Argonne NATIONAL LABORATORY

Present and Future Computing Requirements for:

Molecular Dynamics of PNIPAM Agglomerates and Composite Architectures

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U.S. DEPARTMENT OF ENERGY

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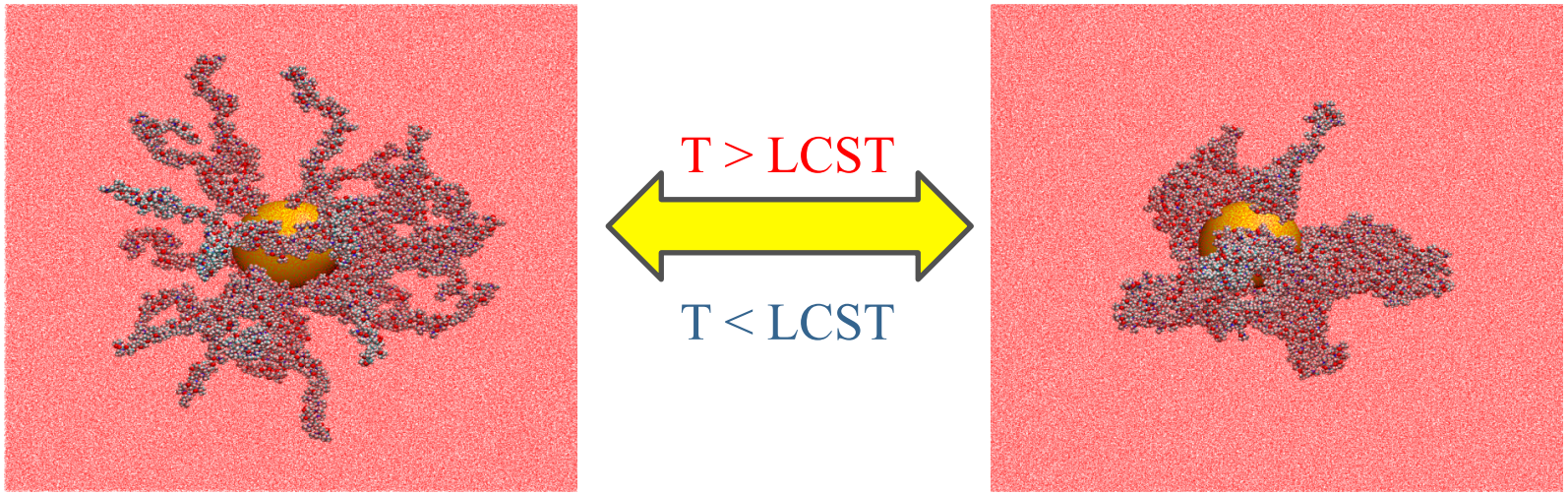
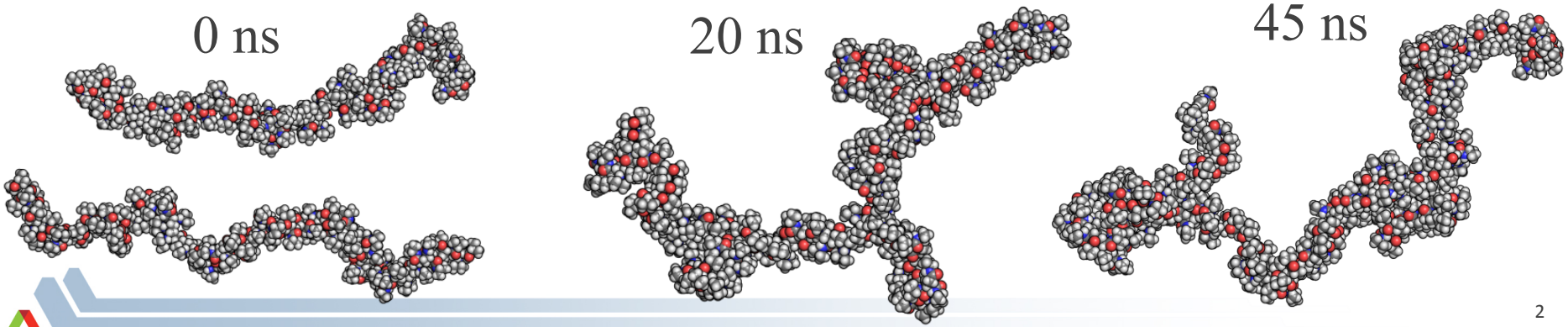
Co-PI: *1. Dr. Ganesh Kamath (University of Missouri-Columbia)*

(1) m1524, Molecular dynamics simulation of PNIPAM-coated gold nanoparticles: Experimental and Simulation Study.

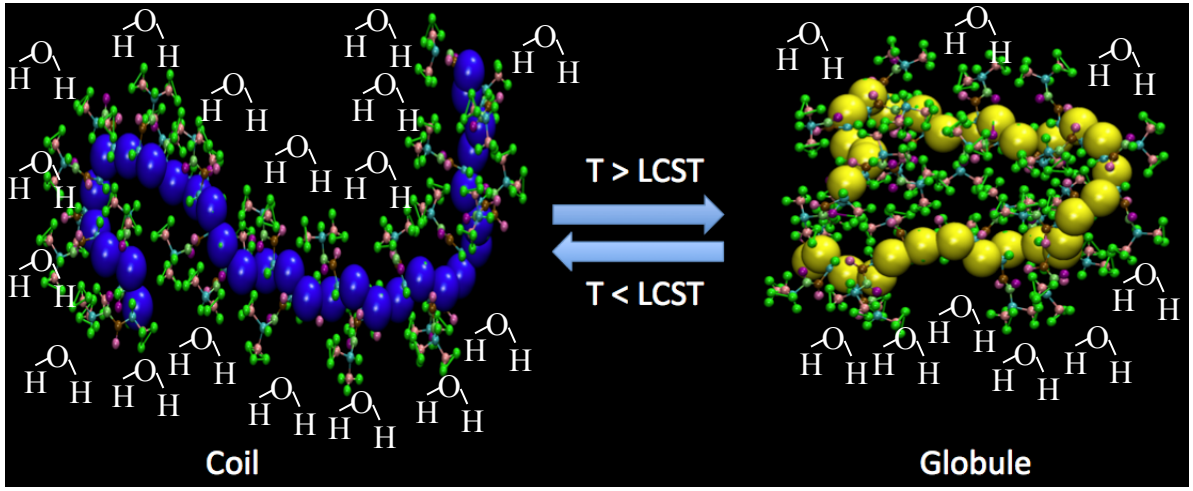


(2) m1528, Agglomeration dynamics in thermo-sensitive polymers across the lower critical solution temperature: Experimental and Simulation Study.



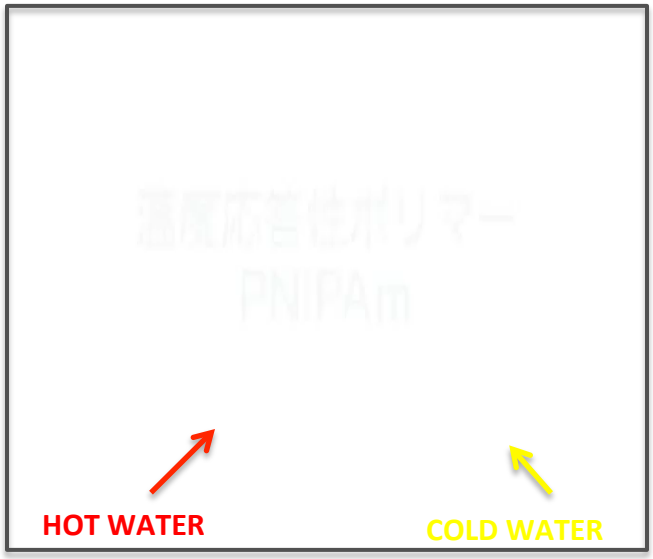
➢ Thermo-Sensitive Polymers: Lower Critical Solution Temperature (LCST)

(A) Hydrophilic — Hydrophobic

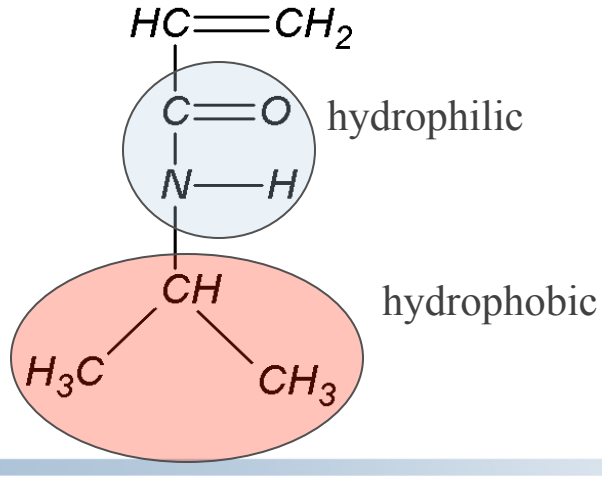


Hydrated Polymer Chain — Collapse of polymer chain

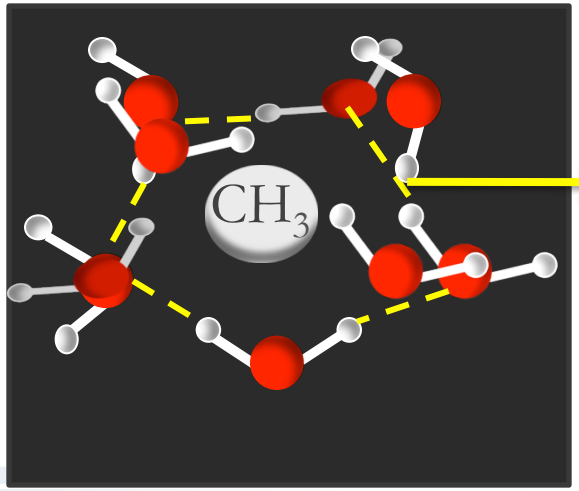
Video



(B) *N-isopropylacrylamide*



(C) *Hydrophobic Effect*



https://www.youtube.com/watch?v=iBZAwhxwHX0

1. Prog. Polym. Sci., Vol. 17, 163-249, 1992

➢ Poly(N-isopropylacrylamide) (PNIPAM)

- ❑ Lower Critical Solution Temperature (LCST): 31-32 ˚C

(A)

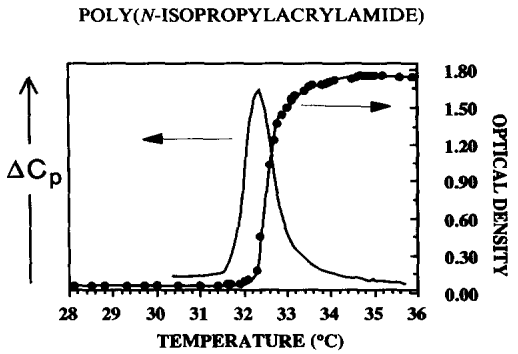
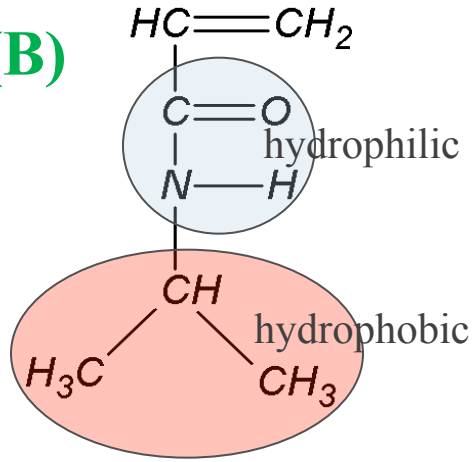


FIG. 4. Cloud point and DSC measurements of the LCST of PNIPAAM chains (0.4 mg/ml).

(B)



➢ Potential Applications

1. Langmuir, 2000, 16 (19), pp 7503–7509.
2. *Macromolecules*, 2008, 41 (4), pp 1512–1520
3. *Prog. Polym. Sci.,* Vol. 17, 163-249, 1992

➢ Motivation

❖ *Key Questions*

❑ What is the atomistic description and mechanism of coil-to-globule transition and agglomeration in PNIPAM?

❑ Is LCST and agglomeration behavior in single chains dependent on the chain length of PNIPAM?

❑ What is the effect of grafting and variation grafting density of PNIPAM chains on their agglomeration?

❑ What is the role of solvation dynamics and structure of proximal water during the coil-to-globule transition of PNIPAM?

❖ *Our Approach*

❑ To examine the agglomeration dynamics and coil-to-globule transition in PNIPAM and role of solvent in inducing the LCST of PNIPAM:

1. PNIPAM single chain agglomeration of varying chain lengths.

2. Simulations of PNIPAM coated gold nanoparticles.

2. Computational Strategies

- ***We approached this problem computationally by:***

1. Building computational models at multi-scale level (atomic- to meso-scale) and conduct molecular dynamics (MD) simulations.

2. We conducted simulations of single chain PNIPAM oligomers with varying chain lengths (3-mer to 500-mer) in presence of explicit water model.

3. To study agglomeration in PNIPAM we conducted simulations of multiple chains of PNIPAM in presence of water e.g. 5 chains of 5-mer, 30-mer, 100-mer.

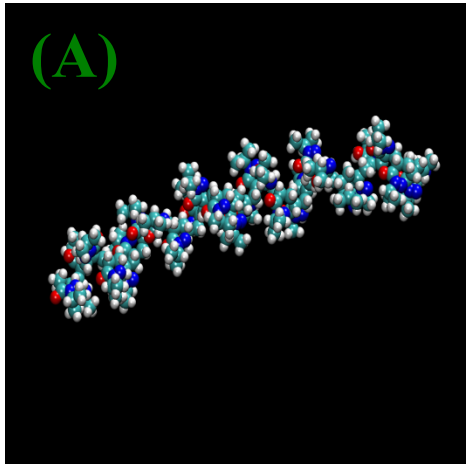
4. Simulations of PNIPAM grafted planar and spherical substrates with varying chain length and grafting density of PNIPAM.

Classical MD codes: NAMD and/or LAMMPS

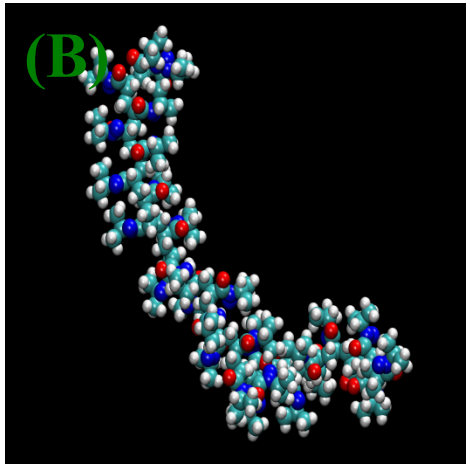
	NAMD	**LAMMPS**
Electrostatic Algorithms	Particle Mesh Ewald (PME) (Nlog(N) scaling)	particle-particle particle-mesh solver (Nlog(N) scaling), standard Ewald summation (N^(3/2)), multi-level summation method solver (scales as N)
Force Field Compatibility	Class-I force-fields (CHARMM, AMBER, OPLS)	Class-I, Class-II force-fields (polymer consistent force-field), reactive force-fields (REAXFF and REBO)
Integrator used for MD simulations	The velocity Verlet integration method	The velocity Verlet integration method

MD Simulations of single chain 30-mer: *(Total atoms = ~40 K)*

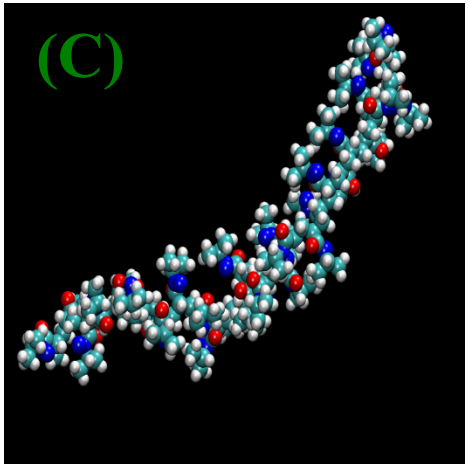
At 278 K after 0 ns



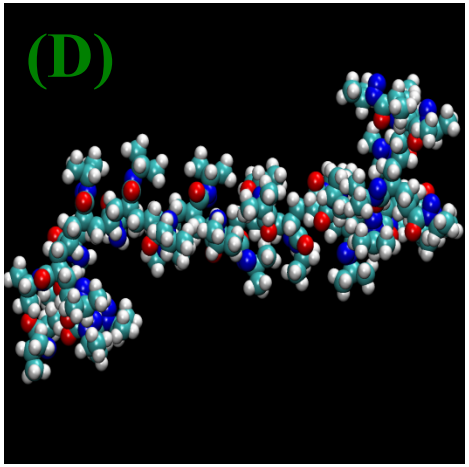
At 278 K after 5ns



At 278 K after 15 ns

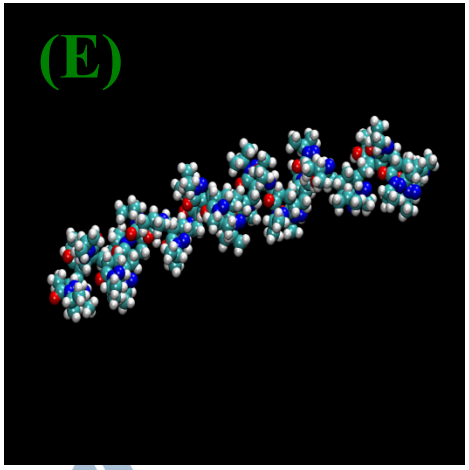


At 278 K after 20ns

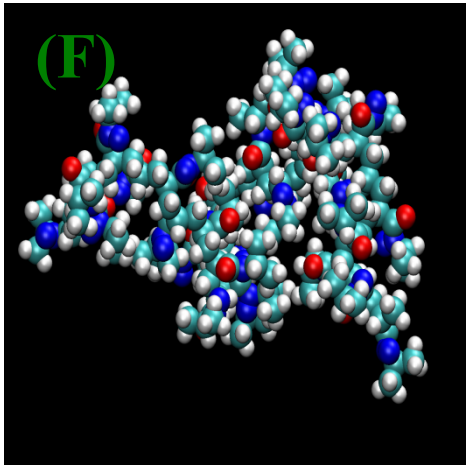


Coil-State

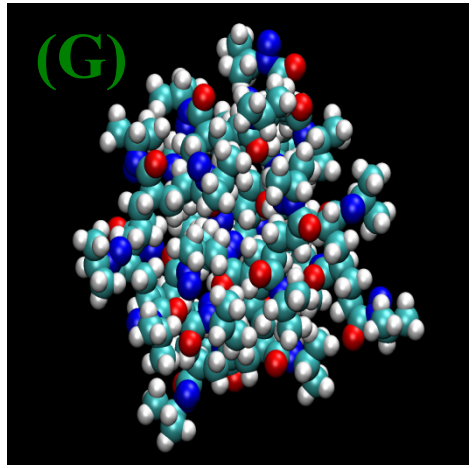
At 310 K after 0 ns



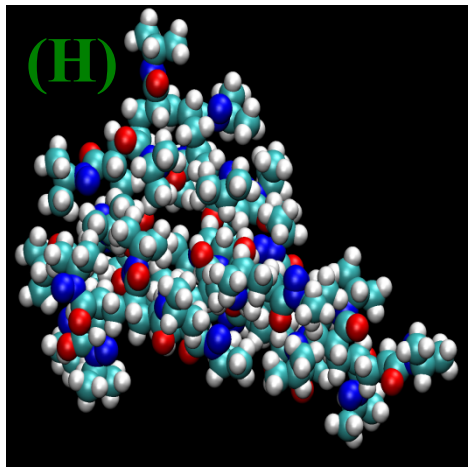
At 310 K after 5 ns



At 310 K after 15 ns



At 310 K after 20 ns



Globule-State

➢ Methods of Analysis: *In-house codes*

❖ Structural Analysis

1. Radial Distribution Function

$$g_{AB}(r) = \frac{v}{tN_A N_B V(r, r+\Delta r)} \sum_{\tau=1}^{t} \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \delta_{\Delta r}\left(r - \left|r_{ij}(\tau)\right|\right)$$

……Equation 2

2. Radius of Gyration (R_g)

$$R_g^{\,2} = \frac{1}{M} \sum_i m_i (r_i - r_{cm})^2$$ ……Equation 3

r_{cm} = Centre of mass of polymer chain

M = Mass of polymer chain

❖ Dynamical Analysis

3. Hydrogen Bond Analysis[1]

$$C_x(t) = \left\langle \frac{\sum_{ij} S_{ij}(t + t_0) \,.\, S_{ij}(t_0)}{\sum_{ij} S_{ij}(t_0) \,.\, S_{ij}(t_0)} \right\rangle$$ ……Equation 4

x = continuous (c)
or intermittent (i)

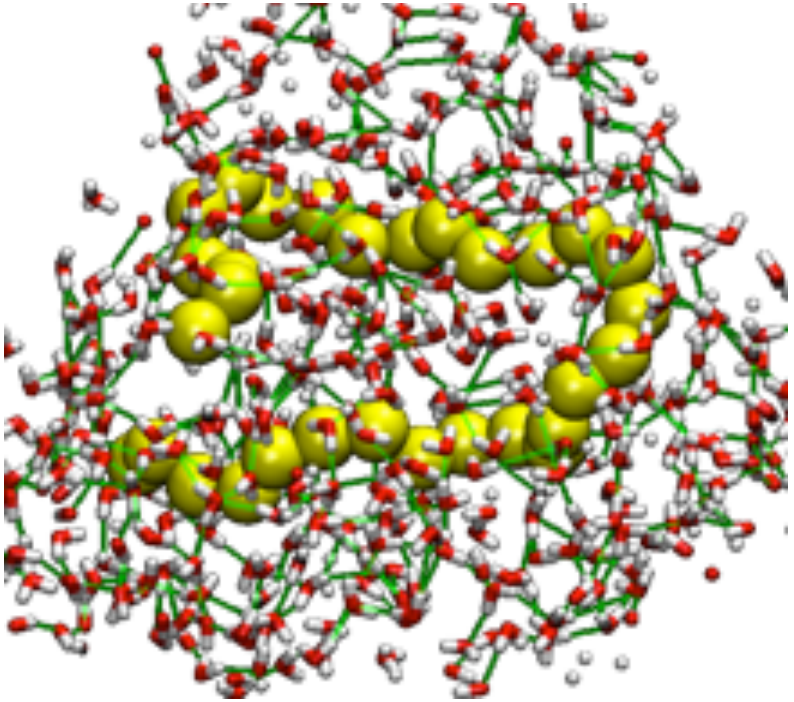
If (hydrogen bond == present at time t) then
  $S_{ij}(t) = 1$
else
  $S_{ij}(t) = 0$
End if

4. Residence Time Probability of water molecules

1. Mol. Phys. **1983**, 50, 1151

Solvent treatment

- For simulating molecules in a solvent, a choice should be made between explicit solvent and implicit solvent.
- Explicit solvent particles must be calculated expensively by the force field, while implicit solvents use a mean-field approach.
- Using an explicit solvent is computationally expensive, requiring inclusion of roughly ten times more particles in the simulation.
- The granularity and viscosity of explicit solvent is essential to reproduce certain properties of the solute molecules. This is especially important to reproduce kinetics.

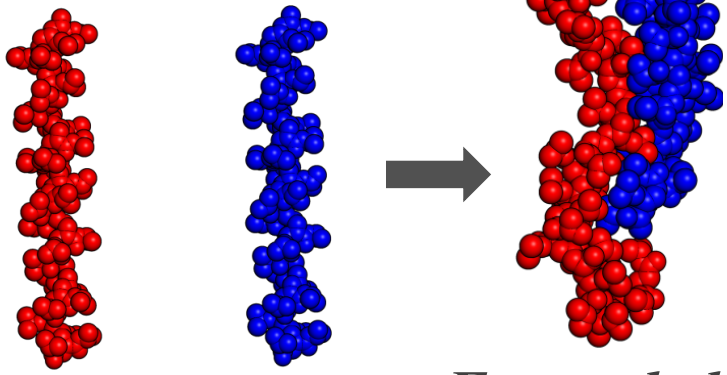


Explicit solvent treatment

PNIPAM (2 chains) 30-mer: TIP3P water model

T = 275 K

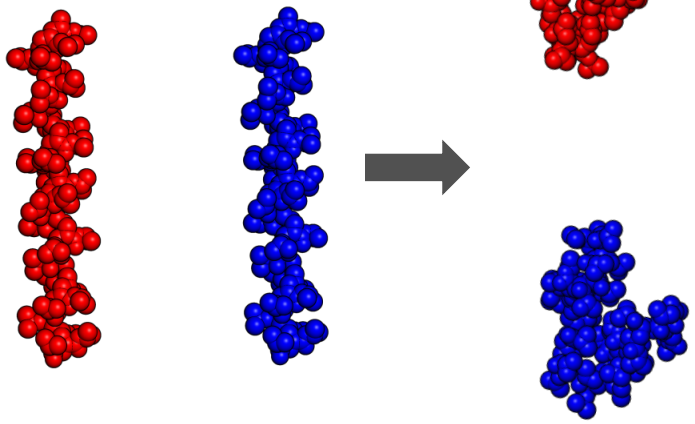
25 ns



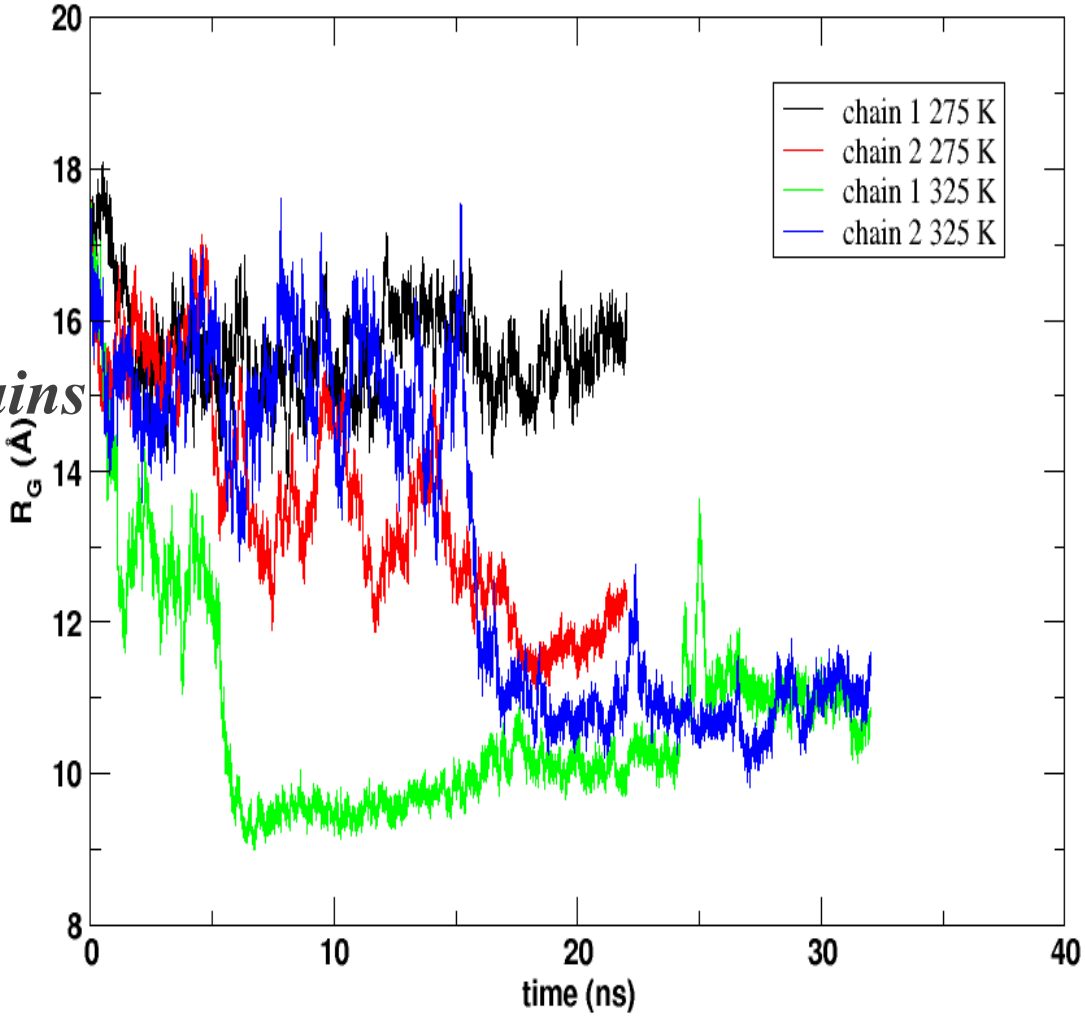
Entangled chains

T = 325 K

30 ns



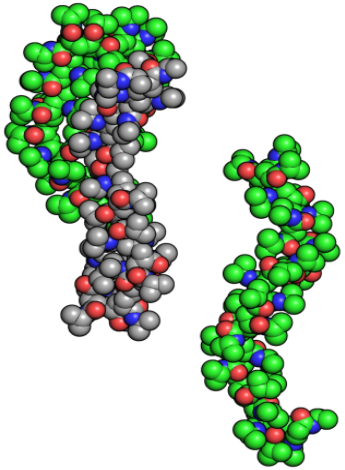
Collapsed chains



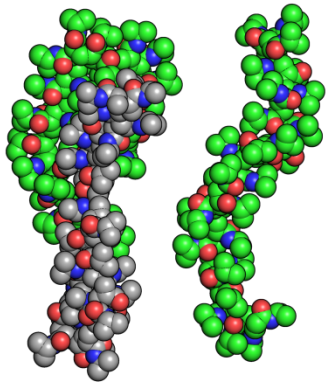
Modeling the third chain 30-mer

275 K

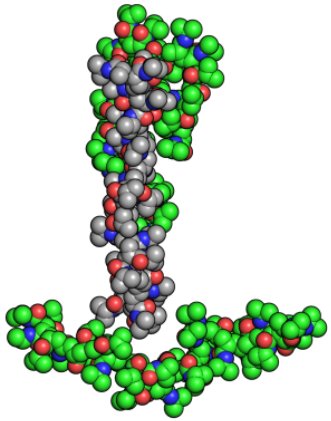
type1



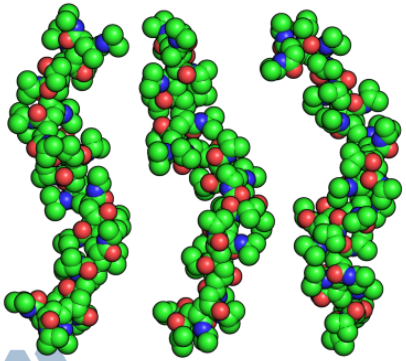
type2



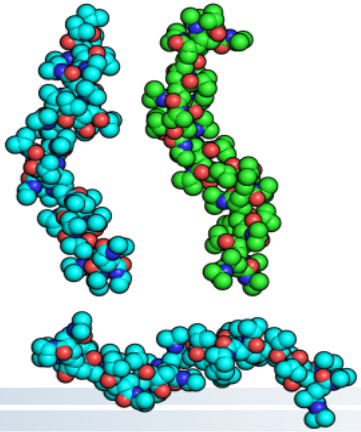
type3



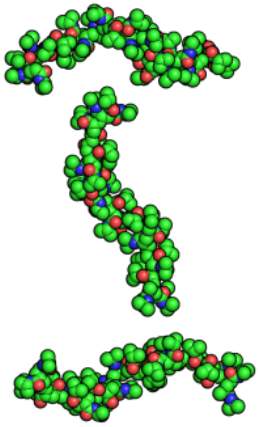
type4



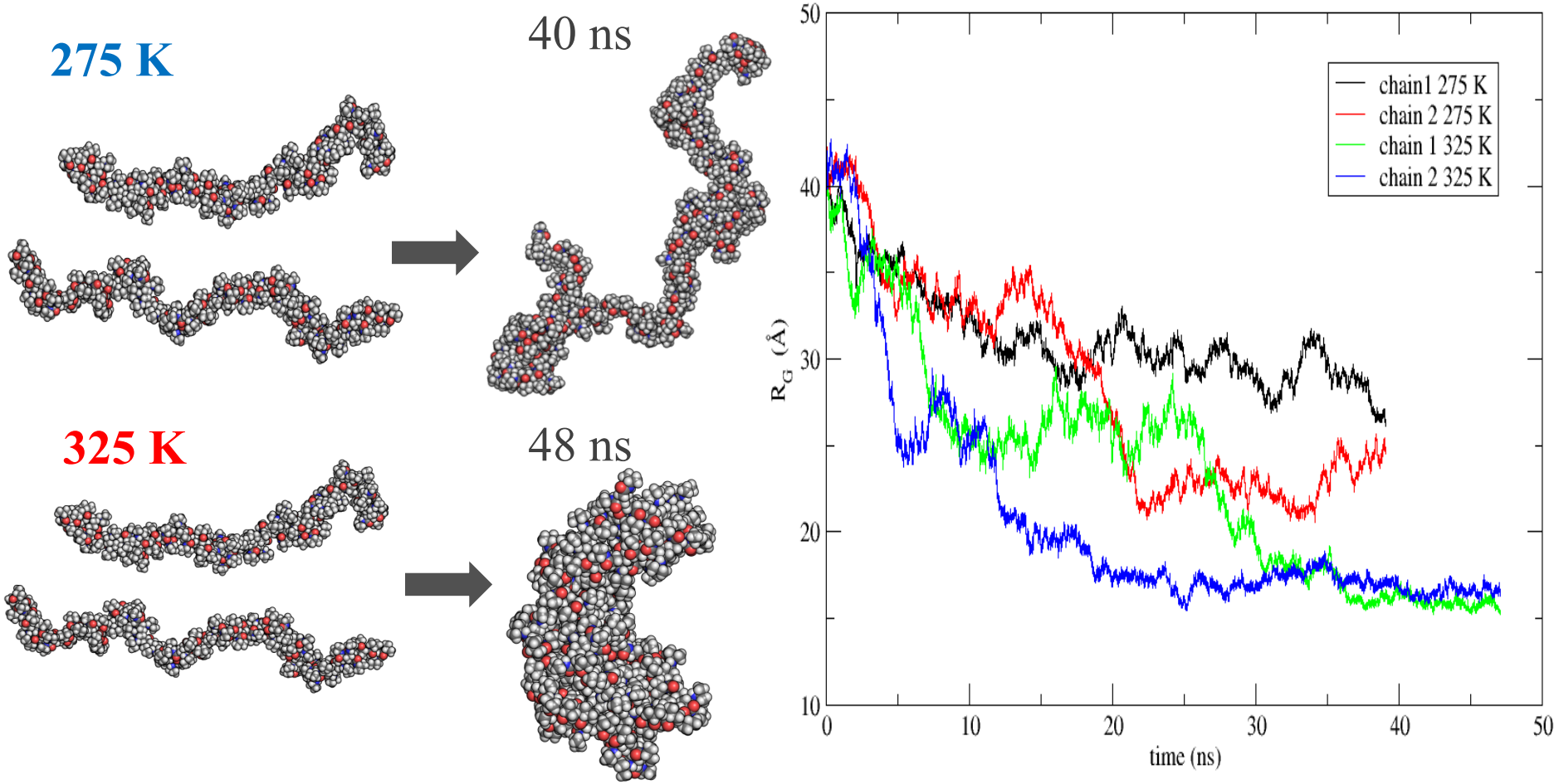
type5



type6



PNIPAM (2 chains) 100-mer: (~400 K atoms)



275 K: agglomeration followed by entanglement of the chains.

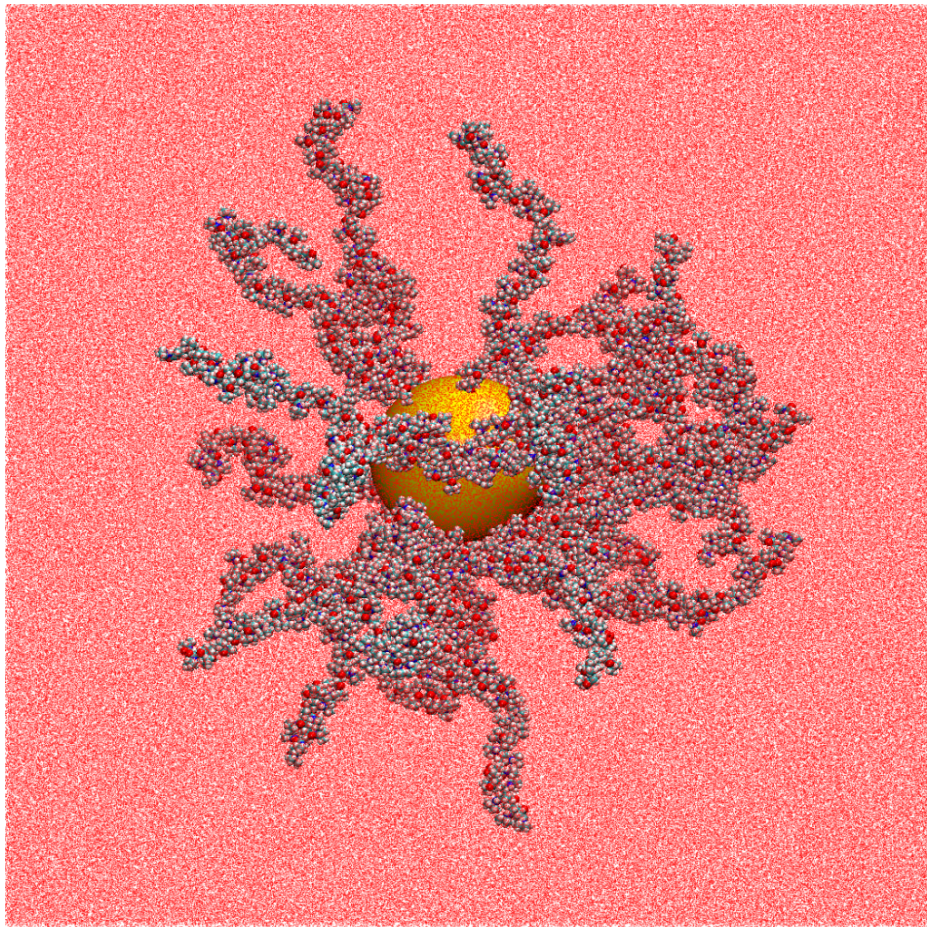
325 K: Collapse of 1 chain; relative collapse of the second chain agglomeration with simultaneous further collapse of the chains.

➢ PNIPAM-coated Gold Nanoparticles: *Effect of Grafting Density*

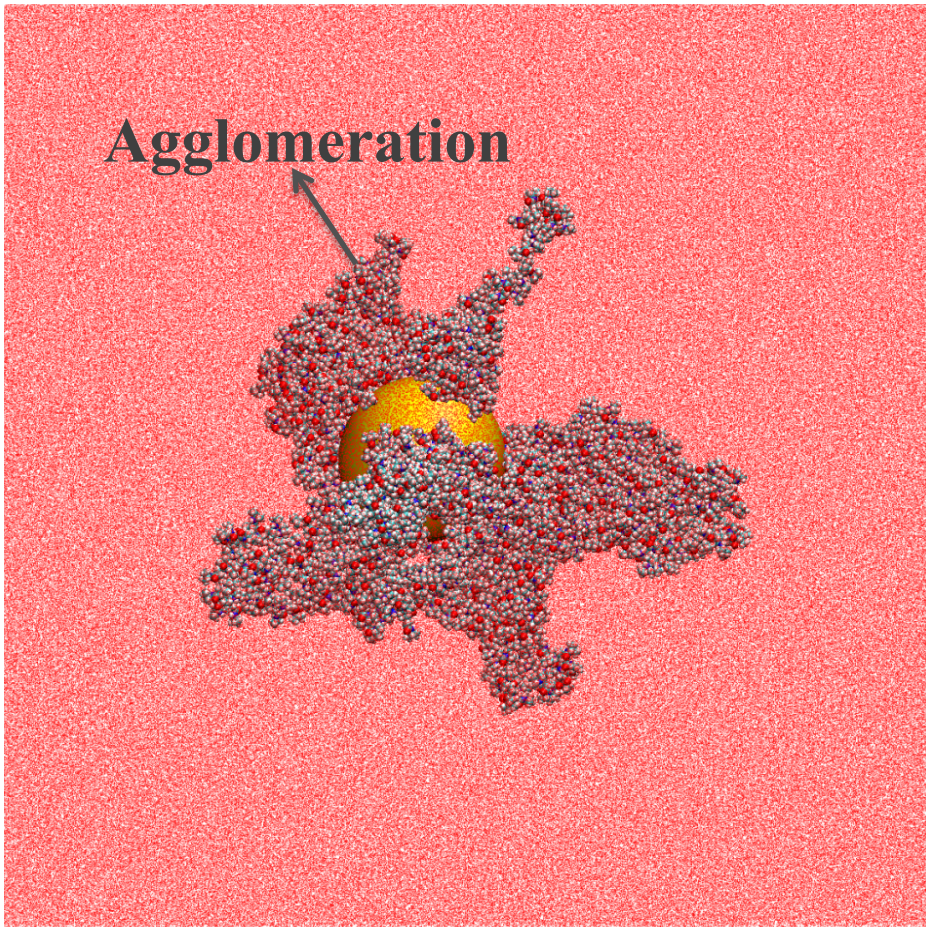
- ❑ To study the agglomeration behavior of polymer chains across the LCST.
- ❑ Current models for grafted polymer are coarse-grained which makes it difficult to study the solvation dynamics in polymers like PNIPAM.
- ❑ Single chain dynamics clearly elucidate the importance of the explicit solvent modelling.
- ❑ Explicit solvent treatment in meso-scopic architectures of these polymer chains is still lacking.

PNIPAM-coated gold nanoparticle (28 chains) 60-mer: (~ 3M atoms)

(A) 275 K



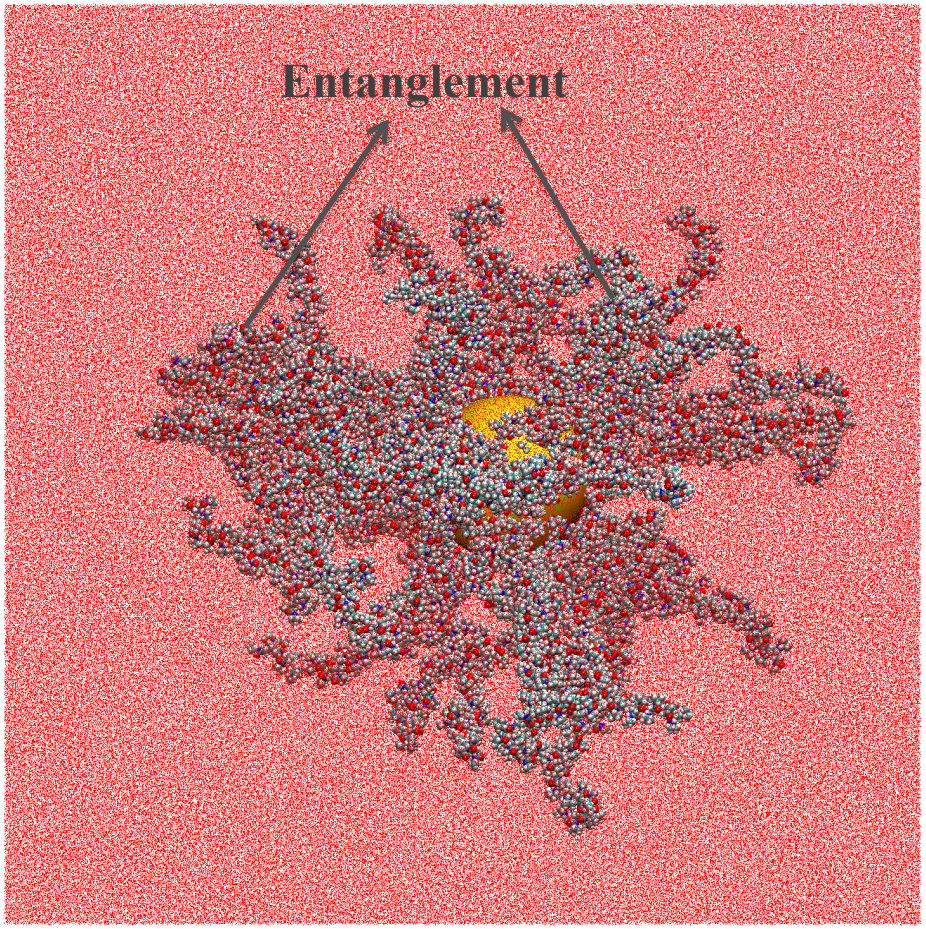
(B) 325 K



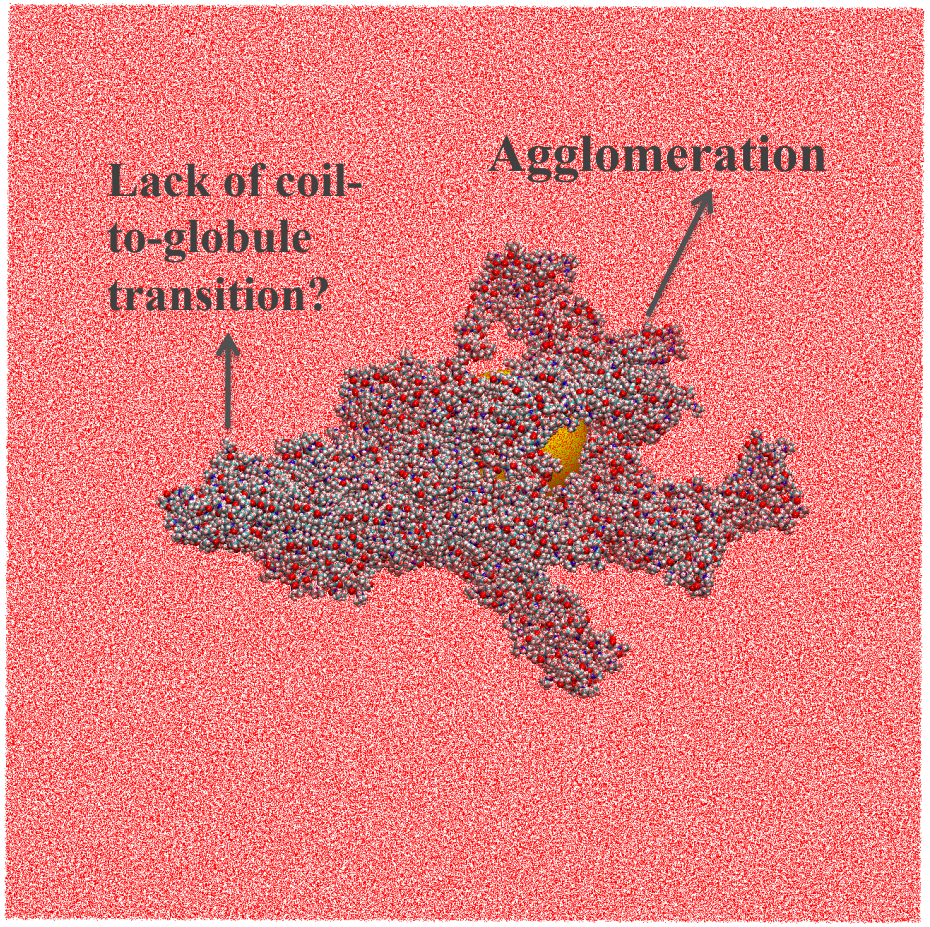
Experimental measurements (SAXS, USAXS etc) are made assuming that the chain is in coil-state below LCST.

PNIPAM-coated gold nanoparticle (56 chains) 60-mer: (~ 3M atoms)

(A) 275 K



(B) 325 K



- **Our biggest computational challenges are:**
  (a) Trajectory files (containing positions and velocities of all atoms) are periodically written during a MD simulation, either for restarting runs or for post-processing visualization and data analysis. Handling of these files could be tedious because of the file size.
  (b) I/O becomes excessively demanding for multi-million-atom simulations.

- **Our parallel scaling is limited by:**

(a) Treatment of long-range electrostatic interaction algorithms/methods.

- **We expect our computational approach and/or codes to change by 2017 in this way:**

(a) We propose to build sophisticated and accurate coarse-grained models of our polymer-water systems which will allow us to implement higher timesteps (30-40 fs) and conduct simulations up to micro-seconds.
(b) Our approach will be to combine atomic- and coarse-grained models and develop hybrid models that will allow us to maintain atomic resolution at the interfaces of interests and coarse-grained approximation for bulk solvent.

3. Current HPC Usage

- **Machines currently using**

  Hopper CRAY XE6 system

- **Hours used in 2012-2013**

Computing Facility	**Core Hours**
NERSC	~24 M
ALCF computing Facility	~50 M + *170 M* = 220 M (ALCC awards)
Carbon Cluster (Argonne National Laboratory)	~0.5 M

- **Data read/written per run**

  System size: 400 K to 10 M atoms, data is stored every picosecond for each simulations. Trajectory can vary between 100-400 GB depending upon system size.

- **Memory used**
  (a) 8-10 GB per core

- **Necessary software, services or infrastructure**
  (a) MD software: NAMD, LAMMPS
  (b) Libraries: MPI, FFTW
  (c) Compilers: FORTRAN, C, C++, PYTHON
  (d) Visualization software: VMD, RASMOL

- **Data resources used (/scratch, HPSS, NERSC Global File System, etc.) and amount of data stored**
  (a) 4-5 TB in /scratch

4. HPC Requirements for 2017

- **Compute hours needed (*in hopper units*)**

Based on the current scaling data for the software on the conventional machines and given the large-scale of simulation models of polymer brush structures and various agglomeration studies of PNIPAM copolymers that will be treated in the proposed work, we expect that a large amount of time will be required, and therefore would request approximately ***~500,000,000*** core hours of CPU time on the conventional machine.

• **Anticipated Number of Cores to be Used in a Typical Production Run**
32 – 64 K computing cores.

•**Anticipated Wallclock to be Used in a Typical Production Run Using the Number of Cores Given Above**
48 – 120 hrs

• **Anticipated Total Memory Used per Run GB**
10-100 GB memory per core

•**Anticipated total data read & written per run**
1 TB to 2 TB

•**Anticipated On-Line File Storage Required (Directly Accesible from a Running Job)**
1 – 2 TB

•**Known or Anticipated architectural requirements (e.g., 2 GB memory/core).**
32 GB memory/core

5. Strategies for New Architectures

Graphics Processing Units (GPU's)

- We are successfully using NAMD on the GPUs on the Carbon cluster at the Center for Nanoscale Material, Argonne National Laboratory. Preliminary observations suggest that NAMD shows strong scaling and is faster on GPUs than traditional cores.

- To be successful on many-core systems we will need help with parallelization of NAMD with strong scaling on multiple GPU nodes.

6. Summary

- *The improvements in computing power now allow for mesoscopic simulations with atomistic level precision. However, we need more computational resources to conduct simulations of realistic system sizes and time scales which will allow the direct comparison with experiments.*

- *Data storage and handling, Data processing (on-the-fly), Data transfer, data visualization represent primary bottlenecks for these systems.*

- ***General:***

  Improved algorithms to improve computational efficiency as well as data handling efficiency are called for.

Acknowledgement

- Dr. Derrick C. Mancini
- Dr. Subramanian K. R. S. Sankaranarayanan
- Dr. Ganesh Kamath
- NERSC computing facility
- ALCF computing facility
- Center for Nanoscale Materials
- LDRD funding source

Thank you!