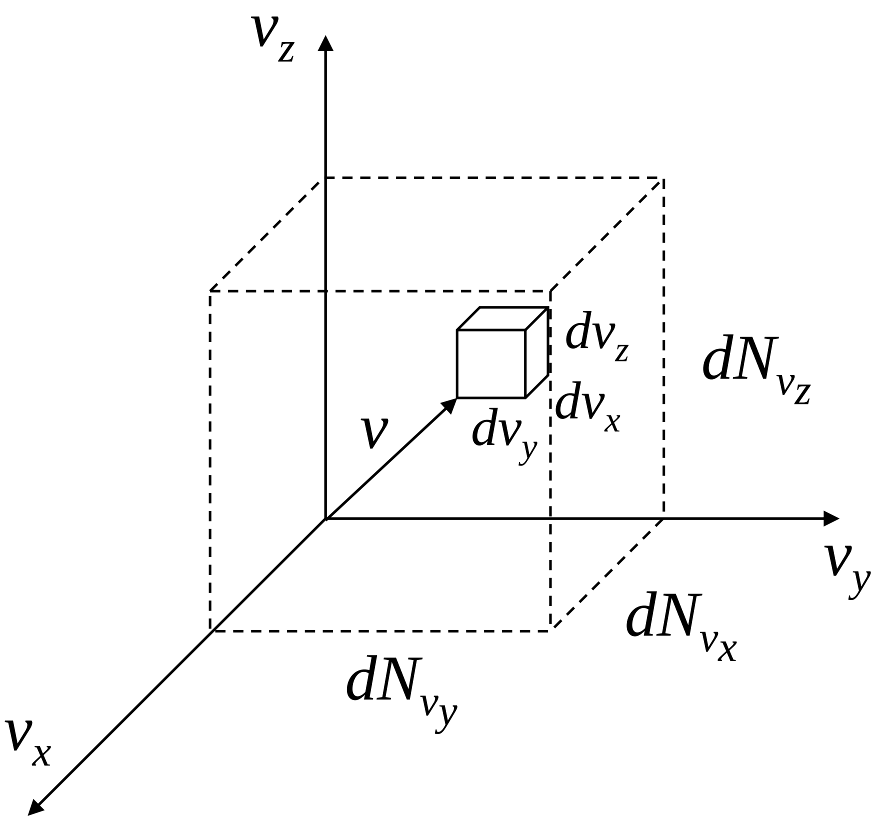
Chapter 11

Kinetic Theory of Gases (2)

Min Soo Kim

Seoul National University

11.6 Distribution of Molecular Speeds



dN_{v_x} ⋯ # of points in the slide

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

\# lying in the slide

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

\# of molecules with $v_x < \quad < v_x + dv_x$

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

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

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

*** Assumption: $\boldsymbol{v_y}$ is not affected by $\boldsymbol{v_x}$**

$d^2N_{v_xv_y}$ ··· # of molecules with $v_x < \quad < v_x + dv_x$

$v_y < \quad < v_y + dv_y$

$\dfrac{d^2N_{v_xv_y}}{dN_{v_x}}$ ··· fraction of v_x component molecules with $v_y < \quad < v_y + dv_y$

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

$Nf(v_x)dv_x$

$$\boldsymbol{d^3N_{v_xv_yv_z} = Nf(v_x)f(v_y)f(v_z)dv_xdv_ydv_z}$$

$v_x < \quad < v_x + dv_x$

$v_y < \quad < v_y + dv_y$

··· # of molecules with $v_z < \quad < v_z + dv_z$

- Density in velocity space

  Consider a velocity space where velocity vectors of particles are distributed

$$d^3N_{v_x}N_{v_y}N_{v_z} = Nf(v_x)f(v_y)f(v_z)dv_xdv_ydv_z$$

$$dN_v = Nf(v)dv_xdv_ydv_z$$

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

Number density of velocity vectors

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

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

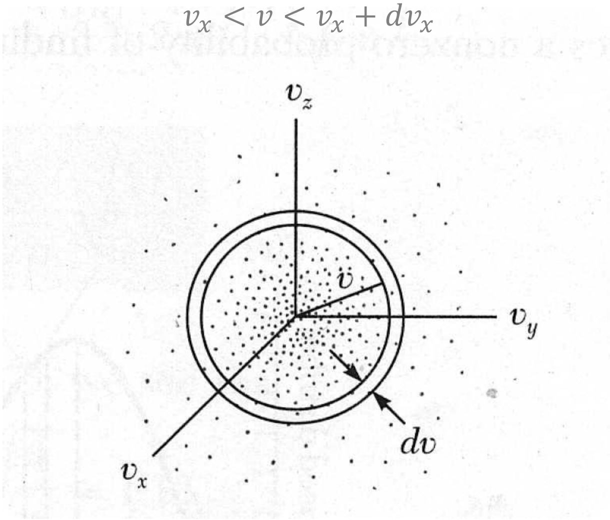


Figure 11.1 Velocity space

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

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

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

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

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

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

$$d^3N_{v_x}N_{v_y}N_{v_z} = Nf(v_x)f\left(v_y\right)f(v_z)dv_xdv_ydv_z$$

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

# of points per unit volume

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

Maxwell velocity distribution function

11.6 Distribution of Molecular Speeds

# of molecules with speed $\boldsymbol{v < \quad < v + dv}$

$$\# = \rho V$$

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

11.6 Distribution of Molecular Speeds

- Maxwell-Boltzmann distribution

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

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

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

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

Finally, the Maxwell-Boltzmann speed distribution is given below

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

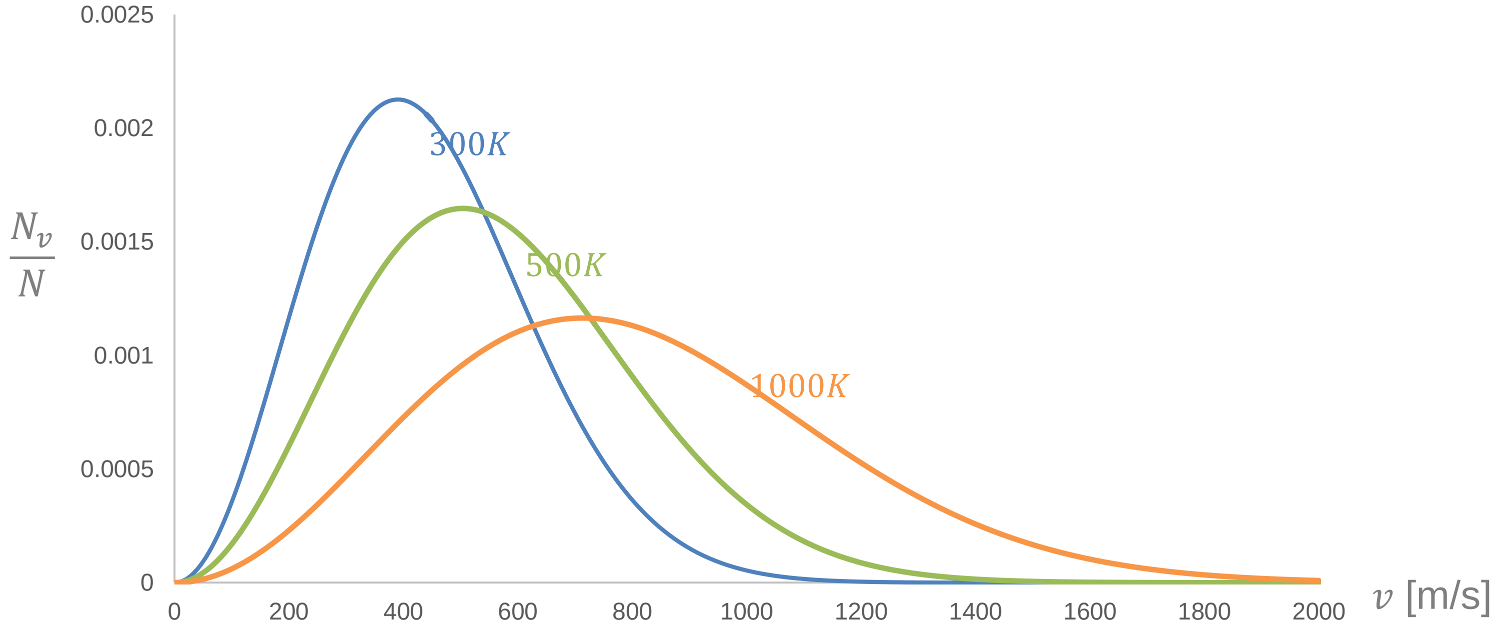


Figure 11.2 Speed distribution of O_2 molecules

11.7 Mean Free Path and Collision Frequency

- 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

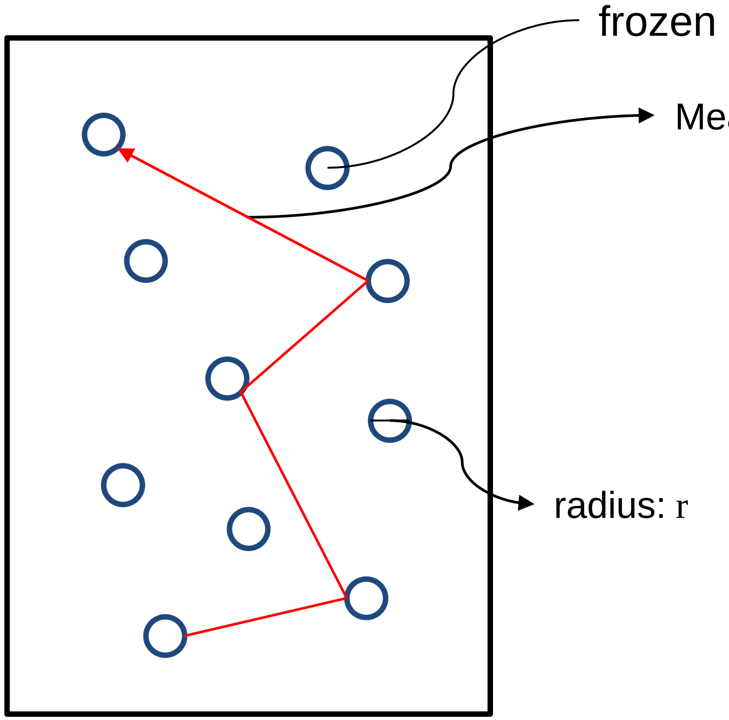
→ # of molecules having particular velocity is unchanged

Molecules — having a finite size

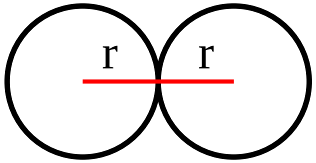
Molecules — colliding with one another

11.7 Mean Free Path and Collision Frequency

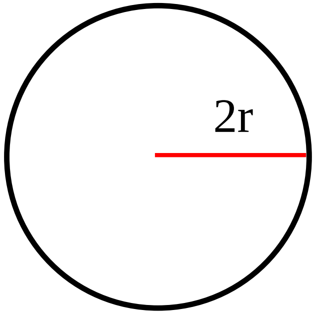
- Mean free path, λ



At collision,



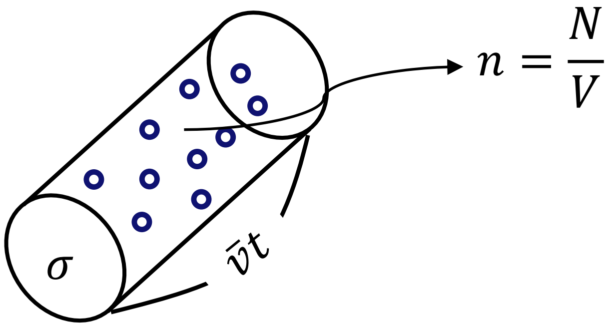
Collision radius = 2r



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

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

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

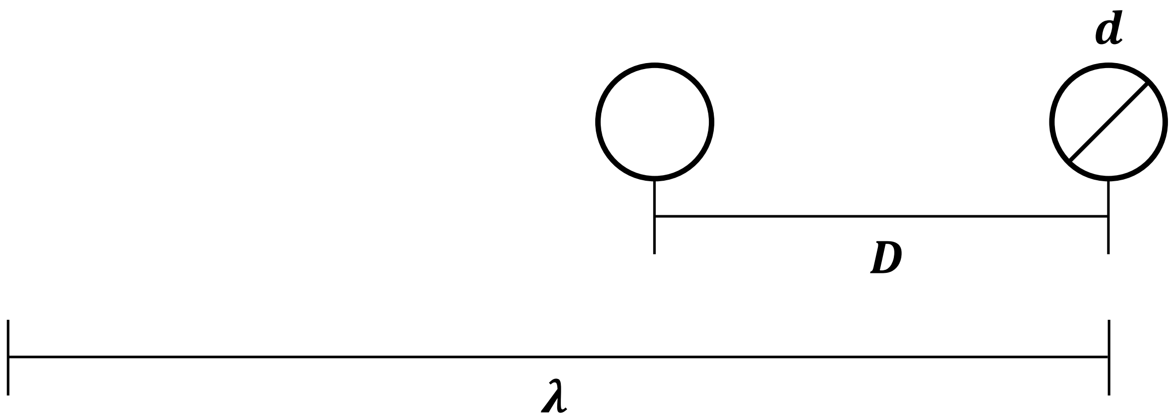


# of molecules in the cylinder swept out by moving molecule :$\sigma\bar{v}tn$

# of collision per unit time : *collision frequency*

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

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-Boltzman speed distribution. If that is done, the result is

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

(corrected)

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

(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 : molecules moving distance

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

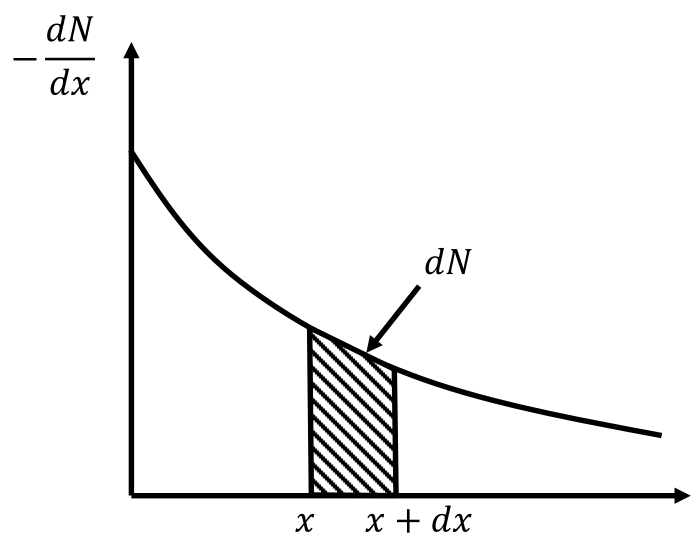
  N : # of molecules that have not yet made a collision
  after traveling a distance x

11.7 Mean Free Path and Collision Frequency

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

- 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 $x <$ $< x + dx$)



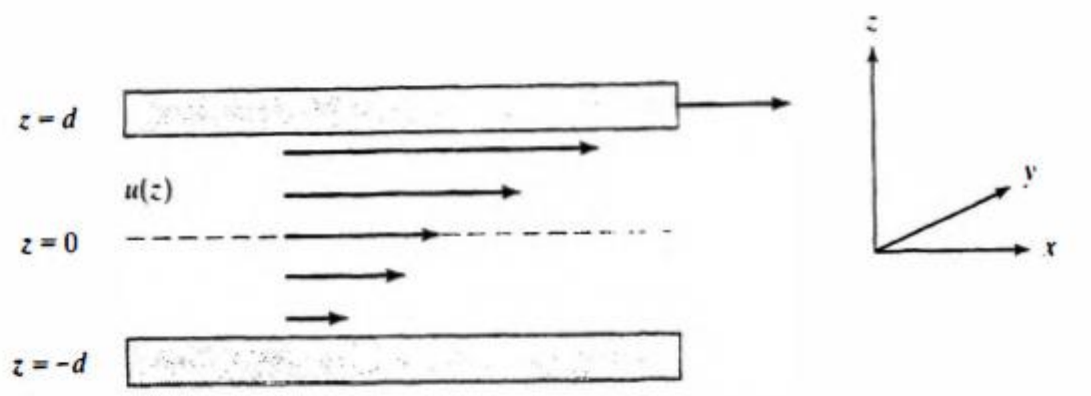


Figure 11.5 Flow of a viscous fluid between a moving upper plate and a stationary lower plate.

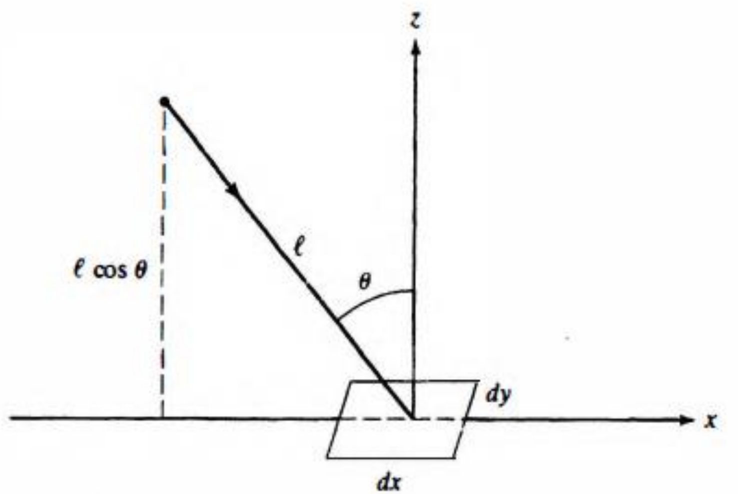


Figure 11.6 Molecule crossing the z=0 plane after its last collision at a distance $\boldsymbol{l\cos\theta}$ above the plane

11.9 Transport Process

- # of molecules in dV: ndv
- # of collisions in dv for dt: $\frac{1}{2}zdtndV$

  z : collision frequency of any one molecule
- # of free paths in dV for dt: $zdtndV$
- # of free paths toward dA: $\frac{dw}{4\pi}zdtndV$
- Fraction of molecules that reach dA without collision (survived eq) : $\frac{N}{N_0} = e^{-\frac{r}{\lambda}}$
- # of molecules leaving dV in dt crossing dA without collision : $\frac{dw}{4\pi}zdtndVe^{-\frac{r}{\lambda}}$

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

$$\longrightarrow \quad \frac{1}{4}zn\lambda dAdt$$

11.9 Transport Process

- 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 : $r cos\theta$

# of molecules crossing dA without collision : $\frac{dw}{4\pi} z dt n dV e^{-\frac{r}{\lambda}} r cos\theta$

11.9 Transport Process

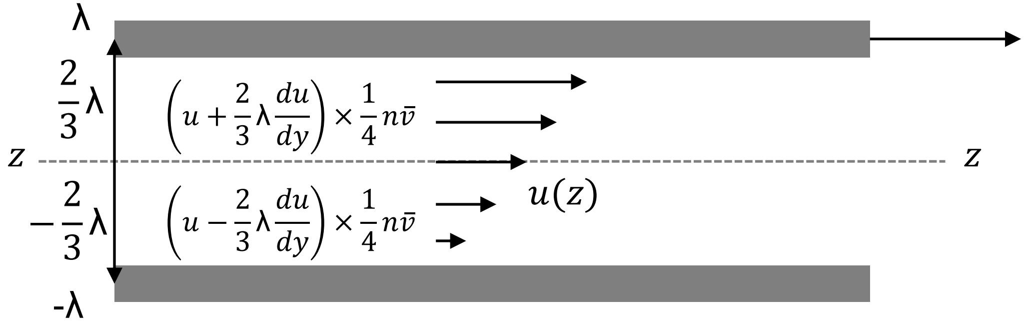


Figure 11.7 Flow of a viscous fluid between a moving upper plate and a stationary lower plate.

- Net rate of momentum transfer per unit area & time : $2 \times \frac{2}{3}λ\frac{du}{dy}m\frac{1}{4}n\bar{v}$
- $\frac{d(mv)}{dt}\frac{1}{A} = \tau = \frac{1}{3}nm\bar{v}λ\frac{du}{dy}$
- $\mu = \frac{1}{3}nm\bar{v}λ$
- $λ=\frac{1}{\sigma m}, \ \bar{v} = \sqrt{\frac{8KT}{\pi m}}$
- $\mu = \frac{2}{3} \times \frac{1}{\sigma}(\frac{2mKT}{\pi})^2$