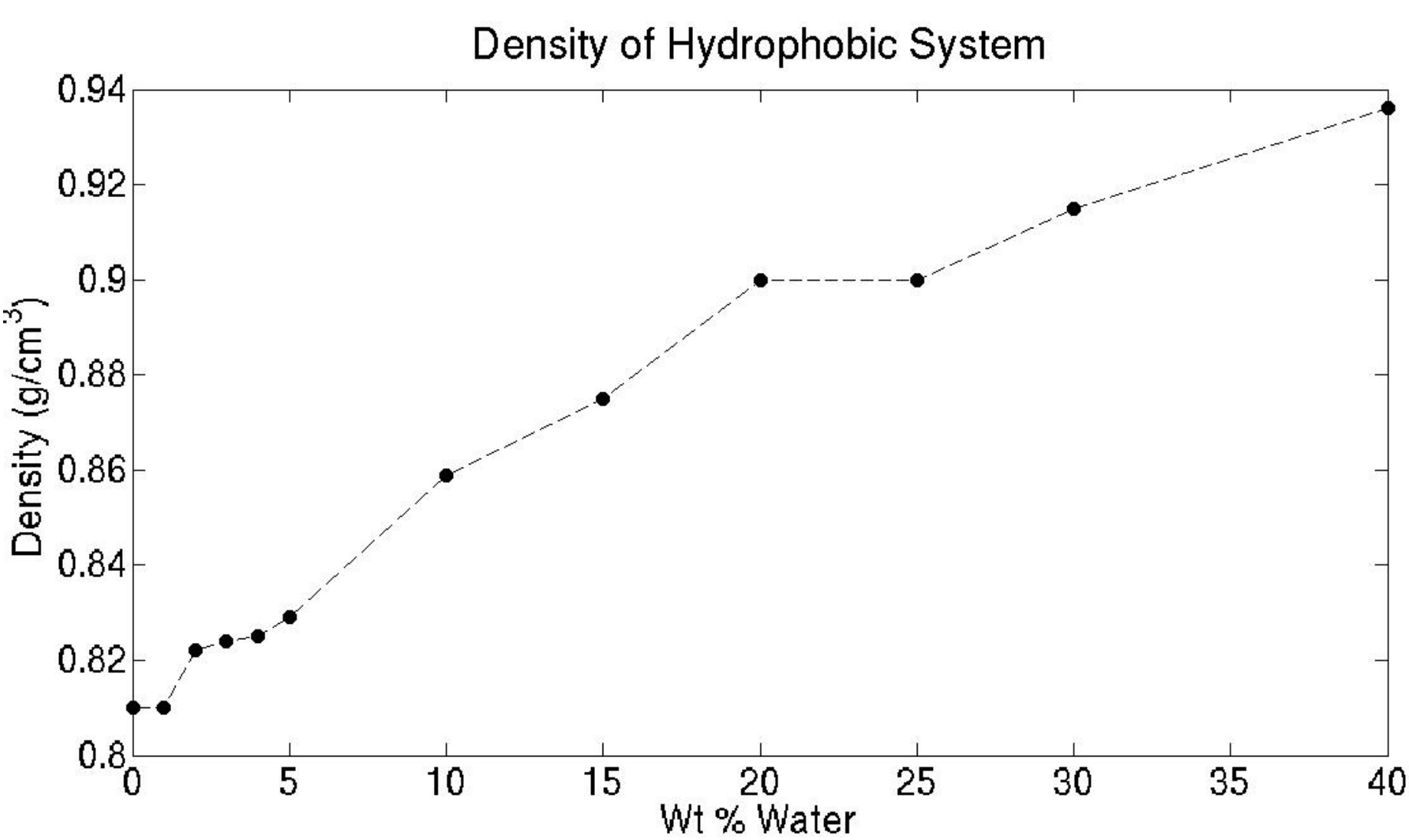
California Institute of Technology

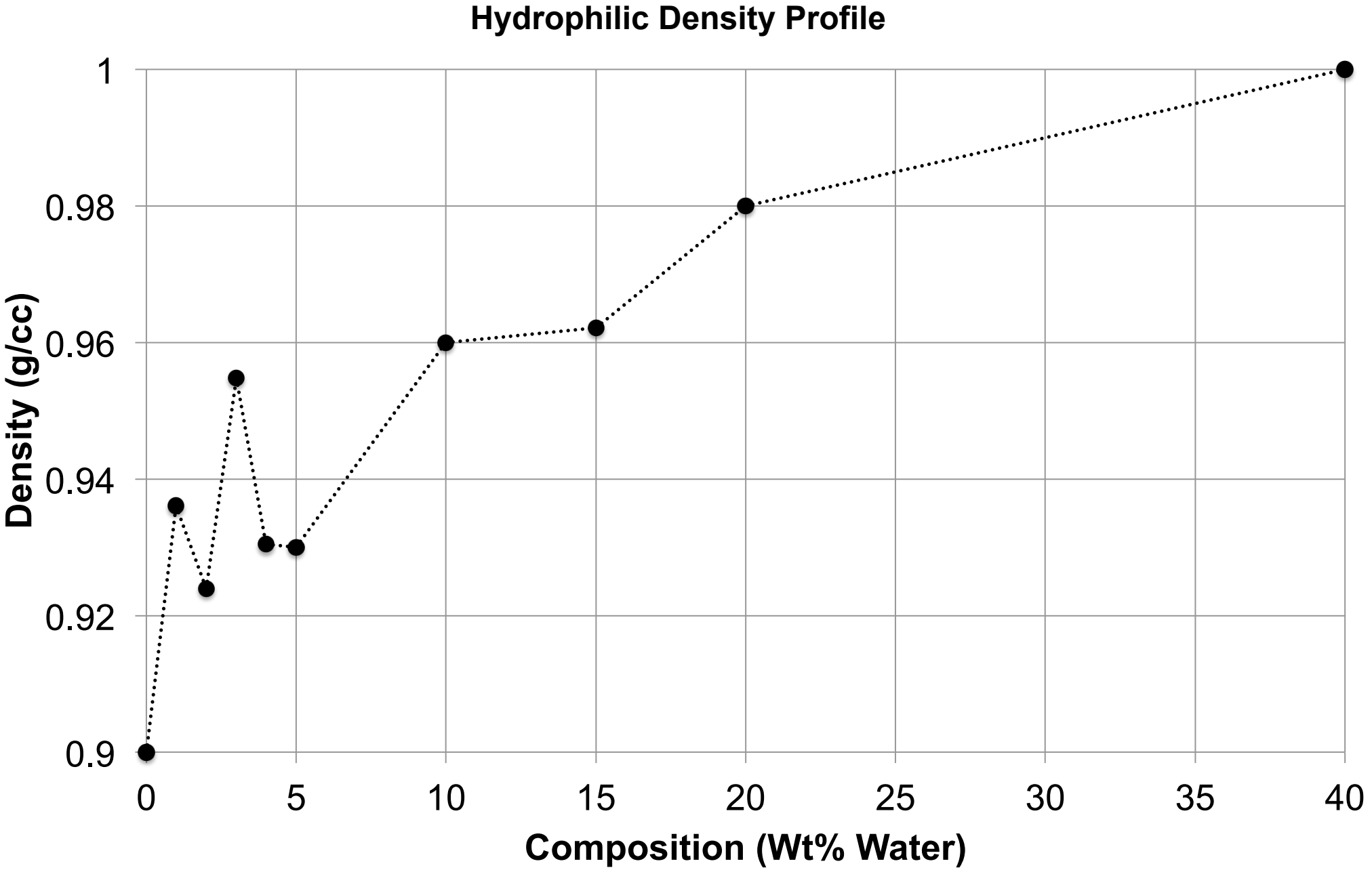
Materials and Process Simulation Center

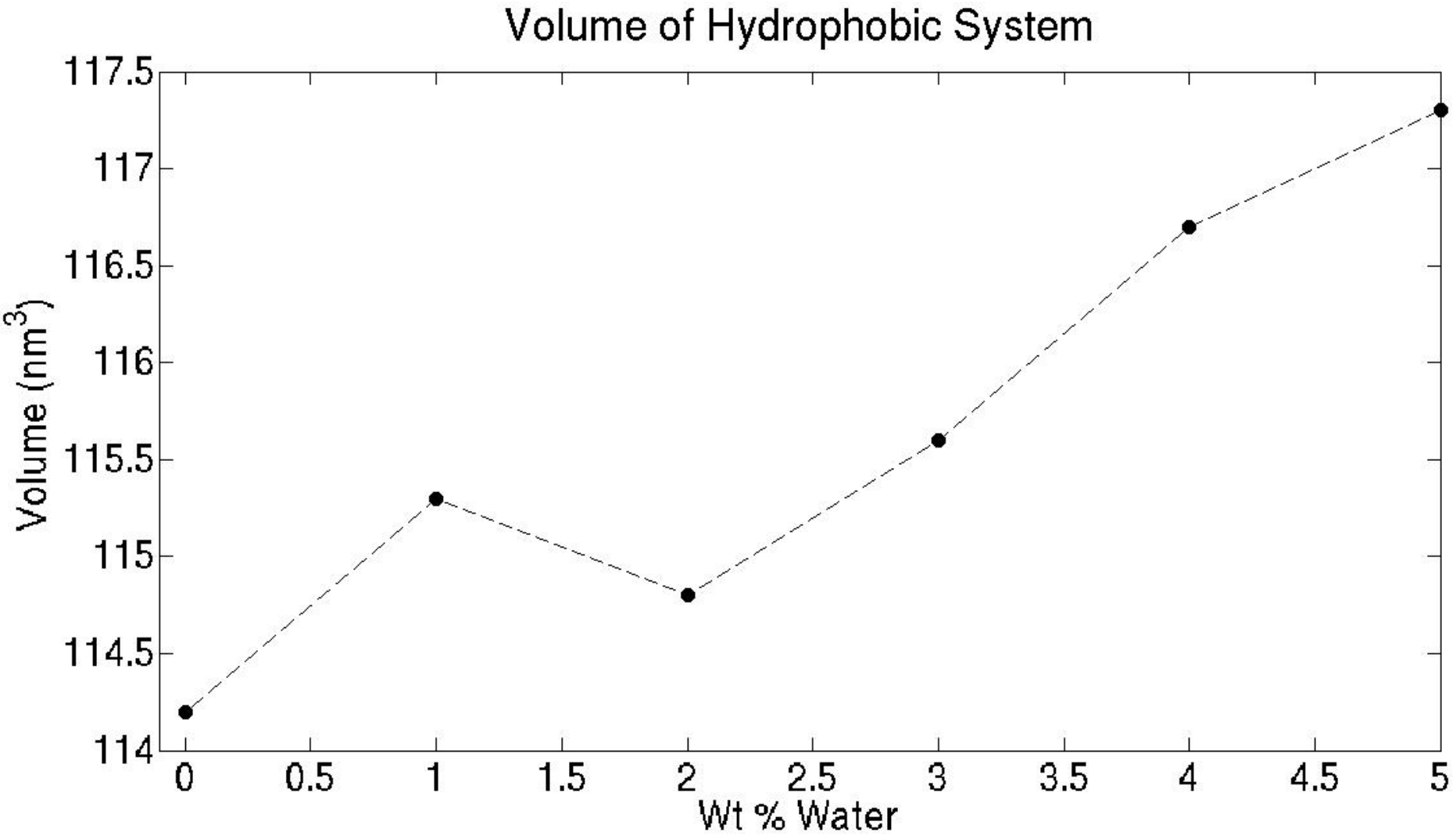
Jason Crowley, David Lehtihet, Seung Geol Lee, Andres Jaramillo-Botero and William A. Goddard III

DOW 11-30-2011



- Density of dry polymer: 0.81 g/cm^3
- Density increases with water content
- Tends toward the density of bulk water at high water content
- Uncertainty in densities: 0.004-0.005

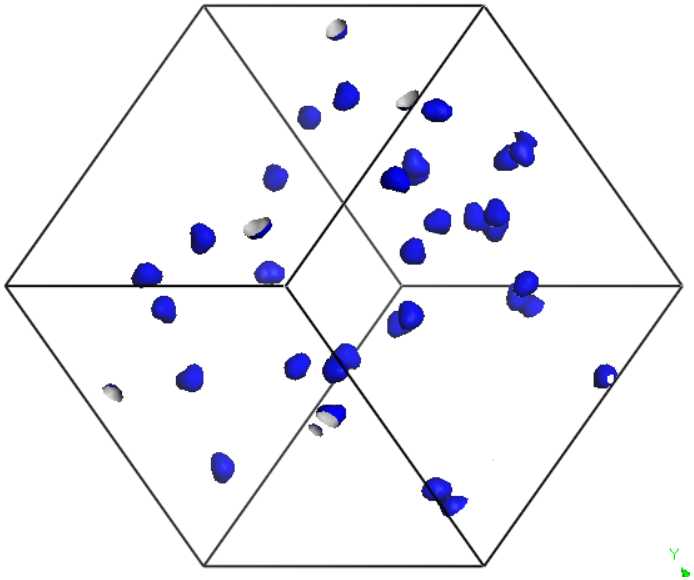

Hydrophilic Density Profile
Density (g/cc)
1
0.98
0.96
0.94
0.92
0.9
0
5
10
15
20
25
30
35
40
Composition (Wt% Water)



Same figure, zoomed in

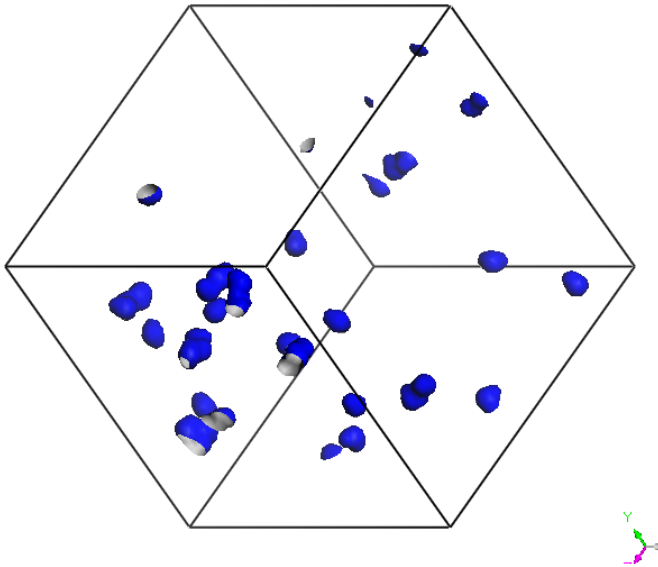
Water phase development

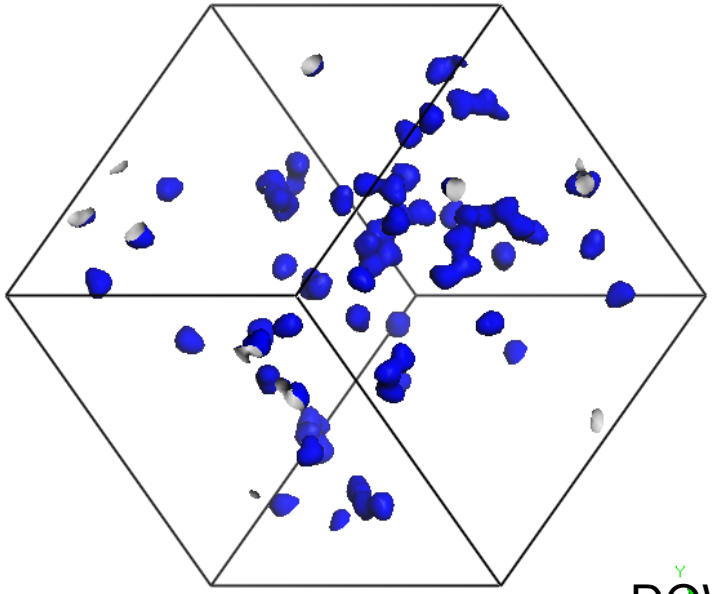
Hydrophobic



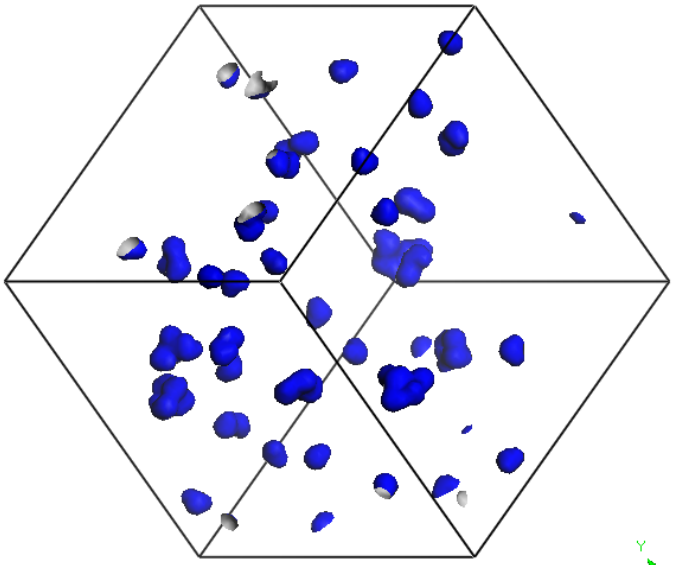
1 wt %
water content

Hydrophilic





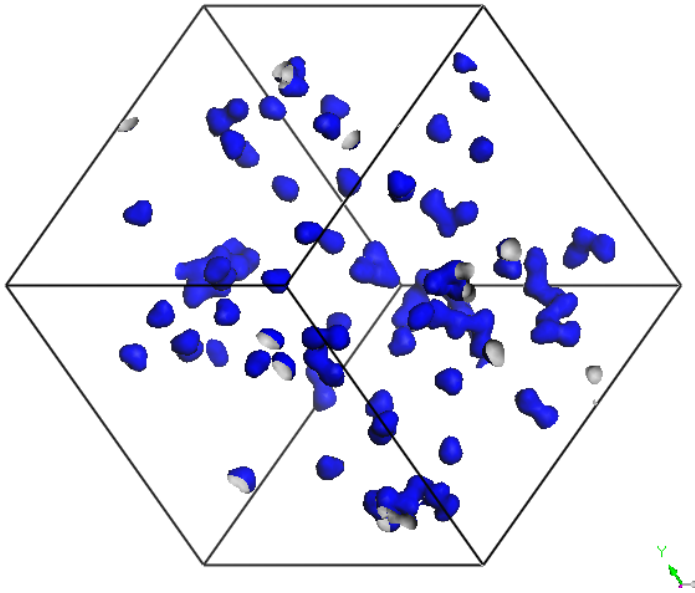
2 wt %
water content



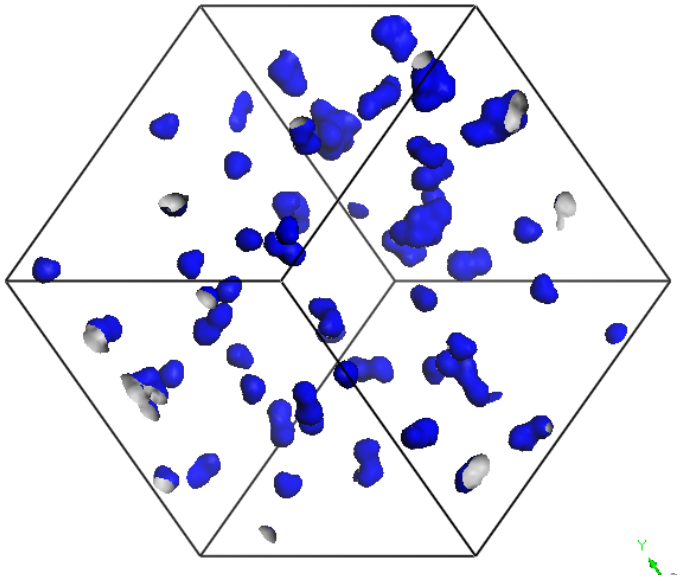
Water phase development

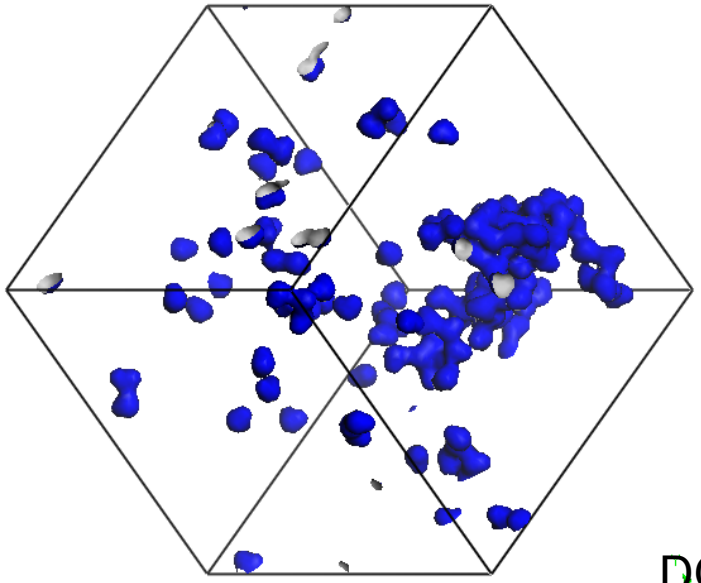
Hydrophobic

Hydrophilic

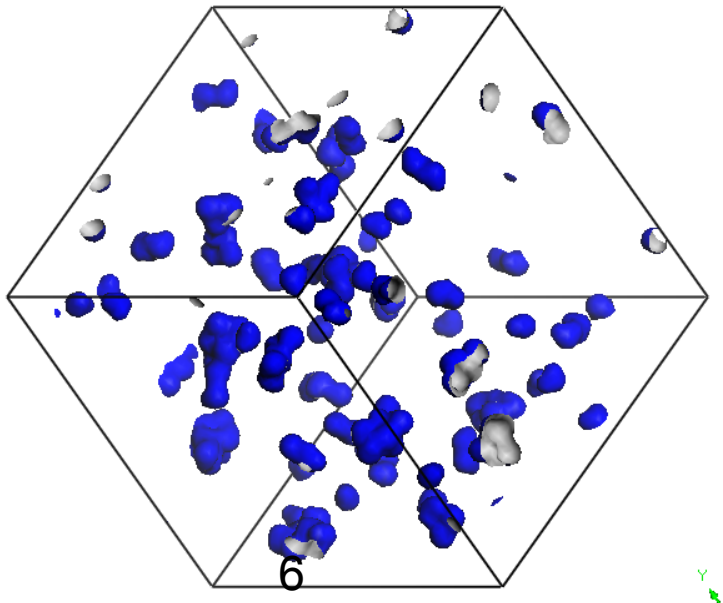


3 wt %
water content





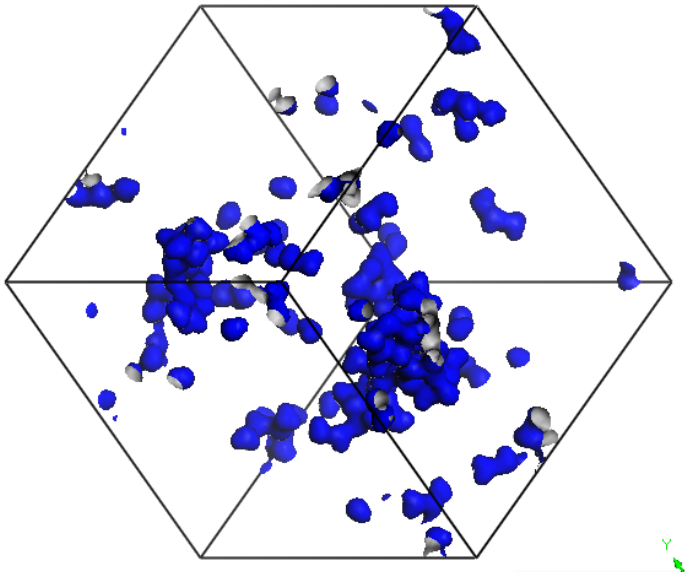
4 wt %
water content



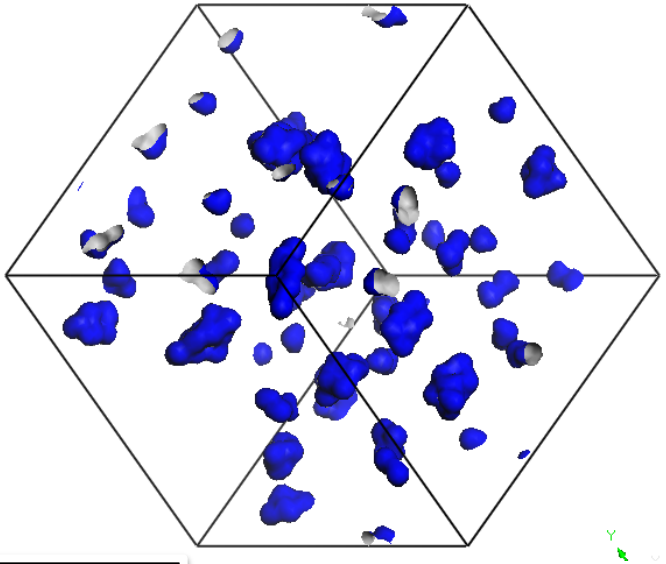
Water phase development

Hydrophobic

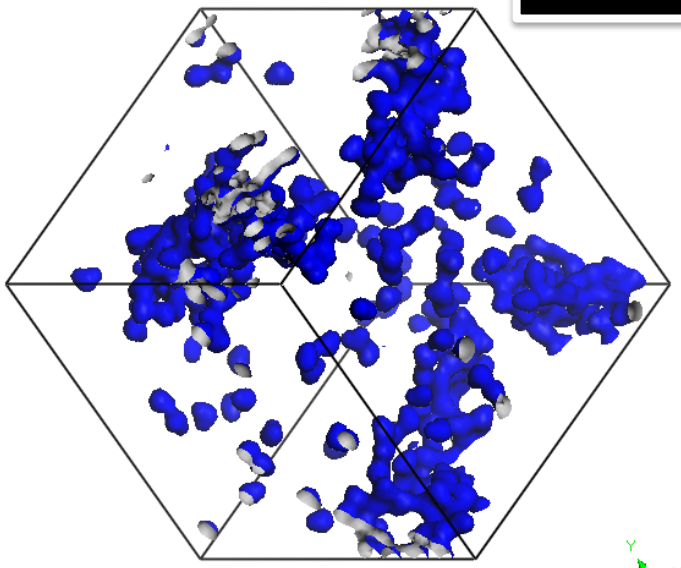
Hydrophilic



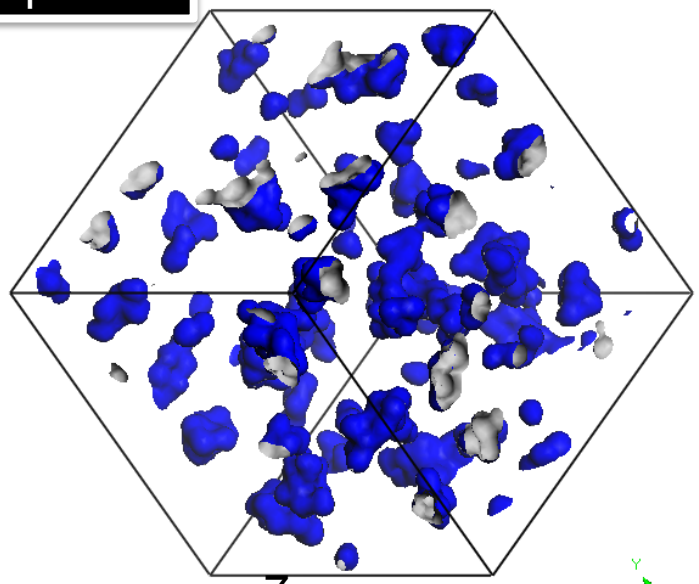
5 wt %
water content



Water is more packed in hydrophobic



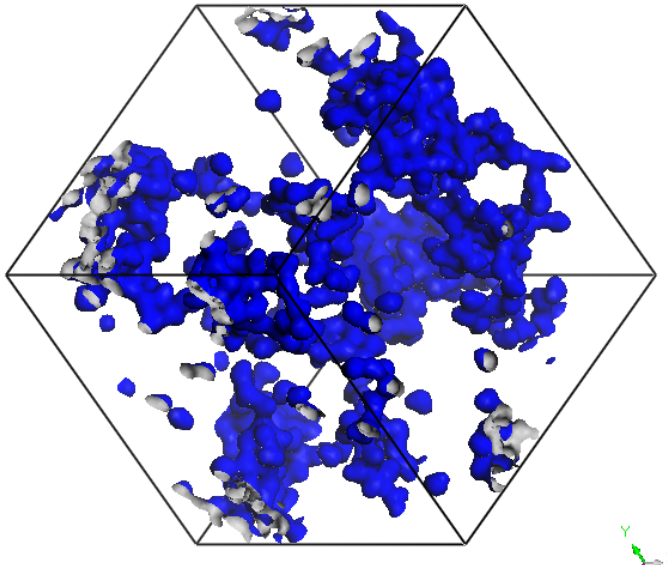
10 wt %
water content



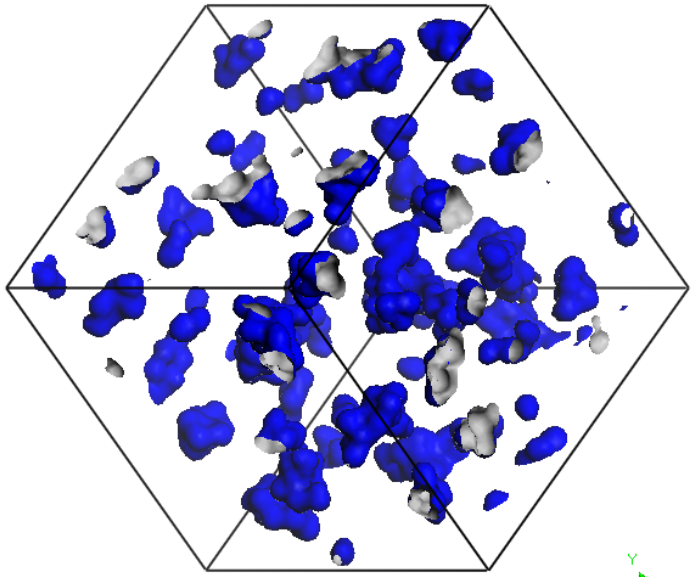
Water phase development

Hydrophobic

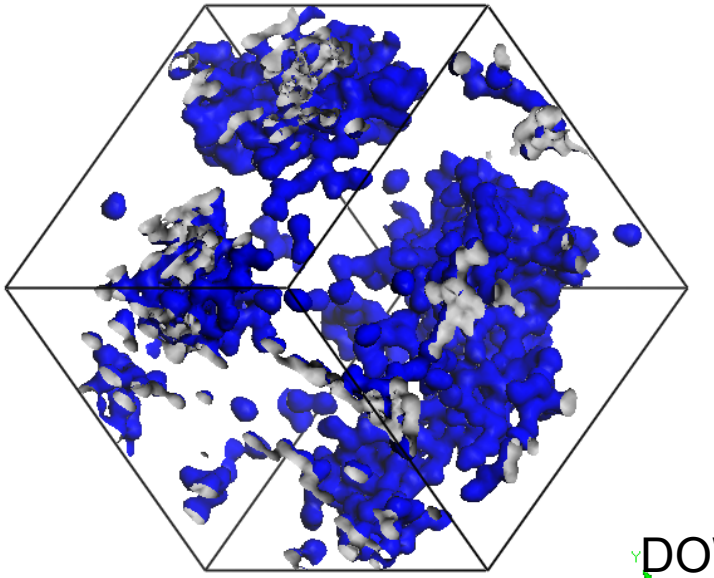
Hydrophilic



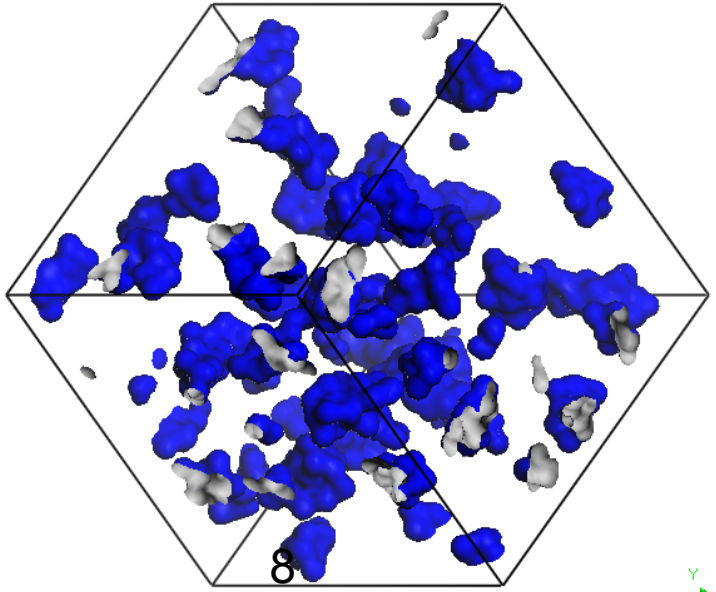
15 wt %
water content



Percolation
Started



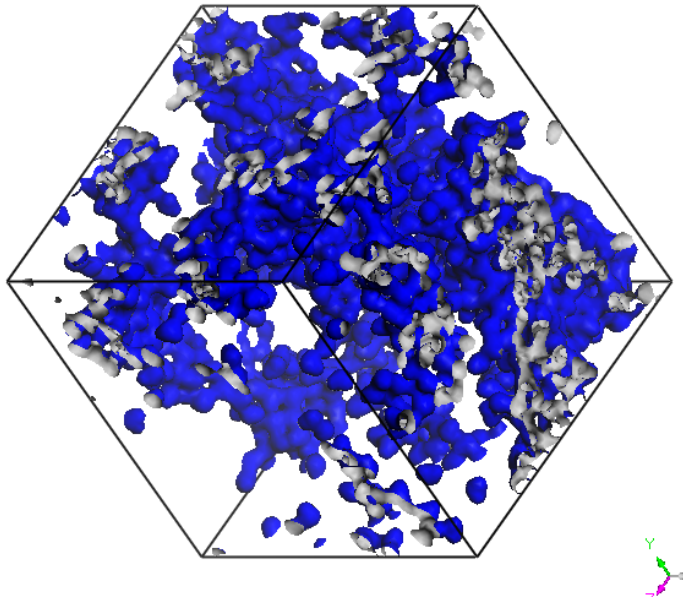
20 wt %
water content



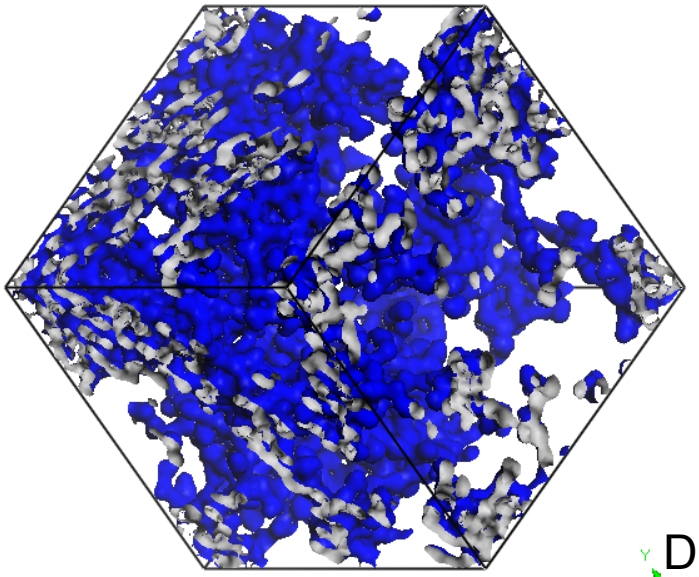
Water phase development

Hydrophobic

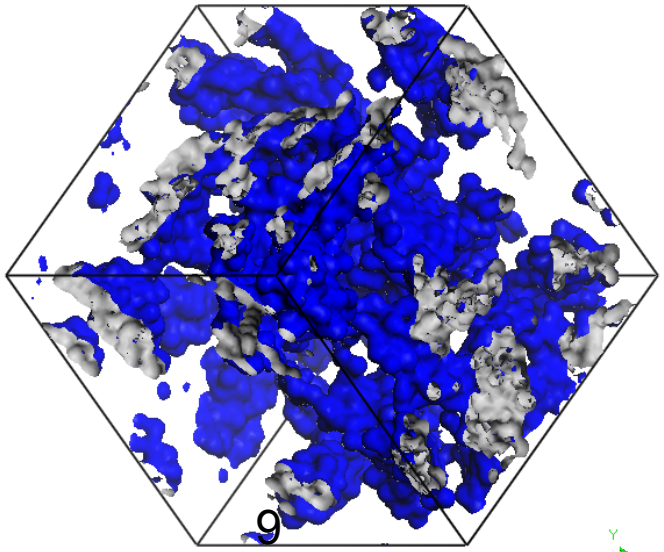
Hydrophilic

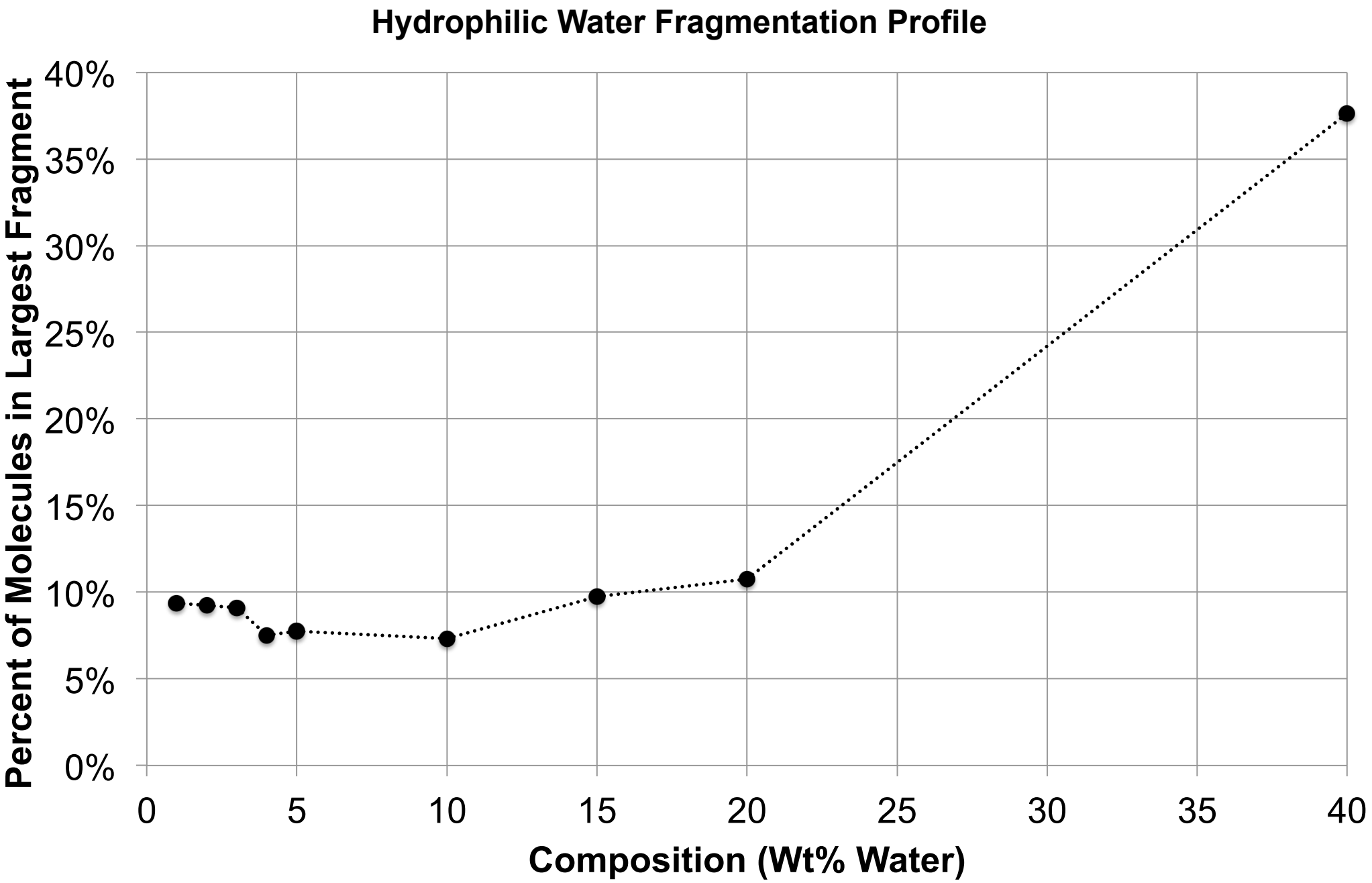


30 wt %
water content

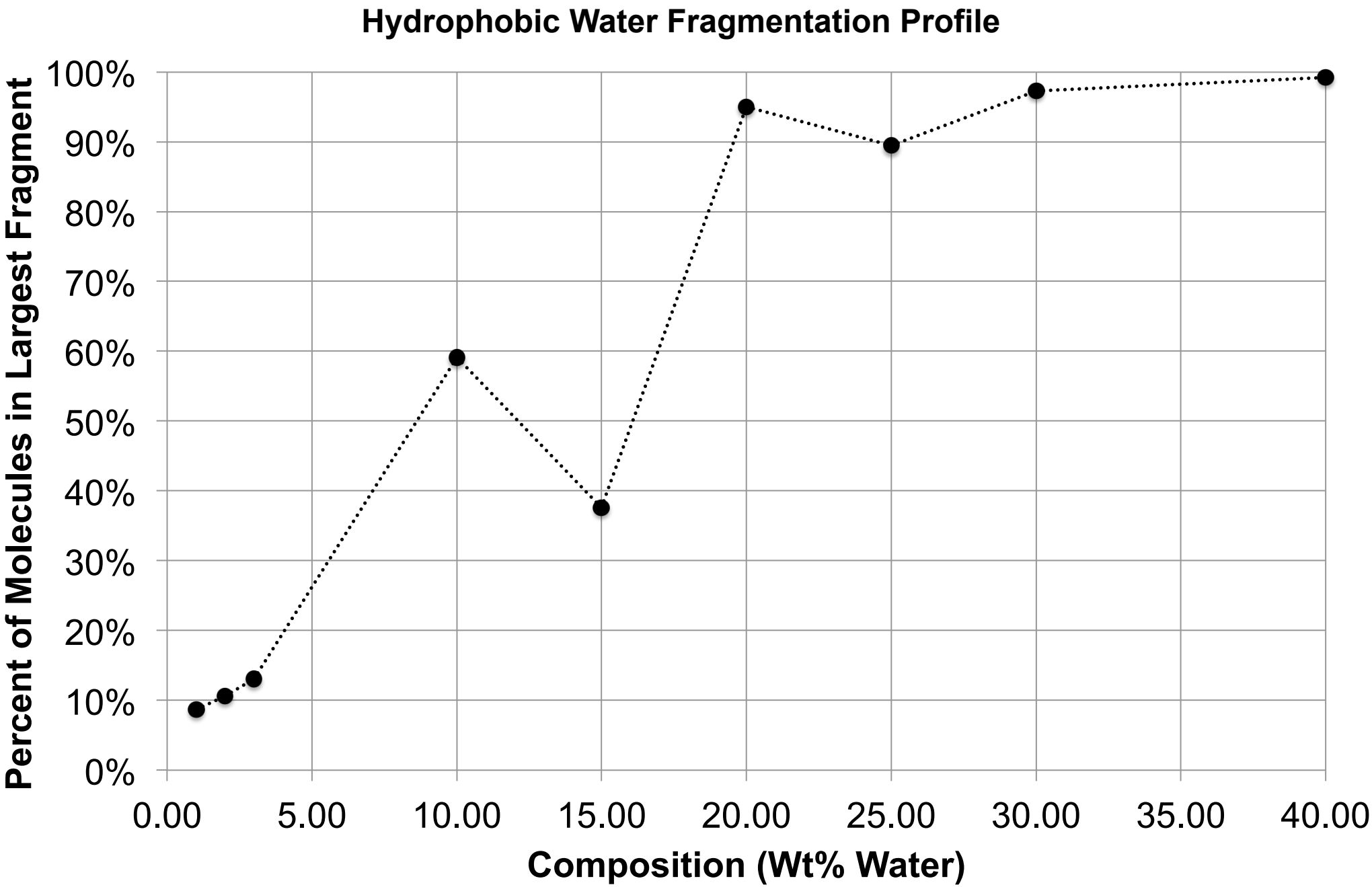


40 wt %
water content



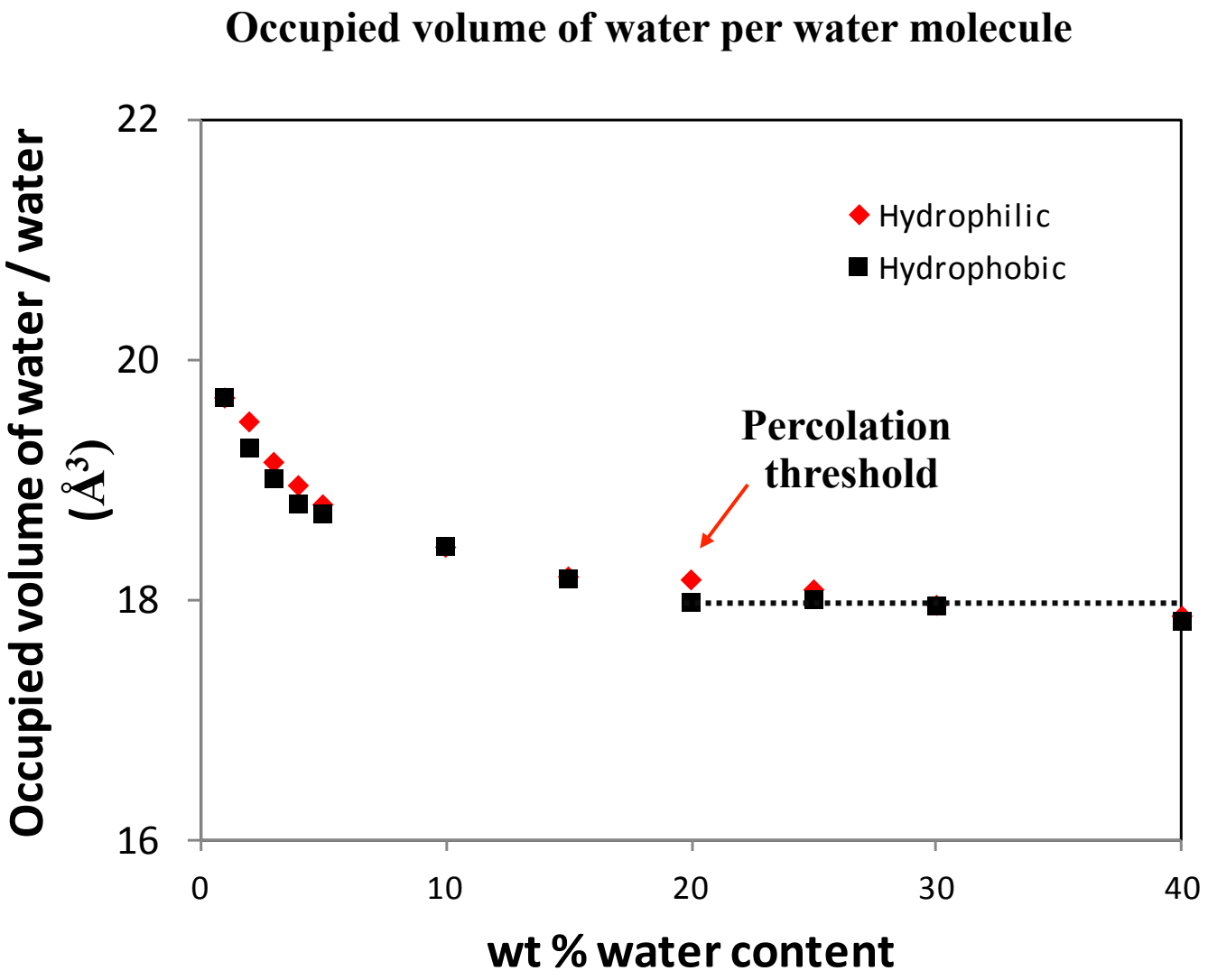


Fragmentation profile. A value of 100% places all water molecules in the same fragment (percolation). The threshold occurs in the 10-15 wt% range for both systems.

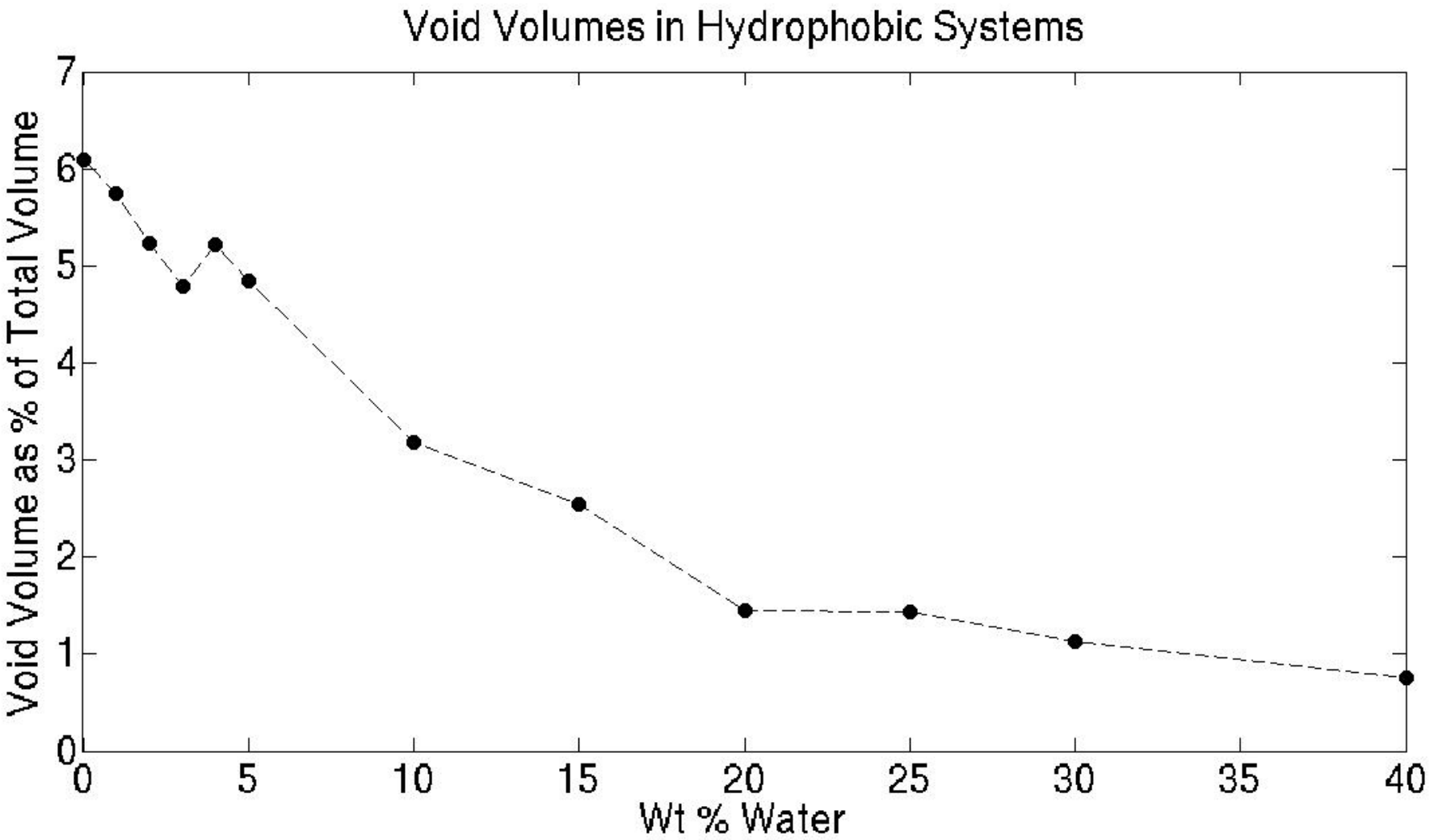


Fragmentation profile. A value of 100% places all water molecules in the same fragment (percolation). The threshold occurs in the 10-15 wt% range for both systems.

Water phase development

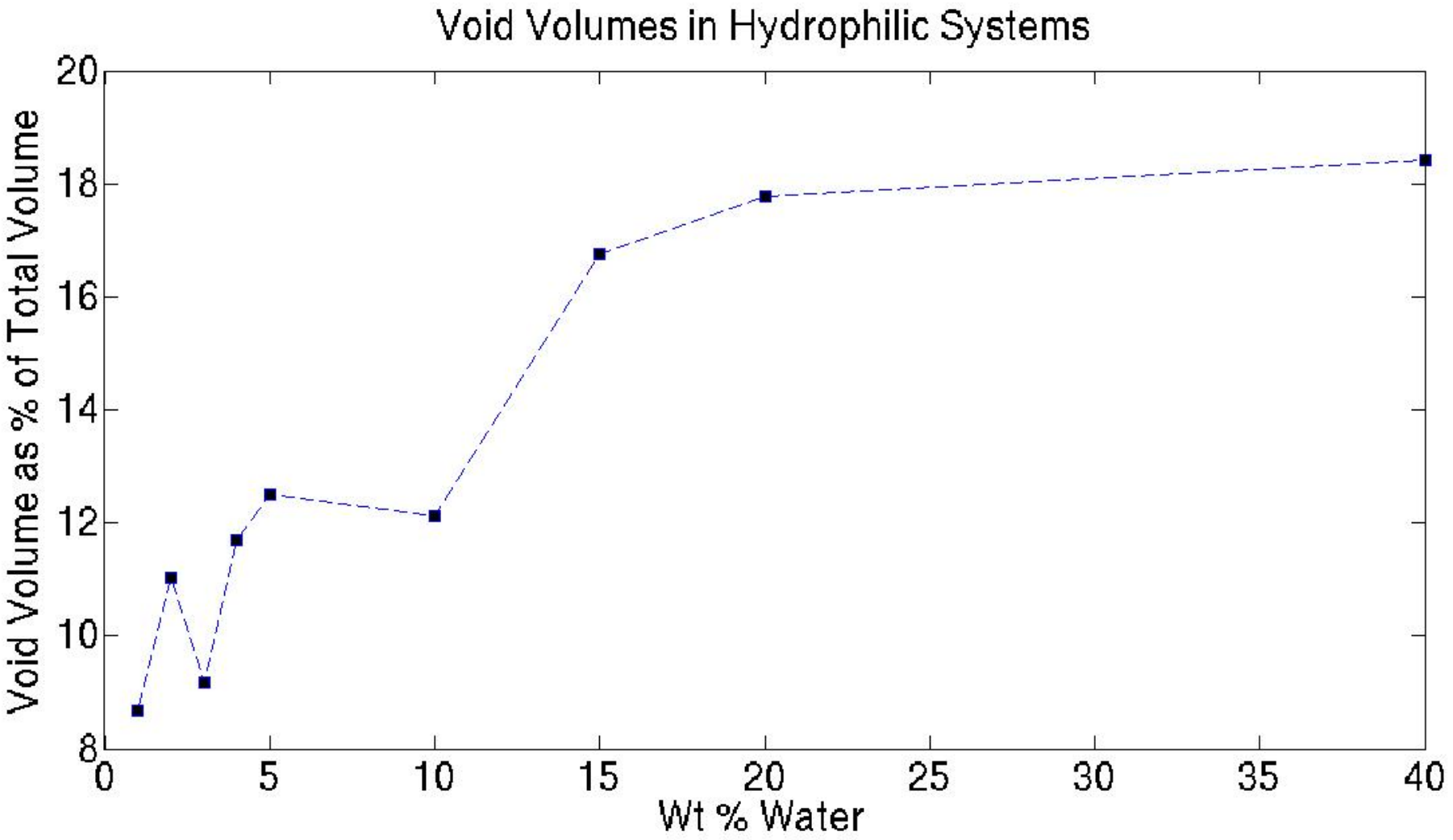


Occupied volume of water per water molecules is decreased with increasing water content & flat after 20 wt % water content.
→ Water molecules are clusterized & percolated.

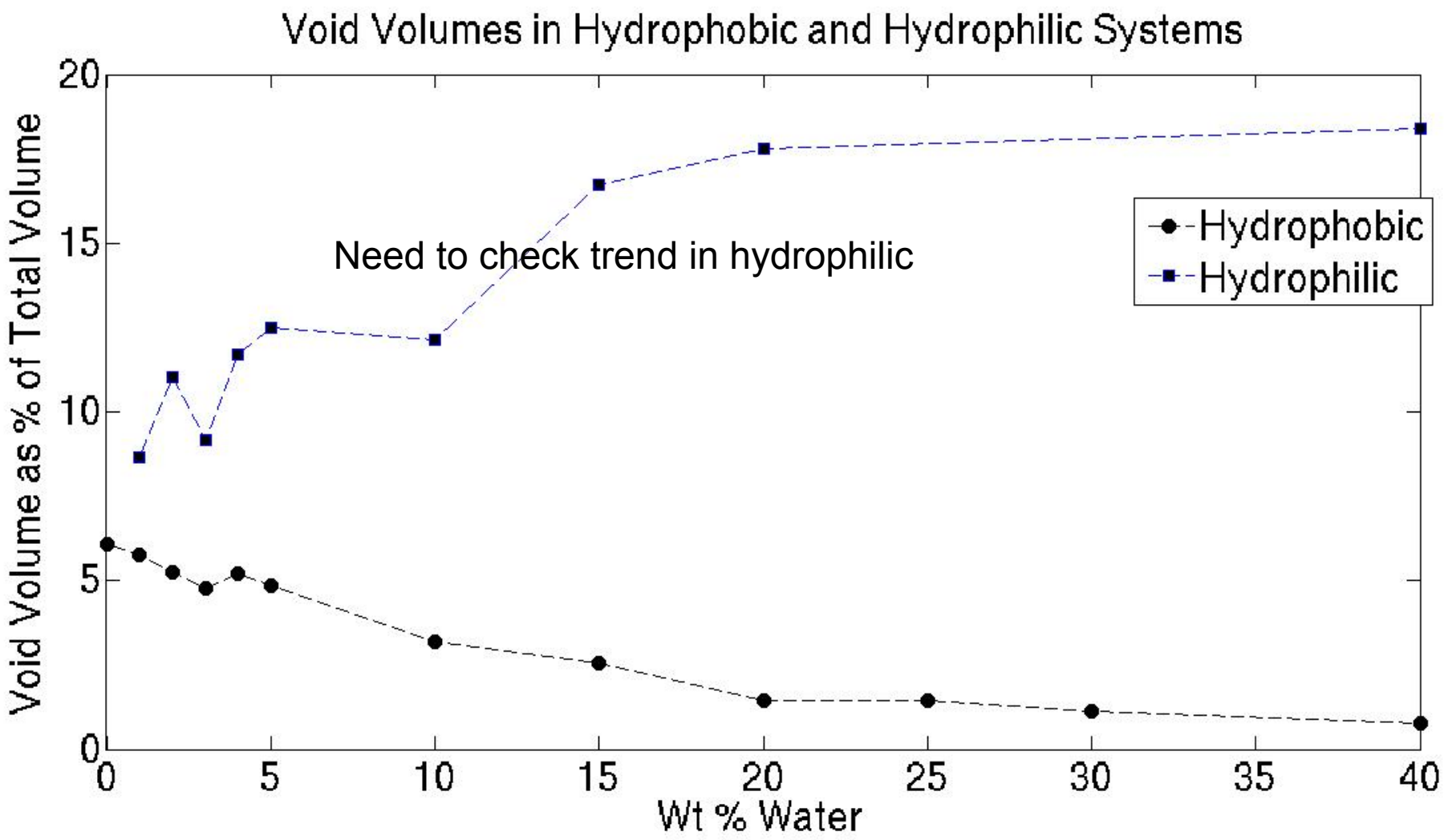


Void volumes tell us how much space we have to put in more waters. The trend is consistent with the density/volume behavior: oscillations at low water content, general decreasing, critical behavior at 20%. Void volume decreases as we add more and more water.

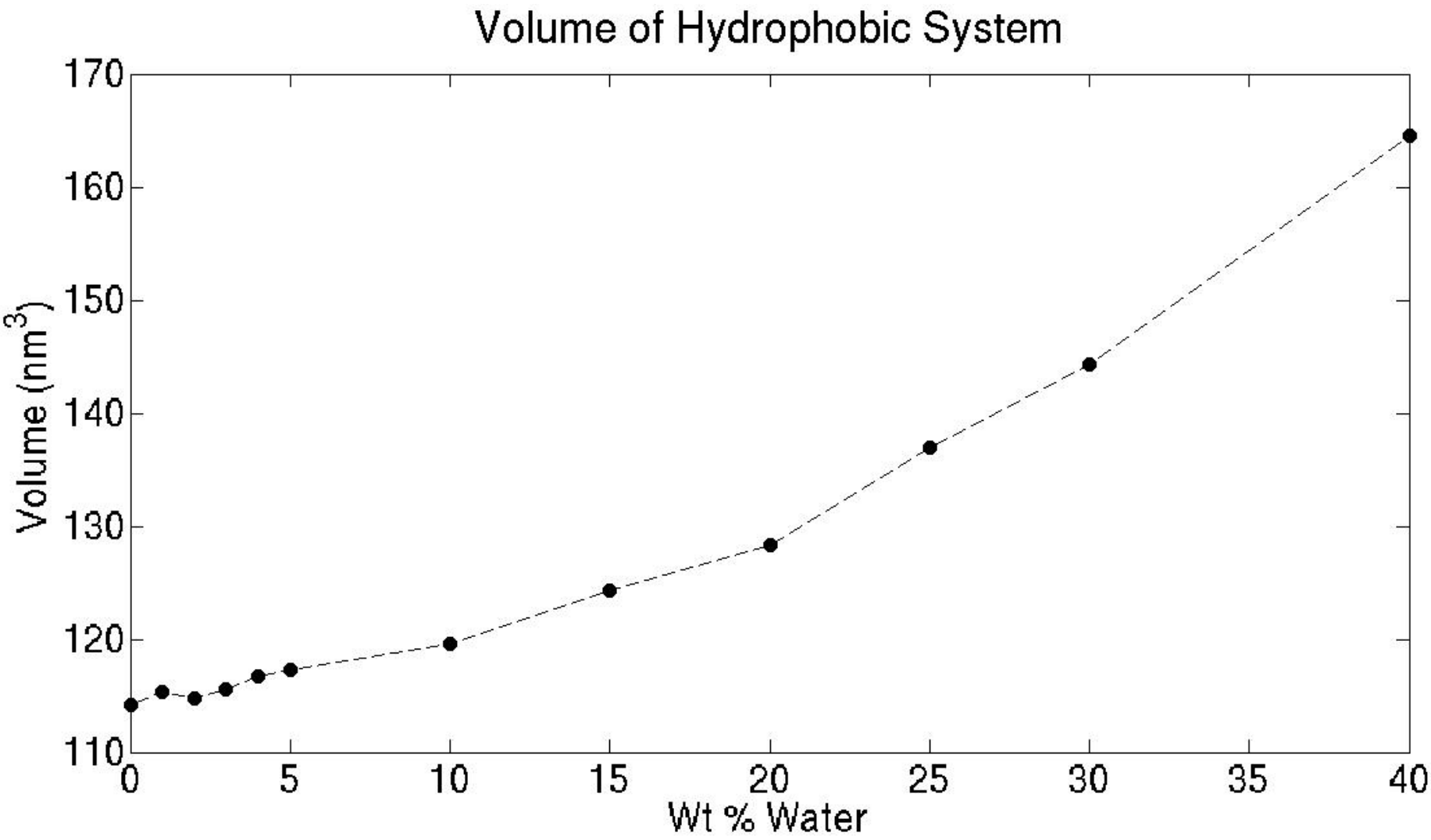
Voids distribution (fewer larger voids)



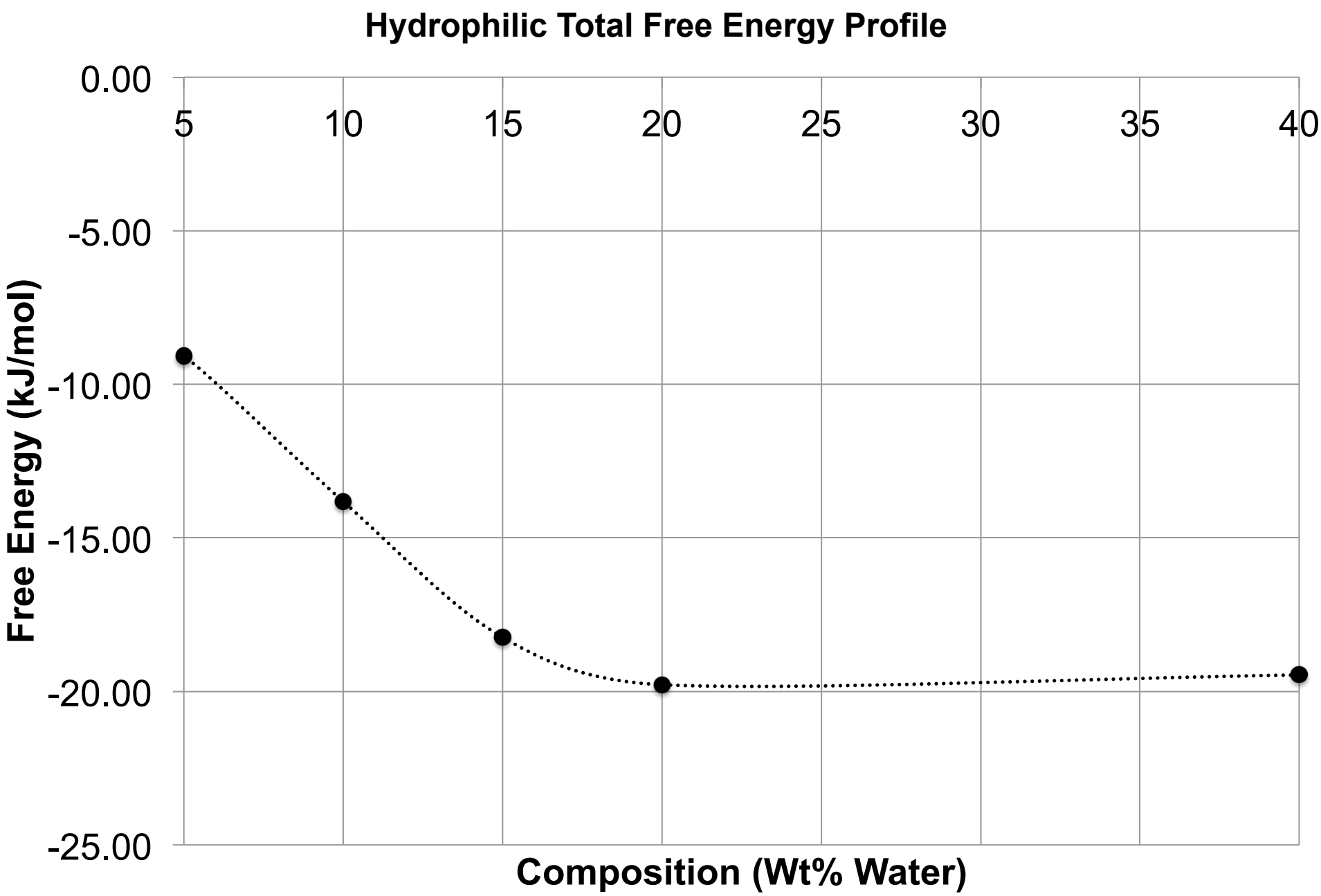
Void volume increases, flattens after water percolates

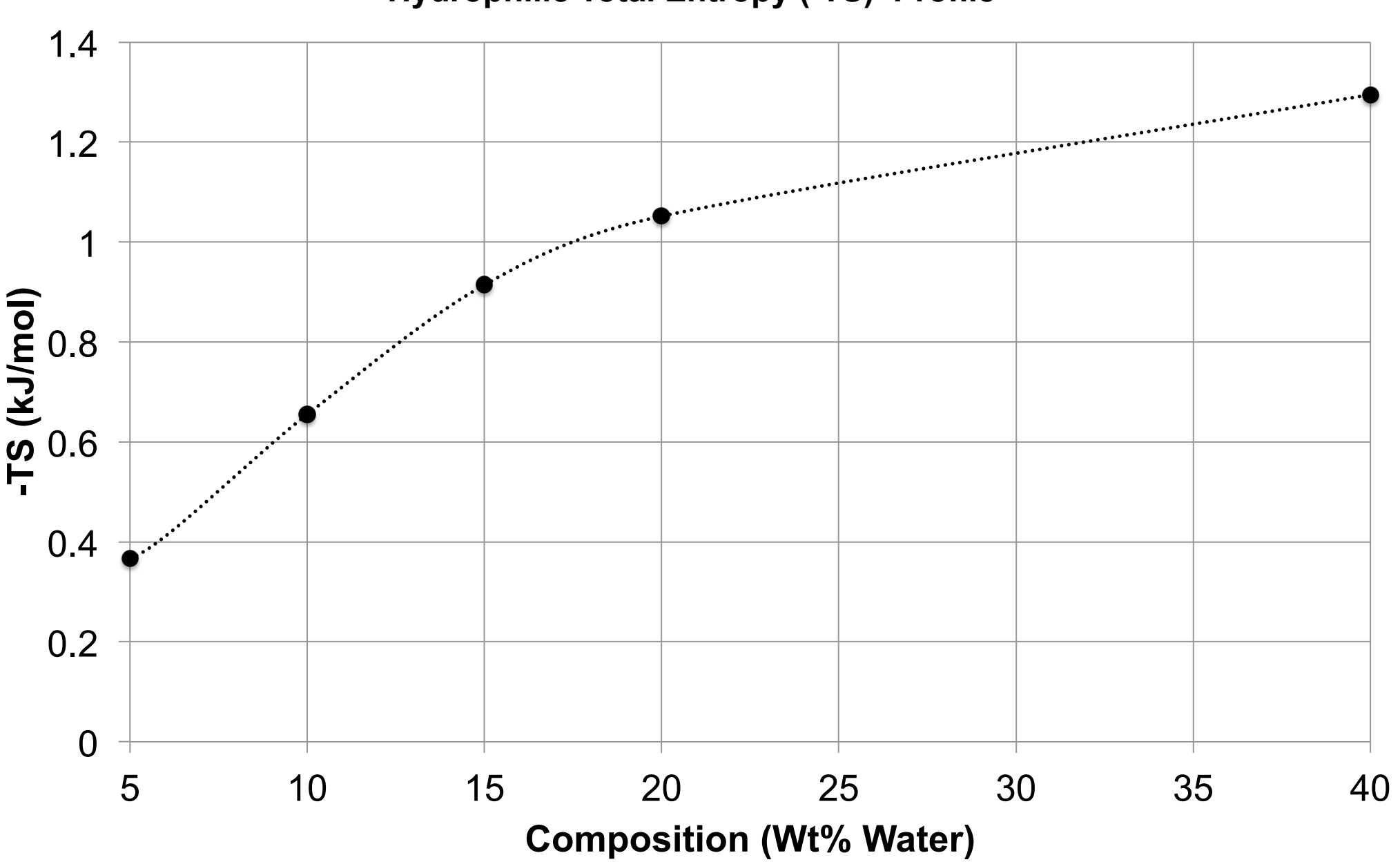


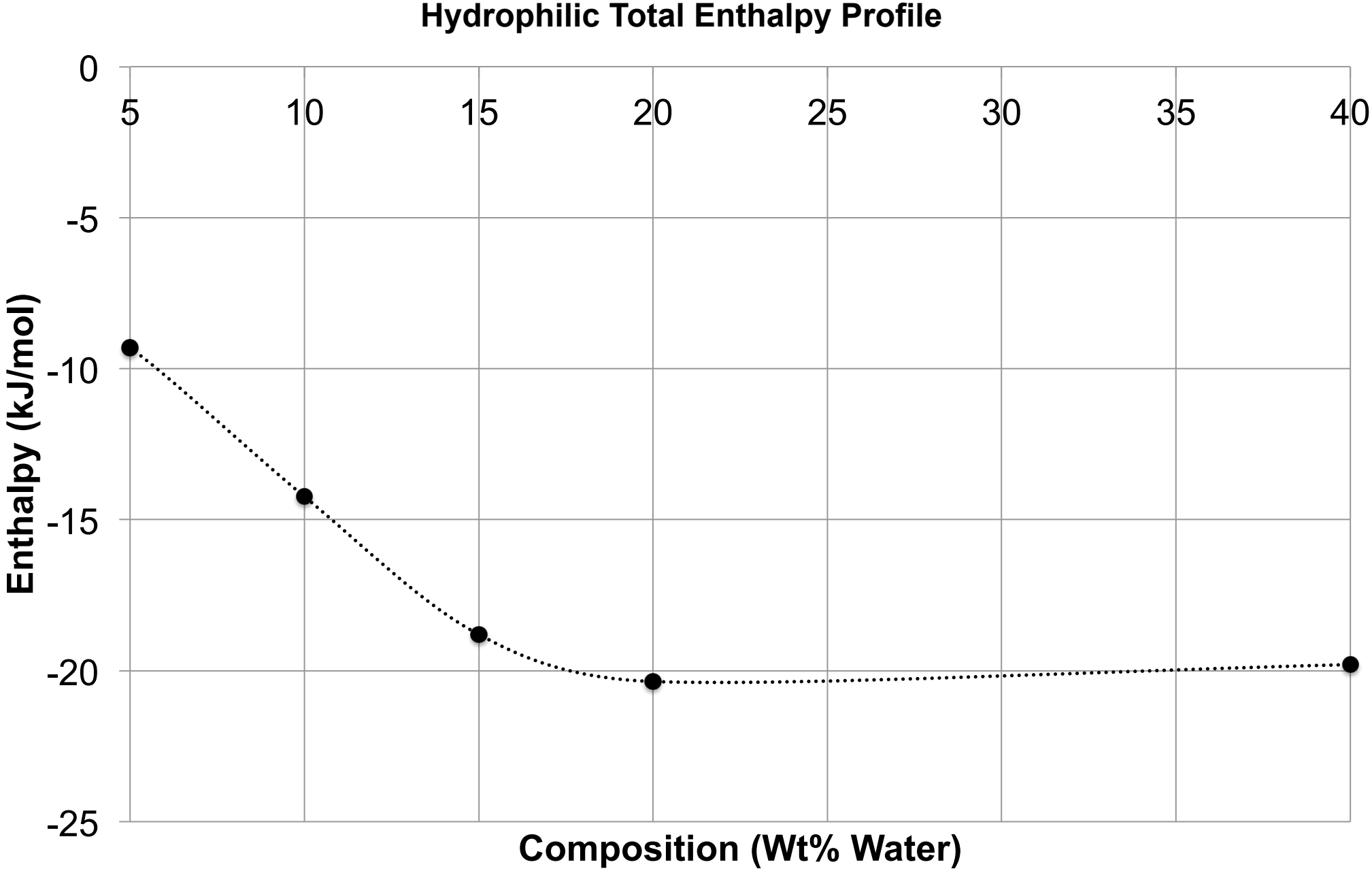
Void volume flattens after water percolates
We will do void+water volume

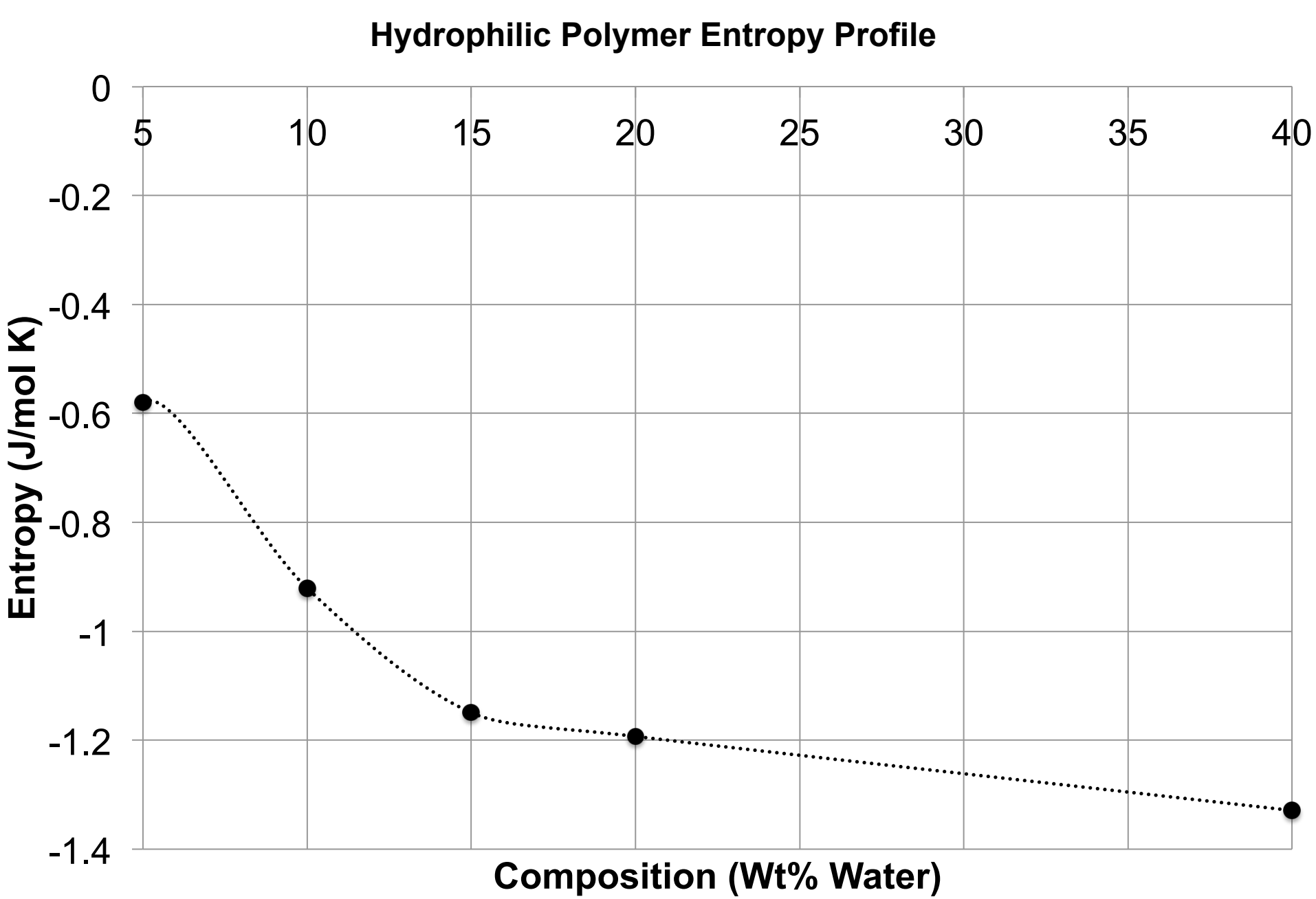


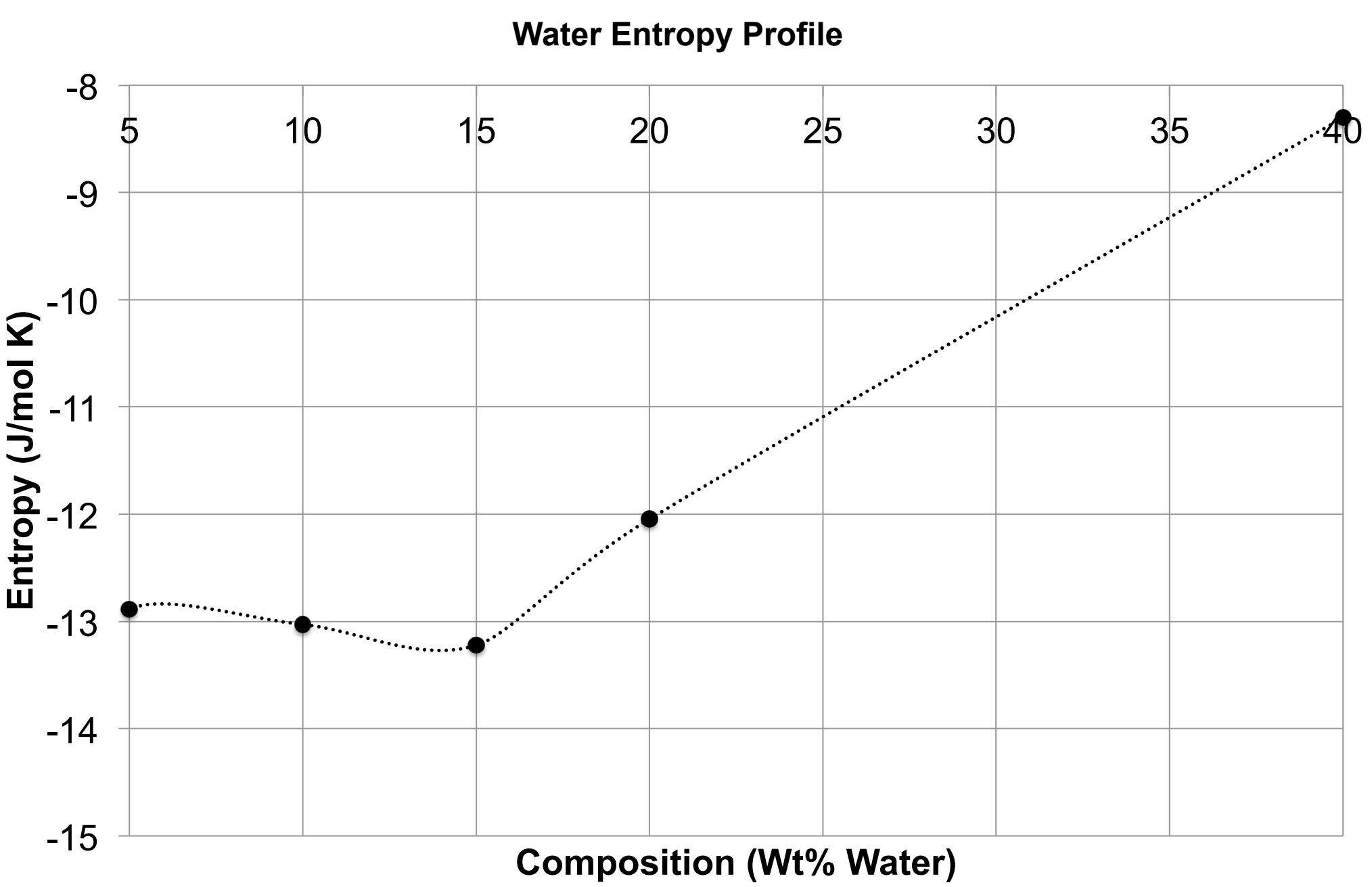
Notice swelling of bulk polymer as water is added

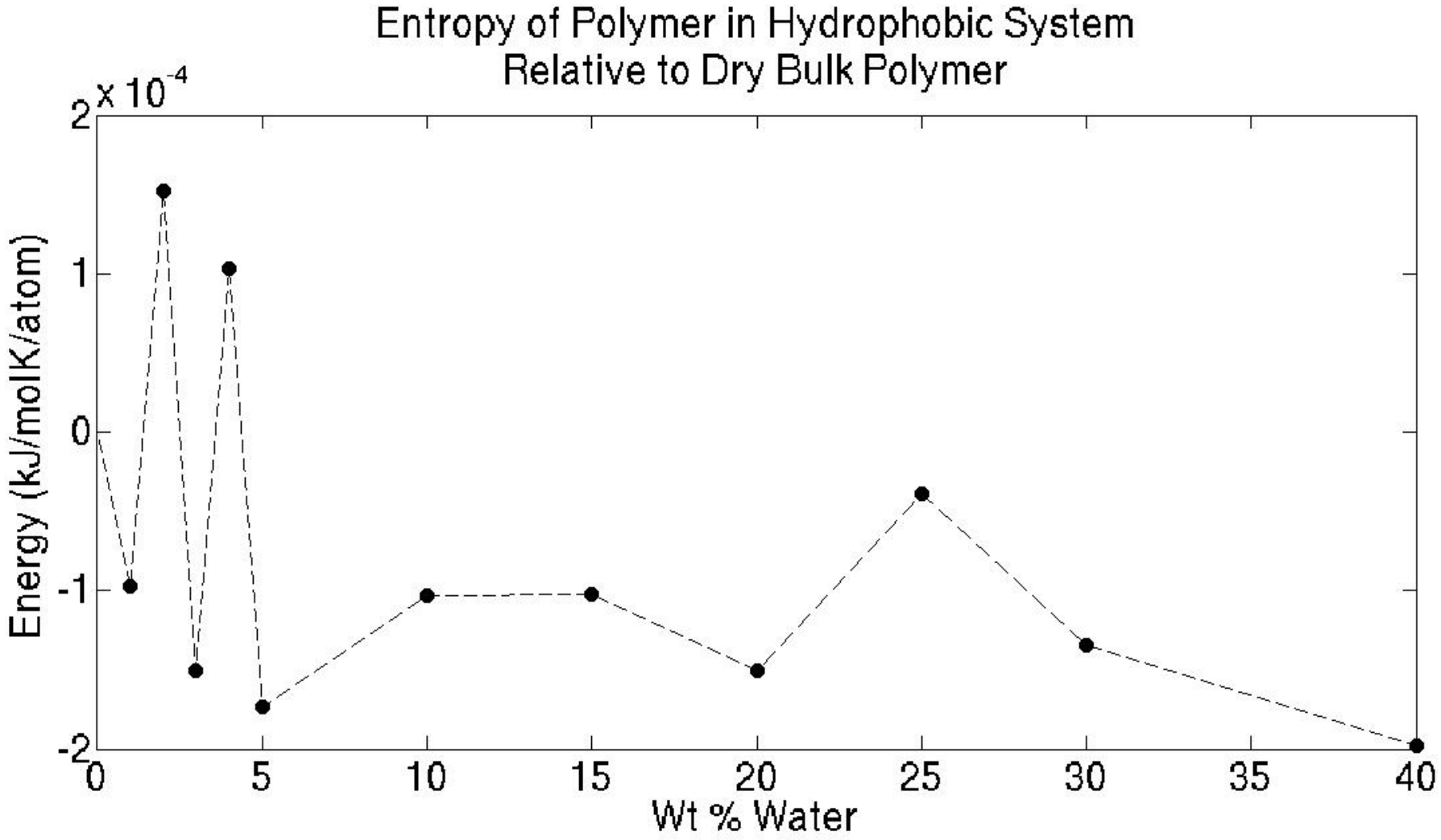

Hydrophilic Total Free Energy Profile
0.00
-5.00
-10.00
-15.00
-20.00
-25.00
5
10
15
20
25
30
35
40
Free Energy (kJ/mol)
Composition (Wt% Water)


Hydrophilic Total Entropy (-TS) Profile
-TS (kJ/mol)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
5
10
15
20
25
30
35
40
Composition (Wt% Water)

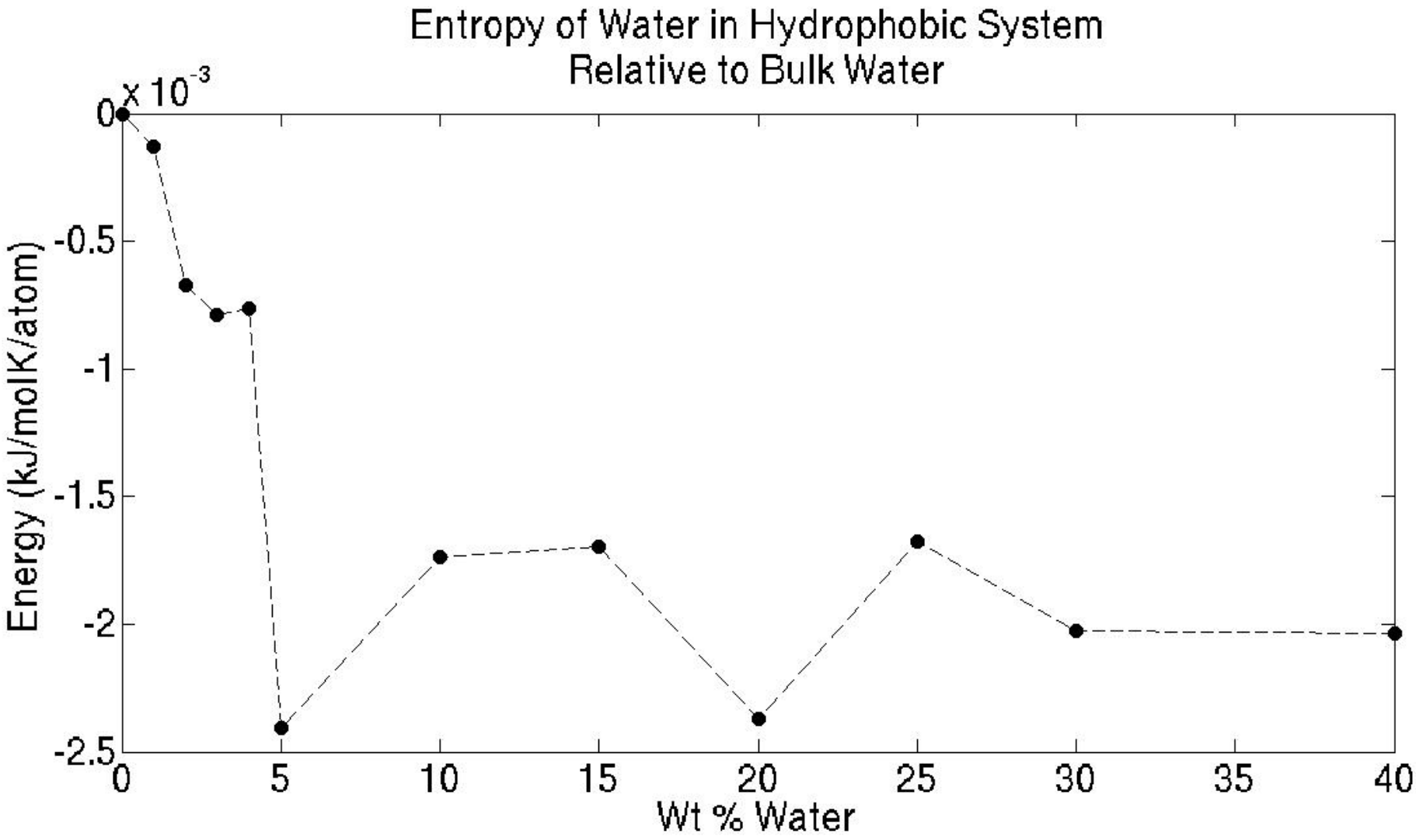

Hydrophilic Total Enthalpy Profile
0
-5
-10
-15
-20
-25
5
10
15
20
25
30
35
40
Enthalpy (kJ/mol)
Composition (Wt% Water)


Hydrophilic Polymer Entropy Profile
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
5
10
15
20
25
30
35
40
Entropy (J/mol K)
Composition (Wt% Water)

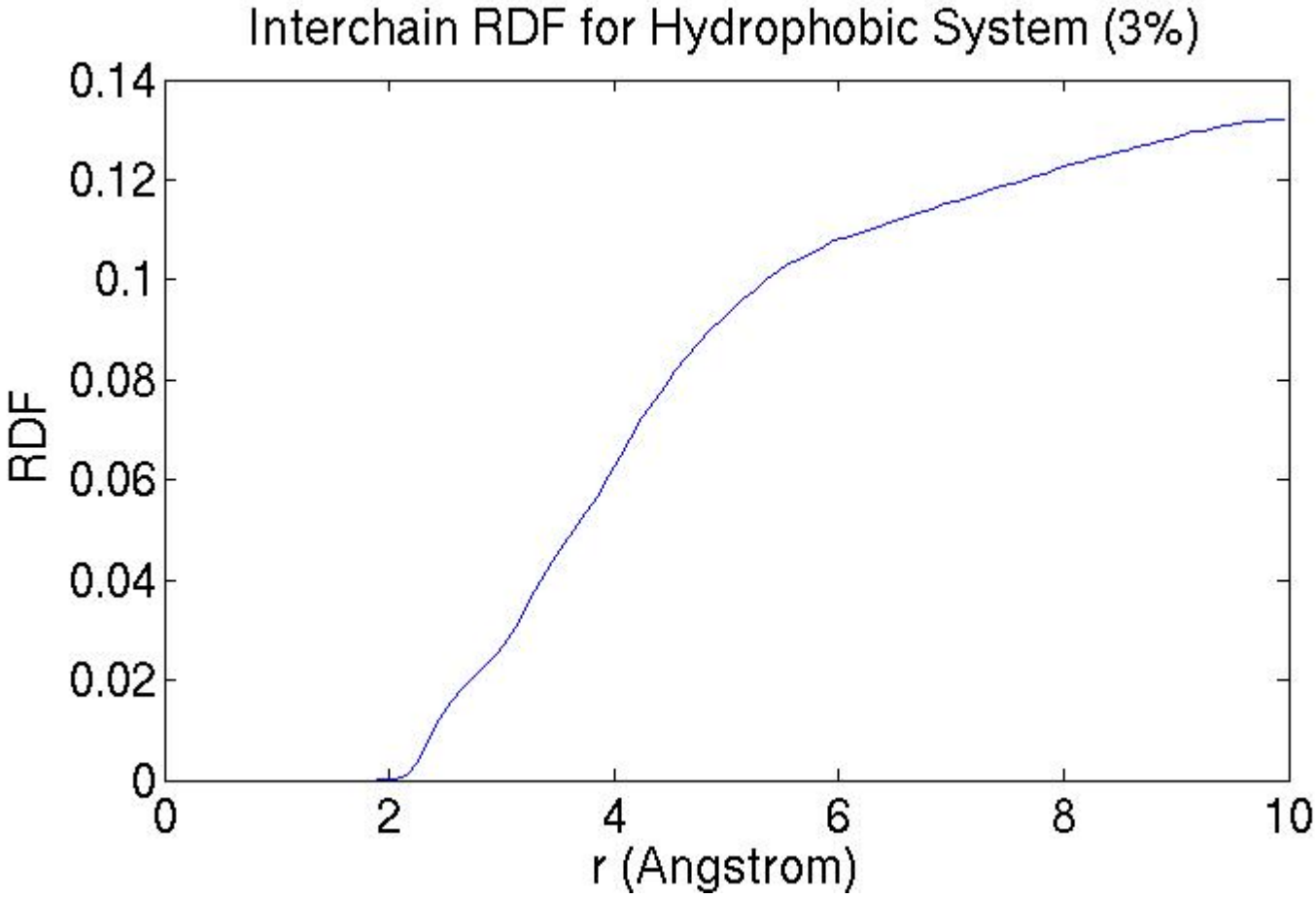

Water Entropy Profile
-8
-9
-10
-11
-12
-13
-14
-15
5
10
15
20
25
30
35
40
Entropy (J/mol K)
Composition (Wt% Water)



Polymer entropy PER ATOM
Entropy, NOT -TS



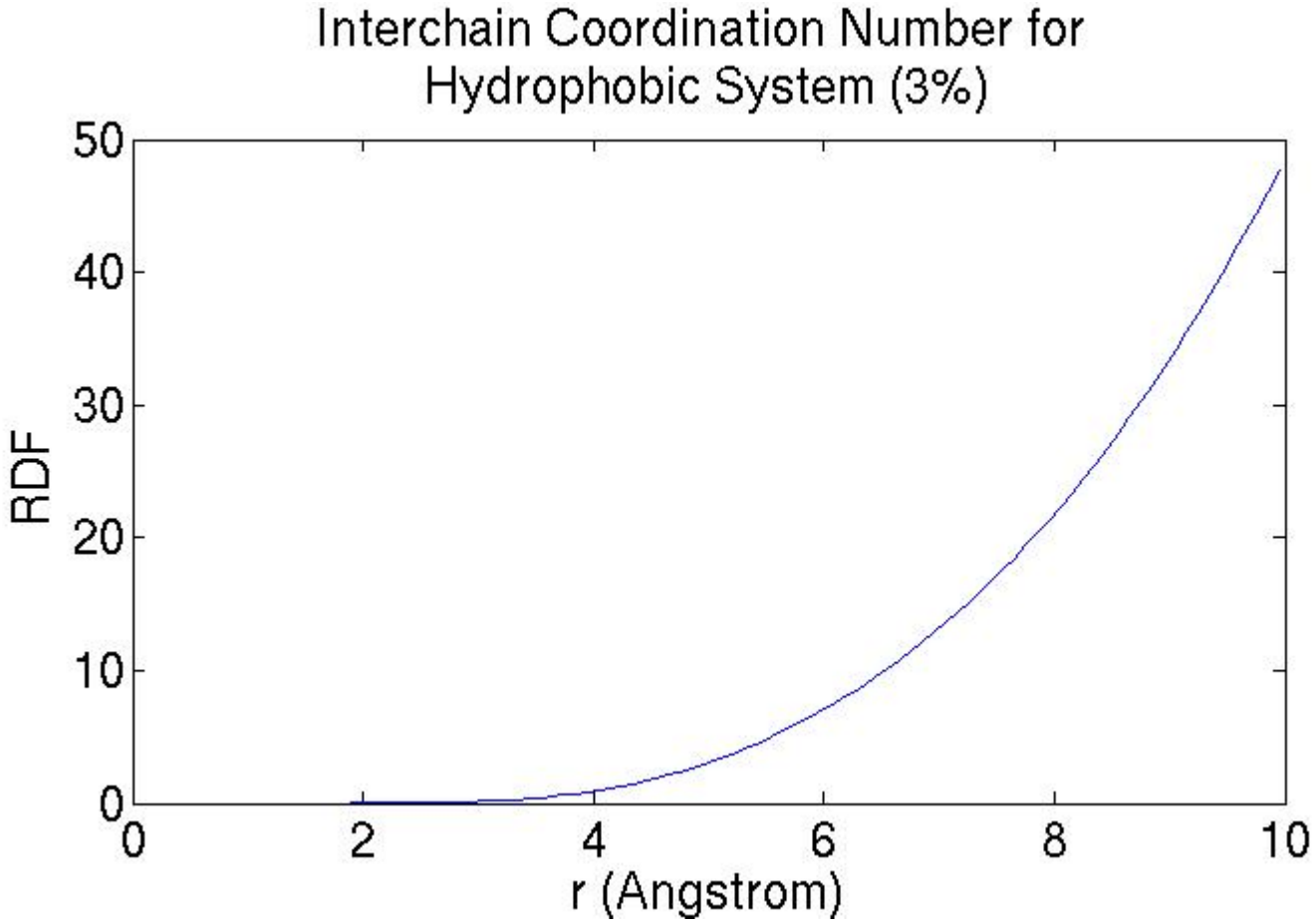
Entropy of water only (PER ATOM)
Entropy, NOT -TS



Consider radial distribution between chains (ie, consider for each atom in one chain all the atoms belonging to a different chain within a certain distance)

If the system is fully entangled, we should see all the atoms of the other chains by one van der Waals radius (first peak). For an amorphous polymer this may not be one van der Waals radius.

This is suggesting we may need larger chains, which was already evident from our entanglement tests (strain)



Coordination number (integral of radial distribution function) would give us this information. The radial distribution function itself gives us the van der Waals radius to use.