



# Polymeric Phase Transitions Driven by Crosslinking Entropy

Jacob Adamczyk, Dr. Miron Kaufman, Dr. Kiril A. Streletzky

Department of Physics, Cleveland State University

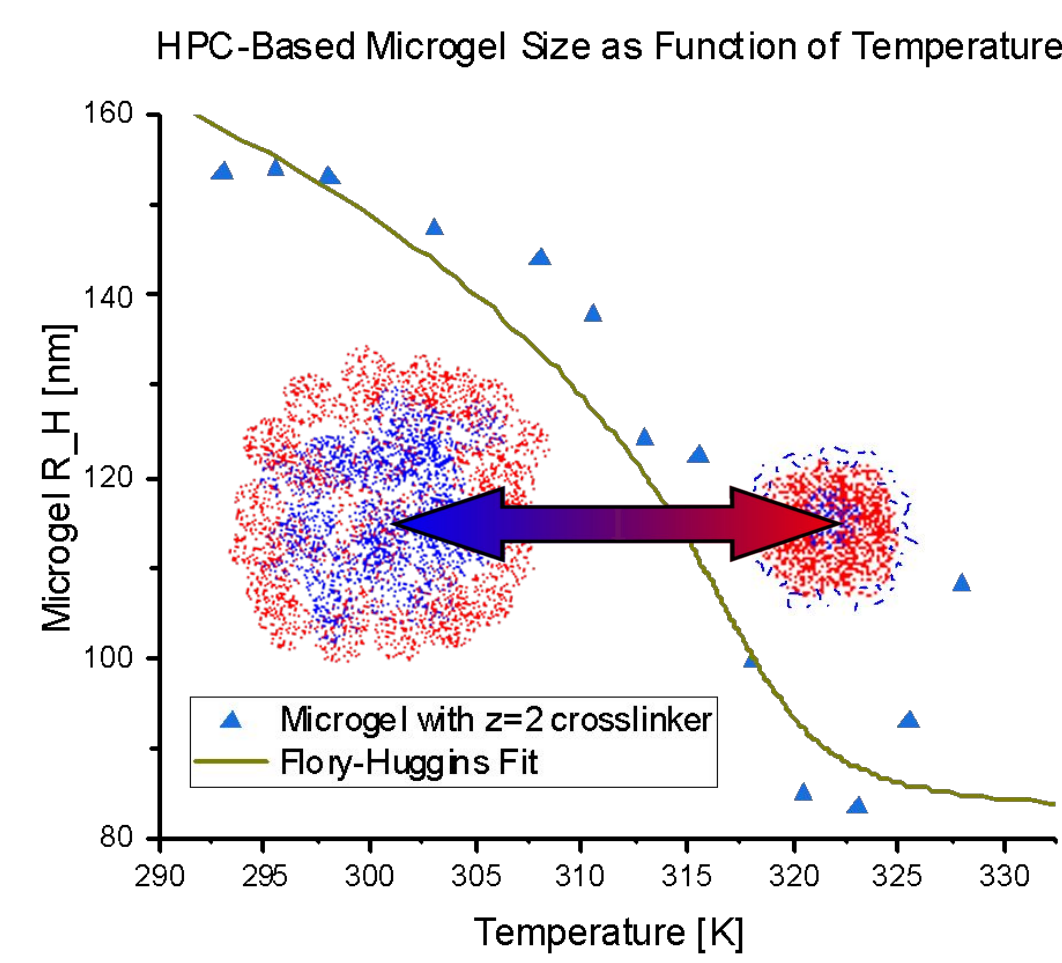
## Abstract

Microgels are polymer-based particles which can change size and shape during volume phase transitions in response to external stimuli. We have specifically investigated microgels which respond to changes in temperature. Hydrodynamic radii were obtained from light scattering data on Hydroxypropylcellulose (HPC) microgels and then modelled with the standard Flory-Huggins theory. We present a numerical study of a thermodynamic theory which includes the entropy associated with crosslinking between polyfunctionals and monomers at the ends of linear polymers. This theory predicts a strong first-order transition due to the saturation of possible crosslinks when the number of polyfunctionals is of the same order of magnitude as the number of polymers. We will present numerical results based on this thermodynamic model.

## Motivation

Polymeric microgels:

- Thermoresponsive nano-structures
- Shrink in size when heated beyond their volume phase transition temperature<sup>[2][3]</sup>



- Crosslinkers in the Flory-Huggins<sup>[2]</sup> (FH) theory have not yet been investigated
- Phase transitions observed as a result of saturation of crosslinking sites

## Entropic Addition to Theory

- The derived crosslinking entropy is broken into two pieces:
  - Below and above saturation of polyfunctionals (crosslinkers) about the polymer chains
- Apply Stirling approximation on the previous formulas
- Find the following molecular entropies, as functions of the chain length ( $L$ ), the number of polymer chains ( $P$ ), crosslinker functionality ( $z$ ) and the number density of solvent and polyfunctional molecules ( $n_0$ ,  $n_z$ ) respectively
- Fix  $L = 3$ ,  $n_0 = 0$  (no solvent as previously stated), and show results for  $z = 2, 3$

$$s = -n_0 \ln(n_0) - n_z \ln(n_z) - (2p - zn_z) \ln(2p - zn_z) + p \ln(p) + (L - \ln(2))p - (z + \ln(z!))n_0 \quad zn_z < 2p$$

$$s = -n_0 \ln(n_0) - \left(n_z - \frac{2p}{z}\right) \ln\left(n_z - \frac{2p}{z}\right) + \frac{z-2}{z} p \ln(p) - \left(L - \ln(2) + 2 + \frac{2}{z} \ln(2(z-1)!)\right)p \quad zn_z > 2p$$

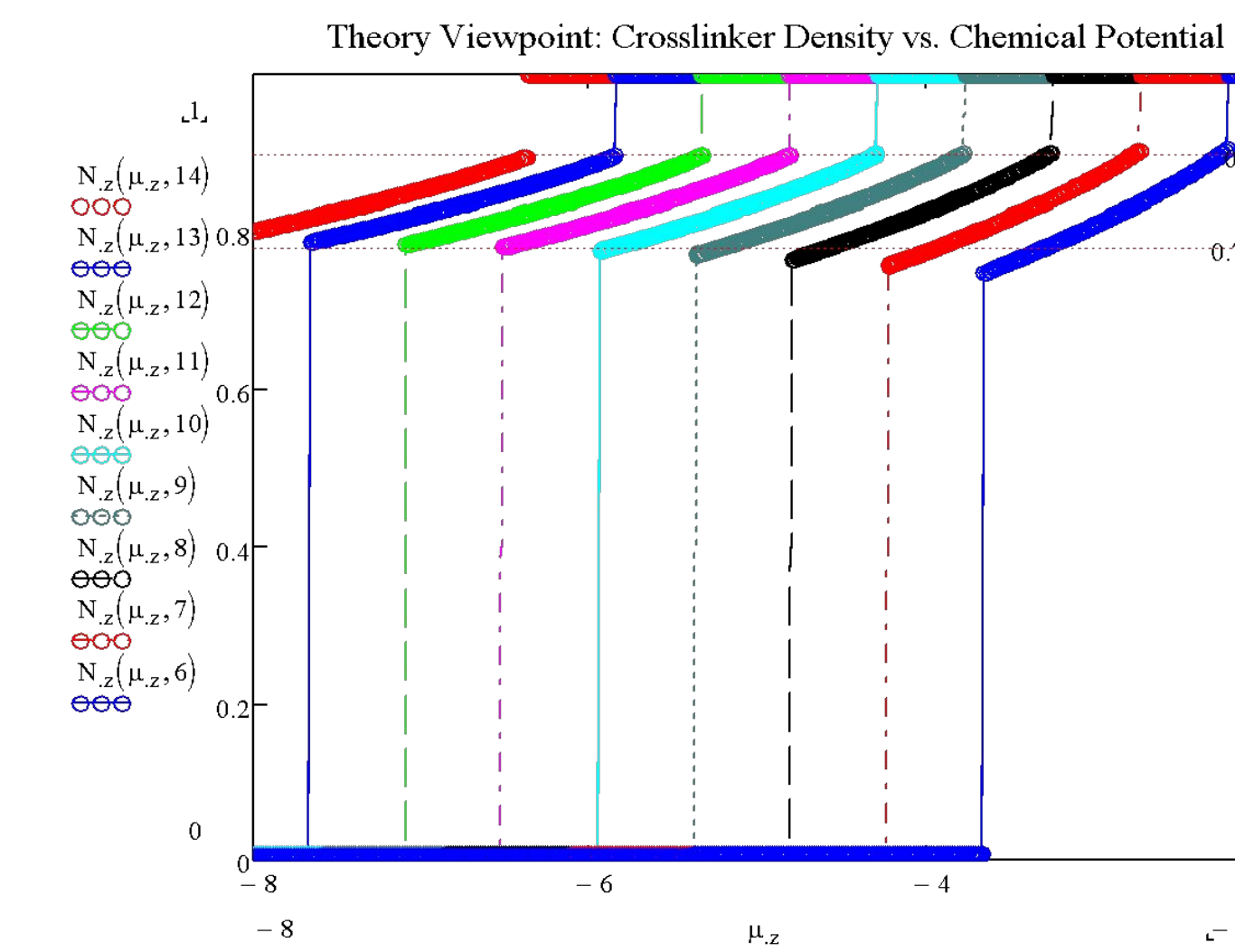
## Evidence of Entropy-Driven Phase Transition

We numerically maximize  $\Omega(N_z, T)$  with respect to the number density of polyfunctionals ( $N_z$ ) as a function of chemical potential for several temperatures (shown on right)

- First evidence of an entropy-driven phase transition based solely on the variability of crosslinkers in the polymer system:
- However, the conjugate variables  $N_z$  and  $\mu_z$  are difficult to interpret, so we must numerically change to a more familiar variable space.

We do this in the Results by:

- Numerically solving for inverse of each phase yielding  $\mu_z(N_z, T)$
- Plugging in the result for  $\Omega$
- Applying Euler equation to obtain  $\Omega(\mu_z, T) = -pV$



## Crosslinking Entropy

We make the following assumptions:

- Dry gels (no solvent)
- No network elasticity
- Same length chains
- Fixed FH  $\chi = -1$  (Flory-chi energy parameter)
- Polymers only accept crosslink connections at ends
- Strongest inter-molecular actions occur between polymer and crosslinker

In this formulation, the effect of the crosslinking alone on the system's thermodynamic variables will be most evident.

- Calculate configurational entropy based on polyfunctionals (crosslinkers)
- Use the grand canonical ensemble to numerically solve for an equation of state.
- There is a specific level of  $n_z$  (density of crosslinkers) at which the polymer ends all become saturated.
- This saturation point determines a phase transition in terms of the crosslinker's chemical potential and density.

We calculate the entropy combinatorially in either regime as follows<sup>[1]</sup>:

$$zn_z < 2p:$$

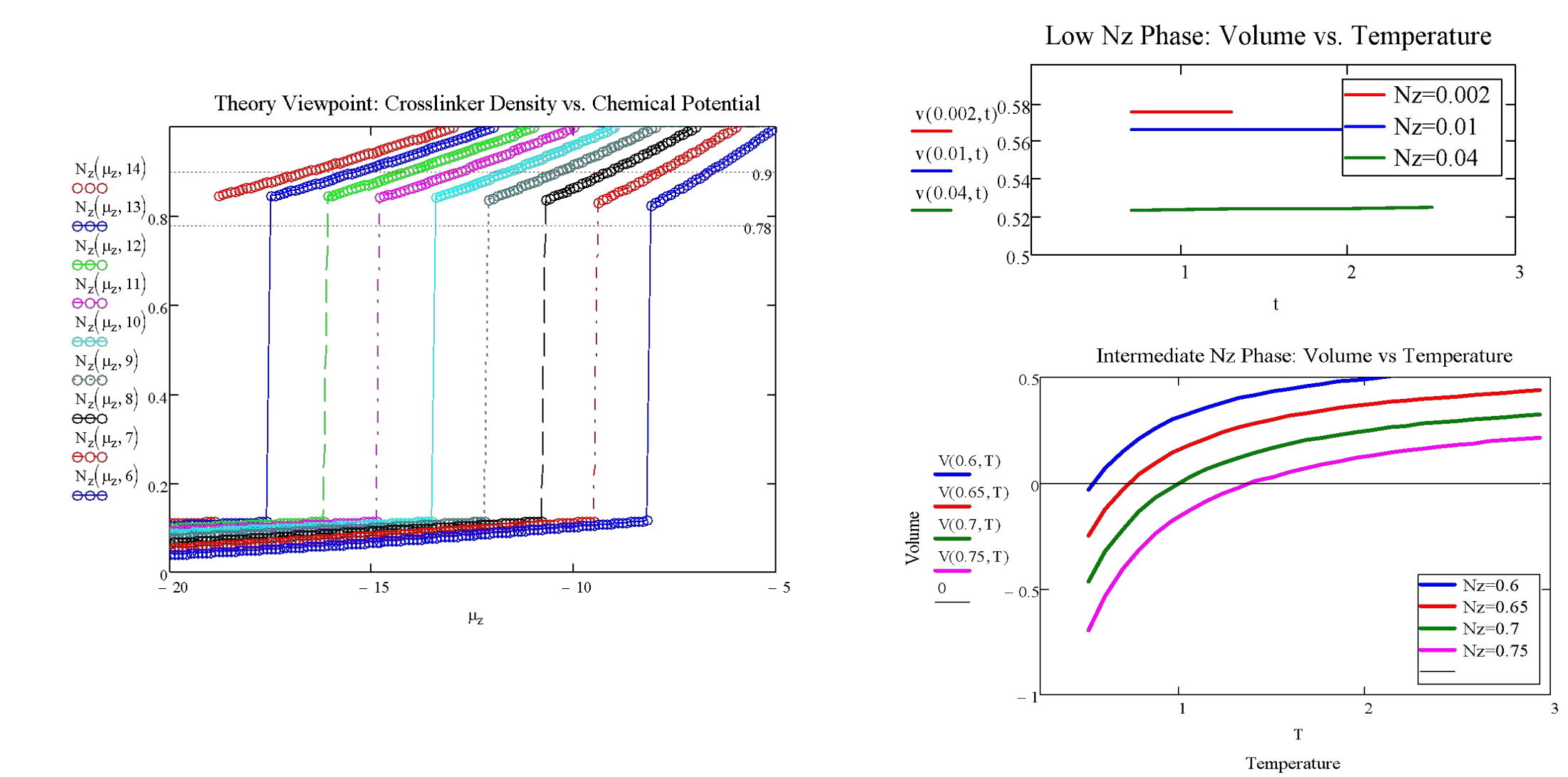
$$e^{S_3} = C(2P, z) * C(2P - z, z) * \dots * C(2P - (N_z - 1)z, z) = \frac{(2P)!}{(2P - zN_z)! (z!)^{N_z}}$$

$$zn_z > 2p:$$

$$e^{S_3} = C(2P, z) * C(2P - z, z) * \dots * C\left(2P - \left(\frac{2P}{z} - 1\right)z, z\right) * C\left(N_z, \frac{2P}{z}\right) = \frac{(2P)! (N_z)!}{(z!)^{\frac{2P}{z}} \left(\frac{2P}{z}\right)! \left(N_z - \frac{2P}{z}\right)!}$$

## Results: Bifunctional Crosslinker

We show results for  $z = 2$  (similar to the microgels in [3])



The boundary phase transitions at  $N_z = 0, 1$  are now continuous.

## Conclusion

The results for  $z = 2, 3$  show:

- The low  $N_z$  phase is stable in the calculable temperature range
- The predicted size of the microgels decreases when increasing crosslinker density
- Agrees with our intuition since we can imagine the crosslinkers as small springs which tighten the connections between polymer chains
- At sufficiently low temperatures, the polymer system becomes unstable (negative volume)

In general:

- Non-trivial dependence of size on temperature for intermediate-high crosslinker densities
- Different than standard FH framework: one would expect that size is monotonically decreasing as a function of temperature<sup>[1]</sup>

## Future Work

- Add this new term to the current standing FH theory
- Apply the new model to wide range of experimental results [ref]
- Expanding to a model including solvent contributions, adding energy contributions from interactions between all types of particles

## References

- [1]: M. Kaufman, Entropy, 20(7), 501, 2018
- [2]: Flory, P.J., "Principles of Polymer Chemistry" (1953)
- [3]: "The Dynamics of Polymeric Microgels with Varying Crosslinker Concentration" S. Tieljen, J. Adamczyk, Dr. K.A. Streletzky, *Bull. Am. Phys. Soc.* **64** G70.00031 (2019)

## Acknowledgements

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## Results: Trifunctional Crosslinker

