Koski, Bollinger, Stevens, Frischknecht, (in Prep.)

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Phase Behavior of Polymer-Grafted Nanoparticles

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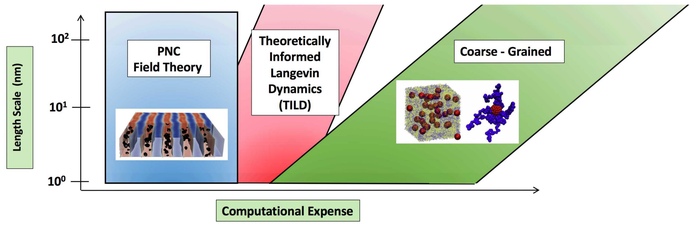
Introduction

A potentially attractive way to control nanoparticle assembly is to graft one or more polymers on the nanoparticle, to control the nanoparticle– nanoparticle interactions. Many parameters control the phase behavior of polymer-grafted nanocompsites, and so efficient and accurate computational methods to predict phase behavior are desireable to help understand and guide experiments and design. We use Theoretically Informed Langevin Dynamics (TILD) to investigate phase behavior of polymer-grafted nanocomposites, and show that the inclusion of thermal fluctuations is needed to match experiment.

Polymer Nanocomposite Models



PNC Field Theory

- polymer field theory + nanoparticles
- can be mean-field or sampled with advanced techniques
- directly calculates the free energy

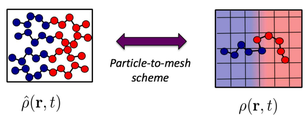
$$\mathcal{Z} = z_1 \int Dw \, \exp(-\mathcal{H}[w])$$ based on equilibrium partition function

Theoretically-Informed Langevin Dynamics (TILD)

$$\frac{d\mathbf{r_i}}{dt} = \beta D F_i + \eta_i(r,t)$$ Langevin Equation

$$\mathcal{Z} = \prod_i \int \mathcal{D}\mathbf{r}_i(t) \left\langle \delta\left[-\frac{d\mathbf{r}_i}{dt} + \beta D F_i + \eta_i(\mathbf{r},t)\right]\right\rangle$$ *Non-equilibrium* partition function

Leverages the advantages of both representations



Explicit access to particle positions

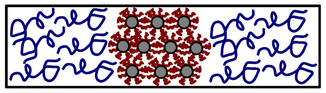
Efficient calculation of non-bonded forces

- each bead moves independently
- interpolate particles to mesh
- calculate nonbond forces from fields on the mesh
- lose access to free energy
- includes thermal fluctuations

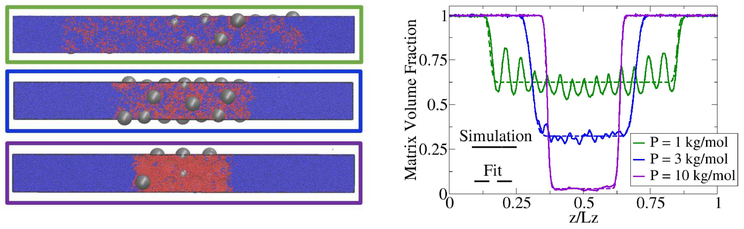
Chao, Koski, Riggleman, *Soft Matter* (2017); Koski, Frischknecht, et al., *Macromolecules* (2017)

Grafted Nanoparticles in Polymer Melts

Calculate binodals from simulations with two explicit interfaces

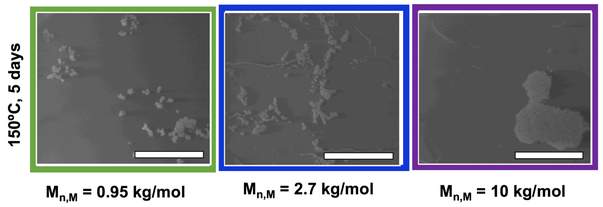


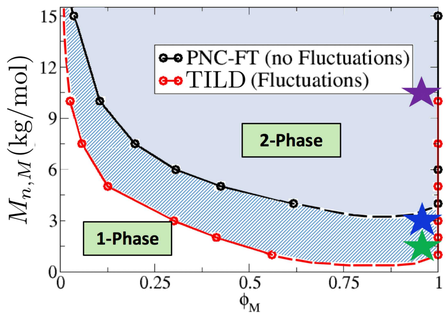
Simulation analysis

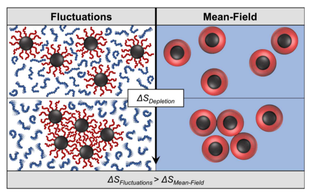


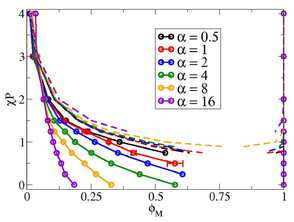
Experiments

PMMA-grafted silica NPs in PS homopolymer melts









dashed = mean-field
solid = TILD

α = P/N
P = matrix length
N = grafted length

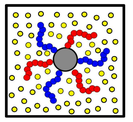
- Experiments show that fluctuations are necessary to properly describe PNC phase behavior.
- Fluctuations capture the full effect of depletion interactions (not fully accounted for at mean-field).
- Field-based simulations allow description of macroscale phase behavior and development of phase diagrams for PNCS!

fluctuations enhance phase separation!

J. P. Koski et al, in review

Mixed Brush Nanoparticles in Solution

Single Particle Brush Structure

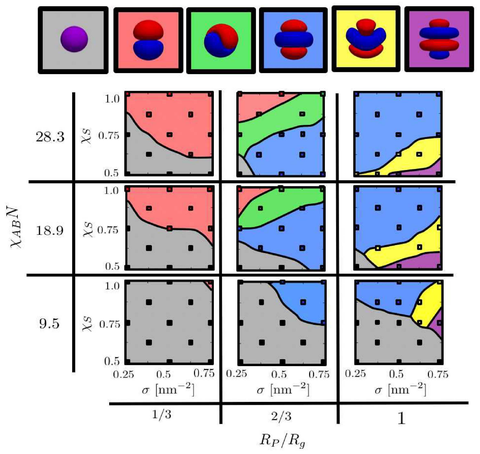


Yellow: Solvent
Red: Dislikes Solvent/Blue
Blue: Dislikes Solvent/Red
Silver: Neutral Particle

- Equal number of Red/Blue chains
- Red and Blue chains same size
- R_p = particle radius
- R_g = size of grafted chains
- σ = grafting density
- χ_{AB} = A-B, χ_s = polymer-solvent interaction

- Phase Diagram generated from mean-field calculations. Allows free energy analysis to asses preferred structure
- Brush phases are a result of competition of minimizing unfavorable Red-Blue contacts and configurational entropy

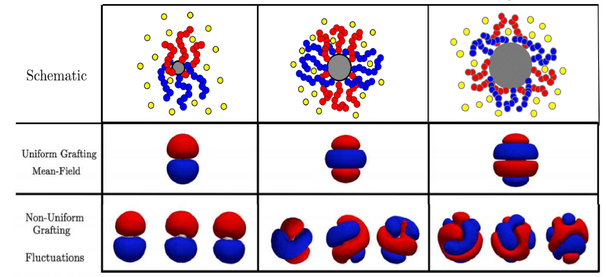
mean-field phase diagram



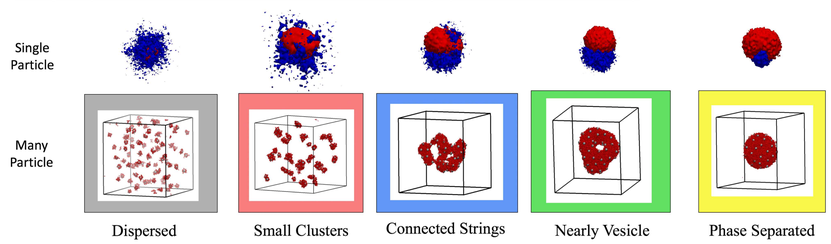
- TILD simulations show defective single particle brush structures
- Janus phase is robust to fluctuations

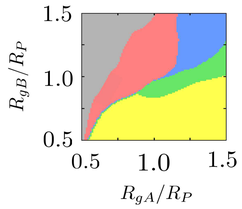
Koski and Frischknecht, *ACS Nano* (2018)

Increasing Particle Size



Single-particle structure dictates many-particle assembly





phase diagram calculated from
- cluster size distribution
- cluster shape (gyration tensor)

Koski, Bollinger, Stevens, Frischknecht, in preperation

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