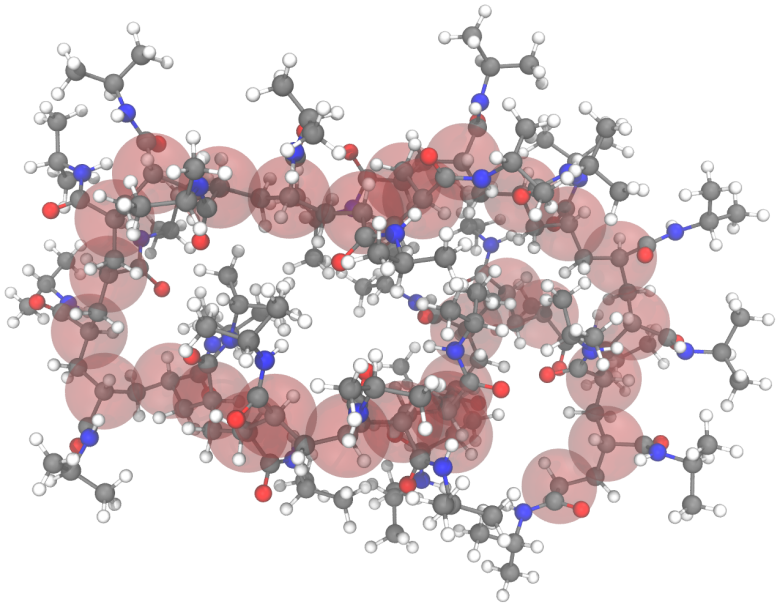
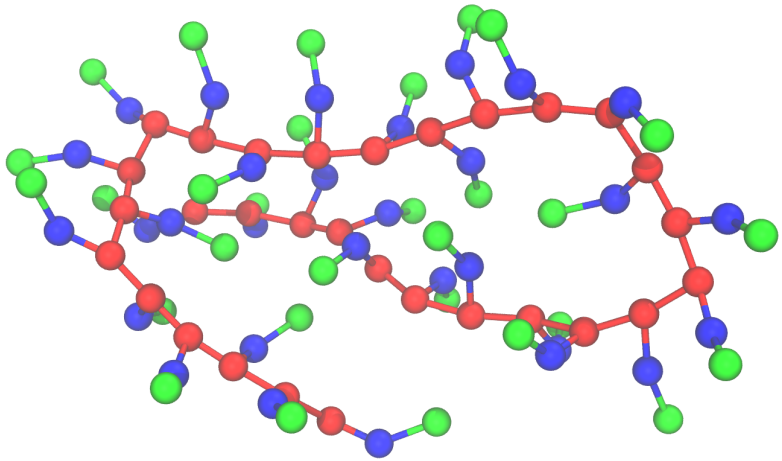
SAND2016-2428C

A Coarse-Grained Model for Thermoresponsive Poly(*N*-isopropylacrylamide)





Lauren J. Abbott and Mark J. Stevens

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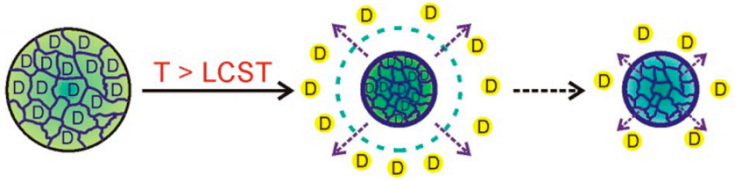
Temperature-responsive behavior useful for many applications

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

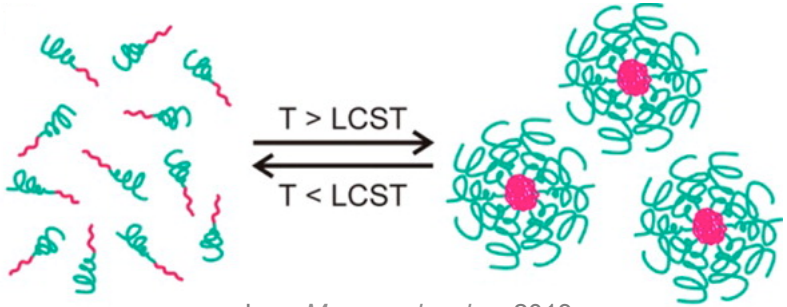
Gibson, *Chem. Soc. Rev.*, 2013

Responsive hydrogels
(e.g., drug delivery, tissue engineering)



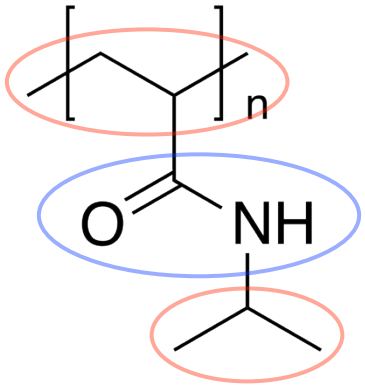
Lee, *Macromolecules*, 2013

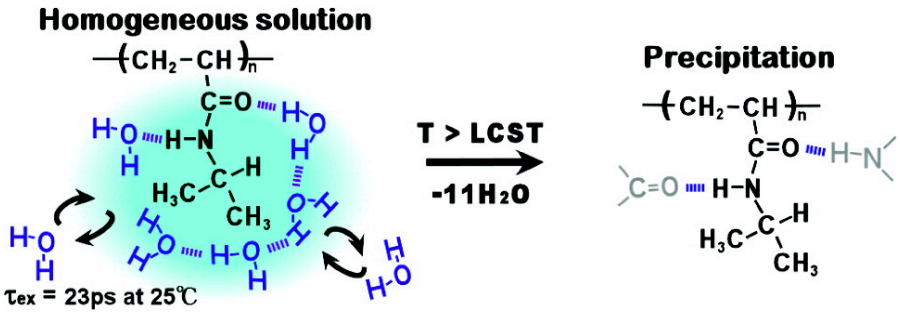
Responsive self-assemblies



Lee, *Macromolecules*, 2013

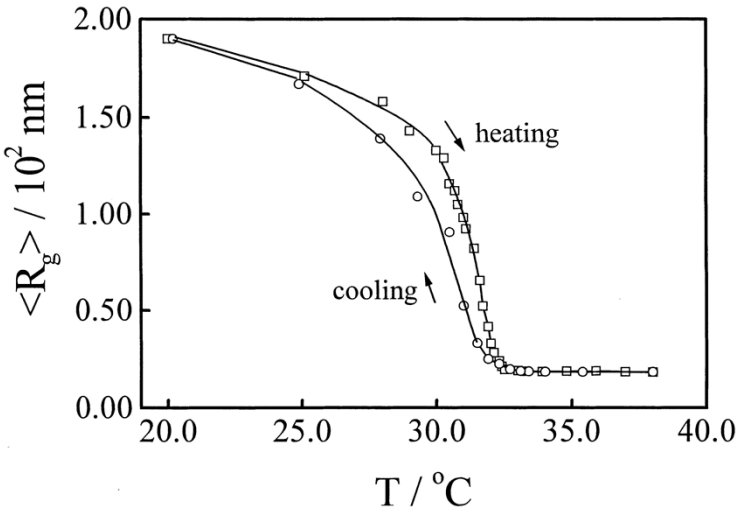
PNIPAM displays a sharp transition at its LCST ~32 °C

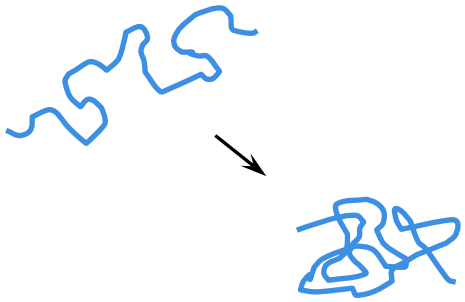




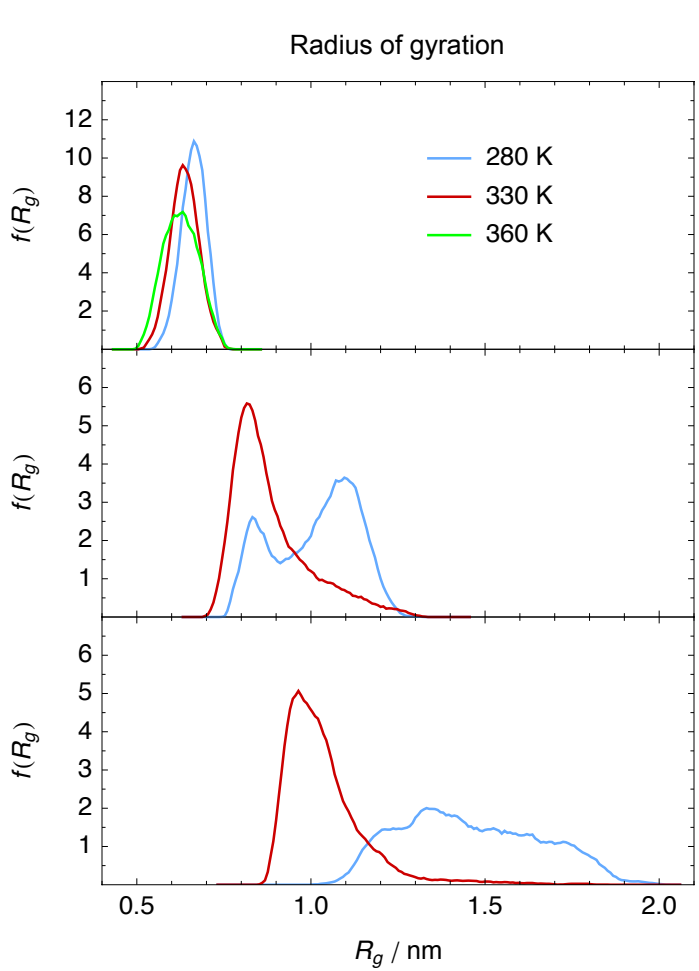
Ono, *J. Am. Chem. Soc.*, 2006

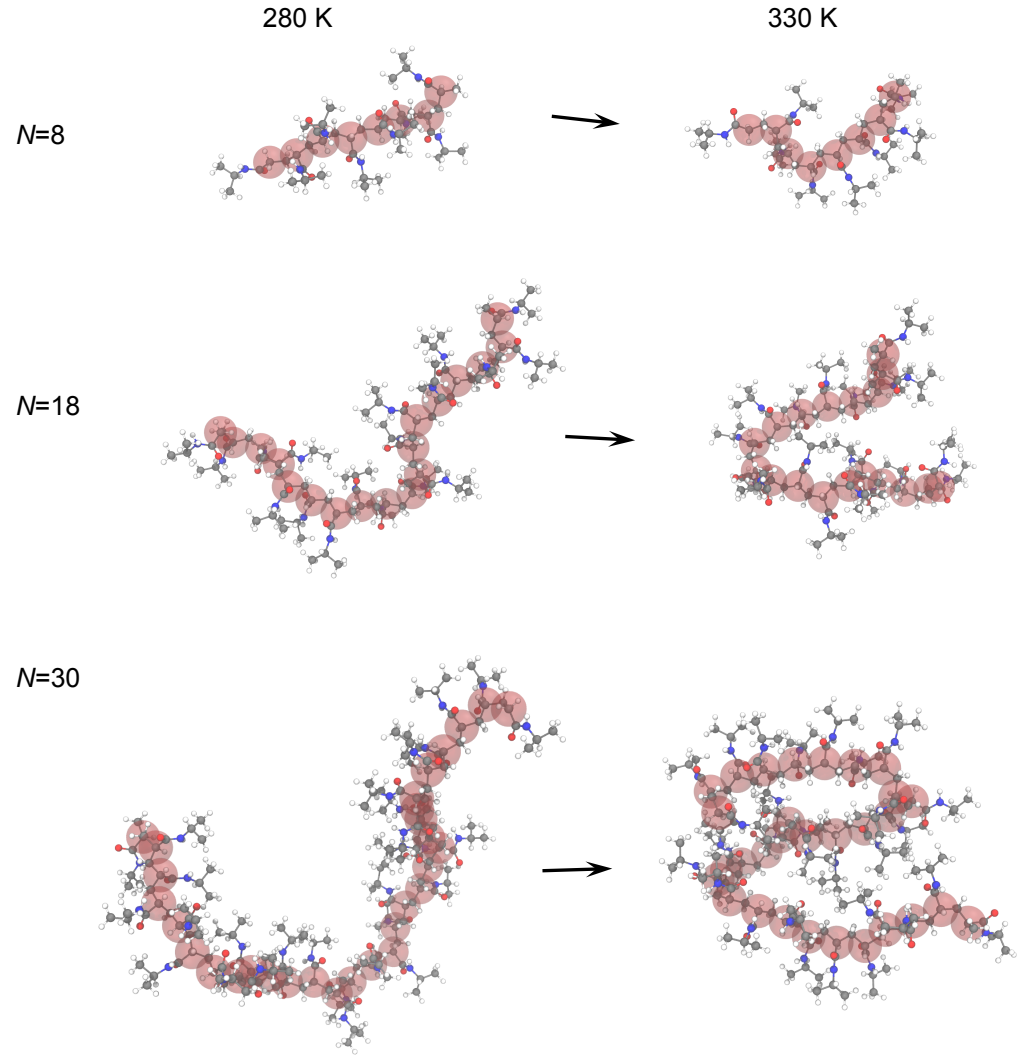
Wang, *Macromolecules*, 1998



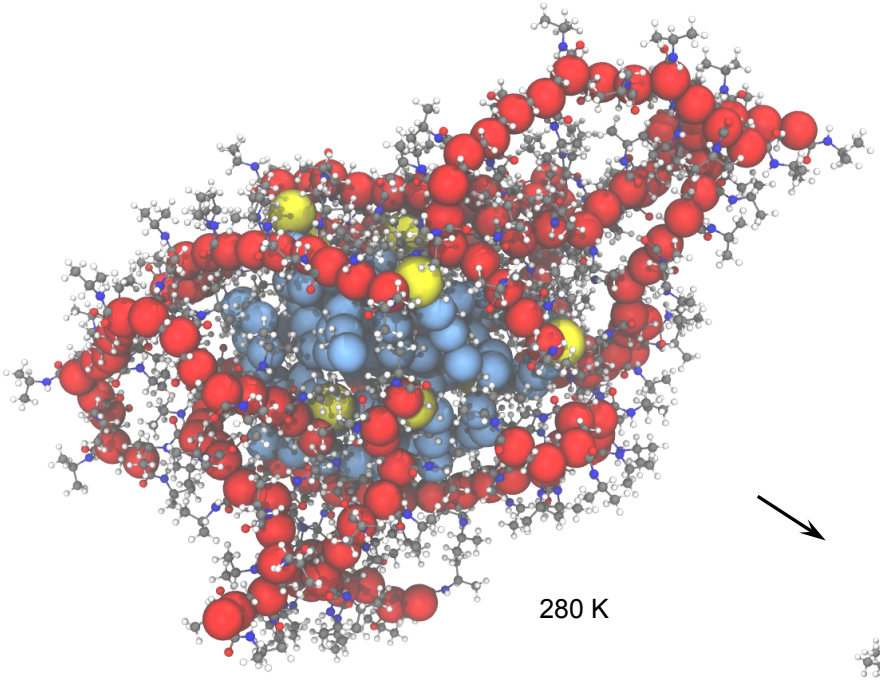


Atomistic simulations capture single-chain behavior

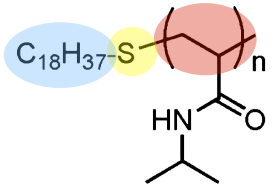




Micelles show temperature-responsive behavior



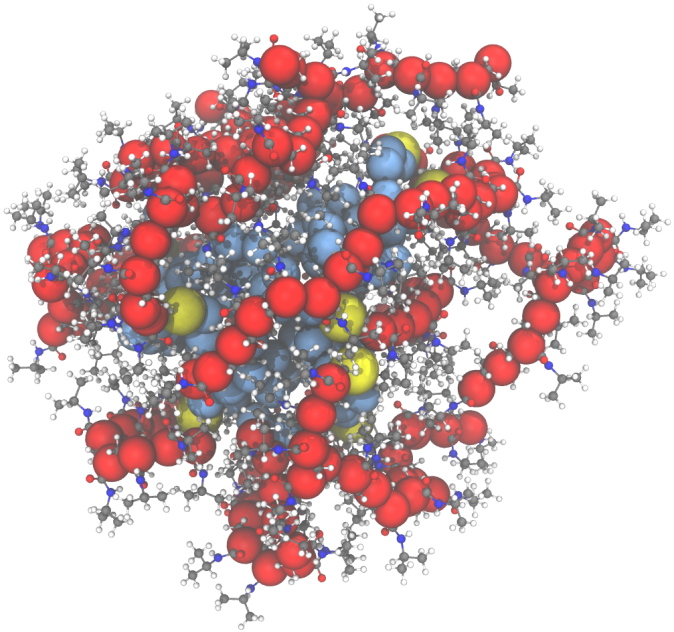
280 K



PNIPAM-C18

Li, *ACS Nano*, 2014

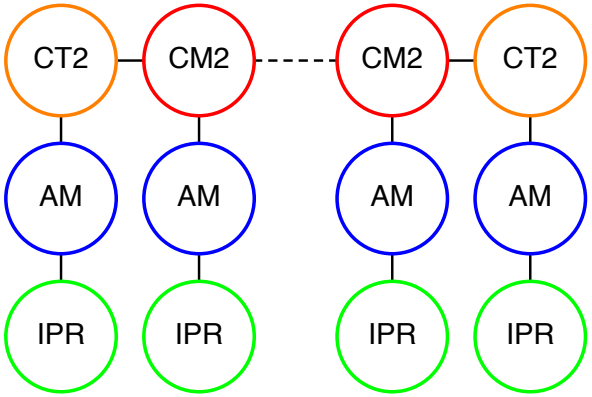
330 K

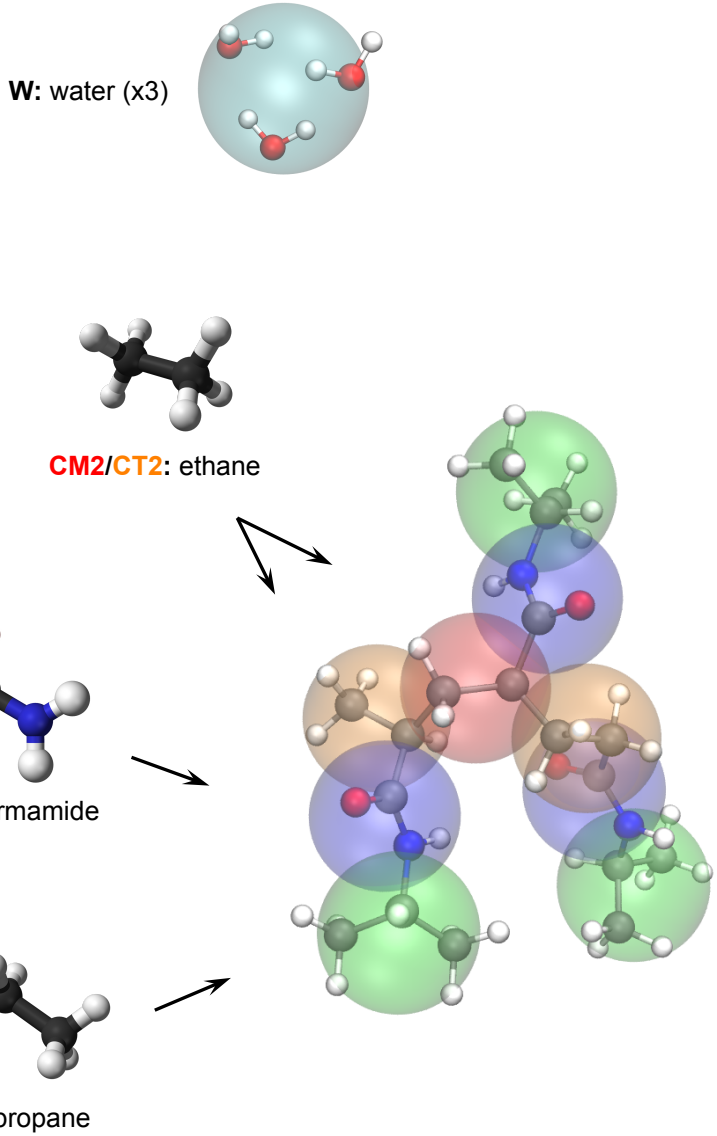


CG model for PNIPAM

Simulation details:

- Following methodology of Shinoda-DeVane-Klein (SDK) CG force field
- CG beads correspond to ~3 heavy atoms
- Explicit water bead = 3 water molecules
- Nonbond: LJ potentials fit to experimental data (e.g., surface/interfacial tension)
- Bonded: Gaussian-based potential fit to distributions from atomistic simulations
- Parameterization performed against *N*=30 oligomer
- MD with HOOMD-blue on GPUs



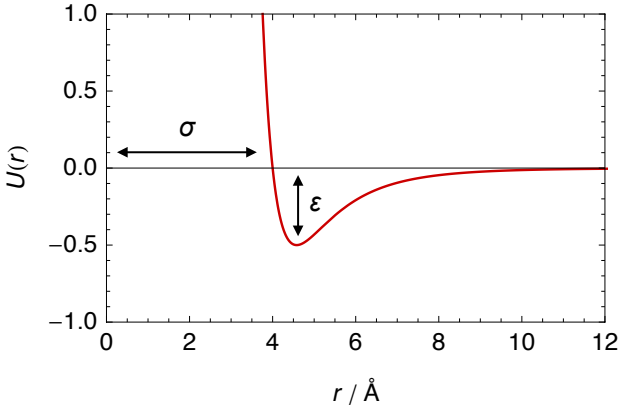


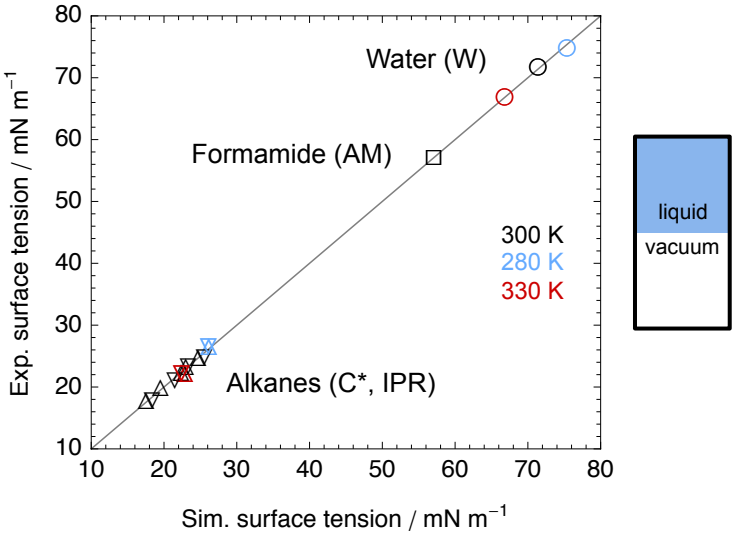
Nonbonded parameters fit to experimental data

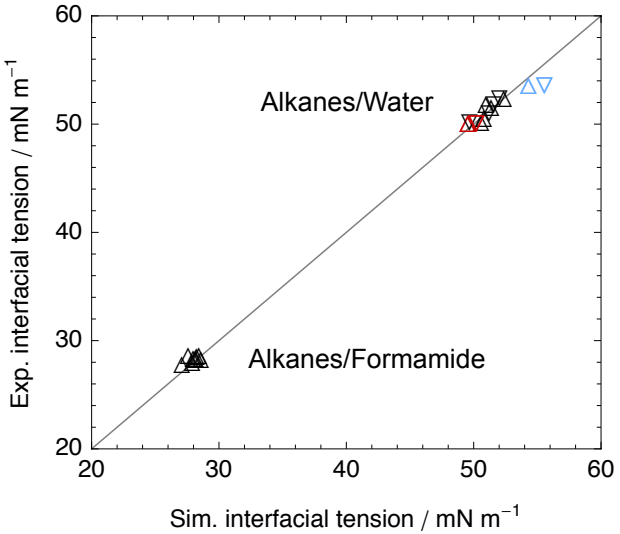
12-4/9-6 Lennard-Jones potentials:

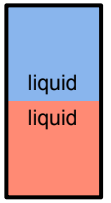
$$U_{\mathrm{LJ}}^{a\text{-}b}\left(r_{ij}\right) = c_{ab}\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{a} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{b}\right]$$

Shinoda, *Mol Simul*, 2007

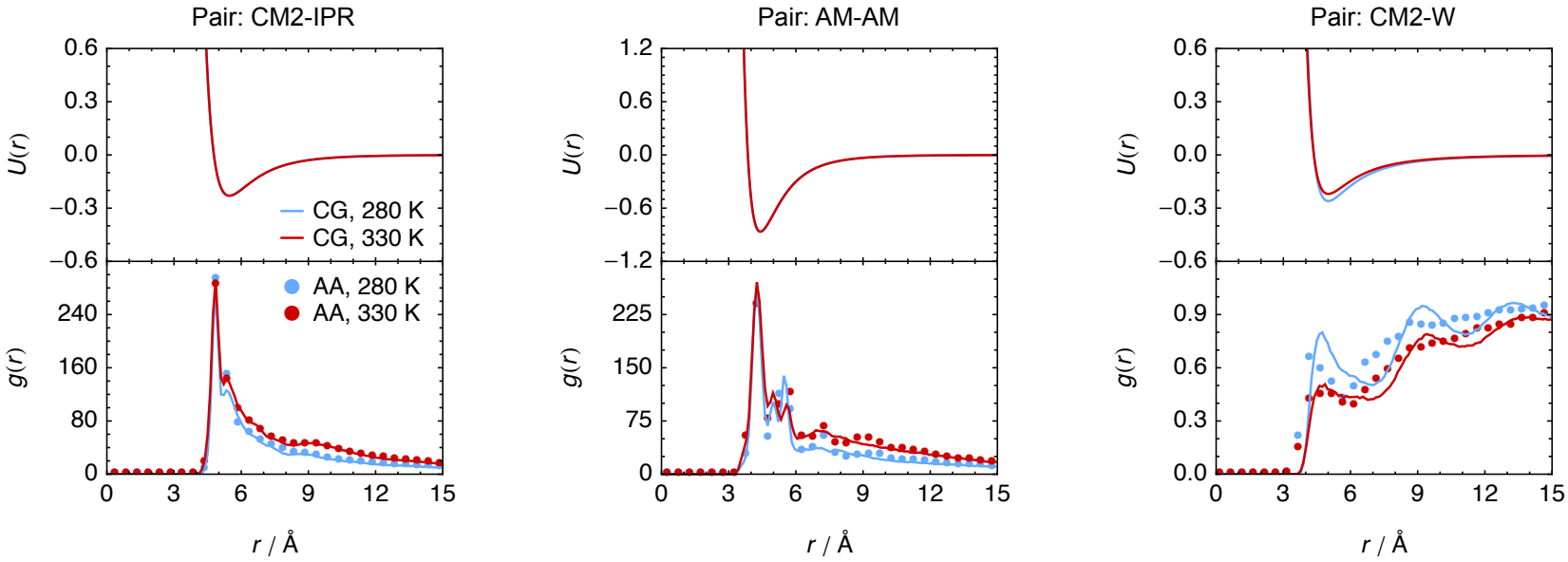








Adjusted for PNIPAM model to better match RDFs



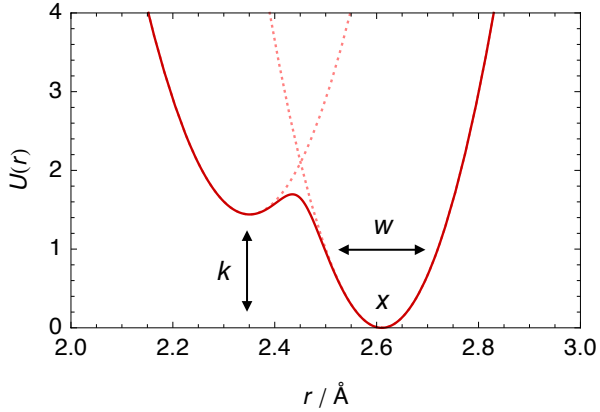
Temperature-dependent nonbonded parameters:
CM2-W, CT2-W, and IPR-W (hydrophobic beads with water)

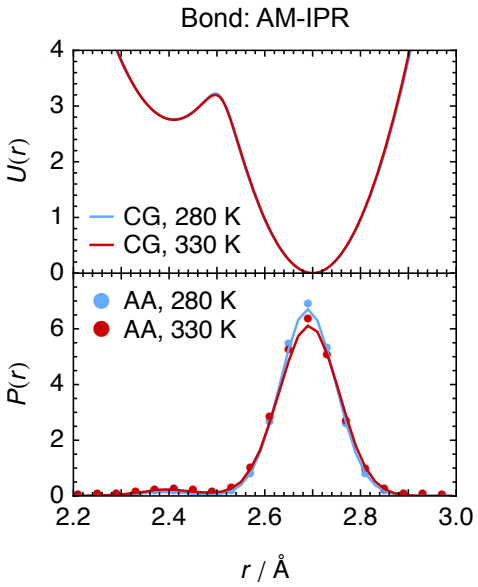
Bonded parameters fit to atomistic simulations

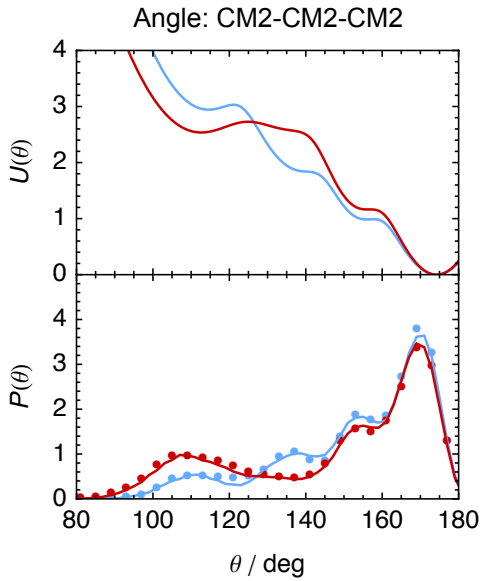
Gaussian-based potentials:

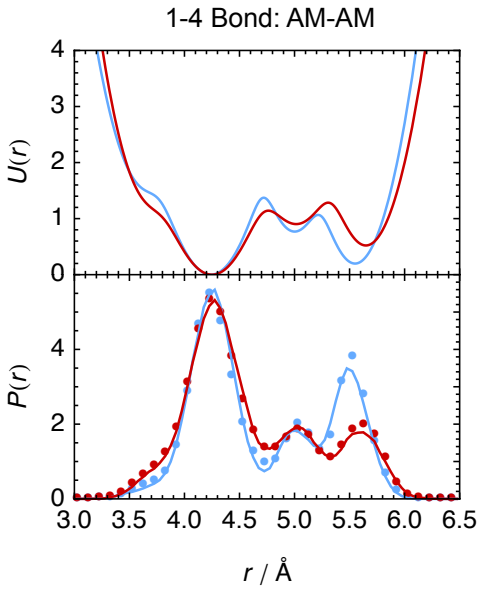
$$U(x,T) = c - k_B T \ln \sum_n k_n \exp\left[-\frac{(x-x_n)^2}{2w_n^2}\right]$$

Milano, *J Polym Sci Part B*, 2005

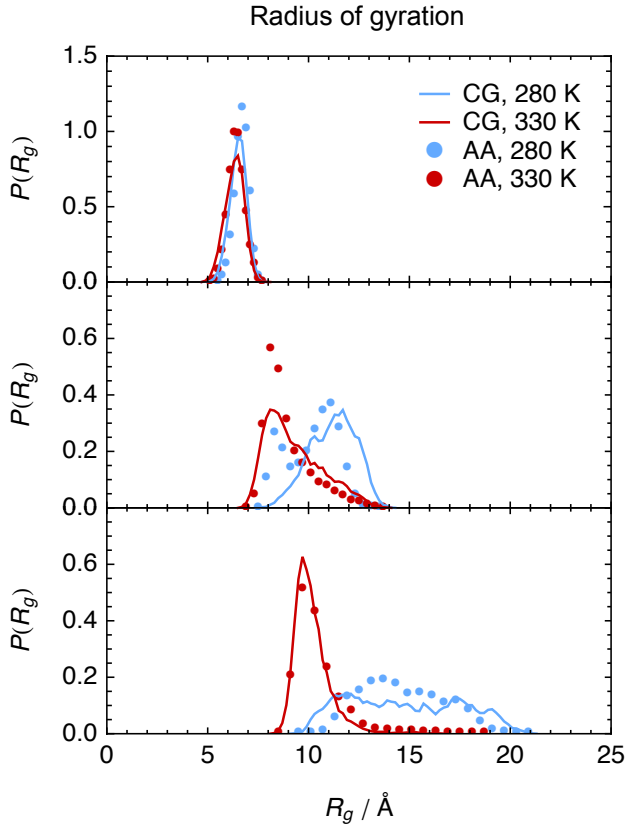








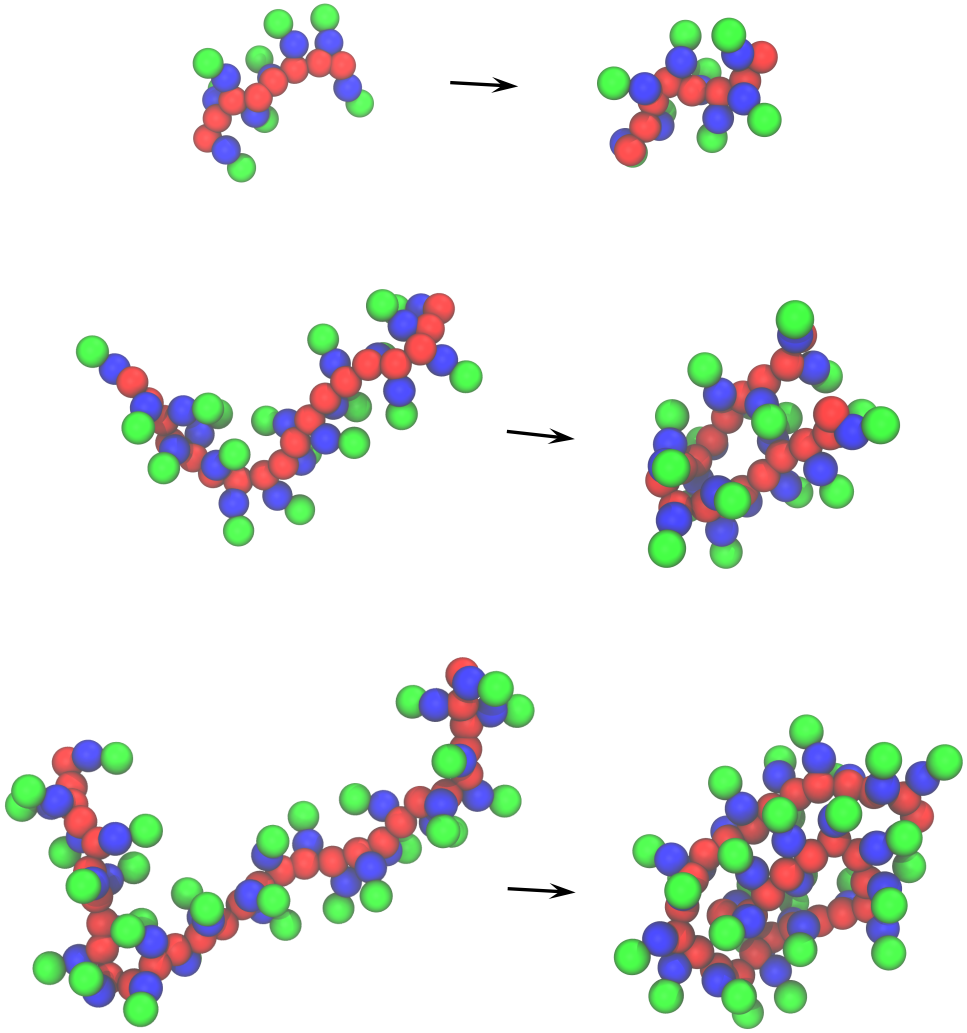
CG model yields correct single-chain behavior



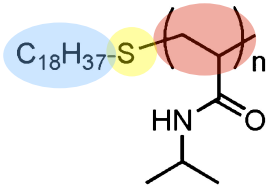
N=8

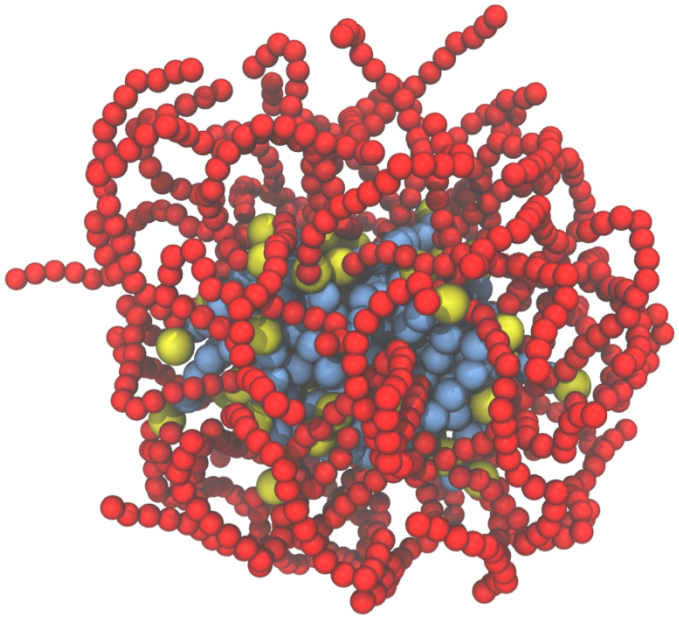
N=18

N=30

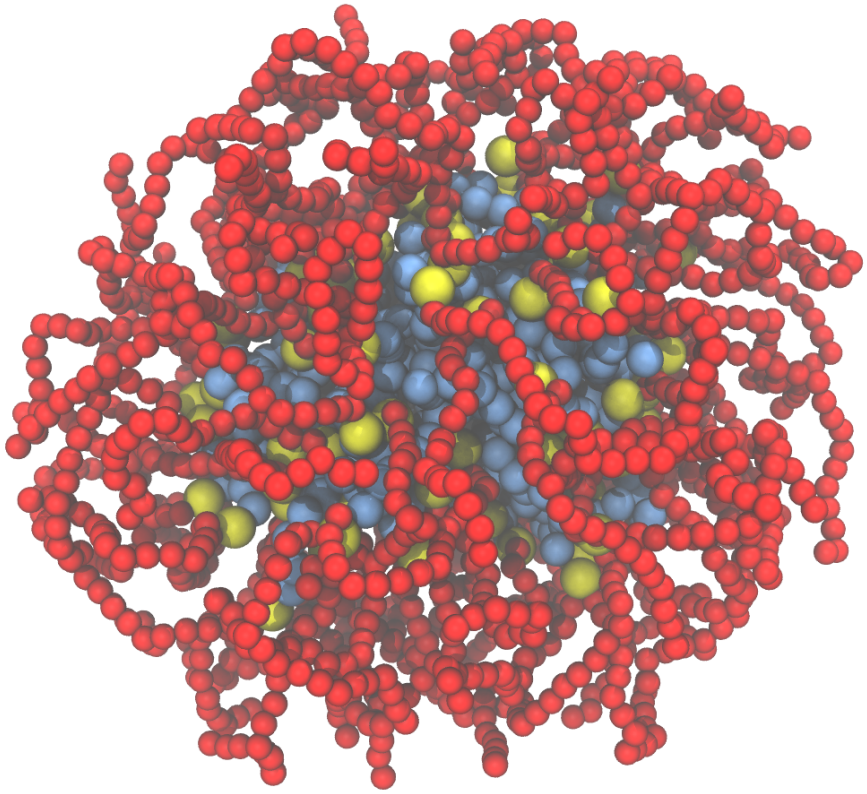


CG model able to simulate micelle self-assembly





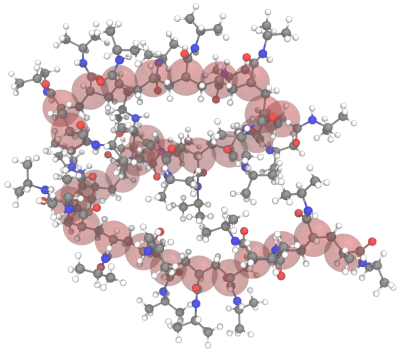
M = 50, 330 K

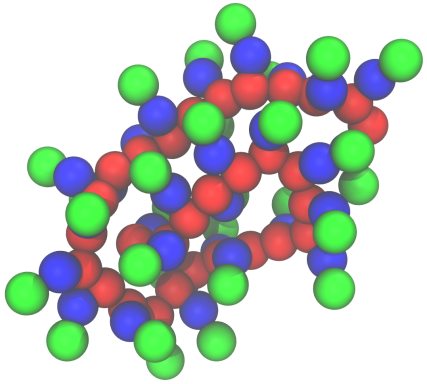


M = 100, 330 K

Summary

- Atomistic simulations of PNIPAM oligomers produce correct single-chain behavior and chain-length dependence
- Small micelles show temperature-dependence, but at the limit of what can be achieved with atomistic models
- Following SDK CG methodology, PNIPAM CG model fit to experimental data and atomistic simulations
- CG model reproduces single-chain behavior and chain-length dependence of atomistic simulations
- Possible to study self-assembly in larger systems with CG model





(1) LJ Abbott et al, *J Phys Chem B*, **2015**, 119, 3837
(2) LJ Abbott and MJ Stevens, *J Chem Phys*, **2015**, 143, 244901

Work was supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division