Differential (Bimolec.) Collision Rate

- What is the collision rate between our molecules?
  - $d\zeta_{AB} \equiv$ **differential collision rate**
    = number of collisions of A's of class c_i with B's of z_i with specific deflection angle (χ) *per unit time per unit vol.*

units: e.g., $cm^{-3}sec^{-1}$

- Depends on:
  1. number density of A molec. in c_i — $= n_A f(c_i)\, dV_c$
  2. number density of B molec. in z_i — $= n_B f(z_i)\, dV_z$
  3. relative speed approaching each other — $= g$
     - if moving slowly, long time between collisions
  4. effective "size" of molecules — $\equiv \sigma_{AB}$ **Differential Collision Cross-section**
     - small $\sigma_{AB} \Rightarrow$ no "collision" unless b small

Equil Kin Theory -7

Differential Cross-Section

- What does σ_{AB} depend on?
  1. molecular force fields (potentials)
     - strength and how molecular potentials vary with distance
  2. duration of interaction, and therefore g
     - higher g means less time for molecules to interact, and strength of interaction = impulse = $\int F\, dt$
  3. scattering angle, χ
     - recall $d\zeta_{AB}$ defined as rate of collisions that result in specific χ
  - therefore $\sigma_{AB}=\sigma_{AB}(g,\chi)$
- Cross-section can be defined by

$$\sigma_{AB}(g,\chi) = \frac{d\zeta_{AB}}{n_A n_B f(c_i) f(z_i) g\, dV_c\, dV_z\, d\Omega}$$

units: area (per solid angle), e.g., $cm^2(sr^{-1})$; numerator: $cm^{-3}sec^{-1}$; $n_A n_B f f\, dV_c dV_z$: cm^{-6}; g: cm/sec; $d\Omega$: sr

cross-section can be interpreted as probability that collision with relative speed g between chosen molecule classes results in deflection into $d\Omega$

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Differential Collision Rate

- So differential collision rate given by

$$d\zeta_{AB} = n_A n_B f(c_i) f(z_i) g \sigma_{AB}(g,\chi) dV_c dV_z d\Omega$$

  – however we required A and B to be distinguishable, if not, then overcounting number of collisions by 2×

$$d\zeta_{AB} = \frac{n_A n_B}{\delta_{AB}} f(c_i) f(z_i) g \sigma_{AB}(g,\chi) dV_c dV_z d\Omega$$

if A=B, δ_{AB}=2
else δ_{AB}=1

- Can also define **total collision cross-section**

units: area, e.g., cm^2

$$\sigma^T_{AB}(g) = \int_0^{4\pi} \sigma_{AB}(g,\chi) d\Omega$$

  – and (total) **bimolecular collision rate** by integrating over all scattering angles and velocity classes

$$z_{AB} = \frac{n_A n_B}{\delta_{AB}} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(c_i) f(z_i) g \sigma^T_{AB}(g) dV_c dV_z$$

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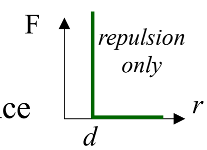
Cross-Section: Elastic Sphere Model

- Molecules are solid spheres
  – "billiard ball model"
  – specular reflection and no g dependence



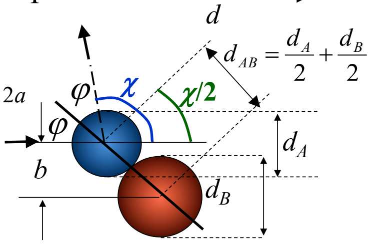
$$b = d_{AB} \cos(\chi/2)$$

$$\sigma_{AB} = \frac{b}{\sin\chi}\left|\frac{\partial b}{\partial \chi}\right|$$

$$\sin a \cos a = \tfrac{1}{2}\sin 2a$$

$$= \frac{d_{AB}\cos\chi/2}{\sin\chi}\frac{(-d_{AB})\sin\chi/2}{2}$$

$$= d_{AB}^2/4$$

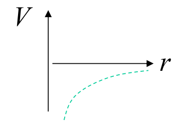


– integrate over $d\Omega$ (4π total steradians)

$$\sigma^T_{AB} = \pi d^2_{AB}$$

Cross-Section: Inverse Power Law

- Can also model attractive forces using simple power law model
  - attraction potential $\sim V = \frac{\omega}{r^{\alpha}}$



- Then can show (see V&K IX.8)

$$\sigma d\Omega = \sigma \sin\chi \, d\chi \, d\phi \qquad \chi = \pi - 2\int_0^{b/r_o} \sqrt{1 - \left(\frac{b}{r}\right)^2 - \frac{2}{\alpha}\left(\frac{b}{\beta r}\right)^{\alpha}} \, d\left(\frac{b}{r}\right)$$

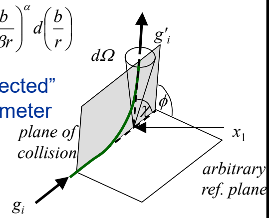
$$\chi = \chi(\beta)$$

large β produce small χ

$$\beta = b\left(\frac{mg^2/2}{\omega\alpha}\right)^{1/\alpha}$$

"energy corrected" impact parameter

$$\sigma d\Omega = \left(\frac{2\alpha\omega}{m}\right)^{2/\alpha} g^{-4/\alpha} \beta d\beta d\phi$$



- Then total cross-section

$$\sigma_{AB}^{T}(g) = 2\pi\left(\frac{2\alpha\omega}{m}\right)^{2/\alpha} g^{-4/\alpha} \int_0^{\infty} \sin^2\chi \, \beta \, d\beta$$

constants — only function of α

Cross-Section: Physical Interpretation

- As noted previously, cross-section is a measure of the "size" of molecules
  - region over which intermolecular forces act
  - larger $\sigma^T_{AB} \Rightarrow$ higher impact parameters (b) will still result in collision
- For elastic sphere model, it represents cross-sectional area of cylinder swept out by two molecules that can have limiting interaction
  - collision occurs only if impact parameter $b \le \boldsymbol{d_{AB}}$