Chapter 11

Kinetic Theory of Gases

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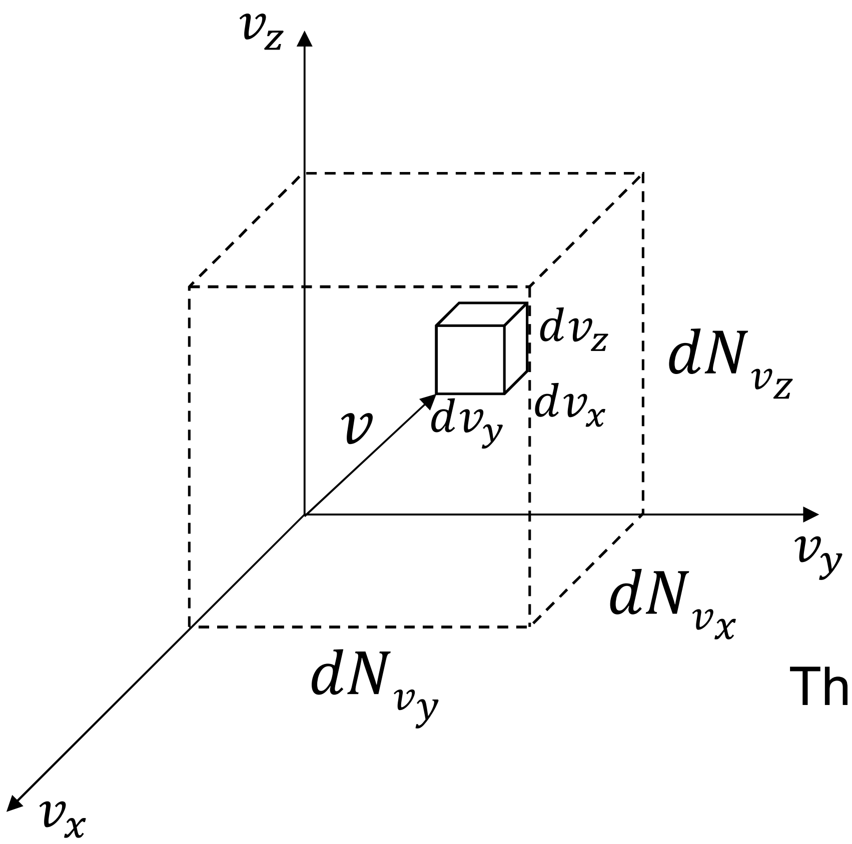
11.6 Distribution of Molecular Speeds



dN_{v_x} ⋯ # of points in the slide

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

\# lying in the slide

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

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

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

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

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

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

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

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

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- 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

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

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

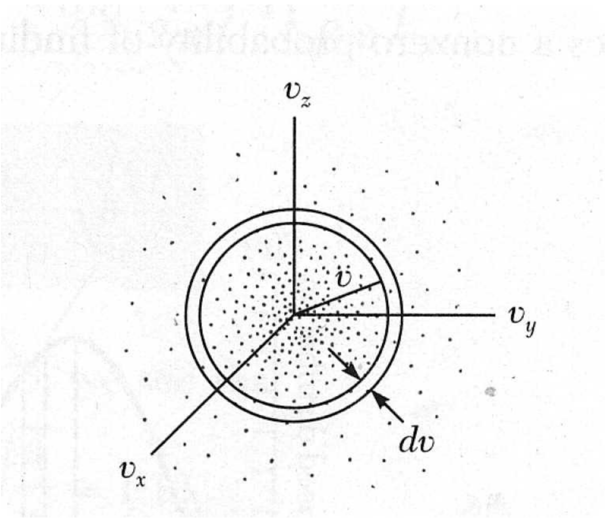

Figure 11.1 Velocity space

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

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

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

1) $d\rho$=0

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

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2) v^2 = constant

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

→ Lagrange's method of undetermined multiplier

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

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

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

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

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

The number of points per unit volume

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

Maxwell velocity distribution function

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

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

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- Maxwell-Boltzmann distribution

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

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

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

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

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Finally, the Maxwell-Boltzmann speed distribution is given below

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

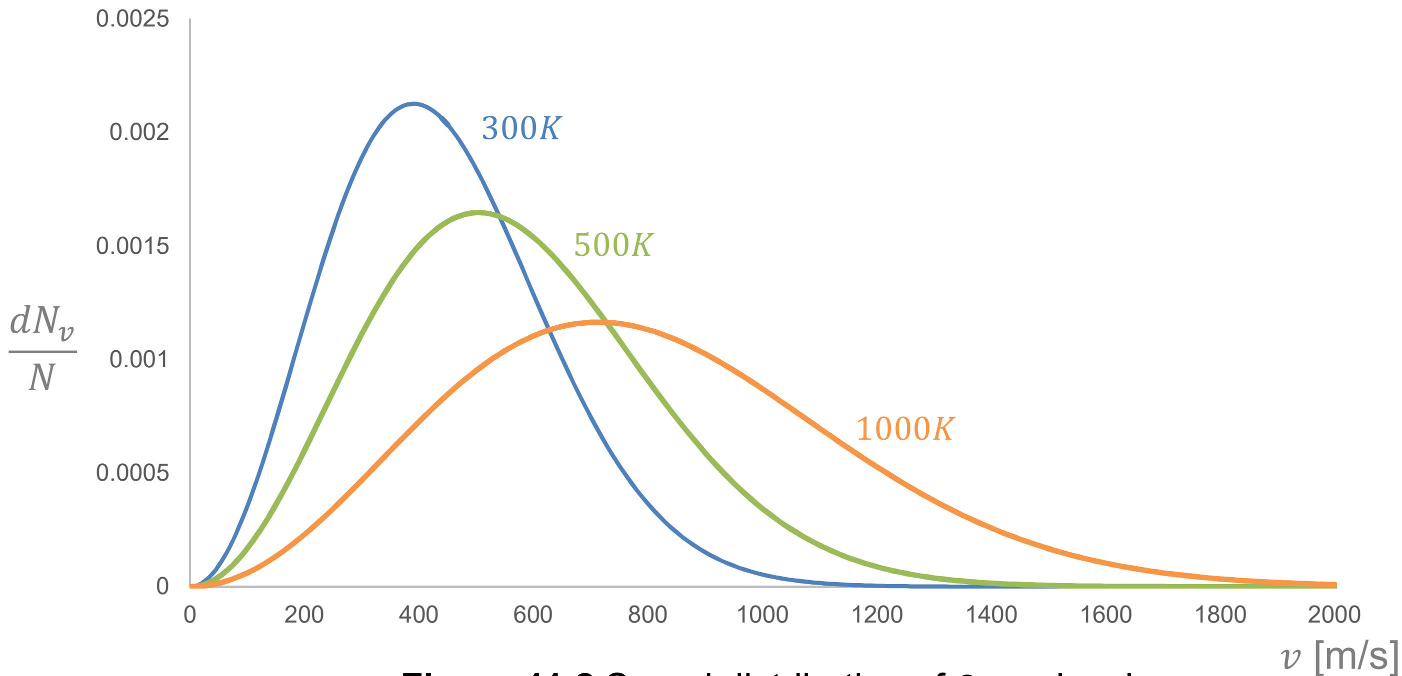

Figure 11.2 Speed distribution of O_2 molecules

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