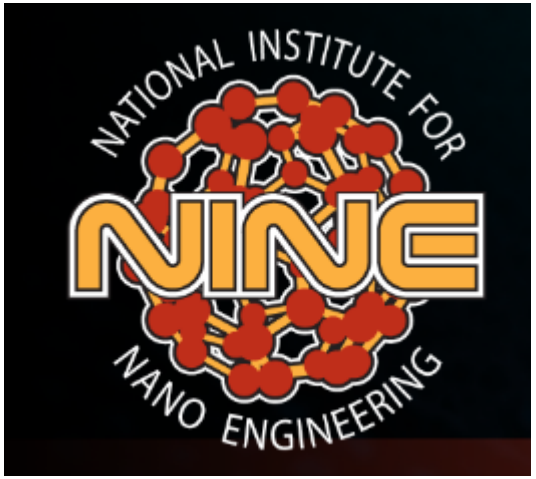
Theoretical Studies of Block Copolymer Lithography

SAND2011-5359C



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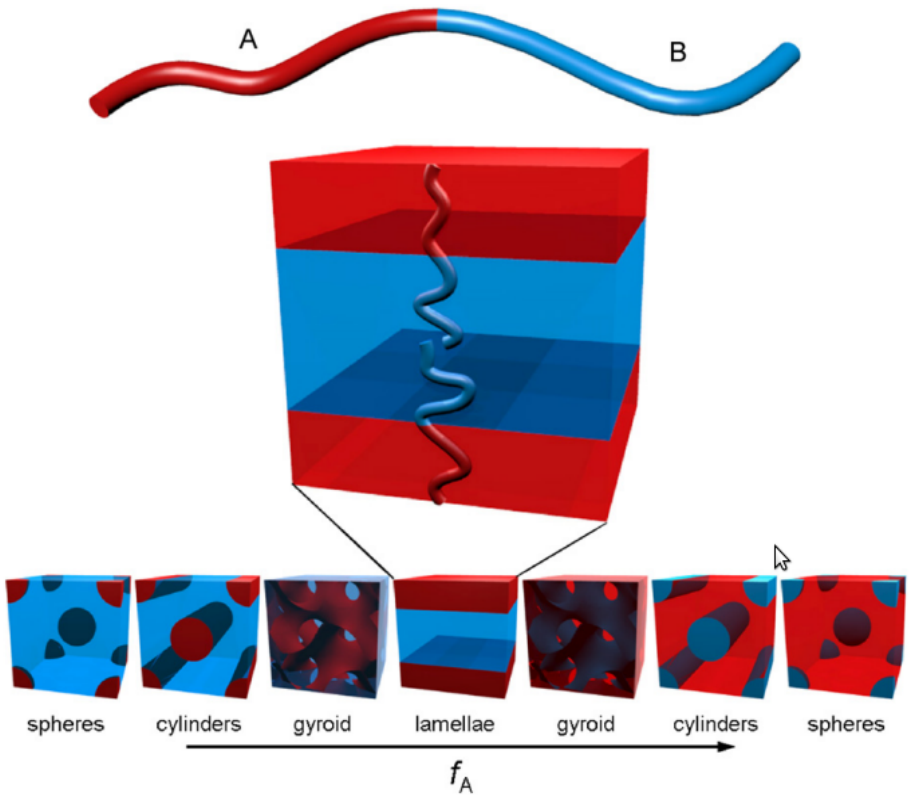
Block Copolymers in Nanotechnology

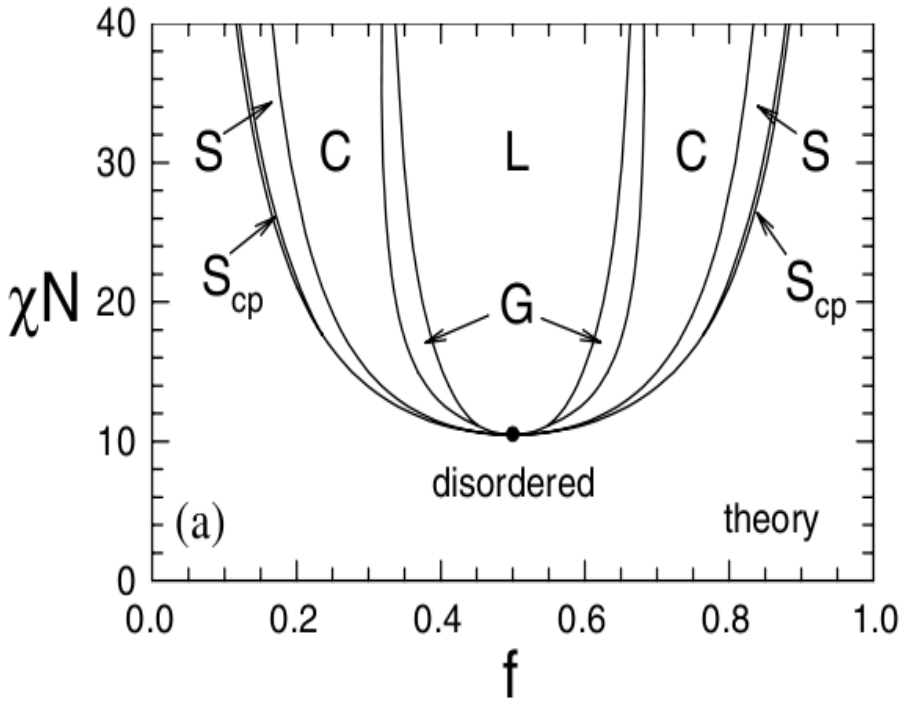
-Block copolymer can make ordered periodic structures (5nm-100nm)

-Micro-phase separation

-In thin films defect free morphologies can be obtained
Information can be used in quantum dots, magnetic storage media, integrated circuits, nanowires, etc.



Darling S.B., Prog. Polym. Sci. (2007)



Matsen, M. Phys.: Condens. Matter (2002)

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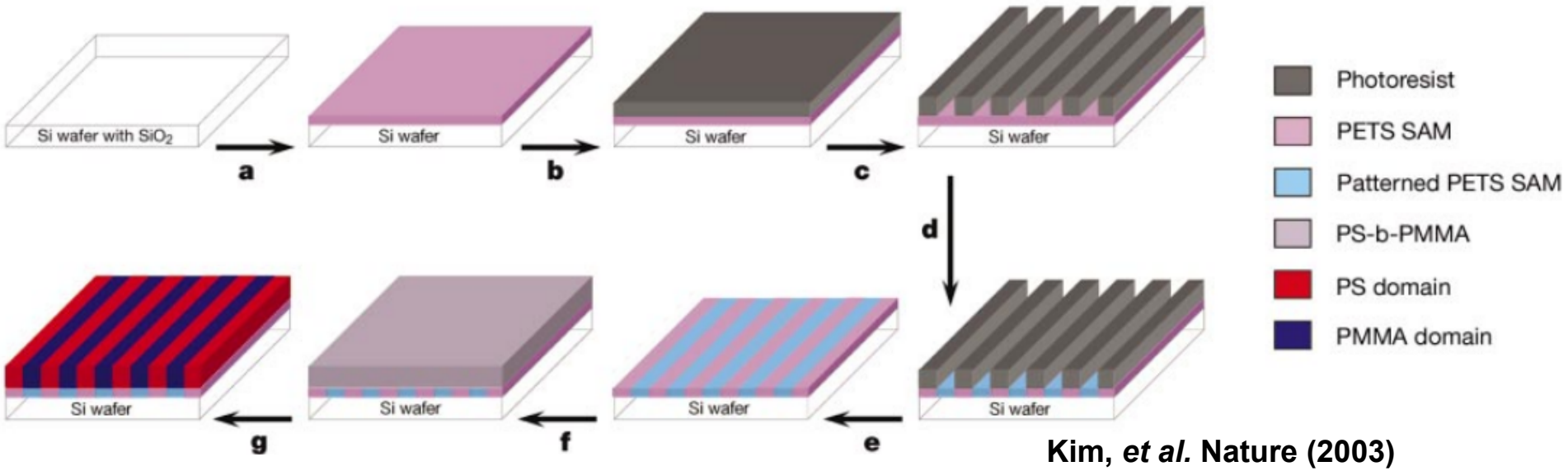
Epitaxial Self-assembly of Block Copolymers Using Nanopatterned Substrates



Kim, *et al.* Nature (2003)

-This method has produced:

-Defect free periodic lamellar structures

-Perfectly ordered vertically oriented cylinders,

-Lamella structures with bends, T-joints, isolated geometries, and jogs

-Hybrid strategy of lithography and molecular level control

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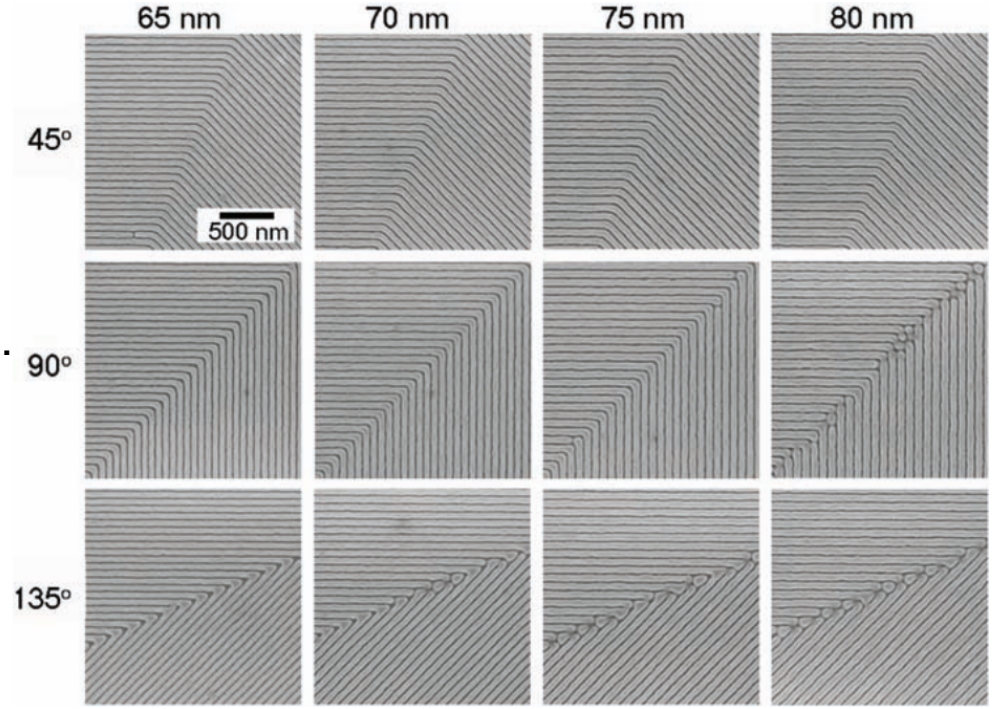
Non Regular Dense Geometries

Bends

-With the help of chemical patterns to trap the block copolymers into non equilibrium morphologies, it was shown that the block copolymers can form structures needed in integrated circuits and perpendicular cylinders.

-Use ternary blends to stabilize structures.

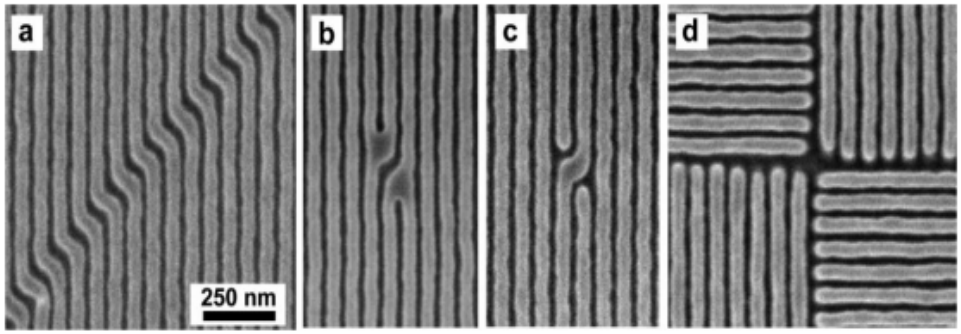
-Long writing times is still an issue.



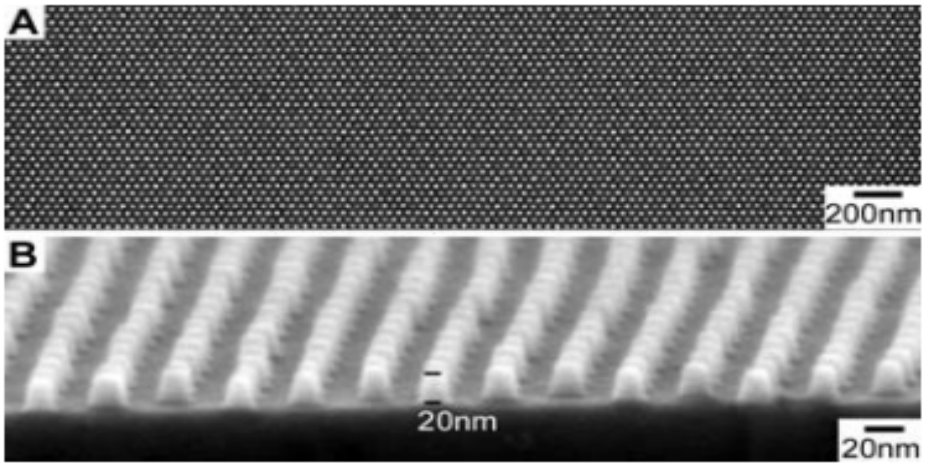
Stoykovich, *et al.* Science (2005)

(b)(c)Isolated Jogs

(a)Jogs (d)T-Junctions



Stoykovich, *et al.* ACS Nano (2007)



Ruiz et al, Science (2008)

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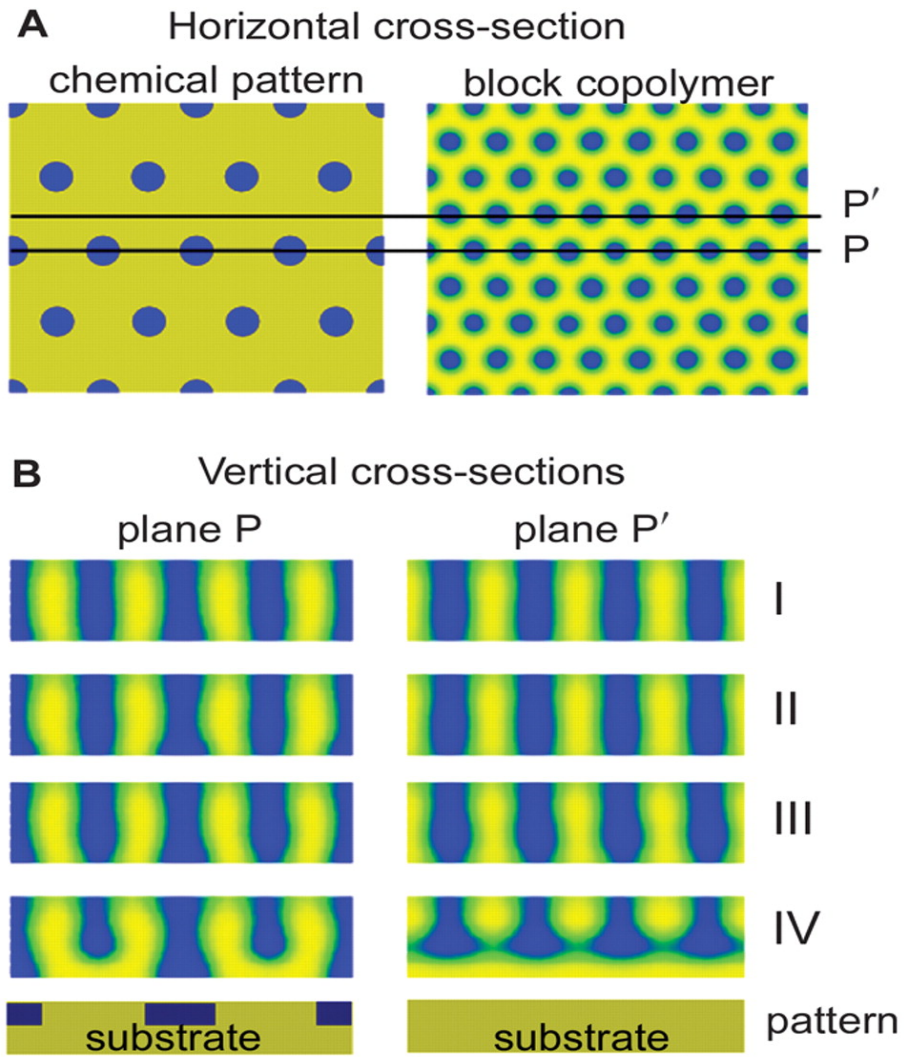
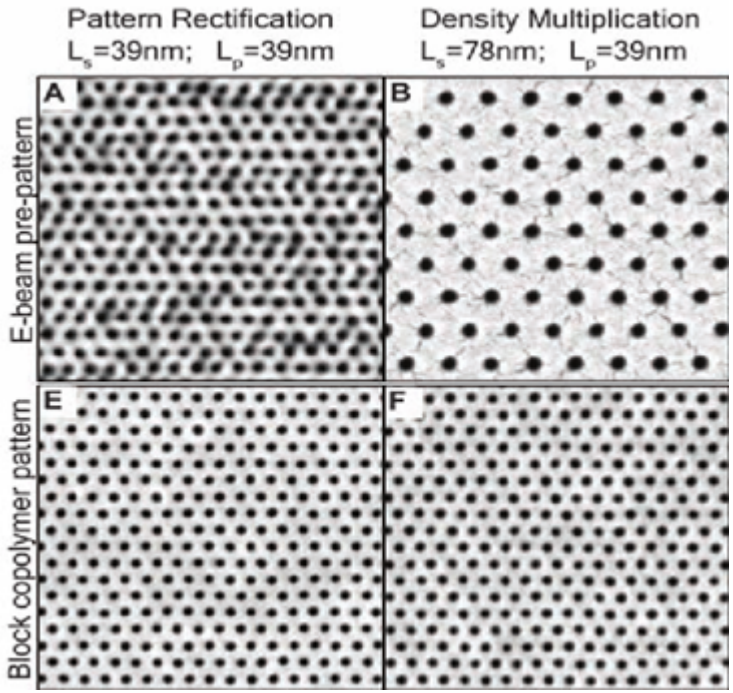
Interpolation of Cylinder Forming Block Copolymers

- Simulations of interpolation of cylinder forming block copolymers.
- Cross section plots of average densities of polymer type A (blue) or B (yellow) across different planes



(I) Weak Λ^{PMMA} and weak Λ^{PS}
(II) Strong Λ^{PMMA} and weak Λ^{PS}
(III) Medium Λ^{PMMA} and medium Λ^{PS}
(IV) Strong Λ^{PMMA} and strong Λ^{PS}



Ruiz et al, Science (2008)

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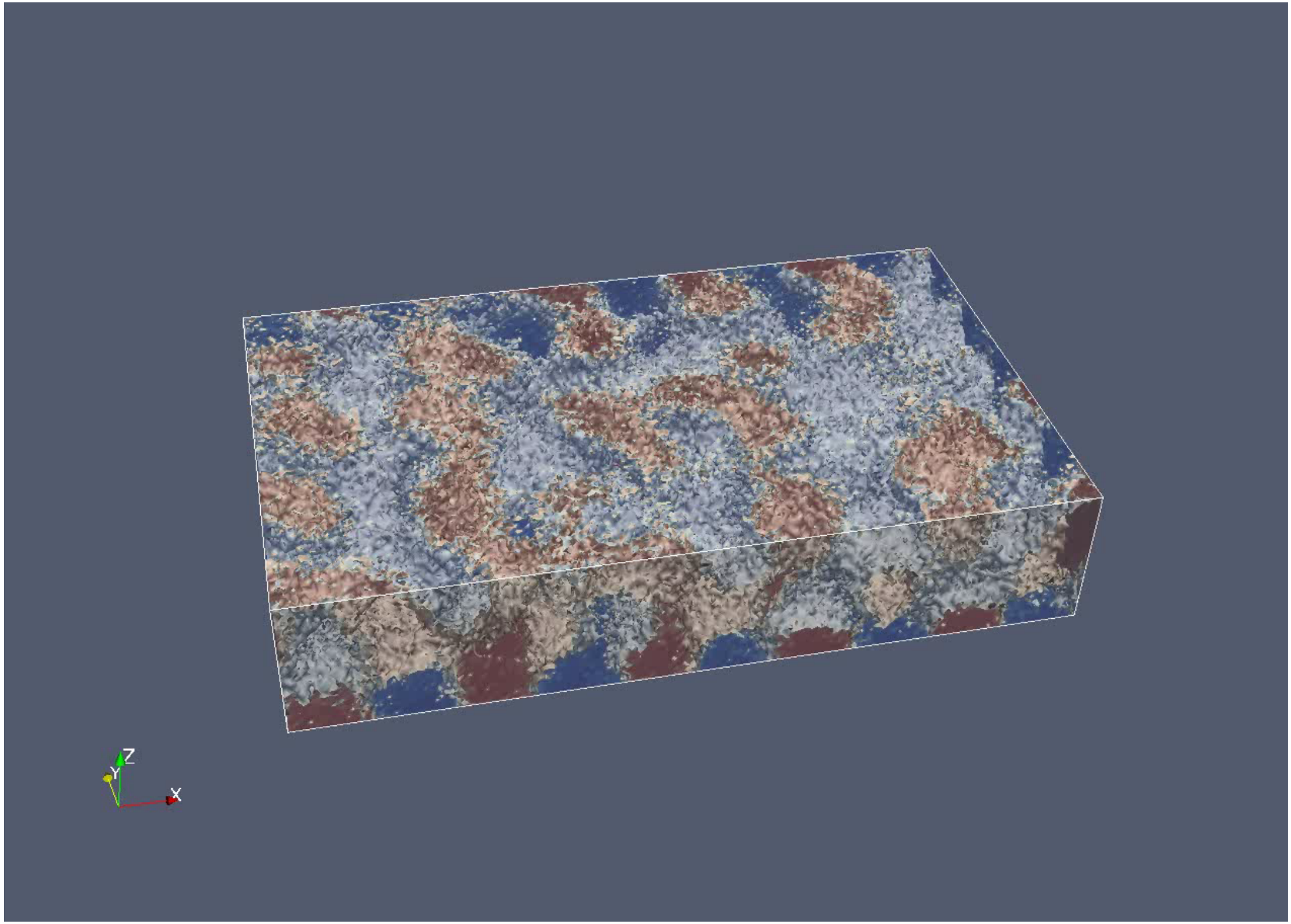
Monte Carlo Simulation of a Lamella Forming Block Copolymers with a Chemical Pattern.



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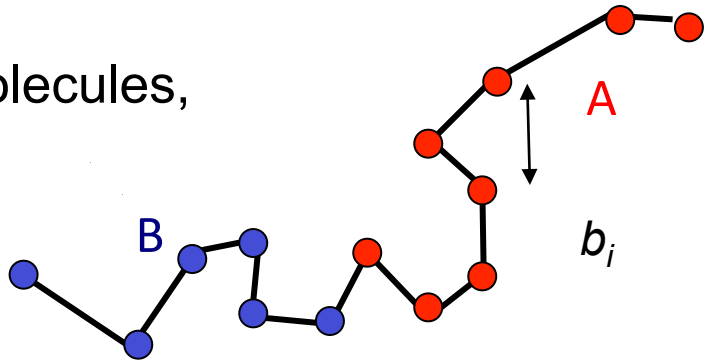
A Coarse-Grained Model

A coarse-grained 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:

Coarse-grained parameters

R_e end-to-end distance

$\sqrt{N} = \rho_{chain} R_e^3$ number of chains in the volume occupied by a chain

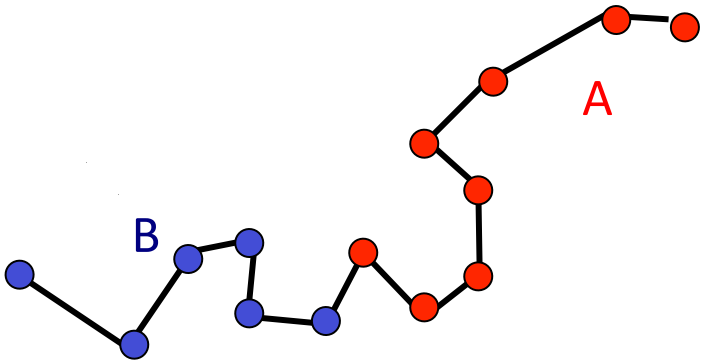
κN *N,* number of beads per chain

Helfand, J. Chem. Phys. (1975)

A Coarse-Grained Model

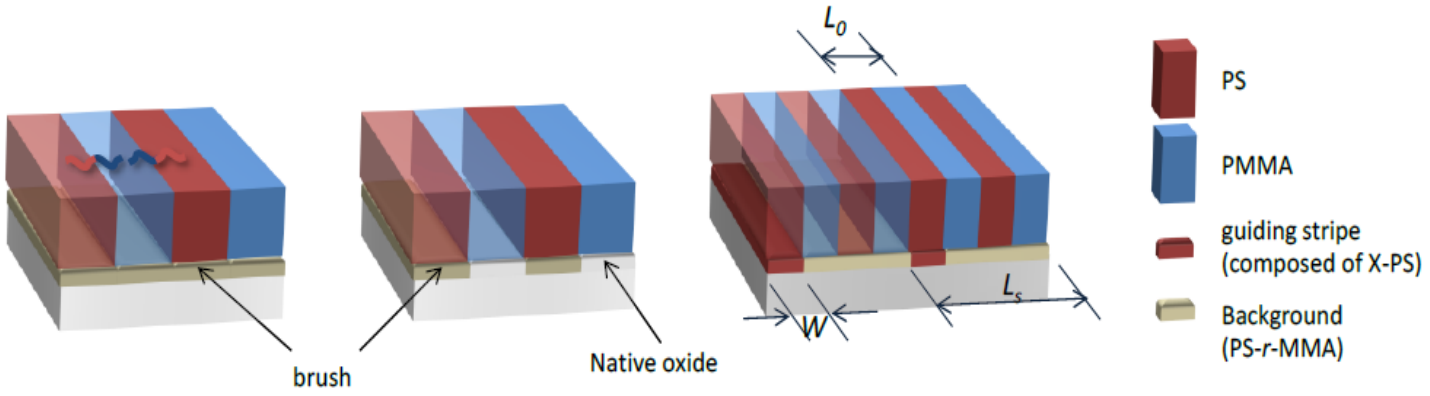
Substrate Potential

$$\frac{U_s(r,K)}{kT} = f(x,y,K)\frac{\Lambda_K}{d_s}\exp\left(\frac{-z^2}{2d_s^2}\right)$$



Use this model in Monte Carlo simulations using the Metropolis Algorithm

In the NVT ensemble the acceptance criteria is: $p_{acc} = \min\left[1, \exp\left(\frac{-\Delta U}{k_B T}\right)\right]$



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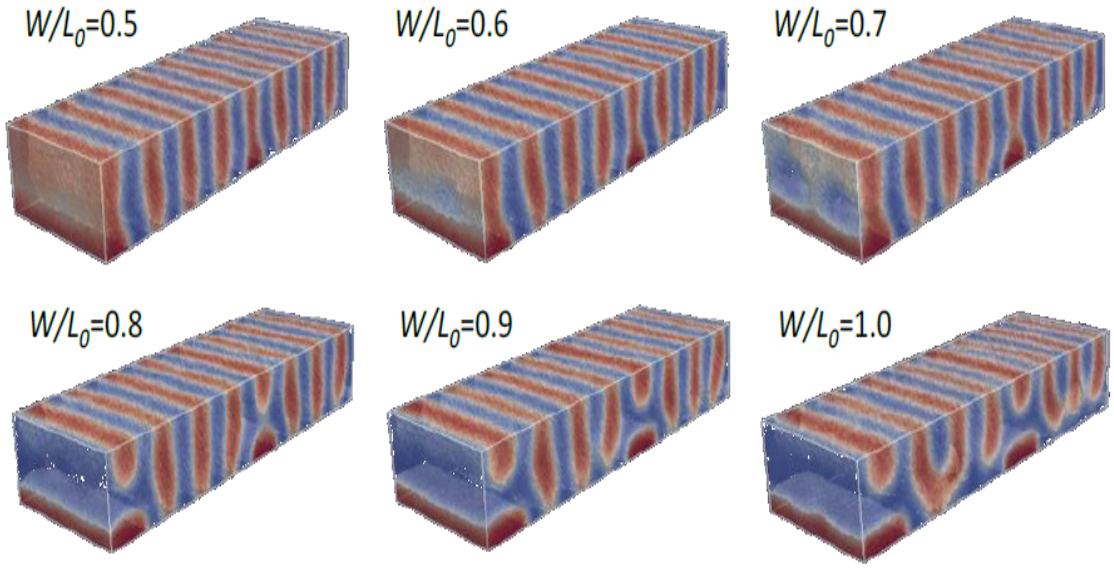
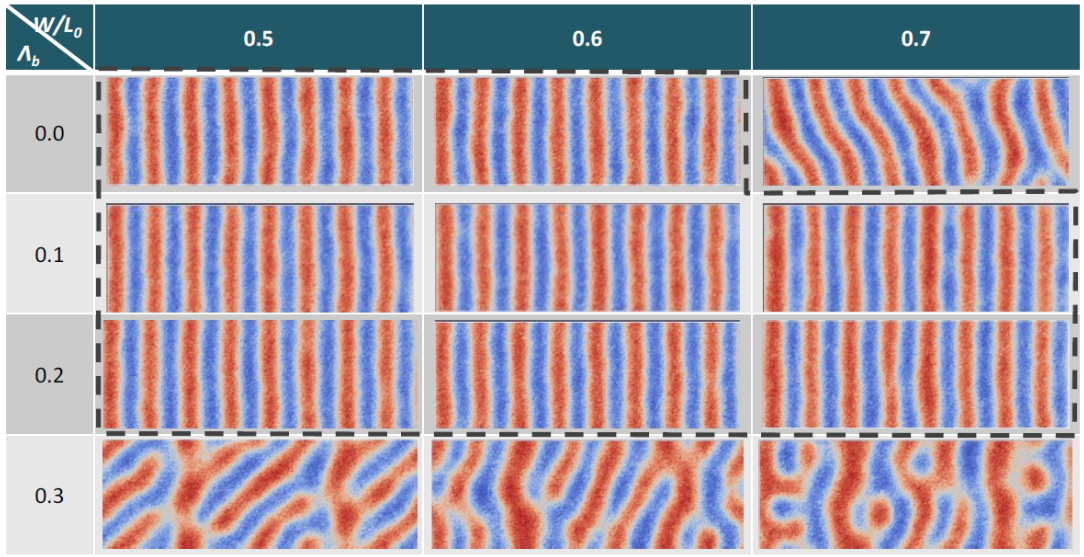
Interpolation of Lamella Forming Block Copolymers





-Simulations for 4x density multiplication (L_s/L_0=4) when varying the value of W.

-As W increases “hovering” lines appear.

-The simulations have a constant value of the strength of chemical patterns ($\Lambda^A N$=2.0 and $\Lambda^B N$=0.15 for the 3D figures).

-As you can see the value of $\Lambda^B N$ also plays an important role in forming topologically defect free structures.

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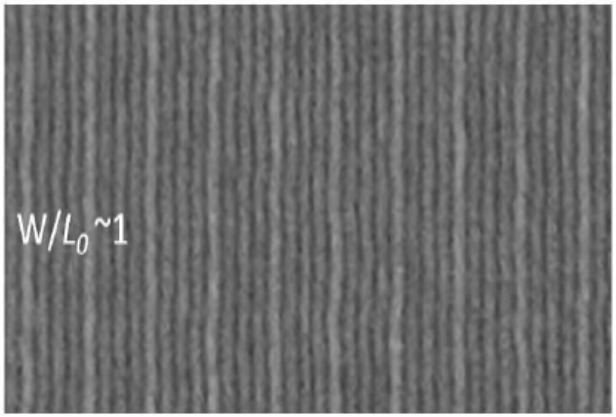
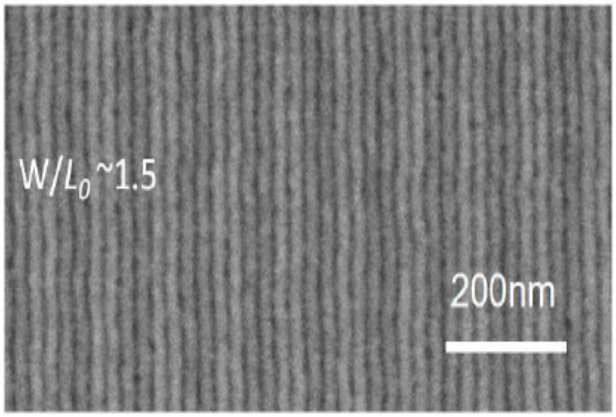
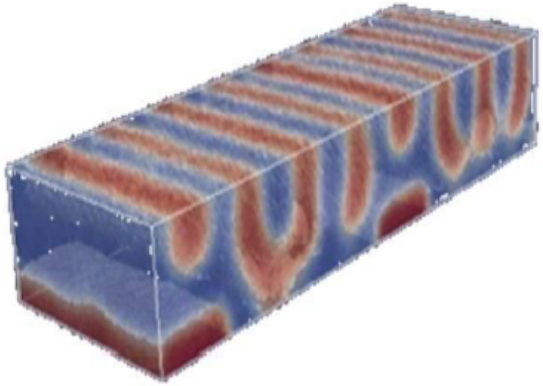
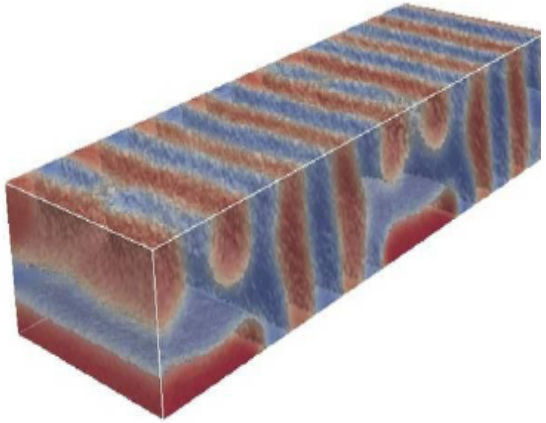
Interpolation of Lamella Forming Block Copolymers









-A side by side comparison of simulations and SEM images of poly(polystyrene-b-methyl methacrylate) for 4x density multiplication (L_s/L_0=4).

-The brighter lines show the “hovering” lines while the darker lines show lamella going through the entire thin film. Results are shown for two values of the width of the stripe(W).

The Free Energy Reversible Path

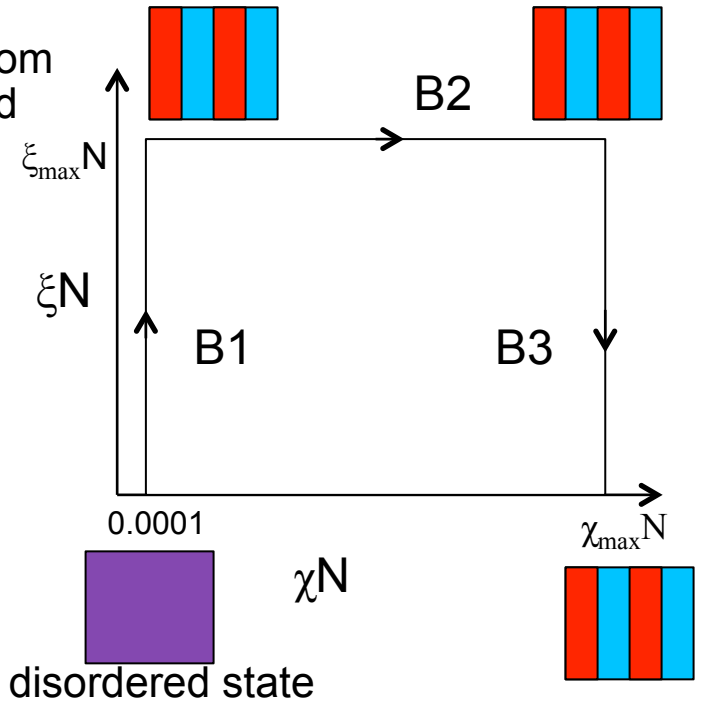
-Construct a reversible path from a disordered state (α) to an ordered state (β) through Thermodynamic Integration

$$\Delta F_{\alpha \longrightarrow \beta} = \int_{\alpha}^{\beta} du \left\langle \frac{\partial H_{ext}}{\partial u} \right\rangle \qquad H_{ext}(r,K) = \sum_{i}^{nN} -\xi f_{ext}(r_i,K)$$

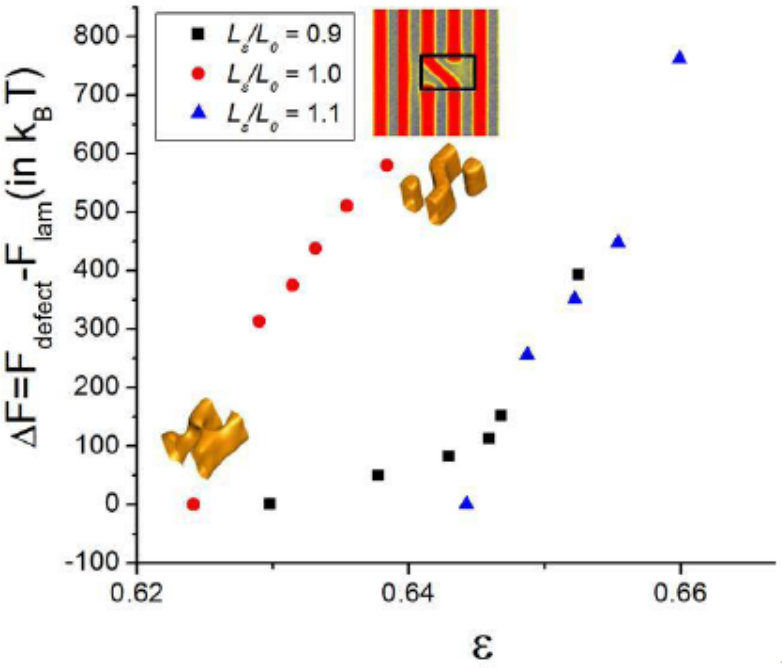
-Can calculate the free energy difference:

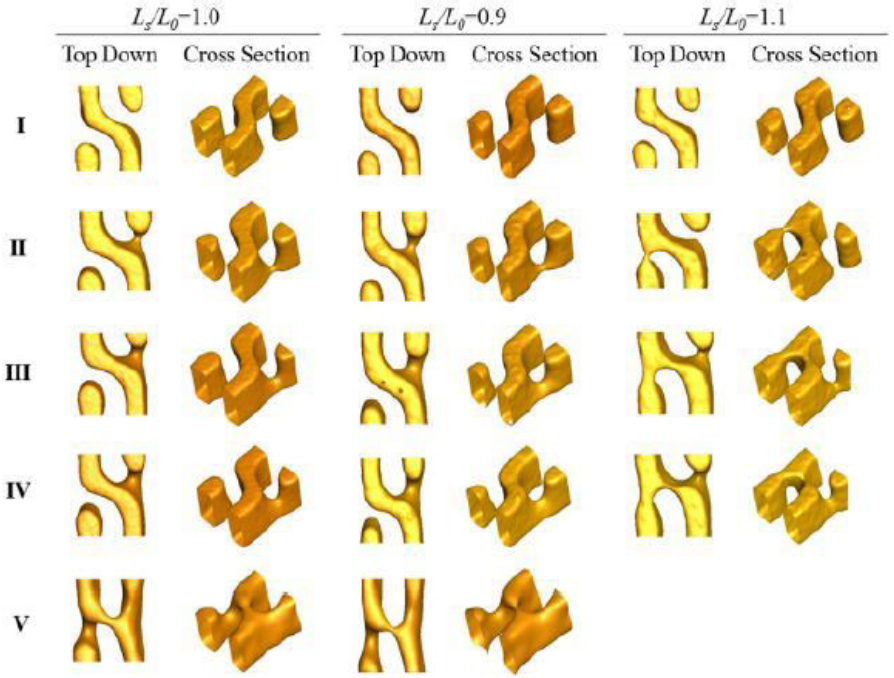
$$\Delta F = \Delta F_p - \Delta F_d$$

where $\Delta F_p = F_p - F_{dis}$, and F_p is the free energy of perfectly aligned lamella, F_{dis} is the free energy of the disordered phase, and F_d is the free energy of a defect in the lamella



Free Energy Calculations for a Jog Defect





$$\varepsilon = \frac{1}{V}\int_{defect}(\phi_A - \phi_B)^2\,dV$$

-An analysis of the partial defects at different annealing times. Stretched, regular, and compressed lamellae are also shown.

-Case I to Case IV for L_s/L_0 =1: the probability of increases from 10^{-237} to 10^{-120} , which shows that the likelihood of forming a defect is non-existent

-Case V for L_s/L_0 =0.9: The probability is 10^{-11}

-This shows that even a small preference of the stripe pattern renders defects unstable

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Conclusions and Future Work

-A field theory influenced coarse grained model has been developed.

-The model has been shown to model experiments and make predictions.

-The block copolymers can be trapped the system in non equilibrium structures and the model can predict and help the understanding of these structures, showing both topological defects and three dimensional defects.

-Dynamic simulations are being performed to help understand the effects of defects in block copolymer thin films and melts.

> -Non equilibrium molecular dynamic simulations, i.e. steady shear simulations
>
> -Incorporating entanglement using the block copolymer melts to help understand the generation and annihilation of defects

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Nealey and de Pablo group members

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