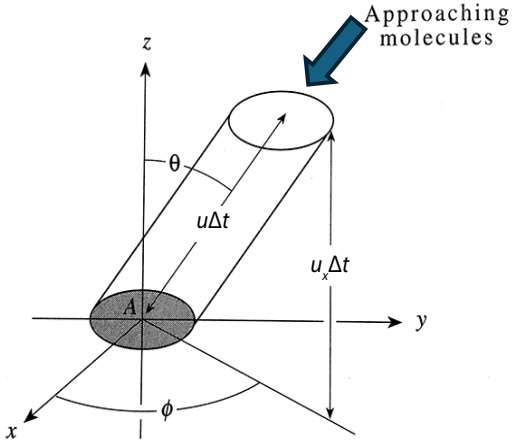
Kinetics & Dynamics of Chemical Reactions

Course CH-310

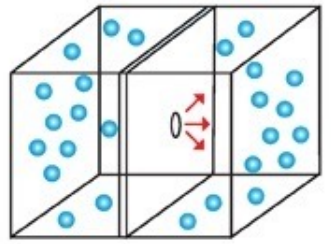
Prof. Sascha Feldmann

Recap from last session

- Collisions with a wall
  - collision flux $z_{\text{coll}} = \frac{\rho}{4}\langle u \rangle = \sqrt{\frac{k_B T}{2\pi\, m}}\rho$ [$s^{-1}m^{-2}$]



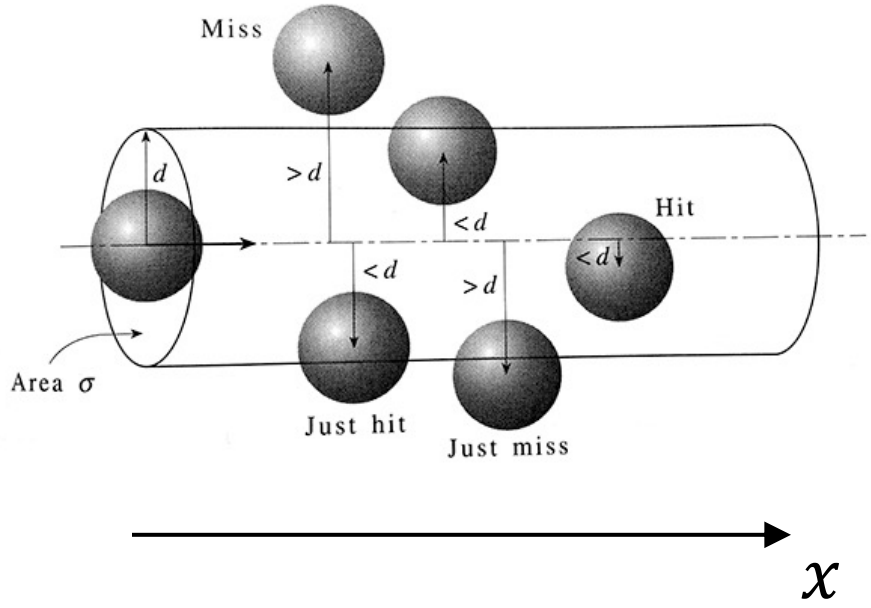
- Effusion
  - low pressure, small hole vs. large mean free path
  - effusion rate $k_{\text{effusion}} = z_{\text{coll}}\, A = \frac{pA}{\sqrt{2\pi m k_B T}}$ [s^{-1}]
  - Knudsen method to measure vapor pressure of liquids



Recap from last session

- Collision rate $z_A = \rho\sigma\langle u_{AB}\rangle = \rho\sigma\sqrt{2}\langle u\rangle$

$$= \sqrt{2}\rho\sigma\sqrt{\frac{8k_BT}{\pi m}} = \rho\sigma\sqrt{\frac{8k_BT}{\pi\mu}}$$



- Mean free path $l = \frac{\langle u\rangle}{z_A} = \frac{1}{\sqrt{2}\rho\sigma}$ [m]

  - number of unscattered molecules as they pass through the volume of other particles and scatter decays as:

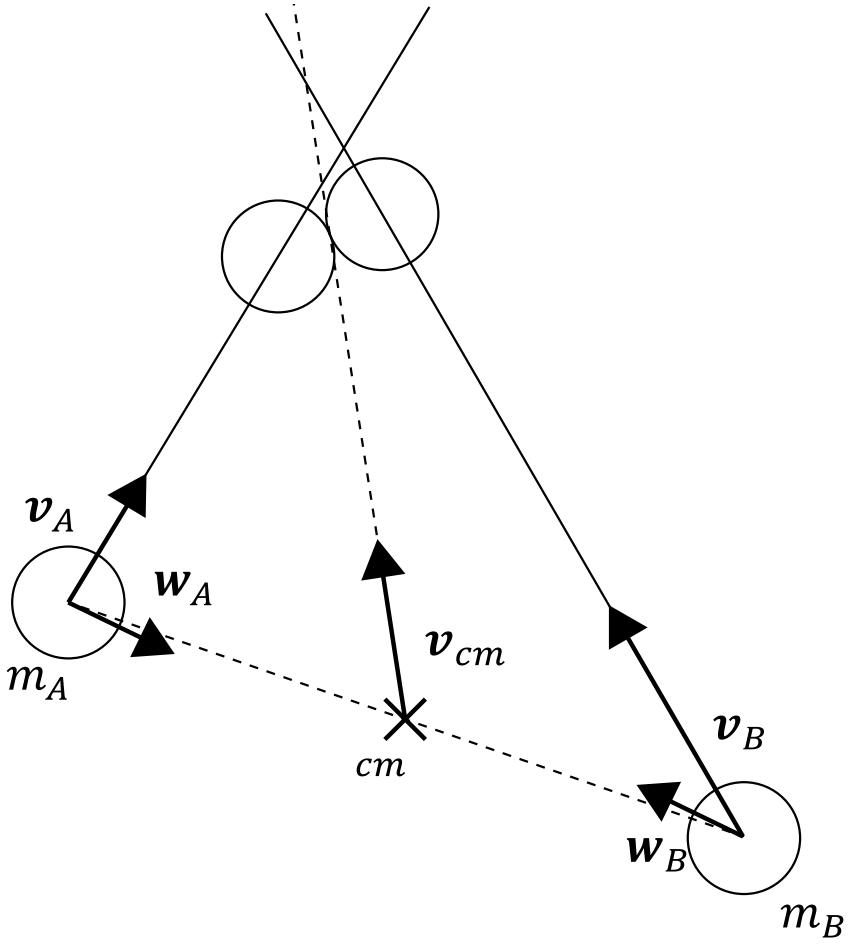
$$n(x) = n_0 e^{-\sigma\rho x} = n_0 e^{-\frac{x}{l}}$$

5.4 Center of mass coordinates

- Useful for collisions, so we derive the coordinate transformation:

$$(\boldsymbol{v}_A, \boldsymbol{v}_B) \rightarrow (\boldsymbol{v}_{cm}, \boldsymbol{w}_{AB})$$

- center of mass velocity $\boldsymbol{v}_{cm}$
- relative velocity $\boldsymbol{w}_{AB}$



- Position vector of center of mass:

$$\boldsymbol{r}_{cm} = \frac{m_A \boldsymbol{r}_A + m_B \boldsymbol{r}_B}{m_A + m_B}$$

- Velocity of *cm*? Time derivative:

$$\frac{d\boldsymbol{r}_{cm}}{dt} = \boldsymbol{v}_{cm} = \frac{m_A \boldsymbol{v}_A + m_B \boldsymbol{v}_B}{m_A + m_B}$$

- Center of mass velocity: $\boldsymbol{v}_{cm} = \frac{m_A \boldsymbol{v}_A + m_B \boldsymbol{v}_B}{m_A + m_B}$
- Subtract this from velocities of molecules to give their relative velocities in a new *center of mass frame* (moving coordinate system):

$$\boldsymbol{w}_A = \boldsymbol{v}_A - \boldsymbol{v}_{cm}$$

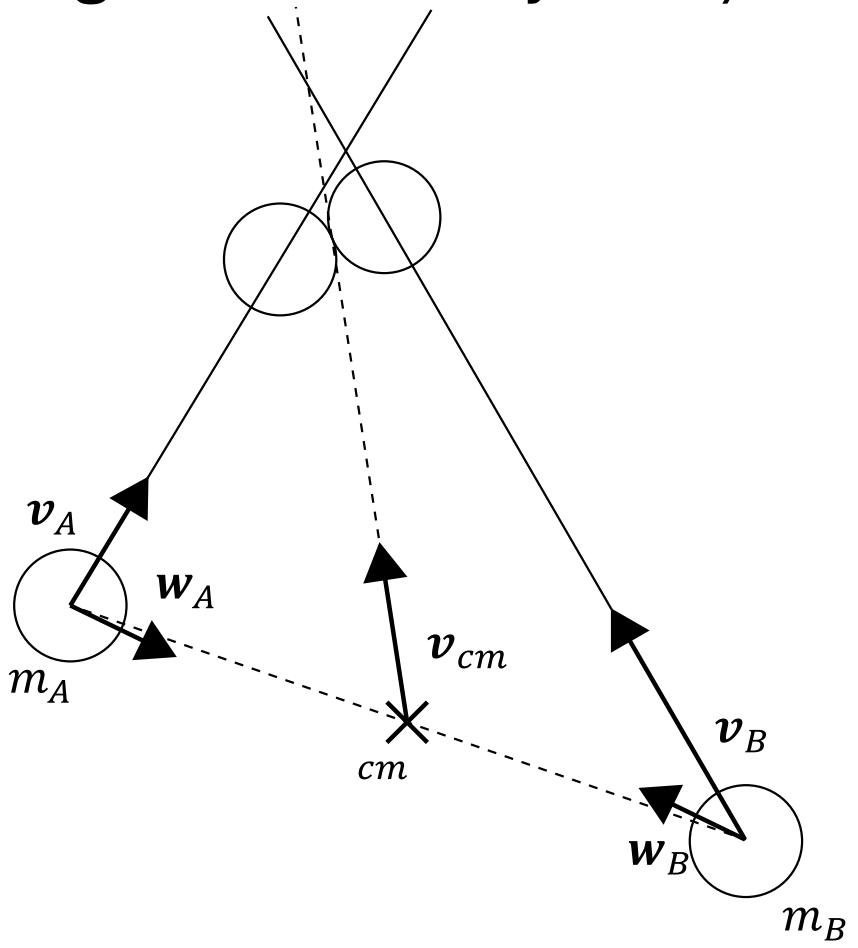
$$\boldsymbol{w}_B = \boldsymbol{v}_B - \boldsymbol{v}_{cm}$$

- Rewrite:

$$\boldsymbol{v}_A = \boldsymbol{v}_{cm} + \boldsymbol{w}_A \quad , \quad \boldsymbol{v}_B = \boldsymbol{v}_{cm} + \boldsymbol{w}_B$$

- Replace $\boldsymbol{w}_A$ and $\boldsymbol{w}_B$ for relative velocity:

$$\boldsymbol{v}_A - \boldsymbol{v}_B = \boldsymbol{w}_A - \boldsymbol{w}_B = \boldsymbol{v}_{AB} = \boldsymbol{w}_{AB}$$



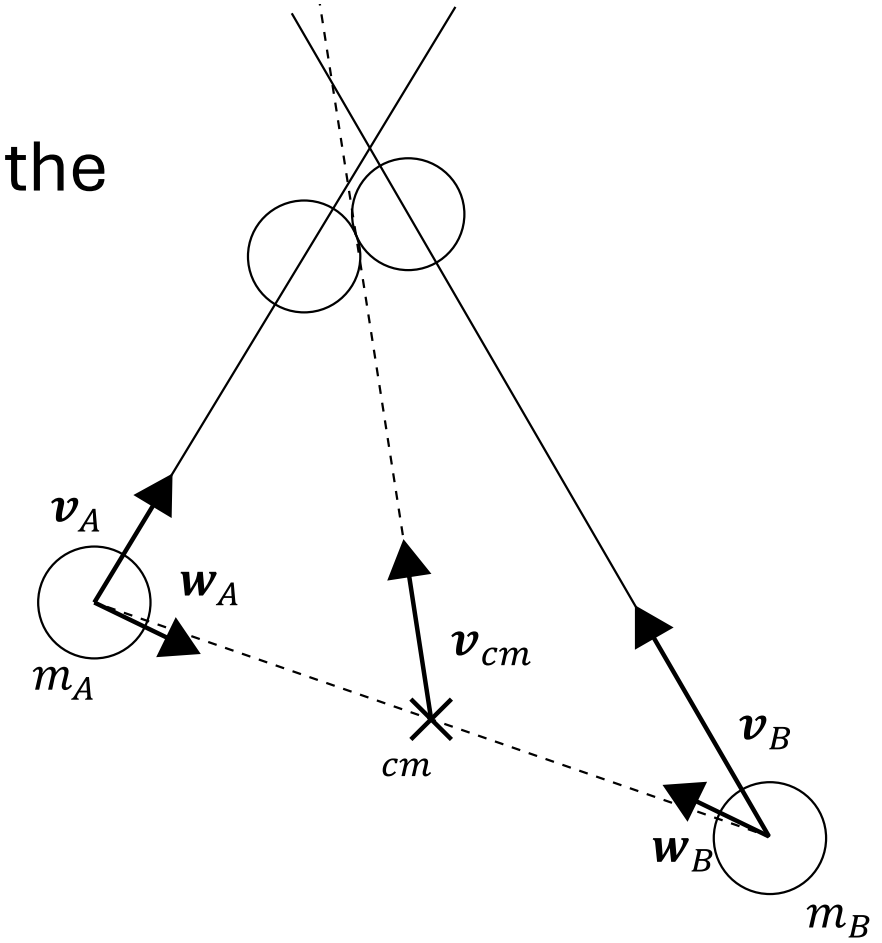
- What is the sum of all momenta within the center of mass frame?

$$m_A\boldsymbol{w}_A + m_B\boldsymbol{w}_B = m_A(\boldsymbol{v}_A - \boldsymbol{v}_{cm}) + m_B(\boldsymbol{v}_B - \boldsymbol{v}_{cm})$$
$$= m_A\boldsymbol{v}_A + m_B\boldsymbol{v}_B - (m_A + m_B)\boldsymbol{v}_{cm}$$
$$= \mathbf{0} \qquad \text{(zero!)}$$

- We can use this to eliminate $\boldsymbol{w}_A$ or $\boldsymbol{w}_B$ from the equation $\boldsymbol{w}_{AB} = \boldsymbol{w}_A - \boldsymbol{w}_B$ to obtain:

$$\boldsymbol{w}_{AB} = \boldsymbol{w}_A + \frac{m_A}{m_B}\boldsymbol{w}_A = m_A\boldsymbol{w}_A \underbrace{\frac{m_A+m_B}{m_A m_B}}_{\frac{1}{\mu}}$$

- Reduced mass: $\mu = \dfrac{m_A m_B}{m_A+m_B}$
- Thus: $\mu\boldsymbol{w}_{AB} = m_A\boldsymbol{w}_A = -m_B\boldsymbol{w}_B$



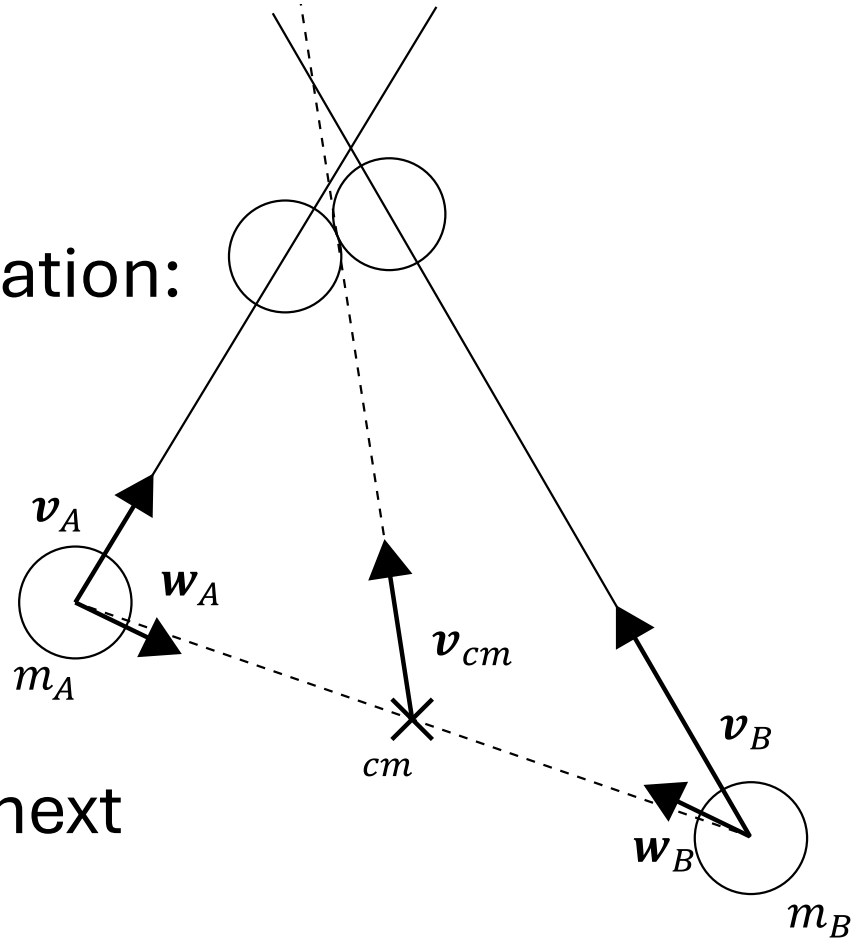
$$\mu \boldsymbol{w}_{AB} = m_A \boldsymbol{w}_A = -m_B \boldsymbol{w}_B$$

- earlier, we found

$$\boldsymbol{v}_A = \boldsymbol{v}_{cm} + \boldsymbol{w}_A \quad , \quad \boldsymbol{v}_B = \boldsymbol{v}_{cm} + \boldsymbol{w}_B$$

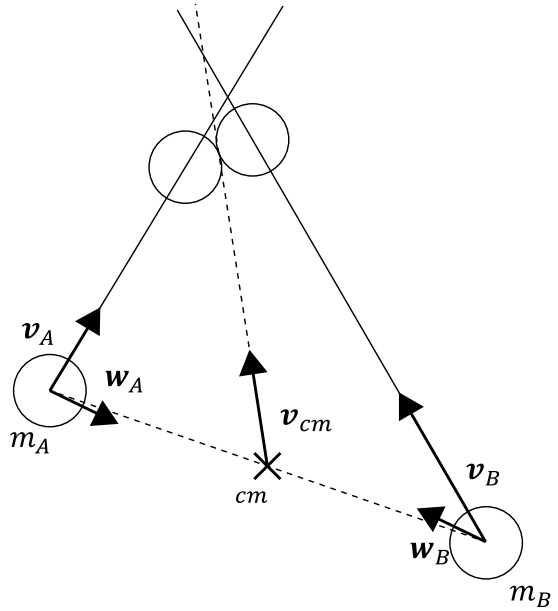
- So we can describe the coordinate transformation:

$$\boldsymbol{v}_A = \boldsymbol{v}_{cm} + \mu \boldsymbol{w}_{AB}/m_A$$
$$\boldsymbol{v}_B = \boldsymbol{v}_{cm} - \mu \boldsymbol{w}_{AB}/m_B$$



- Let's look at the kinetic energy of the system next

$$\boldsymbol{v}_A = \boldsymbol{v}_{cm} + \mu \boldsymbol{w}_{AB}/m_A$$
$$\boldsymbol{v}_B = \boldsymbol{v}_{cm} - \mu \boldsymbol{w}_{AB}/m_B$$



- Kinetic energy of the system:

$$E_{\text{kin}} = \frac{1}{2} m_A \boldsymbol{v}_A^2 + \frac{1}{2} m_B \boldsymbol{v}_B^2$$

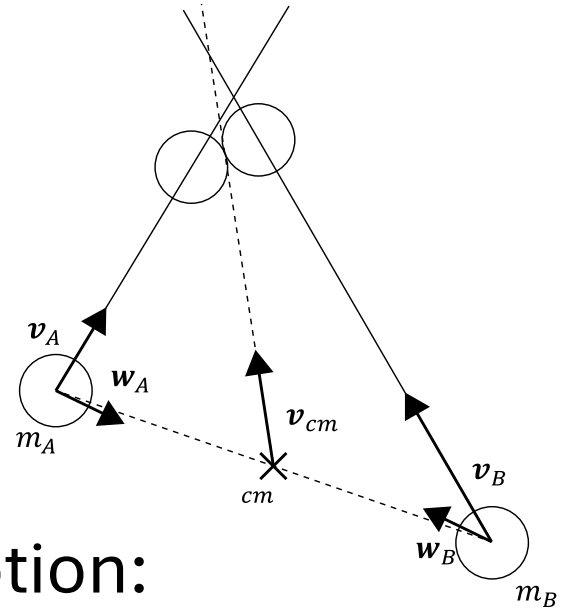
$$= \frac{1}{2} m_A \left(\boldsymbol{v}_{cm} + \frac{\mu \boldsymbol{w}_{AB}}{m_A} \right)^2 + \frac{1}{2} m_B \left(\boldsymbol{v}_{cm} - \frac{\mu \boldsymbol{w}_{AB}}{m_B} \right)^2$$

$$= \frac{1}{2} (m_A + m_B) v_{cm}^2 + \frac{1}{2} \mu w_{AB}^2 + \boldsymbol{v}_{cm} \mu \boldsymbol{w}_{AB} - \boldsymbol{v}_{cm} \mu \boldsymbol{w}_{AB}$$

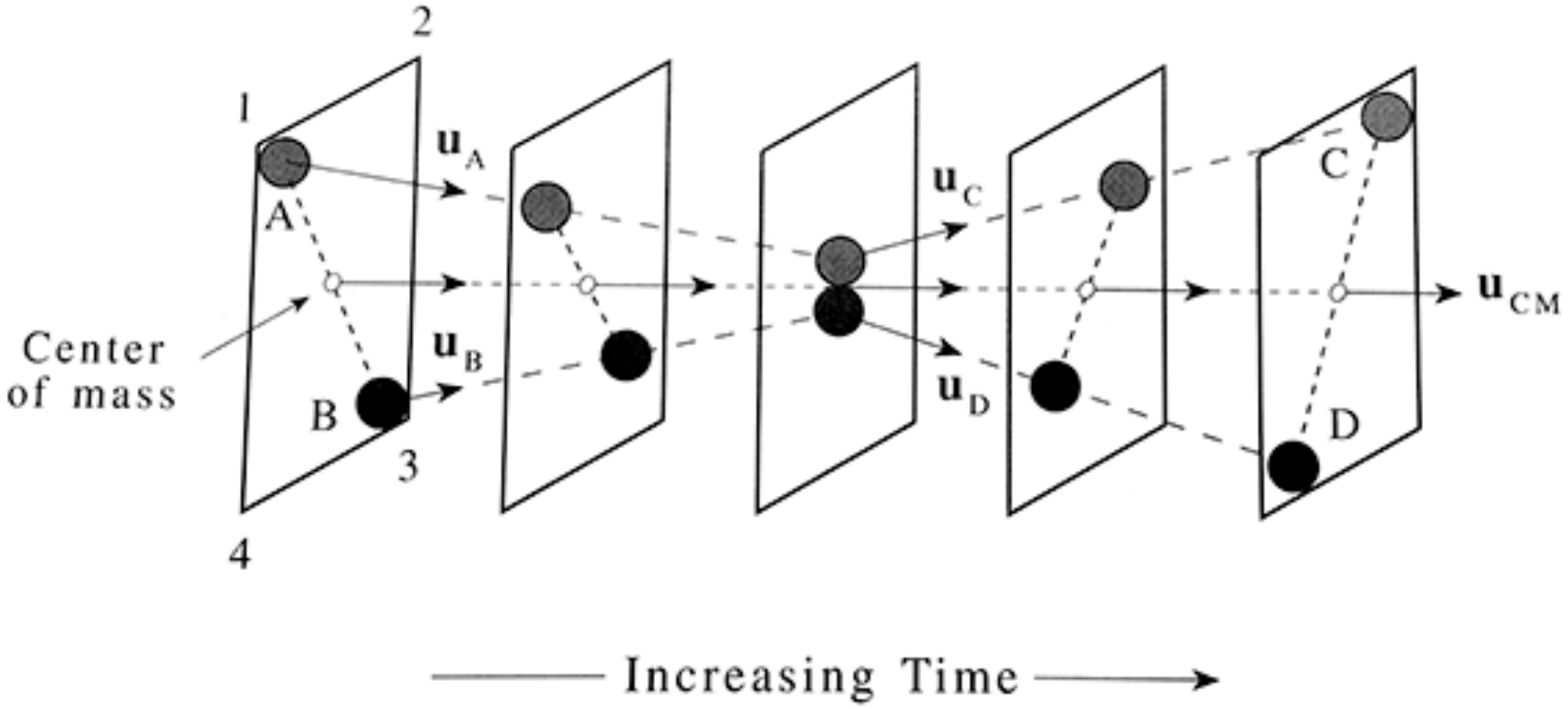
$$= \frac{1}{2} (m_A + m_B) v_{cm}^2 + \frac{1}{2} \mu v_{AB}^2$$ what do these terms mean?

$$= E_{\text{kin, cm}} + E_{\text{kin, AB}}$$

$$E_{\text{kin}} = \frac{1}{2}(m_A + m_B)v_{cm}^2 + \frac{1}{2}\mu v_{AB}^2 = E_{\text{kin, cm}} + E_{\text{kin, AB}}$$



- We can view a collision as the relative motion of the two molecules superimposed on the center of mass motion:

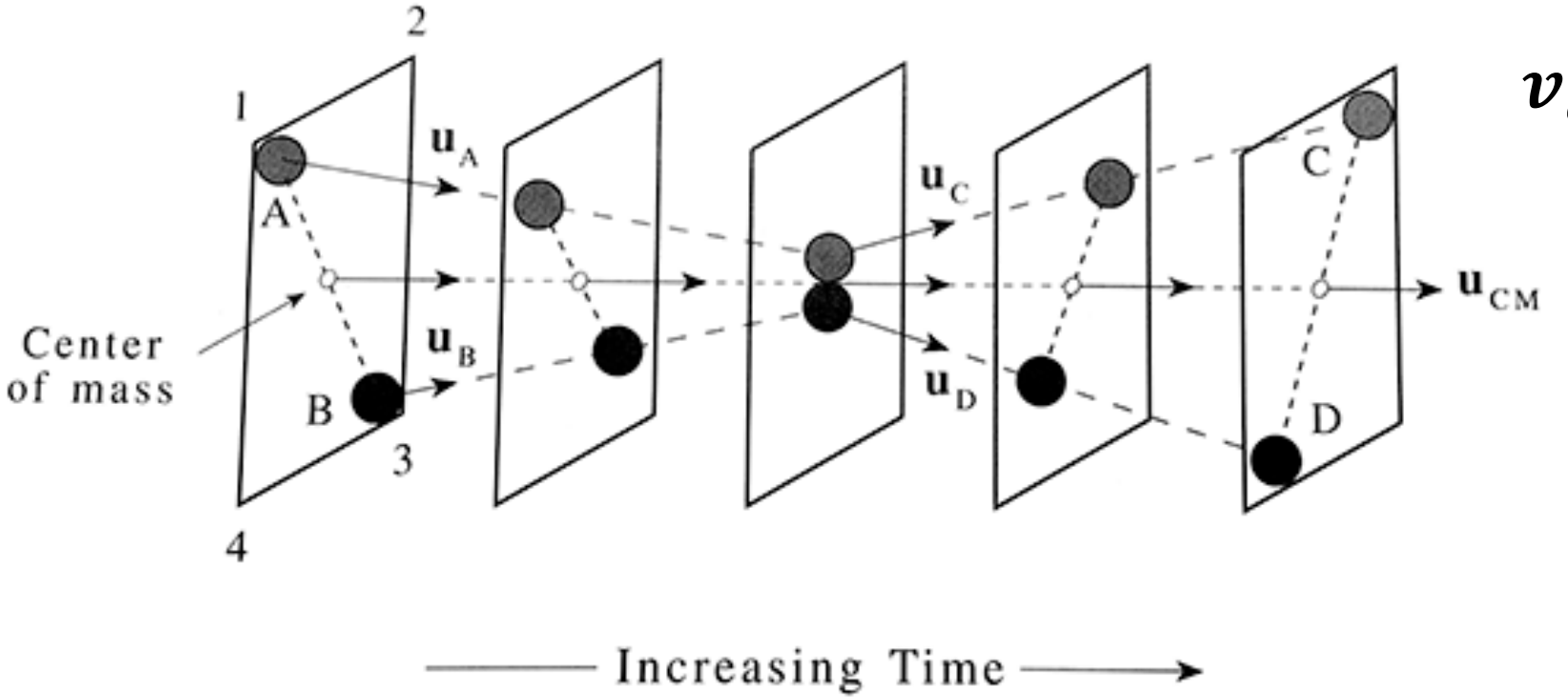


What do you notice?

- The center of mass velocity remains *unchanged* after collision!
- It now corresponds to that of the product molecules C and D (with potentially changed individual masses from A and B):

$$\boldsymbol{v}_{cm} = \frac{m_C \boldsymbol{v}_C + m_D \boldsymbol{v}_D}{m_C + m_D}$$

- Total momentum is conserved: $m_C \boldsymbol{v}_C + m_D \boldsymbol{v}_D = m_A \boldsymbol{v}_A + m_B \boldsymbol{v}_B$



$\boldsymbol{v}_{cm} = const.$

we can neglect c.m. motion in describing the reaction ☺

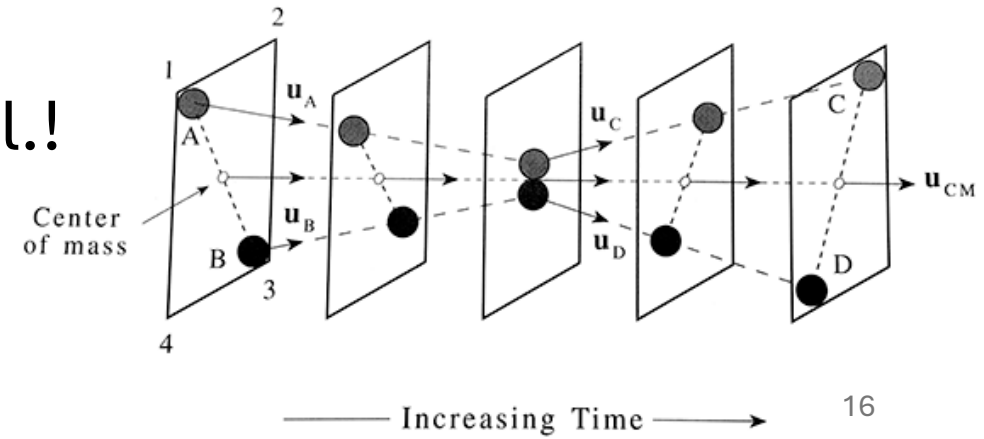
- Kinetic energy of center of mass motion *also* remains unchanged:

$$E_{\text{kin, cm}} = \frac{1}{2}(m_A + m_B)\boldsymbol{v}_{cm}^2 = const.$$

- Can be neglected when describing chemical reactions, so only the kinetic energy associated with the *relative* motion is available for the reaction: $E_{\text{kin, AB}} = \frac{1}{2}\mu\boldsymbol{v}_{AB}^2$
- Relative velocity may change during collision, but the *sum* of relative kinetic energy and internal energy must remain constant:

$$E_{\text{internal, A,B}} + E_{\text{kin, AB}} = E_{\text{internal, C,D}} + E_{\text{kin, CD}} = const.$$

- note: if E_{internal} affected→ *inelastic* coll.!



- Next: we calculate the average relative velocities of the two collision partners – what distribution do we use for this?
- Product of the Maxwell-Boltzmann distributions of the two molecules:

$$f\left(v_{Ax}, v_{Ay}, v_{Az}, v_{Bx}, v_{By}, v_{Bz}\right) dv_{Ax} dv_{Ay} dv_{Az} dv_{Bx} dv_{By} dv_{Bz}$$

$$= \frac{(m_A m_B)^{\frac{3}{2}}}{(2\pi k_B T)^3} e^{-\frac{m_A v_A^2 + m_B v_B^2}{2 k_B T}} \xrightarrow{\text{c.m. frame}} (m_A + m_B) v_{cm}^2 + \mu v_{AB}^2$$

$$dv_{Ax} dv_{Ay} dv_{Az} dv_{Bx} dv_{By} dv_{Bz}$$

- Now we move to the *center of mass coordinate frame*:

$$f\left(v_{cm,x}, v_{cm,y}, v_{cm,z}, v_{ABx}, v_{ABy}, v_{ABz}\right) dv_{cm,x} dv_{cm,y} dv_{cm,z} dv_{AB,x} dv_{AB,y} dv_{AB,z}$$

$$= \frac{(m_A m_B)^{\frac{3}{2}}}{(2\pi k_B T)^3} e^{-\frac{(m_A + m_B) v_{cm}^2 + \mu v_{AB}^2}{2 k_B T}} dv_{cm,x} dv_{cm,y} dv_{cm,z} dv_{AB,x} dv_{AB,y} dv_{AB,z}$$

$$f\left(v_{cm,x}, v_{cm,y}, v_{cm,z}, v_{ABx}, v_{ABy}, v_{ABz}\right) dv_{cm,x} dv_{cm,y} dv_{cm,z} dv_{AB,x} dv_{AB,y} dv_{AB,z}$$
$$= \frac{(m_A m_B)^{\frac{3}{2}}}{(2\pi k_B T)^3} e^{-\frac{(m_A+m_B)v_{cm}^2+\mu v_{AB}^2}{2k_B T}} dv_{cm,x} dv_{cm,y} dv_{cm,z} dv_{AB,x} dv_{AB,y} dv_{AB,z}$$

- We separate out the center of mass term:

$$= (m_A m_B)^{\frac{3}{2}} \left[\frac{1}{(2\pi k_B T)^{\frac{3}{2}}} e^{-\frac{(m_A+m_B)v_{cm}^2}{2k_B T}} dv_{cm,x} dv_{cm,y} dv_{cm,z}\right] \left[\frac{1}{(2\pi k_B T)^{\frac{3}{2}}} e^{-\frac{\mu v_{AB}^2}{2k_B T}} dv_{AB,x} dv_{AB,y} dv_{AB,z}\right]$$

- We eliminate that term through integration over all c.m. velocities:

- $$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{1}{(2\pi k_B T)^{\frac{3}{2}}} e^{-\frac{(m_A+m_B)v_{cm}^2}{2k_B T}} dv_{cm,x} dv_{cm,y} dv_{cm,z} = \frac{1}{(m_A+m_B)^{\frac{3}{2}}}$$

Nice! This simplifies things, from 6 down to 3 dimensions ☺

- We simplified the distribution to:

$$f(v_{ABx}, v_{ABy}, v_{ABz})dv_{AB,x}dv_{AB,y}dv_{AB,z} = \left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{\mu v_{AB}^2}{2k_B T}} dv_{AB,x}dv_{AB,y}dv_{AB,z}$$

- Like we did before for the Maxwell-Boltzmann distribution derivation, we now transform to *spherical coordinates*:

$$f(v_{AB}, \phi, \theta)dv_{AB}d\phi d\theta = \left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} v_{AB}^2 e^{-\frac{\mu v_{AB}^2}{2k_B T}} \sin\theta \, dv_{AB}d\phi d\theta$$

- Now we integrate over the angles (as isotropic) and obtain:

$$f(v_{AB})dv_{AB} = 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} v_{AB}^2 \, e^{-\frac{\mu v_{AB}^2}{2k_B T}} dv_{AB}$$

Distribution of the relative speed v_{AB} of two molecules

- Its expectation value is: $\langle v_{AB} \rangle = \sqrt{2}\langle v_A \rangle$ for $m_1 = m_2 = m$ and $\mu = m/2$

5.5 Dynamics of bimolecular collisions – Reactive hard spheres model

- We had derived the collision rate per unit volume of two molecules

$$z_{AB} = \sigma_{AB}\langle u_{AB}\rangle \rho_A \rho_B$$

- *IF* all collisions would lead to a reaction, then

$$-\frac{\rho_A}{dt} = -\frac{\rho_B}{dt} = z_{AB} = \sigma_{AB}\langle u_{AB}\rangle \ \rho_A \rho_B$$

- Then my rate constant would be just like k_2 $[A][B]$

$$k(T) = \sigma_{AB}\langle u_{AB}\rangle$$

- with $\langle u_{AB}\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$ and $\sigma_{AB} = \pi\left(\frac{d_A+d_B}{2}\right)^2$ we would obtain:

$$k(T) = \sigma_{AB}\langle u_{AB}\rangle = \pi\left(\frac{d_A+d_B}{2}\right)^2 \cdot \sqrt{\frac{8k_BT}{\pi\mu}}$$

But what's wrong with this rate constant…?!

5.5 Dynamics of bimolecular collisions – Reactive hard spheres model

$$k(T) = \sigma_{AB}\langle u_{AB}\rangle = \pi\left(\frac{d_A+d_B}{2}\right)^2 \cdot \sqrt{\frac{8k_BT}{\pi\mu}}$$

But what's wrong with this rate constant…?!

- 1) Not every collision leads to a reaction

  → we likely overestimate our rate here

- 2) What did we find experimentally before in the course for the temperature dependence?

  → Arrhenius eq. like behavior

Above: $k(T) \propto \sqrt{T}$ *vs* Arrhenius: $k(T) \propto e^{-E_{act}/k_BT}$

Let's try to get better than this!

- To get better, let's take into account the *energy* of a particle for its *probability* to successfully collide under reaction:

$$k(T) = \sigma_{AB}\langle u_{AB}\rangle \qquad \rightarrow \qquad k(T) = \langle \sigma_{AB}(E)\, u_{AB}\rangle$$

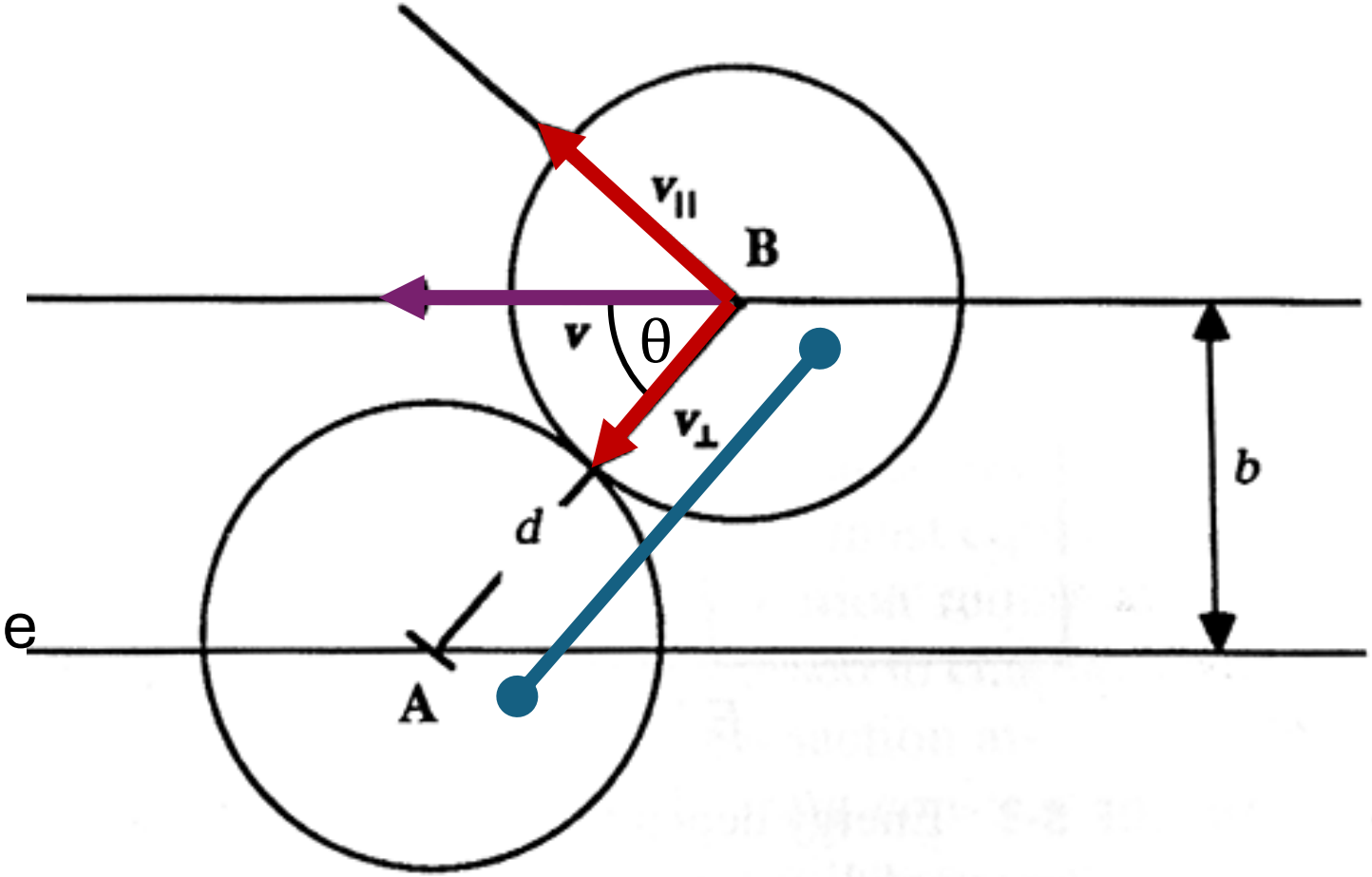
- Let's also take into account that the reactivity depends on the collision *geometry*: we introduce an *impact parameter* b

- We still assume 2 molecules are spheres, and use the center of mass frame, so ignore $\boldsymbol{v}_{cm}$ and only consider the relative velocity $\boldsymbol{v}_{AB} = \boldsymbol{v}$
- Their energy is $E = \frac{1}{2}\mu v^2$ with reduced mass μ
- Their minimum distance for collision is $d = \frac{1}{2}(d_A + d_B)$ from the c.m. origin

$$\boldsymbol{v}_{AB} = \boldsymbol{v} \qquad \text{and} \qquad d = \frac{1}{2}(d_A + d_B)$$

- Decompose into components: $\boldsymbol{v}_{\parallel}$ and $\boldsymbol{v}_{\perp}$
- Angle θ between $\boldsymbol{v}$ and $\boldsymbol{v}_{\perp}$
- Only $\boldsymbol{v}_{\perp}$ can drive reaction!
- Let's accordingly decompose the kinetic energy as

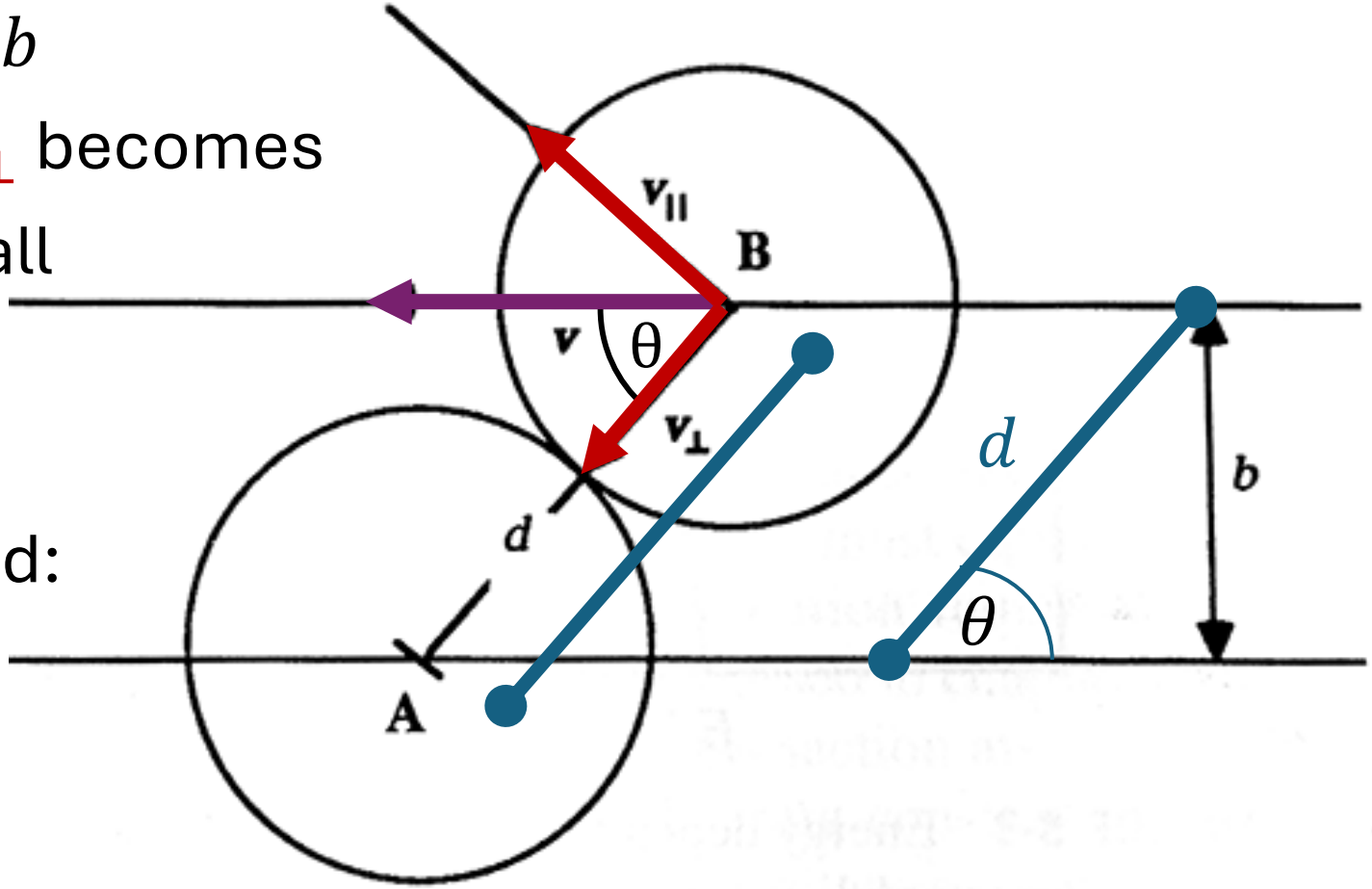
$$E = \frac{1}{2}\mu v_{\parallel}^2 + \frac{1}{2}\mu v_{\perp}^2 = E_{\parallel} + E_{\perp}$$



$$\boldsymbol{v}_{AB} = \boldsymbol{v} \qquad \text{and} \qquad d = \frac{1}{2}(d_A + d_B)$$

- Only $E_\perp = \frac{1}{2}\mu \boldsymbol{v}_\perp^2$ relevant for reaction
- Introduce impact parameter b
- The larger b is, the smaller $\boldsymbol{v}_\perp$ becomes
- To maximize $\boldsymbol{v}_\perp$, make b small

→ more "head-on" collision



- For the energy fraction we find:

$$\frac{E_\perp}{E} = \frac{\boldsymbol{v}_\perp^2}{\boldsymbol{v}^2} = \cos^2\theta$$

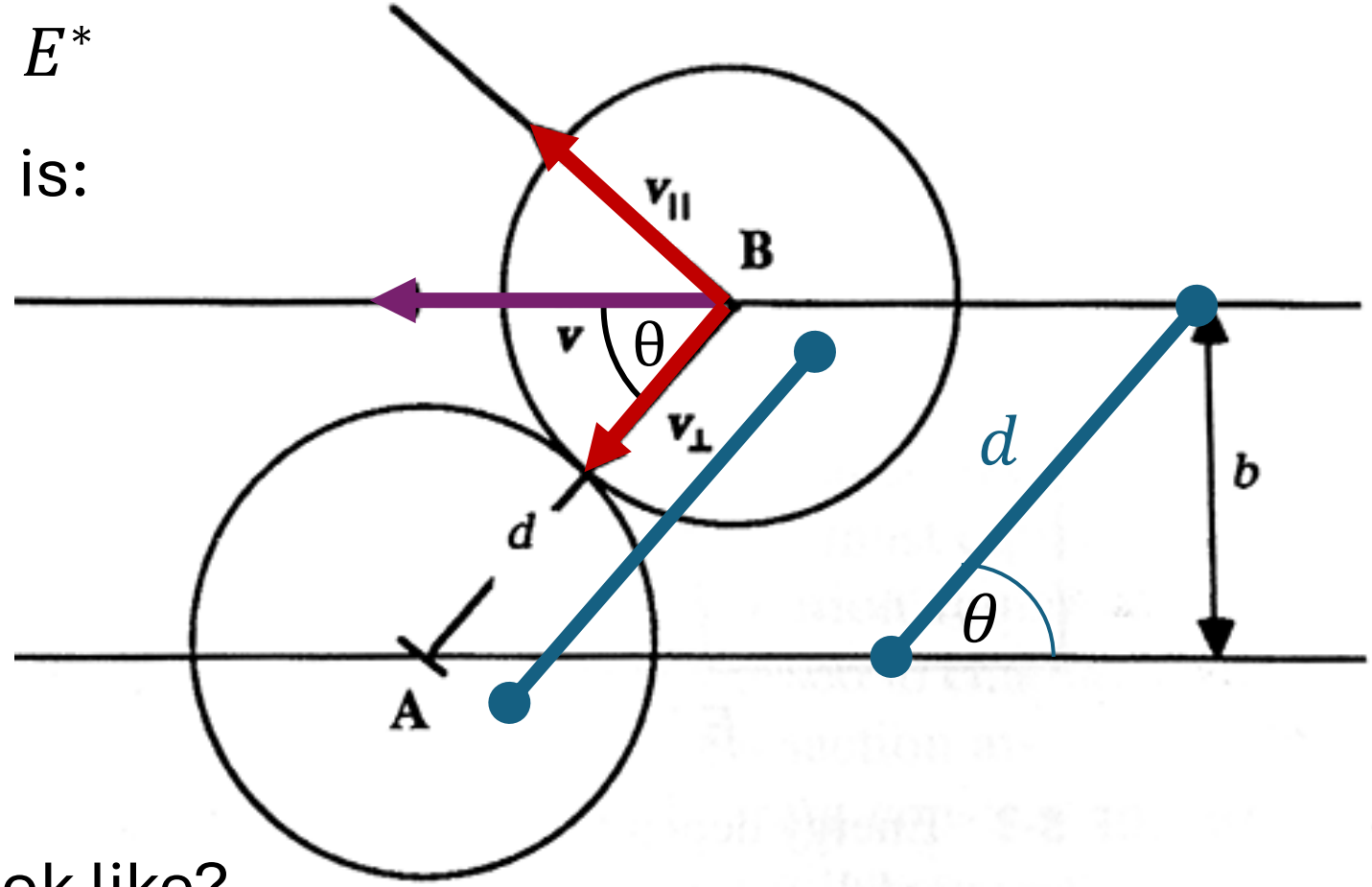
$$= 1 - \sin^2\theta = 1 - \frac{b^2}{d^2}$$

$$\frac{E_\perp}{E} = \frac{v_\perp^2}{v^2} = \cos^2\theta = 1 - \sin^2\theta = 1 - \frac{b^2}{d^2}$$

- For a collision, we need a minimum energy E^*
- So $$E_\perp = E\left(1 - \frac{b^2}{d^2}\right) \overset{!}{\geq} E^*$$
- The reaction probability then is:

$$P_R(E_\perp) = \begin{cases} 0 & \text{if } E_\perp < E^* \\ p & \text{if } E_\perp \geq E^* \end{cases}$$

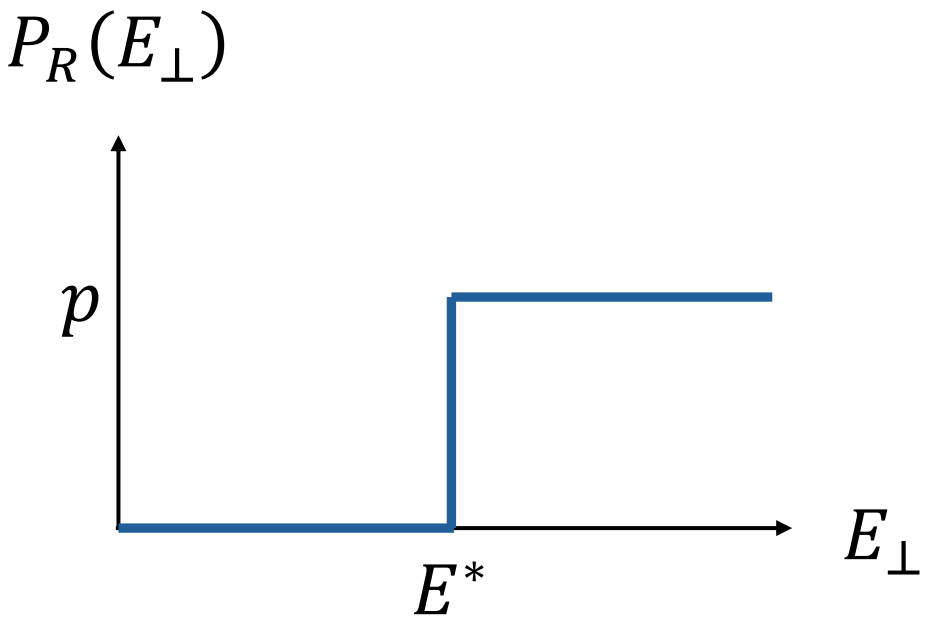
- The probability $\boldsymbol{p}$ we can call the ***steric factor*** (like a fit parameter)

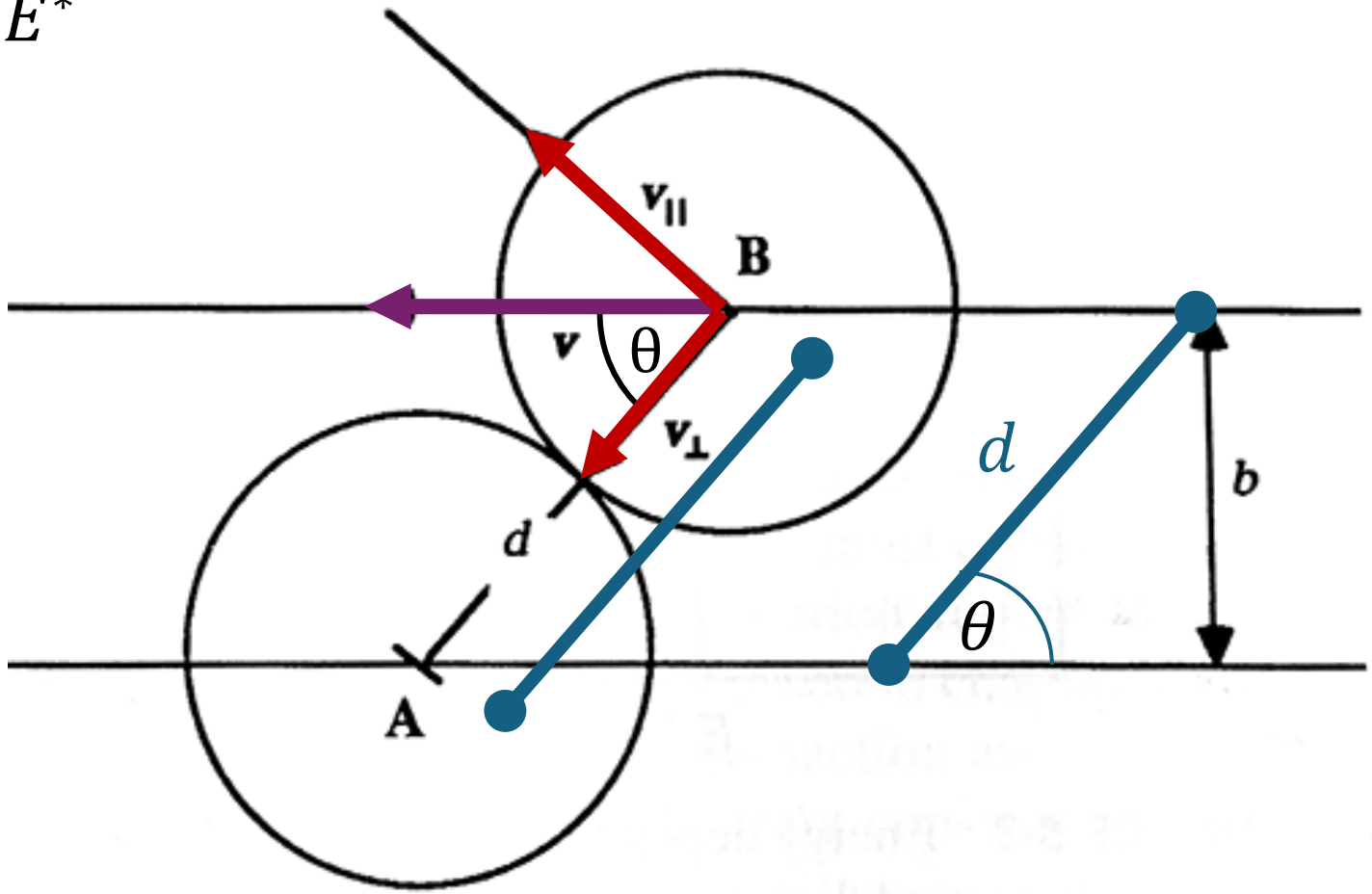


- How does a plot of $P_R(E_\perp)$ look like?

$$E_\perp = E\left(1 - \frac{b^2}{d^2}\right) \overset{!}{\geq} E^*$$

$$P_R(E_\perp) = \begin{cases} 0 & \text{if } E_\perp < E^* \\ p & \text{if } E_\perp \geq E^* \end{cases}$$



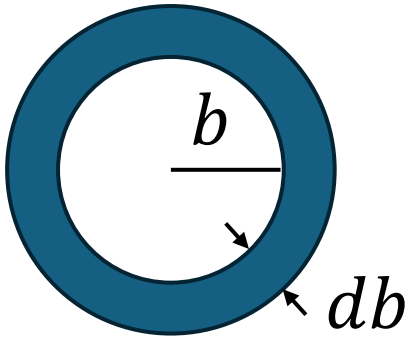


does not look super realistic, but it's a start...

- Let's define a *reaction cross section* $\sigma_R(E)$, taking into account the necessary energy for a reactive collision:
- The surface area A of an infinitesimally thin ring is

  $\mathrm{A} = 2\pi b\ db$

  with radius b and thickness db



- Integrating over all b where a reaction can occur, yields

$$\sigma_R(E) = \int_0^\infty P_R(E_\perp) \cdot 2\pi b\ db$$