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Equilibrium Collision Rates

- 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})

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

  - in order to identify temperature dependence of integral
  - AND to find proper expressions for:
    1. **collision frequency** (θ)
    2. **mean free path** (λ)

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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 relating C_i and Z_i to center-of-mass velocity (w_i), relative velocity (g_i) and reduced mass (m^*_{AB})

$$C_i=w_i-\frac{m^*_{AB}}{m_A}g_i \qquad Z_i=w_i-\frac{m^*_{AB}}{m_B}g_i \qquad m^*_{AB}\equiv\left(\frac{m_A m_B}{m_A+m_B}\right)$$

- Then $e^{-\frac{m_A C^2}{2kT}}e^{-\frac{m_B Z^2}{2kT}}=e^{-\frac{(m_A C^2 m_B Z^2)}{2kT}}$

$$=e^{-\frac{(m_A+m_B)w^2 m^*_{AB}g^2}{2kT}}$$

$$m_A C^2=m_A w^2+\frac{m^{*2}_{AB}}{m_A}g^2-2m^*_{AB}wg$$

$$m_B Z^2=m_B w^2+\frac{m^{*2}_{AB}}{m_B}g^2+2m^*_{AB}wg$$

- and

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

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Bimolecular Collision Rate

- Inserting these into collision rate

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

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

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

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

V&K II.6.9, II.6.10

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

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

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Bimolecular Collision Rate

$$z_{AB} = \frac{n_A n_B}{\delta_{AB}} \left[\int_0^{\infty} \left(\frac{m_A+m_B}{2\pi kT}\right)^{3/2} e^{-\frac{(m_A+m_B)w^2}{2kT}} 4\pi w^2 dw\right] \int_0^{\infty} \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} e^{-\frac{m_{AB}^* g^2}{2kT}} g\sigma_{AB}^T(g) 4\pi g^2 dg$$

- First integral resembles

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

- So

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

Hard Sphere Example

- For hard, elastic spheres $\sigma^T_{AB}(g) = \pi d^2_{AB} \equiv \sigma_{AB}$

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

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

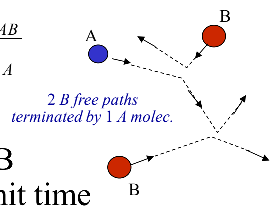
$$= \frac{n_A n_B}{\delta_{AB}} 4\sigma_{AB} \sqrt{\frac{2kT}{\pi m^*_{AB}}} \underbrace{\int_0^\infty y^3 e^{-y^2} dy}_{I_3(1)=1/2}$$

Mean Relative Speed $\bar{g} = \sqrt{\frac{8kT}{\pi m^*_{AB}}}$

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

Collision Frequency

- Recall collision frequency $\theta_{AB} = \frac{z_{AB}}{n_A}$
  - number of collisions/sec of one A molecule with **all** B's
  - it is also the number of free paths of B molecules terminated by one A per unit time



- For hard sphere $\boxed{\theta_{AB} = n_B \sigma_{AB} \bar{g}}$

What happened to δ_{AB}?

if A=B, then each A-A collision terminates 2 A free paths

- For multiple species present

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

$$= \sum_Y n_Y \sigma_{AY} \bar{g}_{AY} \quad \text{hard spheres} \qquad \bar{g} = \sqrt{\frac{8kT}{\pi m^*_{AY}}}$$

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Mean Free Path

- As before $\boxed{\lambda_A = \dfrac{\overline{C}_A}{\theta_A}}$ $\qquad \overline{C}_A = \sqrt{\dfrac{8kT}{\pi m_A}}$

- For single-species and hard sphere

$$\lambda = \frac{\overline{C}}{n\sigma\overline{g}} = \frac{\sqrt{1/m}}{n\sigma\sqrt{1/m^*}} \qquad m^* = \left(\frac{mm}{m+m}\right) = \frac{m}{2}$$

$$\lambda = \frac{1}{n\sigma\sqrt{2}} \quad \propto \frac{1}{n} \propto \frac{T}{p}$$