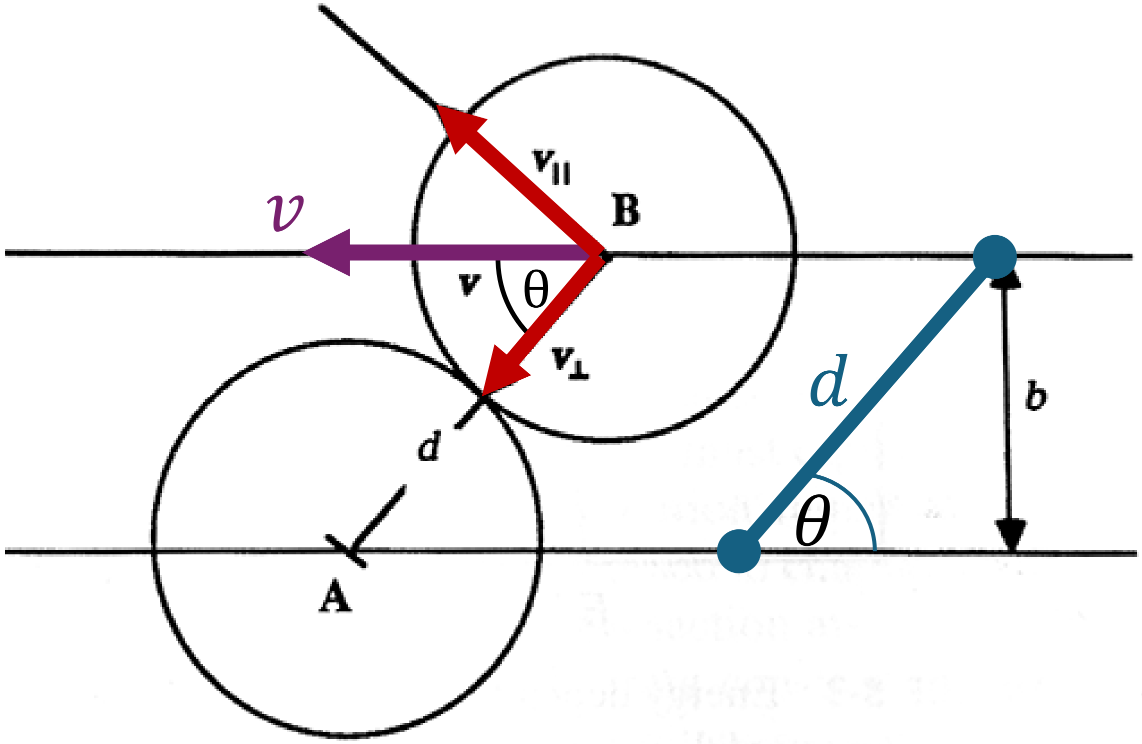
Kinetics & Dynamics of Chemical Reactions

Course CH-310

Prof. Sascha Feldmann

Recap from last session



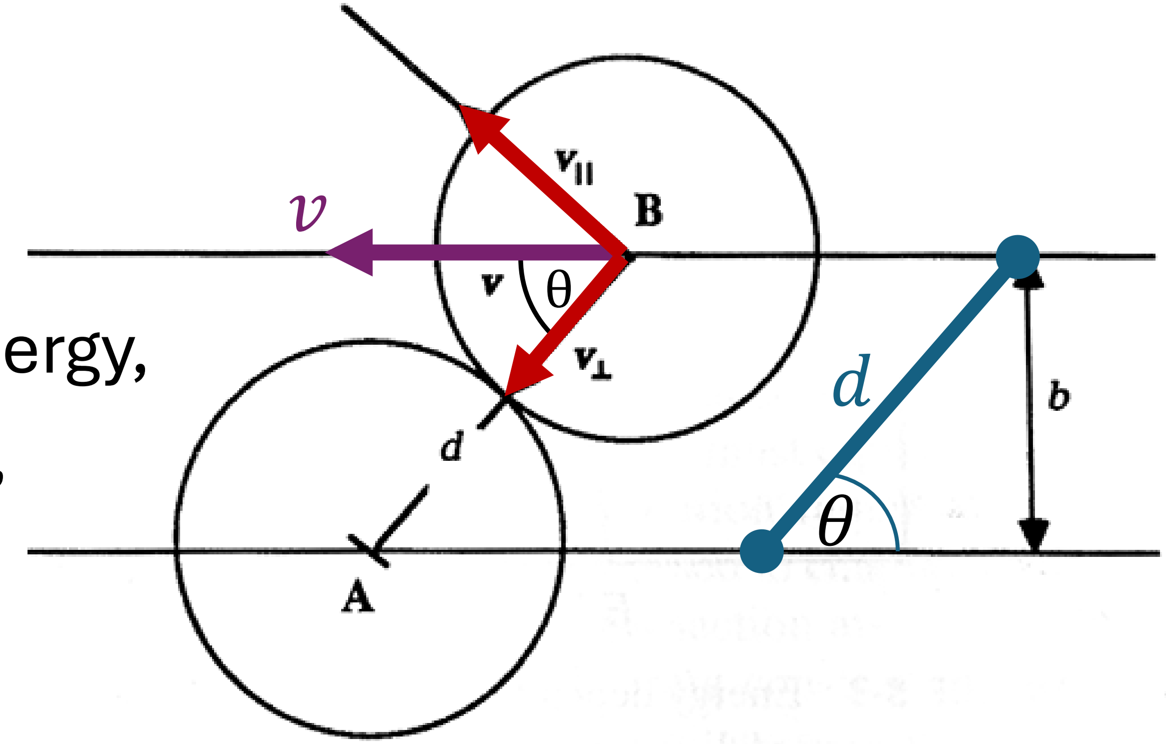
Reactive hard spheres model

- not every collision is reactive, energy dependence
- idea: $k(T) = \langle \sigma_R(E)\, u_{AB} \rangle$
- only orthogonal component can drive reaction
- probability: $P_R(E_\perp) = \begin{cases} 0 & \text{if } E_\perp < E^* \\ p & \text{if } E_\perp \geq E^* \end{cases}$
- Hard sphere collision cross section: $\sigma_{AB} = \pi d^2$
- Reaction cross section: $\sigma_R(E) = \begin{cases} 0 & \text{if } E < E^* \\ \pi d^2 p (1 - \frac{E^*}{E}) & \text{if } E \geq E^* \end{cases}$

Recap from last session

Reactive hard spheres model

- reaction cross section depends on energy, so we calculated the thermal average, using M.B. distribution and got:



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

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

Arrhenius pre-factor A

Recap from last session

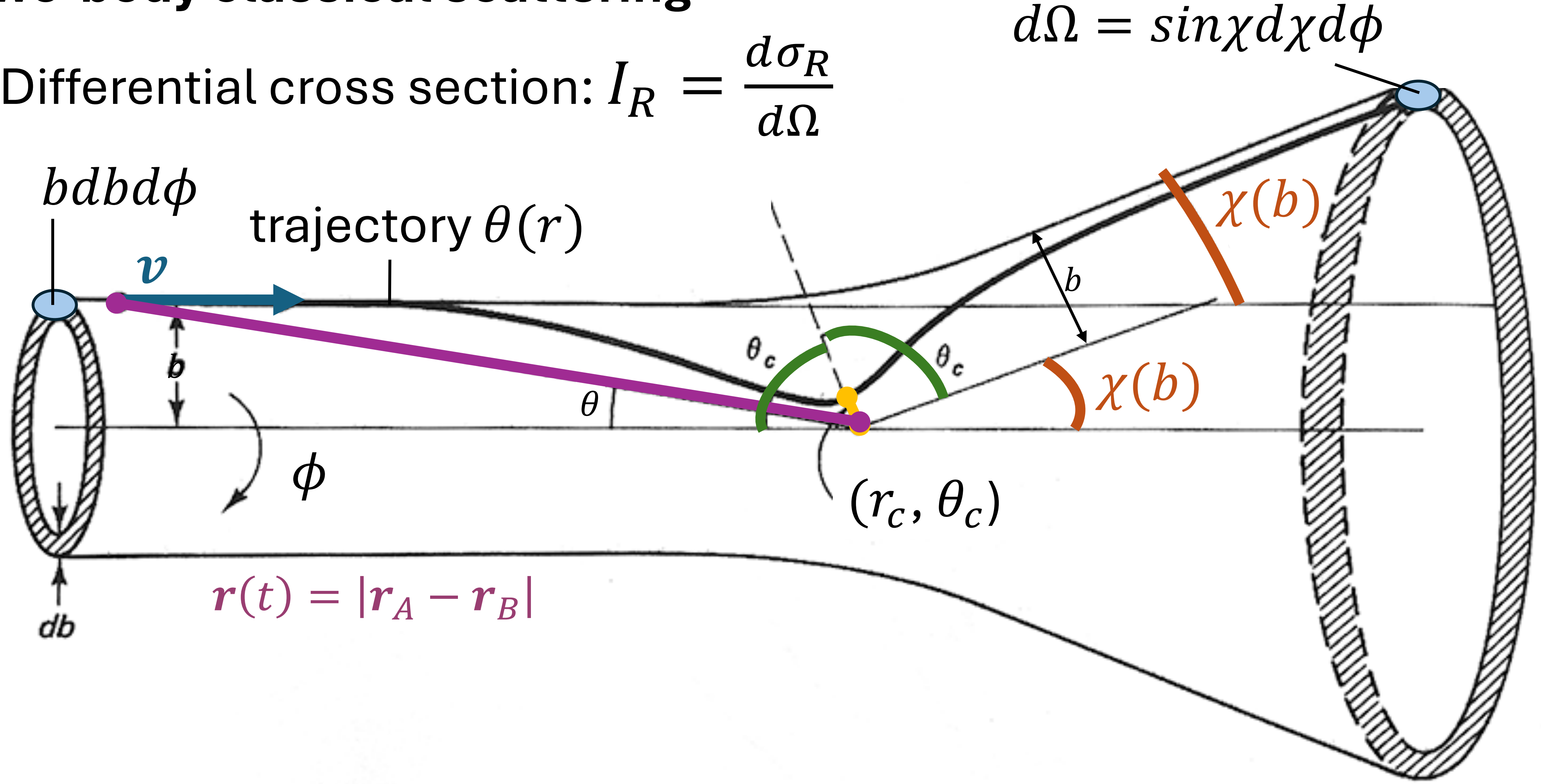
Two-body classical scattering

- Goal is to find *angular* dependence: *differential* reaction cross section I_R
- to learn more details about reaction mechanisms
- use central interaction potential $U(r)$ (at least works for spherical rare gas atoms)
- symmetrical nature of such a potential makes calculations easier
- Again, treat particles in center-of-mass framework
- Ask: What fraction of particles (a part of the total reaction cross section σ_R) scatters into a specific solid angle element (a small element $d\Omega$ of the total solid angle $\Omega = 4\pi$)?

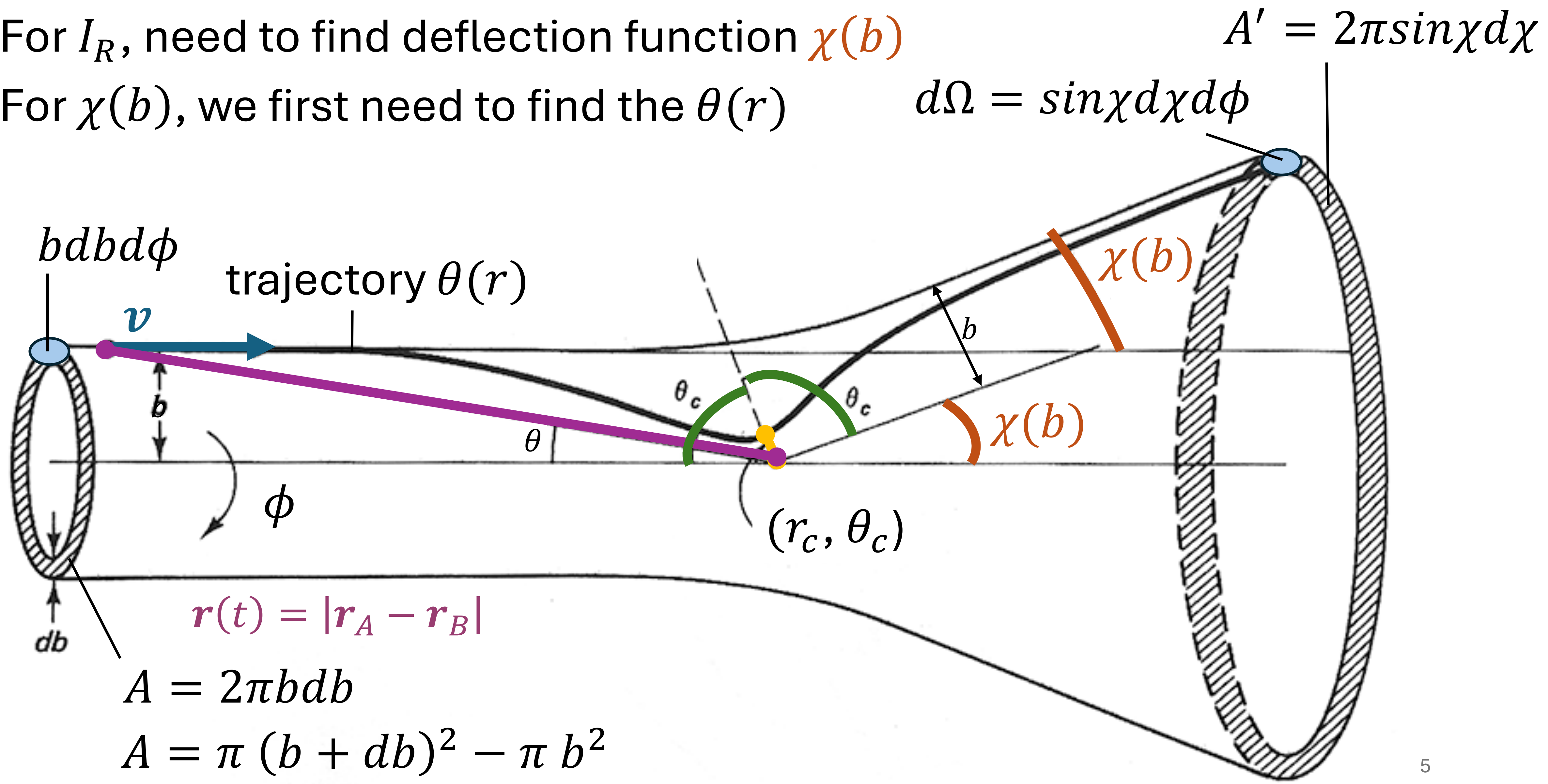
Recap from last session

Two-body classical scattering

- Differential cross section: $I_R = \frac{d\sigma_R}{d\Omega}$

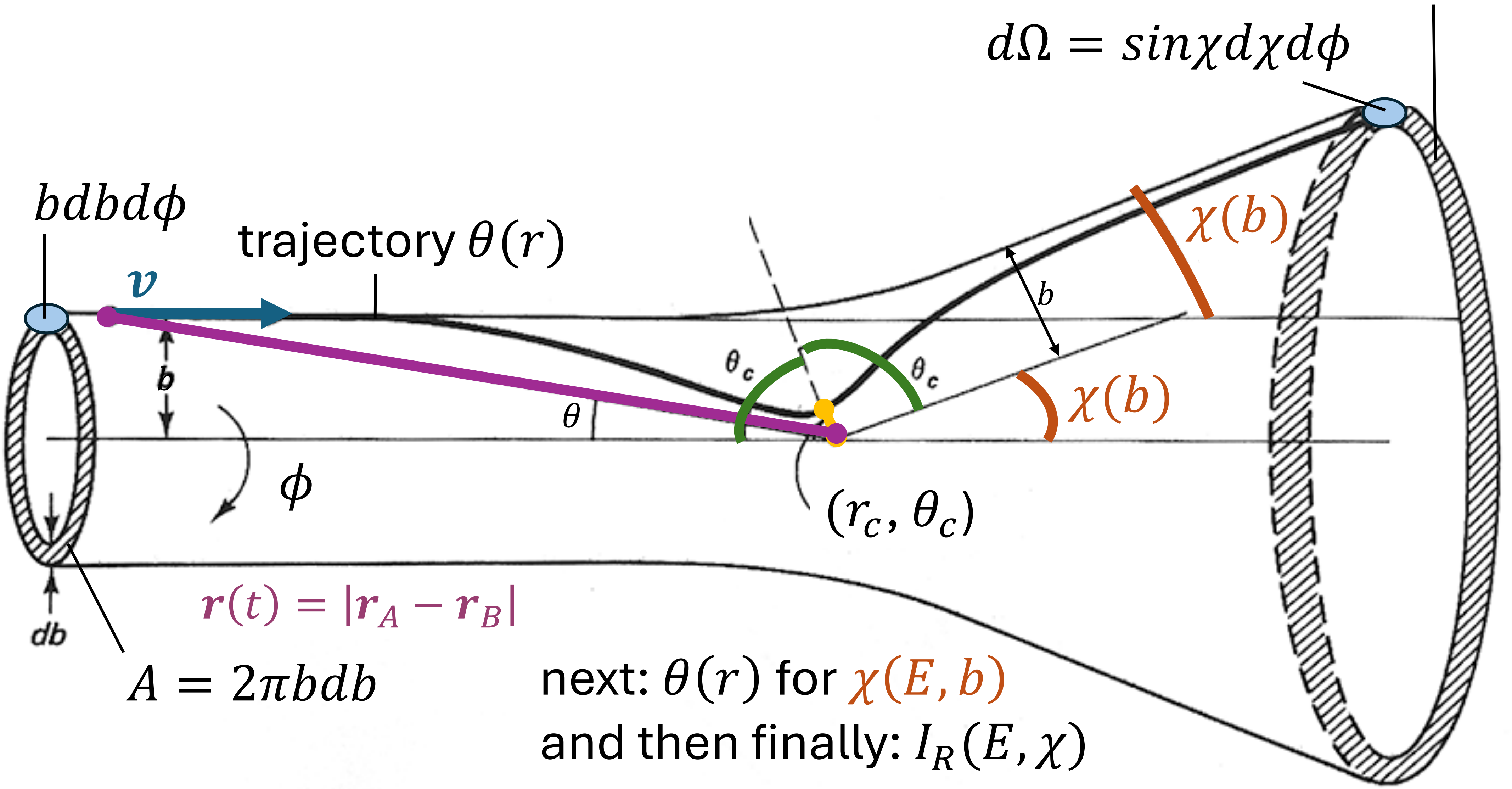


- Wanted: Differential cross section $I_R = \frac{d\sigma_R}{d\Omega} = \frac{2\pi b db}{|2\pi sin\chi(b) d\chi|}$
- For I_R, need to find deflection function $\chi(b)$
- For $\chi(b)$, we first need to find the $\theta(r)$



- Brief reminder about *conservation of particle flux*:

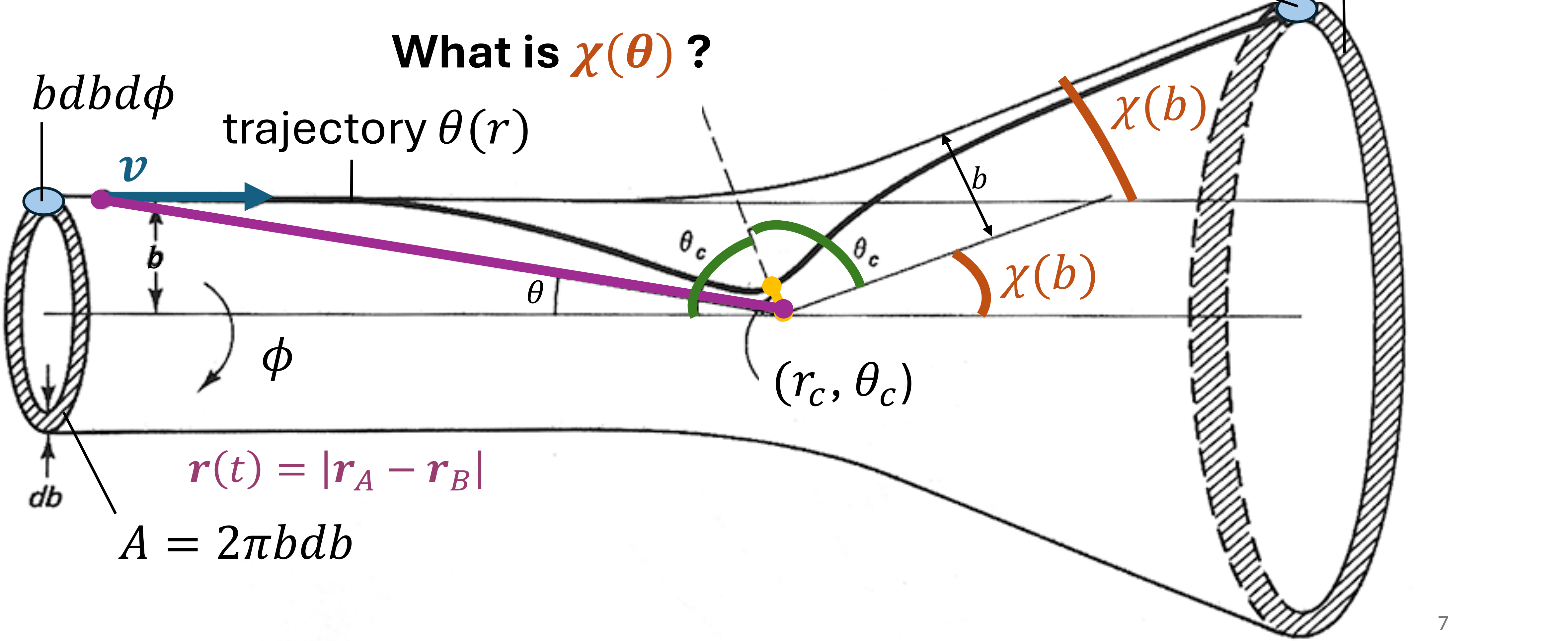
$$\sigma_R(v,\Gamma) = \int P_R(v,b;\Gamma)\, 2\pi b db \;= \iint I_R(\chi,\phi;v,\Gamma) d\Omega$$



next: $\theta(r)$ for $\chi(E,b)$
and then finally: $I_R(E,\chi)$

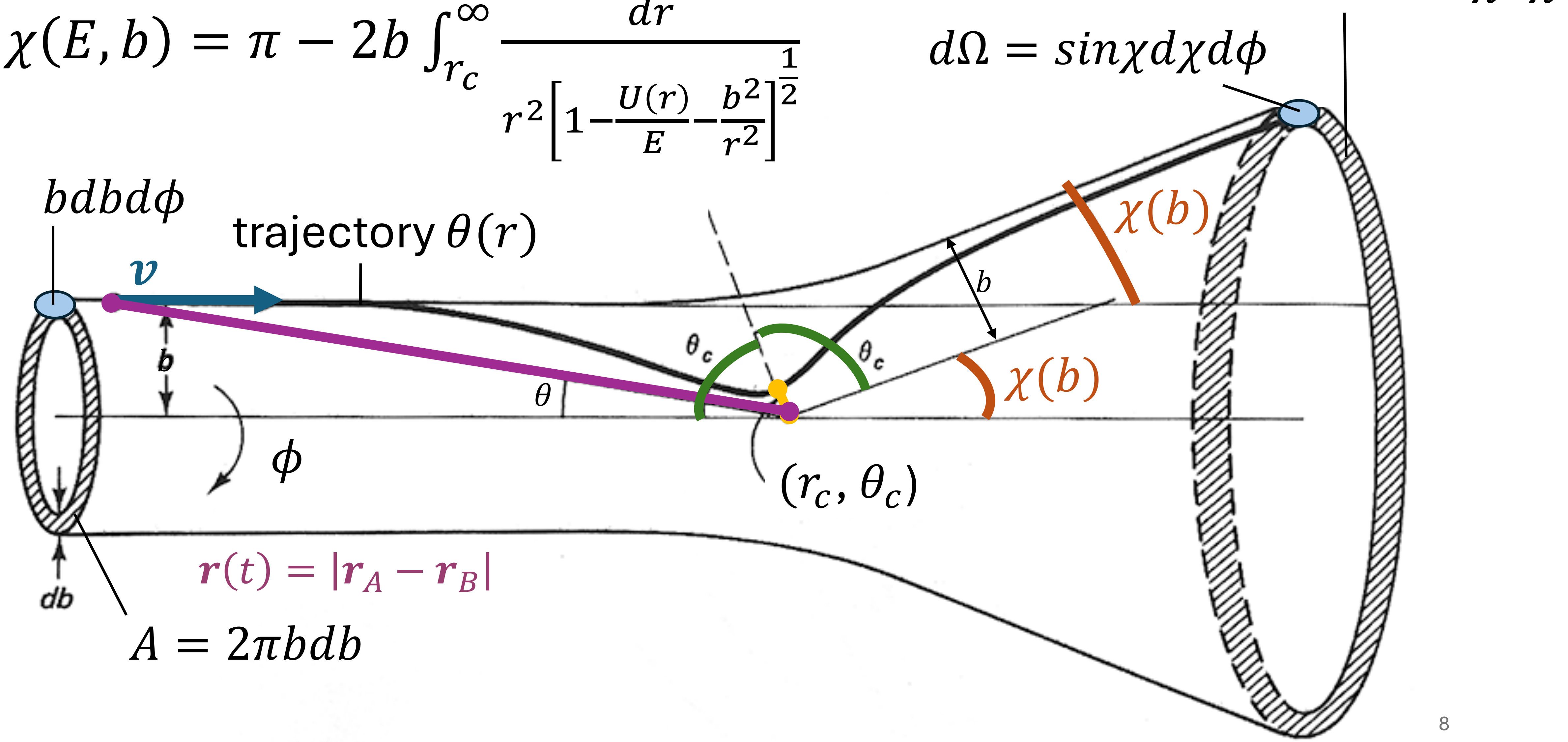
- We found for the trajectory:

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

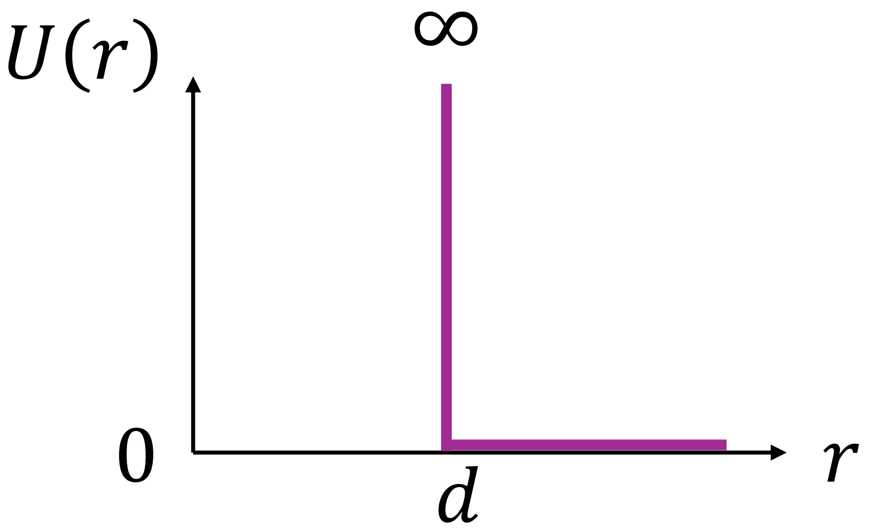


- Deflection function: $\chi(\theta) = \pi - 2\theta_c$
- Inserting our solution from before for $\theta(r)$ yields

$$\chi(E,b) = \pi - 2b\int_{r_c}^{\infty} \frac{dr}{r^2\left[1-\frac{U(r)}{E}-\frac{b^2}{r^2}\right]^{\frac{1}{2}}}$$



- What about the potential $\boldsymbol{U(r)}$? So far, we didn't specify it further!
- How does the *hard-sphere potential* look mathematically?
- Hard-sphere potential: $U(r) = \begin{cases} 0 & (r > d) \\ \infty & (r \leq d) \end{cases}$
- What's the critical distance r_c?
- For hard spheres, $r_c = d$
- Let's insert this into our deflection function

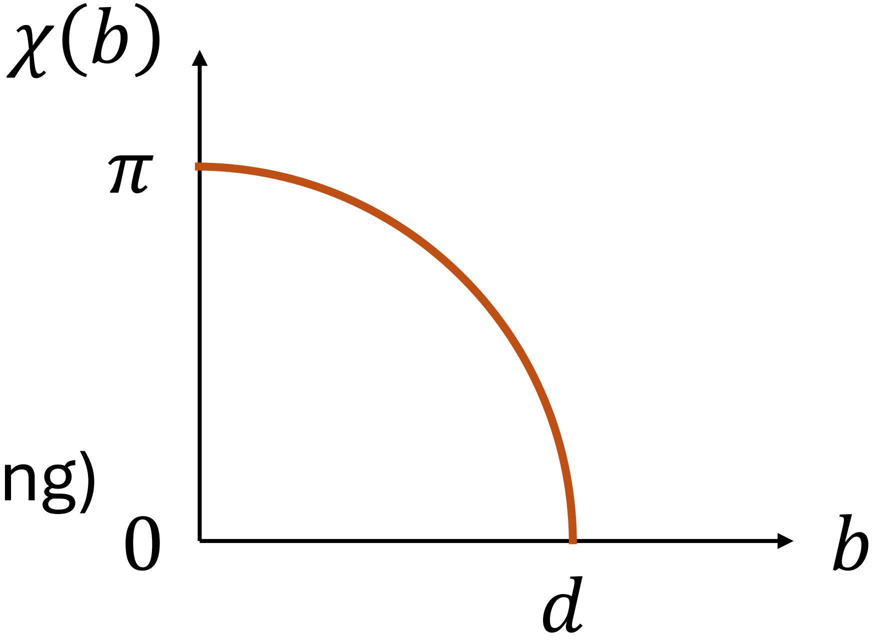


$$\chi(E,b) = \pi - 2b\int_{r_c}^{\infty} \frac{dr}{r^2\left[1-\frac{U(r)}{E}-\frac{b^2}{r^2}\right]^{\frac{1}{2}}}$$ to yield

$$\chi(E,b) = \pi - 2b\int_{d}^{\infty} \frac{dr}{r^2\left[1-\frac{b^2}{r^2}\right]^{\frac{1}{2}}} = \cdots = 2\arccos\frac{b}{d}$$

How does this look plotted?

$$\chi(E,b) = \pi - 2b\int_d^{\infty} \frac{dr}{r^2\left[1-\frac{b^2}{r^2}\right]^{\frac{1}{2}}} = \cdots = 2\arccos\frac{b}{d}$$



- At what b do we have a heads-on collision?

  at $b = 0$

- What is deflection angle χ there?

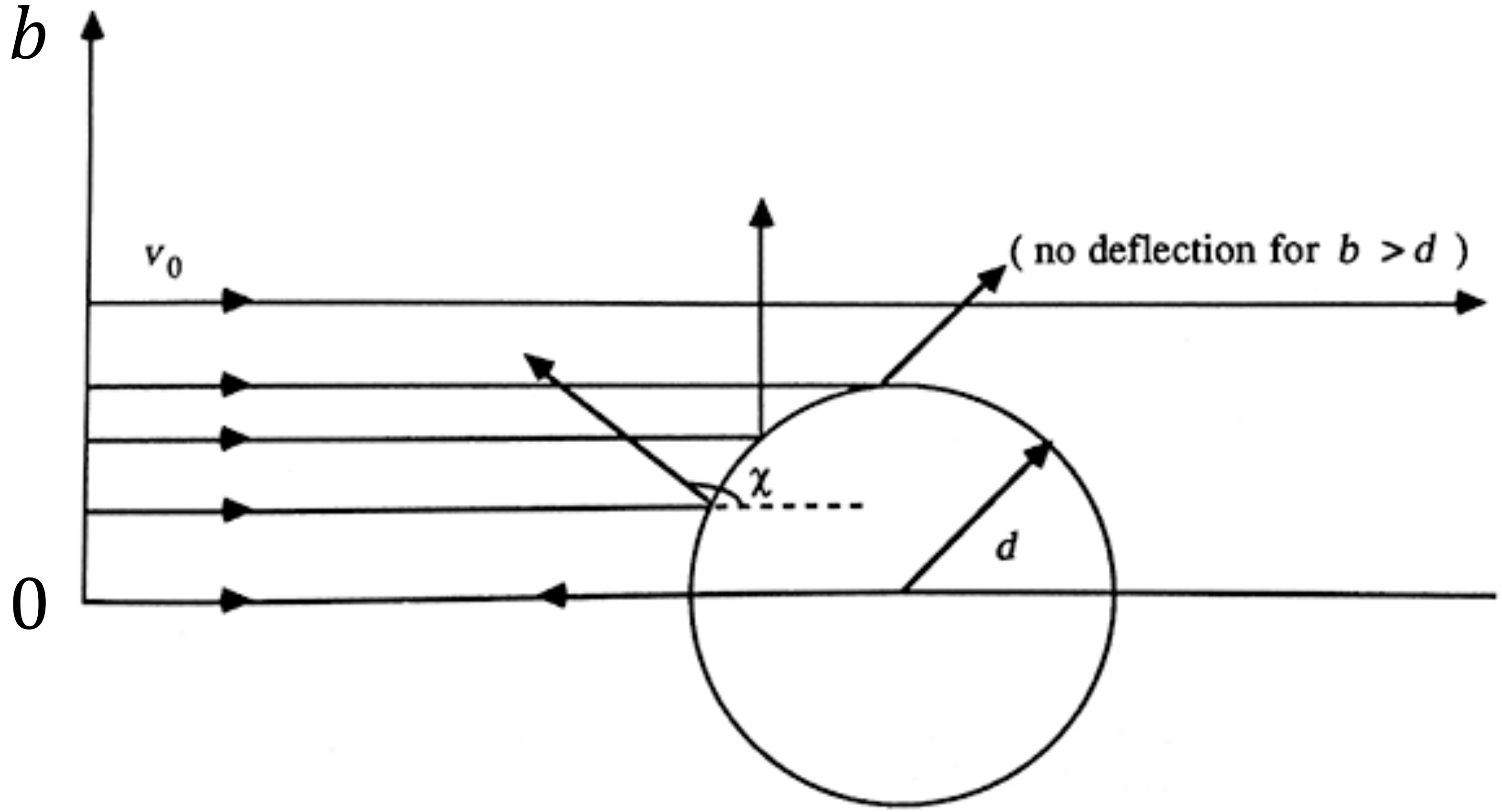
  $\chi(b = 0) = \pi = 180°$ (elastic back-scattering)

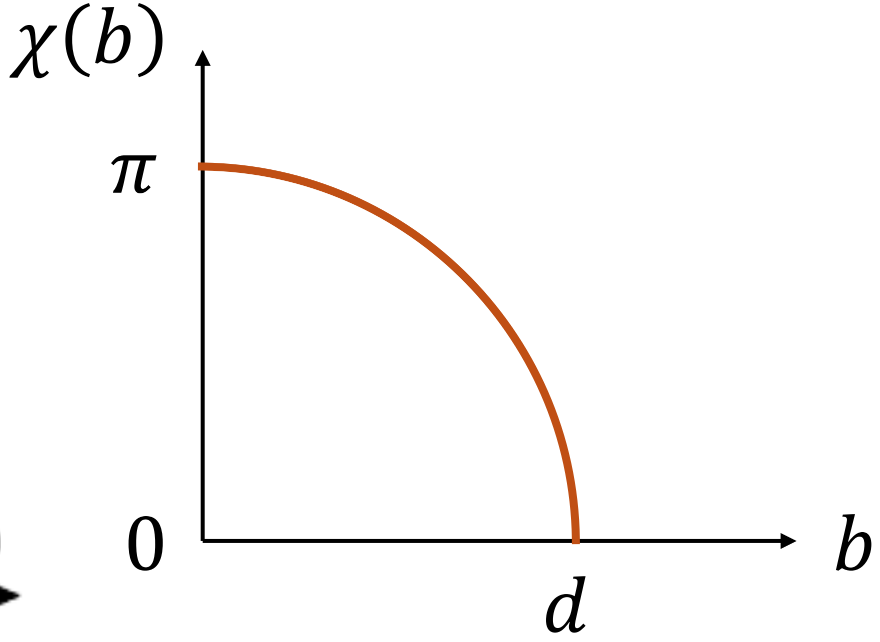
- What happens beyond $b = d$?

  no more collision or deflection, deflection angle is zero

$$\chi(b) = 2\arccos\frac{b}{d} \quad \text{[for hard-spheres potential]}$$

- for hard spheres, χ is energy-independent





Okay, now let's insert our new $\chi(b)$ into I_R !

$$\chi(b) = \pi - 2b\int_d^\infty \frac{dr}{r^2\left[1-\frac{b^2}{r^2}\right]^{\frac{1}{2}}} = 2\arccos\frac{b}{d}$$ [for hard-spheres potential]

- and we had found $$I_R = \frac{d\sigma_R}{d\Omega} = \frac{2\pi bdb}{|2\pi sin\chi(b)d\chi|}$$

- reminder: solid-angle element is $d\Omega = \sin\chi\, d\chi \int_0^{2\pi} d\phi = 2\pi \sin\chi\, d\chi$

$$I_R = \frac{d\sigma_R}{d\Omega} = \frac{2\pi bdb}{|2\pi sin\chi(b)d\chi|} = \frac{b}{\left|\sin\chi\frac{d\chi}{db}\right|} = \frac{b}{\left|\frac{d(\cos\chi)}{db}\right|} = \cdots = \frac{d^2}{4}$$

- It turns out that for the hard-spheres potential the differential cross section is constant, and independent of energy or angle!
- What do we expect when integrating I_R?

$$I_R = \frac{d^2}{4} \quad \text{[for hard-spheres potential]}$$

- What do we expect when integrating this I_R over the solid angle?

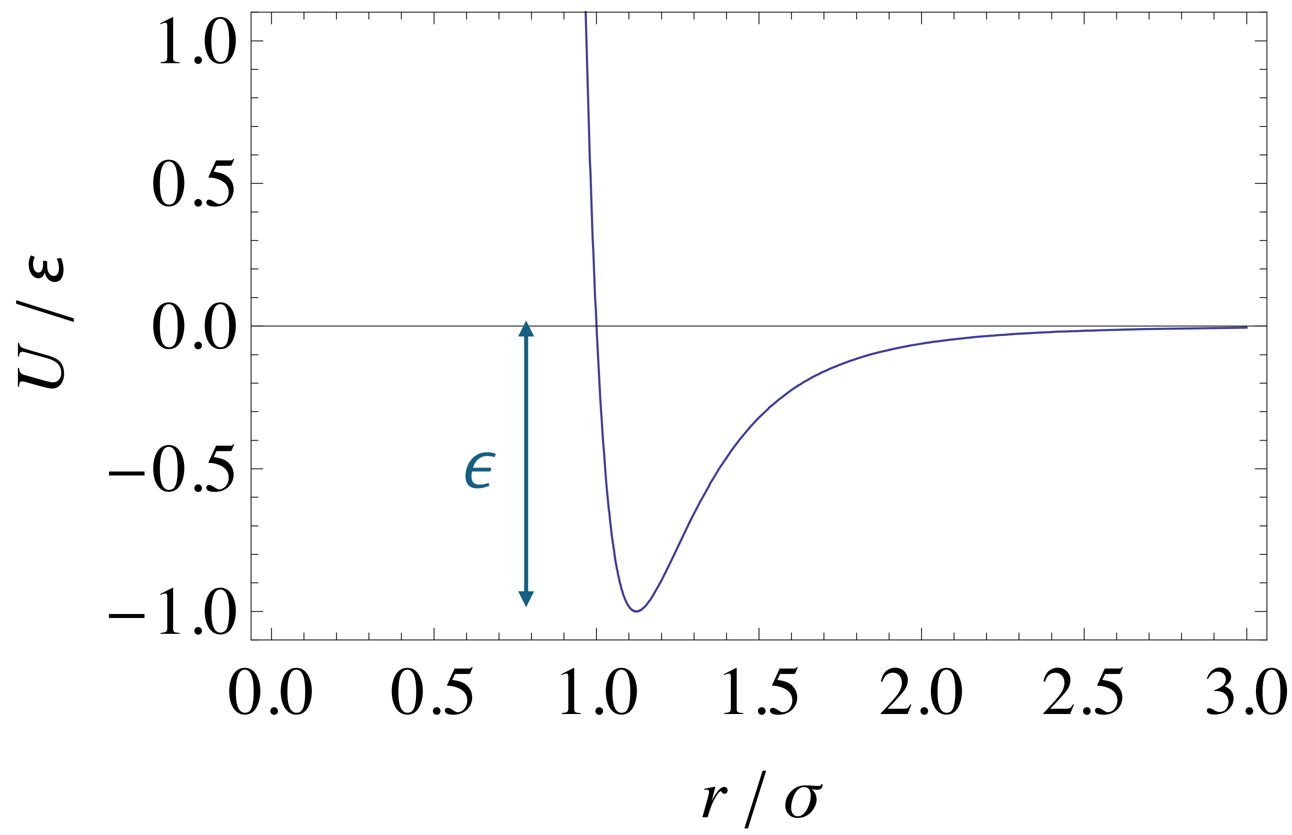
- We should retrieve the total cross section σ!

$$\sigma = \iint I_R d\Omega = \frac{d^2}{4} \iint d\Omega = \frac{d^2}{4}\, 4\pi = \pi d^2$$

- Success! We retrieved the hard-spheres cross section! ☺

- Let’s now move on to a more realistic potential

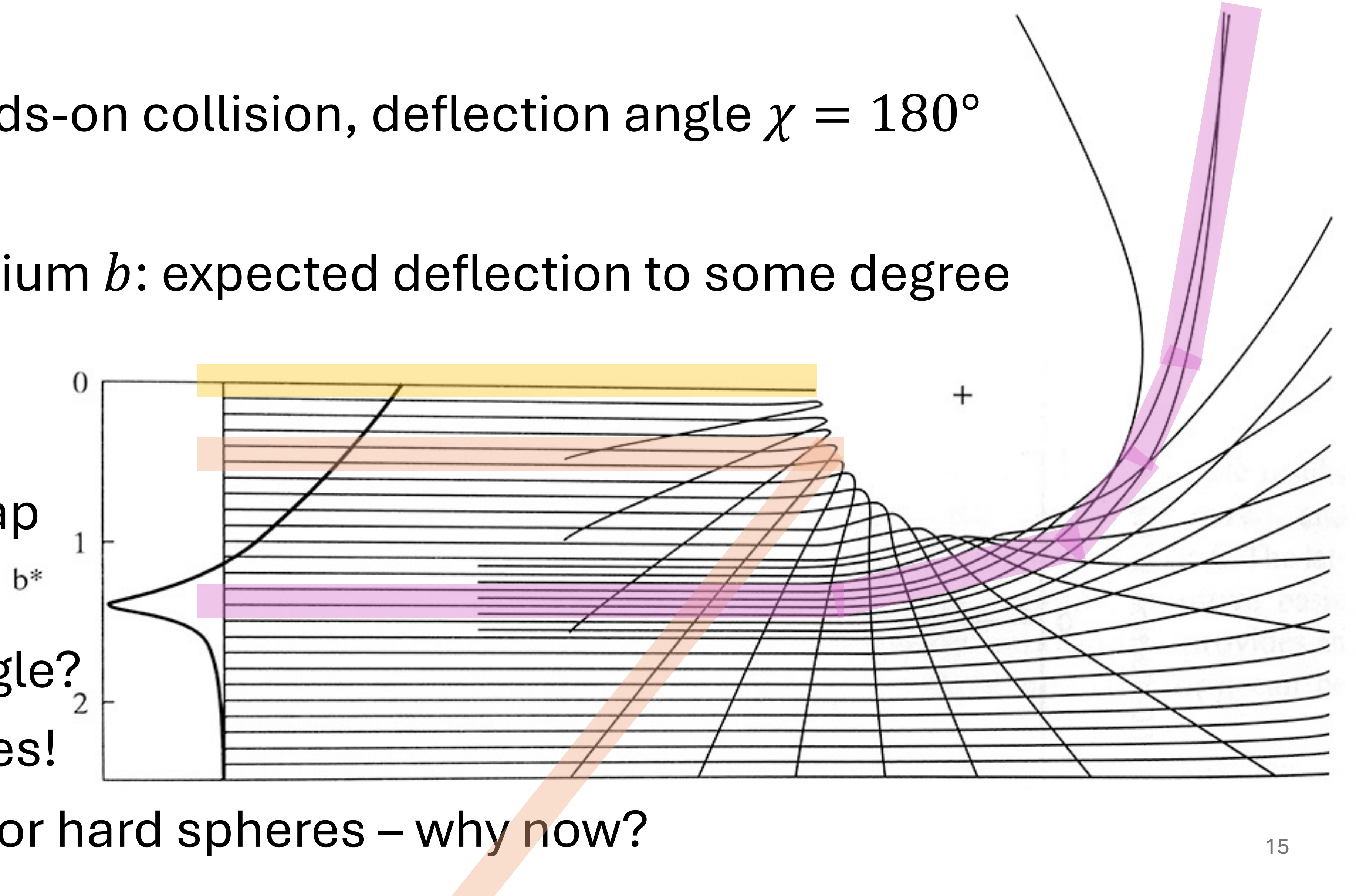
- The ***Lennard-Jones Potential***
- $U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$
- "6-12 potential"
- ϵ depth of potential well
- σ softness of potential
- $-\left(\frac{\sigma}{r}\right)^{6}$ long-range attraction
- $+\left(\frac{\sigma}{r}\right)^{12}$ short-range repulsion



- How will its trajectories look as a function of impact parameter b?

Lennard-Jones Potential: $U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

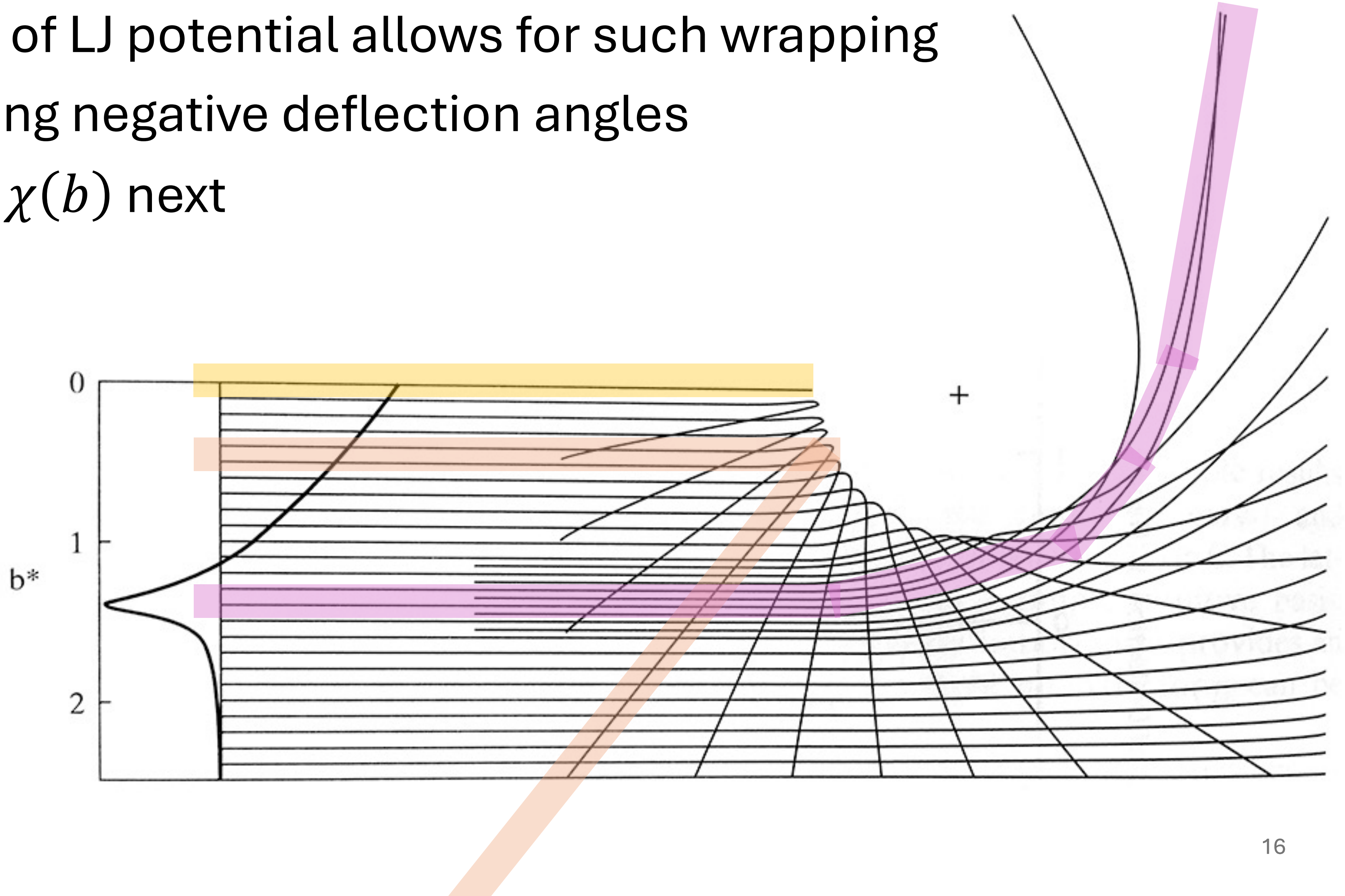
- for $b = 0$: heads-on collision, deflection angle $\chi = 180°$
- for small/medium b: expected deflection to some degree
- for large b: unexpected wrap around center



- Deflection angle? negative values!
- Not possible for hard spheres – why now?

The *Lennard-Jones Potential* $U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

- *Attractive* part of LJ potential allows for such wrapping and the resulting negative deflection angles
- Let's also plot $\chi(b)$ next



The *Lennard-Jones Potential* $U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

- Why do all curves tend to 0 for large b?

→Particles eventually don't feel each other anymore: no deflection

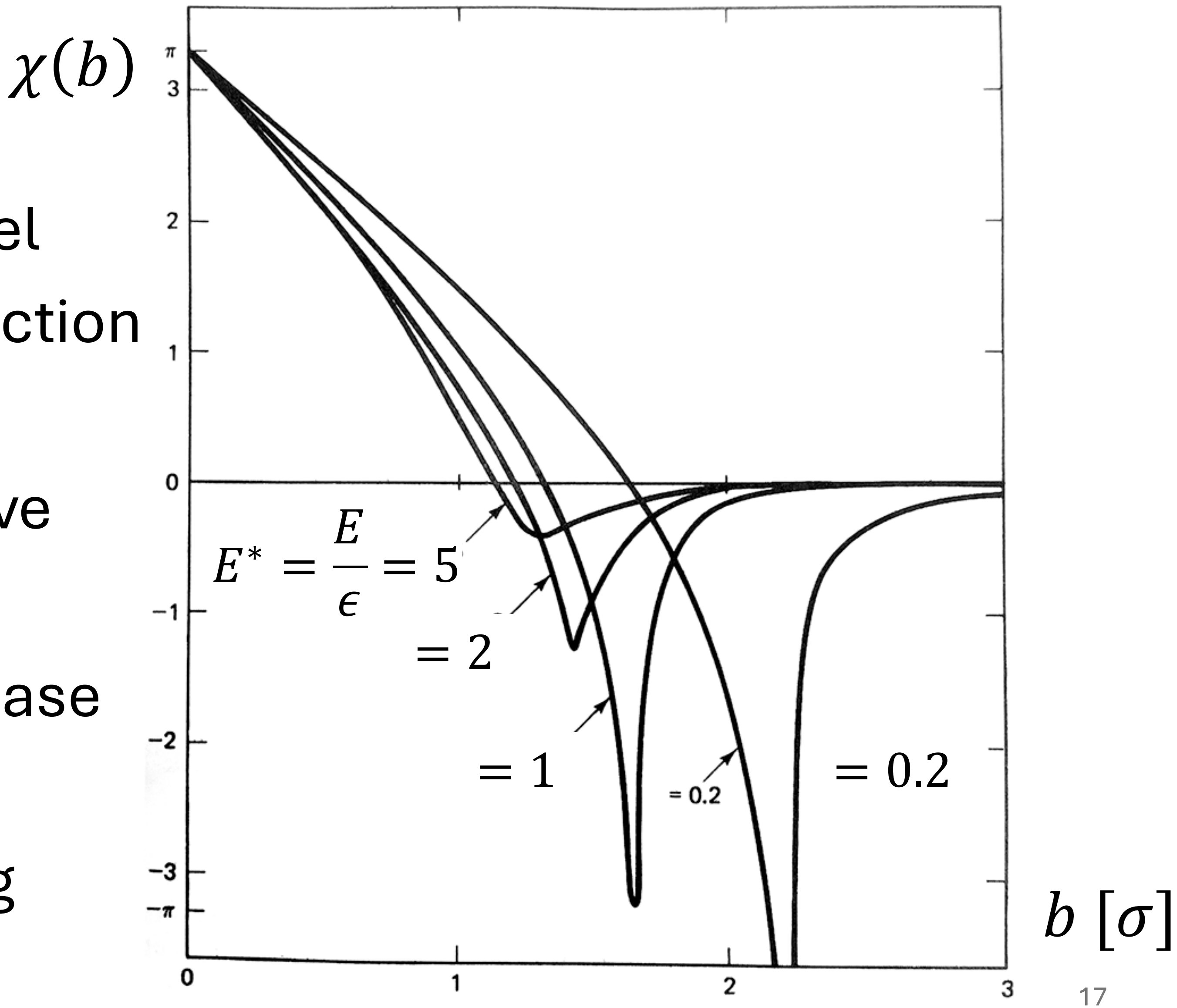
- What happens for small b?

→Particles mostly feel repulsive part of LJ potential

→χ resembles hard-spheres case

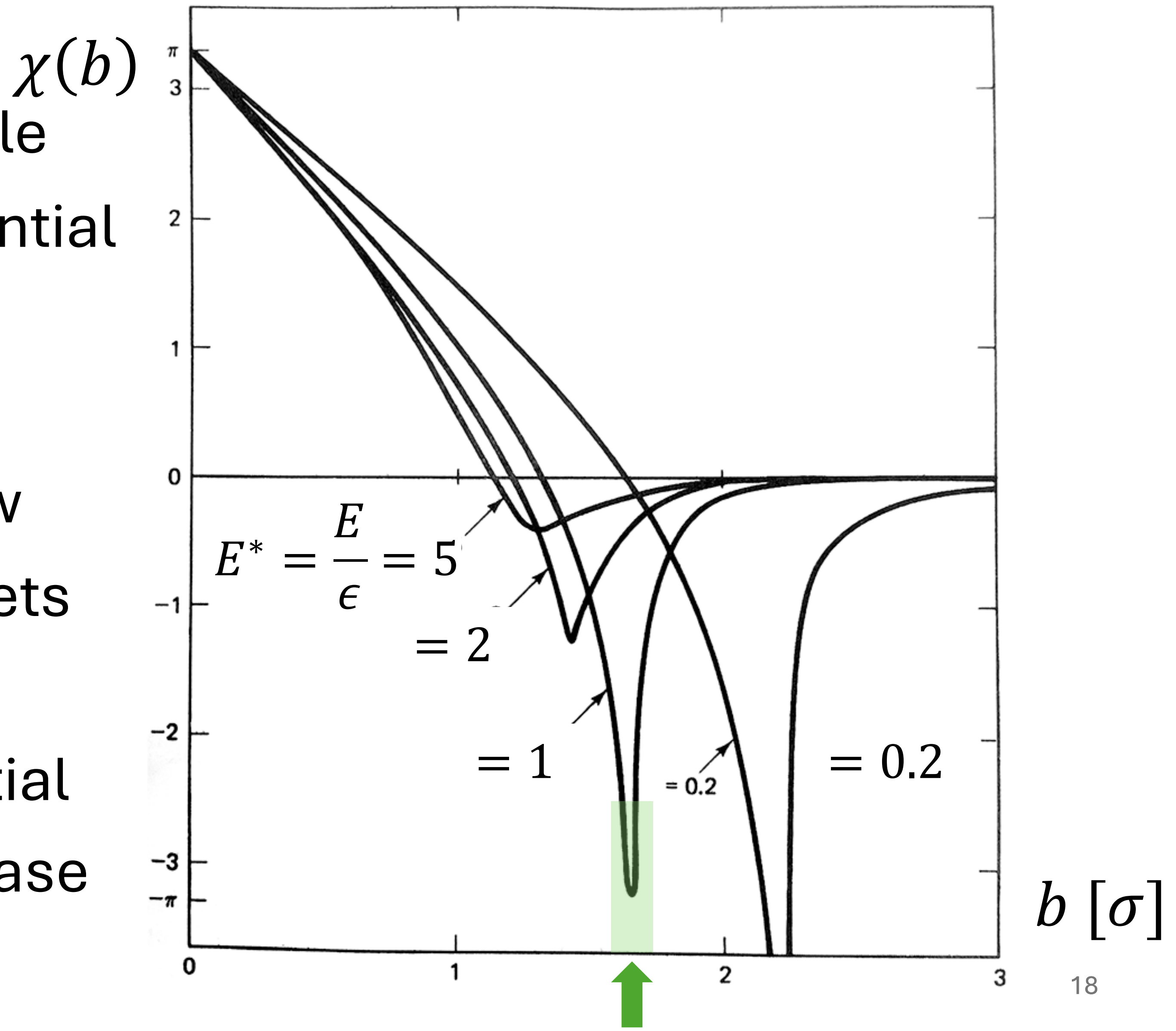
- Different energies plotted:

→ for lower energies, wrapping becomes more pronounced

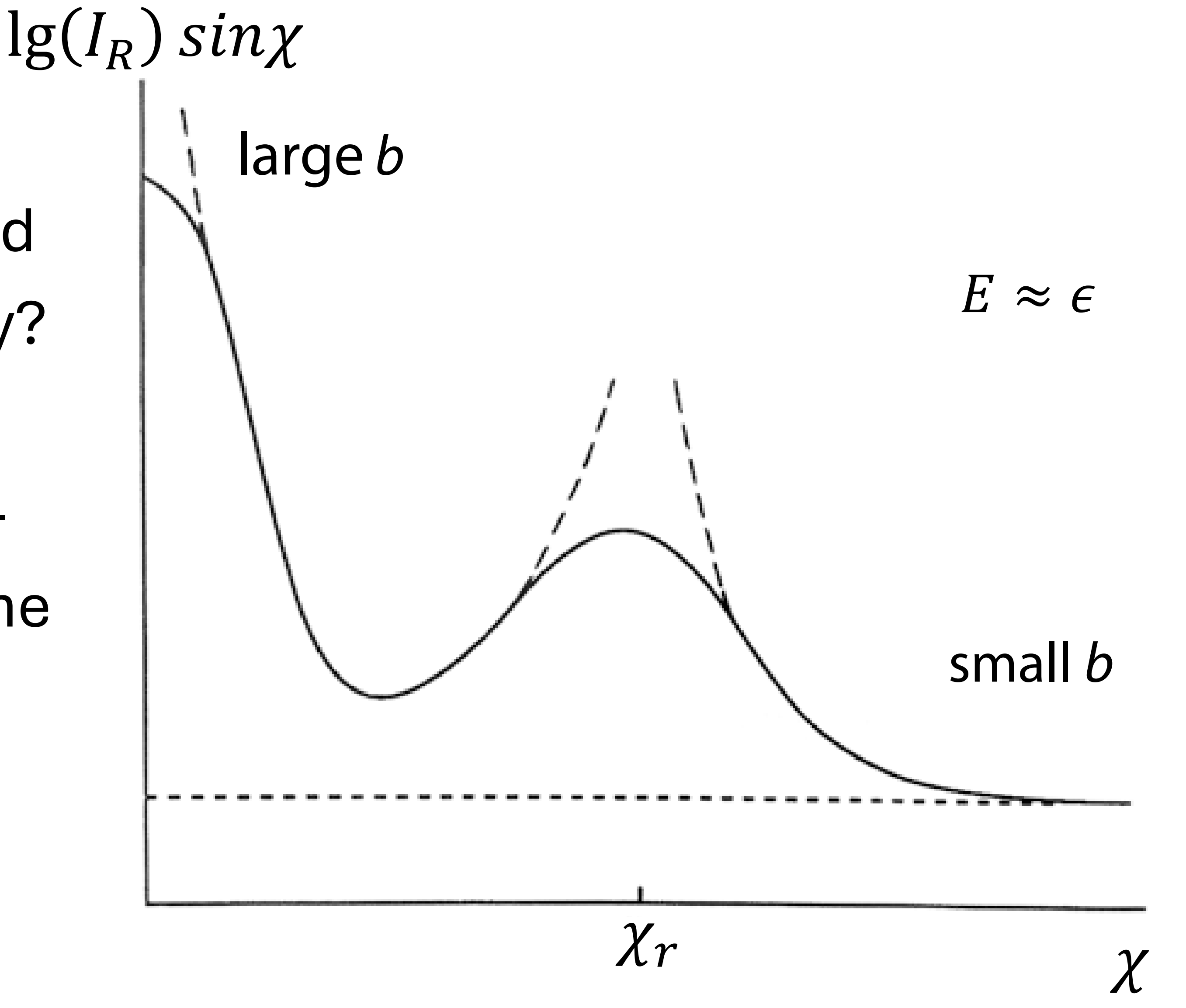


The *Lennard-Jones Potential* $U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

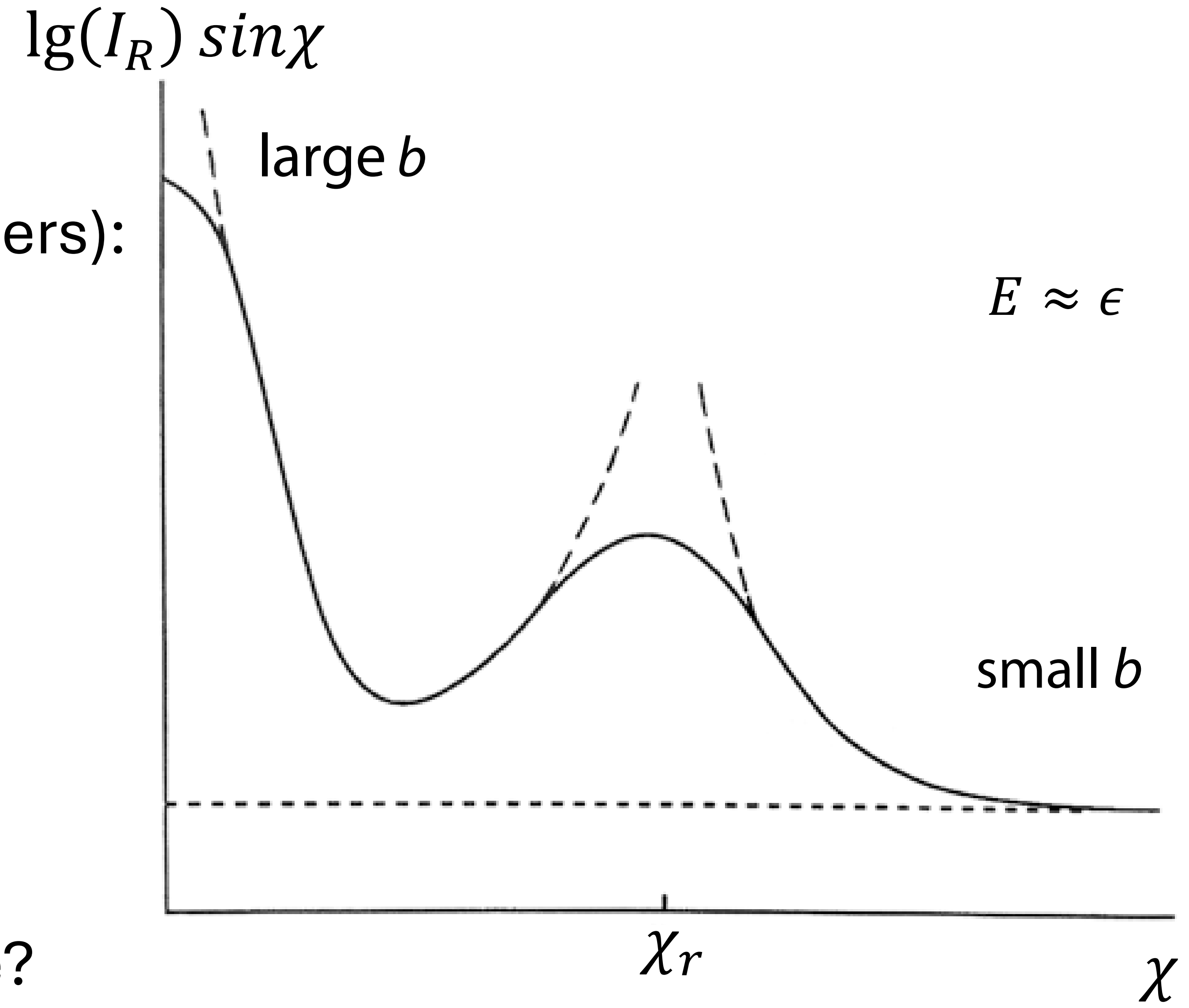
- For high energies, particles are so fast, they barely sample the attractive part of the potential
- At minimum of curve: ***"Rainbow angle"***
- Mathematical analogy to how light scatters from rain droplets to form a rainbow
- Finally, let's plot the differential cross section $I(\chi)$ for the LJ case



- The differential cross section for the LJ potential: $I_R(E,\chi) = b / \left|\frac{d\cos\chi}{db}\right|$
- Dashed curve shows our calculated result – problem?
- It tends to infinity at large b and at the rainbow angle χ_r !!! Why?
- Result of classical treatment
- Would need to treat quantum-mechanically to smooth out the singularities
- At large χ ($\chi \to \pi, \mathrm{b} \to 0$), I_R approaches hard-spheres value of $d^2/4$



The differential cross section for the LJ potential: $I_R(E,\chi) = b / \left|\frac{d\cos\chi}{db}\right|$



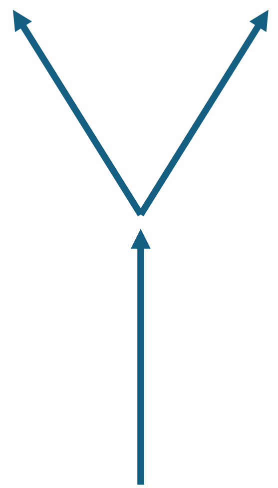
- At the rainbow angle (*i.e.*, at intermediate impact parameters): $\left|\frac{d\cos\chi}{db}\right| \to 0$ meaning $I_R \to \infty$

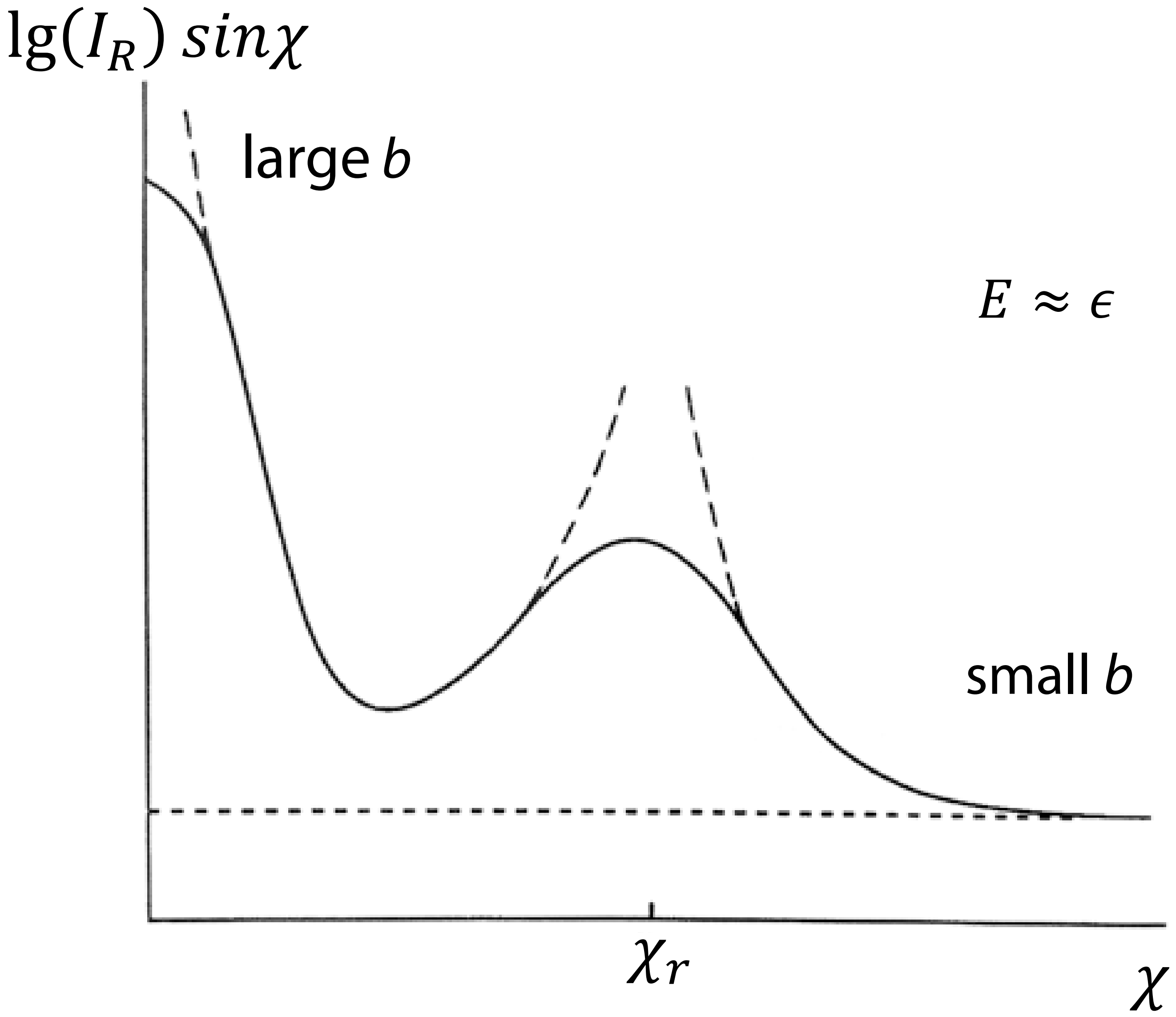
- At small χ ($\chi \to 0, \mathrm{b} \to \infty$): $\left|\frac{d\cos\chi}{db}\right| \to 0$ meaning $I_R \to \infty$

- What about the *negative* deflection angles from before?

What about the *negative* deflection angles from before?

- Experimentally, you can only measure the values plotted
- Due to spherical symmetry of the potential, the negative deflection angles fold into the positive ones ☺

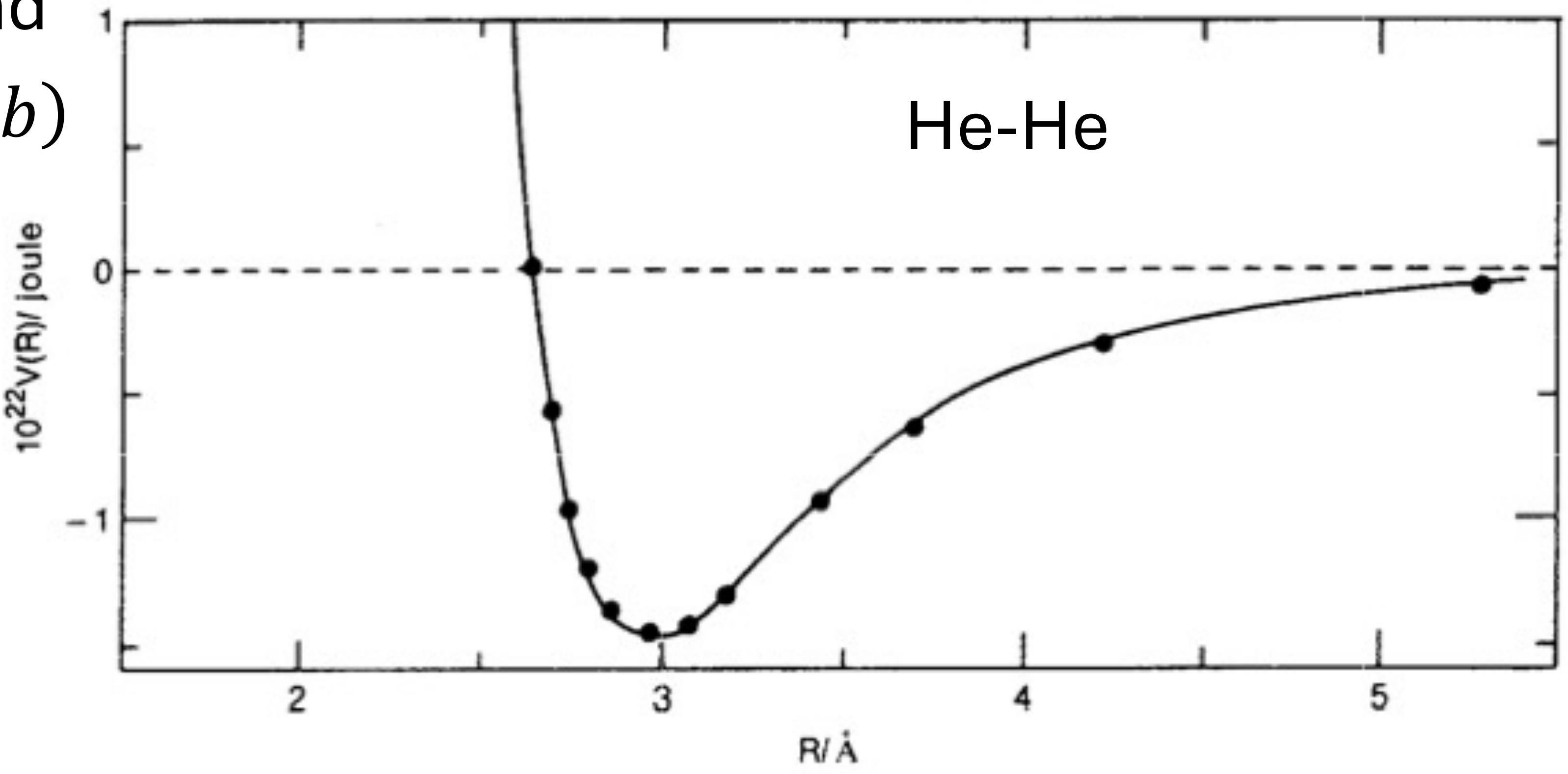




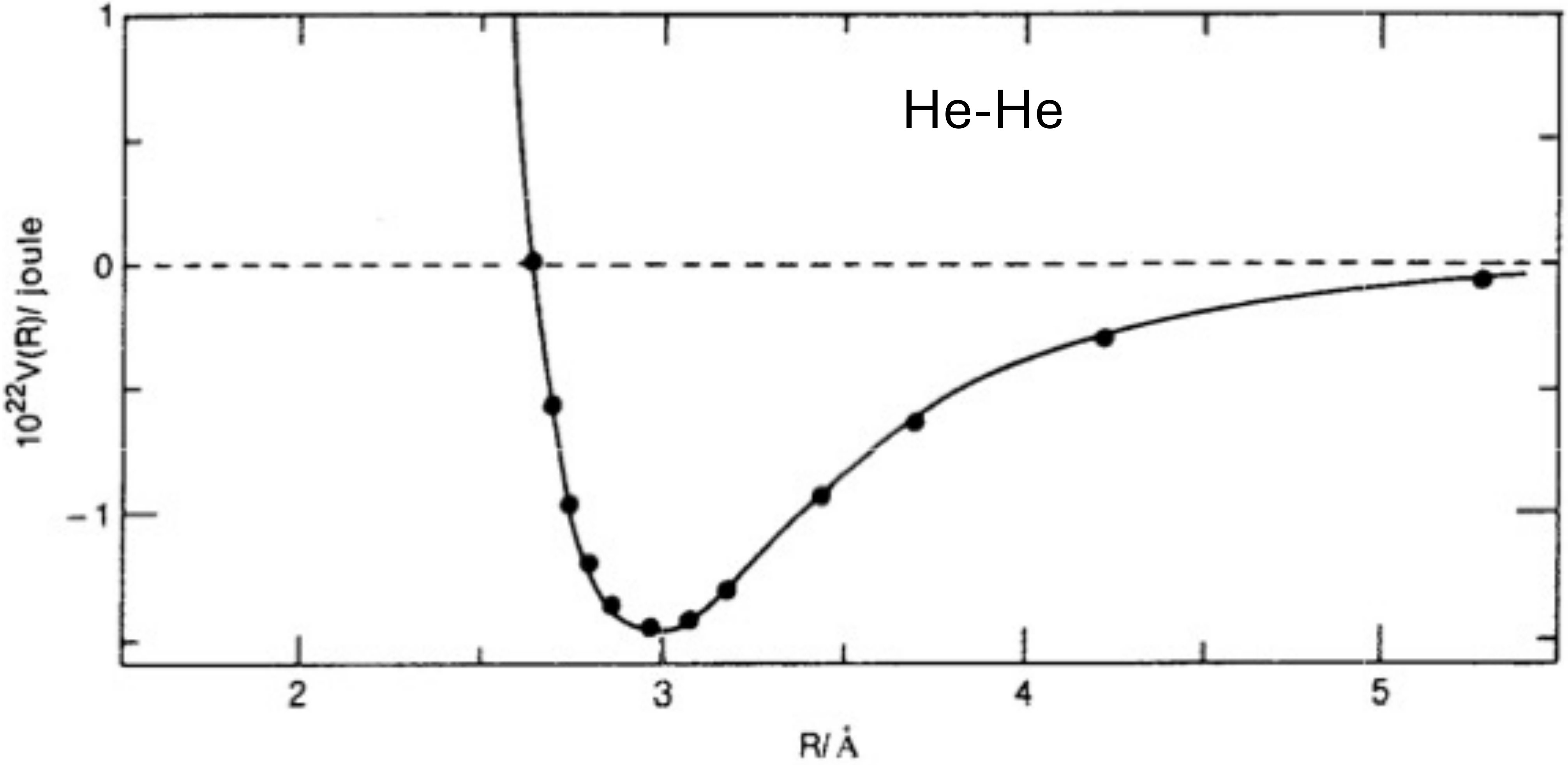
- How can we determine an intermolecular potential *experimentally*?
- By measuring differential cross sections!
- Integrate over a range of deflection angles (e.g., larger than χ_r, from χ_0):

$$\int_{\chi_0}^{\pi} I(E,\chi)|2\pi \sin\chi \, d\chi| = -\int_{b(\chi_0)}^{b(\pi)=0} 2\pi b db = \pi b(\chi_0)^2$$

- From this we now found a means to measure $\chi(b)$
- Then we can re-insert our $\chi(b)$ into the previous formula we solved for finding it, and instead isolate for $U(r)$ ☺



Yuan Tseh Lee won the Nobel Prize for this in 1986 (with Polanyi & Herschbach)



Interatomic potential of He–He. The solid curve represents experimental data; points are theoretical. [Adapted from A. L. Burgmans, J. M. Farrar, and Y. T. Lee, *J. Chem. Phys.*, *64*, 1345 (1976); unpublished computational results by B. Liu and A. D. McLean.]