Collision Frequency and Mean Free Path

- Now that we have expression for the velocity distribution,

$$f_o(C_i) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mC^2}{2kT}}$$

- let's re-examine bimolecular collision rate expression (z_{AB})

$$z_{AB} = n_A n_B \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(C_i) f(Z_i) g \sigma_{AB}^T(g) dV_Z dV_C$$

- Goal is to find proper expressions for:
  1. **collision frequency** (θ)
  2. **mean free path** (λ)

Bimolecular Collision Rate

- Looking at Maxwellian terms

$$f_A(C_i) f_B(Z_i) = \left(\frac{m_A}{2\pi kT}\right)^{3/2} e^{-\frac{m_A C^2}{2kT}} \left(\frac{m_B}{2\pi kT}\right)^{3/2} e^{-\frac{m_B Z^2}{2kT}}$$

- Using previous results for COM coords.

$$m_{AB}^* \equiv \left(\frac{m_A m_B}{m_A + m_B}\right)$$

$$g \equiv \sqrt{(Z_1 - C_1)^2 + (Z_2 - C_2)^2 + (Z_3 - C_3)^2}$$

$$w_i = m_{AB}^* \left(\frac{C_i}{m_B} + \frac{Z_i}{m_A}\right)$$

- We have

$$e^{-\frac{m_A C^2}{2kT}} e^{-\frac{m_B Z^2}{2kT}} = e^{-\frac{(m_A C^2 + m_B Z^2)}{2kT}} = e^{-\frac{(m_A + m_B) w_i^2 + m_{AB}^* g^2}{2kT}}$$

$$\left(\frac{m_A}{2\pi kT}\right)^{3/2} \left(\frac{m_B}{2\pi kT}\right)^{3/2} = \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} \left(\frac{m_A + m_B}{2\pi kT}\right)^{3/2}$$

Bimolecular Collision Rate

- Inserting these into collision rate

$$z_{AB} = n_A n_B \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(C_i) f(Z_i) g \sigma_{AB}^T(g) dV_Z dV_C$$

$$= n_A n_B \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \left(\frac{m_A + m_B}{2\pi kT}\right)^{3/2} e^{-\frac{(m_A+m_B)w^2}{2kT}} \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} e^{-\frac{m_{AB}^* g^2}{2kT}} g\sigma_{AB}^T(g) \underbrace{dV_Z dV_C}_{= dV_w dV_g}$$

$$z_{AB} = n_A n_B \int_0^{\infty} \left(\frac{m_A + m_B}{2\pi kT}\right)^{3/2} e^{-\frac{(m_A+m_B)w^2}{2kT}} 4\pi w^2 dw$$

$$\times \int_0^{\infty} \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} e^{-\frac{m_{AB}^* g^2}{2kT}} g\sigma_{AB}^T(g) 4\pi g^2 dg$$

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$$dV_w = 4\pi w^2 dw$$

$$dV_g = 4\pi g^2 dg$$

Bimolecular Collision Rate

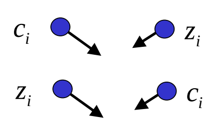
- First integral resembles

$$\int_0^{\infty} \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mw^2}{2kT}} 4\pi w^2 dw = \int_0^{\infty} \chi(w) dw = 1$$

- So

$$z_{AB} = n_A n_B \int_0^{\infty} \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} e^{-\frac{m_{AB}^*}{2kT}g^2} \sigma_{AB}^T(g) 4\pi g^3 dg$$

- What if A=B?
  - then inverting name of c_i and z_i double counts collision



$$z_{AB} = \frac{n_A n_B}{\delta_{AB}} \int_0^{\infty} \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} e^{-\frac{m_{AB}^*}{2kT}g^2} \sigma_{AB}^T(g) 4\pi g^3 dg \qquad \delta_{AB} = \begin{cases} 1 & A \neq B \\ 2 & A = B \end{cases}$$

Hard Sphere Example

- For hard, elastic spheres $\sigma_{AB}^{T}(g) = \pi d_{AB}^{2} \equiv \sigma_{AB}$

$$z_{AB} = \frac{n_A n_B}{\delta_{AB}} \sigma_{AB} \int_0^{\infty} \left(\frac{m_{AB}^*}{2\pi kT} \right)^{3/2} e^{-\frac{m_{AB}^*}{2kT} g^2} 4\pi g^3 dg$$

$$= \frac{n_A n_B}{\delta_{AB}} \frac{4\pi}{\pi^{3/2}} \sigma_{AB} \sqrt{\frac{2kT}{m_{AB}^*}} \int_0^{\infty} e^{-\left[\sqrt{\frac{m_{AB}^*}{2kT}} g\right]^2} \left[\sqrt{\frac{m_{AB}^*}{2kT}} g\right]^3 \left[\sqrt{\frac{m_{AB}^*}{2kT}} dg\right]$$

$$= \frac{n_A n_B}{\delta_{AB}} 4\sigma_{AB} \sqrt{\frac{2kT}{\pi m_{AB}^*}} \underbrace{\int_0^{\infty} y^3 e^{-y^2} dy}_{I_3(1) = 1/2}$$

Mean Relative Speed

$$z_{AB} = \frac{n_A n_B}{\delta_{AB}} \sigma_{AB} \sqrt{\frac{8kT}{\pi m_{AB}^*}} \qquad \overline{C} = \sqrt{\frac{8kT}{\pi m}} \qquad \boxed{z_{AB} = \frac{n_A n_B}{\delta_{AB}} \sigma_{AB} \overline{g}}$$

Collision Frequency

- Recall collision frequency $\theta_{AB} = \frac{z_{AB}}{n_A}$
  – number of coll./sec of one A molecule with all B's
  – also number of free paths of B molecules terminated by one A molecule per unit time
- For hard sphere $\boxed{\theta_{AB} = n_B \sigma_{AB} \overline{g}}$

What happened to δ_{AB}?

If A=B, then A-A collision terminates 2 free paths

- For multiple species present

$$\theta_A \equiv \sum_Y \theta_{AY} \quad \text{Y=all coll. partners, including A}$$

$$= \sum_Y n_Y \sigma_{AY} \overline{g}_{AY} \quad \text{hard spheres}$$

$$\overline{g} = \sqrt{\frac{8kT}{\pi m_{AY}^*}}$$

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Mean Free Path

- As before $\lambda_A = \frac{\overline{C}_A}{\theta_A}$ $\overline{C}_A = \sqrt{\frac{8kT}{\pi m_A}}$
- For single-species and hard sphere

$$\lambda = \frac{\overline{C}}{n\sigma\overline{g}} = \frac{\sqrt{1/m}}{n\sigma\sqrt{1/m^*}}$$

$$m^* = \left(\frac{mm}{m+m}\right) = \frac{m}{2}$$

$$\lambda = \frac{1}{n\sigma\sqrt{2}}$$