California Institute of Technology

Materials and Process Simulation Center

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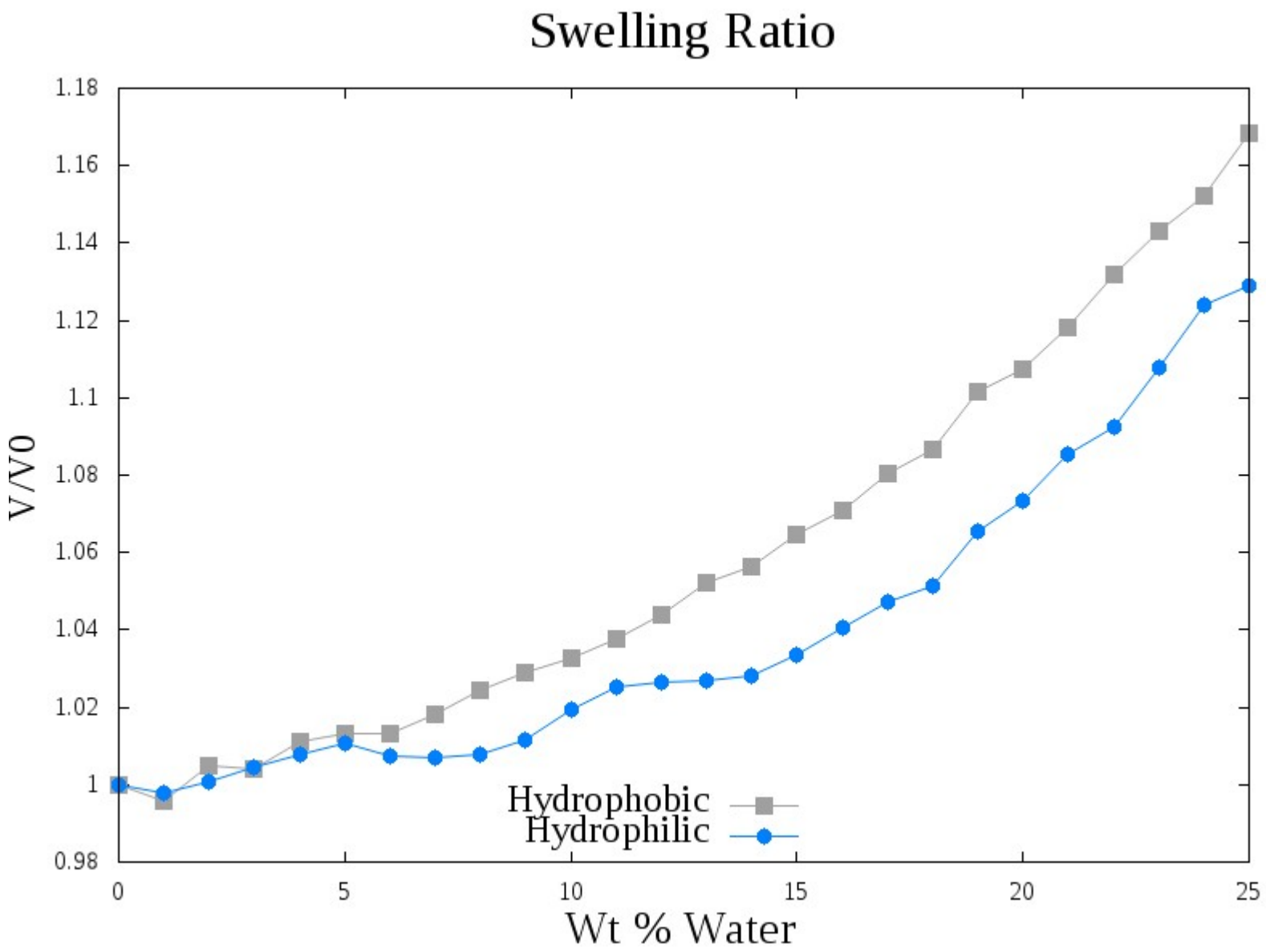
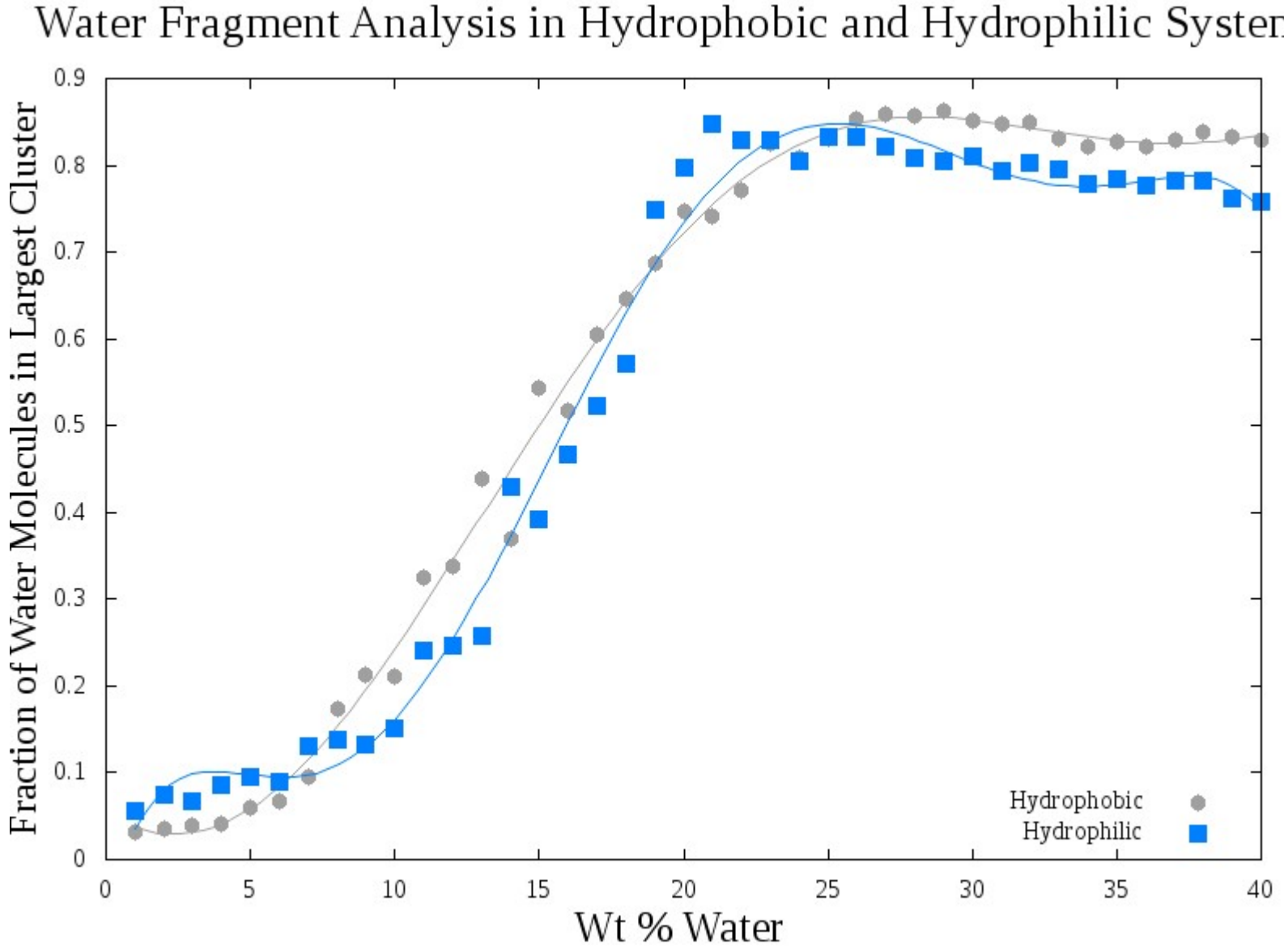
DOW 12-20-2011

27 February 2012 Progress

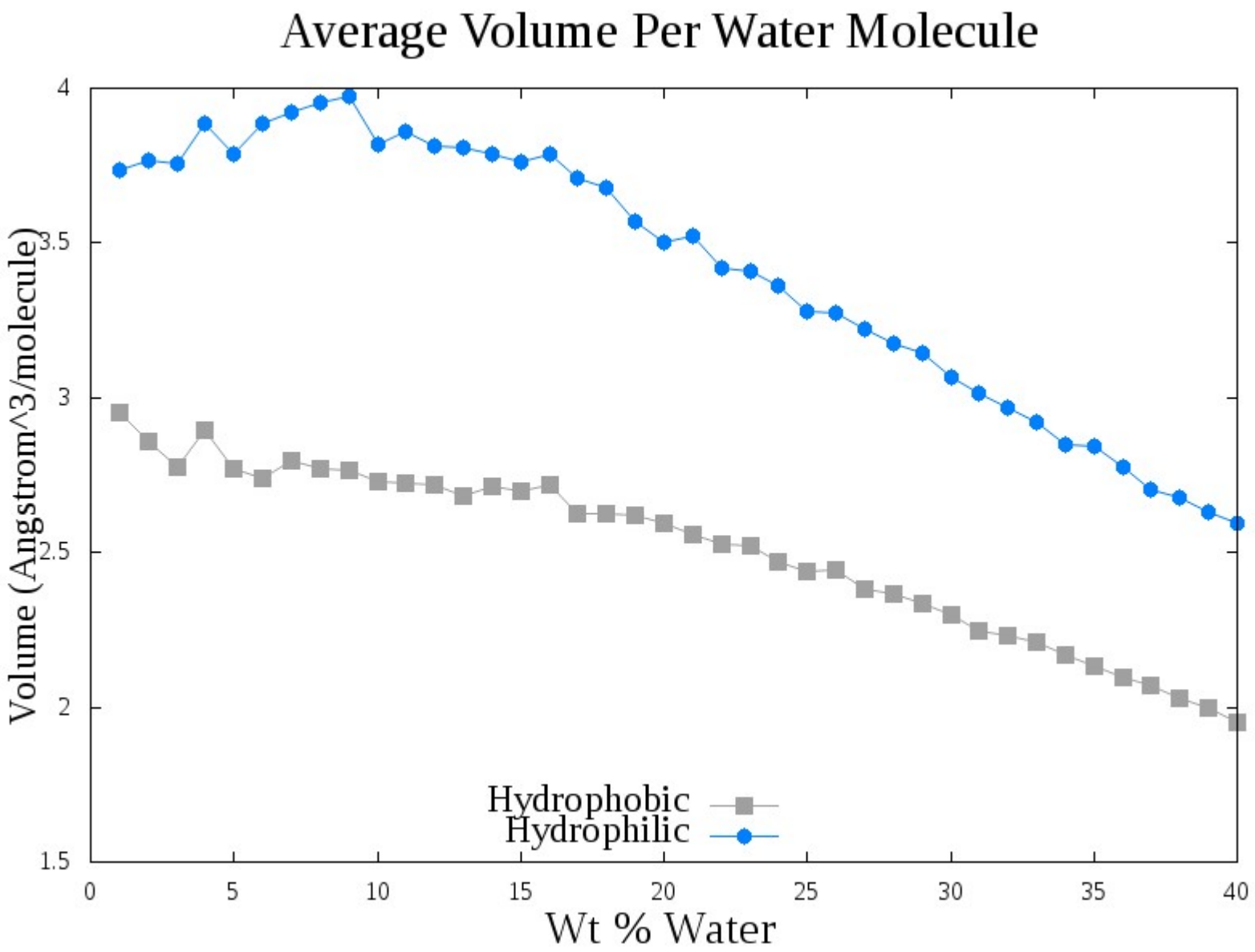
- Completed building structures with new method for water insertions
- Swelling ratios, water fragment analysis (for percolation threshold)
- Stress on water, polymer
- Thermodynamics including chemical potential of water



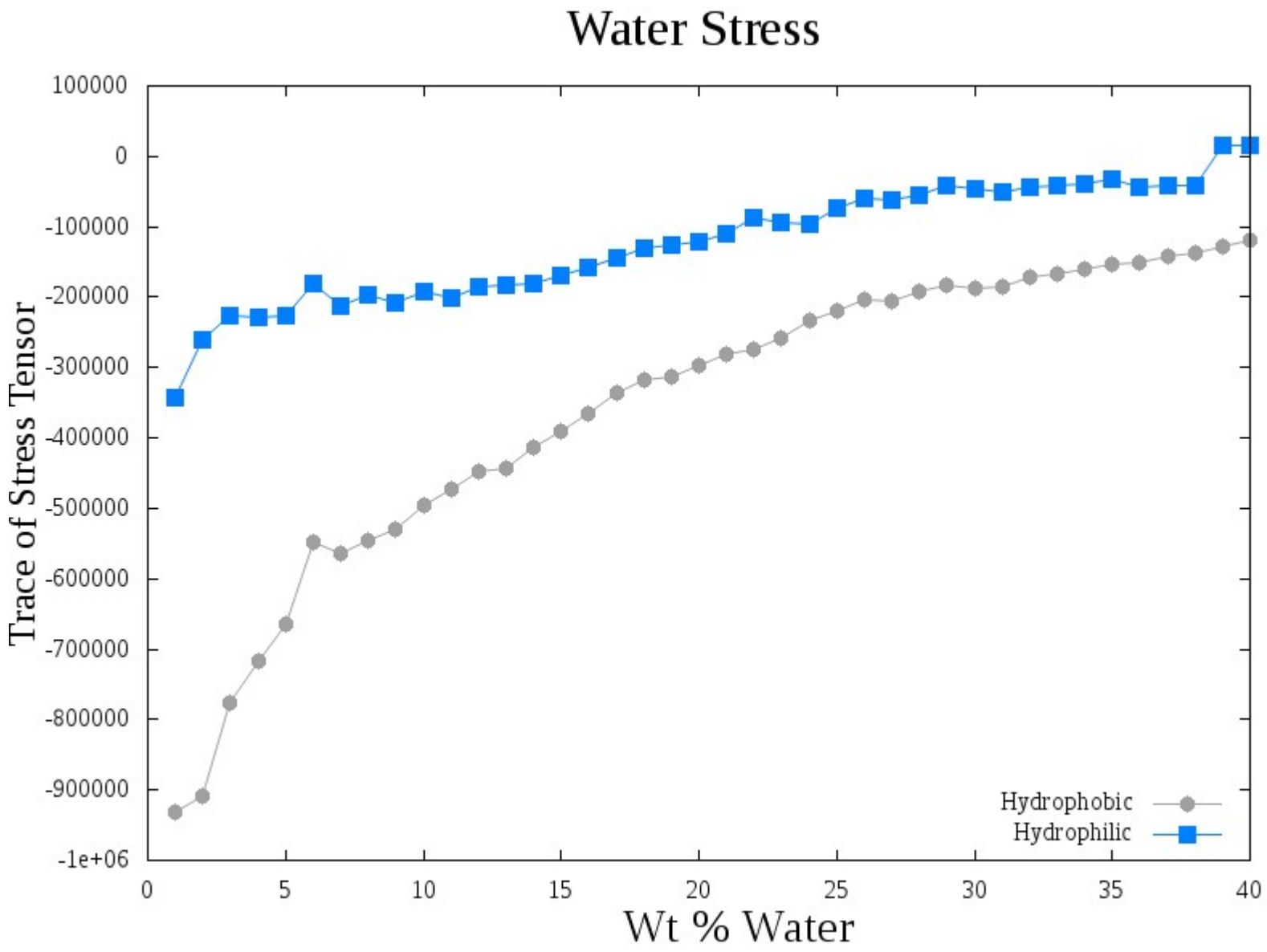
Hydrophobic swells more than hydrophilic. Most pronounced difference 5-15%



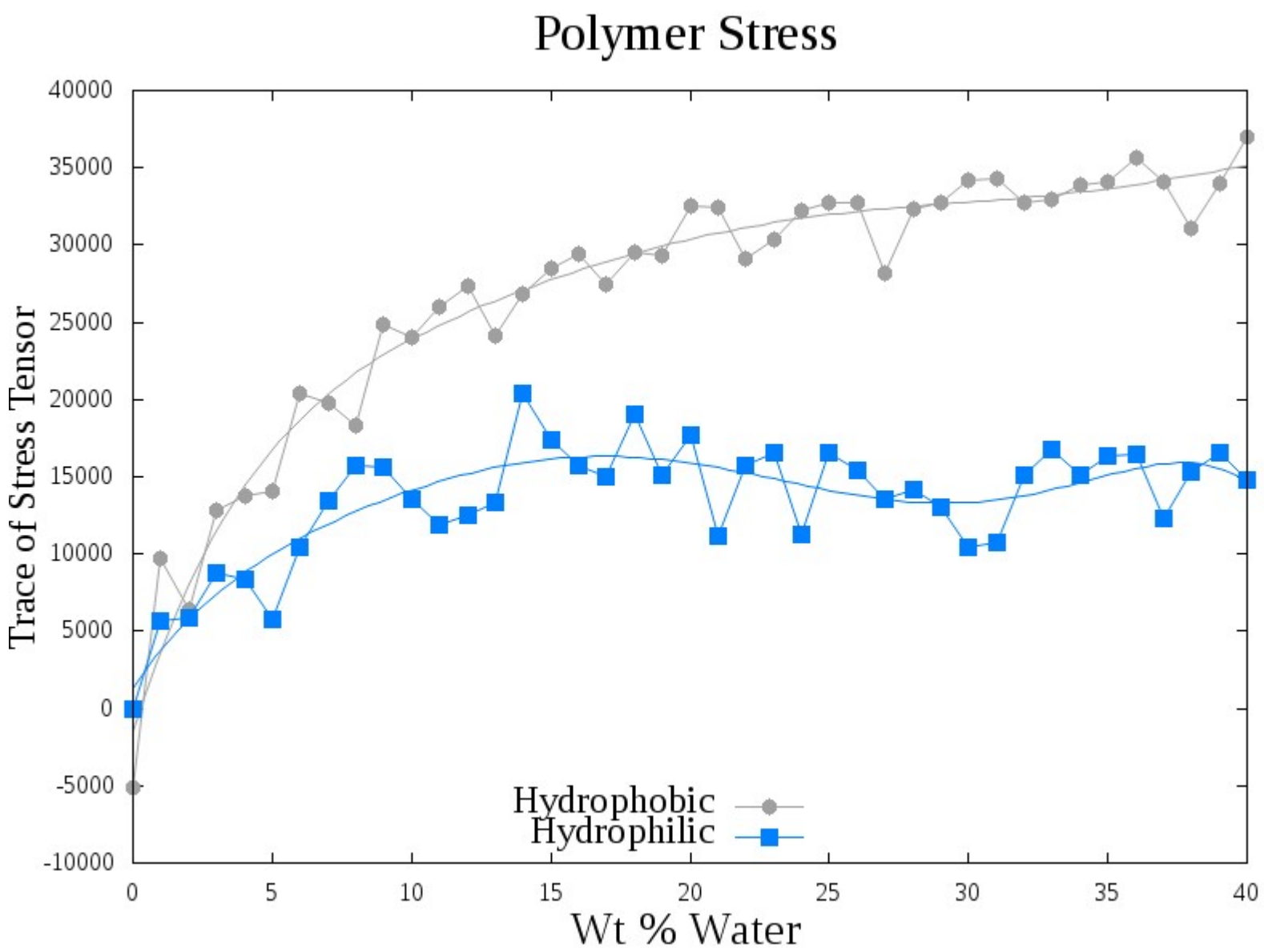
Hydrophobic system has an inflection point at 13%, hydrophilic at 15%
Suggests percolation occurs sooner in hydrophobic than hydrophilic



Volume per water molecule consistently larger in hydrophilic structure. The relatively hydrophilic structure puts less stress on the water, and thus they occupy a larger volume

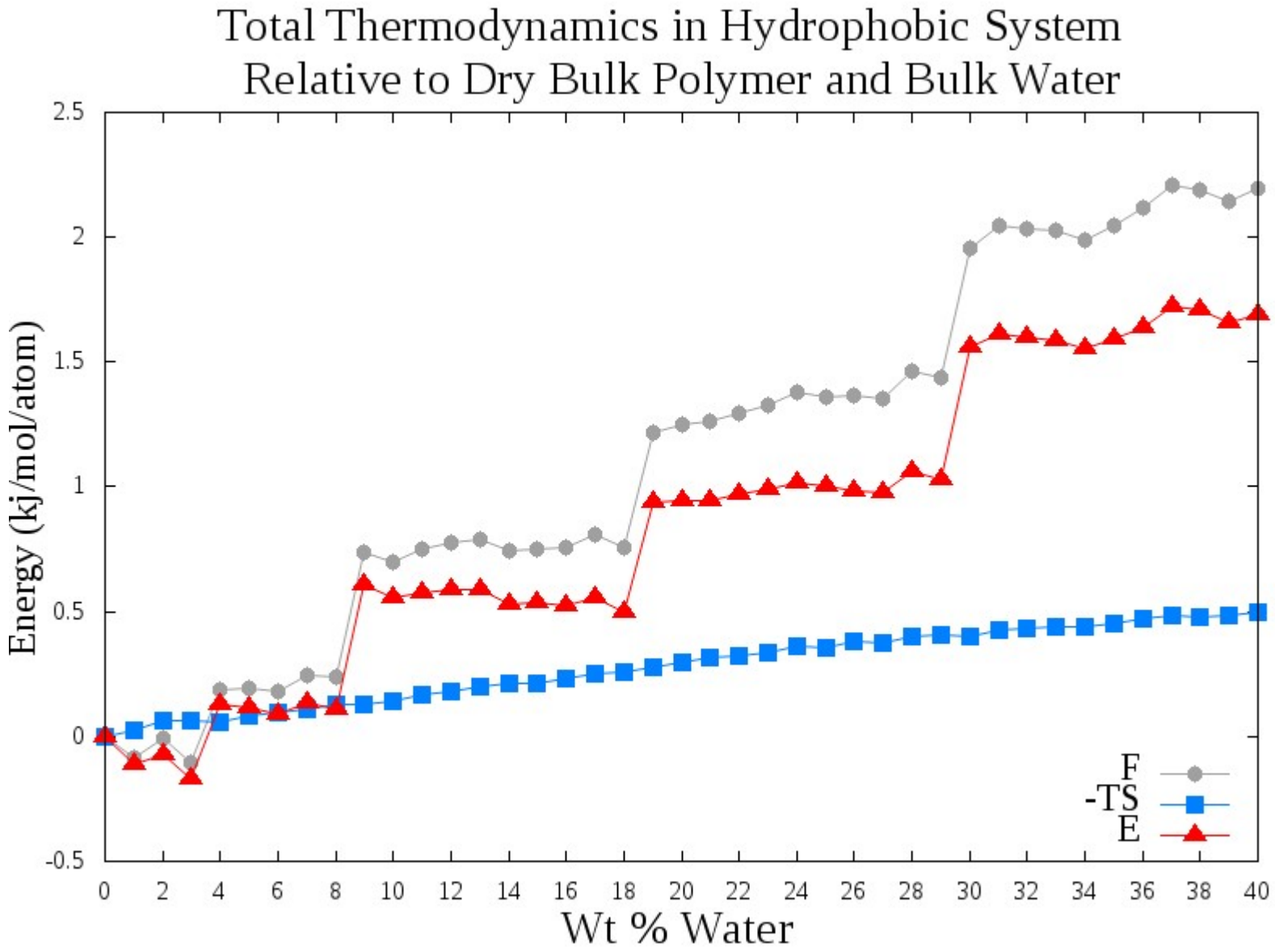


Higher stress on waters in hydrophobic system. Stress on waters reduced with increased water content in both. Tends toward 0.

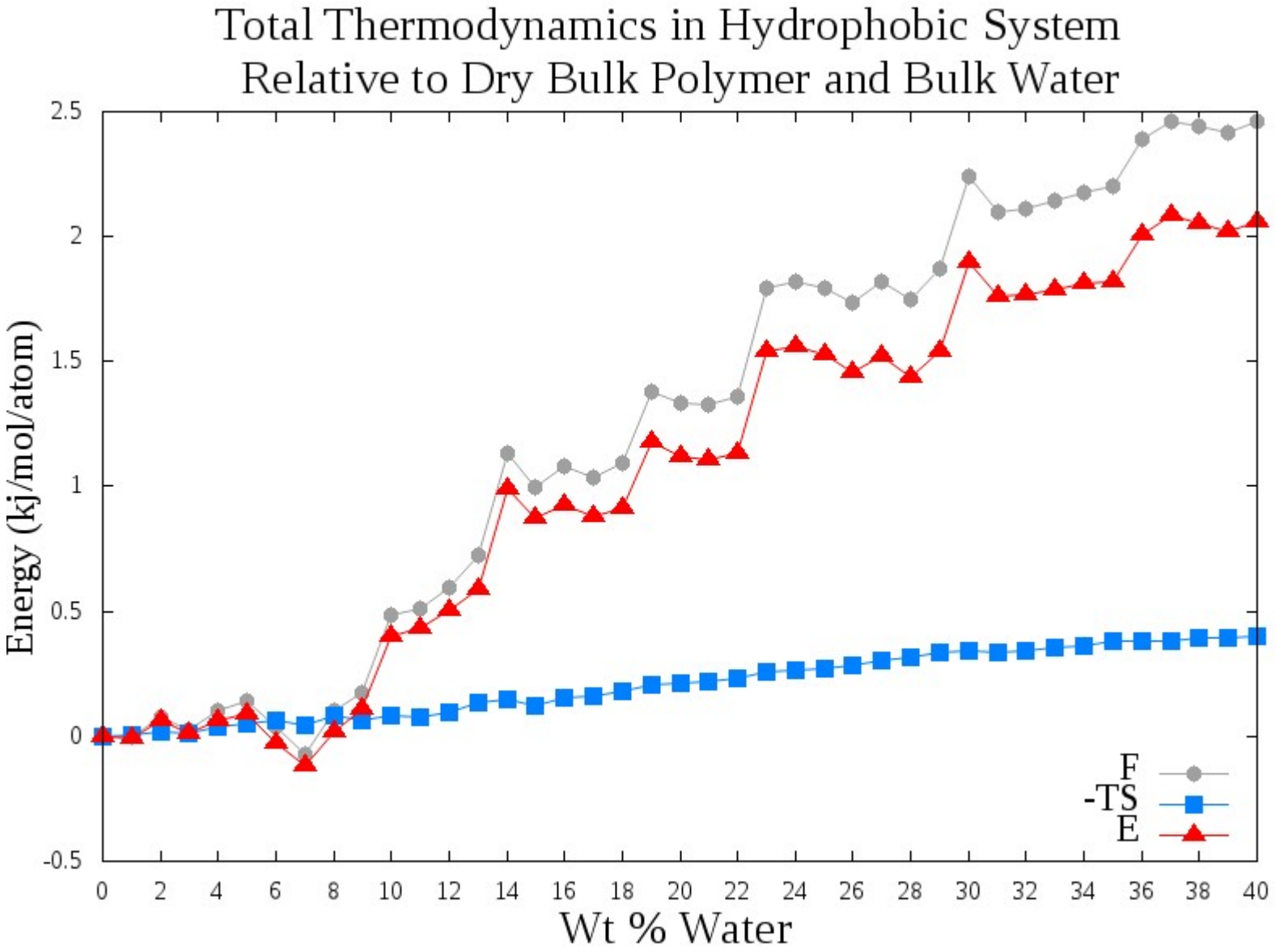


Hydrophobic continues resisting swelling even at 40% (stress on polymer still increasing) Hydrophilic stops resisting at ~15% (stress flattens out)

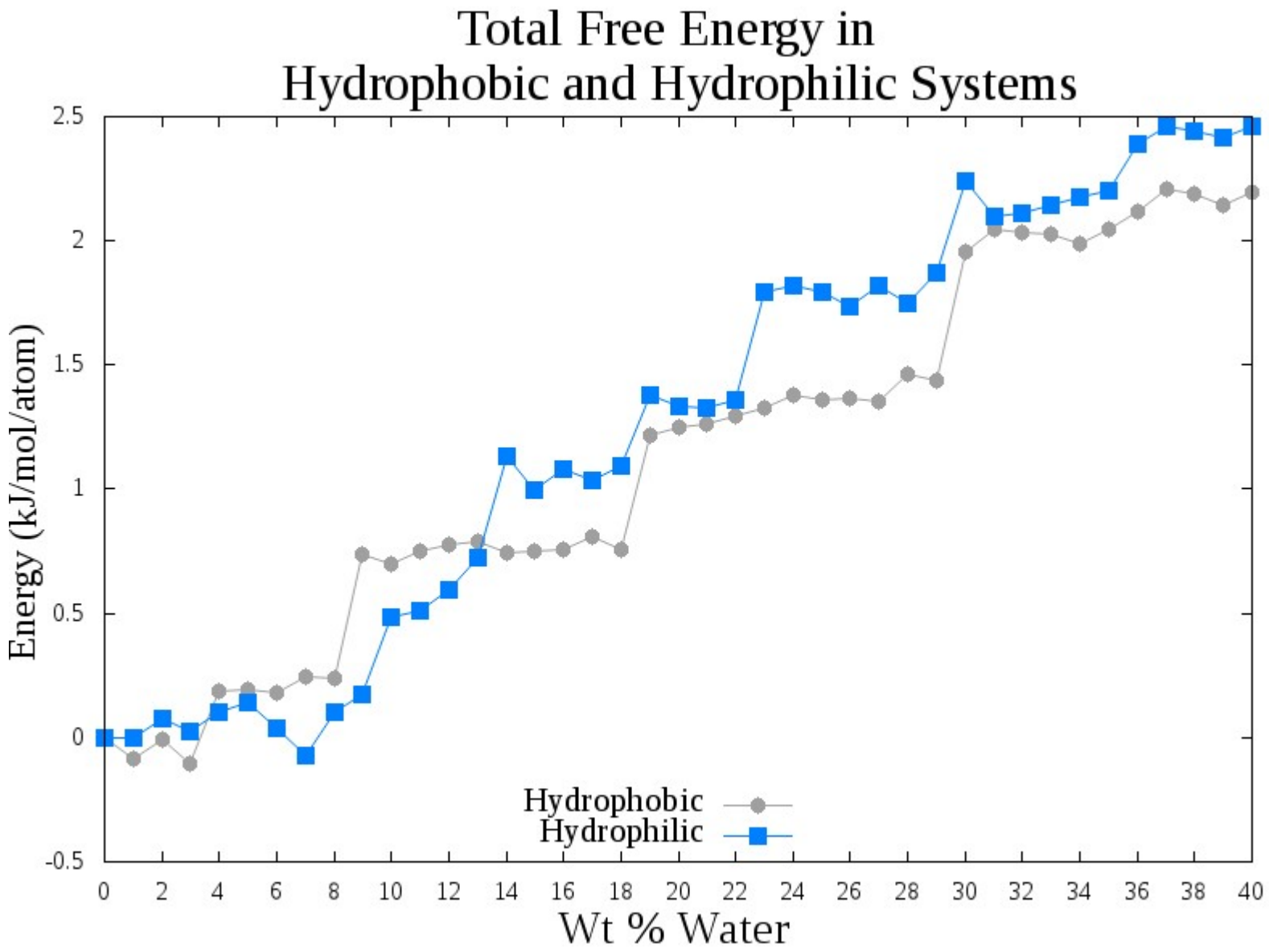
Suggests hydrophobic structure is stronger



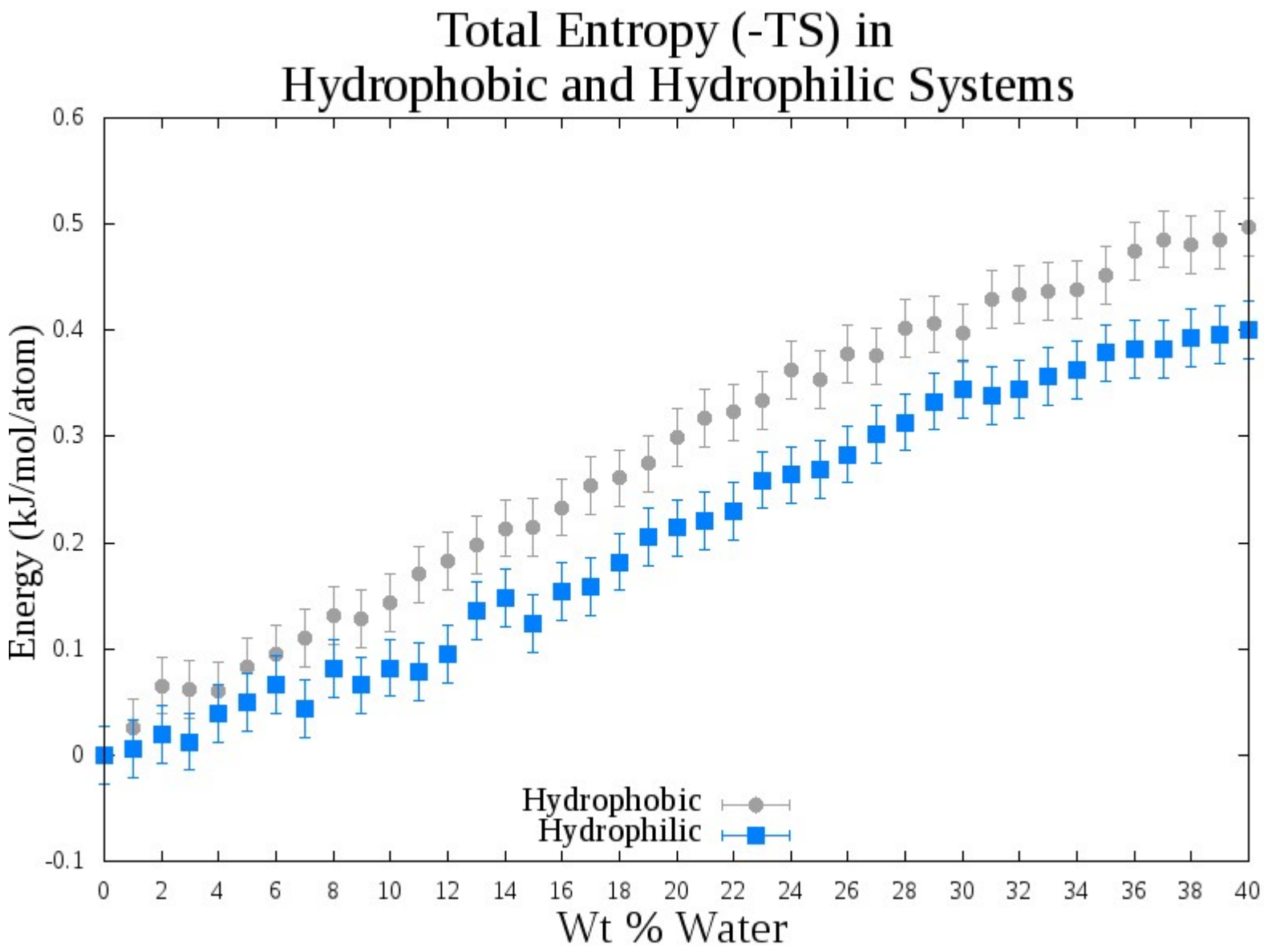
Total (water + polymer) thermodynamics

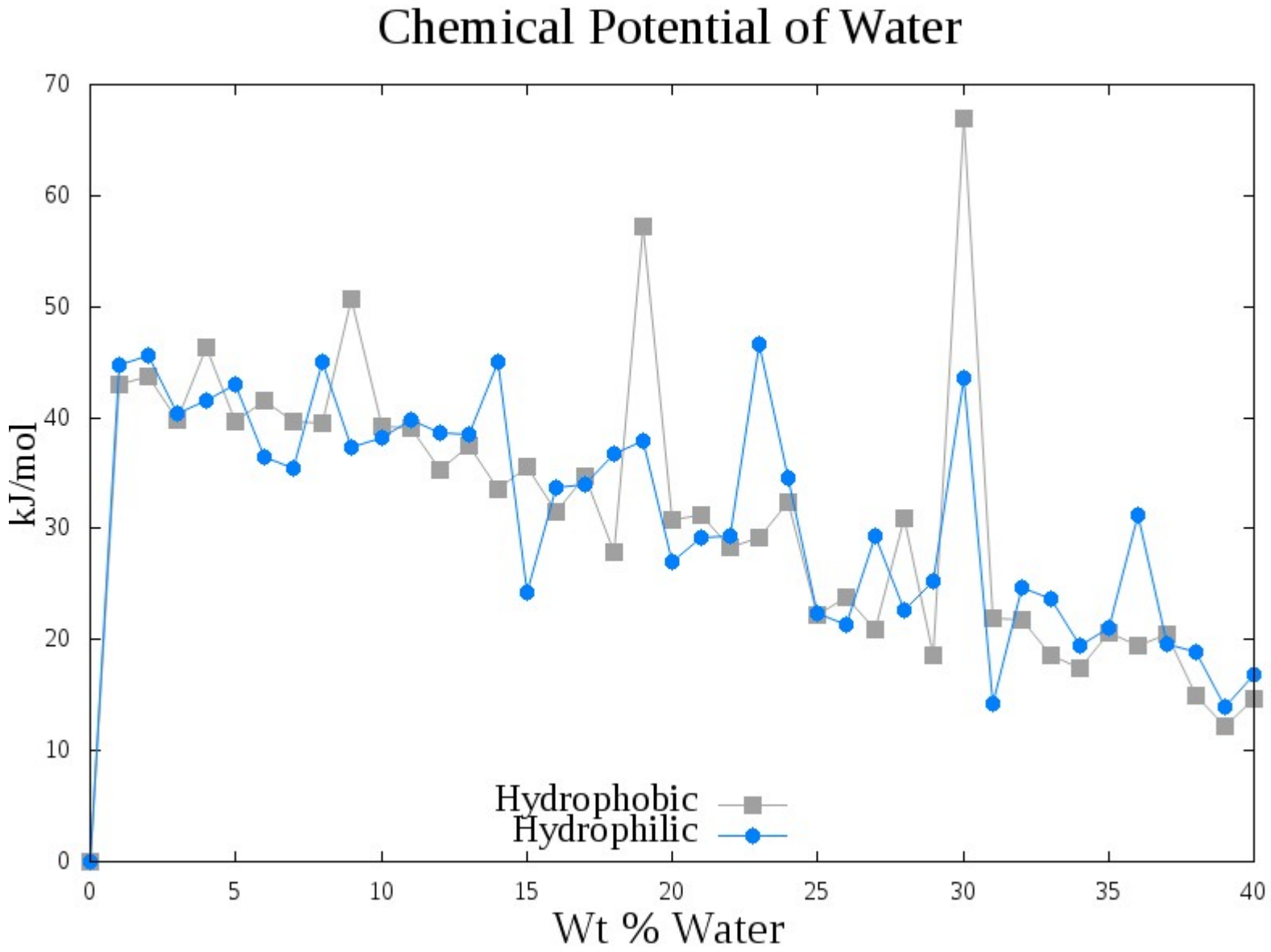


Total (water + polymer) thermodynamics



Free energy lower in hydrophobic system after 12%


Total Entropy (-TS) in
Hydrophobic and Hydrophilic Systems
Energy (kJ/mol/atom)
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
Wt % Water
Hydrophobic
Hydrophilic



From numerical differentiation of water free energy.
Identical in both systems. Decreases approximately linearly with water content (tending toward the chemical potential of bulk water)

Effective Solvent Construction Method:

F factor controls screening of non-bonded interactions.

$$\text{van der Waals} = 4 * \epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

ϵ = interaction strength

σ = effective atom size

$$\text{Electrostatic} = \frac{q_1 * q_2}{\epsilon * r}$$

ϵ = dielectric constant (permitivity)

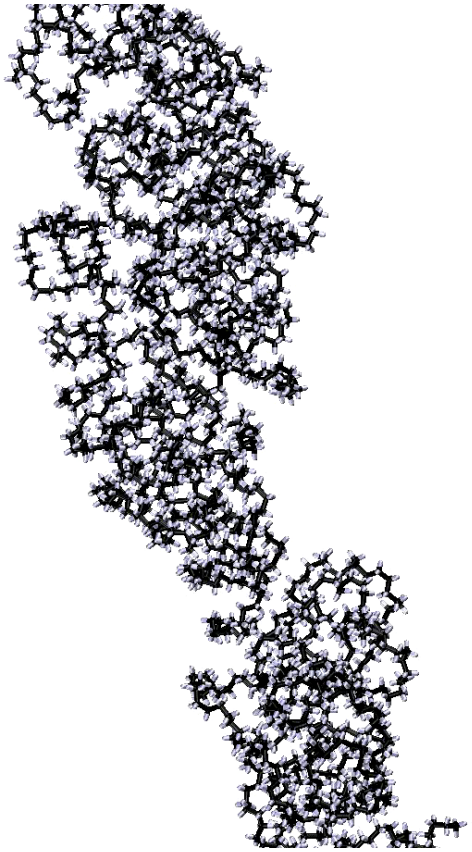
$$\text{van der Waals} \rightarrow \text{F} * \epsilon$$

$$\text{Electrostatic} \rightarrow \frac{1}{F} * \epsilon$$

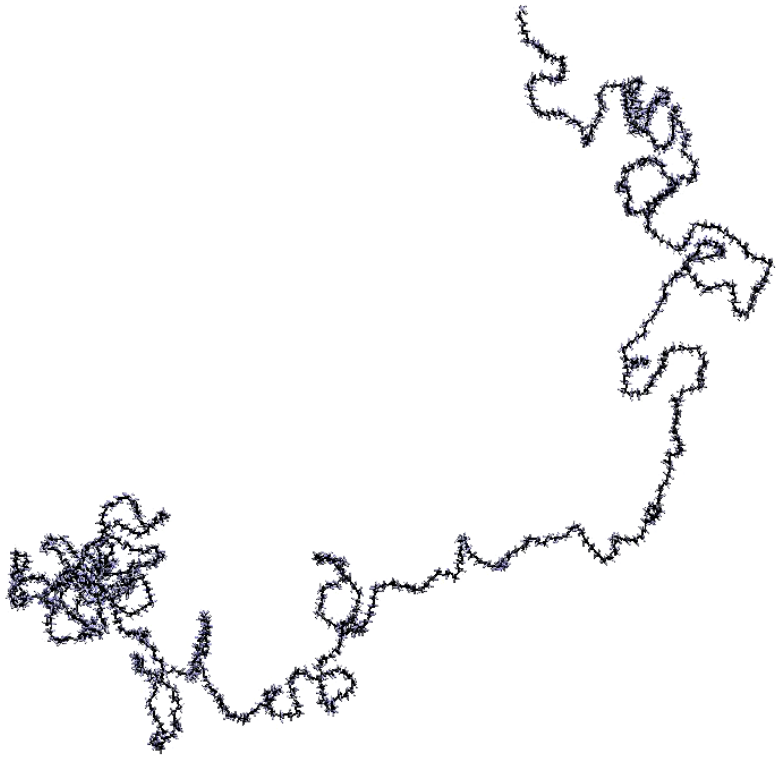
Simulates an effective solvent around polymer

Effective Solvent Construction Method:

Simulates an effective solvent around polymer



F = 1.0

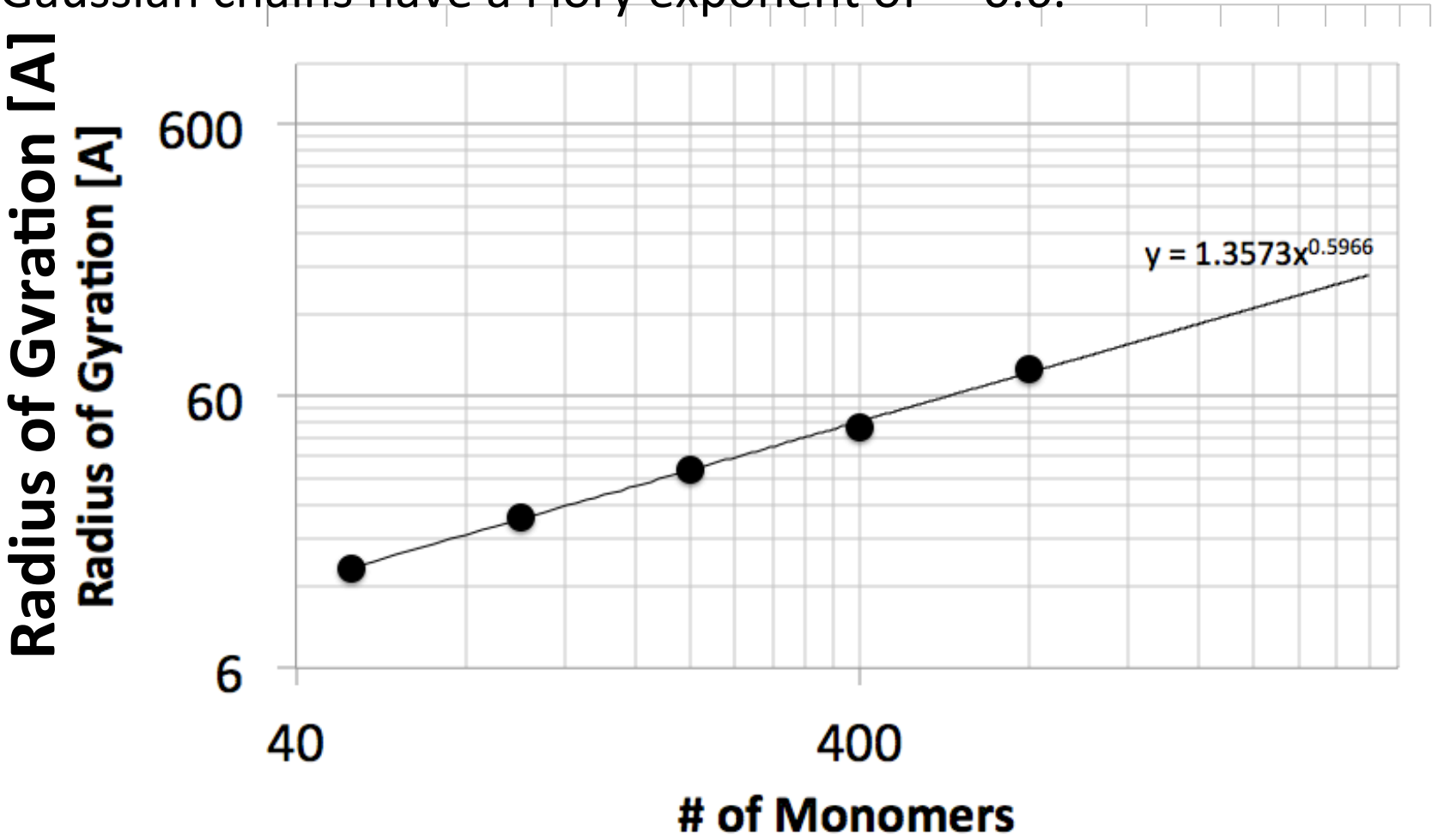


F = 0.1

Effective Solvent Construction Method:

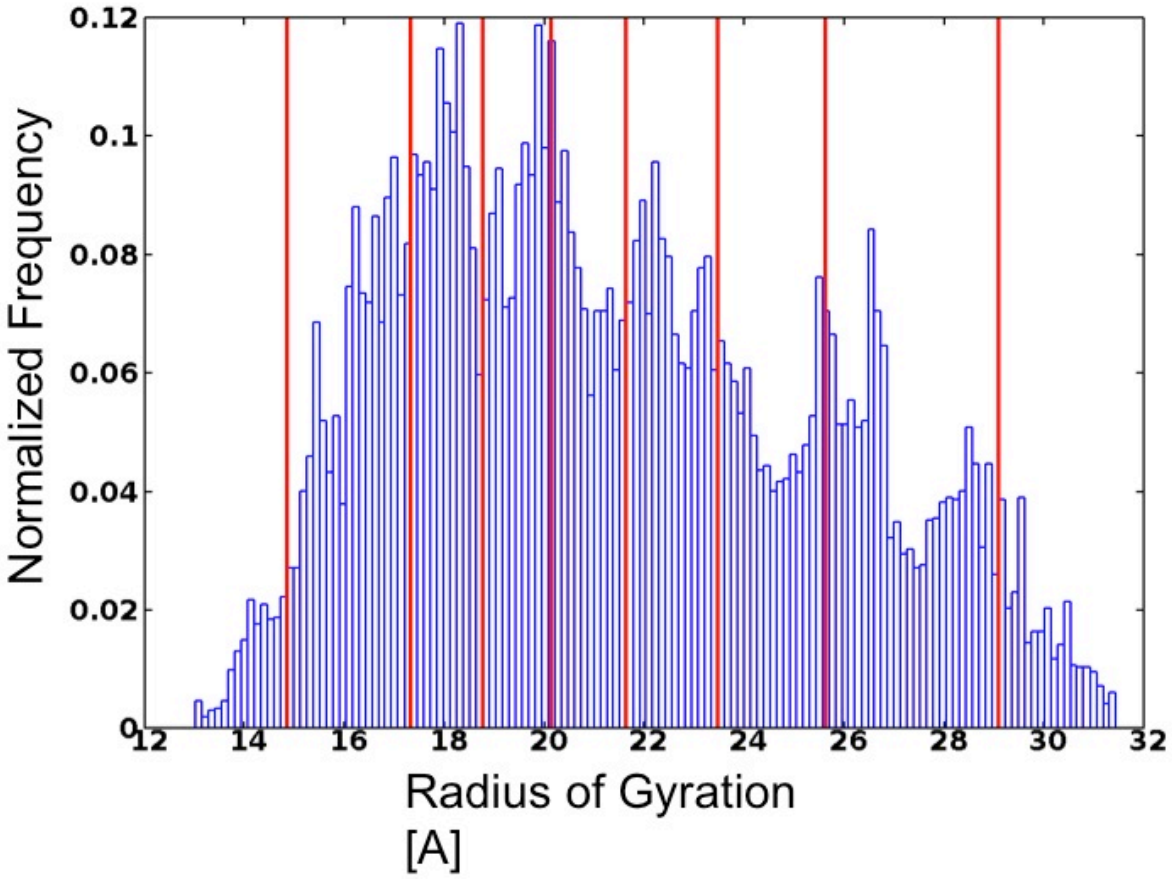
In general: $G(r) \alpha N^{\nu}$ Where N = Number of Monomers,
ν = Flory exponent

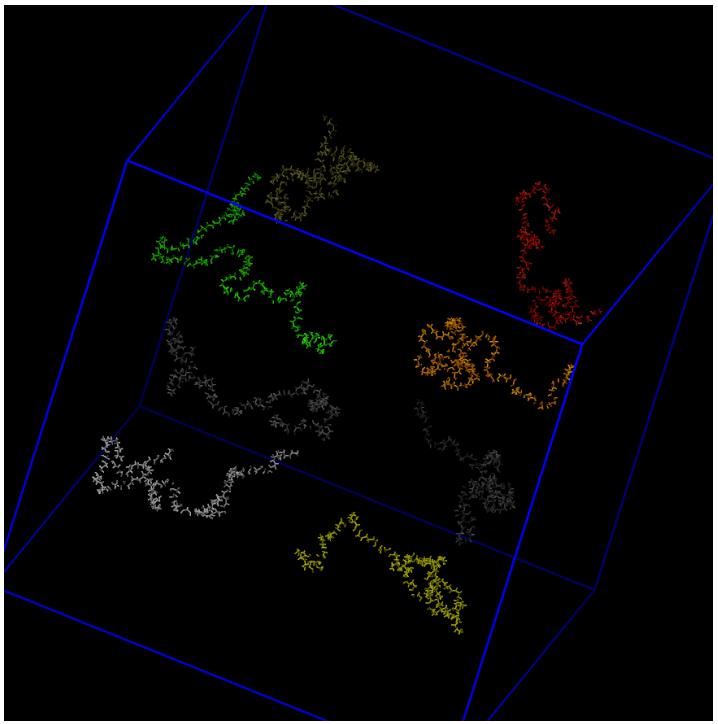
Gaussian chains have a Flory exponent of ~ 0.6.



Effective Solvent Construction Method:

Polymer chains are selected from a distribution of possible configurations to construct a unit cell bulk.

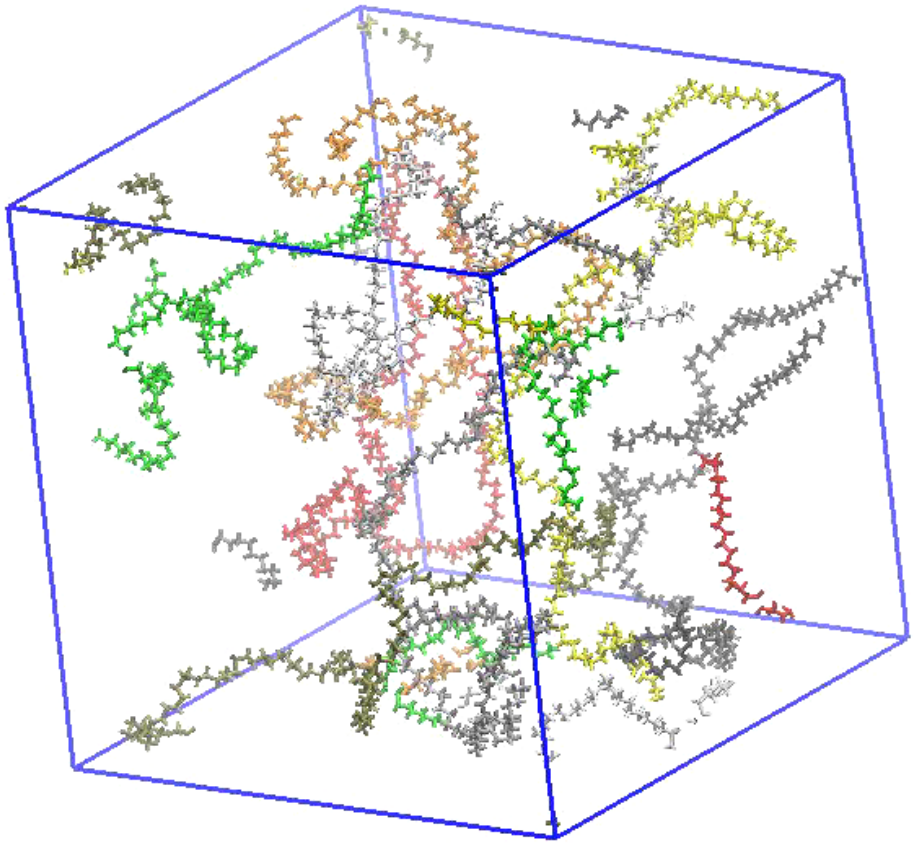




Effective Solvent Construction Method:

Chains are then annealed under slow compression to allow diffusion and inner-penetration.

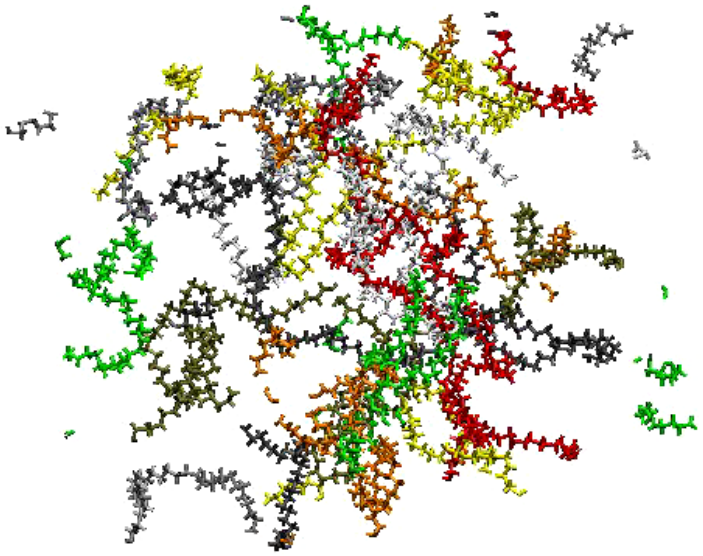
Density = 0.01 – 0.02 g/cc



Effective Solvent Construction Method:

Once annealing is complete, aggressive compression to target density.

Density = 0.02 - 1.1 g/cc



Effective Solvent Construction Method:

Build:
8 Identical Chains under periodic boundary conditions, Density = 0.01 g / cc

Model solution conditions via F factor. F = 0.1

Protocol:

1) **Mixing:** 1.0 ns compression under modeled solution conditions until Density = 0.025 g/cc

2) **Compress:** 1.0 ns compression to 1.1 * experimental density while ramping to real conditions (F factor = 1.0)

3) **Relax:** Allow 0.1 ns NVT relaxation at Density = 1.0 g/cc, T = 300 K

4) **Release:** 0.5 ns equilibration under NPT, P = 1.0 atm, T = 300 K

5) Evaluate bulk density and free energy.