11.B.3. The Collision Frequency

Consider a fluid consists of particles of types $j = A, B, C, \ldots$; each with mass m_j, diameter d_j, number density n_j and velocity $\mathbf{v}_j$.

We shall assume the particles are spatially distributed randomly, while obeying the Maxwell-Boltzmann (velocity) distribution.

Treating the particles as hard balls of diameter d_j, we get

$$d_{ij} = \frac{1}{2}(d_i + d_j) \tag{11.8}$$

= shortest distance between the centers of particles of types i & j.

≡ radius of sphere of influence between particles of types i & j.

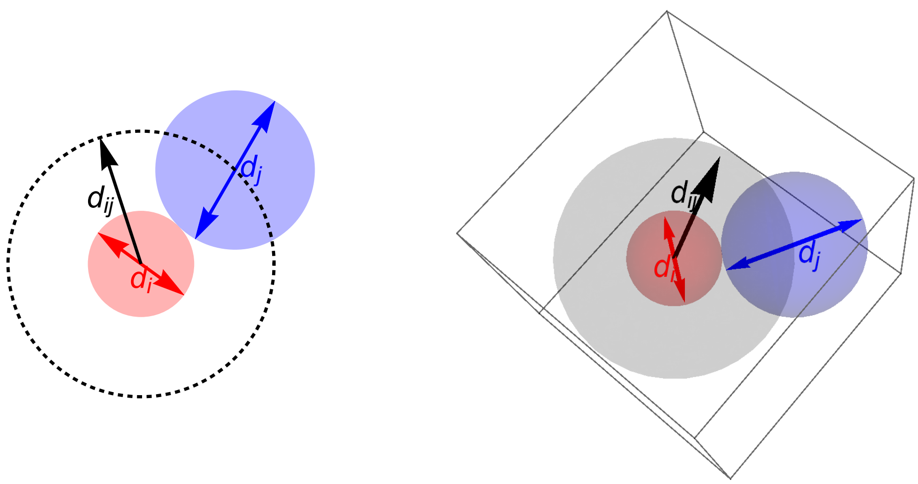

Fig.11.1. Radius of sphere of influence.

For two particles of types i & j, the center-of-mass (CM) velocity is defined as

$$\mathbf{V}_{CM} = \frac{m_i \mathbf{v}_i + m_j \mathbf{v}_j}{m_i + m_j} \tag{11.10}$$

and the relative velocity,

$$\mathbf{v}_r = \mathbf{v}_i - \mathbf{v}_j \tag{11.11}$$

Note that, for the sake of clarity, we have omitted the i, j subscripts in $\mathbf{V}_{CM}$ & $\mathbf{v}_r$.

The average relative speed is therefore

$$\langle v_r \rangle_{ij} = \int d\,\mathbf{v}_i \int d\,\mathbf{v}_j\, F(\mathbf{v}_i)\, F(\mathbf{v}_j) \left| \mathbf{v}_i - \mathbf{v}_j \right| \tag{11.9}$$

Inverting (11.10-1) gives

$$M_{ij}\, \mathbf{v}_i = M_{ij}\, \mathbf{V}_{CM} + m_j\, \mathbf{v}_r \qquad M_{ij}\, \mathbf{v}_j = M_{ij}\, \mathbf{V}_{CM} - m_i\, \mathbf{v}_r \tag{11.9a}$$

where

$$M_{ij} = m_i + m_j = \text{total mass}$$

The Jacobian of the transformation $(\mathbf{v}_i, \mathbf{v}_j) \to (\mathbf{v}_r, \mathbf{V}_{CM})$ is therefore

$$J = \begin{vmatrix} \dfrac{\partial \boldsymbol{v}_i}{\partial \boldsymbol{v}_r} & \dfrac{\partial \boldsymbol{v}_i}{\partial \boldsymbol{V}_{\text{CM}}} \\ \dfrac{\partial \boldsymbol{v}_j}{\partial \boldsymbol{v}_r} & \dfrac{\partial \boldsymbol{v}_j}{\partial \boldsymbol{V}_{\text{CM}}} \end{vmatrix} = \begin{vmatrix} \dfrac{m_j}{M_{ij}} \square & \square \\ -\dfrac{m_i}{M_{ij}} \square & \square \end{vmatrix} = \begin{vmatrix} \square & 0 \\ -\dfrac{m_i}{M_{ij}} \square & \square \end{vmatrix} = 1 \qquad (11.9b)$$

(11.9) thus becomes

$$\langle v_r \rangle_{ij} = \int d\, \boldsymbol{v}_r \int d\, \boldsymbol{V}_{\text{CM}}\; F(\boldsymbol{v}_i)\, F(\boldsymbol{v}_j)\, v_r \qquad (11.12a)$$

Using (11.9a), we have

$$m_i v_i^2 = m_i \left(\boldsymbol{V}_{\text{CM}} + \frac{m_j}{M_{ij}} \boldsymbol{v}_r \right)^2 = m_i V_{\text{CM}}^2 + 2 \frac{m_i m_j}{M_{ij}} \boldsymbol{V}_{\text{CM}} \cdot \boldsymbol{v}_r + m_i \left(\frac{m_j}{M_{ij}} \right)^2 v_r^2$$

$$m_j v_j^2 = m_j \left(\boldsymbol{V}_{\text{CM}} - \frac{m_i}{M_{ij}} \boldsymbol{v}_r \right)^2 = m_j V_{\text{CM}}^2 - 2 \frac{m_i m_j}{M_{ij}} \boldsymbol{V}_{\text{CM}} \cdot \boldsymbol{v}_r + m_j \left(\frac{m_i}{M_{ij}} \right)^2 v_r^2$$

$$\rightarrow \qquad m_i v_i^2 + m_j v_j^2 = M_{ij} V_{\text{CM}}^2 + \mu_{ij} v_r^2 \qquad (11.12b)$$

where

$$\mu_{ij} = \frac{m_i m_j}{M_{ij}} = \text{reduced mass} \qquad (11.12c)$$

Using (11.3) & (11.12b), we have

$$F(\boldsymbol{v}_i)\, F(\boldsymbol{v}_j) = \left(\frac{\sqrt{m_i m_j}\; \beta}{2\pi} \right)^3 \exp\left[-\frac{1}{2} \beta \left(m_i v_i^2 + m_j v_j^2 \right) \right]$$

$$= \left(\frac{\sqrt{m_i m_j}\; \beta}{2\pi} \right)^3 \exp\left[-\frac{1}{2} \beta \left(M_{ij} V_{\text{CM}}^2 + \mu_{ij} v_r^2 \right) \right]$$

so that (11.12a) becomes

$$\langle v_r \rangle_{ij} = \left(\frac{\sqrt{m_i m_j}\; \beta}{2\pi} \right)^3 \int d\, \boldsymbol{v}_r \int d\, \boldsymbol{V}_{\text{CM}}\; \exp\left[-\frac{1}{2} \beta \left(M_{ij} V_{\text{CM}}^2 + \mu_{ij} v_r^2 \right) \right] v_r$$

$$= \left(\frac{\mu_{ij} \beta}{2\pi} \right)^{3/2} \int d\, \boldsymbol{v}_r\; \exp\left(-\frac{1}{2} \beta\, \mu_{ij} v_r^2 \right) v_r$$

$$= \left(\frac{\mu_{ij} \beta}{2\pi} \right)^{3/2} 4\pi \int_0^\infty d\, v_r\, v_r^3\; \exp\left(-\frac{1}{2} \beta\, \mu_{ij} v_r^2 \right)$$

$$= \left(\frac{\mu_{ij} \beta}{2\pi} \right)^{3/2} \frac{8\pi}{\beta^2 \mu_{ij}^2}$$ [See *Mathematica* code below.]

$$= \left(\frac{8}{\pi \beta \mu_{ij}} \right)^{1/2} \qquad (11.13)$$

------------------------------- *Mathematica* code --

Assuming$\left[\beta > 0,\ \int_0^\infty e^{-\beta v^2/2}\, v^3\, dv\right]$

$$\frac{2}{\beta^2}$$

Consider now a type-j particle in its rest frame. In order for it to collide, within the next time interval τ, with a type-i particle travelling with relative velocity $\boldsymbol{v}_r$, the center of the type-i particle must be inside a region of volume $\pi d_{ij}^2 v_r \tau$ [see Fig.11.1a]. The number of such type-i particles is therefore $n_i \pi d_{ij}^2 v_r \tau$. Hence,

$$f_{ij} = n_i \pi d_{ij}^2 \langle v_r \rangle_{ij} \qquad (11.14)$$

= average number of type-i particle collisions the type-j particle suffers per unit time.

= collision frequency of type-i particles against a type-j particle.

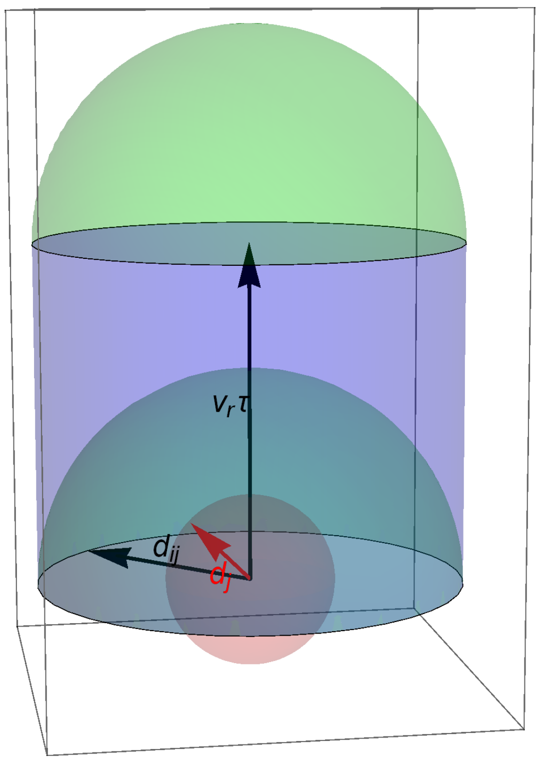

Fig.11.1a. Region $\mathcal{V}$ containing all type-i particles about to collide with the type-j particle (red sphere) is a cylinder (blue) with its end faces replaced by half-spheres (green). The cylinder has axis parallel to $\boldsymbol{v}_r$, radius d_{ij} and length $v_r \tau$. The center of the type-j particle is at the center of an end face of the cylinder. The volume of $\mathcal{V}$ is equal to that of the cylinder, namely, $\pi d_{ij}^2 v_r \tau$.

The total number of collisions between types i & j particles per unit time per unit volume is

$$\nu_{ij} = n_j f_{ij} = n_i n_j \pi d_{ij}^2 \langle v_r \rangle_{ij}$$

$$= n_i n_j \pi d_{ij}^2 \left(\frac{8}{\pi \beta \mu_{ij}} \right)^{1/2} \qquad \text{[(11.13) used.]} \qquad (11.15)$$

Using the same arguments, we get

$$\nu_{ii} = \frac{1}{2} n_i f_{ii} \qquad \text{[No implicit summations.]}$$

where the factor $\frac{1}{2}$ is inserted to compensate for the double counting of each particle: once as target, and once as incoming. Thus,

$$\nu_{ii} = \frac{1}{2} n_i^2 \pi d_{ii}^2 \langle v_r \rangle_{ii} = \frac{1}{2} n_i^2 \pi d_{ii}^2 \left(\frac{8}{\pi \beta \mu_{ii}} \right)^{1/2}$$

$$= \frac{1}{2} n_i^2 \pi d_{ii}^2 \left(\frac{16}{\pi \beta m_i} \right)^{1/2} \qquad \text{[(11.12c) used.]} \qquad (11.16)$$

For a gas of type A particles of average speed $\langle v \rangle$ and collision frequency f_{AA}, we have

$$\tau = \frac{1}{f_{AA}} = \text{time between collisions} = \text{relaxation time}$$

$$\lambda = \langle v \rangle \tau = \frac{\langle v \rangle}{f_{AA}} = \frac{\langle v \rangle}{n_A \pi d_{AA}^2 \langle v_r \rangle} \qquad (11.17a)$$

Now, with $\mathbf{v}_i$ & $\mathbf{v}_j$ representing the velocities of the incoming & target particles, respectively,

$$\langle v_r^2 \rangle = \langle (\mathbf{v}_i - \mathbf{v}_j)^2 \rangle = \langle v_i^2 + v_j^2 - 2\, \mathbf{v}_i \cdot \mathbf{v}_j \rangle$$

$$= \langle v_i^2 + v_j^2 \rangle \qquad \text{[Average over cosine of angle between } \mathbf{v}_i \text{ \& } \mathbf{v}_j \text{ vanishes.]}$$

$$= 2 \langle v^2 \rangle$$

$$\rightarrow \qquad \langle v_r \rangle = \sqrt{2}\, \langle v \rangle \qquad (11.17b)$$

(11.17a) thus becomes

$$\lambda = \frac{1}{\sqrt{2}\, n_A \pi d_{AA}^2} \qquad (11.17)$$