Indicative Student Feedback

- Please help me to improve :)
- Your brief feedback is super helpful!
- It will only take 2 minutes

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SCAN ME

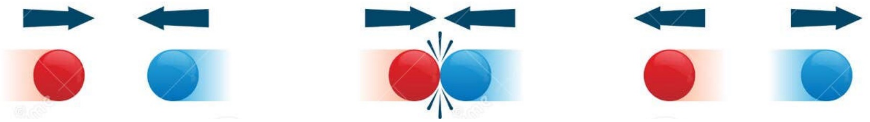
Kinetics & Dynamics of Chemical Reactions

Course CH-310

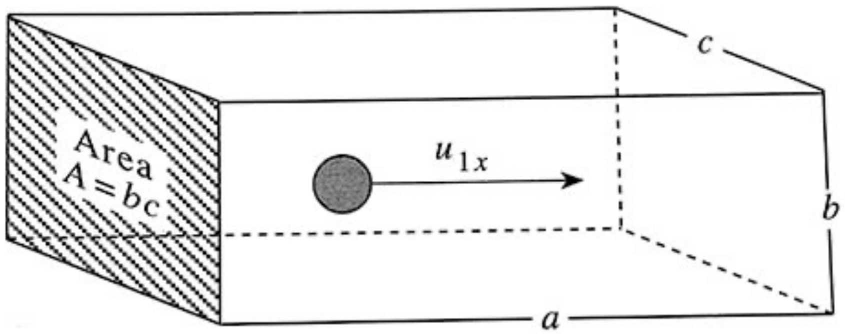
Prof. Sascha Feldmann

Recap from last session

- Polymerization
  - stepwise vs chain type (with 3 steps)
  - kinetic chain length λ and degree of polymerization $\langle N \rangle$



- Kinetic theory of gases
- Ideal Gas Law: $PV = Nk_BT = nRT$
- only kinetic energy, collisions elastic
- $u_{rms} = \sqrt{\langle u^2 \rangle} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_BT}{m}}$



Recap from last session

- Maxwell-Boltzmann velocity distribution

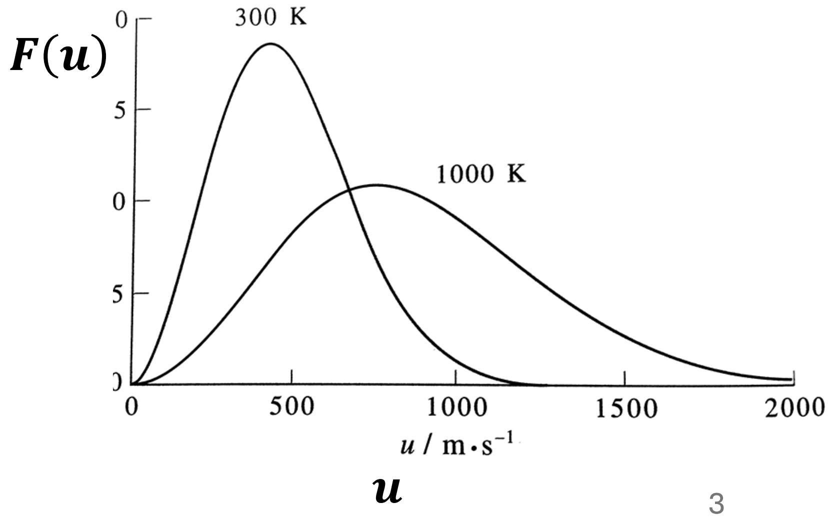
$$\text{in 1D: } f\left(u_j\right)du_i = \sqrt{\frac{m}{2\pi k_B T}}\ \ e^{-\frac{mu_j^2}{2k_BT}}du_i$$

$$\text{in 3D: } F(u)du = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_BT}}du$$

- and how curve changes with composition

  & with temperature

- how to measure speed distributions experimentally (Doppler or slits machine)



Chapter 5

Collisions

5.1 Collisions with a wall

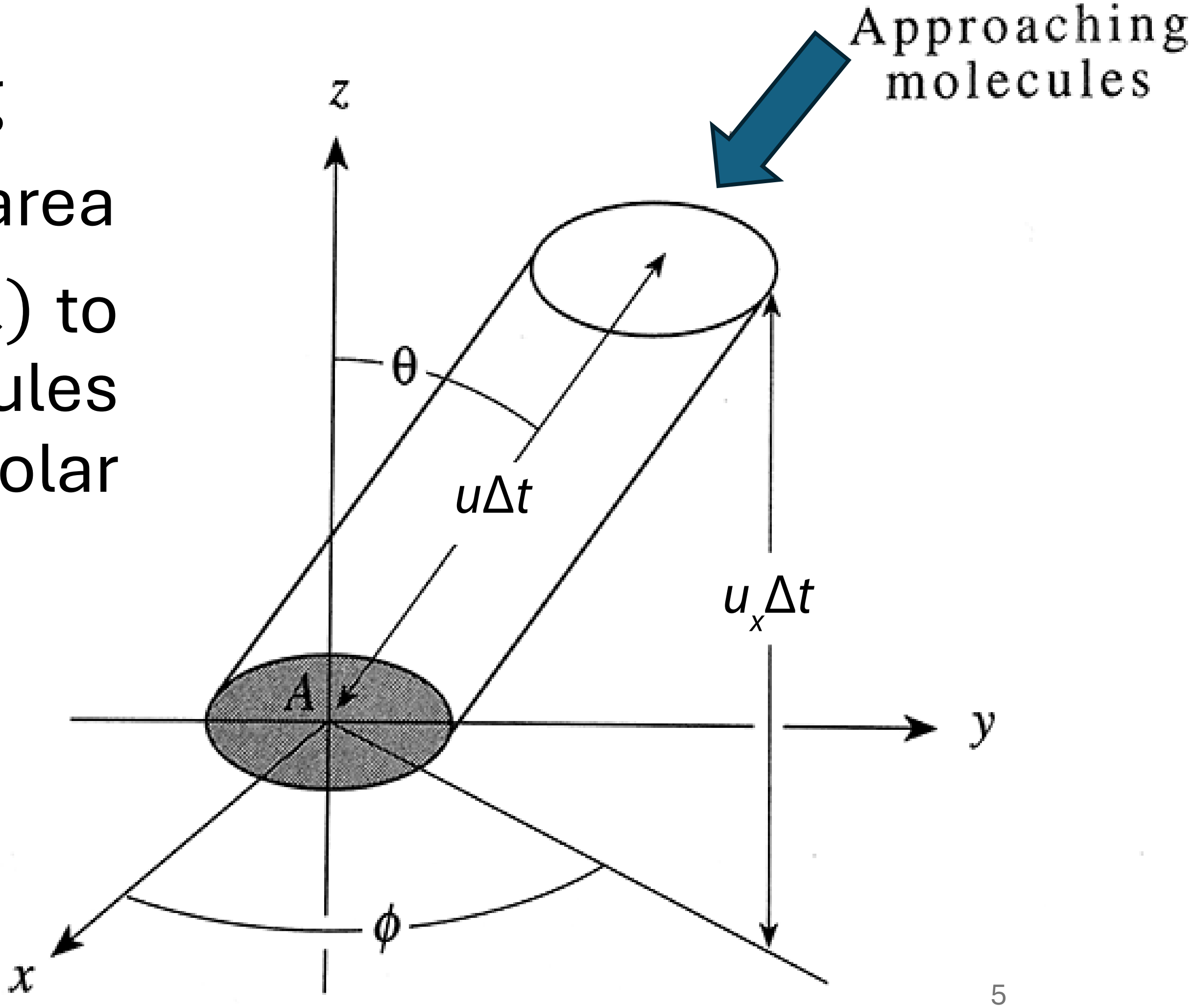
- Wanted: *the collision flux* z_{coll}

z_{coll} = number of molecules hitting a surface per unit time and area

- use Maxwell-Boltzmann distr. $F(u)$ to calculate the *density* of molecules $\rho_{u,\theta,\phi}$ moving with speed u and polar angles θ & ϕ :

$$\rho_{u,\theta,\phi} = \rho\, F(u) du \frac{\sin\theta d\theta d\phi}{4\pi}$$

ρ : gas density (particle number per volume)



- Wanted: *Collision flux* $z_{\mathbf{coll}}$

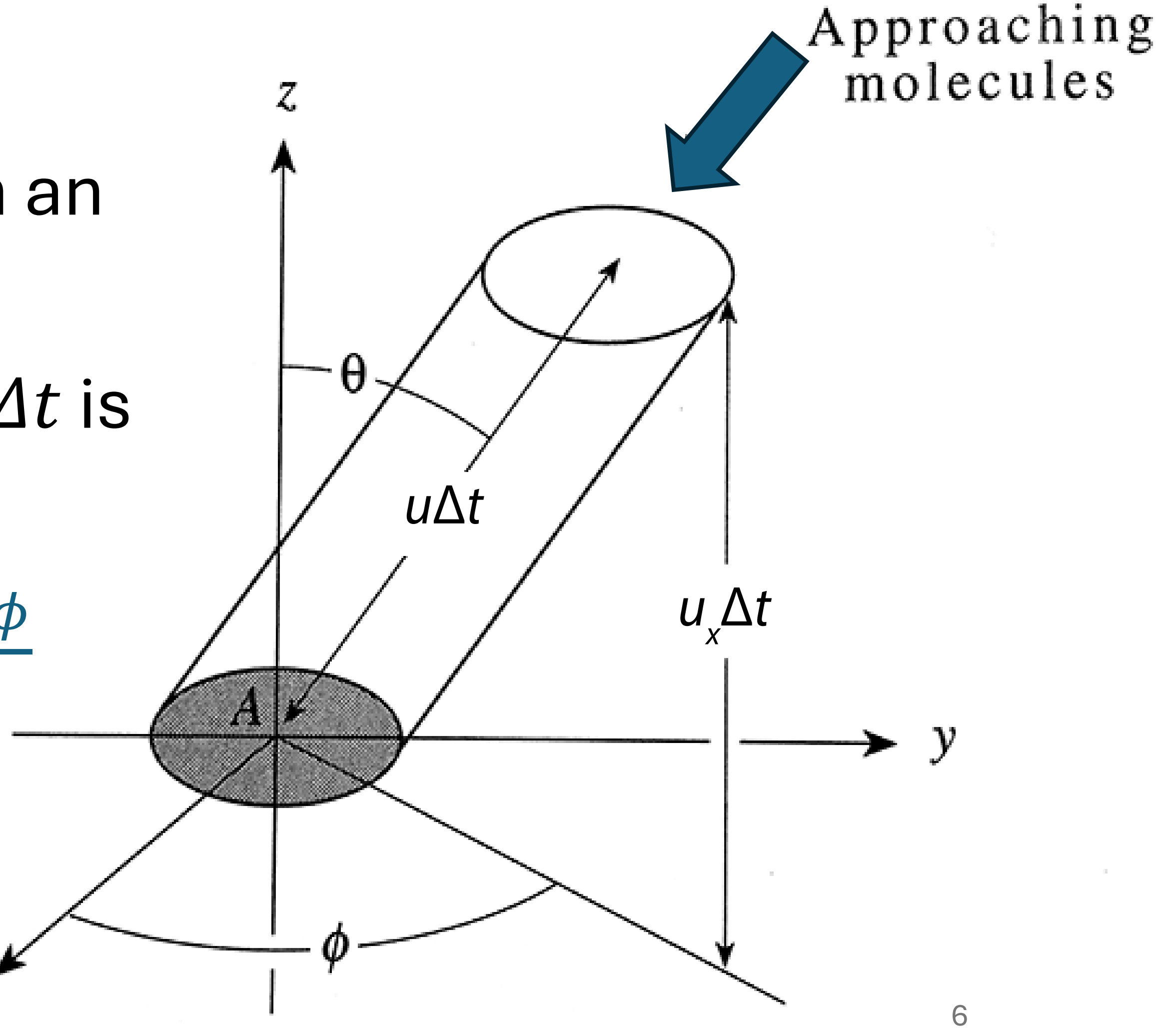
  = number of molecules hitting surface per unit time and area
- particles will take time Δt to hit surface area A
- thus crossing the distance $u_z \Delta t$
- only those count that approach within an oblique cylinder
- the number of molecules in area A in Δt is

$$N_{u,\theta,\phi} = V \rho_{u,\theta,\phi}$$

$$= A \cdot u \cos\theta \, \Delta t \cdot \rho \, F(u) du \frac{\sin\theta \, d\theta \, d\phi}{4\pi}$$

all molecules that move with speed between u and du

relevant surface element / total surface area (4π)



- Wanted: *Collision flux* $z_{\mathbf{coll}}$

  = number of molecules hitting surface per unit time and area

- The number of molecules in area A in Δt is

$$N_{u,\theta,\phi} = A \cdot u\cos\theta\,\Delta t \cdot \rho\, F(u)du\,\frac{\sin\theta\, d\theta d\phi}{4\pi}$$

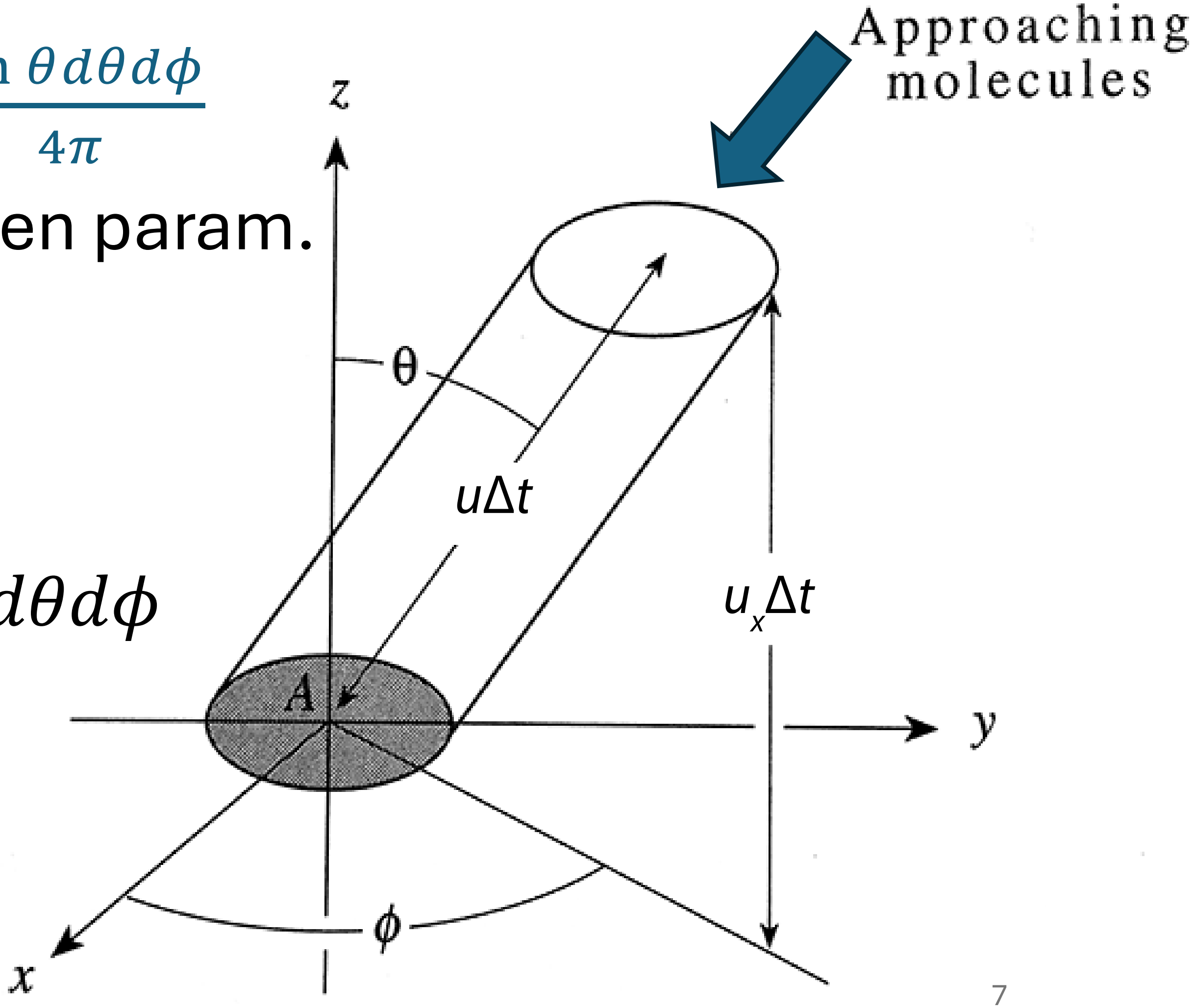
- Flux $z_{\mathrm{coll},u,\theta,\phi}$ of molecules with given param.

  by dividing by $A\,\Delta t$ (as defined):

$$z_{\mathrm{coll},u,\theta,\phi} = \frac{N_{u,\theta,\phi}}{A\Delta t}$$
$$= \frac{\rho}{4\pi} uF(u)du\cos\theta\sin\theta\; d\theta d\phi$$

meaning: $z_{\mathrm{coll},u,\theta,\phi} \propto u^3$

since $u\,F(u) \propto u^3$



- Collision flux $z_{\text{coll},u,\theta,\phi} = \frac{N_{u,\theta,\phi}}{A\Delta t} = \frac{\rho}{4\pi} uF(u)du \cos\theta \sin\theta \, d\theta d\phi$

meaning: $z_{\text{coll},u,\theta,\phi} \propto u^3$

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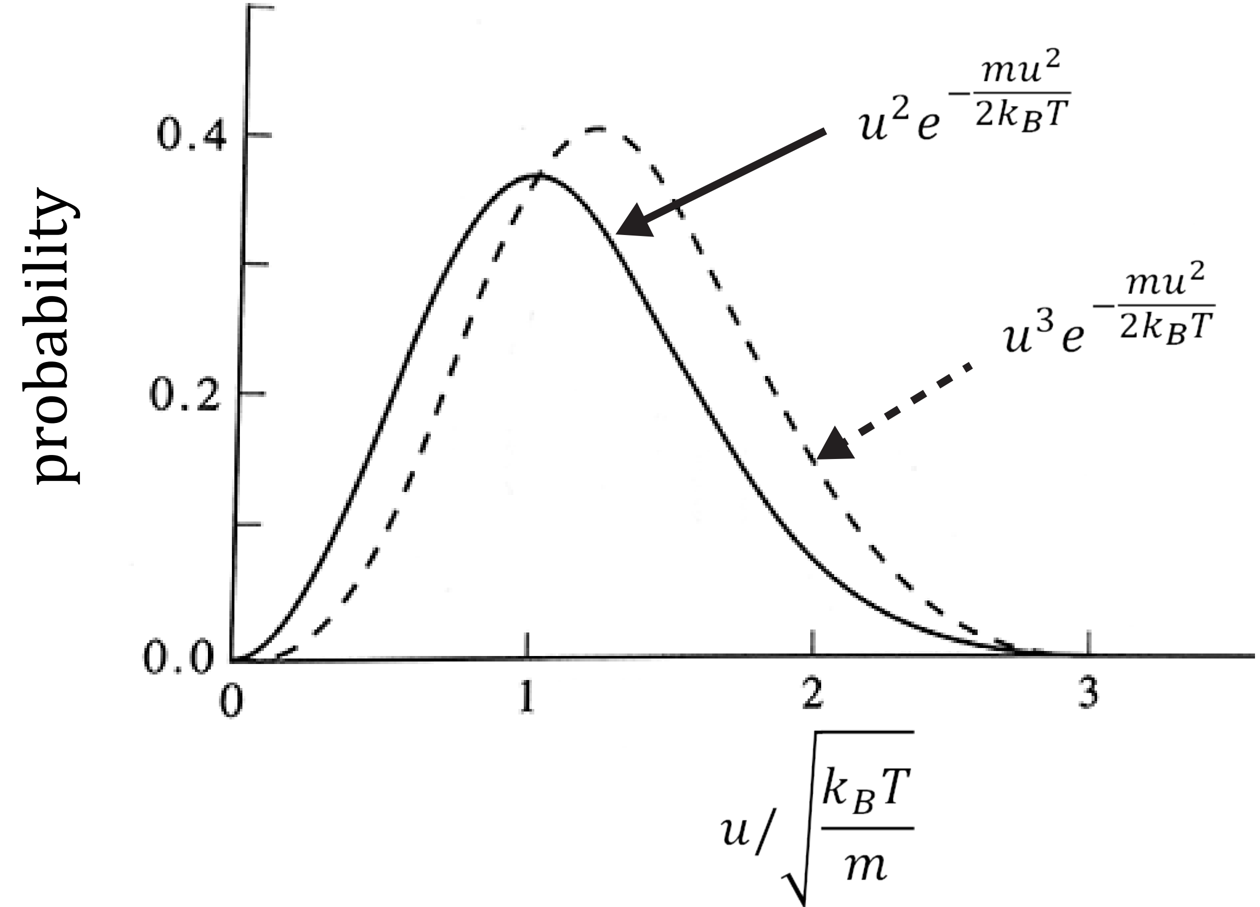
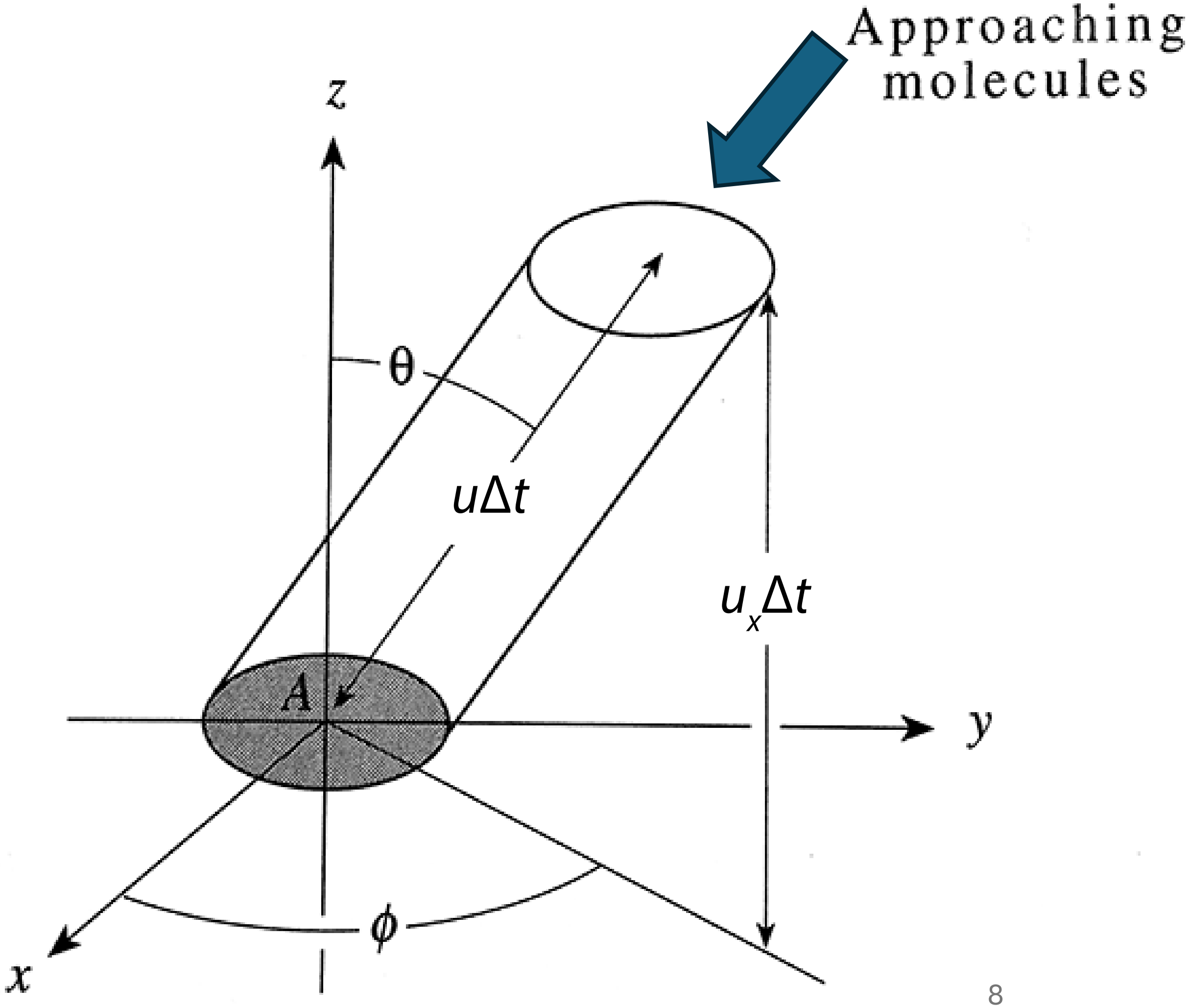
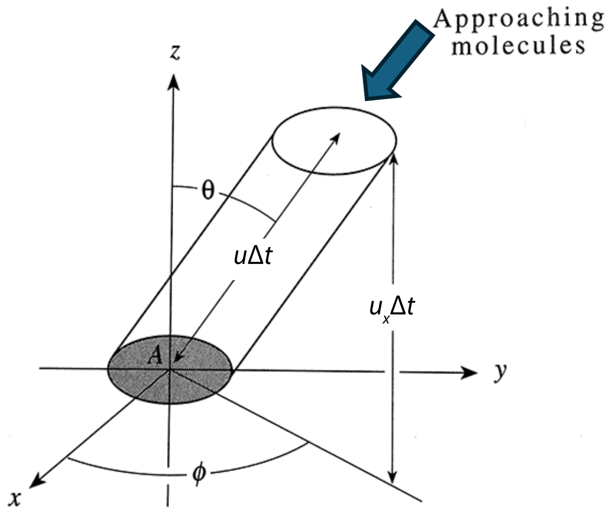




- Collision flux $z_{\text{coll},u,\theta,\phi} = \frac{N_{u,\theta,\phi}}{A\Delta t} = \frac{\rho}{4\pi} uF(u)du \cos\theta \sin\theta \, d\theta d\phi$

- Obtain *total collision flux* z_{coll} by integrating over all speeds & angles
- Note: only molecules with $0 \leq \theta \leq \pi/2$ will hit the surface (molecules can only hit from one side: the top)



$$z_{\text{coll}} = \frac{\rho}{4\pi} \int_0^\infty uF(u)du \underbrace{\int_0^{\pi/2} \cos\theta \sin\theta \, d\theta}_{\frac{1}{2}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

$$= \frac{\rho}{4} \langle u \rangle = \sqrt{\frac{k_B T}{2\pi \, m}} \rho$$

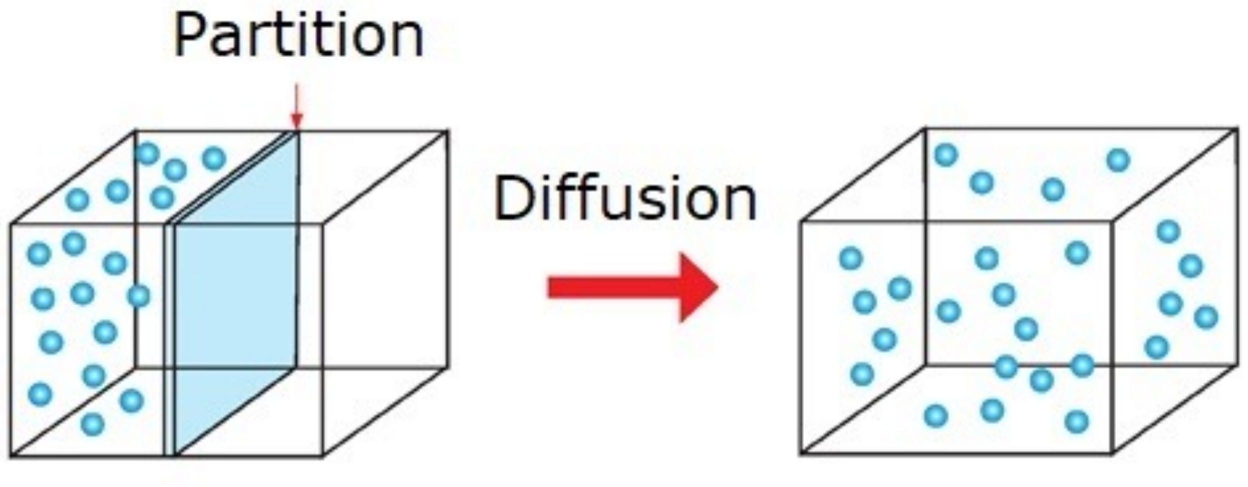
$$z_{\text{coll}} = \sqrt{\frac{k_B T}{2\pi\, m}}\,\rho$$

Quiz: Calculate the collision flux of nitrogen at 300 K and 1 bar.

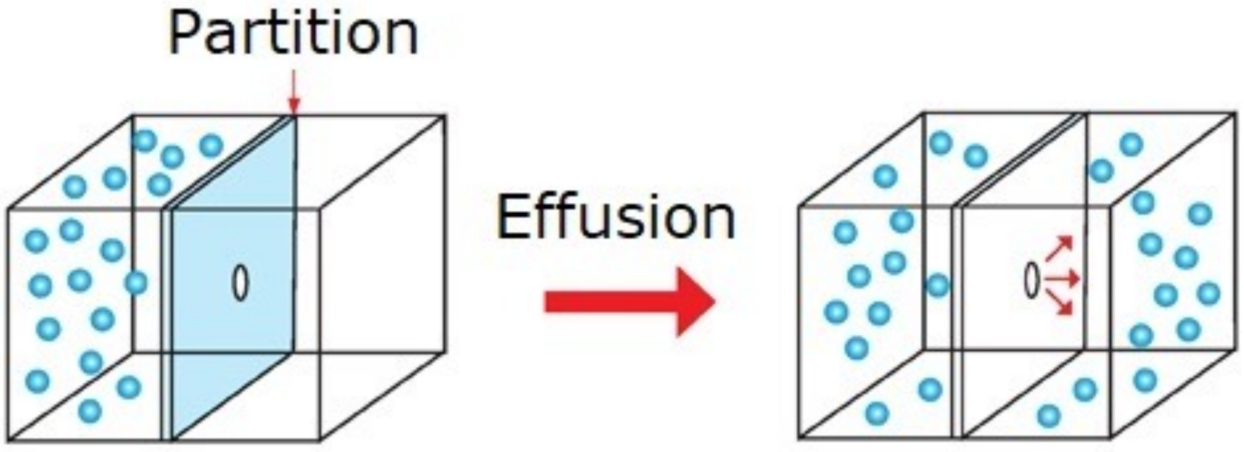
$$z_{\text{coll}} = 3 \text{ x } 10^{27}\ \text{s}^{-1}\text{m}^{-2}$$

that's approx. 3 collisions per ns and per nm^2 !!!

5.2 Effusion

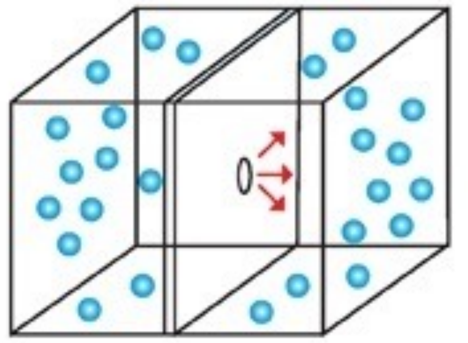


Diffusion through conventional opening: If opening larger than mean free path of molecules

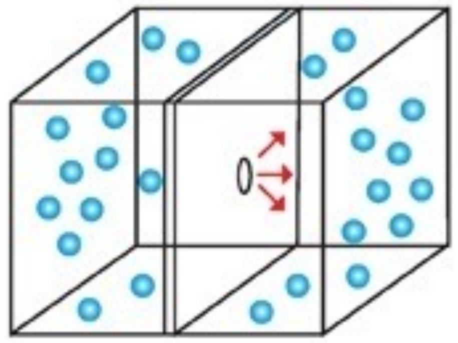


Effusion: when gas escapes through a small hole into vacuum (often in surface science!)

5.2 Effusion



- k_{effusion} is rate of escaping molecules through hole
- from before this just means it is related to collision rate and hole with area A through
- $$k_{\text{effusion}} = z_{\text{coll}}\, A = \sqrt{\frac{k_B T}{2\pi m}}\rho\, A \propto \sqrt{\frac{1}{m}}$$ "Graham's Law"
- How to measure? Through pressure p instead of density ρ
- Ideal Gas Law: $pV = Nk_bT$
- Substitute $\rho = \frac{N}{V} = p/(k_B T)$ $\Rightarrow k_{\text{effusion}} = \sqrt{\frac{k_B T}{2\pi m}}\rho A = \frac{pA}{\sqrt{2\pi m k_B T}}$



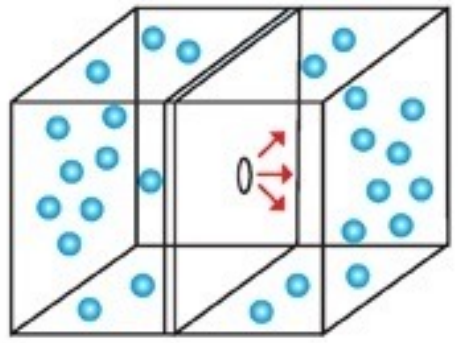
- $k_{\text{effusion}} = \sqrt{\frac{k_B T}{2\pi m}} \rho A = \frac{pA}{\sqrt{2\pi m k_B T}}$

- but also useful for:

Knudsen Method

- Challenge: generally it is hard to determine the vapor pressure p of liquids or solids using just a bulk barometer
- Idea: put compound in container with small hole of known area A
- Put into a vacuum and let gas molecules escape through hole
- Measure rate through mass loss per unit time
- Rate of that is k_{effusion}, so we can derive p knowing A and m

- $k_{\text{effusion}} = \sqrt{\frac{k_B T}{2\pi m}}\rho A = \frac{pA}{\sqrt{2\pi m k_B T}}$



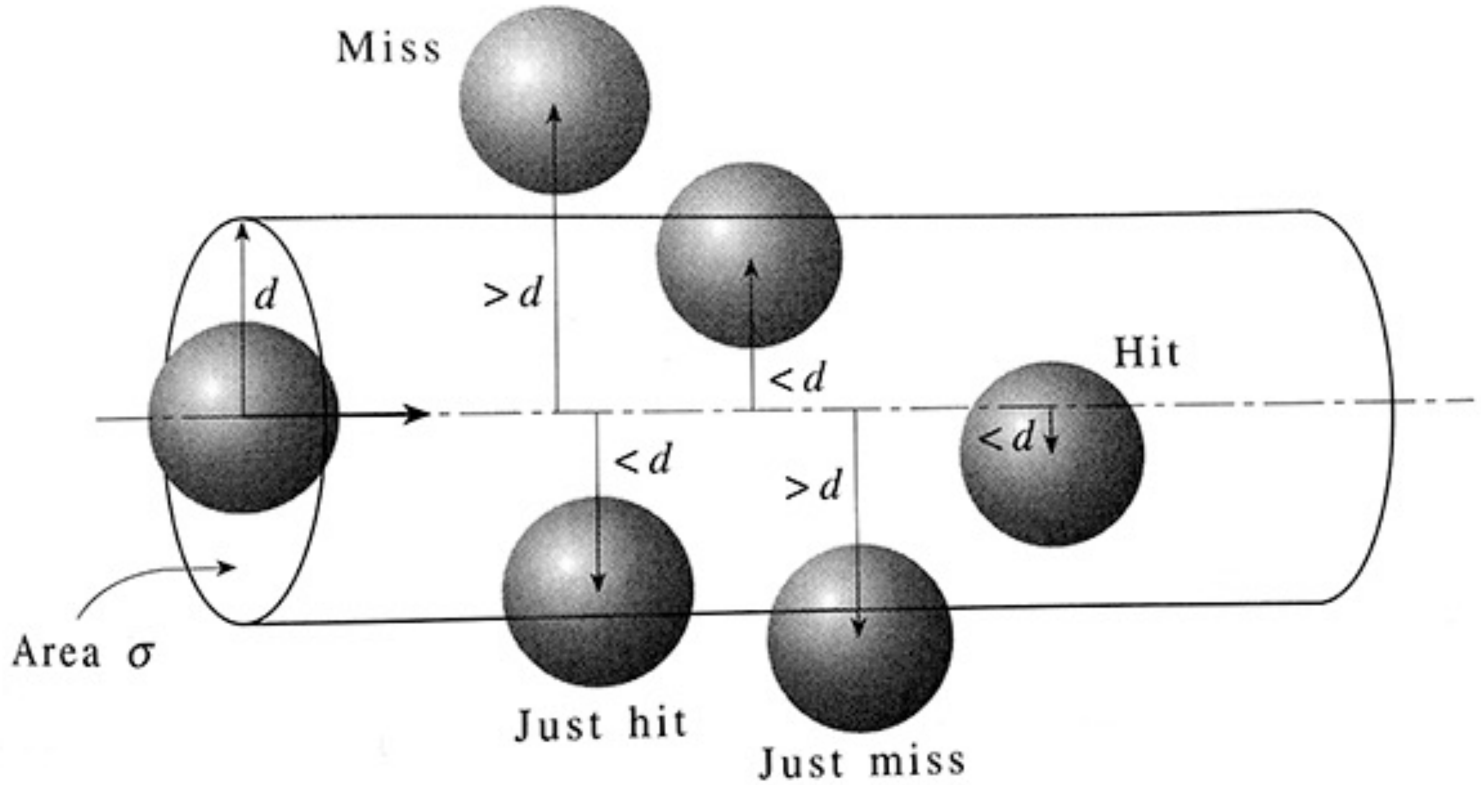
Conditions for Effusion:

- assumes equilibrium (although we got a hole in container!)
- If pressure is really high in container: supersonic expansion (super fast release of molecules into vacuum)
  → need to assume *low* vapor pressure: If gas density is low enough, molecules won't interact with each other, and the equilibrium remains undisturbed
  →*Mean free path* (the molecule travels before colliding with another) needs to be *long* compared to hole size, so no collision/speed distribution alteration through the hole

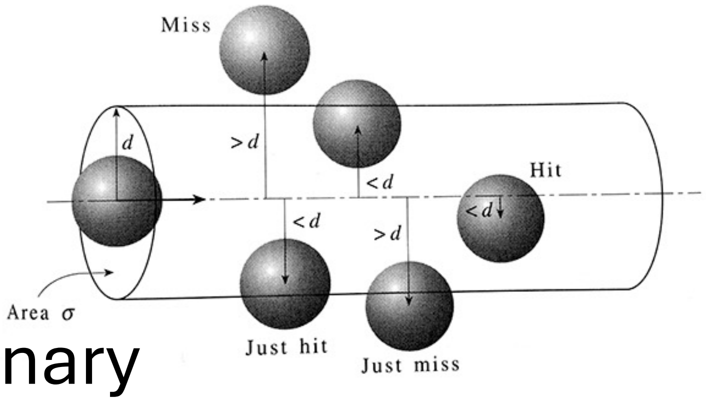
5.3 Collision rate and mean free path

- Assuming molecules are hard spheres again, with diameter d
- Now let molecules collide with each other, want to get collision rate
- Collision if two spheres are closer than their diameter d

Area:
$\sigma = \pi d^2$



- *Collision cross section*: $\sigma = \pi d^2$



- we assume (wrongly) all other molecules are stationary

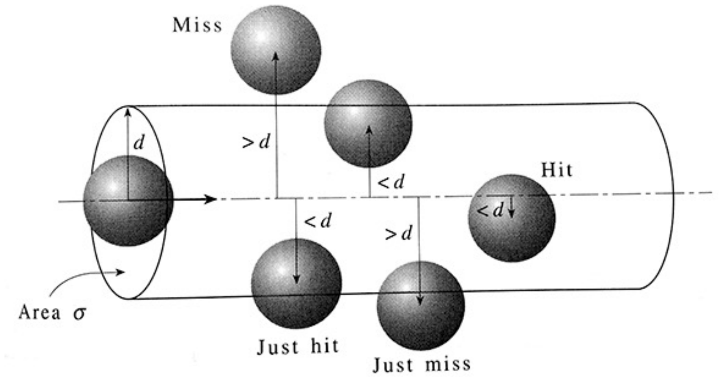
- within a time Δt, a molecule on average sweeps out a cylinder of volume $\langle V \rangle = \sigma \langle u \rangle \Delta t$ with a gas density of ρ

- thus, the molecule undergoes $\Delta N_{\text{coll}} = \rho\, \sigma \langle u \rangle \Delta t$ collisions

- We define the *Collision Rate* z_A as: $z_A = \frac{\Delta N_{\text{coll}}}{\Delta t} = \rho\sigma\langle u \rangle = \rho\sigma\sqrt{\frac{8k_BT}{\pi m}}$

now what about the stationary bit...?

Collision Rate z_A as: $z_A = \frac{\Delta N_{\text{coll}}}{\Delta t} = \rho\sigma\langle u\rangle = \rho\sigma\sqrt{\frac{8k_BT}{\pi m}}$



- Instead of average speed of single molecule $\langle u\rangle$ we use average *relative* speed of two molecules $\langle u_{AB}\rangle = \langle|\vec{u}_A - \vec{u}_B|\rangle$

→ $\langle V\rangle = \sigma\,\langle u\rangle\,\Delta t$ becomes $\langle V\rangle = \sigma\,\langle|\vec{u}_A - \vec{u}_B|\rangle\,\Delta t$

- We move to a center-of-mass coordinate system and find

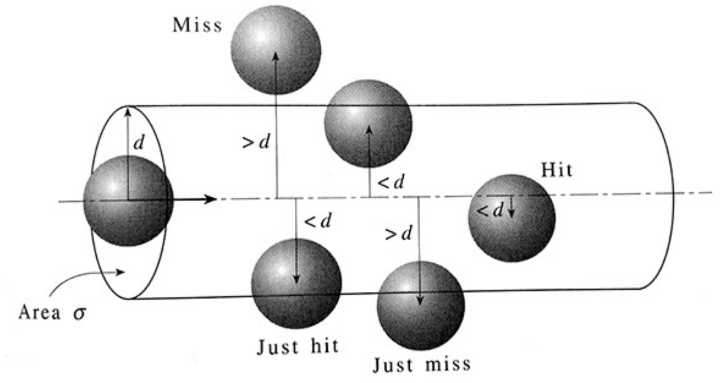
$$\langle u_{AB}\rangle = \langle|\vec{u}_A - \vec{u}_B|\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

with *reduced mass* $\mu = \frac{m_1 m_2}{m_1+m_2}$

- For $m_1 = m_2 = m$ we obtain $\mu = m/2$ and thus

$$z_A = \rho\sigma\langle u_{AB}\rangle = \sqrt{2}\rho\sigma\langle u\rangle = \sqrt{2}\rho\sigma\sqrt{\frac{8k_BT}{\pi m}} = \rho\sigma\sqrt{\frac{8k_BT}{\pi\mu}}$$

$$z_A = \rho\sigma\langle u_{AB}\rangle = \sqrt{2}\rho\sigma\langle u\rangle = \sqrt{2}\rho\sigma\sqrt{\frac{8k_BT}{\pi m}}$$



Quiz: Calculate the collision rate of a single nitrogen molecule at 300 K and 1 bar, assuming $\sigma = 0.450 \cdot 10^{-18}$ m^2.

- We find: $z_A = 10^{10}\ s^{-1}$

→That's a high rate! Every 100 ps one collision on average!

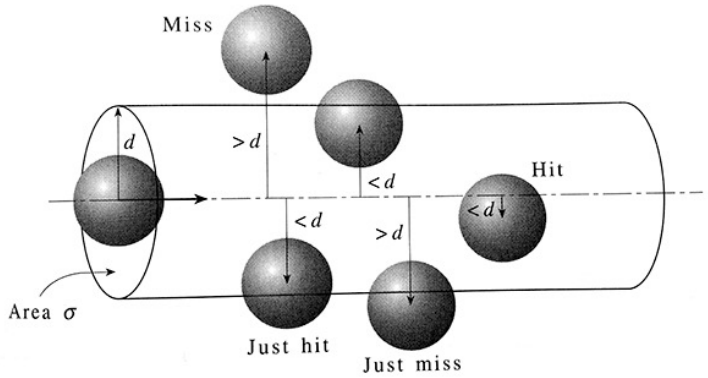
- Let's define the ***mean free path*** $\boldsymbol{l}$ as the average distance a molecule travels between collisions:

$$l = \frac{\langle u \rangle}{z_A} = \frac{1}{\sqrt{2}\rho\sigma}$$

Quiz: Calculate the mean free path of nitrogen at 300 K and 1 bar, assuming $\sigma = 0.450 \cdot 10^{-18}$ m^2.

- We find here $l = 65\ \mathrm{nm}$

<u>Alternative derivation of the *mean free path l:*</u>



- The number of collisions dN per unit length dx is:

$$\frac{dN}{dx} = \sigma\rho \qquad N = \rho V$$

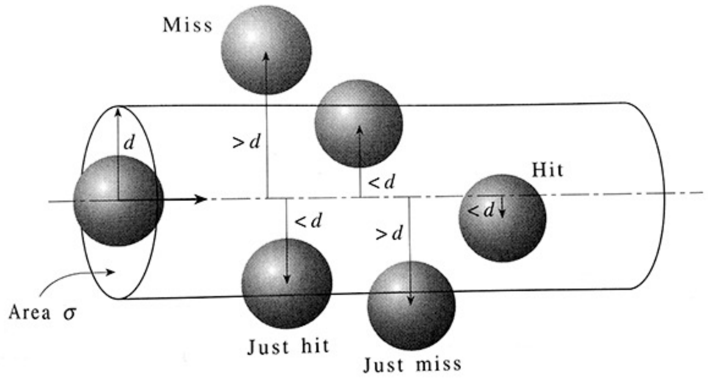
- Consider a beam of n molecules (initially n_0) crossing a volume containing a gas
- The beam gets attenuated because of scattering with that sample

→ the number of unscattered molecules in the beam n *decreases* over distance with rate:

$$\frac{dn}{dx} = -n\frac{dN}{dx} = -n\sigma\rho$$

- Integration yields:

$$n = n_0 e^{-\sigma\rho x}$$



<u>Alternative derivation of the *mean free path l:*</u>

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

- We get an exponential decay with characteristic attenuation length $\frac{1}{e}$ which is the mean free path "l" as $\frac{1}{\sigma\rho}$
- Note: we miss a factor $1/\sqrt{2}$ because again we incorrectly assumed stationary molecules for collision → $l = \frac{1}{\sqrt{2}\sigma\rho}$
- Probability for a molecule to undergo a collision at a distance x is:

$$p(x) = -\frac{\frac{dn}{dx}}{n_0} = \frac{1}{l} e^{-\frac{x}{l}}$$ integration yields

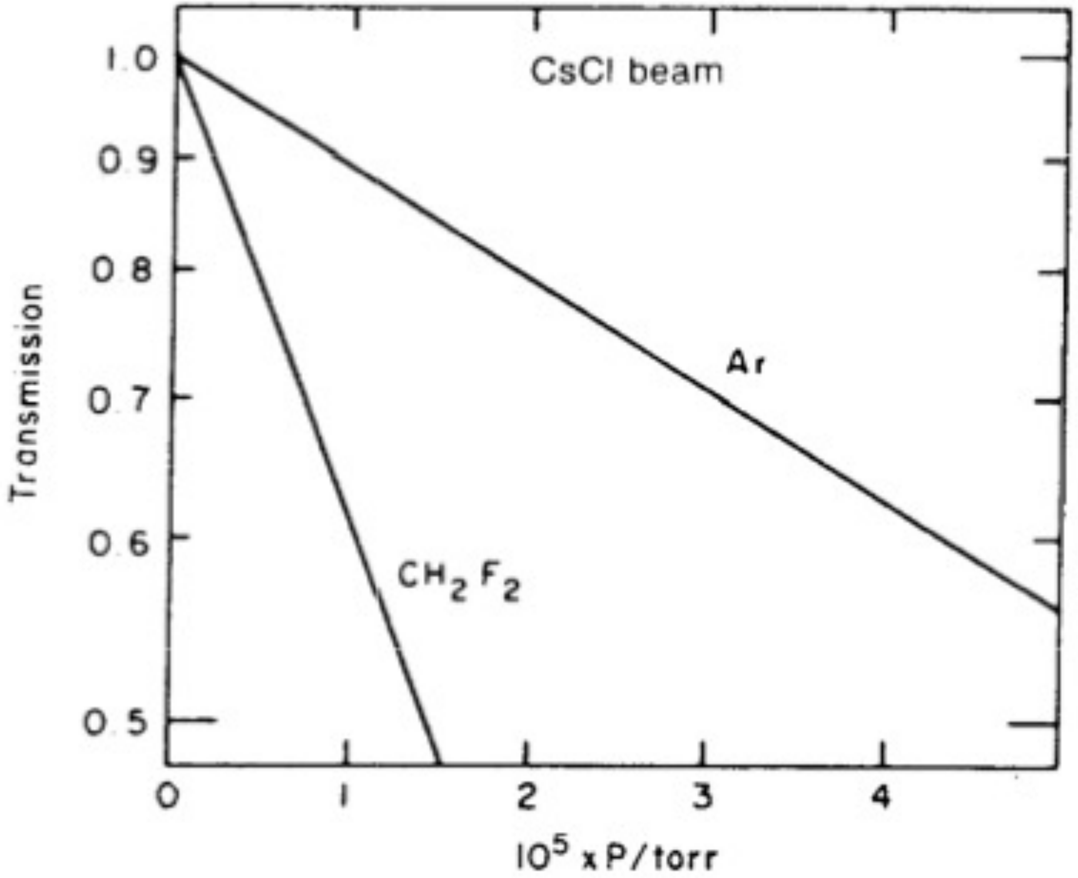
- the expectation value for a scattering event $\langle x \rangle = \int_0^\infty x\, p(x)dx = l$

<u>*Measuring* the collision cross section:</u>

- Measure attenuation of a molecular beam crossing a gas cell as a function of pressure (and composition)

- Transmission drops exponentially, as expected (here plotted as log y)

- From slope can work out mean free path length etc.



Lastly, we define the ***total collision frequency*** $\boldsymbol{z_{AA}}$ or $\boldsymbol{z_{AB}}$:

- In a pure gas, the total frequency of collisions per volume is

$$z_{AA} = \frac{1}{2}\rho z_A = \frac{1}{2}\rho^2 \sigma \sqrt{\frac{8k_BT}{\pi\mu}}$$

- Note: we introduced factor ½ to avoid double-counting collisions

- In a mixture of gases, the collisions between molecules A and B is

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

with $\langle u_{AB}\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$ and $\mu = \frac{m_A m_B}{m_A + m_B}$ and $\sigma_{AB} = \pi\left(\frac{d_A + d_B}{2}\right)^2$