Molecular Dynamics Simulations of Nanoparticle Organization in Polymer/Solvent Mixtures

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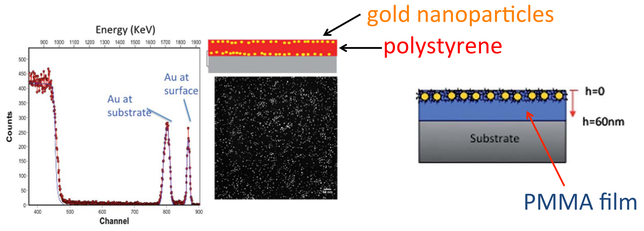
❑ Motivation

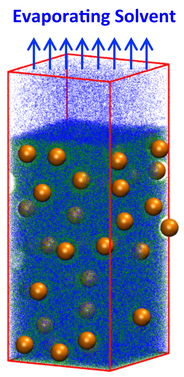
- Evaporating solvent is a widely used technique to disperse nanoparticles in a polymer matrix
- How to control the distribution of nanoparticles?
  - Interactions (nanoparticle/nanoparticle, nanoparticle/solvent, nanoparticle/polymer)
  - Particle size/shape/coating/concentration
  - State of polymers (solution/brush)



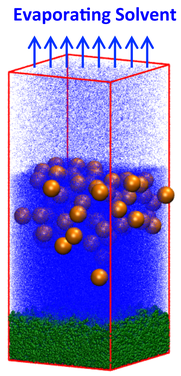
Green, Soft Matter (2012)

Meli and Green, ACS Nano (2008)

❑ Method – Large Scale Molecular Dynamics



Nanoparticles/Polymers

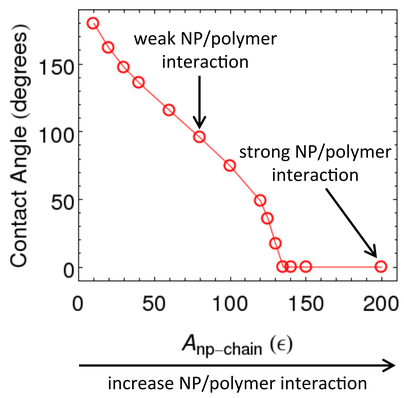


Nanoparticles/Brushes

- Mixtures with dispersed polymers: Lennard-Jones solvent (~ 3 million atoms) + 100-bead polymer chains (~ 3 million beads) + nanoparticles (200, D=20σ)
- Mixtures with grafted polymers: LJ solvent (~ 1 million atoms) + brushes (100-bead chains, grafting density 0.01~0.24σ^{-2} over 100σ × 100σ plane) + nanoparticles (20~100, D=10σ)
- Integrated LJ potential for interactions involving nanoparticles and bead-spring model for polymer chains
- Strong nanoparticle/solvent interaction → solvated nanoparticles
- Vary nanoparticle/polymer interaction
- Remove vapor of solvent → evaporation
- Monitor nanoparticle distribution in polymer/brush matrix

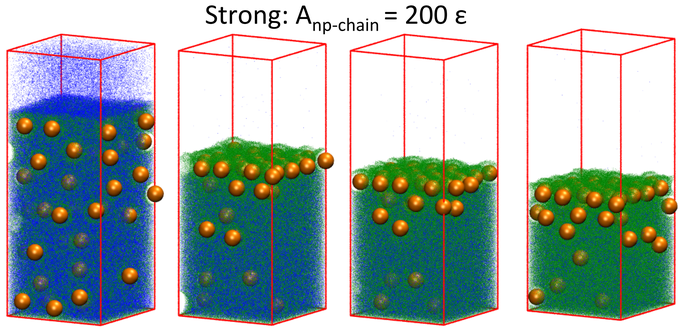
❑ Contact Angle

- Strong (weak) nanoparticle/polymer interaction → small (large) contact angle of nanoparticles on pure polymer melts

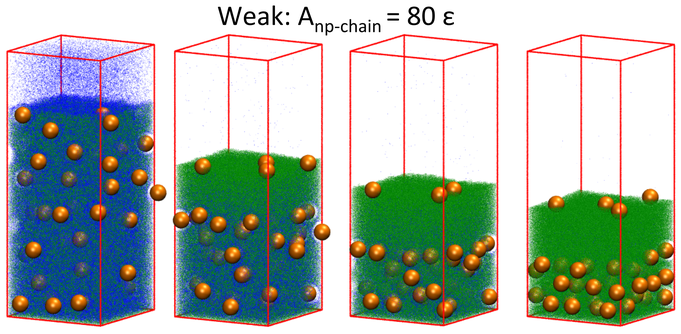


❑ Mixtures with Dispersed Polymers: Strong vs. Weak Nanoparticle/Polymer Interaction

Strong: $A_{np\text{-}chain}$ = 200 ε

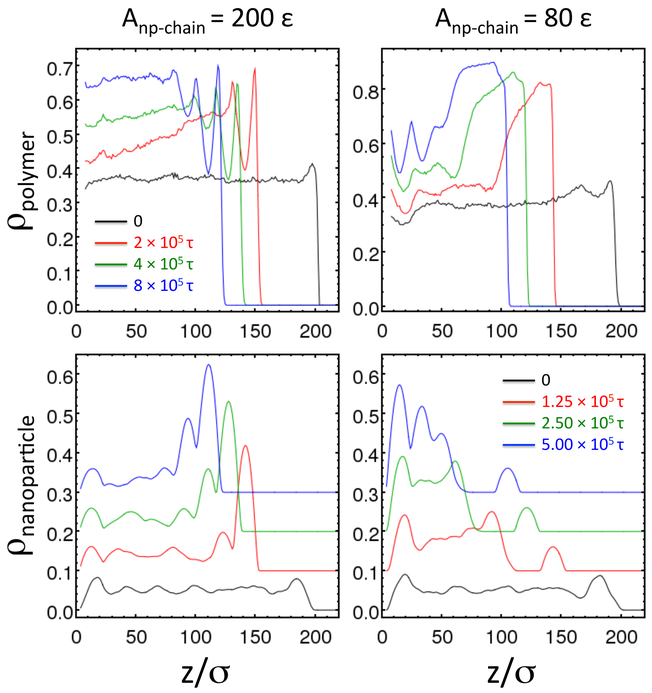


Weak: $A_{np\text{-}chain}$ = 80 ε



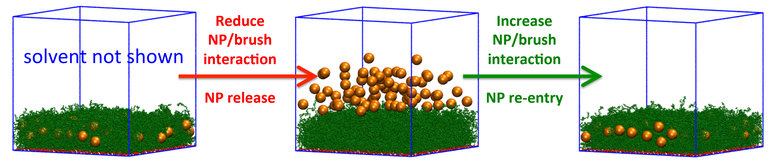
- During evaporation of solvent, density of polymer chains is enhanced at liquid/vapor interface in both cases → a skin layer of polymers forms
- Nanoparticles are accumulated (depleted) in this skin layer of polymers for strong (weak) nanoparticle/polymer interaction
- Strong interaction: nanoparticles form layers near interface → alternating density peaks of nanoparticles and polymers (see density plots below)
- Weak interaction: a few nanoparticles penetrate skin layer of polymers and straddle interface; most nanoparticles are trapped below skin layer and disorderly distributed

❑ Evolution of Polymer/Nanoparticle Distribution



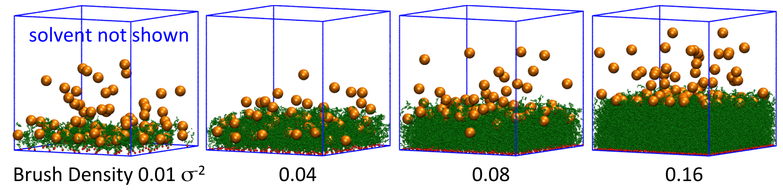
❑ Equilibrate Nanoparticle/Brush/Solvent Mixtures

- Brush density 0.08 σ^{-2}
- Nanoparticle (2D) density 0.75 σ^{-2}
- Reversible nanoparticle capture/release → equilibrated mixtures

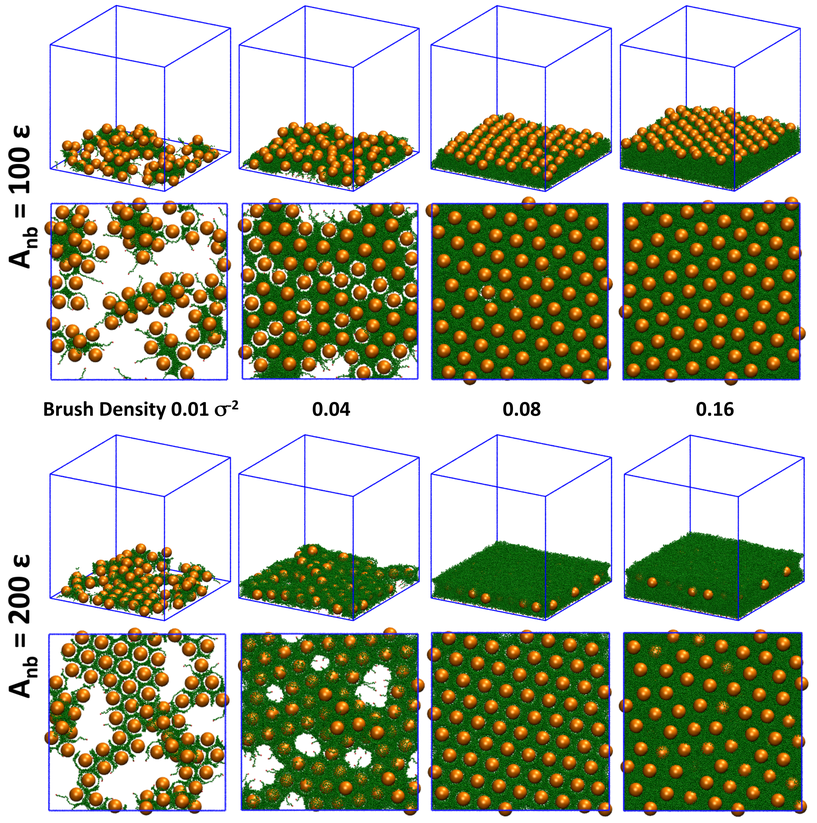


❑ Nanoparticle Distribution with Varying Grafting Density

- Nanoparticle (2D) density 0.75 σ^{-2}
- A_{nb} = 120 ε → nanoparticles straddle surface of pure polymer melt
- Better nanoparticle adsorption at intermediate brush densities



❑ Nanoparticle Organization after Evaporation of Solvent



- Better nanoparticle arrays are formed at:
  - high brush density with weak nanoparticle/brush interaction → nanoparticles form one layer straddling brush surface
  - finely tuned intermediate brush density with strong nanoparticle/brush interaction → brush accommodates just one layer of nanoparticles

All simulations were done with LAMMPS (http://lammps.sandia.gov) on computers at National Energy Research Scientific Computing Center and these resources were obtained through the ALCC grant.

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