Kinetics & Dynamics of Chemical Reactions

Course CH-310

Prof. Sascha Feldmann

Recap from last session

Center of mass coordinates (derivation)

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

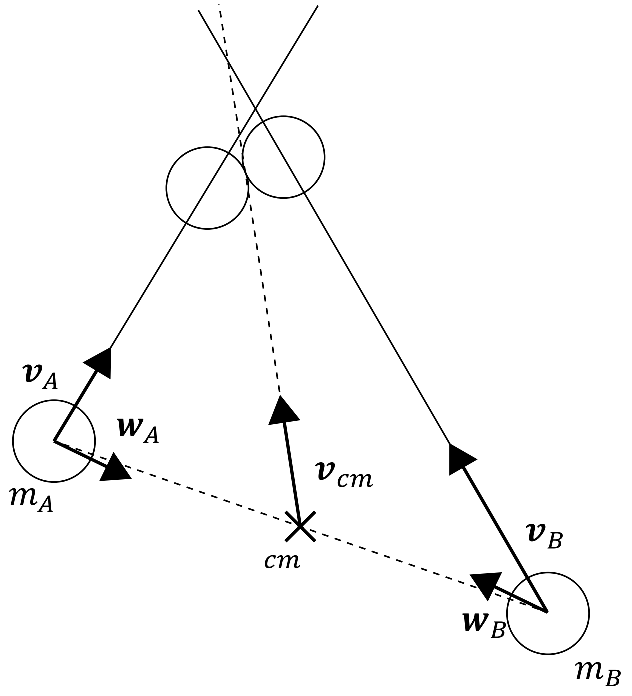
$$\boldsymbol{v}_A = \boldsymbol{v}_{cm} + \mu \boldsymbol{w}_{AB}/m_A$$

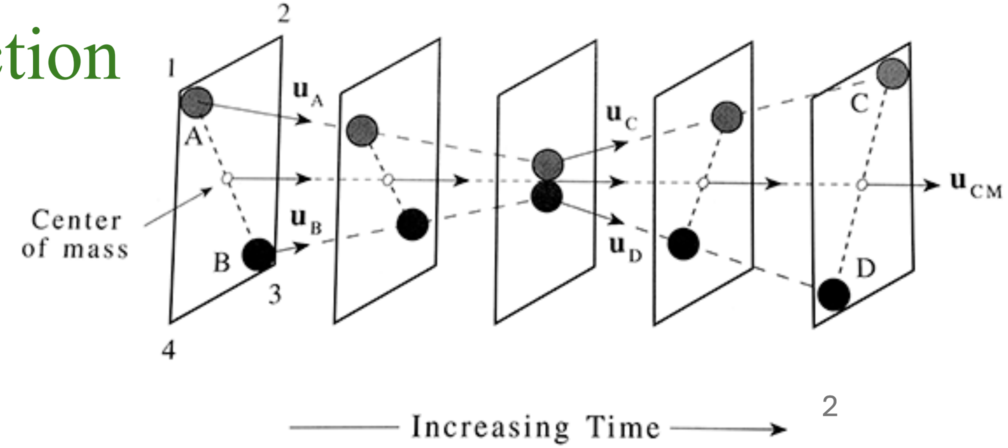
$$\boldsymbol{v}_B = \boldsymbol{v}_{cm} - \mu \boldsymbol{w}_{AB}/m_B$$

- $\mathrm{E}_{\mathrm{kin}} = \frac{1}{2}(m_A + m_B)v_{cm}^2 + \frac{1}{2}\mu v_{AB}^2$

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

conserved! available for reaction





Recap from last session

Center of mass coordinates (derivation)

- distribution of relative velocities:

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

  - transformed to c.m. system
  - integrated out c.m. part

- $f(\ v_{ABx}, v_{ABy}, v_{ABz})dv_{AB,x}dv_{AB,y}dv_{AB,z}$
  - transformed to spherical coordinates
  - integrated out spherical part (isotropic)

- $f(v_{AB})dv_{AB} = 4\pi\left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} v_{AB}^2 \ \ e^{-\frac{\mu v_{AB}^2}{2k_B T}} \ dv_{AB}$ **a M.B. distribution for particles of mass μ**

Recap from last session

Bimolecular collisions – reactive hard spheres ($A + B \rightarrow Products$)

- If *all* collisions were reactive: $-\frac{\rho_A}{dt} = -\frac{\rho_B}{dt} = z_{AB} = \underbrace{\sigma_{AB}\langle u_{AB}\rangle}_{k(T)} \; \rho_A\rho_B$

  $k(T) \quad [A][B]$

- rate is much too high
- temp. dependence wrong: $k(T) \propto \sqrt{T}$ *vs* Arrhenius: $k(T) \propto e^{-E_{act}/k_BT}$

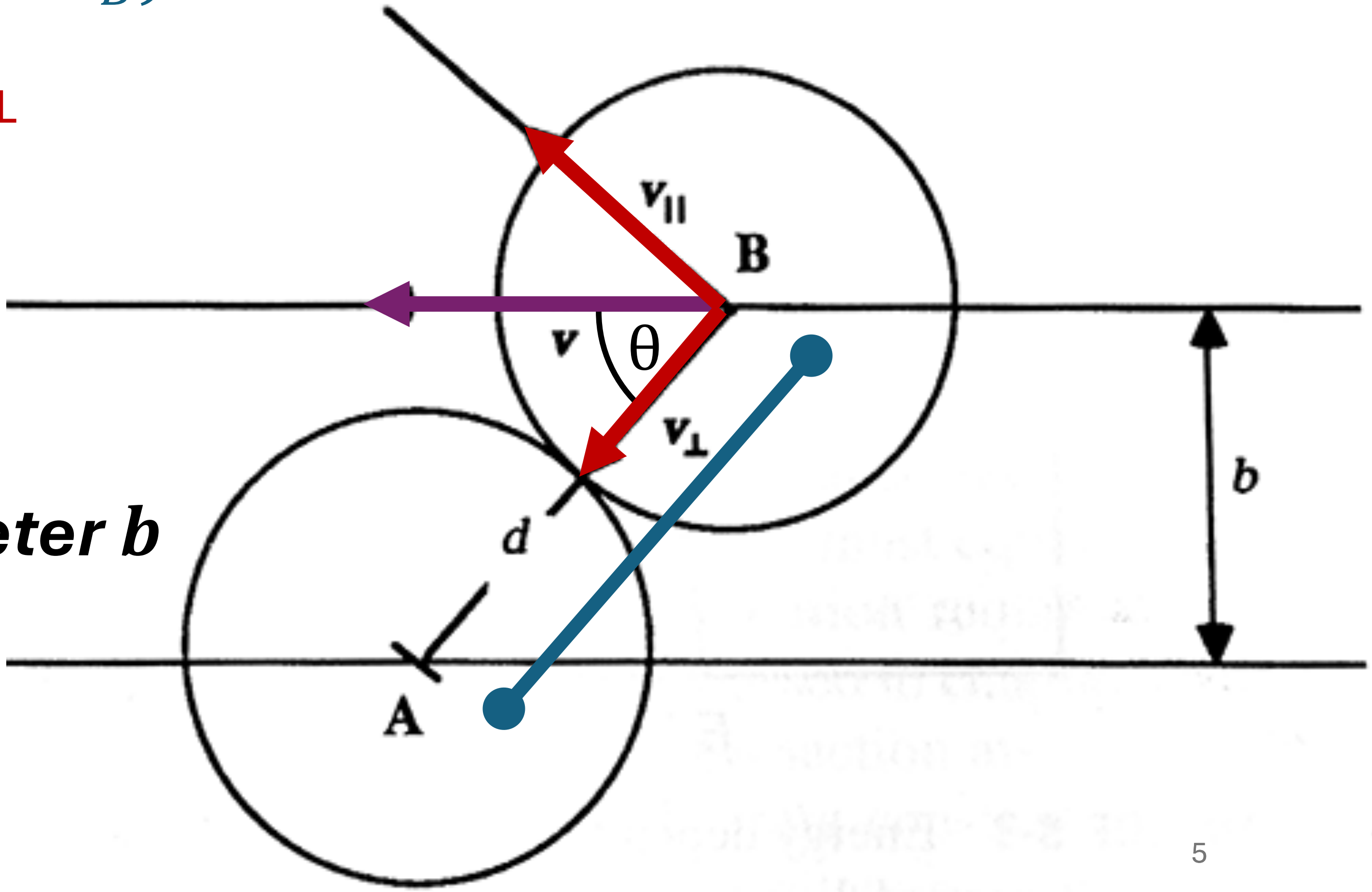
- Idea: $k(T) = \sigma_{AB}\langle u_{AB}\rangle \quad \rightarrow \quad k(T) = \langle \sigma_R(E)\, u_{AB}\rangle$

- we again work in the c.m. frame

Recap from last session

Bimolecular collisions – reactive hard spheres ($A + B \rightarrow Products$)

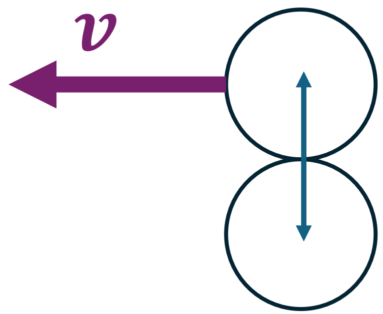
- $\boldsymbol{v}_{AB} = \boldsymbol{v}$ and $d = \frac{1}{2}(d_A + d_B)$
- decomposed into $\boldsymbol{v}_{\parallel}$ and $\boldsymbol{v}_{\perp}$
- angle θ between $\boldsymbol{v}$ and $\boldsymbol{v}_{\perp}$
- only $\boldsymbol{v}_{\perp}$ can drive reaction
- only $E_{\perp} = \frac{1}{2}\mu v_{\perp}^2$ relevant
- introduced ***impact parameter b***
- smaller b → larger $\boldsymbol{v}_{\perp}$



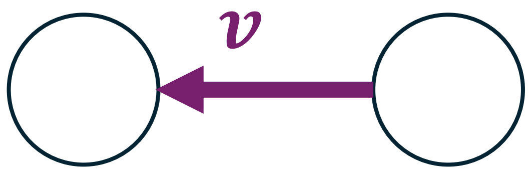
Recap from last session

Bimolecular collisions – reactive hard spheres ($A + B \rightarrow Products$)

- $\boldsymbol{v}_{AB} = \boldsymbol{v}$ and $d = \frac{1}{2}(d_A + d_B)$
- introduced *impact parameter* b



- $b > d$ → no reaction ☹
  as no component of energy directed
  towards collision partner



- $b = 0$ → head-on-collision! ☺
  all the energy directed towards collision partner

Recap from last session

Bimolecular collisions – reactive hard spheres ($A + B \rightarrow Products$)

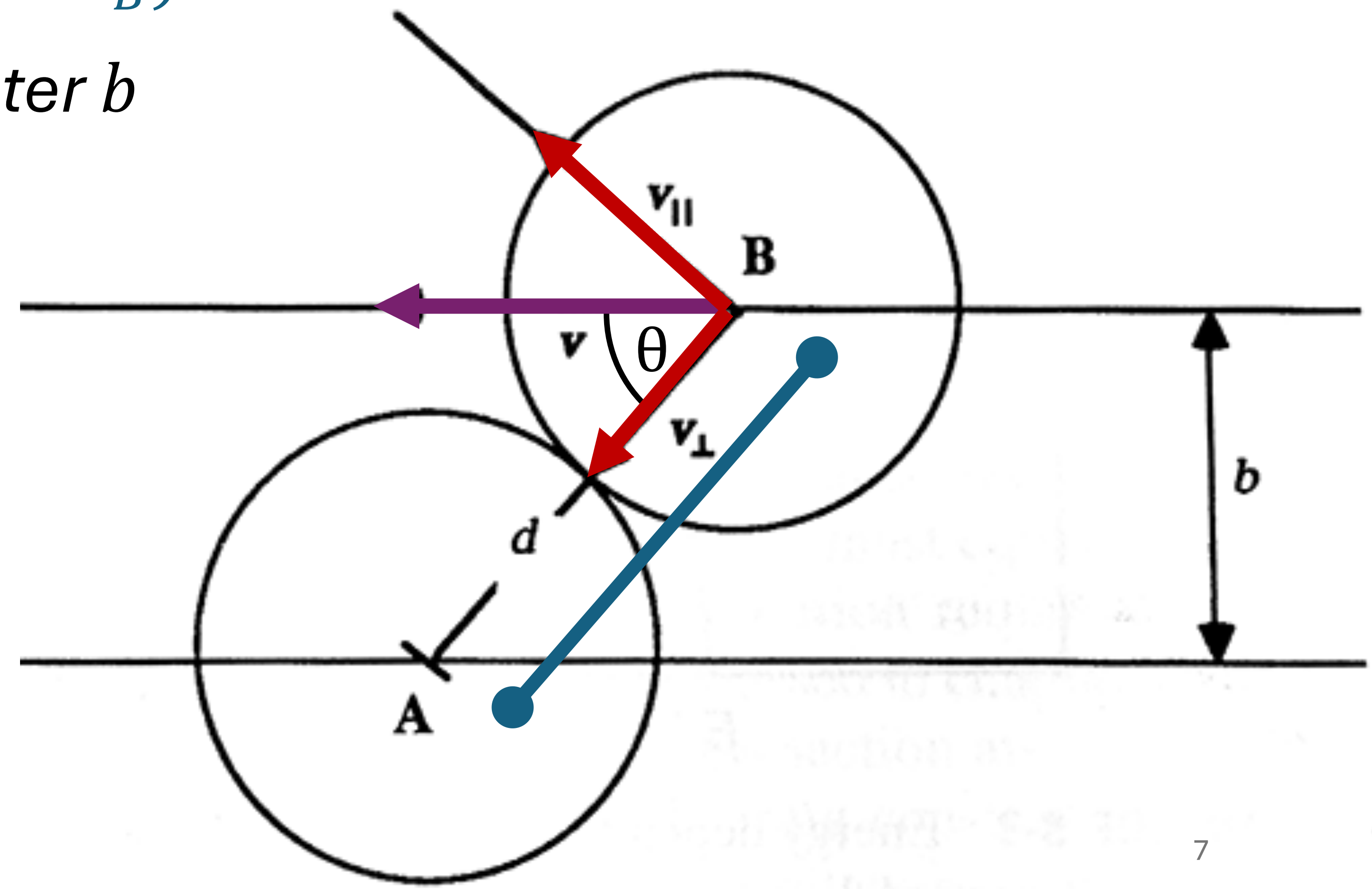
- $\boldsymbol{v}_{AB} = \boldsymbol{v}$ and $d = \frac{1}{2}(d_A + d_B)$
- introduced *impact parameter b*
- smaller b → larger $\boldsymbol{v}_{\perp}$
- Energy fraction is

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

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

- isolating for $E_{\perp}$ yields

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



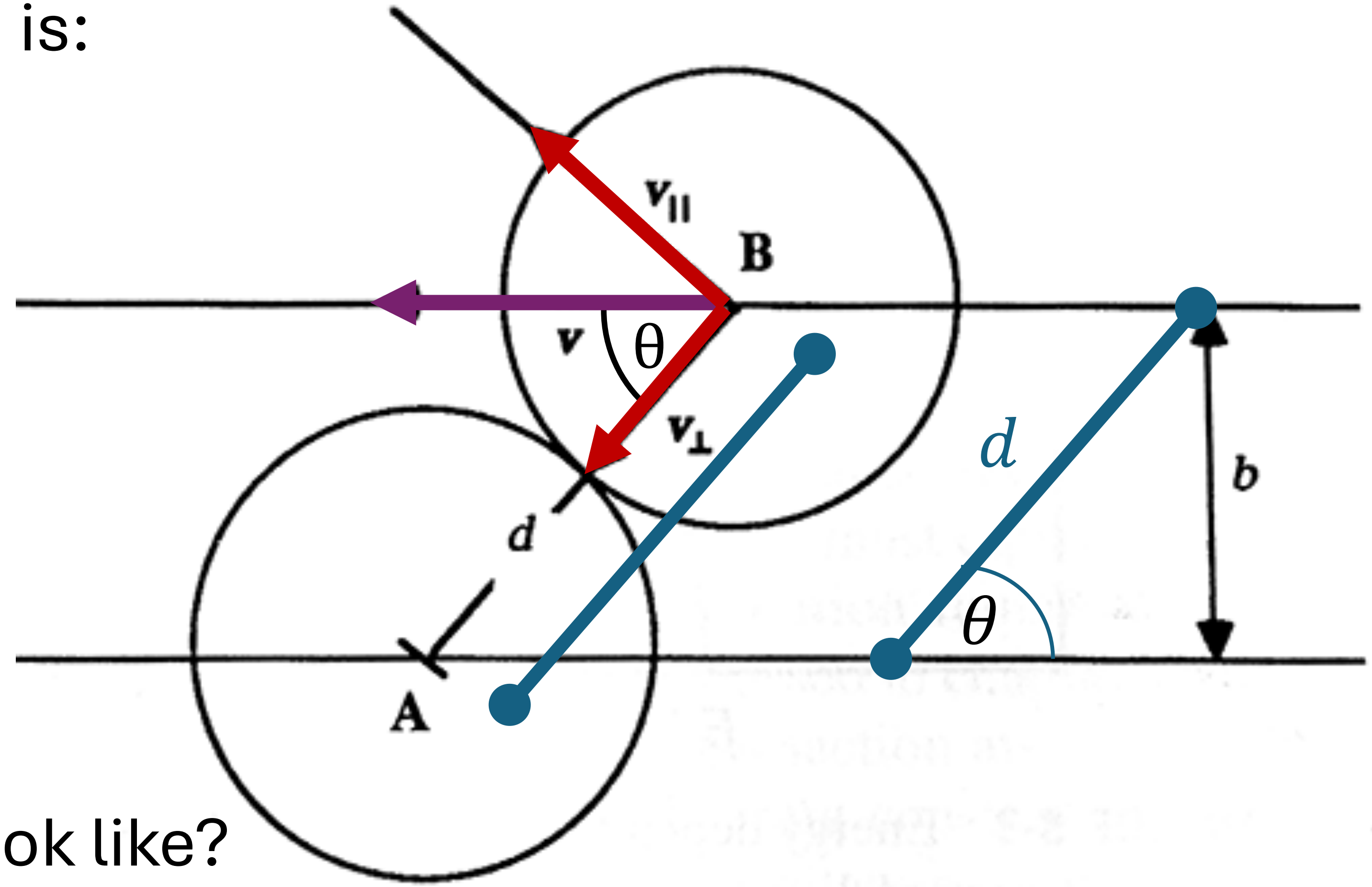
- For a collision, we need a minimum energy E^*

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

- The reaction probability then is:

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

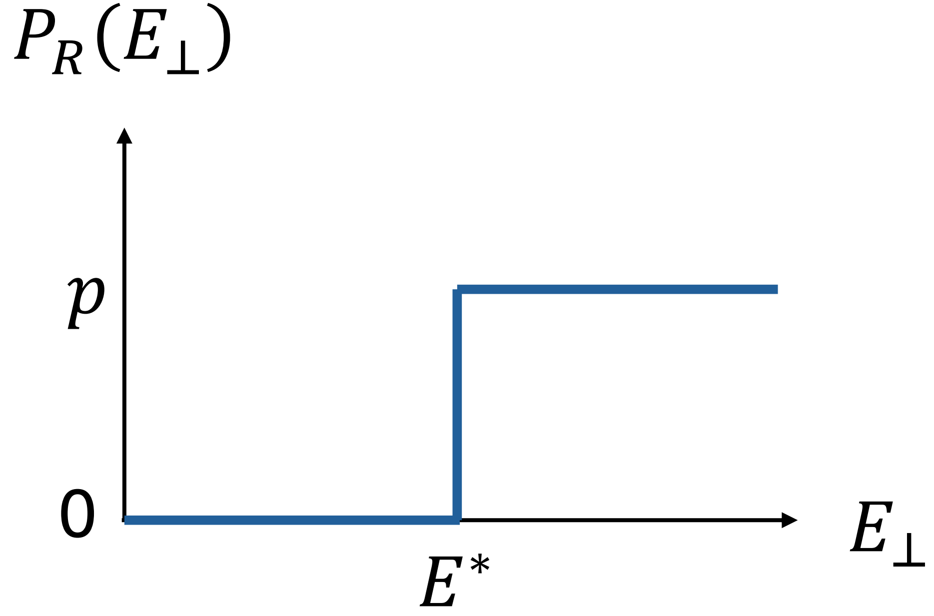
- The probability $\boldsymbol{p}$ we can call the ***steric factor*** (like a fit parameter)



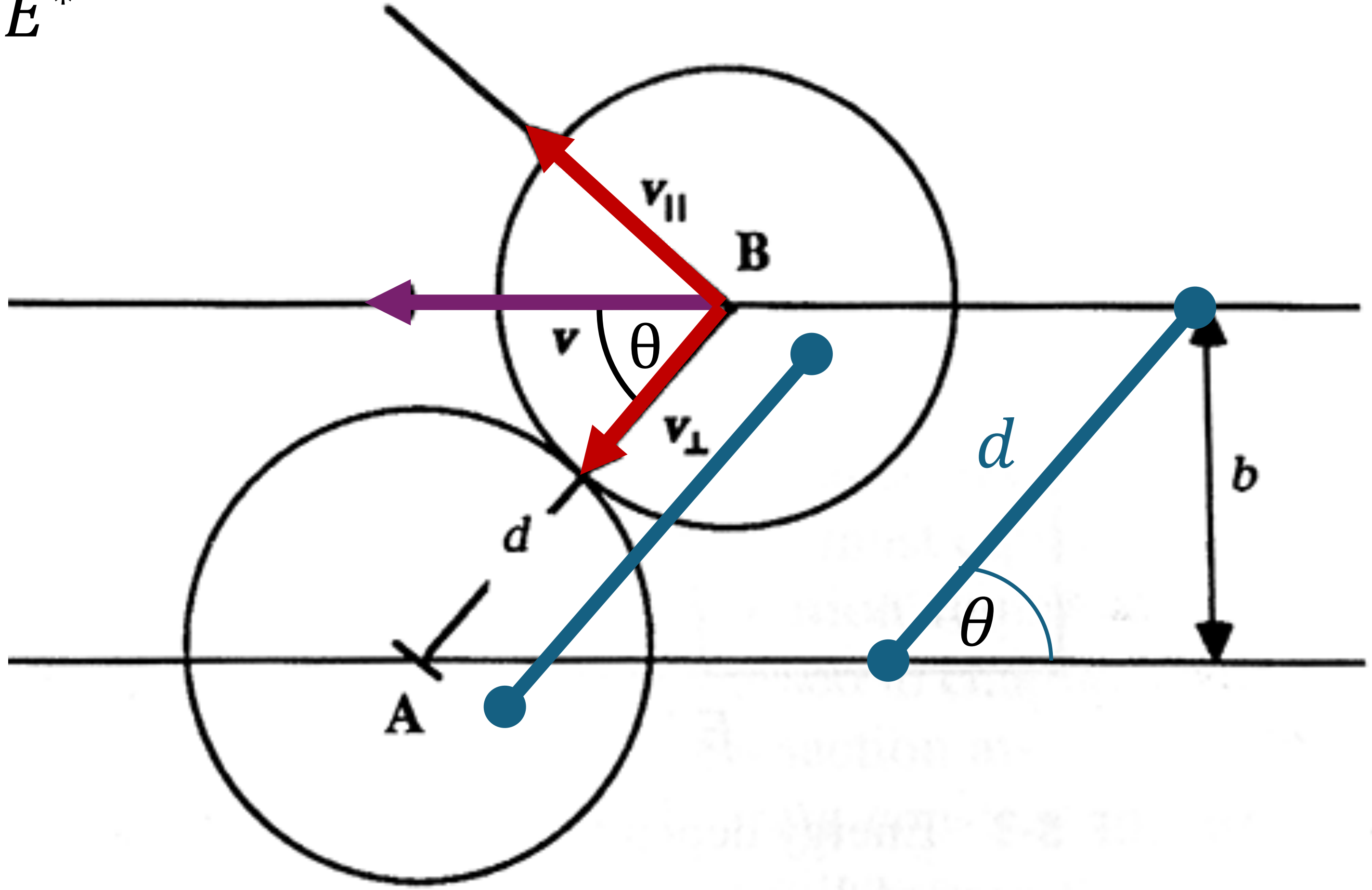
- How does a plot of $P_R(E_\perp)$ look like?

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

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

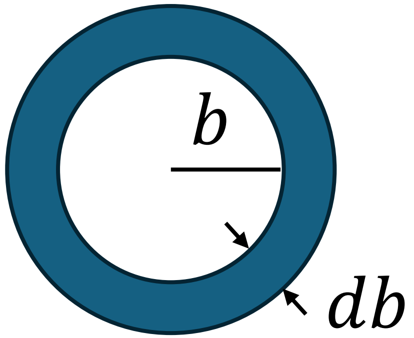


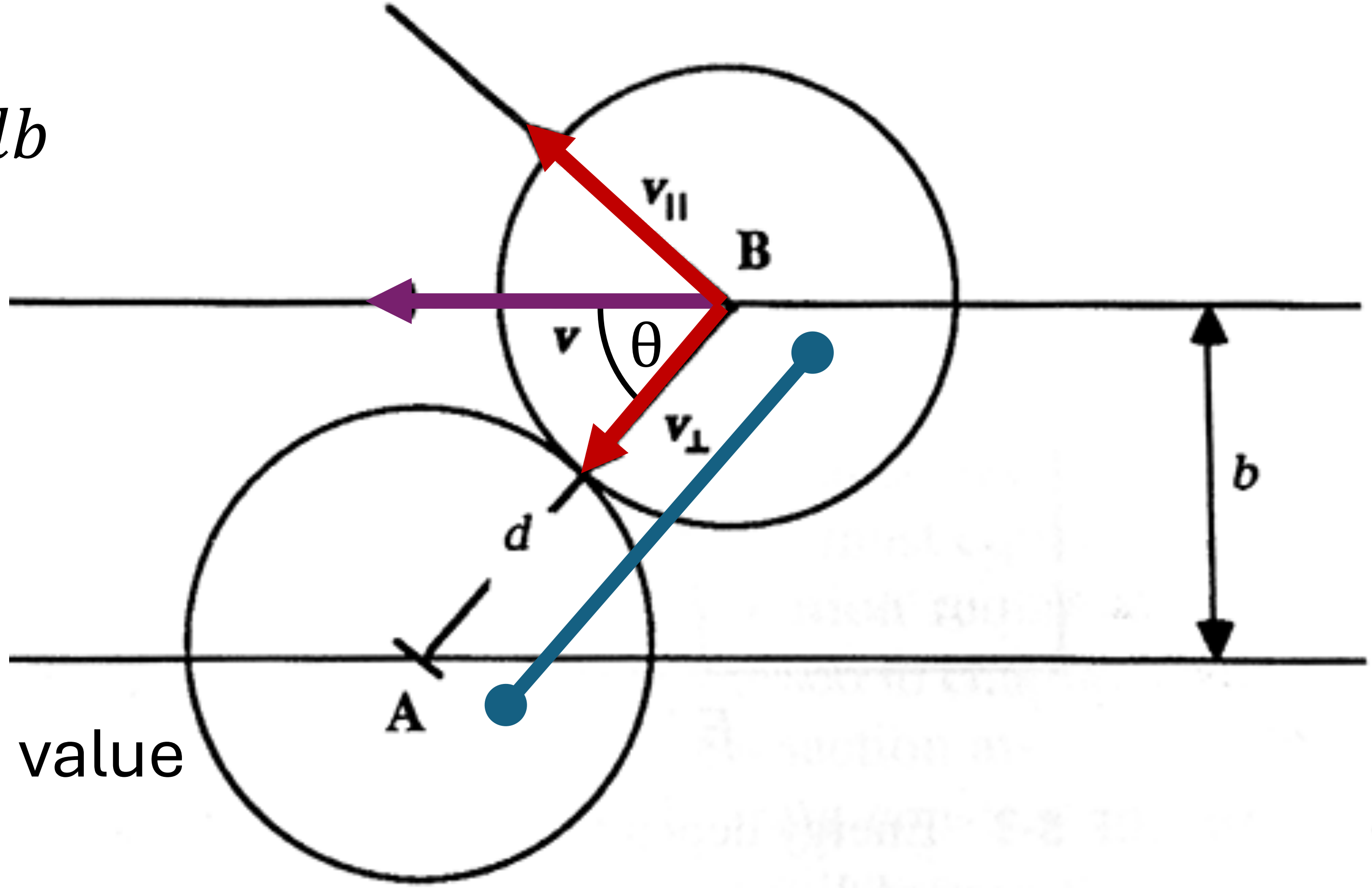
does not look super realistic, but it's a start...



- Let's define a *reaction cross section* $\sigma_R(E)$, taking into account the necessary energy and b for a reactive collision:
- $\sigma_R(E)$ can be understood as surface area A of an infinitesimally thin ring with: $A = 2\pi b\, db$

with radius b and thickness db

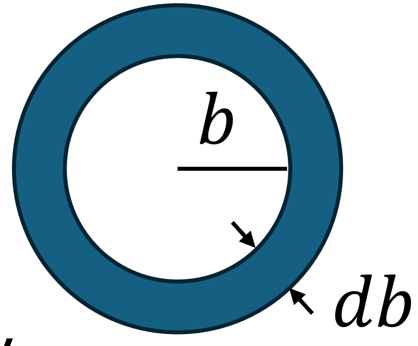




- A reaction occurs only,

if b not larger than a maximum value

- $\sigma_R(E)$ can be understood as surface area A of an infinitesimally thin ring with: $A = 2\pi b\, db$



- A reaction occurs only,

if b not larger than a maximum value

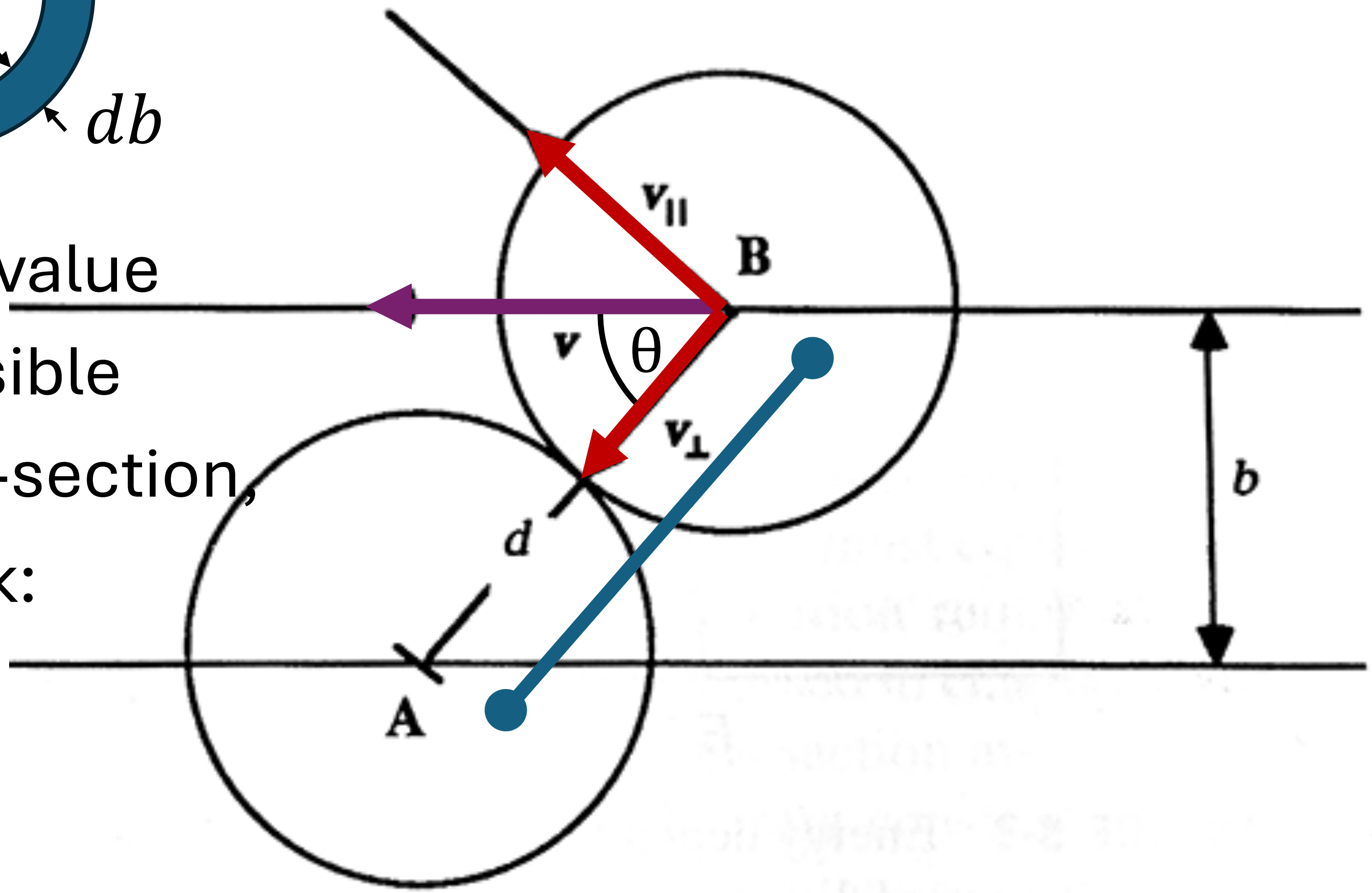
- Integrating over all these possible

b's gives us the reaction cross-section,

i.e., the surface area of the disk:

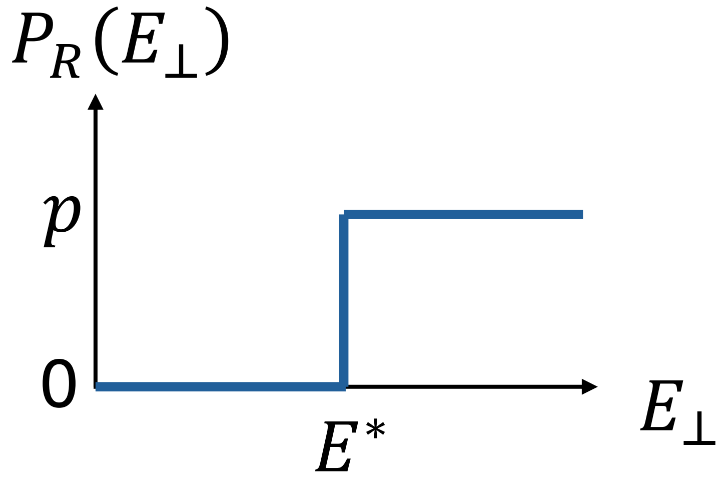
$$\sigma_R(E) = \int_0^{b,max} 2\pi b\, db \quad \text{or}$$

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



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

reaction cross-section for reactive hard spheres



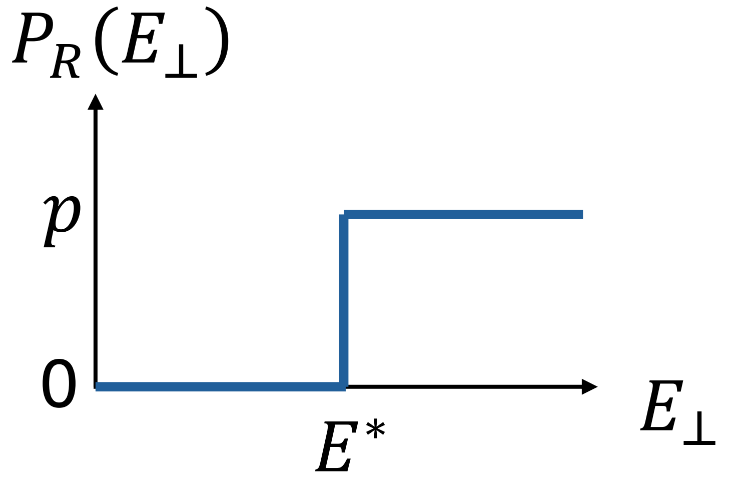
- From $E_\perp = E\left(1 - \frac{b^2}{d^2}\right) \geq E^*$ follows $\quad b \leq d\sqrt{1 - \frac{E^*}{E}} = b_{max}$
- inserting as new integral boundary yields

$$\sigma_R(E) = \int_0^{d\sqrt{1-\frac{E^*}{E}}} p \cdot 2\pi b db = \pi d^2 p(1 - \frac{E^*}{E})$$

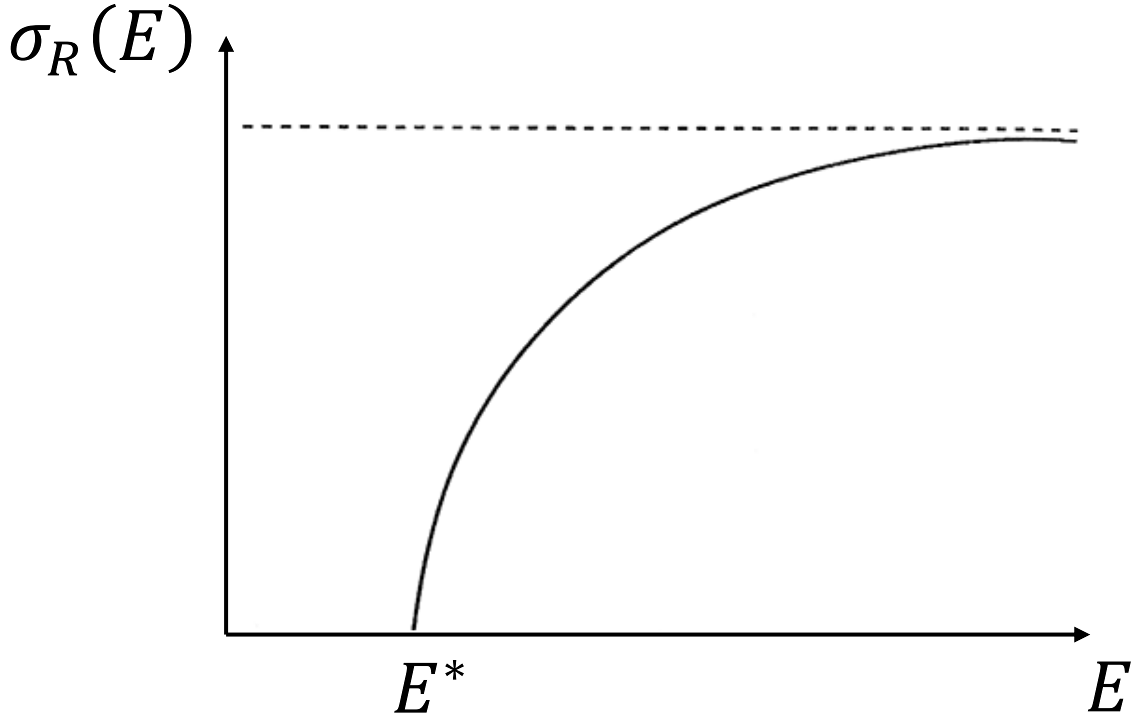
or more generally:

$$\sigma_R(E) = \begin{cases} 0 & \text{if } E < E^* \\ \pi d^2 p(1 - \frac{E^*}{E}) & \text{if } E \geq E^* \end{cases}$$

$$\sigma_R(E) = \begin{cases} 0 & \text{if } E < E^* \\ \pi d^2 p\left(1 - \frac{E^*}{E}\right) & \text{if } E \geq E^* \end{cases}$$



- How does a plot of this look?

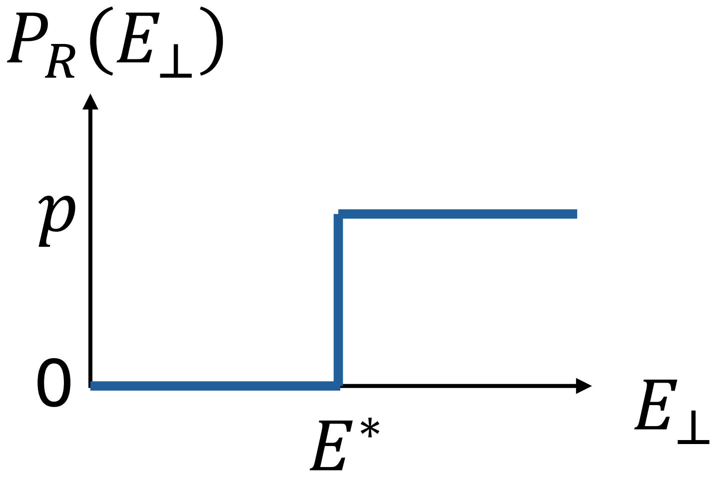


$\pi d^2 p$ ← What does this limit mean?

Hard-sphere collision cross-section
×
Steric factor (probability <1) p

for large E, we approach hard-sphere model! (multiplied with steric correction factor) ☺

$$\sigma_R(E) = \begin{cases} 0 & \text{if } E < E^* \\ \pi d^2 p\left(1 - \frac{E^*}{E}\right) & \text{if } E \geq E^* \end{cases}$$



- How do we get to the desired rate constant $k(T)$?
- How are relative energies distributed for such collisions?
- To obtain $k(T) = \langle \sigma_R(E) v(E) \rangle$

  we average over the thermal population, given by M.B. distribution $F(v)$ of *relative speeds* from before:

$$k(T) = \int_0^\infty \sigma_R(E) v \cdot F(v) dv = \int_0^\infty \sigma_R(E) v \cdot 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{\mu v^2}{2k_B T}} dv$$

- What do we first have to do to solve this?
- bring all to same dependence, so coordinate transform of v to E

$$\sigma_R(E) = \begin{cases} 0 & \text{if } E < E^* \\ \pi d^2 p(1 - \frac{E^*}{E}) & \text{if } E \geq E^* \end{cases}$$

$$k(T) = \int_0^\infty \sigma_R(E) v \cdot F(v) dv = \int_0^\infty \sigma_R(E) v \cdot 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{\mu v^2}{2 k_B T}} dv$$

- What do we first have to do to solve this?
- bring all to same dependence, so transformation of v to E
- use $E = \frac{1}{2}\mu v^2$ and $dv = \frac{dE}{\mu v}$ to obtain

$$k(T) = \frac{1}{k_B T}\left(\frac{8}{\pi \mu k_B T}\right)^{\frac{1}{2}} \int_0^\infty E \sigma_R(E) e^{-\frac{E}{k_B T}} dE$$

$$= \frac{1}{k_B T}\left(\frac{8}{\pi \mu k_B T}\right)^{\frac{1}{2}} \int_{E^*}^\infty \pi d^2 p(E - E^*) e^{-\frac{E}{k_B T}} dE$$

(for $E < E^*$, $\sigma_R(E)$ is zero)

$$k(T) = \frac{1}{k_B T}\left(\frac{8}{\pi\mu k_B T}\right)^{\frac{1}{2}} \int_{E^*}^{\infty} \pi d^2 p(E - E^*) e^{-\frac{E}{k_B T}} dE$$

- integration, using $\int_0^{\infty} x e^{-\frac{x}{a}} dx = a^2$ yields

$$k(T) = \pi d^2 \left(\frac{8 k_B T}{\pi\mu}\right)^{\frac{1}{2}} p\, e^{-\frac{E^*}{k_B T}}$$

What do these terms mean?

hard-sphere cross section × mean velocity × Arrhenius eq.

- Arrhenius pre-factor A now has become a product of correction terms, incl. steric factor $p < 1$, accounting for the fact that even at sufficient energy, not every collision might be reactive due to geometric limitations of molecular orientations

5.7 Dynamics of Bimolecular Reactions – Two-Body Classical Scattering

- Question: At what *angle* do collision partners depart after a collision?
- Or in c.m. frame: At what angle does the pseudo-particle exit the horizontal line?
- We want to become more precise in not just knowing the reaction cross section overall, but also *for a specific angle*
- Why might this extra complication be a useful thing to know?

Because reaction *mechanisms* can often be derived by knowing these angles!!!

→ Let's derive ***differential*** reaction cross-sections as function of angle

- We assume particles A & B collide and use the center of mass frame
- assume they *interact* through a *central potential* $U(r)$
- r is distance between particles

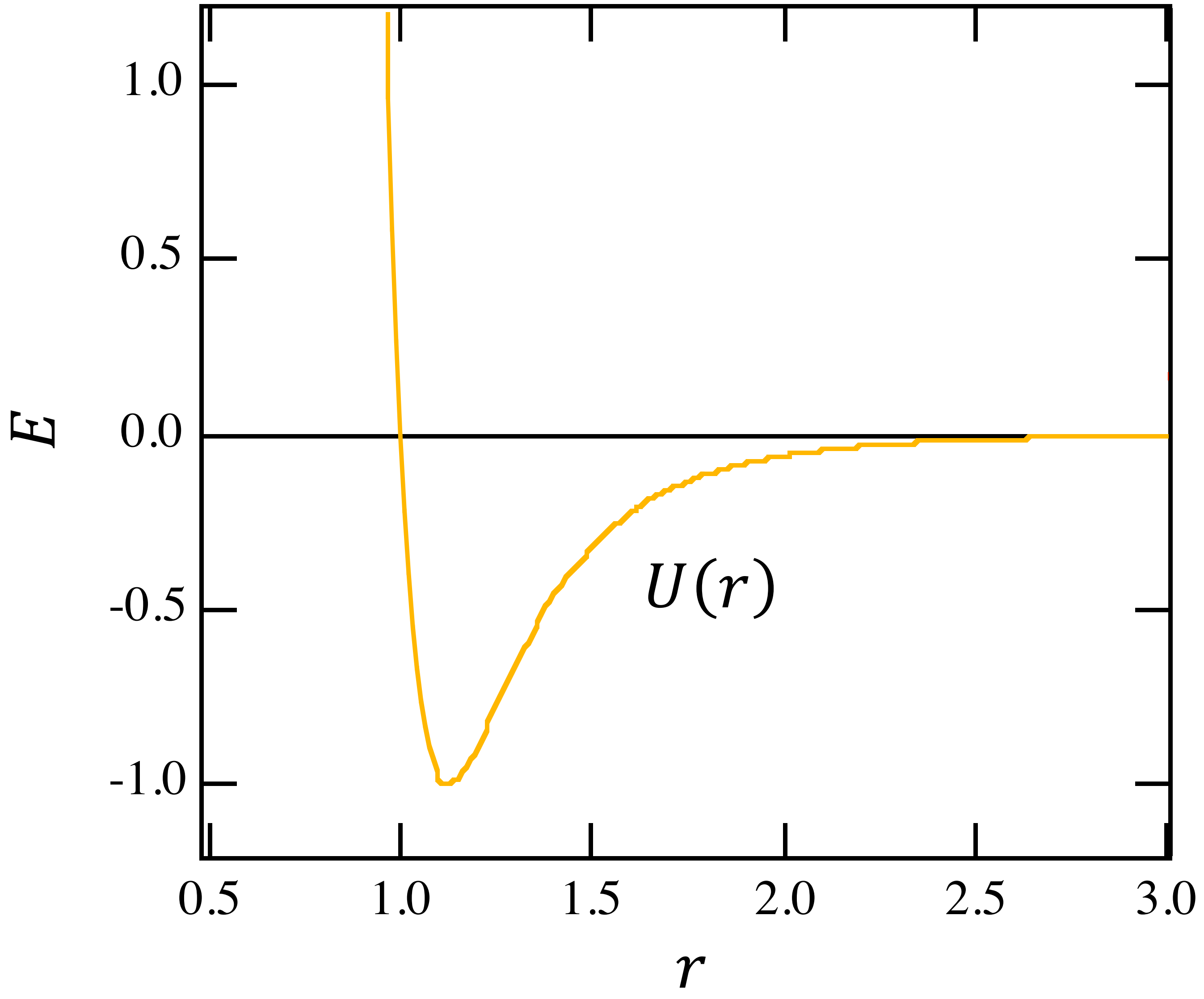
- total energy of collision partners is sum of kinetic, potential and internal energy:

$$E = \frac{1}{2} m v_A^2 + \frac{1}{2} m v_B^2 + U(r) + E_{A,\text{ internal}} + E_{B,\text{ internal}}$$

- we can distinguish *elastic*, *inelastic*, and *reactive* collisions

- How could an interaction potential look like?

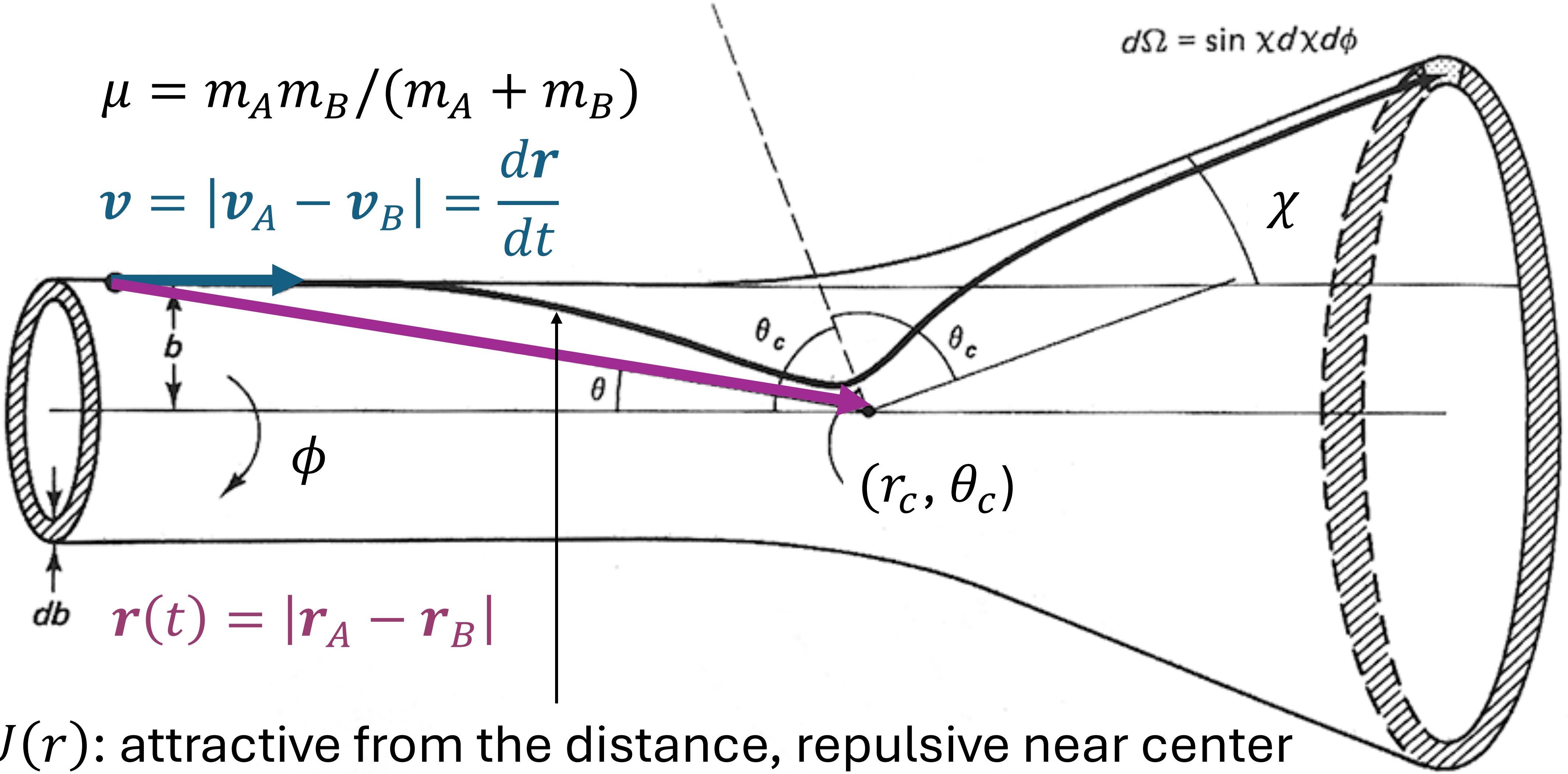
A possible (typical) *central potential* $U(r)$



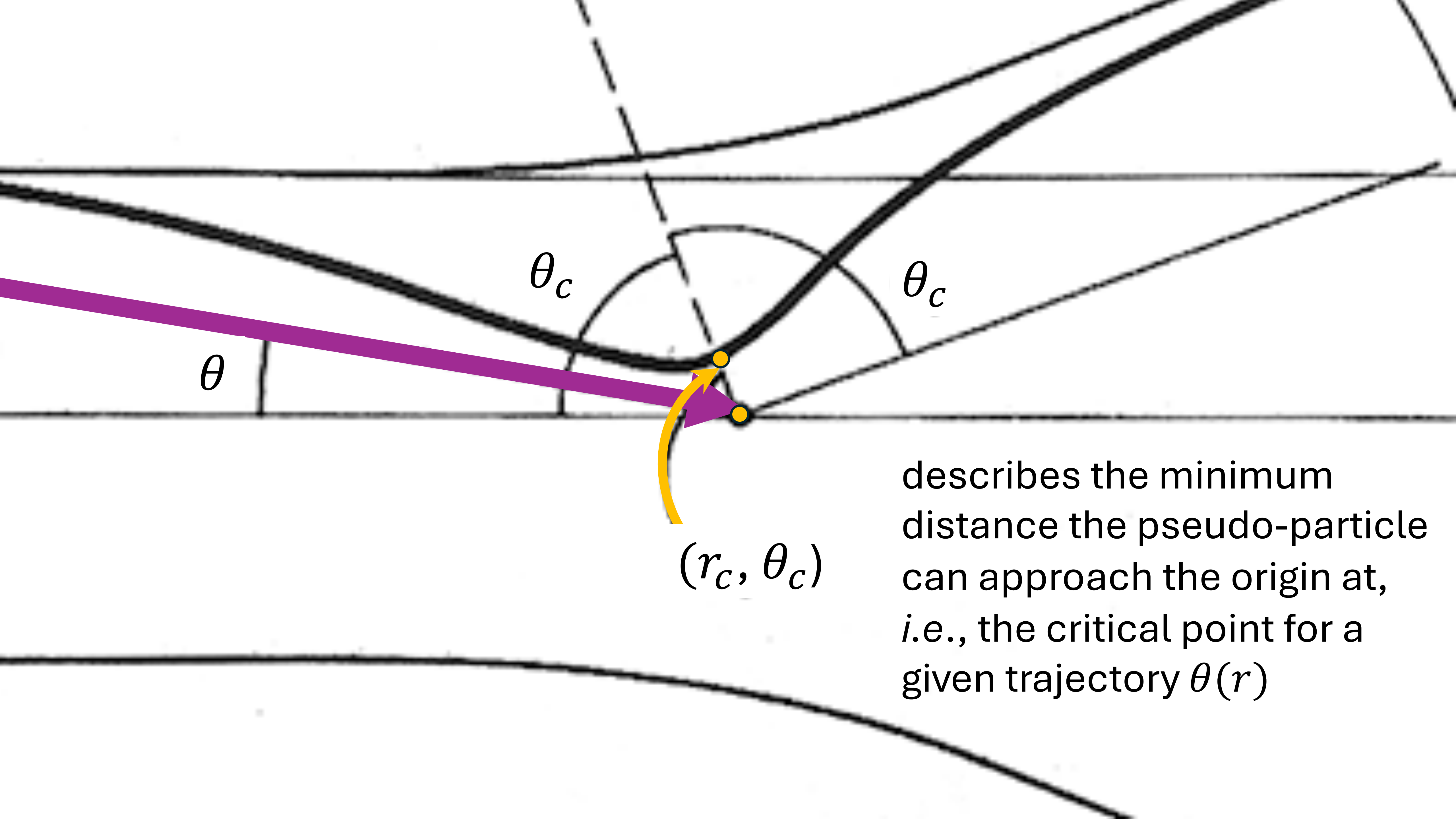
repulsive

attractive

- Fixed center of mass coordinate system, central spherical potential $U(r)$
- Before collision: assume particles approach from infinite distance

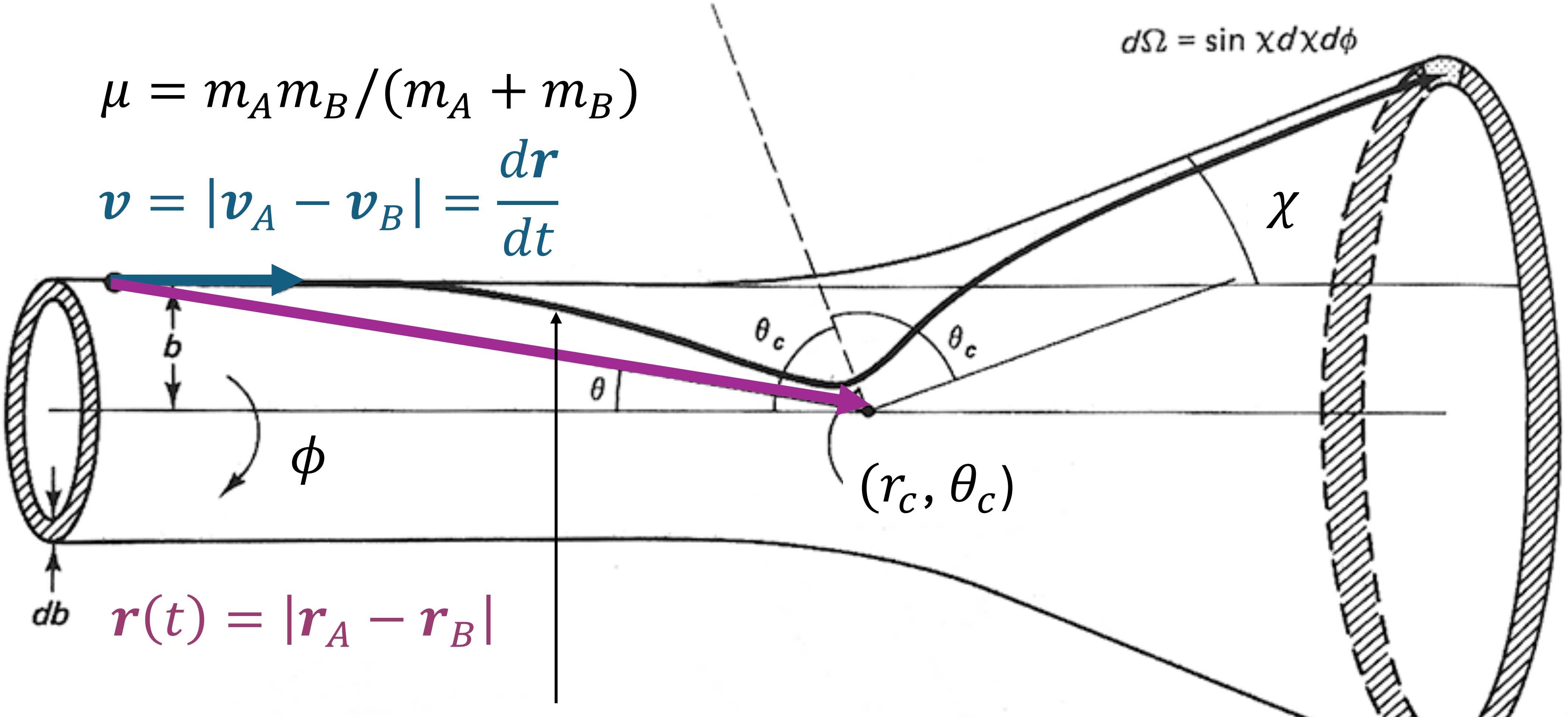


$U(r)$: attractive from the distance, repulsive near center



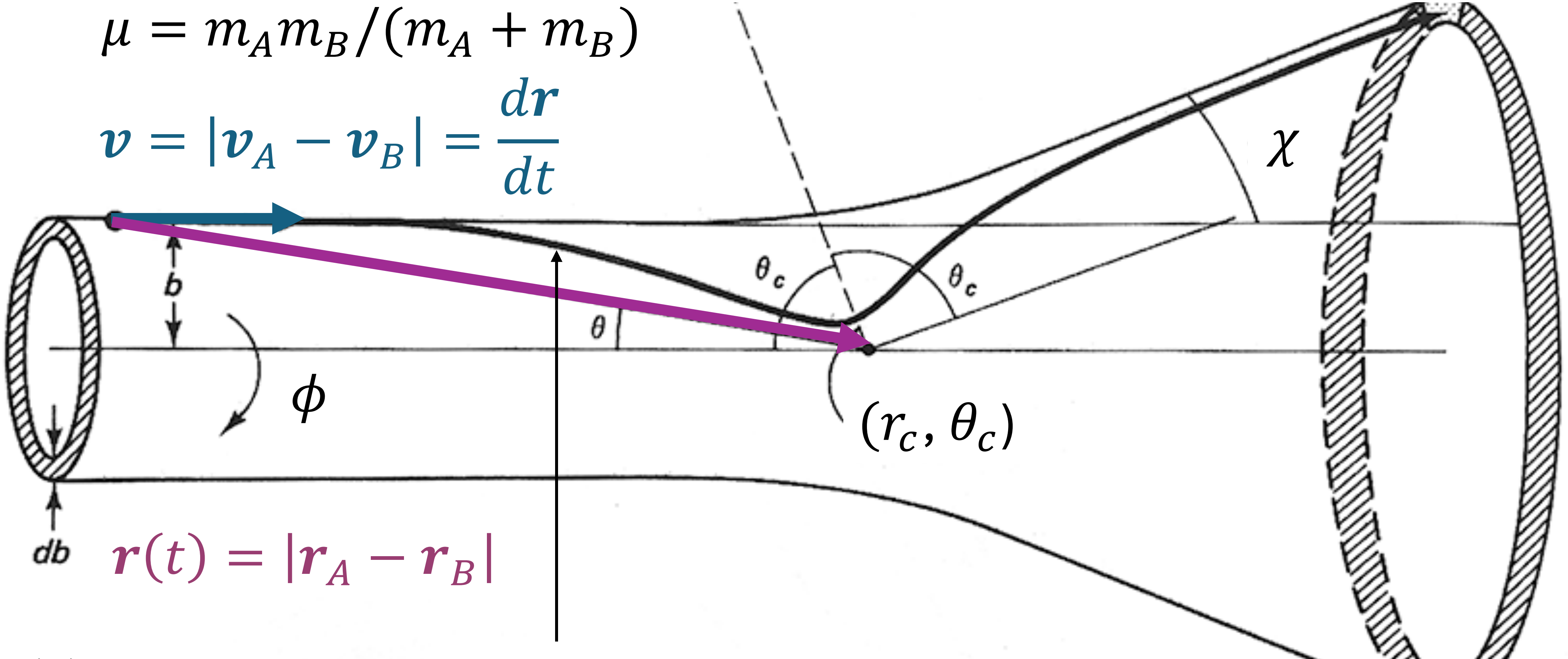
(r_c, θ_c) describes the minimum distance the pseudo-particle can approach the origin at, *i.e.*, the critical point for a given trajectory $\theta(r)$

- Fixed center of mass coordinate system, central *spherical* potential $U(r)$
- Before collision: assume particles approach from infinite distance



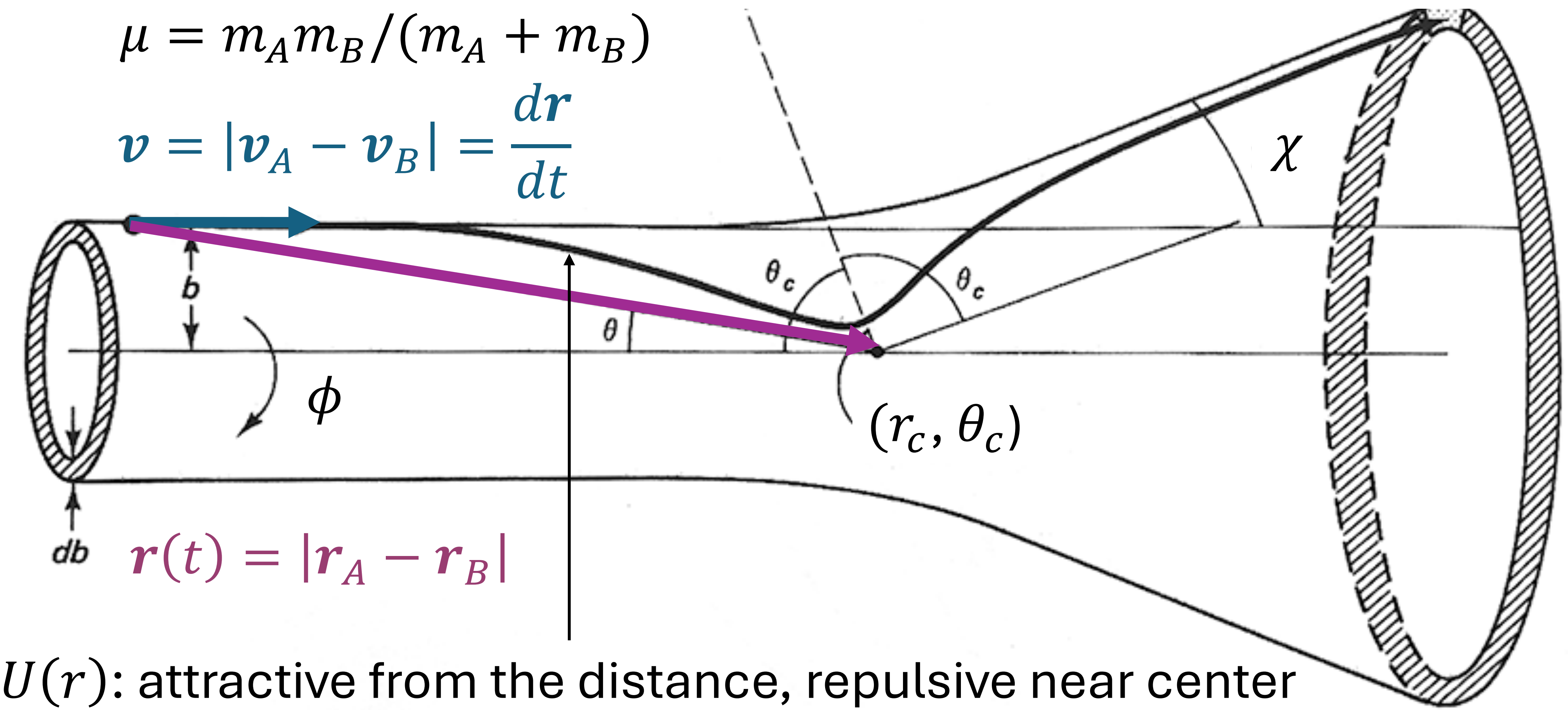
$U(r)$: attractive from the distance, repulsive near center

- The radial velocity at the critical point is: $\dot{r}_{r=r_c} = 0$
- So don't have radial velocity here, only tangential velocity
- Trajectory (like potential $U(r)$) is *symmetrical* around center



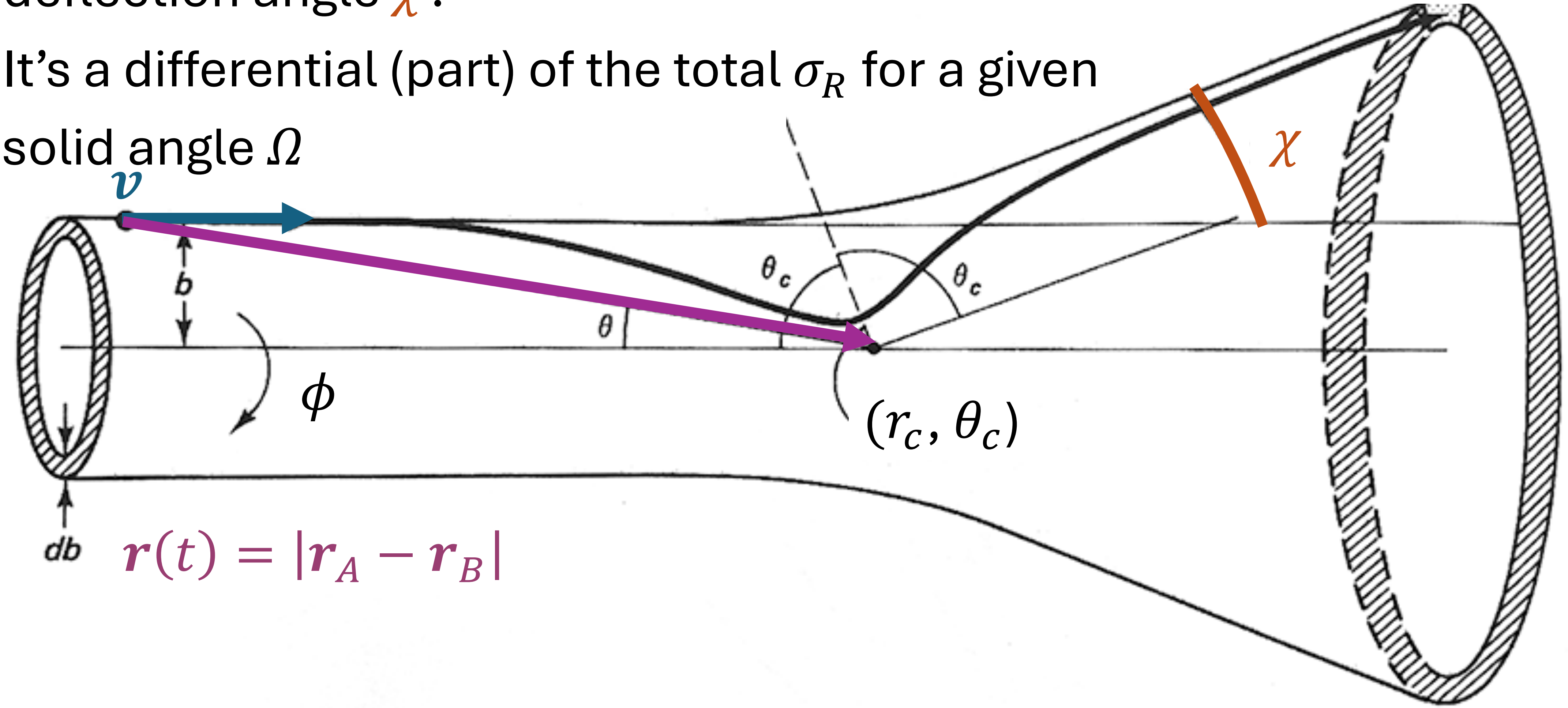
$U(r)$: attractive from the distance, repulsive near center

- What about azimuthal angle ϕ?
- but we got a *spherical* potential $U(r)$
- ϕ does not change during scattering, as trajectory confined to a *plane*! ☺



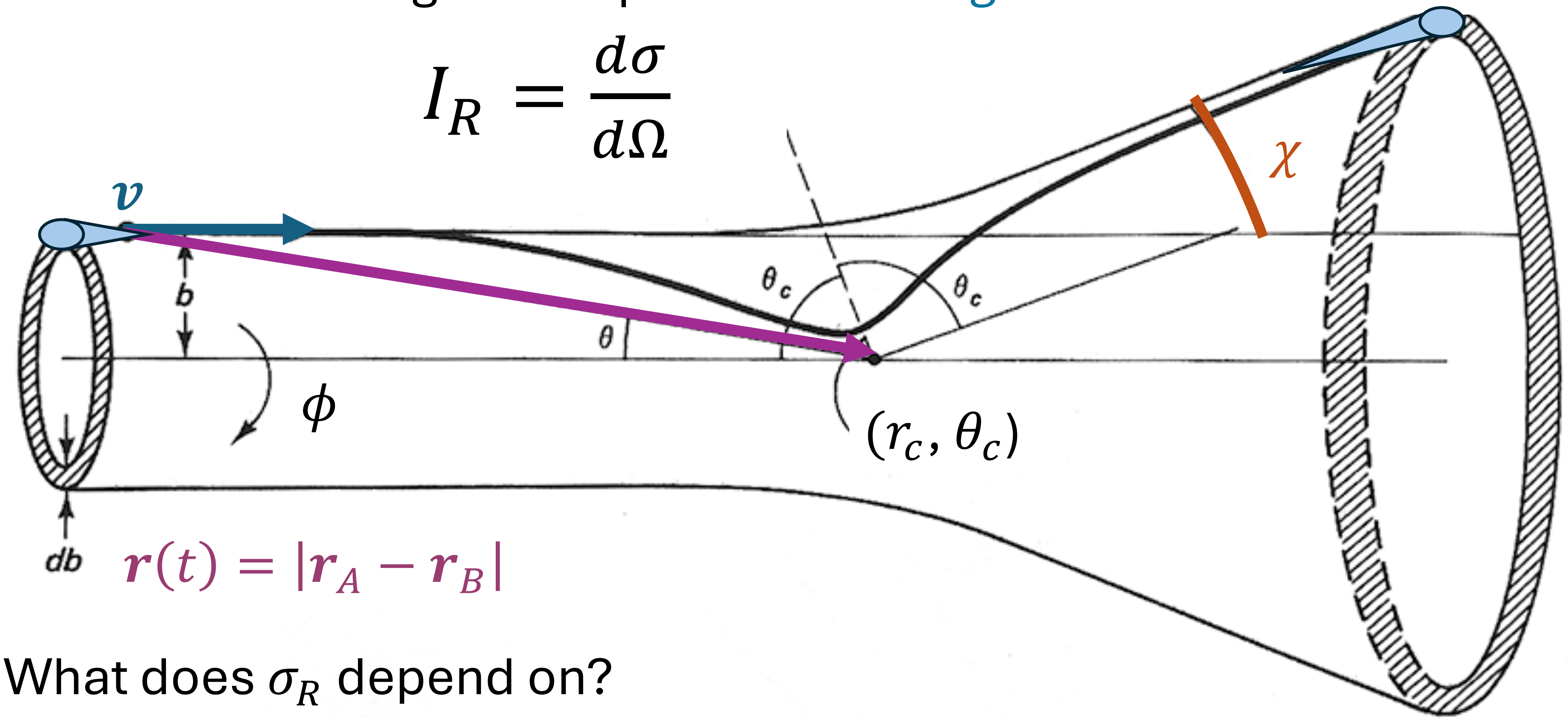
$U(r)$: attractive from the distance, repulsive near center

- Deflection angle χ will be relevant to derive differential cross-section
- From before: (total) reaction cross-section σ_R (= surface area of full disc)
- How large is the disk that will lead to scattering into one specific deflection angle χ?
- It's a differential (part) of the total σ_R for a given solid angle Ω



- How large is the disk that will lead to scattering into one specific deflection angle χ?
- The *differential cross section* I_R is a differential (part) of the total σ_R that leads to scattering into a specific *solid angle Ω* :

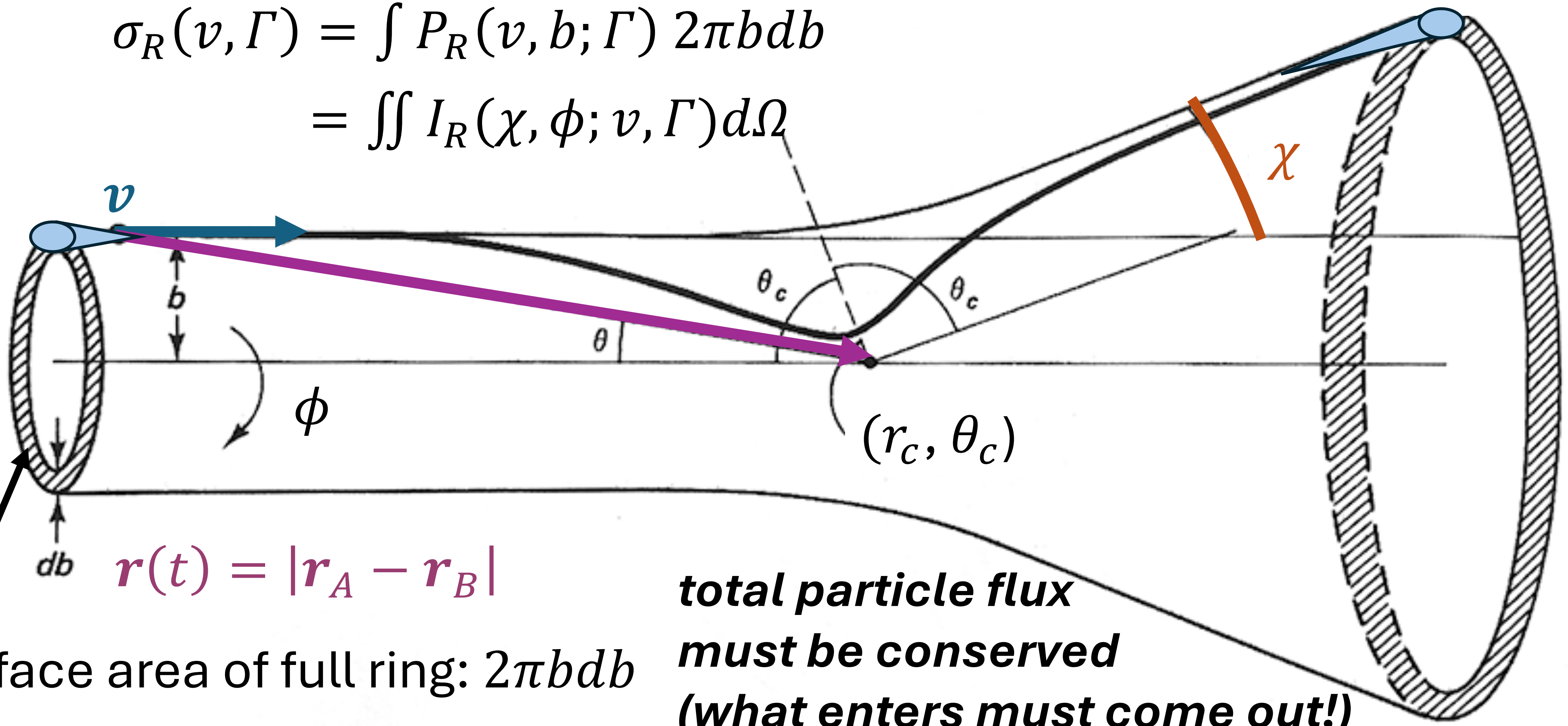
$$I_R = \frac{d\sigma}{d\Omega}$$



- What does σ_R depend on?

- The *differential cross section* I_R is a differential (part) of the total σ_R that leads to scattering into a specific *solid angle Ω* : $I_R = \frac{d\sigma}{d\Omega}$
- What does σ_R depend on? Velocity v, impact param. b, quantum state (Γ)

$$\sigma_R(v, \Gamma) = \int P_R(v, b; \Gamma)\, 2\pi b db$$
$$= \iint I_R(\chi, \phi; v, \Gamma) d\Omega$$



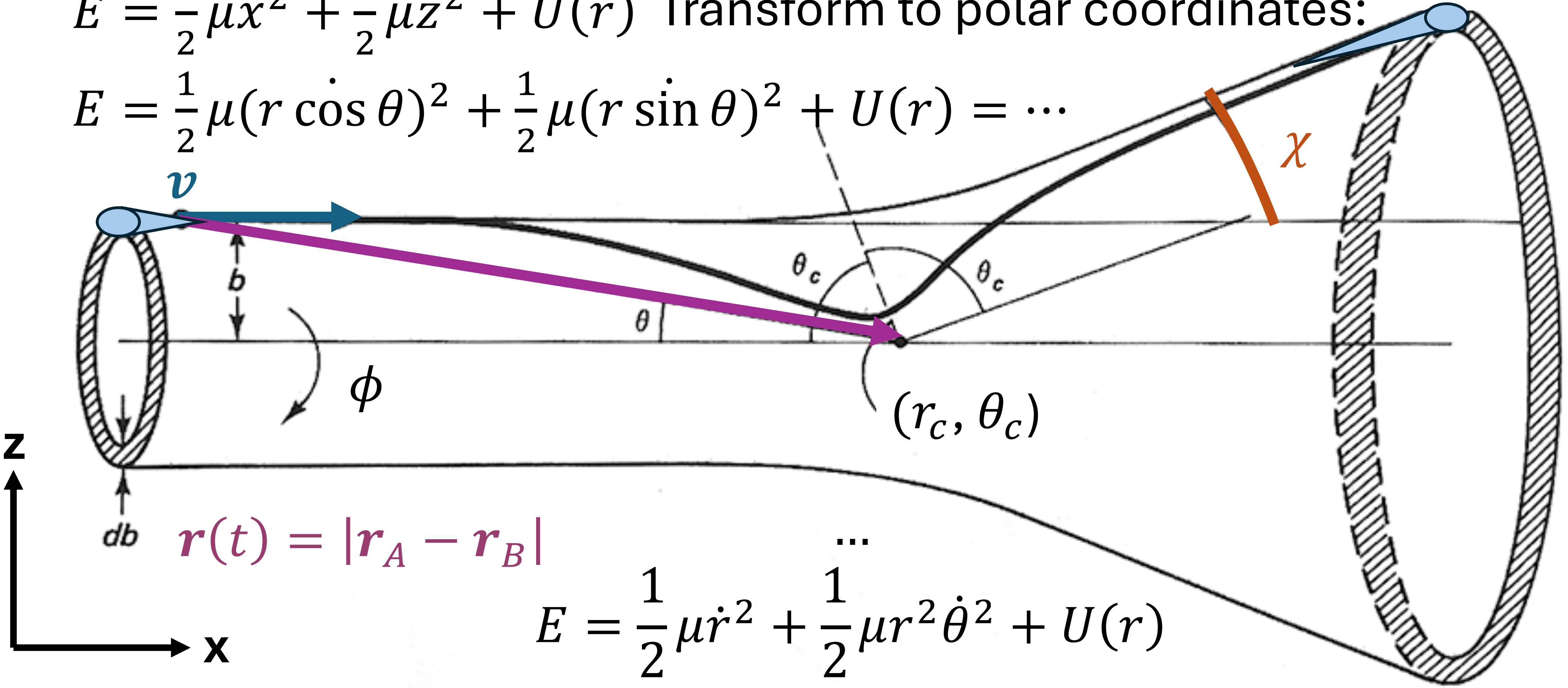
surface area of full ring: $2\pi b db$

total particle flux must be conserved (what enters must come out!)

- To derive the partial scattering cross-section I_R we need to find the *deflection function* $\chi(b)$
- Total energy of particle (Cartesian coordinates) moving in xz plane is:

$$E = \frac{1}{2}\mu\dot{x}^2 + \frac{1}{2}\mu\dot{z}^2 + U(r)$$ Transform to polar coordinates:

$$E = \frac{1}{2}\mu(r\dot{\cos}\,\theta)^2 + \frac{1}{2}\mu(r\dot{\sin}\,\theta)^2 + U(r) = \cdots$$



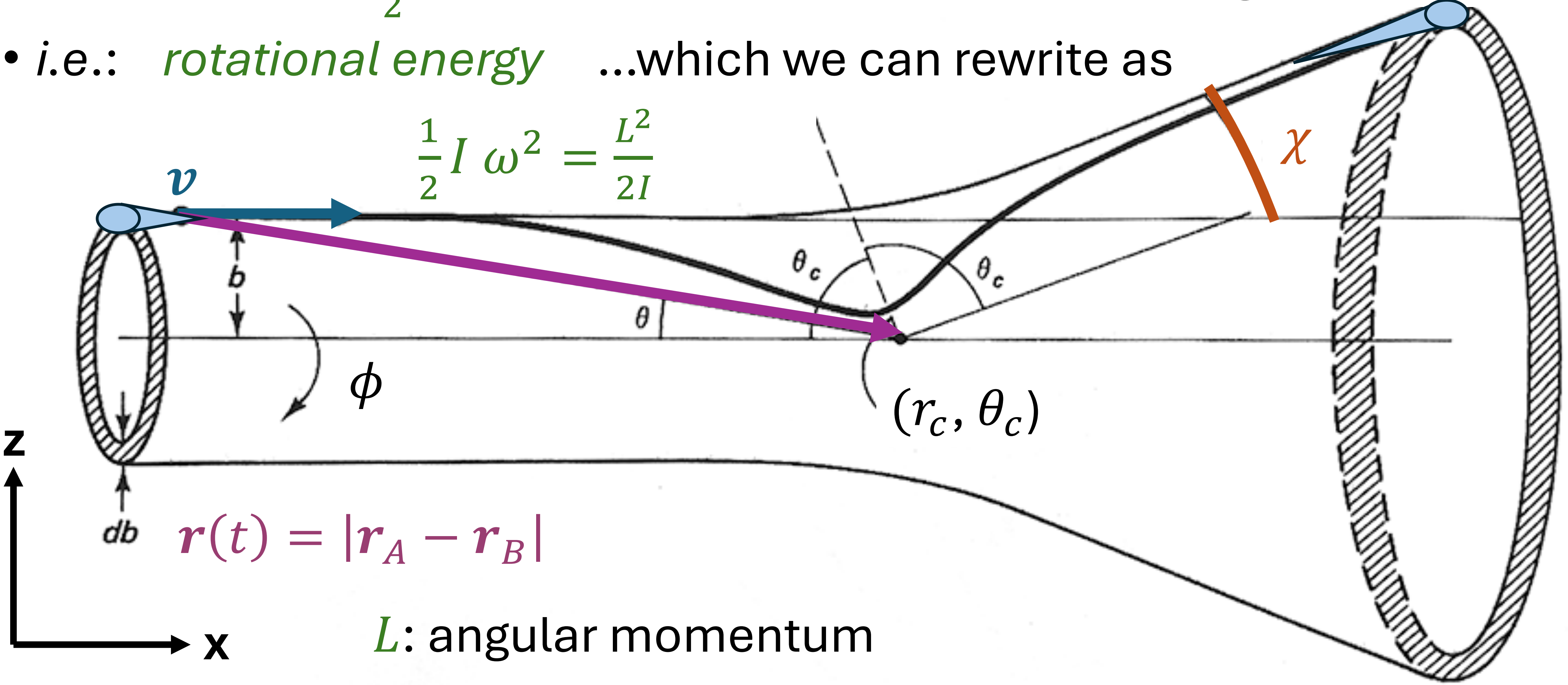
…

$$E = \frac{1}{2}\mu\dot{r}^2 + \frac{1}{2}\mu r^2\dot{\theta}^2 + U(r)$$

$E = \frac{1}{2}\mu\dot{r}^2 + \frac{1}{2}\mu r^2\dot{\theta}^2 + U(r)$ What are the different parts of this sum?

- radial kin. energy & angular motion associated energy (& potential energy)
- or could write: $\frac{1}{2}I\,\omega^2$, with moment of inertia I & angular velocity ω
- *i.e.*: *rotational energy* ...which we can rewrite as

$$\frac{1}{2}I\,\omega^2 = \frac{L^2}{2I}$$



$\boldsymbol{r}(t) = |\boldsymbol{r}_A - \boldsymbol{r}_B|$

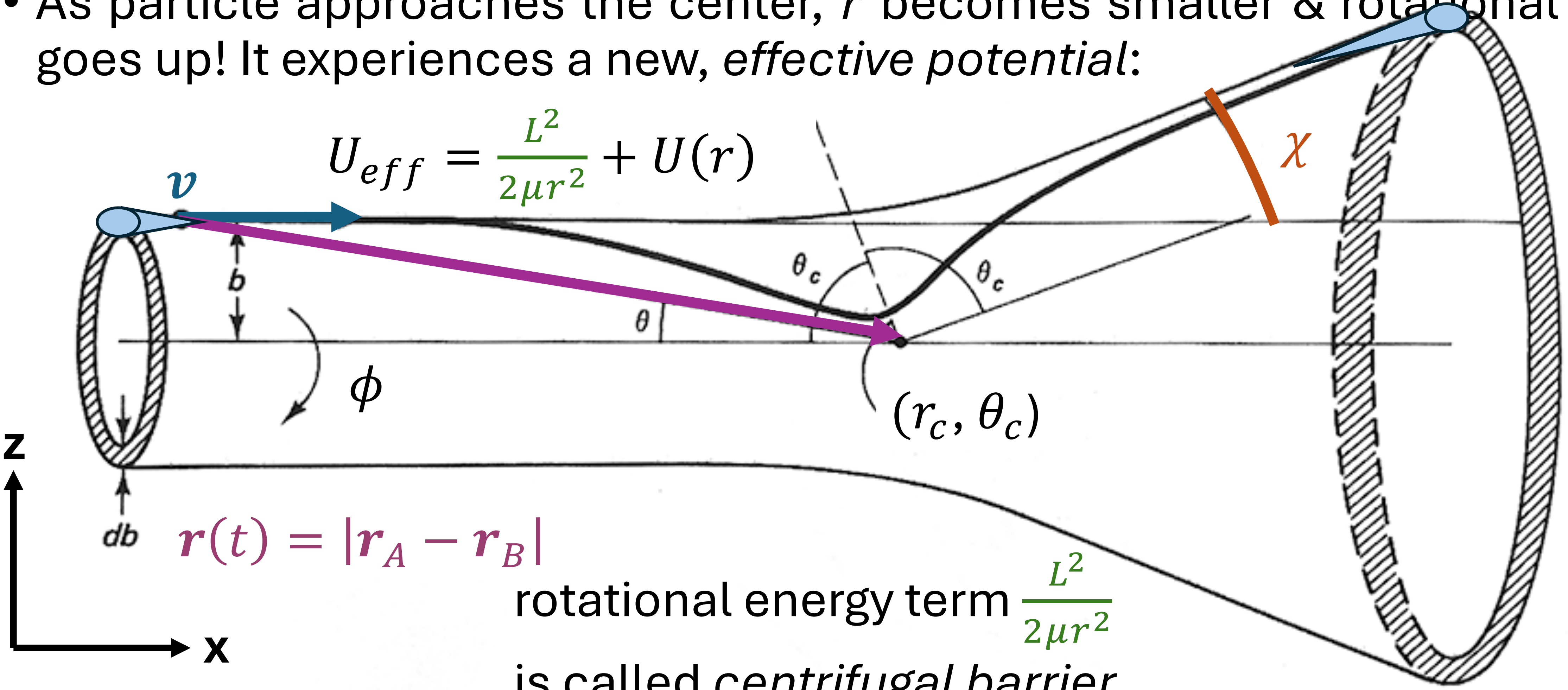
L: angular momentum

$$E = \frac{1}{2}\mu\dot{r}^2 + \frac{1}{2}\mu r^2\dot{\theta}^2 + U(r)$$ we can rewrite as

$$E = \frac{1}{2}\mu v^2 + \frac{L^2}{2\mu r^2} + U(r),$$ L is a const., as angular momentum is conserved

- As particle approaches the center, r becomes smaller & rotational energy goes up! It experiences a new, *effective potential*:

$$U_{eff} = \frac{L^2}{2\mu r^2} + U(r)$$

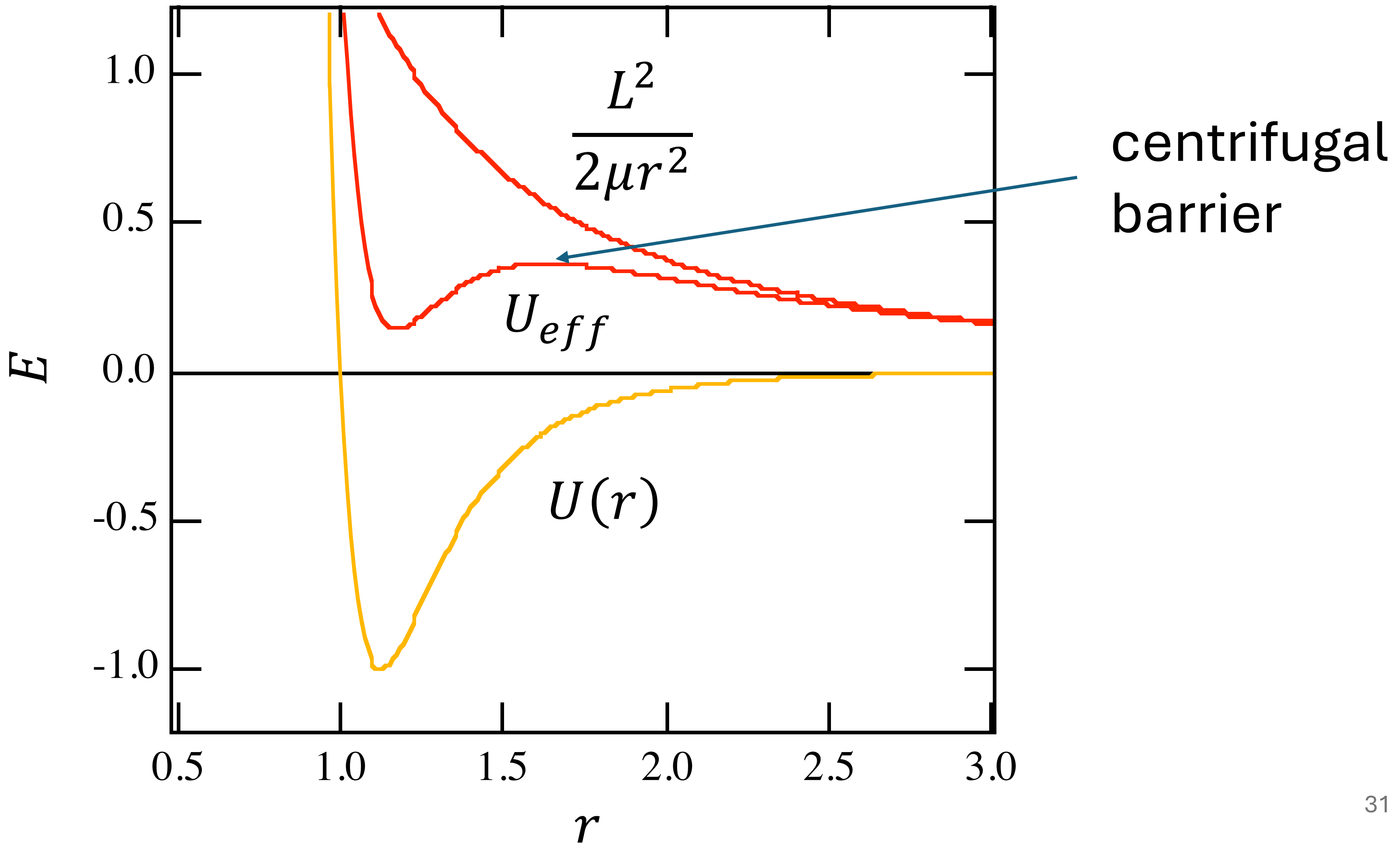


rotational energy term $\frac{L^2}{2\mu r^2}$

is called *centrifugal barrier*

$$U_{eff} = \frac{L^2}{2\mu r^2} + U(r)$$

- How do $U(r)$ and U_{eff} look plotted?



$$E = \frac{1}{2}\mu v^2 + \frac{L^2}{2\mu r^2} + U(r)$$

- How do we calculate L?

$L = |r \times p|$ what's the momentum?

- We derive it from the incoming particle's velocity v_0 and b orthogonal to it:

$$L = |r \times p| = \mu v_0 b$$

- We want to derive the trajectory $\theta(r)$
- we can relate θ to the angular momentum:

$L = \mu r^2 \frac{d\theta}{dt}$ rearrange to $d\theta = \frac{L}{\mu r^2} dt$

- Now let's solve the above differential equation:

$E = \frac{1}{2}\mu \left(\frac{dr}{dt}\right)^2 + \frac{L^2}{2\mu r^2} + U(r)$, rearranged to

$dt = -\left[\frac{2}{\mu}\left(E - U(r) - \frac{L^2}{2\mu r^2}\right)\right]^{-\frac{1}{2}} dr$ which we can substitute into our expression for $d\theta$

$$d\theta = -\frac{L}{\mu r^2}\left[\frac{2}{\mu}\left(E - U(r) - \frac{L^2}{2\mu r^2}\right)\right]^{-\frac{1}{2}} dr$$

- This is great. Integrating this gives us our trajectory $\theta(r)$
  [and from that, we can then get our desired deflection function $\chi(\mathrm{b})$]
- To make life easier, one substitution is still handy to do first:
- We know that $L = \mu v_0 b$ and use $E = \frac{1}{2}\mu v_0^2$
- meaning $L = b(2\mu E)^{\frac{1}{2}}$
- Did we not over-simplify here by reducing E to just a kinetic energy term?!
- No: at infinite distance ($r \to \infty$, $v = v_0$) the potential energy is zero:

$$U(r \to \infty) = 0$$

moreover, the rotational energy must be zero: $\frac{L^2}{2\mu(r\to\infty)^2} = 0$

- Substitution of this L expression yields

$$d\theta = -b \frac{dr}{r^2\left[1 - \frac{U(r)}{E} - \frac{b^2}{r^2}\right]^{\frac{1}{2}}}$$

- Finally, we integrate this:

$$\theta(r) = \int_0^\theta d\theta = -b \int_\infty^r \frac{dr}{r^2\left[1 - \frac{U(r)}{E} - \frac{b^2}{r^2}\right]^{\frac{1}{2}}}$$

- From this, we will be able to derive the deflection function and in the end, the differential scattering cross-section … next time! ☺