Numerical Methods of Polymer Brushes using Self-Consistent Field Theory

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Complex Fluids Design Consortium Annual Meeting
February 2, 2008
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What is a Polymer Brush?

- Polymer brushes refer to an assembly of polymer chains that are attached by one end to a surface or interface.

- Behavior exhibited by polymer brushes is very different than that for non-grafted polymers.

- Dense polymer brushes will exhibit over crowding at the surface which will cause the polymer to stretch away from the grafting surface.
Why are we interested?

- A variety of applications: colloidal stabilization, new adhesive materials, polymer surfactants, membrane surface modification, etc.

- Stimuli-Responsive and Switchable Surfaces: Mixed polymer brushes
  - Segregate at sub-micrometer scale
  - Exhibits switching behavior upon exposure to different environment
  - Use in the fabrication of adaptive/responsive surfaces

• Müller has successfully used the fully spectral method to study a binary brush immersed in solvent
• Spectral methods are an accurate technique for calculating the unit cell of periodic mesophases, but it is only applicable to laterally homogeneous morphologies that must be predetermined in advance
• Poor computational scaling \( \mathcal{O}(N_z^3) \) when the ideal scaling is \( \mathcal{O}(N_zN_s) \)
• Computationally expensive for high resolution, high dimensional simulations
Pseudo-spectral method

- Powerful due to its ability to efficiently transform between the real and spectral representation

- Can be used to calculate large cell in addition to unit cell calculations where advance knowledge of the self-assembly morphology is not required

- The cost is of $O(N_z \log_2 N_z)$ comes closer to achieve the ideal scaling of $O(N_z N_s)$

- Although it has been used to study a variety of polymeric systems, the area of grafted polymers has been untouched
The main problem

Initial condition due to the tethering of the polymer:

\[ q_c(z, 0; [\mu]) = \delta(z - \epsilon) \]

Solving the modified diffusion equation:

\[ \frac{\partial}{\partial s} q_c(z, s; [\mu]) = \frac{\partial^2}{\partial z^2} q_c(z, s; [\mu]) - \mu(z) q_c(z, s; [\mu]) \]

Operator splitting method:

\[ q_c(z, s + \Delta s; [\mu]) = e^{-\Delta s \mu(z)/2} e^{\Delta s \partial^2 / \partial z^2} e^{-\Delta s \mu(z)/2} q_c(z, s; [\mu]) \]
Analytic extension

Solving the modified diffusion equation:

\[ \frac{\partial}{\partial s} q_c(z, s; [\mu]) = \frac{\partial^2}{\partial z^2} q_c(z, s; [\mu]) - \mu(z) q_c(z, s; [\mu]) \]

Taylor Expansion

\[ q_c(z, s + \Delta s; [\mu]) = e^{-\Delta s \mu(z)/2} e^{\Delta s \partial^2 / \partial z^2} e^{-\Delta s \mu(z)/2} q_c(z, s; [\mu]) + O(\Delta s^3) \]

Expression for the propagator at \( s = \Delta s \)

\[ = e^{-\Delta s \mu(z)/2} \int d\tilde{z} G(z, \tilde{z}, \Delta s) e^{-\Delta s \mu(\tilde{z})/2} q_c(\tilde{z}, 0; [\mu]) \]
Analytic extension

Green function for the 1D heat equation

\[
\frac{\partial}{\partial s} G(z, z', s) - \frac{\partial^2}{\partial z^2} G(z, z', s) = \delta(z - z')
\]

\[
G(z, z', \Delta s) = \frac{1}{L_z} + \sum_{m=1}^{\infty} \frac{2}{L_z} \cos \left( \frac{m\pi z}{L_z} \right) \cos \left( \frac{m\pi z'}{L_z} \right) e^{-\Delta s \left( \frac{m\pi}{L_z} \right)^2}
\]

Analytic extension

\[
q_c(z, \Delta s; [\mu]) = \frac{\exp[-\Delta s (\mu(z) + \mu(0)) / 2]}{q(0, 1; [\mu])} \left[ 1 + \sum_{m=1}^{\infty} 2 \cos \left( \frac{m\pi z}{L_z} \right) e^{-\Delta s \left( \frac{m\pi}{L_z} \right)^2} \right]
\]
Gaussian approximation

\[ \delta(z - \epsilon) = \frac{\exp\left[-(z - \epsilon)^2/(2\alpha)\right]}{\sqrt{2\pi\alpha}} \]

- Approximate the Dirac delta function as a Gaussian centered at \( z=\epsilon \) with variance \( \alpha \)

\[ q_c(z, 0; [\mu]) = \frac{\exp\left[-z^2/(2\alpha)\right]}{\sqrt{2\pi\alpha}} \]

- The Dirac delta function is recovered in the limit \( \alpha \to 0 \)
- Initial condition is no longer singular
Density profiles

\[ L = 2R_0, \; f = 0.5, \chi N = 12.5, \; N_z = 4096, \; N_s = 400 \]
AB Binary Blend Brush

- Numerical methods of polymer brushes can be used to look at an AB binary blend brush grafted to a spherical nanoparticle.

- Masking method was used to model an A or B-attractive surface.

- Can compare the self-assembly behavior to a 3D AB diblock copolymer melt confined to the surface of a sphere.
AB Diblock Copolymer Melt
Assumptions and Experimental Validity

- Uniform and thin film in the radial direction

- Difficult to experimentally realize, in the form of colloids and nanoparticles coated with a thin layer of block copolymer

- Neutralize inner and outer surface of layer so that the film is compositionally homogeneous in the radial direction

- Invest in a full 3D SCFT model
Polymers on spherical surfaces

- Multivalent nanoparticles- nanoparticles with precisely controlled number and locations of functional sites: potential application for the self-assembly of useful electronic devices.

- Core-shell and hollow nanospheres: potential application in catalysis, controlled drug delivery, artificial cells, and light fillers.

PtBA/PS brush on silica particles

SiO$_2$-PMMA CSNs
Previous Work: AB Binary Brush in Solvent

- System: AB Binary Brush grafted to the surface of a spherical particle.

- CPU time > 2 years on a 1GHz Pentium 3 machine to obtain self-consistency.

- Our numerical methods can be used to perform a more extensive study of phase space.

Previous Work: AB Diblock Copolymer Thin Film

- System: An AB diblock copolymer thin film covering a nanoparticle
- Investigated the morphology of thin films around a nanoparticle
- Further study the effect of numerous parameters such as surface interactions and film thickness on the morphology.

Masking Method

- Will be used to model surface affinity
- Define a wall volume fraction \( \phi_w \)
  - Decays through a tanh function from 1 to 0
- Surface affinity given by \( \chi_w N \) at \( R_0 \) and \( \chi_{w2} N \) at \( R_f \)
Effect of Curvature on Order to Disorder Transition

\[ f=0.5, \chi_{wN} = \chi_{w2N}=0, Ro=2 \, R_{g0}, Rf=3 \, R_{g0} \]

\[ \chi_N = 8 \]
\[ \chi_N = 6 \]
\[ \chi_N = 5.3 \]
\[ \chi_N = 5.2 \]
\[ \chi_N = 5.22 \]
Effect of Curvature on Order to Disorder Transition

• For a flat substrate the area of the grafting surface is equal to the surface area at the free end.

• In the spherical system, the surface area of the grafting surface is smaller than the area at the free end.

• Dissimilar polymers have more area to move around (conformational entropy).
Lateral vs. Perpendicular Segregation

Brush

Perpendicular Melt Lateral
Effect of Film Thickness (FT):
\( \chi_{N}=12.5, \ f=0.5, \ \chi_{wN}=12.5, \ \chi_{w2N}=-12.5 \)

FT = 1 \( R_{g0} \)  
FT = 1.1 \( R_{g0} \)  
FT = 1.2 \( R_{g0} \)  
FT = 2 \( R_{g0} \)
Effect of Film Thickness (FT):
\( \chi N=20, f=0.7, \chi_w N=20, \chi_{w^2} N =-20 \)

FT = 1 \( R_g_0 \)  
FT = 1.5 \( R_g_0 \)  
FT = 2.5 \( R_g_0 \)
Effect of Surface Interactions:

\( \chi_N = 12.5, f = 0.5, R_0 = 2 R_{g0}, R_f = 3 R_{g0} \)

- \( \chi_{wN} = 14, \chi_{w2N} = -14 \)
- \( \chi_{wN} = 20, \chi_{w2N} = -20 \)
- \( \chi_{wN} = 22, \chi_{w2N} = -22 \)
Effect of Surface Interactions: Brush
\[ \chi_N = 6.0, \ f = 0.5, \ R_0 = 2 \ R_{g0}, \ R_f = 3 \ R_{g0} \]

\[ \chi_w N = 10, \ \chi_w^2 N = -10 \]
\[ \chi_w N = 15, \ \chi_w^2 N = -15 \]
\[ \chi_w N = 20, \ \chi_w^2 N = -20 \]
Conclusions and Future Plans

- Curvature minimal affects the value $\chi N$ corresponding to the order-disorder transition for our brush system.

- By varying film thickness and surface attraction, we can produce the lateral or perpendicular morphologies for both the brush and melt systems.

- Perform a more comprehensive study of the effect of curvature on the morphology of the thin film.
Acknowledgements

• Glenn H. Fredrickson, Ed Kramer, Carlos J. Garcia-Cervera, Hector Ceniceros

• Fredrickson group

• Funding