SAND2008-0386P

Structure and Interactions in Nanoparticle/Polymer Blends

Amalie L. Frischknecht

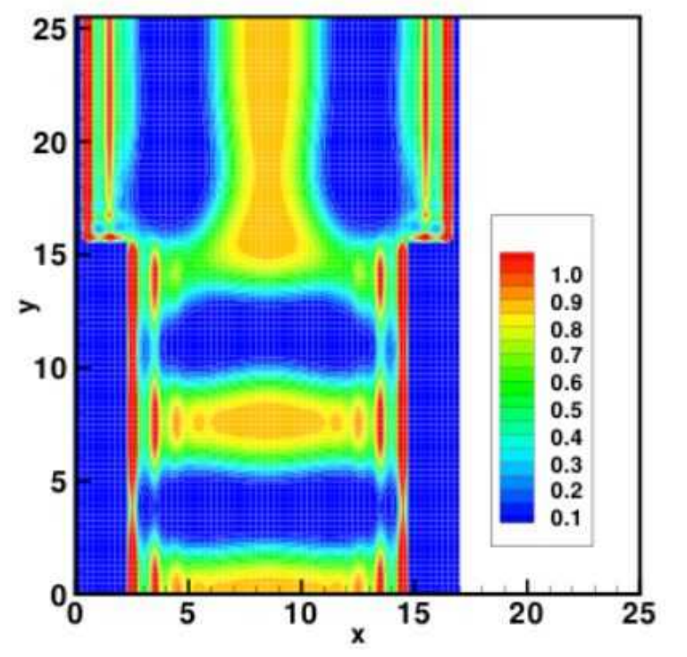
Tramonto: a fluids-DFT code

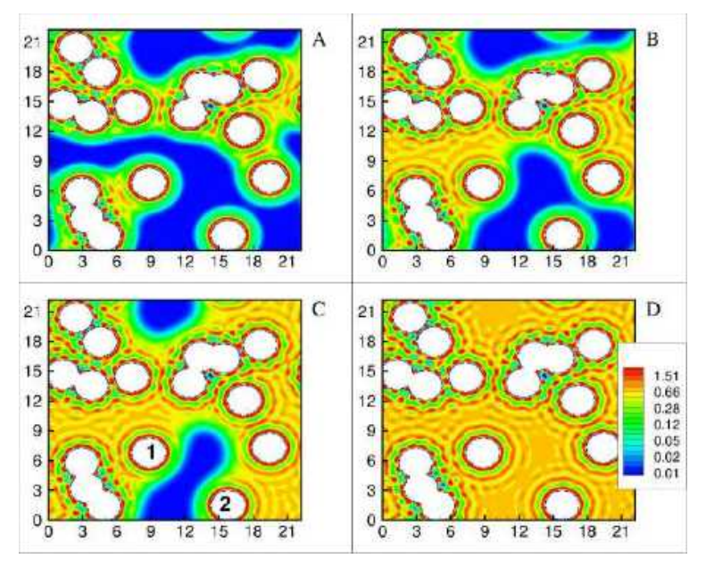
http://software.sandia.gov/tramonto/index.html

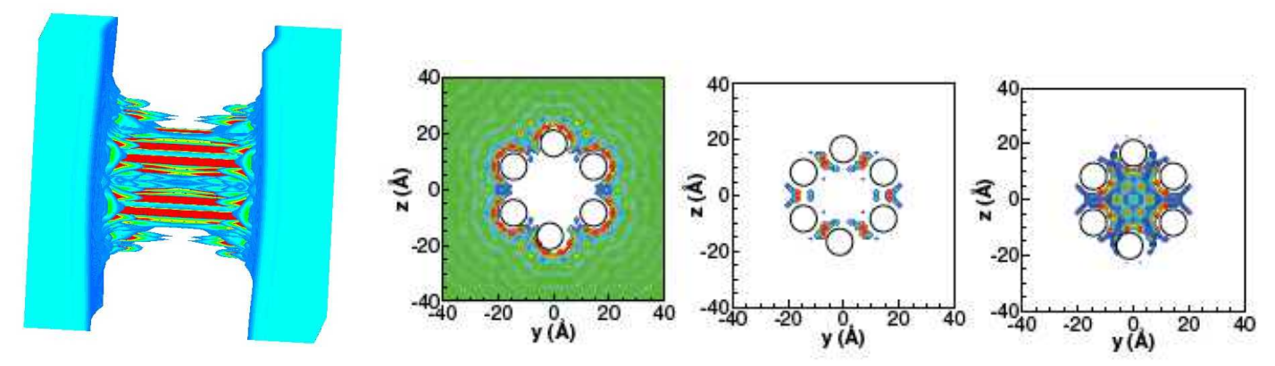
Laura Frink, PI

DFTs = nonlinear integral equations

- minimize grand free energy
  - obtain inhomogeneous fluid densities
  - adsorption, minimum energy, force, etc.
- solve in 3D, Cartesian grid, real space
- complex geometries
- parallel
- sophisticated linear solver algorithms
- arc-length continuation algorithms

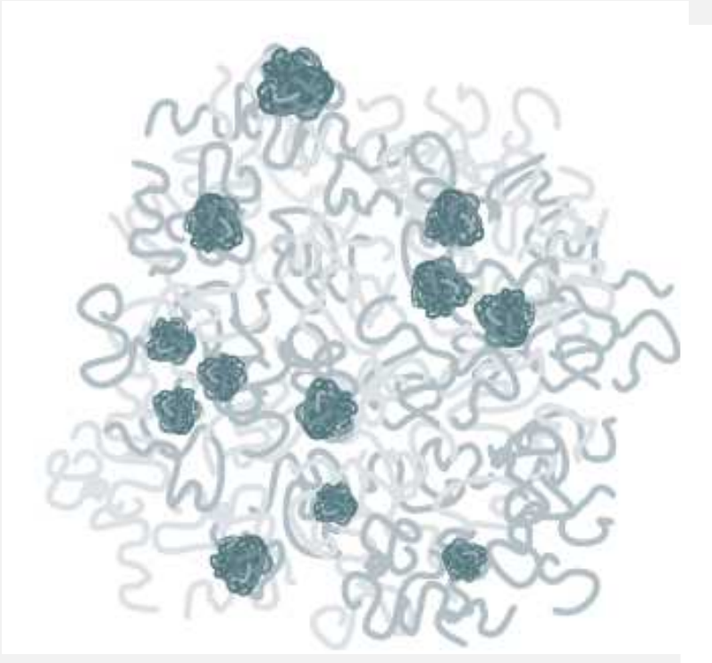




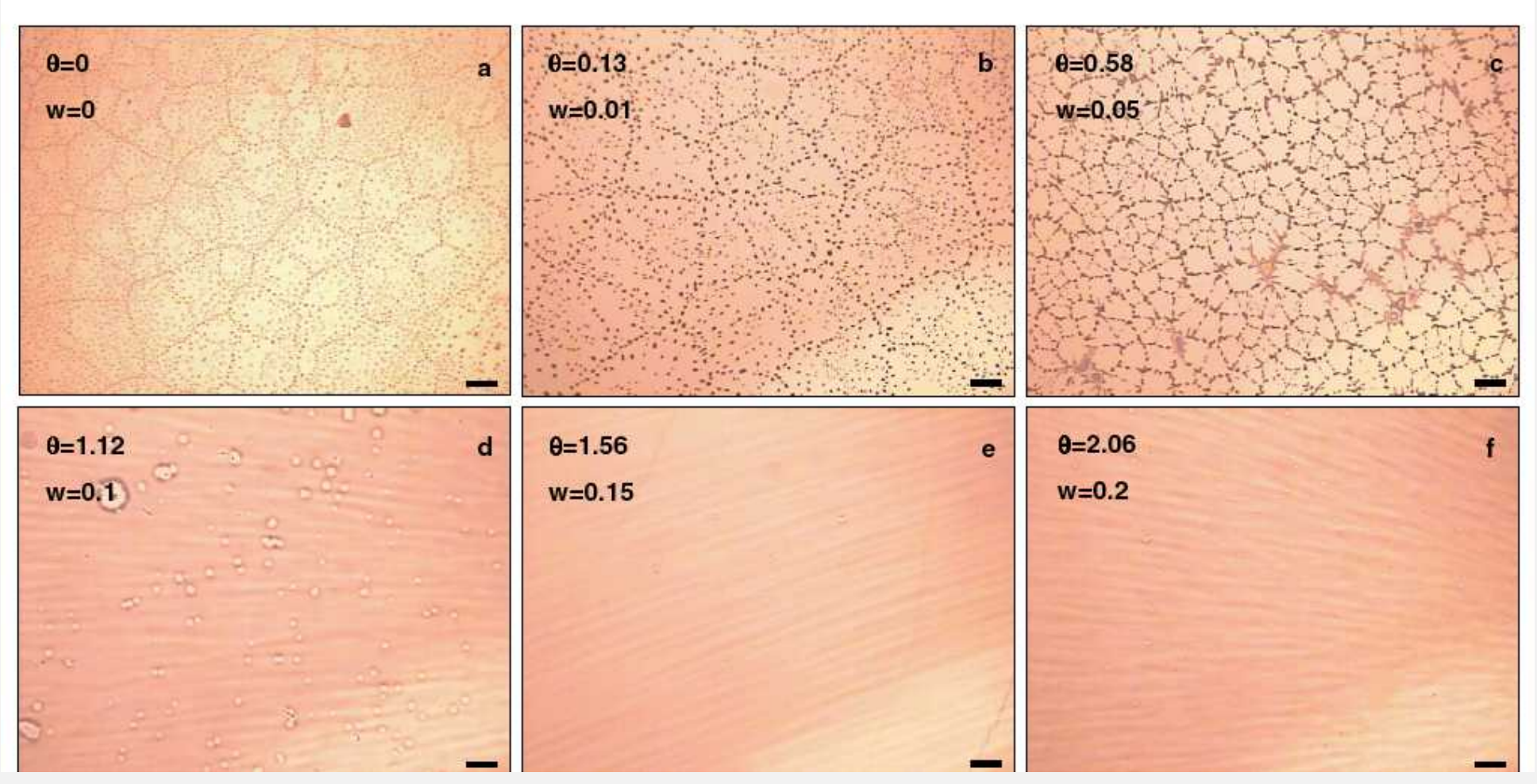


NP/Polymer Blends Near a Substrate

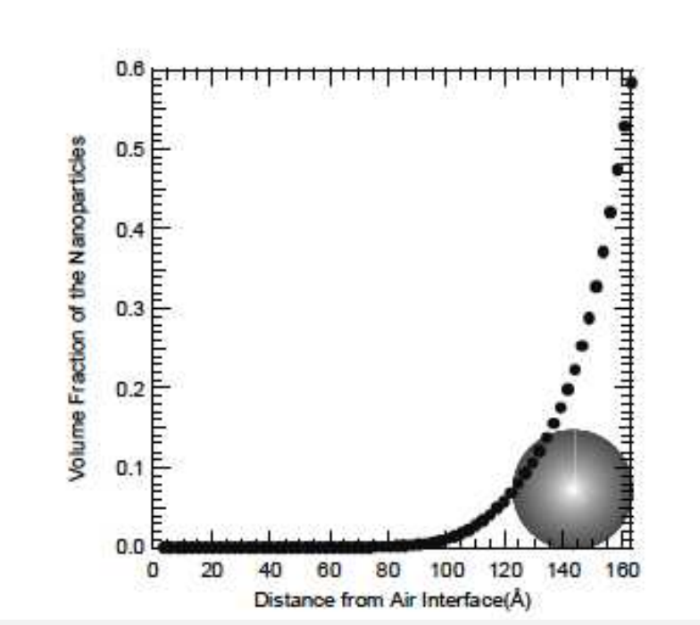
Observations on Polymer/NP Thin Films



PS nanoparticles blended with PS on silicon
40 nm thick film
NPs prevent dewetting!



neutron reflectivity shows NPs go to substrate

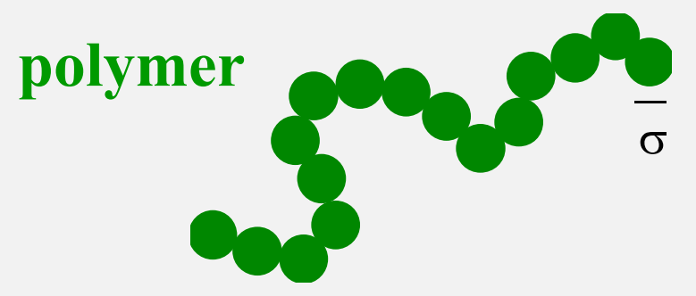


Mackay et al., Nature Mat., 2003
Krishnan et al, Langmuir, 2005

Can we explain with theory?

why do NPs segregate to the substrate?
what effect does this have on the polymer?

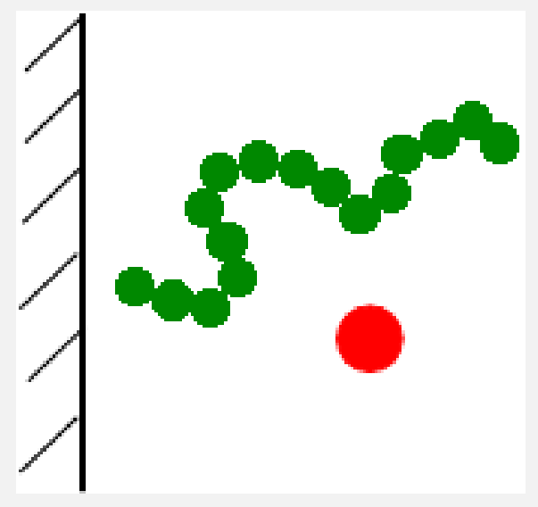
athermal system: model as hard spheres
only interactions are entropic

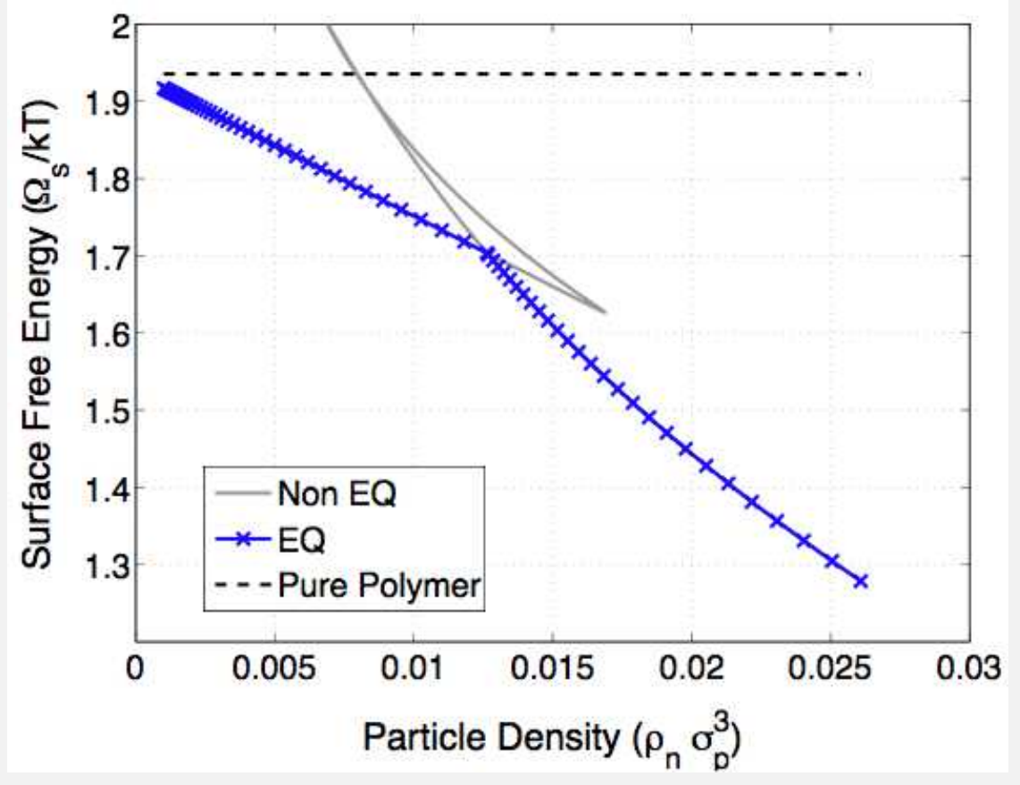


Kuhn length for PS: 1.485 nm

D = 2.0σ = 2.97 nm
D = 3.0σ = 4.45 nm

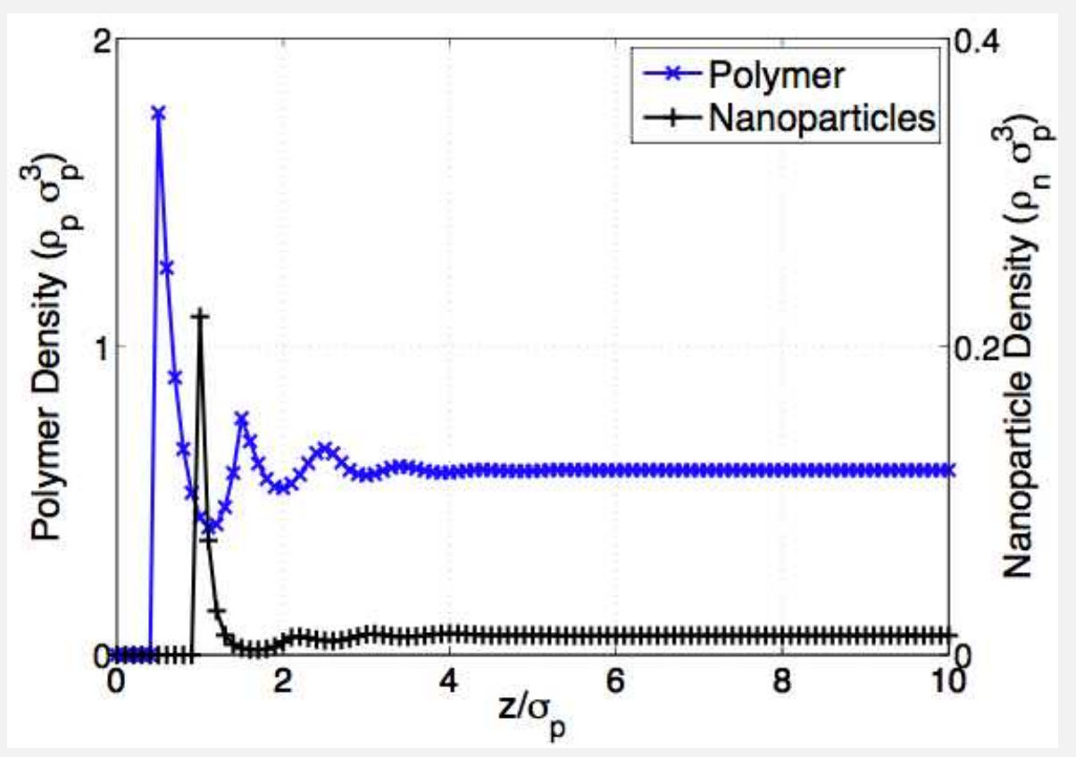
A Layering Phase Transition!



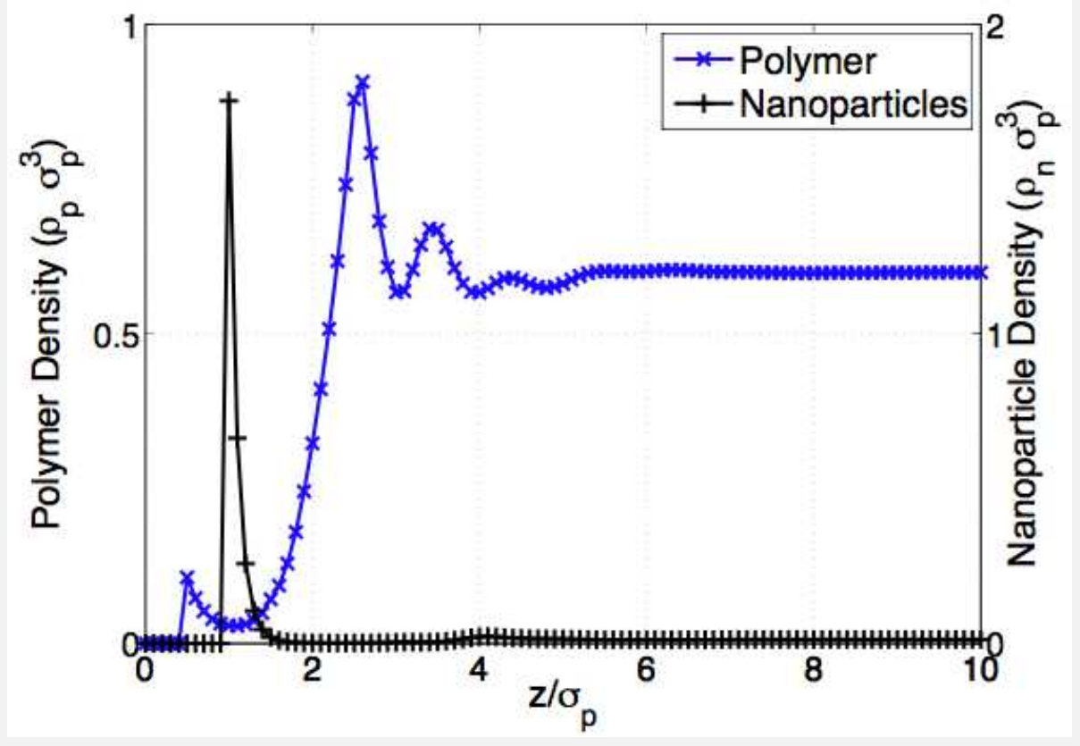


N = 40, D=2σ
≈3nm

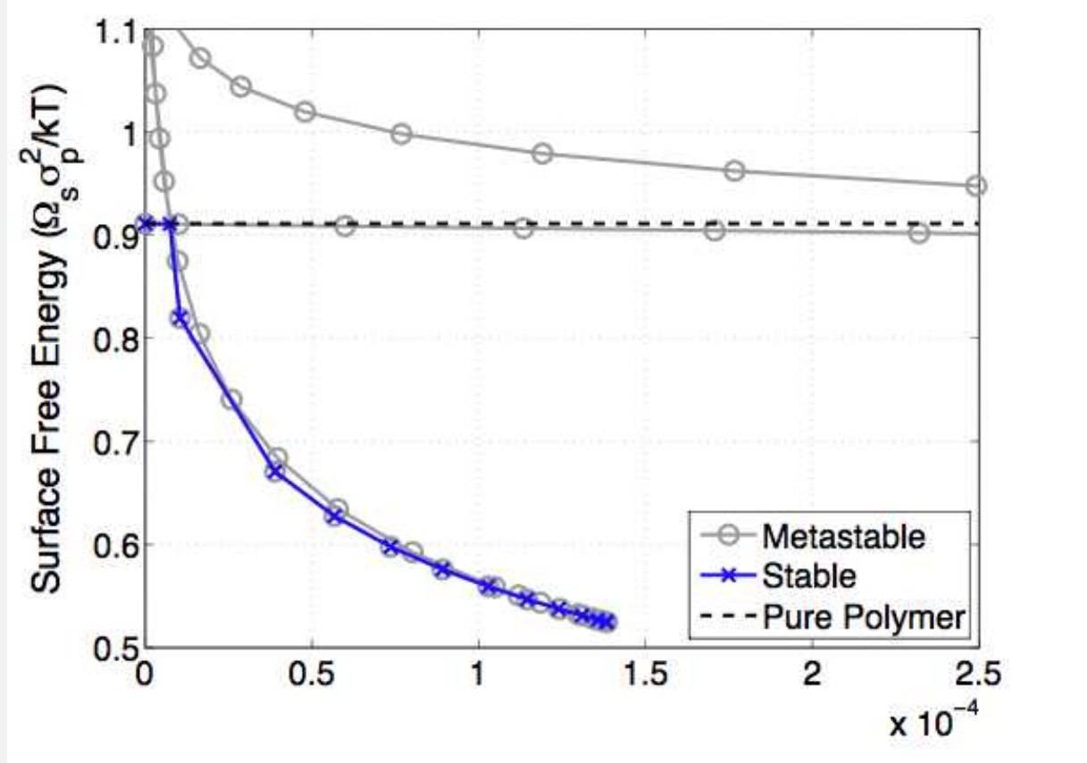
- first-order transition
- entropy-driven
- lower energy when add NPs



typical fluid structure

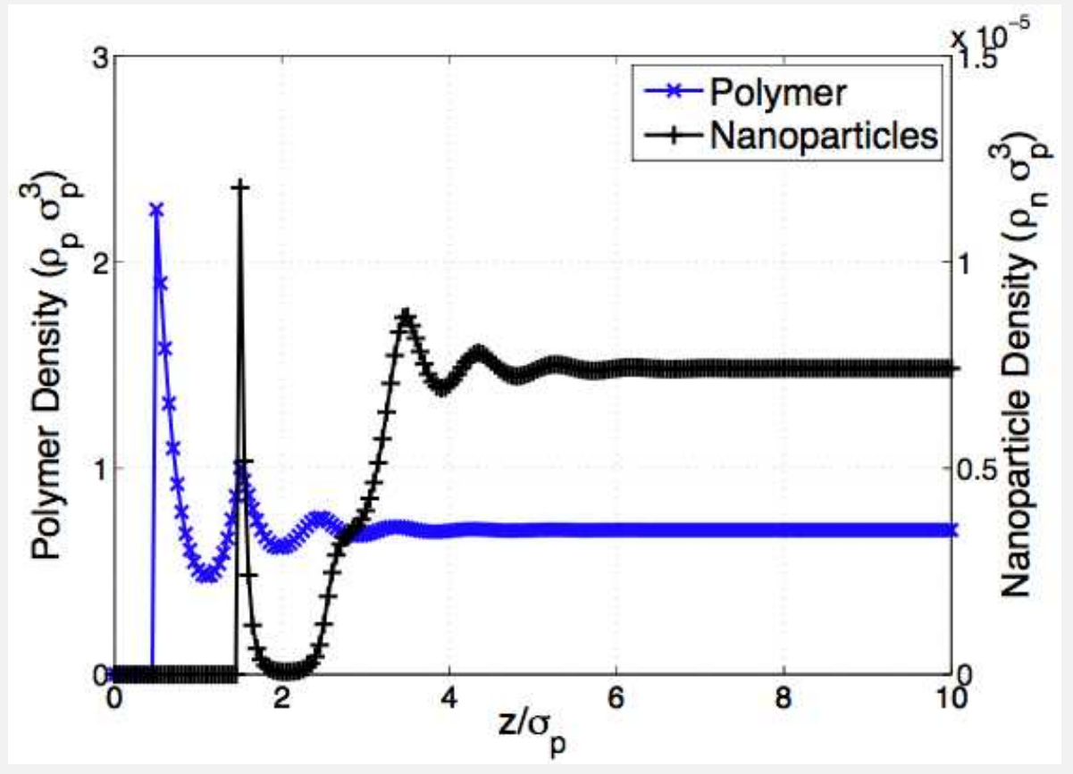


NP layer, areal coverage 0.82

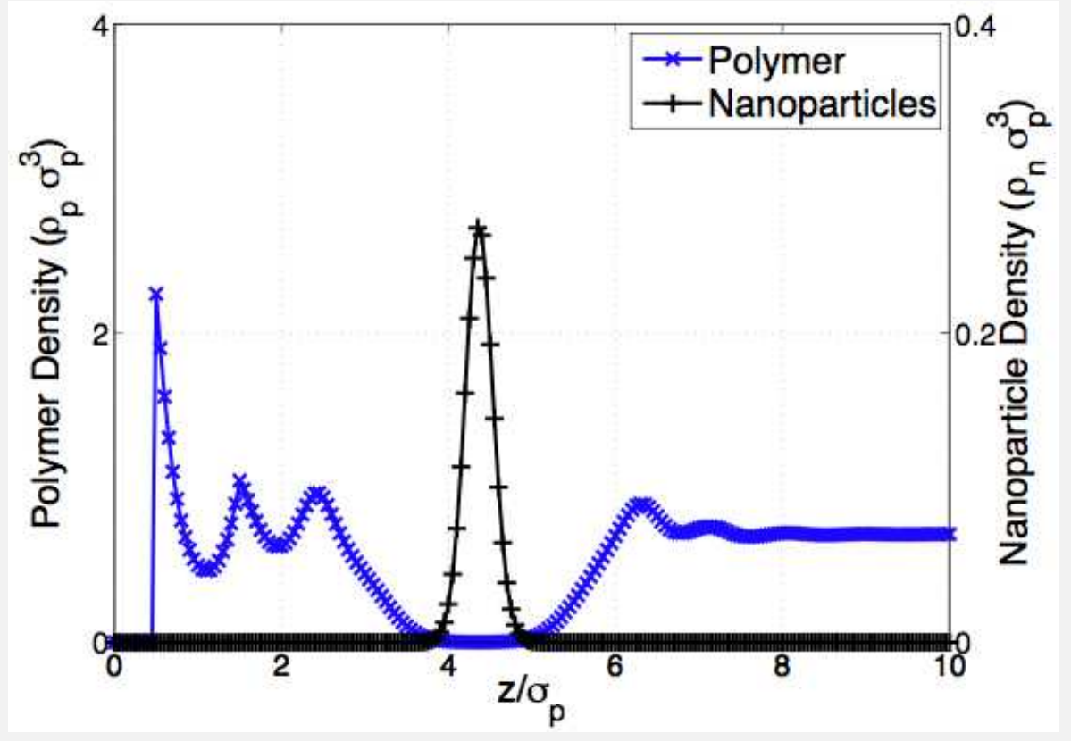


Larger Particles

N = 100, D = 3.0σ
≈ □□□nm



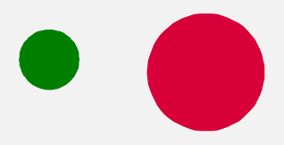
typical fluid structure



NP layer, areal coverage 0.35

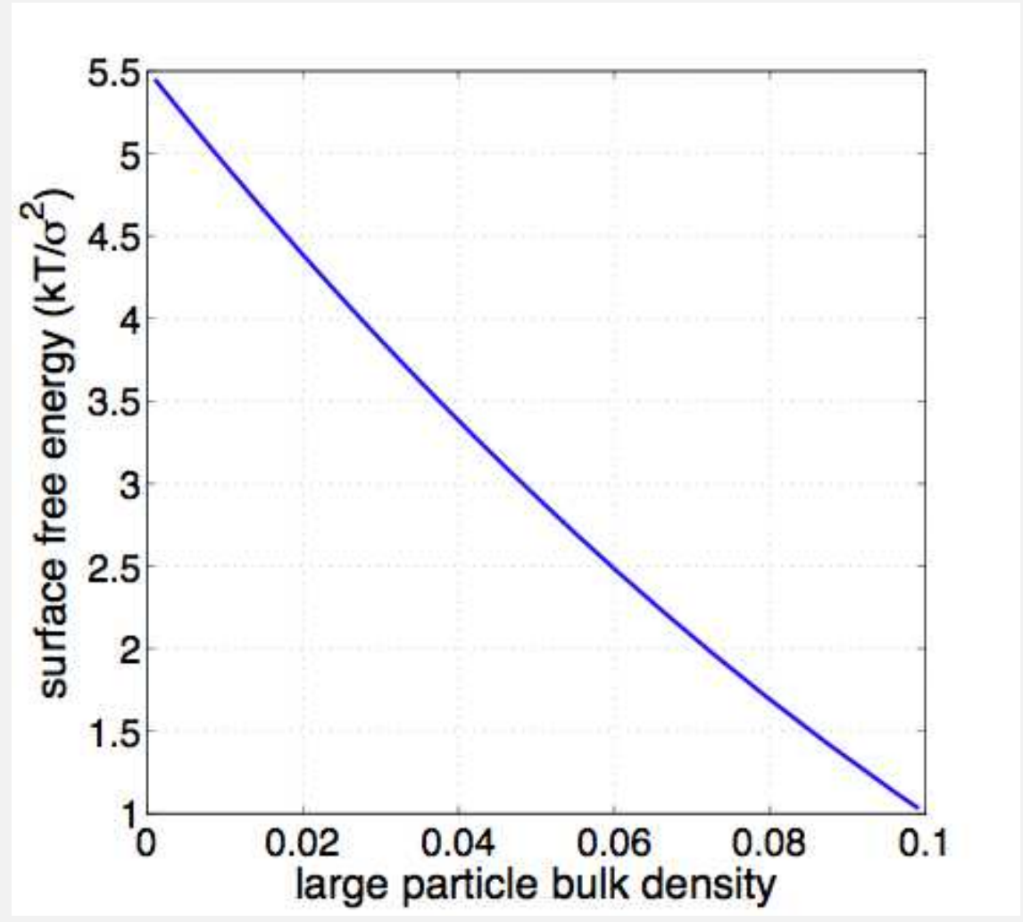
This is a polymer effect!

binary hard sphere mixture

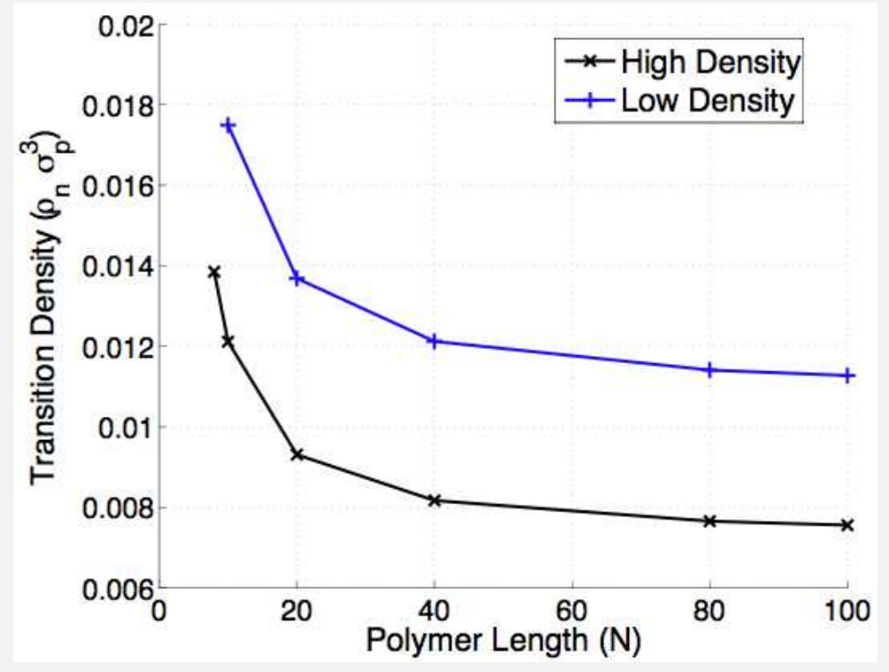


$D_s = 1\sigma$
$D_b = 2\sigma$

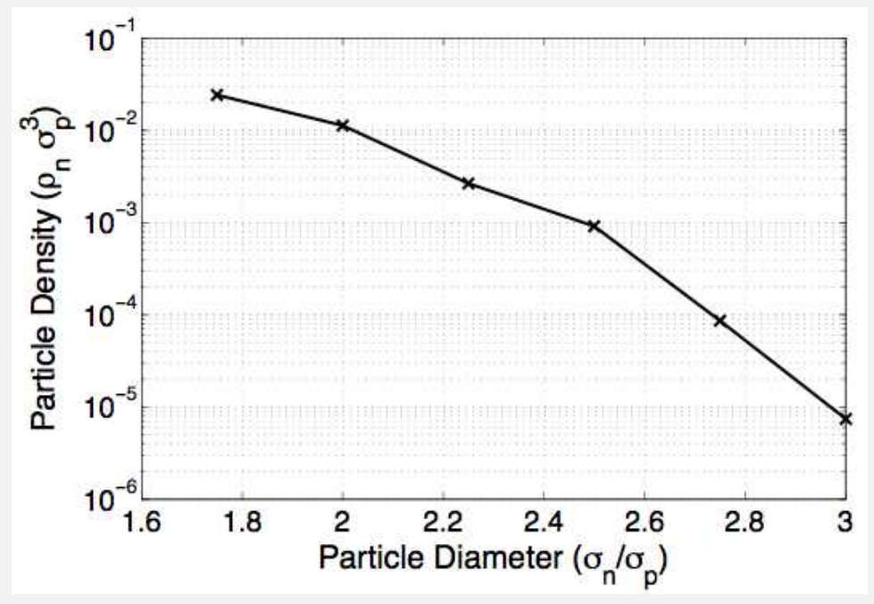
no phase transition:



dependence on chain length



dependence on NP size



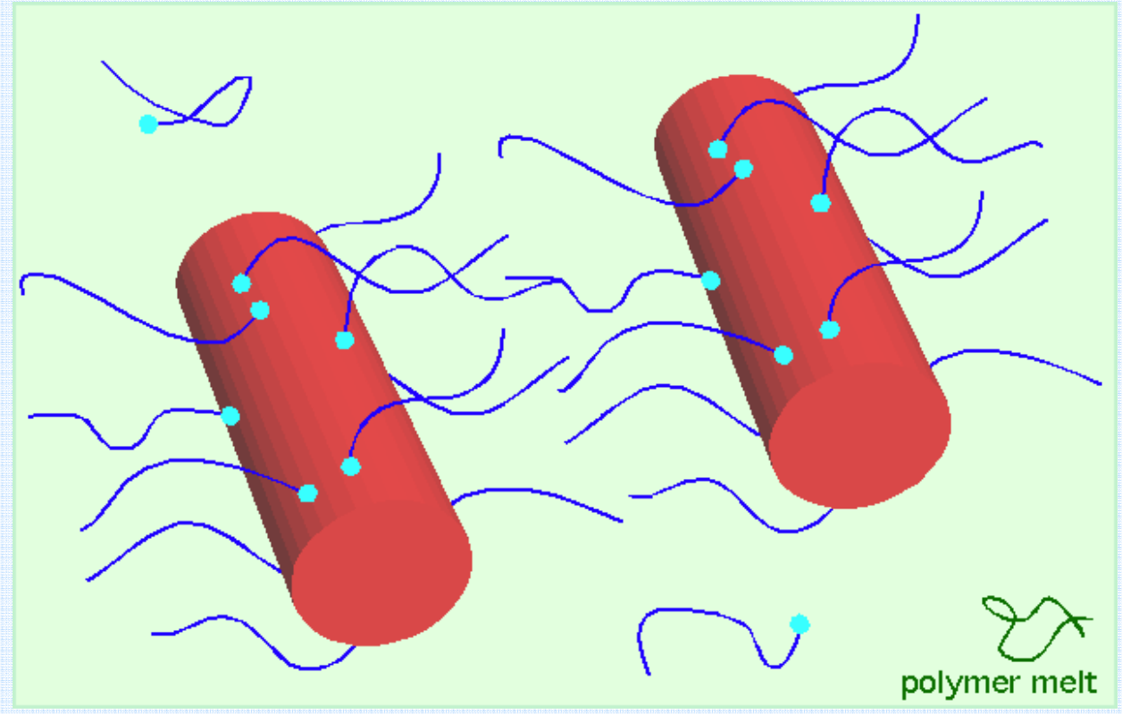
Conclusions

- **found a new first order phase transition**
  - **NPs form layer near substrate**
- **polymeric effect**
- **free energy goes down when add NPs**
  - **should contribute to observed suppression of dewetting**
- **entropy alone is sufficient to cause NPs to segregate to the surface: "entropic push"**

Thanks to CINT: User Project "Effect of Nanoparticle Surface Segregation on Polymer Film Dewetting"

- E. S. McGarrity, A. L. Frischknecht, L. J. D. Frink, and M. E. Mackay, Phys. Rev. Lett., **99**, 238302, 2007.
- E. S. McGarrity, A. L. Frischknecht, and M. E. Mackay, J. Chem. Phys., *in review*, 2007.

Stabilization of Nanoparticles in Polymer Melts

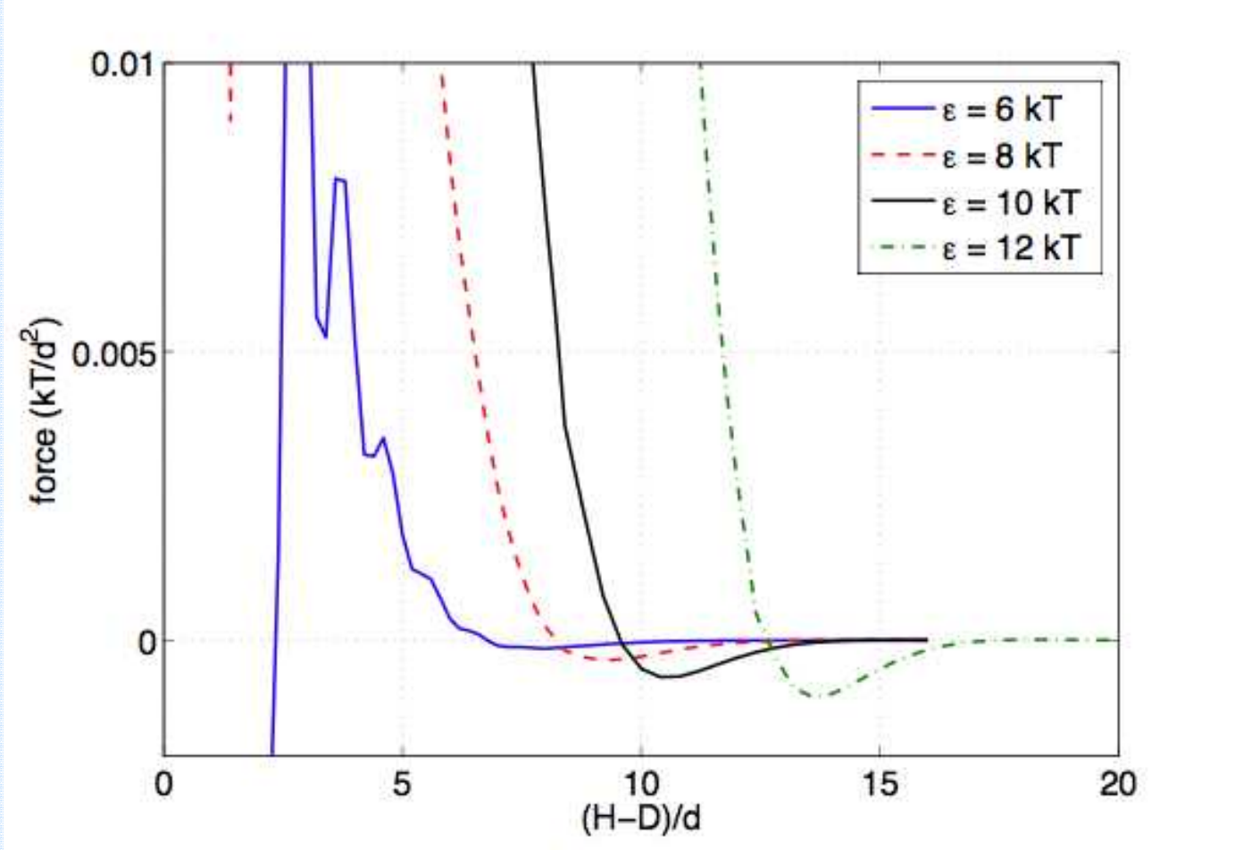


- adsorbed chains of length N, sticky ends
- matrix chains of length P
- nanorods with diameter D

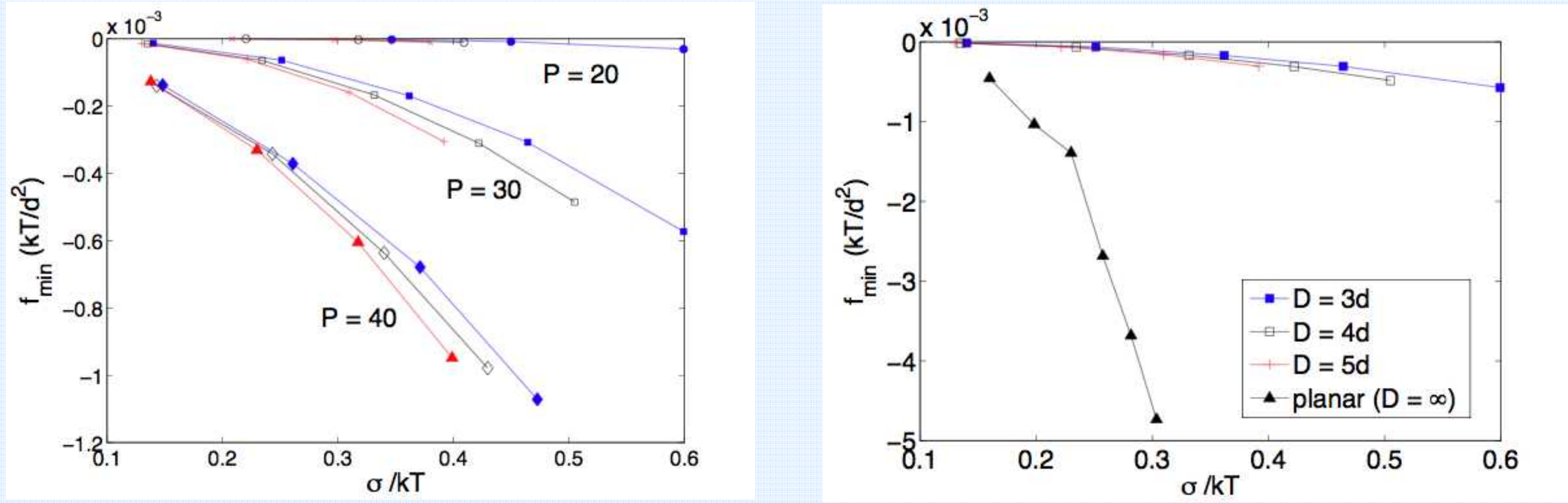
Will the rods aggregate?

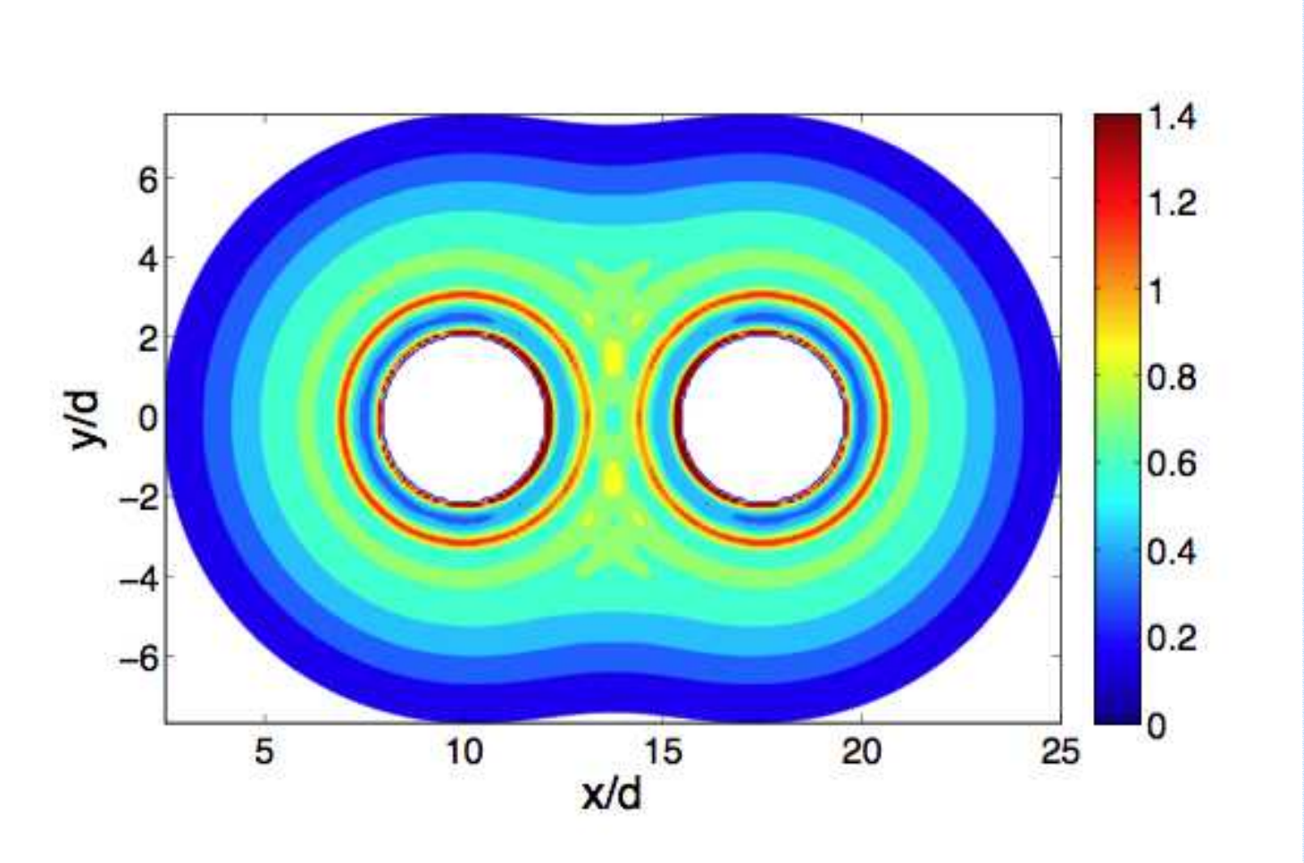
force per unit area between nanorods
D = 4d, P = 40

- attractive force when brushes contact
- repulsive force at shorter distances



minimum in force per area





- force more attractive:
  - for longer matrix chains
  - stronger "sticky" ends
  - larger particles
- chains rearrange as nanorods approach, lowers force
- nanorods will disperse better than larger-sized particles

Thanks to LDRD, C2

A. L. Frischknecht, J. Chem. Phys., to be submitted.

National Nuclear Security Administration

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