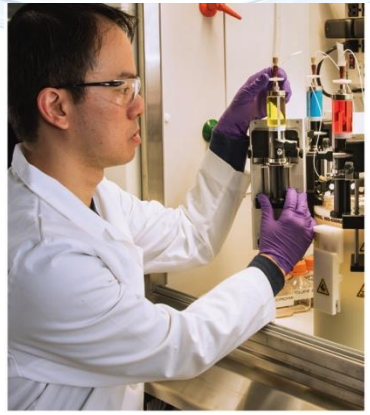

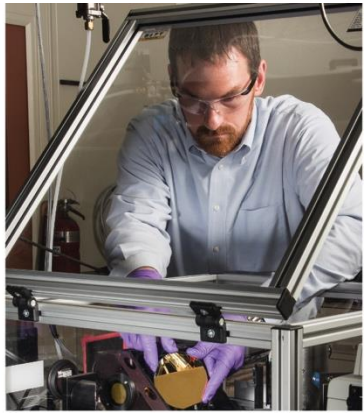

Molecular Dynamics Study of the Conformational Properties of Polymers in an Explicit Solvent and the Identification of the θ-Temperature

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[1]Le Moyne College, [2]National Institute of Standards and Technology(NIST), U.S. Department of Commerce, Gaithersburg, Maryland, USA

NIST National Institute of Standards and Technology U.S. Department of Commerce

LE MOYNE · COLLEGE · A·D·1946

MATERIAL MEASUREMENT LABORATORY

POLYMERS

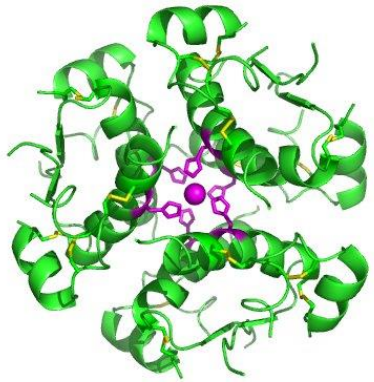
Large molecule/macromolecule composed of repeating subunits called monomers

Polystyrene(Styrofoam)

Image from:
https://www.theodysseyonline.com/new-year-no-more-styrofoam

Polyisoprene(rubber)

Image from:
https://www.tirerack.com/content/tirerack/desktop/en/homepage.html



Insulin Hexamer

Image from:
https://en.wikipedia.org/wiki/Insulin

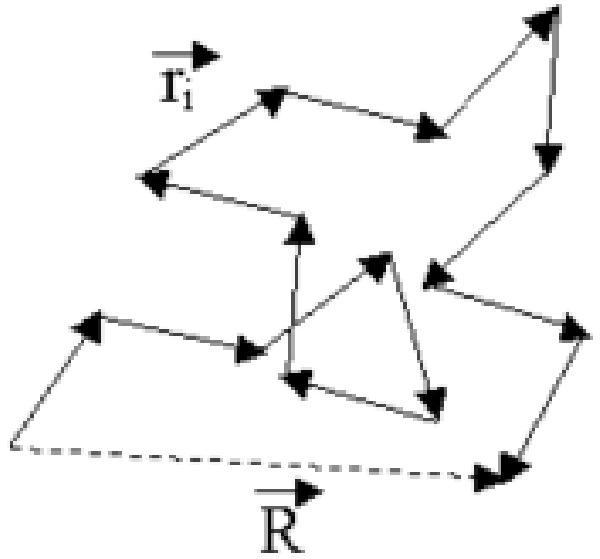
DNA

Image from:
http://exchange.smarttech.com/search.html?q=%22DNA%20structure%22

POLYMER MODELS

- Ideal Chain:
  - Modeled after a random walk model (no attractions, no repulsions)

- "Real Chain":
  - Incorporates interactions between all segments
    - Includes a repulsive excluded volume interaction and an attractive component that allows us to account for the quality of the solvent



A typical ideal chain

https://en.wikipedia.org/wiki/Ideal_chain

FLORY THEORY/SCALING LAW

$$R_g \sim N^{\nu} \qquad R_g^2 = \frac{1}{N}\sum_{k=1}^{n}(r_k - r_{mean})^2$$

R_g is the radius of gyration of the polymer

N is the degree of polymerization(# of segments)

ν Is the Flory exponent

For a good solvent, $\nu \approx 3/5$

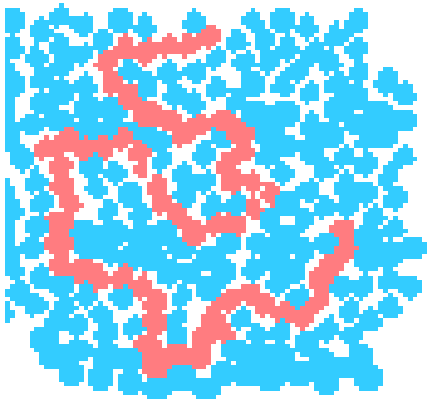
For the θ-solvent, $\nu \approx 1/2$

For a poor solvent, $\nu \approx 1/3$

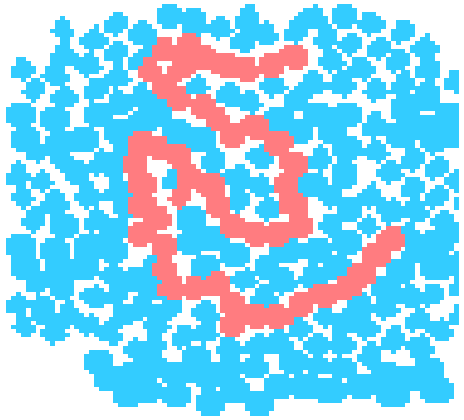
Solvent quality depends on chemistry and temperature

SOLVENT QUALITY

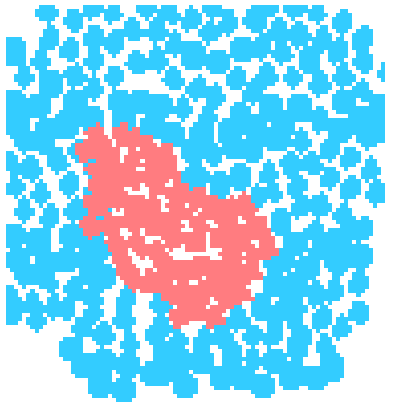
- **“Good solvent”:**
  - Monomers prefer to interact with the solvent particles rather than with other monomers
  - Repulsive interactions dominate
  - Polymer swells



- **“θ-solvent”:**
  - Attractive and repulsive interactions are equal
  - Polymer behaves as if it’s an ideal chain



- **“Poor solvent”**
  - Monomers prefer to interact with other monomers rather than with solvent particles
  - Attractive forces dominate
  - Polymer contracts and behaves more as a hard sphere



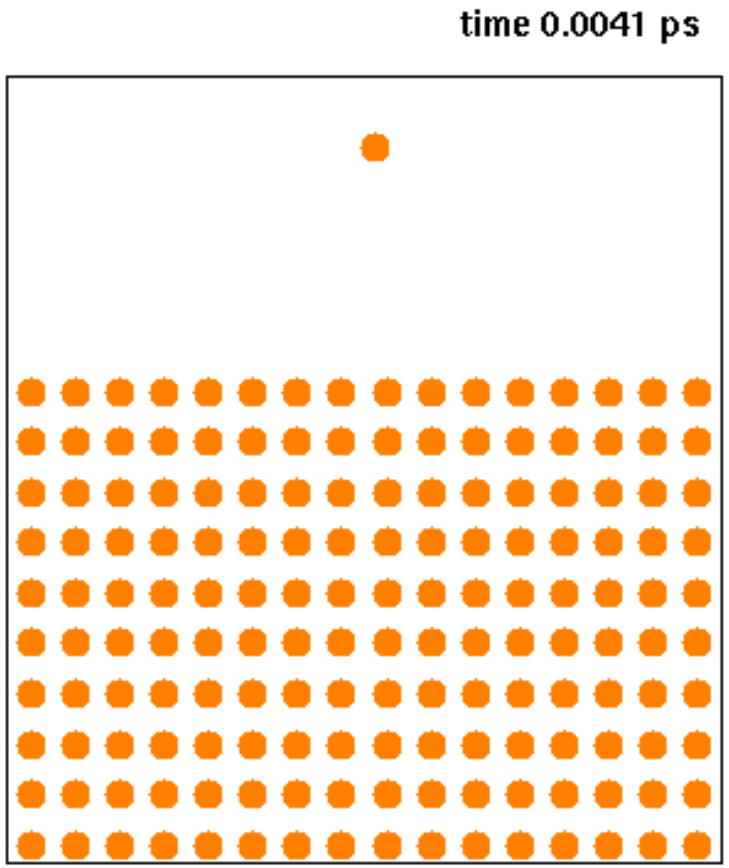
Images from: http://rkt.chem.ox.ac.uk/lectures/pol.html

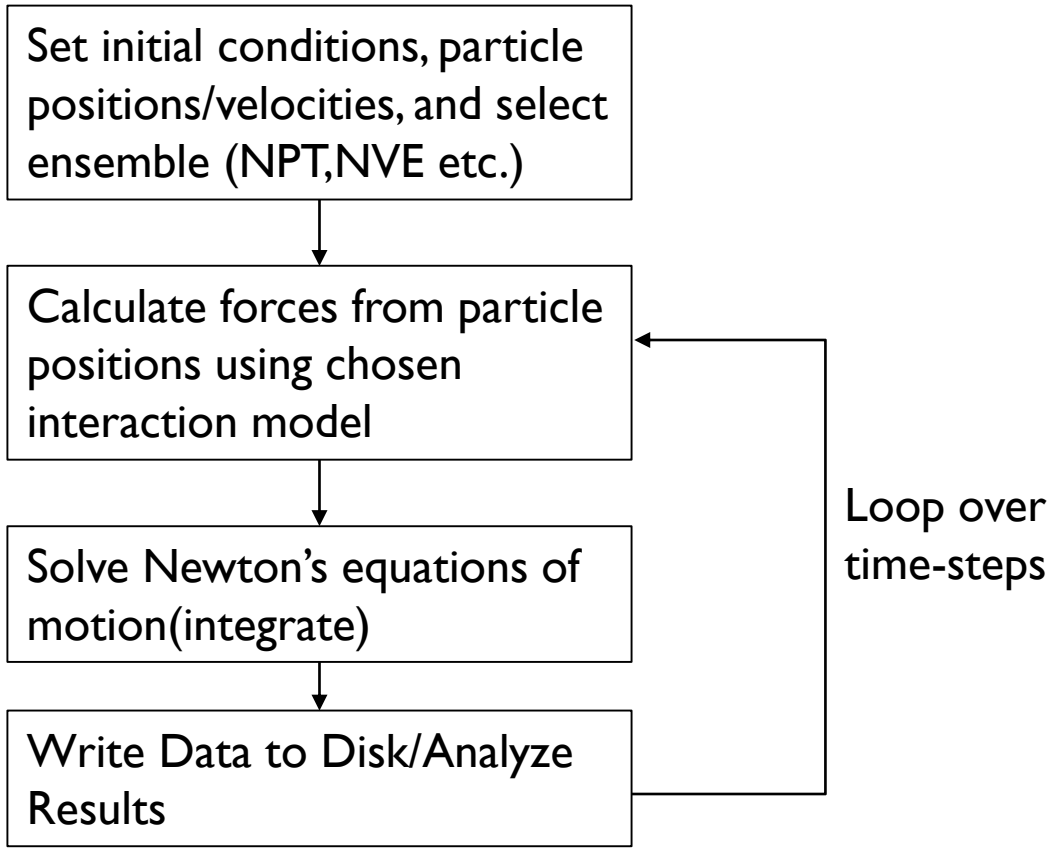
OBJECTIVES

- Develop a model that can identify the θ-temperature of a polymer solution
- Use molecular dynamics to simulate polymers of varying chemistries and molecular architectures in an explicit solvent

MOLECULAR DYNAMICS SIMULATIONS

Animation from https://en.wikipedia.org/wiki/Molecular_dynamics





IMPLICIT SOLVATION WORK

- Implicit solvation work on this topic has been done by Steinhauser M.O. In J. Chem. Phys. 122(2005) on flexible linear polymer chains of varying molecular masses
- Used a coarse grained bead-spring model that introduced a dimensionless parameter λ which determines the depth of the intermolecular potential
- Larger λ=greater attractive forces between segments
- The overall intermolecular potential has the form

$$V_{inter}(r) = \begin{cases} V_{WCA}(r) - \lambda\epsilon, & 0 < r < 2^{1/6}\sigma \\ \lambda V_{cos}(r), & 2^{1/6} \le r < r_{cut} \\ 0 & else \end{cases}$$

$$V_{WCA}(r) = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} + \epsilon$$

$$V_{cos}(r) = \left[\frac{1}{2}\cos(\alpha r^2 + \beta) + 0.5\right]\epsilon$$

Where α and β are parameters that fit the cosine curve to smoothly approach 0 at the cutoff

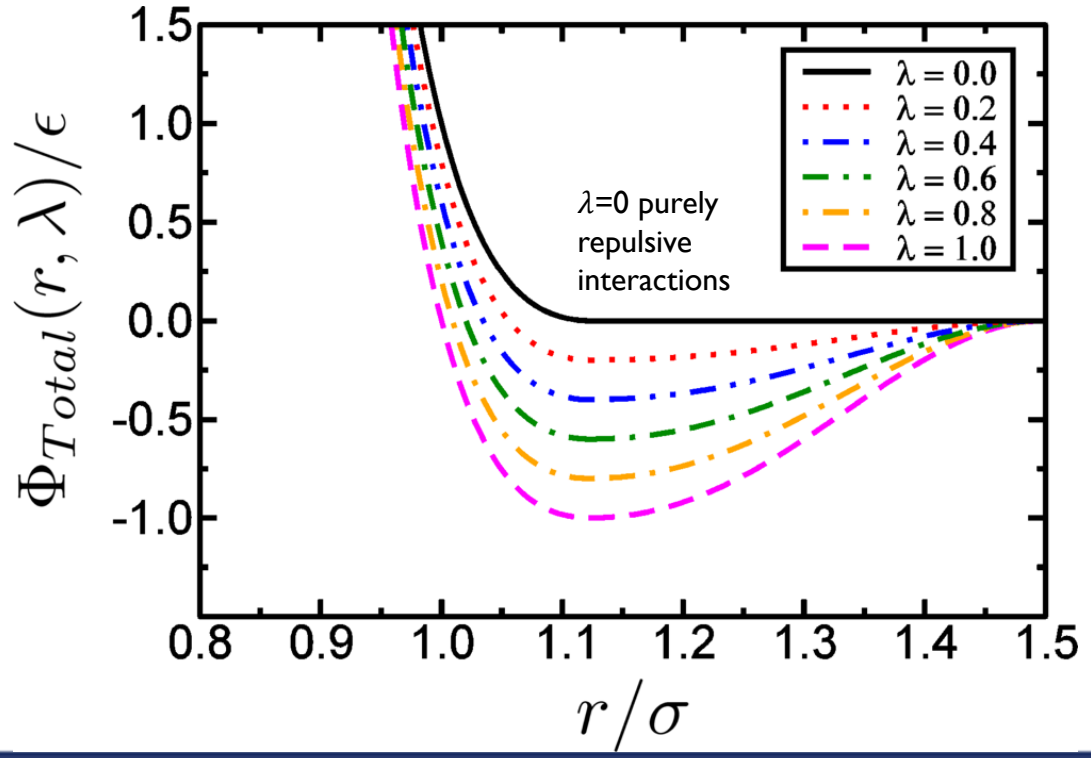


Image from:
Steinhauser M.O *Int. J. Mol. Sci.* 2009, *10*(12)

Steinhauser M.O. *J. Chem. Phys* 122(2005)

IMPLICIT SOLVATION WORK

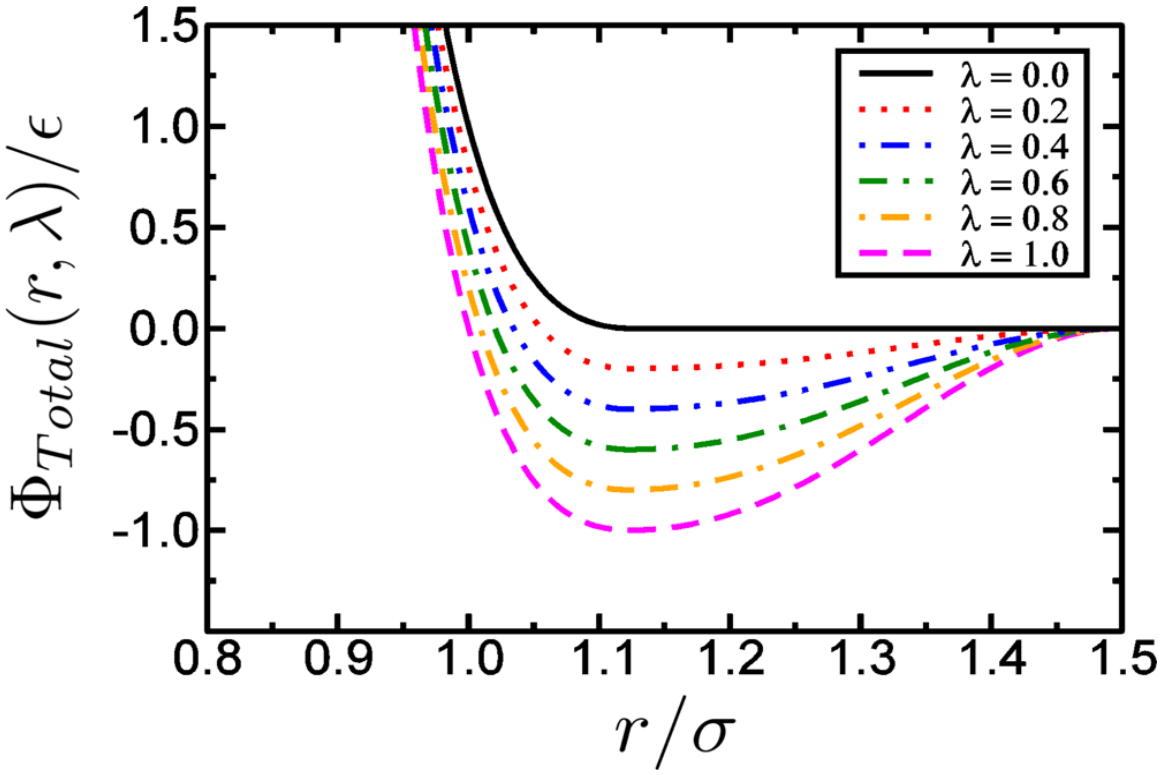
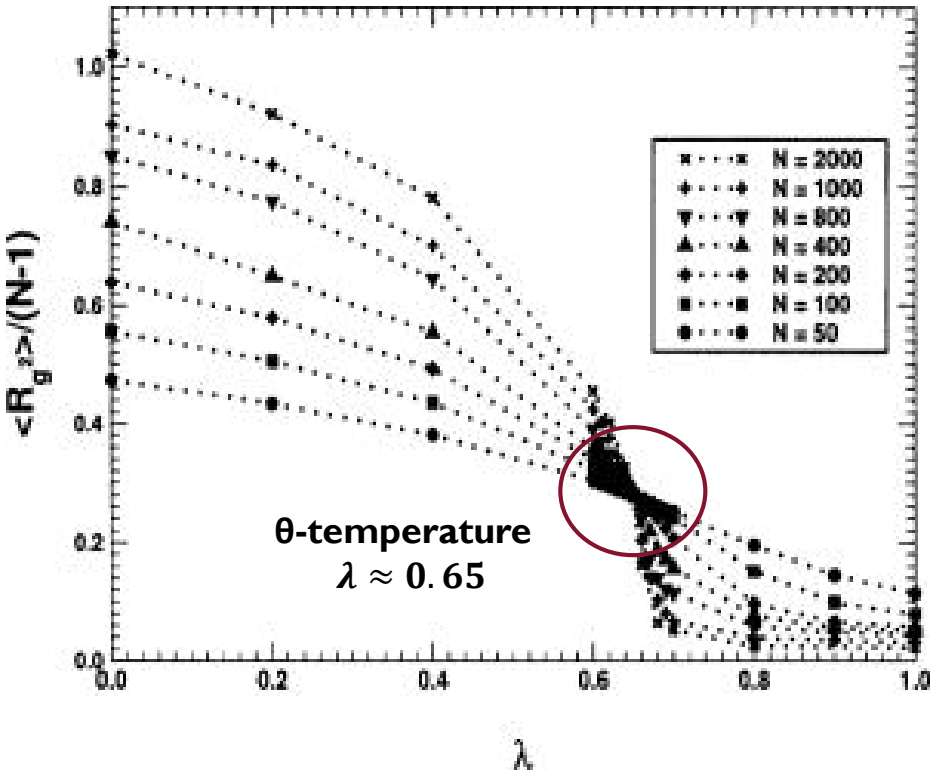


Image from: Steinhauser M.O *Int. J. Mol. Sci.* 2009, *10*(12)



Steinhauser M.O. *J. Chem. Phys* 122(2005)

WHY USE AN EXPLICIT SOLVENT?

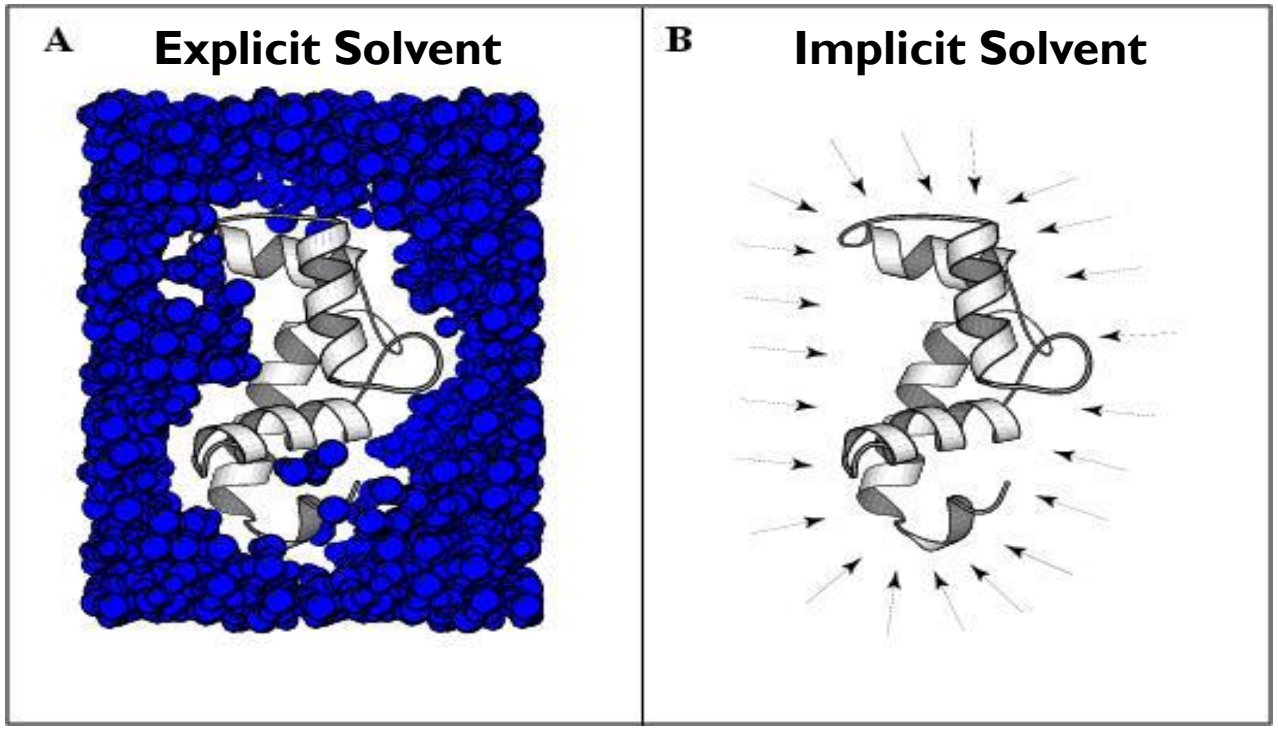
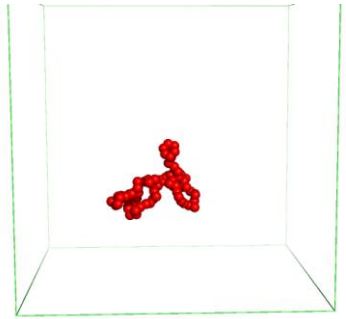


Image from: http://csb.stanford.edu/~koehl/ProShape/born.php

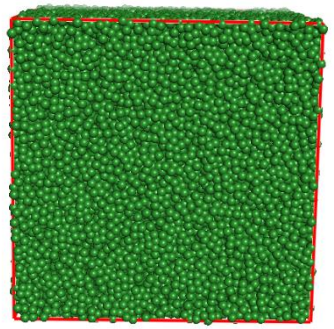
- Provides a more realistic and detailed full-atom description of the system
- Essential to reproduce certain properties of solute molecules
  - Reaction kinetics
  - Dynamics
- Computationally expensive… but worth it

SIMULATION DETAILS

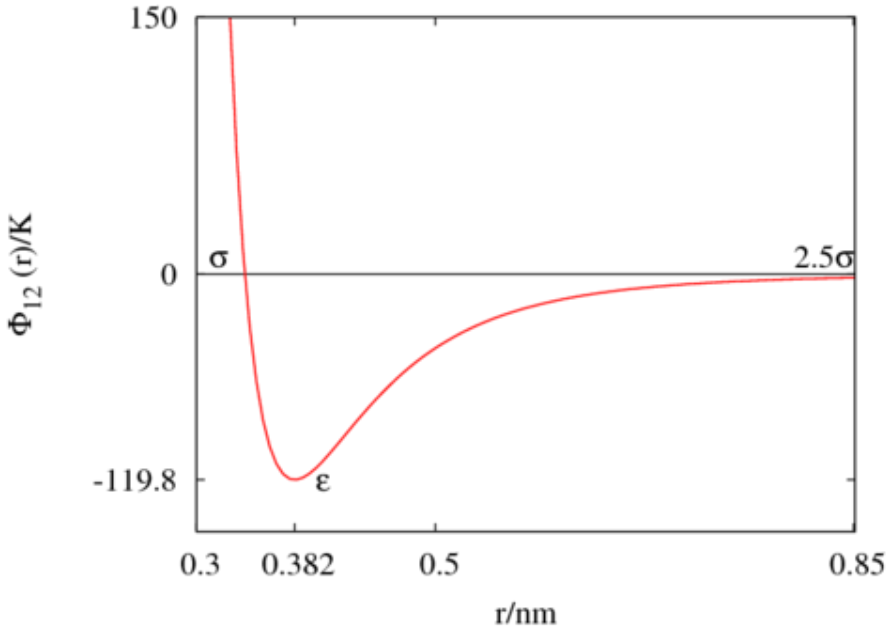
- Used a coarse grained bead model with an explicit solvent to try and determine the θ-temperature of various polymers of different molecular architectures and chemistries
- NPT Ensemble
- The Lennard Jones Potential was used with a cutoff of 2.5σ
- Used ZENO numerical path integration software to obtain conformational properties of the generated polymer chains (radius of gyration, hydrodynamic radius, etc)



Polymer chain with 41 monomers



72000 solvent particles + polymer



$$V_{LJ}(r) = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

Image from: http://www.sklogwiki.org/SklogWiki/index.php/Lennard-Jones_model

SYSTEMS STUDIED

Molecular Mass: 41,81,161,321

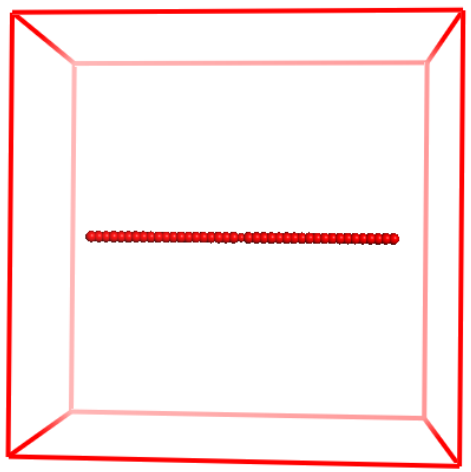
Temperature=0.5,0.7,0.9

ε_{pp} for polymer-polymer interactions: 1.0
ε_{ss} for solvent-solvent interactions: 1.0

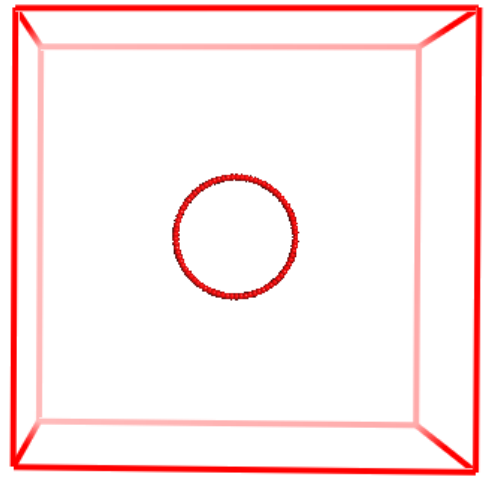
ε_{sp} cross interactions: Modified Lorentz Berthelot mixing rule

$$\varepsilon_{sp} = \sqrt{\varepsilon_{pp} * \varepsilon_{ss}}(1 - \alpha)$$

α=.0, α=.02, α=.04, α=.06, α=.08, α=.1, α=.12, α=.14, α=.16,



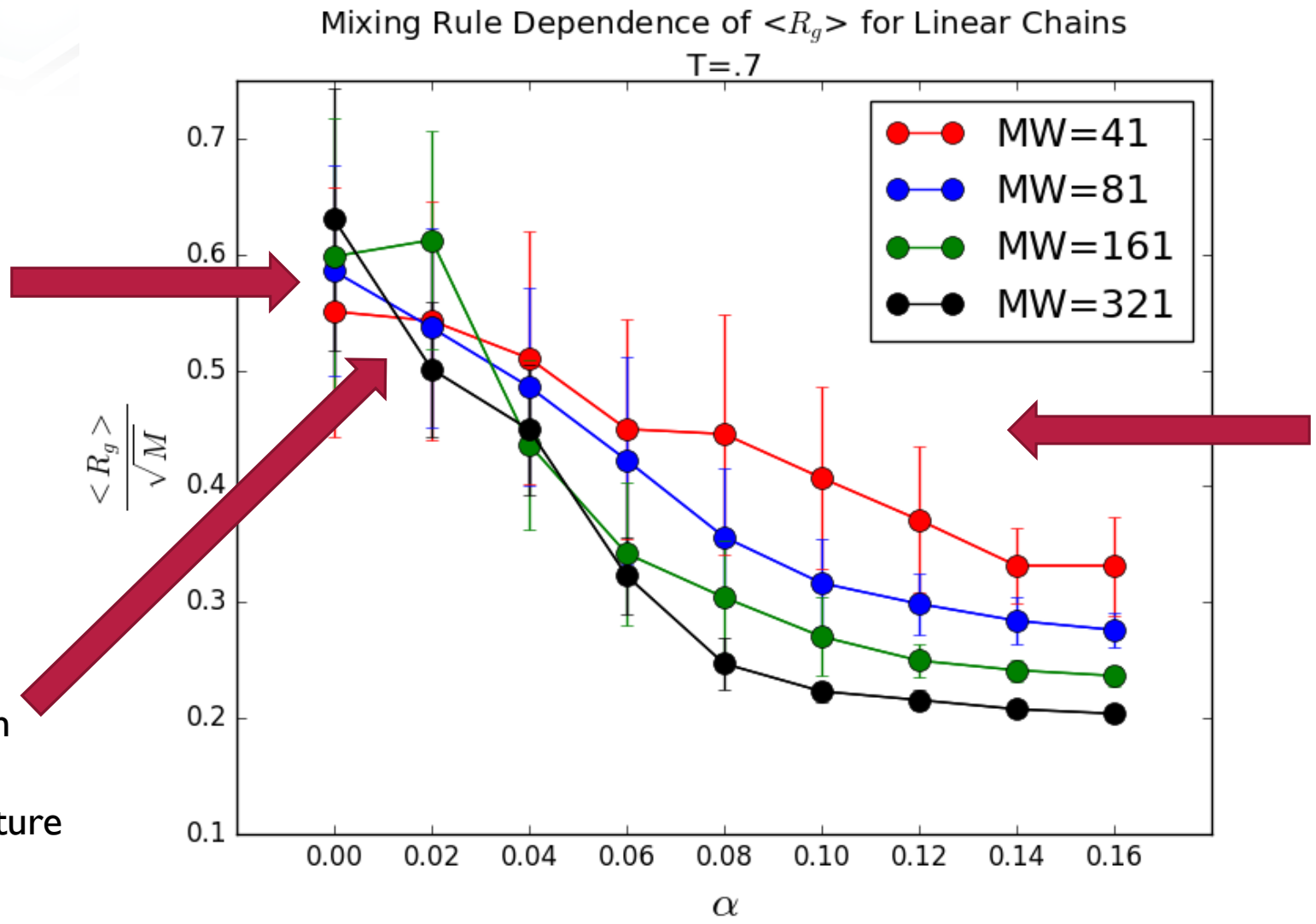
Linear Chain



Ring Polymer

WHAT SHOULD OUR MIXING RULE BE?

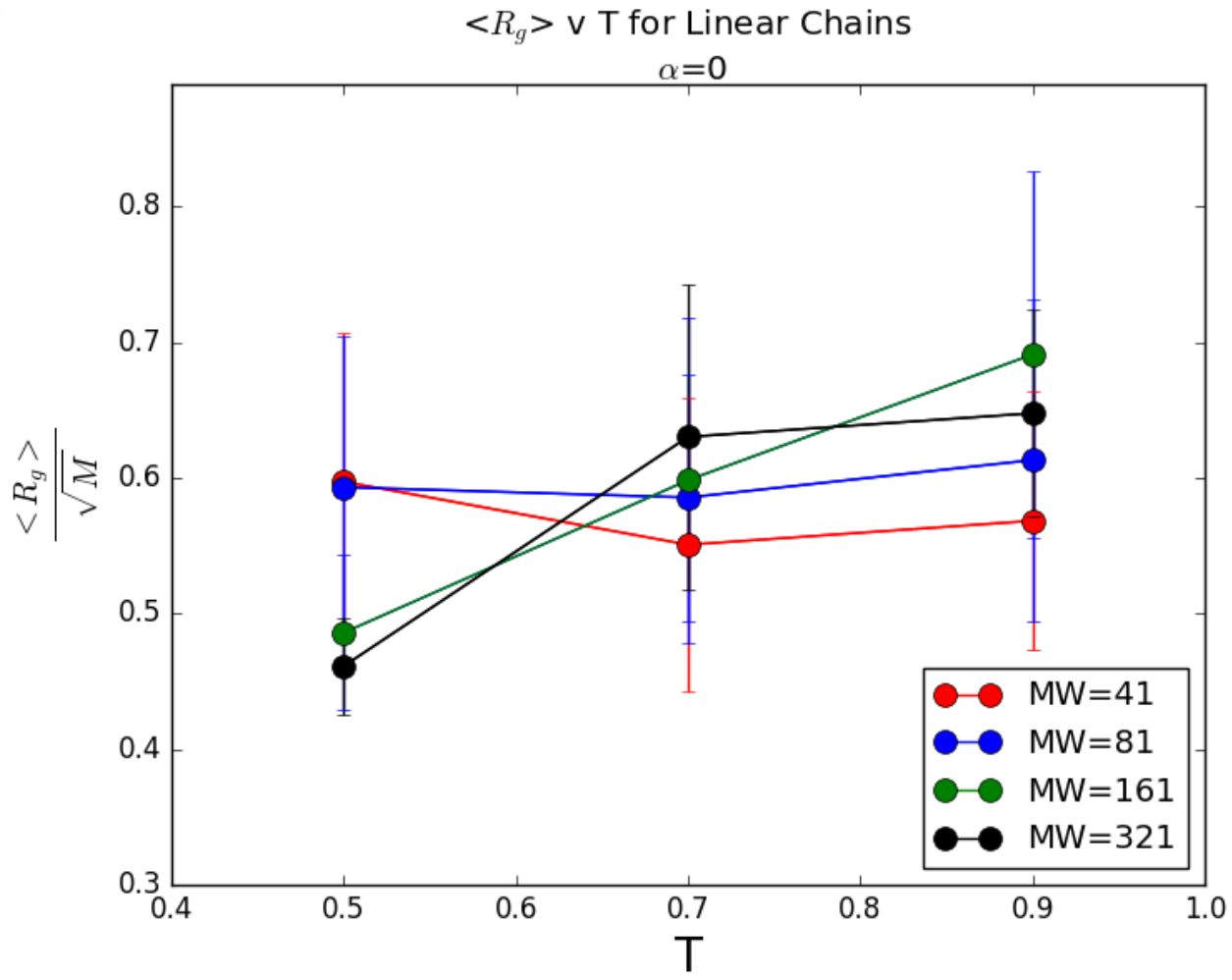
α=0
Swollen Region
Good solvent conditions



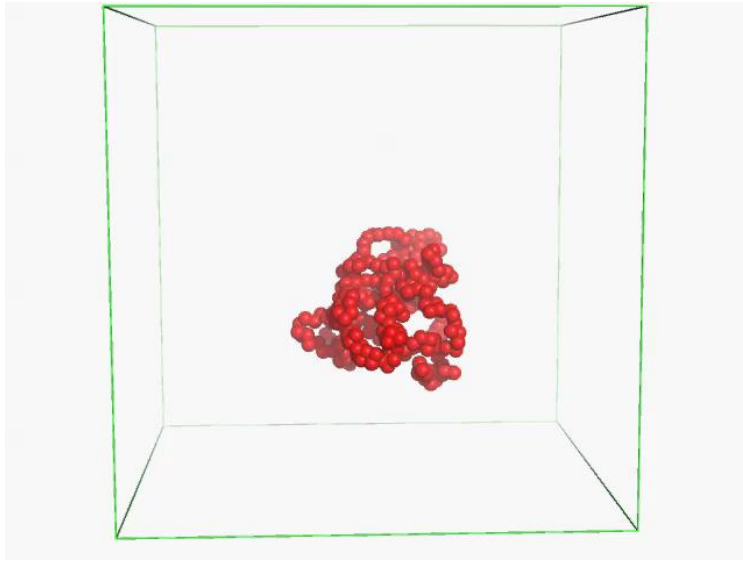
$\alpha \geq 0.06$
Collapsed Region
Always poor solvent conditions

0.02<α<0.04
Intermediate Region
R_g is sensitive to changes in temperature

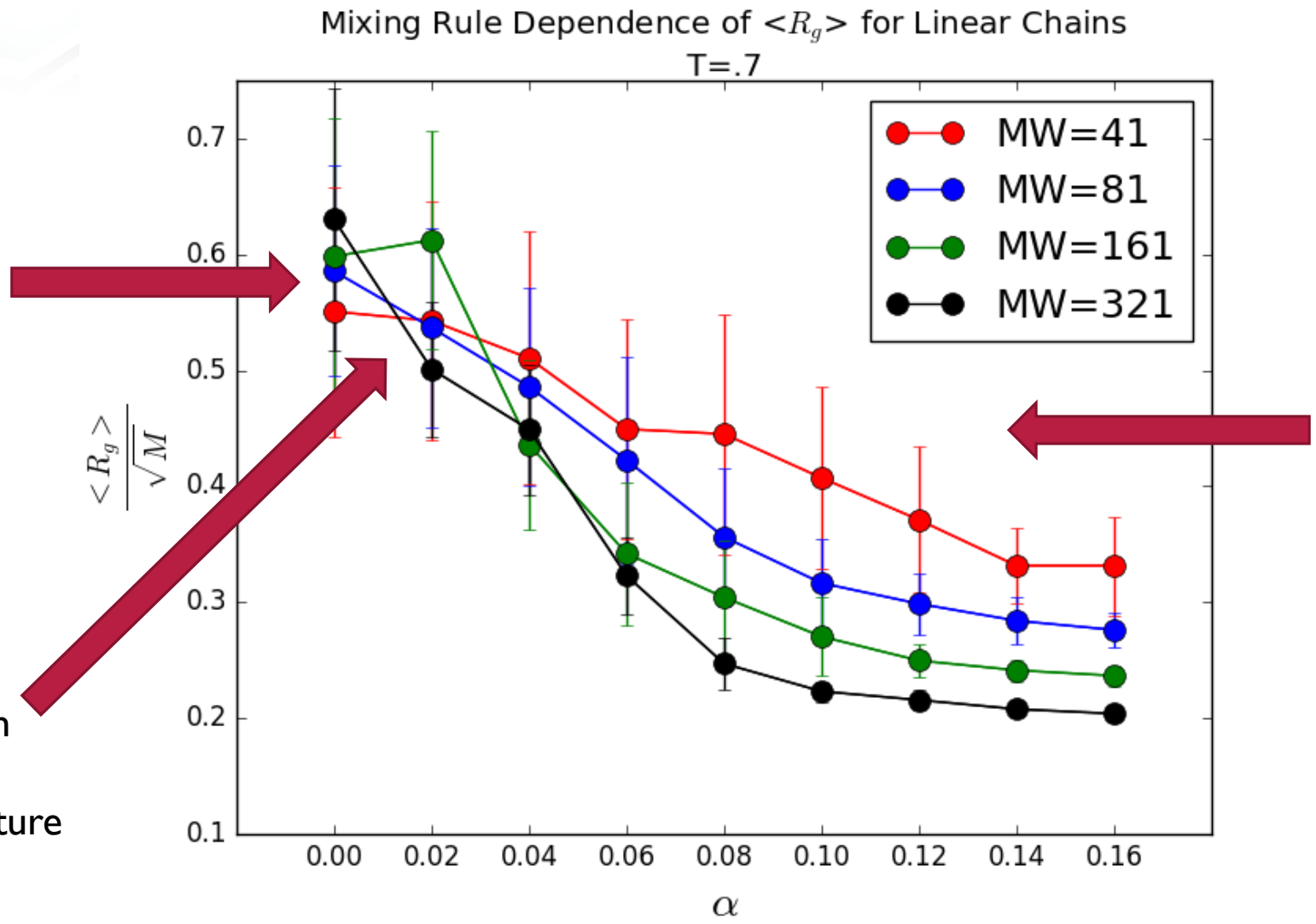
SWOLLEN REGION-LINEAR



- α=0
- No clear trend between <R_g> and temperature, difficult to identify θ-temperature
- Chains are more swollen, cross interactions too attractive (good solvent conditions)
- Cannot naively choose mixing rule



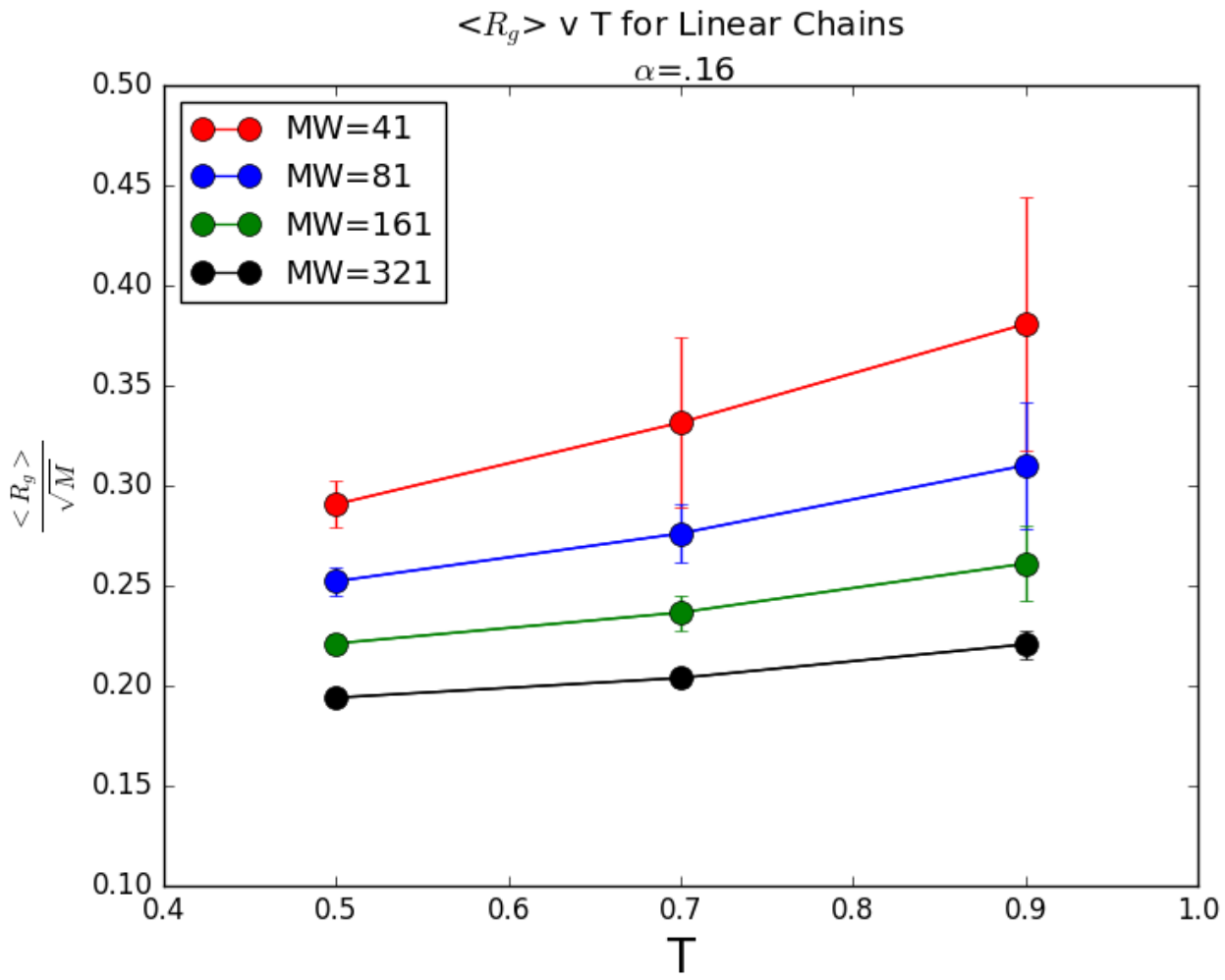
α=0
Swollen Region
Good solvent conditions



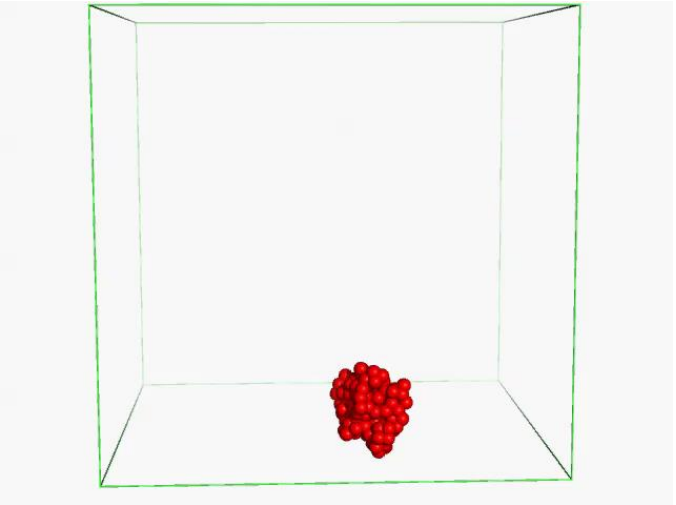
$\alpha \geq 0.06$
Collapsed Region
Always poor solvent conditions

0.02<α<0.04
Intermediate Region
<R_g> is sensitive to changes in temperature

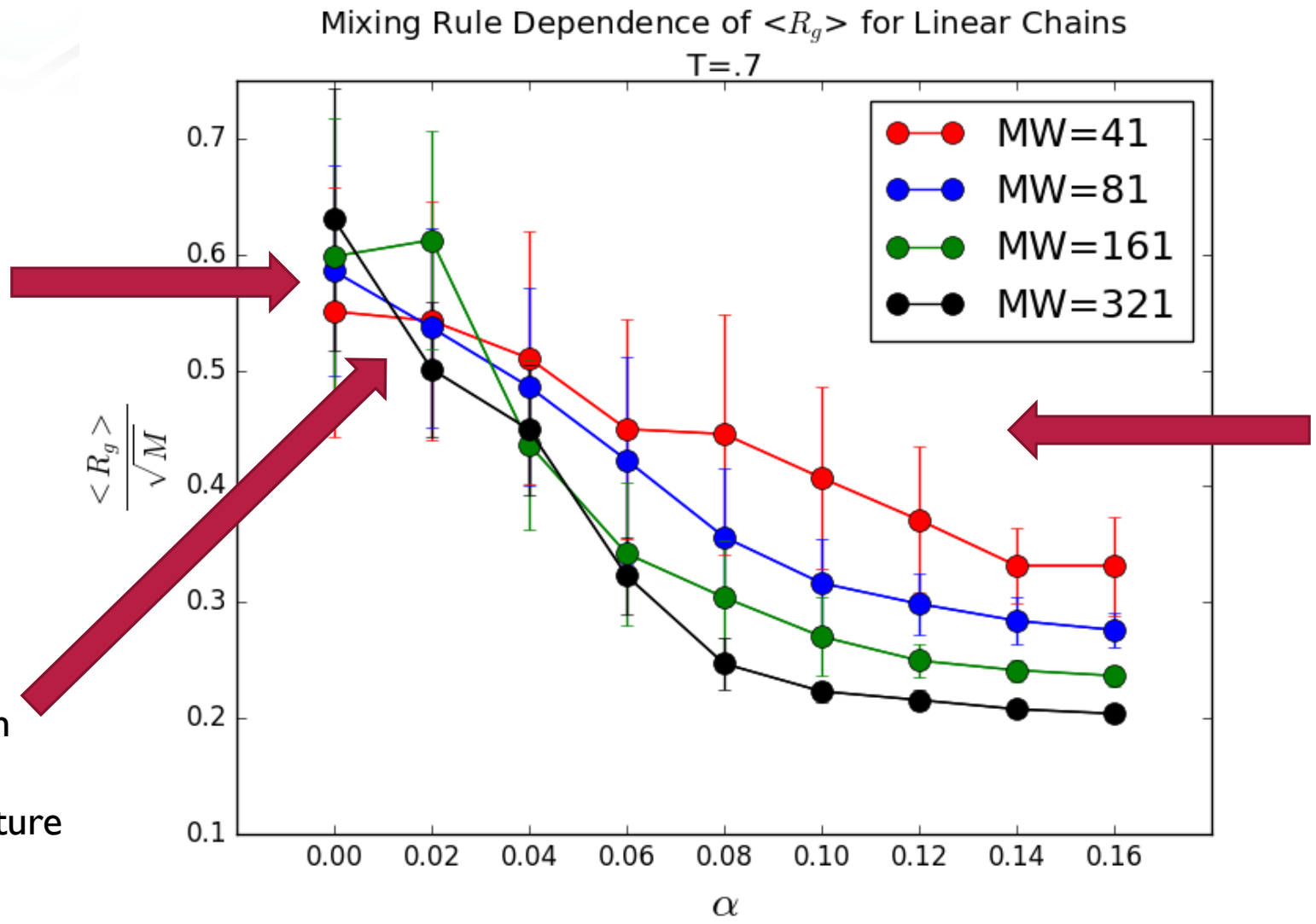
COLLAPSED REGION-LINEAR



- $\alpha \geq 0.06$
- Chain is always collapsed, cross interactions too repulsive (bad solvent conditions)
- Desired behavior was not achieved for these simulations, no crossover occurs



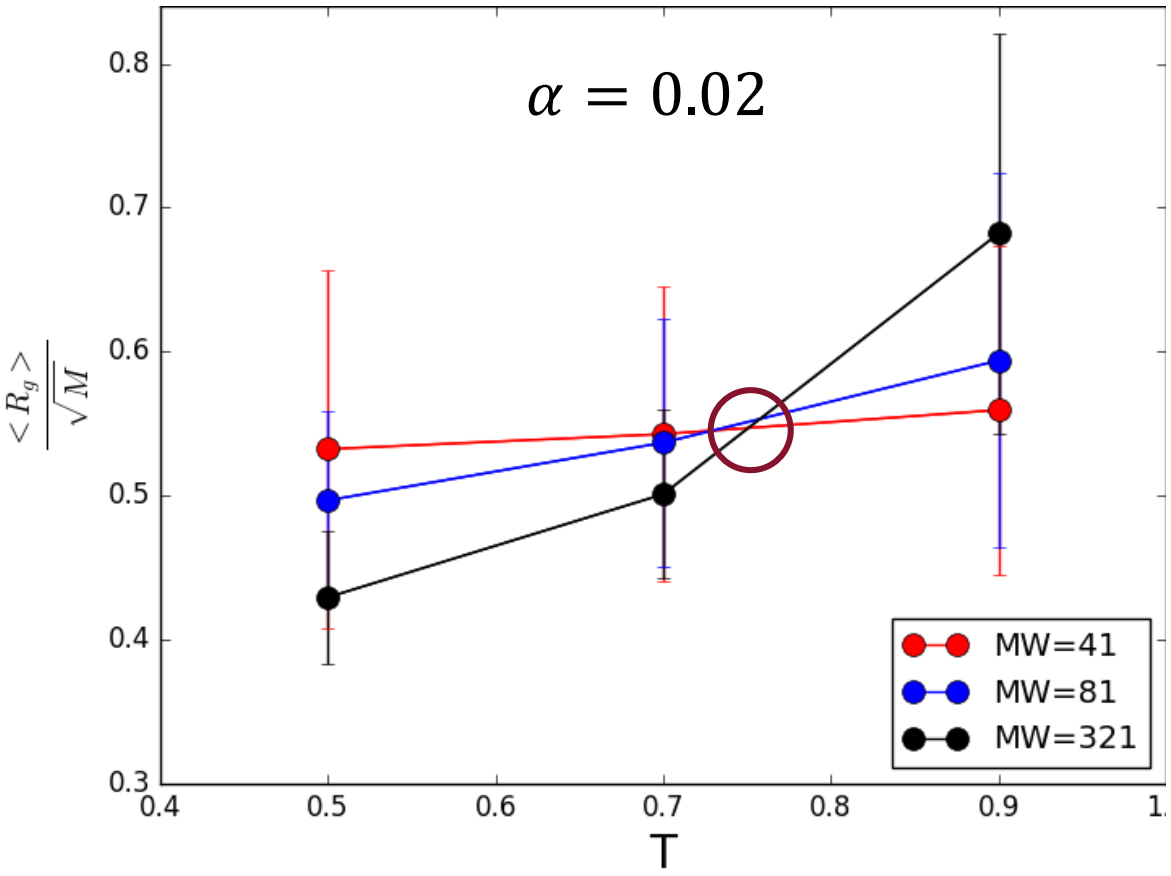
α=0
Swollen Region
Good solvent conditions

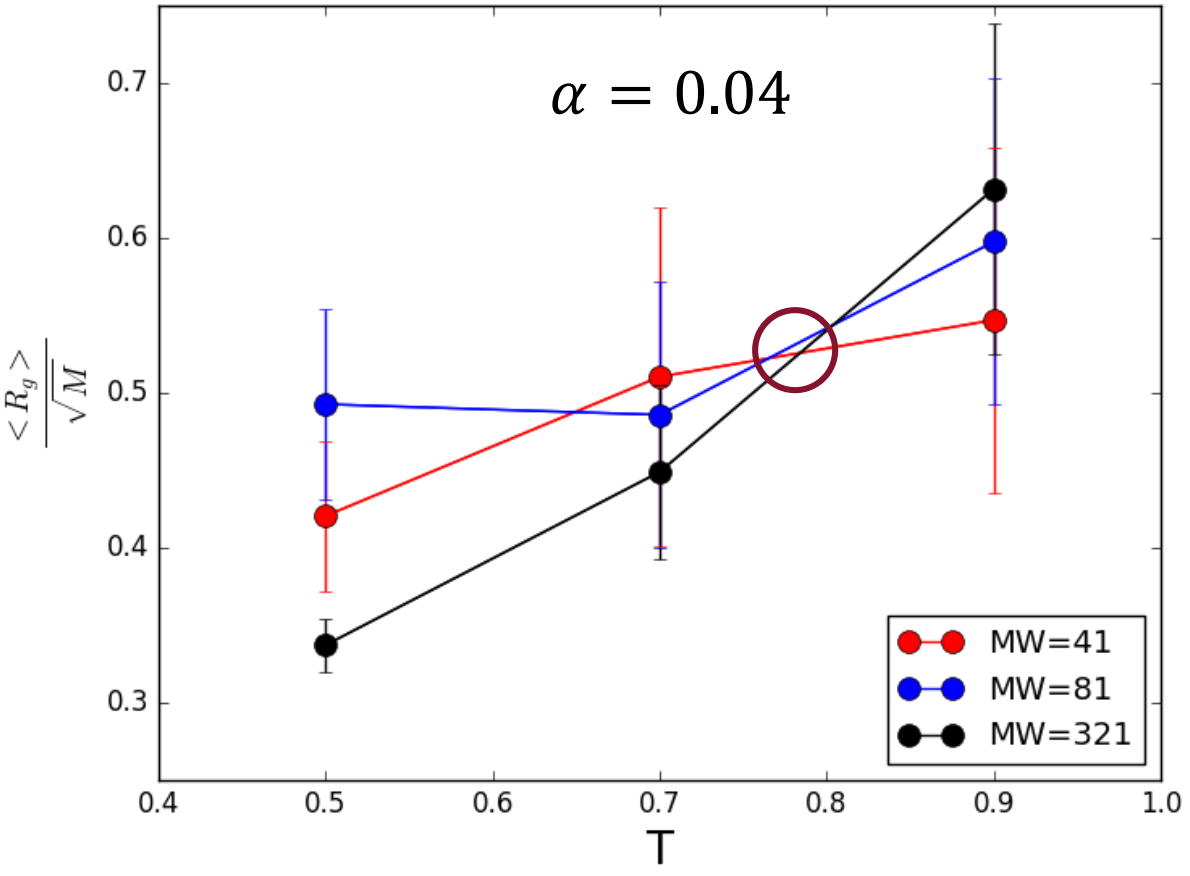


$\alpha \geq 0.06$
Collapsed Region
Always poor solvent conditions

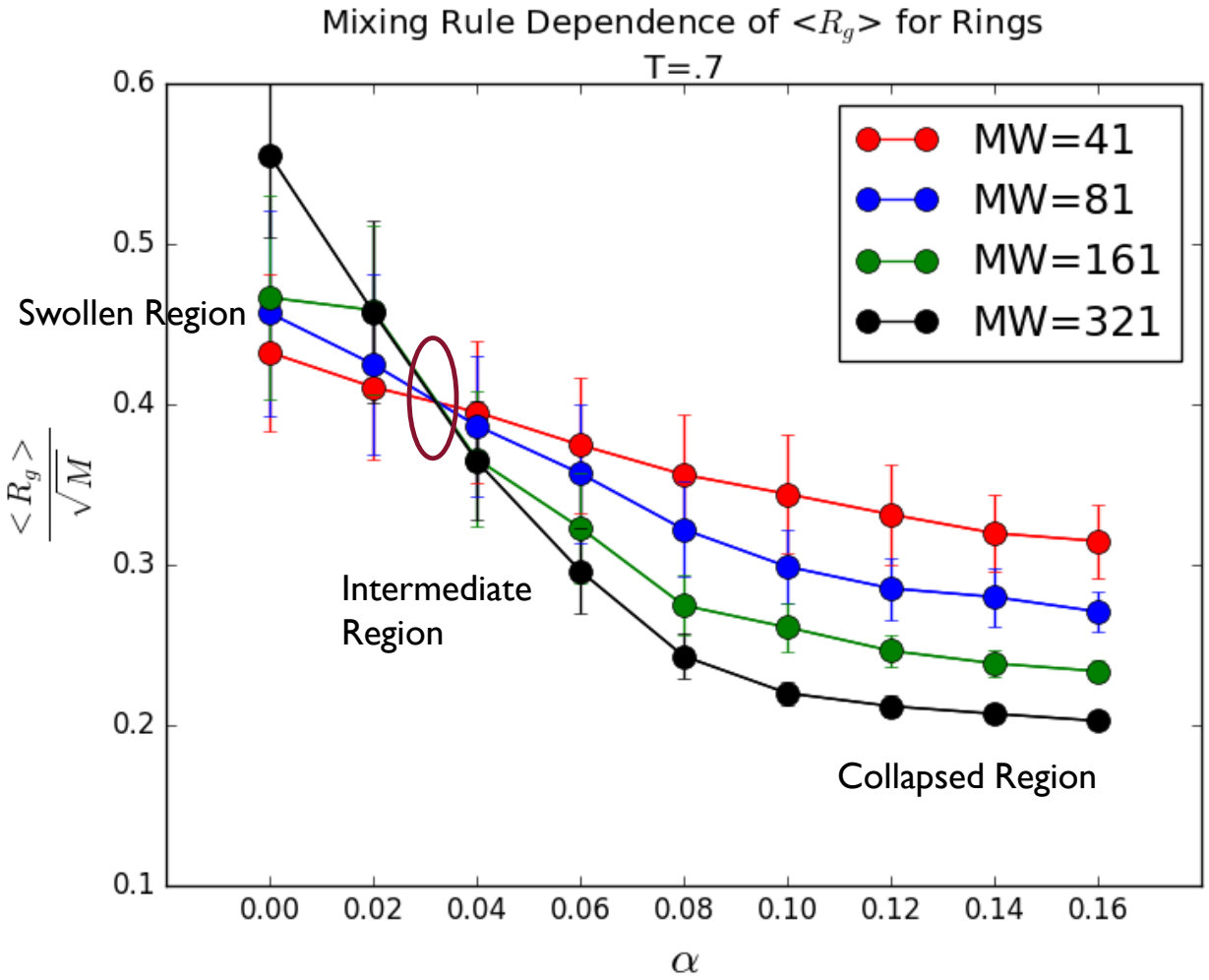
0.02<α<0.04
Intermediate Region
R_g is sensitive to changes in temperature

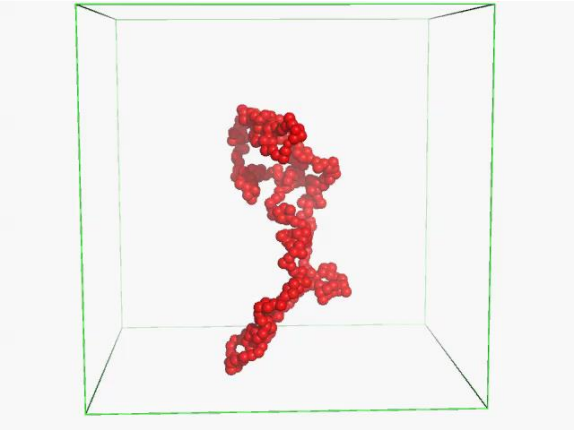
INTERMEDIATE REGION-LINEAR



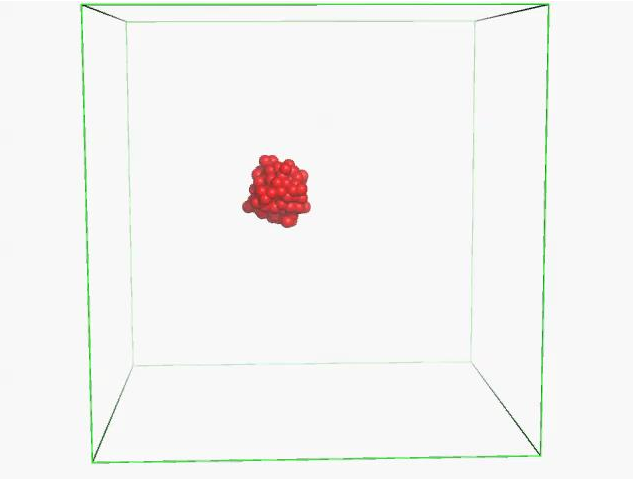


RING POLYMERS



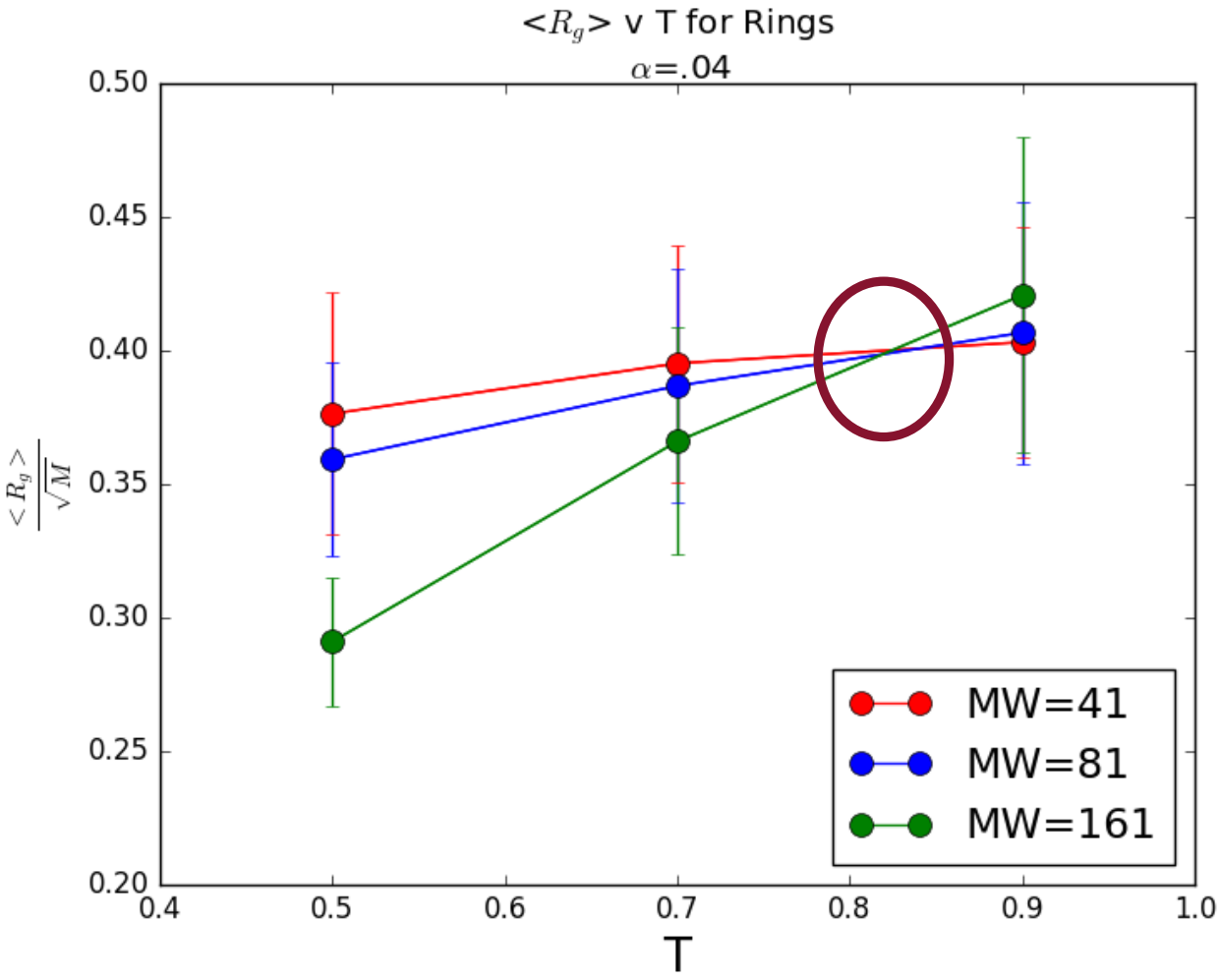


Swollen Ring



Collapsed Ring

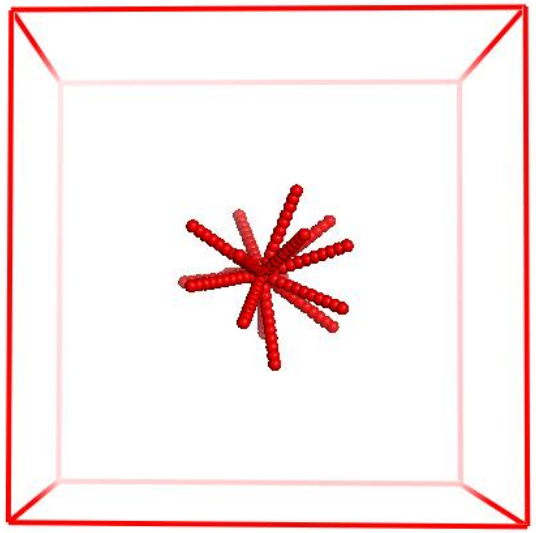
INTERMEDIATE REGION-RINGS



- α=0.04
- θ-temperature in range
  0.8< θ<0.9

FUTURE WORK

- Increase resolution of search for θ-temperature
  - Explore $0 < \alpha < 0.06$
  - Explore more temperatures within range $0.5<T<0.9$
- Explore different types of molecular architectures
  - Find θ-temperature for branched polymers



Branched/Star Polymer

ACKNOWLEDGMENTS

- Dr. Alexandros Chremos
- Dr. Jack Douglas
- Computational Soft Materials Working Group (COMSOFT)
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