Chapter 11

Kinetic Theory of Gases (2)

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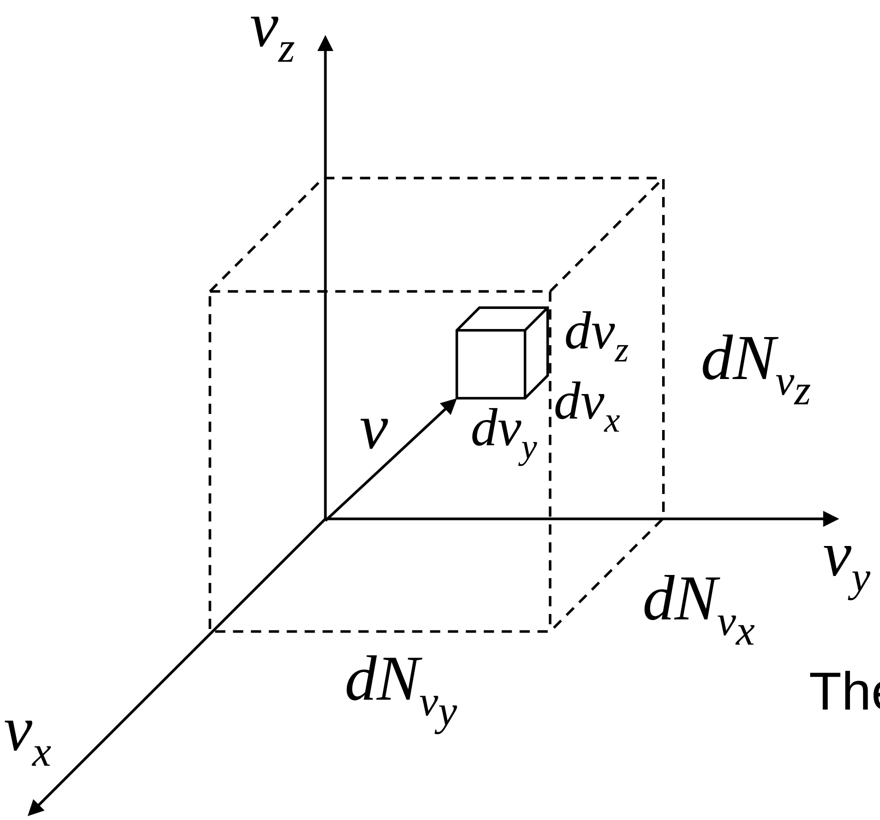


dN_{v_x} ⋯ # of points in the slide

$\frac{dN_{v_x}}{N}$ ⋯ fraction of the total

lying in the slide

$$\frac{dN_{v_x}}{N} = f(v_x)dv_x$$

The number of molecules with $v_x \sim v_x + dv_x$

$$dN_{v_x} = Nf(v_x)dv_x$$

$$dN_{v_y} = Nf(v_y)dv_y$$

$$dN_{v_z} = Nf(v_z)dv_z$$

*** Assumption: v_y is not affected by v_x**

$d^2N_{v_x v_y}$ ⋯ the number of molecules with $v_x \sim v_x + dv_x, \quad v_y \sim v_y + dv_y$

$\dfrac{d^2N_{v_x v_y}}{dN_{v_x}}$ ⋯ fraction of v_x component molecules with $v_y \sim v_y + dv_y$

$$d^2N_{v_x v_y} = dN_{v_x}\frac{dN_{v_y}}{N} = dN_{v_x} f(v_y)dv_y$$

$\quad\quad\quad\quad\quad\quad \hookrightarrow Nf(v_x)dv_x$

$$\boldsymbol{d^3N_{v_x v_y v_z} = Nf(v_x)f(v_y)f(v_z)dv_x dv_y dv_z}$$

the number of molecules with $v_x \sim v_x + dv_x,\ v_y \sim v_y + dv_y,\ v_z \sim v_z + dv_z$

- Density in velocity space

  Consider a velocity space where velocity vectors of particles are distributed

$$d^3N_{v_x v_y v_z} = Nf(v_x)f(v_y)f(v_z)dv_x dv_y dv_z$$

$$dN_v = Nf(v)dv_x dv_y dv_z$$

※ dN_{v_x} : number of molecules in the slice $v_x < v < v_x + dv_x$

Number density of velocity vectors

$$\rho(v) = \frac{d^3N_{v_x v_y v_z}}{dv_x dv_y dv_z} = Nf(v_x)f(v_y)f(v_z)$$

$$v^2 = {v_x}^2 + {v_y}^2 + {v_z}^2$$

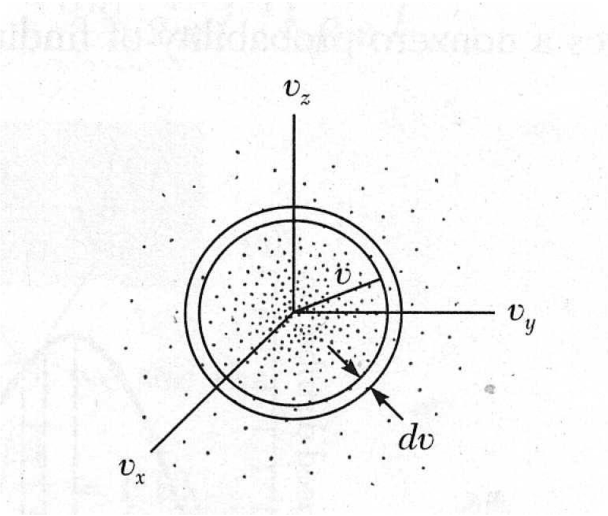


Figure 11.1 Velocity space

$$d\rho = \frac{\partial \rho}{\partial v_x} dv_x + \frac{\partial \rho}{\partial v_y} dv_y + \frac{\partial \rho}{\partial v_z} dv_z$$

$$\frac{\partial \rho}{\partial v_x} = N \frac{\partial}{\partial v_x} [(f(v_x)] f\left(v_y\right) f(v_z) = N f'(v_x) f\left(v_y\right) f(v_z)$$

Because of homogeneity of direction of particles,
there exist constraints along spherical shell of the velocity space

1) $d\rho$=0

$$\frac{f'(v_x)}{f(v_x)} dv_x + \frac{f'(v_y)}{f(v_y)} dv_y + \frac{f'(v_z)}{f(v_z)} dv_z = 0$$

2) $v^2 = \text{constant}$

$$\lambda[v_x dv_x + v_y dv_y + v_z dv_z] = 0$$

→ Lagrange's method of undetermined multiplier

$$\left[\frac{f'(v_x)}{f(v_x)} + \lambda v_x\right] dv_x + \left[\frac{f'(v_y)}{f(v_y)} + \lambda v_y\right] dv_y + \left[\frac{f'(v_z)}{f(v_z)} + \lambda v_z\right] dv_z = 0$$

$= 0$ $\quad$ $= 0$ $\quad$ $= 0$

$$\frac{f'(v_x)}{f(v_x)} + \lambda v_x = 0, \longrightarrow \ln f = -\frac{\lambda}{2} {v_x}^2 + \ln\alpha$$

$$\boldsymbol{f(v_x) = \alpha e^{-\frac{\lambda}{2}{v_x}^2} = \alpha e^{-\beta^2 {v_x}^2}}$$

$$d^3N_{v_x v_y v_z} = Nf(v_x)f(v_y)f(v_z)dv_x dv_y dv_z$$

$$= N\alpha^3 e^{-\beta^2(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z$$

The number of points per unit volume

$$\rho = \frac{d^3N_{v_x v_y v_z}}{dv_x dv_y dv_z} = N\alpha^3 e^{-\beta^2 v^2}$$

Maxwell velocity distribution function

The number of molecules with speed $v \sim v + dv$

$$dN_v = \underbrace{\left(N\alpha^3 e^{-\beta^2 v^2}\right)}_{\rho} \times \underbrace{(4\pi v^2 dv)}_{V} = 4\pi N\alpha^3 v^2 e^{-\beta^2 v^2} dv$$

- Maxwell-Boltzmann distribution

  Two, obvious relations are used to obtain α, β of $N(v)$

$$N = \int_0^\infty dN_v = 4\pi N\alpha^3 \underline{\int_0^\infty v^2 e^{-\beta^2 v^2} dv} \quad \frac{\sqrt{\pi}}{4\beta^3} \qquad \alpha = \frac{\beta}{\sqrt{\pi}}$$

$$E = \frac{3}{2}NkT = \frac{1}{2}m\int_0^\infty v^2 dN_v = 2\pi m N\alpha^3 \underline{\int_0^\infty v^4 e^{-\beta^2 v^2} dv} \quad \frac{3\sqrt{\pi}}{8\beta^5}$$

$$\therefore \alpha = \sqrt{\frac{m}{2\pi kT}}, \qquad \beta = \sqrt{\frac{m}{2kT}}$$

Finally, the Maxwell-Boltzmann speed distribution is given below

$$dN_v = 4\pi N(\frac{m}{2\pi kT})^{3/2} v^2 e^{-mv^2/2kT} dv$$

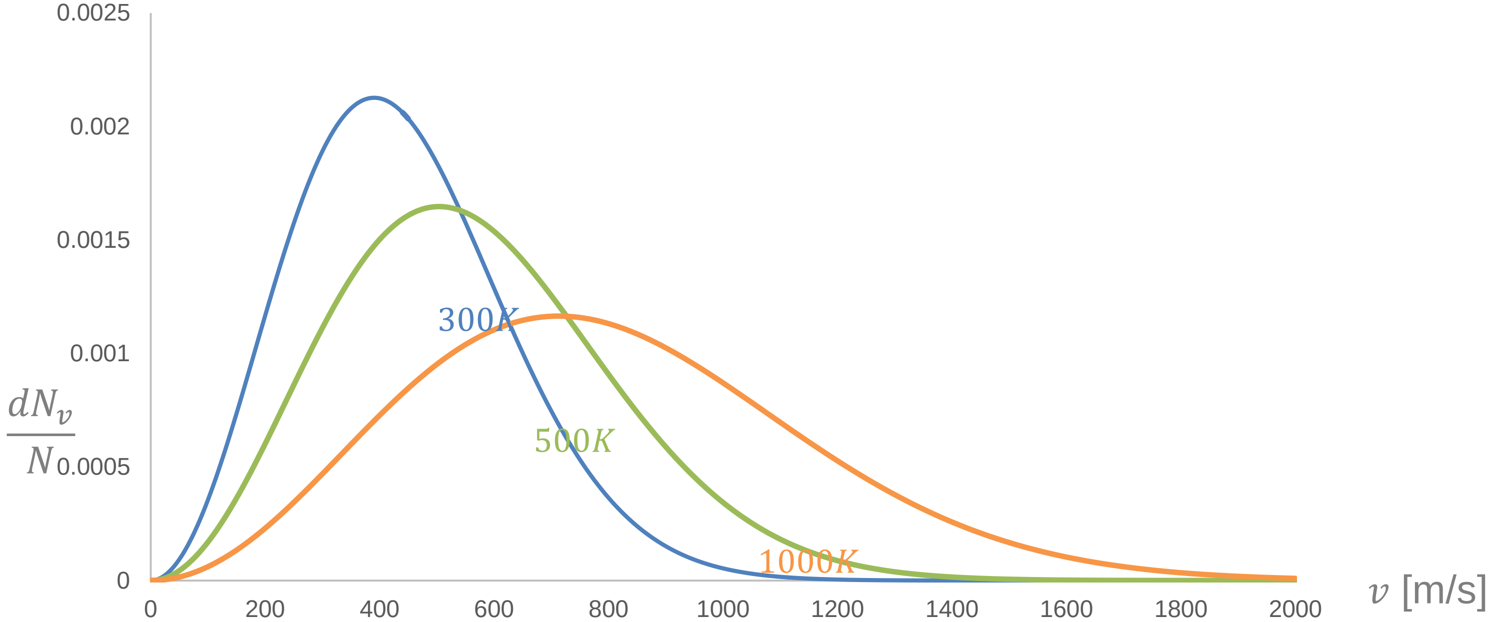


Figure 11.2 Speed distribution of O_2 molecules

$$d^3N_{v_x v_y v_z} = N(\frac{m}{2\pi kT})^{3/2} e^{-mv^2/2kT} dv_x v_y v_z \qquad dN_{v_x} = N(\frac{m}{2\pi kT})^{1/2} e^{-mv_x^2/2kT} dv_x$$

- Mean free path and collision frequency

Equation of state

Collisions between molecules ··· ignored

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

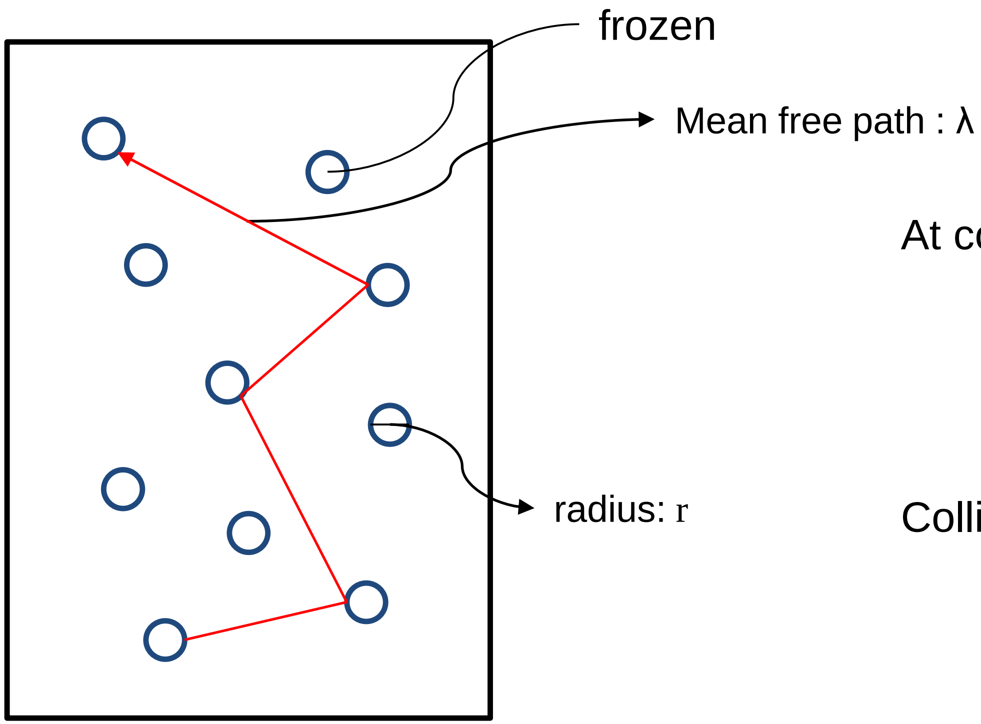
→ Will change the velocity of individual molecules

→ The number of molecules having particular velocity is unchanged

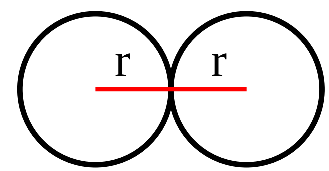
Molecules ─┬─ having a finite size
           └─ colliding with one another

11.7 Mean Free Path and Collision Frequency

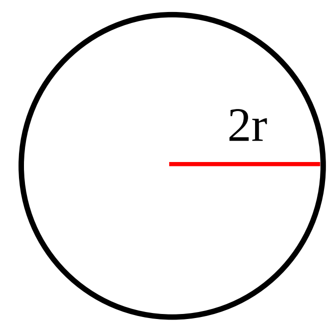
- Mean free path, λ



At collision,



Collision radius = 2r

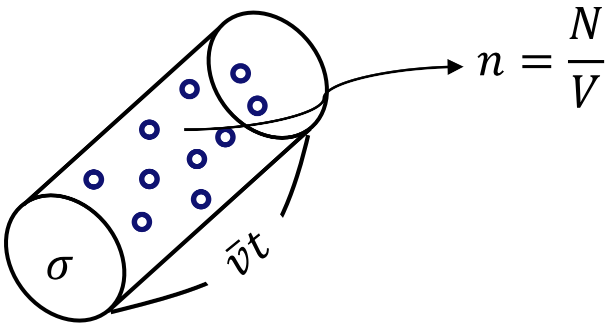


Collision cross section : $\sigma = 4\pi r^2$

11.7 Mean Free Path and Collision Frequency

Collision cross section : $\sigma = 4\pi r^2$

Moving distance in the time interval $t = \bar{v}t$



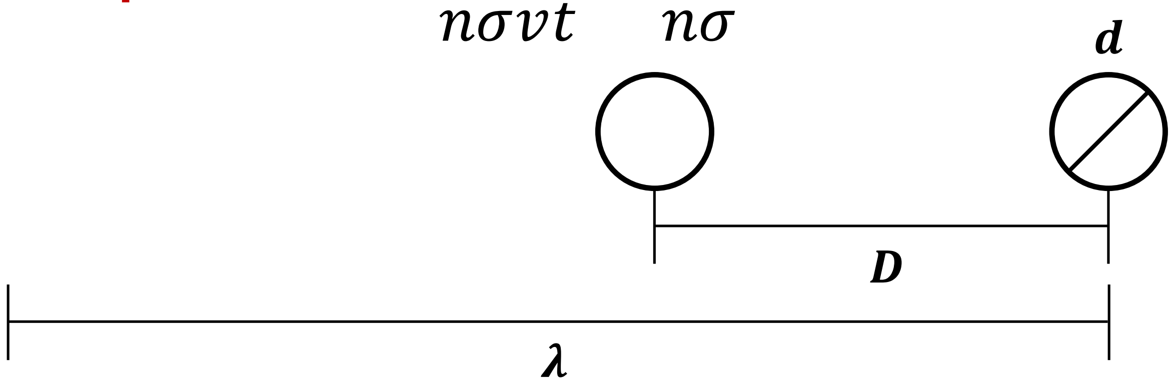
The number of molecules in the cylinder swept out by moving molecule: $\sigma\bar{v}tn$

The number of collision per unit time : *collision frequency*

$$\boldsymbol{collision\ frequency = z = \frac{n\sigma\bar{v}t}{t} = n\sigma\bar{v}}$$

11.7 Mean Free Path and Collision Frequency

Mean free path : $\lambda = \dfrac{\bar{v}t}{n\sigma\bar{v}t} = \dfrac{1}{n\sigma}$



This answer is only approximately correct because we have used the mean speed $\bar{v}$ for all the molecules instead of performing an integration over the Maxwell-Boltzmann speed distribution. If that is done, the result is

Mean free path : $\lambda = \dfrac{1}{\sqrt{\dfrac{8}{\pi}}n\sigma}$

(corrected)

Collision frequency : $f_c = \dfrac{\bar{v}}{\lambda} = \sqrt{\dfrac{8}{\pi}}\bar{v}n\sigma$

(corrected)

11.7 Mean Free Path and Collision Frequency

- The distribution of free path, $x <$ $< x + dx$

- $dN = -P_c N dx$

  dN : number of molecules decreasing after collision
  P_c : collision probability
  dx : molecule's moving distance

- $N = N_0 e^{-P_c x}$
  $dN = -P_c N_0 e^{-P_c x} dx$

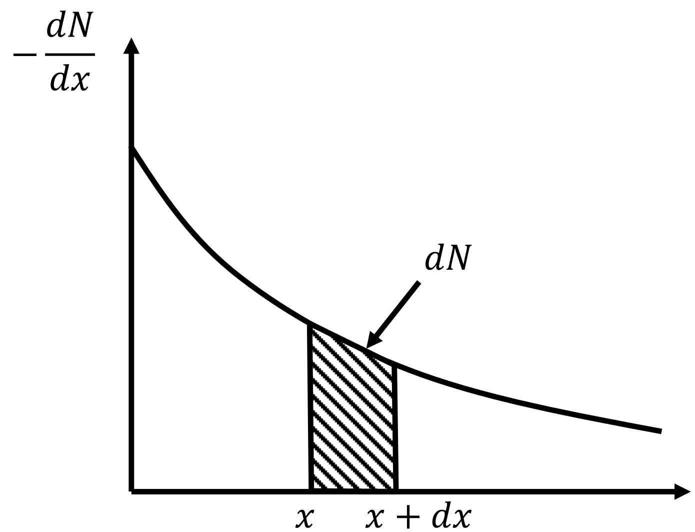
  N : The number of molecules that have not yet made a collision after traveling a distance x

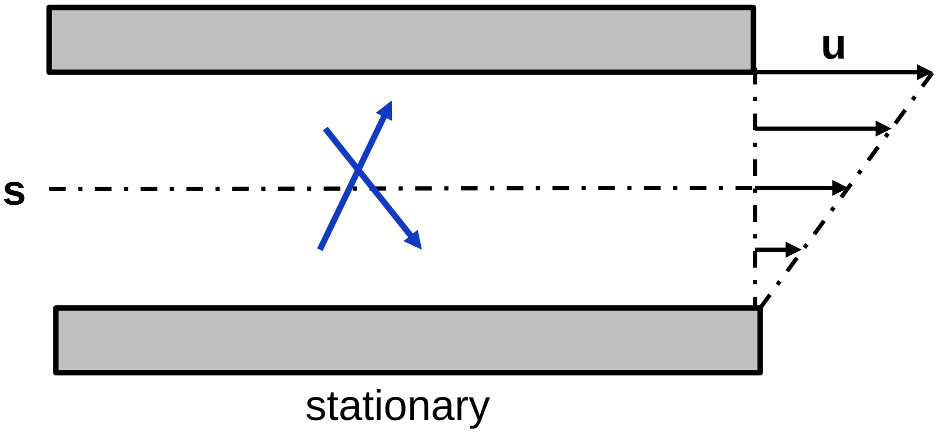
11.7 Mean Free Path and Collision Frequency

- $$\lambda = \frac{\int x(-dN)}{N_0} = \frac{\int_0^\infty P_c N_0 x\, e^{-P_c x} dx}{N_0} = P_c \left\{ \left[\frac{x e^{-P_c x}}{-P_c} \right]_0^\infty - \frac{1}{-P_c} \int_0^\infty e^{-P_c x}\, dx \right\}$$
$$= P_c \left\{ 0 - \frac{1}{{P_c}^2} \left[e^{-P_c x} \right]_0^\infty \right\} = \frac{1}{P_c}$$

- Survival equation : $N = N_0 e^{-\frac{x}{\lambda}}$ (# having free paths $x <$)

$$dN = -\frac{N_0}{\lambda} e^{-\frac{x}{\lambda}} dx$$ (# with free path $x <$ $< x + dx$)



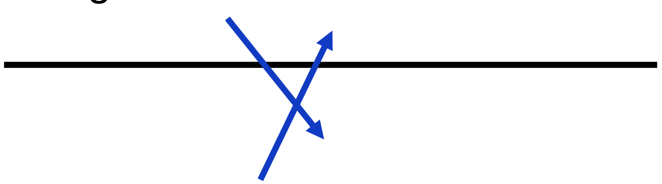


- Velocity of gas << thermal velocity

Thermal velocity distribution can be used even though the gas is not in equilibrium

Figure 11.5 Flow of a viscous fluid between a moving upper plate and a stationary lower plate.

$$\tau = \eta \frac{du}{dy} \qquad F = \eta A \frac{du}{dy}$$

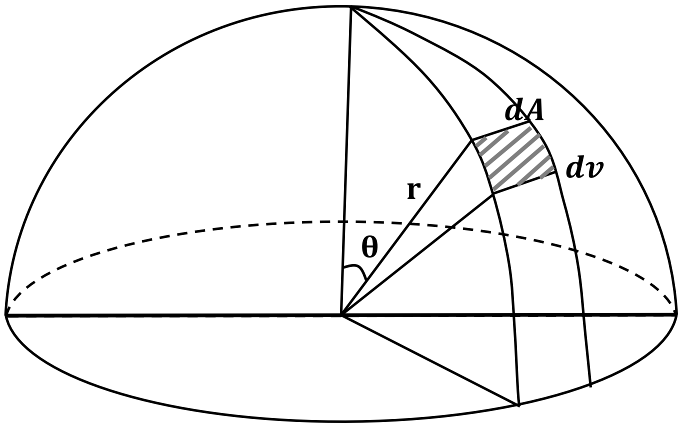


- Net momentum change : $\dfrac{d(mv)}{dt}$

$$P = {}^{F}\!/_{A} = {}^{\frac{d(mv)}{dt}}\!/_{A}$$

Frictional force (?)

momentum across a surface (O)



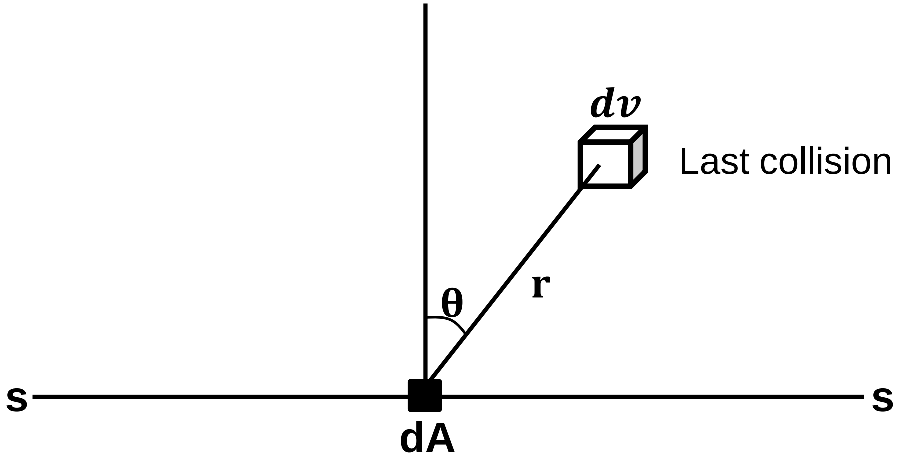


Figure 11.6 Molecule crossing the z=0 plane after its last collision at a distance $l\ cos\theta$ above the plane

11.9 Transport Process

- The number of molecules in $dV = ndV$
- The number of collisions in dV for $dt = \frac{1}{2}zdt \cdot ndV$

  z : collision frequency of any one molecule
- The number of free paths in dV for $dt = zdt \cdot ndV$
- The number of free paths toward $dA = \frac{d\omega}{4\pi} \cdot zdt \cdot ndV$ $\quad [d\omega = \frac{dA\cos\theta}{r^2}]$
- Fraction of molecules that reach dA without collision (survival eq.) : $\frac{N}{N_0} = e^{-\frac{r}{\lambda}}$
- # of molecules leaving dV in dt crossing dA without collision = $\frac{d\omega}{4\pi} \cdot zdt \cdot ndV \cdot e^{-\frac{r}{\lambda}}$

$$= \frac{dA\cos\theta}{4\pi r^2} \cdot zdt \cdot nr^2\sin\theta d\theta d\varphi dr \cdot e^{-\frac{r}{\lambda}} \qquad [dV = r^2\sin\theta d\theta d\varphi dr]$$

- # of molecules leaving dV in dt crossing dA without collision = $\frac{d\omega}{4\pi}\cdot zdt\cdot ndV\cdot e^{-\frac{r}{\lambda}}$

  $= \frac{dA\cos\theta}{4\pi r^2}\cdot zdt\cdot nr^2\sin\theta d\theta d\varphi dr\cdot e^{-\frac{r}{\lambda}}$

$$\int_0^{\frac{\pi}{2}}\sin\theta\cos\theta\, d\theta = \int_0^{\frac{\pi}{2}}\frac{\sin 2\theta}{2}\mathrm{d}\theta = \left[-\frac{1}{4}\cos 2\theta\right]_0^{\frac{\pi}{2}} = \frac{1}{2} \qquad \int_0^{2\pi}\mathrm{d}\varphi = 2\pi \qquad \int_0^{\infty} -\lambda e^{-\frac{r}{\lambda}}\mathrm{dr} = \lambda$$

$$0 < \theta < \frac{\pi}{2}$$
$$0 < \emptyset < 2\pi$$
$$0 < r < \infty$$

→ $\frac{1}{4}zn\lambda dAdt$

- Collision frequency : $z = \frac{\bar{v}}{\lambda}$

- Total # of collision with the wall per dA, dt for all direction & speed = $\frac{1}{4}n\bar{v}$

- Average height of last collision before crossing

The height of the volume element = $r\cos\theta$

The number of molecules crossing dA without collision = $\frac{d\omega}{4\pi} zdt \cdot ndV \cdot e^{-\frac{r}{\lambda}} \cdot r\cos\theta$

$[d\omega = \frac{dA\cos\theta}{r^2},\ dV = r^2 \sin\theta d\theta d\varphi dr]$

$$\bar{y} = \frac{\int_0^{\frac{\pi}{2}} \int_0^{2\pi} \int_0^{\infty} \frac{dA\cos\theta}{4\pi r^2} \cdot zdt \cdot nr^2 \sin\theta \cdot e^{-\frac{r}{\lambda}} \cdot r\cos\vartheta\, dr d\varphi d\vartheta}{\int_0^{\frac{\pi}{2}} \int_0^{2\pi} \int_0^{\infty} \frac{dA\cos\theta}{4\pi r^2} \cdot zdt \cdot nr^2 \sin\theta \cdot e^{-\frac{r}{\lambda}}\, dr d\varphi d\vartheta}$$

$$= \frac{\frac{1}{6} zn\lambda^2 dAdt}{\frac{1}{4} zn\lambda dAdt}$$

$$= \frac{2}{3}\lambda$$

11.9 Transport Process

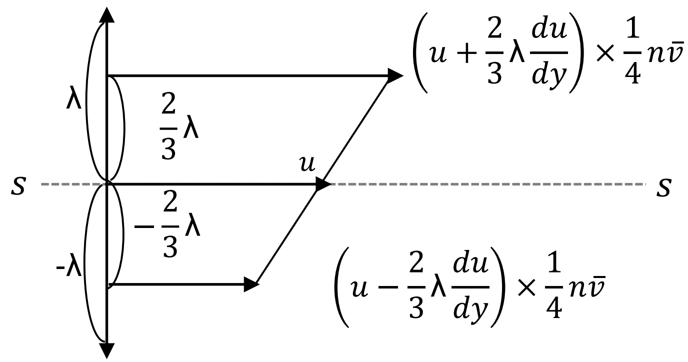


Figure 11.7 Flow of a viscous fluid between a moving upper plate and a stationary lower plate.

- Net rate of momentum transfer per unit area & time : $\frac{4}{3}\lambda\frac{du}{dy}\cdot m\cdot\frac{1}{4}n\bar{v}$
- $\frac{d(mv)}{dt}\frac{1}{A}=\frac{F}{A}=\tau=\frac{1}{3}nm\bar{v}\lambda\frac{du}{dy}$
- $\eta=\frac{1}{3}nm\bar{v}\lambda$
- $\lambda=\frac{1}{\sigma n},\ \bar{v}=\sqrt{\frac{8kT}{\pi m}}$
- $\eta=\frac{2}{3}\cdot\frac{1}{\sigma}(\frac{2mkT}{\pi})^{\frac{1}{2}}$ $\qquad$ $\eta=\frac{5}{16}\cdot\frac{1}{\sigma}(\frac{2mkT}{\pi})^{\frac{1}{2}}$ (considering speed distribution)