Frontiers of Computational Polymer Field Theory

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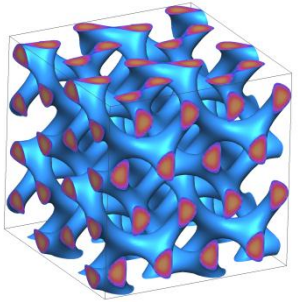
Acknowledgements



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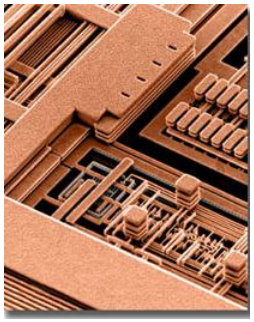
Funding:

NSF DMR-CMMT
NSF DMR-MRSEC
ACS-PRF

Complex Fluids Design Consortium:

Rhodia
Mitsubishi Chemical
Arkema
Dow Chemical
GE CR&D
Nestlé
Kraton Polymers
DSM
Intel, IBM, JSR, Asahi Kasei
SNL, LANL

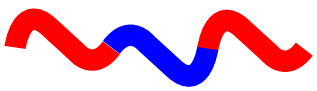
www.mrl.ucsb.edu/cfdc



We aim to develop simulation tools that can guide the design of nano/meso-structured polymer formulations

Why Nano-structured Polymers?

Nano-structuring is a way to achieve functionality that differentiates and adds value to existing and new families of polymers



SIS triblock copolymer

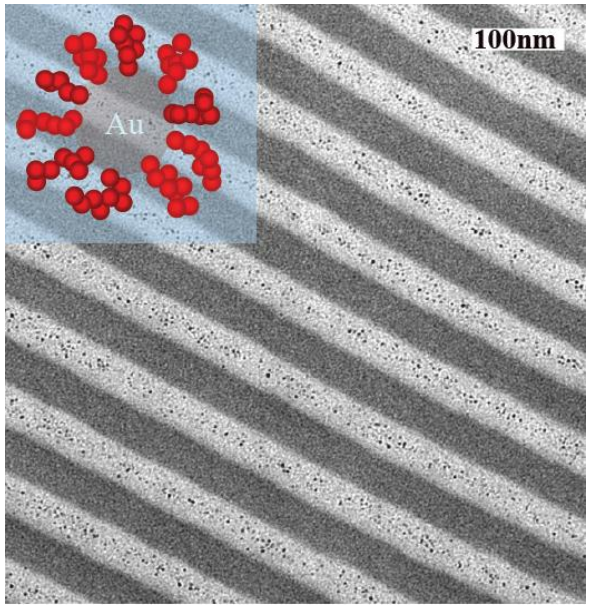
Outline

- Introduction to *equilibrium* polymer field theory
- Computational approaches
  - Self-Consistent Field Theory (SCFT)
  - Field Theoretic Simulations (FTS)
- Coarse-graining by force-matching
- Discussion and outlook

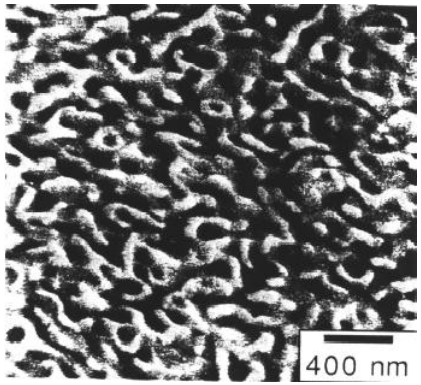
Why Field-Based Simulations?

Nano/meso: 1 nm to 1 μm

- Relevant spatial and time scales challenging for fully atomistic, classical "particle-based" simulations
- Use of fluctuating fields, rather than particle coordinates, has computational advantages:
  - Simulations become easier at high density & high MW
  - Systematic coarse-graining similar to numerical RG
  - Seamless connection to continuum mechanics



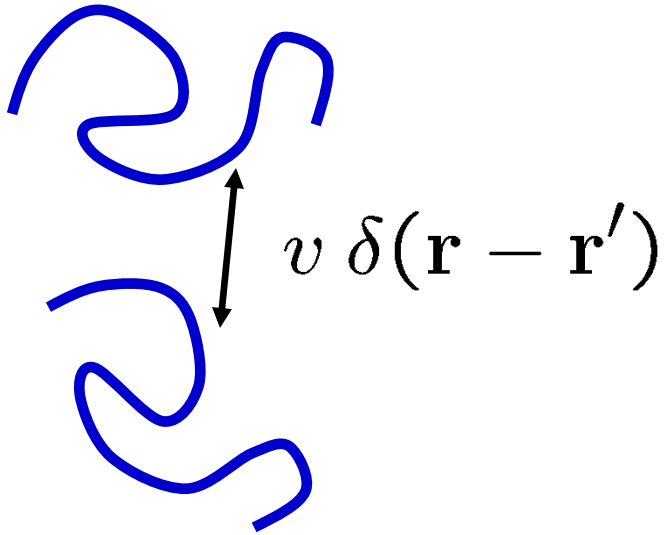
Copolymer nanocomposite
BJ Kim

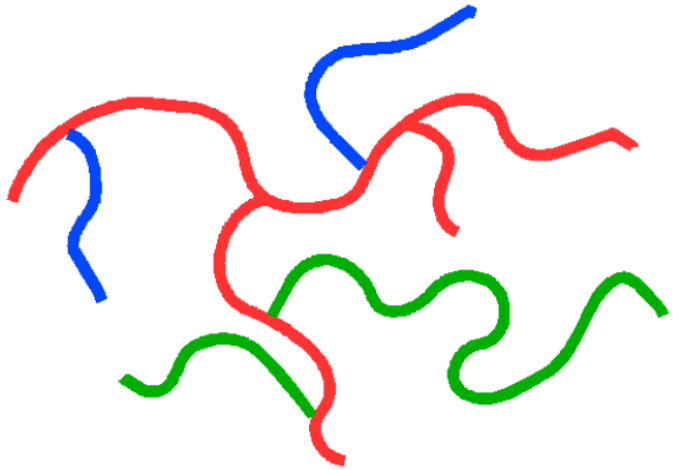


Polymeric microemulsion
F. S. Bates

Models

- Starting point is a coarse-grained particle model
- Continuous Gaussian chains
- Pairwise contact interactions
  - Excluded volume v, Flory χ parameters
- Easily added:
  - Electrostatic interactions
  - Incompressibility (melt)
- Arbitrary branched architectures



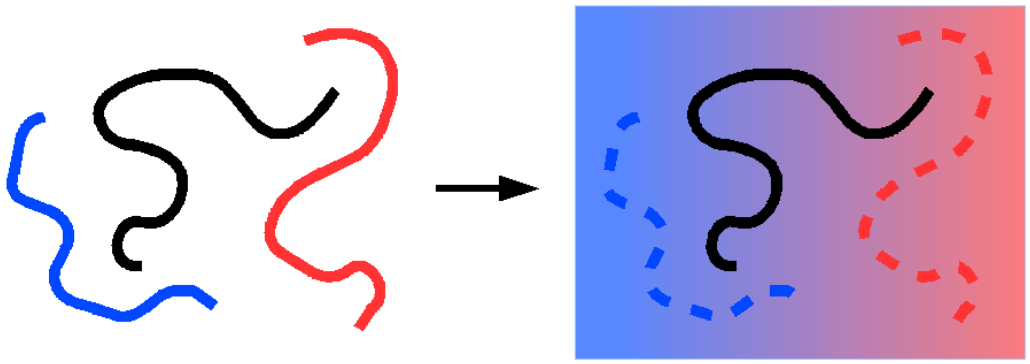


A branched "multiblock" polymer

From Particles to Fields

We convert the many-body problem into a statistical field theory

$$Z(n,V,T) = \int d\mathbf{r}^n \, e^{-U(\mathbf{r}^n)} \rightarrow \int \mathcal{D}w \, e^{-H[w]}$$



Polymers decoupled!

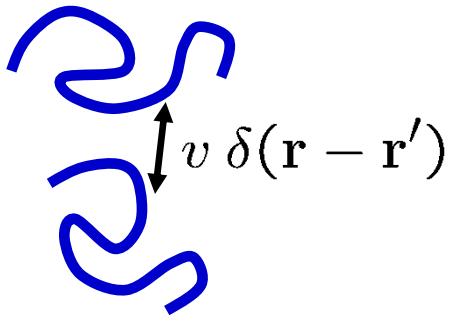
$$e^{-U(\mathbf{r}^n)} = e^{-\frac{1}{2}\int\int \hat{\rho} v \hat{\rho}}$$

$$\propto \int \mathcal{D}w \, e^{-\int i w \hat{\rho} - \frac{1}{2}\int\int w v^{-1} w}$$

Boltzmann weight is a complex number!

The Edwards Model

- Model of flexible homopolymers dissolved in good, implicit solvent (S. F. Edwards, 1965)



- Field-theoretic form

$$Z(n,V,T) = \int \mathcal{D}w\ \exp(-H[w])$$

$$H[w] = \frac{1}{2v}\int d\mathbf{r}\, w^2 - n \ln Q[iw]$$

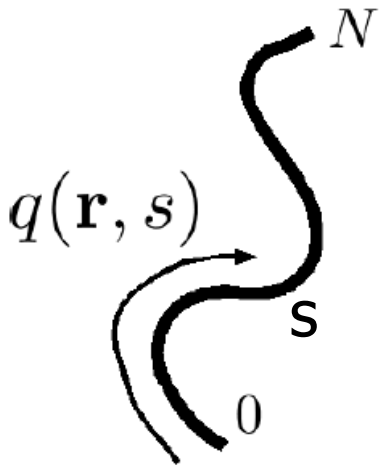
- Q[iw] is the single-chain partition function for a polymer in an imaginary potential field iw(r)

Formalism known to Edwards: numerical simulations new

Single-chain statistics

- Q[iw] calculated from propagator q(**r**,s) for chain end probability distribution

$$Q[iw] = V^{-1} \int d\mathbf{r}\, q(\mathbf{r}, N)$$



- Propagator obtained by integrating a complex diffusion (Fokker-Planck) equation along chain contour s

$$\frac{\partial}{\partial s} q(\mathbf{r}, s) = \frac{b^2}{6} \nabla^2 q(\mathbf{r}, s) - iw(\mathbf{r}) q(\mathbf{r}, s), \quad q(\mathbf{r}, 0) = 1$$

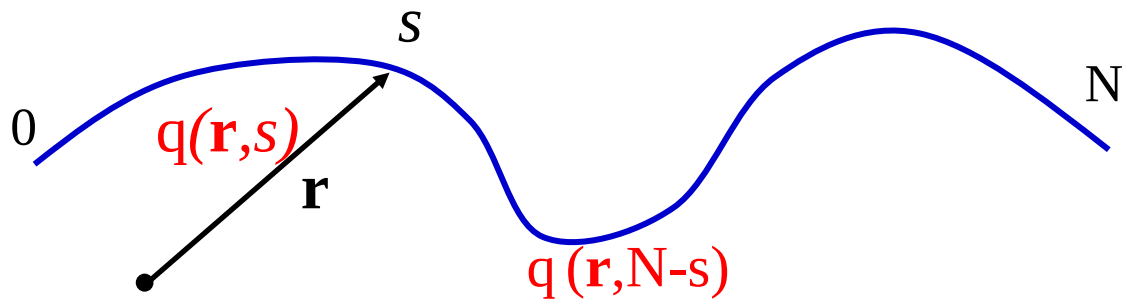
Numerically limiting "inner loop" in field-based simulations!

Observables and Operators

- Observables can be expressed as averages of **operators** O[w] with complex weight exp(-H[w])
- Density and stress operators (complex) can be composed from solutions of the Fokker-Planck equation

$$\rho(\mathbf{r};[iw]) = \frac{n}{VQ}\int_0^N ds\; q(\mathbf{r},s)q(\mathbf{r},N-s)$$

$$\sigma_{\alpha\beta}(\mathbf{r};[iw]) = \frac{nb^2}{3VQ}\int_0^N ds\; q(\mathbf{r},s)\nabla_\alpha\nabla_\beta\, q(\mathbf{r},N-s)$$



Types of Field-Based Simulations

- The theory can be simplified to a "mean-field (SCFT)" description by a *saddle point* approximation:

$$e^{-F} = Z = \int \mathcal{D}w\, e^{-H[w]} \approx e^{-H[w^*]} \qquad \left.\frac{\delta H[w]}{\delta w(\mathbf{r})}\right|_{w^*} = 0$$

- SCFT is accurate for $C \equiv nR_g^3/V \to \infty$ high MW melts

- We can simulate a field theory at two levels:

"Mean-field" approximation (SCFT): F ≈ H[w*]

Full stochastic sampling of the complex field theory: "Field-theoretic simulations" (FTS)

SCFT: Finding Saddle Points

- Relax to a saddle point in complex plane with fictitious dynamics

$$\frac{\partial}{\partial t} w(\mathbf{r}, t) = -\frac{\delta H[w]}{\delta w(\mathbf{r}, t)}$$

- Numerical algorithms should have excellent stability; accuracy in t not important

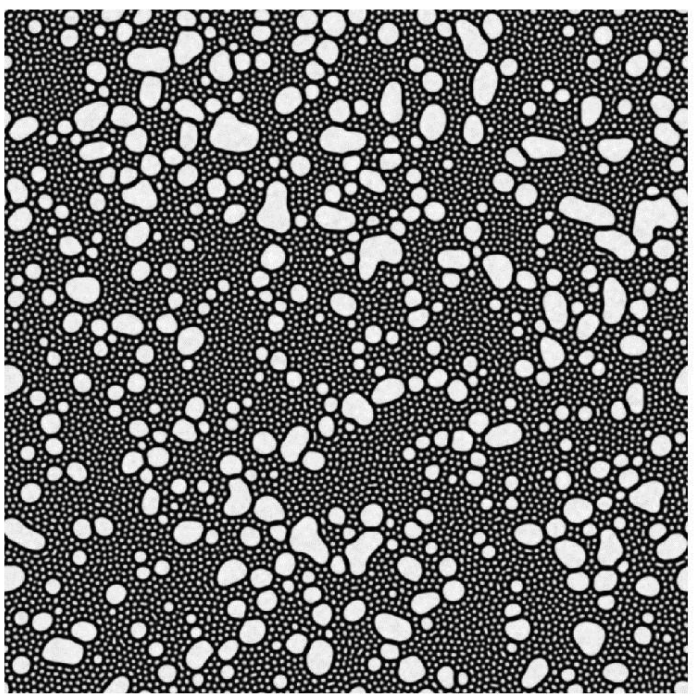
- Pseudo-spectral methods largely adopted from computational fluid mechanics, not statistical mechanics!

Implement with plane wave spectral collocation and parallel FFTs

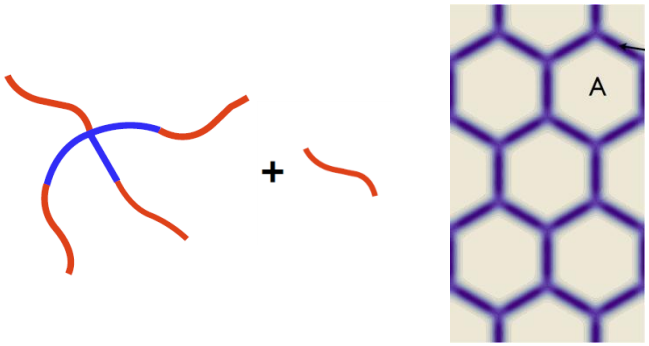
H. D. Ceniceros and G. H. Fredrickson,
SIAM Multiscale Modeling and Simulation **2**, 452-474 (2004)

High-Resolution SCFT Simulations

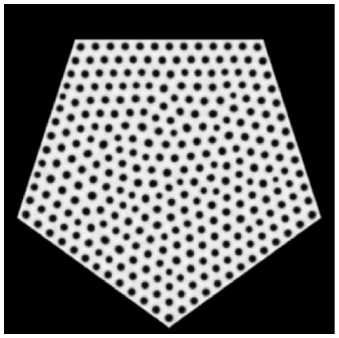
- By spectral collocation methods we can resolve fields using up to ~10^7 basis functions
  - Unit cell calculations for ordered phases with variable cell shape to relax stress
  - Large cell calculations for exploring self-assembly in new systems
- A broad range of complex polymer melts, solutions, alloys, and copolymers can be treated



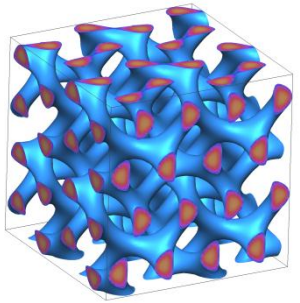
Block copolymer-homopolymer blend



High internal phase emulsions



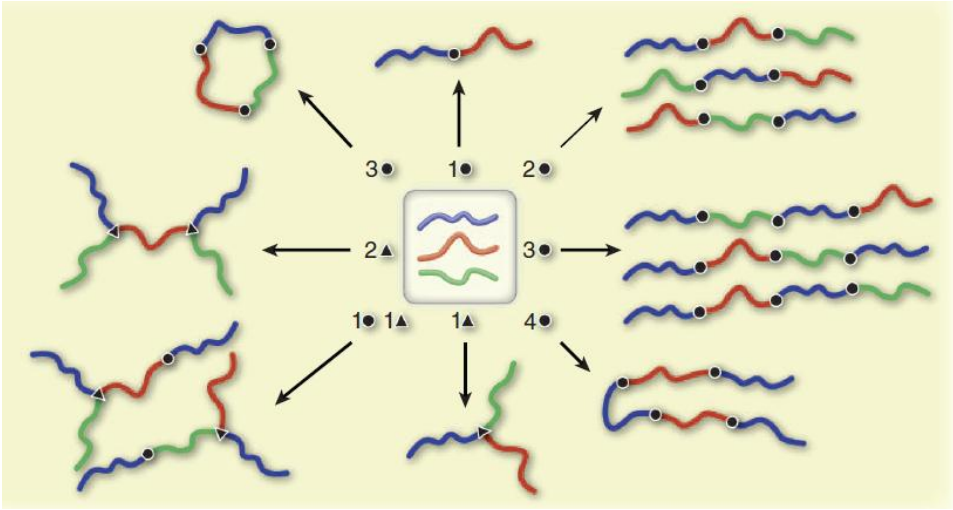
Confined BC films



Triply-periodic gyroid phase of BCs

Mènages en blocs

Mènage problem:
E. Lucas, 1891



Multiblock polymers have a multiplicity of designs that can be realized by modern polymer chemistry
What is the relationship between sequence and *collective* mesoscopic structure and materials properties?

Number of distinct linear polymers with k species and n blocks:

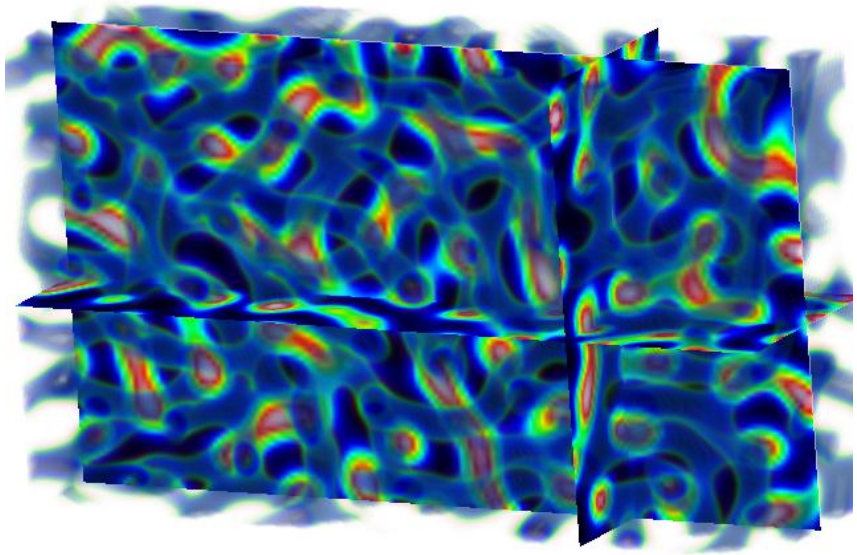
k/n	2	3	4	5	6	7	8	9	10
2	1	2	1	2	1	2	1	2	1
3	0	3	9	24	45	102	189	402	765
4	0	0	12	72	300	1092	3612	11,664	36,300
5	0	0	0	60	600	3900	21,000	102,120	466,200
6	0	0	0	0	360	5400	50,400	378,000	2,502,360

SCIENCE VOL 336 27 APRIL 2012

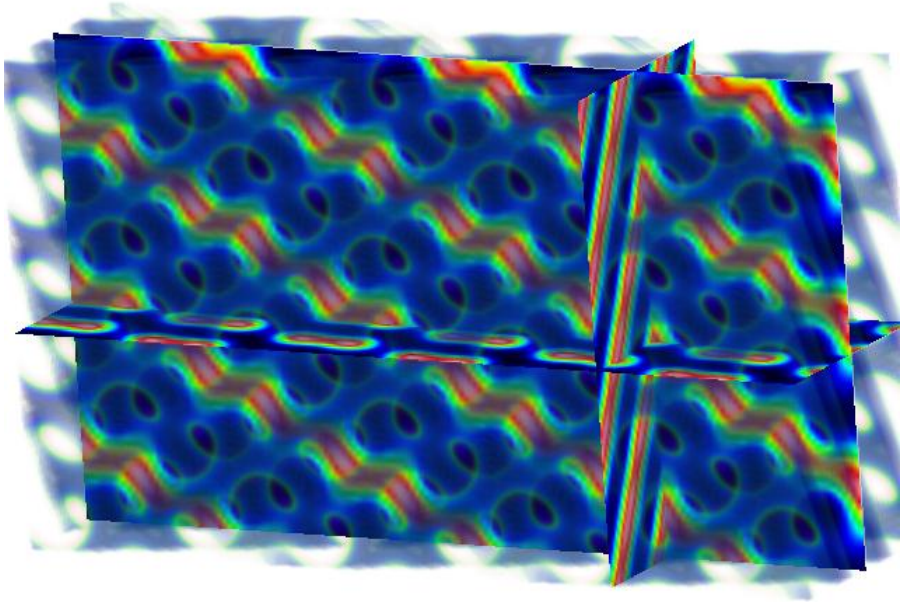
Large Cell SCFT of an ABC Triblock Melt

Parameters for PI-PS-PEO known to exhibit a stable **orthorhombic Fddd (O^{70}) phase:**

$f_A = 0.275$, $f_B = 0.55$, $\chi_{AB}N = \chi_{BC}N = 13$, $\chi_{AC}N = 35$



Relaxed from random seed



Defect free 3x3x3 unit cells. Relaxed from leading harmonics of Fddd

Abundant metastable states!

K. Delaney, using GPUs

Beyond Mean-Field Theory

- In many situations, mean-field theory (SCFT) is inaccurate
  - Polymer solutions, especially polyelectrolytes
  - Melts near a critical point or order-disorder transition

- We need to sample field configurations far from any saddle point

- But… H[w] is complex; exp(-H) not positive!

- This "sign problem" is familiar in other branches of chemistry and physics
  - QCD, lattice gauge theory, correlated electrons
  - Quantum rate processes

How do we statistically sample the full field theory?

Complex Langevin Dynamics

G. Parisi, J. Klauder 1983; V. Ganesan & GHF 2001

- A Langevin dynamics in the complex plane for sampling complex field theories and avoiding the sign problem

$$\frac{\partial}{\partial t} w_R(\mathbf{r},t) = -\mathrm{Re}\frac{\delta H[w]}{\delta w(\mathbf{r},t)} + \theta(\mathbf{r},t)$$

$$\frac{\partial}{\partial t} w_I(\mathbf{r},t) = -\mathrm{Im}\frac{\delta H[w]}{\delta w(\mathbf{r},t)}$$

- Thermal noise is asymmetrically placed and is Gaussian and white satisfying usual fluctuation-dissipation relation:

$$\langle\theta\rangle = 0, \quad \langle\theta(\mathbf{r},t)\theta(\mathbf{r}',t')\rangle = 2\delta(t-t')\delta(\mathbf{r}-\mathbf{r}')$$

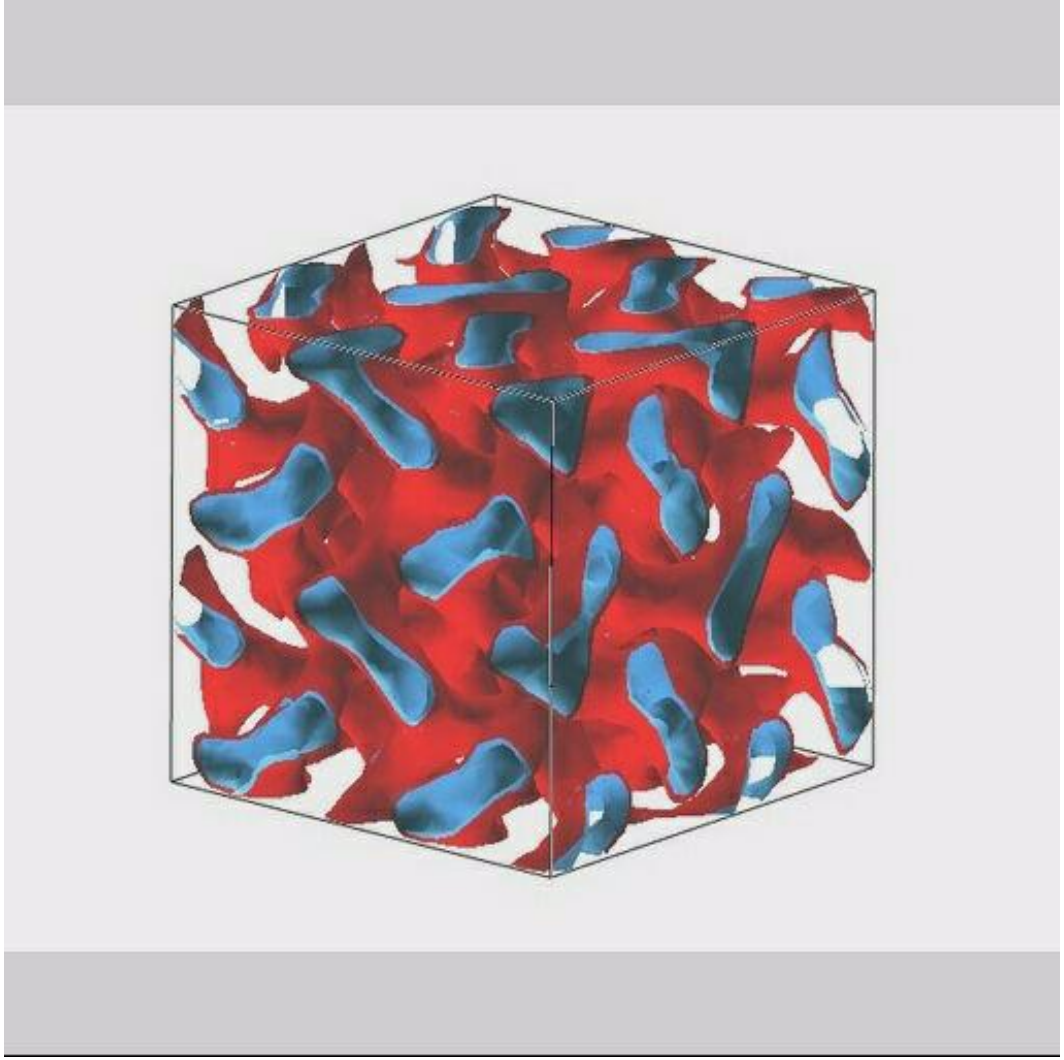
The stochastic lattice field equations are stiff, nonlocal, nonlinear

Fluctuation-mediated order-disorder transition: AB diblock copolymer melt

$\chi N = 14 \rightarrow 11$

f = 0.396

IC: 2^3 unit cells of stress-free gyroid from SCFT



E. M. Lennon, G. O. Mohler, H. D. Ceniceros, C. J. Garcia-Cervera, and G. H. Fredrickson, *SIAM Multiscale Modeling and Simulation* **6**, 1347 (2008)

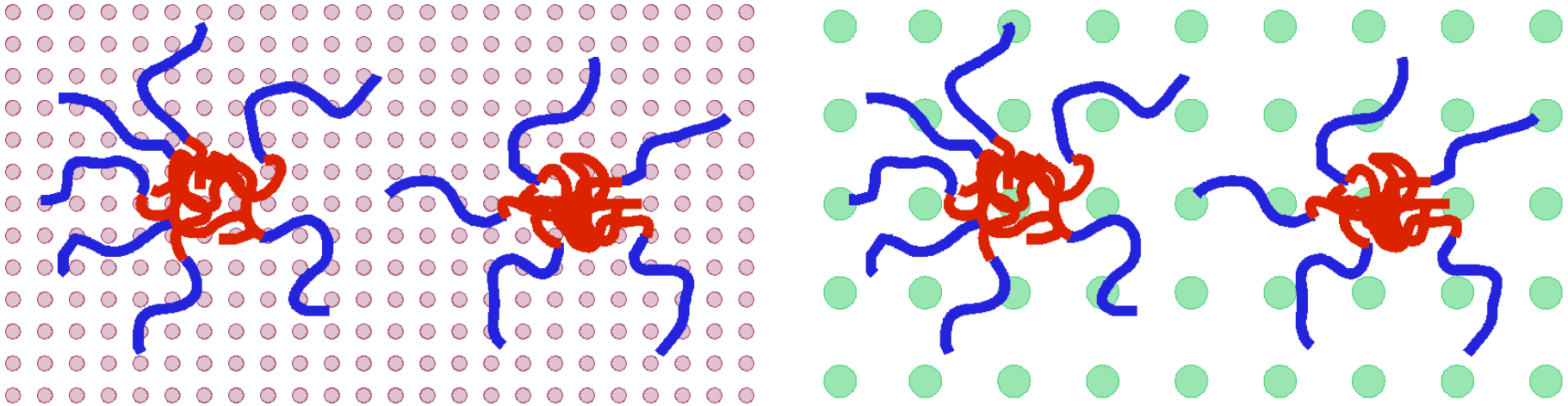
Large Multiscale Systems: Coarse-Graining

- Complex Langevin simulations require lattice discretization

$$Z_C \propto \int Dw\, e^{-H[w]} \rightarrow \int d\mathbf{w}\, e^{-H(\mathbf{w})}$$

- **Ideal efficiency:** lattice spacing commensurate with largest structures, CG/RG to embed fine-scale fluctuation physics

Example: solvent swollen micellar phases



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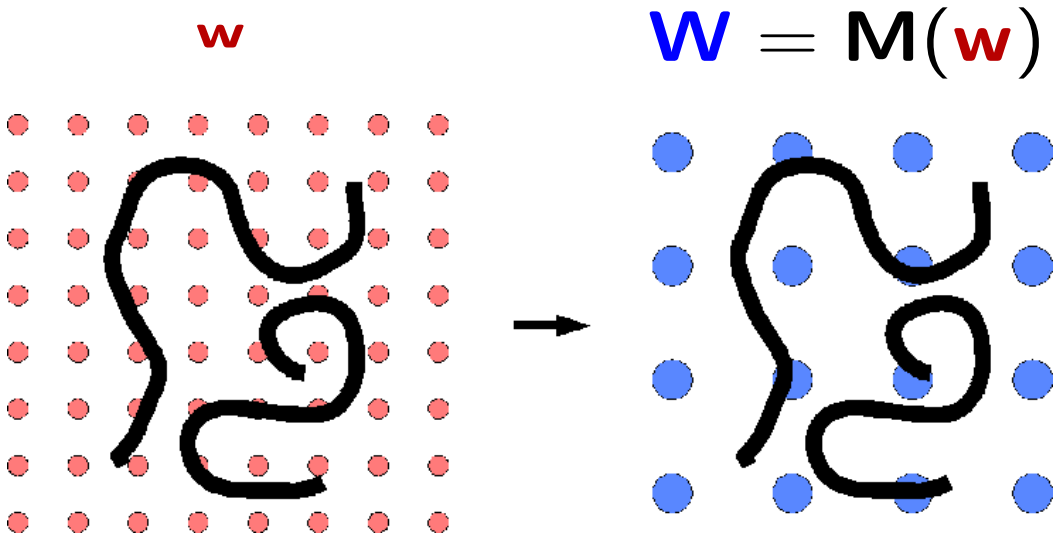
Systematic Coarse-Graining (CG)

Define CG mapping **M**(**w**) from fine to coarse lattice:



Mapping defines complex PDF of a coarse-grained model:

$$e^{-H(\mathbf{w})} \rightarrow e^{-H'(\mathbf{W})} \sim \int d\mathbf{w}\ \delta\big(\mathbf{W} - \mathbf{M}(\mathbf{w})\big)\ e^{-H(\mathbf{w})}$$

Linear basis function approx: $H'(\mathbf{W}) \approx \sum_{\alpha} K'_{\alpha} H'_{\alpha}(\mathbf{W})$

Parameterizing the CG Model

"Force-Matching" metric:

(adapted from Noid et al. formalism)

$$\left\langle \left| \frac{\partial H'(\mathbf{M}(\mathbf{w}))}{\partial \mathbf{W}} - \mathbf{M}\left(\frac{\partial H(\mathbf{w})}{\partial \mathbf{w}} \right) \right|^2 \right\rangle$$

Minimize with respect to **K'**: → Linear system

CG Hamiltonian parameters obtained from
a single fine-grained simulation

Operators coarse-grained using identical framework:

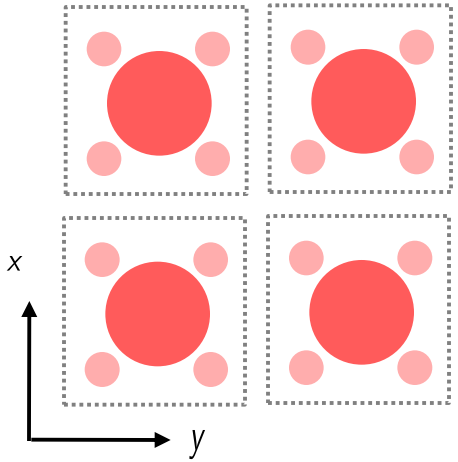
$$\tilde{\mu}(\mathbf{w}) \rightarrow \tilde{\mu}(\mathbf{W}) \approx \sum_{\alpha_\mu} K'_{\alpha_\mu} \tilde{\mu}_{\alpha_\mu}(\mathbf{W})$$

New to numerical RG literature?

Noid, Voth, Andersen et. al. JCP 2008
Villet and Fredrickson, JCP 2010

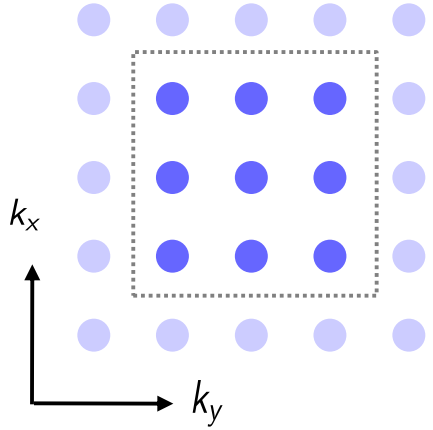
Coarse-Graining Mapping Schemes

Real-Space Block Averaging



Compatible with even number of lattice points:
FFT efficiency improved by 2^n grids

Fourier Mode Elimination



More flexible rate of coarse-graining

Fourier-space properties (e.g. structure factor) can be computed for CG models

Requires odd number of lattice points

c.f., Wilson-style RG

The Gaussian-Regularized Edwards Model

Edwards model is **UV divergent**: regularize with repulsive Gaussian interaction

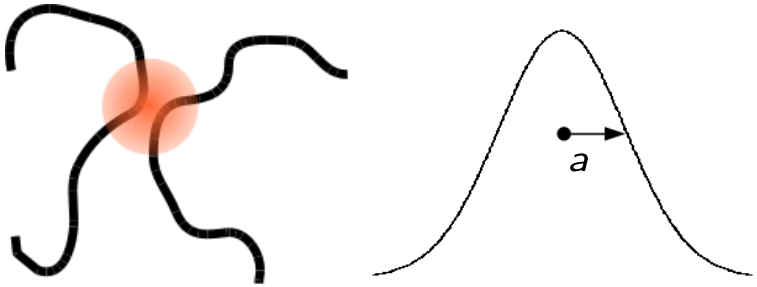
$$H[w] = \frac{1}{2B}\int d\mathbf{r}\; w(\mathbf{r})^2 - C\,V \ln Q\left[i\, e^{a^2\nabla^2} w\right]$$

Excluded Volume — Single-Chain Statistics

Excess chemical potential: $\mu_{ex}(B, C, a, V) = \langle -\ln Q\rangle \equiv \langle \tilde{\mu}\rangle$

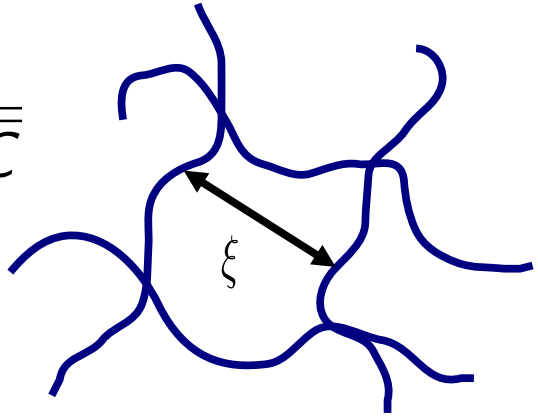
Length Scales (scaled by R_g):

Excluded Volume Range



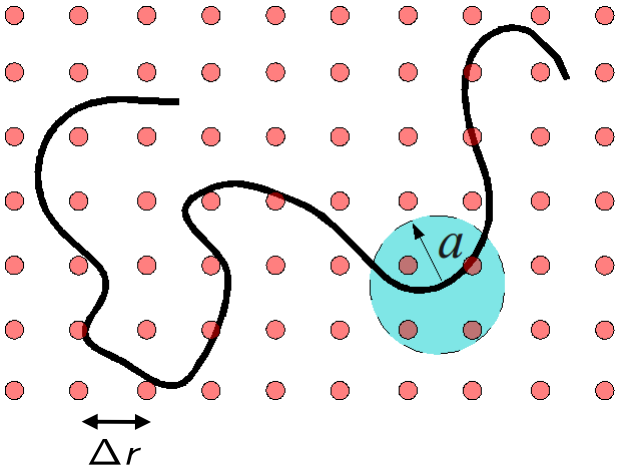
Solution Correlation Length

$$\xi \sim \frac{1}{\sqrt{2BC}}$$



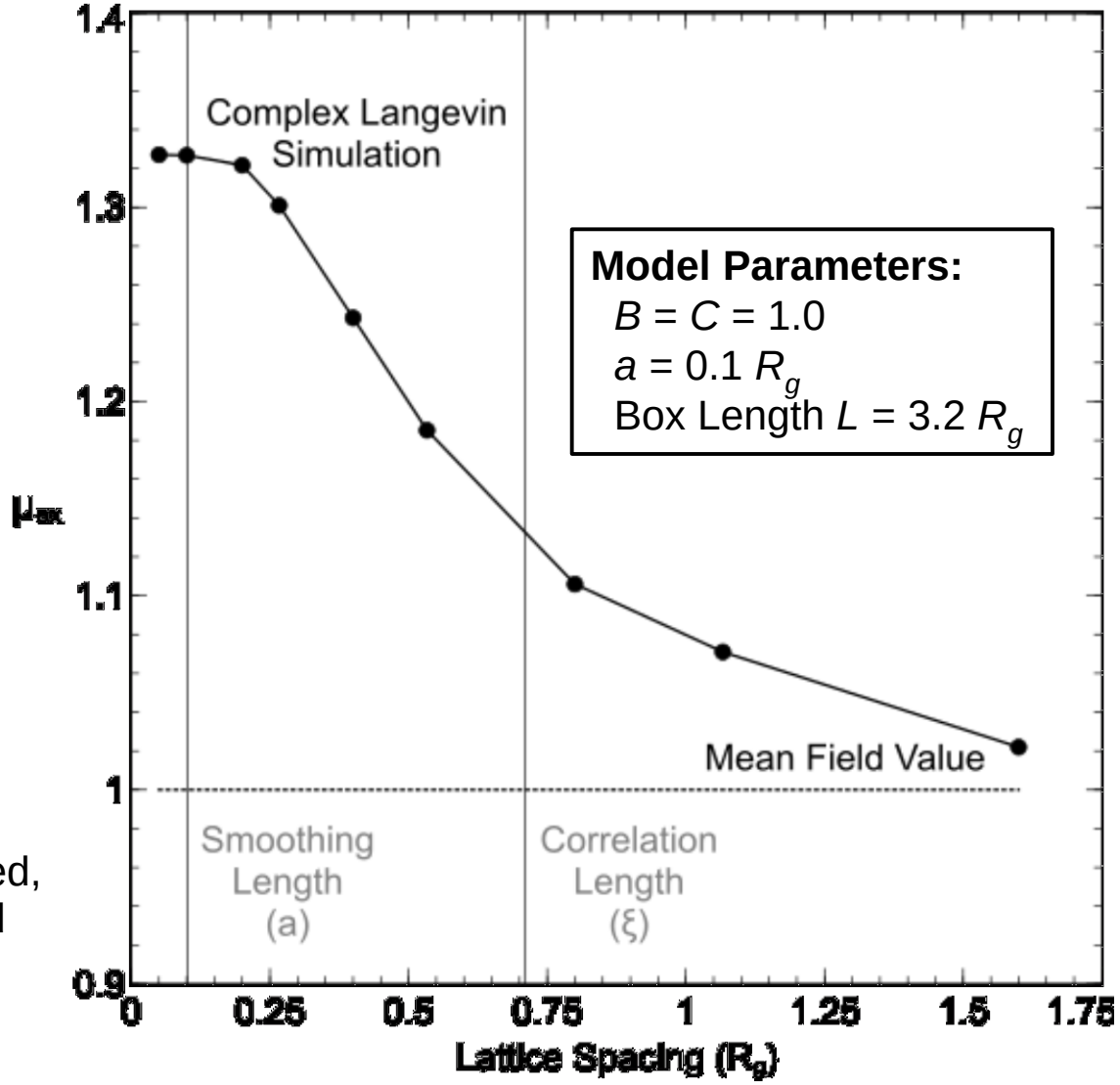
Lattice Resolution and Accuracy

Lattice spacing constrained by excluded volume range *a*



$\Delta r \lesssim a$: Accurate simulation

$\Delta r > a, \xi$: Fluctuations suppressed, mean-field recovered



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Coarse-Grained Trial Functionals

Minimal “3+2” basis for regularized Edwards model:

- Allow renormalization of existing parameters
- Add simple extra functionalities to improve coarse-graining accuracy

$$H[w] = \frac{1}{2\,B}\int d\mathbf{r}\; w(\mathbf{r})^2 - C\,V \ln Q\left[i\,e^{a^2\nabla^2} w\right]$$

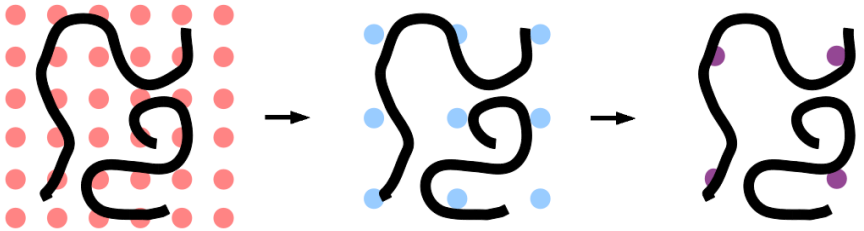
$$H'[W] = \frac{K_1'}{2}\int d\mathbf{r}\, W(\mathbf{r})^2 - K_2' V \ln Q\left[i\,e^{a^2\nabla^2} W\right] + K_3'\int d\mathbf{r}\, W(\mathbf{r})$$

$$\tilde{\mu}[w] = -(1)\ln Q\left[i\,e^{a^2\nabla^2}\; w\right]$$

$$\tilde{\mu}'[W] = -K_{\mu_1}' \ln Q\left[i\,e^{a^2\nabla^2}\; W\right] + K_{\mu_2}'$$

Fixed-Volume Coarse Graining

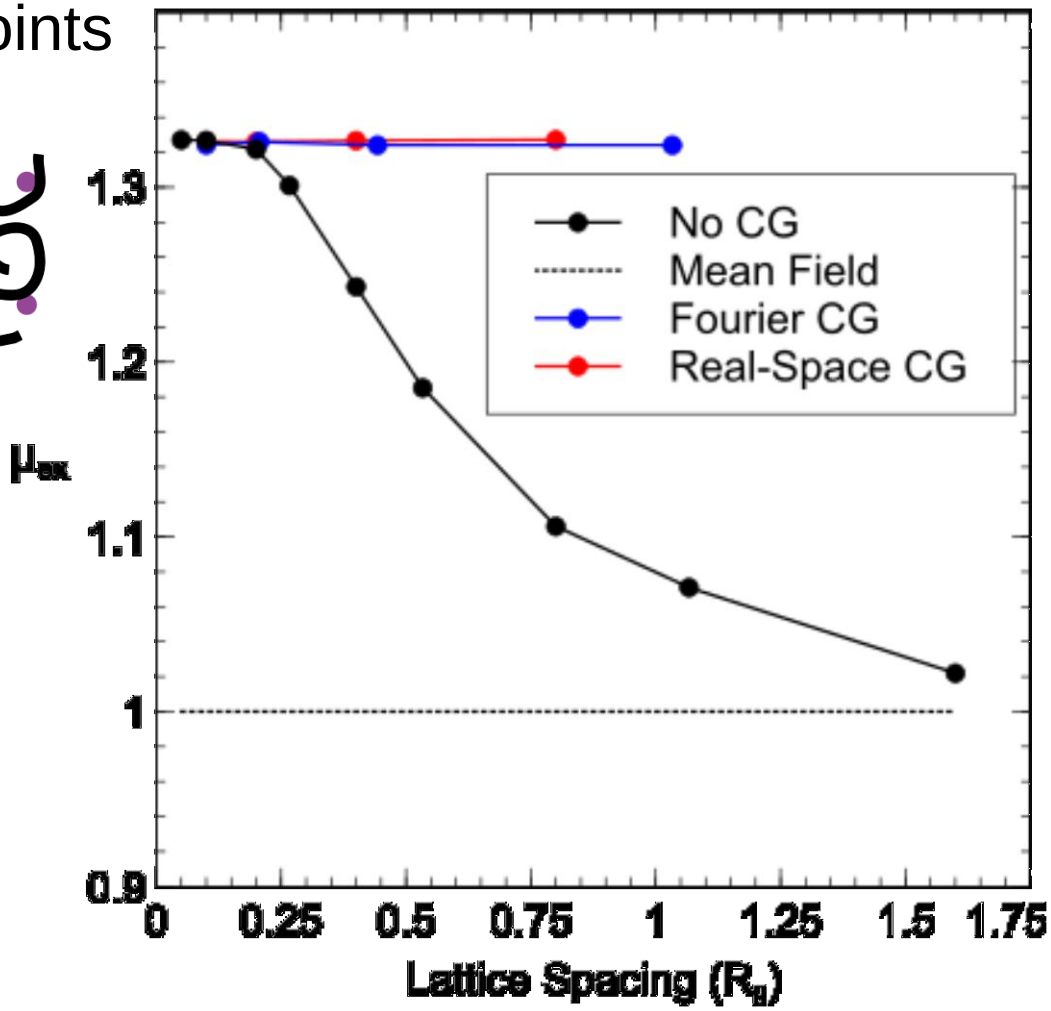
Represent same system with progressively fewer lattice points



Initial System:
$\Delta r = 0.1\ R_g$
$L = 3.1 / 3.2\ R_g$ (Fourier/Real CG)

CG Protocol:
Real-Space: 2^3 Cubic Blocking
Fourier: ~ $(½)^3$ mode elimination

CG models accurate at low resolution!



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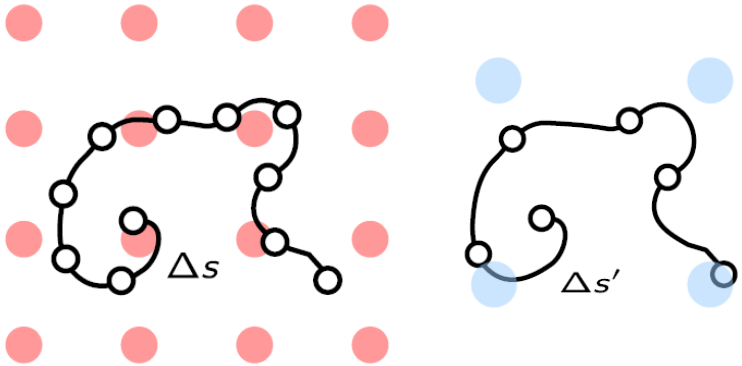
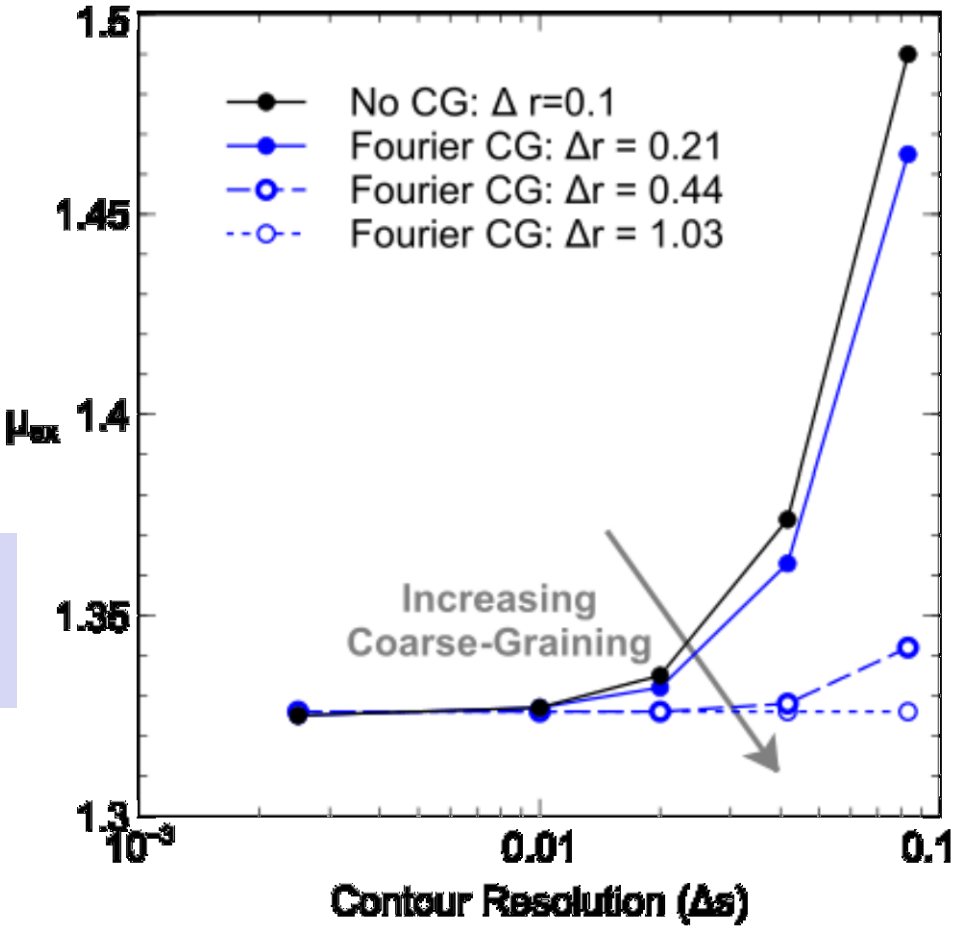
Coarse-Graining and Contour Resolution

Can lower contour resolution be used with CG models?

Algorithm of choice: second-order splitting with Richardson extrapolation
(J. Qin 2009, D. Audus (in prep))





CG models accurate at low contour resolution!

$$\Delta s' \sim (\Delta r)^{1.6}$$

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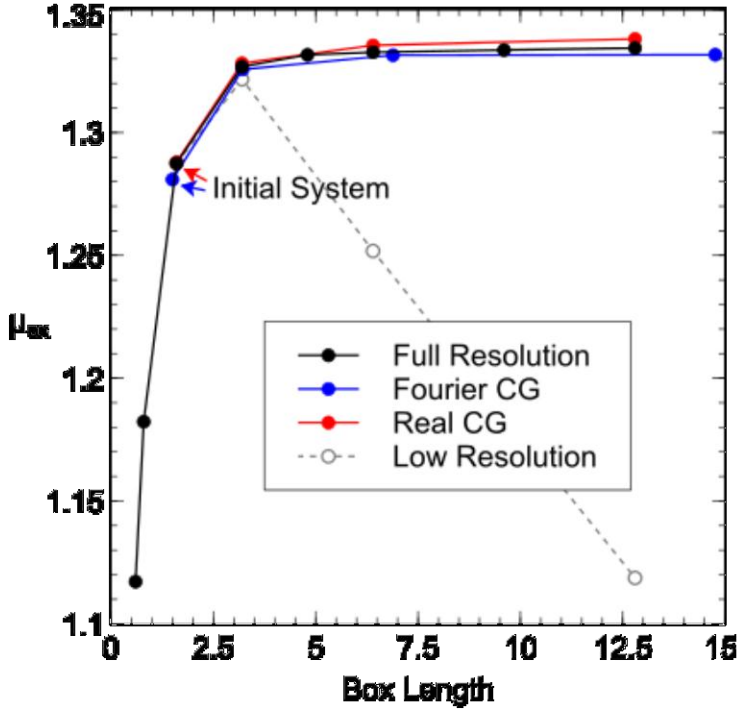
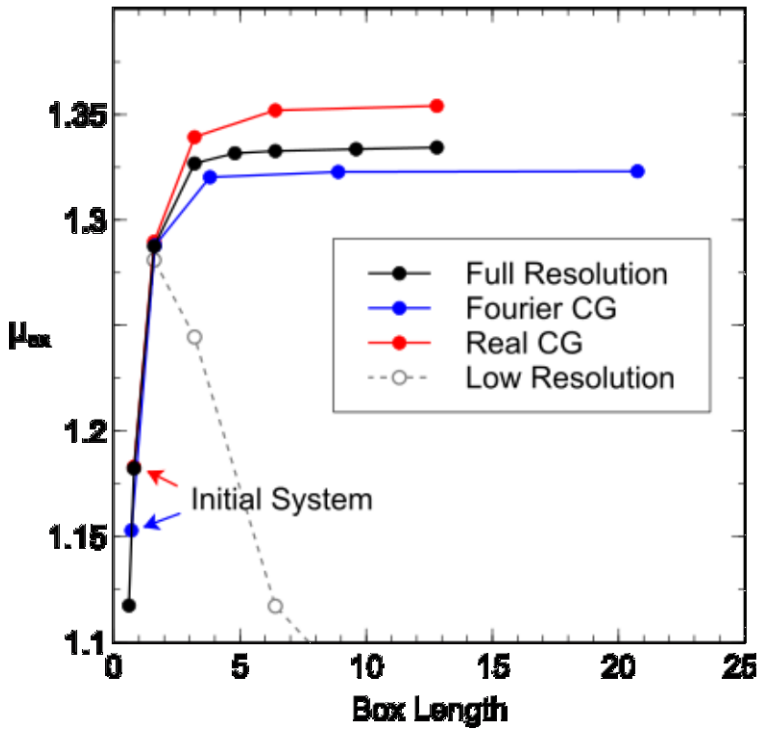
Box Expansion: Coarse-Graining "Cascades"

Iteratively progress to larger system volumes at fixed number of grid points :

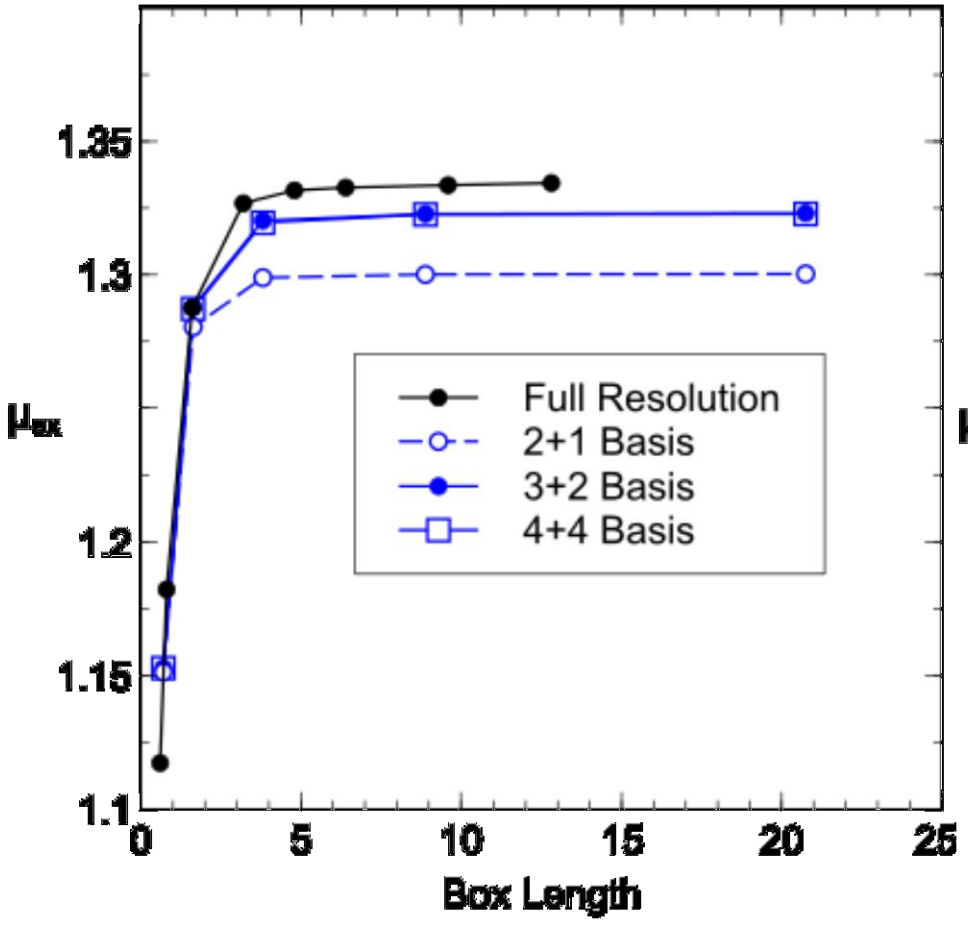




Finite size effects are reasonably described by CG cascades!

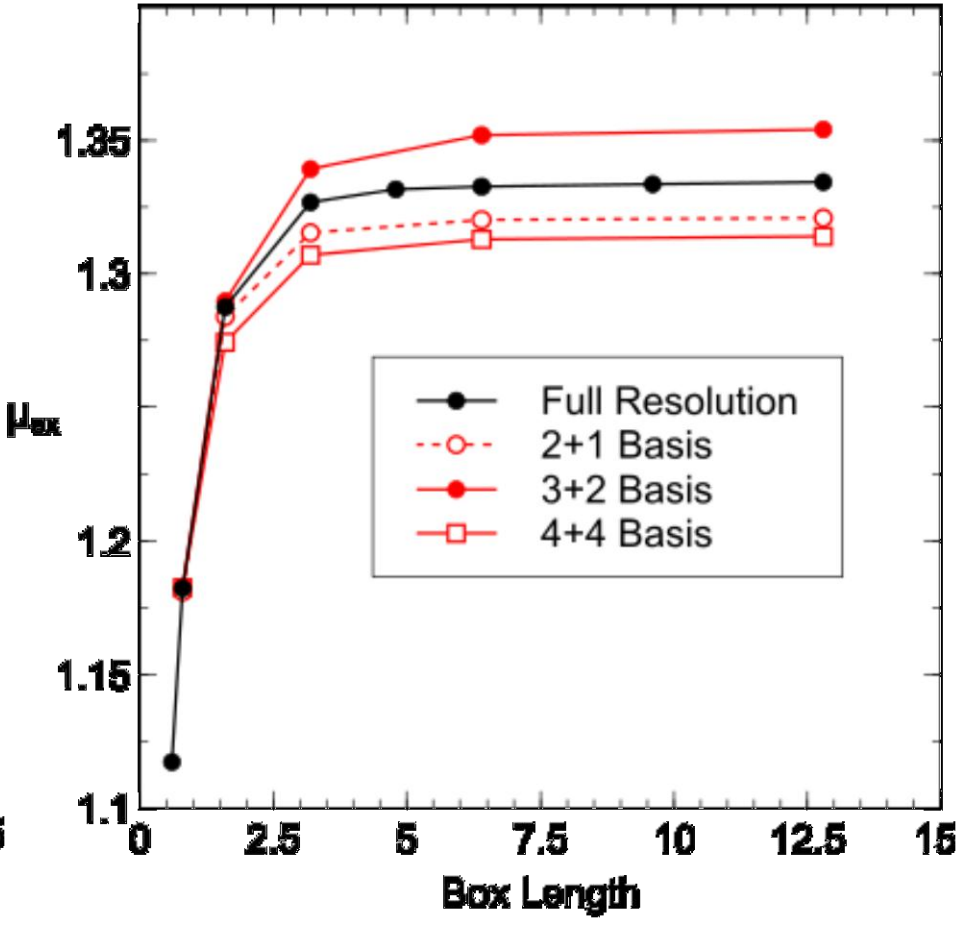
Coarse-Grained Basis Comparison

Fourier CG



Systematic improvement to a limiting value

Real-Space CG



Inconsistent results from larger basis sets

Basis identification plagued by nonlocal, nonlinear character of field theory

Coarse-graining in FTS: Future studies

- **Force field parameterization** is currently a limitation -- can a different field theoretic representation help?

"Coherent states" representation of Edwards Model (GCE):

$$H[\phi,\widehat{\phi}] = \int ds \int d\mathbf{r}\ \widehat{\phi}(\mathbf{r},s)[\partial_s - (b^2/6)\nabla^2]\phi(\mathbf{r},s)$$
$$+ \frac{1}{2}v\int d\mathbf{r}[\tilde{\rho}(\mathbf{r};[\phi,\widehat{\phi}])]^2 - \sqrt{z}\int d\mathbf{r}[\widehat{\phi}(\mathbf{r},0)+\phi(\mathbf{r},N)]$$

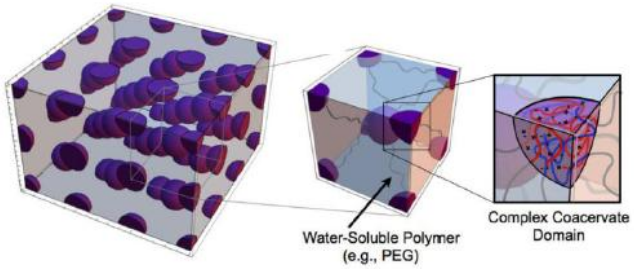
$$\tilde{\rho}(\mathbf{r};[\phi,\widehat{\phi}]) = \int ds\ \widehat{\phi}(\mathbf{r},s)\phi(\mathbf{r},s)$$

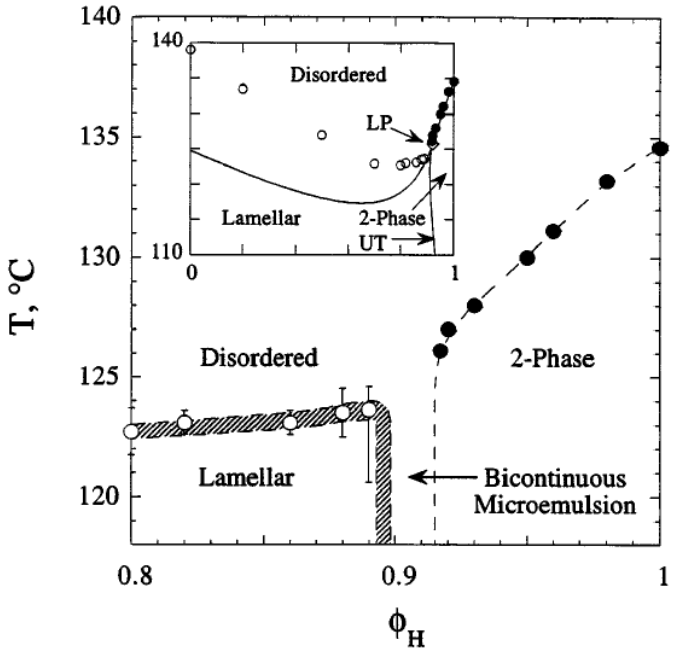
Theory is finite polynomial order in fields and gradients!

X. Man, K. Delaney, M. Villet, H. Orland, GHF

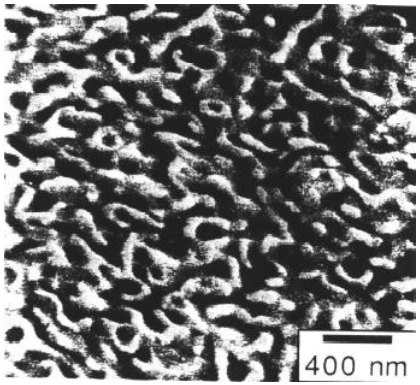
Applications of Coarse-Graining

- Solvent swollen block copolymer mesophases
  - Coarse grain until SCFT accurate





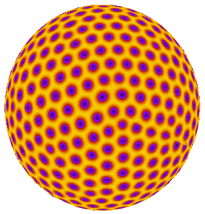
- Bicontinuous microemulsions in A+B+AB blends
  - Coarse grain to finest feature size ~25nm
  - FTS of coarse model to study long-wavelength fluctuation physics



Bates et. al. *PRL* 79, 849 (1997)

Analytically intractable: $d_{uc}=8$!

Discussion and Outlook



- "Field-based" computer simulations are powerful tools for exploring equilibrium self-assembly in polymer formulations

- Good numerical methods are essential!
  - Complex Langevin sampling is our main tool for addressing the sign problem
  - Free energy and variable cell shape methods progressing
  - **Coarse-graining/RG techniques improving**

- Emerging application areas are
  - Multiblock phase diagrams
  - Thin films: directed self-assembly
  - Polyelectrolyte complexes
  - Bicontinuous microemulsions
  - Hybrid simulations with nanoparticles and colloids
  - Supramolecular polymers
  - **Nonequilibrium extensions** to coupled flow and structure

The Equilibrium Theory of Inhomogeneous Polymers (Oxford, 2006)
G. H. Fredrickson et. al., *Macromolecules* **35**, 16 (2002)