# Latex Films

Dow Chemical Project

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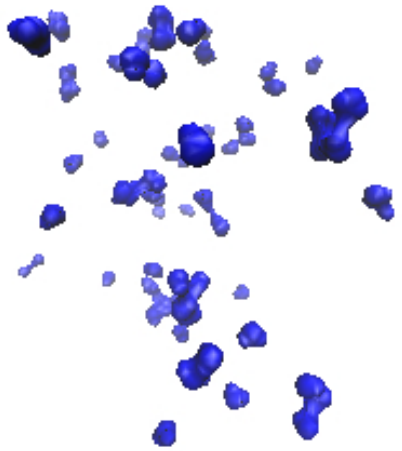
# Solvated Hydrophobic Polymer

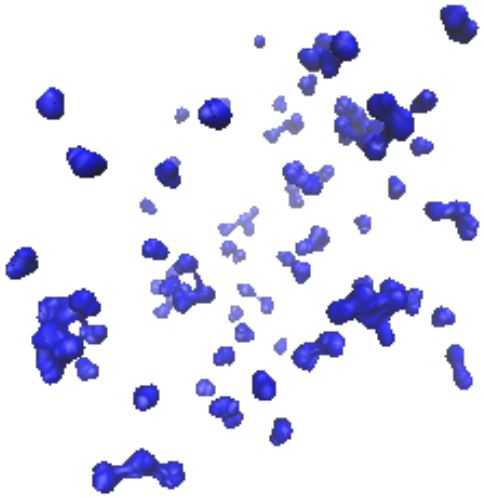
- Equilibrate 40 wt% structure
- Remove water molecules at random to get 30, 25,20,15,10,5,4,3,2,1%
- Equilbration: CED as before, 1 ns NPT (constant number, pressure, temperature)
- Take snapshots once energy equilibrated. 5 snapshots (one every ~100ps)
- 2PT analysis on each snapshot for thermodynamics

Water Molecules Represented as Solid Surfaces

1 %

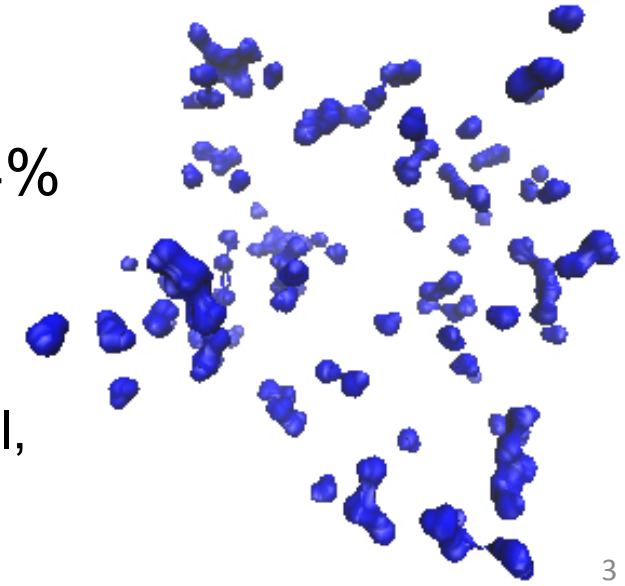
2%



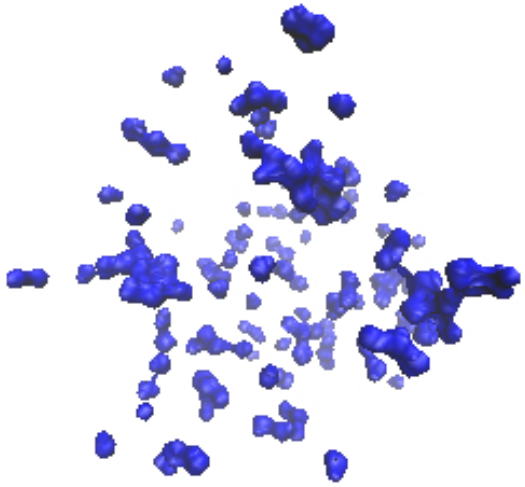


3%

4%

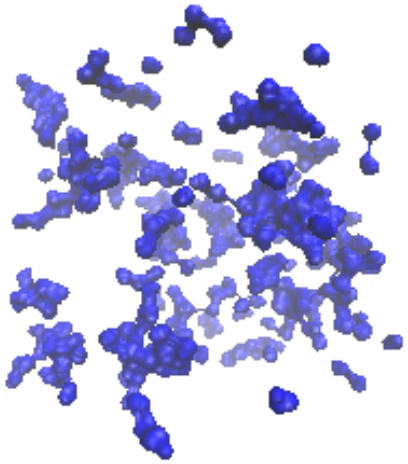


Water molecules in small, separated clusters

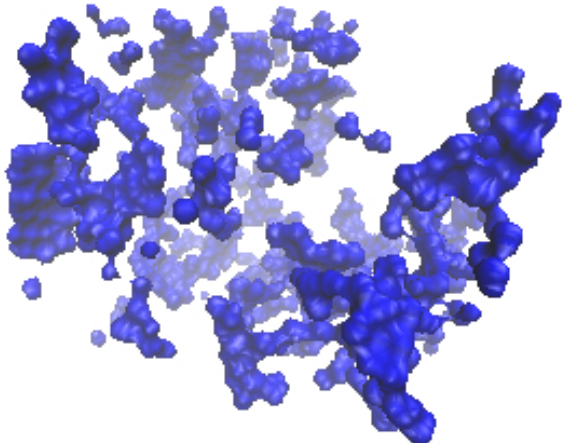


5%

10%

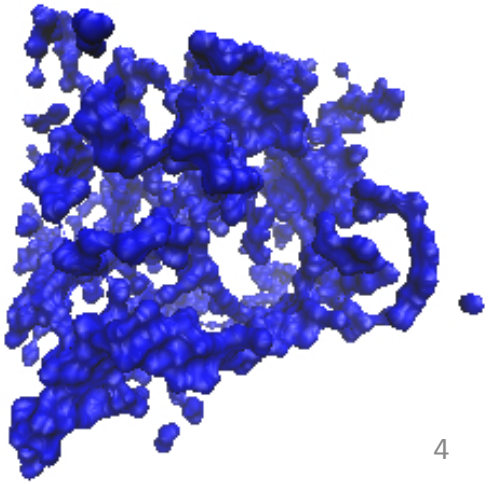


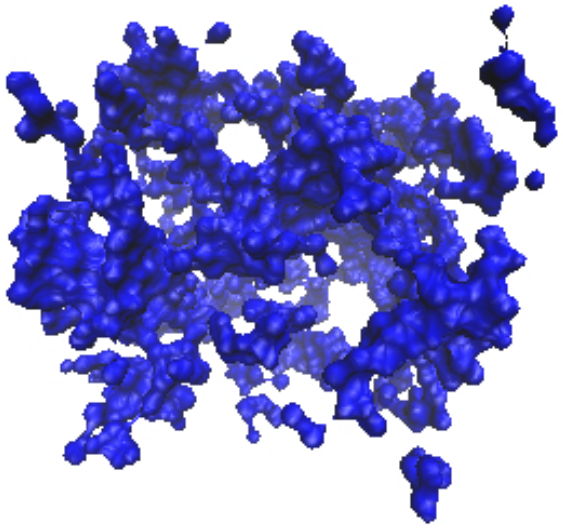
Clusters grow, start joining together.
Percolation at 15-20%



15%

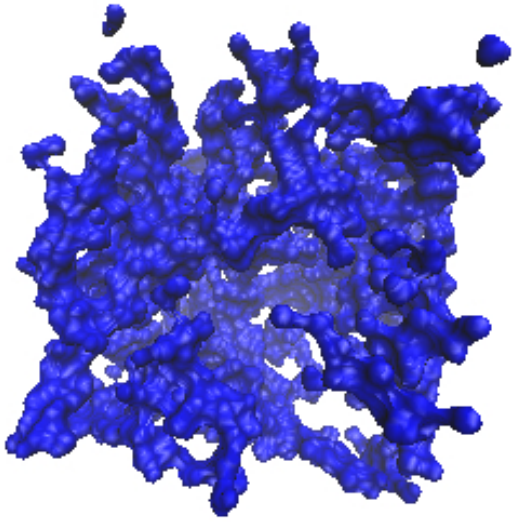
20%

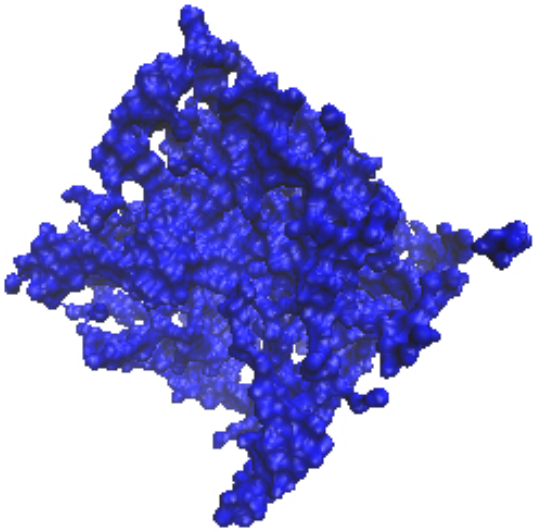




25%

30%





Increasing percolation

40%

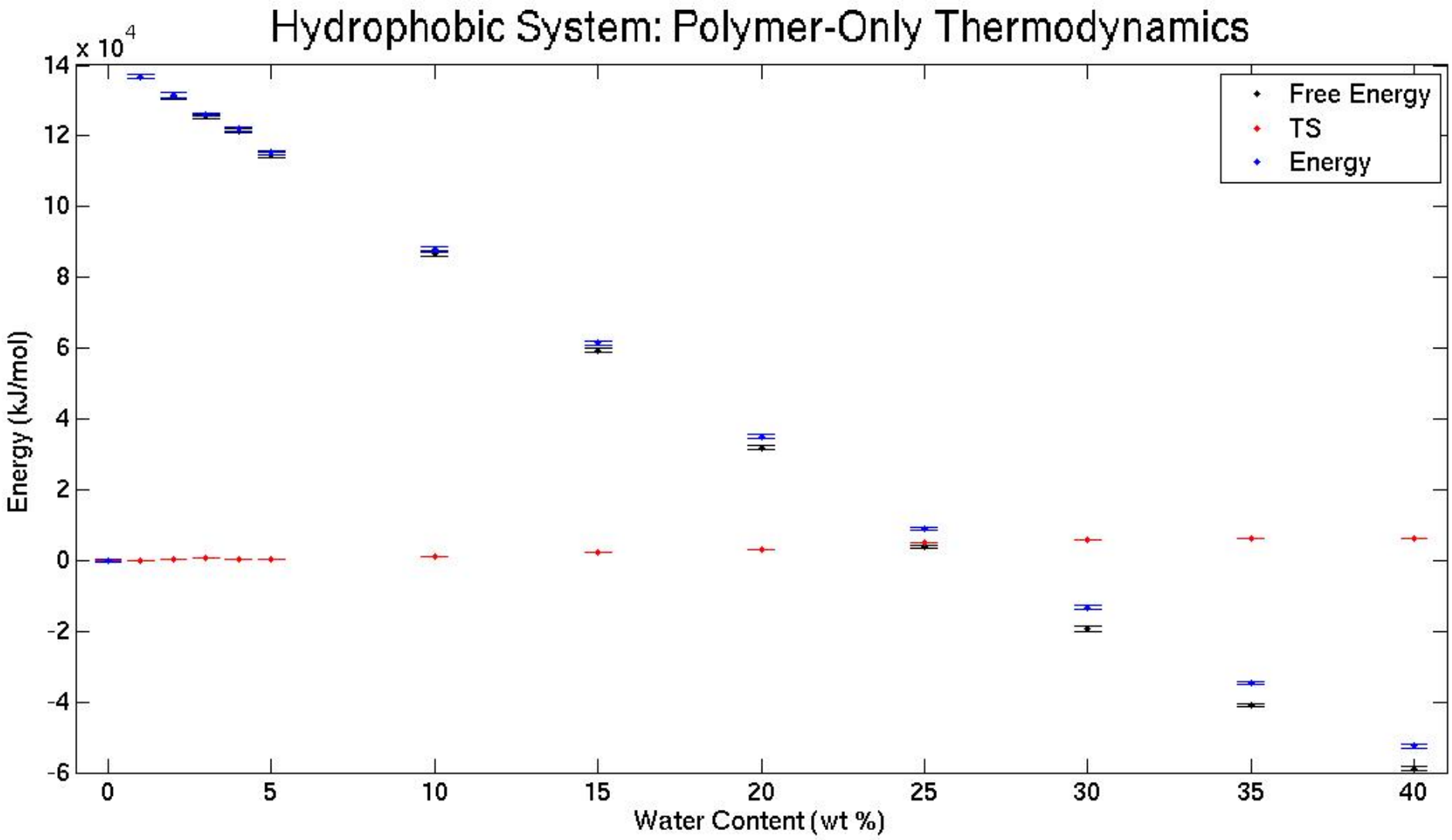
Determine percolation threshold

# Hydrophobic System: Thermodynamics of Polymer Part

- Consider polymer, water separately to examine the effects of each on total thermodynamics
- Free energy (black), energy (blue), and TS (temperature * entropy, red)
- Referencing to dry polymer tells us if the polymer is more or less stable with the addition of water. If the free energy increases relative to the dry polymer (or, is positive in the figure on the next slide), then the polymer is "less happy" (ie, it is unfavorable for the polymer to add water). The converse also holds.
- Free energy dominated by energetic contributions

# Hydrophobic System: Thermodynamics of Polymer Part

- Entropy plays an increasing role as water content increases
- Very unfavorable to add water to dry case until 25% (free energy is greater than that of the dry system until then)
- >30% water more favorable than dry case (for polymer part) (free energy is lower than that of the dry system)
- Always favorable to add water to *solvated* polymer. (Increasing the water decreases the free energy relative to the dry polymer)

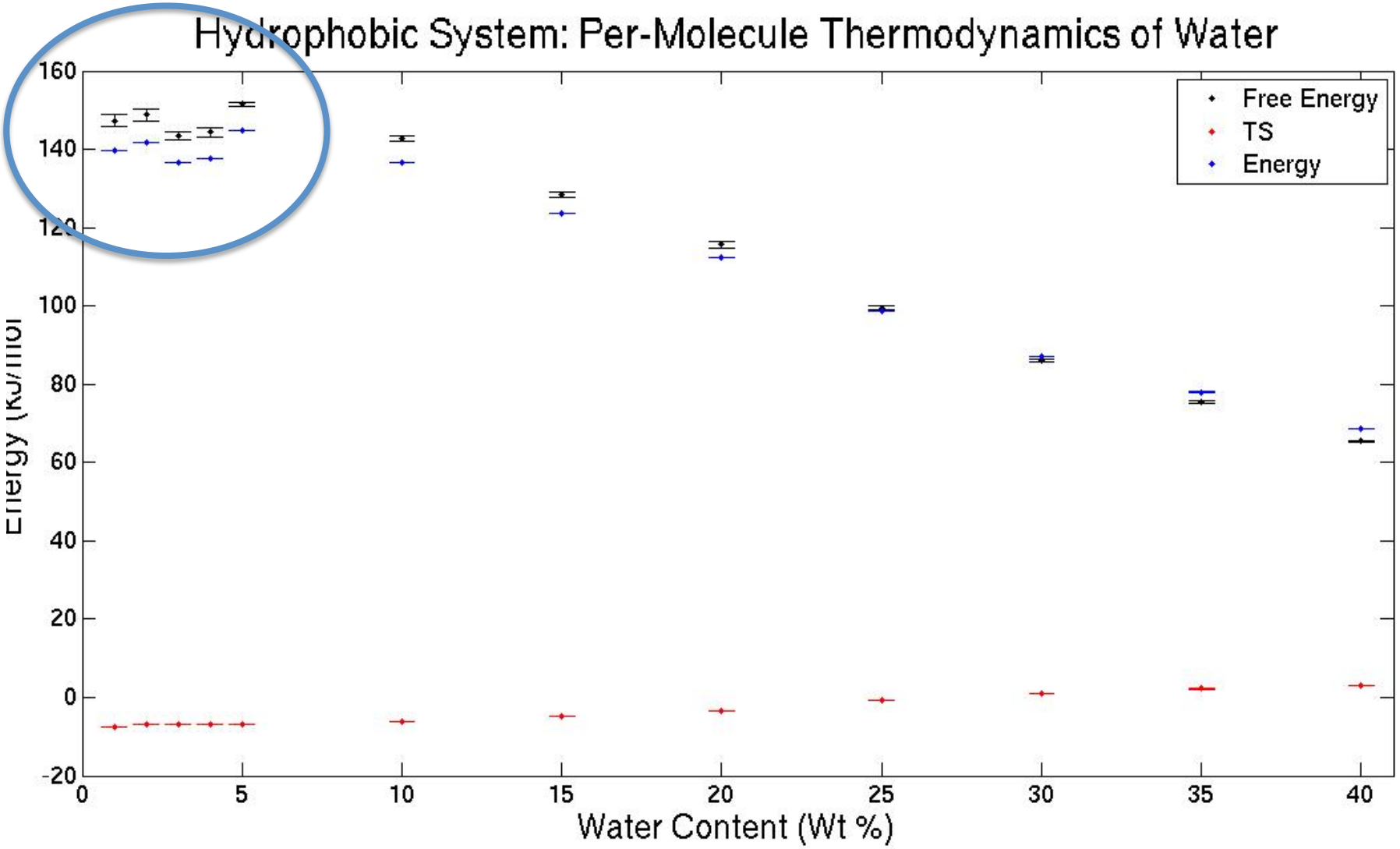

Hydrophobic System: Polymer-Only Thermodynamics
x 10^4
Energy (kJ/mol)
Water Content (wt %)
Free Energy
TS
Energy
14
12
10
8
6
4
2
0
-2
-4
-6
0
5
10
15
20
25
30
35
40

# Hydrophobic System: Thermodynamics of Water Part

- Reference to a system of pure water of the correct size. For example, if there are 1000 water molecules in the solvated system, reference the water thermodynamics to a box of 1000 waters
- Thermodynamics here are per water molecule
- As for the polymer part, entropy plays a small role that increases with water content

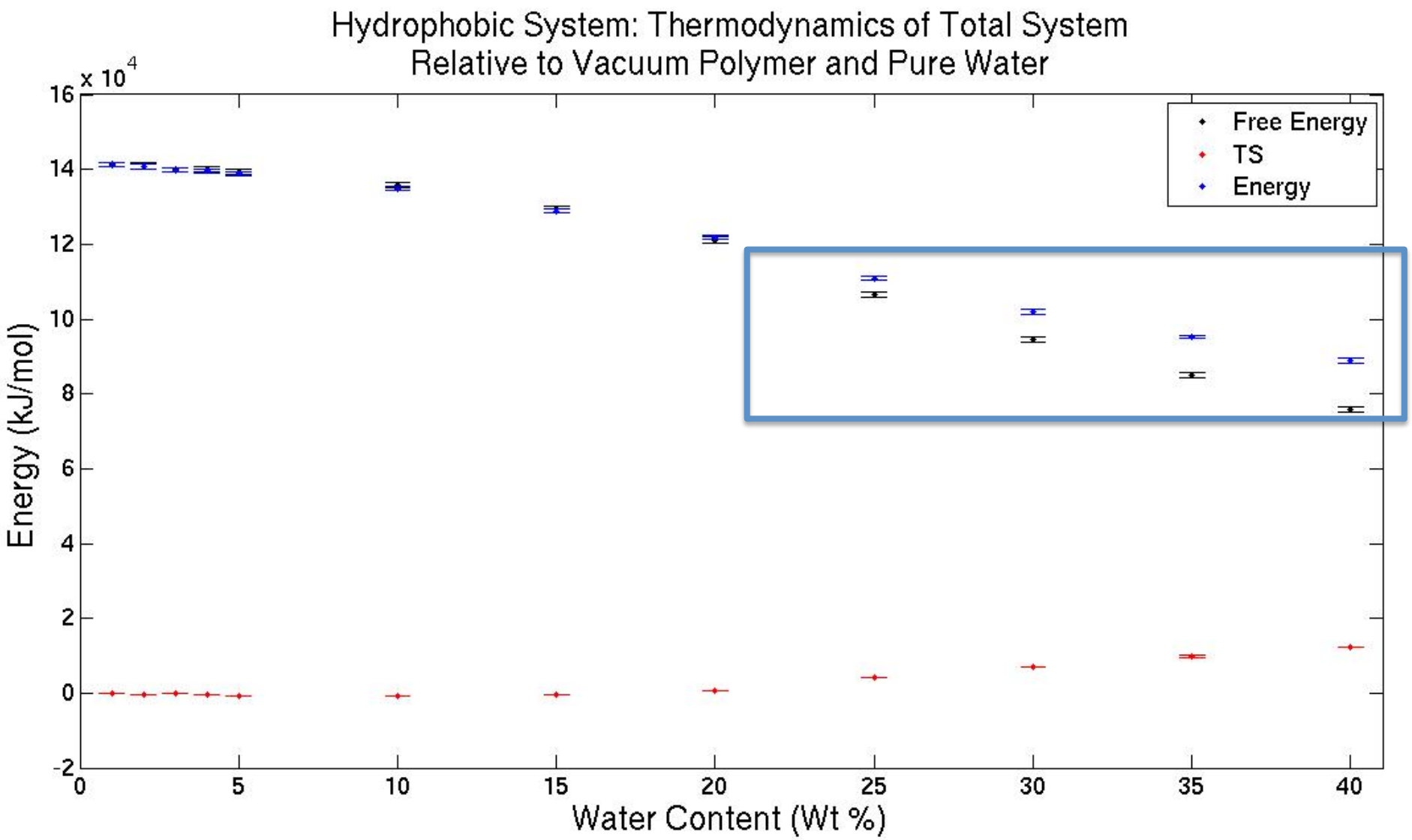
# Hydrophobic System: Thermodynamics of Water Part

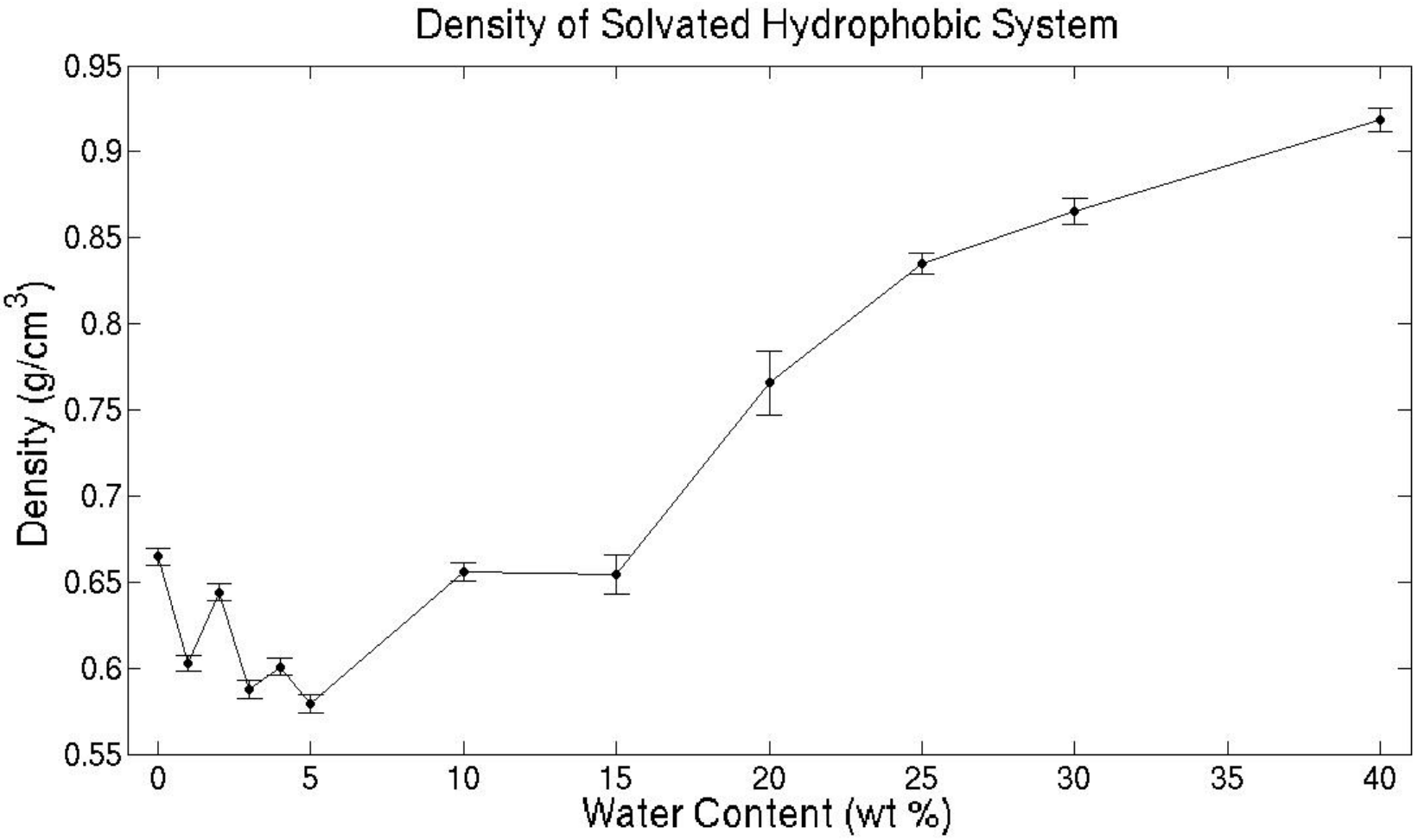
- Larger increase in entropy with water content than in polymer part, reflects increased entropy of water molecules
- The free energy is always greater than 0, so the waters in the solvated system are less “happy” than those in pure water
- Note local minimum at ~2-3%


Hydrophobic System: Per-Molecule Thermodynamics of Water
Free Energy
TS
Energy
Energy (KJ/mol)
Water Content (Wt %)
160
140
120
100
80
60
40
20
0
-20
0
5
10
15
20
25
30
35
40

# Hydrophobic System: Total Thermodynamics

- Slight local minimum at ~2-3% (from water part, need to investigate physical origin)
- Suggests that hydrophobic system, if completely dry, would resist water uptake (free energy at 1% >> free energy of dry polymer)
- System could be metastable at ~2-3%, but if enough water is available, thermodynamics predicts that the system will continue to pick up water
- Note: Recall that this says nothing about the kinetics of water uptake

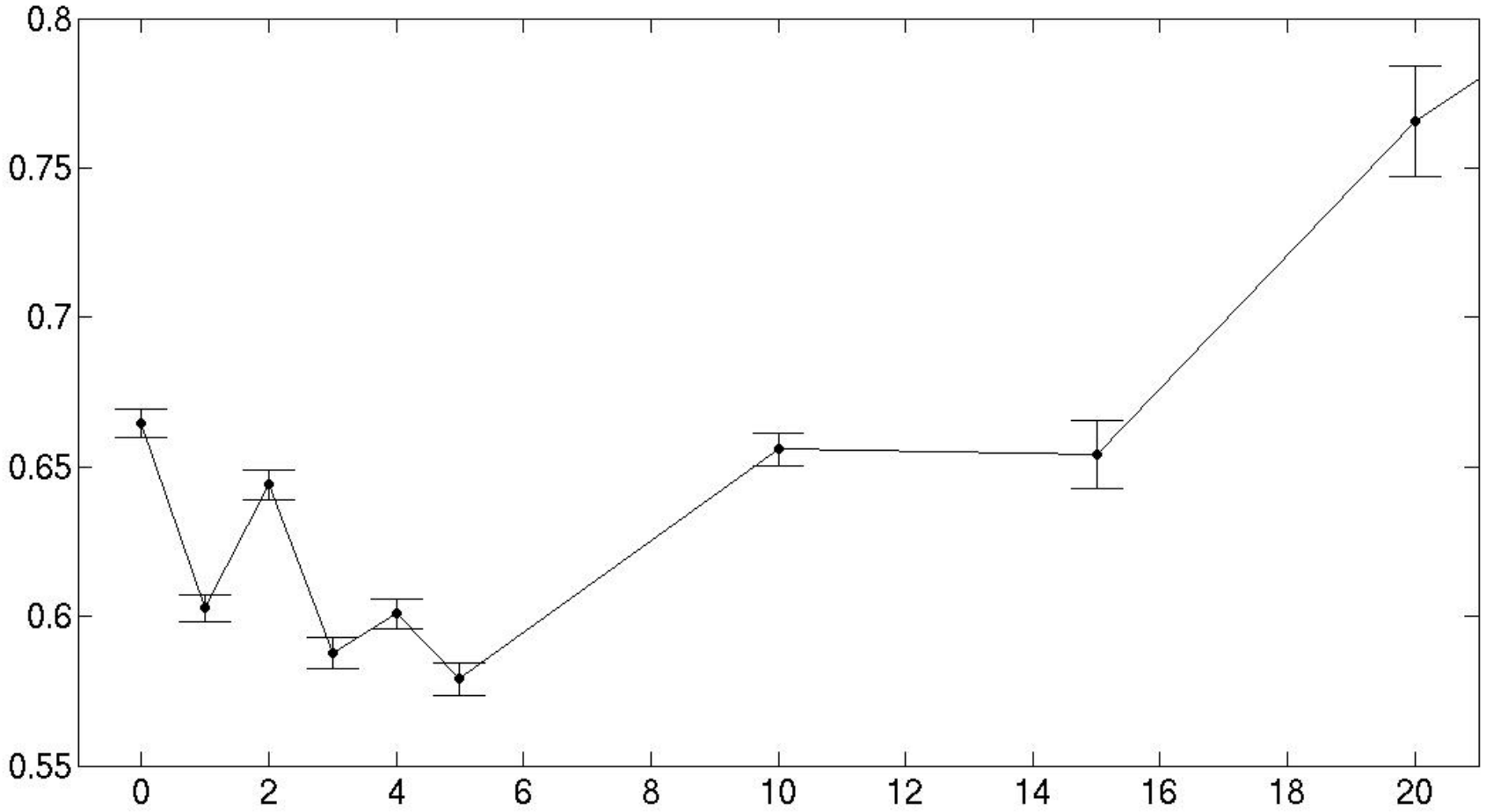

Hydrophobic System: Thermodynamics of Total System
Relative to Vacuum Polymer and Pure Water
x 10^4
Energy (kJ/mol)
Water Content (Wt %)
Free Energy
TS
Energy
16
14
12
10
8
6
4
2
0
-2
0
5
10
15
20
25
30
35
40




Generally swells at low water content. Consistent with hydrophobic polymer.

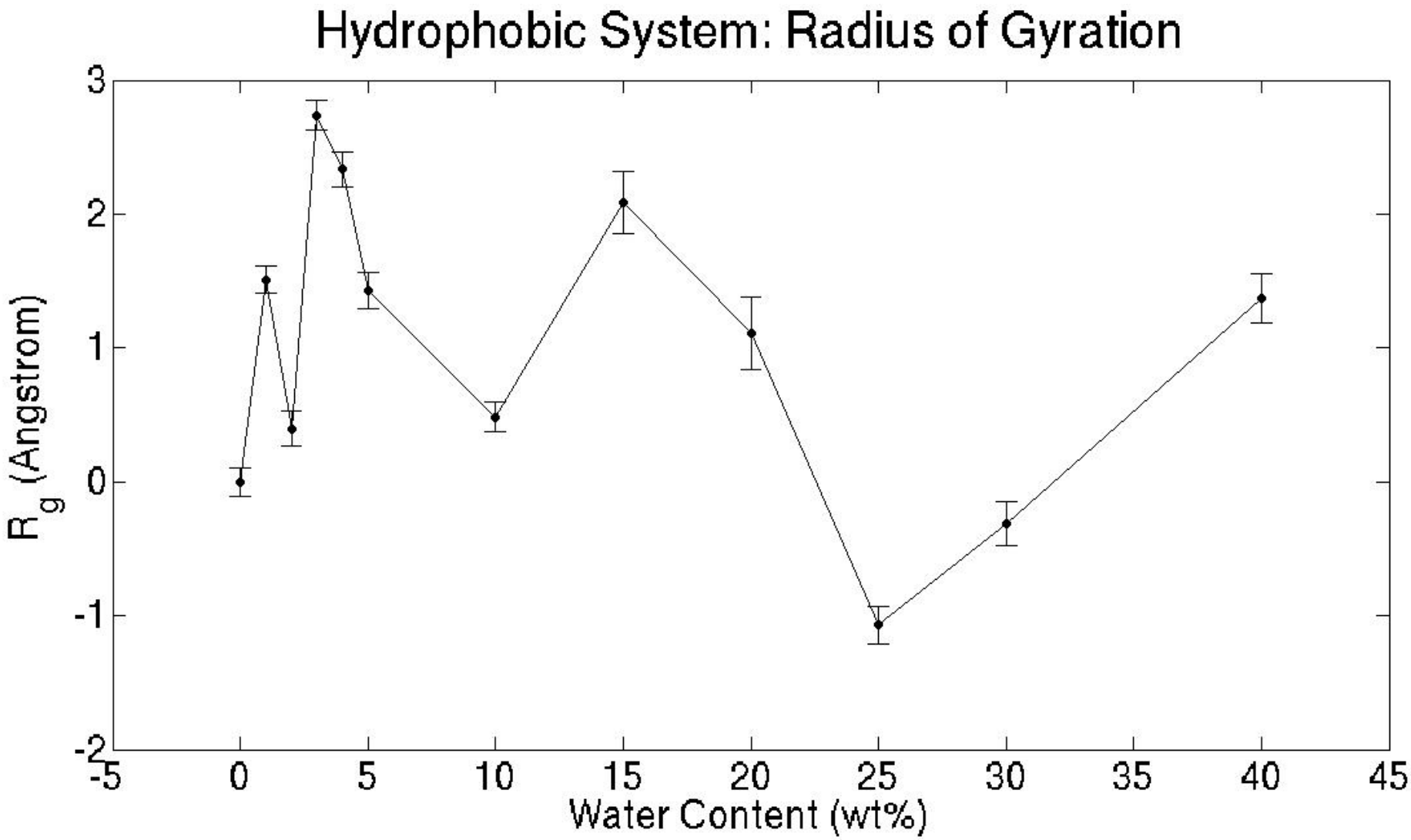
At higher water contents, density dominated by bulk-like water

# Same Figure, Zoomed in



# Radius of Gyration

- Equilibrate structures a further 1ns under NPT (constant number, pressure, temperature)
- Calculate average radius of gyration
- Should indicate degree to which polymer "hides" from water



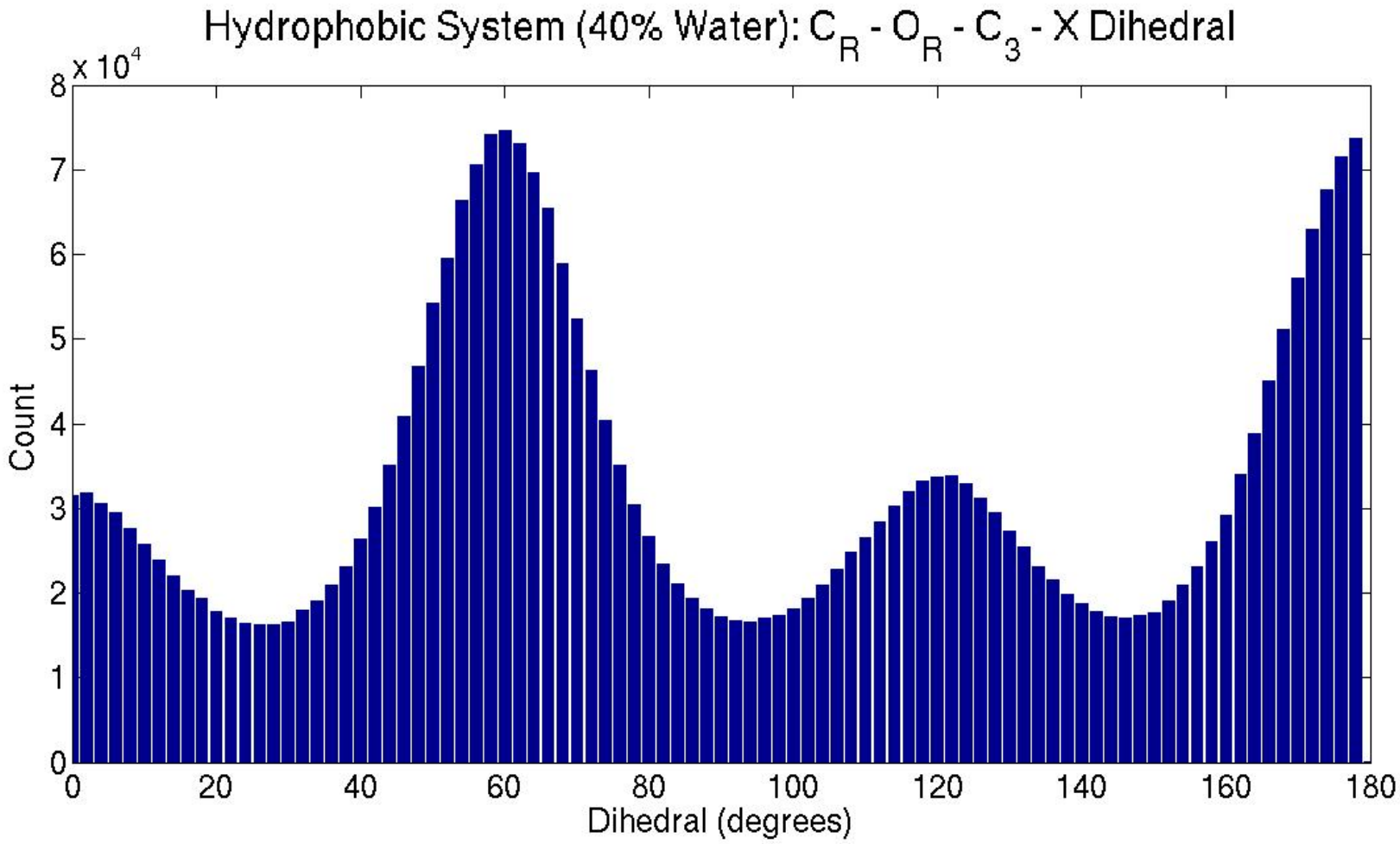

Consistent with density behavior. Polymer generally spreads out as system swells at low water content

# Glass Transition

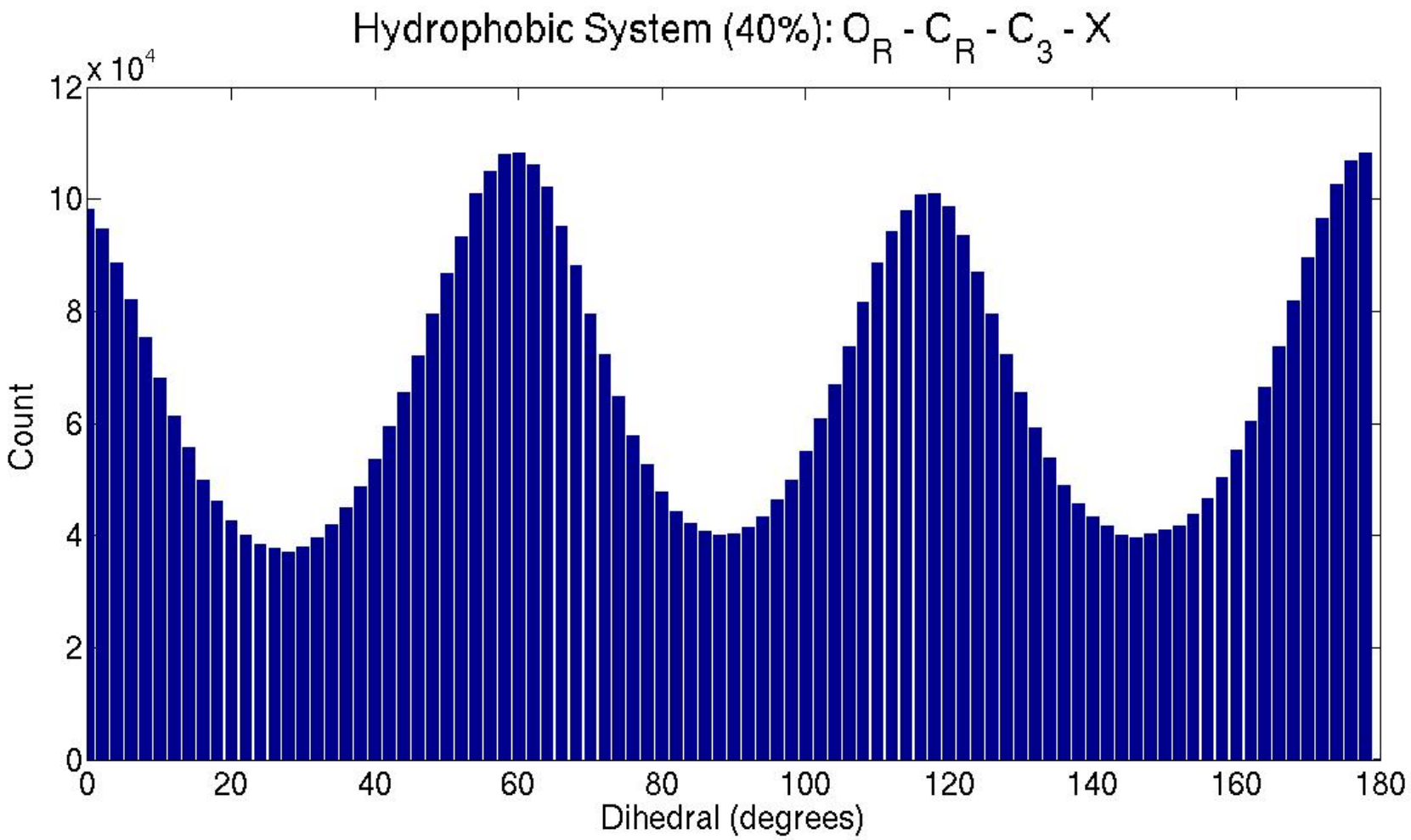
- Compute free energy, entropy, energy at various temperatures using 2PT ("Two-Phase Thermodynamics")
- Expect a "kink" at the glass transition temperature
- Heat system over 50ps
- Equilibrate 500ps, acquire data 100ps (5 snapshots at 20ps intervals)
- (These equilibrations too short, only a demonstration. Do ~1ns for better data)

# Dihedrals

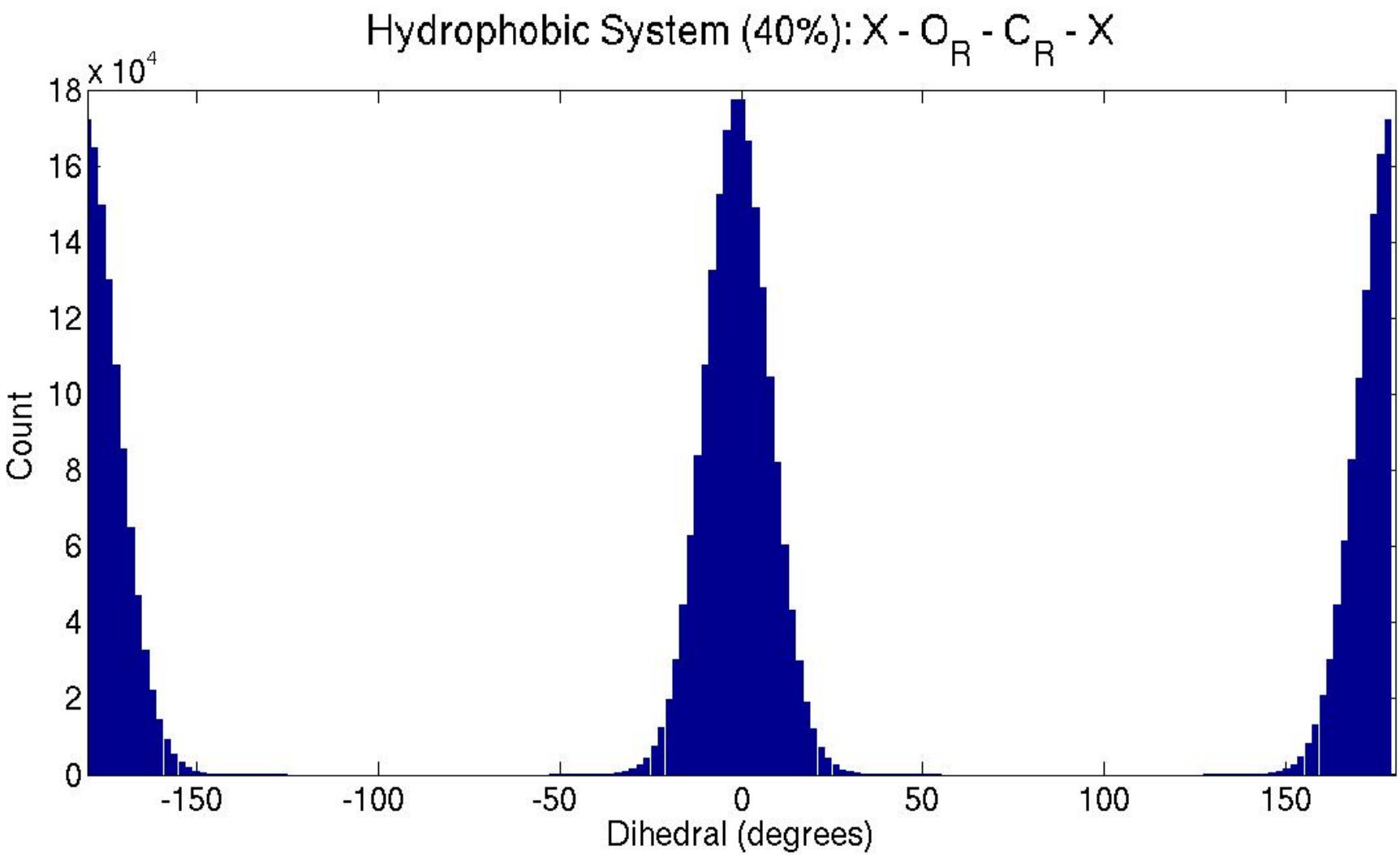
- Distribution of dihedrals in the structure could give insight into structural changes in the polymer with the addition of water
- Will compare dry polymer to polymer with 40 wt% water (calculation for dry polymer still running)
- Statistics of dihedrals also inform the coarse-graining process



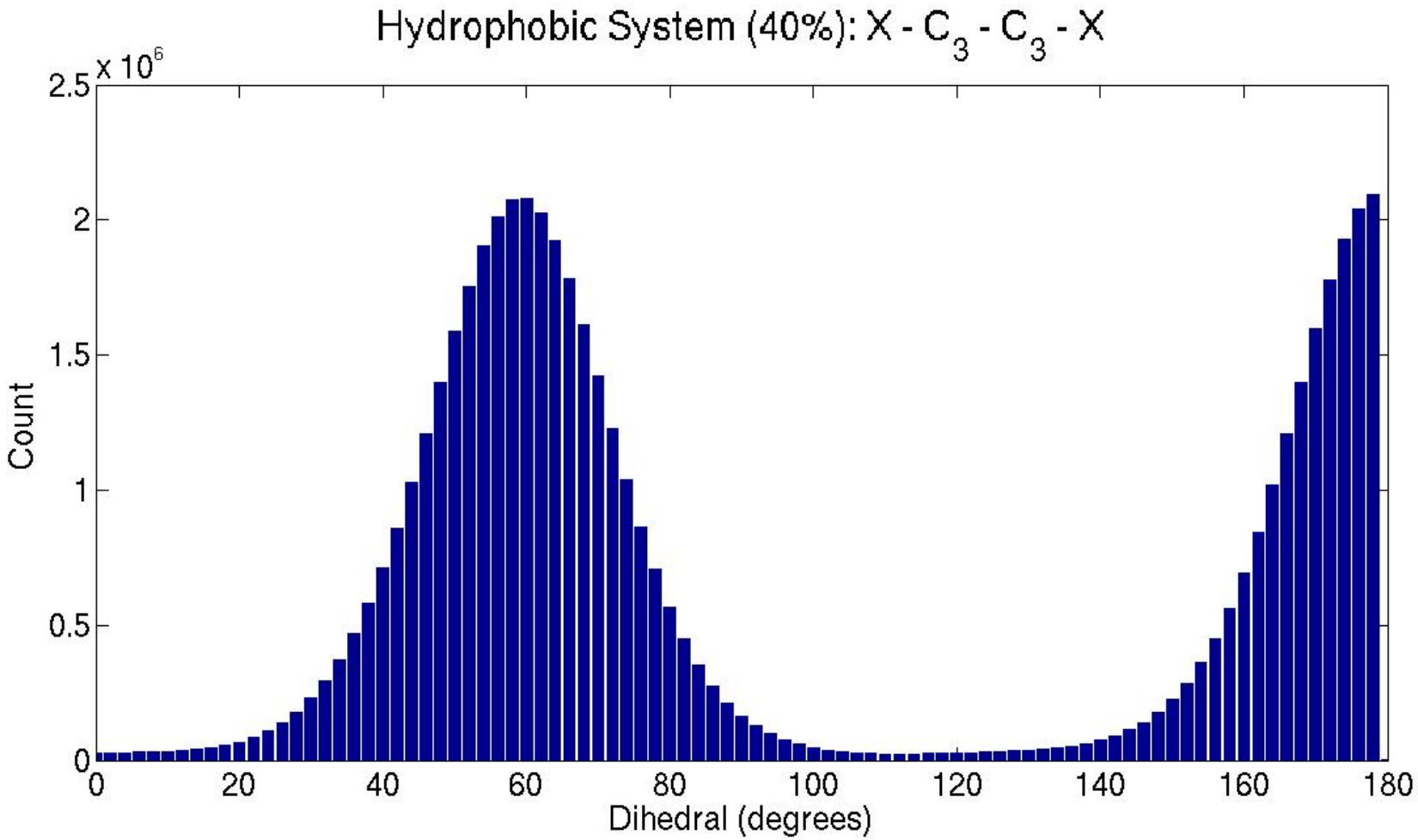

~60 degrees most probable, ~120 degrees less likely.
Somewhat rigid dihedral




Like CR-OR-C3-X, but “floppier”. ~60 and ~120 almost equally probably


Hydrophobic System (40%): X - O_R - C_R - X
x 10^4
18
16
14
12
10
8
6
4
2
0
Count
-150
-100
-50
0
50
100
150
Dihedral (degrees)

Very rigid.



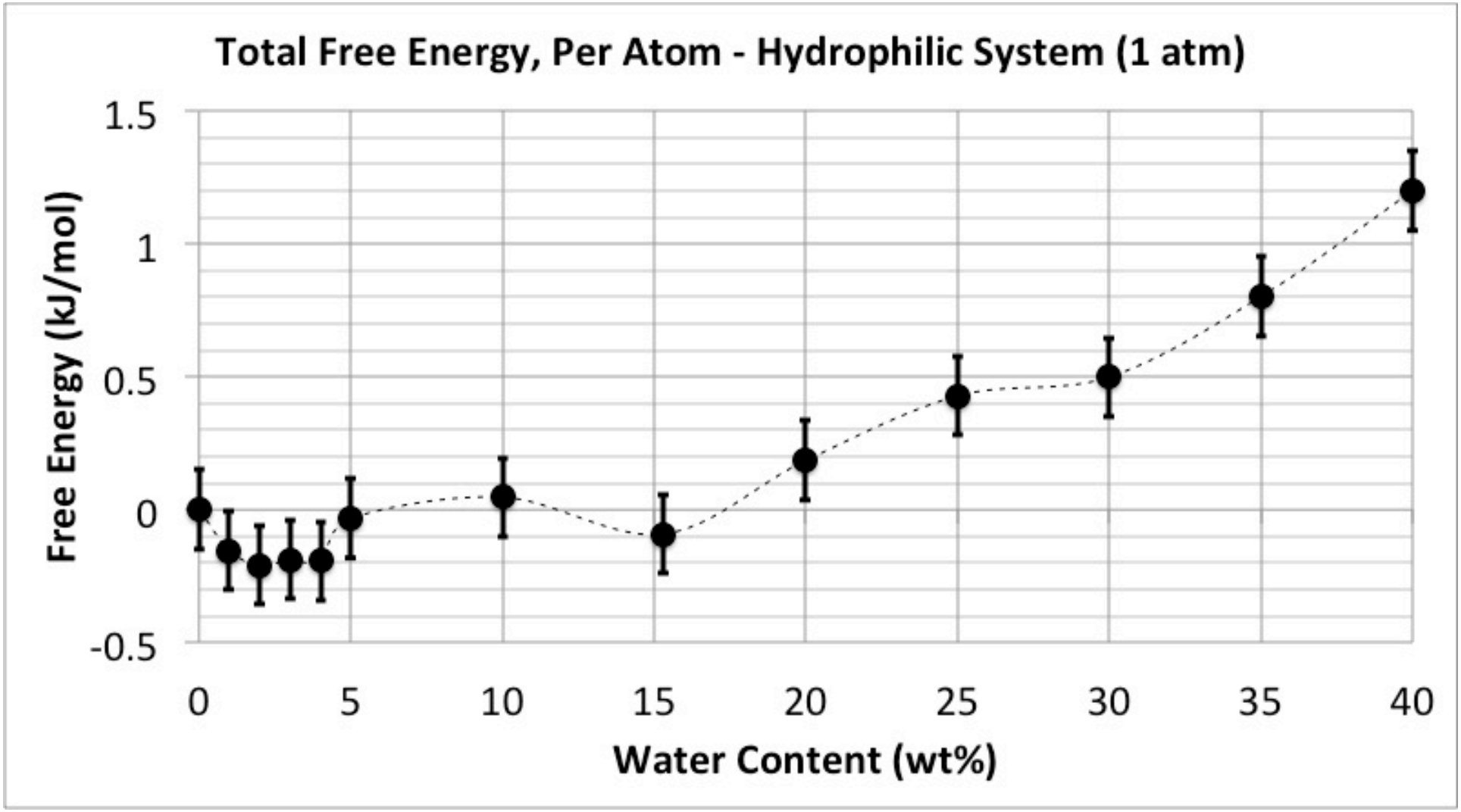

Backbone carbons (C3-C3) prefer 60 or 180

**General Description:**

**Hydrophilic System Composition**
DREIDING Polymer, F3C Water
Lennard-Jones, fixed partial charge, hydrogen-bonding between MMA* and water

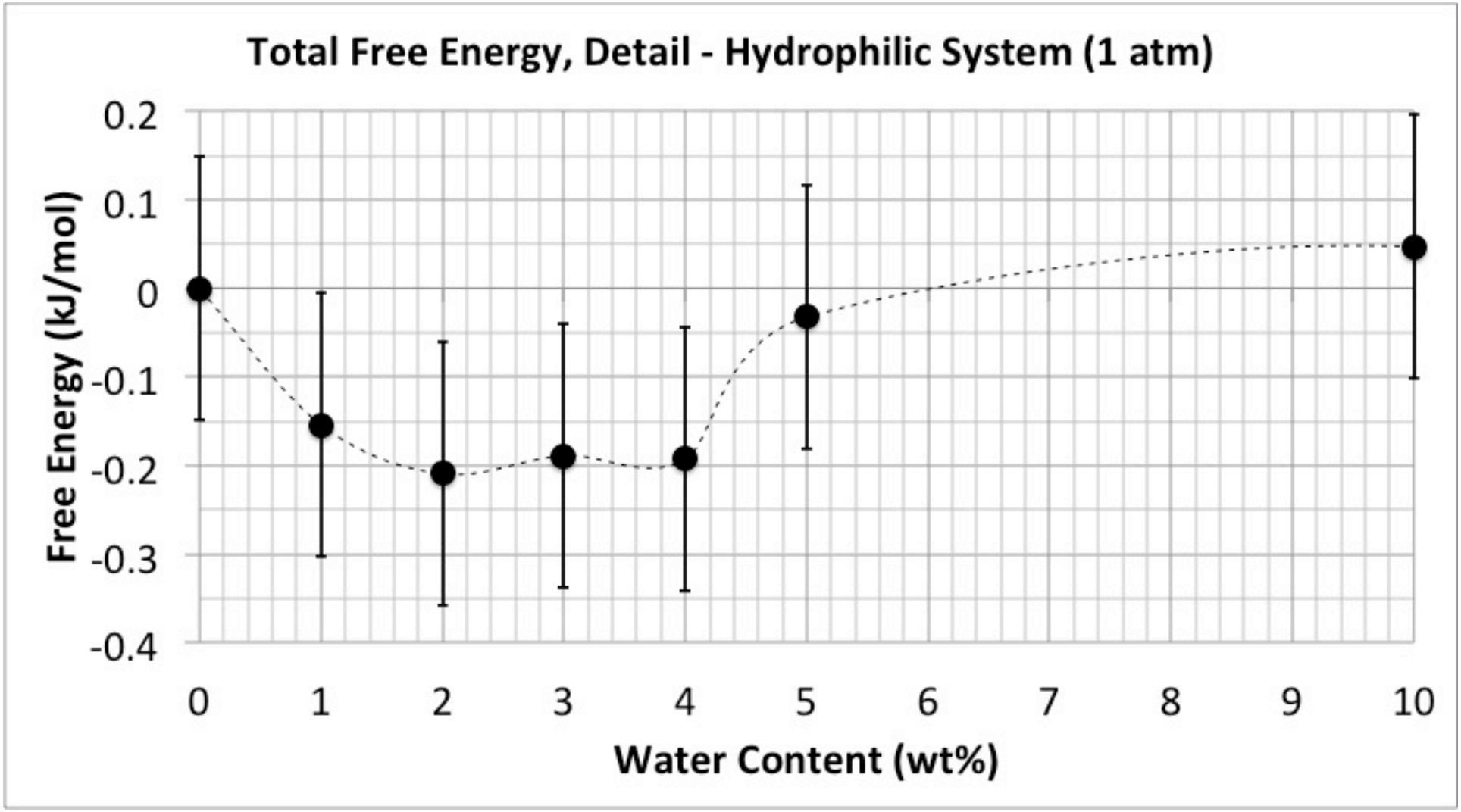
2PT data gathered for 20ps at 4fs intervals, NVT @ 300K
9163 polymer atoms

**Thermodyanmic References:**
**Entropy Reference** – Bulk Water (F3C => 62.18 J/mol K), Vacuum Polymer
**Internal Energy Reference** – Bulk Water (F3C => 6.5180 kJ/mol]), Vacuum Polymer
**Free Energy Reference** – Bulk Water (F3C => -12.0689), Vacuum Polymer

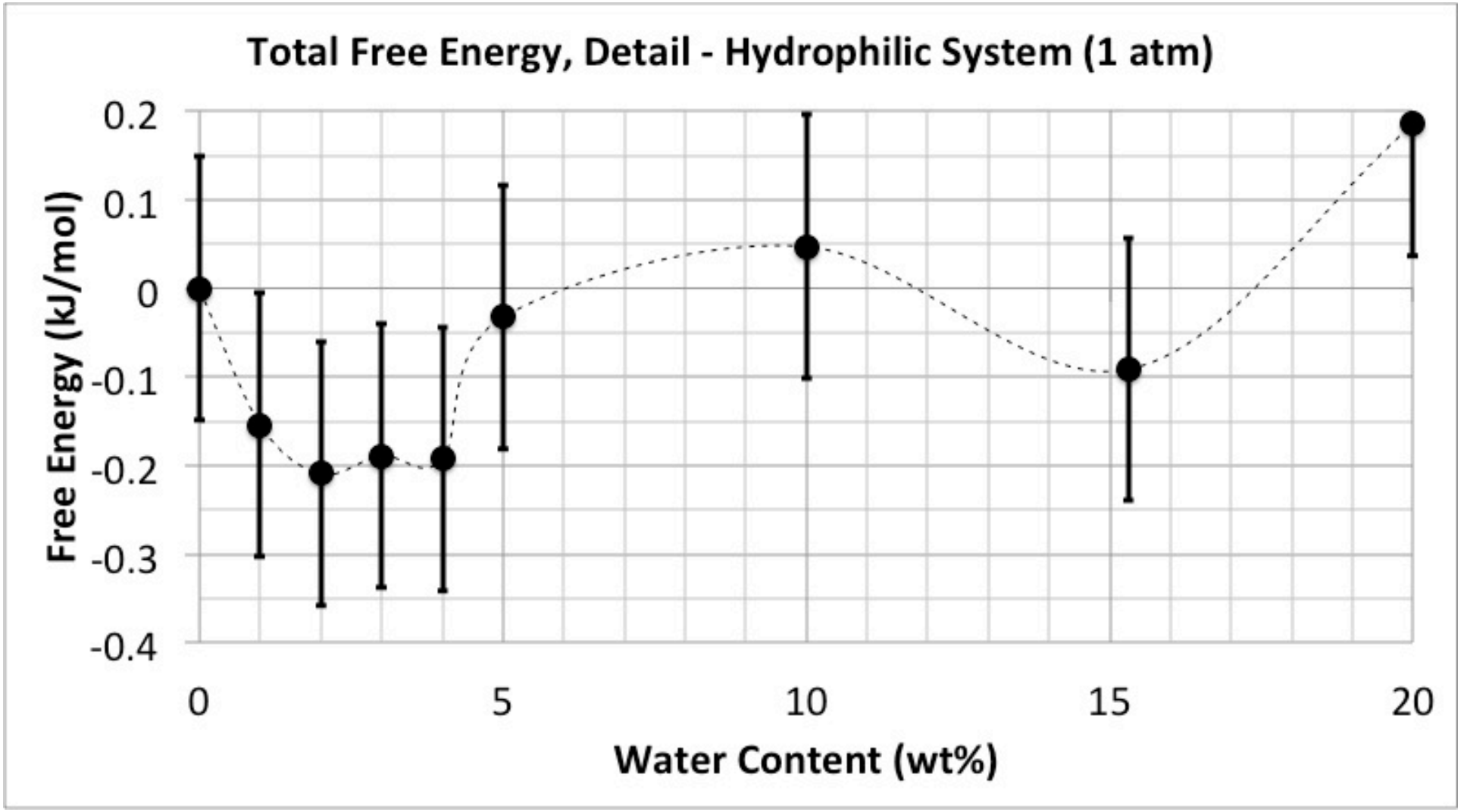



Free energy profile of the system. Generally with increasing water, there is an unfavorable increase in free energy, but there are local minima slightly below 5wt% and again at 15wt%.

This suggests that though generally resistant to water, the polymer-water system is fraught with locally stable metastates, that undermine the resistance of the system.



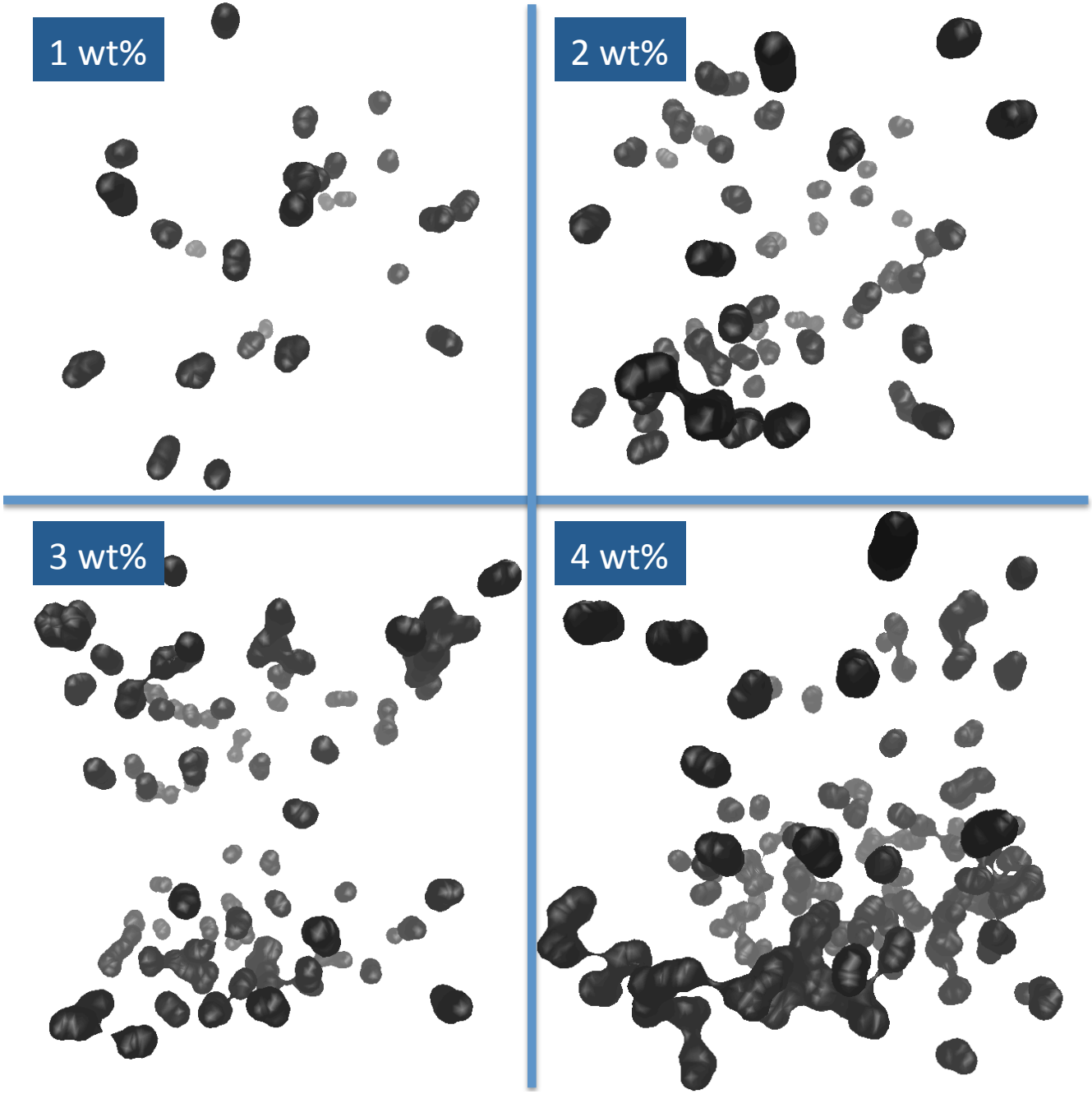

Free energy profile of the system, low water content detail. This highlights the local minima slightly below 5wt%, Below 5w% uncertainty makes it difficult to pinpoint a specific energy minimum, but it is clear that completely dry polymer readily takes on water, until approaching a barrier.




Free energy profile of the system, low water content detail. This highlights the local minima slightly below 5wt% and again at 15wt%. While there is a barrier to water absorption above 4 wt%, this is undermined by a higher water content energy minimum.

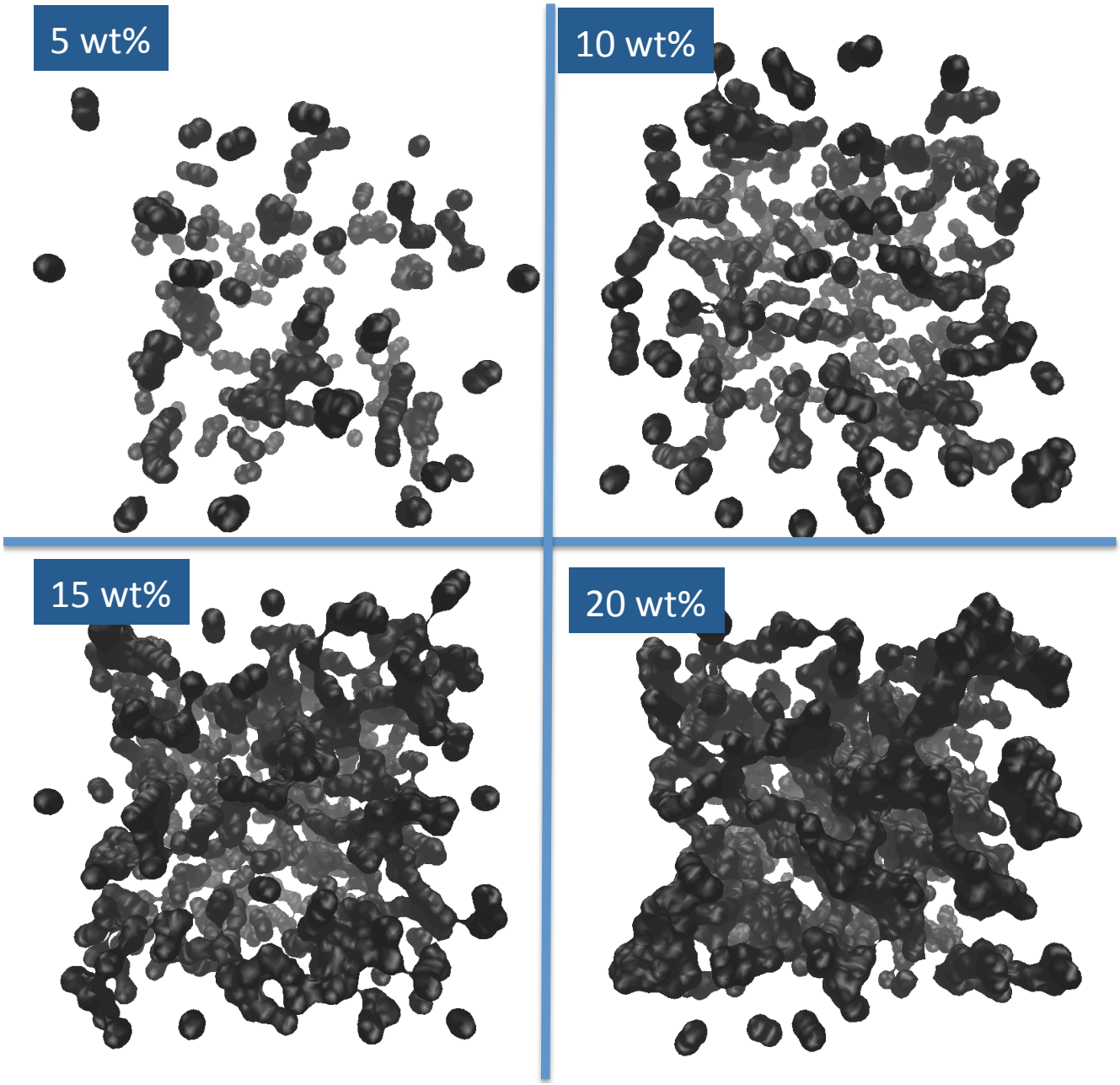
There is evidence to suggest this stabilizes a state of percolation, severely reducing effectiveness as a water barrier.

# Surface Representation of Water in Hydrophilic System




Low water content systems initially exhibit dispersed water molecules. Adding water causes "clumping" an anisotropic distribution of molecules, which becomes most pronounced at the energy barrier seen in the free energy profile.

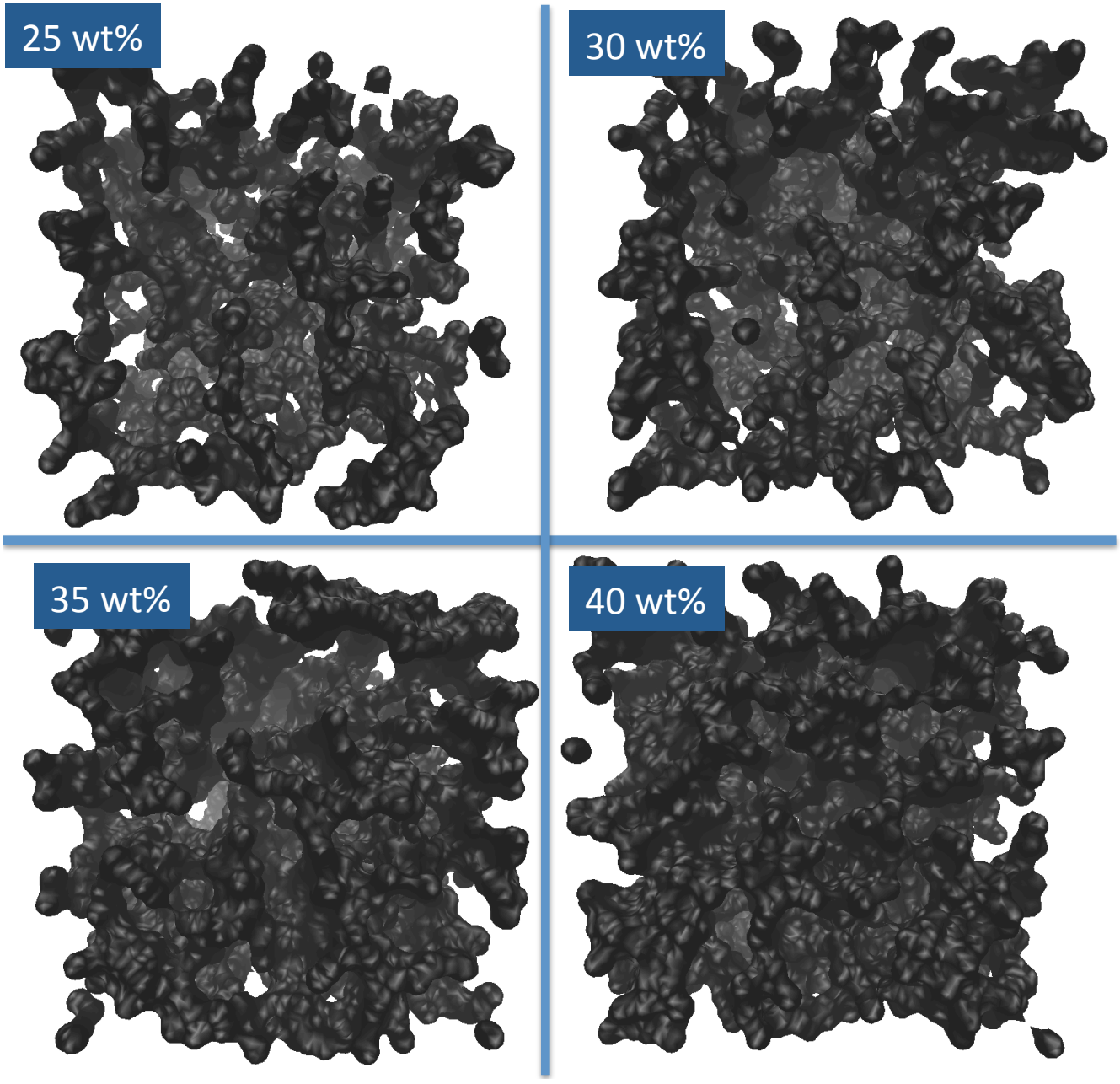
# Surface Representation of Water in Hydrophilic System



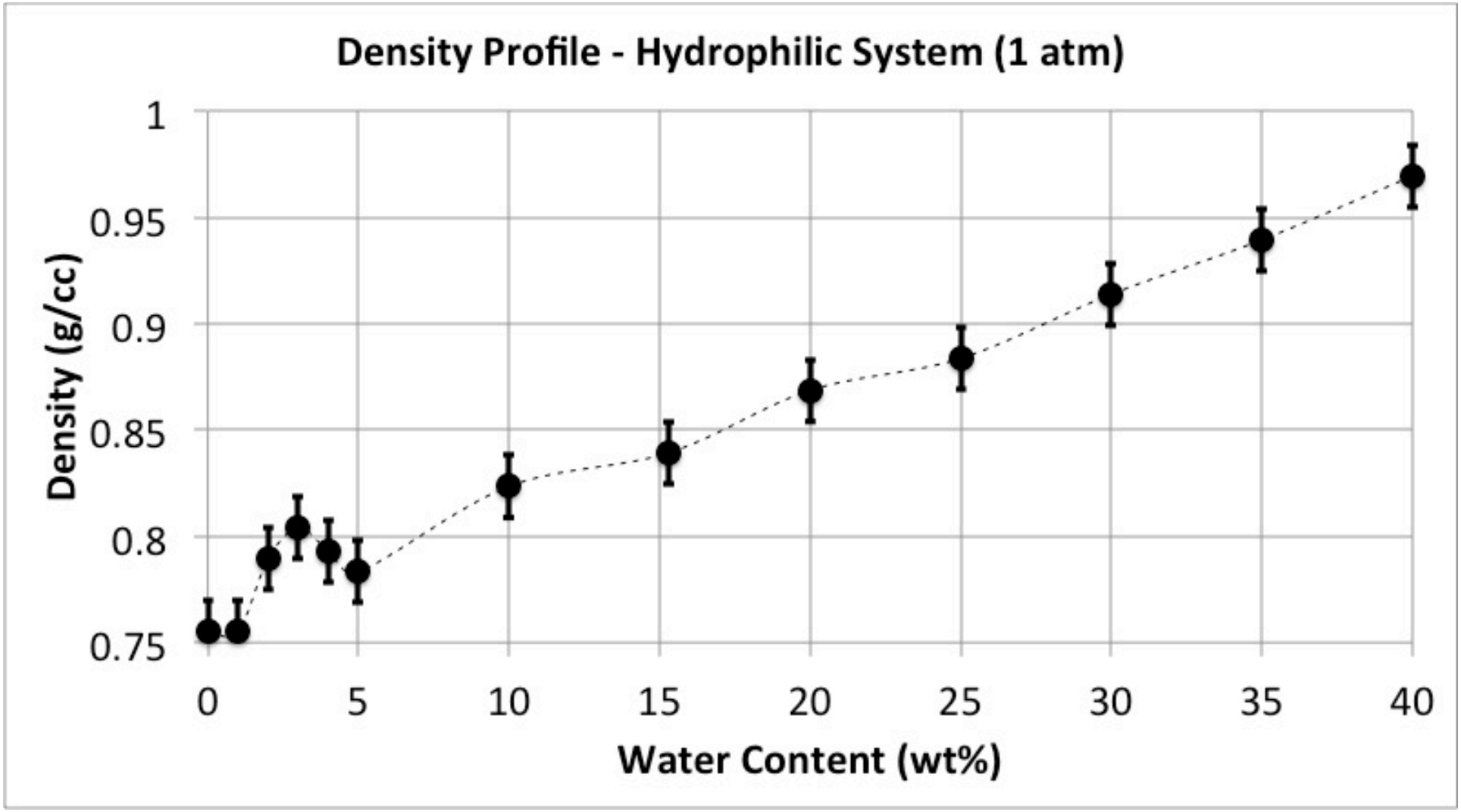

After crossing the first barrier, the water molecules again become dispersed, but now are not isolated as single water molecules.

Additional waters find their way near existing water molecules, but the system is not as capable of anisotropic "clumping". Eventually, the water regions begin to touch, which may be the source of the minimum seen in the free energy profile.

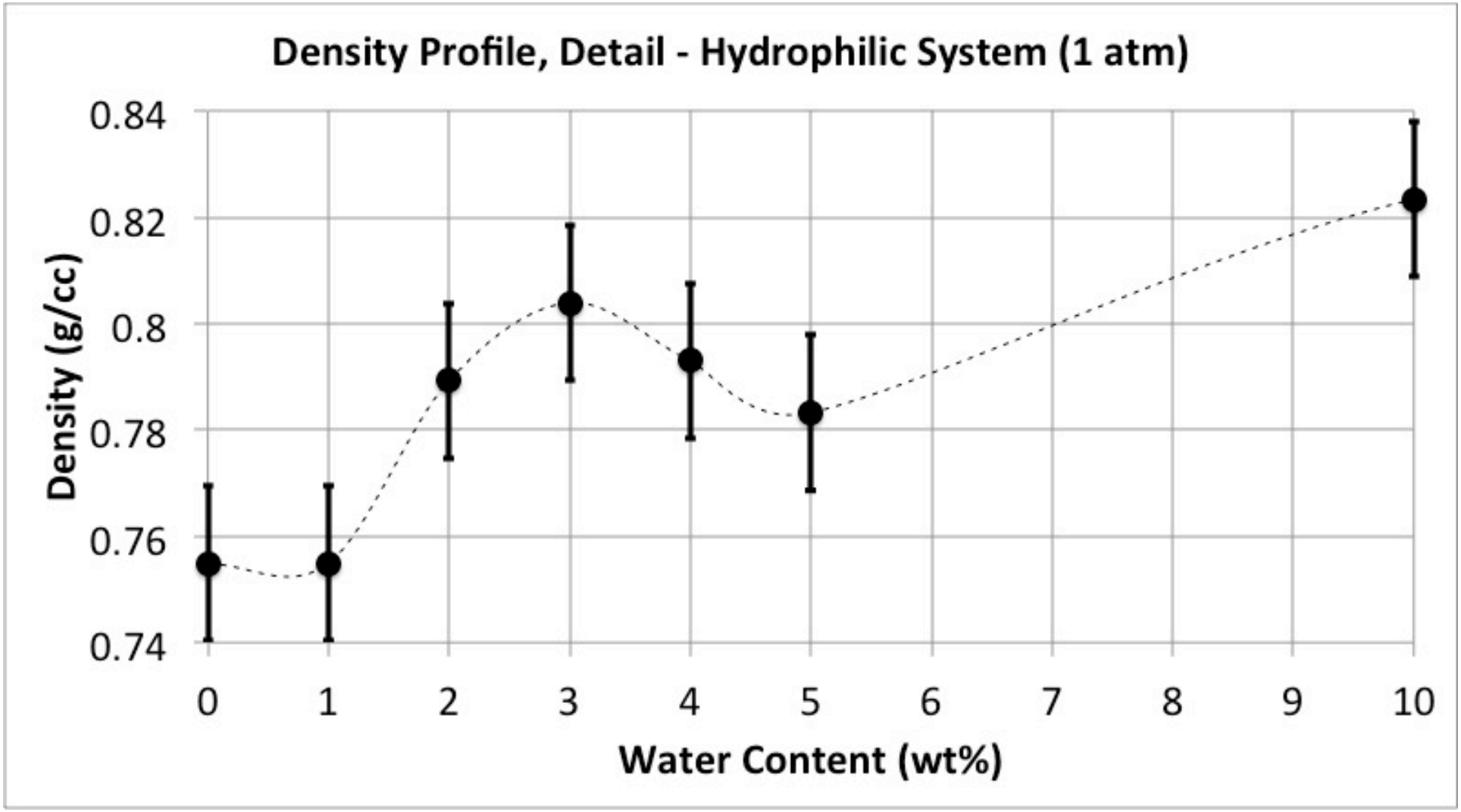
# Surface Representation of Water in Hydrophilic System



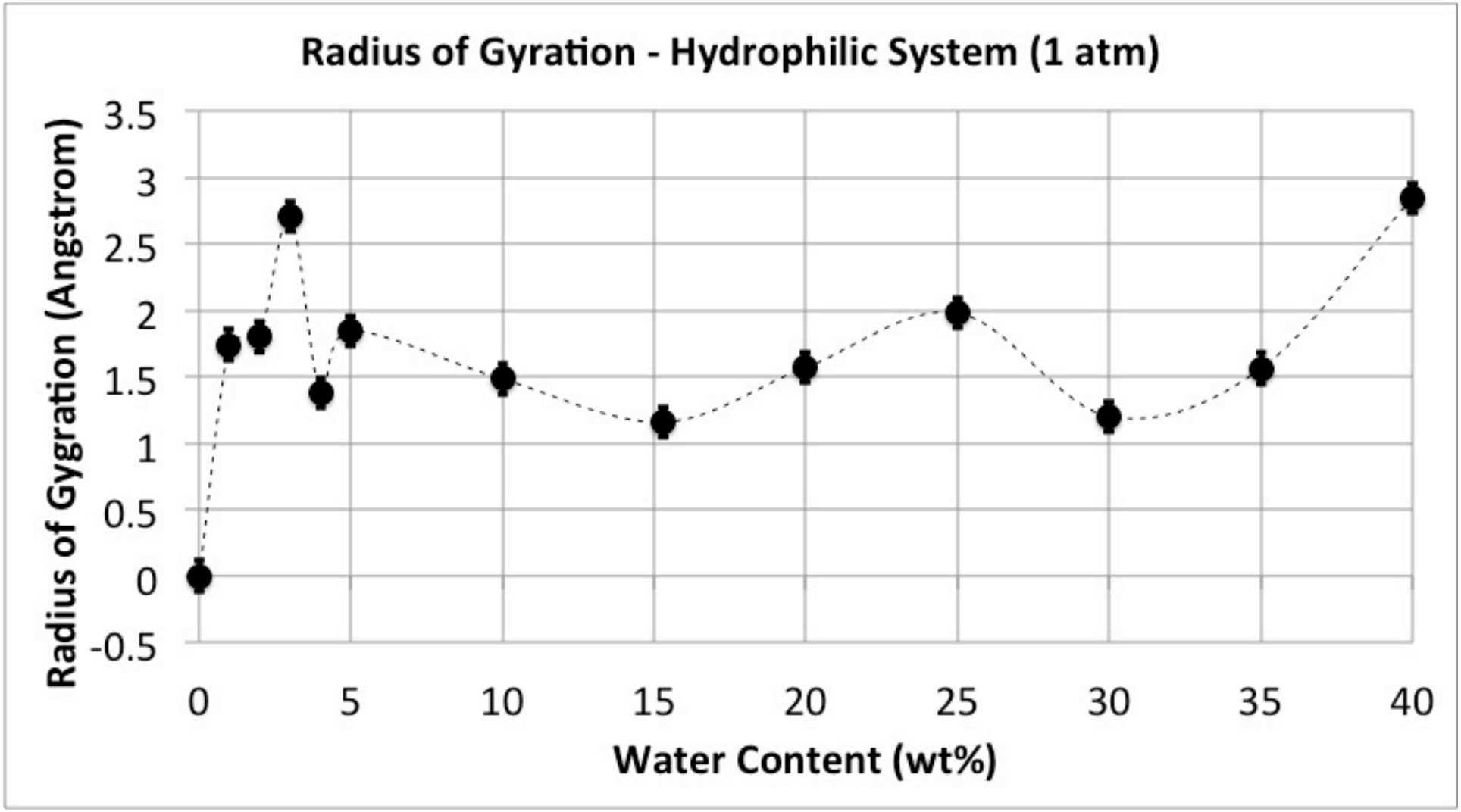

Eventually, the water regions go from touching to merging into one unified region…. These water channels are responsible for percolation and the failure of the film as a barrier to water.



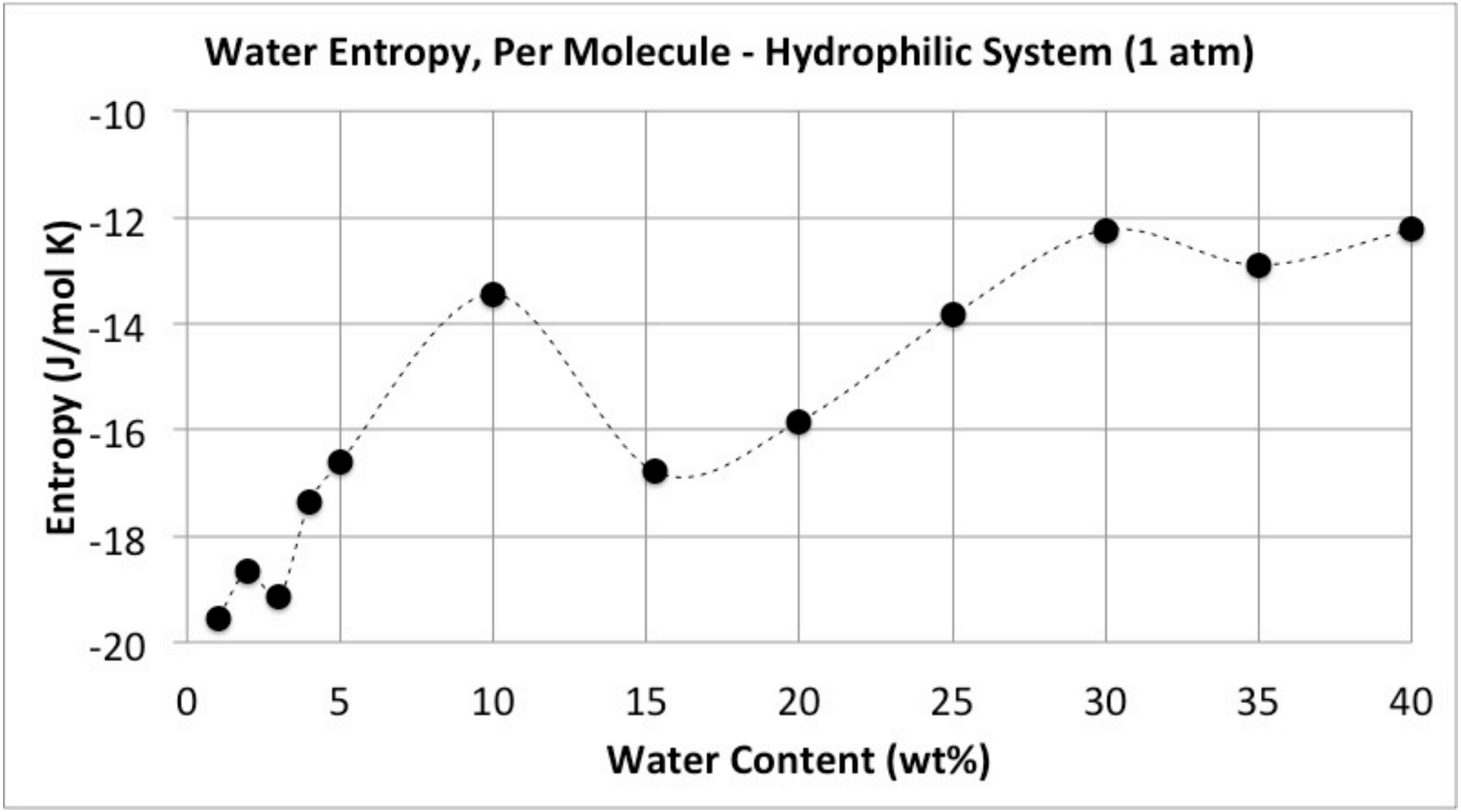

Hydrophilic density profile. For low water content, water polymer interactions lead to increased density, but the general trend is toward bulk water density with increasing water content.



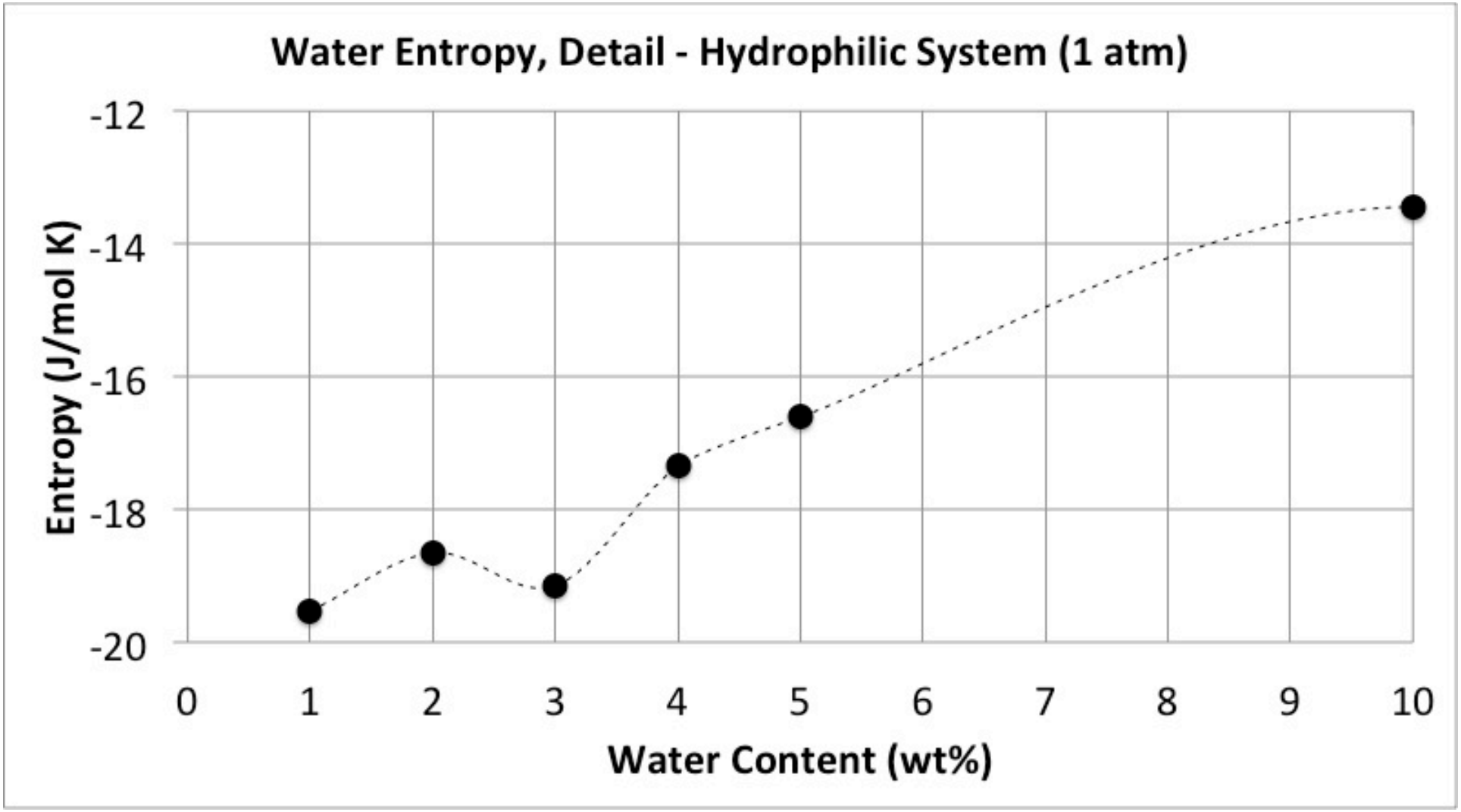

Hydrophilic density profile, low water content detail. For low water content, water polymer interactions lead to a density local maximum, indicating a possible favorable energy minimum. For increasing water content, the density approaches bulk water density.



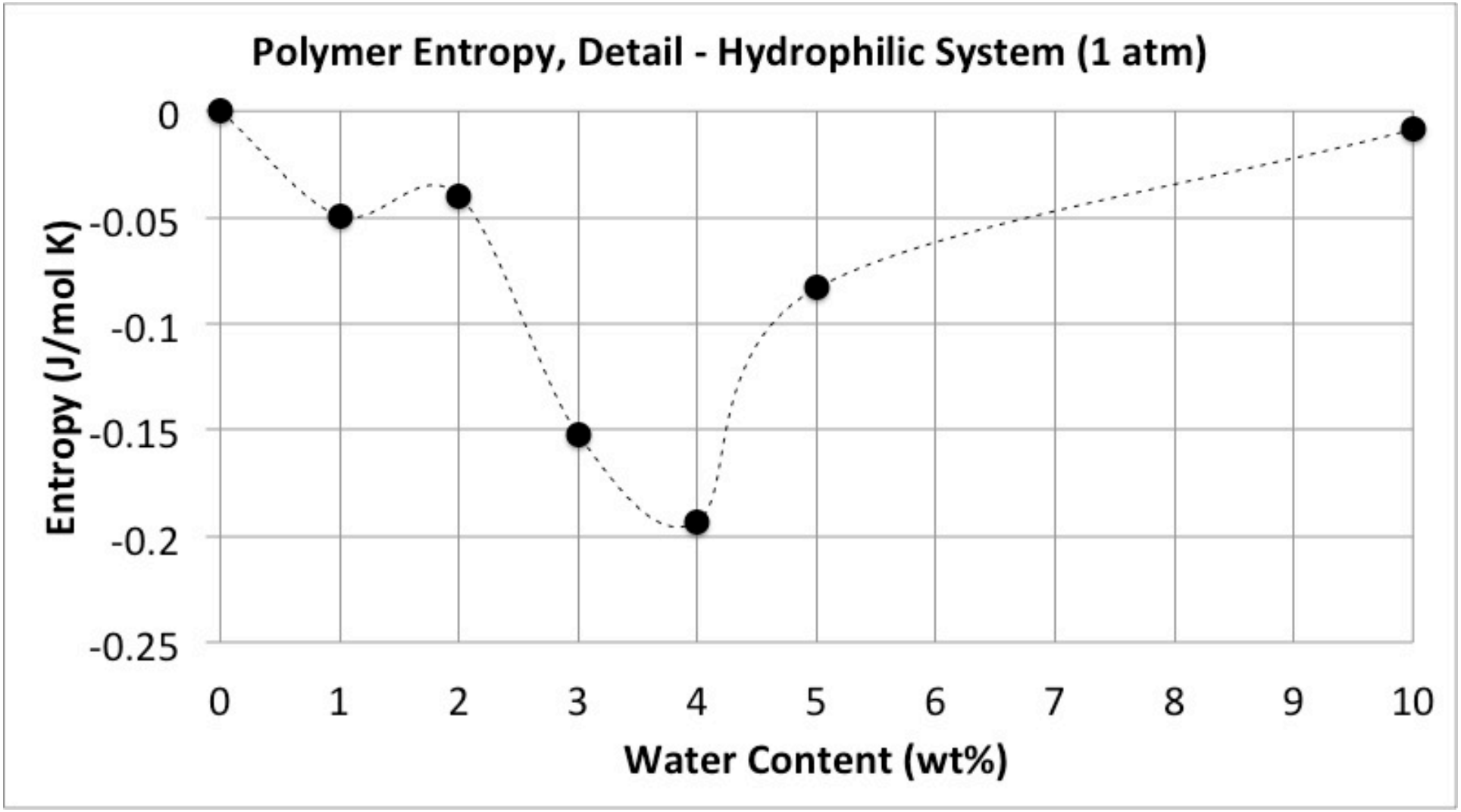

Polymer radius of gyration relative to the vacuum system. Less informative about the energy than the density, but notice the steep decrease after 3wt%, which indicates a structural change in the polymer.



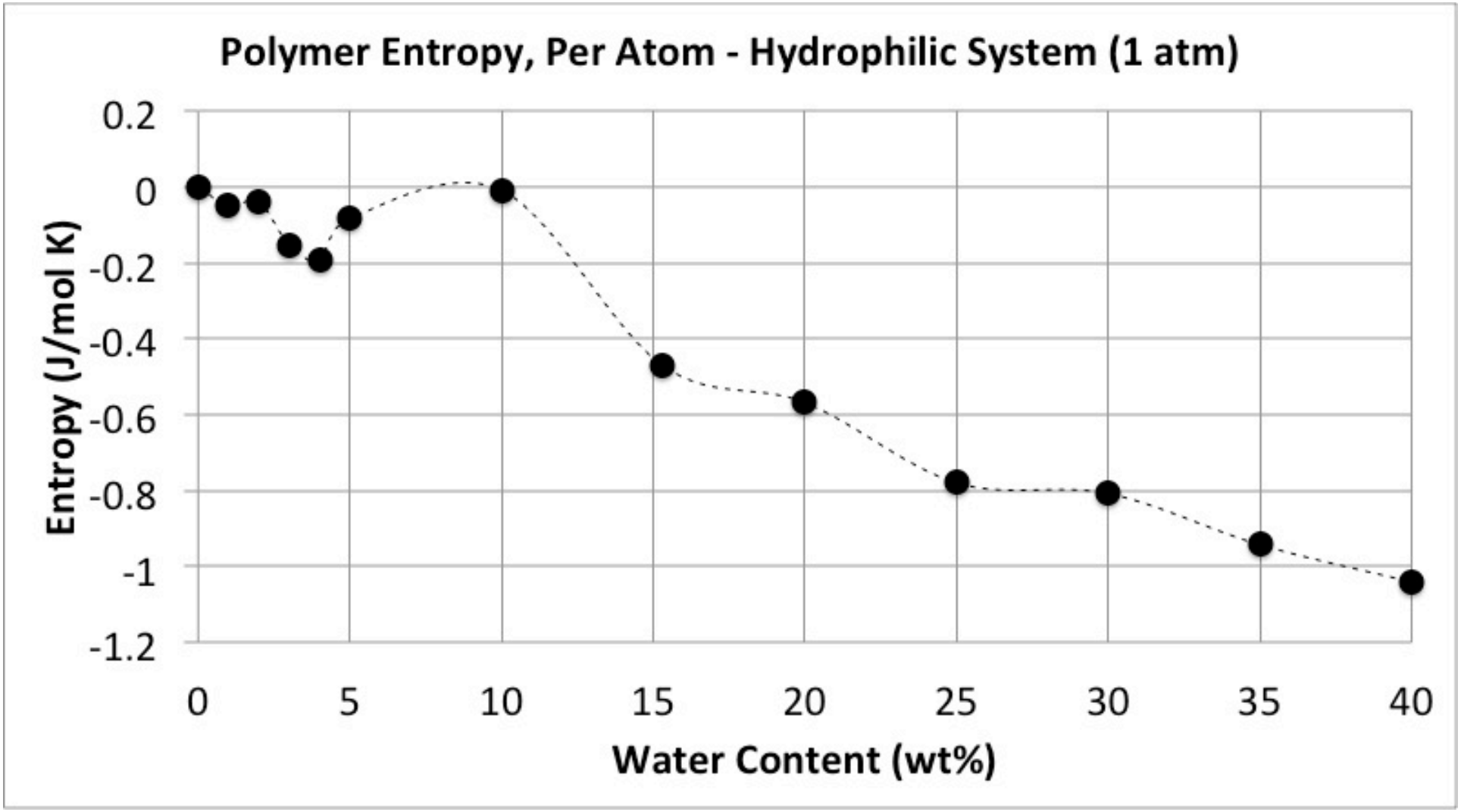

Entropy profile of water. At low water content, the waters are adsorbed to the polymer and have relatively low entropy. As water content increases, the entropy approaches bulk water (here set to 0). Notice the minima at 3 wt% and ~15 wt% which show an interaction other than the general trend.



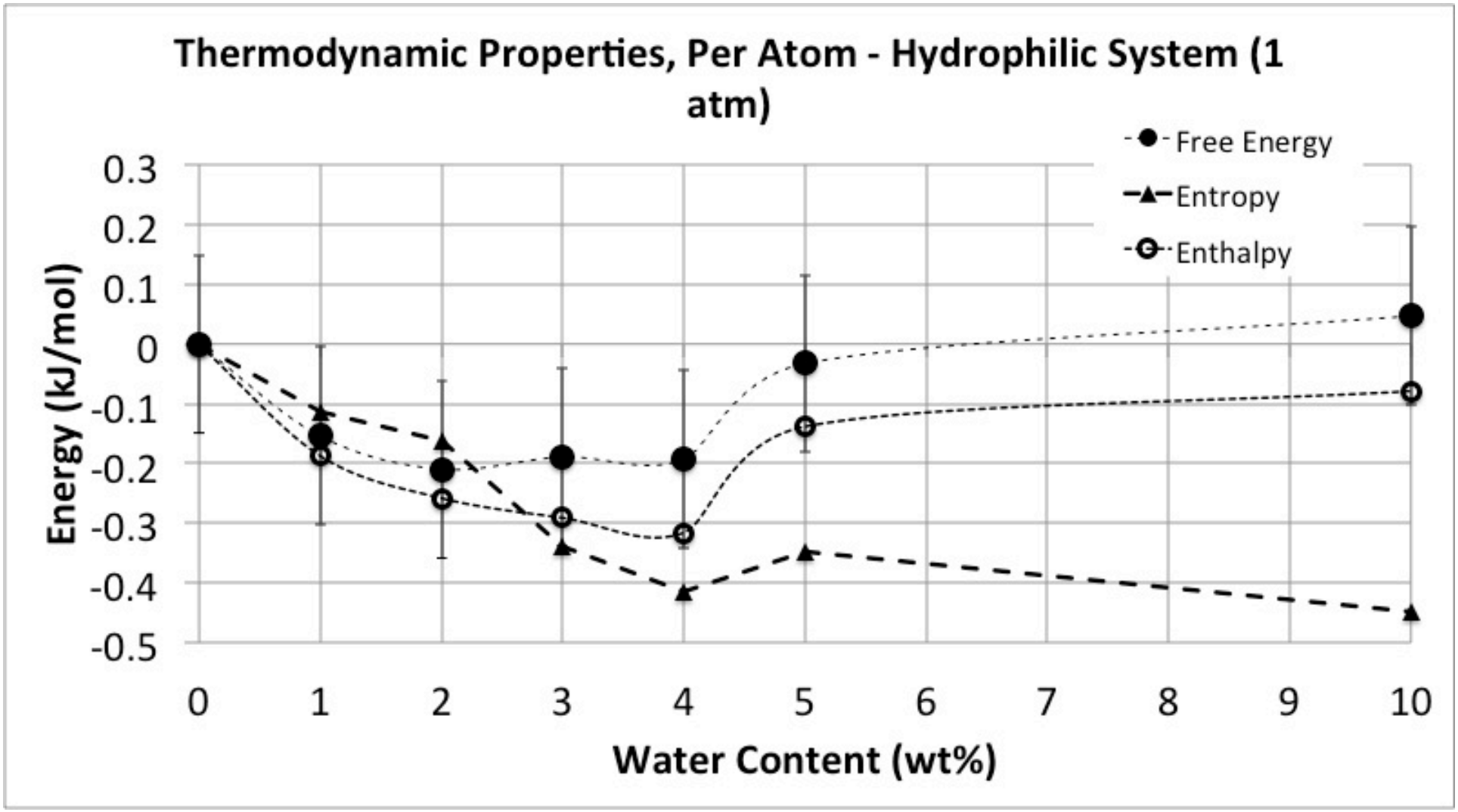

Entropy profile of water, low water content detail. At low water content, the waters are adsorbed to the polymer and have relatively low entropy. As water content increases, the entropy approaches bulk water (here set to 0). Notice the minimum at 3 wt% which shows an interaction other than the general trend.



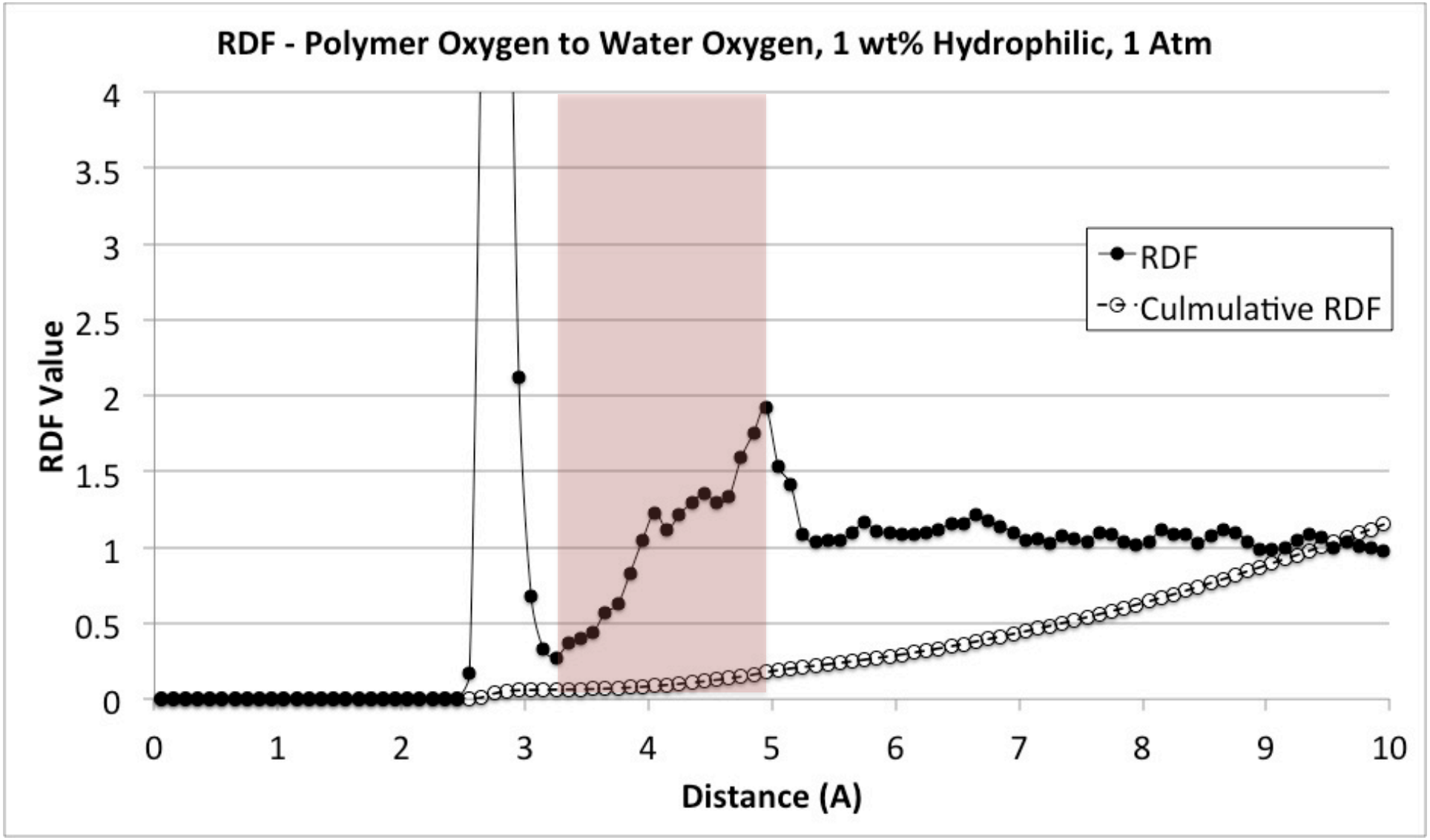

Entropy profile of the polymer, detail of low water content. There is a clear minimum at 4 wt%. This is different than the entropy minimum at 3wt% for water molecules.

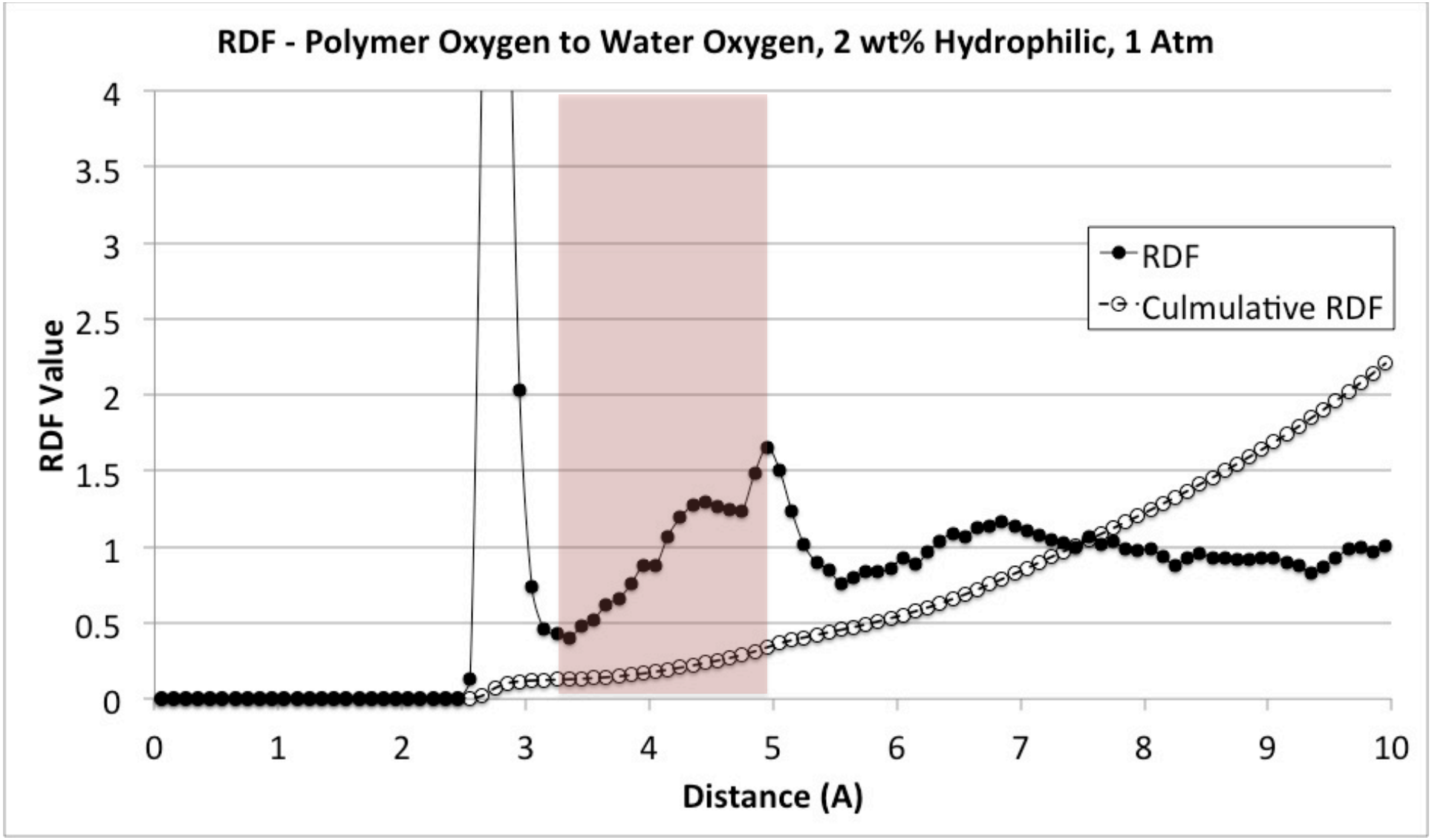


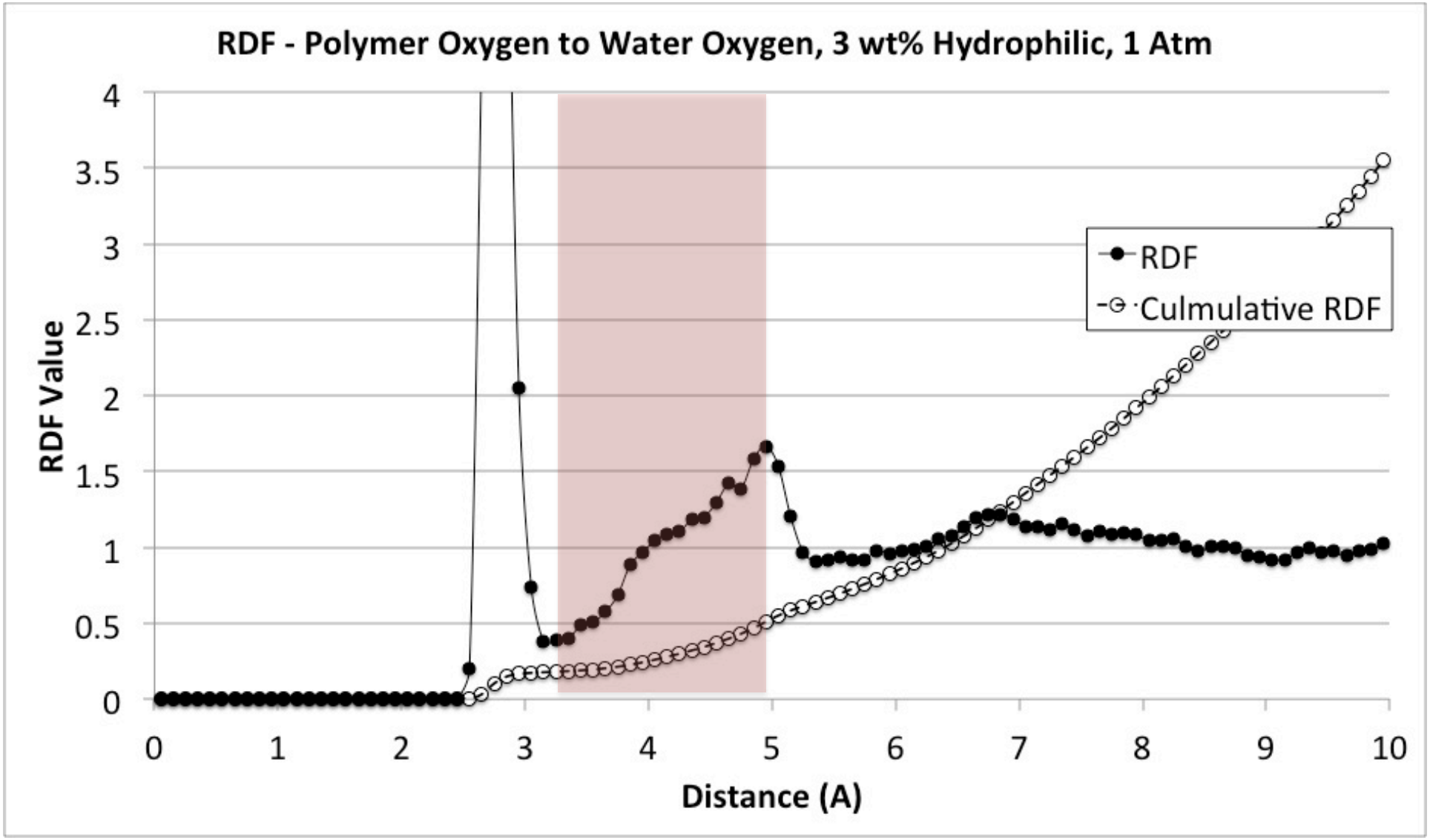

Entropy profile of the polymer. The entropy of the vacuum polymer has been set to zero for reference. Overall there is a trend of decreasing entropy with increasing water content. Notice the minimum at 4 wt% which shows an interaction other than the general trend.

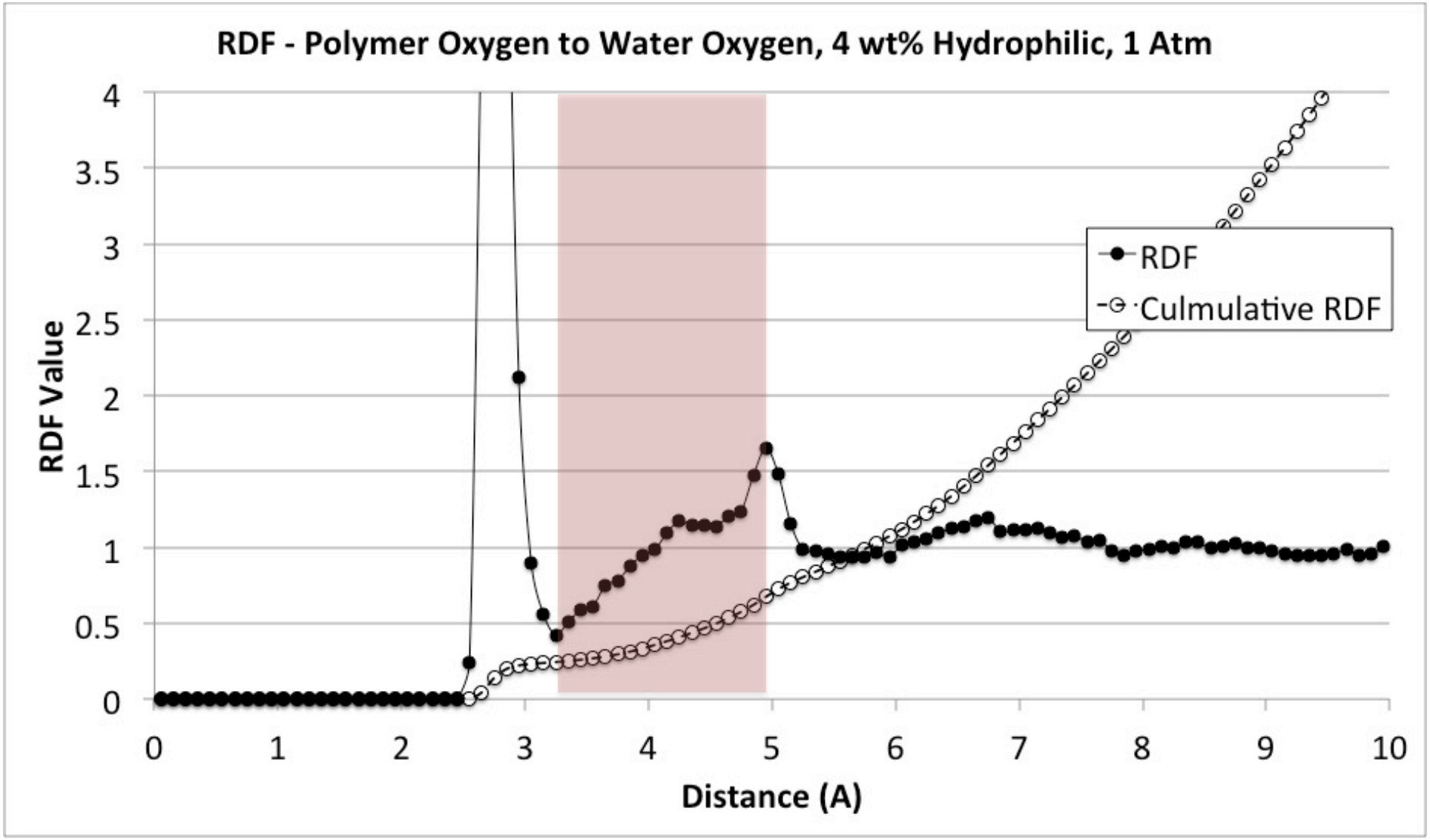


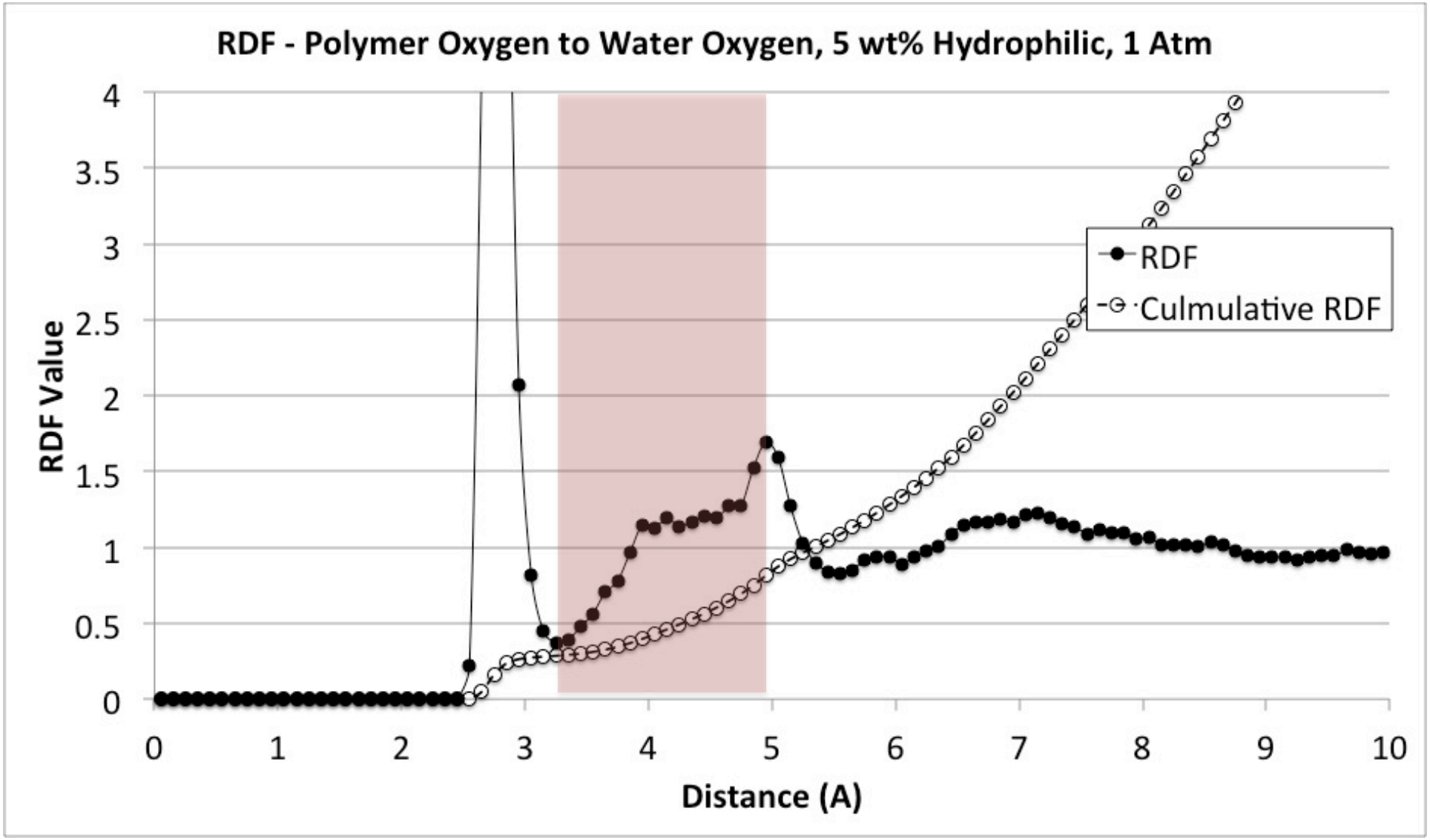

Total thermodyanmic profile. The overall trend of the free energy curve is dominated by the enthalpy curve, but the shape is influenced slightly by entropy.

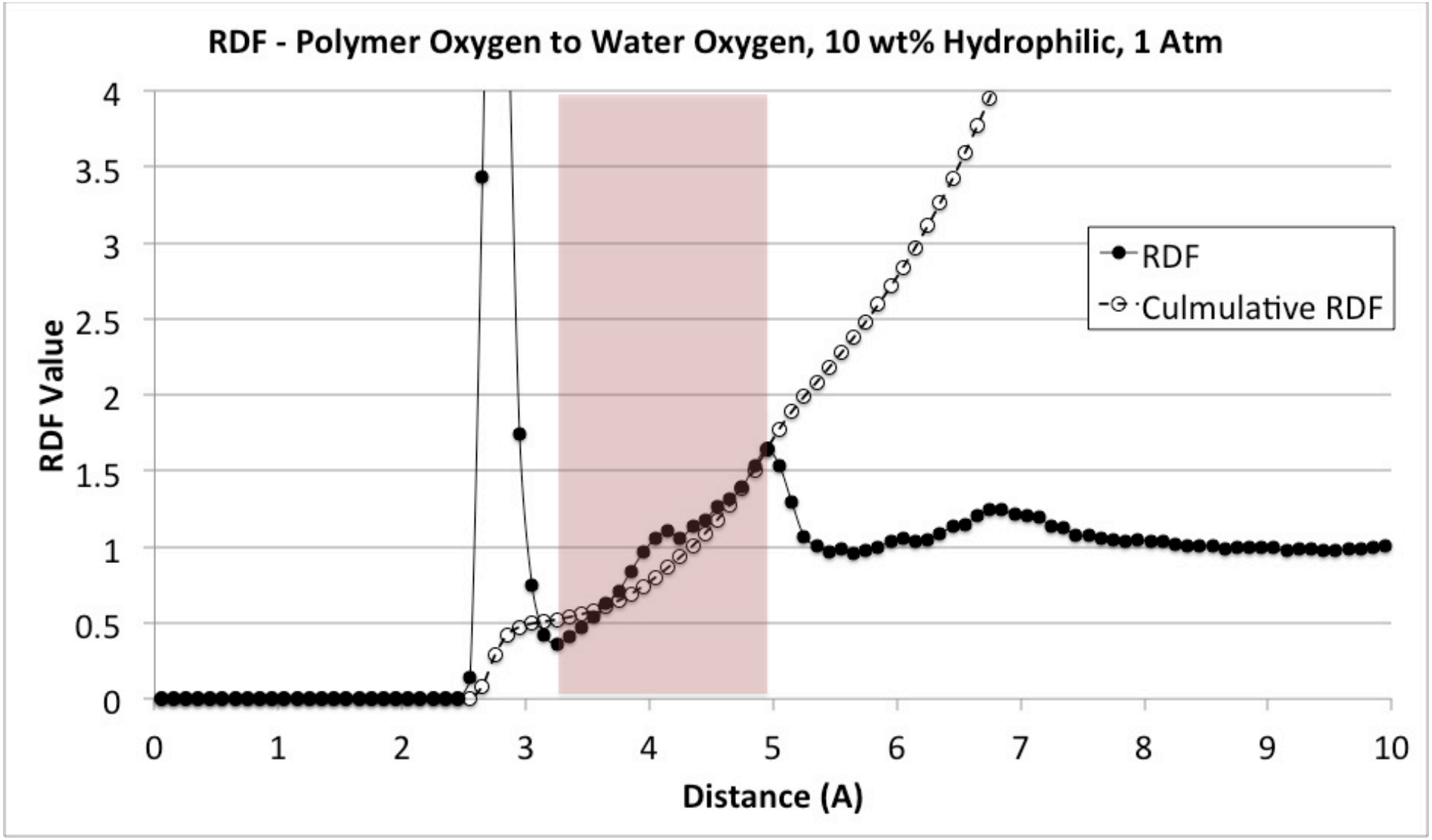

RDF - Polymer Oxygen to Water Oxygen, 1 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
2
3
4
5
6
7
8
9
10

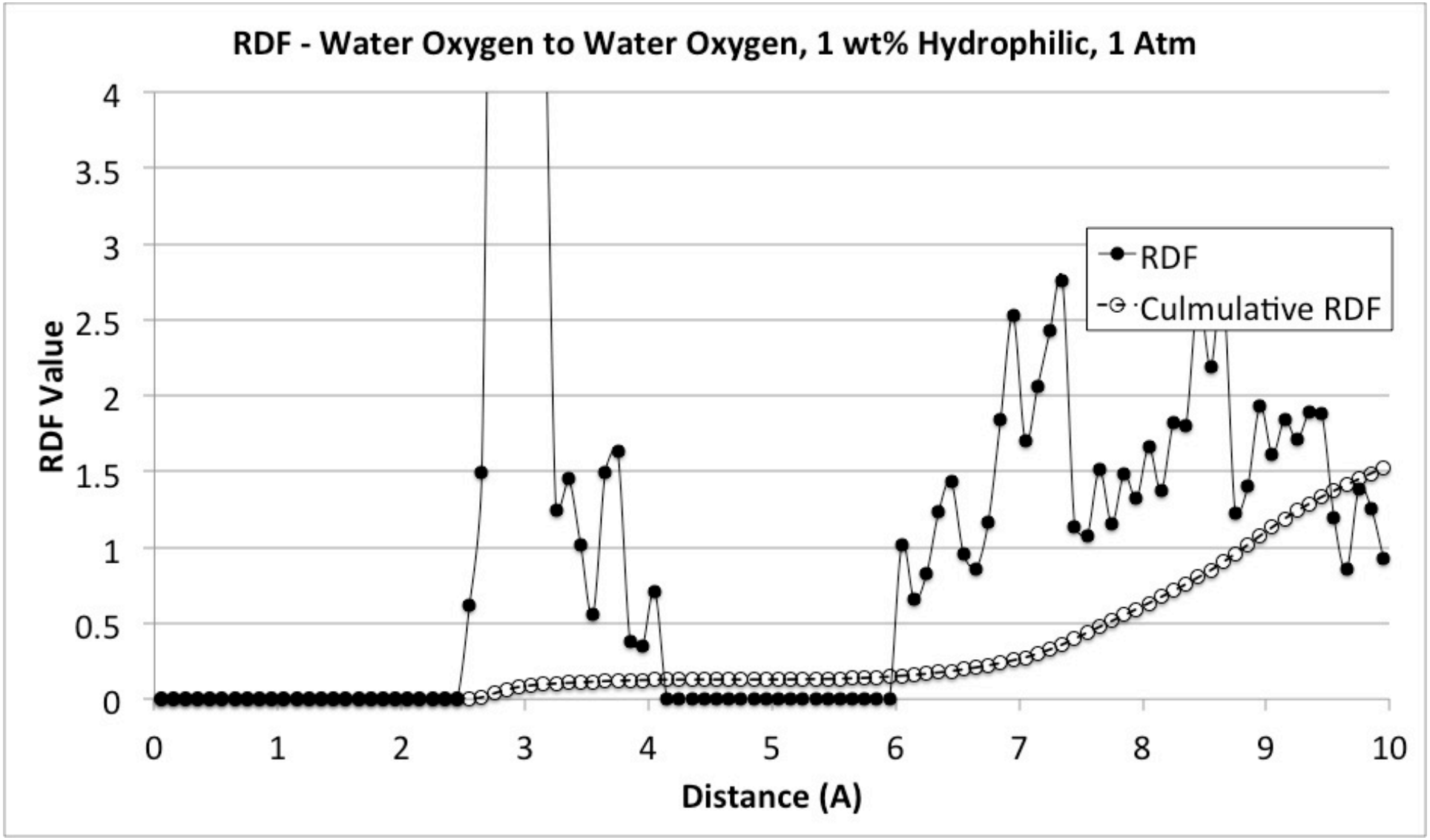

RDF - Polymer Oxygen to Water Oxygen, 2 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
2
3
4
5
6
7
8
9
10

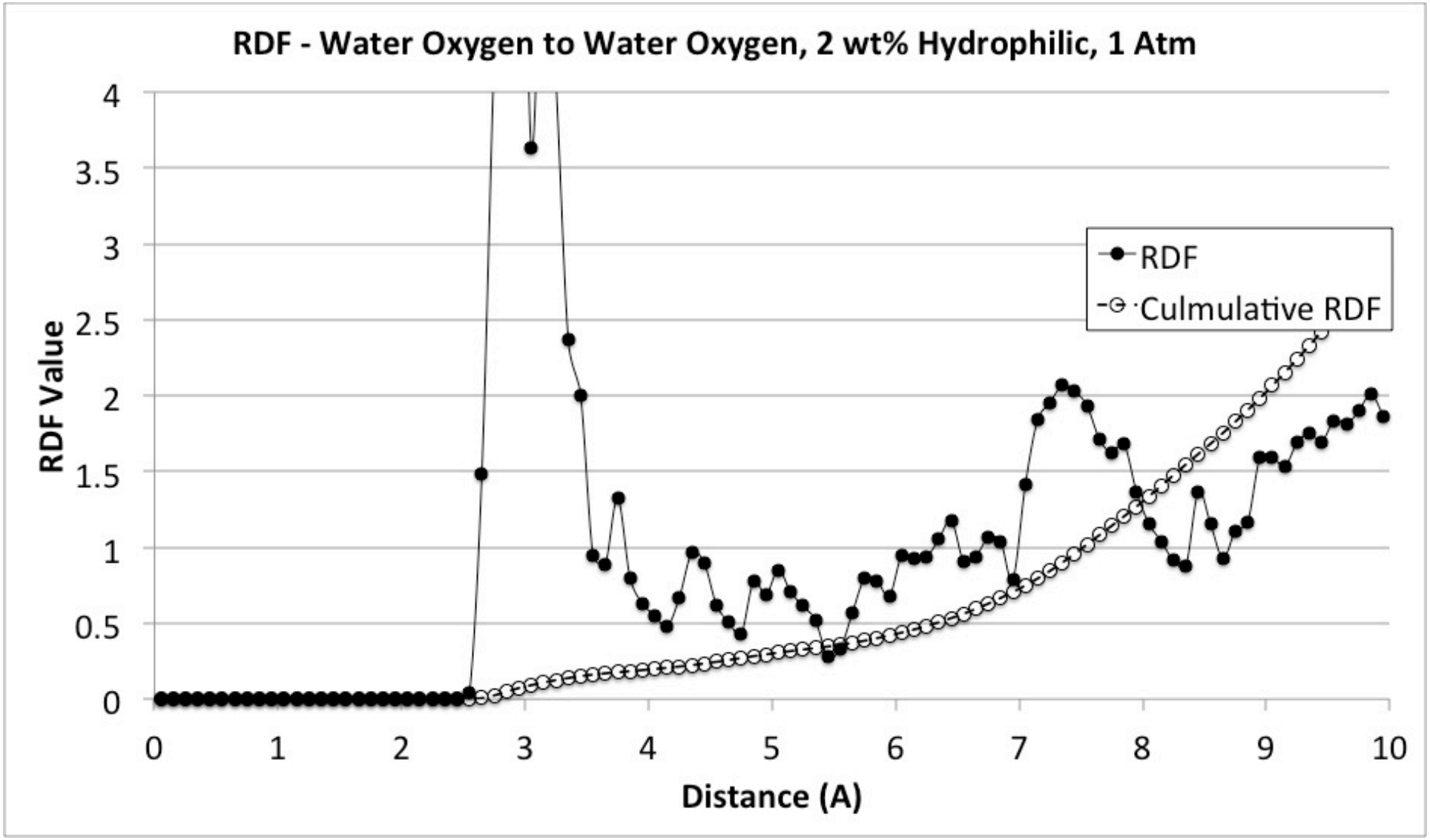

RDF - Polymer Oxygen to Water Oxygen, 3 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
2
3
4
5
6
7
8
9
10

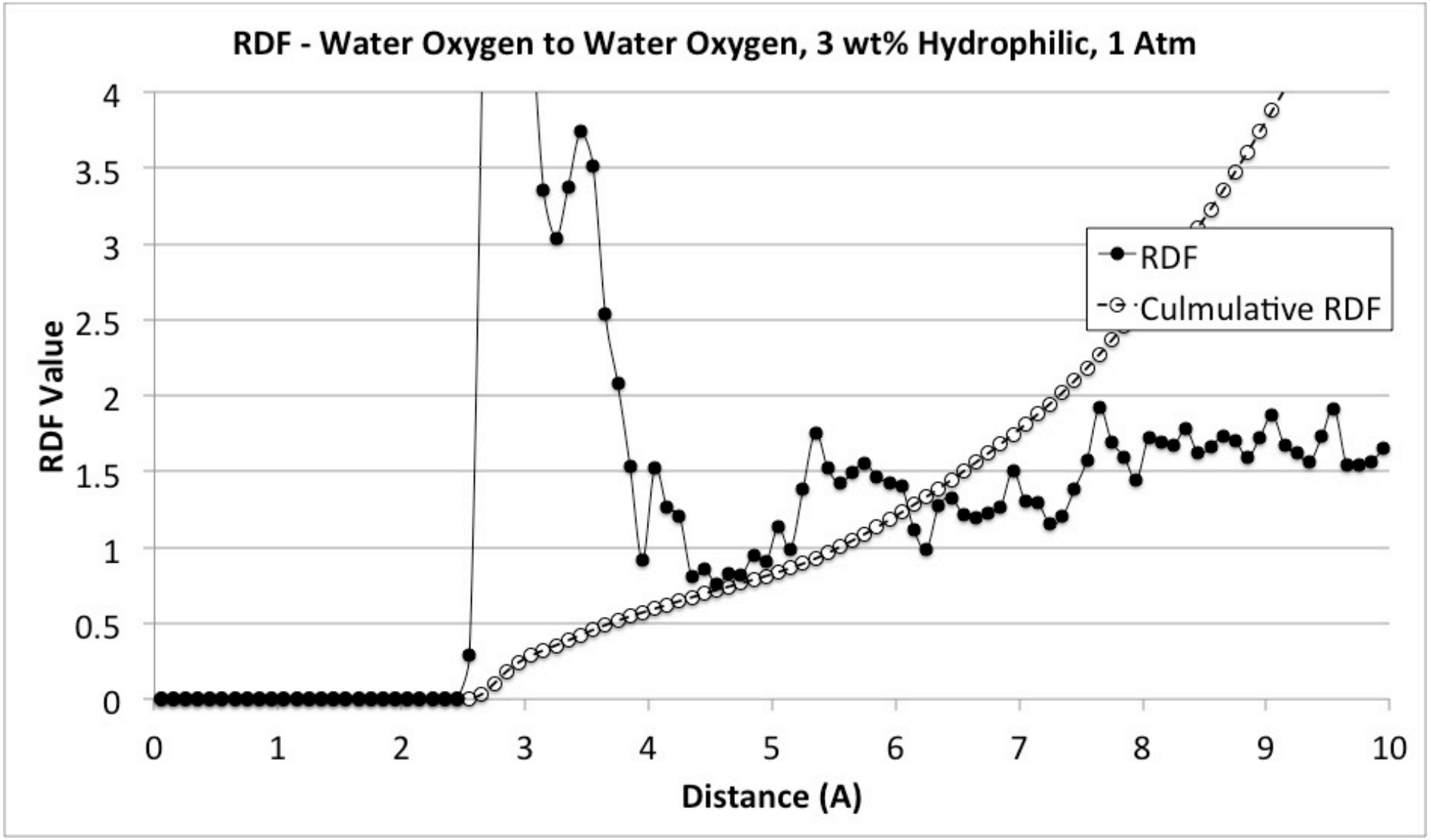

RDF - Polymer Oxygen to Water Oxygen, 4 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
2
3
4
5
6
7
8
9
10


RDF - Polymer Oxygen to Water Oxygen, 5 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
2
3
4
5
6
7
8
9
10


RDF - Polymer Oxygen to Water Oxygen, 10 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
2
3
4
5
6
7
8
9
10


RDF - Water Oxygen to Water Oxygen, 1 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
2
3
4
5
6
7
8
9
10


RDF - Water Oxygen to Water Oxygen, 2 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
2
3
4
5
6
7
8
9
10


RDF - Water Oxygen to Water Oxygen, 3 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
2
3
4
5
6
7
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9
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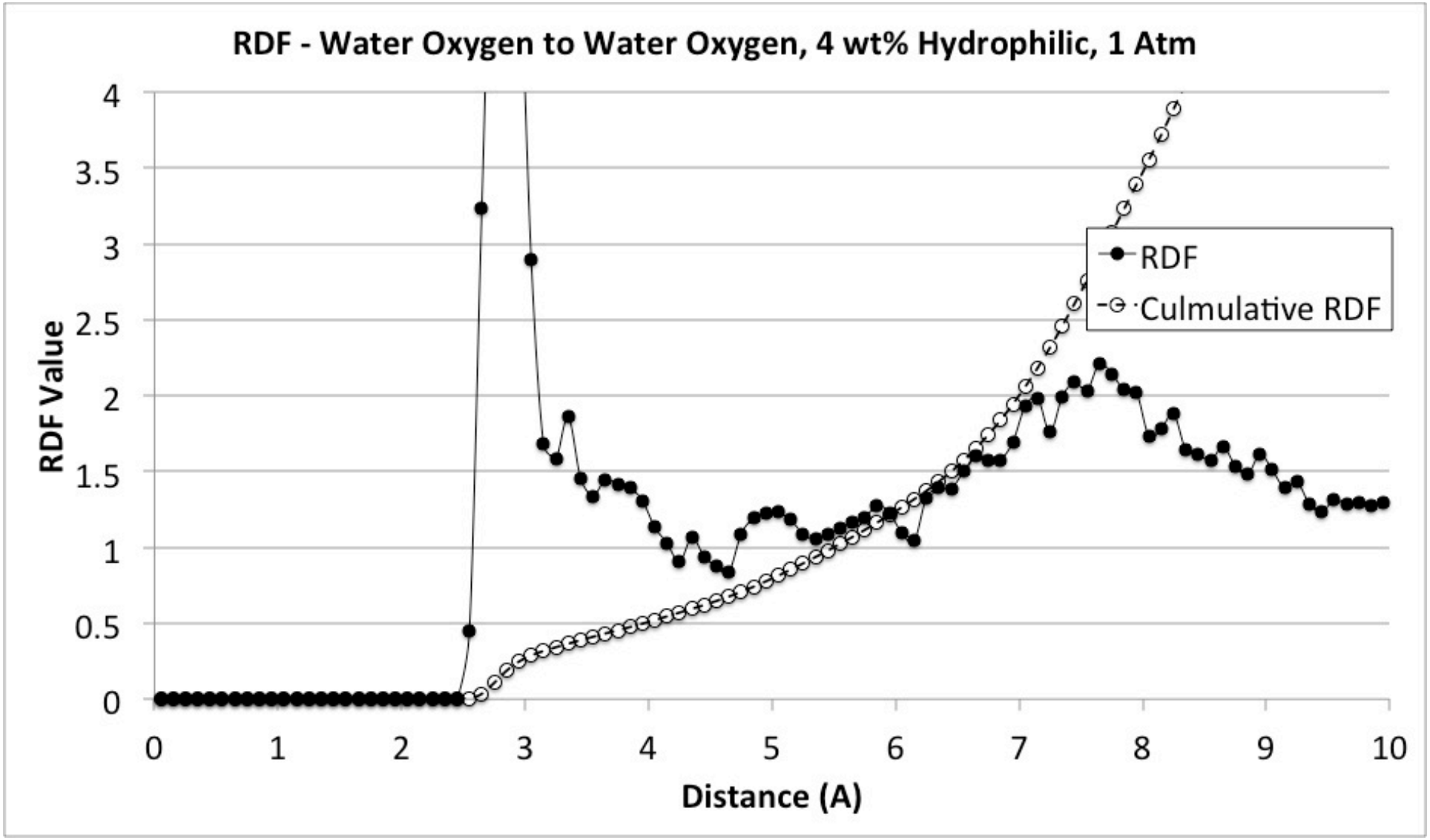
RDF - Water Oxygen to Water Oxygen, 4 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
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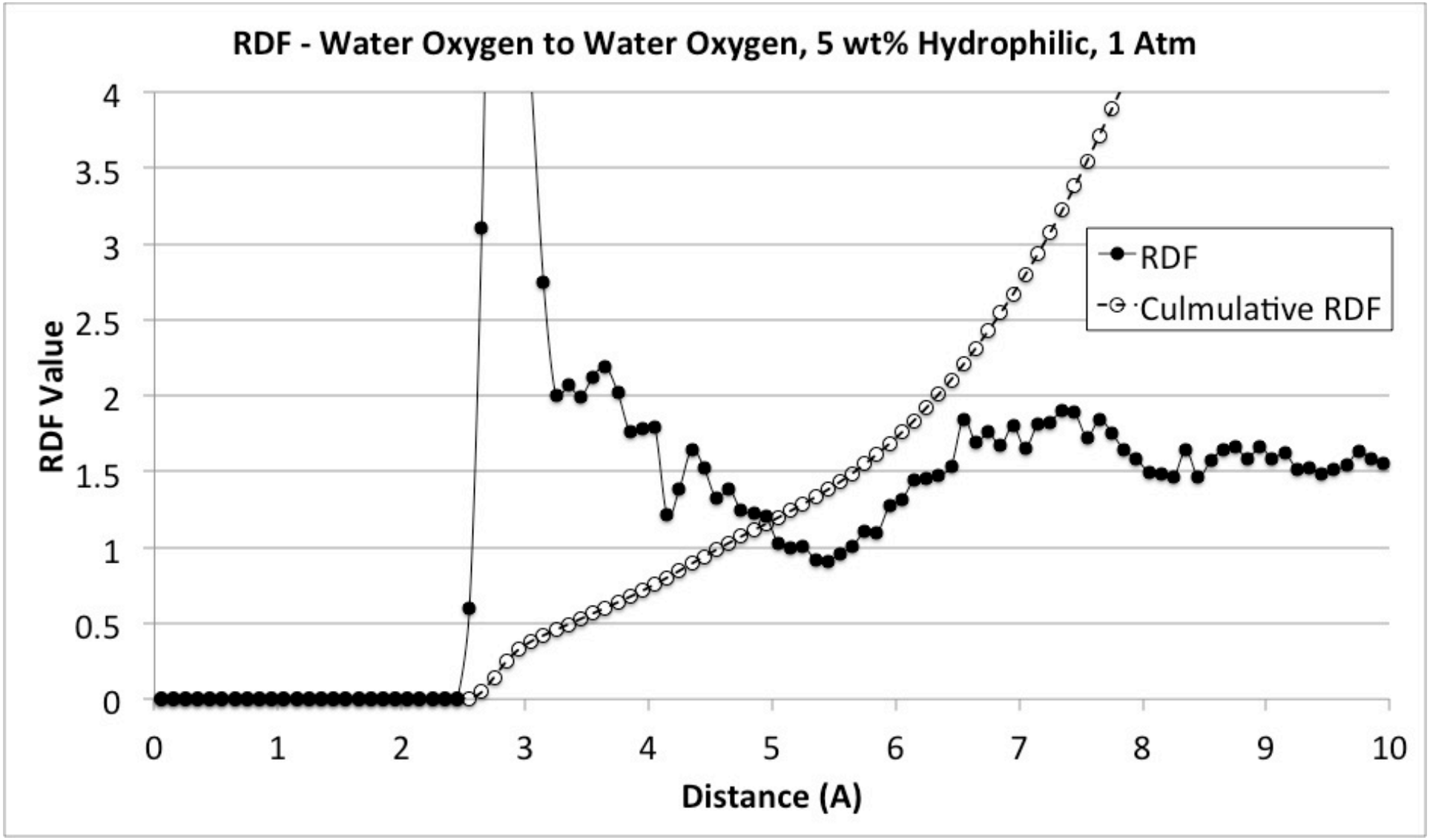
RDF - Water Oxygen to Water Oxygen, 5 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
2
3
4
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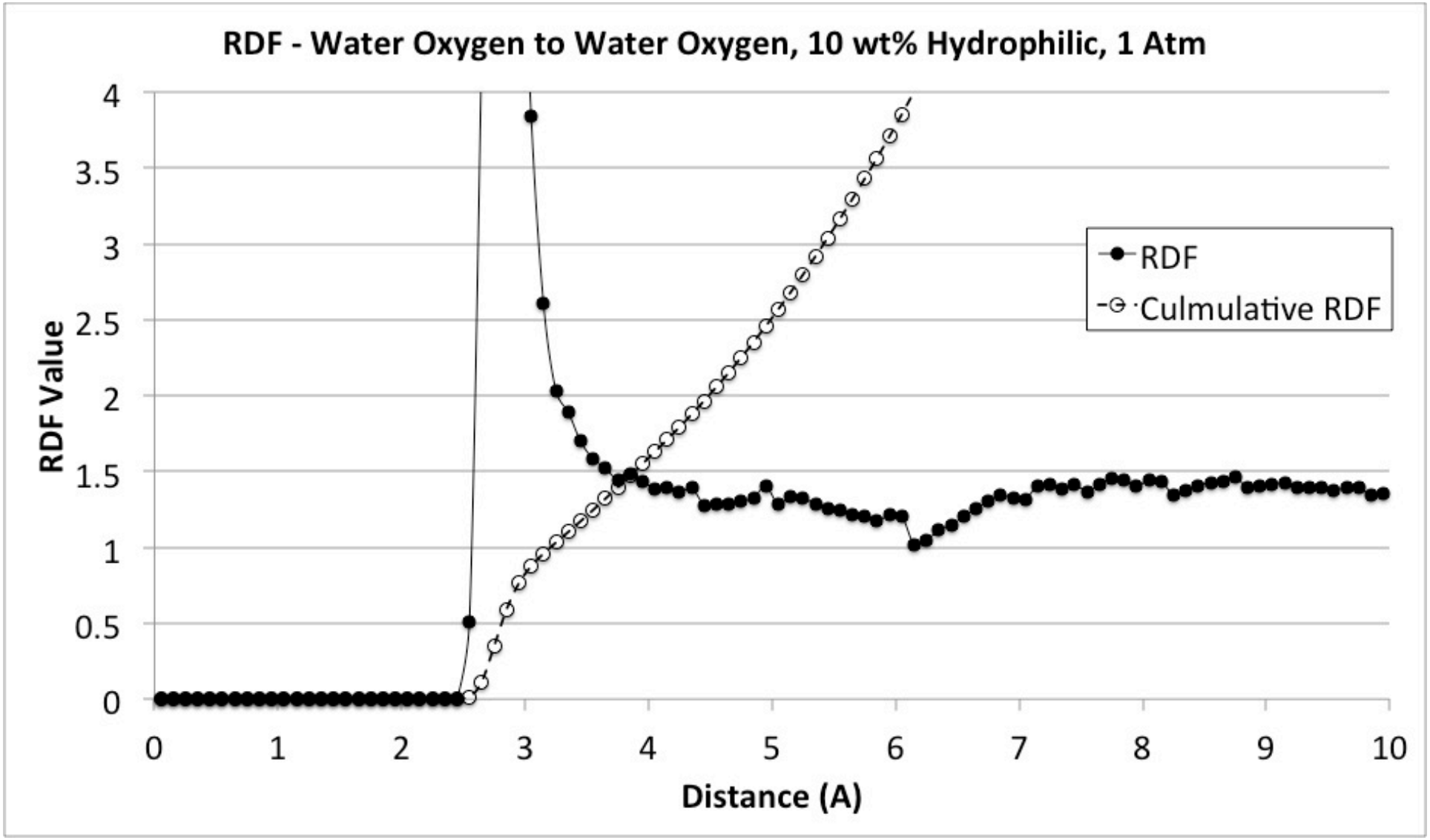
RDF - Water Oxygen to Water Oxygen, 10 wt% Hydrophilic, 1 Atm
RDF Value
Distance (A)
RDF
Culmulative RDF
0
0.5
1
1.5
2
2.5
3
3.5
4
0
1
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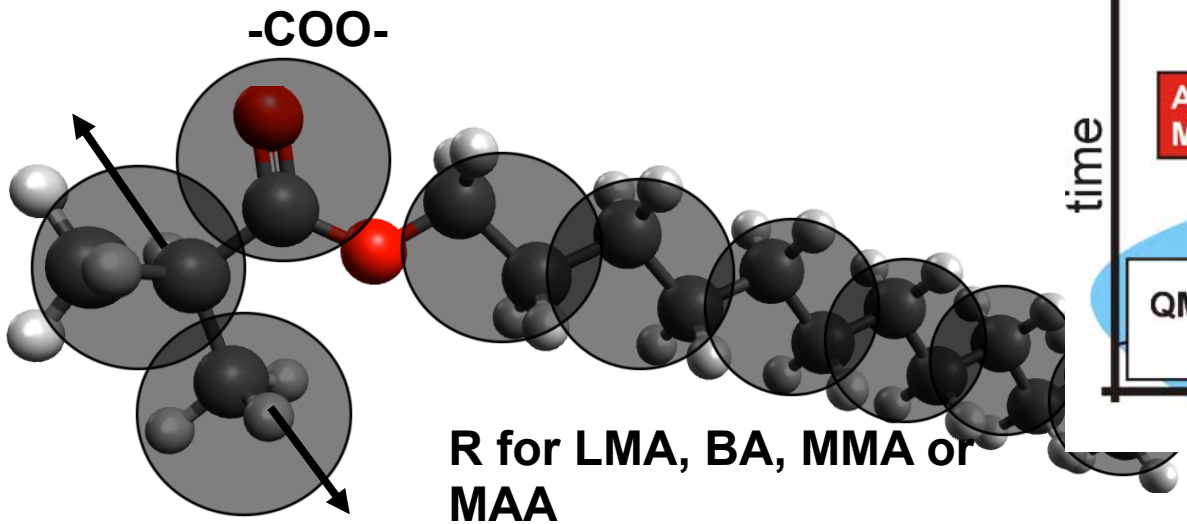
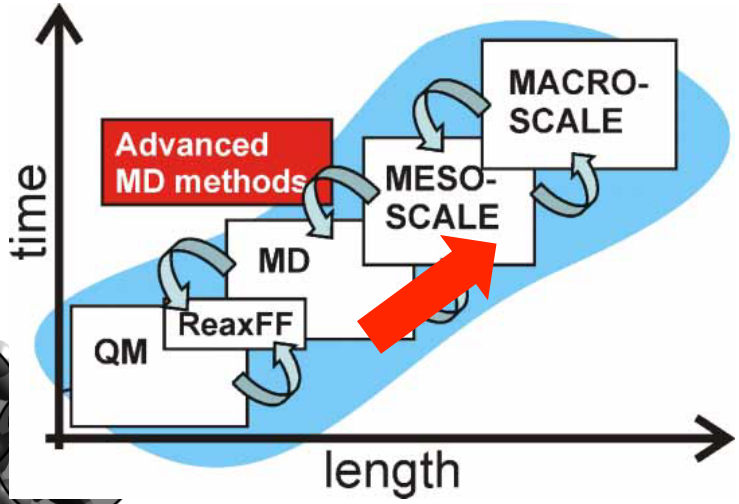
# *Coarse-Grain (CG) Molecular Dynamics*

■CG can reduce the computational costs with a large number of atoms. (~$10^{9\text{-}12}$ atoms with μs.)



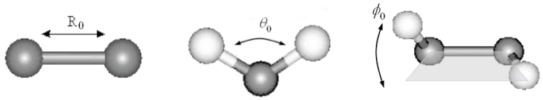




■Bead represents several atoms (up to 6~7) into pseudo-particles (rigid-body)

→ Clusters of atoms (Beads) interact with others through CG force fields to s

$$E_{Total} = E_{Bonds} + E_{Angles} + E_{Torsions} + E_{nonBond} + E_{hBond}$$

Same as classic MD



# Building the coarse-grain model

## x100 w/r to atomistic

- Bond stretch: Harmonic

$$V_{Bonds} = \tfrac{1}{2}\kappa(r - r^{eq})^2$$

- Angle bend: Cosine Harmonic

$$V_{Angles} = \tfrac{1}{2}\beta(\cos\Theta - \cos\Theta^{eq})^2$$

- Torsion: Harmonic

$$V_{Torsions} = \tfrac{1}{2}\gamma(1 + \cos(n\varphi - d))$$

- Hydrogen Bonds: Dreiding

$$V_{HBond} = D_0\left[5\left(\frac{r_0}{r}\right)^{12} - 6\left(\frac{r_0}{r}\right)^{10}\right]\cos^4\Theta$$

- van der Waals: Morse Potential

$$V_{R_{ij}} = D_0\left\{\left(e^{-0.5\alpha\left(R_{ij}/R_0 - 1\right)}\right)^2 - 2\left(e^{-0.5\alpha\left(R_{ij}/R_0 - 1\right)}\right)\right\}$$

- **Backbone structure**
- Beads for monomer
- Bead for water molecule
- Bead for ions
- Quasi-bead for hydrogen
  - Bonds, angles not calculated during dynamics
  - Move as rigid body with parent nucleotide
- Statistics obtained from explicit water atomistic simulations
- All beads neutral, Morse potential for nonbonds (vdW + Coulomb)

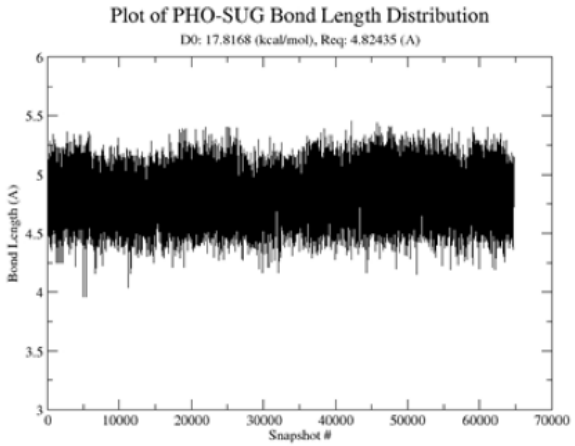
Exemplified with DNA

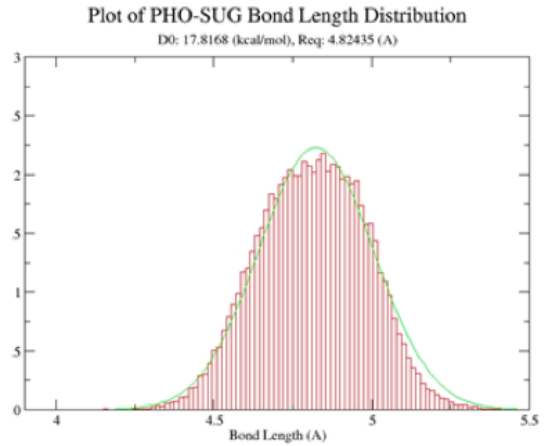
# Valence (bond) interactions

Bond Parameters (excluding hydrogens)

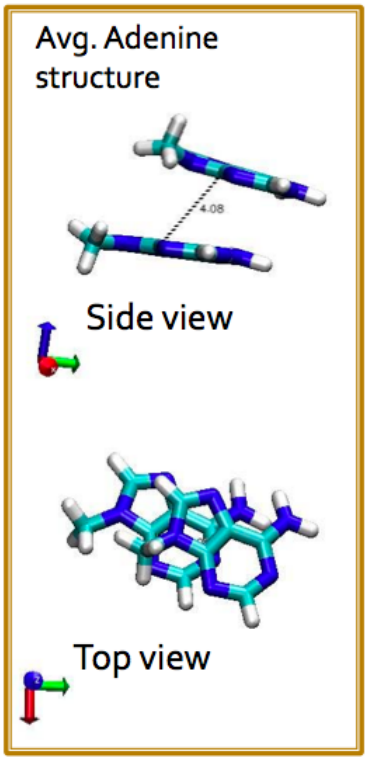
| | $k_0$(kcal/m²) | $r_0$(m) |
|---|---|---|
| SUG-THY | 168 | 4.2 |
| SUG-ADE | 156 | 4.6 |
| SUG-GUA | 143 | 4.7 |
| SUG-CYT | 193 | 4.1 |
| SUG-PHO | 46 | 4.0 |
| SUG-PHP | 18 | 4.4 |

- Calculate bonds/angles/torsions from atomistic simulations
  - 10 independent DNA simulations of random sequences
  - Take snapshots of last 2ns of 5ns NVT MD, every 10ps
- Assume distributions to be Boltzmann, get parameters by non-linear curve fitting

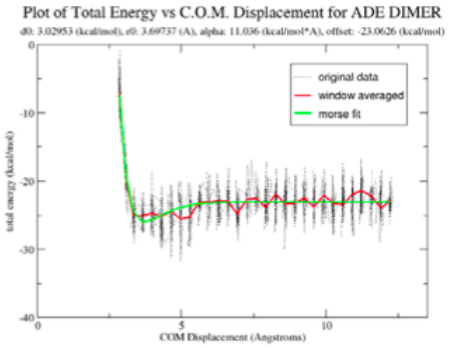


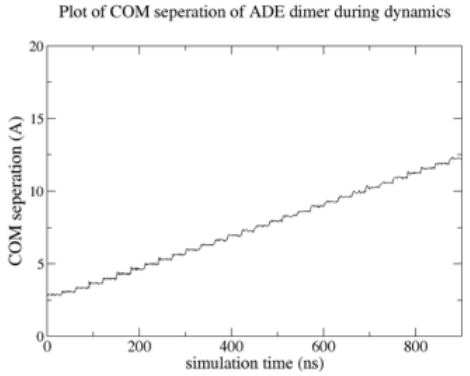



# Non-bonded interactions

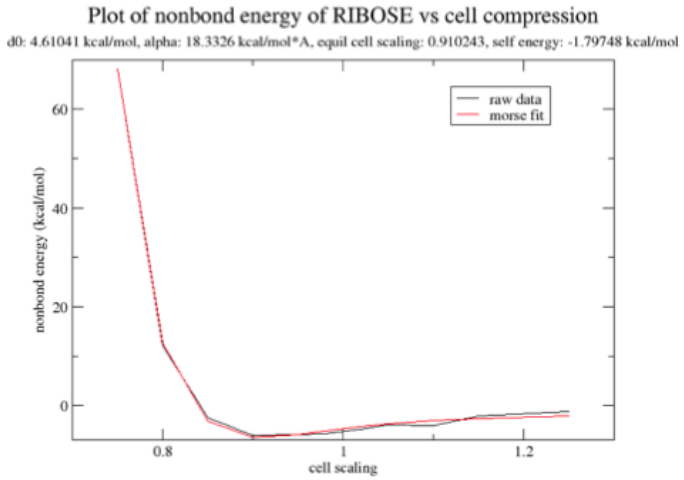


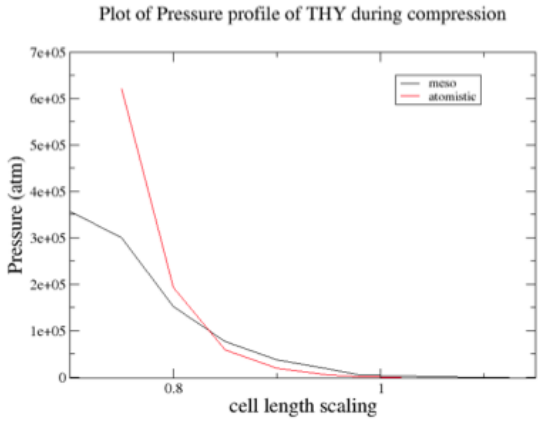

- Solvate 2 atomistic units in waterbox
- Equilibrate structure
- Attach 500 kcal/mol spring to C.O.M.
- Calc nonbond energy:
  - Start: 0.33Å
  - End: 17Å
  - Increment: 0.33Å
- Fit to Morse Potential (VDW + Coulomb)



# Optimizing nonbond: compression simulations




- Equilibrate Meso and atomistic units in waterbox
- Isobaric compression of cell length x: 1.25, 1.15, 1.1, 1.05, 1.02, 0.98, 0.95 – 0.7 every 0.05
- Record solute energy and system pressure for each compression
- Iterate Meso parameters until profile match atomistic