Illustrations (non-data)

* SCF build-up
  + PB build up in Rui electrostatics textbook
* Chain block (mod diff eq)
* Block disc process
* Individual chain conformation
* SCF code flowchart

Equation List

* Interactions (general)
* Partition function
  + Fourier transform
  + Saddle point approx
* Free energy
* SCF eqns
* Simple mixing vs. Anderson Mixing
* Anderson error

Figure (data) List

* Data build up (a0)
  + Free energy
  + Polymer density distribution
  + Height profile (multiple codes)
* a0 vs. prev lit
  + TEM support
* a3 video (w/free energy transitions)
* full ax video (no free energy)
* Multiple videos with correct stopping point for presentation

Reference Slides

* SCF derivation
* PB derivation (coulomb operator, HS transform)
* Free energy for all transitions

Misc.

* Action buttons
  + Add ref to table of contents to master slide

Outline

* Introduction
  + Polymer brush history
  + “Theoretically solved” RSC 2013 paper
  + Polyelectrolyte lit review (only by Borisov, 1991)
  + Most (if not all) current publications use lattice model
    - Known to have artifacts
    - Inaccurate chain assumption
  + Applications for accurate polyelectrolyte brush
    - General lack of systematic theories accurately describing coupled interactions
    - Biomaterials engineering (e.g. surface modifiers for membranes)
      * Collab with Kumar
    - Hydrogen fuel cells
      * Collab with Radke
* Model and Theory
  + Semi-canonical ensemble (canonical in chain, grand in solvent/ions)
  + Interactions (operator form)
  + “Standard field-theoretic transformations” (?)
    - Fourier transform for operators
    - Hubbard-Stratonovich for Coulombic
    - Saddle-point approximation for solvable free energy
  + Block discretization process
    - Based on CUSUM method for signal processing noisy data
    - Cumulative sum monitoring and block breakpoints when cusum changes a certain amount
  + “Self-consistency”
    - Numerically solve equations, convergence achieved when fields change less than some thresh from iter to iter
    - Combination of simple mixing and Anderson mixing
* Results and Discussion
  + Good match with prev. lit (theory and experiments) in terms of neutral chain
  + xC convention created for distinction between coexisting phases
  + 2nd order phase transition btw coil and 1C
  + Coil -> max C -> max C-1, C-2,… -> 1C
  + Existence of xCd, a dilute extended layer coexisting with condensed phases
  + 1Cd previously found in neutral system, grafted coil on condensed inner
  + Additional repulsion effects from coulombic interactions allow for x>1
  + End point distributions show each layer(condensed or otherwise) individual chain
  + Height is effective order parameter, but relation between theoretically determined and experimentally recorded heights are not well studied (future work, 2nd moment, density thresh, AFM, spherical ellipsometry, neutron scattering)
  + If space and enough results
    - Prelim results for Nafion project and neurofilament project
* Conclusion and future works
  + Results show although sufficient work has been done on neutral chains, polyelectrolyte chains exhibit non trivial results
  + New laterally layered conformations results from addition of coulombic interactions and should be a great field of exploration
    - Ex. Smart valves with transitions corresponding to certain shears, smart sensors corresponding to different layers, etc.
  + Immediate next step is to study effect of forces on polyelectrolyte brushes, particularly for interpretation of experimental results using AFM and engineering of biofouling
  + Ongoing collaborations with Kumar and Radke show the breadth of possible applications

On the Theory of Grafted Polyelectrolyte Brushes

Takashi Yokokura, Chao Duan, Rui Wang

**Introduction**

Uncharged polymer brushes have been of interest since 1977, first probed by Alexander as a polymer layer procured by polarity-induced adsorption. As opposed to polyelectrolyte solutions, which are free to explore the entire volume of solution, polymer brushes are either chemically or physically attached to an impermeable surface and thus have an intrinsic entropic penalty for collapsing upon itself. This entropic penalty is further increased by packing chains closer together, i.e. the grafting density. Progress in charged polymer brushes, or polyelectrolyte brushes, has been mostly led by Zhulina, Leermakers, Fleer, and Borisov, particularly for applications in neurofilaments, a neuronal component which controls structure and rigidity and thought to be a key player in neurodegeneration. However, the advances in polyelectrolyte brushes have been almost exclusively calculated on a lattice-constrained model, which are known to have numerical shortcomings and artifacts. Further, a systematic study across charge and solubility has yet to be reported.

**Model and Theory**

We perform our calculations within a semi-canonical ensemble in which the number of polymer chains are kept constant while the number of solvent molecules and ions are enforced by their respective chemical potentials.

Illus

We consider the interplay between four interactions: polymer chain elasticity using the Gaussian chain model, Flory-Huggins interactions between monomers and solvent molecules, electrostatic interactions, and the incompressibility of monomers and solvent molecules.

Eqs

Following standard field-theoretic transformations (Fourier transforms, Hubbard-Stratonovich transformation), a partition function can be constructed.

Eq

By performing the saddle-point approximation, we focus on only equilibrium states.

Eq

The system is now fully solvable by a system of self-consistent field (SCF) equations.

Eqs

We solve the above system numerically by beginning with an initial guess, computing through the SCF equations, and iterating towards self-consistency. We use a combination of Simple Mixing and Anderson Mixing to determine new field values. Self-consistency is declared once the following mean-squared error is below a threshold of 0.001.

Eq

For the study of complex charge and solubility distributions along the chain (e.g. for each amino acid sequence on a protein), chains need to be discretized accurately and efficiently. We proceed with a numerical method commonly applied in data processing, CUSUM, which is used to interpret signals confounded with noise. By monitoring the charge/Flory-Huggins parameters of each monomer, two hyperparameters can be adjusted to form block boundaries.

Fig

**Results and Discussion**

1. Systematic Study of Homopolyelectrolyte Brushes
2. Preliminary Collaboration Results