

The Physics and Applications of Block Copolymer Films

StatMech Day IV, WIS --- 23/6/11



The Physics and Applications of Block Copolymer Films

coworkers:

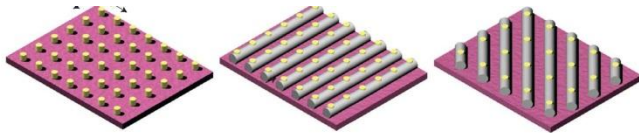
Xingkun Man (TAU) & H. Orland (Saclay)

Experiments: J. Daillant & P. Guenoun (Saclay)

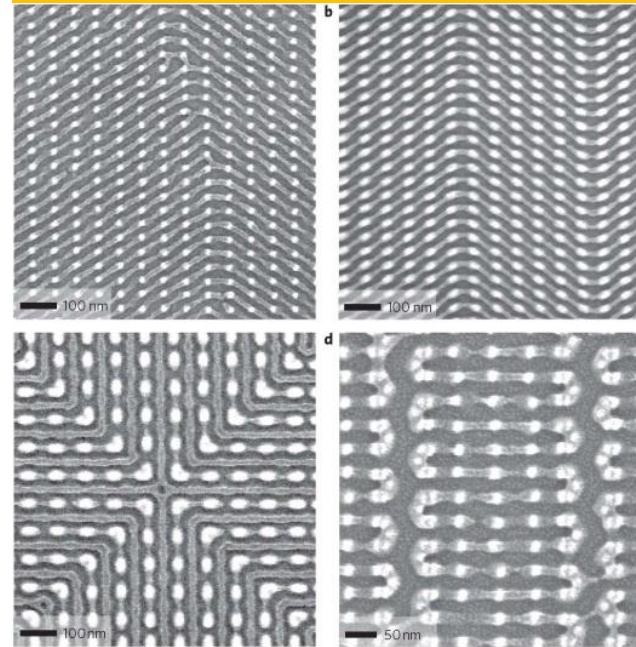
- Introduction: the physics of block copolymers
- Surfaces & Electric Fields: nanostructures, chemical surface patterns & nano-imprint templates, surface-induced orientation, electrically-induced orientation

Polymer Self-assembly on Surfaces: Future Nano-Lithography

cylinders on
dot-patterned
surfaces



directed patterns to
replace photomasks?

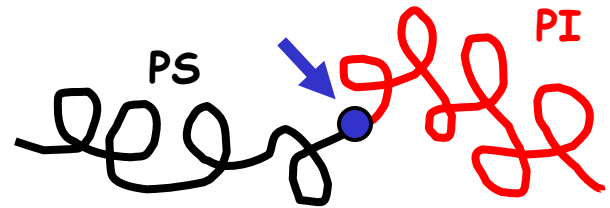


100 nm

What are Block Co-Polymers?

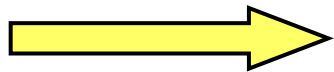
- Repulsive Interaction: *polystyrene-polyisoprene*

- Phase separation: PS/PI



- Competition: chemical link & entropy

- Self-Assembly



Micro-phase separation (nano-scale)

Applications:

Nano-Structures; Bottom-up Functional Composites

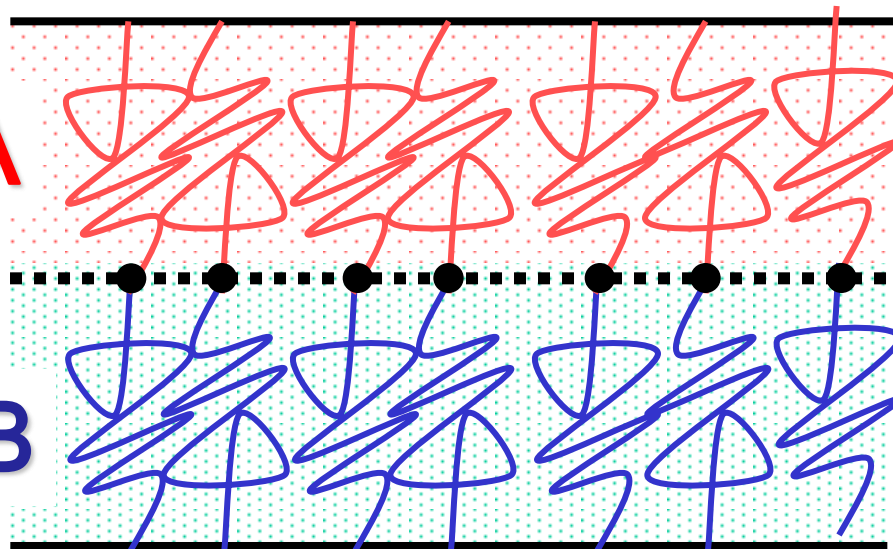
Why periodic structures ?

interfacial
tension

$$\gamma_{AB}$$

A

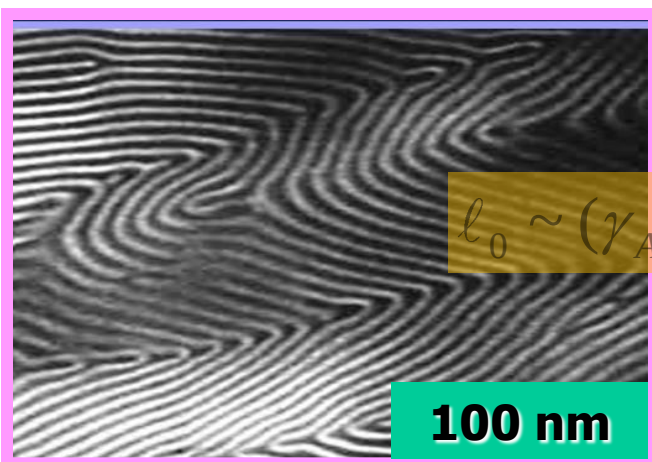
B



$$\ell_0 = 2\pi / q_0$$

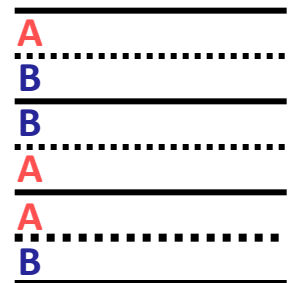
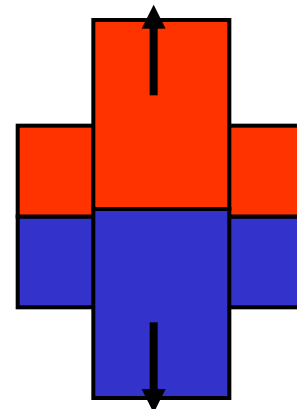
10 - 100 nm

TEM: lamellae

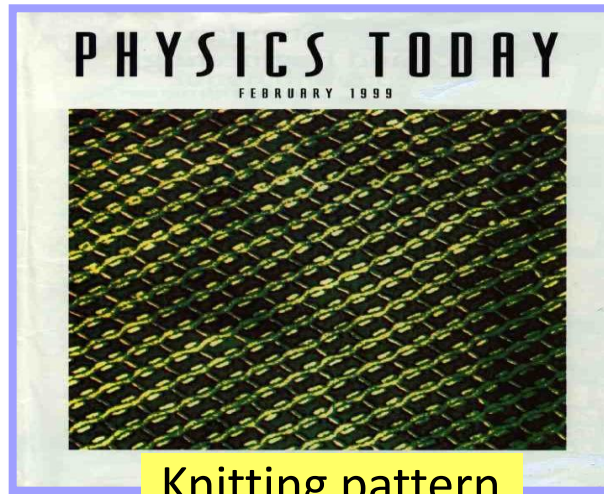


$$\ell_0 \sim (\gamma_{AB})^{1/3} N^{2/3}$$

100 nm



Tri-Blocks: other phases

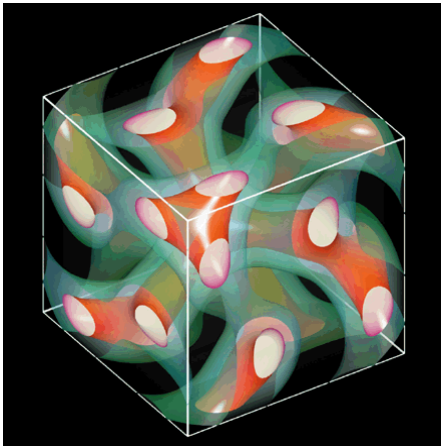


Knitting pattern

Stadler

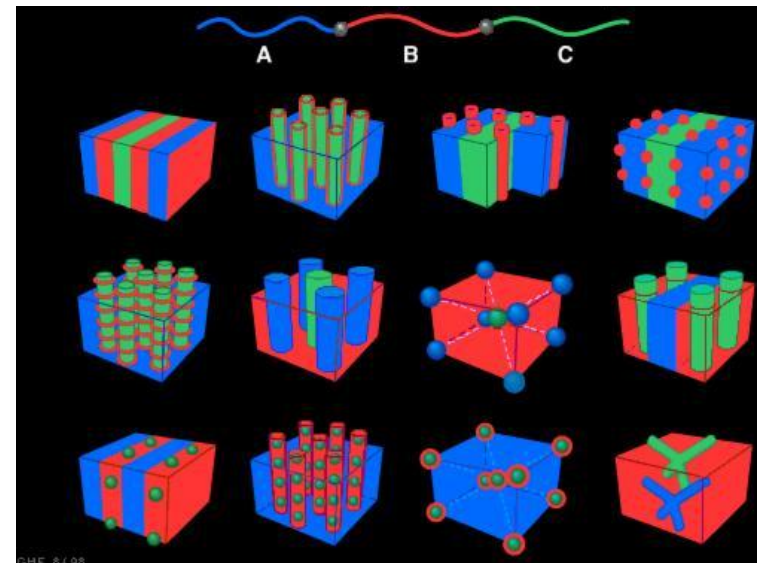
A — B — C

bi-continuous



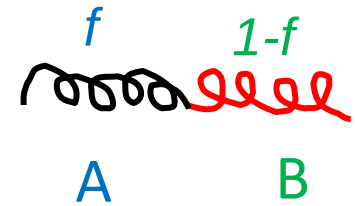
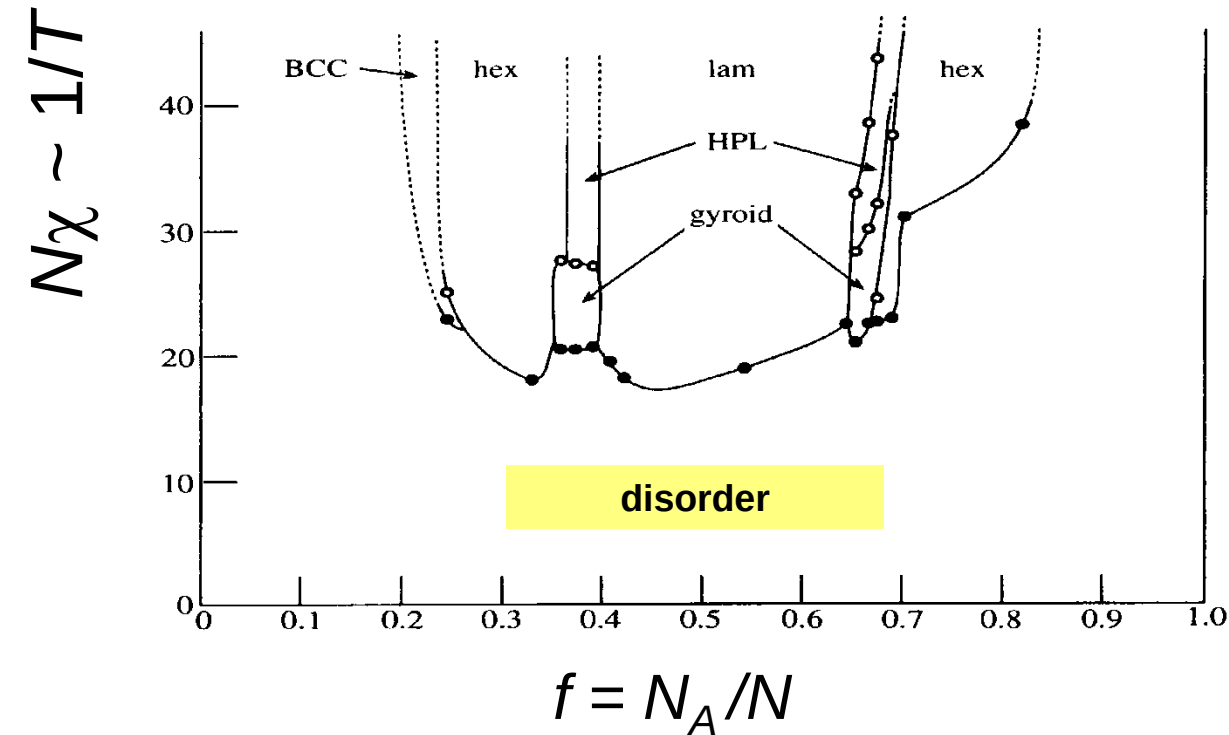
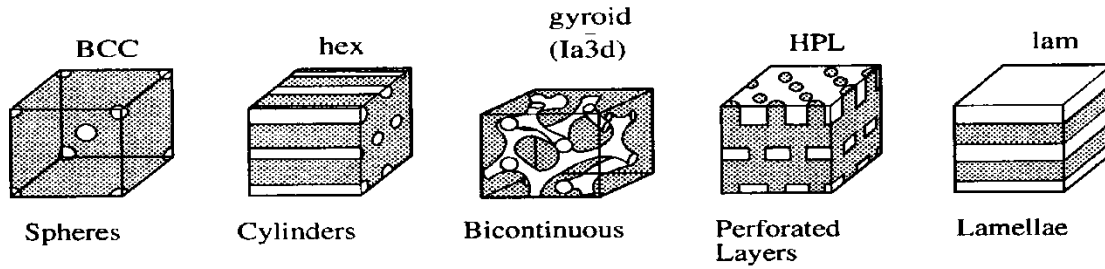
Thomas

many complex morphologies



Zheng & Wang '95

Phase Diagram of di-Blocks



f fraction of A

χ Flory parameter

Block Co-Polymers: Coarse-grained Models

Bulk Free Energy : Ginzburg-Landau expansion

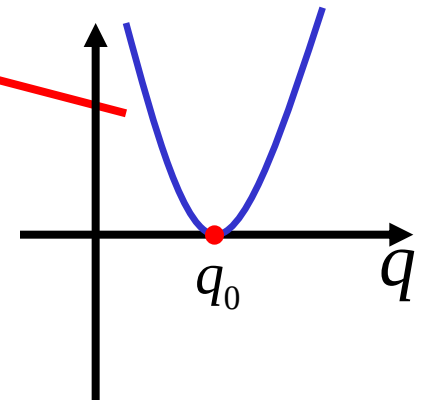
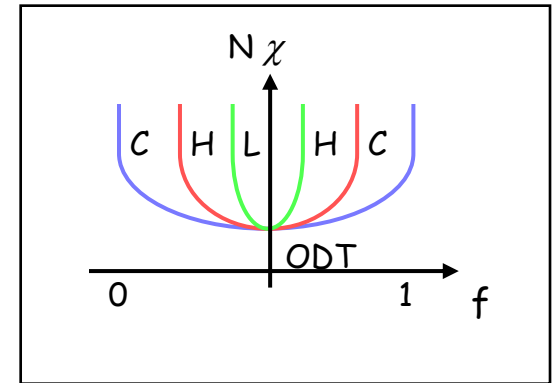
$$F_{\text{bulk}} = \int \left\{ \frac{\tau}{2} \phi^2 + \frac{h}{2} \underbrace{\left(q_0^2 \phi + \nabla^2 \phi \right)^2}_{\text{dominant mode}} + \frac{\lambda}{3!} \phi^3 + \frac{u}{4!} \phi^4 \right\} d^3 r$$

$\phi(\mathbf{r}) = \phi_A - f$ order parameter

χ Flory parameter $N\chi_c \approx 10.49$

$\tau = 2N(\chi_c - \chi)$ reduced temperature

$q_0 \approx 1.9/R_g$ dominant mode close to ODT

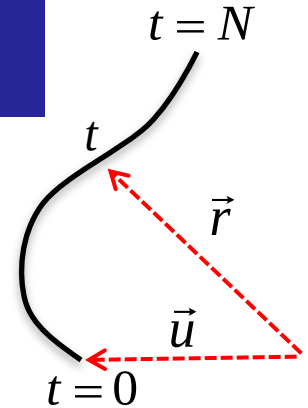


ODT = **O**rders **D**isorder **T**emperature

Self-Consistent Field Theory: The Edwards' Method

$Q(t, \vec{r} | \vec{u})$ The probability of finding the t monomer at $\vec{r}$,
given that the end-point is at $\vec{u}$

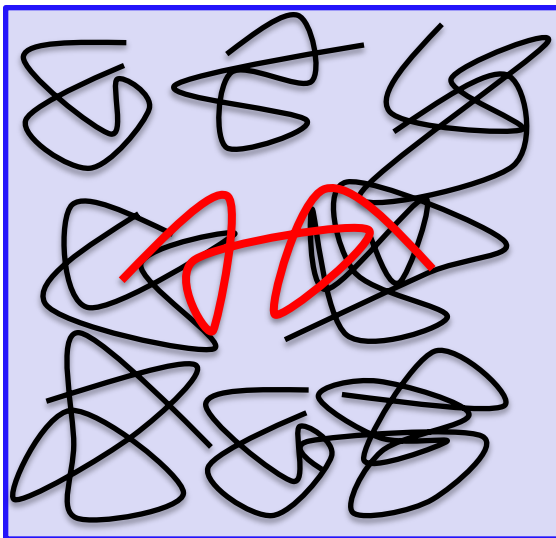
$q(t, \vec{r}) = \int d\vec{u} Q(t, \vec{r} | \vec{u})$ End-integrated polymer propagator:



$$\frac{\partial q(t, \vec{r})}{\partial t} = \frac{a^2}{6} \nabla^2 q(t, \vec{r}) - \omega(\vec{r}) q(t, \vec{r})$$

Schrödinger-like eq.

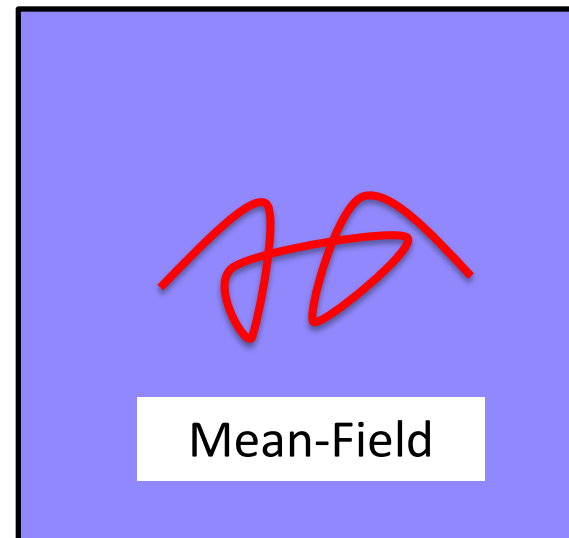
Concentration $\phi(r)$



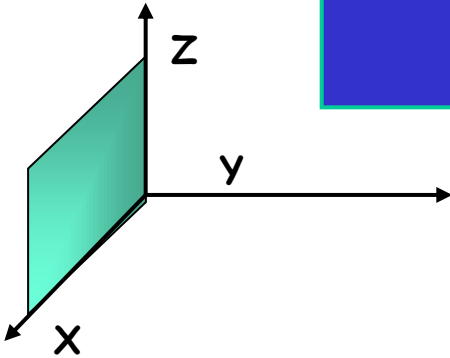
$\phi(r) \square \omega(r)$



Auxiliary field $\omega(r)$



Effect of Surface: Arbitrary Chemical Patterns



Total Free Energy

$$F = F_{\text{bulk}} + F_{\text{surf}}$$

Patterned surfaces: $u(x, z)$

$$F_{\text{surf}} = \int u \cdot \phi \, d^2r$$

BCP concentration: $\phi(x, y, z)$

Minimize the total free energy respecting the boundaries

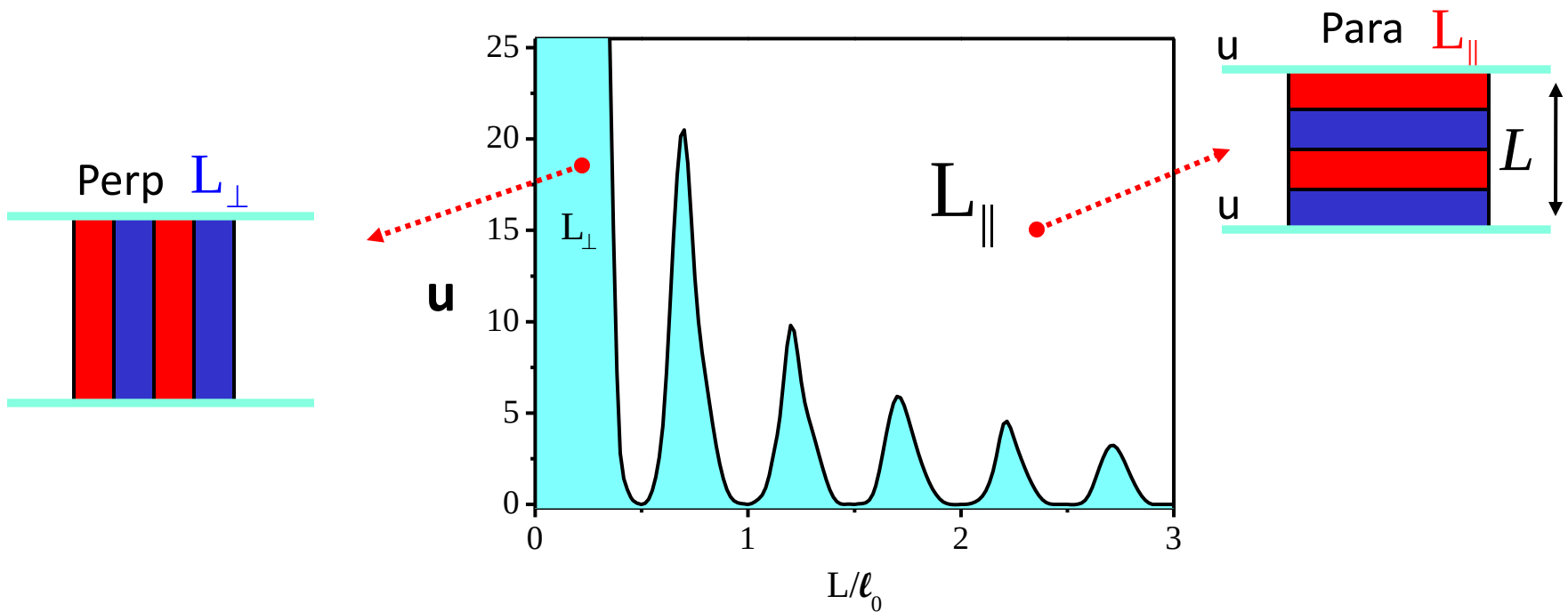
u_B surface energy of B monomers

u_A surface energy of A monomers

$u = u_A - u_B$ strength of surface interaction

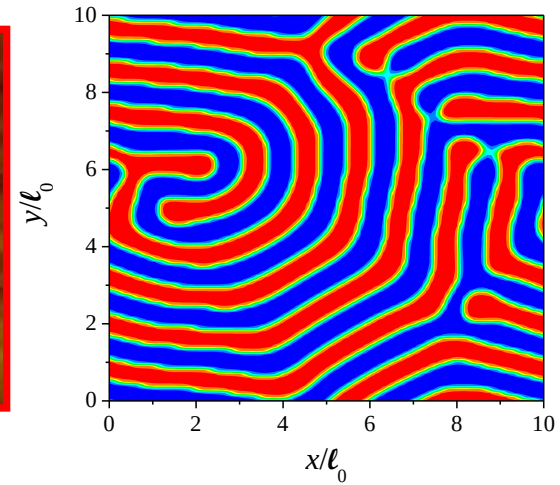
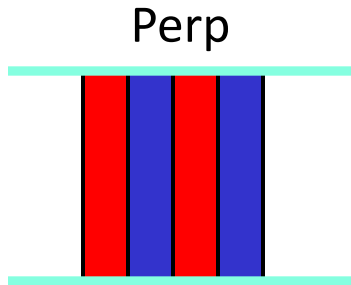
Orientation Transition of Lamellae

surface treatment u vs. thickness L



Parallel to Perpendicular Transition

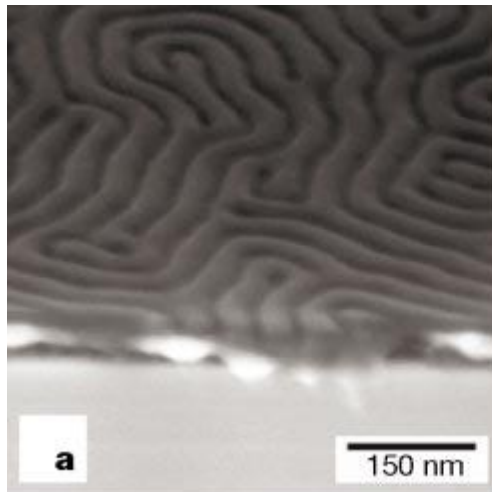
Top view



- Problem: the Perp phase is not aligned in the plane
- How to align ? Directed Self-Assembly...

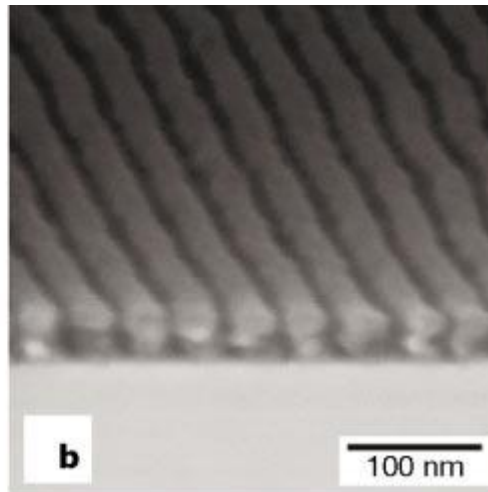
Chemical nano-patterned surface

uniform
surface

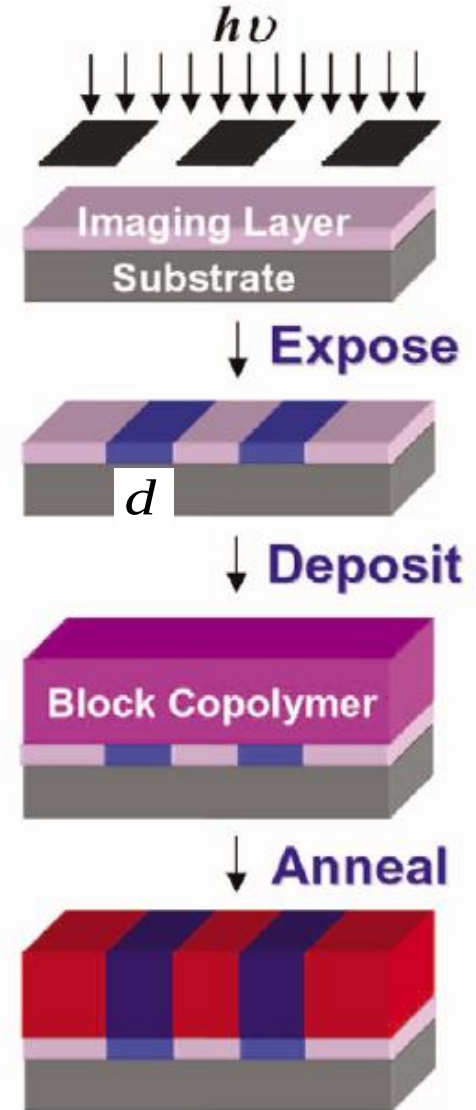


Kim et al '03

BCP replicates
the patterns

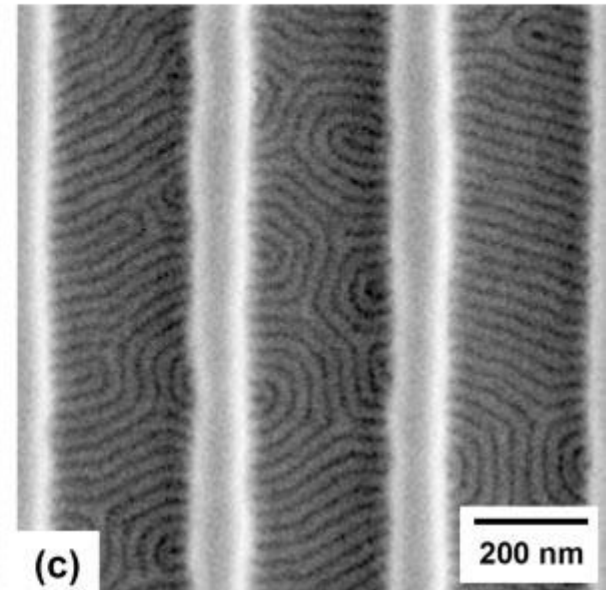
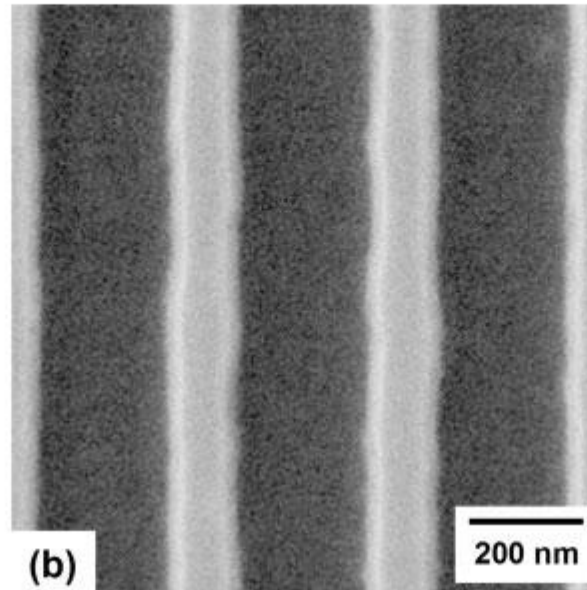
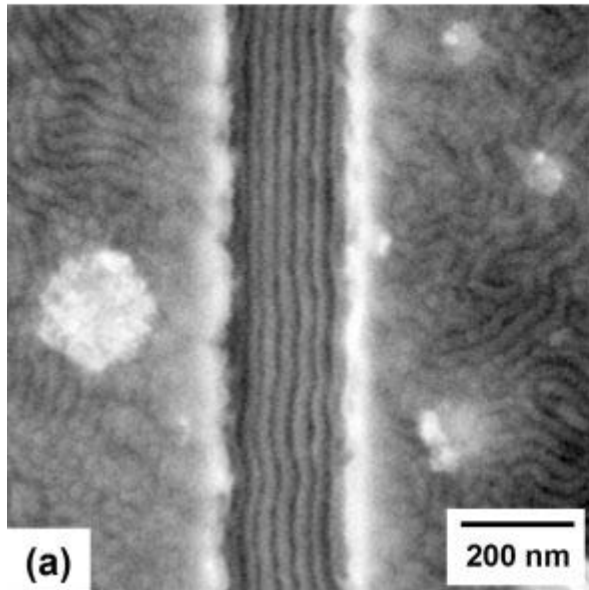
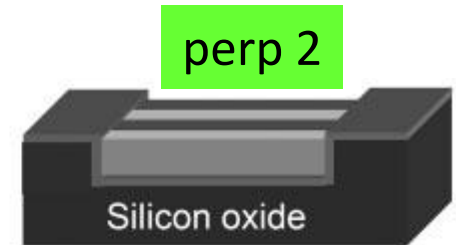
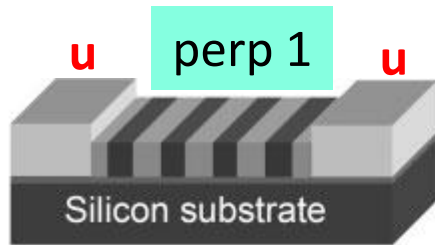


$$d \ll \ell_0$$



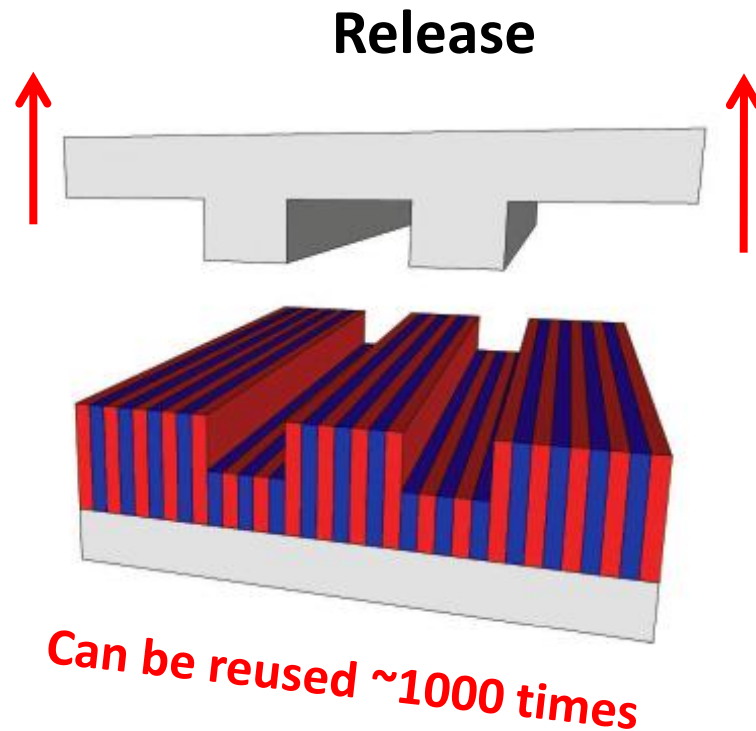
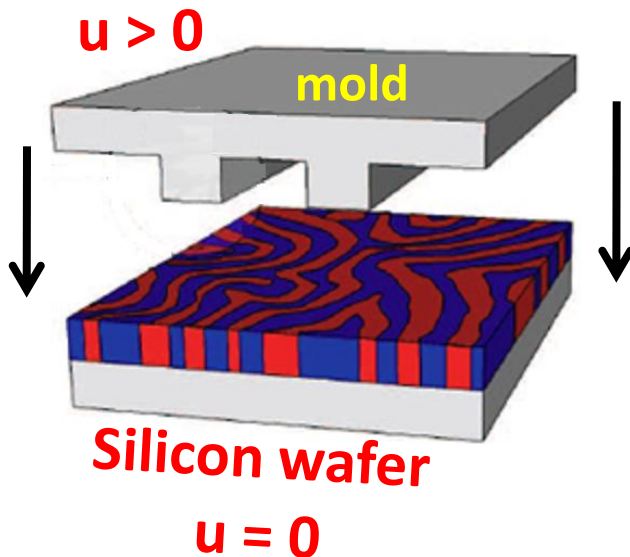
Char et al; Nealey et al

Topographic Guiding Patterns



Problem: The wafer has to be modified for each repeated sample

Nano Imprint Lithography - NIL



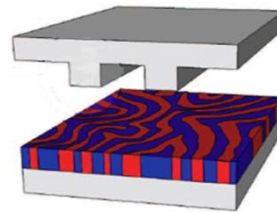
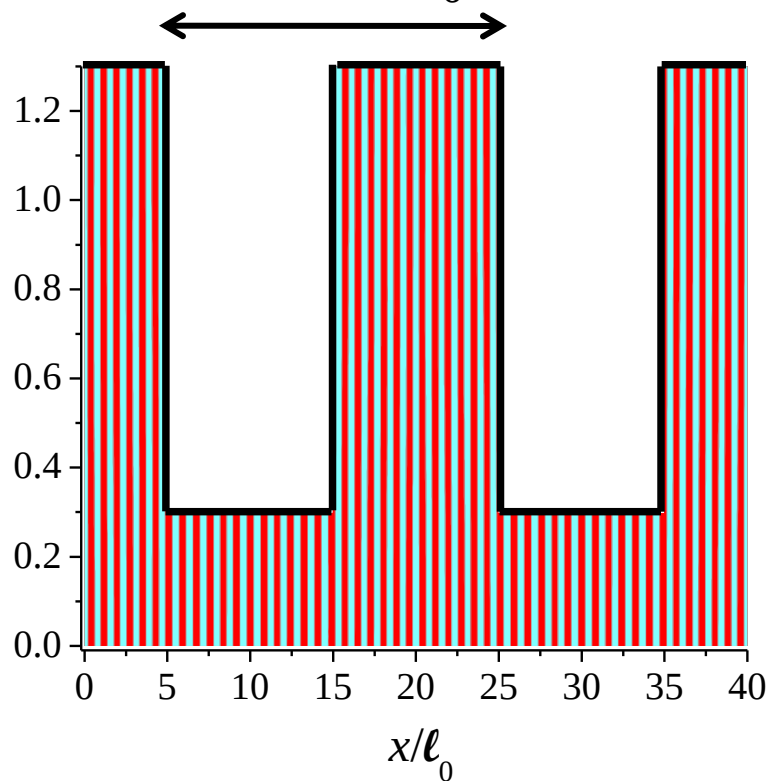
Directed Perp Phase

$$d \gg \ell_0$$

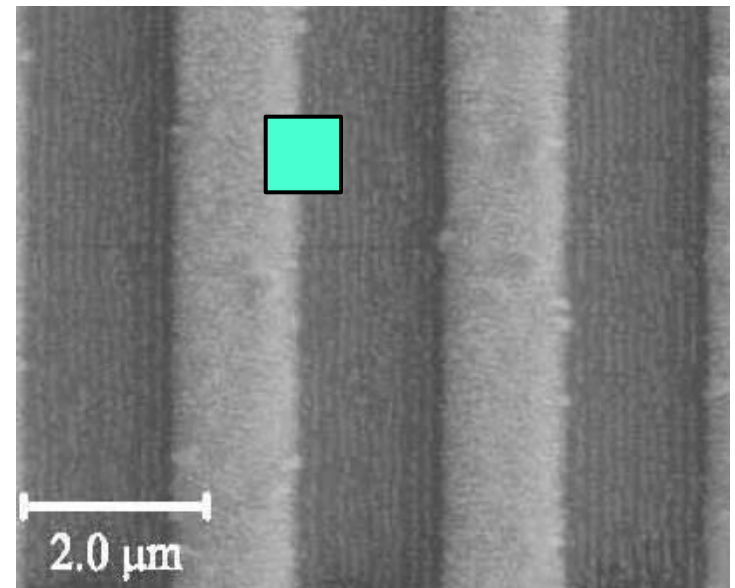
Perfect Perp phase

side view

$$d = 20\ell_0$$



Top view: SEM



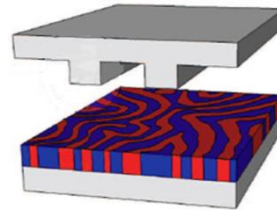
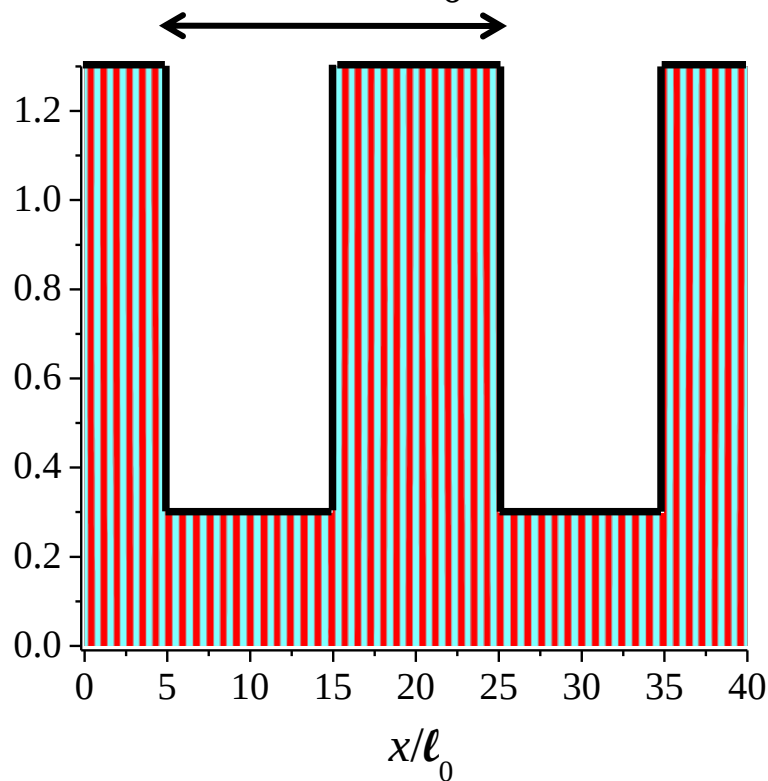
Produce Perp Phase

$$d \gg \ell_0$$

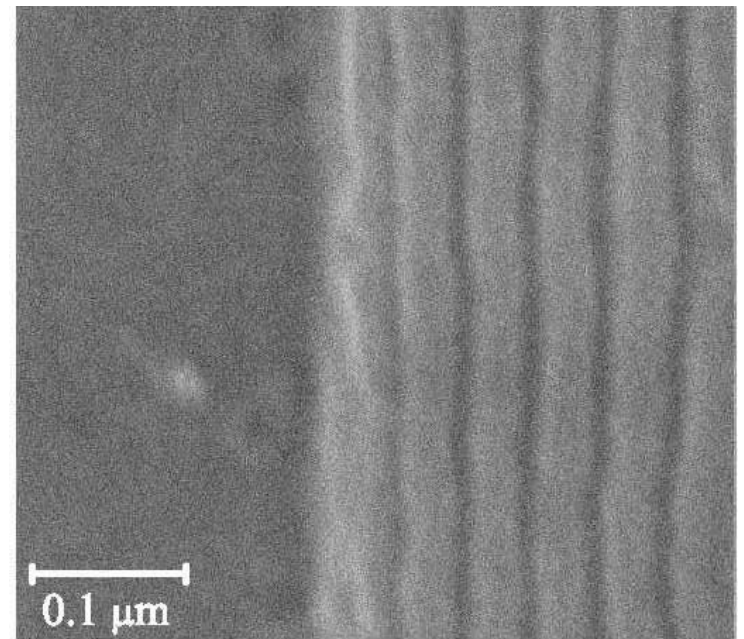
Perfect Perp phase

side view

$$d = 20\ell_0$$

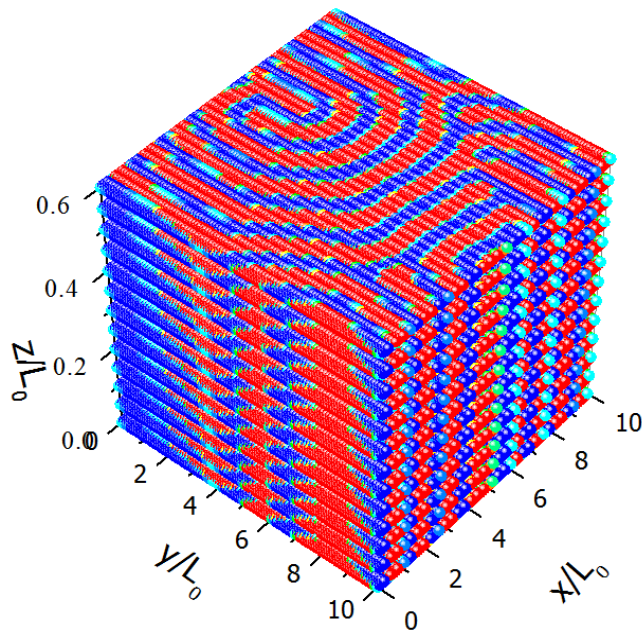


Zoom in

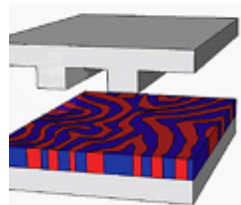


SCF calculations

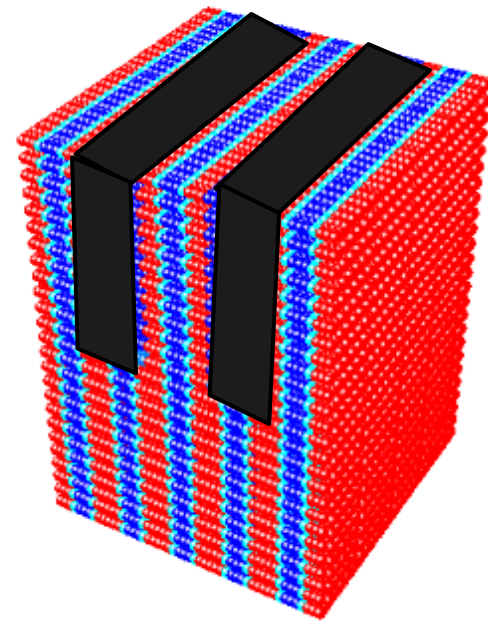
Flat Surfaces



In-plane
defects

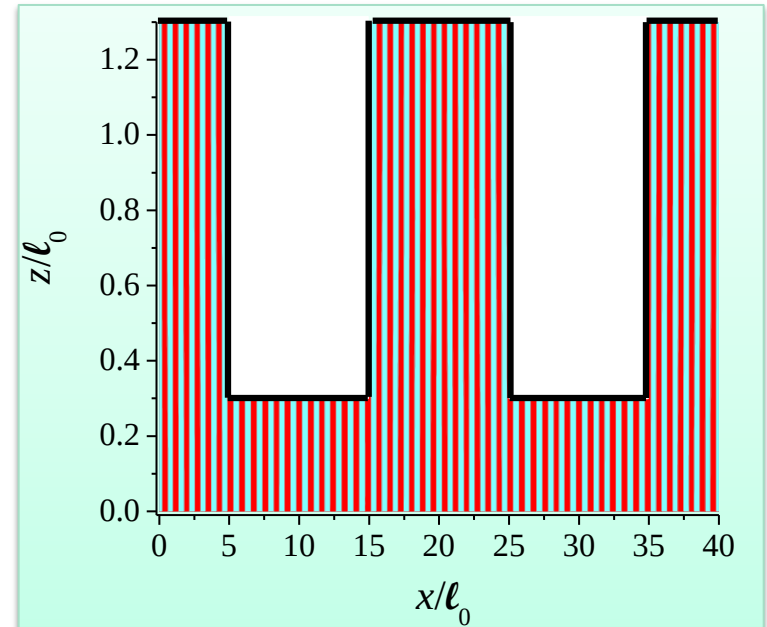
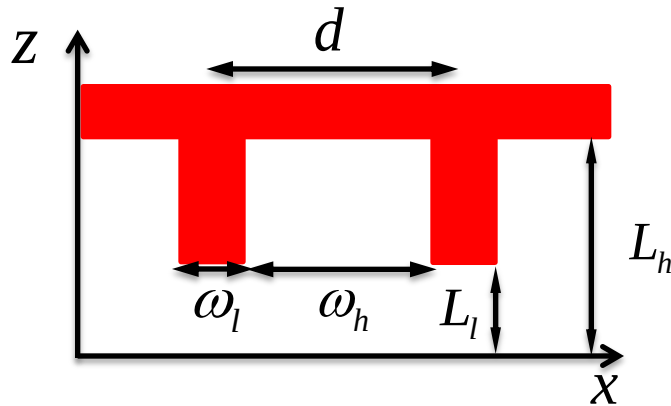


NIL



In-plane
alignment

Three important findings for NIL



1

Gradual temperature quench

2

$d = \omega_l + \omega_h \approx 20\ell_0 \square 30\ell_0$ **in experiments** $\omega_l = \omega_h$

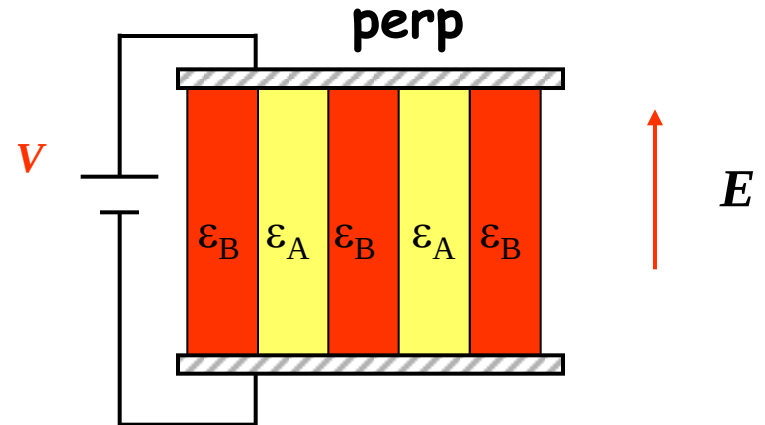
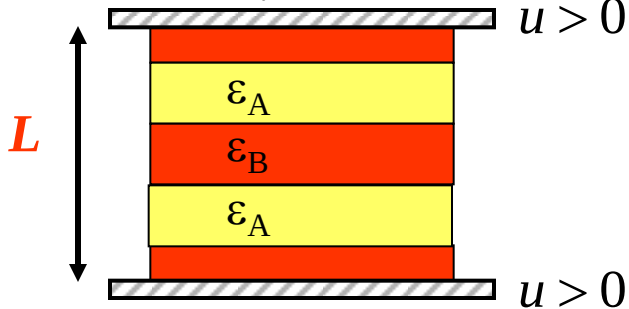
3

The top surface preference $u \approx 0.02$

Orientation with Electric Field

Confined lamellae

para



$$U = -\frac{1}{2} C V^2$$

$$C = \frac{1}{4\pi} \frac{\epsilon S}{L}$$

$$\begin{aligned} L &\sim 10 \mu\text{m} \\ V &\sim 100 \text{ V} \\ E &\sim 10 \text{ V}/\mu\text{m} \end{aligned}$$

moderate voltages

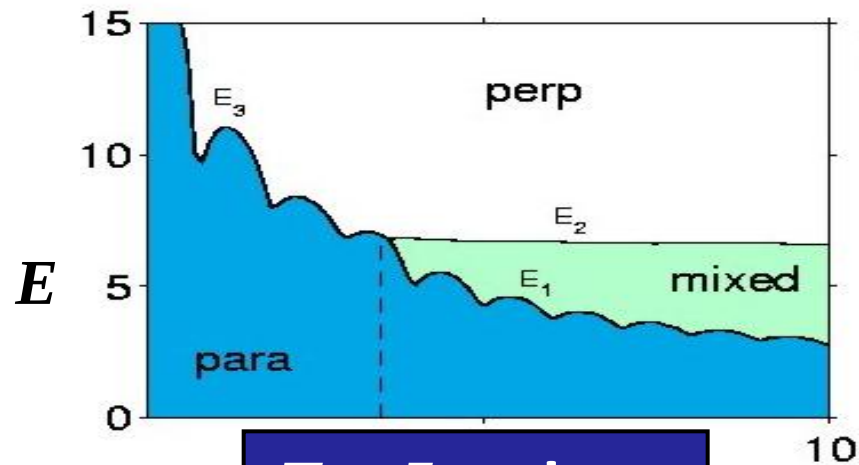
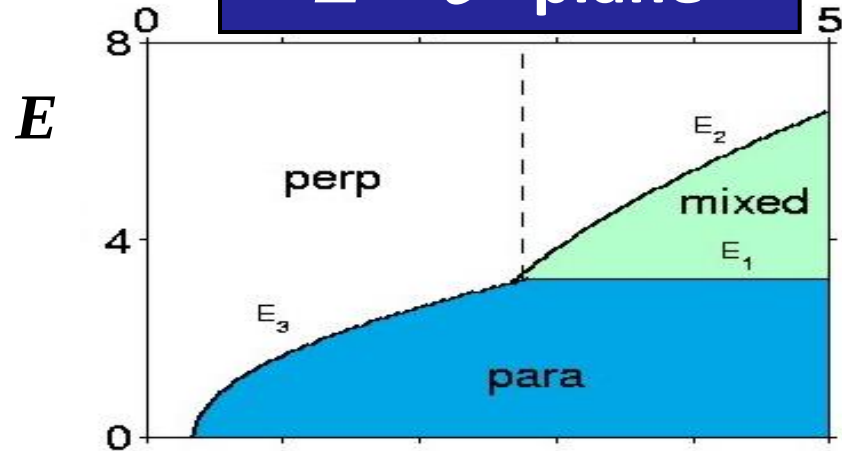
high fields

- Surface interactions prefer para orientation
- Dielectric boundaries prefer to align **parallel** to E (perp)

Anything in between?

Phase Diagrams

$E - \delta$ plane

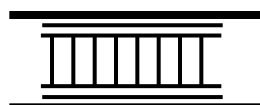


$E - L$ plane

perp



mixed

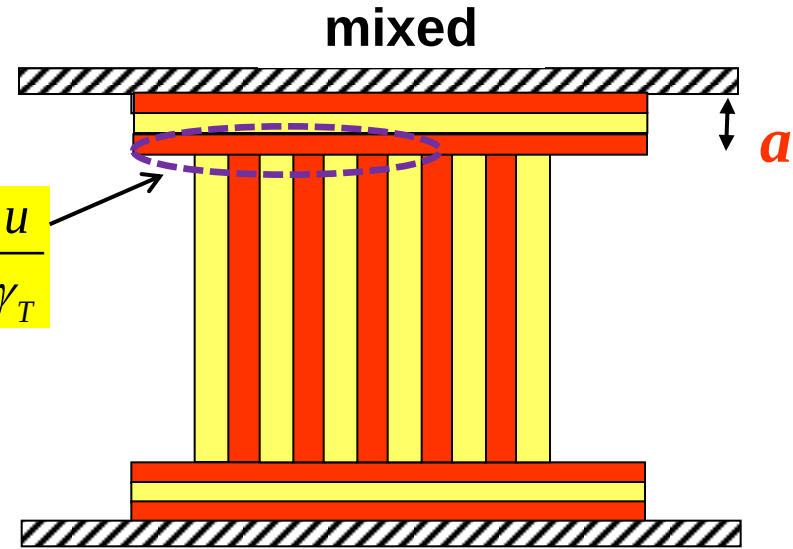


para



L

$$\delta = \frac{u}{\gamma_T}$$

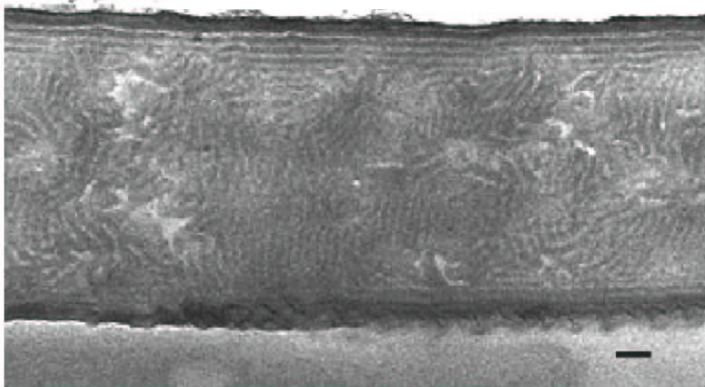


Mixed Morphology

Electron Microscopy

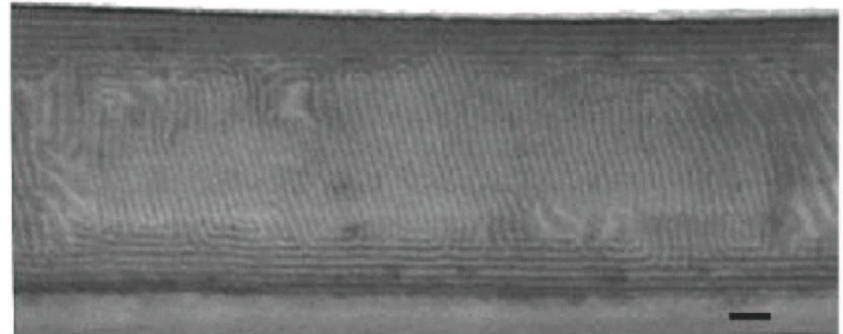
- PS-PMMA block copolymer
- Annealing in E -field $40 \text{ V}/\mu\text{m}$
- *Competition:* Surface & E -field

6 hours



0.6 μm

16 hours



Para

Perp

Para

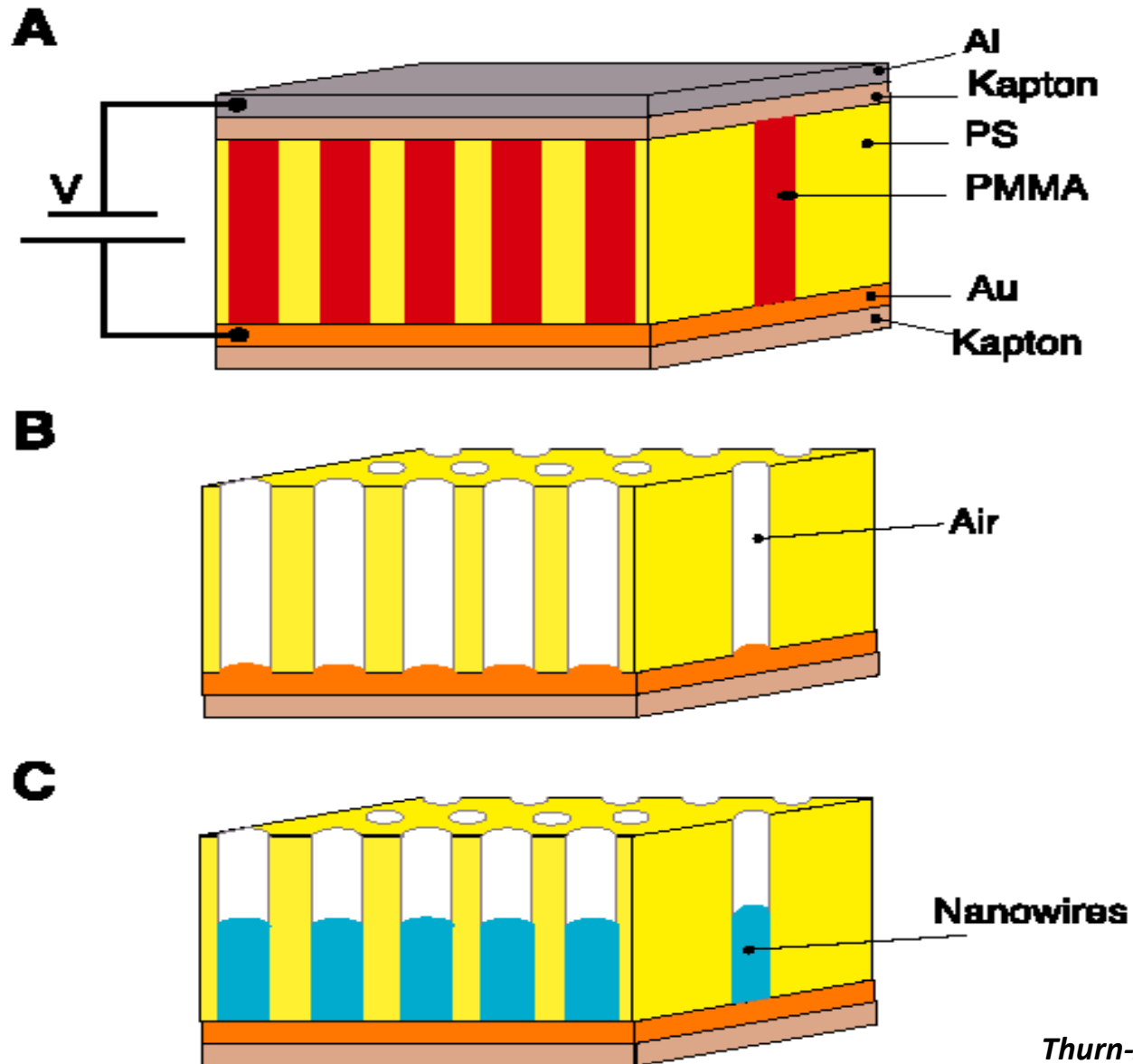
Conclusions

- Surface patterns, templates & electric fields for Block Copolymers
 - self-assembly, nano-patterns and structures: *applications to nano-lithography*
- **Challenge:** defect-free orientation & alignment with minimal surface treatment
- **Challenge:** Metastability, traps, film rheology

Electric Field

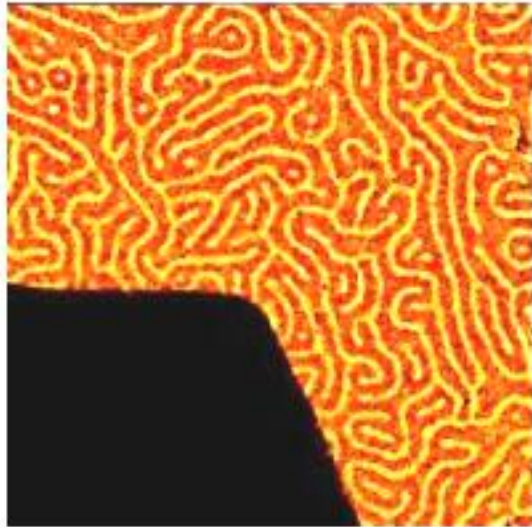
Orientation of lamellae

BCP Films : Templates for Nano-wires

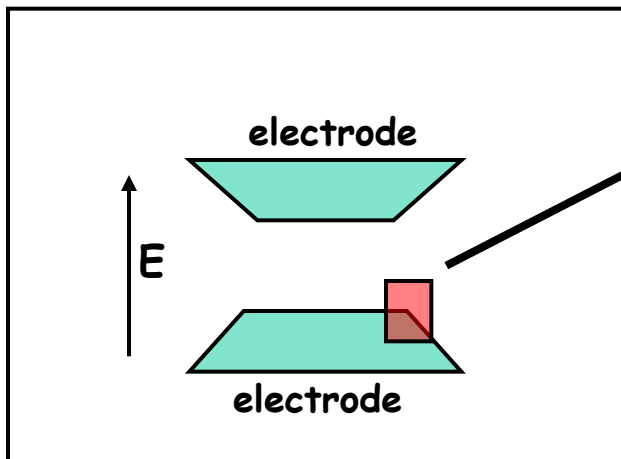
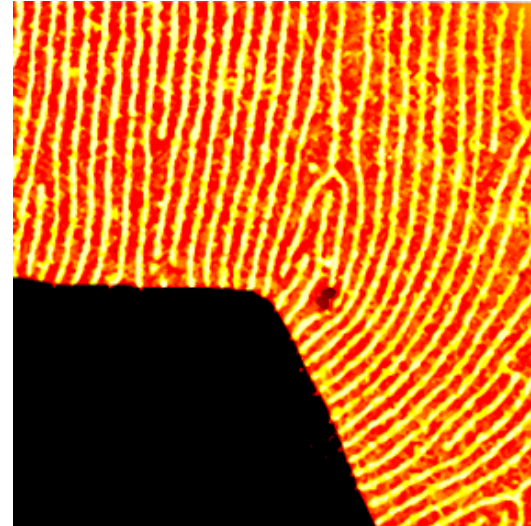


TEM Micrographs of PS-PMMA

No Applied Field



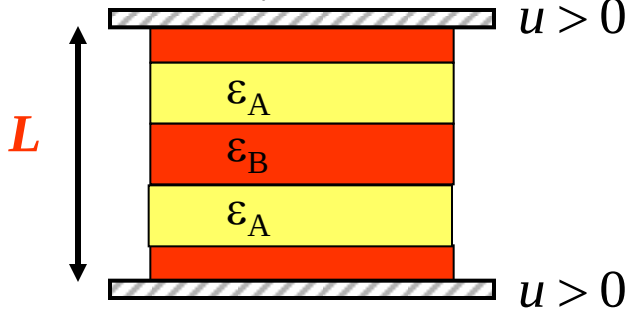
Annealed Under Applied Field



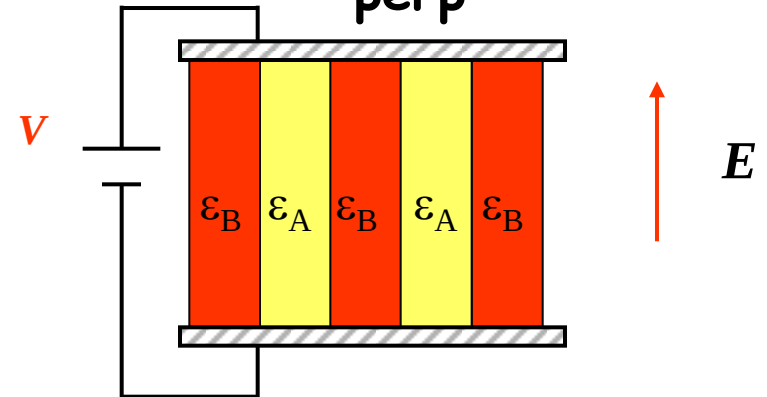
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para



perp



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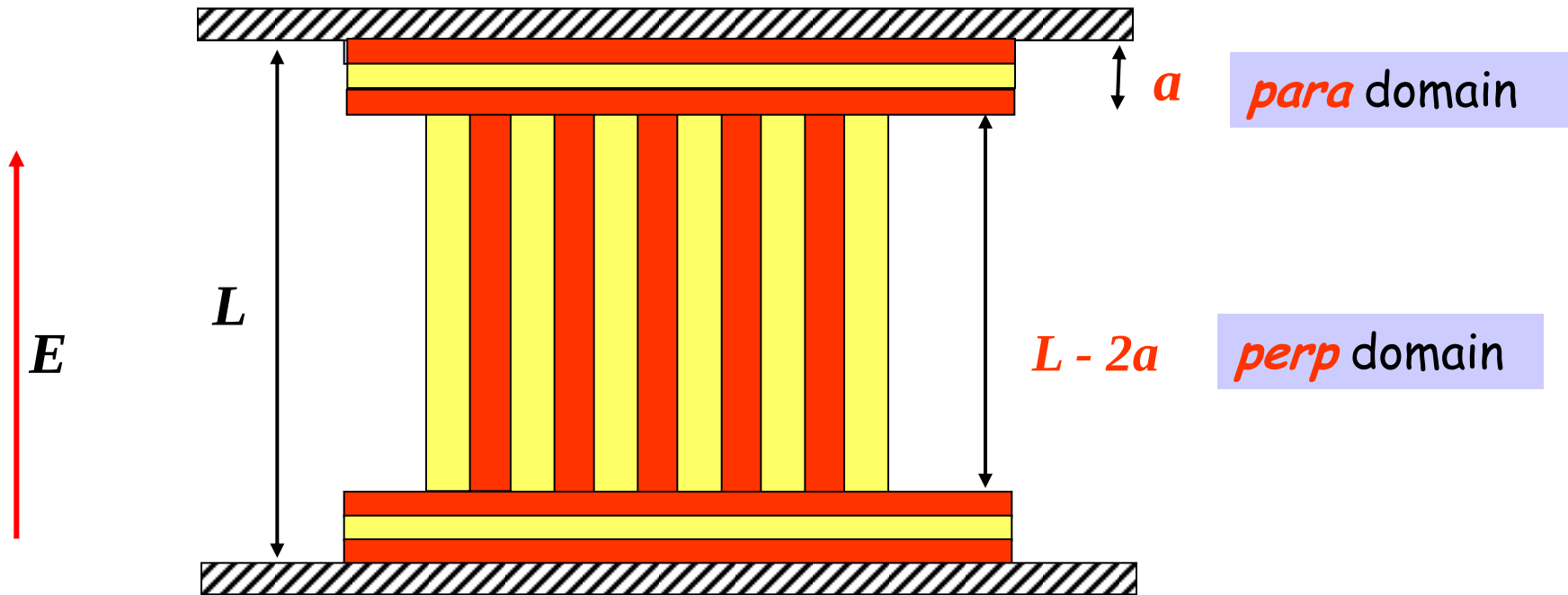
moderate voltages

high fields

- Surface interactions prefer para orientation
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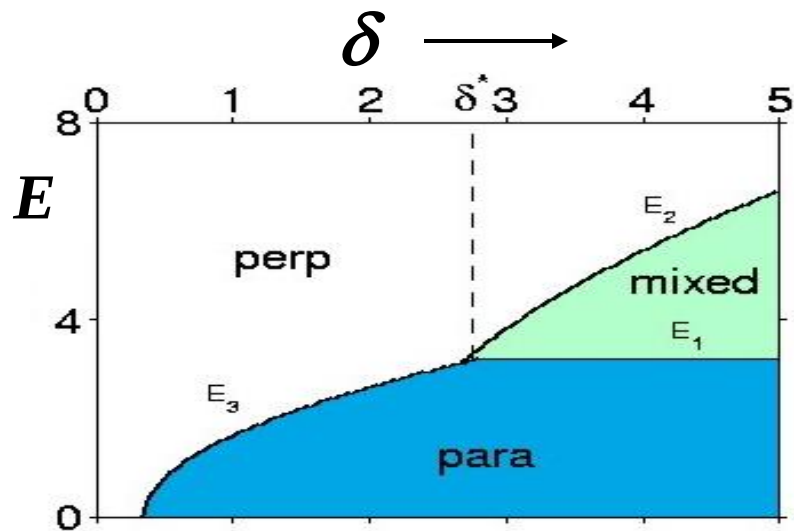
Anything in between?

MIXED MORPHOLOGY

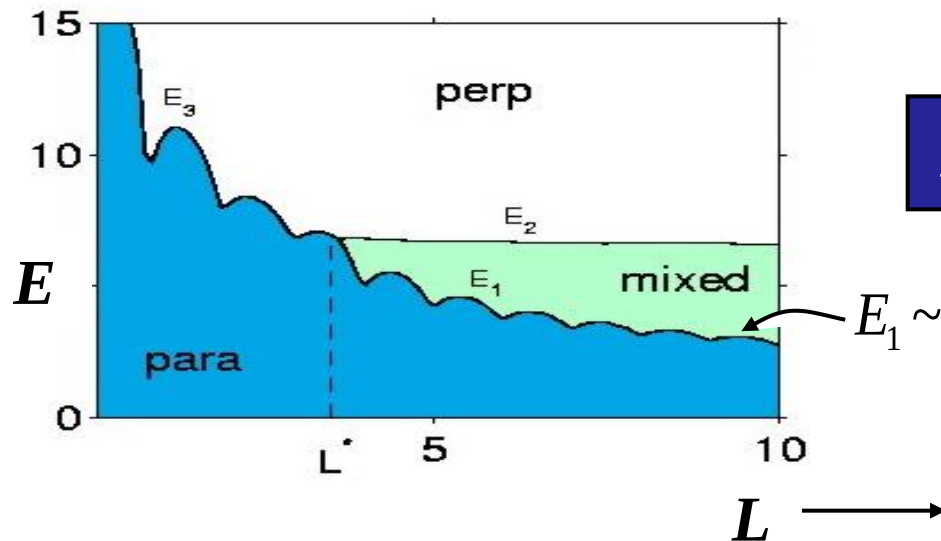


- Sharp interfaces (strong segregation)
- Effect of surfaces has finite range
- *Mixed* State:
 - Two parallel layers of width a
 - Perpendicular domain in the middle: $L - 2a$

Phase Diagrams



$$\delta = \frac{u}{\gamma_T}$$



Conclusions

- Surface patterns & templates for Block Copolymers
 - self-assembly, nano-patterns and structures
 - **Challenge:** defect-free orientation & alignment with minimal surface treatment
 - **Challenge:** Metastability, traps, film rheology
- Nanolithography: - 'bottom up' approach
 - Device Design & Fabrication? Pattern Quality? Multi-mask?
 - There is potential but we are not yet there...
- E-field: Versatile tool in Block Copolymer
 - Orientation control of block copolymer films;
 - Phase transitions; roles of ionic impurities