

Kinetics & Dynamics of Chemical Reactions

Course CH-310

Prof. Sascha Feldmann

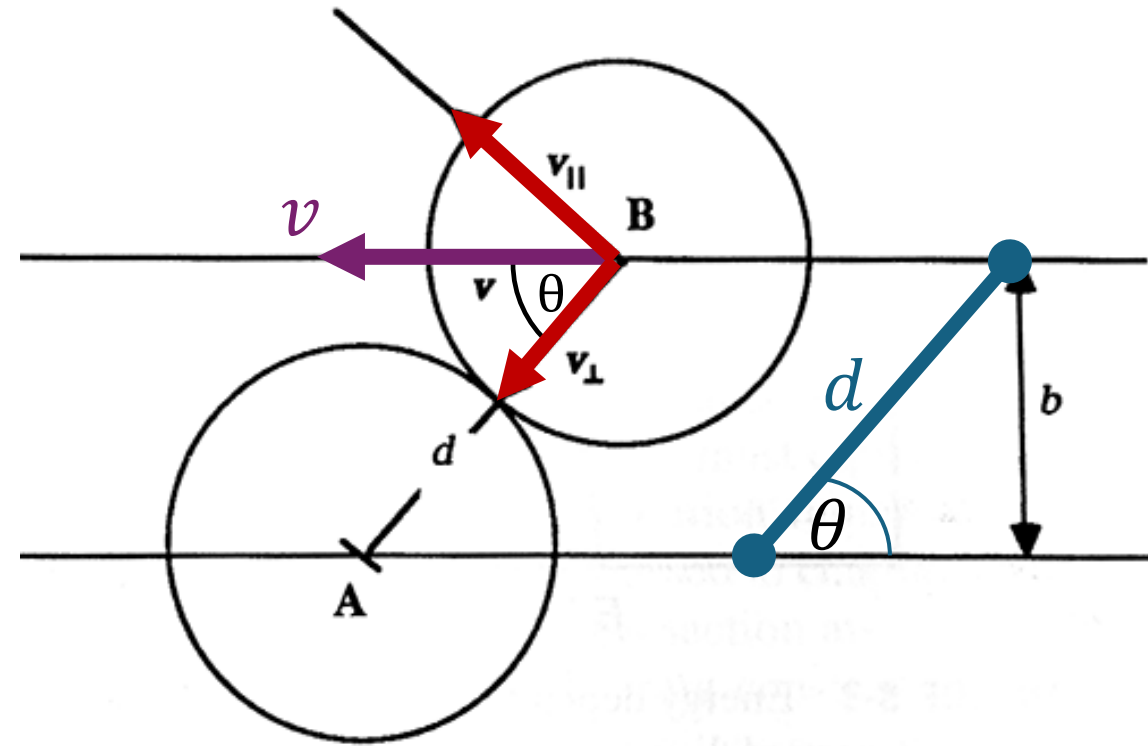
Exam:

Friday, 17 January 2025, 9.15 am - 12.15 pm,
in room BCH2201

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

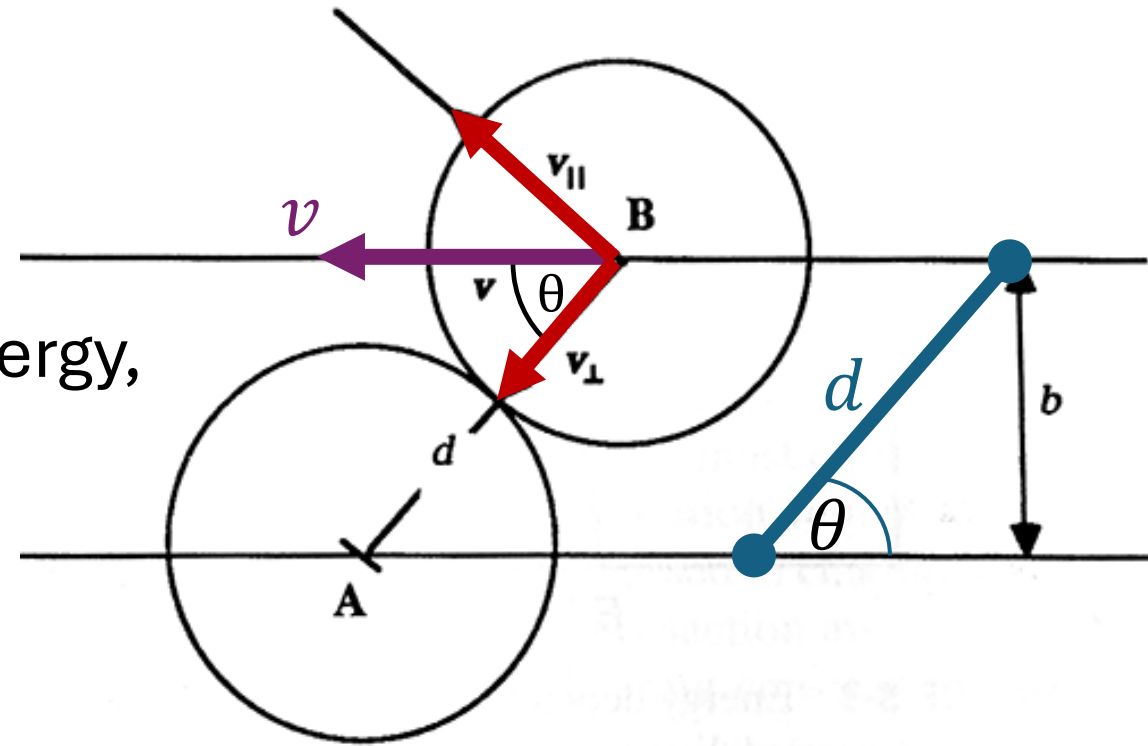


Recap from last session

Reactive hard spheres model

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

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



hard-sphere cross section $\times$ mean velocity $\times$ Arrhenius eq.

Arrhenius pre-factor A

Recap from last session

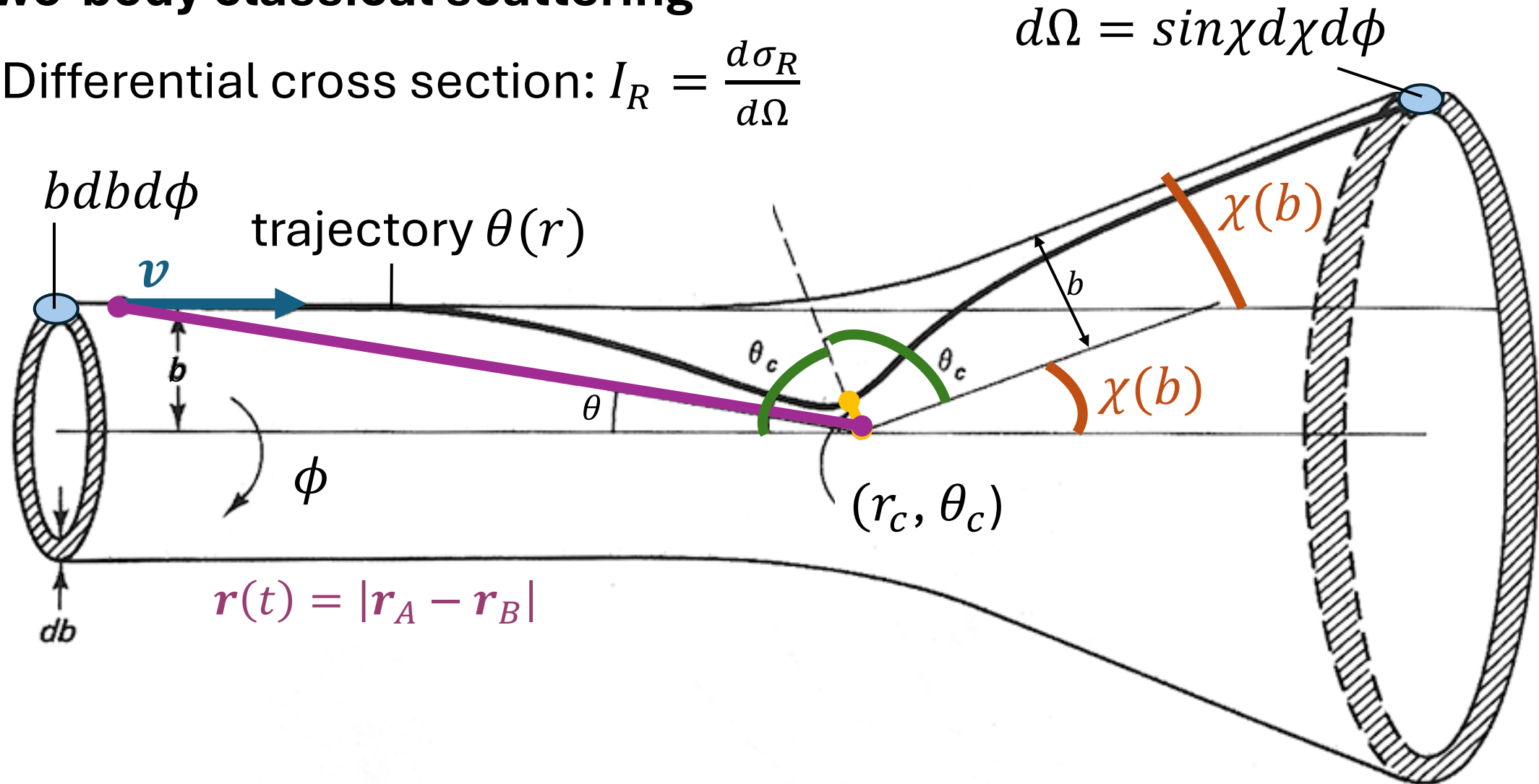
Two-body classical scattering

- angular dependence and *differential* reaction cross section I_R
- to learn more details about reaction mechanisms
- central interaction potential $U(r)$ (at least works for spherical rare gas atoms)
- The symmetrical nature of such a potential will make our life easier
- Again, treat all 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 (a small element $d\Omega$ of the total solid angle Ω)?

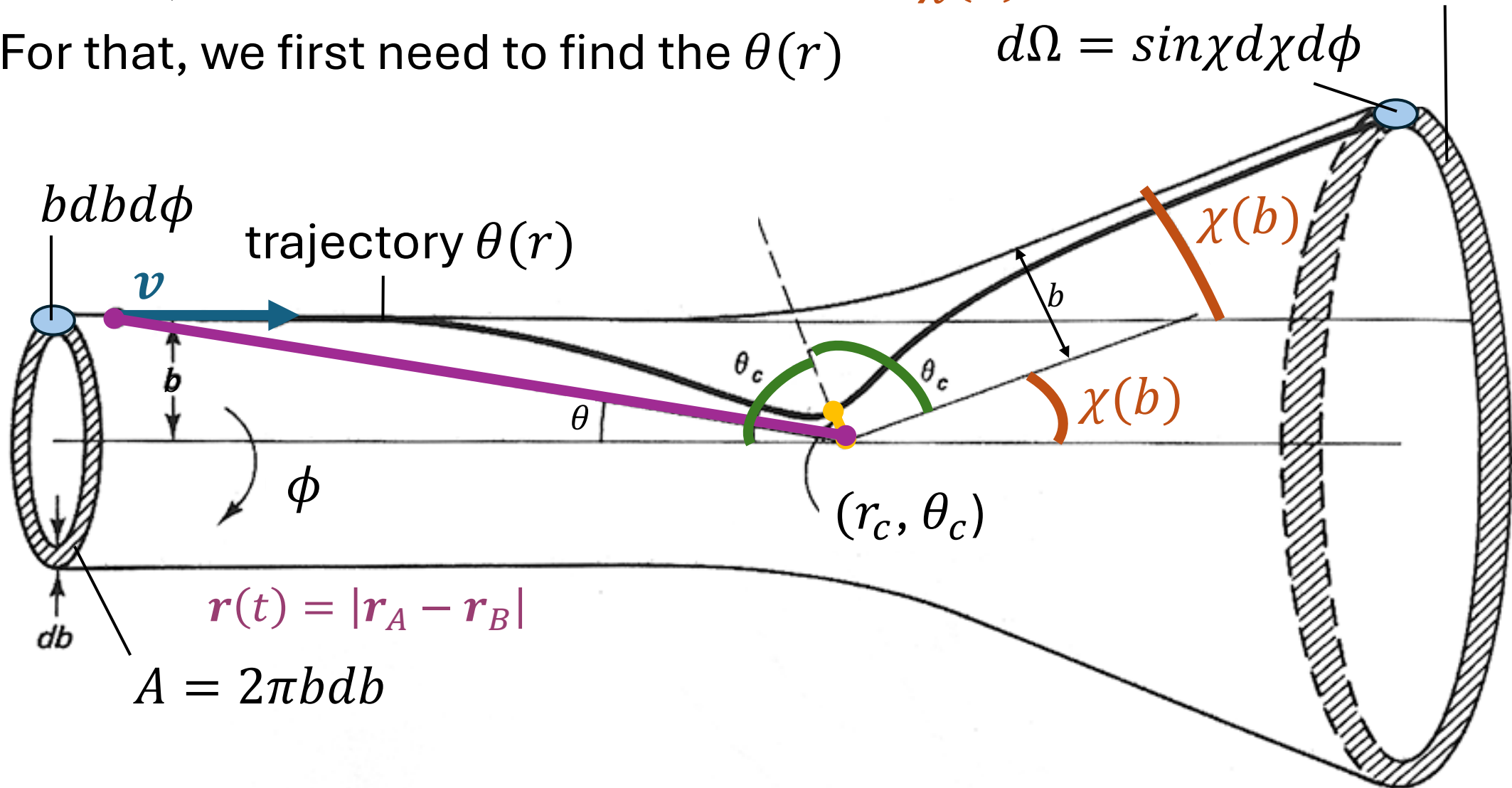
Recap from last session

Two-body classical scattering

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

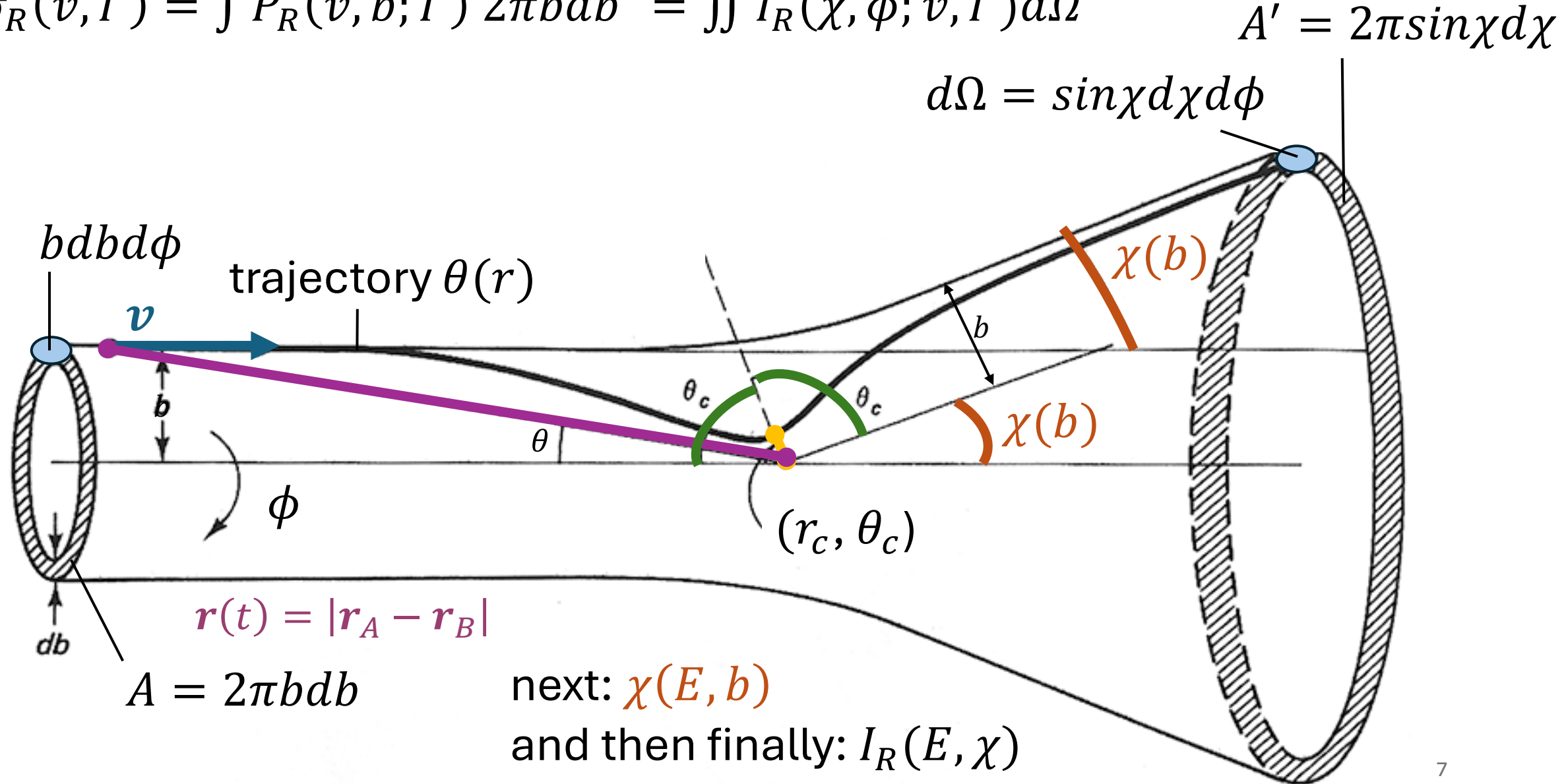


- Wanted: Differential cross section $I_R = \frac{d\sigma_R}{d\Omega} = \frac{2\pi b db}{|2\pi \sin\chi(b) d\chi|}$
- For this, need to find deflection function $\chi(b)$ $A' = 2\pi \sin\chi d\chi$
- For that, we first need to find the $\theta(r)$ $d\Omega = \sin\chi d\chi d\phi$ |



- Brief reminder about *particle flux conservation*:

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

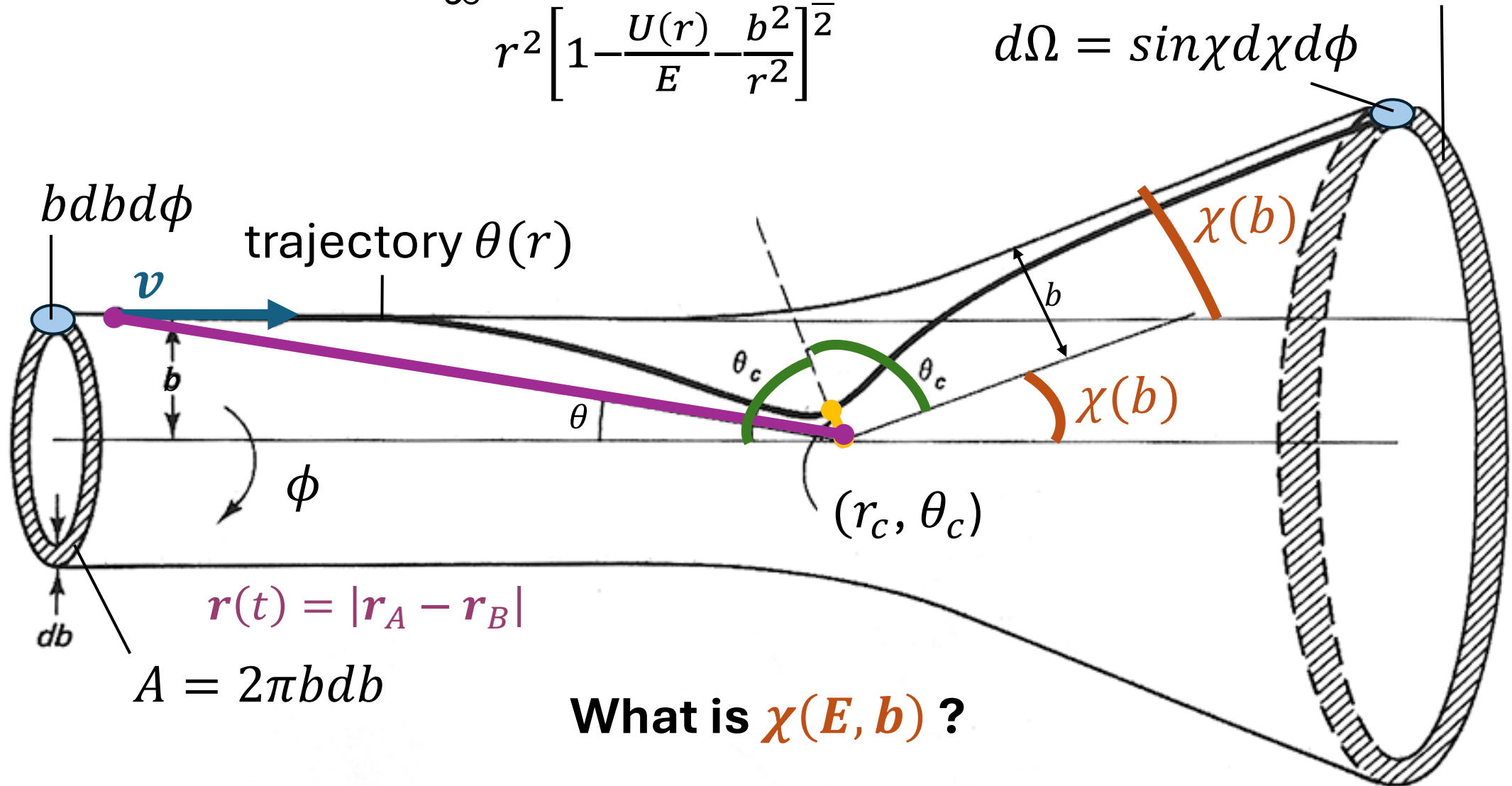


- We found for the trajectory

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

$$d\Omega = \sin\chi d\chi d\phi$$

$$A' = 2\pi \sin\chi d\chi$$

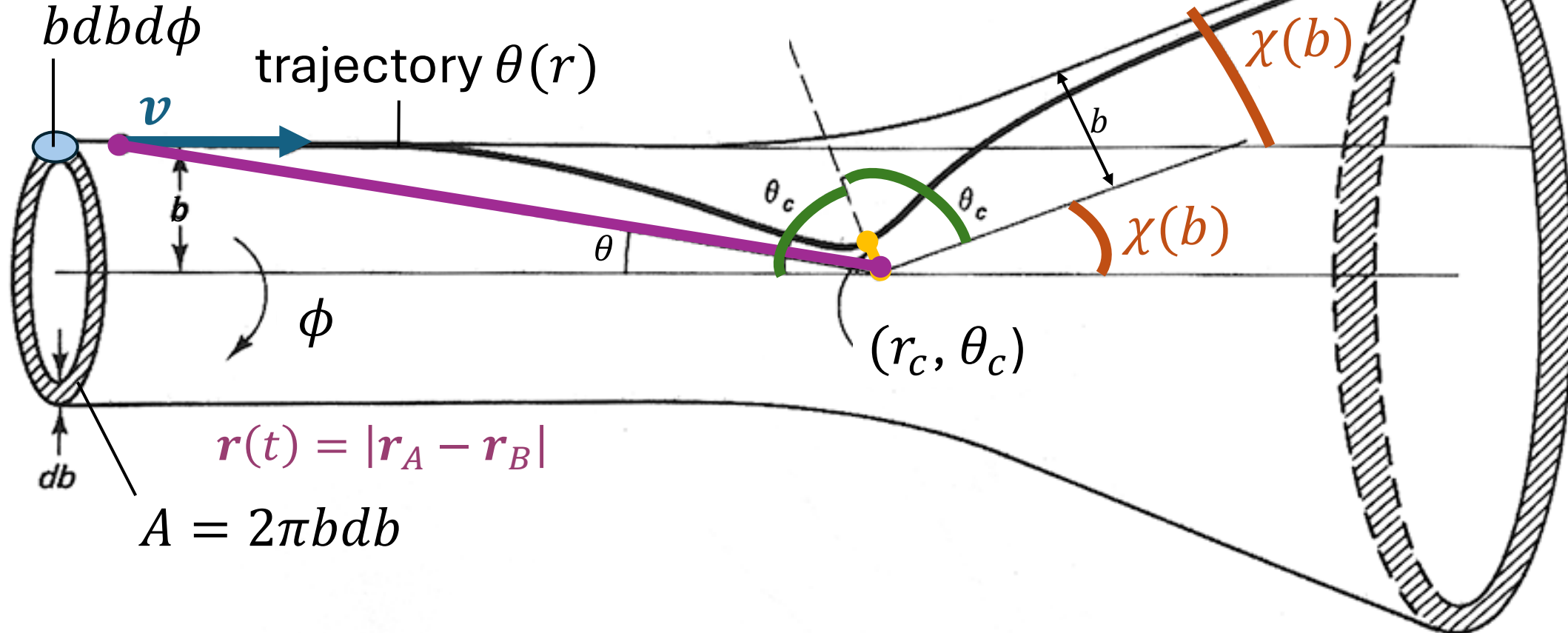


What is $\chi(E, b)$?

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

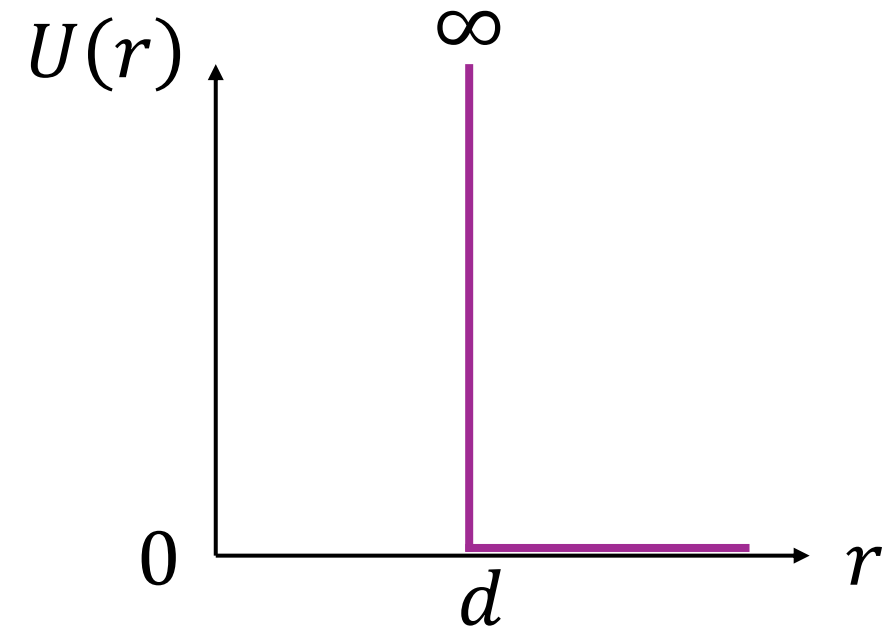
$$\chi(E, b) = \pi - 2b \int_{r_c}^{\infty} \frac{dr}{r^2 \left[1 - \frac{U(r)}{E} - \frac{b^2}{r^2} \right]^{\frac{1}{2}}}$$

$$d\Omega = \sin\chi d\chi d\phi$$



- What about the potential $\mathbf{U(r)}$? 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

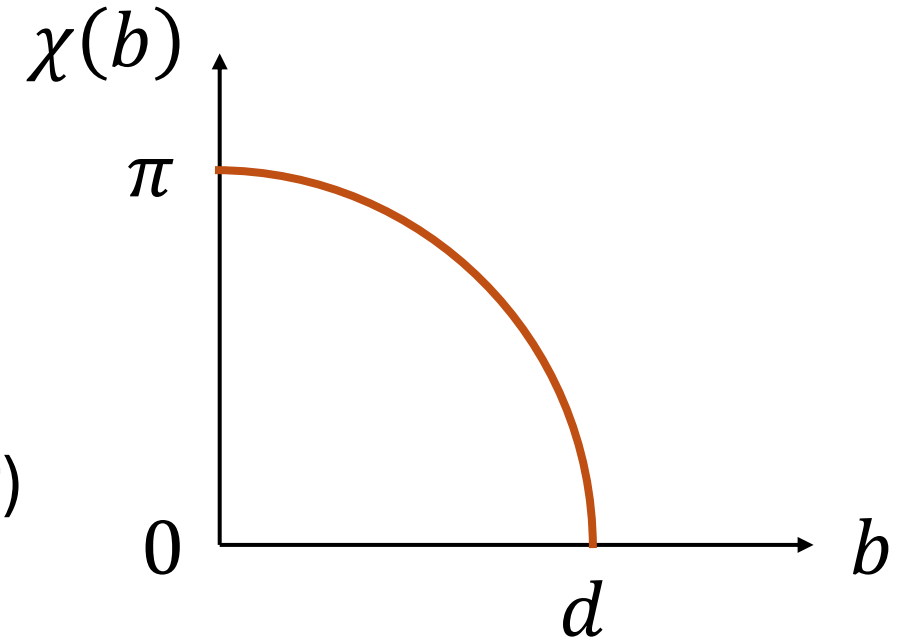
$$\chi(E, b) = \pi - 2b \int_{r_c}^{\infty} \frac{dr}{r^2 \left[1 - \frac{U(r)}{E} - \frac{b^2}{r^2} \right]^{\frac{1}{2}}} \text{ to yield}$$

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

How does this look plotted?

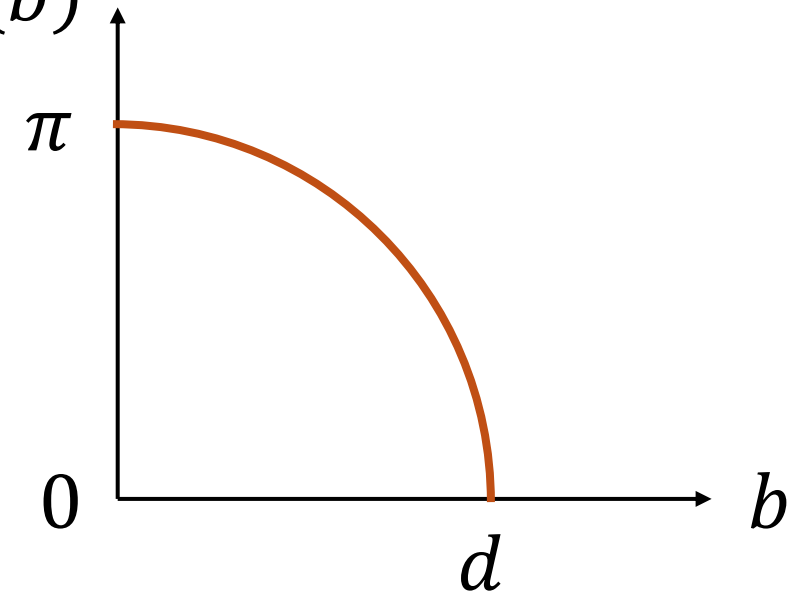
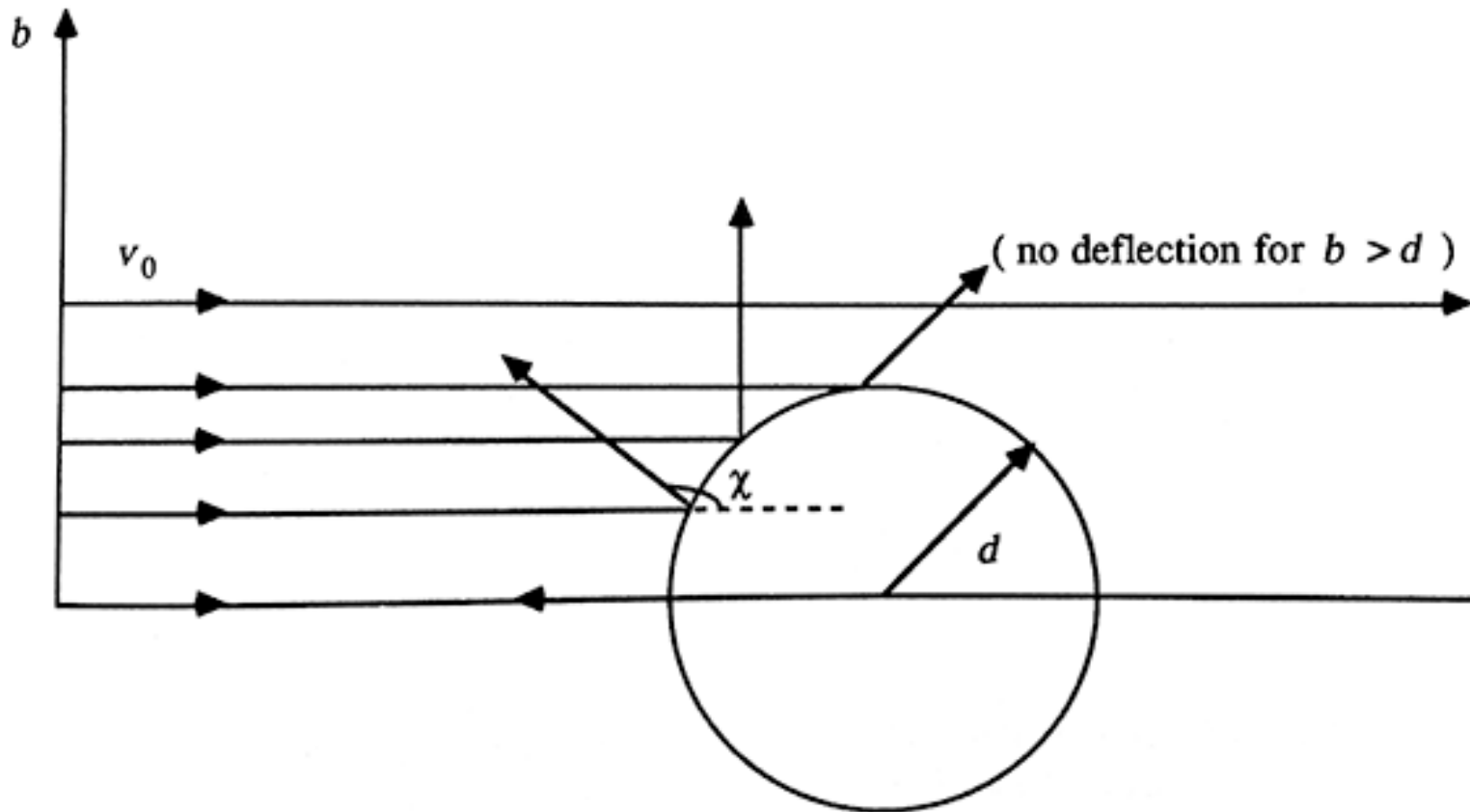
$$\chi(E, b) = \pi - 2b \int_d^\infty \frac{dr}{r^2 \left[1 - \frac{b^2}{r^2} \right]^{\frac{1}{2}}} = \dots = 2 \arccos \frac{b}{d}$$

- At what b do we have heads-on collision?
at $b = 0$
- What is deflection angle χ there?
 $\chi(b = 0) = \pi = 180^\circ$ (elastic back-scatter)
- What happens beyond $b = d$?
no more collision or deflection, deflection angle is zero



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

- for hard spheres, χ is energy-independent $\chi(b)$



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

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

• and we had derived

$$I_R = \frac{d\sigma_R}{d\Omega} = \frac{2\pi b db}{|2\pi \sin \chi(b) d\chi|}$$

• reminder: solid angle element is

$$\sin \chi d\chi \int_0^{2\pi} d\phi = 2\pi \sin \chi d\chi$$

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

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

We find $I_R = \frac{d^2}{4}$ for hard spheres

What do we expect when integrating this I_R ?

- 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-sphere 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”

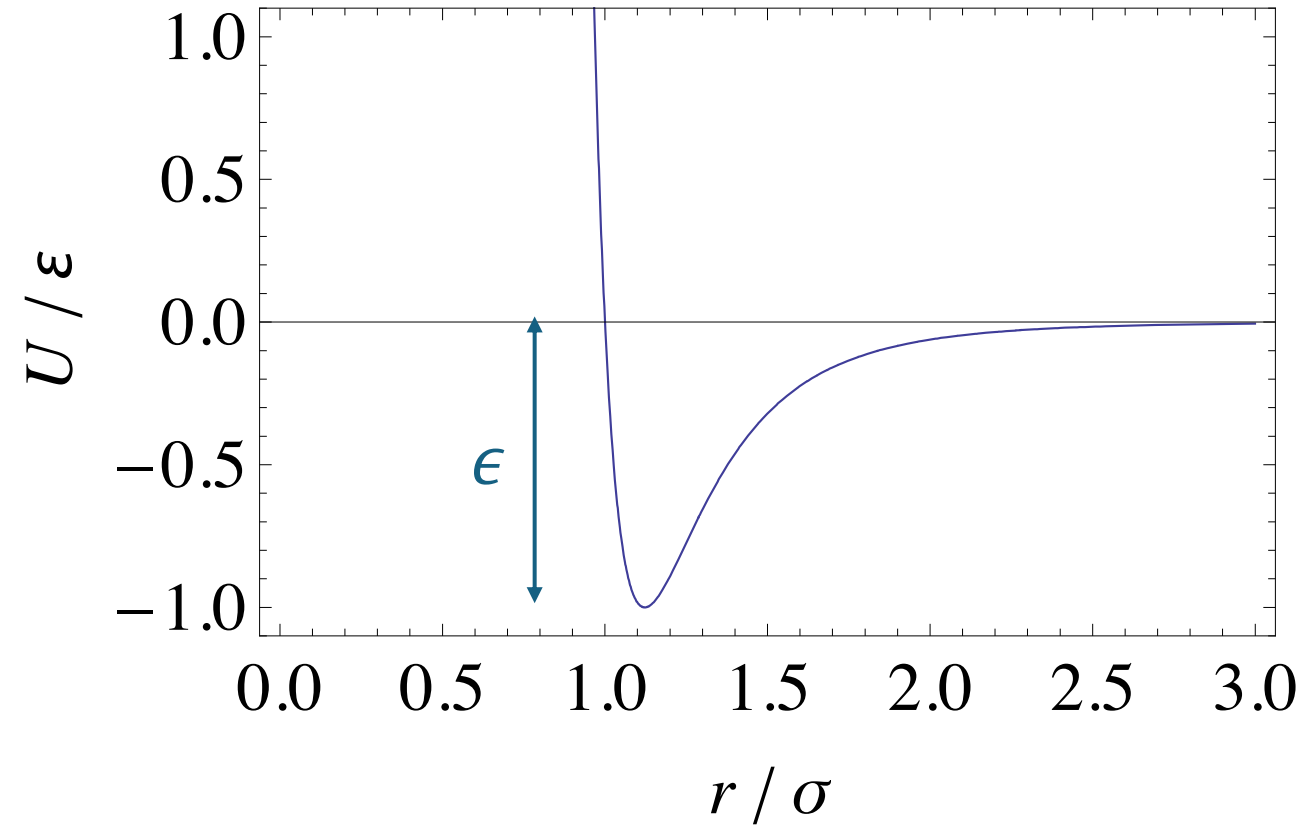
- ϵ depth of potential well

- 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 ?



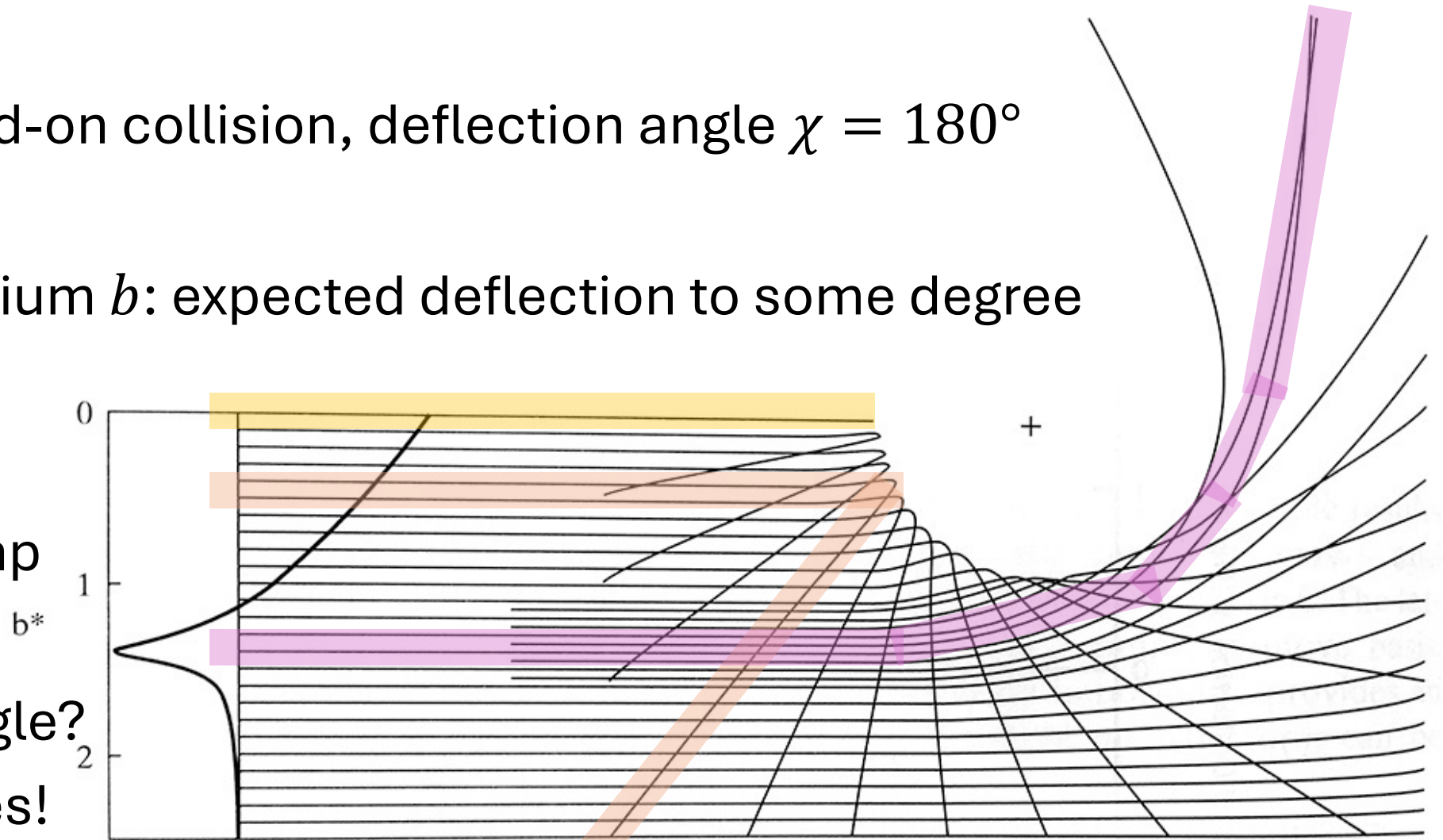
The *Lennard-Jones Potential* $U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$

- for $b = 0$: head-on collision, deflection angle $\chi = 180^\circ$
- for small/medium b : expected deflection to some degree

- for large b :
unexpected wrap
around center

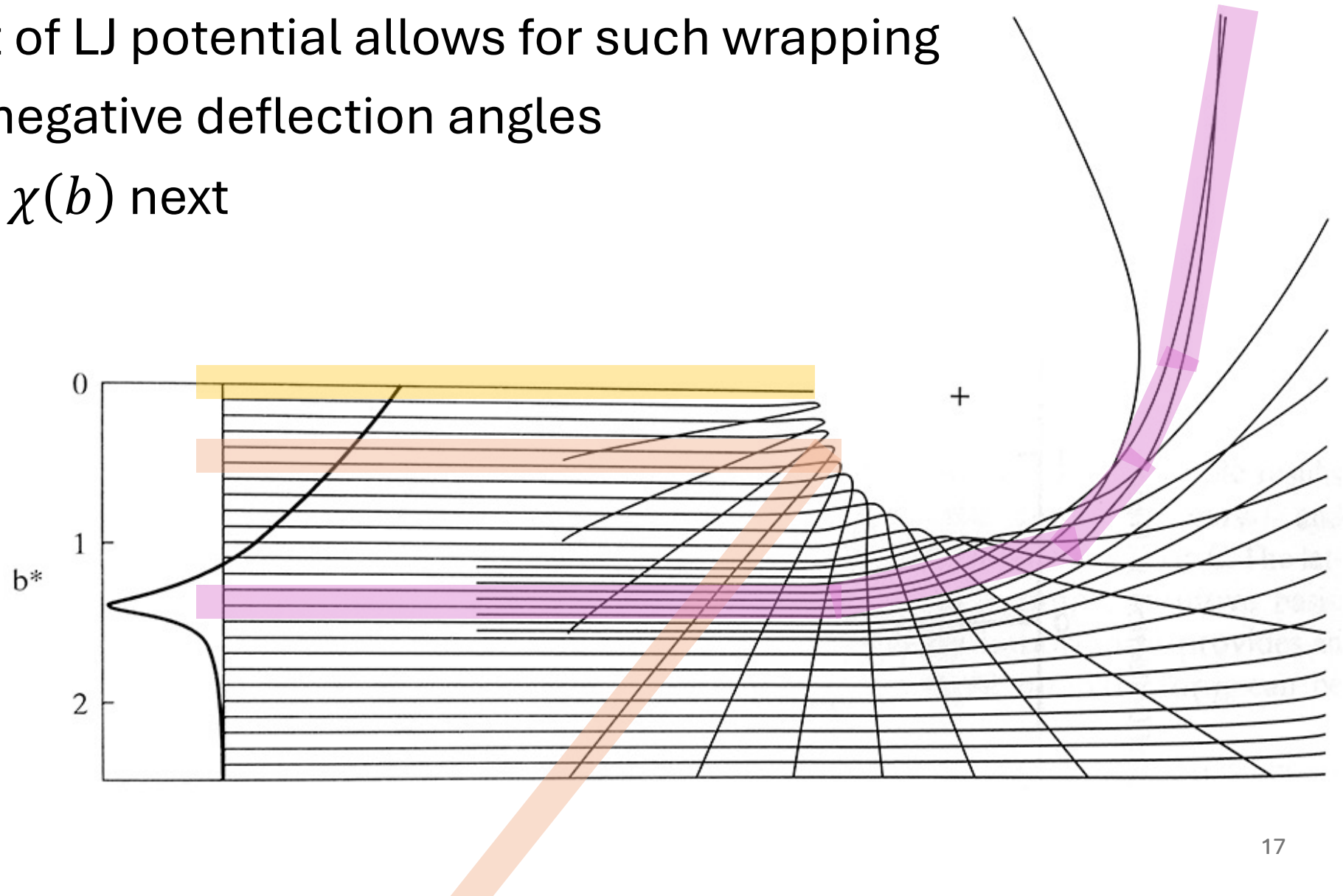
- Deflection angle?
- negative values!

- Not possible for hard spheres, why now?



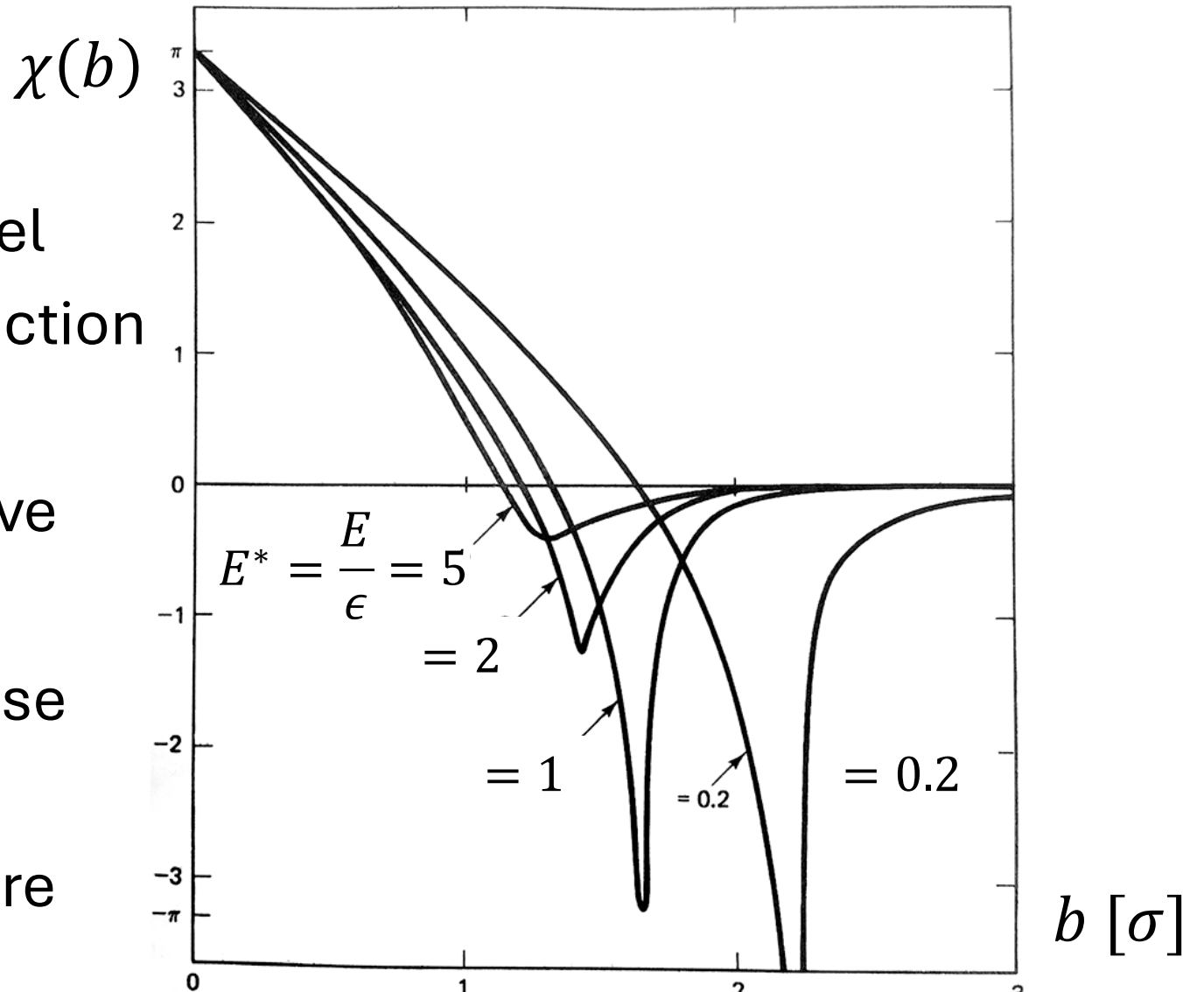
The *Lennard-Jones Potential* $U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$

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



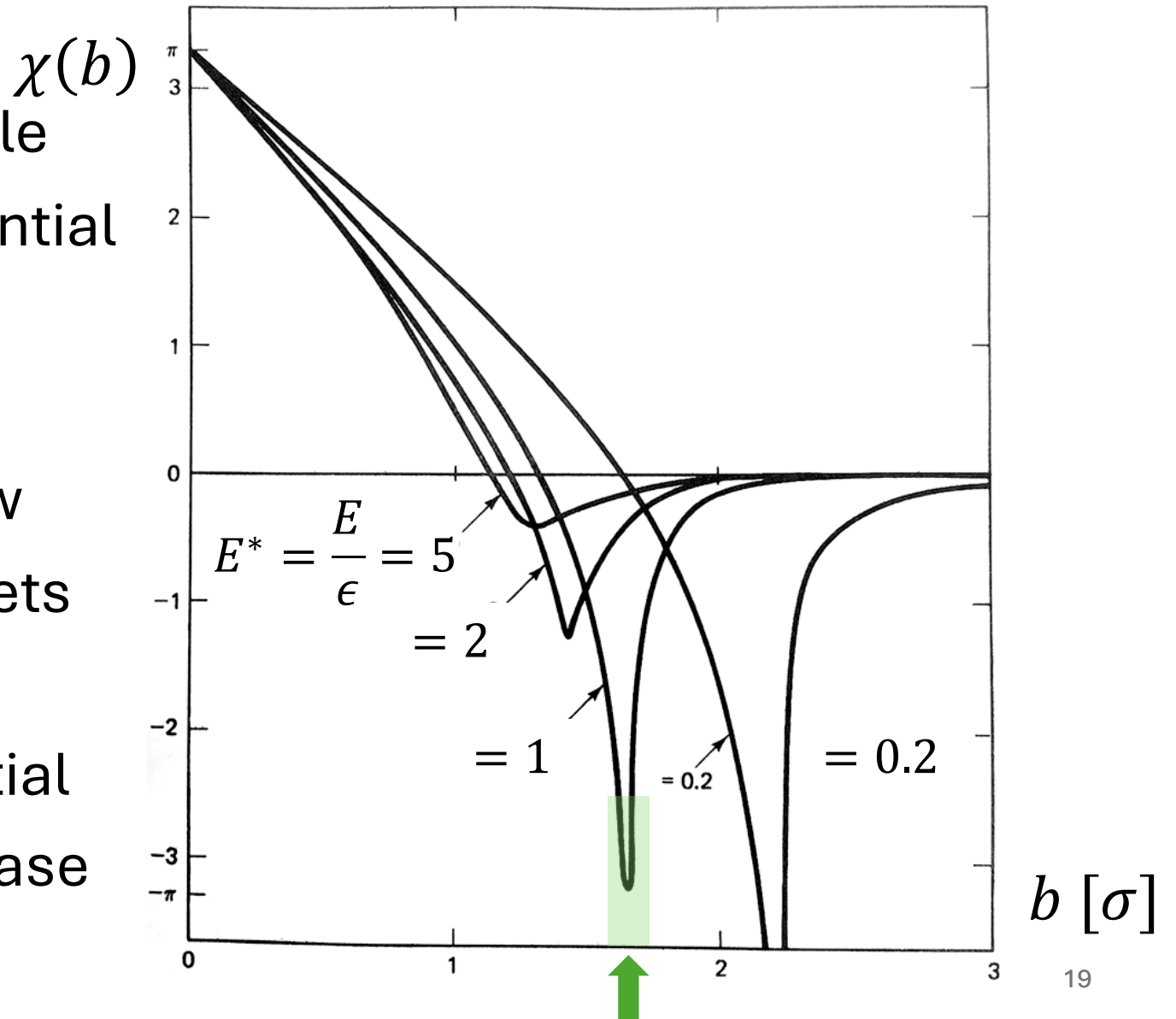
The *Lennard-Jones Potential* $U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$

- Why do all curves tend to 0 at 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 sphere case
- Different energies plotted
→ for lower energies, even more pronounced wrapping

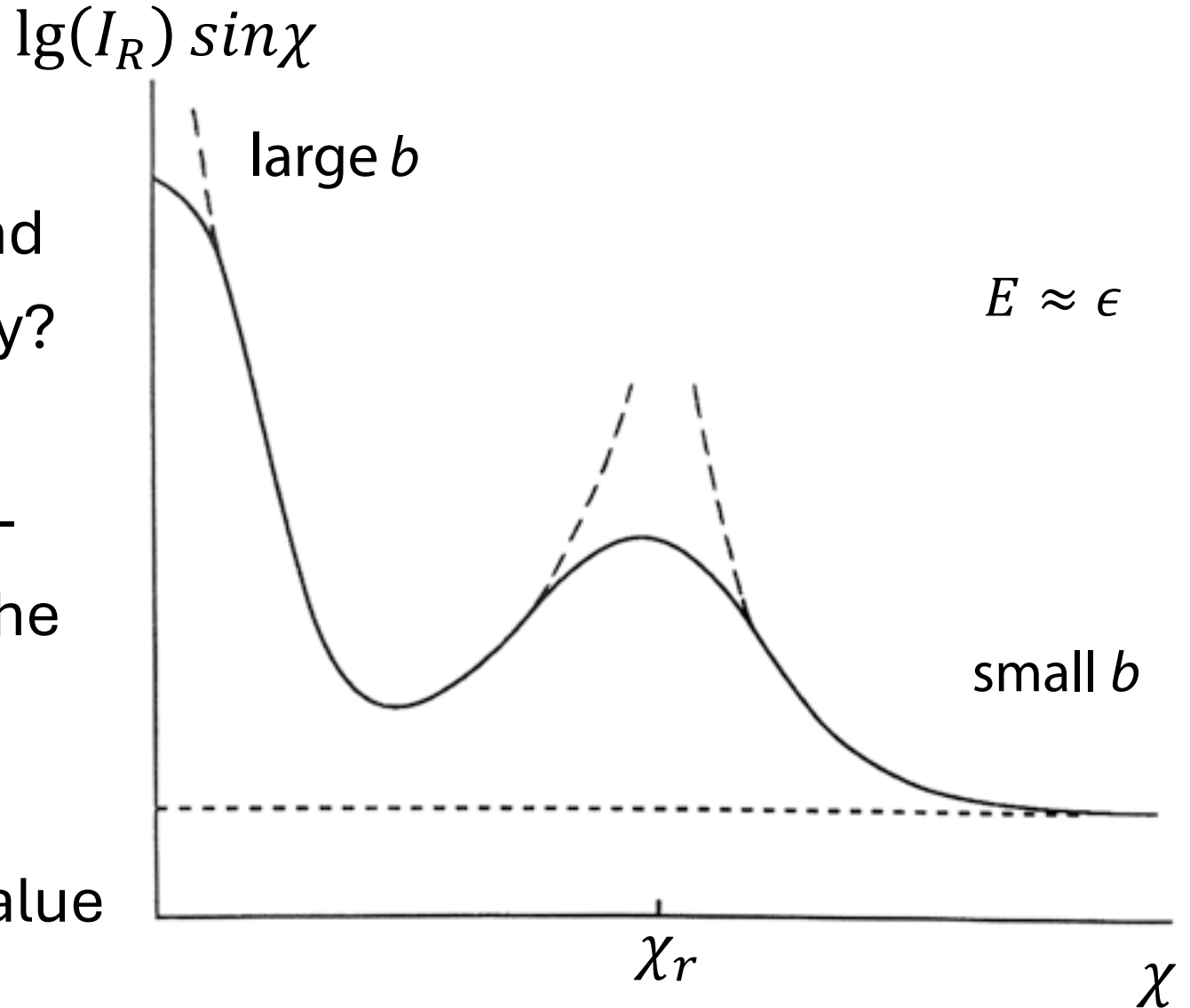


The *Lennard-Jones Potential* $U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$

- 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 rainbows
- Finally, let's plot the differential cross section $I(\chi)$ for the LJ case



- The differential cross section for a 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 ($\chi \rightarrow \pi, b \rightarrow 0$),
 I_R approaches hard sphere value
of $d^2/4$



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

$\lg(I_R) \sin \chi$

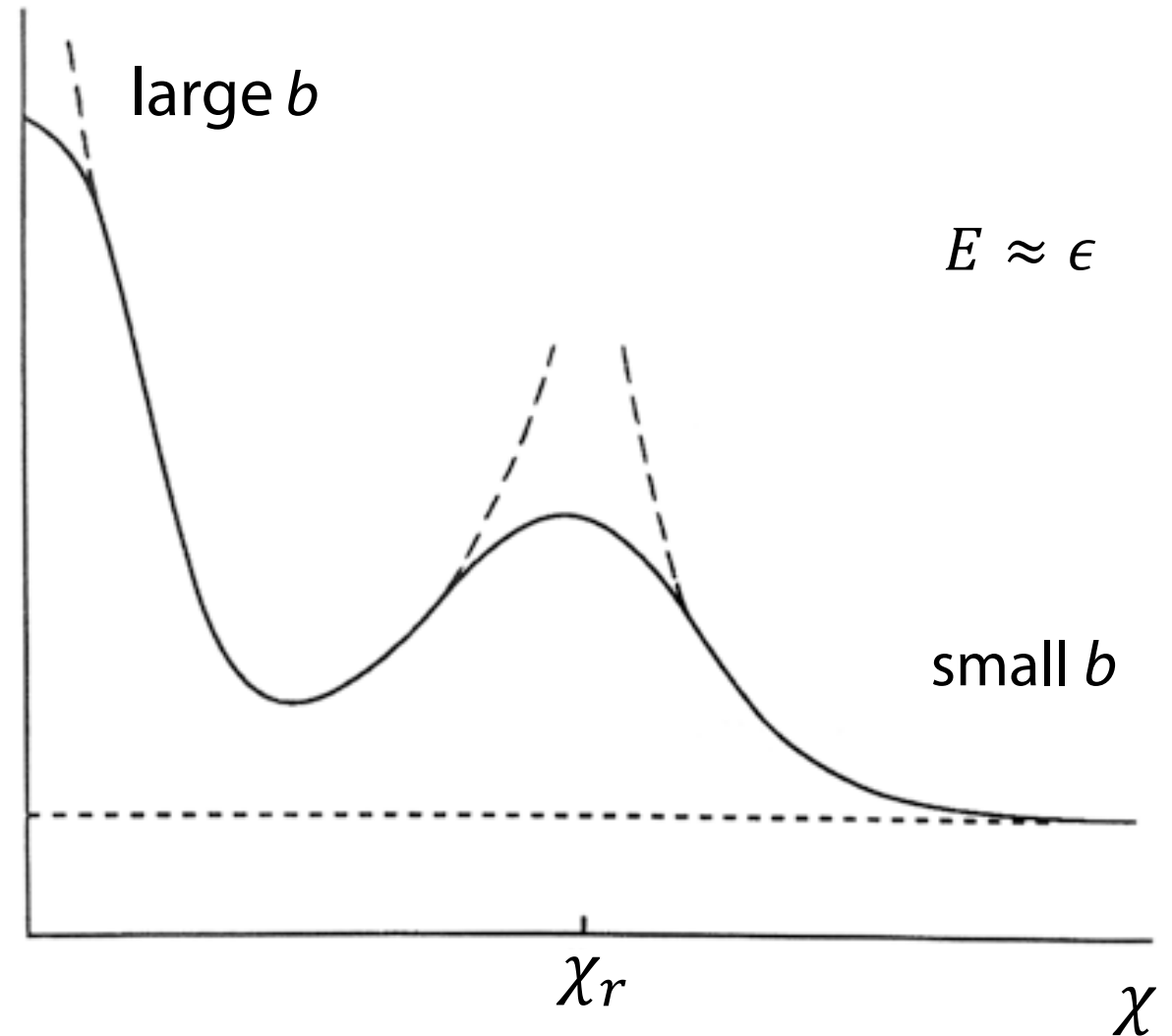
- At the rainbow angle (*i.e.*, at intermediate impact parameters):

$$\left| \frac{d \cos \chi}{db} \right| \rightarrow 0 \text{ meaning } I_R \rightarrow \infty$$

- At small χ ($\chi \rightarrow 0, b \rightarrow \infty$):

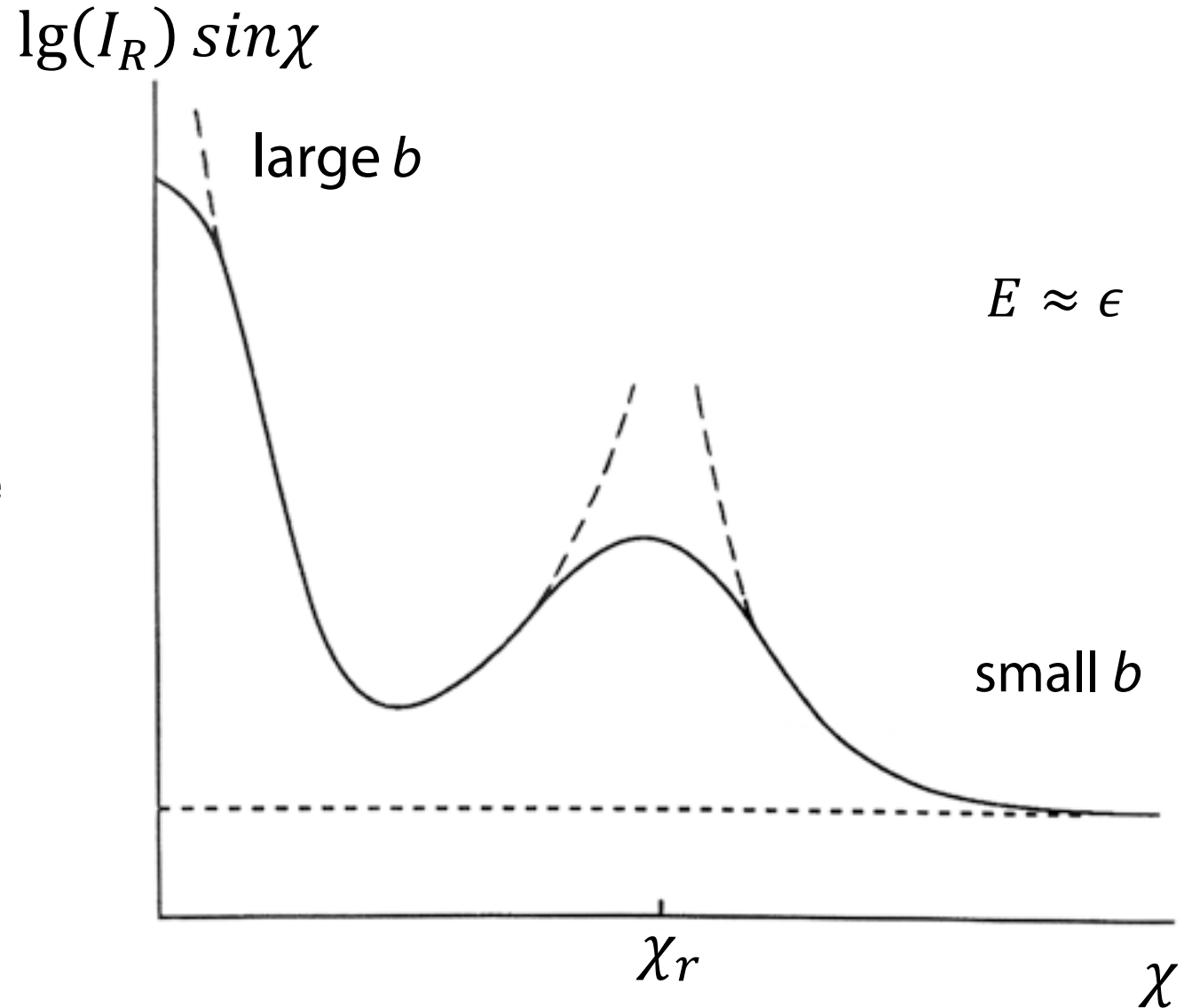
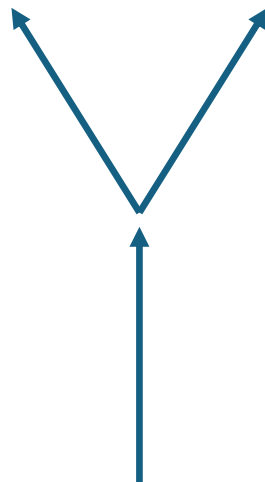
$$\left| \frac{d \cos \chi}{db} \right| \rightarrow 0 \text{ meaning } I_R \rightarrow \infty$$

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



What about the *negative* deflection angles from before?

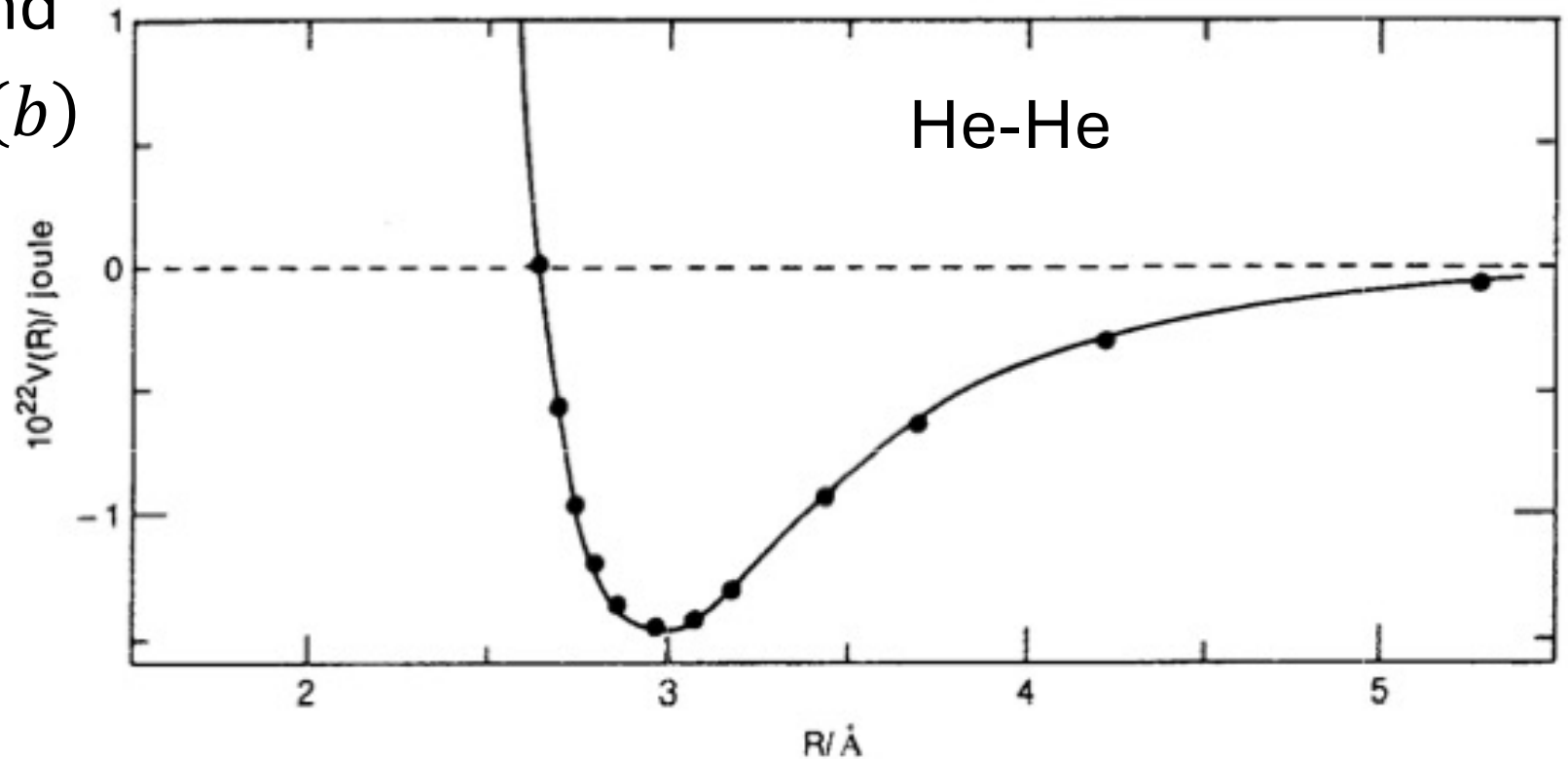
- Experimentally, you can only measure the values plotted
- Due to spherical symmetry of the potential, the negative deflection angles fold into the positive ones ☺



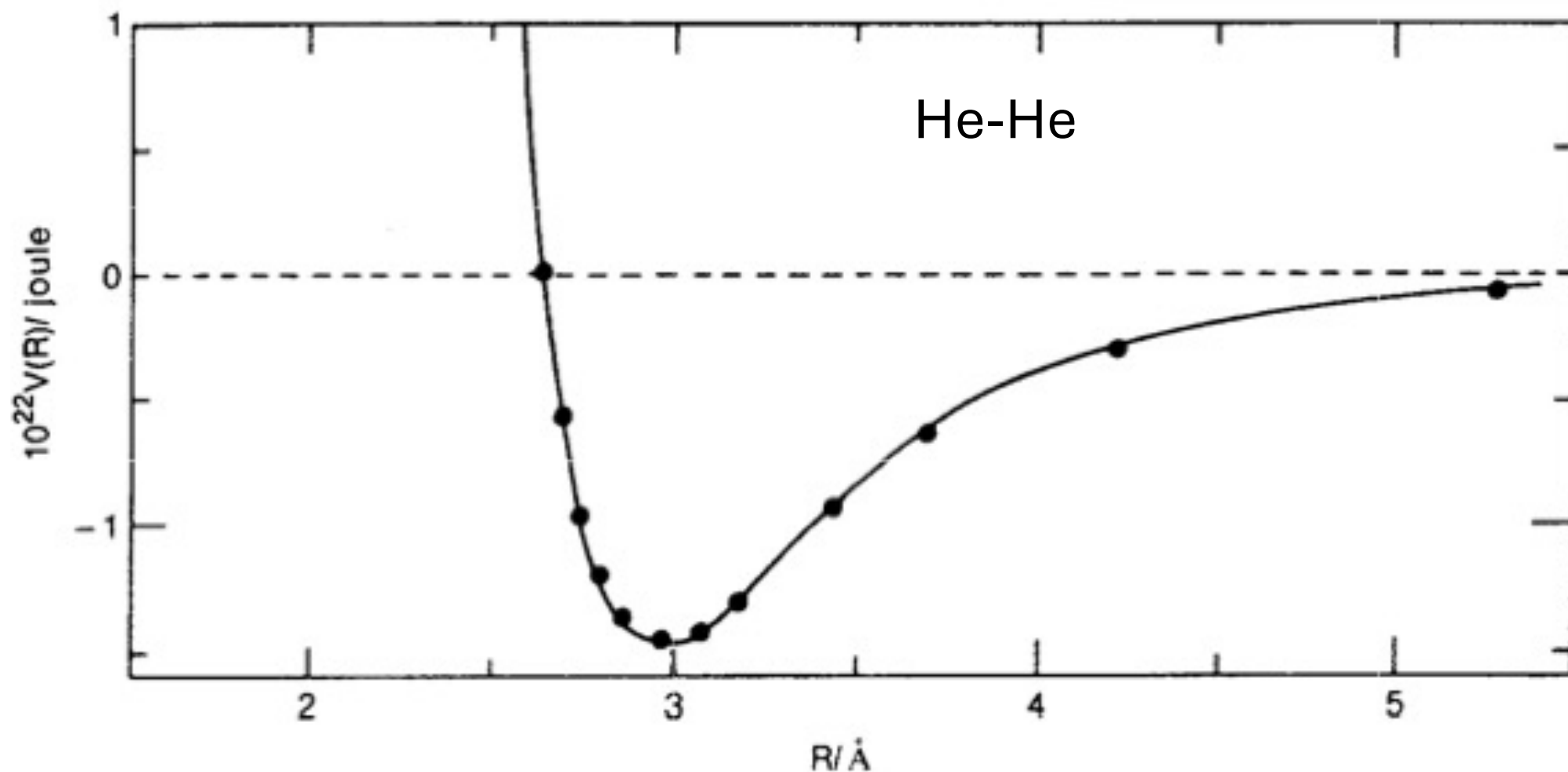
- How can we determine an intermolecular potential *experimentally*?
- By measuring differential cross sections!
- Integrate over a range of deflection angles (e.g., larger than χ_r , from χ_0):

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

- From this we now found a means to measure $\chi(b)$
- Then we can re-insert our $\chi(b)$ into our earlier 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.]