Examining the Aggregation Behavior of Polymer Grafted Nanoparticles using Molecular Simulation and Theory

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Motivation

Significant scientific and technological interest has focused on polymer inorganic nanocomposites (PINCs) over the past few decades

Without polymer brush   With Polymer brush
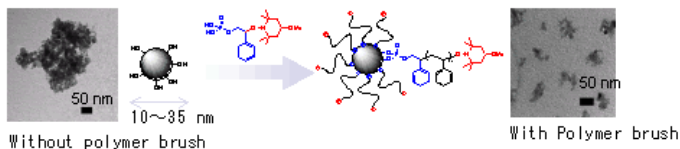
- The mixing of polymers and nanoparticles is opening pathways for engineering flexible composites that exhibit advantageous magnetic, electrical, optical, or mechanical properties.
  - Grafted buckyball systems provide up to a 3 order of magnitude increase in fracture toughness
  - Ionic liquid grafted zirconia nanoparticles have been shown to provide excellent mechanical, electrochemical,and thermal stability for use in Li-ion batteries

http://www.q-eaep.kyushuu.ac.jp/project/en/env_g006.html

Motivation

- The greatest hindrance to the large-scale
  production and commercialization of PINCs
  or tethered nanoparticles(TNPs)
  is the absence of cost-effective methods for
  controlling the dispersion of the
  nanoparticles
  - The nanoscale particles typically aggregate,
    which cancels out any benefits associated
    with the PINCs
  - Obtaining well-dispersed nanoparticles
    composites with high homogeneity presents
    a challenge.
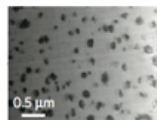
$\sigma = 0.01$ chains nm^{-2}
$M_g = 25$ kg mol^{-1}

$\sigma = 0.01$ chains nm^{-2}
$M_g = 158$ kg mol^{-1}

$\sigma = 0.1$ chains nm^{-2}
$M_g = 24$ kg mol^{-1}

Polystyrene coated silica nanoparticles
Akcora, et al. Nature Materials, 8 (2009)

Goal

- We want a systematic way to explore the aggregation/dispersion trends as a function of: tether length, tether density, and temperature/interaction strength
  - The goal is to avoid costly large scans of parameter space
- A convenient way of capturing the aggregation/dispersion in a systematic way is to look at the VLE
  - We can consider the VLE to be more of a general measure of phase behavior
    - The vapor phase is viewed as a dispersed phase in an implicit solvent and the liquid phase can be compared to a higher density aggregated phase
- Molecular simulations and SAFT calculations are used to examine this behavior, coupling the detailed structural understanding gleaned from simulation with the efficiency of SAFT for thermodynamic properties.

Simulation Model

We want a model that balances the following:

- Directly relatable to experiment (e.g., realistic relative interaction strengths)
- Generic enough to be applicable to a wide range of systems
- Computationally efficient
- Lends itself easily to SAFT calculations

Coarse-grained (CG)/united atom (UA) model was chosen

- Silica nanoparticle treated as a single CG site
- Grafted polymers modeled as UA alkanes

Simulation Model

- Silica nanoparticles (1 nm) are modeled with a 12-6 Lennard-Jones potential
    - Parameters come from Lee and Hua derived for Si_6O_{12}: σ=6.2 Å and ϵ= 3.1 kcal/mol

- Polymers are modeled as UA chains with TraPPE potential
    - Following Martin and Siepmann:
      CH_2 : σ=3.95Å, ϵ=0.191 kcal/mol
      CH_3 : σ= 3.75 Å, ϵ=0.0914 kcal/mol
      ...+ bonds + angles + dihedrals
    - free to move around the surface of the nanoparticle

- Lorentz-Berthelot mixing rules applied

Si_6O_{12}

alkane
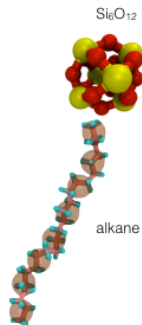
Lee and Hua J. Chem. Phys. 132 (2010)
Martin and Siepmann, J. Phys. Chem B, 102, (1998)

Simulation Method

- Simulations performed using the GPU-enabled HOOMD-Blue
  - Quench dynamics (QD) is used to estimate the VLE
    1. Start with a single phase liquid system
    2. Rapidly expand the box in one direction
    3. Calculate the density profile along the long dimension of the box
    4. Repeat for different temperatures
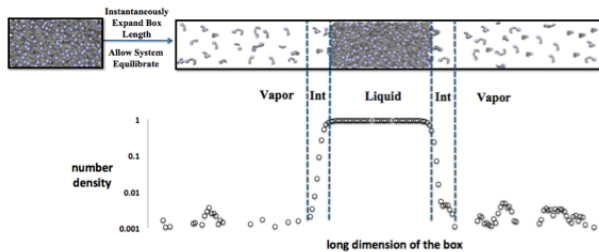
Anderson, et al. J. Comput. Phys. 227, (2008); in't Veld, et al. J. Chem. Phys. 129, (2008)

SAFT Theory
Background

- Molecular based equation of state

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{mono}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT}$$

  - Molecules modeled as hard spheres
  - Spheres interact through dispersion interactions
  - The spheres tangentially bond together
  - Molecules can interact through association interactions
    - Mimics hydrogen bonds

- Several different versions of the SAFT equation have been proposed

Chapman, Gubbins, Jackson, Radosz, *Fl. Ph. Eq.*, 52, 31 (1989); *Ind. Eng. Chem. Res.*, 29, 1709 (1990)
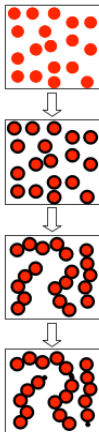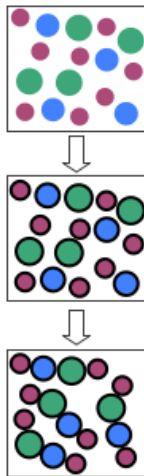
Hetero-SAFT VR

Background

- Describes chains composed of segments of different size and/or energy of interaction

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{mono}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT}$$
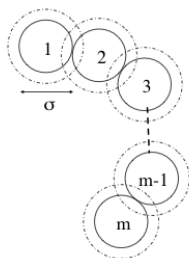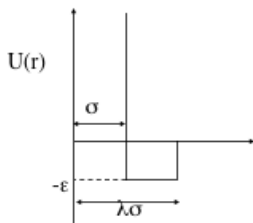
- Modification of the chain term

$$\frac{A^{chain}}{NkT} = -m \ln y_i^{SW}(\sigma_i) \Rightarrow -\sum_{ijbonds} \ln y_i^{SW}(\sigma_{ij})$$

- Hetero-SAFT-VR validated through extensive NPT and GEMC simulations of diblock heteronuclear chains

Peng, Zhao, and McCabe, *Mol. Phys.*, 104, 571, (2006)

Hetero-SAFT VR

- Dispersion interactions modeled through a potential of variable range
  - 3 adjustable parameters: σ, ϵ, and λ
- Nanoparticles:
  - Fit to reproduce high quality Lennard-Jones VLE from NIST
- Alkanes:
  - UA Atom: $m = (C\text{-}1)/3 + 1$
  - Parameters taken from McCabe and Jackson (PCCP, 1999)
- Mixtures
  - Lorentz-Berthelot combining rules

Gil-Villegas, et al., *J. Chem. Phys.*, 106(10), 4168, (1997); Galindo, et al., *Mol. Phys.*, 93(2), 241, (1998)
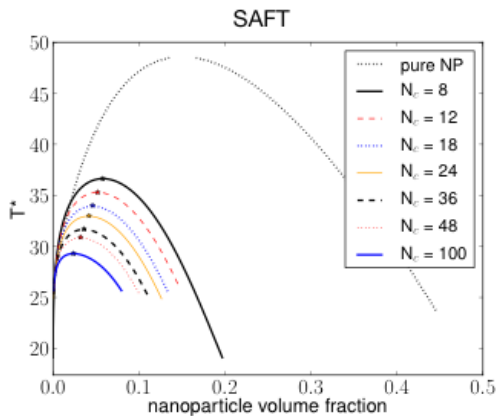
Connecting VLE to Aggregation/Dispersion Behavior

- T^* can be thought of as inverse interaction strength
  - Low T^* means strongly interacting, high T^* more weakly interacting
  - Strongly interacting systems:
    - Volume fraction greater than 0.20 results in single uniform liquid,
    - Volume fraction less than 0.20 system will form aggregates in equilibrium with very low density dispersed phase
  - Weakly interacting systems:
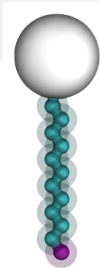   - transition to uniform phase will occur at lower volume fraction
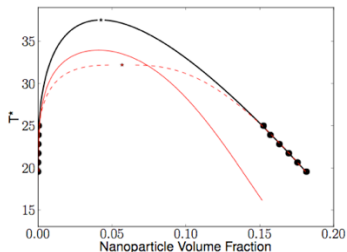
Grafted vs. Bare NPs

- Single graft system compared to the pure NP VLE
  - Behavior is significantly altered as compared to the pure NP system
    - Polymers disrupt strong NP-NP interactions

SAFT

Jessica D. Haley, Christopher R. Iacovella, Cl=Examining the Aggregation Behavior of Polyn   September 25, 2014   12 / 17

Monotethered Nanoparticle Systems

- Consider a system with a single polymer
  - critical temperature drops as chain length increases
    - inverse of what is seen for a pure polymer system
  - critical density drops as chain length increases
   - consistent with pure polymer systems
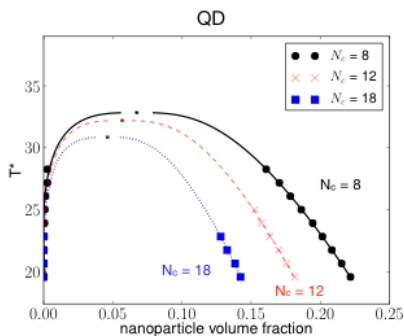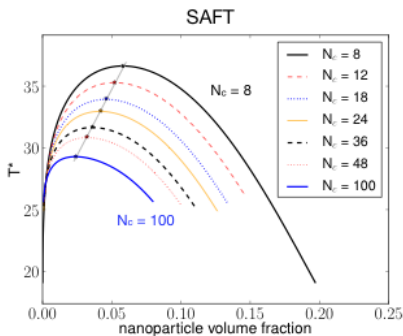
Change in Topology

- Changing the number of grafts has a similar effect to changing the interaction strength
  - Potential of mean force (PMF) between grafted nanoparticles
    - volume fraction = 0.003 and $T^* = 40$
  - Increasing the number of grafts shields the strong nanoparticle-nanoparticle interactions
    - effective interaction for $N_{graft} = 6$ is essentially a repulsive shoulder
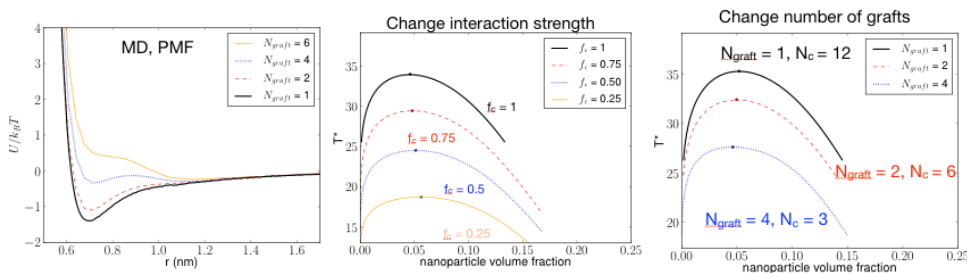
Varying Number of Grafts/Beads

- Reduction in critical temperature as the number of grafts is increased is seen with longer grafts having a lower critical temperature than shorter grafts

- Transition point is reached at 6 grafts where this trend is reversed and shorter grafts result in a lower critical temperature.
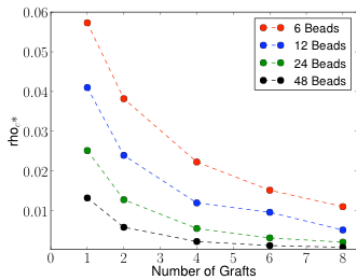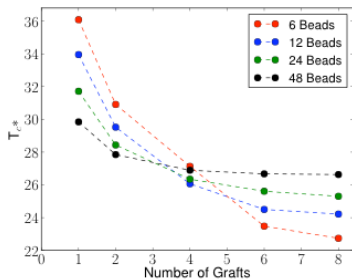
Conclusions

- Agreement between VLE calculations performed using quench dynamics (QD) and SAFT for tethered nanoparticles
    - VLE provides us with a convenient way to examine the changes in aggregation/dispersion behavior

- Tether length increases, the coexistence region shrinks
    - Both critical density and temperature are reduced, the latter of which is the opposite of what is seen for pure alkanes
    - SAFT calculations reveal transition point at 6 grafts where this trend is reversed and shorter grafts result in a lower critical temperature.

- As tether density increases, strong interactions between nanoparticles are shielded
    - PMF shows reduced interaction, matching behavior seen when reducing NP interaction
    - VLE behavior converges at higher grafting density

- We can investigate how to further modify behavior through solvent to develop design rules for controlling this fundamental behavior

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