Georgia Tech College of Engineering School of Aerospace Engineering

Equilibrium Velocity Distribution

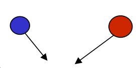
- Pressure and diffusion results were found without knowing the form of $f(c_i)$
  - just needed to know there was such a distribution, and that we assumed we were in equilibrium for p expression
- **What is f at equilibrium $\equiv f_o$?**
  - note: even when not in equilibrium, may be able to use $f = f_o + f'$ (small perturbation from equilibrium)
- Original approach taken by Maxwell used statistical argument and constraint equations
- Here we will employ physical approach based on collision rates, focus on bimolecular collisions

Georgia Tech College of Engineering School of Aerospace Engineering

Bimolecular Collisions

- Consider two molecules
  - molecule of species A and from velocity class c_i colliding with molecule of species B moving at z_i

$n_A, m_A, c_i\,dV_c$



$n_B, m_B, z_i\,dV_z$

  - collision occurs because force fields from the two molecules interact, causing a deflection
    - so collision involves momentum transfer
- Most convenient to analyze collision in **center-of-mass** coordinate system
  - center-of-mass velocity $\equiv w_i$

reduced mass $\equiv \frac{m_A m_B}{m_A + m_B}$

$$(m_A + m_B) w_i = m_A c_i + m_B z_i \Rightarrow w_i = \frac{m_A c_i + m_B z_i}{m_A + m_B} = m_{AB}^* \left[\frac{c_i}{m_B} + \frac{z_i}{m_A} \right]$$

Center of Mass Coordinates

- Can rewrite molecular velocities in CM coordinates

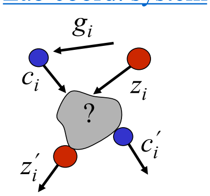
velocity in CM coord $\tilde{c}_i = c_i - w_i = c_i\left(1-\frac{m_{AB}^*}{m_B}\right) - z_i\frac{m_{AB}^*}{m_A} = \frac{m_{AB}^*}{m_A}\left(c_i - z_i\right) = \frac{m_{AB}^*}{m_A}\left(-g_i\right)$

  – similarly $\tilde{z}_i = z_i - w_i = \frac{m_{AB}^*}{m_B} g_i$

relative velocity $\equiv z_i - c_i$

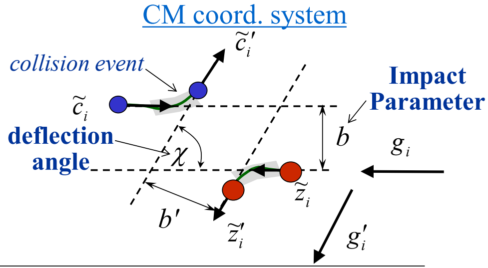
- Molecular motion in plane of collision

Lab coord. system



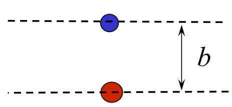
$' \Rightarrow$ *after collision*

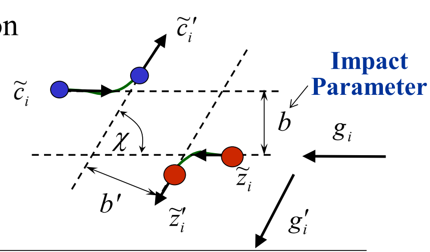
CM coord. system



Impact Parameter

- What does impact parameter (b) represent?
  – closest distance that would occur between centers of particles if no trajectory change
  – for larger b, less likely that a collision with large deflection angle (χ) would occur
    - $\chi = 0$ means no collision occurred
      – no momentum transferred between molecules





CM Collision Conservation Eqns

- Want to relate velocities after collision to before
  - **conserv. of momentum**

$$m_A\tilde{c}_i + m_B\tilde{z}_i = m^*_{AB}\left(-g_i\right) + m^*_{AB}\left(g_i\right) = 0$$

$$m_A\tilde{c}'_i + m_B\tilde{z}'_i = 0$$ *total mom. in CM coord = 0*

$$w_i = w'_i$$ *CM velocity constant (no external forces)*

  - **conserv. of energy** (elastic)

$$KE = \frac{1}{2}m_A c_i^2 + \frac{1}{2}m_b z_i^2 \qquad c_i^2 = \left(w_i - \frac{m^*_{AB}}{m_A}g_i\right)^2 \qquad z_i^2 = \left(w_i - \frac{m^*_{AB}}{m_B}g_i\right)^2$$

$$= \frac{1}{2}\left(m_A + m_B\right)w_i^2 + \frac{1}{2}m^*_{AB}g_i^2$$

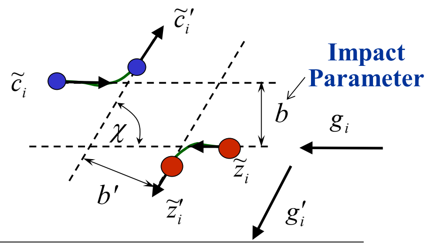
$$=$$

$$= \frac{1}{2}\left(m_A + m_B\right)w_i'^2 + \frac{1}{2}m^*_{AB}g_i'^2$$

relative speed unchanged $\Rightarrow \left|g_i\right| = \left|g'_i\right| \equiv g$

  - **conserv. angular mom.**

impact parameter unchanged $\left|g_i\right| b = \left|g'_i\right| b' \Rightarrow b = b'$



Differential Solid Angle

- Now look at collision in 3-d space
- Can define which part of space molecules "enter" after collision using **differential solid angle** of collision, $d\Omega$
  - solid angles have units of steradians (*sr*)

$$d\Omega = \sin\chi\, d\chi\, d\phi$$

$$\int_{all\ space} d\Omega = \int_0^{2\pi}\int_0^{\pi} \sin\chi\, d\chi d\phi$$

$$\Omega_{total} = -\cos\chi\Big|_0^{\pi}\phi\Big|_0^{2\pi}$$

$$= -\left(-1-1\right)2\pi$$

$$= 4\pi$$