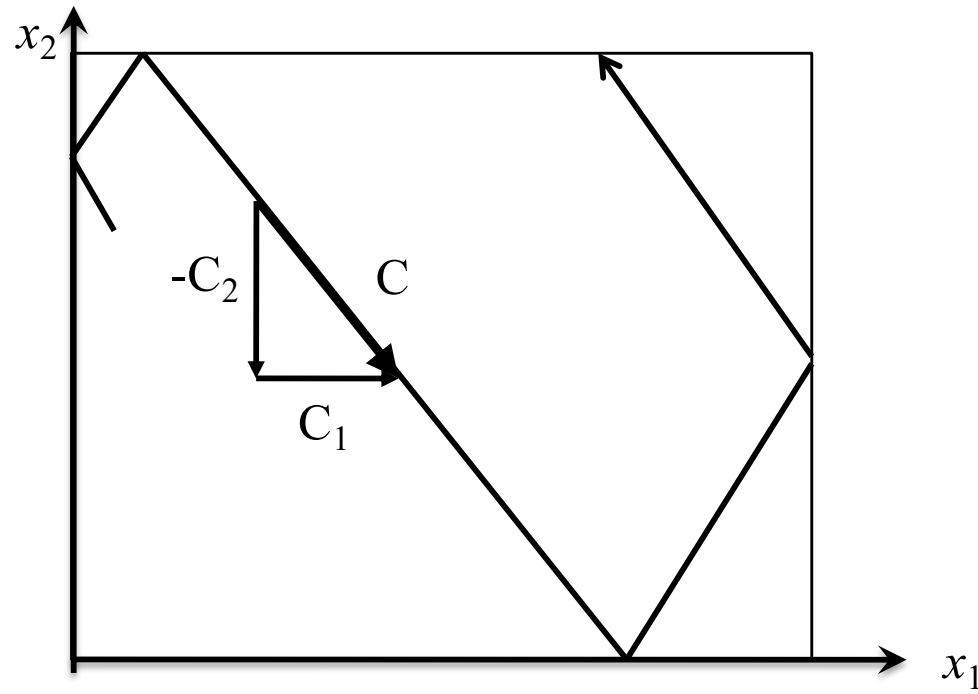


A Molecular Picture of Dynamic Behavior

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A Molecular Picture of Dynamic Behavior

- Consider a gas in a state of equilibrium inside a cubical box.
- Assume the molecules do not collide with each other and that collisions with the wall take place specularly and with speed unchanged. (These assumptions are untrue, but for an ideal gas do not matter.)
- Given these assumptions, this situation is as in the following figure.



- The molecule moves at constant speed C , irrespective of its direction.
- When it collides with the wall its velocity perpendicular to the wall is reversed, but speed is unchanged.
- The magnitudes of the components have fixed values

$$\begin{matrix} |C_1| & |C_2| & |C_3| \\ C_1^2 + C_2^2 + C_3^2 = C^2 \end{matrix}$$

- and



- The force on a given wall depends on the number of collisions per unit time and the change in momentum per collision.
- If l is the length of the box, the time to travel between walls is, say

$$l/|C_1|$$

- Since there are two traverses per collision with one wall, the number of collisions per unit time is

$$|C_1|/2l$$

- The change in x_1 -momentum per collision is

$$2m|C_1|$$

- The magnitude of the total change in x_1 momentum per unit time, which is the total force exerted on the wall by the molecule is

$$2m|C_1| \times |C_1| / 2l = \frac{mC_1^2}{l}$$

- Since the area of the wall is l^2 , the pressure on the wall is

$$\frac{mC_1^2}{l^3} = \frac{mC_1^2}{V}$$

- The gas mixture is composed of a large number of molecules of different mass $m_a, m_b, \dots$ and speed $C_a, C_b, \dots$, so that the total pressure exerted on the wall is

$$p = \frac{1}{V} \sum_z m_z C_{z1}^2$$

- Since the gas is in equilibrium this will also be the pressure on all the other walls. Taking the sum and dividing by three

$$p = \frac{1}{3V} \sum_z m_z (C_{z1}^2 + C_{z2}^2 + C_{z3}^2) = \frac{1}{3V} \sum_z m_z C_z^2$$



- Since the total energy of translation, E_{tr} of the molecules is

$$E_{tr} = \frac{1}{2} \sum_z m_z C_z^2$$

- We can write

$$pV = \frac{2}{3} E_{tr}$$

- Now, consider the perfect gas law (N is number of moles)

$$pV = NR_u T$$

- Comparing

$$E_{tr} = \frac{3}{2} NR_u T$$

- R_u is the universal gas constant per mole.

$$R_u = 8.3144621 \frac{J}{\text{mol } K}$$

- The gas constant per molecule is Boltzmann's Constant

$$k = 1.38 \times 10^{-23} \frac{J}{K}$$

- So, the average translational energy per mole/molecule is

$$\hat{e}_t = \frac{3}{2} R_u T \qquad e_t = \frac{3}{2} kT$$

- We have ignored any internal molecular structure so translation provides the entire internal energy of the gas. Thus, the specific heat is

$$\hat{c}_v = \left(\frac{\partial e}{\partial T} \right)_v = \frac{de_r}{dT} = \frac{3}{2} R_u$$

- For an ideal gas $c_p - c_v = R$

- and
$$\hat{c}_p = \frac{5}{2} R_u$$

- The ratio of specific heat is
$$\gamma = \frac{5}{3}$$

- We can estimate molecular speeds. The mean square speed is

$$\overline{C^2} \equiv \frac{\sum_z m_z C_z^2}{\sum_z m_z}$$

- Noting that the density is $\rho = m/V$

$$\frac{p}{\rho} = \frac{1}{3} \overline{C^2}, \quad \frac{p}{\rho} = RT, \quad R_{air} = 0.287 \text{ kJ/kgK}$$

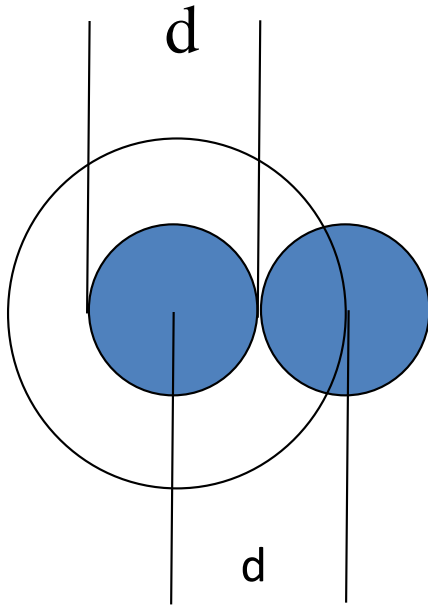
- AT STP for air $\sqrt{\overline{C^2}} = 506.5 \text{ m/sec}$

Collisions

- Consider collisions between molecules
- Average spacing is $l_0 = \sqrt[3]{1/n}$
- However, the average distance between collisions can be larger.
- The average distance is called the Mean Free Path

Mean Free Path

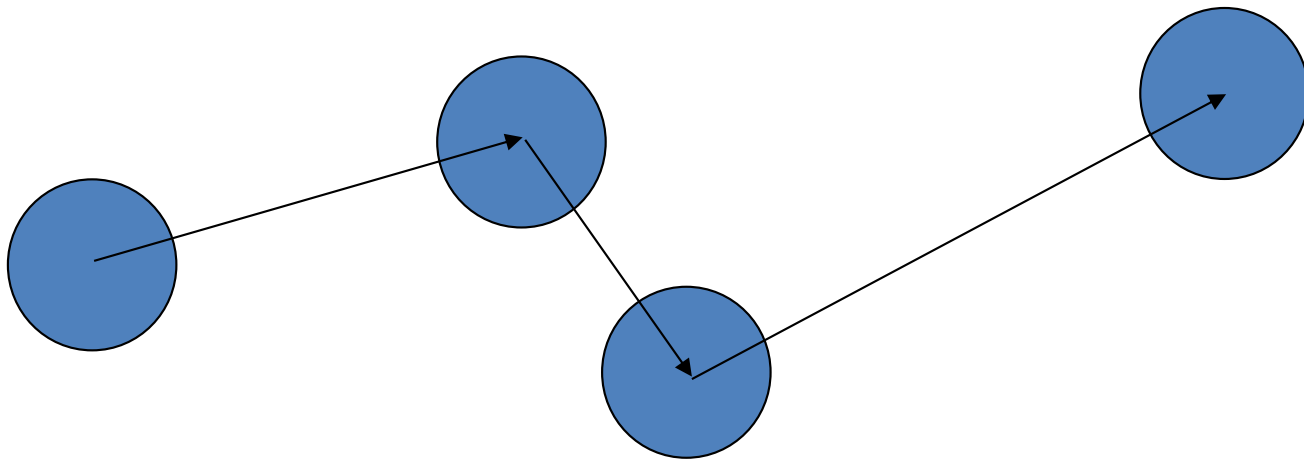
- Sphere of Influence



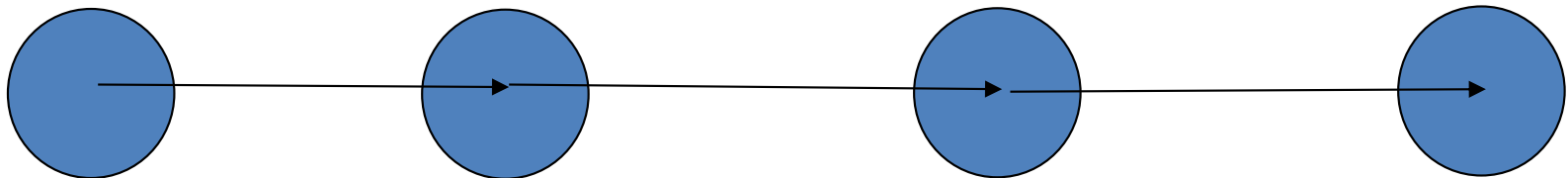
Every molecule has a “sphere of influence.” If the center of another molecule enters the sphere then a collision has occurred.

Mean Free Path

- The actual path followed



- Simplify by straightening



Mean Free Path

- Assume $c = \bar{c}$
- Then the sphere of influence sweeps out a cylindrical volume/unit time of

$$\pi d^2 \bar{c} \quad [L^3/t]$$

- The number of collisions per unit time is

$$\theta = \pi d^2 \bar{c} n \quad [\#/t]$$

Mean Free Path

- Average distance traveled per collision

$$l = \frac{\bar{c}}{\theta} = \frac{1}{\pi d^2 n} \quad [\text{L}]$$

- Better theory gives

$$l = \frac{1}{\sqrt{2}\pi d^2 n} \quad \theta = \sqrt{2}\pi d^2 \bar{c} n$$

Collision Cross Section

- The quantity $\sigma = \pi d^2$ can be thought of as a cross section for the collision. So that

$$l = \frac{1}{\sqrt{2}\sigma n} \quad \theta = \sqrt{2}\sigma \bar{c} n$$

- Note

$$\frac{l}{l_0} = \frac{n^{1/3}}{\sqrt{2}\pi d^2 n} = \frac{1}{\sqrt{2}\pi d^2 n^{2/3}} = \frac{1}{\sqrt{2}\pi} \frac{l_0}{d}$$



Numbers (H₂)

- Number density at STP = $2.7 \times 10^{24} \text{ m}^{-3}$
- Collision diameter = 2.7 Angstroms

$$l_0 = 3.445 \times 10^{-9} \text{ m} = 34.45 \text{ Ang}$$

$$l = 1.262 \times 10^{-7} \text{ m} = 1262 \text{ Ang}$$

$$\frac{l}{l_0} = 36.6$$



Numbers

- Average speed

$$\bar{c} = 1782 \text{ m/sec}$$

- Collision frequency

$$\theta = 1.412 \times 10^{10} \text{ sec}^{-1}$$