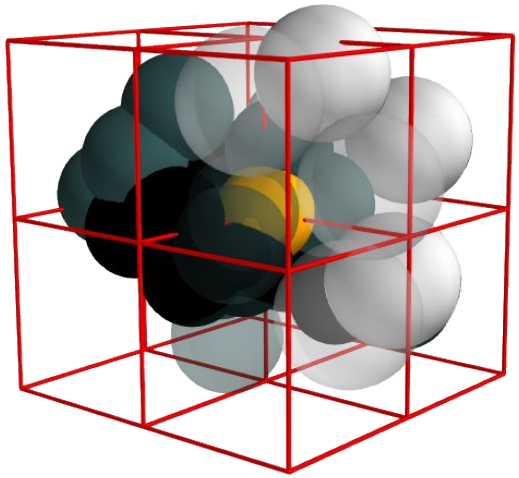
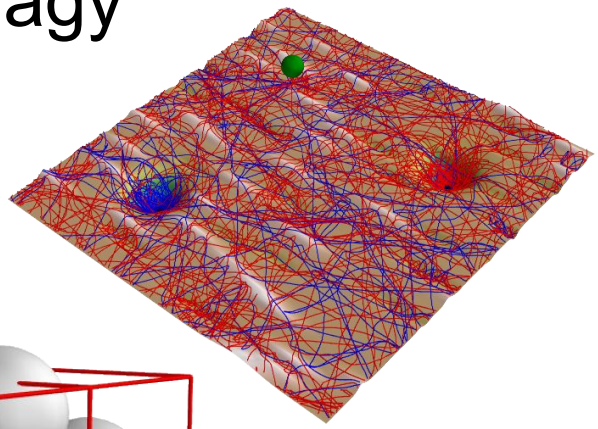
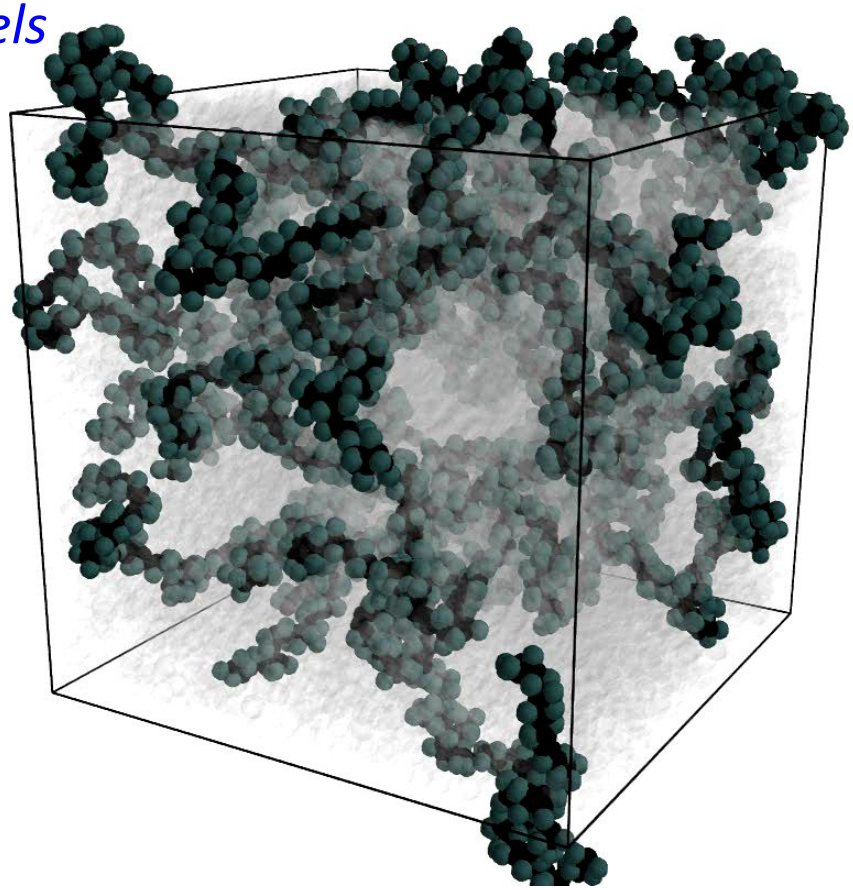
Molecular-Level to Macro-Level Dynamics of Polystyrene/Toluene Solutions

Development of Methods for Dynamical Simulation of Non-Uniform Coarse-Grained Models

Matt Hagy





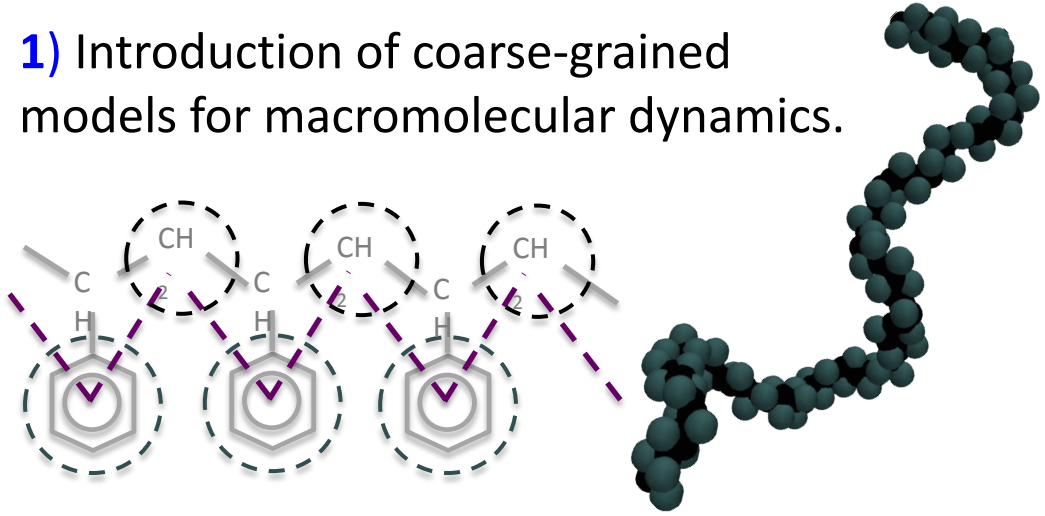


May 14th 2010

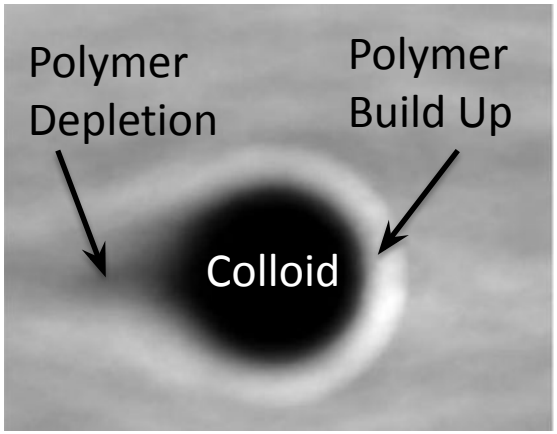
Ph.D. Candidacy Examination

Overview of Proposal

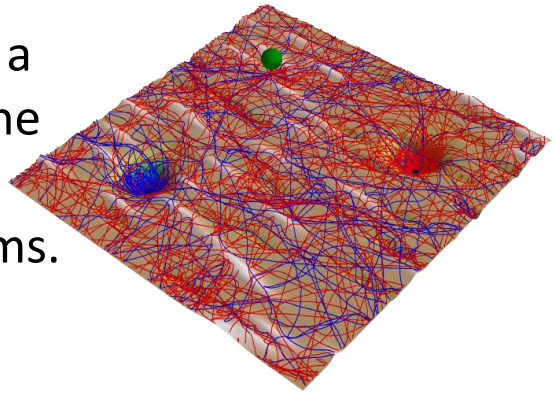
1) Introduction of coarse-grained models for macromolecular dynamics.

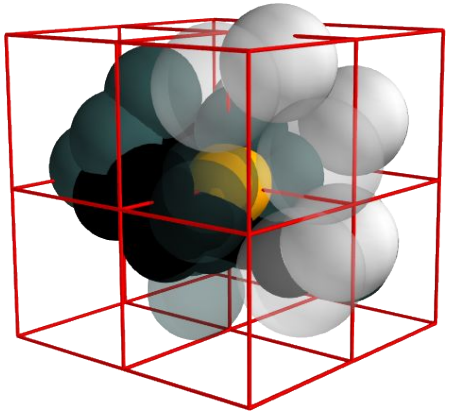


2) Discussion of special considerations for the dynamics of non-uniform coarse-grained models.



3) Development of a simple model for the dynamics of non-uniform systems.





5) Application of generalized time-rescaling to the coarse-grained polystyrene/toluene model.

4) Generalization of time-rescaling for non-uniform systems.

$$\xi_i[\vec{r}(t)] = \frac{\zeta_i^{(D)}[\vec{r}(t)]}{\zeta_i^{(CG)}[\vec{r}(t)]}$$

Coarse-Grained Models for the Dynamic Simulation of Macromolecules

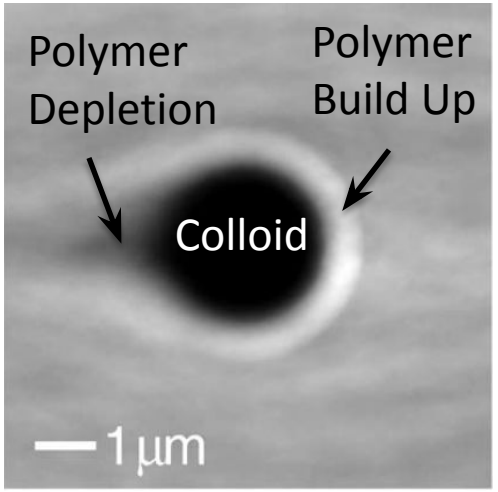
A better understanding of macromolecular dynamics is needed for nonequilibrium polymer applications. i.e.:

- Electrospinnning of nanofibers from polymer solutions
- Block copolymer self-assembly
- Aggregation of colloids in polymer solutions

Recently, coarse-grained models have been used to simulate the molecular-level dynamics of uniform polymer melts.*

In this proposal, I will develop methods to simulate the dynamics of coarse-grained models for non-uniform macromolecular systems (i.e. polymer solutions).

Driven Colloid in Polymer Solution Experiment



Gutsche, C.; Kremer, F.; Krüger, M.; Rauscher, M.; Weeber, R.; Harting, J. *J. Chem. Phys.* **2008**, 129.

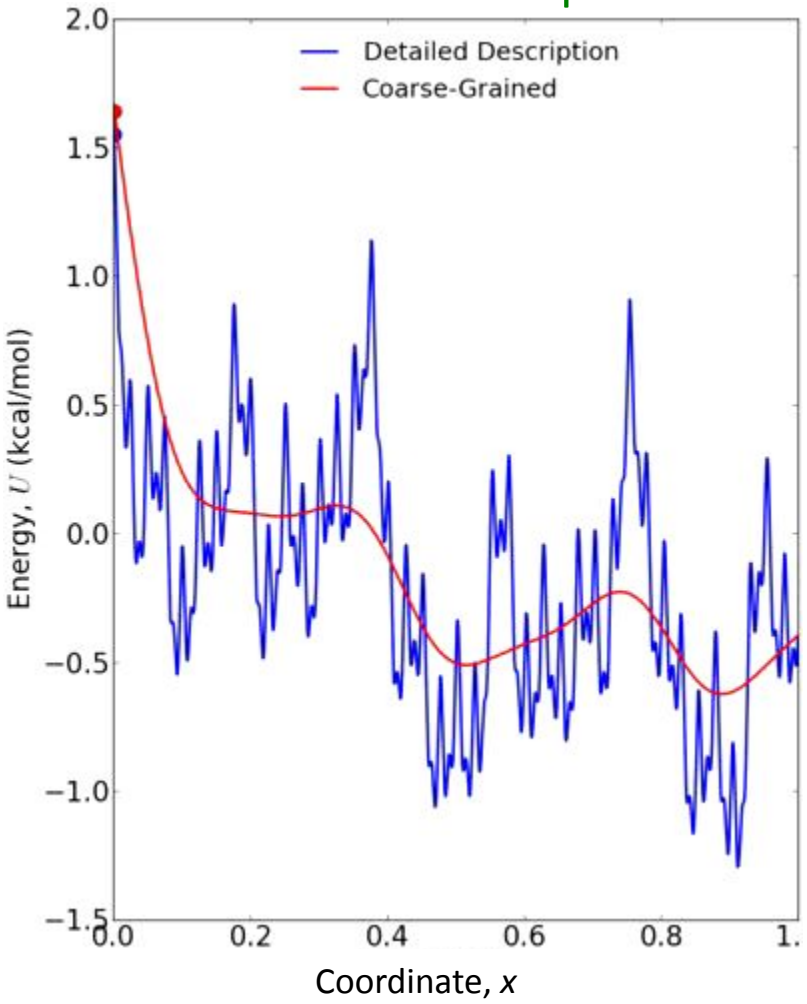
*a) Tschöp, W.; Kremer, K.; Batoulis, J. *Acta. Polym*. **1998**, 49. b) Müller-Plathe, F. *Chem. Phys. Chem.* **2002**, 3(9), 754–769. c) Harmandaris, V.; Adhikari, N.; Van der Vegt, N.; Kremer, K. *Macromolecules*. **2006**, 39(19), 6708–6719. d) Harmandaris, V.; Kremer, K. *Macromolecules.* **2009**, 42(3), 791–802.

Challenges of Coarse-Grained Dynamics

- **Requires reproducing essential modes of molecular motion in coarse-grained model.**
  - Example: Bead-spring model successful for static properties, but doesn't model modes of motion as needed for dynamics.

- **Dynamics of a coarse-grained model are accelerated relative to true dynamics.[1]**
  - Results from reduced friction for constitutive unit motion in coarse-grained model.
  - Requires a time-rescaling relationship to relate the simulated coarse-grained dynamics to the real-time scale.
    - Generally accomplished with a bulk time-rescaling factor.[2]

Diffusion in coarse-grained vs. detailed description



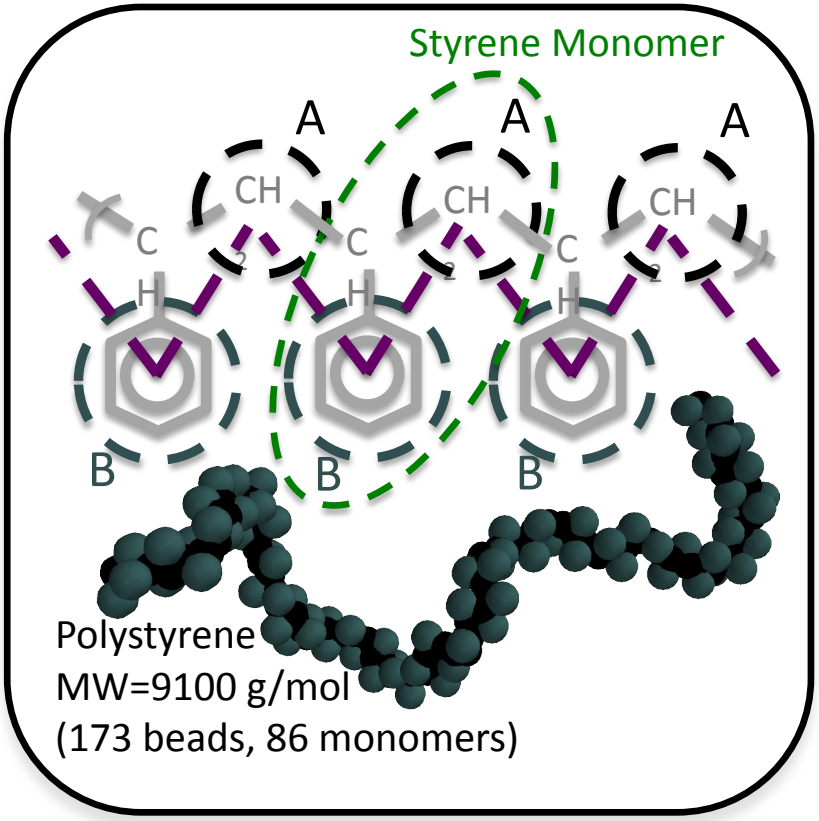
1. Forrest, B.; Suter, U. *J. Chem. Phys*. **1995**, 102.

2. Tschöp, W.; Kremer, K.; Batoulis*, J. Acta. Polym*. **1998**, 49. b) Müller-Plathe, F. *Chem. Phys. Chem.* **2002**, 3(9), 754–769. c) Harmandaris, V.; Kremer, K. *Macromolecules.* **2009**, 42(3), 791–802.

Coarse-Grained Polystyrene Model

Harmandaris & coworkers have developed a model for polystyrene melts.*

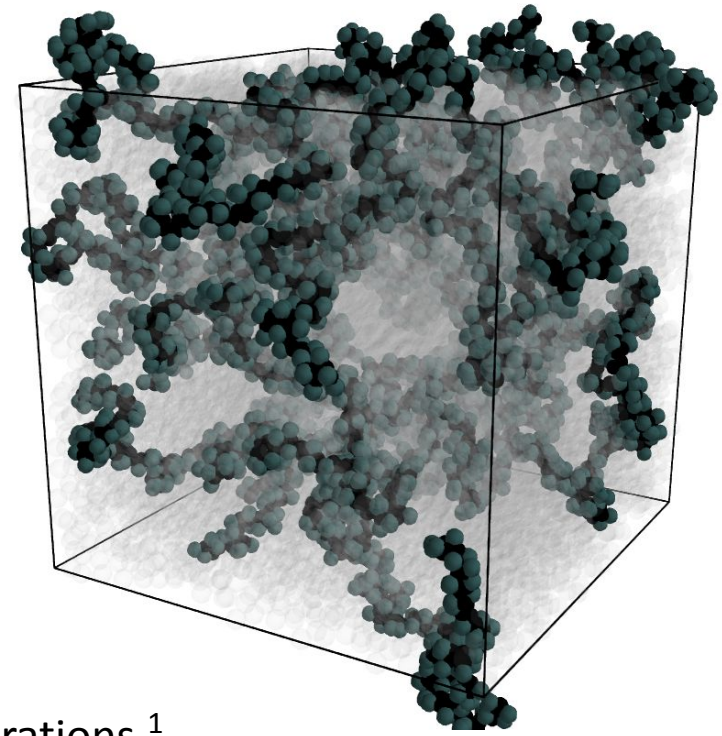
- Based on 2 coarse bead types: **A** & **B.**
- Potentials of mean force between beads properly model modes of molecular motion.
- Calculate a bulk time-rescaling factor by comparing short-time monomer diffusion constants in all-atom and coarse-grained simulations.
  - Generally on the order of 100 to 1000 real ns to each coarse-grained 1 ns of simulation.
- Their results agree exceptionally well with experimental data.



To this model, I propose the addition of a coarse-grained representation of toluene to investigate polystyrene/toluene solutions.

*a) Harmandaris, V.; Adhikari, N.; Van der Vegt, N.; Kremer, K. *Macromolecules*. **2006**, 39(19), 6708–6719.
b) Harmandaris, V.; Reith, D.; van der Vegt, N.; Kremer, K. *Macro. Chem. Phys*. **2007**, 208. c) Harmandaris, V.; Kremer, K. *Macromolecules.* **2009**, 42(3), 791–802.

Polystyrene/Toluene Model

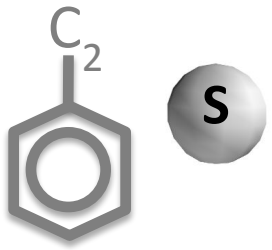


Propose modeling toluene as a sphere.

- Construct a new bead type: **type S**.
- Introduce 3 new non-bonded interactions to be modeled as lennard-jones potentials.
  - Parameterized from pair correlation statistics sampled by all-atom simulation.

Spherical approximation supported by:

- High level quantum calculations of toluene dimer interaction energies in spherically different configurations.[1]
  - Differ by at most 0.68 kcal/mol.
  - Thermal energy RT=0.6 kcal/mol comparable at T=300K.
- Experimental[2] & simulation[3] work shows a lack of preferential pair orientation in standard benzene solutions.
  - Toluene should be less prone to ordering due to reduced symmetry.



Toluene Explicit Solvent

1. Sinnokrot, M.O.; Sherrill, C.D. *J. Phys. Chem. A.* **2004**, 108(46), 10200–10207.
2. 2. a) Joo, T.; Albrecht, A. *J. Chem. Phys.* **1993**, 99, 3244. b) Cabaco, M.; Danten, Y.; Besnard, M.; Guissani, Y.; Guillot, B. *J. Phys. Chem. B.* **1997**, 101(35), 6977–6987. c) Kirkwood, J.; Ulness, D.; Albrecht, A. *Chem. Phys. Let.* **1998**, 293, 167–172.
3. 3. a) Cabaco, M.; Danten, Y.; Besnard, M.; Guissani, Y.; Guillot, B. *J. Phys. Chem. B.* **1997**, 101(35), 6977–6987. b) Nakagawa, T.; Umemura, J.; Hayashi, S.; Oobatake, M.; Miwa, Y.; Machida, K. *Mol. Phys.* **1996**, 88(6), 1635–1643. c) Chelli, R.; Cardini, G.; Procacci, P.; Righini, R.; Califano, S.; Albrecht, A. *J. Chem. Phys.* **2000**, 113, 6851.

Friction Reduction in Coarse-Graining Non-Uniform Systems

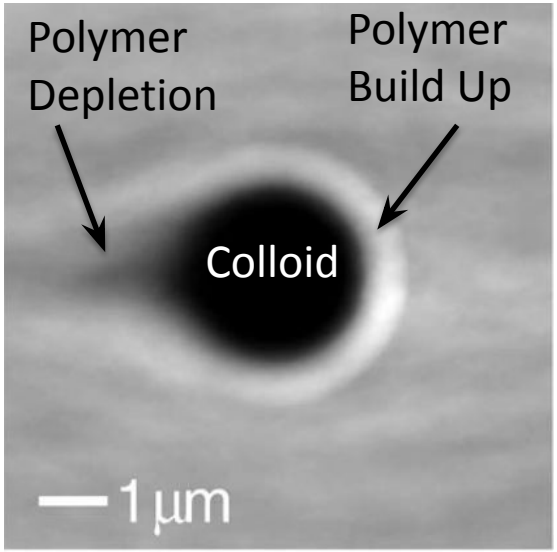
Existing bulk time-rescaling methods are not valid for non-uniform systems.

- Non-uniformities imply different microscopic-friction-determining environments about different degrees of freedom.
- In the coarse-grained model, the friction in some regions may be reduced more so than in other regions.
- Existing bulk time-rescaling methods assume a uniform reduction of friction.

New methods are needed to properly simulate the dynamics of coarse-grained models for non-uniform systems!

Non-Uniformities in Nonequilibrium Polymer Solutions

Driven Colloid in Polymer Solution Experiment



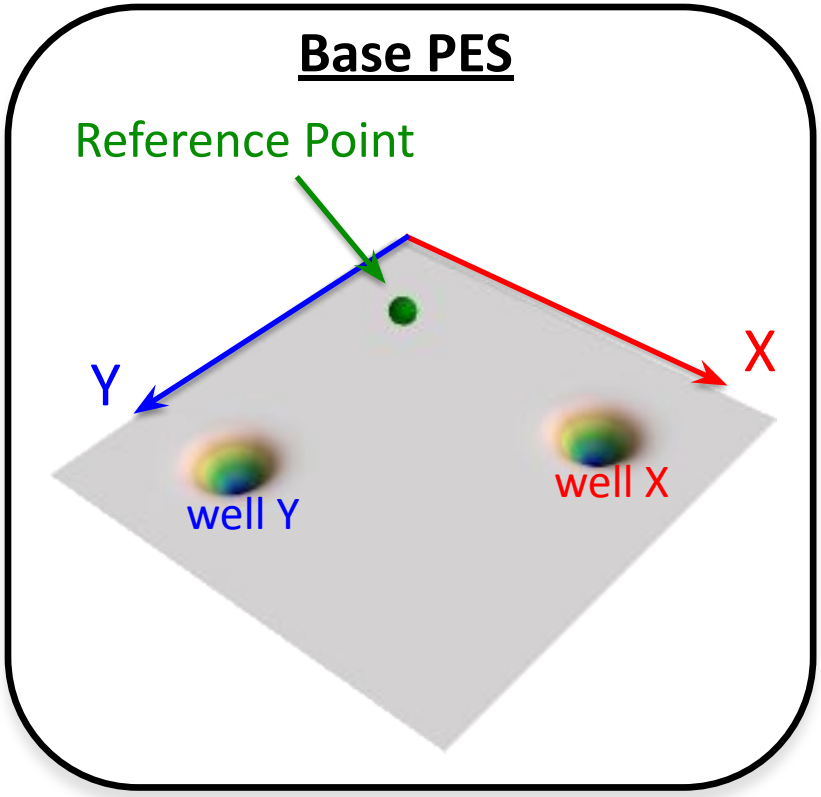
Gutsche, C.; Kremer, F.; Krüger, M.; Rauscher, M.; Weeber, R.; Harting, J. *J. Chem. Phys.* **2008**, 129.

Model System for Non-Uniform Friction Reduction

Simple 2-dimensional system used to investigate how dynamics are affected by non-uniform changes in friction.

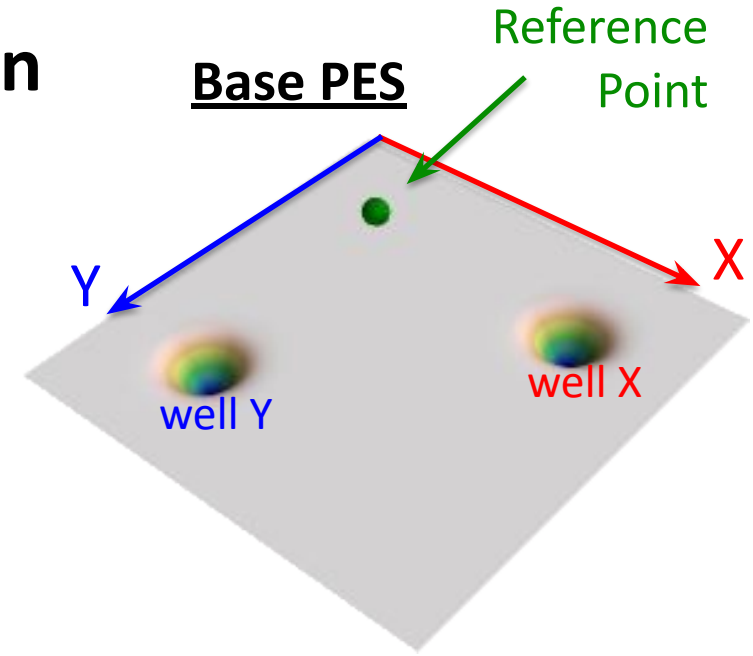
- Study 2-dimensional potential energy surfaces (PESs).
- PESs have 2 absorbing energy wells equidistant from a reference point.
  - In orthogonal directions.

Will introduce methods to vary friction in each direction (X & Y) independently.

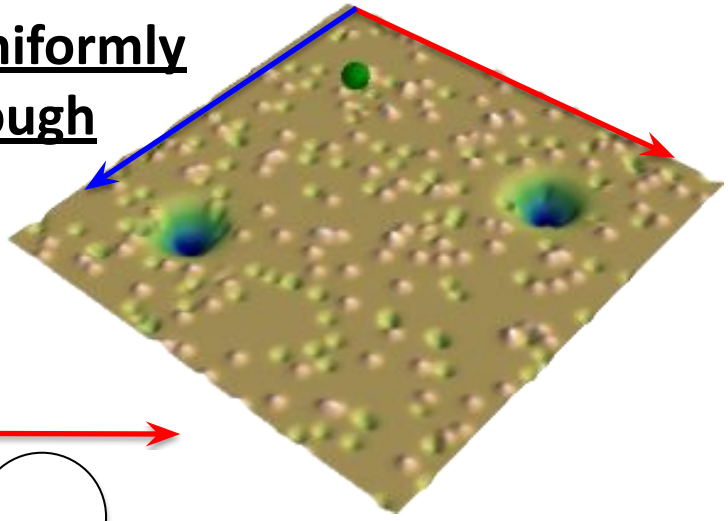


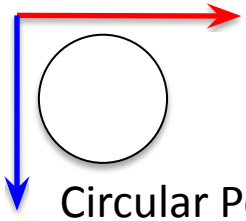
Non-Uniform Friction Modulation

- Stochastic perturbation used to increase the roughness (friction) of the base PES.
  - Can be modulated non-uniformly.
- Allows for the construction of PESs with the same global structure and variable friction in each direction (X & Y).



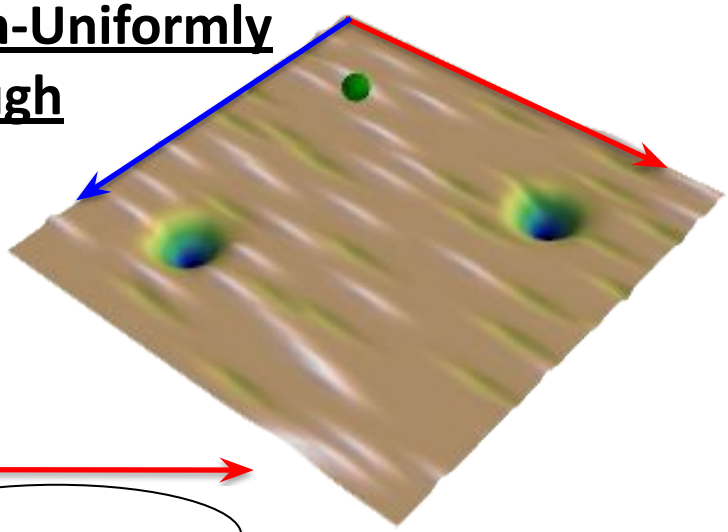
Uniformly Rough

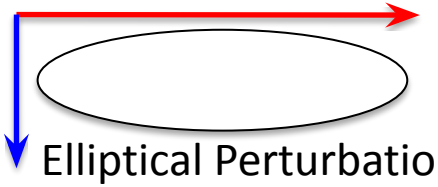




Circular Perturbations

Non-Uniformly Rough





Elliptical Perturbations

Mathematical Model Definitions

- PES defined as a sum of Gaussians.

$$U(x,y) = \sum_i A_i \exp\left[-\kappa_{x,i} l_p \left(x - x_{0,i}\right)^2 + -\kappa_{y,i} l_p \left(y - y_{0,i}\right)^2\right]$$

- Function l_p implements periodic boundaries.

$$l_p(d) = \begin{cases} d - L & : d > 0.5L \\ d + L & : d \leq -0.5L \\ d & : -0.5L < d \leq 0.5L \end{cases}$$

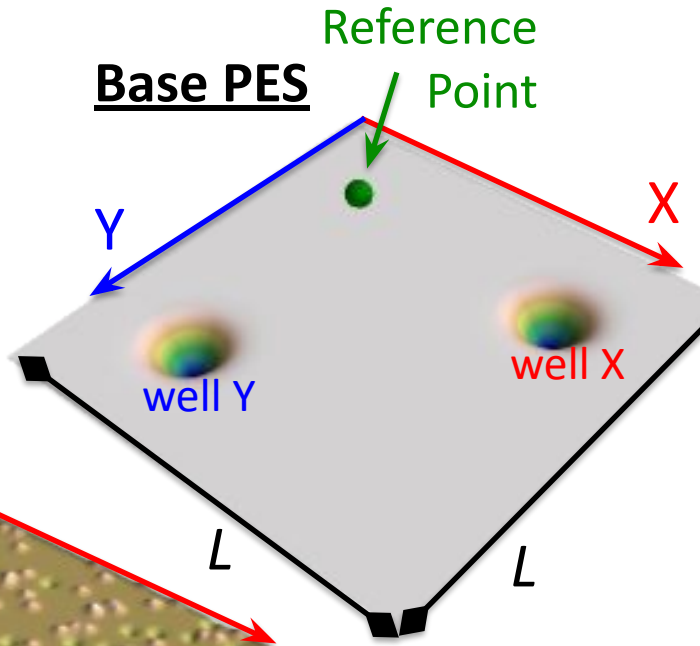
where *L* is the length of the surface in each direction.

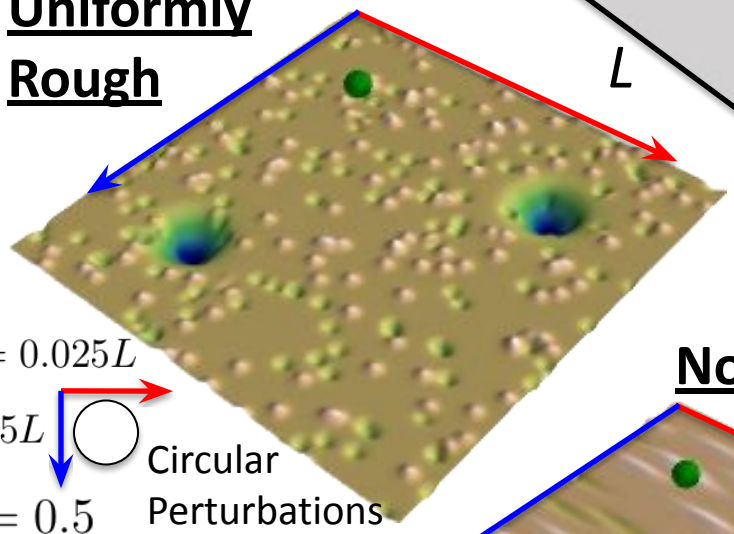
- Fall offs defined in terms of perturbation radius *r*.
  - Direction dependent

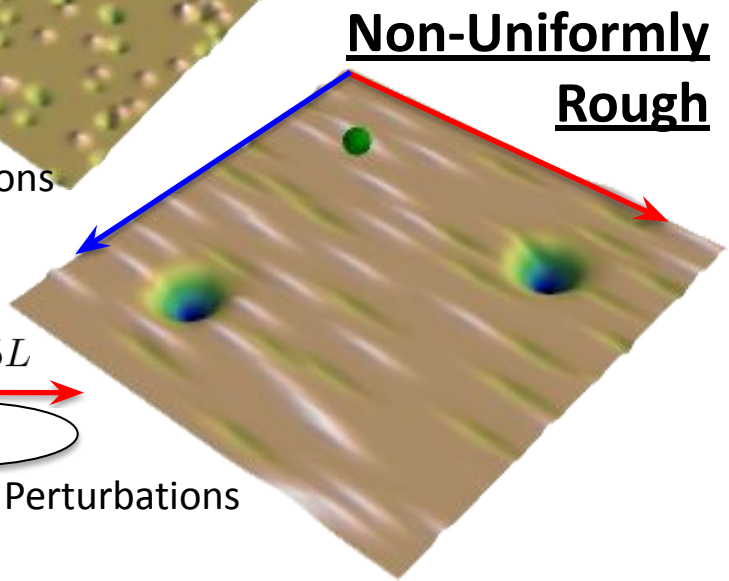
$$\kappa = -\ln(0.05)/r^2$$

- Extent of perturbation defined by reduced perturbed area *ρ*.

$$\rho = L^{-2}\pi \sum_i^n r_{x,i} r_{y,i}$$

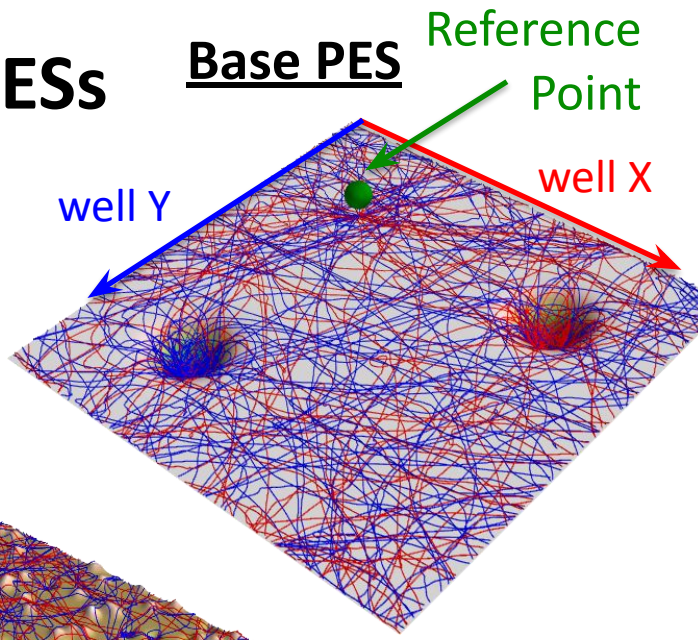






Sampling Dynamics Across Model PESs

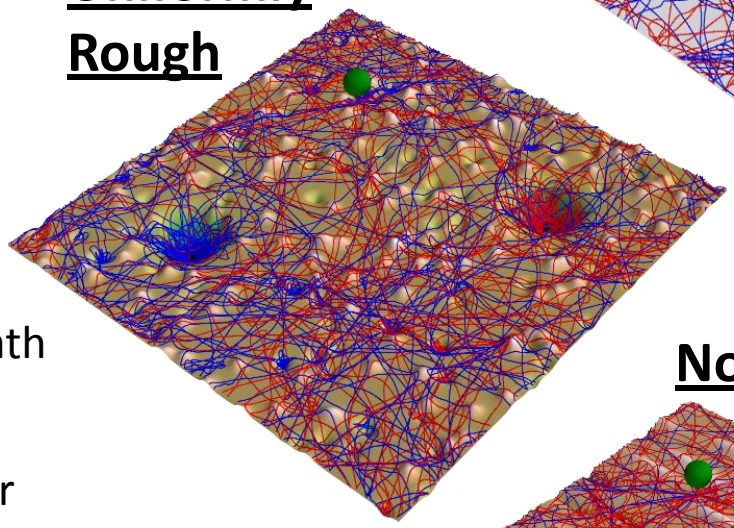
Calculate mean-first-passage times of a tracer from the reference point to each well.



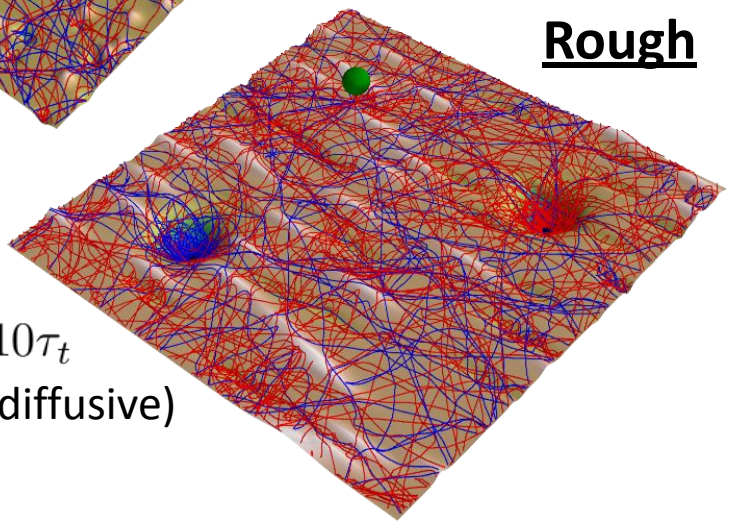
32 example trajectories shown for each PES.

Red trajectories terminate in Well X.

Blue trajectories terminate in Well Y.

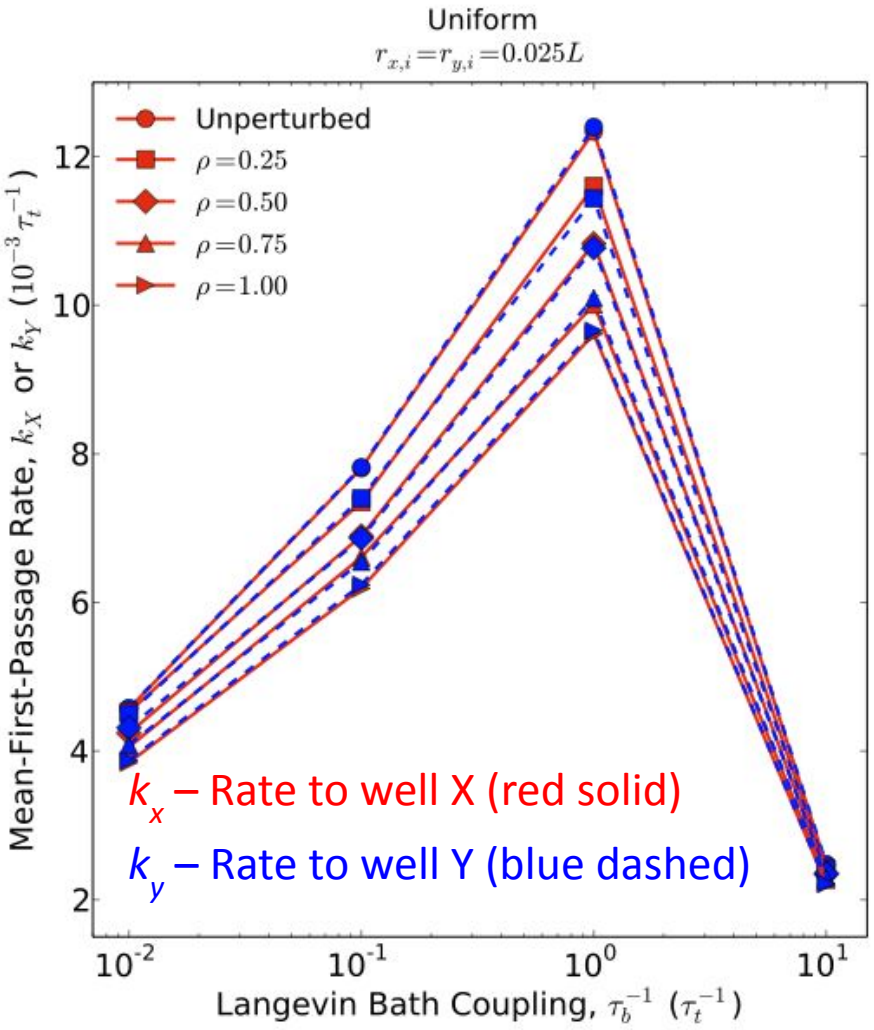


- Couple tracer to Langevin bath.
  - Simulates lesser degrees freedom (i.e. solvent) as Markovian noise.
- Strength of coupling quantified by bath thermalization time τ_b.
- Relative to τ_t, a characteristic time for ballistic motion of tracer.
  - $\tau_b >> \tau_t$: ballistic tracer (weak coupling)
  - $\tau_b \approx \tau_t$: diffusive tracer (strong coupling)
- Study a range of τ_b from ballistic to diffusive.



$\tau_b = 10\tau_t$
(mildly diffusive)

Effect of Uniform Friction Reduction on Dynamics

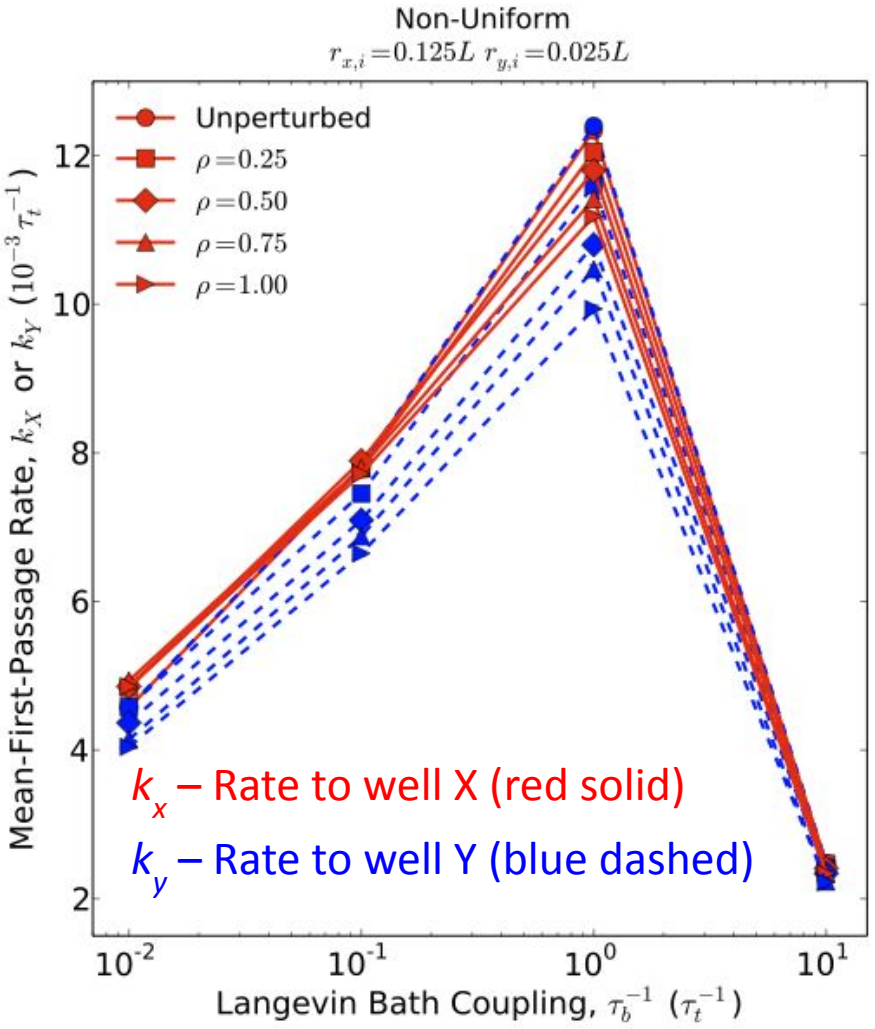


Uniformly decreasing friction (decreased extent of perturbative roughness ρ) increases rates for absorption in both wells in concert.

- Comparable to dynamic acceleration when coarse-graining a uniform system.
  - i.e. polymer melts
- The detailed model has a uniformly higher extent of friction for constitutive unit motion relative to the coarse-grained model.
  - Coarse-graining comparable to decreasing ρ.
- A single bulk time-rescaling factor is sufficient to describe the acceleration of coarse-grained dynamics.
- Similar to existing work where bulk time-rescaling is appropriate.

Effect of Non-Uniform Friction Reduction on Dynamics

Non-uniformly decreasing friction increases k_y more so than k_x; disparity in rates.



- Comparable to dynamic acceleration when coarse-graining a non-uniform system.
  - i.e. polymer solutions
- The detailed model has a non-uniformly higher extent of friction for constitutive unit motion relative to the coarse-grained model.
  - Coarse-graining comparable to decreasing ρ
- A single bulk time-rescaling factor is **insufficient** to relate the accelerated dynamics of the coarse-grained model to the true physical time scale of the detailed model.

New methods are needed to simulate the dynamics of coarse-grained models for non-uniform systems where friction is reduced non-uniformly

Generalization of Time-Rescaling

- Propose rescaling the dynamics of each i^{th} degree of freedom r_i independently.
- Rescaling factor ξ_i dependent on current configuration $\vec{r}(t)$.
- Results in a different integration time step $\Delta t_i^{(CG)}$ for each degree of freedom r_i.

Definition of time-rescaling factor

$$\xi_i[\vec{r}(t)] = \frac{\zeta_i^{(D)}[\vec{r}(t)]}{\zeta_i^{(CG)}[\vec{r}(t)]}$$

Relation to integration time step

$$\Delta t^{(D)} = \xi_i[\vec{r}(t)]\Delta t_i^{(CG)}$$

- Propose approximating time-rescaling factors ξ_i's from simulated short-time diffusion constants of a test bead in coarse-grained and detailed descriptions.
  - Simulate anisotropic friction-determining environment to mimic that around $r_i(t)$ for the test bead.
  - Each set of simulations provides ξ_i estimates for 3 r_i's of bead coordinates.

Numerical approximation of time-rescaling factor

$$\xi_i[\vec{r}(t)] \approx \frac{D_i^{(CG)}[\vec{r}(t)]}{D_i^{(D)}[\vec{r}(t)]}$$

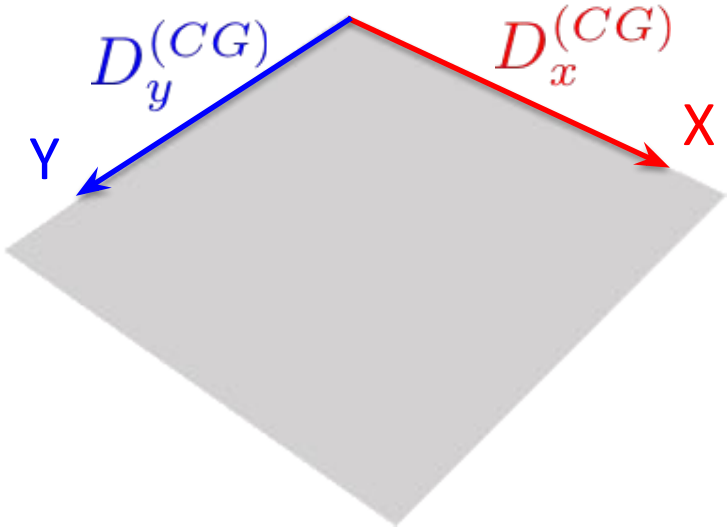
Sample short-time diffusion constant in both coarse-grained and detailed description for this approximation.

Model PESs Test of Generalized Time-Rescaling

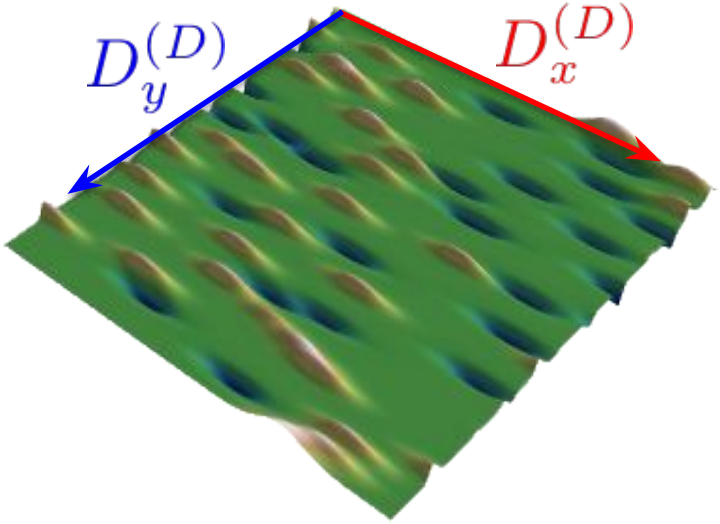
- Take smooth PES as characteristic of a coarse-grained (CG) model and rough PES as characteristic of a detailed (D) model.
- Attempt to simulate dynamics across smooth PES using frictional environment of rough PES.
- Exploit uniform roughness for each degree of freedom
  - Only need two time-rescaling factors ξ_x and ξ_y.
- Sample diffusion constants in each direction for different PESs to calculate time-rescaling factors.

$$\xi_x = \frac{D_x^{(CG)}}{D_x^{(D)}}$$

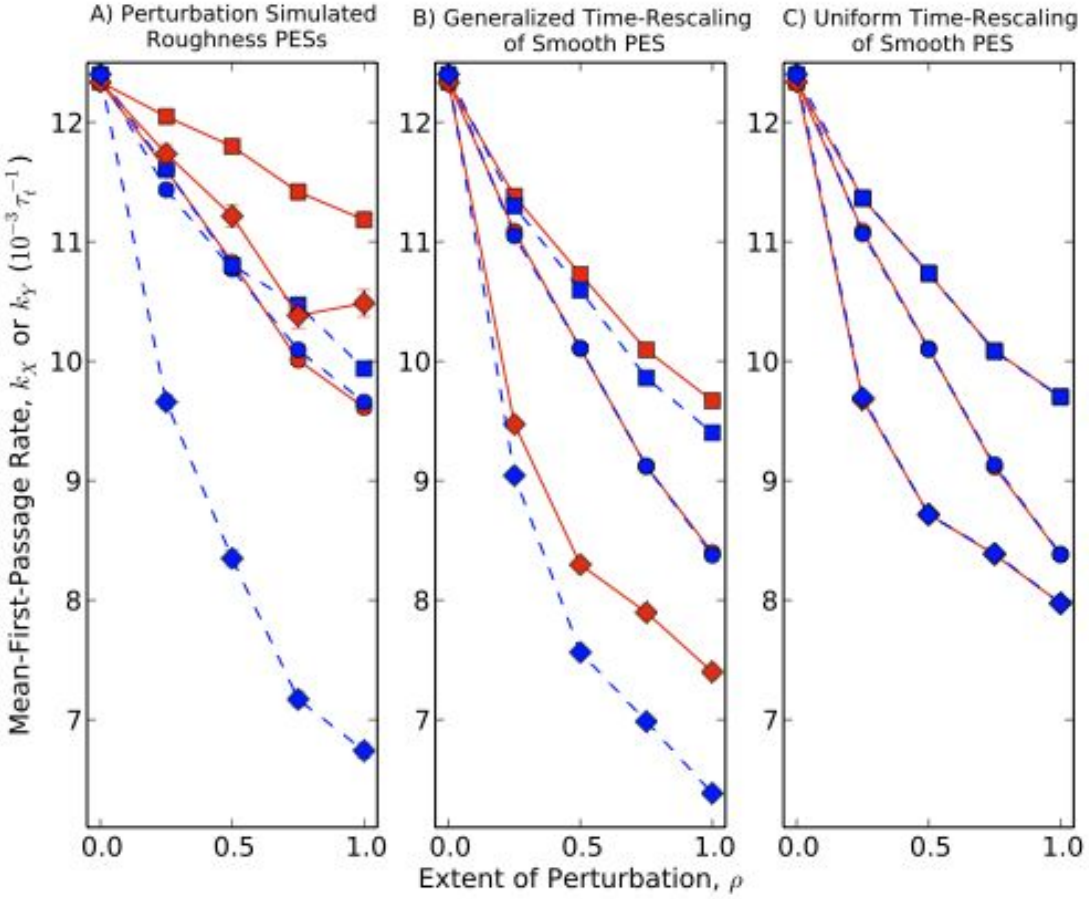
$$\xi_y = \frac{D_y^{(CG)}}{D_y^{(D)}}$$



Smooth PES characteristic of coarse-grained (CG) description



Rough PES characteristic of detailed (D) description



Results

k_x – Rate to well X (red solid)

k_y – Rate to well Y (blue dashed)

□ - Uniform Perturbation

$r_x = r_y = 0.025L$

■ - Non-Uniform Perturbation

$r_x = 0.125L \quad r_y = 0.025L$

◆ - Non-Uniform Perturbation

$r_x = \infty L \quad r_y = 0.025L$

$\tau_p = \tau_t$ (Diffusive)

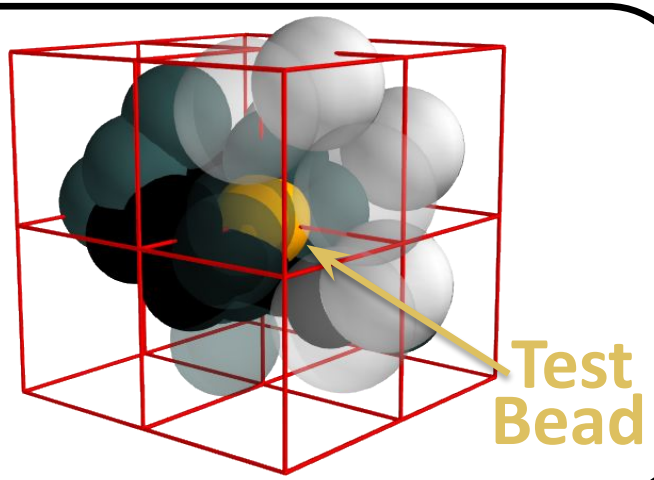
- Overall, generalized time-rescaling is found to be an improvement over uniform time-rescaling for systems with non-uniform changes in friction.
- Quantitative deviations can be explained by finite-size effects.
  - Each trajectory encounters only approximately 6 friction “bumps.”
    - Average of frictional environment not a good a approximation
  - Higher dimensional models needed (i.e. block copolymer phase separation with different scale models).

Applying Generalized Time-Rescaling to Polystyrene/Toluene Model

- Computationally inefficient to perform auxiliary simulations at every integration cycle.
- Instead, classify the environment about each bead as one of a few canonical environments.
  - Friction reduction ξ_i in each environment can be precomputed for each bead type.

Characterization Scheme

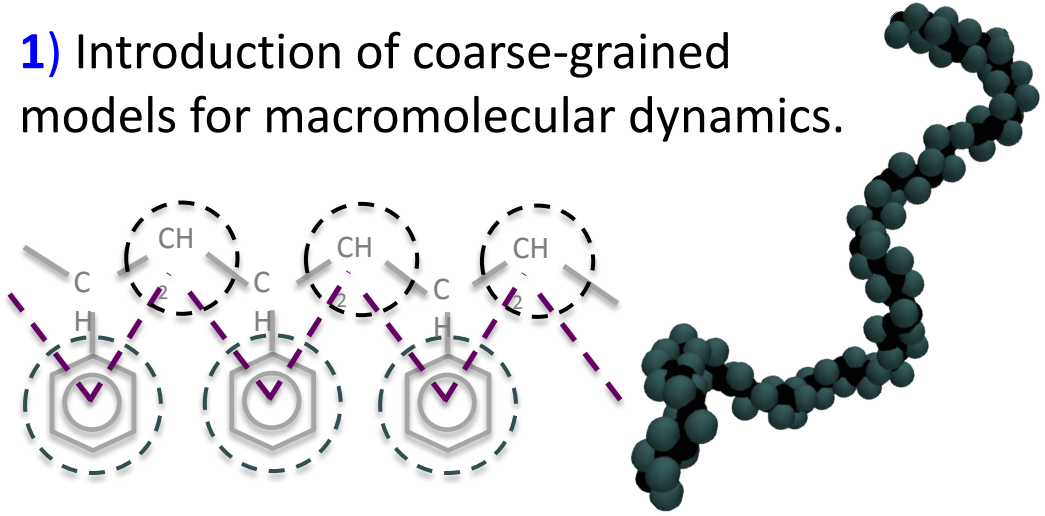
Propose discretizing the first solvent shell about the test bead into eigths, then counting the number of each bead type per an octant.



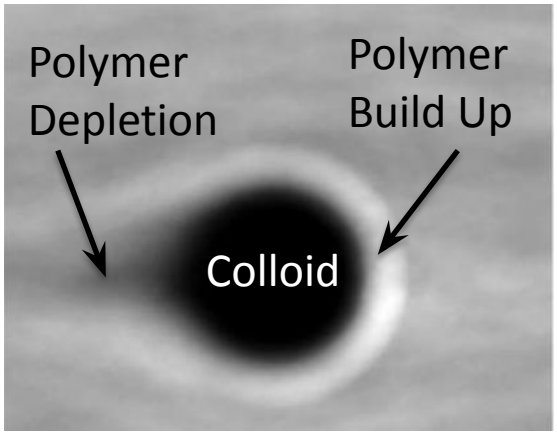
- For each canonical enviroment, stochastic methods can be used to generate multiple initial configurations satisfying this classification.
- Diffusion constants of a test bead in this environment are then to be measured in both the coarse-grained and detailed descriptions to calculate time-rescaling factors.

Summary of Proposal

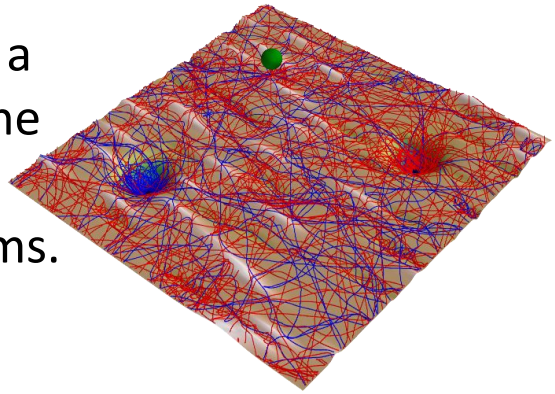
1) Introduction of coarse-grained models for macromolecular dynamics.

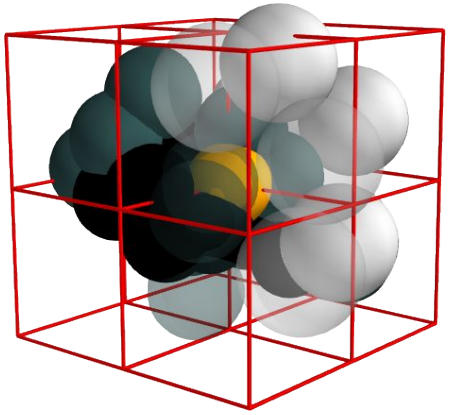


2) Discussion of special considerations for the dynamics of non-uniform coarse-grained models.



3) Development of a simple model for the dynamics of non-uniform systems.





5) Application of generalized time-rescaling to the coarse-grained polystyrene/toluene model.

4) Generalization of time-rescaling for non-uniform systems.

$$\xi_i[\vec{r}(t)] = \frac{\zeta_i^{(D)}[\vec{r}(t)]}{\zeta_i^{(CG)}[\vec{r}(t)]}$$

Supplemental Slides

Applications

Equilibrium Dynamics

Background

Nonequilibrium Polymer Solutions

Have a good understanding of the equilibrium behavior of polymer solutions

- Scaling of size of molecular weight
- Solvent effects on size
- Etc.

Nonequilibrium Applications

- Electrospinning
- Polymer Colloid Gels
- Solvent Casting Films

Know very little about dynamics

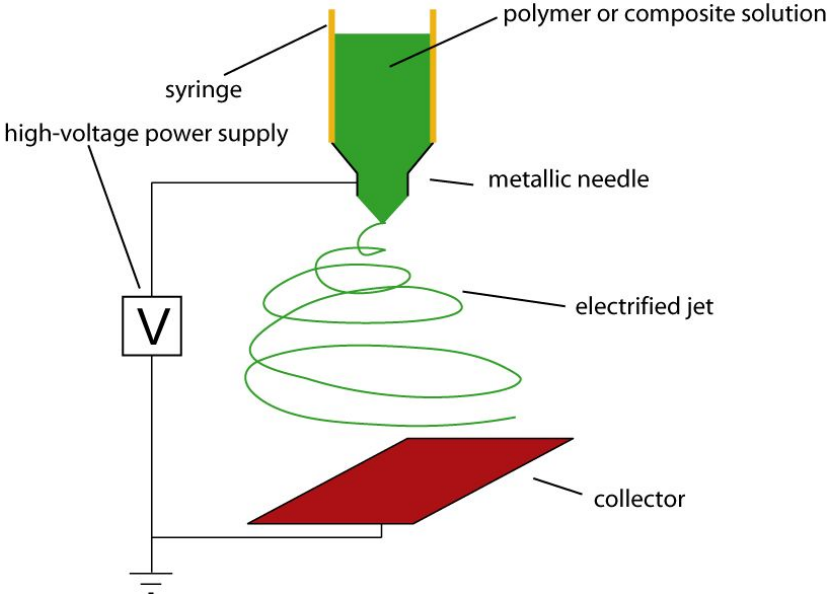
i.e. Time & length scales of equilibrium fluctuations

Know even less about far-from-equilibrium behavior

i.e. How does an extended chain relax to equilibrium size & shape

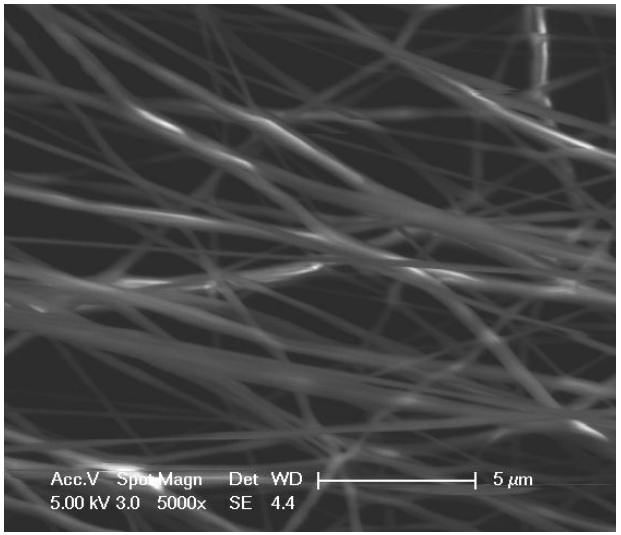
Electrospinning

- Electric field creates a jet of polymer solution
- Flowing polymer solution aligns polymer chains
- Solvent partially evaporates before deposits on surface
- Creates uniform nanofibers



Methodical experimentation with different solvents to create quality fibers

Essential sufficient solvent evaporation before deposited, otherwise lose ordering



References

Polymer/Colloids Systems

- Colloids in polymer solution weakly aggregate through depletion forces
- Used extensively in industry
- Current theoretical understanding assumes polymer component at equilibrium with respect to colloid

Images

Recent experimental evidence suggests nonequilibrium behavior of polymer important when colloids in motion

References

Experimental Knowledge of Polymer Solutions

Diffusion constants from spectroscopy

- List techniques

NMR has provided information on range of time scales for internal motion (nanoseconds)

Plots of diffusion constant

Diffusion of small molecule tracers has provided some information on dynamics of free volume

References

Theoretical Models

Rouse & Zimm model for dynamics of chains in solutions

Analytic models and numerical experiments for scaling of time scales for internal motion with length chain for generic chain like molecules

Figures

References

Simulations to Incorporate Molecular Detail

Molecular dynamics simulation used to investigate local dynamics in hydrogen bonding polymer polyethyleneoxide

Similar techniques employed for polymer melts

Figures

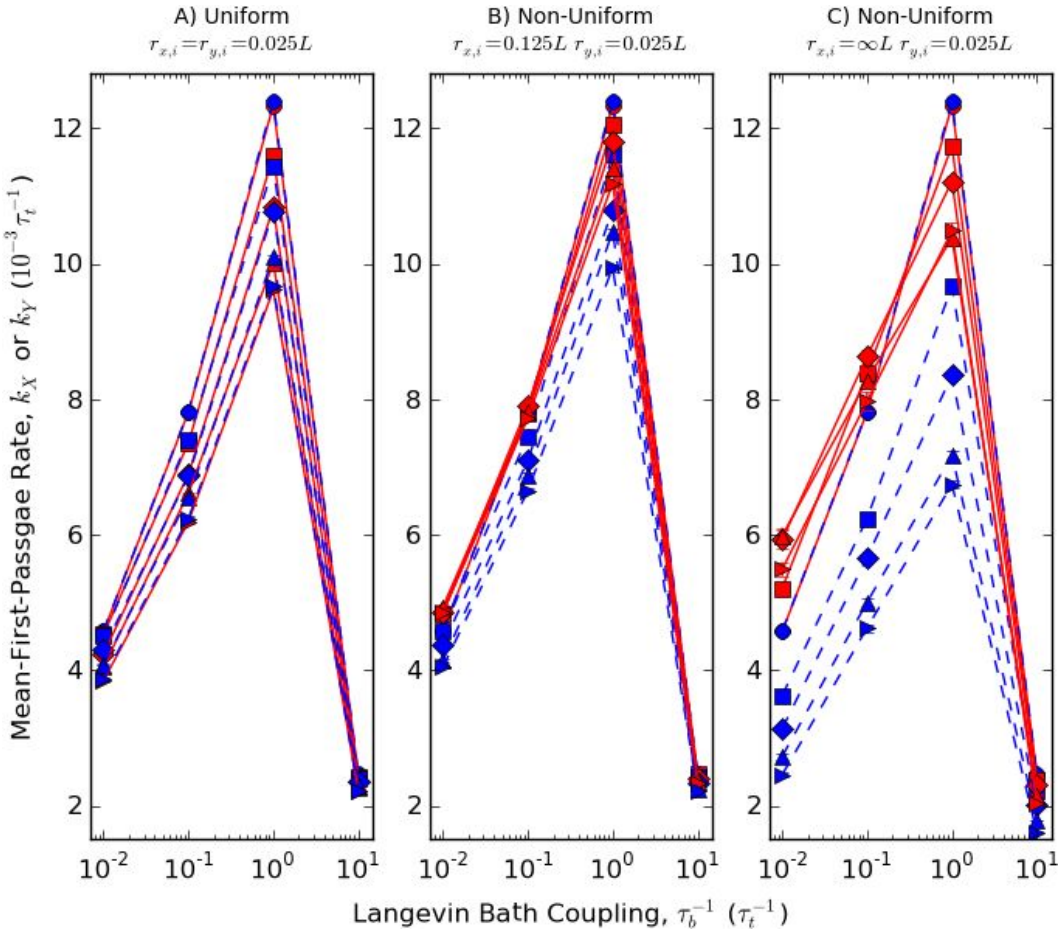
Such methods currently limited to small systems and only time scales on the order of motion of small segments

References

Extra

Rates to Each Well

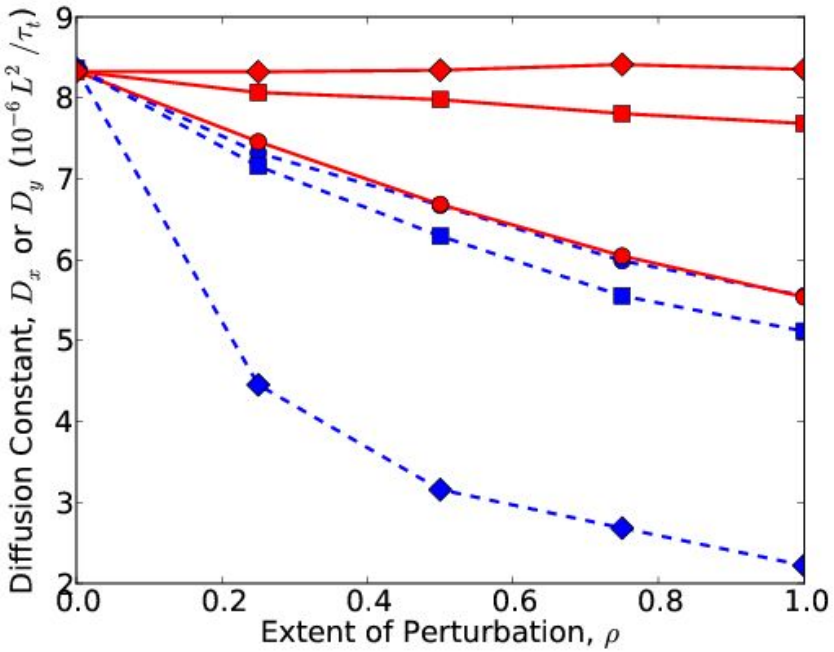
- Surfaces exhibit Kramer's Turnover behavior (good)
- Increasing friction decreases rates
- For uniform roughness, k_x and k_y decrease in concert
- For non-uniform roughness disparity in rates is observed
- Model demonstrates consequences of non-uniform reduction on dynamics



Test of Generalized Time-Rescaling

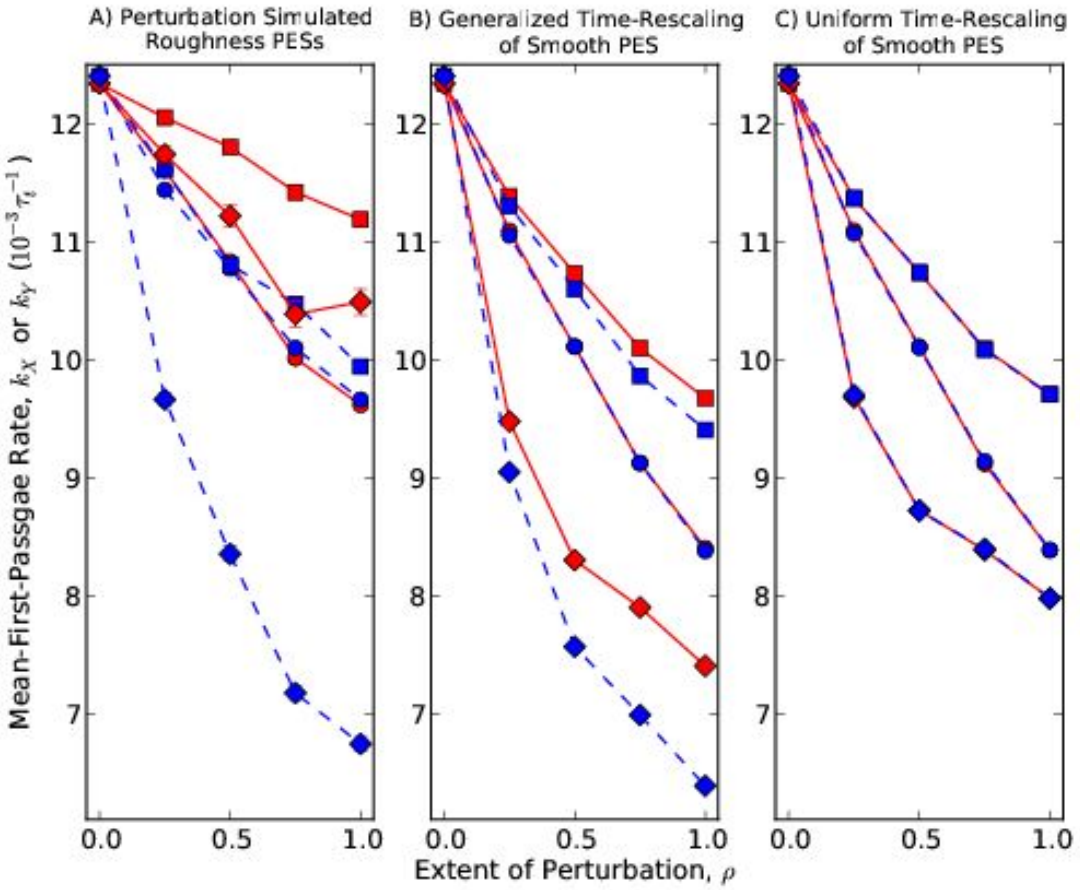
- Take smooth PES as characteristic of a coarse-grained (CG) model and rough PES as characteristic of a detailed (D) model
- Attempt to simulate dynamics across smooth PES using frictional environment of rough PES
- Exploit uniform roughness for each degree of freedom
  - Only need two rescaling factors ξ_x and ξ_y and these are time independent
- Sample diffusion constants in each direction for different PESs

$$\xi_x = \frac{D_x^{(CG)}}{D_x^{(D)}} \quad \xi_y = \frac{D_y^{(CG)}}{D_y^{(D)}}$$



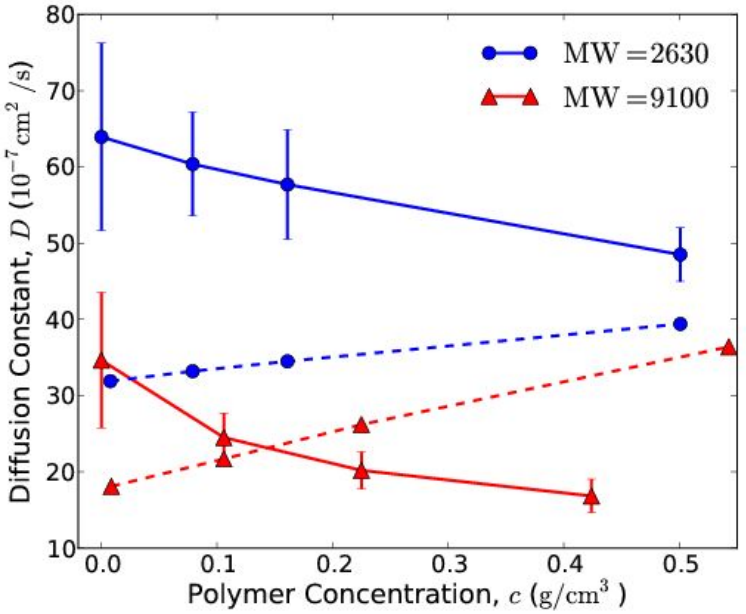
Results for Generalized Time-Rescaling

- Overall generalized time-rescaling provides an improvement over uniform time-rescaling
- Quantitative deviation likely due to finite size effects of roughness in model system
    - Effects mitigated with increasing dimensionality



Validation of Model and Methods

- Diffusion constant of polystyrene in toluene has been measured by several experiments and well accepted values exists
- Simulate different MW polystyrene over range of concentration and compare against experimental data
    - Dilute concentration, validate structural properties of individual chain
    - Higher semidilute concentrations, test intricate interchain interactions in



- Validation of preliminary methods shows accurate within a factor of 2
- More rigorous methods proposed needed for higher quantitative accuracy & qualitative scaling with concentration

Test of simplified methods used for a preliminary investigation of polystyrene/toluene solutions

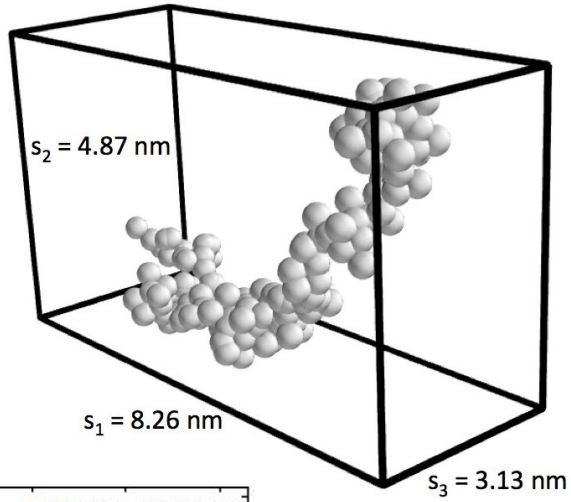
Simulation – solid lines

Experiment – dashed lines

Quantify Length Scales of Equilibrium Fluctuations

- Measure size through end-to-end length R_E and radius of gyration R_g
- Quantify shape through primary axis analysis
- Quantify fluctuations with root-mean-square deviation from the mean

$$R_E = |\vec{r}_N - \vec{r}_1| \qquad R_g = \sqrt{\frac{1}{N}\sum_{i=1}^{N} |\vec{r}_i - \vec{r}_{\text{com}}|^2}$$



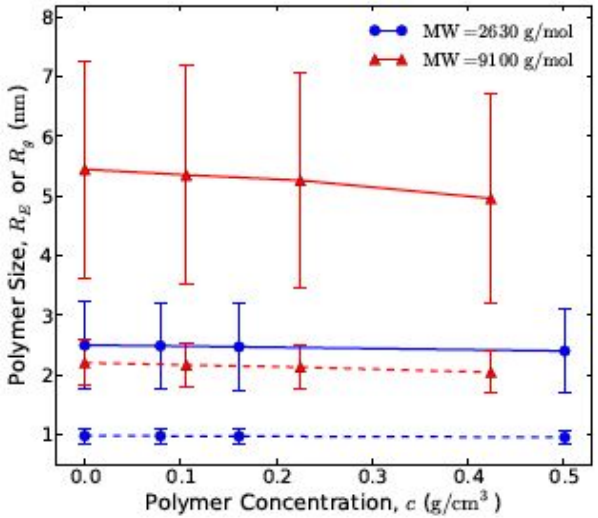


FIG. 8: Preliminary results for polystyrene molecular size with equilibrium fluctuations in size σ_x show by error bars (not uncertainty of measurement, which is negligible). Size is quantified by either end-to-end length R_E (solid lines) or by radius of gyration R_g (dashed lines). Results are shown for two polymer molecular weights of 2630 g/mol (blue circle ◯) and 9100 g/mol (red triangle △) as a function of polymer concentration c.

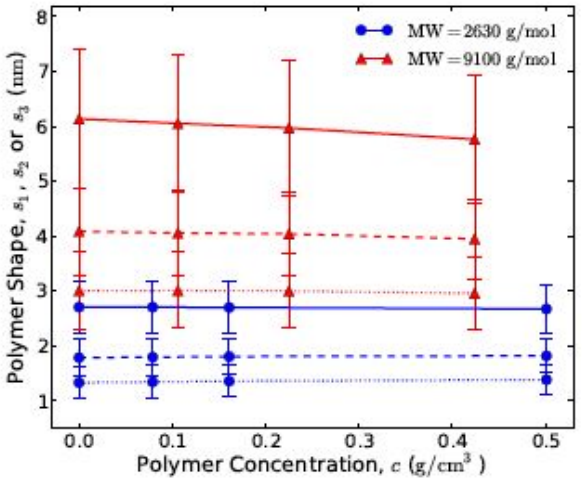


FIG. 10: Preliminary results for average polymer molecular shape s_i, with equilibrium fluctuations in shape σ_{s_i} show by error bars (not uncertainty of measurement). The length along different principle axes are described by line style with s_1 shown as a solid line, s_2 is dashed and a dotted line shows s_3. Results are shown for two polymer molecular weights of 2630 g/mol (blue circle ◯) and 9100 g/mol (red triangle △) as a function of polymer concentration c.

Quantify Time Scales of Equilibrium Fluctuations

Quantify time scales of fluctuation correlations using time correlation functions

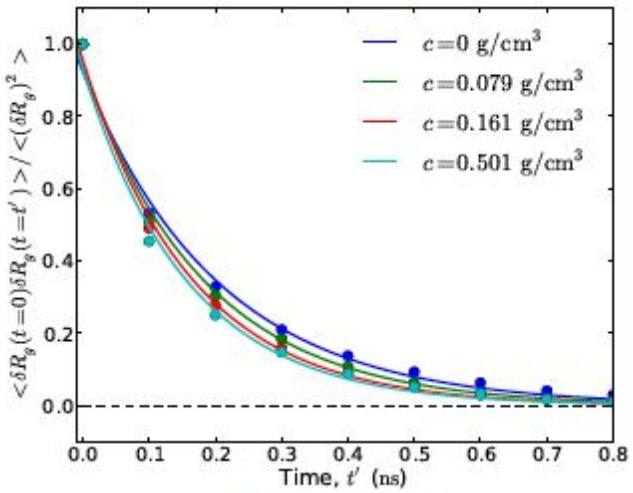
$$\xi_x^n(t') = \frac{\langle \delta x(t=0)\delta x(t=t')\rangle}{\langle (\delta x)^2\rangle}$$

Exponential behavior shows linear-regression can be used to model behavior

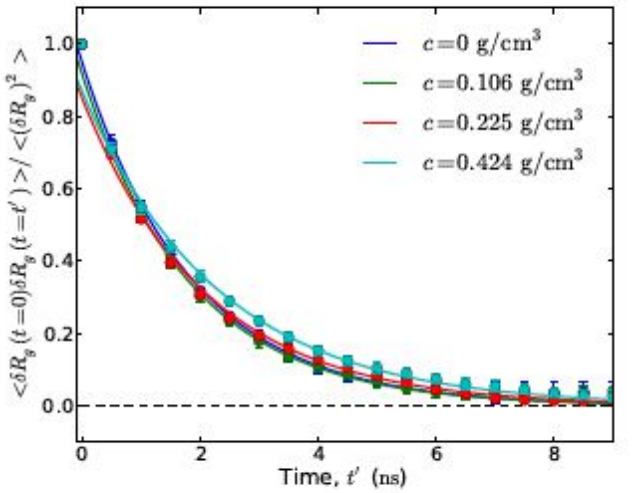
$$\Delta F = k\delta x$$

$$\xi_x^n(t') = \exp\left(-t'/\tau_x\right)$$

Allows calculation of characteristic times



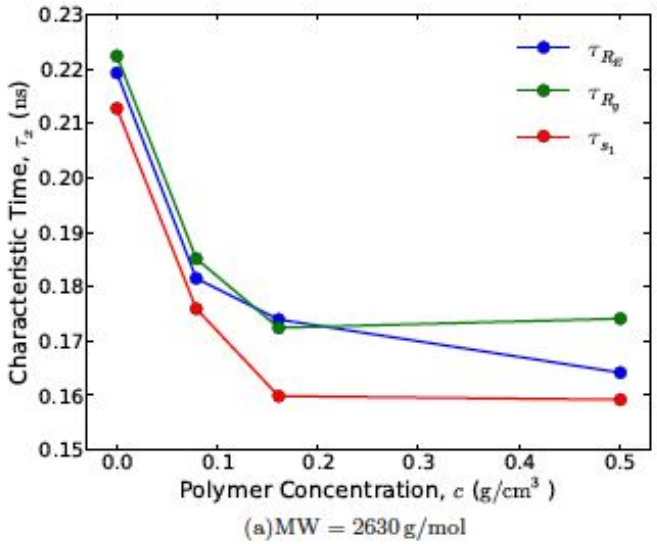
(a)MW = 2630 g/mol



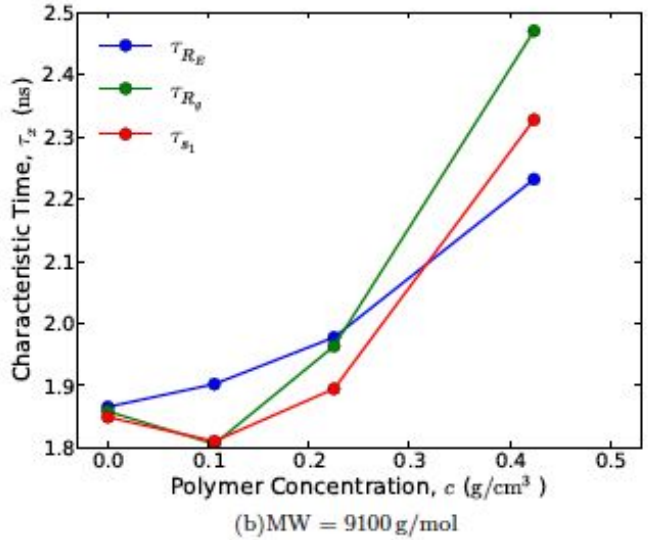
(b)MW = 9100 g/mol

FIG. 11: Preliminary results for fluctuation dynamics of polymer radius of gyration R_g as quantified by the normalized time correlation function $\xi^n_{R_g}(t')$ given by Equation 6. Points are results of simulation and error bars are smaller than the size of markers. Lines are exponential fits to the data. Different molecular weights are plotted separately with MW = 2630 g/mol shown in Figure 11(a) and MW = 9100 g/mol shown in Figure 11(b) as their times-scales differ by roughly an order of magnitude.

Characteristic Times



(a)MW = 2630 g/mol



(b)MW = 9100 g/mol

FIG. 12: Preliminary results for characteristic times τ_x of polymer size and shape correlation fluctuations. Results shown for the size metrics of end-to-end length $x = R_E$, radius of gyration $x = R_g$ and for the shape metric of primary axis length $x = s_1$. Different molecular weights are plotted separately with MW = 2630 g/mol shown in Figure 12(a) and MW = 9100 g/mol shown in Figure 12(b) due to the large difference in time scales.

Relaxation Dynamics of Extended Chain

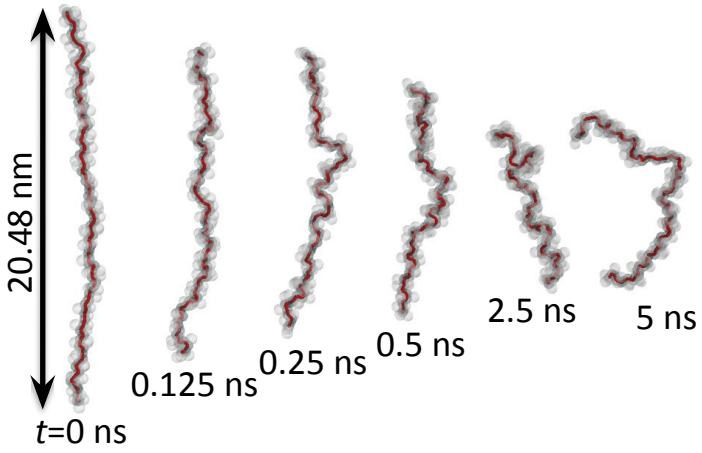
Extend on chain to a specific end-to-end length

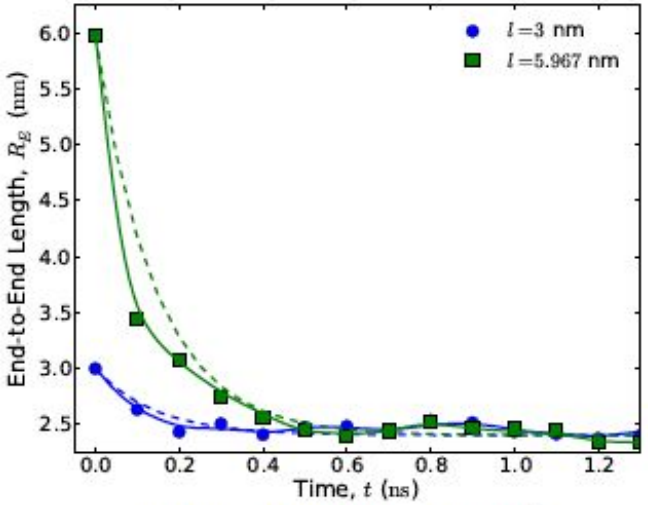
Observe relaxation dynamics when chain is released

Results relevant to electrospinning

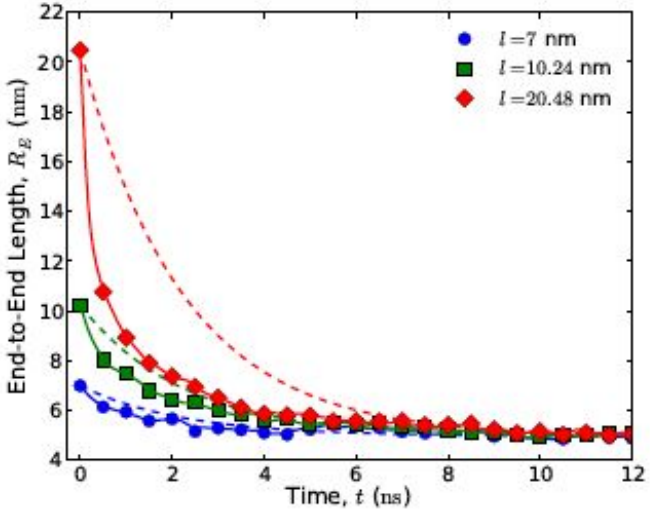
Small extension should relax through a fluctuation-dissipation relationship from equilibrium time scales

$$x(t') =< x > +(l- < x >) \exp(-t'/\tau_x)$$





(a)MW = 2630 g/mol c = 0.501 g/cm^3



(b)MW = 9100 g/mol c = 0.424 g/cm^3

FIG. 14: Preliminary results for relaxation dynamics of an extended polymer chain in polystyrene/toluene solutions. End-to-end length dynamics are averaged over 100 simulation trajectories and error bars are smaller than plotting marker. Simulation results are shown with solid lines and markers as labeled on each plot. Additionally, the relaxation predicted by Equation 8 is shown by dashed lines.

Driven Spherical Probe

Drag a spherical particle through polymer solutions to study nonequilibrium behavior in polymer colloid system

Monitor force on particle and investigate deviations from Stokes Law

Investigate structure of polymer about sphere using spherical density correlation functions