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2

Single Chain Properties

2.1

The Ideal Polymer Chain

What Do They Have in Common?

a polymer chain

a drunk person

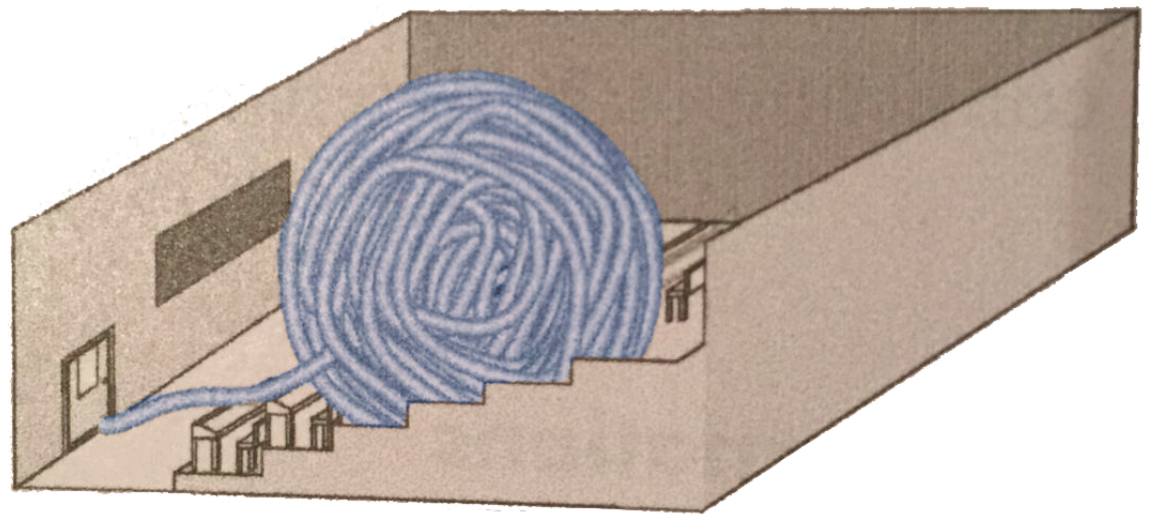
Brownian motion
(gas particles)

- **… can be described by the same statistical approach (the random walk model)**
- How can this be used to express the polymer chain size? How does it relate to polymer molecular weight?

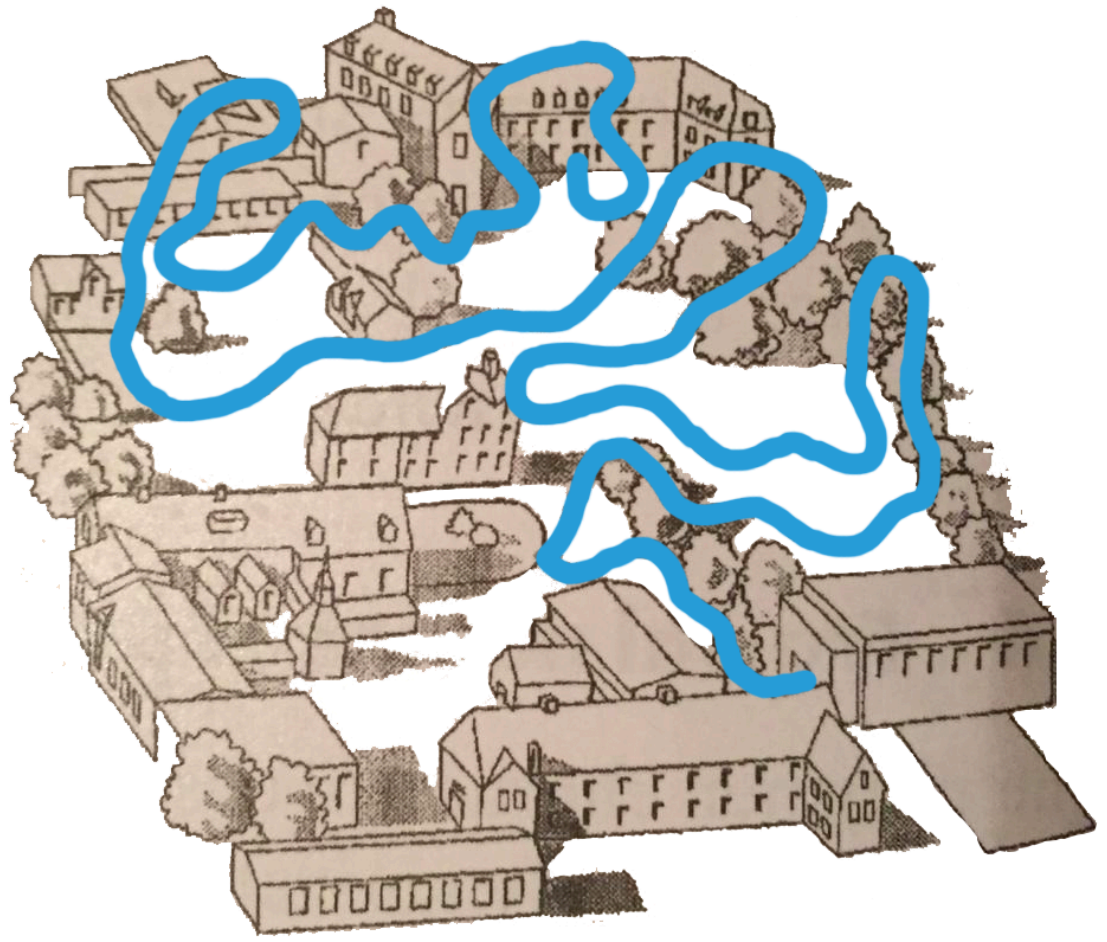
Chain Dimensions

- polymer conformation depends on chain flexibility, interactions between repeat units, and interactions with the surrounding medium
- example of a hypothetical polymer size: 10^{10} monomers; magnification factor: 10^{8}

collapsed globule
(attractive interactions)



random walk
(no effective interaction)



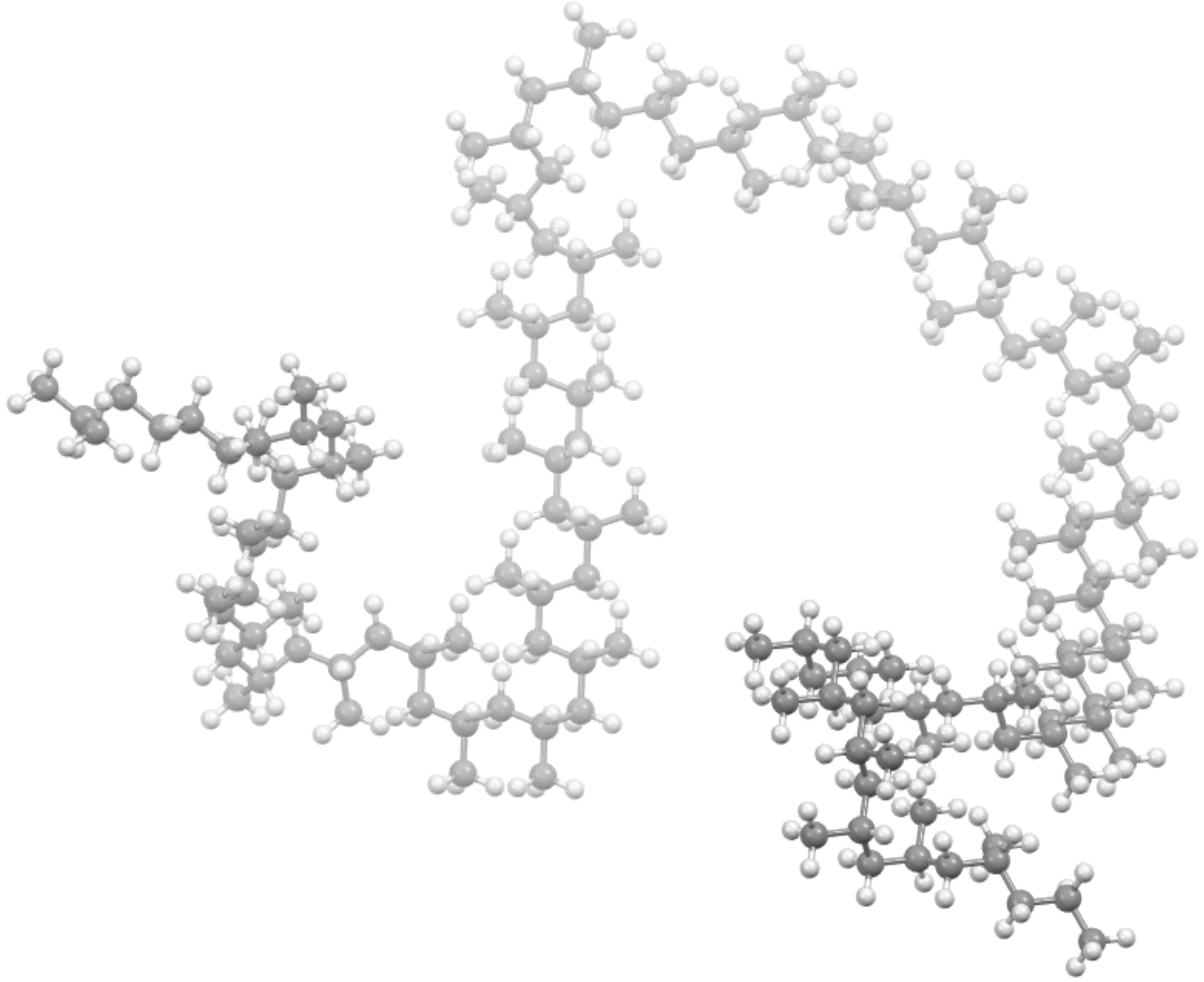
the ideal polymer chain

extended conformation
(long-range repulsion)

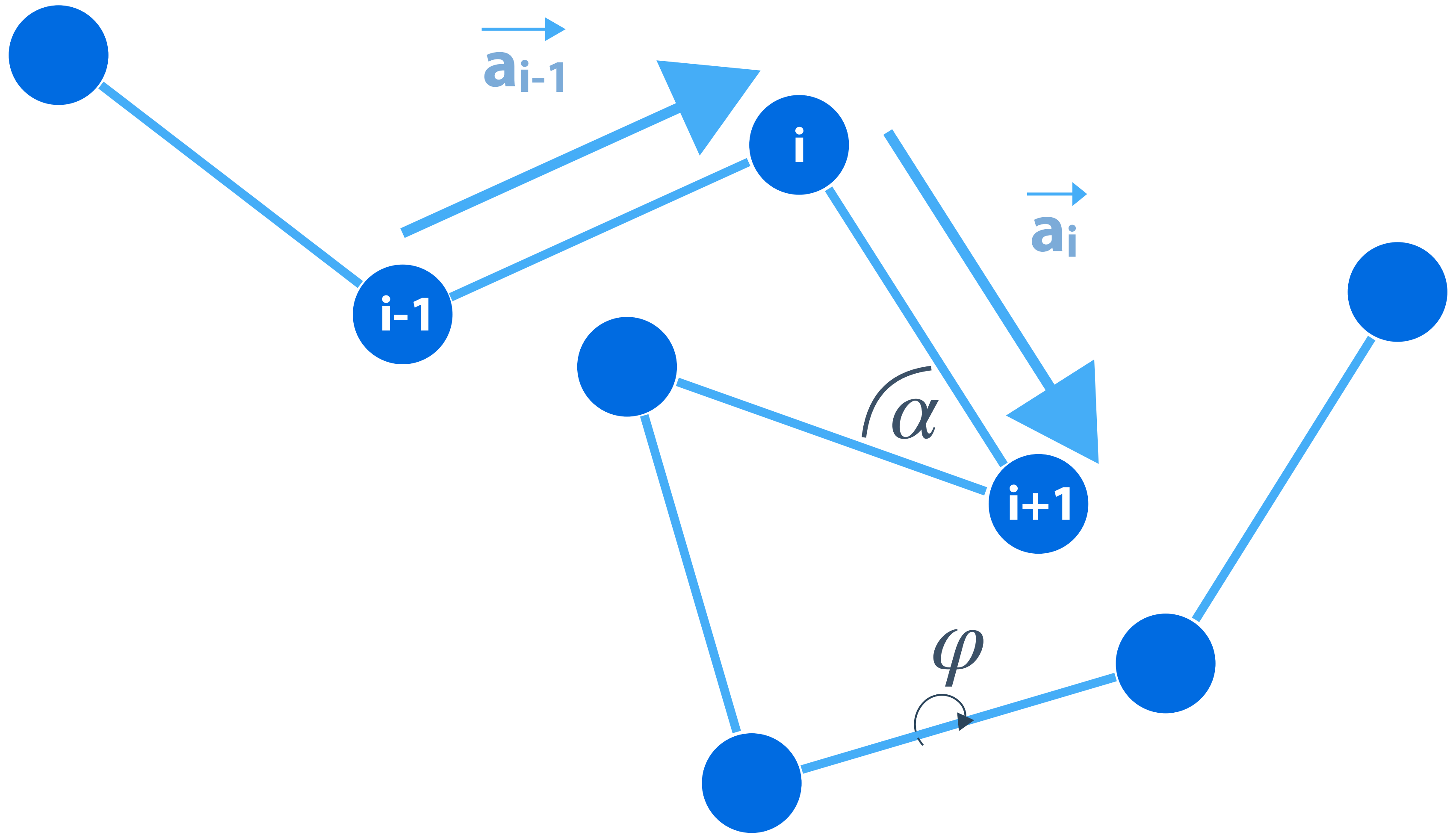
- **chain sizes may be of vastly different dimensions, strongly depending on parameters like *T* or solvent**

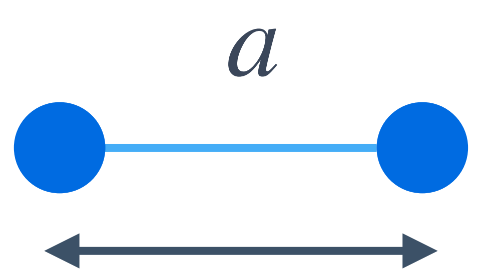
Simplification of the Polymer Chain

- from atoms and bonds to a chain of beads and links: models with variable repeating unit size, link sizes, bending and torsion angles



snapshot of PP (50 repeating units)





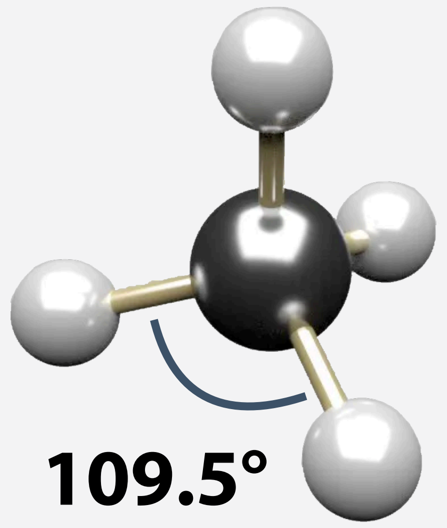
$$V_{stretch} = \frac{\kappa}{2}(a - a_0)^2$$

- **ideal polymer chain: no energetic interactions between repeating units**
- **accurate description of polymer melts and solutions**

Polymer Conformations

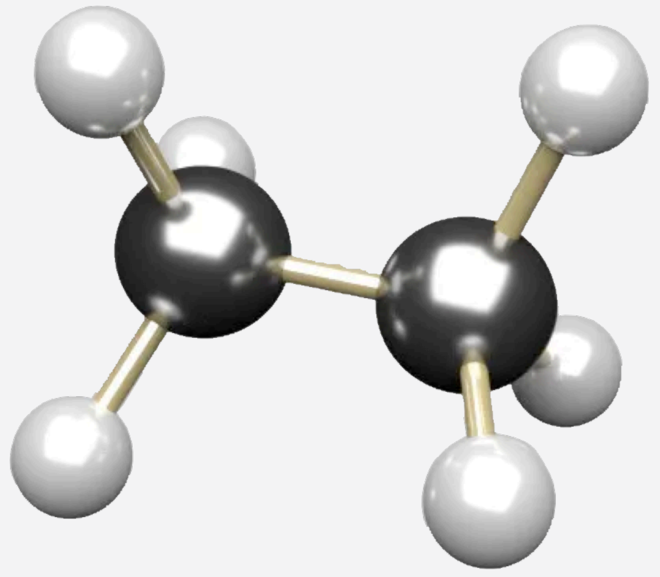
- conformation: the shape of a molecule resulting from rotation around fixed bonds

methane



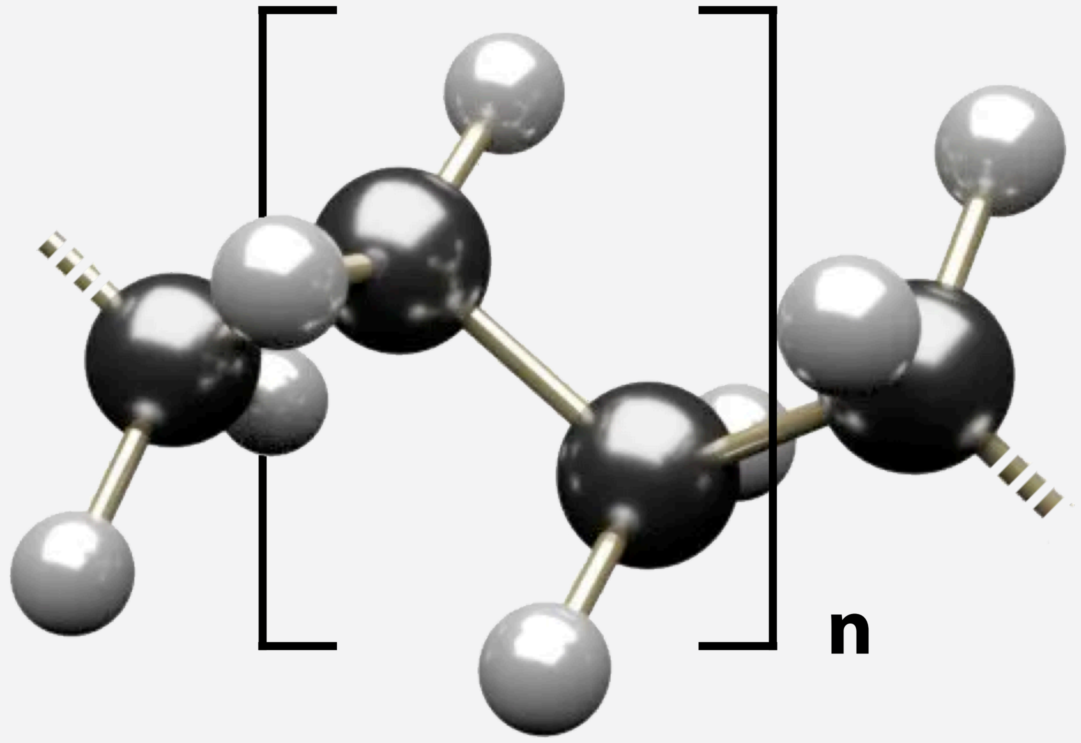
1 conformation
(fixed bond length
and angles)

ethane



3 conformations
(almost free rotation
around C-C bond)

polyethylene

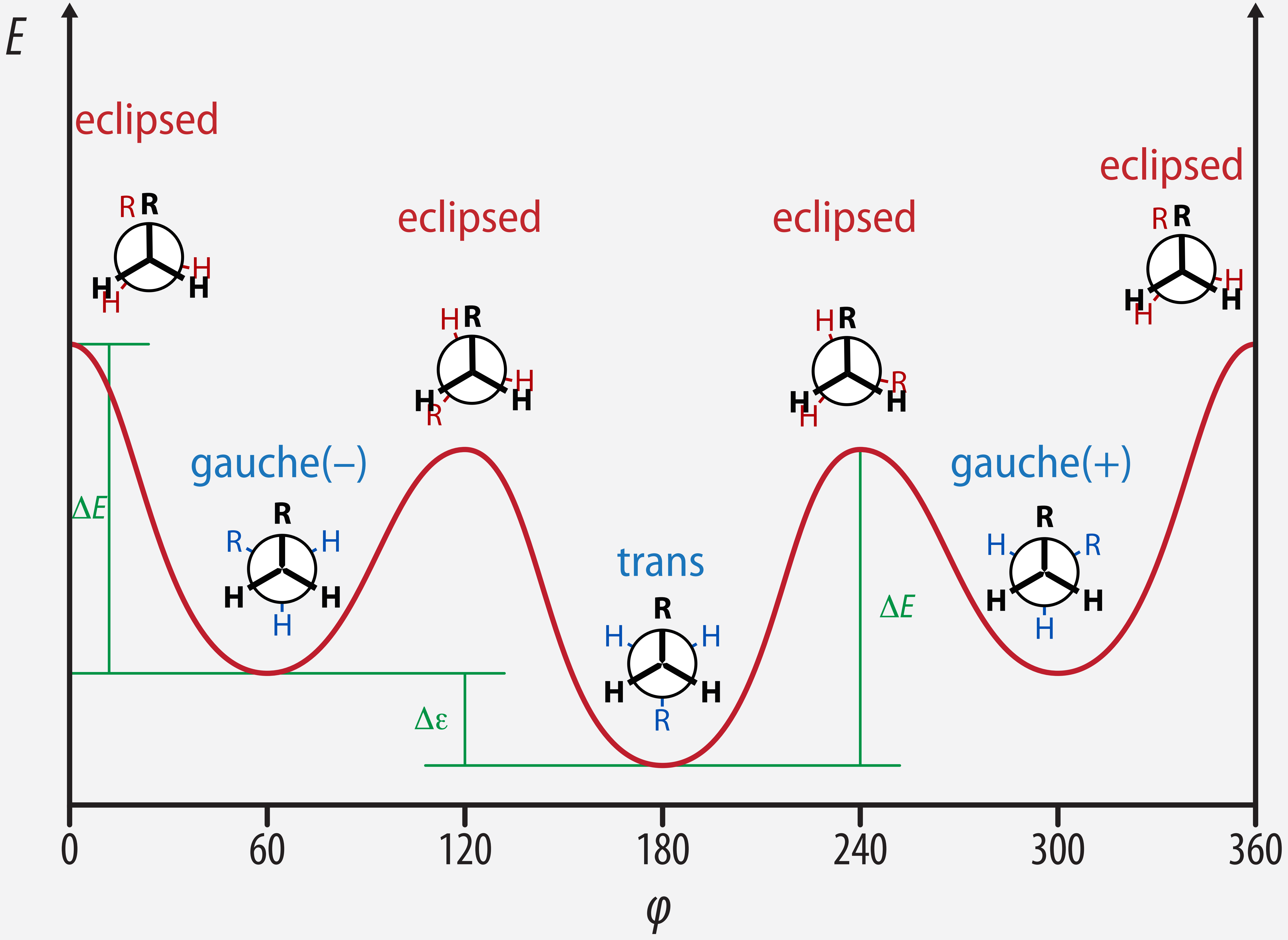


3^{2n} conformations

- **the number of possible conformations increases drastically with the chain length**
- **conformational changes happen on the picosecond time scale**

Energy Landscape of Polymer Conformations

main source of flexibility is the variation of torsion angles.



- **rotation around single bonds at r.t. is governed by ΔE (thermal equilibrium) and $\Delta \epsilon$ (energy barrier)**

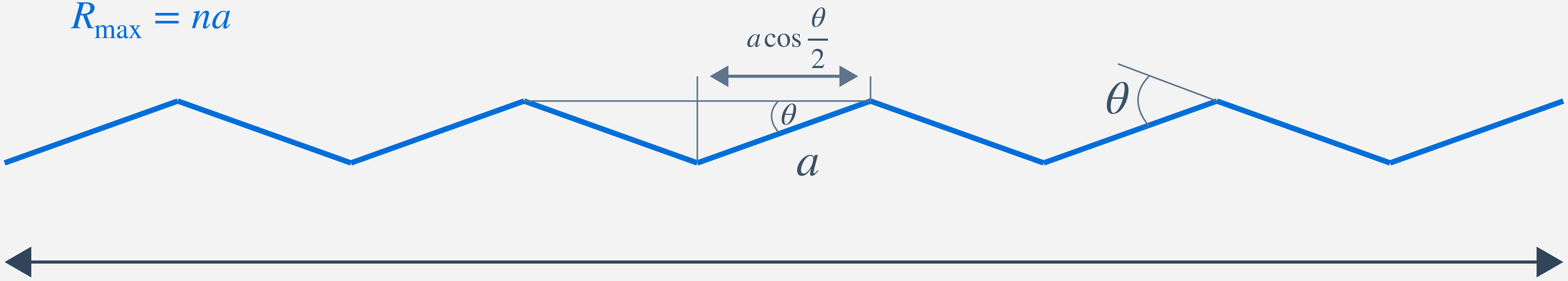
Contour Length

- the largest possible end-to-end distance (contour length or projection length), R_{max}, is an all-*trans* (zig-zag) conformation.

contour length:

$$R_{\max} = na$$

all-*trans* conformation



projection length: (maximum end-to-end distance)

$$R_{\max} = na\cos\frac{\theta}{2}$$

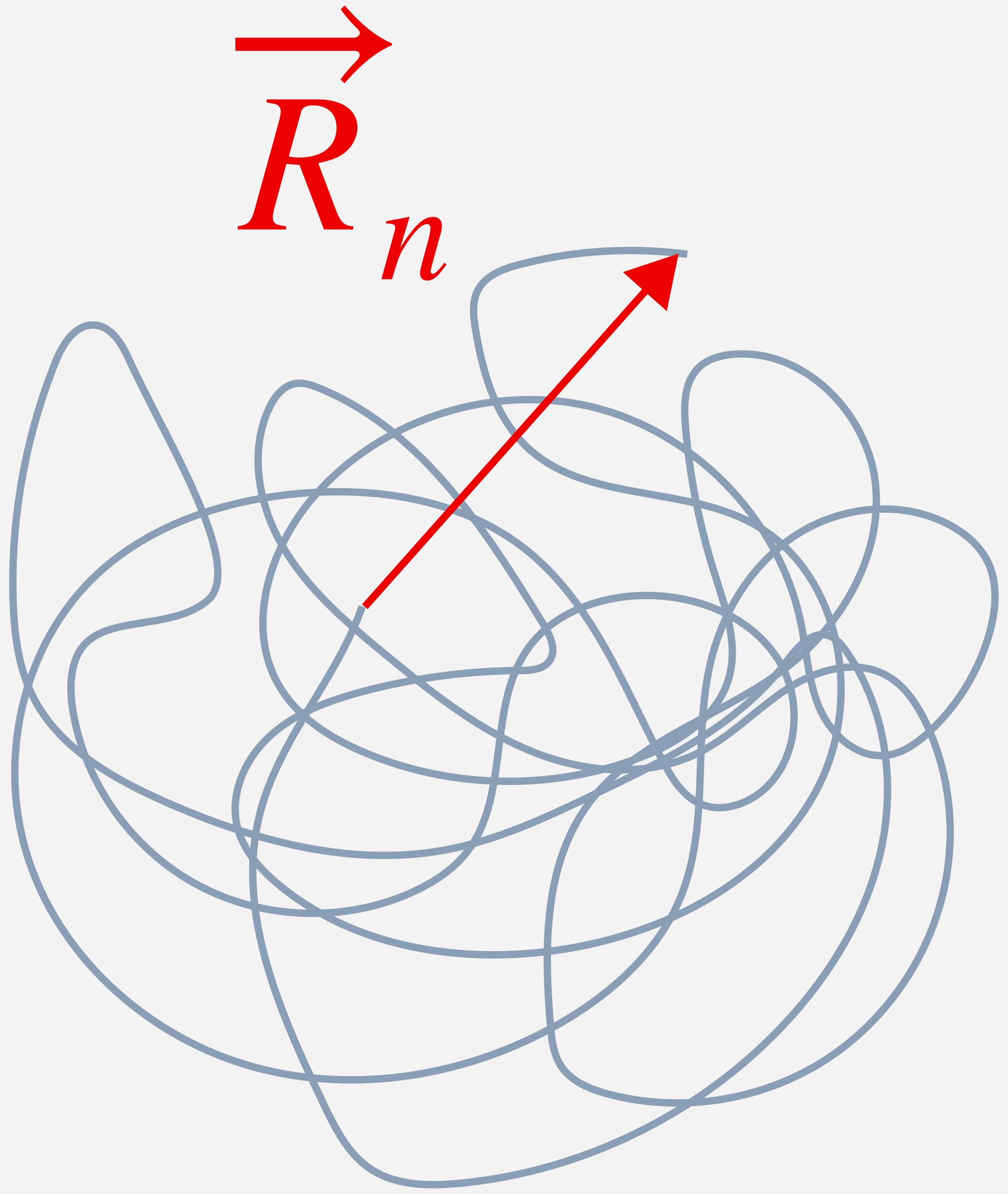
Example: PE

tetrahedral angle: θ = 68°,
bond length: *a* = 1.54 Å

- **However, *gauche* states of torsion angles lead to flexibility in the chain conformation**

Gauche and *Trans* States in PE

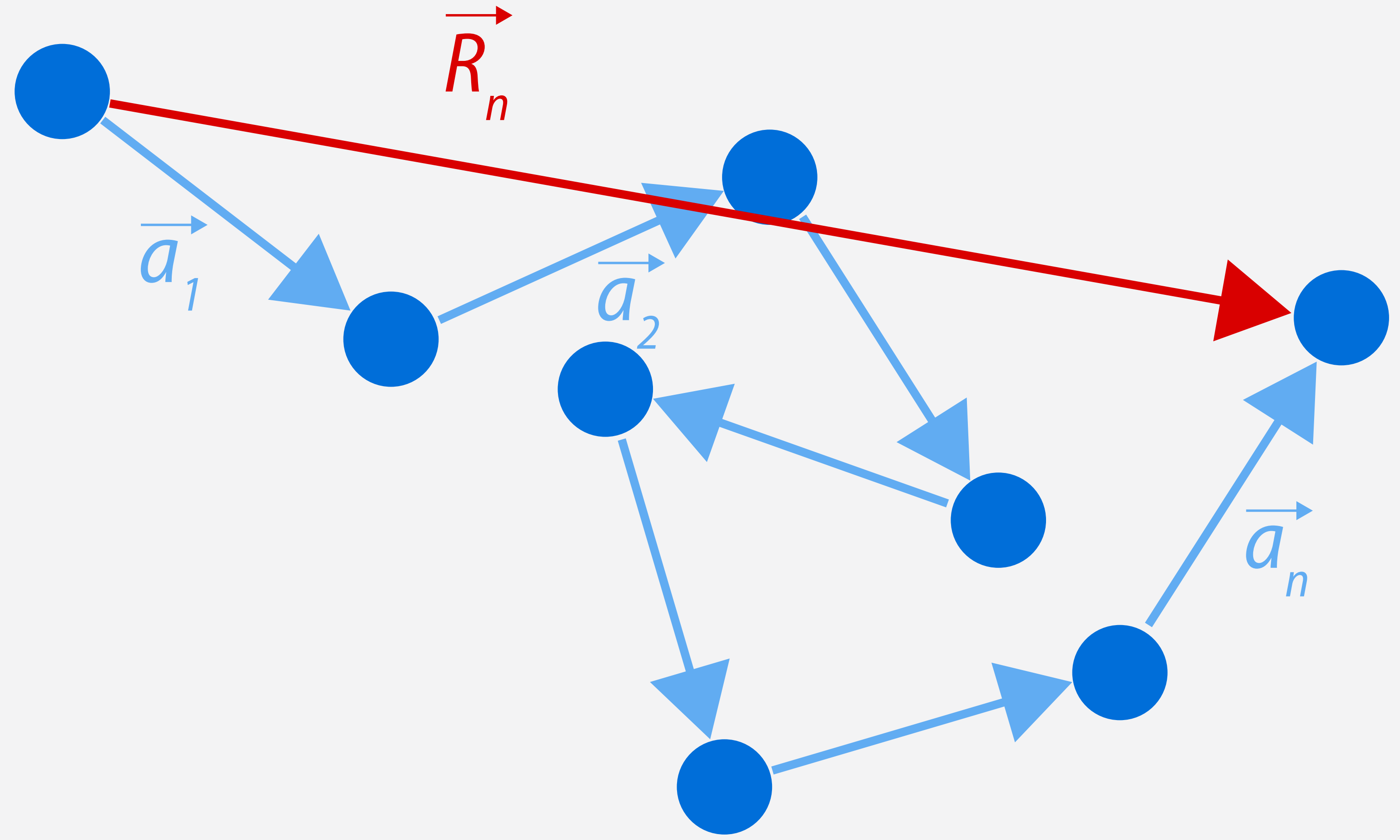
- polyethylene chain with 10’000 carbon atoms



- **typically, all-*trans* rod-like chain sections comprise fewer than 10 main-chain bonds**
- **most synthetic polymers are hence quite flexible and are represented as random coils**

Freely Jointed Chain Model

- no restriction upon bond angle and bond rotation
- however, $< \overrightarrow{R_n} >$ is zero for an isotropic collection of ideal chains



$$\vec{R}_n = \vec{a}_1 + \vec{a}_2 + \ldots + \vec{a}_n$$

polymer chain size

$$< R_n^{\ 2} >^{\frac{1}{2}} \cong \sqrt{n}\ a$$

- **polymer chain size represented by the mean-square end-to-end distance**

$$< R_n^2 > \equiv < \vec{R}_n \cdot \vec{R}_n > = < \sum_{i=1}^{n} \vec{a}_i \cdot \sum_{j=1}^{n} \vec{a}_j > = \sum_{i=1}^{n} a_i^2 + \sum_{i \neq j} \vec{a}_i \cdot \vec{a}_j = n|a|^2 + < \sum_{i \neq j} \vec{a}_i \cdot \vec{a}_j > = n|a|^2 \equiv na^2$$

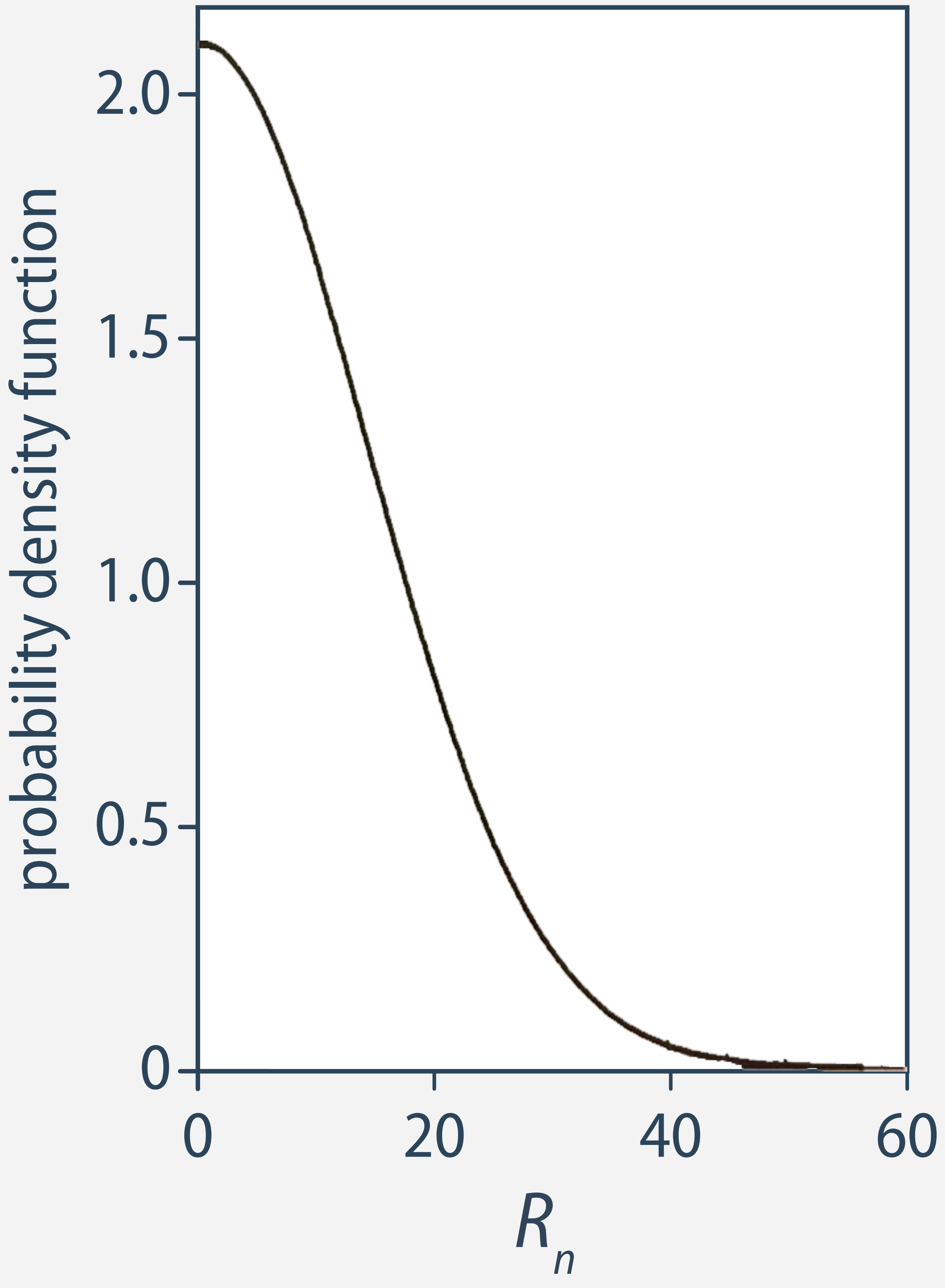
- **hence, the root mean-square end-to-end distance is proportional to** $\sqrt{M}$

$$< R^2 >^{\frac{1}{2}} \propto \sqrt{n} \propto \sqrt{M}$$

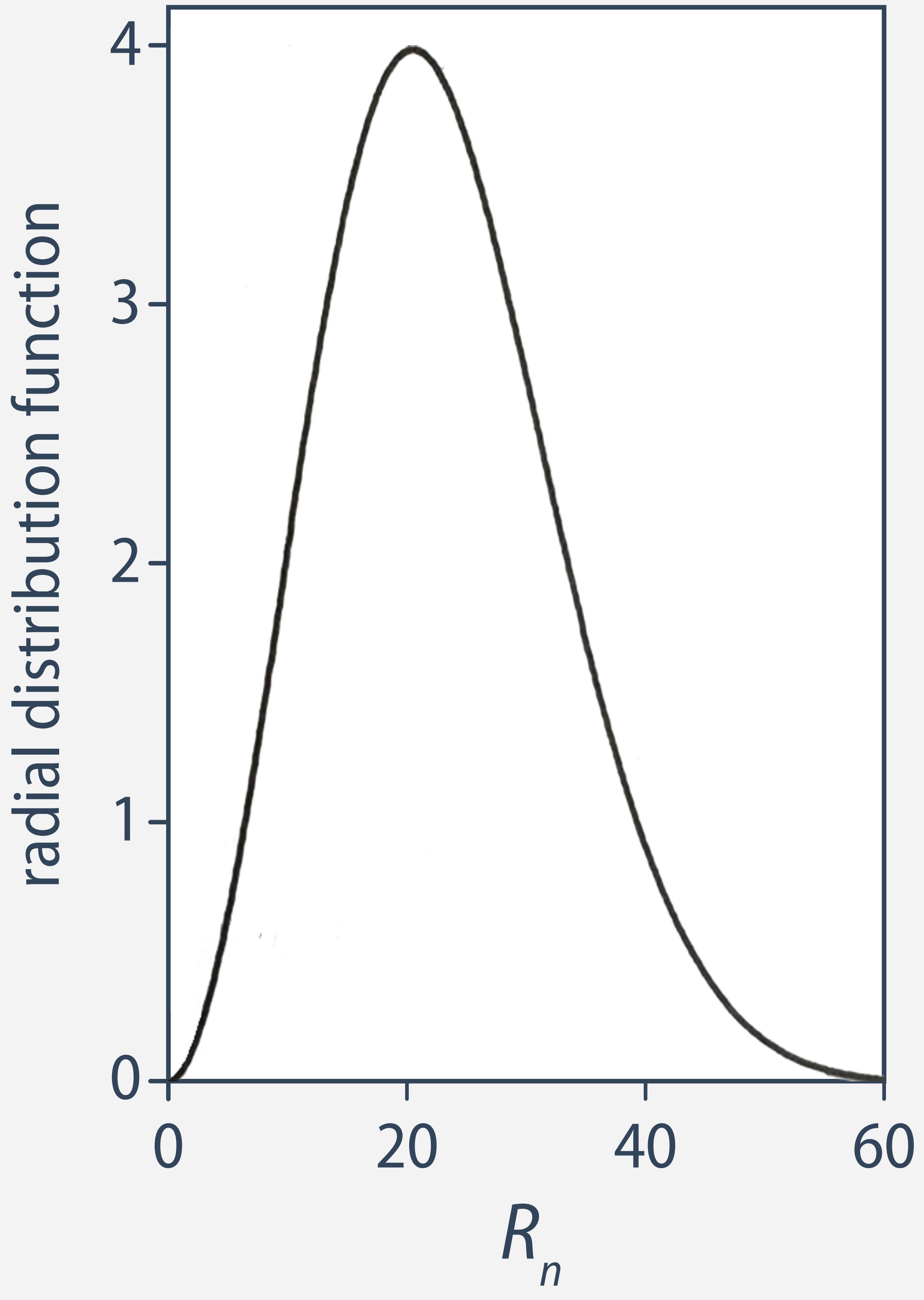
The “Gaussian” Chain

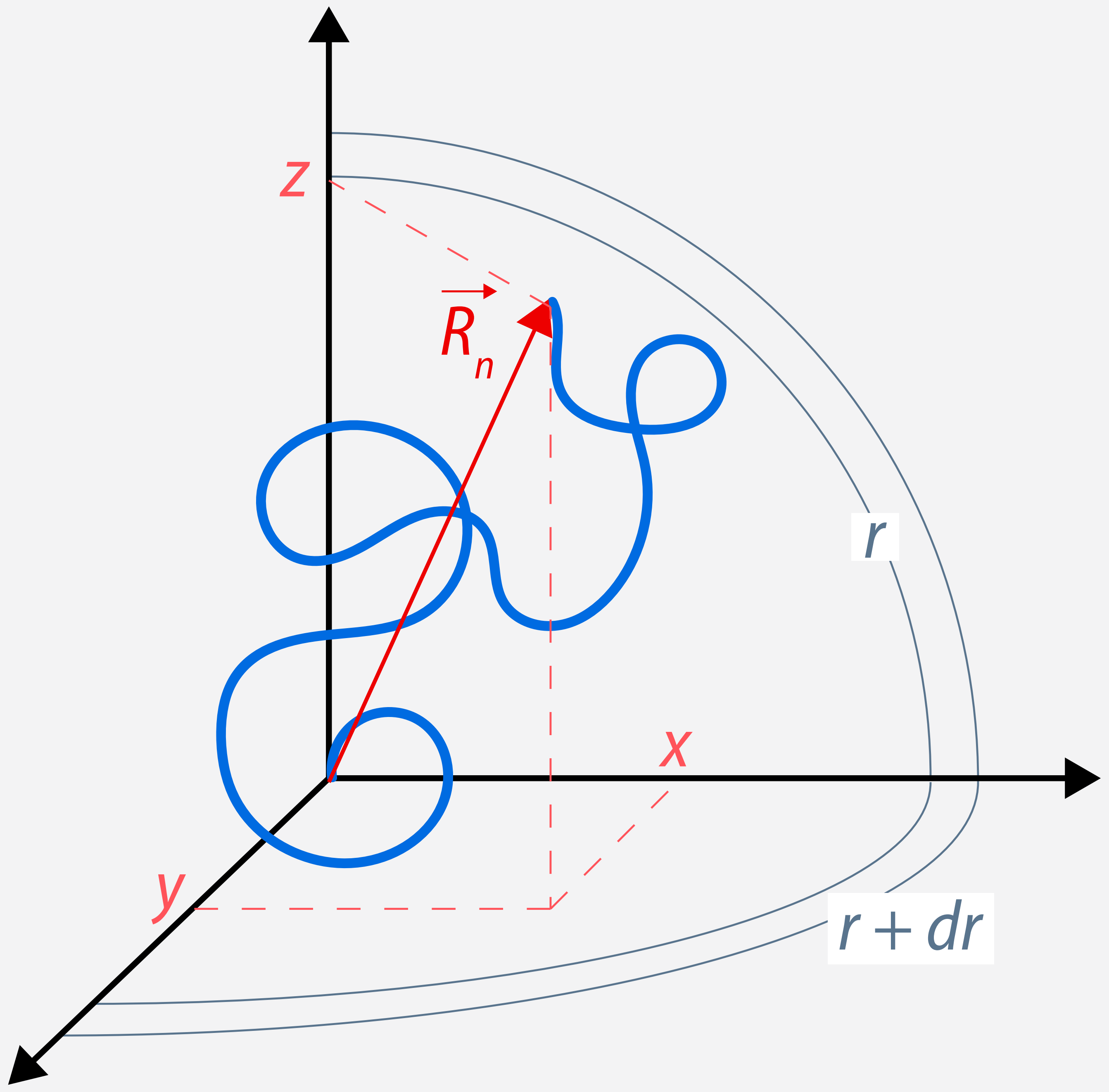
- an ideal chain can be mapped onto a random walk and obeys Gaussian statistics

$$P = (\frac{3}{2\pi na^2})^{3/2}\exp(-\frac{3R_n^2}{2na^2})$$



$$P4\pi R^2 dr = 4\pi(\frac{3}{2\pi na^2})^{3/2}\exp(-\frac{3R_n^2}{2na^2})R_n^2 dr$$





- most probable are conformations with $\vec{R}_n = 0$, but it’s *rms* value is finite and proportional to $\sqrt{n}$

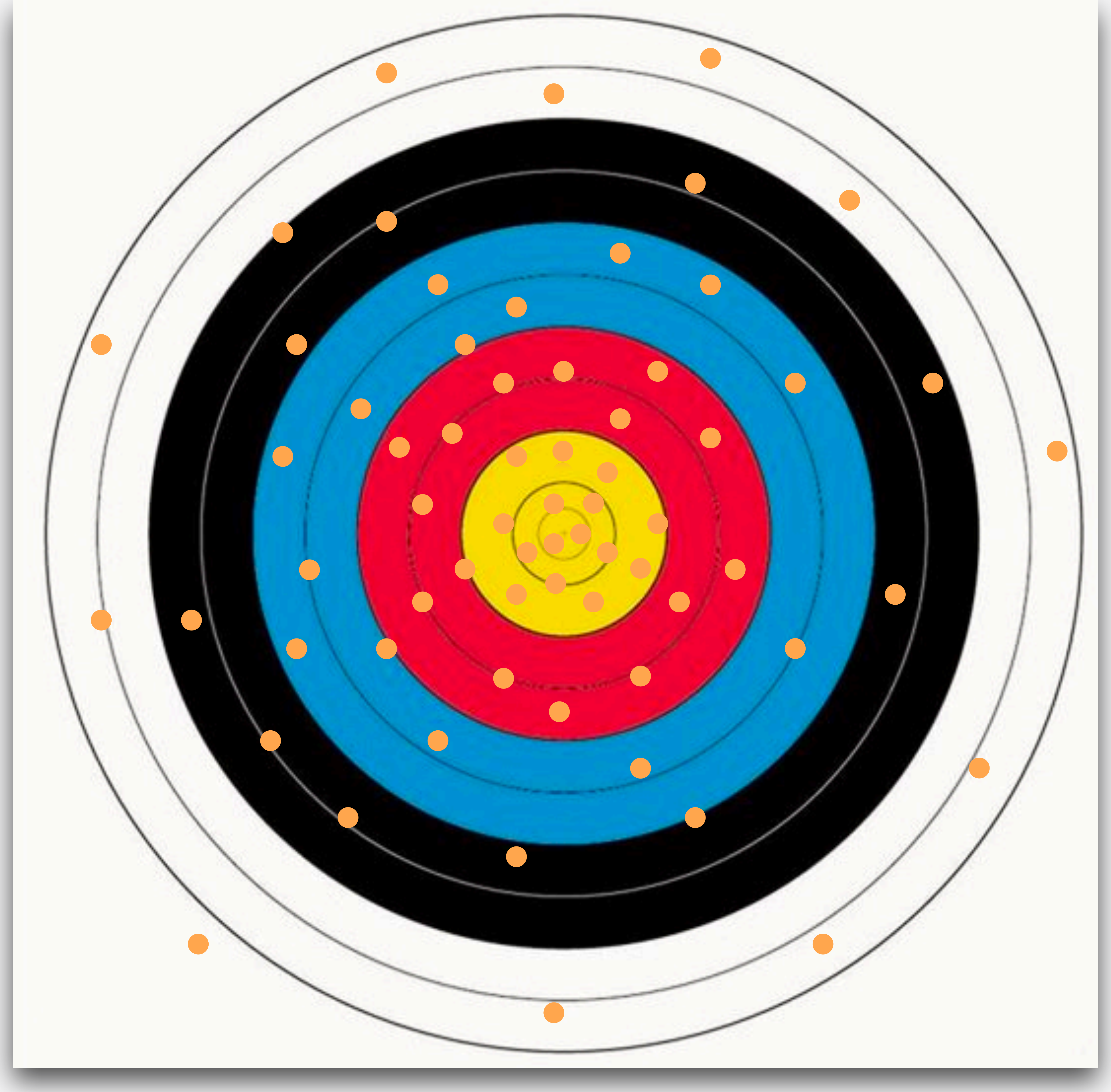
see Reading Recommendation: Takamasa Sakai, Physics of Polymer Gels, 2020

Analogy for Probability Density and Radial Distribution Function

- consider archery:

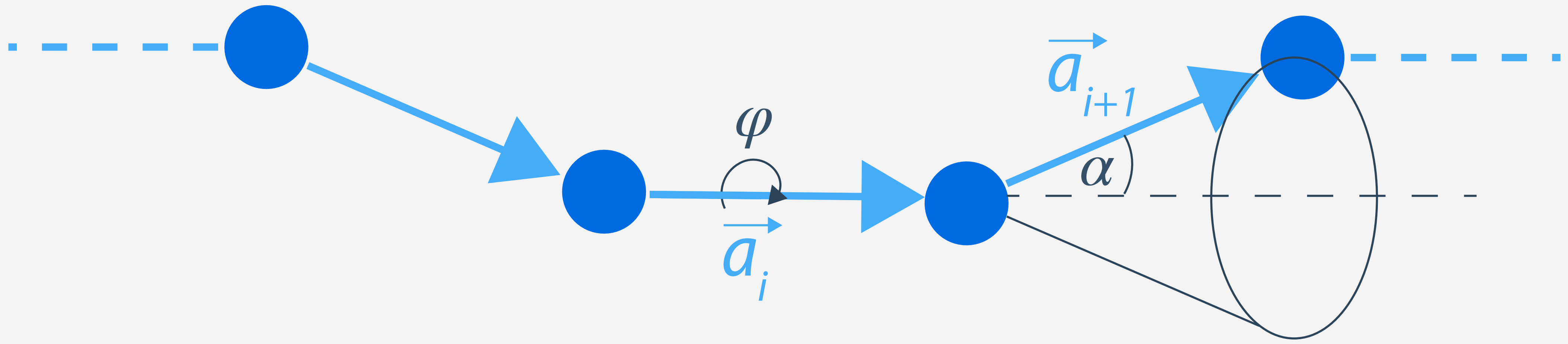
Where is the most probable position of any shot?

What would your average points be?



Freely Rotating Chain Model

- all torsion angles $-\pi < \varphi \leqslant \pi$ are assumed to be equally probable; tetrahedral angles α are fixed.



average projection from $\vec{a}_{i+1}$+1 on $\vec{a}_i$: $|a|cos\alpha$

average projection from from $\vec{a}_{j}$+1 on $\vec{a}_i$: $|a|cos^{|j-i|}\alpha$

mean square end-to-end distance:

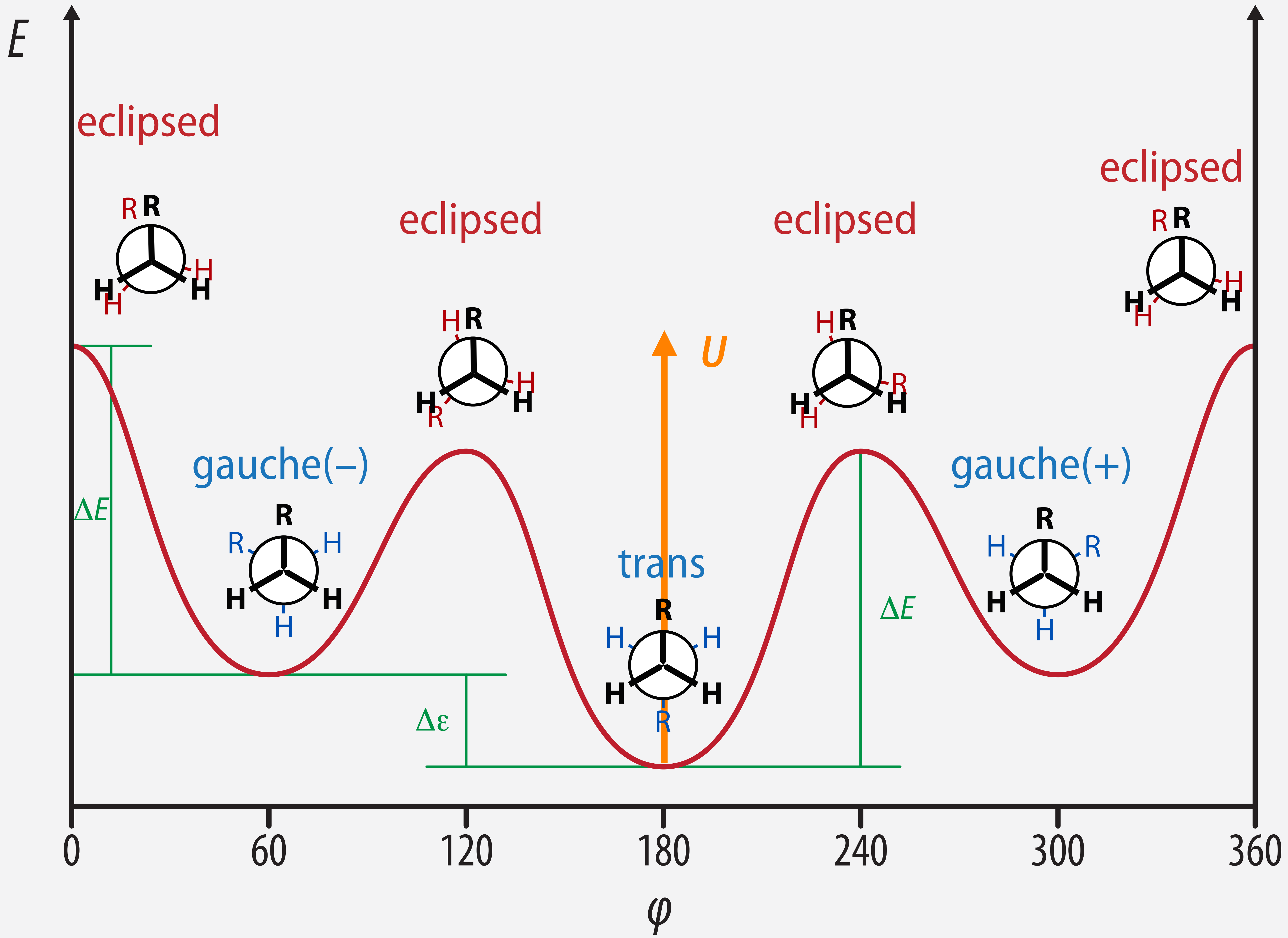
$$< R_n^2 > = n|a|^2 + < \sum_{i \neq j} \vec{a}_i \cdot \vec{a}_j > = n|a|^2 + 2|a|^2 \sum_{i<j}^{n} cos^{j-i}\alpha$$

- dependence of $< R^2 >$ of an ideal linear chain on number of bonds, bond length, and bond angle:

for large n: $< R_n^2 > = na^2 \left(\dfrac{1 + cos\alpha}{1 - cos\alpha} \right)$

Hindered Rotation Model

- **constant bond lengths and angles, independent torsion angles with rotation hindered by a potential, *U***



for large n:

$$< R^2 > = na^2 \left(\frac{1 + cos\alpha}{1 - cos\alpha} \right) \left(\frac{1 + < cos\varphi >}{1 - < cos\varphi >} \right)$$

Chain Flexibility and the Characteristic Ratio

- **the mean-square end-to-end distance can be approximated for long chains:**

Flory's characteristic ratio

$$< R^2 > \cong C_\infty n a^2$$

freely jointed chain: $C_\infty = 1$

freely rotating chain $C_\infty = \dfrac{1 + cos\alpha}{1 - cos\alpha}$

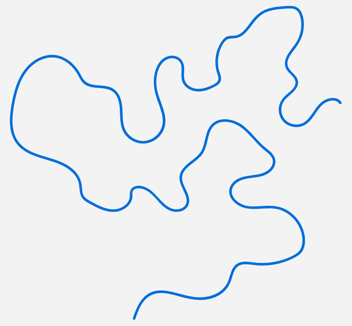
hindered rotation $C_\infty = \left(\dfrac{1 + cos\alpha}{1 - cos\alpha}\right)\left(\dfrac{1 + < cos\varphi >}{1 - < cos\varphi >}\right)$

- **the characteristic ratio is a correction term for chain ridigity/flexibility.**

random coil:

$C_\infty = 1$

stretched conformation:



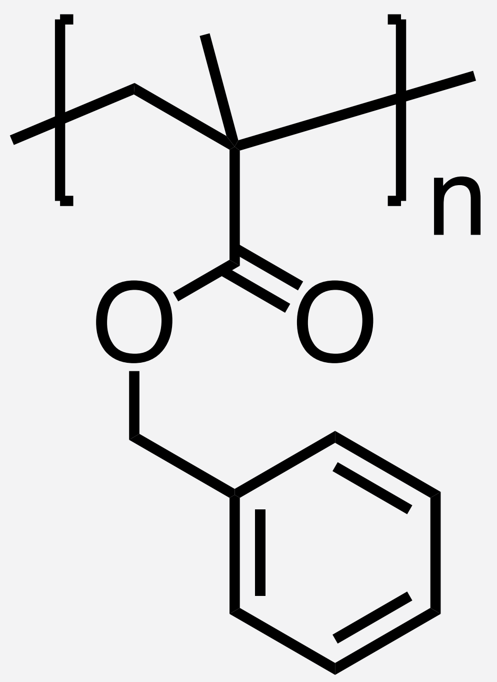
$C_\infty \gg 1$

$$< R^2 > \cong \begin{cases} n \cdot a^2 & \text{freely jointed chain} \\ 2n \cdot a^2 & \text{freely rotating chain} \\ 3n \cdot a^2 & \text{hindered rotation} \end{cases}$$

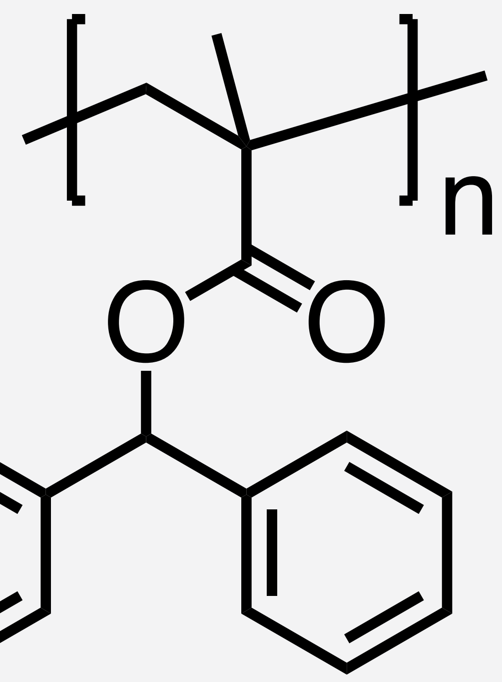
↓ **chain ridigity**

Examples

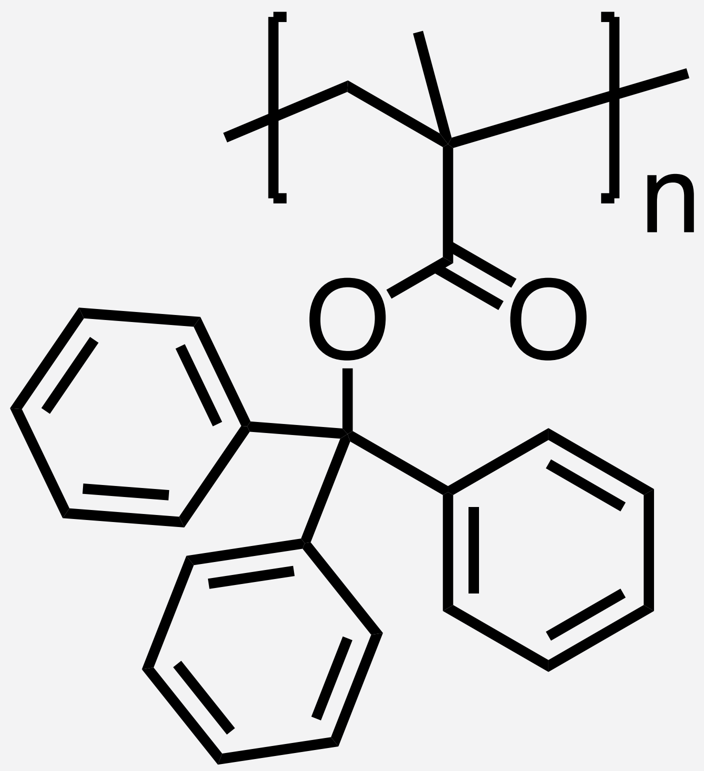
several
poly(methylmethacrylate)s



$C_\infty = 10$

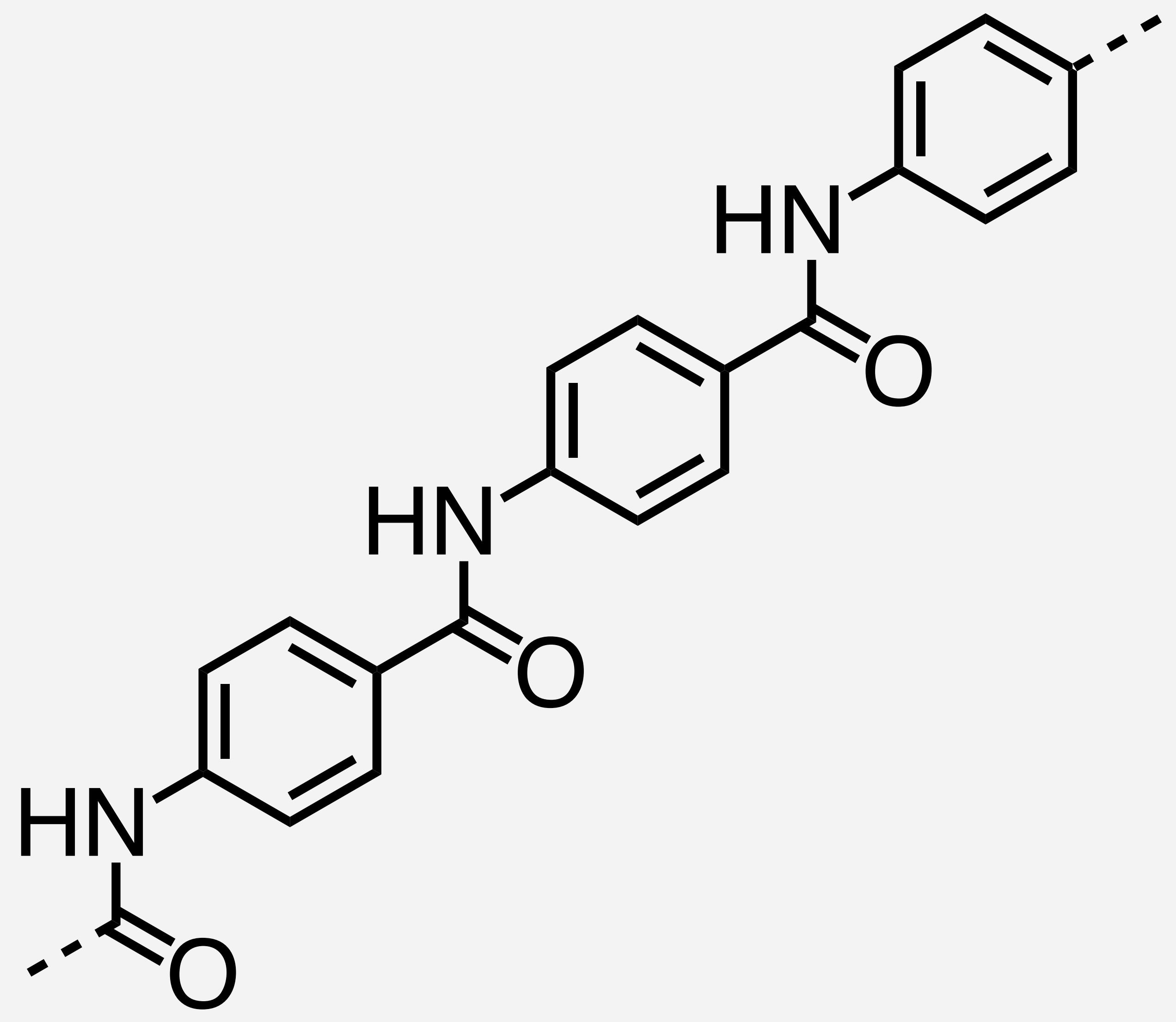


$C_\infty = 14$



$C_\infty = 20.3$

poly(*p*-benzamide)



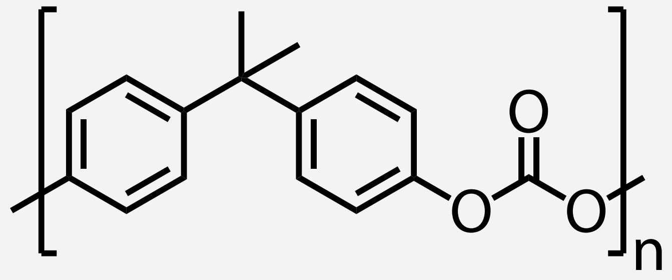
$C_\infty = 325$ why?

- **chain stiffness increases with increasing side chain bulkiness (limited rotation around main chain bonds)**
- **aromatic rings, double bonds increase the rigidity of a polymer chain**

Typical Values of C_∞ in Solution

Polymer	**Solvent**	***T* [°C]**	C_∞
polyethylene	1-dodecanol	138	6.7
polystyrene (atactic)	cyclohexane	35	10.2
polypropylene (atactic)	cyclohexane	92	6.8
polyisobutylene	benzene	24	6.6
polyvinylacetate	*i*-pentanone + hexane	25	8.9
polyoxomethylene	aqueous K_2SO_4	35	4.0
polycarbonate	methylenechloride	25	2.2
poly(benzobisoxazole)			93
poly(*p*-benzamide)			325

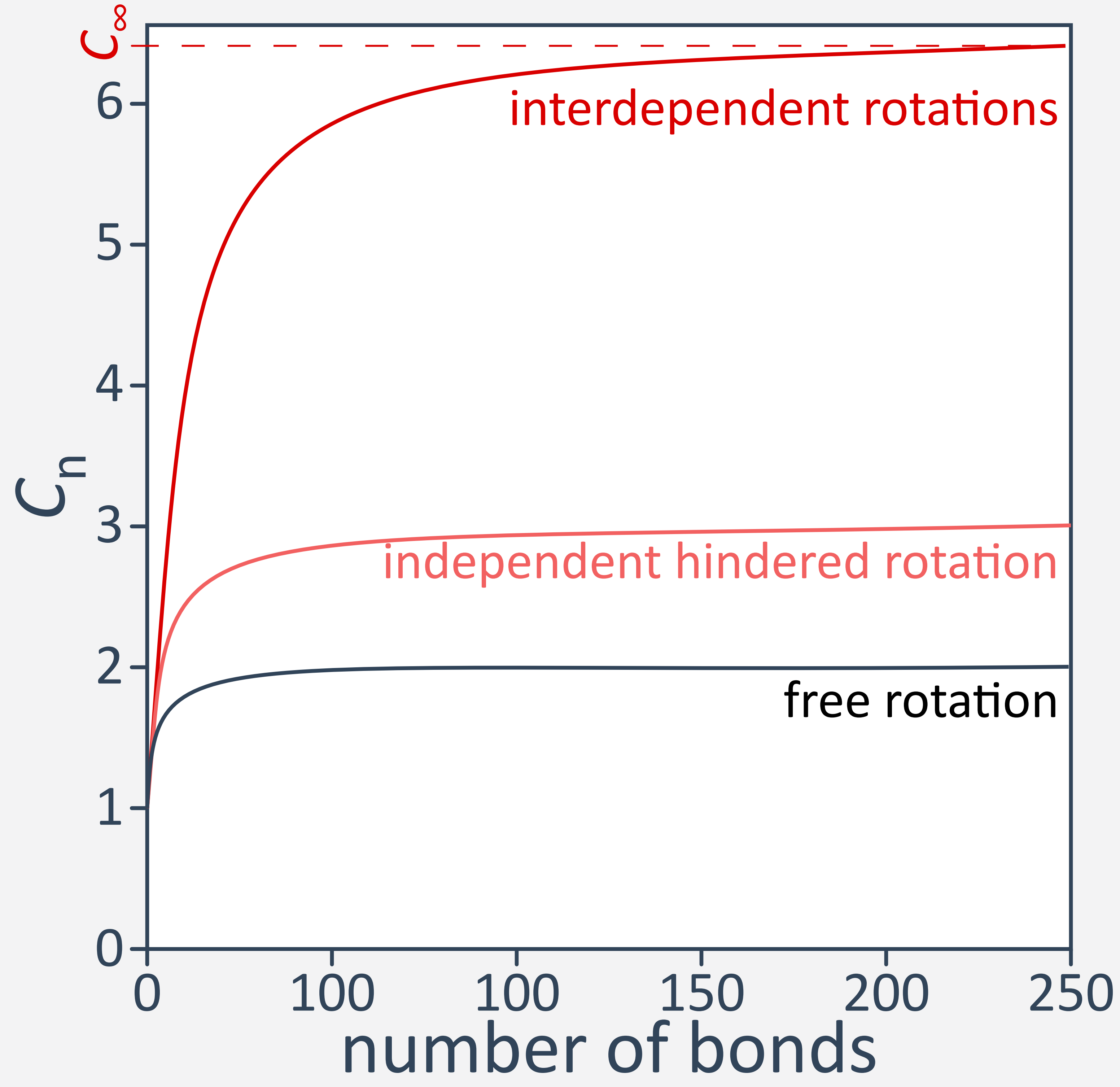
- **be careful with an interpretation (see Exercise Sheet):**



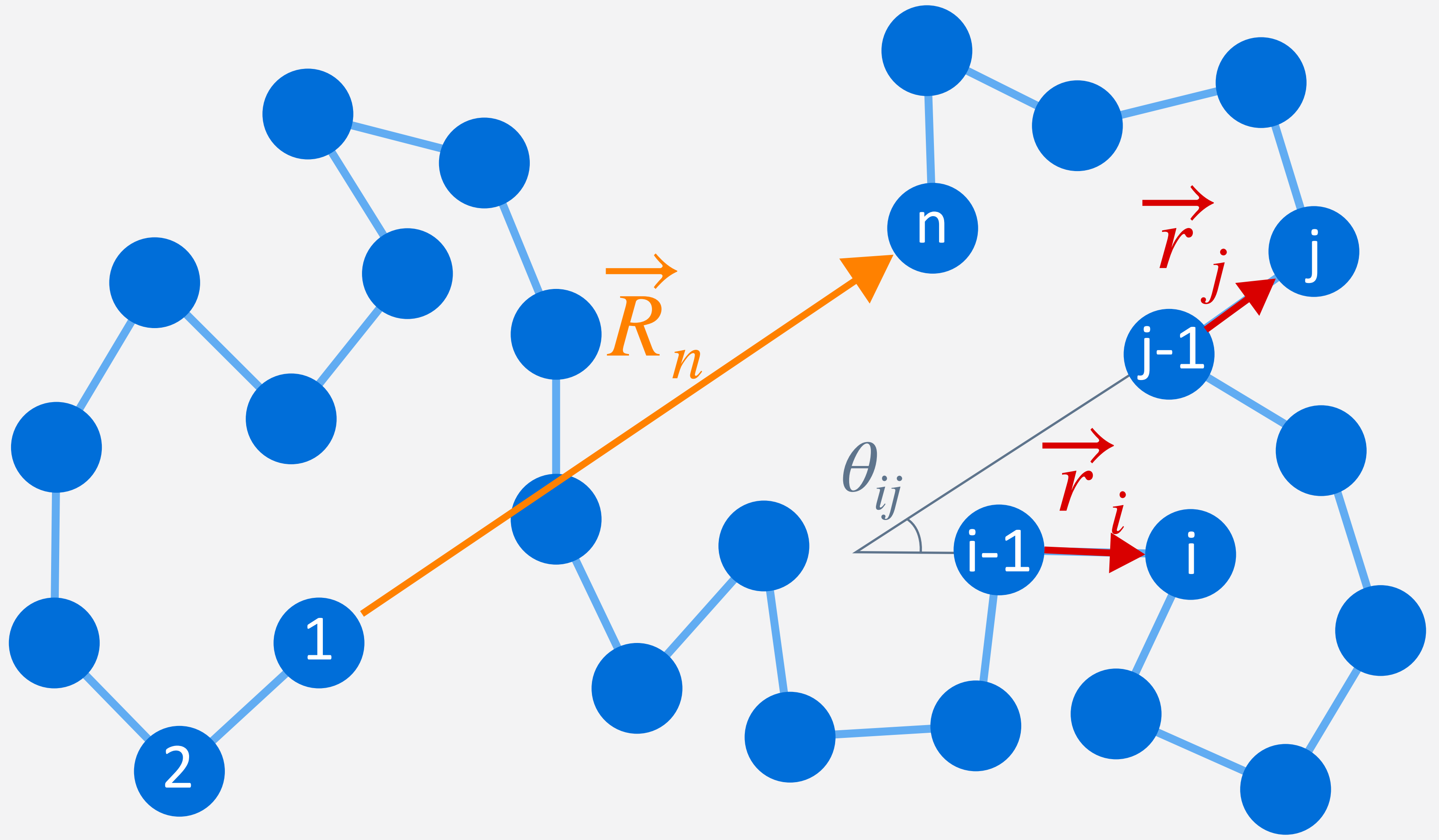
$C_\infty = 2.2?$

Deviations from Ideal-Chain Behaviour in PE

- Flory's characteristic ratio, C_n, approaches a finite value only for $n \rightarrow \infty$ ($C_\infty = 6.7$ for PE)



$$C_n = \frac{1}{n}\sum_{i=1}^{n} C'_i \qquad C'_i \equiv \sum_{j=1}^{n} < cos\theta_{ij} >$$

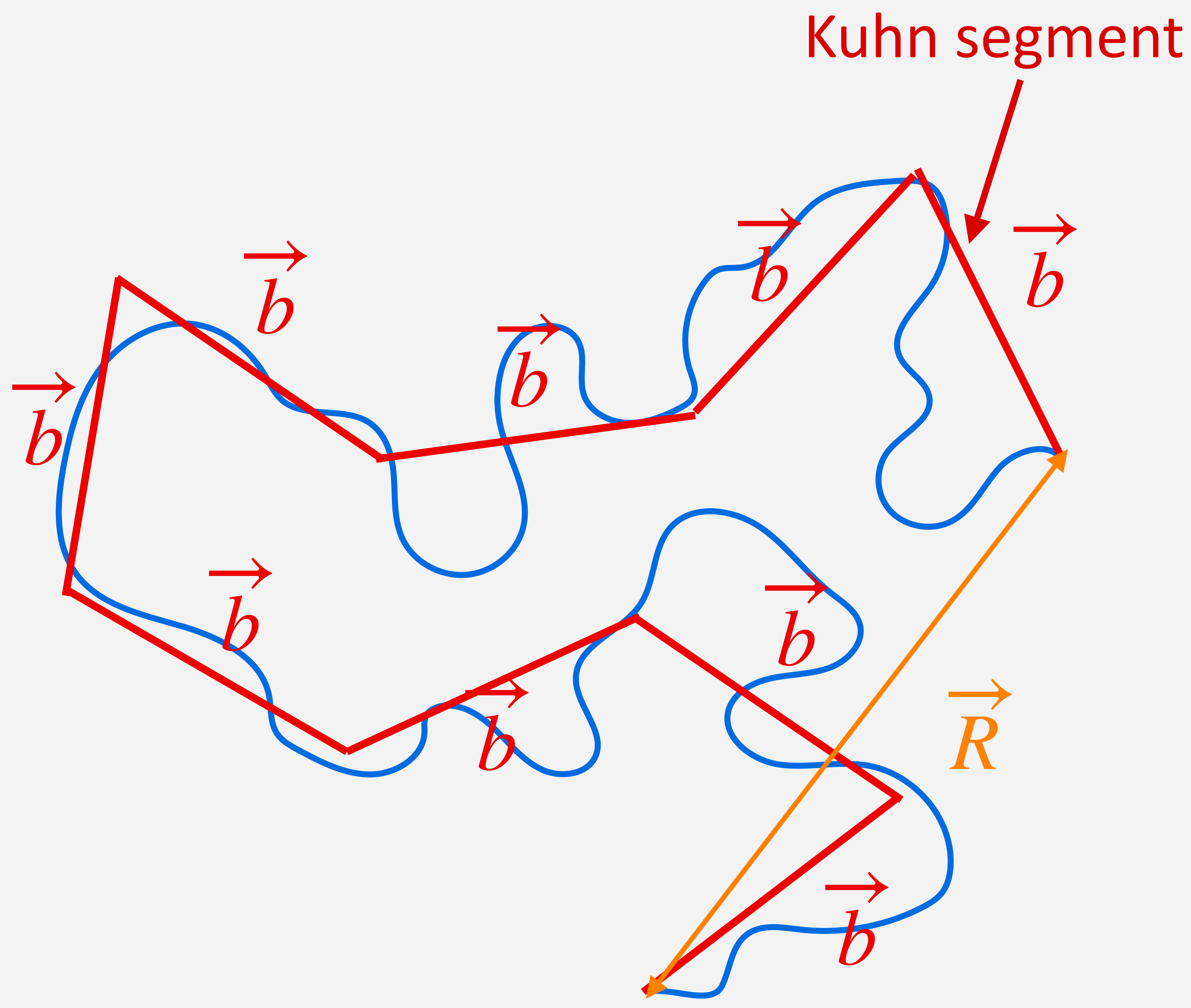


local and non-local, more far reaching interactions

- **real chains: further correlations between bond vectors due to forces acting on individual chain elements**

Kuhn Segments

- real polymer chains can be represented by an equivalent freely-jointed chain:



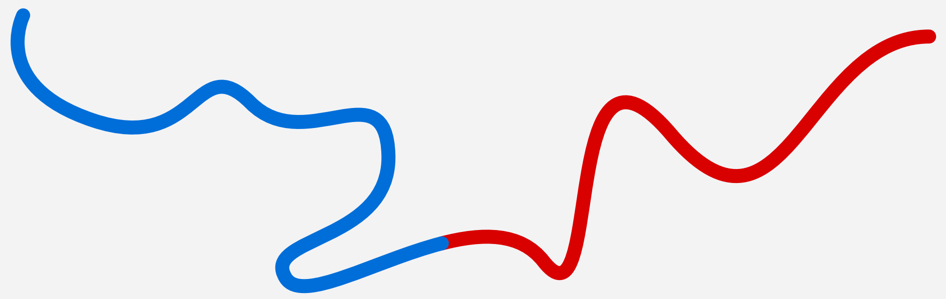
same projection length: $na = Nb$
(maximum end-to-end distance)

same end-to-end distance: $< R^2 > = Nb^2 = C_\infty na^2$

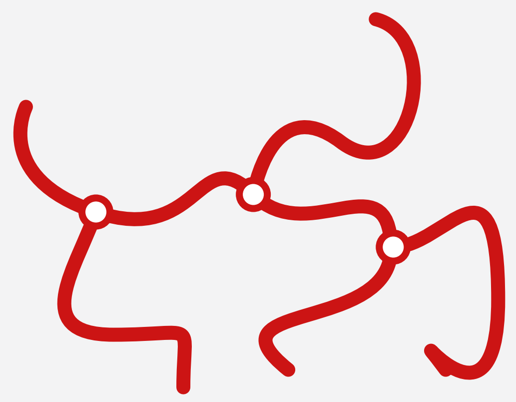
$$b = \frac{C_\infty na^2}{R_{max}} = aC_\infty$$

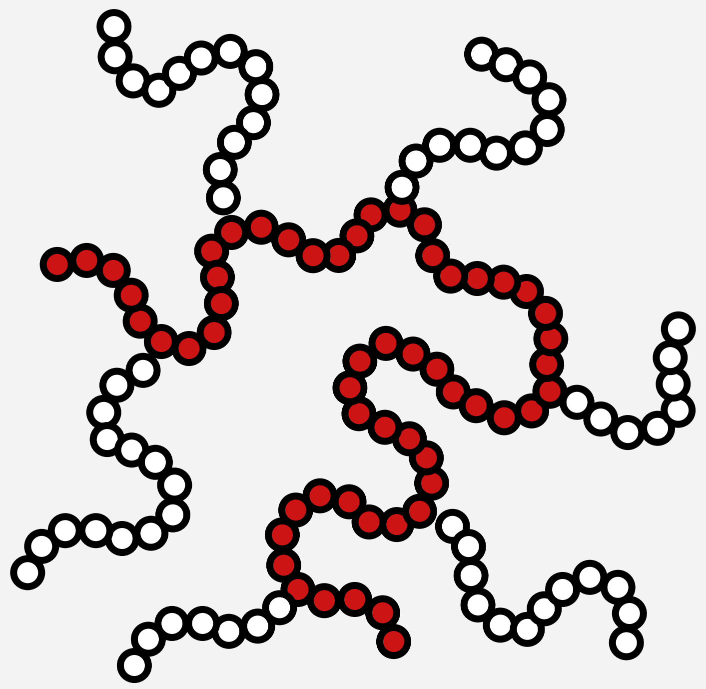
- b **is the Kuhn segment length which increases with chain stiffness (see also Exercise)**

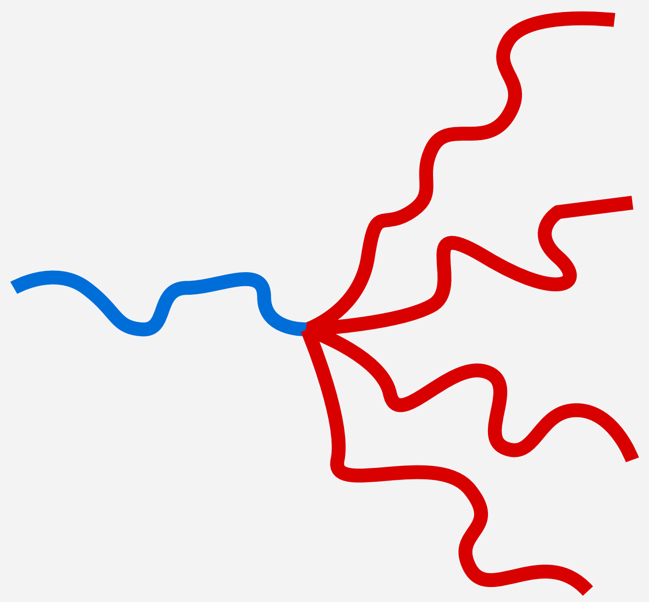
End-to-End Distance: Not Always An Appropriate Measure

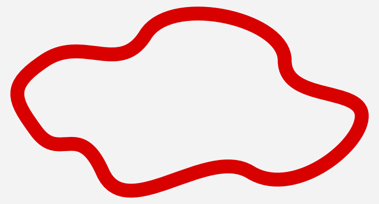

block copolymer

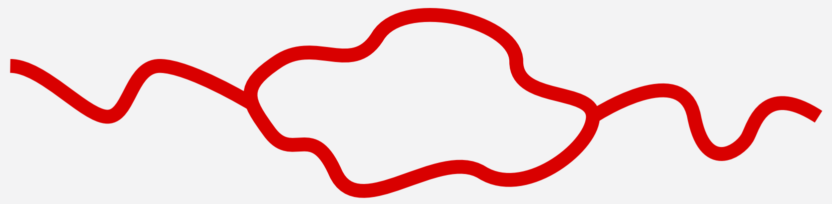

star polymer

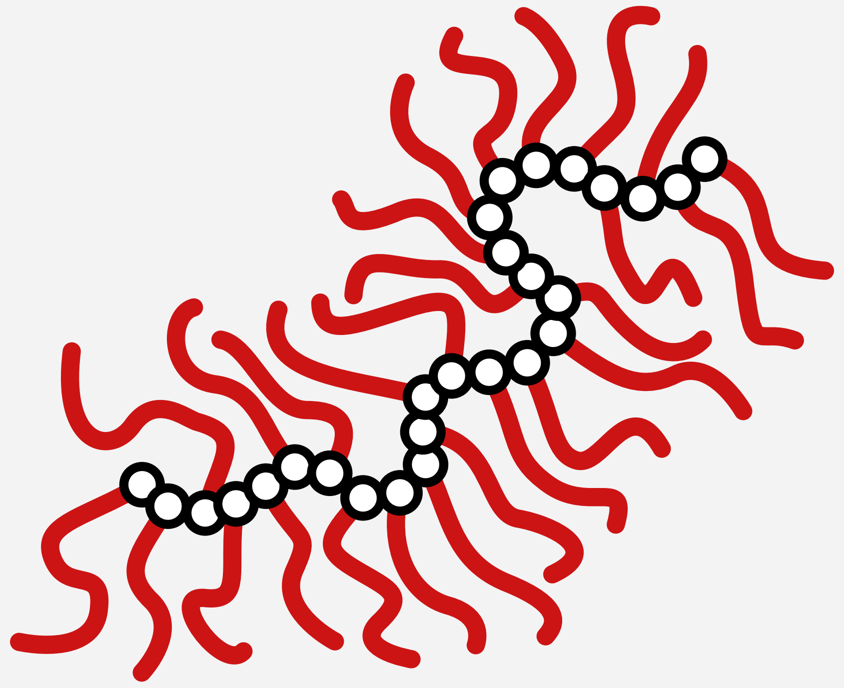

branched polymer


grafted polymer


palm-tree AB_n


ring

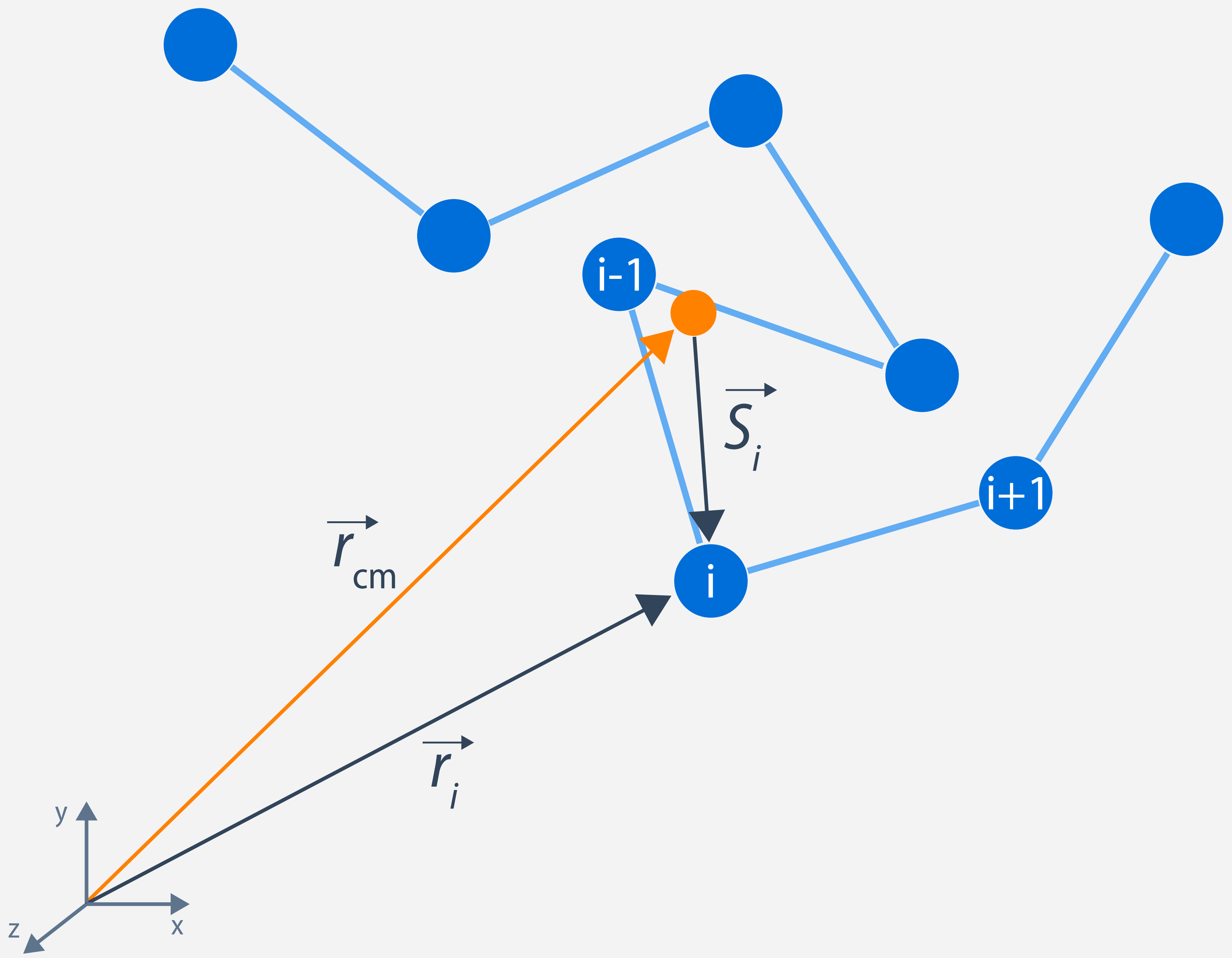

coil-cycle-coil


brush polymer

- **the end-to-end distance of some polymers can not be defined unambiguously**

Radius of Gyration

- **radius of gyration**, R_g, characterises the polymer size of any architecture (including branched or rings)



$$R_g^2 = \frac{1}{N}\sum_{i=1}^{N}(\vec{r}_i - \vec{r}_{cm})^2 = \frac{1}{N}\sum_{i=1}^{N} S_i^2$$

$$\sum_{1}^{N} \vec{S}_i = 0$$

- **the mean-square of R_g relates to the mean-squared end-to-end distance for an ideal linear chain:**

for large n: $$< R_g^2 > = \frac{nl^2}{6} = \frac{< R_n^2 >}{6}$$

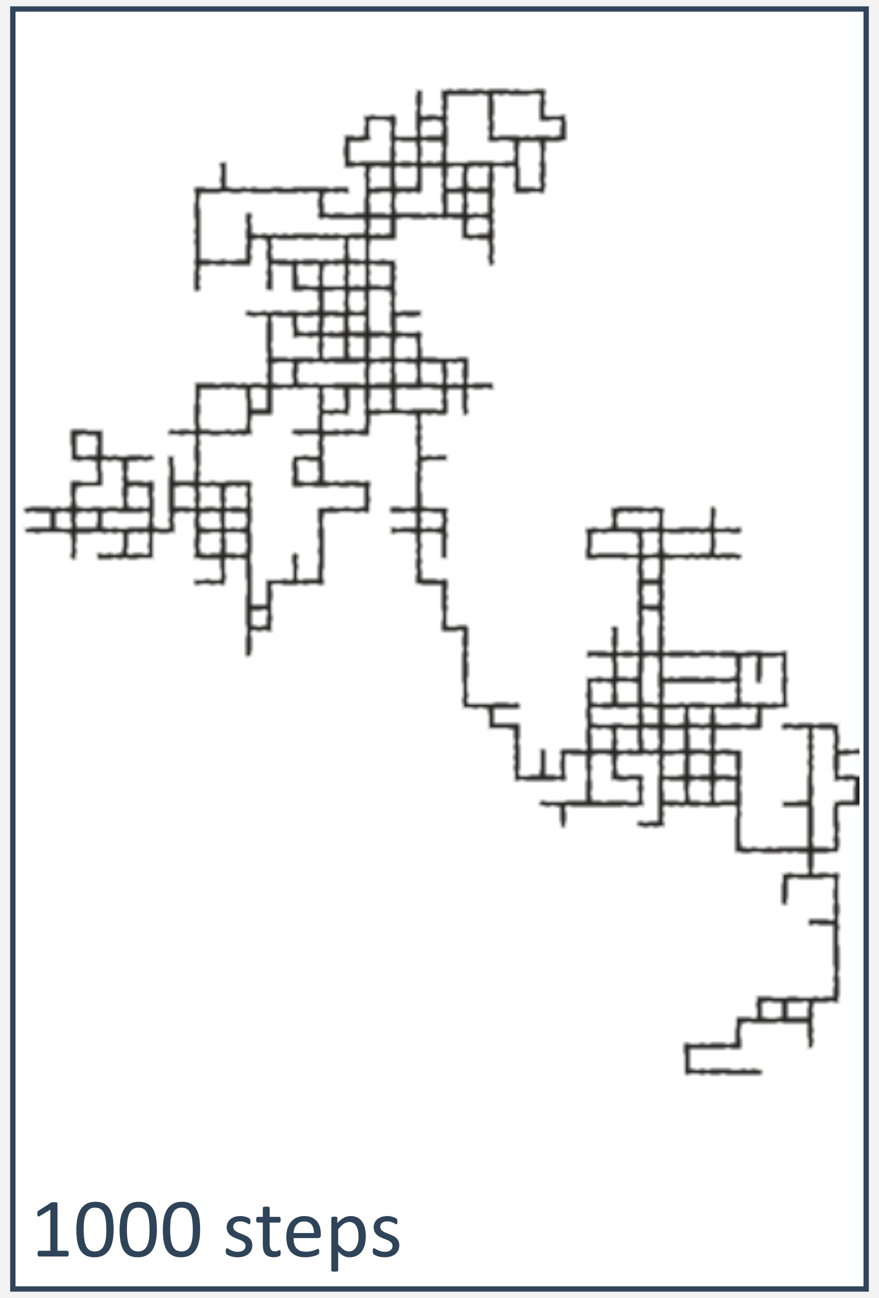
2.2

Real Polymer Chains

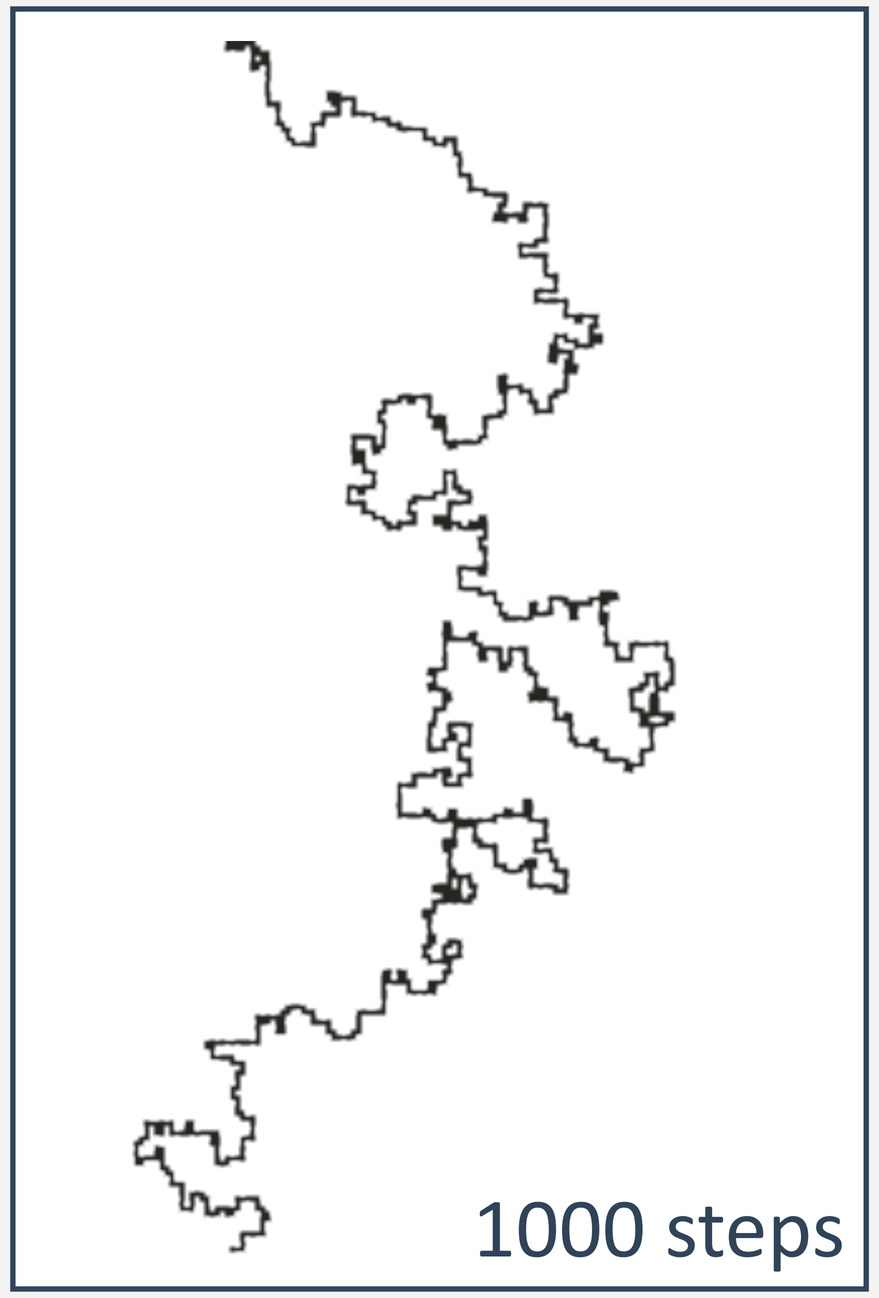
Self-Avoiding Random Walk

- real chain: chain segments have a finite volume and they undergo interactions with their surrounding

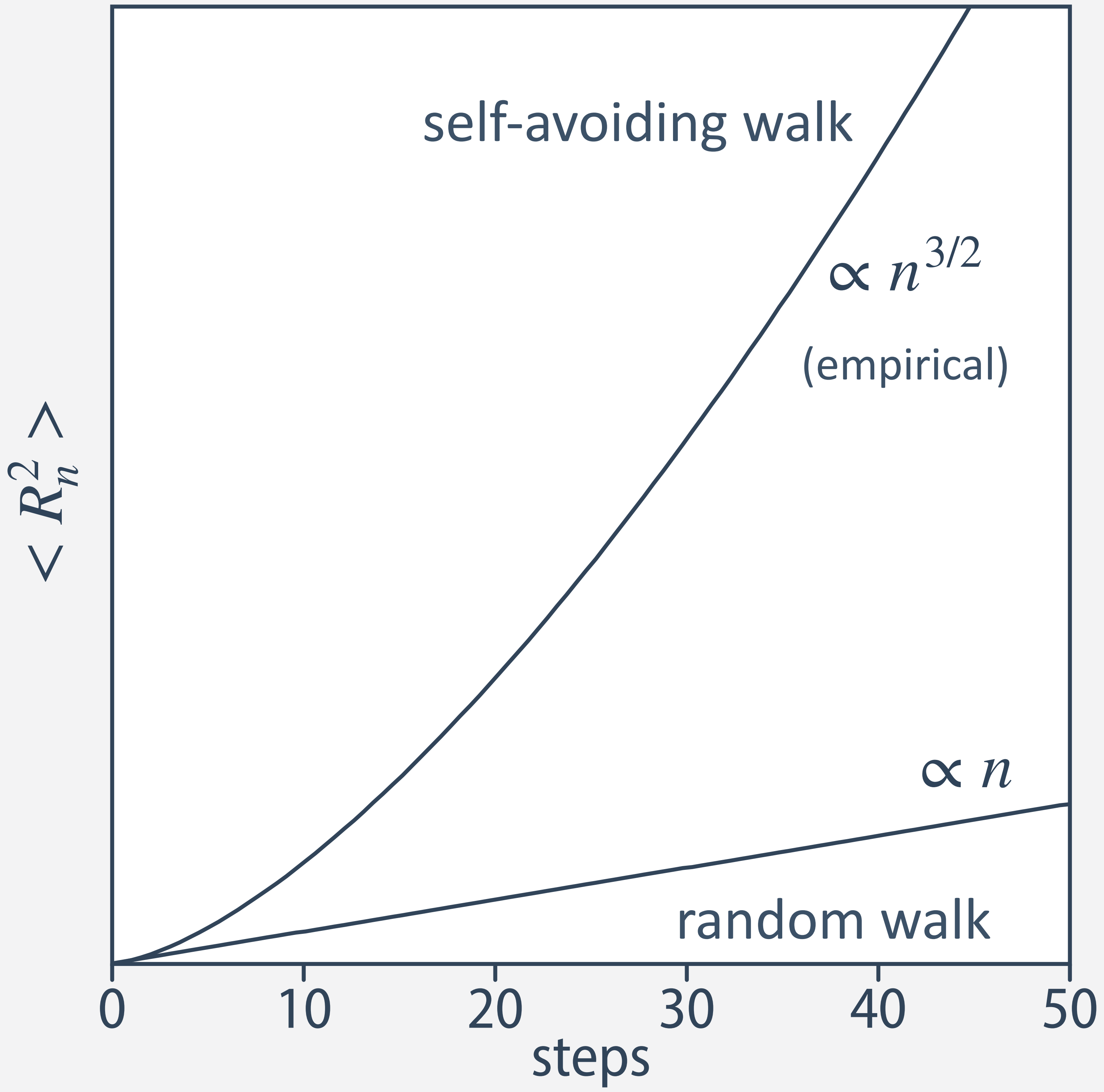
random walk



self-avoiding walk



end-to-end distance

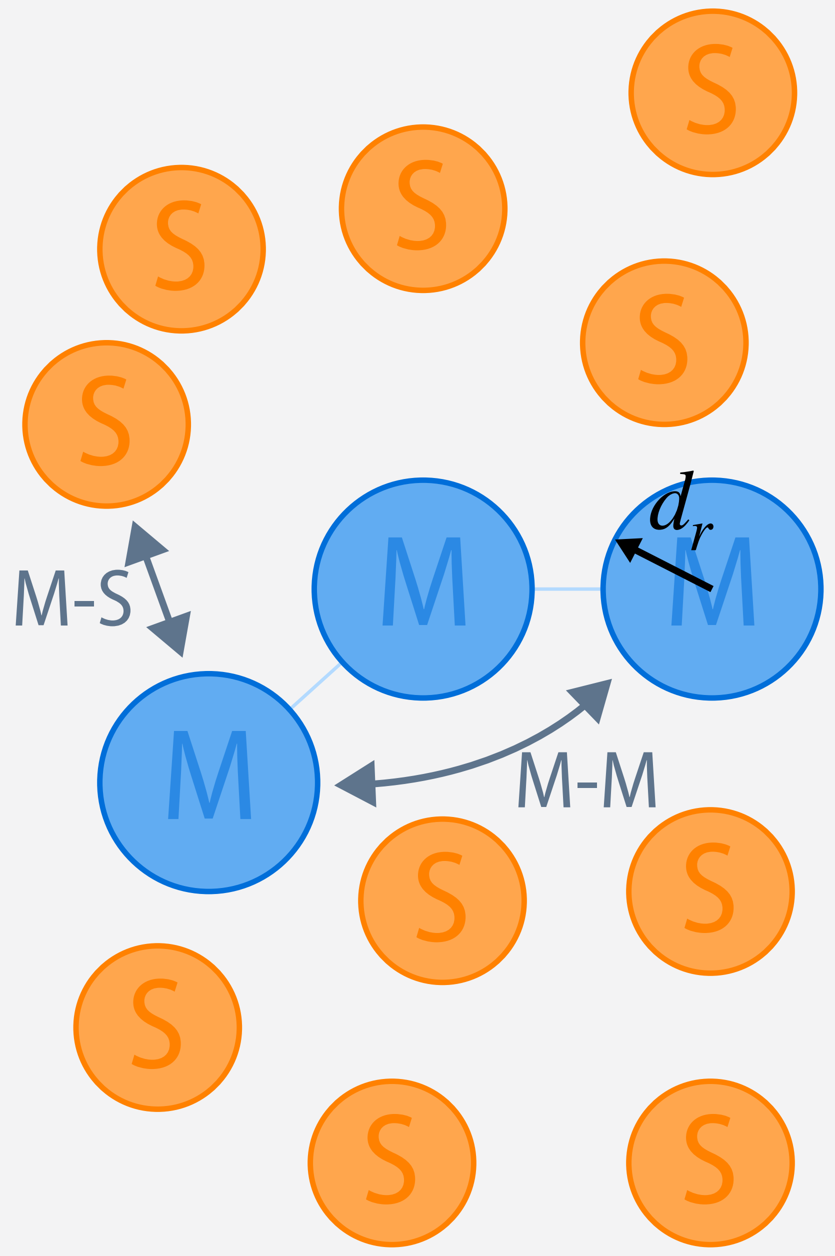


- **real polymer chains may be mapped onto self-avoiding walks (volume excluded by other monomers)**

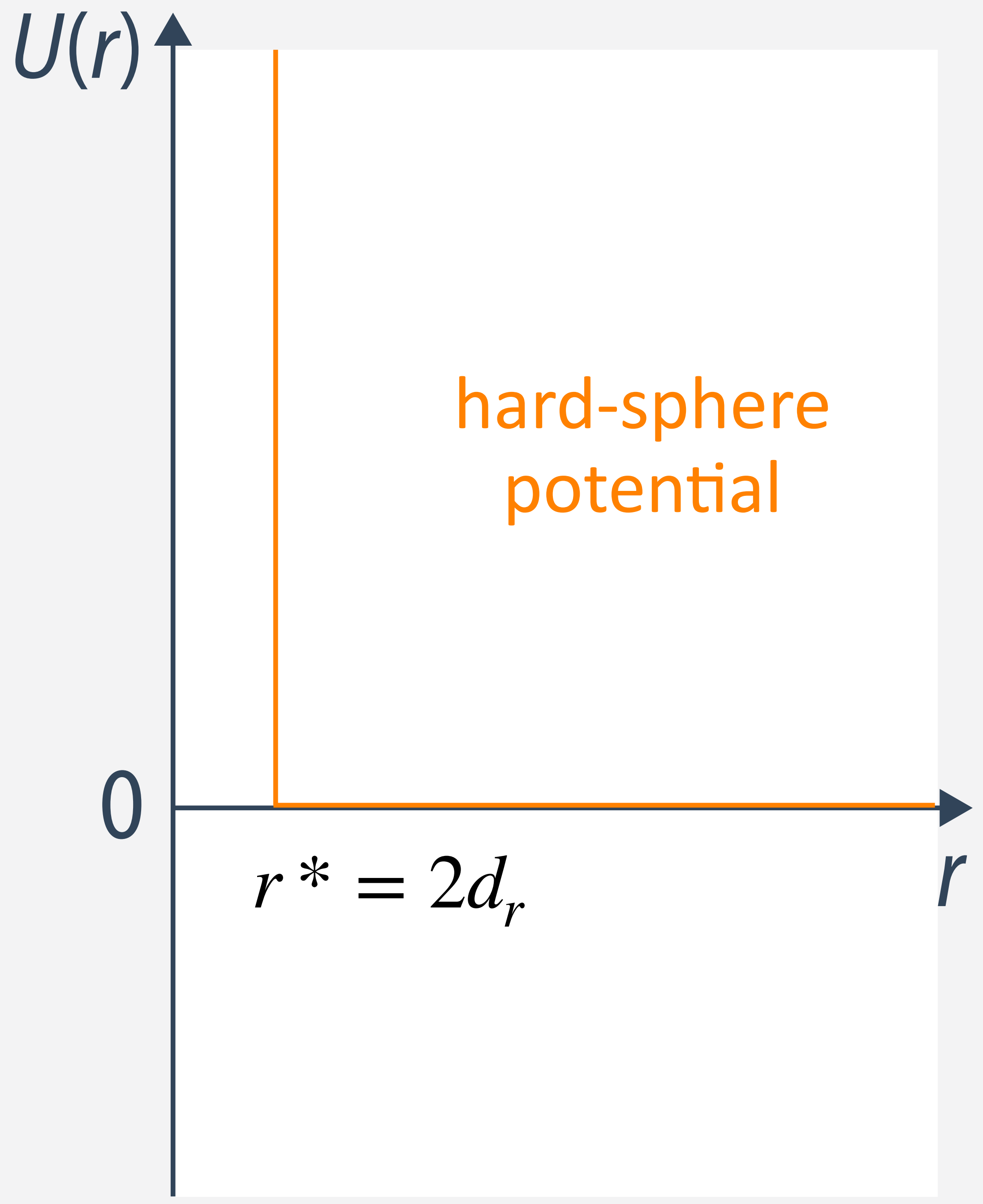
Effective Interaction Potentials

- **polymer conformation is determined by monomer-monomer and monomer-solvent interactions**

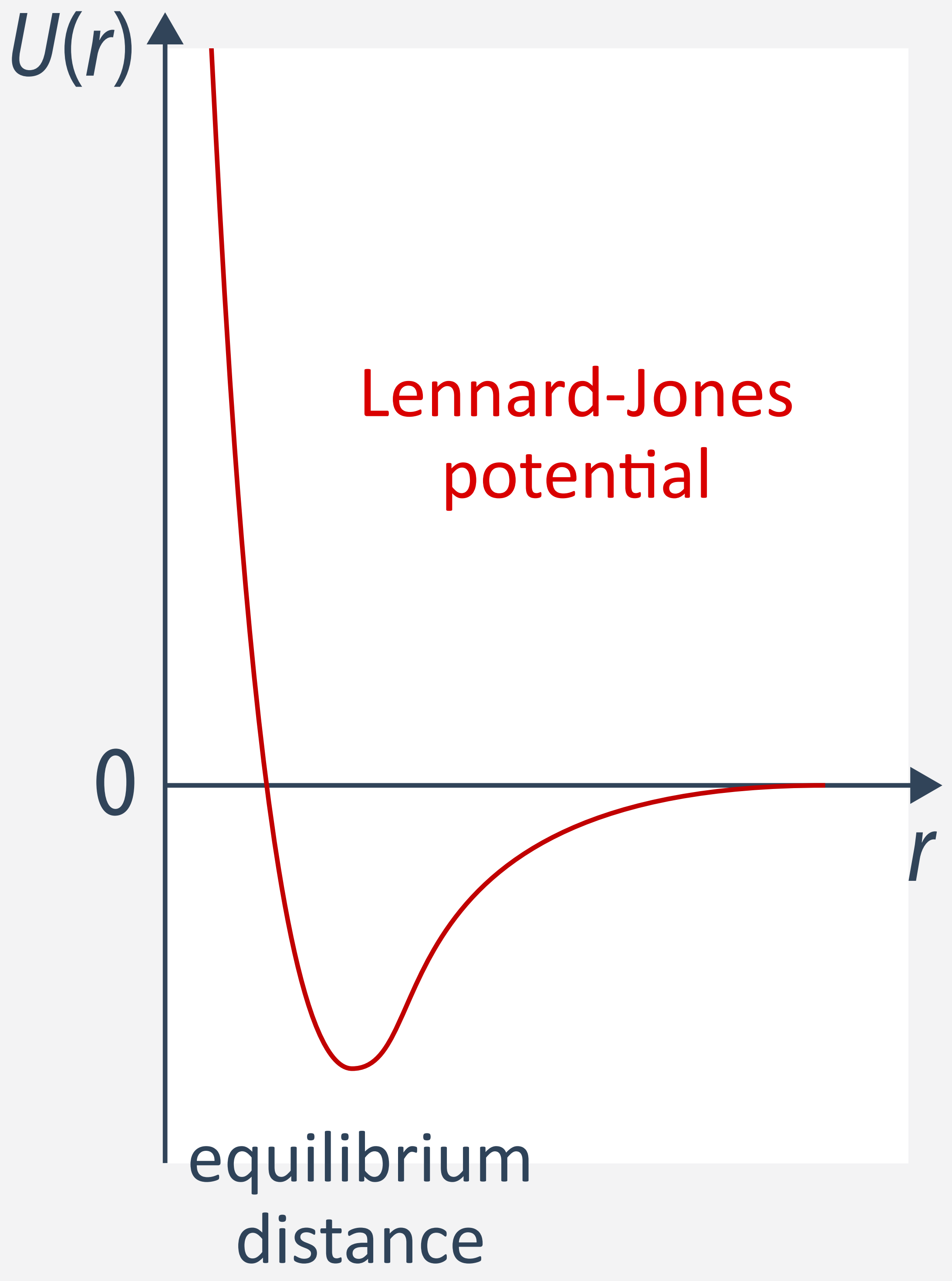
polymers in solution



zero monomer-monomer net interaction



attractive monomer-monomer interaction



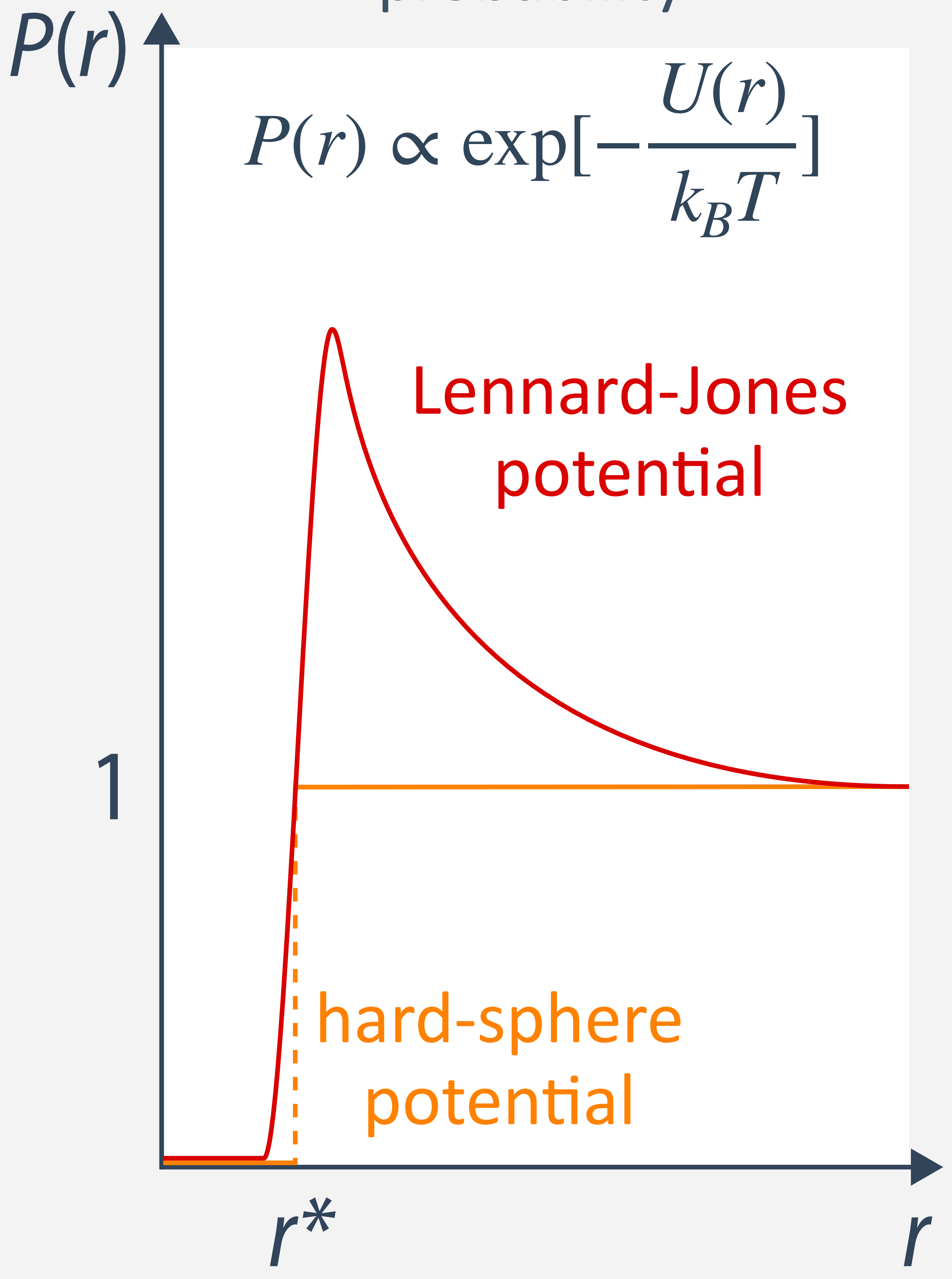
- **Lennard Jones potential: monomer-monomer attraction, but strong repulsion at short distances**

more about the **Lennard-Jones potential** in **Chapter 3.1**

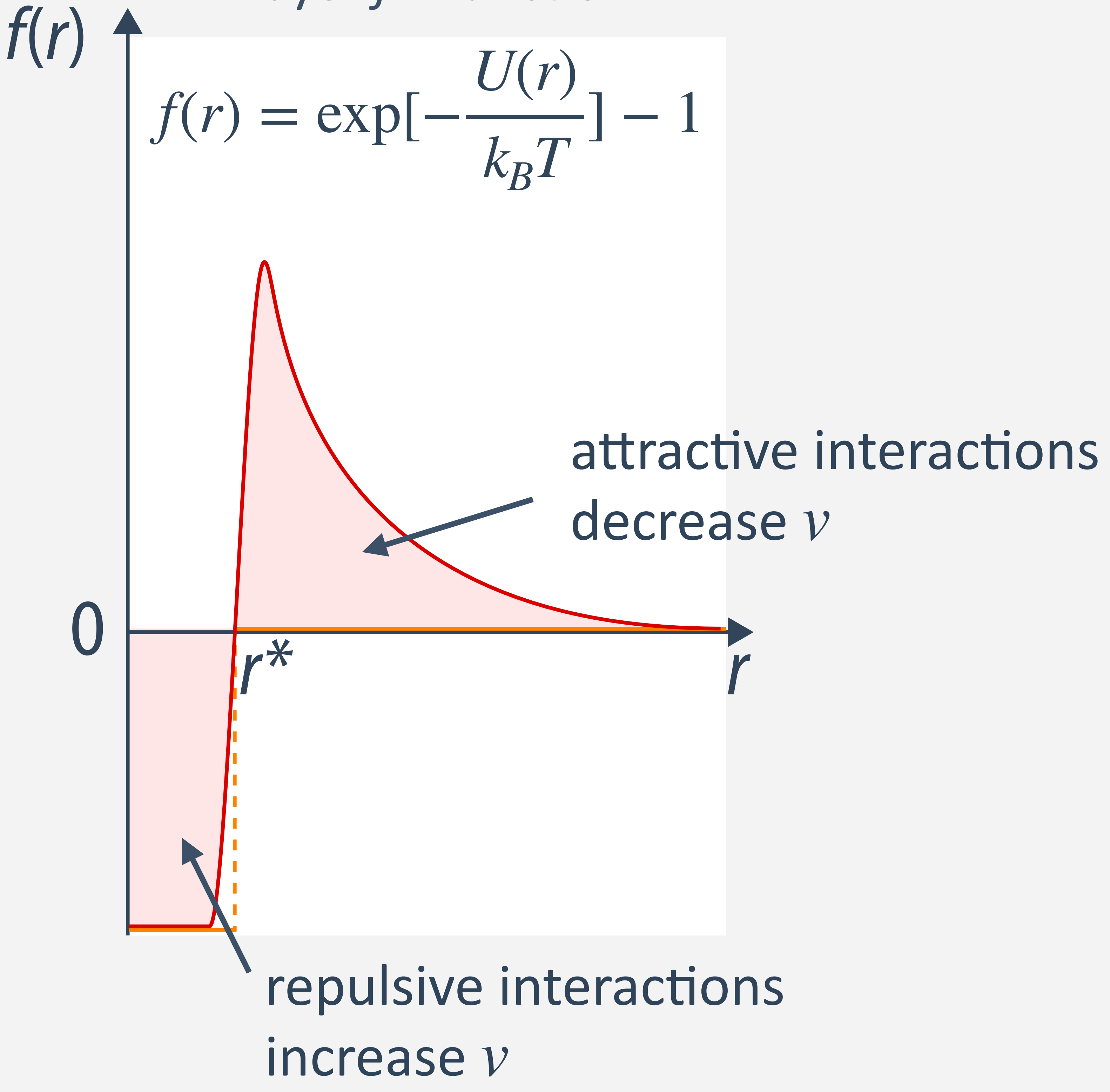
Excluded Volume

- probability of distance r between 2 monomers expressed by Boltzmann's distribution or Mayer f-function

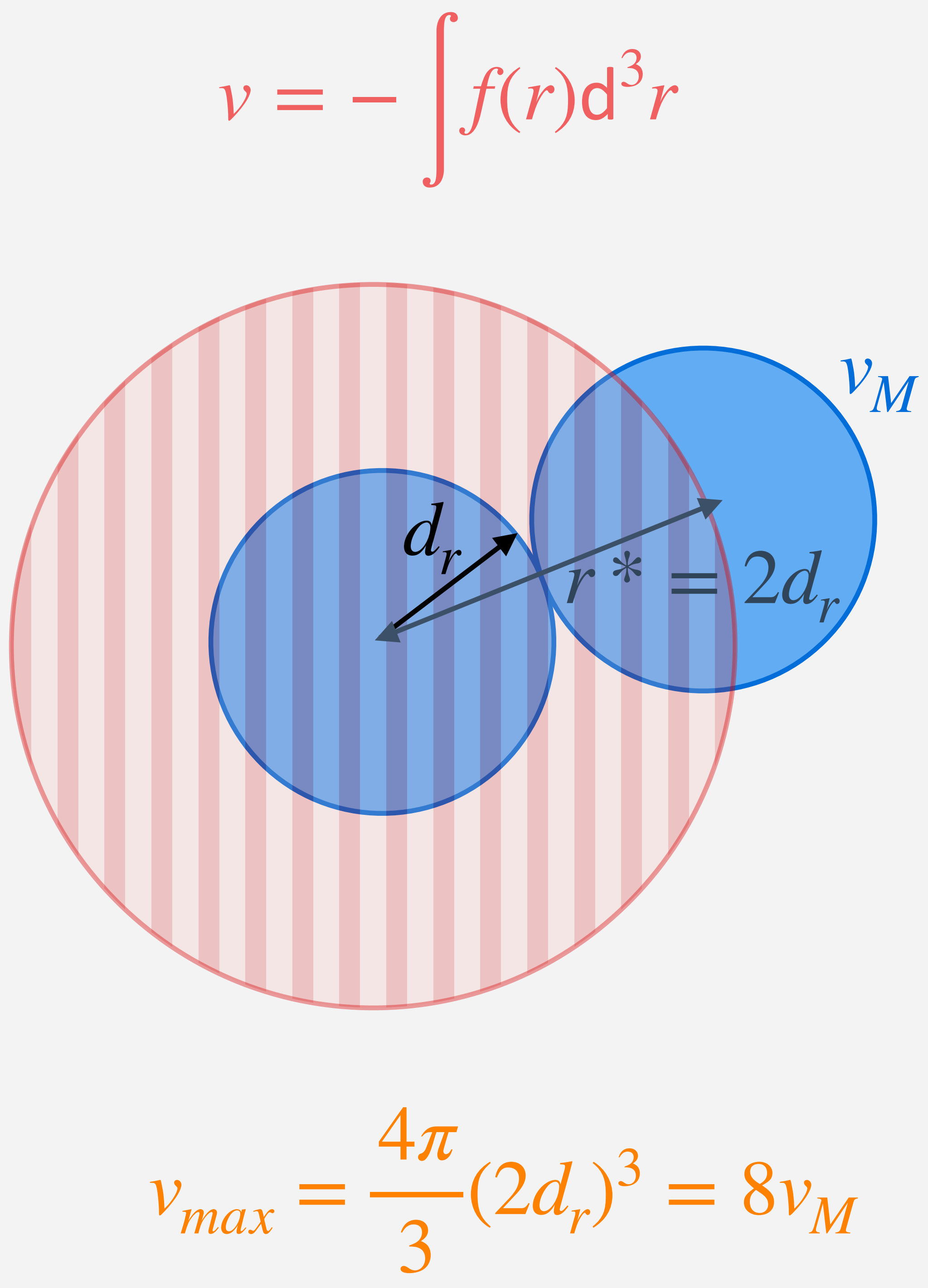
probability



Mayer f—function



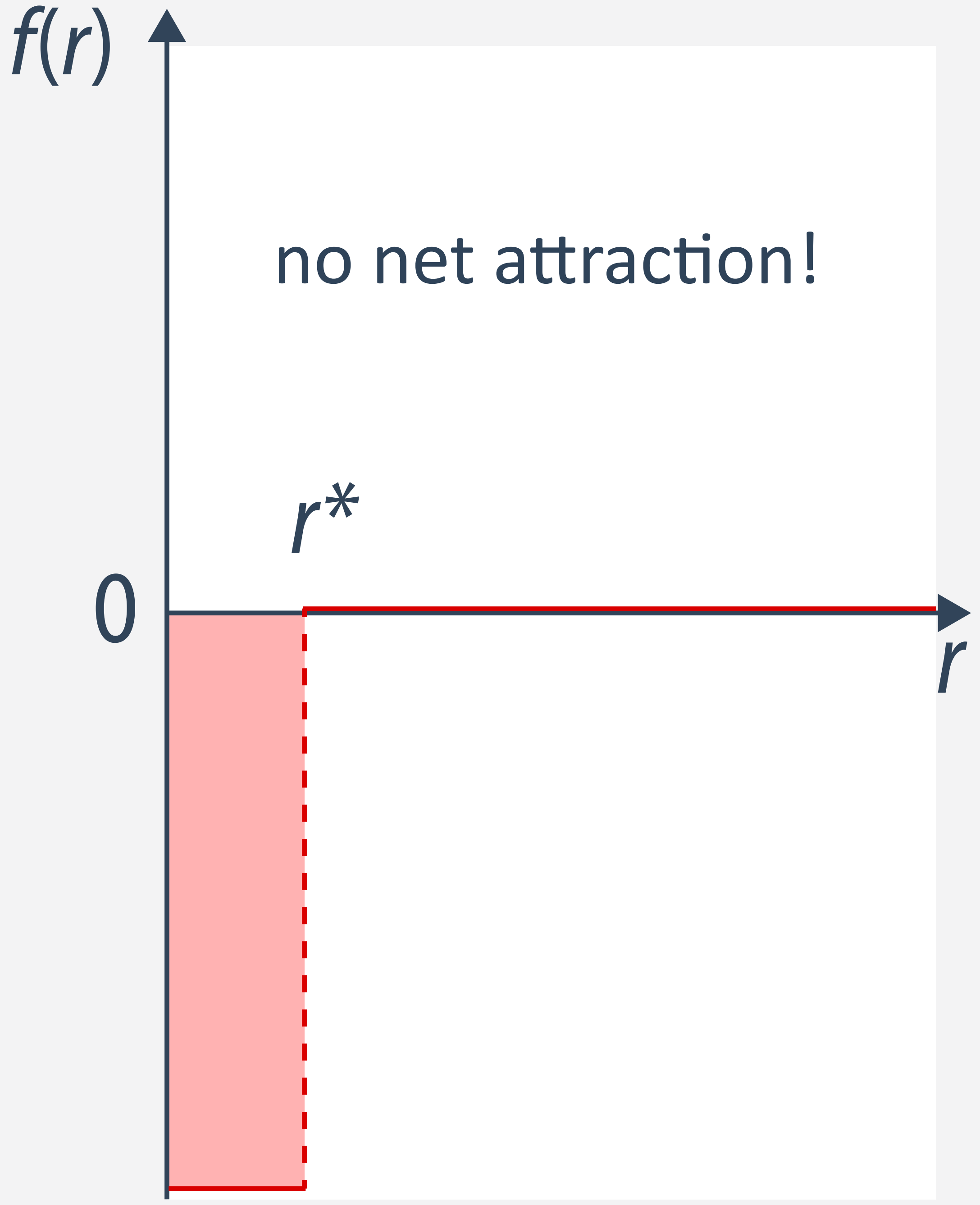
excluded volume



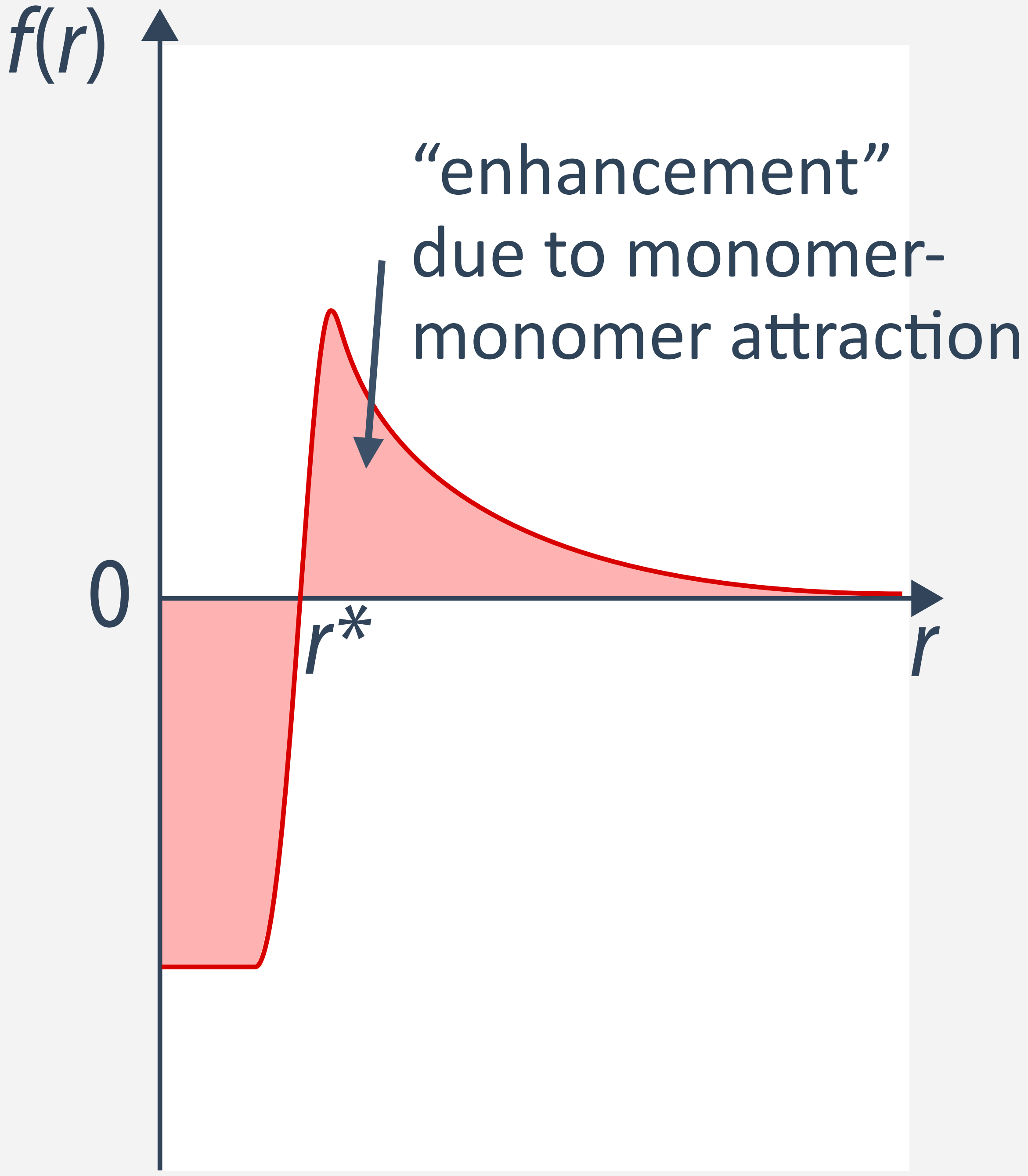
- **excluded volume: space that each chain segment blocks to its surrounding**

Classification of Solvents

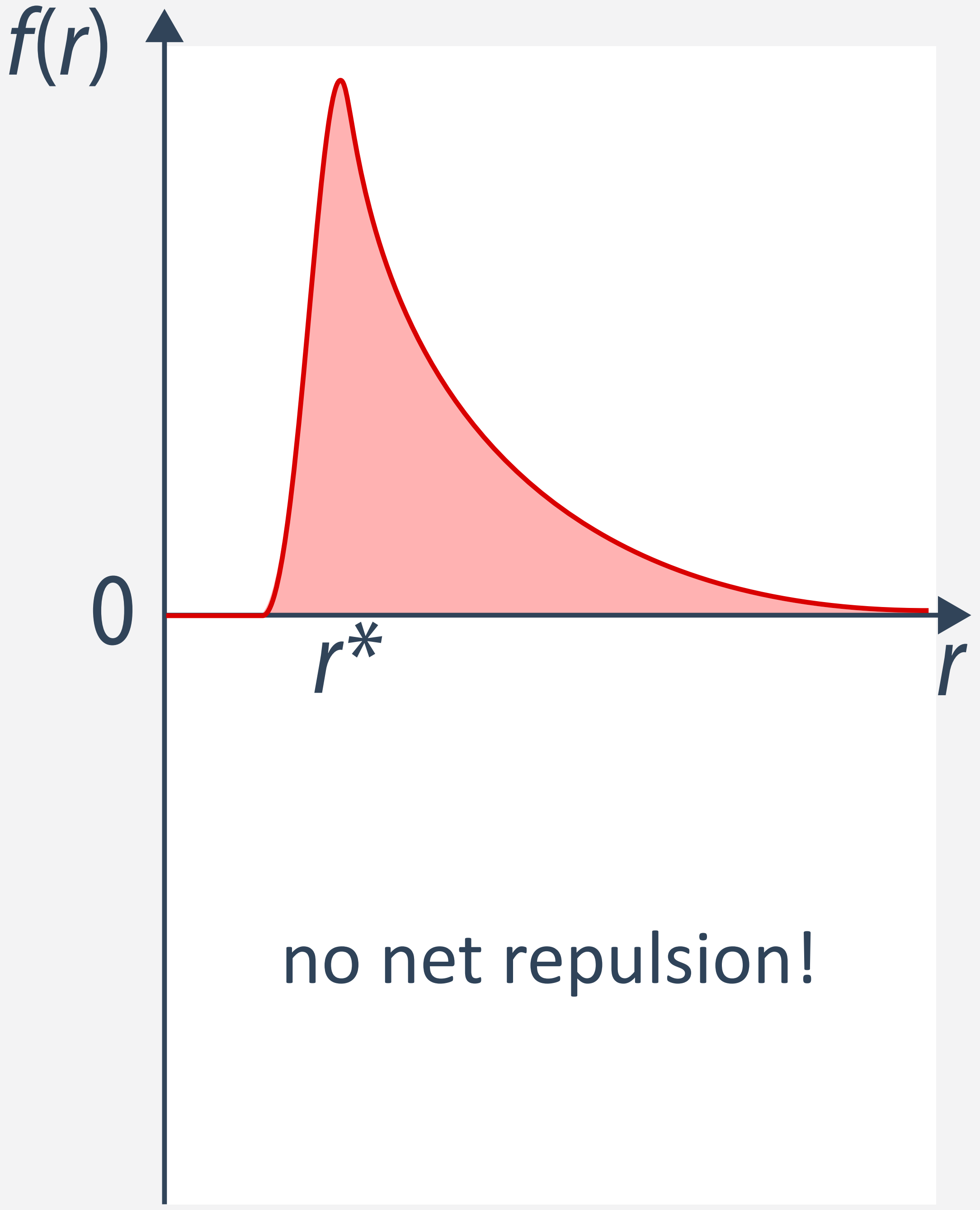
athermal $v = (2d_r)^3$ → **good** $0 < v < (2d_r)^3$ → **theta** $v = 0$ → **poor** $-(2d_r)^3 < v < 0$ → **non-solvent** $v = -(2d_r)^3$



chains are swollen



ideal chain behaviour



chains are collapsed

ethyl benzene & PS

toluene & PS

cyclohexane & PS (T_θ = 34.5 °C)

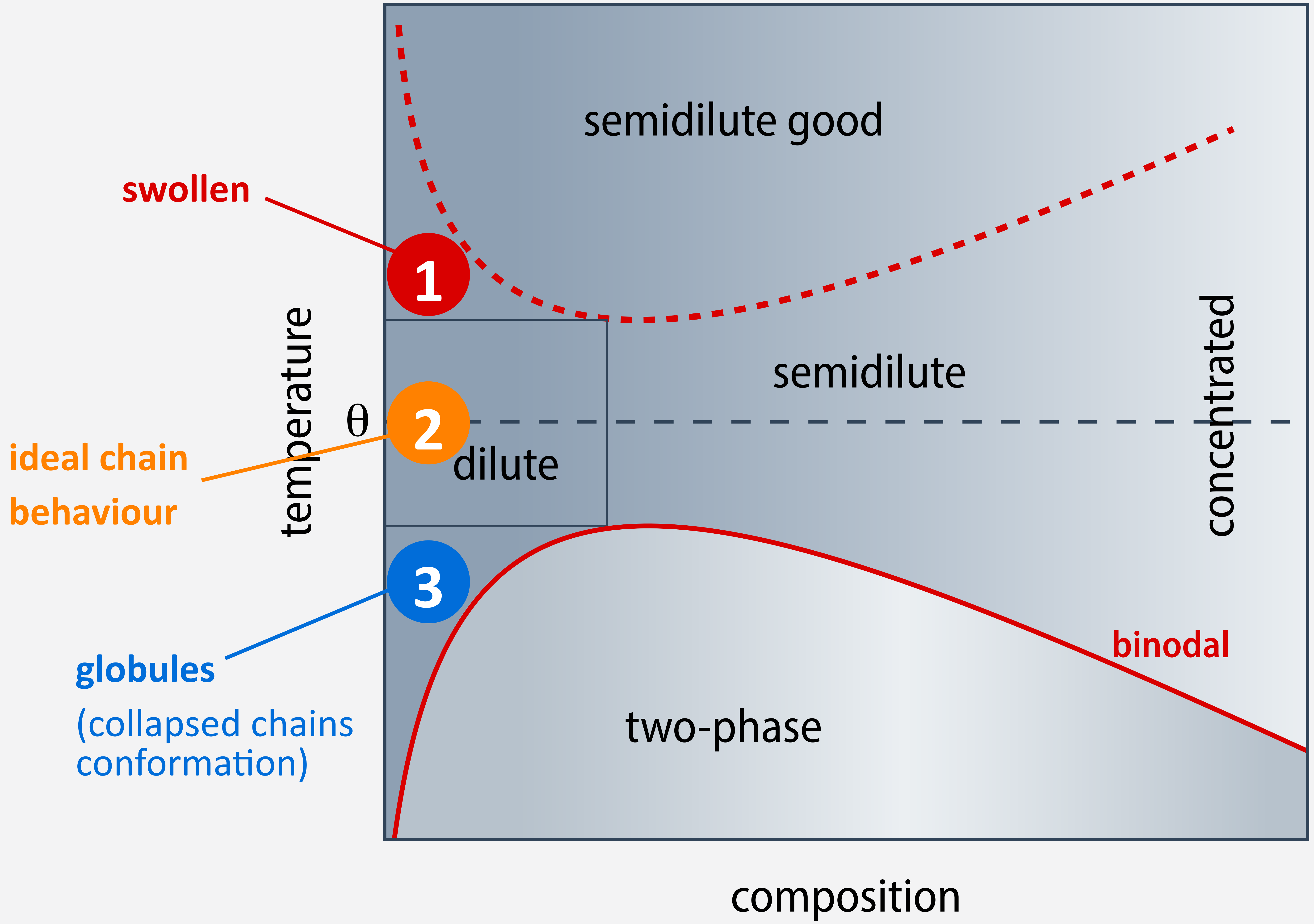
EtOH & PS

water & PS

- **better solvent quality leads to polymer coil expansion, and a lower segmental density in the coil interior**

Phase Diagram of Polymer Solutions

- at sufficiently low concentration, chains are well dispersed and do not phase-separate from the solvent



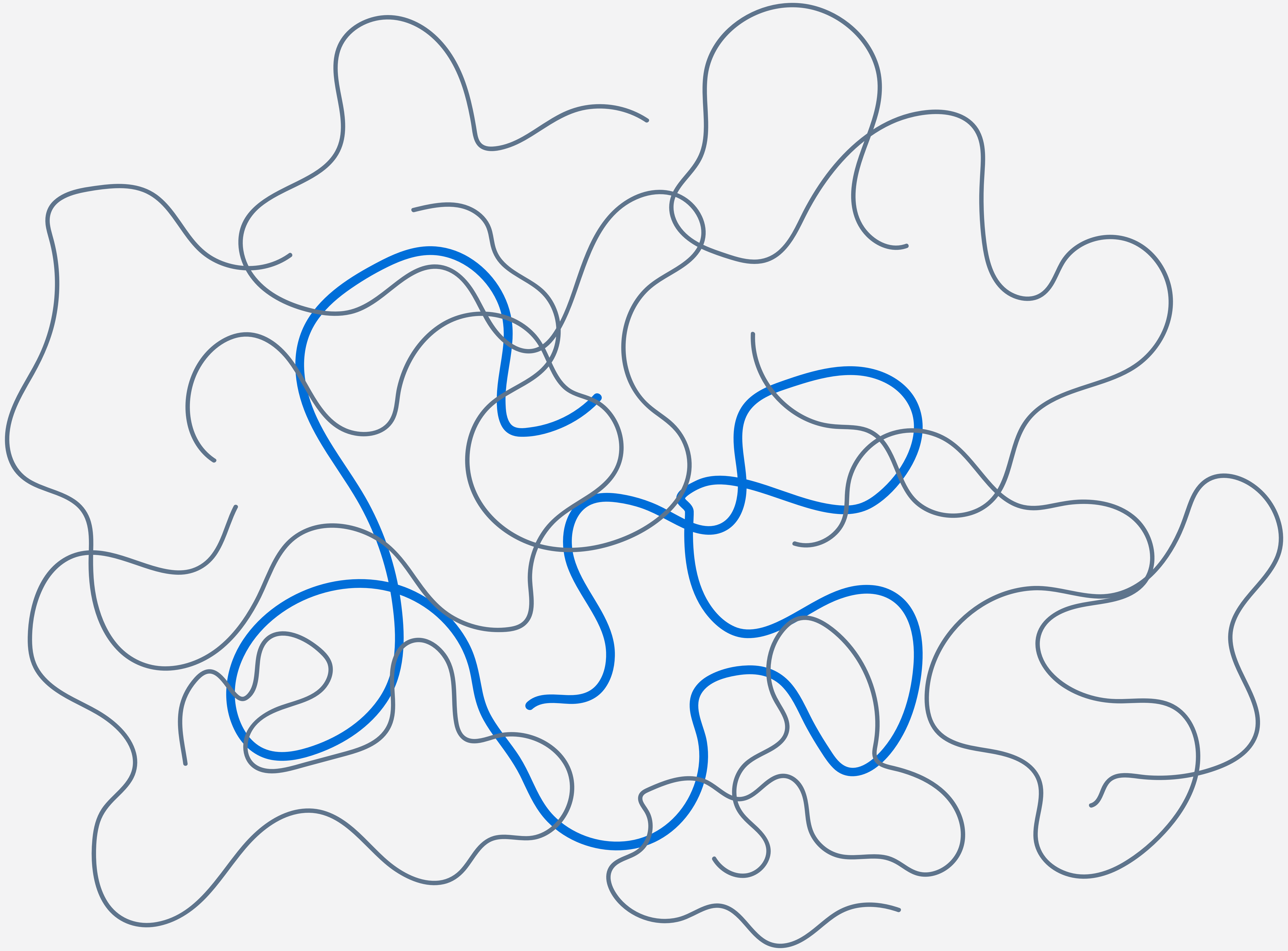
example:

cyclohexane & PS
T_θ = 34.5 °C

- **at the θ-temperature, polymer behave ideal and are miscible with the solvent at any concentration**

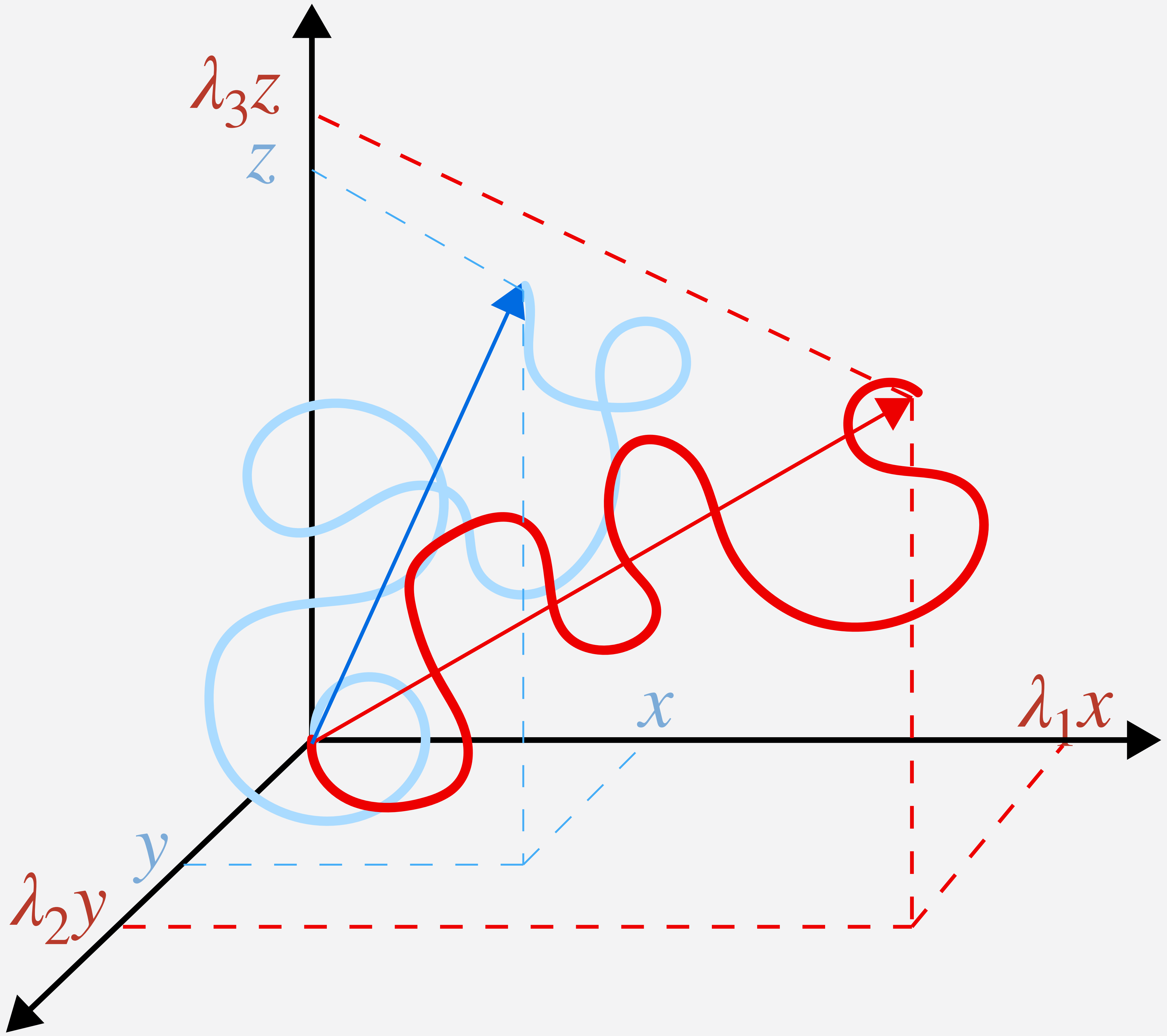
Omnipresence of the θ-State in Polymer Melts

- polymer melts constitute an athermal state (identical “monomer-monomer” & ”monomer-solvent” interactions)
- same tendency of all chains to expand
- as a result, no chain can expand (excluded volume interactions are screened by overlapping segments of other coils)



- **polymer chains adopt their random coil conformation in polymer melts at any temperature!**

Outlook



How does the end-to-end distance change upon deformation?

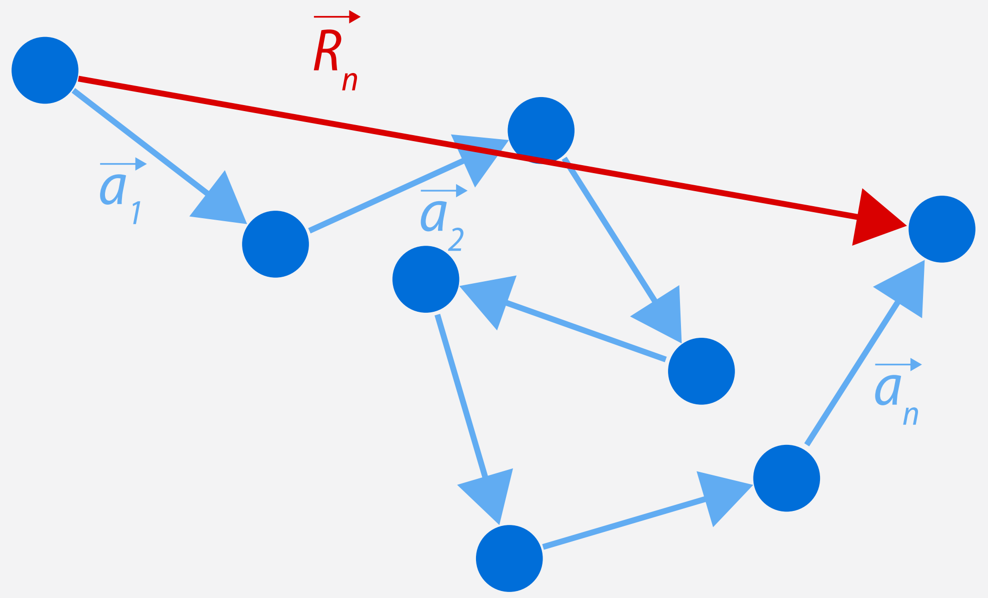
see Chapter 4.1 (Rubber Elasticity)

Learning Outcome

- every possible conformation of an ideal chain can be mapped onto a random walk
- a common feature to all ideal chain models is that size scales with $\sqrt{M}$ for large n
- restrictions in available chain conformation with respect to the freely jointed chain is expressed using C_∞, a measure of chain “stiffness”.
- accurate description of all polymer melts and certain behaviour in solution with the ideal chain model

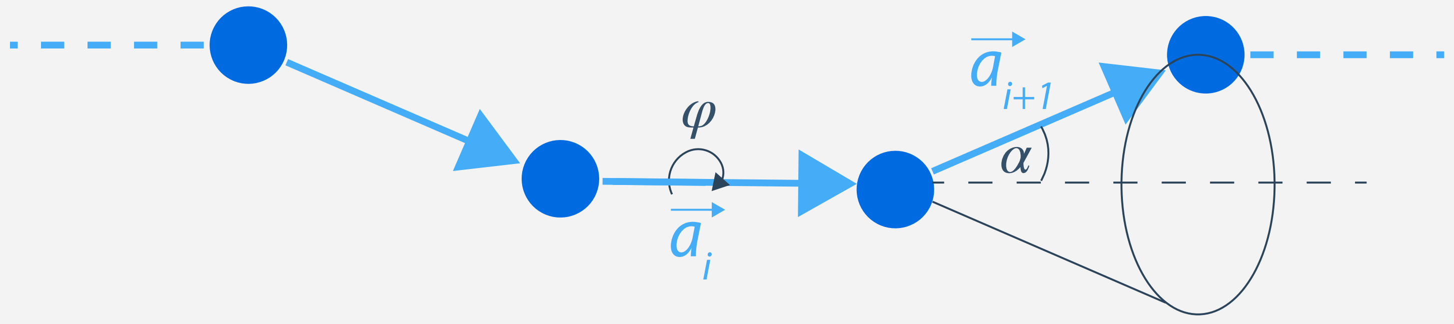
$$\boxed{< R_n{}^2 > \cong C_\infty n a^2}$$

freely jointed chain



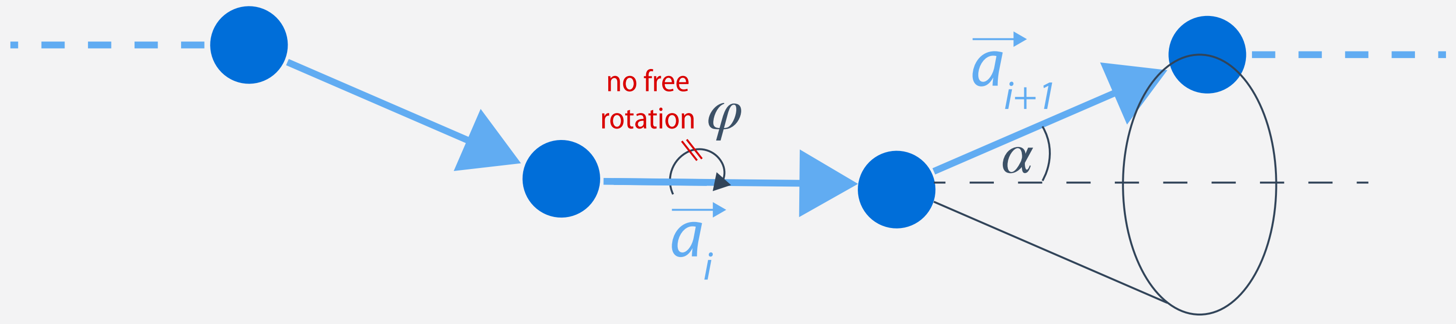
no torsion and bond angle restriction

freely rotating chain



bond angle restriction

hindered rotating chain



torsion and bond angle restriction

$C_\infty = 1$

increased chain rigidity