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Nanoparticle Simulations & Theory

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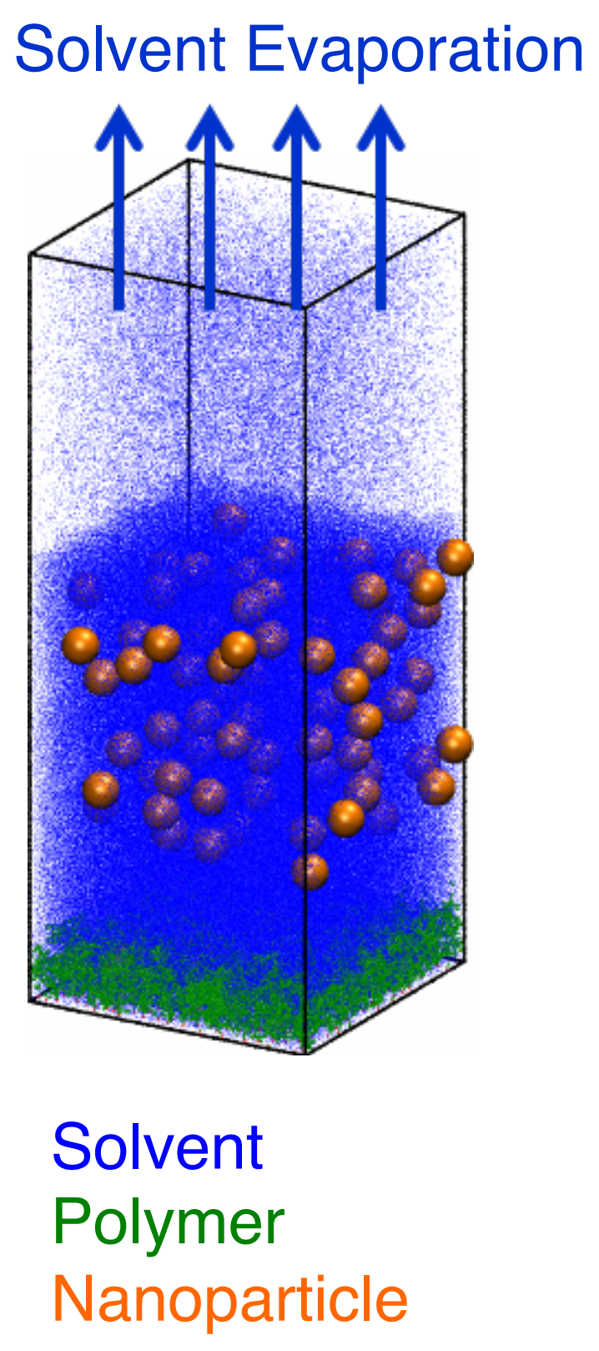
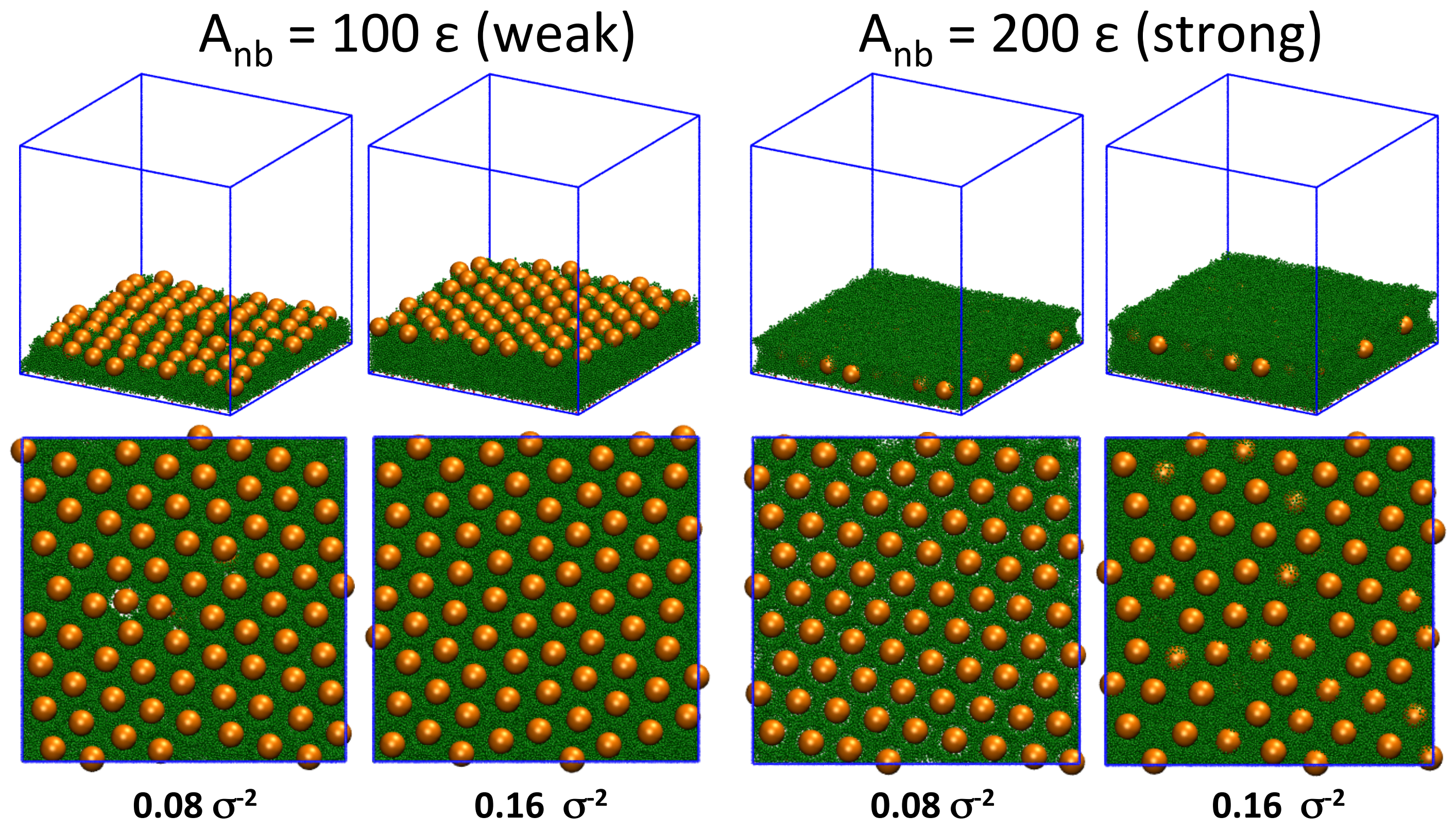
Introduction

The TSNP thrust works to understand and predict the behavior of systems of nanoparticles embedded in diverse environments. Our efforts focus on calculating the interactions in such systems and understanding how to control their structure and properties. In order to study these complex systems, we are using state-of-the-art classical atomistic and coarse-grained molecular dynamics (MD) simulations and statistical mechanics methods, particularly classical density functional theory (c-DFT). Here, three examples of the work are presented. MD is being used to study the organization of nanoparticles at the interface between polymers and solvent, especially after evaporation. Atomistic MD simulations show that the interplay between the coating on the nanoparticle and the solvent has strong effects on the individual nanoparticle shape and on the interactions between nanoparticles. Using classical density functional theory, nanorods coated with a polymer brush are studied to determine when they will will aggregate or disperse in a polymer melt.

Nanoparticle Organization in Polymer/Solvent Mixtures

MD simulations of nanoparticles (gold spheres), polymers (green) and solvent (blue) after evaporation show
- Polymer density increases at liquid/vapor interface
- Organization of nanoparticles depends on polymer-nanoparticle interaction:
  - Strong interaction: nanoparticles form layers near interface
  - Weak interaction: most nanoparticles reside below skin layer





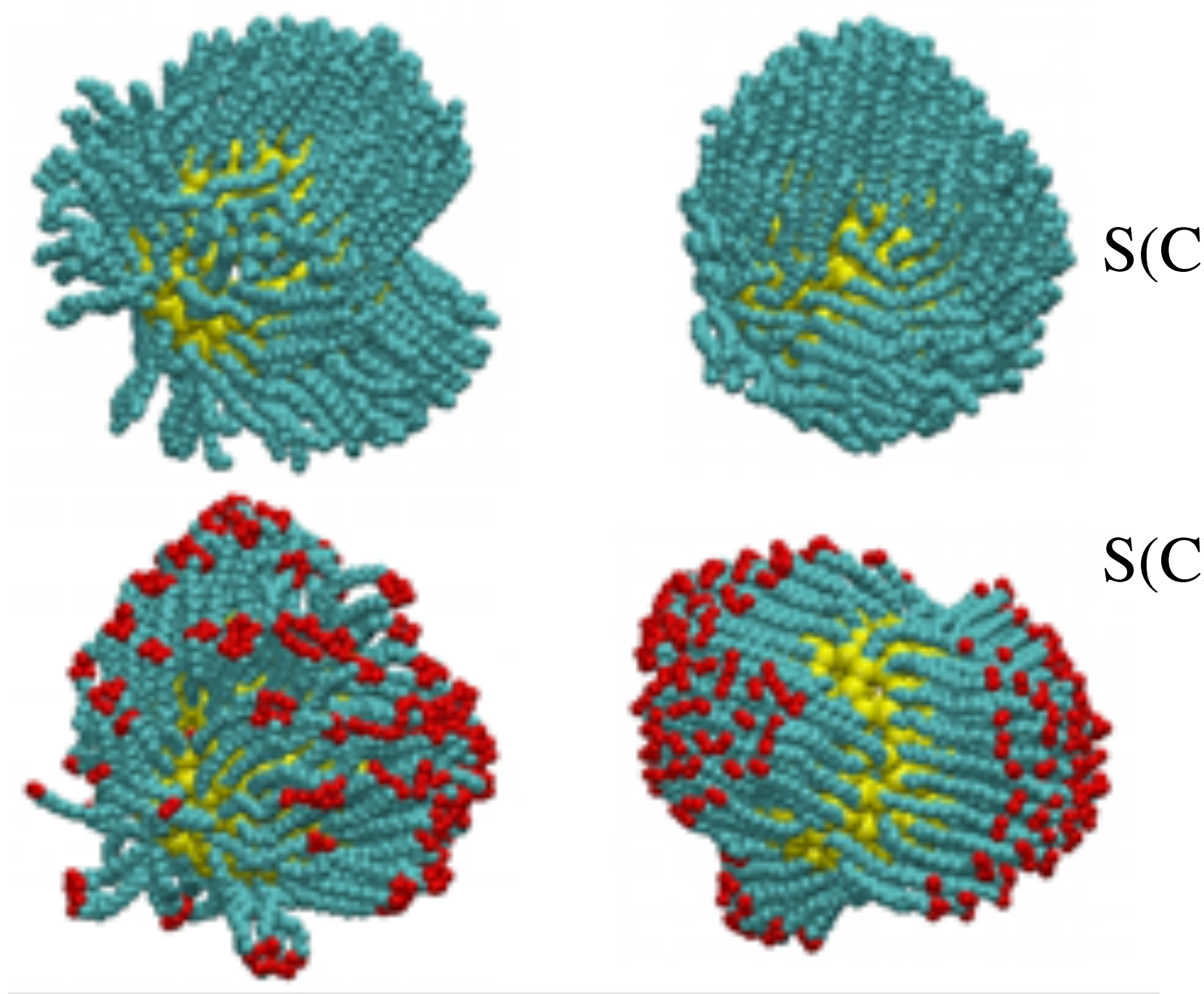
Well ordered arrays of nanoparticle formed at nanoparticle-polymer brush interface when brush density is high and nanoparticle/brush interaction is weak.

Atomistic Simulations of Coated Nanoparticles

Symmetry and Size Effects in Coated Nanoparticles

– Symmetric Coating Leads to Asymmetric Shapes
– Small changes affect structure → change potential activity/solubility

4 nm diameter Au nanoparticles with alkanethiol ligands
in decane (left) and water (right)

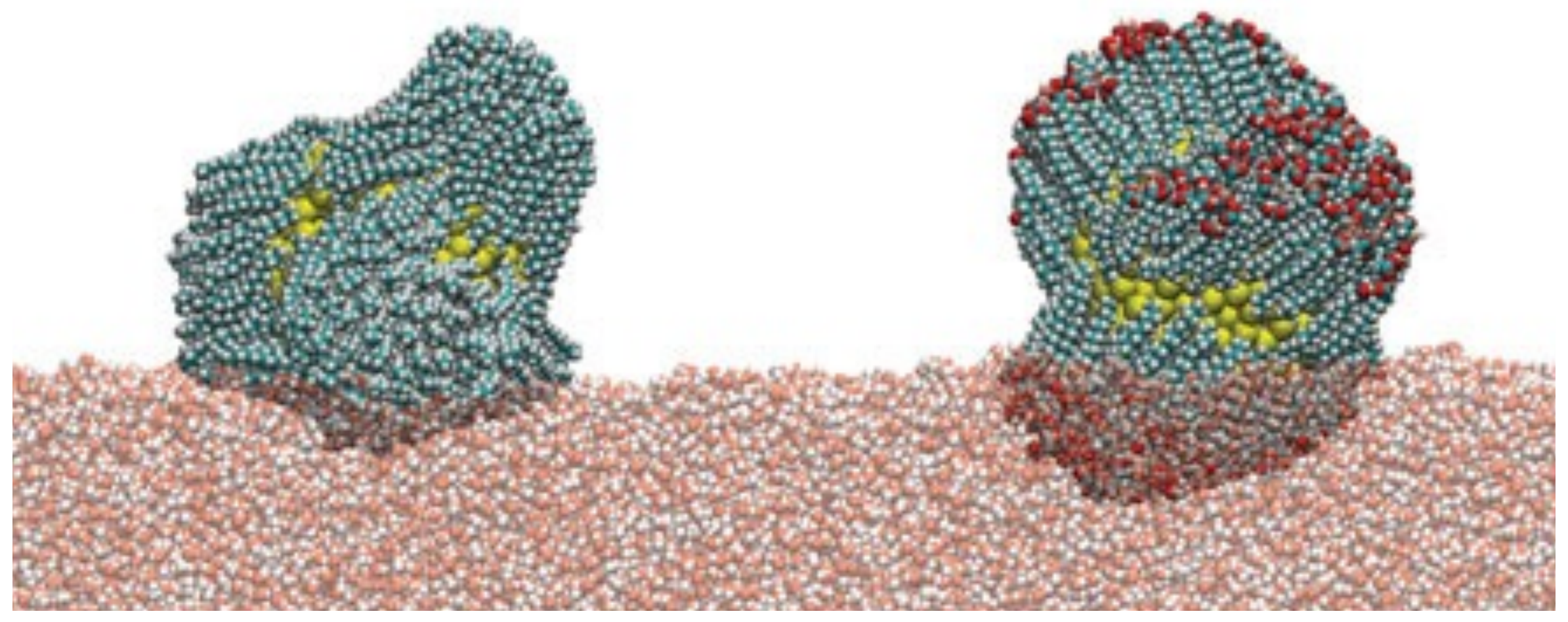


$S(CH_2)_{17}CH_3$

$S(CH_2)_{17}COOH$

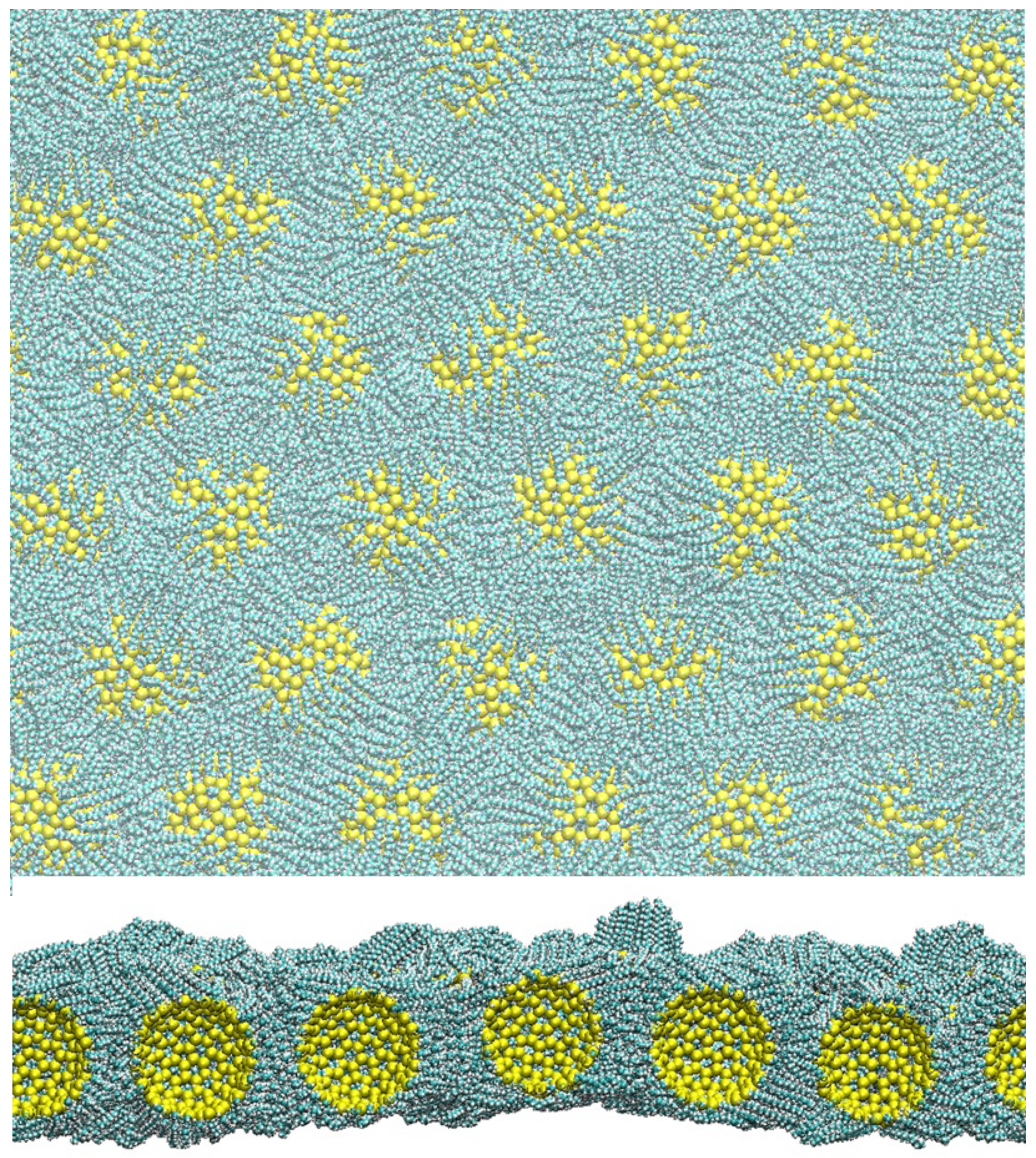
Coatings Distortion and Orientation at Liquid/Vapor Interface

$S(CH_2)_{17}CH_3$ $S(CH_2)_{17}COOH$



water

Self-Assembly into 2 Films at Water/Vapor Interface



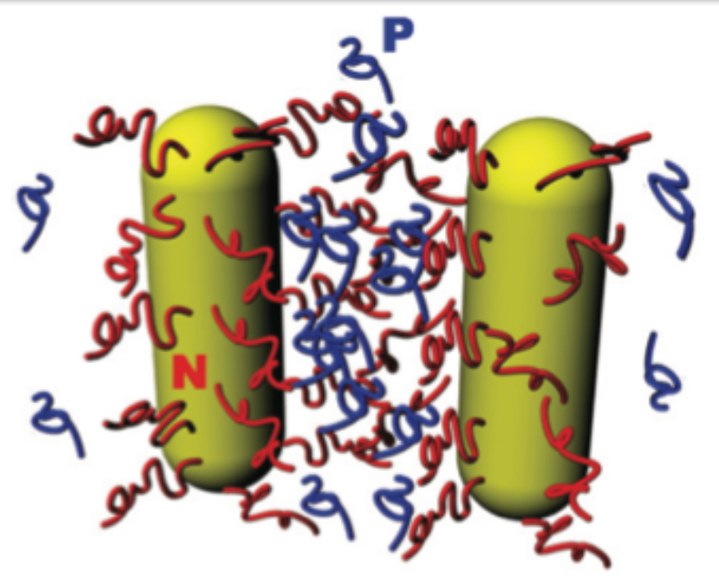
Many 4 nm Au nanoparticles with coating of $S(CH_2)_{17}CH_3$ at water/vapor interface.

Top and side views.

Dry films are mechanically stable

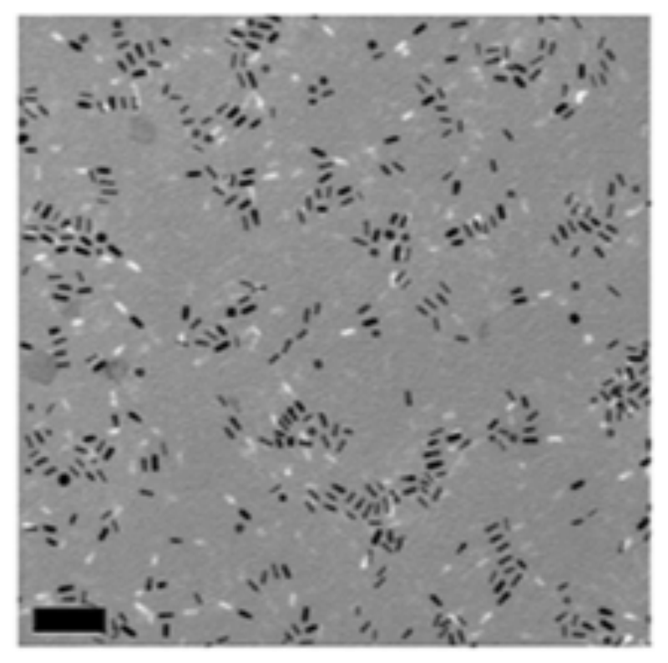
Dispersion of Polymer-Grafted Nanorods

Polymer brushes on gold nanorods (NRs) mixed in a homopolymer melt film.

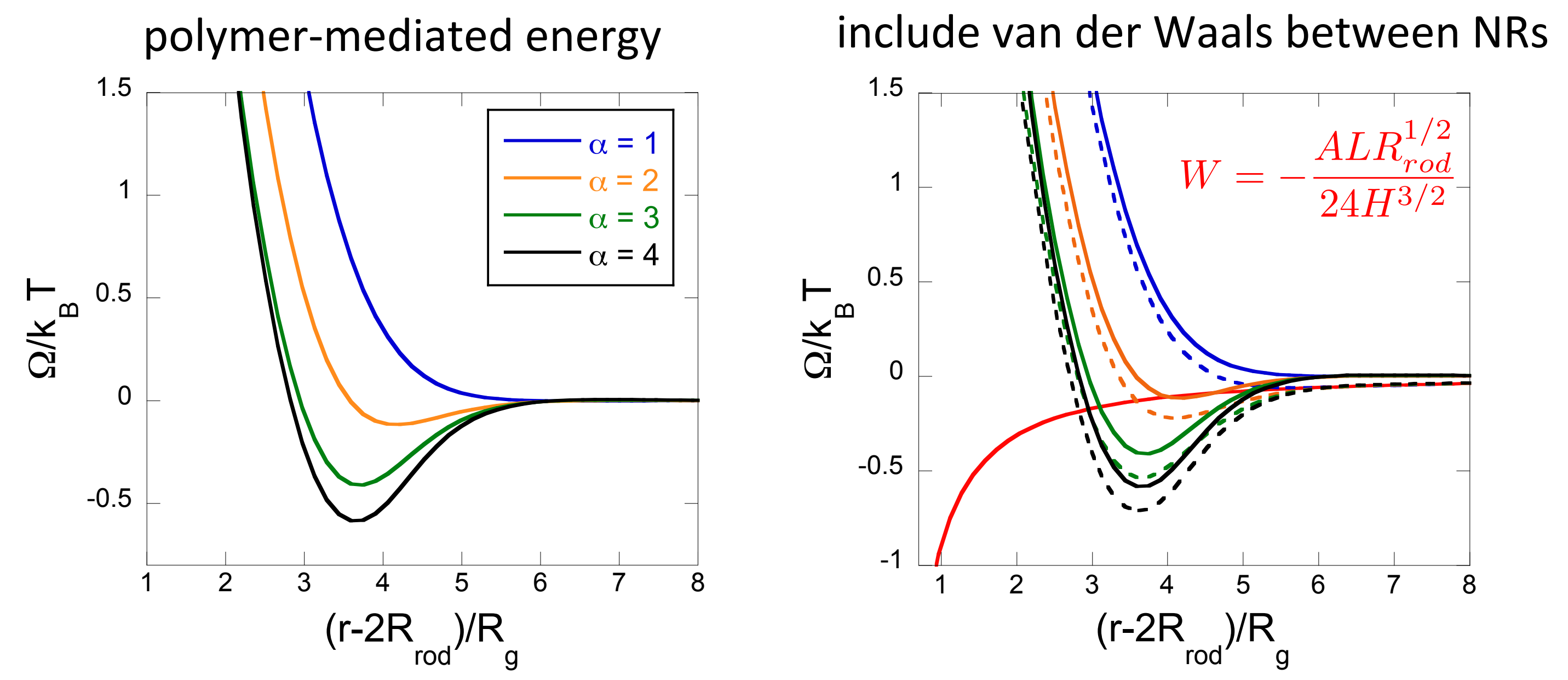


What determines dispersion/aggregation?
- molecular weights of brush (N), matrix (P)
- grafting densities
- NR radius R_{rod}

Classical Density Functional Theory
- freely-jointed chains
- calculate interaction energy between 2 parallel rods

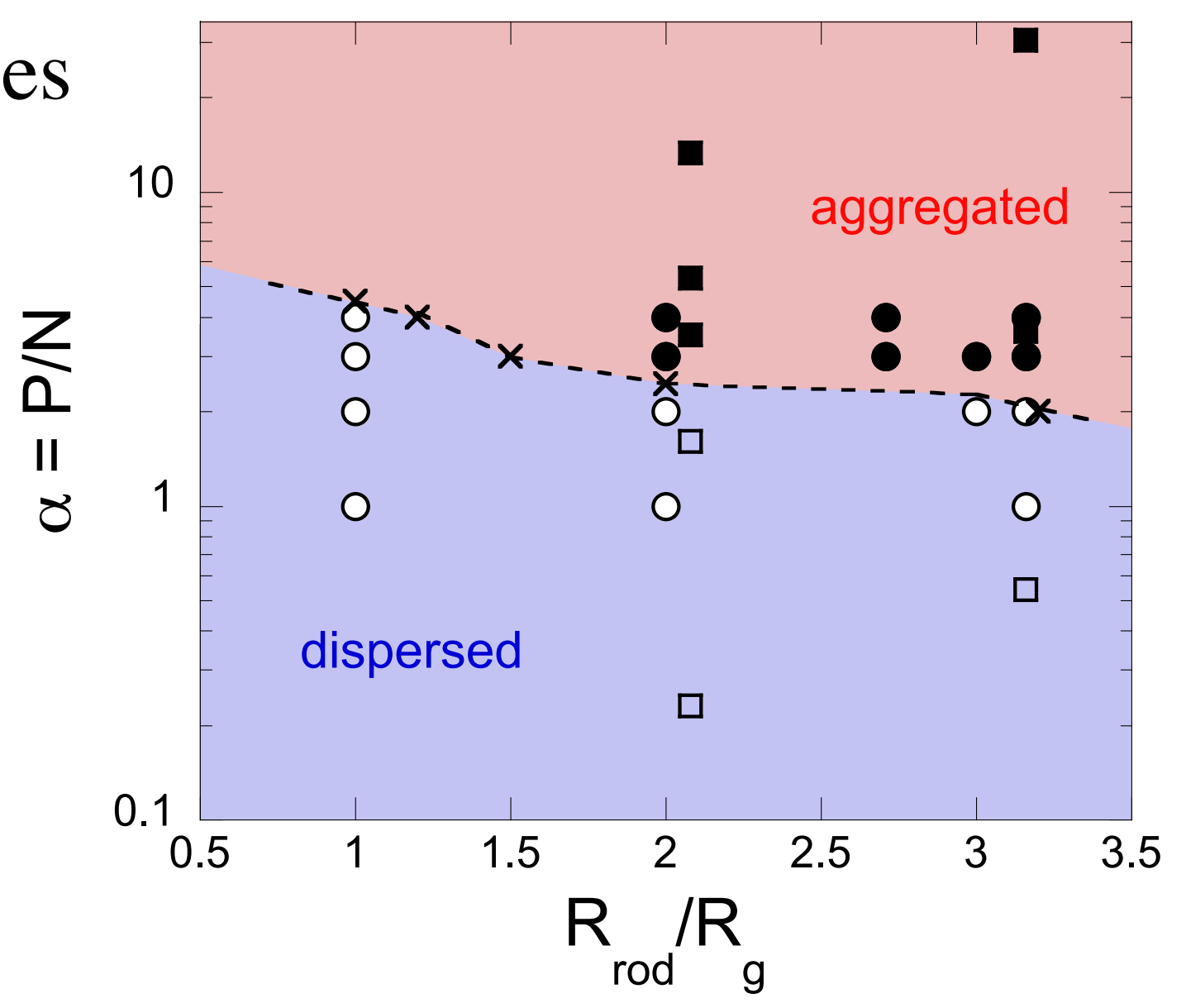


TEM of aggregated rods



- repulsion at short distances
- attractive well at intermediate distances
  - leads to aggregation
- depth of well increases with α = P/N

- NRs will aggregate for energies > 5 kT
- good agreement with experiment
  - circles = c-DFT
  - squares = experiment
- dispersion state determines optical properties



M. J. A. Hore, A. L. Frischknecht, and R.J. Composto, *ACS Macro Lett.* **1**, 115 (2012); A. L. Frischknecht, M. J. A. Hore, J. Ford, and R. J. Composto, *Macromolecules* **46**, 2856 (2013).

Future Work

We will continue to address fundamental issues concerning the structure of nanoparticles coatings and the structure of ensembles of nanoparticles. Using molecular simulations at different scales and molecular theories, we will investigate how the molecular interactions yield the observed structures and what the material properties are.

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