# Thermodynamics of Supramolecular Polymers with Hydrogen Bonding Ends

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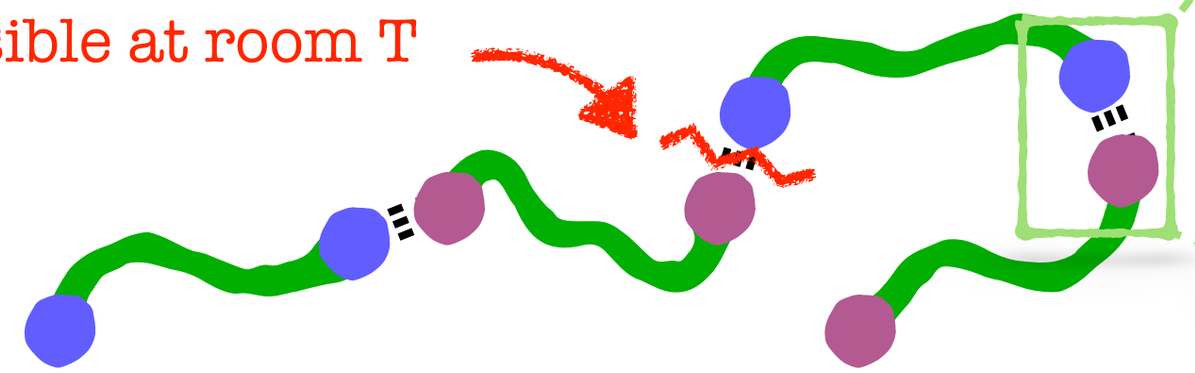
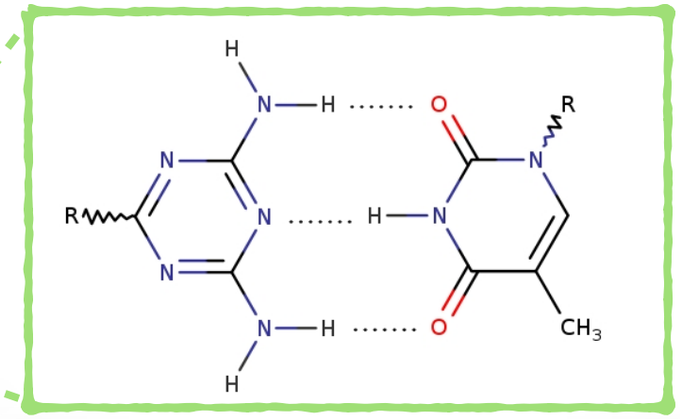
# Supramolecular Polymers

- **Thermo-responsive polymer**

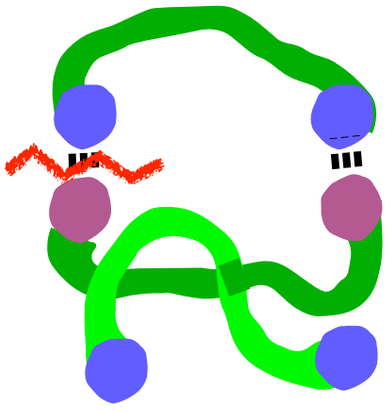
Reversible at room T






Hydrogen bonds
π-π interaction
ionic interaction
metal-ligand binding

- **Ring Aggregates**

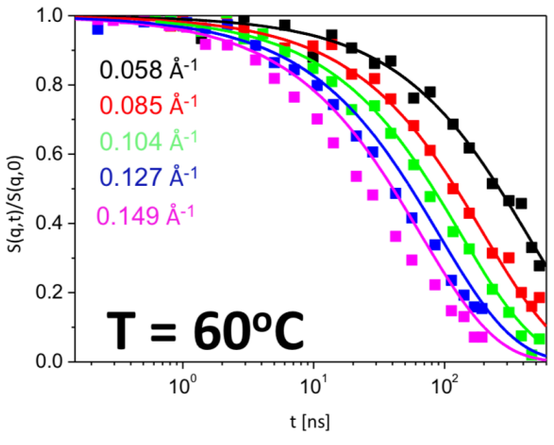


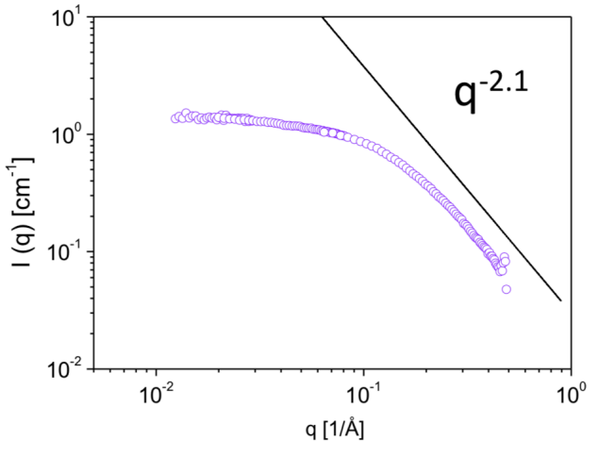
Ring opening?

Chain relaxation

Threading dynamics?

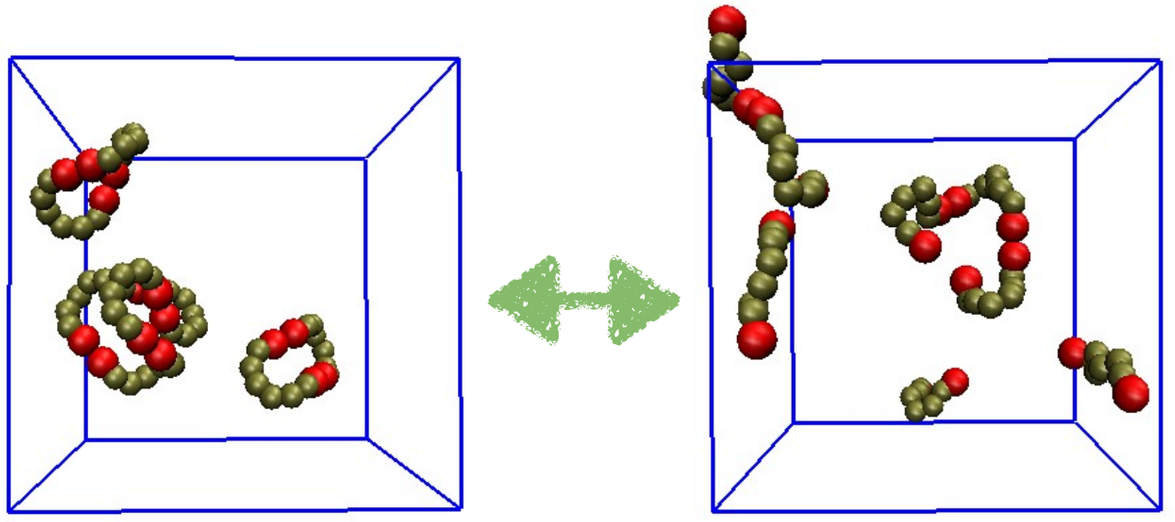
Neutron Scattering Experiment (Brás et. al, unpublished)

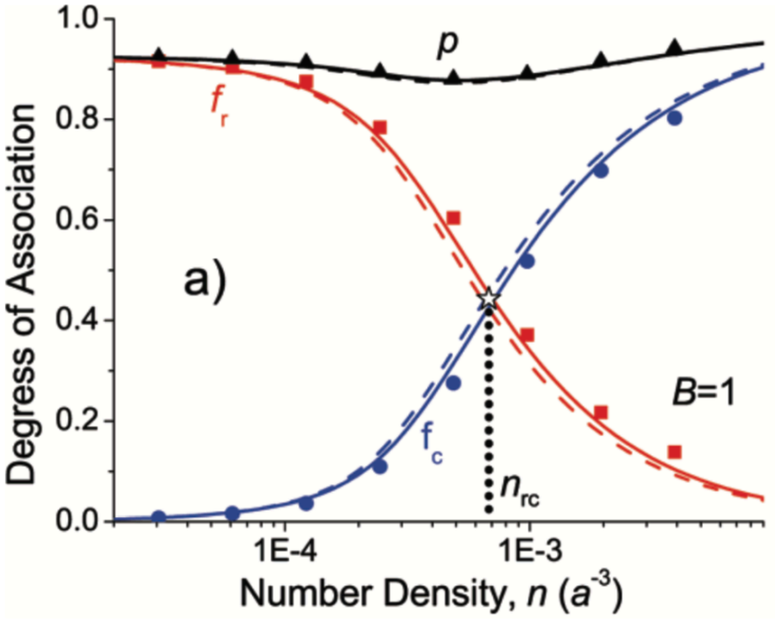


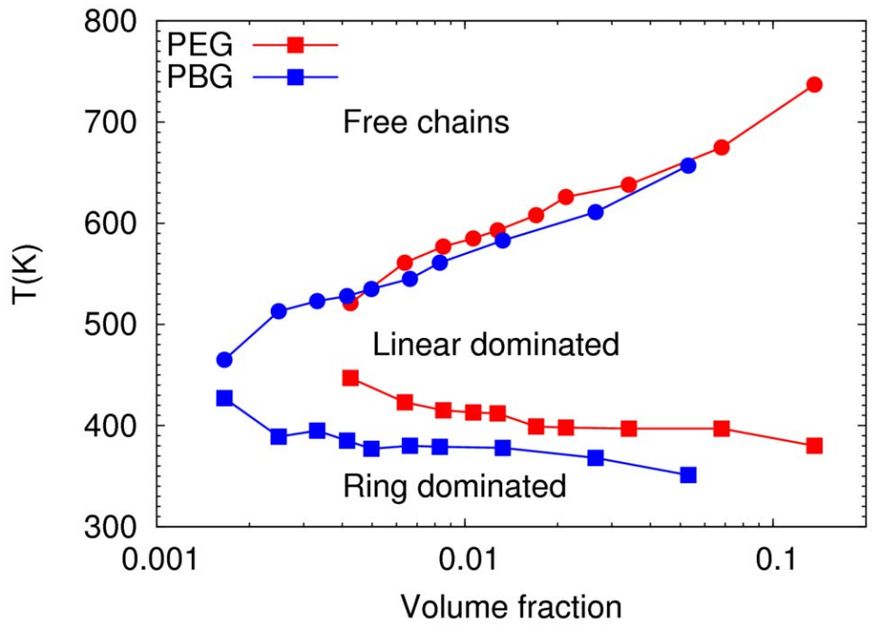
# Ring-Linear Transition

- **Ring aggregates**
  - Energetically favorable (no free associating ends)
  - Entropically unfavorable (two ends should meet in space)





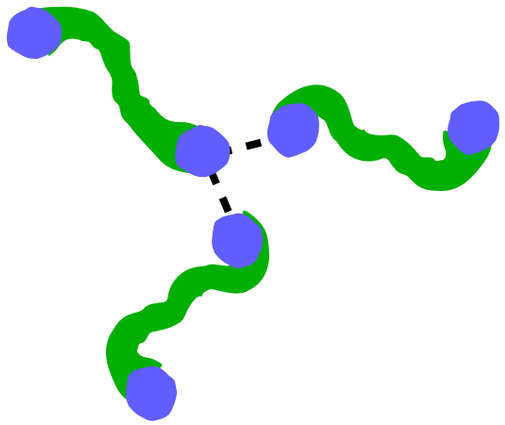

Haggy et al, Macromolecules, 2007

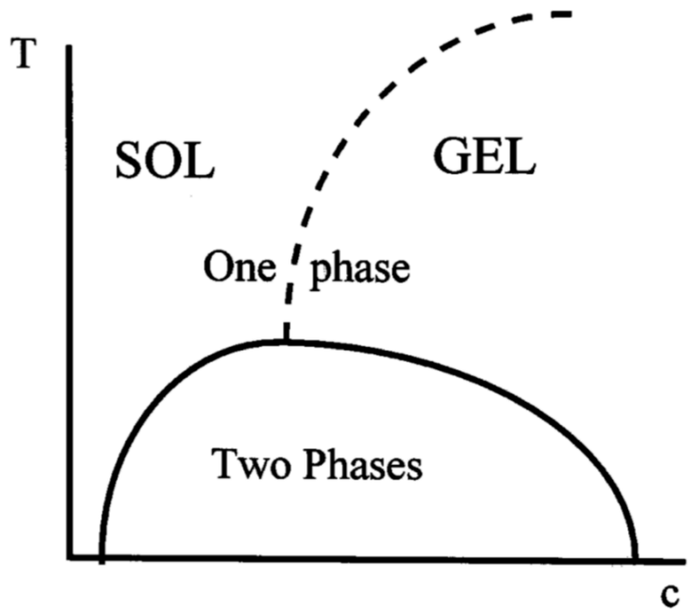



Lee et al, in preparation

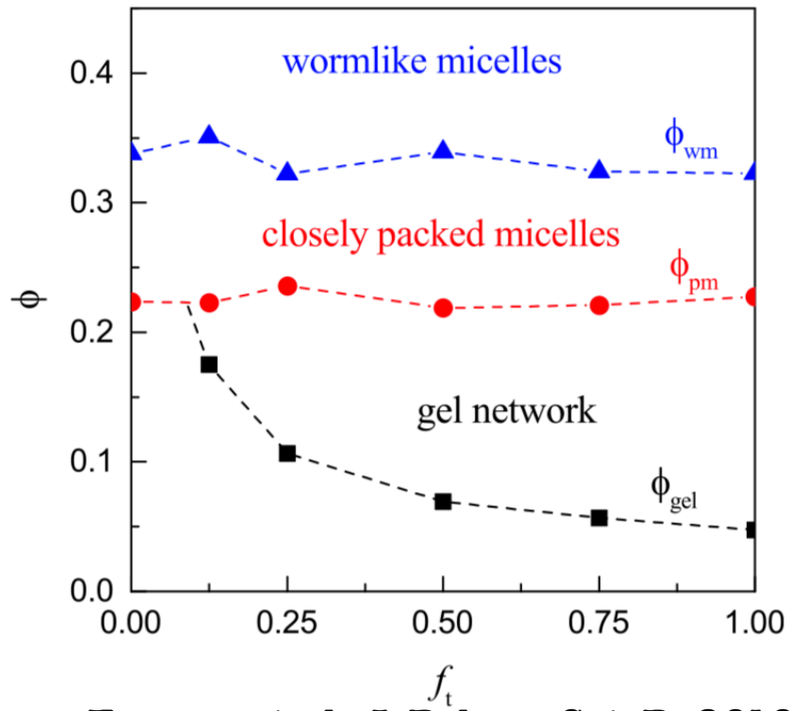
# Sol-Gel Transition

- **Critical functionality** $f^*=2$






Rubinstein et al, Curr. Opin. Colloid Interface Sci. 1999

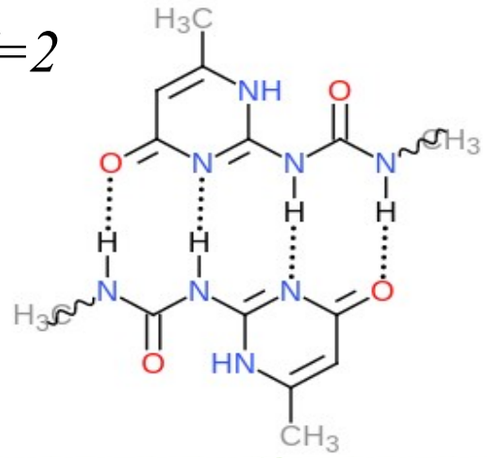



Fuyura et al, J. Polym. Sci. B. 2018

# Functionality of Stickers

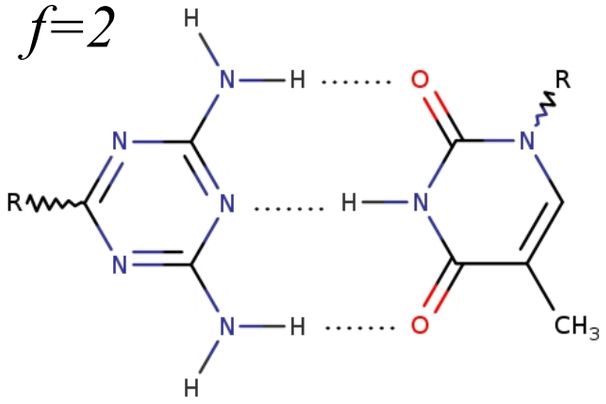
- **Hydrogen bonding stickers**

*f*=2



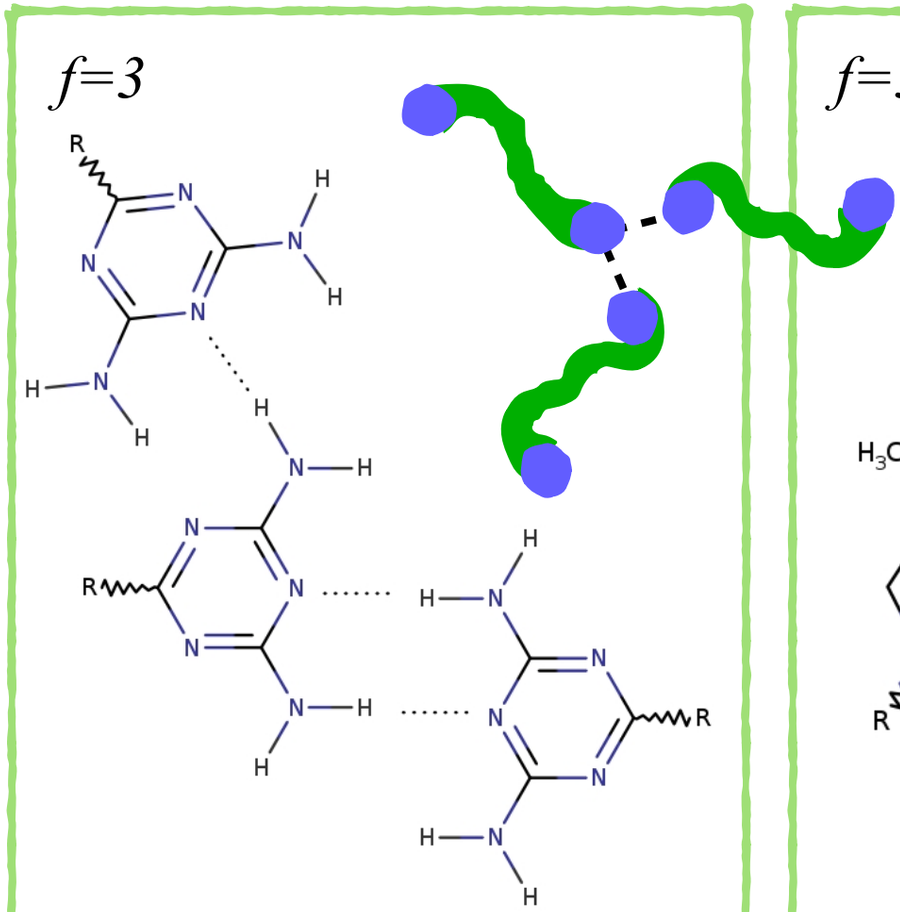
Upy-Upy

*f*=2



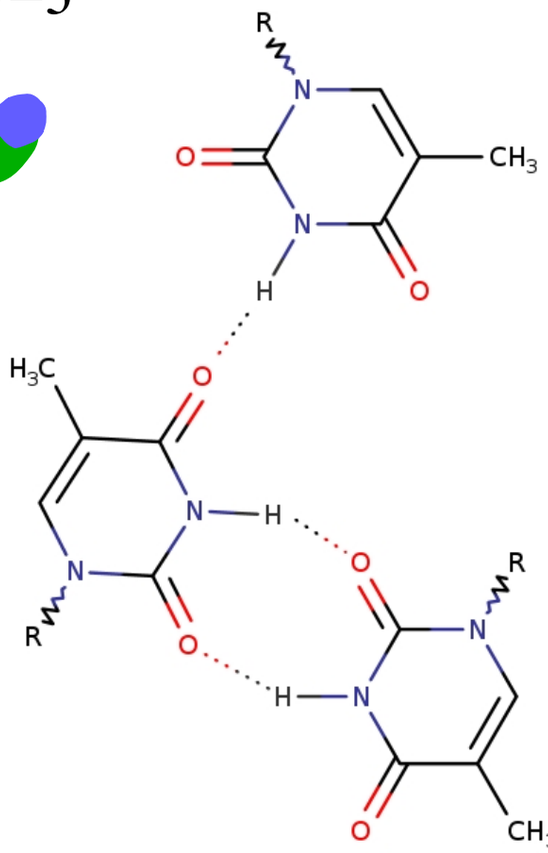
DAT-THY

*f*=3



DAT-DAT

*f*=3

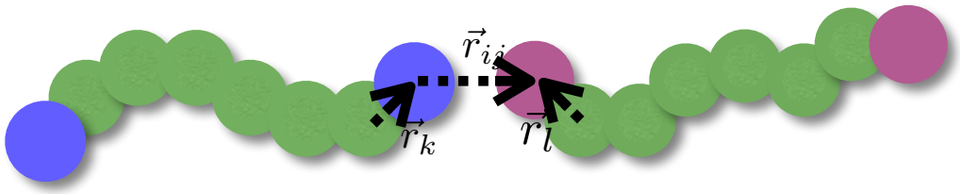


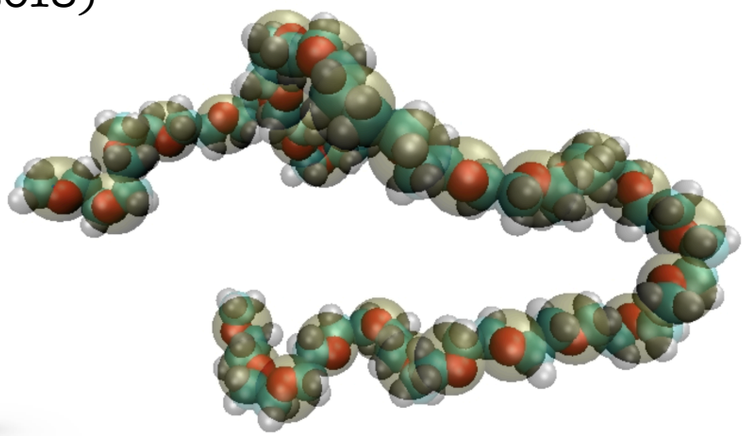
THY-THY

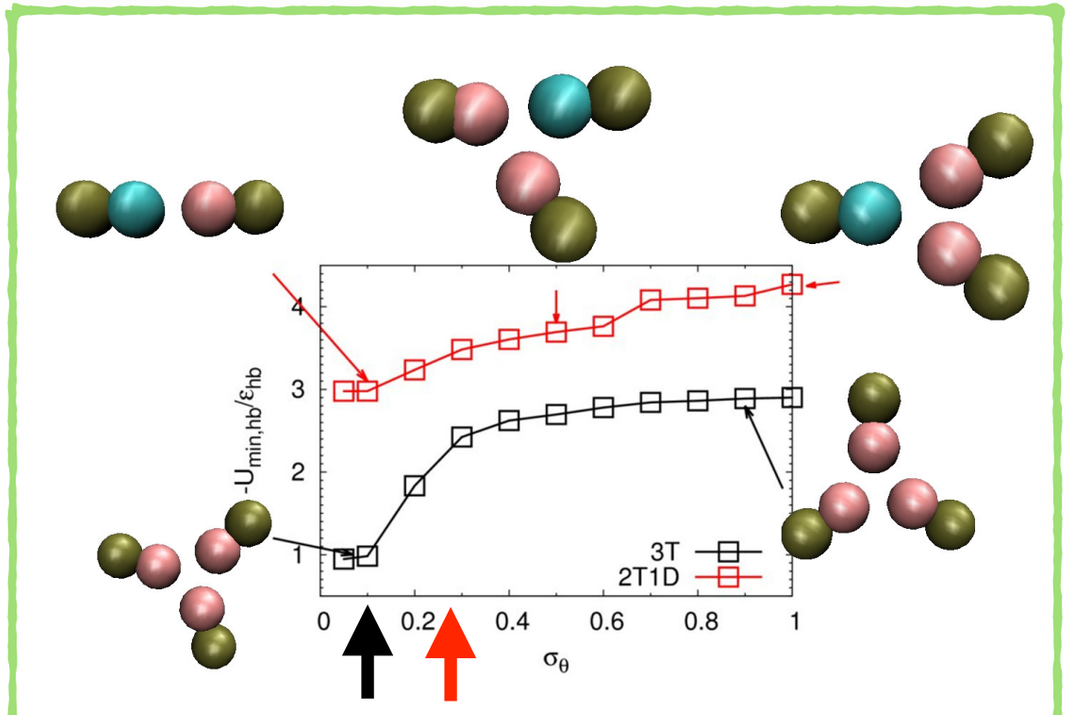
# Coarse-Grained Model for SMPs

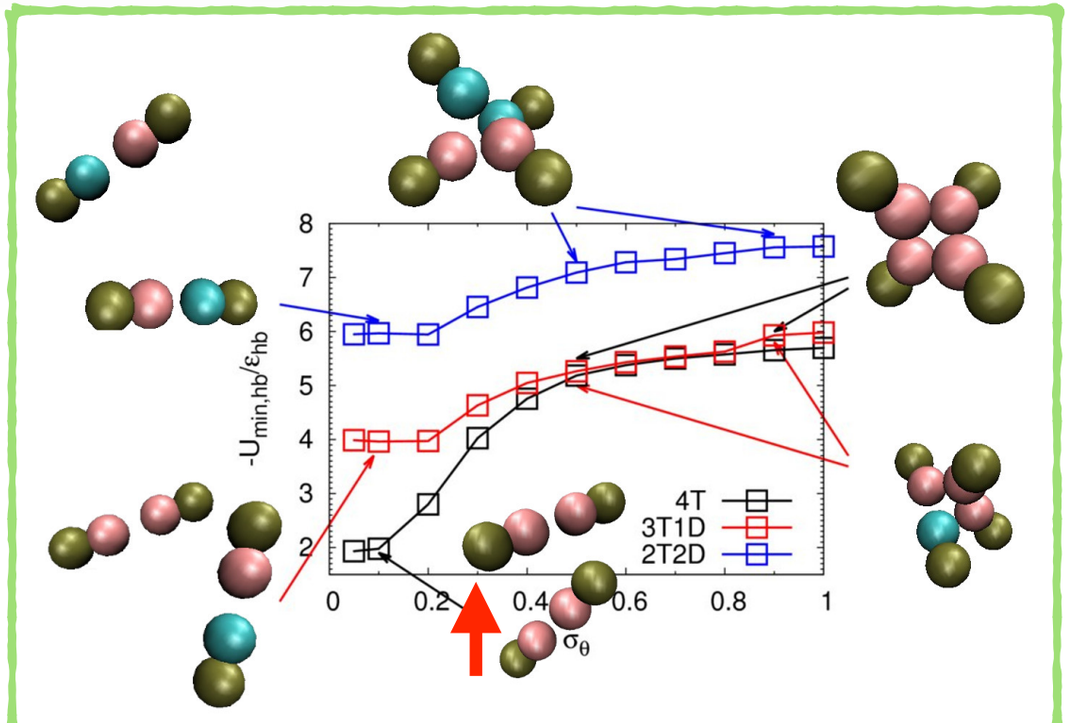
- **United Atom Model for Polyethylene and polybutylene glycols**
- **Hydrogen bonding stickers** (Lee et al, J. Chem. Phys. 2018)

$$U_{\rm hb}(r_{ij},\vec{i}_k,\vec{j}_l) = -\epsilon_{\rm hb} G(r_{ij};R_{\rm hb},\sigma_R)\times G(\vec{i}_k\hat{r}_{ij};1,\sigma_\theta)G(\vec{i}_l\hat{r}_{ij};-1,\sigma_\theta),$$





# Sampling Methods

- **Stochastic Approximation Monte Carlo (SAMC)**
  - Wang-Landau algorithm (Landau et al, Am. J. Phys. 2004)

    $$w(U_{\text{old}} \to U_{\text{new}}) = \min\left[\frac{g(U_{\text{old}})}{g(U_{\text{new}})}, 1\right]$$

  - SAMC (Liang et al, J. Am. Stat. Assoc, 2007)

    $$\ln[g(U)] \to \ln[g(U)] + \gamma_t(\delta_{U,U_{\text{new}}} - p^*(U)) \qquad \gamma_t = \gamma_0 \frac{t_0}{\max(t_0, t)}$$

- **Replica Exchange SAMC** (Vogel et al, Phys. Rev. Lett. 2013)

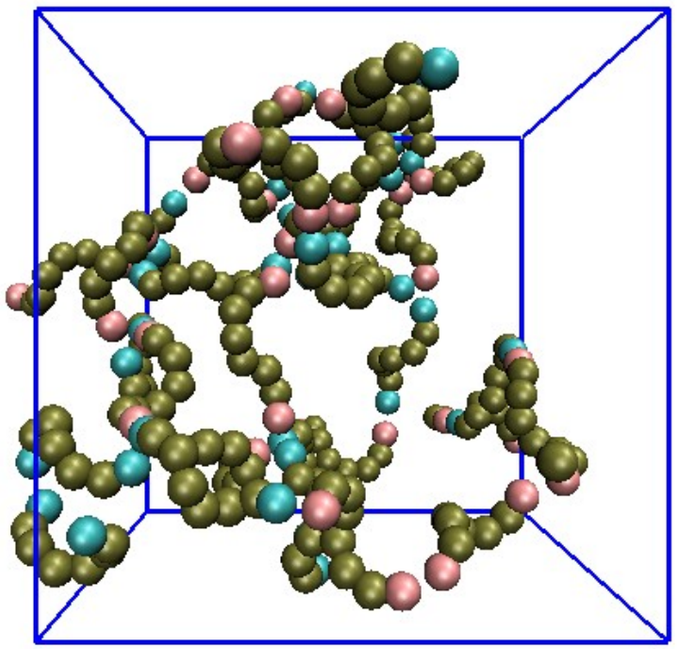
  $$w_{\text{ex}}(x_i \leftrightarrow y_j) = \min\left(1, \frac{g_i(U(x))}{g_i(U(y))}\frac{g_j(U(y))}{g_j(U(x))}\right)$$

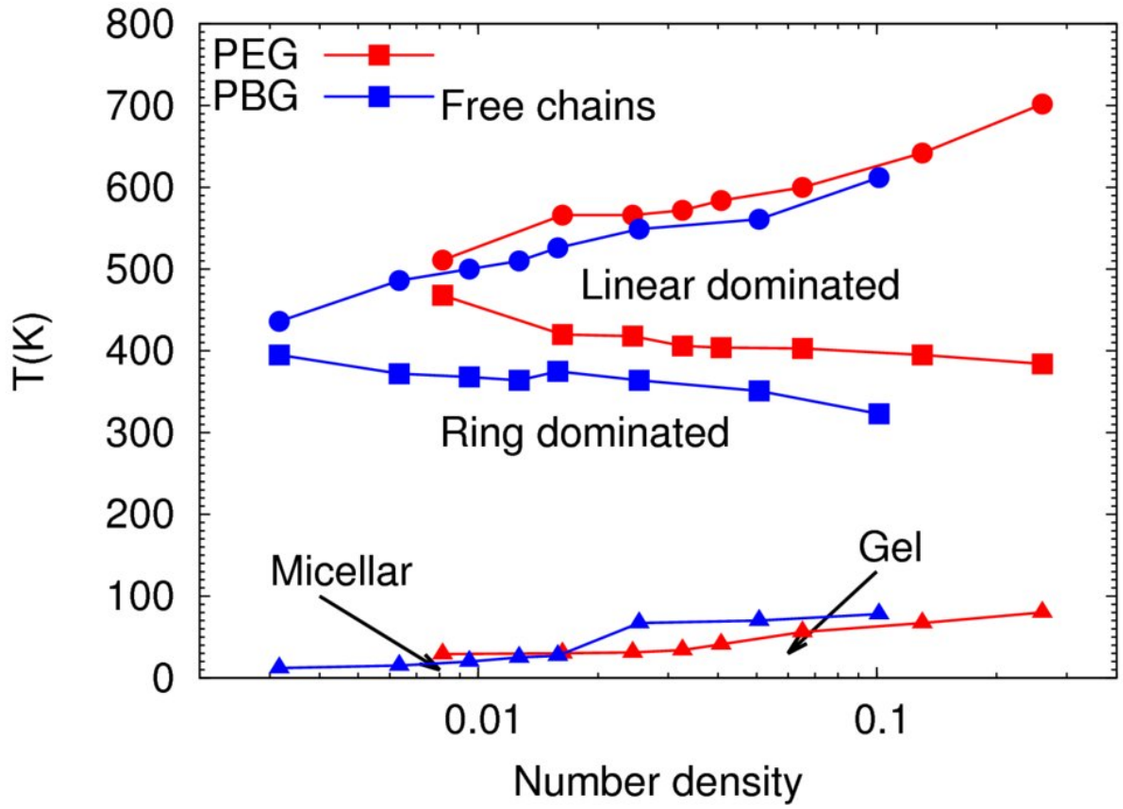
- **Density of States for Total Energies** (Shakirov et al, Eur. Phys. J. 2016)

  $$g(E) = \sum_{U=U_{\min}}^{U_{\max}} g(U) g_{\text{id}}(E-U)\Theta(E-U)$$

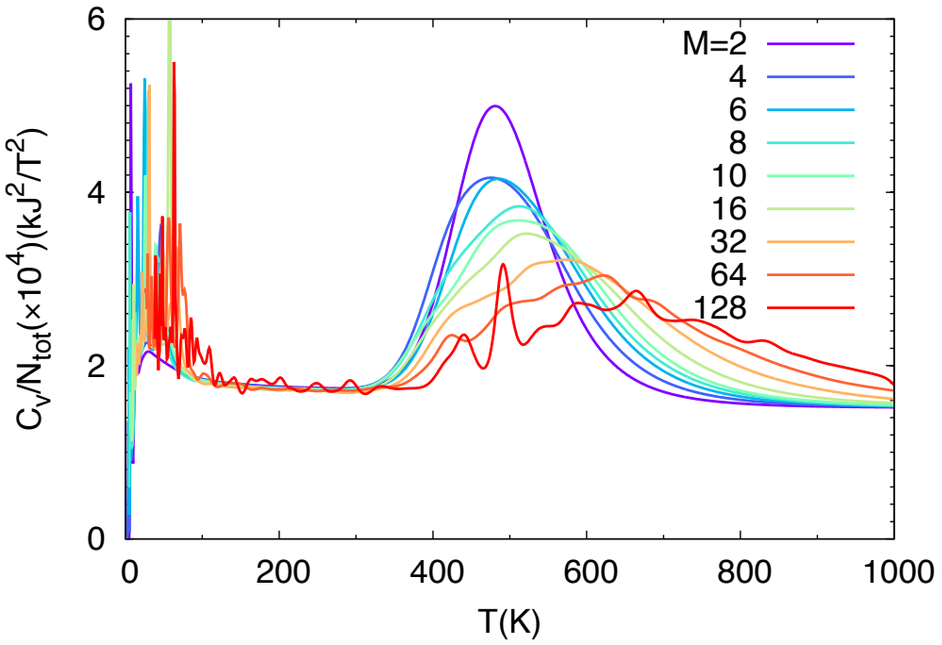
# Heterocomplementary SMPs

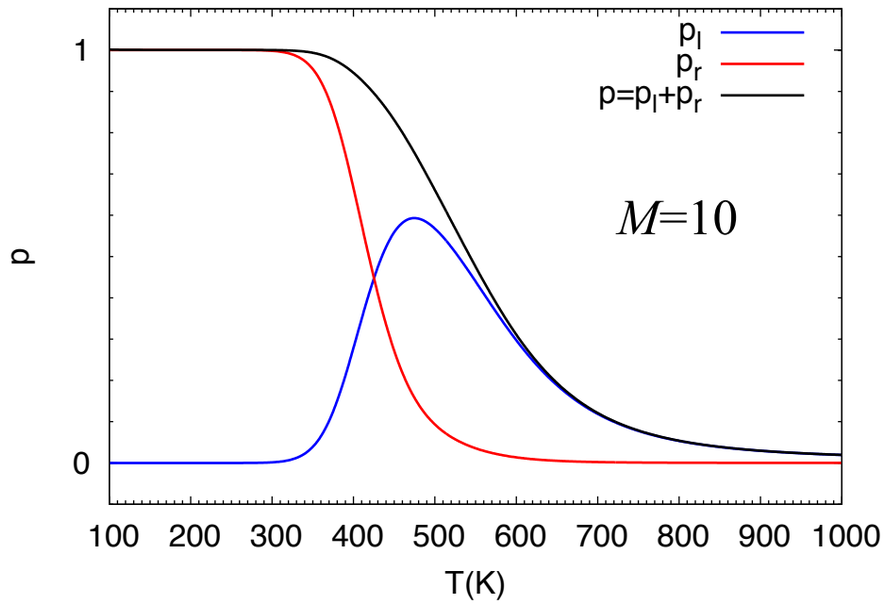
- THY-PEG(PBG)-THY and DAT-PEG(PBG)-DAT

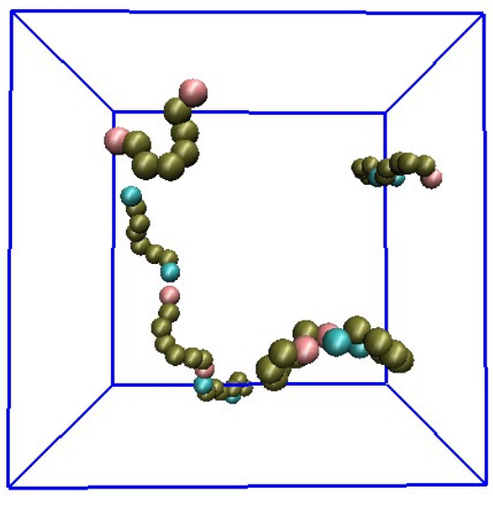




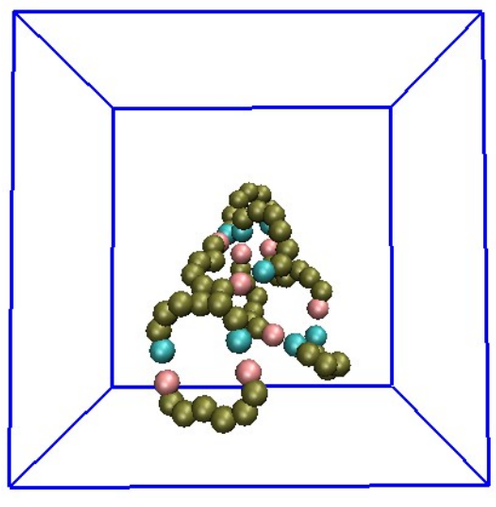
# Ring-Linear Transition



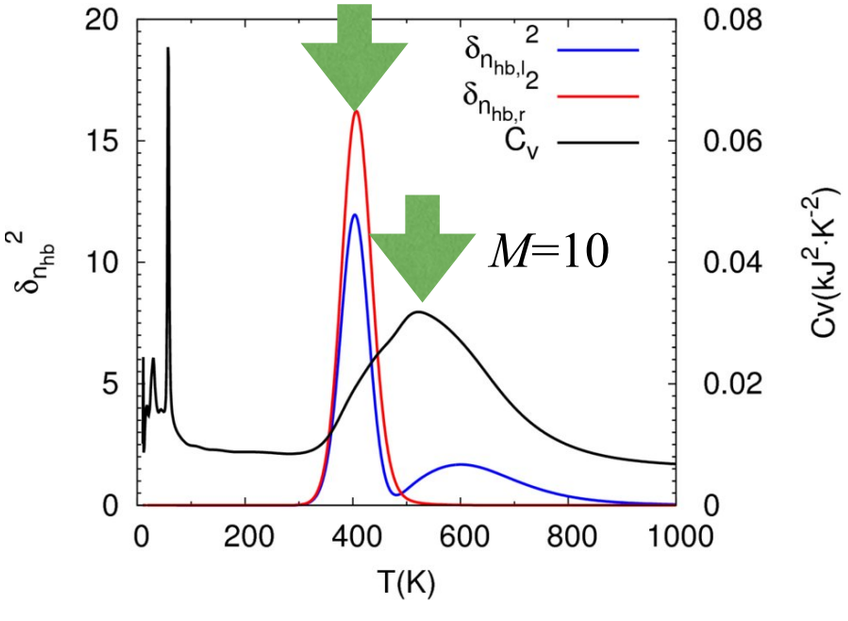



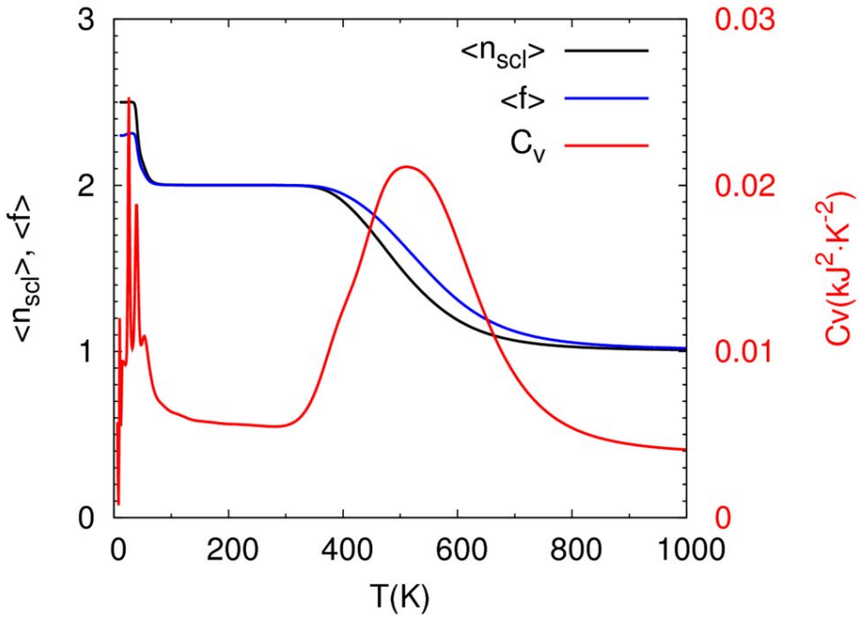
Linear-aggregates

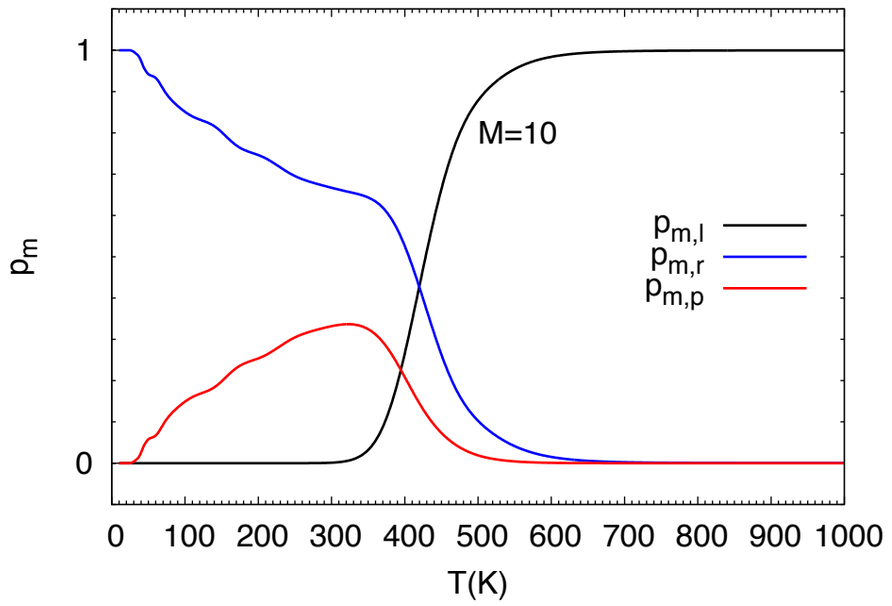


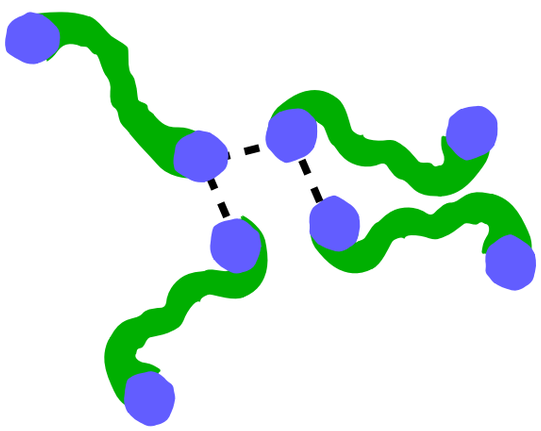
Ring-aggregates

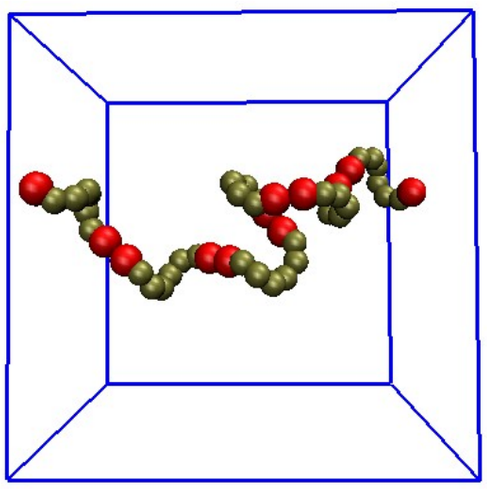


# Flower-like Micelle

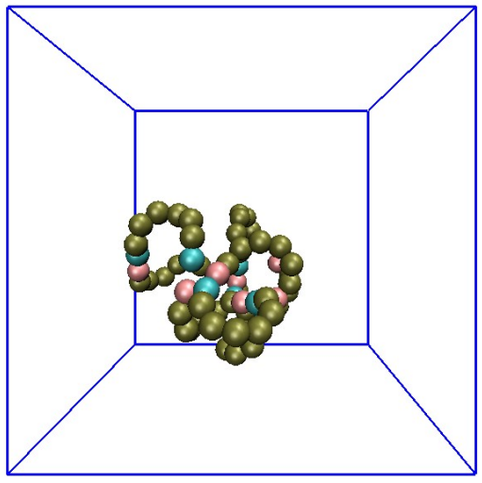


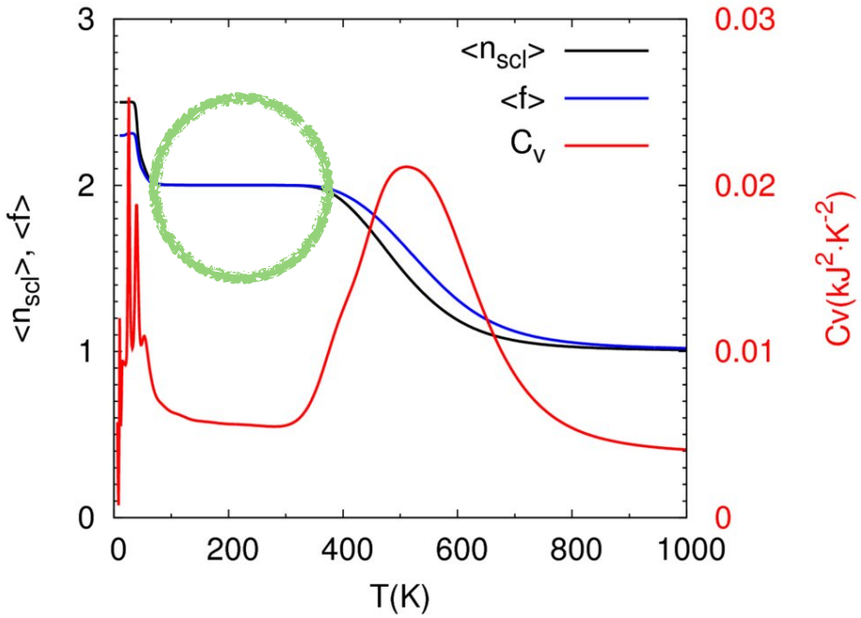


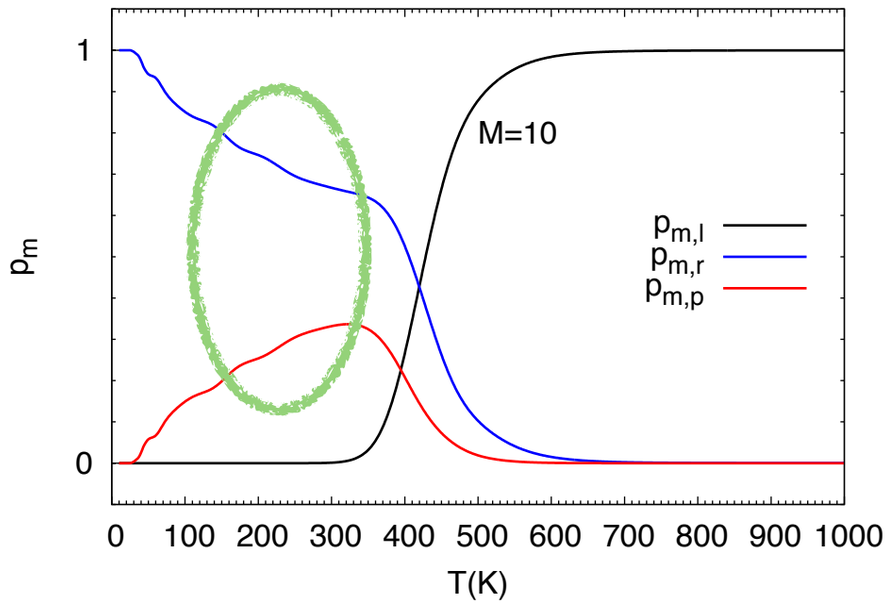
Percolating ring with $f$=2
ring (finite size)

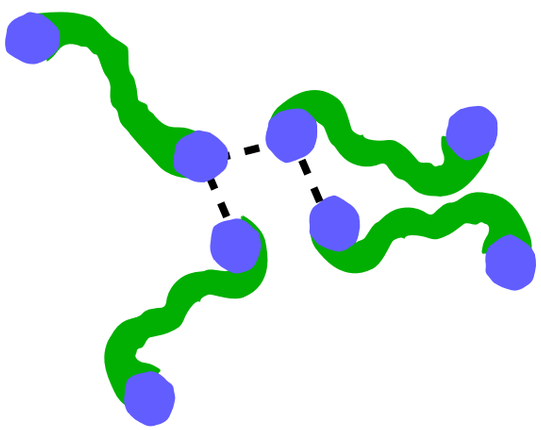


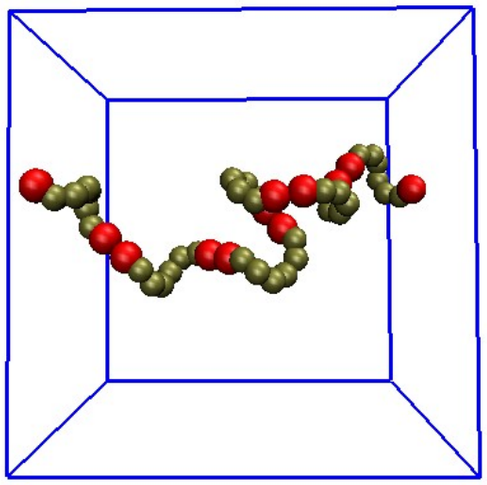
non-percolating ring with $f$>2
flower-like micelle

# Flower-like Micelle

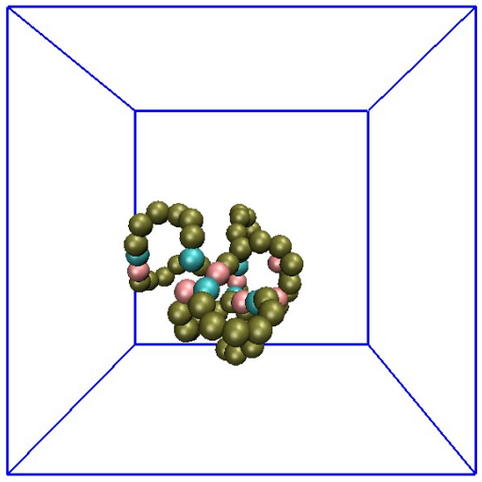


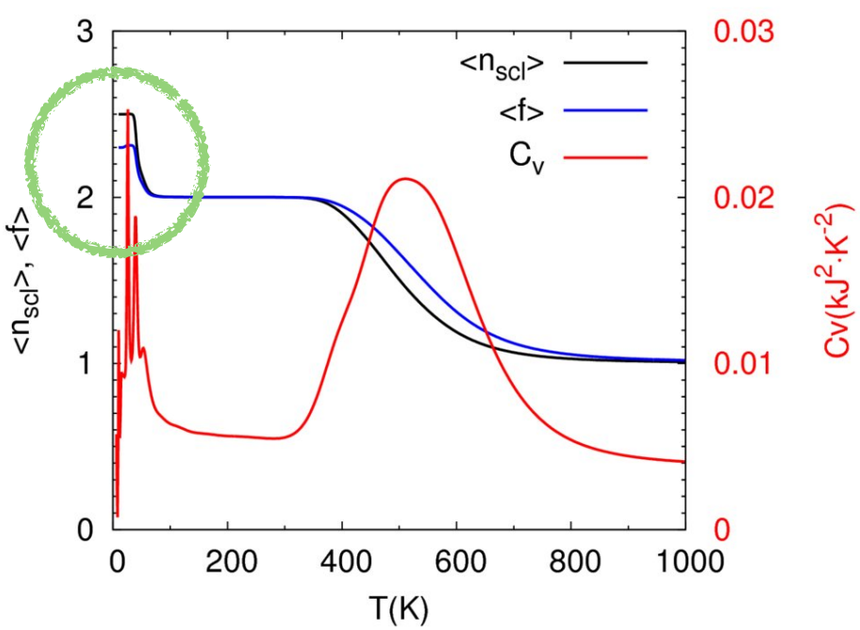


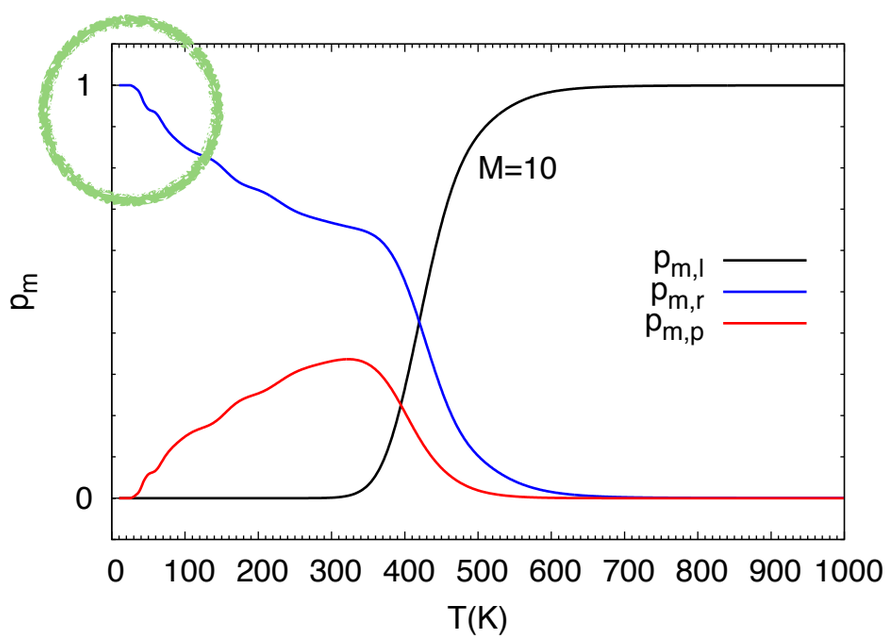
Percolating ring with $f$=2
ring (finite size)

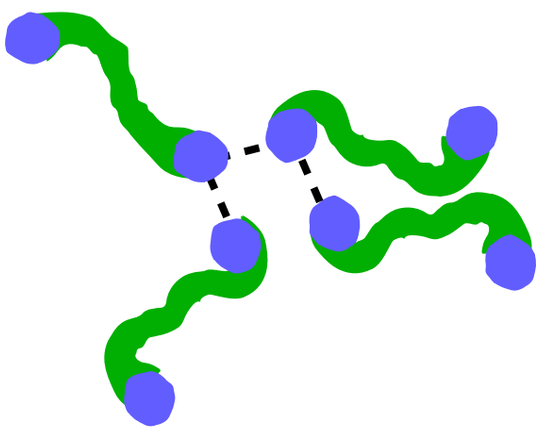


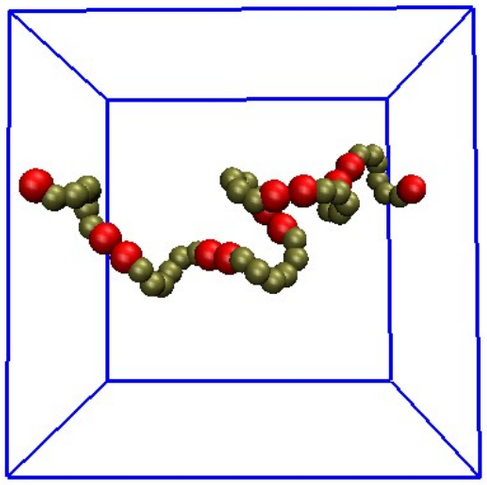
non-percolating ring with $f$>2
flower-like micelle

# Flower-like Micelle

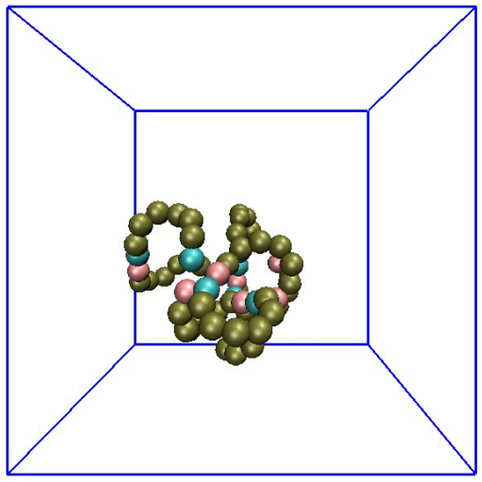




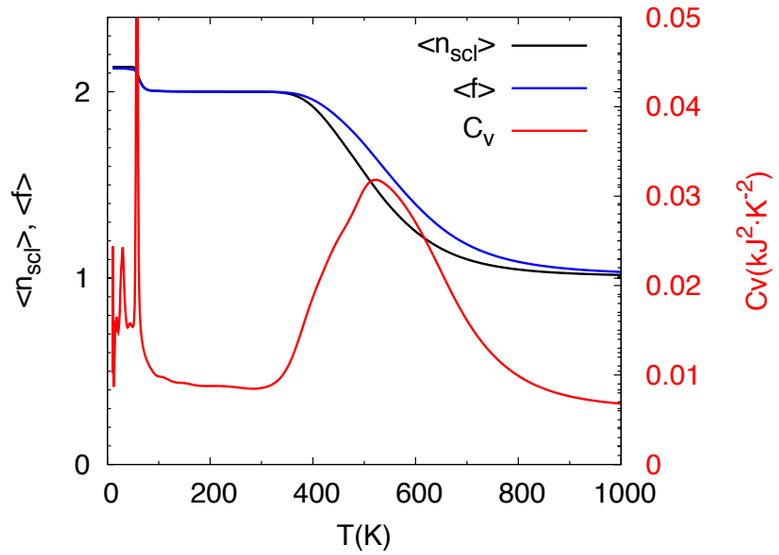
Percolating ring with $f$=2
ring (finite size)

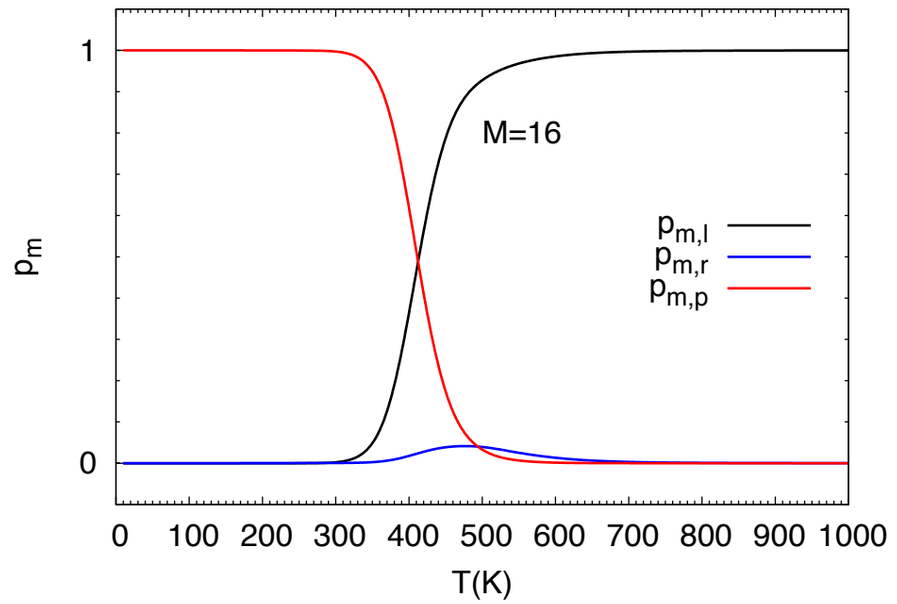


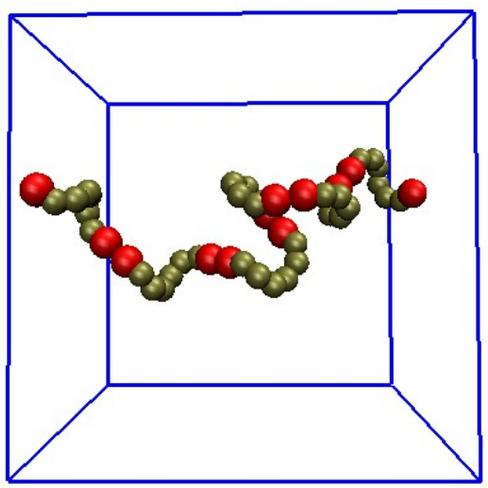
non-percolating ring with $f$>2
flower-like micelle

# Ring-Gel Transition

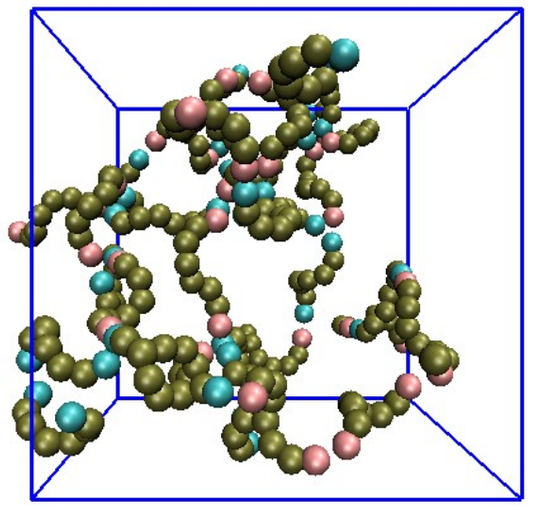
Critical functionality of gelation $f^*=2$



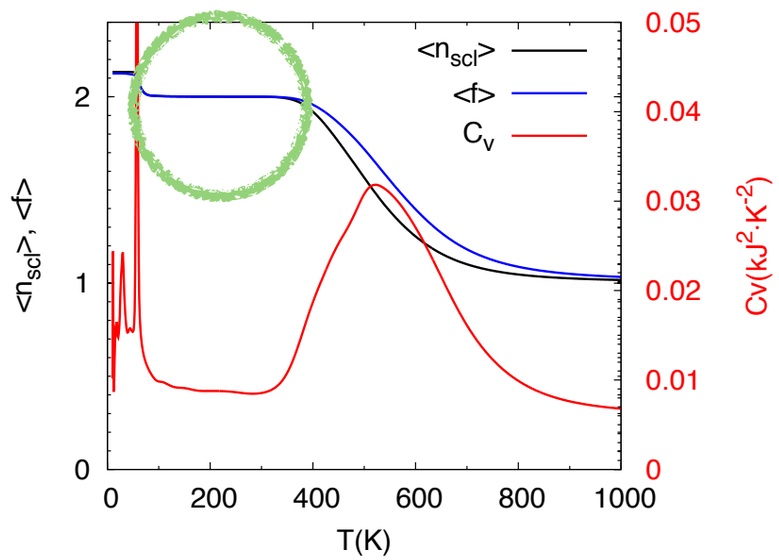
Percolating ring with $f$=2
ring (finite size)

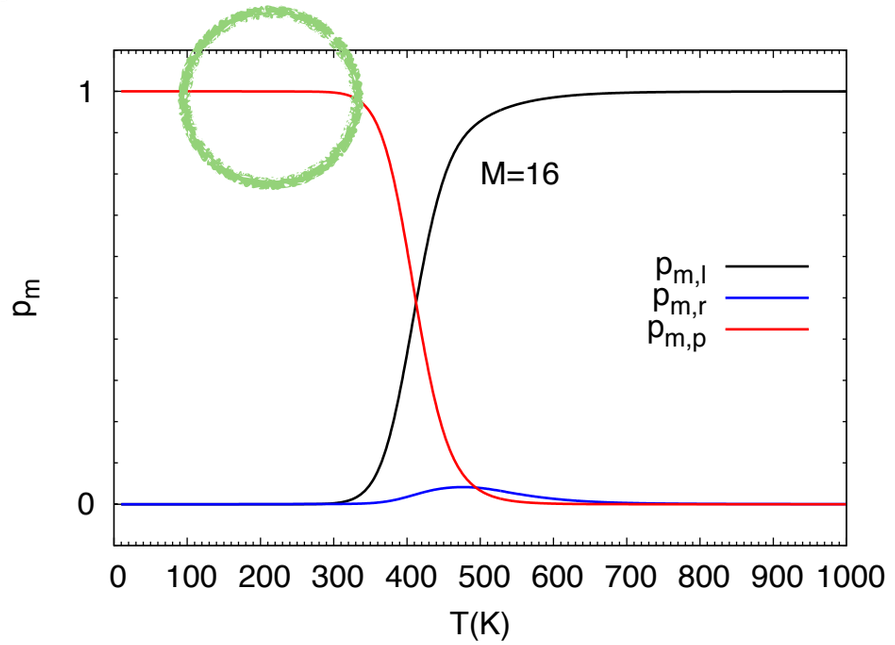


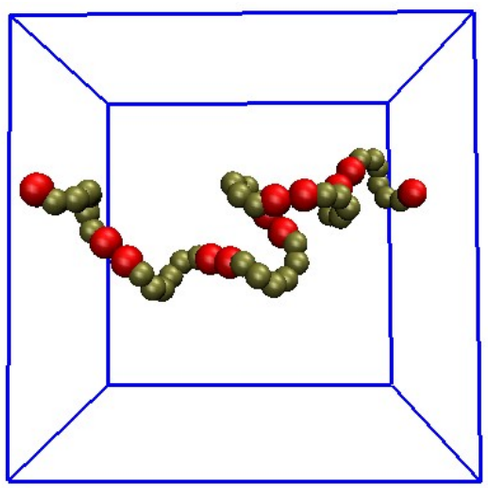
Percolating ring with $f$>2
gel

# Ring-Gel Transition

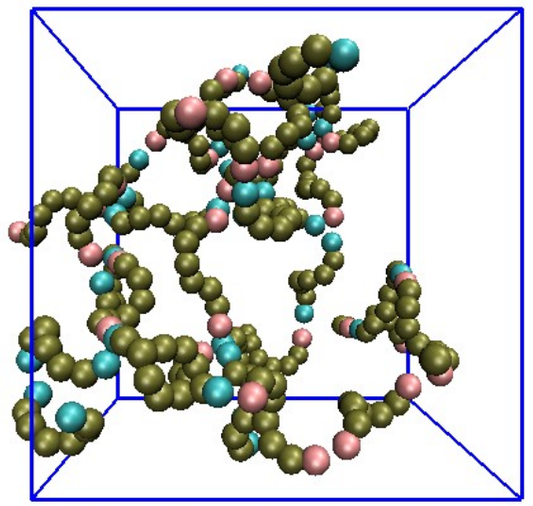
Critical functionality of gelation $f^*=2$



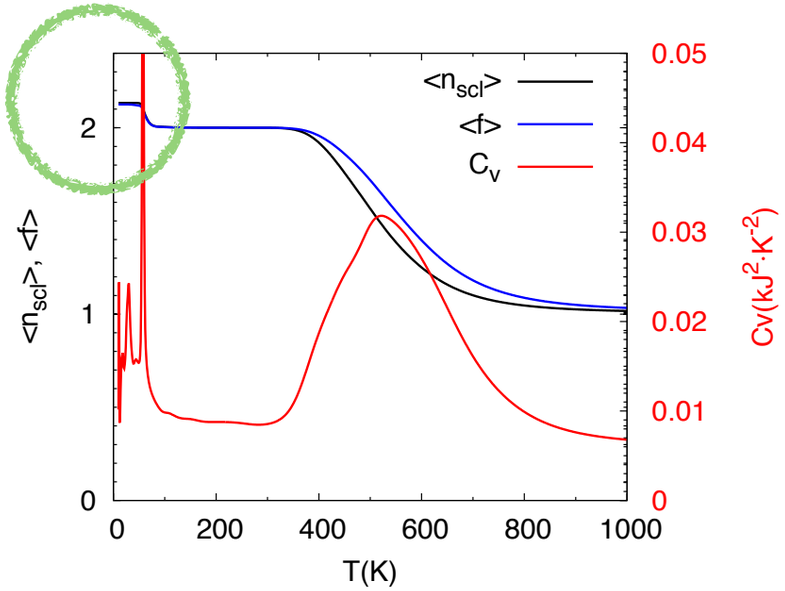
Percolating ring with $f$=2
ring (finite size)

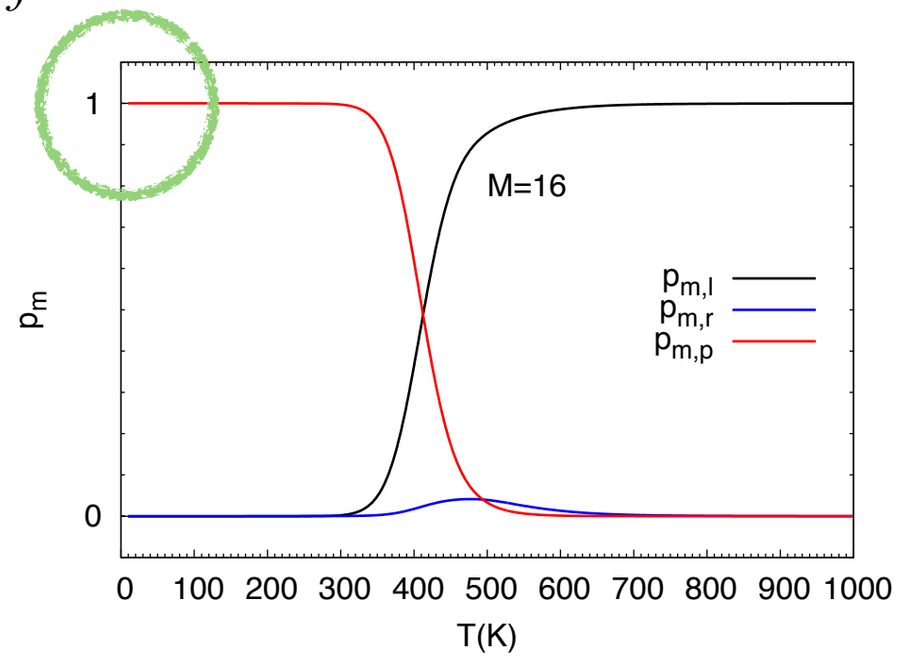


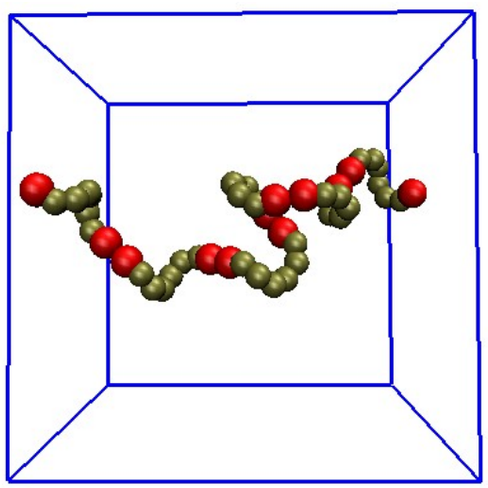
Percolating ring with $f$>2
gel

# Ring-Gel Transition

Critical functionality of gelation $f^*=2$

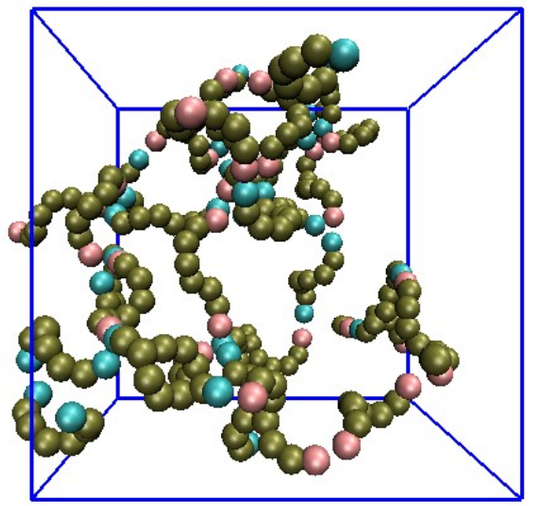


Percolating ring with $f$=2

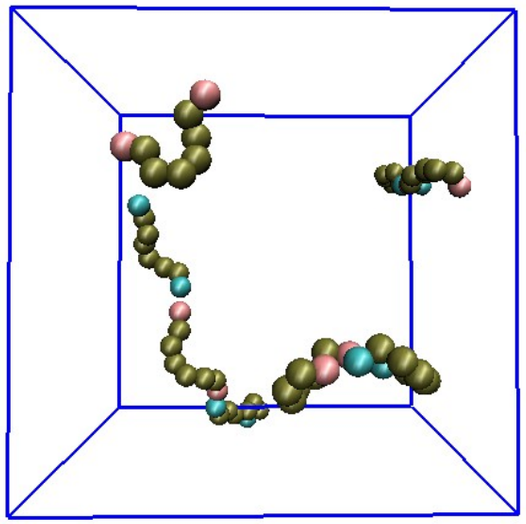
ring (finite size)



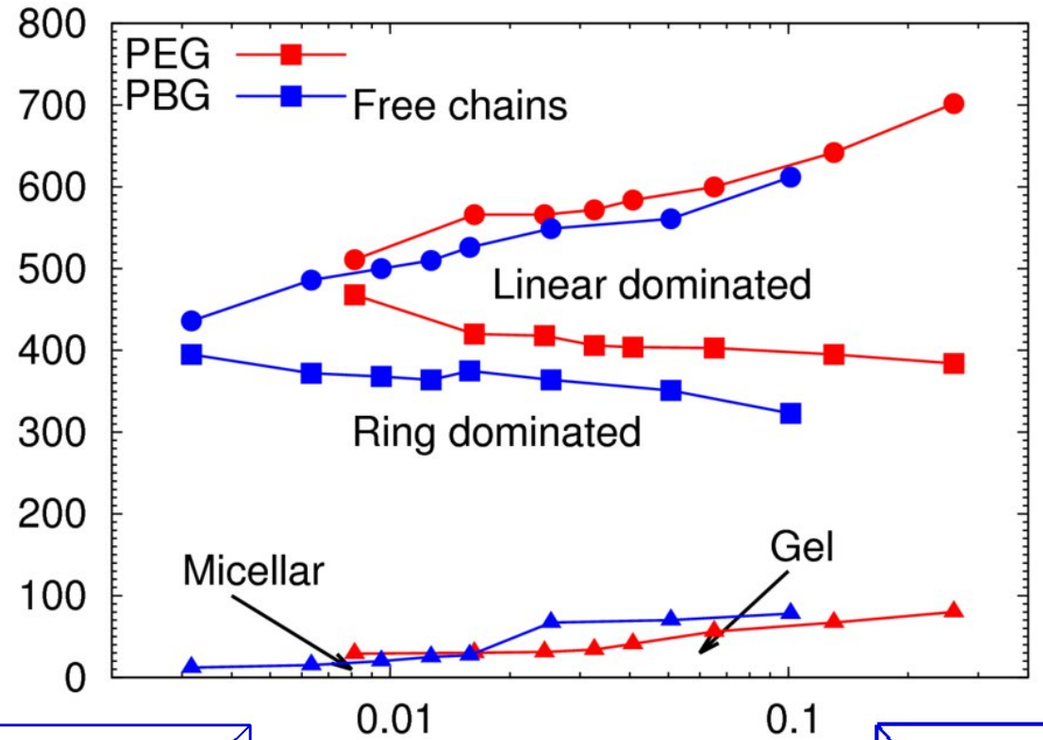
Percolating ring with $f$>2

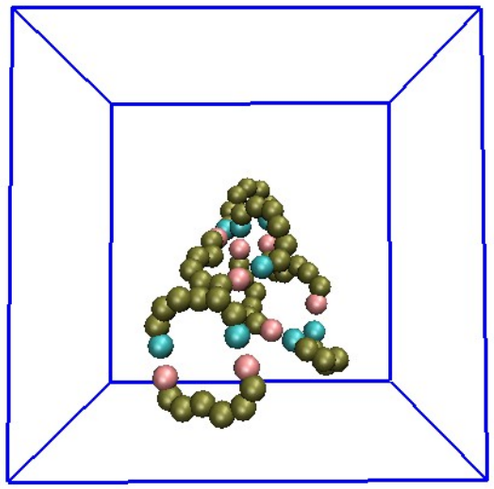
gel

# Phase Diagram

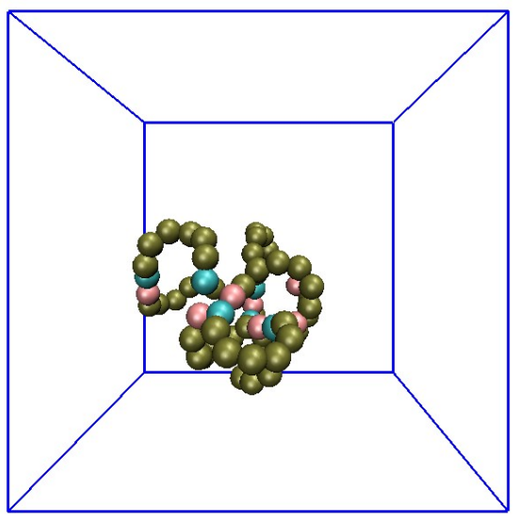


Linear

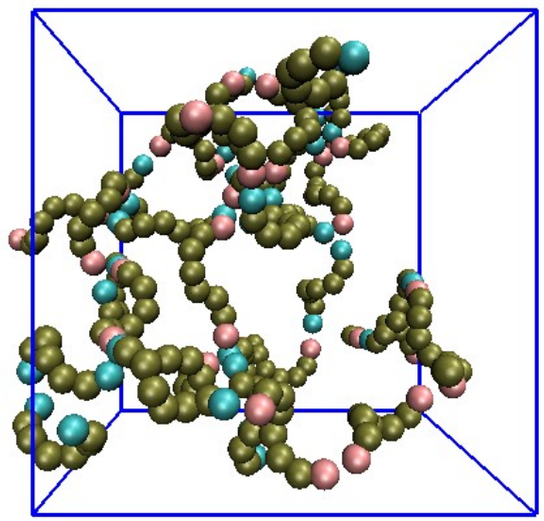


Ring



Flower-like micelle



Gel

# Conclusion

- SMPs with a temperature-dependent functionality sticker show a micelle (or gel)-ring transition.
- At intermediate temperature, SMPs undergo a ring-linear transition.
- At very low temperature, dilute SMPs form flower-like micelles and semi-dilute SMPs over overlap concentration form a gel.

**Thank you for your attention!**