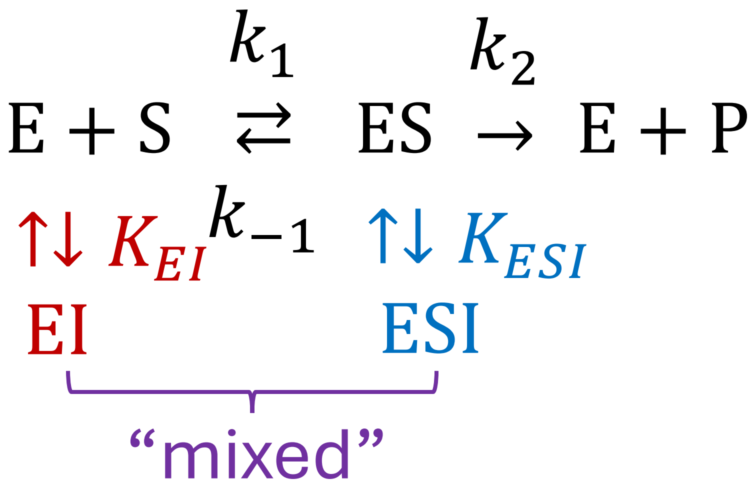
# Kinetics & Dynamics of Chemical Reactions

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

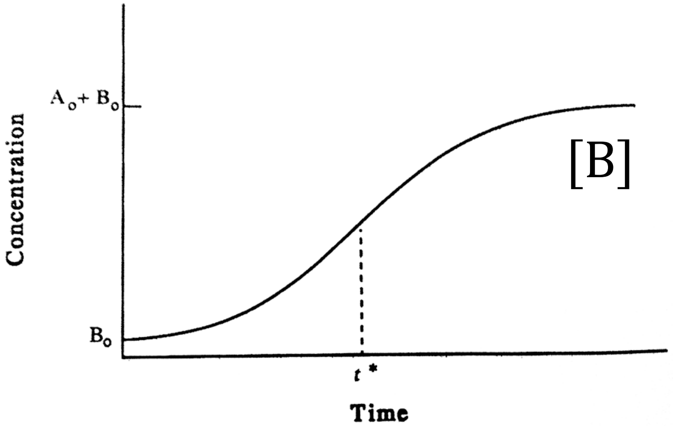


$$\begin{tikzcd} E + S \arrow[r, shift left, "k_1"] \arrow[d, shift left] & ES \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] \arrow[d, shift left] & E + P \\ EI \arrow[u, shift left, "K_{EI}"'] & ESI \arrow[u, shift left, "K_{ESI}"'] \end{tikzcd}$$

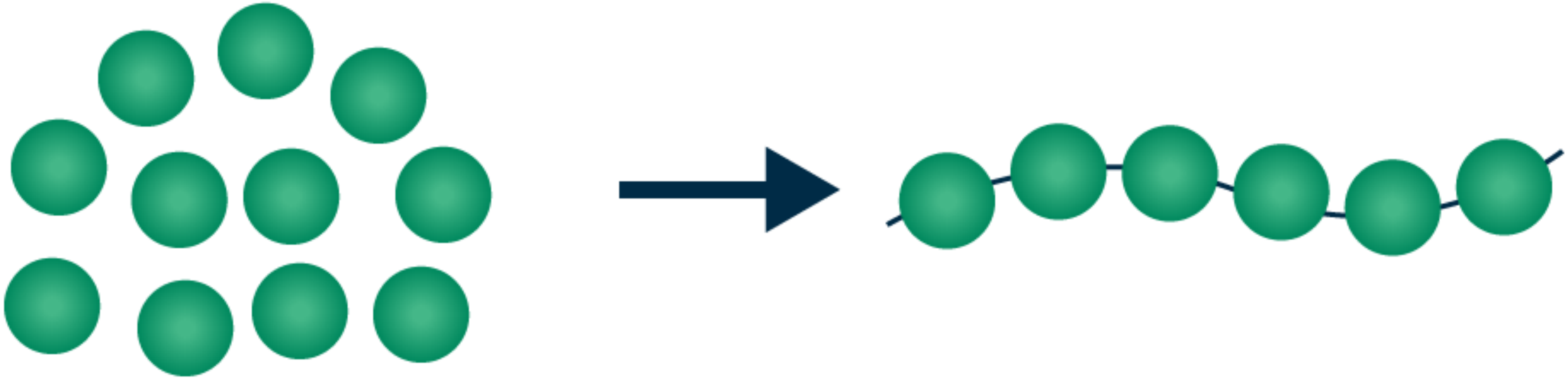
$\underbrace{\text{EI} \qquad\qquad \text{ESI}}_{\text{“mixed”}}$

- Autocatalysis (follows an “S curve”)

$$A + B \xrightarrow{k} 2B$$



# 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 hydroxyacid to from a polyester:

$$\mathrm{HO{-}R{-}COOH} + \mathrm{HO{-}R{-}COOH} \rightarrow \mathrm{HO{-}R{-}COO{-}R{-}COOH} + \mathrm{H_2O}$$

- Rate equation for consumption of acid groups:

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

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

$$\mathrm{HO{-}R{-}COOH + HO{-}R{-}COOH \rightarrow HO{-}R{-}COO{-}R{-}COOH + H_2O}$$

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

- Integration yields:

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

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

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

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

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

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

# Chain polymerization

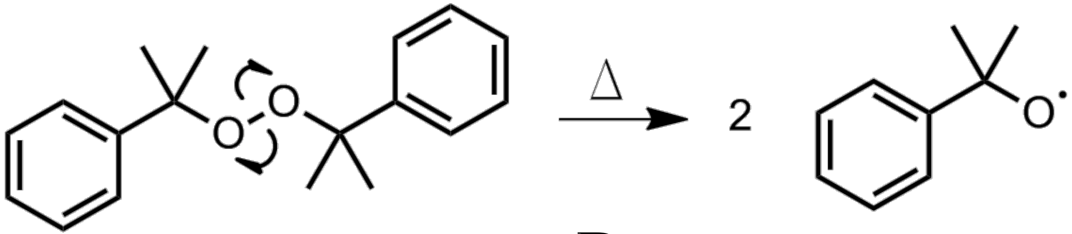
- proceeds by adding monomers to end of growing chain
- e.g. radical polymerization of ethylene to polyethylene:

$$\mathrm{R{-}CH_2CH_2\cdot\ + CH_2CH_2 \rightarrow R{-}CH_2CH_2{-}CH_2CH_2\cdot}$$

- Proceeds in <u>3 distinct steps</u>:

<u>A) Initiation</u>

- e.g. thermally



$$\mathrm{In} \xrightarrow{k_i} 2\,\mathrm{R}\cdot \qquad \text{with rate equation:} \qquad \frac{d[\mathrm{R}\cdot]}{dt} = 2k_i[\mathrm{In}]$$

*slow reaction*

- Radical reacts with monomer M to give radical $\mathrm{M_1}\cdot$

$$\mathrm{R\cdot + M} \xrightarrow{\text{fast}} \mathrm{M_1}\cdot$$

*fast reaction*

# Chain polymerization

B) Propagation (chain growth)

- Addition of further monomers M for chain growth

$$\mathrm{M}_1\cdot\ +\mathrm{M}\overset{k_p}{\rightarrow}\ \mathrm{M}_2\cdot$$

$$\mathrm{M}_2\cdot\ +\mathrm{M}\overset{k_p}{\rightarrow}\ \mathrm{M}_3\cdot$$

$$\dots$$

- We simplify by assuming same rate const. $k_p$ independent of chain length
- Rate of growth: $v_p = k_p[\mathrm{M}_1\ \cdot][\mathrm{M}]$

## Chain polymerization

C) Termination

- when 2 radicals combine

$$\mathrm{M}_n \cdot + \mathrm{M}_m \cdot \xrightarrow{k_t} \mathrm{M}_{n+m} \quad \text{(mutual termination)}$$

- We will not consider things like

$$\mathrm{M}_n \cdot + \mathrm{M}_m \cdot \rightarrow \mathrm{M}_n + \mathrm{M}_m \quad \text{(disproportionation)}$$

$$\mathrm{M}_n \cdot + \mathrm{M} \rightarrow \mathrm{M}_n + \mathrm{M} \cdot \quad \text{(chain transfer)}$$

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

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

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

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

initiation termination

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

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

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

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

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

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

  - where we assume initiator radicals react instantaneously to form radical chains with efficiency $f$
  - and took the second term from mutual termination

- Separate variables and integrate to yield

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

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

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

inserting $$[\mathrm{M}\cdot] = \left(\frac{f k_i}{k_t}\right)^{\frac{1}{2}}[\mathrm{In}]^{\frac{1}{2}}$$

- yields

$$v_p = -\frac{d[\mathrm{M}]}{dt} = k_p\left(\frac{f k_i}{k_t}\right)^{\frac{1}{2}}[\mathrm{In}]^{\frac{1}{2}}[\mathrm{M}]$$

- We define the *kinetic chain length* $\lambda$:

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

- We estimate $\lambda$ by taking the ratio of the corresponding *rates*
- …and by assuming steady-state conditions, so

$$\text{rate of activated center production} = \text{rate of termination}$$

- $\lambda \approx \dfrac{\text{rate of monomer consumption}}{\text{rate of activated center production}} = \dfrac{v_p}{v_i} = \dfrac{k_p[\mathrm{M}\cdot][\mathrm{M}]}{2fk_i[\mathrm{In}]} \approx \dfrac{k_p[\mathrm{M}\cdot][\mathrm{M}]}{2k_t[\mathrm{M}\cdot]^2}$

$$= \frac{k_p[\mathrm{M}]}{2k_t[\mathrm{M}\cdot]} = \frac{k_p}{2(fk_ik_t)^{\frac{1}{2}}}[\mathrm{In}]^{-\frac{1}{2}}[\mathrm{M}]$$

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

$$\langle N \rangle = 2\lambda$$

$$= \frac{k_p}{(f k_i k_t)^{\frac{1}{2}}} [\mathrm{In}]^{-\frac{1}{2}} [\mathrm{M}]$$

- What happens when using smaller initiator concentrations?

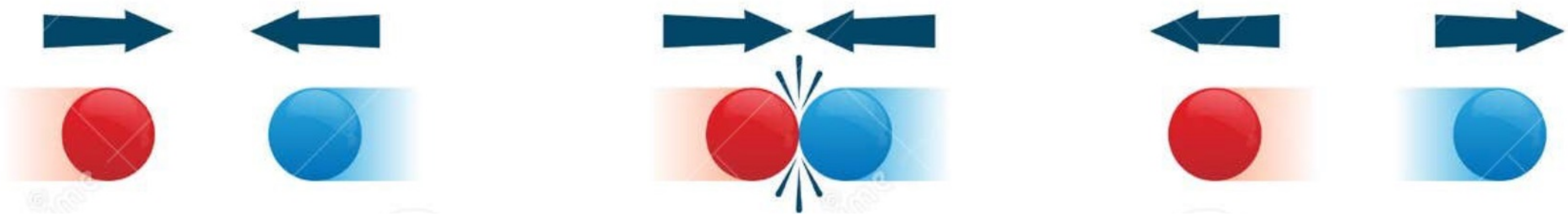
→ Polymers with higher molecular weight are obtained

# Chapter 4

## Kinetic Theory of Gases

# 4.1 Average Translational Kinetic Energy

assume elastic collisions between hard spheres



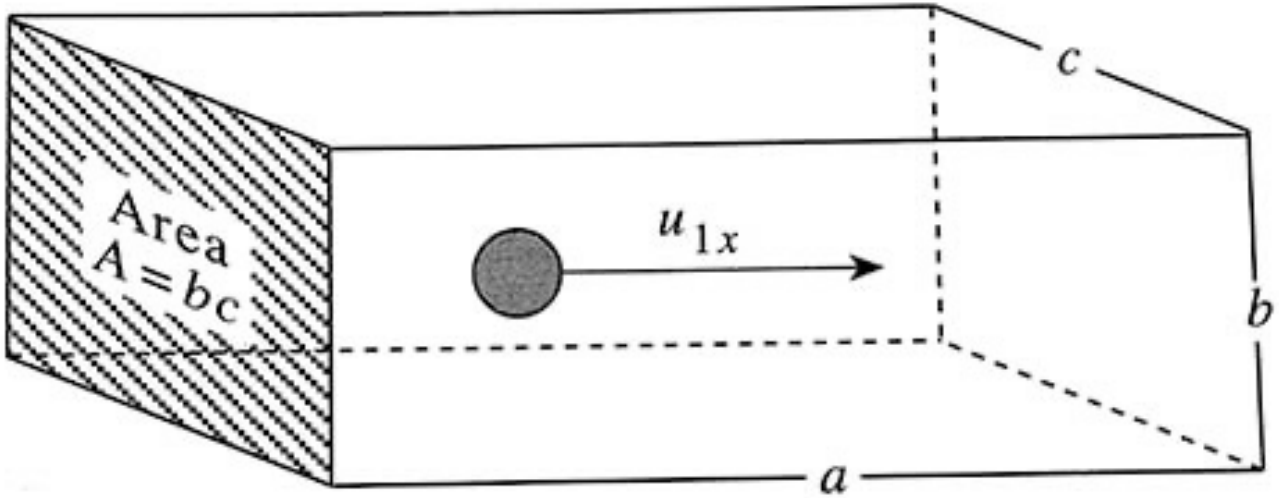
# 4.1 Average Translational Kinetic Energy

## Deriving the Ideal Gas Law

Assumptions:

- Ideal gas behavior independent of composition at sufficiently low pressure, so no interactions (average distance >> 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

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



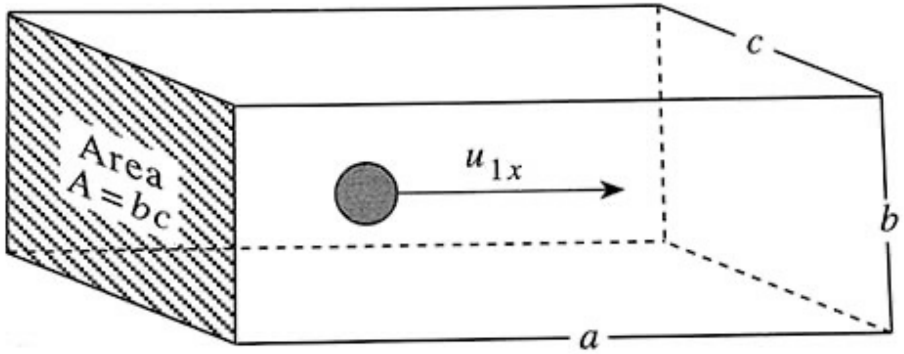
- Momentum $\mathrm{p} = m\, u_{1x}$
- After elastic collision → $-mu_{1x}$
- Force exerted on wall is

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

- Absolute change in momentum upon collision:

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

- Absolute change in momentum upon collision:



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

- Time period it takes for a round trip:

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

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

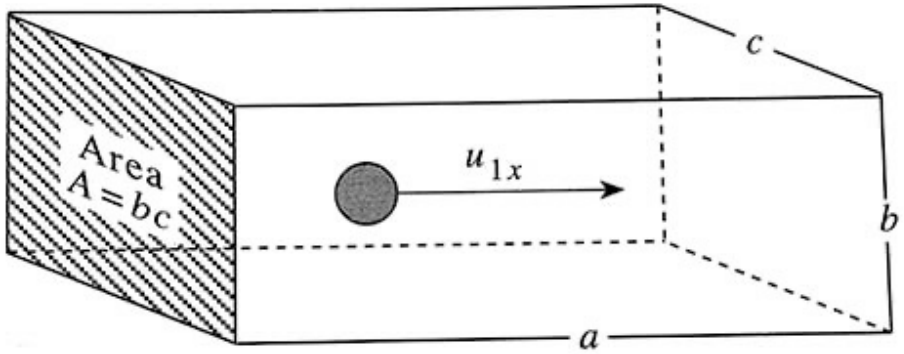
$$\frac{\Delta(m\,u_{1x})}{\Delta t} = \frac{m\,u_{1x}^2}{a} = F_1$$

- Newton's 2nd law: force on molecule = force on wall
- Associated pressure $P_1$ by dividing by surface area of right wall $bc$:

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

with volume $V = abc$

- Summing over all molecules for total pressure



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

- 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

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

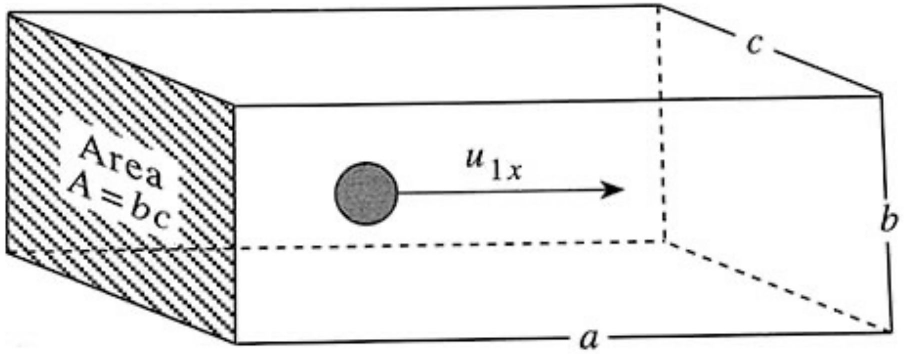
- Since $u^2 = u_x^2 + u_y^2 + u_z^2$, it follows that

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

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

- 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

$$\langle \frac{1}{2}mu^2 \rangle = \frac{1}{2}m\langle u^2 \rangle = \frac{3}{2}k_BT \qquad (\frac{1}{2}k_BT \text{ per direction})$$

- Substitute into above eq. yields

$$\boxed{PV = Nk_BT = nRT}$$

**Ideal Gas Law**

$$PV = Nk_BT = nRT$$

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

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

- 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 I go to a lighter gas molecule/element?*

# 4.2 The Maxwell-Boltzmann Distribution

## Goal: to find speed distribution of a gas

- Historically earlier: somewhat heuristic treatment by **Maxwell**

→No need to learn, but take a look at the lecture notes for the derivation, if you are interested :)

- We will here derive **Boltzmann's** general approach

- Use ***Boltzmann distribution*** from statistical thermodynamics:
- In thermal equilibrium, the probability $P_i$ of finding the system in 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, sum over all energy levels

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 $\frac{1}{2}mu_x^2$ we substitute to get:

$$P_{(u_{x,i})} = \frac{e^{-\frac{mu_{x,i}^2}{2\,k_BT}}}{Q}$$

$$\text{with Q} = \int_{-\infty}^{\infty} e^{-\frac{mu_{x,j}^2}{2\,k_BT}}\,du_x$$

- Use that $\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$
- to find for the partition function $\text{Q} = \sqrt{\frac{2\pi k_BT}{m}}$
- And overall $\boxed{f(u_j) = \sqrt{\frac{M}{2\pi RT}}\,e^{-\frac{Mu_j^2}{2RT}} = \sqrt{\frac{m}{2\pi k_BT}}\;e^{-\frac{mu_j^2}{2k_BT}}}$

**probability distribution for a single velocity component**

- To derive the *speed* distribution of an ideal gas (i.e. distribution of the *magnitude* of velocity), we now write down the 3-dimensional velocity distribution function $\mathrm{P}\left(u_x, u_y, u_z\right)$:

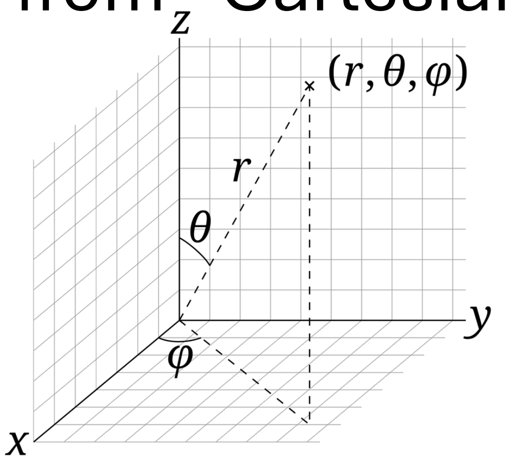
$$\mathrm{P}\left(u_x, u_y, u_z\right) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{m(u_x^2+u_y^2+u_z^2)}{2k_B T}}$$

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

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

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

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



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

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

- We perform a coordinate transformation from Cartesian to spherical coordinates:
  - using $u_x^2 + u_y^2 + u_z^2 = u^2$
  - and $du_x du_y du_z = \left|\frac{\partial(u_x, u_y, u_z)}{\partial(u, \varphi, \theta)}\right| du\, d\varphi\, d\theta = u^2 \sin\theta\, du\, d\varphi\, d\theta$
- We eliminate the angular part through integration over all directions the molecule can travel
- $\tilde{\mathrm{P}}(u)du = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_B T}} du \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta\, d\theta$

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

- We thus obtain the **_Maxwell-Boltzmann distribution_**:

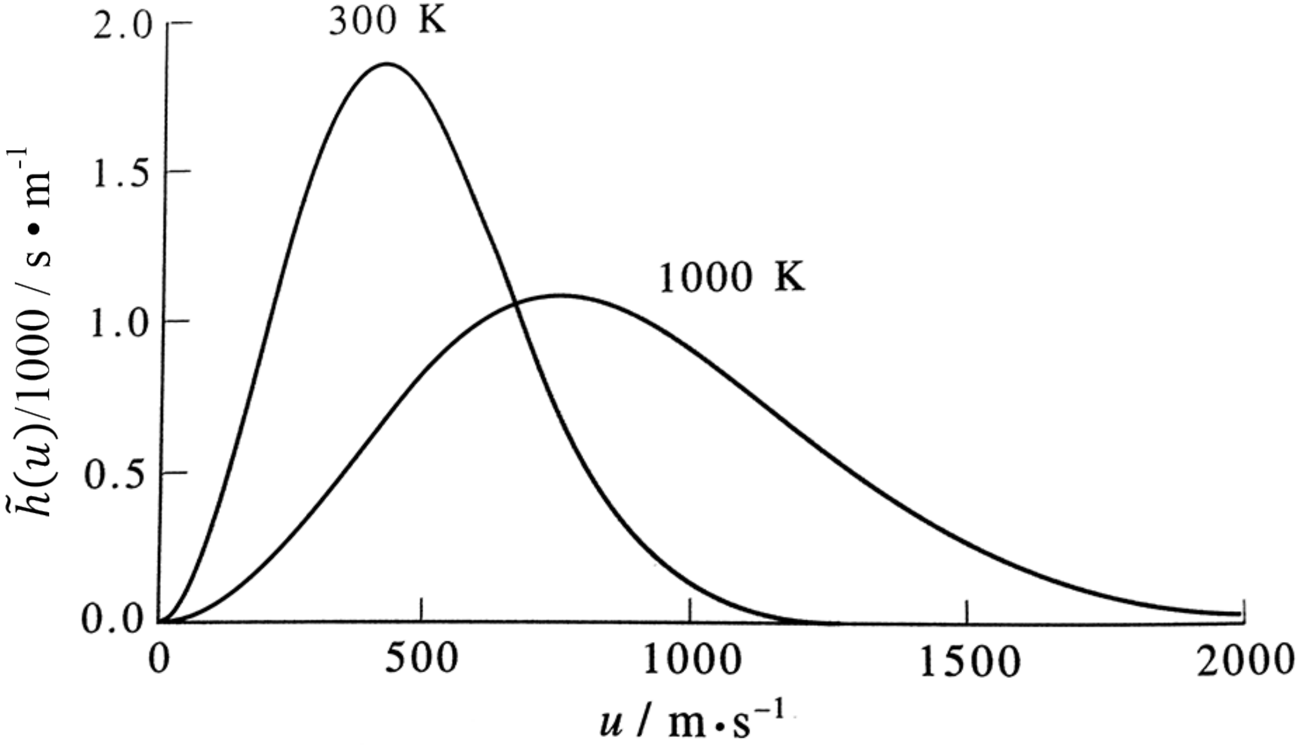
$$\boxed{\tilde{\mathrm{P}}(u)du = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_B T}} du}$$

**Maxwell-Boltzmann distribution**:

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

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 gas $PV = \frac{1}{3}Nm\langle u^2\rangle$
- and that the rms-velocity is $u_{rms} = \sqrt{\langle u^2\rangle} = \sqrt{\frac{PV}{N\,m}}$
- We want to verify that generally across all values this holds true:

$$P_{(u_x)} = \frac{e^{-\frac{mu_x^2}{2\,k_B T}}}{Q}$$

But how?

- Idea:

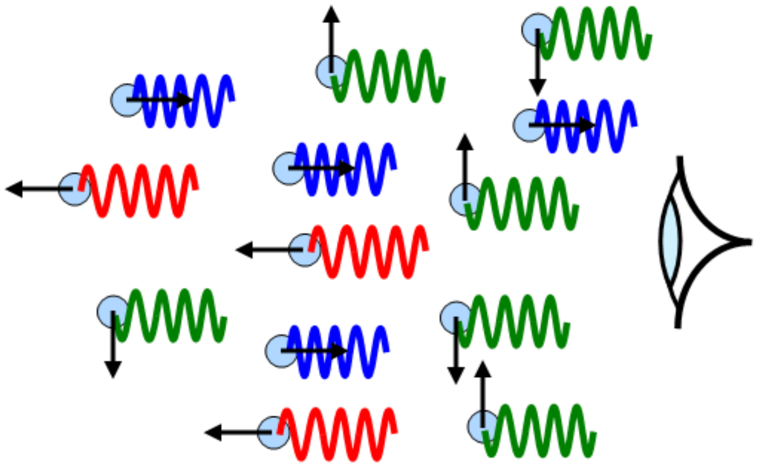
Measure something easily observable, that is *influenced* by $u_X$

→ Spectroscopy! Measure absorption or emission of light

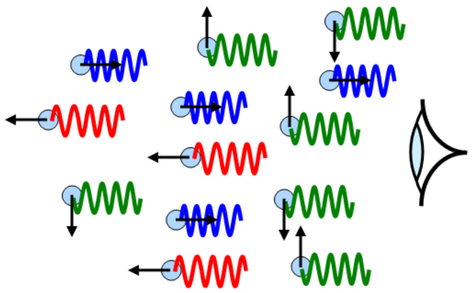
**A)** Measure ***Doppler broadening*** of your absorption or emission spectrum of molecules in gas phase

- 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 :)



$E = h\,\nu$



- Frequency of light emitted or absorbed:

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

$\nu_0$: transition frequency of static molecule

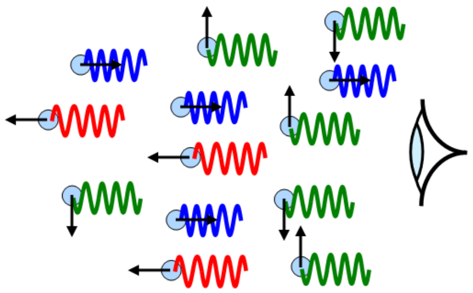
$$\rightarrow u_x = \left(\frac{\nu}{\nu_0} - 1\right)c$$

- 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:

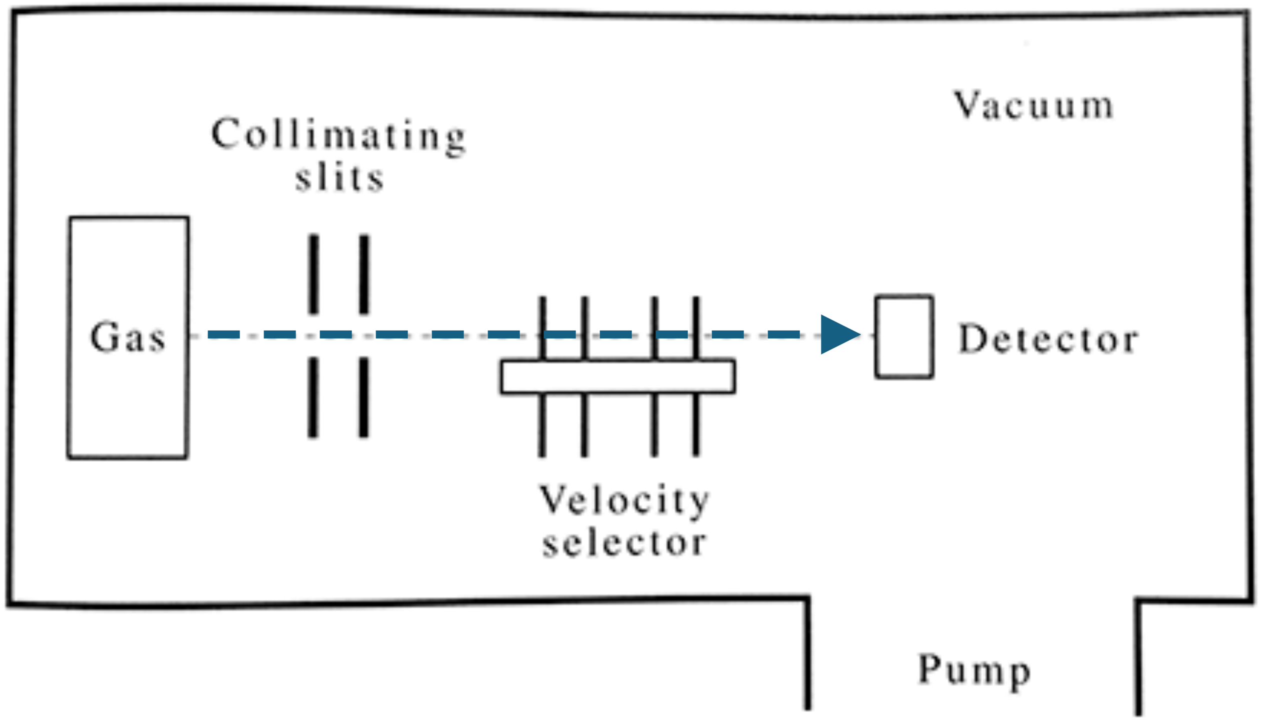
$$I(\nu) \propto e^{-\frac{mu_x^2}{2k_BT}} \propto e^{-\frac{mc^2(\nu-\nu_0)^2}{2\nu_0^2k_BT}}$$

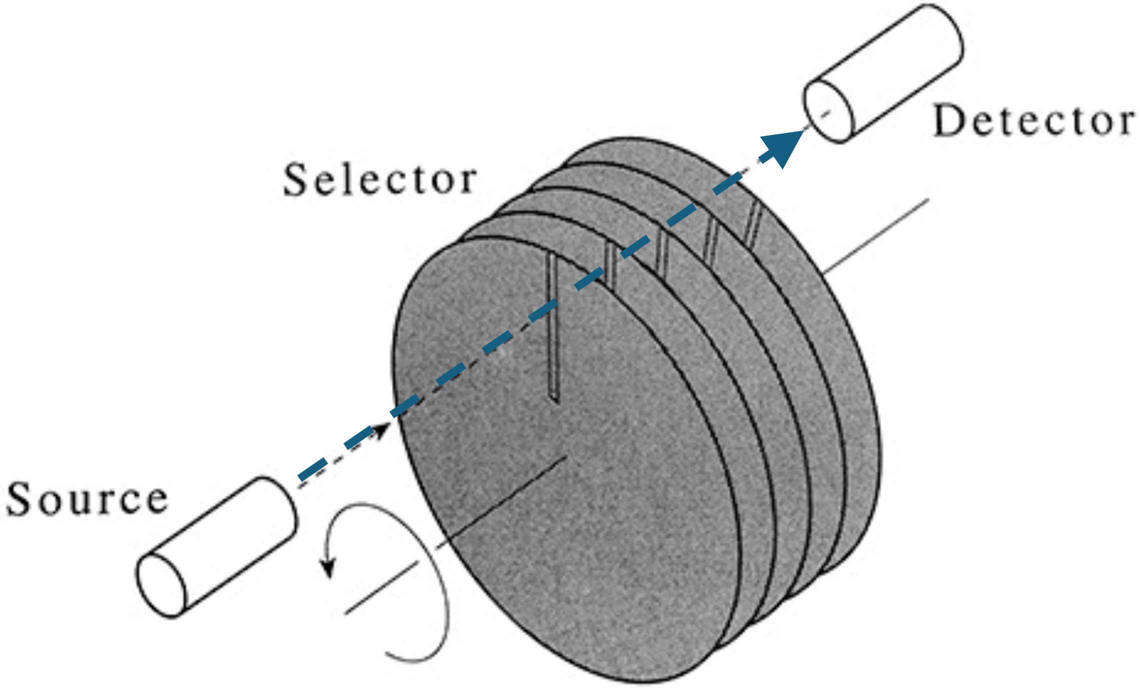
$$I(\nu) \propto e^{-\frac{mc^2(\nu-\nu_0)^2}{2\nu_0^2 k_B T}}$$



- We see a broadening of the line shape following a gaussian
- With variance $\sigma^2 = \frac{\nu_0^2 k_B T}{mc^2}$
- Meaning the width of the spectrum increases with 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