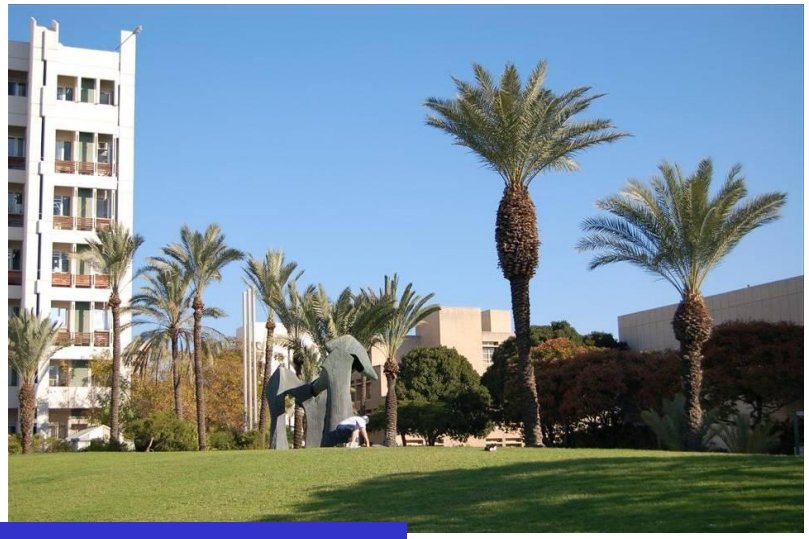
The Physics and Applications of Block Copolymer Films

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



TEL AVIV UNIVERSITY אוניברסיטת תל-אביב

The Physics and Applications of Block Copolymer Films

coworkers:

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

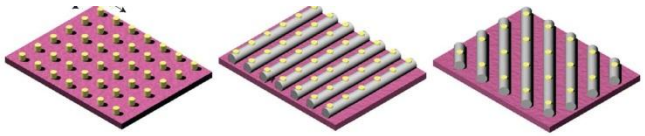
Experiments: J. Daillant & P. Guenoun (Saclay)

- Introduction: the physics of block copolymers

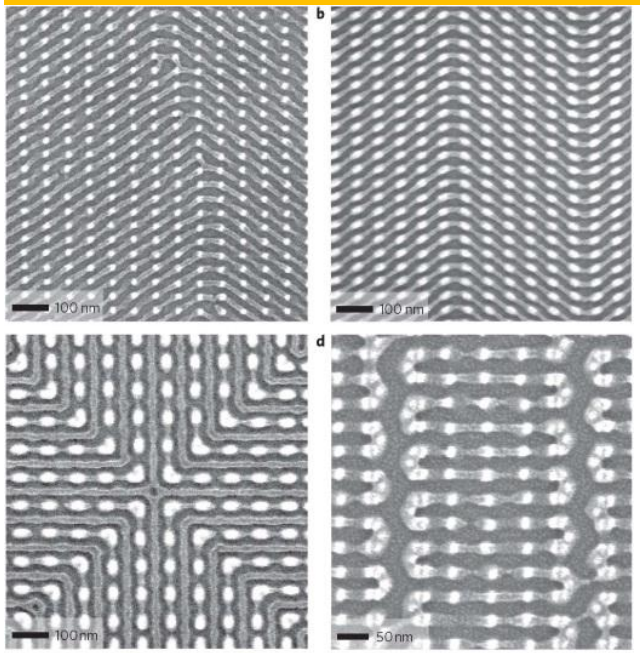
- Surfaces & Electric Fields: nanostructures, chemical surface patterns & nano-imprint templates, surface-induced orientation, electrically-induced orientation

Polymer Self-assembly on Surfaces: Future Nano-Lithography

cylinders on dot-patterned surfaces



directed patterns to replace photomasks?

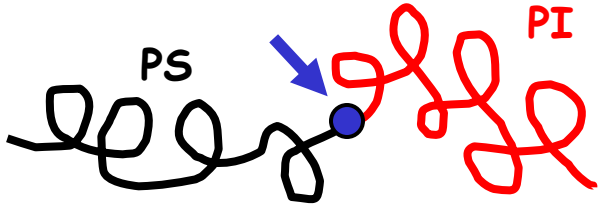


100 nm

Yang et al '10

What are Block Co-Polymers?

- Repulsive Interaction: *polystyrene-polyisoprene*
  - ***Phase separation***: PS/PI



- Competition: chemical link & entropy
  - ***Self-Assembly***

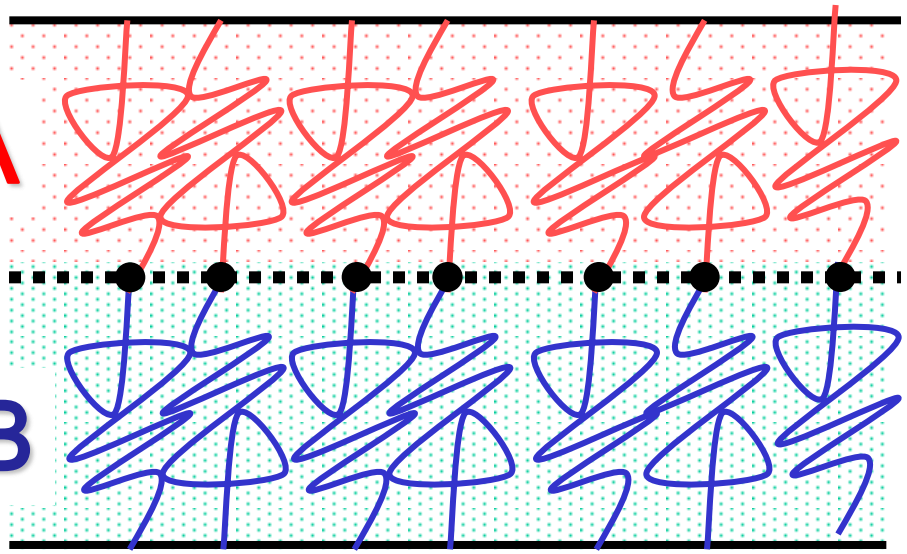
→ Micro-phase separation (nano-scale)

Applications:

Nano-Structures; Bottom-up Functional Composites

Why periodic structures ?

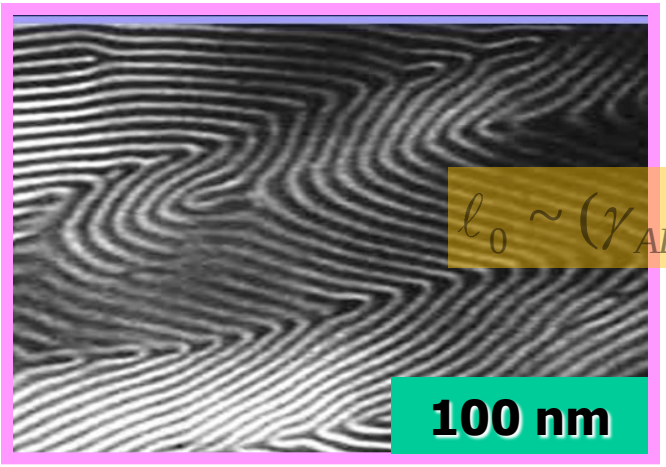
interfacial tension γ_{AB}



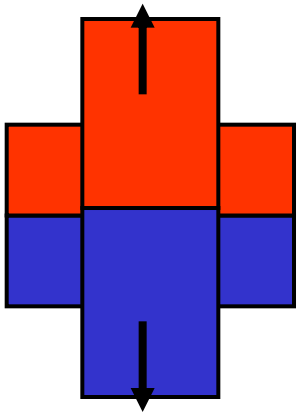
$\ell_0 = 2\pi / q_0$

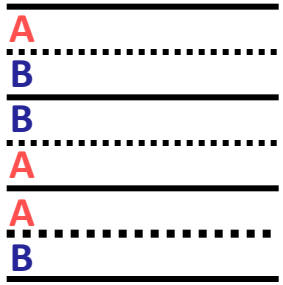
10 - 100 nm

TEM: lamellae



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





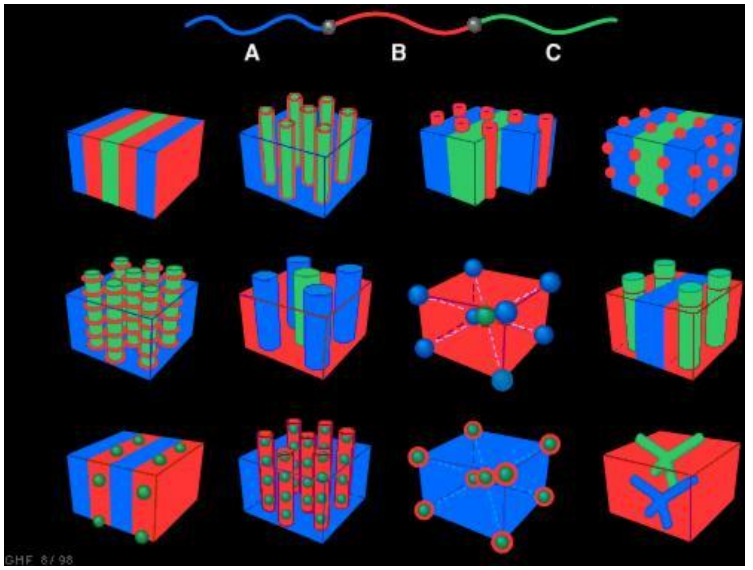
Tri-Blocks: other phases

Knitting pattern

Stadler

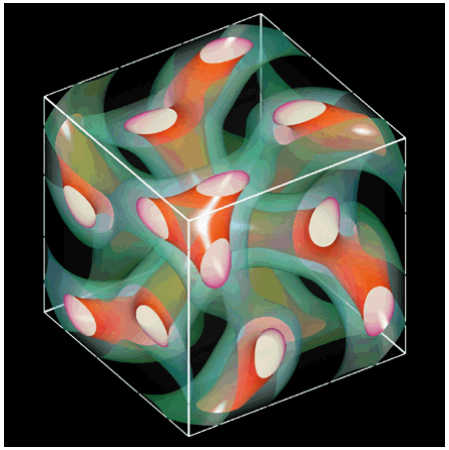
A – B – C

many complex morphologies



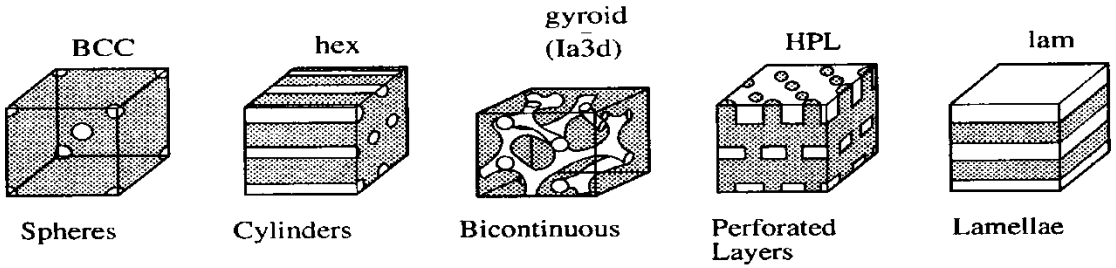
Zheng & Wang '95

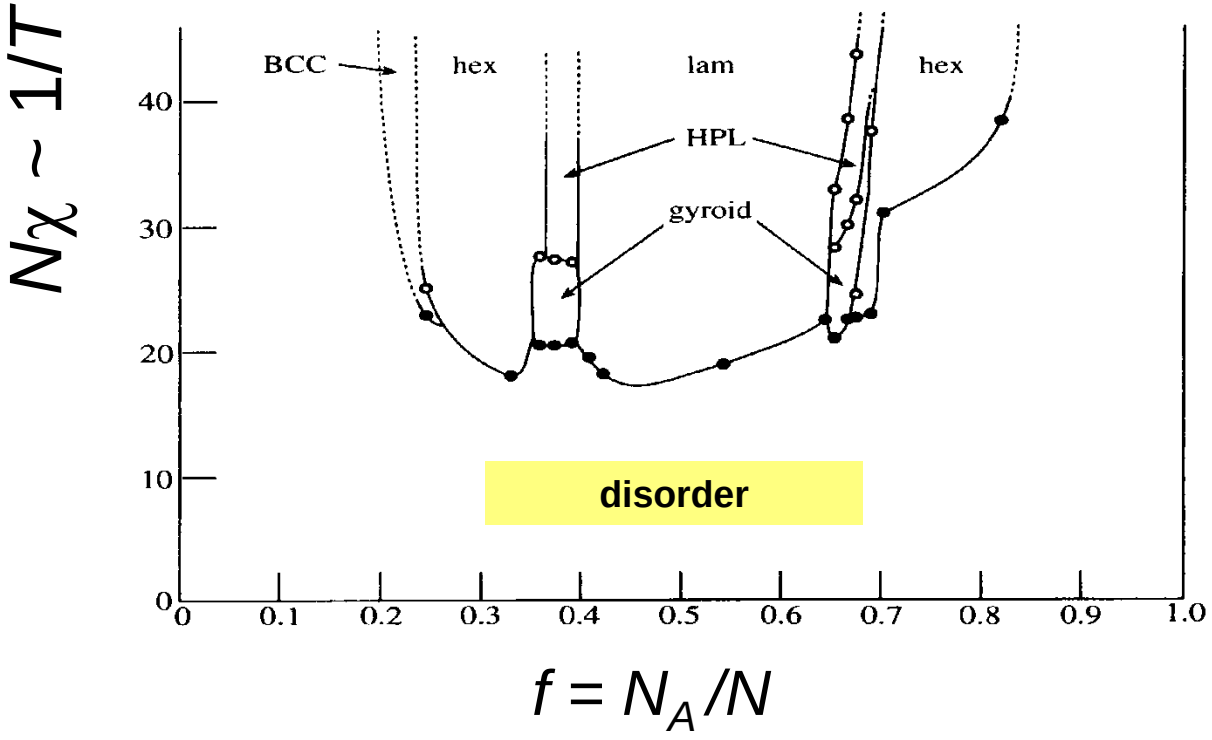
bi-continuous

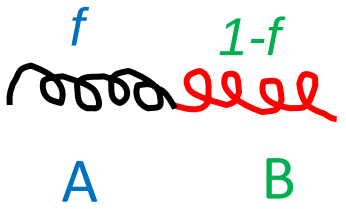


Thomas

Phase Diagram of di-Blocks





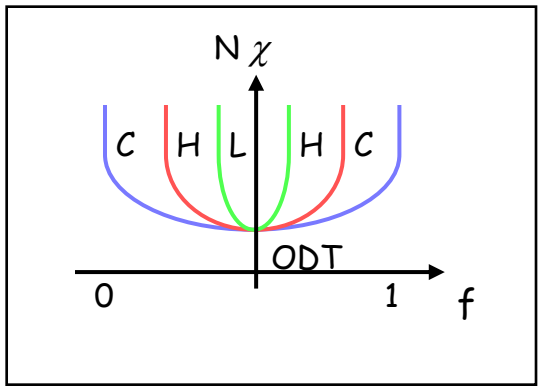


f fraction of A

χ Flory parameter

Khandpur '95

Block Co-Polymers: Coarse-grained Models



Bulk Free Energy : Ginzburg-Landau expansion

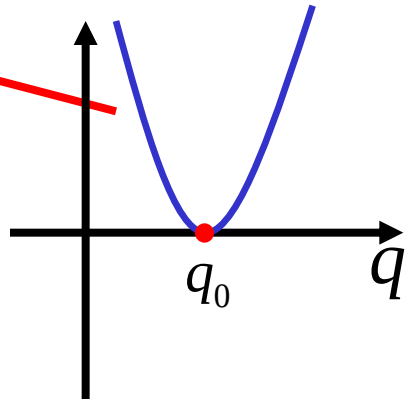
$$F_{\text{bulk}} = \int \left\{ \frac{\tau}{2}\phi^2 + \frac{h}{2}\left(q_0^2\phi + \nabla^2\phi\right)^2 + \frac{\lambda}{3!}\phi^3 + \frac{u}{4!}\phi^4 \right\} d^3r$$

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

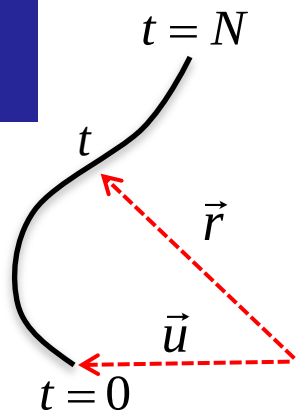


ODT= Order Disorder Temperature

Leibler '80

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 $\vec{u}$



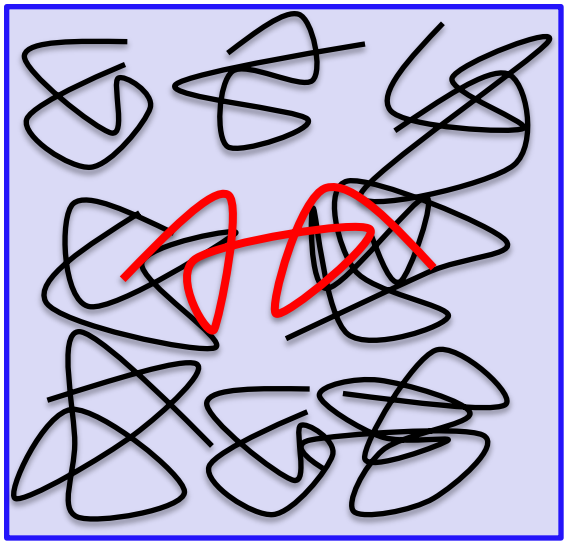
$$q(t,\vec{r}) = \int d\vec{u}\; Q(t,\vec{r}|\vec{u})$$

End-integrated polymer propagator:

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

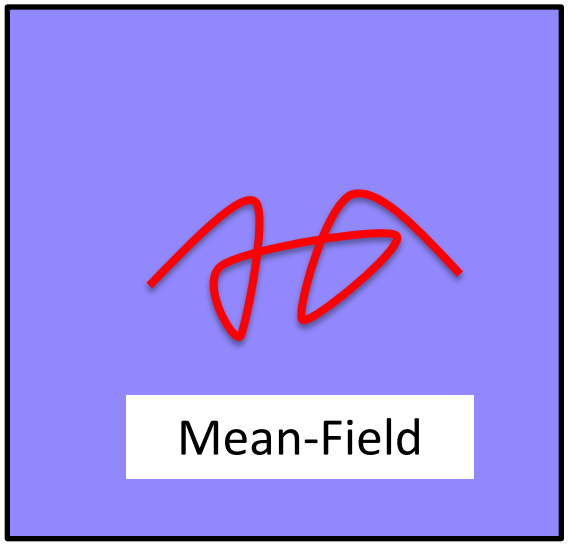
Schrödinger-like eq.

Concentration $\phi(r)$



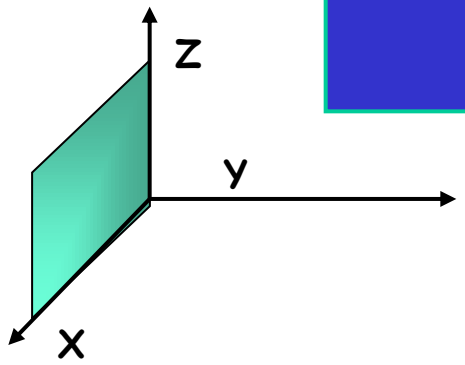
$\phi(r)$ $\omega(r)$

Auxiliary field $\omega(r)$



Effect of Surface:

Arbitrary Chemical Patterns



Total Free Energy

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

Patterned surfaces: $u(x,z)$

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

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

Minimize the total free energy respecting the boundaries

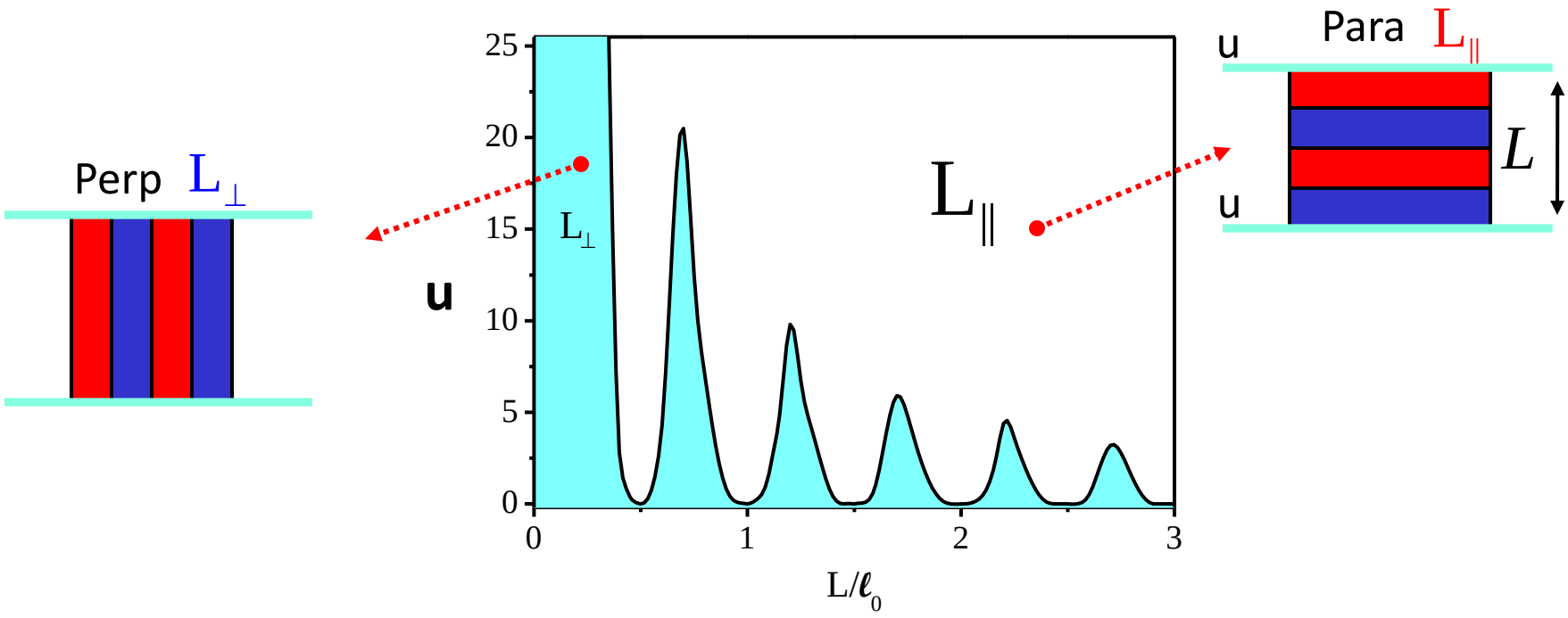
u_B surface energy of B monomers

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***

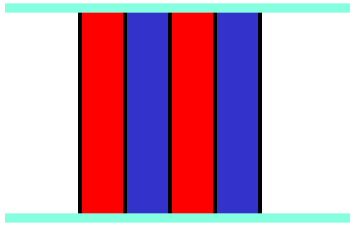


AFM: Guenoun & Daillant

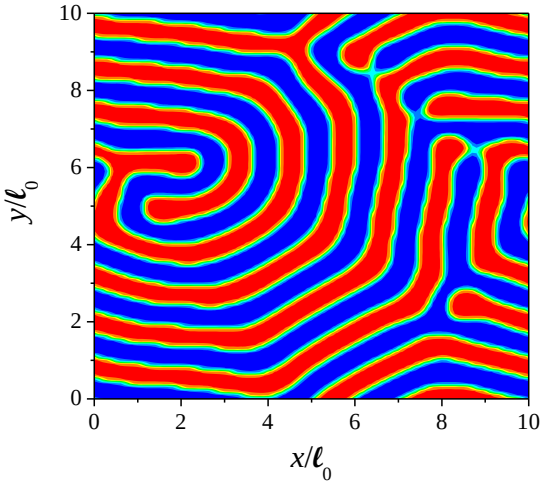
Theory: Masten; Tsori & DA

Parallel to Perpendicular Transition

Perp



Top view

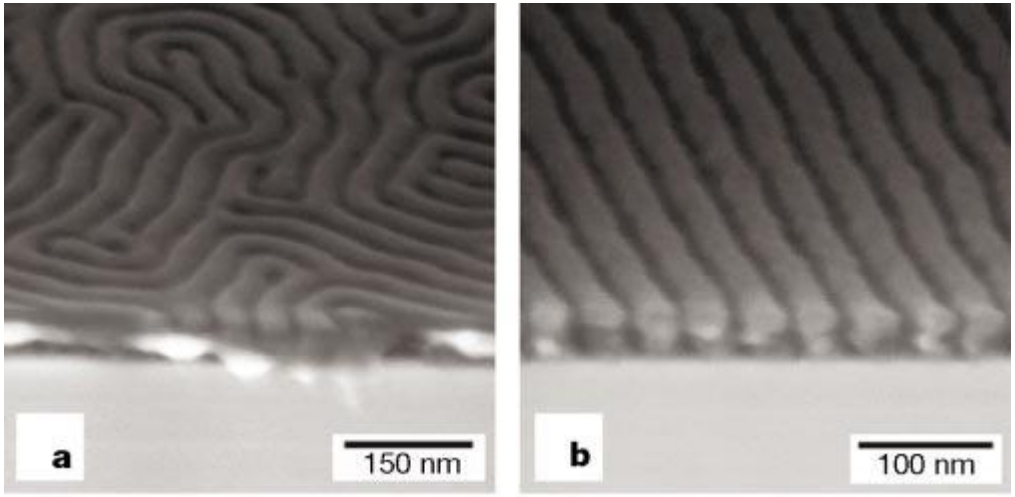


- **Problem: the Perp phase is not aligned in the plane**
- **How to align ? Directed Self-Assembly…**

Chemical nano-patterned surface

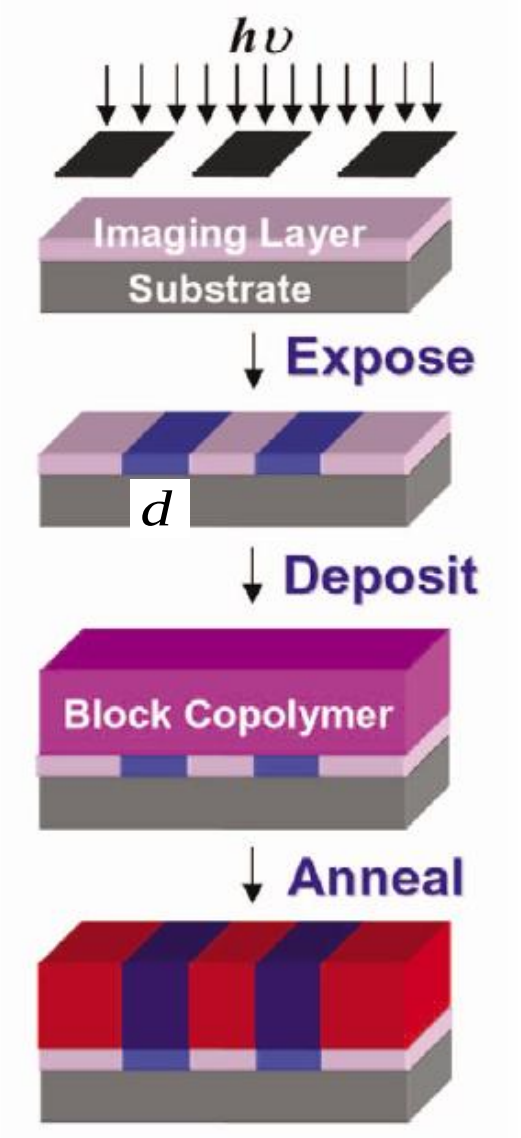
uniform surface

BCP replicates the patterns



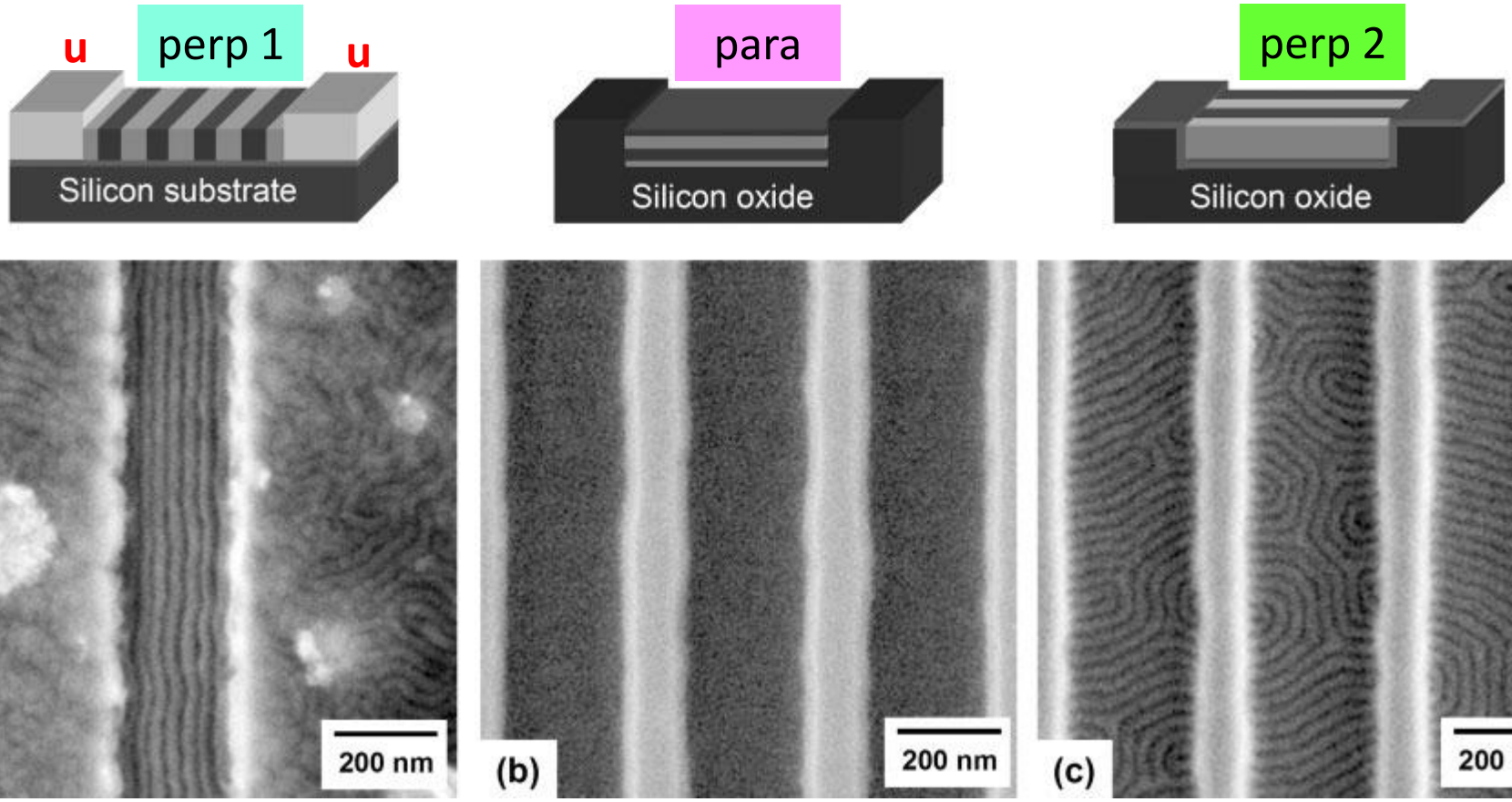
Kim et al '03

$d \sim \ell_0$



Char et al; Nealey et al

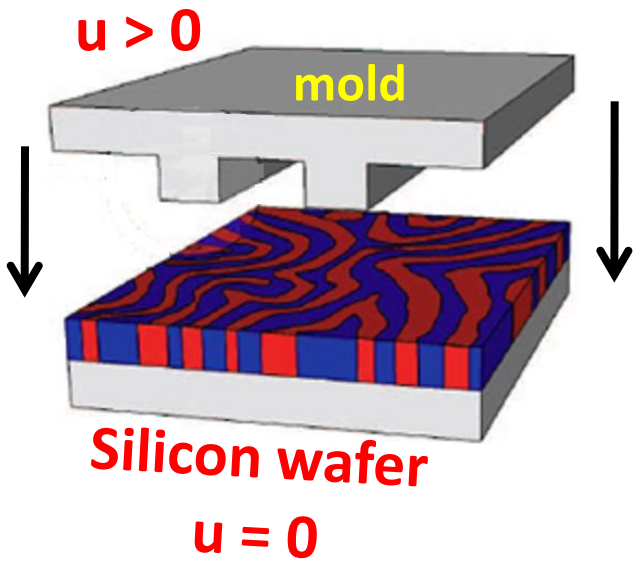
Topographic Guiding Patterns

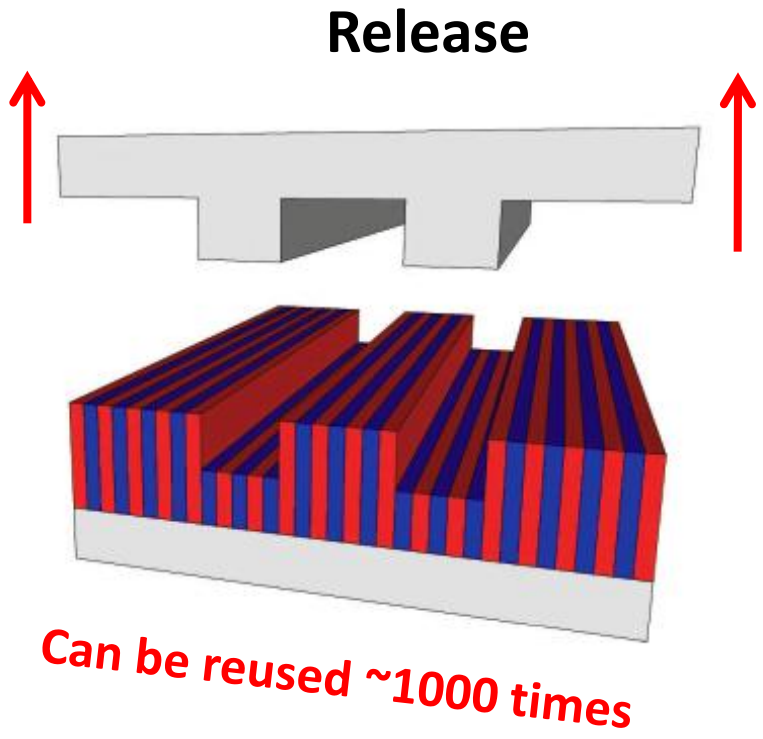


Problem: The wafer has to be modified for each repeated sample

Park et al '07

Nano Imprint Lithography - NIL





Li & Huck; Char et al; Daillant & Guenoun

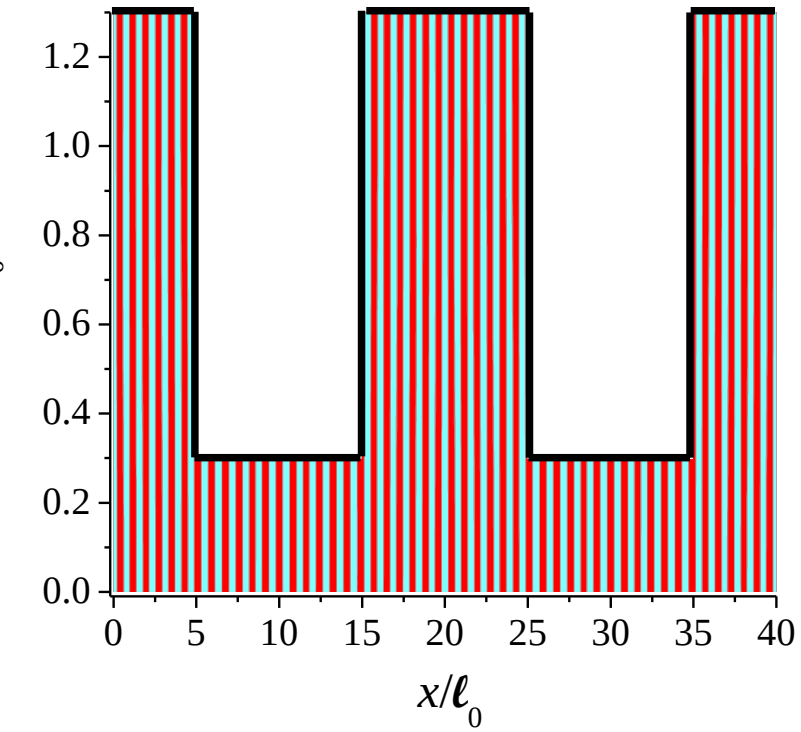
Directed Perp Phase

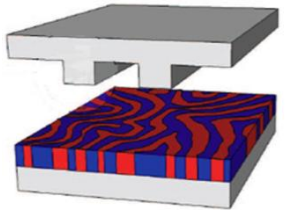
$d \gg \ell_0$

Perfect Perp phase

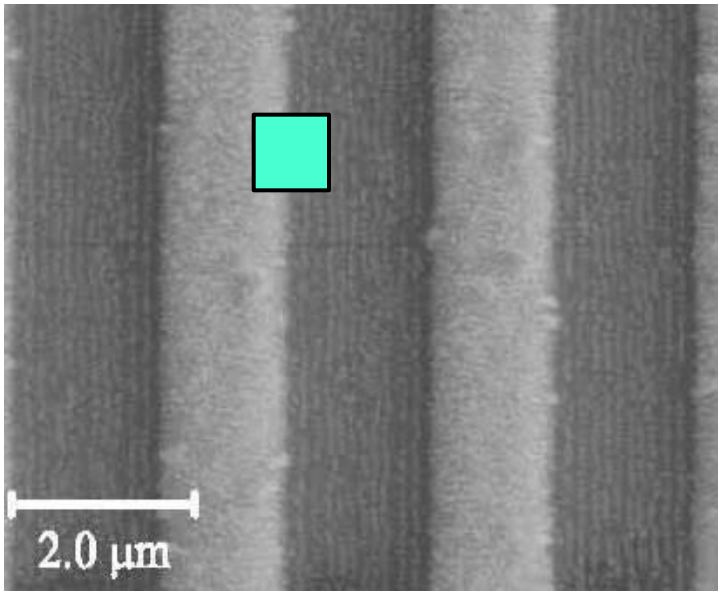
side view

$d = 20\ell_0$





Top view: SEM



Man, Orland & DA ' 10

Daillant & Guenoun ' 10

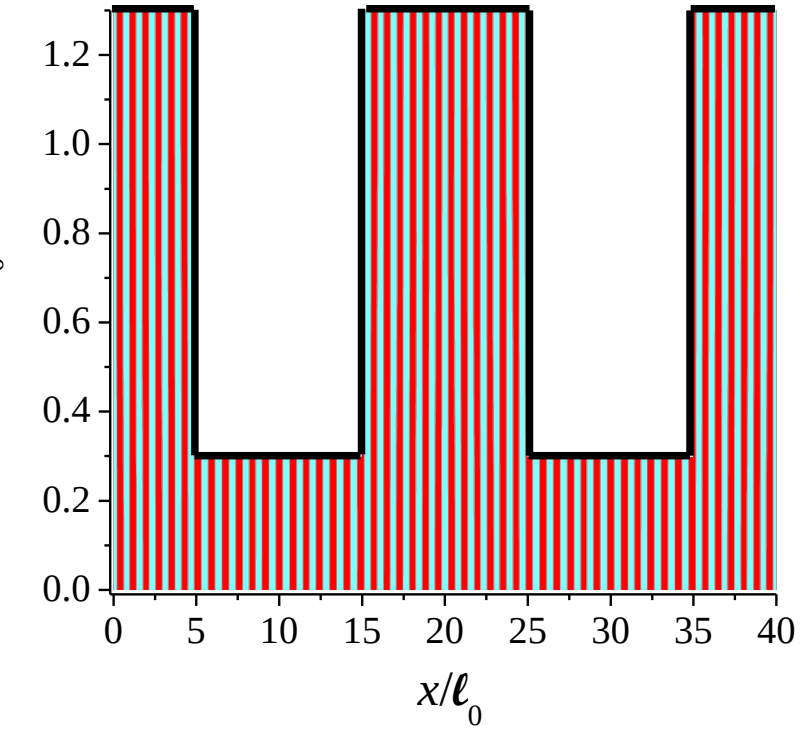
Produce Perp Phase

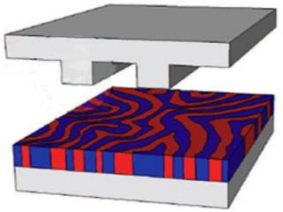
$d \gg \ell_0$

Perfect Perp phase

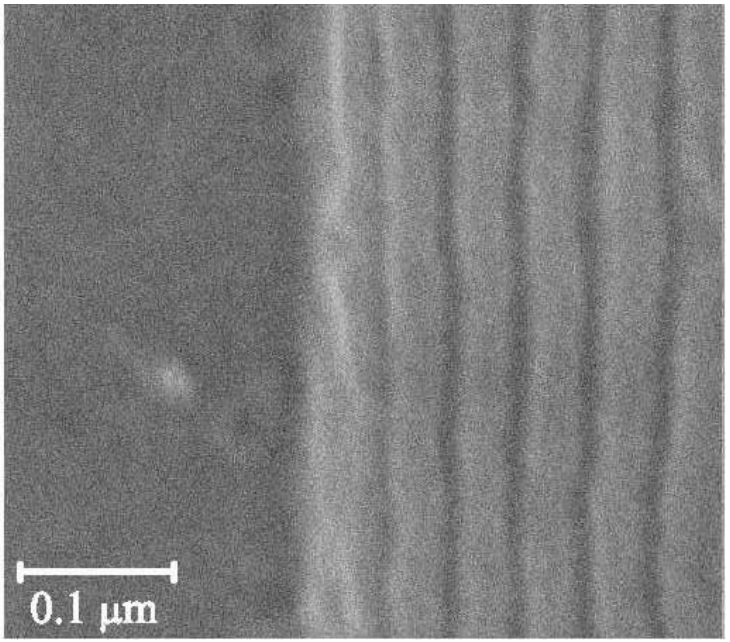
side view

$d = 20\ell_0$





Zoom in

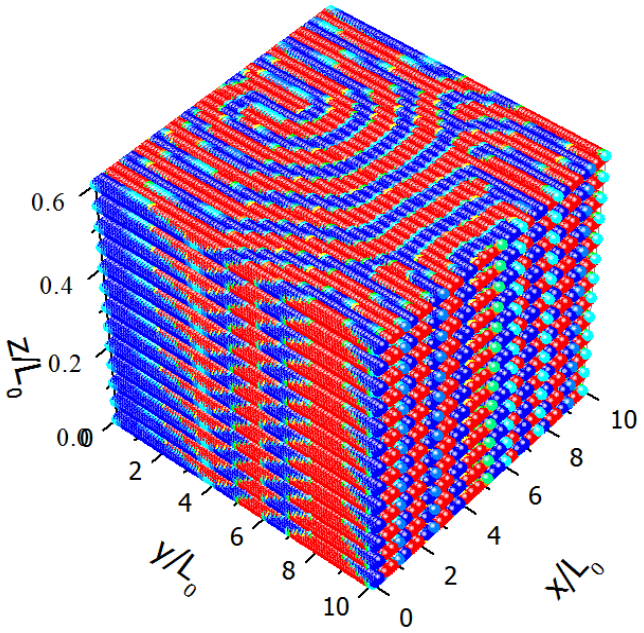


Man, Orland & DA ' 10

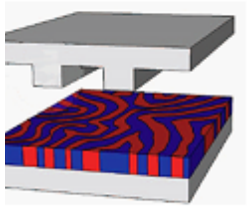
Daillant & Guenoun ' 10

SCF calculations

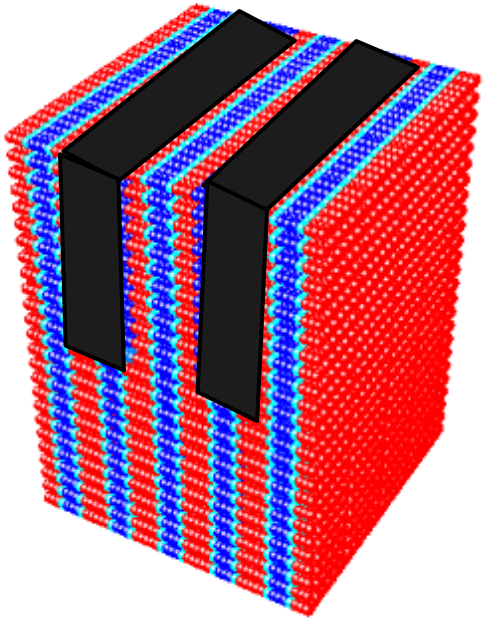
Flat Surfaces



In-plane
defects

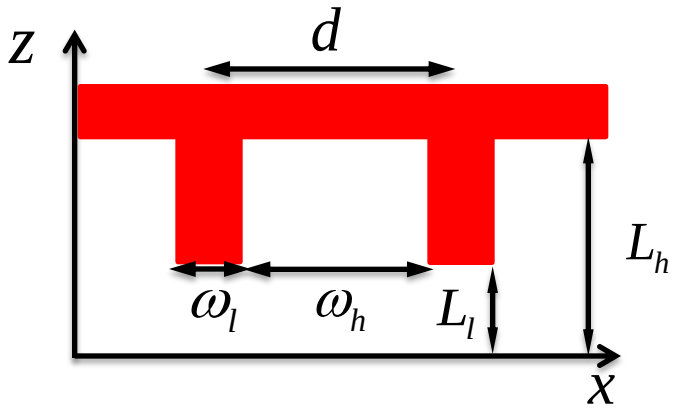


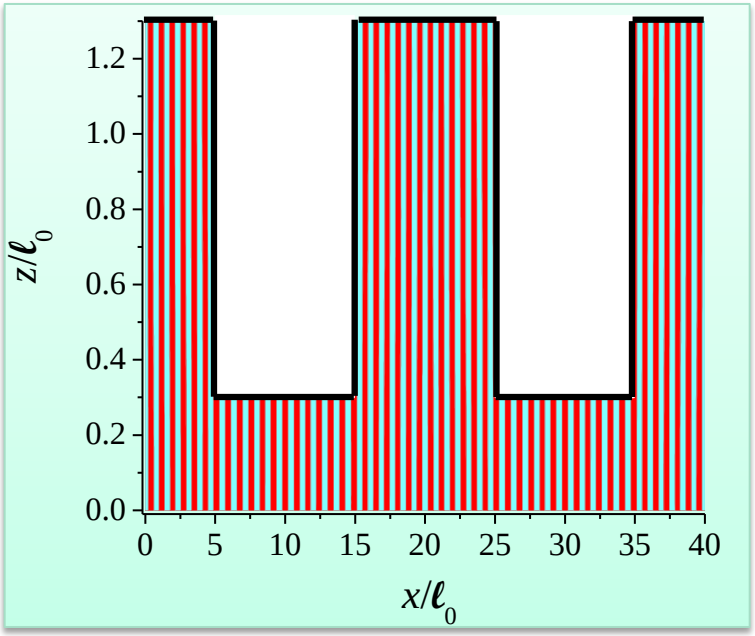
NIL



In-plane
alignment

Three important findings for NIL





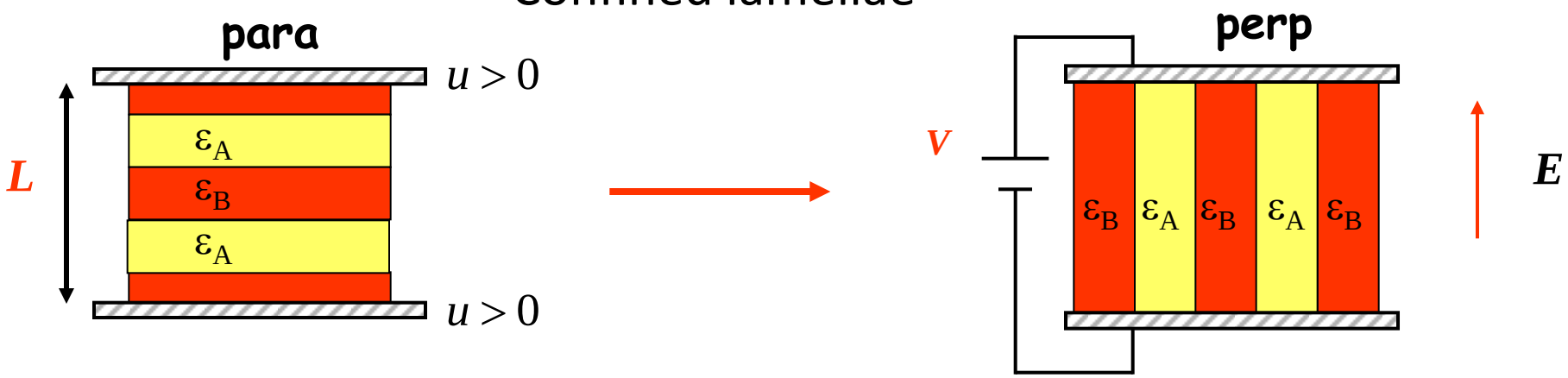
1. **Gradual temperature quench**

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



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

$L \sim 10\ \mu m$
$V \sim 100\ V$
$E \sim 10\ V/\mu m$

moderate voltages

high fields

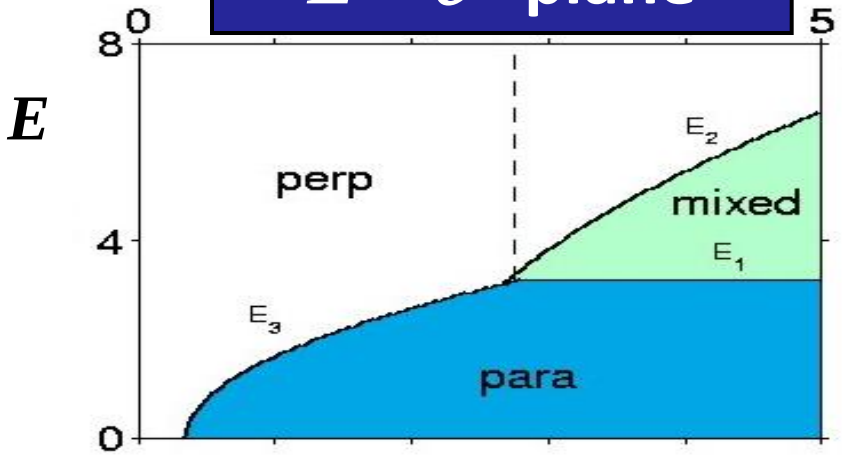
$$C = \frac{1}{4\pi} \frac{\varepsilon S}{L}$$

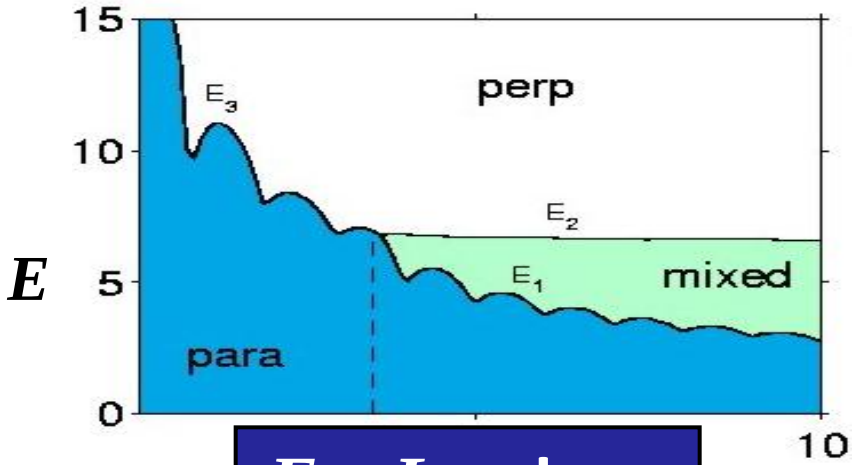
- Surface interactions prefer para orientation
- Dielectric boundaries prefer to align parallel to ***E*** (perp)

Anything in between?

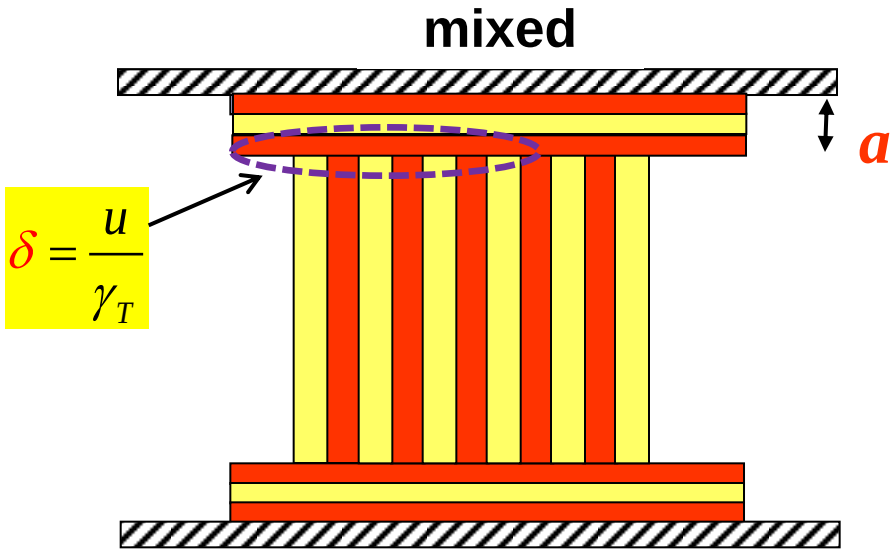
Phase Diagrams

$E - \delta$ plane





$E - L$ plane

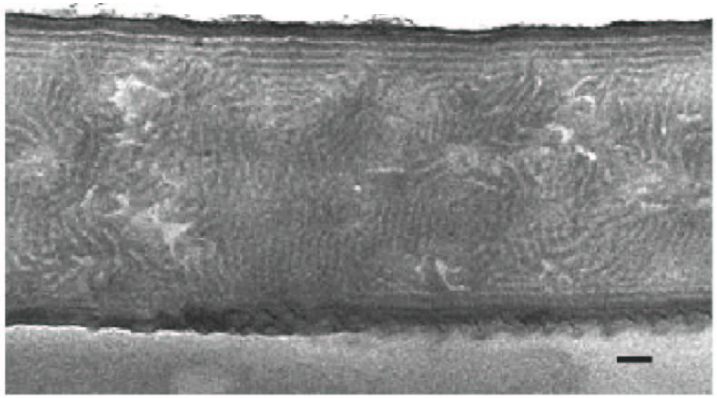


Tsori & DA '02

Mixed Morphology
Electron Microscopy

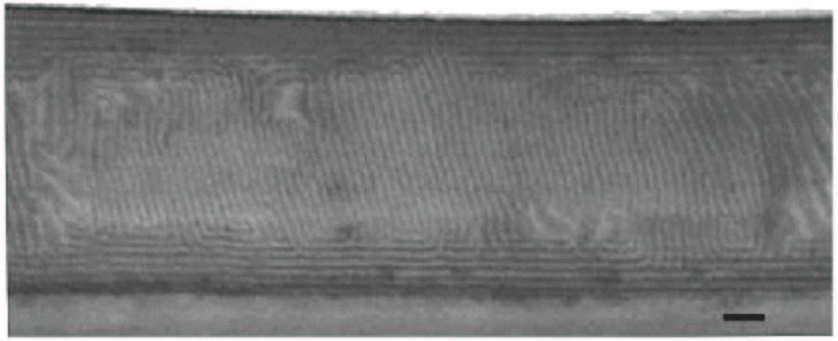
- PS-PMMA block copolymer
- Annealing in ***E***-field $40\ \mathrm{V}/\mu m$
- *Competition:* Surface & ***E***-field

6 hours



$0.6\ \mu m$

16 hours



Para

Perp

Para

Russell + Gido '03

Conclusions

- Surface patterns, templates & electric fields for Block Copolymers
  - self-assembly, nano-patterns and structures: *applications to nano-lithography*

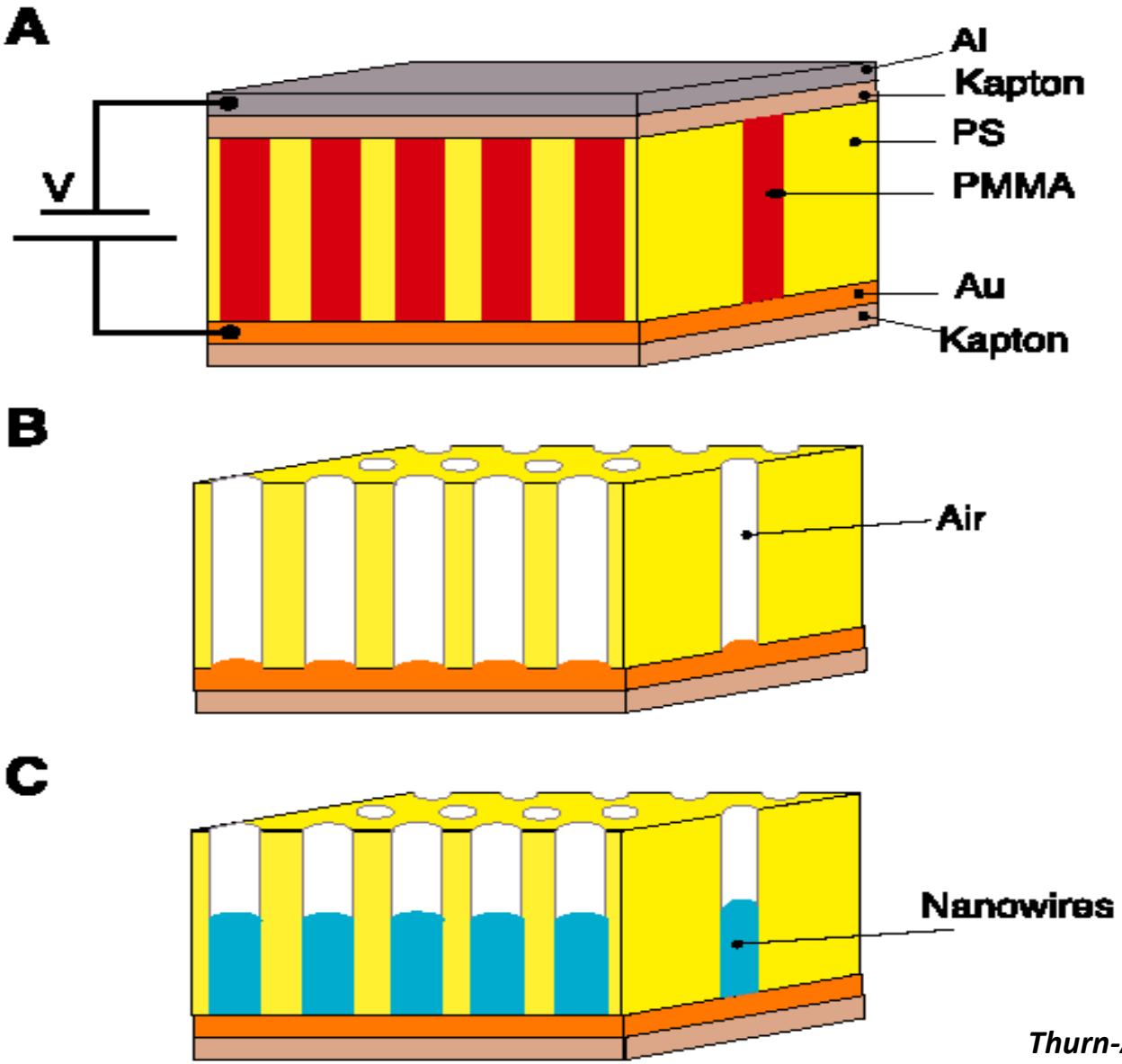
- **Challenge**: defect-free orientation & alignment with minimal surface treatment

- **Challenge**: Metastability, traps, film rheology

Electric Field

Orientation of lamellae

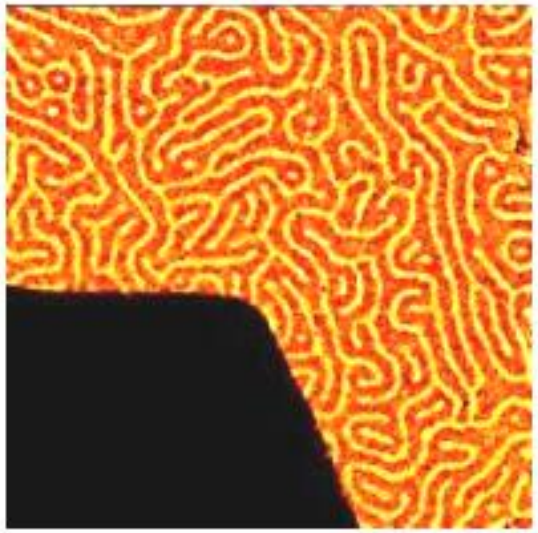
BCP Films : Templates for Nano-wires



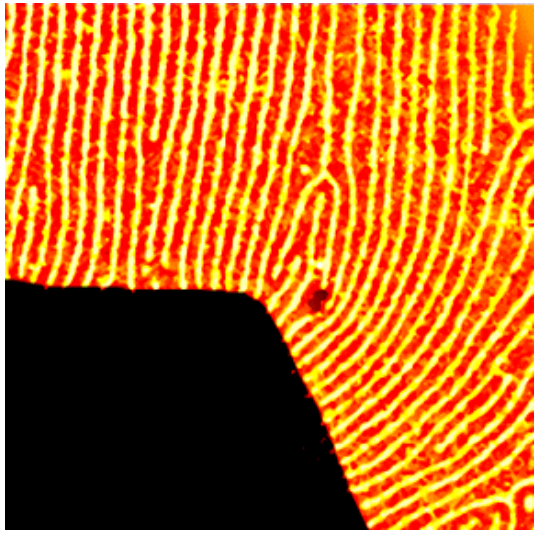
Thurn-Albrecht, Russell et al.
Nature '00

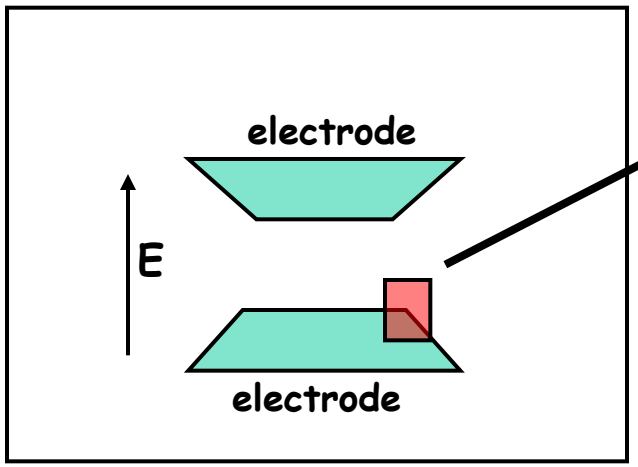
TEM Micrographs of PS-PMMA

No Applied Field



Annealed Under Applied Field

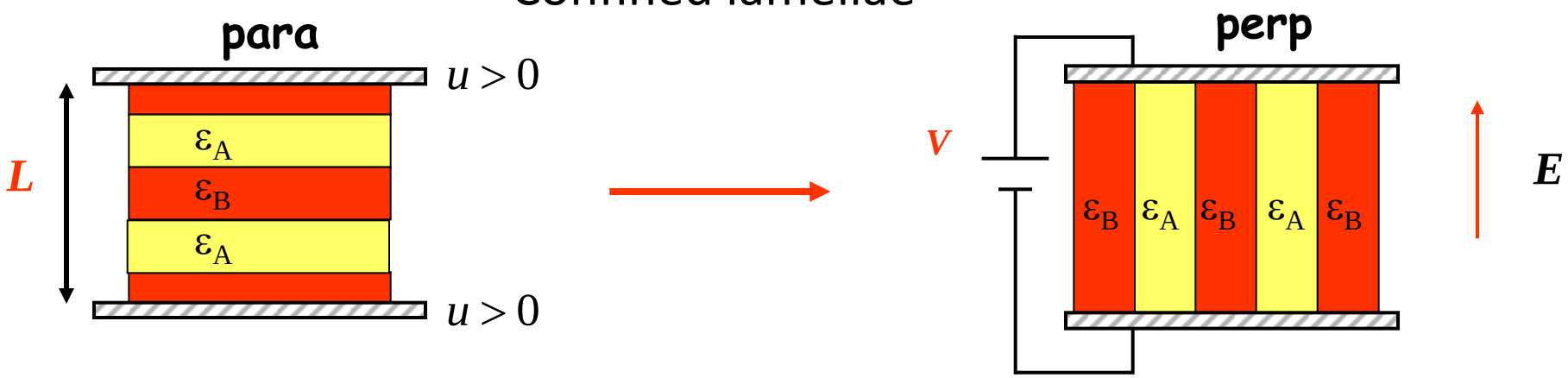




Russell et al, Science '96

Orientation with Electric Field

Confined lamellae



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

$L \sim 10\ \mu m$
$V \sim 100\ V$
$E \sim 10\ V/\mu m$

moderate voltages

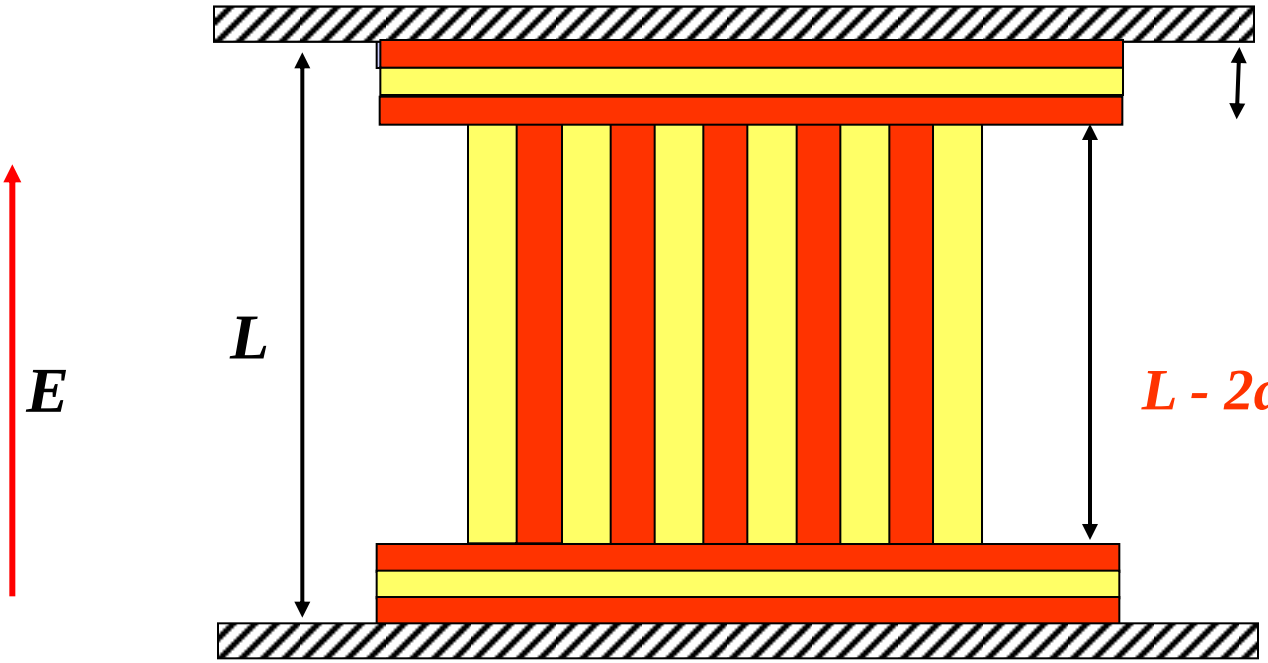
high fields

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

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

Anything in between?

MIXED MORPHOLOGY

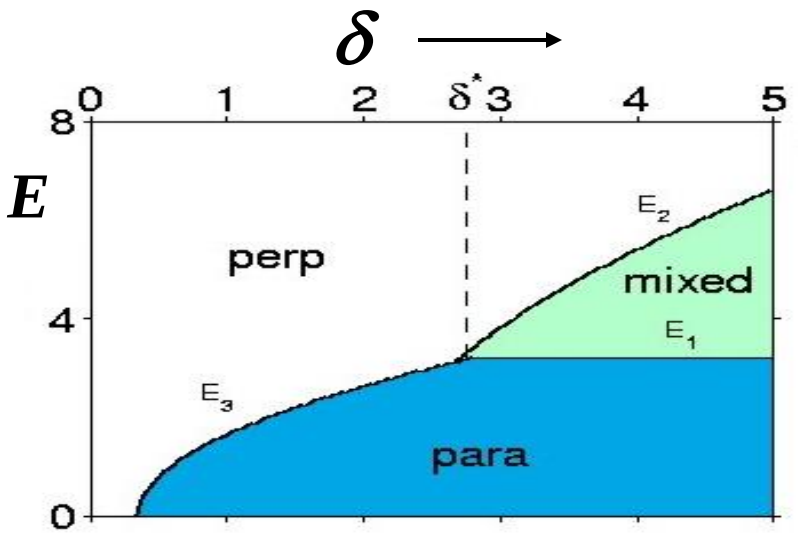


- Sharp interfaces (strong segregation)
- Effect of surfaces has finite range
- ***Mixed*** State:

  Two parallel layers of width ***a***

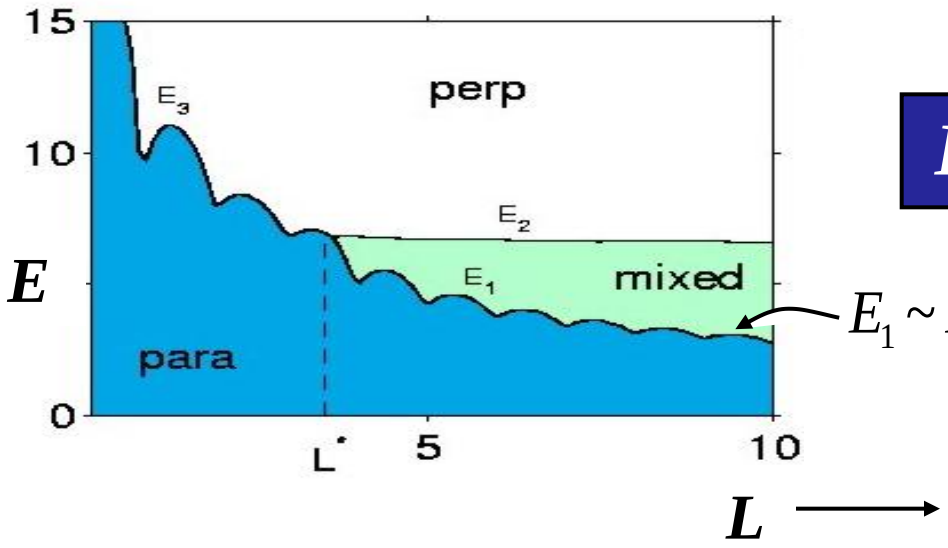
  Perpendicular domain in the middle: ***L - 2a***

Phase Diagrams



$E - \delta$ plane

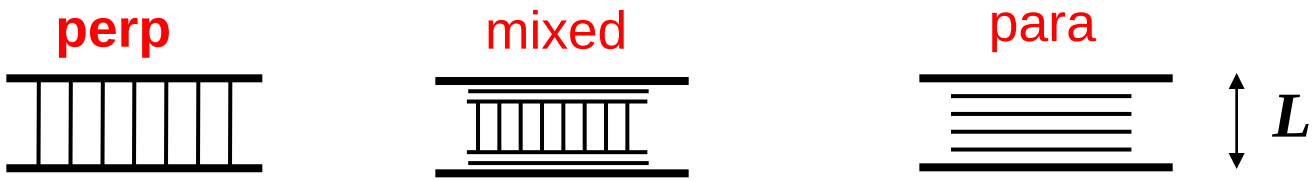
$$\delta = \frac{u}{\gamma_T}$$



$E - L$ plane

$E_1 \sim L^{-1/2}$

$E_1 \leq 30\text{V}/\mu$



Tsori & DA '02

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