Self-Assembly of a Lamellae-Forming Block Copolymer on Sparse Nanopatterns

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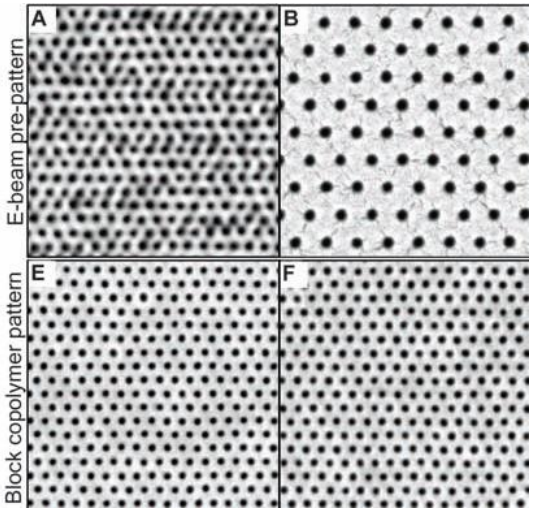
Interpolation on spare nanopatterns

Block-copolymers can form defect-free structures on sparse patterns.

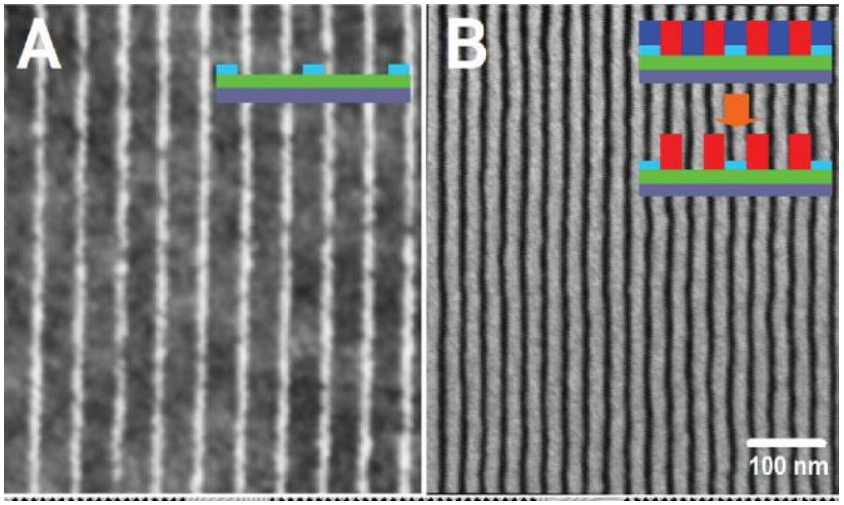
cylinder- forming copolymer



Ruiz, R. *et al*. *Science*, **2008**.

One spot for 4 cylinders

lamellae-forming copolymer



Cheng, J. Y. *et al. Adv. Mat.*, **2008**

One stripe for 2 lamellae

What morphologies arise in density multiplication with symmetric copolymers?
How robust is the multiplication process ?

Interpolation on spare nanopatterns

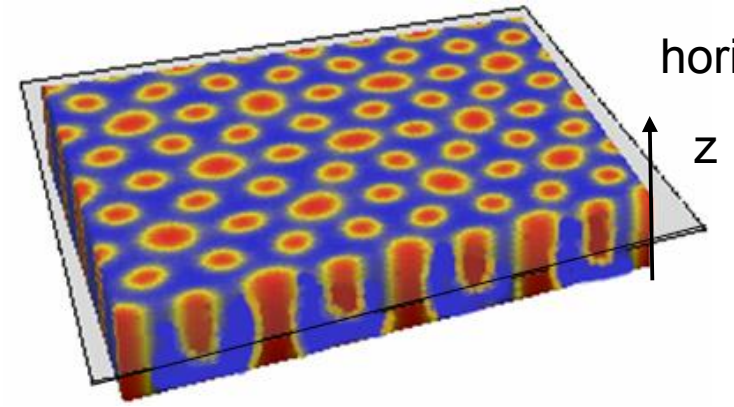
What are the conditions for a successful interpolation?

Two ways to envision the problem:

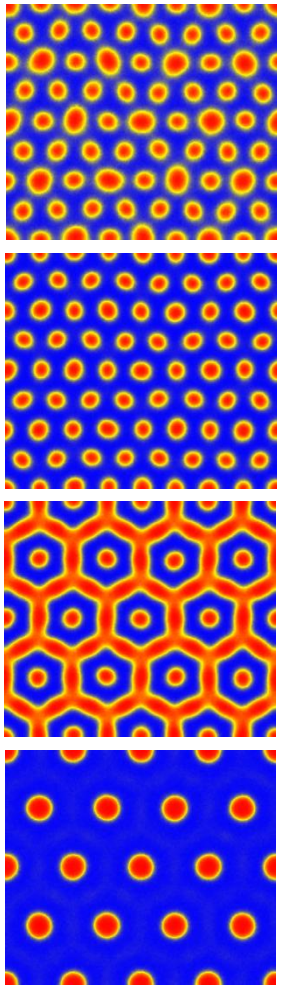
1. The block copolymer mostly adopts its bulk morphology. The nanopattern serves only to pin the domains and enforce long-range alignment.

2. The nanopattern induces non-bulk morphologies and interpolation is only possible with a careful choice of the pattern properties

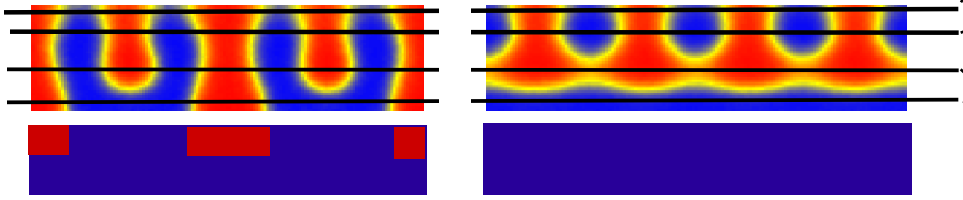
Non-bulk morphology in interpolation of cylinders



horizontal cross-sections



vertical cross-sections



patterned line

non-patterned line

strong PMMA/spot attraction favors defect-free assembly but leads to hour-glass shaped domains.

Experimental system

A symmetric diblock on a stripe-patterned substrate

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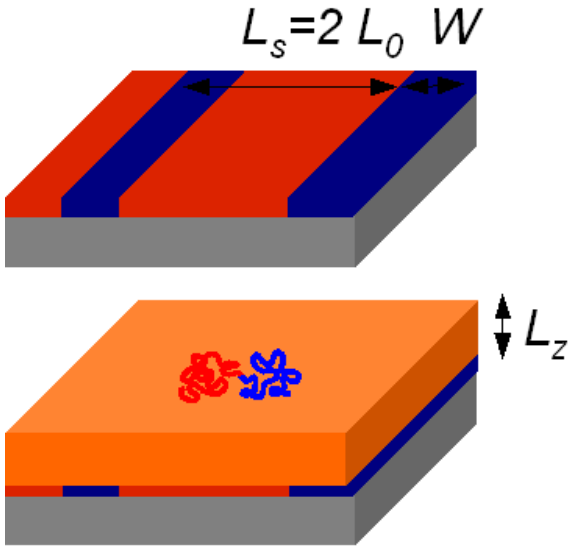
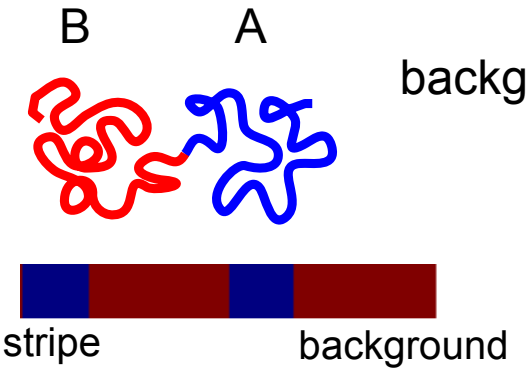


A large parameter space

- film thickness L_z
- pattern periodicity L_s
- stripe width W
- block/pattern strength of interaction



	A	B
background	$-\Lambda_b$	Λ_b
stripe	Λ_s	$-\Lambda_s$

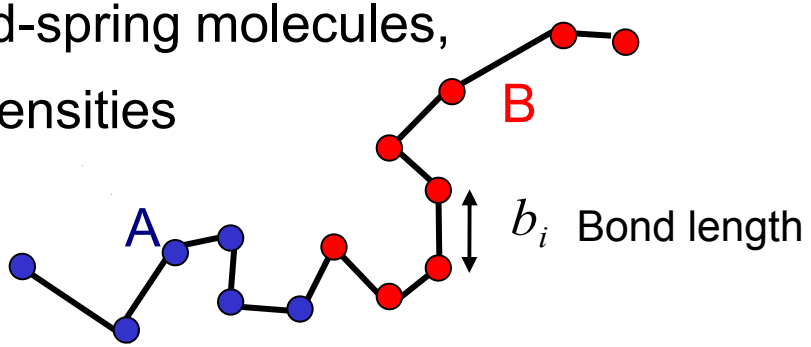
A combinatorial exploration of the parameter space is needed

A coarse-grained model

A mesoscopic description

Gaussian chains, discretized into bead-spring molecules, interact via a functional of the local densities

$$H/kT = 3/2\sum_i b_i^2 + E_{int}\left[\varphi_A, \varphi_B\right]$$



Interaction energy:

$$E_{int}\left[\varphi_A, \varphi_B\right]/\sqrt{N} \sim \chi N \int dr \varphi_A \varphi_B + \kappa N \int dr \left(1 - \varphi_A - \varphi_B\right)^2$$

incompatibility — finite compressibility

Helfand, J. Chem. Phys. (1975)

Coarse-grained parameters

R_e end-to-end distance

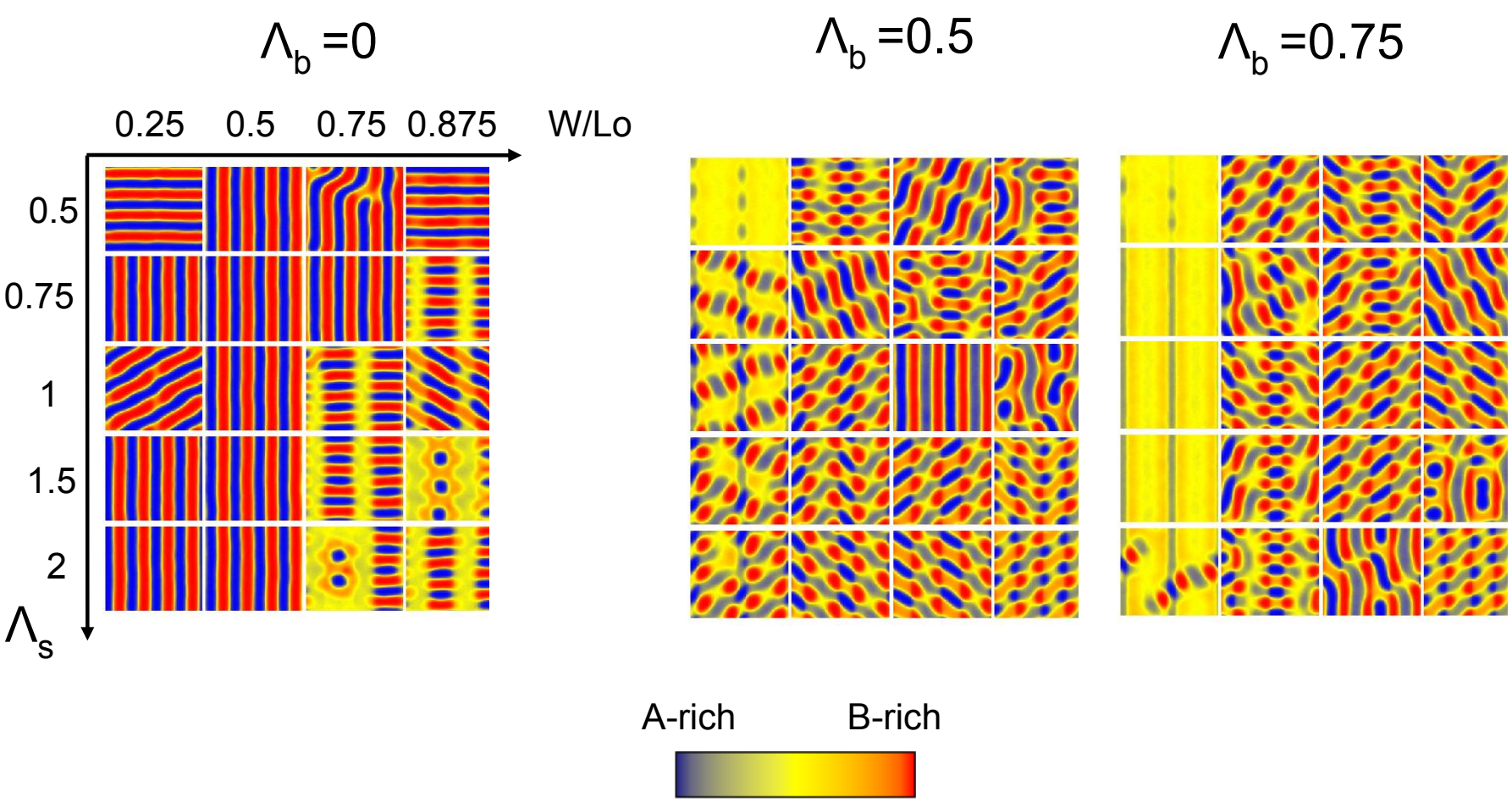
$\sqrt{N}$ number of chains in the volume occupied by a chain

$\chi N, \kappa N$ N, number of beads per chain $\sqrt{N} = \rho_{chain} R_e^3$

A combinatorial approach

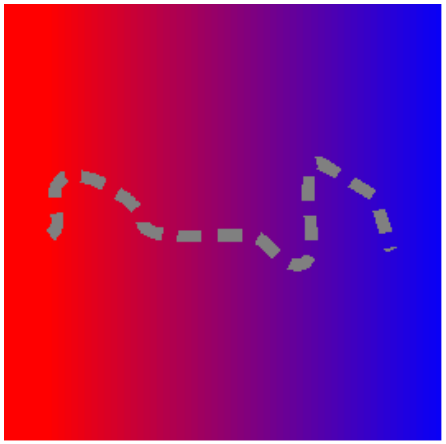
A simulated system typically includes 10000 chains.

The method is efficient enough to consider hundreds of parameter combinations.



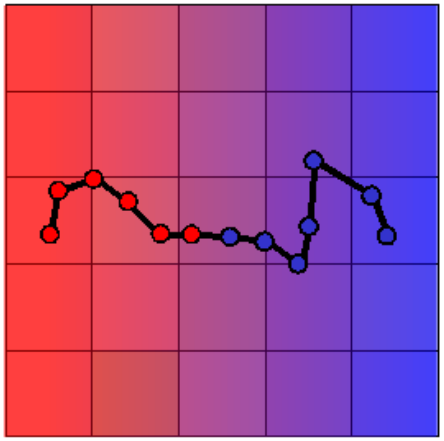
Methods

Self-consistent field theory



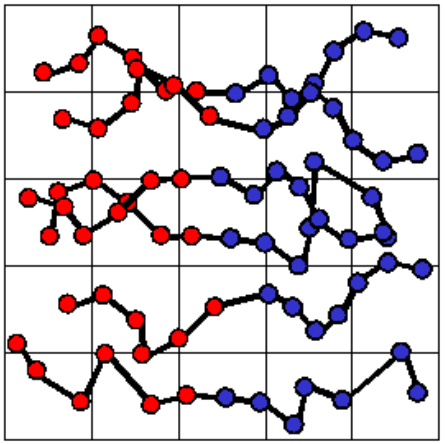
- field-based
- neglect fluctuations
- modified diffusion equation

Single-chain in mean-field simulations



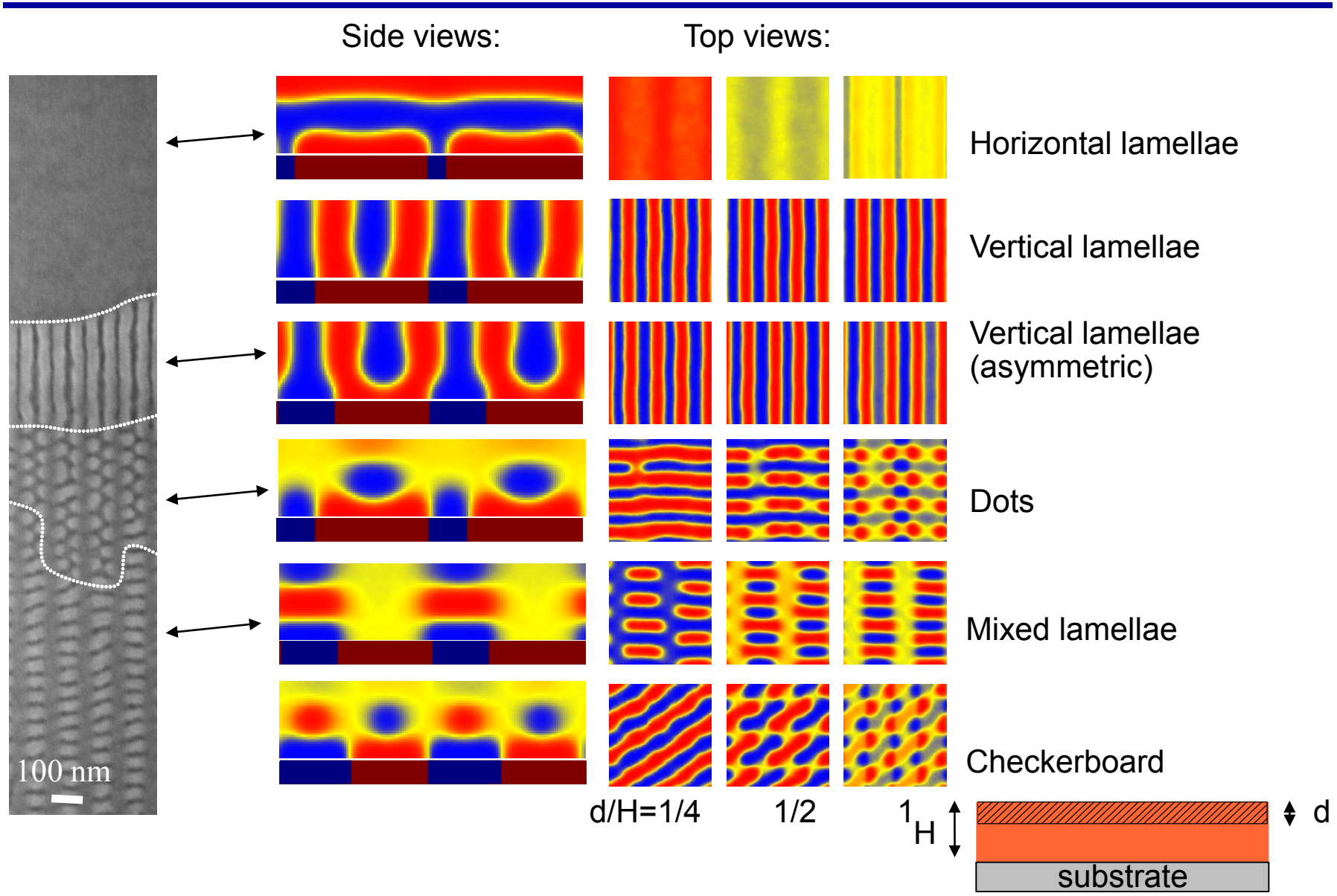
- particle-based but fields
- includes fluctuations
- two-step cycle

Monte Carlo simulations



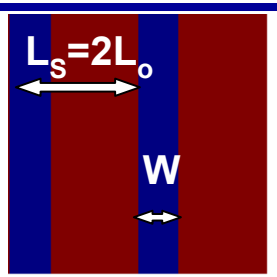
- particle-based, no fields
- includes fluctuations
- genuine MC simulation

A variety of morphologies



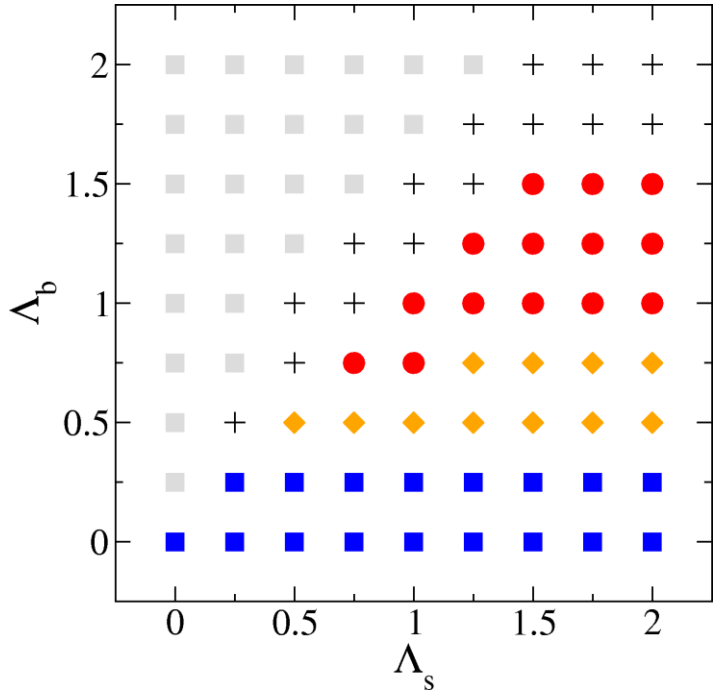
Exploring the parameter space

Effect of changing the pattern selectivity

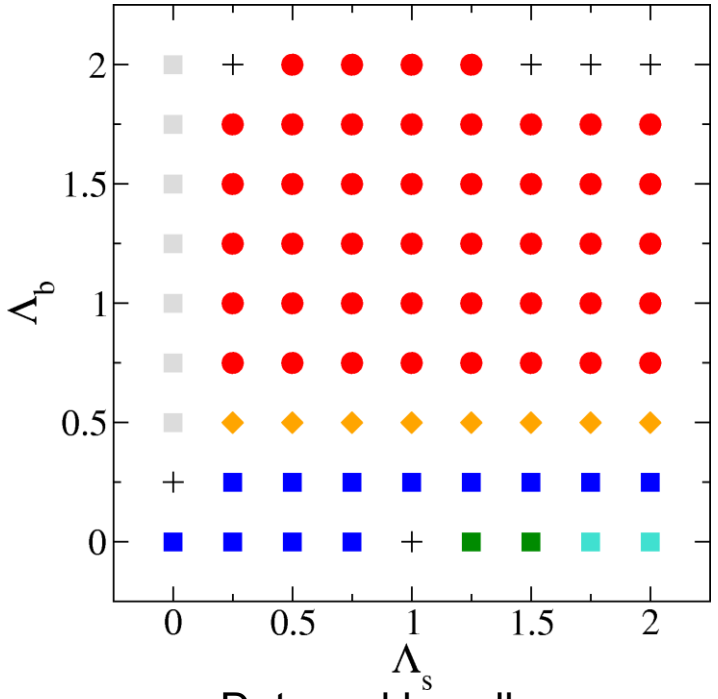


Fixed interpolation ratio $L_s/L_o=2$
Fixed thickness $H=Lo$

$W/L_o=0.5$



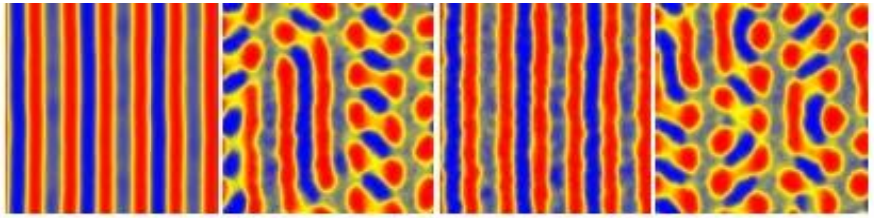
$W/L_o=0.75$



- Horizontal Lamellae
- Vertical Lamellae
- Mixed lamellae
- Dots
- Checkerboard
- Dots and lamellae
- Horizontal and mixed lamellae
- Hybrid

Thermodynamic integration

- Two competing morphologies
  Which one is equilibrium?



4distinct
simulations

- Free energy difference going from state 1 to state 2 :

$$\Delta F_{1\to 2} = \int du \left\langle \frac{\partial H}{\partial u} \right\rangle$$

The integration path must be fully reversible and continuous.

- Impose an external field that constrains the system to stay in the desired state:

$$H_{ext} = \sum U_{ext}(r_i, K_i) \qquad U_{ext}(r, K) = -\zeta f_{ext}(r)\,\varepsilon_K$$

A Reversible path: from lamellae to dots

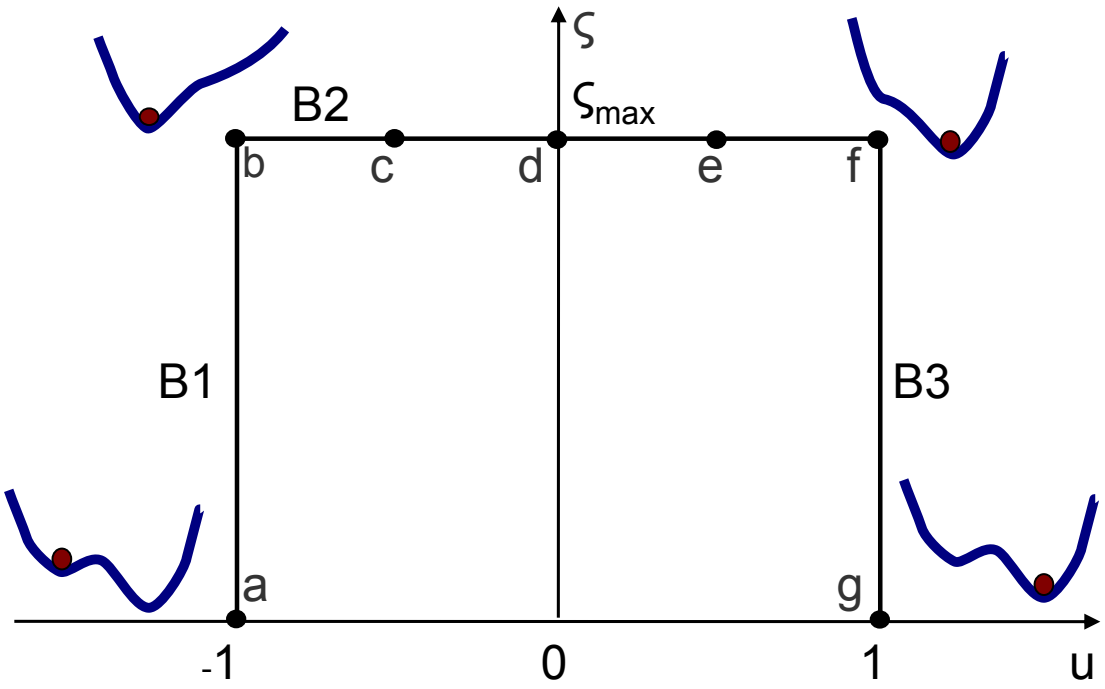
$\Delta F = F_{dot} - F_{lam}$

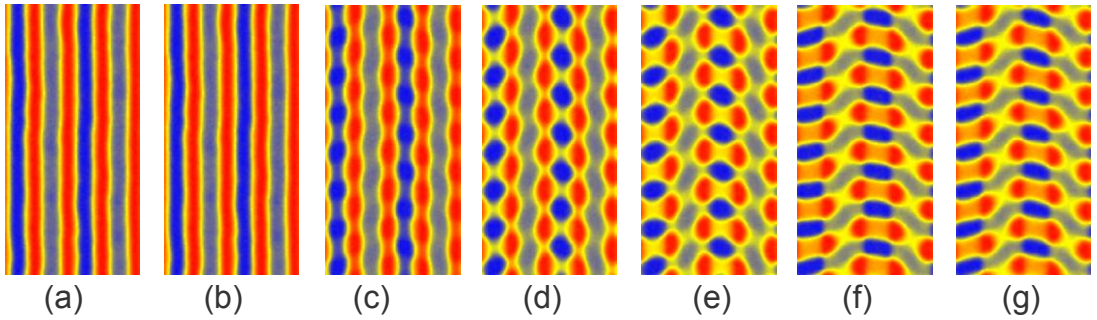
Three branches:

- Field branch B1: Start from lamellae and impose a lamellae-like external field to further stabilize morphology of the lamellae

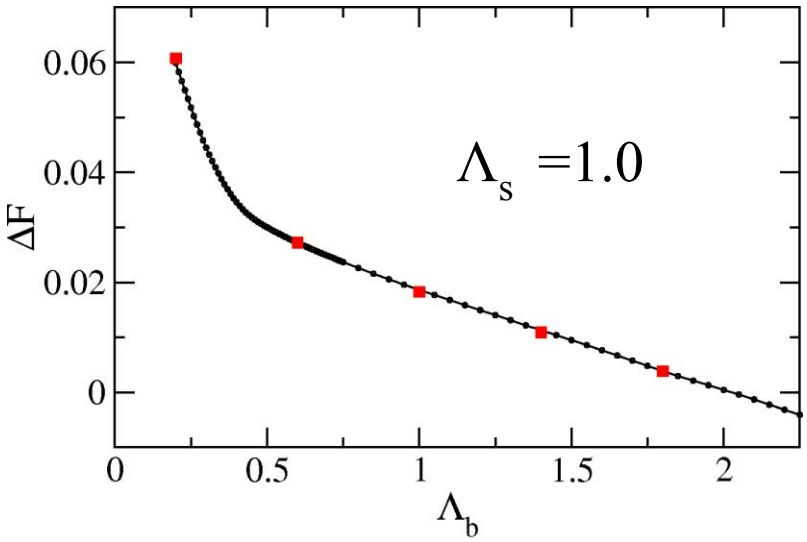
- Mixing branch B2 : gradually convert lamellae into dots using an inter-polated field

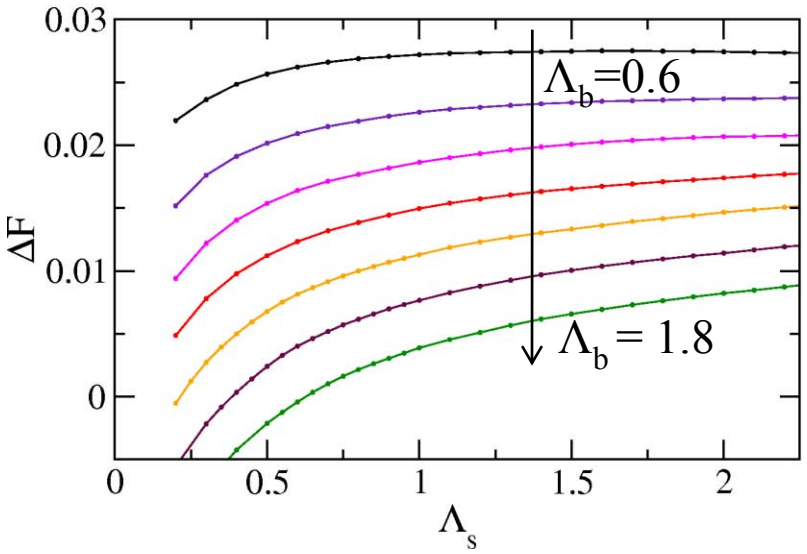
- Field branch B3 : decrease the dot-like field to zero.





Free energy calculations





$\Delta F = F_{dot} - F_{lam}$ ΔF in $k_b T$/chain

■ Absolute value of ΔF computed along the external field path

● ΔF computed from the reference point by simple thermodynamic integration:

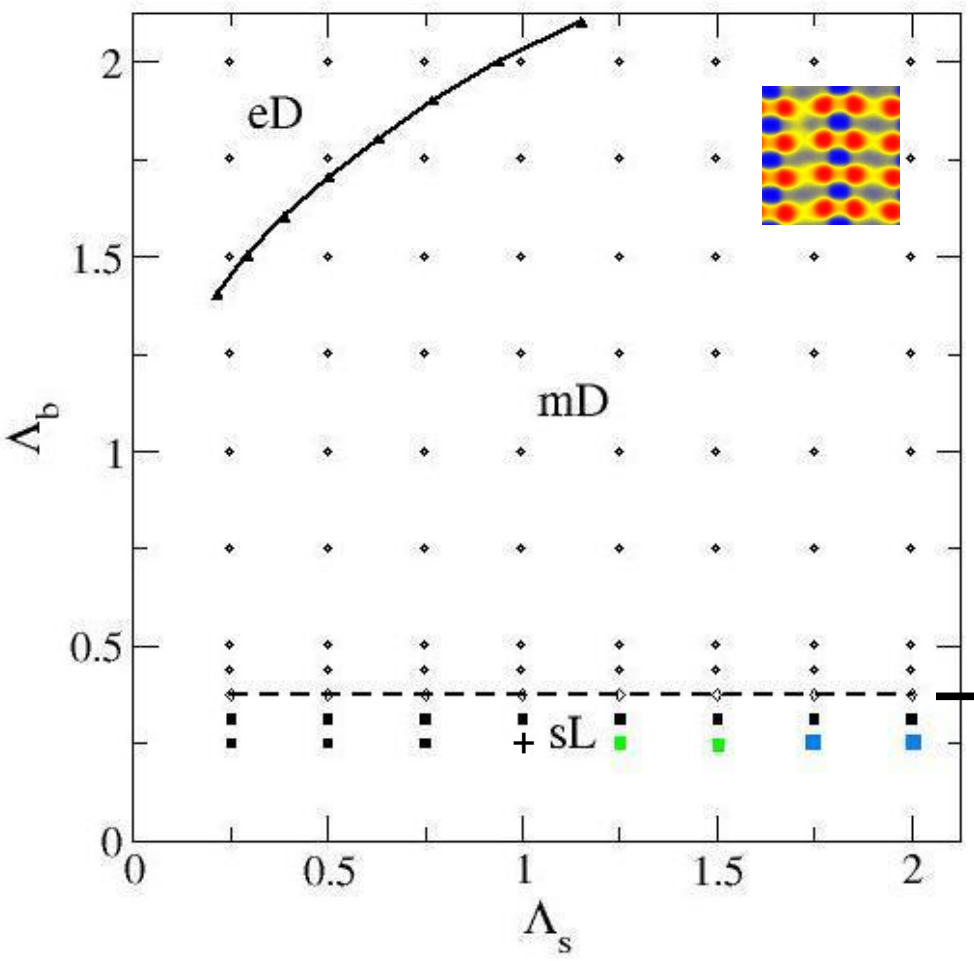
$$\Delta F = \int d\lambda_b \left\langle \frac{\partial H}{\partial \lambda_b} \right\rangle$$

→ good agreement between the two procedures

ΔF can then be computed for the entire plane Λ_s-Λ_b.

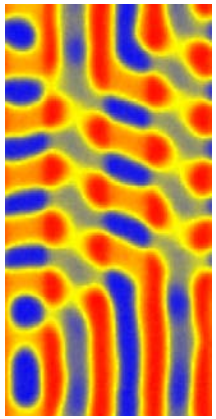
Metastability vs equilibrium

$W/L_o=0.75$



Morphology obtained in simulations:
: lamellae
: dots

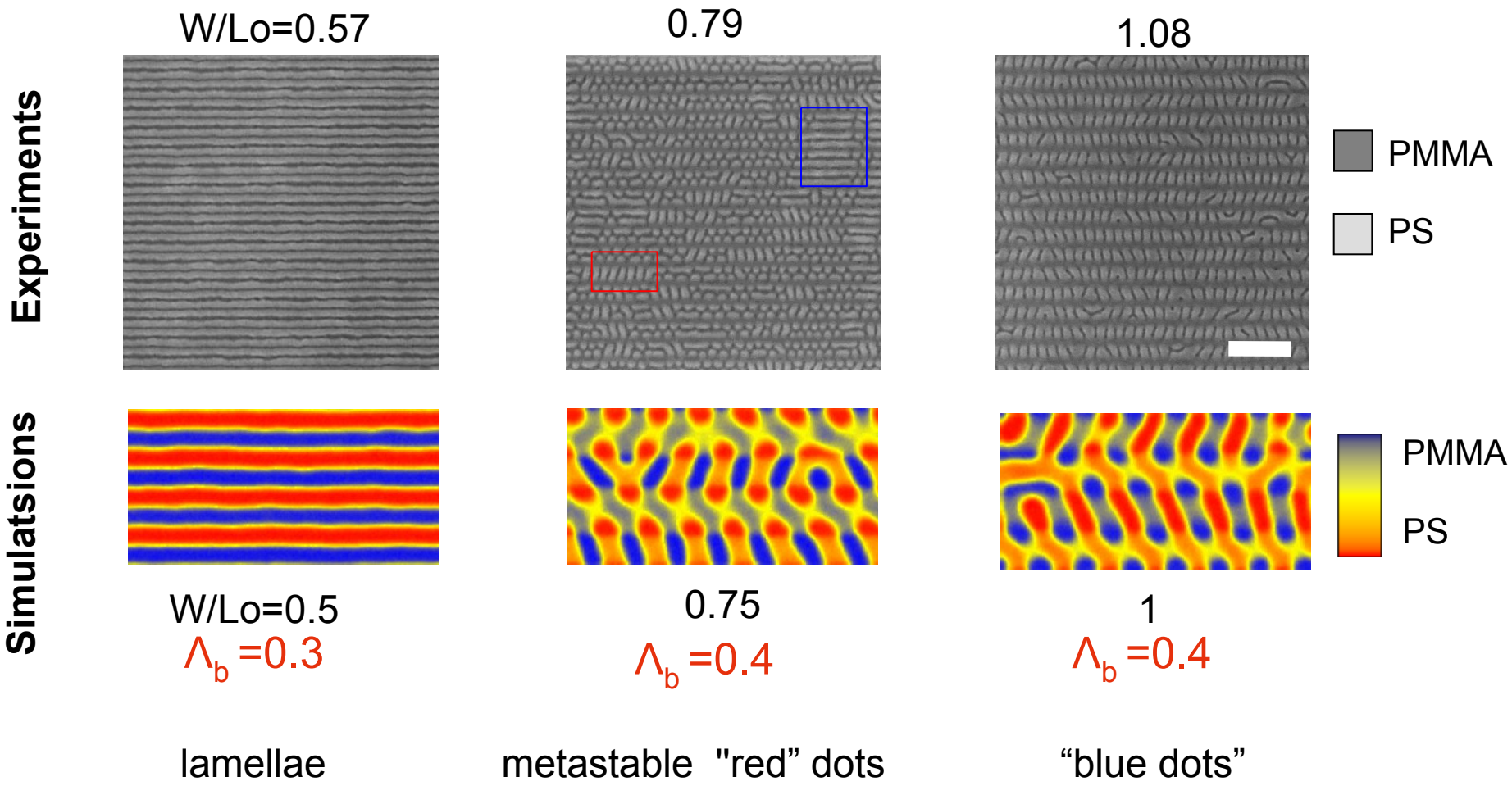
Three regions:
- eD : equilibrium dots
- mD: metastable dots
- sL : stable lamellae



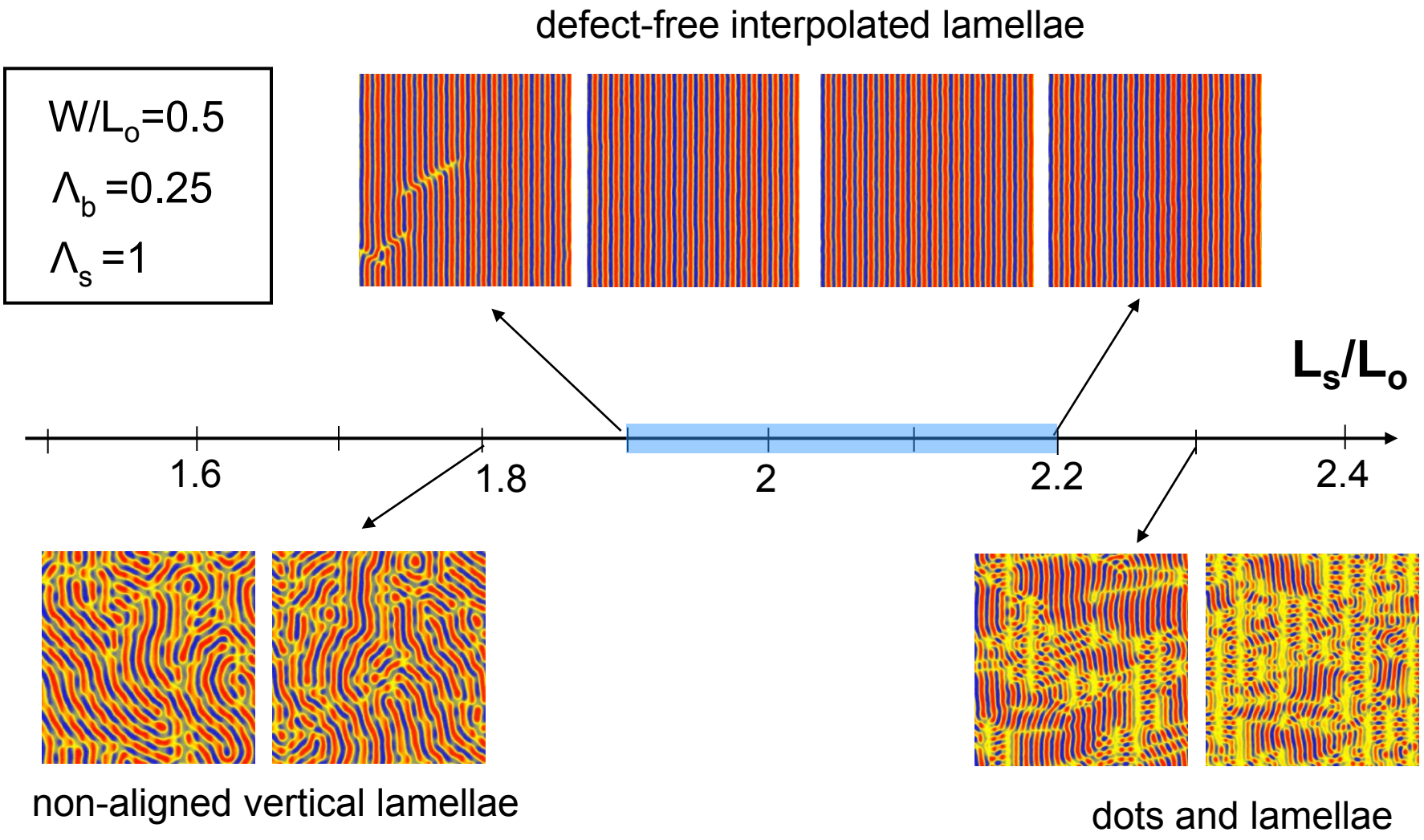
Formation of dots and lamellae in the same simulation box

This region of the parameter space is dominated by metastable dots.

Interpretation of experiments



Effect of pattern commensurability



Conclusions

- Using MC simulations of a coarse-grained model, we can efficiently simulate three-dimensional systems and explore wide regions of parameter space.

- Thermodynamic integration can be used to determine the free energy difference between two ordered morphologies.

- The process of pattern interpolation with lamellae produces distinct morphologies: horizontal, vertical, vertical asymmetric , mixed lamellae, dots and checkerboard .

- In the vicinity of $W/L_0=0.5$, metastable dot structures are predominant. Only low strength of the background are lamellae preferred both thermodynamically and dynamically.

Control of characteristic period, range of interpolation, and defects through homopolymer addition

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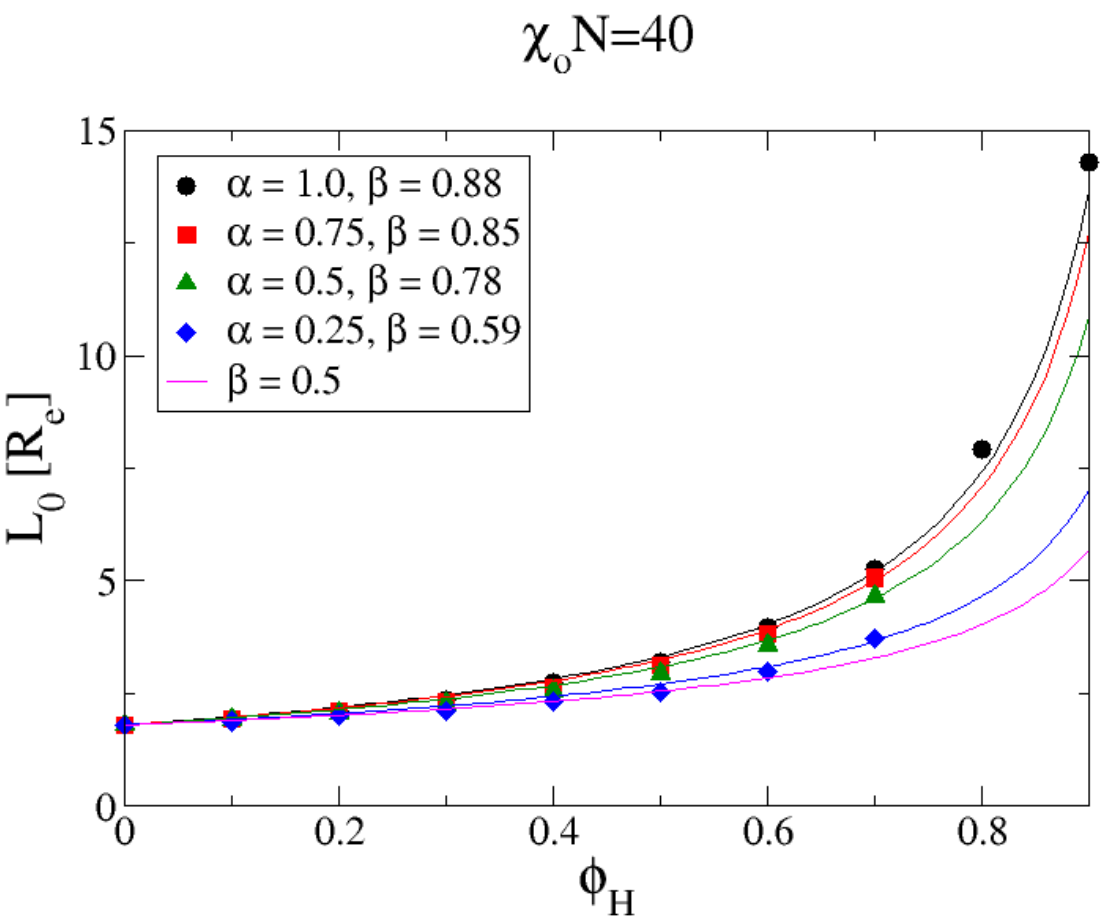
Ternary Mixtures, Optimal Period

The diblock copolymer can be swollen by each homopolymer, increasing the period.

The swelling can be fitted to the equation

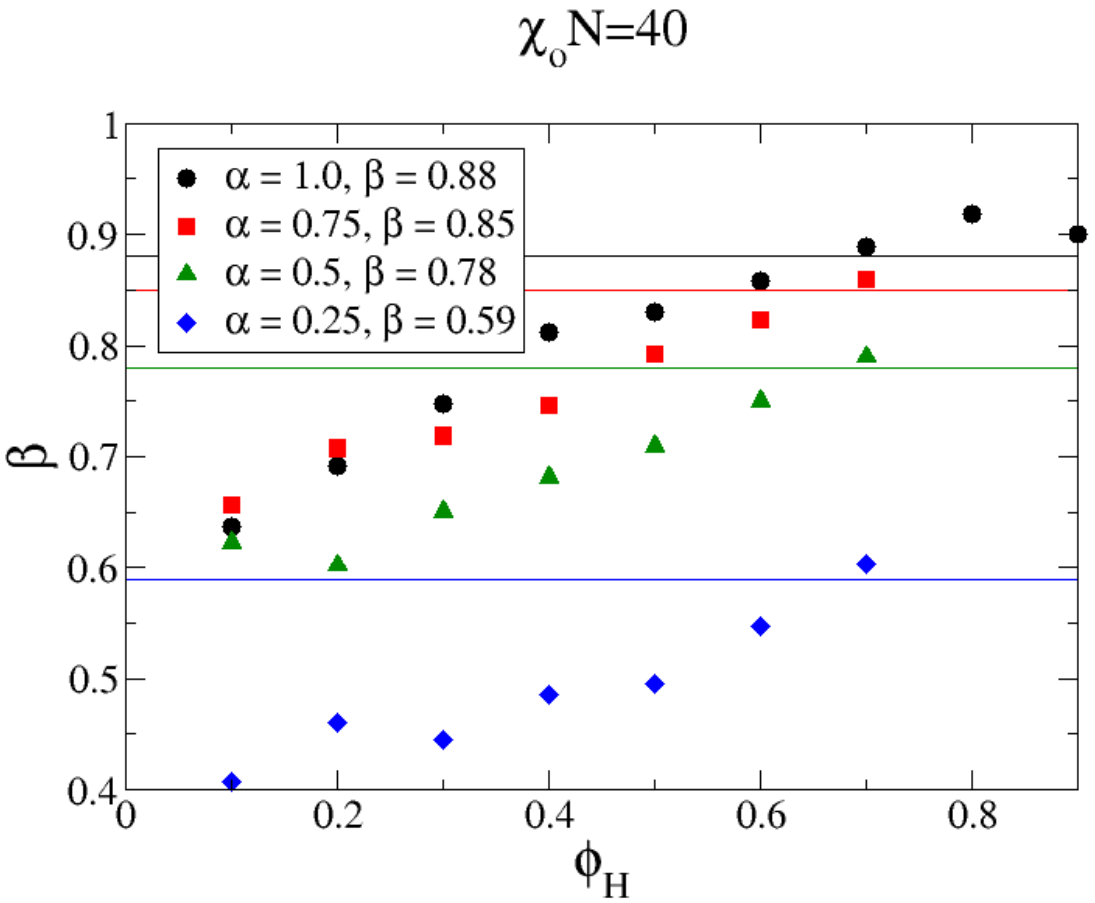
$$L_0(\varphi_H) = \frac{L_0(\varphi_H = 0)}{(1-\varphi_H)^{\beta}}$$



Values of β

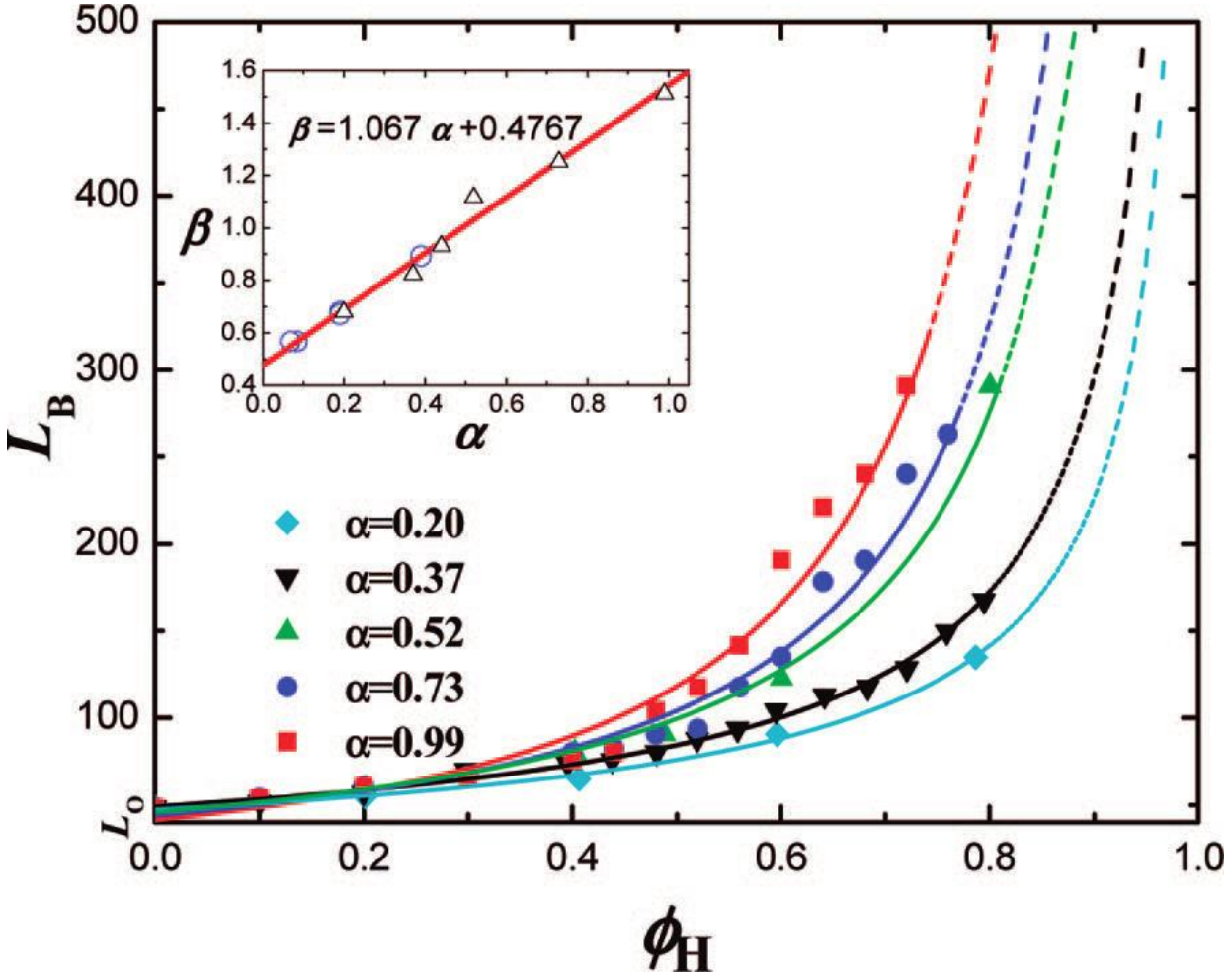
The value of β drifts as the lamellae become more swollen with homopolymers.

The curves on the preceding slide use the β values at around $\varphi_H = 0.7$.



Experimental Results

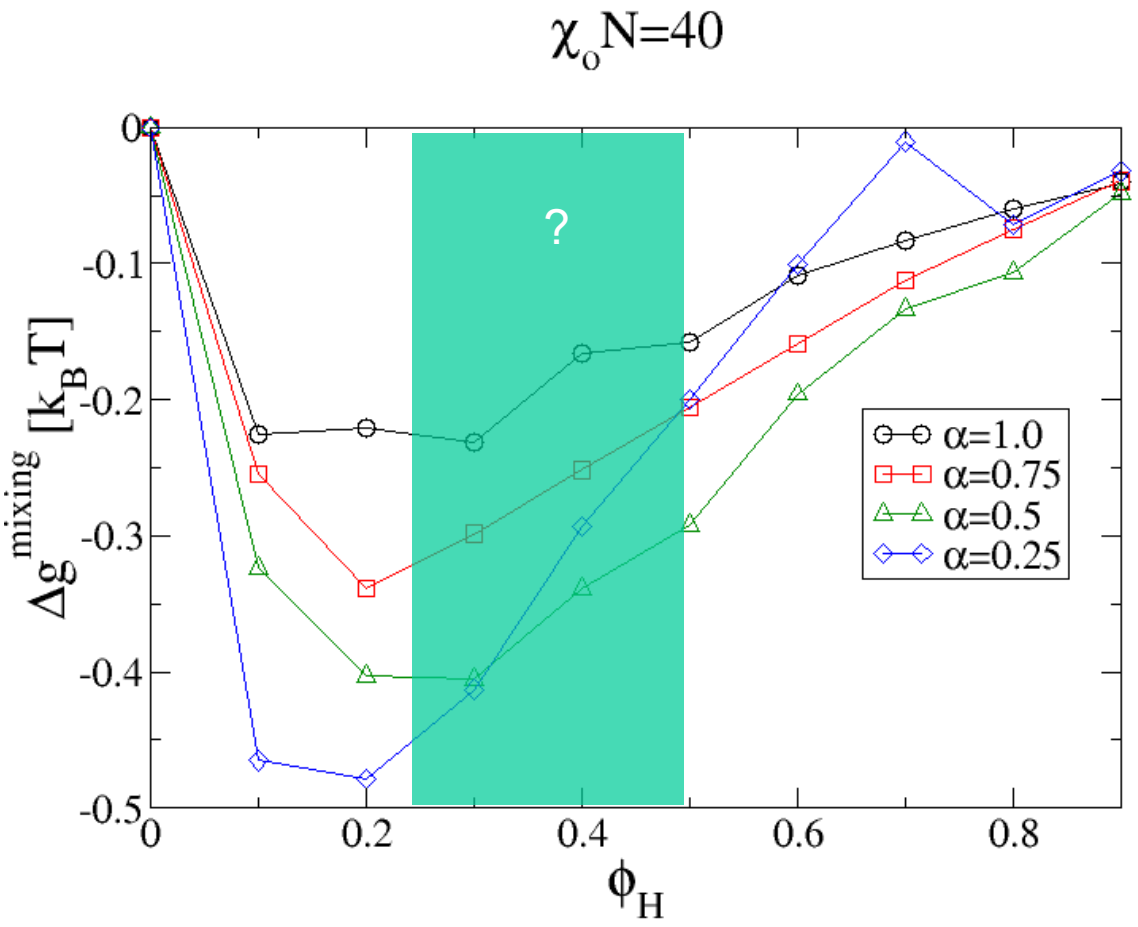
Experimentally, Guoliang produced larger values of β with a linear dependence in α.



Energy of Mixing

Free energy of mixing can be determined from Monte Carlo simulations.

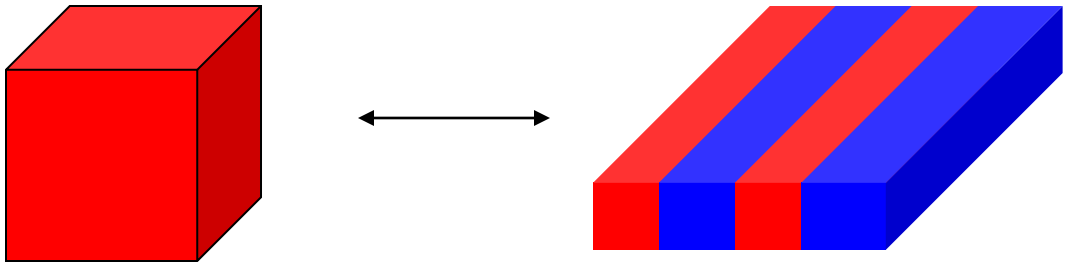
This value, along with interfacial energy and surface energy, can be used to determine where defect free structures are possible.



Optimal Swelling with Gibbs ensemble

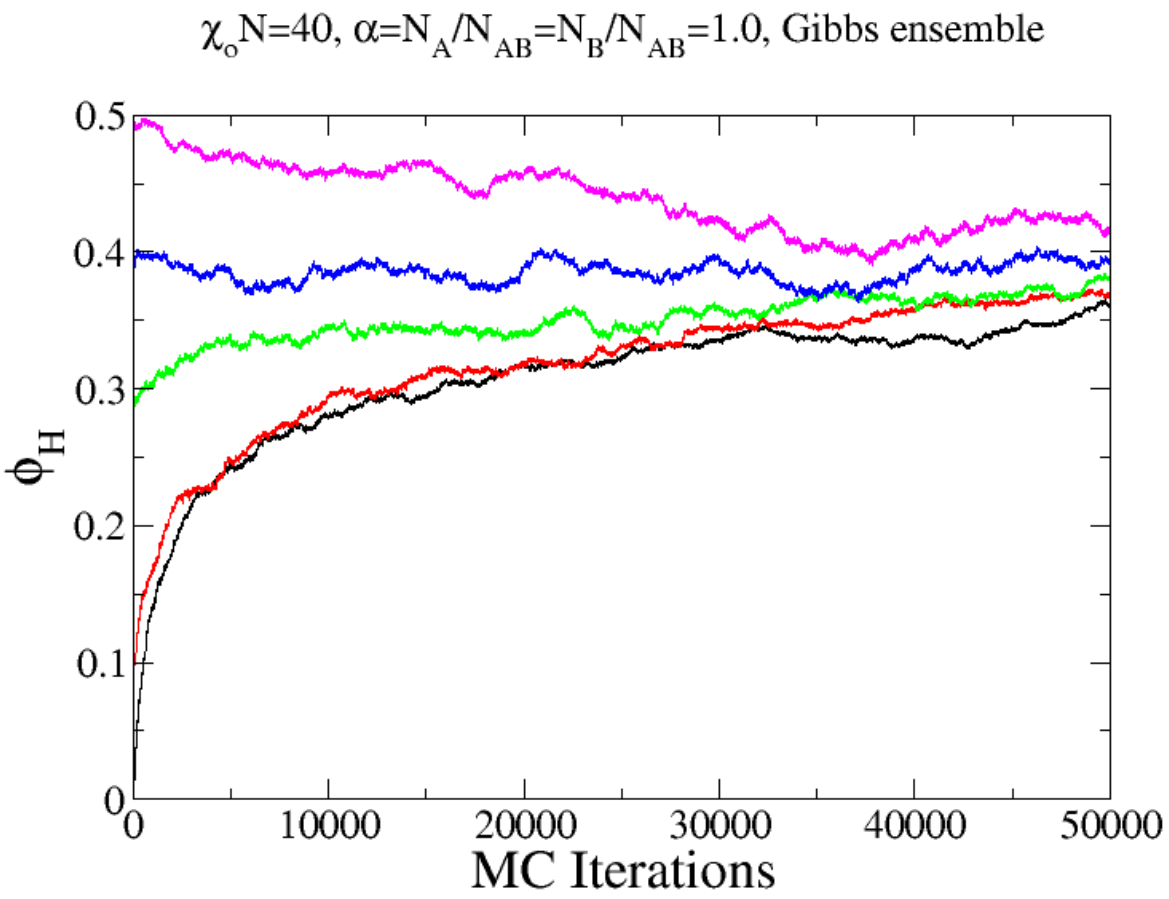
To determine the ideal swelling of the lamellae with homopolymers, a Gibbs ensemble simulation is run.

One simulation box is lamellae, the other is A-rich. The A-rich simulation box doubles as a B-rich simulation box.



Optimal Swelling with Gibbs ensemble

Optimally, the lamellae is swollen with a volume fraction of 0.39 homopolymers when all chains are the same length.



Comparing chemical potential

μ^{ex} includes the ideal mixing term.

	Lamellar phase	A-rich phase
μ^{ex} of copolymer	47.6	47.8
μ^{ex} of A polymer	43.3	43.3
μ^{ex} of B polymer	43.3	-

The average volume fraction of copolymers in the A-rich phase is $2.1*10^{-5}$. The error in this value may be up to 20%, so it is close enough to $1.8*10^{-5}$, the value that gives $\mu^{ex}=47.6$.

For μ^{ex} of the B homopolymer to match in the 2 phases listed above, the volume fraction in the A-rich phase must be $8.3*10^{-14}$. In the Monte Carlo simulation, there is never a B homopolymer in the A-rich phase. The simulation would need to be run over 100 years before a B homopolymer ends up in the A-rich phase.

Comparing to SCFT

The ideal MC volume fractions in the A-rich phase (from chemical potential calculations) match closely with the SCFT:

A-rich phase	MC, $\chi_o N$=40, χN=32.8	SCFT, χN=30	SCFT, χN=35
$\varphi_{copolymer}$	$1.8*10^{-5}$	$2.7*10^{-5}$	$3.0*10^{-6}$
$\varphi_{B\ homopolymer}$	$8.3*10^{-4}$	$9.4*10^{-4}$	$6.8*10^{-6}$

The SCFT predicts slightly less homopolymers in the lamellar phase:

Lamellar phase	MC, $\chi_o N$=40, χN=32.8	SCFT, χN=30	SCFT, χN=35
$\varphi_{homopolymers}$	0.39	0.36	0.34

Optimal Period

The A-rich phase is almost pure A.

Thus, the maximally swollen lamallae can be approximated by equating the chemical potential of the homopolymers in the pure phase with that in the lamallae.

I will verify this trend with Gibbs ensemble, as it is opposite to what is expected.