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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Inhomogeneity of Dense Polymer Systems

Polymer Mesophase/Polymer Nano-Composites

Microphase Separation in Blockcopolymer Melt

Salami Structure in HIPS (PS/PB)

Chain structure

Viscoelasticity

Koubunshi Shashinshu

Macromolecules 29, 2498 (1996)
Viscoelasticity of Dense Polymer Systems

Die Swell (extrusion from a channel)

Viscous fluid  Viscoelastic fluid

extended

recoil
**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)

\[
\nabla \cdot \mathbf{v} = 0 \quad (\mathbf{v} \equiv \phi_A \mathbf{v}_A + \phi_B \mathbf{v}_B)
\]

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

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

Constitutive Equation: Johnson-Segalman (JS) model

\[
\frac{\sigma_i}{\tau_i} + \frac{d\sigma_i}{dt} = G_i \left( \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right) \quad \sigma \equiv \sum_{i=1}^{3} \sigma_i
\]
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

\[
\frac{\sigma_i}{\tau_i} + \frac{d\sigma_i}{dt} = G_i \left( \nabla \mathbf{v} + \left( \nabla \mathbf{v} \right)^T \right) \quad \sigma \equiv \sum_{i=1}^{3} \sigma_i
\]
Simulation of Viscoelastic Flow Model
(Jupp, Yuan & Kawakatsu, 2003)

Simulation results
(shear-induced demixing case)

Stability diagram

\[ We = \frac{\text{elastic force}}{\text{viscous force}} = \kappa \tau_A \]

\[ \tau' = \frac{\tau_B}{\tau_A} = 0.2 \]

\[ We = 4.0 \]

\[ \chi \]

\[ \phi \]

O homogeneous
X two-phase

Shear-induced demixing
Simulation of Viscoelastic Flow Model
(Jupp, Yuan & Kawakatsu, 2003)

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

Uniform shear rate \(\rightarrow\) Inhomogeneous distribution of shear rate

instability
Introducing information on chain structure into flow simulation

Relation between Macroscopic and Microscopic Phenomena

Probability distribution of chain conformation (spatially-folding shape)

Self-Consistent Field (SCF) Theory
Density Functional Theories (SCF vs. GL)

Segment density
\[ \phi(r) \]

Fee energy functional
\[ F = F[\{\phi(r)\}] \]

Phase diagram of blockcopolymer melt

- Self-consistent field (SCF)
- Strong segregation
- Weak segregation
- Ginzburg-Landau (GL)
Basic Formalism of Static SCF Theory

Path integral for equilibrium chain conformation

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

Mean field (SCF)

Equilibrium structures

F = F \left[ \{ Q(n, r; m, r') \} \right] = F \left[ \phi(r) \right]
Static SCF Simulation: Phase Diagram & Domain Structures

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

- **l**amellar
- **c**ubic
- **g**yroid
- **c**ylinder

Periodic structure ➔ Fourier space analysis

\[ f = \frac{N_A}{N_A + N_B} \]
Prediction of Complex Domain Structures
(Morita, Kawakatsu, Doi, Yamaguchi, Takenaka & Hashimoto)

PS-PI diblock copolymer mixture

experiment

3d simulation

$\phi_{\text{long}} : \phi_{\text{short}} = 0.2 : 0.8$
Prediction of Complex Domain Structures
(Morita, Kawakatsu, Doi, Yamaguchi, Takenaka & Hashimoto)

experiment

2d simulation

Prediction of Complex Domain Structures
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Prediction of Complex Domain Structures
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\[ \phi_{\text{long}} : \phi_{\text{short}} = 0.2 : 0.8 \]

Prediction of exotic structures
Dynamical Extension of SCF Theory

- Growth of irregular domains
- Structural phase transitions

Dynamical model

Density distribution
\[ \phi(r, t) \]

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

Chain structure

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

Local diffusion
\[
\frac{\partial \phi(r, t)}{\partial t} + \nabla \cdot \{\phi(r, t) v(r, t)\} = L \nabla^2 \frac{\delta F}{\delta \phi(r, t)}
\]

Diffusion/Hydrodynamics
Structural Phase Transition between Mesophases

- Growth of unstable modes
- Kinetic pathway
- Conformation change
SAXS Experiment on Microemulsion

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

Diffuse scattering

Modulation fluctuation layer

GL Model
(Weak segregation)

$C_{16}E_6 : CH_3(CH_2)_15(OC_2H_4)_6OH$
Stability Analysis on GL Model  

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

**Amplitude modulation**

\[ \lambda_{03}^- = 0 \]

**Undulation**

(b) 

![Image of amplitude modulation](image)

(a) 

![Image of undulation](image)

**Bright region**: majority phase (surfactant)  
**Dark region**: minority phase (water)
Dynamics of Structural Phase Transition

Gyroid $\rightarrow$ Cylinder

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

Changes in symmetry & periodicity (a few %)

Many modes (12 + 6)

Gyroid(1,1,1) $\rightarrow$ Cylinder: epitaxial growth
Dynamics of Structural Phase Transition under Shear Flow (T.Honda and T.Kawakatsu)

Gyroid $\rightarrow$ 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
\[ \phi(r, t) \]

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

Chain architecture

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

Local diffusion
\[ \frac{\partial \phi(r, t)}{\partial t} + \nabla \cdot \{\phi(r, t)v(r, t)\} = L \nabla^2 \frac{\delta F}{\delta \phi(r, t)} \]

Hydrodynamic effect

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, $\chi N = 20 \rightarrow 15$ ($G \rightarrow G/C$)

Real space dynamic SCF simulation with weak shear

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


Dissipative Particle Dynamics (DPD)

With hydrodynamic effect

Without hydrodynamic effect

Brownian Dynamic (BD)

Artificial stabilization of interconnected transient structure
Kinetic Pathway

DPD simulation of kinetic pathway in block copolymer melt
Viscoelastic Properties of Mesophases

- Sheared mesophase
- Sheared brushes
  - Highly-deformed conformation
  - Entanglements
  - External/internal flow

Standard dynamic SCF
Limitations of standard SCF

Basic assumption of DSCF

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

Local equilibrium (Canonical ensemble)

Non-equilibrium conformation (Viscoelasticity, etc.)

Sheared polymer brushes
Viscoelasticity and Reptation Motion in Concentrated Polymer Systems

Polymer melt

Step shear deformation

Stress relaxation by reptation

Polystyrene

Large deformation

(1)

(γ)

(G(t; γ))

Extension of SCF to Highly Deformed Chains

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

Bond orientation tensor \( S(n, r) \)

Path Integral

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

Bond orientation \( S(n, r) \) +

reptation, flow deformation, constraint release
Extension of SCF to Highly Deformed Chains

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

Path Integral

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

Reptation dynamics for \( S(n, r, t) \)

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

\[ + \left[ \kappa(r, t) \cdot S(n, r, t) + S(n, r, t) \cdot \kappa^T(r, t) \right] + \frac{\partial}{\partial t} S(n, r, t) \]

\( \kappa(r, t) \equiv \nabla v(r, t) \) Velocity gradient tensor

Constraint release
Simulation of Polymer Melt Under Step Shear Deformation
(Shima, Kuni, Okabe, Doi, Yuan, and Kawakatsu, 2003)

Comparison with reptation theory for uniform systems

Stress relaxation

Polystyrene

Large deformation

experiment

simulation

$G(t;\gamma)$

$t$

$\gamma$

$G(t;\gamma)$
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

Dynamic Extension of SCF Theory

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

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END