Latex Films

Dow Chemical Project

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9-2-2011

Outline

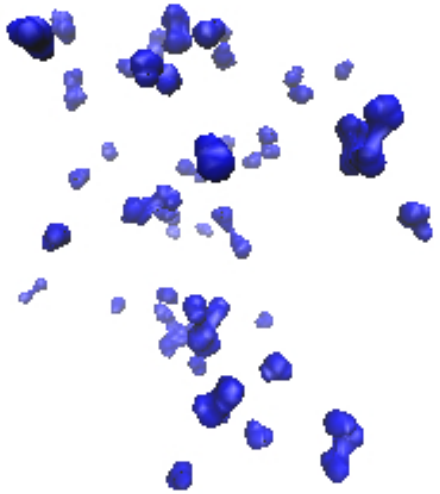
Thermodynamics as a function of water content (continued)

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 to finish
- Take snapshots once energy equilibrated. 5 snapshots (one every ~100ps)
- 2PT analysis on each snapshot for thermodynamics

Water Molecules Represented as Solid Surfaces

1 %



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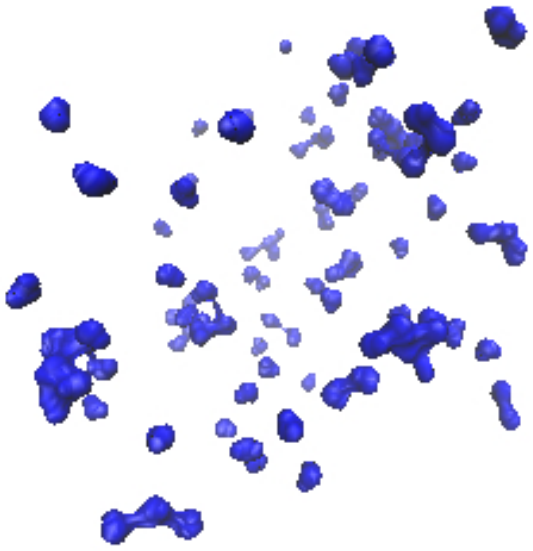

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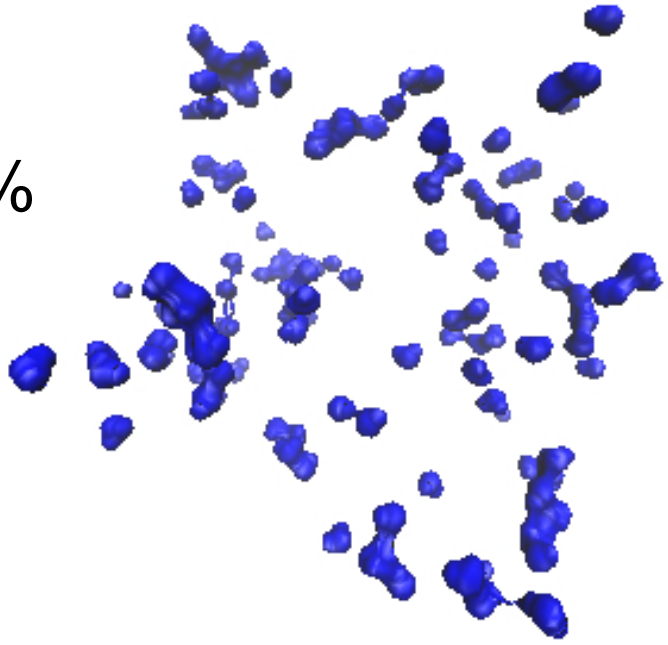

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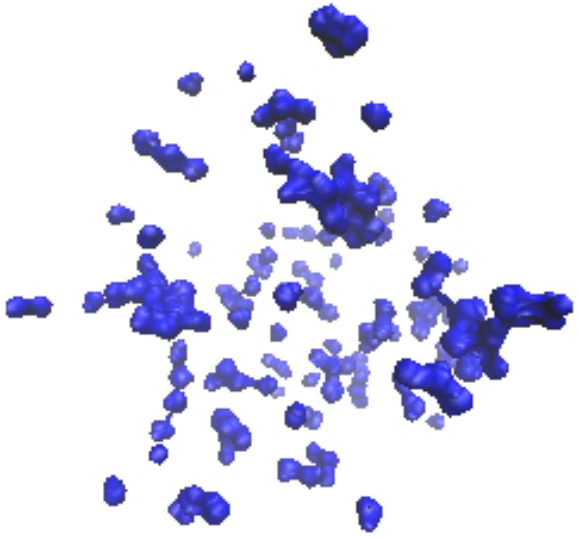
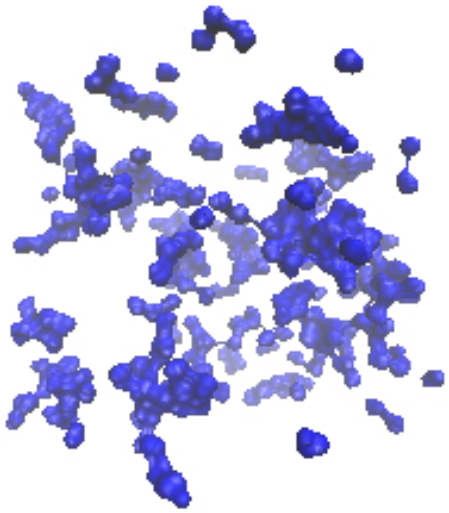
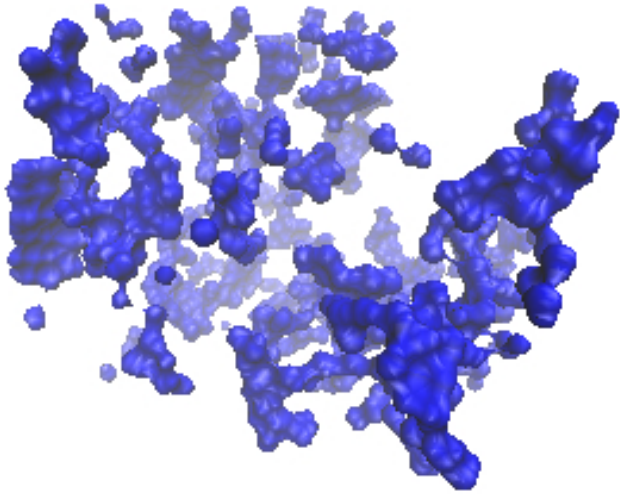


5%

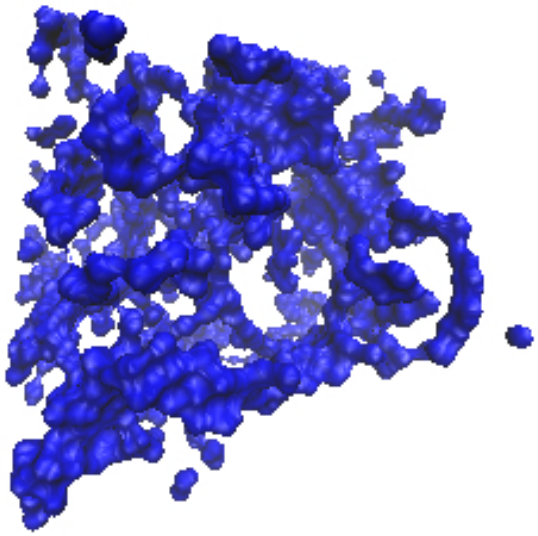
10%

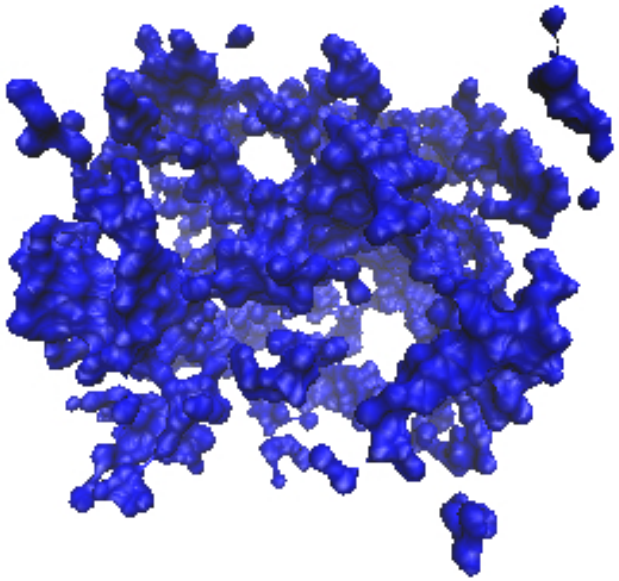




15%

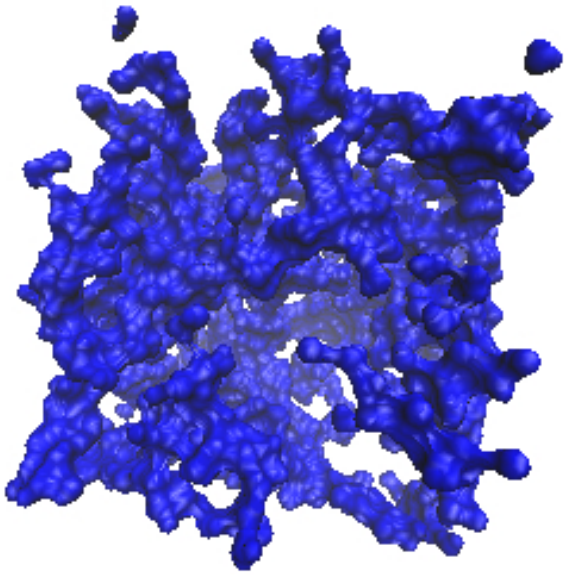
20%

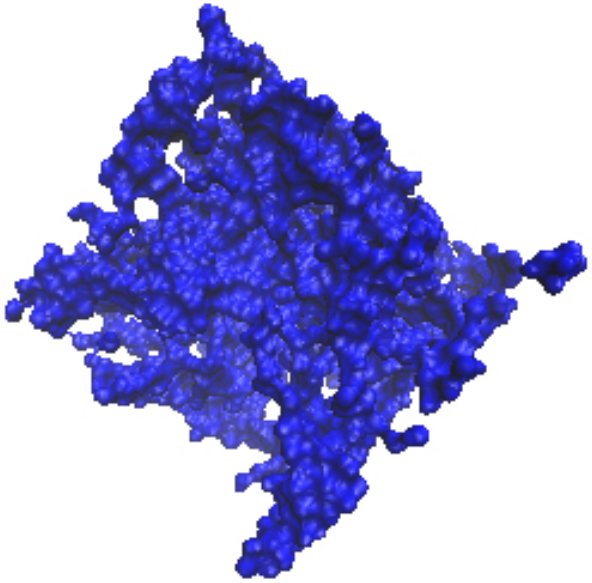




25%

30%





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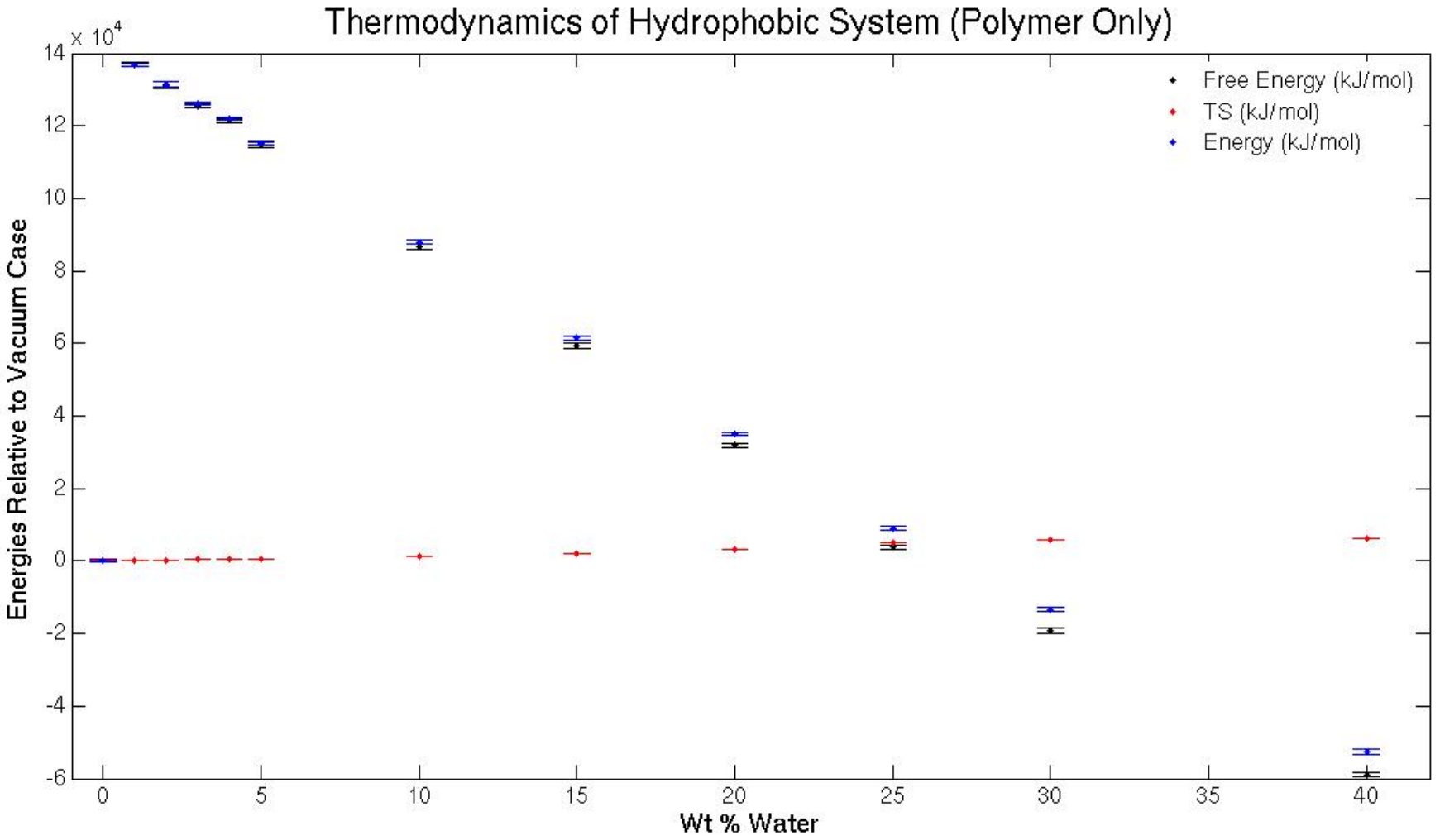
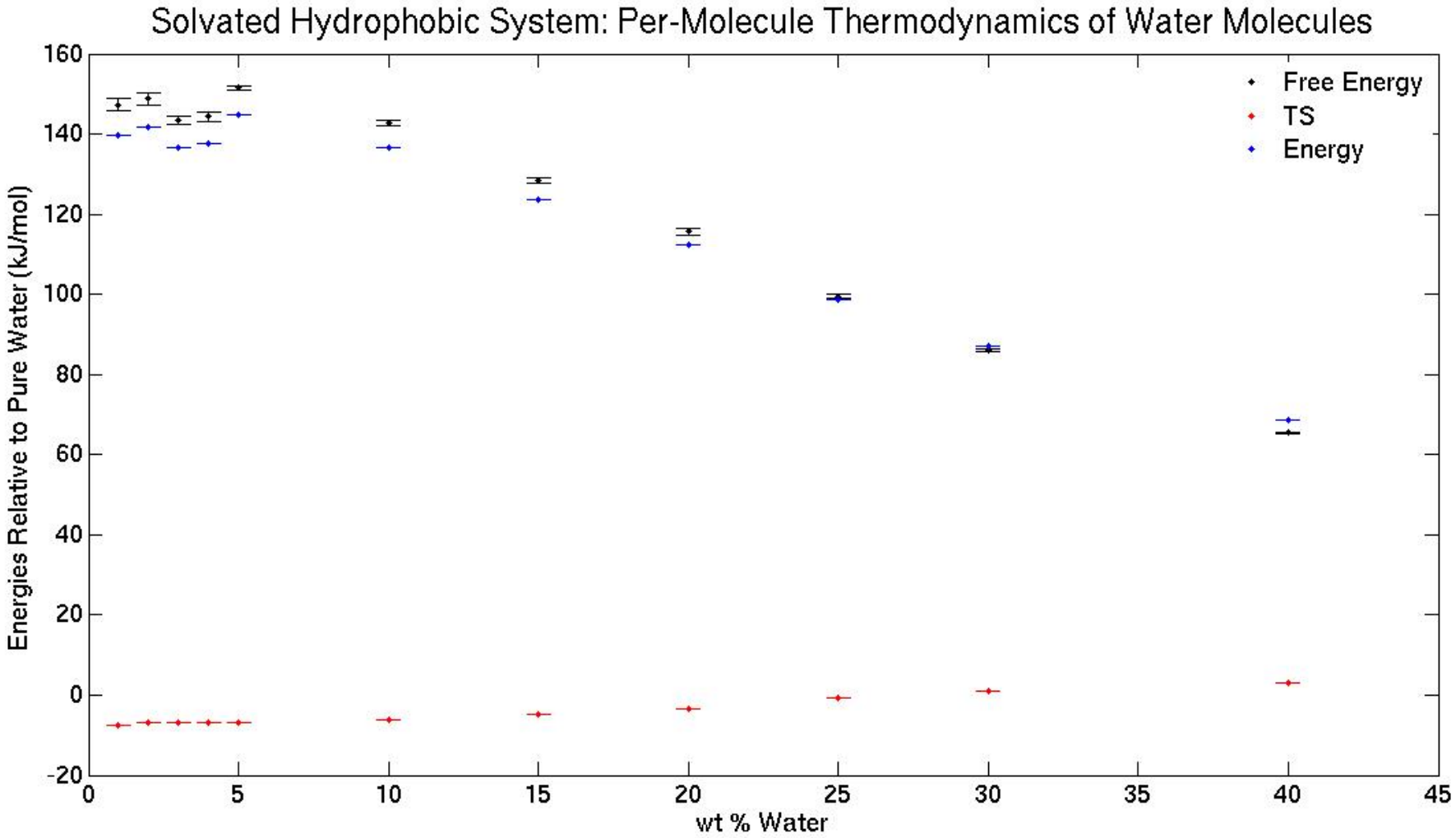
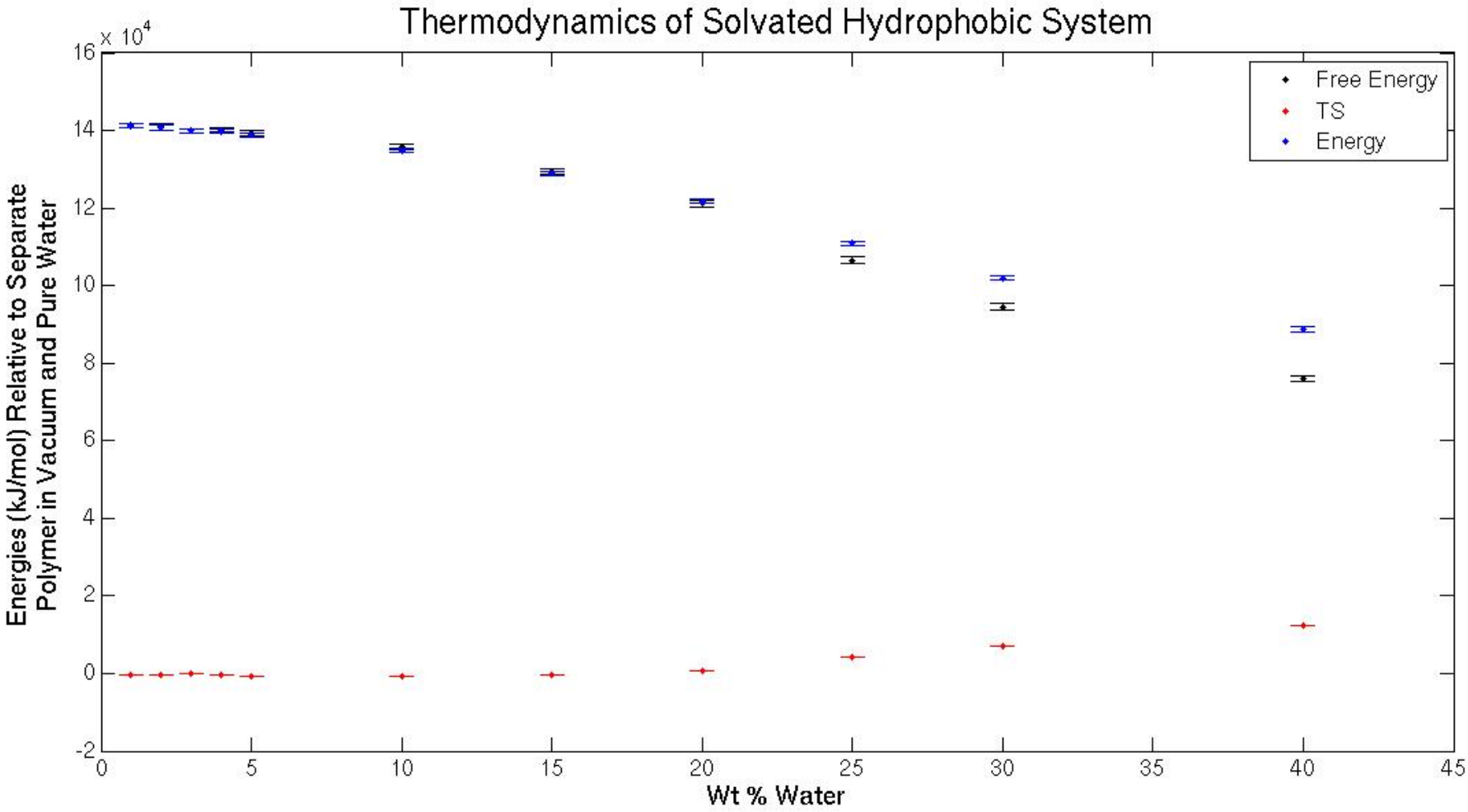
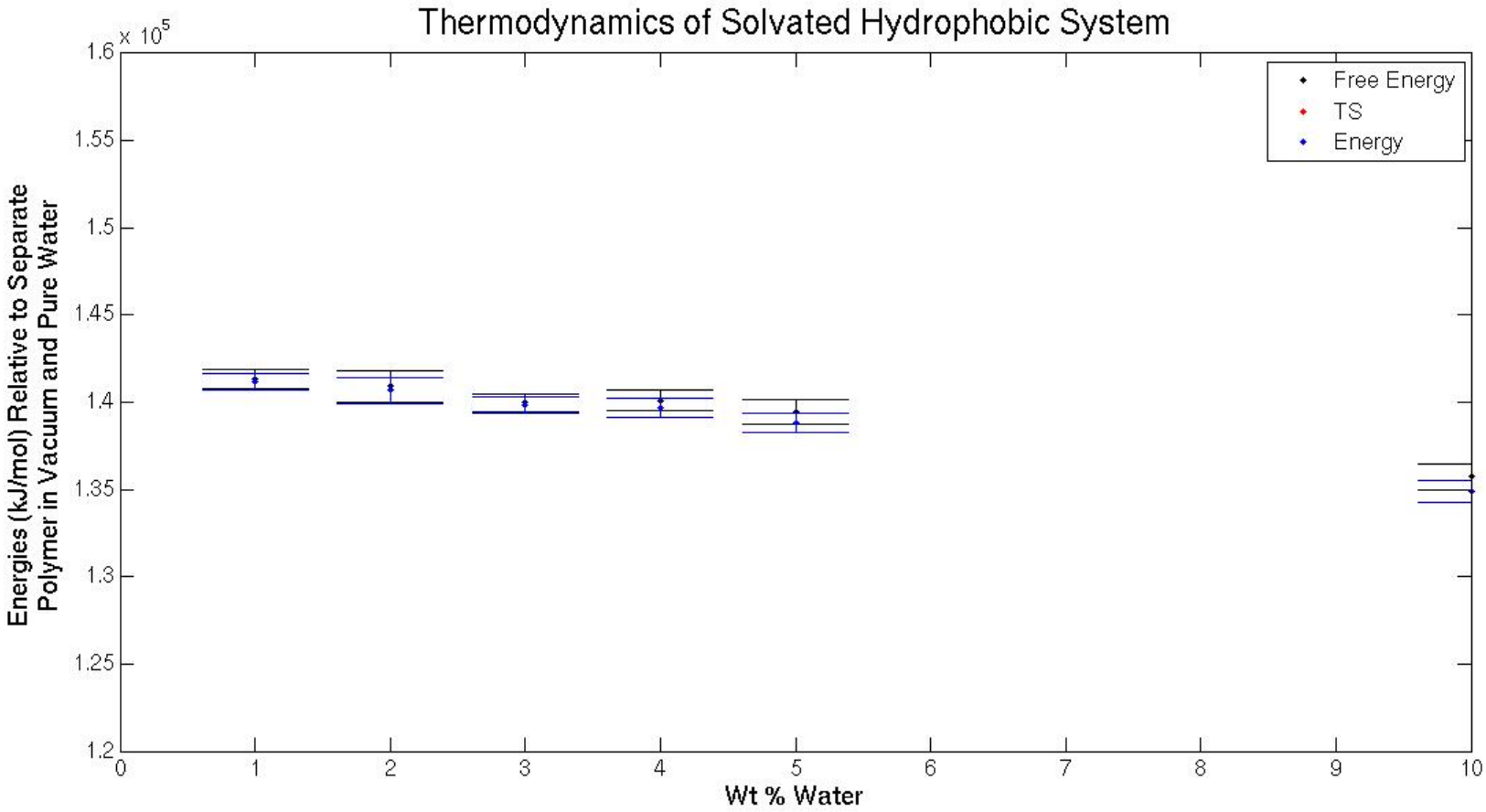

Thermodynamics of Hydrophobic System (Polymer Only)
x 10^4
14
12
10
8
6
4
2
0
-2
-4
-6
Energies Relative to Vacuum Case
0
5
10
15
20
25
30
35
40
Wt % Water
Free Energy (kJ/mol)
TS (kJ/mol)
Energy (kJ/mol)


Solvated Hydrophobic System: Per-Molecule Thermodynamics of Water Molecules
Free Energy
TS
Energy
Energies Relative to Pure Water (kJ/mol)
wt % Water
160
140
120
100
80
60
40
20
0
-20
0
5
10
15
20
25
30
35
40
45


Thermodynamics of Solvated Hydrophobic System
x 10^4
16
14
12
10
8
6
4
2
0
-2
0
5
10
15
20
25
30
35
40
45
Energies (kJ/mol) Relative to Separate Polymer in Vacuum and Pure Water
Wt % Water
Free Energy
TS
Energy

Same Figure, Zoomed in on Energy



Solvated Hyrophilic Polymer

For the data plotted here:

Hydrophilic System Composition

DREIDING Polymer, F3C Water

Lennard-Jones, fixed partial charge, hydrogen-bonding between MMA* and water

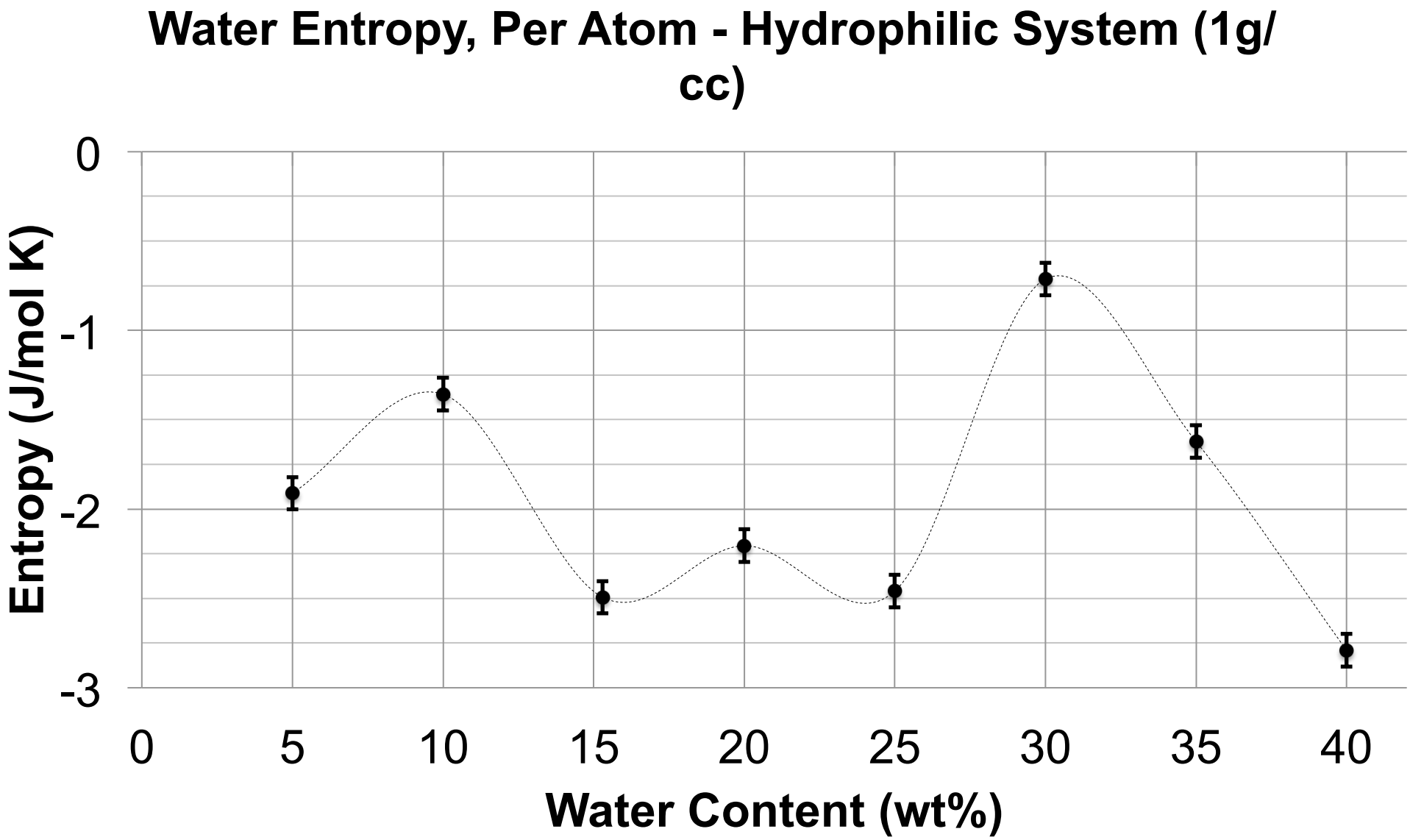
2PT data gathered for 20ps at 4fs intervals, NVT @ 300K and 1 g/cc

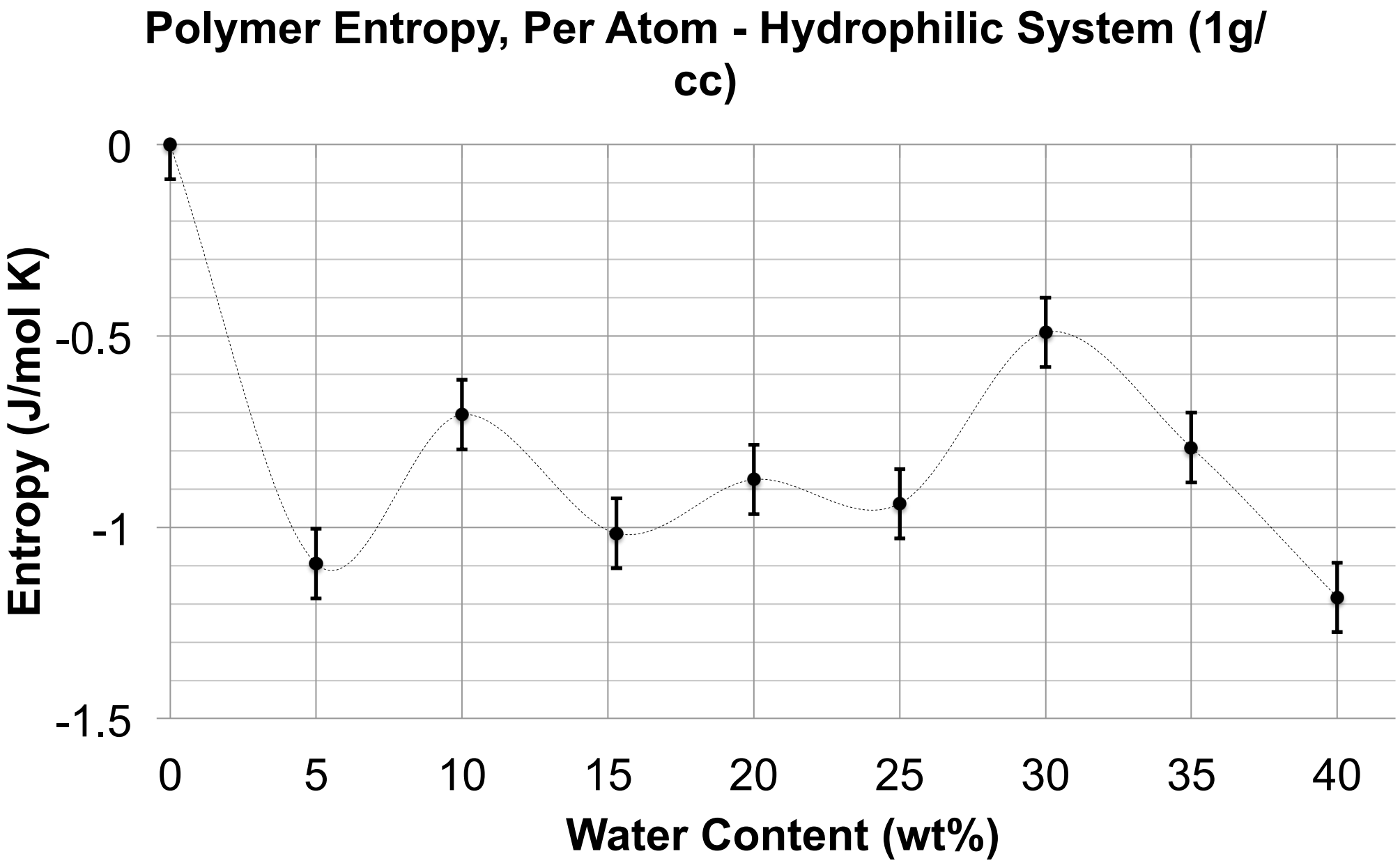
9163 polymer atoms

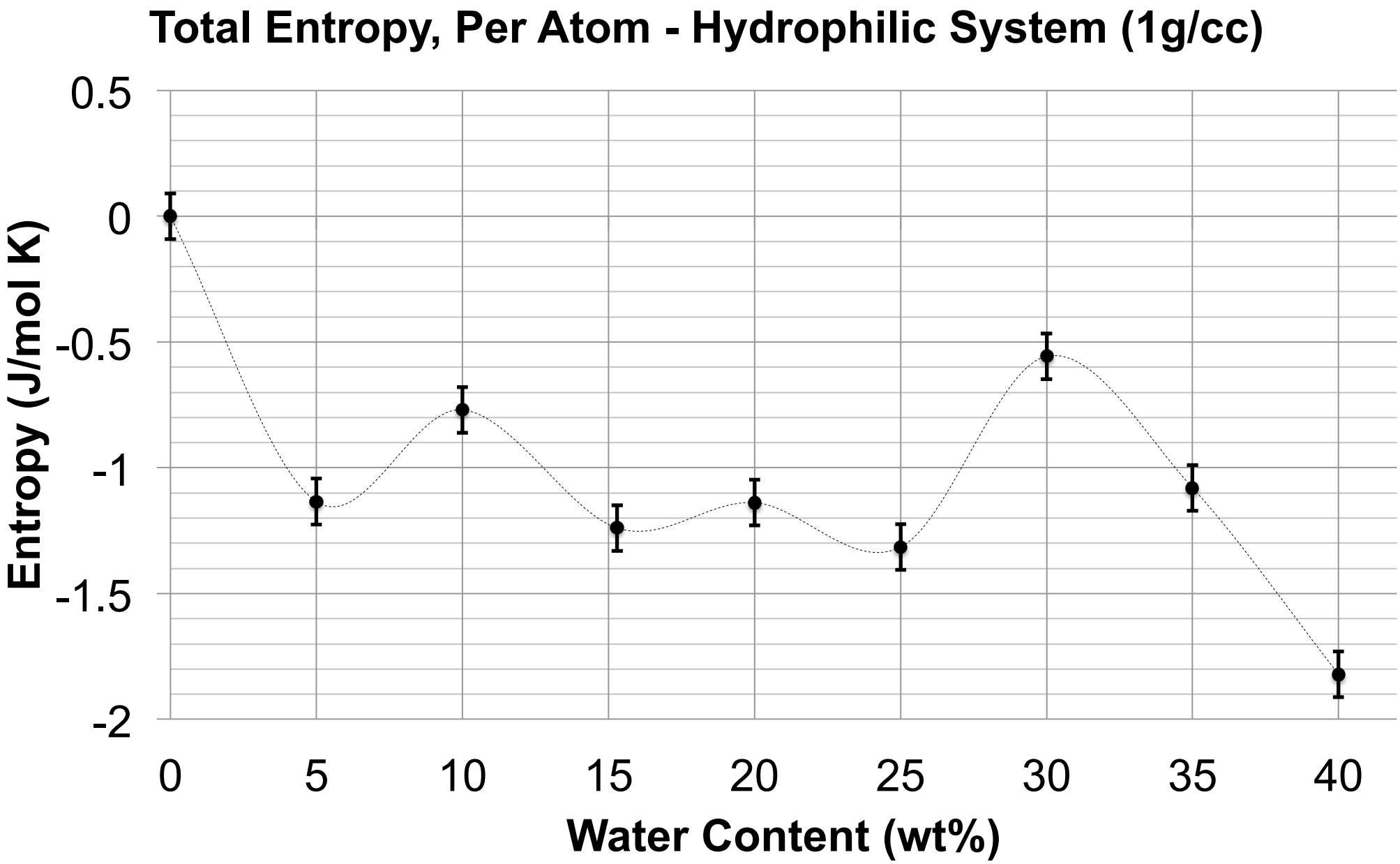
Entropy Reference – Bulk Water (F3C => 62.18 J/mol K), Vacuum Polymer

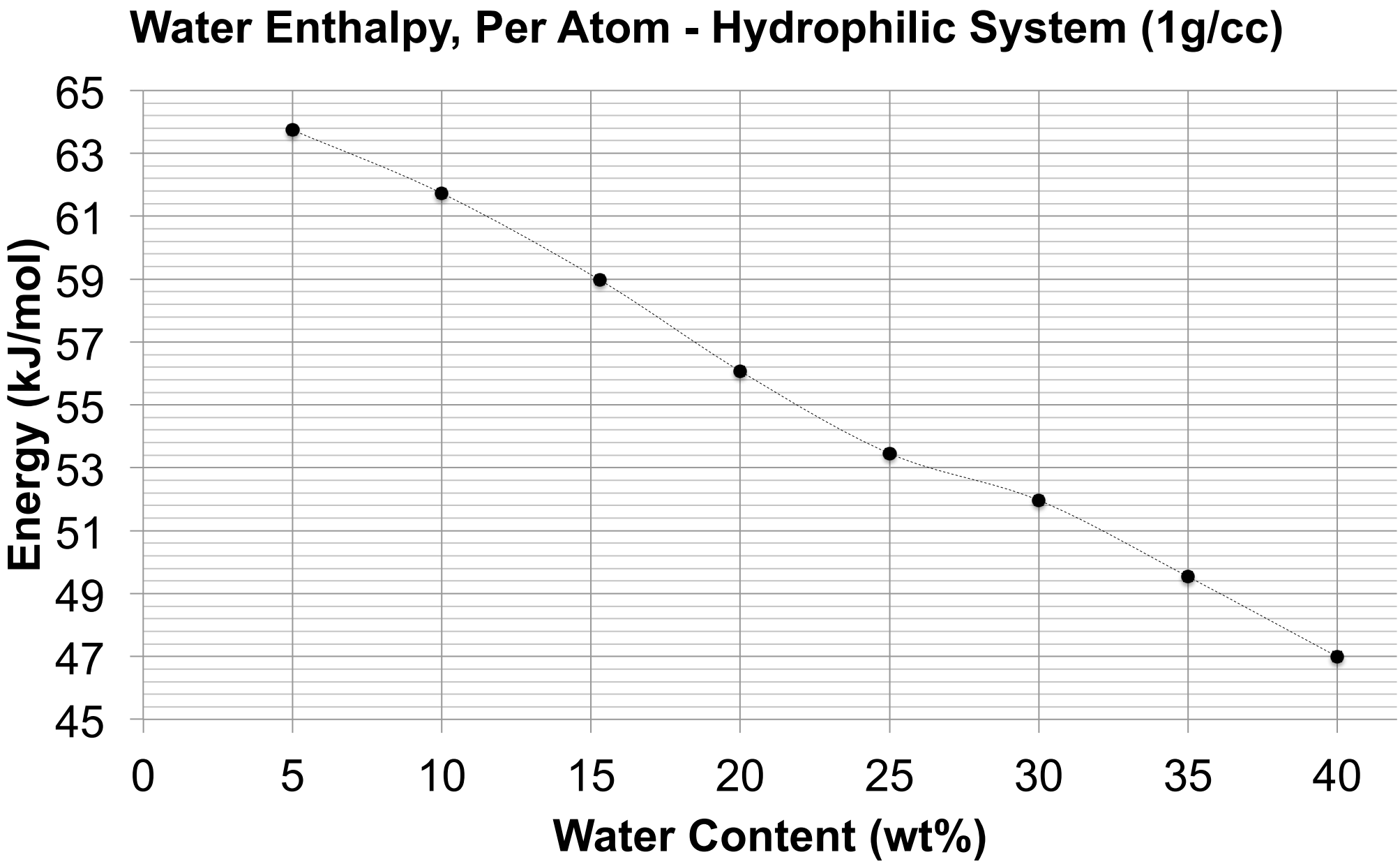
Internal Energy Reference – Bulk Water (F3C => -9.6 kcal/mol [-40.1664kJ/mol]), Vacuum Polymer

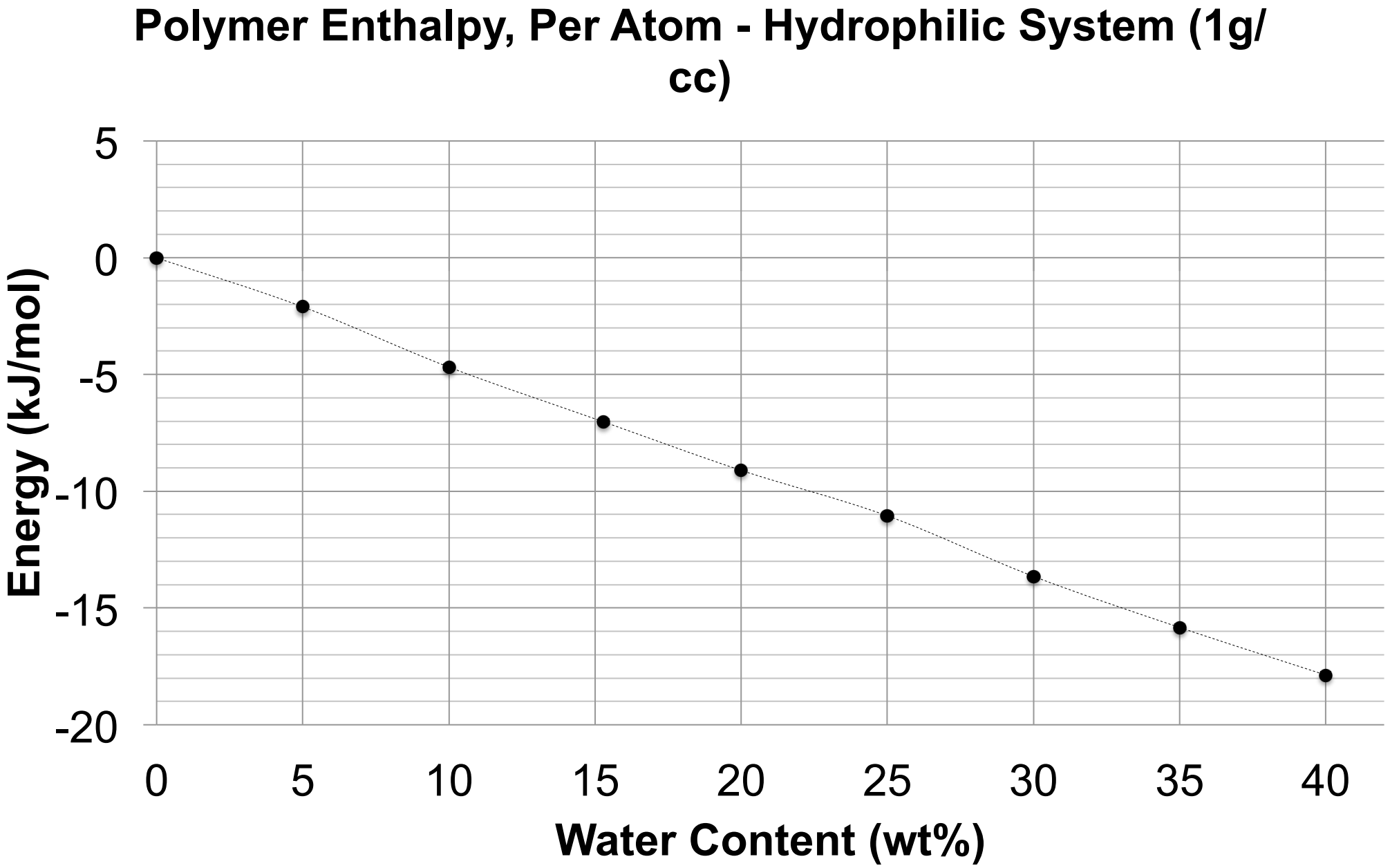
Free Energy = H-T*S

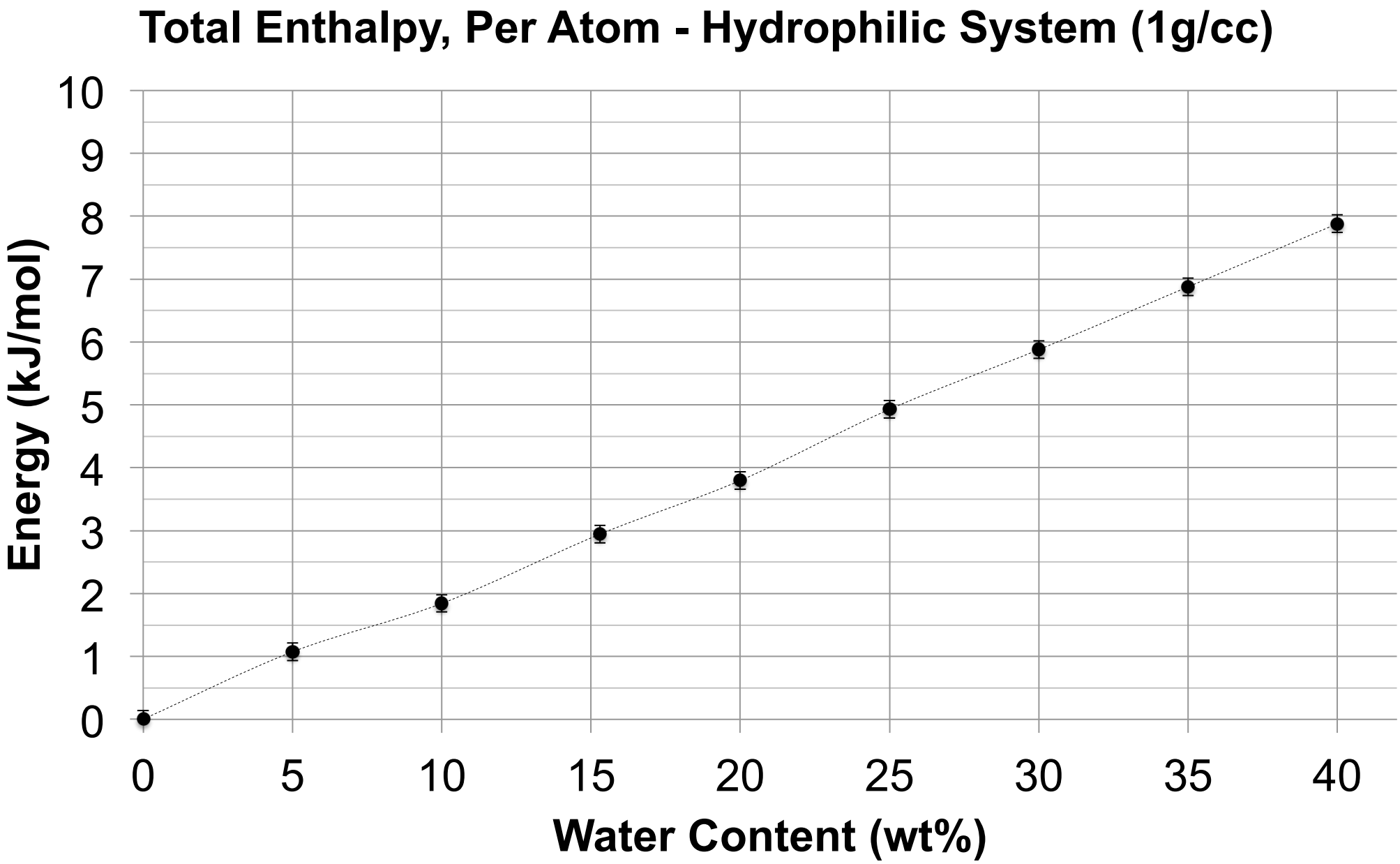

Water Entropy, Per Atom - Hydrophilic System (1g/cc)
Entropy (J/mol K)
0
-1
-2
-3
0
5
10
15
20
25
30
35
40
Water Content (wt%)

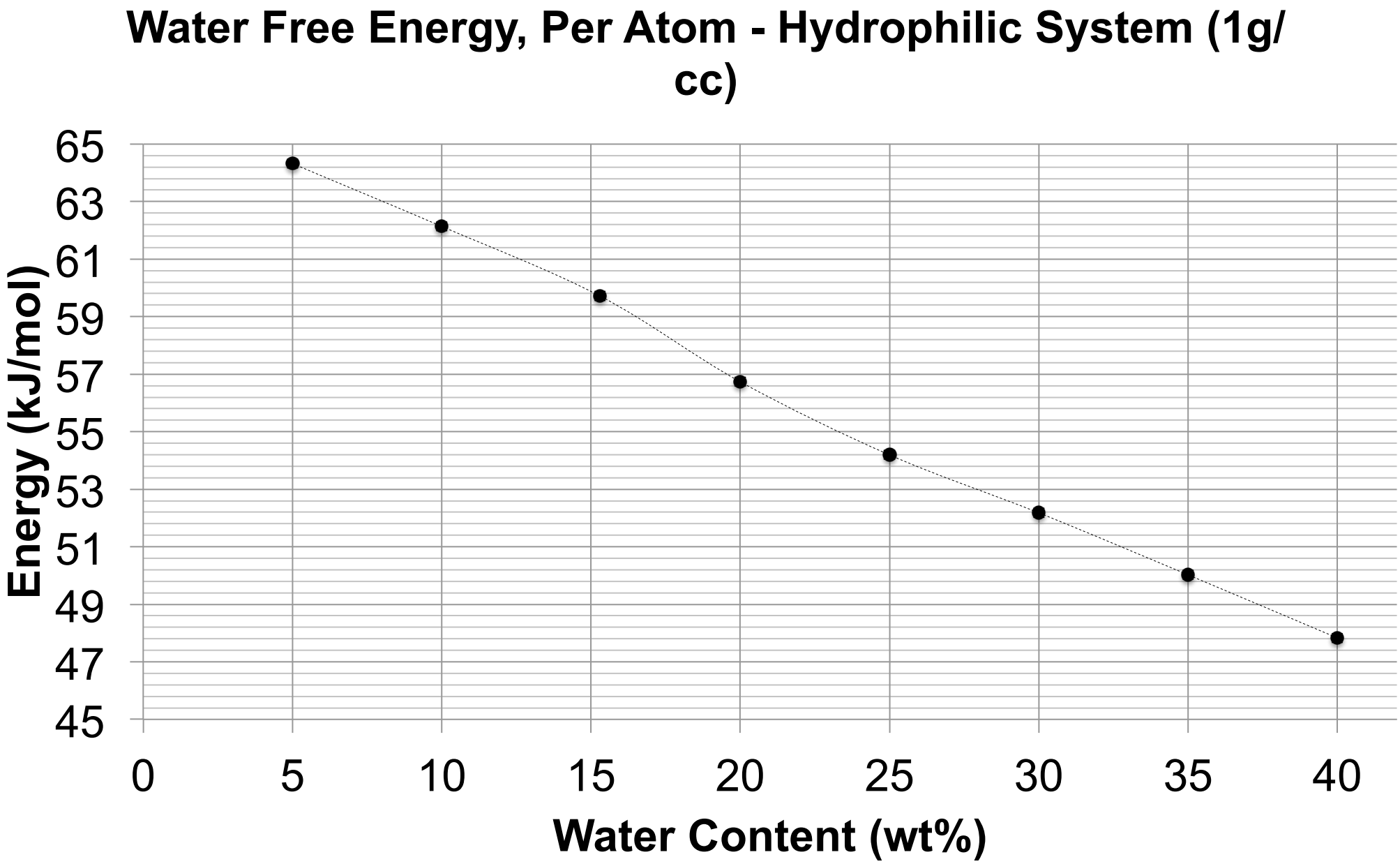

Polymer Entropy, Per Atom - Hydrophilic System (1g/cc)
Entropy (J/mol K)
0
-0.5
-1
-1.5
0
5
10
15
20
25
30
35
40
Water Content (wt%)

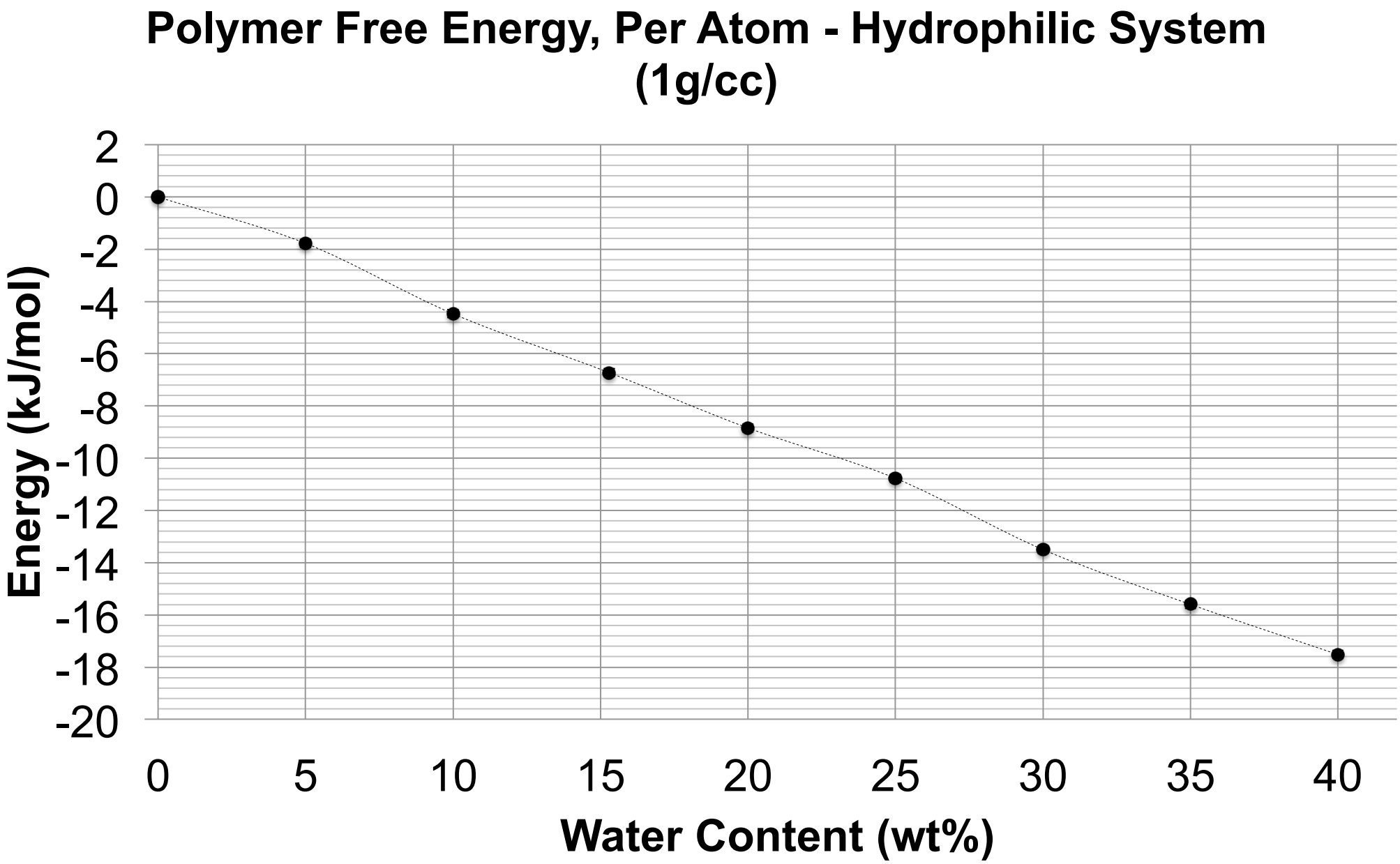

Total Entropy, Per Atom - Hydrophilic System (1g/cc)
Entropy (J/mol K)
0.5
0
-0.5
-1
-1.5
-2
0
5
10
15
20
25
30
35
40
Water Content (wt%)

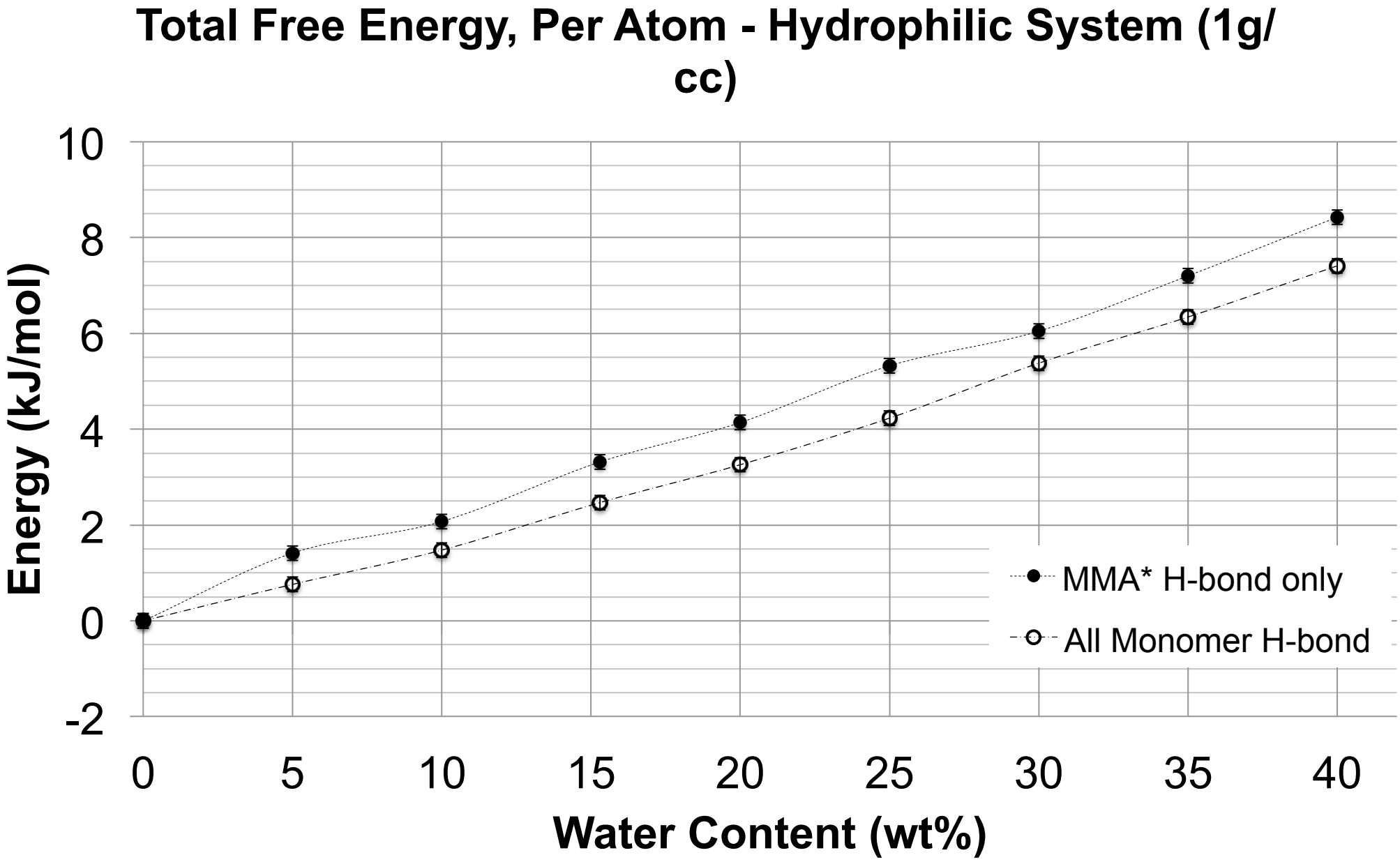

Water Enthalpy, Per Atom - Hydrophilic System (1g/cc)
Energy (kJ/mol)
65
63
61
59
57
55
53
51
49
47
45
0
5
10
15
20
25
30
35
40
Water Content (wt%)


Polymer Enthalpy, Per Atom - Hydrophilic System (1g/cc)
Energy (kJ/mol)
5
0
-5
-10
-15
-20
0
5
10
15
20
25
30
35
40
Water Content (wt%)


Total Enthalpy, Per Atom - Hydrophilic System (1g/cc)
Energy (kJ/mol)
10
9
8
7
6
5
4
3
2
1
0
0
5
10
15
20
25
30
35
40
Water Content (wt%)


Water Free Energy, Per Atom - Hydrophilic System (1g/cc)
Energy (kJ/mol)
65
63
61
59
57
55
53
51
49
47
45
0
5
10
15
20
25
30
35
40
Water Content (wt%)


Polymer Free Energy, Per Atom - Hydrophilic System (1g/cc)
Energy (kJ/mol)
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
0
5
10
15
20
25
30
35
40
Water Content (wt%)


Total Free Energy, Per Atom - Hydrophilic System (1g/cc)
Energy (kJ/mol)
10
8
6
4
2
0
-2
0
5
10
15
20
25
30
35
40
Water Content (wt%)
MMA* H-bond only
All Monomer H-bond

Contributions to Thermodynamic Properties:

40wt% Water	Polymer (%)	Water (%)
Entropy	42.5	57.5
Enthalpy	58.7	41.3
Energy	60.6	39.4

20wt% Water	Polymer (%)	Water (%)
Entropy	68.8	31.2
Enthalpy	79.6	20.4
Energy	80.4	19.6

Traditional

Entropy-based

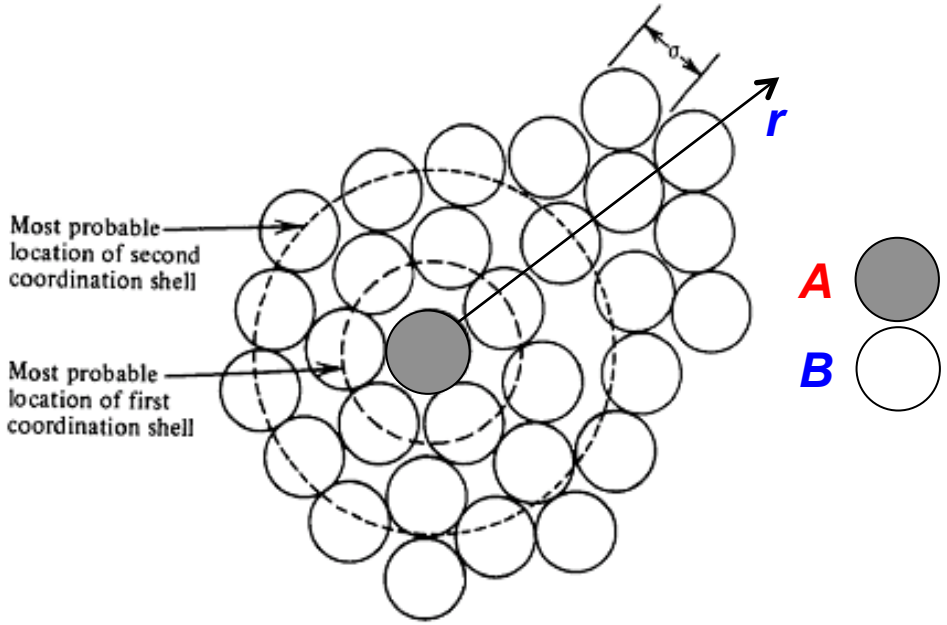
SWELLING

Future Approaches: Pair Correlation Function

Pair correlation function (PCF)

$$g_{A-B}(r) = \left(\frac{n_B}{4\pi r^2 \Delta r} \right) / \left(\frac{N_B}{V} \right)$$

n_B is the number of particle B located at the distance r in a shell of thickness from particle A, N_B is the number of B particles in the system, and is the total volume of the system.



PCF is probability density (or distribution density) of finding B molecule around A molecule at a distance r.

We expect:

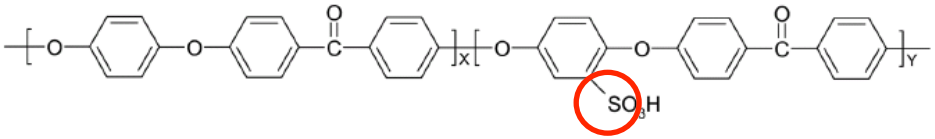
As increasing water contents,

Polymer-polymer PCF → decrease (due to swelling of the system)

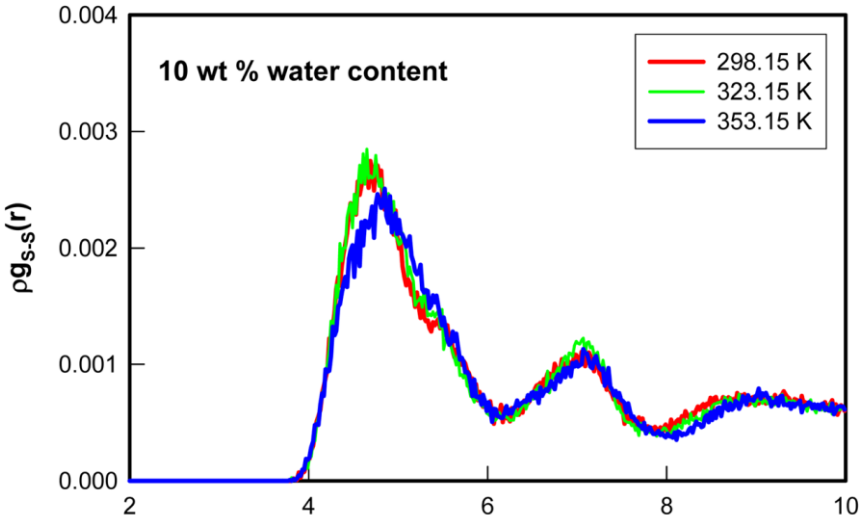
Polymer-water PCF → increase (due to high water content)

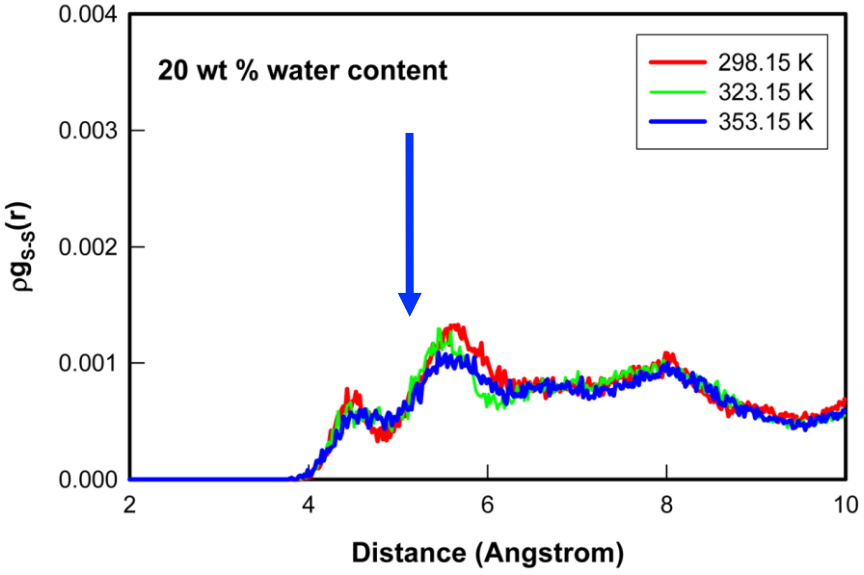
Future Approaches: Pair Correlation Function

Case Study: Fuel Cell Membrane

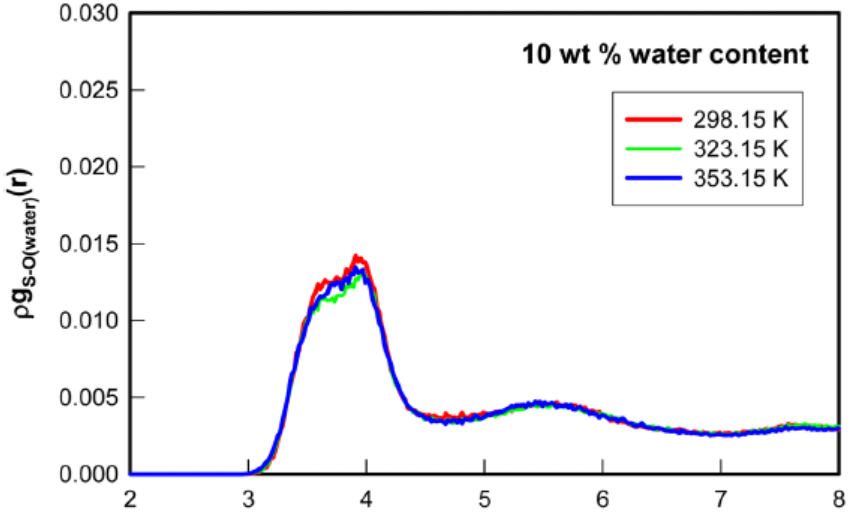


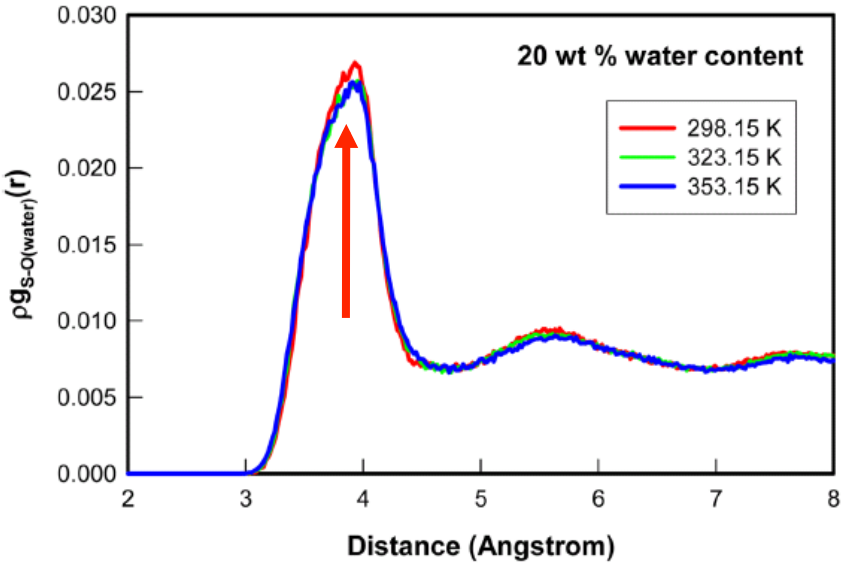
$S_{polymer}$-$S_{polymer}$





$S_{polymer}$-O_{water}





9-2-2011

GF Brunello, WR Mateker, SG Lee, JI Choi and SS Jang, J Renewable Sustainable Energy, 3, 043111, 2011.

Future Approaches: Mean Square Displacement

Mean Square Displacement (MSD)

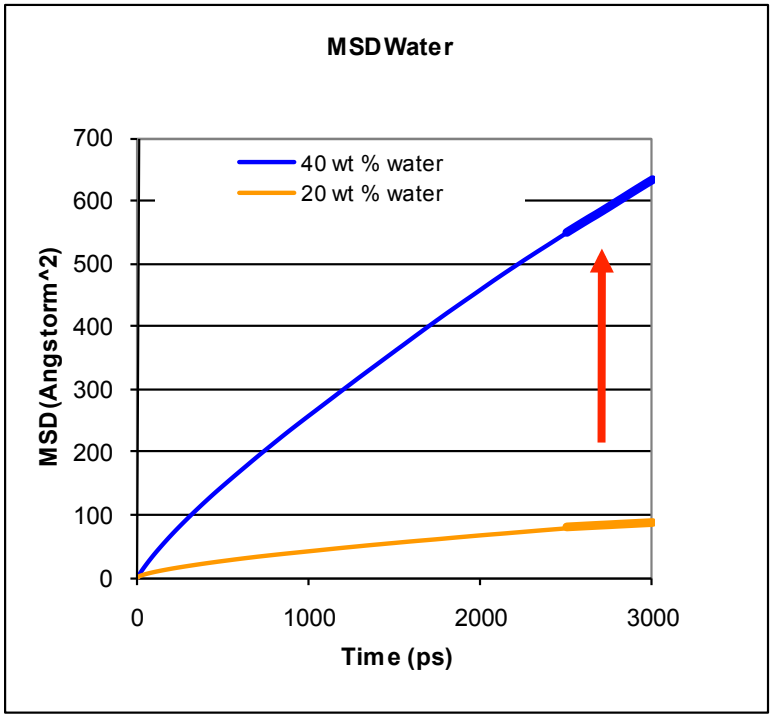
$$D = \lim_{t\to\infty} \frac{1}{6t} \left\langle \left(r(t) - r(0)\right)^2 \right\rangle$$

r(t) and r(0) are the positions of the target molecules at a time, t, greater than 0 and at t = 0, respectively

Diffusion coefficient can be determined by MSD of the target molecules.

We expect:

As increasing water contents, MSD of water → increase (due to swelling, free water > bound water)



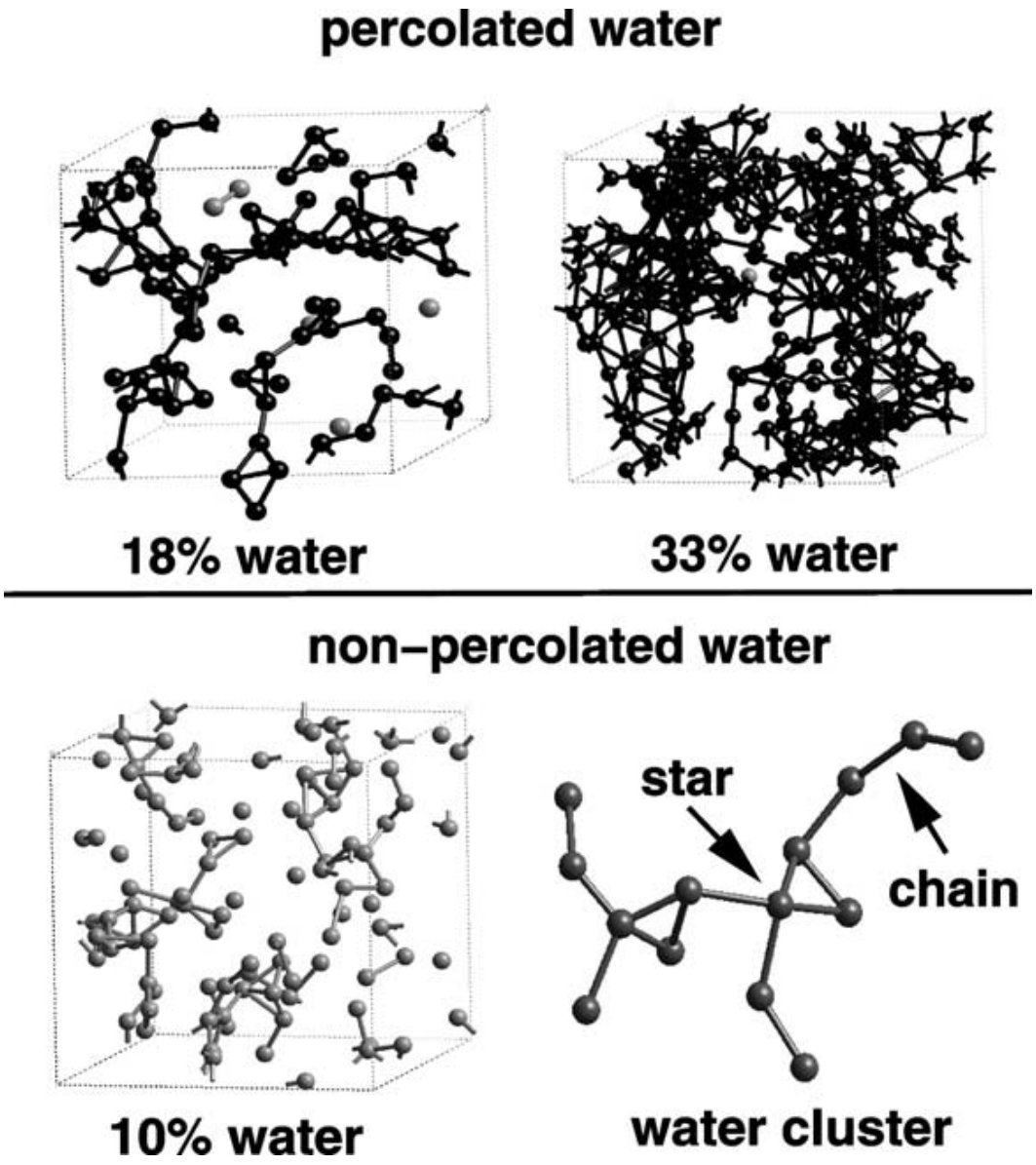
Case Study: Hydrogel

Diffusion coefficients of water (10^{-5} cm^2/s) in hydrogel:

0.03 (20 wt %) → 0.28 (40 wt %)

SG Lee, GF Brunello, DG Bucknall and SS Jang, Biomaterials, 30, 6130, 2009

Future Approaches: Percolation of water



Case Study: water in sucrose solution

Threshold distance for the percolation : 4 Å

As increasing water contents, water connectivity is enhanced. (due to swelling)

V Molinero, T Cagin, WA Goddard III, Chem Phys Lett, 377, 469, 2003.