Atomistic and Coarse-Grained Simulations of PNIPAM

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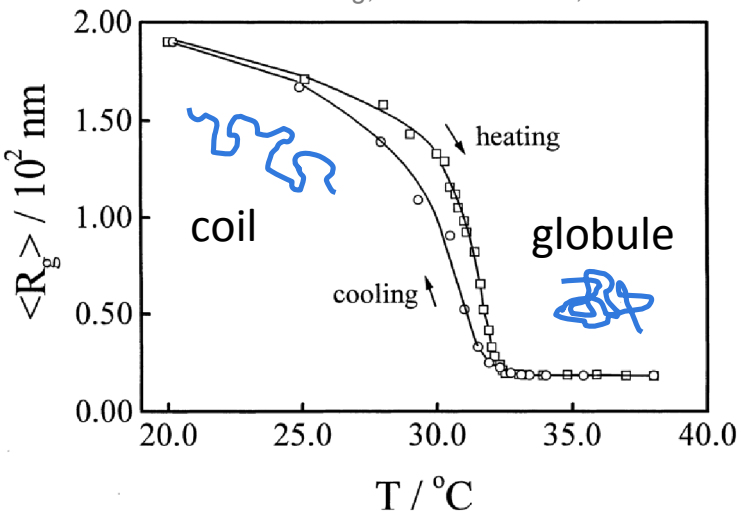
U.S. DEPARTMENT OF ENERGY | Office of Science

PNIPAM LCST & Copolymer

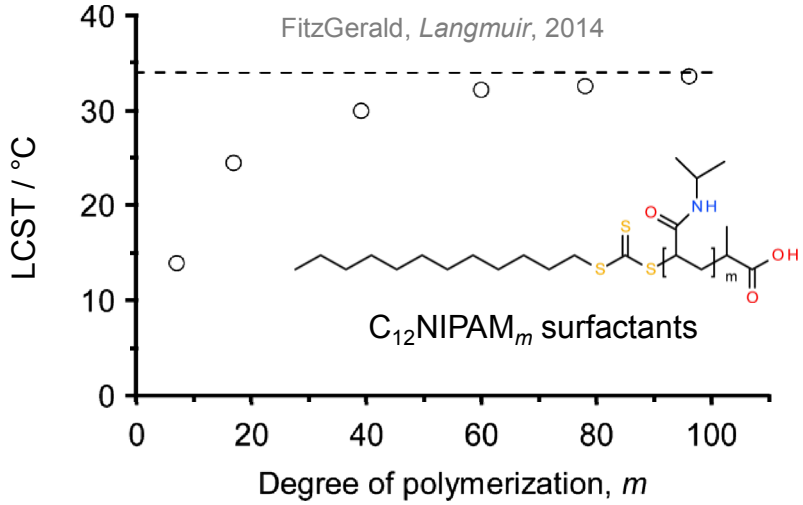
PNIPAM has LCST at ~ 32C

Wang, *Macromolecules*, 1998

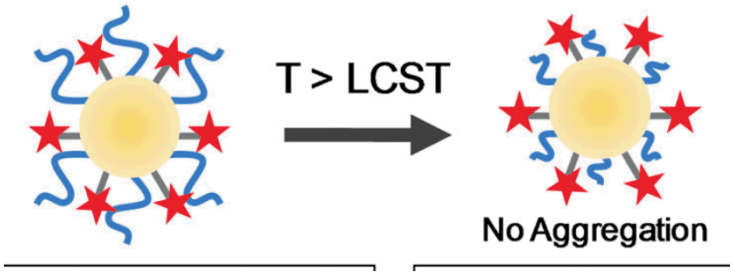


PNIPAM copolymers

FitzGerald, *Langmuir*, 2014

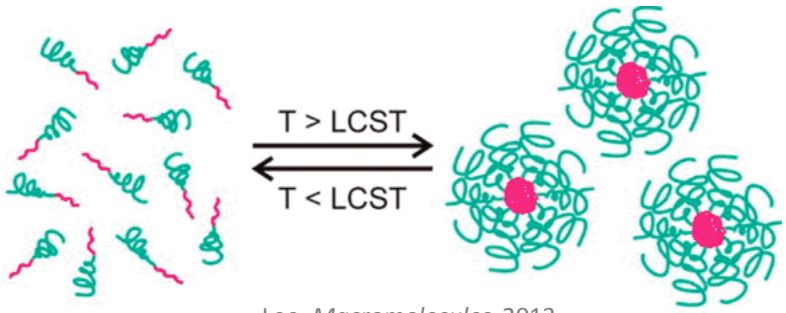


Responsive surface coatings (e.g., sensors, catalysis)



Gibson, *Chem. Soc. Rev.*, 2013

Responsive self-assemblies



Lee, *Macromolecules*, 2013

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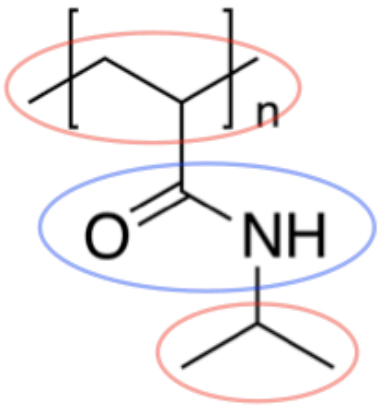
PNIPAM



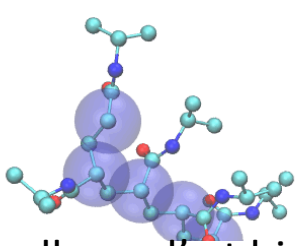
hydrophobic

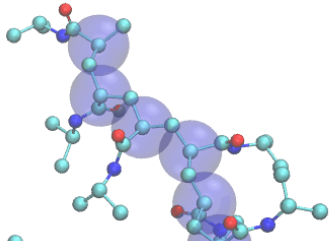
hydrophilic

hydrophobic

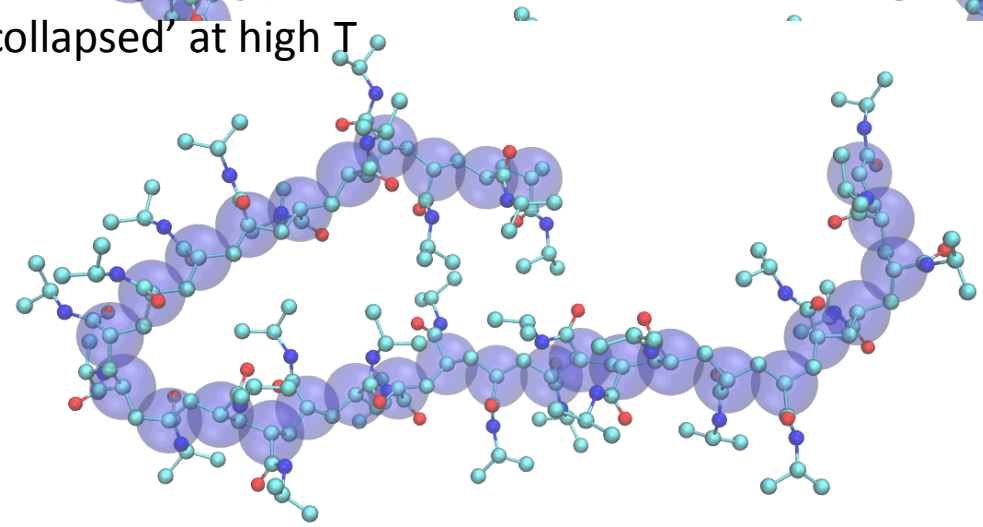
N = 30
Single chain in water
LCST

extended at low T





'collapsed' at high T



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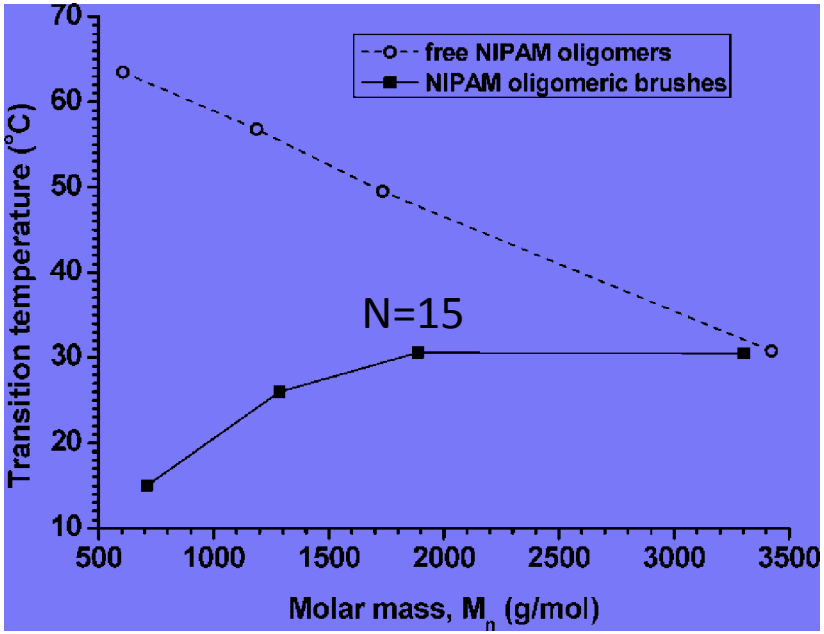
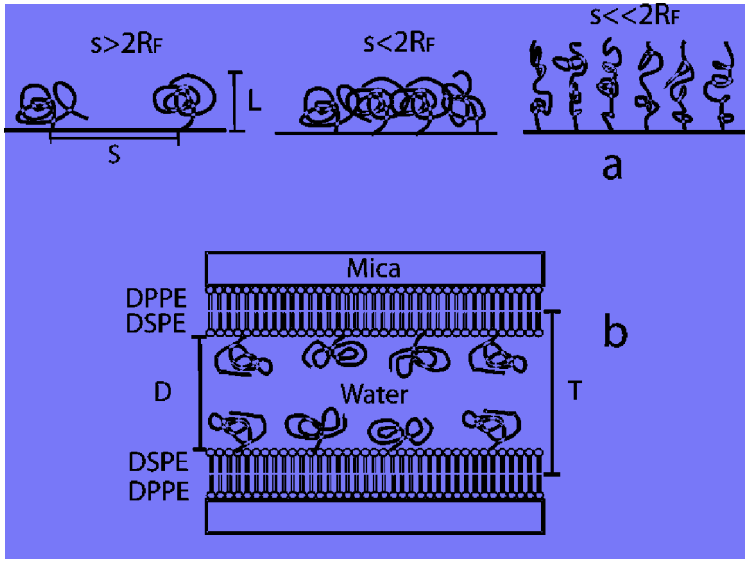
PNIPAM Oligomers





Shan et al. Macromolecules 2009
PNIPAM coated nanoparticles
Chain length dependent transition

Winnick & Leckband et al. Langmuir '07
SFA measurements of grafted PNIPAM.
At low grafting densities, short PNIPAM does not collapse above the LCST.

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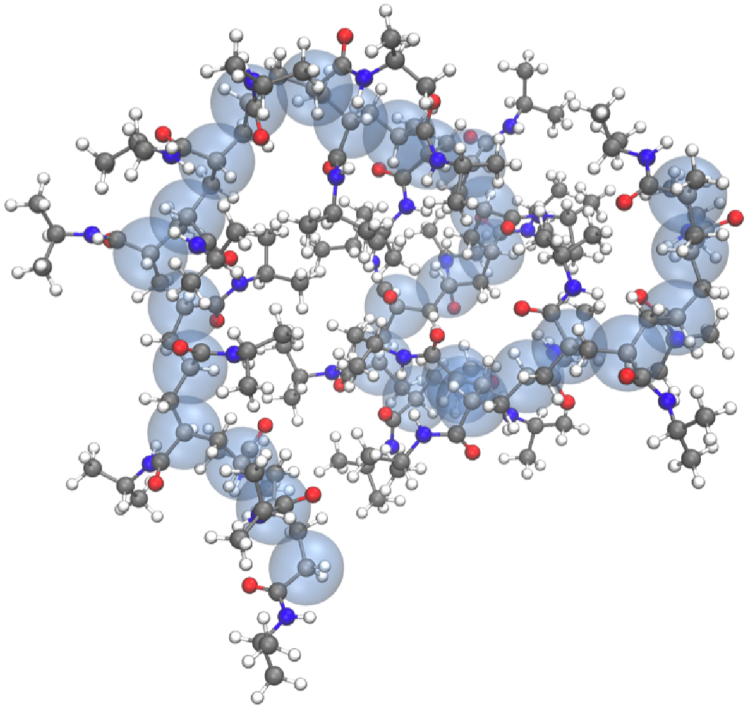
Oligomer simulations

Single chain in water

- OPLS with modified dihedrals (Siu, *JCTC*, 2012)
- TIP4P/2005 water model
- Gromacs 4.6.5
- **100-400 ns production in NPT ensemble**
- 2 fs time step
- Canonical thermostat
- Parrinello-Rahman barostat
- Short-range nonbond with 1.0 nm cutoff
- Long-range electrostatics with PME
- Cubic box with PBC, 4.0-9.0 nm



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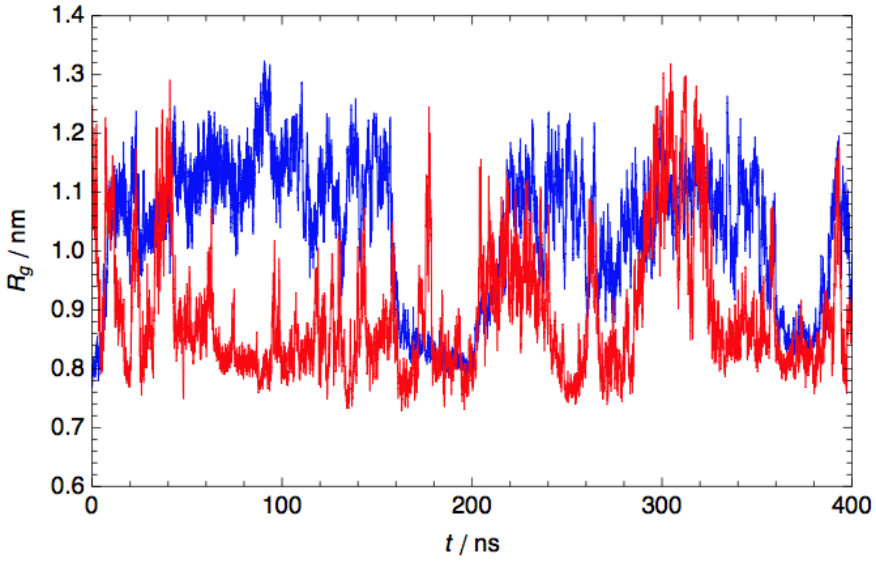
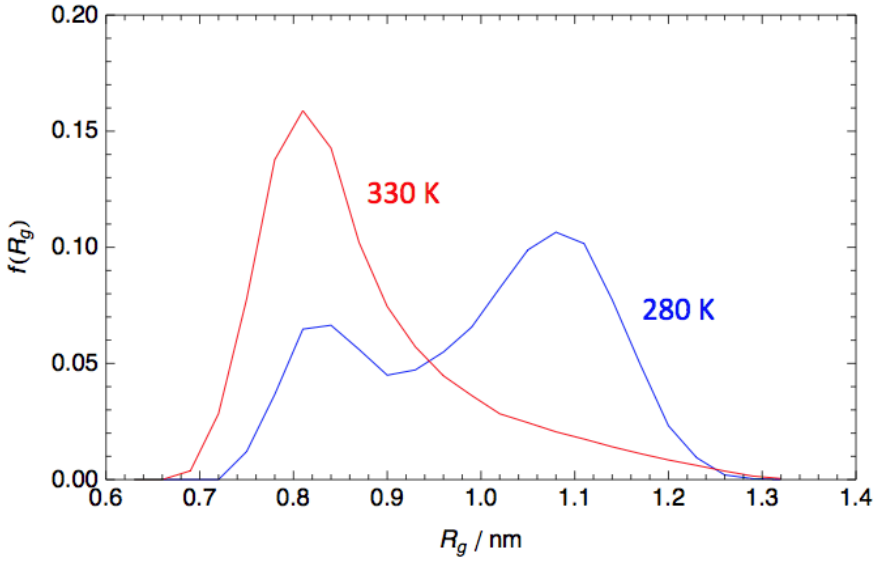
PNIPAM dynamics

N=18 400 ns simulation. Yes, have to run *very* long to get distributions accurately.





Hydrogen bonding dynamics results in slow variation in structure and demands very long simulation times.

Equilibration determined in terms of **distribution** of R_g.

Adds to motivation for coarse-grained model.

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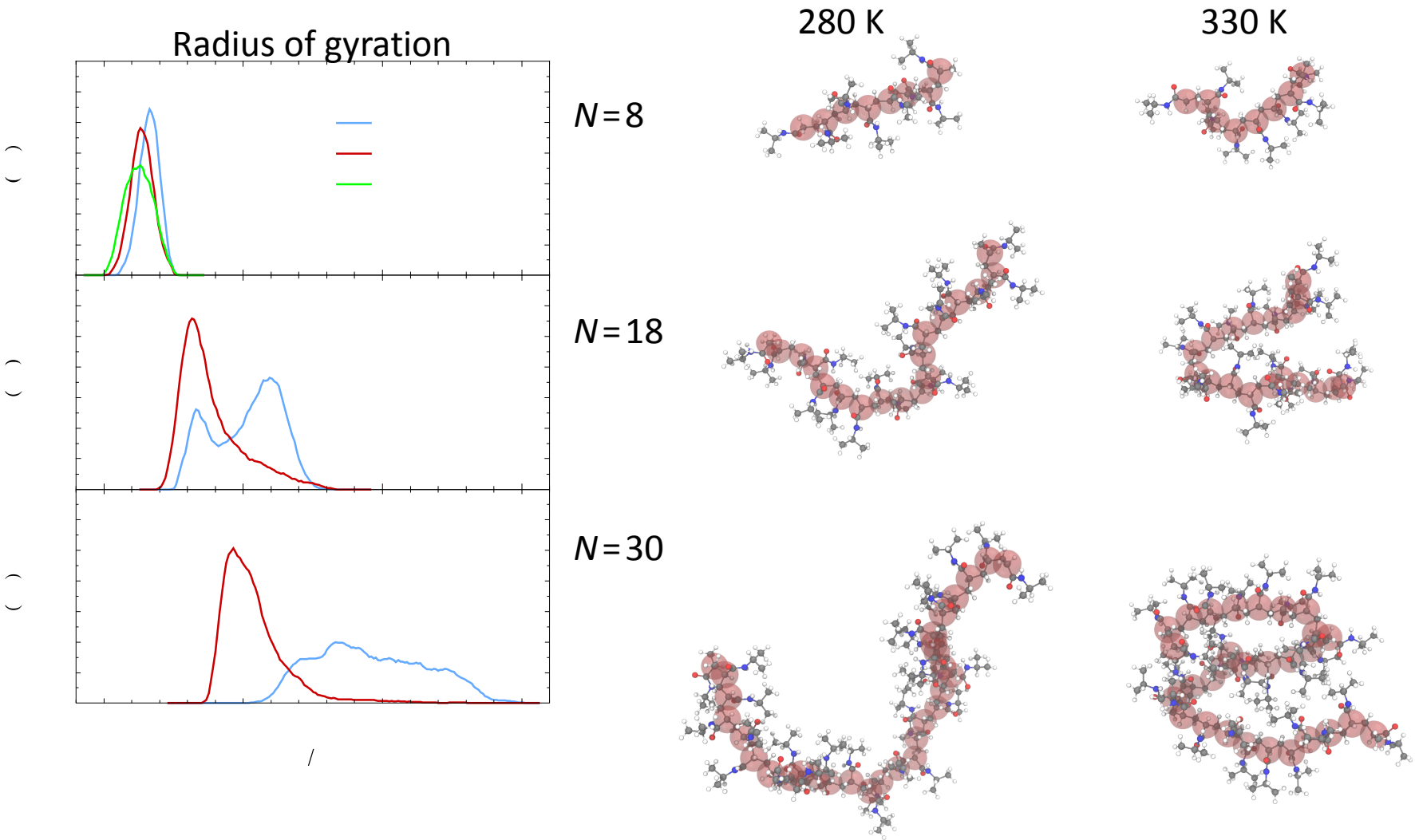
Oligomer Structure



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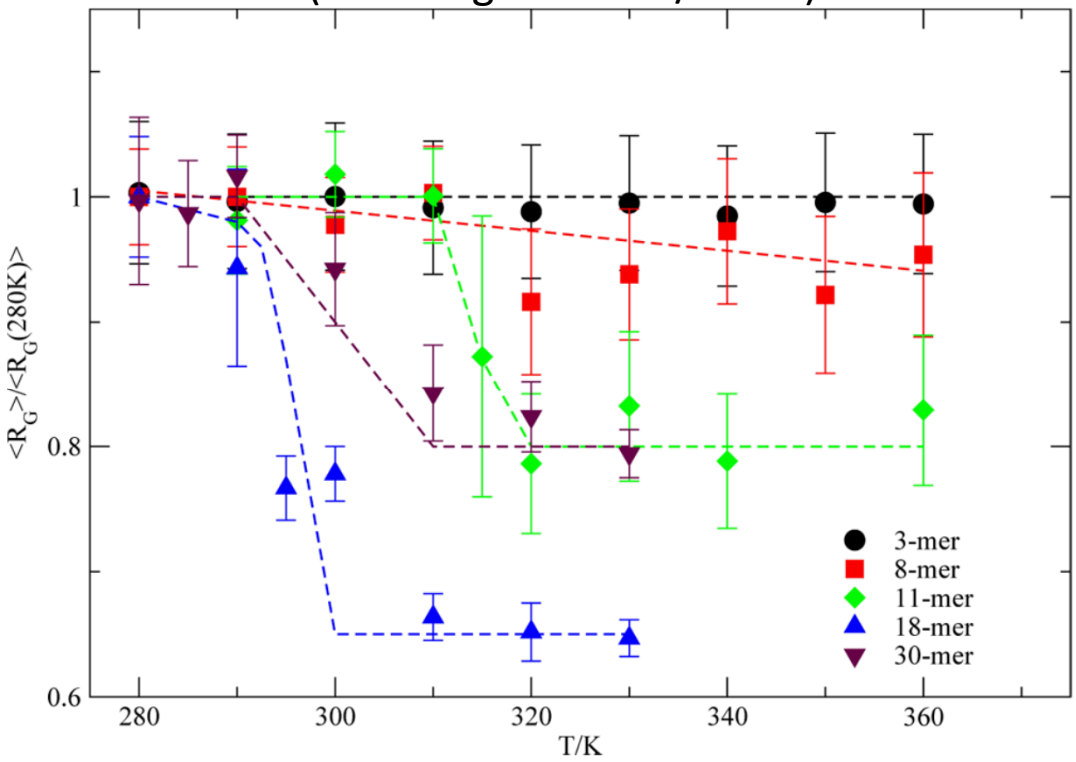
Oligomer LCST

(with original OPLS/TIP3P)



Minimum length required for a single chain to bend ⟹ Minimum length required for *single* chain LCST

This corresponds to the experimental behaviors seen.

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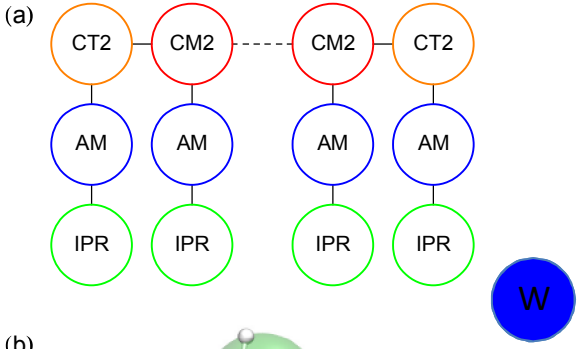
Coarse-graining PNIPAM

Need CG model to treat the interesting PNIPAM systems.

- relaxation/equilibration slow
- gels are large
- micelles slower



1. implicit solvent model does not work
2. ?Koga JPCB 2016: water + LJ polymer
3. Started with CG model of Shinoda, DeVane, Klein

0) Two parameter sets for 280K and 330K
1) New bead types for AM & IPR and CM2
2) Match experimental thermodynamic data for analogous chemical compounds at 300 K.
3) CG bond parameters were fit to atomistic distributions for PNIPAM single chains at 280 K and 330 K.
4) Nonbonded parameters (from step 2) were adjusted to yield better agreement with RDFs for PNIPAM single chains at 280 K and 330 K. (Iterative Boltzmann + Tweaking)

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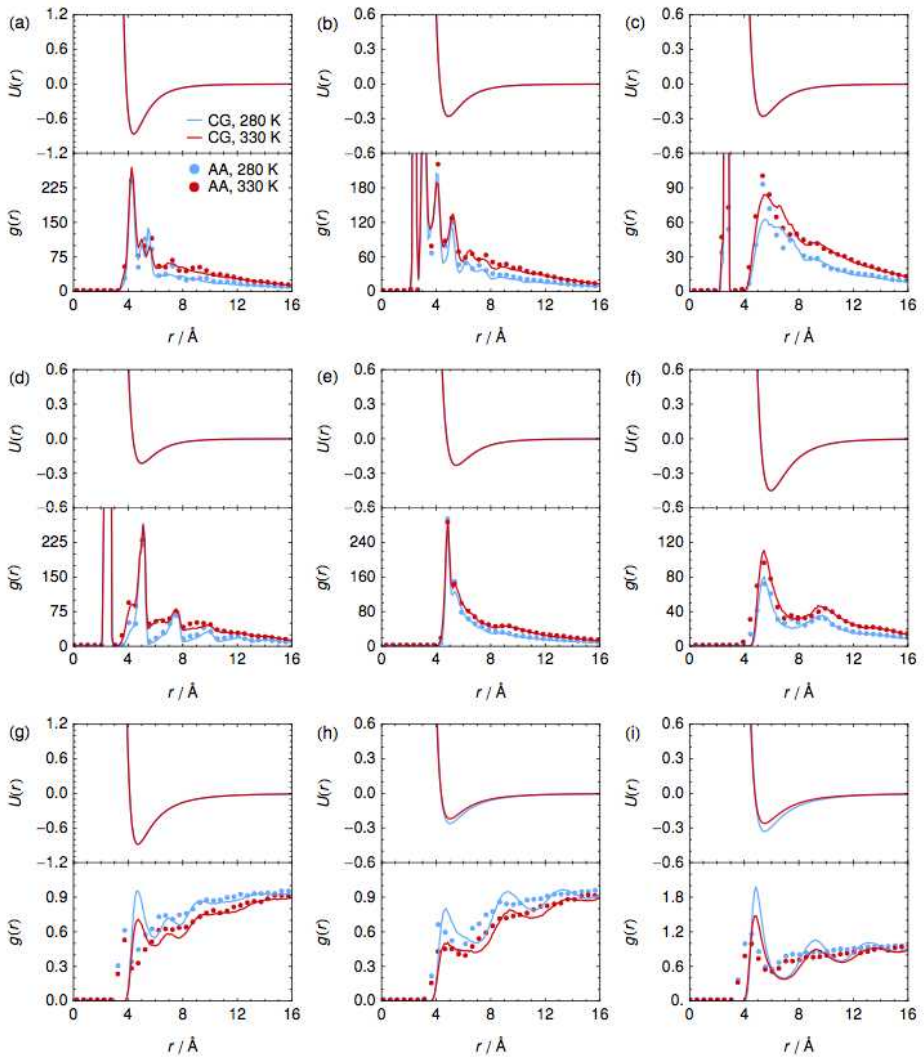
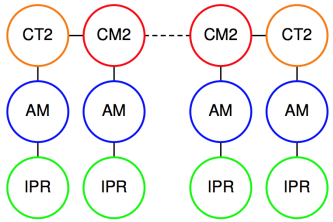
Lots of cross-term calculations

(a) AM–AM
(b) AM–CM2
(c) AM–IPR
(d) CM2–CM2
(e) CM2–IPR
(f) IPR–IPR
(g) AM–W
(h) CM2–W
(i) IPR–W



280 K
330 K
points are atomistic data



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Adjustments

The starting LJ parameters are for $\sigma_{AM} = \sigma_{AM-AM}$

σ_{AM-AM} reflects a bead size for hydrogen bond formation between AM & AM.

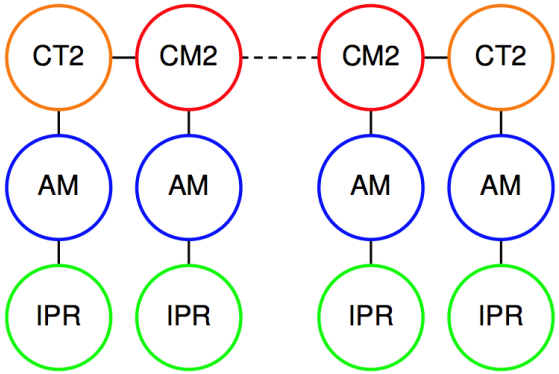
For AM-X, where X is hydrophobic,

cannot use Berthelot combination rules

must adust σ_{AM-X} to be larger

the get correct rdf peak positions

ε_{AM-X} was decreased to maintain the same interaction strength at long distances.



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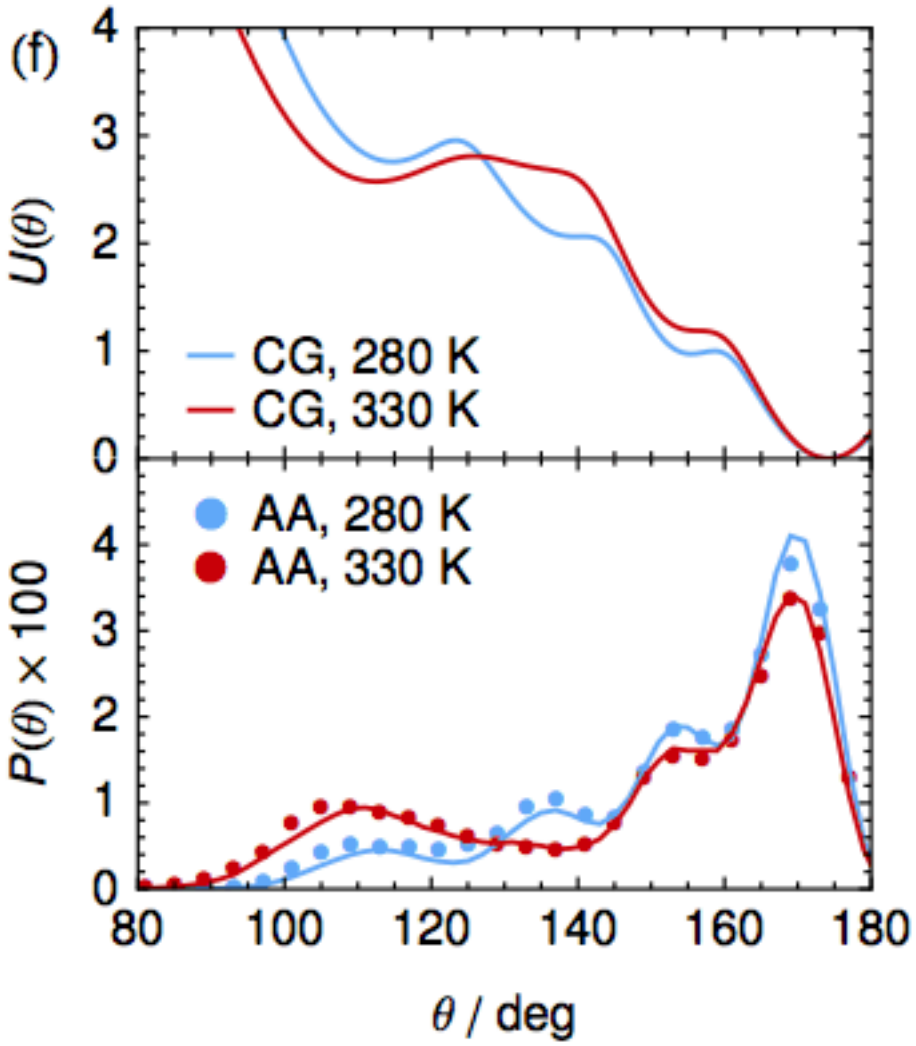
More T-dependence

Backbone CM2-CM2-CM2 angle
Can match with CG for each T.



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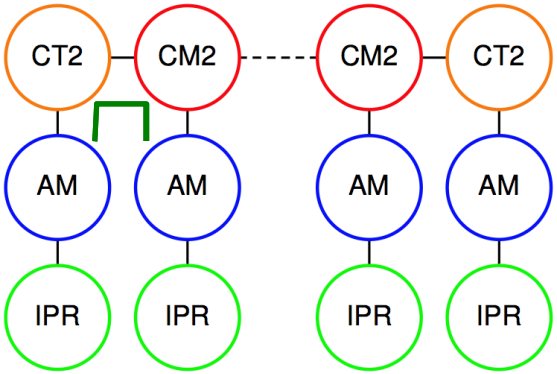
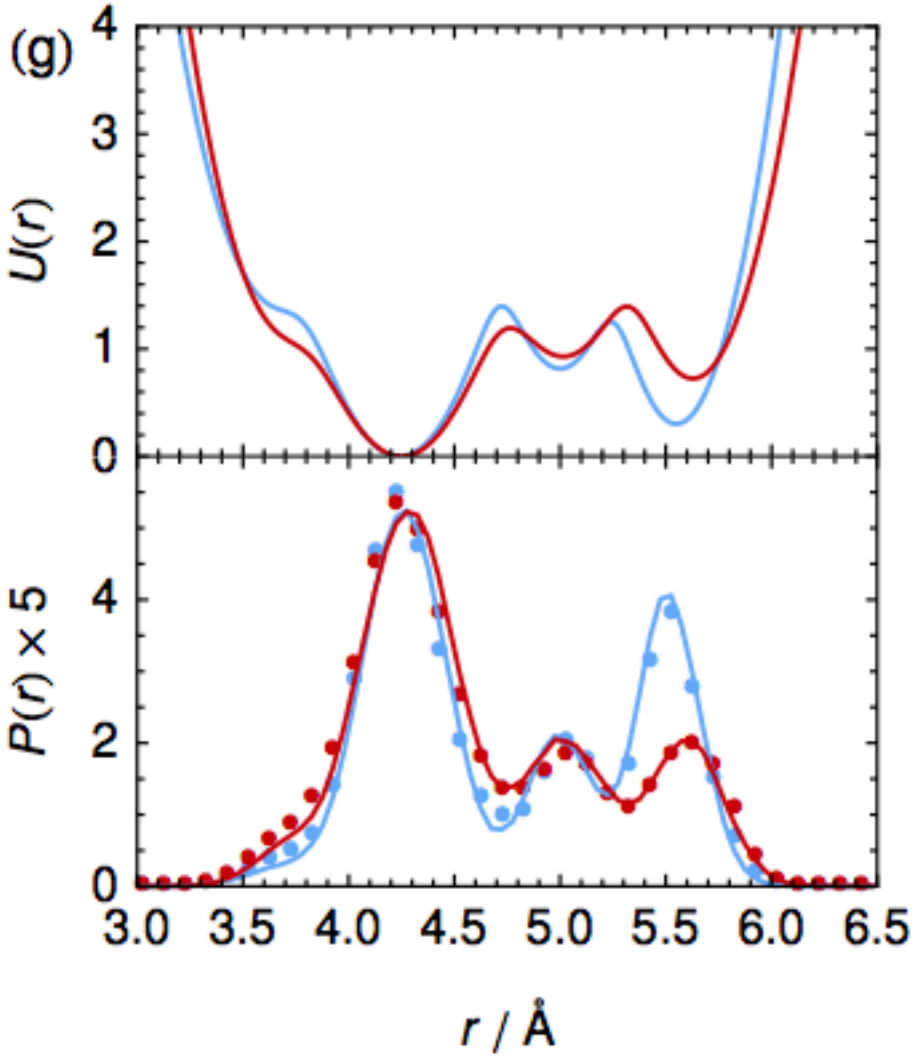
More T-dependence

AM-AM 1-4 interaction



tacticity



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CG PNIPAM Model

Summary points

- lots of parameters
- interdependent and sensitive
- need some parameters at two temperatures

- better model would incorporate hydrogen bonding,
  but may have fewer atoms/CG bead

But it works!

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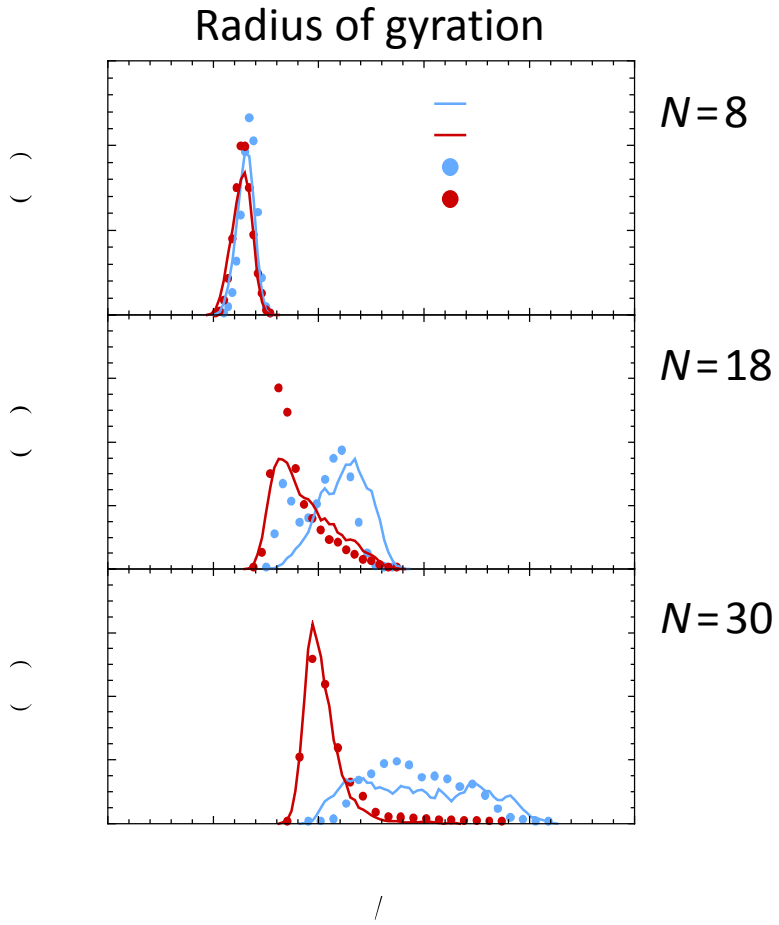
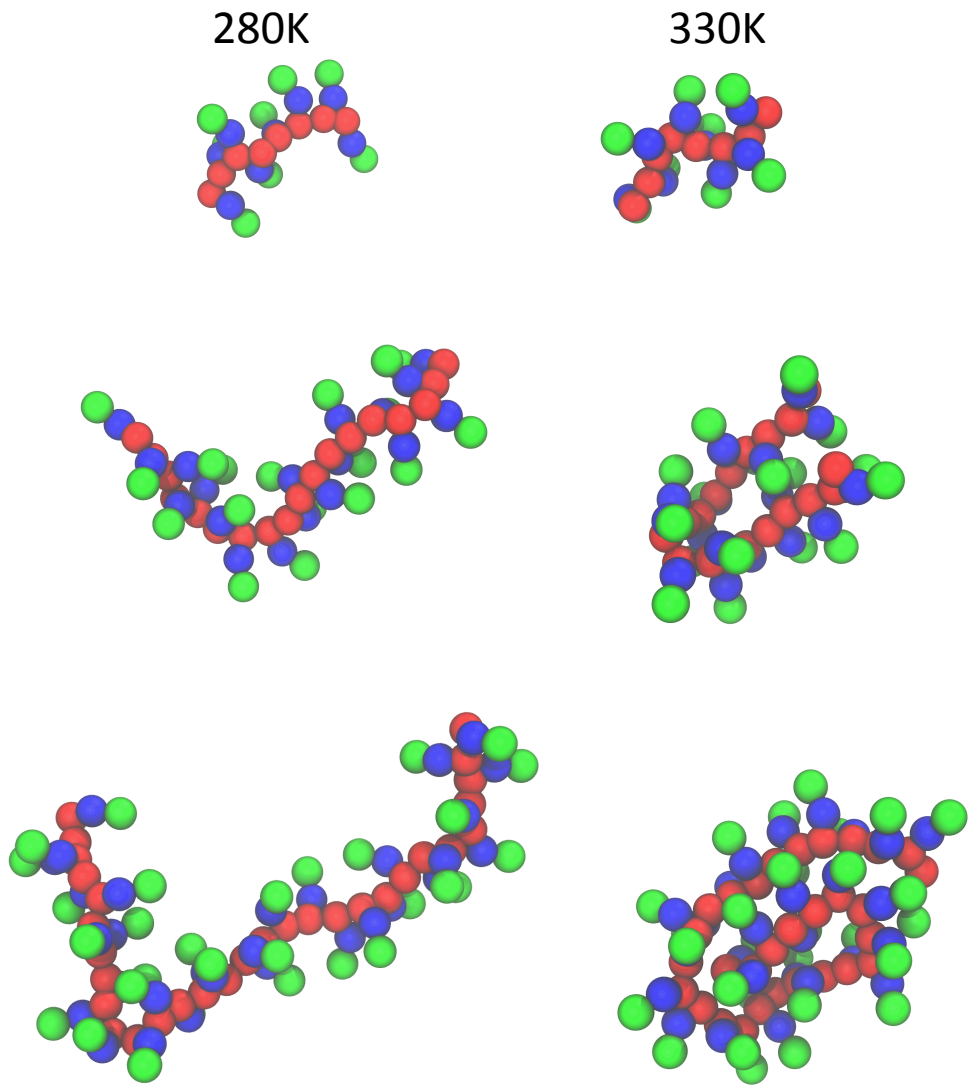
How good is CG model?





CG model yields correct single chain structure and N dependence.

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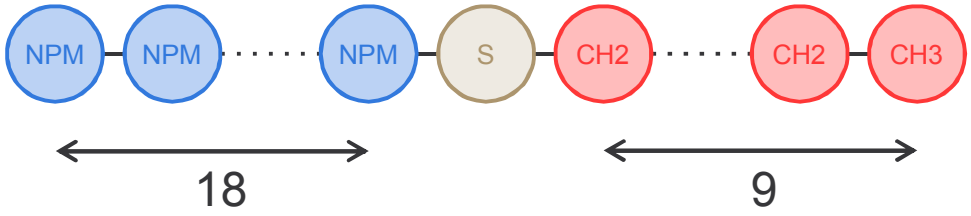
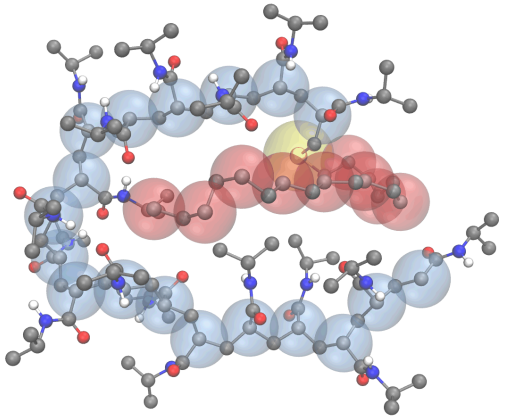
Atomistic Simulations of Single Copolymer

PNIPAM-C18 surfactant:



or 36 C in backbone



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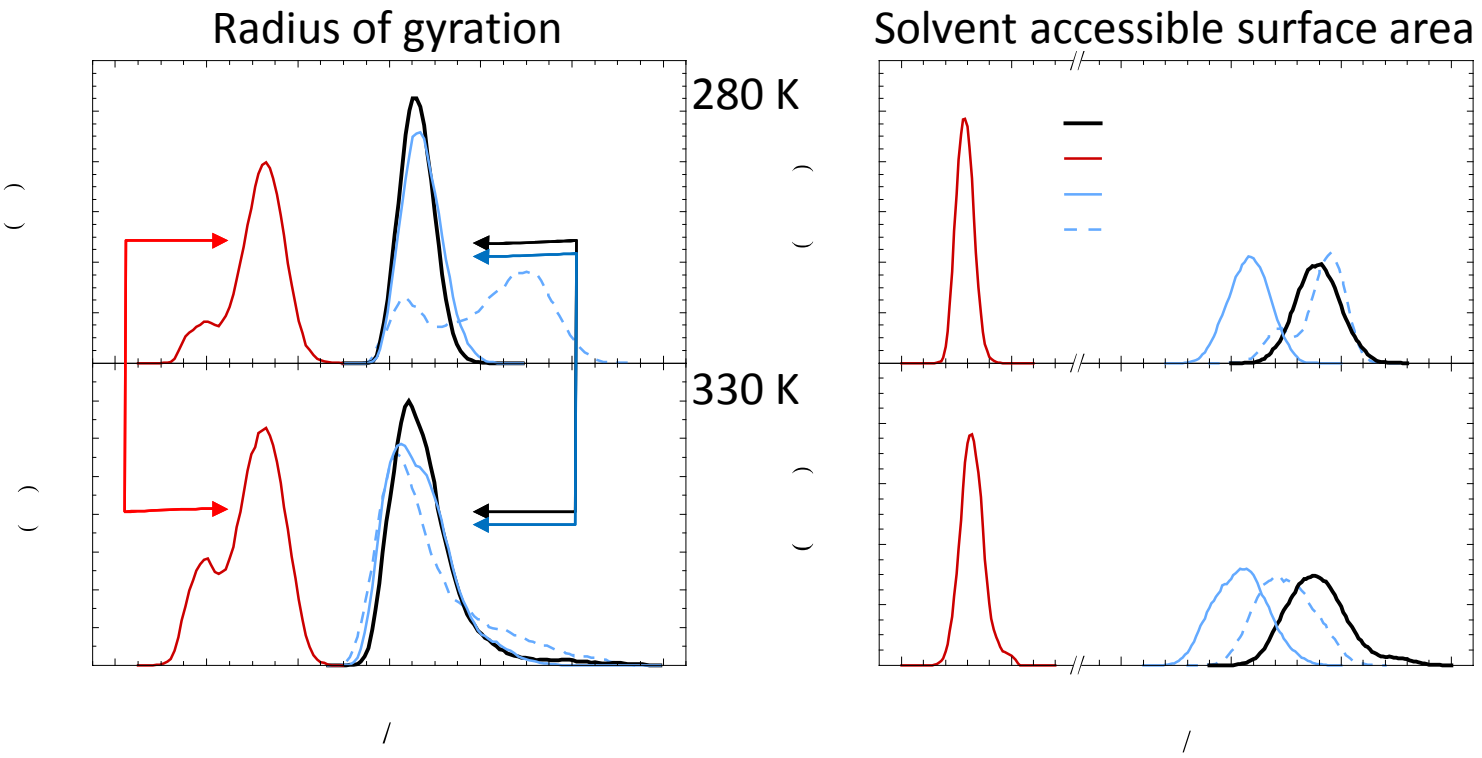
Copolymer Structure



Whole Chain is compact at both T.

PNIPAM part

Alkane part

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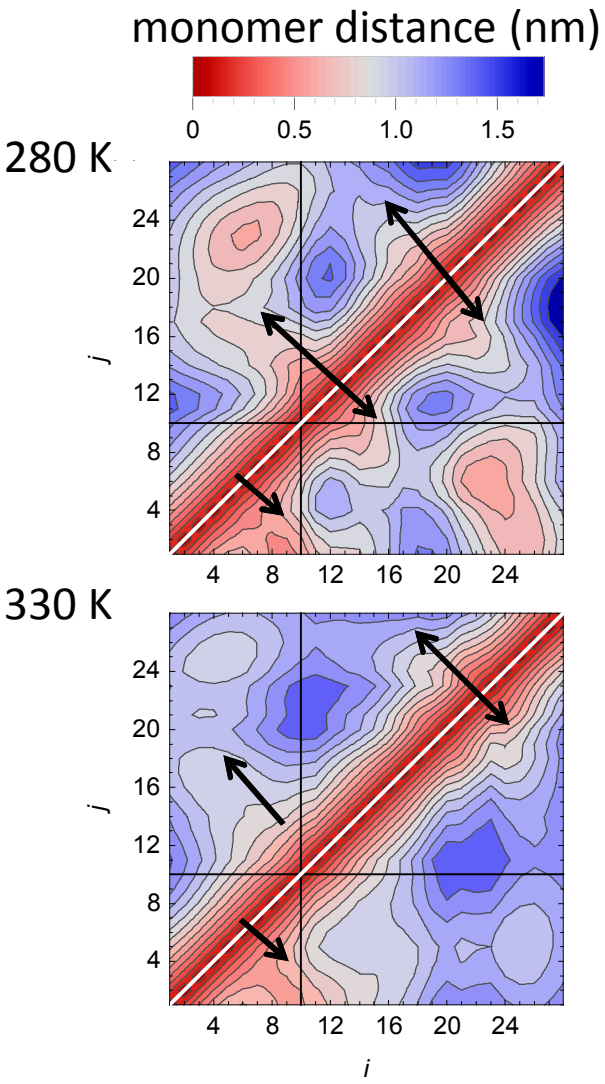
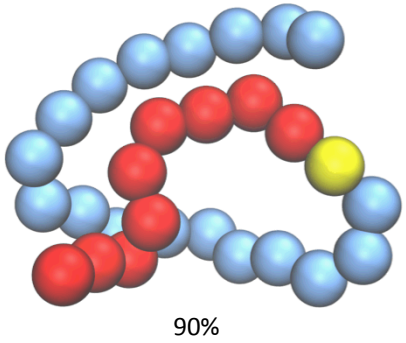
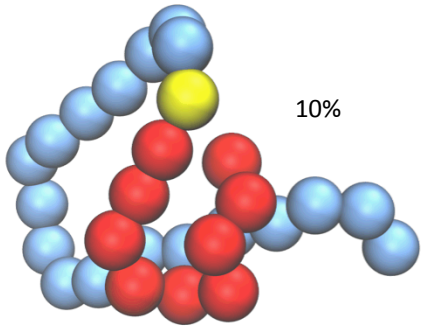
Copolymer Structure

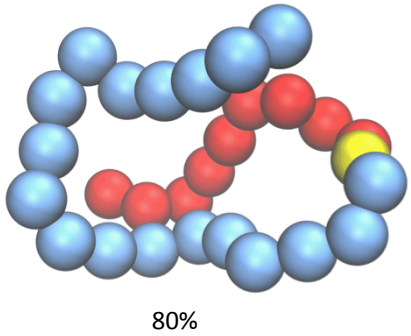
Contact Maps

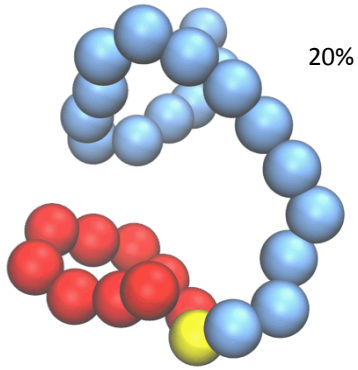


In majority structure, alkane part bends to be next to PNIPAM backbone









1 bead = 2 C atoms

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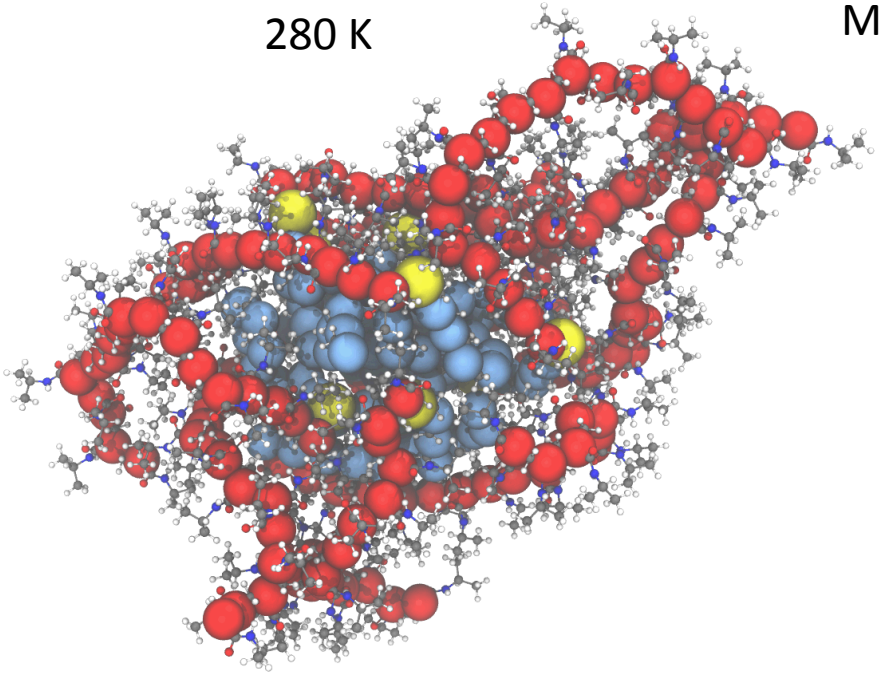
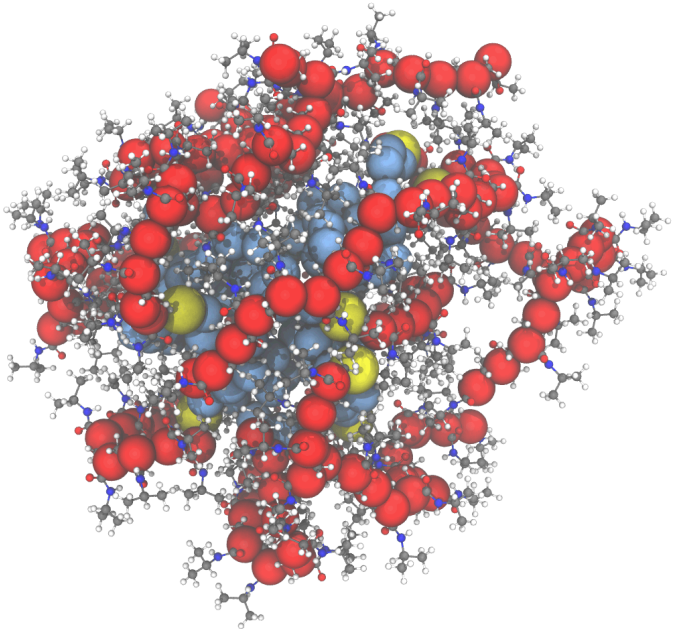
Atomistic Micelle Simulations

280 K

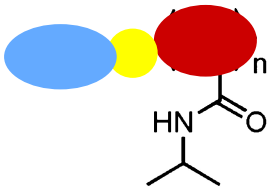
M=10

330 K





Prebuilt micelles show T-responsive behavior
Below LCST, larger PNIPAM outer region



PNIPAM-C18

Li, *ACS Nano*, 2014

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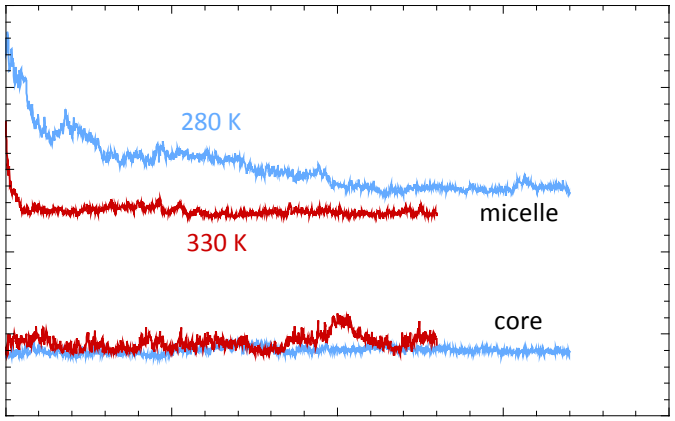
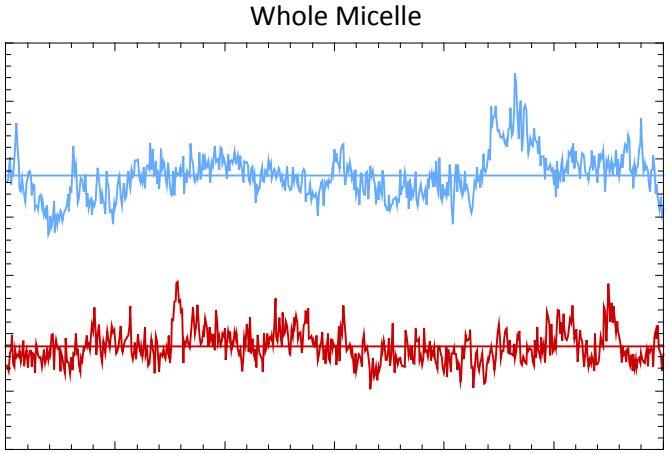
Micelle microsecond simulations



after initial transient



CG model are really needed to treat micelles and large systems, in general.

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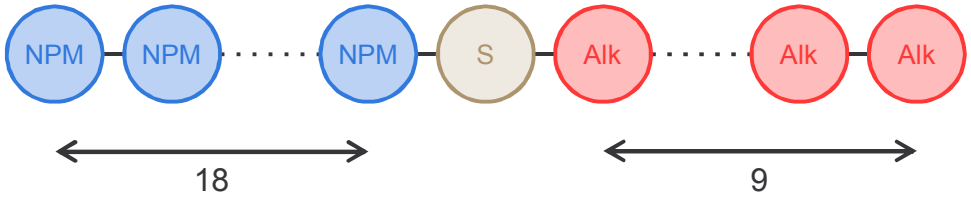
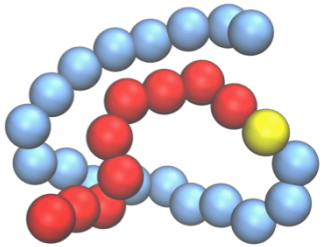
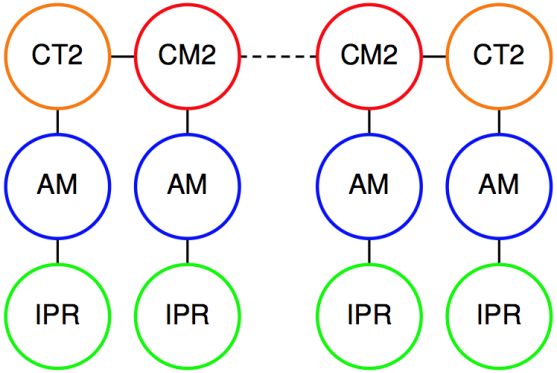
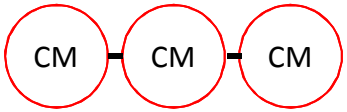
CG model of Copolymer

PNIPAM-C18 surfactant:









need CM-* cross terms and revise

Work in Progress

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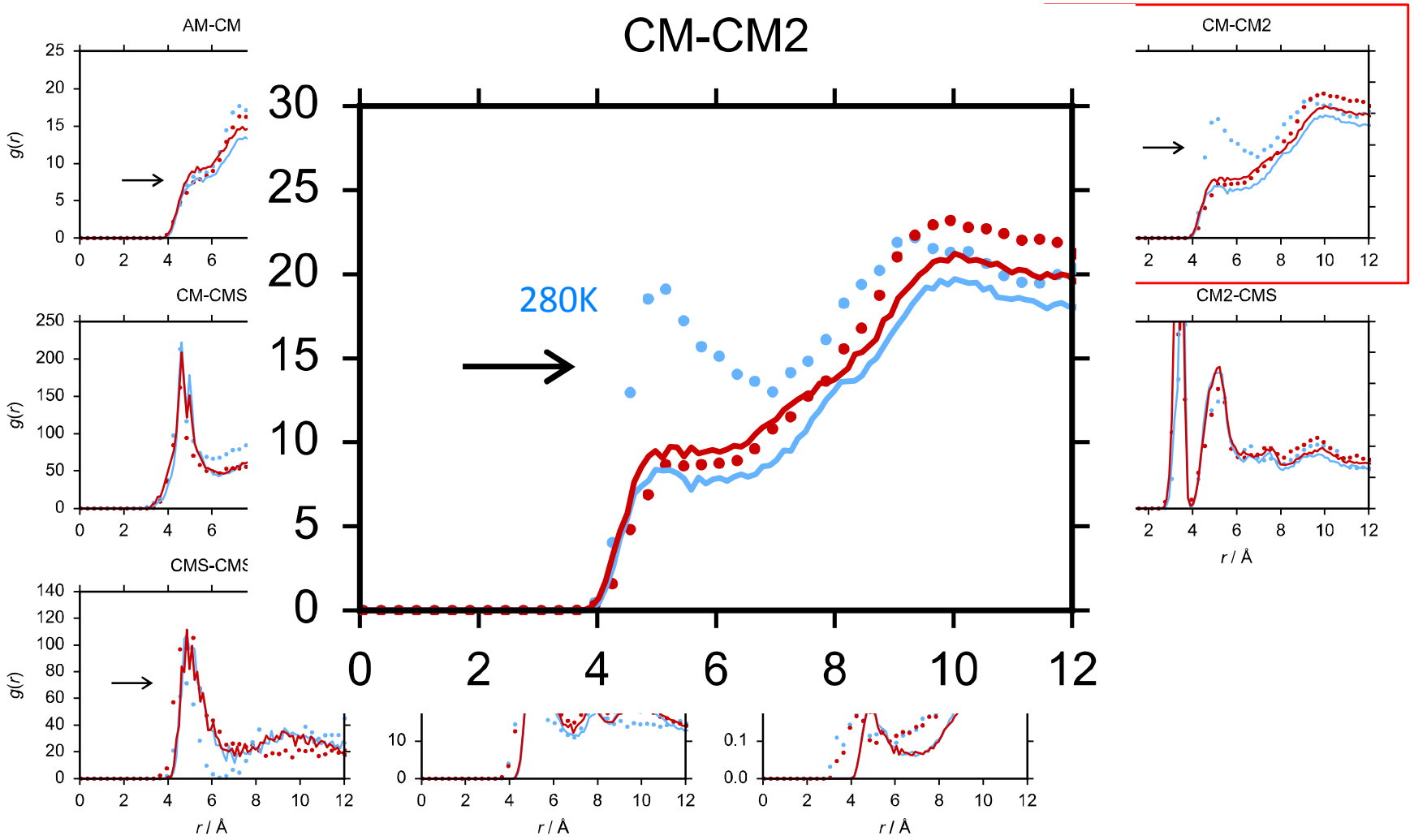
Cross-Term g(r) comparison



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Tweaking nonbond parameters

To better match peak intensities in g(r) [in kcal/mol]

1. Decreased $\varepsilon_{AM\text{-}AM}$: 0.39 to 0.20
2. Decreased $\varepsilon_{CM\text{-}W}$: 0.34 to 0.28
3. Decreased $\varepsilon_{CMS\text{-}IPR}$: 0.55 to 0.40

For better matching T dependence:

1. Increased $\varepsilon_{CM\text{-}CM2}$: 0.2984 to 0.45/0.35
2. Decreased $\varepsilon_{CM\text{-}IPR}$: 0.32 to 0.18/0.30
3. Decreased $\varepsilon_{CMS\text{-}CM2}$: 0.82 to 0.30/0.40

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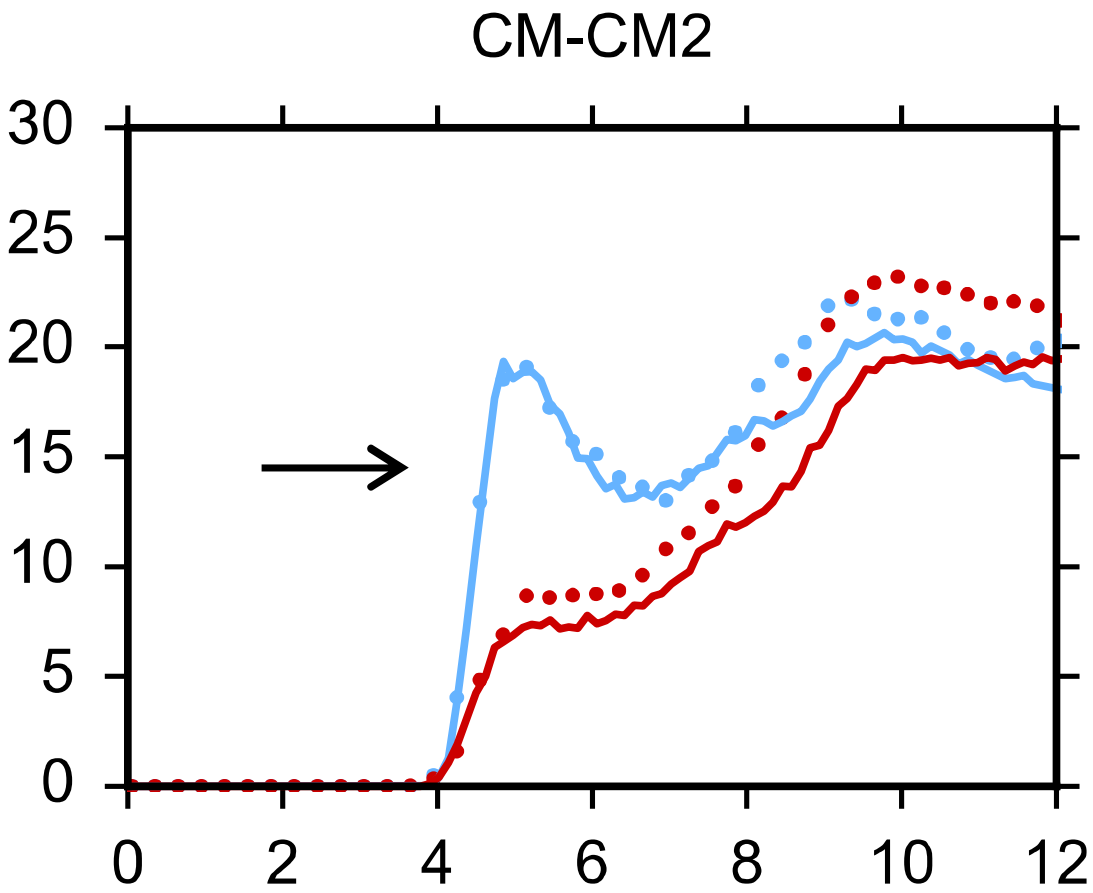
Better Matching



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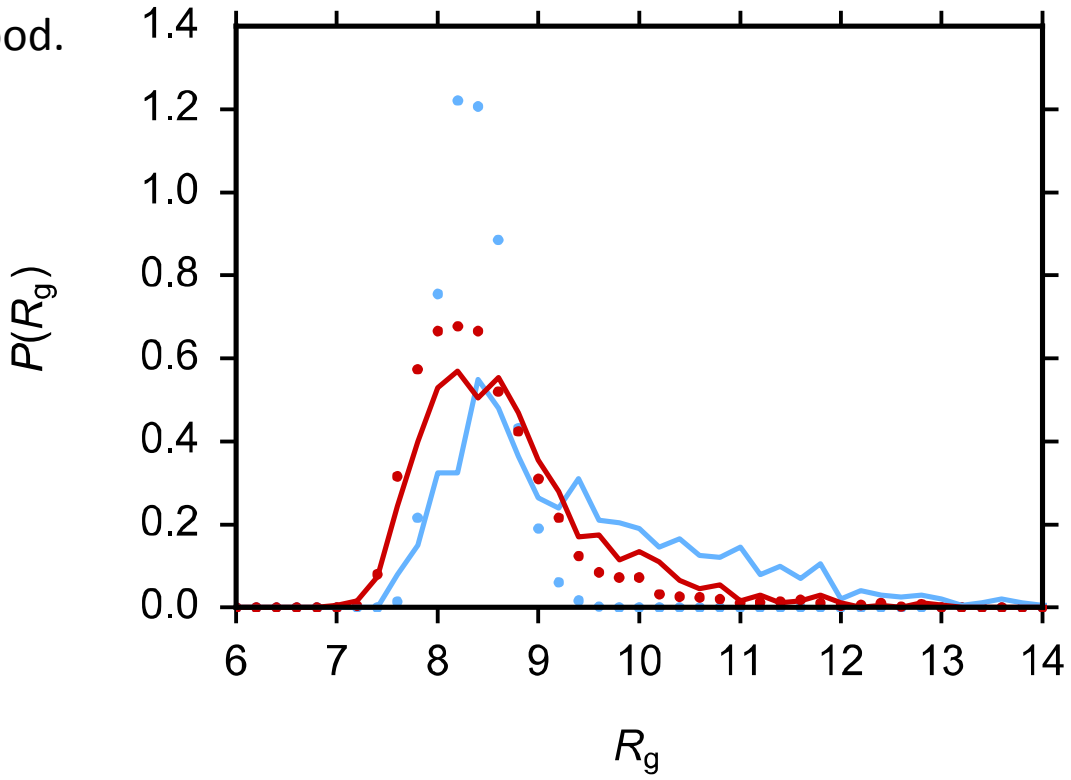
CG Copolymer Structure

R_g distribution at 330K is good.

But, needs work at 280K



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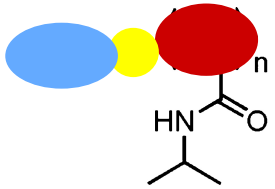
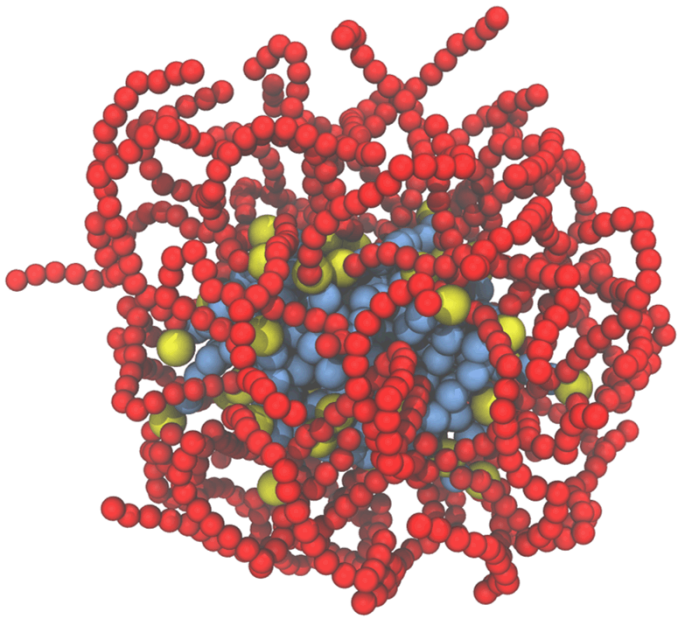
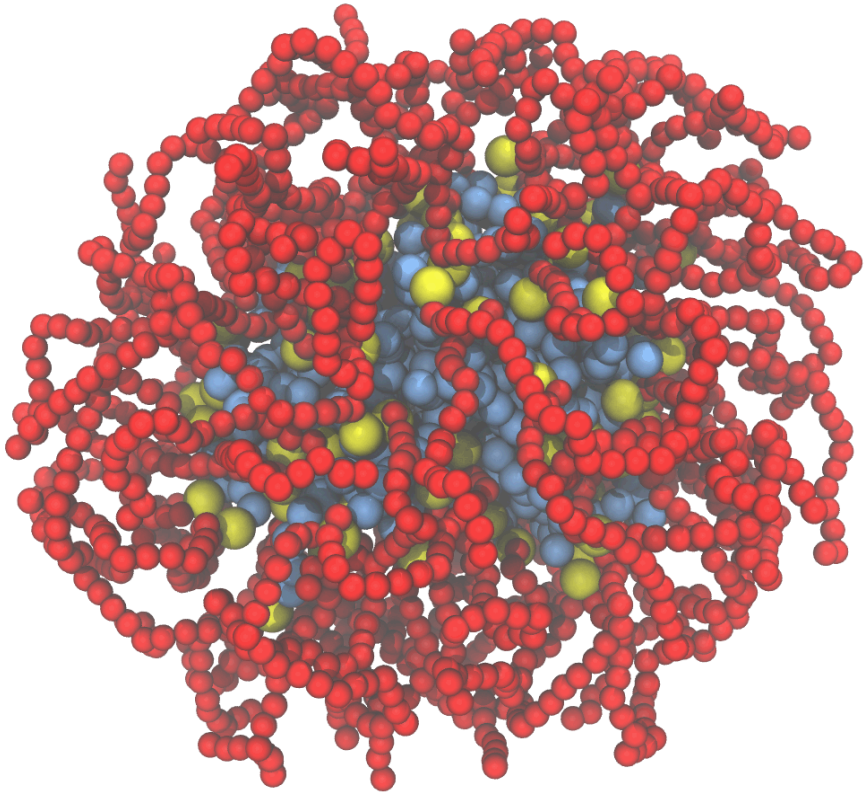
CG will enable Micelle simulations.





M = 50, 330 K



M = 100, 330 K

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Conclusions

Atomistic simulations

Minimum length is required for backbone to bend.
No structural transition for short oligomers.

In copolymer single chain, the alkane part bends back to be next to nipam backbone.

In prebuilt micelles of copolymer with PNIPAM on outside,
T dependence does appear in PNIPAM structure

CG Model

Have PNIPAM CG model at two T (above & below LCST)
Matches atomistic structure

Copolymer model and micelles are work in progress

Lessons in Coarse-Graining

CG models with many types (and T dependence) are complex.

Need a better CG water model.

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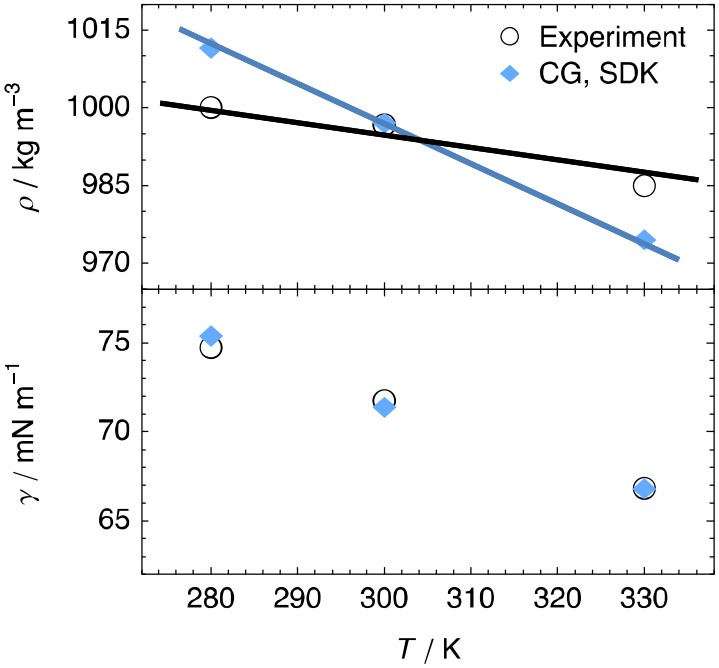
Limitations & Weakness in CG method



water

LJ variants of CG water do not get the density as a function T correct.
This is a critical aspect of the hydrophobic effect(s). Koga JPCB 2016
Missing hydrogen bonding in almost all CG models.
No CG model for *multiple* waters exists that does this.
Molinari water model for a single water molecule does.
Plus need means to treat other hydrogen bonding groups, e.g. amides in PNIPAM.

What is entropy & enthalpy of PNIPAM & water as a function of T?

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