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

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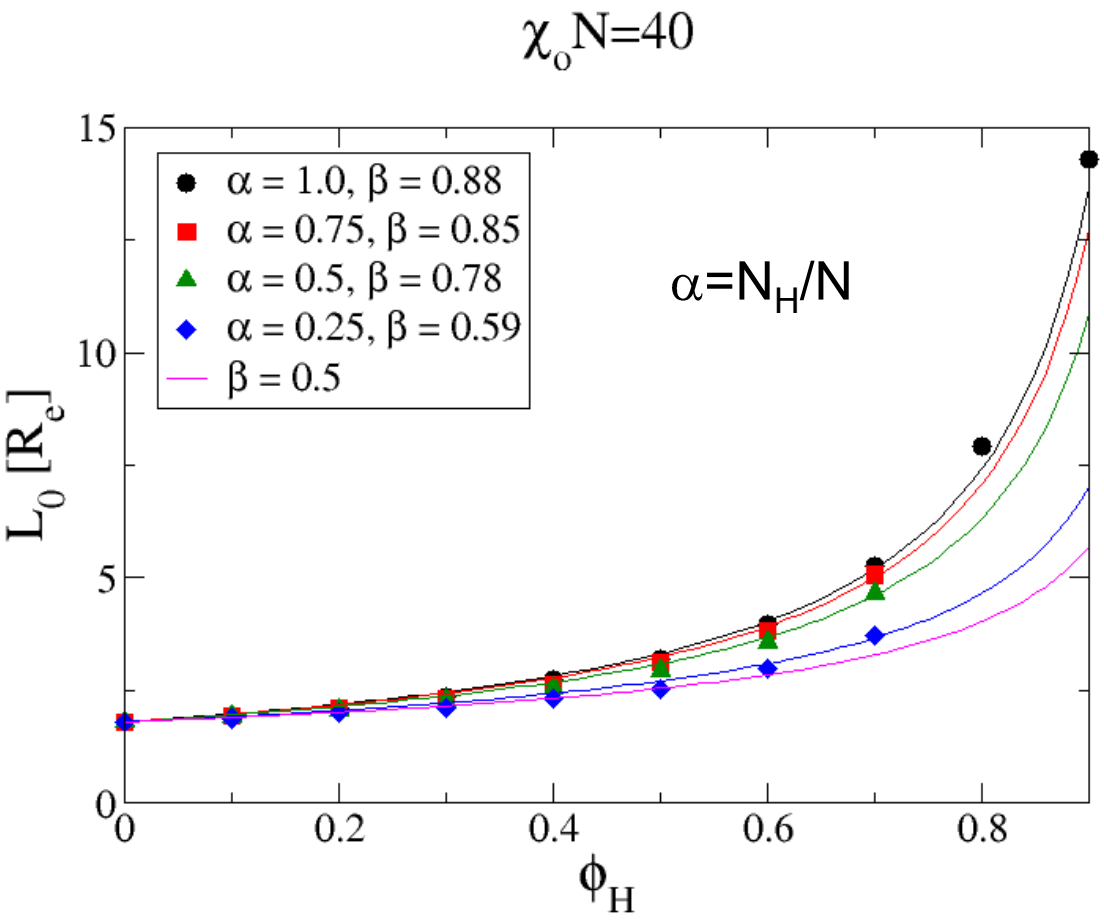
Ternary Mixtures, Optimal Period

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

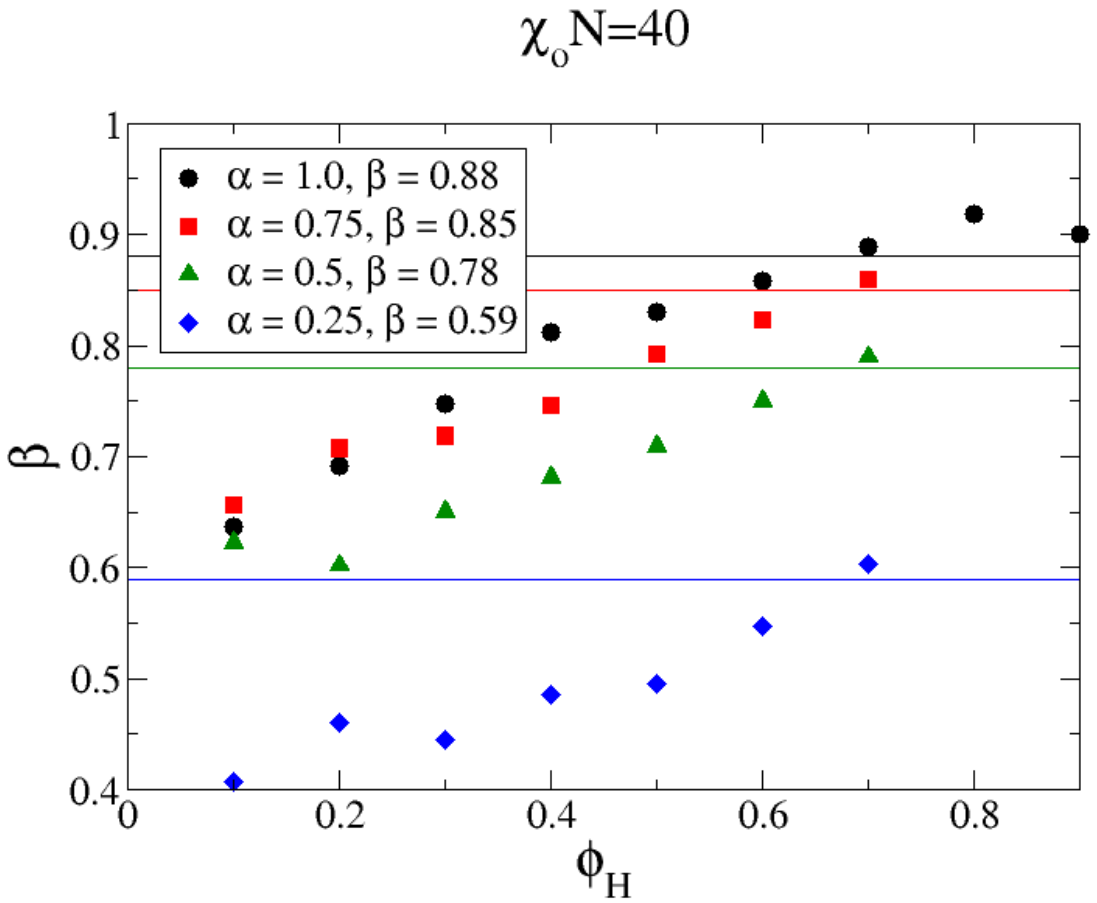
- The swelling can be fitted to the equation

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



Values of β

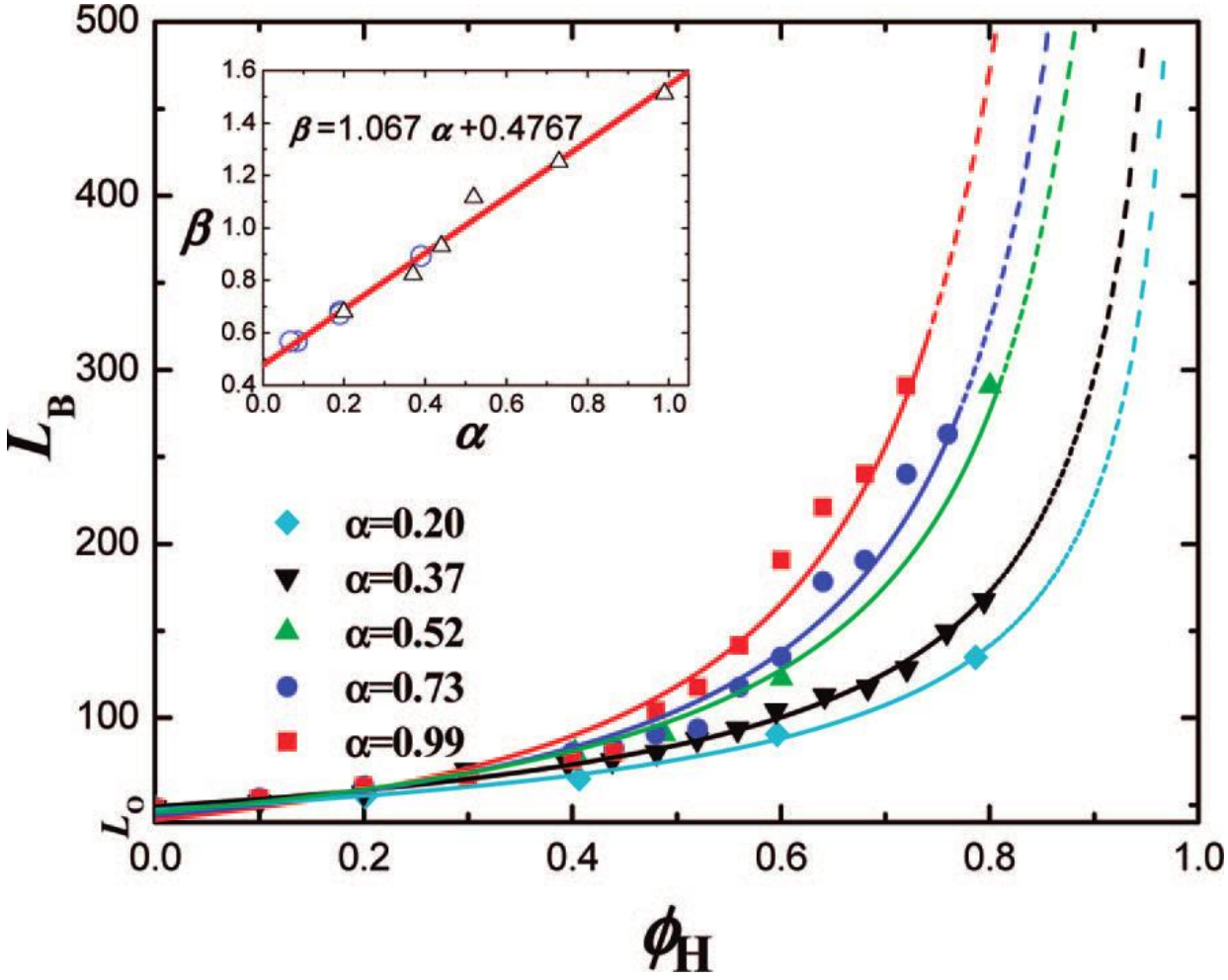
- The value of β drifts as the lamellae become more swollen with homopolymers.
- The curves on the preceding slide use the β values at around $\varphi_H = 0.7$.



Experimental Results

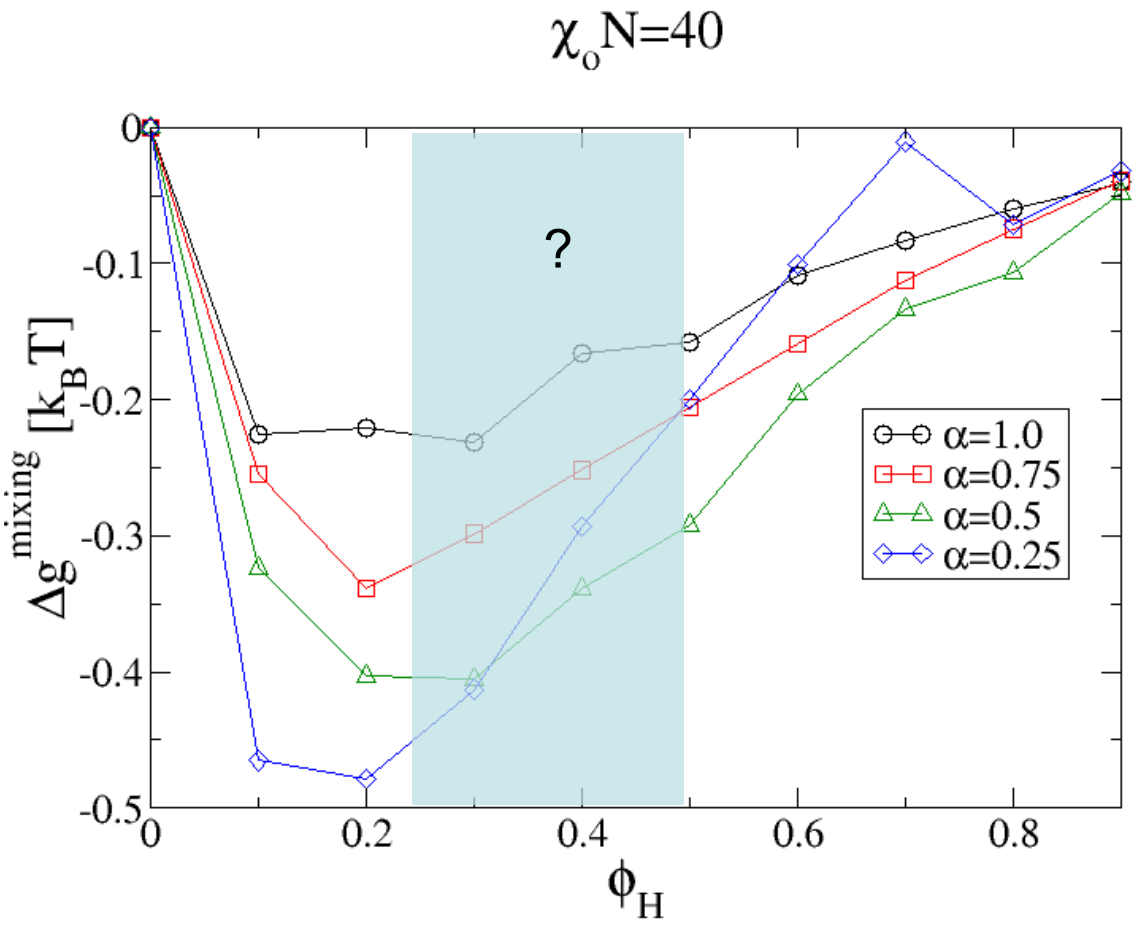
- Experimentally, Guoliang produced larger values of β with a linear dependence in α.

Liu et. al. *Macromolecules* **2009**, *42*, 3063-3072.



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.

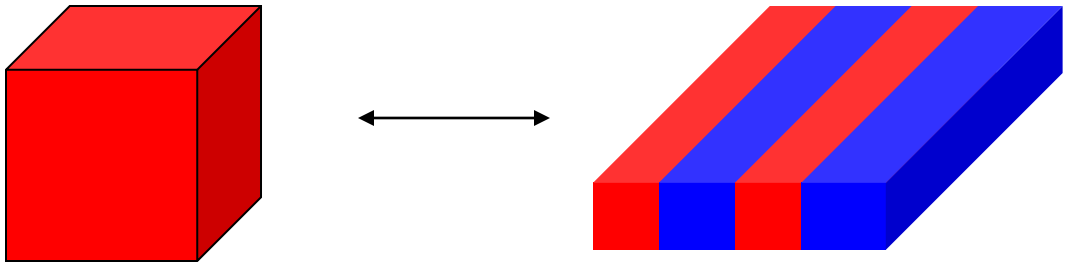


? First order transition ?

Optimal Swelling with Gibbs ensemble

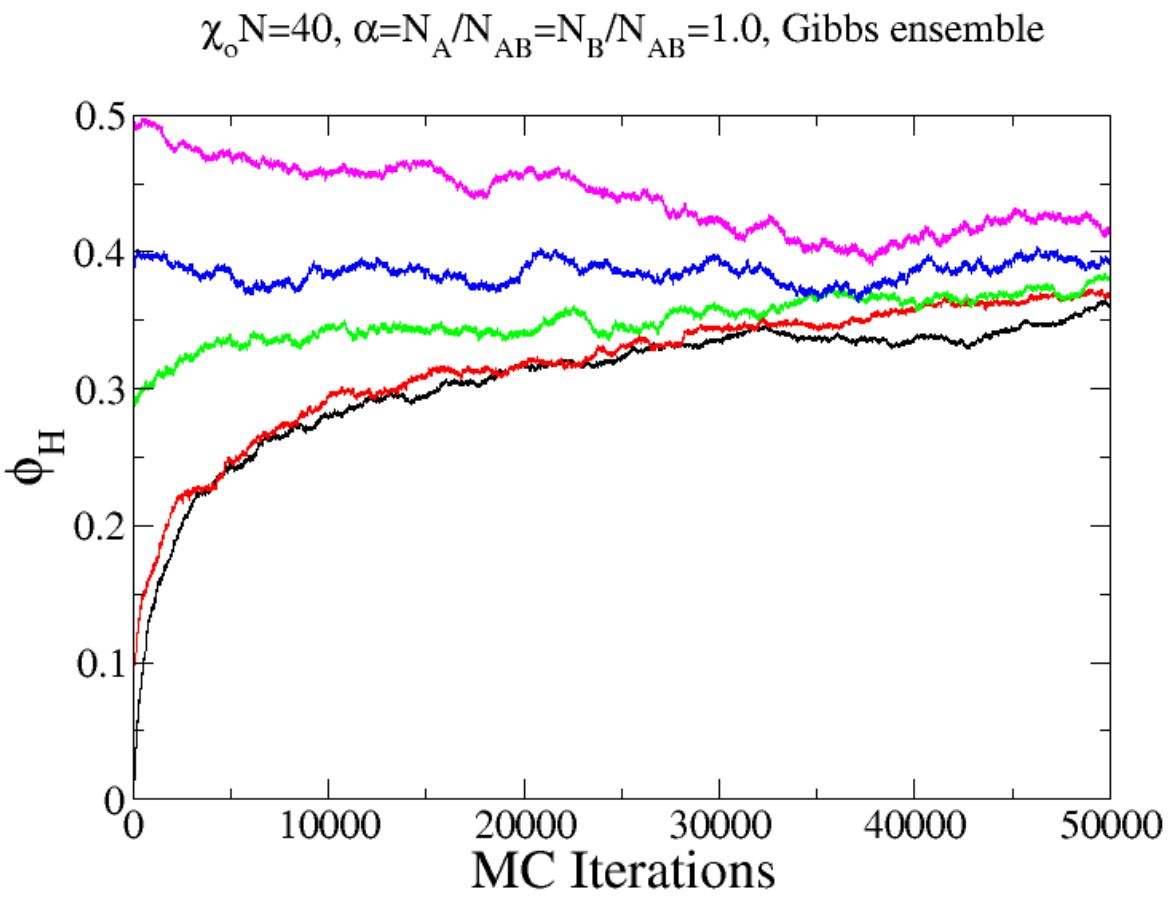
- To determine the ideal swelling of the lamellae with homopolymers, a Gibbs ensemble simulation is run.

- 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
$\varphi_{copolymer}$	$1.8*10^{-5}$	$2.7*10^{-5}$	$3.0*10^{-6}$
$\varphi_{B\ homopolymer}$	$8.3*10^{-14}$	$9.4*10^{-14}$	$6.3*10^{-16}$

- 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.