

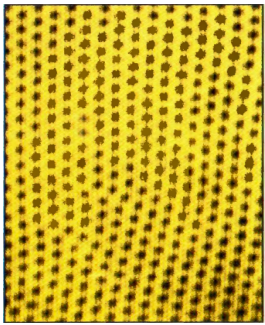
# Phase Behaviour of Polyelectrolyte/Homopolymer Blends

Ashkan Dehghan, Youhai Sun and An-Chang Shi

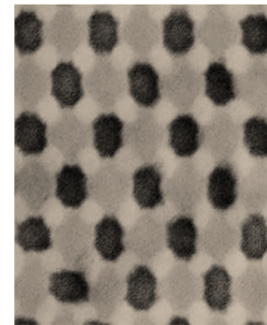
Department of Physics and Astronomy, McMaster University, Hamilton, Canada



# Pattern Formation In Nature:



Ferrofluid

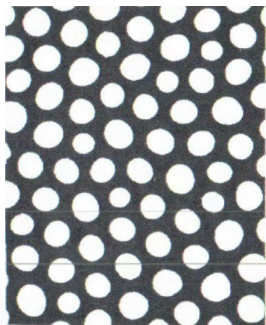
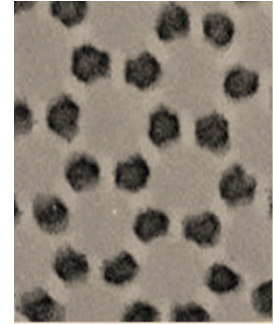
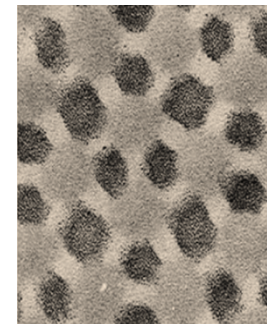


Polymers

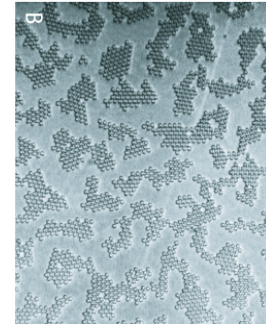
Organic Films



Polymers



Magnetic



Colloids

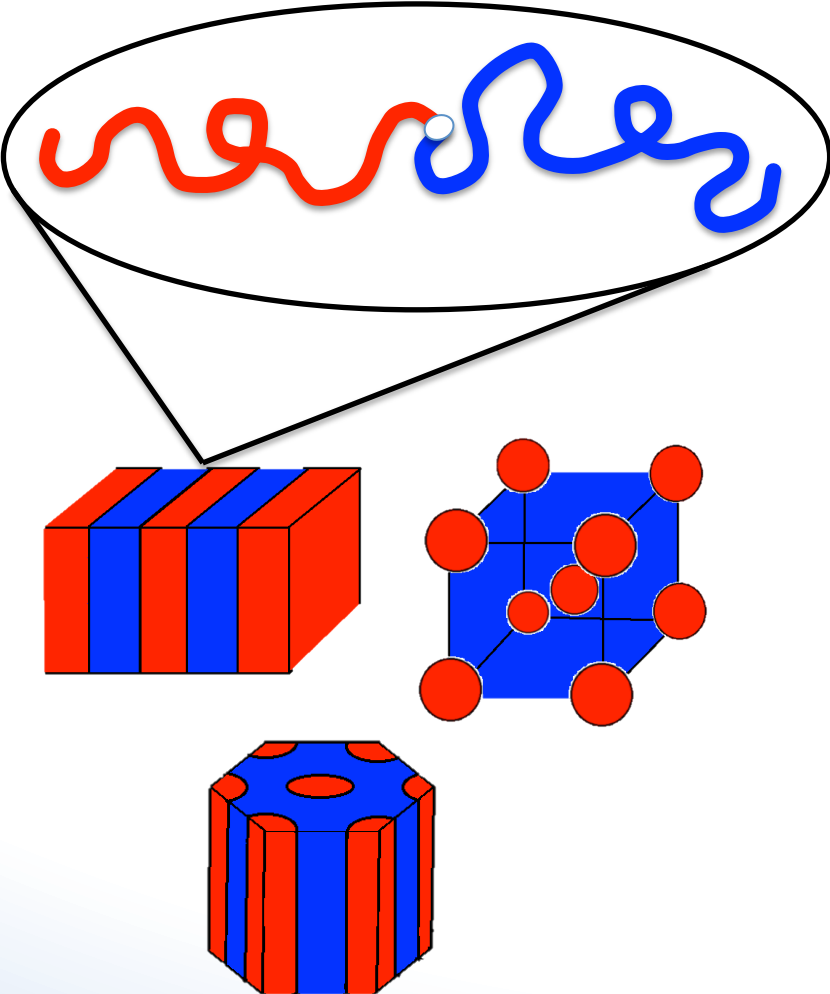
<http://physics.nyu.edu/grierlab/surface14c/>

Seul, Michael, and David Andelman. "Domain shapes and patterns: the phenomenology of modulated phases." *Science* 267.5197 (1995): 476-483.

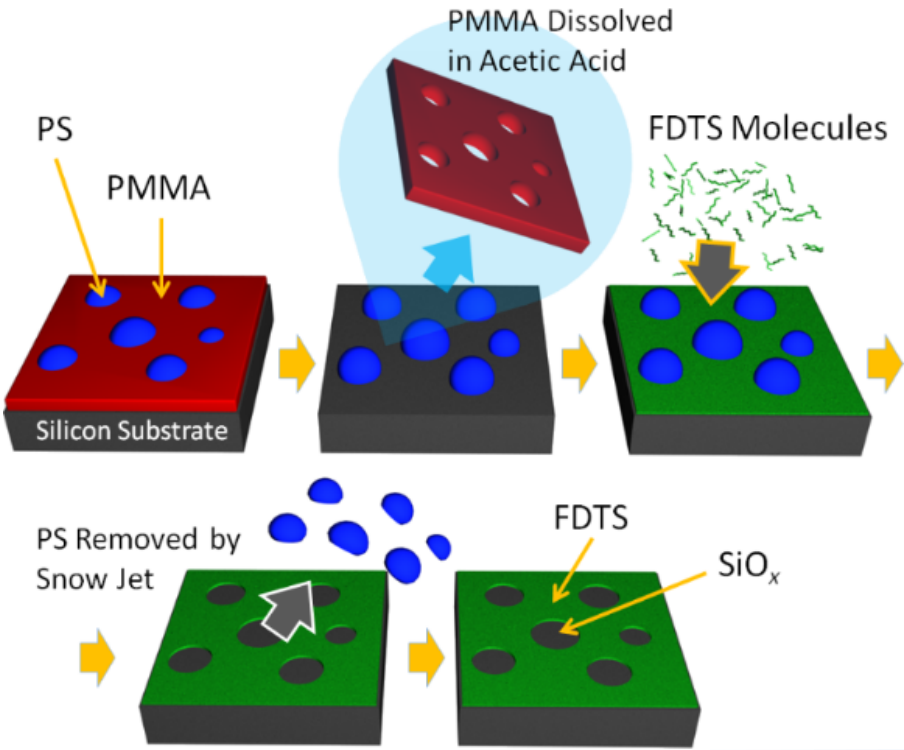
**Observation of Cylinder-Based Microphase-Separated Structures from ABC Star-Shaped Terpolymers Investigated by Electron Computerized Tomography**

A. Takano,<sup>\*</sup> †, ‡, §, S. Wada,<sup>‡</sup>, S. Sato,<sup>†</sup>, T. Araki,<sup>†</sup>, K. Hirahara,<sup>†</sup>, T. Kazama,<sup>†</sup>, S. Kawahara,<sup>†</sup>, B. Y. Isono,<sup>†</sup>, A. Ohno,<sup>§</sup>, N. Tanaka,<sup>§</sup> and, and Y. Matsushita<sup>‡</sup>  
*Macromolecules* **2004** 37 (26), 9941-9946

# Self-Assembly in Polymers:



## Lithography



Cheng Huang<sup>1,2,3</sup>, Markus Moosmann<sup>1,2</sup>, Jiehong Jin<sup>1,2</sup>, Tobias Heiler<sup>1,2</sup>, Stefan Walheim<sup>1,2</sup> and Thomas Schimmel<sup>1,2</sup>

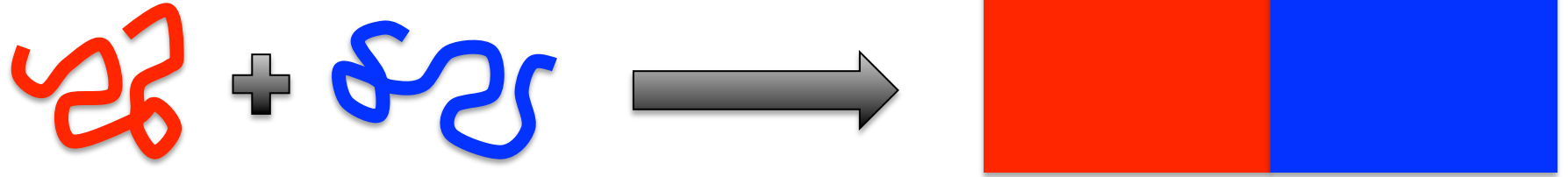
<sup>1</sup>Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany

<sup>2</sup>Institute of Applied Physics and Center for Functional Nanostructures (CFN), Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany

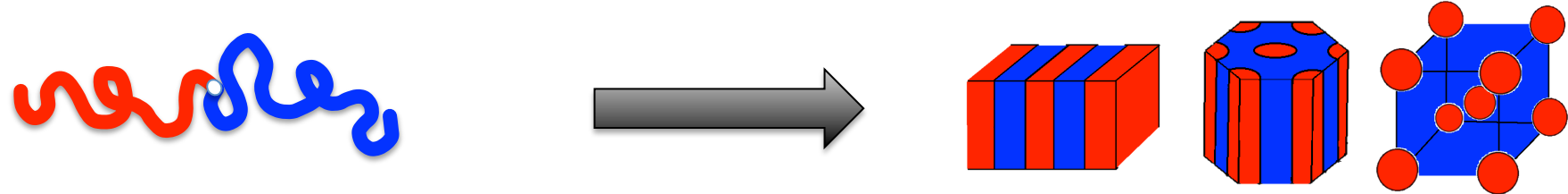
<sup>3</sup>Joint Research Laboratory Nanomaterials Karlsruhe Institute of Technology (KIT)/Darmstadt University of Technology, 64287 Darmstadt, Germany

# Introducing the Model:

Binary Blends of Homopolymers:



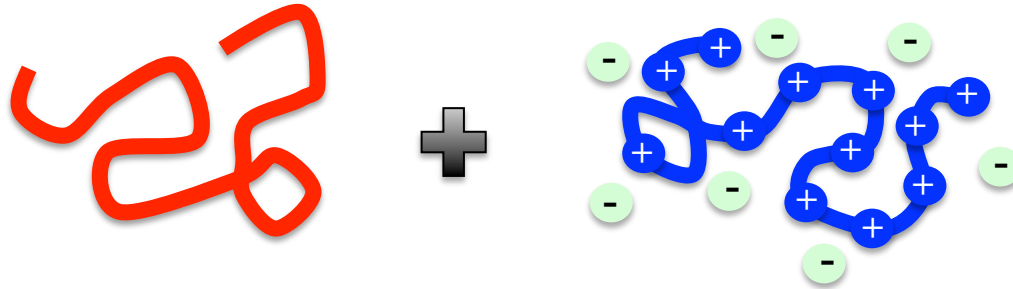
Block Copolymer Blends:



Polyelectrolyte/Homopolymer Blends:



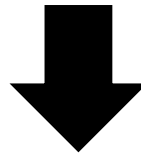
# Introducing the Model:



$$H_0 = \frac{3}{2b^2} \int_0^N ds \left[ \frac{d\mathbf{R}(s)}{ds} \right]^2$$

$$H_1 = \int d\mathbf{r} \chi \phi_A(\mathbf{r}) \phi(\mathbf{r})$$

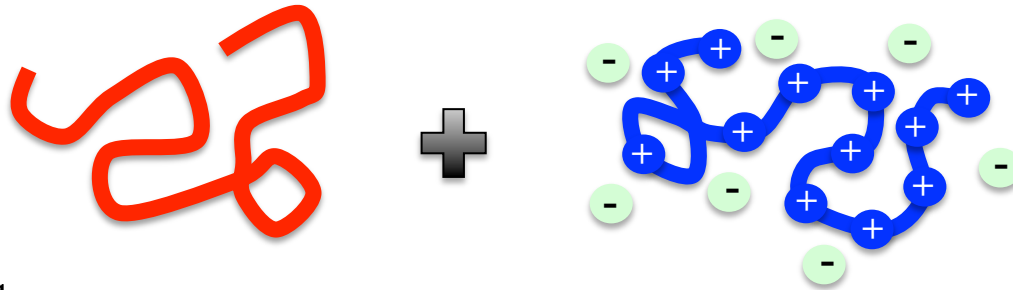
$$H_2 = \int d\mathbf{r} \left[ \phi_e(\mathbf{r}) \psi(\mathbf{r}) - \frac{\epsilon}{8\pi e^2} |\nabla \psi(\mathbf{r})|^2 \right]$$



$$\frac{\partial q(\mathbf{r}, s)}{\partial s} = \left[ \nabla^2 - \omega(\mathbf{r}) \right] q(\mathbf{r}, s)$$

$$\nabla \cdot \left[ \epsilon \nabla \psi(\mathbf{r}) \right] = -\phi_e(\mathbf{r})$$

# Introducing the Model:



$$\phi_A(\mathbf{r}) = \frac{\bar{\phi}_A}{Q_A} \int_0^1 ds q_A(\mathbf{r}, s) q_A(\mathbf{r}, 1 - s)$$

$$\phi_C(\mathbf{r}) = \frac{\bar{\phi}_C}{Q_C \kappa} \int_0^\kappa ds q_C(\mathbf{r}, s) q_C(\mathbf{r}, \kappa - s)$$

$$\phi_I(\mathbf{r}) = \frac{\bar{\phi}_I}{Q_I} q_I\left(\mathbf{r}, \frac{1}{N}\right)$$

$$\omega_A(\mathbf{r}) = \chi_{AC} \phi_C(\mathbf{r}) + \eta + P_A \psi(\mathbf{r})$$

$$\omega_C(\mathbf{r}) = \chi_{AC} \phi_A(\mathbf{r}) + \eta$$

$$\omega_I(\mathbf{r}) = -\psi(\mathbf{r})$$

$$\nabla^2 \psi(\mathbf{r}) = -\frac{N}{\epsilon} \left[ P_A \phi_A(\mathbf{r}) - \phi_I(\mathbf{r}) \right]$$

$$1 = \phi_A(\mathbf{r}) + \phi_C(\mathbf{r})$$

## Parameters:

$$\phi_A(\mathbf{r}) \quad \phi_C(\mathbf{r})$$

$$\kappa = \frac{N_C}{N_A}$$

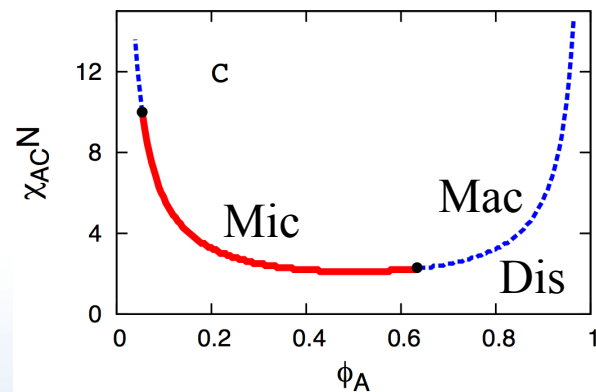
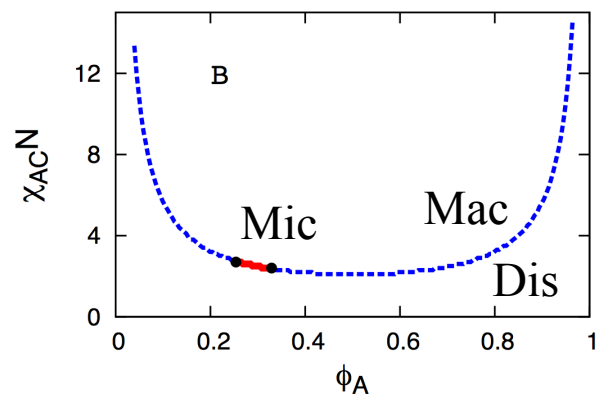
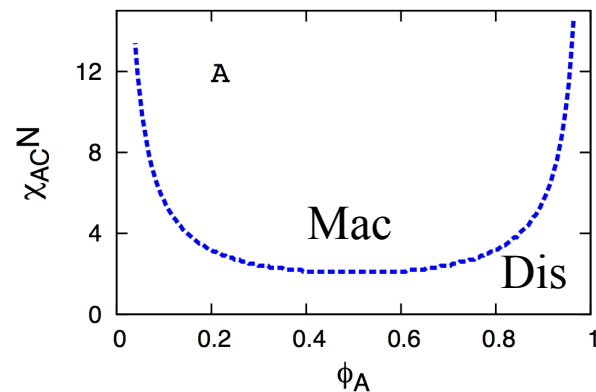
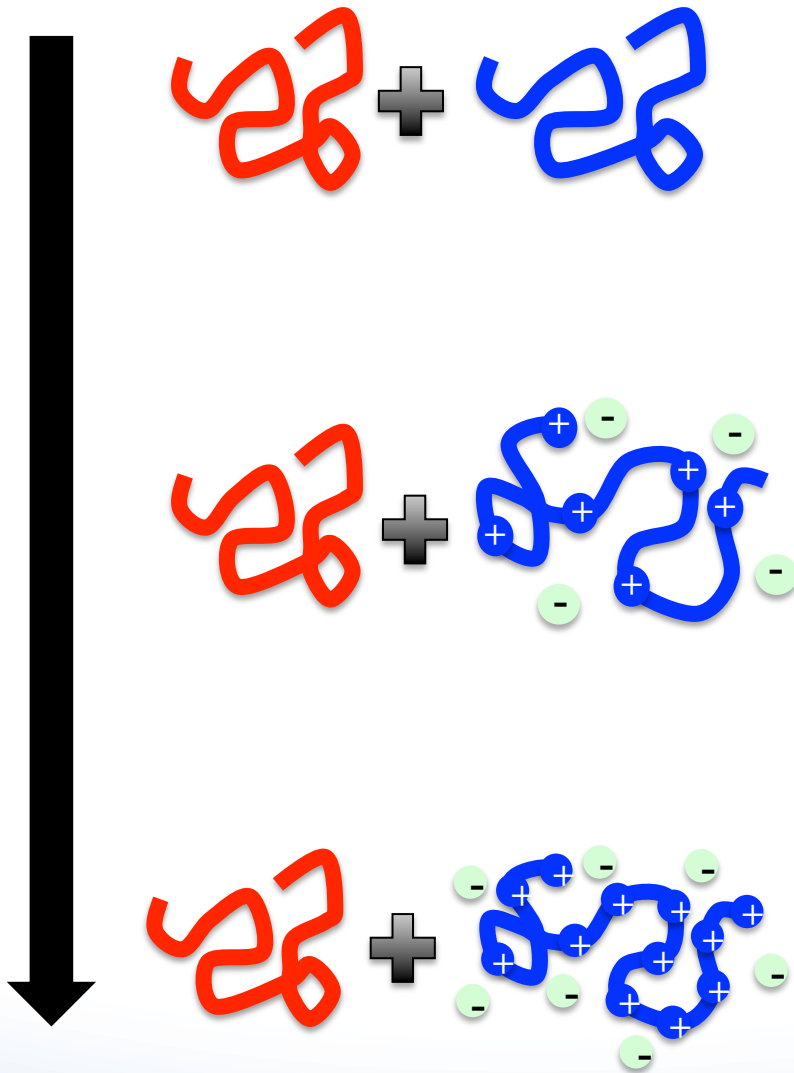
$\epsilon$

$P_A$

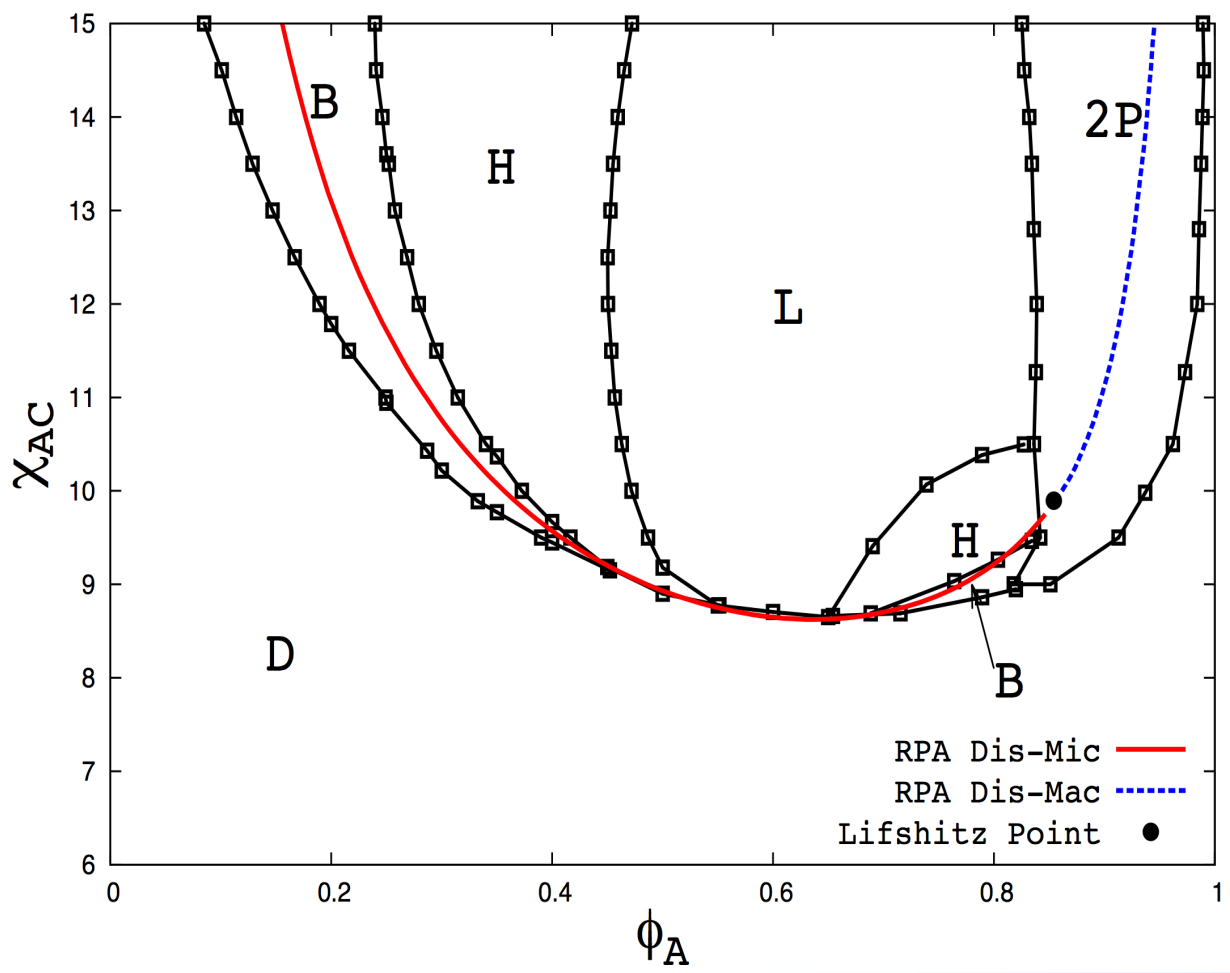
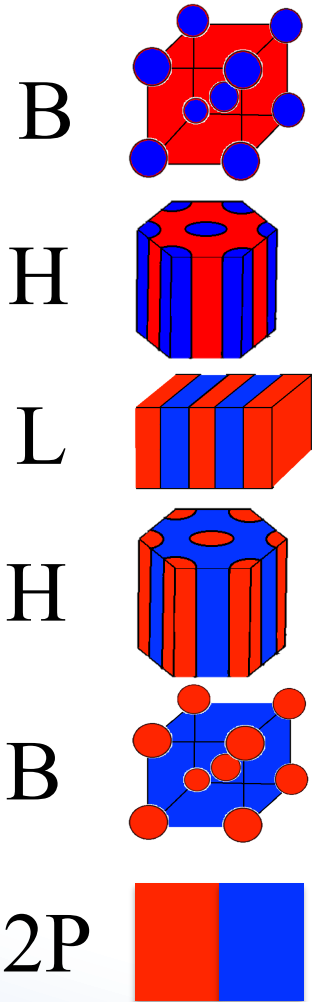
$\chi_{AC}$

# Studying the Phase Diagram Using Random Phase Approximation:

Increasing  $P_A$



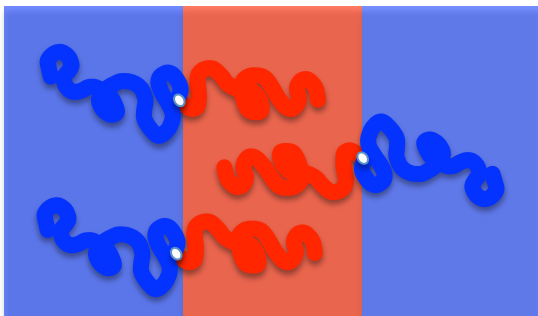
# Studying the Phase Diagram Using Self-Consistent Field Theory:



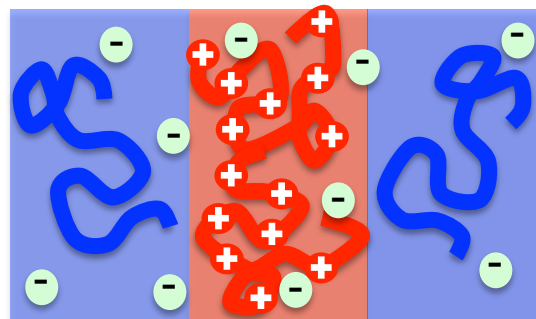


# Unique Properties of The Polyelectrolyte/ Homopolymer System:

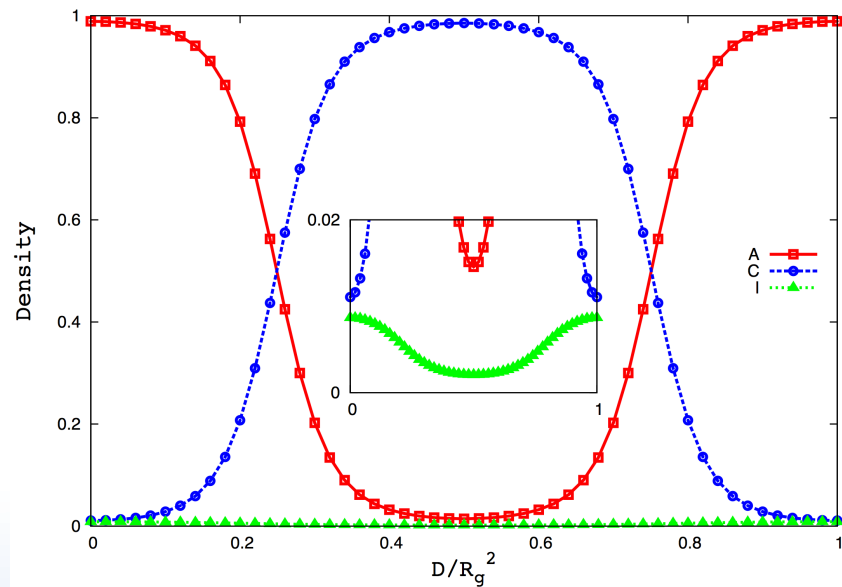
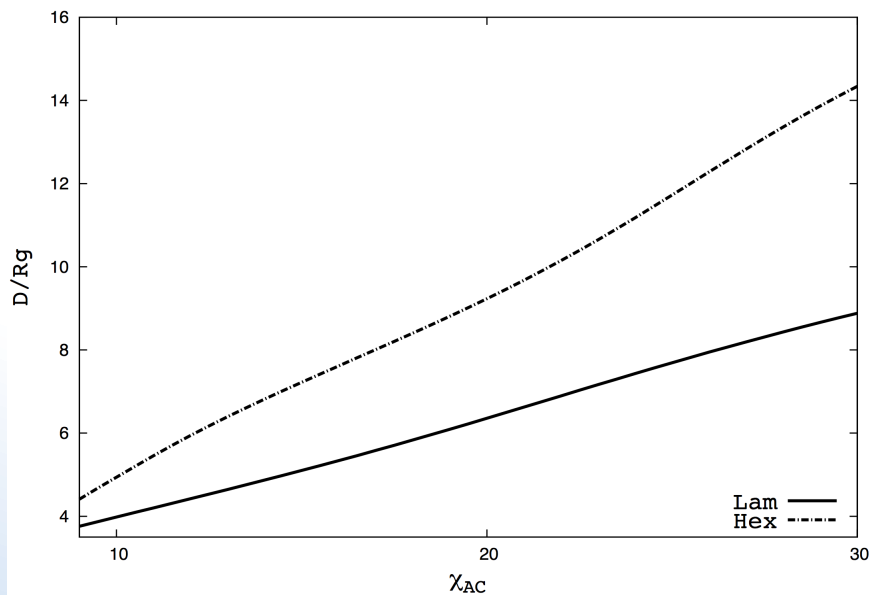
## Block Copolymer Blends



## Polyelectrolyte/Homopolymer Blends



## Polyelectrolyte/Homopolymer Blends



# Understanding the Underlying Physics:

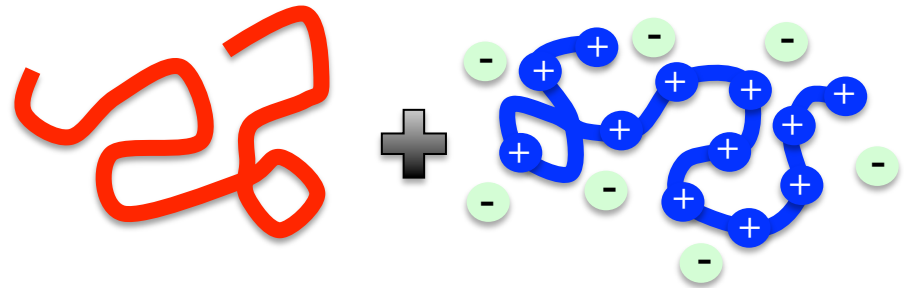
## Demixing

Repulsive interaction between the A and C segments.

Electrostatic interaction between Ions and Counter-Ions.

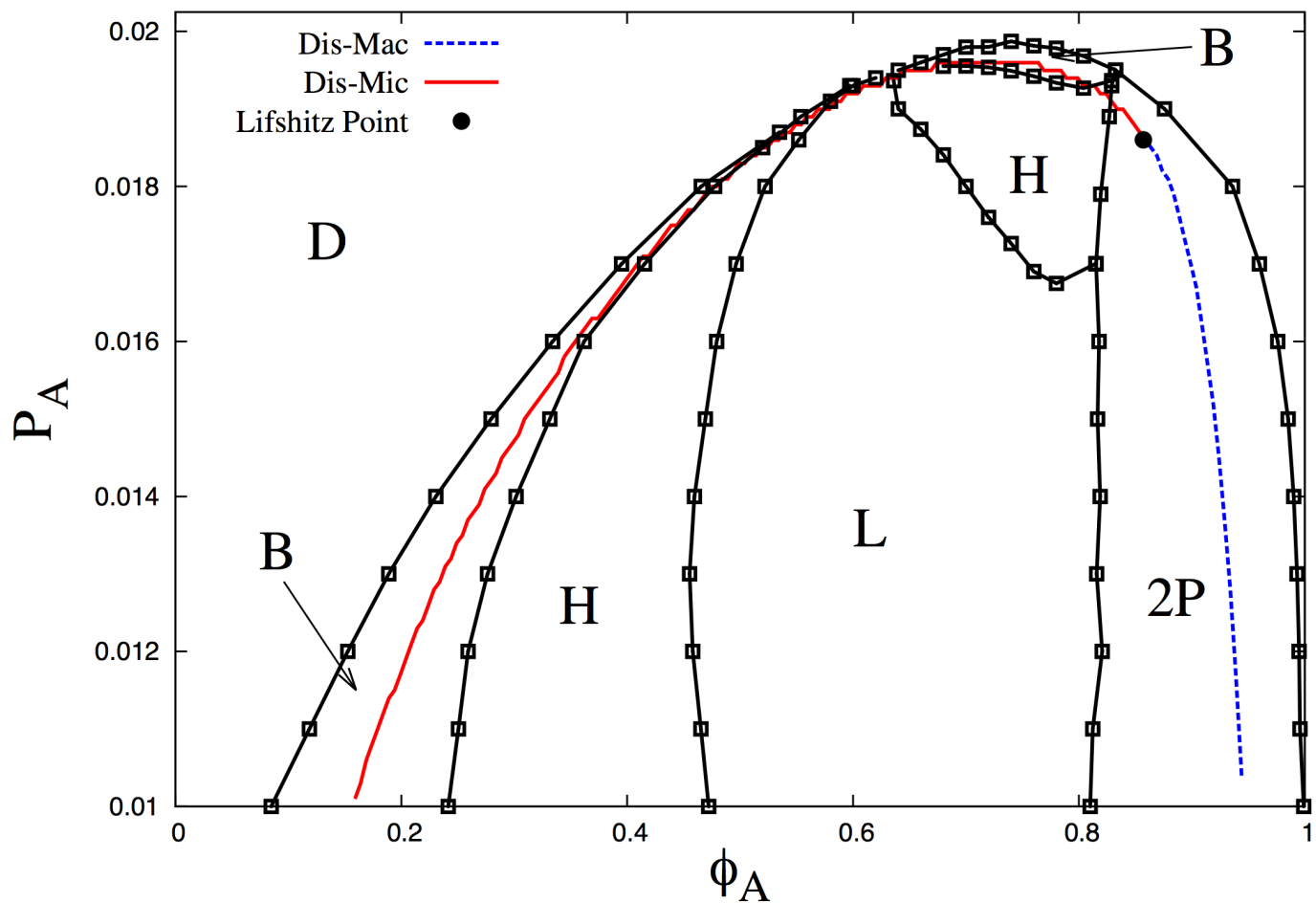
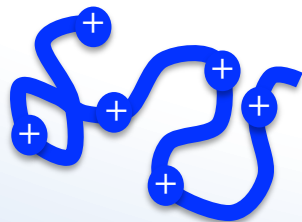
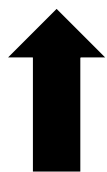
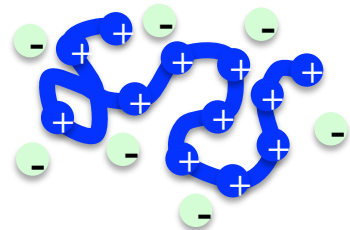
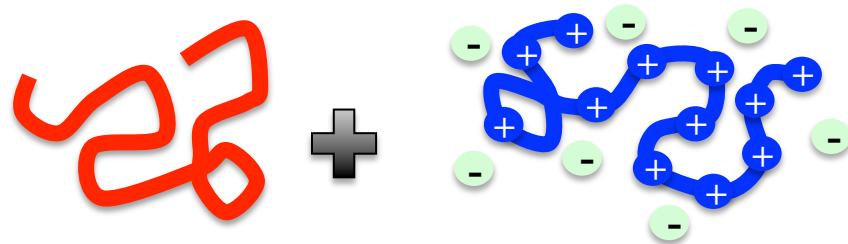
## Mixing

Mixing entropy of polymers and Ions.



**Balance between the short/long interactions  
and the mixing entropy.**

# Sensitivity of The System to Charge Density:



# Conclusion:

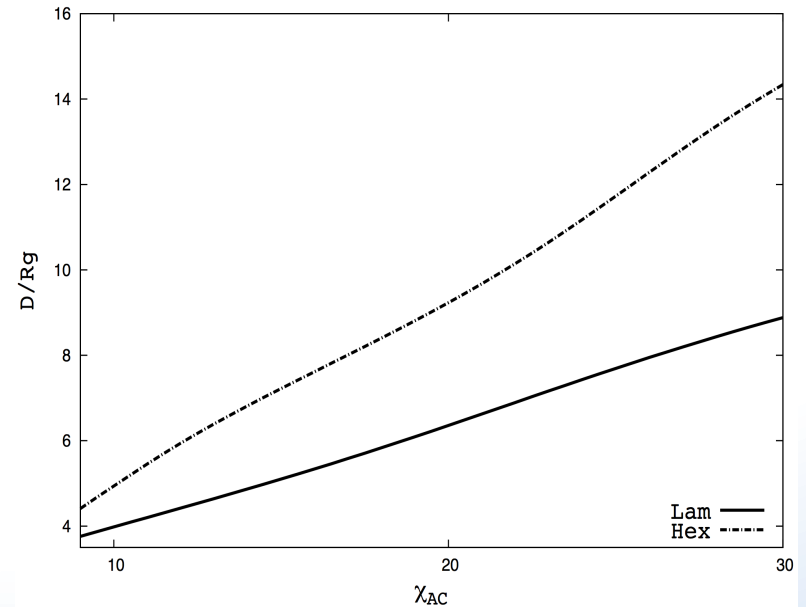
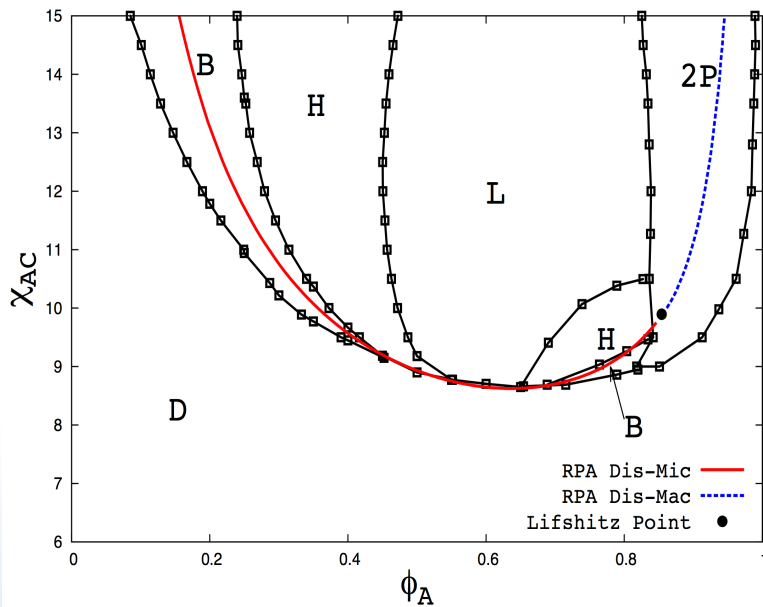
1. The phase behavior of the Homopolymer/Polyelectrolyte blends includes:

Microphase Separation

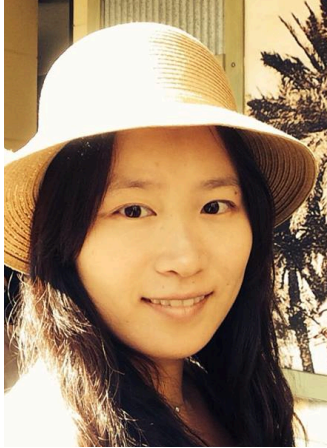
and

Macrophase Separation

2. Highly tunable domain sizes.



# Collaborators and Resources:



Dr. Youhai Sun



Dr. An-Chang Shi

