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Stabilization of Nanorods in Polymer Melts by End-Adsorbed Chains

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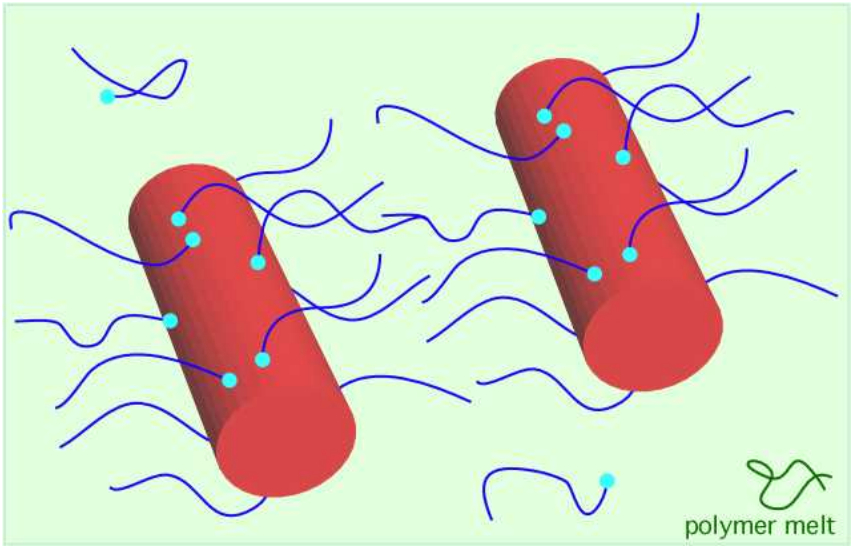
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

The Problem:

dispersion of nanosized objects in a polymer melt

same rules as for polymer-stabilized colloids?

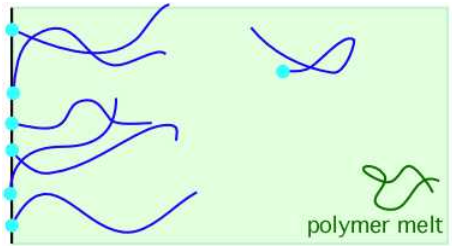


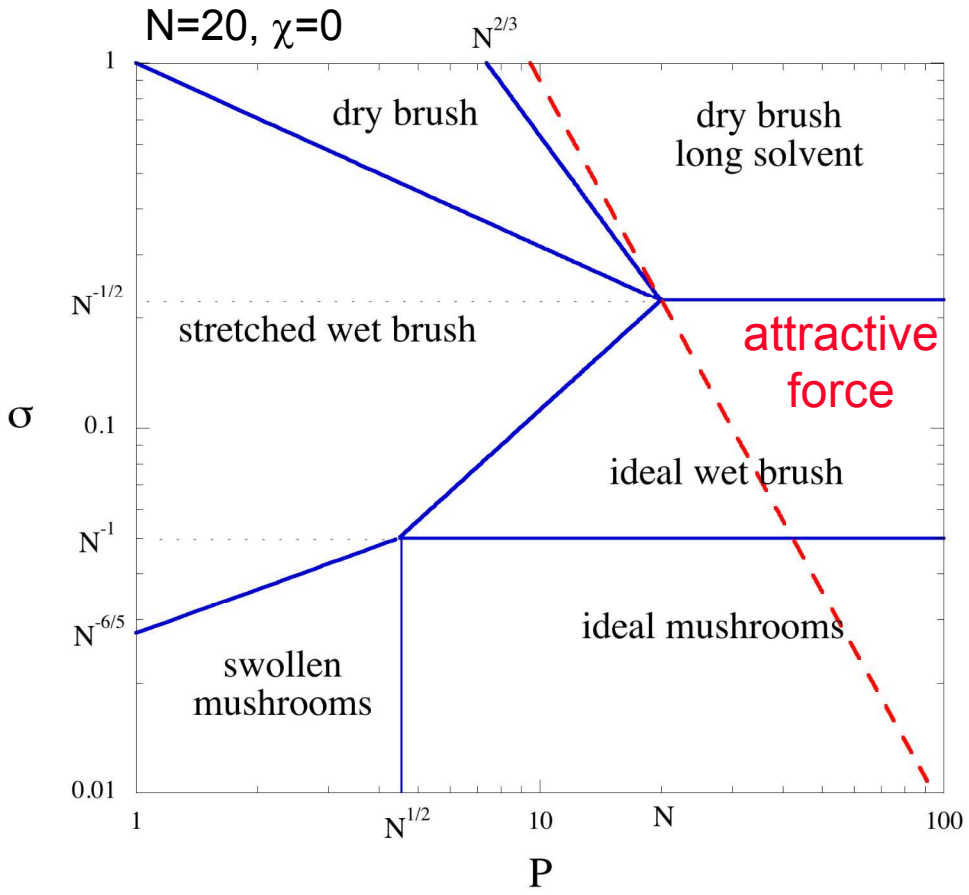
- adsorbed chains length N
  - -sticky ends, energy ε_w
- matrix chains length P
- athermal ($\chi = 0$)
- nanorods with diameter D

is the force always repulsive?
will the chains desorb?

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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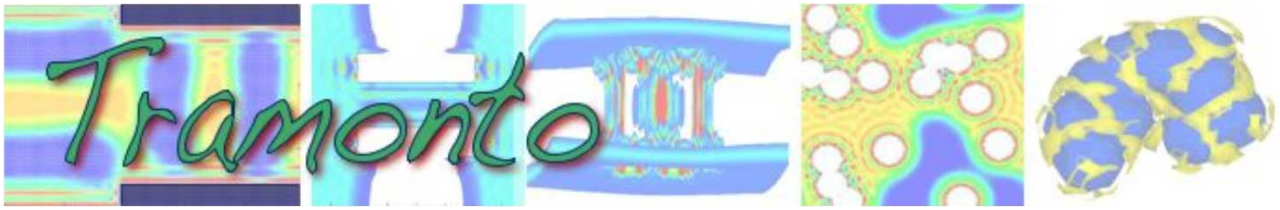
Density Functional Theory



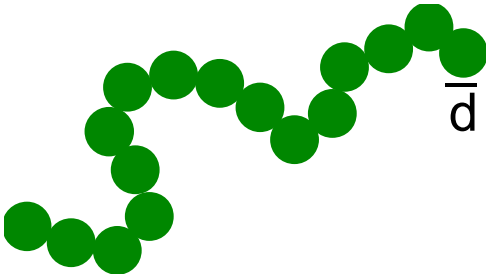
http://software.sandia.gov/tramonto/index.html

- **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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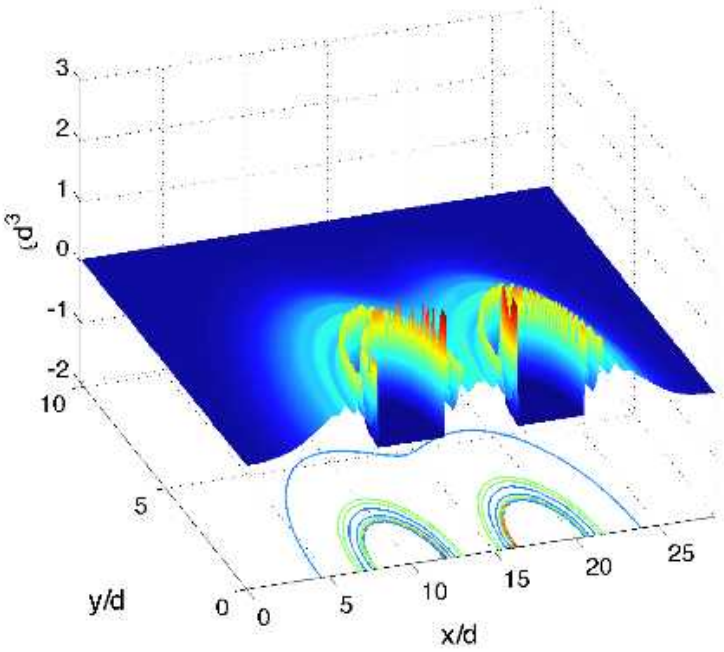
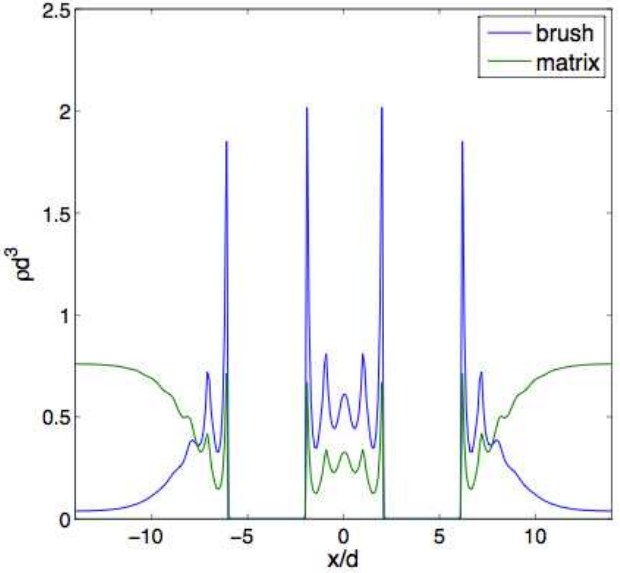
Density Profiles

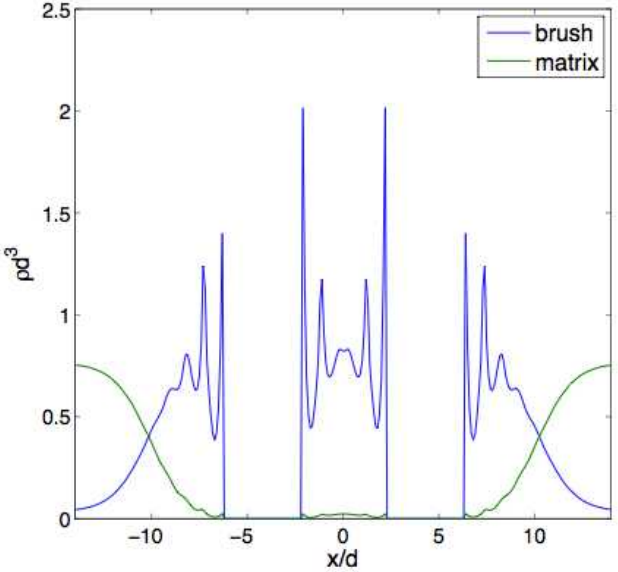
N = 20, P = 20, D = 4d



ε_w = 6kT



ε_w = 10kT



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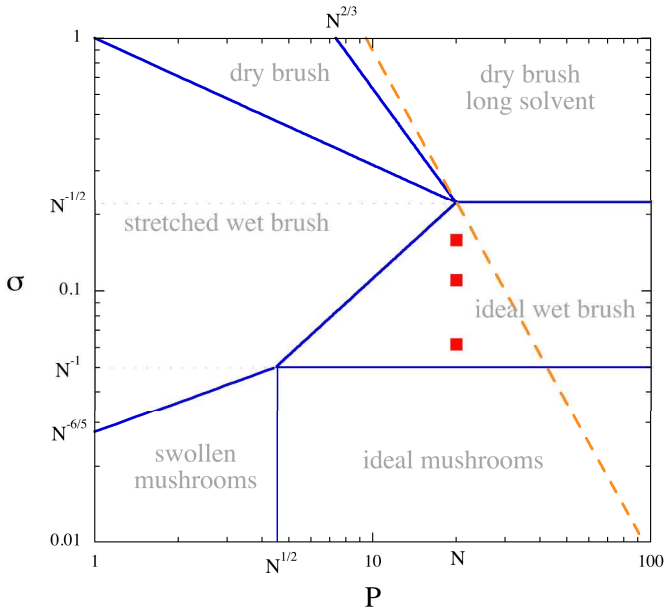
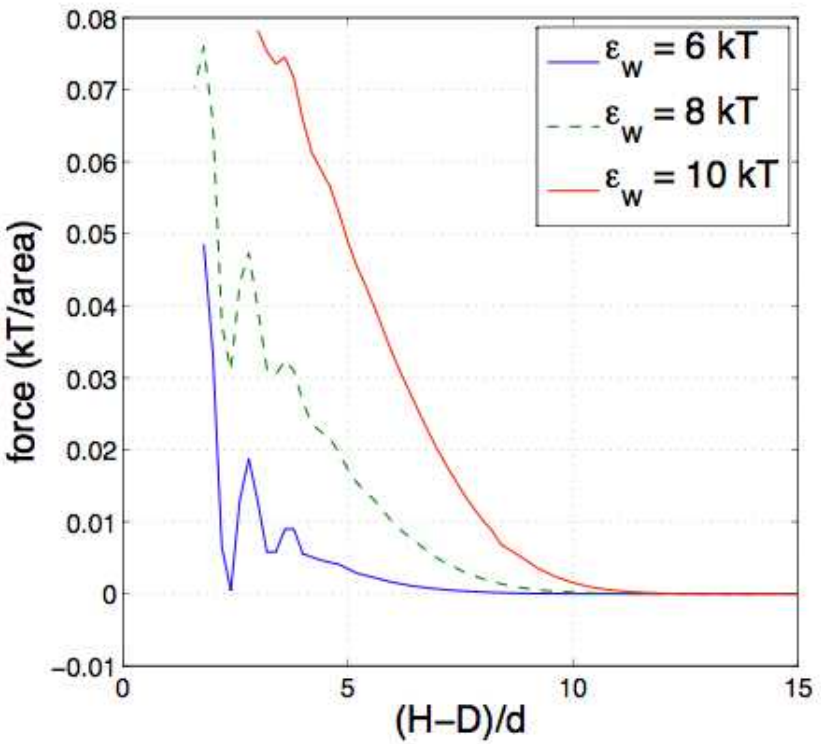
Force between rods



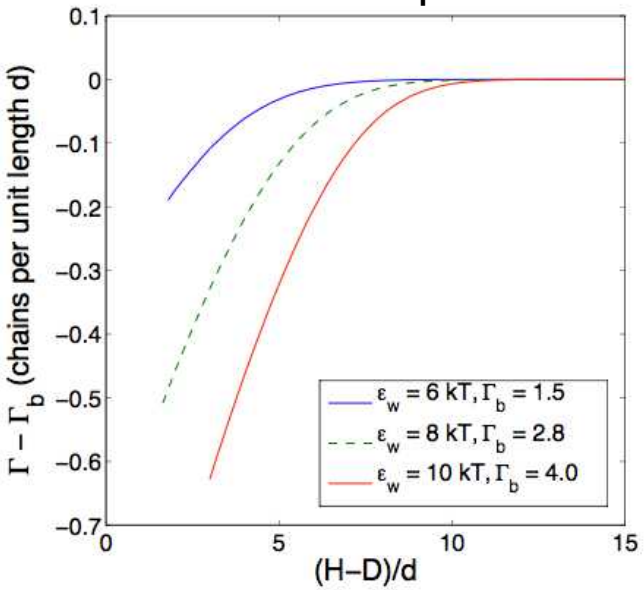
N = 20, P = 20, D = 4d

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

force



chain adsorption



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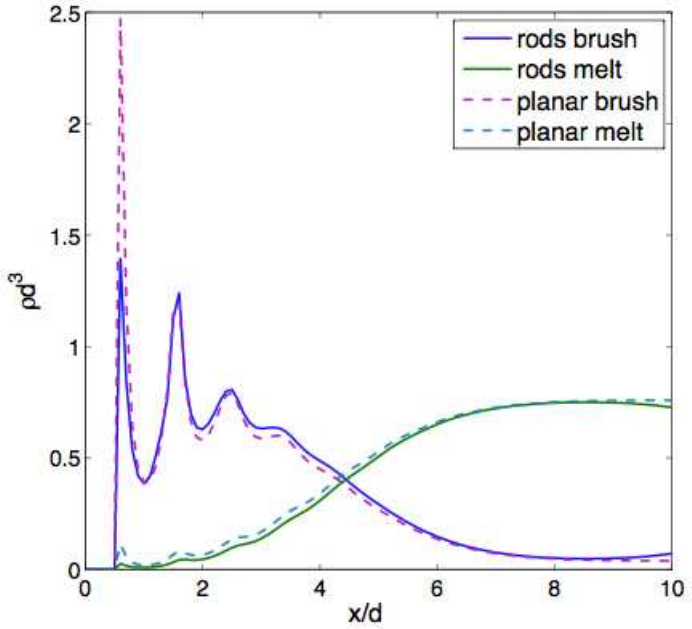
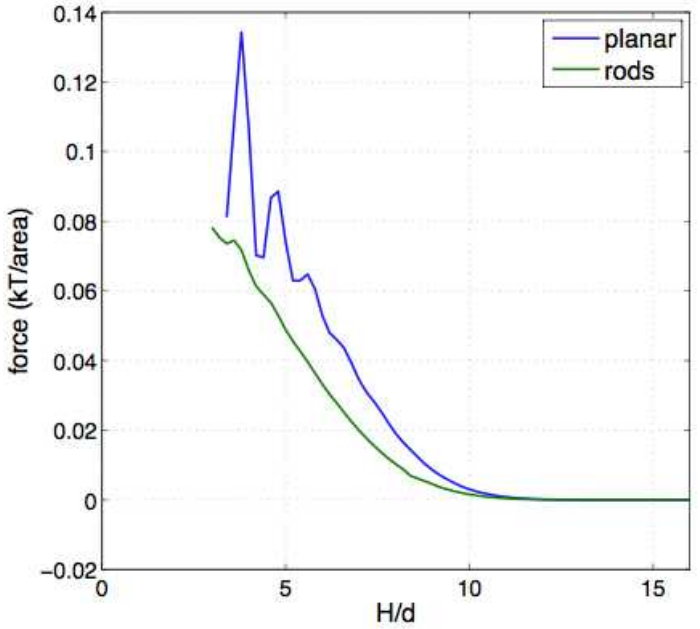
Less force due to curvature

N = 20, P = 20

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

similar brush heights, profiles
force less in curved system





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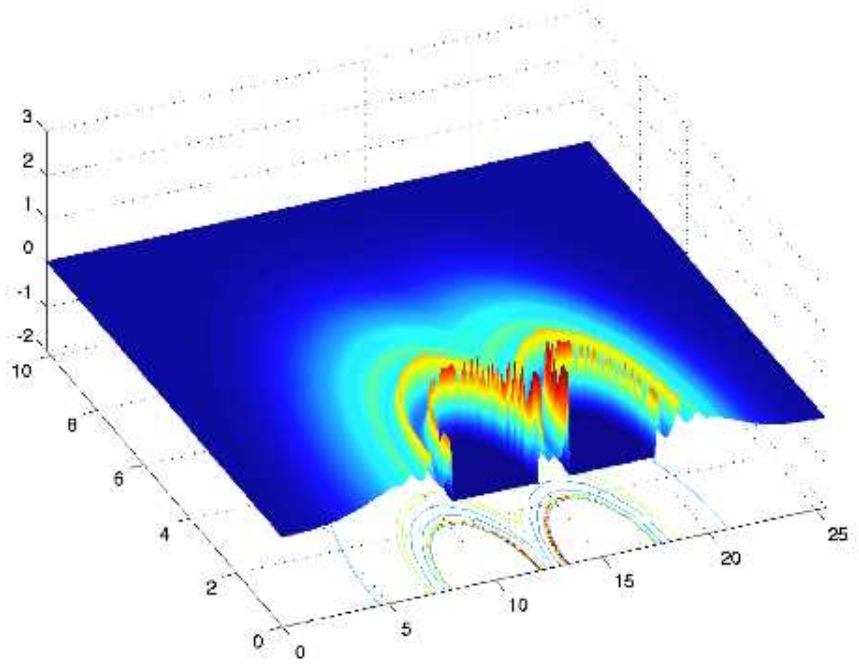
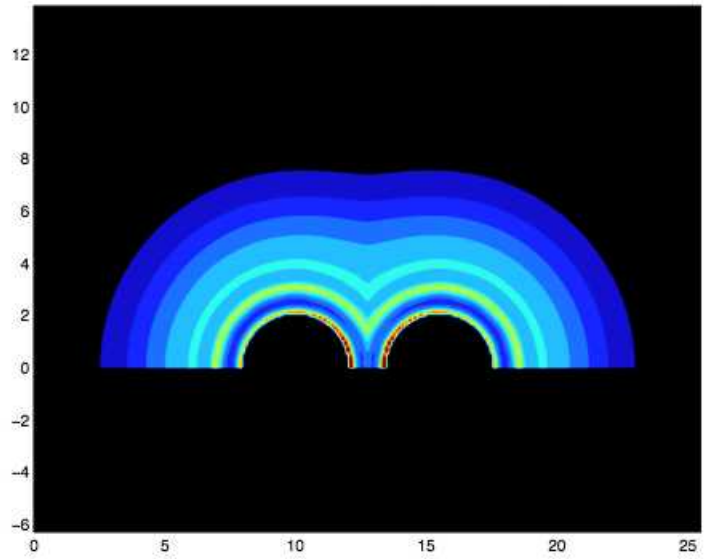
Chains go around rods





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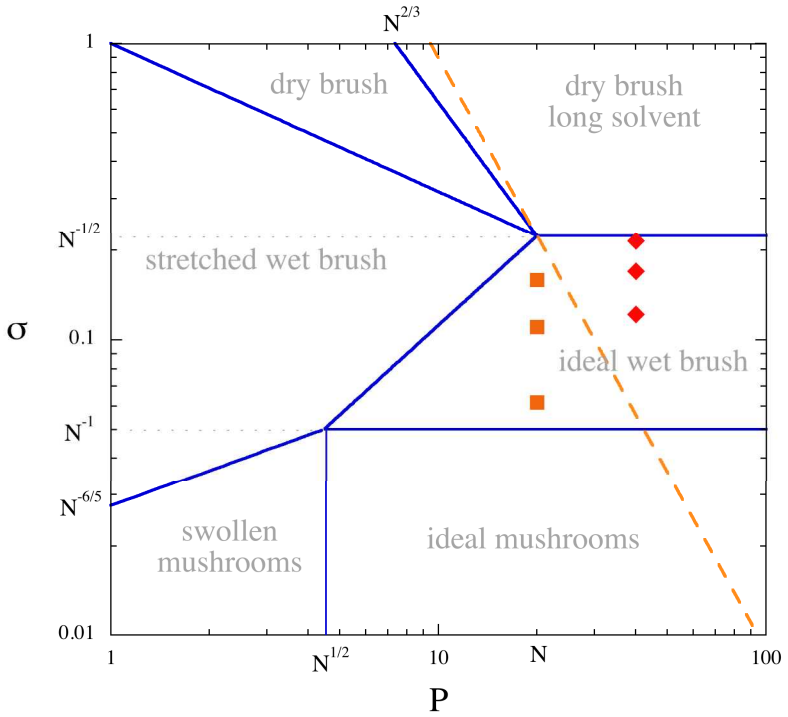
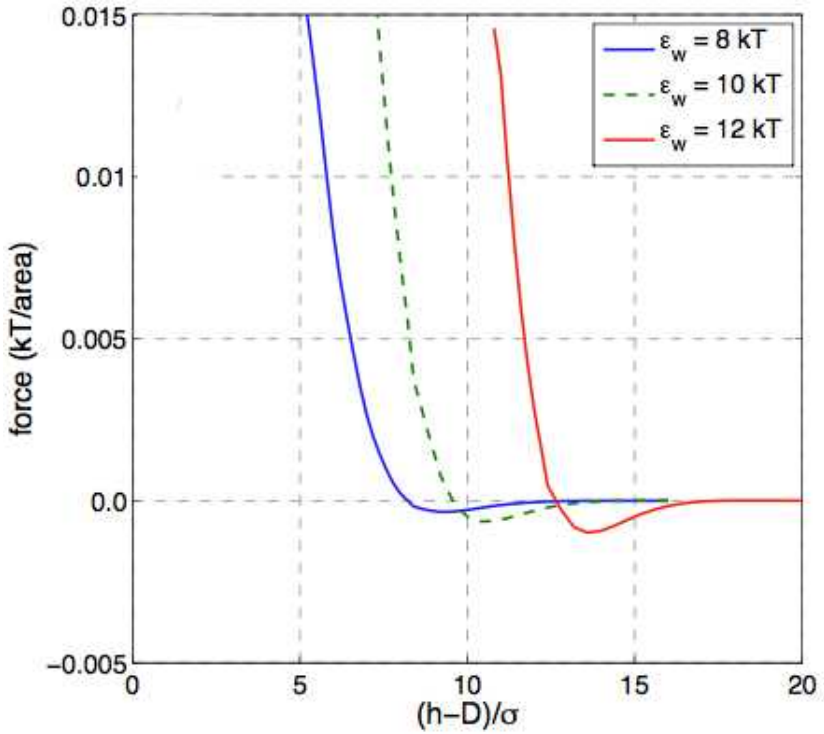
Attractions

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





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Summary and Future Work

- chains desorb but still get repulsions
- forces can be attractive
- follow flat brush behavior (so far)
- force less for same brush height due to curvature

Future

- escape transition?
- more phase space
  - particle size
  - strongly stretched regime
- spheres

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