Ground-state properties of thick flexible polymers

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Abstract

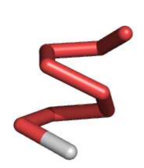
We investigate ground-state properties of a simple model for flexible polymers, where the steric influence of monomeric side chains is effectively introduced by a thickness constraint. Thickness is defined via the global radius of curvature. From parallel tempering and flat-histogram computer simulations, we find a strong thickness dependence of the conformational topology of the ground-state structures. A systematic analysis for short polymers allows for a thickness-dependent classification of the dominant ground-state topologies. It turns out that helical structures, strands, rings, and coils are natural, intrinsic geometries of such line-like objects.

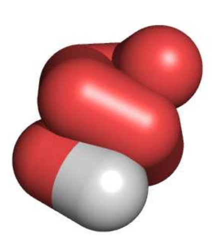
Model – Interaction Potential and Thickness

- flexible homopolymer with fixed bond length, off-lattice
- pure Lennard–Jones interaction

$$E_{LJ}(r_{ij}) = 4 \sum_{i,j=i+2} \left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right).$$

- Here: $\sigma = 1$, i.e. $E_{LJ}(r_{ij}) = 0$ for $r_{ij} =$ bond length





→ How to implement thickness?

Global curvature, thickness, and the ideal shapes of knots

O. Gonzalez and J.H. Maddocks: Proc. Natl. Acad. Sci. USA **96**, 4769 (1999)

- **Thickness of a curve** d: the (constant, maximal) radius of a smooth, non-self-intersecting tube centered on the curve
- **Global radius of curvature** r_{gc}: smallest radius of all circumcircles defined by any three points on the curve

"...the notion of global radius of curvature provides a concise characterization of the thickness of a curve, ..."

$$d = r_{gc}$$

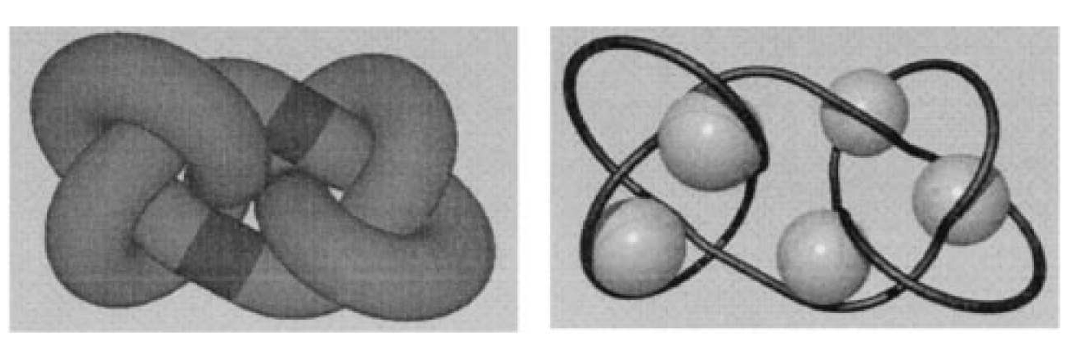


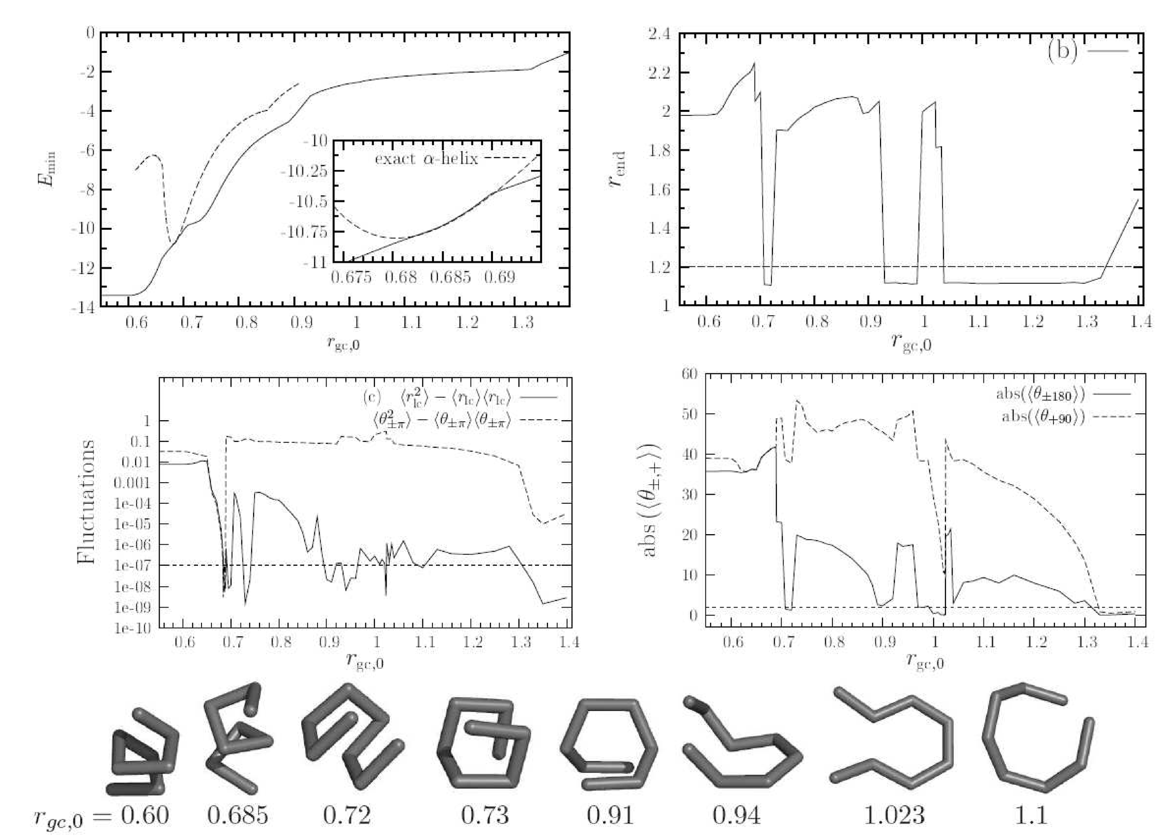
Figure from Gonzales, Maddocks. "Interpretation of the minimum global radius of curvature for a numerically computed ideal knot. **Left: The tube interpretation.** The minimal value of r_{gc} is the radius of the tube shown here. **Right: The sphere interpretation.** Any spherical shell of radius less than the minimum value of r_{gc} cannot intersect the curve at three or more points."

Observables and Examples

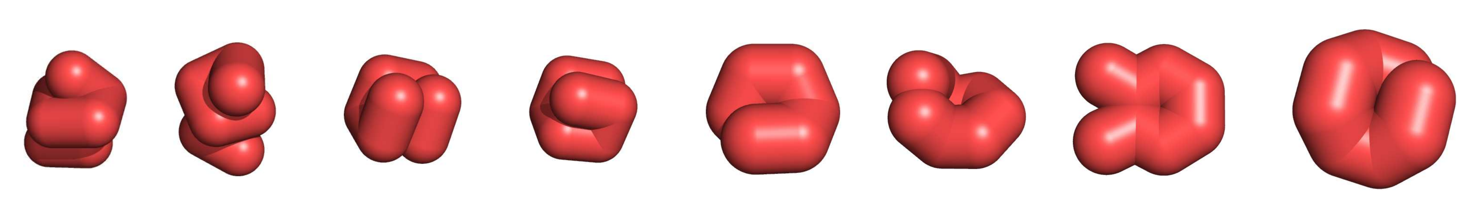
- **Observables**
  - **Total Energy**
  - **End to End Distance** r_{end}
  - **Radius of Gyration** $r^2_{gyr} \propto \sum_i (x_i - x_{cms})^2$
  - **Radial Distribution Function** $P(r_{ij})$
  - **Local Radii of Curvature** (related to Bond Angle) $r_{c,i} := r_{c,(i,i+1,i+2)}$
  - **Torsion Angles** (w/wo orientation)
- **Examples of Ground-State Properties**
  - "Closed": $r_{end} \to 1.12\ldots$ (minimum of LJ potential)
  - κ_0: $r_{c,i} =$ const., i.e. $\langle r_c \rangle^2 - \langle r_c \rangle \langle r_c \rangle \to 0$
  - τ_0: $\theta_{i,\pm} =$ const.
  - "planar": $\langle \theta_+ \rangle \to 0$
- **Illustrating Examples**
  - perfect helix: κ_0, τ_0
  - bended saddle shaped ring ("windschiefer Kreis"): κ_0, "closed"
  - planar ring: κ_0, "closed", "planar"

Ground-State Analysis $N = 8$

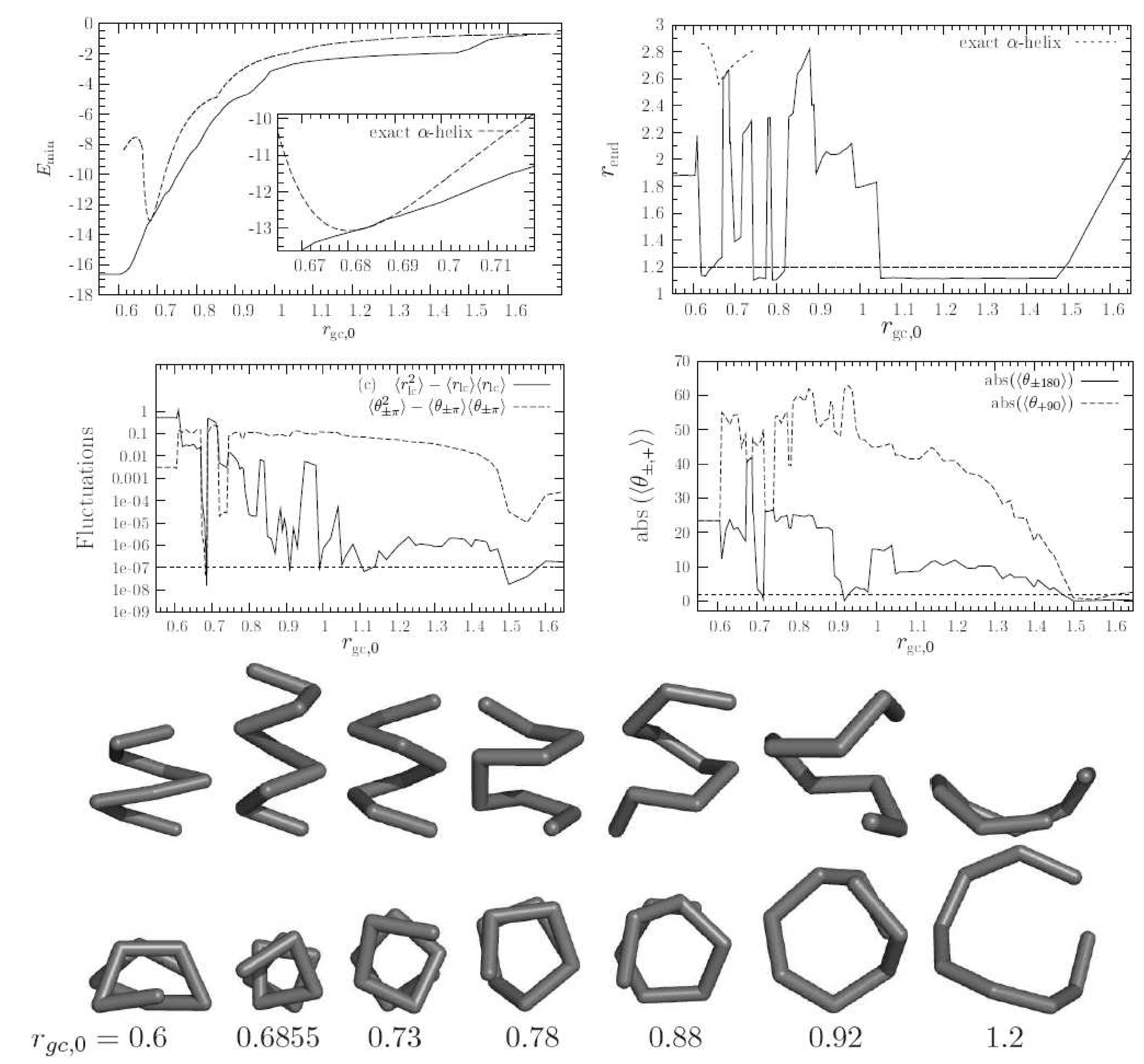
Charakteristics of ground states with increasing thickness



How they "really" look (thickness increasing from $r_{gc} = 0.6$ to 1.2)

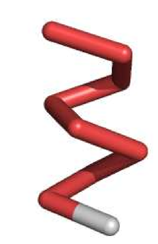


Ground-State Analysis $N = 9$



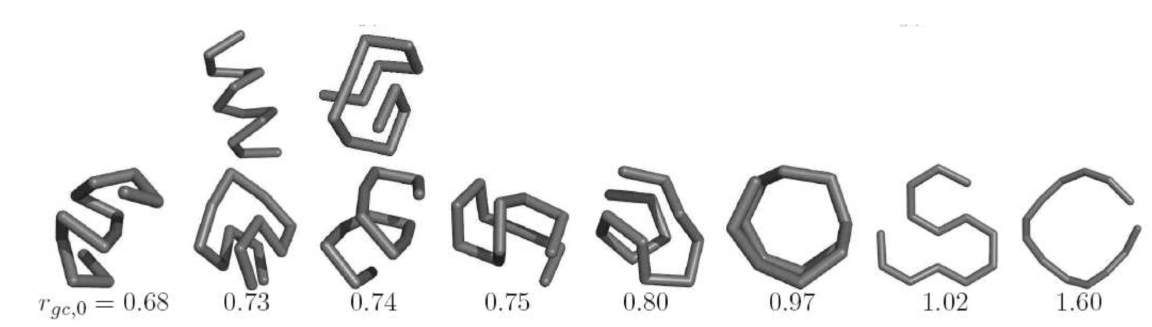
The α-Helix with $N = 9$ Monomers

Exact α-Helix
- About 3.6 monomers/turn
- $r_c = 0.688\ldots$
- $\theta = 41.66°$



Ground State at $r_{gc,0} = 0.68$
- 3.55 ... 3.6 monomers/turn
- $r_c \in (0.680 \ldots 0.688)$
- $\theta = 41.05° \ldots 41.62°$

Ground States $N = 13$



Upper row: Conformatitions with energy slightly above ground-state energy. **Lower row:** Ground-state conformations.

Summary

- Simple, general model with thickness constraint
- Differentiation between structural classes (controlled by thickness)
- Helicees, turns, rings
- α-helix exists in model without H-bonds

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