

Multiscale modeling of polymer-induced interactions between colloids in waterborne coatings

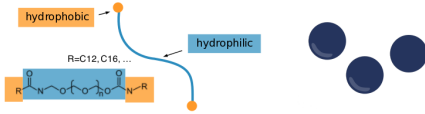
Alyssa Travitz¹, Wenlin Zhang², Ronald G. Larson^{1,2}

¹Department of Macromolecular Science and Engineering, ²Department of Chemical Engineering, University of Michigan, Ann Arbor



Introduction

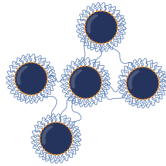
The primary components of waterborne coatings are colloidal particles and rheology-modifying polymers.



Rheology-modifying polymers consist of a hydrophobic backbone and hydrophilic end caps that adsorb to the colloids' surfaces.

In waterborne systems, HEUR polymers form a layer of loops around each colloid, increasing the range of the colloids' repulsive interactions.

We quantify these repulsive interactions through Brownian dynamics simulations and self-consistent field theory to inform our multiscale modeling efforts to understand and predict the behavior of waterborne coatings.



Simulation model system

We use a stiff bead-spring model to resolve each kuhn step of the polymer and bead-bead repulsions account for the excluded volume effects of polymer interactions

All simulations are performed using the molecular dynamics package in HOOMD-blue¹.

Harmonic spring potential:

$$U_{bond}(r) = \frac{1}{2}k(r - r_0)^2$$

$$k = 400 \frac{k_B T}{\sigma_{bb}^2}$$

$$r_0 = 1b_K$$

Bead-bead repulsive potential:

$$U_{bb}(r) = \begin{cases} 4\epsilon_{bb} \left[\left(\frac{\sigma_{bb}}{r} \right)^{12} - \left(\frac{\sigma_{bb}}{r} \right)^6 + \frac{1}{4} \right] & r < 2^{1/6} \sigma_{bb} \\ 0 & r \geq 2^{1/6} \sigma_{bb} \end{cases}$$

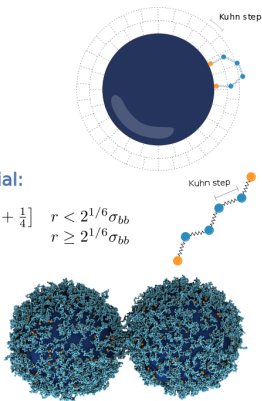
$$\sigma_{bb} = 0.4b_K$$

$$\epsilon_{bb} = 1k_B T$$

Langevin integrator:

$$m \frac{d\vec{v}}{dt} = \vec{F}_C - \gamma \cdot \vec{v} + \vec{F}_R$$

\vec{v} = velocity
 γ = drag coefficient
 \vec{F}_C, \vec{F}_R = conservative and random forces



Self-consistent field theory

Spherical lattice self-consistent field theory for an isolated colloid

In a chemical potential field $w(r) = v\phi(r)$, where $\phi(r)$ is the local segment density, and v is the excluded volume parameter, we can compute the evolution of the chain propagator $P(m, n)$:

$$P(m, n) = [\lambda_- P(m-1, n-1) + \lambda_0 P(m, n-1) + \lambda_+ P(m+1, n-1)] e^{-w(m)} e^{-v(m, n)}$$

$\lambda_-, \lambda_0, \lambda_+$ = probability that a segment transitions to an adjacent layer on step n
 $v(m, n)$ = attractive strength of a sticker end

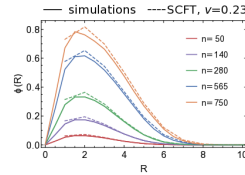
so that the Boltzmann weight for segment n to reside in layer m is:

$$Q(m, n) = P(m, n) P(m, N_K - n + 1) e^{w(m)} e^{v(m, n)}$$

allowing us to calculate the density of segments for each layer m :

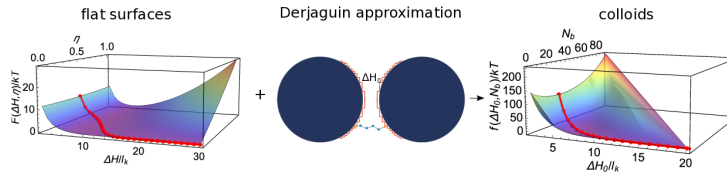
$$\phi(m) = \frac{J N_K \sum_{n=1}^{N_K} Q(m, n)}{\sum_{m=1}^M \sum_{n=1}^{N_K} A(m) Q(m, n)}$$

$J N_K$ = total # of chain segments
 $A(m)$ = # of sites per lattice shell



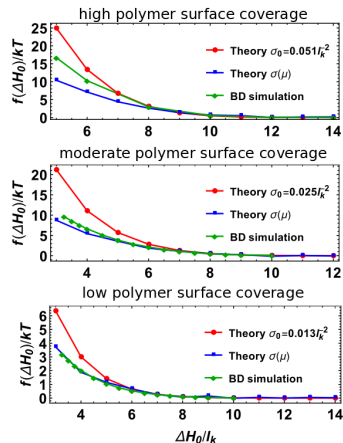
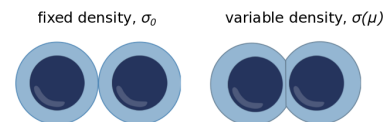
Lattice self-consistent field theory for two interacting colloids with bridging

To calculate the free energy of two interacting polymer-coated colloids, we solve the SCFT equations for two flat surfaces on a cubic lattice. We apply the Derjaguin approximation to the flat surface calculations to estimate the effective interactions between two spherical colloids:



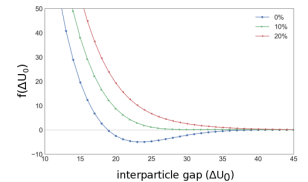
Effective repulsions between colloids

We compare the SCFT predictions to BD simulations of the same set-up. In the BD simulations, the polymer loops have translational freedom on the surface of the colloid, whereas in the SCFT approach, the loops are fixed without translational movement. Therefore, we introduce SCFT with non-uniform polymer density, $\sigma(\mu)$.



Phase stability from polymer defects

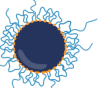
Using our SCFT approach, we can calculate the effective pair potential between colloids that results from the equilibrium number of bridges and loops at each interparticle gap:



no defects, all polymers have one hydrophobe on each end



10% of polymers are missing a hydrophobe on one end

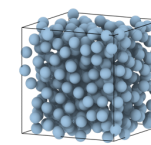
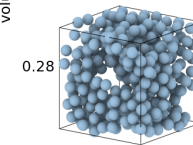
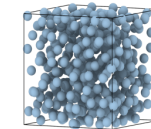
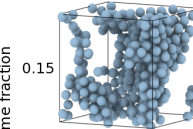


percent of polymers defective

0%

10%

volume fraction



We see that phase separation occurs if all polymers have two hydrophobes (one on each end). However, if more than 10% of the polymers are missing a hydrophobic end-cap, the formulation remains dispersed.

Conclusions and future work

We present two approaches, SCFT and Brownian dynamics, to quantifying the effective interactions between colloidal particles coated in rheology modifying polymers. We show that our Brownian dynamics simulations validate the lattice self-consistent field theory approach, which is ultimately used to calculate equilibrium effective potentials inaccessible by simulations. The resulting effective potentials demonstrate the importance of polymer defects to formulation phase stability.

These studies will inform our multiscale modeling approach to predicting and understanding the rheology of waterborne coatings in quiescent conditions and under shear.

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