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Forces Between Nanorods with End-Adsorbed Chains in Polymer Melts

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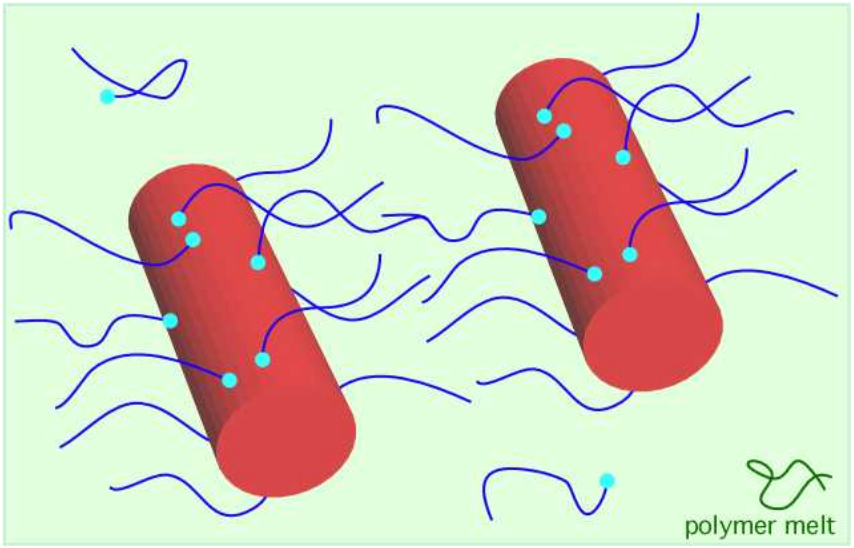
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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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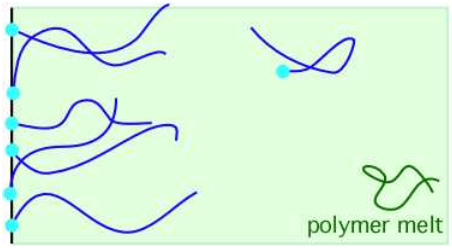
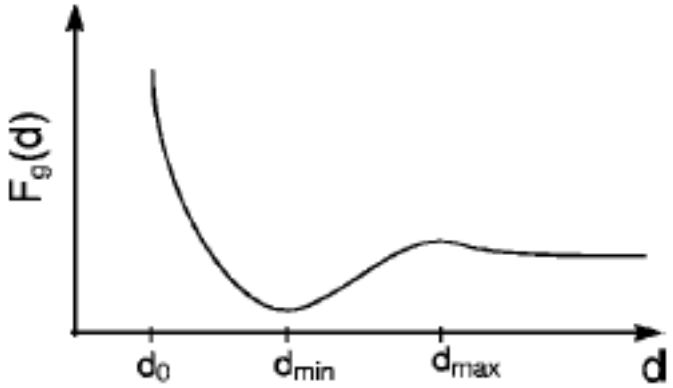
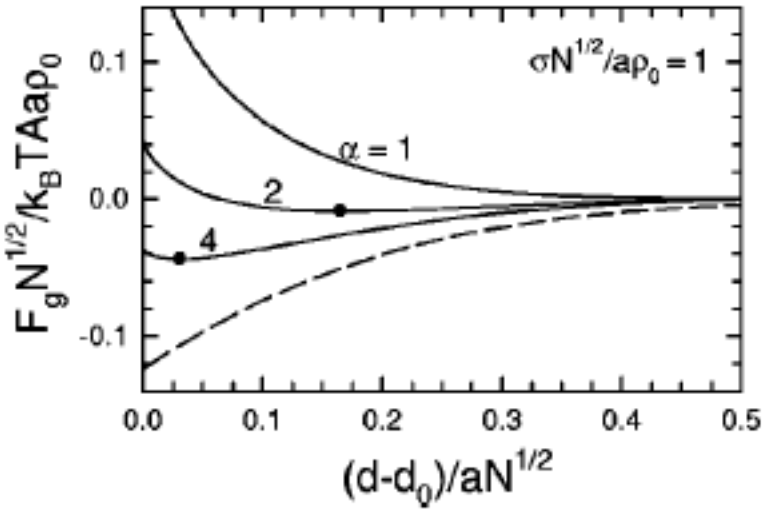
Forces Between Flat Surfaces

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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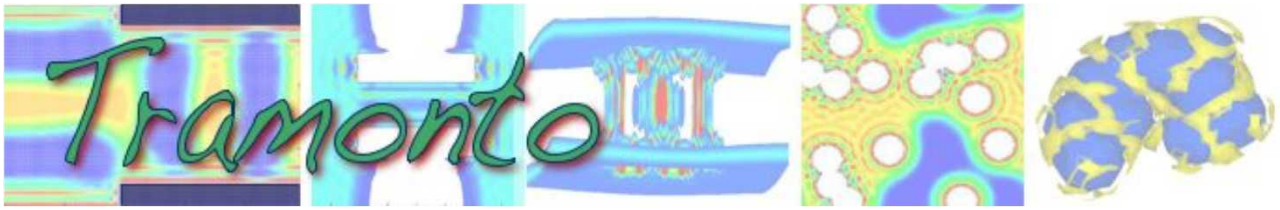
Density Functional Theory



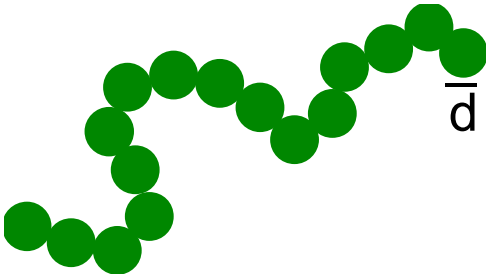
http://software.sandia.gov/tramonto/index.html

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

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

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

- **CMS-DFT**
- **main features:**
  - **freely-jointed chains**
  - **bulk thermo from PRISM**
  - **accurate at melt densities**
  - **today: all repulsive fluid interactions**



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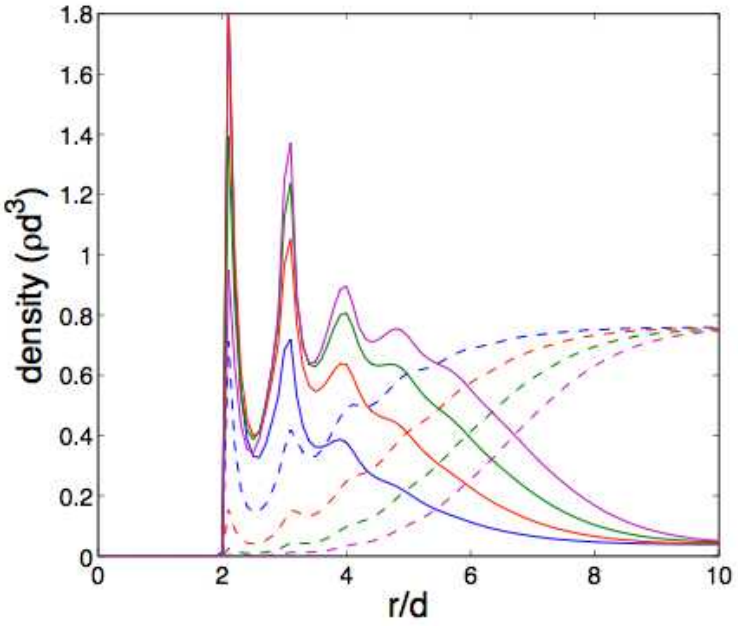
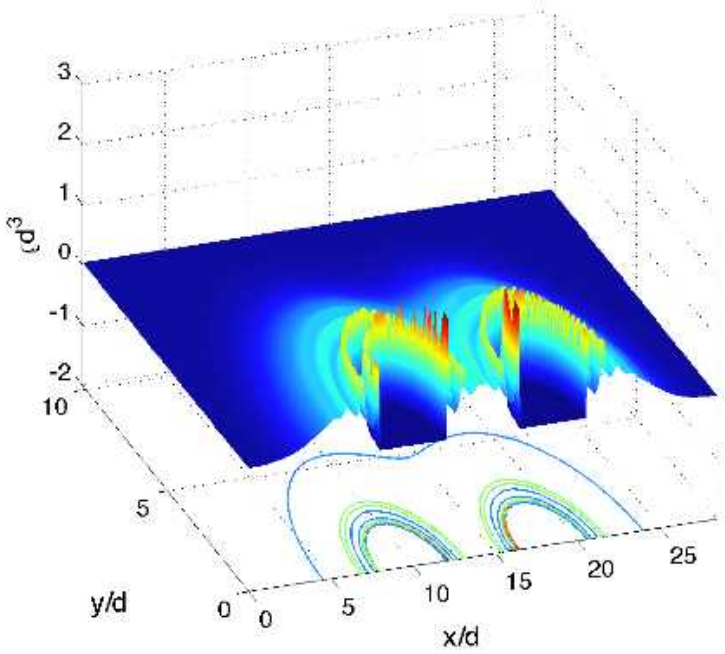
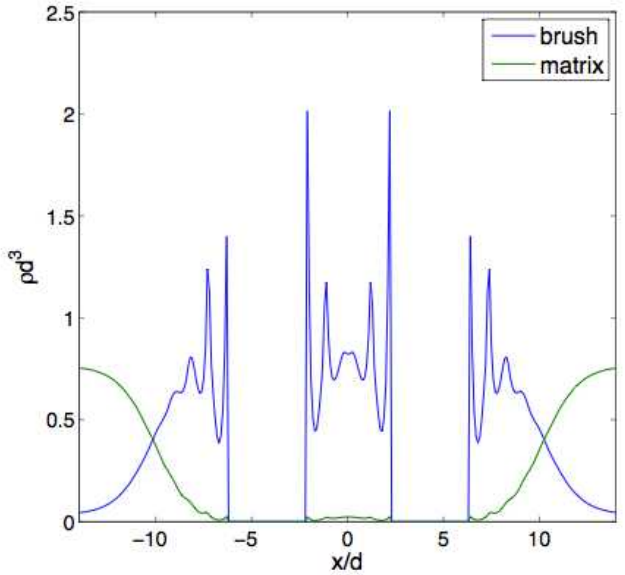
Density Profiles

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

isolated brush







ε = 10kT

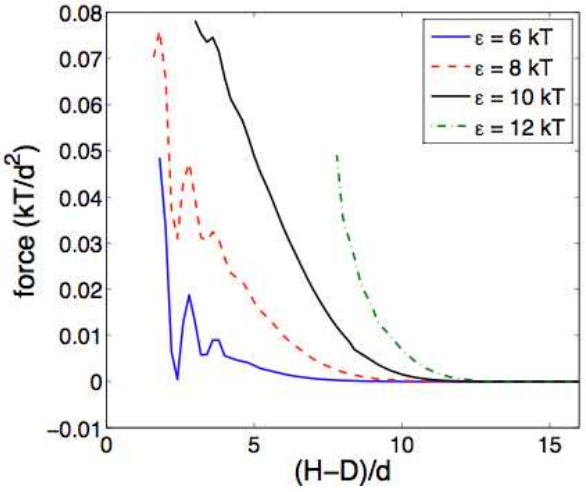
Force between rods

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

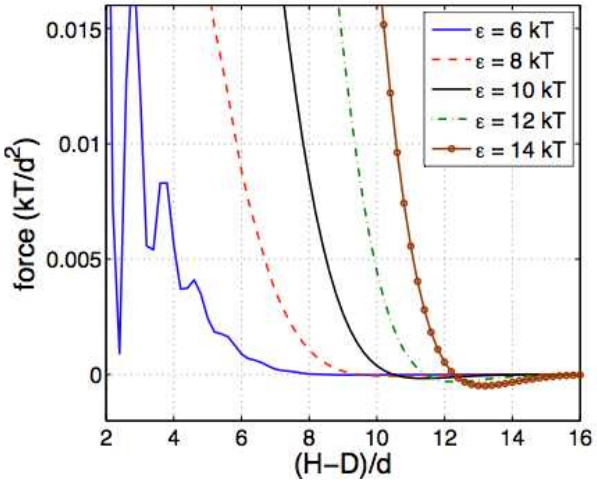
N = 20
P = 20, 30, 40
D = 3d, 4d, 5d
ε = 6 - 15 kT

D = 4d

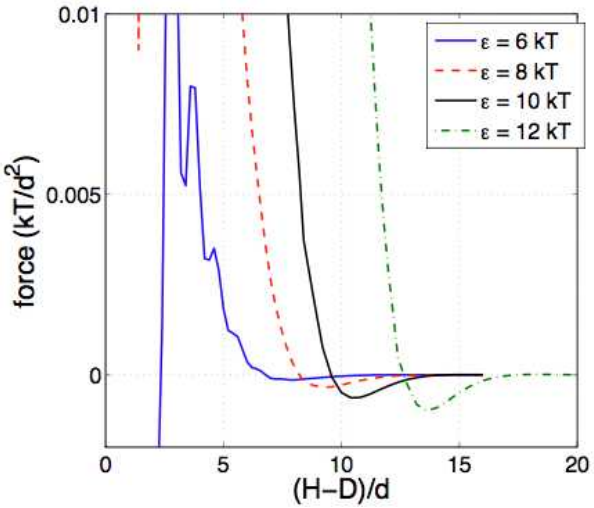
P = 20



P = 30



P = 40



autophobic dewetting still present
always some attraction at contact

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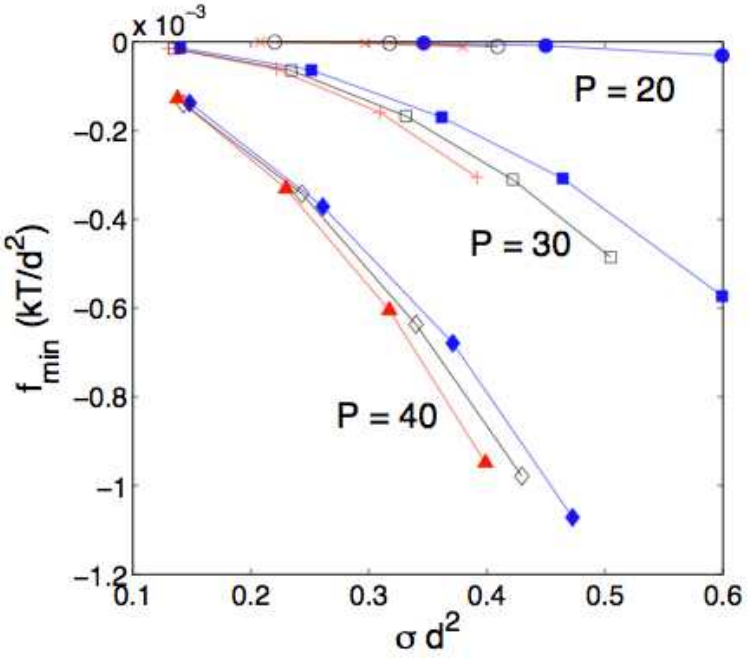
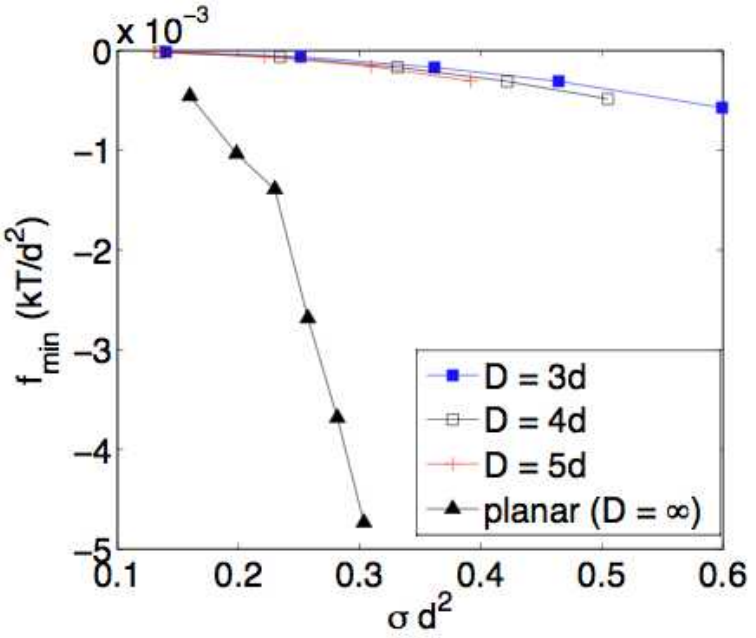
Attractive Minimum

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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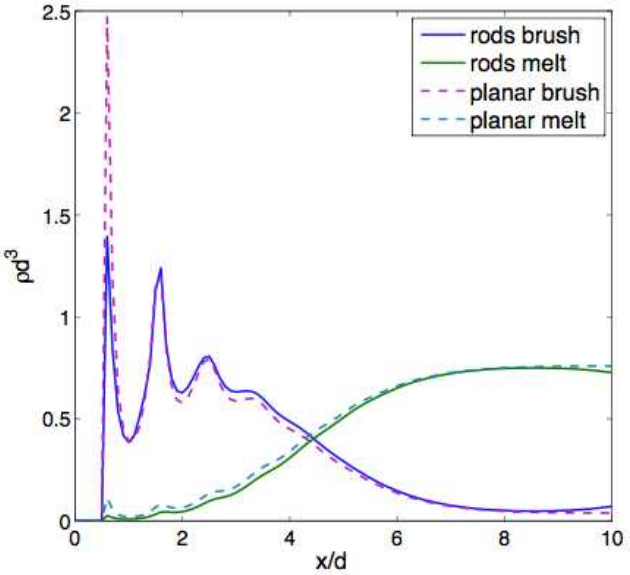
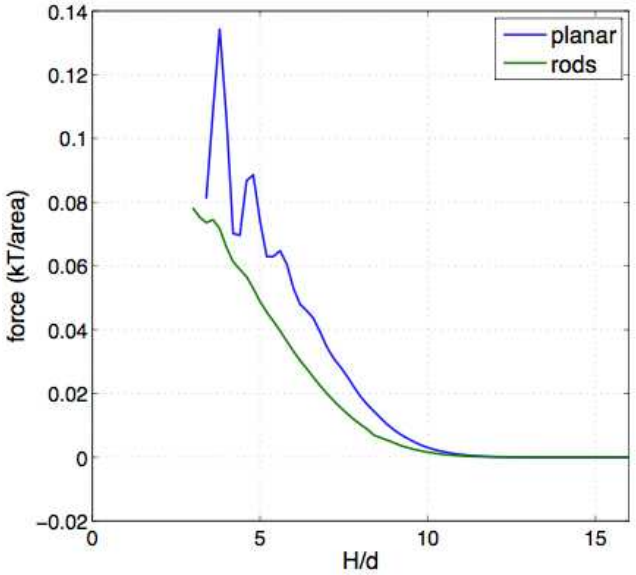
Less force due to curvature

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

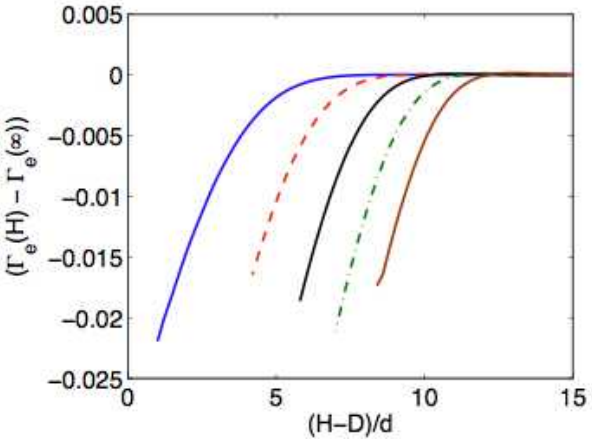


similar brush heights, profiles
force less in curved system



P = 20
D = 4d

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



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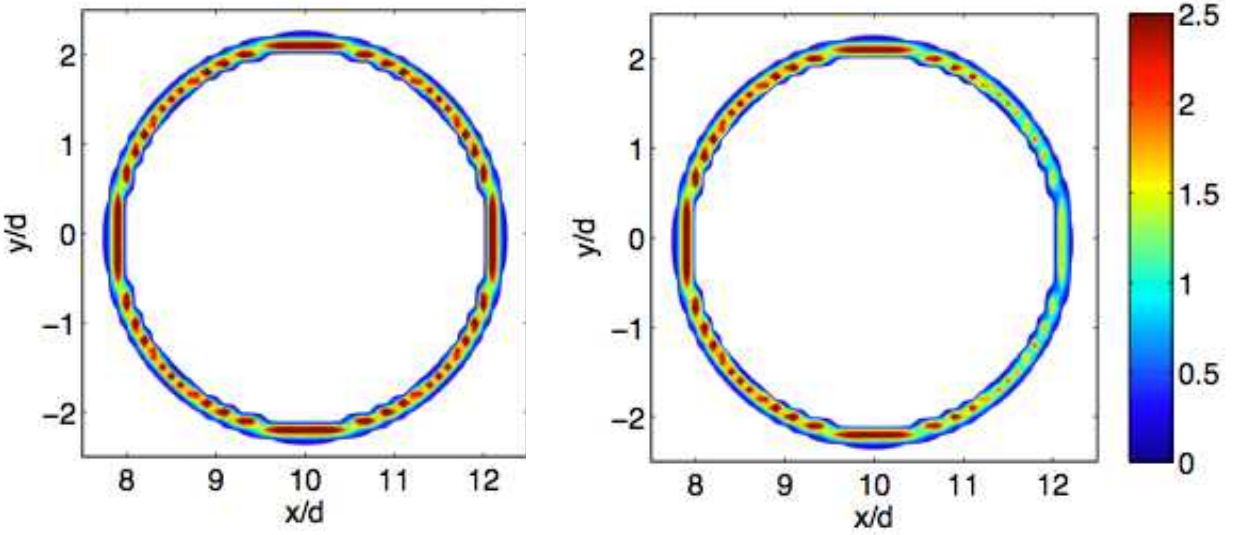
Chains rearrange as rods approach

D = 4d, P = 20,
ε = 10 kT

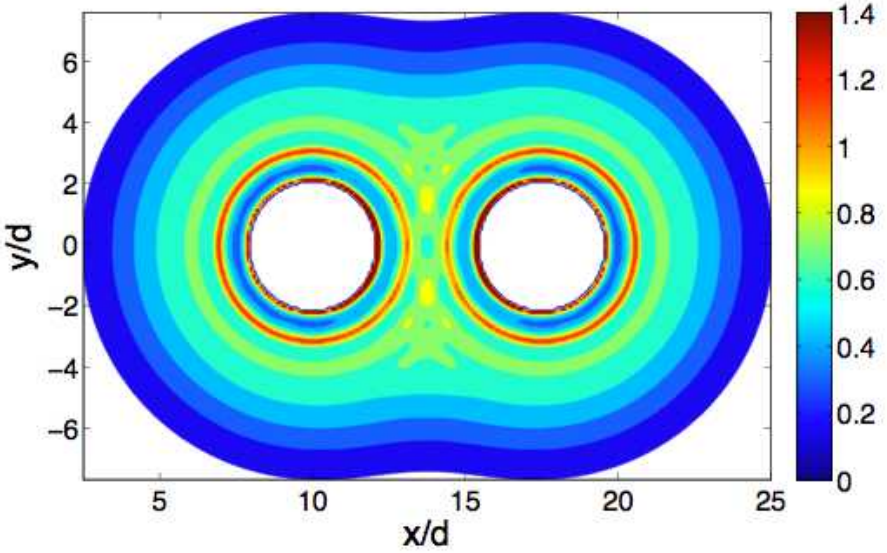
(H-D)/d = 16

(H-D)/d = 3.5

end densities



brush density



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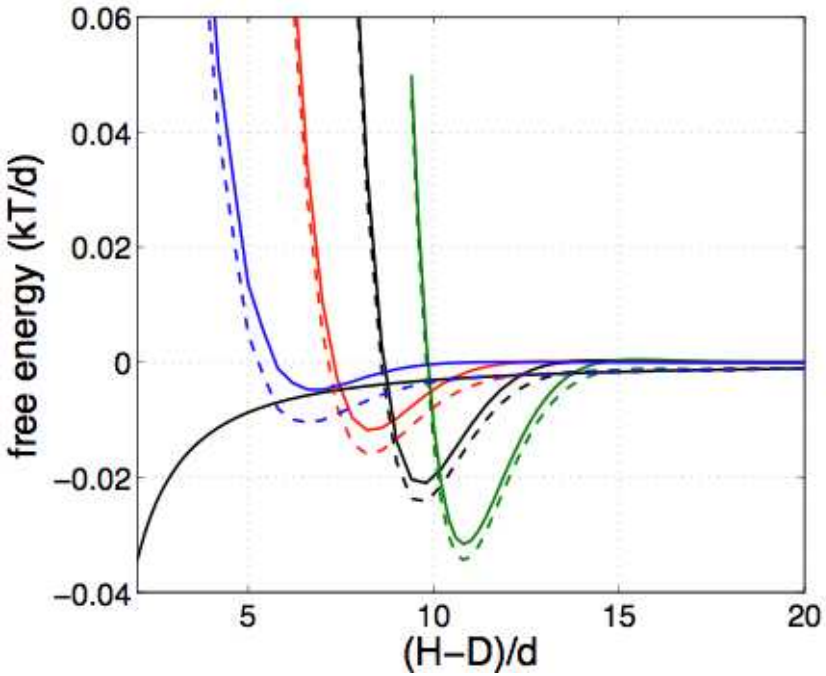
Experimental Implications

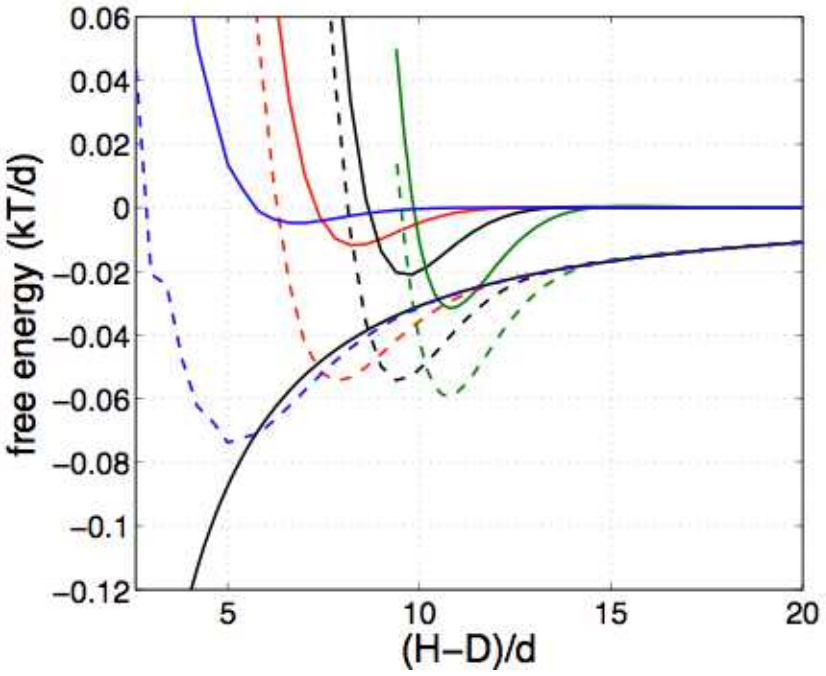
D = 5d, P = 40

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., 2008, submitted.

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Thanks:
Sandia LDRD program

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