SAND2008-7501C

Forces Between Nanorods with End-Adsorbed Chains in Polymer Melts

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Main Question

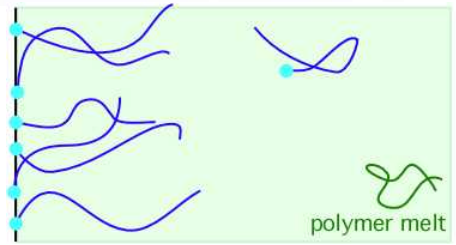
- how best to disperse a nanoparticle in a polymer?
  - –what materials?
  - –use surfactant or polymer brush?
  - –what molecular weight vs. nanoparticle size?
- colloidal size-particles: treat as flat
- nanoparticles: must treat curvature

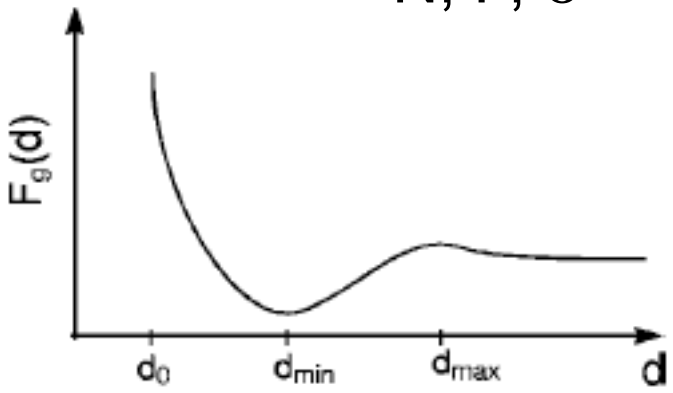
<u>This talk</u>

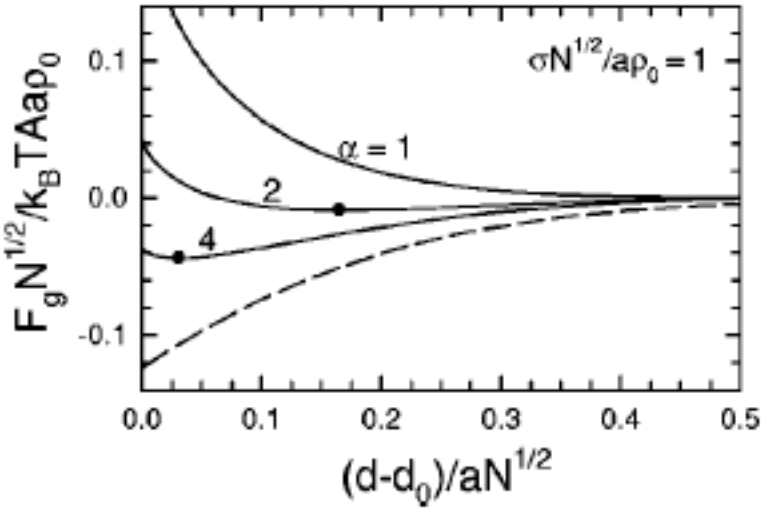
- focus on entropic interactions
  - – particles coated with polymer
  - – immersed in homopolymer of same type
  - – $\chi = 0$

Forces Between Flat Surfaces

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







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

Matsen and Gardiner,
J Chem Phys, 2001

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What happens on curved surfaces?

from Xu et al., *J. Polym. Sci. B Polym. Phys.* **44,** 2811, (2006)

SCF calculations
N = P = 50, D=30a

QuickTime™ and a
decompressor
are needed to see this picture.

QuickTime™ and a
decompressor
are needed to see this picture.

do see attractions due to autophobic dewetting

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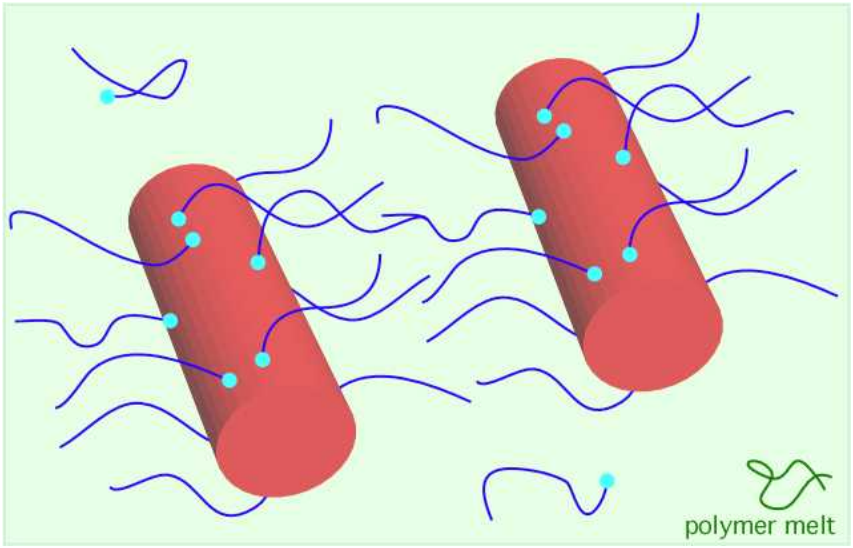
The Problem:

dispersion of nanosized objects in a polymer melt

same rules as for polymer-stabilized colloids?



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

is the force repulsive or attractive?
will the chains desorb?
is there a curvature effect?

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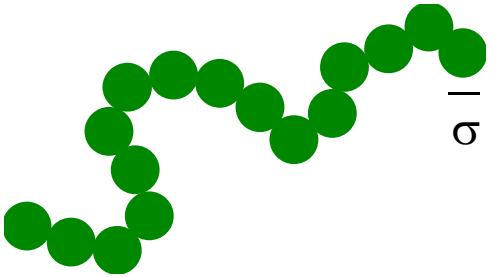
Coarse-Grained Calculations

athermal system: only interactions are entropic
polymer: model as chain of hard spheres
nanorod: model as impenetrable cylinder

polymer



nanorod

Kuhn length for PS: 1.485 nm

calculate force using
fluids density functional theory (DFT)

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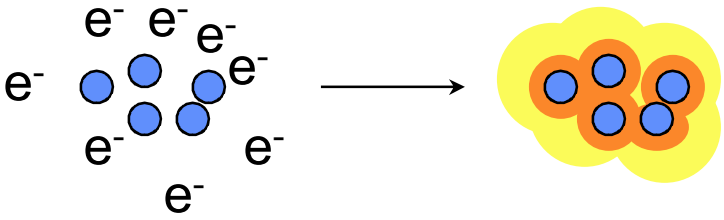
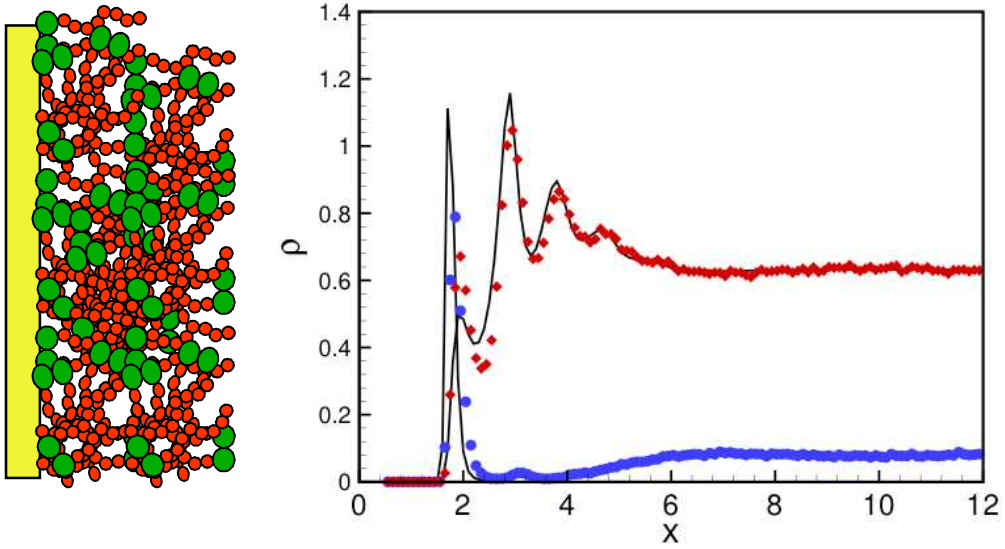
Density Functional Theory (DFT)

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

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

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

Laura Frink, PI

http://software.sandia.gov/tramonto

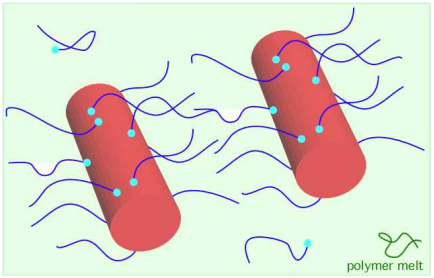
F-DFTs = nonlinear integral equations

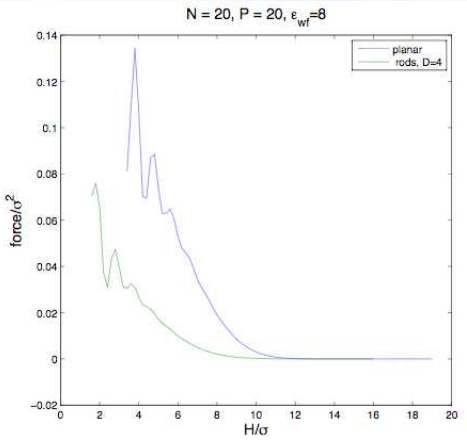
- solve in 3D, Cartesian grid
- Newton-Raphson solver
- parallel
- sophisticated linear solver algorithms
- arc-length continuation algorithms

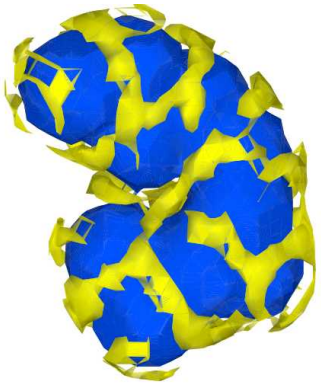
The Trilinos Project

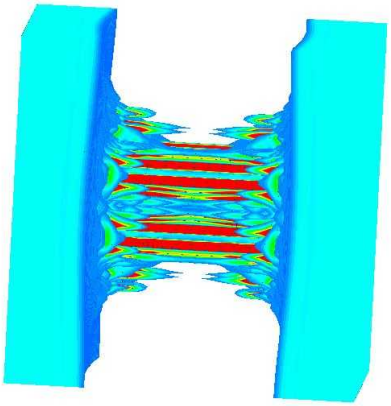
What can F-DFT do?

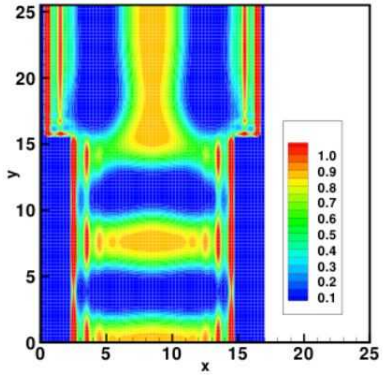
- forces between particles
- phase behavior
- solvation free energies
  - implicit solvent
- complex geometries
- complex chain architectures
- compare to simulation (MD)

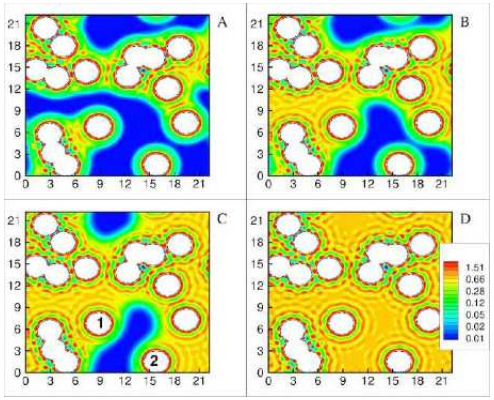


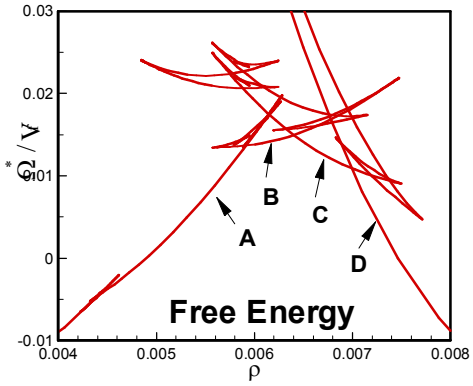












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Our approach: CMS-DFT

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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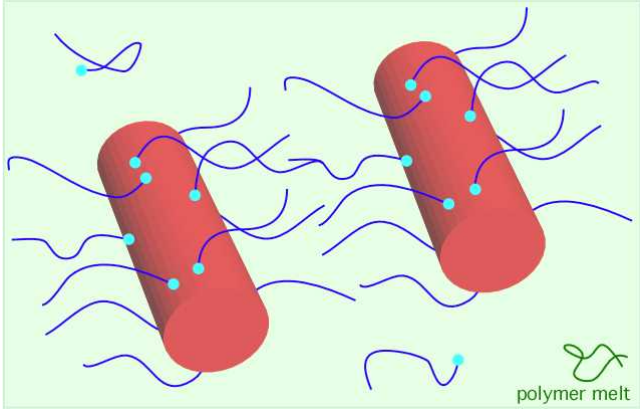
Calculation Details

- parallel cylinders
- athermal (repulsive interactions)
- adsorbed chains
  - N = 20
  - $\rho_b d^3 = 0.04$
- matrix chains
  - P = 20,30,40
  - $\rho_b d^3 = 0.76$



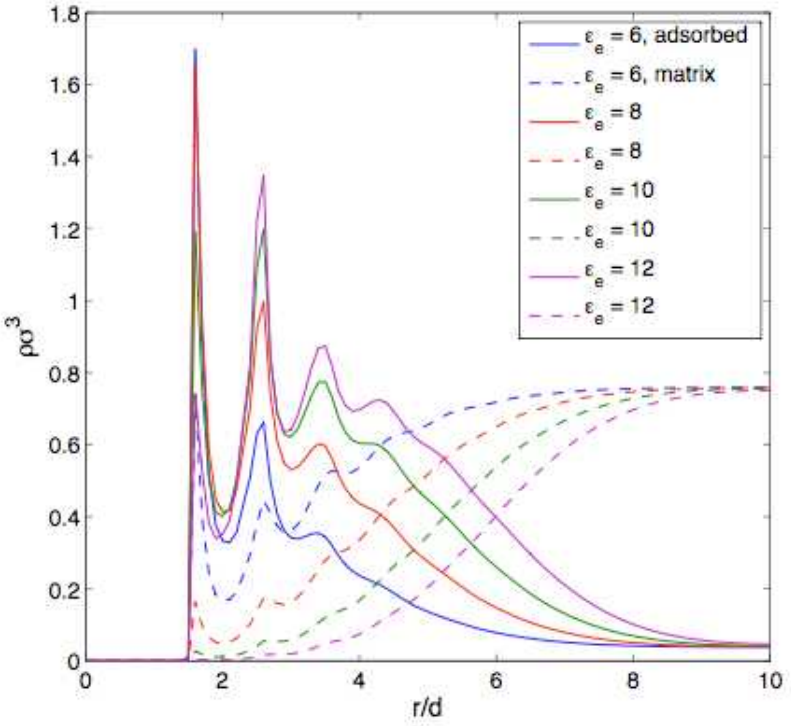
surface interactions:

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

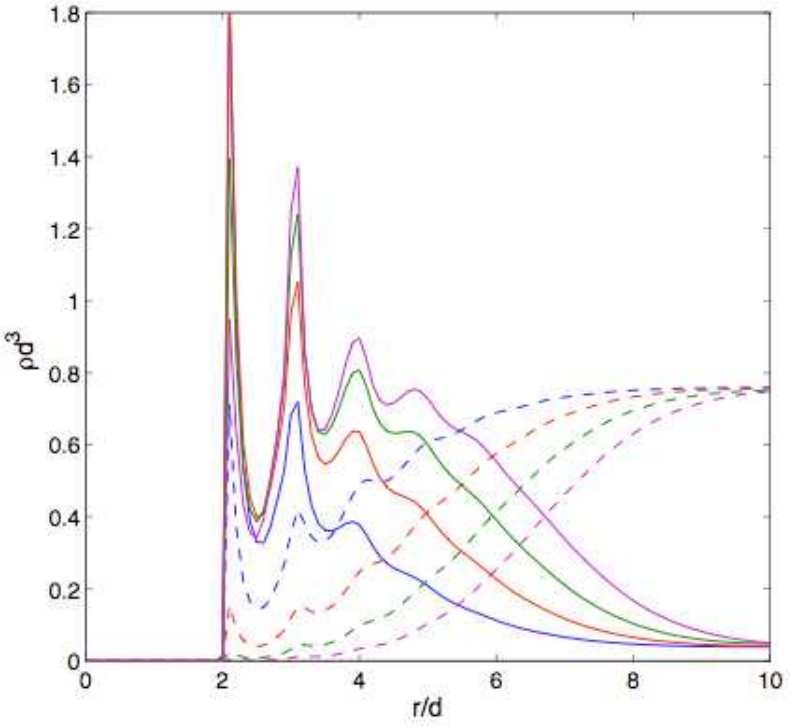
Nanorods: Brush Profiles

N = 20, P = 20

D = 3d



D = 4d



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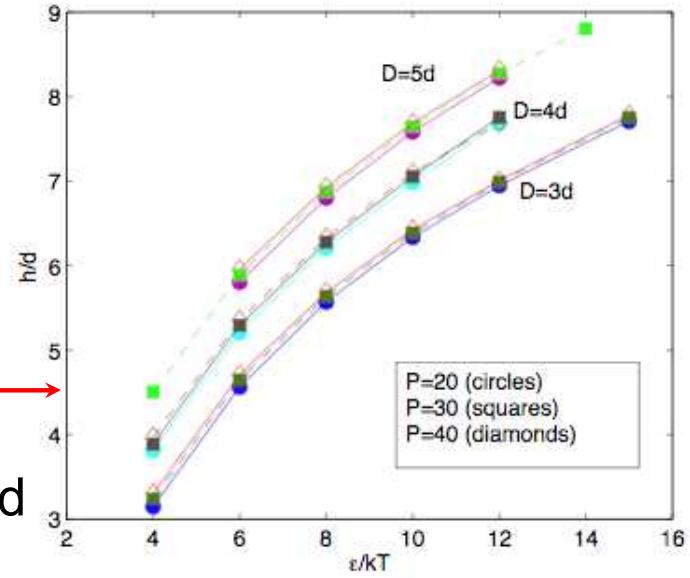
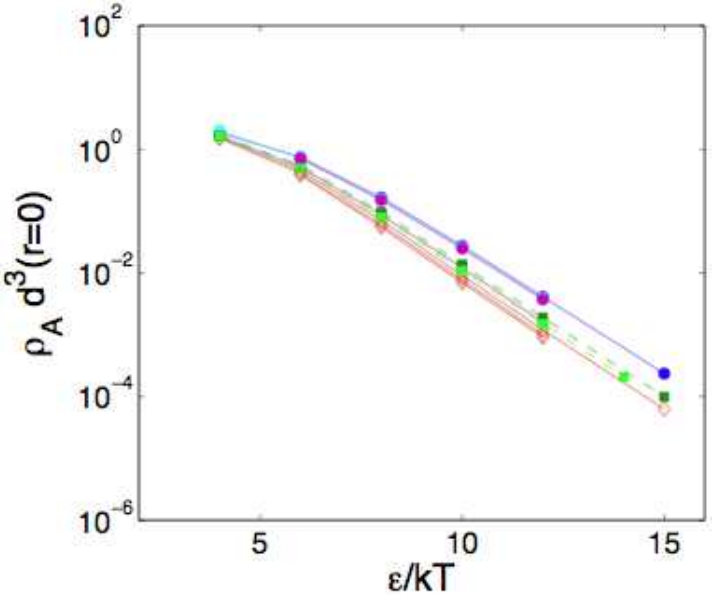
Brush Structure

height of brush



ideal
R = 4.5d

penetration of matrix chains



small ε: wet ideal brush
larger ε: towards dry brush

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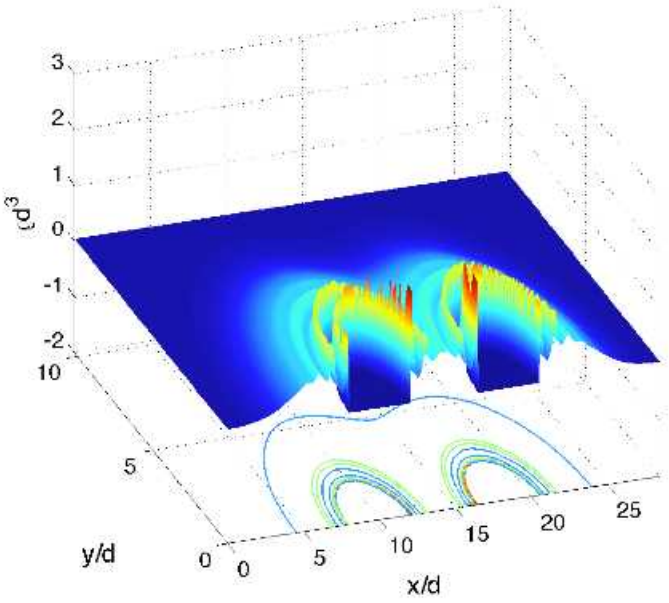
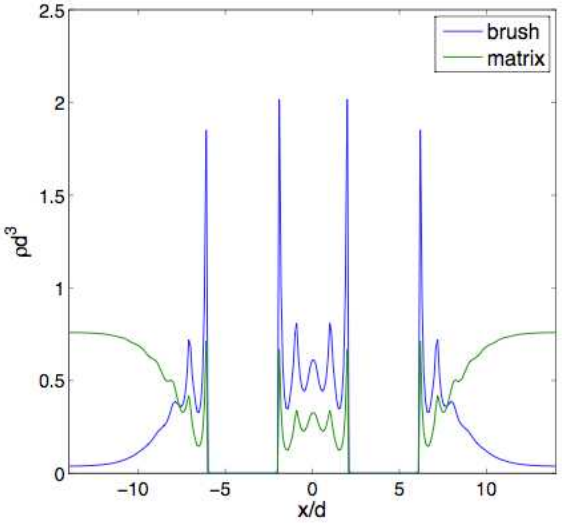
Two Nanorods

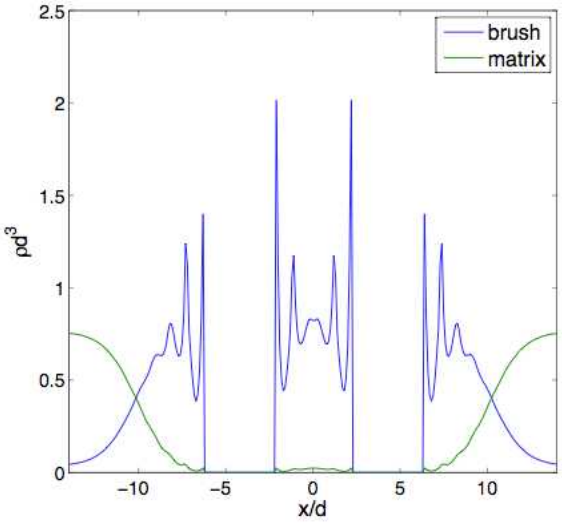
N = 20, P = 20, D = 4d



ε_e = 6kT



ε_e = 10kT



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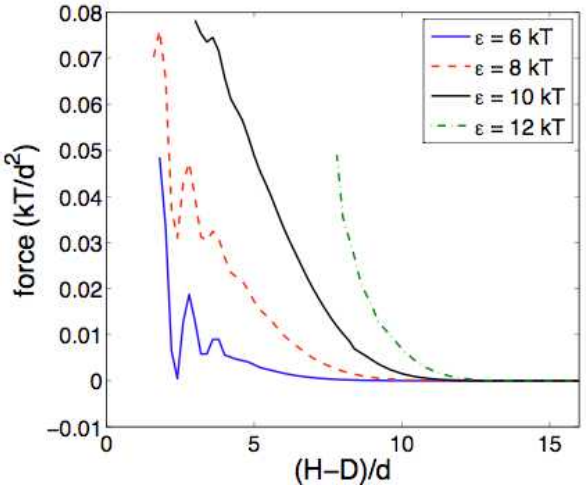
Force between rods

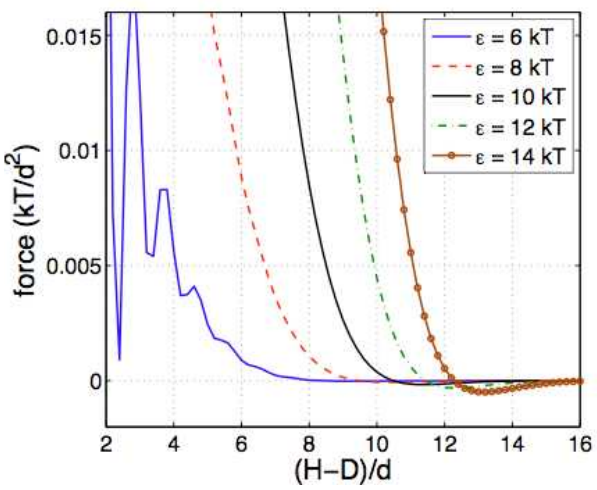
$$F = \frac{1}{A}\frac{\partial \Omega}{\partial H} = \frac{1}{\pi D}\frac{\partial (\Omega / L)}{\partial H}$$

D = 4d

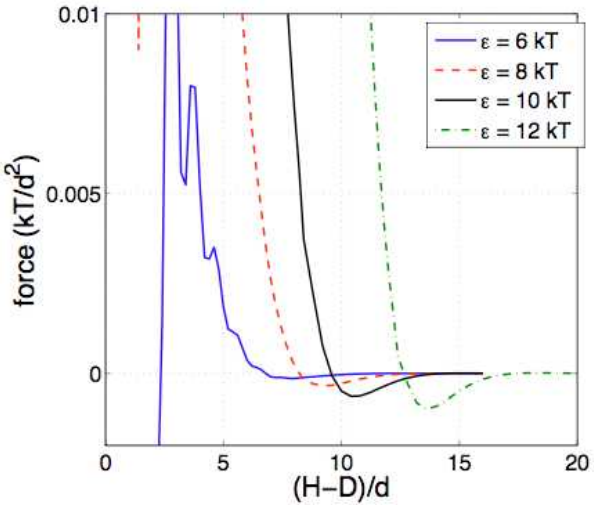
P = 20



P = 30



P = 40



autophobic dewetting still present
always some attraction at contact

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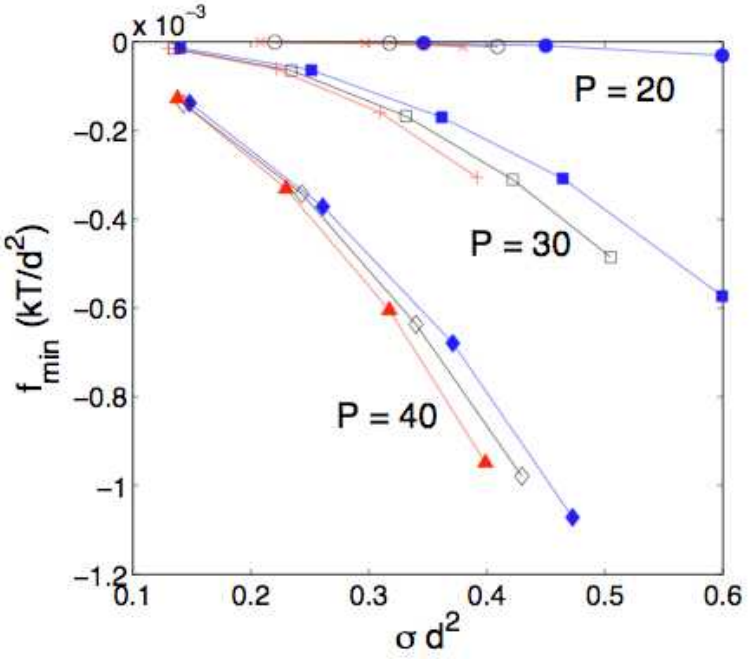
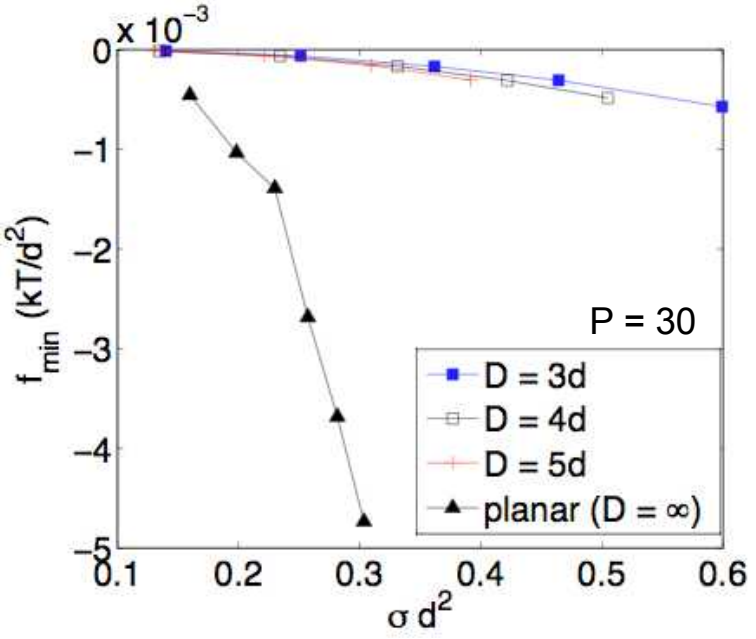
Attractive Minimum

depth of minimum vs. density of adsorbed chains





- depth increases for:
  - longer matrix chains
  - more adsorbed chains
  - larger rod diameter

- trends consistent with SCF for flat, spherical brush interactions
  (Matsen and Gardiner, J Chem Phys, 2001; Xu et al., J. Polym. Sci B, 2006)

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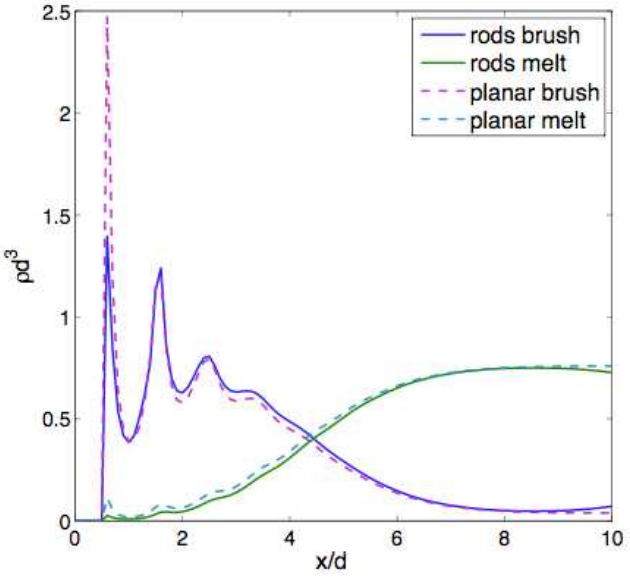
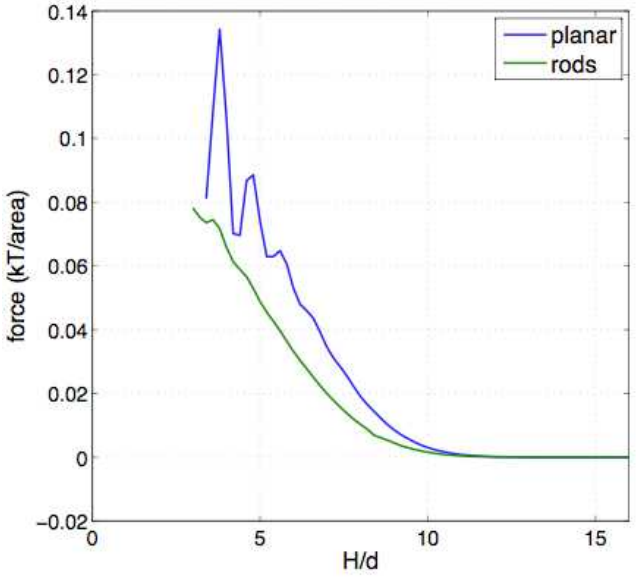
Less force due to curvature

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

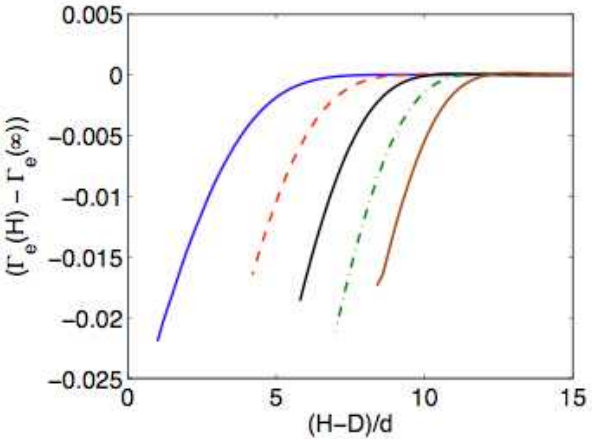
similar brush heights, profiles
force less in curved system





P = 20
D = 4d

chains do desorb
(D=4d, P=30)



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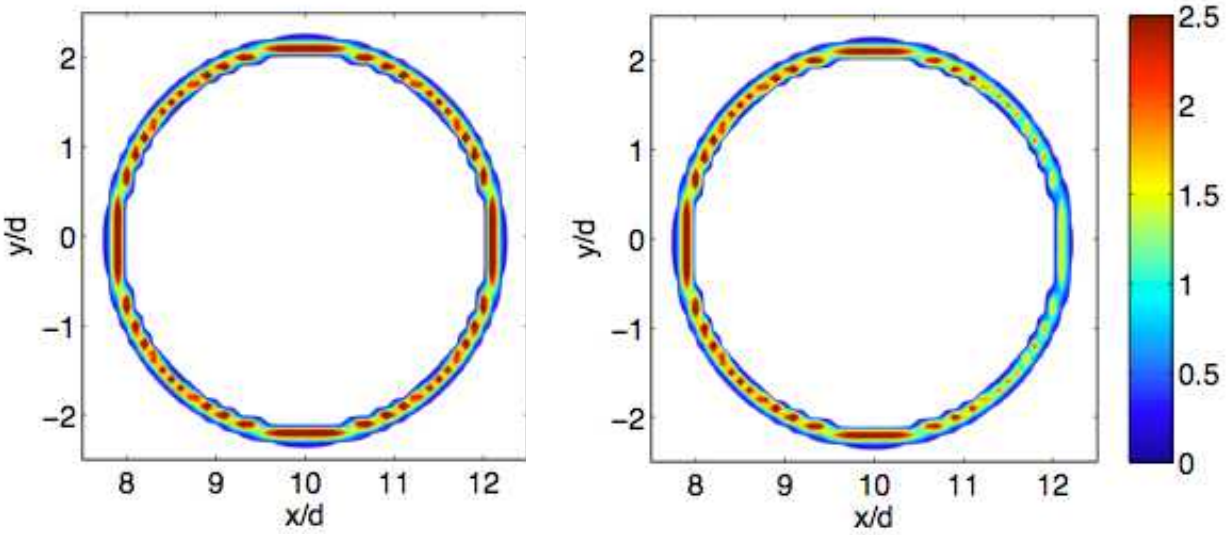
Chains rearrange as rods approach

D = 4d, P = 20,
ε = 10 kT

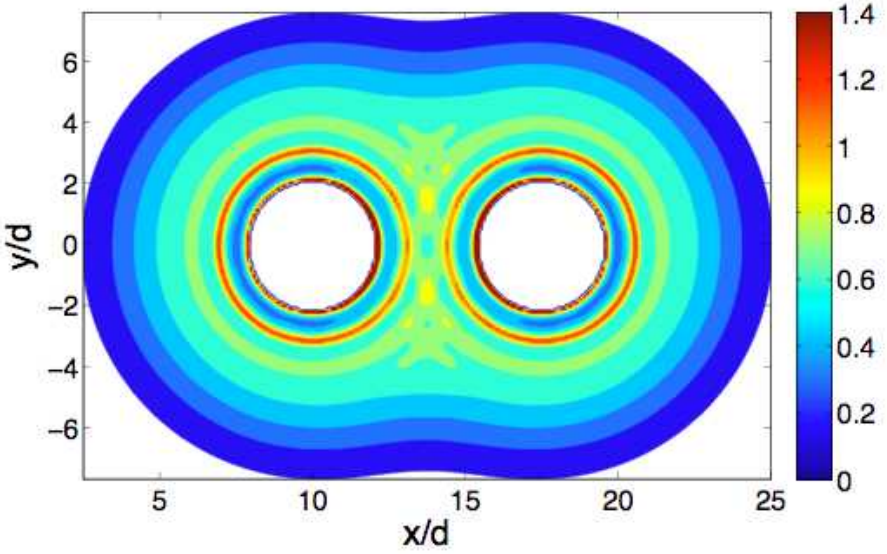
(H-D)/d = 16

(H-D)/d = 3.5

end densities



brush density



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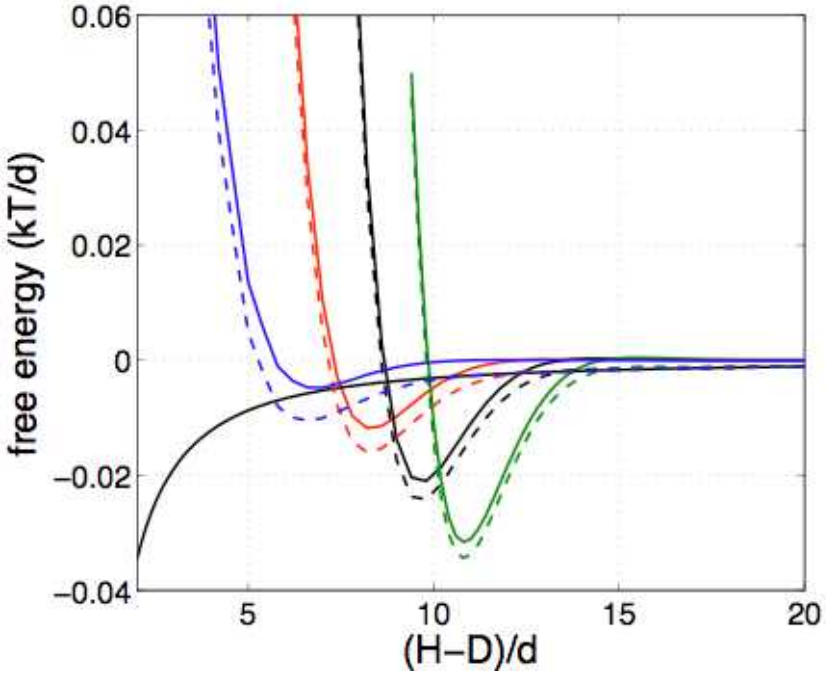
Experimental Implications

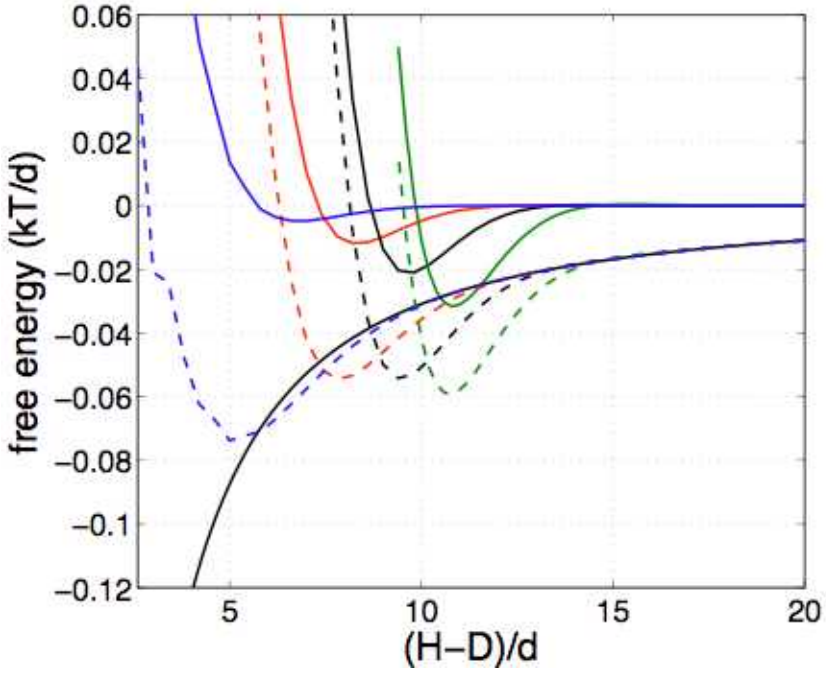
D = 5d, P = 40

rod-rod van der Waals: $$W = -\frac{ALR^{1/2}}{24H^{3/2}}$$

A = 1.2 kT



A = 12 kT



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Summary

- chains desorb but still get repulsions
- repulsive force less for same brush height due to curvature
- always an attractive force present
  - autophobic dewetting
  - smaller than for flat brushes
  - increases with P, ε, D
- attractions can be significant

A. L. Frischknecht, *J. Chem. Phys.*, **128**, 224902 (2008)

Thanks

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

- LDRD
- C2
- Laura Frink
- Nelson Bell

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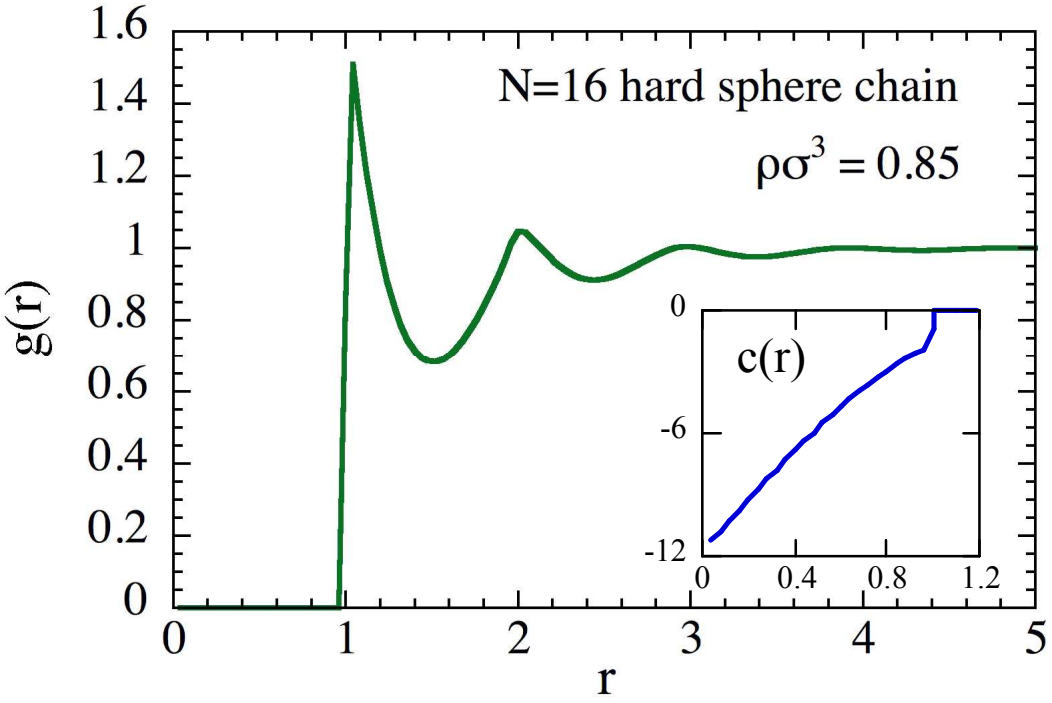
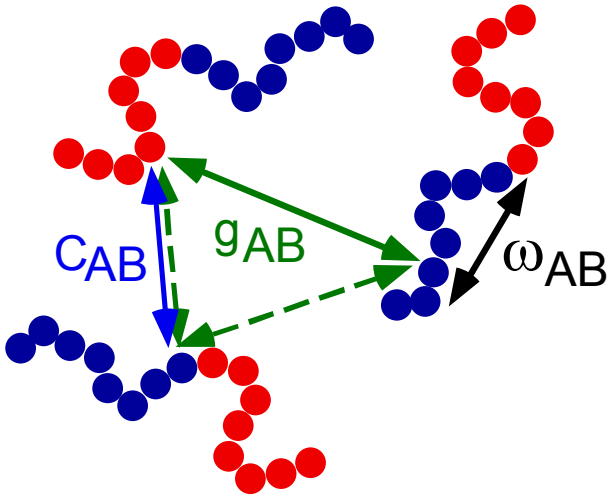
Input to CMS-DFT: PRISM Theory

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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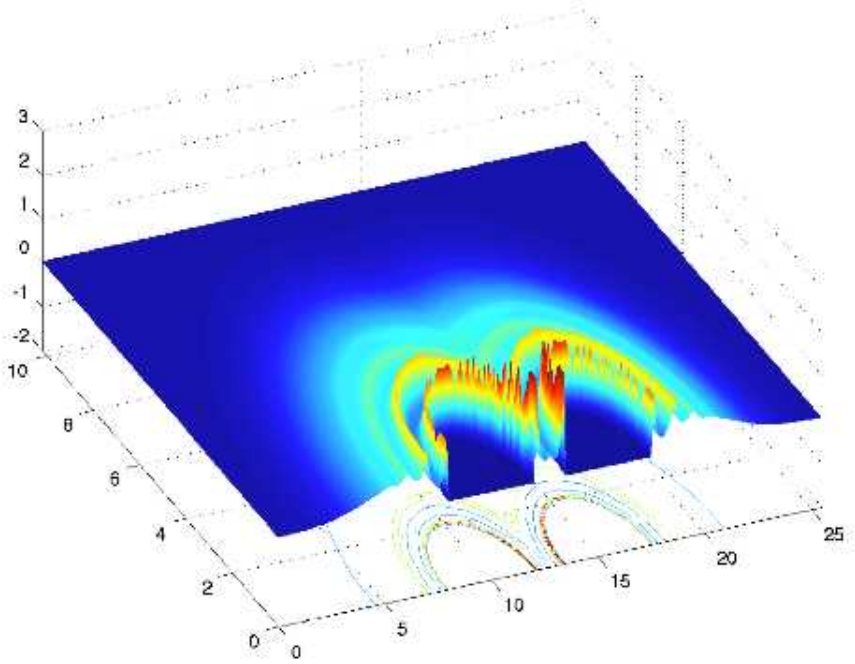
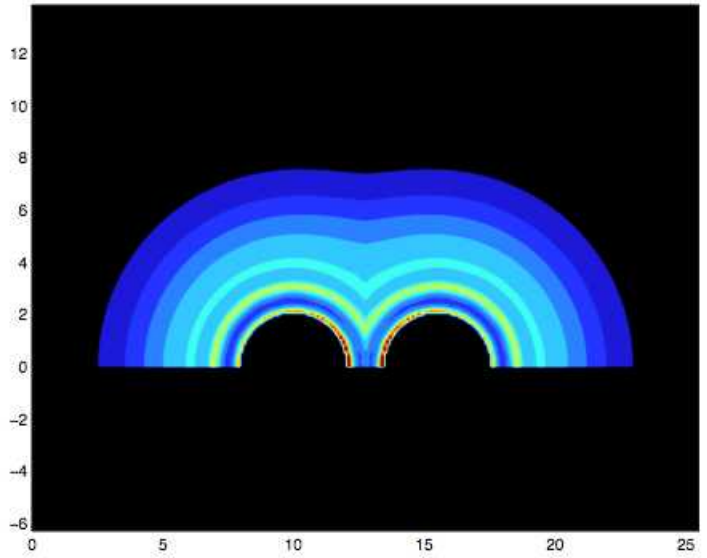
Chains go around rods





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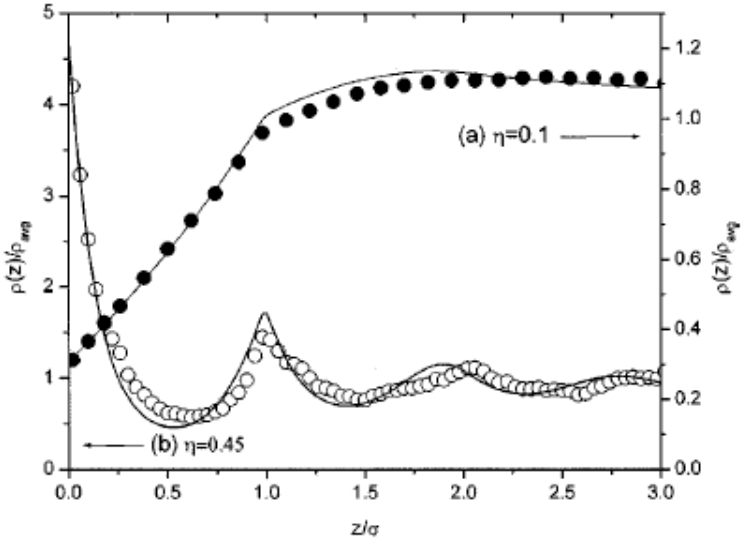
Advantages/Capabilities of F-DFT

- 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



Tripathi & Chapman, PRL, 2005

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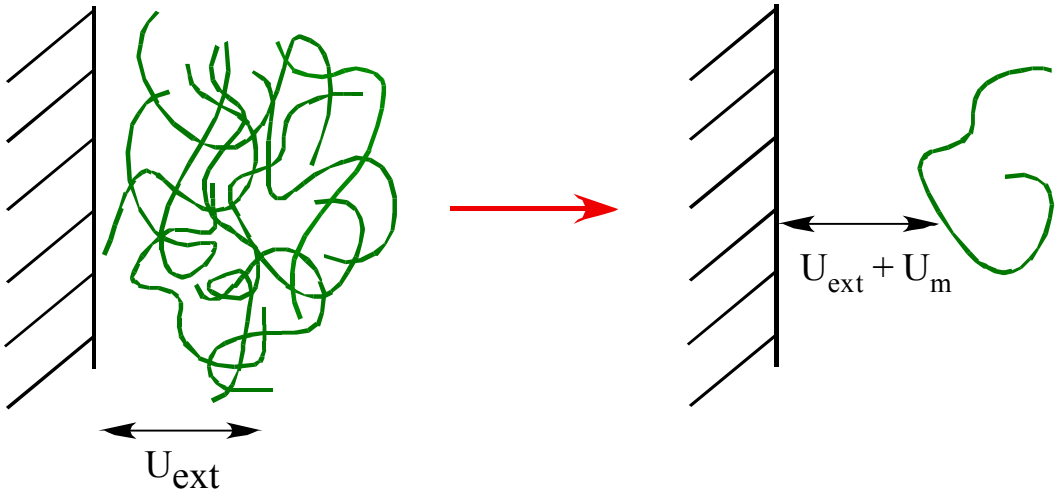
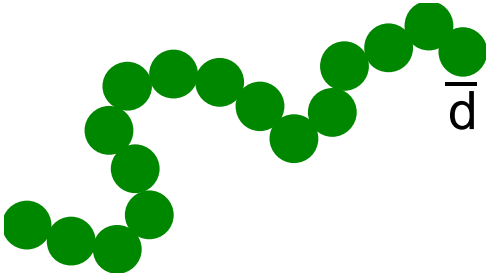
CMS-DFT

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



- **Minimize free energy, $\Omega[T,V,\mu; \rho(\mathbf{r})]$**
- **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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