Confined Self-Assembly of Block Copolymers

An-Chang Shi

Department of Physics & Astronomy

McMaster University

Hamilton, Ontario Canada

Collaborators:

Bin Yu and Baohui Li, Nankai University Peng Chen and Haojun Liang, USTC Diblock Copolymers: Bulk Structures

Competition between entropy and energy



Leads to <u>microphase</u> separation of diblock copolymers



Self-Assembly of Block Copolymers

Using block copolymer self-assembly to produce and control nanostructures

- Phases and phase transitions of block copolymer systems: multiblock, blends, solutions, rod-coil
- Kinetics of order-order transitions: theory of spinodal decomposition and nucleation
- Effects of external degrees of freedom: polydispersity, electric fields, confinements

Confined Self-Assembly of Block Copolymers

(1) Engineer new structures through confinement.
 (2) Understand confined self-assembly of amphiphilic molecules.

- Surface interactions
 Selective or neutral
- Structural frustration
 - Confinement size and domain period
- Geometries
 - Dimension and shape of confinement



Confinements naturally occur in nanomaterials and biological systems

1D Confinement: Structural Frustration



Symmetric Diblock Copolymer in Cylinders

THE JOURNAL OF CHEMICAL PHYSICS 126, 024903 (2007)

Symmetric diblock copolymers in nanopores: Monte Carlo simulations and strong-stretching theory

Qiang Wang^{a)}

Department of Chemical and Biological Engineering, Colorado State University, Fort Collins, Colorado 80523-1370

THE JOURNAL OF CHEMICAL PHYSICS 124, 104906 (2006)

Effect of surface field on the morphology of a symmetric diblock copolymer under cylindrical confinement

Peng Chen

Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China and Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Xuehao He

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Haojun Liang^a

Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China and Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China



Nanocylindrical Tubes

Jie Feng and Eli Ruckenstein*

Self-assembly of the symmetric diblock copolymer in a confined state: Monte Carlo simulation

Xuehao He

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

Mo Song Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough LEII 3TU, United Kingdom

Haojun Liang and Caiyuan Pan⁸⁾ Department of Polymer Science and Engineering, University of Science and Technology of China, Hefel, Anhui, 32002, People's Republic of China Department of Chemical and Biological Engineering, State University of New York at Buffalo, Buffalo, New York 14260-4200

Morphologies of AB Diblock Copolymer Melts Confined in

Motivation from Experiments



Decreasing pore diameter



H. Xiang, et al. J. Polym. Phy. B43,3377 (2005)



Y. Y. Wu et al., Nature Materials. 3, 816 (2004)

2D Morphologies

Cylindrical pore



W. Li, R. A. Wickham, and R. A. Garbary, Macromolecules 39, 806 (2006).

Model Block Copolymers

Cylinder-forming asymmetric diblock copolymers

DBCP 1: f=0.18, χN ~ 80

- Close to C-S boundary
- Robust cylinders
- DBCP 2: f=0.36, χN = 14
- Close to C-L boundary
- Deformable cylinders



Model System I: Lattice Model

- Bond-fluctuation model of polymers (Carmesin & Kremer, Larson)
- Equilibrium structures obtained with a simulated annealing method (Kirkpatrick et al)
- Cylinder forming diblock copolymers confined in a cylindrical pore
- Structure as a function of wallpolymer interactions and pore diameter

$A(N_A)-b-B(N-N_A); N=12$





B. Yu, B. Li, and ACS

Model System II: Self-consistent Field Theory

$$\phi_{\alpha}(\vec{r}) = \frac{1}{Q_c} \int_{0}^{f_{\alpha}} ds \ q_{\alpha}(\vec{r}, s) q_{\alpha}^{+}(\vec{r}, f_{\alpha} - s),$$

$$\omega_{\alpha}(\vec{r}) = \chi N \left[\phi_{\beta}(\vec{r}) - f_{\beta} \right] + \eta(\vec{r}),$$

$$\phi_{A}(\vec{r}) + \phi_{B}(\vec{r}) = 1.$$

$$Q_{c} = \frac{1}{V} \int d\vec{r} \ q_{A}^{+}(\vec{r}, f_{A})$$
$$\frac{\partial}{\partial s} q_{\alpha}(\vec{r}, s) = \sigma_{\alpha}^{2} \nabla^{2} q_{\alpha}(\vec{r}, s) - \omega_{\alpha}^{(0)}(\vec{r}) q_{\alpha}(\vec{r}, s)$$

$$q_{\alpha}(\vec{r},0) = 1, q_{\alpha}^{+}(\vec{r},0) = q_{\beta}(\vec{r},f_{\beta})$$
$$\frac{N}{\rho_{0}R_{g}^{3}V}F = \frac{1}{V}\int d\vec{r} \left[\chi N \phi_{A}(\vec{r})\phi_{B}(\vec{r}) - \sum_{\alpha}\omega_{\alpha}(\vec{r})\phi_{\alpha}(\vec{r})\right] - \ln Q_{c}(\{\omega_{\alpha}\}).$$

Model System II: Self-consistent Field Theory

Mean-fields:	$\omega_A(r) = \chi N \phi_B(r) - H(r) + \eta(r)$ $\omega_B(r) = \chi N \phi_A(r) + H(r) + \eta(r)$
Monomer densities:	$\phi_{A}(r) = \frac{1}{Q} \int_{0}^{f} dsq(r,s)q^{\dagger}(r,s) $ Surface $\phi_{B}(r) = \frac{1}{Q} \int_{f}^{1} dsq(r,s)q^{\dagger}(r,s) $ field
Incompressibility:	$\phi_A(r) + \phi_B(r) = 1$ inside the pore

Surface field: H(r): Short ranged potential

Split-step FT method is used to solve the modified diffusion equations

W. LI and R. A. Wickham; P. Chen, H. Liang and ACS

Bulk Structures: DBCP I

A(N_A)-*b*-B(N-N_A); N=12 ε_{AB} =1.0







- ► N_A=6,5: Lamellae
- > N_A=4: Gyroid
- $> N_A = 3,2$: Cylinders

Confinement Induced Structures: DBCP 1

Case 1: Wall attracts the majority blocks

 $f_{A}=1/6, \epsilon_{AB}=1.0, \epsilon_{WA}=1.0, \epsilon_{WB}=-1.0$





Why Helix?

Packing of flexible linear objects in cylinders

Strong segregation leads to fixed cylinder size d

Geometry leads to a cylinder length L

ize d
$$L = f_A \frac{D^2}{d^2} L_z$$
$$\frac{L_z}{S} L' = \frac{L_z}{S} \sqrt{(2\pi R)^2 + S^2}$$

L =

$$R = \frac{S}{2\pi} \sqrt{f_A^2} \frac{D^4}{d^4} - 1$$

sin $\alpha = \frac{d^2}{f_A D^2}$
 $\frac{L}{L_z} = f_A \frac{D^2}{d^2}$

$$C = 2\pi R$$

$$L' = \sqrt{(2\pi R)^2 + S^2}$$

$$\tan \alpha = \frac{S}{2\pi R}$$



Properties of Helix

Back of the envelop calculation leads to





Good qualitative agreement

B. Yu, P. Sun, T. Chen, Q. Jin, D. Ding, B. Li, and A. C. Shi, 2007

Confinement Induced Structures: DBCP 1

Case 2: Wall attracts the minority blocks

 $f_{A}=1/6, \epsilon_{AB}=1.0, \epsilon_{WA}=-1.0, \epsilon_{WB}=1.0$





Morphologies are controlled by the ratio D/L_0 Effective diameter: $D-3L_0/2$

Effective diameter: $D-3L_0/2$



Confinement Induced Structures: DBCP 1

Case 3: Neutral wall

 $f_{A}=1/4, \epsilon_{AB}=1.0, \epsilon_{WA}=0.0, \epsilon_{WB}=0.0$



Morphologies are controlled by the ratio D/L_0 New morphologies induced by neutral wall



Free Energy Comparison: 1st Order Transitions



Weihua Li and Rob Wickham, 2006

Properties of helices



Weihua Li and Rob Wickham, 2006

Confined Self-Assembly of Diblock Copolymers: DBCP 2

One-dimensional confinement



The cylinders can deform!

P. Chen, HJ Liang and ACS (2007)

Confined Self-Assembly of Diblock Copolymers: DBCP 2

Deformation of cylinders leads to complex structures



Effects of Confining Geometry



f = 1/6

B. Yu, et al, JCP 2007

Effects of Confining Geometry

The shape of the pores matters!



f = 1/6

B. Yu, et al, JCP 2007

Effects of Confining Geometry

One-dimensional and three-dimensional confinements



B. Yu, et al 2007

f = 1/6

Summary and Discussion

- Confined self-assembly leads to rich variety of morphologies which are not found in the bulk
- Structure formation is correlated with the parameter
 D/L₀ \Log structural frustration effect
- A generic morphological transition sequence, from string of spheres to cylinder to helix then toroids, is predicted
- Morphologies are consistent with known experiments and theory
- More challenges ahead: mechanisms, geometries, more complex copolymers, etc.