Latex Films

Dow Chemical Project

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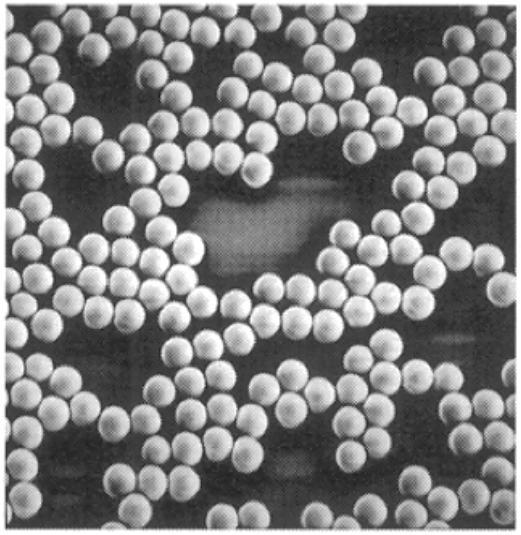
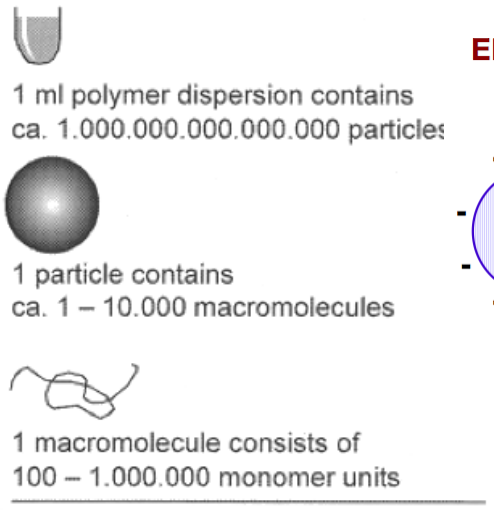
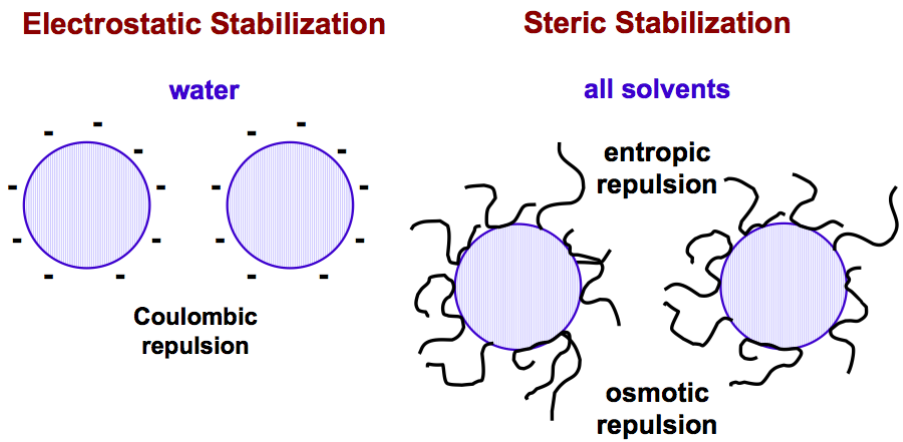
Colloids

- A latex is a colloidal dispersion (suspension) of polymer particles in water
- Latex particles consist of polymer molecules of any molar mass (typically 5000 to 1 x 10^6)
- Colloidal stability is coulombic or steric in origin





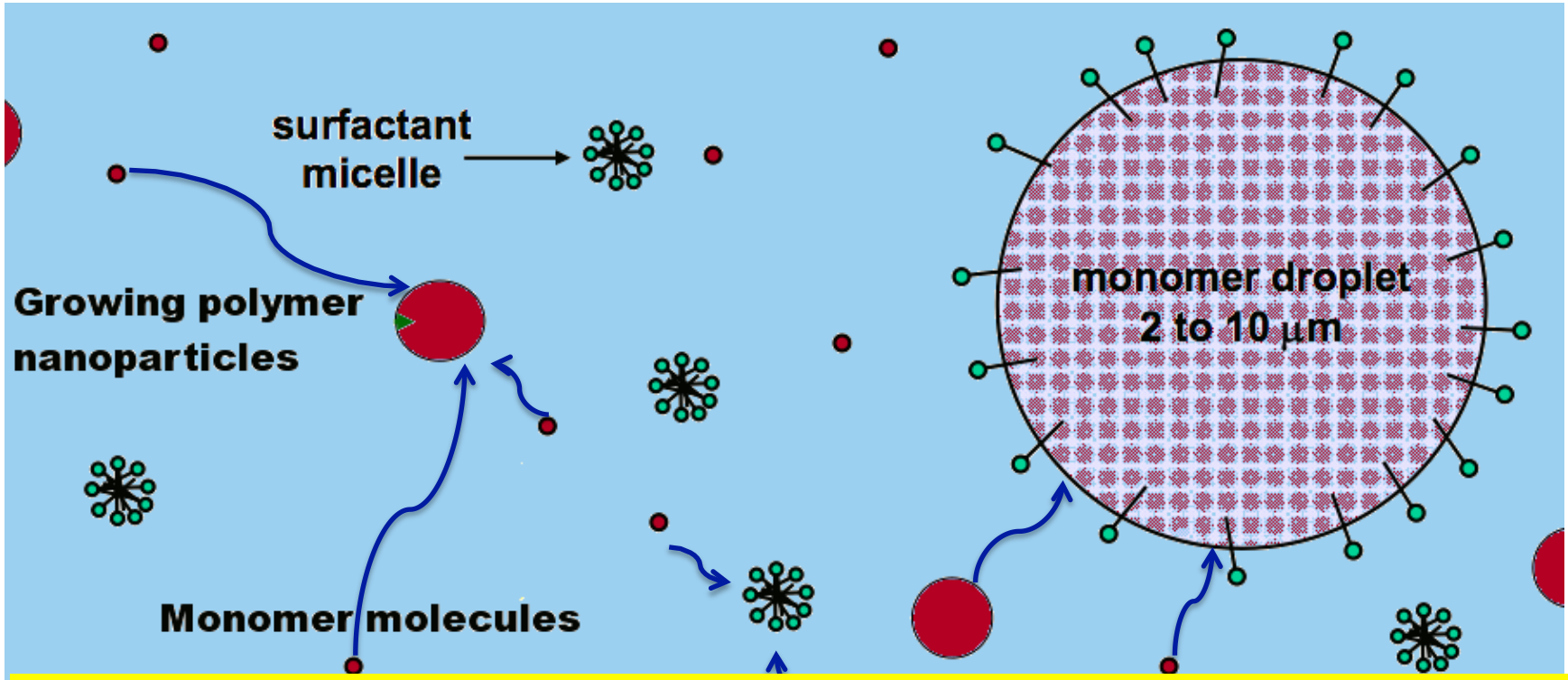


Grafted polymer acts as steric stabilizer

DOW stage 2 predominant (Dr. Willie Lau will send description)

Latex formation process

1. Particle nucleation (homogeneous or micellar)
2. Growth fed my monomer molecules in solution



Initiation occurs in water phase
Polymerization occurs in water phase and in the particles
Oligomers "eaten" by larger particles (in water they exceed solubility)

General Latex composition

- LMA (Lauryl methacrylate) or SMA (Stearyl methacrylate):
- BA (butyl acrylate): controls Tg and other film properties
- MMA* (methacrylic acid): improve colloidal stability, control the reaction kinetics and viscosity
- MMA (Methyl methacrylate): main functional polymer, provide mechanical stability
- (Divinyl benzene) crosslinker: polymer crosslinker, crosslinker may be used after film is formed !

- Surfactant C12H25(OC2H4)4SO4-Na+ (Dodecil benzene sulphonic acid - Disponil FES 32IS). Emulsifier that also controls kinetics and acts as an electrosteric stabilization agent

What influences latex's colloidal properties

- Particle size and particle size distribution,
- Particle surface charge density,
- Particle surface area covered by stabilizers,
- Conformation of the hydrophilic polymer adsorbed or coupled onto the particle surface,
- Type and concentration of functional groups on the particle surface,
- Optical and rheological properties
- Colloidal stability

What has DOW characterized from their latex ?

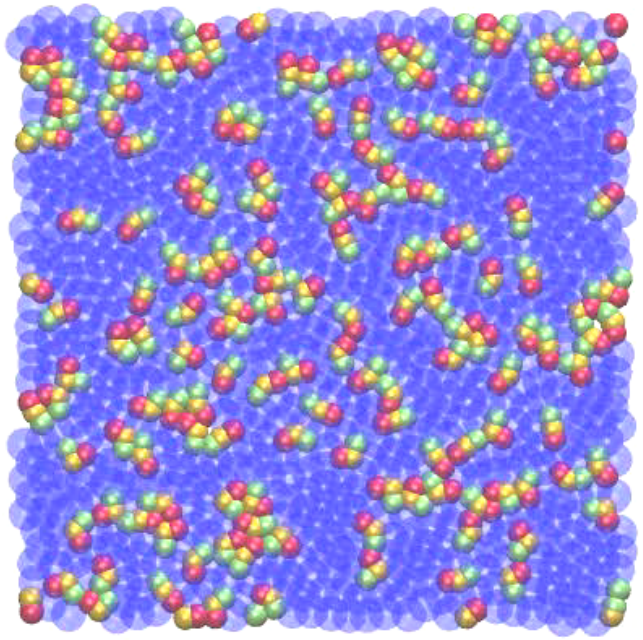
What influences latex' colloidal properties: particle nucleation

- Emulsion polymerization->segregation of free radicals among monomer-swollen polymer particles->reduced probability of bimolecular termination of free radicals
- This leads to faster polymerization rate and emulsion polymer with a higher molecular weight
- Transport of monomer, free radicals, and surfactant to the growing latex particles and partition of these reagents among the continuous aqueous phase, the monomer emulsion droplets (the monomer reservoir), and the monomer-swollen polymer particles (the primary reaction loci) play a crucial role in the particle growth stage.

Micelle formation and Colloid dynamics

(Coarse-grain models)

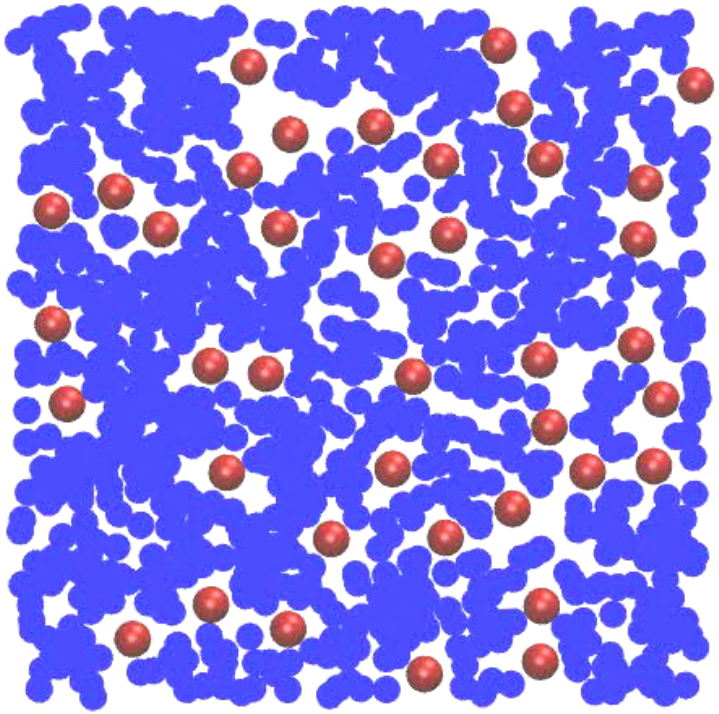
Micelle (FENE)



Increased length- and time-scales

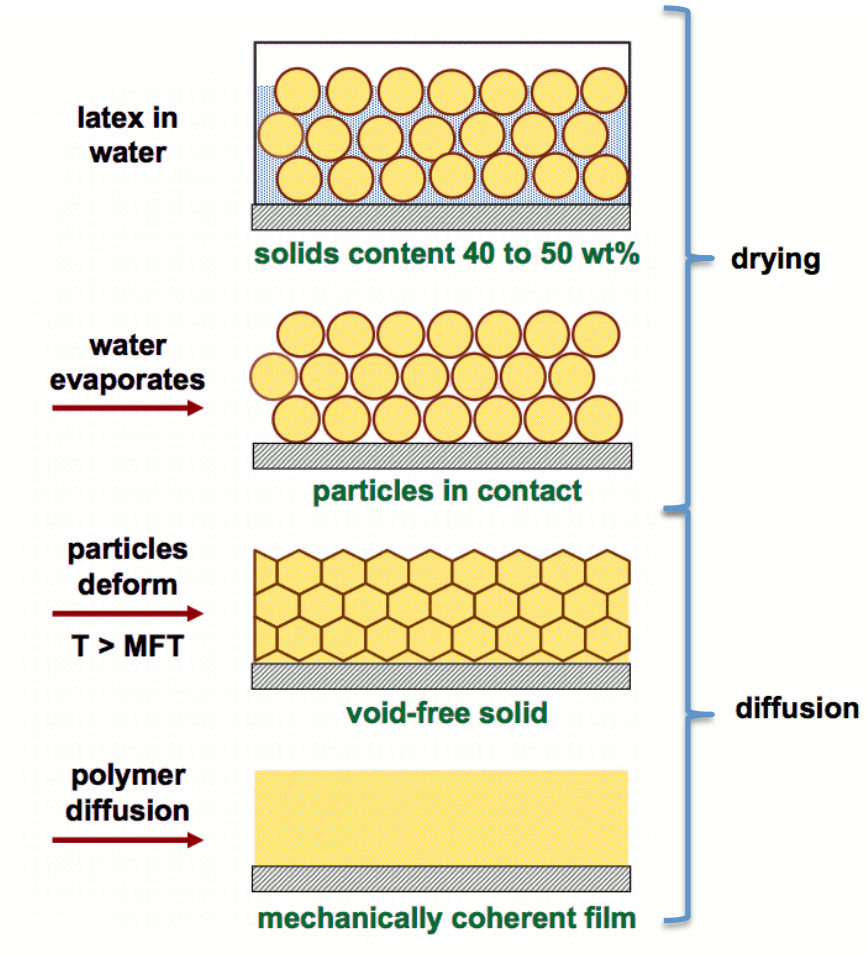
→

Colloid (LJ)

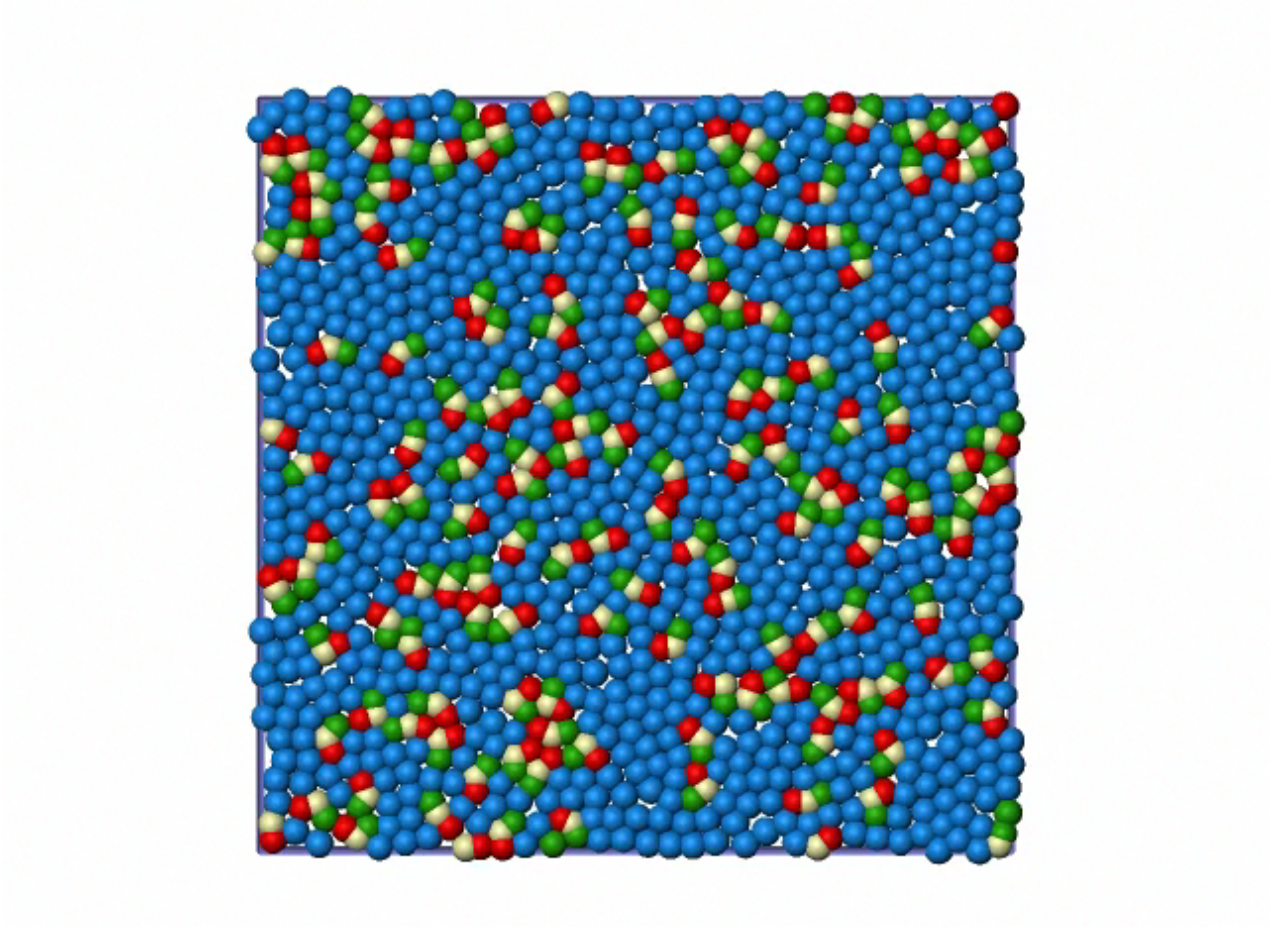


Micelle formation, polymer nanoparticle formation, polymer-to-micelle migration, hydrophilic stabilizers, interfaces and mechanical properties during/after water evaporation

Film formation process

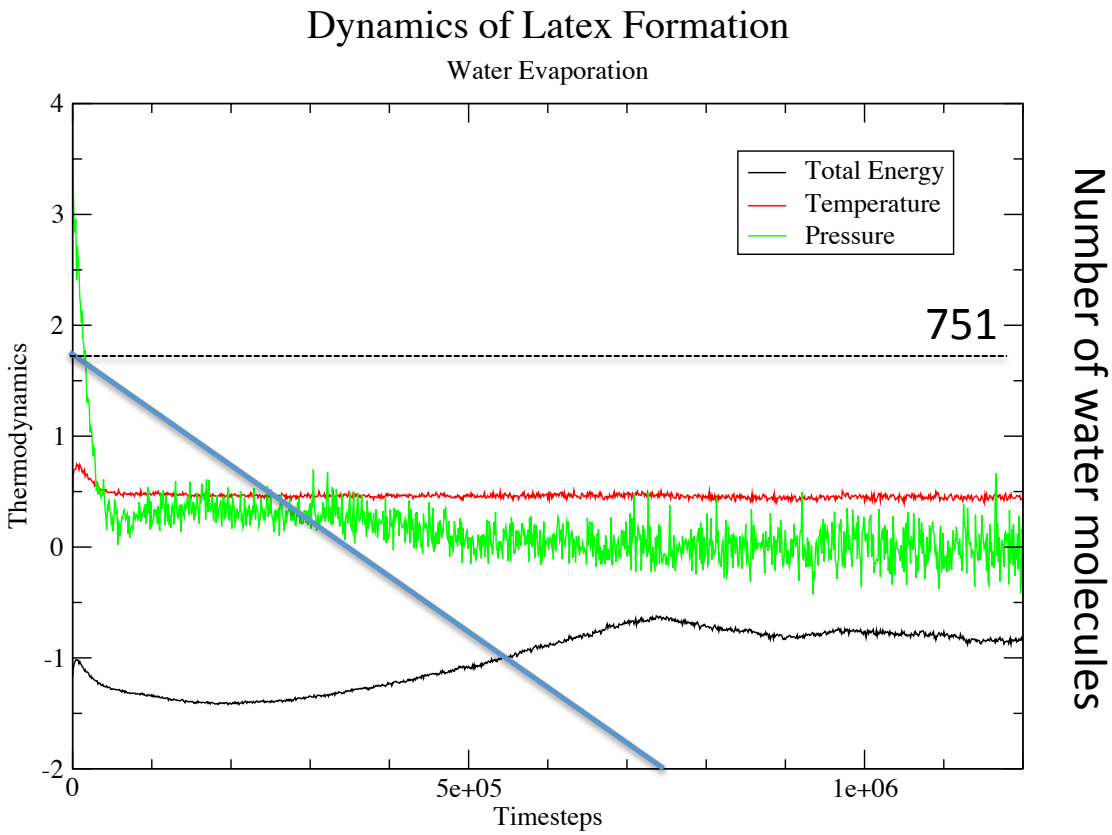


Water evaporation
$1H_2O/1000$ t.u. @P=1,T=0.45

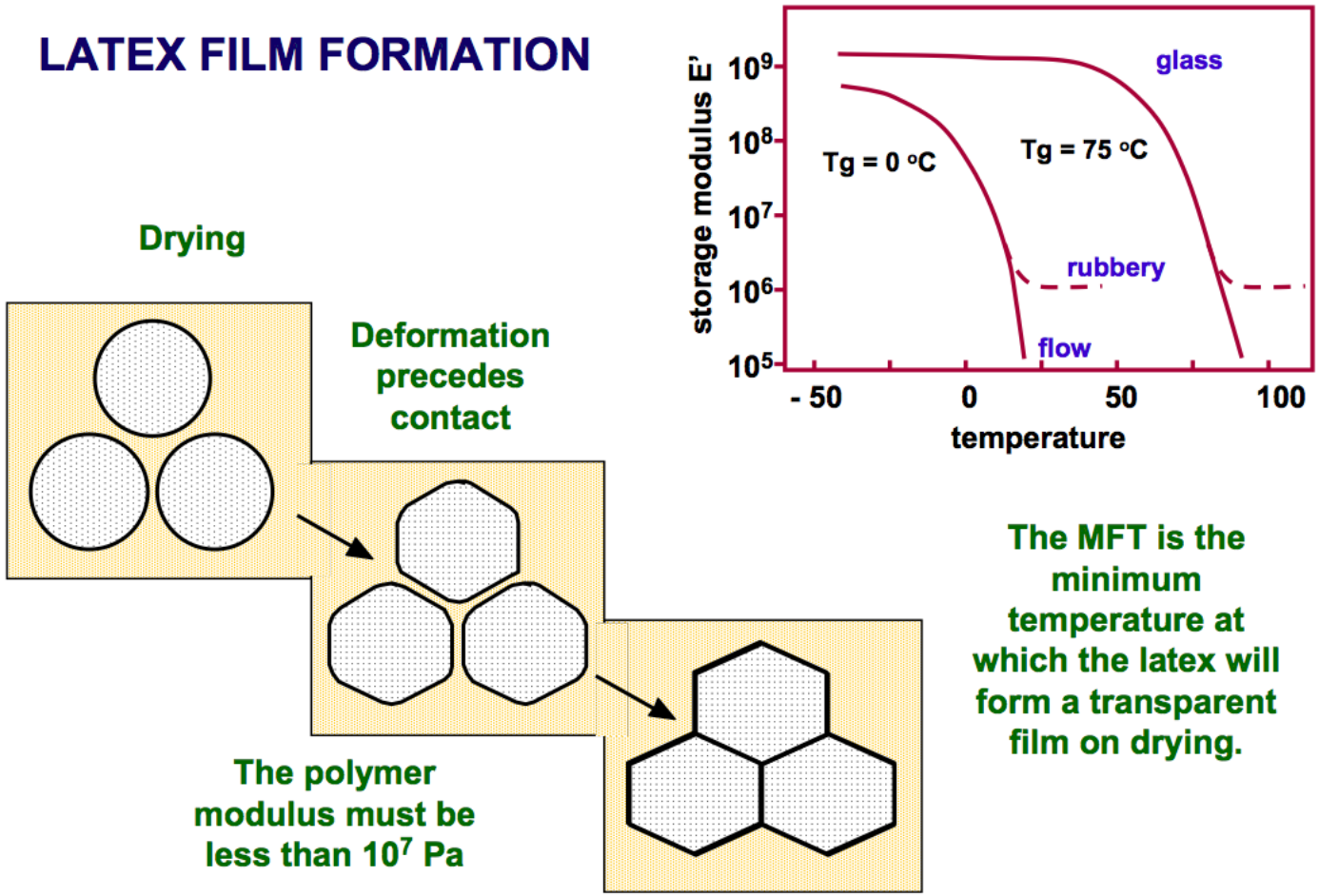


Induced evaporation (i.e. no surface yet), mixture dries and polymer diffuses

Thermodynamics during evaporation



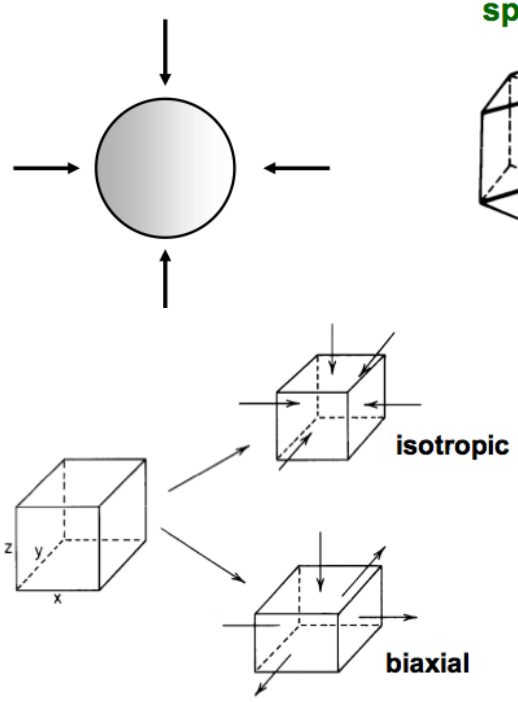
Minimum Film Formation Temperature (MFT)



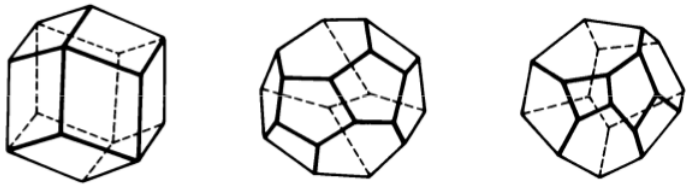
Dynamic Modulus = storage modulus + *i* loss modulus

Nanoparticle packing

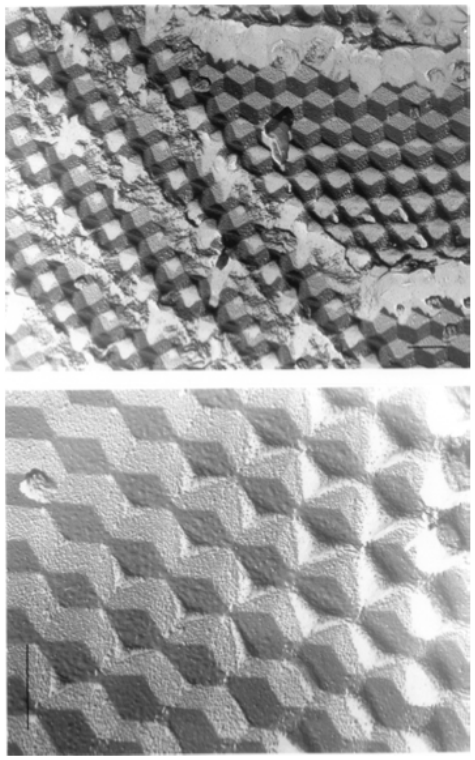
- Isotropic deformation of fcc packed latex particles leads to rhombic dodecahedra



Forces associated with drying deform latex spheres into space-filling polyhedral cells.



Capillary forces, surface tension .

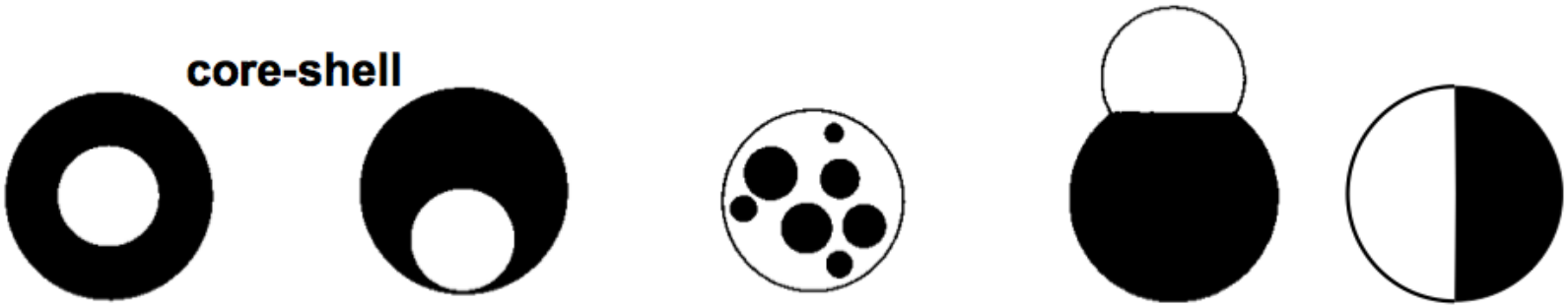


Freeze-fracture TEM images of a poly(butyl methacrylate) latex film

PBMA d = 337 nm
20 h at 36 °C

Structured Latex Nanoparticles

- Monomers inserted in stages or all at once? i.e. second stage co-polymerization may be used to obtain structured latex particles
  - crosslinked core, hard core-soft shell, soft core-hard shell



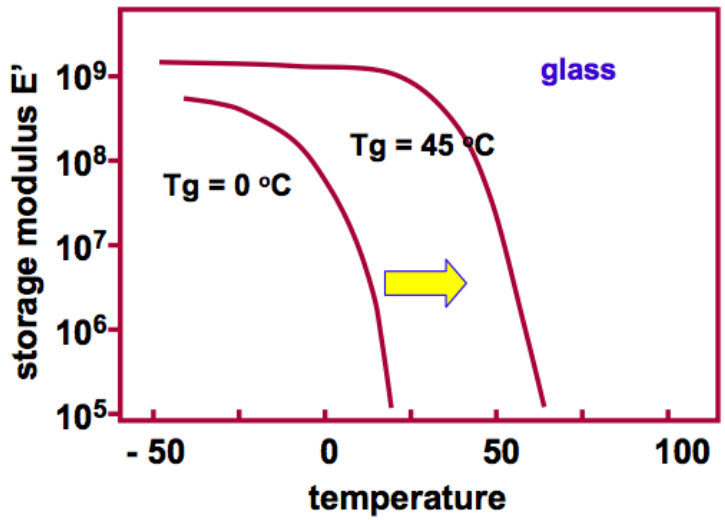
DOW DOES NOT STAGE FORMATION

Tuning

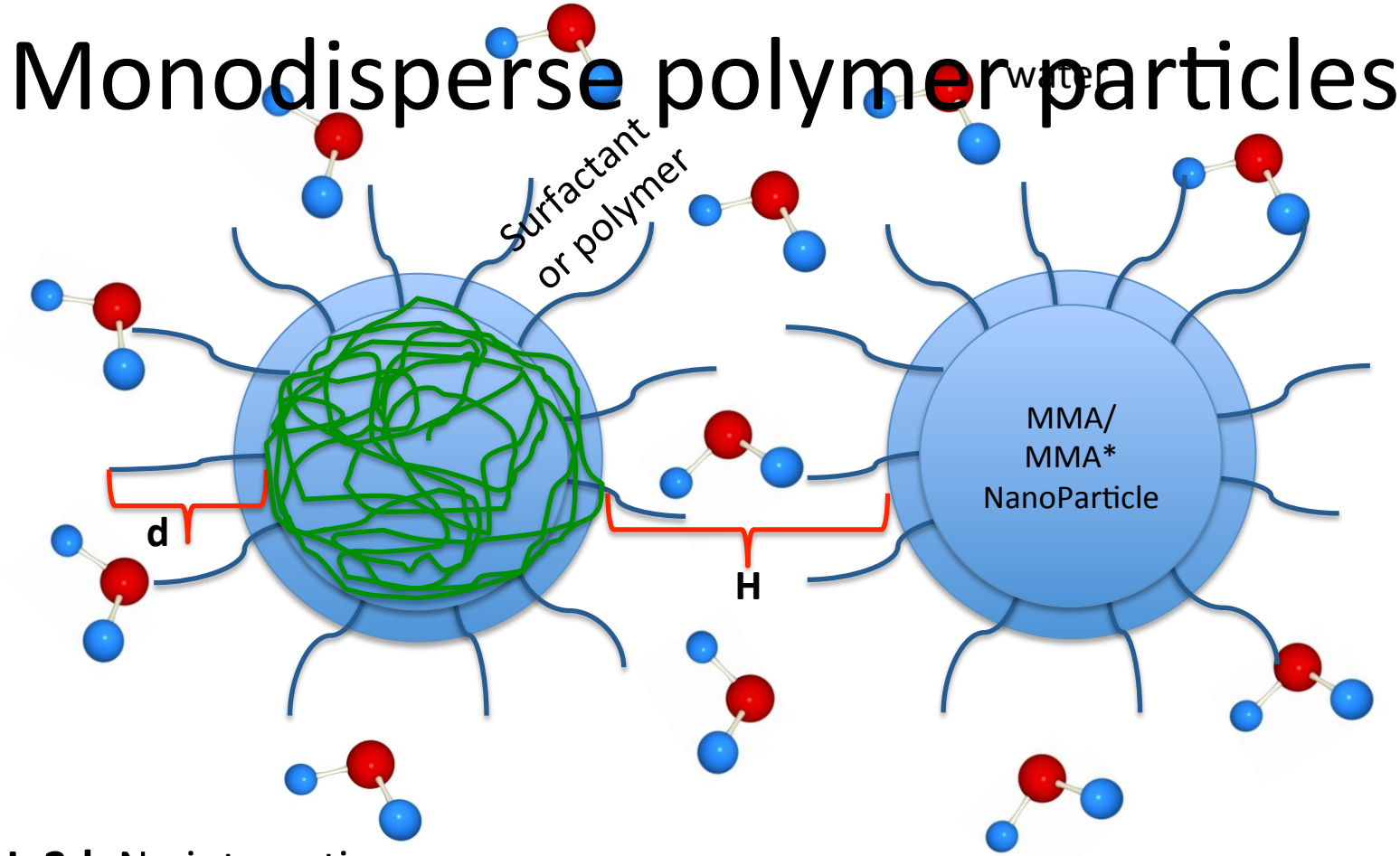
- Plasticizers lower Tg and decrease the modulus (i.e. enhanced coallesence)
  - If an organic solvent is added to the latex and dissolves in the particles, it will act as a plasticizer
  - Volatile solvents added to the dispersion, lower the modulus of the polymer in the particles

$$\frac{1}{T_g} = \frac{w_{pol}}{T_{g,pol}} + \frac{w_{solv}}{T_{g,solv}}$$

Fox equation



Monodisperse polymer particles



H>2d: No interaction

d<H<2d: High density of macromolecular segments leads to drop in osmotic pressure and flux of water into zone which causes repulsion

H<=d: Elastic compression of the surfactant caused by physical repulsion of the surfaces and hydrophilic heads.

Entanglement

- For certain polymers above a critical molar mass (M_e), the melt viscosity increases as $M^{3.4}$. This behavior is attributed to the effect of entanglements
  - Solutions of polymers with $M >> M_e$ have very high viscosity
  - There is an increase in strength associated with entanglements
- The confining effect of the surrounding chains act like a confining tube
- **Latex dispersions maintain low viscosity for high solids even for high M polymers**

Entanglement: Graessley, 1974; Tonelli, AE Polymers from the Inside Out, Wiley, 2001 p 139
Strength: R. Wool, *Polymer Interfaces*, 1997

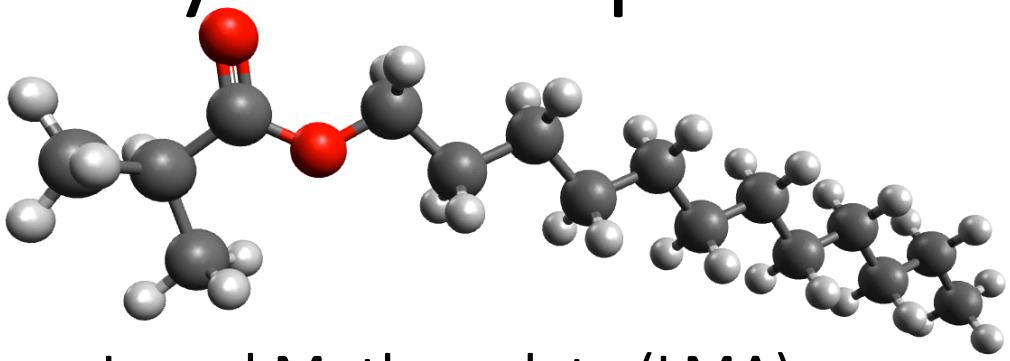
Molecular Model Polymer Compositions

Composition (co-polymerized)

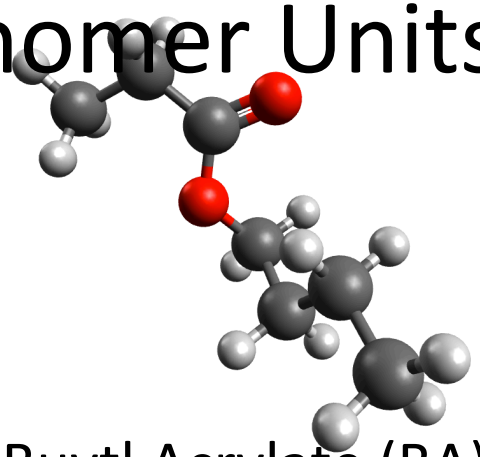
- Hydrophobic:
  - 20% BA, 40%LMA, 39% MMA, 1%MMA* (Mass Fraction)
  - 23.4% BA, 21.3%LMA, 53.0%MMA, 2.2%MMA* (Mole Fraction)
- Hydrophilic:
  - 60% BA, 39% MMA, 1%MMA* (Mass Fraction)
  - 56% BA, 42.2%MMA, 1.8%MMA* (Mole Fraction)
- 0.2 nDDM
- Tg ~10°C
- Neutralization: NH_4OH, NaOH (OH, Na+, Cl-)

- Constructed 4/5 100-mer strands for system sizes ~10,000 atoms (vacuum)

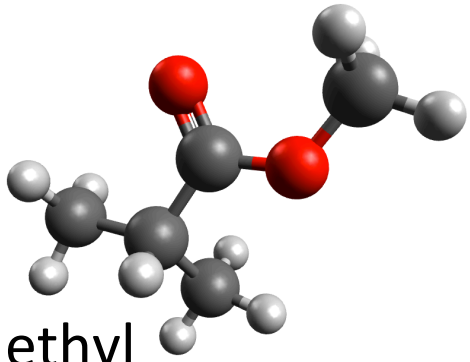
System Preparation: Monomer Units



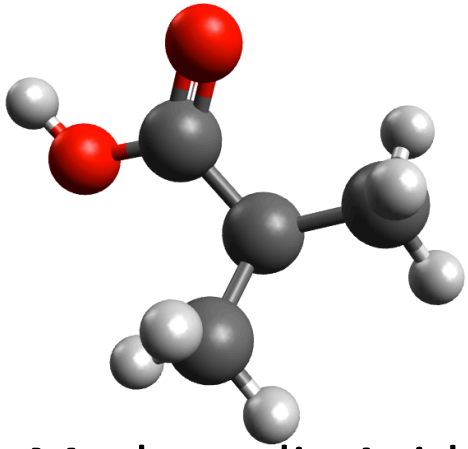
Lauryl Methacrylate (LMA)



Buytl Acrylate (BA)



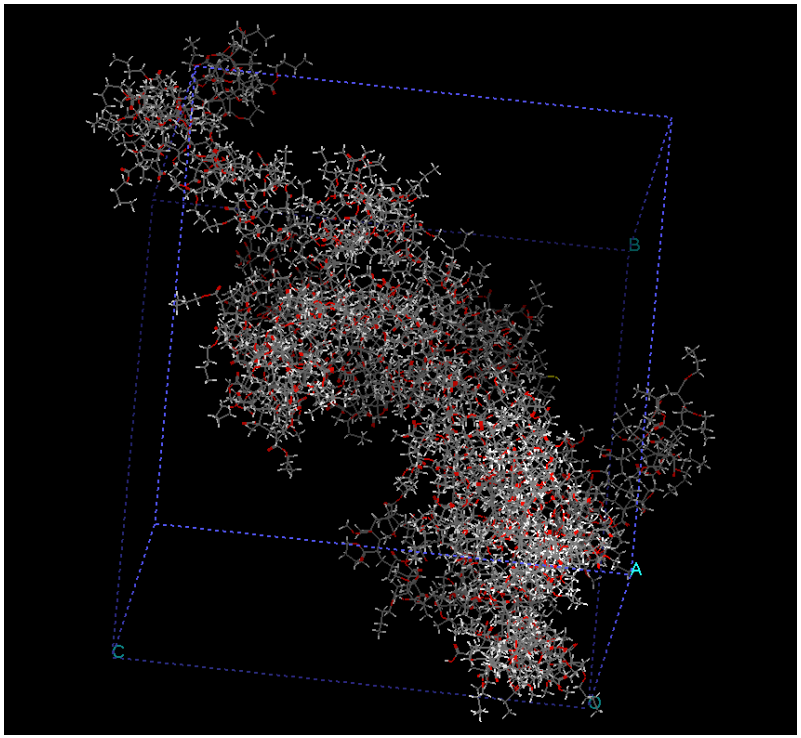
Methyl Methylacrylate (MMA)



Methacrylic Acid (MMA*)

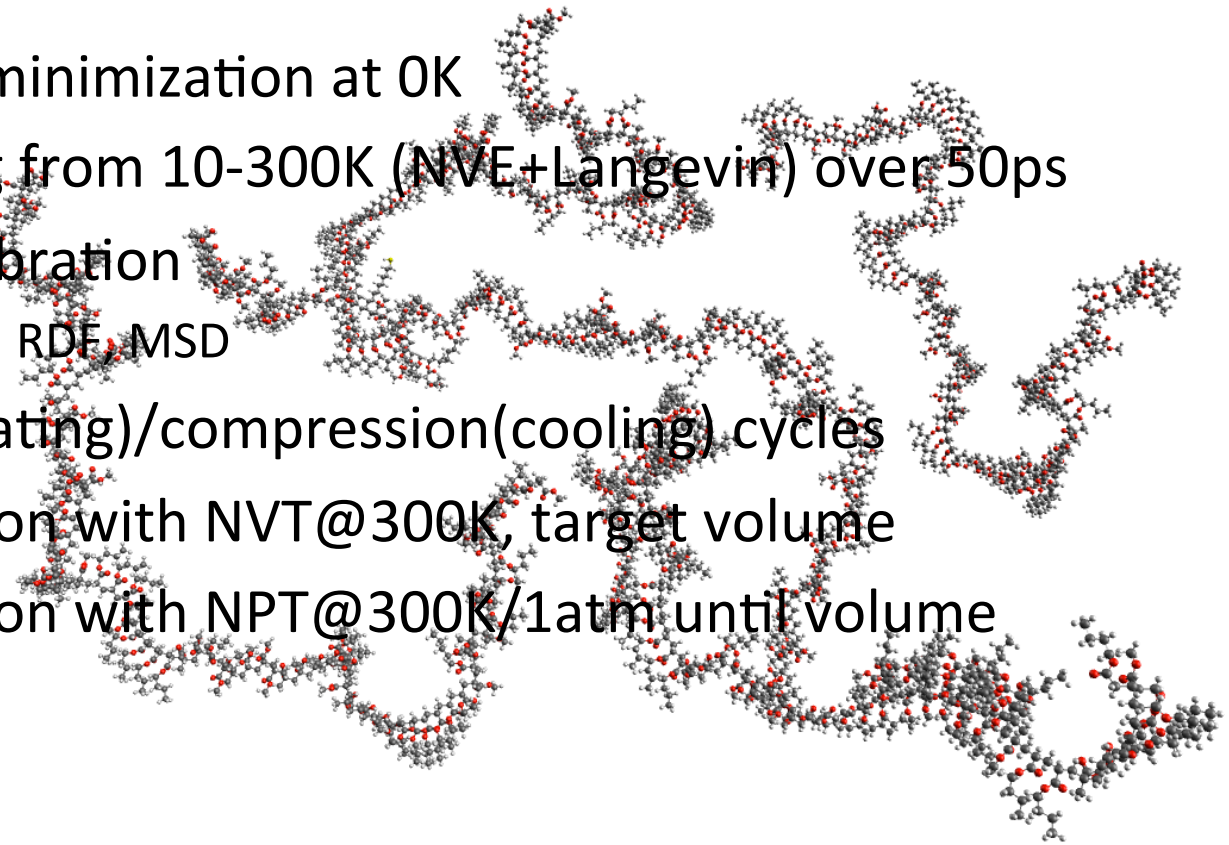
System Preparation: Amorphous Structure

- The strands are then arranged in a random conformation within a cell defined by periodic boundary conditions.



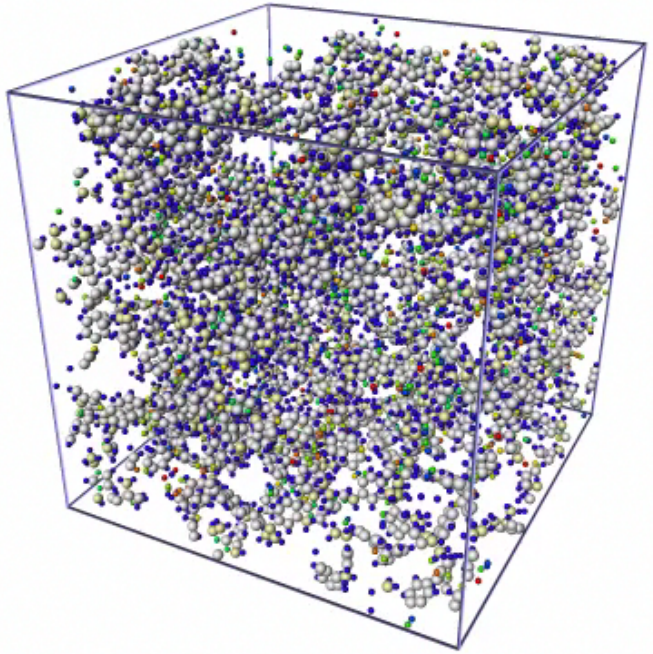
Polymer Structure Preparation

- 1000 Steps CG minimization at 0K
- Gradual heating from 10-300K (NVE+Langevin) over 50ps
- 50ps NVE equilibration
  - Compute initial RDF, MSD
- 5 expansion(heating)/compression(cooling) cycles
- 50ps equilibration with NVT@300K, target volume
- 50ps equilibration with NPT@300K/1atm until volume converges



Heating/Expansion Cycles

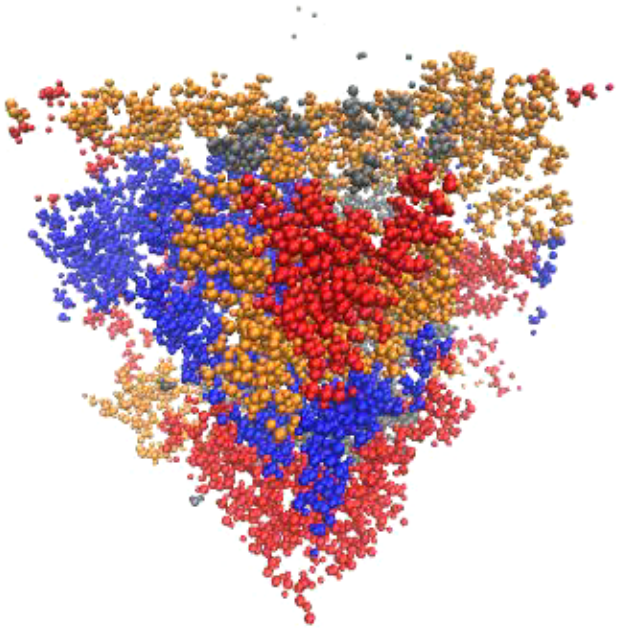
- Start at half target density
- Heat from 300-1200K over 50ps, simultaneously doubling the volume (half the start density)
- Equilibrate @high temperature for 50ps
- Cool back to 300K over 50ps, simultaneously compressing to 1/4th the volume (twice the start density)
- Repeat



Applies to vacuum and solvated systems

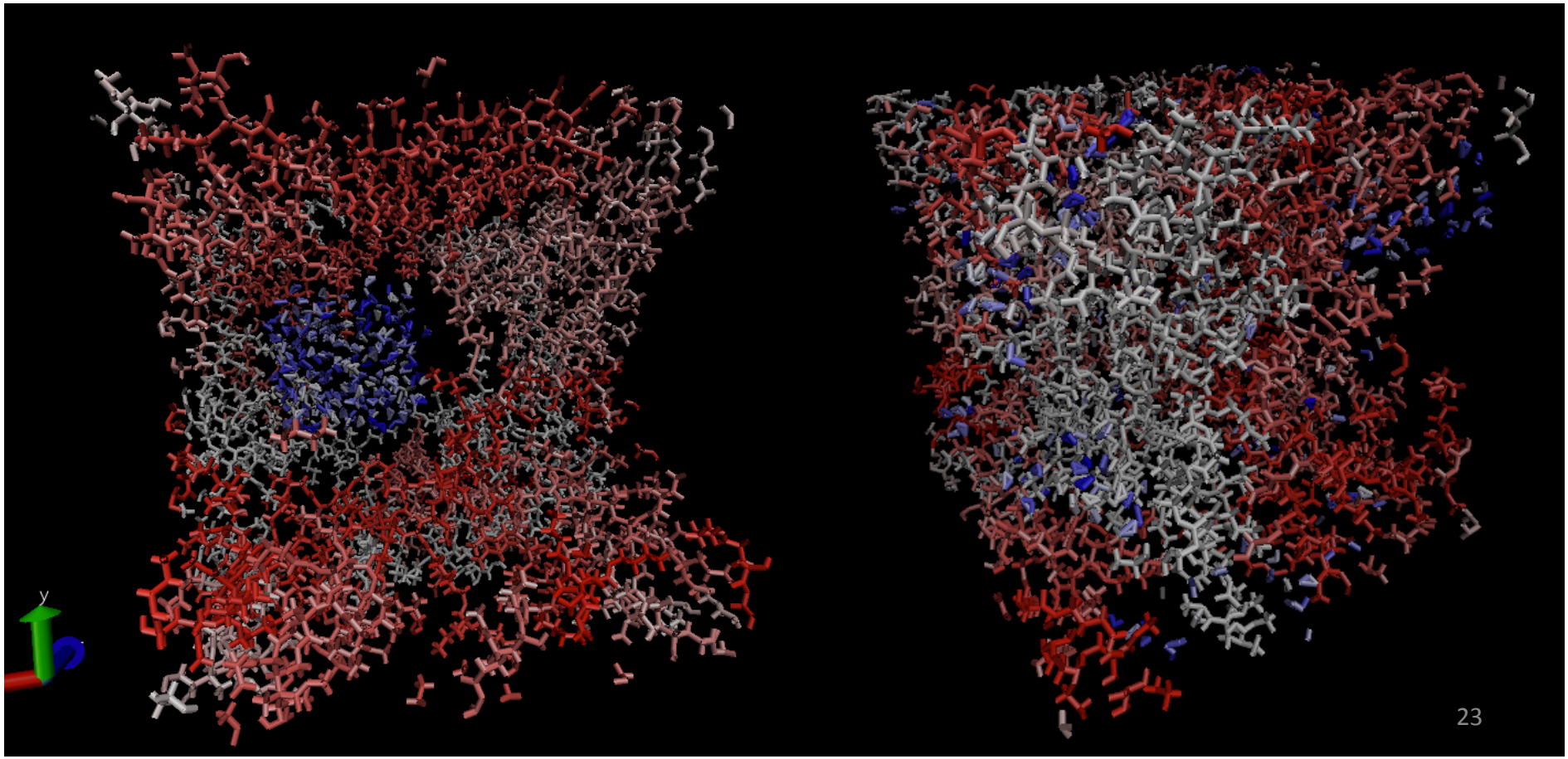
Conjugate Energy Density (CED) approach

Equilibration of Hydrophobic System:

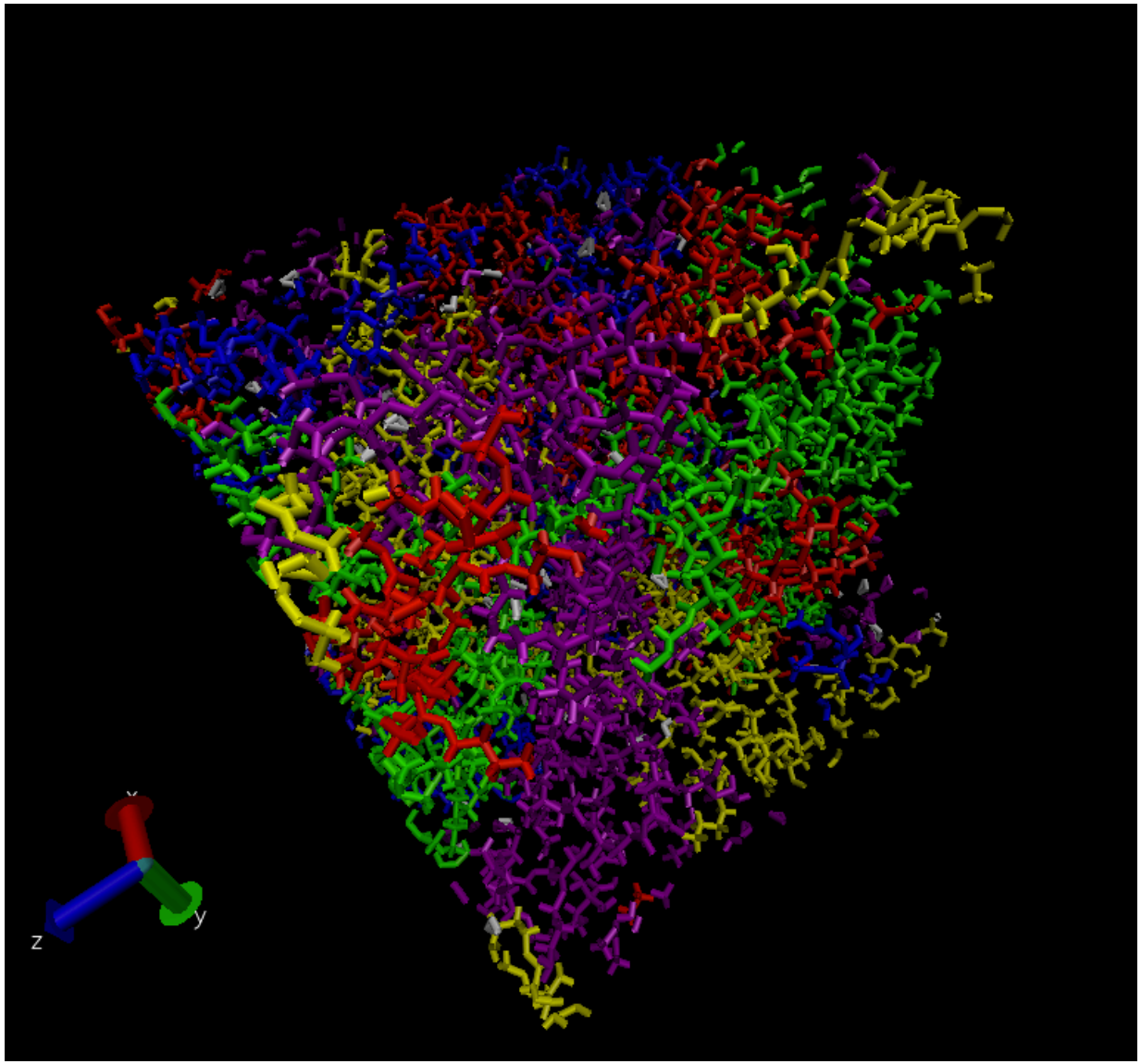


Solvation

- Hydrophilic: 246 water molecules (9 wt%)
- Hydrophobic: 362 water molecules (10 wt%)



System Entanglement



Analysis: Glass Transition Temperature

T_g calculated from MD.[1]

Step 1) A characteristic length is defined for the system:

$$L_c = \frac{\langle R_{O-O} \rangle}{2}$$

Where R is the first peak of the radial distribution function (RDF). In this system, the distribution of carboxyl oxygens is tracked.

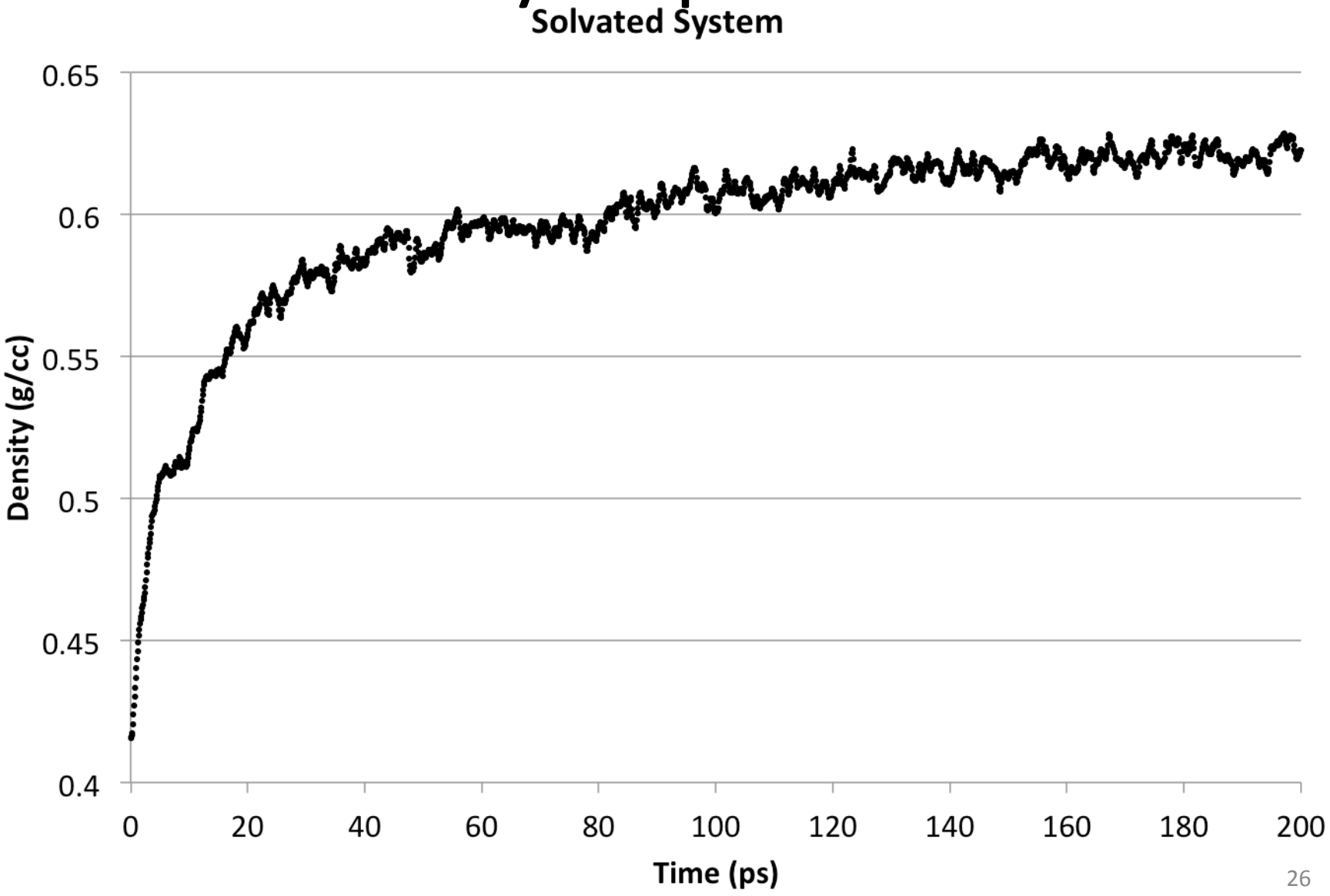
Step 2) dynamics are performed for 100ps at a range of temperatures

Step 3) The root mean square displacement (RMSD) is measured for the atoms of interest (oxygens)

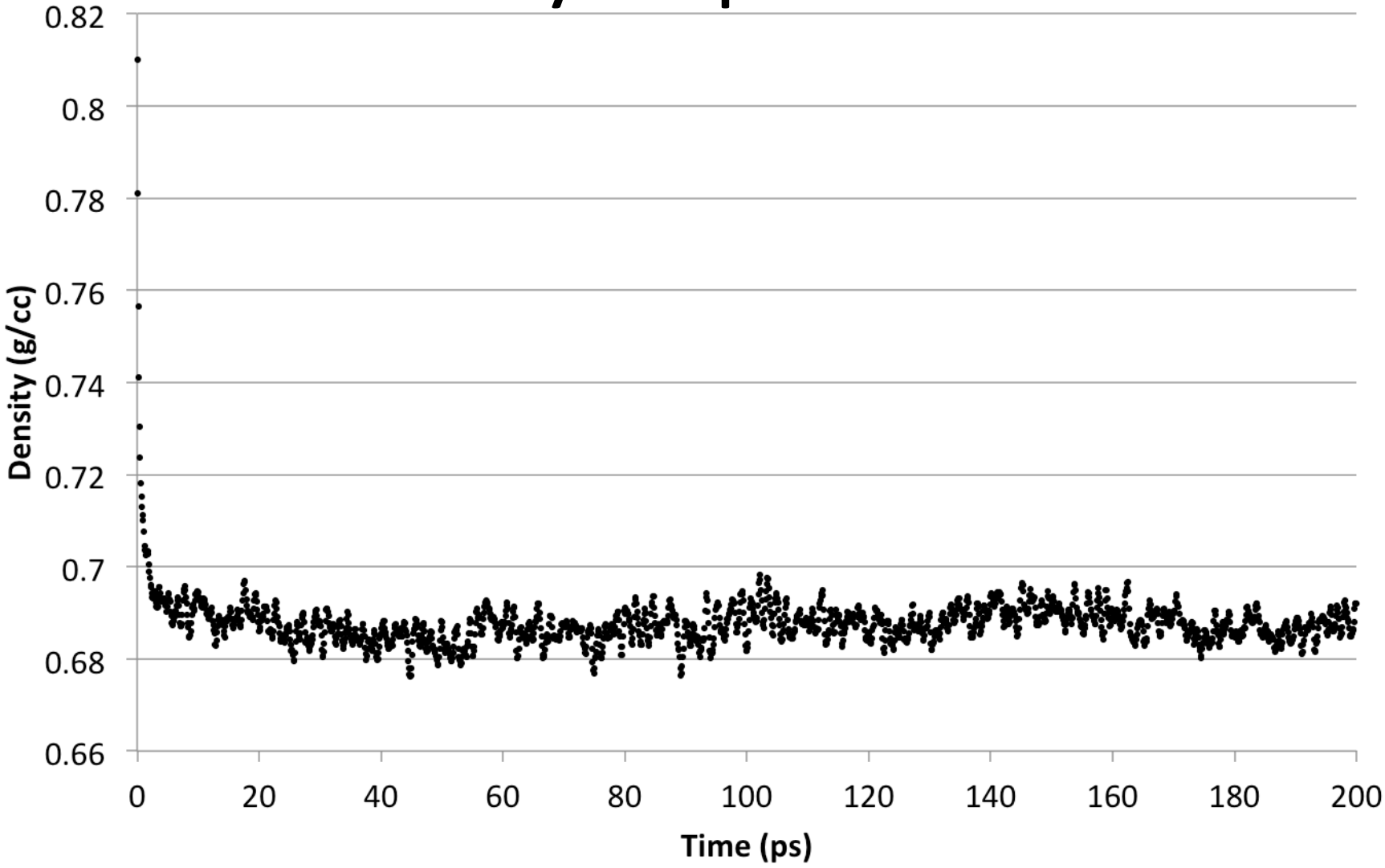
Step 4) The temperature at which the RMSD equals the L_c is the glass transition temperature.

[1]Tamai, Yoshinori, "A practical method to determine glass transition temperature in molecular dynamics simulation of mixed ionic glasses", *Chemical Physics Letters*, vol. 351 (2002) pp. 99-104

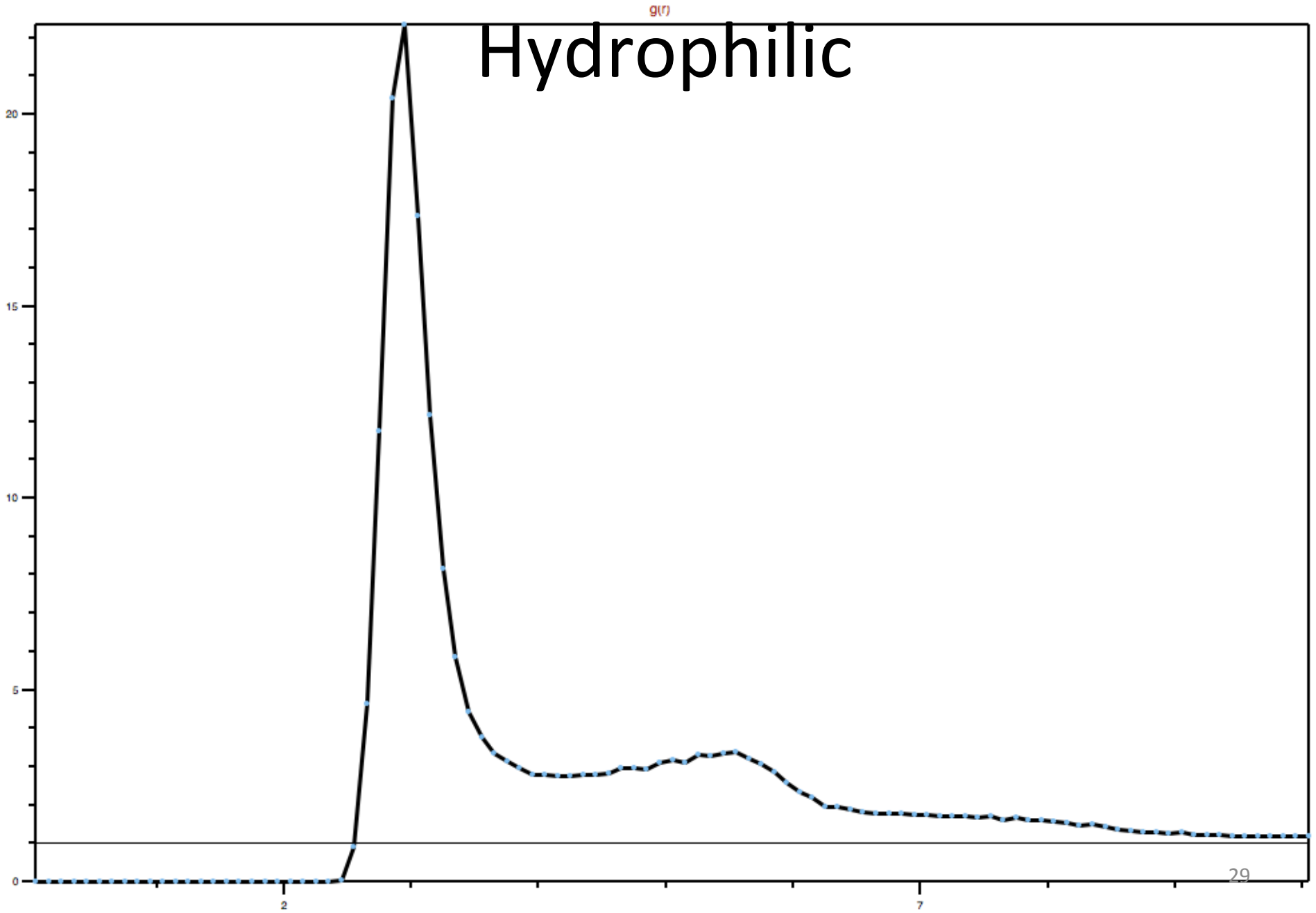
Hydrophilic



Hydrophilic

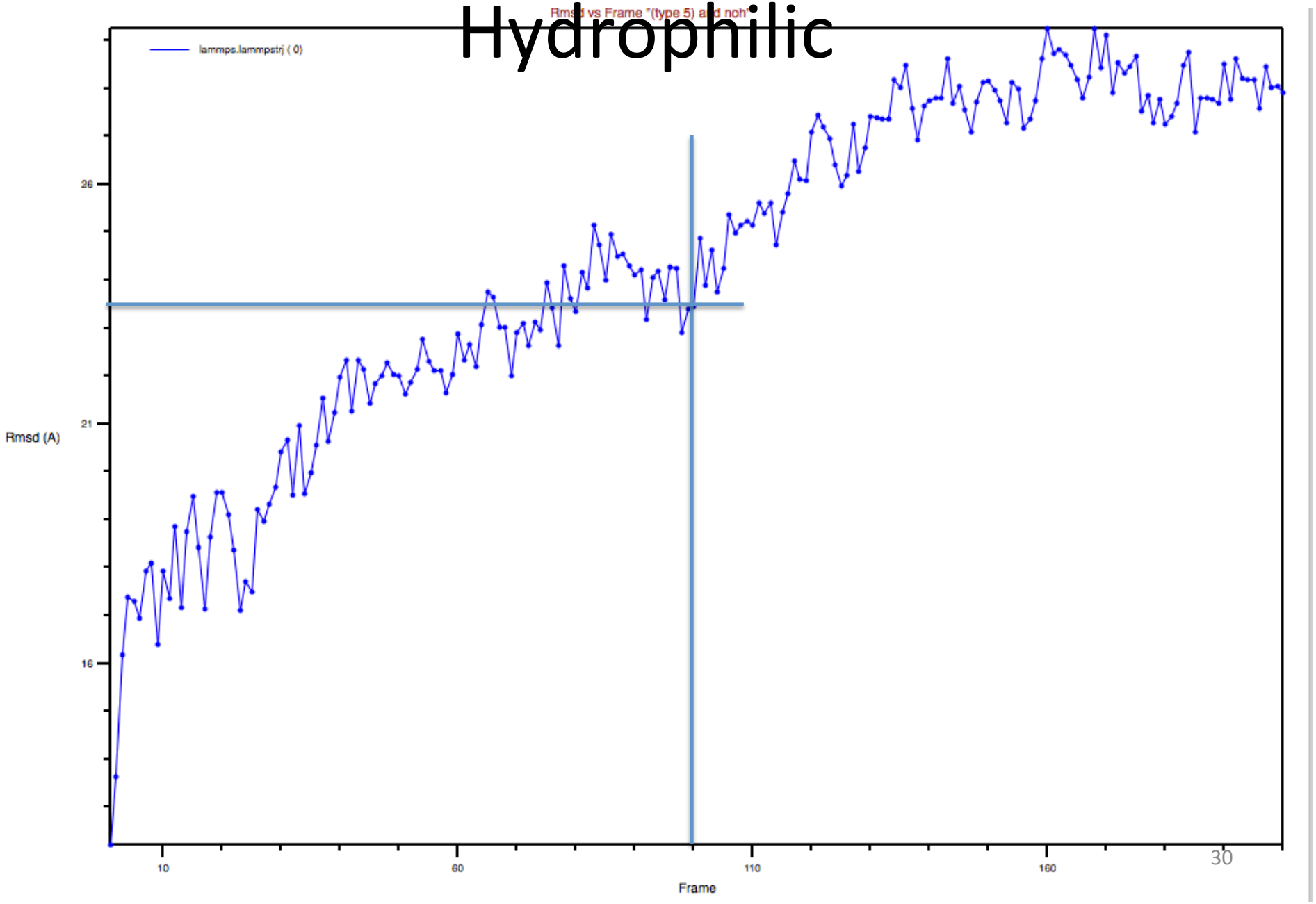


Analysis: RDF of carbonyl oxygens: 1st peak at 3 angstroms (L_c=1.5)



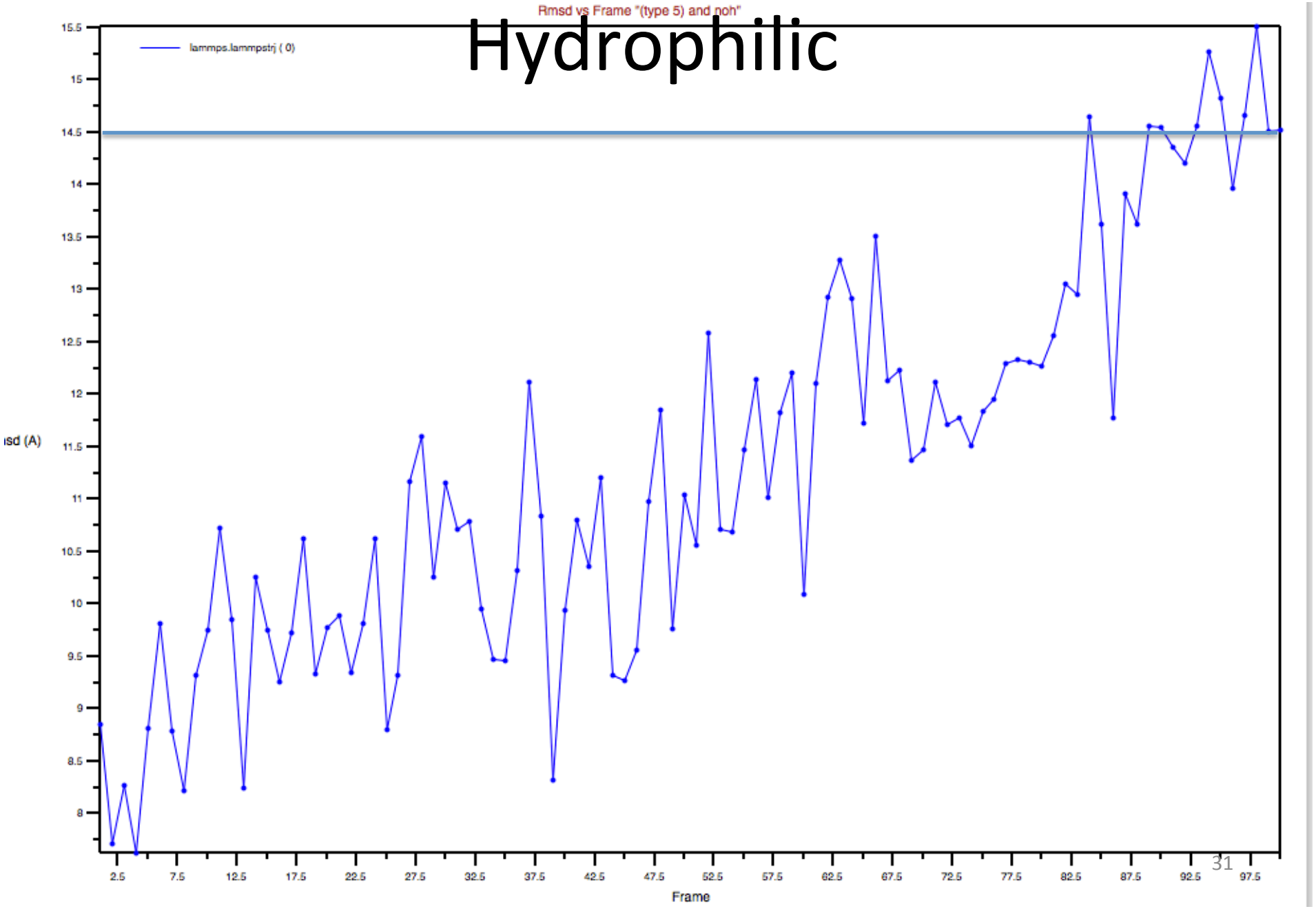
At 300 K, RMSD = 11.5 angstrom

Hydrophilic

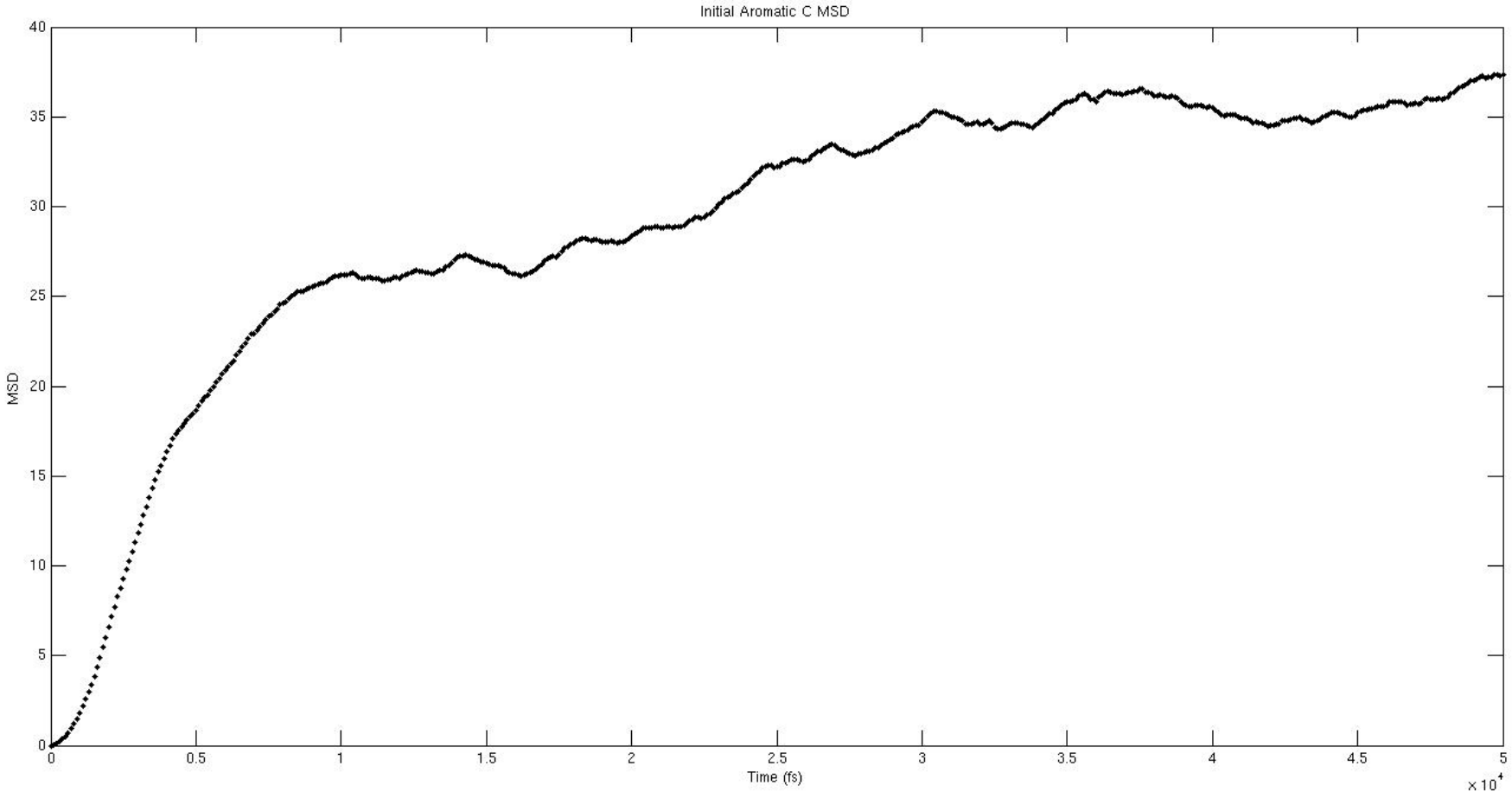


At 170 K, RMSD = 5.75 angstrom

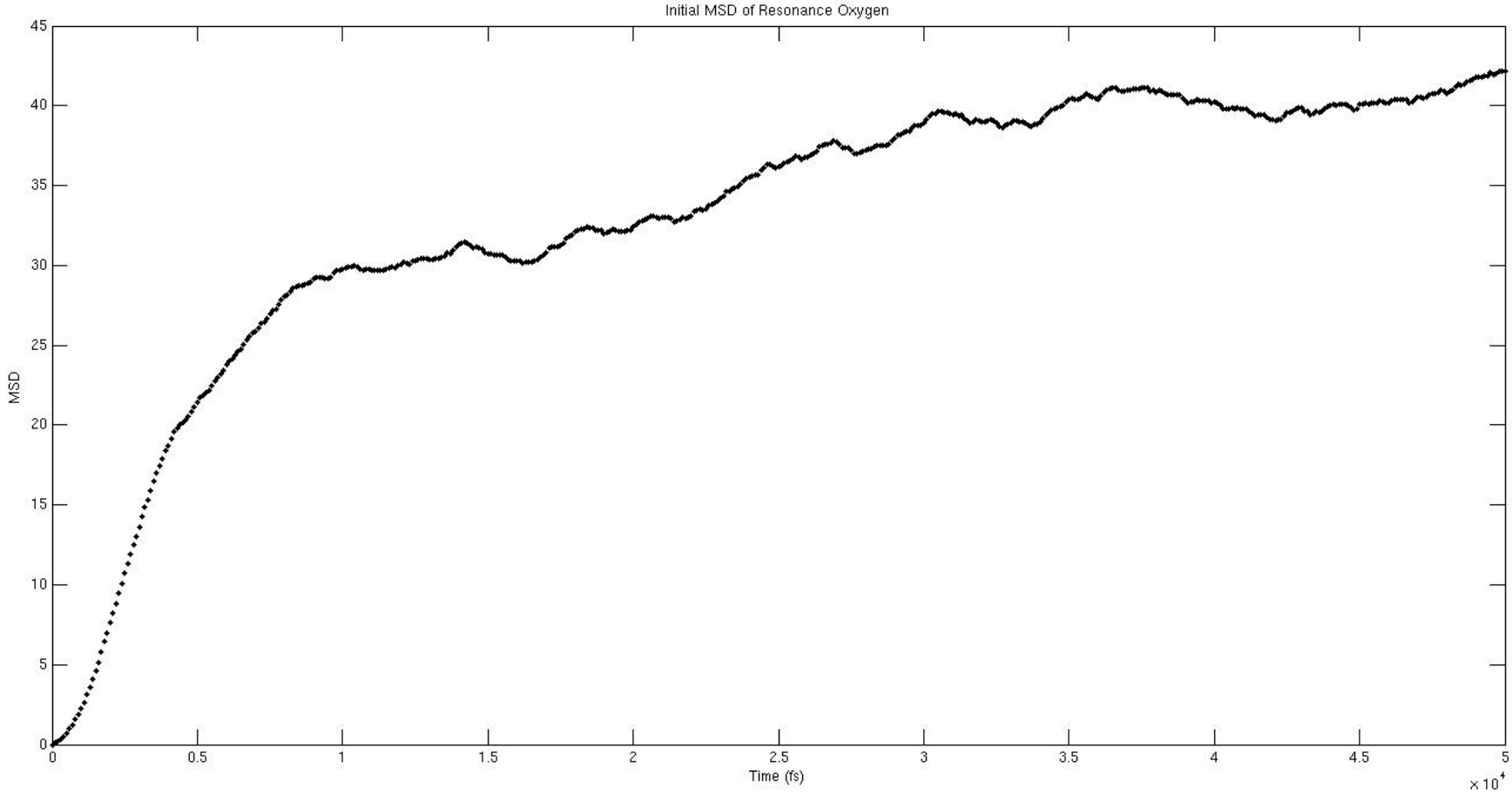
Hydrophilic



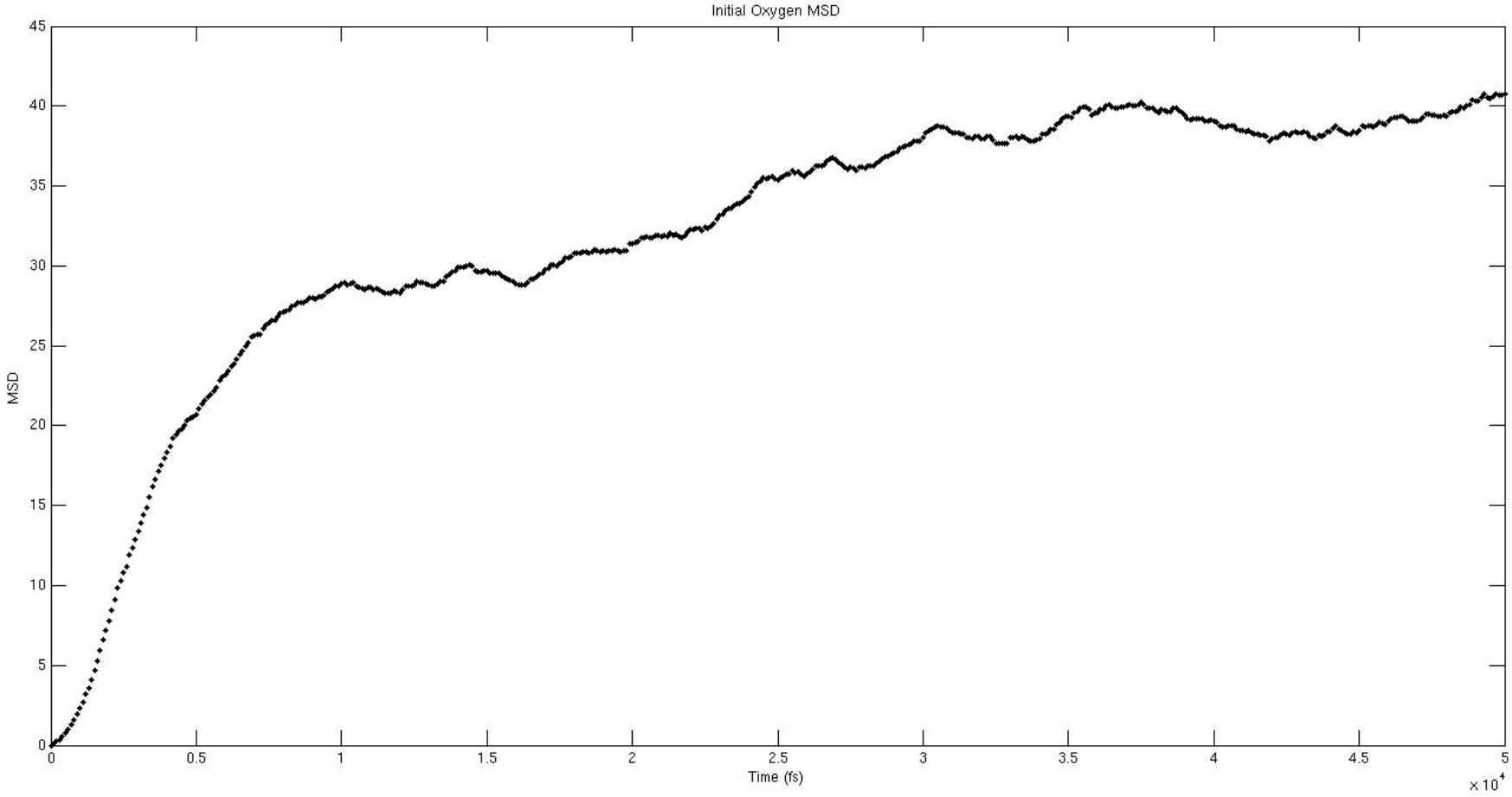
Hydrophobic (initial equilibration)



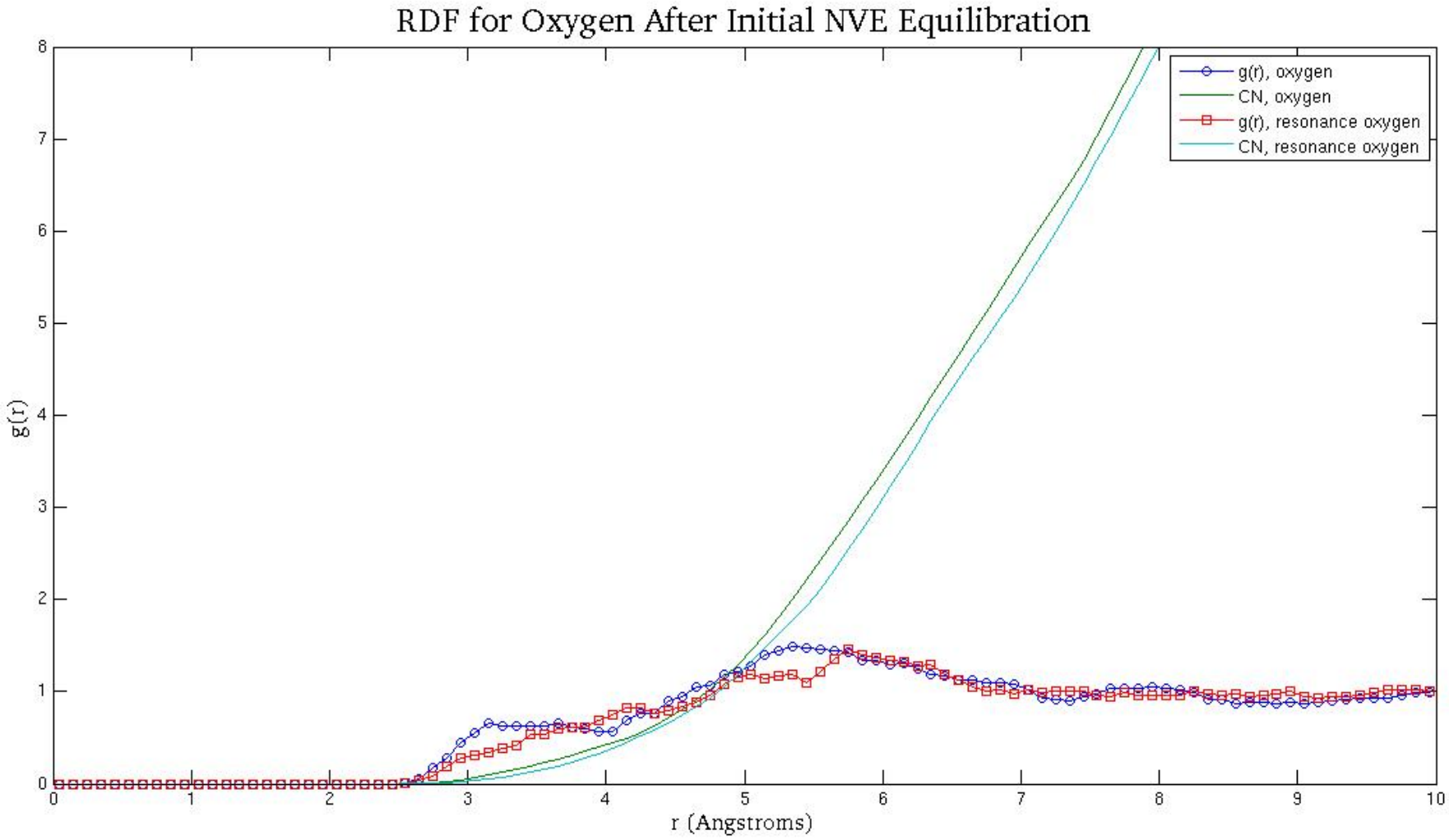
Hydrophobic (initial resonance O MSD)



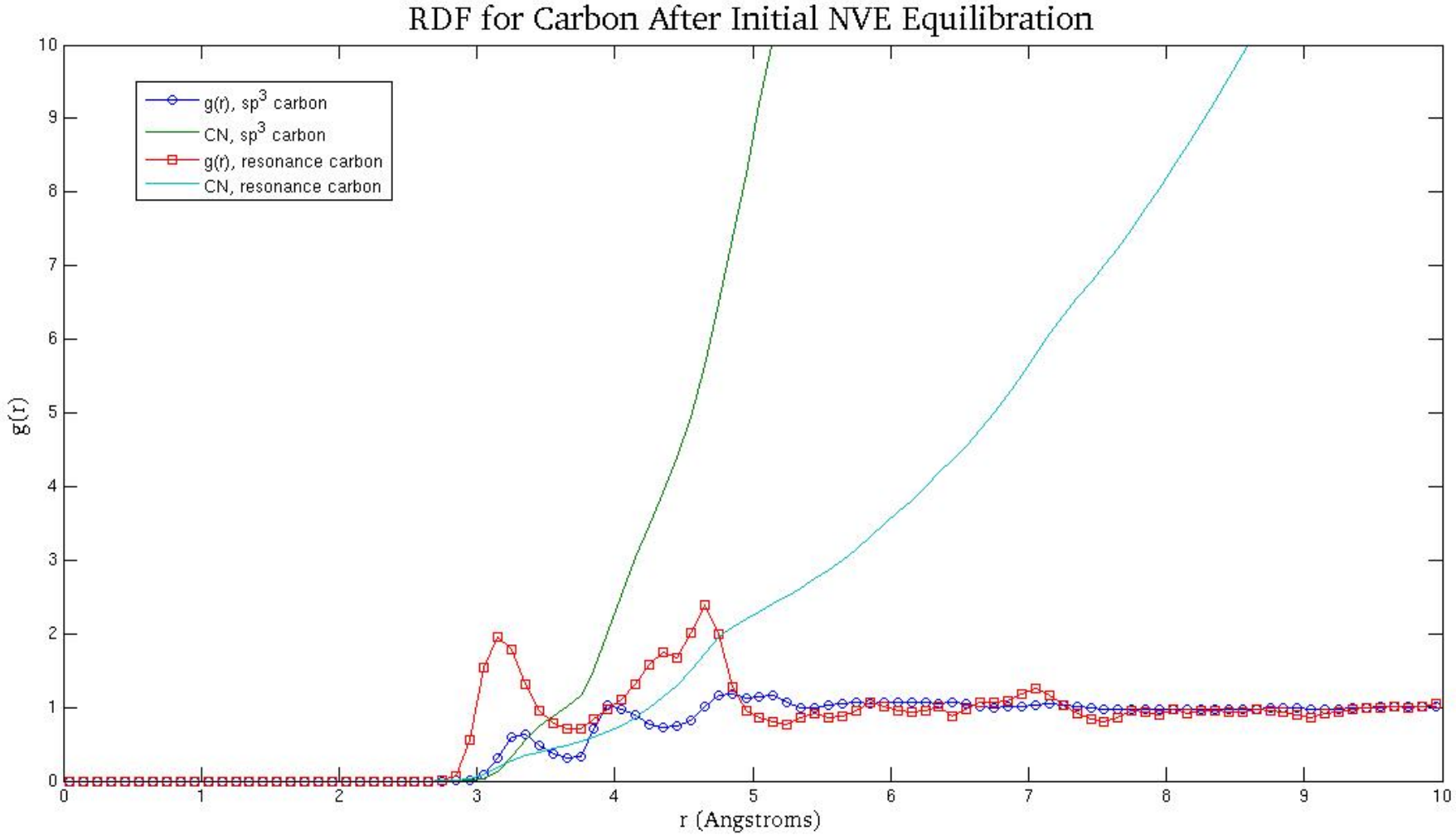
Hydrophobic (initial O MSD)



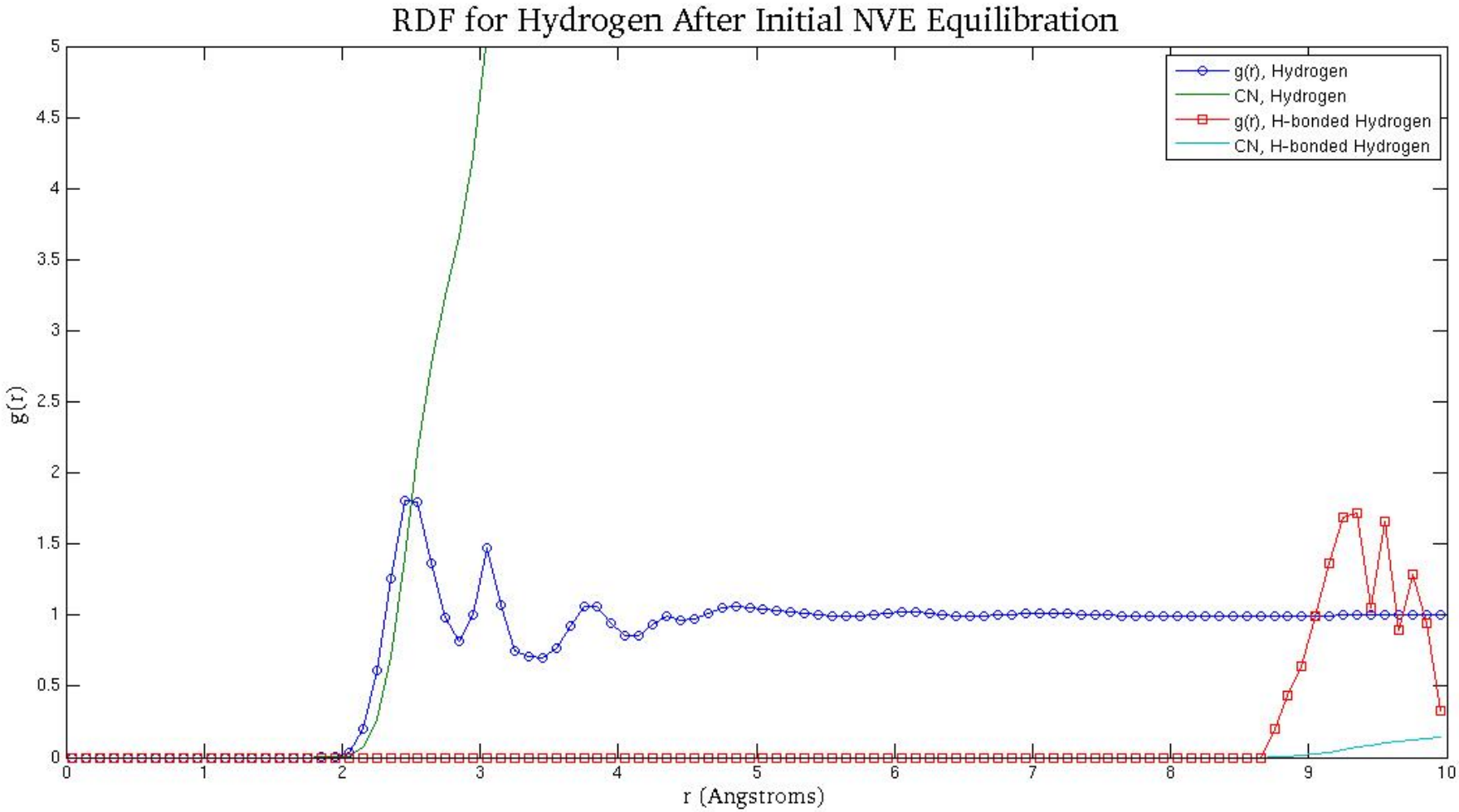
Hydrophobic: O RDF



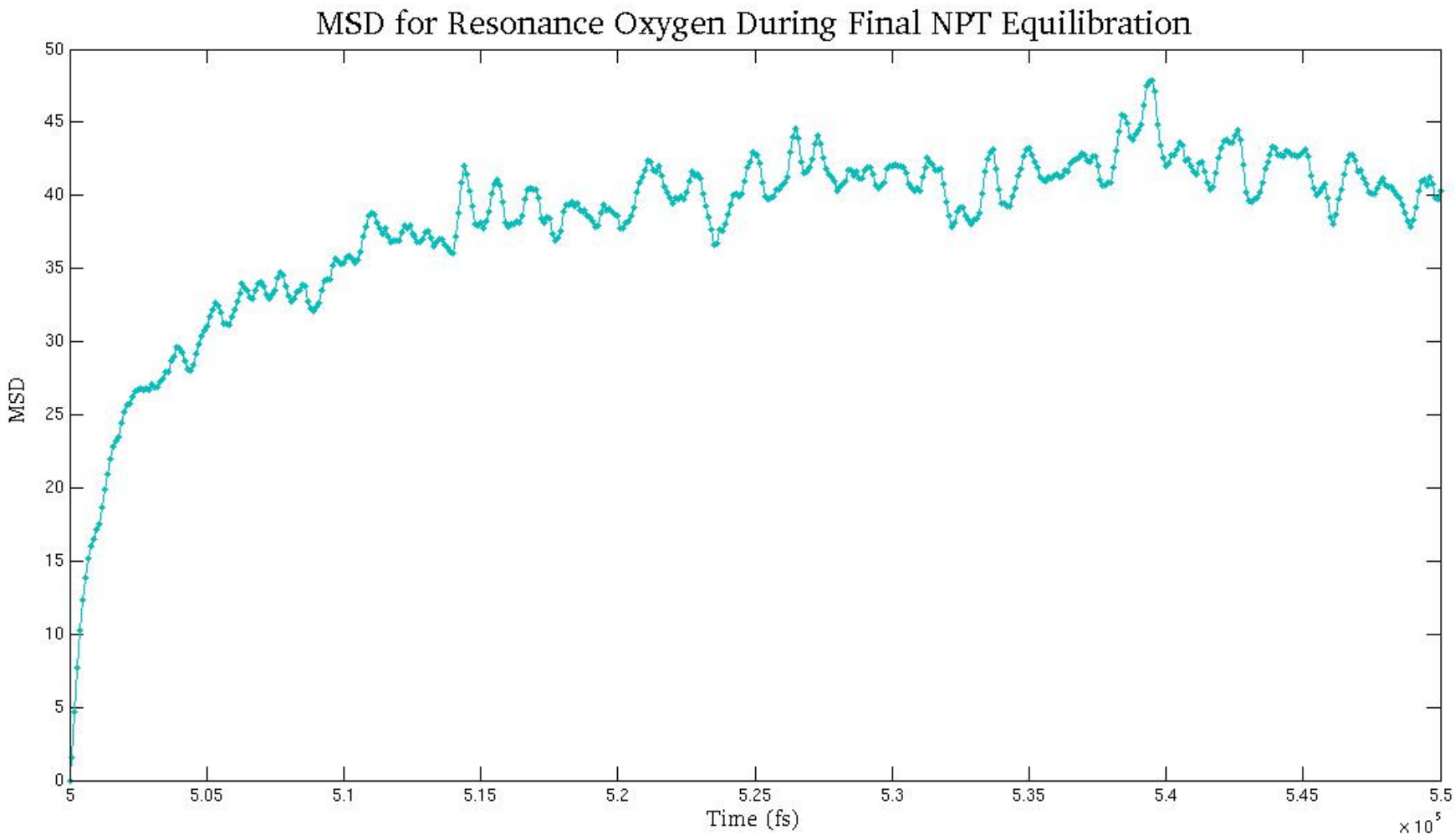
Hydrophobic: C RDF



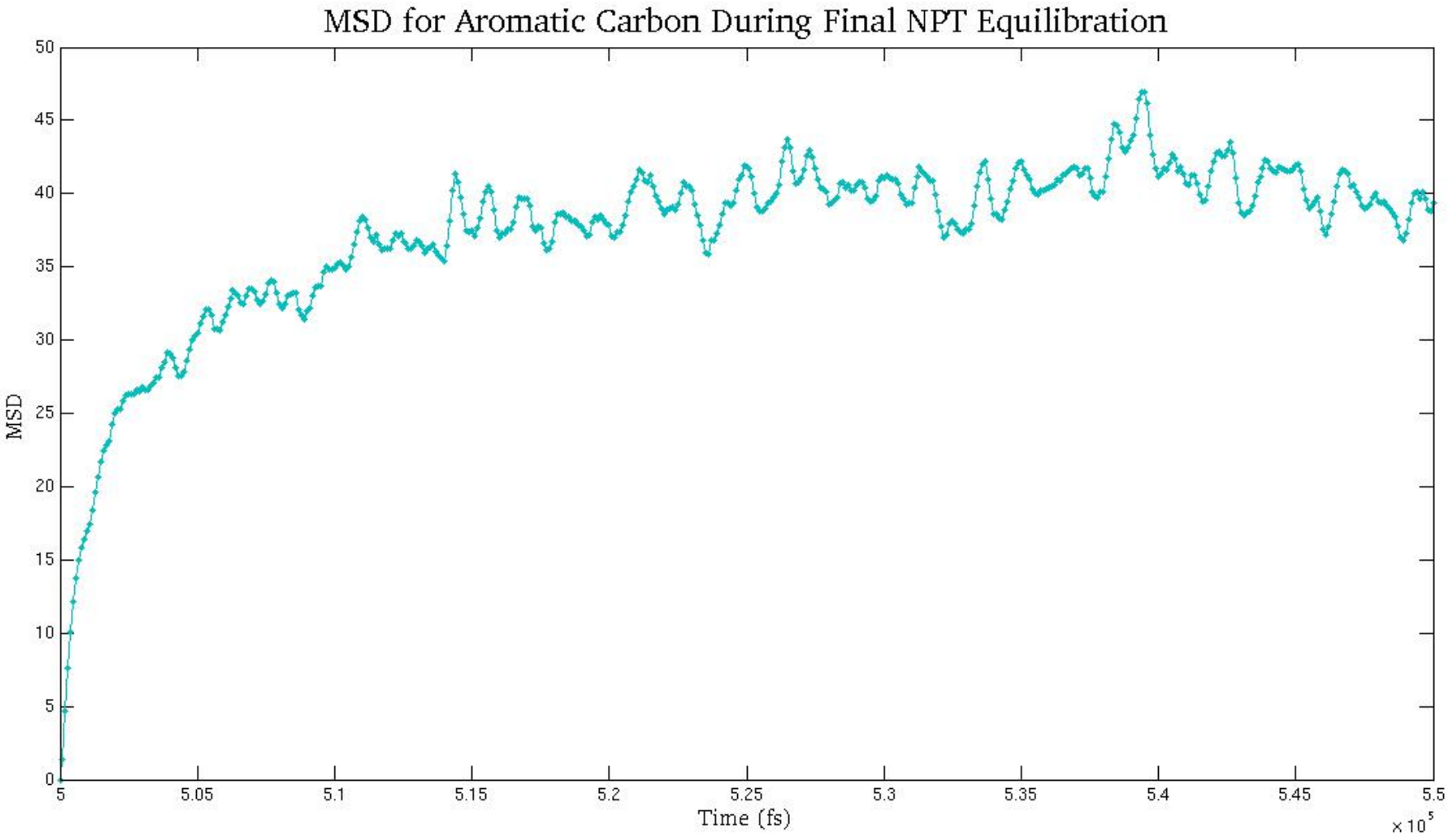
Hydrophobic: H RDF



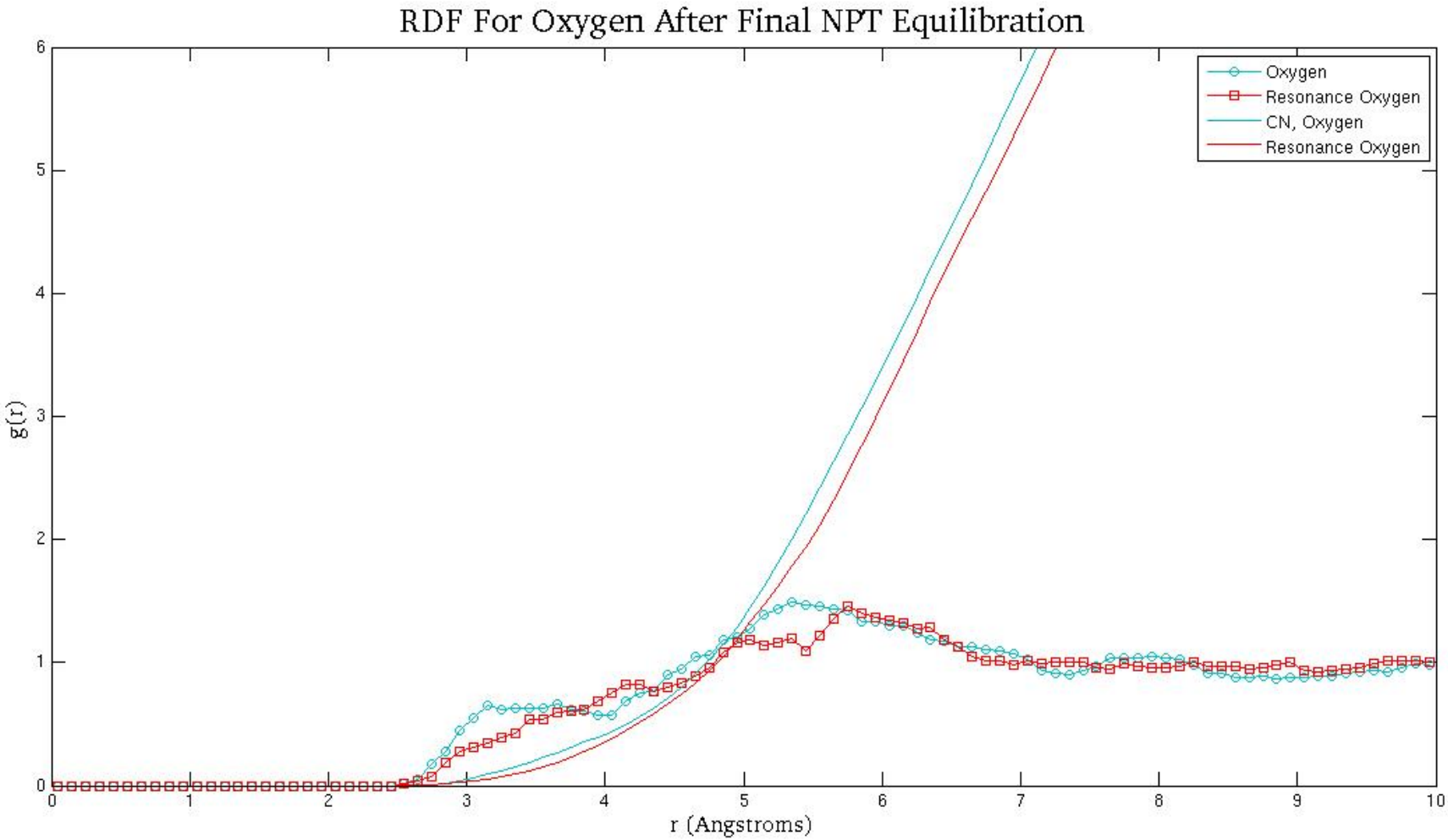
Hydrophobic: resonance O MSD



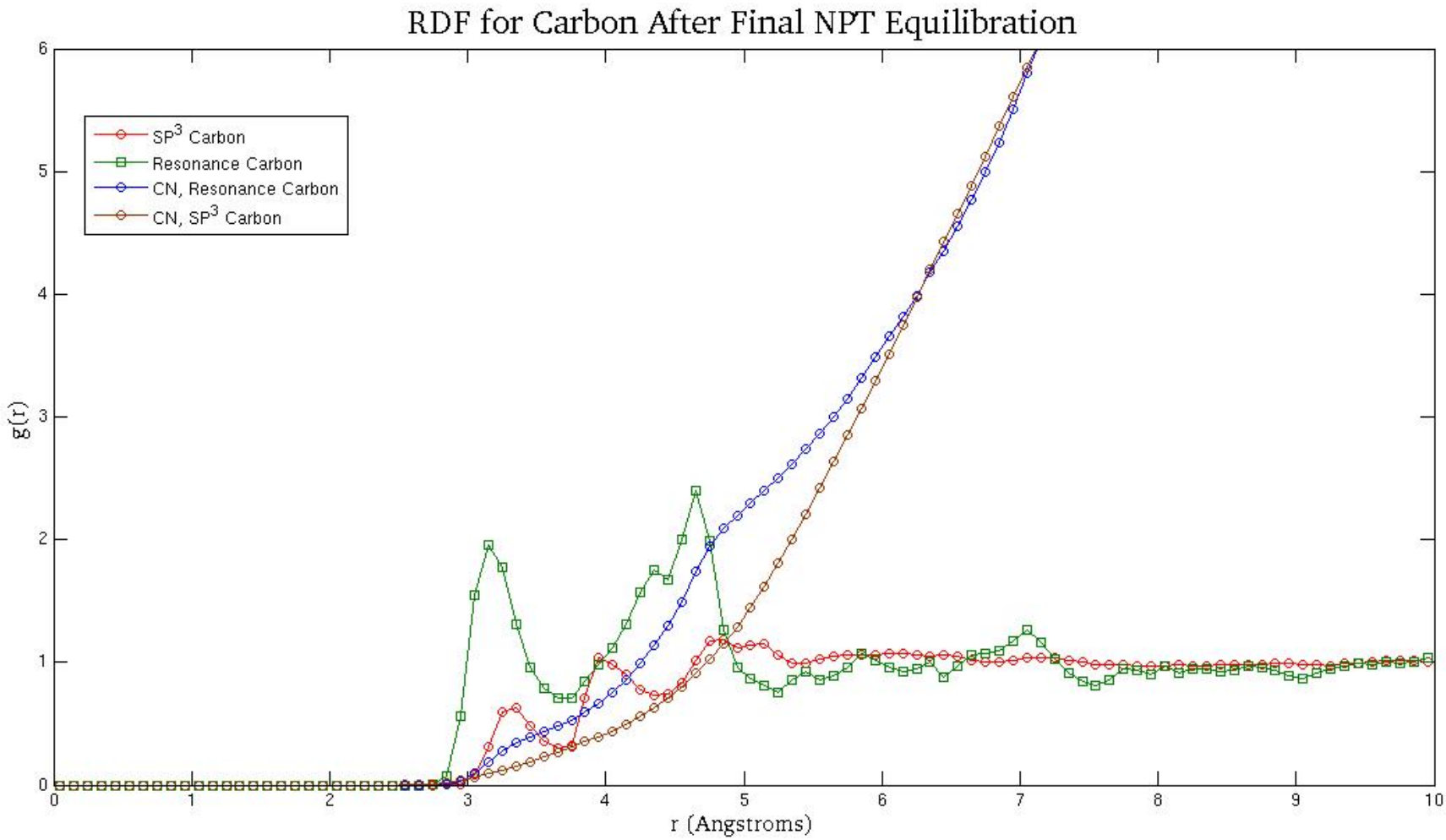
Hydrophobic: aromatic C MSD



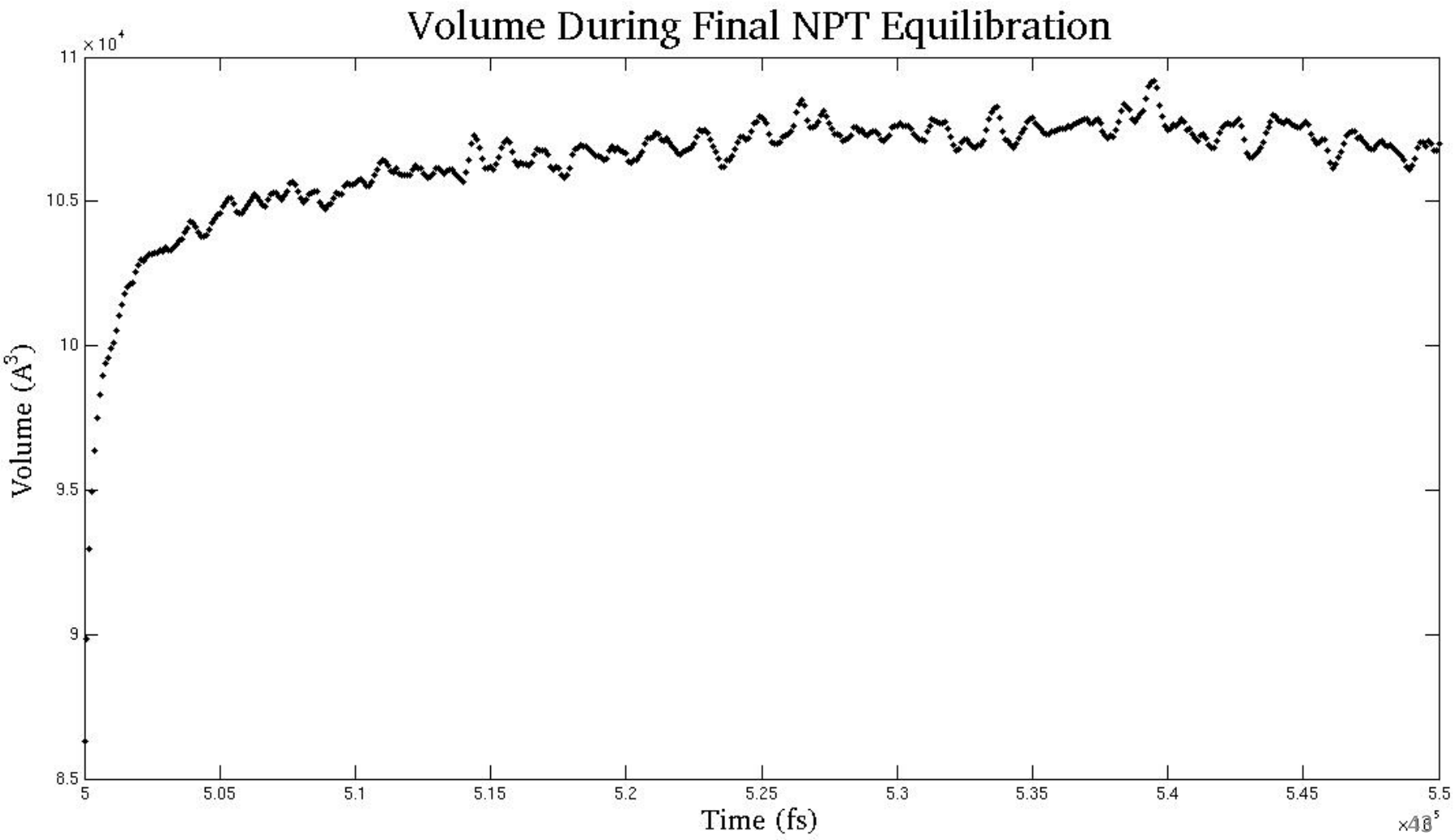
Hydrophobic: O RDF

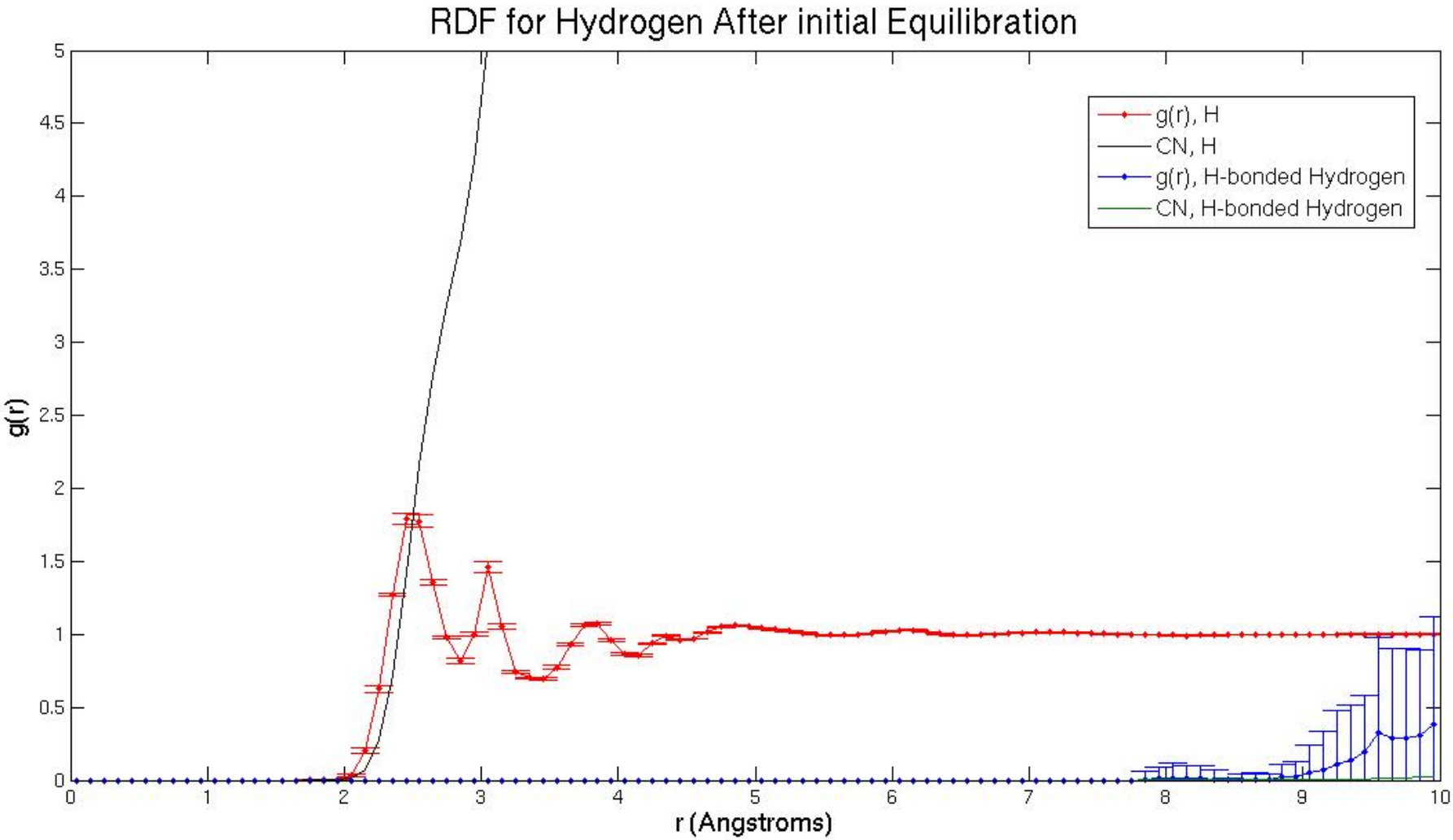


Hydrophobic: C RDF

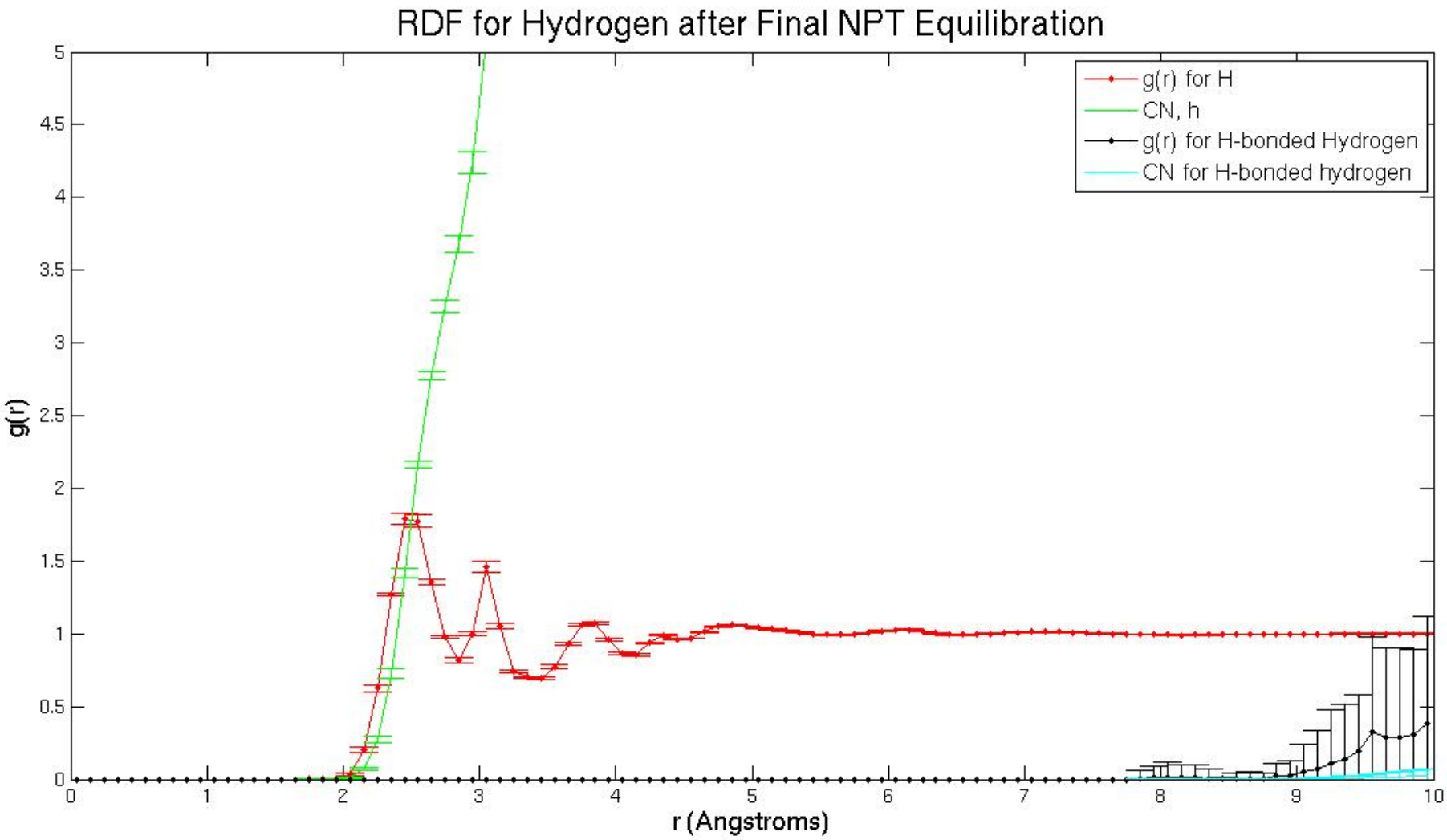


Hydrophobic: final volume

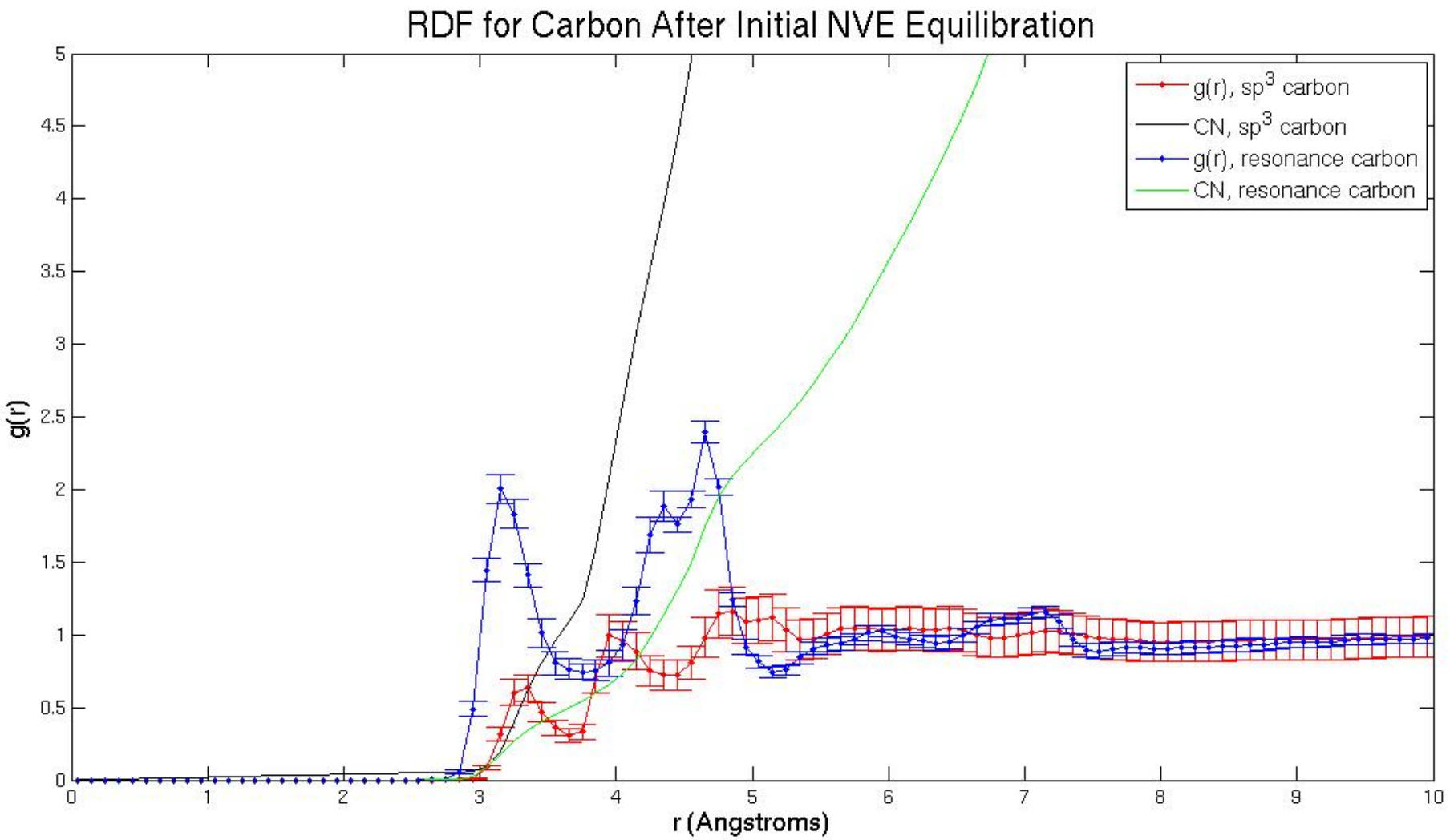




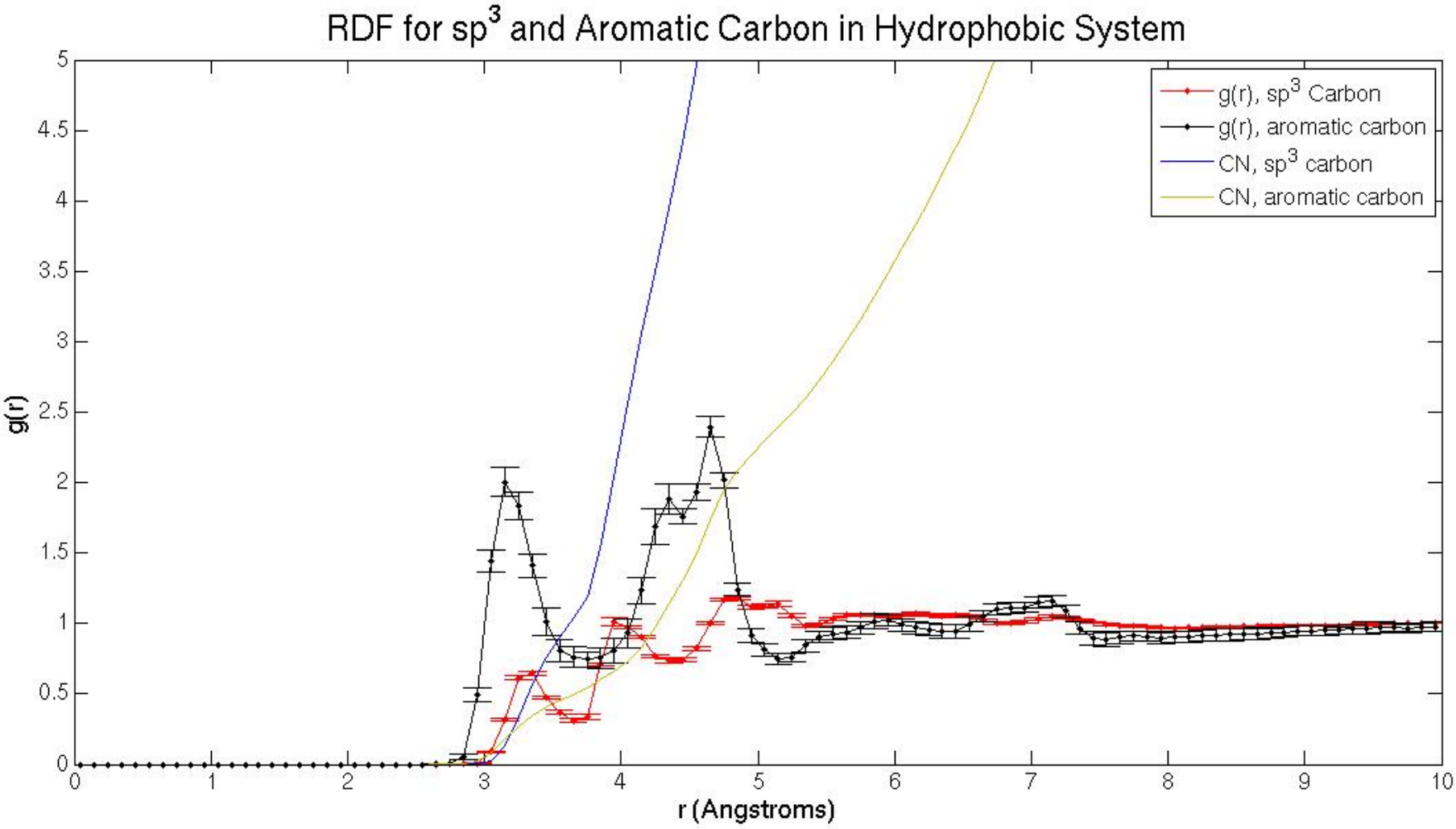
Hydrophobic System



Hydrophobic System

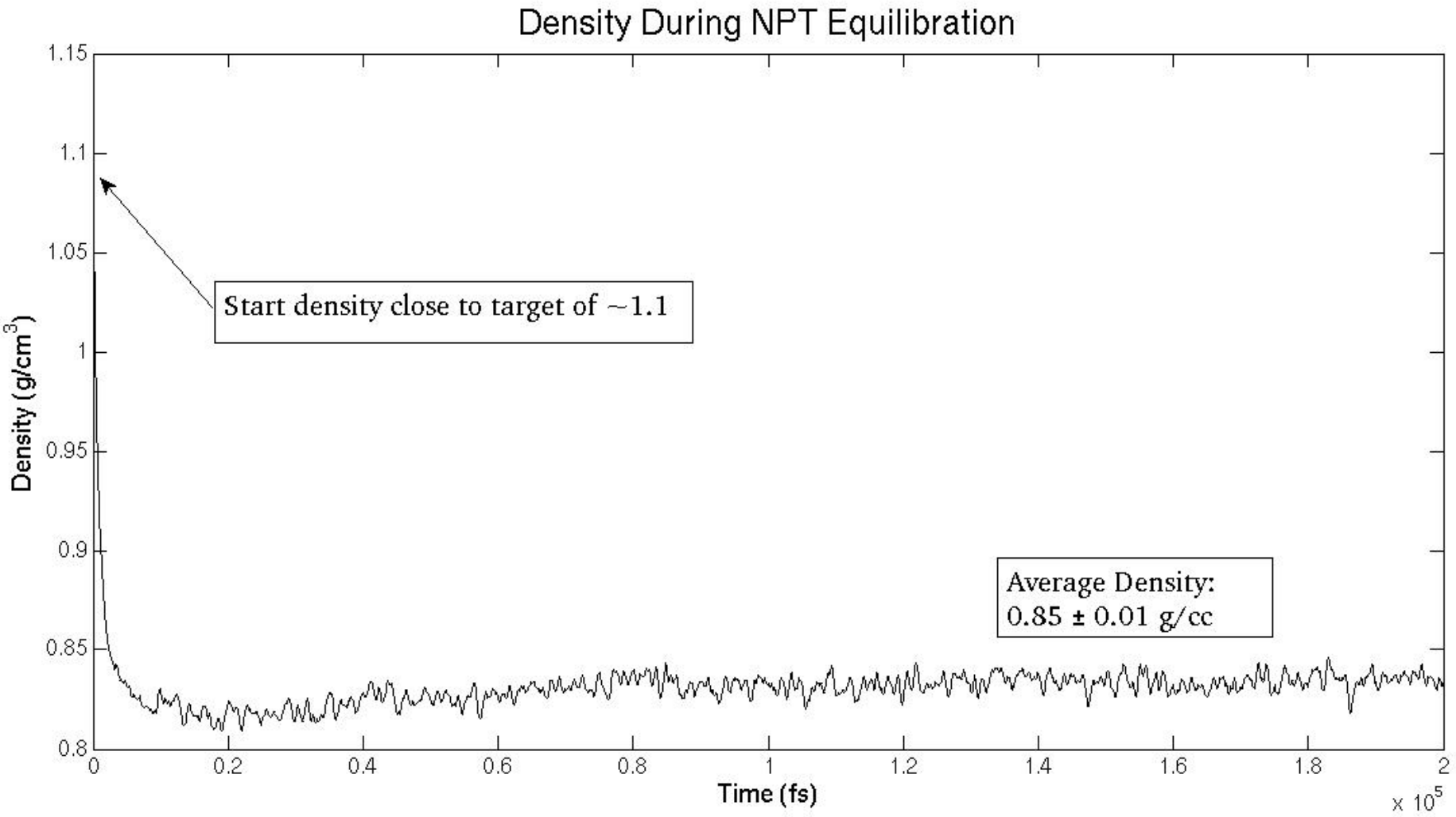


Hydrophobic System



Hydrophobic System, after final NPT equilibration

No change for either H or C, indicates equilibration times too short



Final density still too low. Indicates equilibration times too short

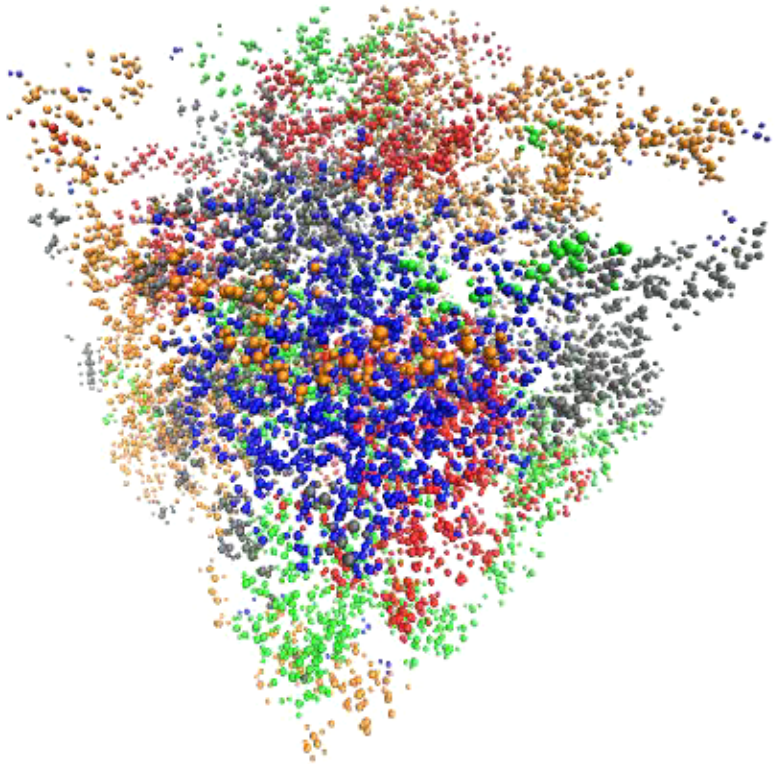
Density

- From final NPT equilibration:
  - Volume: 107385 $Å^3$, or 1.07 X 10^{-19} cm^3
- Mass: 55781 amu, or 9.26 X 10^{-20} g
- Density: 0.86 g/cm^3

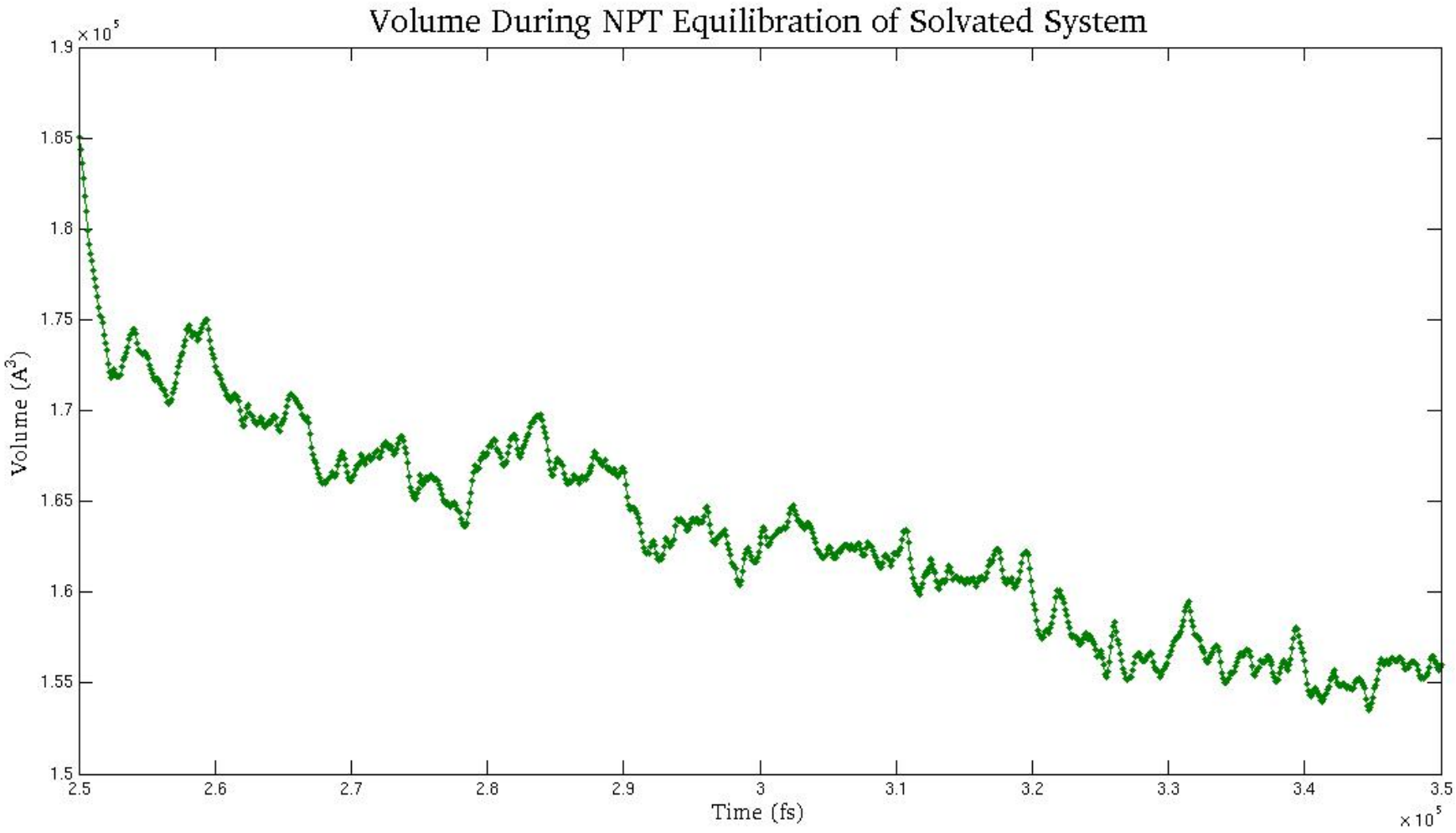
Solvation

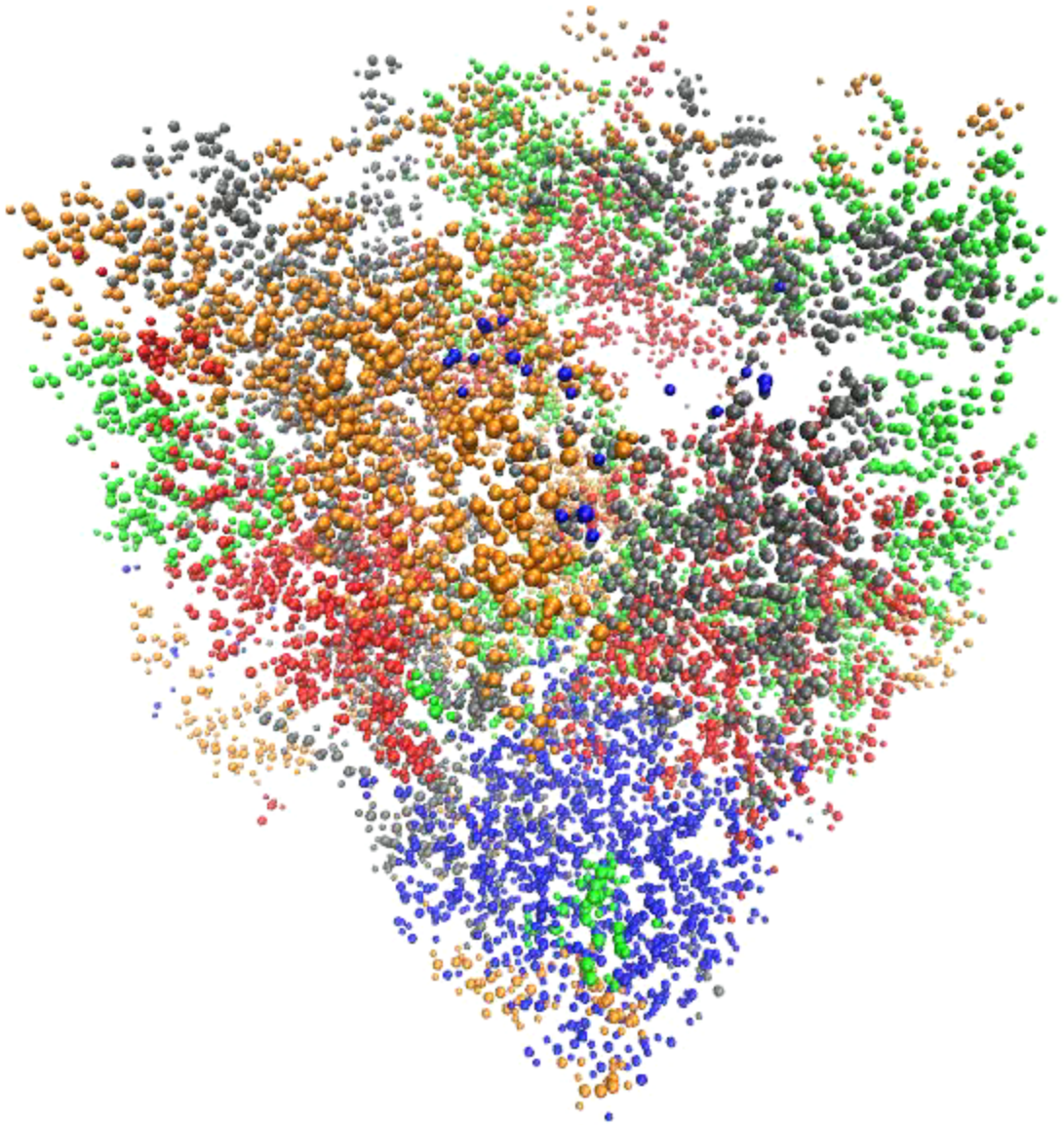
- 10 wt% water
- Added water box to low-density polymer
- 1000 steps CG minimization
- Heated 10-300K over 50ps
- Equilibrated at 300K (NVE) 100ps
- 100ps NVT at 300K
- 100ps NPT at 300K, 1atm

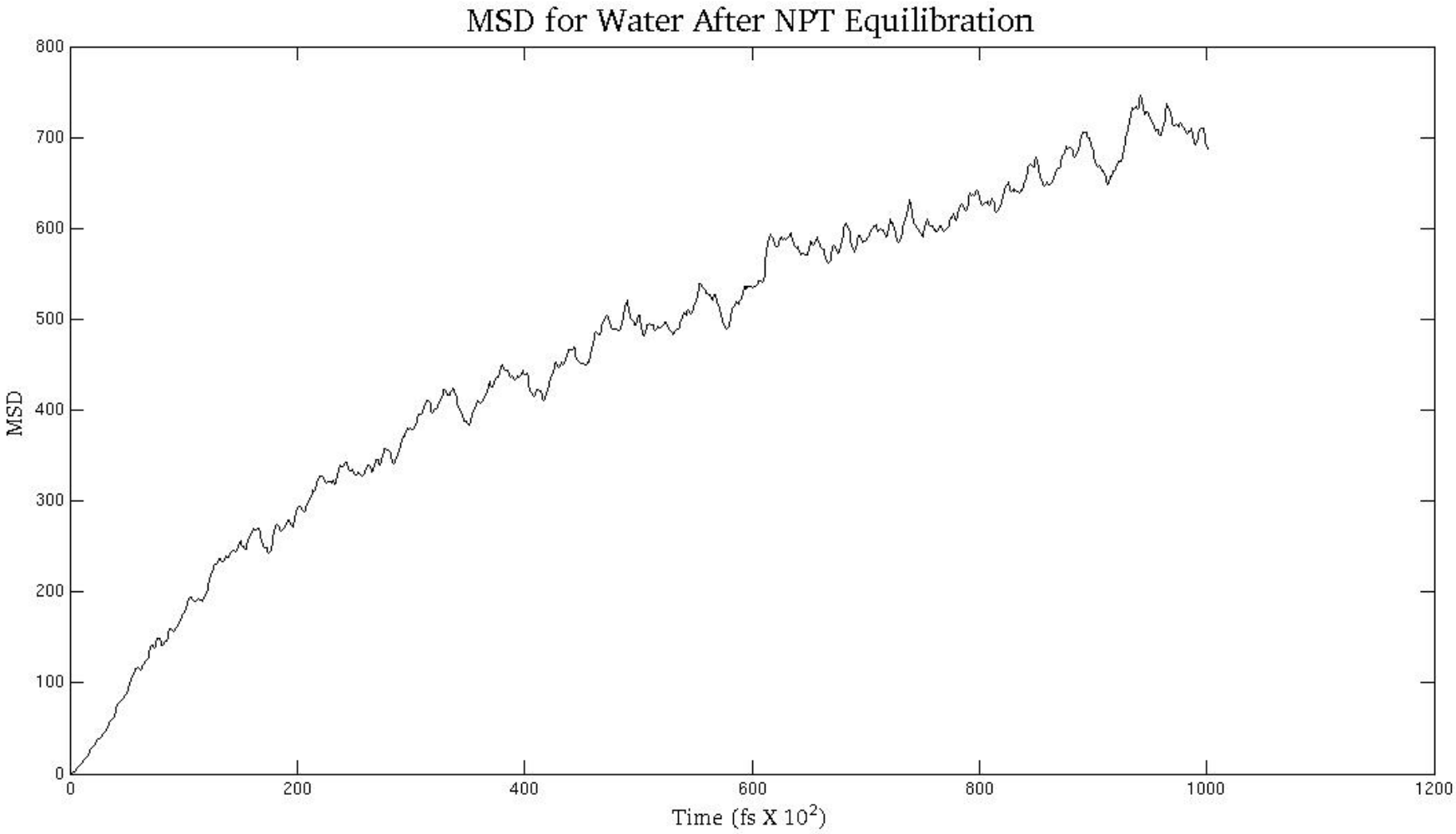
Solvation- 10wt% Water

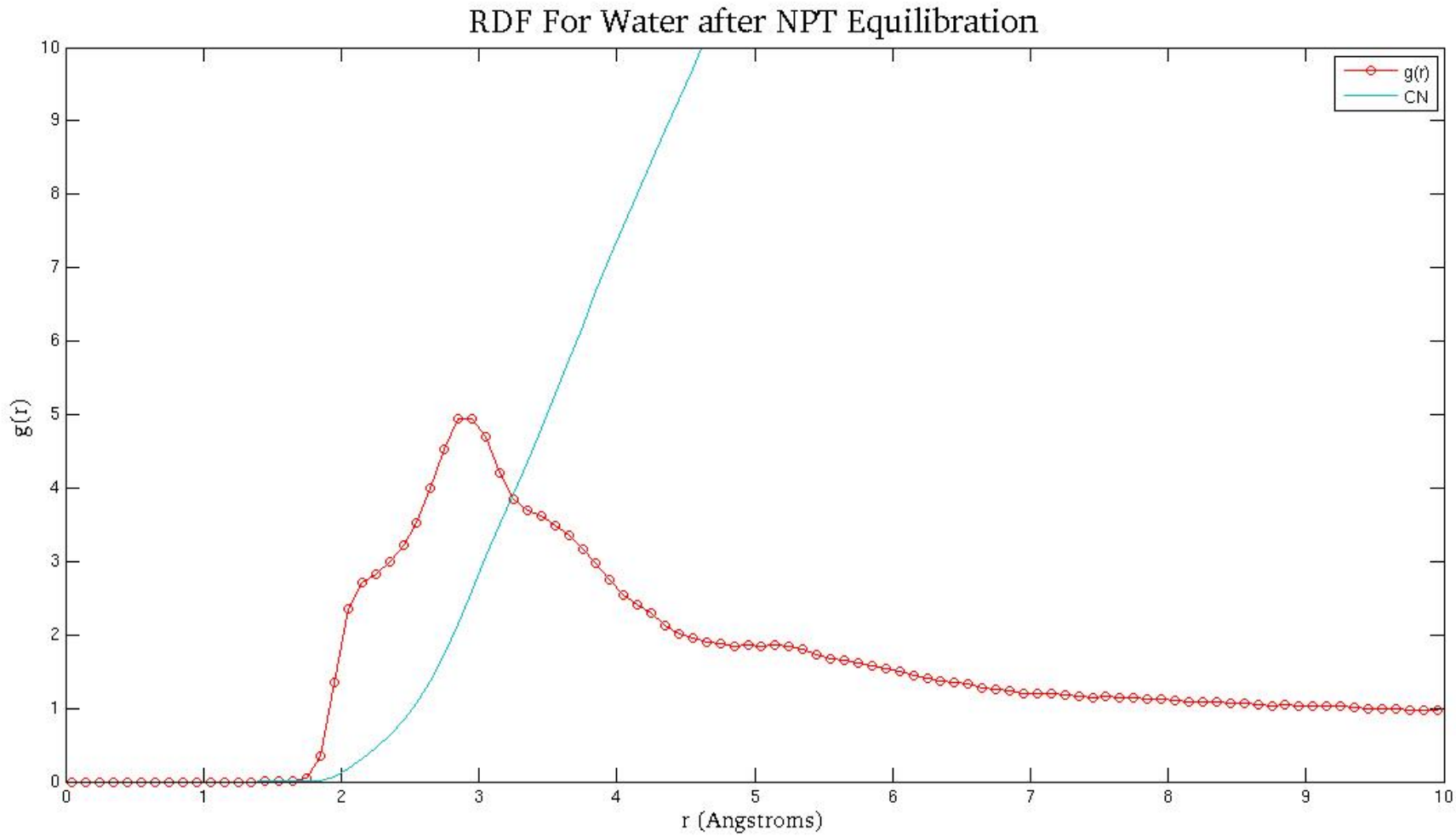


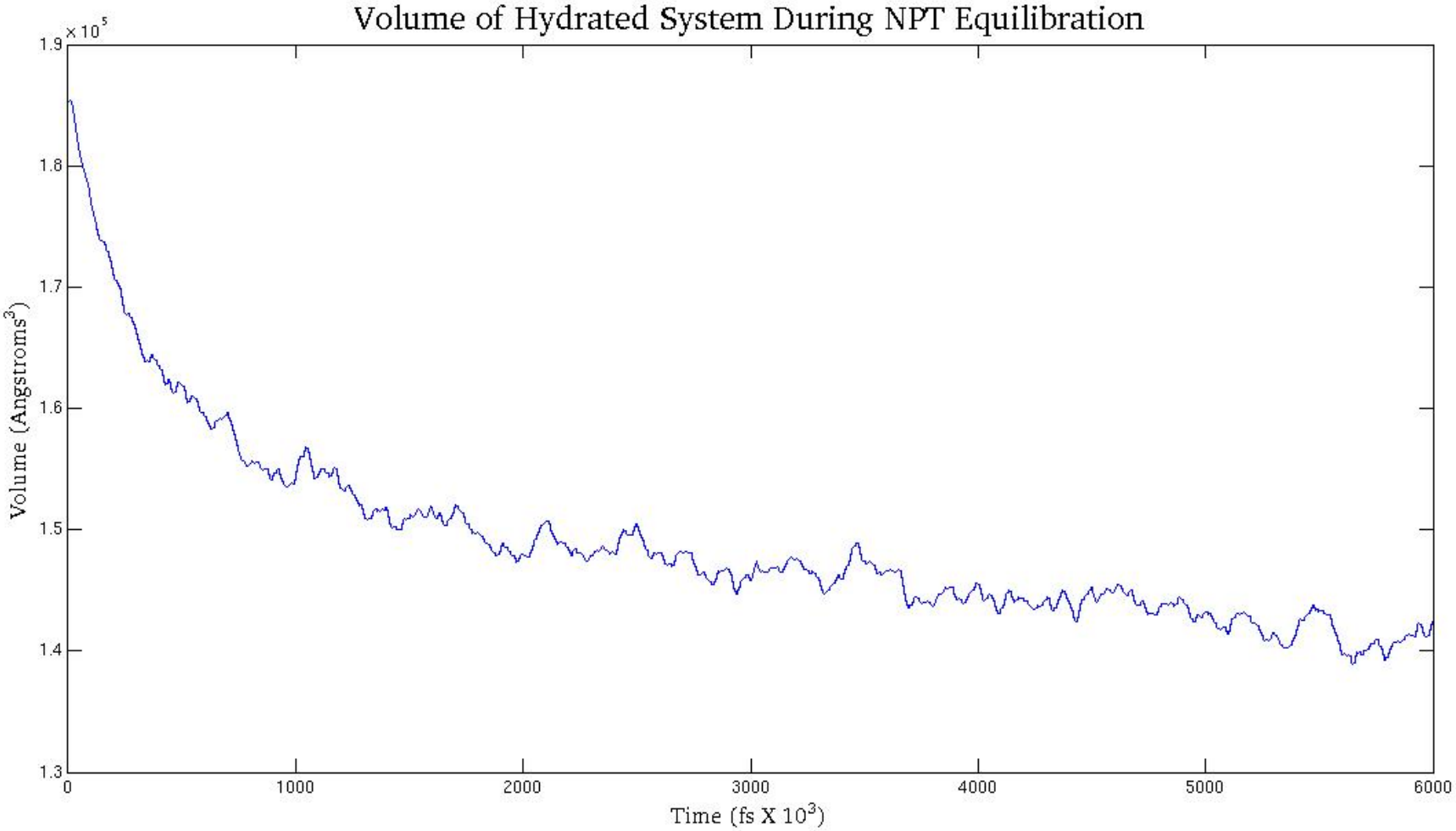
Hydrophobic: solvated volume






MSD for Water After NPT Equilibration
MSD
Time (fs X 10^2)
0
100
200
300
400
500
600
700
800
0
200
400
600
800
1000
1200

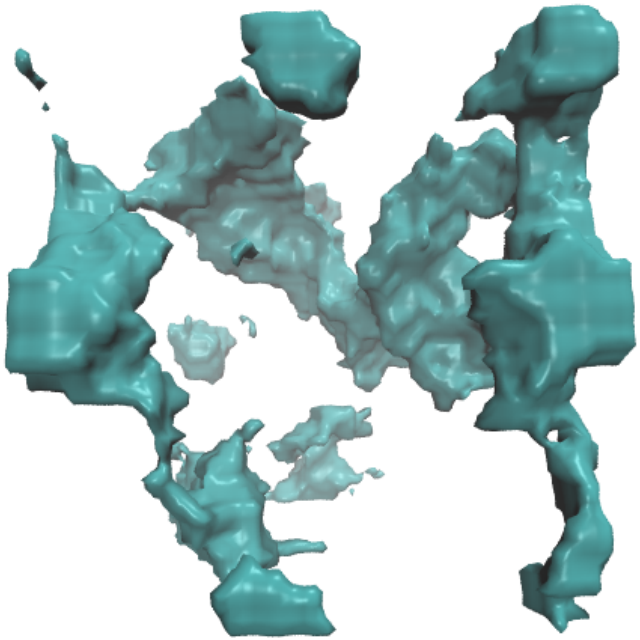

RDF For Water after NPT Equilibration
g(r)
CN
g(r)
r (Angstroms)
0
1
2
3
4
5
6
7
8
9
10


Volume of Hydrated System During NPT Equilibration
×10^5
1.9
1.8
1.7
1.6
1.5
1.4
1.3
Volume (Angstroms^3)
0
1000
2000
3000
4000
5000
6000
Time (fs X 10^3)

Void analysis in dry systems

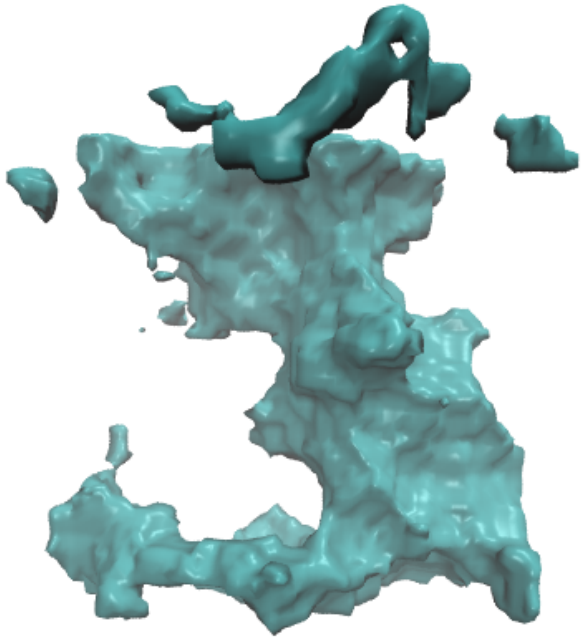
Void % and volume for low density systems (~0.6 g/cc)

Hydrophobic



12.023%
18.7 nm^3

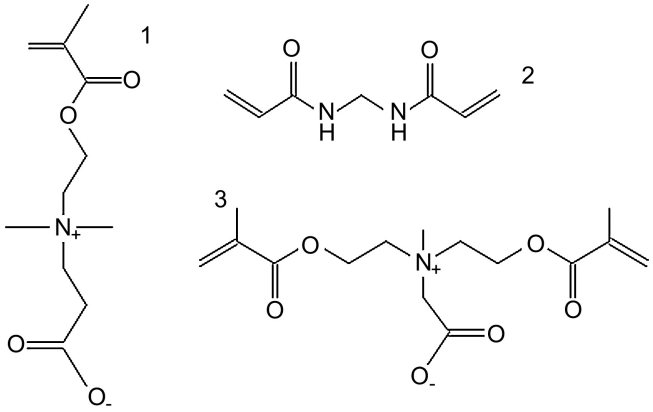
Hydrophilic



13.451%
20.3 nm^3

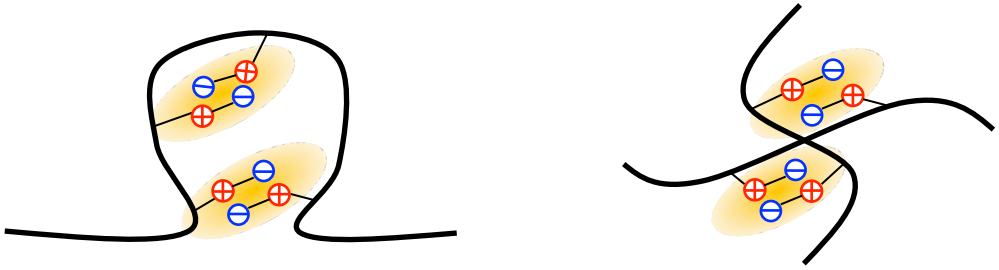
PREDICTING THE EQUILIBRIUM WATER CONTENT IN CBMA HYDROGELS FROM FIRST PRINCIPLE SIMULATIONS

Carboxybetain methacrylate Hydrogels



1. carboxybetain methacrylate (CBMA), **2**. *N,N'*-methylenebis (acrylamide) crosslinker **3.** carboxybetain dimethacrylate crosslinker

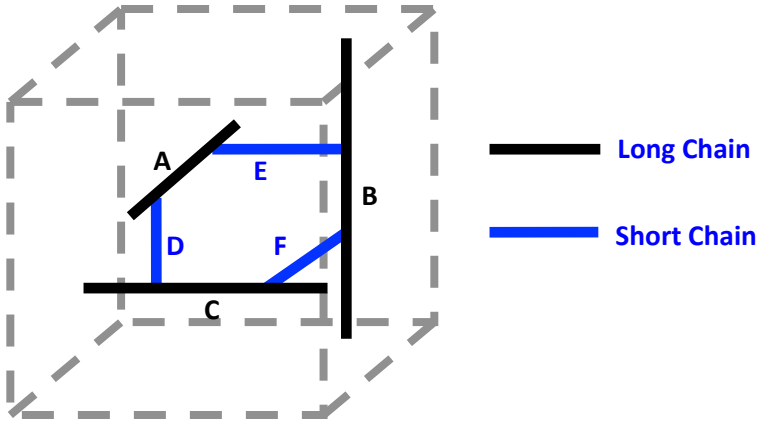
- superior suitability for biomedical applications
  - high hydration and ultra-low fouling
- Used as scaffolds in tissue engineering and joint replacment



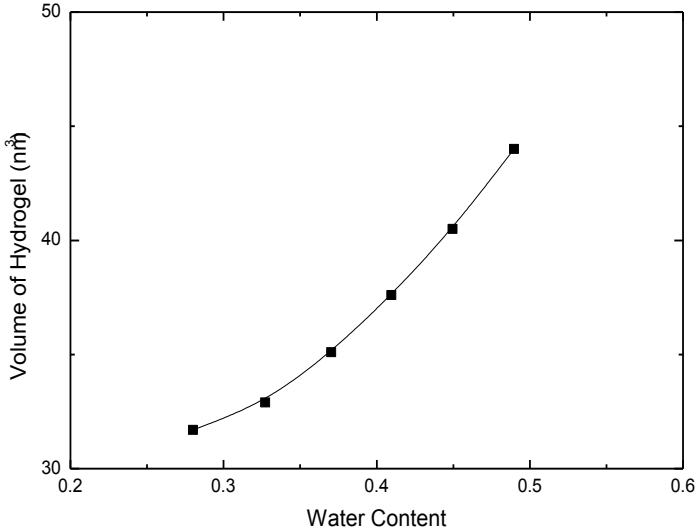
Physical crosslinking of zwitterionic polymer chains. (a) Inter-chain crosslinking; (b) Intra-chain crosslinking

Molecular Dynamics simulations

Water Content of Hydrogel	Number of Water Molecules
28%	335
33%	415
37%	502
41%	592
45%	697
49%	819
62%	1396
71%	2120
81%	3630
86%	5250
90%	8200

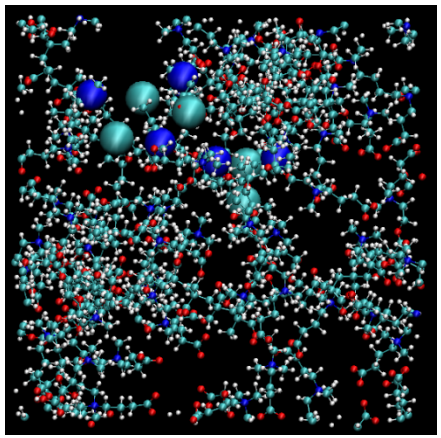


- Fully atomistic simulations
- Investigating the structural properties of water molecules in matrix

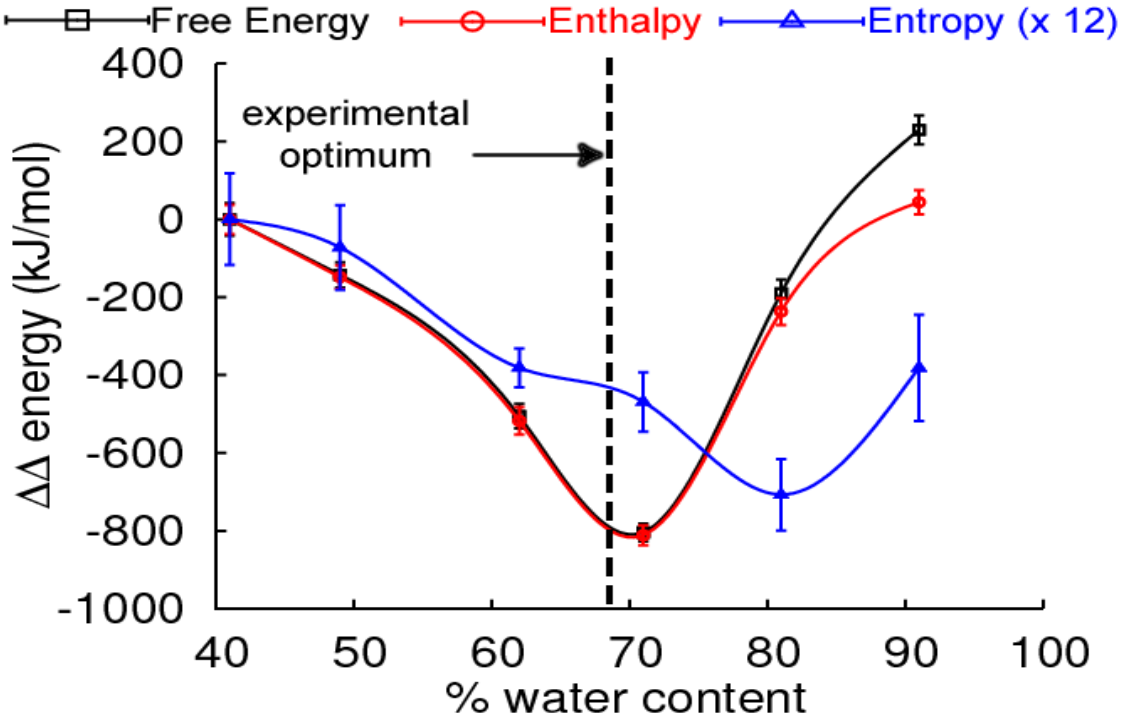


Volumes of hydrogels with various water contents.

Free Energy MD Simulations

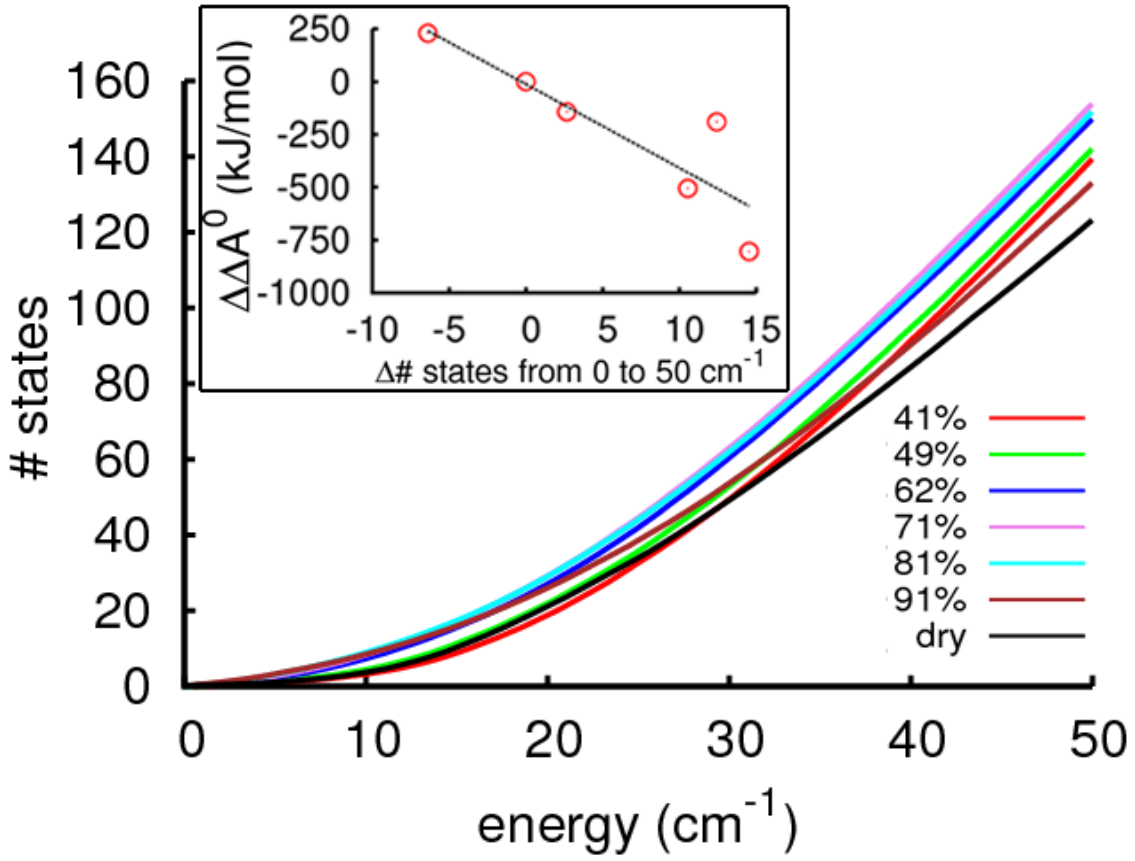


Snapshot of simulation cell



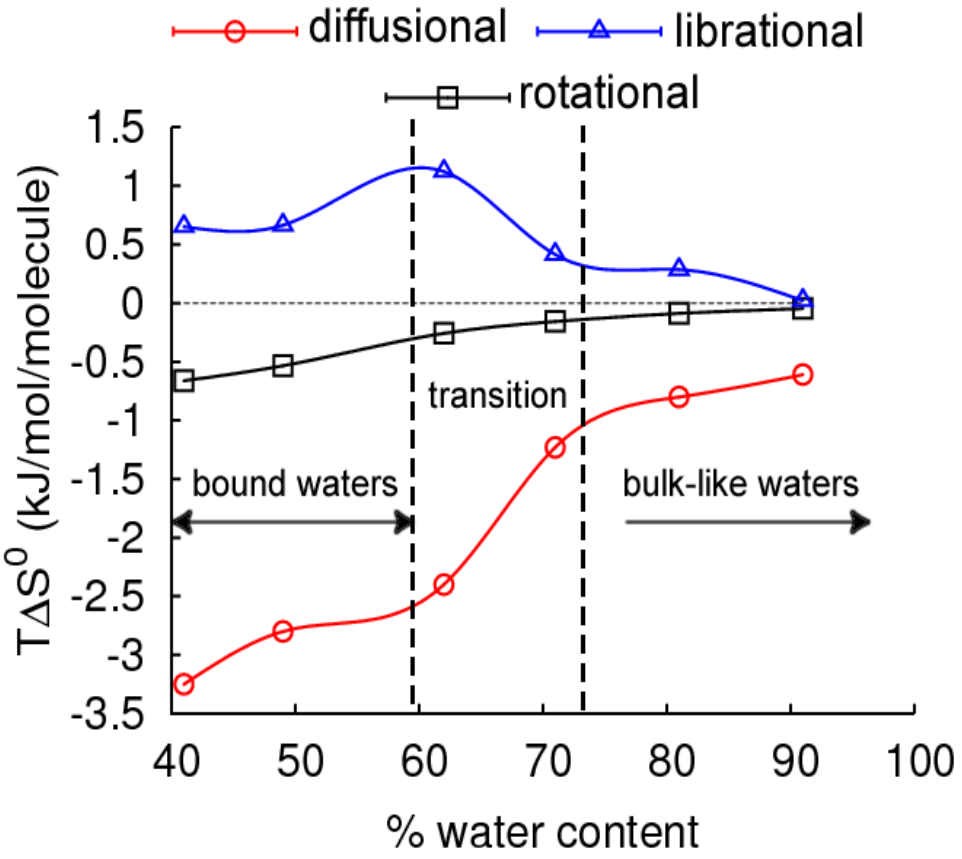
Able to predict the experimental optimal water content by considering the entropy of hydrogel

Insights into the role of water



Water enhances the low frequency breathing modes of the hydrogel at low water content

The entropy of water inside hydrogels



- Diffusional entropy increases continously
- Librational entropy decreases as water molecules leave surface of hydrogel and enters quasi-liquid state in hydrogel pore

Conclusions

- Using computational tools developed at Goddard lab, we are able to predict the experimental optimal water content of CBMA hydrogel
- The enthalpy dominates the interactions in the systems
- Water acts to enhance the low energy vibrational state of the hydrogel before equilibrium by binding to surface
- Water transitions into a quasi-liquid phase at higher content, destabilizing hydrogel matrix