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Polymer Field Theories and Classical DFT: Applications to Polymer Brushes and Nanocomposites

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Sandia National Laboratories

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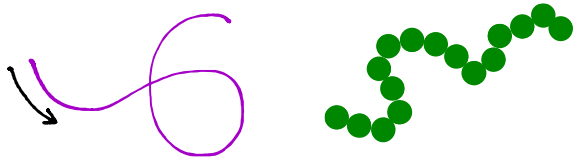
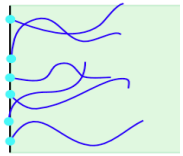
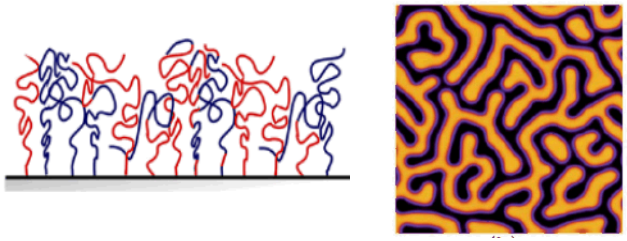
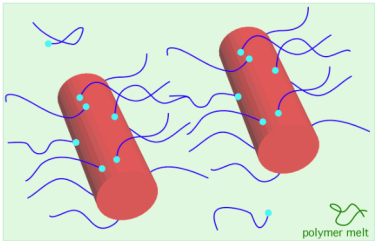
Outline of the talk

- polymer theories
  - self-consistent field theory (SCFT)
  - classical density functional theory (DFT)
- intro to end-grafted polymers
- pattern formation in mixed brushes
  - SCFT calculations
  - comparison to experiment
- polymer brushes on nanoparticles
  - DFT and SCFT calculations
  - comparison to experiment







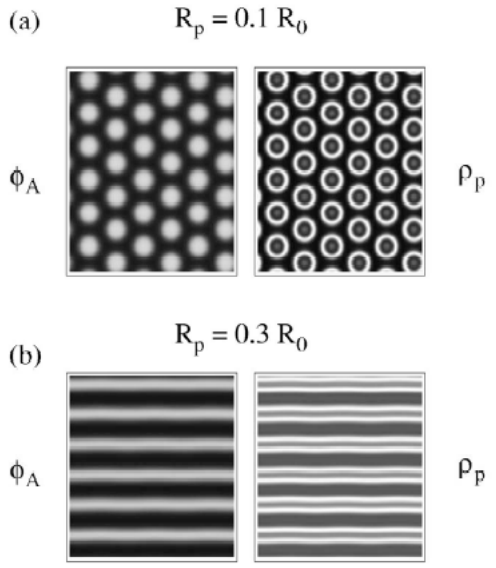


Polymer Theories

- treat larger length/time scales than simulation
- direct access to free energy
- exploration of phase space
- *but* approximate

bulk
- equations of state
- PRISM

inhomogeneous
- self-consistent field theory (SCF)
- classical density functional theory (DFT)
- hybrid SCF/DFT

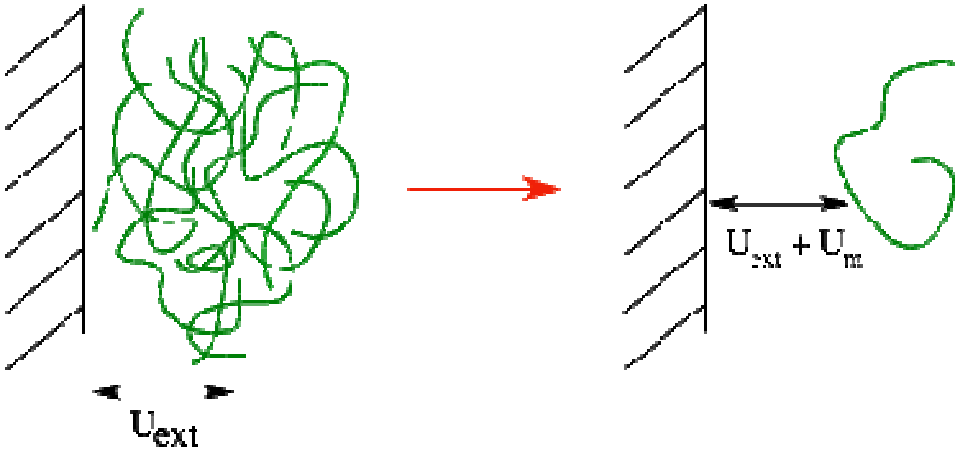


Balazs, Curr. Opin. Solid St. & Mat. Sci., 2003

Inhomogeneous Theories

SCFT and DFT

basic idea: replace many chain problem with single chain in a field



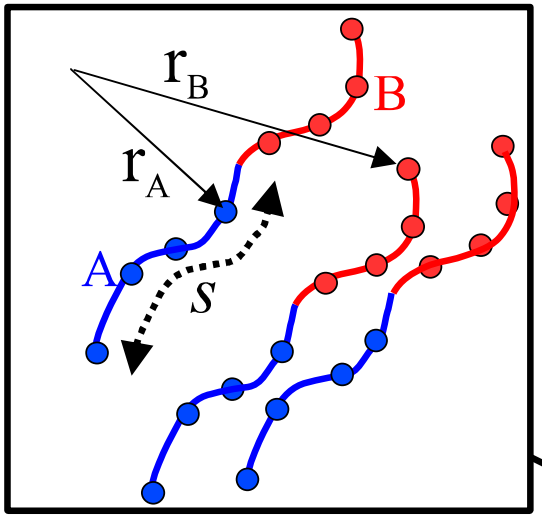
input: a model for the system
chain type
interactions

output: minimized free energy
density profiles

Self-Consistent Field Theory

From Particles to Fields

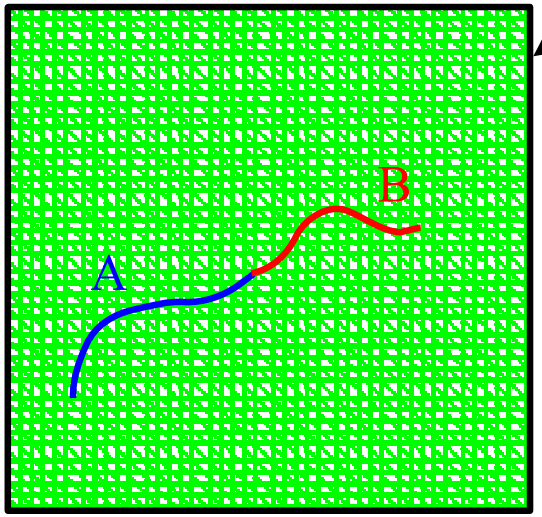
Example: diblock copolymers



$$Z = \int \mathcal{D}\mathbf{r}_A \, \mathcal{D}\mathbf{r}_B \, e^{-\beta H[\mathbf{r}_A, \mathbf{r}_B]}$$

$$\beta H = \frac{3}{2b^2} \sum_{\alpha=1}^{n} \int_0^N ds \left(\frac{d\mathbf{r}_\alpha(s)}{ds} \right)^2 + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \, \hat{\rho}_K(\mathbf{r}) v_{KL}(\mathbf{r} - \mathbf{r}') \hat{\rho}_L(\mathbf{r}')$$

Hubbard-Stratonovich transformation



$$Z = \int \mathcal{D}w_A \, \mathcal{D}w_B \, e^{-\beta H[w_A, w_B]}$$

$$\beta H = \int d\mathbf{r} \, h(w_A(\mathbf{r}), w_B(\mathbf{r})) - n \, \ln Q[iw_A, iw_B]$$

Q = *single-chain partition function*

G. H. Fredrickson

Sandia National Laboratories

Mean-Field Approximation: SCFT

- SCFT is derived by a *saddle point* approximation to the FT:

$$e^{-F} \equiv Z = \int \mathcal{D}[w] e^{-H[w]} \sim e^{-H[w^*]}$$

- The approximation is asymptotic for $C \to \infty$
- We can simulate the field theory at two levels:
  - "Mean-field" approximation (SCFT): F ≈ H[w*]
  - Full stochastic sampling of the complex field theory: "Field-theoretic simulations" (FTS)

Typical Features of SCFTs

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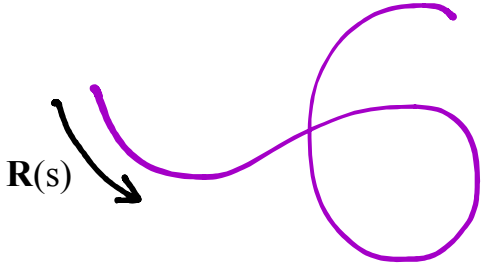
typically (but not always):

- use Gaussian thread model of chain
  - leads to PDE for chain propagators

$$U_0[\mathbf{R}(s)] = \frac{3}{2a^2}\int_0^N ds \left|\frac{\partial \mathbf{R}(s)}{\partial s}\right|^2$$



- use Flory-Huggins free energy for interactions

$$U[\mathbf{R}_A(s), \mathbf{R}_B(s)] = v_0 \int d\mathbf{r}\chi_{AB}\phi_A(\mathbf{r})\phi_B(\mathbf{r})$$

- incompressible (or nearly incompressible)
- many numerical solution methods (nonlinear equations)
  - real space
  - Fourier space

- model polymers on the length scale of the chain (R_g)
- great for phase behavior, structure

To learn more about SCFT

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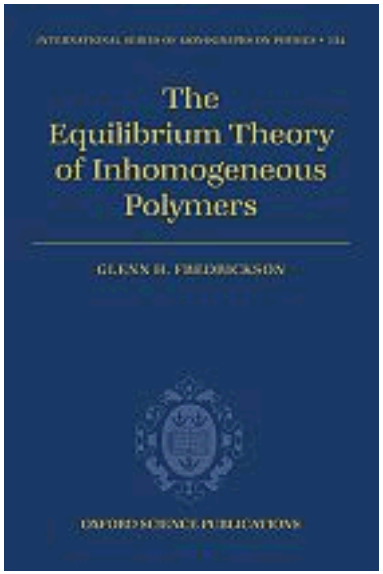
Read Glenn Fredrickson's book!

The Equilibrium Theory of Inhomogeneous Polymers

Glenn H. Fredrickson

Oxford Univ. Press, 2006



Density Functional Theory (DFT)

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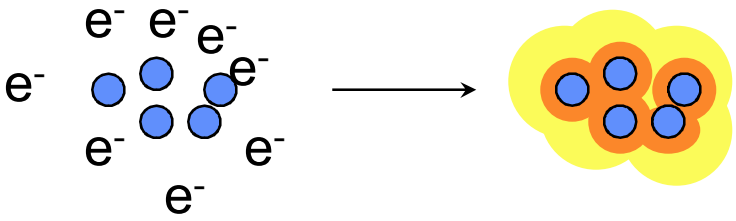
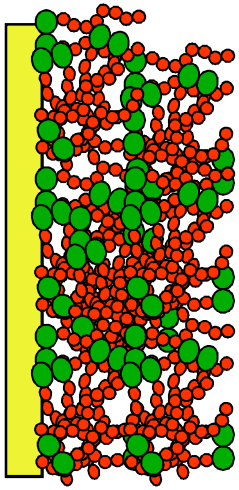
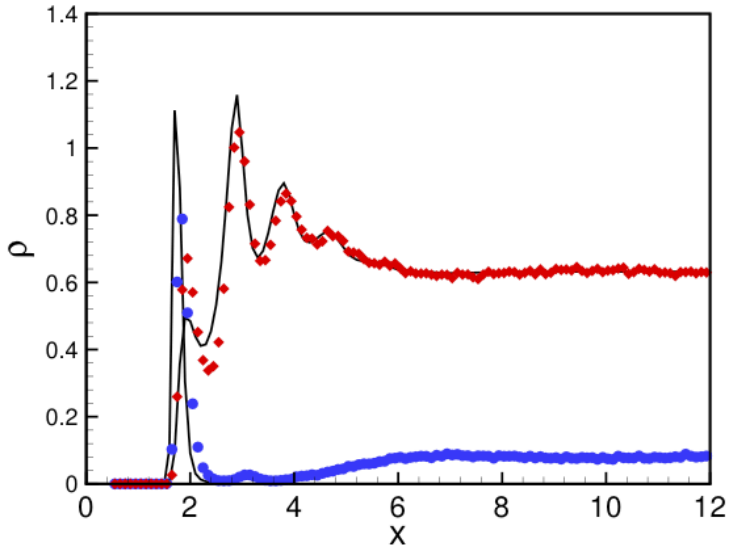
$$\Omega[\rho(r)] : V(r) \rightarrow \rho(r)$$

External field — Density profile



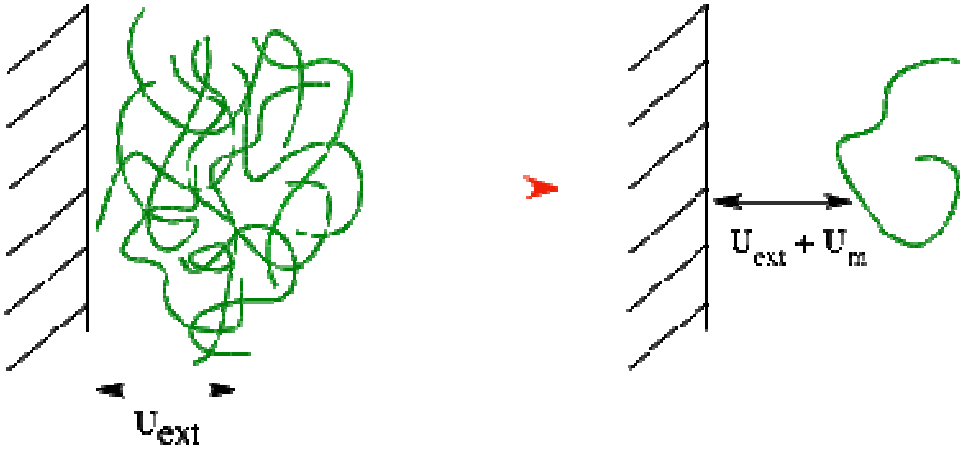
Electronic Structure
Minimizing quantum Hamiltonian





Fluid Structure
Minimizing free energy
(Often open system with fixed chemical potential)

Structure of Fluids 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, hard sphere, attractions, bonding, ...

minimize free energy

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

Typical Features of Polymer DFTs

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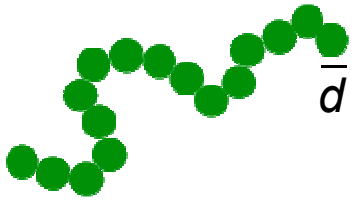
- use freely-jointed chain of hard spheres for model
  - includes segment length scale *d*
  - leads to integral equations for chain propagators



- use hard sphere repulsions + LJ attractions for interactions
  - directly comparable to MD, MC simulations

- compressible
- different types of classical DFTS:
  - CMS-DFT (Chandler, McCoy, Singer)
    - based on 2nd order expansion of free energy
  - weighted DFTs (esp. Wu, Chapman)
    - based on perturbations to hard sphere reference fluid

    - model packing effects + chain length scale
    - great for comparison to simulation
    - local structure, phase behavior, mixtures with particles, etc.

Tramonto: Sandia's DFT Code

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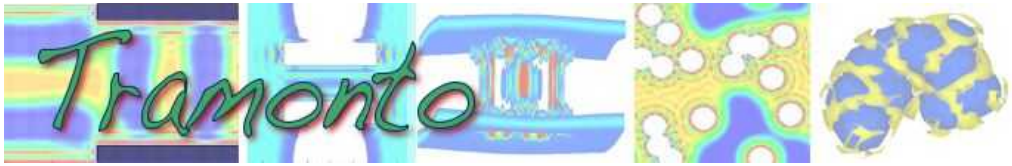

http://software.sandia.gov/tramonto

F-DFTs = nonlinear integral equations

- solve in 3D, Cartesian grid
- modified Newton's method, Picard solver
- parallel
- sophisticated linear solver algorithms
- arc-length continuation algorithms

- hard spheres
- polymers
  - CMS-DFT
  - modified iSAFT
- mean-field attractions
- charged systems
  - includes Poisson solver

The Trilinos Project

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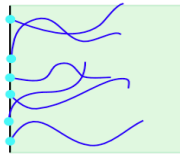
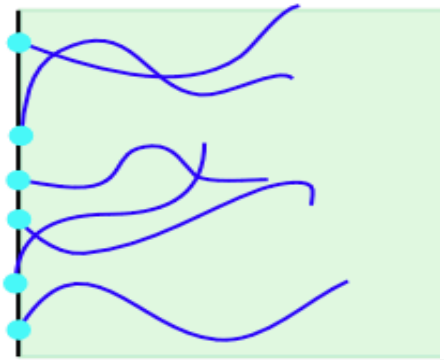
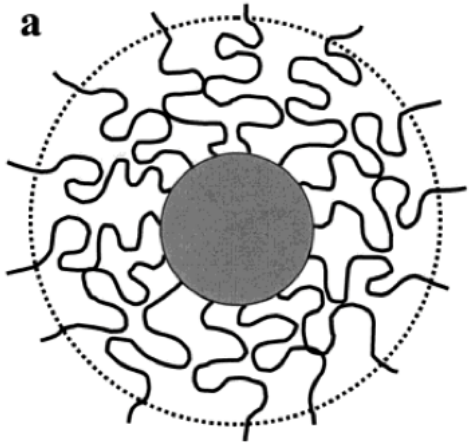


Polymer Brushes



- graft or adsorb polymer to surface
- if dense enough, chains stretch away from surface

height of brush:
balance stretching energy penalty vs. interactions



curved brushes

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

Theory for Polymer Brushes

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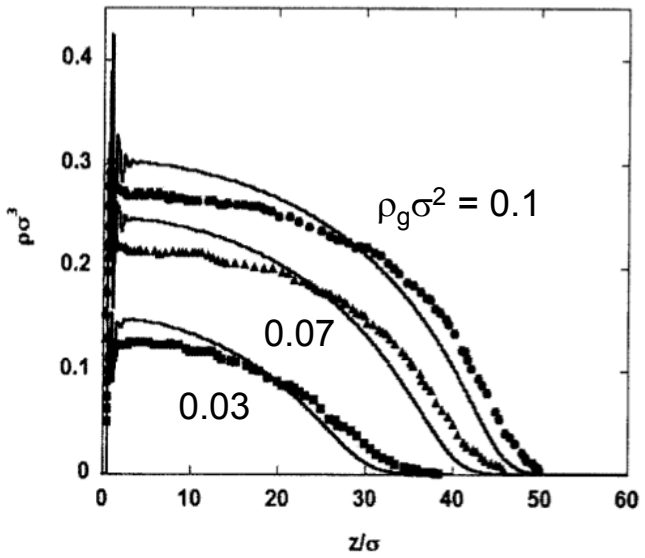
DFT and SCFT capture basic physics

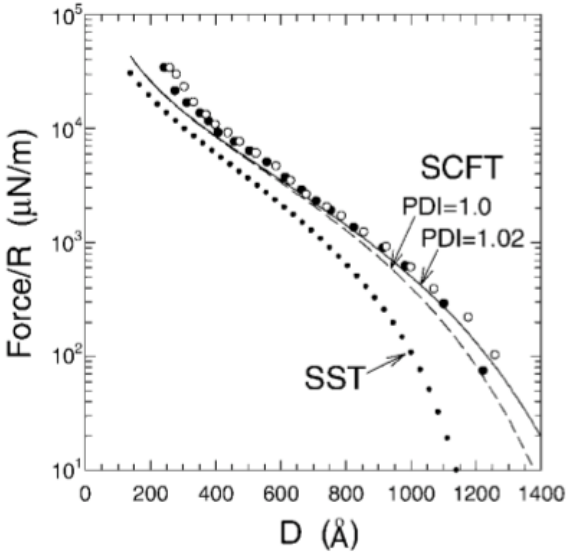
DFT vs. MD simulation



brush in vacuum
N = 100

Jain et al., J. Chem. Phys. 128, 154910 (2008); (simulations from Grest and Murat, 1989)

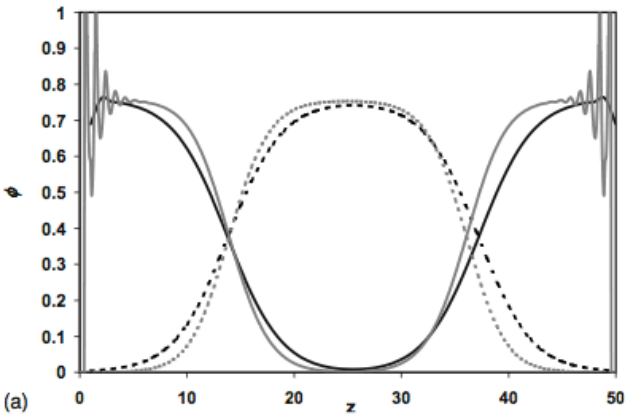
SCFT vs. Experiment



force between brushes in solvent

Kim and Matsen, Macromolecules 42, 3430 (2009); (exp. from Taunton et al, 1988)

DFT vs. SCFT



brushes in polymer melt
N = P = 100, ρ_g = 0.1

Jain et al., J Chem Phys 131, 044908 (2009)

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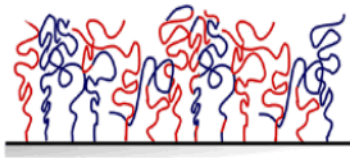
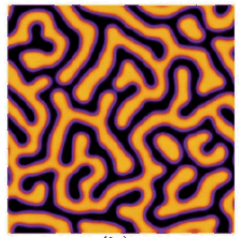
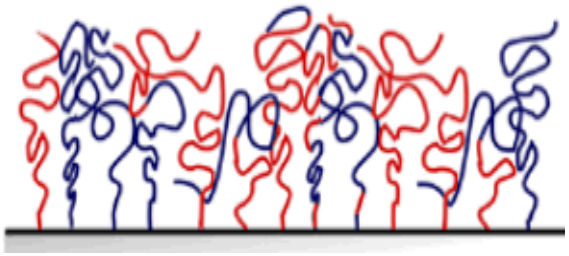


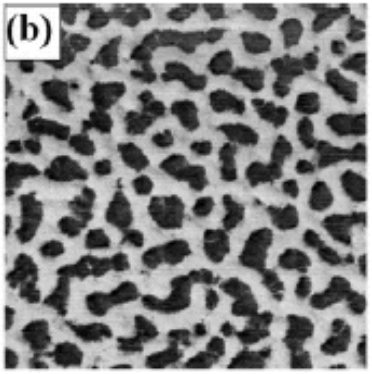


Mixed Polymer Brushes

- A mixture of two polymers in which one end of each polymer chain is tethered to the substrate
- Phase separate in a manner similar to block copolymer thin films

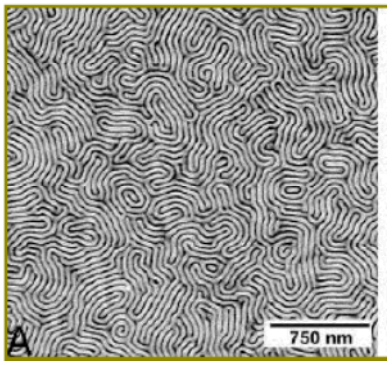


"Ripple" phase of symmetric mixed brush (PS – PMMA) under non-selective solvent



Usov et al., *Macromolecules*, *40,* 8774 (2007)

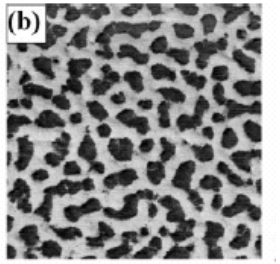
Perpendicular lamella of PS-b-PMMA block copolymer thin film

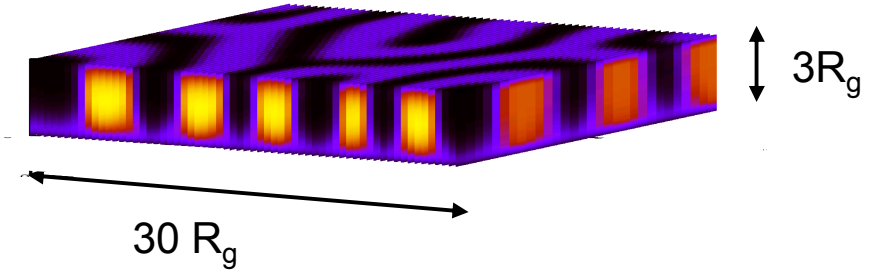


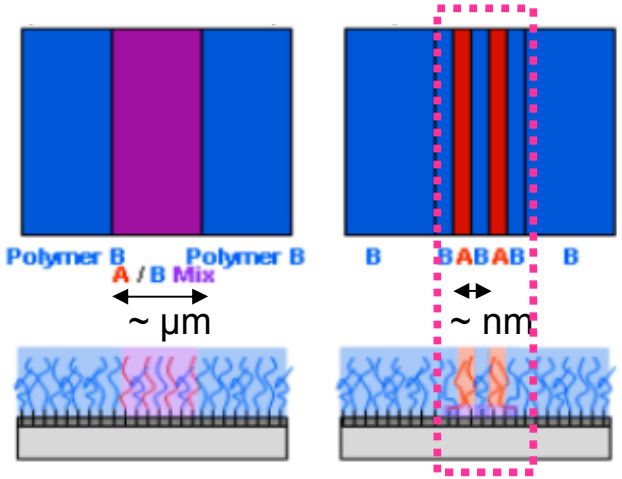
Daniel J.C. Herr, *Future Fab. Intl. Sec.5.* Issue 18 (2005)

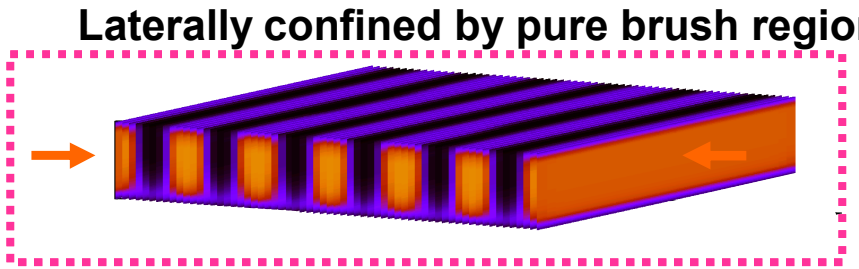
Directed Assembly?

- New graphoepitaxy-type technique
- Mixed polymer brushes laterally confined by pure brush region



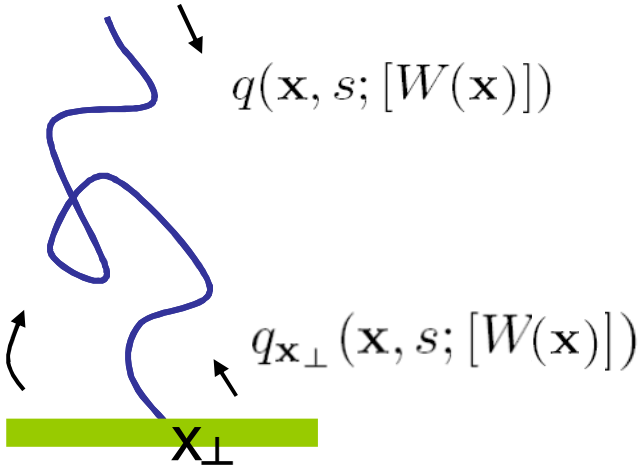






SCFT of Melt Mixed Brush

- melt with high grafting density
- brush chains A, B: Flory interaction energy χ
- large polymer/air surface tension so flat top surface
- “walls” in z-direction (substrate + top surface)
- periodic boundaries in (x,y)



Free-end: uniform initial condition

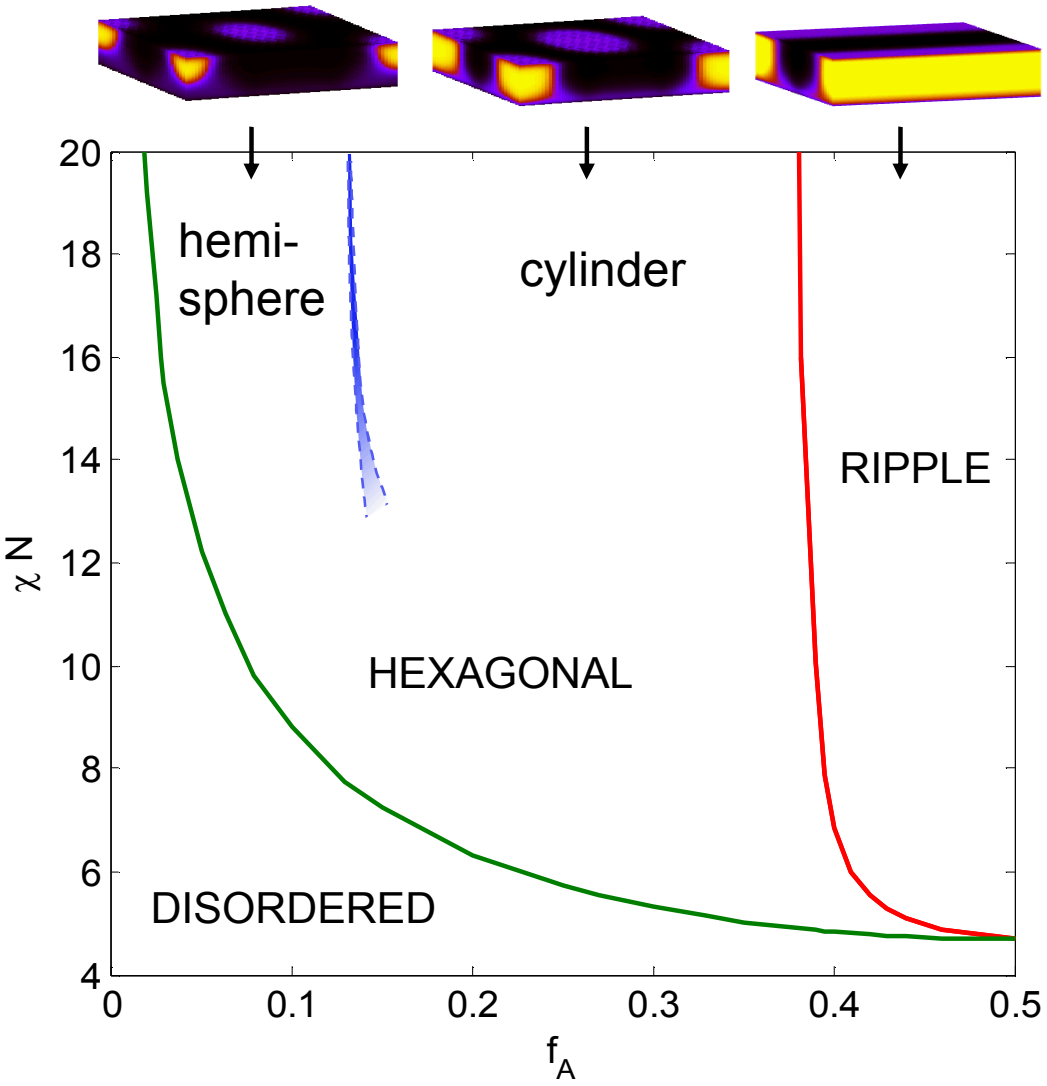
Tethered-end: initialized with a delta function

$$q_{\mathbf{x}_\perp}(\mathbf{x}, 0; [W]) = \delta(\mathbf{x} - \mathbf{x}_\perp)$$

Generalize to arbitrary grafting density distribution

$$g_{A,B}(\mathbf{x}_\perp, z)$$

SCFT Phase Diagram



Directed Assembly in SCFT

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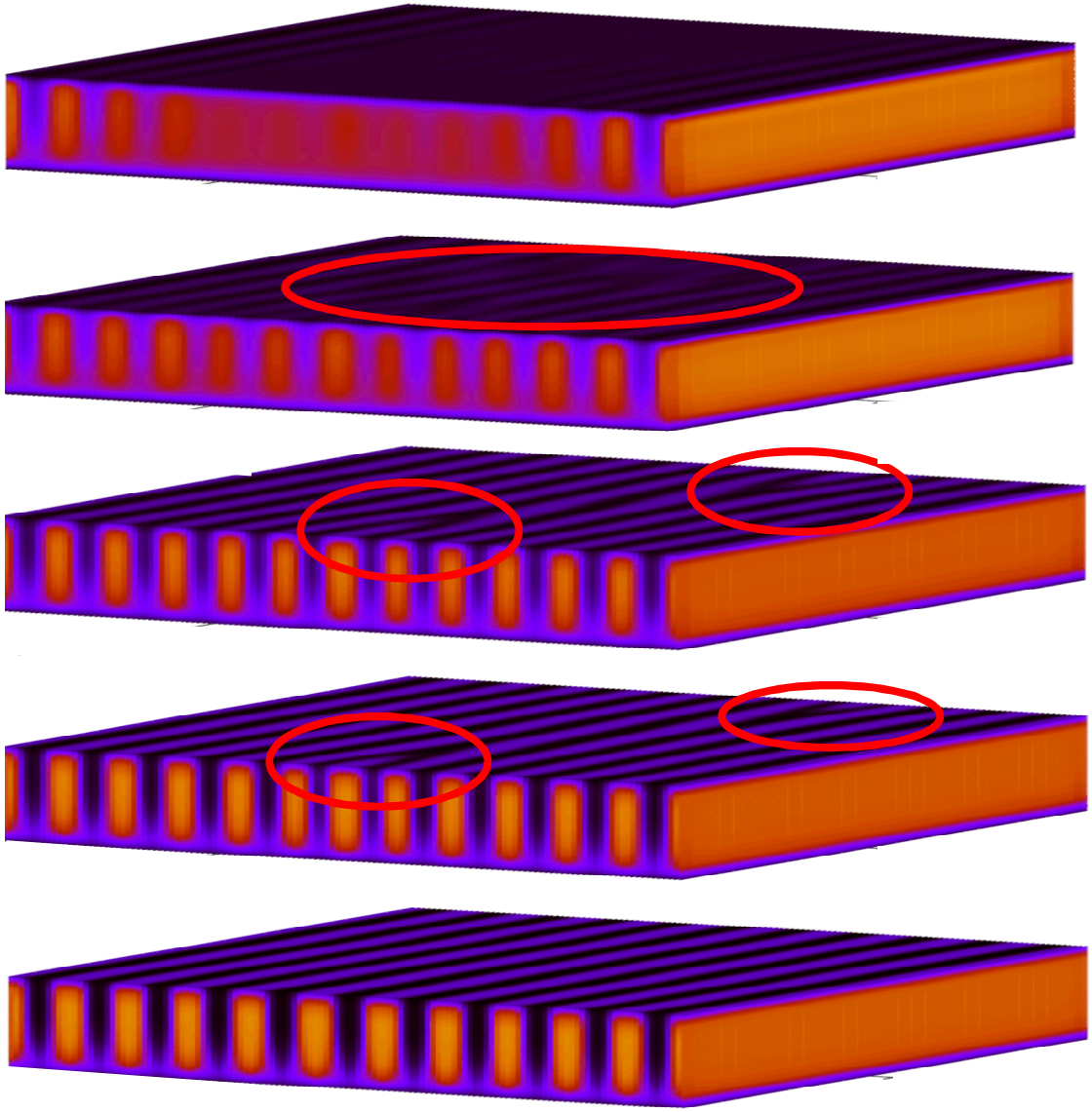
$f_A = 0.5$
system size
~ 56 R_g

Evolution of long-ranged ordering

anneal χN slowly



Directed Assembly of Cylinders

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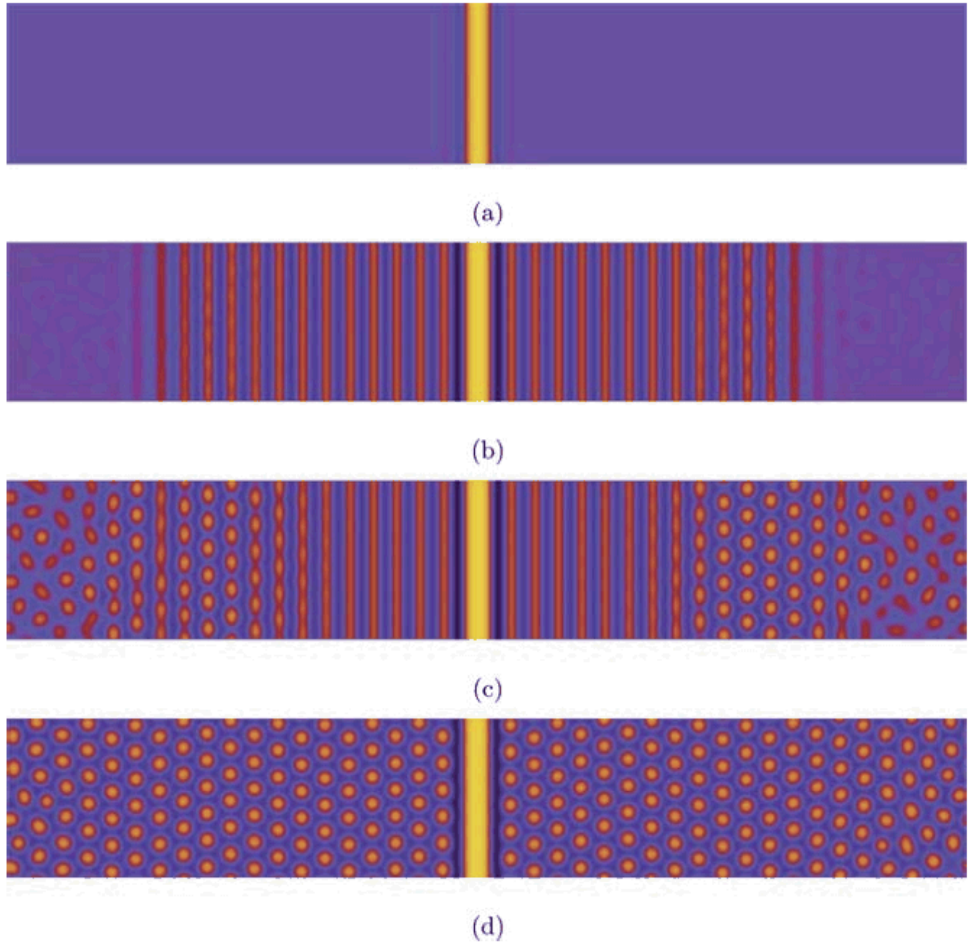
$f_A = 0.3$

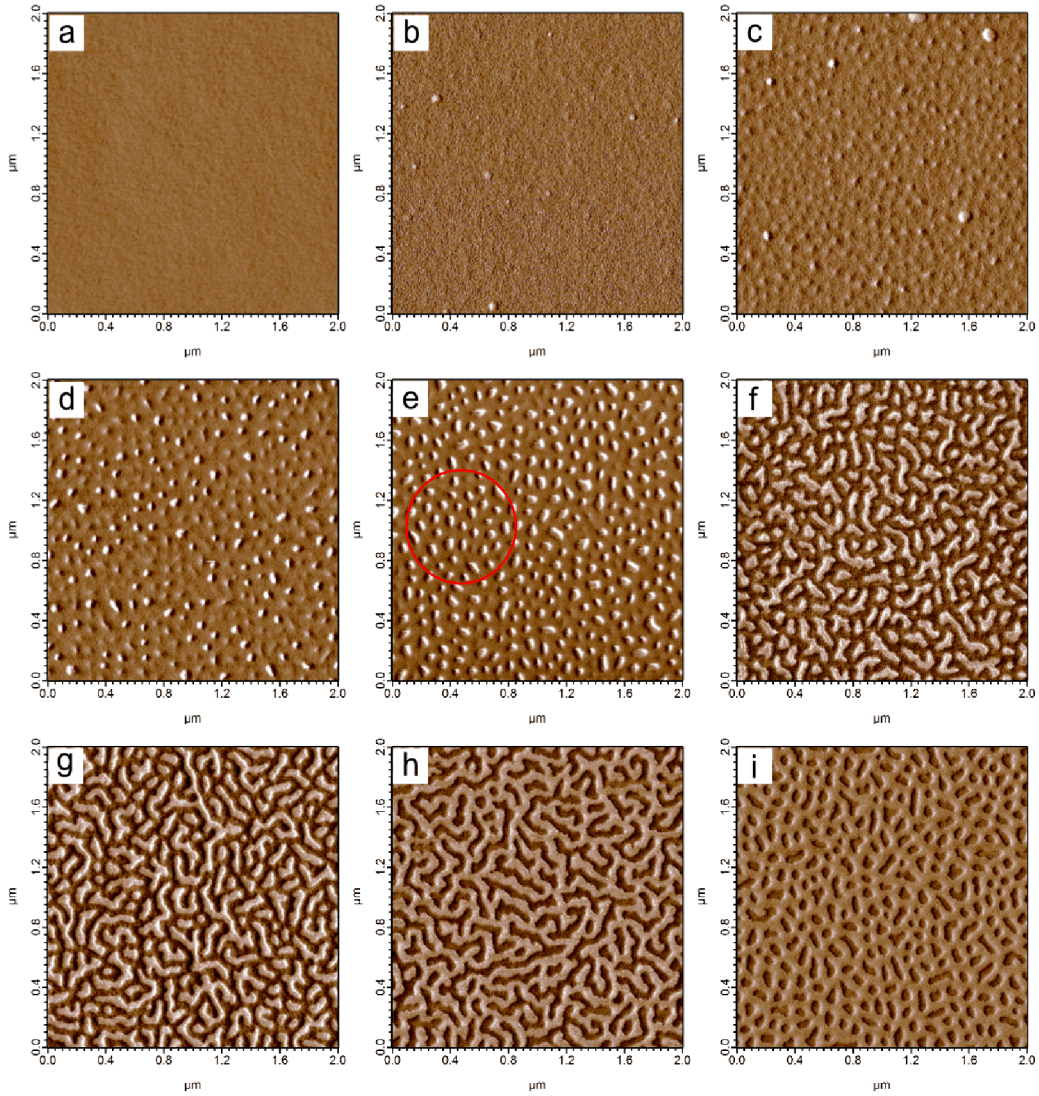
$\chi N = 4.5$

$\chi N = 6.0$



Experimental Phases

- PS-PMMA mixed brushes
- solvent anneal
- PS volume fraction from 0.0 to 0.68
- AFM phase contrast images



Price et al., *Macromolecules* **45**, 510 (2012)

Why the difference?

spatial variations in grafting density!

SCFT

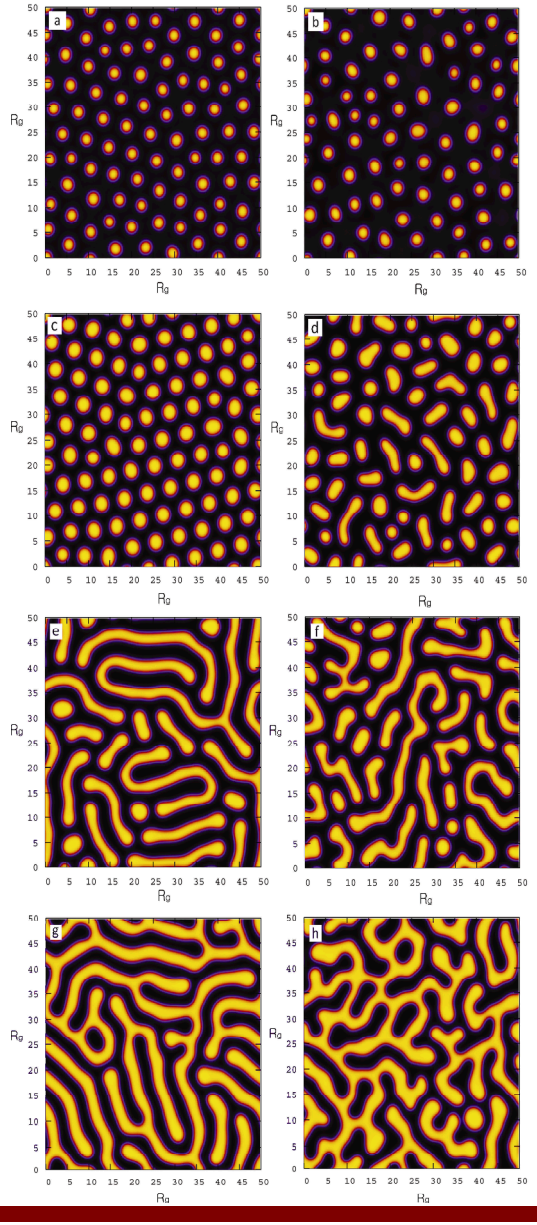
uniform grafting density (left)

$$g_A(\mathbf{x}_\perp) = f_A$$

Gaussian random distribution of grafting (right)

$$\langle (g_A(\mathbf{x}_\perp) - f_A)(g_A(\mathbf{x'}_\perp) - f_A) \rangle = \Lambda^2 \exp(-|\mathbf{x}_\perp - \mathbf{x'}_\perp|^2 / 2\sigma^2)$$

$\sigma = 0.5 R_g$, $\Lambda^2 = 0.02$



$f_A = 0.1$

$f_A = 0.3$

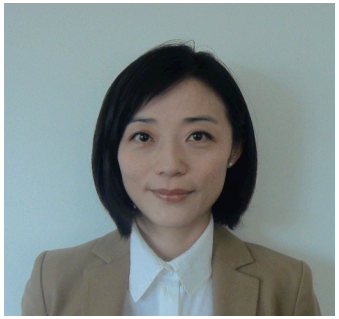
$f_A = 0.4$

$f_A = 0.5$

Conclusions

- spatial variations in grafting destroy long-range order
- good qualitative agreement in phase diagram
- can direct self-assembly
  - with sufficiently uniform grafting density

Acknowledgments:



Su-Mi Hur

Glenn Fredrickson

Dale Huber

UC Santa Barbara

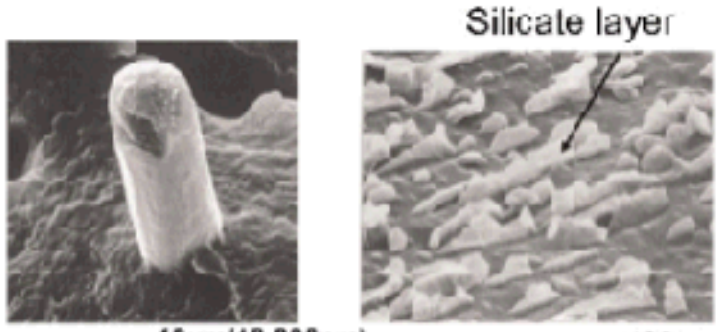
Hur et al., *Soft Matter* **7**, 8776 (2011); Price et al., *Macromolecules* **45**, 510 (2012)

S-M. Hur, A. L. Frischknecht, D. L. Huber, and G. H. Fredrickson, *Soft Matter* **9**, 5341 (2013).

Polymer Nanocomposites

majority component: polymer
minority component: particle with dimensions < 100 nm

- improved material properties
- mechanical
- electrical
- optical
  - need control over dispersion

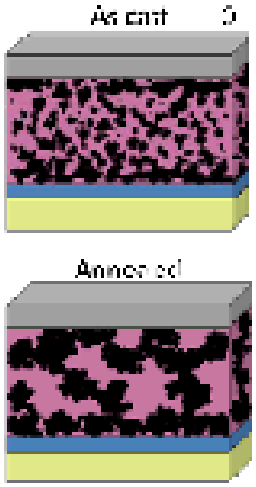


glass fiber

clay particle (in nylon)

Okada & Usuki, Macromol. Mater. Eng., 2006

- functional materials
- self-healing
- photovoltaics
- others...
  - need control over interfaces

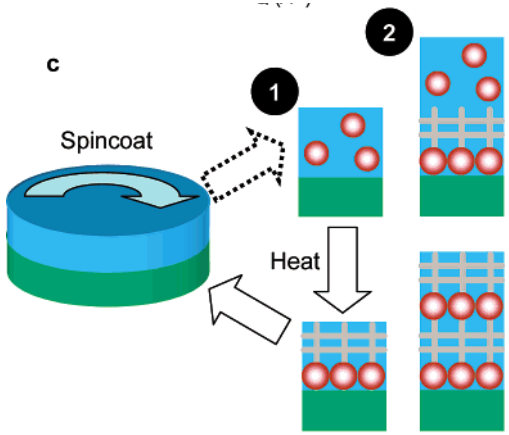


Cartoon of PCBM/P3HT solar cell

Kiel et al, Phys Rev Lett, 2010

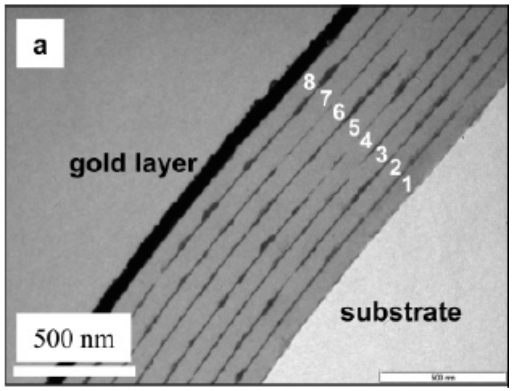
Digression: NPs in Polymer Films

nanoparticles tend to go to surfaces

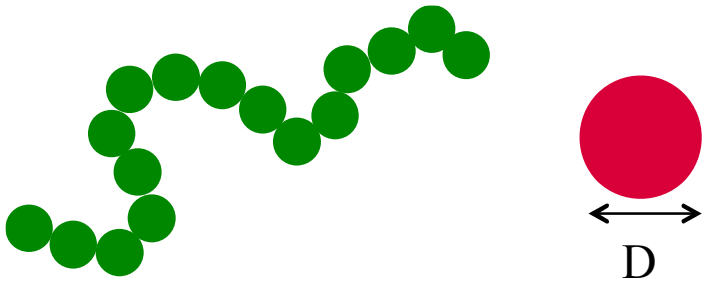


athermal system: model as hard spheres
only interactions are entropic
polymer and particles are fluid components

ideal for DFT: capture packing interactions



Krishnan et al., *Nano Lett* (2007)



Weighted DFT: iSAFT

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

$$F = F^{id} + F^{hs} + F^{ch}$$

ideal gas part:

$$F^{id}[\rho_\alpha(\mathbf{r})] = kT \sum_\alpha \int d\mathbf{r}\rho_\alpha(\mathbf{r})\,[\ln \rho_\alpha(\mathbf{r}) - 1]$$

hard sphere functional:

$$F^{hs}[\rho_\alpha(\mathbf{r})] = kT \int d\mathbf{r}\Phi[n_\gamma(\mathbf{r})]$$

("White Bear" FMT, Roth et al., 2002)

chain bonding contribution:

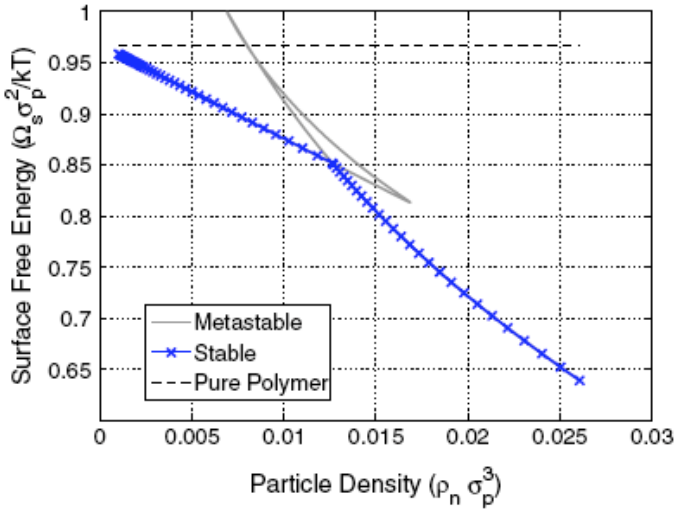
$$F^{ch}[\rho_\alpha(\vec{r})] = kT \int d\vec{r}' \sum_{\alpha=1}^{m} \rho_\alpha^{\text{seg}}(\vec{r}') \sum_{\alpha}^{\{\alpha'\}} \left(-\frac{1}{2} \ln \int d\vec{r}'' \frac{\delta(|\vec{r}' - \vec{r}''| - \sigma^{\alpha\alpha'})}{4\pi(\sigma^{\alpha\alpha'})^2} y^{\alpha\alpha'}(\vec{r}', \vec{r}'') \rho_{\alpha'}^{\text{seg}}(\vec{r}'') + \frac{1}{2} \right)$$

minimize free energy

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

S. Tripathi and W.G. Chapman, *Phys. Rev. Lett.* **94**, 087081 (2005); *J. Chem. Phys.* **122**, 094506 (2005); S. Jain et al., *J. Chem. Phys.* **127**, 244904 (2007)

A Layering Phase Transition

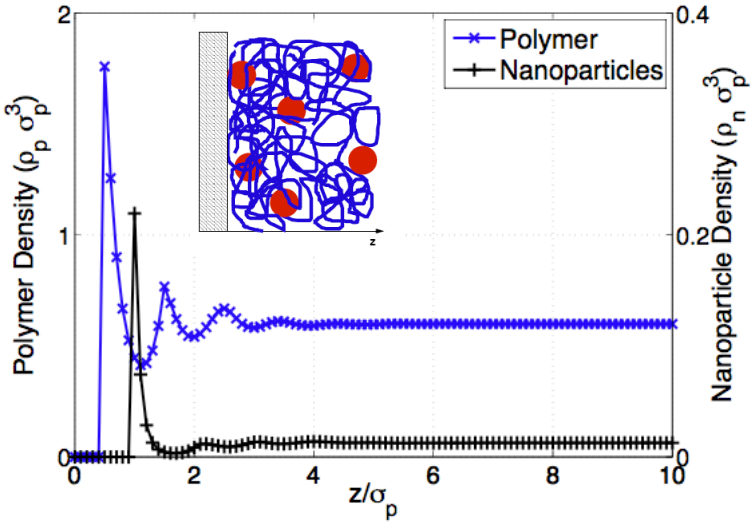


N = 40, D=2 ∫ H3nm

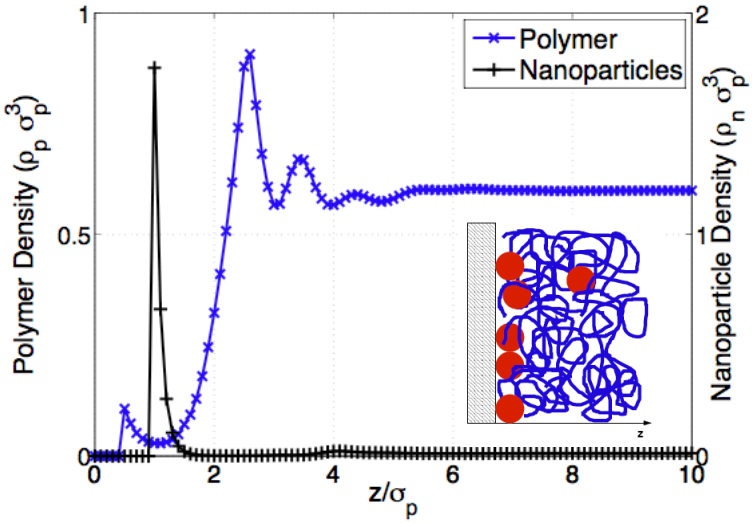
- fixed total packing fraction

$$\rho_p \sigma^3 + \rho_{np} \sigma_{np}^3 = 0.79$$

- first-order transition
- entropy-driven



typical fluid structure



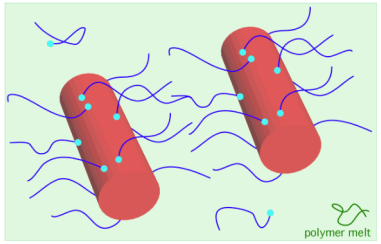
NP layer, areal coverage 0.82

E. S. McGarrity et al., *Phys. Rev. Lett.*, **99**, 238302 (2007).

Outline of the talk

Sandia National Laboratories

- polymer theories
  - self-consistent field theory (SCFT)
  - classical density functional theory (DFT)
- intro to end-grafted polymers
- pattern formation in mixed brushes
  - SCFT calculations
  - comparison to experiment
- polymer brushes on nanoparticles
  - DFT and SCFT calculations
  - comparison to experiment



Polymer-Grafted Nanorods

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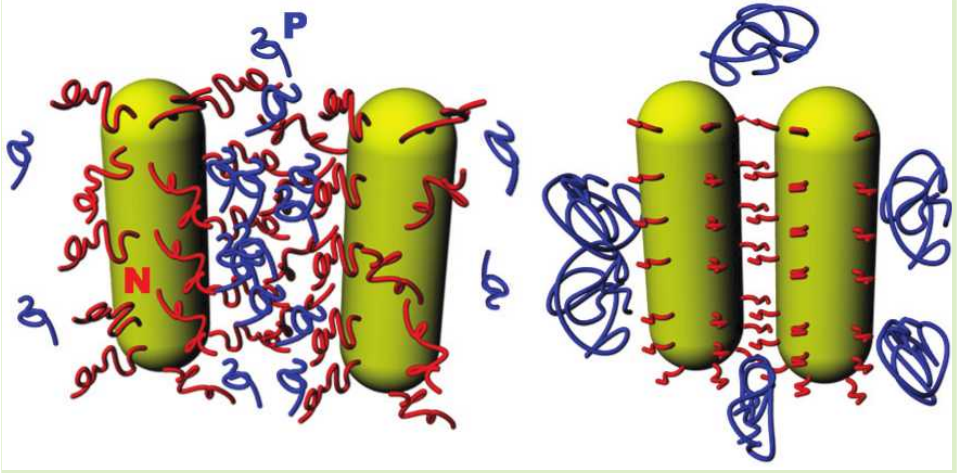
What controls nanorod dispersion/aggregation?

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

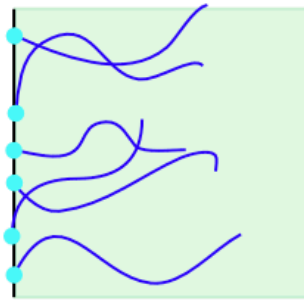


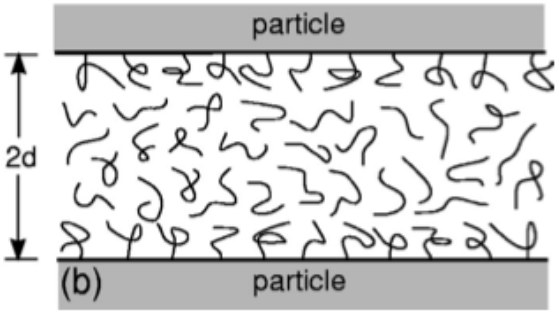
athermal systems:

PS brush in PS

PEO brush in PEO

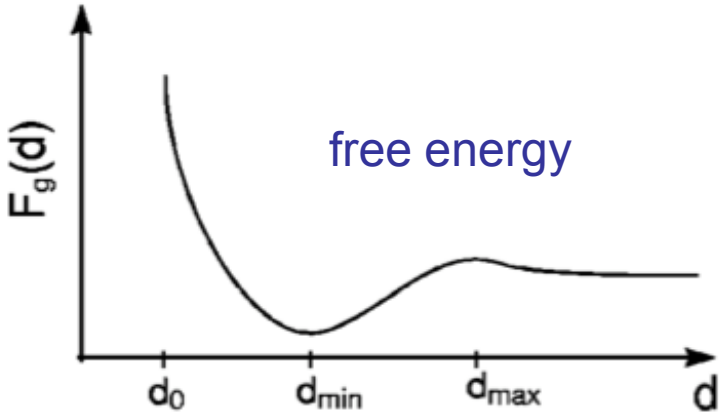
Brush-Brush Interactions

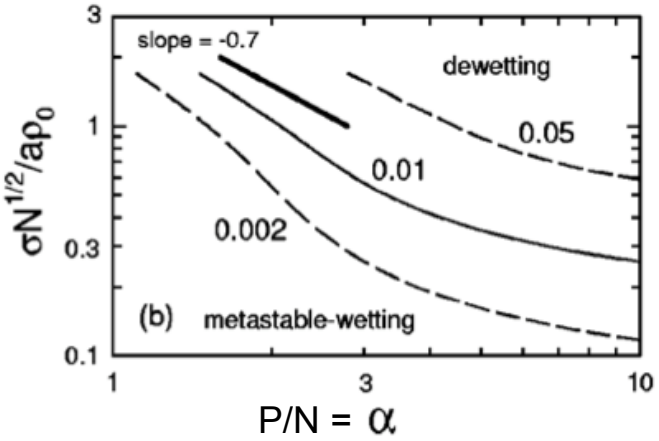




autophobic dewetting:

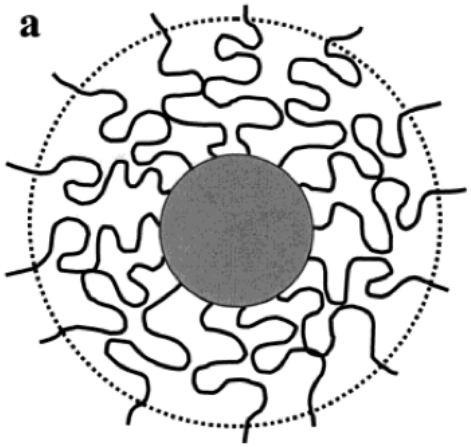
- entropy cost for matrix chains to enter brush
- leads to positive brush-matrix surface tension
- brushes are attracted





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

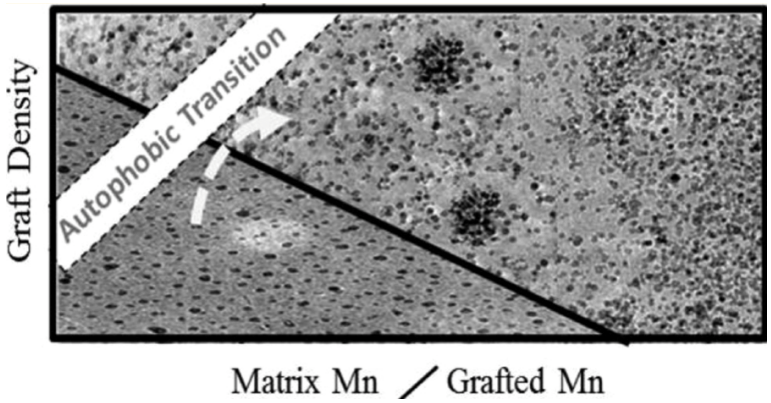
Brushes on Curved Surfaces

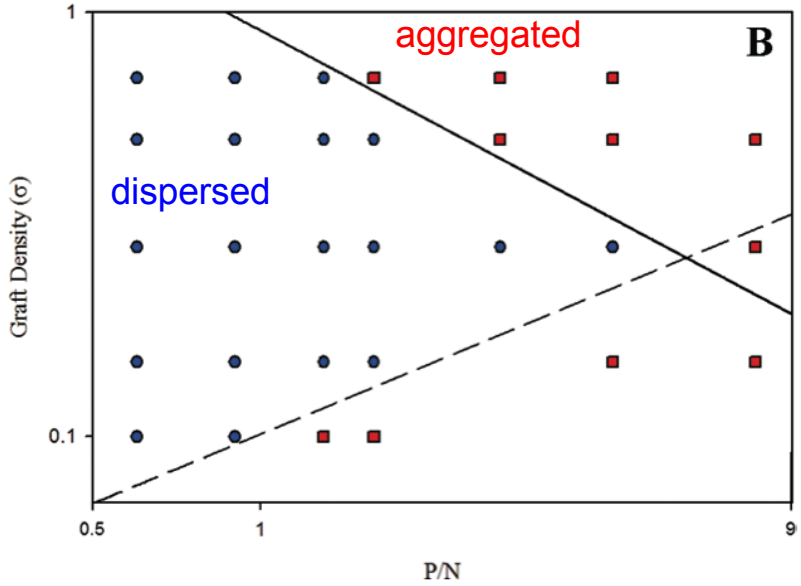


- more volume than on flat surface at same grafting density
- chains splay out more
- brush is less extended

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

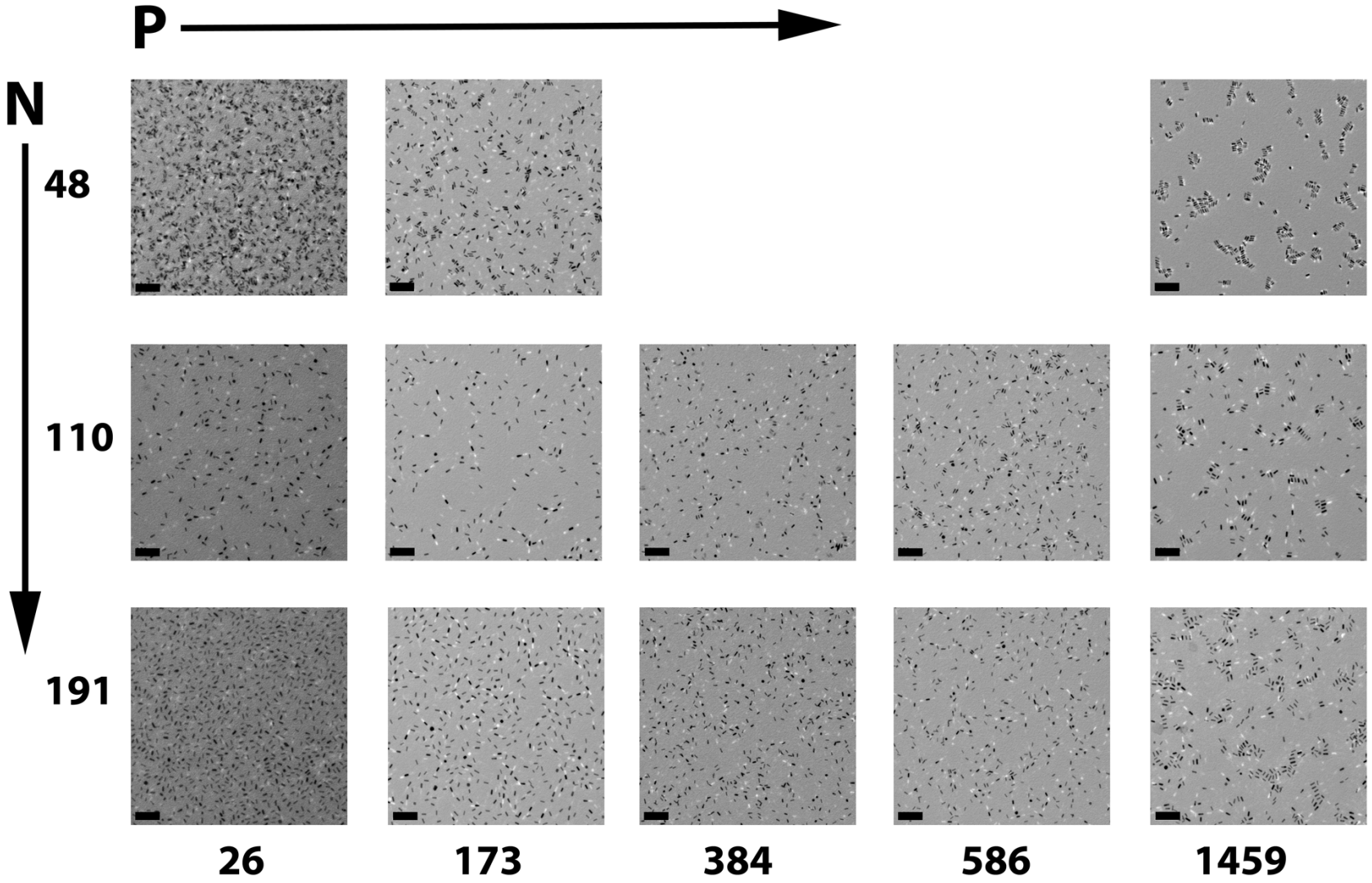
PS-silica in PS





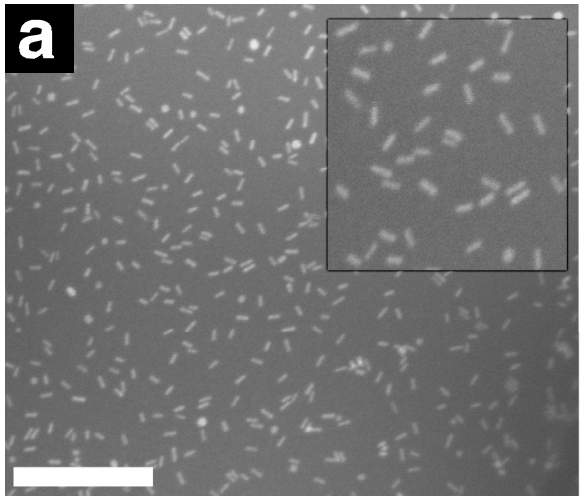
Sunday, D., Ilavsky, J., & Green, D. L. (2012). *Macromolecules*, *45*, 4007–4011.

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

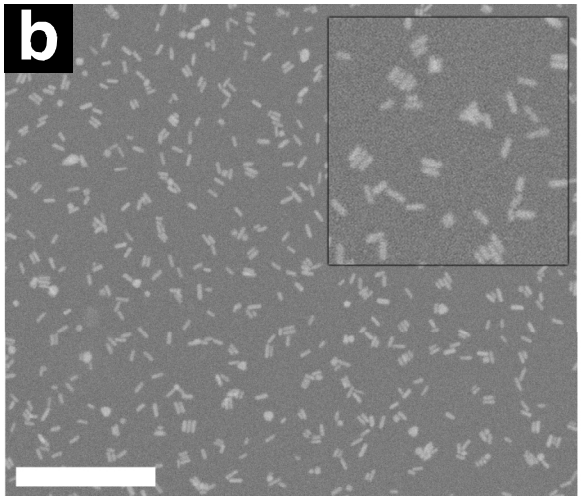


Hore, M. J. A., Frischknecht, A. L., & Composto, R. J. (2012), *ACS Macro Letters*, *1*, 115–121.

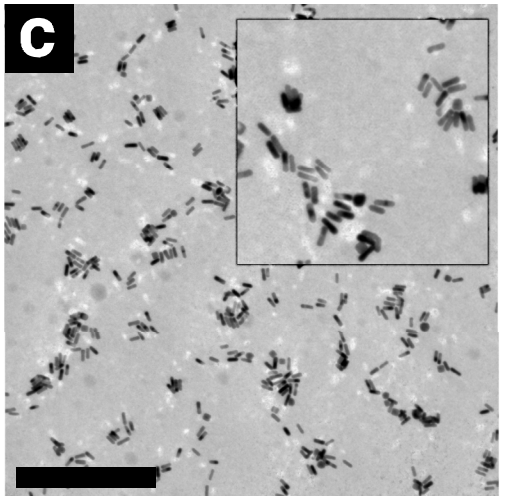
PEO-Au(*N*):PEO(*P*)



P/N = 0.43

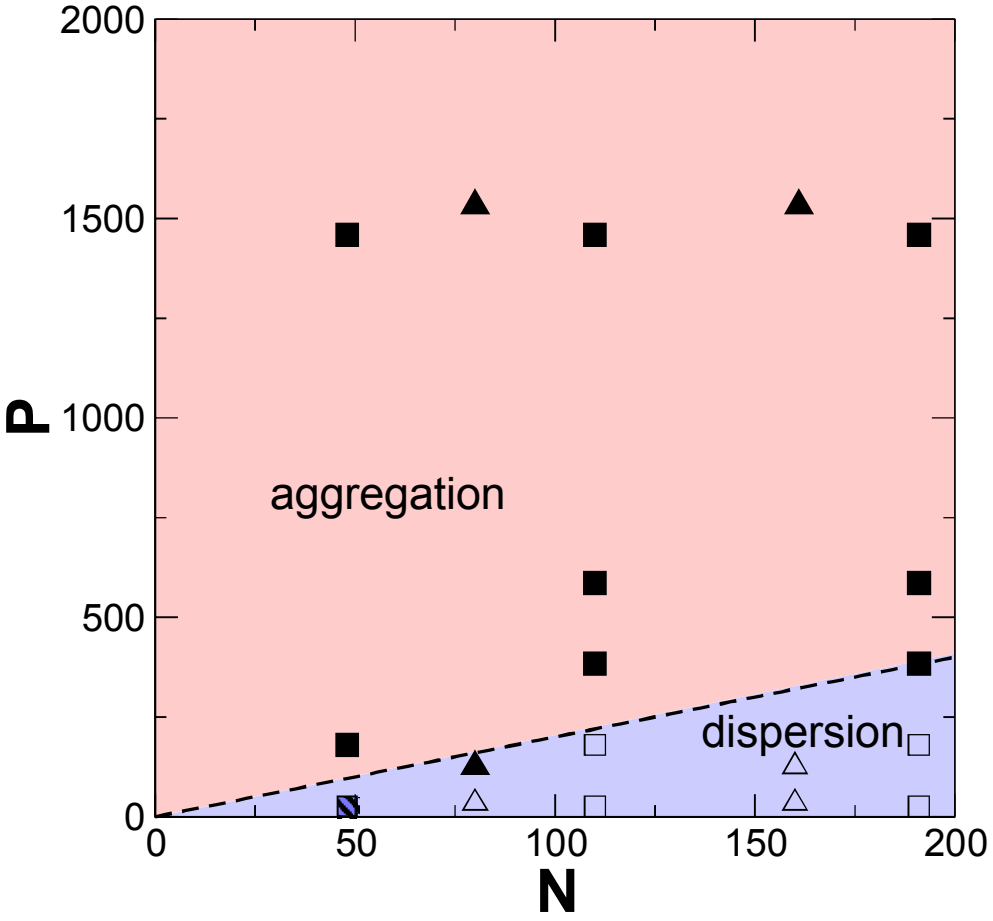


P/N = 1.58



P/N = 19.2

Dispersion "Map" for NRs



dispersion for $P < 2N$

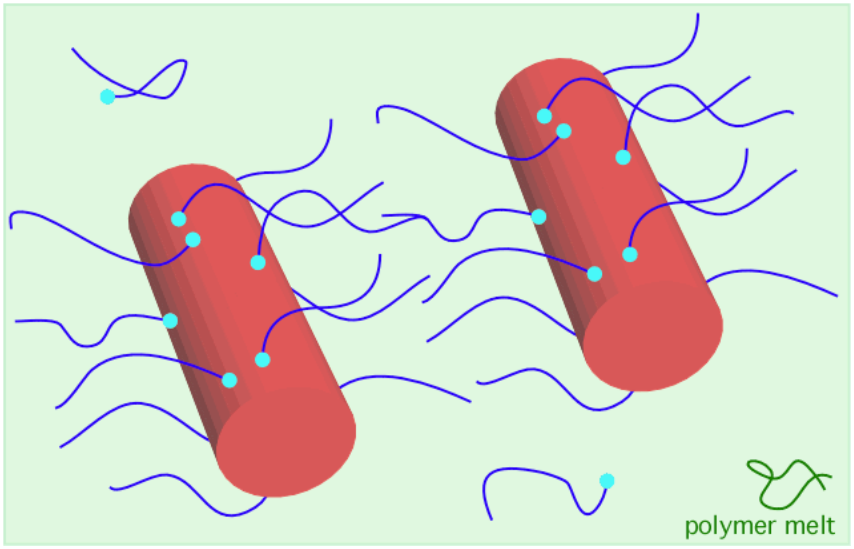
ignores possible effects of:

- 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

note nanorods exclude chains from interior are not part of the fluid in the theory

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)

DFT 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

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

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

$$G_1 = G_N^i = e^{-\beta U(r)} \qquad w(r) = \frac{1}{4\pi\sigma^2}\delta(|r| - \sigma)$$

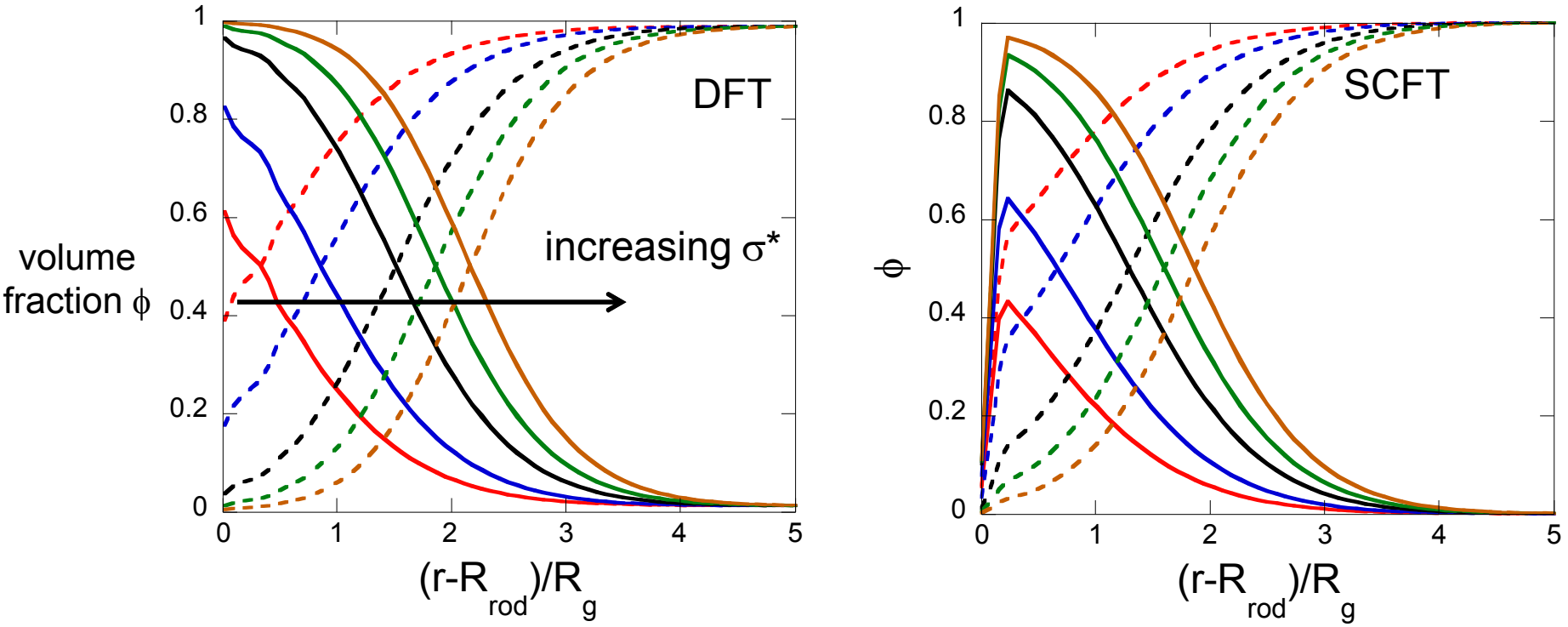
Chain Architecture (freely-jointed chains)

free energy

$$\Delta\Omega = -\frac{1}{N_L} \sum_\alpha \int d\mathbf{r} \, (\rho_\alpha(\mathbf{r}) - \rho_{b,\alpha}) + \frac{1}{2} \sum_{\alpha\beta} \int \int d\mathbf{r} d\mathbf{r}' c_{\alpha\beta}(\mathbf{r} - \mathbf{r}') \left[\rho_\alpha(\mathbf{r}) \rho_\beta(\mathbf{r}') - \rho_{b,\alpha}\rho_{b,\beta}\right]$$

Single Nanorod: Brush Profiles

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



grafting density important

Single Nanorod: Brush Profiles

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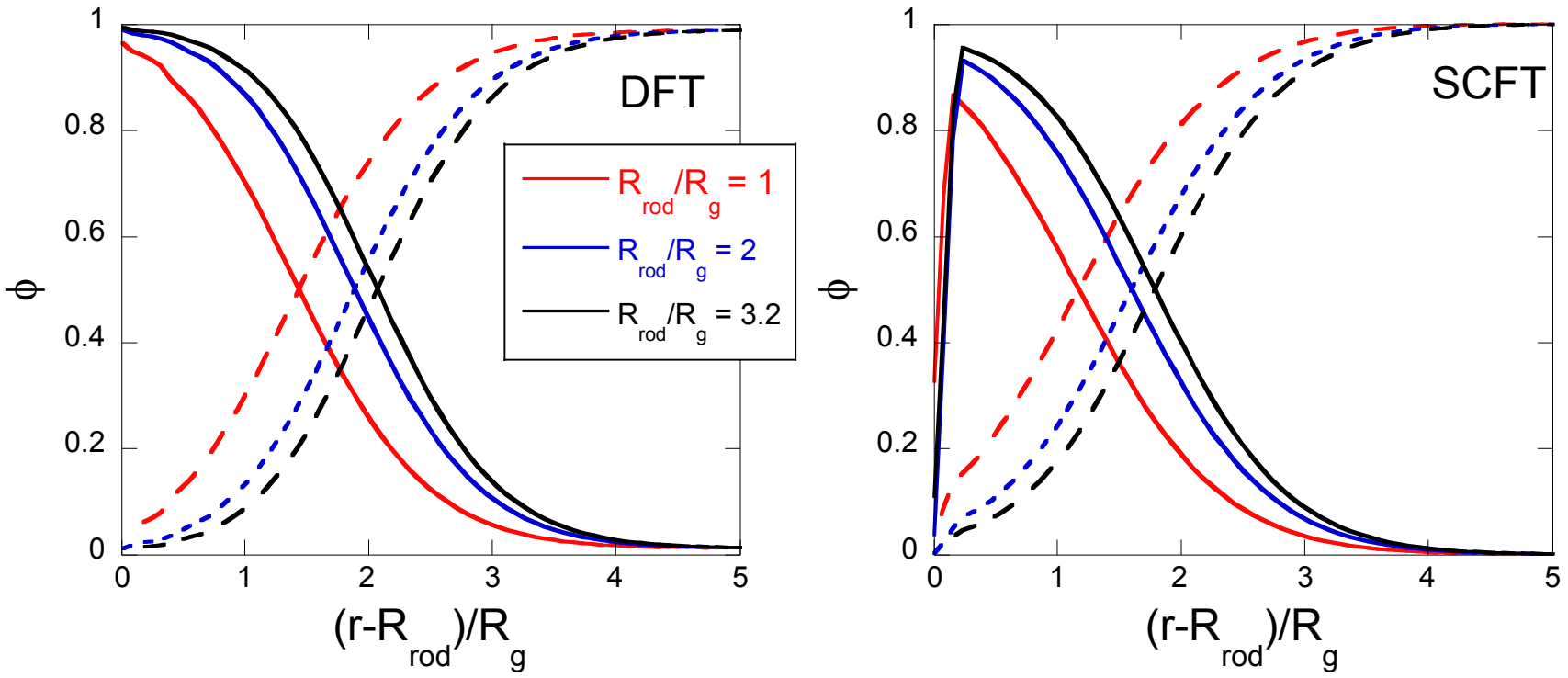
$\alpha = 2, \sigma^* = 2.38$



nanorod curvature important

Single Nanorod: Brush Profiles

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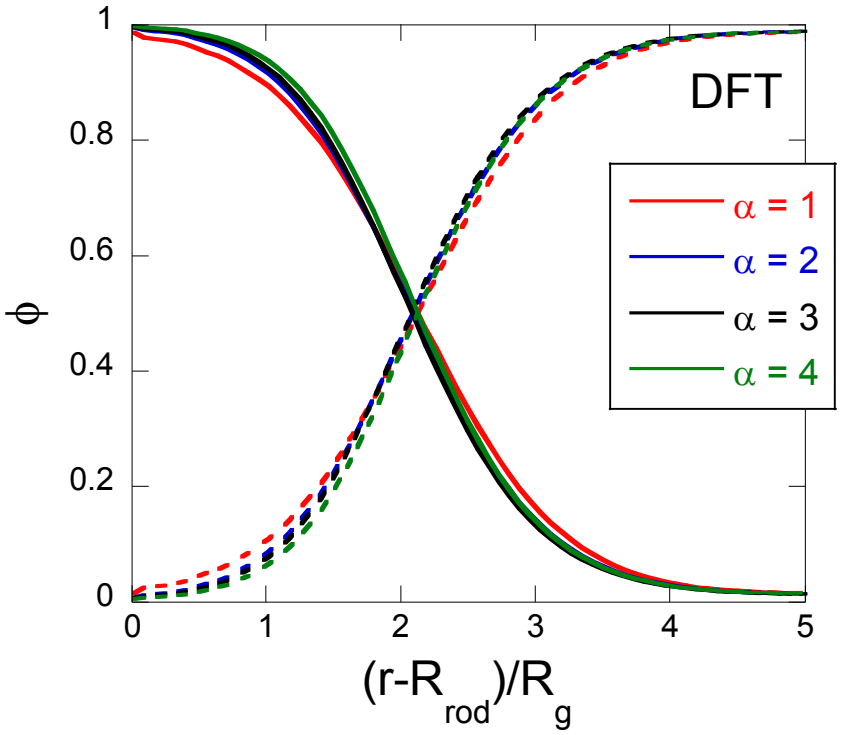
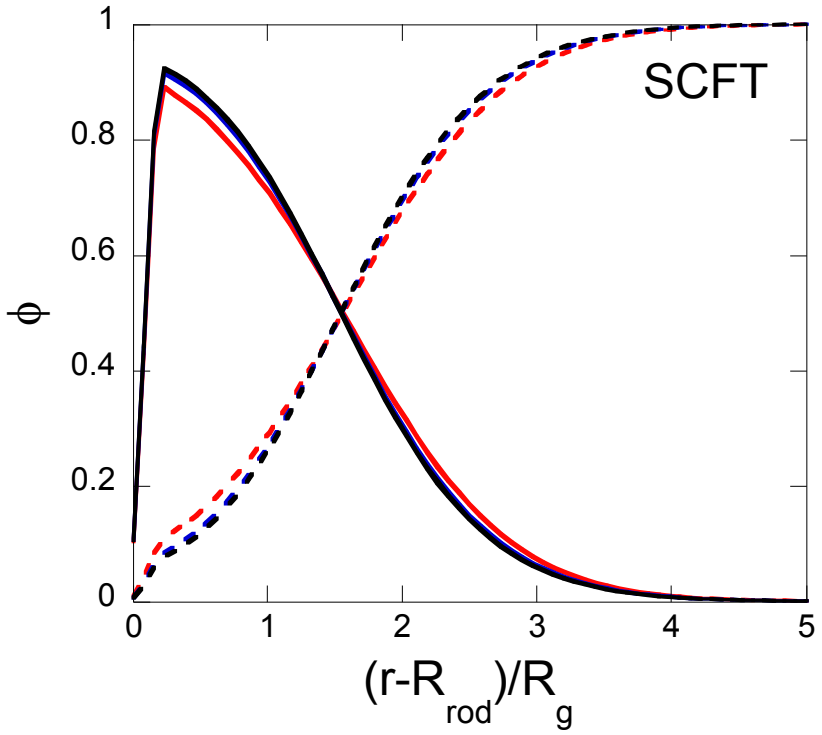
$R_{rod}/R_g = 3.2$, $\sigma^* = 2.38$

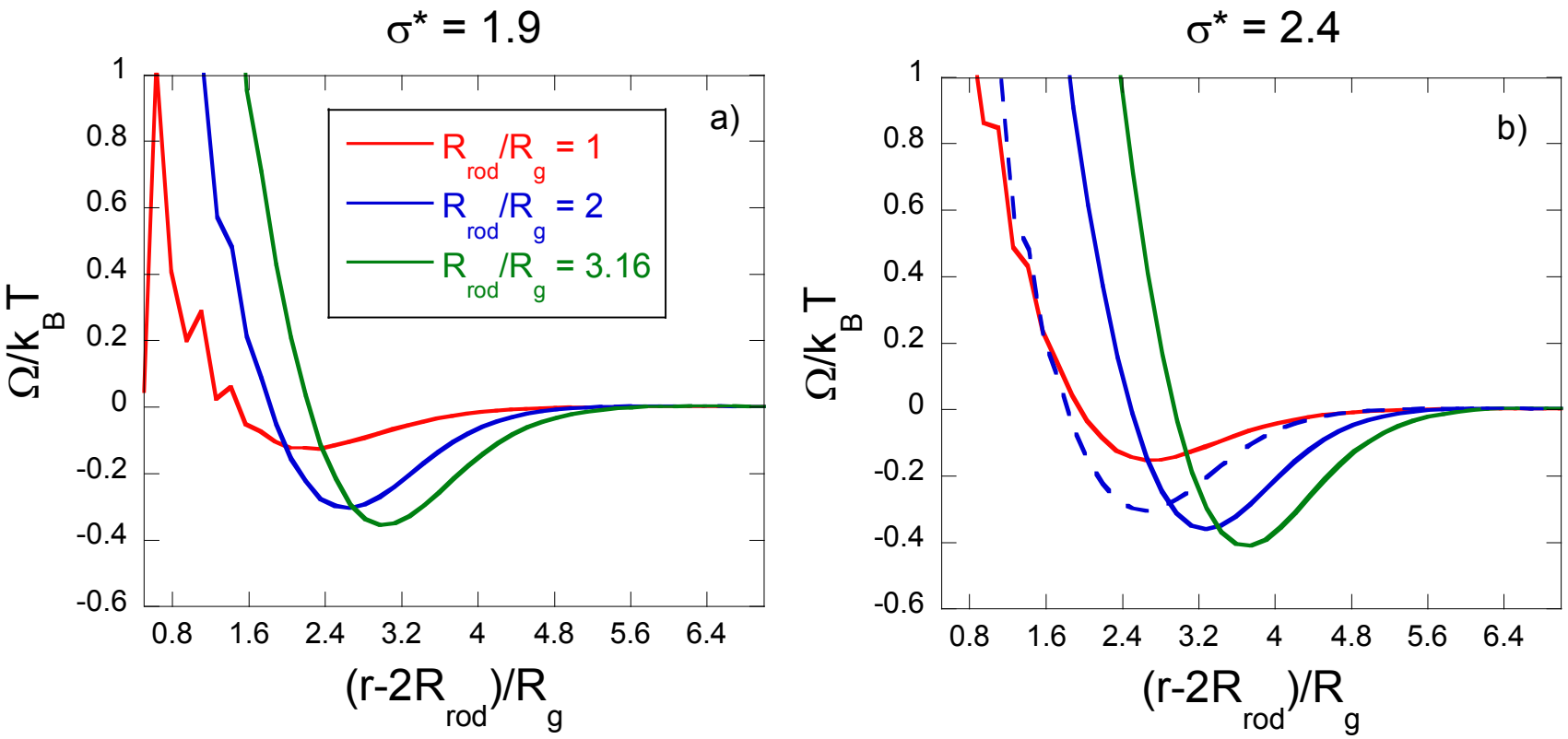




matrix chain length doesn't affect brush profiles much

Rod-rod interaction energy

P/N = α = 3



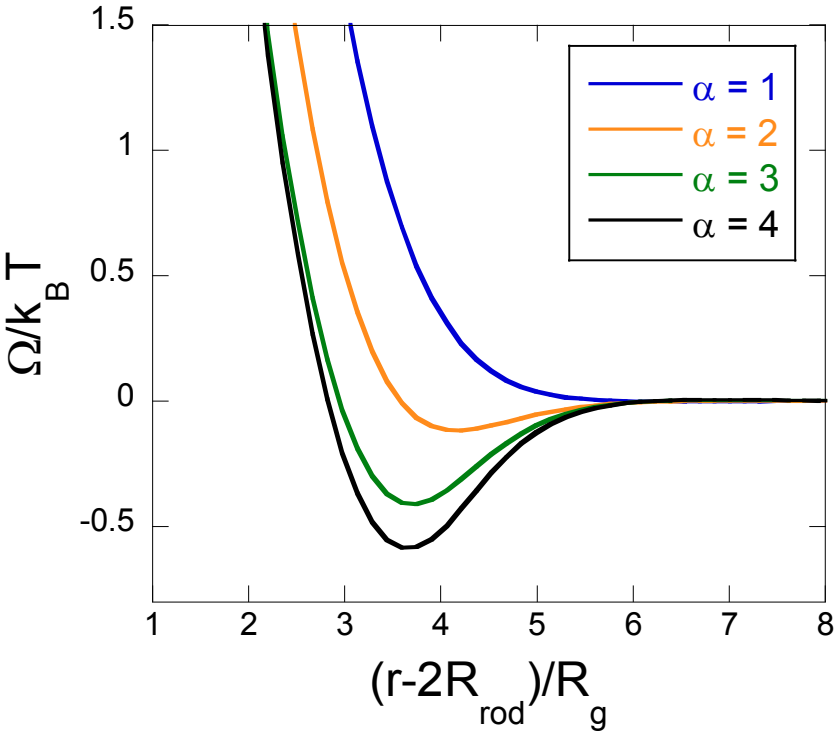
deeper attractive well as:

- grafting density increases
- R_{rod} increases

Rod-rod interaction energy

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

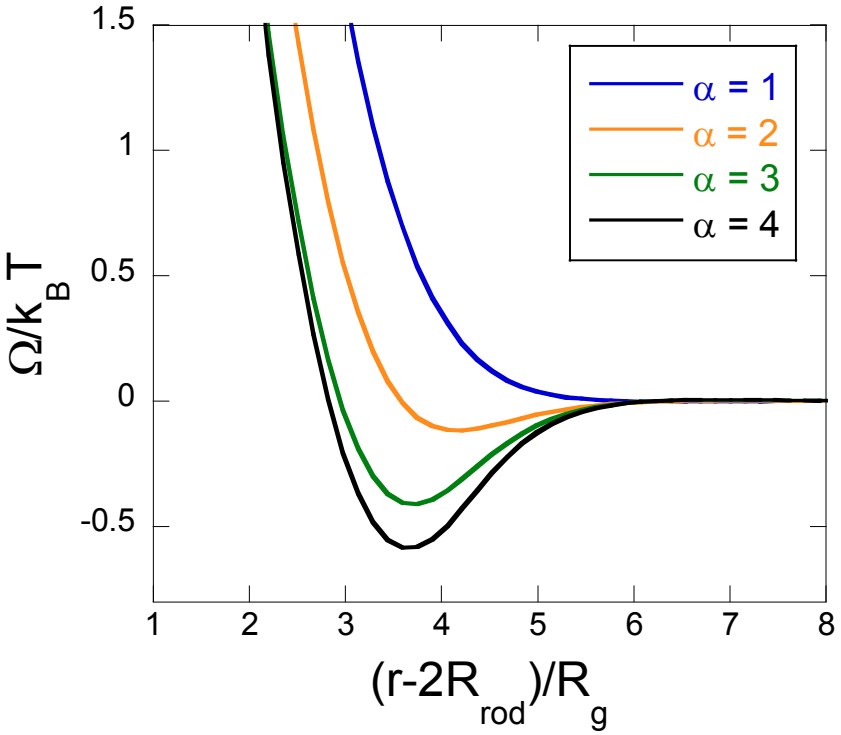
matrix chain length crucial!



Rod-rod interaction energy

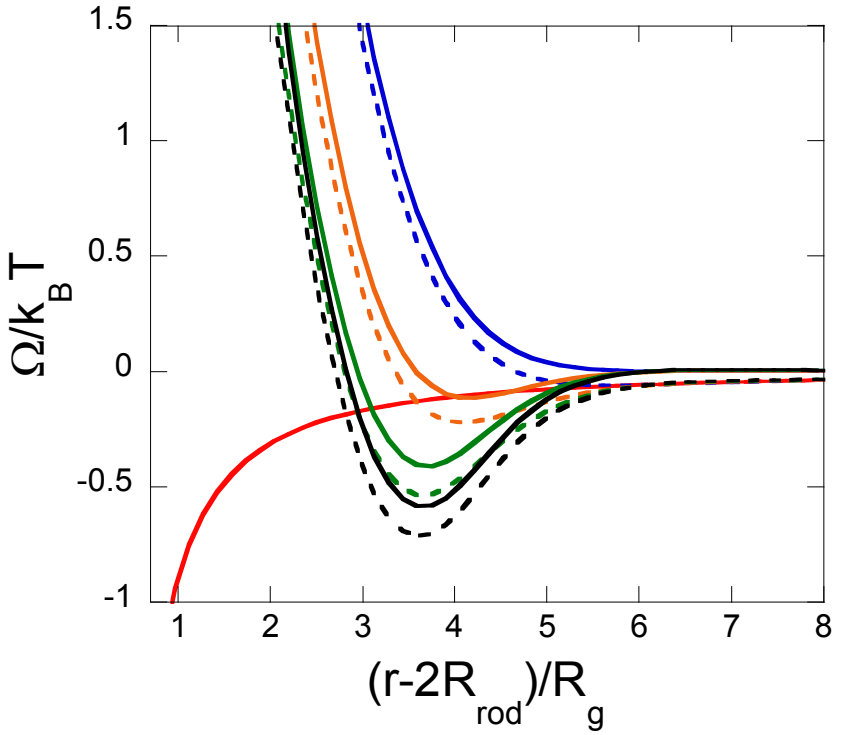
$R_{rod}/R_g = 3.2$, $\sigma^* = 2.4$

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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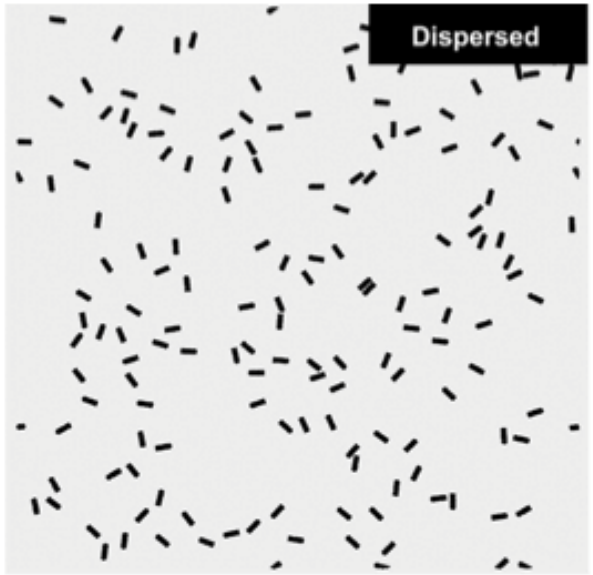
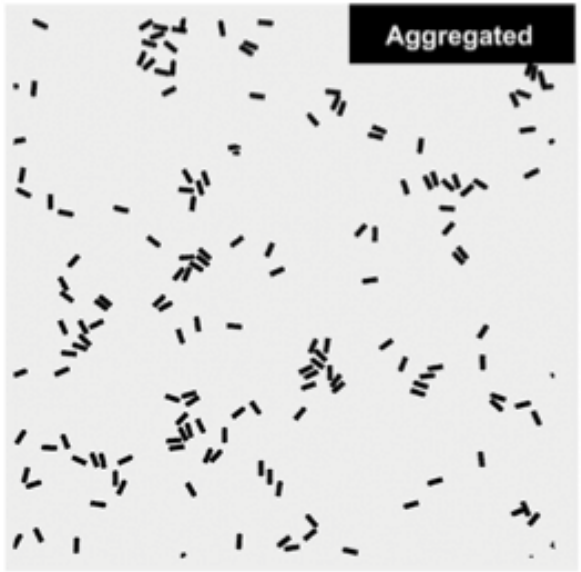
Monte Carlo simulations
square-well potential



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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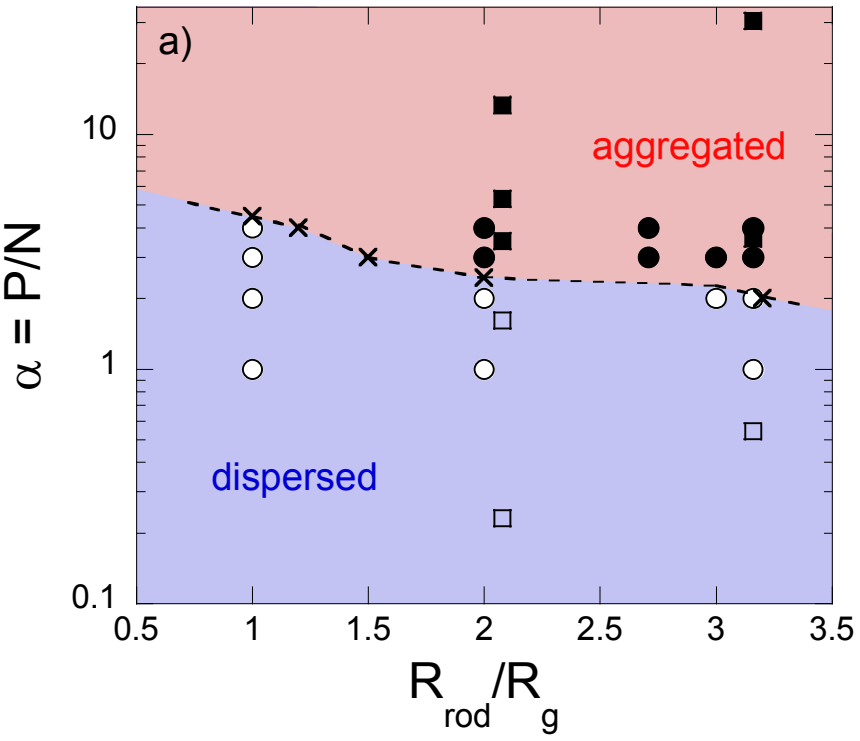
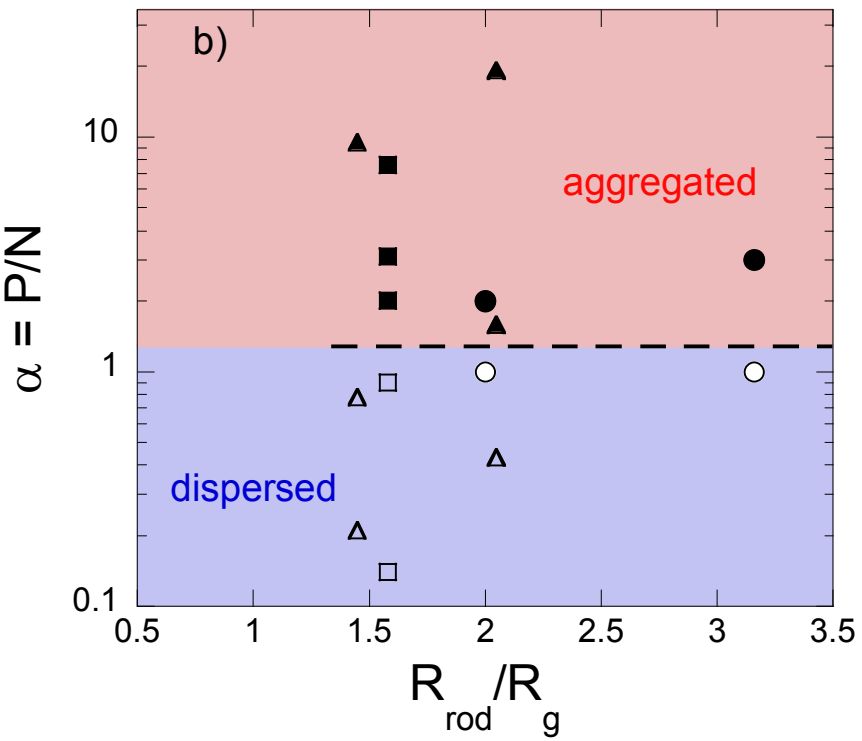
$1.9 < \sigma^* < 2.4$



$1 < \sigma^* < 1.4$

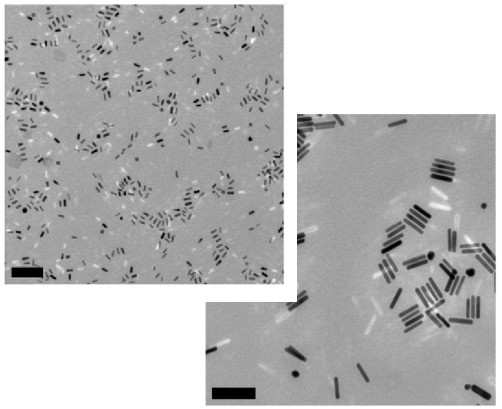


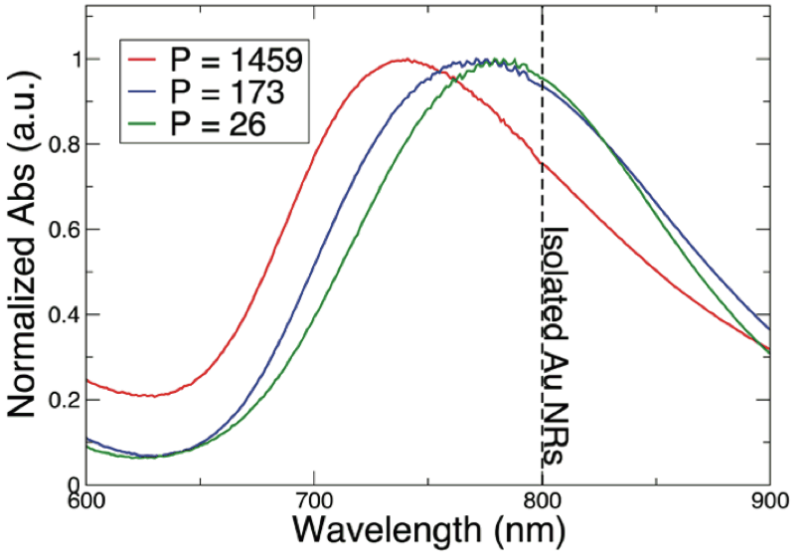
circles = DFT
squares = PS/PS
triangles = PEO/PEO

good overall agreement

Conclusions

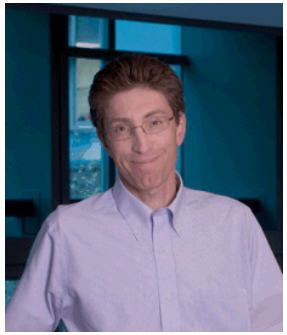
- brush profiles remarkably insensitive to α
- interaction energy sensitive to σ^*, R_{rod}, and α
- DFT captures correct trends
  - transition to aggregation near *P/N = 2*
- design: promote dispersion for
  - small σ^*, R_{rod}, or α
  - can potentially control rod spacing in aggregates
    - to control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





Frischknecht, Hore, Ford, & Composto, *Macromolecules* **46**, 2856 (2013)

Acknowledgments



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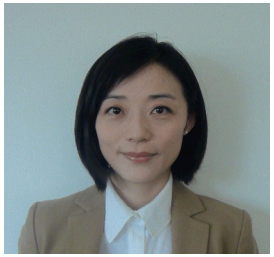
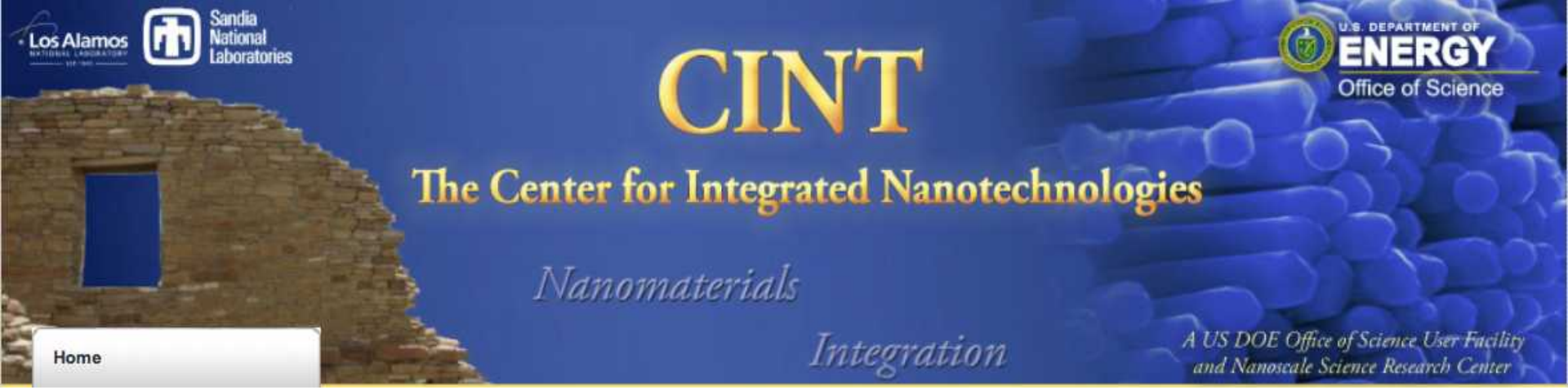


Su-Mi Hur Glenn Fredrickson Dale Huber

UC Santa Barbara

Funding

- CINT User Program
- LDRD



http://cint.lanl.gov

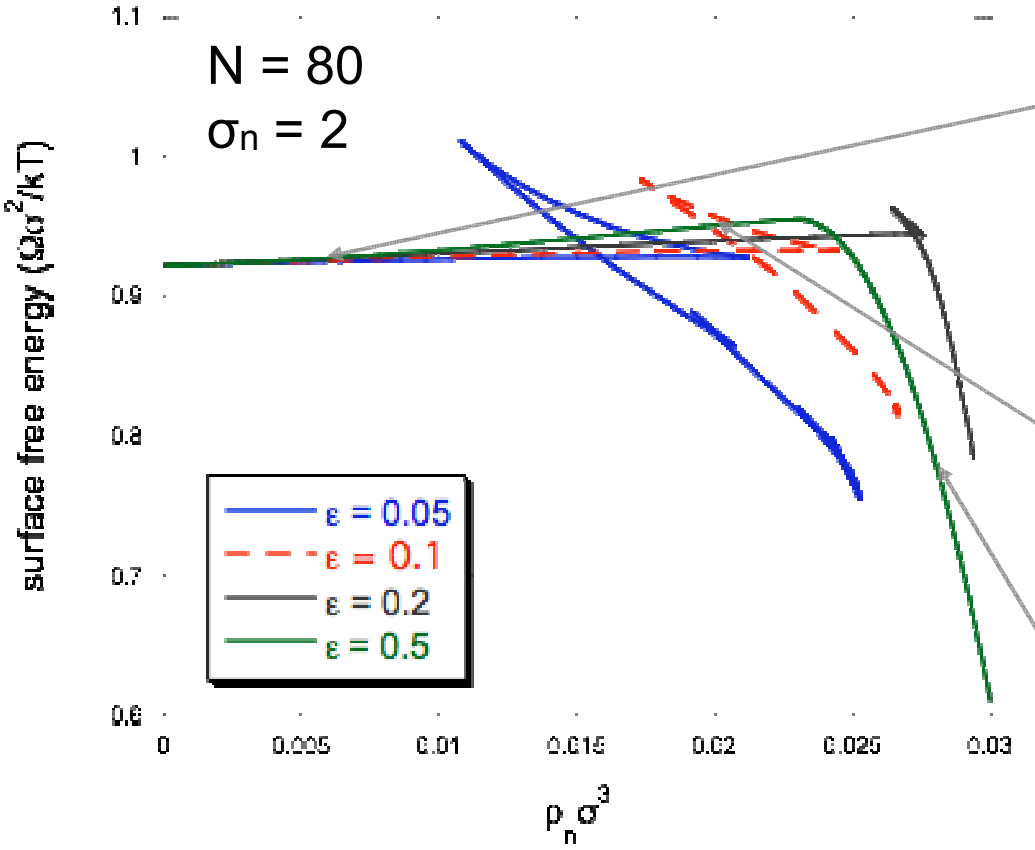
- **Focus on nanoscale integration**
- **User facility with a diverse portfolio of customers (academia, labs, industry)**

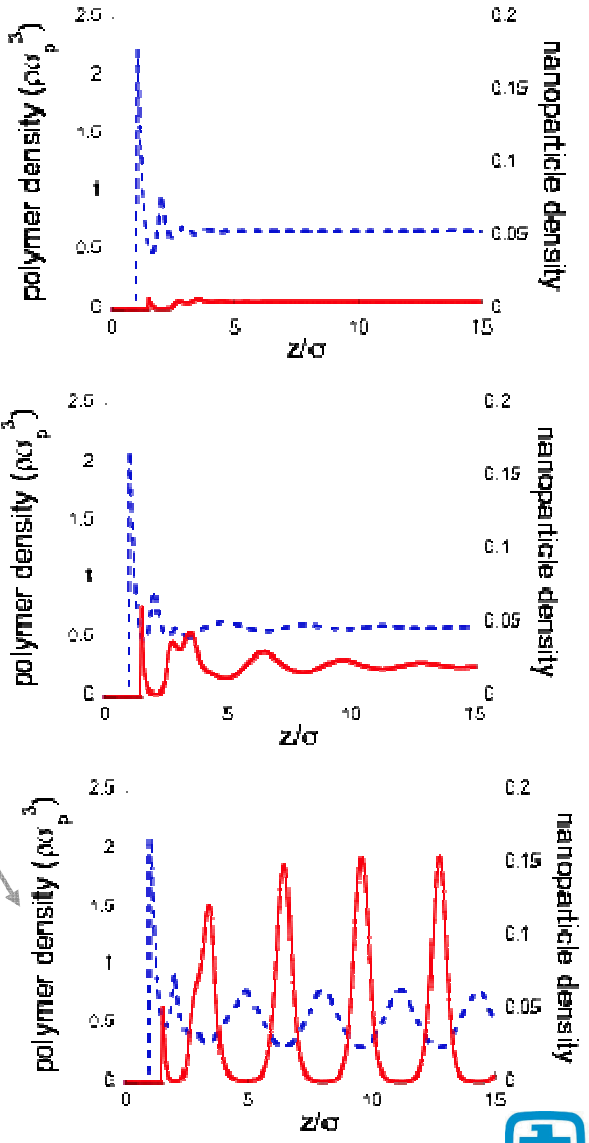

CINT Core Facility
Albuquerque, NM


CINT Gateway Facility
Los Alamos, NM

Los Alamos NATIONAL LABORATORY
Sandia National Laboratories

Effect of Attraction Strength





- van der Waals loop vanishes at high ε
- transition becomes continuous

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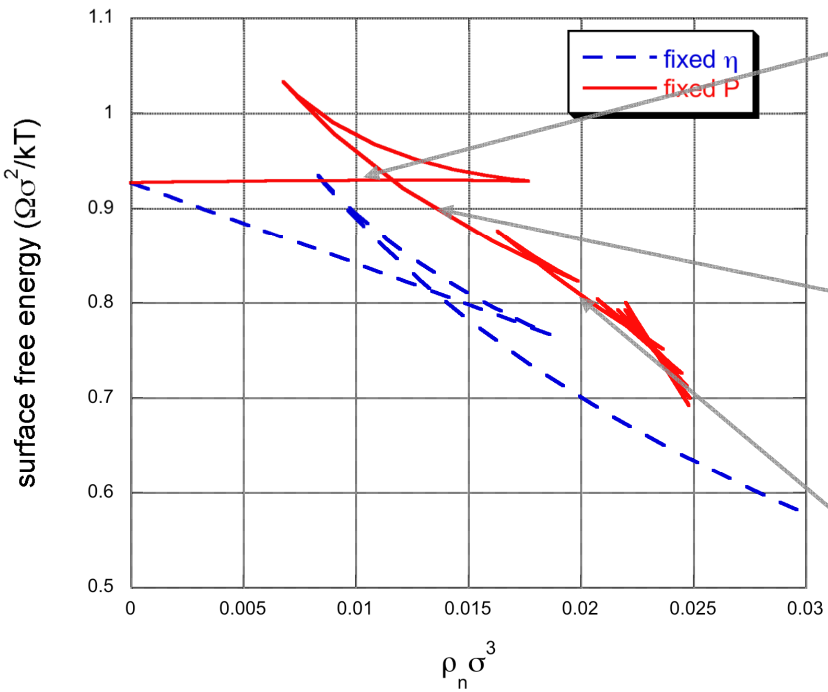
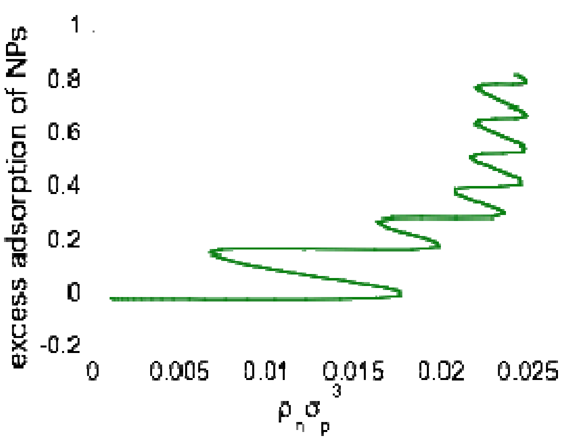
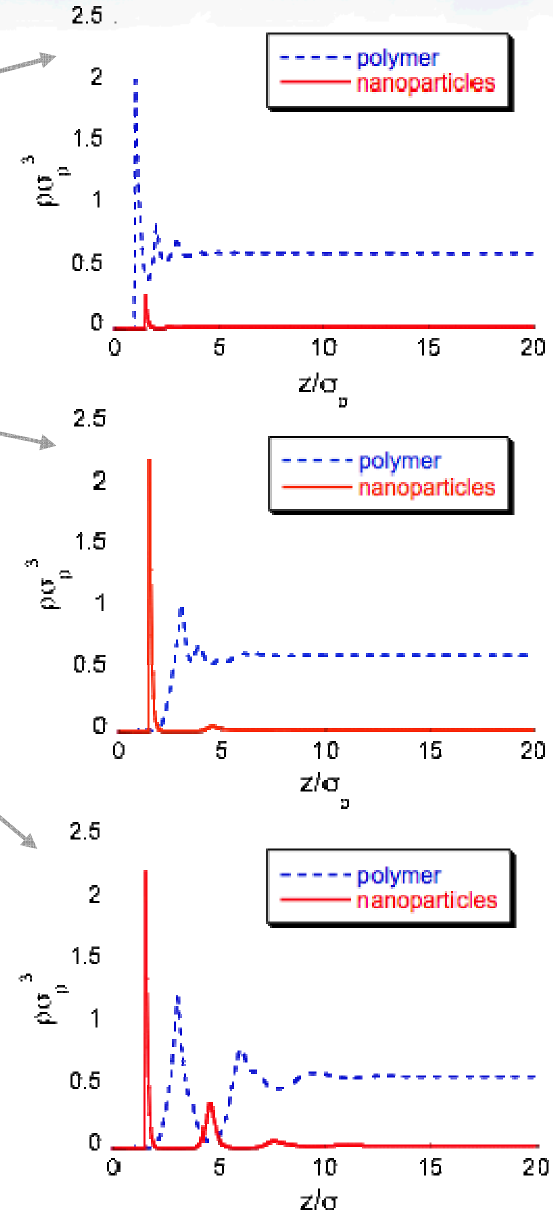
Constant pressure: still a transition

$N=30, D=2\sigma, \eta_0 = 0.37$

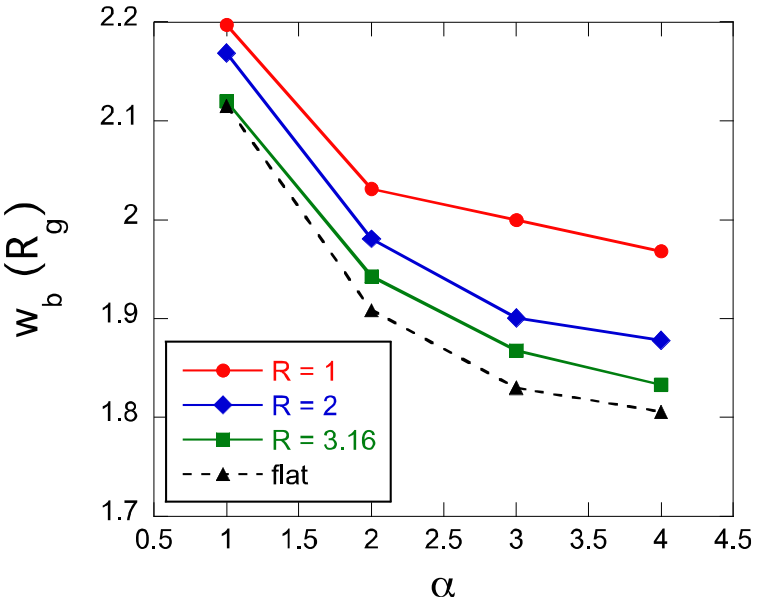




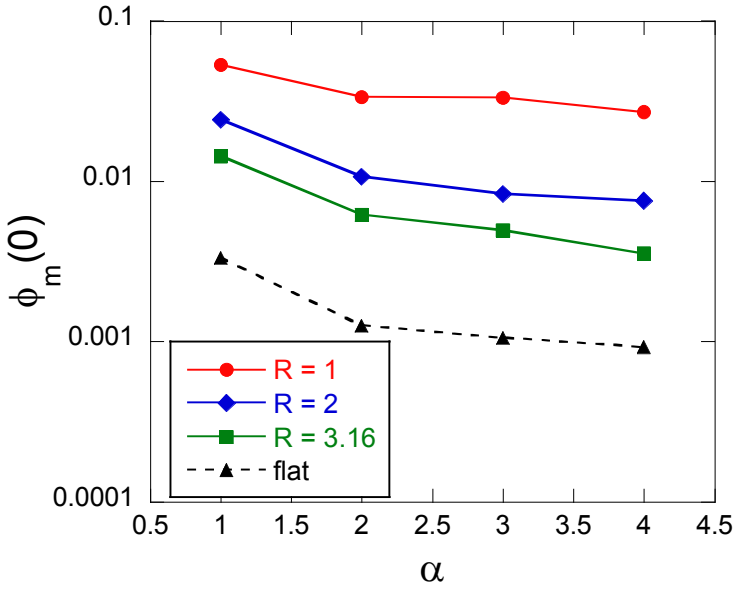


Brush Characteristics vs α

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)

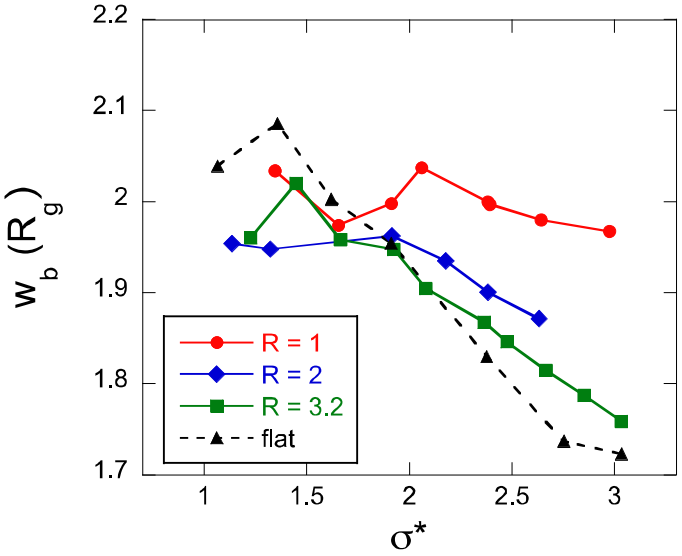
$$\phi_b(h_b) = \frac{1}{2}\phi_b(0)$$

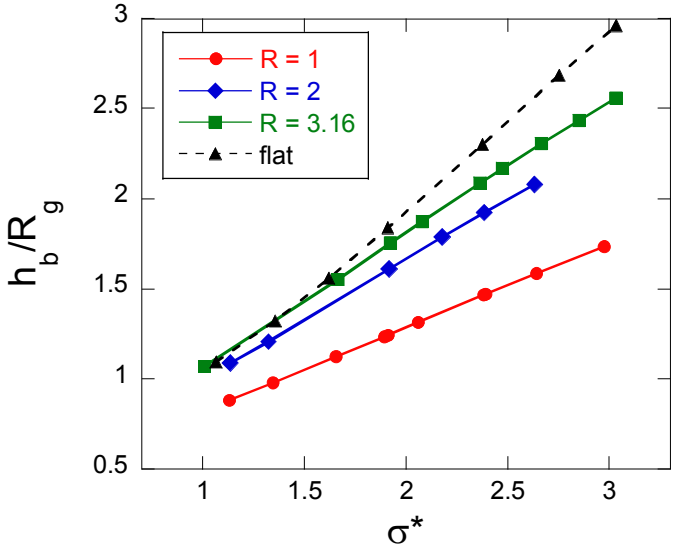
width w_b

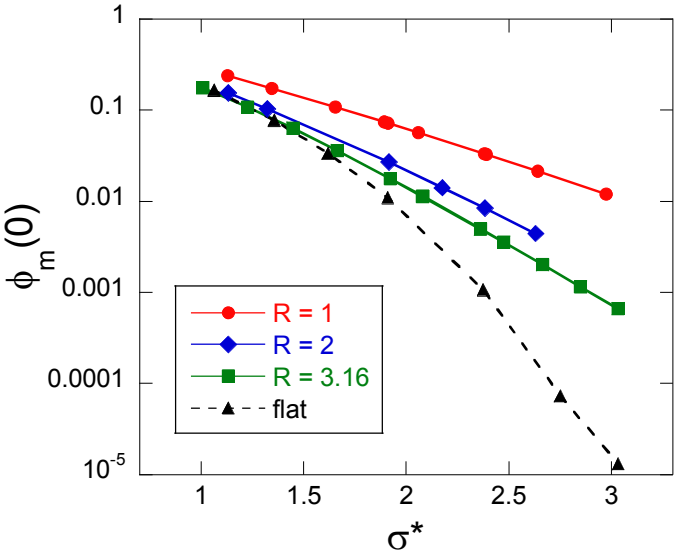
$$w_b = \frac{\phi_b(0)}{|\phi_b'(h)|}$$

matrix fraction at rod surface

$$\phi_m(0)$$

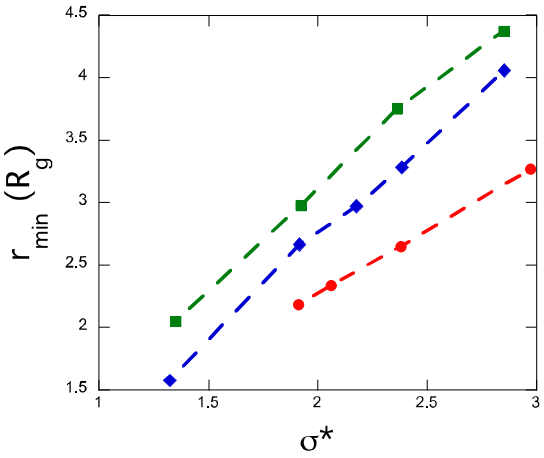


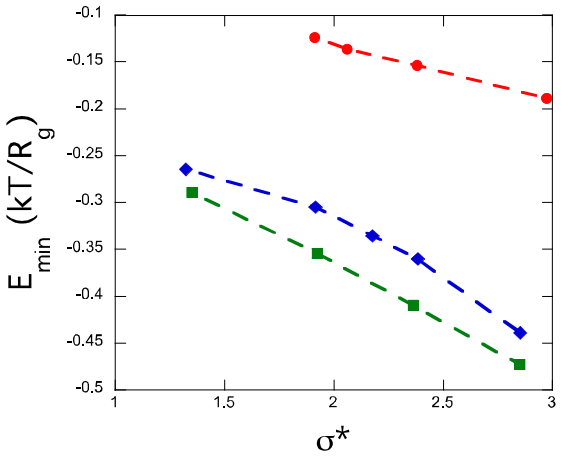




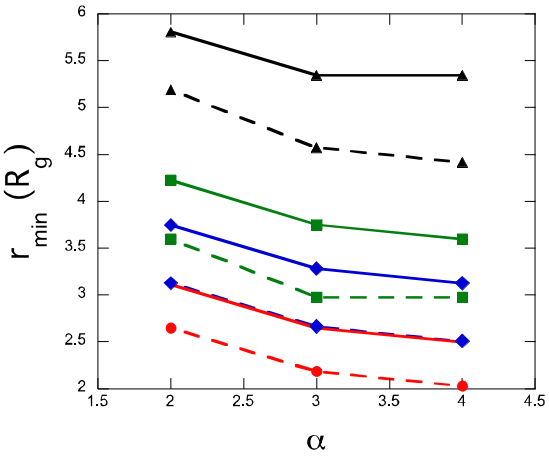
Interactions vs σ^* and α

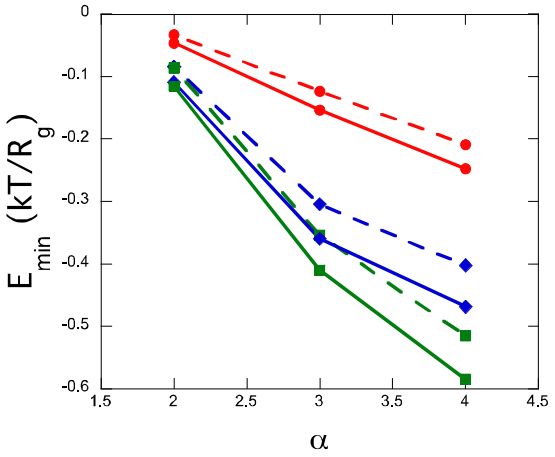
grafting density





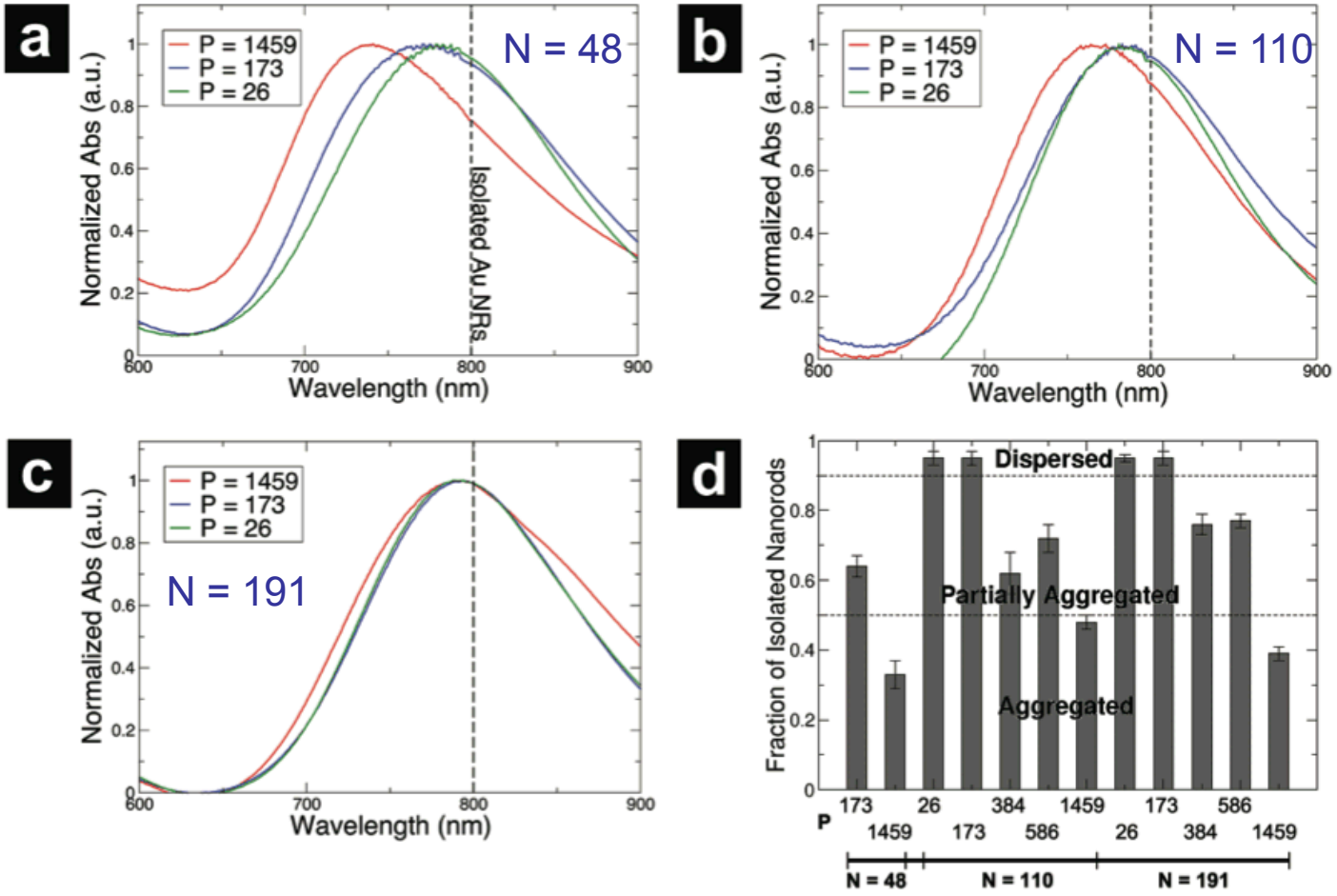
chain ratio





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

Surface Plasmon Resonance

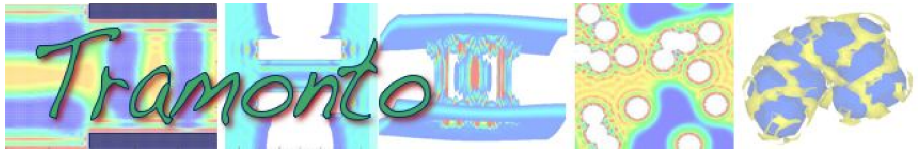


Hore, M. J. A., Frischknecht, A. L., & Composto, R. J. (2012), *ACS Macro Letters*, *1*, 115–121.

Fluids-DFT Implementation

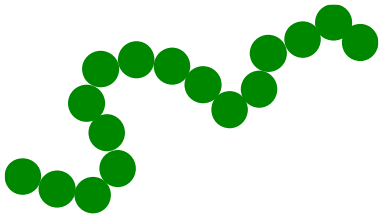
Sandia National Laboratories

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

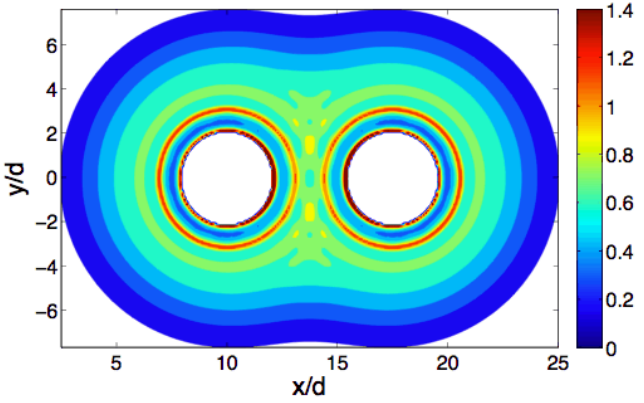


http://software.sandia.gov/tramonto

- **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, ...

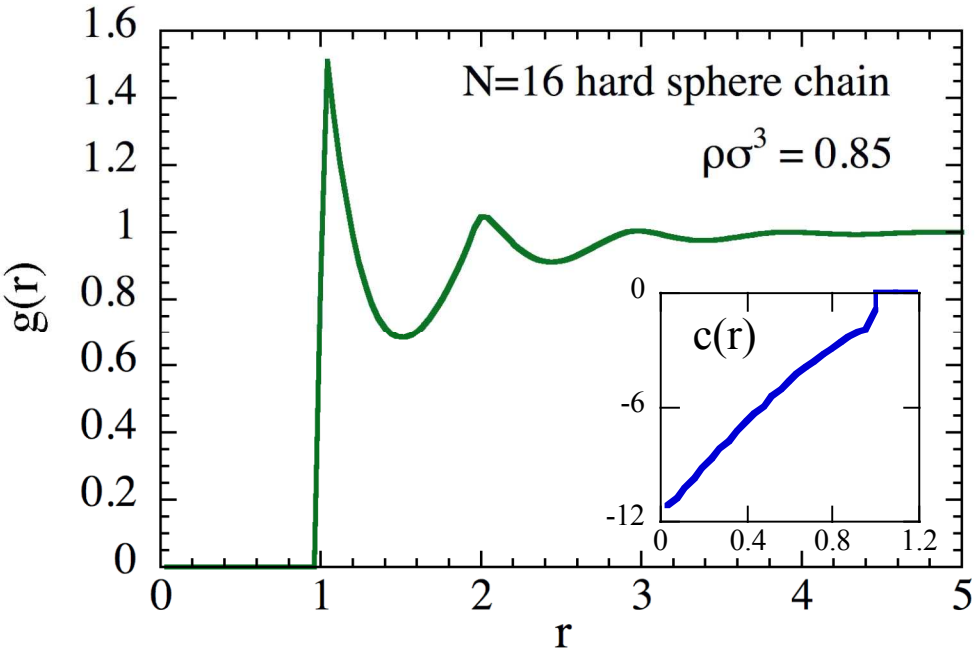


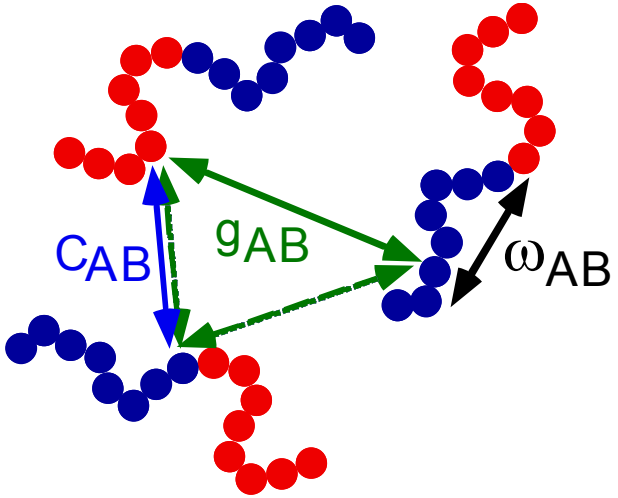
Input to CMS-DFT: PRISM Theory

Sandia National Laboratories

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

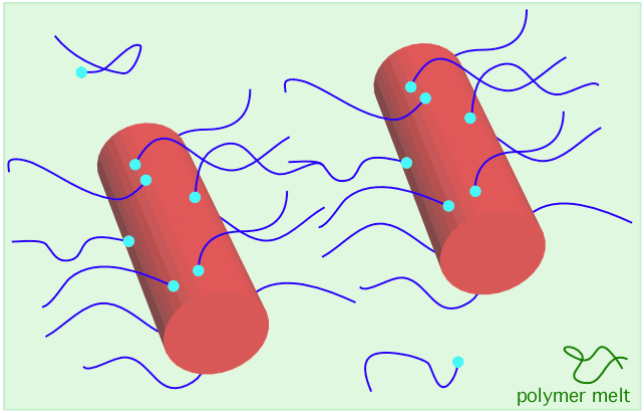




Calculation Details

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