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.

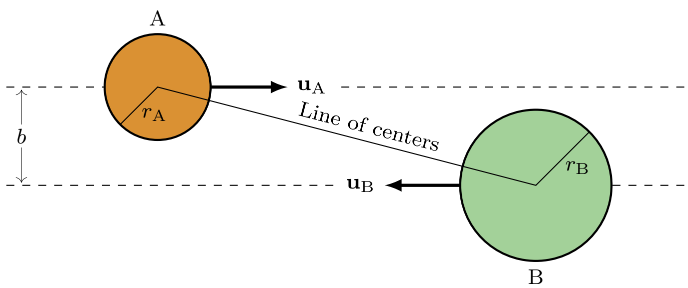

Figure 6.1: Line-of-centers model.

  - 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.