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Advanced School and Conference on Knot Theory and its Applications to Physics and Biology

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Random Knots and Polymers

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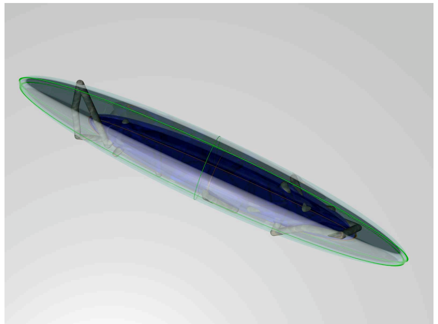
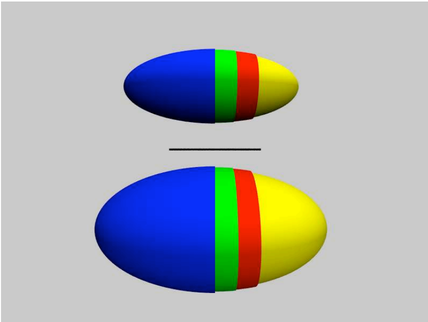
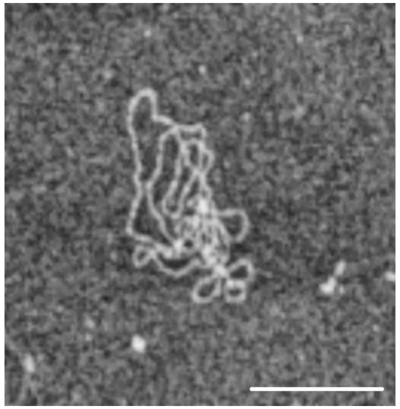
May 19, 2009

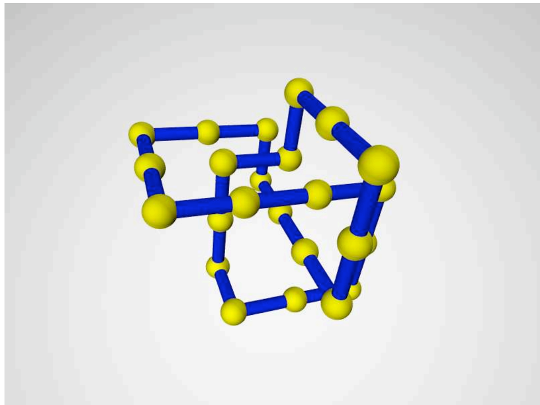




Outline

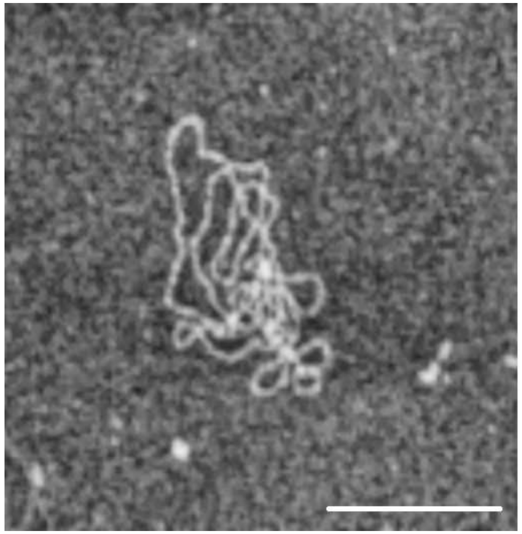
- Random polygons and polymers
- Measuring size and shape
- Open problems

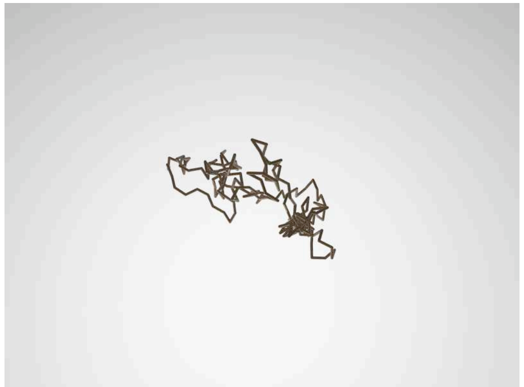




Random polygons and polymers

- Polymers are long chains of molecules made of repeated units (e.g. DNA, proteins, plastics)
- Polymers derive their properties from their structure
- Researchers study systems of polymers and single polymers
- We concentrate of studying the structure of single polymer chains, in particular, closed polymers which can form knots
- Basic idea - single polymer chains can be modeled by random chains



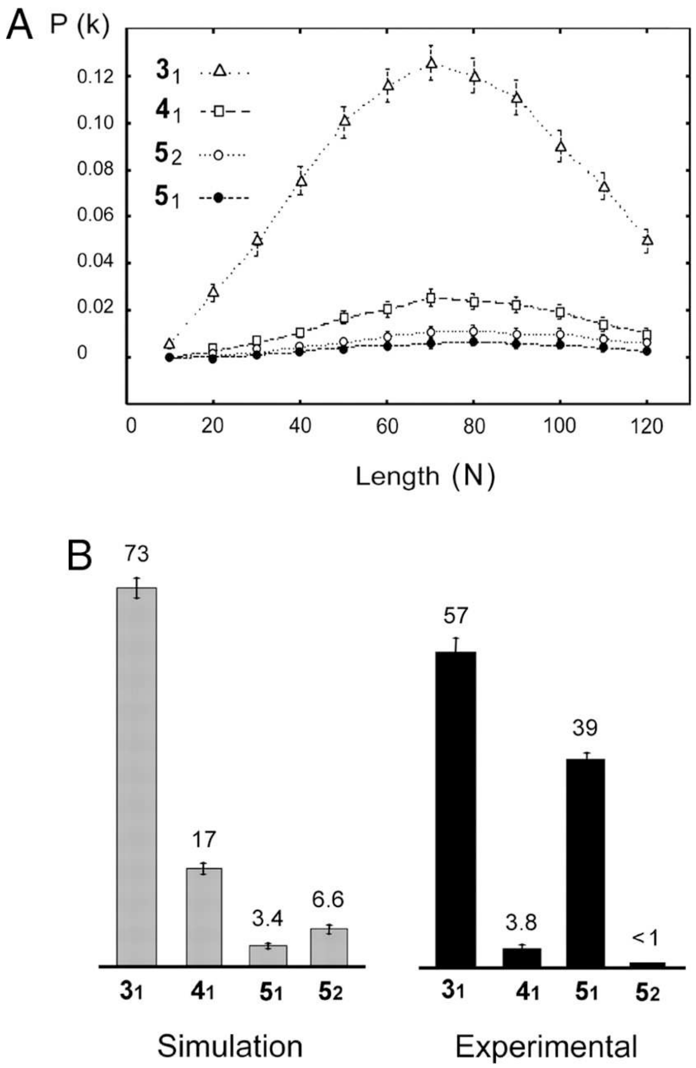


Polymer Model

- Polymers are modeled as random open and closed chains
  - Walk means open
  - Polygon means closed
- Art - generating realistic chains
- Model depends on the level of detail you want and situation
- A number of monomers are modeled as one longer segment with more flexibility

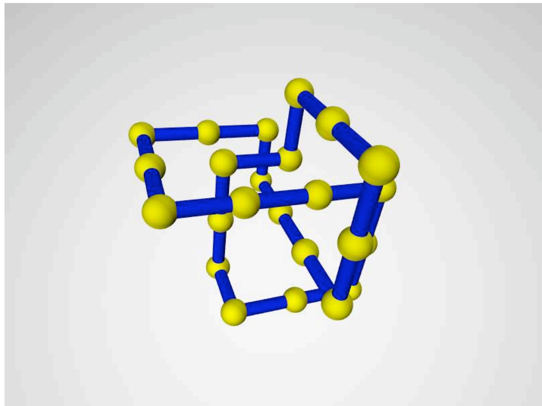
[1, 2] Arsuaga++, *Proc. Natl. Acad. Sci. USA* (2002, 2005)

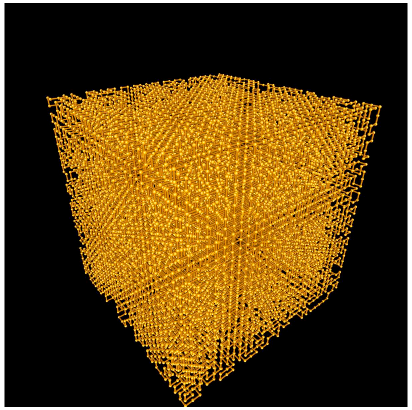
[3] Micheletti++, *J. Chem. Phys.* (2006)

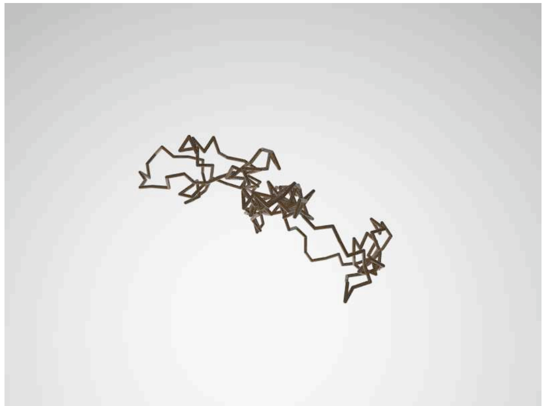


Solvents and Polymer Behavior

- Good solvent - chains repel each other
  - Chains are given some thickness (swollen, excluded volume)
  - Modeled on the unit lattice (nice because one can prove theorems)
- Bad solvent - chains attract each other
  - Several models
- Θ solvent - no attraction or repelling
  - Modeled with freely jointed chains (equilateral)
  - Gaussian polygons (edge vectors are Gaussian, not chain lengths)







Solvent Quality and Scaling

Radius of gyration

$$R_g = \sqrt{\frac{1}{N}\sum_{k=1}^{N} |r_k - r_{\mathbf{mean}}|^2}$$

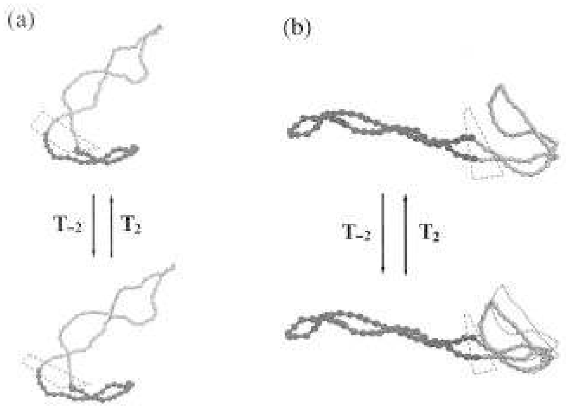
Scaling of radius of gyration

- Good solvent - $\overline{R_g} \sim N^{0.588}$
- Bad solvent - $\overline{R_g} \sim N^{1/3}$
- Θ solvent - $\overline{R_g} \sim N^{1/2}$

DNA Model

Wormlike chains

- Monte Carlo (roughly energy minimization with some wiggle)
- Energy based on some combination of:
  - Trying to keep edge length the same
  - Bending energy $\sum(\text{bending angles})^2$
  - Twisting energy $(\text{writhe} - \text{writhe}_{\text{goal}})^2$
  - Electrostatic repelling
  - Excluded volume (small thickness to avoid knot type changes)

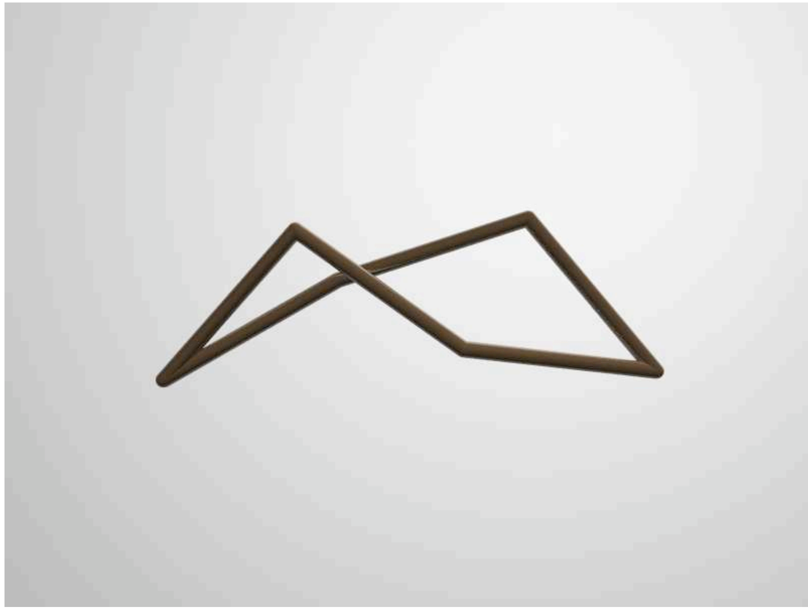


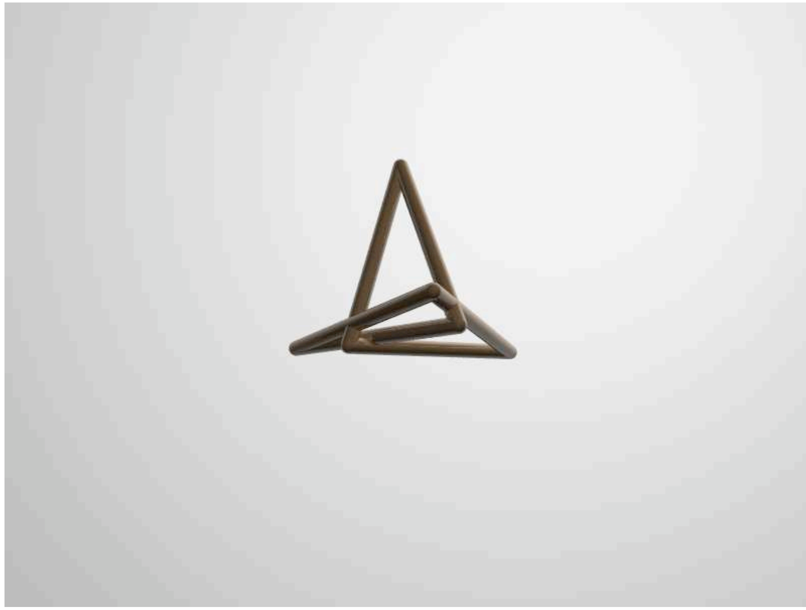
[4] Liu and Chan, *J. Chem. Phys.* (2008)

Topological Effects

Topology and size

- Knot takes up some of the length
- You would expect the structure of knotted polymers to be different for different knot types
- Question - Does this happen asymptotically?





Excluded Volume and Topological Effects

How does topology affect the size for freely jointed chains?

- No topological constraints $R_g \sim N^{1/2}$
- For a fixed knot type $R_g \sim N^{0.588}$ (numerically)
- Recall, excluded volume $R_g \sim N^{0.588}$ (numerically)
- Topological restriction acts like excluded volume (edges having some thickness)
- Topological effects are interesting because nothing can be derived exactly

[5] des Cloizeaux and Mehta, *J. Phys.I France* (1979)

How to Generate Random Polygons: Freely Jointed Chains

Freely jointed chains model

- No repelling, no attraction between edges
- Open chains (random walks) - Easy, just generate random directions
- Closed chains (random polygons) - More challenging
  - Crankshaft rotations - Monte Carlo approach [6]
  - Hedgehog method [7] (we've used this)
  - Generalized hedgehog [8]
  - Hybrid versions (now we're using this)

[6] Millett, *Random knotting and linking* (1994)

[7] Klenin++, *J. Biomol. Struct. Dyn.* (1988)

[8] Varela++, *J. Phys. A* (2009)

How to Determine the Knot Type

Rely on knot polynomials

- Alexander polynomial (crude but fast)
- Jones polynomial
- Kauffman polynomial
- HOMFLYPT polynomial (slower)
    - Ewing and Millett program (we use)
    - Knotscape
    - KnotPlot (Jenkins algorithm)
    - Gouesbet et al.
- Get distribution of HOMFLYPT polynomials, contamination is low

Piotr Pieranski

[9] Ewing and Millett, *Progress in knot theory and related topics* (1997)

[10] Hoste and Thistlethwaite, `Knotscape`, http://www.math.utk.edu/∼morwen/knotscape.html

[11] Scharein, `KnotPlot`, http://www.knotplot.com

[12] Jenkins, Masters thesis (1992)

[13] Gouesbet++, *Appl. Math. Comput.* (1999)

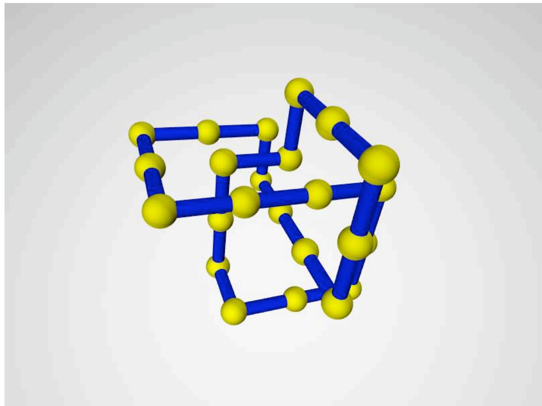
Summary

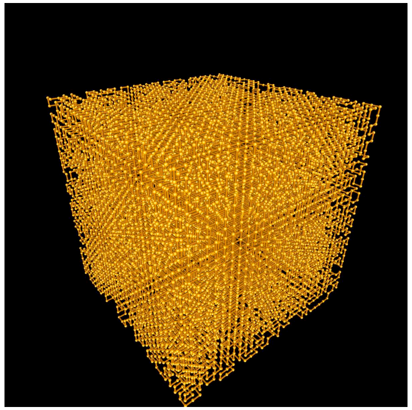
So far

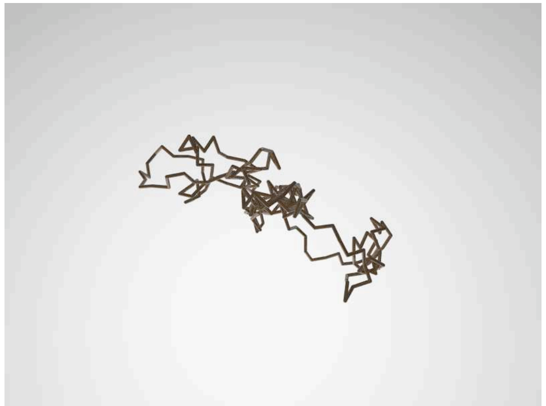
- Single polymers can be modeled as different types of random walks/polygons
- Use computational tools to determine “knot type” for random polygons
- Topology affects the size of the polygons

Now

We will go through some recent work we have done





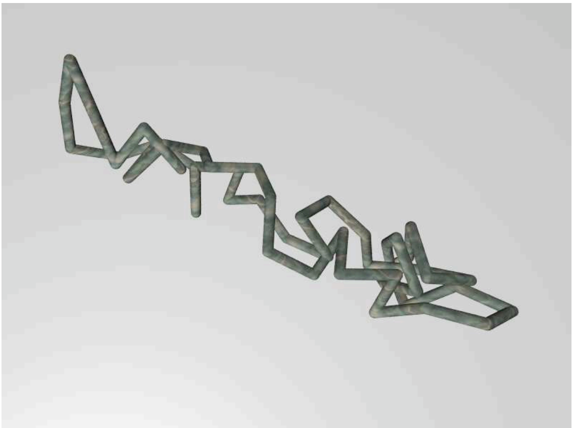


Work on Size and Shape of Knotted Polymers

Joint work with Akos Dobay, John Kern, Ken Millett, Michael Piatek*, Patrick Plunkett*, and Andrzej Stasiak

This study

- Goals
  - Measure the size and shape of polymer loops
  - Determine the effect of knotting
- Polymer model
  - Freely jointed model (larger length scales)
  - Equilateral closed polygons
  - No repulsion or attraction between edges



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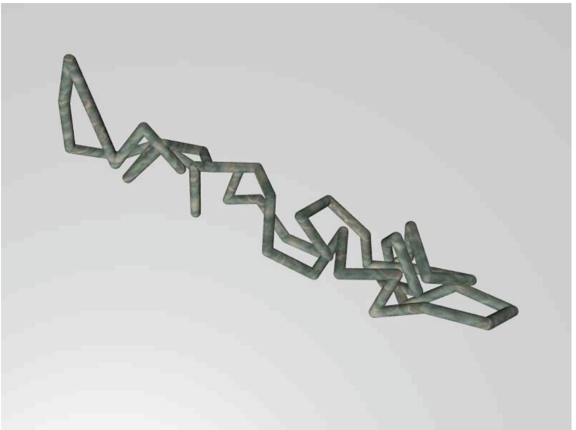
Goals

- Interested in universal descriptors (long and skinny vs sphere-like)
  - Size (R_g)
  - Shape
- Want to know what sort of shape polygons are converging to, on average
- Quantify measurements of shape
- See how knotting affects the overall shape, short term and asymptotically

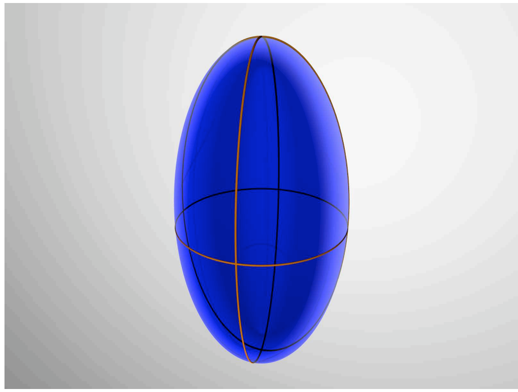


$\not\sim$

Describing Polymer Size and Shape

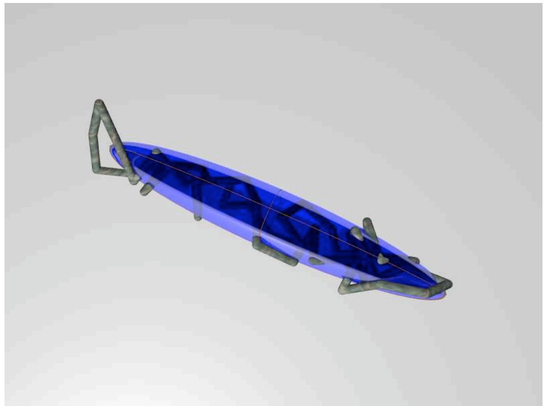
Ellipsoids

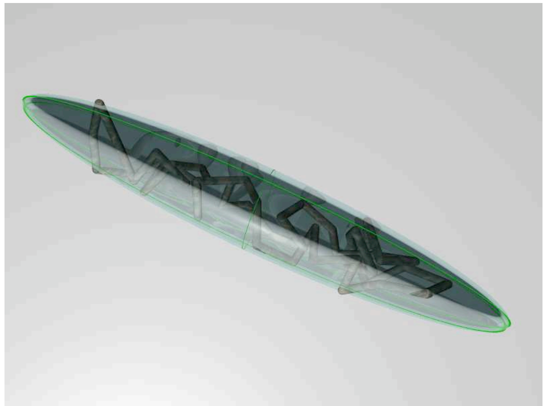
- Kuhn - basic shape is prolate ellipsoid
- Question - what is the ellipsoid?
- Question - how should we quantitatively characterize the shape of ellipsoid?



Types of ellipsoids

- Inertial ellipsoid (moment of inertia tensor)
- Enveloping ellipsoid (smallest volume enclosing ellipsoid)

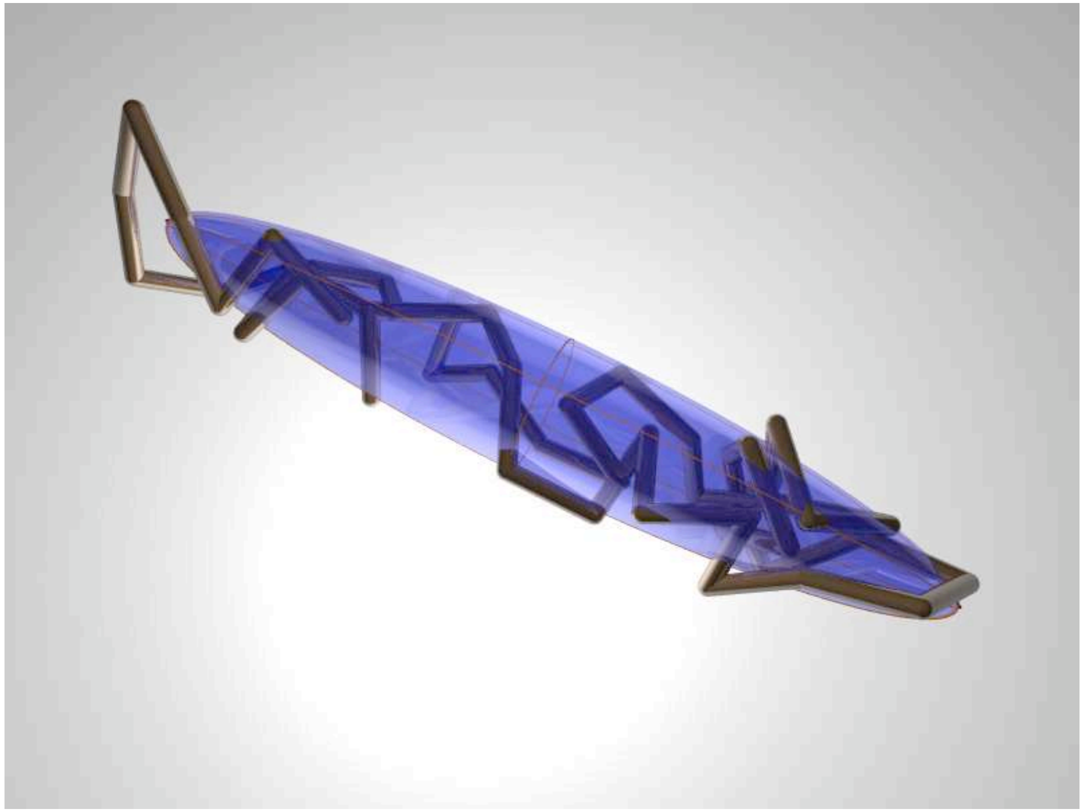




Characteristic Inertial Ellipsoid

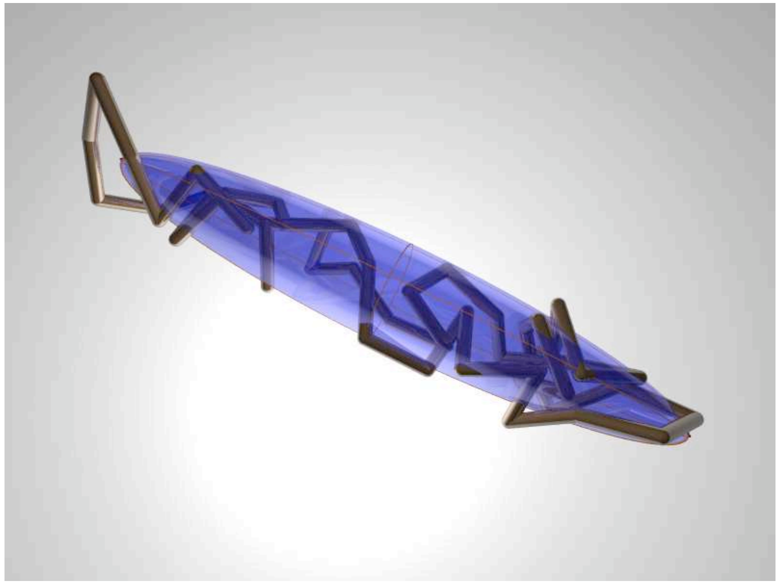
Definition

- Axes are principal axes
- Semi-axis lengths are $\sqrt{3 \cdot \text{eigenvalues}}$



Are You Suddenly Hungry For Fish?

What fish is this?



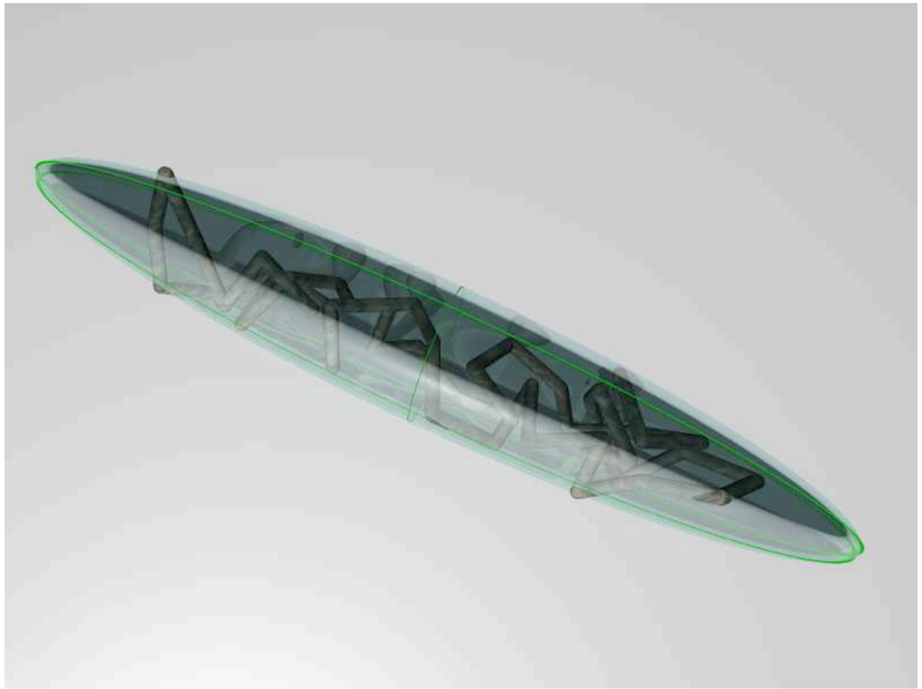
Doug Arnold (IMA and UMN)

The Northern Pike

Enveloping Ellipsoid

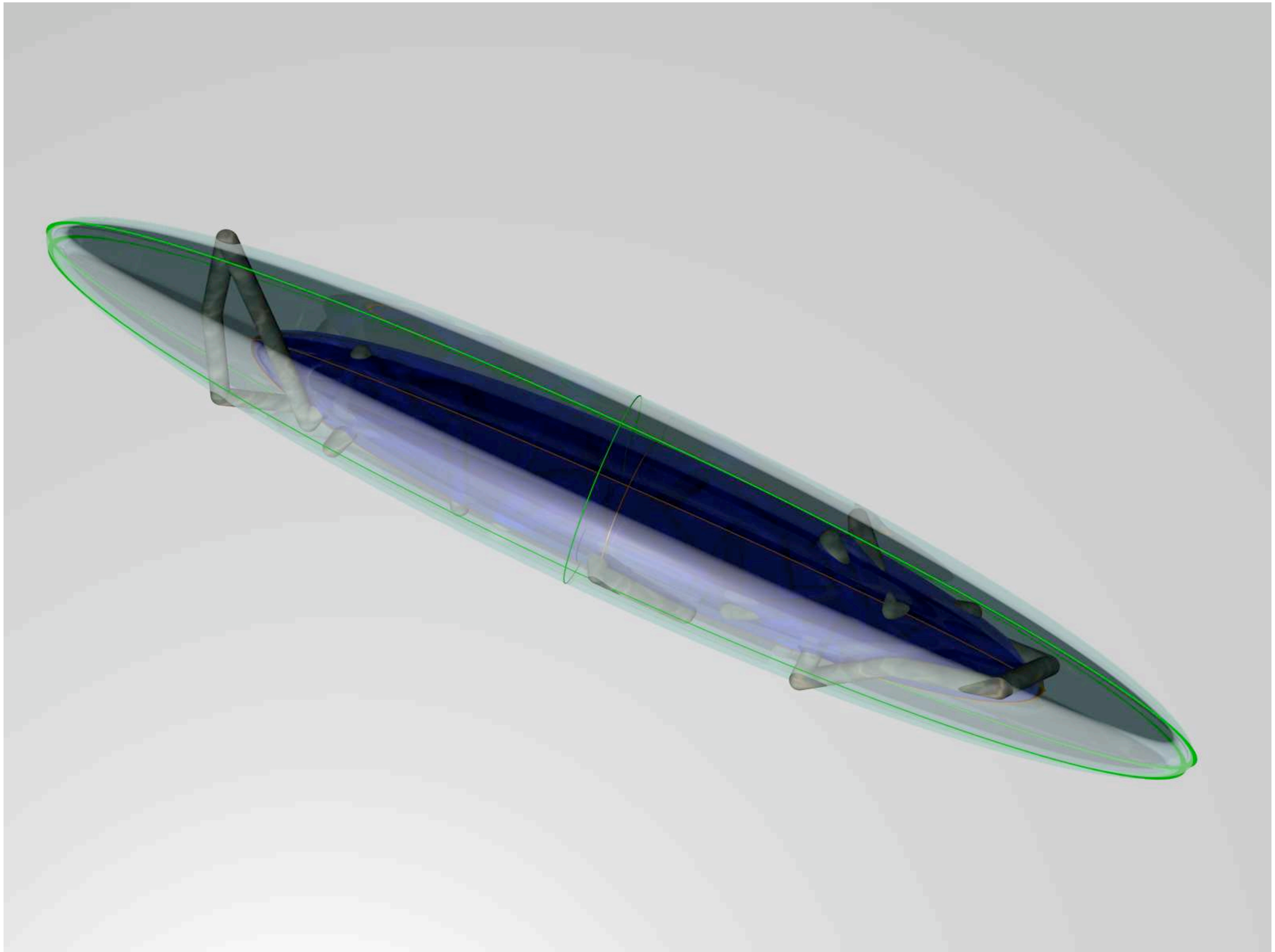
Definition

- Minimal volume enclosing ellipsoid
- Algorithm due to Sven Schönherr



[15] Sven Schönherr, Diplomarbeit, Freie Universität Berlin (1994)

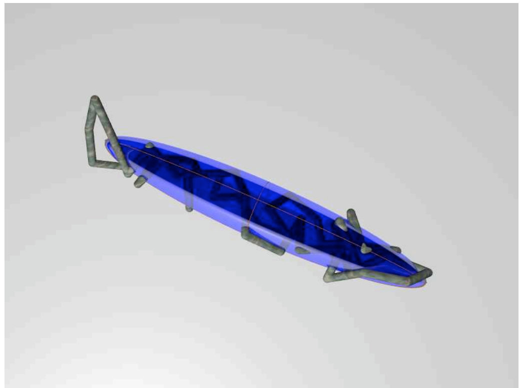
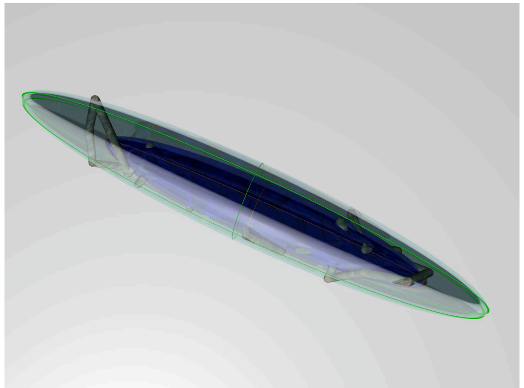
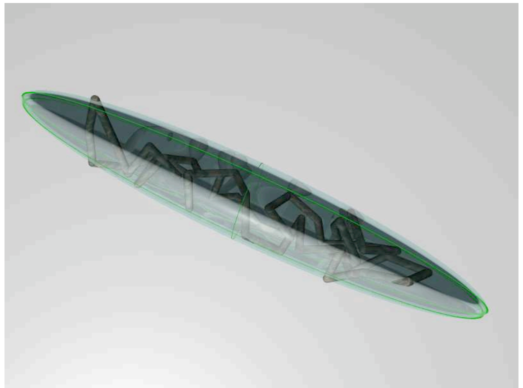
Characteristic Inertial and Enveloping Ellipsoids



Review

Notes

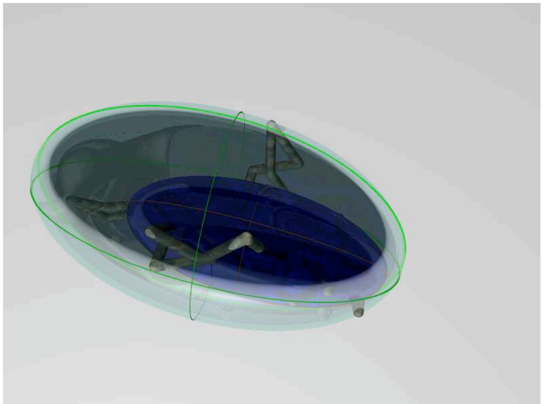
- For a simulated polymer, we have two ellipsoids
  - Characteristic inertial ellipsoid
  - Enveloping ellipsoid
- Axes appear to be in similar directions
- Centers are not likely the same
- Enveloping is bigger than inertial

Measuring the Size and Shape

Goal

- Analyze the size and shape of the polymers, with an eye towards the effect of knotting
- Size
  - Squared radius of gyration
- Shape
  - Asphericity
  - Prolateness (nature of asphericity)



Size

Squared radius of gyration, denoted R

- Suppose λ_1, λ_2, λ_3 eigenvalues of moment of inertia tensor
- $R = \lambda_1 + \lambda_2 + \lambda_3$
- $R = R_g^2$ (from previous slides)

- Semi-axis of characteristic inertial ellipsoid
  - $a = \sqrt{3\lambda_1}$
  - $b = \sqrt{3\lambda_2}$
  - $c = \sqrt{3\lambda_3}$

- $R = \frac{a^2+b^2+c^2}{3}$

Shape

Asphericity

- $0 \leq A \leq 1$
- $A = 0$ means perfectly spherical
- $A = 1$ means rod-like, i.e. collinear points
- Symmetric in arguments
- Scale invariant

Definition

- Traditionally, $A = \frac{(\lambda_1-\lambda_2)^2+(\lambda_1-\lambda_3)^2+(\lambda_2-\lambda_3)^2}{2(\lambda_1+\lambda_2+\lambda_3)^2}$
- Better, $A = \frac{(a-b)^2+(a-c)^2+(b-c)^2}{2(a+b+c)^2}$

[16] Aronovitz and Nelson, *J. Physique I* (1986)

[17] Rudnick and Gaspari, *J. Phys. A: Math. Gen.* (1986)

Why Better?

"...the contribution to a measure from each configuration is biased by its overall size ..."

Bias

- $B(x, y, z) = x + y + z$ (eigenvalues)
- $R(x, y, z) = \frac{x^2+y^2+z^2}{3}$ (semi-axis lengths)
- $A(x, y, z) = \frac{(x-y)^2+(x-z)^2+(y-z)^2}{2(x+y+z)^2}$ (both)

- $\nabla B \cdot \nabla A \neq 0$
- $\nabla R \cdot \nabla A = 0$

[18] Cannon, Aronovitz, and Goldbart, *J. Physique I* (1991)

Shape II

Prolateness (*nature of asphericity*)

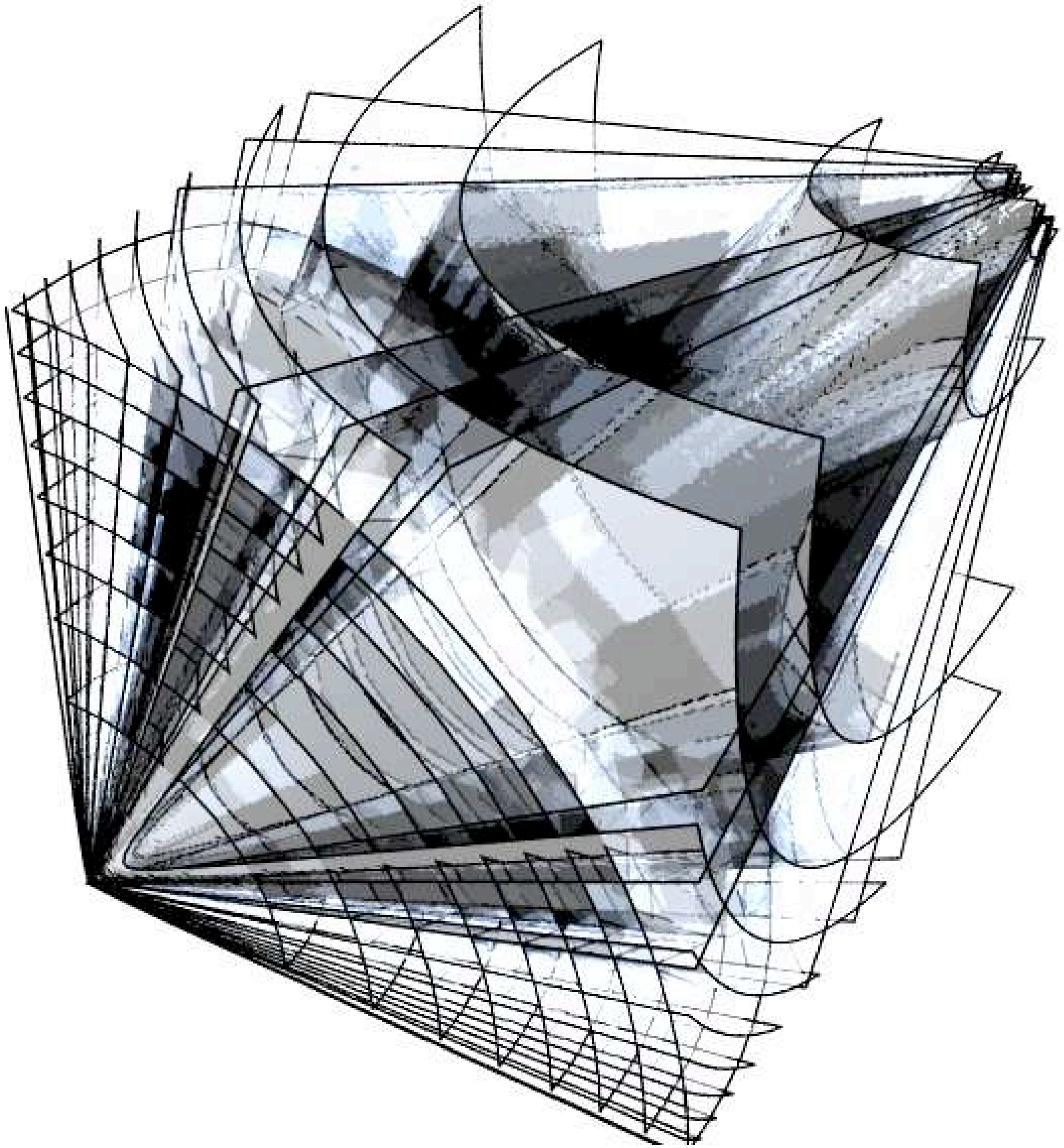
- $-1 \leq P \leq 1$
- $P = -1$ means perfectly oblate
- $P = 1$ means perfectly prolate
- For a sphere P is undefined
- Symmetric in arguments
- Scale invariant

Definition

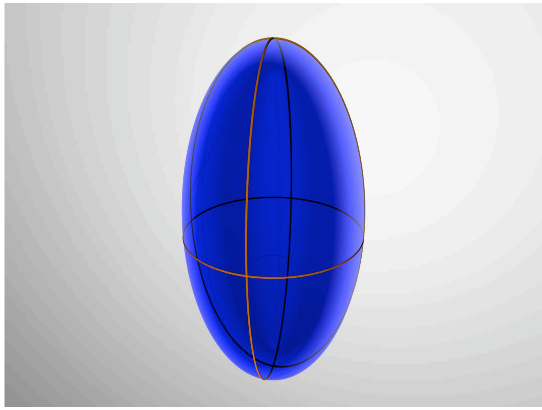
- $P(x, y, z) = \frac{(2x-y-z)(2y-x-z)(2z-x-y)}{2(x^2+y^2+z^2-xy-xz-yz)^{3/2}}$
- $\nabla P \cdot \nabla R = 0$
- $\nabla P \cdot \nabla A = 0$
- $\nabla P \cdot \nabla B = 0$

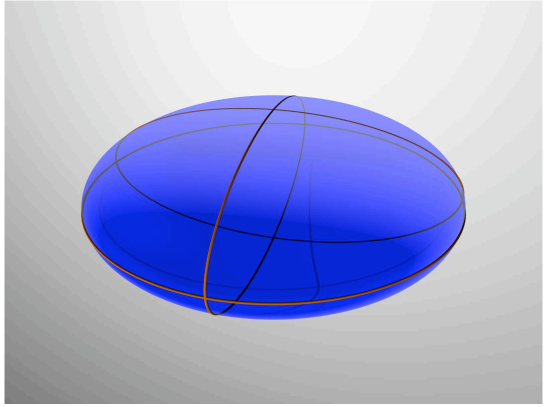
[16] Aronovitz and Nelson, *J. Physique I* (1986)

Unbiased (Orthogonal) System



Examples





Left - Prolate (rugby ball)

- $(1, 0.5, 0.5)$ semi-axis lengths
- $A = 0.0625$
- $P = 1$

Right - Oblate (M&M candy)

- $(1, 1, 0.4)$ semi-axis lengths
- $A = 0.0625$
- $P = -1$

Review

Ellipsoids

- Characteristic inertial ellipsoid
- Enveloping ellipsoid

Unbiased system of descriptors

- Squared radius of gyration R (size)
- Asphericity A (primary shape descriptor, $0 \leq A \leq 1$)
- Prolateness P (secondary shape descriptor, $-1 \leq P \leq 1$)

Goal

- Length effects
- Topological effects

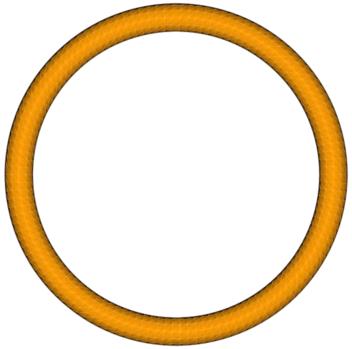
Data Generation

How

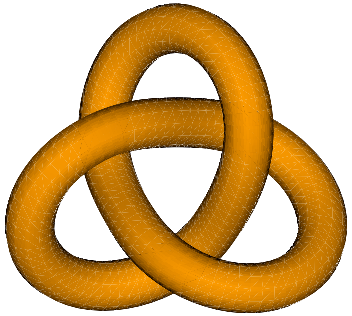
- Hedgehog method
- From 50 edges to 500 edges by 10, 6 to 48 by 2
- 400,000 knots for each number of edges
- Knot types “determined” using Ewing/Millett HOMFLYPT code
- Computations took several weeks on 40 node cluster

Who

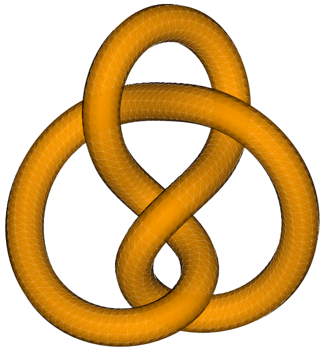
Thanks to Rob Scharein and KnotPlot
www.knotplot.com



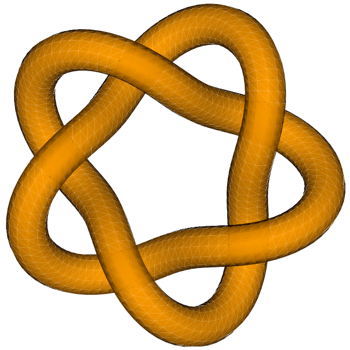
0_1



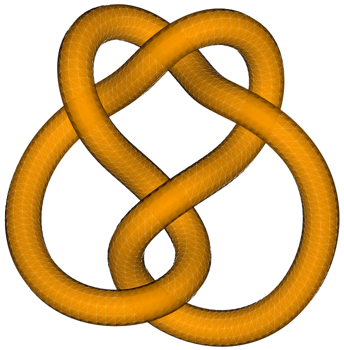
3_1



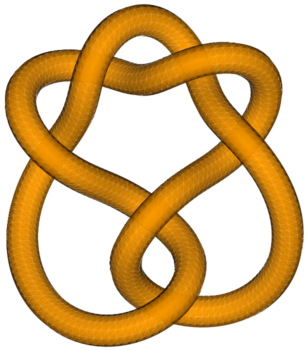
4_1



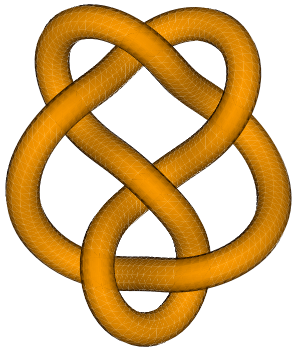
5_1



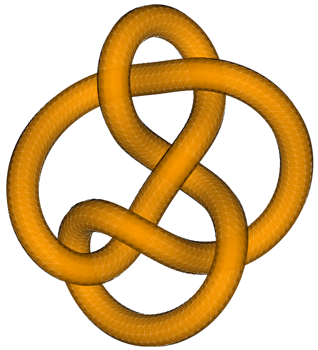
5_2



6_1

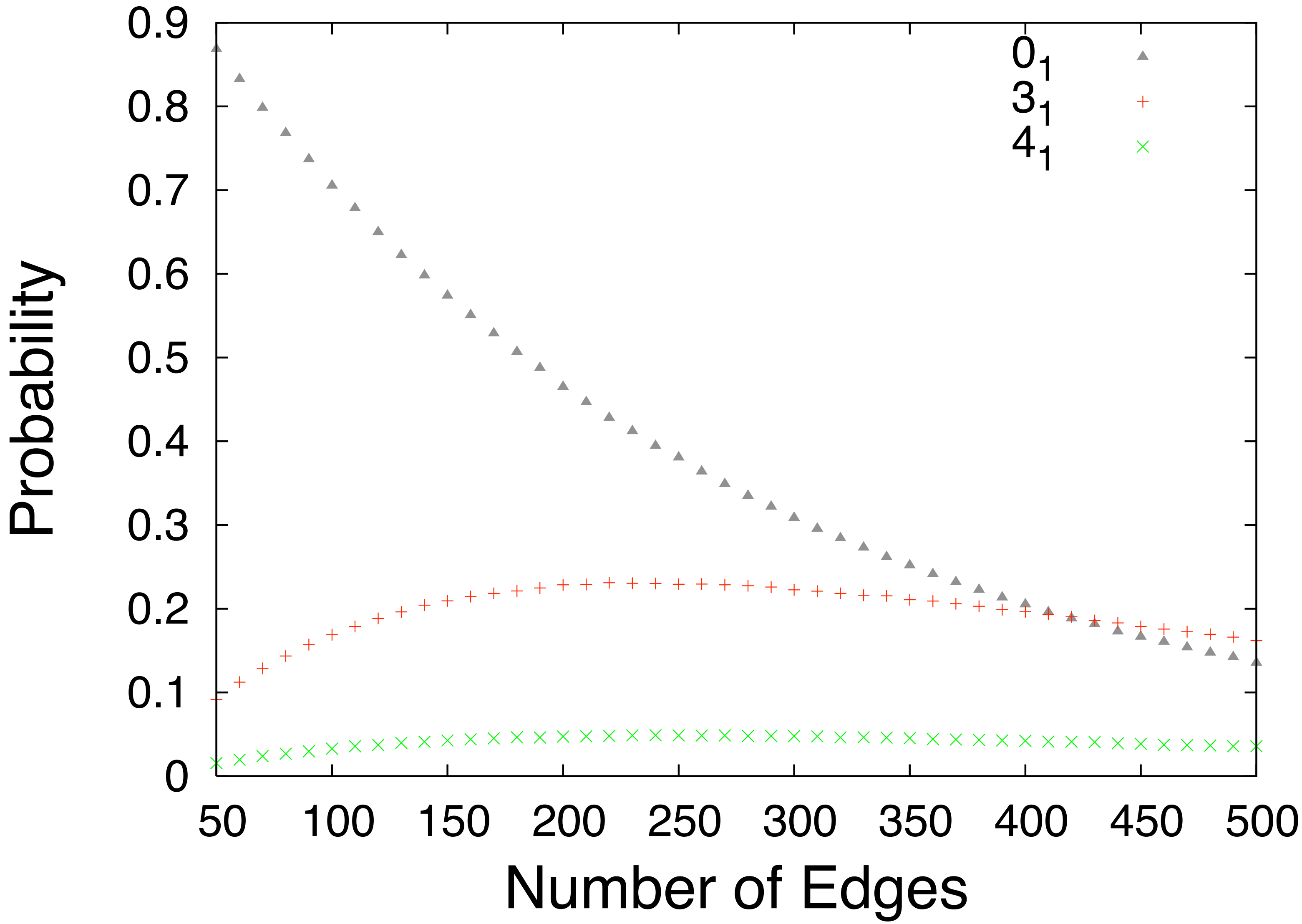


6_2

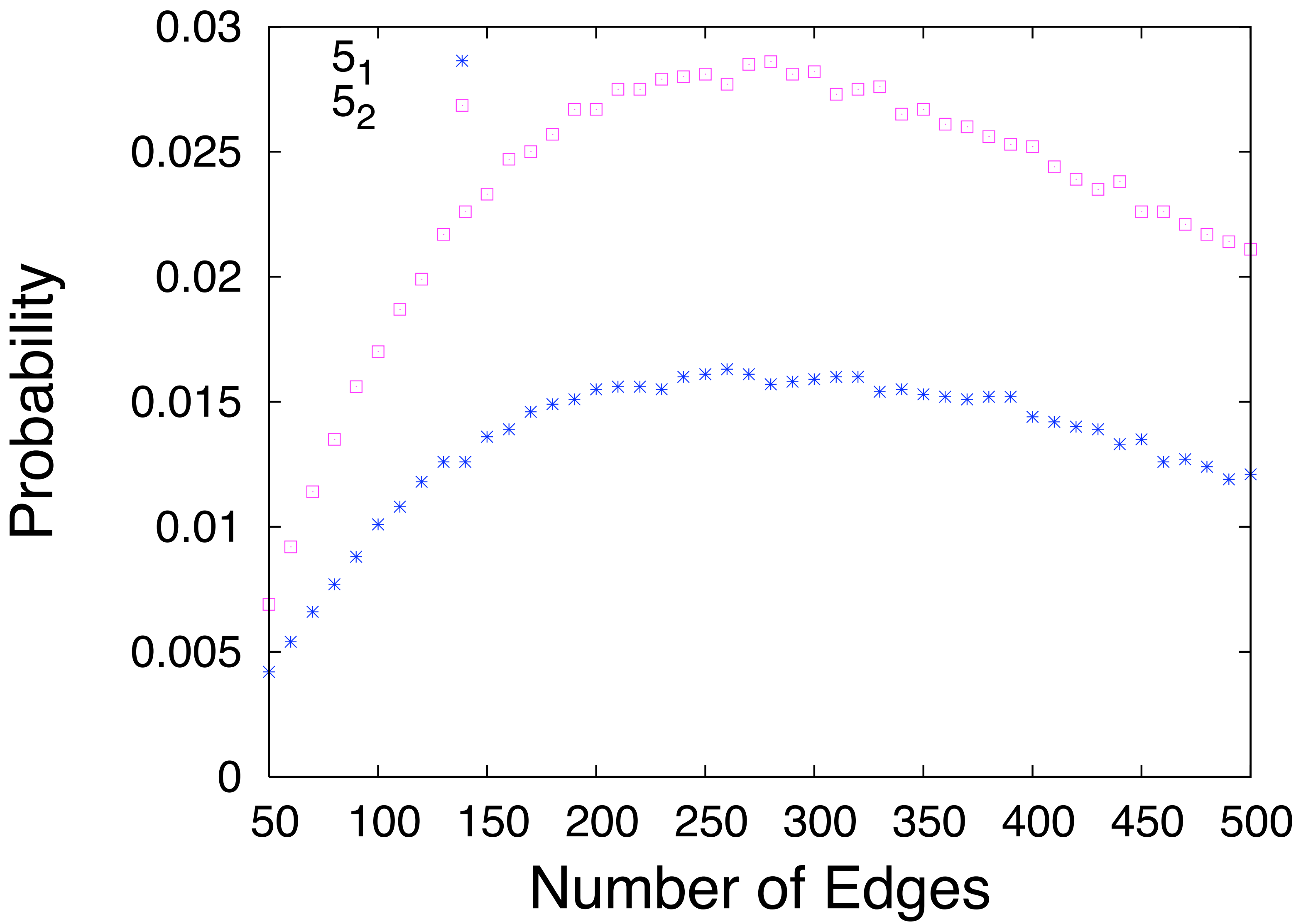


6_3

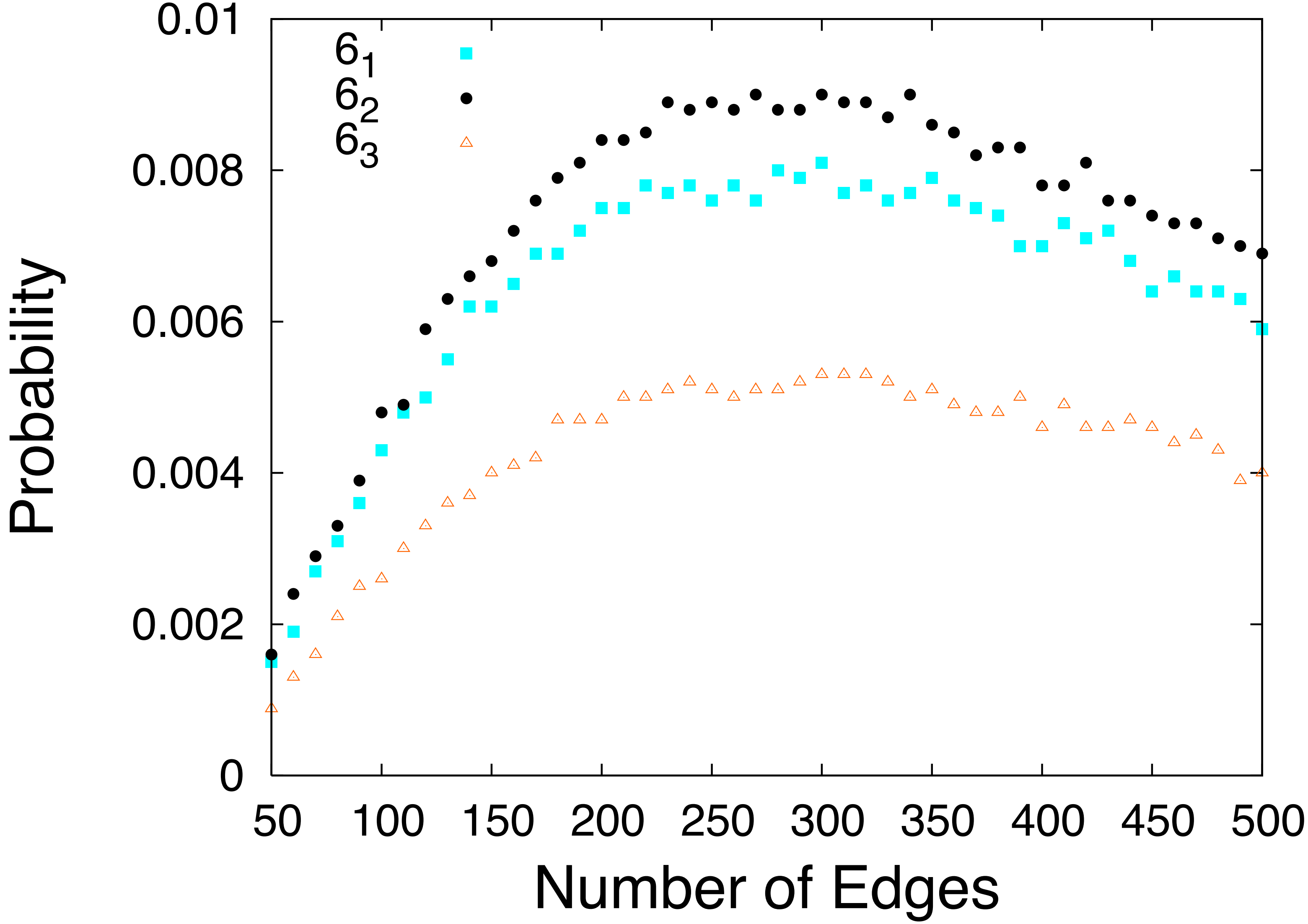
Probability Data: Unknot, Trefoil, and Figure-8



Probability Data: 5-Crossing Knots



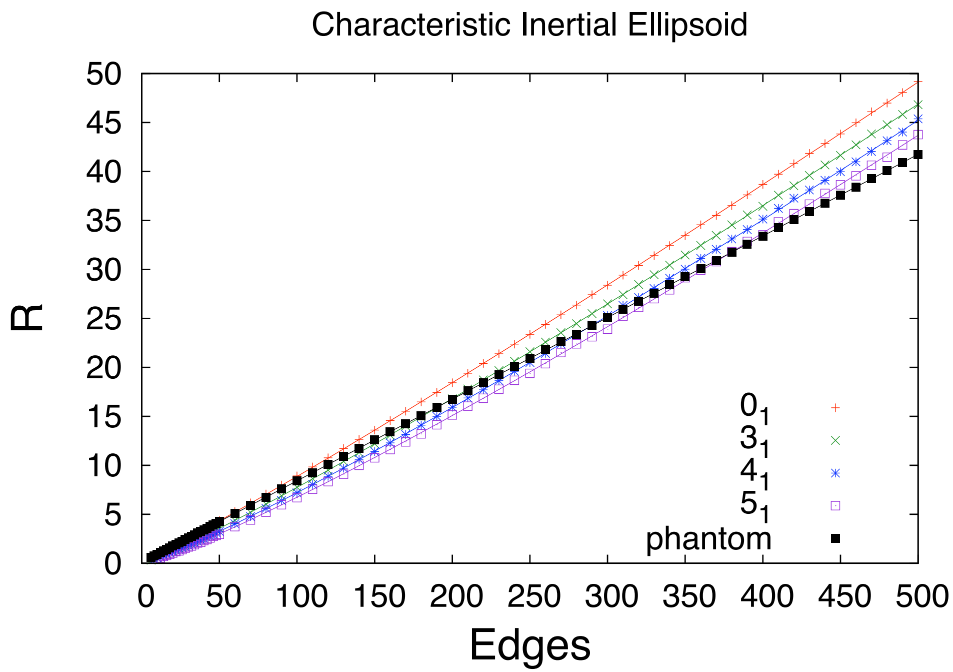
Probability Data: 6-Crossing Knots



Characteristic Inertial Ellipsoid - R_I

Note

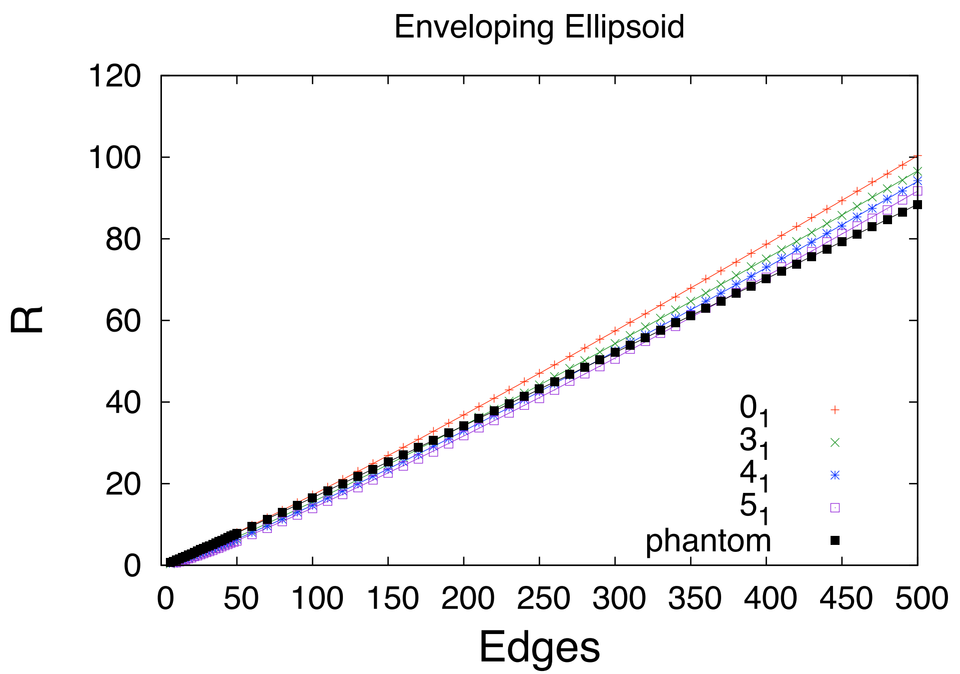
- R_I is the squared radius of gyration of the vertex set
- Each point is an average R_I
- Phantom polygons = All of the possible states
- $n^{2\nu}\left(A + B/\sqrt{n} + C/n\right)$, $\nu = 0.5(\text{phantom}), 0.588(\text{knot type})$



Enveloping Ellipsoid - R_E

Note

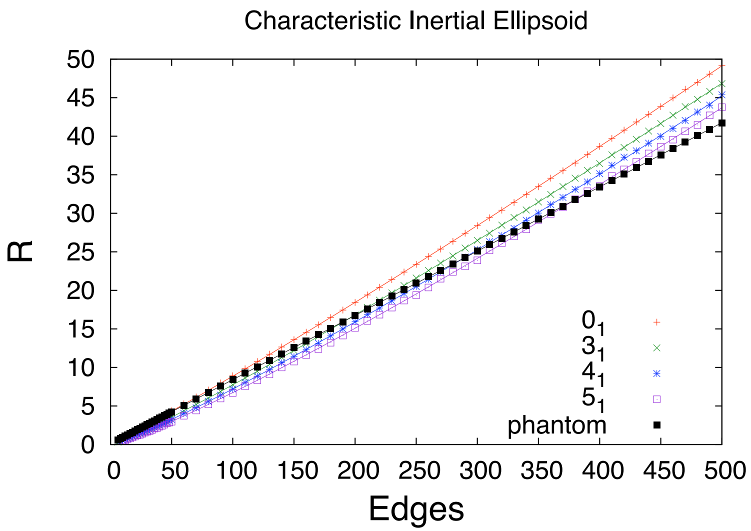
- $R_E = \frac{a^2+b^2+c^2}{3}$ is a bit artificial here
- R_E is the SRGN of a vertex set whose inertial ellipsoid is this enveloping ellipsoid
- Measurable sense of scale for comparison sake

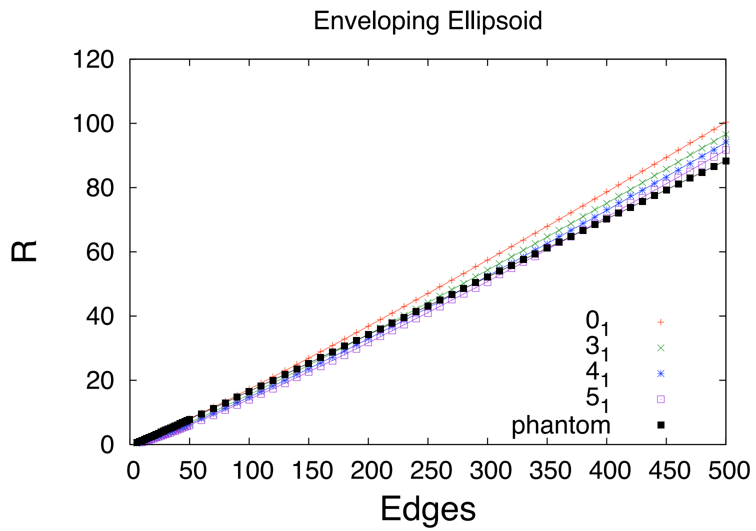


Analysis of R

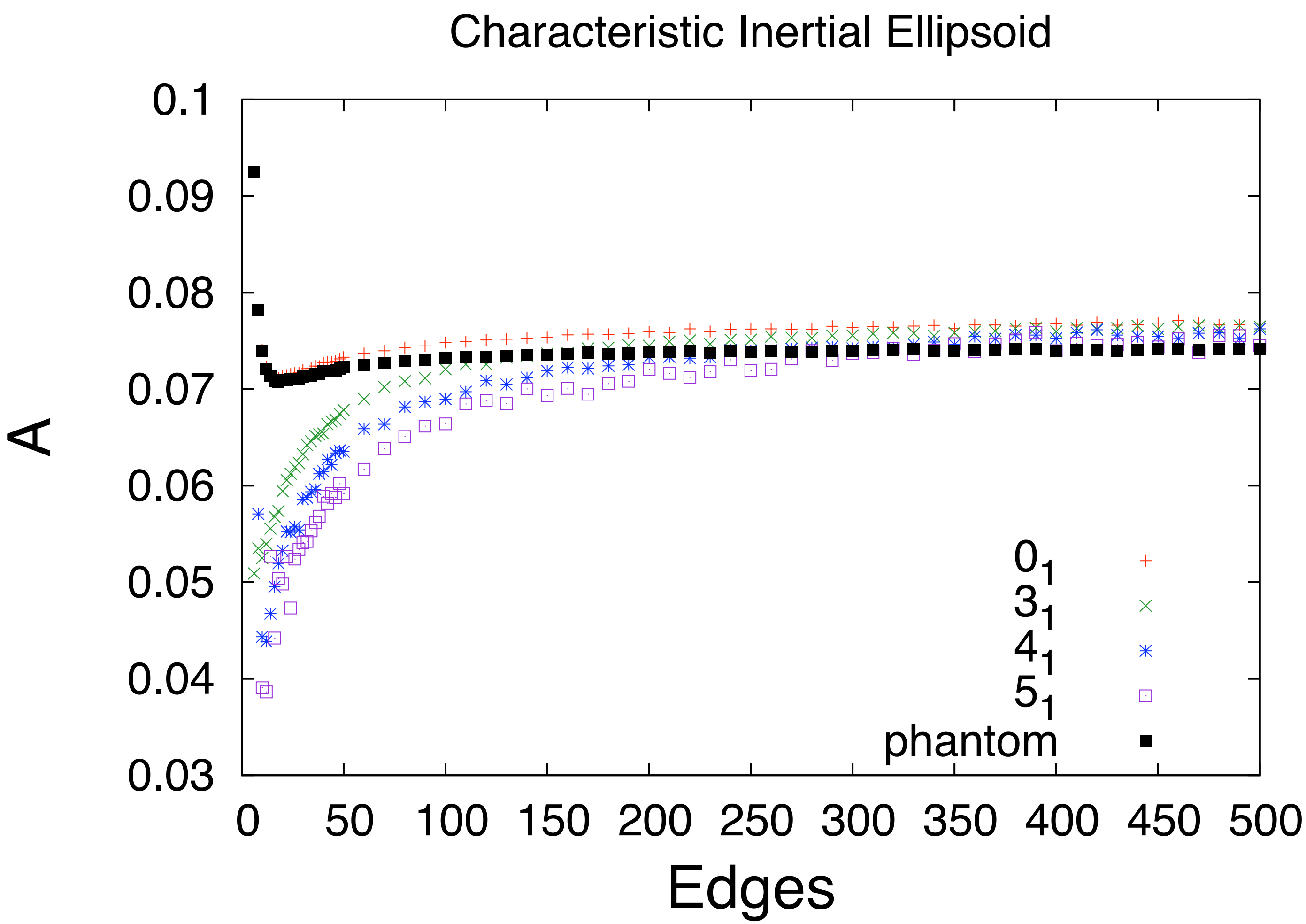
Comparison

- Same scaling function holds for R_E
- $R_E \approx 2R_I$

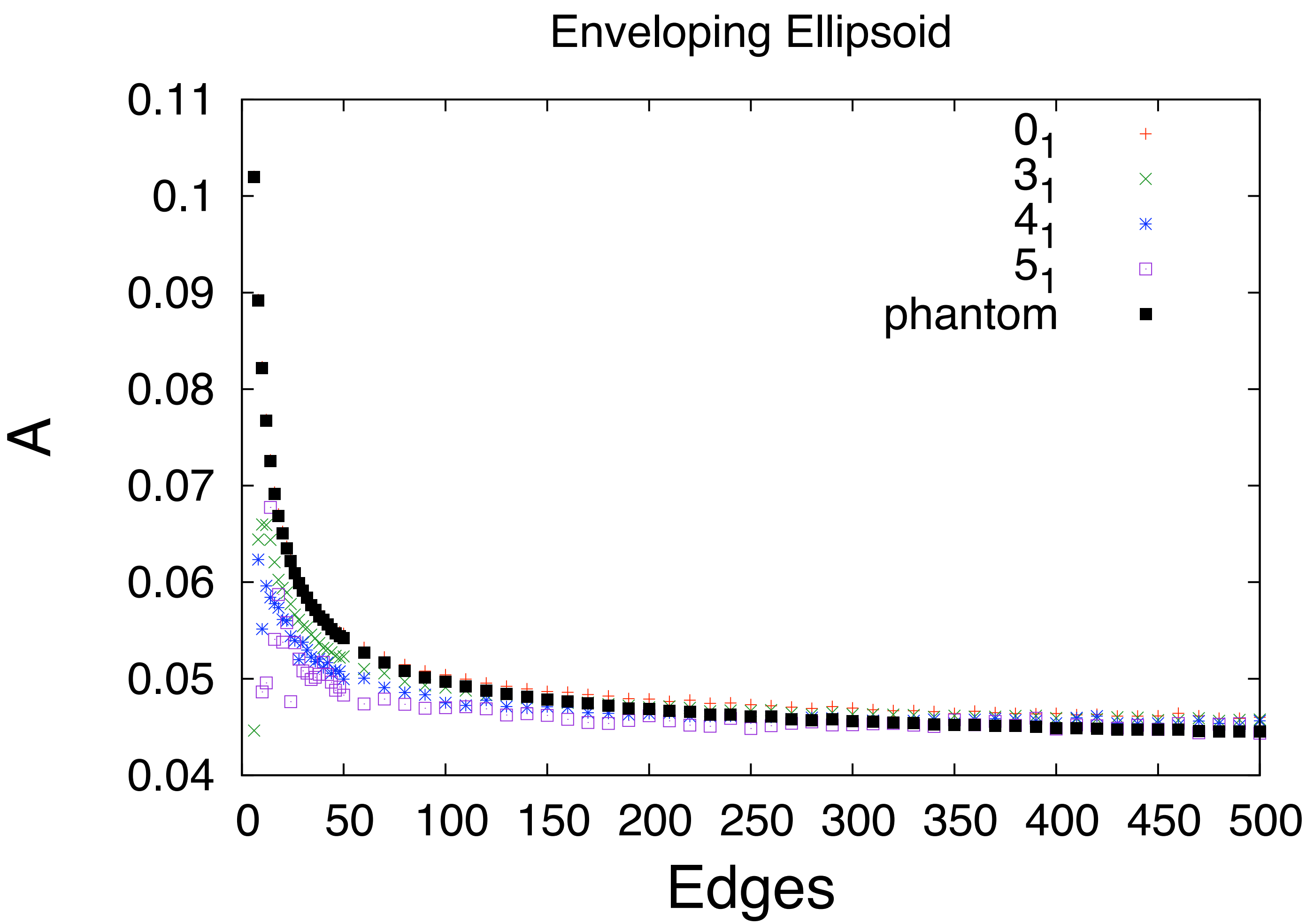




Characteristic Inertial Ellipsoid - A_I

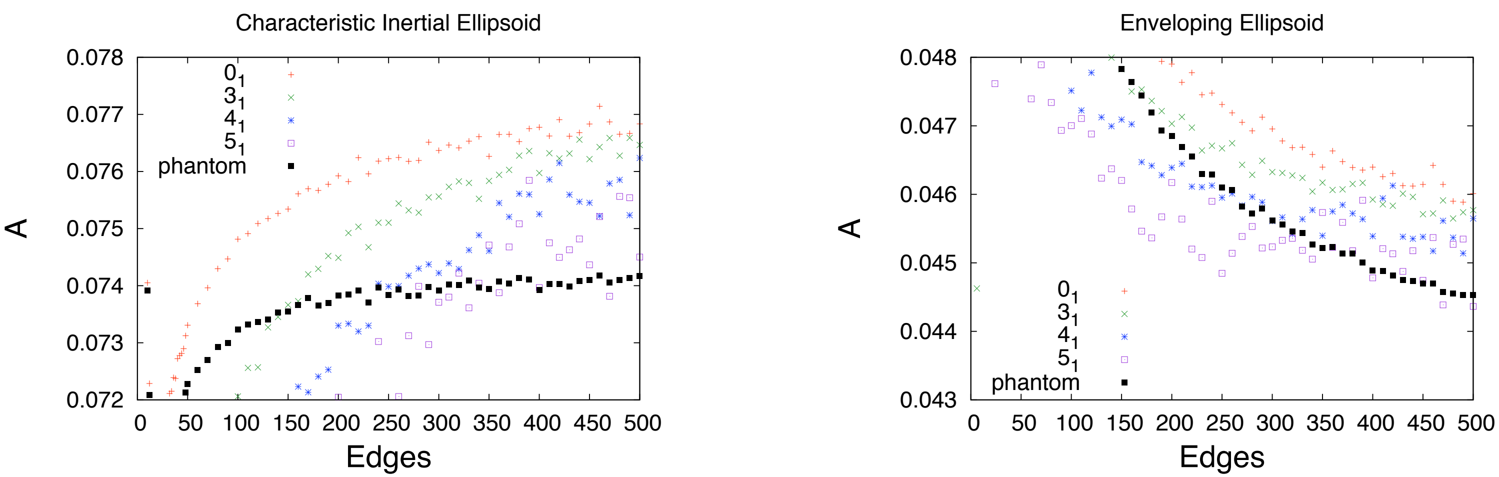


Enveloping Ellipsoid - A_E



Comparison

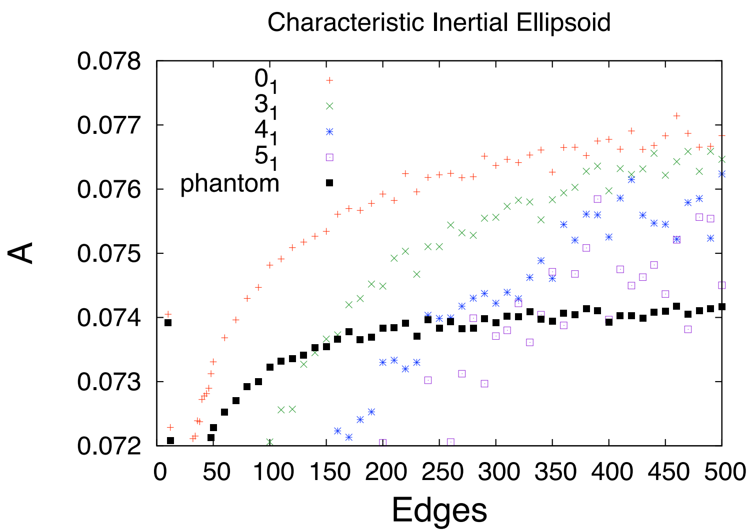
- Knot types appear to approach a similar limiting value
- Phantom polygons appear to approach different limiting value
- More complex knots are more spherical
- Approach limiting value from below versus above
- Enveloping ellipsoids are more spherical than inertial ellipsoids

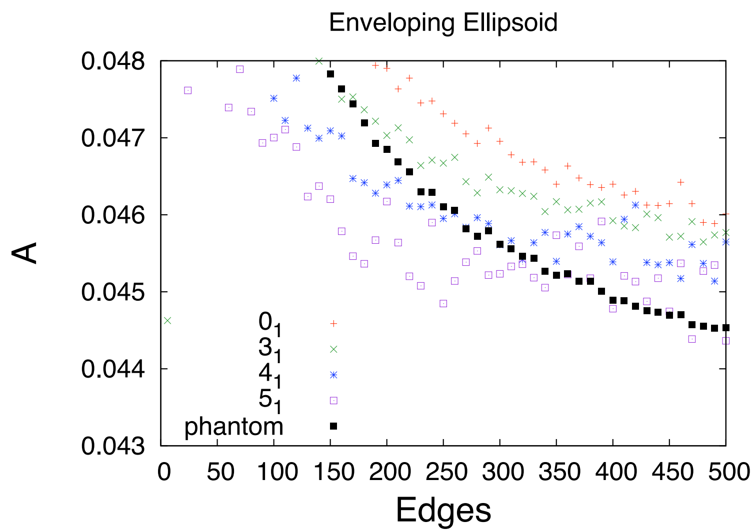


Explanations

Limiting values

- Knot localization explains the seemingly same limiting value for knot types
- Phantom polygons contain many complex knots (which have yet to "localize")





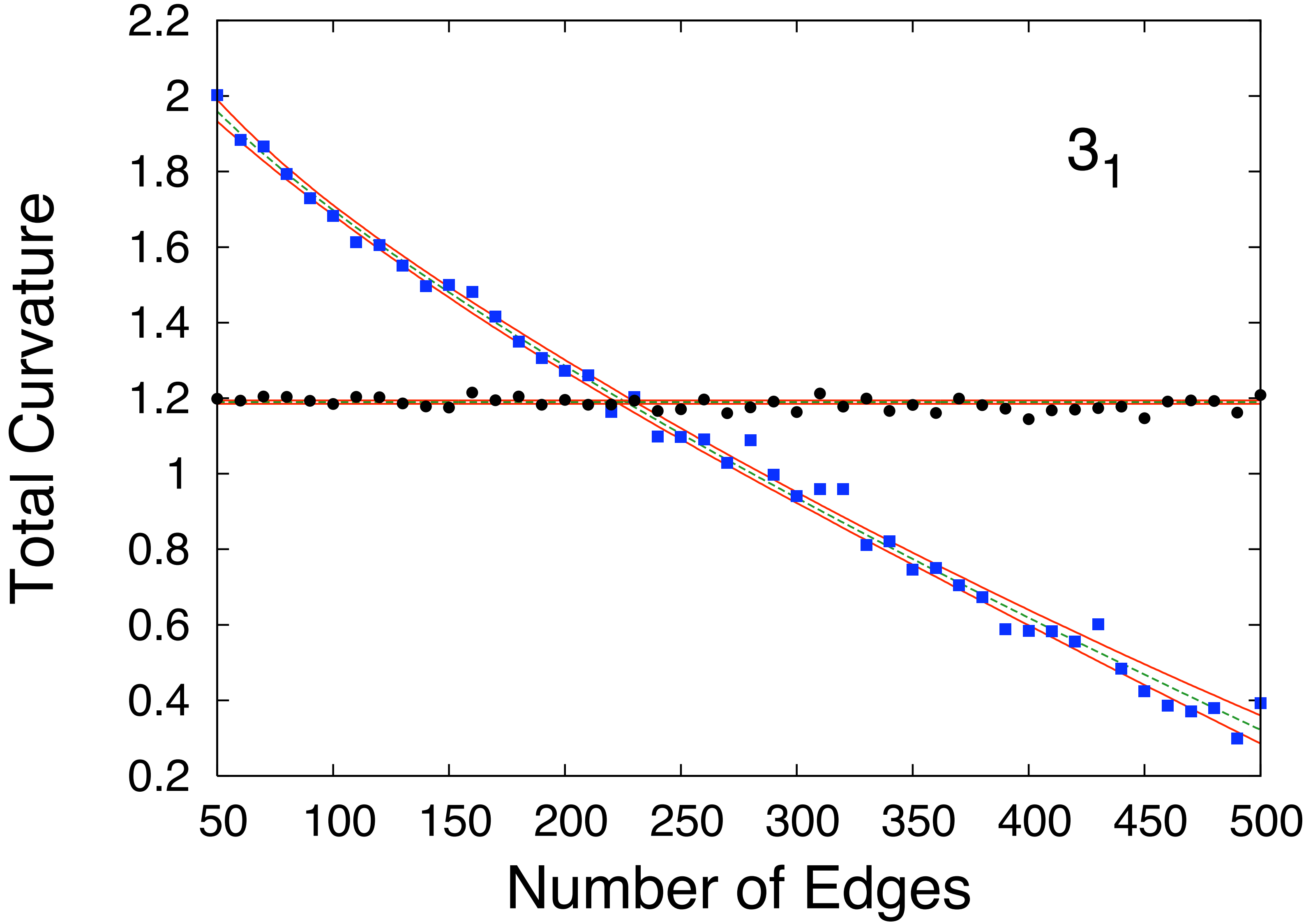
Estimating Limiting Values

Monte Carlo estimates of limiting values

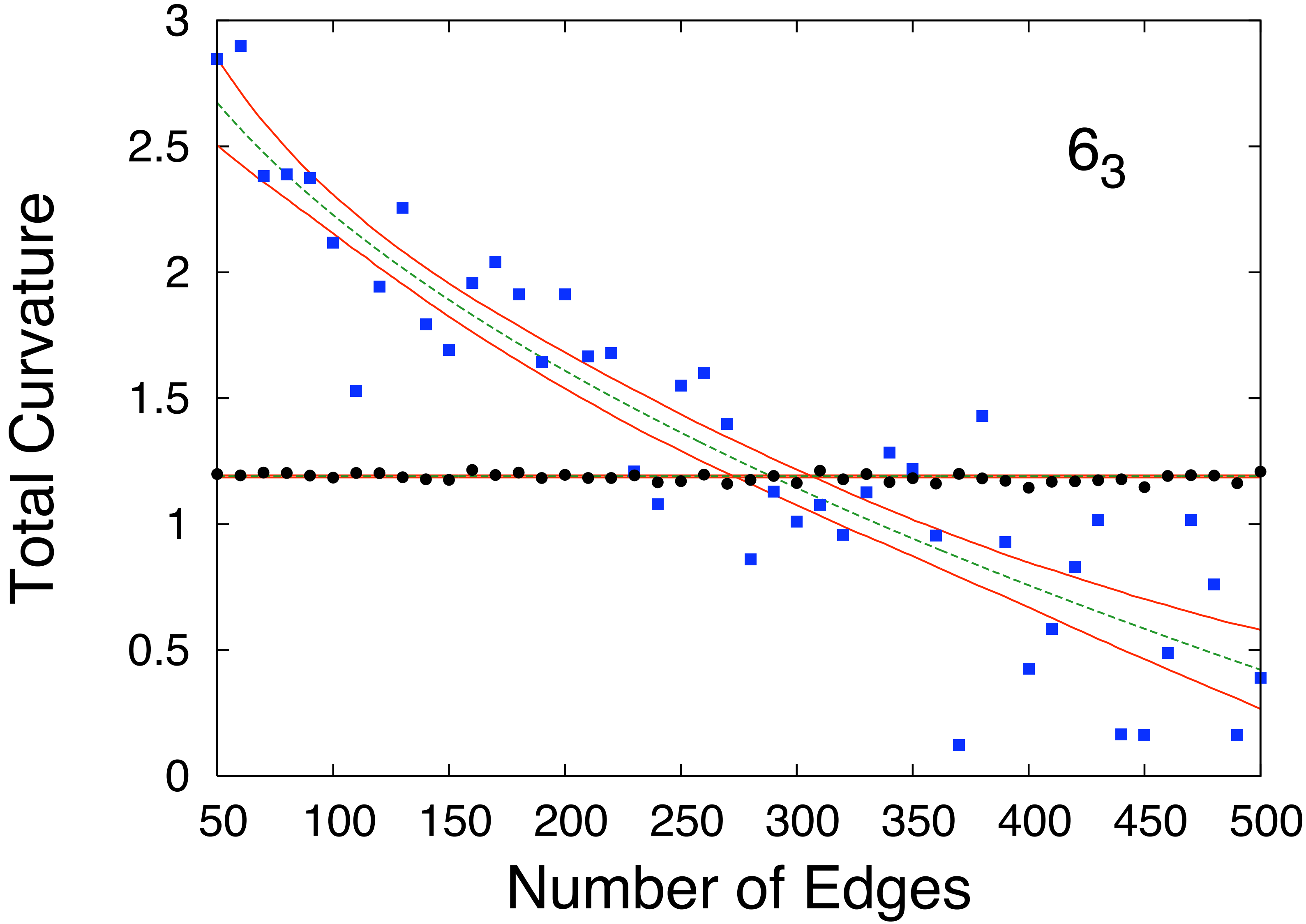
$$A + B/\sqrt{n} + C/n$$

Knot	Limiting A_I	Limiting A_E
phantom	0.07436 ± 0.00042	0.04092 ± 0.00028
0_1	0.07875 ± 0.00074	0.04353 ± 0.00048
3_1	0.0793 ± 0.0010	0.04424 ± 0.00063
4_1	0.0797 ± 0.0021	0.0445 ± 0.0014
5_1	0.0814 ± 0.0037	0.0461 ± 0.0024
5_2	0.0819 ± 0.0029	0.0455 ± 0.0018
6_1	0.0853 ± 0.0055	0.0467 ± 0.0035
6_2	0.0807 ± 0.0051	0.0446 ± 0.0033
6_3	0.0782 ± 0.0063	0.0430 ± 0.0042

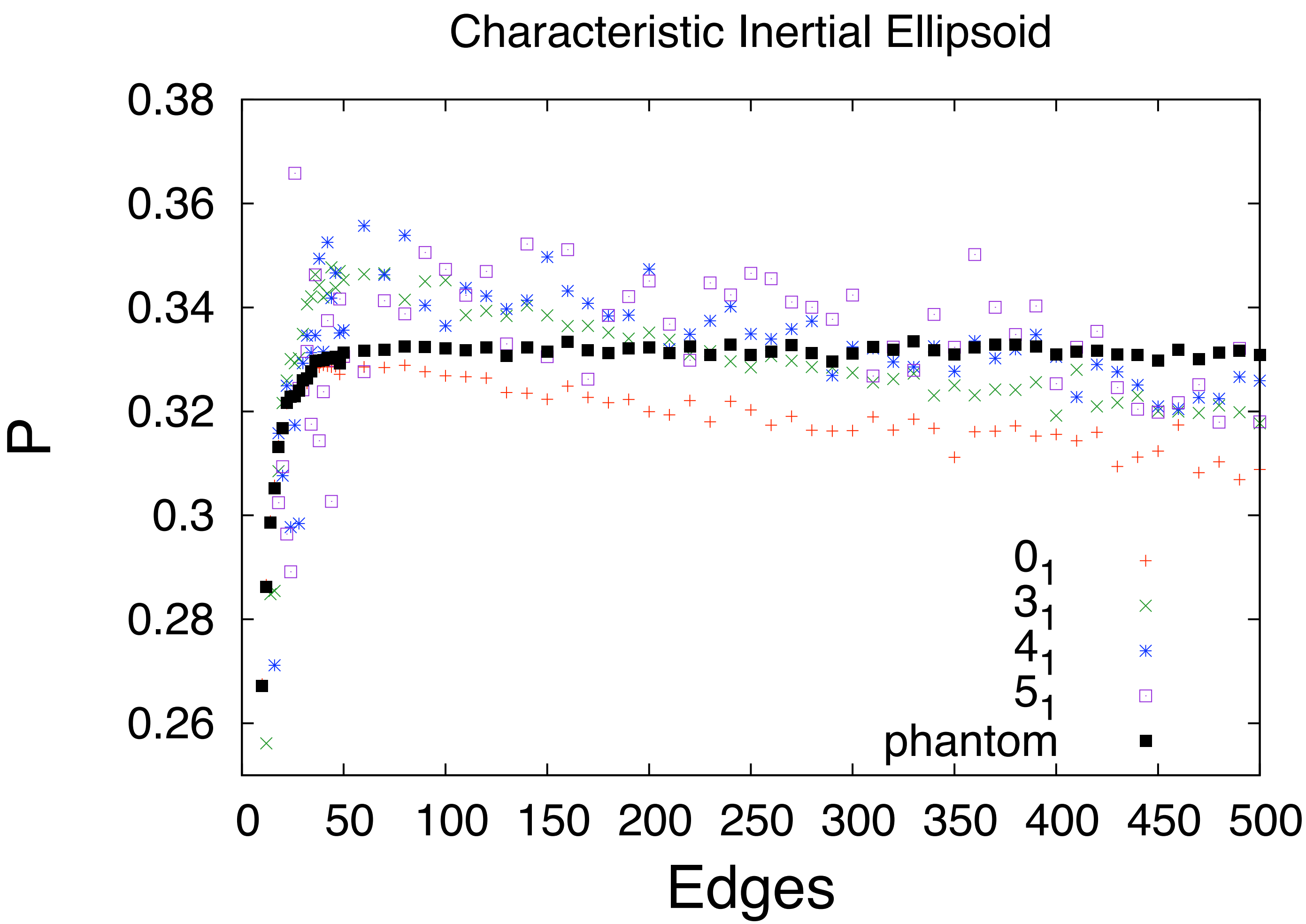
Total Curvature of 3_1



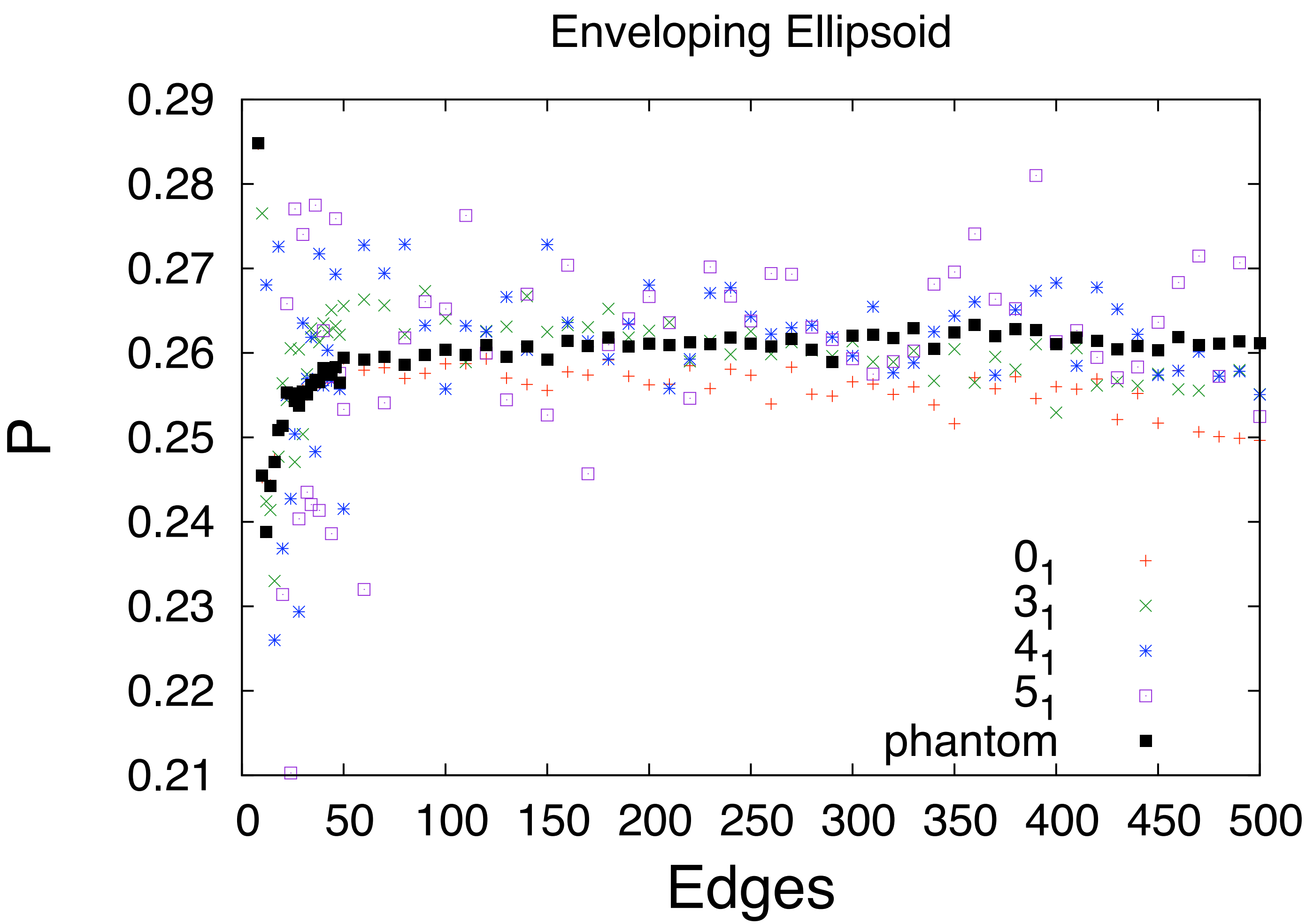
Total Curvature of 6_3



Characteristic Inertial Ellipsoid - P_I



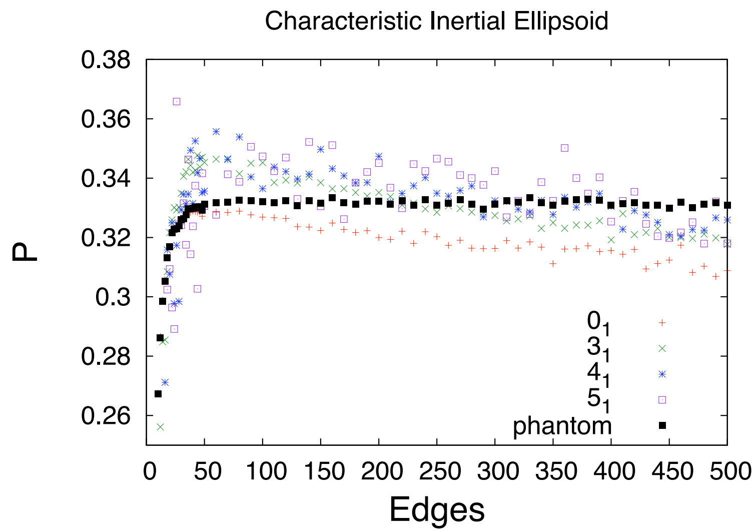
Enveloping Ellipsoid - P_E

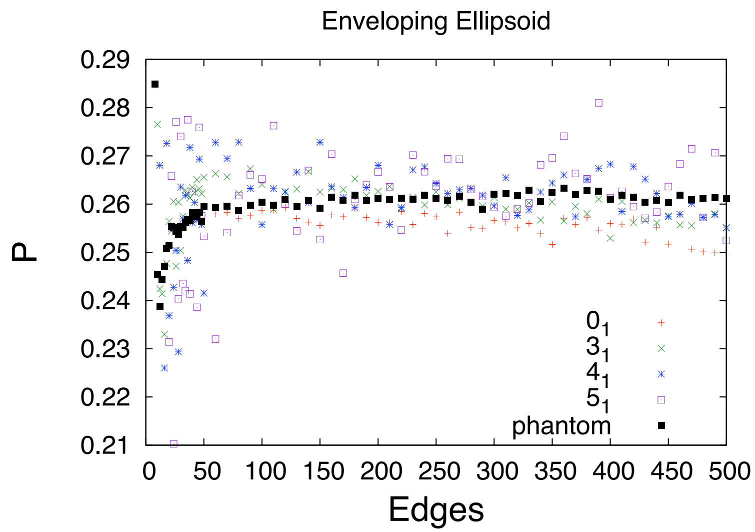


Analysis of P

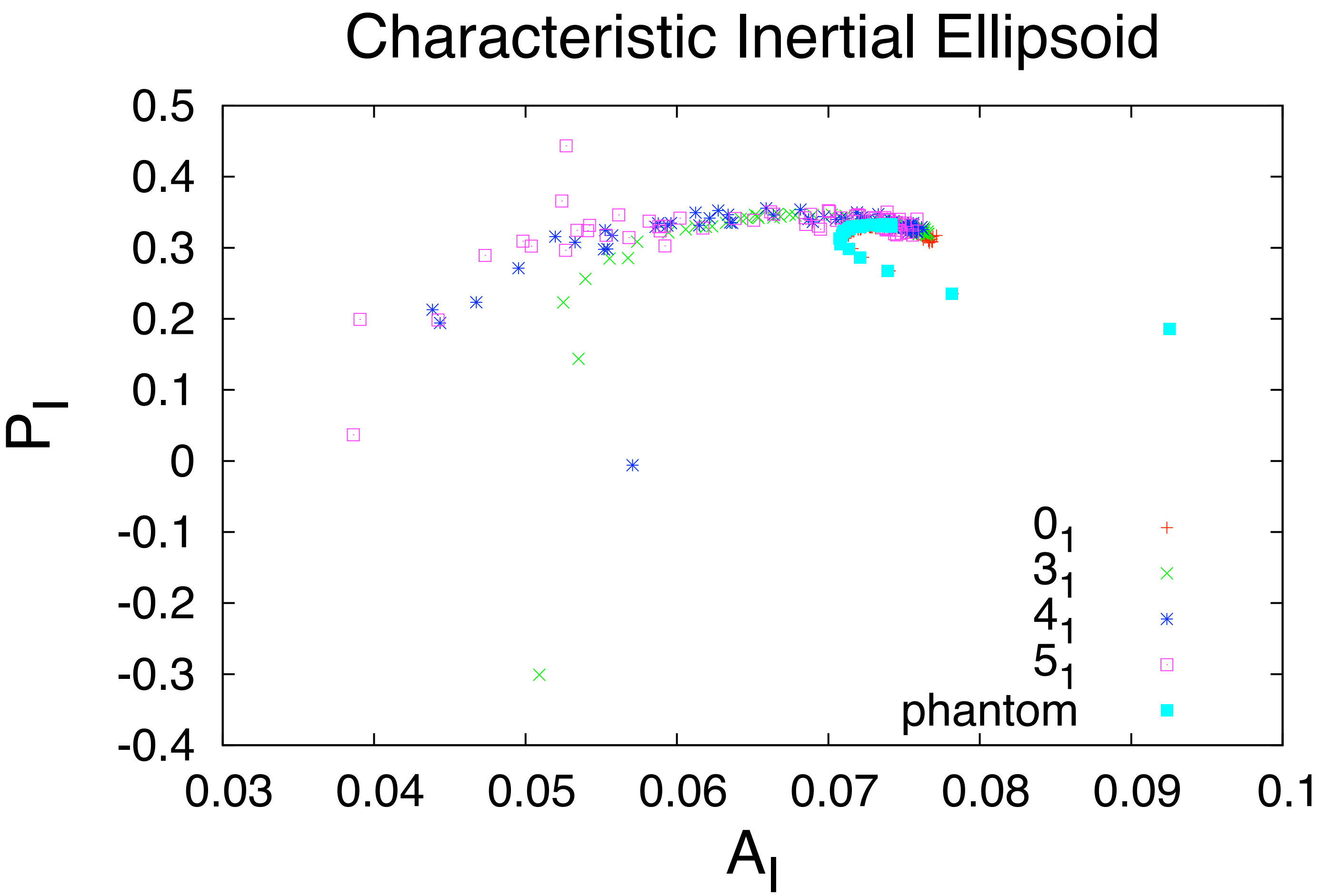
Comparison

- Phantom polygons are at a limiting value
- Inertial more prolate than enveloping
- Knot types are still decreasing (what happens beyond?)

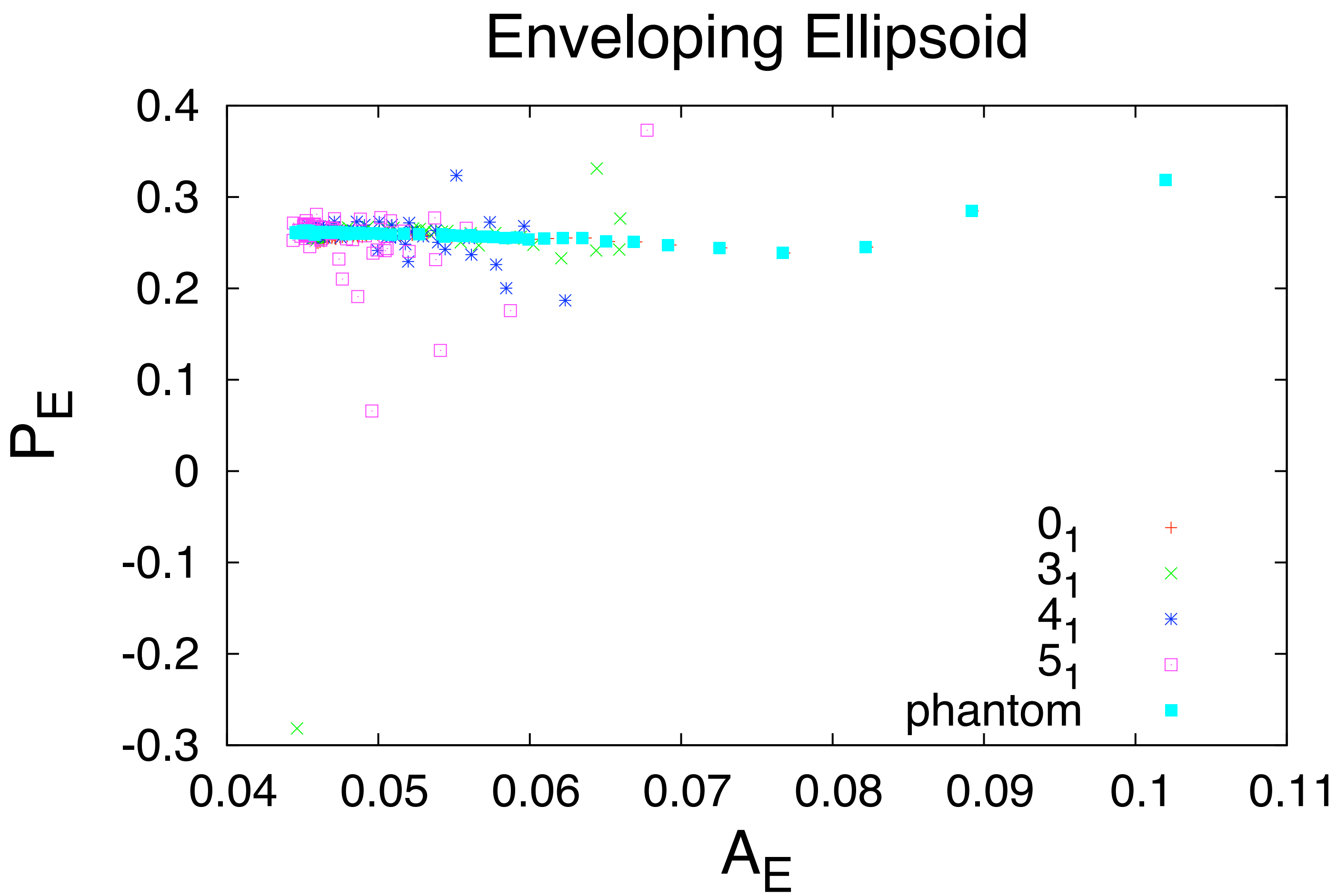




Prolateness versus Asphericity

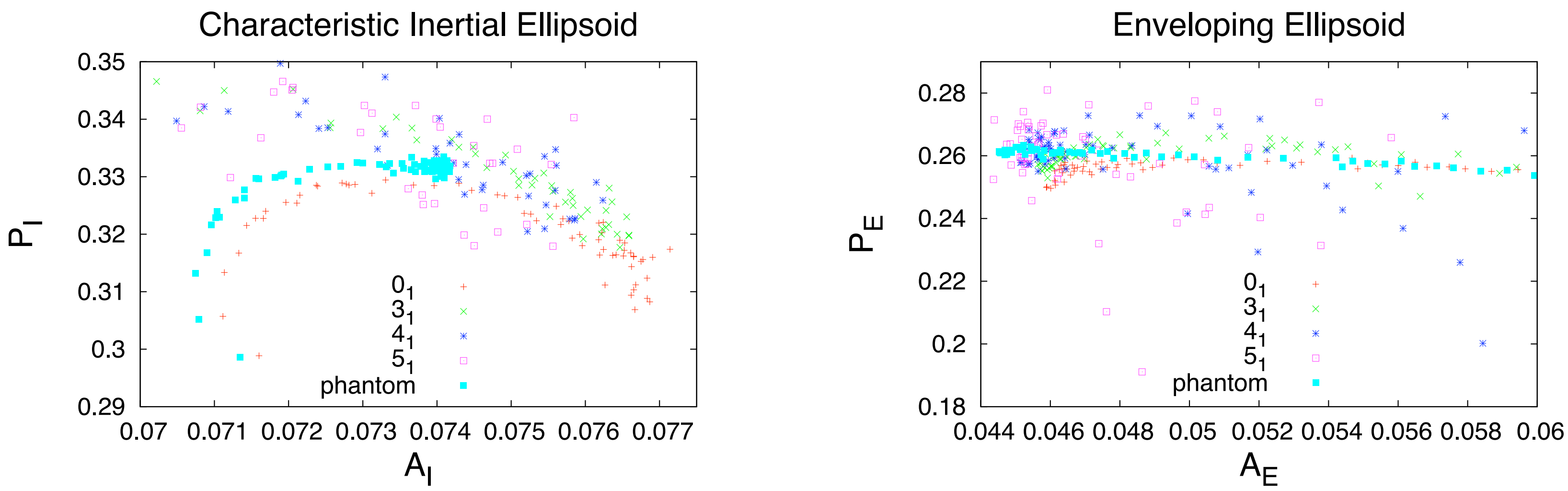


Prolateness versus Asphericity



Comparison

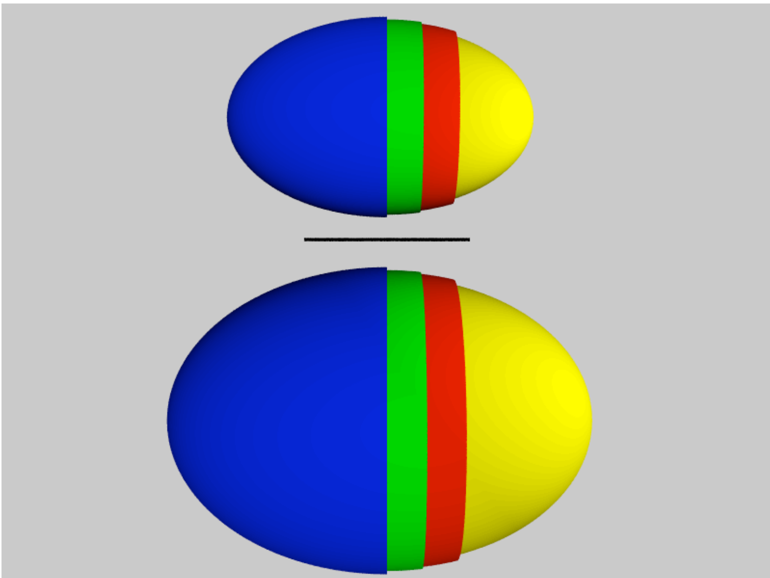
- Inertial: clustering is clear where phantom $\neq$ knot type
- Enveloping: clustering less clear but still there
- Knot types are still decreasing (what happens beyond?)

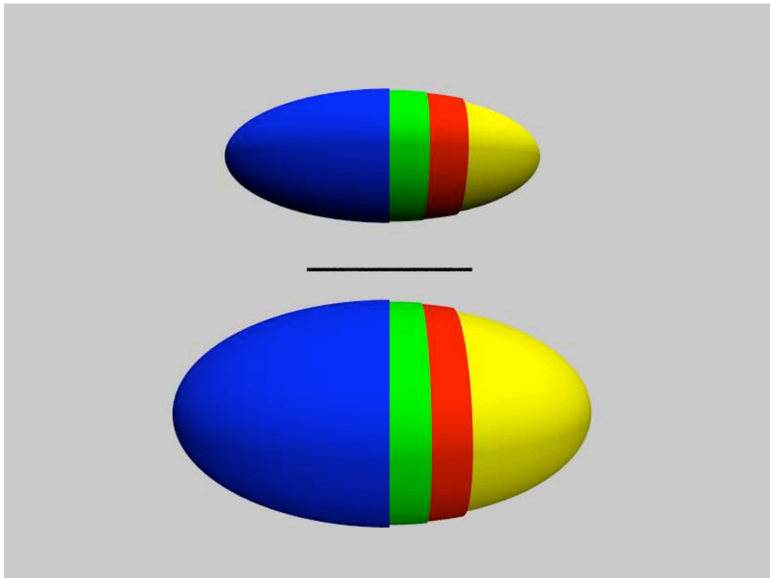


Typical Ellipsoids - 500 Edges

Key

- 0_1 – blue
- 3_1 – green
- 4_1 – red
- phantom – yellow

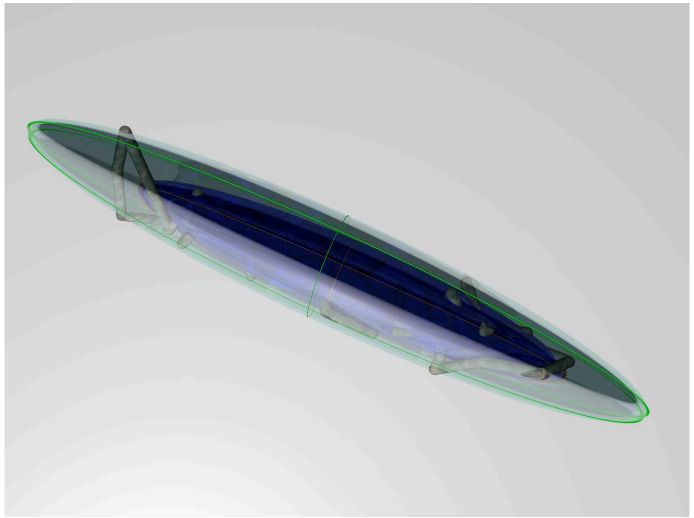


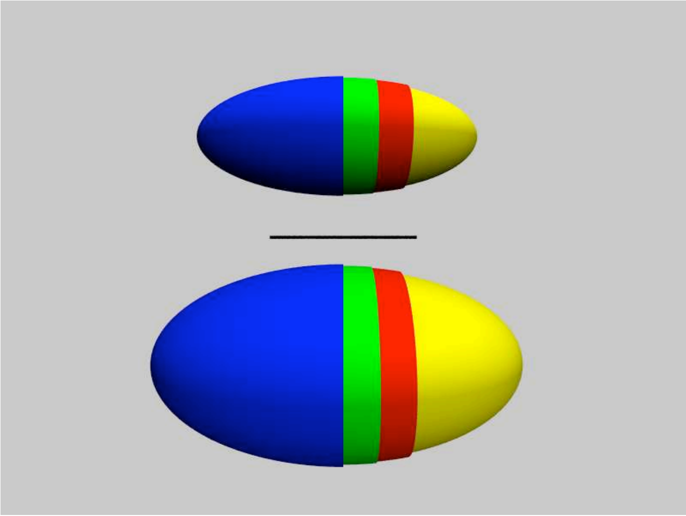


Shape and Size of Knotted Polymers

Conclusions

- Inertial and enveloping ellipsoids tell different stories
- A and P should use axis lengths for unbiased system
- Limiting values for phantom polygons differ from knot types





[19] Millett++, *J. Chem. Physics* (2009)

[20] Plunkett++, *Macromolecules* (2007)

[21] Rawdon++, *Macromolecules* (2008)

[22] Rawdon++, *Macromolecules* (2008)

Things To Do

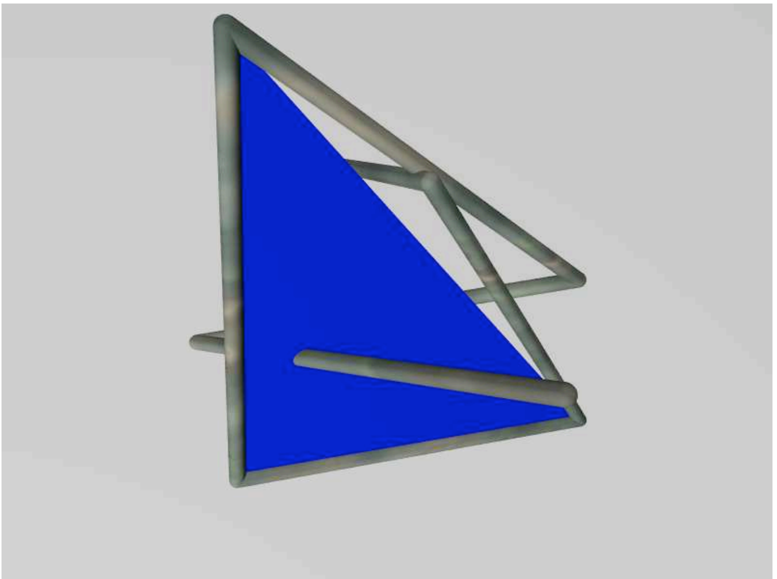
Software

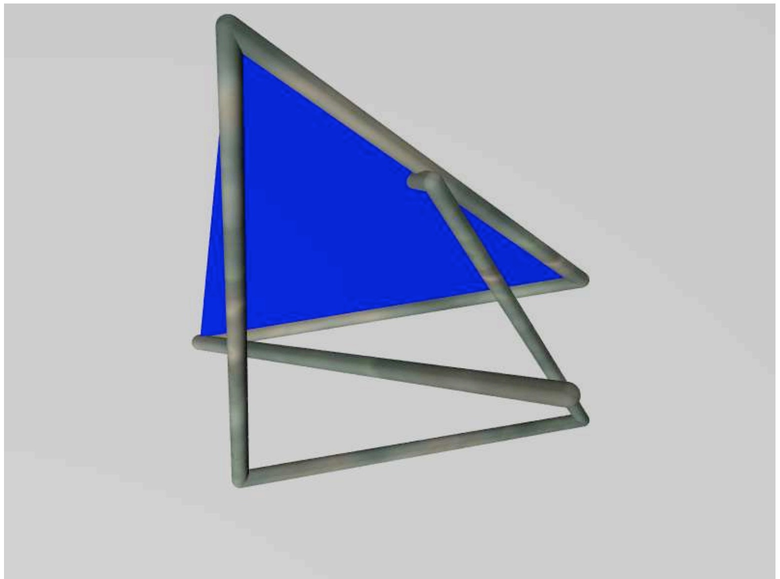
- New HOMFLYPT software
  - Simplification schemes
- Other fast algorithms to determine “knot type”
- Freeware for generating random polygons
- Freeware for generating wormlike chains
- Crossing converter in $n\ln(n)$ time (or faster)

Open Problem

Open Knots

- Researchers have found knotted (and slip-knotted) proteins
- What does it mean for an open string to be knotted?
- This a nice little problem intersecting with science
- Problem - How long is the knotted (open) portion in a knot?

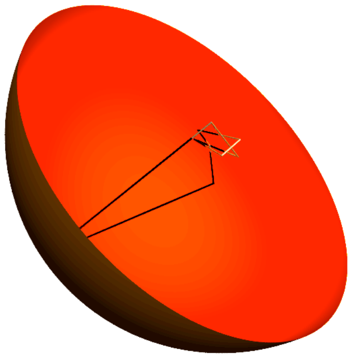


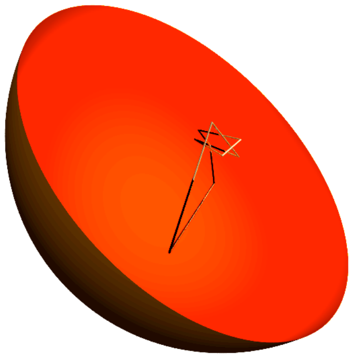


Length of Knots

Definition of knotting in arcs

- Generate closure points on a large sphere enclosing arc
- Determine knot type for each closure
- Accept if 50% are of a common knot type

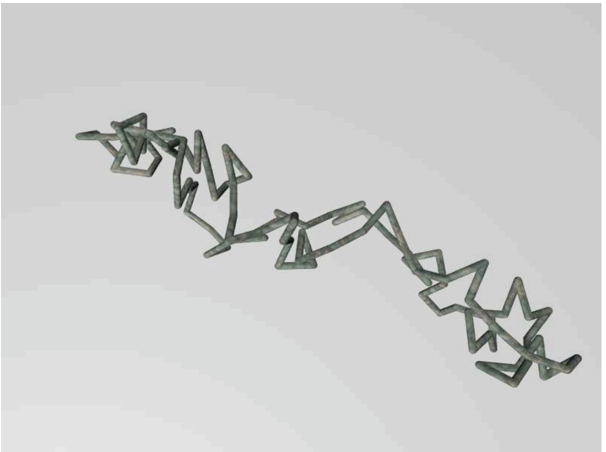




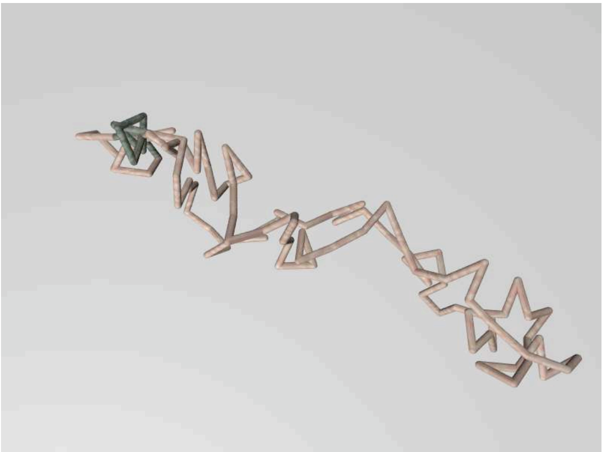
[23] Millett and Sheldon, *Physical and numerical models in knot theory* (2005)

[24] Millett++, *Macromolecules* (2005)

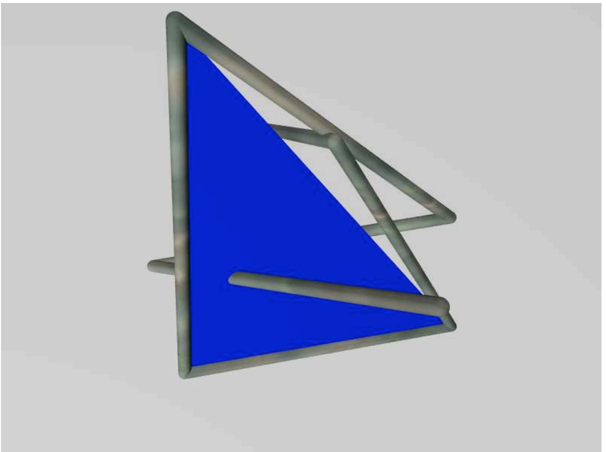
Example of 7 Edge Local Knot



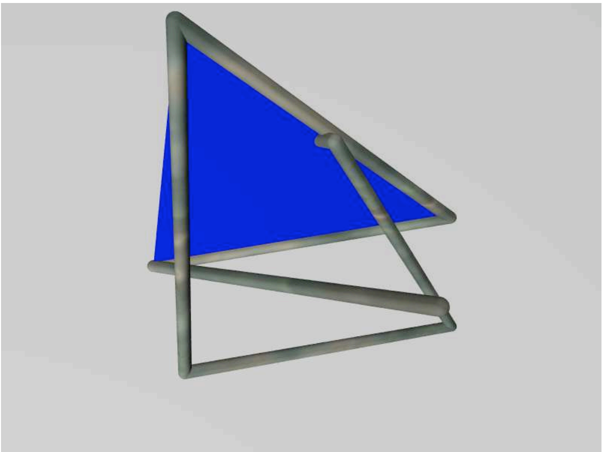
(a) 100 edge trefoil



(b) Knotting highlighted

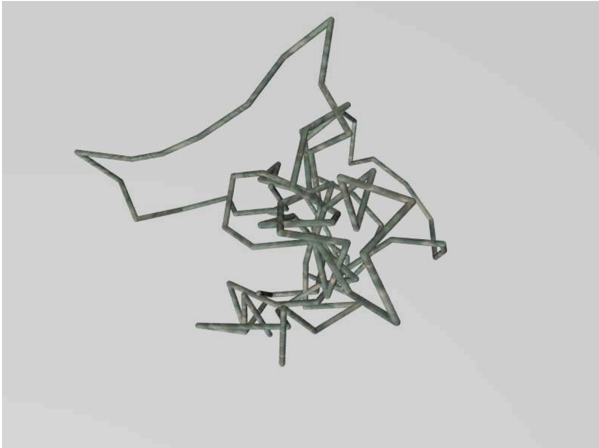


(c) First piercing triangle

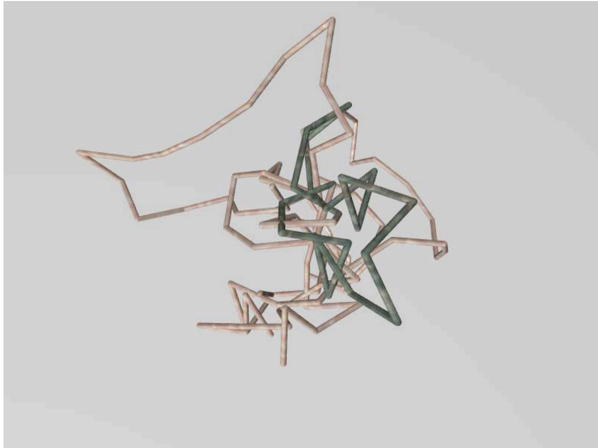


(d) Second piercing triangle

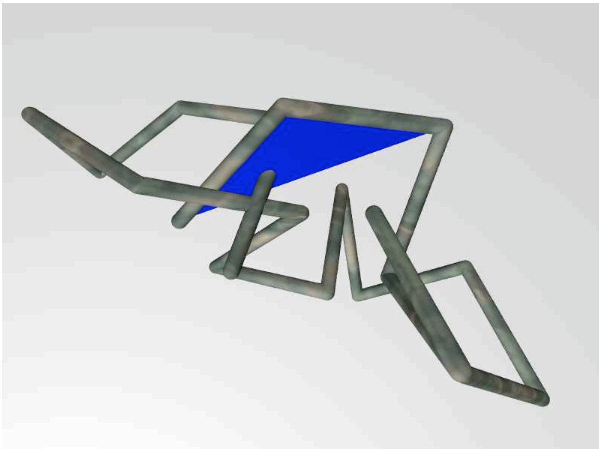
Example of 19 Edge Local Knot



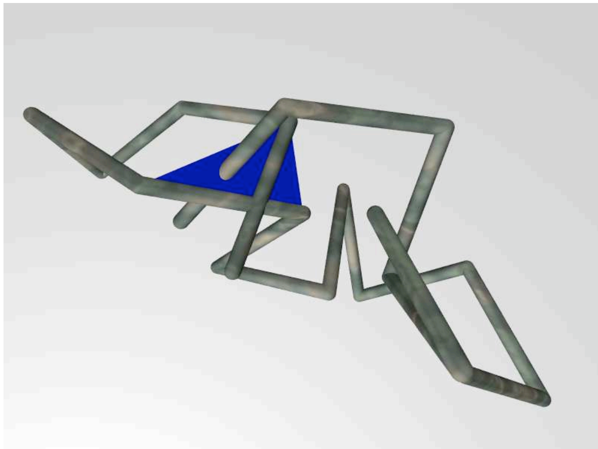
(a) 100 edge trefoil



(b) Knotting highlighted

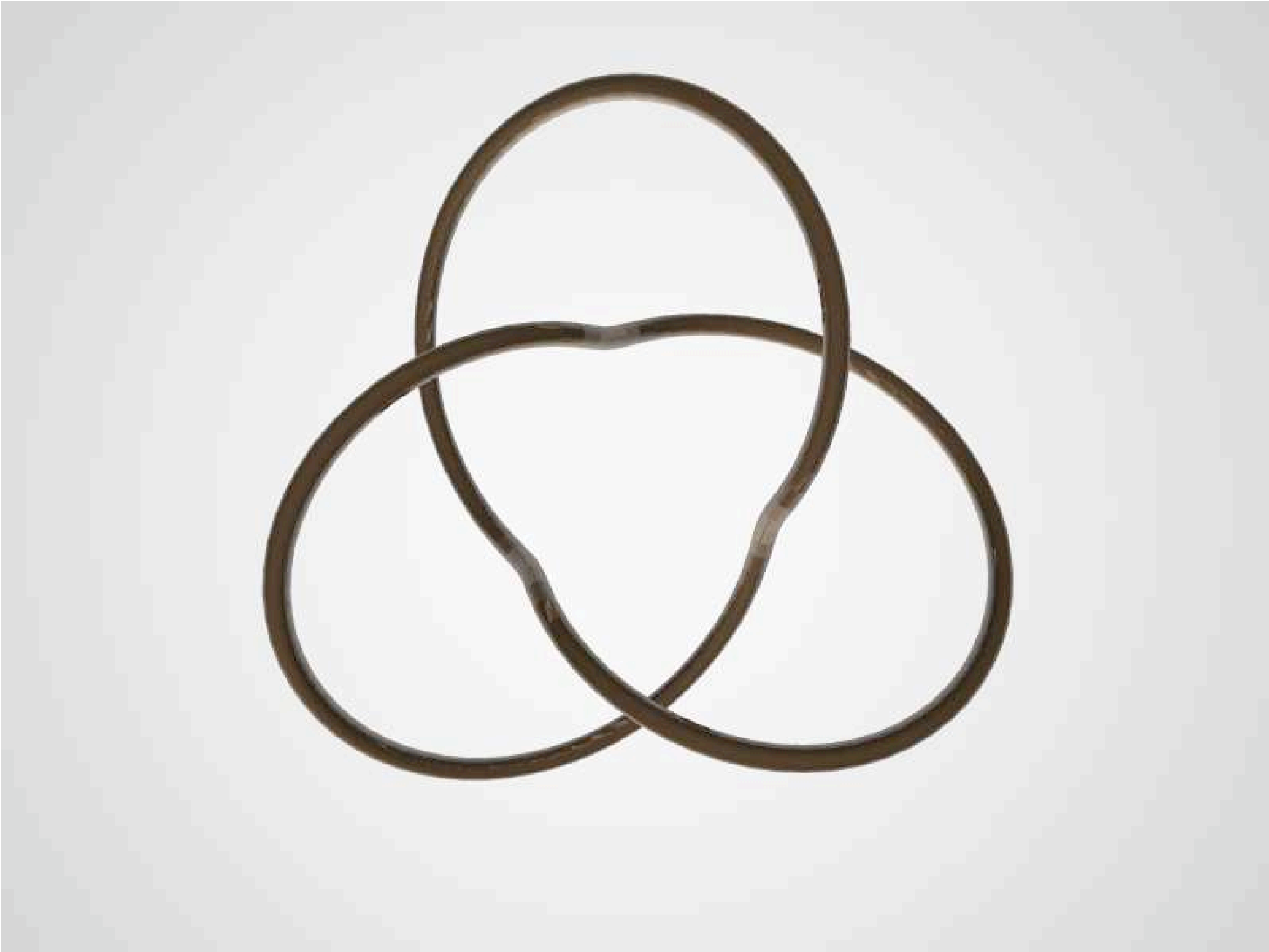


(c) First piercing triangle



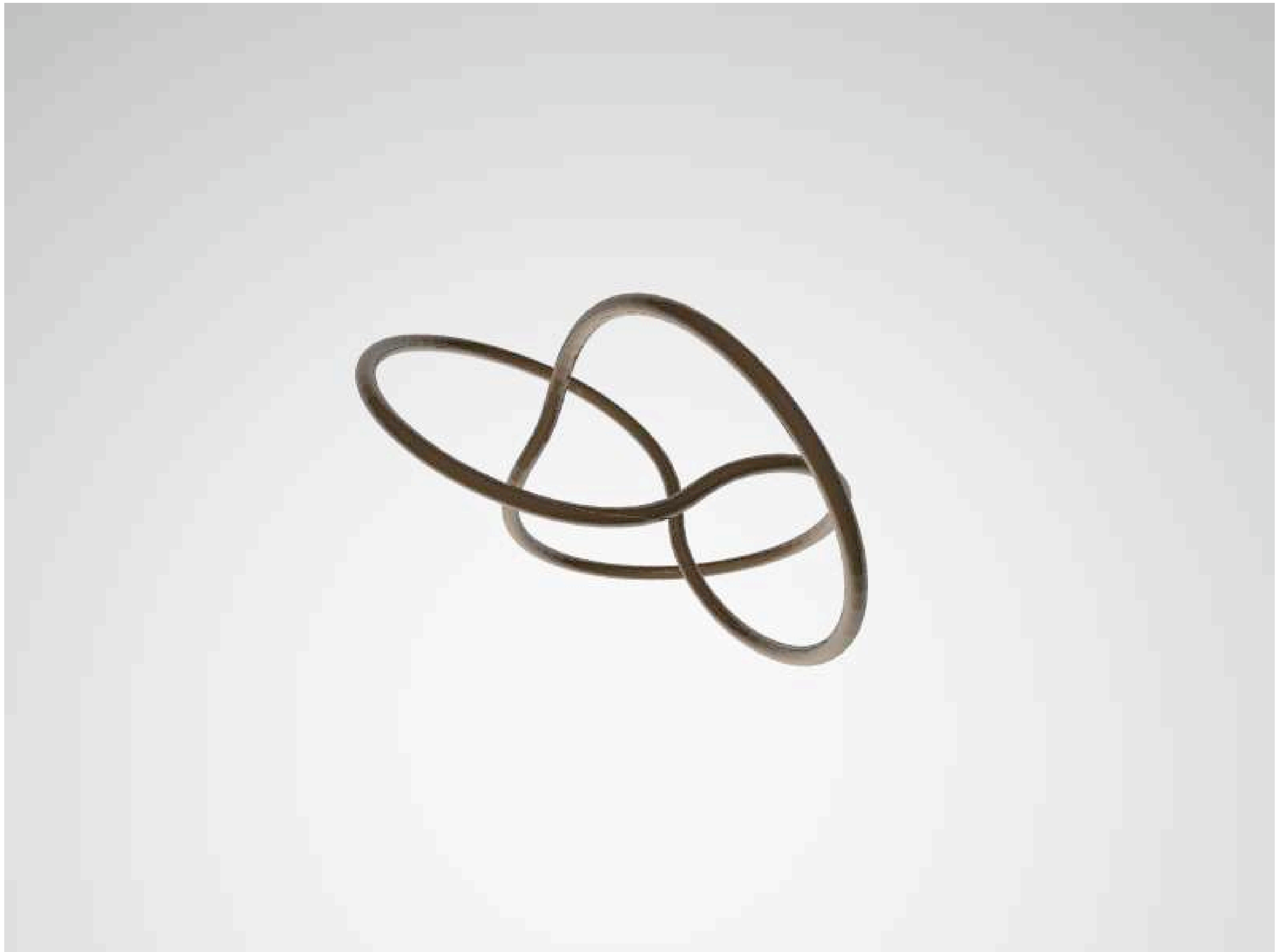
(d) Second piercing triangle

Measuring the Size of Knots



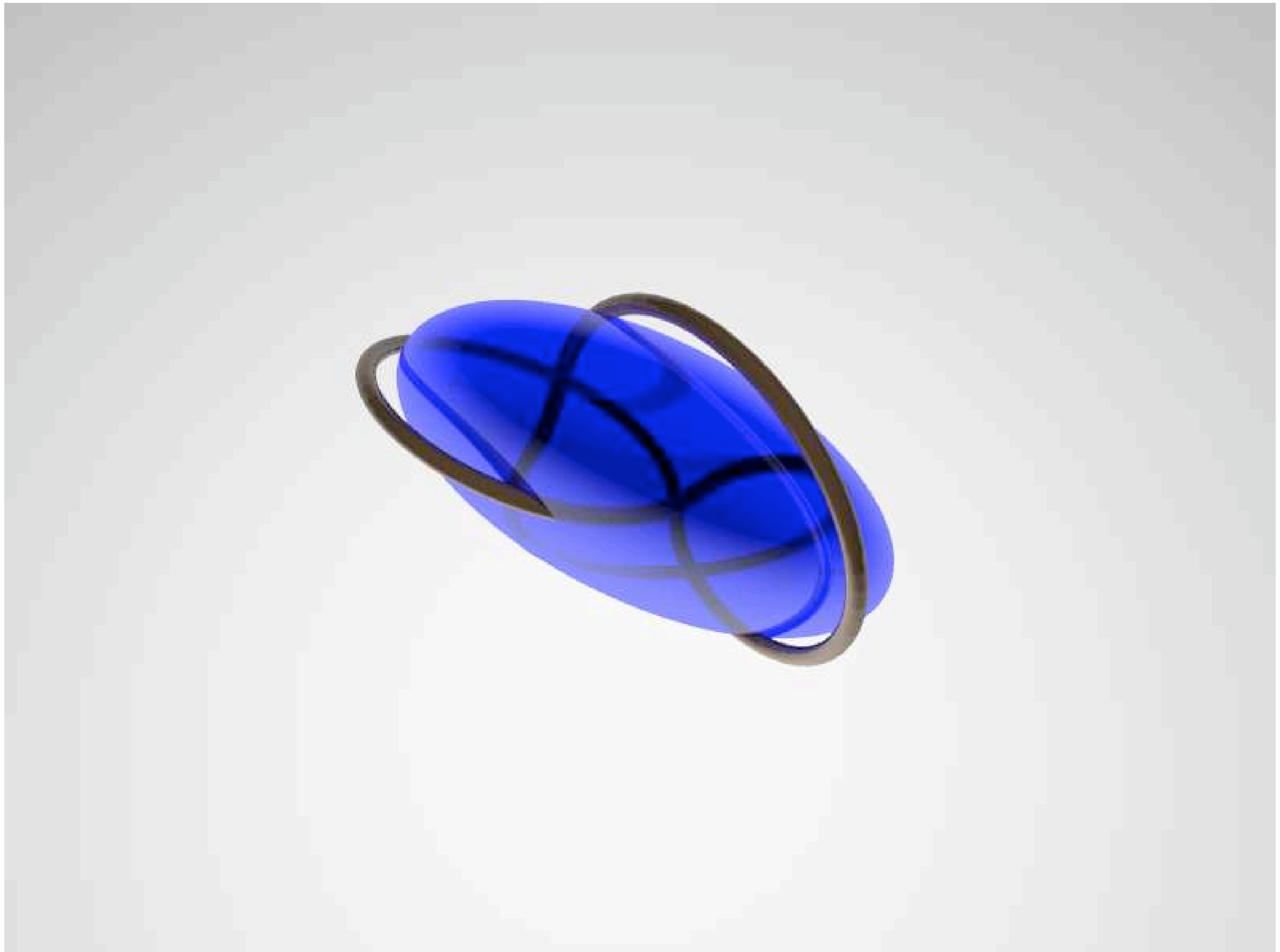
Straight on View

Measuring the Size of Knots

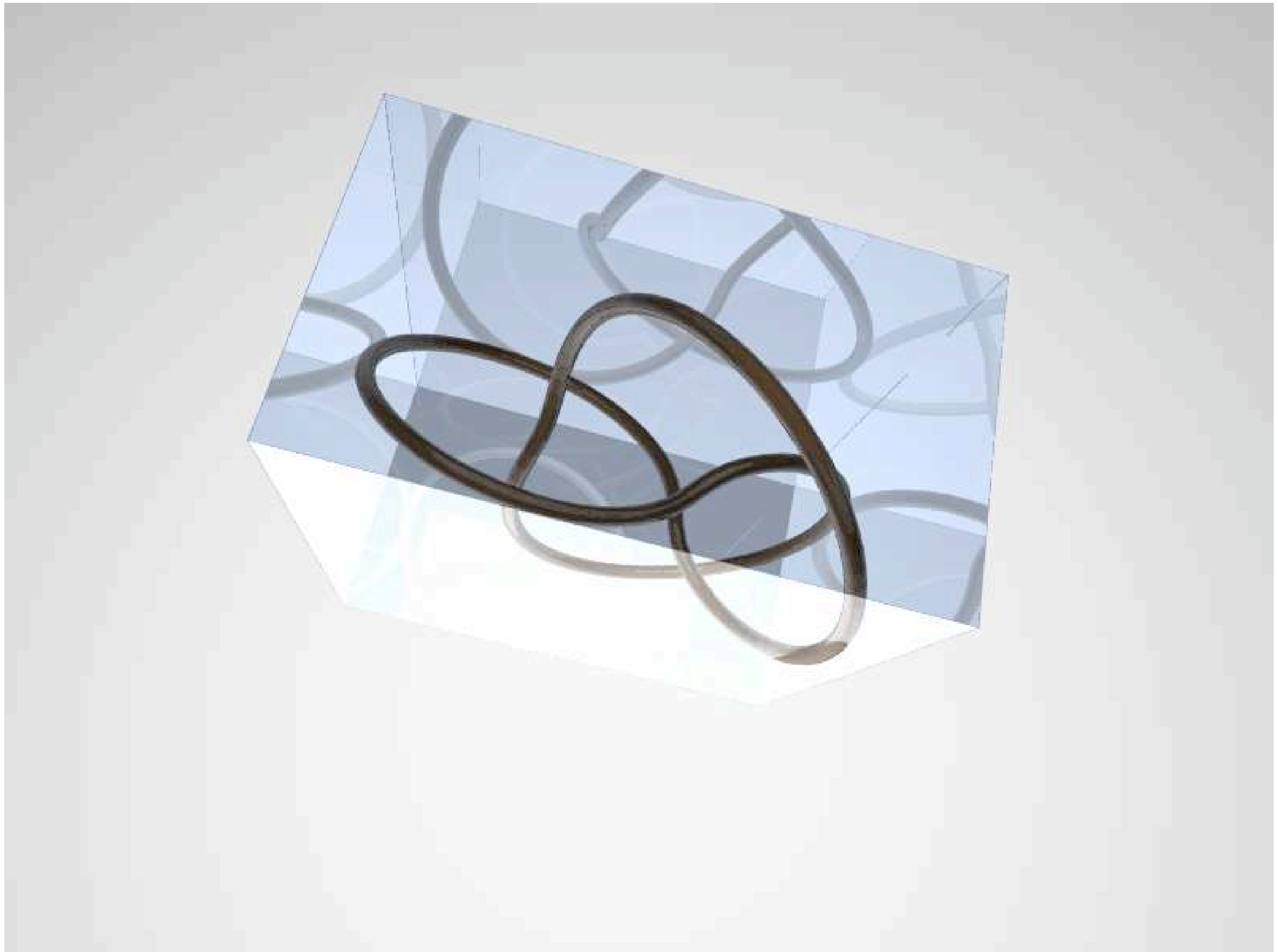


Tilted View

Measuring the Size of Knots

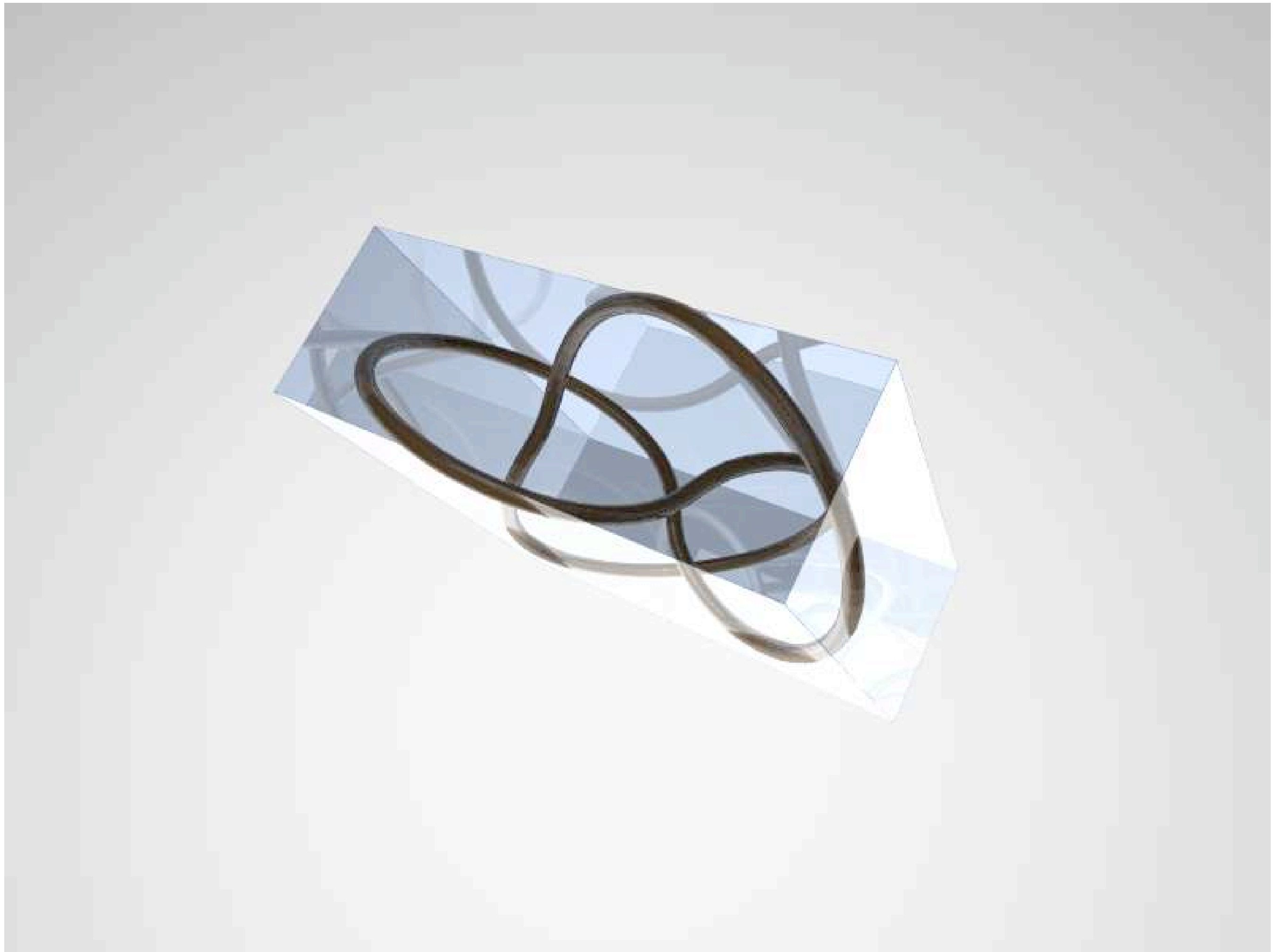


Characteristic Ellipsoid of Inertia



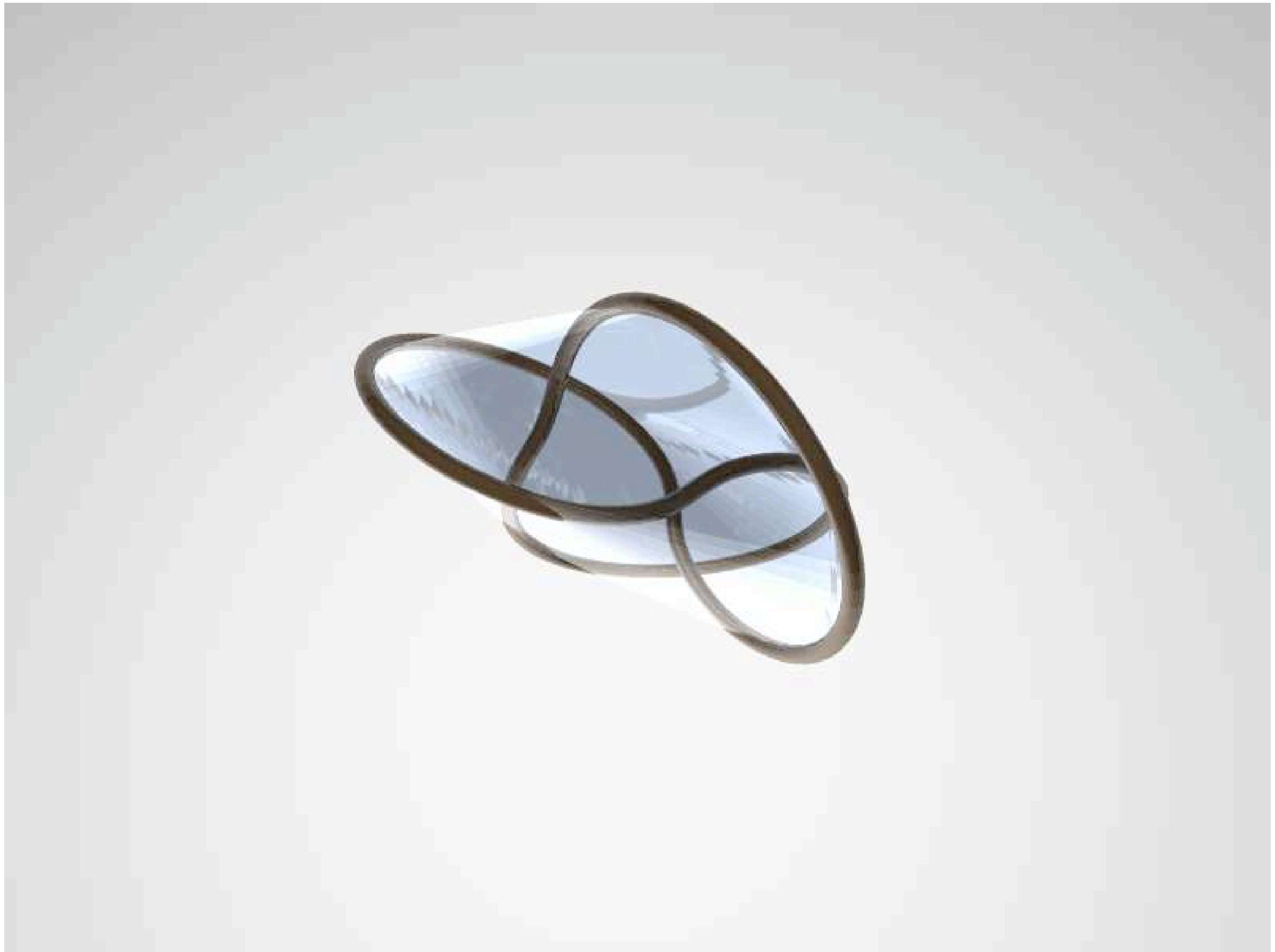
Smallest Box

Measuring the Size of Knots



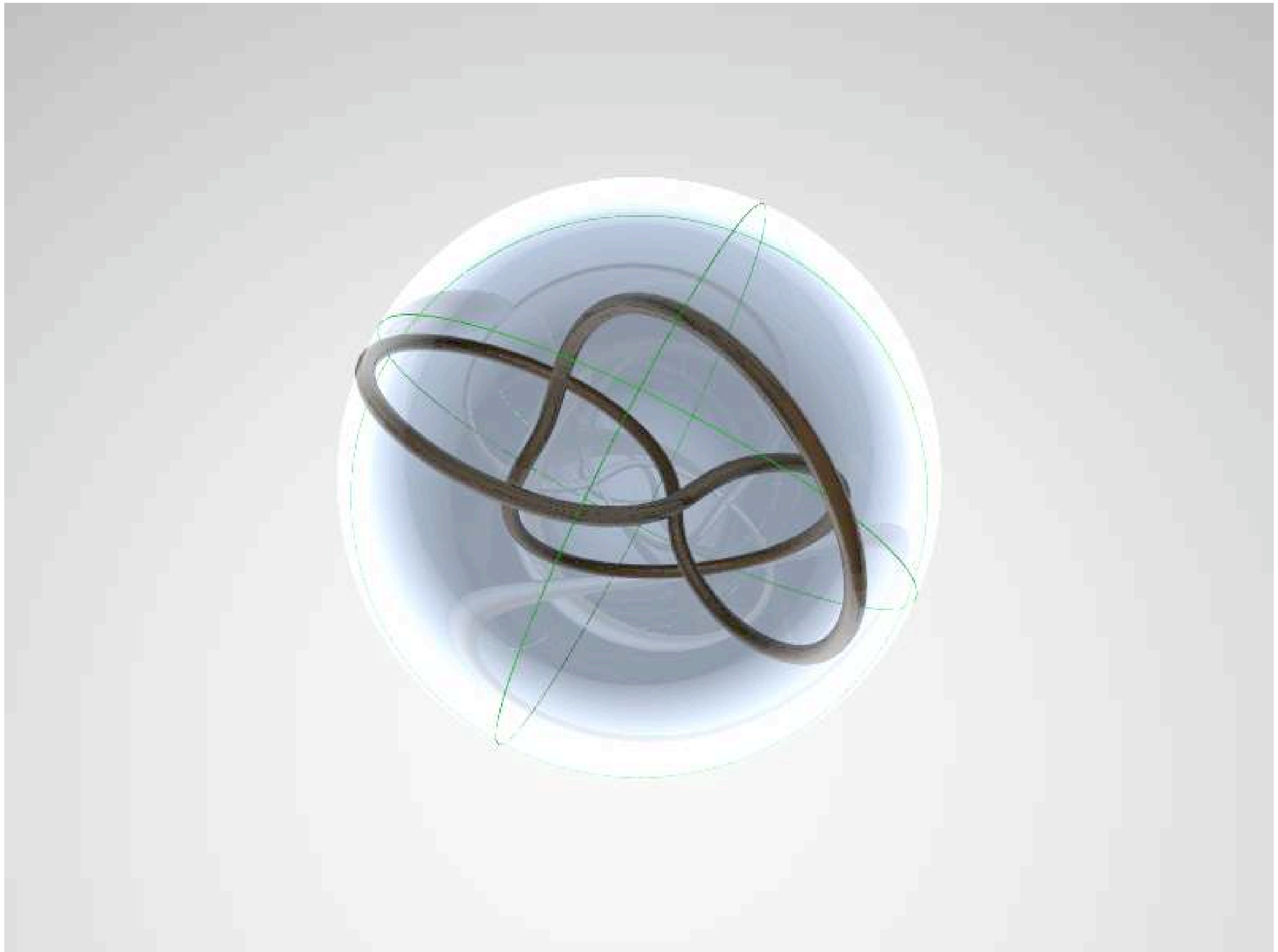
Skinny Box

Measuring the Size of Knots



Convex Hull

Measuring the Size of Knots



Smallest Sphere

Measuring the Size of Knots

Smallest Volume Enveloping Ellipsoid

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Macromolecules, 38(2):601–606, 2005.

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