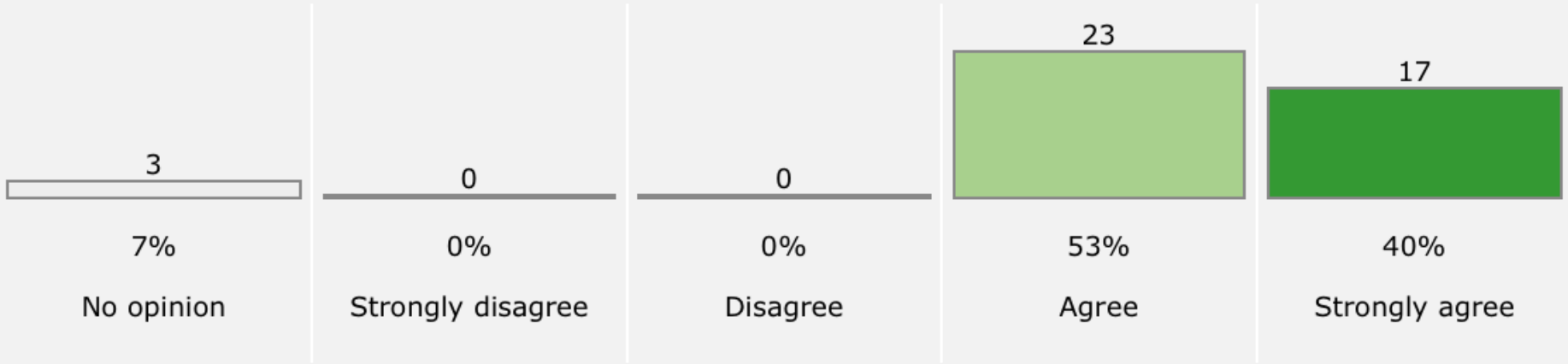
Results are in: Indicative student feedback

Year	2025-2026
Course	Dynamics and kinetics
Questionnaire	Indicative feedback of teaching (since 2022-2023)
Nb Registered	64
Nb Answered	43

THANK YOU! <3

The running of the course enables my learning and an appropriate class climate



Results are in: Indicative student feedback

- **Can we do more exercises during the lecture?**
  → Unfortunately, due to time constraints this is not possible. This part is covered by the exercise sessions, while I need to deliver key concepts.
- **Mode of the exercise sessions:**
  - 50% of you highlighted they enjoy that the TAs walk them through the most important solution aspects
  - 50% of you would prefer solving the questions during the session and have the TAs answer questions arising

  → If they change the mode, they will lose again half of you. So they will for now stick to the former style, but can always answer questions arising separately outside the session, of course!

Results are in: Indicative student feedback

"Interesting course. The series help a lot to understand the key concepts of the lectures. The time needed is perfect, it is worth the credits.
- The course is well given and well structured.
- The course is well structured and the exercise session are really helpful to understand the theory of the course.
- The exercises as well as the course part are well organized, I particularly enjoy the way the exercise session is carried out with the assistants.
- The explanations that go with the slides are really clear and helpful.
- The is interesting and demands a lot of intuition, the professor follows a steady rhythm which is helpful when looking at difficult subjects. Some more examples similar to the exercises would be nice to have to help.
- Very good course. It is well structured, well explained. The way in which the exercises are presented makes it easy to understand how to solve the problems
- Very good course. Explanations and slides are clear. Exercises are of great help to understand the concepts and practice!
- Very interesting course, the teacher creates a pleasant atmosphere for participation and understanding."

Exam slot has been allocated to us:

- Thursday, 15th January 2026: 9.15 am – 12.15 pm
- Location: BS 260/BS270

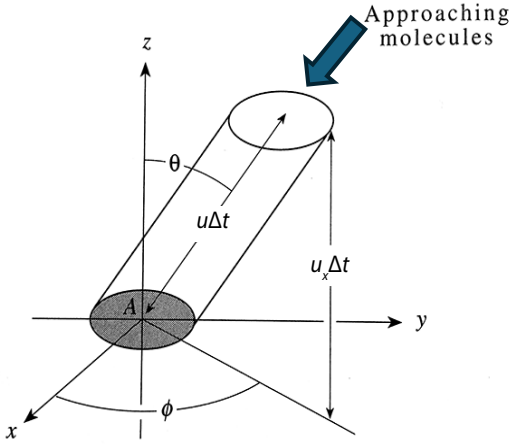
Kinetics & Dynamics of Chemical Reactions

Course CH-310

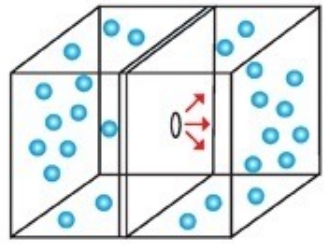
Prof. Sascha Feldmann

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}]



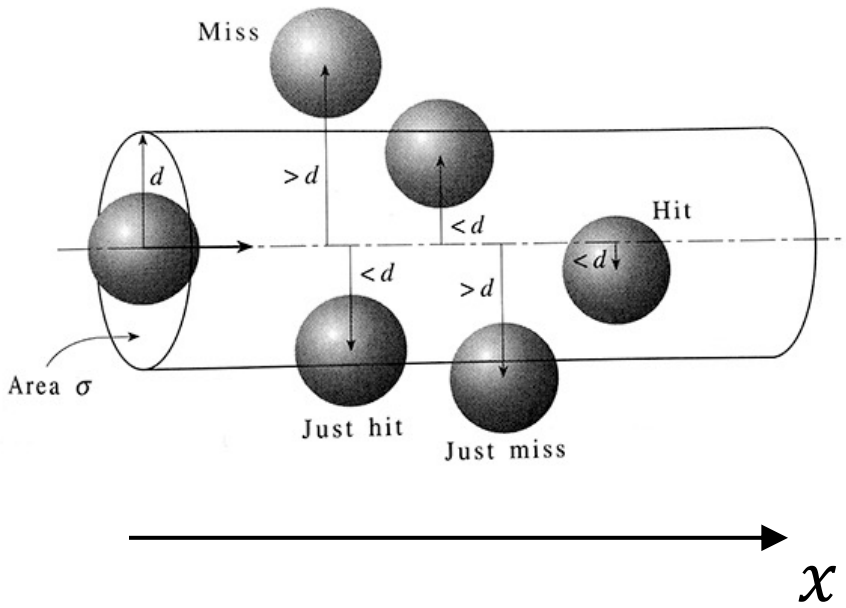
- Effusion
  - low pressure, small hole vs. large mean free path
  - effusion rate $k_{\text{effusion}} = z_{\text{coll}}\, A = \frac{pA}{\sqrt{2\pi m k_B T}}$ [s^{-1}]
  - Knudsen method to measure vapor pressure of liquids



Recap from last session

- Collision rate $z_A = \rho\sigma\langle u_{AB}\rangle = \rho\sigma\sqrt{2}\langle u\rangle$ [s^{-1}]

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



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

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

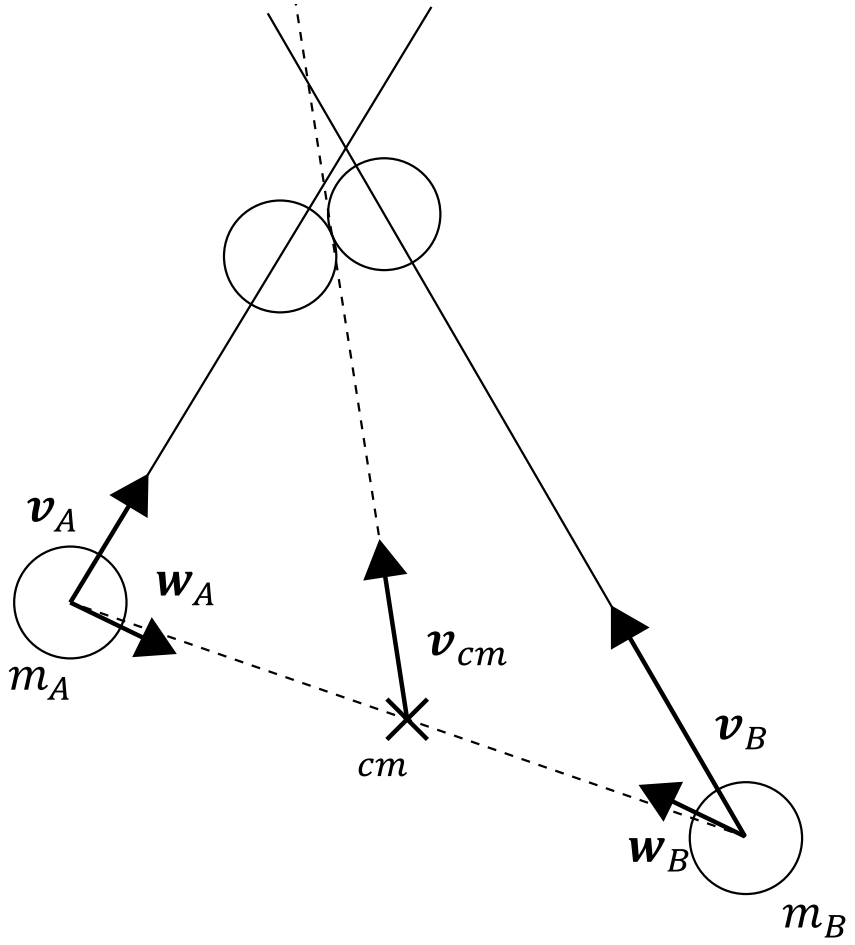
$$n(x) = n_0 e^{-\sigma\rho x} = n_0 e^{-\frac{x}{l}}$$

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 find their relative velocities in a new *center of mass frame* (a moving coordinate system):

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

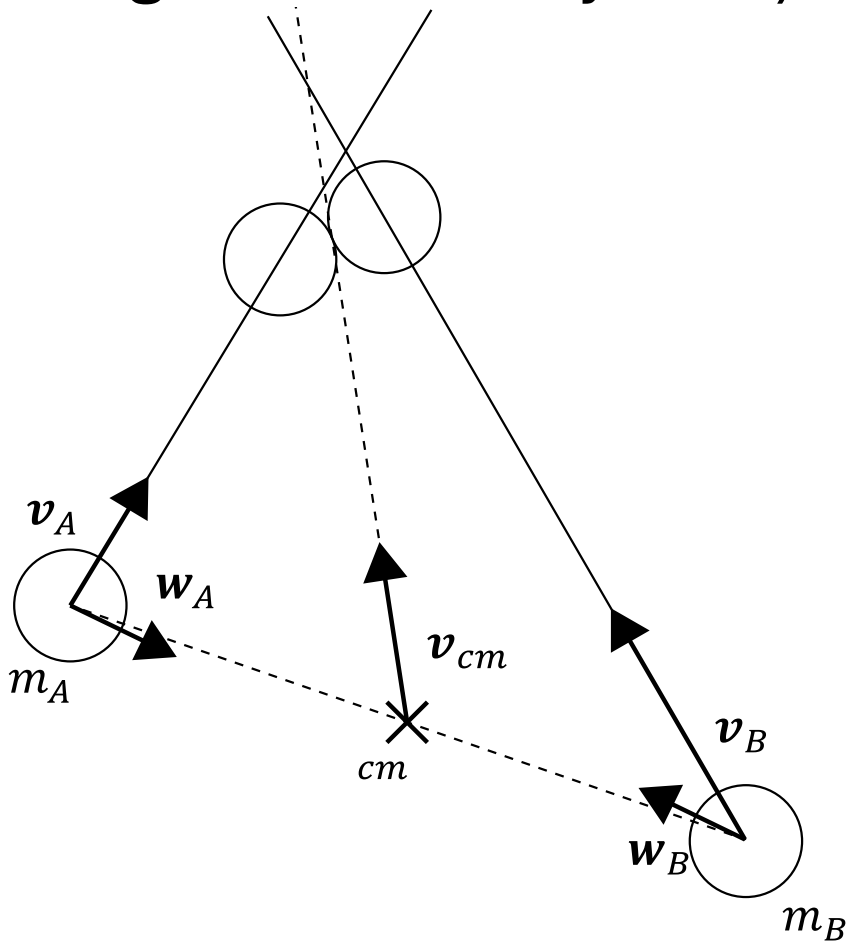
$$\boldsymbol{w}_B = \boldsymbol{v}_B - \boldsymbol{v}_{cm}$$

- 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 the relative velocity:

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



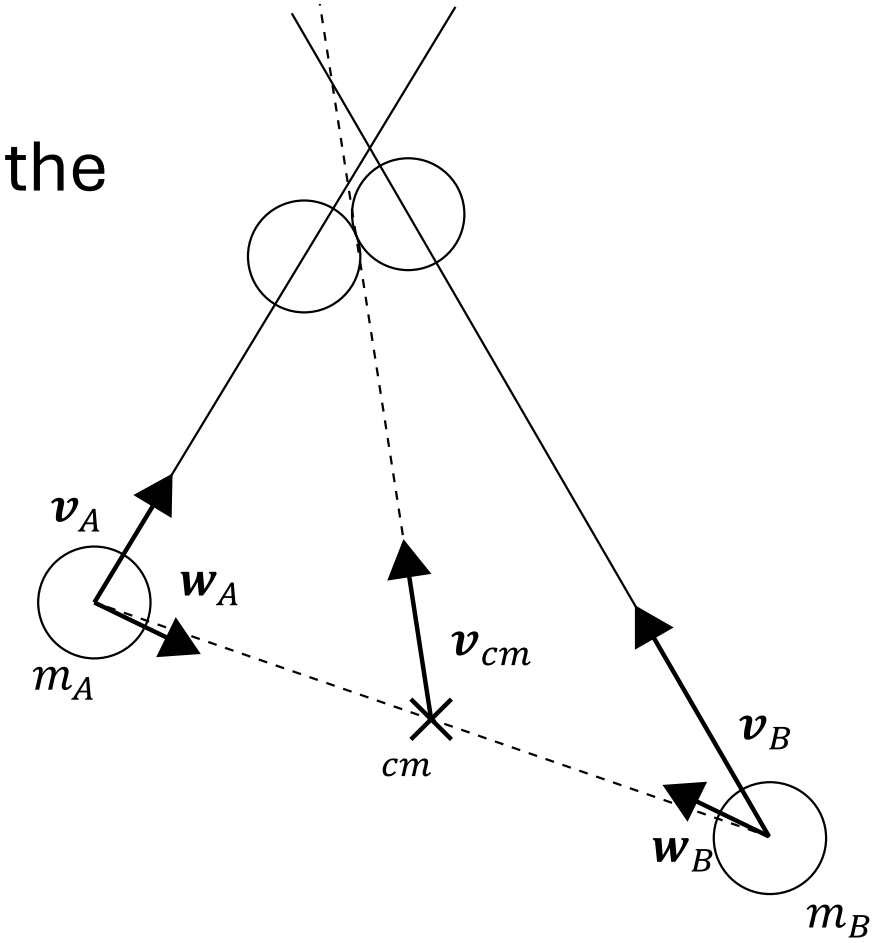
- What is the sum of all momenta within the center of mass frame?

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

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



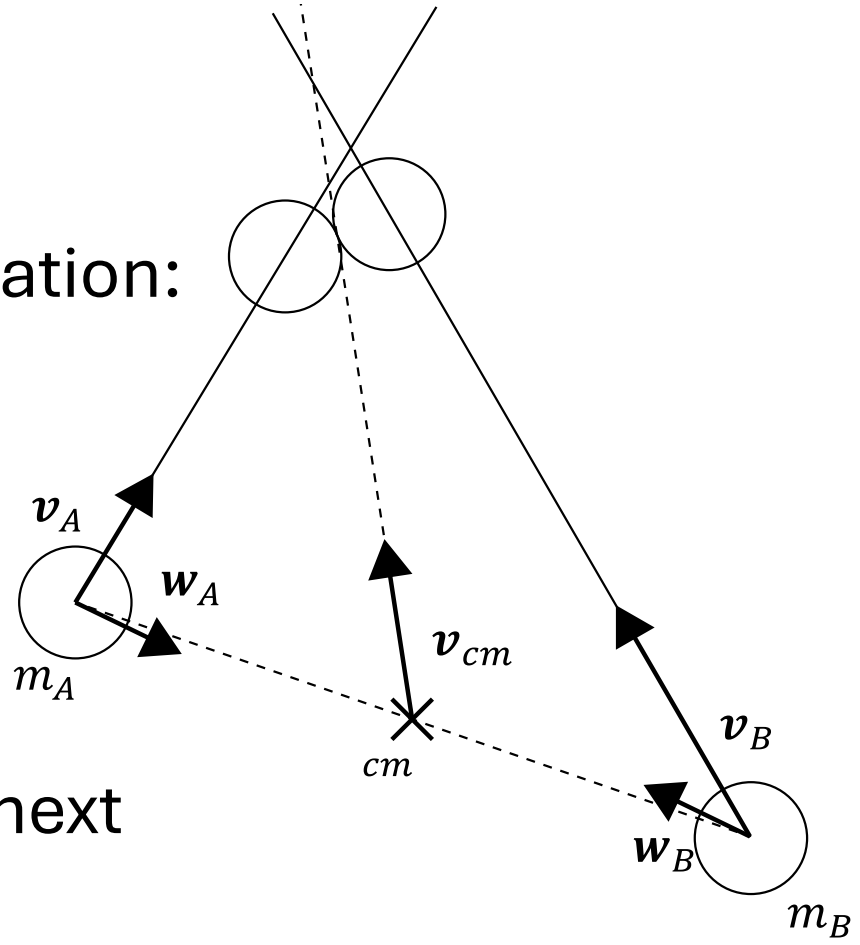
$$\mu \boldsymbol{w}_{AB} = m_A \boldsymbol{w}_A = -m_B \boldsymbol{w}_B$$

- earlier, we found

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

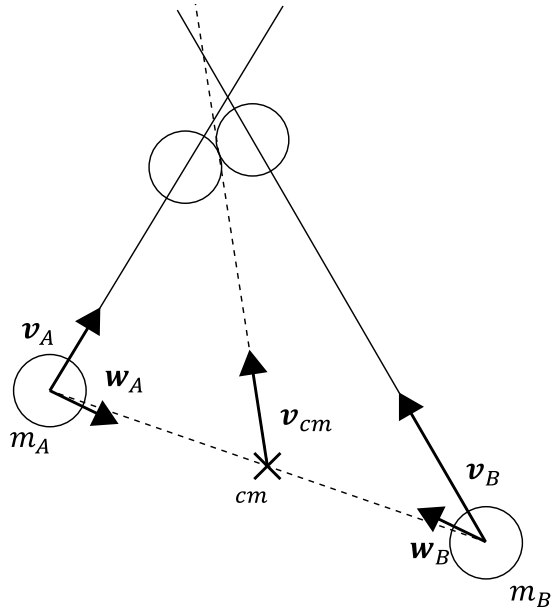
- So we can describe the coordinate transformation:

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



- 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:

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

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

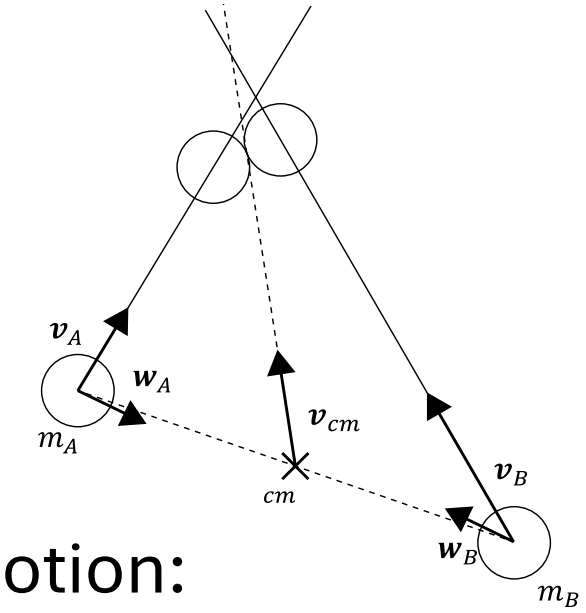
$$= \frac{1}{2} (m_A + m_B) v_{cm}^2 + \frac{1}{2} \mu w_{AB}^2 + \boldsymbol{v}_{cm} \mu \boldsymbol{w}_{AB} - \boldsymbol{v}_{cm} \mu \boldsymbol{w}_{AB}$$

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

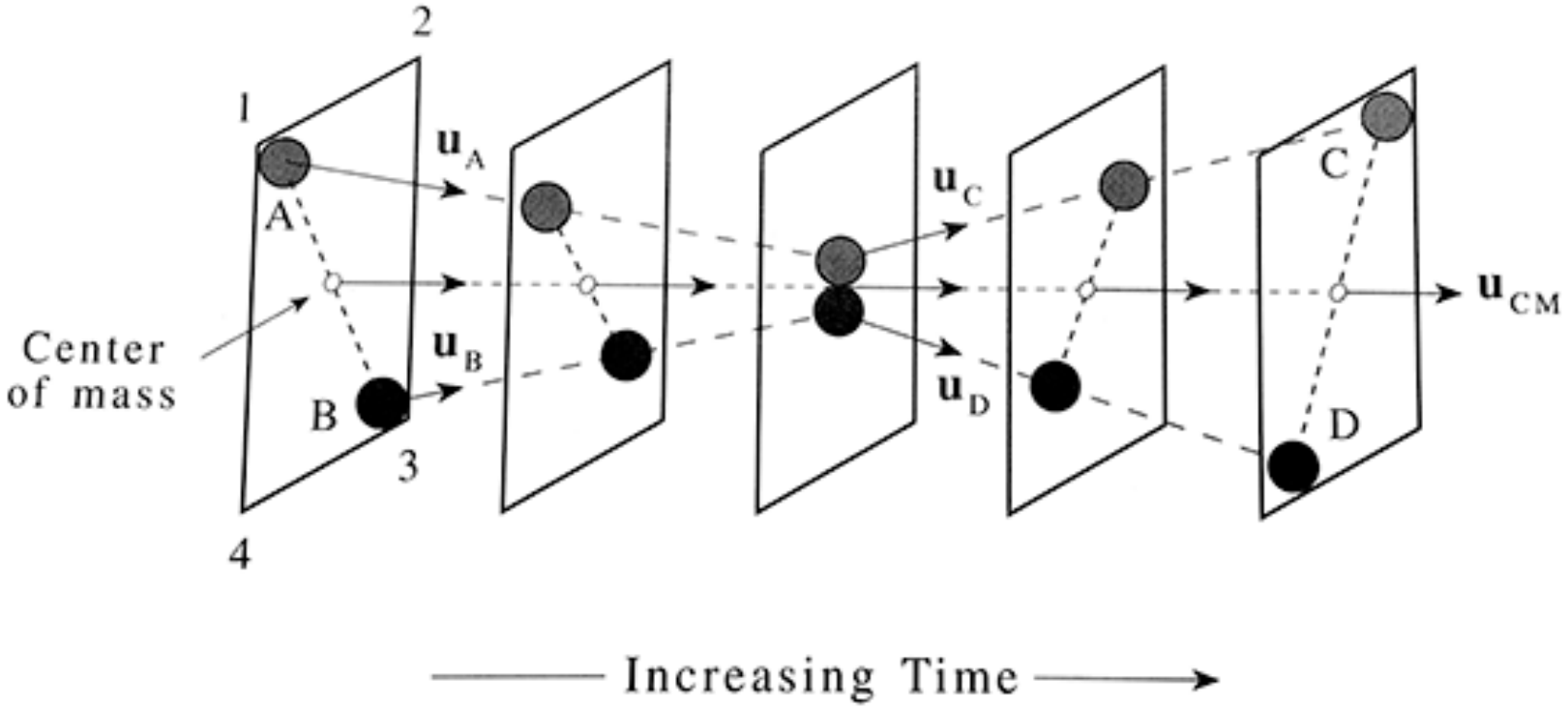
what do these terms correspond to?

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

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



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

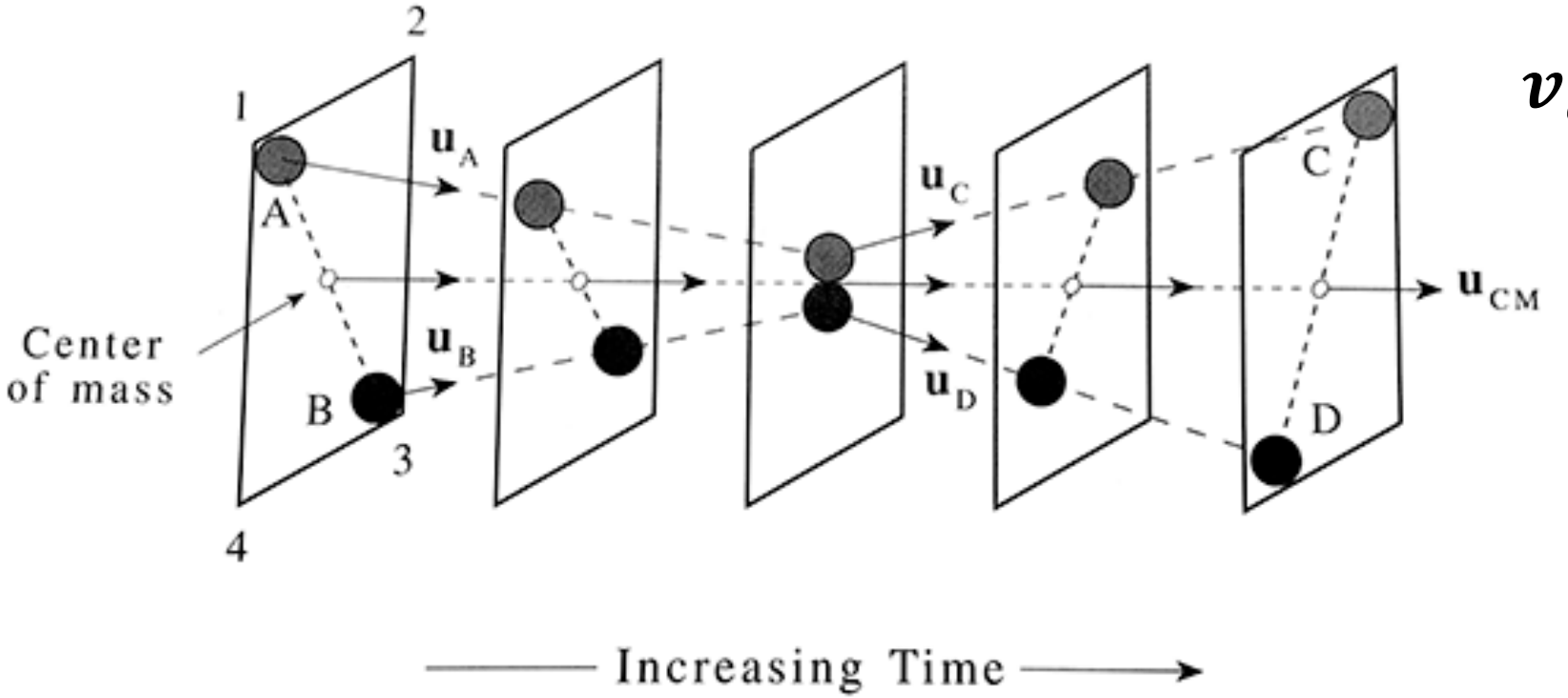


What do you notice?

- 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):

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

- The 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 the c.m. motion for describing the reaction ☺

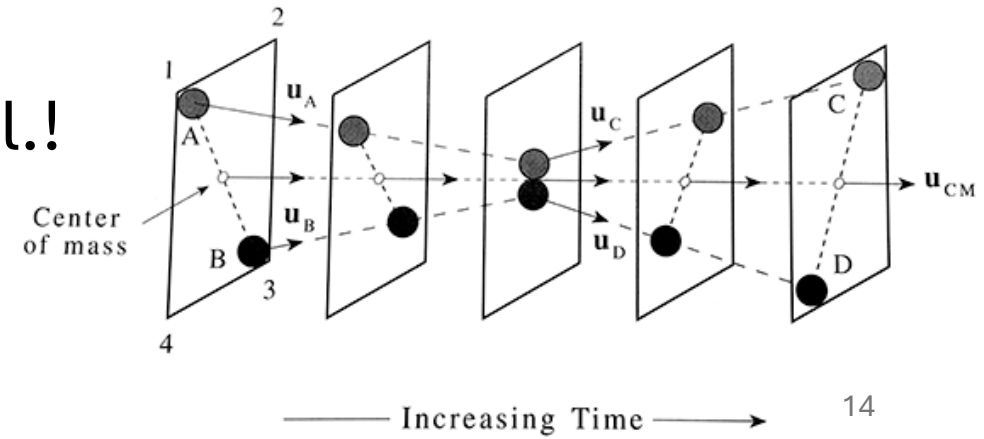
- Kinetic energy of center of mass motion *also* remains unchanged:

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

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

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

- 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:

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

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

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

- Next, 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 the center-of-mass term from the relative-motion 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 just 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 all 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 $\mu = m/2$

i.e. the result we used in the last session, now proven ☺

5.5 Dynamics of bimolecular collisions – Reactive hard spheres model

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

$$z_{AB} = \sigma_{AB}\langle u_{AB}\rangle \rho_A \rho_B \quad [\mathrm{s^{-1}\,m^{-3}}]$$

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

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

… the rate constant would just be like $k_2 \times [A][B]$

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

- 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 empirically before in the course for the temperature dependence?

  → Arrhenius Eq. 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 estimate 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*** $\boldsymbol{b}$

- 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 $E = \frac{1}{2}\mu \boldsymbol{v}^2$ with reduced mass μ
- minimum distance for collision is $d = \frac{1}{2}(d_A + d_B)$ from the c.m. origin

Relative velocity: $\boldsymbol{v}_{AB} = \boldsymbol{v}$ distance: $d = \frac{1}{2}(d_A + d_B)$

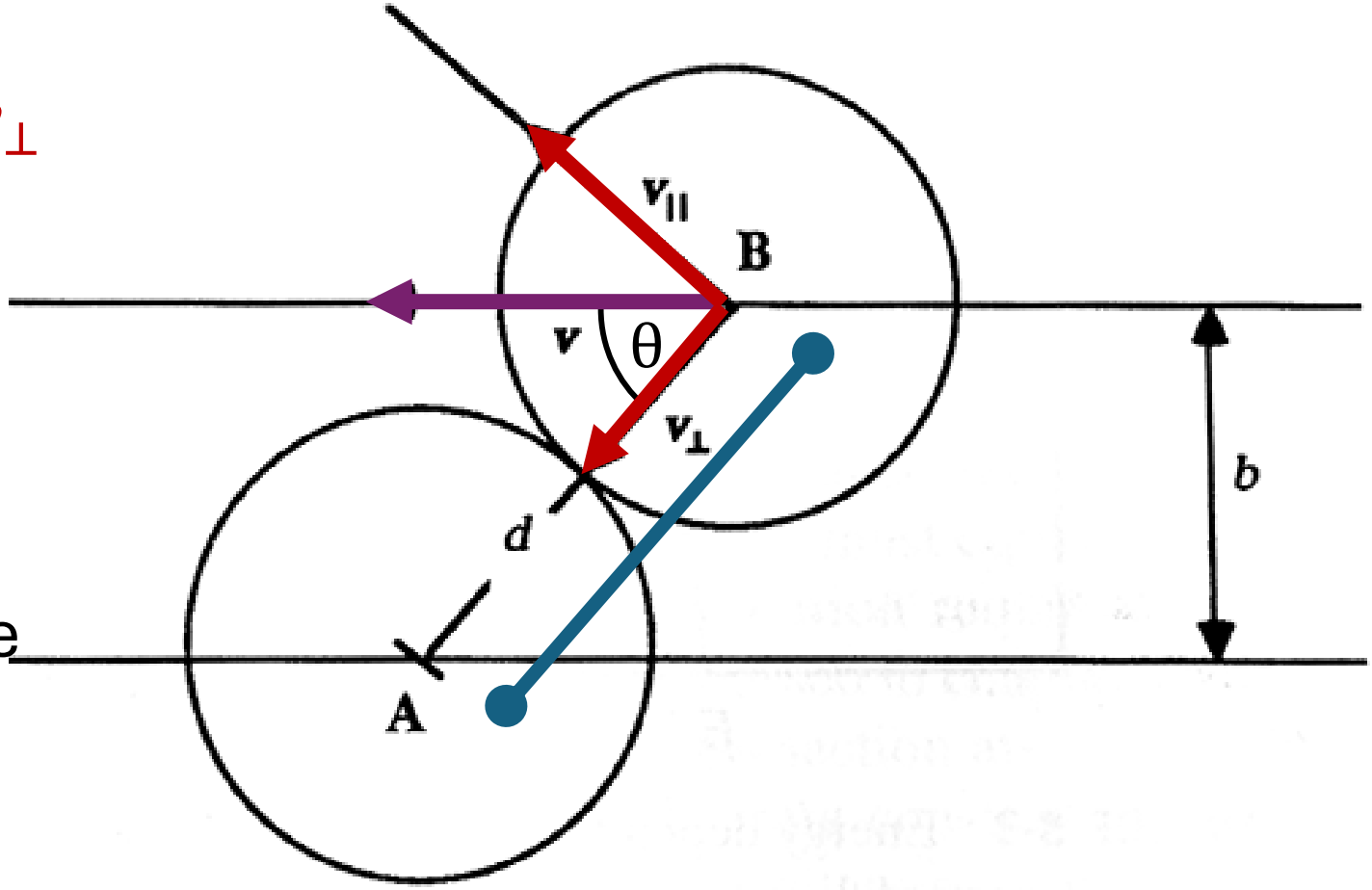
- Decompose into components: $\boldsymbol{v}_{\parallel}$ and $\boldsymbol{v}_{\perp}$

  and angle θ between $\boldsymbol{v}$ and $\boldsymbol{v}_{\perp}$

- Which component matters?
- Only $\boldsymbol{v}_{\perp}$ can drive reaction!

- Let's accordingly decompose the kinetic energy into

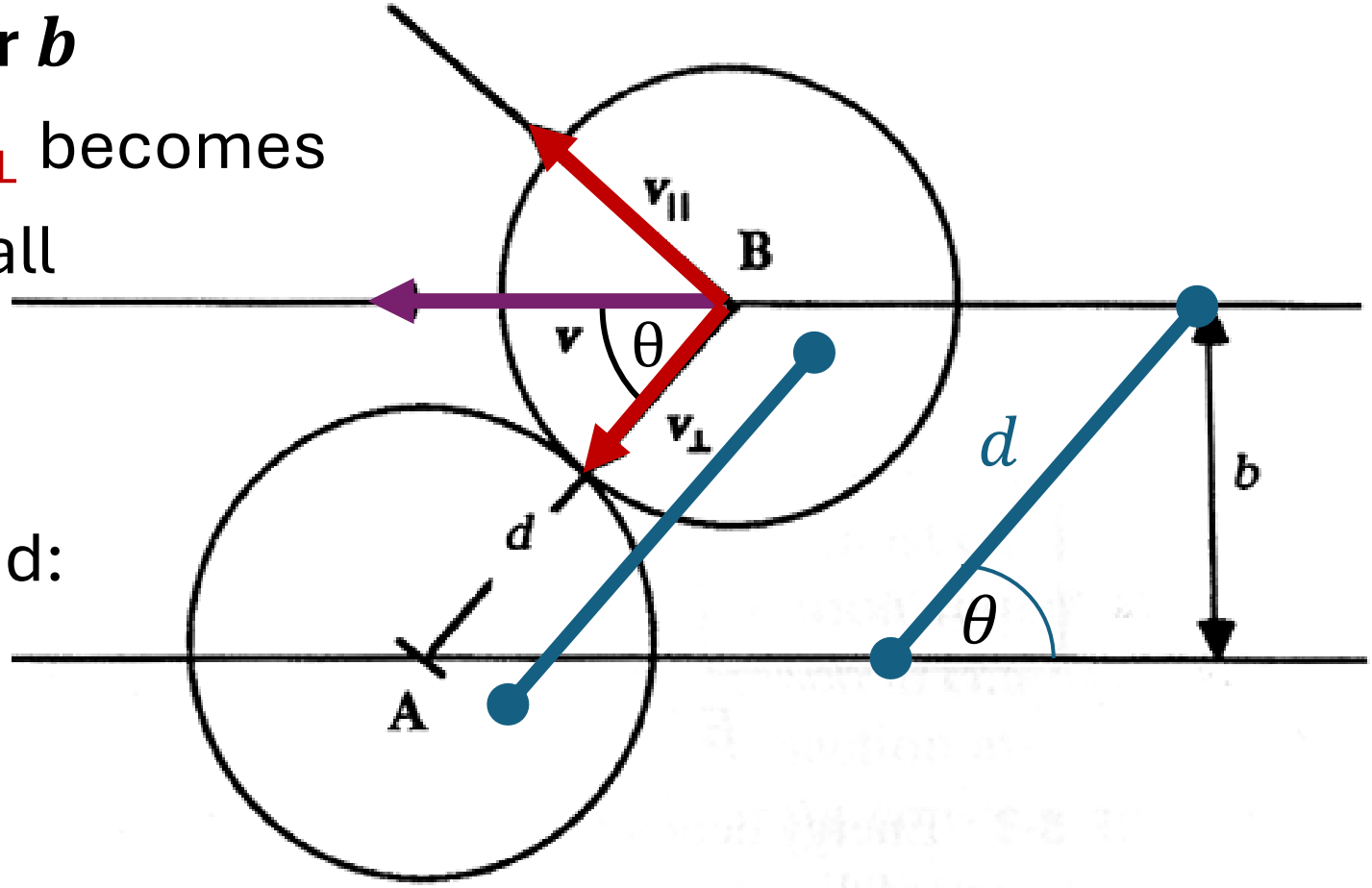
$$E = \frac{1}{2}\mu v_{\parallel}^2 + \boxed{\frac{1}{2}\mu v_{\perp}^2} = E_{\parallel} + E_{\perp}$$



Relative velocity: $\boldsymbol{v}_{AB} = \boldsymbol{v}$ distance: $d = \frac{1}{2}(d_A + d_B)$

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

→ more "heads-on" collision



- For the energy fraction we find:

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

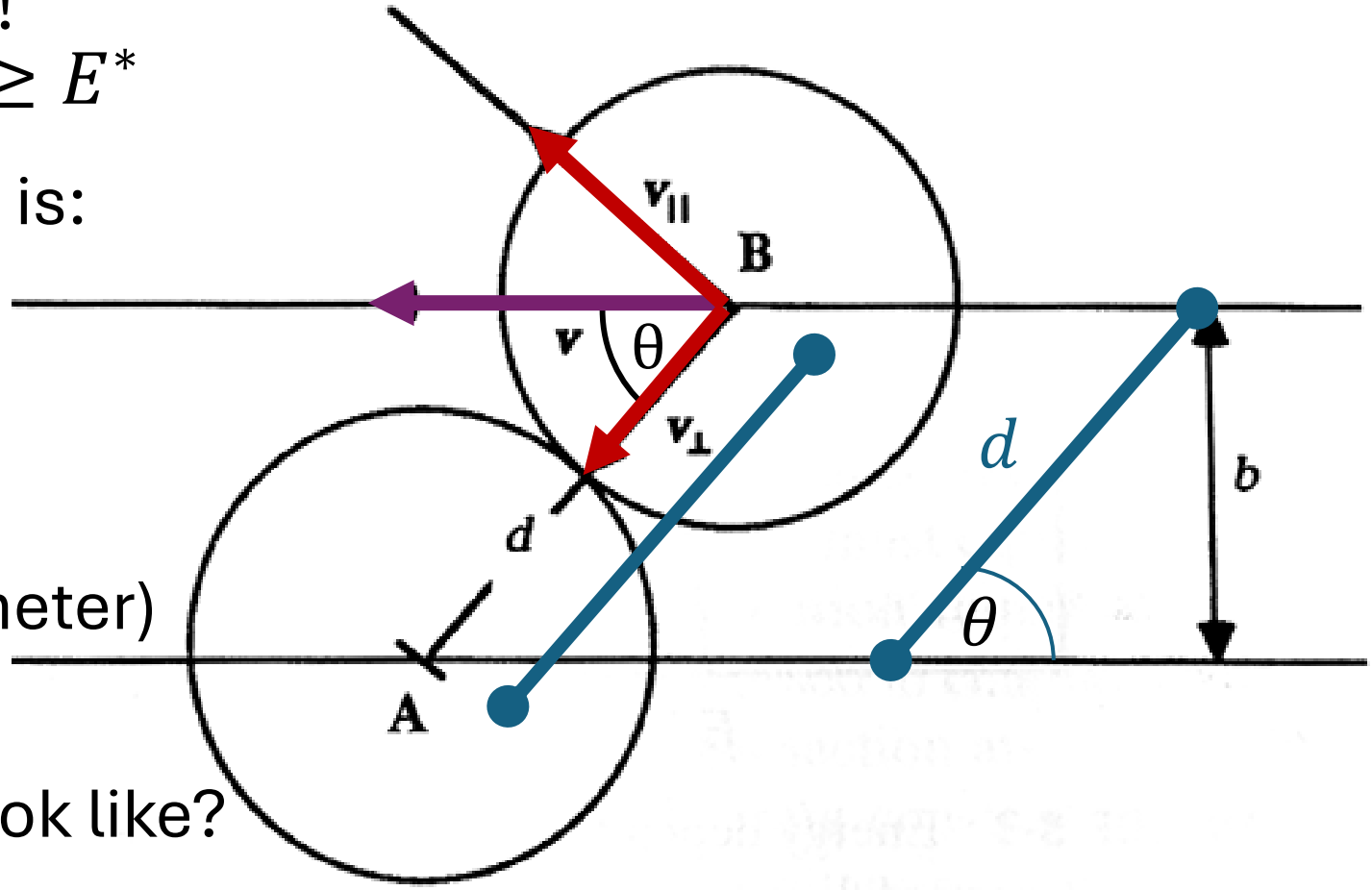
$$= 1 - \sin^2\theta = 1 - \frac{b^2}{d^2}$$

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

- 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:

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

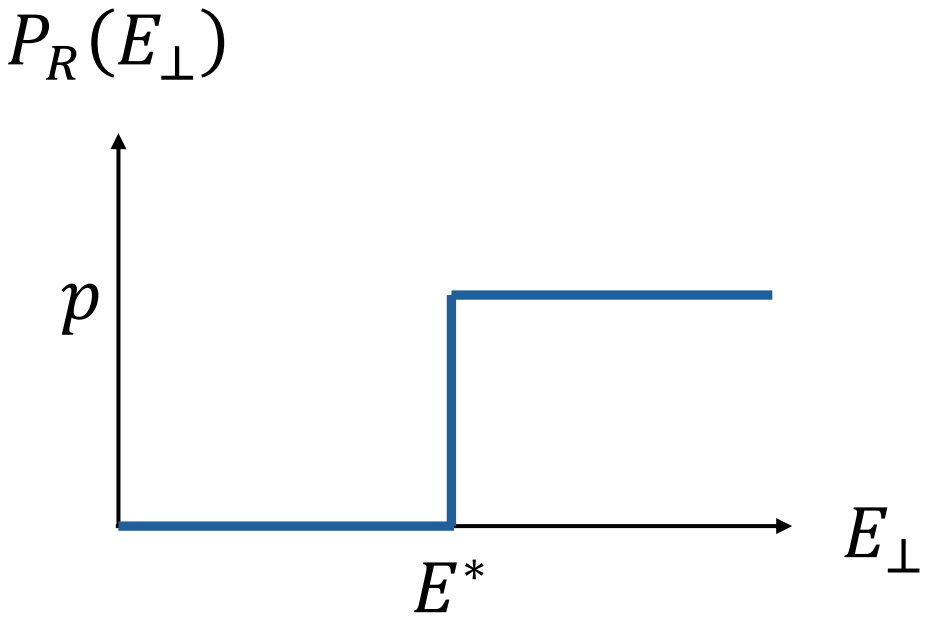
- $\boldsymbol{p}$ we can call the ***steric factor*** (like a fit parameter)

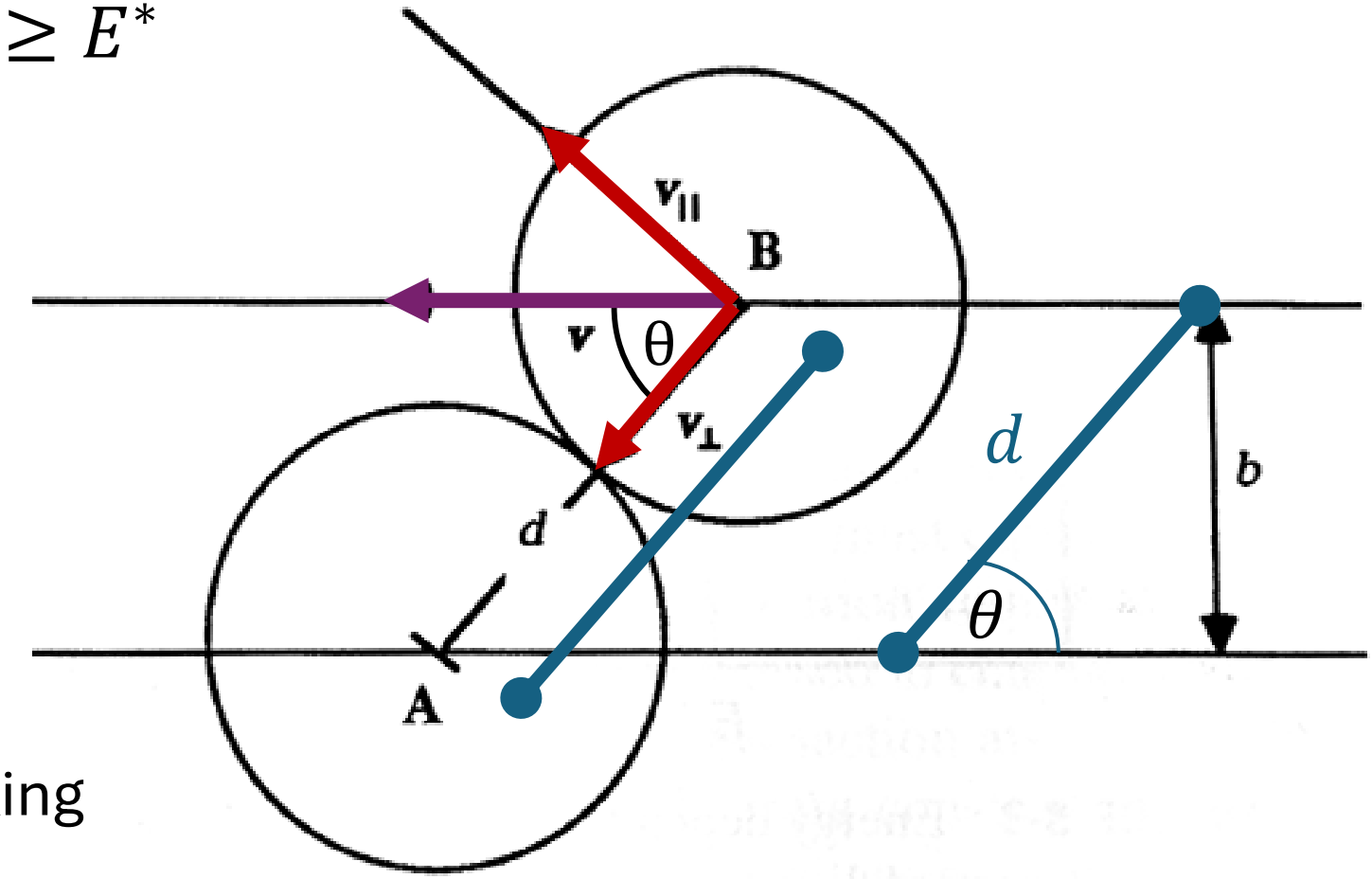


- How does a plot of $P_R(E_\perp)$ look like?

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

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





something like this; not yet looking super realistic, but it's a start…