March 5, 2004
The 21st Century COE Program
of Tohoku university
COE International Symposium

Dynamical Self-Consistent Field Theory for Inhomogeneous Dense Polymer Systems

---- Bridging the Gap between Microscopic Chain Structures and Dynamics of Macroscopic Domains ---

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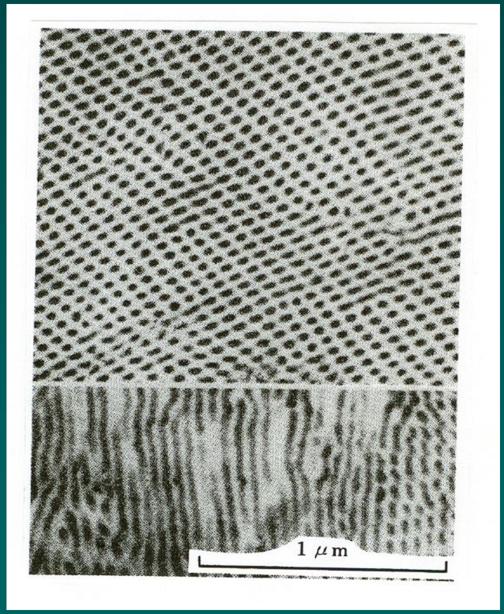
CONTENTS

Inhomogeneity of Dense Polymer Systems

Polymer Mesophase/Polymer Nano-Composites

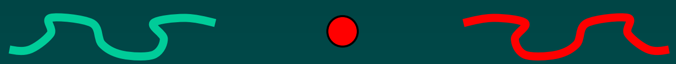
Microphase Separation in Blockcopolymer Melt

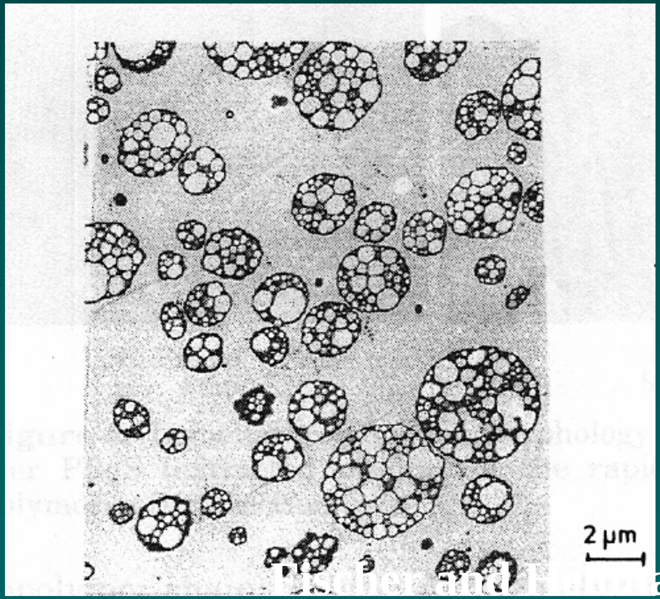


Koubunshi Shashinshu

Chain structure

Salami Structure in HIPS (PS/PB)



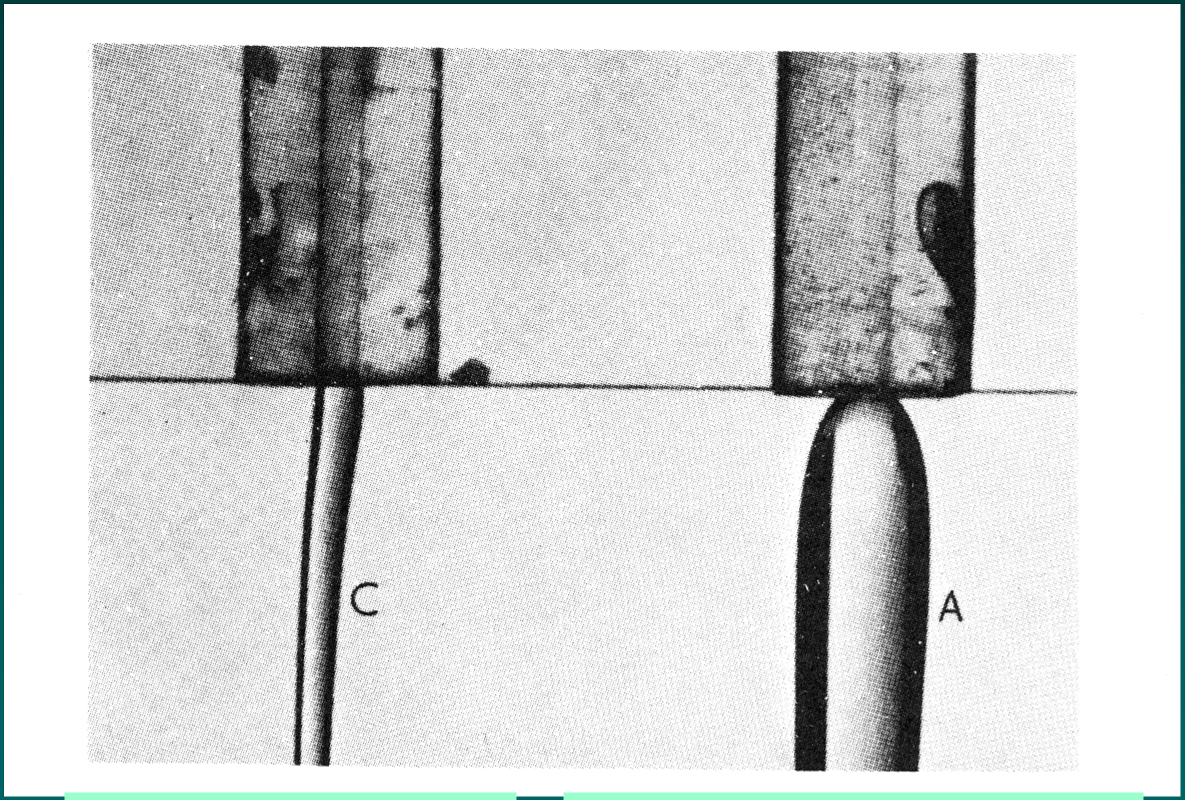


Fischer and H[illegible]an,
Macromolecules 29, 2498 (1996)

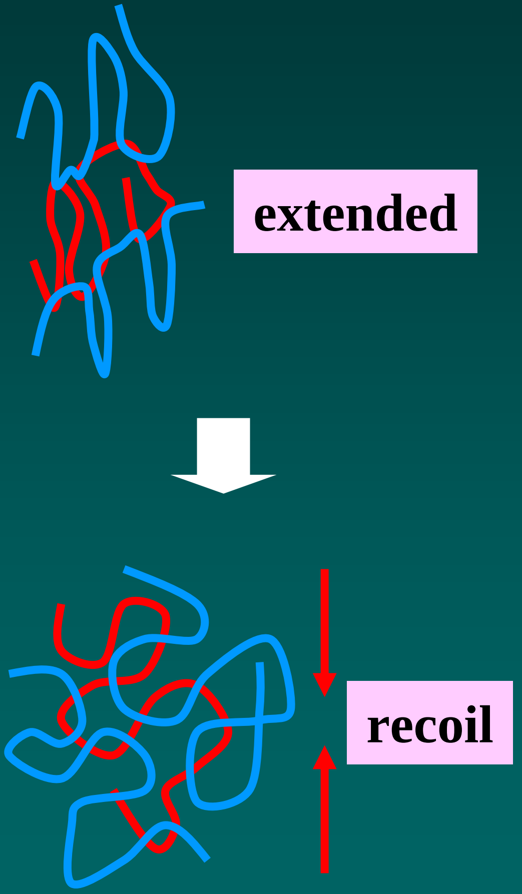
Viscoelasticity

Viscoelasticity of Dense Polymer Systems

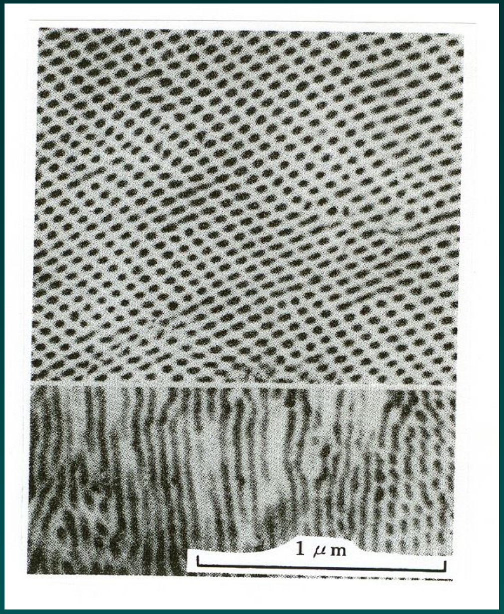
Die Swell (extrusion from a channel)

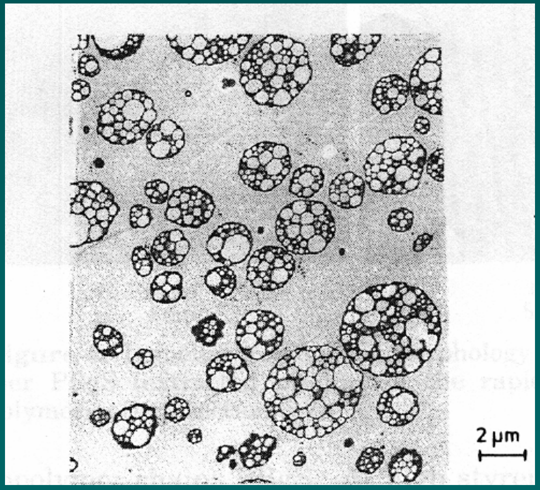


Viscous fluid **Viscoelastic fluid**



Purpose of the Study

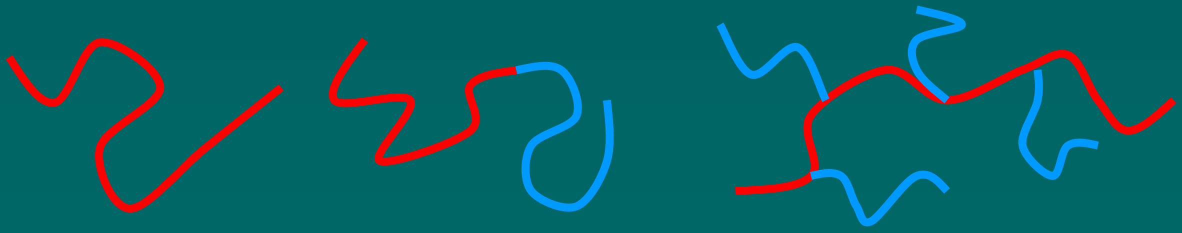




Viscoelastic fluid + Inhomogeneity

Quantitative prediction of structure/dynamics of domains

- **Phase separation (meso/macroscale)**
- **Chain structure (microscale)**



Macroscopic Phenomenological Approach

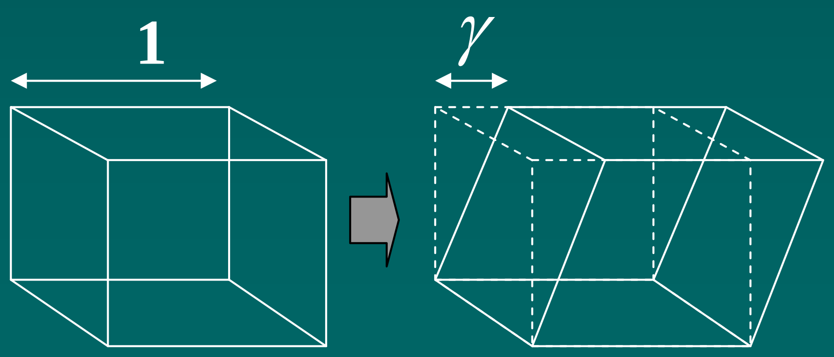
(Jupp, Yuan & Kawakatsu, 2003)

Macro/mesoscopic flow simulation
(Stokes Equation & Phase separation)

+

Phenomenological constitutive equation

$$\sigma(t) = \int_{-\infty}^{t} G(t-s) \frac{d\gamma(s)}{ds} ds$$



$\sigma(t)$: stress

$\gamma(t)$: deformation

$\frac{d\gamma(t)}{dt}$: deformation rate

Simulation of Viscoelastic Flow Model

(Jupp, Yuan & Kawakatsu, 2003)

Dynamics of Viscoelastic Body

Density Field: Two fluid model (Doi & Onuki)

$$\nabla \cdot \boldsymbol{v} = 0 \qquad \left(\boldsymbol{v} \equiv \phi_A \boldsymbol{v}_A + \phi_B \boldsymbol{v}_B\right)$$

$$\boldsymbol{v}_A - \boldsymbol{v}_B = \frac{\phi_A \phi_B}{\varsigma}\left[-\nabla \mu + \alpha \nabla \cdot \sigma\right]$$

$$\frac{\partial \phi_A}{\partial t} = -\boldsymbol{v} \cdot \nabla \phi_A + \nabla \cdot \left[\frac{\phi_A^2 \phi_B^2}{\varsigma}\left(\nabla \mu - \alpha \nabla \cdot \sigma\right)\right]$$

Constitutive Equation: Johnson-Segalman (JS) model

$$\frac{\sigma_i}{\tau_i} + \frac{d\sigma_i}{dt} = G_i\left(\nabla \boldsymbol{v} + \left(\nabla \boldsymbol{v}\right)^T\right) \qquad \sigma \equiv \sum_{i=1}^{3} \sigma_i$$

Simulation of Viscoelastic Phase Separation

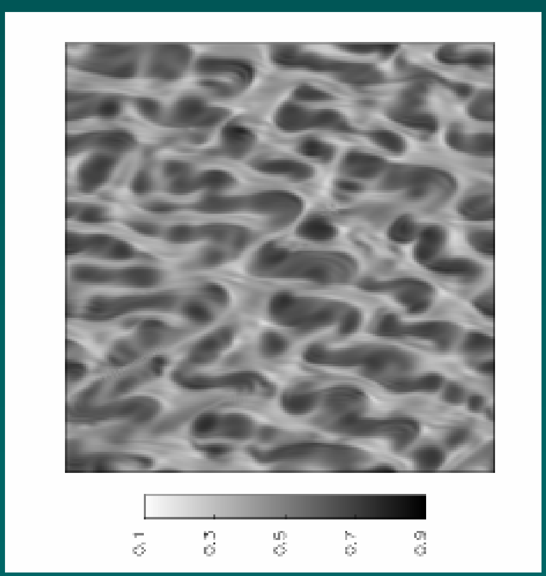
(Jupp, Yuan & Kawakatsu, 2003)

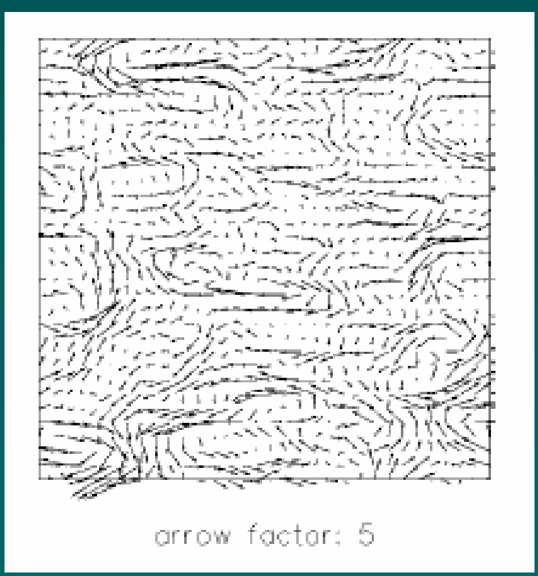
2d Simulation under steady shear ($\dot{\gamma} = \text{const.}$)

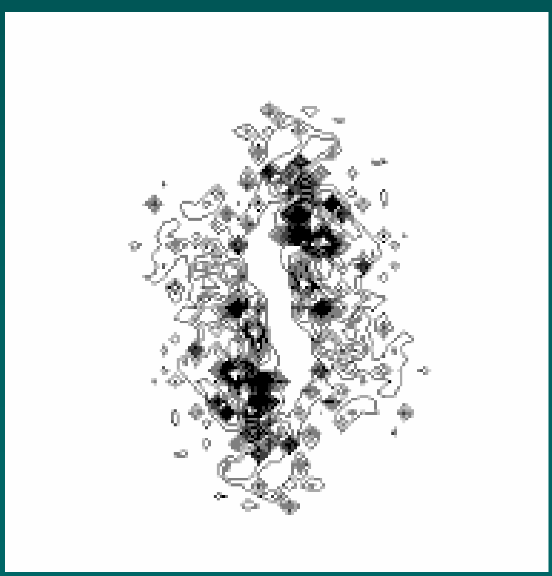
- **Two fluid model**
- **Johnson-Segalman (JS) model**

$$\frac{\sigma_i}{\tau_i} + \frac{d\sigma_i}{dt} = G_i\left(\nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^T\right) \qquad \sigma \equiv \sum_{i=1}^{3} \sigma_i$$

Segment density | **Flow field** | **Scattering intensity**



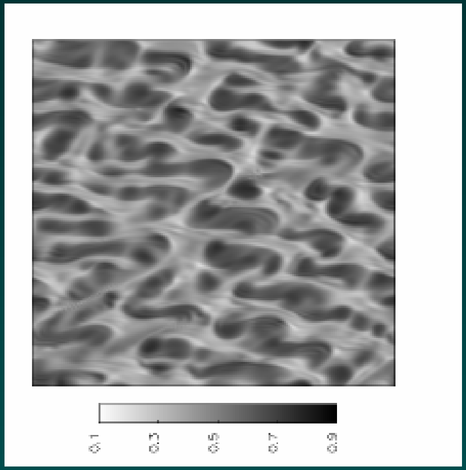




Simulation of Viscoelastic Flow Model

(Jupp, Yuan & Kawakatsu, 2003)

Simulation results
(shear-induced demixing case)



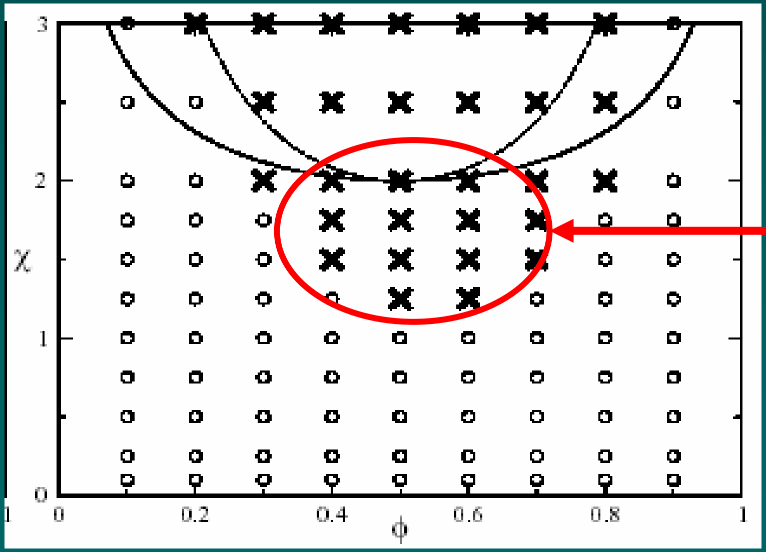
Stability diagram

$$We \equiv (\text{elastic force})/(\text{viscous force}) \equiv \kappa\tau_A$$

$$\tau' \equiv \tau_B/\tau_A = 0.2$$

$$We = 4.0$$

χ



ϕ

Shear-induced demixing

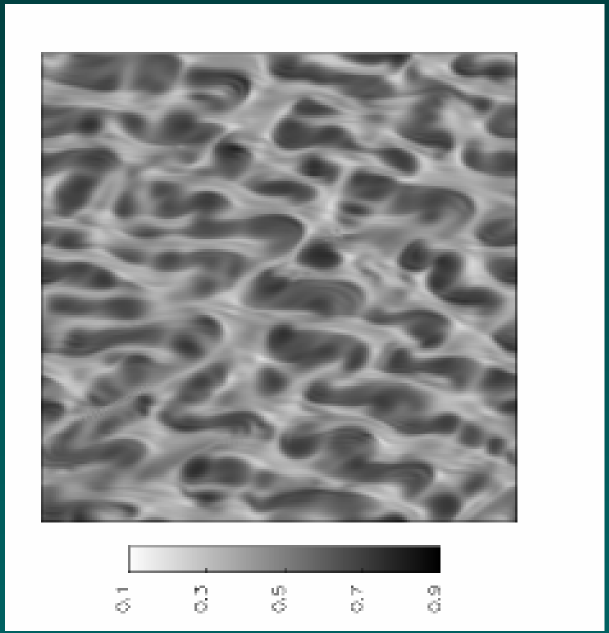
○ homogeneous

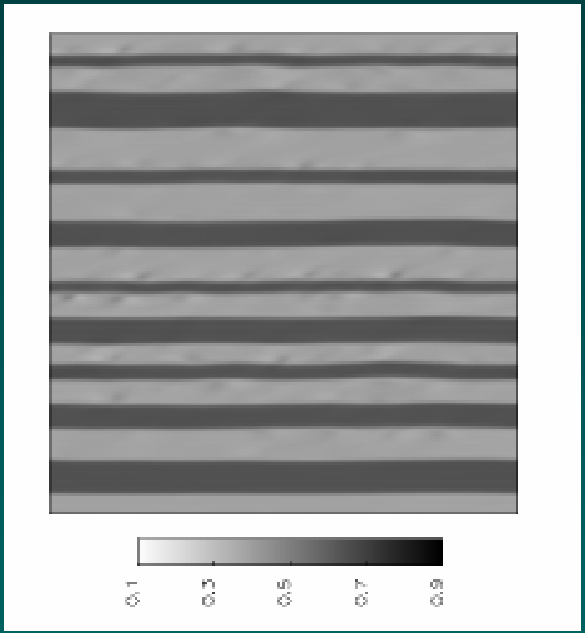
× two-phase

Simulation of Viscoelastic Flow Model

(Jupp, Yuan & Kawakatsu, 2003)

2d Simulation of shear banding
(steady shear $\dot{\gamma} = \text{const.}$)



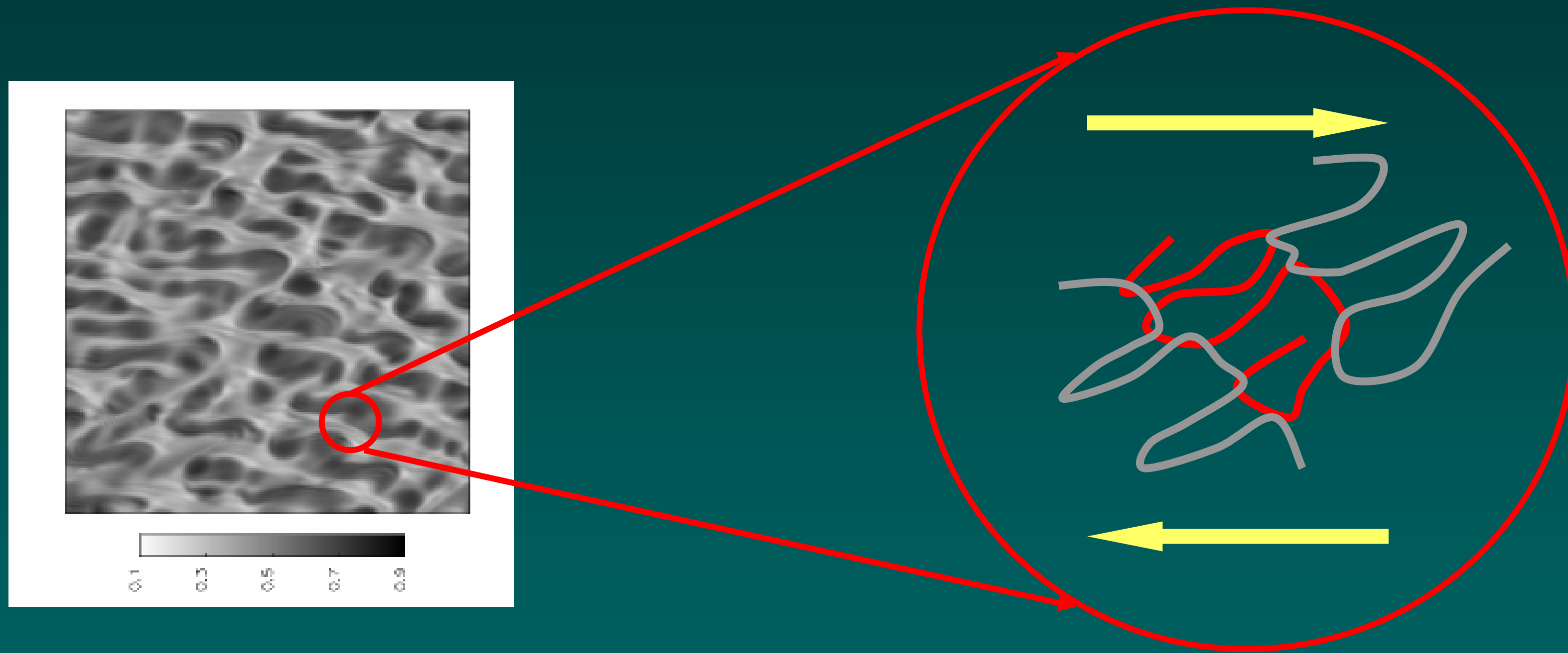


instability

Uniform shear rate → **Inhomogeneous distribution of shear rate**

Relation between Macroscopic and Microscopic Phenomena

Introducing information on chain structure into flow simulation

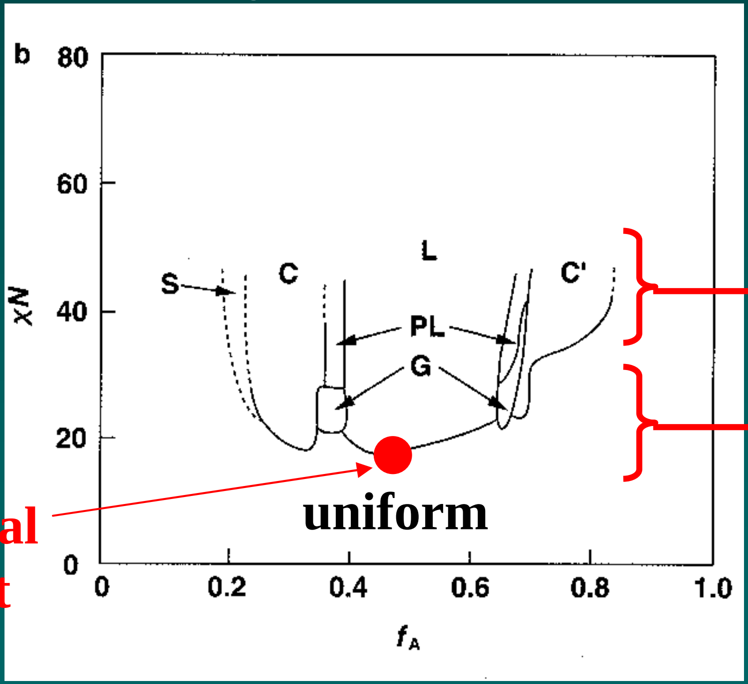


Probability distribution of chain conformation (spatially-folding shape) ⬅ **Self-Consistent Field (SCF) Theory**

Density Functional Theories (SCF vs. GL)

Segment density $\phi(\boldsymbol{r})$ → **Fee energy functional** $F = F\left[\{\phi(\boldsymbol{r})\}\right]$

Phase diagram of blockcopolymer melt



Critical point

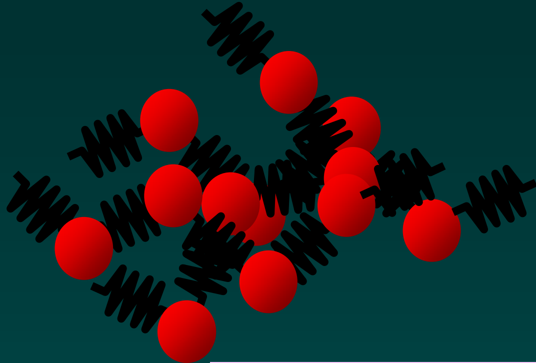
Self-consistent field (SCF)

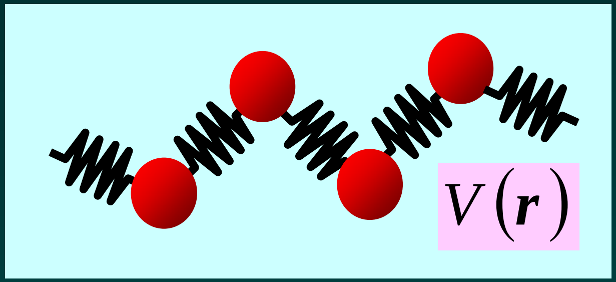
Strong segregation

Weak segregation

Ginzburg-Landau (GL)

Basic Formalism of Static SCF Theory





$$Q(n,\mathbf{r};m,\mathbf{r}') = \sum_{\text{all conformation}} \exp\left[-\frac{1}{k_{\mathrm{B}}T}H\right]$$

Path integral for equilibrium chain conformation

$V(\mathbf{r})$ **Mean field (SCF)**

$$\frac{\partial}{\partial n}Q(n,\mathbf{r};m,\mathbf{r}') = \left[\frac{b^2}{6}\nabla^2 - \beta V(\mathbf{r})\right]Q(n,\mathbf{r};m,\mathbf{r}')$$

$\phi(\mathbf{r})$

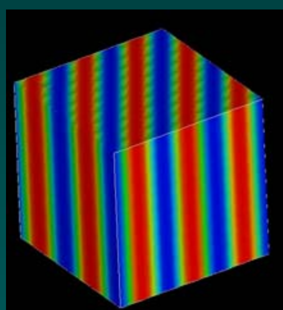
$$F = F\left[\{Q(n,\mathbf{r};m,\mathbf{r}')\}\right] = F\left[\phi(\mathbf{r})\right]$$

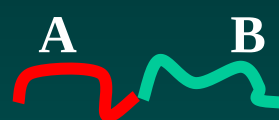
Equilibrium structures

Static SCF Simulation : Phase Diagram & Domain Structures

Block copolymer melt (Matsen & Schick; *Phy. Rev. Lett.* 72 (1994) 2660.)

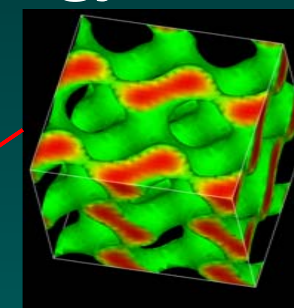
lamellar

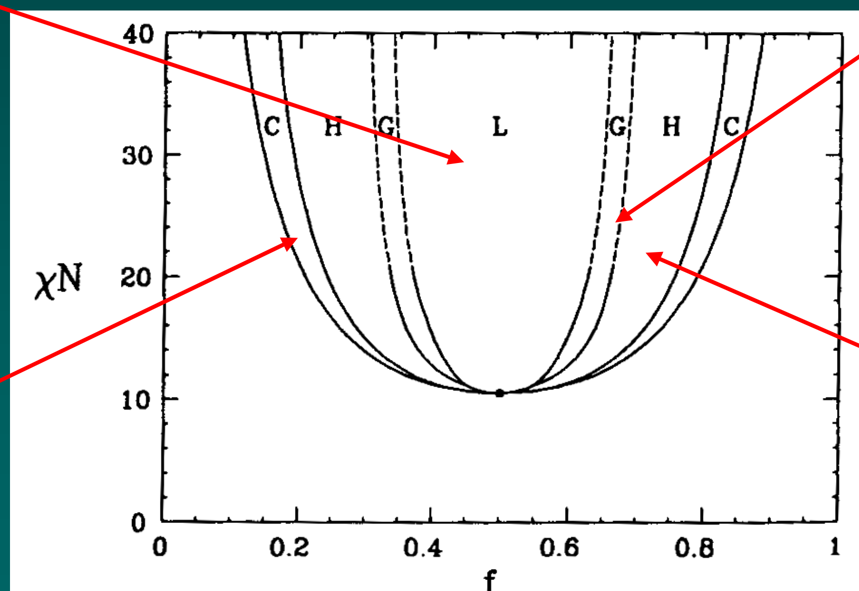




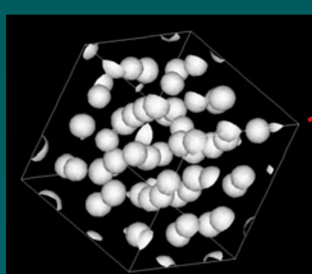
$$f = \frac{N_A}{N_A + N_B}$$

gyroid

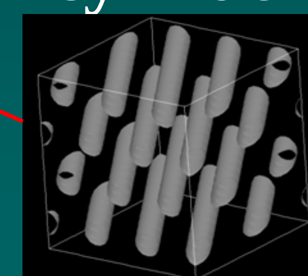




cubic



cylinder



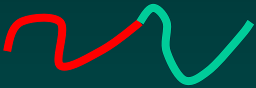
Periodic structure ⇒ Fourier space analysis

Prediction of Complex Domain Structures

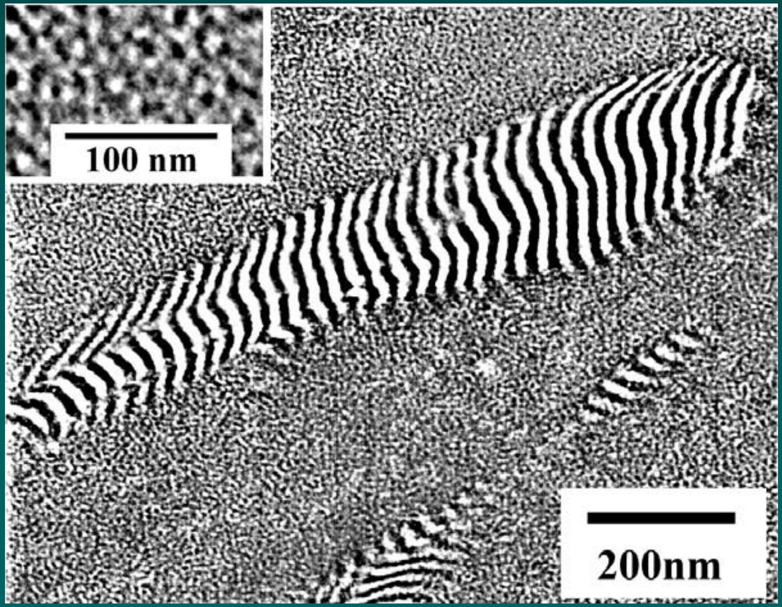
(Morita, Kawakatsu, Doi, Yamaguchi, Takenaka & Hashimoto)

PS-PI diblock copolymer mixture

+

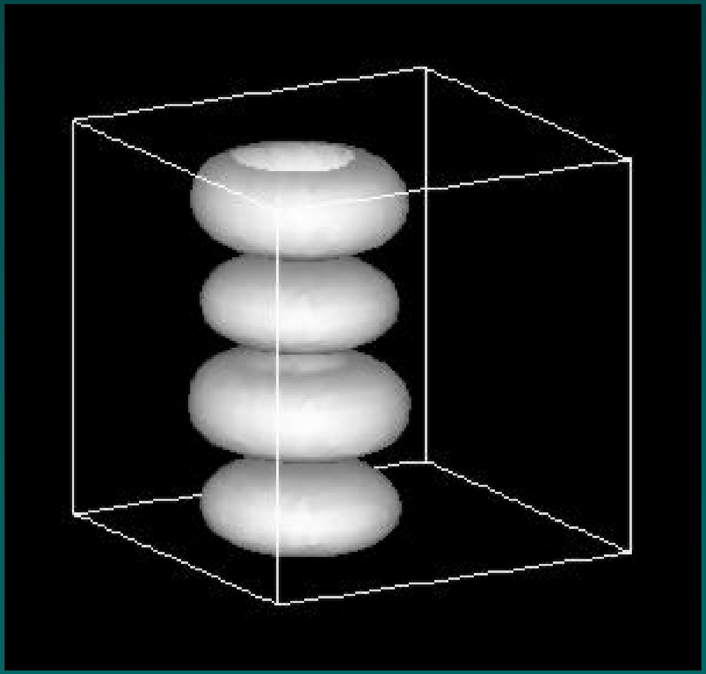


experiment



$$\phi_{\text{long}} : \phi_{\text{short}} = 0.2 : 0.8$$

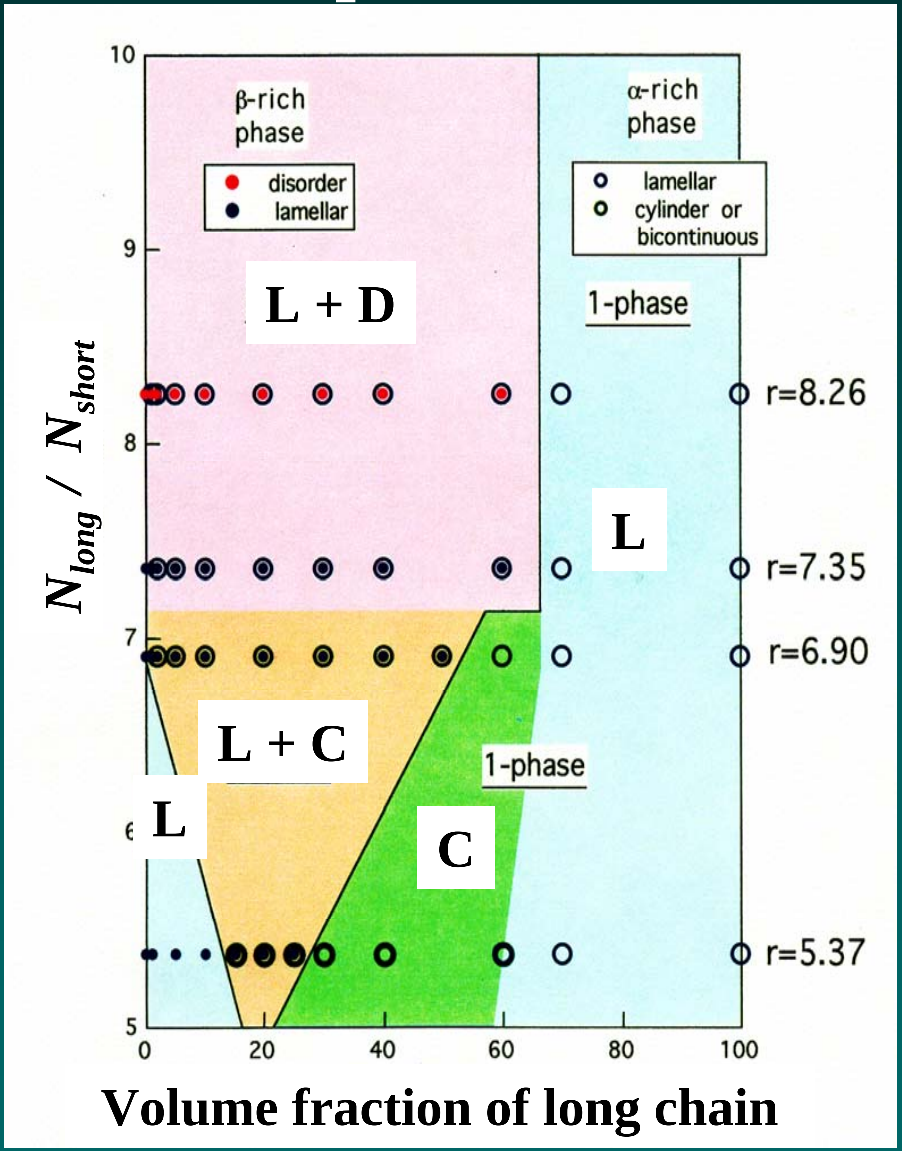
3d simulation



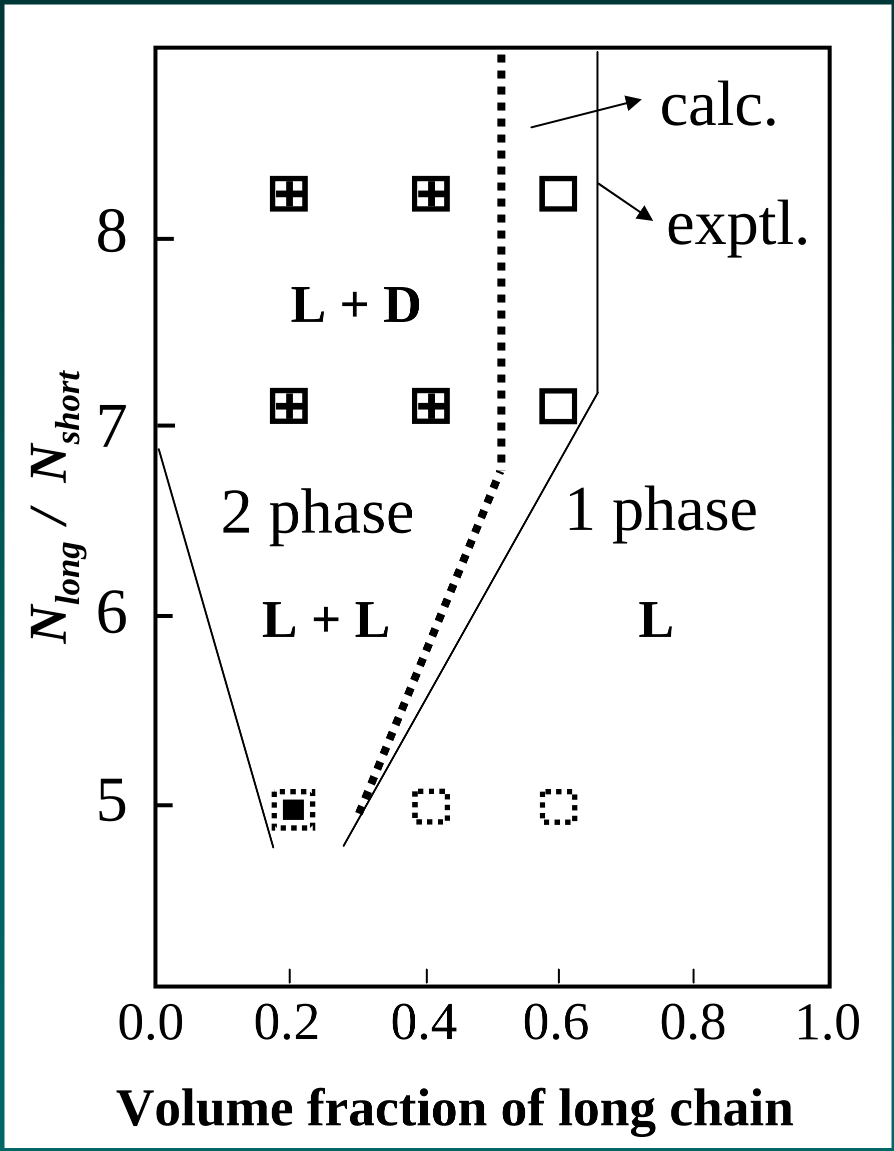
Prediction of Complex Domain Structures

(Morita, Kawakatsu, Doi, Yamaguchi, Takenaka & Hashimoto)

experiment

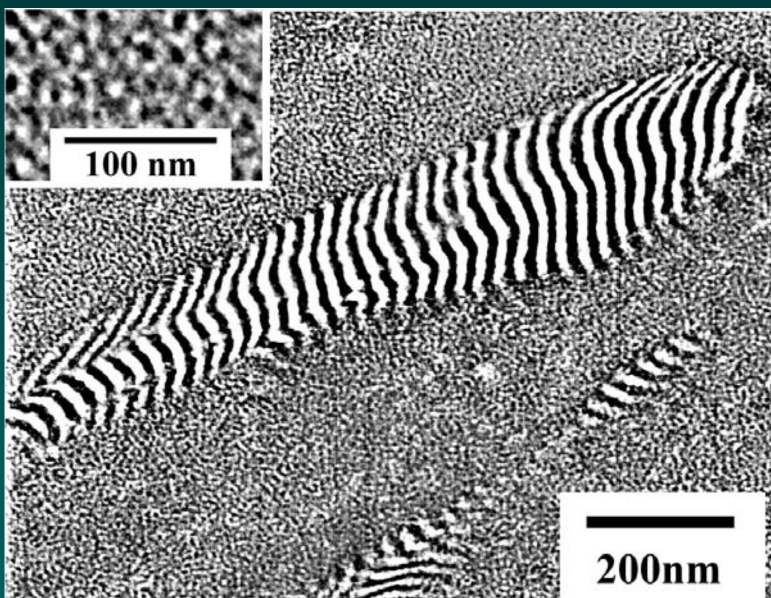


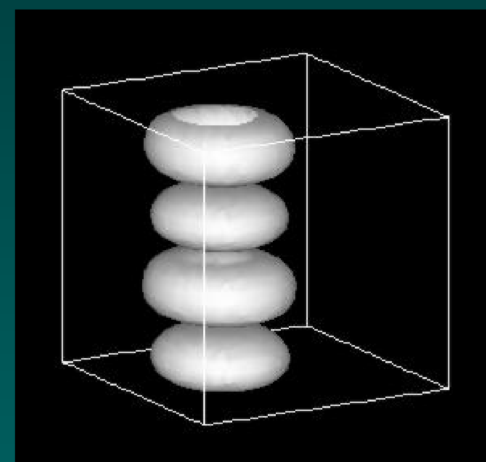
2d simulation

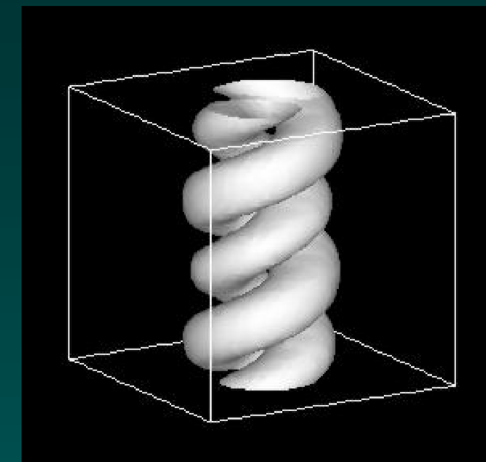


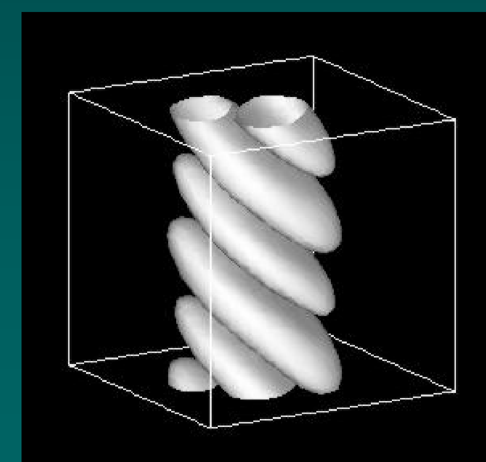
Prediction of Complex Domain Structures

(Morita, Kawakatsu, Doi, Yamaguchi, Takenaka & Hashimoto)









$$\phi_{\text{long}} : \phi_{\text{short}} = 0.2 : 0.8$$

→ **Prediction of exotic structures**

Dynamical Extension of SCF Theory

- Growth of irregular domains
- Structural phase transitions

→ Dynamical model

Density distribution $\phi(\boldsymbol{r}, t)$

↓

SCF calculation **Chain structure**

$$\frac{\partial}{\partial n} Q(n, \boldsymbol{r}; n', \boldsymbol{r}') = \left[\frac{b^2}{6} \nabla^2 - \beta V(\boldsymbol{r}) \right] Q(n, \boldsymbol{r}; n', \boldsymbol{r}')$$

↓

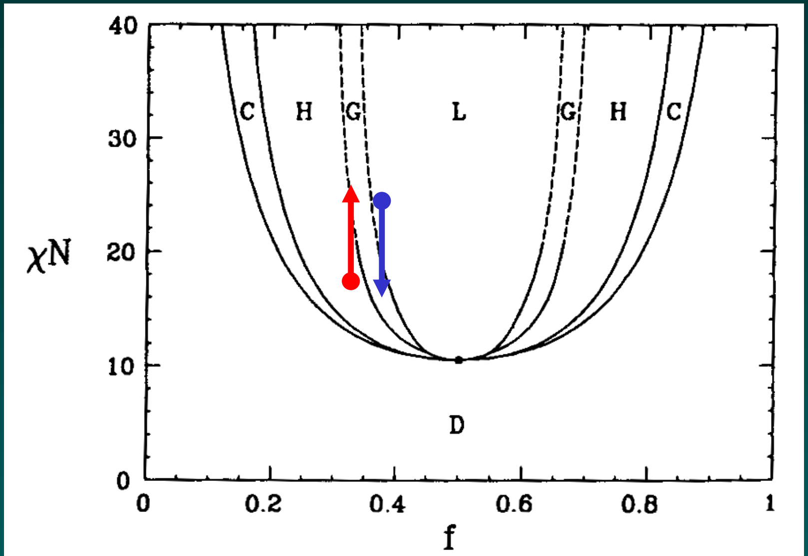
Free energy $F[\{\phi(\boldsymbol{r})\}]$

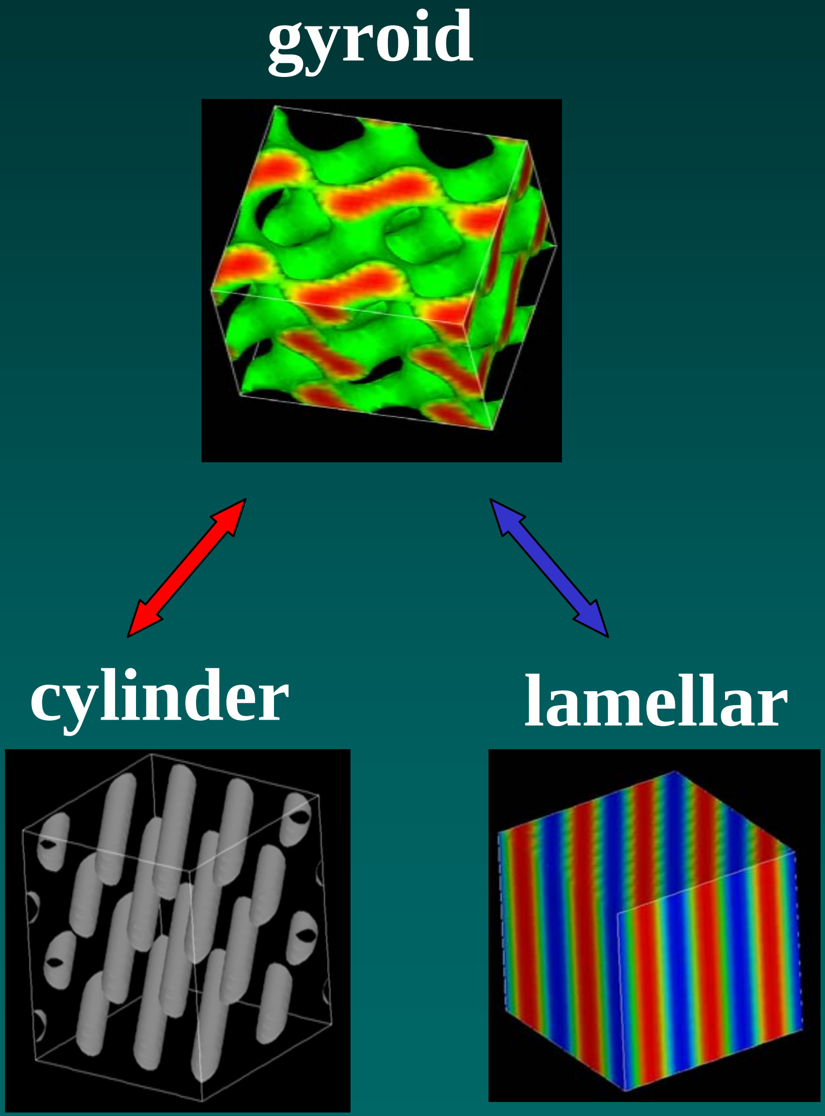
↓

Local diffusion **Diffusion/Hydrodynamics**

$$\frac{\partial \phi(\boldsymbol{r}, t)}{\partial t} + \nabla \cdot \{\phi(\boldsymbol{r}, t) \boldsymbol{v}(\boldsymbol{r}, t)\} = L \nabla^2 \frac{\delta F}{\delta \phi(\boldsymbol{r}, t)}$$

Structural Phase Transition between Mesophases



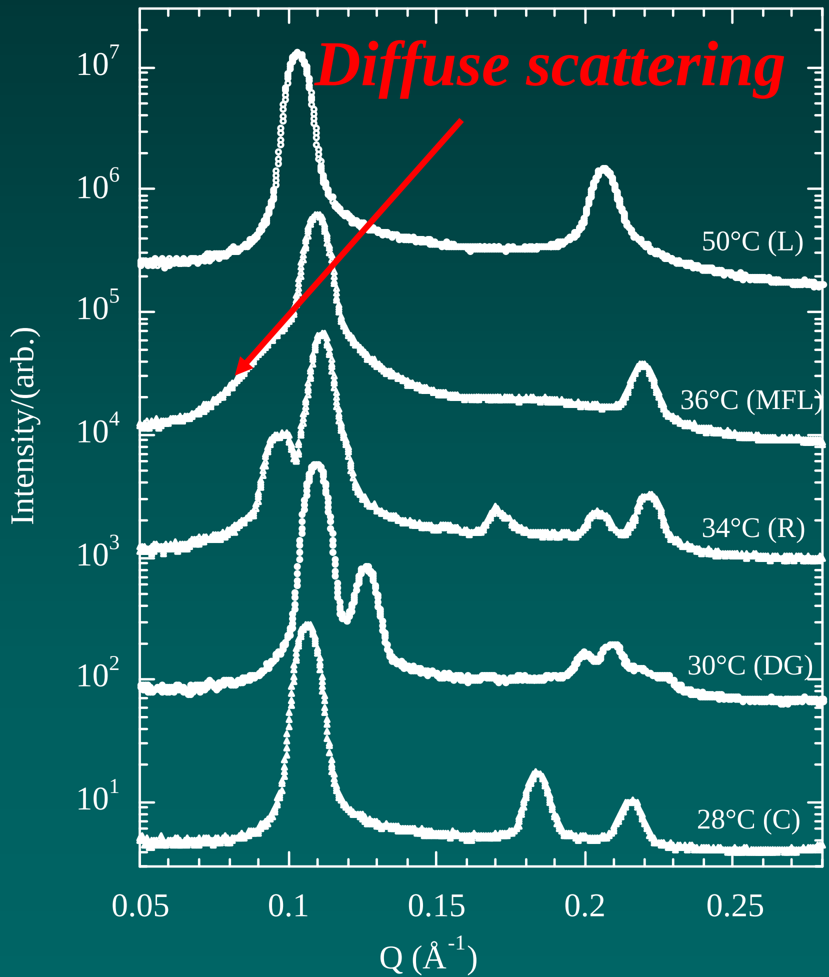


- Growth of unstable modes
- Kinetic pathway
- Conformation change

SAXS Experiment on Microemulsion

(Imai, *et al.*, *J. Chem. Phys.* 119 (2003) 8103.)

55% $C_{16}E_6$ / D_2O system



L

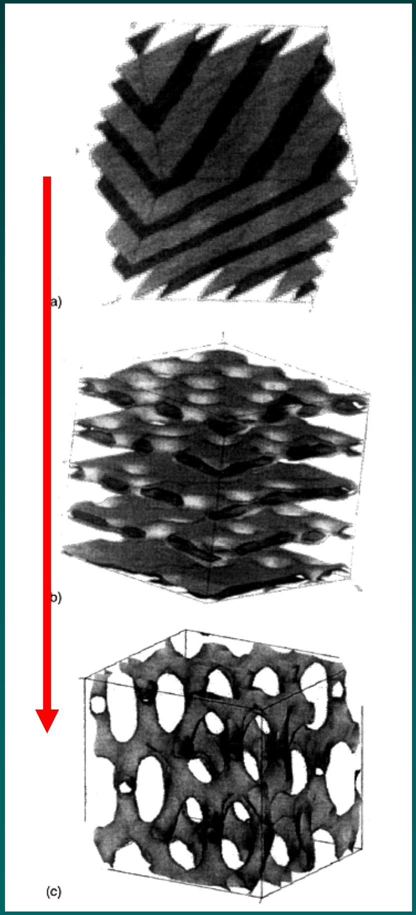
Modulation fluctuation layer

R

G

H

GL Model (Weak segregation)



L

PL

R

$C_{16}E_6 : CH_3(CH_2)_{15}(OC_2H_4)_6OH$

Stability Analysis on GL Model

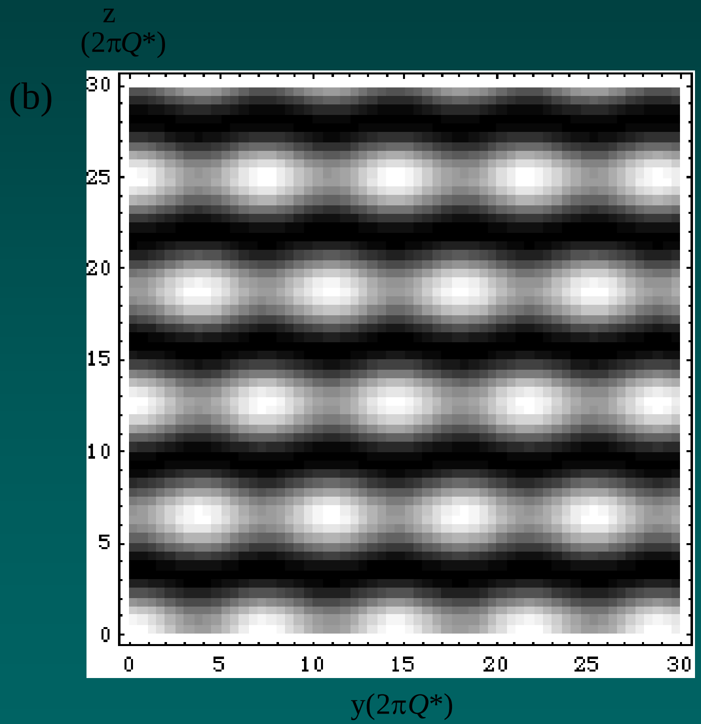
(Imai, *et al.*, *J. Chem. Phys.*, 119 (2003) 8103.)

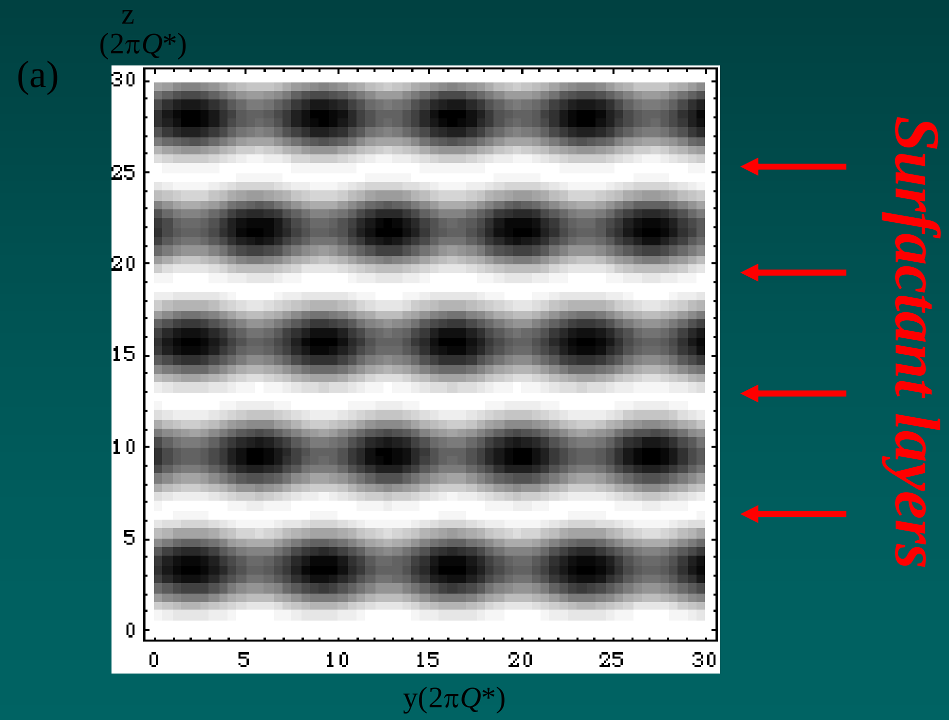
$$\lambda_{03}^{+} = 2\tau Q^{*2}$$

Amplitude modulation

$$\lambda_{03}^{-} = 0$$

Undulation





Bright region : majority phase (surfactant)

Dark region: minority phase (water)

Dynamics of Structural Phase Transition

(M.Nonomura, *et al., J. Phys. Condens. Matt.* 15 (2003) L423.)

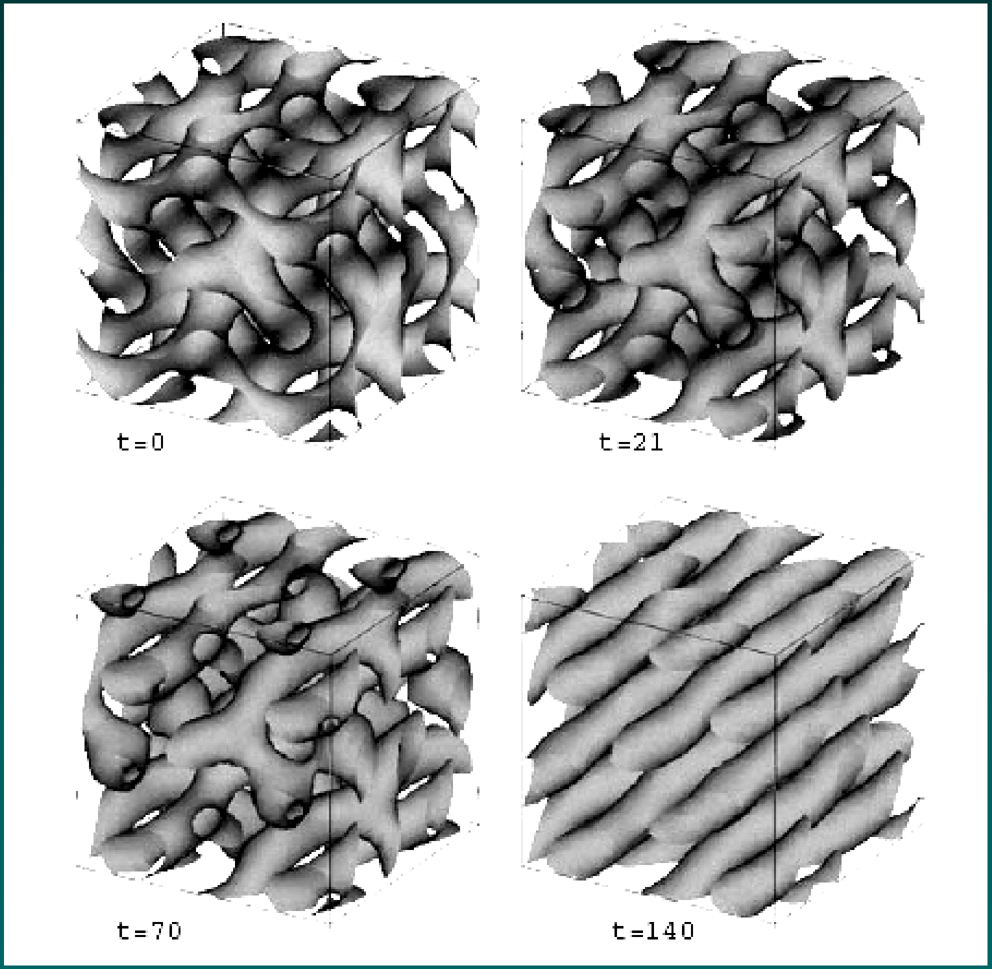
Gyroid → Cylinder

Ginzburg-Landau model
(weak segregation)
+
Fourier mode expansion

Changes in symmetry & periodicity (a few %)

⇩

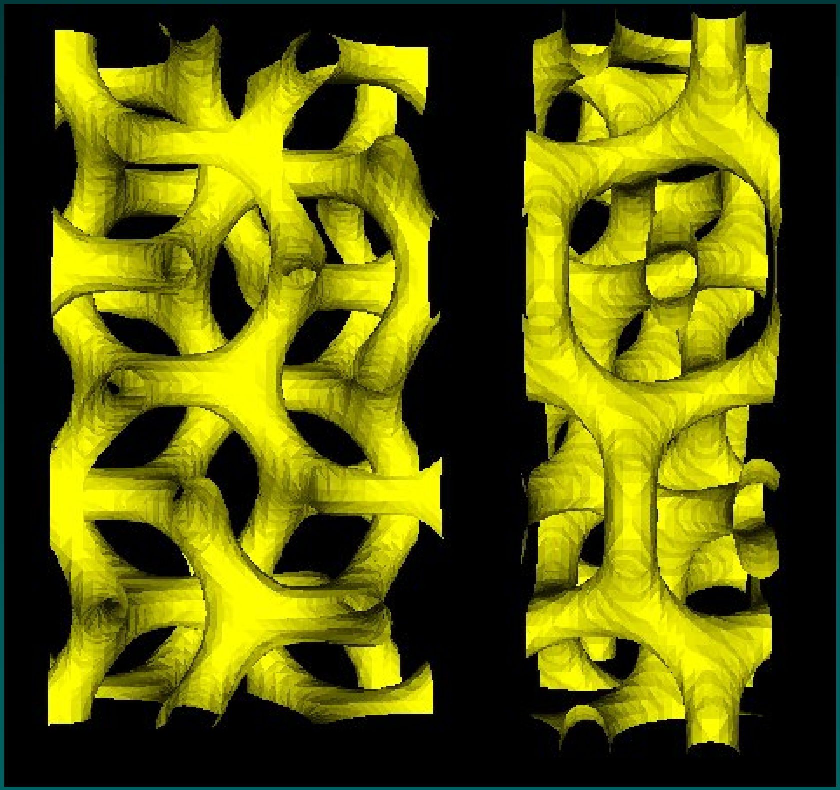
Many modes (12 + 6)



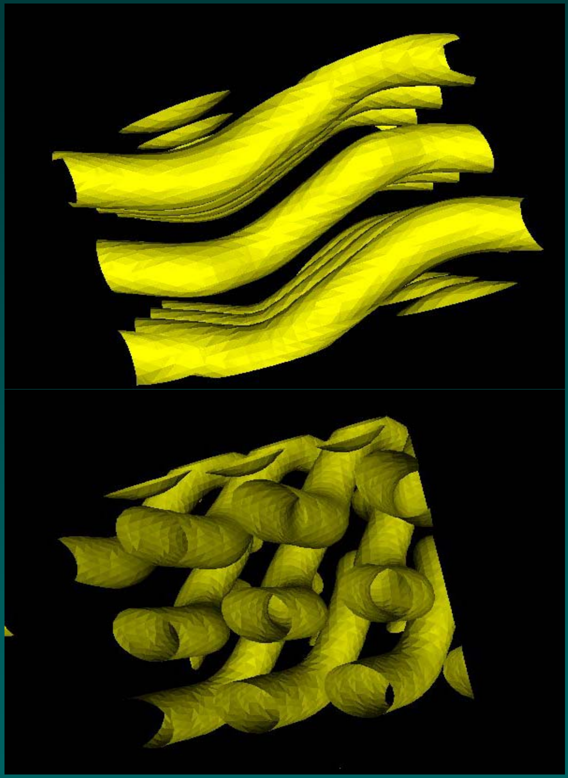
Gyroid(1,1,1) → Cylinder: epitaxial growth

Dynamics of Structural Phase Transition under Shear Flow (T.Honda and T.Kawakatsu)

Gyroid → Cylinder (Strong segregation)



Shear flow
in (1,0,0)
direction



Real space dynamic SCF + variable system size

Chain architecture
& stability

Automatic adjustment
of periodicity

Dynamics of Structural Phase Transition under Shear Flow (T.Honda and T.Kawakatsu)

Density distribution

$$\phi(\mathbf{r}, t)$$

SCF calculation

Chain architecture

$$\frac{\partial}{\partial n} Q(n, \mathbf{r}; n', \mathbf{r}') = \left[\frac{b^2}{6} \nabla^2 - \beta V(\mathbf{r}) \right] Q(n, \mathbf{r}; n', \mathbf{r}')$$

Free energy

$$F[\{\phi(\mathbf{r})\}]$$

Local diffusion

Hydrodynamic effect

$$\frac{\partial \phi(\mathbf{r}, t)}{\partial t} + \nabla \cdot \{\phi(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)\} = L \nabla^2 \frac{\delta F}{\delta \phi(\mathbf{r}, t)}$$

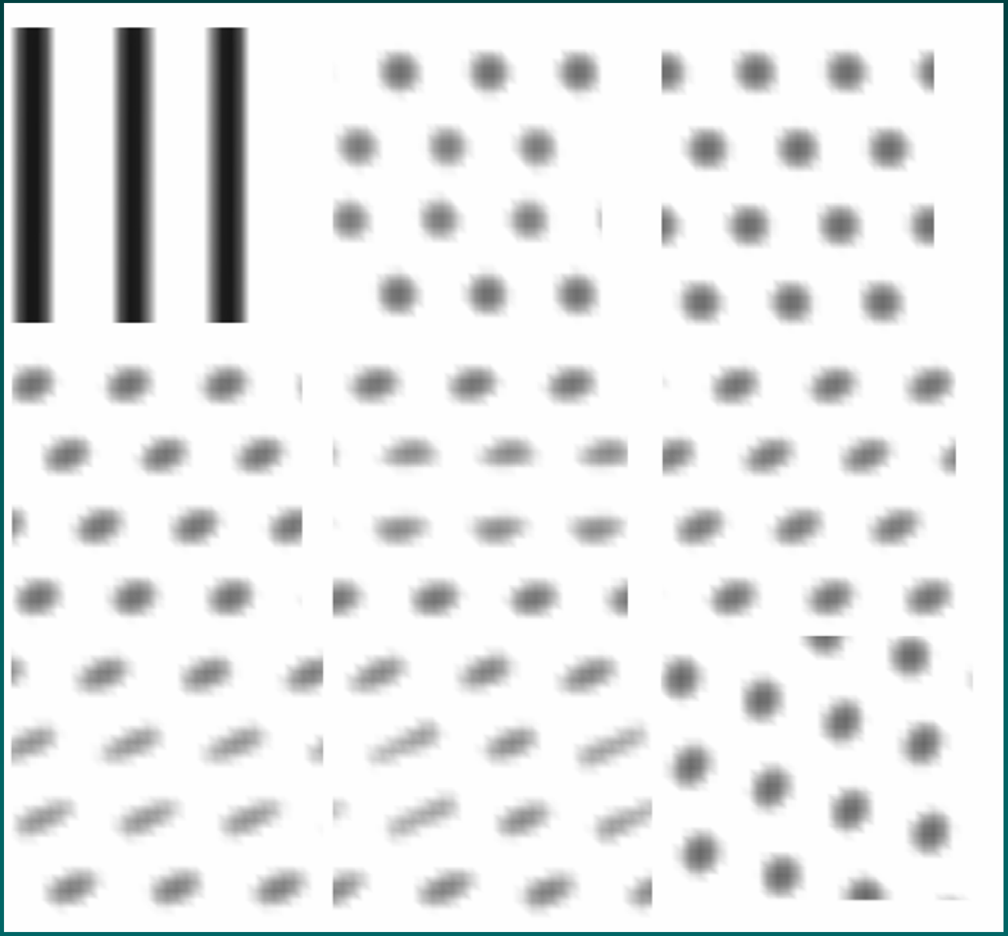
Box size adjustment

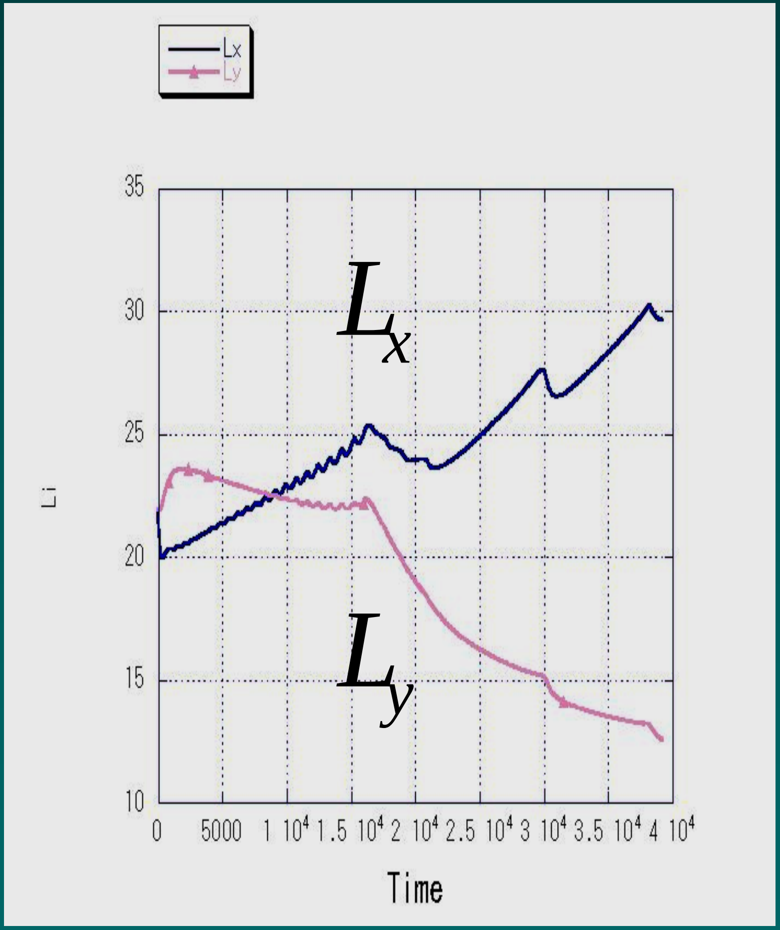
$$\frac{\partial}{\partial t} L_\alpha = -M_\alpha \frac{\partial (F/V)}{\partial L_\alpha}$$

Change in periodicity

Dynamics of Structural Phase Transition under Shear Flow (T.Honda and T.Kawakatsu)

A_8-B_{12} blockcopolymer melt, $\chi N = 20$
Real space 2-d dynamic SCF simulation with weak shear

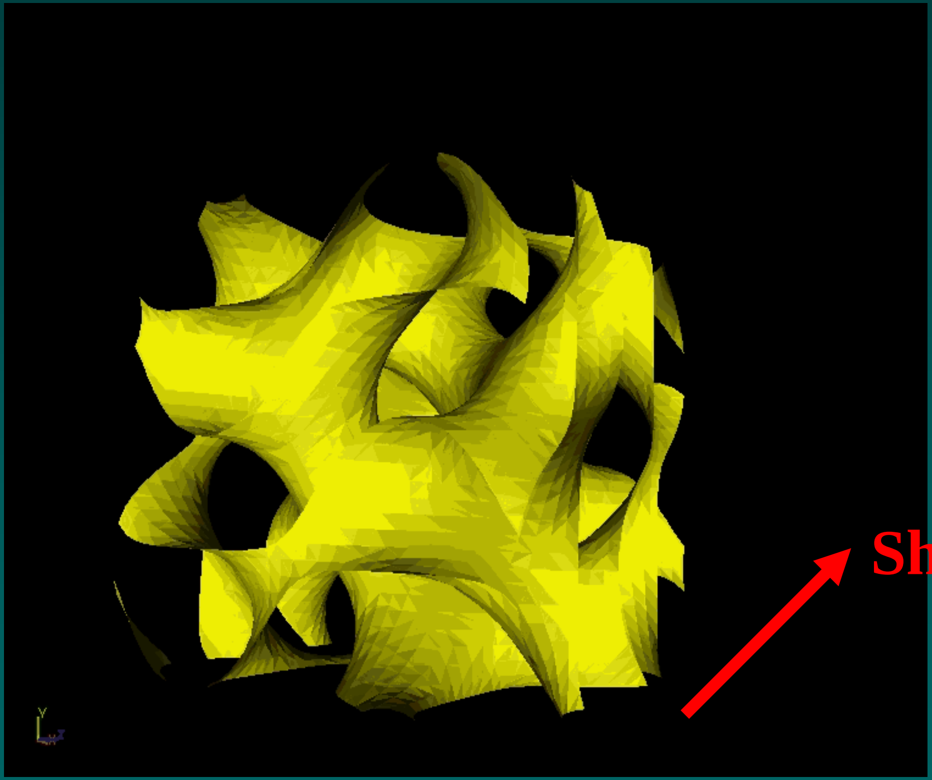




Dynamics of Structural Phase Transition under Shear Flow (T.Honda and T.Kawakatsu)

A_7-B_{13} blockcopolymer melt, $\chi N = 20 \rightarrow 15$ (G → G/C)

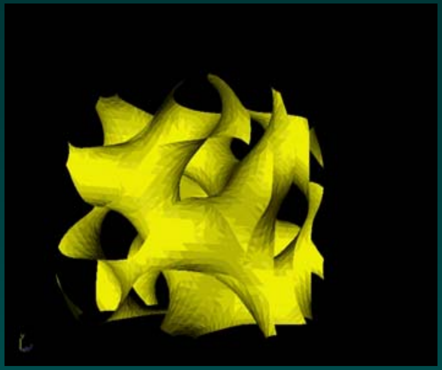
Real space dynamic SCF simulation with weak shear

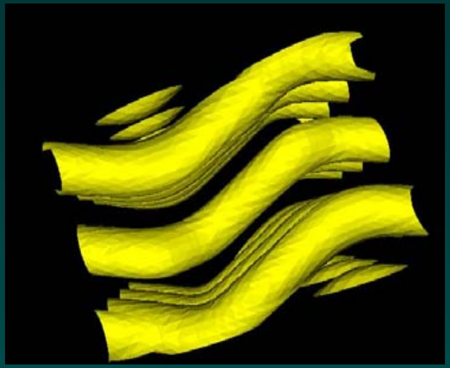


Shear direction (1,0,0)

→ Direct observation of the kinetic pathway

Dynamics of Structural Phase Transition under Shear Flow (T.Honda and T.Kawakatsu)



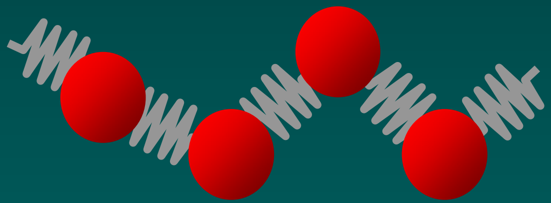


(1,0,0)-growth	→	Non-epitaxial
Real space dynamics under shear	→	Modulated cylinder (Metastable)
Variable box size	→	Change in periodicity in perpendicular direction

Effect of External Flow & Kinetic Pathway

(Groot, Madden & Tildesley, *J. Chem. Phys.* 110 (1999) 9739.)

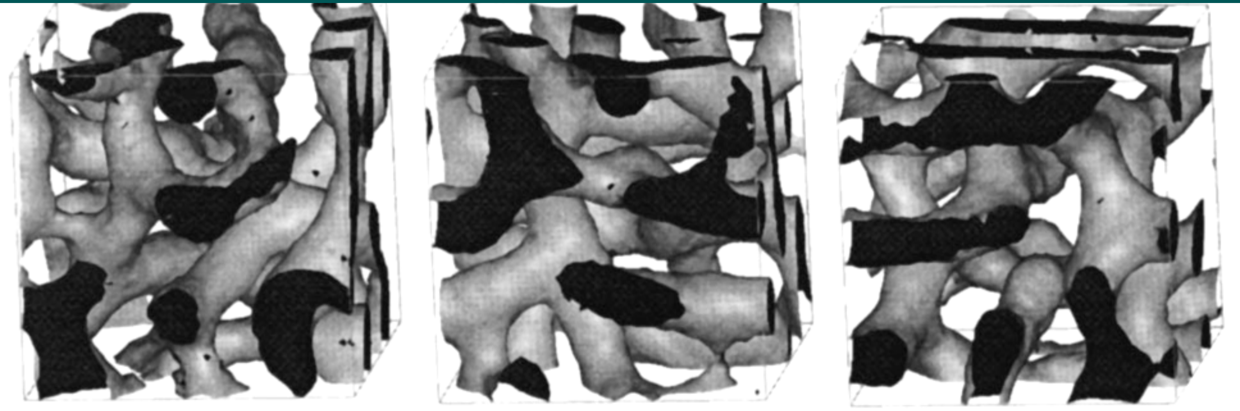
Dissipative Particle Dynamics (DPD)



With hydrodynamic effect

Brownian Dynamic (BD)

Without hydrodynamic effect

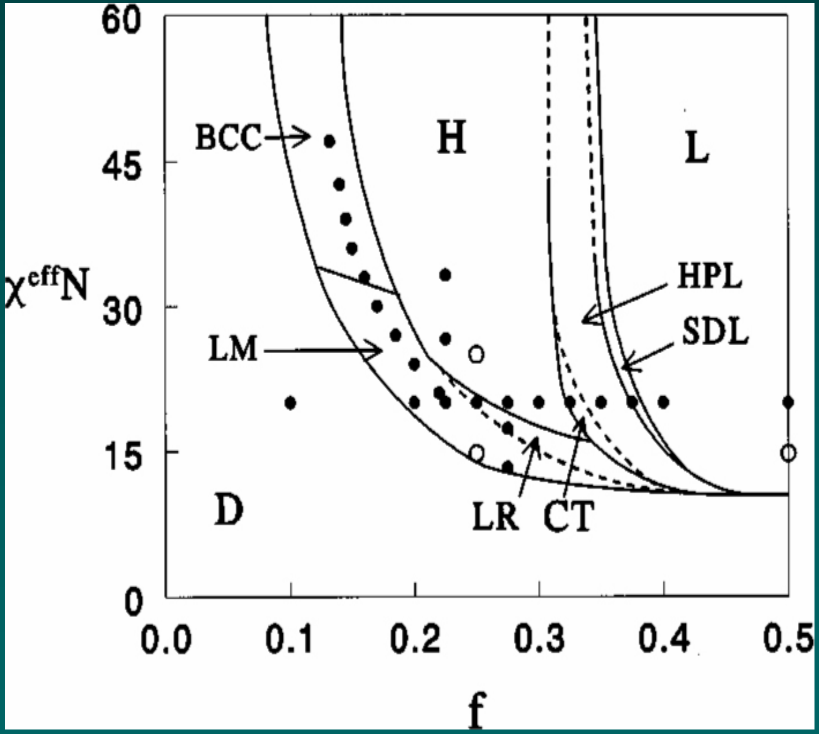


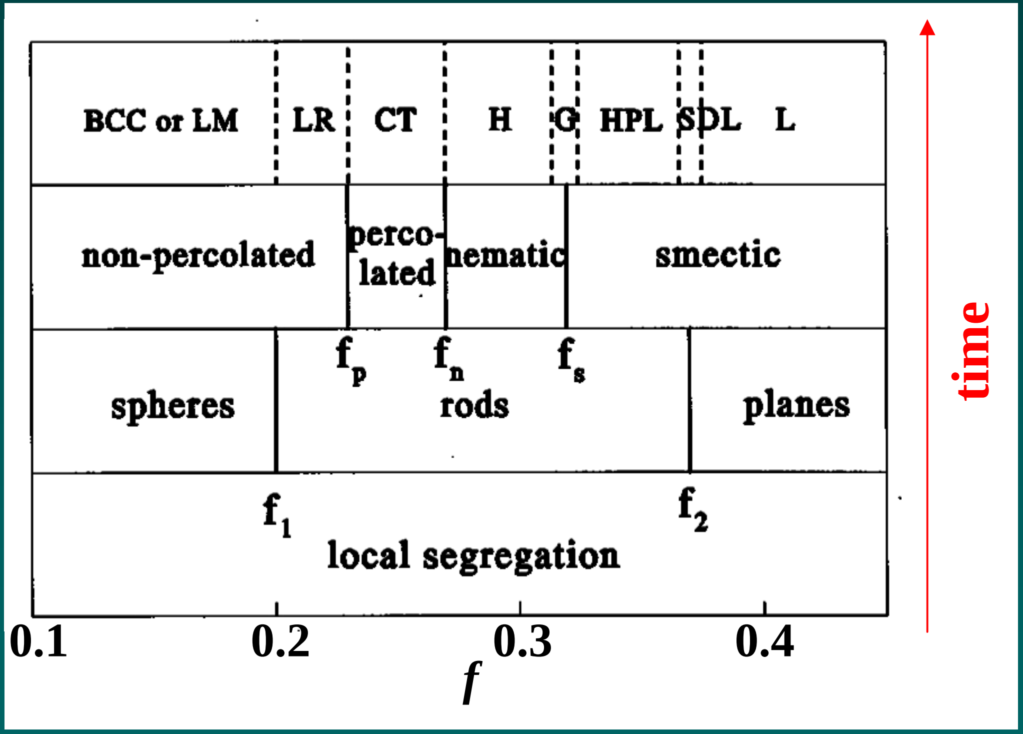
Artificial stabilization of interconnected transient structure

Kinetic Pathway

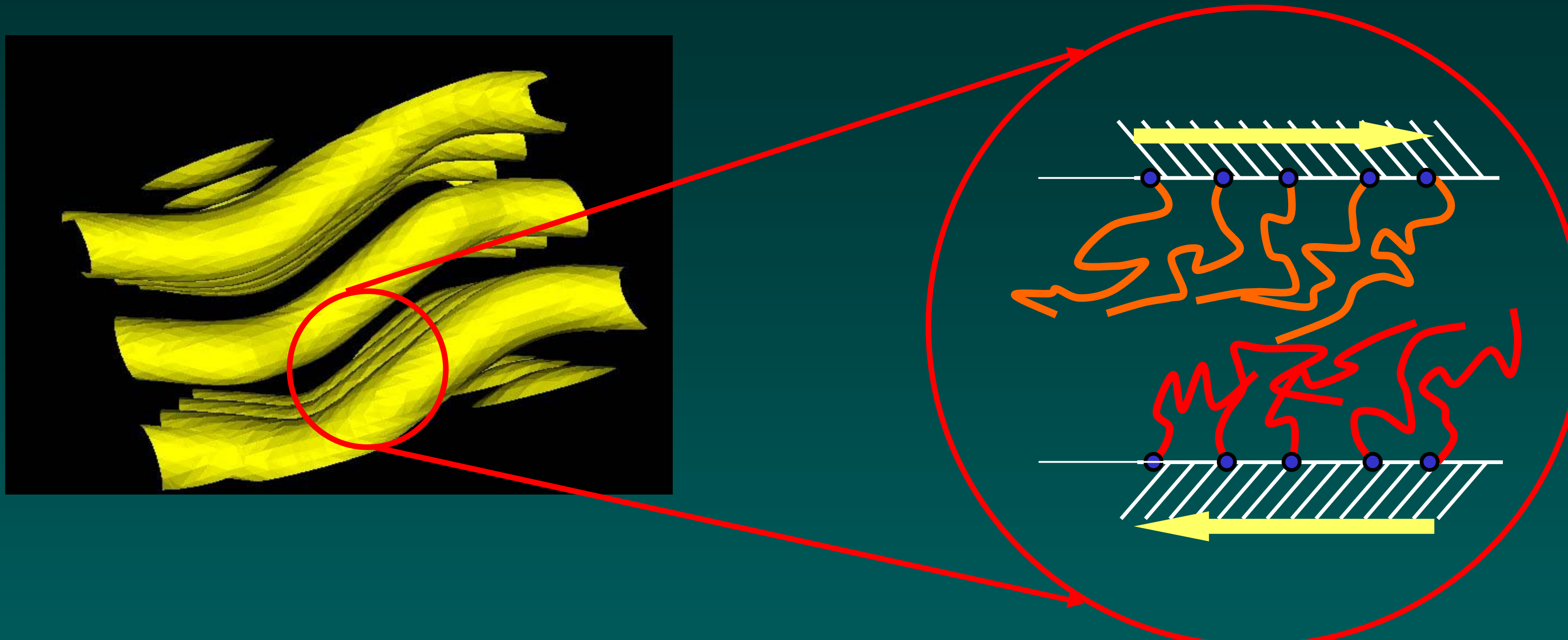
(Groot, Madden & Tildesley, *J. Chem. Phys.* 110 (1999) 9739.)

DPD simulation of kinetic pathway in block copolymer melt





Viscoelastic Properties of Mesophases



Sheared mesophase

Sheared brushes

Standard dynamic SCF

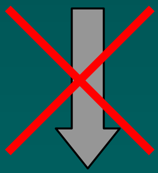
- **Highly-deformed conformation**
- **Entanglements**
- **External/internal flow**

Limitations of standard SCF

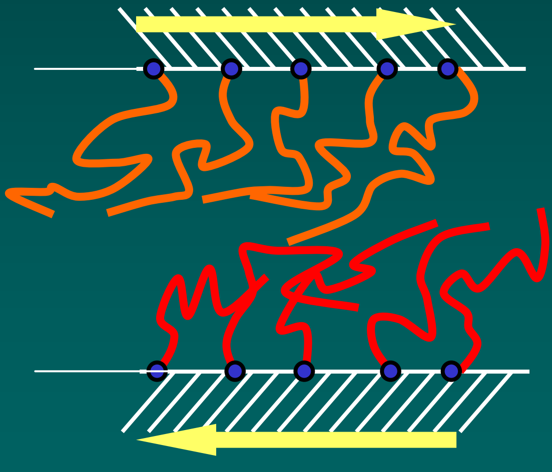
Basic assumption of DSCF

$$Q(n,\boldsymbol{r};n',\boldsymbol{r}') \equiv \sum_{\text{all conformation}} \exp\left[-\beta \sum_k V(\boldsymbol{r}_k)\right]$$

Local equilibrium (Canonical ensemble)

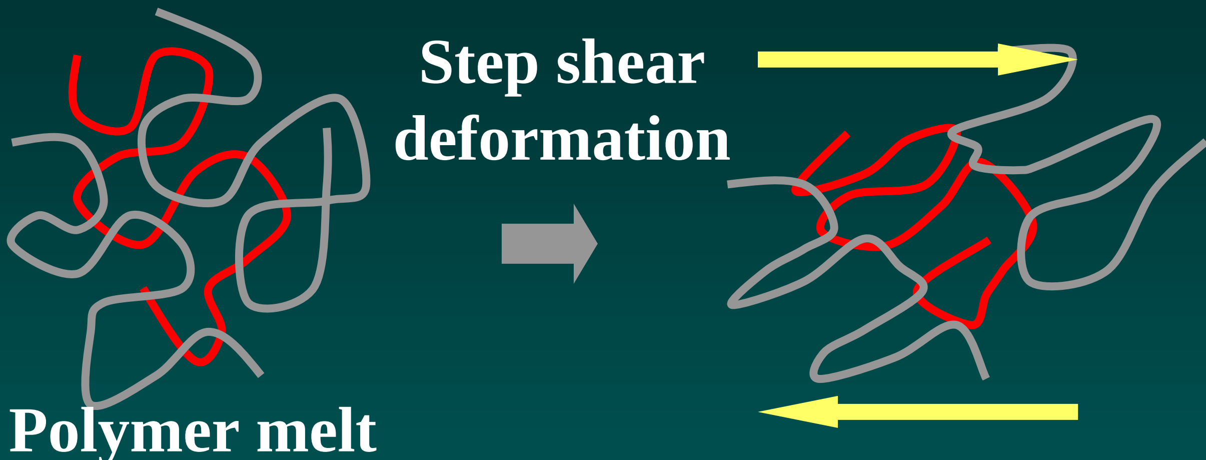


Non-equilibrium conformation (Viscoelasticity, *etc.*)

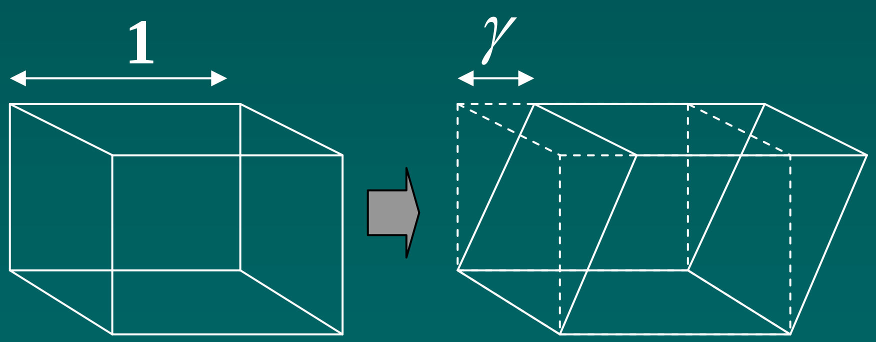


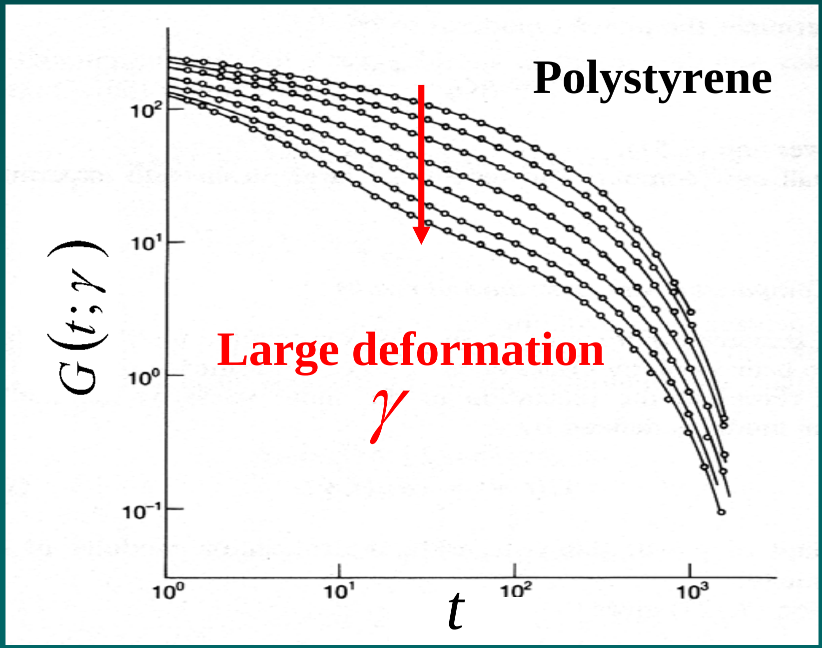
Sheared polymer brushes

Viscoelasticity and Reptation Motion in Concentrated Polymer Systems



Stress relaxation by reptation



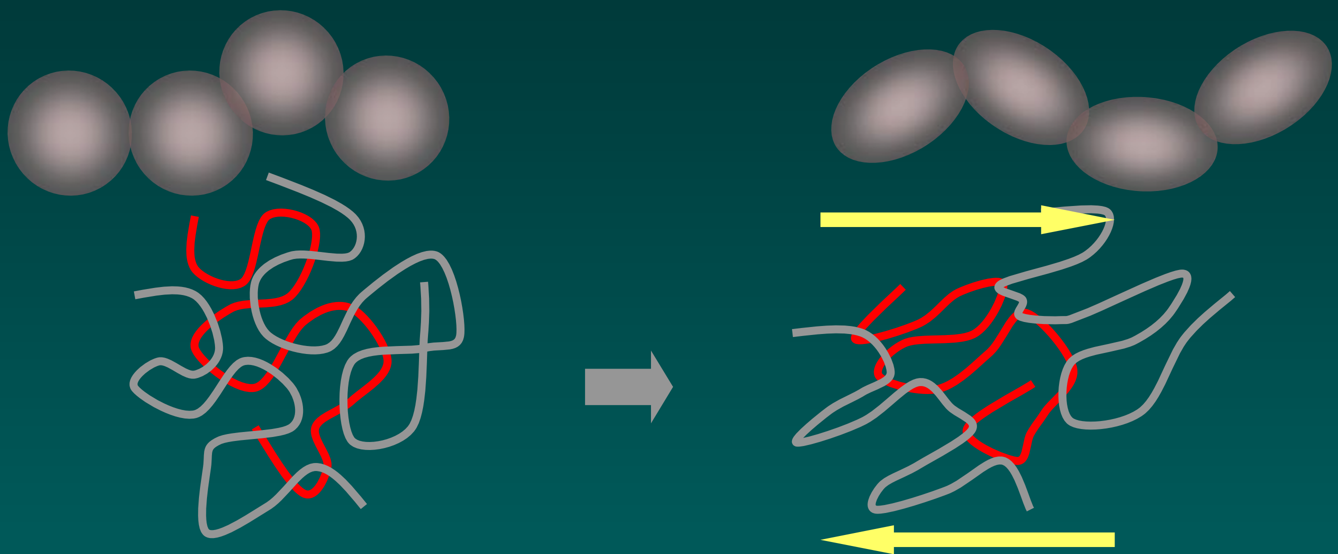


(Osaki, *et al.*, *Macromolecules* 15 (1982) 1068.)

Extension of SCF to Highly Deformed Chains

(Shima, Kuni, Okabe, Doi, Yuan, and Kawakatsu, 2003)

Bond orientation tensor $\boldsymbol{S}(n,\boldsymbol{r})$



Path Integral

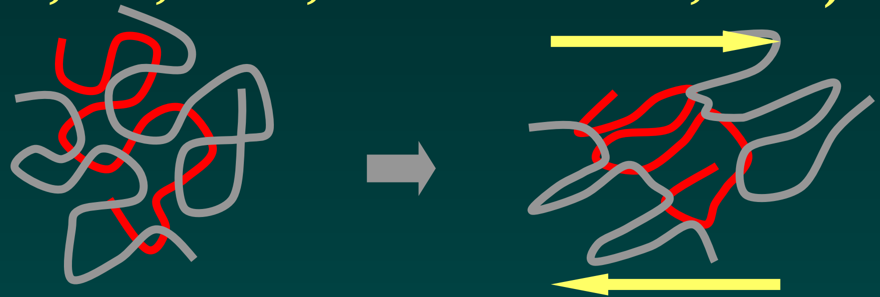
$$\frac{\partial}{\partial n}Q(n,\boldsymbol{r};m,\boldsymbol{r}') = \left[\underline{\boldsymbol{S}(n,\boldsymbol{r})}:\nabla\nabla - \beta V(\boldsymbol{r})\right]Q(n,\boldsymbol{r};m,\boldsymbol{r}')$$

Bond orientation $\boldsymbol{S}(n,\boldsymbol{r})$ **+**

reptation, flow deformation, constraint release

Extension of SCF to Highly Deformed Chains

(Shima, Kuni, Okabe, Doi, Yuan, and Kawakatsu, 2003)



Path Integral

$$\frac{\partial}{\partial n} Q(n, \boldsymbol{r}; m, \boldsymbol{r}') = \left[\underline{\boldsymbol{S}(n, \boldsymbol{r}):} \nabla\nabla - \beta V(\boldsymbol{r})\right] Q(n, \boldsymbol{r}; m, \boldsymbol{r}')$$

Reptation dynamics for $\boldsymbol{S}(n, \boldsymbol{r}, t)$

$$\frac{\partial}{\partial t} \boldsymbol{S}(n, \boldsymbol{r}, t) = -\frac{\partial}{\partial n} \boldsymbol{j}(n, \boldsymbol{r}, t) - \nabla \cdot \left[\boldsymbol{v}(\boldsymbol{r}, t) \cdot \boldsymbol{S}(n, \boldsymbol{r}, t)\right]$$

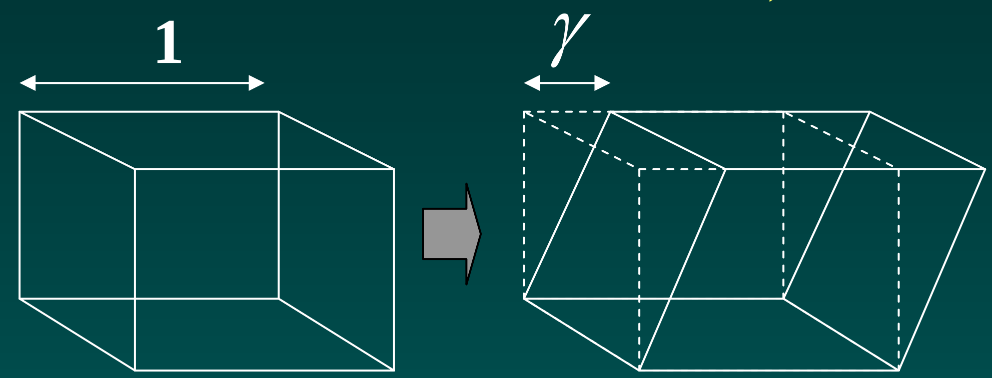
$$+ \left[\kappa(\boldsymbol{r}, t) \cdot \boldsymbol{S}(n, \boldsymbol{r}, t) + \boldsymbol{S}(n, \boldsymbol{r}, t) \cdot \kappa^{T}(\boldsymbol{r}, t)\right] + \left.\frac{\partial}{\partial t} \boldsymbol{S}(n, \boldsymbol{r}, t)\right|_{\text{constraint release}}$$

$$\kappa(\boldsymbol{r}, t) \equiv \nabla \boldsymbol{v}(\boldsymbol{r}, t)$$ **Velocity gradient tensor**

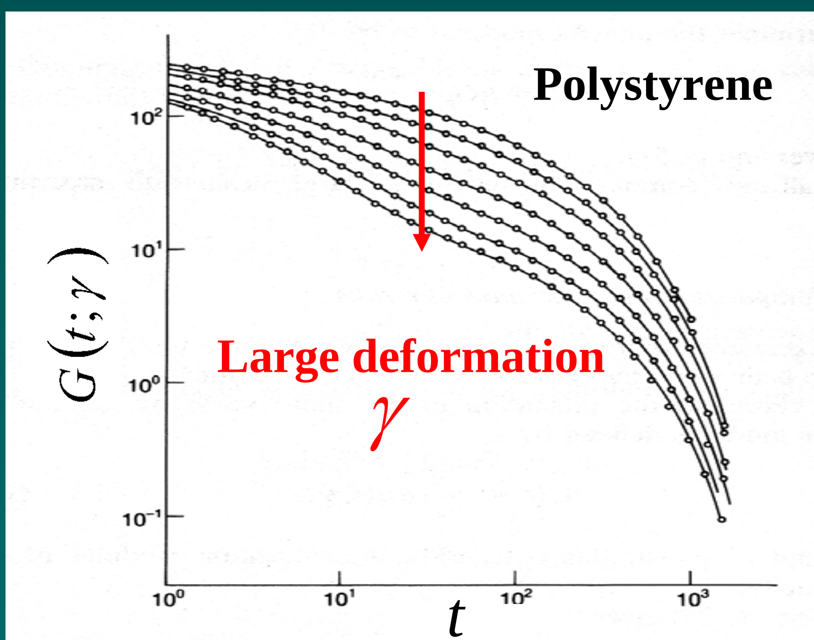
Simulation of Polymer Melt Under Step Shear Deformation

(Shima, Kuni, Okabe, Doi, Yuan, and Kawakatsu, 2003)

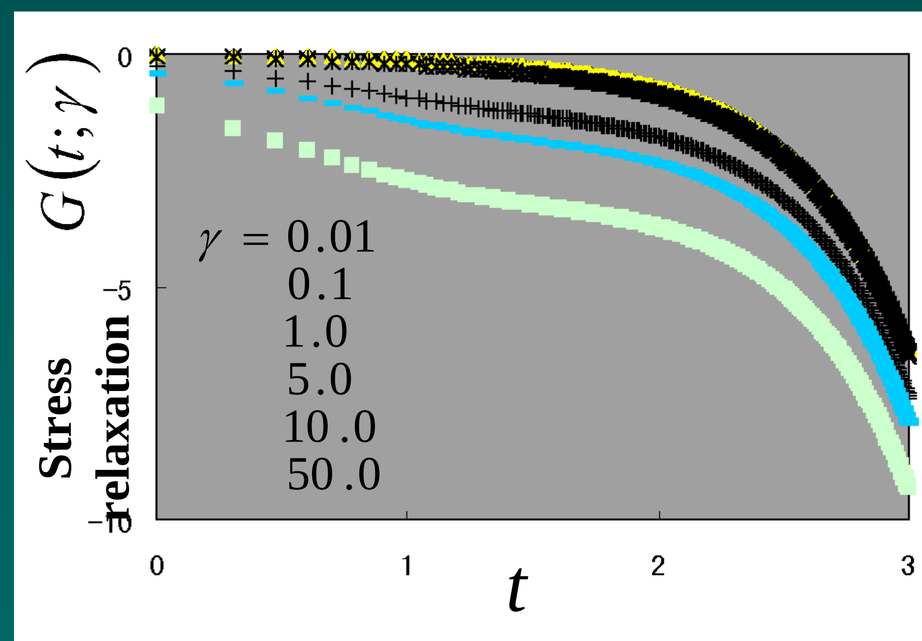
Comparison with reptation theory for uniform systems



experiment

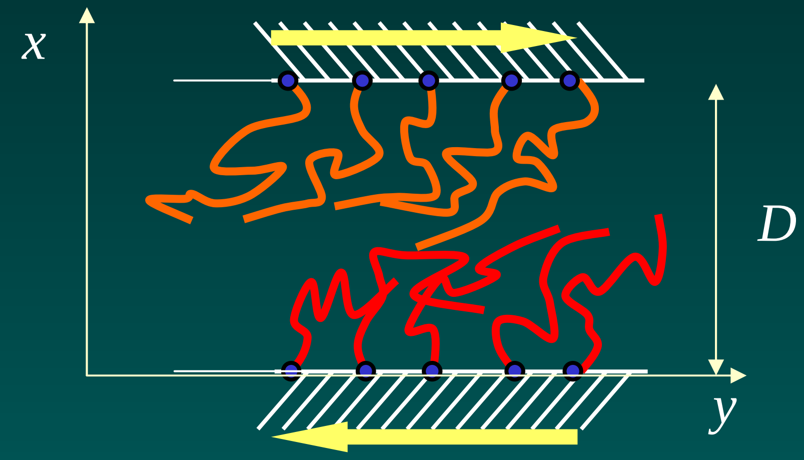


simulation

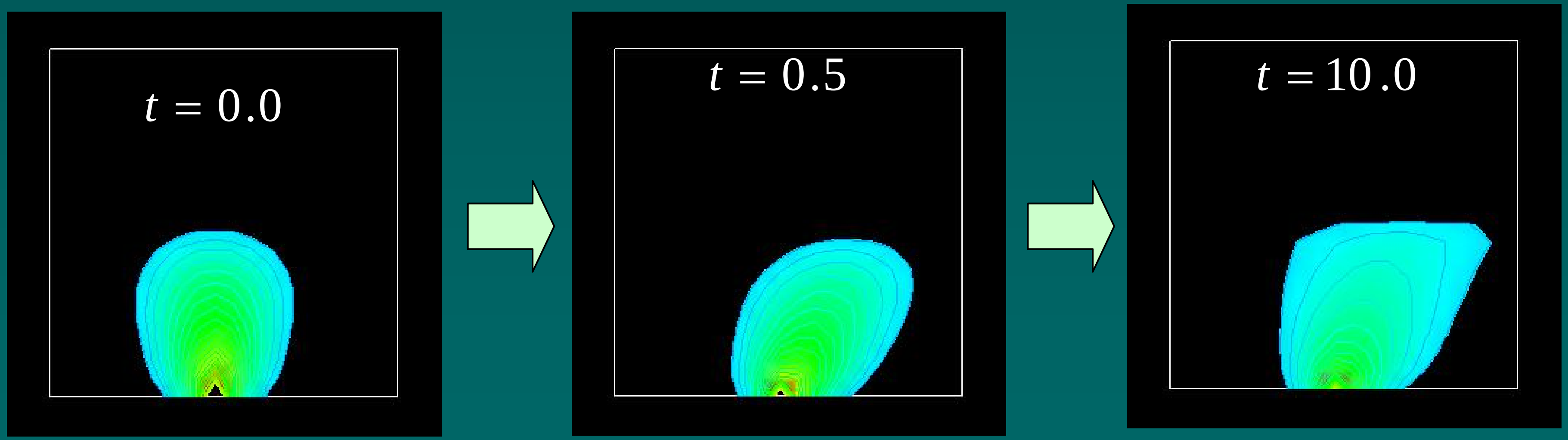


Simulation of Polymer Brushes Under Steady Shear Deformation

(Shima, Kuni, Okabe, Doi, Yuan, and Kawakatsu, 2003)



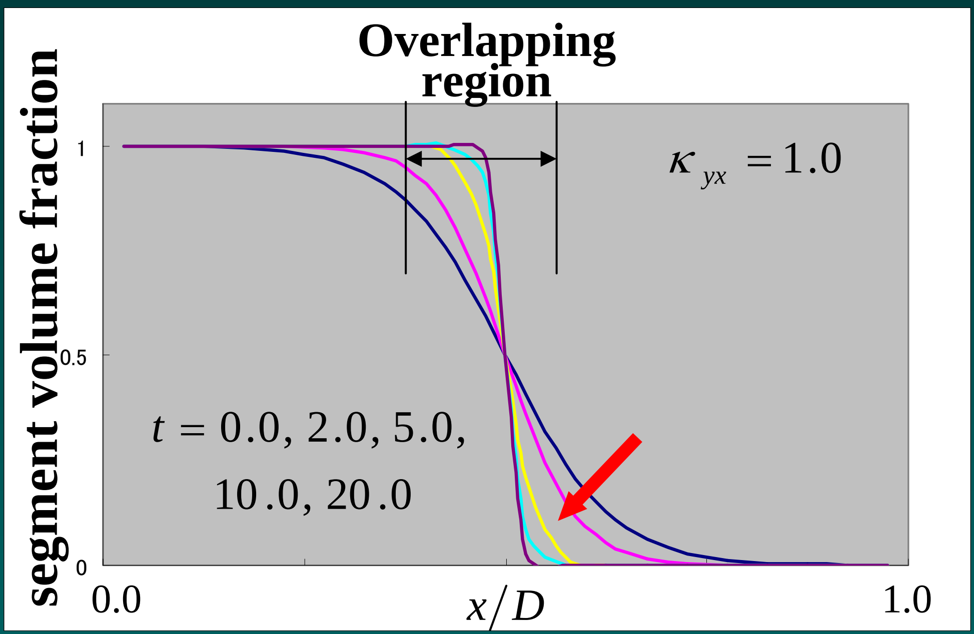
Single Chain Conformation ($\kappa_{yx} = 1.0$)



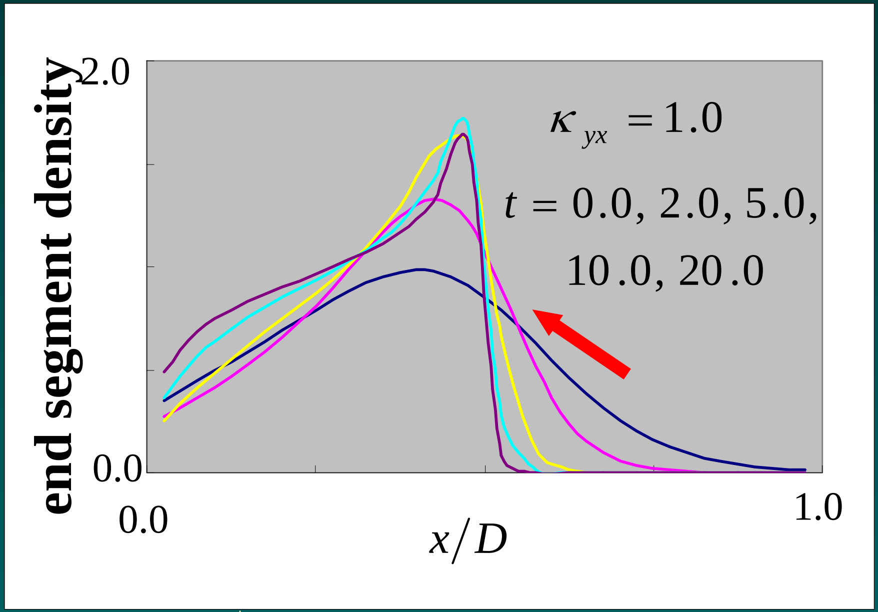
Simulation of Polymer Brushes Under Steady Shear Deformation

(Shima, Kuni, Okabe, Doi, Yuan, and Kawakatsu, 2003)

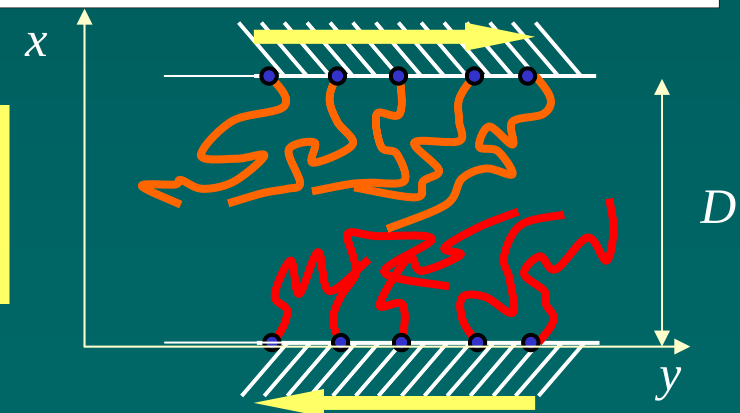
Segment Distribution



End Segment Distribution

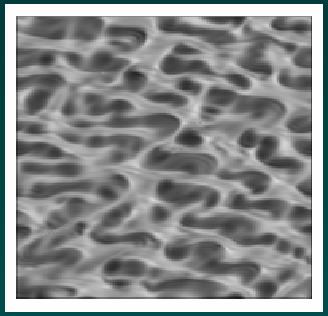


Dynamical properties that cannot be reproduced by standard SCF



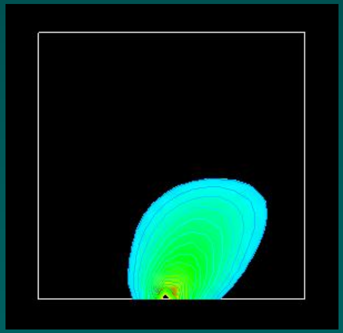
Conclusion and Future Direction

Polymer Mesophase/Polymer Nano-Composites



Numerical Analysis of Viscoelastic Equations ⇐ **Macroscopic flow**

+



Dynamic Extension of SCF Theory ⇐ **Chain structure**

⇓

Predictions on structural transition/viscoelastic behavior based on microscopic chain structure

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END