SAND2019-11372C

Assembly of Polymer-Grafted Nanoparticles

Amalie L. Frischknecht

Center for Integrated Nanotechnologies

Sandia National Laboratories

CINT Annual Meeting

September 23, 2019

Jason Koski

Rob Riggleman

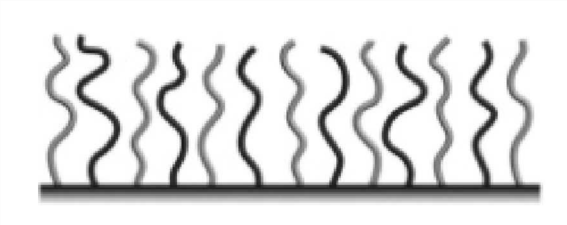
Russ Composto

U Penn

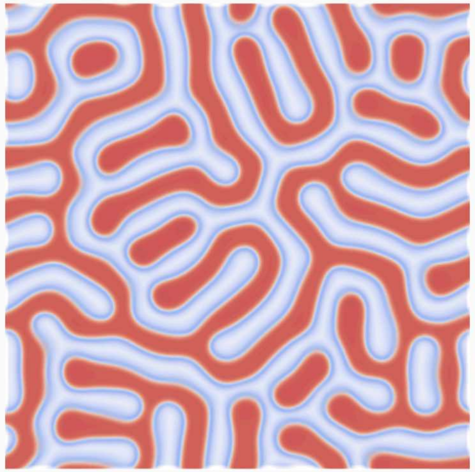
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

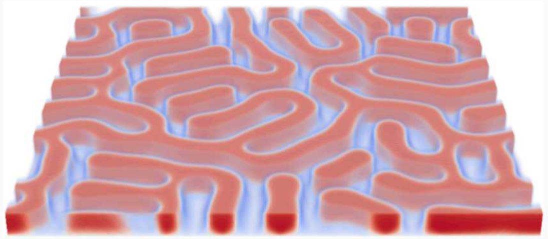
Mixed polymer brushes

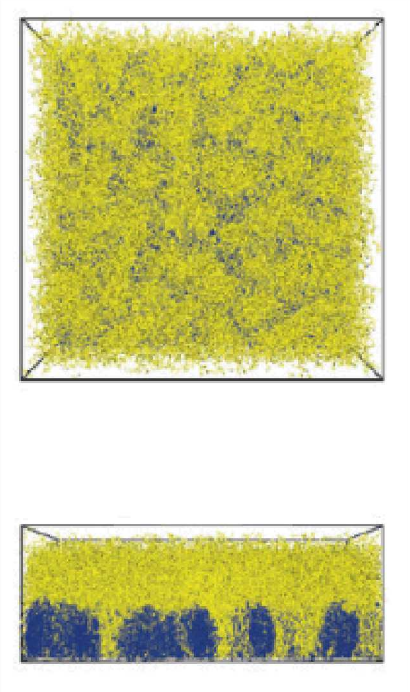
- multiple polymer species grafted to surface
- microphase separation
  - lateral
  - vertical



lateral phase separation





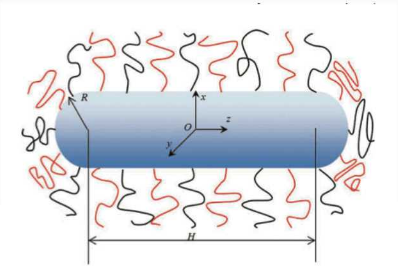


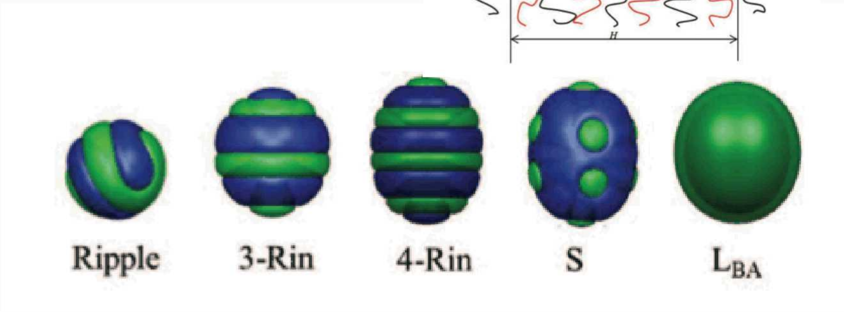
vertical phase separation

Wang, J. & Mueller, M. *J Phys Chem B* **113,** 11384–11402 (2009).

Mixed polymer brushes

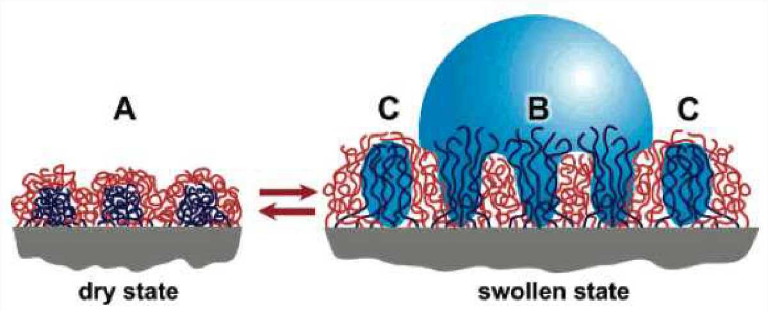
patchy
nanoparticles





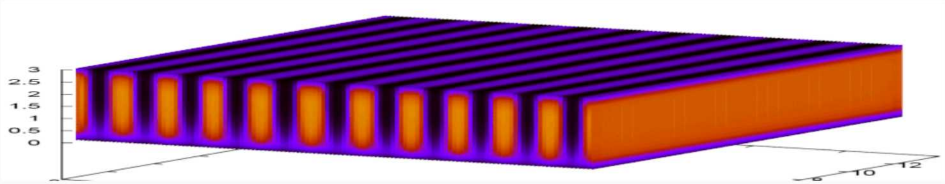
X. Ma, et al J Chem Phys **139**, 214902 (2013).

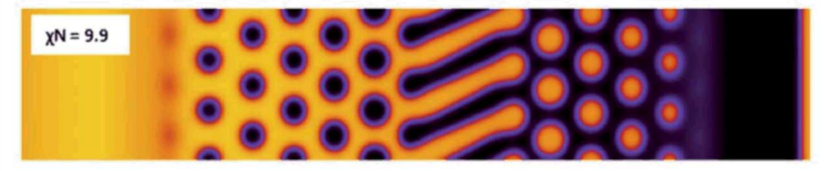
switchable surfaces



Motornov, M., Sheparovych, R., Tokarev, I.,
Roiter, Y. & Minko, S. *Langmuir* **23,** 13–19 (2007).

surface patterning



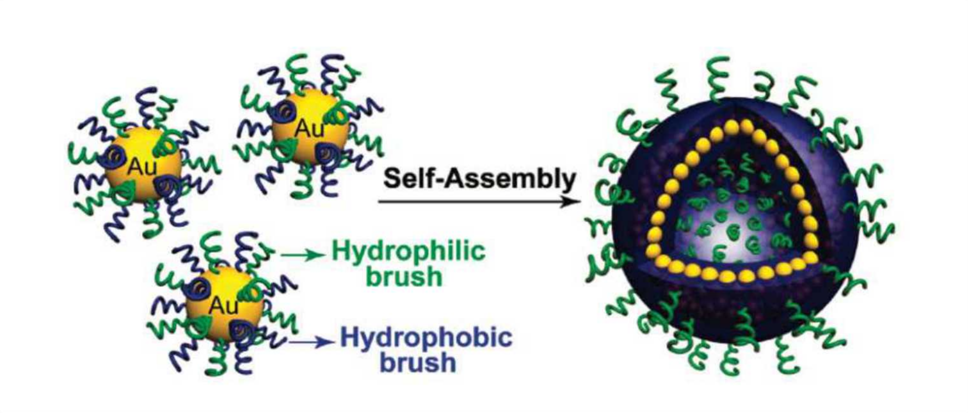


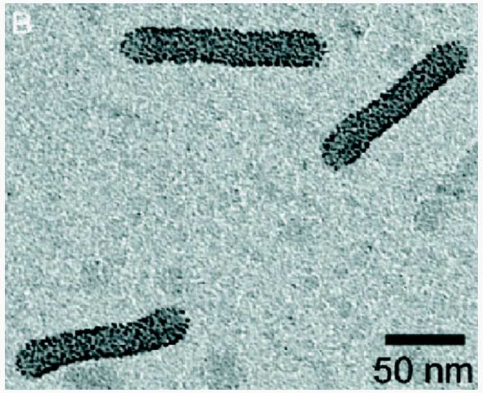
S-M. Hur, et al, *Soft Matter* **7**, 8776 (2011);
Soft Matter **9**, 5341 (2013).

Assembly of mixed-brush nanoparticles in solution

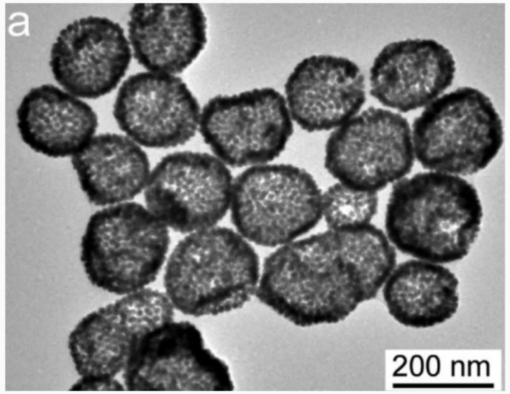
Interest for

- solvent processing of nanocomposites
- optical applications (eg sensing, plasmonics)
- catalysis
- drug delivery

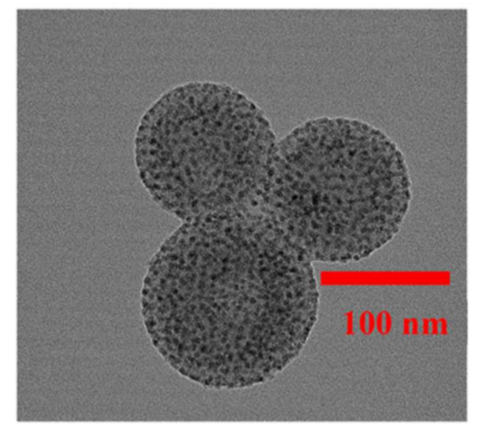




Zubarev *et al.*, JACS, 2006



Song *et al.*, JACS, 2012



Guzman-Juarez et al, Macromolecules, 2018

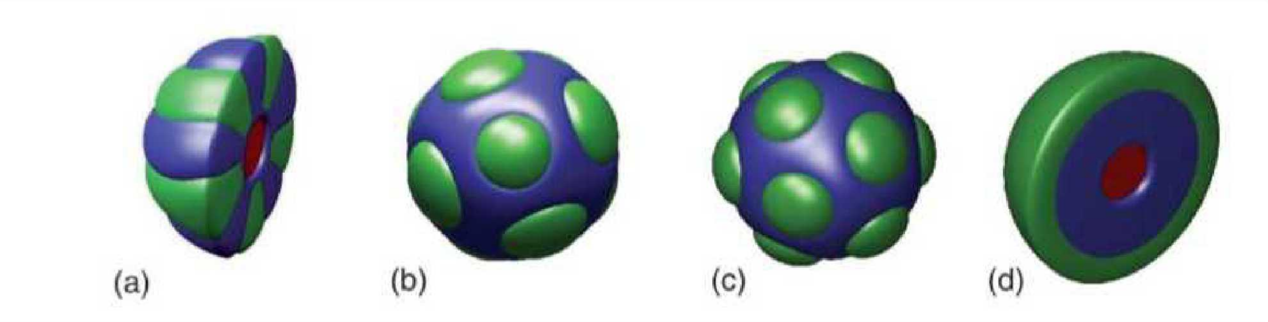
What is the structure of mixed-brush nanoparticles?

What governs the self-assembly of mixed-brush nanoparticles?

Previous modeling of mixed brush nanoparticles

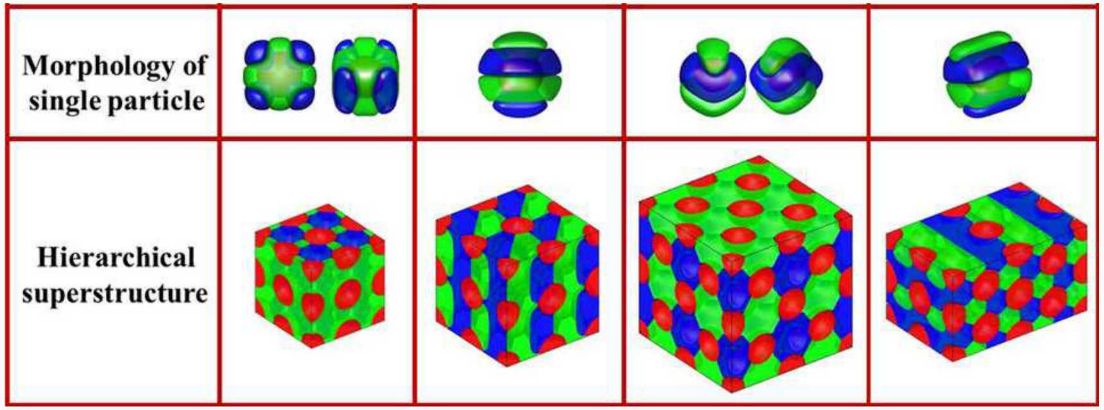
polymer self-consistent field theory (SCFT)

non-selective good solvent
$\chi_{AB}N = 40$



Wang et al., *J. Chem. Phys.*, 2011

neat particles
$\chi_{AB}N = 20$



Chen et al., *ACS Macro Lett.*, 2016

How realistic are these structures? What about fluctuations?

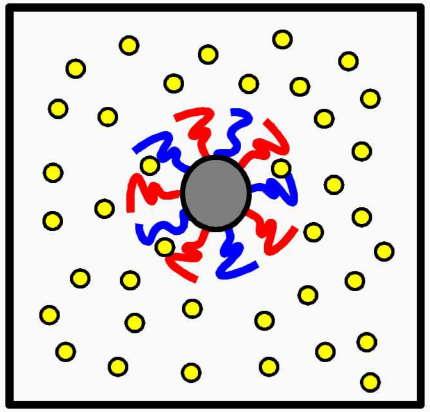
Theoretically-Informed Langevin Dynamics (TILD)

discrete Gaussian chains + NPs

monomer shape function $h_m(\mathbf{r}) = (2\pi a^2)^{-3/2} e^{-|\mathbf{r}|^2/2a^2}$

nanoparticle shape function $h_P(\mathbf{r}) = \frac{\rho_0}{2}\mathrm{erfc}\left(\frac{|\mathbf{r}| - R_P}{\zeta}\right)$

bond length b, a = ζ = b/2



Langevin eq for chains, particles:

$$m_i \frac{d^2\mathbf{r_i}}{dt^2} = \mathbf{F}_i - D\frac{d\mathbf{r_i}}{dt} + \eta_i(t)$$

$F_i = F_{bond} + F_{int}$

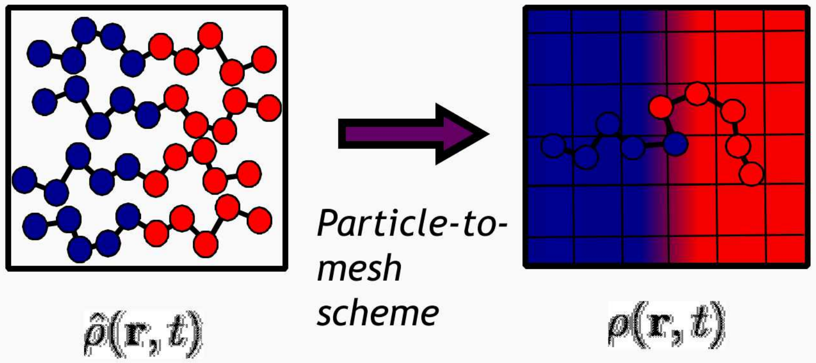
η_i = Gaussian white noise

monomer-monomer interactions: $u(\mathbf{r}) = \frac{\chi_{AB}}{\rho_0}(h_A * h_B)(\mathbf{r})$

repulsive interactions: $u_c(\mathbf{r}) = \frac{\kappa}{2\rho_0}(h_i * h_j)(\mathbf{r})$

bonding potential: $\beta u_{bond} = \frac{3}{2b^2}|\mathbf{r}_s - \mathbf{r}_{s+1}|^2$

Theoretically-Informed Langevin Dynamics (TILD)



1. Evaluate bonded forces on all particles (beads in chains)
2. Interpolate particle positions to density on mesh
3. Calculate non-bond forces as fields on the mesh → evaluate $F_{int}(\mathbf{r}, t) = -\int d\mathbf{r}' \nabla u(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}', t)$

   (in k-space with FFT)
4. Translate to forces on each particle; update particle positions

Similar to:

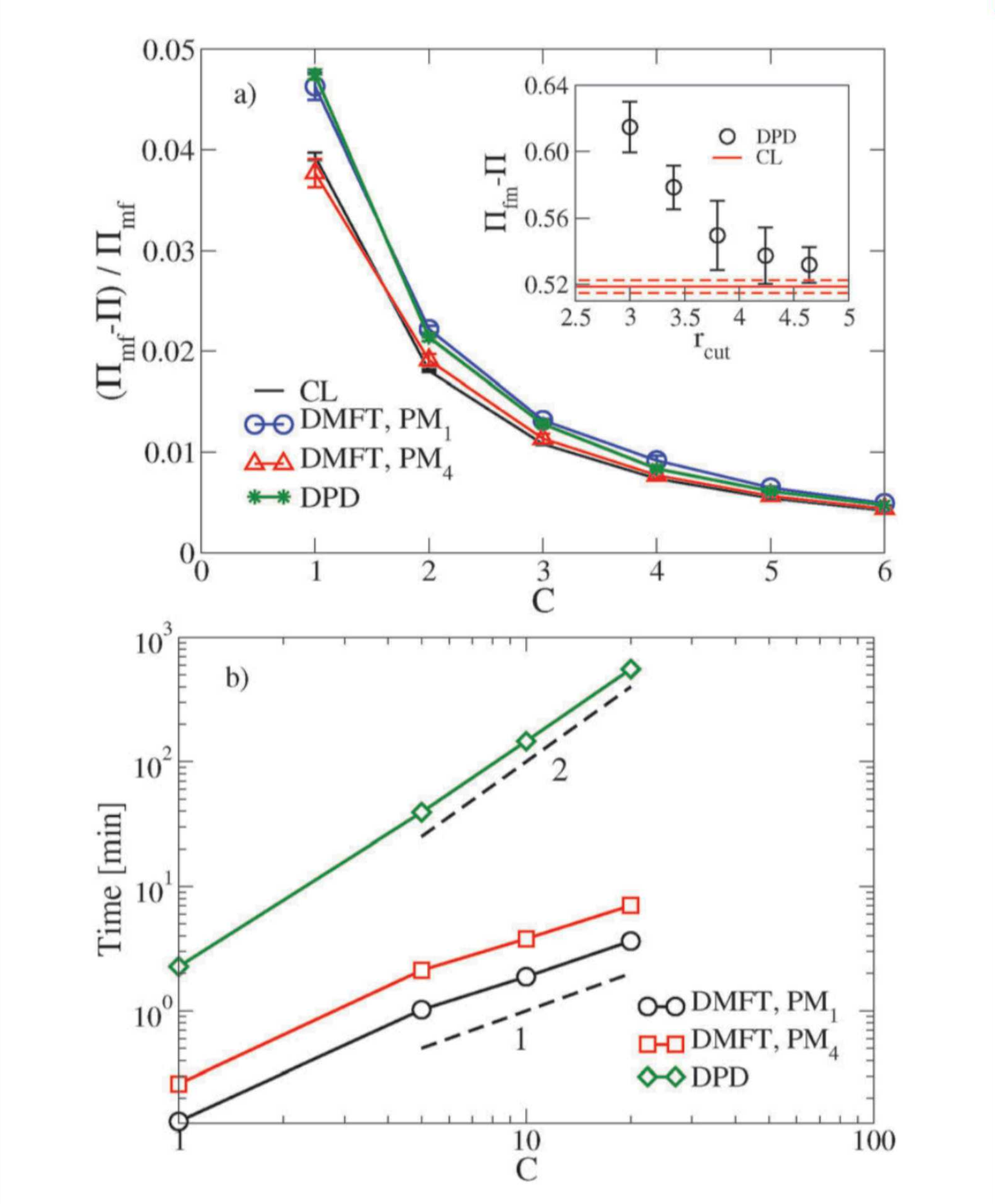
- Ganesan (SCBD: self-consistent Brownian dynamics)
- Müller (SCMF: single-chain-in-mean-field)
- de Pablo (TICG: theoretically-informed coarse-grained sims)

Riggleman group implementation

Include torques on grafted nanoparticles

Solve Langevin equation with Gronbech-Jensen and Farago (GJF) scheme

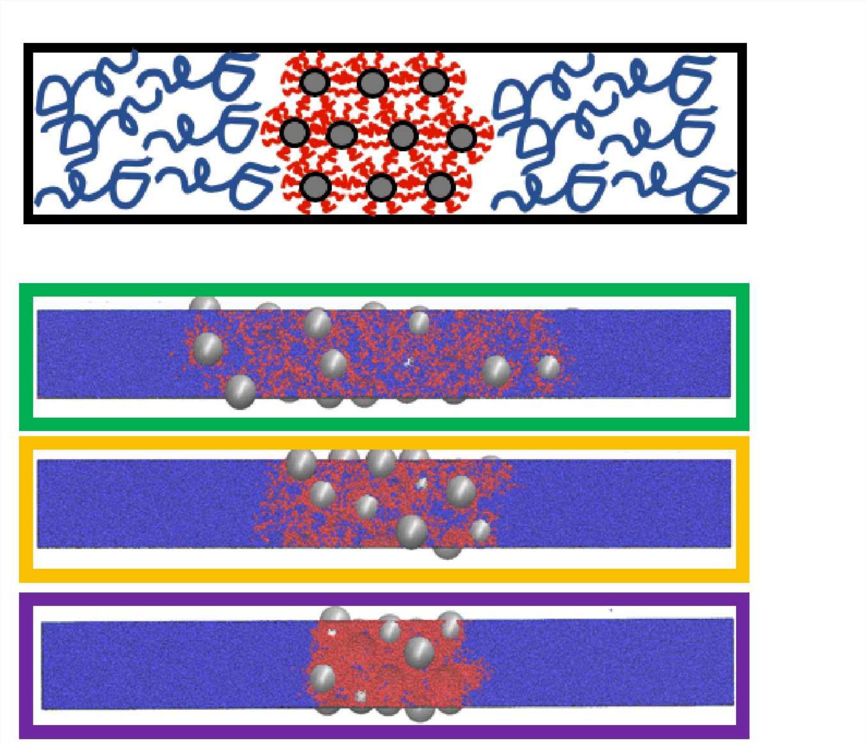
allows large timesteps
good performance compared to DPD simulation

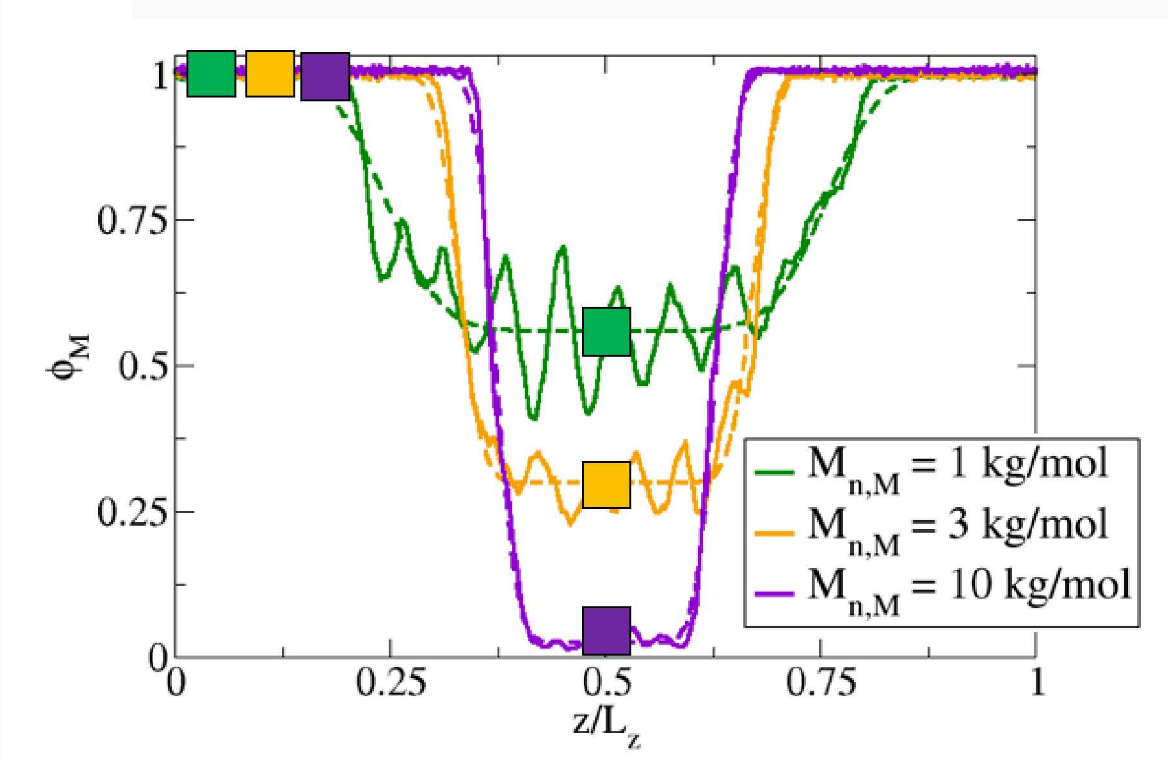


N. Gronbech-Jensen and O. Farago, Molecular Physics (2013)

Chao, H., Koski, J. & Riggleman, R. A. *Soft Matter* **13,** 239–249 (2017).

Digression: grafted NPs in homopolymer matrix

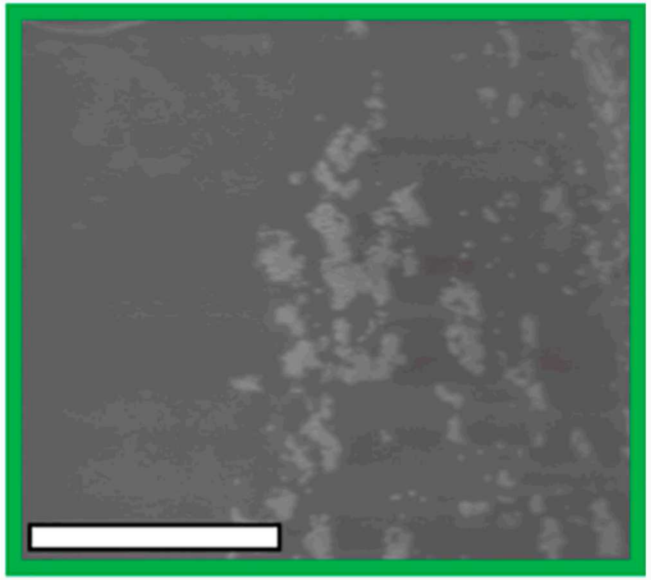




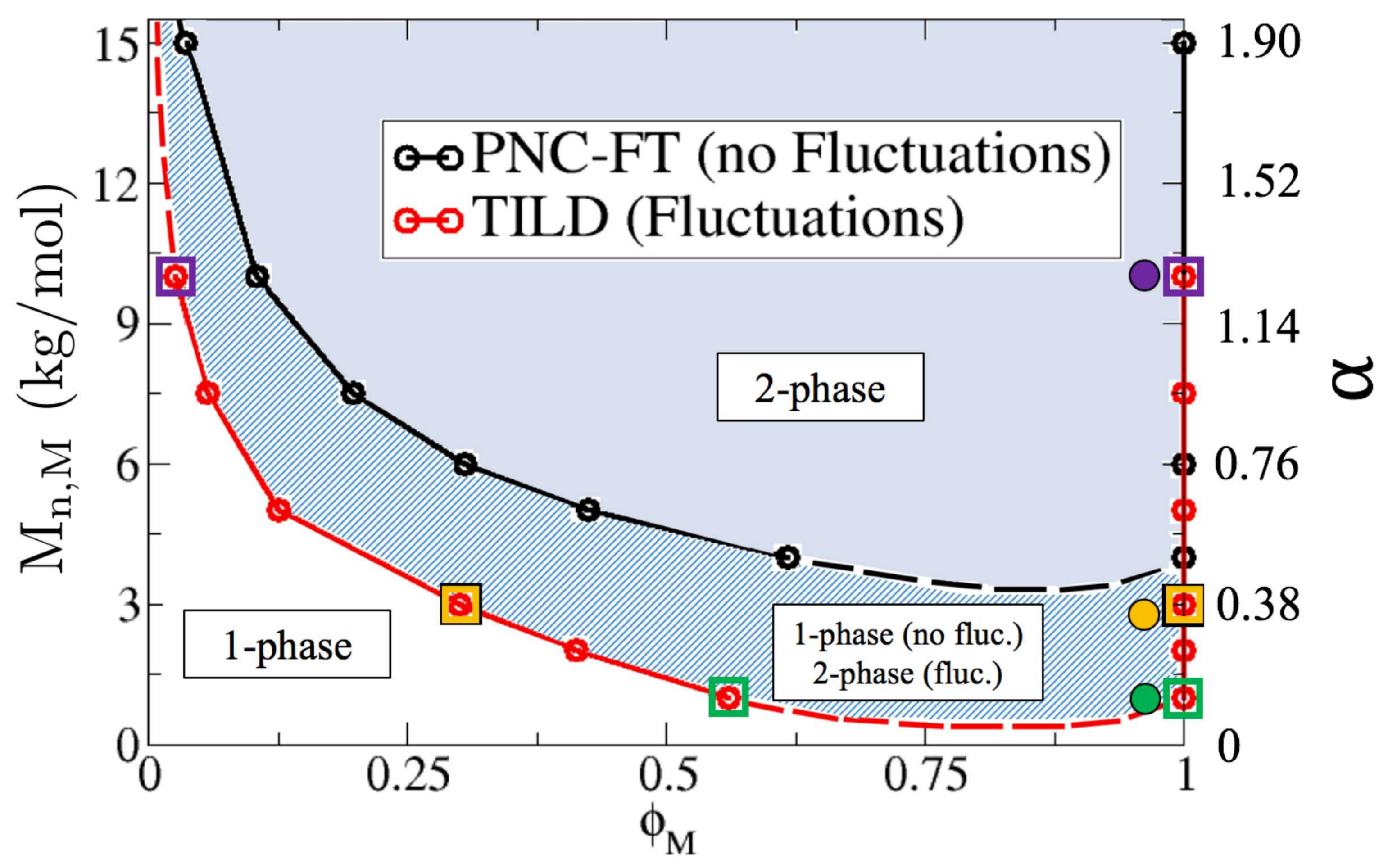
Digression: grafted NPs in homopolymer matrix

PMMA-g-SiO_2 in PS

$M_{n,M}$ = 0.95 kg/mol (PS)
$M_{n,G}$ = 7.9 kg/mol (PMMA)
σ = 0.26 chains/nm^2

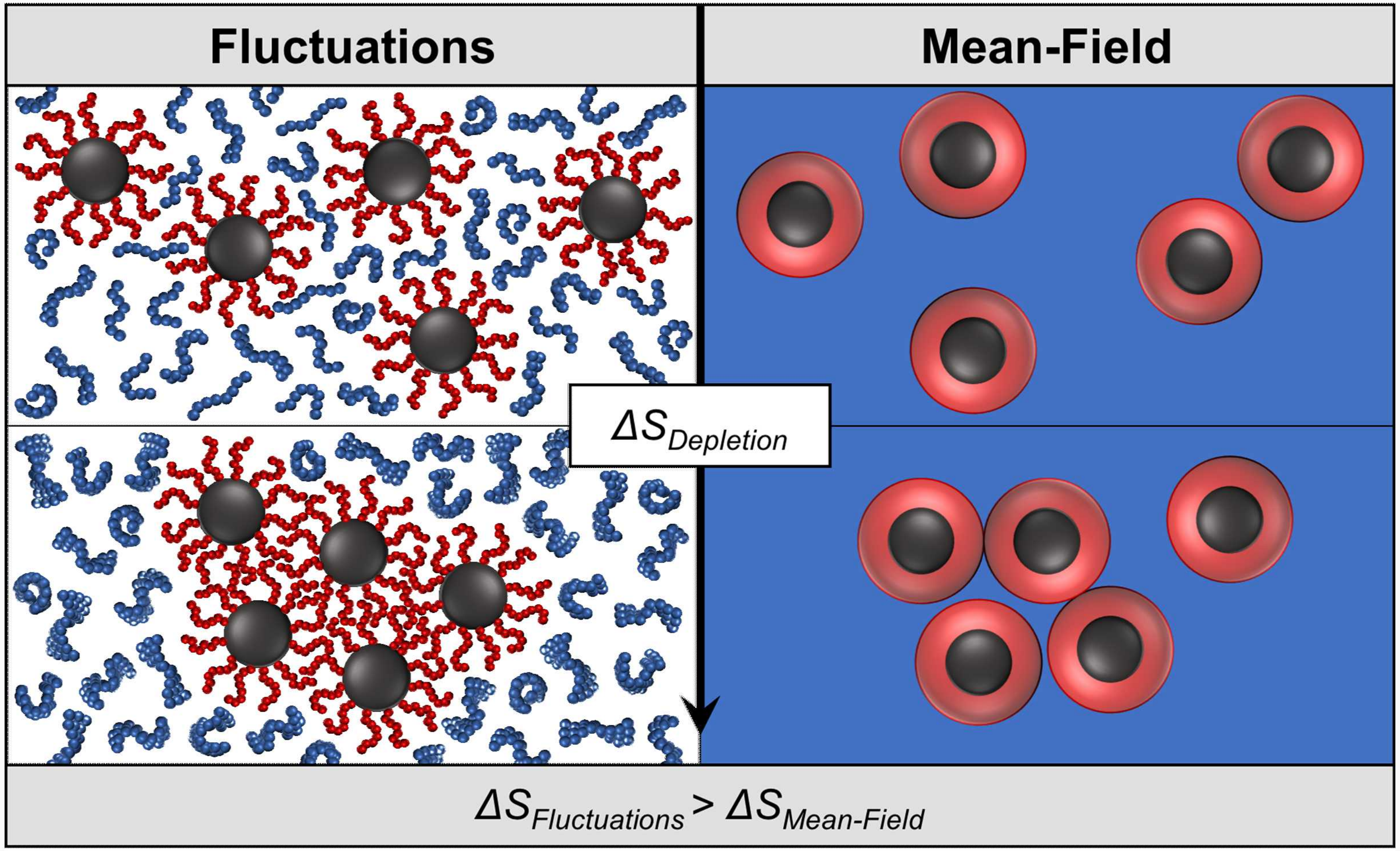


scale = 1 μm



Koski et al, Macromolecules (2019)

Digression: grafted NPs in homopolymer matrix

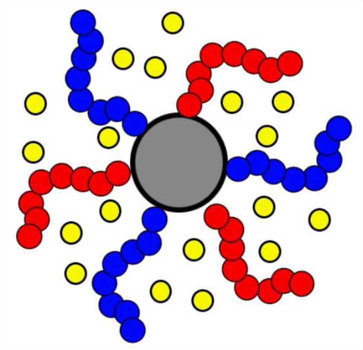


extra entropy leads to extra depletion interactions

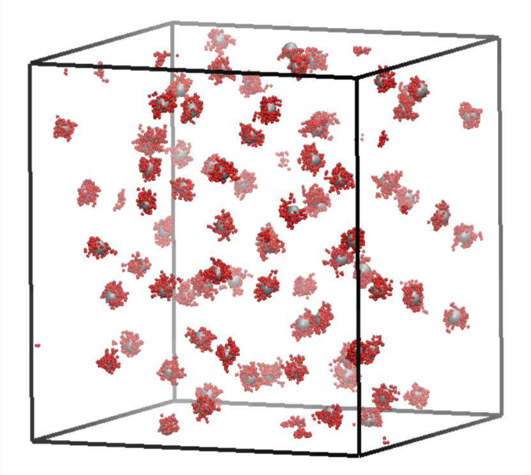
Koski et al, Macromolecules (2019)

Rest of the talk

- mixed brushes on single particles
  - SCFT structure
  - TILD structures



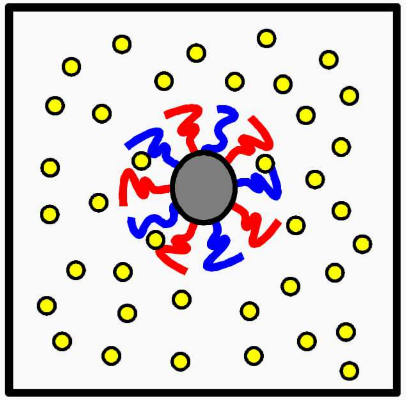
- assembly of mixed brush NPs
  - TILD only



Single mixed brush NPs: nonselective solvent

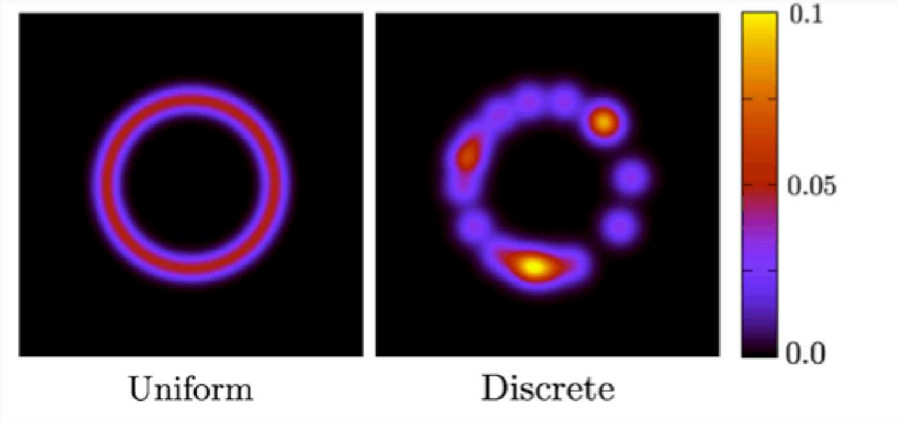
equal chain lengths, $N_A = N_B = 60$
equal fractions, $f_A = f_B = 0.5$
monomer size $d = 0.73b$
$\chi_{AB}N = 28.3$
$\chi_{AS} = \chi_{BS} = \chi_S$

vary: R_P/R_g, σ, χ_S



Three calculations:

1. SCFT with uniform grafting density
2. SCFT with random grafting density
3. TILD with random grafting density



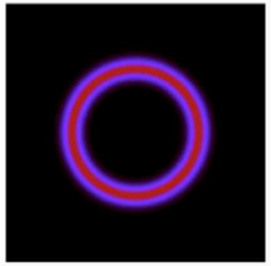
SCFT for single particles

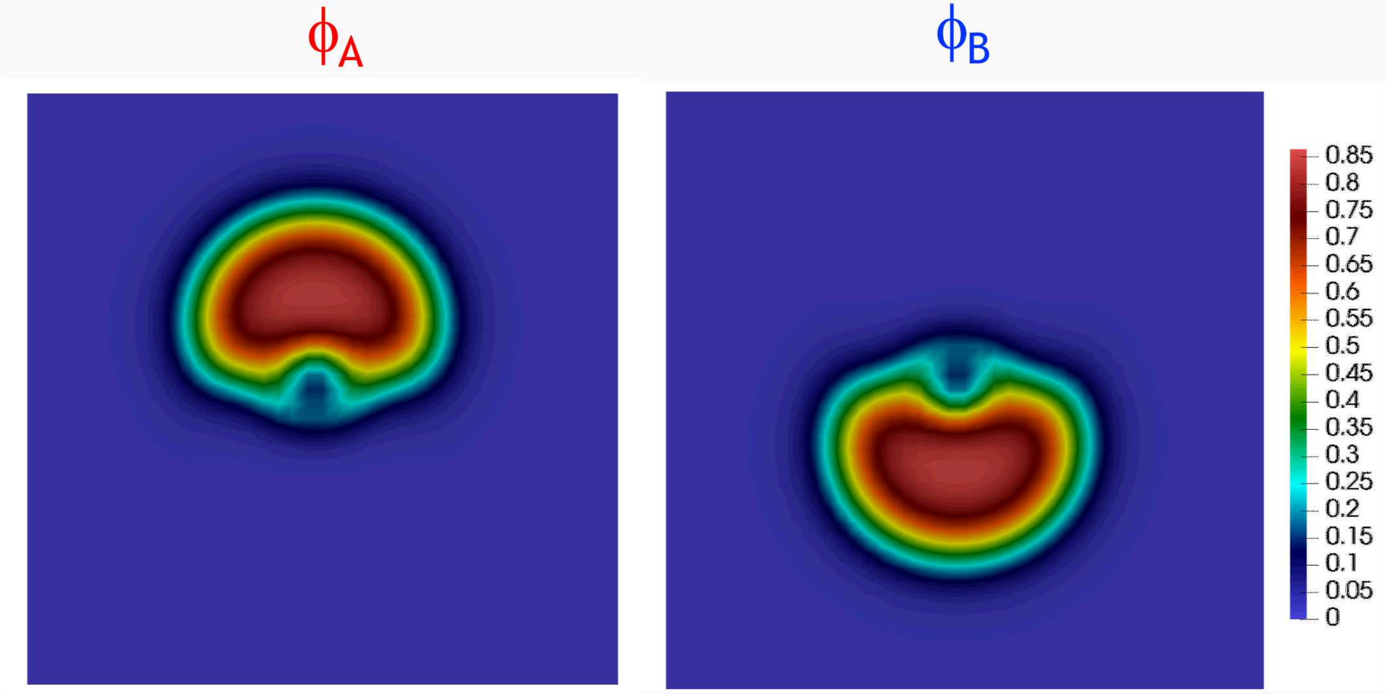
$\chi_{AB}N = 28.3$

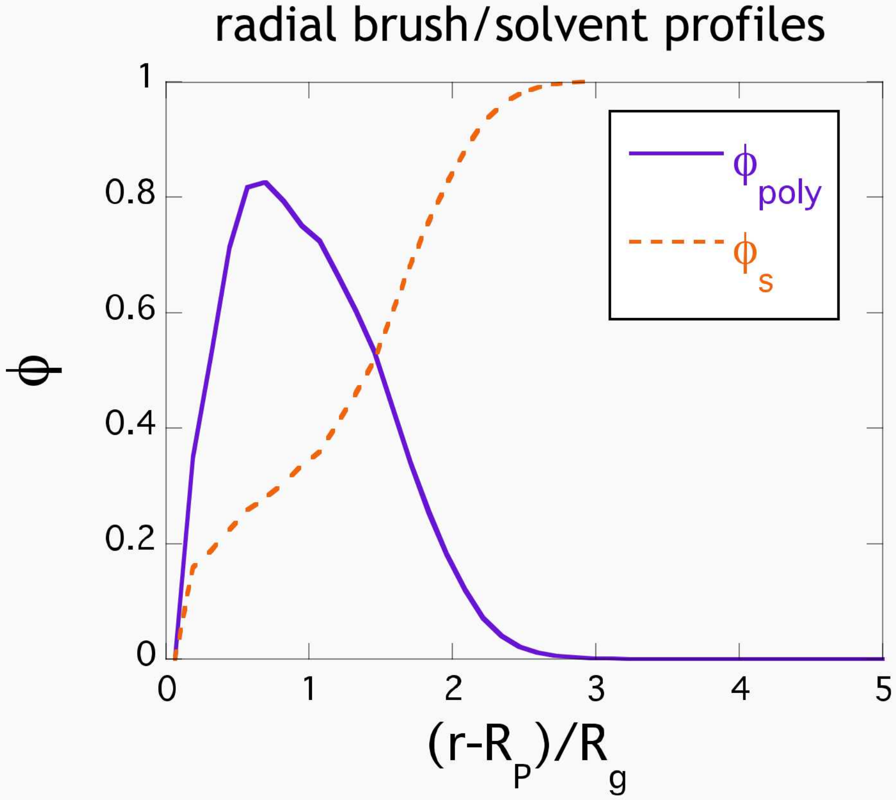
$\chi_S = 1$

$R_p/R_g = 1/3$

$\sigma = 1.7/d^2$







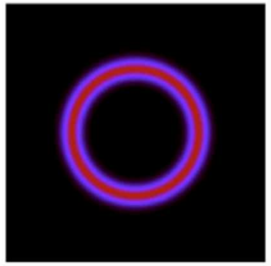
SCFT for single particles

$\chi_{AB}N = 28.3$

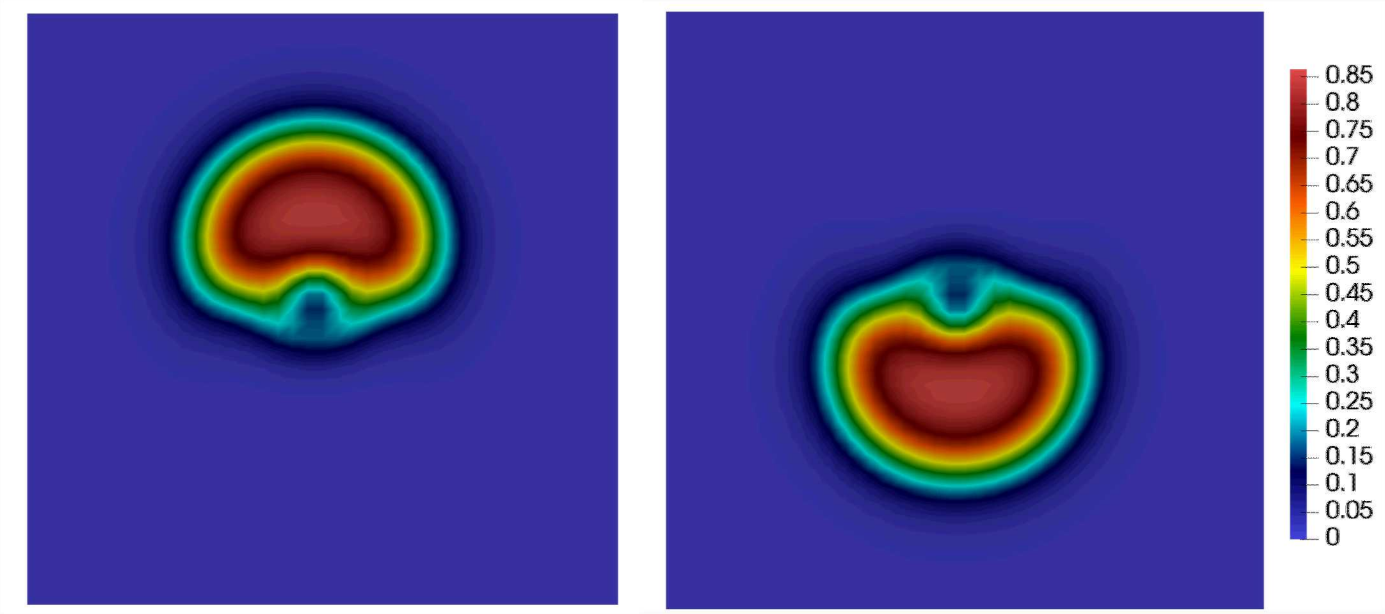
$\chi_S = 1$

$R_p/R_g = 1/3$

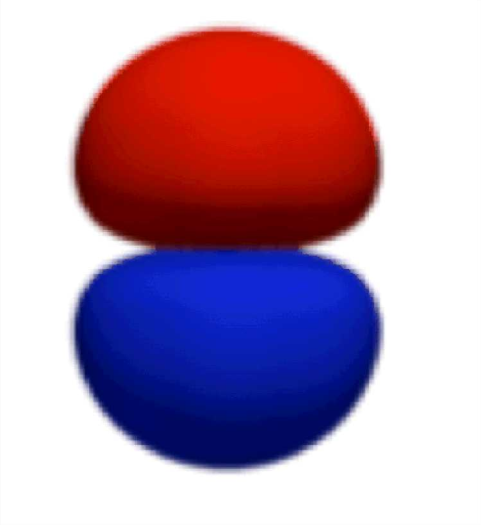
$\sigma = 1.7/d^2$



ϕ_A ϕ_B



density isosurfaces at $\phi = 0.5$

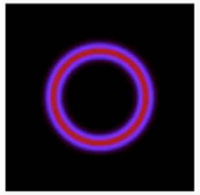


SCFT for single particles

$\chi_{AB}N = 28.3$

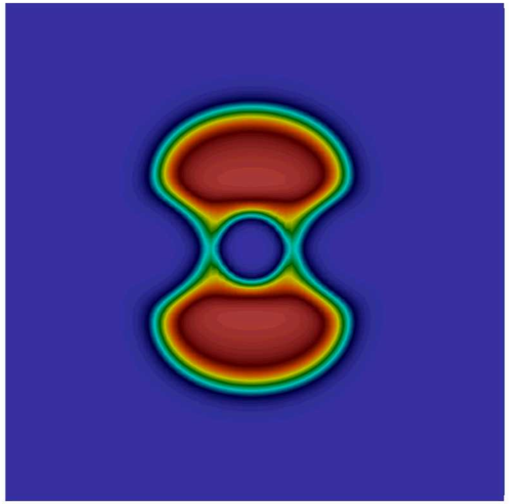
$\chi_S = 1$

$\sigma = 1.7/d^2$

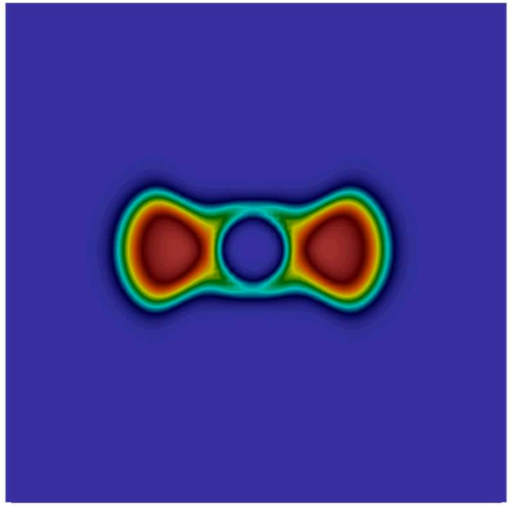


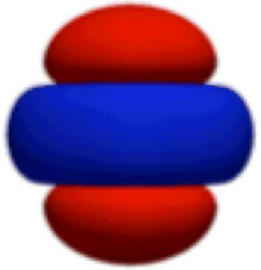
$R_p/R_g = 1$

ϕ_A



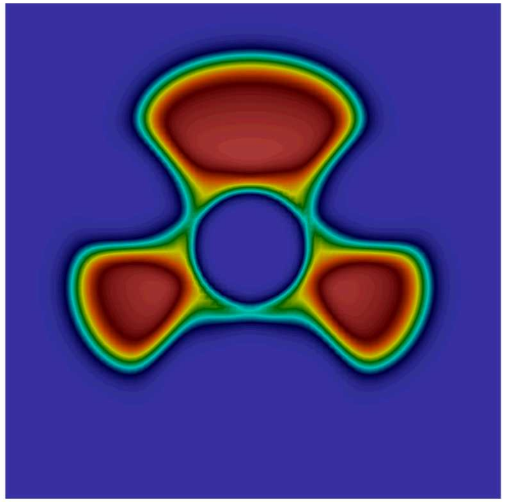
ϕ_B



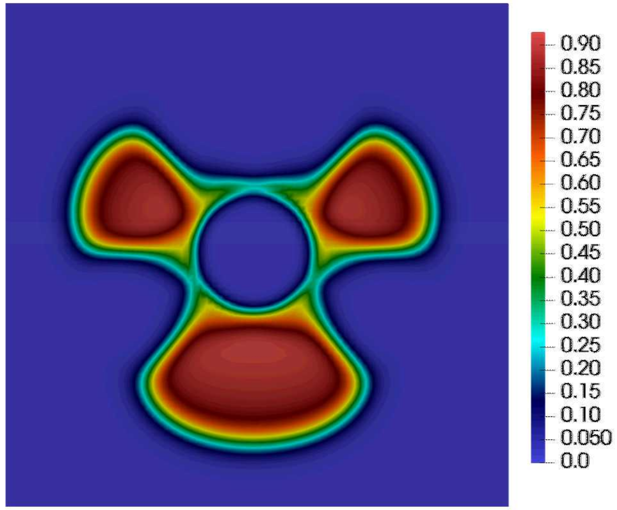


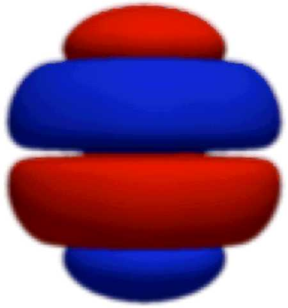
$R_p/R_g = 5/3$

ϕ_A



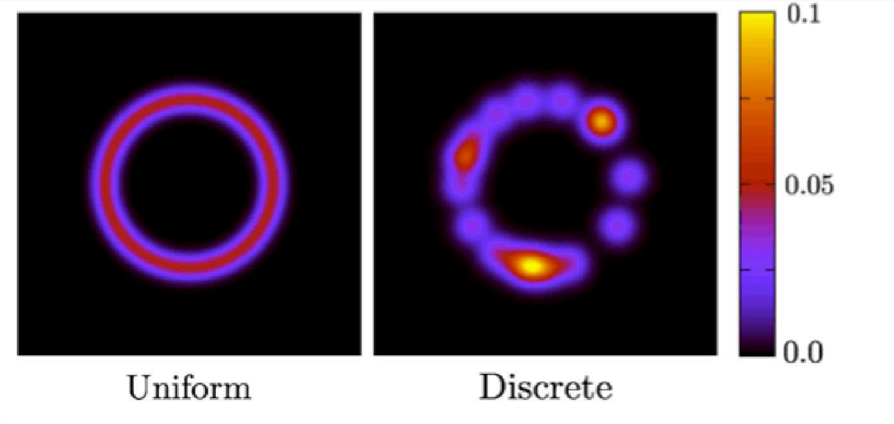
ϕ_B





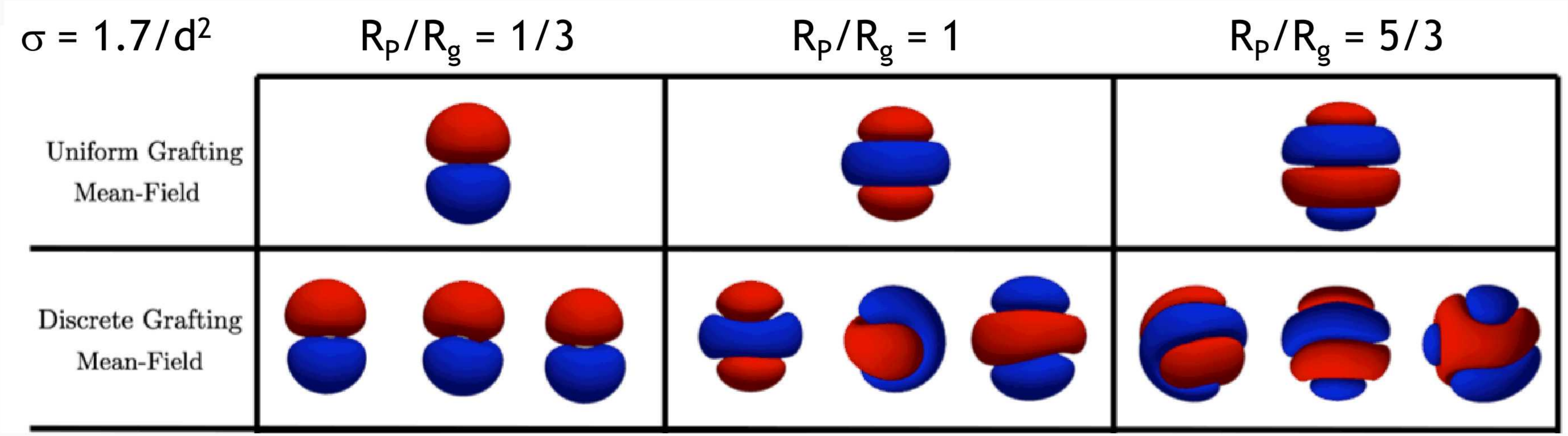
Random discrete grafting sites, SCFT

uniform grafting is unlikely
allow random discrete grafting



$\chi_{AB}N = 28.3$

$\chi_S = 1.0$

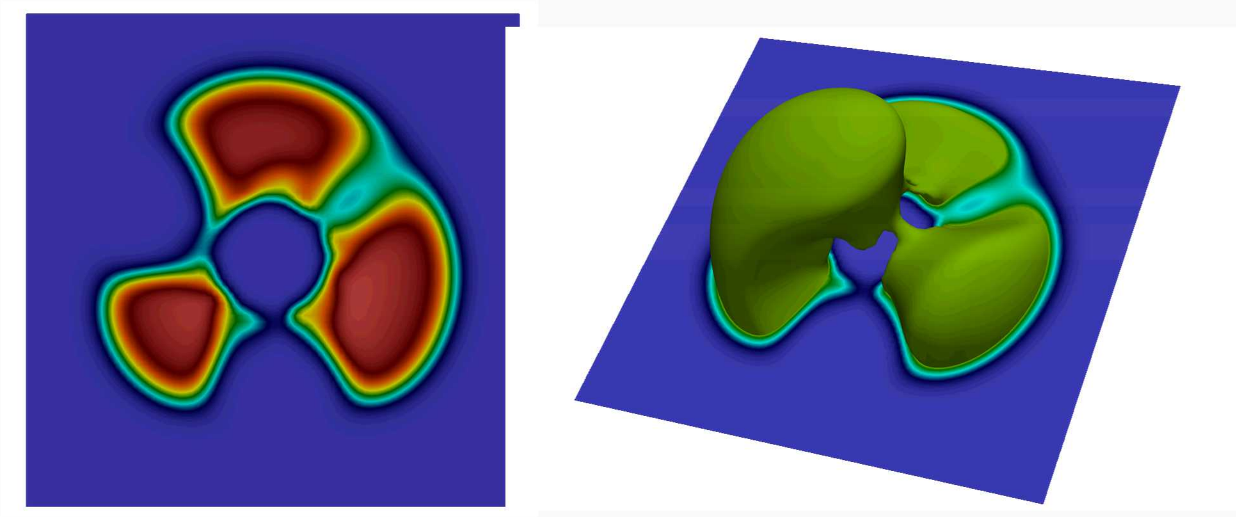


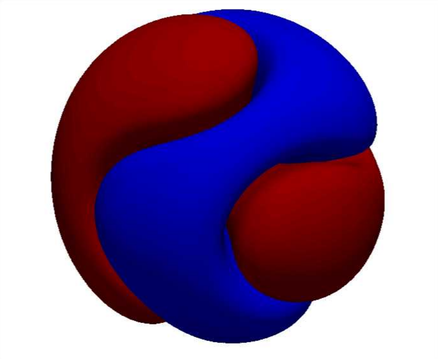
random grafting structures are less ordered

Disordered brush structures, R_P/R_g = 5/3

SCFT, random grafting

ϕ_A

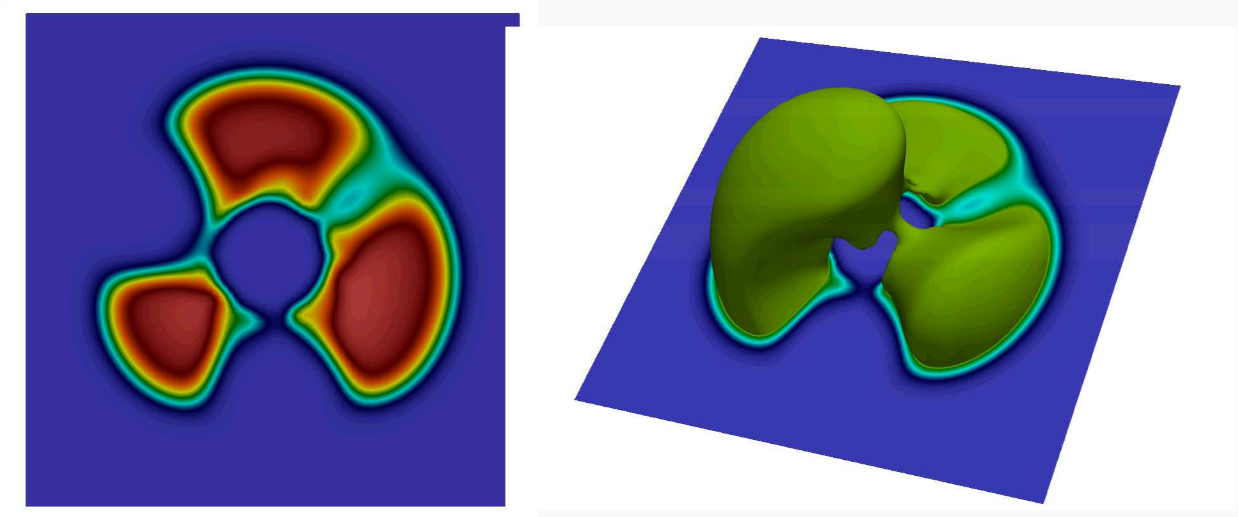


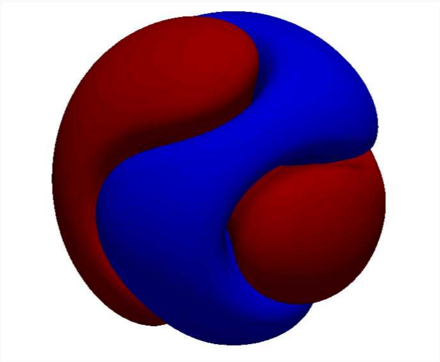


Disordered brush structures, R_P/R_g = 5/3

SCFT, random grafting

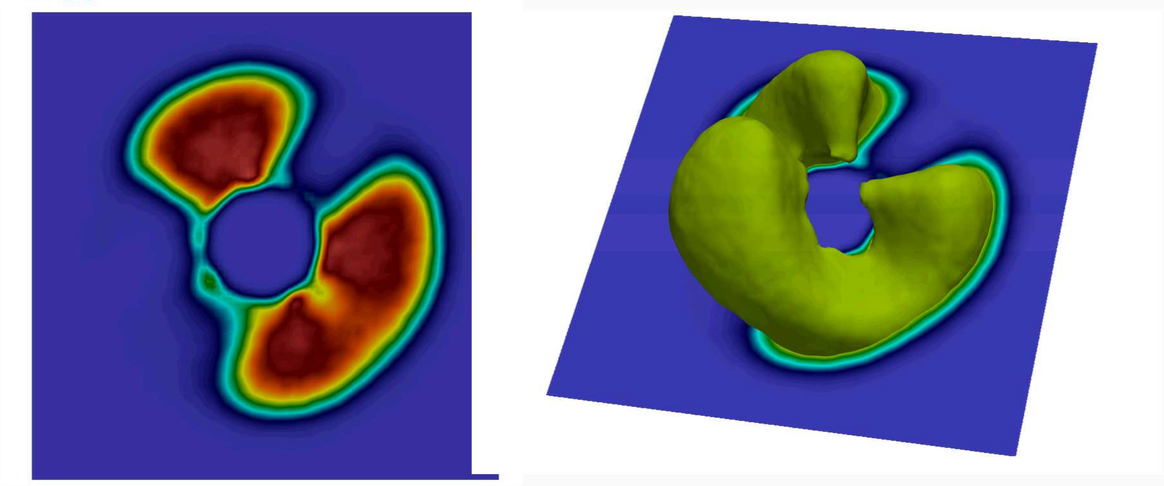
ϕ_A

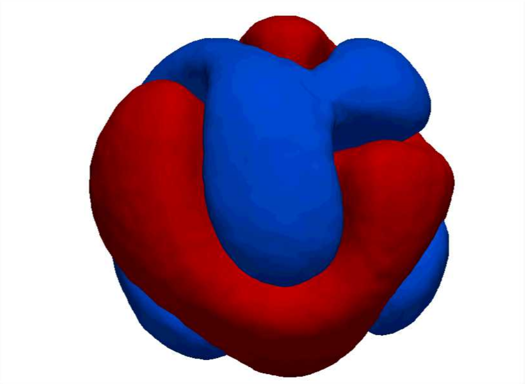




TILD, random grafting

ϕ_A

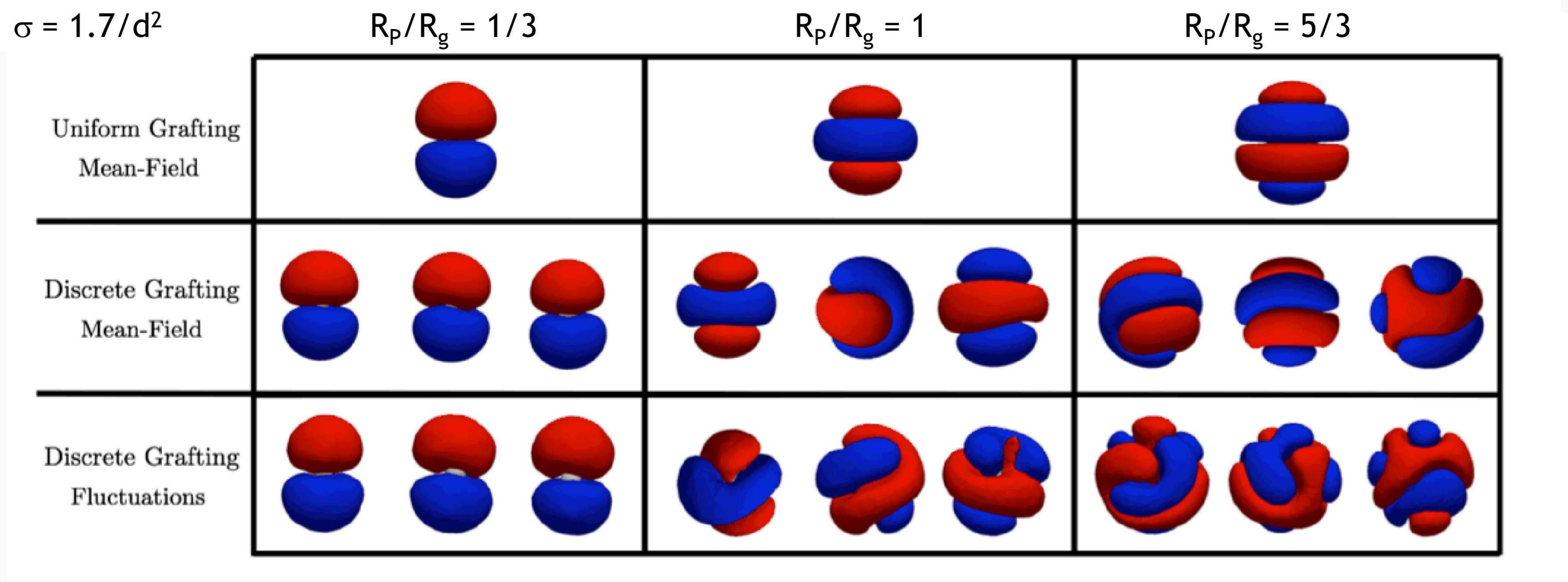




TILD vs SCFT

random grafting + thermal fluctuations

$\chi_{AB}N = 28.3$
$\chi_S = 1.0$



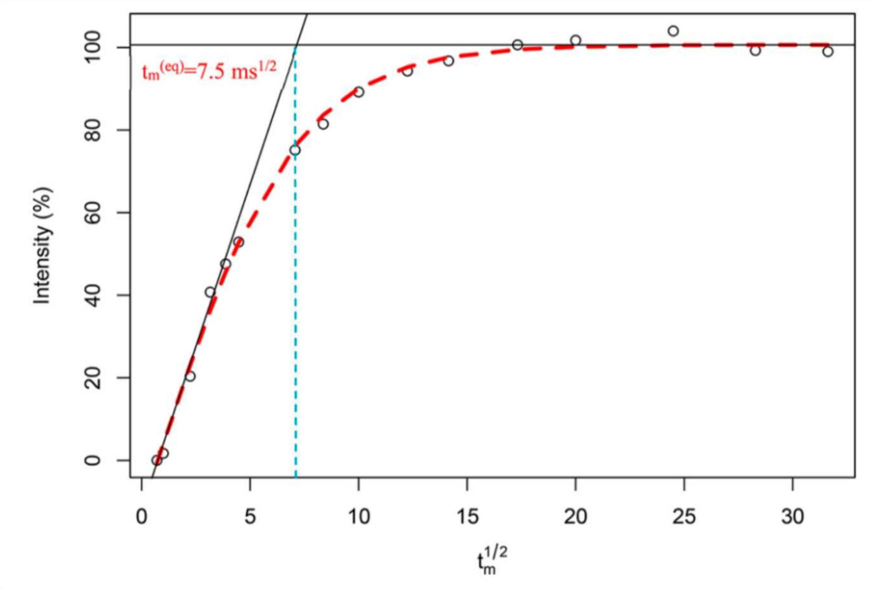
prediction: Janus phase robust to fluctuations!

J.P. Koski and A.L. Frischknecht, ACS Nano **12**, 1664 (2018).

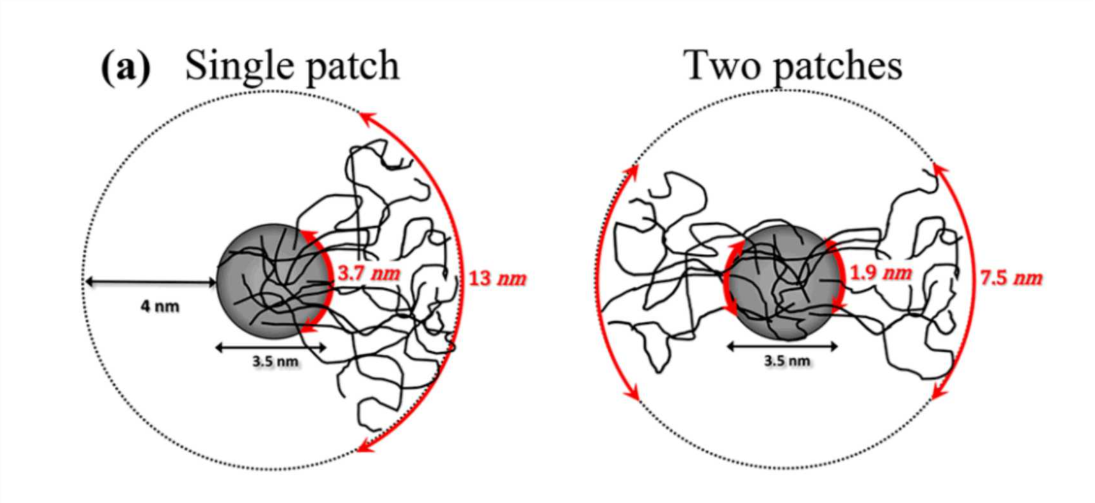
Experimental evidence of grafted Janus NPs?

PS-PEO on ZrO_2 NPs

[1]H NMR spin diffusion



consistent with

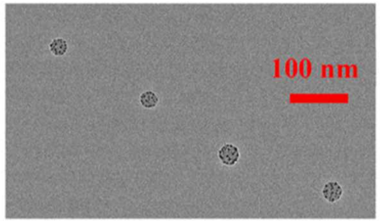
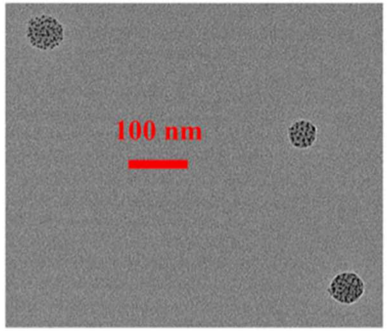
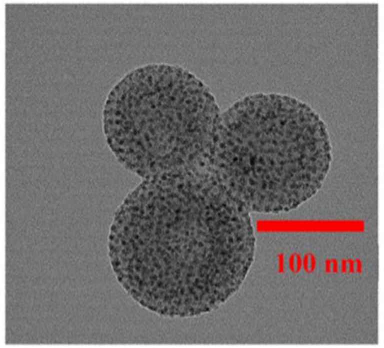


Guzman-Juarez, B., Abdelaal, A., Kim, K., Toader, V. & Reven, L.
Macromolecules **51,** 9951–9960 (2018).

Mixed brush NP assembly in selective solvent

example: PEO-PS on ZrO_2 in THF/water

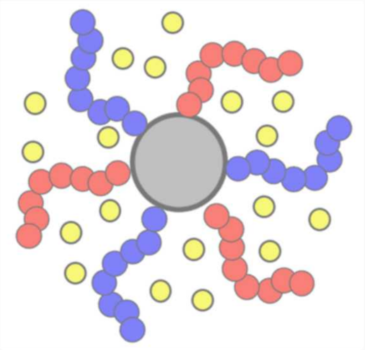
PS fraction

0.19	Densely packed spheres (dia. 30-36 nm)	
0.40	Densely packed spheres (dia. 45-60 nm)	
0.93	Vesicles, (dia. 75-115 nm)	

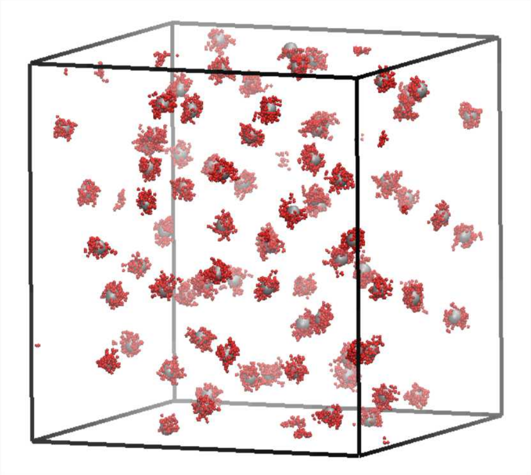
Guzman-Juarez, et al, *Macromolecules* **51,** 9951–9960 (2018).

Rest of the talk

- mixed brushes on single particles
  - SCFT structure
  - TILD structures



- assembly of mixed brush NPs
  - TILD only



Mixed brush NPs in selective solvent

Rest of talk:

A chains in bad solvent: $\chi_{AS} = \chi_S$

B chains in good solvent: $\chi_{BS} = 0$

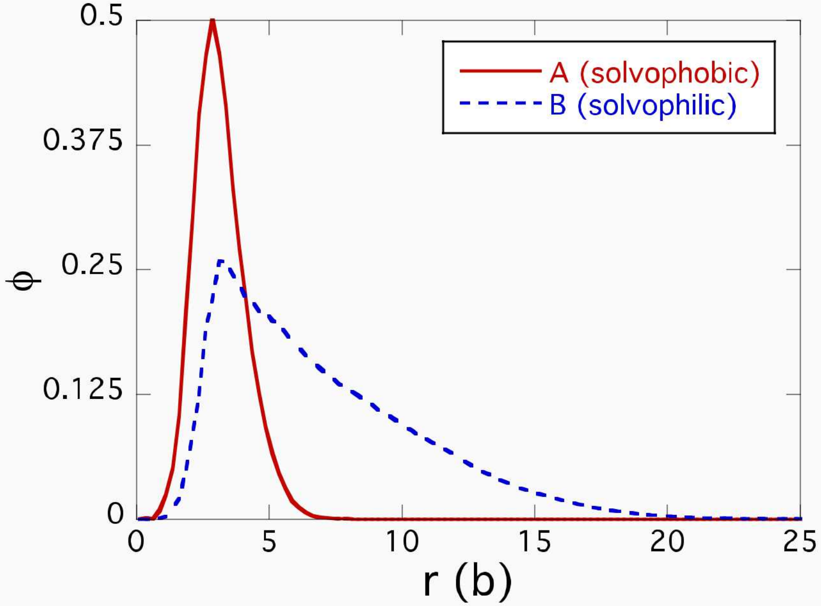
immiscible chains: $\chi_{AB} = 1$

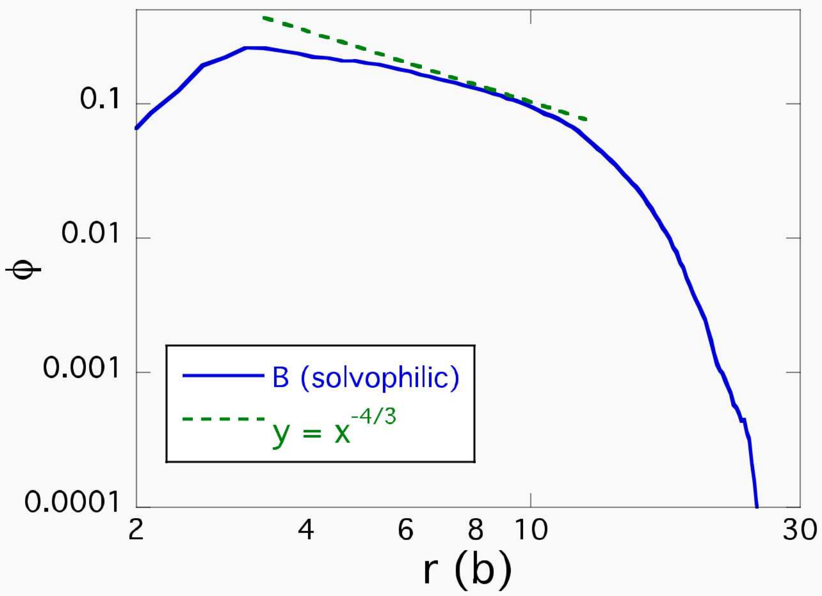
$R_p = 2b$, $\sigma = 1/b^2$ (50 grafted chains per particle)

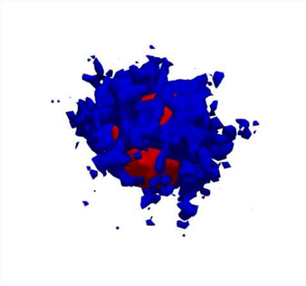
For asymmetric chain lengths, get vertical phase separation

$\chi_S = 1.25$, $N_A = 6$, $N_B = 54$

$f_A = 0.5$







Daoud-Cotton for stars

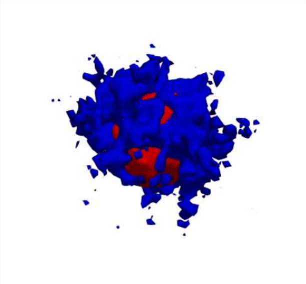
$$\phi(r) \sim r^{-4/3}$$

Dispersed phase

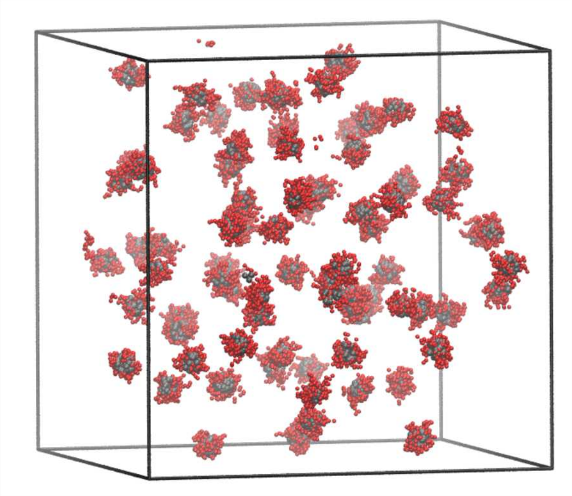
$\chi_S = 1.25$, $N_A = 6$, $N_B = 54$

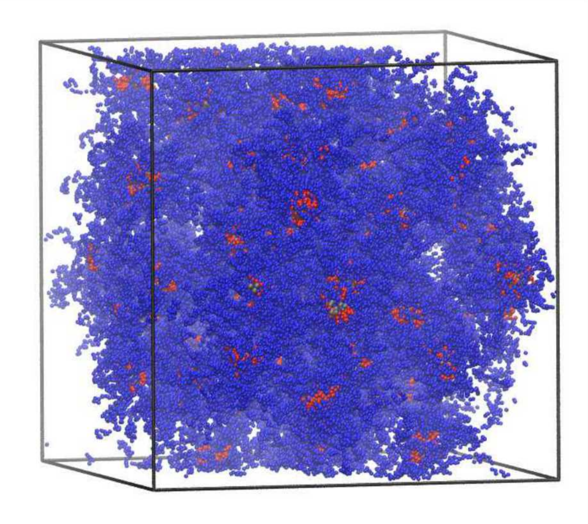
$f_A = 0.5$

long solovphilic chains
short solvophobic chains



80 particles initially in center of box



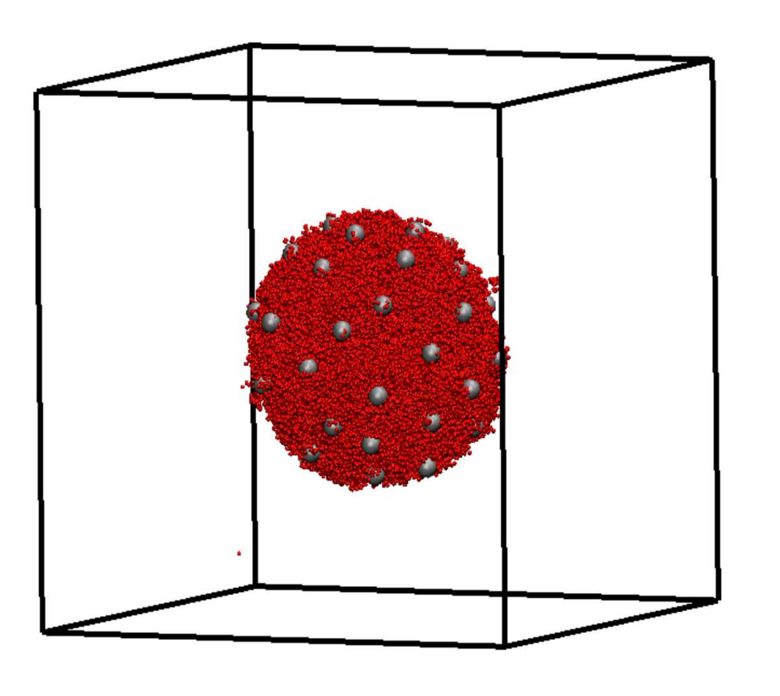


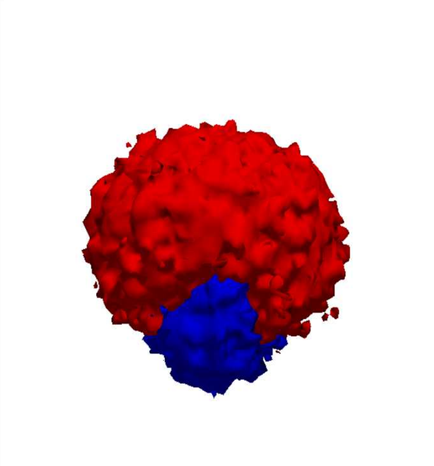
Macrophase separation

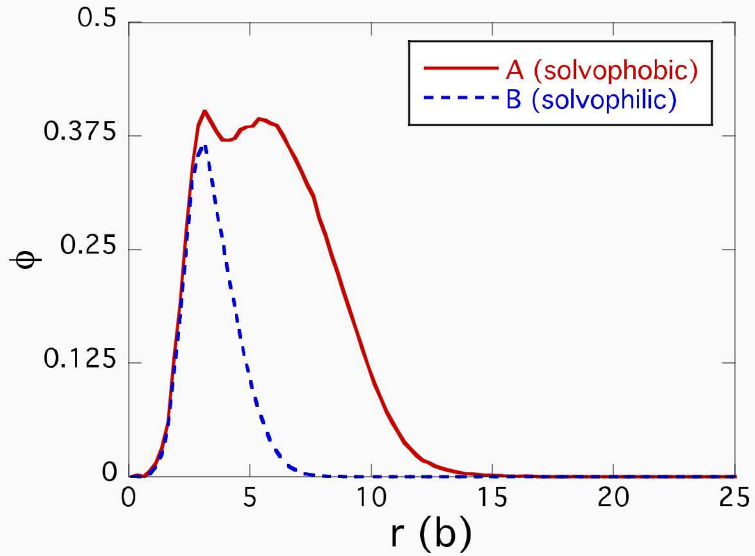
$\chi_S = 2$, $N_A = 54$, $N_B = 6$

$f_A = 0.5$

short solovphilic chains
long solvophobic chains







"Ordered" NP assemblies: similar chain lengths

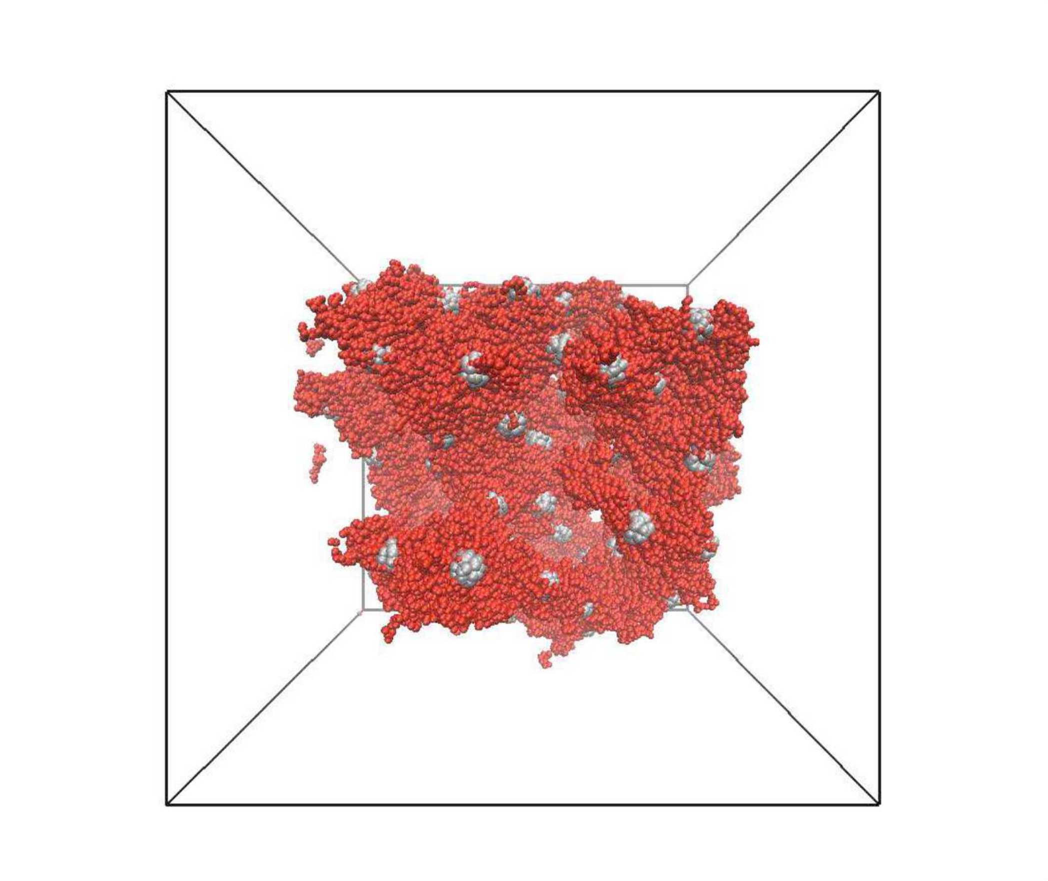
A chains in bad solvent: $\chi_{AS} = 1.25$

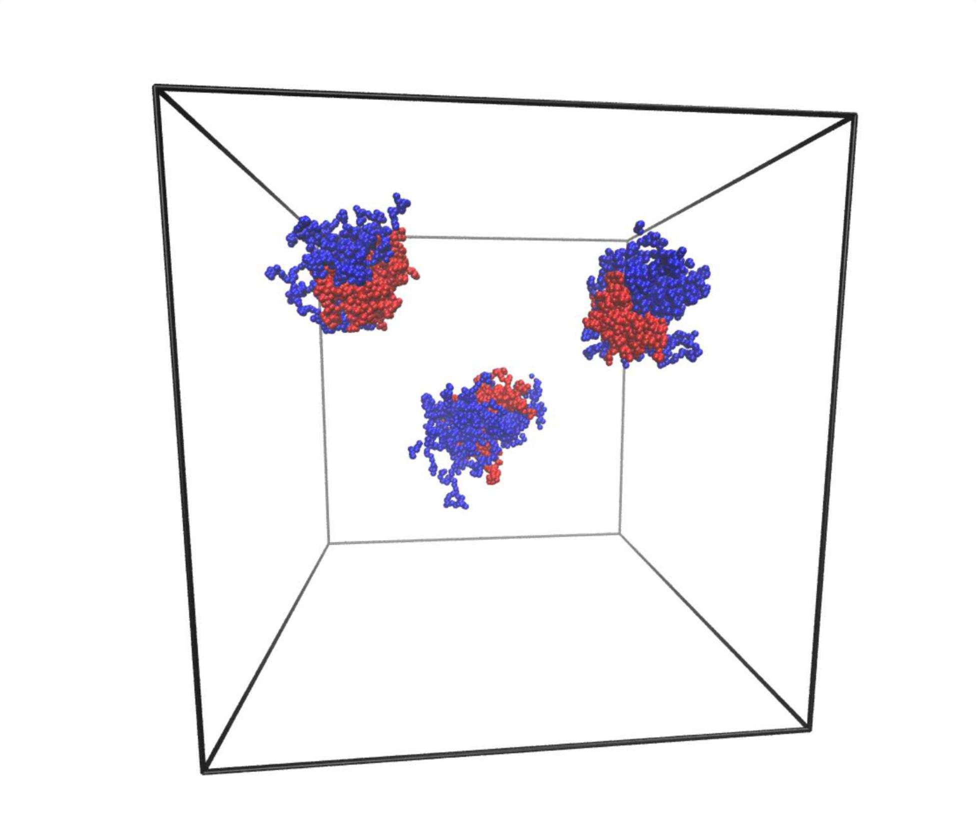
B chains in good solvent: $\chi_{BS} = 0$

immiscible chains: $\chi_{AB} = 1$

80 particles initially in center of box

$N_A = N_B = 54$, $f_A = 0.5$, $\sigma = 1/b^2$





“Ordered” NP assemblies

A chains in bad solvent: χ_{AS} = 1.25

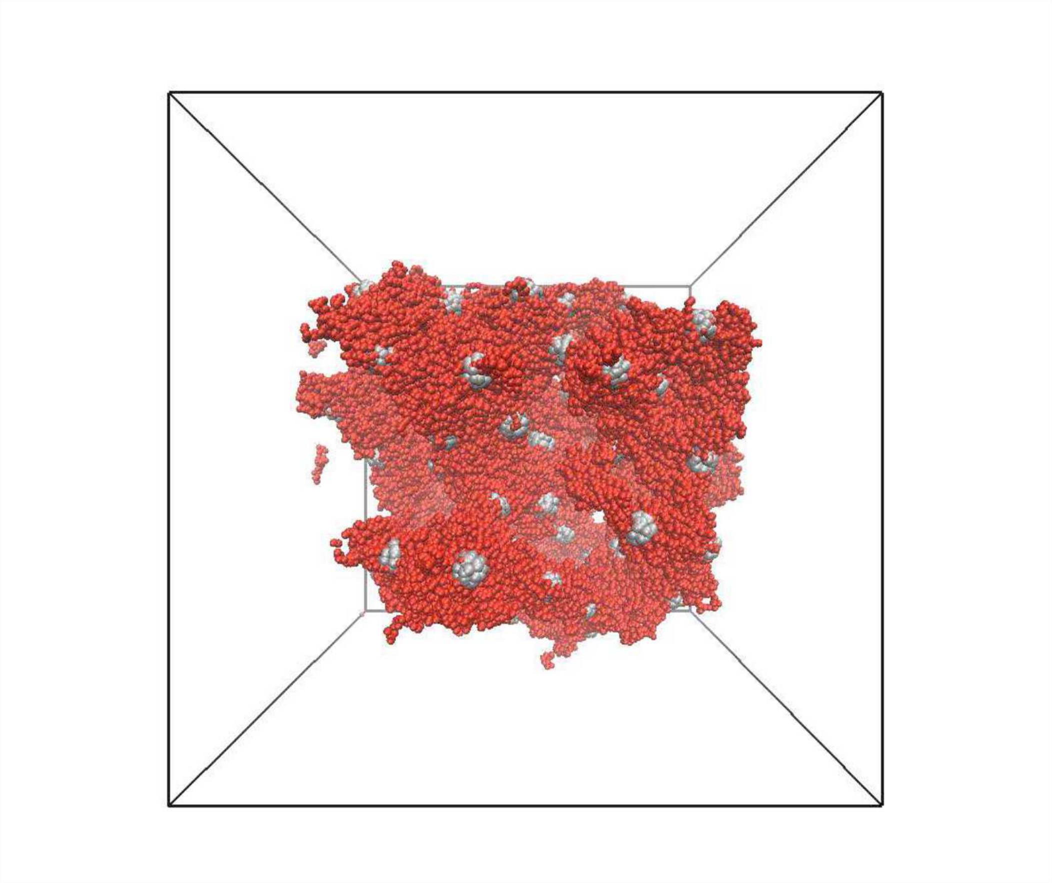
B chains in good solvent: χ_{BS} = 0

immiscible chains: χ_{AB} = 1

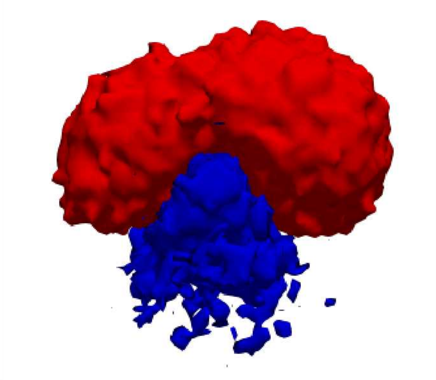
80 particles initially in center of box

$N_A = N_B = 54$, $f_A = 0.5$, $\sigma = 1/b^2$

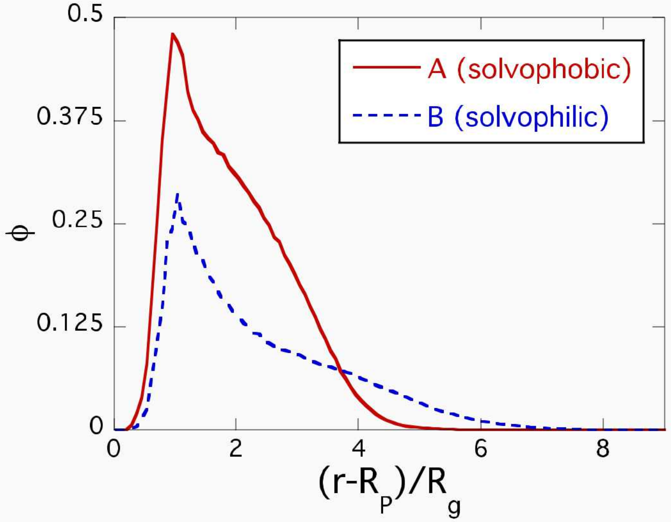
$R_P = 0.7R_g$



equivalent single NP



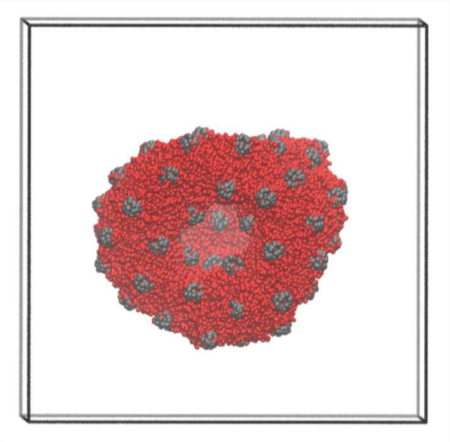
average configuration

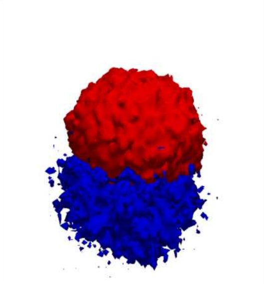


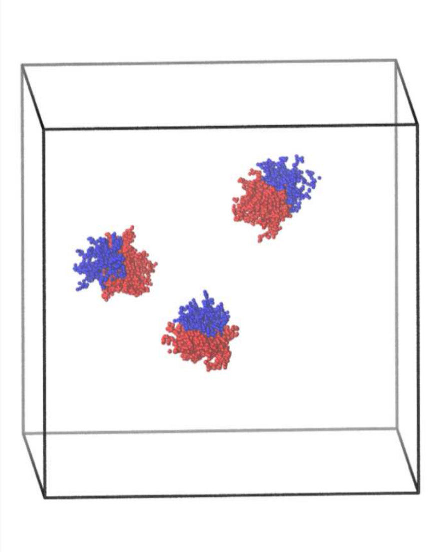
"Nearly Vesicle"

$\chi_S = 2$, $N_A = 54$, $N_B = 24$

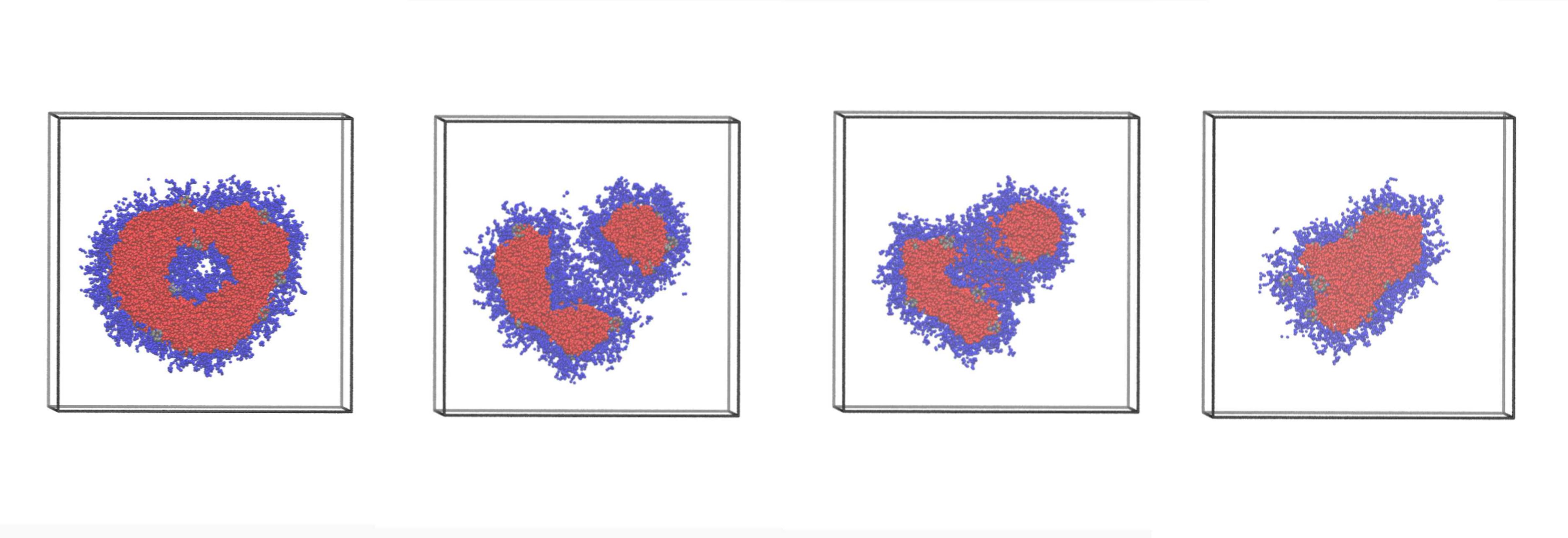
$f_A = 0.5$







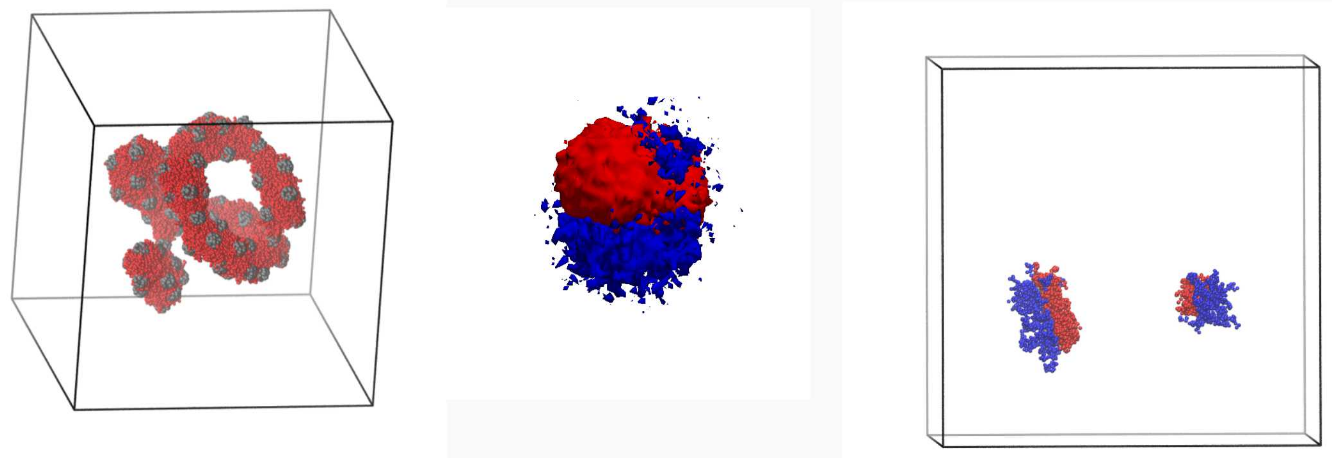
10b thick slices:



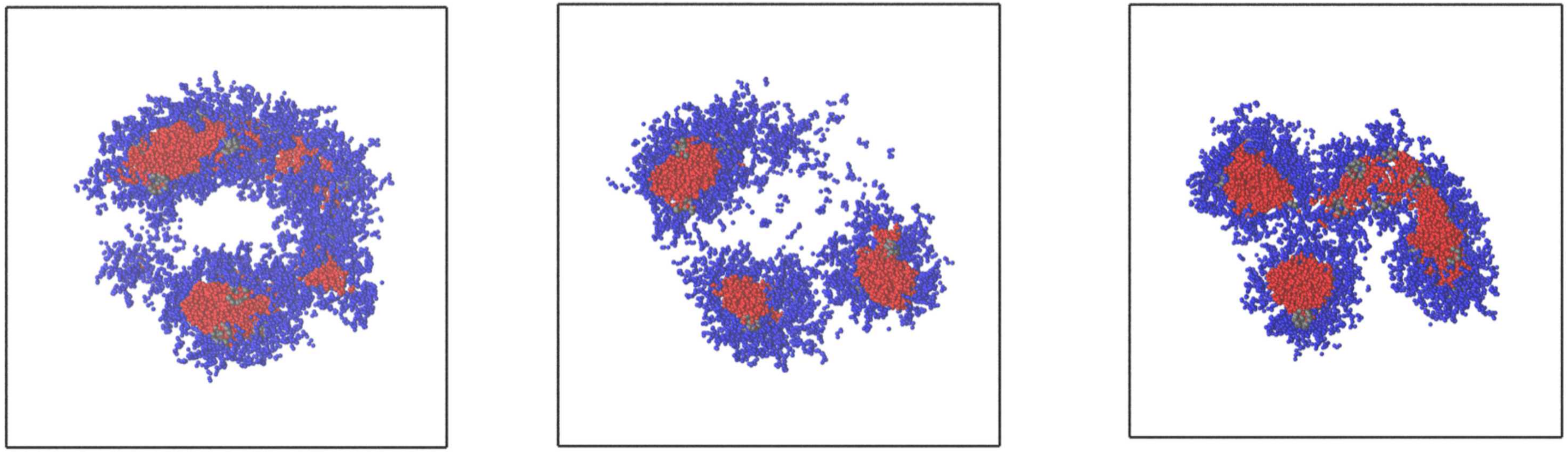
"Connected strings"

$\chi_S = 2$, $N_A = 24$, $N_B = 24$

$f_A = 0.5$

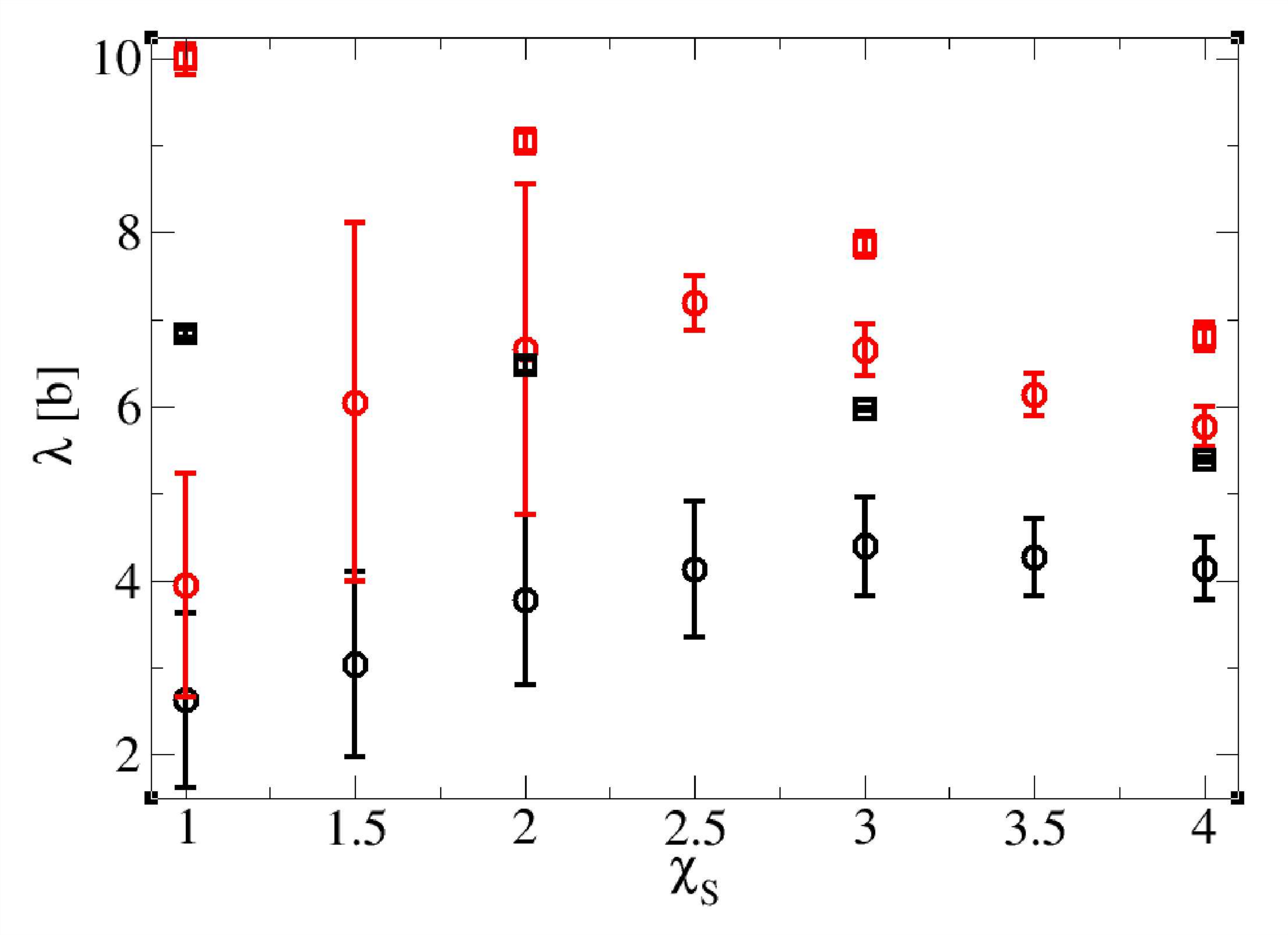


10b thick slices:



"Janus" nature of mixed brush NPs

$\lambda = ||(com_A) - (com_B)||$



mixed, $N_A = N_B = 24$

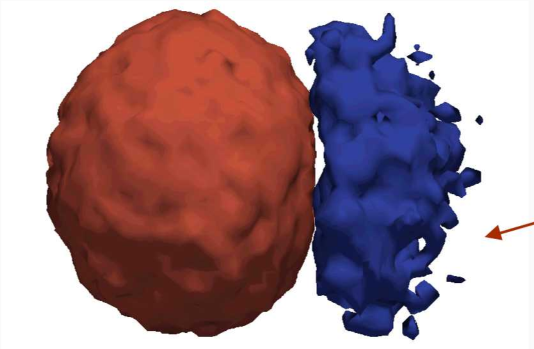
mixed, $N_A = N_B = 54$

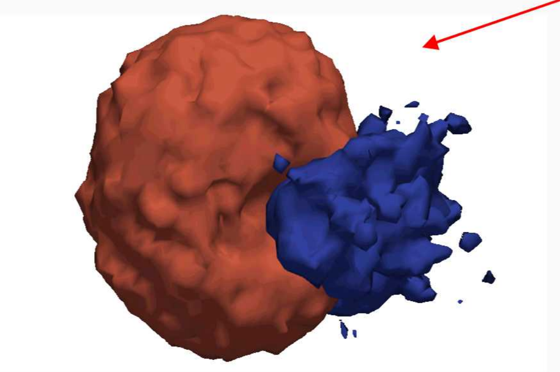
Janus, $N_A = N_B = 24$

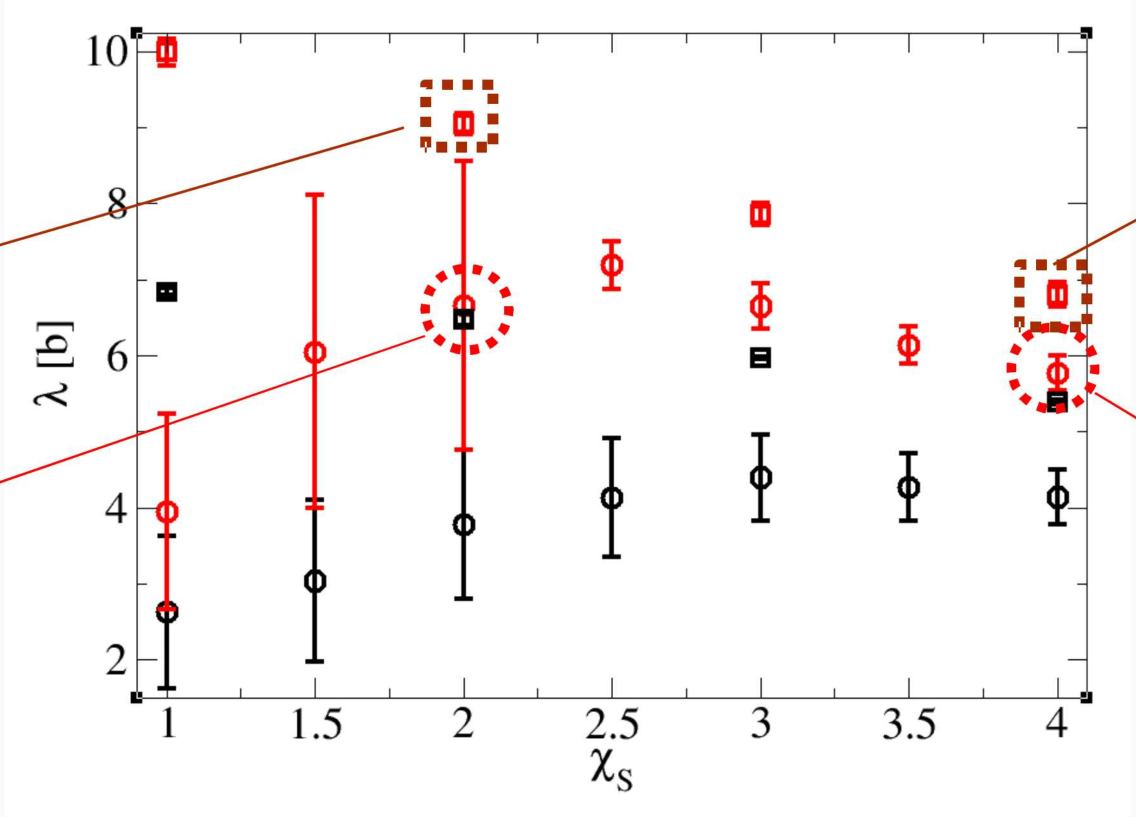
Janus, $N_A = N_B = 54$

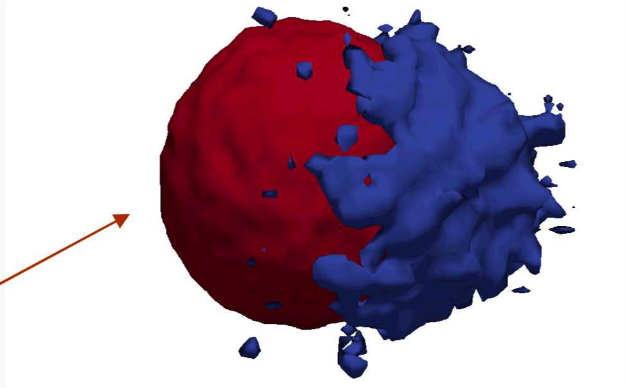
“Janus” nature of mixed brush NPs

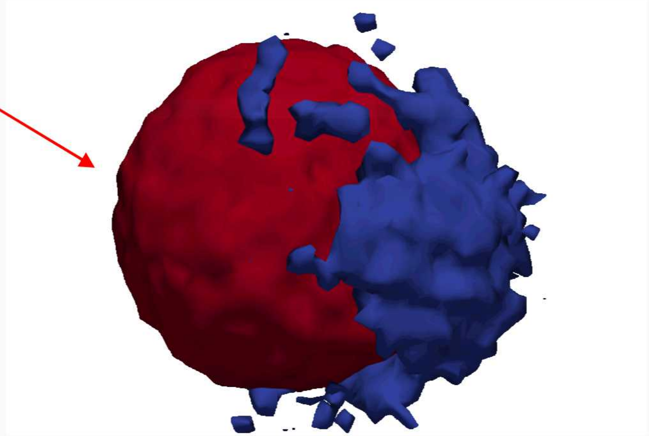
$\lambda = ||(com_A) - (com_B)||$







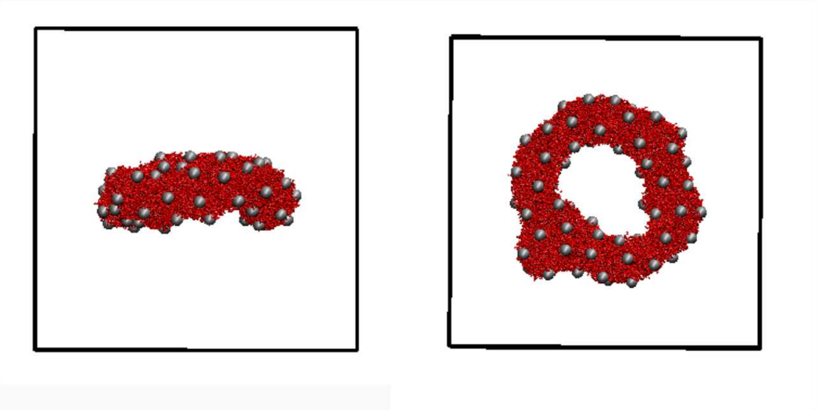




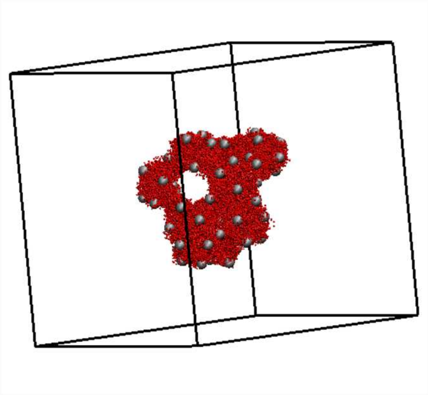
Janus-grafted vs random-grafted NPs

χ_S = 3, Na = 24, Nb = 24

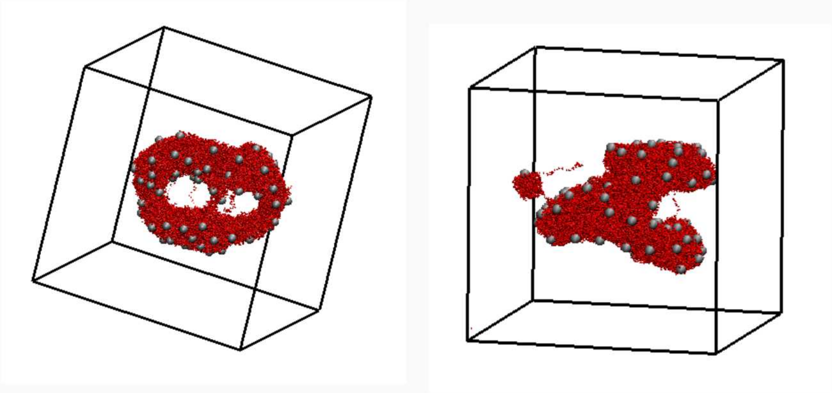
Janus

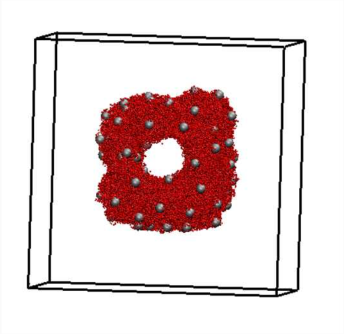


random



χ_S = 3, Na = 54, Nb = 54

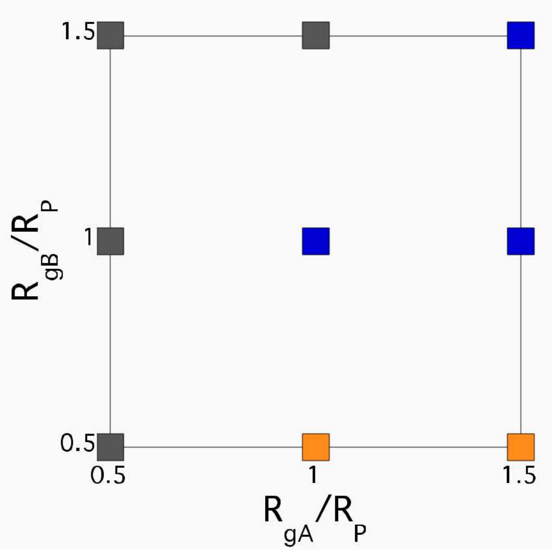




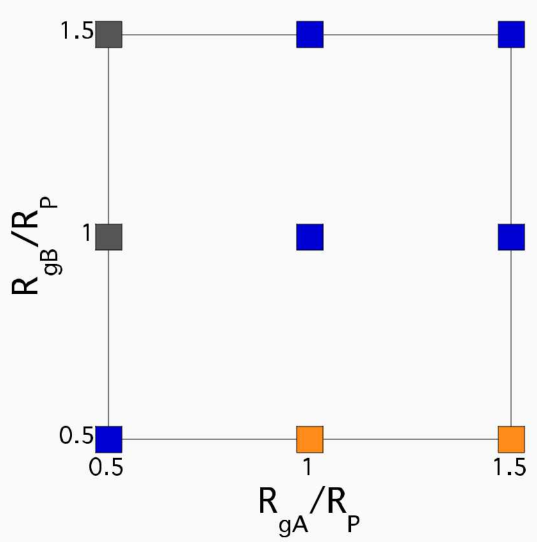
Phase maps for random-grafted

$\chi_S = 2$

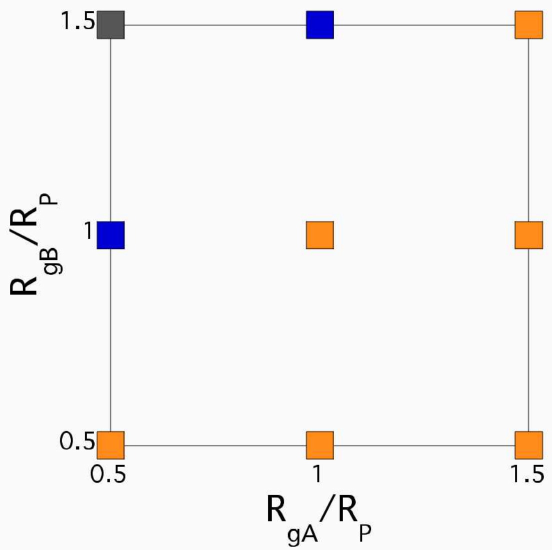
$f_A = 0.25$

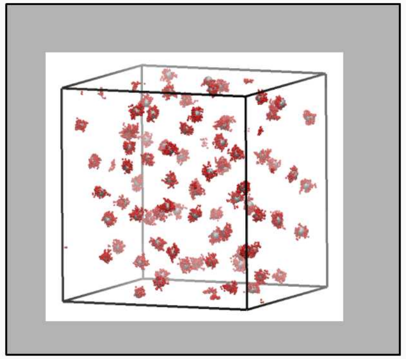


$f_A = 0.5$



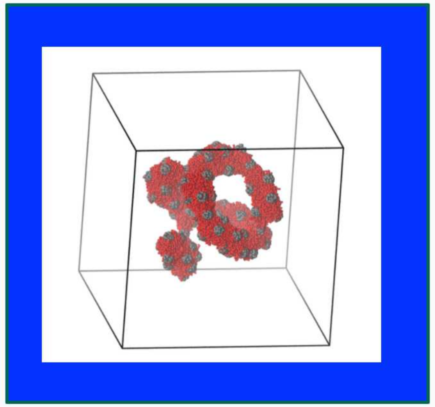
$f_A = 0.75$





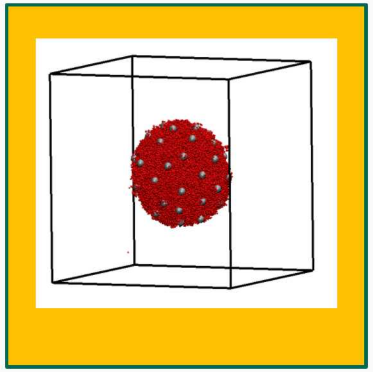
Dispersed

long solovphilic
short solvophobic



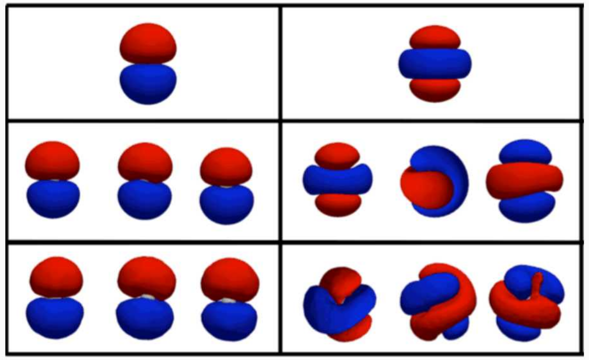
“Janus”: Ordered

short solovphilic
long solvophobic

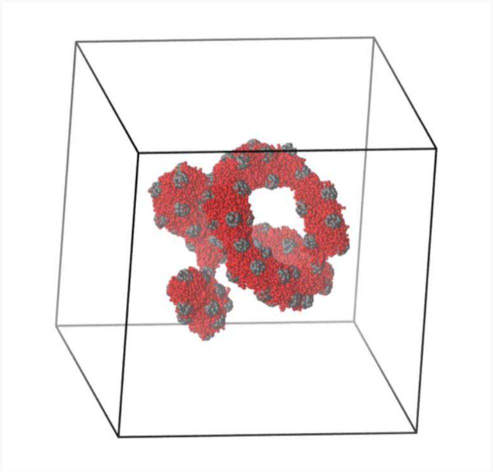


Phase Separated

Conclusions



- single mixed brush NPs
  - TILD predicts more defective NPs than SCFT
  - Janus phase robust to fluctuations

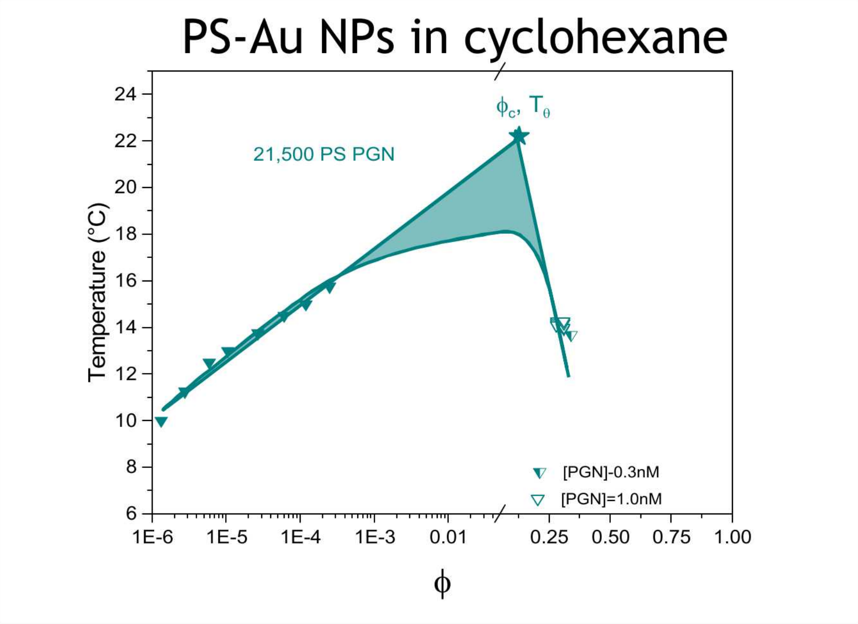


- mixed brush NP assembly
  - very asymmetric systems: dispersed or phase separated
  - similar chain lengths, volume fractions
    - Janus-like single particles
    - stringy or vesicle-like aggregates
    - more clear structure for higher χ_S

Future Directions

- further quantify assembly

- phase behavior of homopolymer-grafted NPs in solvent



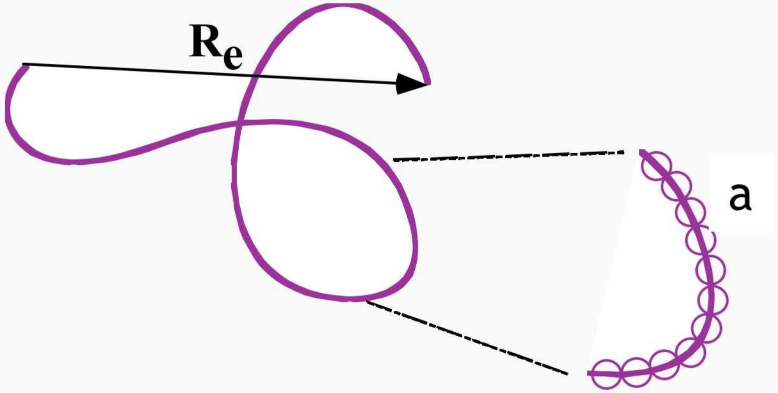
courtesy Rich Vaia

- dynamics?

Structure of polymer brushes

free polymers are random walks

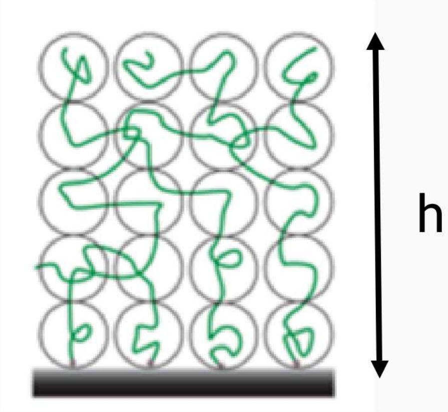
$$R_e \sim N^{1/2}$$



brush: put σ chains/unit area

if close enough in a brush,
polymers must stretch:

$$F = k_B T \left[\underbrace{\frac{3h^2}{2Na^2}}_{\text{stretching entropy}} + \underbrace{\frac{wN^2\sigma}{h}}_{\text{interactions}} \right]$$



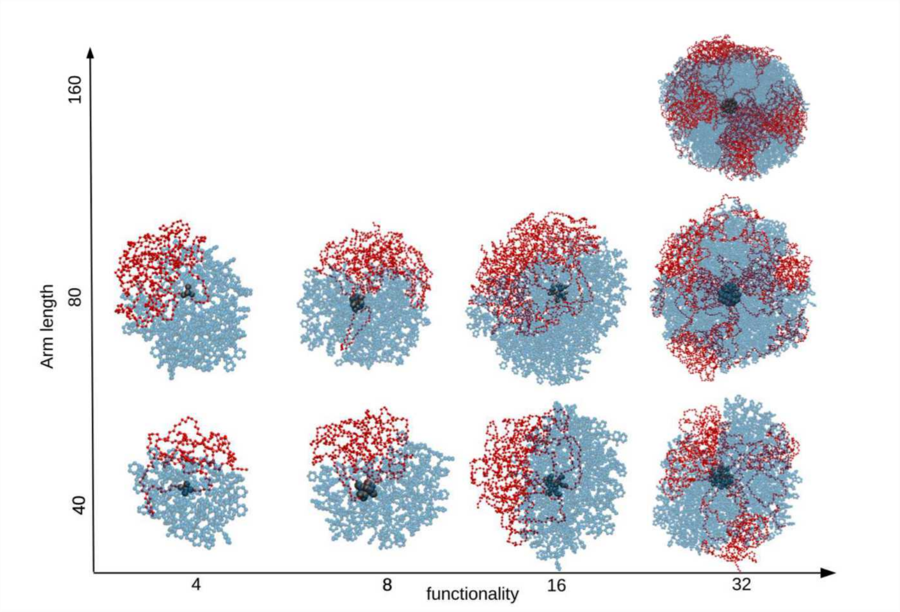
minimize free energy:

$$h \sim N(\sigma w)^{1/3}$$

Challenges in modeling mixed brush nanoparticles

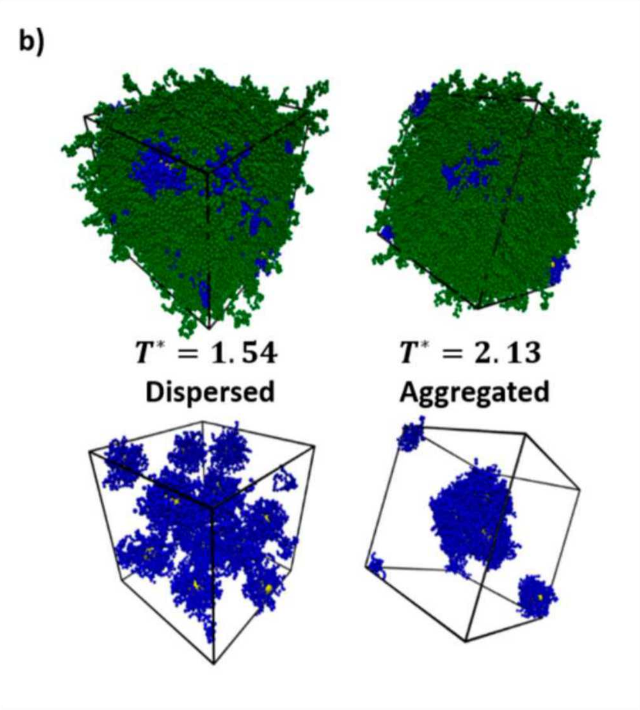
challenge 1: size scales make direct particle simulations difficult

atomistic: miktoarm stars



Bačová, P., Glynos, E., Anastasiadis, S. H. and Harmandaris, V. *ACS Nano* **13,** 2439-2449 (2019).

Brownian dynamics



Martin, T. B. *et al. J Am Chem Soc* **137,** 10624–10631 (2015).

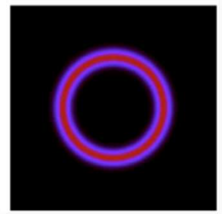
N = 10
P = 50

SCFT for single particles

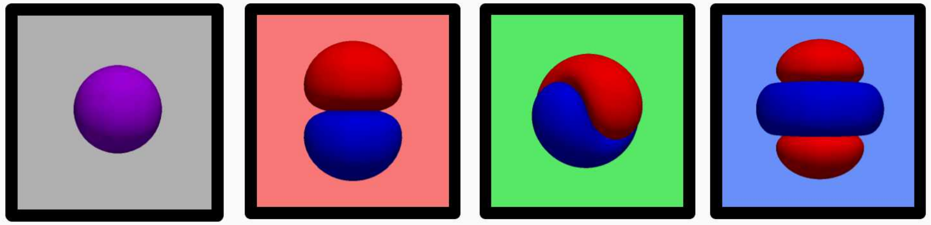
$$\chi_{AB}N = 18.9$$

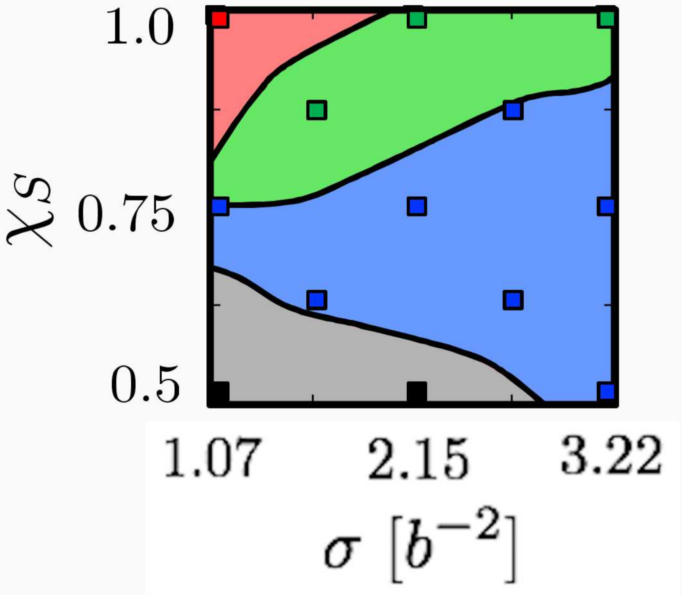
$$R_P = (2/3)R_g$$

uniform grafting density



$\chi_{AB}N$ = 28.3
χ_S = 1.0

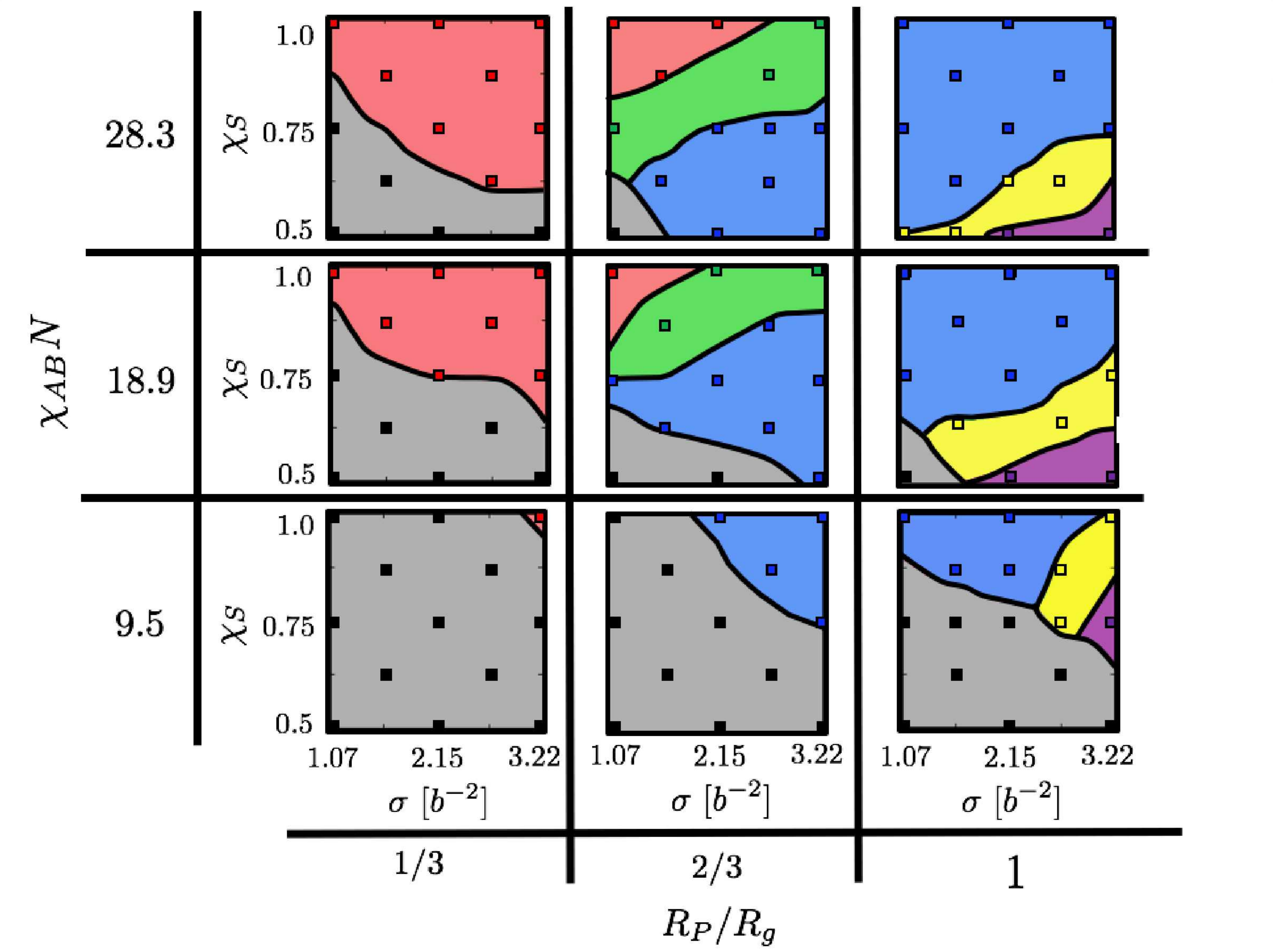


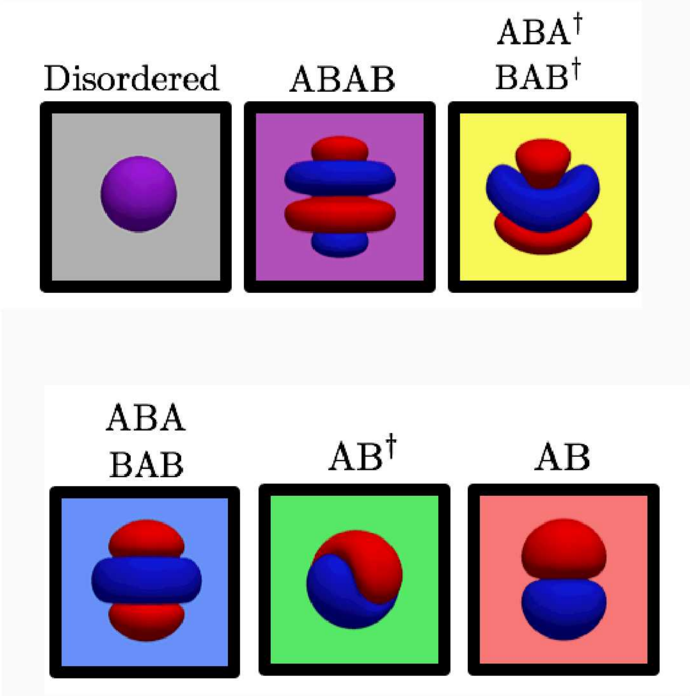


use Boltzmann weight to interpolate phase boundaries

$$P_i = \frac{\exp(-\beta F_i)}{\sum_j \exp(-\beta F_j)}$$

Full SCFT phase diagram





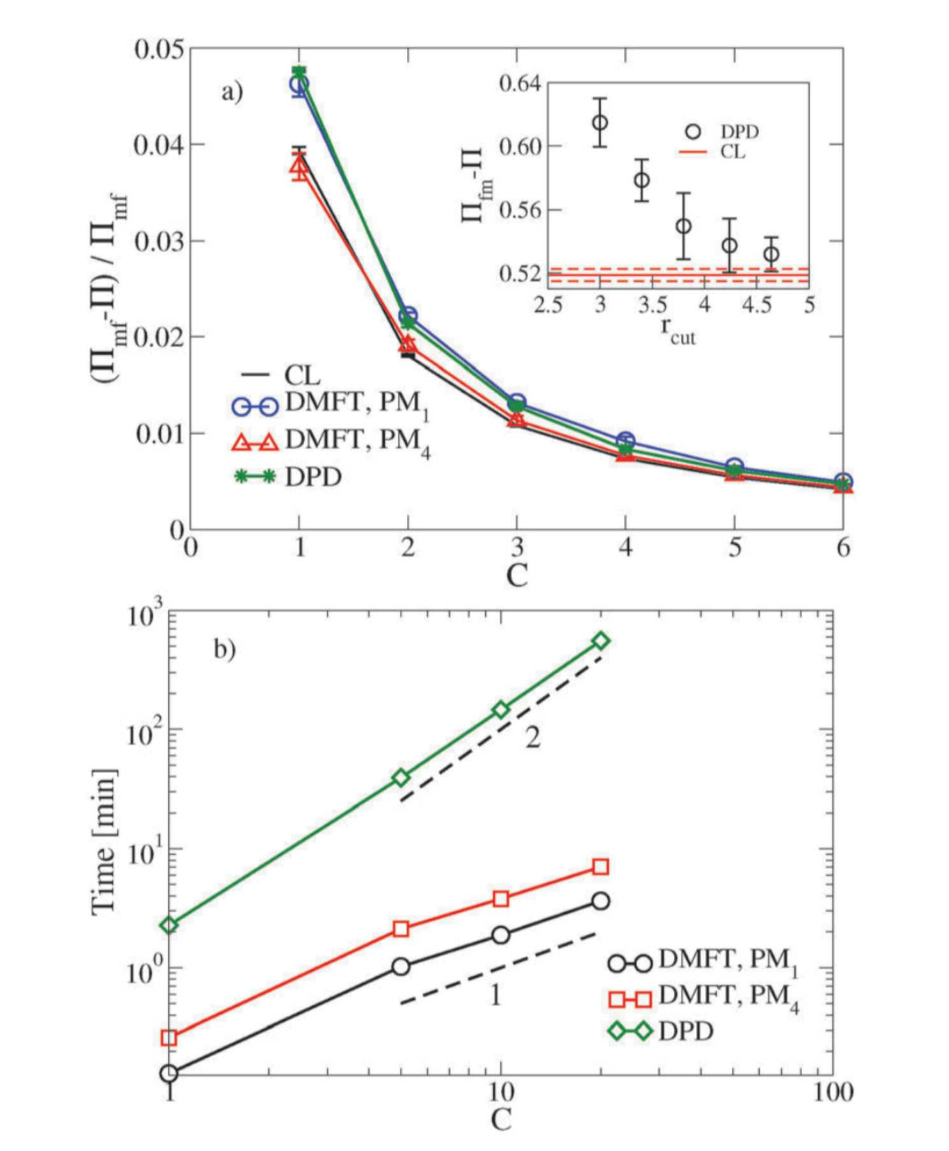
Riggleman group implementation

Include torques on grafted nanoparticles

Solve Langevin equation with Gronbech-Jensen and Farago (GJF) scheme

$$\mathbf{r}_{k,s}(t_n) = 2\,b\,\mathbf{r}_{k,s}(t_{n-1}) - a\,\mathbf{r}_{k,s}(t_{n-2}) + b\,\delta t^2[\mathbf{f}^{(\mathrm{b})}_{k,s}(t_{n-1}) + \mathbf{f}^{(\mathrm{nb})}_{k,s}(t_{n-1})] + \frac{b\,\delta t}{2}[\theta_{k,s}(t_n) + \theta_{k,s}(t_{n-1})],$$

allows large timesteps
good performance compared to DPD simulation

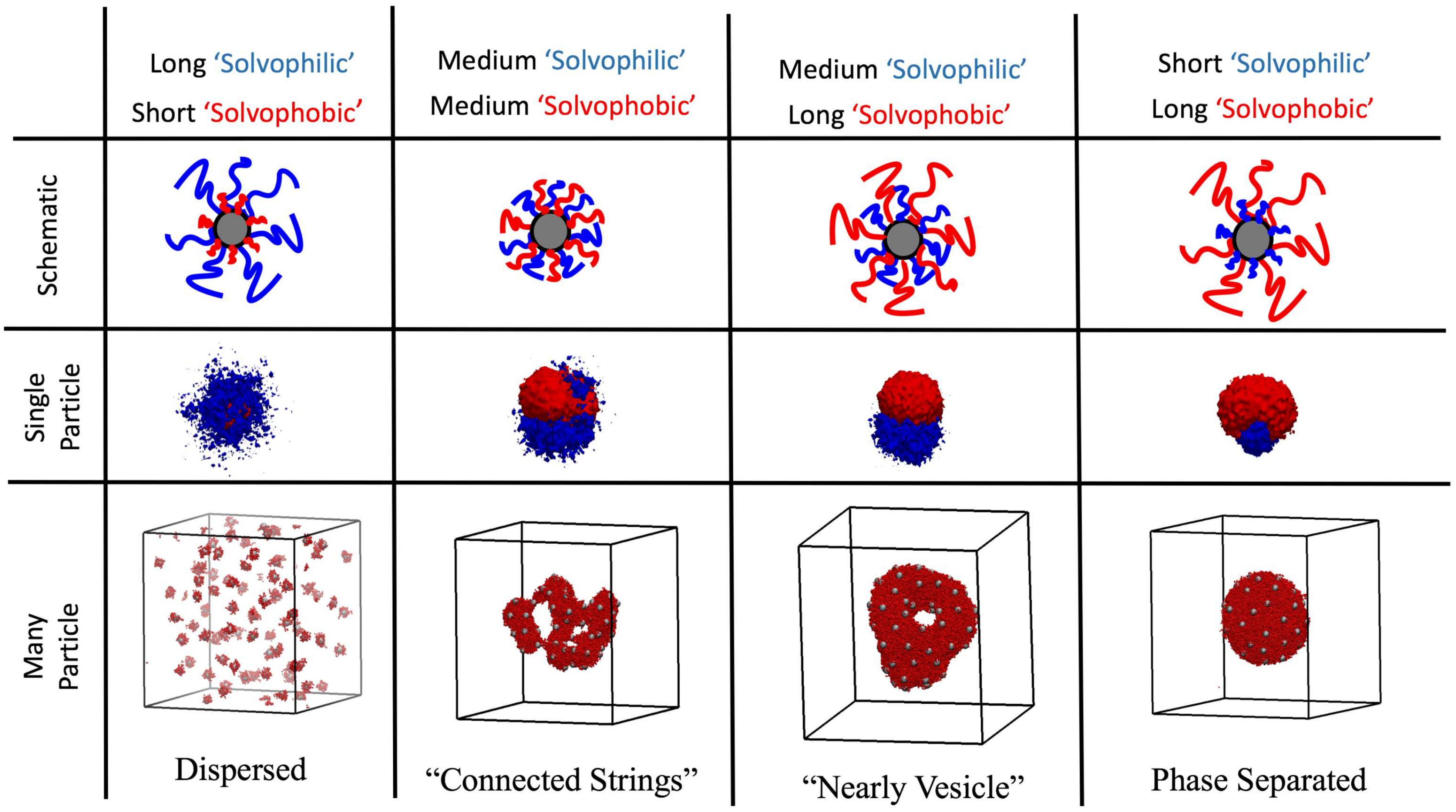


N. Gronbech-Jensen and O. Farago, Molecular Physics (2013)

Chao, H., Koski, J. & Riggleman, R. A. *Soft Matter* **13,** 239–249 (2017).

Vary chain lengths

$\chi_S = 2$
$f_A = 0.5$



Classify observed assemblies

define cluster: all particles with at least 1 A monomer located within 2b of another A monomer on a different particle

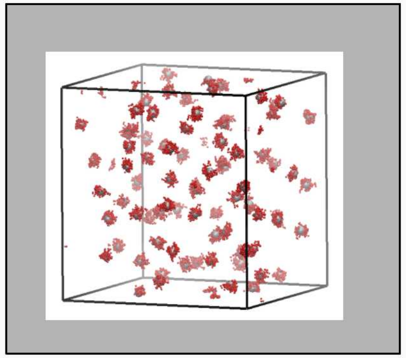
n_C = number of clusters

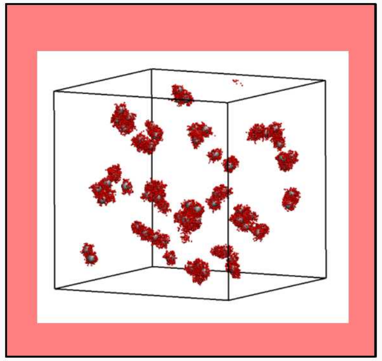
n_A = avg # of particles per cluster

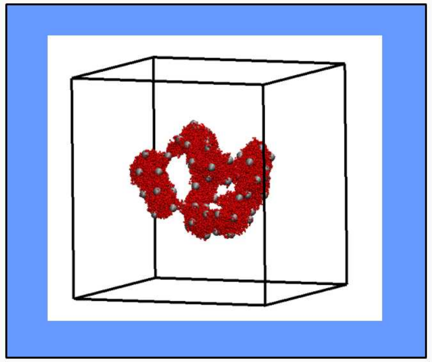
κ^2 = relative shape anisotropy of clusters

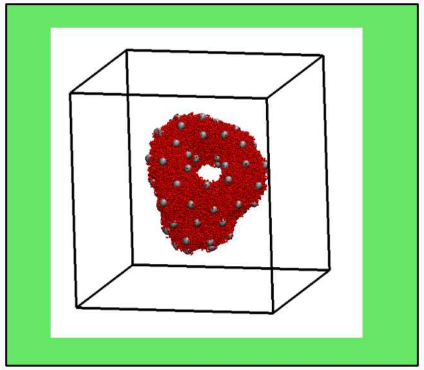
κ^2 = 0: sphere
κ^2 = 1: rod

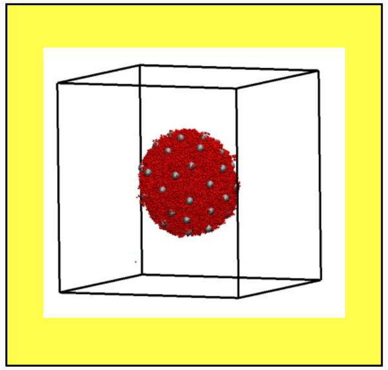
$n_A < 1.5$		dispersed
$1.5 < n_A < 3$		small clusters
$3 < n_A < n_{max}$	$\kappa^2 > 0.22$	stringy aggregates
	$0.13 < \kappa^2 < 0.22$	loops/vesicles/?
	$\kappa^2 < 0.13$	macrophase separated
$n_A = n_{max}$		macrophase separated


Dispersed

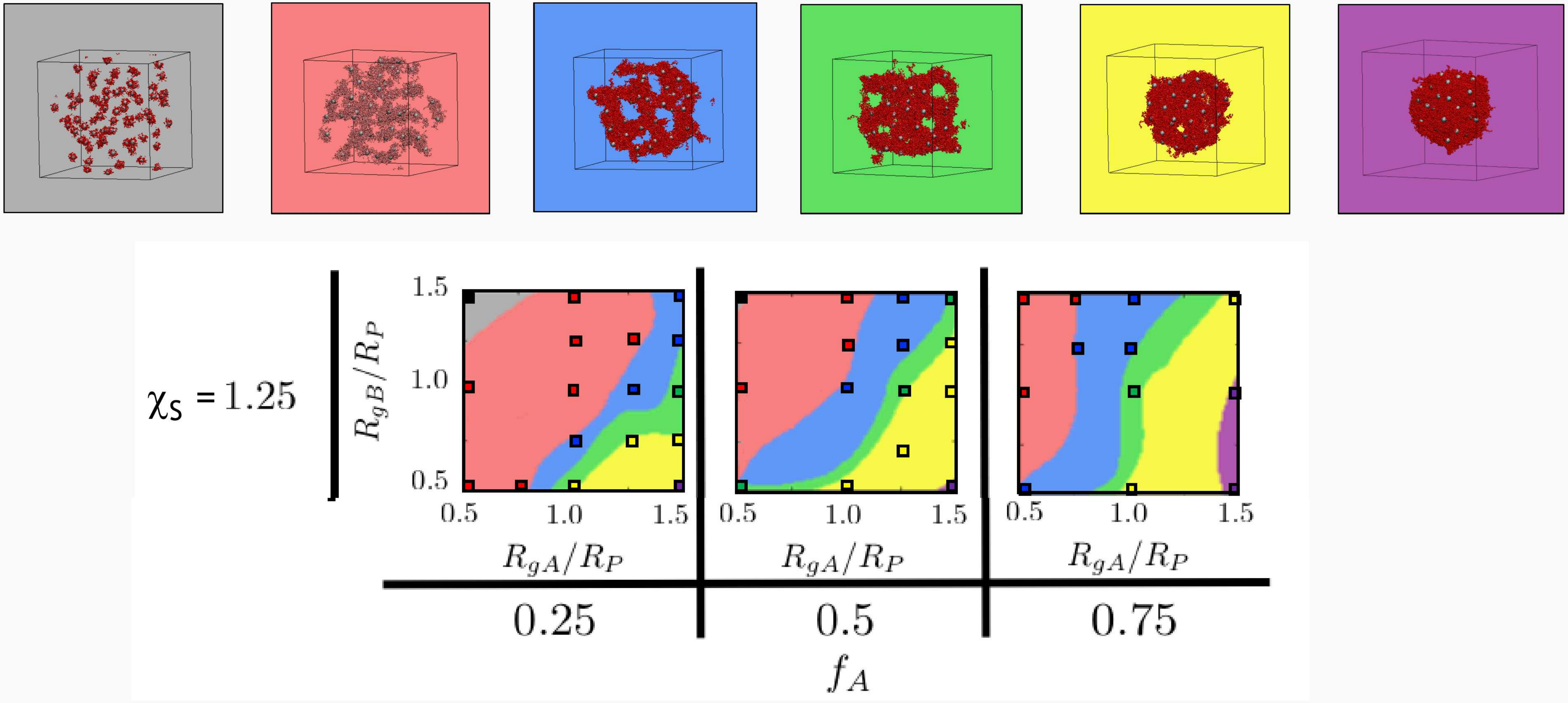

Small Clusters


Connected Strings

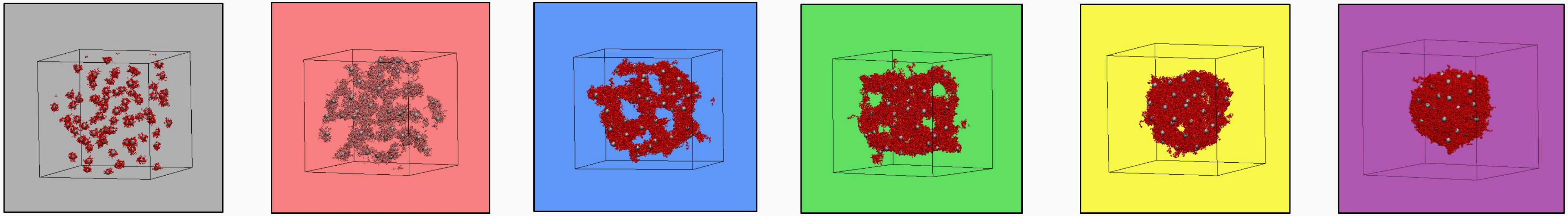

Nearly Vesicle

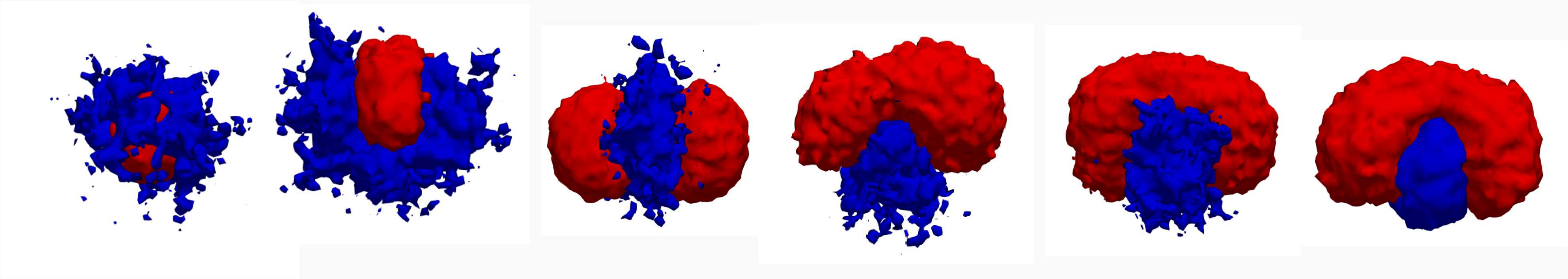

Phase Separated

Lower χ_S



Lower χ_S

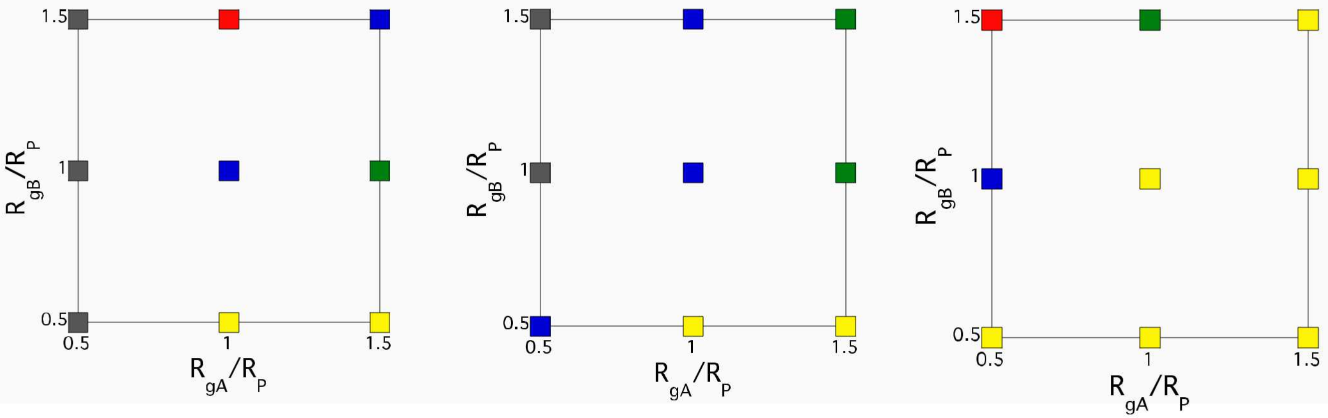




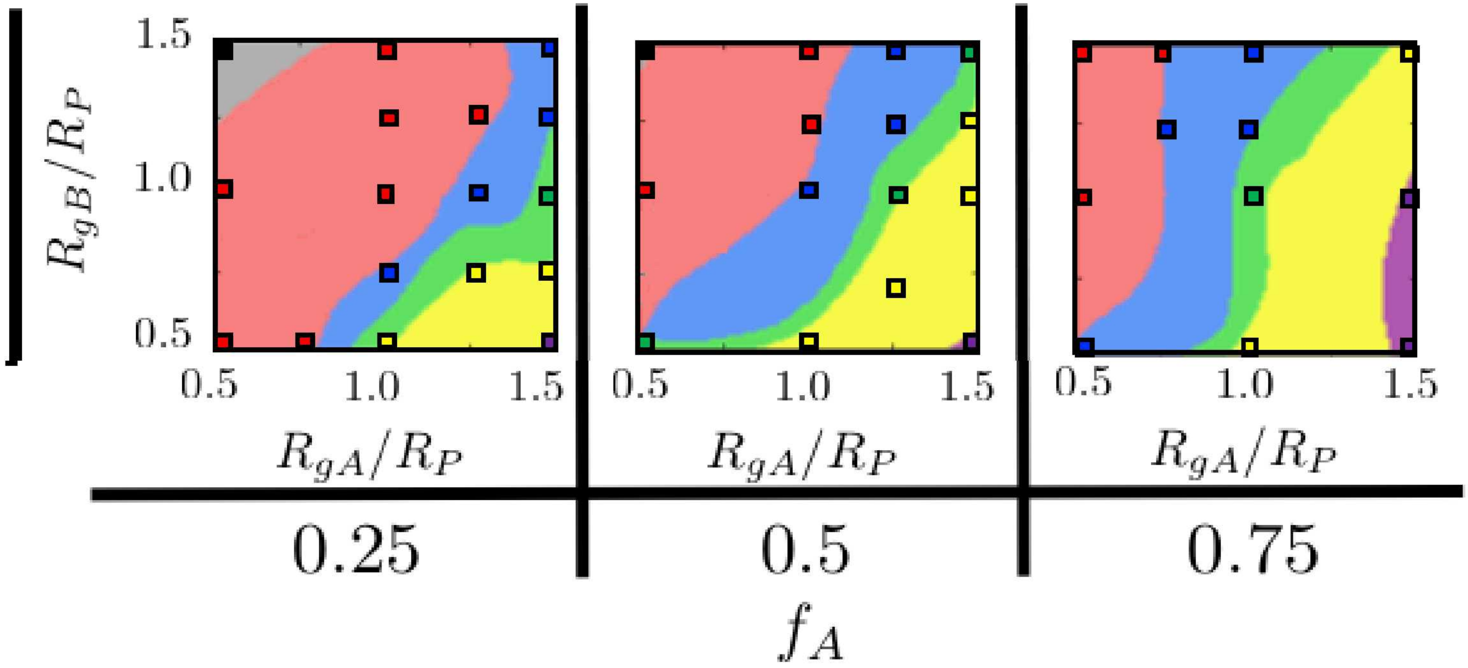
- less distinct brush structures
- more “messy” assmblies

Comparison of solvent qualities

$\chi_S = 2$



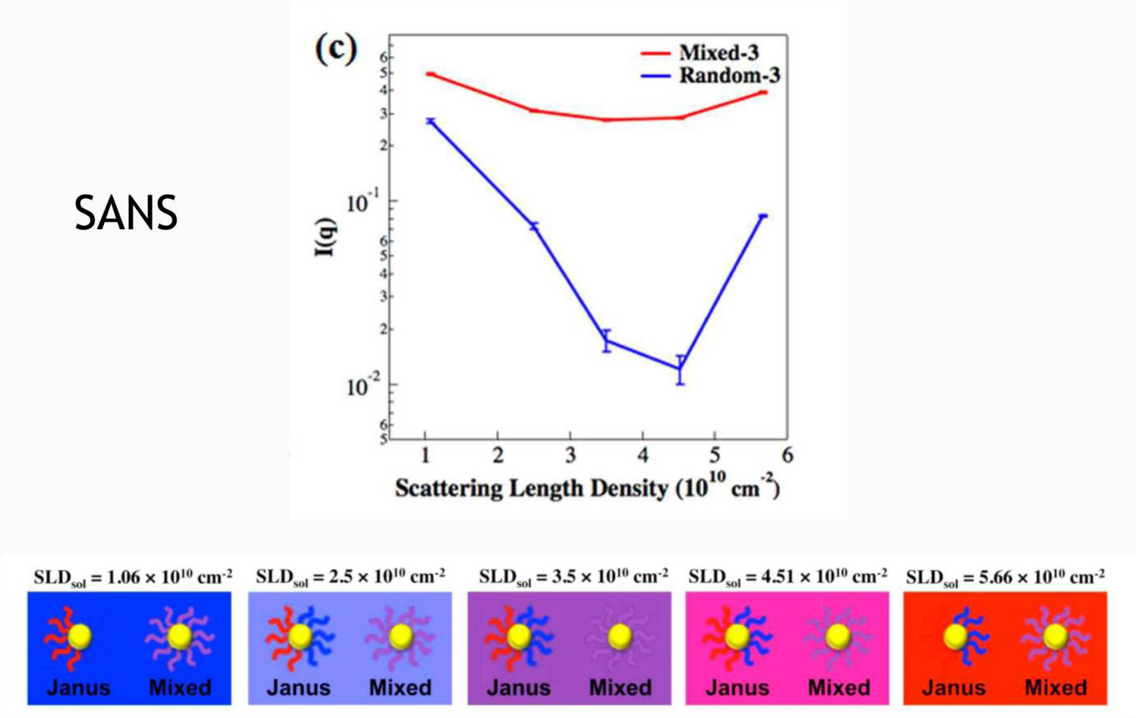
$\chi_S = 1.25$



Experimental evidence of grafted Janus NPs?

dPS-PMMA on Au NPs

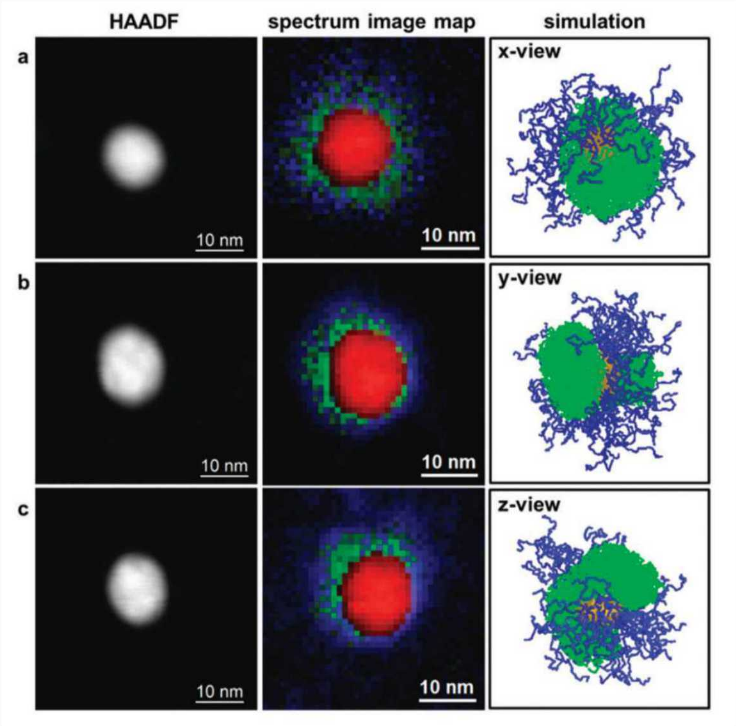
SANS



Kim, S., Kim, T.-H., Huh, J., Bang, J. & Choi, S.-H. *ACS Macro Lett.* **4,** 417–421 (2015).

PS-PMMA on Au NPs

EELS for polymers



Rossner, C., Tang, Q., Müller, M. & Kothleitner, G. *Soft Matter* **14,** 4551–4557 (2018).