SAND2007-2444P

Structure and Interactions in Nanoparticle/Polymer Blends

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Sandia National Laboratories

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Outline

- overview
- density functional theory (DFT)
- coated nanorods in melts
- nanoparticles in polymer films

Some Experimental Questions

- how best to disperse a nanoparticle in a polymer?
  - what materials?
  - use surfactant or polymer brush? what chain lengths?
  - what molecular weight vs. nanoparticle size?

- interfacial properties of nanocomposites
  - where do the particles go?
  - segregation, e.g. in block copolymer domains?
  - what happens at a substrate?

Challenges in Modeling

nanoparticle sizes:

7Å (buckeyball)
2 - 10 nm (cross-linked polymers, dendrimers)
2 - 50 nm (metals, oxides, ...)

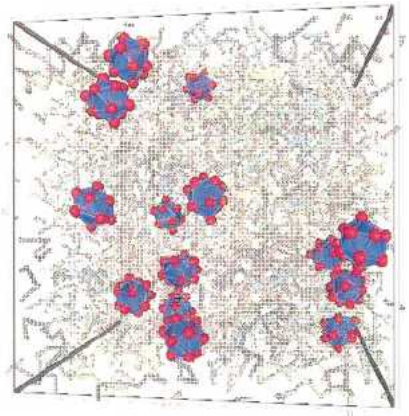
polymer sizes

e.g. PS at entanglement length 18kDa
$R_g \approx 3.6$ nm

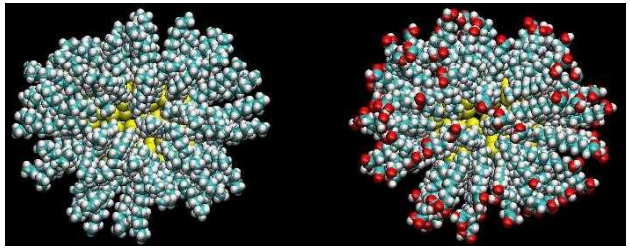
$\Longrightarrow$ can't treat nanoparticles as flat surfaces

Simulations

- length scales large for atomistics
- coarse-grained models
  - dilute limit
    - polymer dynamics near 1 nanoparticle
    - calculate PMF between two particles
  - small particles, D = 2 or 3x monomer size



Starr et al., Macromolecules, 2003



alkanethiols on Au nanoclusters

Grest, Stevens, 2007

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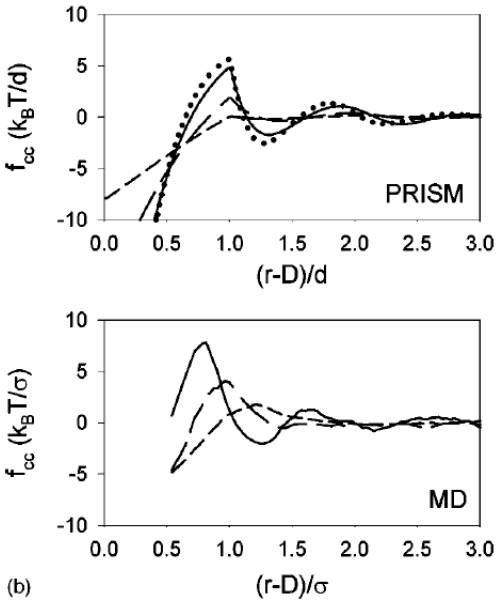
Bulk: Liquid State Theory

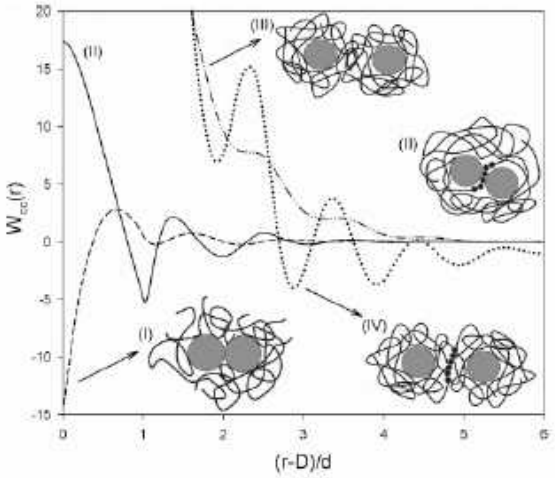
PRISM theory

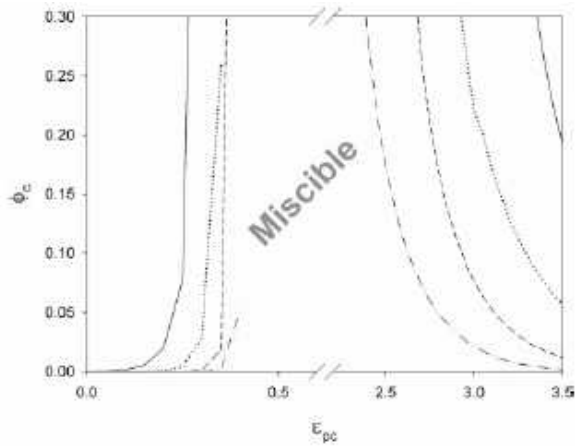
athermal: phase separation due to depletion attraction

Hooper and Schweizer, *J. Chem. Phys.* 124, 6986 (2004)



with nanoparticle-polymer attractions





Hooper and Schweizer, *Macromolecules* 39, 5133 (2006)

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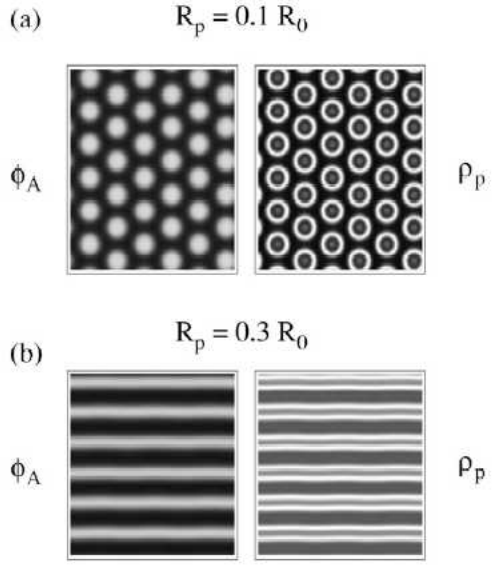
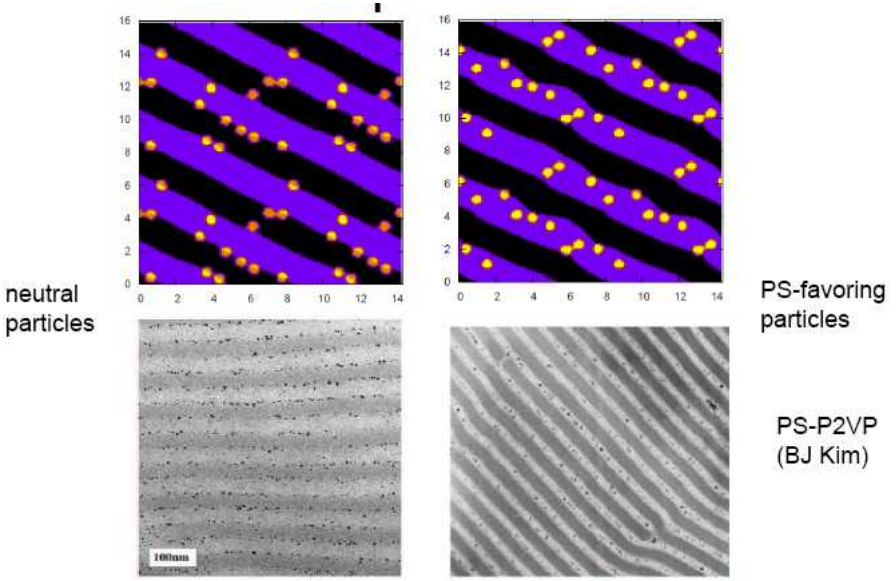
Hybrid SCF Theories

- self-consistent field theory for polymers
  - especially diblocks
- particles
  - density functional theory (e.g. hard spheres)
  - treat as surfaces



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



Düchs, Fredrickson, Sides, 2007

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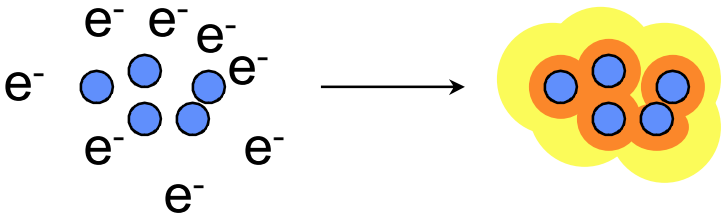
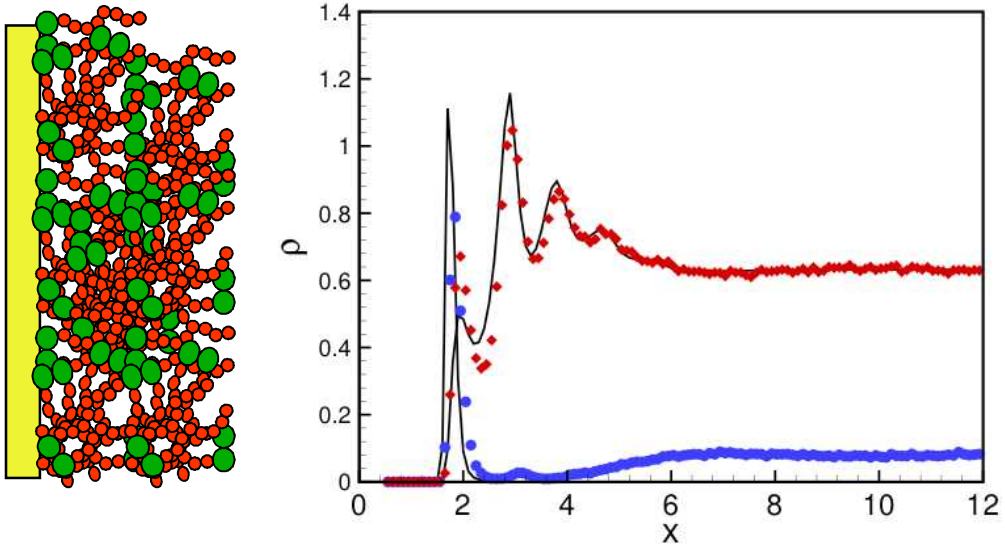
Density Functional Theory (DFT)

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

External field — Density profile



Electronic Structure
(Closed system with N-electrons)



Fluid Structure
(Often open system with fixed chemical potential)

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Structure of a Fluids-DFT

ansatz for Helmholtz free energy:

$$
\begin{aligned}
F[\rho(\mathbf{r})] &= F^{id} + F^{HS} + F^{att} + \ldots \\
&= \int \rho(\mathbf{r})[\ln(\rho(\mathbf{r}) - 1]d\mathbf{r} + \int \Phi(\{n_\gamma\})d\mathbf{r} \\
&\quad + \sum_i \sum_j \int d\mathbf{r} \int d\mathbf{r}' \, \rho_i(\mathbf{r})\rho_j(\mathbf{r}')u_{ij}^{att}(|r - r'|) + \ldots
\end{aligned}
$$

form in grand canonical (open) ensemble

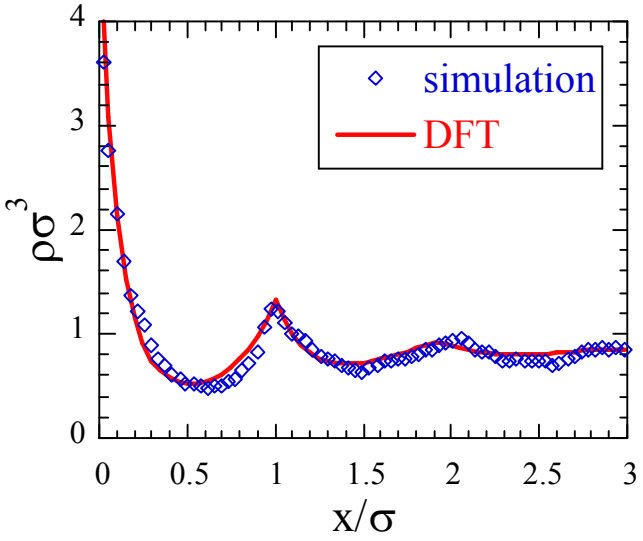
$$
\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int \rho(\mathbf{r})[V^{ext}(\mathbf{r}) - \mu)]d\mathbf{r}
$$

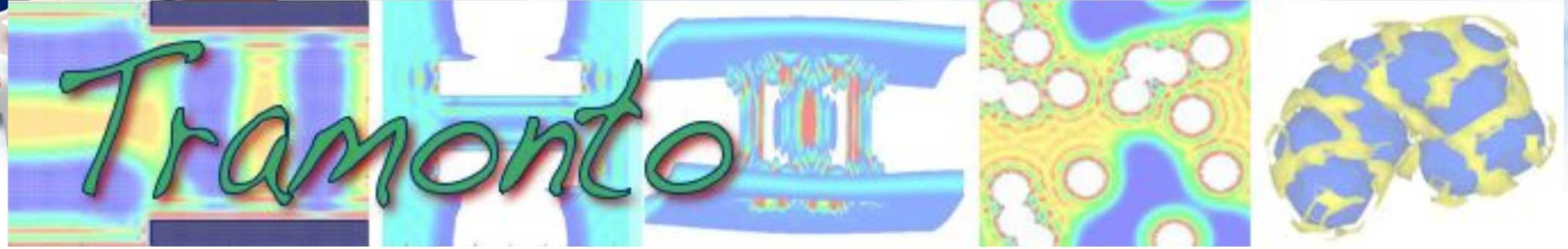
minimize free energy

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

Advantages/Capabilities of DFT

- treat different length scales
  - packing of individual “atoms” or sites
  - nano to mesoscopic length scales
- different kinds of fluids
  - hard spheres
  - attractive, Coulombic interactions
  - polymers
- compare directly to simulation results
- phase-space studies





Laura Frink, PI

http://software.sandia.gov/tramonto/index.html

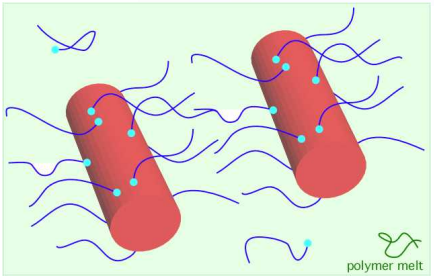
DFTs = nonlinear integral equations

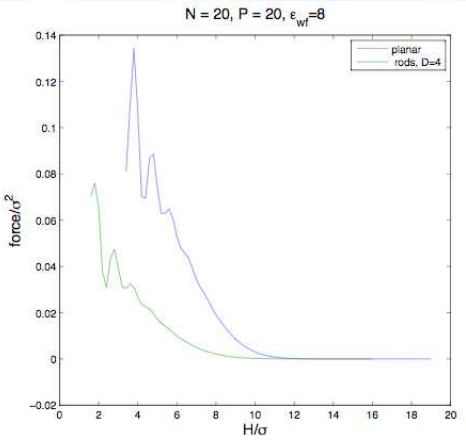
- solve in 3D, Cartesian grid
- Newton-Raphson solver
- parallel
- sophisticated linear solver algorithms
- arc-length continuation algorithms

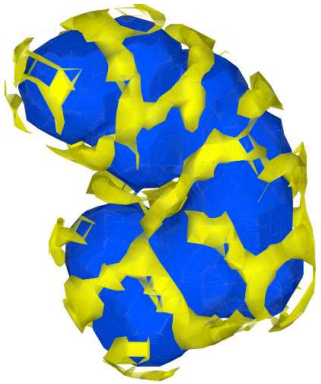
The Trilinos Project

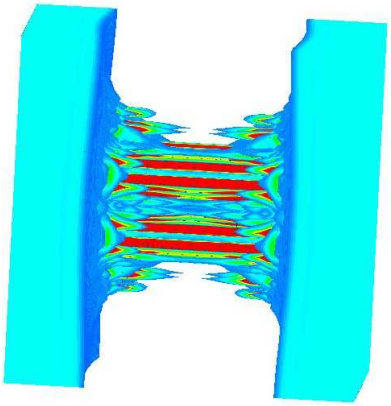
What can F-DFT do?

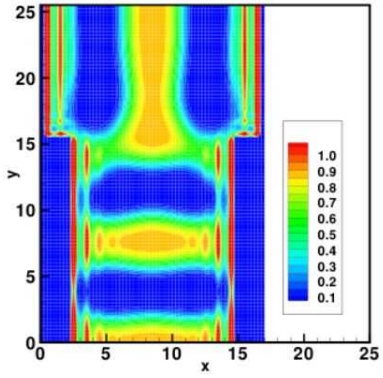
- forces between particles
- phase behavior
- solvation free energies
  - implicit solvent
- complex geometries
- complex chain architectures
- compare to simulation (MD)

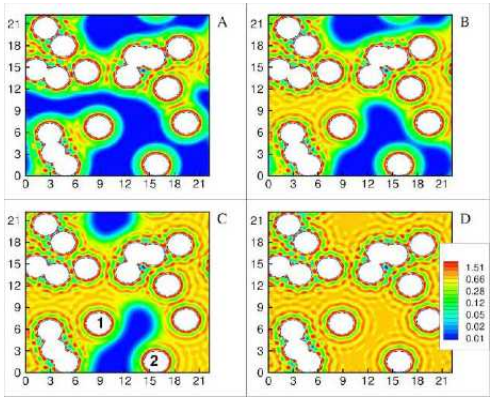


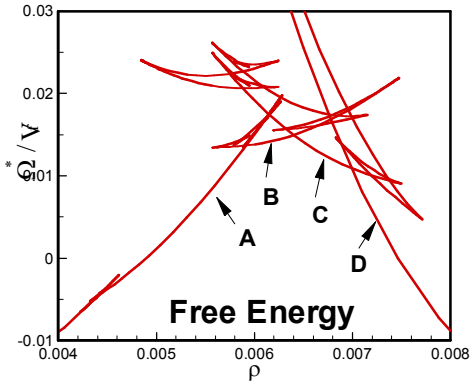












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Outline

- overview
- density functional theory (DFT)
- **coated nanorods in melts**
- nanoparticles in polymer films

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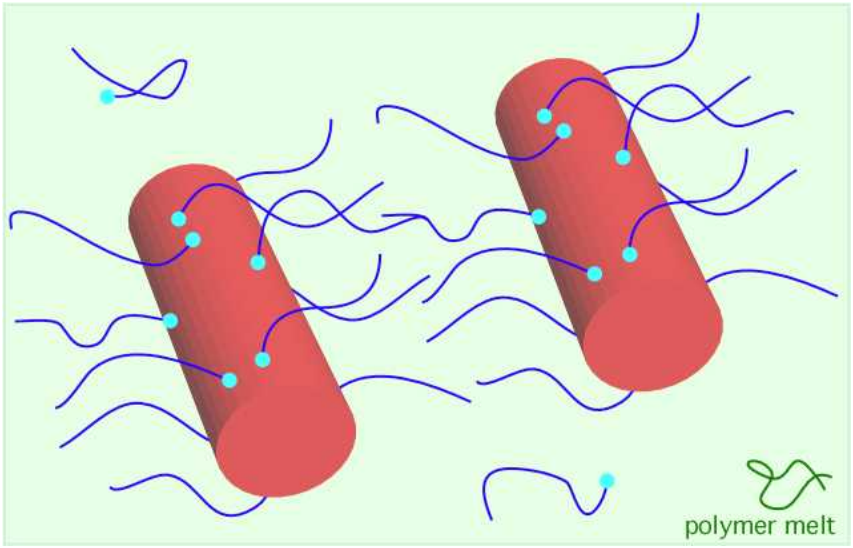
The Problem:

dispersion of nanosized objects in a polymer melt

same rules as for polymer-stabilized colloids?

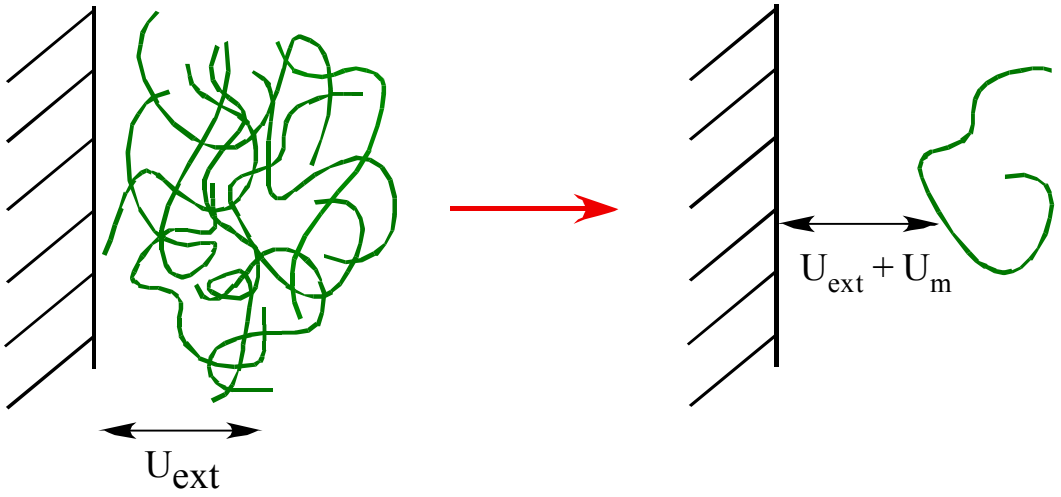


- adsorbed chains length N
  - -sticky ends, energy ε_e
- matrix chains length P
- athermal ($\chi = 0$)
- nanorods with diameter D

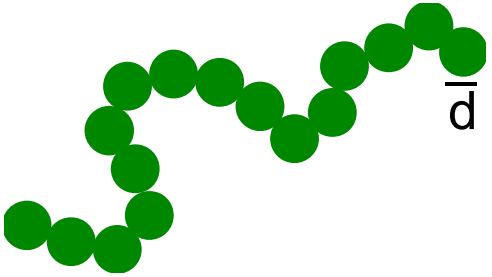
is the force always repulsive?
will the chains desorb?

CMS-DFT

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



- **Minimize free energy, $\Omega[T,V,\mu; \rho(r)]$**
- **Solve self-consistently for density profile and mean field:**



$$\rho(r) = G\left[U_{eff}(r)\right]$$

$$U_{eff}(r) = U_{ext}(r) + U_M\left[\rho(r)\right]$$

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Our approach: CMS-DFT

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

- chains are flexible
- 2nd order density expansion

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

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 (gaussian chains)

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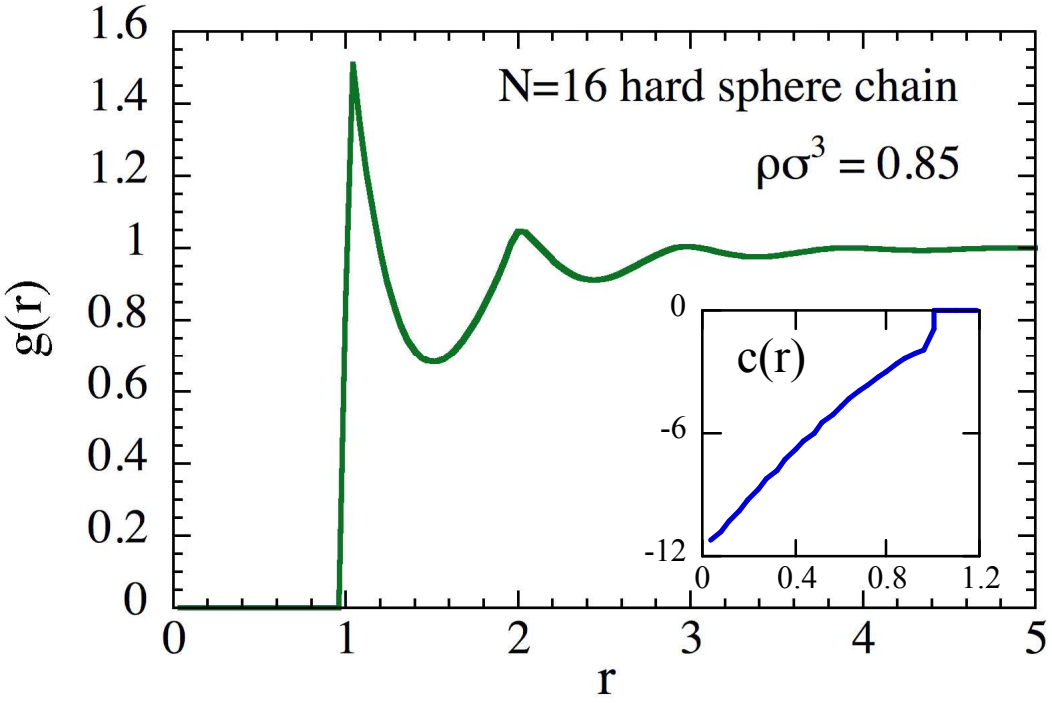
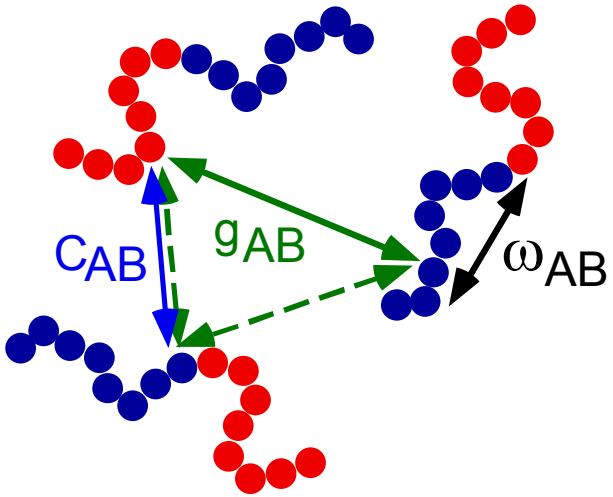
Input to CMS-DFT: PRISM Theory

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





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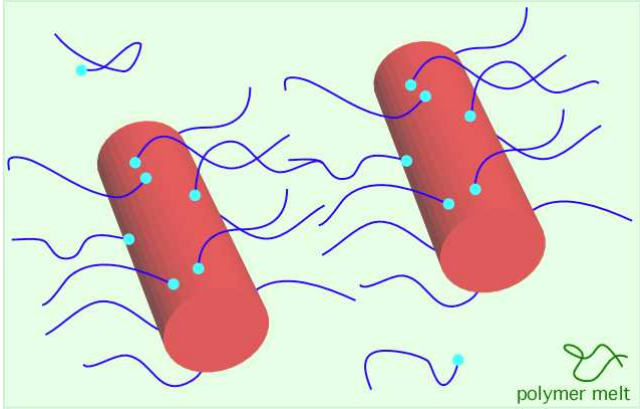
Calculation Details

- parallel cylinders
- athermal (repulsive interactions)
- adsorbed chains
  - N = 20
  - $\rho_b d^3 = 0.04$
- matrix chains
  - P = 10,20,40
  - $\rho_b d^3 = 0.76$

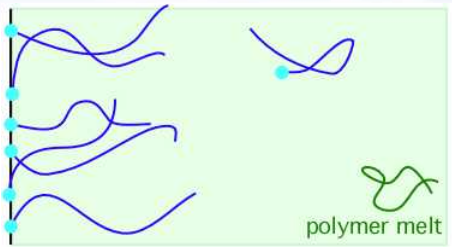


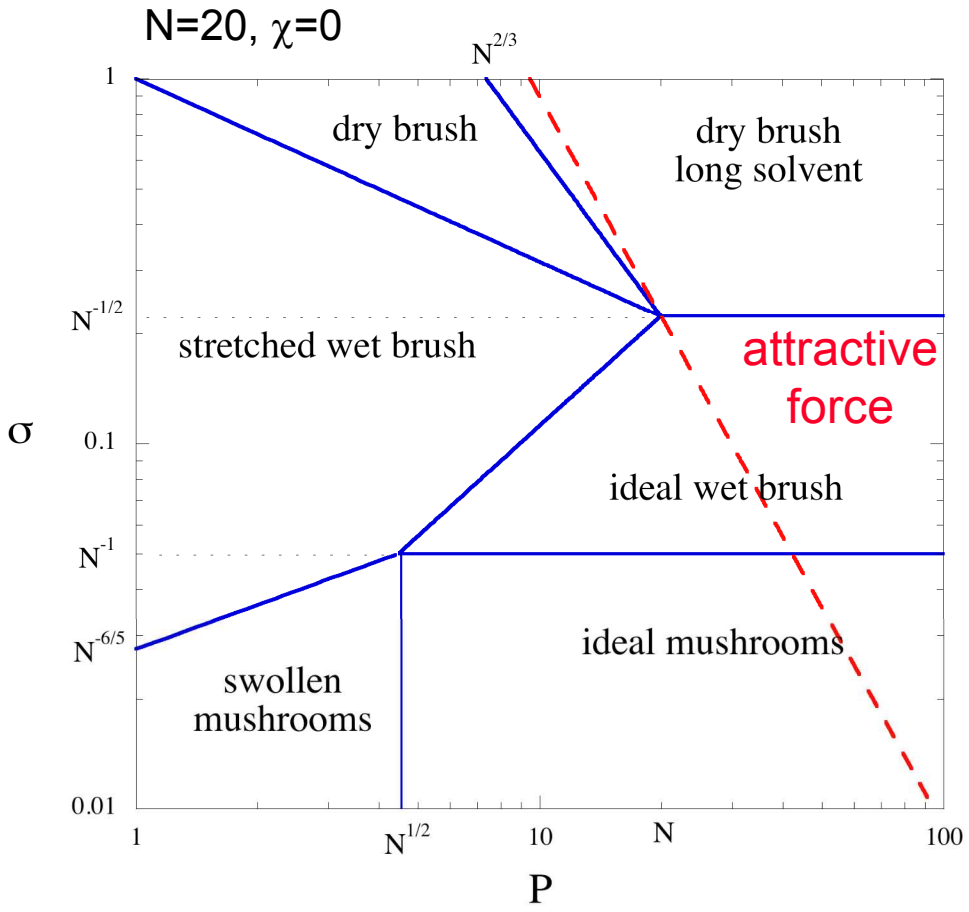
surface interactions:

- repulsive for matrix chains, sites 2-20 on adsorbing chains
- attractive to one end of adsorbing chains, depth ε_e

Diagram of State for Flat Surfaces

grafted chains on flat surfaces
behavior depends on:
N, P, σ





cause of attraction:
surface tension between brush and melt
- for long matrix chains
- high surface coverage

Gay, Macromolecules, 1997
Ferreira et al., Macromolecules, 1998

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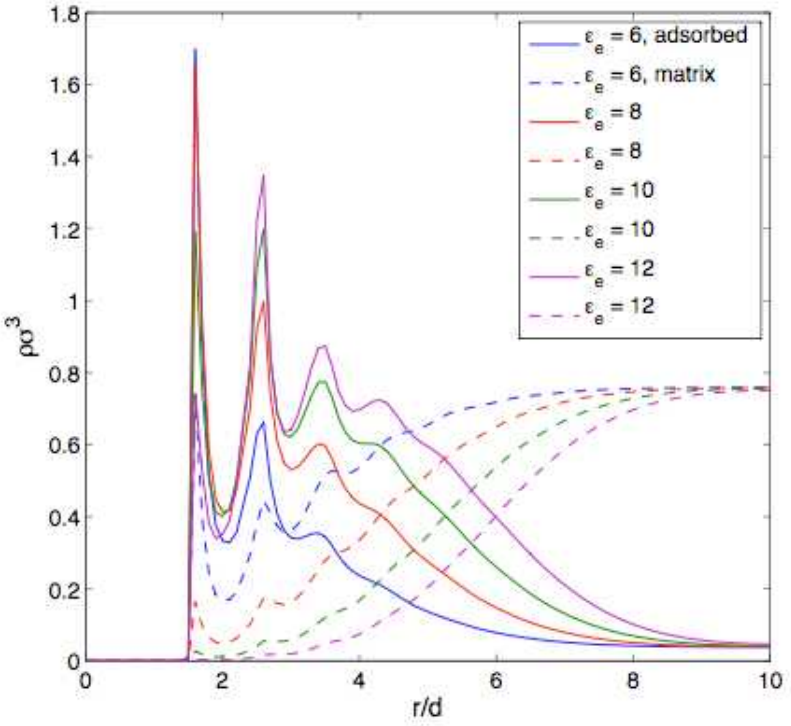
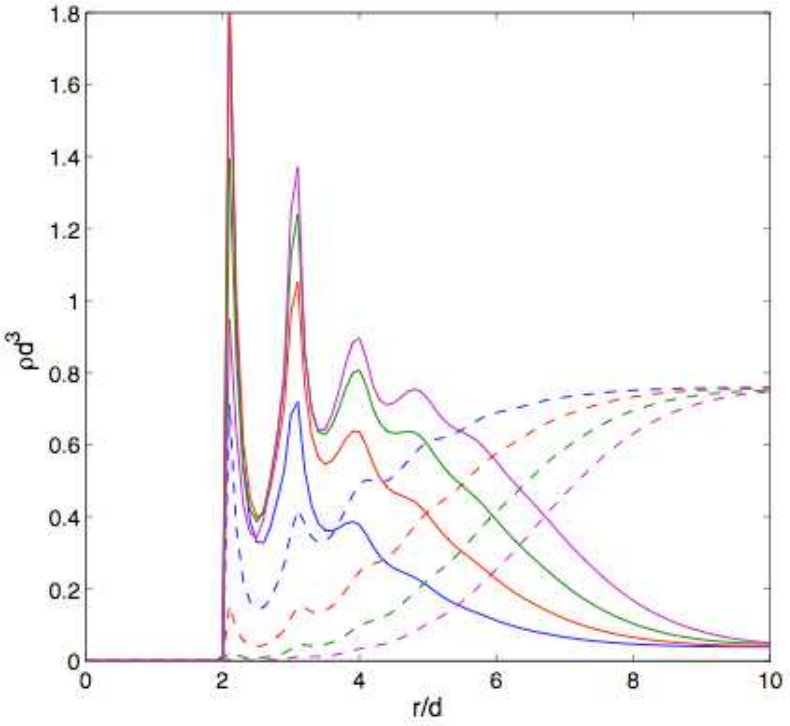
Nanorods: Brush Profiles

N = 20, P = 20

D = 3d



D = 4d



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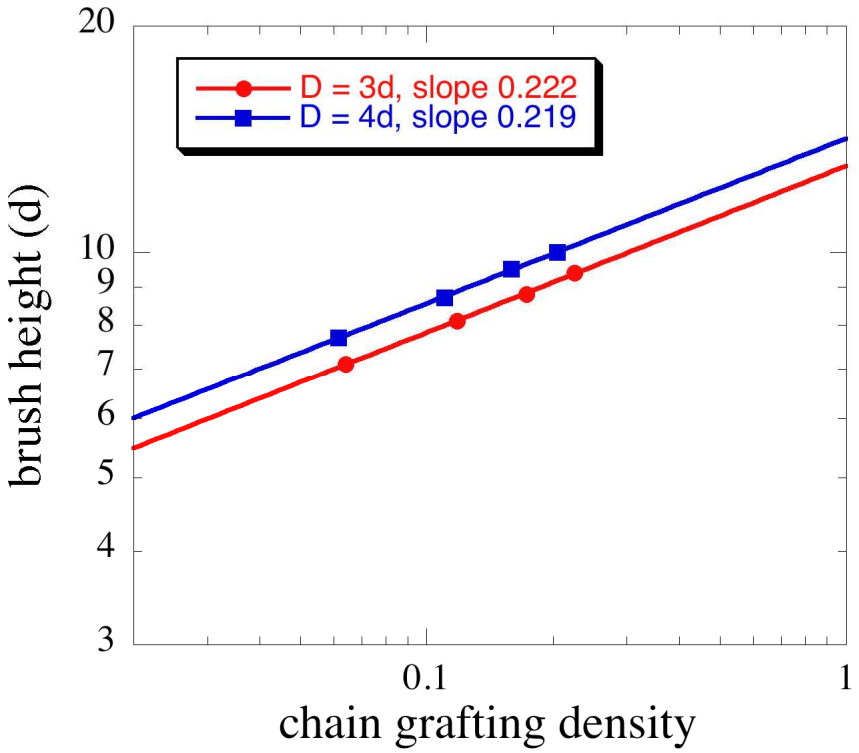
Brush Scaling

Flory argument: $$F \sim \frac{h^2}{V} + \frac{wnV^2}{v} \sim \frac{h^2}{V} + \frac{w\sigma V^2}{h^2} \qquad n = 2\pi RL\sigma, v = \pi h^2 L$$

$$h \sim (Rw\sigma N^3)^{1/4}$$

Ball et al., Macromolcules, 1991



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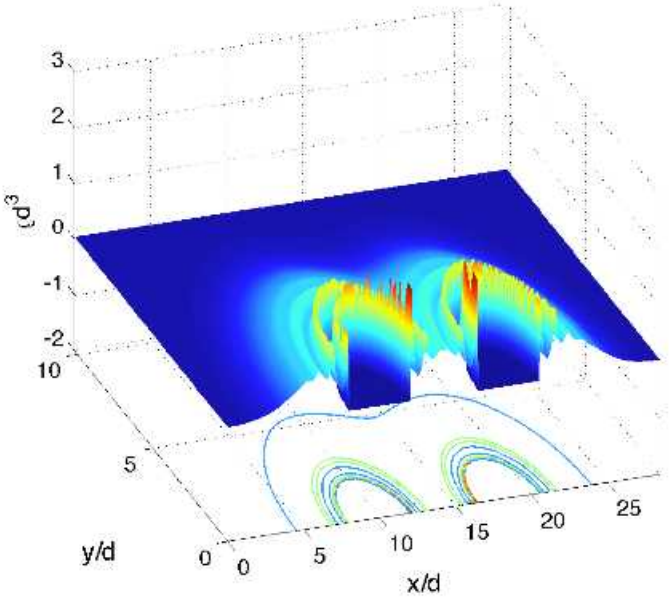
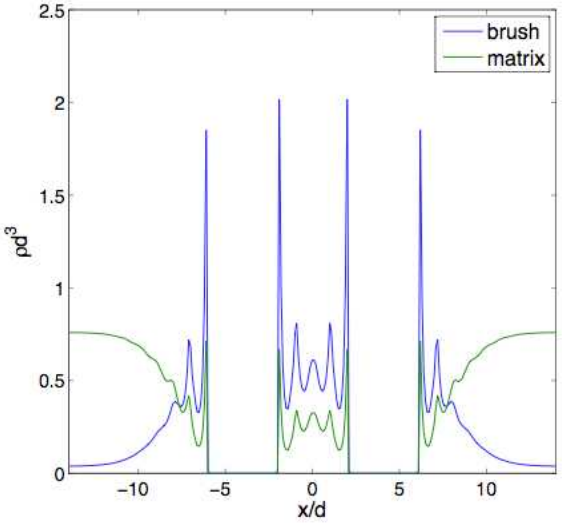
Two Nanorods

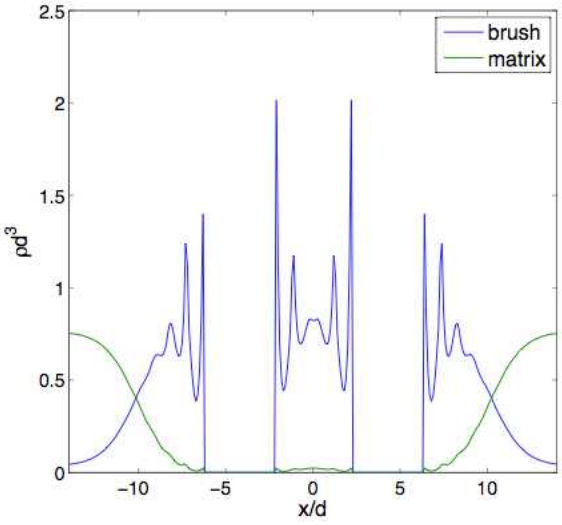
N = 20, P = 20, D = 4d



ε_e = 6kT



ε_e = 10kT



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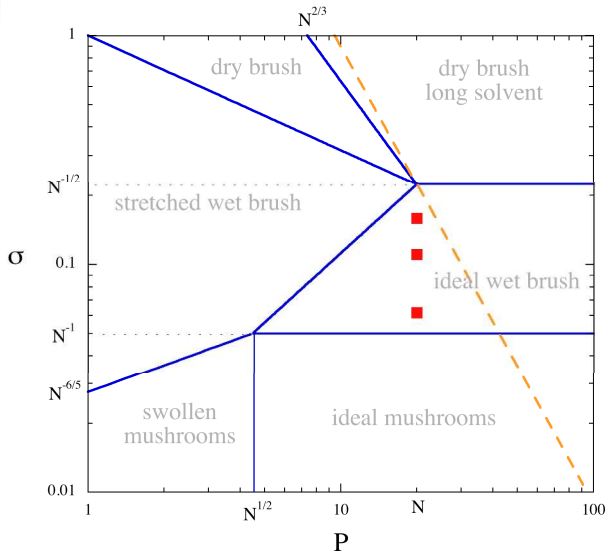
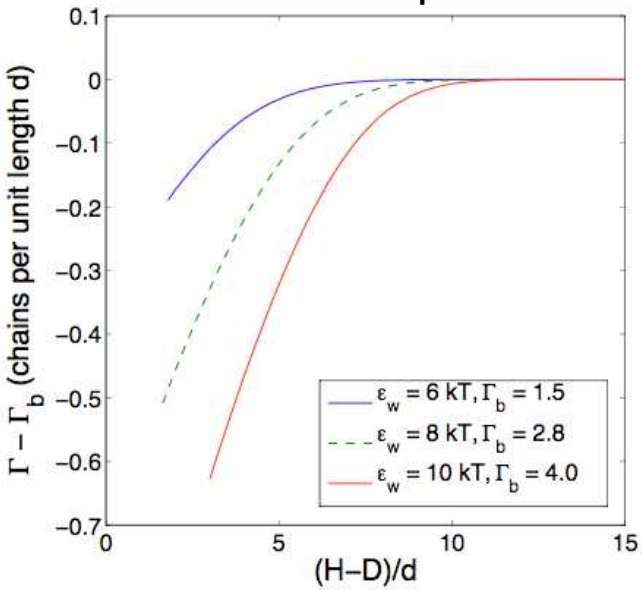
Force between rods



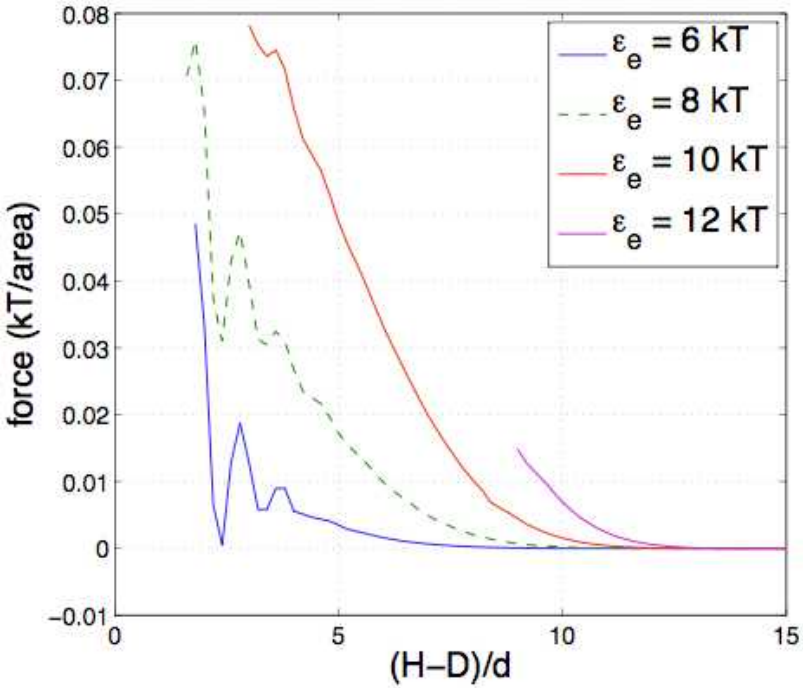
N = 20, P = 20, D = 4d

$$F = \frac{1}{A}\frac{\partial \Omega}{\partial H} = \frac{1}{\pi D}\frac{\partial(\Omega / L)}{\partial H}$$

chain adsorption



force



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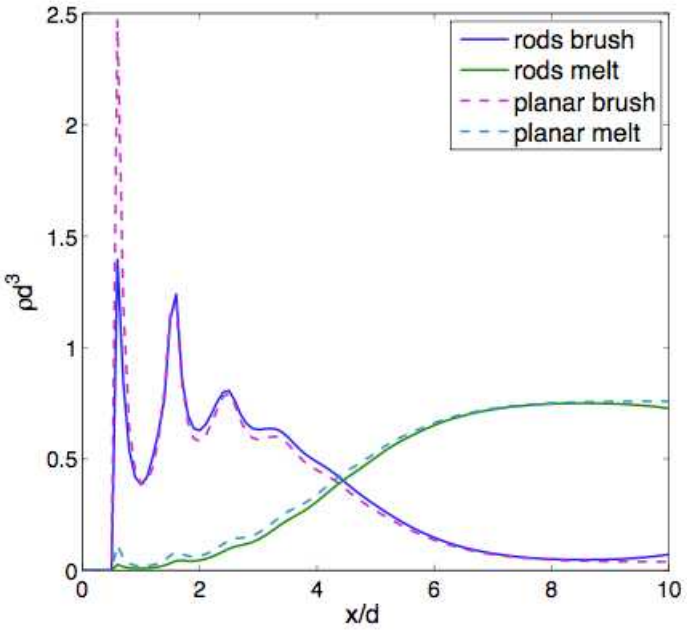
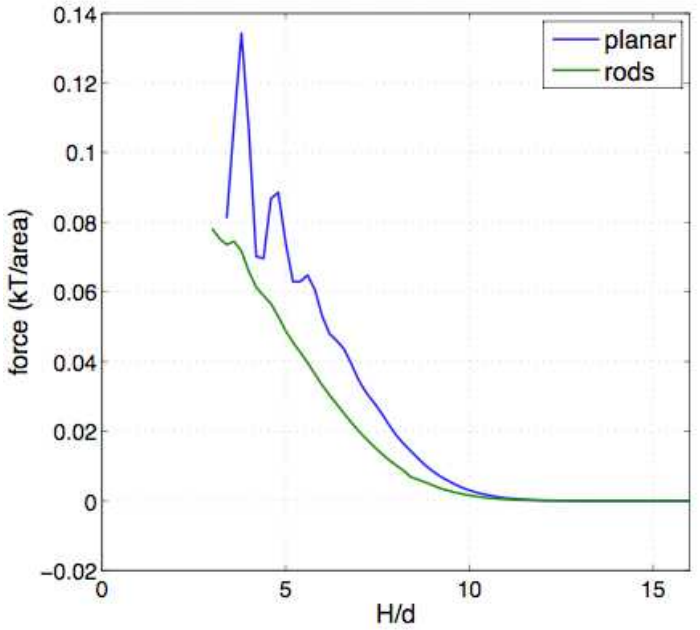
Less force due to curvature

N = 20, P = 20, D = 4d

planar brush: ε_e = 8 kT
cylindrical brush: ε_e = 10 kT

similar brush heights, profiles
force less in curved system





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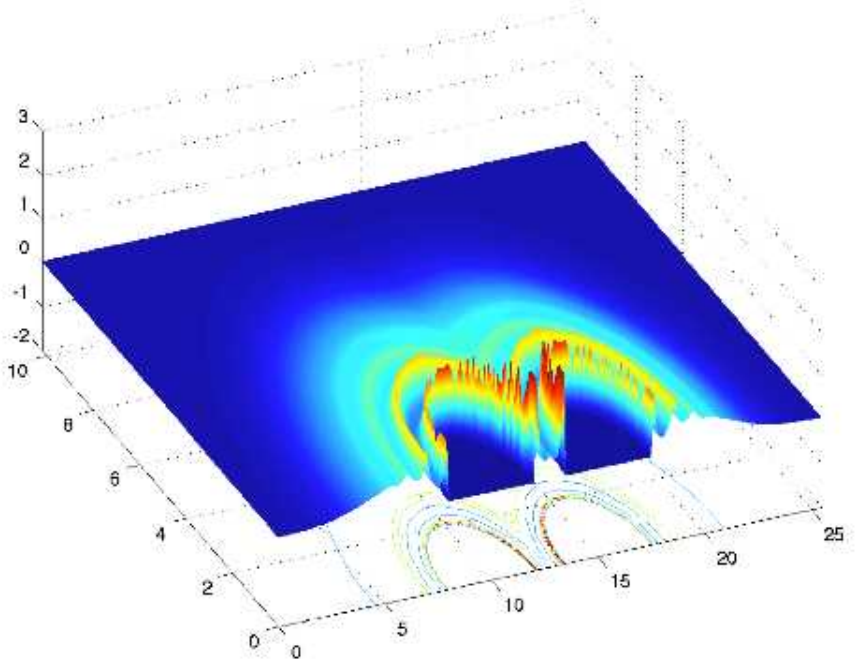
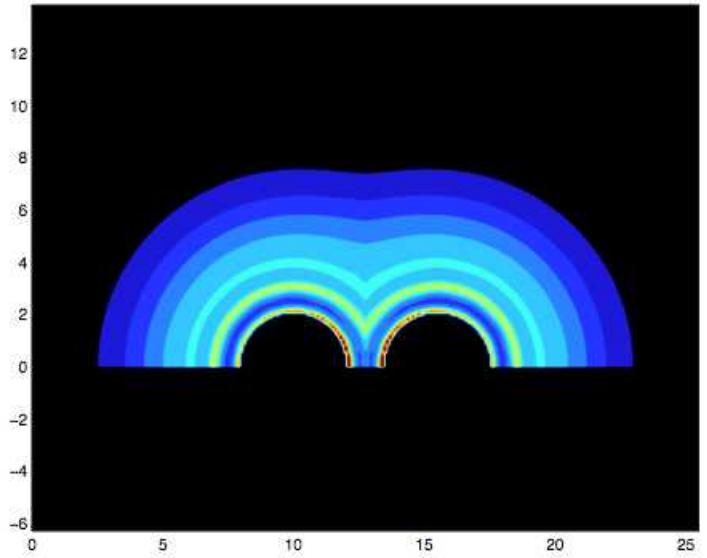
Chains go around rods





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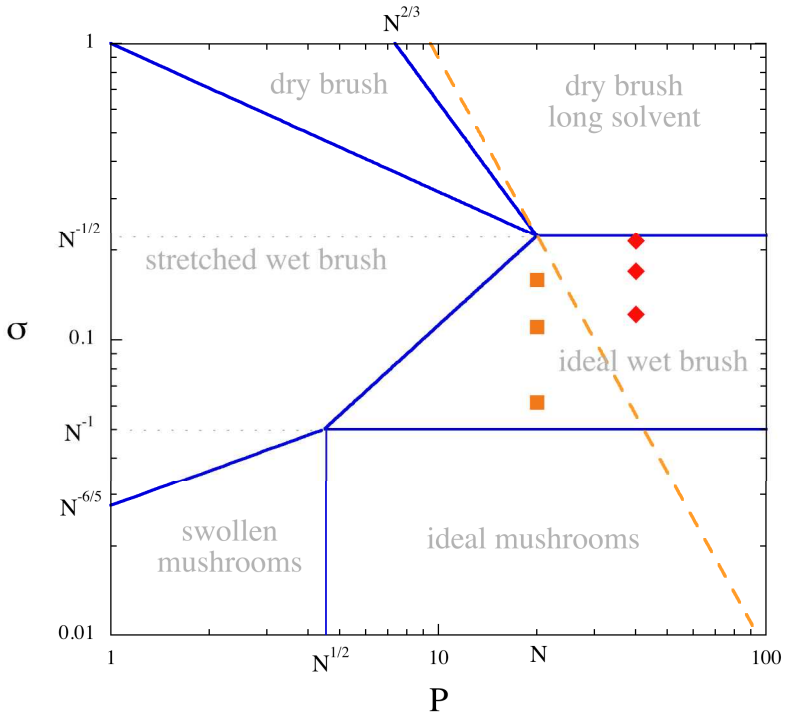
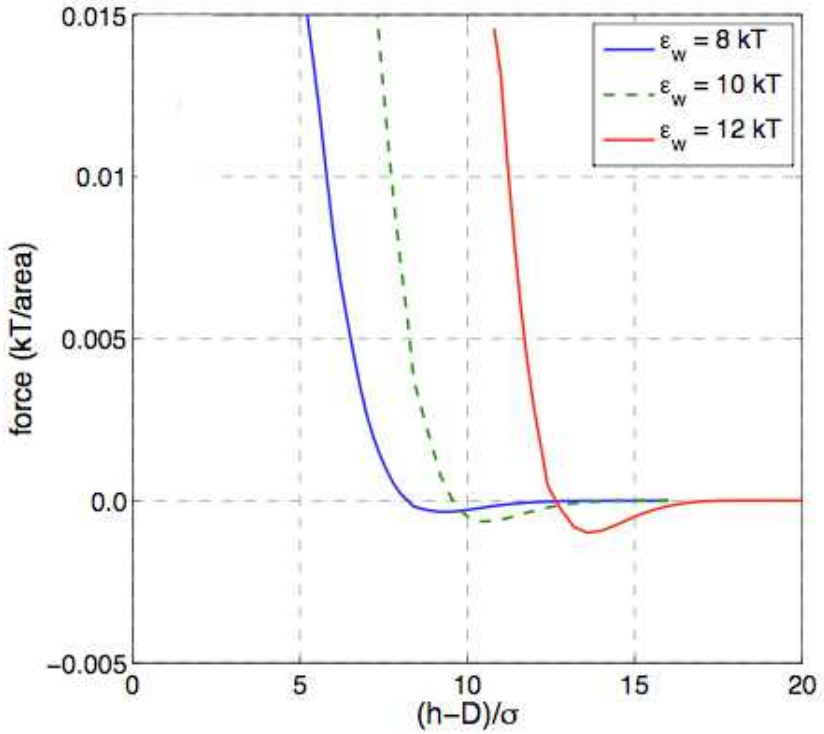
Polymer-Mediated Attractions

N = 20, P = 40, D = 4d





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Outline

- overview
- density functional theory (DFT)
- coated nanorods in melts
- **nanoparticles in polymer films**

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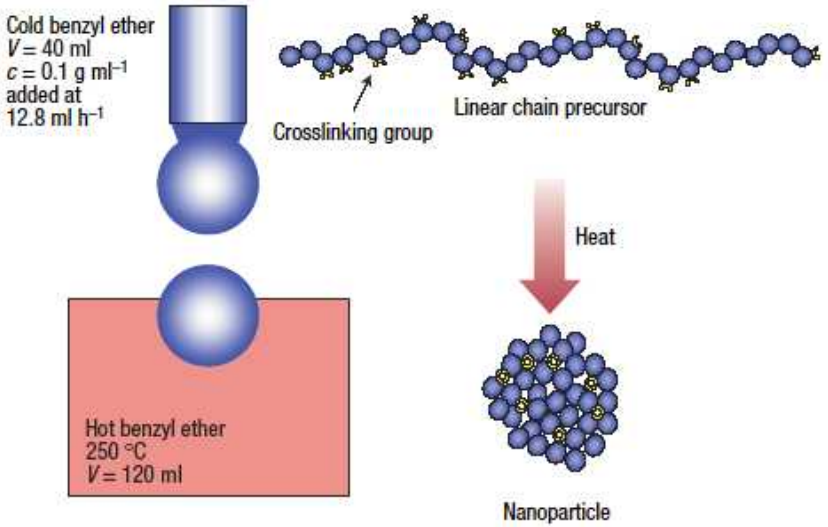
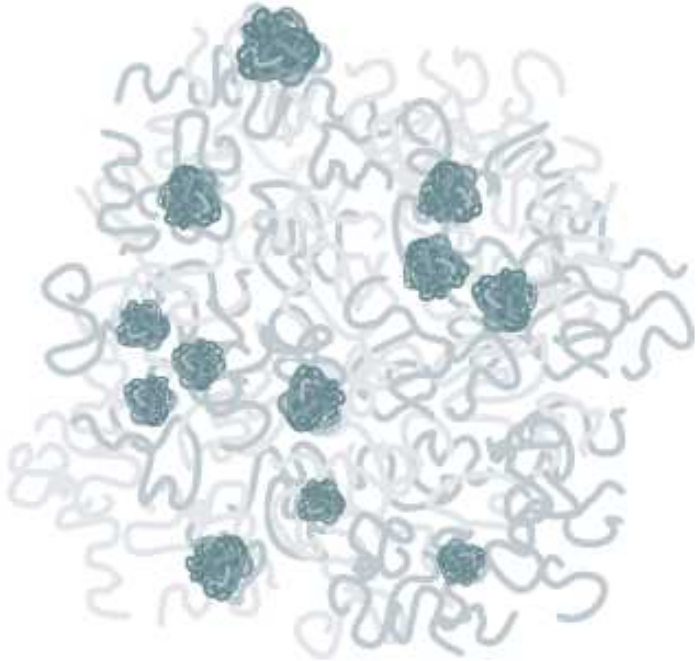
A Model Athermal System: PS NPs in PS

hard-sphere like nanoparticles



mix in melt PS



NPs stay dispersed!
(for $R_{NP} < R_g$)

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Mackay et al., Nature Mat., 2003
E. Harth, J. Am. Chem. Soc., 2002

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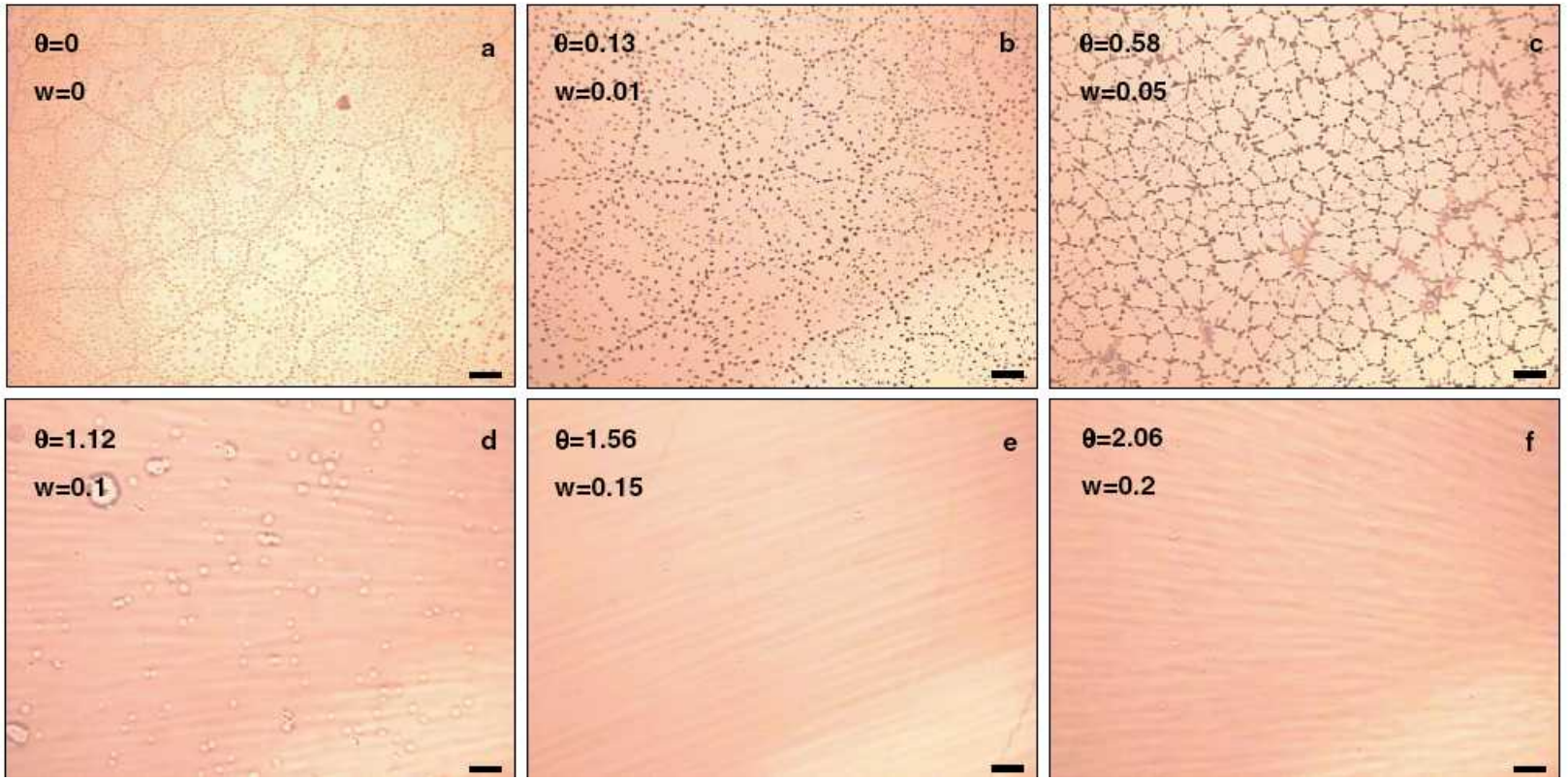
Polymer/NP Thin Films

PS nanoparticles blended with PS on silicon

40 nm thick film

NPs prevent dewetting!



Krishnan et al, Langmuir, 2005

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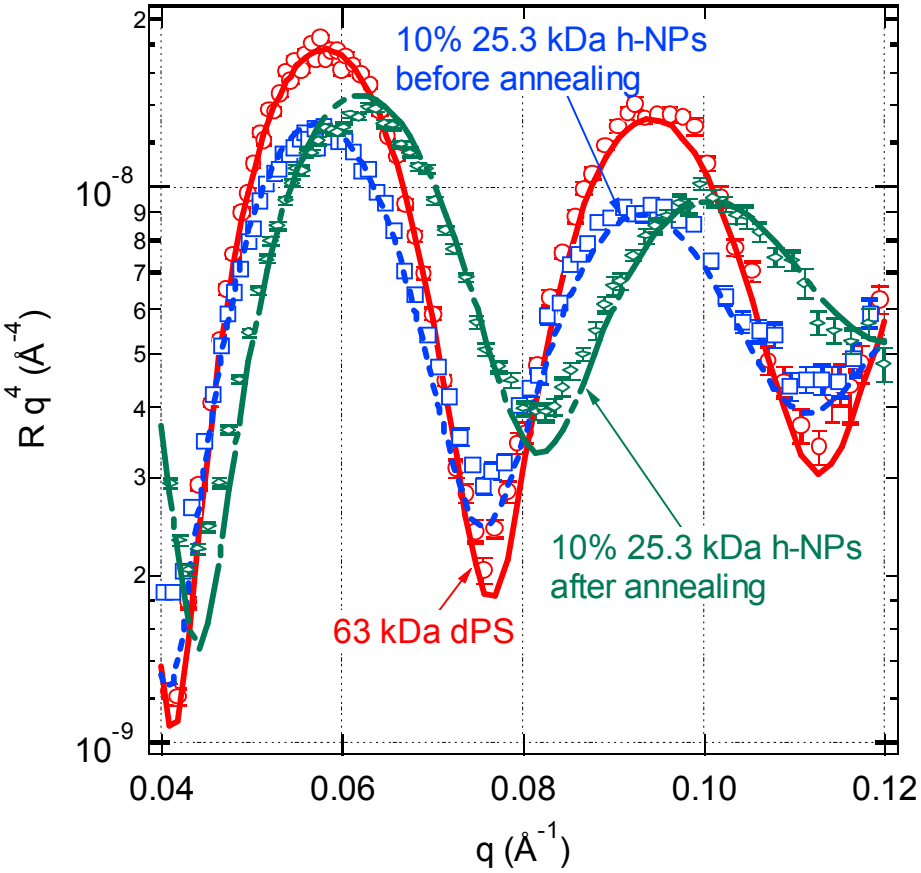
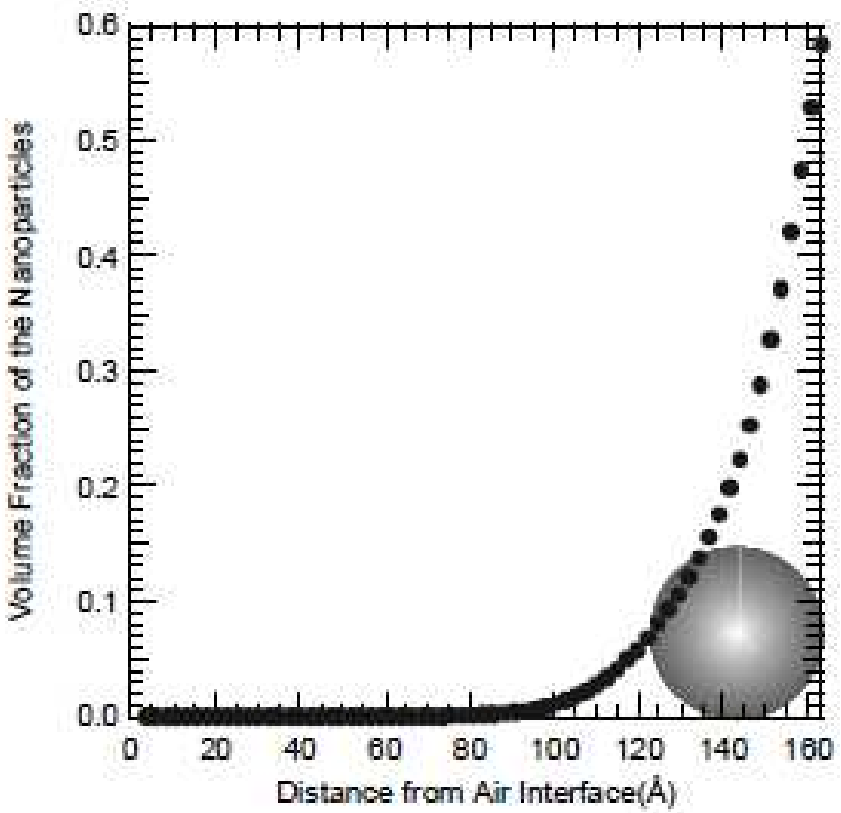
Where are the nanoparticles?

neutron reflectivity





- nanoparticles segregate to surface
- lower surface energy/more surface roughness

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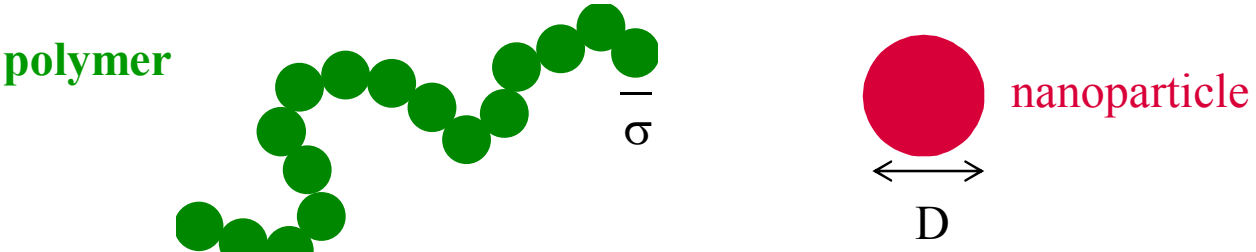
Coarse-Grained Model

athermal system: repulsive LJ spheres



Kuhn length for PS: 1.485 nm

$D = 2.0\sigma = 2.97$ nm

$D = 2.5\sigma = 3.71$ nm

What's an appropriate DFT?

treat particles, polymers in same framework

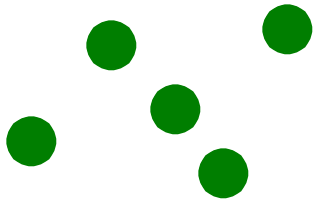
accuracy for mixtures of diff. size sites

"WTC"-DFT

based on associating fluids

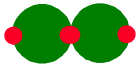
(Wertheim's TPT1 theory for bulk)

reference fluid: monomers



bonding sites

monomers bond:



as bonding energy $\rightarrow \infty$ get polymers

S. Tripathi and W.G. Chapman, *Phys. Rev. Lett.* **94**, 087081 (2005); *J. Chem. Phys.* **122**, 094506 (2005)

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Elements in WTC functional

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

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

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

chain bonding contribution:

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

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Calculational Details

surface potential:

$$V_\alpha(z) = \frac{2}{15}\left(\left(\frac{\sigma}{z-\delta_\alpha}\right)^9 - \left(\frac{\sigma}{z-\delta_\alpha}\right)^3\right), \quad z < z_{cut}$$

monomers $\delta_p = 0$

nanoparticles $\delta_{np} = (\sigma_{np} - 1)/2$

- start at low particle concentrations
- keep total packing fraction fixed:

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

- follow solution as particle concentration increases

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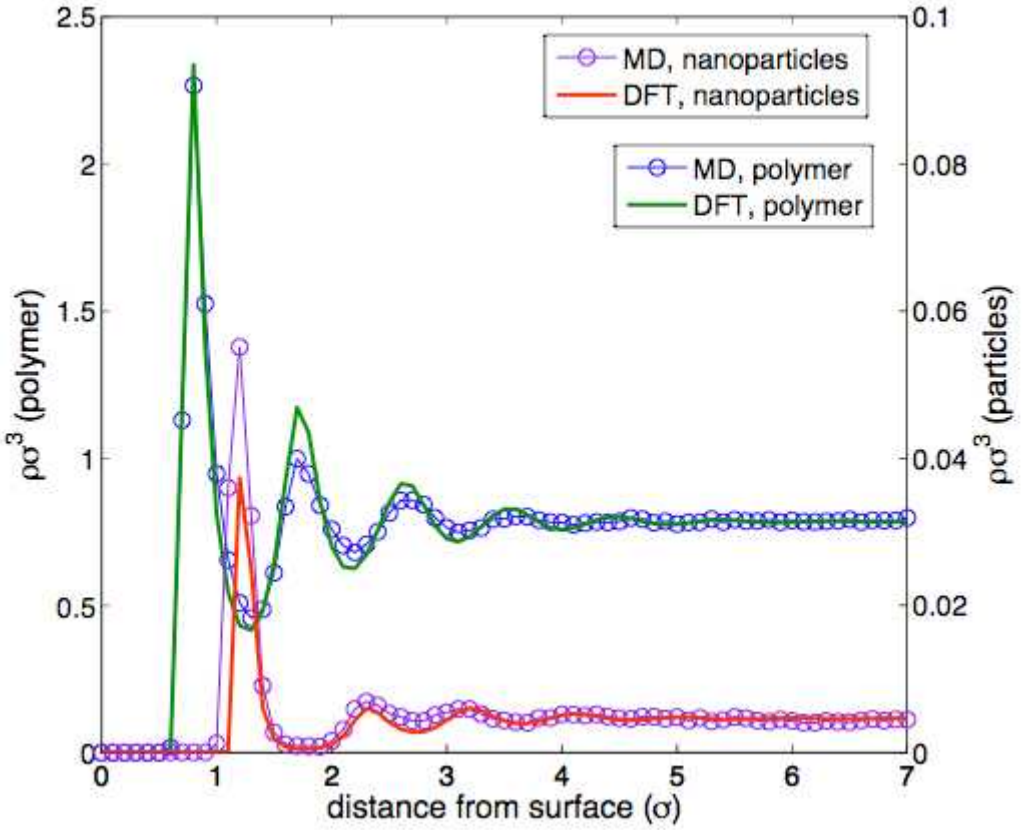
Nanoparticle/Polymer Thin Films

with E. S. McGarrity and M. E. Mackay (MSU)

F-DFT matches simulation

N = 20, D = 2σ



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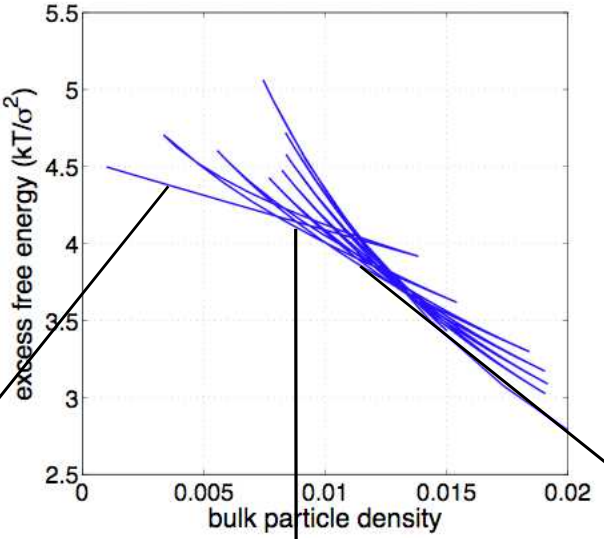
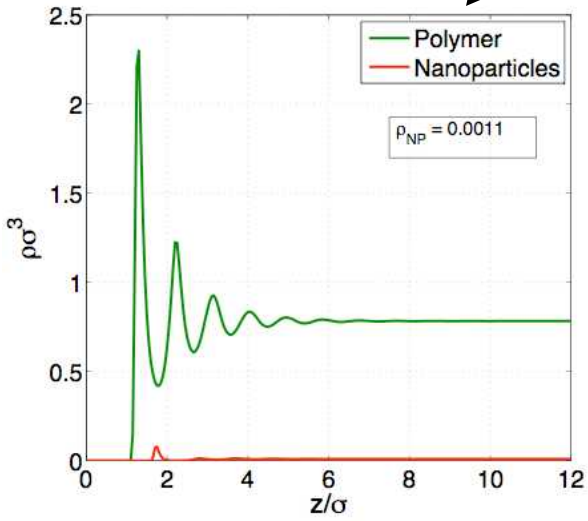
Layering Transitions

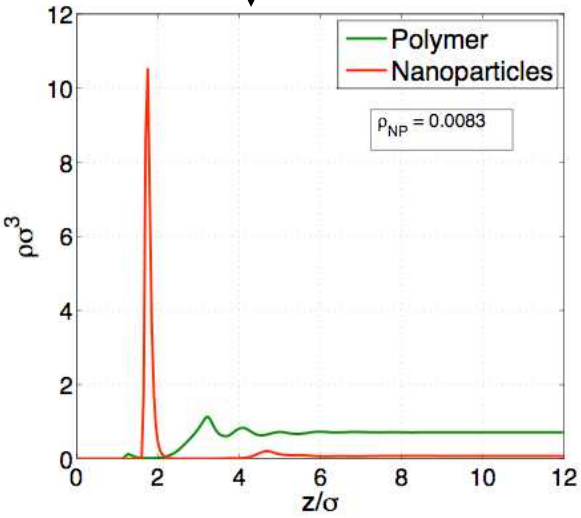
N = 20, D=2σ



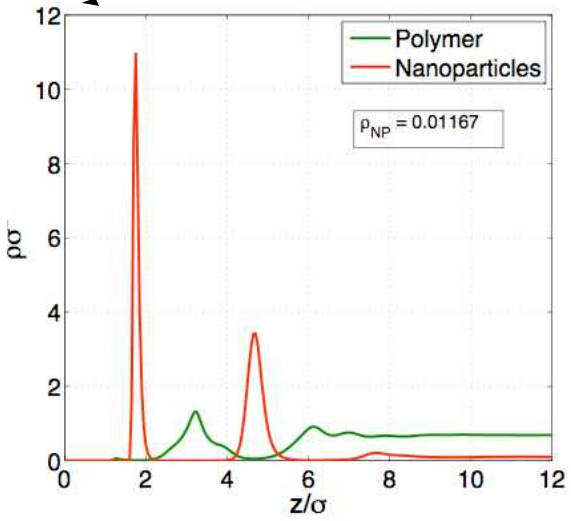
no layers



1 layer



2 layers



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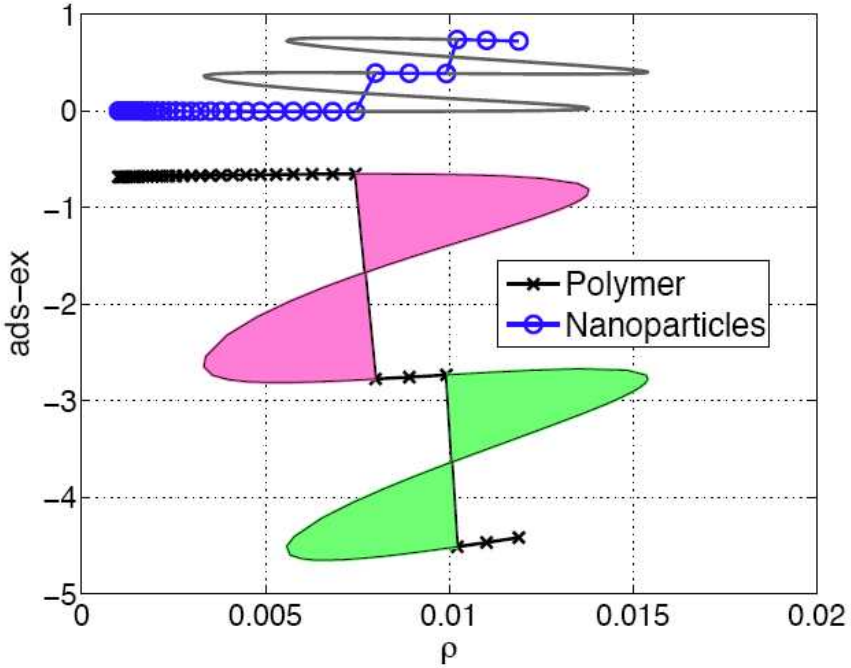
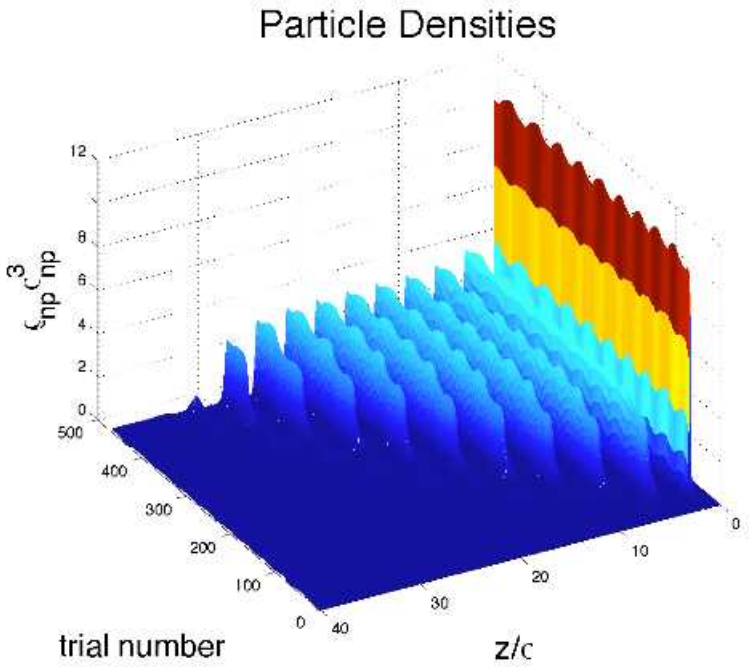
Layering

Excess adsorptions



Particle Densities



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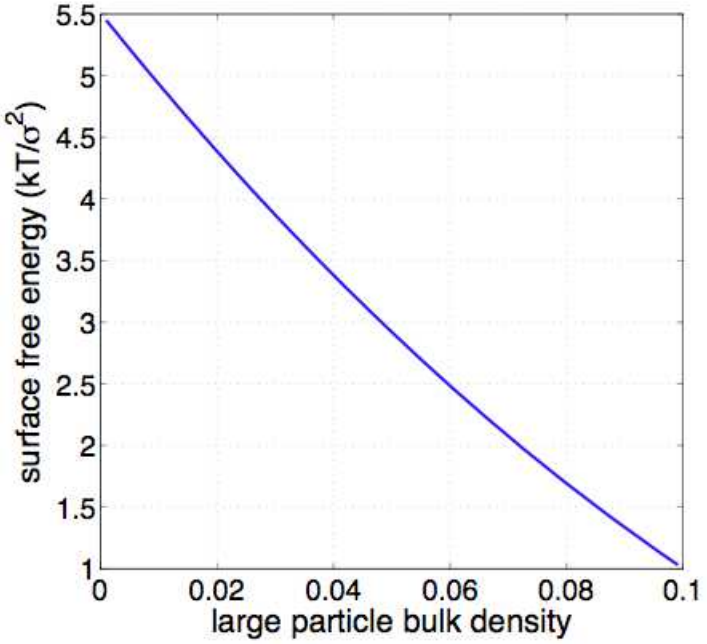
This is a polymer effect!

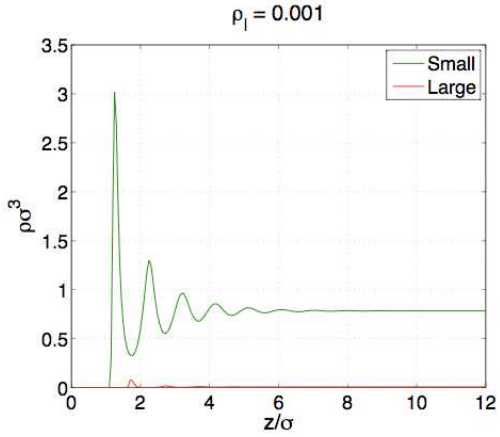
binary hard sphere mixture

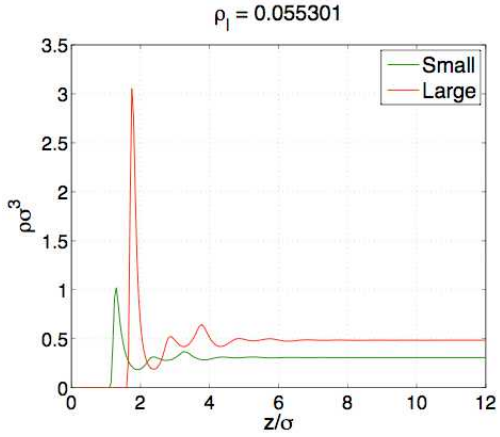
$D_s = 1\sigma$

$D_b = 2\sigma$

no phase transition:







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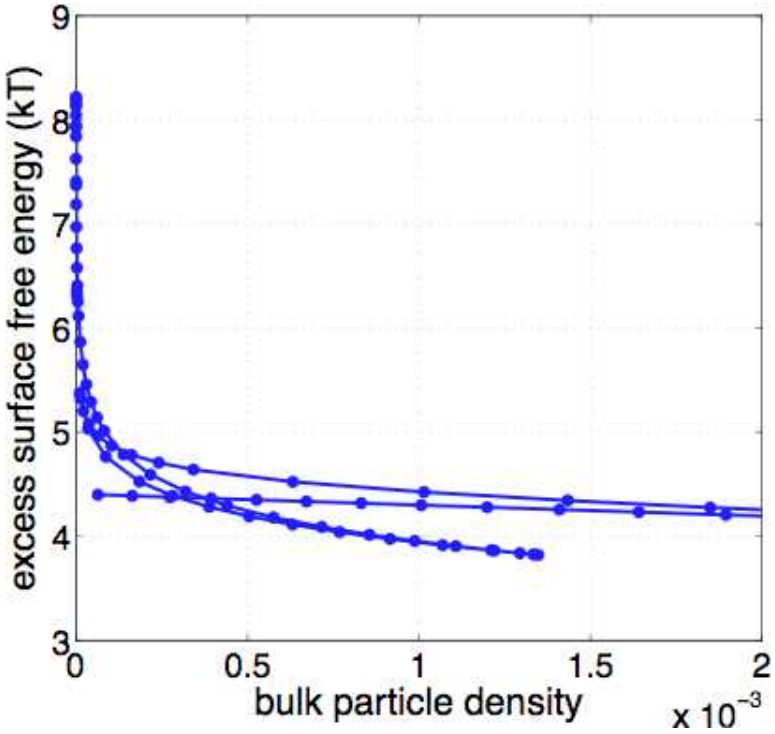
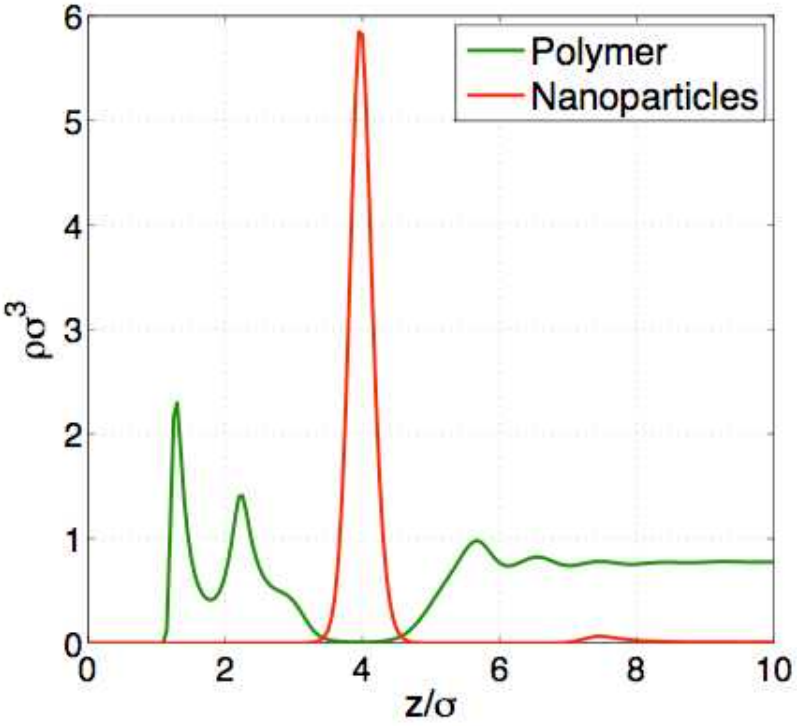
Larger Particles

N = 20, D = 2.5σ





- ongoing study
- effects of attractions?

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Summary

- nanorods
  - brush profiles similar to scaling
  - attractions for P>N
  - repulsions for P=N despite some desorption

- nanoparticle/polymer films
  - DFT appears accurate compared to MD
  - first-order layering transitions
  - polymer effect

Thanks

Collaborators

Erin McGarrity (MSU)
Michael Mackay (MSU)

Laura Frink (SNL)
Nelson Bell (SNL)
John Curro (SNL)

Funding

Sandia LDRD
CINT

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