Beyond the Mean Field: Efficiently Implementing the Complex Langevin Method

Erin M. Lennon
Glenn H. Fredrickson

Department of Chemical Engineering
University of California, Santa Barbara

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Disorder in Self-Assembly

- Goal: Increase epoxy toughness
- Amphiphilic block copolymers
- 5% copolymer loading yields 40x to 70x increase in fracture resistance

Dean et al; *Macromolecules* 2003
Mean Field Results

- Model as a blend of copolymer and homopolymer
- Hypothetical micellar region

Matsen; Phys. Rev. Letters 1995
Mean Field Assumption

- Assume a single configuration dominates the partition function
- Fluctuations are suppressed

\[ Z = \int D[W] e^{-H[W]} \approx e^{-H[W^*]} \]
Complex Langevin Solution

- Stochastic sampling of fields
- Simultaneous excitation and relaxation

\[
\frac{\partial}{\partial t} W(r,t) = -\lambda \frac{\delta H[W]}{\delta W(r,t)} + \eta(r,t)
\]

\[
\langle \eta(r,t) \rangle = 0
\]

\[
\langle \eta(r,t) \eta(r',t') \rangle = 2\lambda \delta(r - r') \delta(t - t')
\]
Numerical Limitations

- System stability and accuracy require restrictively small step sizes
Novel Method: SDE Splitting

- 2nd order Semi-Implicit method

\[
dx = (A(x) + B(x))dt + \eta
\]

\[
x^{n+1} = x^{n} + \frac{\Delta t}{2} \left[ A_{x^{n+1}} + B_{\tilde{x}} + A_{x^{n}} + B_{x^{n}} \right] + \eta
\]

\[
\tilde{x} = x^{n} + \Delta t \left[ A_{x^{n}} + B_{x^{n}} \right] + \eta
\]
Novel Method: SDE Splitting

- Example:

\[
\begin{align*}
W_{n} &= W_{n} + \Delta t \frac{\delta H}{\delta W} + \eta \\
\hat{W}_{n+1} &= \frac{1}{2 + \Delta t \hat{g}_T} \left( \hat{W}_n + \hat{\eta} + (\Delta t \hat{g}_T + 1)\hat{W}_n + \Delta t \frac{\delta \hat{H}}{\delta \hat{W}} \right)
\end{align*}
\]
Method Comparison

![Data comparison chart showing results for Modified First Order Scheme and Second Order Scheme across different timestep values. The chart includes error bars for each data point.]
Diblock Copolymer Model

- Pressure and Difference Fields

\[ H[W_{\pm}] = C \left[ \int dr [(2f - 1)W_+ - iW_- \\
+ W_-^2 (\chi N)^{-1}] - V \ln Q \right] \]
Appearance of Micelles

Density Profile

![Density Profile Image]
Shift in the Order Parameter

C = 240
Shift in the Order Parameter

\[ C = 60 \]
Shift in the Order Parameter

C = 30
Future Work

- Continue work on efficient numerical methods
- Extend simulations into larger systems
- Address physical phenomena intractable by current methodology
Diblock/Homopolymer Blends

A-B Diblock
A Homopolymer

Matsen; *Phys. Rev. Letters* 1995
Micelles in Disorder

- New ODT
- Unbinding transition

Critical Micelle Concentration

SCFT

Experiments

Fluctuations
Diblock/Homopolymer Blend

- Diblock as Surfactant
- Ternary Blend
  - A-B Diblock
  - A Homopolymer
  - B Homopolymer

SCFT Experiments

Fluctuations
Microemulsions

- Fluctuation Destroy Unbinding Transition
- Narrow Region!

Bates et al; *PRL* 1997
Stabilizing Microemulsions

- Polydispersity
  - A-B asymmetries
  - Chain Length Variations

Hillmyer et al; *J Phys Chem B* 1999
Stabilizing Microemulsions

Homopolymers

Diblocks
- Varied Length
- Symmetric
- Varied Composition

Hillmyer et al; *J Phys Chem B* 1999
Summary

- Improved Numerical Methods
  - Full Complex Langevin Dynamics tractable
- Application to Neat Diblock System
- Future Work with Diblock Homopolymer Blends
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