Simulation Utilities for Soft and Hard Interfaces

SUSHI

Simulation Utilities for Soft and Hard Interfaces

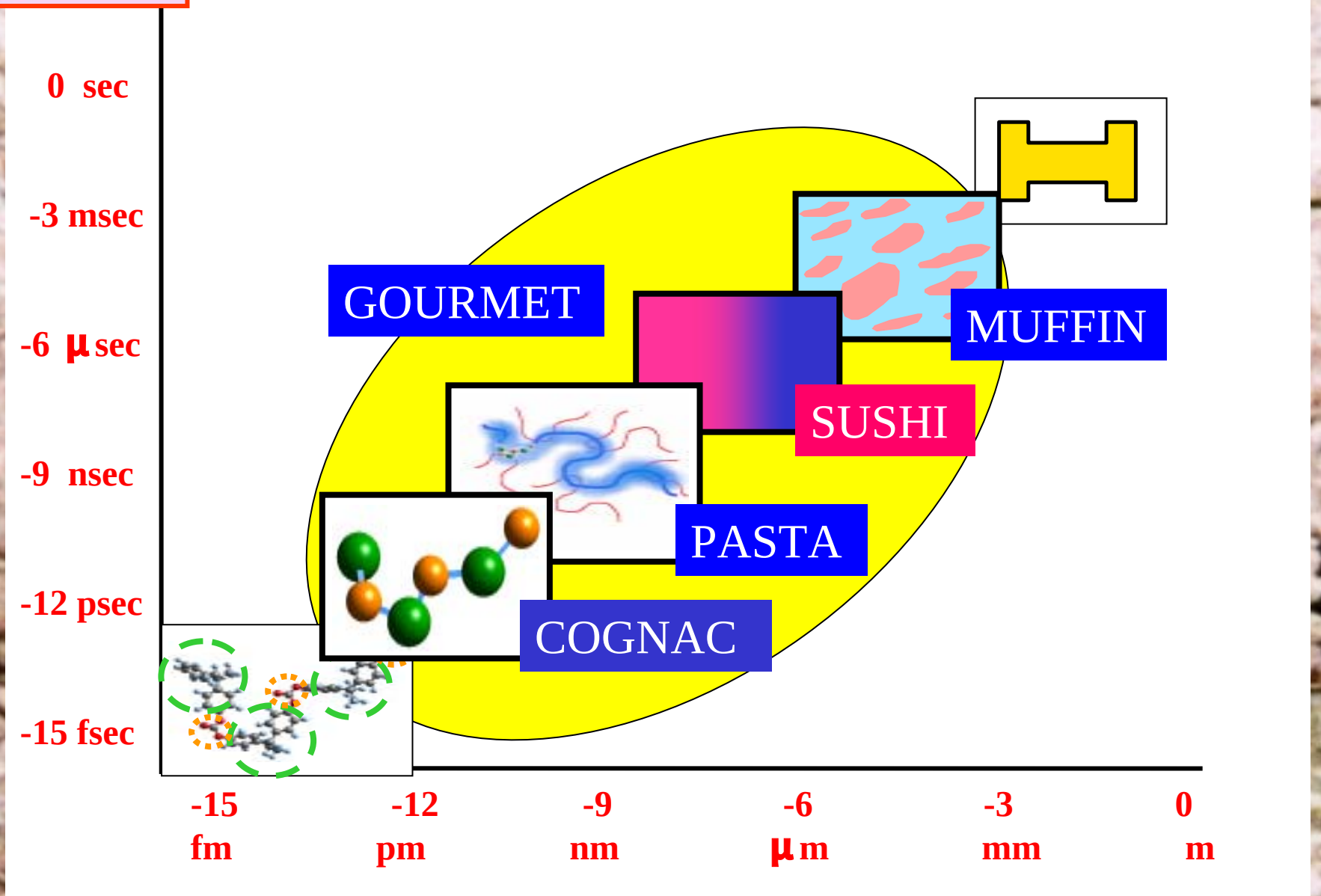
Simulator for polymeric materials on mesoscopic scale based on Self-Consistent Field theory

Developed by Working Group 2 of Doi Project

T. Honda, H.Kodama, J.-R. Roan,
Y.Morita, S.Urashita, R.Hasegawa, K.Yokomizo,
T.Kawakatsu, M.Doi

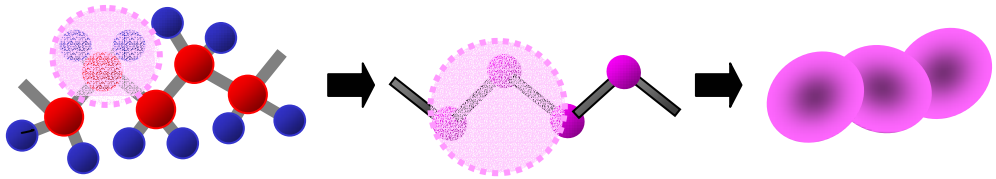
OCTA

Position of SUSHI on length and time scale



Characteristics

The field of segment density is used to describe the system.



1. **Various polymer architecture**

   Homo, block, star, comb, ring, any types of topology, fixed sequence(tapered block)
2. **Off lattice mean field method**
3. **Enhanced SCF methods**

   Grand canonical dynamics, chemical Reaction, polyelectrolyte, etc.
4. **Open source software**

Characters of Components

1. Polymers

Any topologies,

Any sequences

Monomers

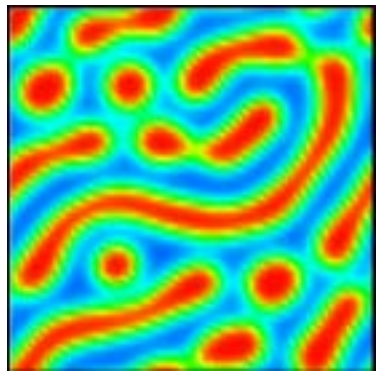
Specific volume,

Effective bond length,

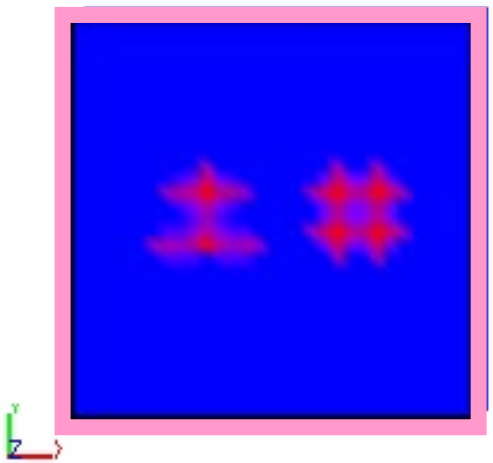
Electric charge

2. Solvents

Specific volume



Anti-symmetric block copolymer
$b_{eff\,A}=2$, $b_{eff\,B}=1$, $N_A=N_B=20$, $\chi_{AB}=0.4$,
System 64×64, A：red, B:blue



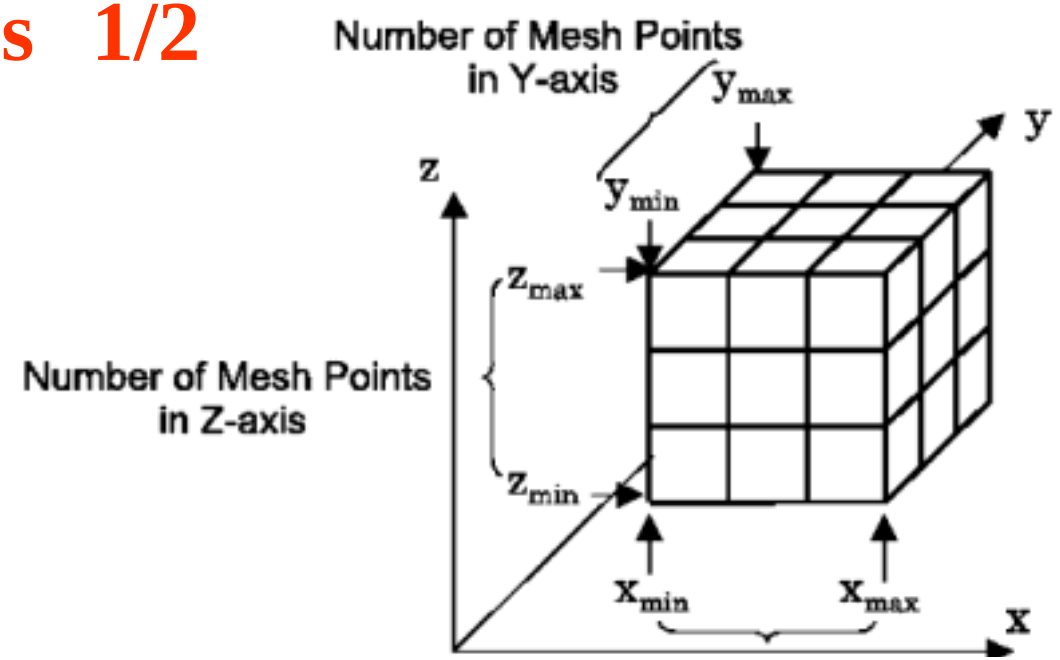
Polymers in solution

Meshes 1/2

1. Regular Mesh

One~three dimension

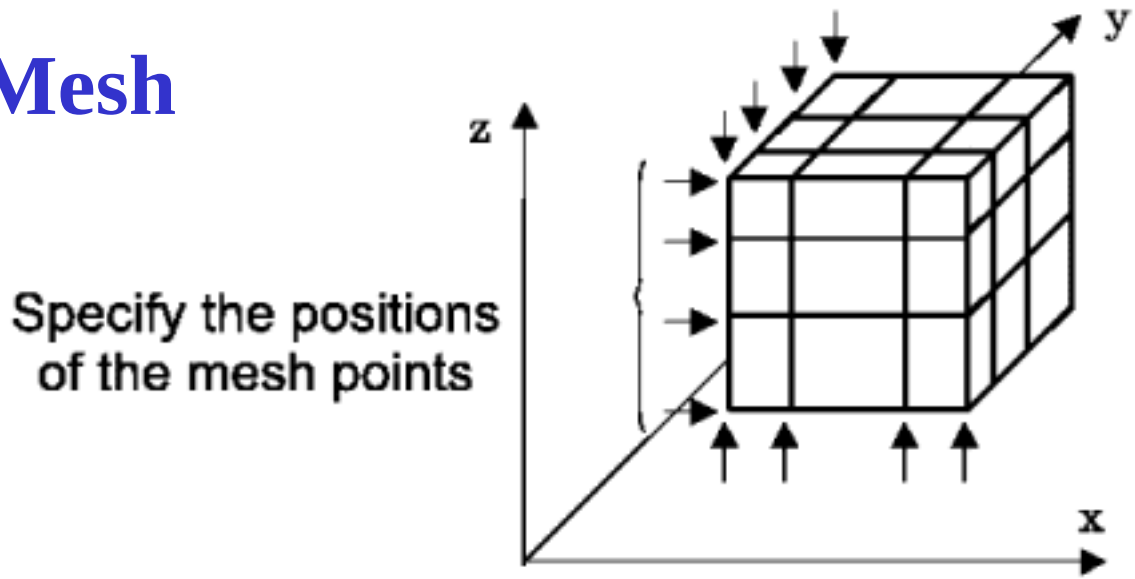
general purpose



2. Rectangular Mesh

One~three dimension

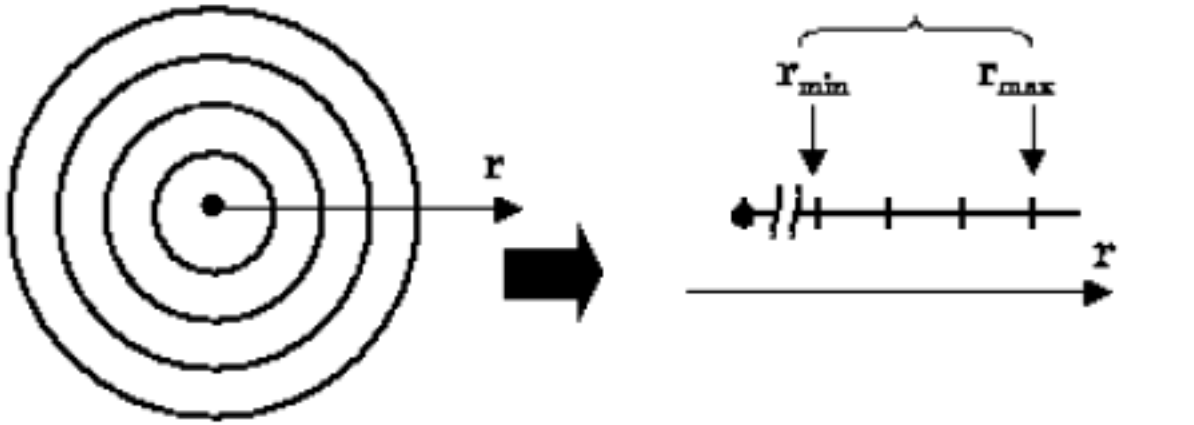
Interfaces



Meshes 2/2

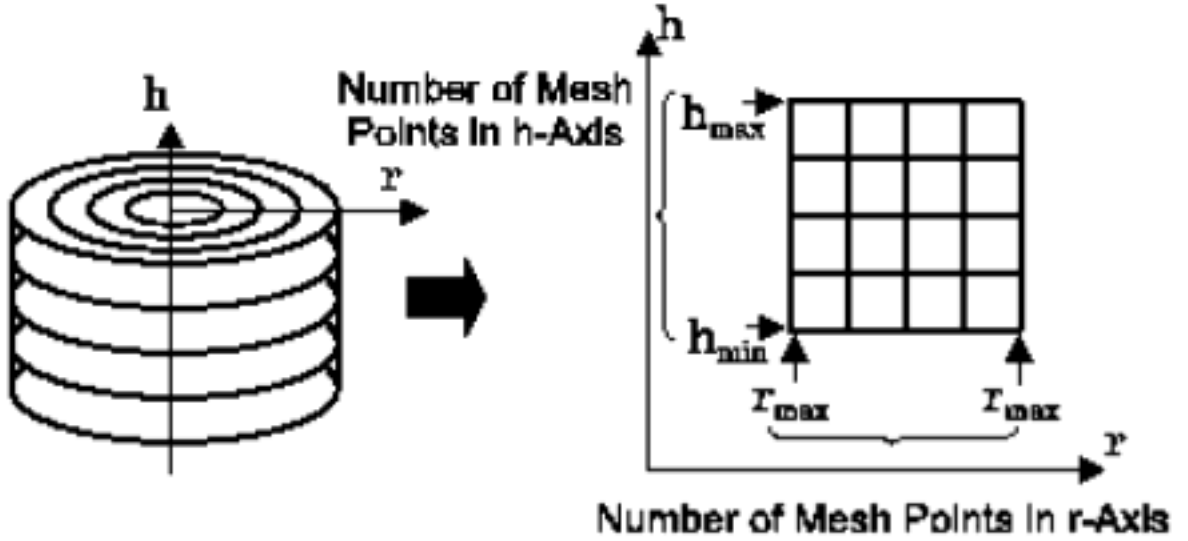
3. Circular Mesh

One dimension
Micelles



4. Cylindrical Mesh

Two dimension
Micelles,
vesicles,
mushrooms,
pancakes



Boundary conditions and Ensembles

Boundary Conditions

1. Periodic boundary condition

Infinite systems

2. Hard wall

Adsorptions, depletions, grafts

3. Reflective boundary condition

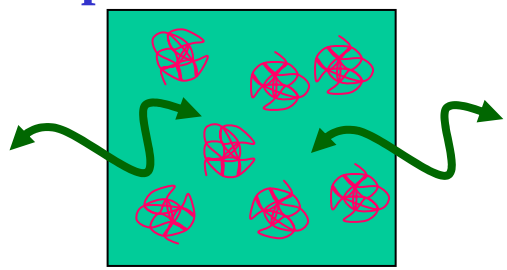
The boundaries for bulk systems

Ensembles

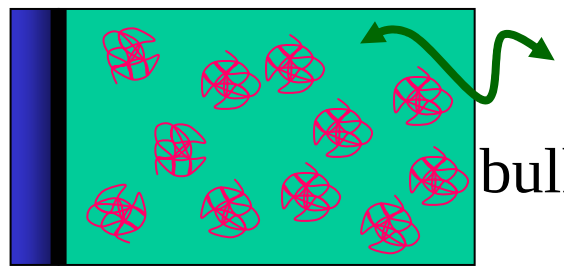
1. Canonical Ensemble

2. Grand canonical Ensemble

Examples



periodic system
canonical ensemble



wall reflective
grand canonical ensemble

Calculation methods

1. Static Equilibrium Calculation
   Calculates equilibrium states.

2. Dynamics Calculation
   Time dependent simulation of phase separation.

3. Monte Carlo Calculation
   Search for lower energy states
   (avoids being trapped in a local minimum)

Basic Equations

Edwards Equation for the Path Integral

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

Segment Density

$$\phi_K(\mathbf{r}) = C_K \sum_i \int d\mathbf{r}_0 \int d\mathbf{r}_{N_K} Q_K(0, \mathbf{r}_0; i, \mathbf{r}) Q_K(i, \mathbf{r}; N_K, \mathbf{r}_{N_K})$$

Canonical Ensemble

$$C_K = \frac{M_K}{\int d\mathbf{r}_0 \int d\mathbf{r}_{N_K} Q_K(0, \mathbf{r}_0; N_K, \mathbf{r}_{N_K})}$$

Grand Canonical Ensemble

$$C_K = \frac{\phi_K^{(\mathrm{bulk})}}{N_K} \exp\left[N_K (W_K^{(\mathrm{bulk})} + \mathrm{constant}) \right]$$

Segment Segment Interaction

$$W_K(\mathbf{r}) = \sum_{K'} \chi_{KK'} \phi_{K'}(\mathbf{r}),$$

M_K: total number of the chain in the system

Self Consistent Field

$$V_K(\mathbf{r}) = W_K(\mathbf{r}) - \frac{\delta F[\{\phi(\mathbf{r})\}]}{\delta \phi_K(\mathbf{r})}$$

Static Equilibrium Method

The segment interactions and chemical potentials are updated at each iteration.

$$V_K(\mathbf{r}) = W_K(\mathbf{r}) - \mu_K(\mathbf{r})$$

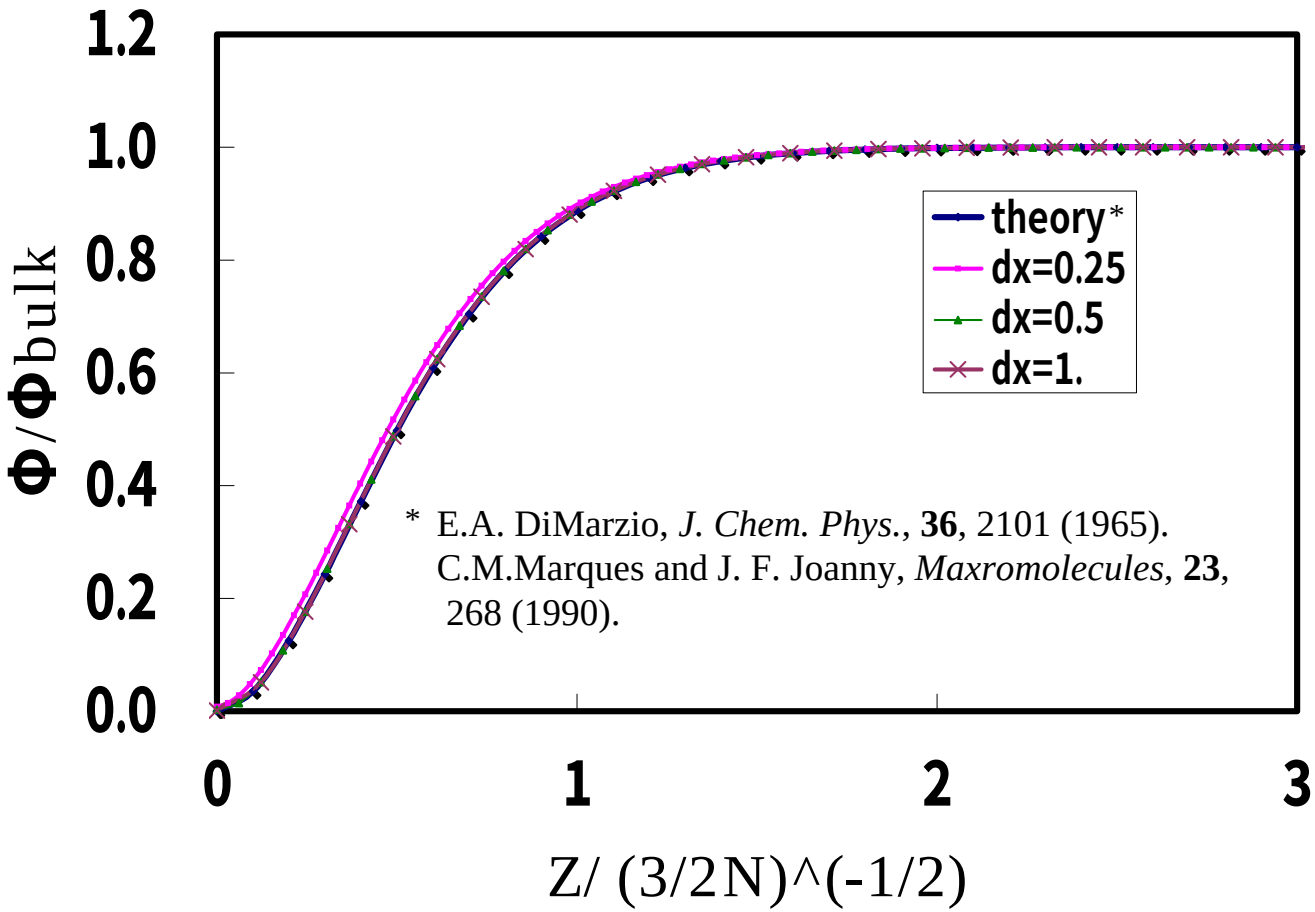
$$W_K(\mathbf{r}) \longrightarrow W_K(\mathbf{r}) + \mathrm{constW} \times \left(\sum_{K'} \chi_{KK'} \phi_{K'}(\mathbf{r}) - W_K(\mathbf{r}) \right)$$

$$\mu_K(\mathbf{r}) \longrightarrow \begin{cases} \mu_A(\mathbf{r}) - \mathrm{constV} \times \left(1 - \sum_{K'} \phi_{K'}(\mathbf{r}) \right) & \text{for } K = A \\ \mu_K(\mathbf{r}) - \mathrm{constV} \times \left(\mu_K(\mathbf{r}) - \mu_A(\mathbf{r}) \right) & \text{for } K \neq A \end{cases}$$

$$\chi_{KK'} = z\beta \left[\epsilon_{KK'} - \frac{1}{2}(\epsilon_{KK} + \epsilon_{K'K'}) \right]$$

Meshes
Off lattice model

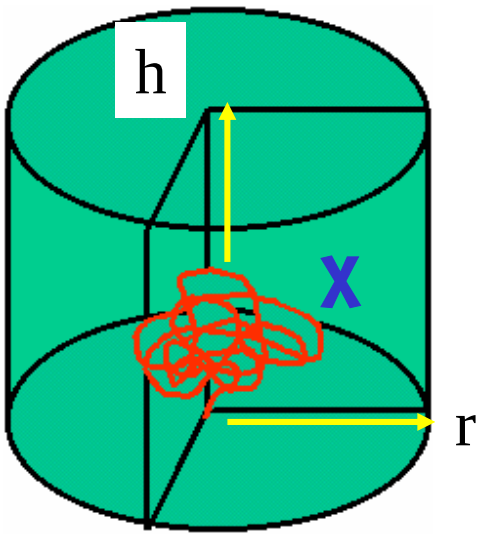
Depletion of polymer near solid wall in solution.
N=100, χ=0.5, Φ^{bulk}=0.001, dx=0.25, 0.5, and 1.



A polymer grafted to a wall
Mushroom

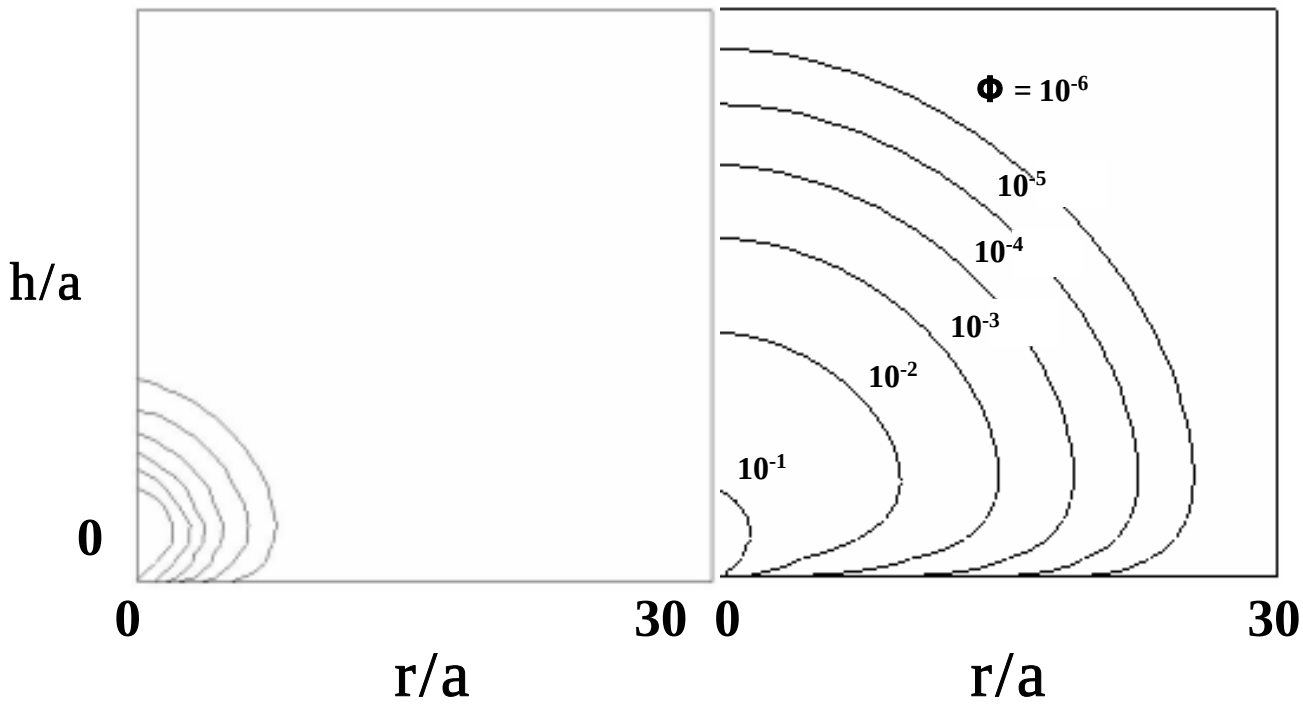
The mushroom shrinks with increasing χ.

Interaction parameter
χ_s polymer-wall = 0.
χ polymer-solvent



Shrunk mushroom
N=100, χ=1.5

Swollen mushroom
χ=0.25

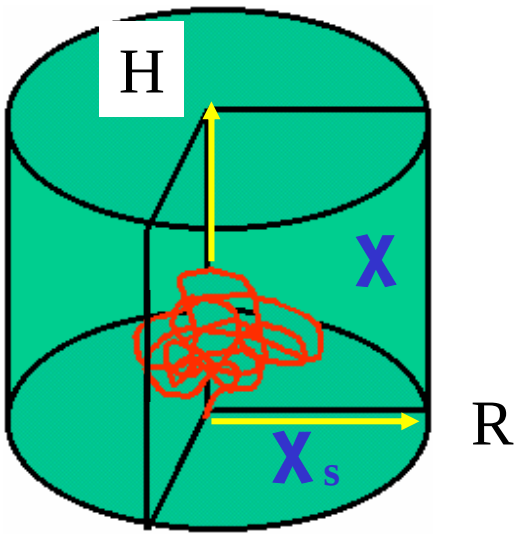


A polymer grafted to a wall
Mushrooms and Pancakes

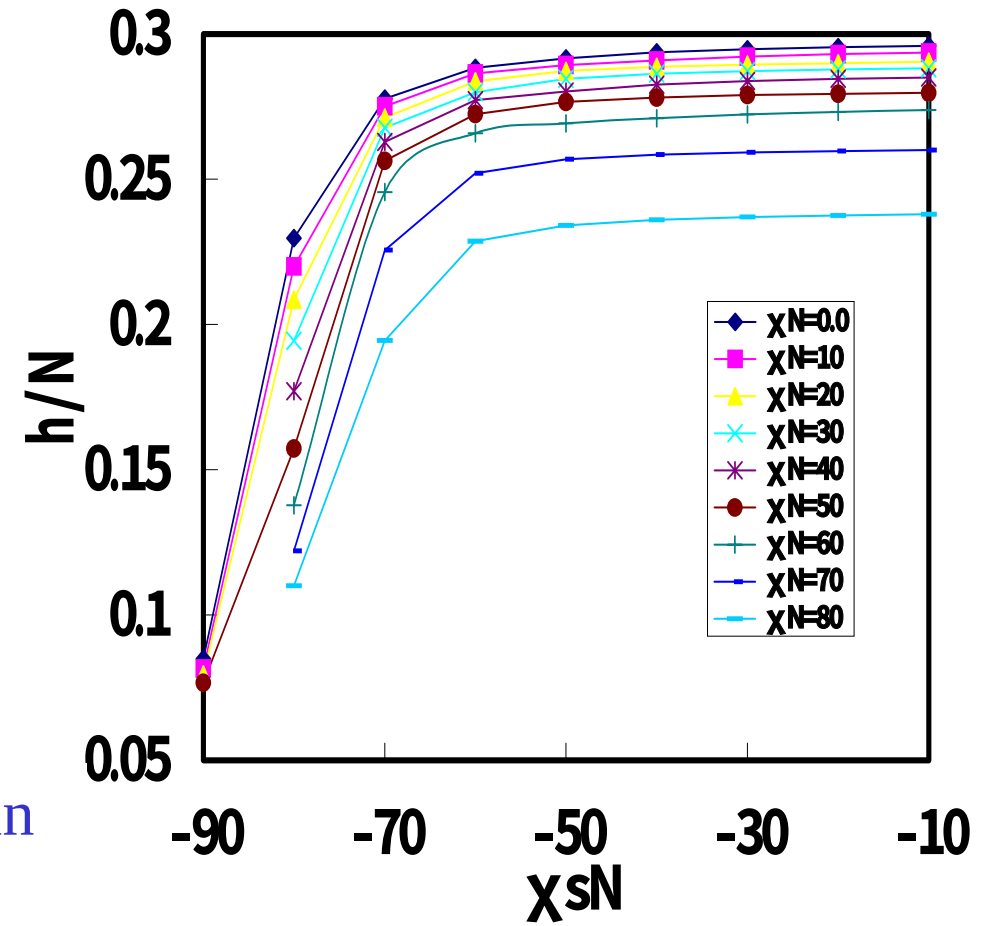
Changes from mushroom to pancake with decreasing surface chi parameter χ_s .

Interaction parameter
χ_s polymer-wall
χ polymer-solvent

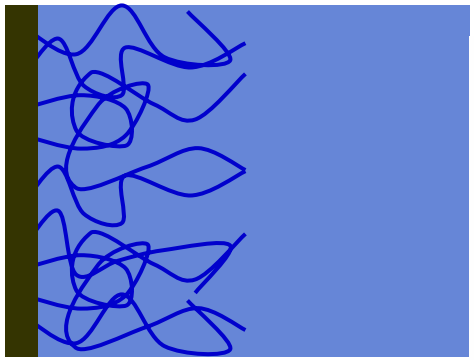
N=100



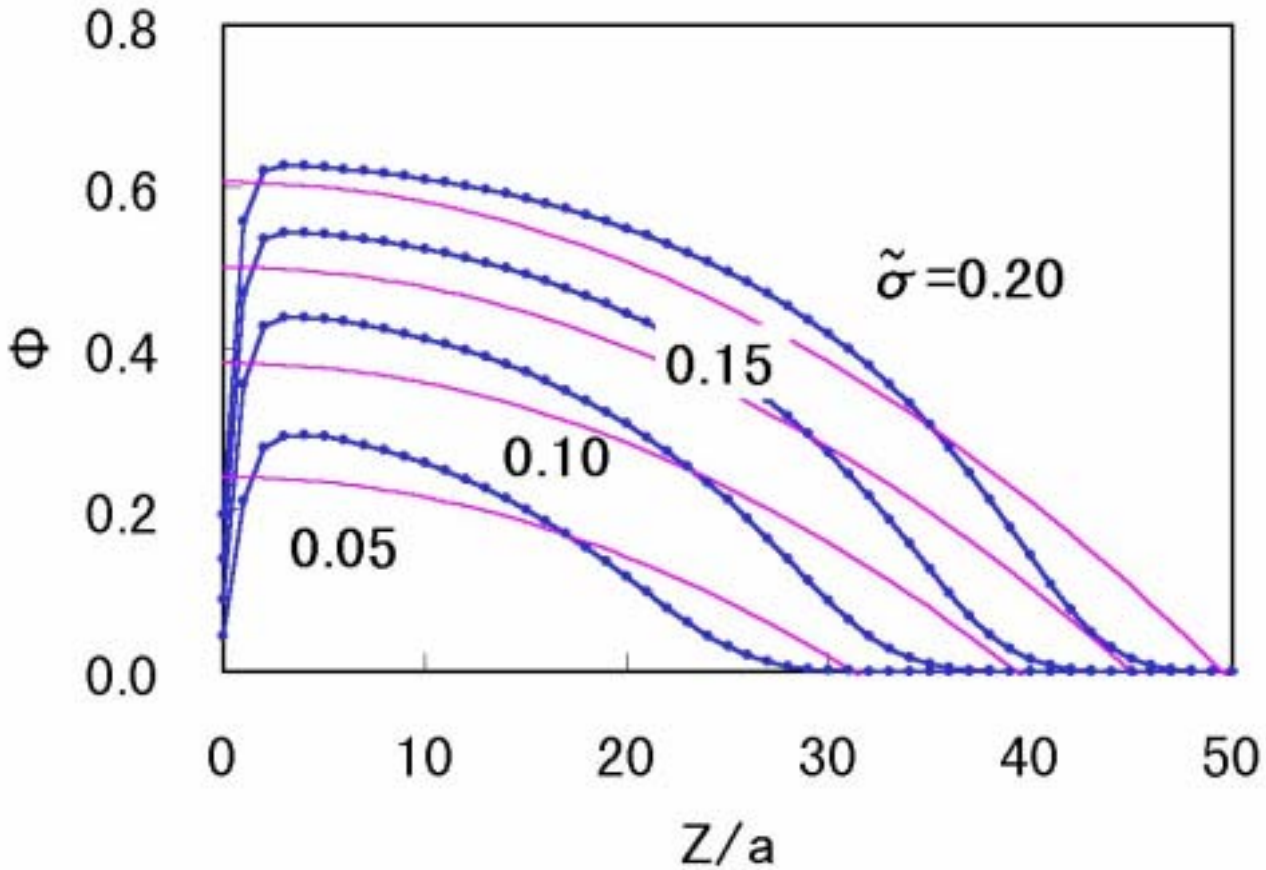
Single grafted polymer chain in cylindrical mesh system



Polymers grafted to a wall
Brushes



N=100,
χ=0.25



— Milner, Witten and Cates, *Europhys. Lett.*, **5**, 413 (1988)

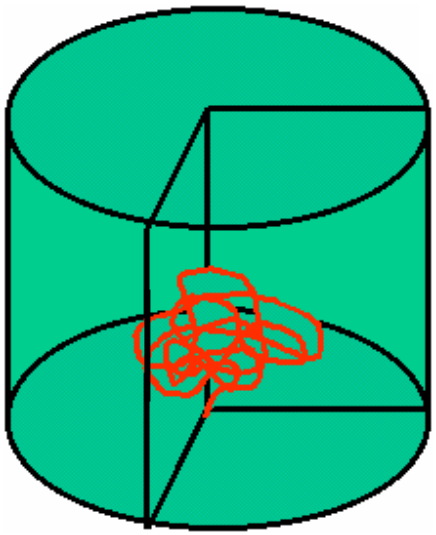
Polymers grafted to a wall
Mushrooms and Brushes

The grafted polymer should be considered as mushrooms and brush.

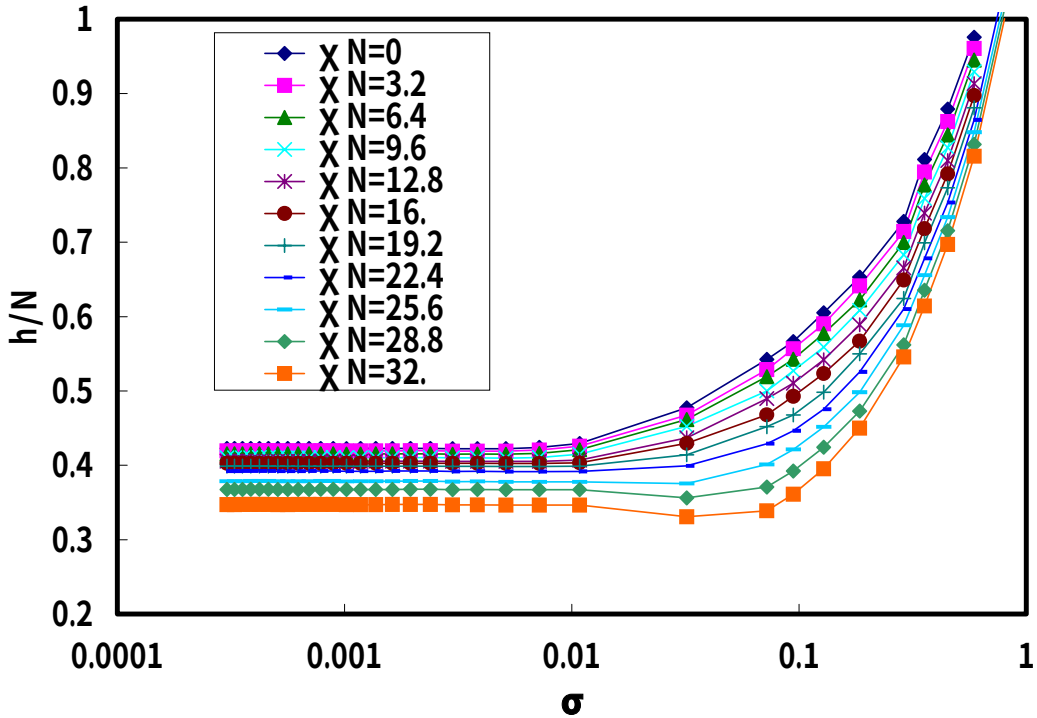
Interaction parameter

χ_s polymer-wall = 0.

χ polymer-solvent

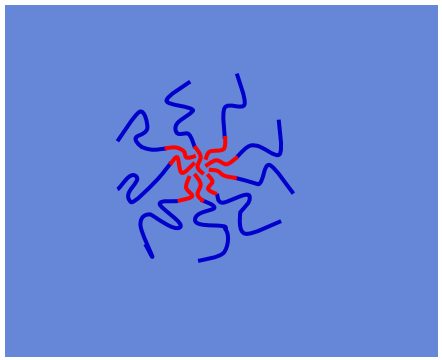


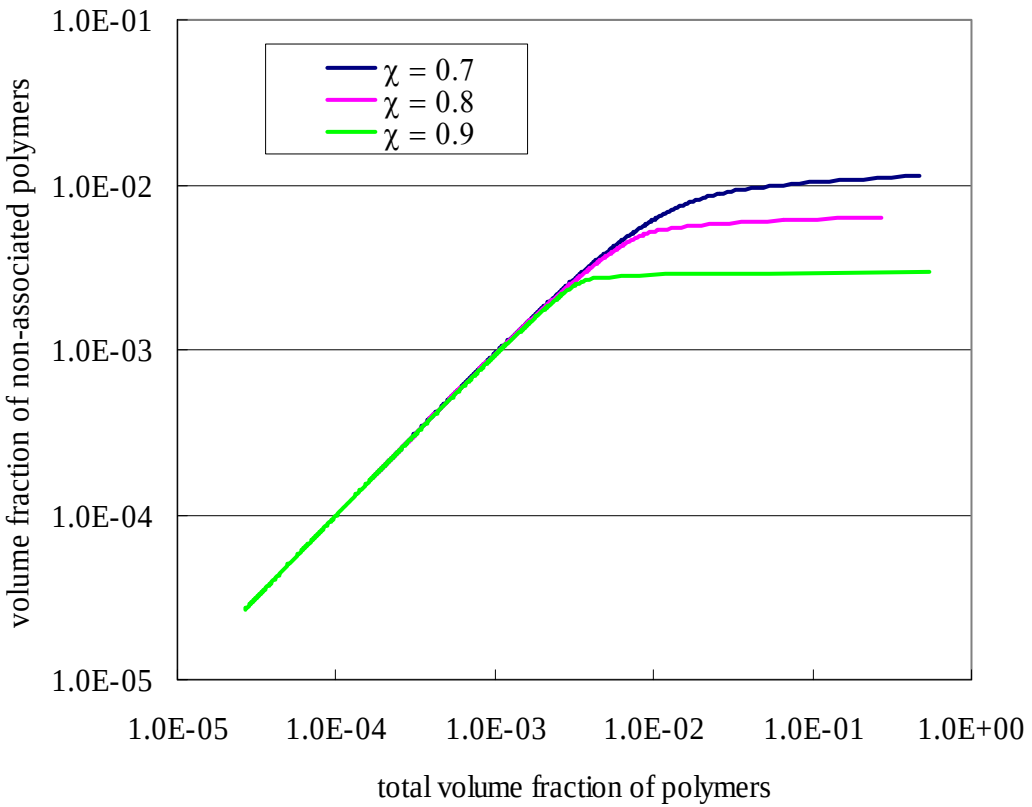
N=32



Result of the 3D system

Micelle
Associated polymer in solution





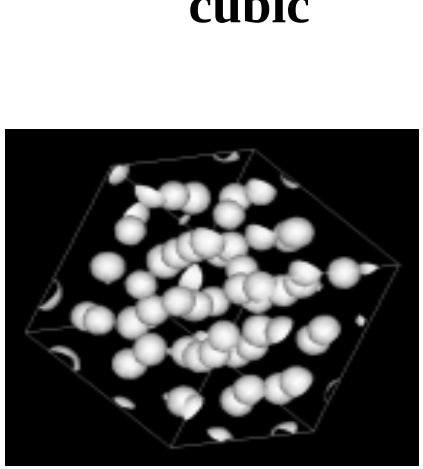
Volume fraction of non-associated A10B20 block copolymers as a function of total volume fraction of block copolymers. Monomeric solvent C is selective for B block. Interaction parameters are chosen as $\chi_{AB}= \chi_{AC}$ =2.0 and χ_{BC} =χ is changed from 0.7 to 0.9.

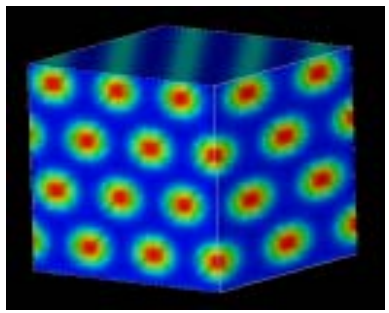
Block copolymer typical structures

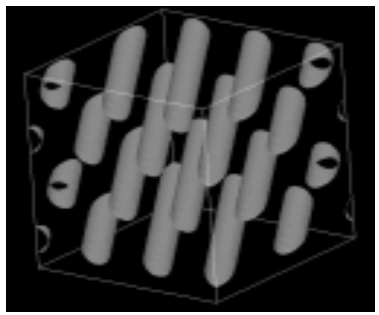
hexagonal

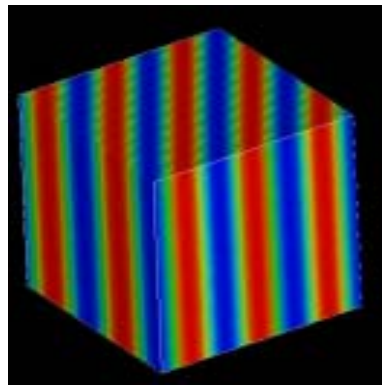
cubic

lamellar









f=0.225

f=0.5

N=40，χN=20，32^3

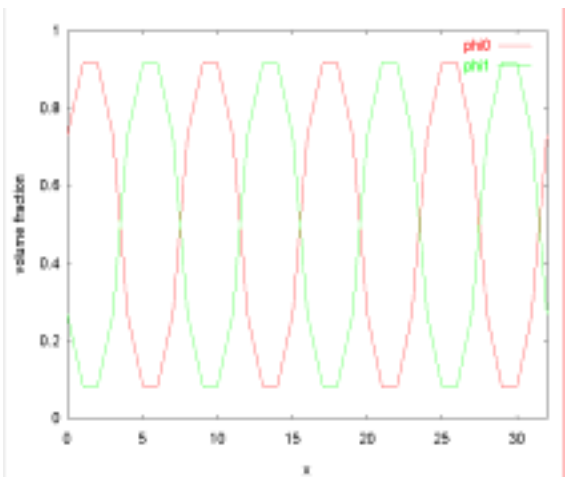
f=0.25

Block copolymer typical structures 1/2

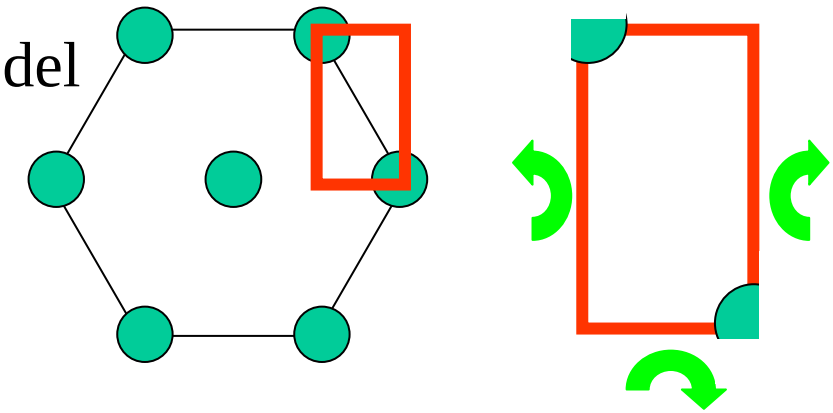
Good initial guess of Self-Consistent Field is required to obtain the morphology at the global minimum of free energy.

Lamellar model

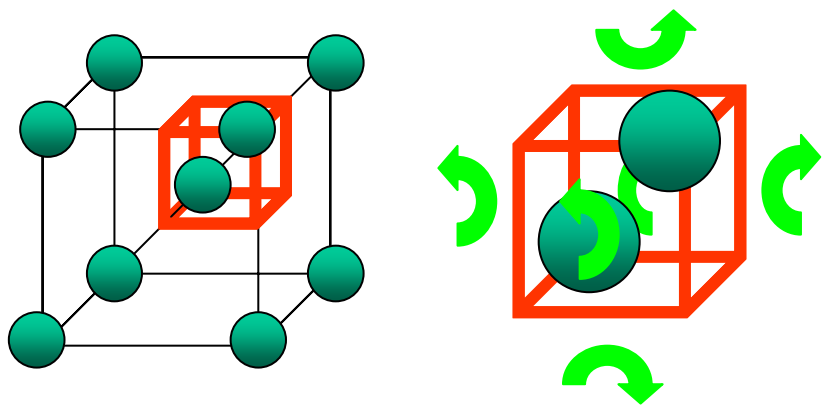
One dimensional calculation



Cylinder model



Cubic model



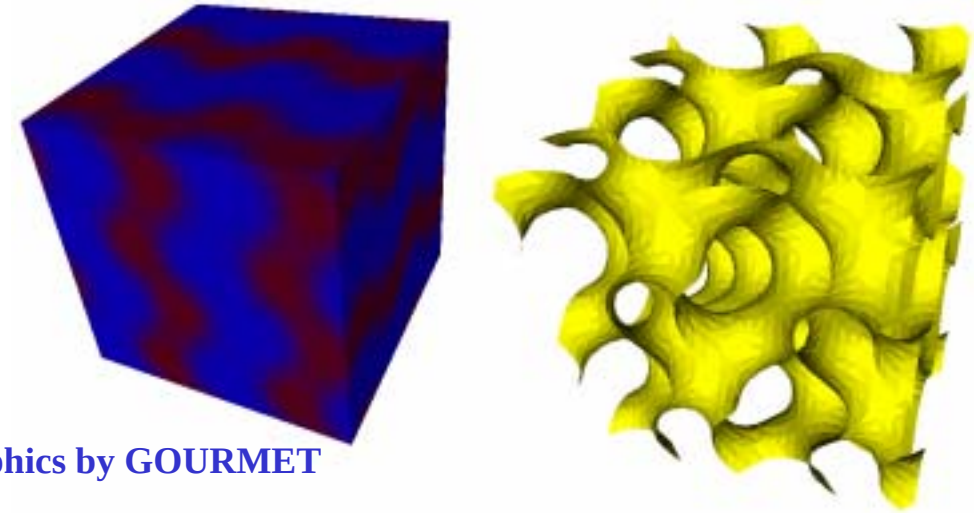
Block copolymer typical structures 2/2

Gyroid model

Using triply periodic level surface for initial V.

V = c (cos x * sin y +
sos y * sin z +
cos z * sin x)
c: scale factor

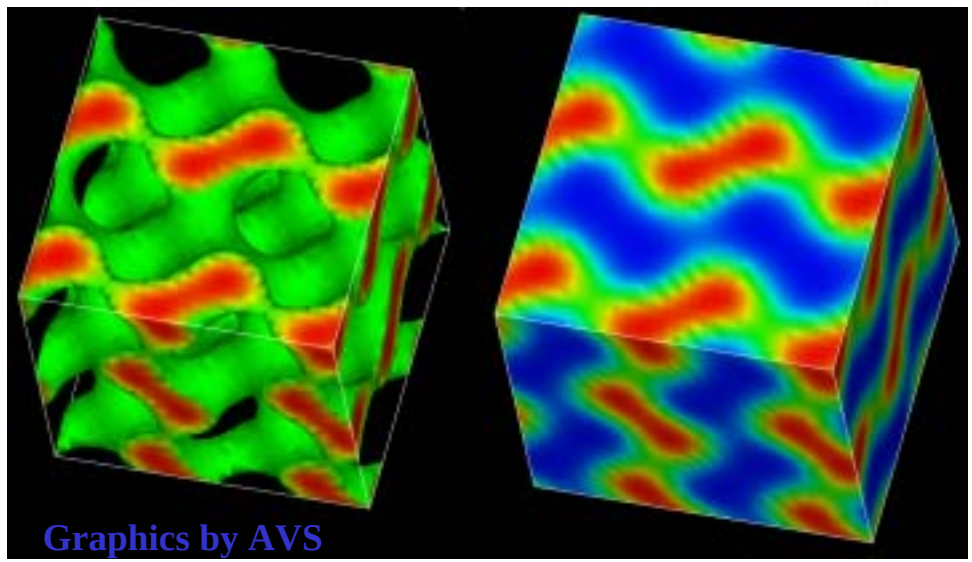
http://www.msri.org/publications/sgp



Graphics by GOURMET

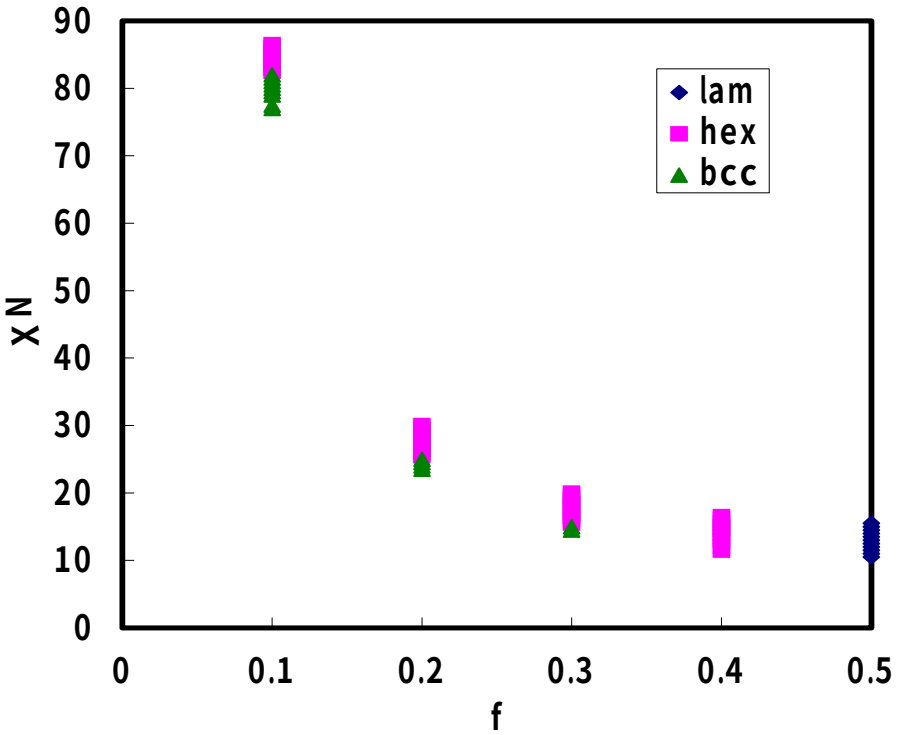
Simulation Result

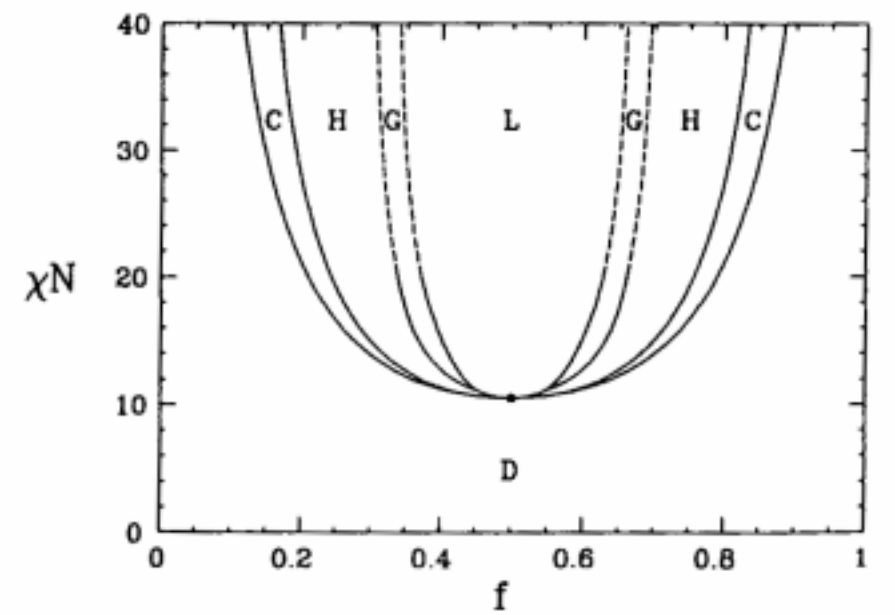
N=30, f=0.4, χN=14,
System size = 32^3



Graphics by AVS

Block copolymer
Phase diagram





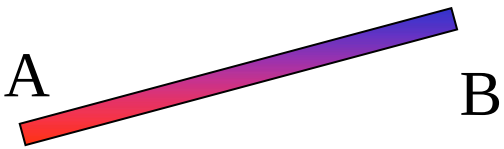
Calculated by optimizing lattice constants

Matsen **&** Schick
Phy. Rev. Lett. , **72,** 2660 (1994) .

Tapered polymer
Multi-State Path Integral

Path integral equations for K-th type monomers

$$Q_K(s+ds,\mathbf{r}) = \exp\left[-\beta r_K V_K(\mathbf{r})ds/2\right] \sum_{K'} T_{KK'}(s)\left(1+\frac{b_{K'}^2}{6}\nabla^2 ds\right) \left(\exp\left[-\beta r_{K'} V_{K'}(\mathbf{r})ds/2\right] Q_{K'}(s,\mathbf{r})\right)$$



Sum of the path integrals

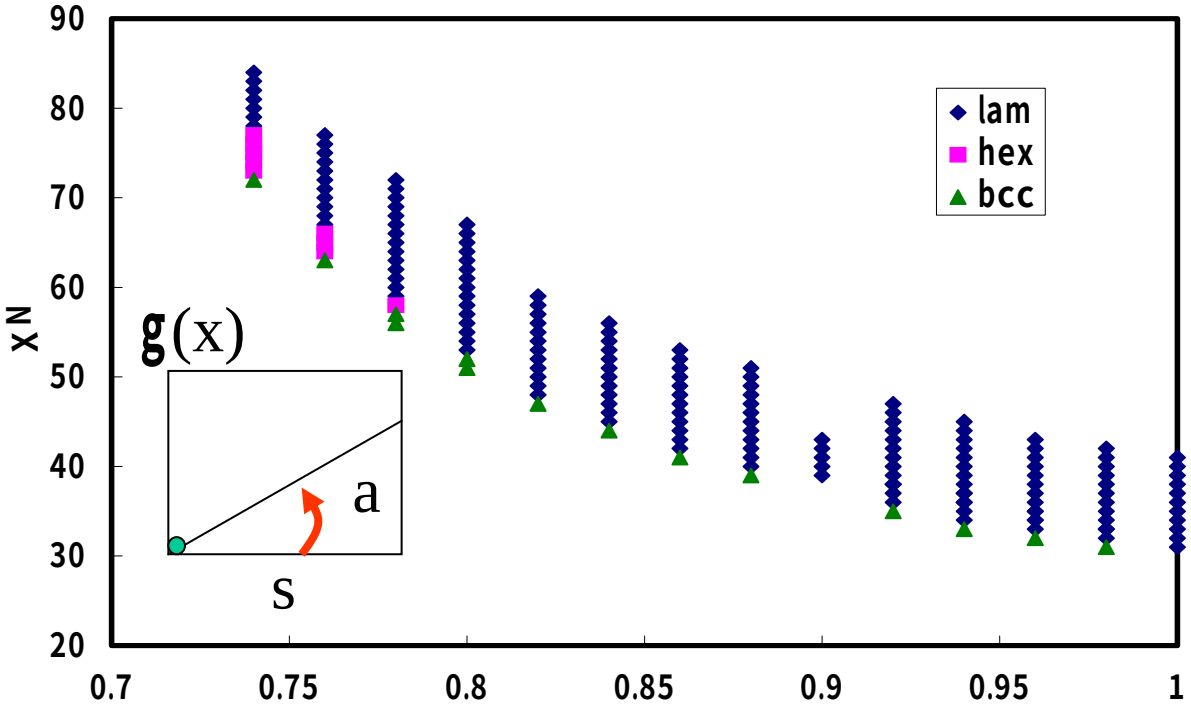
$$Q(s,\mathbf{r}) = \sum_K Q_K(s,\mathbf{r})$$

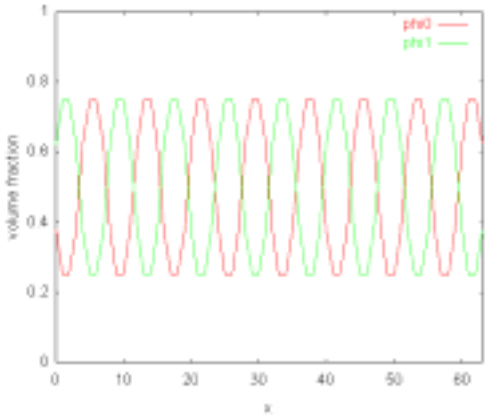
Volume fraction of K-th type segment

$$\phi_K(\mathbf{r}) = M_n \frac{\int ds Q(s,\mathbf{r})\tilde{Q}(N-s,\mathbf{r})g_K(s)}{\int d\mathbf{r}_N Q(N,\mathbf{r}_N)}$$

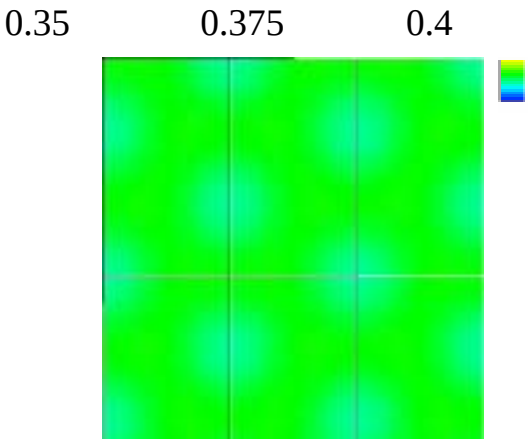
G.J.Fleer et al. "Polymers at Interfaces", Chapman & Hall (1993)

Tapered polymer

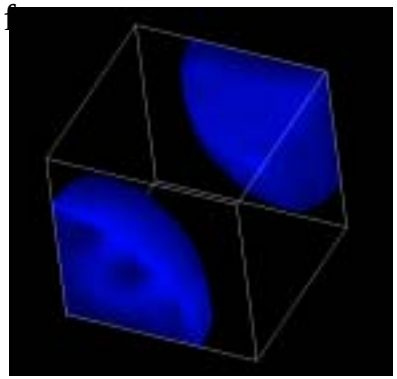




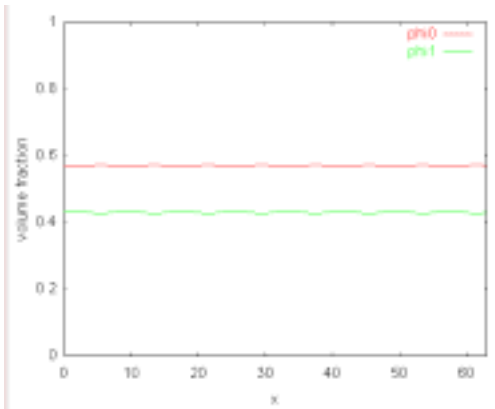
a=1.00, χN=44



a=0.78, χN=58, 18×18・3 $^{1/2}$



a=0.78, χN=57, 5^3



a=0.86, χN=44

Strong polyelectrolyte

A polymer solution in which almost all the ionizable atomic groups are ionized.

SCF method

Total charge distribution is calculated by the charge density ρ_K of the segment.

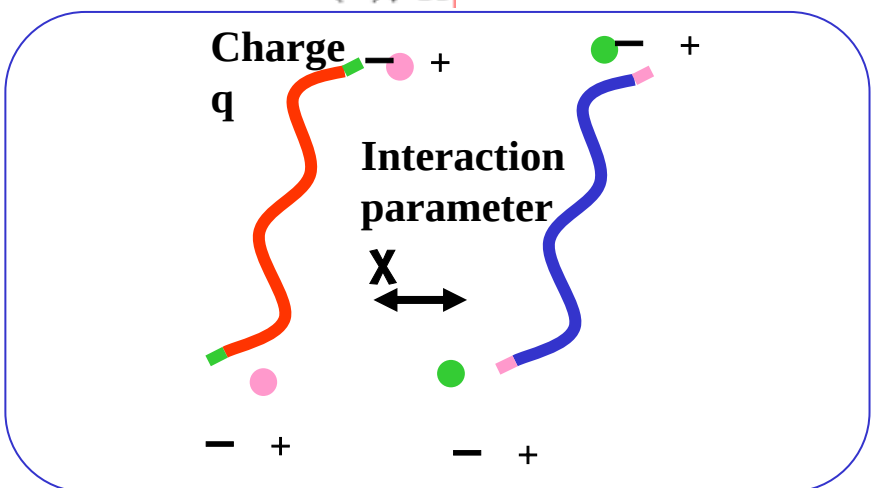
$$\rho(\mathbf{r}) = \sum_K \rho_K \phi_K(\mathbf{r})$$

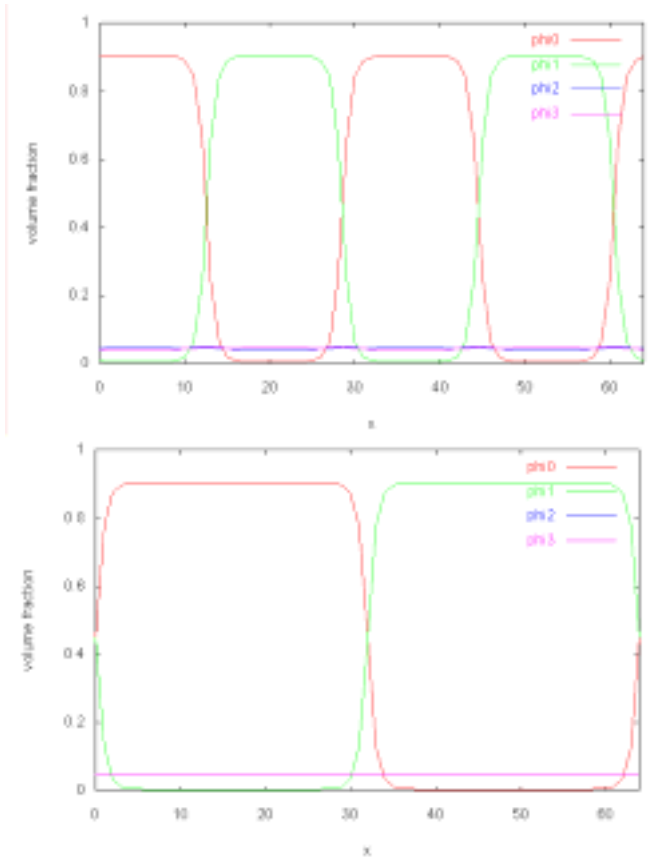
Solve the Poisson equation

$$\nabla^2 U(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{\epsilon}.$$

Add this electrostatic potential to V_k.

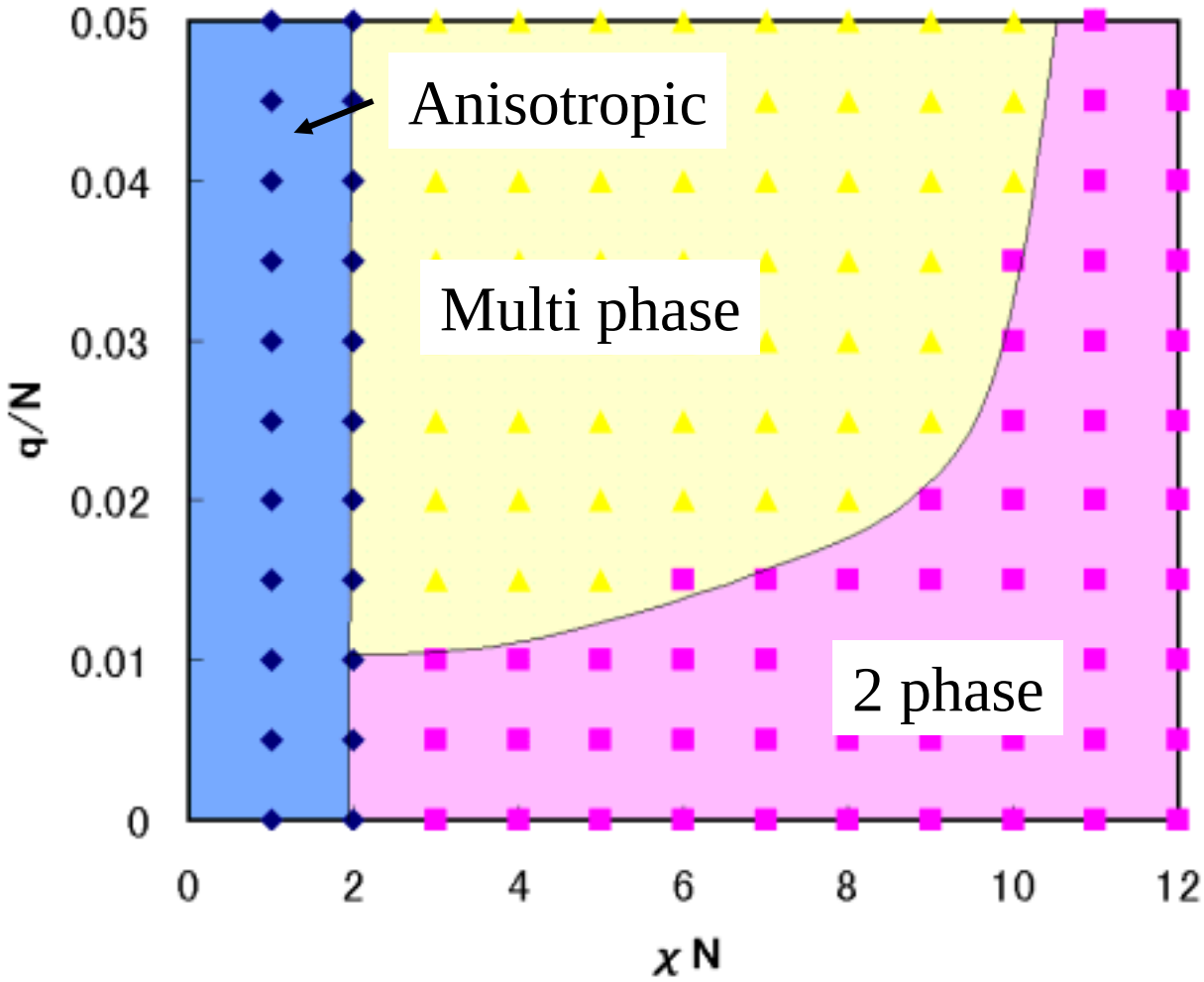
$$U(\mathbf{r})\rho_K$$





Strong polyelectrolyte

Phase diagram of polyelectrolyte blend; ions are located at each end of polymers.



Dynamics Simulation

Diffusion Equation

$$\mu_K(\mathbf{r}) = -V_K(\mathbf{r}) + \sum_{K'} \epsilon_{KK'}\phi_{K'}(\mathbf{r}) = -V_K(\mathbf{r}) + W_K(\mathbf{r})$$

$$\frac{\partial}{\partial t}\phi_K(\mathbf{r},t) = \nabla[L_K(\mathbf{r},t)\nabla\{\mu_K(\mathbf{r},t) + \lambda(\mathbf{r},t)\}]$$

$L_K(\mathbf{r},t)$: mobility coefficient

Rouse Dynamics condition

$$L_K(\mathbf{r},t) = L_0\phi_K(\mathbf{r},t)$$

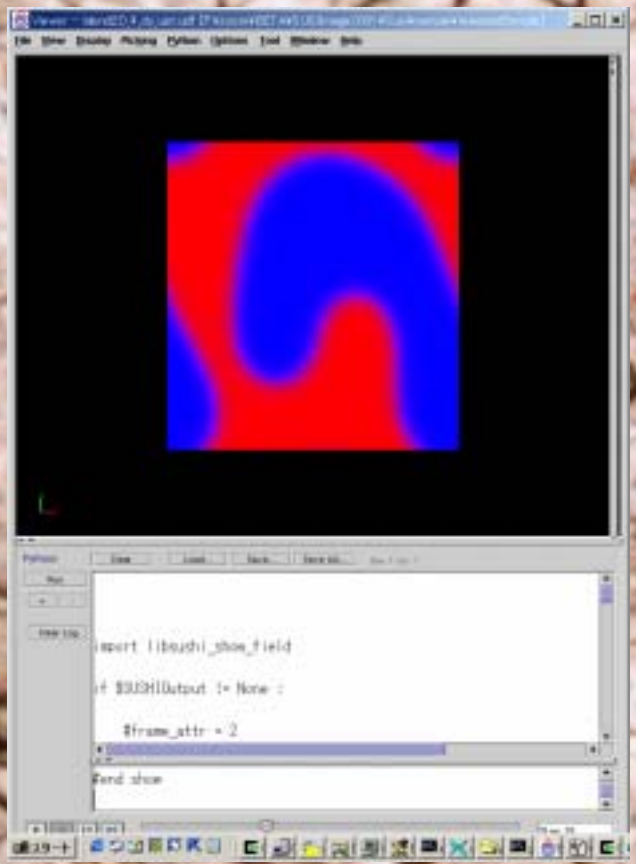
Reptation Dynamics condition

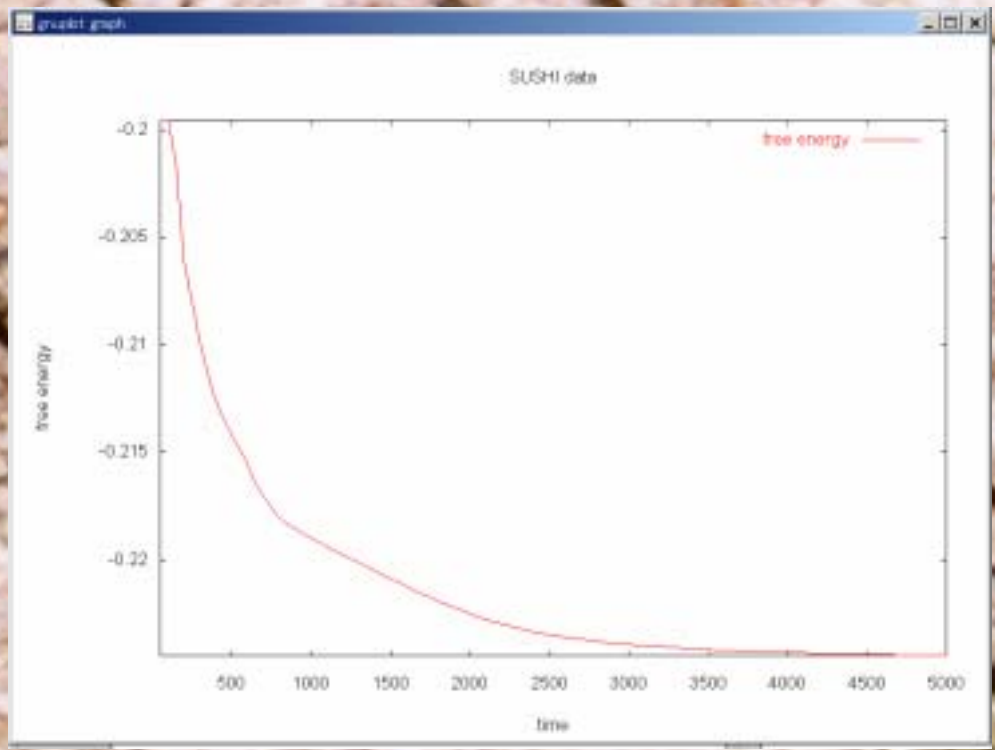
$$L_K(\mathbf{r},t) = \frac{L_0}{N^{(total)}}\phi_K(\mathbf{r},t)$$

$N^{(total)}$ is the total number of segments in the chain.

$\lambda(\mathbf{r},t)$: Lagrange multiplier for the local incompressibility condition

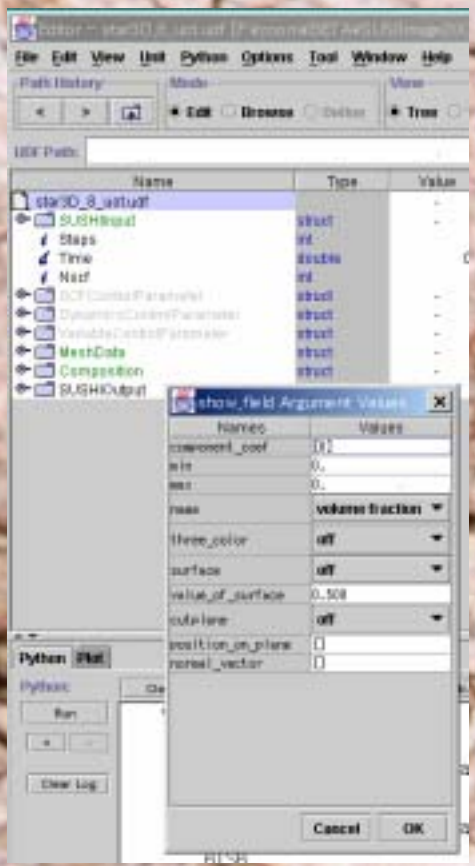
Dynamics Simulation

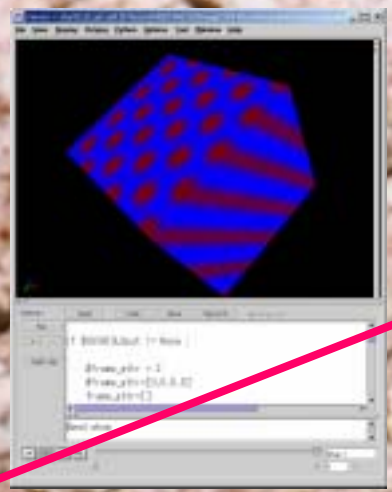


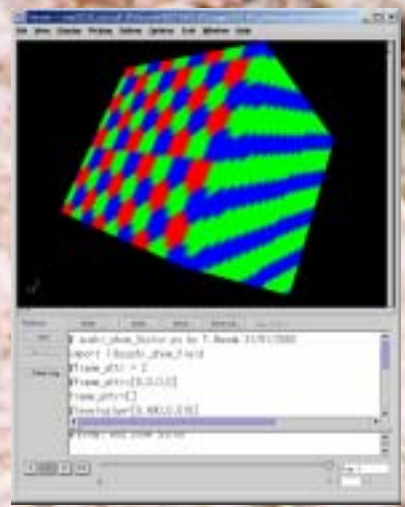


Dynamics Simulation

Star polymer and analysis by GOURMET





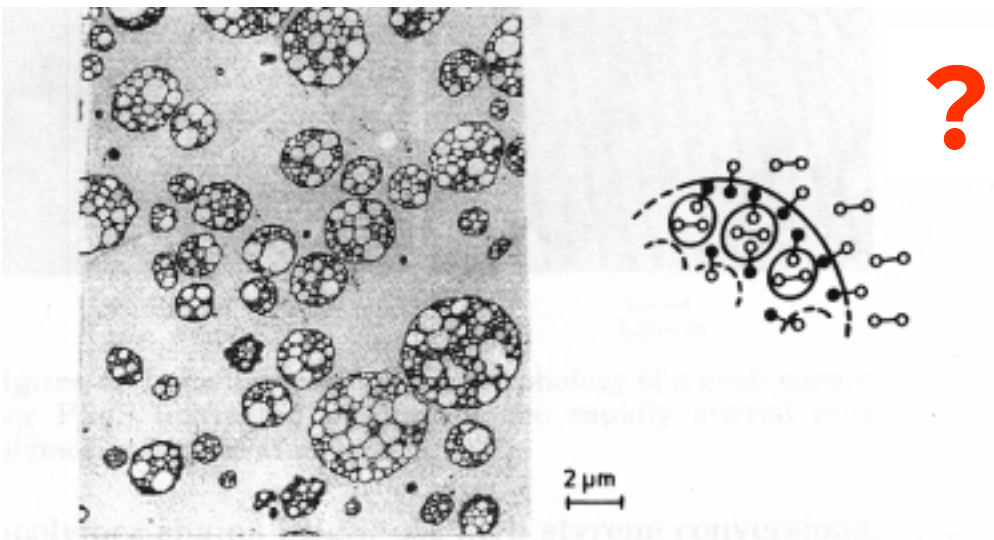


Reaction induced phase separation

HIPS

GOAL

HIPS (High-Impact-Modified Polystyrene)



?

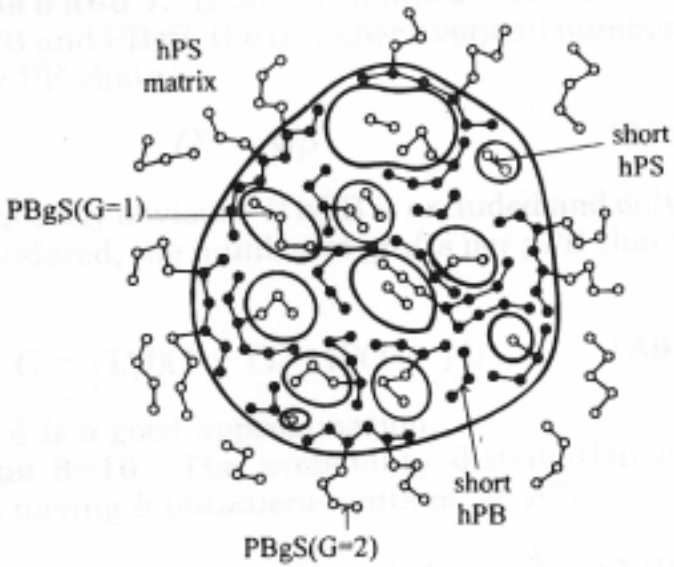
Figure 1. Salami structures in commercial HIPS (from BASF AG), made of PS (○–○) and the graft copolymer PBgS (●–○) (In all electron micrographs of this paper: (black) butadiene, (white) styrene phases.)

Fischer and Hellman, Macromolecules **29**, 2498 (1996)

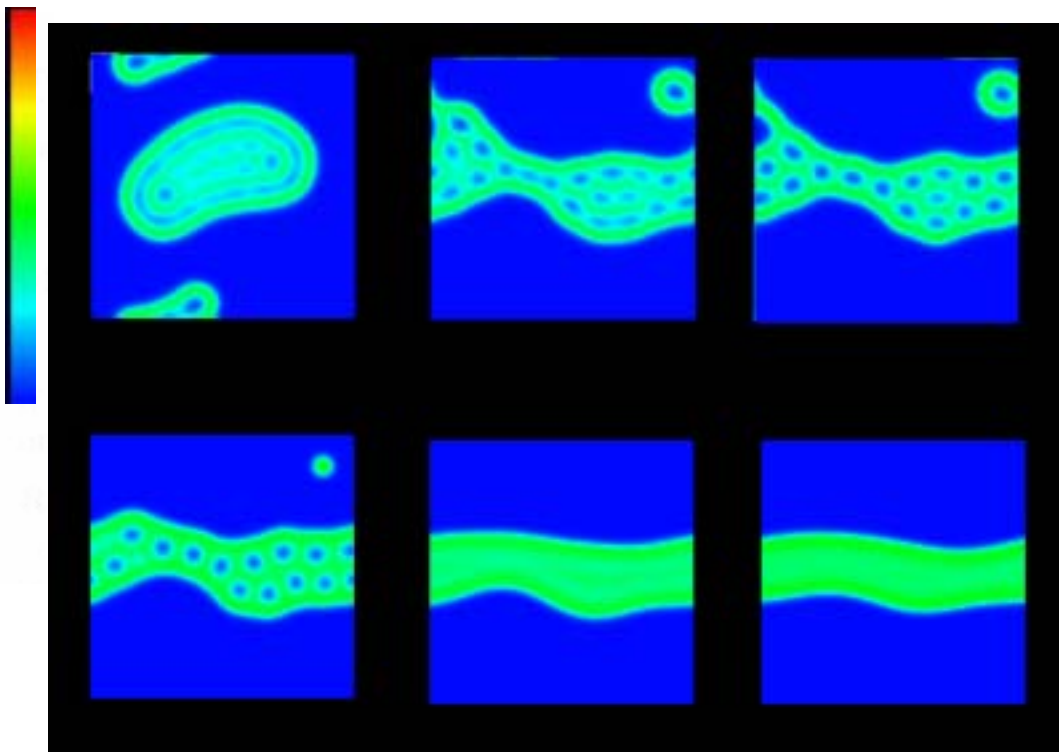
Reaction induced phase separation

HIPS

Morphology of mixed PS, grafted PBs and S

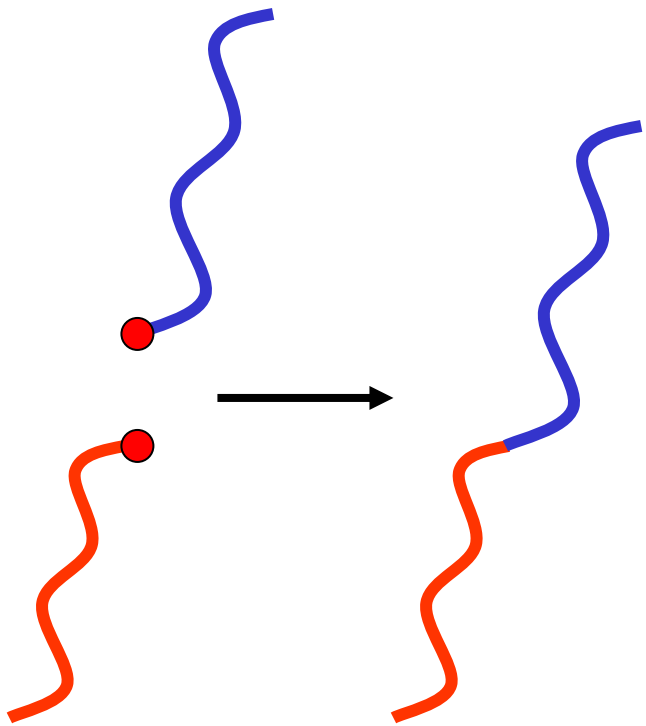


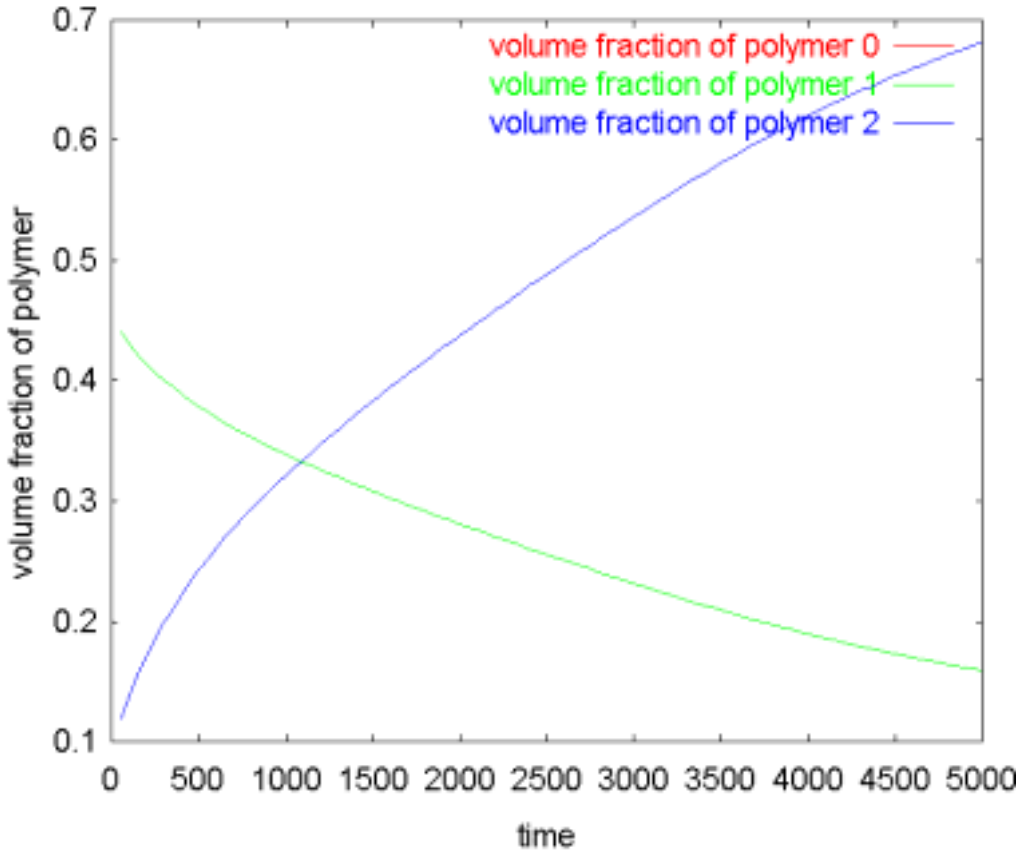
Model of Salami Domain by
Fischer and Hellman



Block copolymer creation

a block copolymer was created by a reaction of A and B polymers at their ends.

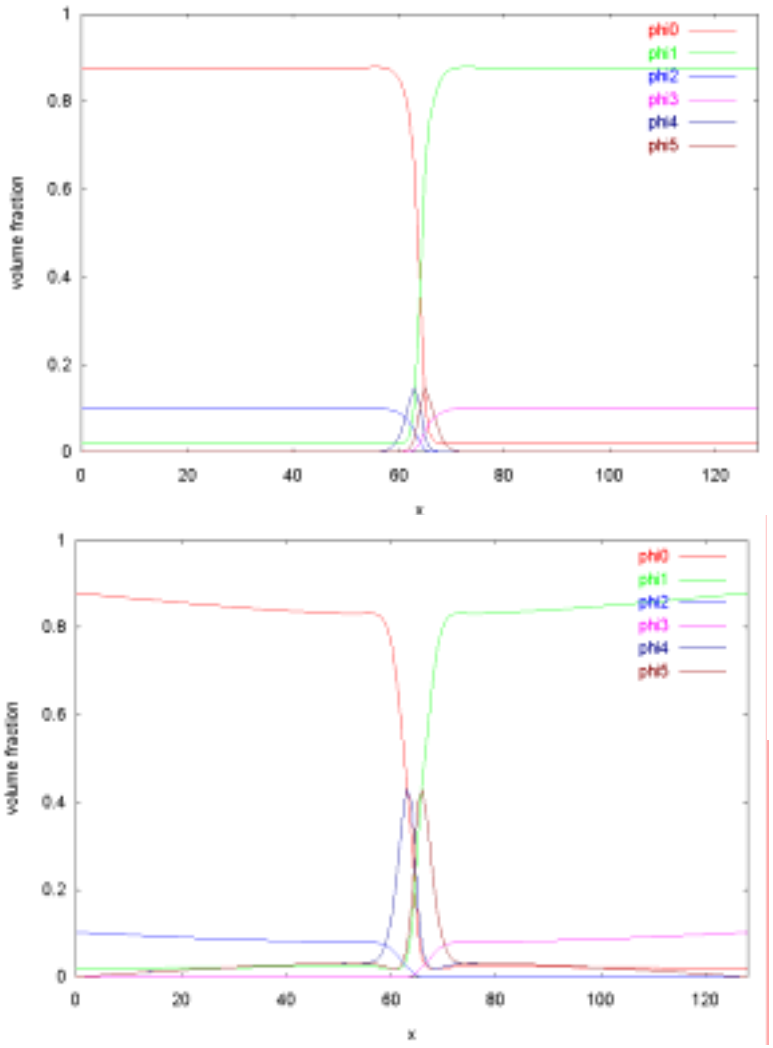




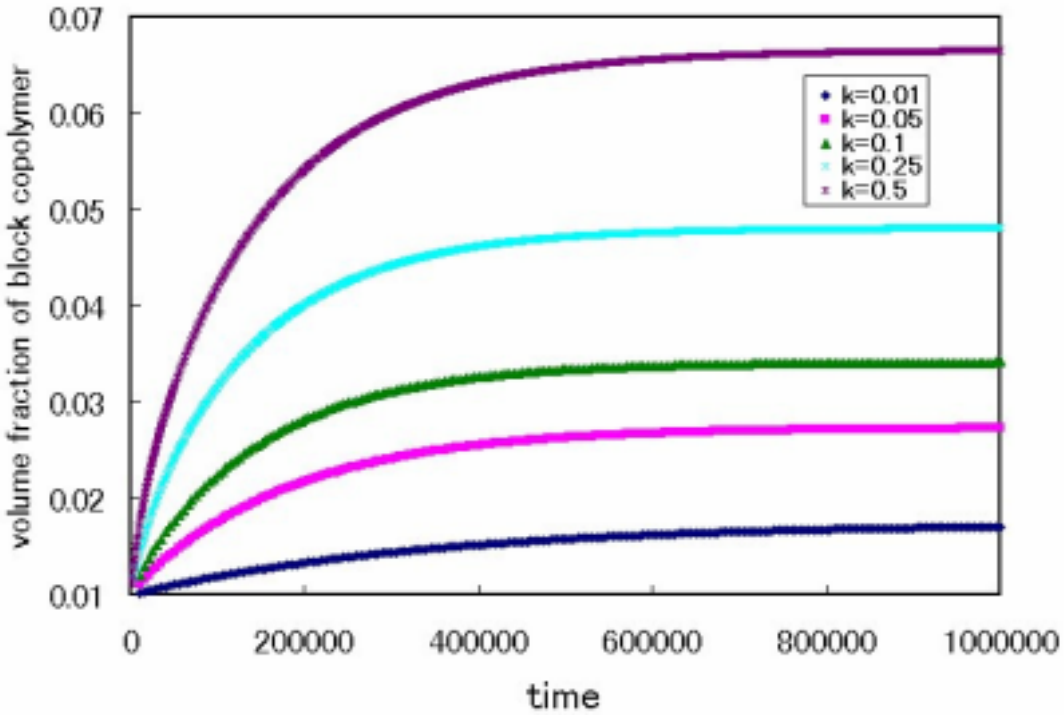
Active site reaction

The volume fraction of active group was calculated by SCF

Block copolymer creation at interface

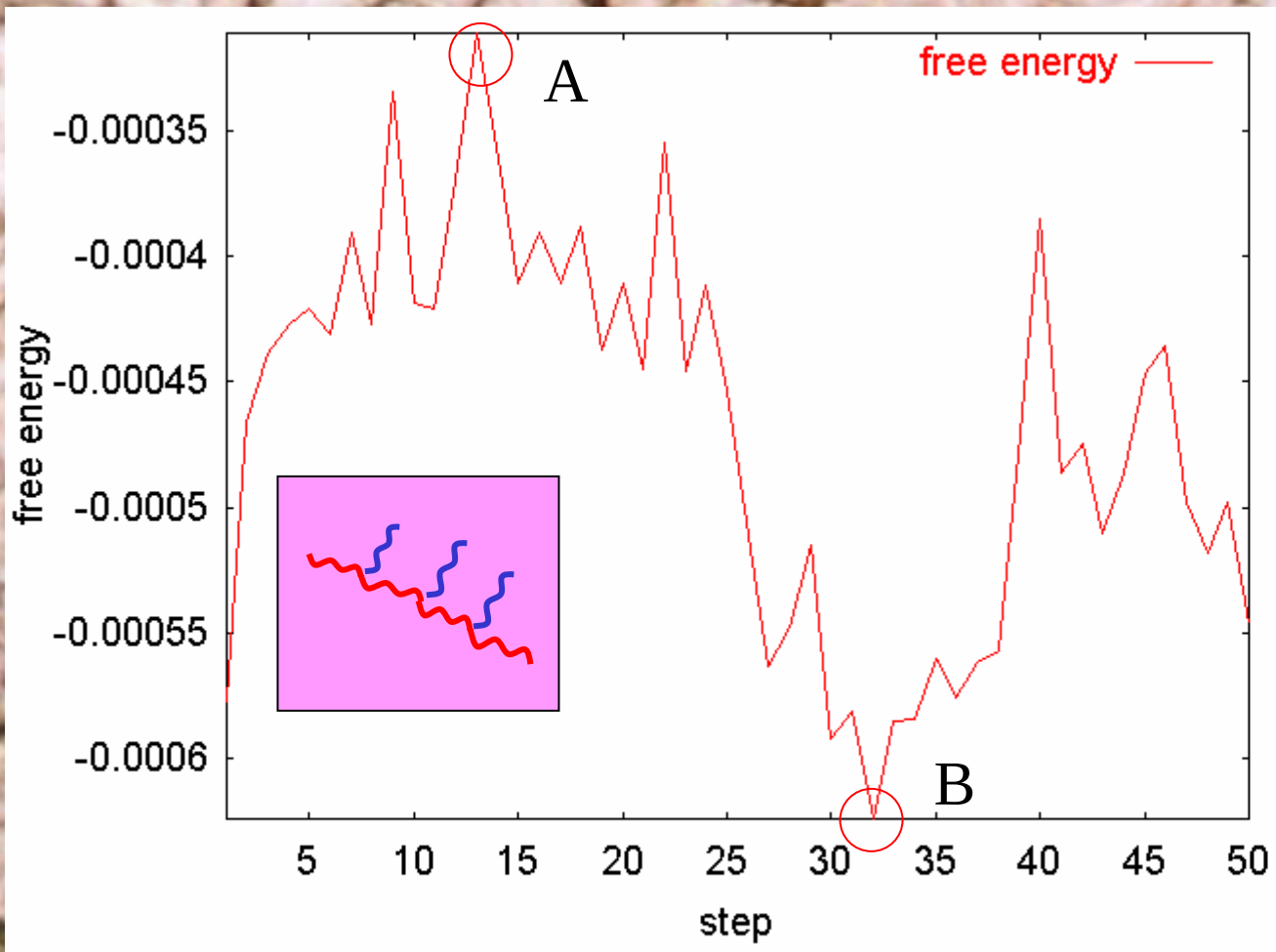


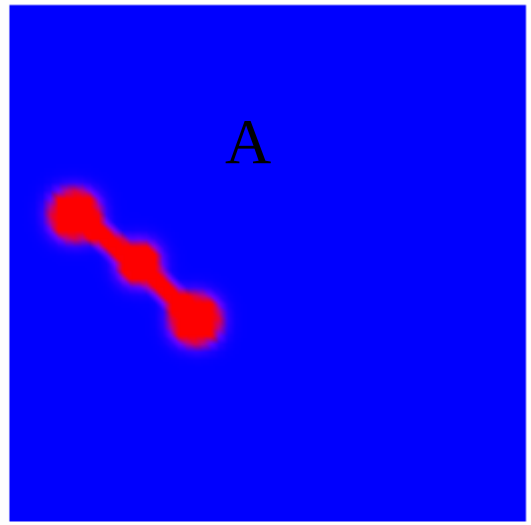
Matrix polymer: $N_A=N_B=10$, reactrive and block copolymer: $N_A=N_B=20$, $\chi_{AB}=0.4$, $\Phi_{block\_initial}=0.01$

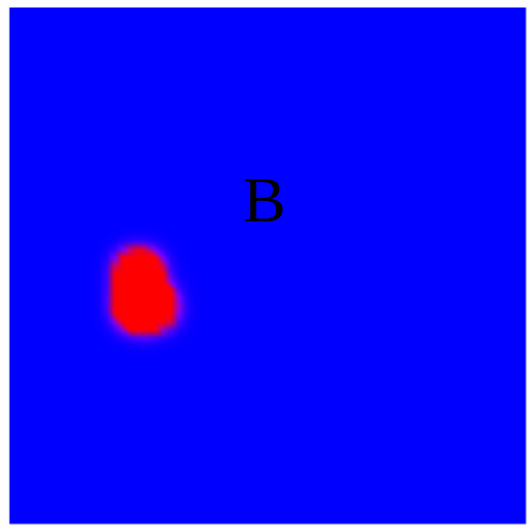


Monte Carlo simulation

The method to study an isolated chain in a dilute solution or a single chain in a many chain system.







Linking to other layers

Morphology

MUFFIN

χ parameters

SUSHI

PASTA

COGNAC

Multi-phase structure,
Interaction parameters

Summary

- SUSHI is a general purpose simulator of meso-scale structures in polymeric materials.
- SUSHI has many functions and there is an infinite variety of systems by combining the functions.
- An open source software written in C++ ; there are no restrictions to use SUSHI for your research.

We hope that SUSHI will be a useful tool for your research.

Acknowledgement

This work is supported by the national project, which has been entrusted to the Japan Chemical Innovation Institute (JCII) by the New Energy and Industrial Technology Development Organization (NEDO) under METI's Program for the Scientific Technology Development for Industries that Creates New Industries.