SAND2013-2261C

Dispersion of Polymer-Grafted Nanorods in Polymer Films

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APS March Meeting
March 19, 2013

Sandia National Laboratories

Exceptional service in the national interest

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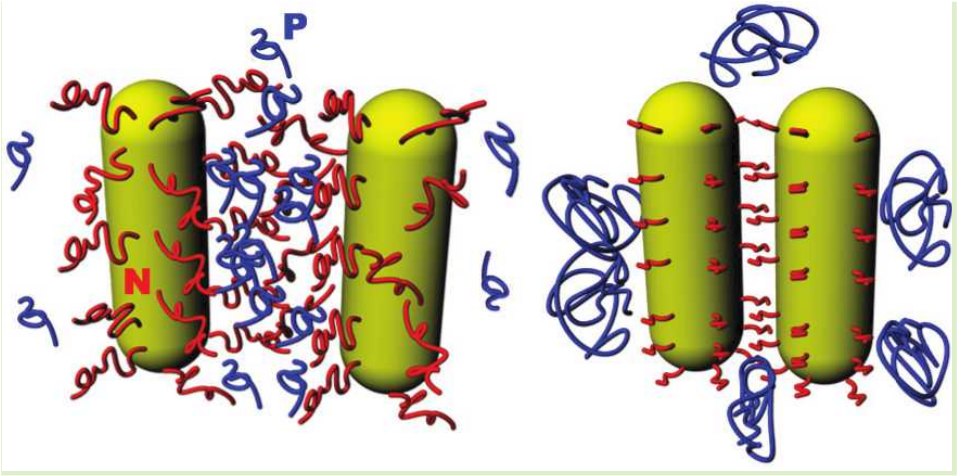
Experimental System

- gold nanorods
- polymer brush coating
- 5% rods in polymer thin film
  - rods confined in the plane of the film



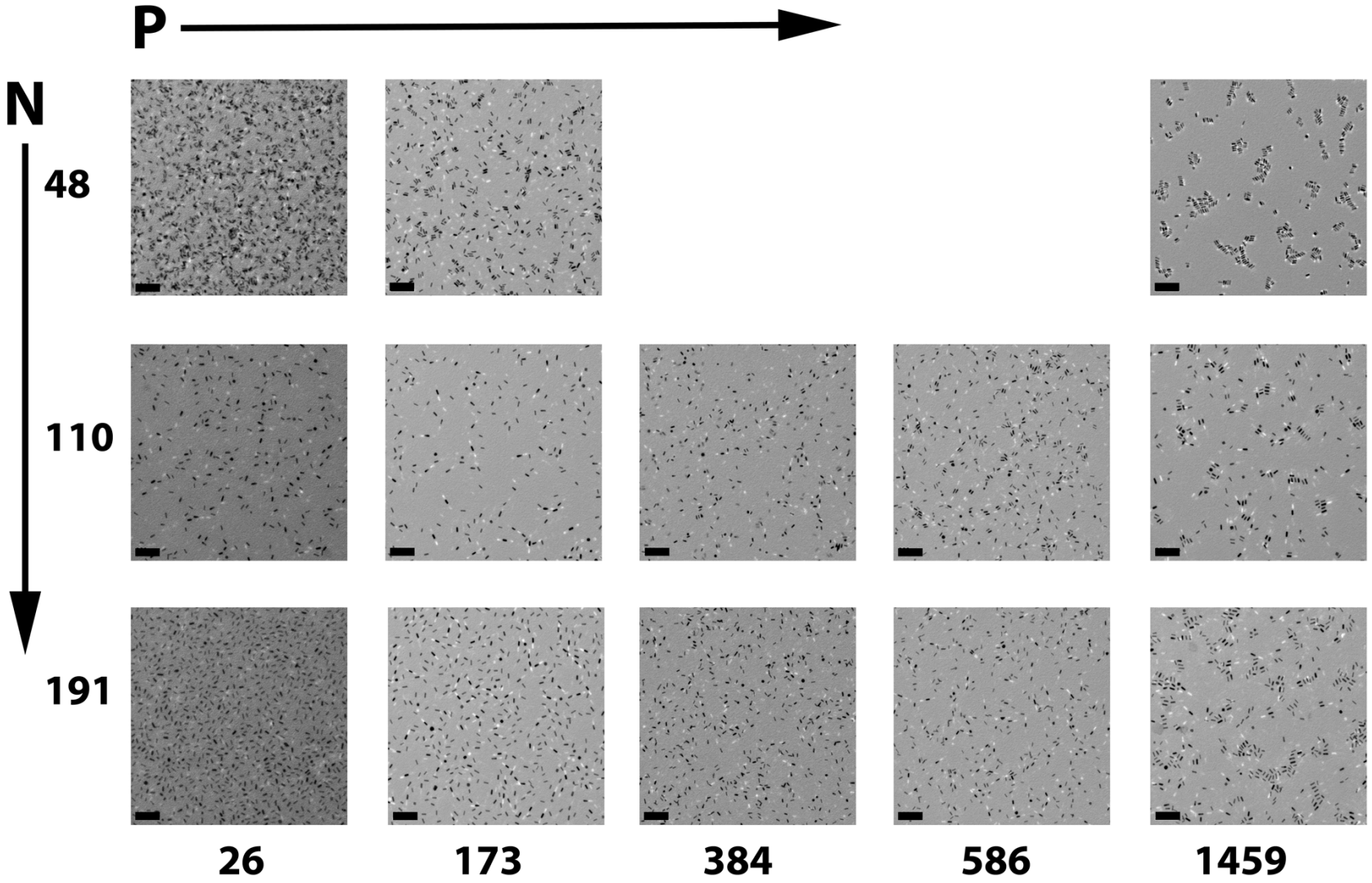
athermal systems:

PS brush in PS

PEO brush in PEO

What controls nanorod dispersion/aggregation?

Nanorods: PS-Au(*N*):PS(*P*)



Hore, M. J. A., Frischknecht, A. L., & Composto, R. J. (2012), *ACS Macro Letters*, *1*, 115–121.

PEO-Au(*N*):PEO(*P*)

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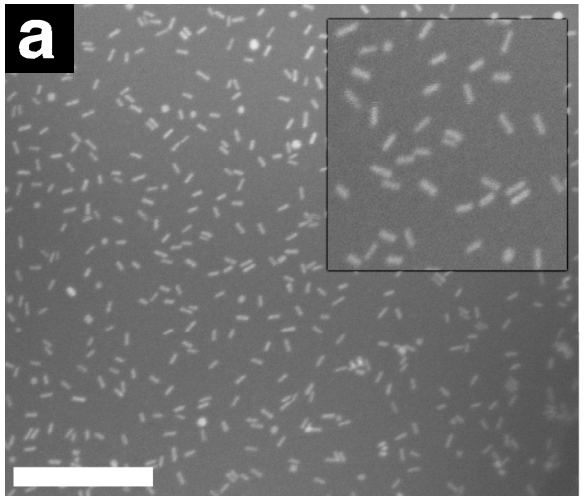
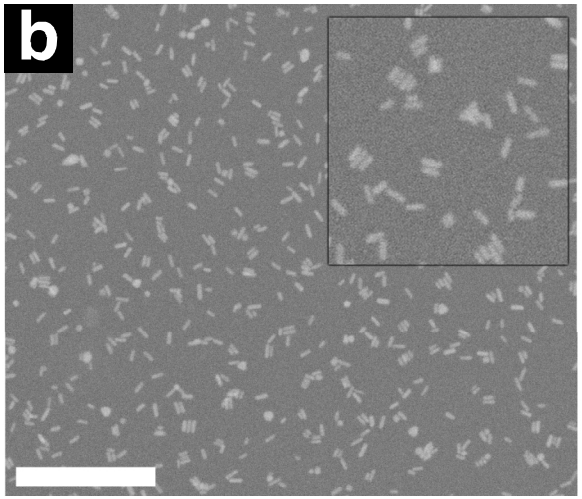
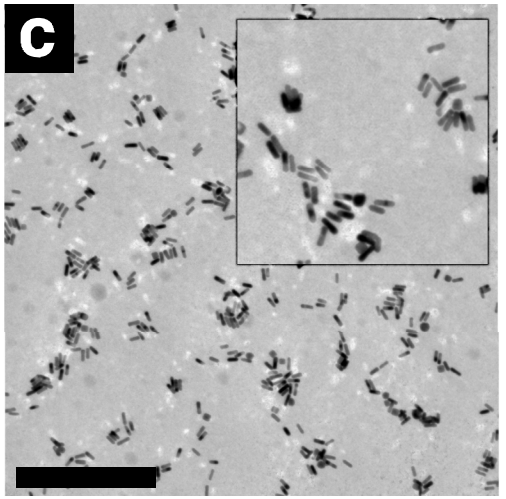


P/N = 0.43

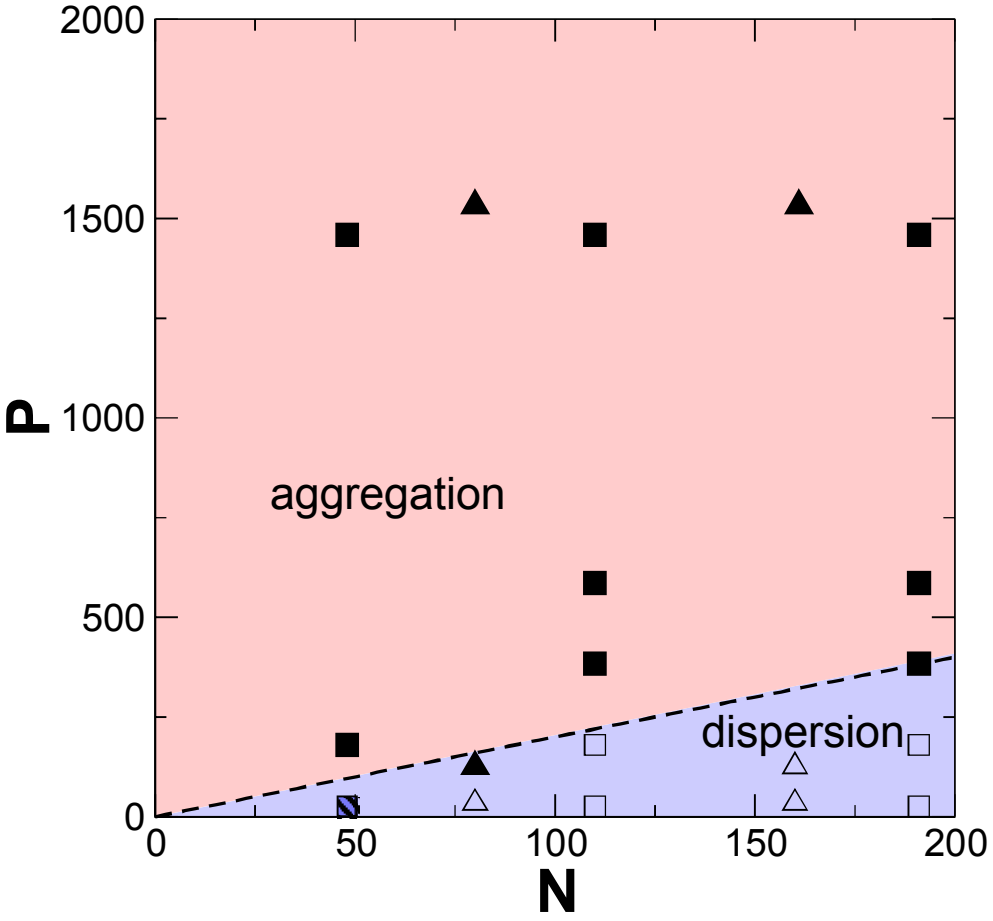


P/N = 1.58



P/N = 19.2

Dispersion "Map" for NRs



dispersion for $P < 2N$

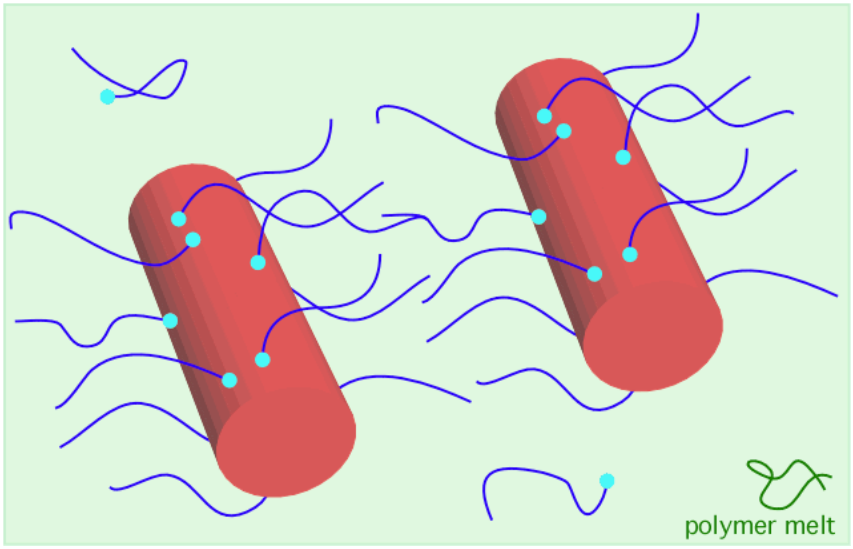
ignores possible effects of:

- rod curvature
- grafting density
- rod length

squares: PS
triangles: PEO

Hore, M. J. A., Frischknecht, A. L., & Composto, R. J. (2012), *ACS Macro Letters*, *1*, 115.

Modeling



classical DFT and SCFT

- brush chains length *N*
- matrix chains length *P*
- athermal ($\chi = 0$)
- nanorods with radius R_{rod}
- grafting density σ

goal: calculate polymer-mediated interaction free energy

variables: $\alpha = P/N$

R_{rod}/R_g

$$\sigma^* \equiv \frac{\sqrt{6}\sigma N^{1/2}}{a\rho_0}$$

experimental ranges:

$\alpha = P/N = 0.15 - 30$

$R_{rod}/R_g = 1.5\text{-}3.2$

$\sigma^* = 0.95\text{-}2.38$

earlier work: Frischknecht, J. Chem. Phys., **128**, 224902 (2008)

Single Nanorod: Brush Profiles

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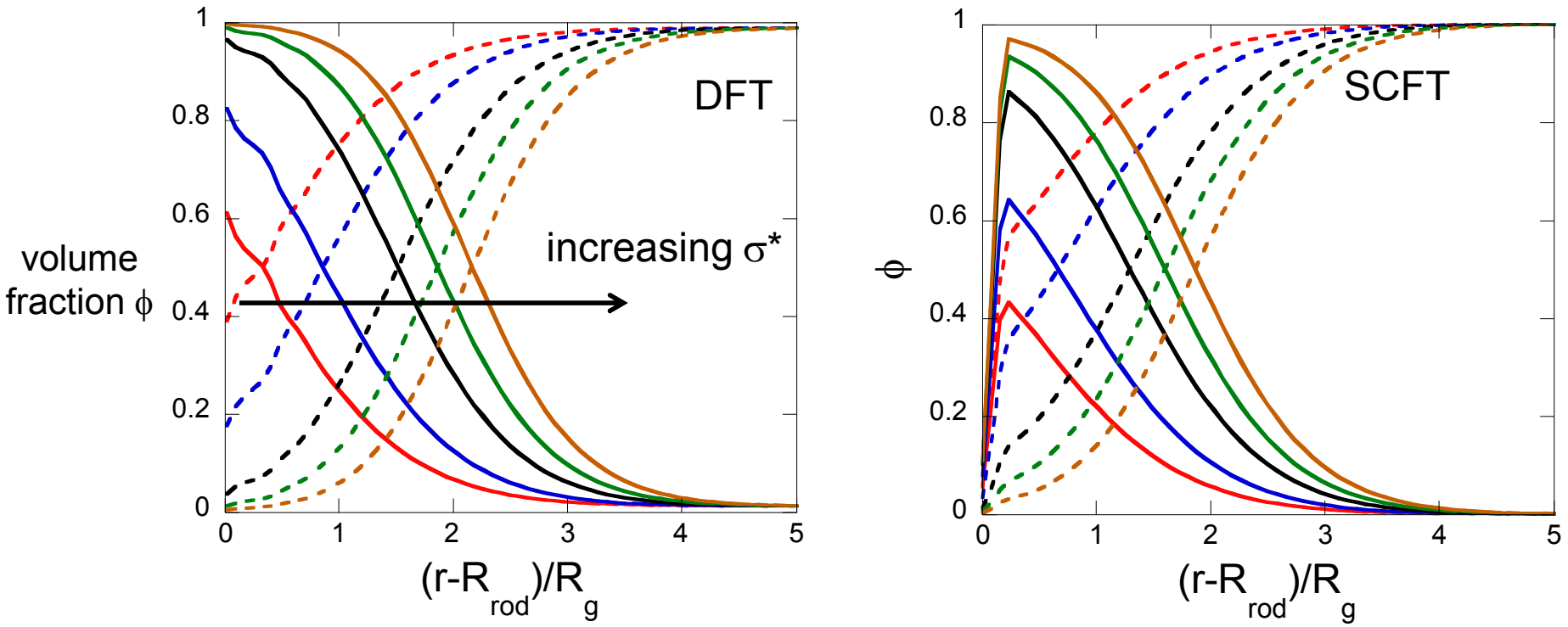
$R_{rod}/R_g = 3.2$, $P/N = \alpha = 3$



grafting density important

Single Nanorod: Brush Profiles

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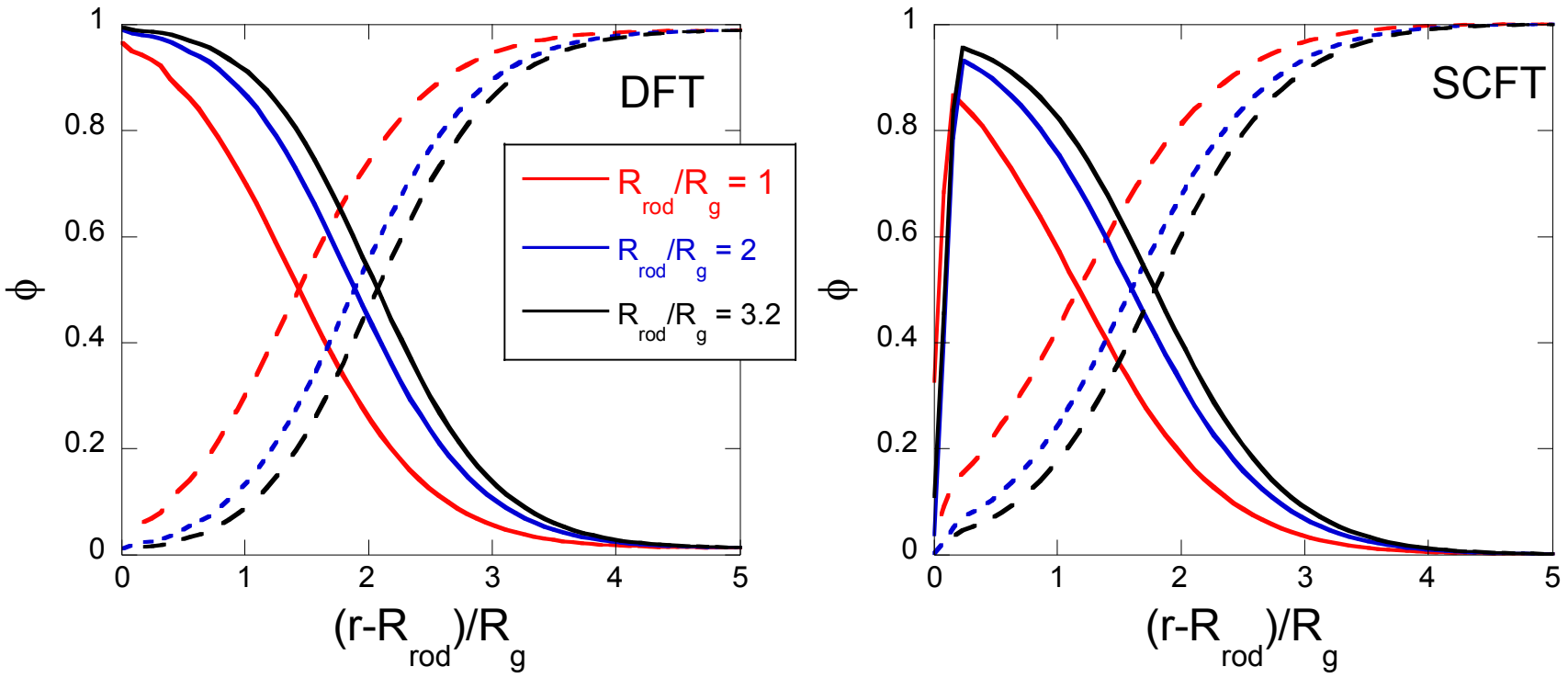
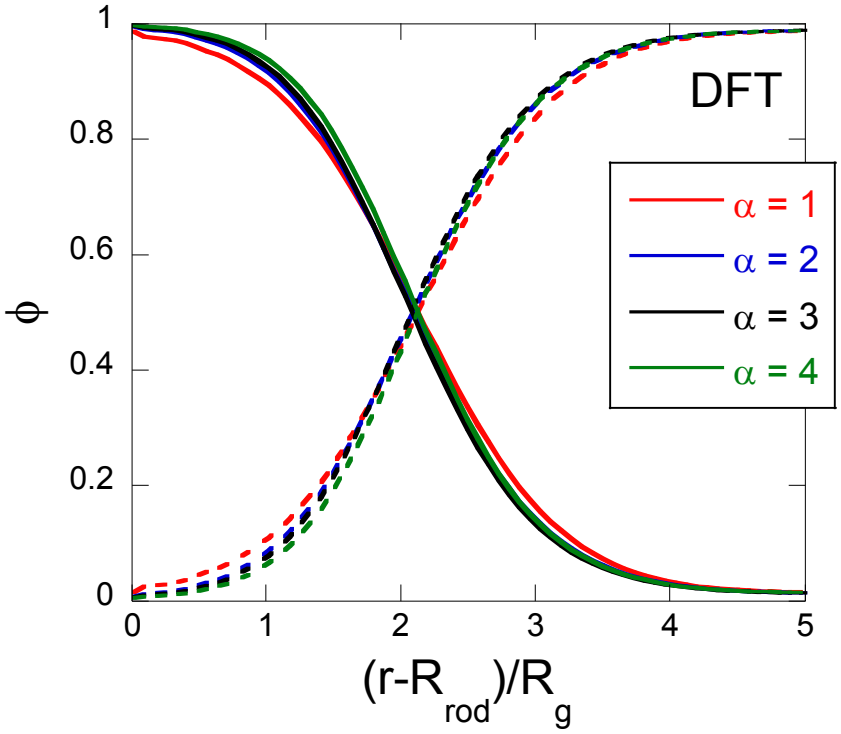
$\alpha = 2, \sigma^* = 2.38$

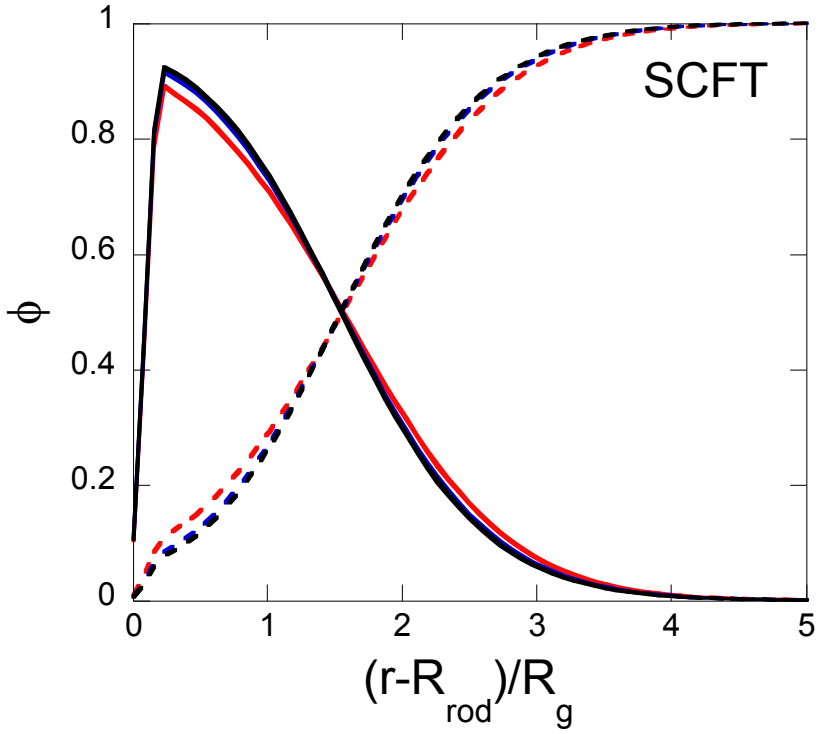


nanorod curvature important

Single Nanorod: Brush Profiles

$R_{rod}/R_g = 3.2$, $\sigma^* = 2.38$





matrix chain length doesn't affect brush profiles much

Rod-rod interaction energy

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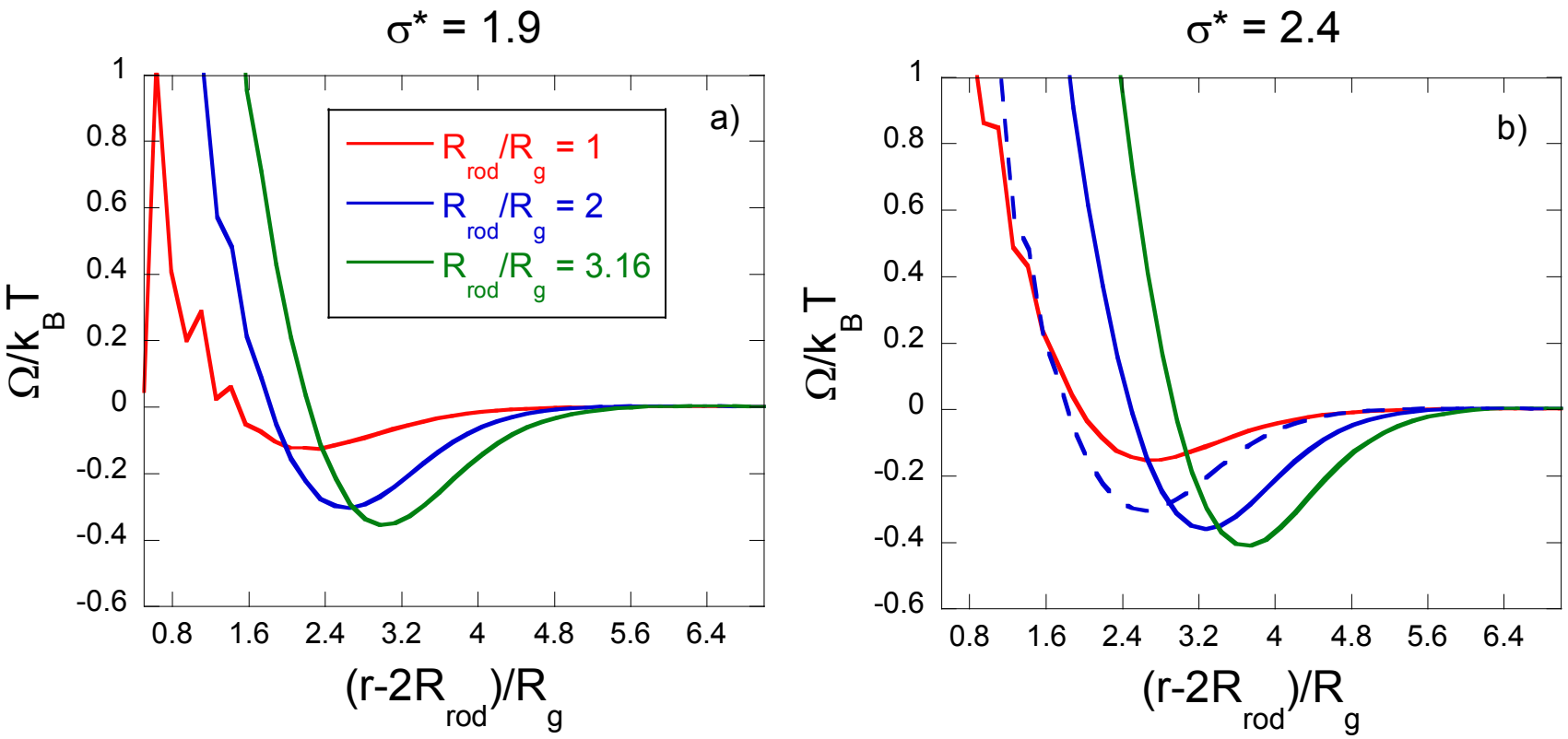
$P/N = \alpha = 3$



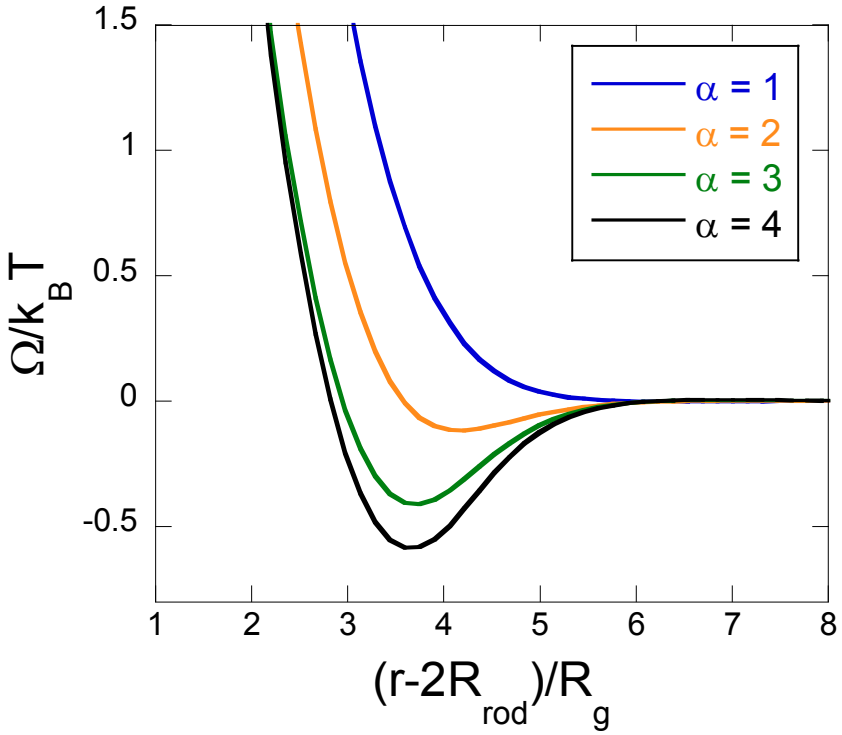
deeper attractive well as:

- grafting density increases
- R_{rod} increases

Rod-rod interaction energy

$R_{rod}/R_g = 3.2$, $\sigma^* = 2.4$

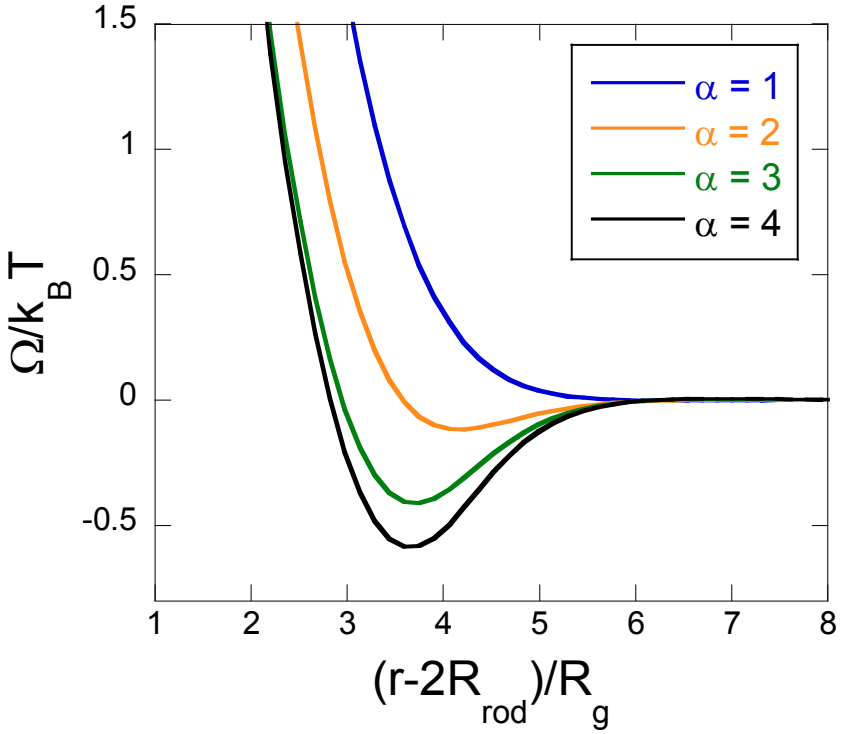
matrix chain length crucial!



Rod-rod interaction energy

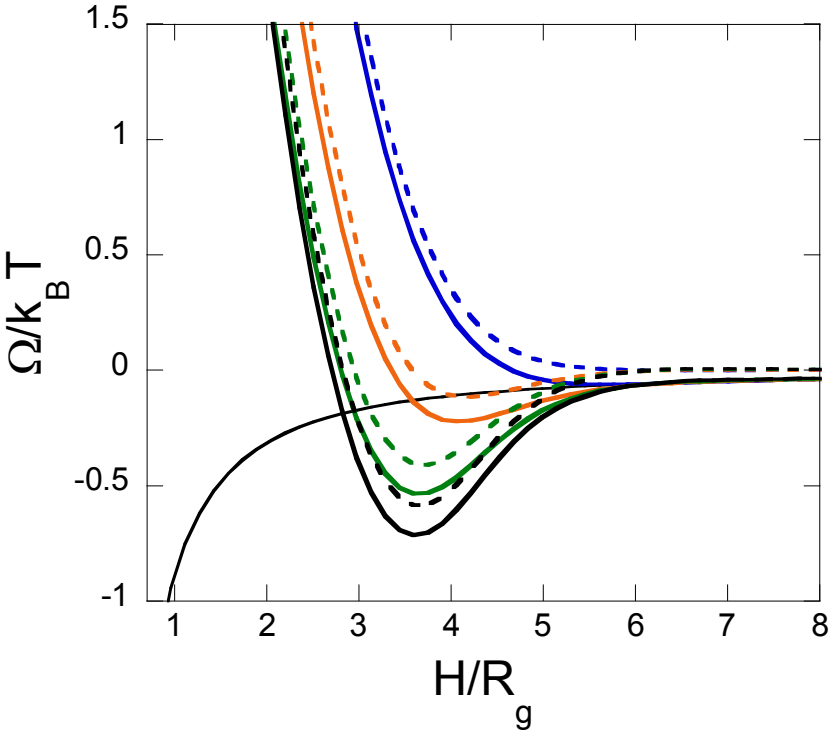
$R_{rod}/R_g = 3.2$, $\sigma^* = 2.4$

matrix chain length crucial!



include van der Waals between Au rods:

$$W = -\frac{ALR_{rod}^{1/2}}{24H^{3/2}}$$



Criterion for Aggregation?

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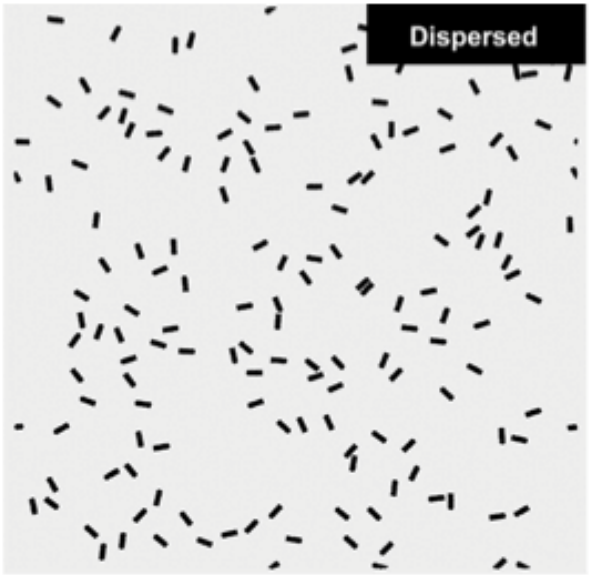
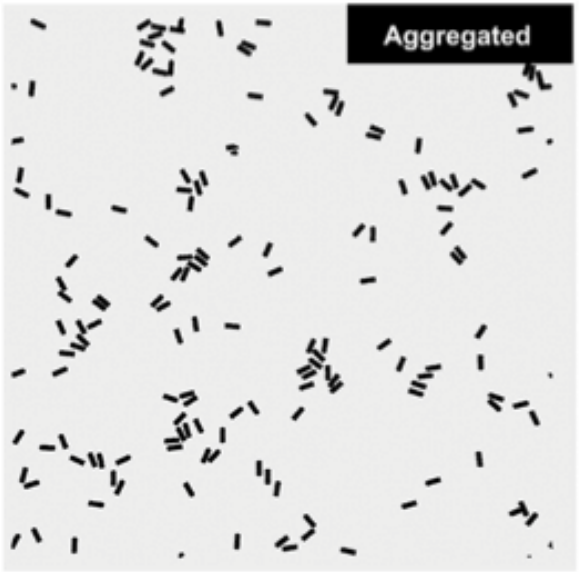
Monte Carlo simulations
square-well potential



0 kT



5 kT

10 kT

assume aggregation for $E_{tot} > 5$ kT

Hore, M. J. A., et al. (2012), *ACS Macro Letters*, *1*, 115–121.

Comparison with experiment

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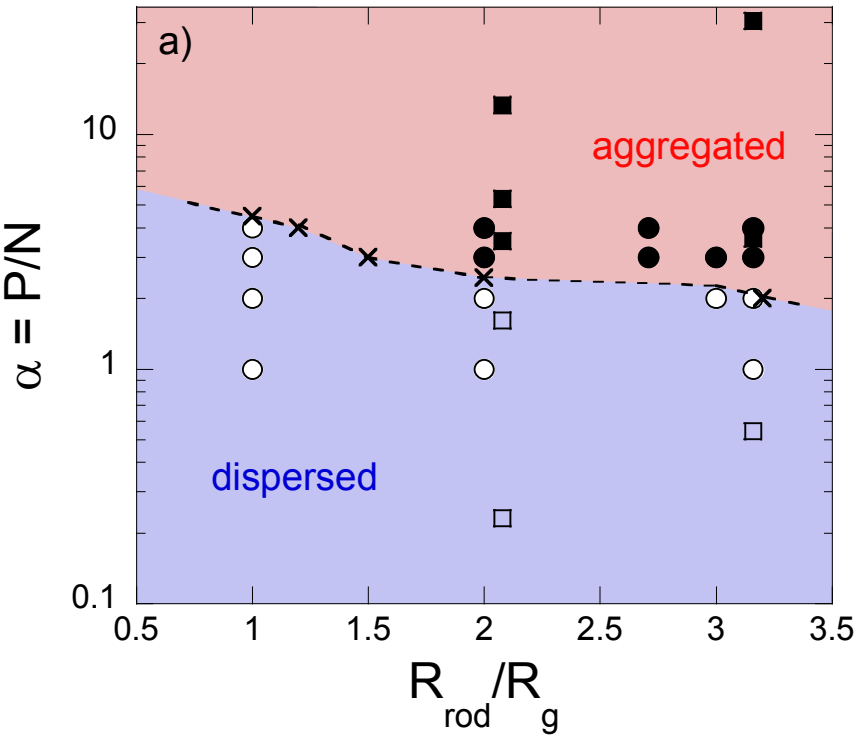
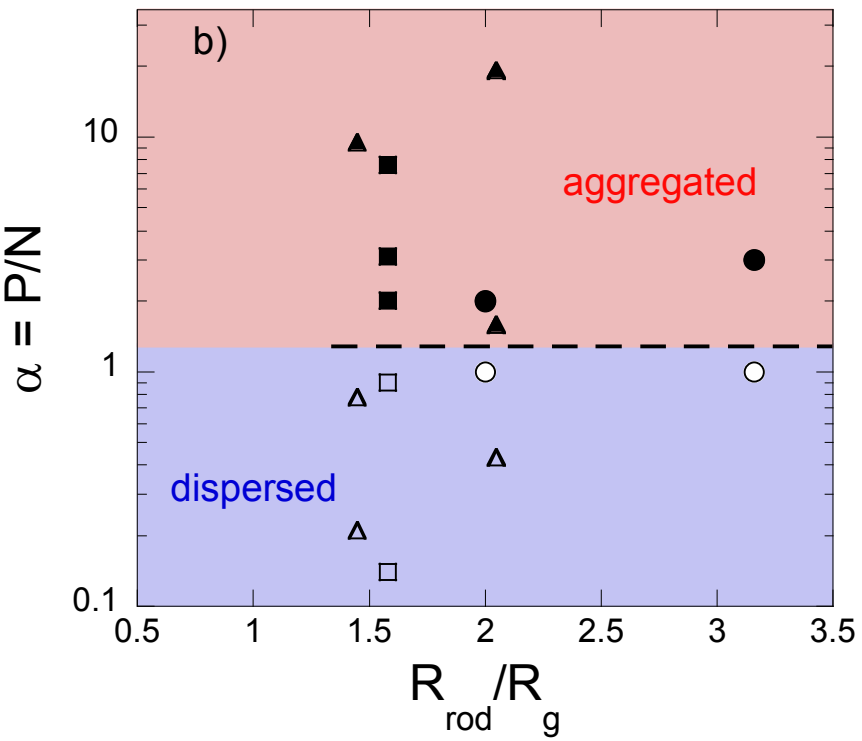
$1.9 < \sigma^* < 2.4$



$1 < \sigma^* < 1.4$

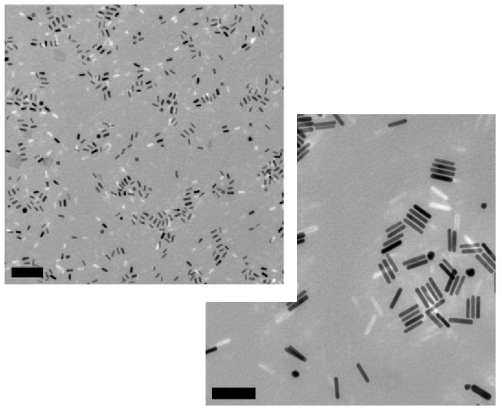


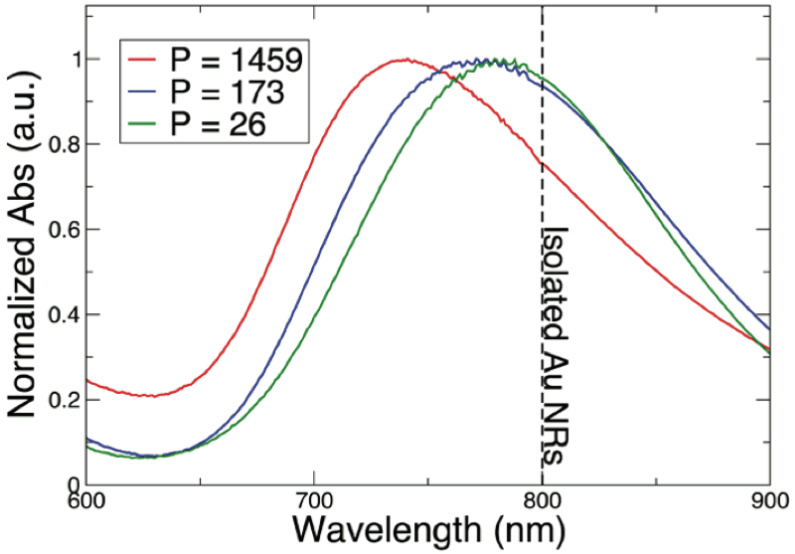
circles = DFT
squares = PS/PS
triangles = PEO/PEO

good overall agreement

Conclusions

- brush profiles remarkably insensitive to α
- interaction energy sensitive to σ^*, R_{rod}, and α
- DFT captures correct trends
  - transition to aggregation near *P/N = 2*
- design: promote dispersion for
  - small σ^*, R_{rod}, or α
  - can potentially control rod spacing in aggregates
    - to control optical properties





Frischknecht, Hore, Ford, & Composto, *Macromolecules* (in press)

Acknowledgments

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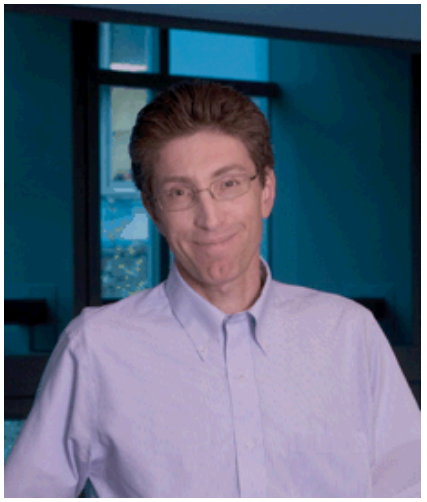
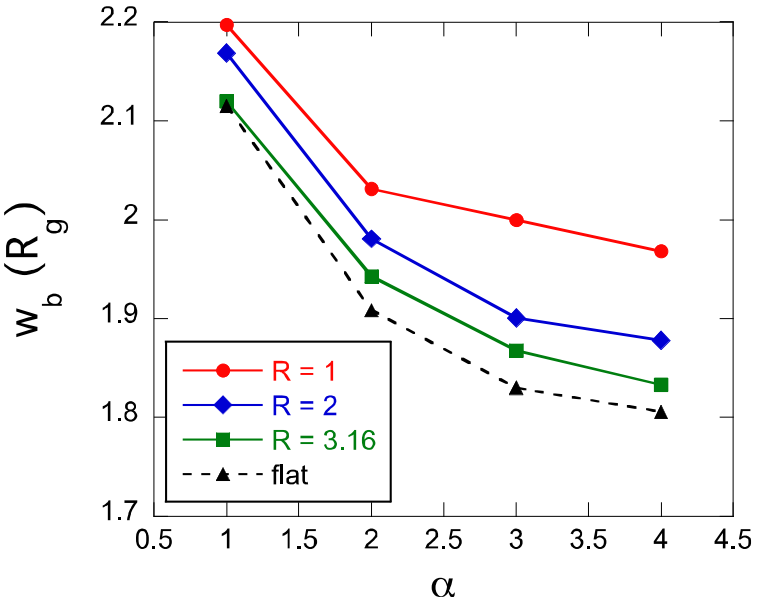


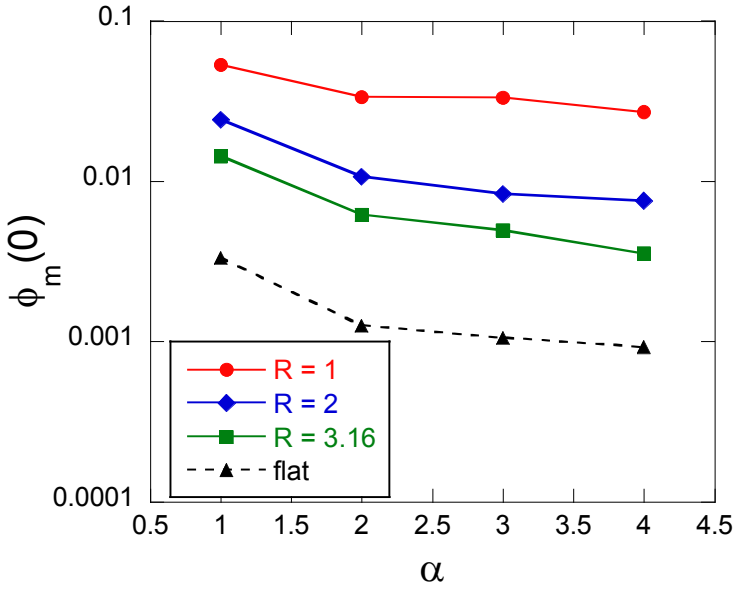
CINT User Program

Brush Characteristics vs α

brush width



volume fraction of matrix chains at NR surface



- brush height insensitive to α
- details of interface matter for interactions

Brush Characteristics vs σ*

height h_b (nearly linear)

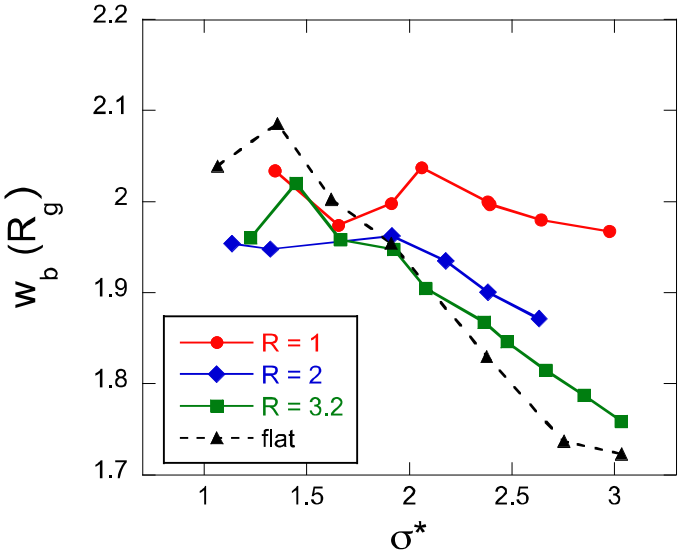
$$\phi_b(h_b) = \frac{1}{2}\phi_b(0)$$

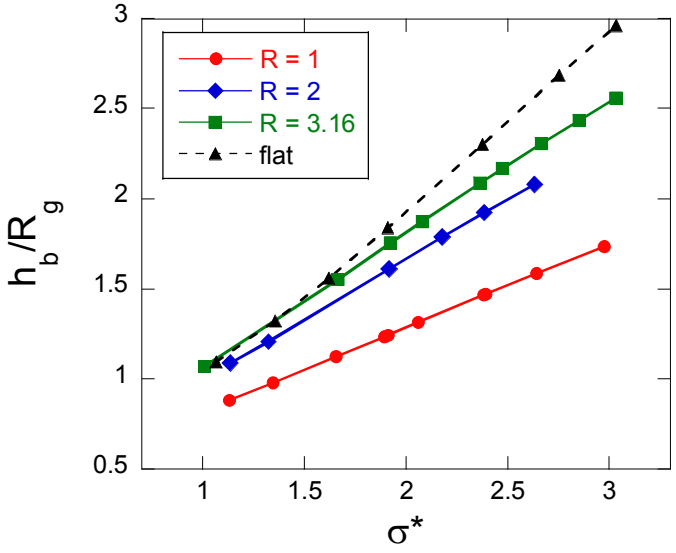
width w_b

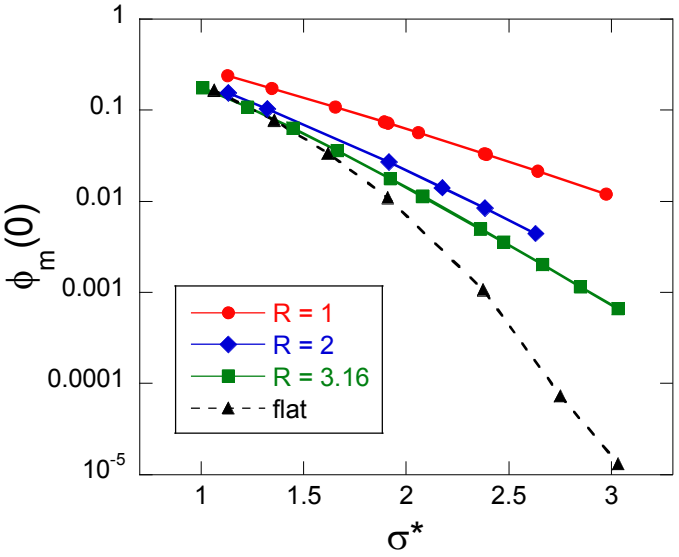
$$w_b = \frac{\phi_b(0)}{|\phi_b'(h)|}$$

matrix fraction at rod surface

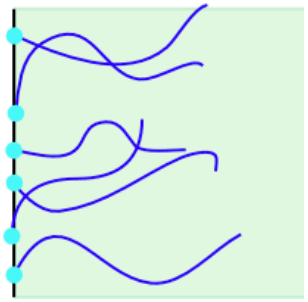
$$\phi_m(0)$$

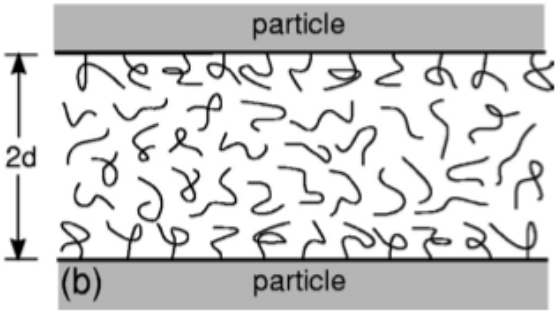






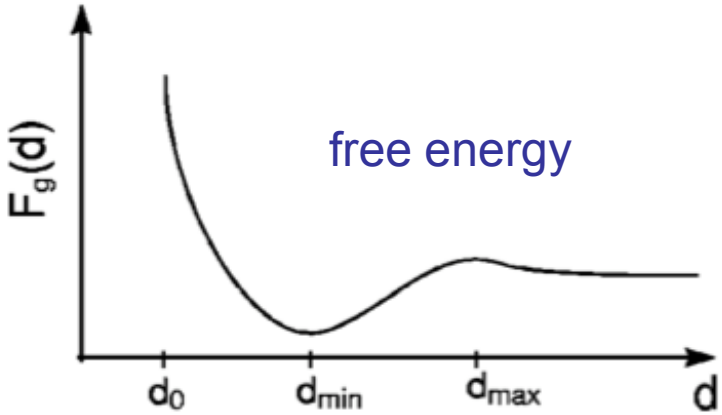
Brush-Brush Interactions

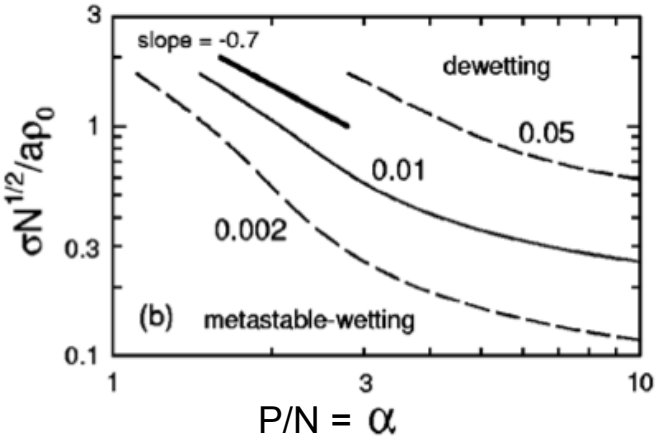




autophobic dewetting:

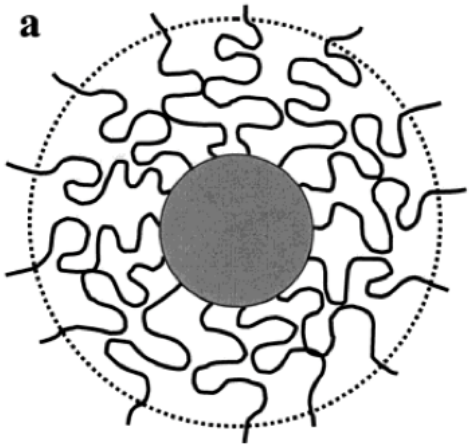
- entropy cost for matrix chains to enter brush
- leads to positive brush-matrix surface tension
- brushes are attracted





Matsen, M. W., & Gardiner, J. (2001). *J Chem Phys*, *115*, 2794–2804.

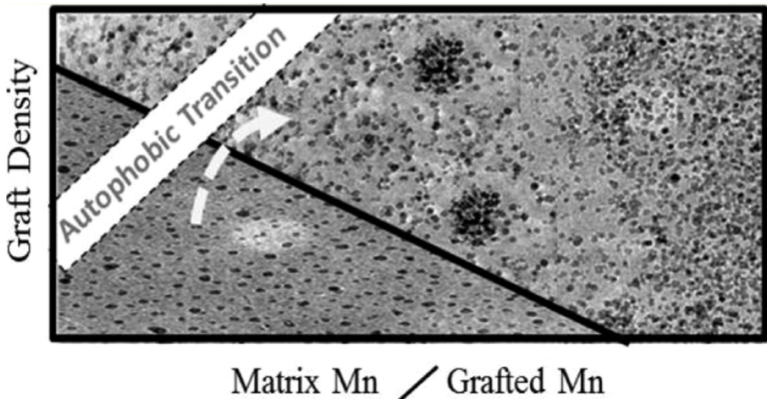
Brushes on Curved Surfaces

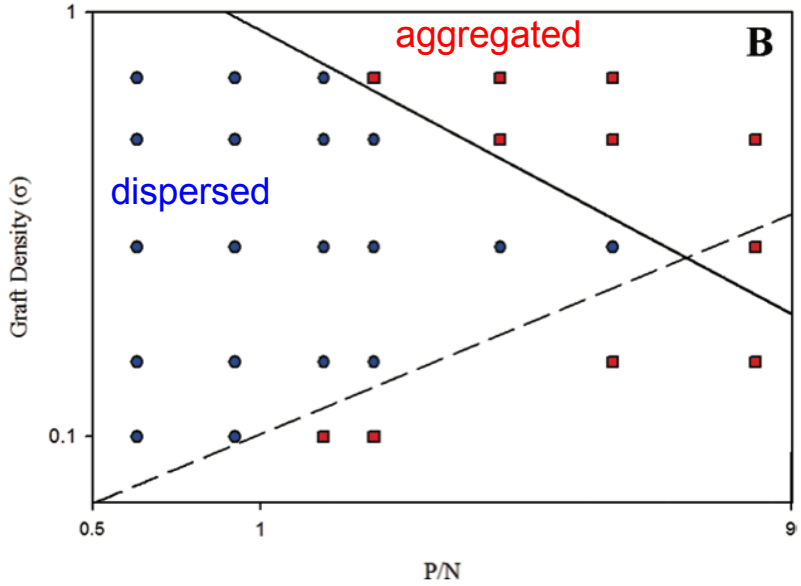


- more volume than on flat surface at same grafting density
- chains splay out more
- brush is less extended

expect wet to dry transition to occur for
- larger grafting densities
- larger P/N

PS-silica in PS

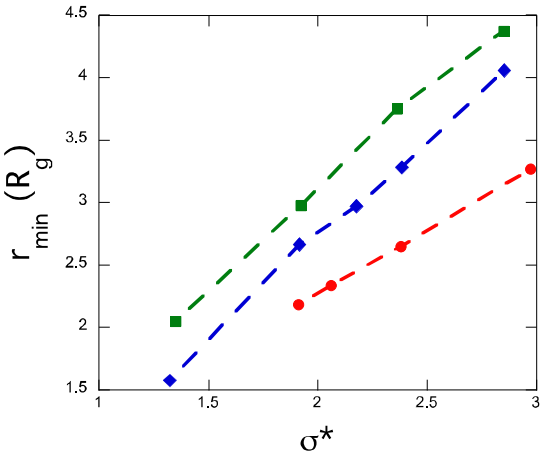


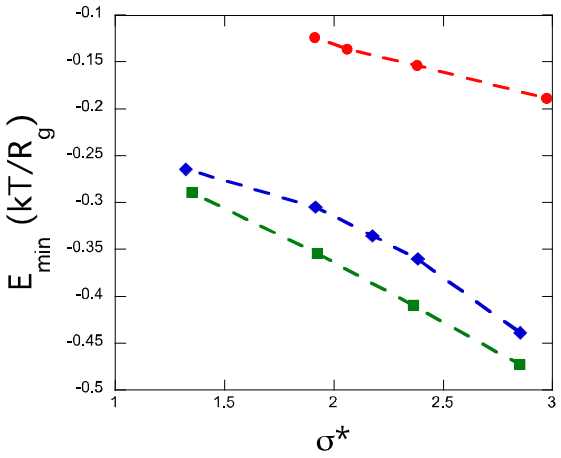


Sunday, D., Ilavsky, J., & Green, D. L. (2012). *Macromolecules*, *45*, 4007–4011.

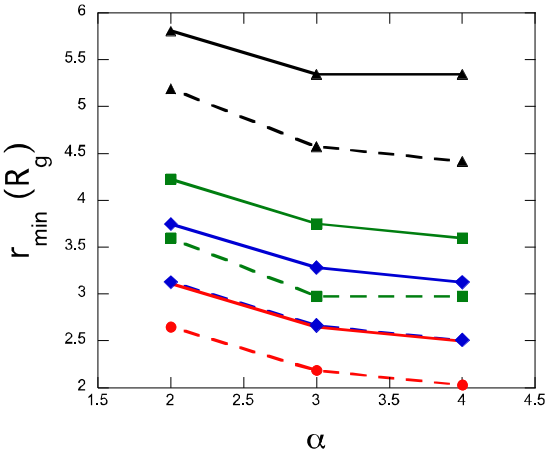
Interactions vs σ* and α

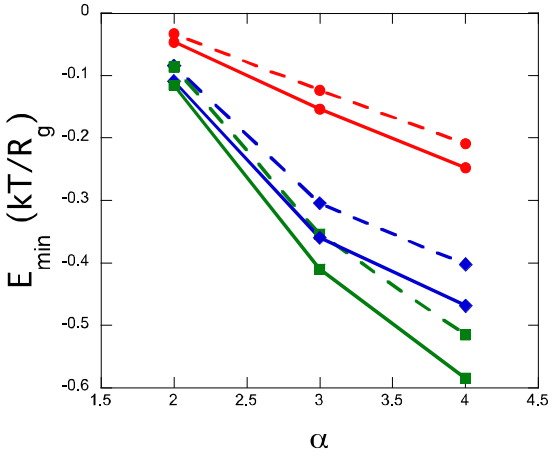
grafting density





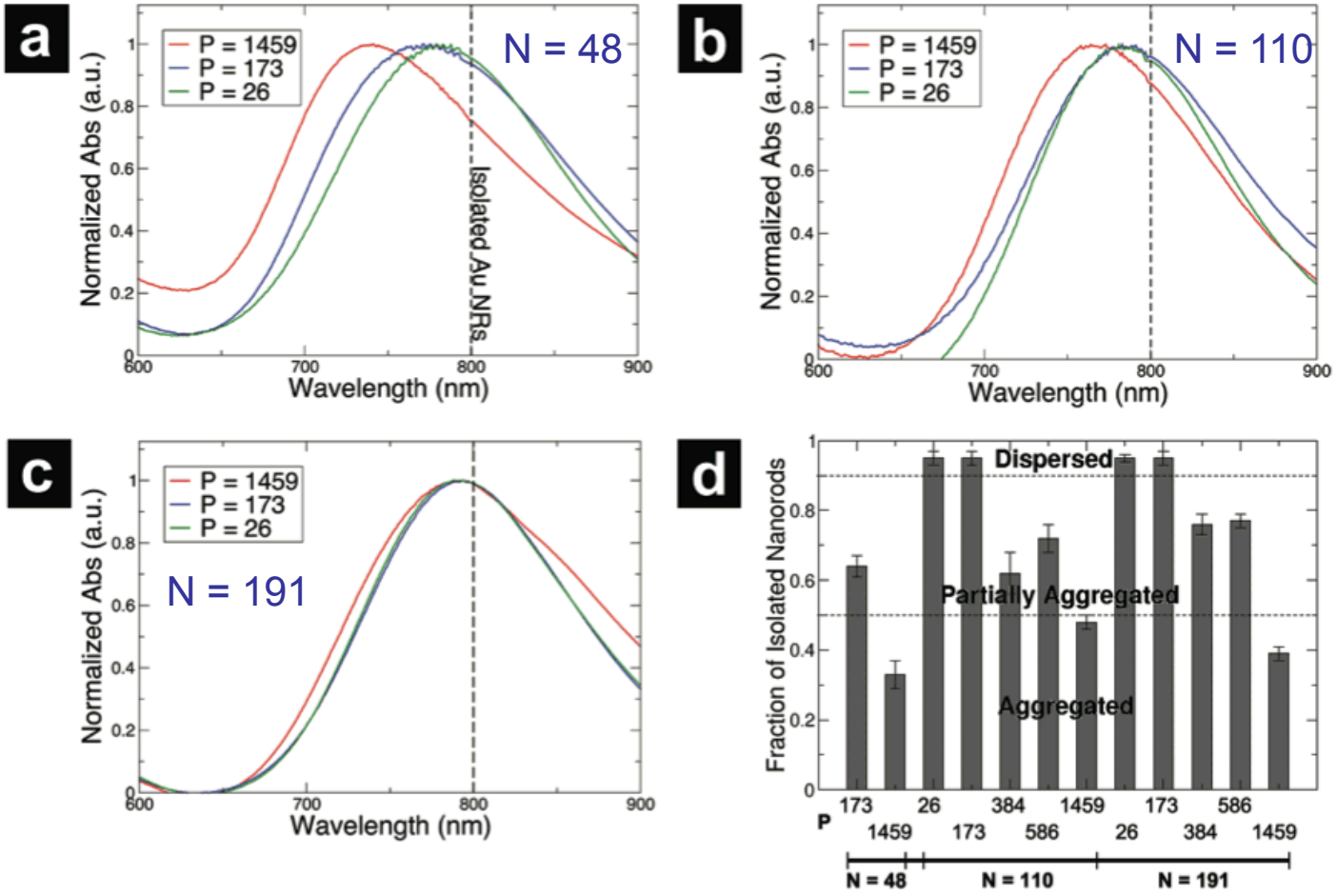
chain ratio





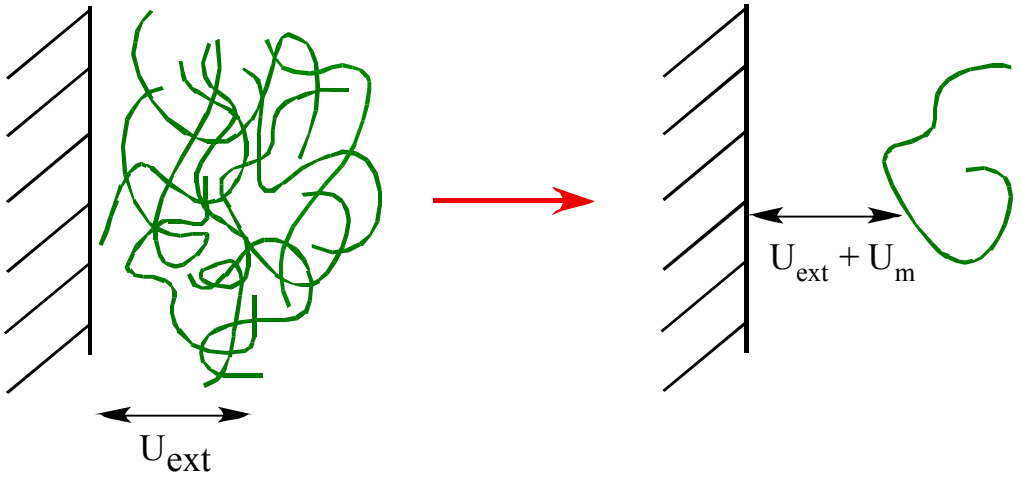
- depth of well decreases with both σ*, α
- r_{min} increases with increasing σ*, decreases with increasing α

Surface Plasmon Resonance



Hore, M. J. A., Frischknecht, A. L., & Composto, R. J. (2012), *ACS Macro Letters*, *1*, 115–121.

Classical (Fluids) Density Functional Theory (DFT)



$$\Omega[\rho_\alpha(\mathbf{r})] = F[\rho_\alpha(\mathbf{r})] + \sum_\alpha \int d\mathbf{r}\rho_\alpha(\mathbf{r})\,[V_\alpha(\mathbf{r}) - \mu_\alpha]$$

Helmholtz free energy *F*: ideal gas term, monomer interactions, bonding

CMS-DFT
(Chandler, McCoy, Singer)

minimize free energy

$$\frac{\delta\Omega}{\delta\rho(\mathbf{r})} = 0 \longrightarrow$$ equations to solve for $\rho(r)$

Fluids-DFT Implementation

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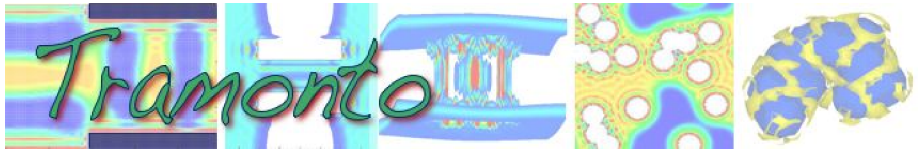
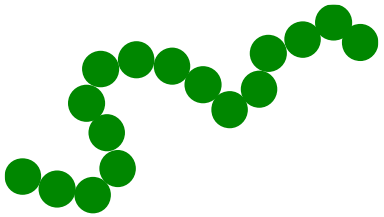
solve nonlinear integral eqtns
- in 3D, Cartesian grid
- modified Newton solver
- parallel

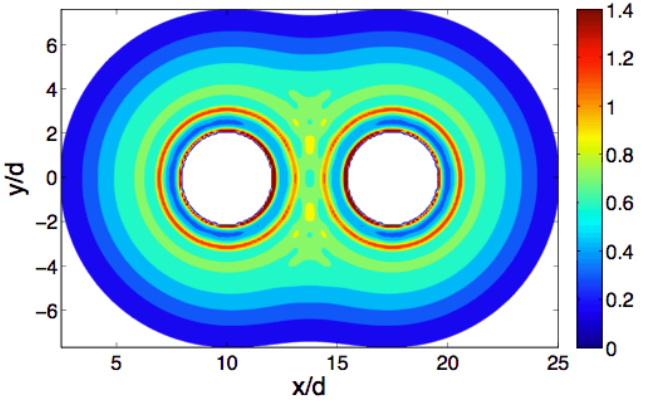


http://software.sandia.gov/tramonto

- **inputs**
  - model of the fluid
    - freely-jointed tangent chains
    - repulsive LJ interactions
  - bulk fluid densities (chemical potentials)
  - surface geometry
    - NR exclude polymer
    - sticky ends attracted with LJ energy



- **outputs**
  - fluid density profiles
  - equilibrium free energy
    - phase diagrams
  - adsorption, stress profiles, ...



Our approach: CMS-DFT

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- chains are flexible
- 2nd order density expansion

Chandler, McCoy, Singer (1986);
McCoy et al. (1990s)

$$\rho_\alpha(r) = \frac{\rho_\alpha^b}{N_\alpha} \sum_{s=1}^{N_\alpha} \frac{G_s(r) G_s^i(r)}{e^{-\beta U_\alpha(r)}}$$

Chain density distribution

$$U_\alpha(r) = V_{ext}(r) - \sum_\gamma \int c_{\alpha\gamma}(r-r')[\rho_\gamma(r') - \rho_\gamma^b]dr'$$

Unknown field

$$c(r) = c_{rep}(r) - u_{att}(r)$$

PRISM Theory RPM Approx

$$G_s(r) = e^{-\beta U_{\alpha,s}} \int w(r-r') G_{s-1}(r') dr'$$

$$G_s^i(r) = e^{-\beta U_{\alpha,s}} \int w(r-r') G_{s+1}^i(r') dr'$$

$$G_1 = G_N^i = e^{-\beta U(r)}$$

$$w(r) = \frac{1}{4\pi\sigma^2}\delta(|r| - \sigma)$$

Chain Architecture (freely-jointed chains)

Input to CMS-DFT: PRISM Theory

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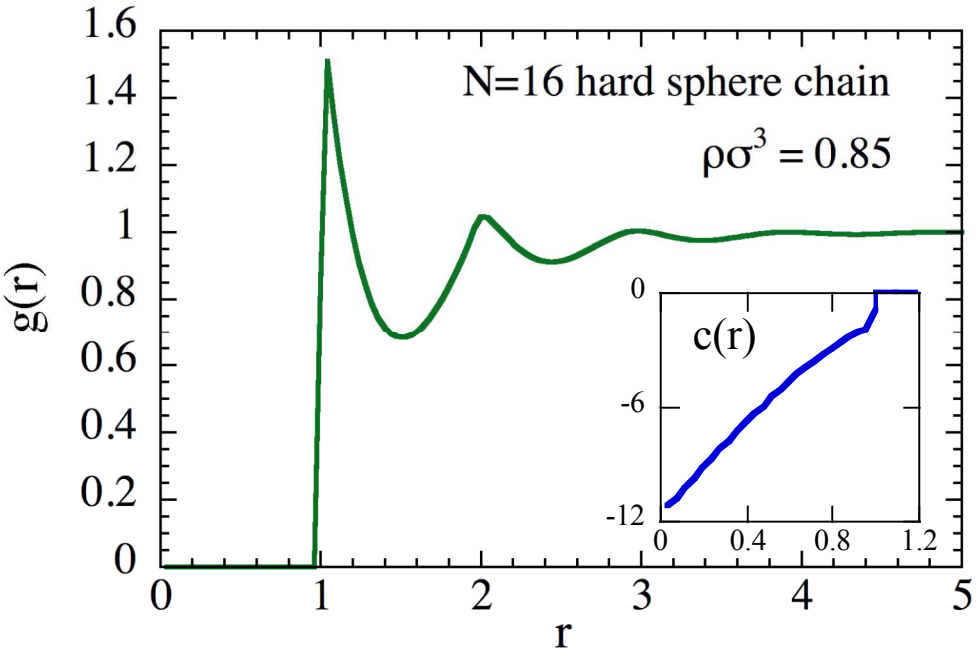
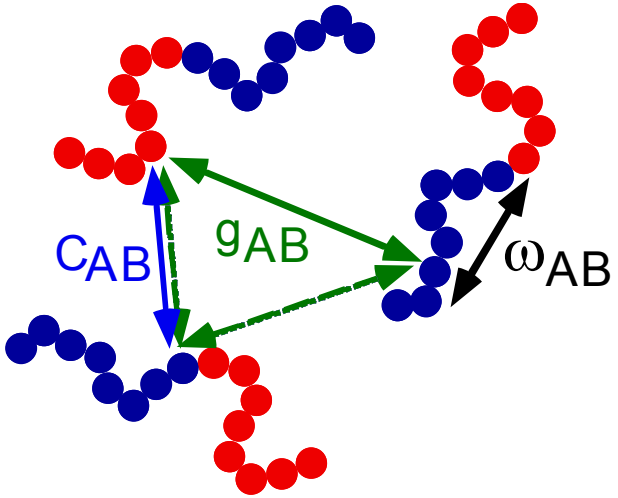
Curro and Schweizer

- Liquid state theory for homogeneous polymer fluids
  - intramolecular correlations ω_{AB}
  - intermolecular correlations $g_{AB}(r)$, $c_{AB}(r)$
- Excellent for repulsive interactions

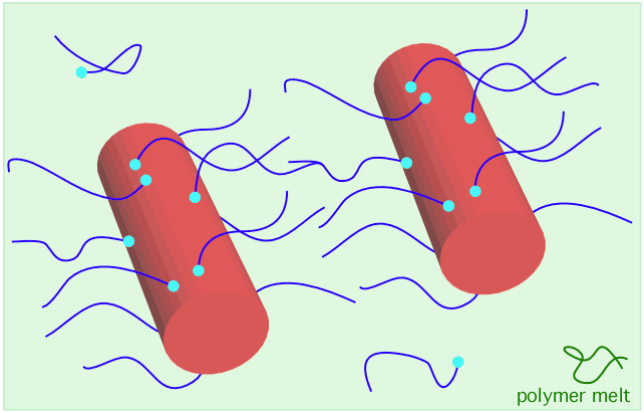




Calculation Details

Sandia National Laboratories

- parallel cylinders
- athermal (repulsive interactions)
- adsorbed chains
  - N = 40
  - $\rho_b a^3 = 0.01$
- matrix chains
  - P = 40,80,120,160
  - $\rho_b a^3 = 0.85$



surface interactions:

- repulsive for matrix chains, all except end on adsorbing chains
- attractive to one end of adsorbing chains, depth ε_e