

Rotational Isomeric State Model

- fraction of *gauche* increases with T
- - factor 2 because 2 gauche states (g^+ , g^-), only 1 trans
- $\Delta E_g \approx 1\text{-}2 \text{ kJ/mol}$
 - \rightarrow at r.t. $f_g \approx 0.5$

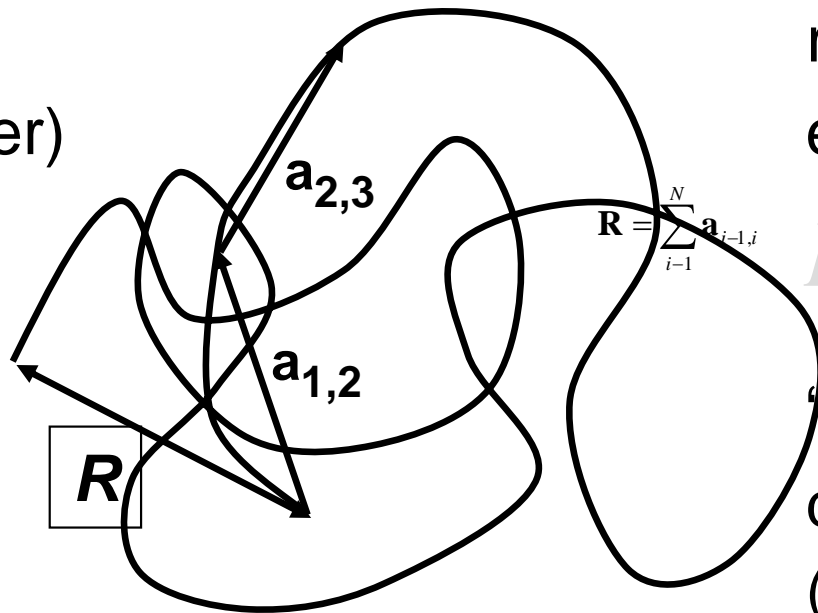
Rotational Isomeric State Model

- RIS model – an approximation
- neglects all dihedral (torsion) angles other than 180° and $\pm 60^\circ$ (Flory)

Random Coil

- Polymer chain in solution, melt, or amorphous glass

segment
(monomer)



root-mean-square
end-end distance:

$$R_0 \equiv \langle R^2 \rangle^{1/2} = aN^{1/2}$$

“random walk”:

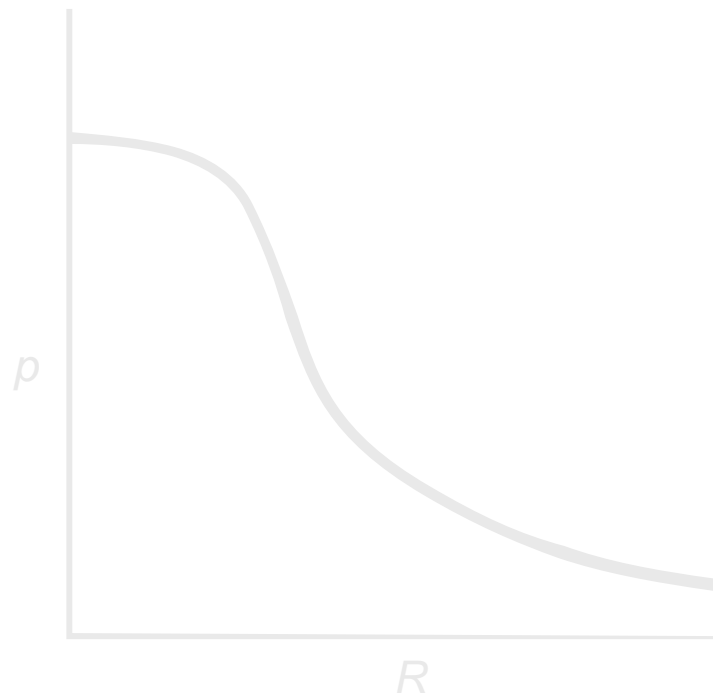
distance \propto no. of steps

(strictly true only for “ideal chains”)

- **End-to-end distance:** $\mathbf{R} = \sum_{i=1}^N \mathbf{a}_{i-1,i}$

Gaussian Coil

- “ideal chain” = freely-jointed non-self-avoiding chain
 - freely jointed: any angle between a_i and a_{i+1} equally probable
 - non-self-avoiding: chain can overlap with itself
- Distribution of end-to-end distances
 - e.g. for one chain over time – Gaussian distribution



Persistence Length

- Theory of worm-like chains (Kratky and Porod)
- Persistence length is the distance along the chain at which orientational correlation with the starting segment drops to $1/e$.
- Persistence length is a measure of the **rigidity** of a polymer chain

