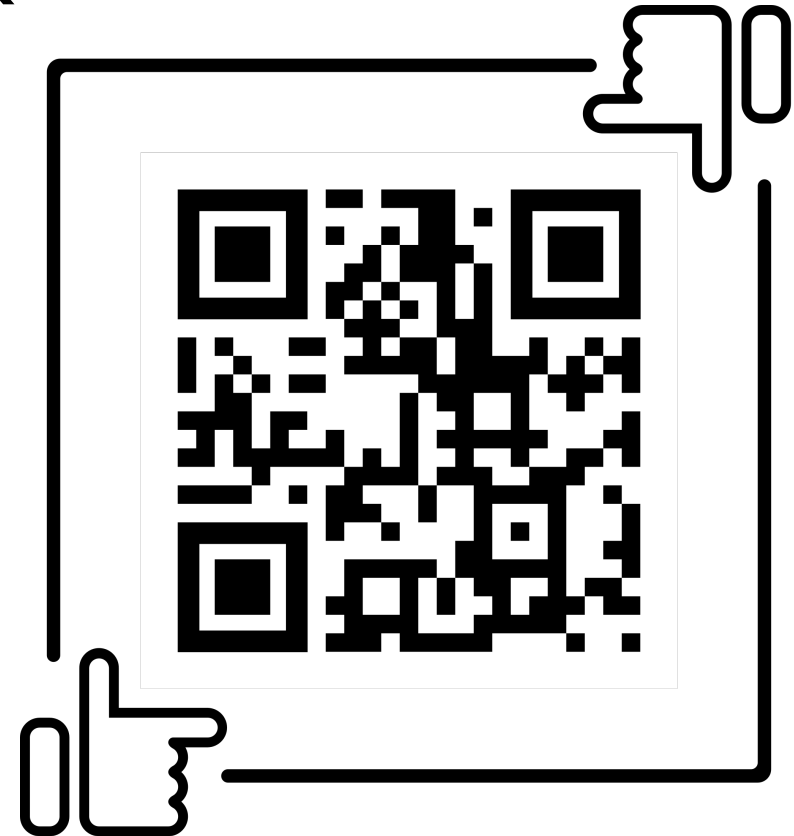


Indicative Student Feedback

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

https://isa.epfl.ch/imoniteur_ISAP/!etuevalreponses.htm



SCAN ME

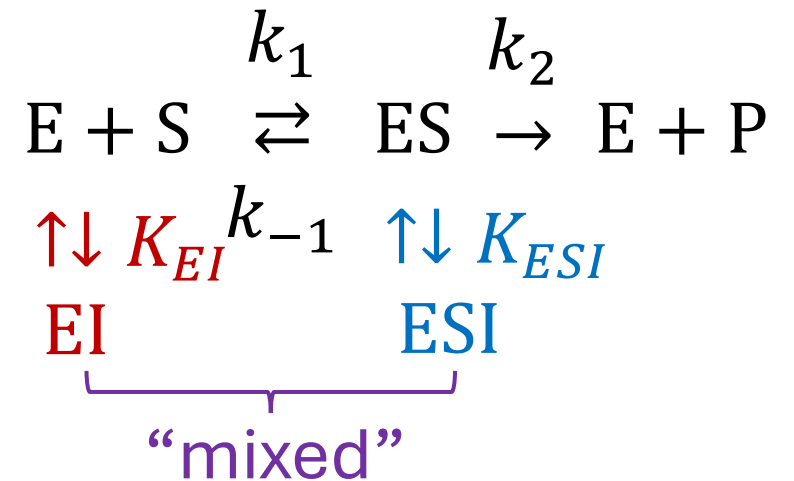
Kinetics & Dynamics of Chemical Reactions

Course CH-310

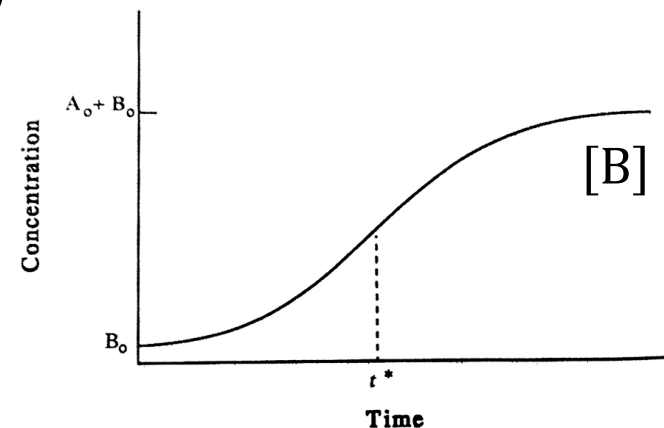
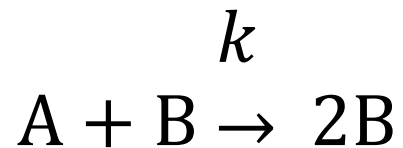
Prof. Sascha Feldmann

Recap from last session

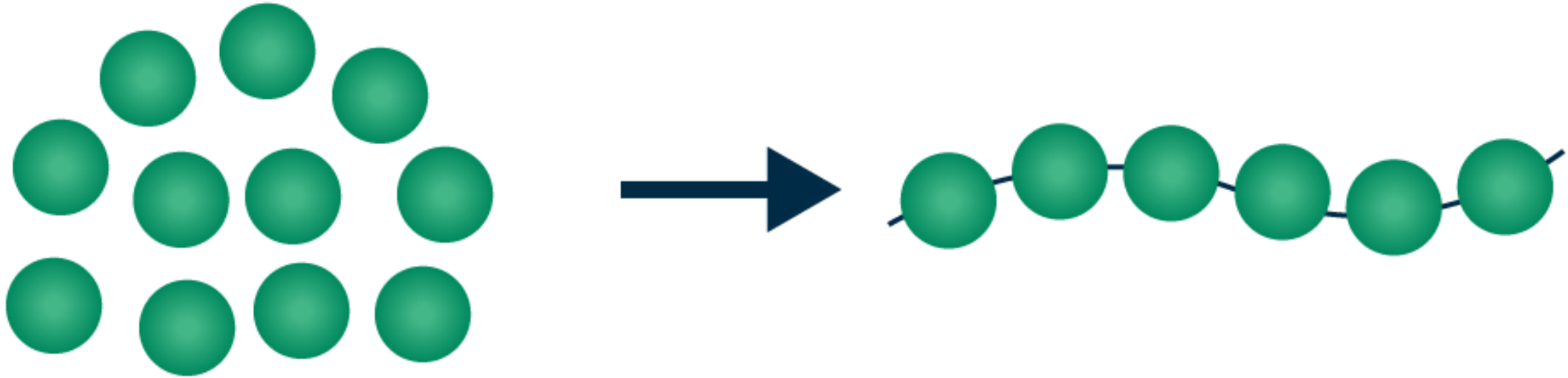
- Michaelis-Menten mechanism for enzyme kinetics
 - various assumptions made
 - different ways of plotting
 - different forms of inhibition



- Autocatalysis (follows an “S curve”)



3.5 Polymerization

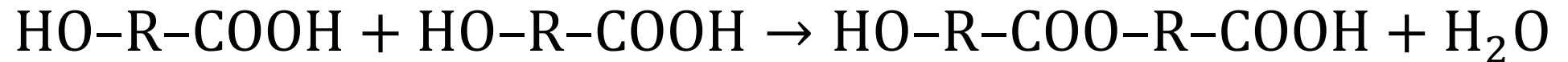


3.5 Polymerization

- 2 cases of polymerization reactions: stepwise & chain type

Stepwise polymerization

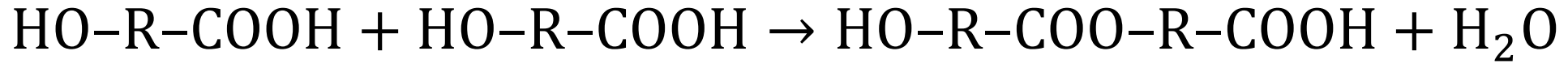
- Any 2 monomers may react at any time or add to chain growth
- E.g. polycondensation of a hydroxy-acid to form a polyester:



- Rate equation for consumption of acid groups:

$$-\frac{d[A]}{dt} = -\frac{d[\text{COOH}]}{dt} = k[\text{COOH}][\text{OH}] = k[A]^2$$

$$\text{using } [\text{COOH}] = [\text{OH}] = [A]$$



$$-\frac{d[A]}{dt} = -\frac{d[\text{COOH}]}{dt} = k[\text{COOH}][\text{OH}] = k[A]^2$$

- Integration yields:

$$[A]_t = \frac{[A]_0}{1+kt[A]_0}$$

- We define the ***fraction p of monomers*** that reacted:

$$p = \frac{[A]_0 - [A]}{[A]_0} = \frac{kt[A]_0}{1+kt[A]_0}$$

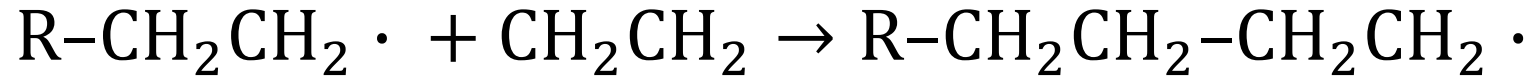
- We define the ***degree of polymerization, i.e. average chain length $\langle N \rangle$*** :

$$\langle N \rangle = \frac{[A]_0}{[A]} = \frac{1}{1-p} = 1 + kt[A]_0$$

- How does the average chain length increase with time? **Linearly!**

Chain polymerization

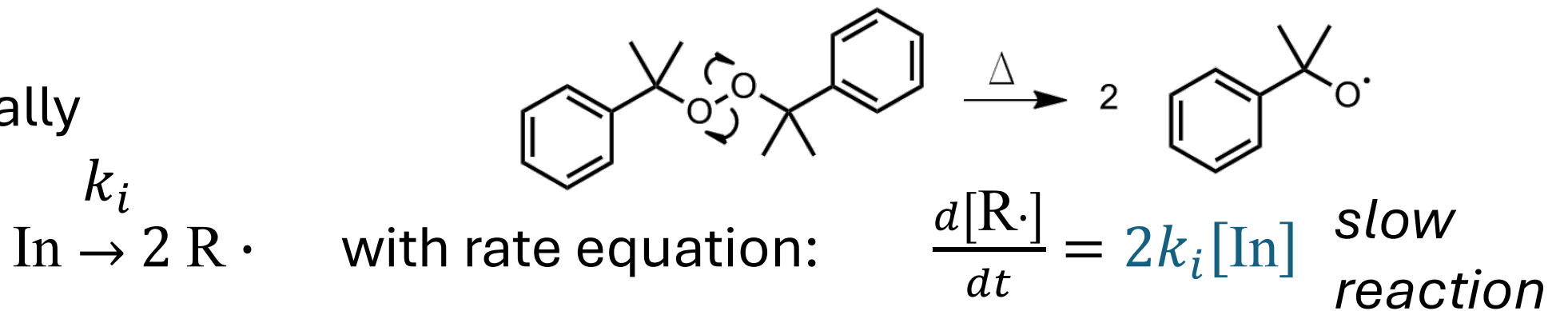
- proceeds by adding monomers to the end of the growing chain
- e.g. radical polymerization of ethylene to polyethylene:



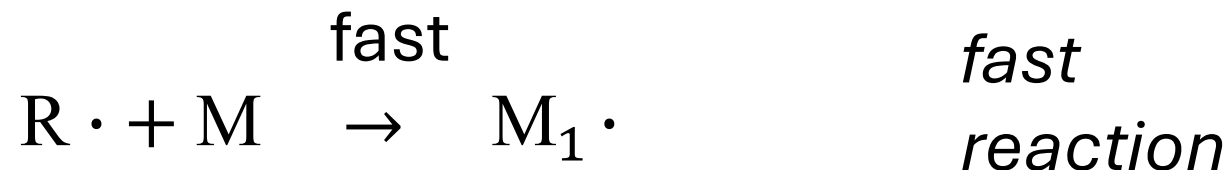
- Proceeds in 3 distinct steps:

A) Initiation

- e.g. thermally



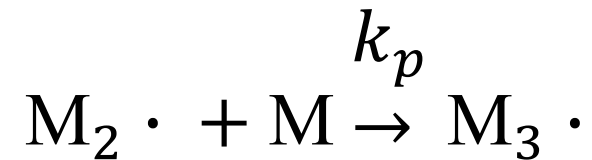
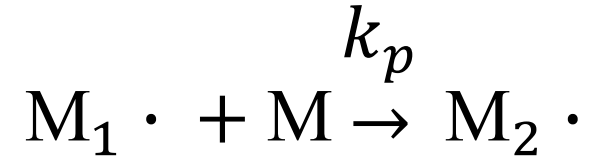
- Radical reacts with monomer M to give radical $\text{M}_1 \cdot$



Chain polymerization

B) Propagation (chain growth)

- Addition of further monomers M leads to chain growth:



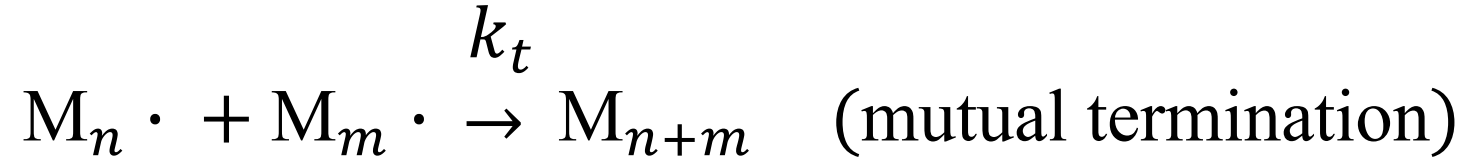
...

- here, we simplified by assuming the same rate constant k_p independent of chain length
- Rate of growth: $v_p = k_p [M_1 \cdot][M]$

Chain polymerization

C) Termination

- when 2 radicals combine:



- We will *not* consider things like



- How to get a solution for the rate of polymer growth v_p ???

$$v_p = k_p [M \cdot] [M]$$

- How to get a solution for the rate of polymer growth v_p ?

$$v_p = -\frac{d[M]}{dt} = k_p [M \cdot] [M]$$

$$\frac{d[M \cdot]}{dt} = \text{production} - \text{depletion}$$

← initiation ← termination

$$= 2fk_i[\text{In}] - \text{depletion}$$

with efficiency of initiation $f = \frac{\text{radical initiating reaction}}{\text{total number of radicals}}$

$$= 2fk_i[\text{In}] - 2k_t[M \cdot]^2$$

- How high is the conc. of $M \cdot$ typically compared to rest?

What trick does this allow us to apply?

- We can apply the steady-state approximation to the radical chains:

$$\frac{d[\text{M}\cdot]}{dt} = 0 = 2fk_i[\text{In}] - 2k_t[\text{M}\cdot]^2$$

- we assumed initiator radicals react instantaneously to form radical chains with efficiency f
 - and took the second term from mutual termination
- Separation of variables and integration yields:

$$[\text{M}\cdot] = \left(\frac{fk_i}{k_t}\right)^{\frac{1}{2}} [\text{In}]^{\frac{1}{2}}$$

- Back to our question: How to get a solution for the rate of polymer growth v_p ?

$$v_p = -\frac{d[M]}{dt} = k_p [M \cdot] [M]$$

- We insert $[M \cdot] = \left(\frac{fk_i}{k_t}\right)^{\frac{1}{2}} [In]^{\frac{1}{2}}$

- and find: $v_p = -\frac{d[M]}{dt} = k_p \left(\frac{fk_i}{k_t}\right)^{\frac{1}{2}} [In]^{\frac{1}{2}} [M]$

- We define the ***kinetic chain length*** λ :

$$\lambda = \frac{\text{monomer units consumed}}{\text{activated centers produced}}$$

- We estimate λ through the ratio of the corresponding *rates*
- ...and by assuming steady-state conditions, so

rate of activated center production = rate of termination

$$\begin{aligned} \lambda &\approx \frac{\text{rate of monomer consumption}}{\text{rate of activated center production}} = \frac{v_p}{v_i} = \frac{k_p[\text{M}\cdot][\text{M}]}{2fk_i[\text{In}]} \approx \frac{k_p[\text{M}\cdot][\text{M}]}{2k_t[\text{M}\cdot]^2} \\ &= \frac{k_p[\text{M}]}{2k_t[\text{M}\cdot]} = \frac{k_p}{2(fk_ik_t)^{\frac{1}{2}}} [\text{In}]^{-\frac{1}{2}}[\text{M}] \end{aligned}$$

- We obtain the **degree of polymerization** $\langle N \rangle$ by assuming all chains are terminated eventually through mutual termination, yielding the “real” chain length:

$$\begin{aligned}\langle N \rangle &= 2\lambda \\ &= \frac{k_p}{(fk_i k_t)^{\frac{1}{2}}} [\text{In}]^{-\frac{1}{2}} [\text{M}]\end{aligned}$$

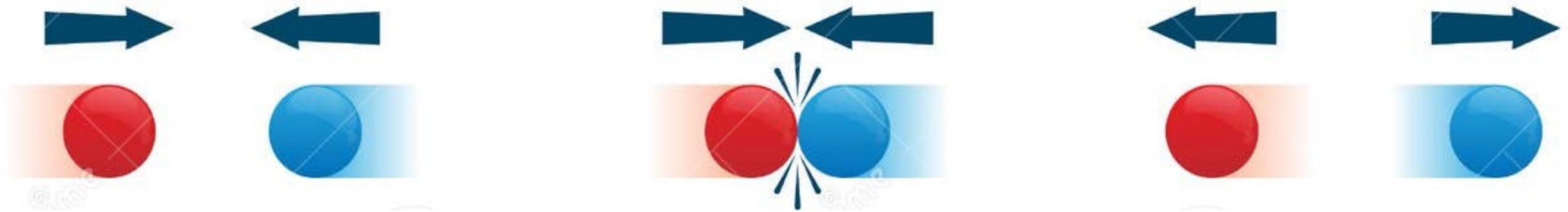
- What happens when using a smaller initiator concentration?
→ Polymers with higher molecular weight are obtained

Chapter 4

Kinetic Theory of Gases

4.1 Average Translational Kinetic Energy

assume elastic collisions between hard spheres



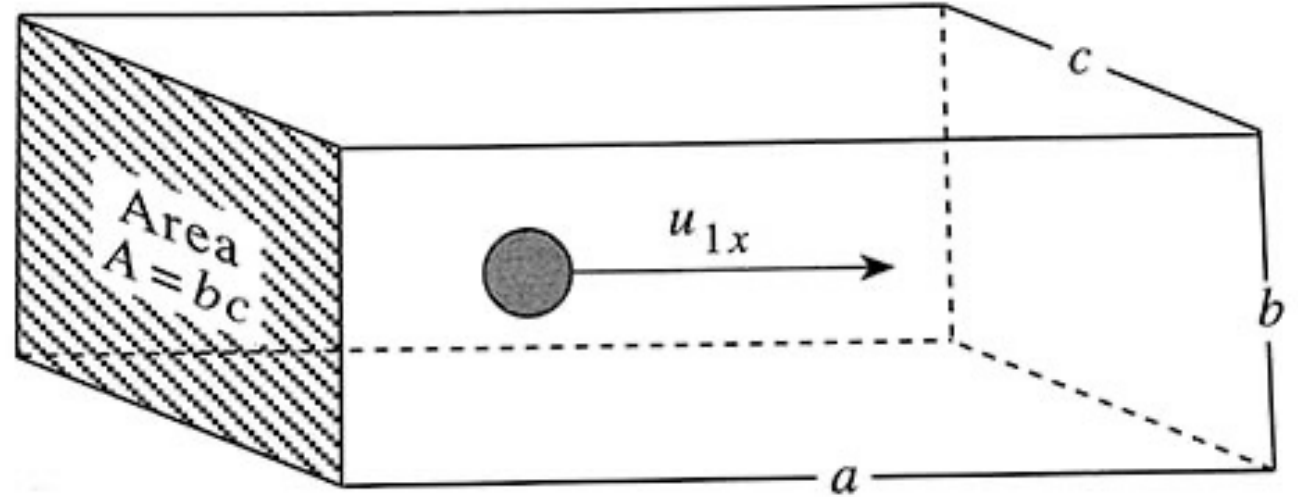
4.1 Average Translational Kinetic Energy

Deriving the Ideal Gas Law

Assumptions:

- Ideal gas behavior independent of composition at sufficiently low pressure, so no interactions (average distance \gg diameter of gas particle)
- Thus, no potential energy, only kinetic energy
- Collisions (for now) are fully elastic between hard spheres
- No change to total translational energy upon collision, *i.e.*, no internal degrees of freedom (vibrations & rotations) excited during collision

- Goal: Determine the pressure of an ideal gas with mass m and with velocity u_1 and its components u_{1x}, u_{1y}, u_{1z} in this rectangular box



- Momentum $p = m u_{1x}$
- After elastic collision becomes $\rightarrow -m u_{1x}$
- Force exerted on the right wall is change of momentum over time:

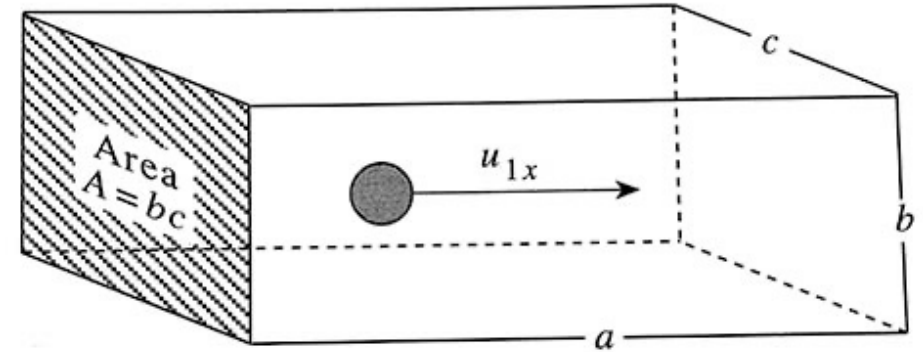
$$F = \frac{\Delta p}{\Delta t} = \frac{m \Delta u_{1x}}{\Delta t}$$

- Absolute change in momentum upon collision:

$$\Delta(m u_{1x}) = |-m u_{1x} - m u_{1x}| = 2m u_{1x}$$

- Absolute change in momentum upon collision:

$$\Delta(mu_{1x}) = |-mu_{1x} - mu_{1x}| = 2mu_{1x}$$



- Time period it takes for a round trip ($2a$):

$$\Delta t = 2 \frac{a}{u_{1x}}$$

- Momentum per unit time (force) imparted on right wall is therefore:

$$\frac{\Delta(m u_{1x})}{\Delta t} = \frac{m u_{1x}^2}{a} = F_1$$

- Newton's 2nd law: force on molecule = force on wall

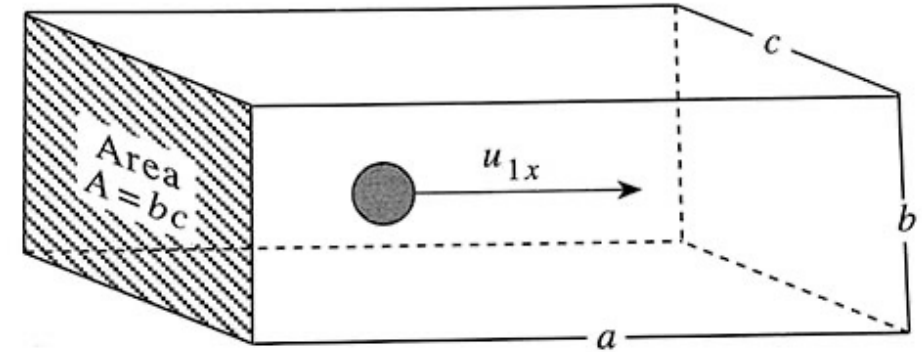
- Associated pressure P_1 by dividing by surface area of right wall bc :

$$P_1 = \frac{F_1}{bc} = \frac{m u_{1x}^2}{abc} = \frac{m u_{1x}^2}{V}$$

with volume $V = abc$

- We sum over all molecules for the total pressure P :

$$P = \sum_{j=1}^N P_j = \sum_{j=1}^N \frac{m u_{jx}^2}{V} = \frac{m}{V} \sum_{j=1}^N u_{jx}^2$$



- With $\sum_{j=1}^N u_{jx}^2 = N \langle u_x^2 \rangle$ we obtain:

$$PV = m N \langle u_x^2 \rangle$$

- Gas is isotropic, so

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$$

- Since $u^2 = u_x^2 + u_y^2 + u_z^2$, it follows that

$$\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle$$

$$\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle$$

- Hence $\langle u_x^2 \rangle = \frac{1}{3} \langle u^2 \rangle$

- and $PV = \frac{1}{3} Nm \langle u^2 \rangle$

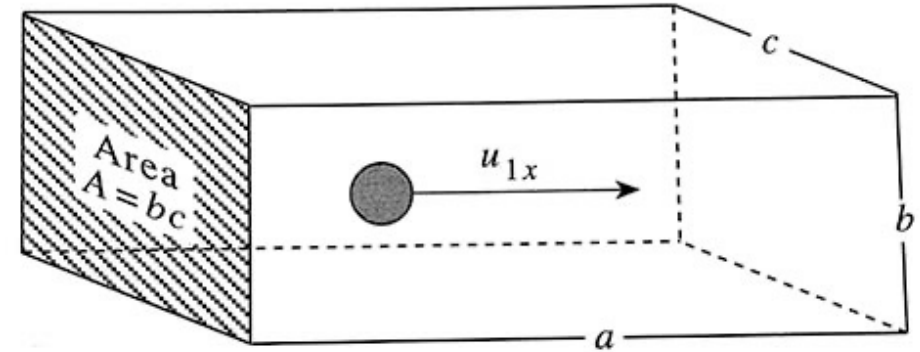
- From statistical thermodynamics we know that the average translational energy per molecule of an ideal gas is

$$\left\langle \frac{1}{2} m u^2 \right\rangle = \frac{1}{2} m \langle u^2 \rangle = \frac{3}{2} k_B T \quad \left(\frac{1}{2} k_B T \text{ per direction} \right)$$

- Substitution into the above equation yields:

$$PV = Nk_B T = nRT$$

The Ideal Gas Law



$$PV = Nk_B T = nRT$$

- For the **root-mean-square velocity** of a gas molecule we find:

$$u_{rms} = \sqrt{\langle u^2 \rangle} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}}$$

- Note, in general $\langle u^2 \rangle \neq \langle u \rangle^2$, so $u_{rms} \neq \langle u \rangle$ $\langle u \rangle$: average speed
- How does u_{rms} look plotted against temperature?
- What happens, if we go to a lighter gas molecule/element?

4.2 The Maxwell-Boltzmann Distribution

Goal: to find an expression for the **speed distribution of a gas**

- Historically earlier: somewhat heuristic treatment by **Maxwell**
→ no need to learn the derivation by heart, but please take a look at the lecture notes for the derivation, if you are interested :)
- We will here derive **Boltzmann's** general **approach**

- we use the **Boltzmann distribution** from statistical thermodynamics:
- In thermal equilibrium, the probability P_i of finding the system in a state of a certain energy E_i is:

$$P_i = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_j e^{-\frac{E_j}{k_B T}}} = \frac{e^{-\frac{E_i}{k_B T}}}{Q}$$

with $Q = \sum_j e^{-\frac{E_j}{k_B T}}$: the partition function, summed over all energy levels

$$\text{and } \int_{-\infty}^{\infty} e^{-\frac{E_j}{k_B T}} dE = 1$$

- Using that the translational energy for one velocity component (e.g. x) of a gas molecule is $\frac{1}{2} m u_x^2$, we substitute to get:

$$P(u_{x,i}) = \frac{e^{-\frac{m u_{x,i}^2}{2 k_B T}}}{Q}$$

$$\text{with } Q = \int_{-\infty}^{\infty} e^{-\frac{m u_{x,j}^2}{2 k_B T}} du_x$$

- Use that $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$

to find for the partition function: $Q = \sqrt{\frac{2\pi k_B T}{m}}$

- And overall $f(u_j) = \sqrt{\frac{M}{2\pi RT}} e^{-\frac{M u_j^2}{2RT}} = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m u_j^2}{2k_B T}}$

M.B.-probability distribution for a single velocity component (1D)

- To derive the *speed distribution* of an ideal gas (i.e., distribution of the *magnitude* of velocity), we next write down the *3-dimensional* velocity distribution function $P(u_x, u_y, u_z)$:

$$P(u_x, u_y, u_z) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{m(u_x^2 + u_y^2 + u_z^2)}{2k_B T}}$$

- But we want to find the actual probability for any given, very small interval (meaning it is approximated to be constant):

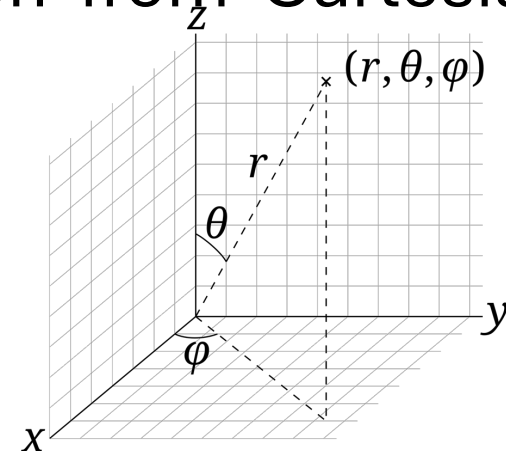
$$\tilde{P} = P(u_x, u_y, u_z) du_x, du_y, du_z$$

- We next perform a coordinate transformation from Cartesian to spherical coordinates:

$$x = r \sin\theta \cos\varphi$$

$$y = r \sin\theta \sin\varphi$$

$$z = r \cos\theta$$



$$P(u_x, u_y, u_z) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{m(u_x^2 + u_y^2 + u_z^2)}{2k_B T}}$$

$$\tilde{P} = P(u_x, u_y, u_z) du_x, du_y, du_z$$

- We perform a coordinate transformation from Cartesian to spherical coordinates using:

- $u_x^2 + u_y^2 + u_z^2 = u^2$

- and $du_x du_y du_z = \left| \frac{\partial(u_x, u_y, u_z)}{\partial(u, \varphi, \theta)} \right| du d\varphi d\theta = u^2 \sin \theta du d\varphi d\theta$

- Then, we eliminate the angular parts by integrating over all directions the molecule can travel:

- $\tilde{P}(u) du = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_B T}} du \int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta$

$$\tilde{P}(u)du = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_B T}} du \underbrace{\int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta}_{= 4\pi}$$

- We thus obtain the

Maxwell-Boltzmann distribution:

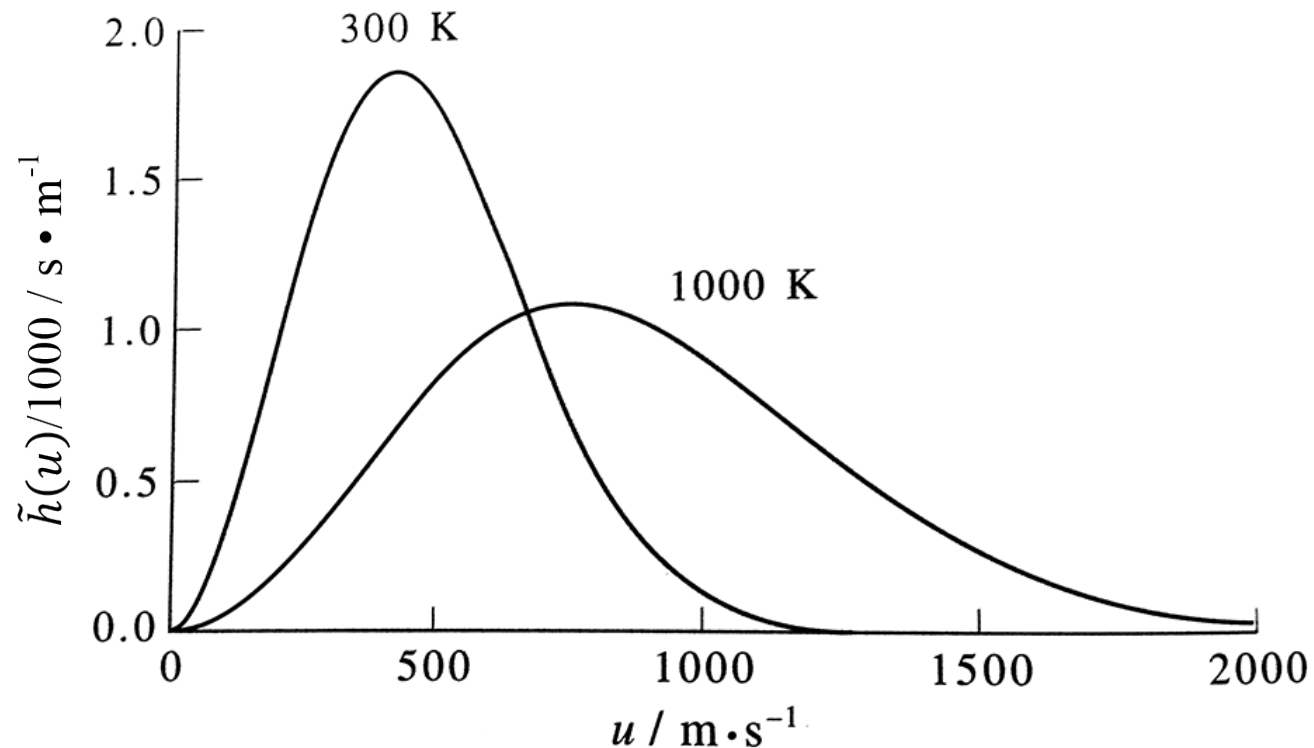
$$\tilde{P}(u)du = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_B T}} du$$

Maxwell-Boltzmann distribution:

$$\tilde{P}(u)du = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_B T}} du$$

also called $F(u)du$

Example: Speed distribution of nitrogen at 300 K and 1000 K:



4.3 Measurements of the Velocity Distribution

- We remember from before that for ideal gases $PV = \frac{1}{3}Nm\langle u^2 \rangle$
- and that the rms-velocity is $u_{rms} = \sqrt{\langle u^2 \rangle} = \sqrt{\frac{PV}{Nm}}$
- We want to verify that generally across all values this holds true:

$$P(u_x) = \frac{e^{-\frac{mu_x^2}{2k_B T}}}{Q} \quad \text{But how?}$$

- Idea:

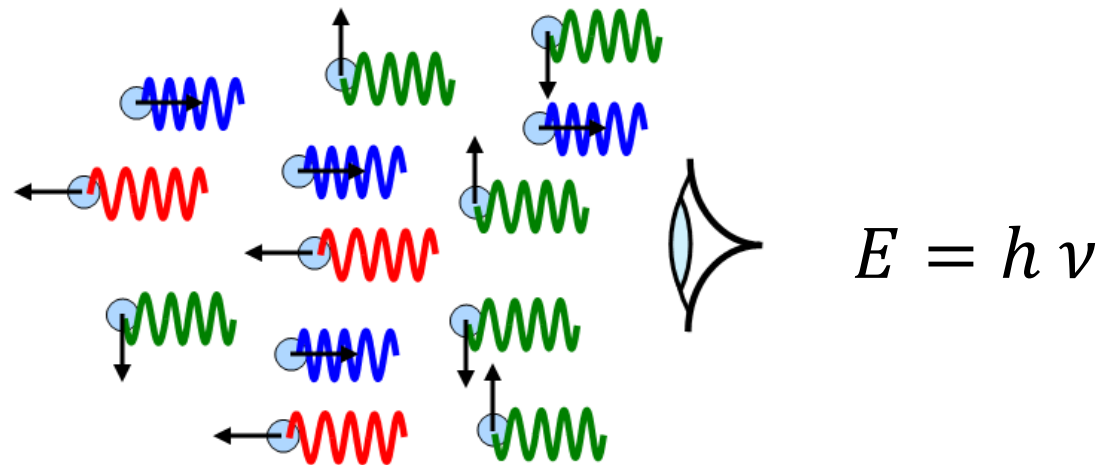
Measure something easily observable, that is *influenced* by u_x

→ E.g.: Measure absorption or emission of light (spectroscopy)

A) Measure the Doppler broadening of the absorption or emission spectrum of molecules in gas phase

- if molecule moves towards us: blue-shift/frequency increase of light
- if molecule moves away from us: red-shift/frequency decrease of light

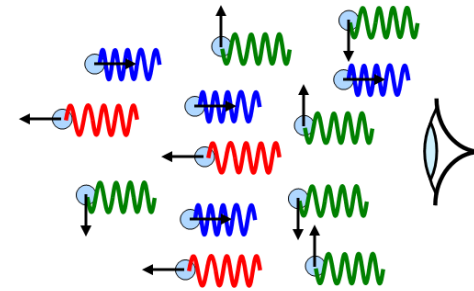
→ Use this to infer speed distribution of molecules, or temperature of the gas :)



- Frequency of light emitted or absorbed:

$$\nu = \nu_0 \left(1 + \frac{u_x}{c} \right)$$

ν_0 : transition frequency of static molecule

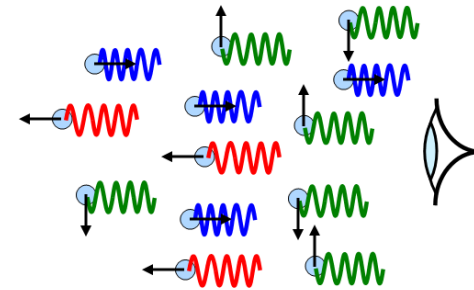


$$\rightarrow u_x = \left(\frac{\nu}{\nu_0} - 1 \right) c$$

- How does intensity distribution of light frequencies $I(\nu)$ look if u_x follows Boltzmann distribution?
- Substitute into the 1D velocity distribution (along observer direction only!) to find:

$$I(\nu) \propto e^{-\frac{m u_x^2}{2k_B T}} \propto e^{-\frac{m c^2 (\nu - \nu_0)^2}{2 \nu_0^2 k_B T}}$$

$$I(\nu) \propto e^{-\frac{mc^2(\nu-\nu_0)^2}{2\nu_0^2k_B T}}$$

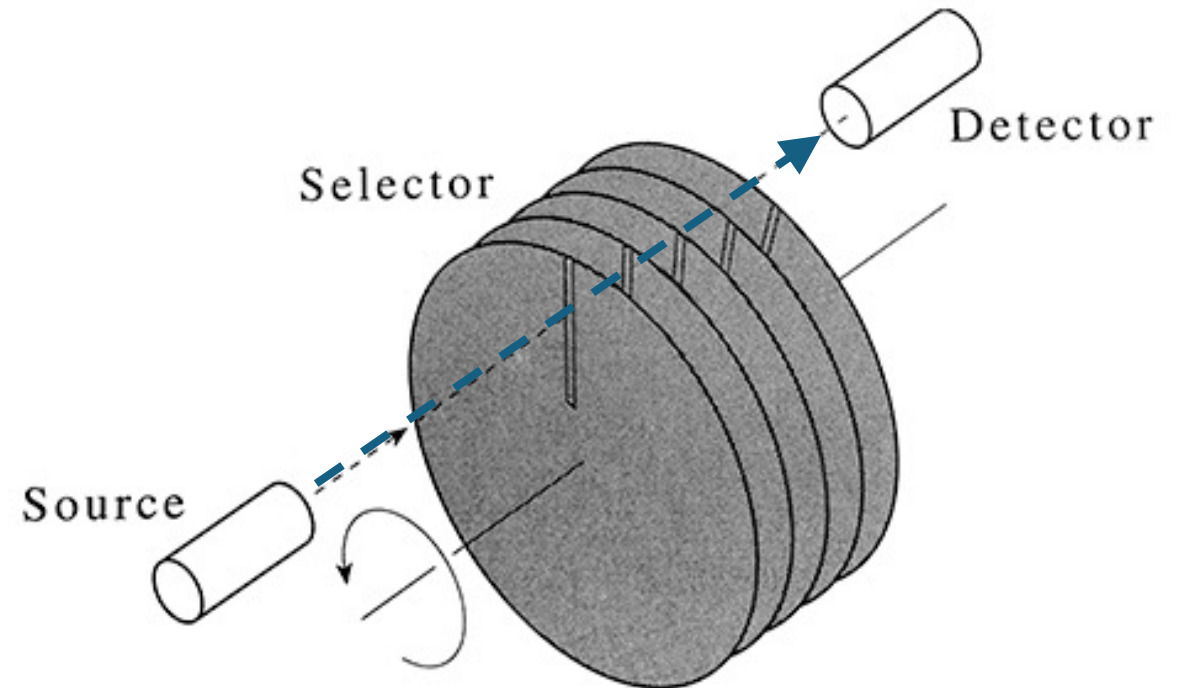
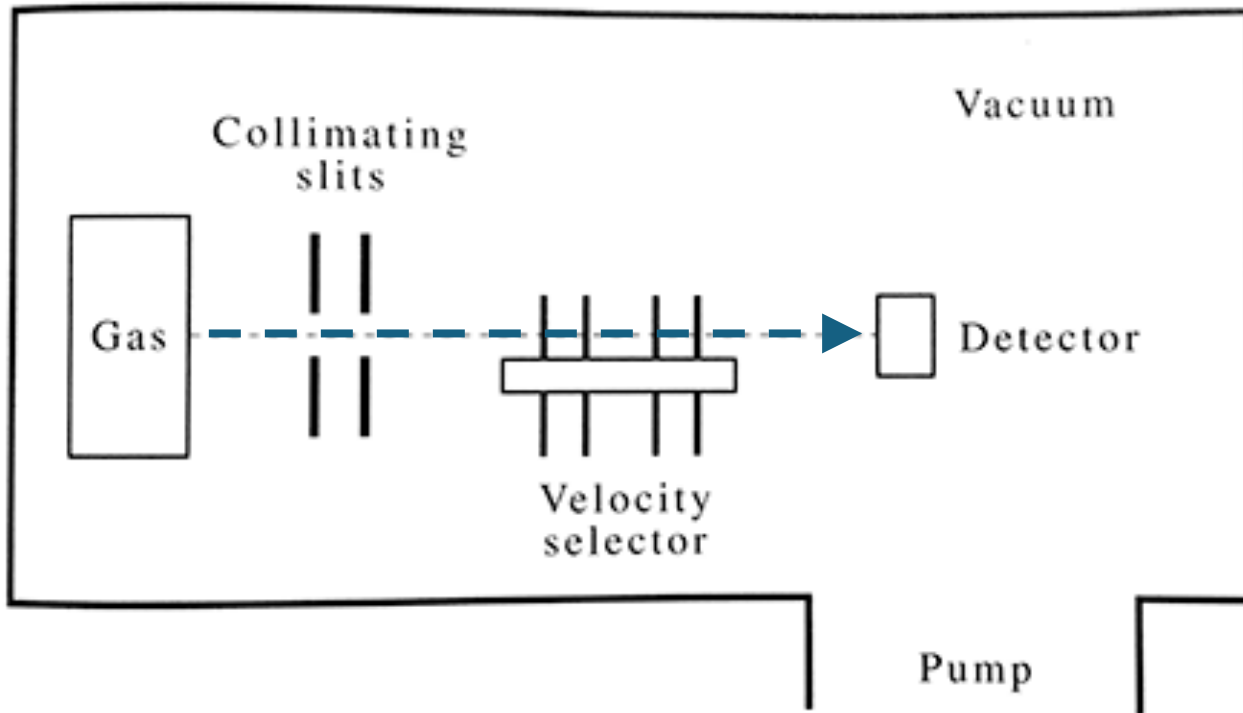


- We see a broadening of the line shape following a gaussian

with variance $\sigma^2 = \frac{\nu_0^2 k_B T}{mc^2}$

- the width of the spectrum increases with ν_0 and is proportional to the temperature

B) Measure gas particles arriving at a detector



- slits cut into series of spinning discs
- a given rotation speed will only allow molecules of one specific velocity to pass
- measurement of the gas flux exiting the discs as a function of the rotation frequency yields the velocity distribution