Numerical advances in Self-Consistent Field Theory simulations of Block Copolymers

Carlos Garcia-Cervera
Mathematics Department, UCSB
IPAM, UCLA, 2013
Collaborators

- Hector D. Ceniceros, Mathematics, UCSB
- Kris Delaney, MRL, UCSB
- Glenn H. Fredrickson, MRL, UCSB
- Edward Kramer, Materials, UCSB

- Su-Mi Hur, Chemical Eng., U. Wisconsin-Madison
- Tanya Chantawansri, Army Research Lab, Maryland
- Sean Paradiso, Chemical Eng., UCSB
- Per Von Soosten, Mathematics, UCSB
Block Copolymer Lithography

- Thermodynamic incompatibility & chemical bonding → microscopic phase separation

- Self-assembly of block copolymer thin films: a promising high resolution, next generation lithographic tool

Bulk Phases of Diblock Copolymers

- In 3D we can see 6 bulk phases
  - L: Lamellar
  - C: Cylindrical
  - S: Spherical
  - G: Gyroid
  - PL: Perforated-lamellar
  - D: Double Diamond

- In 2D we can only see 2 of these phases
  - L: Lamellar
  - C: Cylindrical

Directed Self-Assembly

- Long range dimensional control – removal of defects and grain boundaries
- Placement accuracy: satisfying alignment and registration tolerances

**Chemically Patterned Substrate**


**Topographically Patterned Substrate (graphoepitaxy)**


Requirements for Block Copolymer Lithography

- Improved long range dimensional control
- Placement accuracy: satisfying alignment and registration tolerances
- Improved resolution and linear density - beyond the 10 nm?
- Basis set of essential features

Non-natural structures

- Features with multiple sizes and pitches in the same layer
- Satisfying pattern transfer requirements and integration
- Enhanced process window
- Achieving throughput requirements, either via single wafer or batch processing: average net throughput of ~1 wafer per 1-2 minutes

International Technology Roadmap for Semiconductors
Evaporation Dynamics

http://www1.eere.energy.gov/solar/sunshot/pv_organic.html

Pattern Selection via Controlled Evaporation

Self-Consistent Field Theory (SCFT)

- Particle based model: many Gaussian chains interacting with each other (\(\sim\) Wiener Process)

\[
Z = \int \mathcal{D}r \exp(-\beta U[r]) \quad U[r] : \text{potential energy}
\]

Hubbard-Stratonovich Transformation

- Field based model: single-chain in the field

\[
Z = \int \mathcal{D}w \exp(-H[w]) \quad H[w] = C \int_V dx h(w) - n \ln Q[w]
\]

\(H[w]\) : effective Hamiltonian (energy functional of field \(w\))

\(C\) : coordination number (dimensionless chain concentration)

\(Q[w]\) : a single chain partition function in an external field \(w\)

- Mean field approximation: single configuration dominates the partition

\[
Z = \int \mathcal{D}w \exp(-H[w]) \xrightarrow{\infty} Z \approx \exp(-H[w^*]) \quad \beta A = -\ln Z \approx H[w^*]
\]
Self-Consistent Field Theory

- Single-chain partition function $Q$

$$Q[w] = \frac{1}{V} \int_V E_x \left[ \exp \left\{ - \int_0^1 w(X_s) \, ds \right\} \right] \, dx$$

- Energy functional $H[w]$ and density operators can be evaluated from chain propagator $q(x, s; [w])$ (Feynman-Kac)

$$Q[w] = \frac{1}{V} \int_V q(x, 1) \, dx$$

$$\frac{\partial}{\partial s} q(x, s; [w]) = \Delta q(x, s; [w]) - w(x)q(x, s; [w]),$$

$$q(x, 0; [w]) = 1, \text{ plus b.c.}$$


SCFT Equations

- **Effective Hamiltonian:**

\[ H[W, \Sigma] = \int_V \left( (1 - 2f)W - \Sigma + \frac{1}{\chi N} W^2 \right) dx - V \ln Q[W, \Sigma], \]

where

\[ Q[W, \Sigma] = \frac{1}{V} \int_V q(x, 1) dx, \]

and \( q \) satisfies the diffusion equation

\[ \frac{\partial q}{\partial s} = \Delta q - \psi q, \quad x \in V, \quad s \in (0, 1), \]

\[ q(x, 0) = 1. \]

We have defined

\[ \psi = \begin{cases} 
\Sigma - W, & 0 \leq s \leq f, \\
\Sigma + W, & f < s \leq 1.
\end{cases} \]
SCFT Equations – Gradient Flow

- **Dynamics:**
  - Mean field (saddle point) solution (SCFT)
  - Solving for Q and densities: most numerically expensive step.

\[
\frac{\partial W}{\partial t} = \phi_A(x; W, \Sigma) - \phi_B(x; W, \Sigma) + 1 - 2f - \frac{1}{\chi_N} W,
\]

\[
\frac{\partial \Sigma}{\partial t} = \phi_A(x; W, \Sigma) + \phi_B(x; W, \Sigma) - 1,
\]

\[
\phi_A(x; W, \Sigma) = \frac{1}{Q} \int_0^f q(x, s)q^\dagger(x, 1 - s) \, ds,
\]

\[
\phi_B(x; W, \Sigma) = \frac{1}{Q} \int_f^1 q(x, s)q^\dagger(x, 1 - s) \, ds,
\]

\[
Q = \frac{1}{V} \int_V q(x, 1) \, dx.
\]
Basic Schematic

Start: Generate Random Initial Field Configurations $W_{r}(u,0)$ and $W_{r}(u,0)$

Solve Modified Diffusion Equations

Solve the Single Chain Partition Function

Calculate the Densities

Update the Fields $W_{r}(u,t)$ and $W_{r}(u,t)$

Convergence Criterion Met? Yes

End

No
Existence of Solutions

- Dynamics equations: ODE in a Banach space.
  \[
  \frac{dy}{dt} = F(y); \quad F : (L^p(V))^2 \rightarrow (L^p(V))^2, \quad p \geq \frac{3}{2}
  \]

- F is Lipschitz: Follows from Kato-Rellich + semigroup estimates:
  \[
  q(s) = e^{s(\Delta - \psi)} q_0
  \]

- F is in fact Fréchet differentiable:
  \[
  q(s) = e^{s\Delta} q_0 - \int_0^s (s-t)^{\Delta} \psi e^{t\Delta} q_0 \, dt + O(\|\psi\|^2)
  \]

- Picard’s theorem: (Local) Existence and Uniqueness.
- Global existence: Extension of local solutions.
Phase separation: Bifurcation

- We consider symmetric solutions:
  \[ F(W, \Sigma, \chi_N) = 0; \quad F : (L^p(V))^2 \times (0, \infty) \to (L^p(V))^2, \quad p \geq \frac{3}{2} \]

- Homogeneous solution: \( F(0, 0, \chi_N) = 0 \quad \forall \chi_N \)

- Fréchet derivative:
  \[ F'(0, 0, \chi_N) = \begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix}, \]

where

\[
T_{11} = 2\Delta^{-1} + 2\Delta^{-2} \left( I - e^{\Delta} \right), \\
T_{12} = 2(1 - 2f)\Delta^{-1} + 2\Delta^{-2} \left( e^{f\Delta} - e^{(1-f)\Delta} \right), \\
T_{21} = -T_{12}, \\
T_{22} = -2\Delta^{-1} - 2\Delta^{-2} \left( 3I - 2e^{f\Delta} - 2e^{(1-f)\Delta} + e^\Delta \right) - \frac{2}{\chi_N}.
\]
Phase separation: Bifurcation (cont.)

- Crandall-Rabinowitz-type of bifurcation.

SCFT Equations: Numerics

- **Dynamics:**
  - Mean field (saddle point) solution (SCFT)
  - Solving for $Q$ and densities: most numerically expensive step.

\[
\frac{\partial W}{\partial t} = \phi_A(x; W, \Sigma) - \phi_B(x; W, \Sigma) + 1 - 2f - \frac{1}{\chi_N} W,
\]

\[
\frac{\partial \Sigma}{\partial t} = \phi_A(x; W, \Sigma) + \phi_B(x; W, \Sigma) - 1,
\]

\[
\phi_A(x; W, \Sigma) = \frac{1}{Q} \int_0^f q(x, s)q^\dagger(x, 1-s) \, ds,
\]

\[
\phi_B(x; W, \Sigma) = \frac{1}{Q} \int_f^1 q(x, s)q^\dagger(x, 1-s) \, ds,
\]

\[
Q = \frac{1}{V} \int_V q(x, 1) \, dx.
\]
SCFT Equations: Challenges

- **Main ingredients:**
  - Time-stepping of the chemical potentials.
  - Solver for modified diffusion equation.
  - Integration along the polymer chain.
- Nonlinear, nonlocal equations.
- Fully implicit: too costly.
- **Semi-Implicit Scheme via Linearization:**

\[
\frac{W^{n+1} - W^n}{\Delta t} = \mathcal{L}[W^{n+1}] + F[W^n] - \mathcal{L}[W^n]
\]
Semi-Implicit Scheme for SCFT

- Consider: \[
\frac{\partial q}{\partial s} = \Delta q - \epsilon \omega q; \]

- **Asymptotic expansion (RPA):**

  \[
  q(x, s) = 1 + \varepsilon \sum_{k \neq 0} \hat{q}_1(k, s)e^{ikx} + O(\varepsilon^2),
  \]

  \[
  q^\dagger(x, s) = 1 + \varepsilon \sum_{k \neq 0} \hat{q}_1^\dagger(k, s)e^{ikx} + O(\varepsilon^2).
  \]

- **Leading term in the density:**

  \[
  \phi_A(x) = f + \varepsilon \sum_{k \neq 0} e^{ikx} \int_0^f (\hat{q}_1(k, s) + \hat{q}_1^\dagger(k, 1-s)) \, ds + O(\varepsilon^2),
  \]

  \[
  \phi_B(x) = 1 - f + \varepsilon \sum_{k \neq 0} e^{ikx} \int_f^1 (\hat{q}_1(k, s) + \hat{q}_1^\dagger(k, 1-s)) \, ds + O(\varepsilon^2).
  \]
Semi-Implicit Scheme for SCFT

\[
\frac{\Sigma^{n+1} - \Sigma^n}{\Delta t} = -(g_{AA} + 2g_{AB} + g_{BB}) \ast \Sigma^{n+1} + (\phi_A^n + \phi_B^n - 1) + (g_{AA} + 2g_{AB} + g_{BB}) \ast \Sigma^n,
\]

\[
\frac{W^{n+1} - W^n}{\Delta t} = \phi_A^* - \phi_B^* + 1 - 2f - \frac{2}{\chi N} W^{n+1}.
\]

\[
\hat{g}_{AA}(k) = \frac{2}{|k|^4} \left( f|k|^2 + e^{-|k|^2f} - 1 \right),
\]

\[
\hat{g}_{AB}(k) = \frac{1}{|k|^4} \left( 1 - e^{-|k|^2f} \right) \left( 1 - e^{-|k|^2(1-f)} \right),
\]

\[
\hat{g}_{BB}(k) = \frac{2}{|k|^4} \left( (1 - f)|k|^2 + e^{-|k|^2(1-f)} - 1 \right).
\]

This scheme is unconditionally stable.

Modified Diffusion Equation

\[ \frac{\partial q}{\partial s} = \Delta q - \psi q, \quad x \in V, \quad s \in (0, 1), \]

\[ q(x, 0) = 1, \]

Operator Splitting (2\textsuperscript{nd} order):

\[ q_{n+1} = e^{-\frac{\psi \Delta s}{2}} e^{\Delta s \Delta} e^{-\frac{\psi \Delta s}{2}} q_n \]

G. Strang, *Numerische Mathematik*, 6, 1964

Solving the Modified Diffusion Equation

**Modified Diffusion Equation:** \[
\frac{\partial q}{\partial s} = \Delta q - \psi q
\]

**Fourth Order BDF, initialized with Backward Euler + Extrapolation:**

\[
\frac{25}{12} q_{n+1} = 4q_n - 3q_{n-1} + \frac{4}{3} q_{n-2} - \frac{1}{4} q_{n-3} + \Delta s \left[ \Delta q_{n+1} - w(u)(4q_n - 6q_{n-1} + 4q_{n-2} - q_{n-3}) \right]
\]

**Trapezoidal rule with endpoint corrections:**

\[
\int_I f \, ds = \Delta x \sum_{i=0}^{m'} f_i - \frac{\Delta s^2}{12} \left( \frac{3f_m - 4f_{m-1} + f_{m-2}}{2\Delta s} - \frac{3f_0 - 4f_1 + f_2}{2\Delta s} \right) + O(\Delta s^4)
\]

Stability of the gyroid phase


Block-Copolymers on Curved Surfaces

Total of 446 domains: 69 (5-fold) , 350 (6-fold) , and 57 (7-fold)
Lamellar phase

**Lithography: AB in a Square Well**

\[ f_A = 0.7 \]

B-cylinders in hexagonal arrays w/o confinement

\[ \chi N = 13.75 \quad 15.75 \quad 17 \]

Tetragonal ordering is induced by the square lateral confinement during annealing stage.

Lattice subsequently twists into hexagonal ordering in order to reduce the stress in the interstitial sites.

AB + A in a Square Well

- A-homopolymer additive stabilizes tetragonal ordering

\[ f_A = 0.7 \]
B-cylinder forming diblock

\[ \alpha = 1.75 \quad (N_{Ah}/N) \]
\[ V_{Ah} = 0.23 \]
A(major block)-homopolymer

- B-attractive wall

\[ L = 23 \ R_g \]

A-homopolymer localization decreases the free energy of the square configuration such that it is energetically more favorable than the hexagonal configuration.
Bent Lines: AB + A + Confinement

\[ f_A = 0.5, \quad \text{Channel Width} = 9 \, R_g \]

- AB + neutral wall
- AB + A-attractive wall

+ A (\( \alpha = 0.5 \, (N_{Ah}/N), \quad V_{Ah}=0.2 \))

Dynamical Self-Consistent Field Theory

\[ \partial_t \phi_K = \nabla \cdot M_K \nabla \mu_K^{SCFT} + J_S \delta_{KS} \]

\( K = \{A, B, S\} \)

Density flux from SCFT free energy
Solvent removal from surface of film

SCFT Free Energy

Free energy $\Rightarrow$ Legendre Transform of $H[w]$

$$F[\rho] = \sup_w \left\{ \int_V \rho w - H[w] \right\}$$

$\downarrow$

$$\rho(x) = \phi(x; w^*) \ (\text{Feynman} - \text{Kac})$$

Nonlinear, Nonlocal equation
Chemical Potential: SCFT Free Energy

\[
\mu(r,t)_K^{SCFT} = \left. \frac{\delta H}{\delta \phi(r,t)_K} \right|_{w^*}
\]

\[
= C \left\{ \sum_J \chi_{kJ} \phi(r,t)_j - w(r,t)_K^* + \zeta \left( \left( \sum_J \phi(r,t)_j \right) - 1 \right) \right\}
\]

\[
\hat{\phi}_K (r; w^*) = \int q(r,s; w^*) q'(r,s; w^*) ds = \phi_K (r,t)
\]
Parameters Involved In Our Study

\[ \chi_{AB} \chi_{AS} \chi_{BS} \]

\[ f, N \]

\[ \phi_S^{eq} \]

\[ \chi_{AB}^\text{eff} N = (1 - \phi_S^{eq}) \chi_{AB} N \]

\[ J_S = \lambda (\phi_s - \phi_s^{eq}) \]
Moving Boundary Model

\[ \partial_t \phi_K = \nabla \cdot M_K \nabla \mu_K^{SCFT} + J_S \delta_{KS} \]

\[ \bar{z} = \frac{z}{L(t)} \]

\[ \left( \frac{\partial \phi}{\partial t} \right)_{\bar{z}} = \left( \frac{\partial \phi}{\partial t} \right)_z + \left( \frac{\partial \phi}{\partial z} \right)_t \left( \frac{\partial z}{\partial t} \right)_{\bar{z}} \]

\[ = \nabla \cdot M \nabla \mu^{SCFT} + \bar{z}L'(t) \left( \frac{\partial \phi}{\partial z} \right)_t \]
Verification of Continuum Dynamics

MD Simulation Details:
- 6-12 LJ Fluid
- FENE bonds
- Strong 10-4 LJ interaction with z=0 surface prevents a ‘floating’ film

Typical Moving Boundary Model Profiles:

Evaporation Dynamics in 2D: Lamellae

\begin{align*}
\chi_{AB}N &= 22 \\
\phi_{BCP}^e &= 0.5 \\
\phi_S^e &= 0.3
\end{align*}

\begin{align*}
\chi_{AB}N &= 22 \\
\phi_{BCP}^e &= 0.5 \\
\phi_S^e &= 0.18
\end{align*}
Morphology Guided by Secondary Patterns

- Ordered phase *induces density correlations* in near-critical fluid beneath it.
  - Every dynamical result exhibits some form of this pattern.
Block connectivity

- Stripes terminate in dangling chain ends of the opposite type
- Results in an increase in the probability of finding B segments beneath A-rich Lamellae
Control Experiments

Evaporation simulations on a symmetric blend (a) and diblock (b) system implicate chain connectivity in patterning at the front.

Cylinder-forming systems (d) emerge a pattern analogous to the “struts” in (b) and (c)
Evaporation Trajectories
Trends in Surface Morphology

\[ \phi_s^{eq} \]

\[ 0.17 \]

\[ 0.26 \]

\[ 0.35 \]

\[ \chi_{AB}^{\text{eff}} N \]

\[ 16.0 \]

\[ 16.2 \]

\[ 16.5 \]

\[ 16.7 \]

\[ 17.0 \]
Trends in Surface Morphology

- Parameters $\phi_S^\text{eq}$ and $\chi_{AB}^\text{eff}$ are changed independently.
- $\chi_{AB}^\text{eff}$ increased: morphologies transition from perpendicular to horizontal.
- Changes in evaporation rate have minor effect.
Evaporation-driven Ordering
Evaporation-driven Ordering

- No order observed until unstable region near the surface forms: A layer of spheres appears.
- Spheres organize into a hexagonal lattice.
- A bifurcation occurs: For high $\chi_{AB}^{\text{eff}}$, spheres are unstable as seen in phase diagram.
- Lower values of $\chi_{AB}^{\text{eff}}$ or slower evaporation rates provide sufficient time for solvent gradients to advance, and spheres to stretch.
Molecular Origin of Induced Patterns

- **Block connectivity**
  - Stripes terminate in dangling chain ends of the opposite type
  - Results in an increase in the probability of finding B segments beneath A-rich Lamellae
Mitigating the Correlation-Hole

- The correlation-hole pattern that forms beneath $C_{\perp}$ presents an increased density of minority-block segments.

- Hypothesis: solvent selective for majority block will provide a barrier to forming this pattern and stabilize $C_{\perp}$ fronts
Selective Solvent Results

Minority-Selective  Neutral  Majority-Selective
Selective Solvent Stabilizes Cylinder Formation

Increasing Solvent Selectivity
Overview and Future Work

- Developed efficient predictive numerical methodologies.
- Numerical experiments guide design of lithographic approaches and elucidate evaporation-induced pattern selection.

- Further understanding of evaporation processes needed.
- Hydrodynamics: Coupling to Navier-Stokes?.
- Dynamic density functional theory: Can we invert the density? $\rho_0 = \rho(x; W, \Sigma) \rightarrow$ Can we recover $W$ and $\Sigma$?
- Framework too complicated: Can we obtain reduced models?

Acknowledgments

- We received partial support from the MARCO Center on Functional Engineered Nano Architectonics (FENA).
- This work made use of MRL Central Facilities supported by the MRSEC and MRI-R2 Programs of the National Science Foundation under award No. DMR05-20415 and NSF MRI-R2 0960316.
- Support provided by NSF CAREER, and NSF SOLAR awards.