A Unified Computing Framework for Self-Consistent Field Theory

Applications in Charged Polymers

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Outline

- A unified computing framework for self-consistent field theory
  Polyorder
- Microphase separation of weakly charged block copolymers
  SCFT studies
- Summary
- Acknowledgments

Polyorder:
A Unified Computing Framework for Self-consistent Field Theory

Follow or fork this software package at
https://bitbucket.org/liuyxpp/polyorder

Scientific Software Packages

Mathematics

- LAPACK/BLAS/FETK
- MUDPACK/FISHPACK/SPHEREPACK (Computational Information Systems Laboratory, NCAR)
- Matlab/Mathematica, Numpy/Scipy, Octave (GNU)/Sage

Molecular Modelling

- Gaussian (The author John Pople received the Nobel Prize in 1998 for "his development of computational methods in quantum chemistry"!)
- GAMESS/MOPAC/AMBER/CHARMM
- NAMD (The Theoretical and Computational Biophysics Group and the Parallel Programming Laboratory at UIUC)
- LAMMPS (Sandia National Laboratories, a US Department of Energy laboratory)
- OpenMD (created mostly by graduate students in the Gezelter group at the University of Notre Dame)

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Any well known software in POLYMER field? NONE!

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The Way to Go: Open Source and DVCS

OPEN SOURCE comes from the academic society

- The science should be open.
- For colleagues to check your realization is correct.
- Receive responses from your colleagues.
- Share and collaborate.

Distributed version control system (DVCS)

- EASY to keep track of the history of your code.
- EASY to to branch your code to add new features.
- EASY to revert your work.
- EASY to track issues and fix bugs.
- EASY to collaborate with others.

Recommendation in practice:

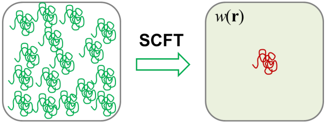
- Mercurial + https://bitbucket.org
- Git + https://github.com

Open Source in Action: the Polyorder Project

Background

Self-consistent field theory is one of the most successful polymer theories.

SCFT is a field-based theory.



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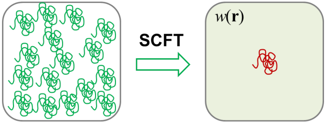
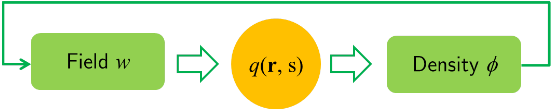


SCFT equations mostly should be solved numerically.

$$\omega_p = \chi_{ps} N\phi_s\left(\vec{r}\right) + \sum_{p\neq p'} \chi_{pp'} N\phi_{p'}\left(\vec{r}\right) + \eta\left(\vec{r}\right)$$



$$\frac{\partial q_p}{\partial s} = \nabla^2 q_p - \omega_p q_p$$

$$\phi_p = \frac{\bar{\phi}_p}{Q_p f_p} \int_0^{f_p} ds q_p\left(\vec{r}, s\right) q_p^*\left(\vec{r}, f_p - s\right)$$

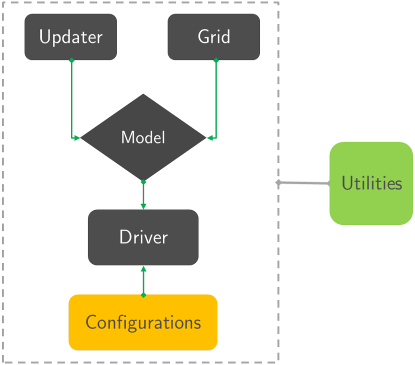
The Polyorder Project

Overview

The Goal

Polyorder is a C++ library which aims to ease the development of polymer self-consistent field theory (SCFT) programs.

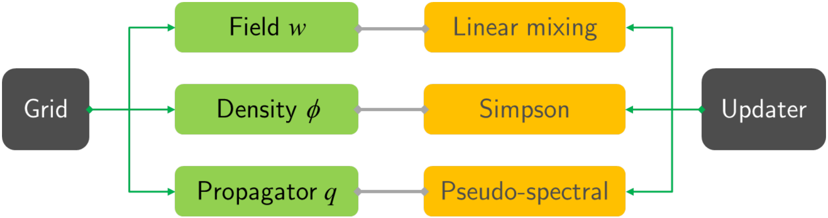
The Framework



The Polyorder Project

Design

A self-updating mechanism



Grid

Field w

Density ϕ

Propagator q

Linear mixing

Simpson

Pseudo-spectral

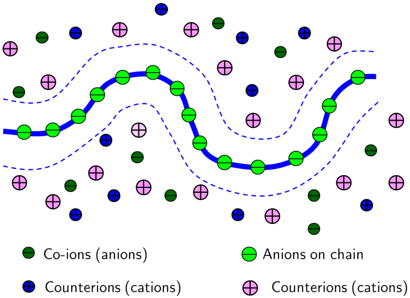
Updater

Application: Microphase Separation of Weakly Charged Block Copolymers

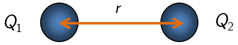
Y. X. Liu*, et al. *Macromolecules* **2011**, *44*, 8261.

Charged Polymer Solutions and Poisson-Boltzmann Equation

Chain connectivity



Long range electrostatic interaction



$$U(r) = \frac{Q_1 Q_2 e^2}{4\pi\epsilon\epsilon_0 k_B T} r^{-1}$$

The interaction decays much slower than van der Waals interaction.

Charged Polymer Solutions and Poisson-Boltzmann Equation

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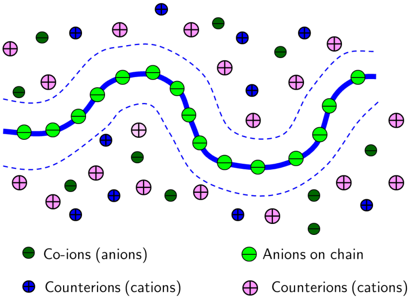
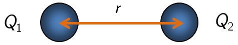


Long range electrostatic interaction



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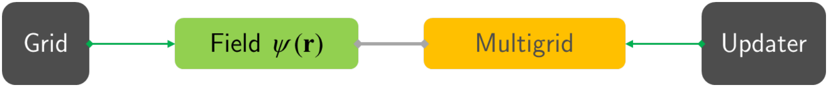
The interaction decays much slower than van der Waals interaction.

In the mean-field level, the electronic interaction can be described by the Poisson-Boltzmann (PB) Equation:

$$\nabla \cdot [\epsilon(\vec{r}) \nabla \psi(\vec{r})] = -N \sum_i \upsilon_i \phi_i(\vec{r})$$

The Electric Potential Field

It is updated by multigrid Updaters.

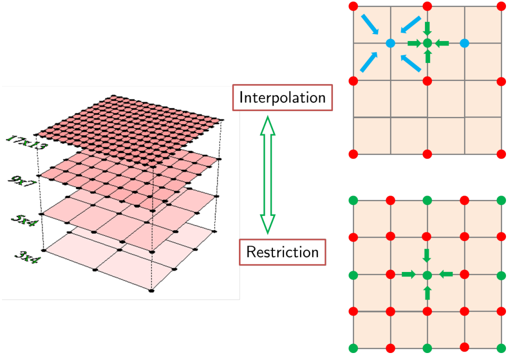

Grid

Field $\psi(\mathbf{r})$

Multigrid

Updater

Multigrid algorithm approaches the ideal computational complexity $O(M)$



Multigrid in Non-orthogonal Unit Cell

For 2D hexagonal unit cell:

$$\begin{aligned}\nabla\cdot\left[\epsilon\left(\vec{r}\right)\nabla\psi\left(\vec{r}\right)\right]=&\frac{4}{3}\epsilon\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial x\partial y}+\frac{\partial^2\psi}{\partial y^2}\right)+\\&\frac{4}{3}\left[\left(\frac{\partial\epsilon}{\partial x}+\frac{1}{2}\frac{\partial\epsilon}{\partial y}\right)\frac{\partial\psi}{\partial x}+\left(\frac{\partial\epsilon}{\partial y}+\frac{1}{2}\frac{\partial\epsilon}{\partial x}\right)\frac{\partial\psi}{\partial y}\right]\end{aligned}$$

For 3D hexagonal unit cell:

$$\begin{aligned}\nabla\cdot\left[\epsilon\left(\vec{r}\right)\nabla\psi\left(\vec{r}\right)\right]=&\frac{4}{3}\epsilon\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial x\partial y}+\frac{\partial^2\psi}{\partial y^2}+\frac{3}{4}\frac{\partial^2\psi}{\partial z^2}\right)+\\&\frac{4}{3}\left[\left(\frac{\partial\epsilon}{\partial x}+\frac{1}{2}\frac{\partial\epsilon}{\partial y}\right)\frac{\partial\psi}{\partial x}+\left(\frac{\partial\epsilon}{\partial y}+\frac{1}{2}\frac{\partial\epsilon}{\partial x}\right)\frac{\partial\psi}{\partial y}+\frac{3}{4}\frac{\partial\epsilon}{\partial z}\frac{\partial\epsilon}{\partial z}\right]\end{aligned}$$

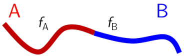
Results and Discussion

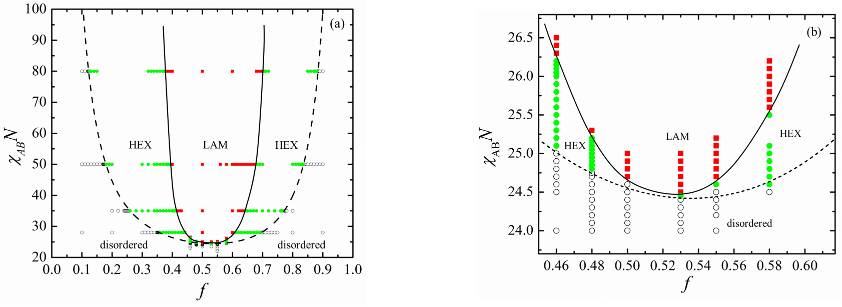
Phase Digram of Charged-Neutral Diblock Copolymer Solutions in 2D Space

Two features of the phase diagram:

1. The critical point moves upward.

2. The diagram is asymmetric.



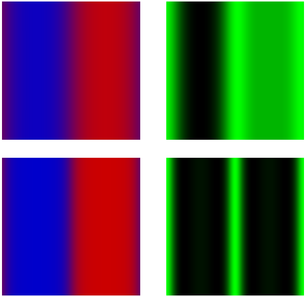


Results and Discussion

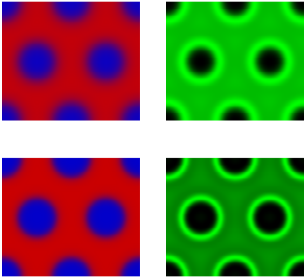
Morphologies of Charged-Neutral Diblock Copolymer Solutions in 2D Space

Main predictions:

1. Interfaces of neutral polymers is much sharper than charged polymers.
2. Solvent molecules tends to distribute inside charged domains.



Density distribution of type A (red) and B (blue) segments (left columns), and solvent molecules (right columns) with $f = 0.5$, $\chi_{AB}N = 35$.

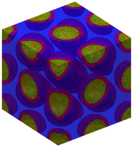


Density distribution of type A (red) and B (blue) segments (left columns), and solvent molecules (right columns) with $f = 0.7$, $\alpha_A N = 20$.

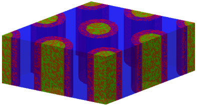
Results and Discussion

Possible Morphologies in 3D Space

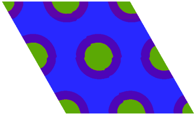
Dielectric constant is position-independent.



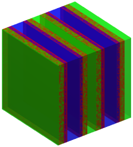
$fA = 0.24$
$\chi_{AB}N = 35$
$\alpha_A N = 2$



$fA = 0.3$
$\chi_{AB}N = 20$
$\alpha_A N = 2$



Top view



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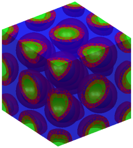

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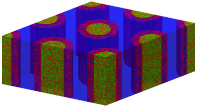

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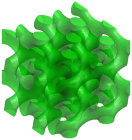

$fA = 0.38$
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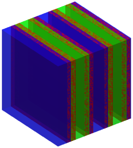
$\alpha_A N = 2$



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Thanks!