Week 6

Enhancing Collision Theory

6.1 Threshold Energy and Line-Of-Centers Model

5/2: • Picking up from the previous lecture...

- It follows by plugging in the energy substitutions from last time that

$$u_r f(u_r)\,\mathrm{d}u_r = \left(\frac{2}{k_\mathrm{B}T}\right)^{3/2}\left(\frac{1}{\mu\pi}\right)^{1/2} E_r \mathrm{e}^{-E_r/k_\mathrm{B}T}\,\mathrm{d}E_r$$

- Thus,

$$\begin{aligned}
k &= \int_0^\infty \mathrm{d}u_r\, f(u_r)k(u_r)\\
&= \left(\frac{2}{k_\mathrm{B}T}\right)^{3/2}\left(\frac{1}{\mu\pi}\right)^{1/2}\int_0^\infty \mathrm{d}E_r\, E_r\mathrm{e}^{-E_r/k_\mathrm{B}T}\sigma_r(E_r)
\end{aligned}$$

- Now assume that only those collisions for which the relative kinetic energy exceeds a threshold energy E_0 result in a collision. Thus, define

$$\sigma_r(E_r) = \begin{cases} 0 & E_r < E_0\\ \pi d_\mathrm{AB}^2 & E_r \geq E_0 \end{cases}$$

- Consequently,

$$\begin{aligned}
k &= \left(\frac{2}{k_\mathrm{B}T}\right)^{3/2}\left(\frac{1}{\mu\pi}\right)^{1/2}\int_{E_0}^\infty \mathrm{d}E_r\, E_r\mathrm{e}^{-E_r/k_\mathrm{B}T}\pi d_\mathrm{AB}^2\\
&= \left(\frac{8k_\mathrm{B}T}{\mu\pi}\right)^{1/2}\pi d_\mathrm{AB}^2\mathrm{e}^{-E_0/k_\mathrm{B}T}\left(1+\frac{E_0}{k_\mathrm{B}T}\right)\\
&= \langle u_r\rangle\,\sigma_\mathrm{AB}\mathrm{e}^{-E_0/k_\mathrm{B}T}\left(1+\frac{E_0}{k_\mathrm{B}T}\right)
\end{aligned}$$

- We can use

$$E_a = k_\mathrm{B}T^2\frac{\mathrm{d}\ln k}{\mathrm{d}T}$$

  to relate the above to the activation energy.

• Another simplification we've made is that the reaction cross section is not constant, but actually depends on relative speed.

- Accounting for the collision geometry between the two hard spheres gives rise to the **line-of-centers model**.
- **Line-of-centers model**: A model for $\sigma_r(E_r)$ in which the cross section depends on the component of the relative kinetic energy that lies along the line that joins the centers of the colliding molecules.

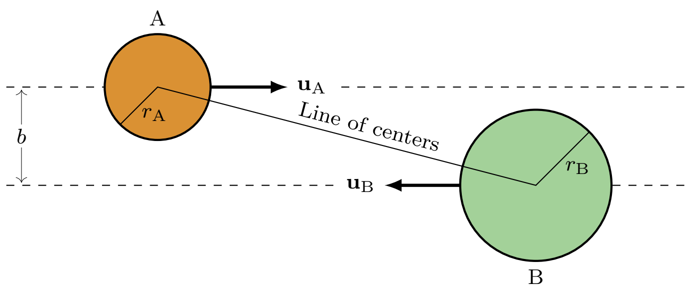

Figure 6.1: Line-of-centers model.

  - If we denote the relative kinetic energy along the line of centers by E_{loc}, then we are assuming that a reaction occurs when $E_{loc} > 0$.
  - The main thrust of this model is that we are redefining E_r instead of $\sigma_r(E_r)$ overall.
- The line-of-centers model asserts that two molecules will collide only if the **impact parameter** is less than the sum of the radii of the colliding molecules.
  - In particular, we (re)define

$$\sigma_r(E_r) = \begin{cases} 0 & E_r < E_0 \\ \pi d_\mathrm{AB}^2 \left(1 - \frac{E_0}{E_r}\right) & \end{cases}$$

  - It follows from math similar to the above that

$$\begin{aligned} k &= \left(\frac{2}{k_\mathrm{B}T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} \int_0^\infty \mathrm{d}E_r \, E_r \mathrm{e}^{-E_r/k_\mathrm{B}T} \sigma_r(E_r) \\ &= \left(\frac{8k_\mathrm{B}T}{\mu\pi}\right)^{1/2} \pi d_\mathrm{AB}^2 \mathrm{e}^{-E_0/k_\mathrm{B}T} \\ &= \langle u_r \rangle \, \sigma_\mathrm{AB} \mathrm{e}^{-E_0/k_\mathrm{B}T} \end{aligned}$$

- **Impact parameter**: The perpendicular distance between the two dashed lines in Figure 6.1. *Denoted by* $\boldsymbol{b}$.
- The cross section exhibits a threshold energy.
  - The dependence of the reaction cross section on the relative kinetic energy of the collision is consistent with the line-of-centers model.
- Relating E_0 to the Arrhenius equation parameters.
  - For the activation energy E_a, we have

$$\begin{aligned} E_a &= k_\mathrm{B}T^2 \frac{\mathrm{d} \ln k}{\mathrm{d}T} \\ &= k_\mathrm{B}T^2 \frac{\mathrm{d}}{\mathrm{d}T} \left\{ \ln \left[\left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{1/2} \pi d_\mathrm{AB}^2 \right] - \frac{E_0}{k_\mathrm{B}T} \right\} \end{aligned}$$

$$
\begin{aligned}
&= k_\mathrm{B}T^2\frac{\mathrm{d}}{\mathrm{d}T}\left\{\ln T^{1/2} - \frac{E_0}{k_\mathrm{B}T} + \text{terms not involving } T\right\} \\
&= E_0 + \frac{1}{2}k_\mathrm{B}T
\end{aligned}
$$

- Tian wants us to memorize the last line above.

– Considering the line-of-centers collision model and the Arrhenius equation yields

$$A = \langle u_r\rangle\,\sigma_\mathrm{AB}\mathrm{e}^{1/2}$$

- Tian goes through a practice problem.

6.2 Isotropy, Internal Energy, and Center of Mass Assumptions

5/4: • Doing away with the assumption that the spheres are isotropic.

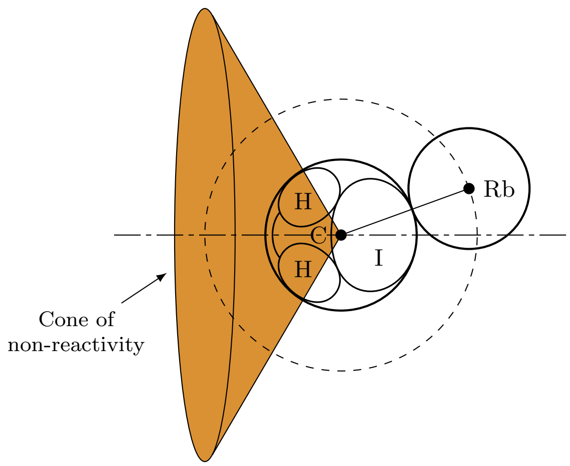

Figure 6.2: Molecules are not isotropic.

– Consider the reaction

$$\mathrm{Rb\,(g) + CH_3I\,(g) \Longrightarrow RbI\,(g) + CH_3\,(g)}$$

– The rubidium atom must collide with the iodomethane in the vicinity of the iodine atom for a reaction to occur.

– Indeed, many molecules have a **cone of non-reactivity**.

- Additionally, the internal energy of the reactants can affect the cross section of a reaction.

– Consider the reaction

$$\mathrm{{H_2}^+\,(g) + He\,(g) \Longrightarrow HeH^+\,(g) + H\,(g)}$$

– As the reactant molecule ${H_2}^+$ passes through different vibrational states, its reaction cross section changes.

– We only need to understand that other types of energy can have an effect qualitatively; we do not need to work with the shape of the curves quantitatively.

- A reactive collision can be described in a center-of-mass coordinate system.

– Consider the collision and subsequent scattering process for the bimolecular reaction

$$\mathrm{A\,(g) + B\,(g) \Longrightarrow C\,(g) + D\,(g)}$$

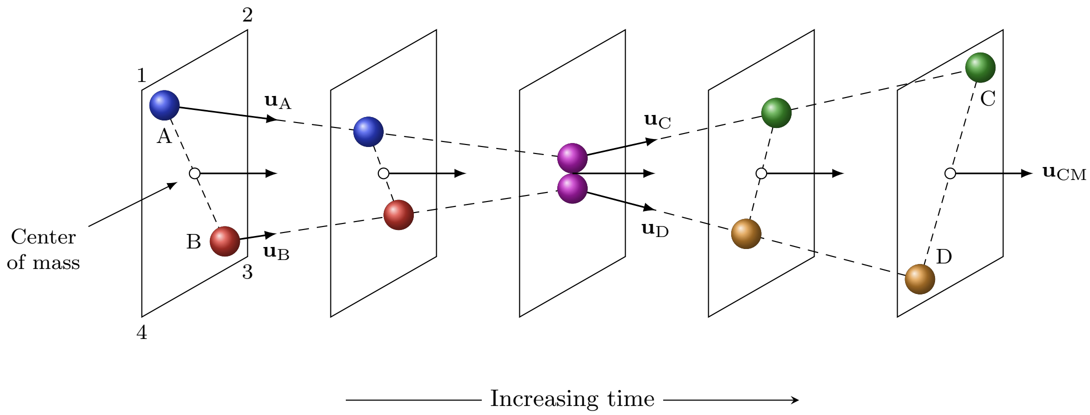

Figure 6.3: Center-of-mass coordinate system.

- Before the collision, A and B are traveling with velocities $\mathbf{u}_{\mathrm{A}}$ and $\mathbf{u}_{\mathrm{B}}$, respectively.
- The collision generates molecules C and D, which then move away from each other with velocities $\mathbf{u}_{\mathrm{C}}$ and $\mathbf{u}_{\mathrm{D}}$, respectively.
- $\mathbf{R}$, the location of the center of mass, is given by

$$\mathbf{R} = \frac{m_{\mathrm{A}}\mathbf{r}_{\mathrm{A}} + m_{\mathrm{B}}\mathbf{r}_{\mathrm{B}}}{M} \qquad\qquad M = m_{\mathrm{A}} + m_{\mathrm{B}}$$

- The velocity $\mathbf{u}_{\mathrm{cm}}$ of the center of mass is the time derivative of the position vector. Therefore, it is given by

$$\mathbf{u}_{\mathrm{cm}} = \frac{m_{\mathrm{A}}\mathbf{u}_{\mathrm{A}} + m_{\mathrm{B}}\mathbf{u}_{\mathrm{B}}}{M}$$

- We assume that this is an elastic collision (thus, energy is conserved).
- The total kinetic energy is given by

$$\mathrm{KE}_{\mathrm{react}} = \frac{1}{2}m_{\mathrm{A}}u_{\mathrm{A}}^2 + \frac{1}{2}m_{\mathrm{B}}u_{\mathrm{B}}^2$$

- Combining the fact that the relative speed of the two molecules is given by $\mathbf{u}_{\mathrm{r}} = \mathbf{u}_{\mathrm{A}} - \mathbf{u}_{\mathrm{B}}$ with the definition of $\mathbf{u}_{\mathrm{cm}}$ yields

$$\mathbf{u}_{\mathrm{A}} = \mathbf{u}_{\mathrm{cm}} + \frac{m_{\mathrm{B}}}{M}\mathbf{u}_{\mathrm{r}} \qquad\qquad \mathbf{u}_{\mathrm{B}} = \mathbf{u}_{\mathrm{cm}} - \frac{m_{\mathrm{A}}}{M}\mathbf{u}_{\mathrm{r}}$$

  - Note that the change in plus to minus sign between the two above forms hails from our definition of relative speed as A minus B and not the other way around (as we could also very well define it). In other words, it's just a convention thing, and all that matters is that we're consistent.
- It follows that

$$\begin{aligned}\mathrm{KE}_{\mathrm{react}} &= \frac{m_{\mathrm{A}}}{2}\left(\mathbf{u}_{\mathrm{cm}} + \frac{m_{\mathrm{B}}}{M}\mathbf{u}_{\mathrm{r}}\right)^2 + \frac{m_{\mathrm{B}}}{2}\left(\mathbf{u}_{\mathrm{cm}} - \frac{m_{\mathrm{A}}}{M}\mathbf{u}_{\mathrm{r}}\right)^2 \\ &= \frac{1}{2}Mu_{\mathrm{cm}}^2 + \frac{1}{2}\mu u_{\mathrm{r}}^2\end{aligned}$$

- Thus, the kinetic energy is composed of two contributions: one due to the motion of the center of mass, and one due to the relative motion of the two colliding molecules.
- We can do a similar analysis for the products to determine that

$$\mathrm{KE}_{\mathrm{prod}} = \frac{1}{2}Mu_{\mathrm{cm}}^2 + \frac{1}{2}\mu' {u_{\mathrm{r}}'}^2$$

- Note that momentum is conserved, i.e.,

$$m_{\mathrm{A}}\mathbf{u}_{\mathrm{A}} + m_{\mathrm{B}}\mathbf{u}_{\mathrm{B}} = m_{\mathrm{C}}\mathbf{u}_{\mathrm{C}} + m_{\mathrm{D}}\mathbf{u}_{\mathrm{D}}$$

- This implies that $\mathbf{u}_{\mathrm{cm}}$ does not change from reactants to products.
- The energy associated with the motion of the center of mass is therefore constant, and we will ignore its constant contribution to the total kinetic energy.

$$E_{\mathrm{react,int}} + \frac{1}{2}\mu u_{\mathrm{r}}^2 = E_{\mathrm{prod,int}} + \frac{1}{2}\mu' {u_{\mathrm{r}}'}^2$$

  - $E_{\mathrm{react,int}}$ and $E_{\mathrm{prod,int}}$ are the total internal energies of the reactants and products, respectively.
  - This internal energy takes into account all the degrees of freedom other than translation.