Advanced Institute for
Materials Research
Tohoku University

MS GH-0-19 (11:00-13:00)
Phase field method and applications in biology and materials science
ICIAM2019, 19th July 2019, Valencia

From Janus to Ashura
-A hierarchical structure of nanopolymer particles-

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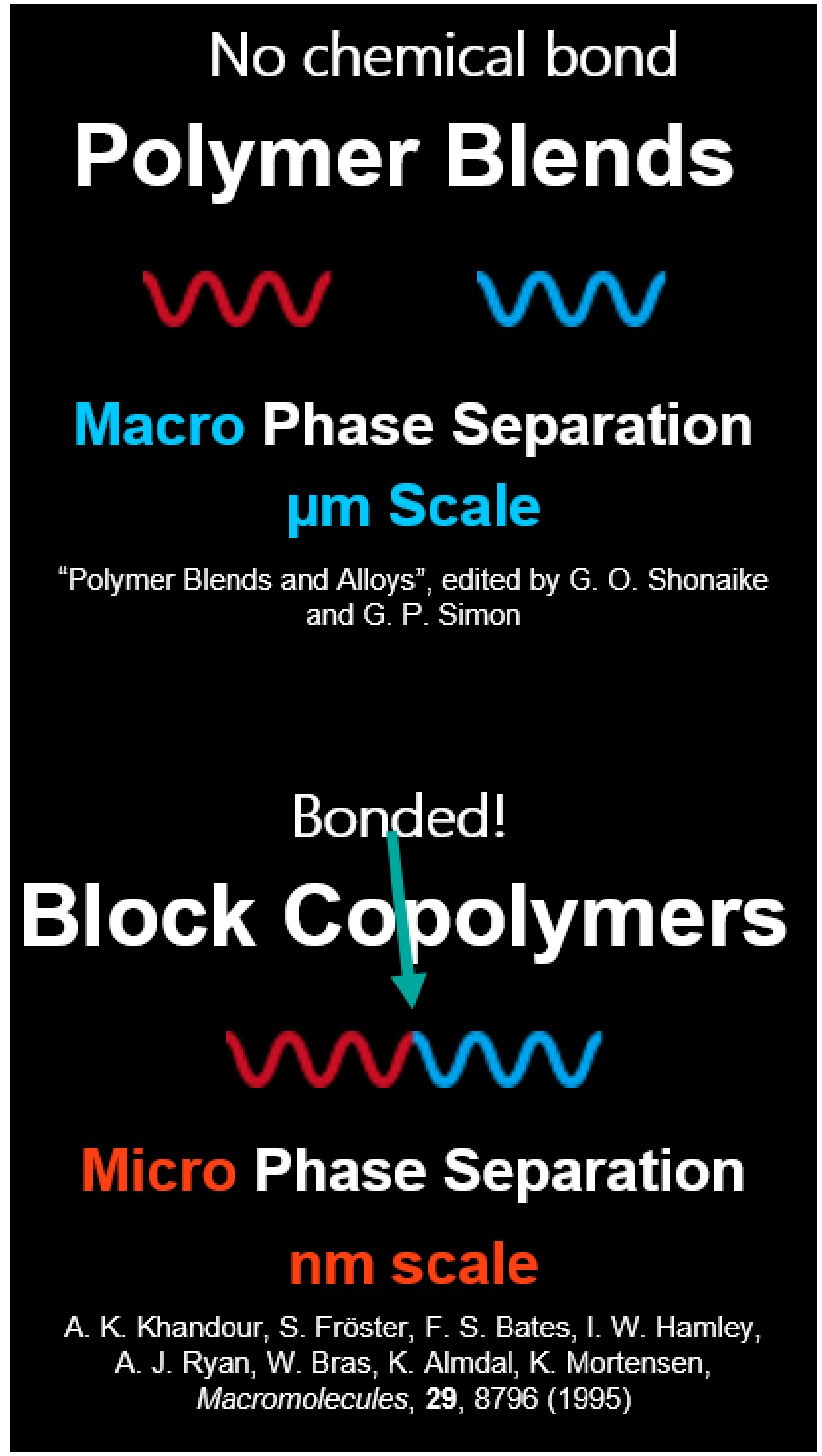
Tohoku University, AIMR

Collaborators: E. Avalos, T.Teramoto, H.Yabu

TOHOKU UNIVERSITY

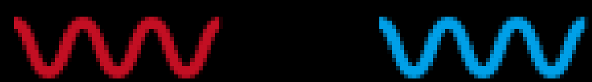
Polymer Blends vs Block Copolymer



Phase Separated Structures of Polymer Materials

No chemical bond

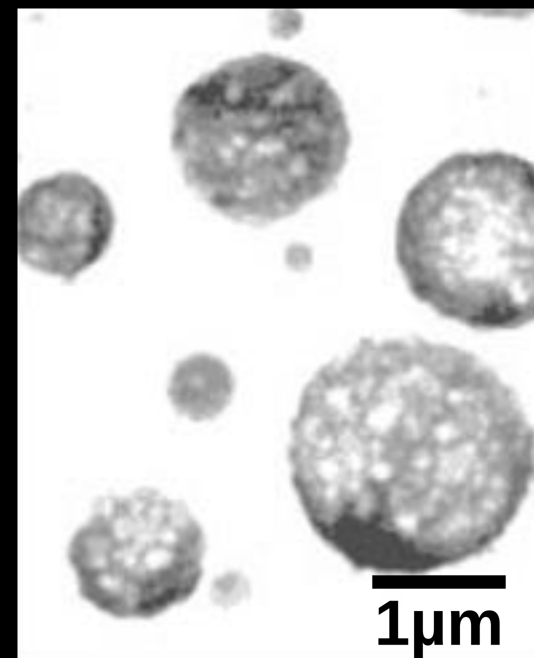
Polymer Blends



Macro Phase Separation

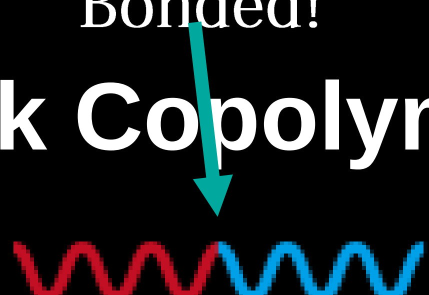
µm Scale

“Polymer Blends and Alloys”, edited by G. O. Shonaike and G. P. Simon



Bonded!

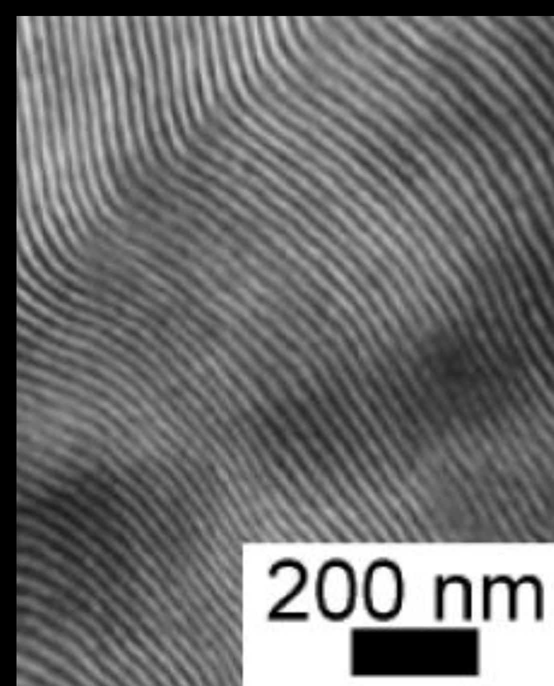
Block Copolymers



Micro Phase Separation

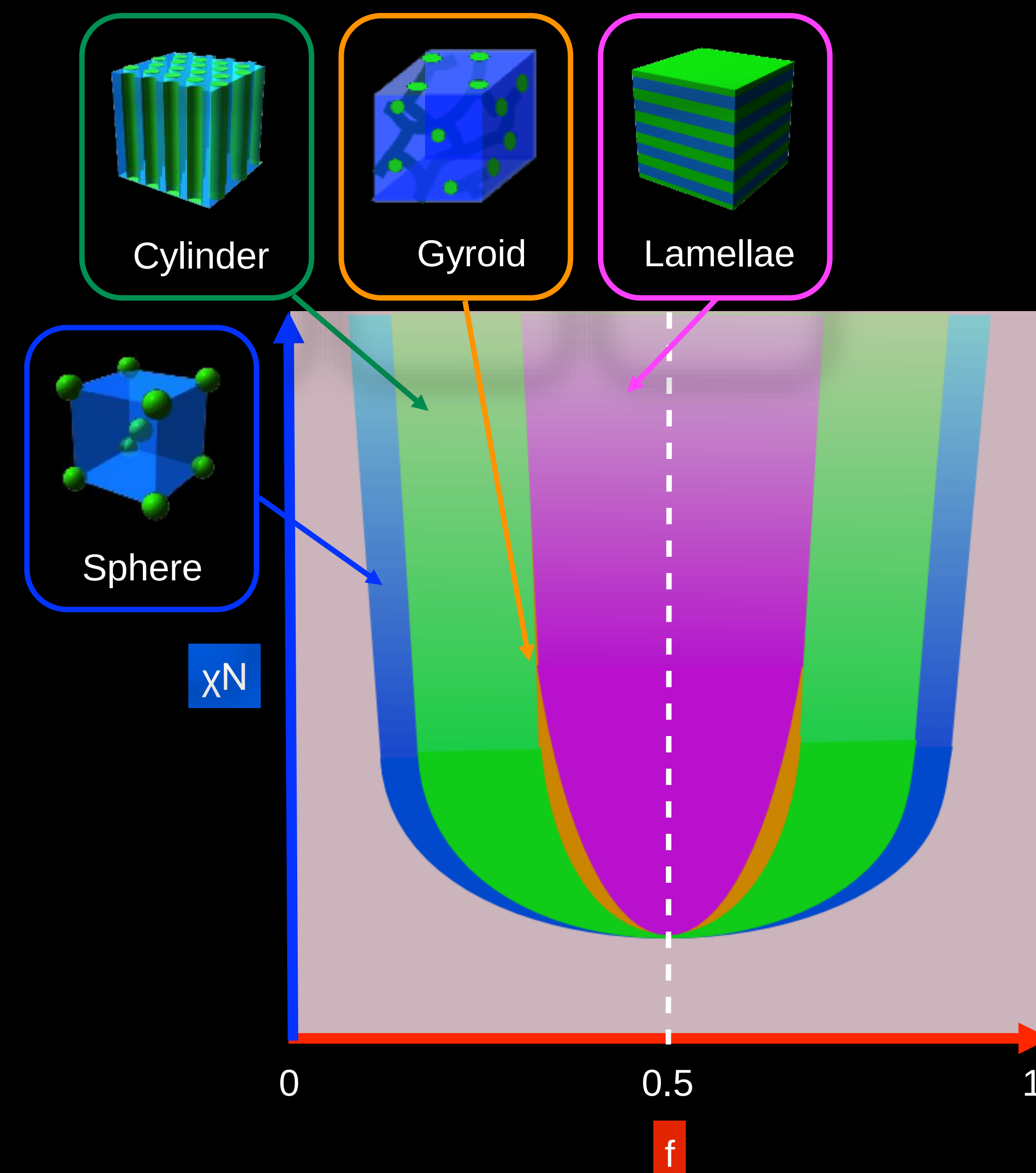
nm scale

A. K. Khandour, S. Fröster, F. S. Bates, I. W. Hamley, A. J. Ryan, W. Bras, K. Almdal, K. Mortensen, *Macromolecules*, **29**, 8796 (1995)



Micro Phase Separation

Nanoscale structuring by changing copolymerization ratios, molecular weights, and miscibility of polymers.

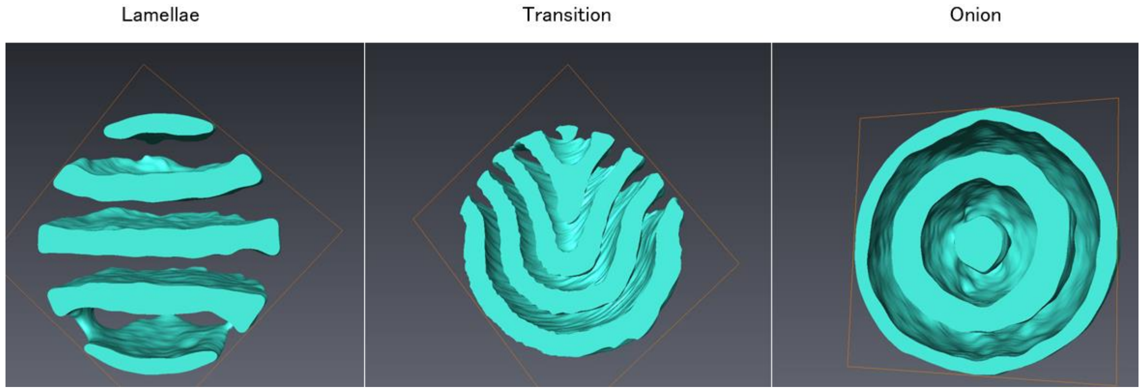


morphology: copolymerization ratio, χN, periodicity: N

Polymer particles with phase separated structure?

Questions

- **Metamorphose from lamellar to onion**



- **Ashura particle for three homopolymers**

What we did

- **Mathematical modeling and computations for these phenomena**
- **Appropriate parameters for temperature change?**
- **Answer to mutual exclusiveness among polymers of Asyura**

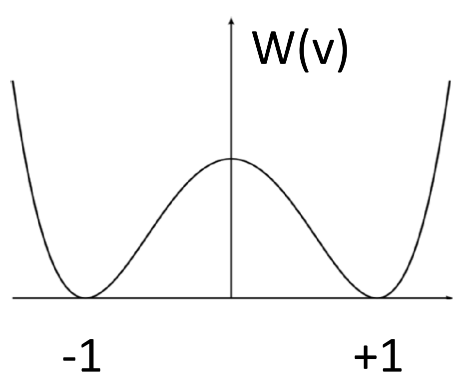
Modeling of diblock copolymer

What is an appropriate free energy!

No bondings

Free energy

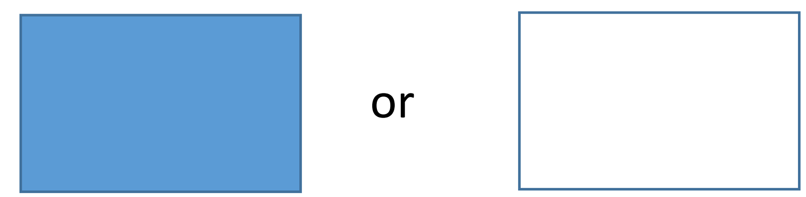
$$F_\epsilon(v) = \int_\Omega \left\{ \frac{\epsilon^2}{2} |\nabla v|^2 + W(v) \right\} dr$$



Double well potential

Allen-Cahn equation: Non-conservative

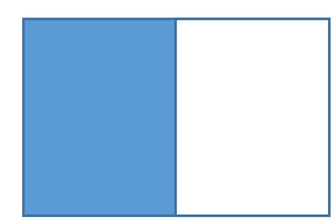
$$\tau v_t = \epsilon^2 \Delta v + (1-v)(1+v)v$$



No phase separation

Cahn-Hilliard equation: Mass is conserved

$$\tau v_t = -\Delta \left\{ \epsilon^2 \Delta v + (1-v)(1+v)v \right\}$$



No chemical bonding → **Macro** phase separation

Free energy for block copolymers

micro-phase separation

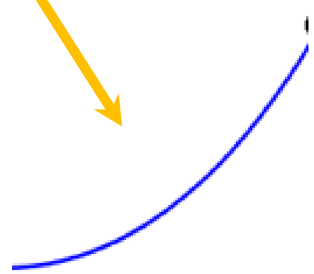
A and B are bonded

Bulk Phase (No solvent)

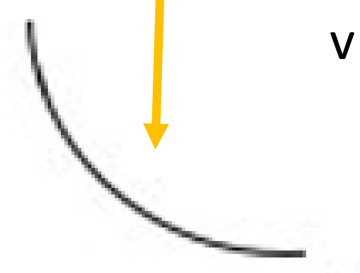
Model the bonding

Chemical bonding ➔ Micro-phase separation

$$F_{\epsilon,\sigma}(v) = \int_{\Omega} \left\{ \frac{\epsilon^2}{2} |\nabla v|^2 + W(v) + \boxed{\textbf{?}} \right. dr$$



k^2

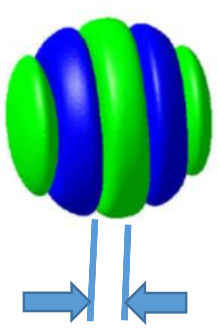


$k^{-\beta}$

v oscillates rapidly around v^bar

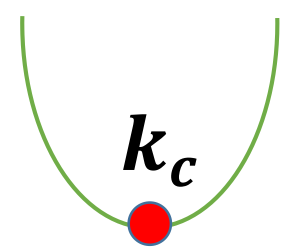
Converges weakly to zero

Fourier space



k_c

Decrease the interface area



Increase the interface area

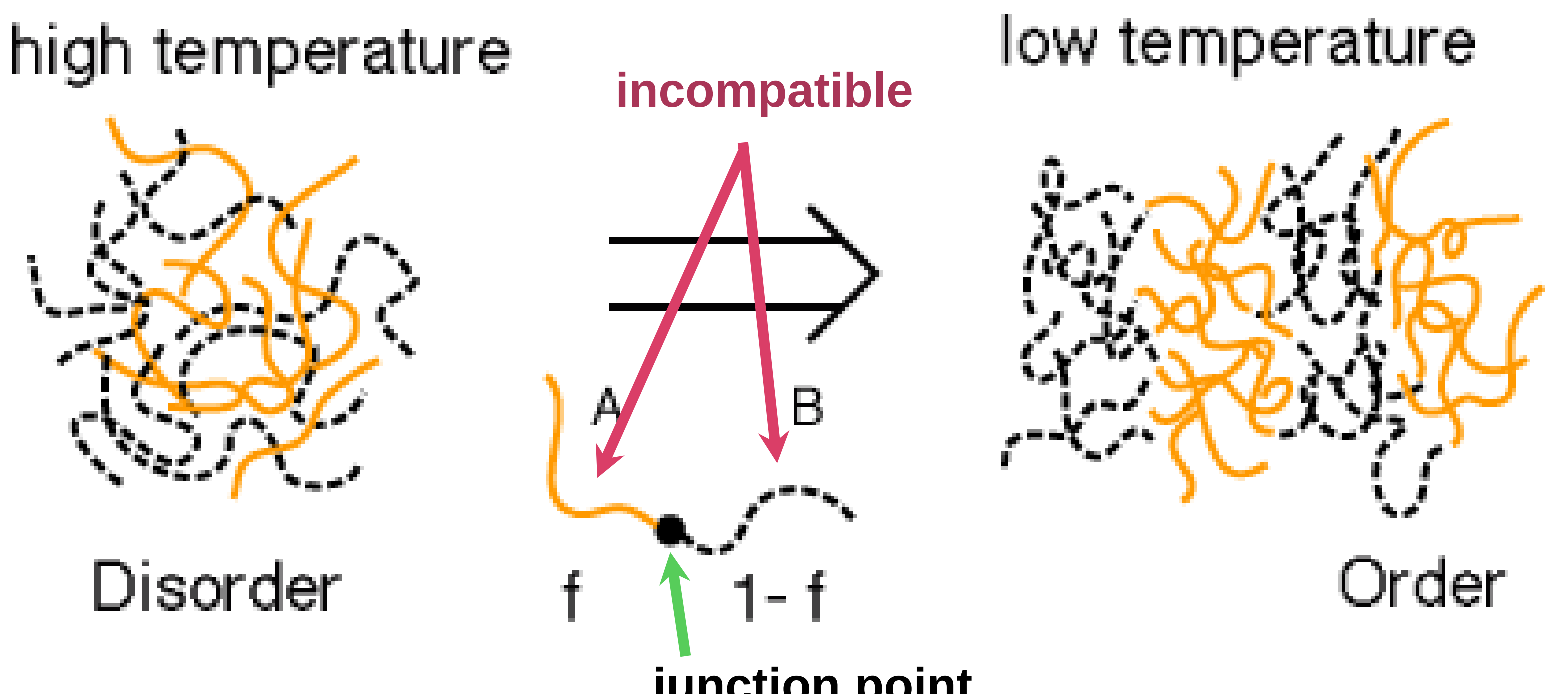
β Is determined by experiments

These two opposite effects characterize the micro-phase wave number k_c .

v ~ +1 : A-polymer rich
v ~ -1 : B-polymer rich

v ~ 0 : interface

They are repulsive, but bonded together.



Segregation

Bonded: nonlocal

$$F_{\epsilon,\sigma}(u) = \int_\Omega \left(\frac{\epsilon^2}{2} |\nabla u|^2 + W(u) + \frac{\sigma}{2} |(-\triangle)^{-1/2}(u - \overline{u})|^2 \right) \mathrm{d}r.$$

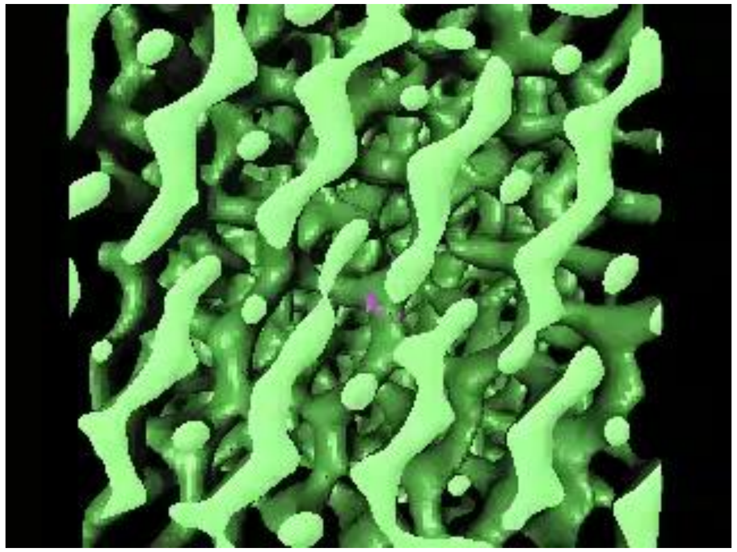
$u(r, \mathrm{t})$: local concentration at the position r, time t

Ohta, Kawasaki (86,90)

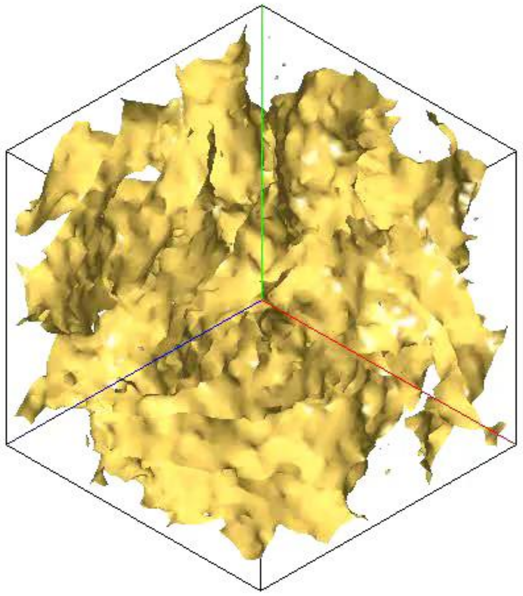
Reformulated: Nishiura,Ohnishi (94), Choksi, Ren(03)

Block Copolymer Melts

Two different types of homopolymers are bonded



3D image by X-ray computerized tomography
by Prof.Jinnai



3d double gyroid

T.Teramoto and Y. Nishiura : Dynamics and morphologies of micro-phase Separation, JJIAMJ 27 (2010),

A short history of Ohta-Kawasaki dynamics

- A model of density functional type for micro-phase separation

T. Ohta and K. Kawasaki, Macromolecules 19 (1986) 261.

- A mathematical formulation of O-K model and its singular limit were introduced by

Y.Nishiura and I.Ohnishi, Physica D (1995) 31

$$F_{\varepsilon,\sigma}(u) := \int_\Omega \{\tfrac{1}{2}\varepsilon^2|\nabla u|^2 + W(u) + \tfrac{1}{2}\sigma|(-\Delta_N)^{-1/2}(u-\overline{u})|^2\}dx,$$

$$\overline{u} := \frac{1}{|\Omega|}\int_\Omega u\,dx, \qquad u \in \mathrm{H}^1(\Omega),$$

- **Singular Limit Equations**

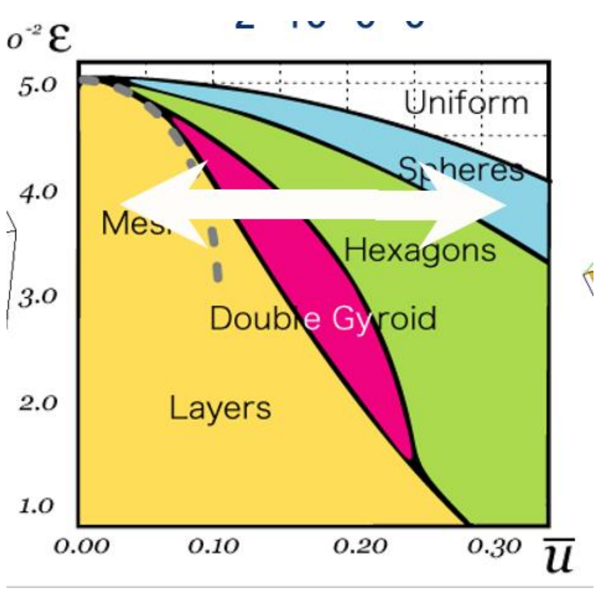
$$\begin{aligned}
&-\Delta v = (1-2\chi_{\hat\Omega^-_{p,t}}) - \frac{1}{|\hat\Omega_p|}(|\hat\Omega^+_{p,t}| - |\hat\Omega^-_{p,t}|), && \text{in } \hat\Omega_p \setminus \Gamma_t,\\
&\frac{\partial v}{\partial n} = 0, && \text{on } \partial\hat\Omega_p,\\
&v = C\kappa_{\Gamma_t},\\
&V = \tfrac{1}{2}\left[\frac{\partial v}{\partial n}\right]_{\Gamma_t},\\
&\Gamma_0 = \Gamma_{00},
\end{aligned}$$

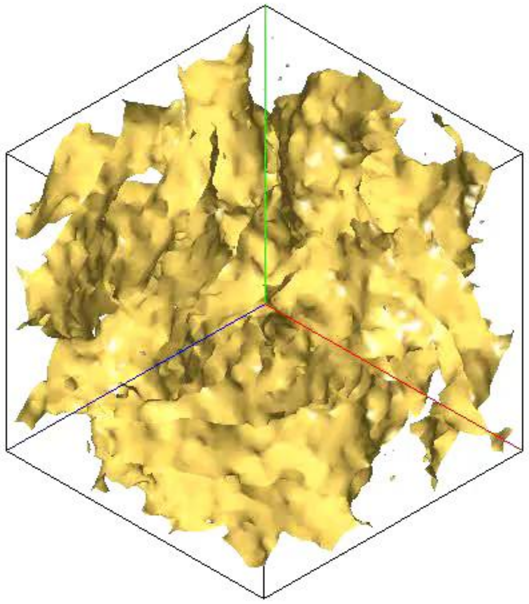
Modified Hell-Shew equations

- **Many mathematicians started to work on this problem after this.**
R.Choksi, M.Peletier, J. Williams, …

Exploring 3D morphology

★ **T.Teramoto and YN, J.Phys.Soc.Japan (2002)**

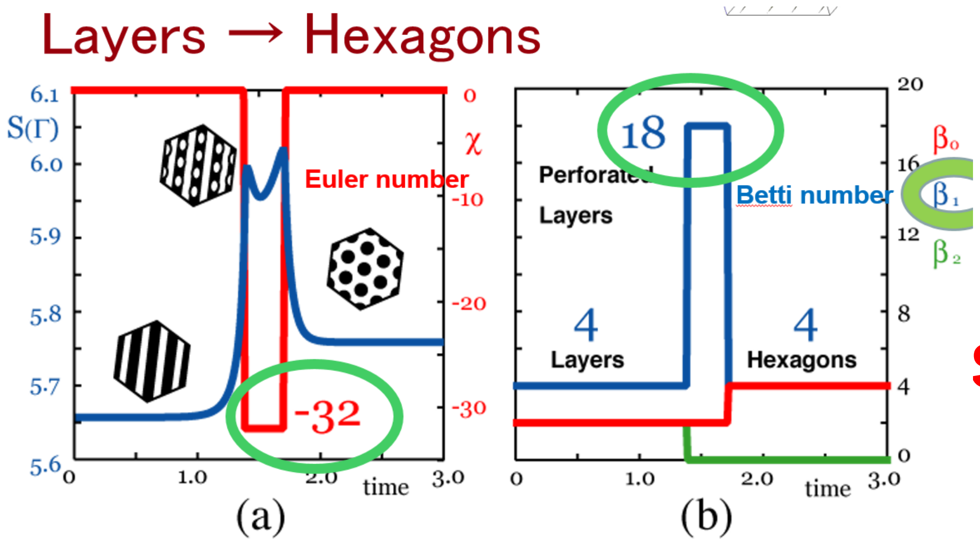




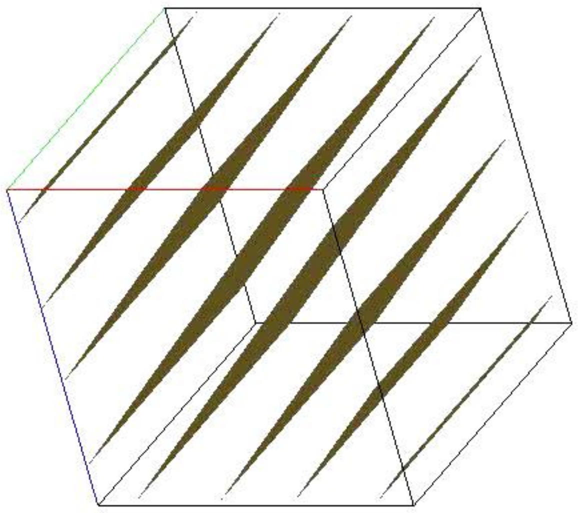
★ **T.Teramoto and YN, JJIAM (2010)**

Morphological characterization of the diblock copolymer problem with Topological computation

Layers → Hexagons

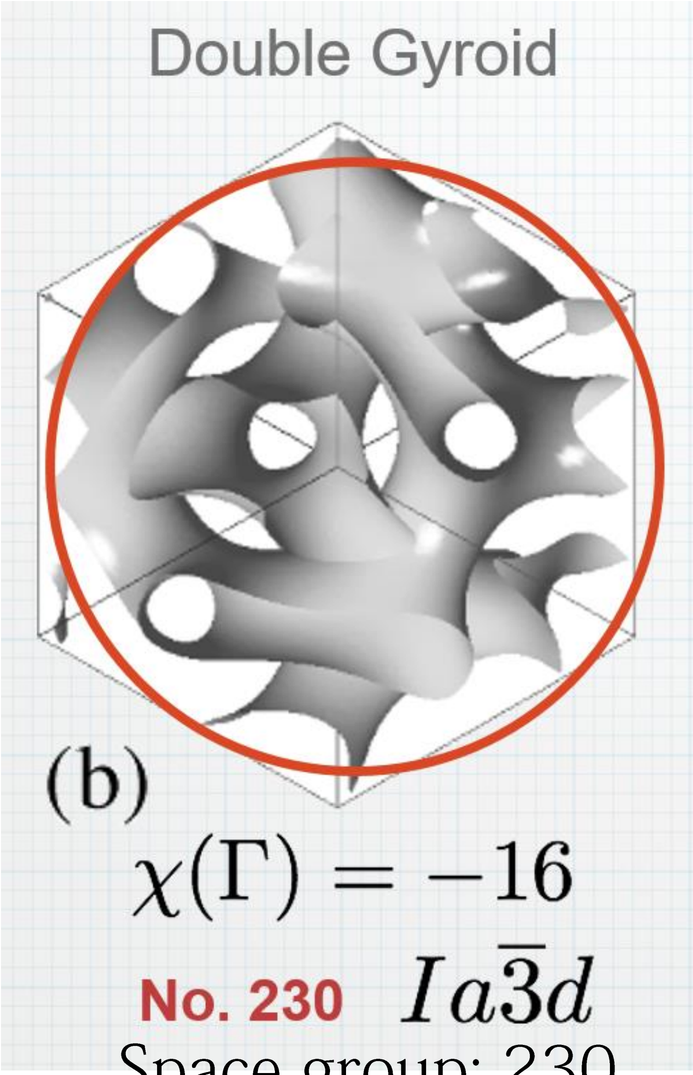


Application of ChomP
to copolymer problem.
Scaling law for Betti numbers



Perforated lamellar appears during the deformation..

Rigorous Existence for Double Gyroids



Space group: 230

*T. Wanner, 1D problem, Disc. And Cont. Dyn.Sys., 37(2) (2017)
*J.-P.Lessard, E. Sander, and T.Wanner, J.Comp.Dyn. (2018), bif. point
*Jan Bouwe van den Berg and J.F.Williams, preprint (2018)
Contraction mapping in a gyroid symmetric space in 3D

Introduce the solvent

Particles are floating in water!

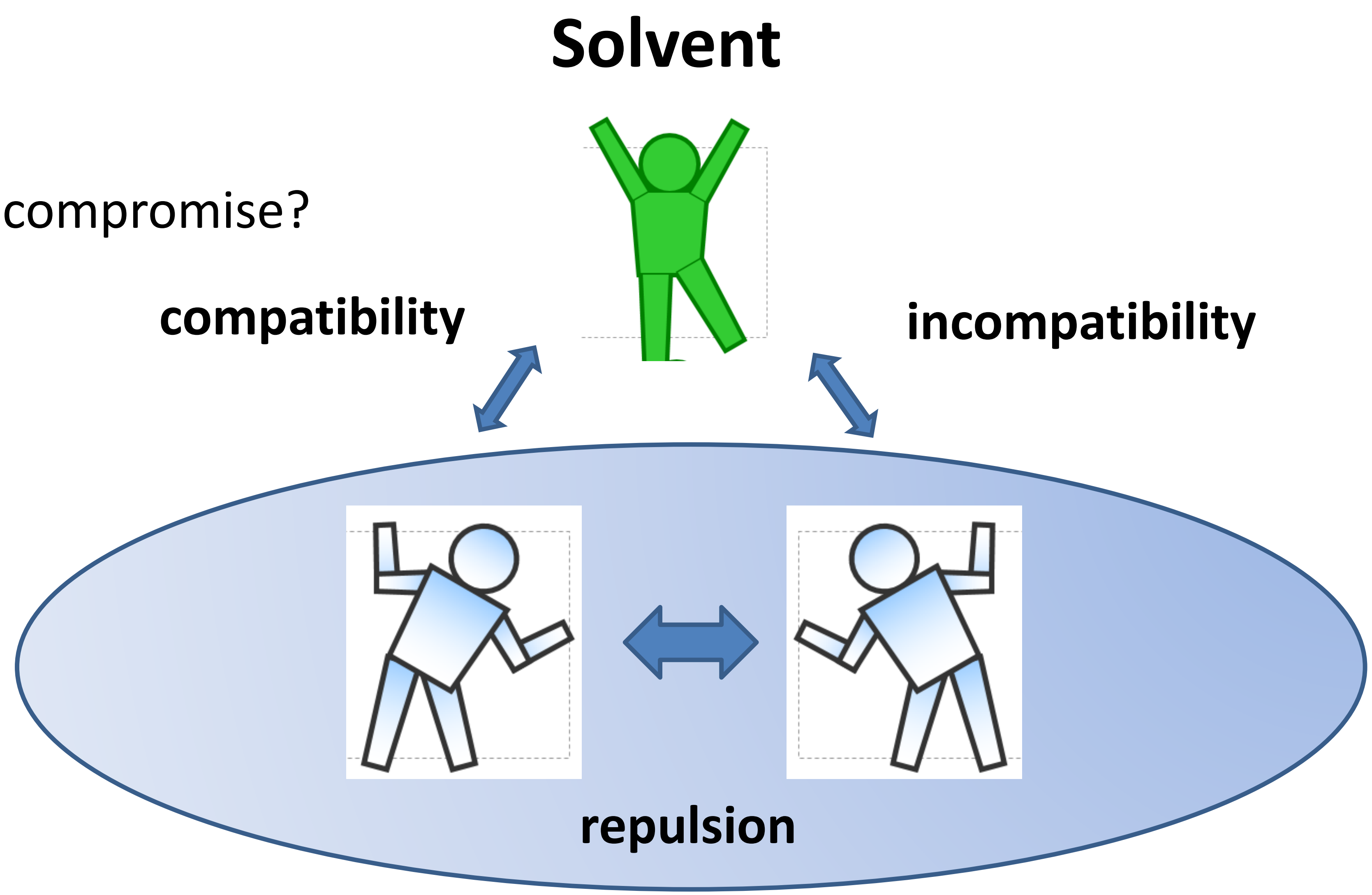
Bulk phase to Particle phase

Modeling the trilateral problem

- **P1: Confinement effect**
  - Divide **copolymer-rich** and **solvent-rich phases**.
    - We introduce a new variable separating two regimes.
  - Shape itself is formed spontaneously (not always spheres)
- **P2: Micro-phase separation**
  - Two polymers are bonded, but repel each other
  - Non-local effect
- **P3: Compatibility to external solvent**
  - Each component of diblock copolymer may have **different affinity to solvent**.
  - If outside is water, then hydrophilic (phobic) one prefers closer (distant) place to water.
    - We introduce a new term in the potential W(u,v)

Internal vs External

How to compromise?



- ◆ Shape variable: Cahn–Hilliard equation
- ◆ Microphase separation: Diblock copolymer model

Model free energy for constrained Diblock Copolymer

Confined particle by solvent micro-phase separation occurs inside only

E.Avalos, T. Higuchi, T. Teramoto, H. Yabu and Y. Nishiura：“Frustrated phases under three-dimensional confinement simulated by a set of coupled Cahn–Hilliard equations”, **Soft Matter** 27 (2016)12 : 5905--5914（2016）

Minimize the Free Energy

u: shape variable

v: micro-phase variable

$$F_{\epsilon,\sigma}(u,v) = \int_{\Omega} \left\{ \frac{\epsilon_u^2}{2} |\nabla u|^2 + \frac{\epsilon_v^2}{2} |\nabla v|^2 + \boxed{W(u,v)} + \frac{\sigma}{2} \left| (-\Delta)^{-1/2} (v - \overline{v}) \right|^2 \right\} dr,$$

σ: strength of bonding

where

$$\overline{v} = \frac{1}{|\Omega|} \int_{\Omega} v dr,$$

b1: affinity to solvent
Hydrophilic or Hydrophobic

b2: shape parameter

$$\boxed{W(u,v)} = \frac{(u^2-1)^2}{4} + \frac{(v^2-1)^2}{4} + \boxed{b_1 uv + b_2 \frac{uv^2}{2}}$$

- E.Avalos, T. Higuchi, T. Teramoto, H. Yabu and Y. Nishiura : “Frustrated phases under three-dimensional confinement simulated by a set of coupled Cahn–Hilliard equations”, **Soft Matter** 27 : 5905--5914（2016）

Coupled Cahn-Hilliard equations for constrained di-block copolymer

u : shape variable

$$\tau_u u_t = \triangle \left(\frac{\delta F}{\delta u} \right) = -\triangle \left\{ \epsilon_u^2 \triangle u + (1-u)(1+u)u + b_1 v + b_2 \frac{v^2}{2} \right\}$$

u divides **copolymer-rich** and **solvent-rich phases**.

$$\tau_v v_t = \triangle \left(\frac{\delta F}{\delta v} \right) = -\triangle \left\{ \epsilon_v^2 \triangle v + (1-v)(1+v)v + b_1 u + b_2 uv \right\} - \sigma (v - \overline{v})$$

v : phase−separation variable

v describes **micro-phase separation**

V = ±1: A-polymer-rich, B-polymer-rich
V = 0 : No copolymer

Shape variable "u"
uv^2 forms particle shape

A new variable **u** defines the shape coupled with uv^2 term

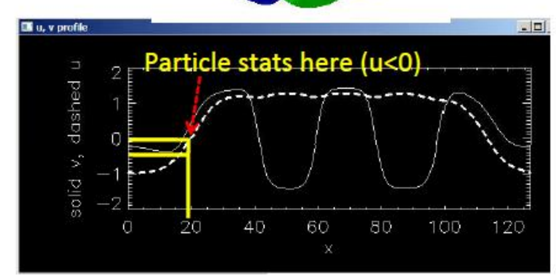
$-uv^2$ reperesents the effect of confinement

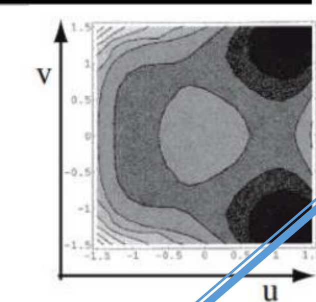
Micro-phase separation **occurs only inside of confinement**

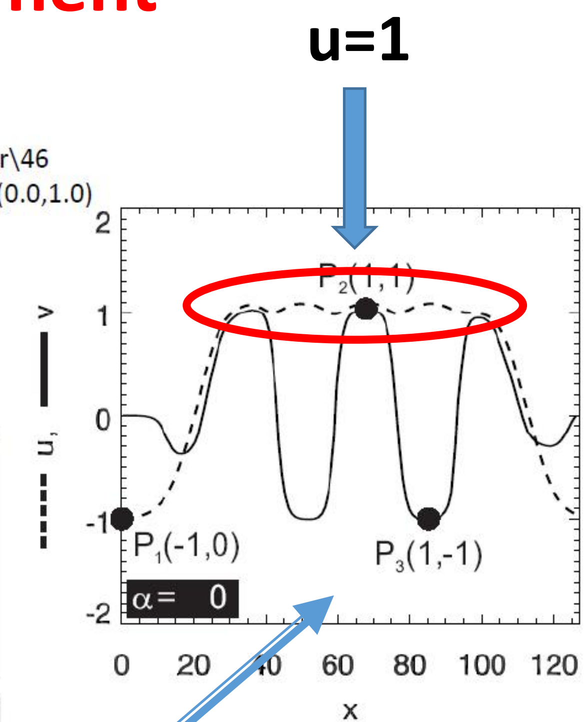
A and B polymers exist only in the region of u = 1.

Monomial $-uv^2$ is a good candidate!

This term decreases energy when v oscillates between 1 and -1.







(b) Confined layered particle in one dimension. This is the case of $b_1 = 0$ where the confinement surface has equal preference for $v < 0$ or $v > 0$. Notice the confinement surface defined by u is not rigid but rather it adopts the undulations of v at the surface of the particle.

u: - - - - -

v: ———

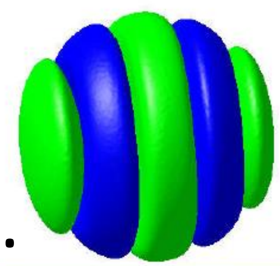
Affinity toward solvent
(Trilateral)

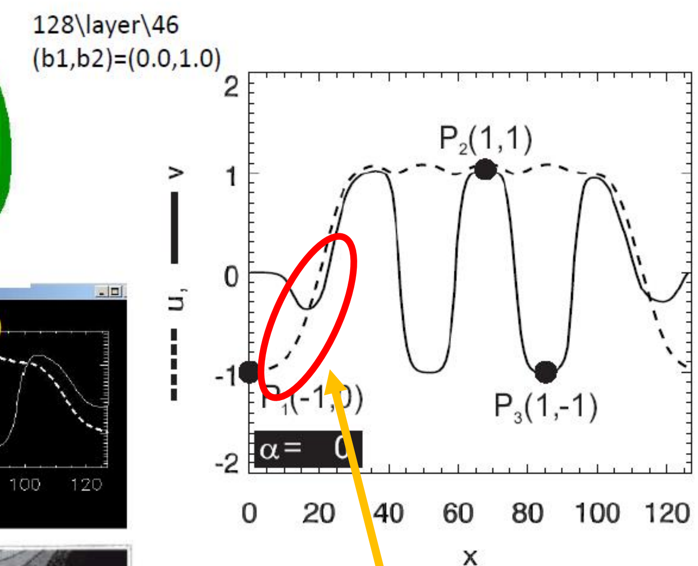
The product **uv** plays a key role for affinity effect

uv reperesents the effect of compatibility

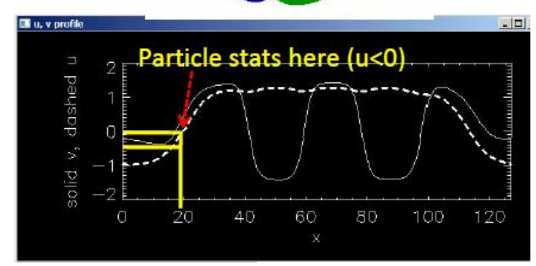
Compatibility or incompatibility to external solvent

Near the boundary of confinement,
u changes its sign from positive to negative.

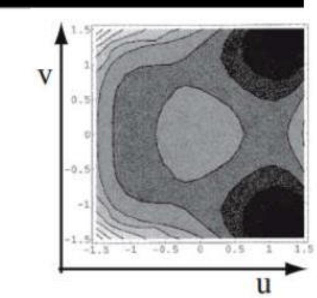




(b) Confined layered particle in one dimension. This is the case of $b_1 = 0$ where the confinement surface has equal preference for $v < 0$ or $v > 0$. Notice the confinement surface defined by u is not rigid but rather it adopts the undulations of v at the surface of the particle.



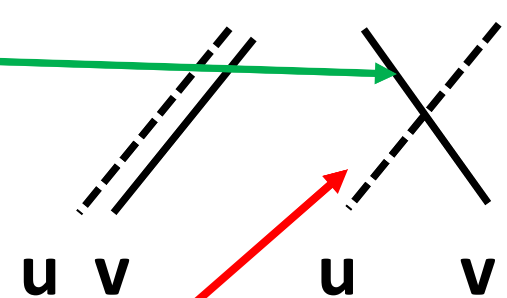
b1=0, b2!=0



Monomial uv is a good candidate!

Parallel or Crossing

v=1: hydrophilic (A-polymer),
v=-1: hydrophobic (B-polymer)



uv < 0 decreases the energy

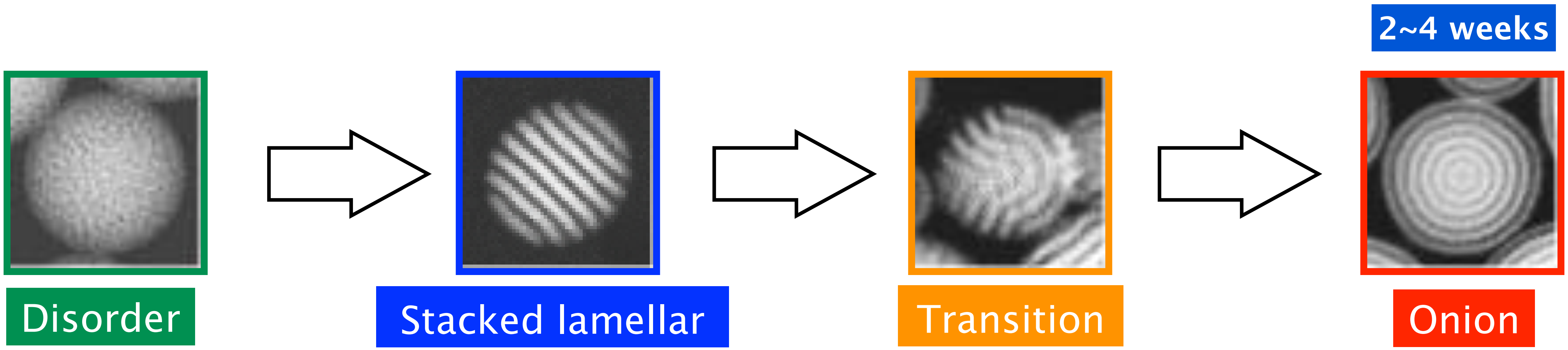
u changes sign from positive to negative near the interface.

Metamorphose
from lamellar to onion

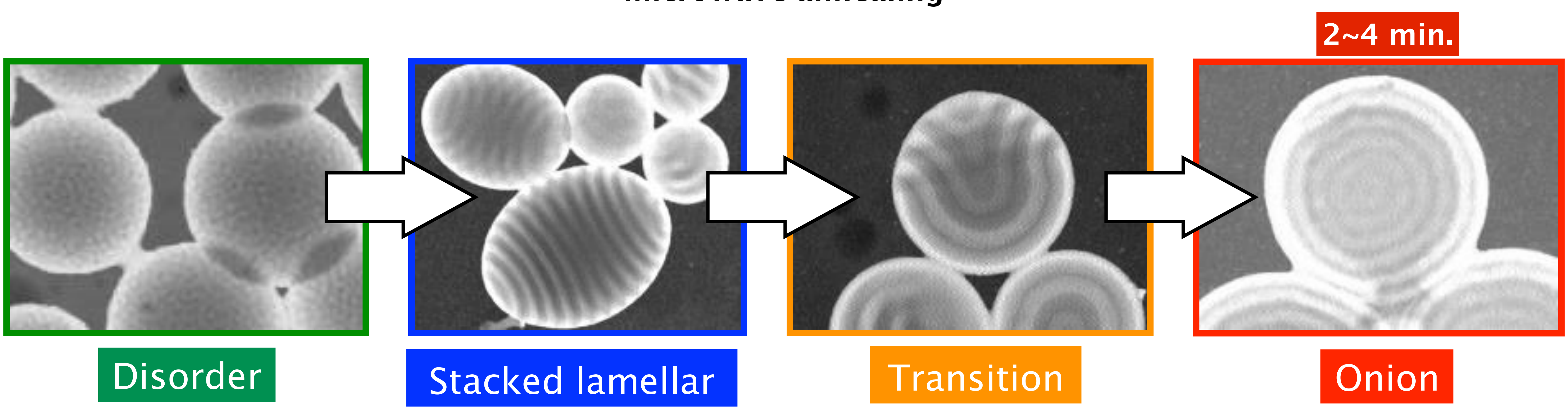
"Transformation of block copolymer nanoparticles from ellipsoids with striped lamellae into onion-like spheres and dynamical control via coupled Cahn–Hilliard equations"
Avalos, E., Teramoto, T., Komiyama, H., Yabu, H., Nishiura, Y. **ACS Omega** (2018)

Microwave Annealing

annealed in a water bath at 40 °C



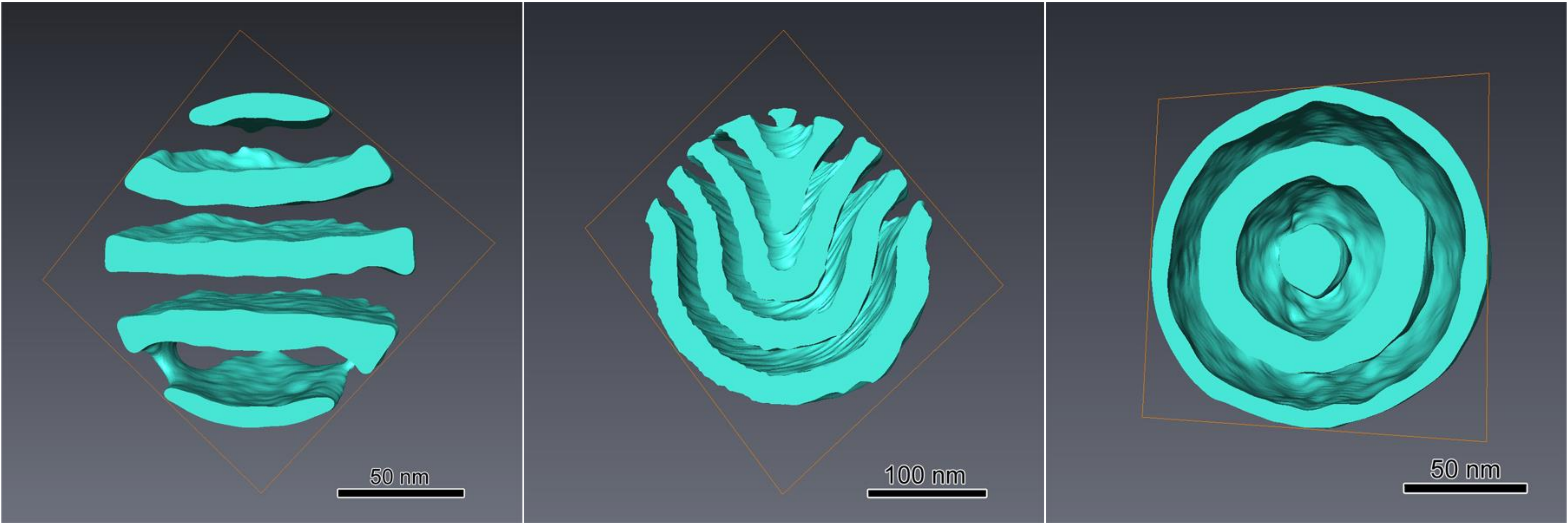
microwave annealing



Macromolecules, 46(10), 4064-4068 (2013)PAT. P. JP2009-188892

Transformation Process from Lamellae to Onion: Electron Tomography

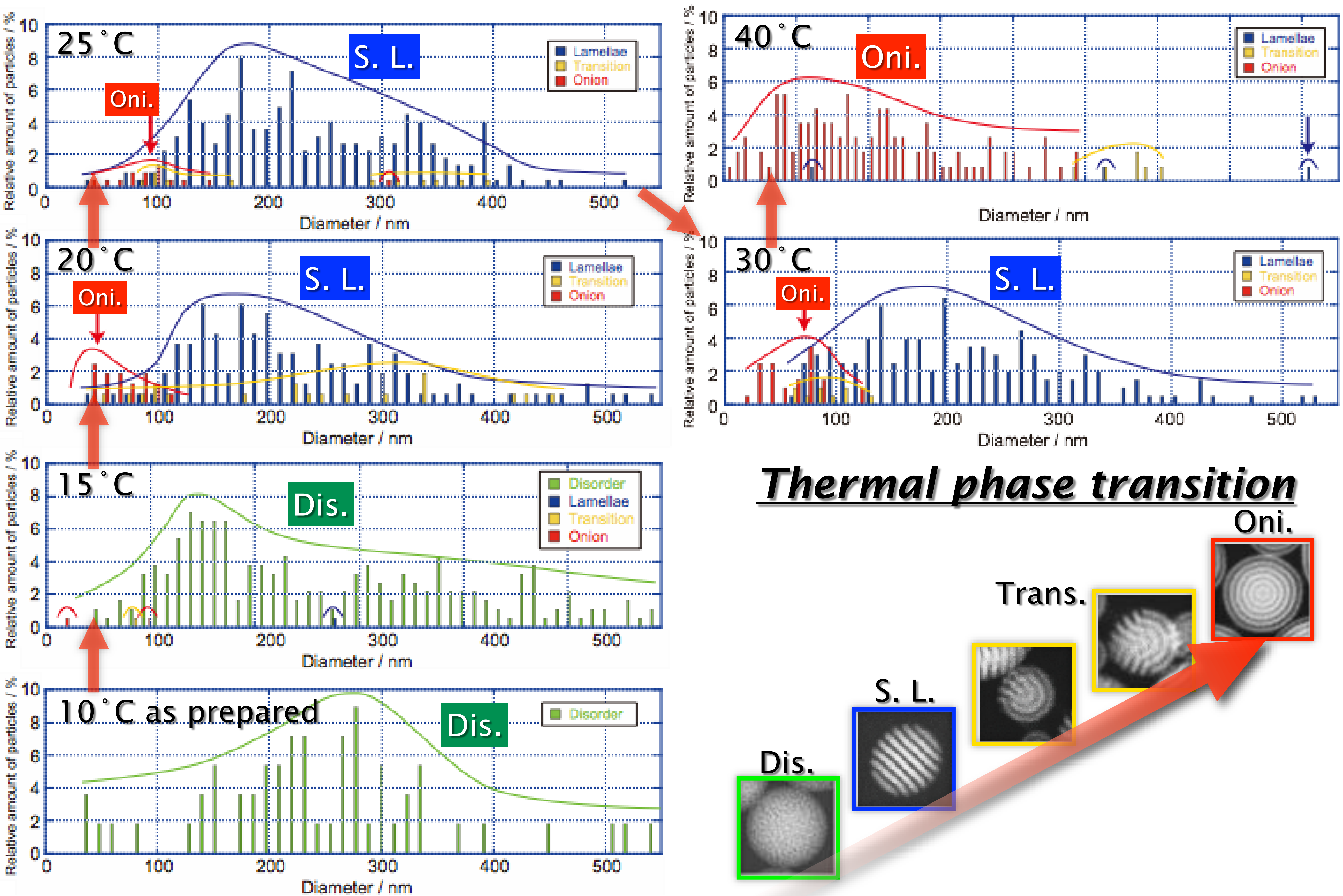
Lamellae | Transition | Onion



$-60^\circ < \theta < 60^\circ$, step 2°

Macromol. Rap. Commun. 2010, 31(20), 1773-1778

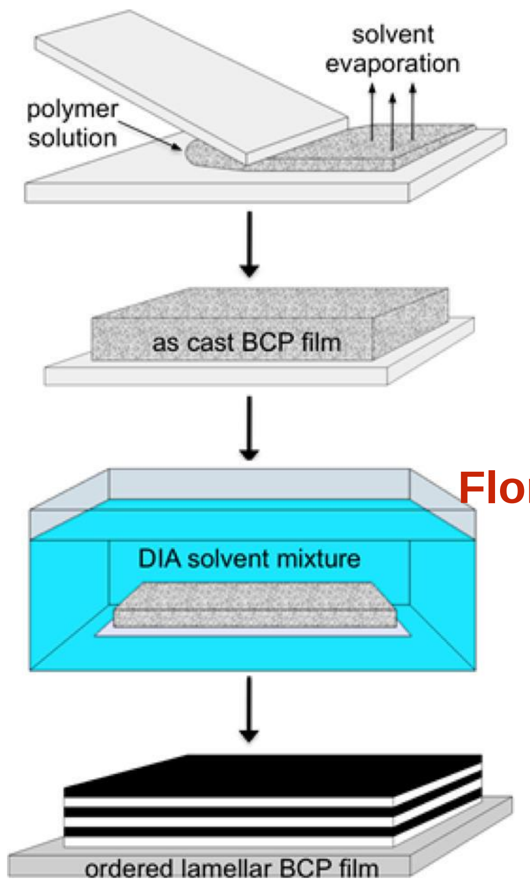
Transformation Process from Lamellae to Onion: Size Effect



Macromol. Rap. Commun. 2010, 31(20), 1773-1778

Temperature T is related to one of the parameters in our model through the following two relations.

Relation between temperature and χ



Direct Immersion Annealing (DIA)
:Annealing in solvent

Macromolecules
Article
pubs.acs.org/Macromolecules

Reduced Domain Size and Interfacial Width in Fast Ordering Nanofilled Block Copolymer Films by Direct Immersion Annealing

Melanie Longanecker,[†] Arvind Modi,[†] Andrey Dobrynin,[⊥] Seyong Kim,[§] Guangcui Yuan,[‡] Ronald Jones,[‡] Sushil Satija,[‡] Joona Bang,[§] and Alamgir Karim*[,†]

F-H χ Parameter between polymer 1 and solvent

F-H χ Parameter between polymer 2 and solvent

gas constant

Flory-Huggins (F-H) χ Parameter between polymer A and B

$$\chi_{12} = \frac{(\chi_{1s} - \chi_{2s})^2}{(\delta_1 + \delta_2 - 2\delta_s)^2}\frac{RT}{v}$$

temperature

molar volume

Solubility Parameter of Polymer 1

Solubility Parameter of Solvent

Solubility Parameter of Polymer 2

Macromolecules 1972, 5, 513−516.

$(\chi_{1s} - \chi_{2s})^2 \uparrow$ ・Temperature $\uparrow$ ・・・ $\chi_{12} \uparrow$

Relation between Interfacial Thickness and χ

Length of Monomer Unit

Interfacial Thickness of Polymer A and B

$$\epsilon_v = \frac{2a}{\sqrt{6\chi_{AB}}}$$

F-H χ Parameter between polymer A and B

$\chi_{12} \uparrow$ ・・・ $w \downarrow$

Increase of b1 ・・・ increase of $(\chi_{1s}-\chi_{2s})^2$

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 56, NUMBER 7 1 APRIL 1972

Theory of the Interface between Immiscible Polymers. II

EUGENE HELFAND AND YUKIKO TAGAMI*
Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974

(Received 4 November 1971)

Interfacial thickness ε_v controls the temperature!

$$\varepsilon_v \propto 1/T^{\frac{1}{2}}.$$

Experiments

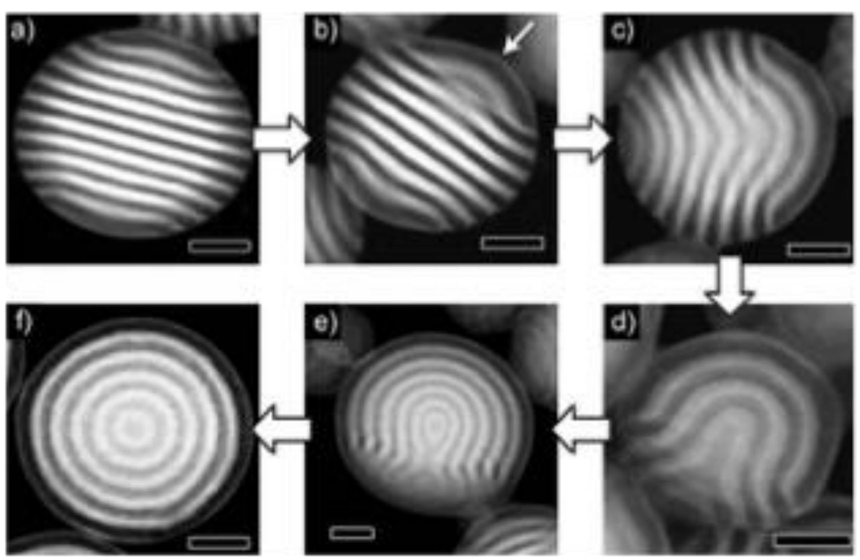
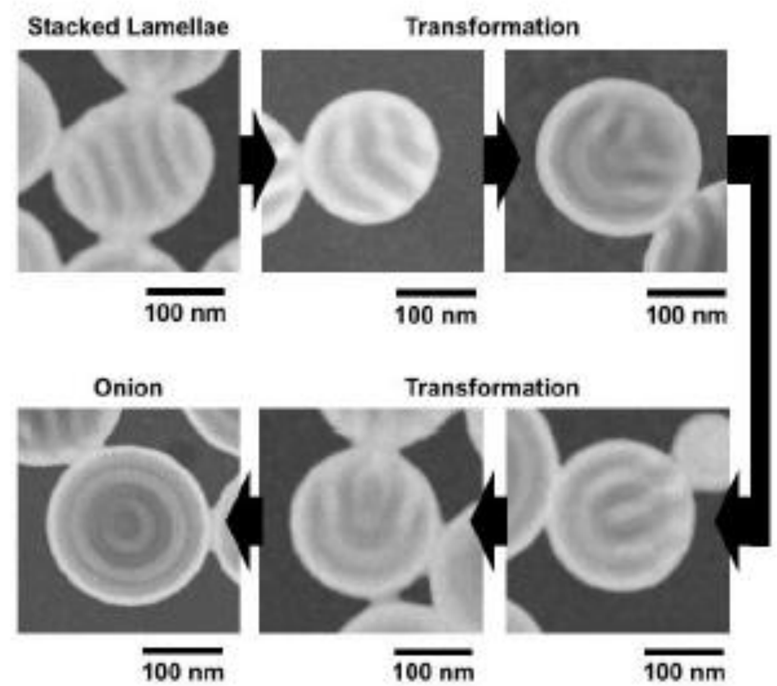


Figure 3. STEM images (dark field) of PSt-PI-76 nanoparticles prepared at 35 °C. Nanoparticles with various transformed lamellar structures were observed. Scale bars indicate 100 nm.

Macromol. Rapid Commun. 2010, 31, 1773–1778



Interfacial thickness ε_v controls the temperature!

$$\tau_v v_t = -\triangle \left\{ \epsilon_v^2 \triangle v + (1-v)(1+v)v - b_1 u + b_2 uv \right\} - \sigma (v - \overline{v})$$

Temperature is increased ⇒ ε_v **becomes smaller**

Simulation

ε_v 0.0020 0.018 0.014 0.010

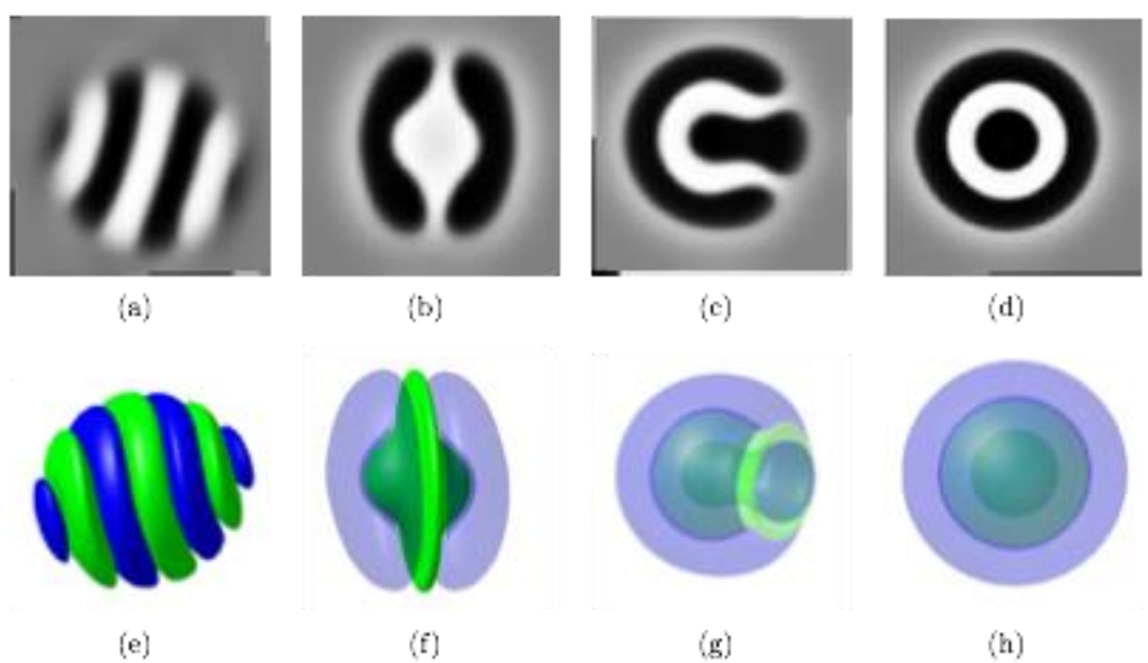
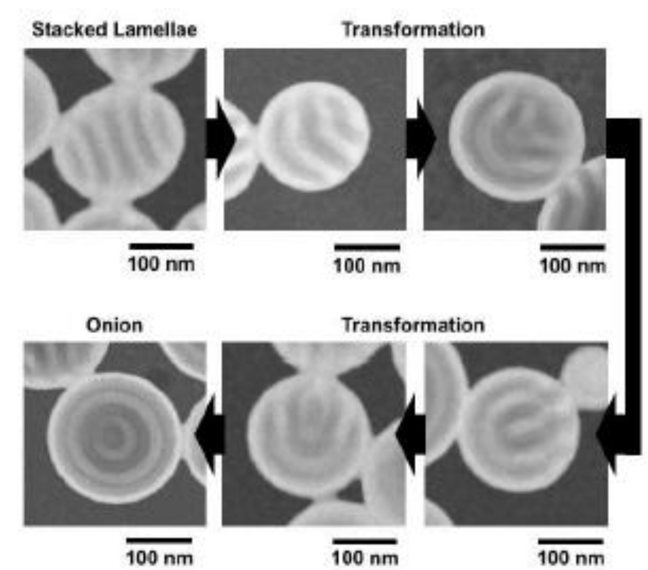
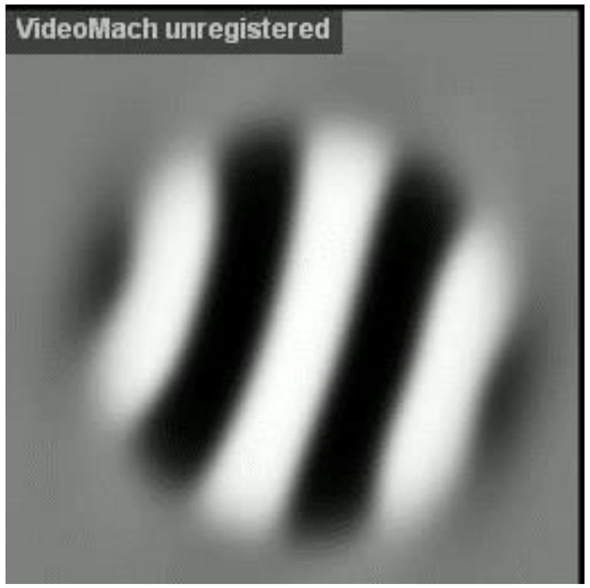


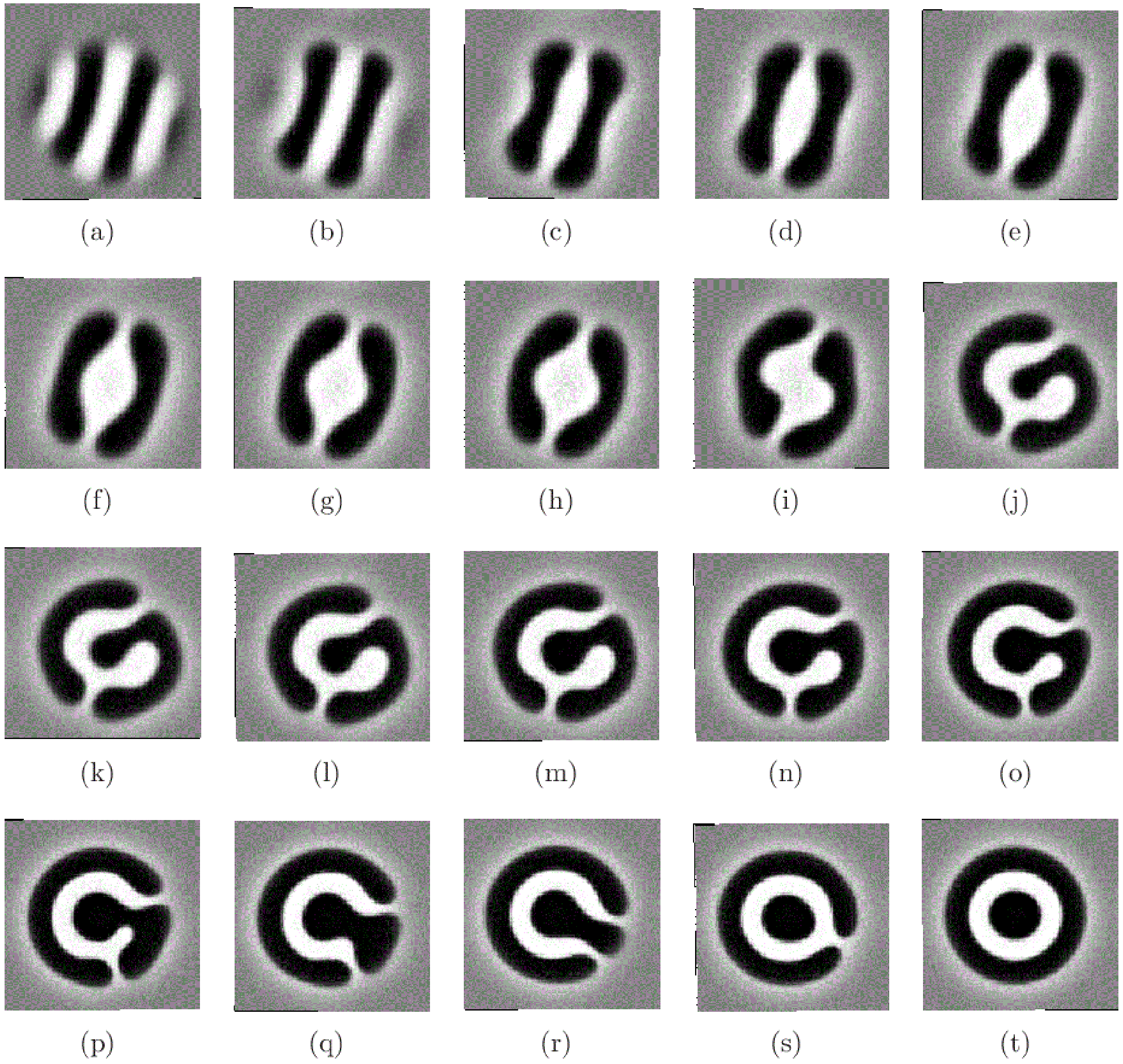
Figure 1: Changes in morphology as ϵ_v decreases. $b_1 = 0.4$. From left to right: $\epsilon_v = 0.020, 0.018, 0.014$ and 0.010. Top: cross section. Bottom: isosurface of order parameter v.

Experiments



ε_v is decreased





Small difference of compatibility initially

b1 = 0.40

If **b1 =0**, no morphological change even if ε_v becomes smaller!

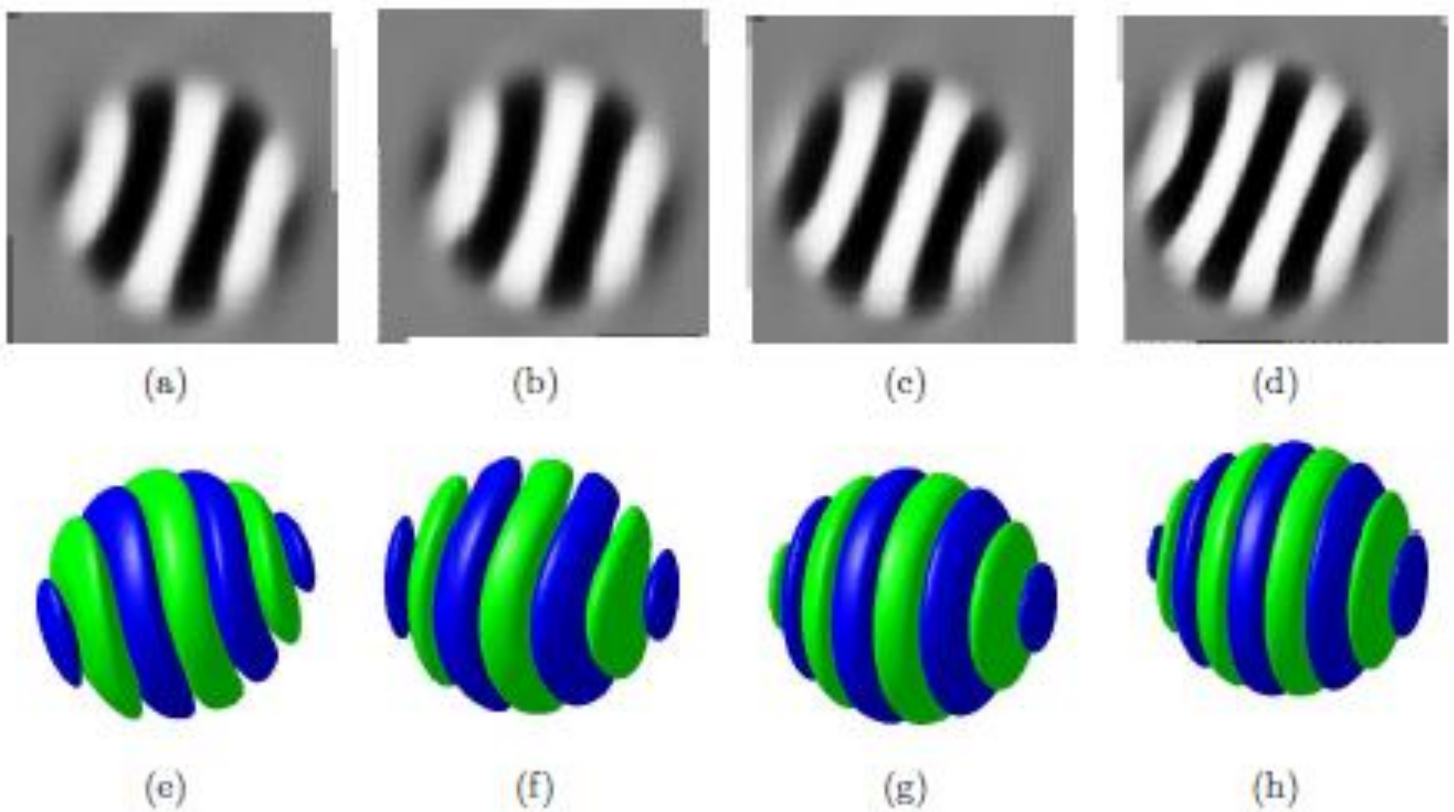
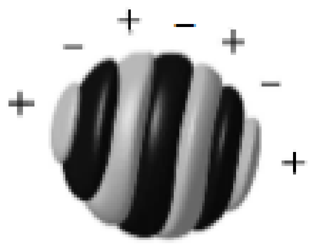


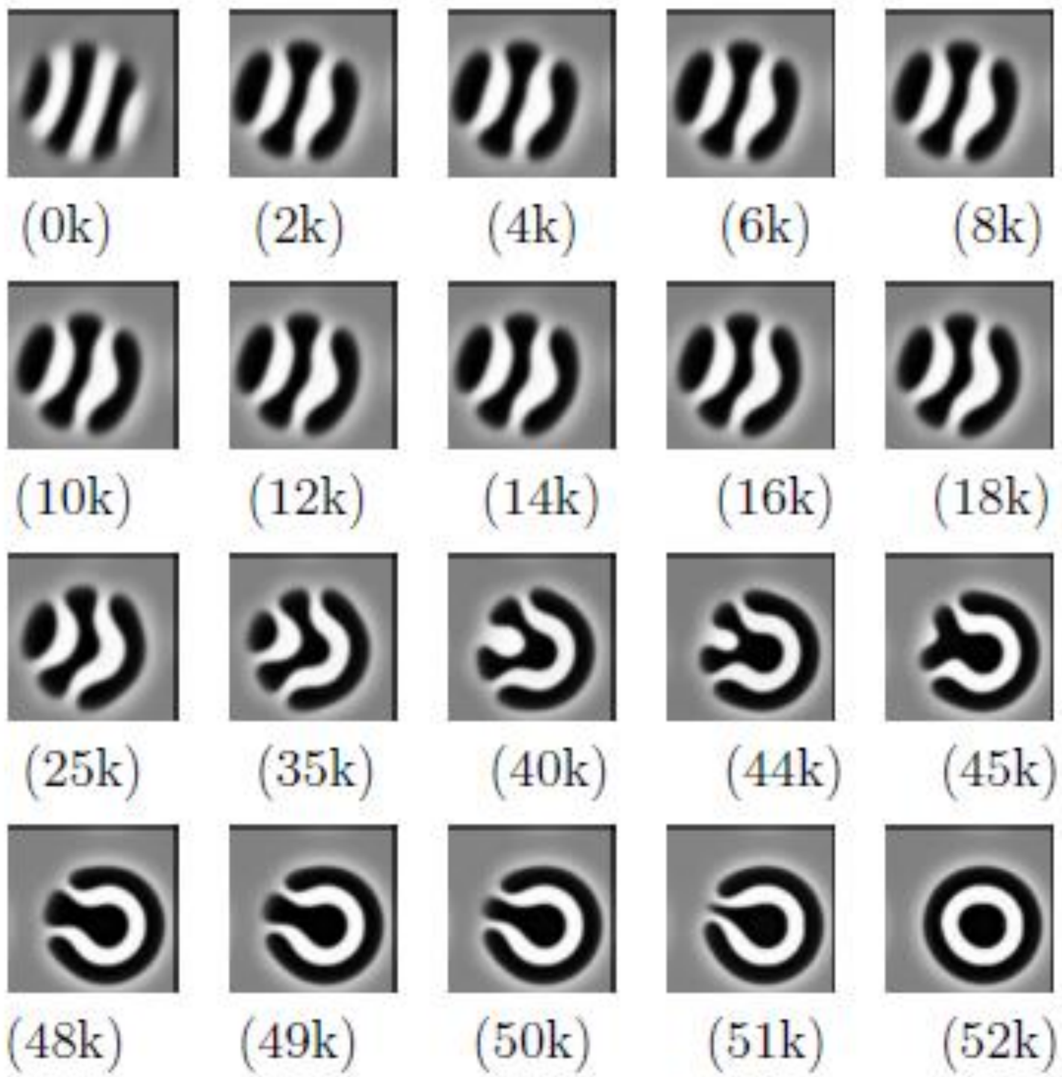
Figure 6: System with $b_1 = 0.0$. 10k time steps. From left to right: $\epsilon_v = 0.020$, 0.018, 0.014 and 0.010. Top: cross section. Bottom: isosurface of order parameter v. Notice that the number of layers increases with decreasing values of ϵ_v, as expected.

No affinity difference, nothing happens!

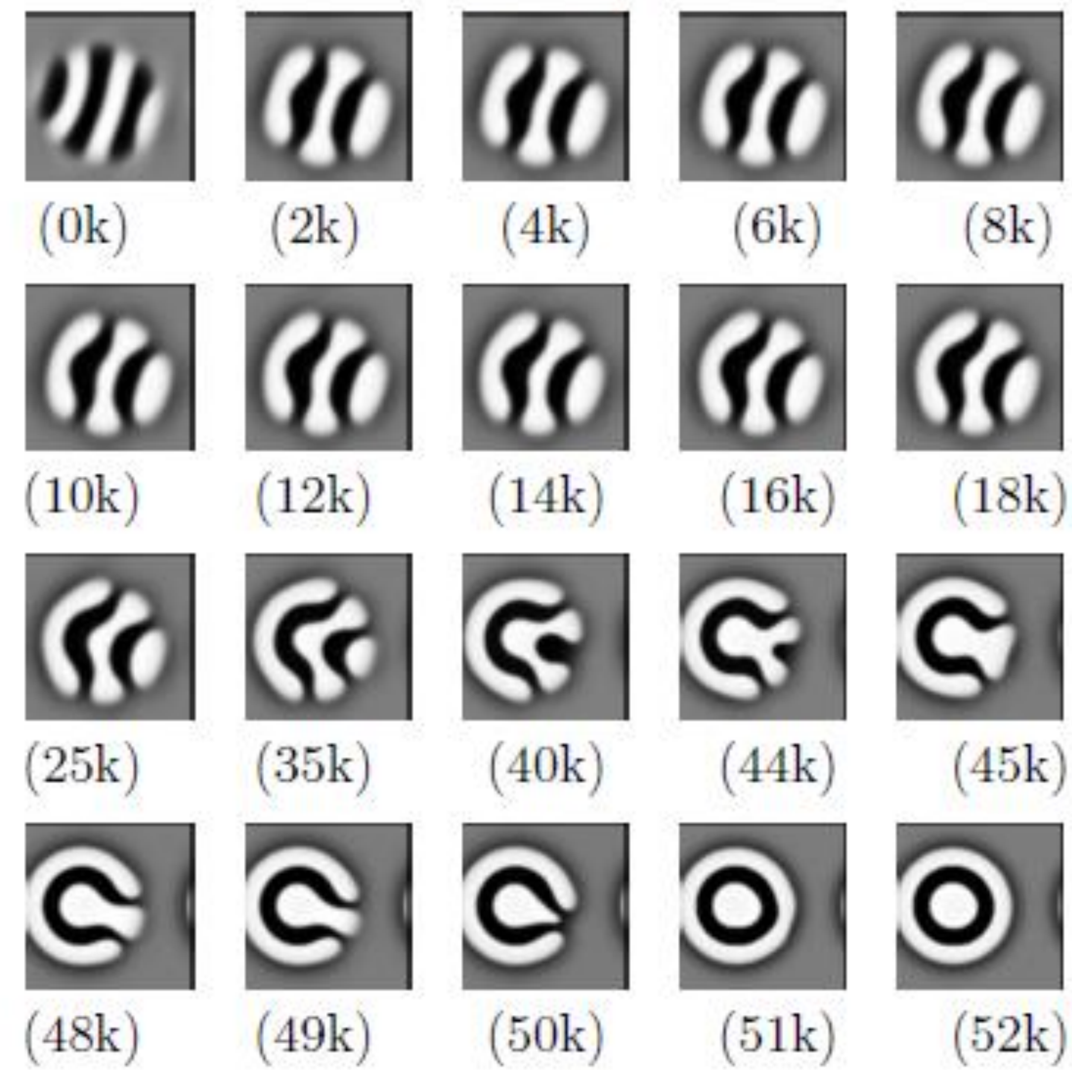


Reverse-onion?

$b_1 > 0$ b1 > 0



$b_1 < 0$ b1 < 0



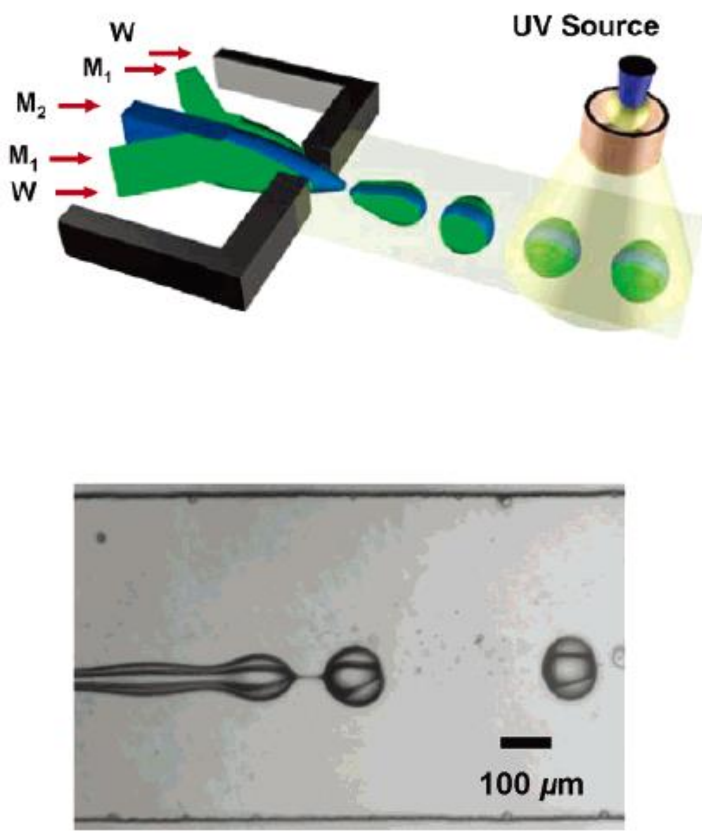
Our model has predicted this phenomenon.

Reverse onion is also confirmed experimentally!

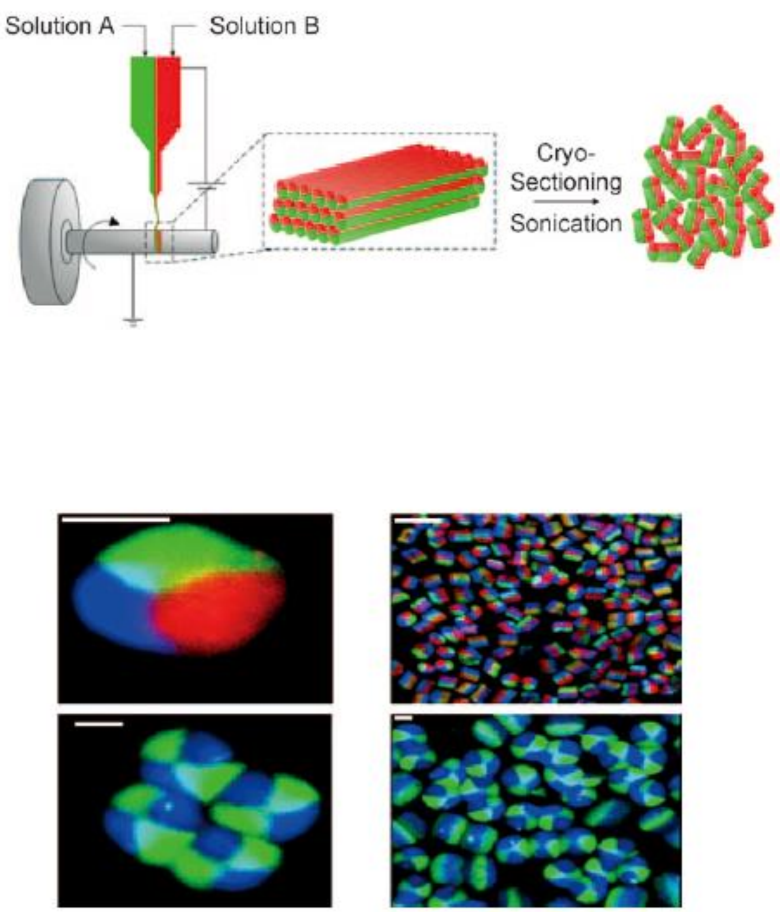
Asyura
（阿修羅）
3 different homopolymers

Not easy to make submicron particles

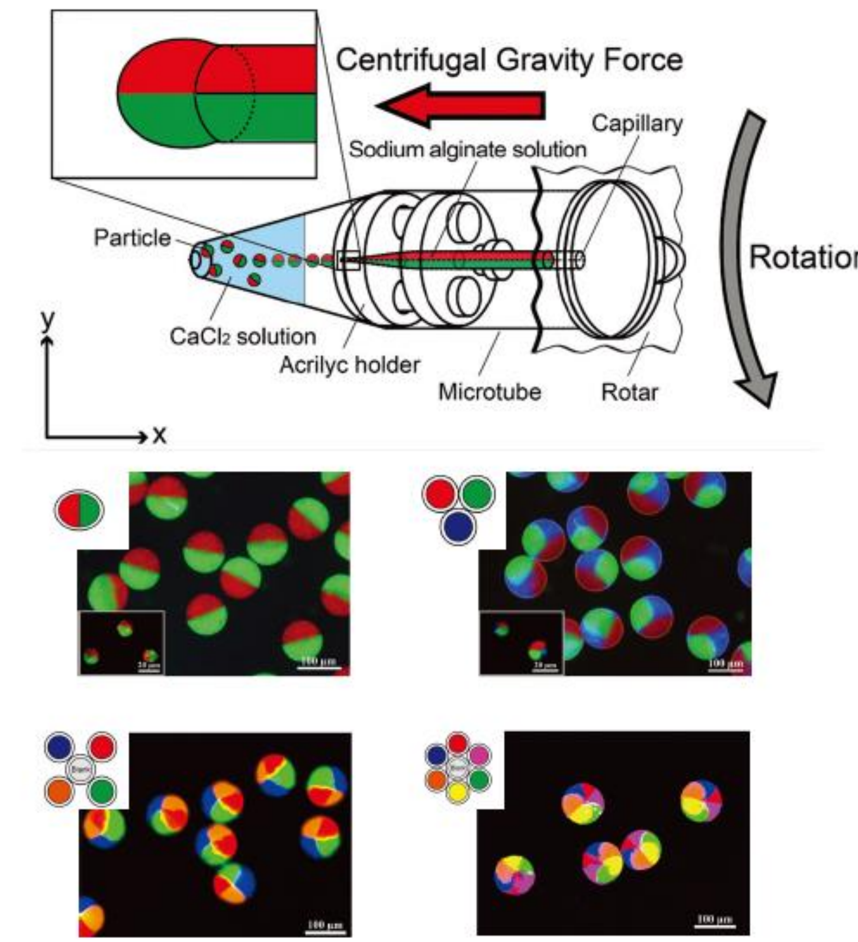
(a)



(b)



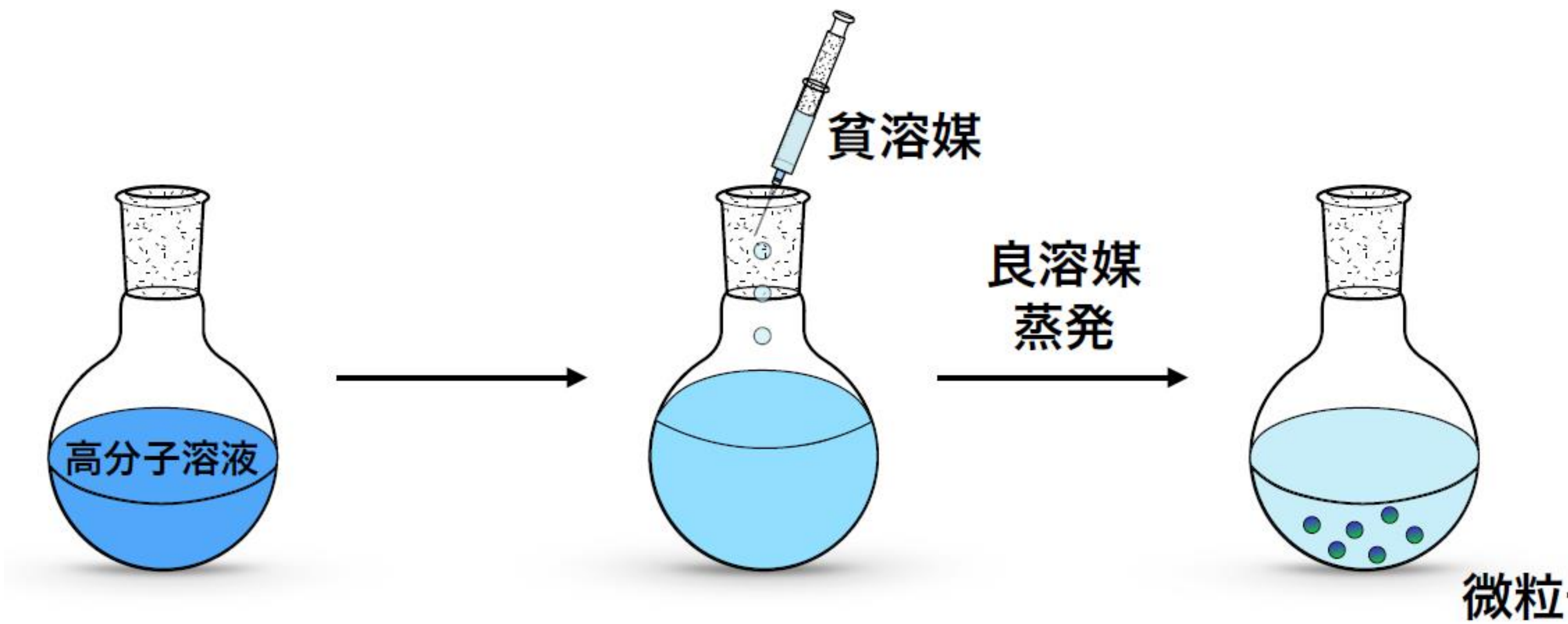
(c)



Z. Nie et al., J. AM. CHEM. SOC, 2006, 128, 9408-9412 S. Bhaskar et al., Macromol. Rapid Commun. 2008, 29, 1655-1660 K. Maeda et al., Adv. Mater., 2012, 24, 1340-1346

手法	Microfluidic tips	electrohydrodynamic cojetting	centrifuge droplet shooting
直径	c.a. 100 μm	several 10~100μm	c.a. 100 μm
構造	層状分割	等分割	等分割
材料	光硬化性樹脂	PLGA, NIPAM etc.	アルギン酸

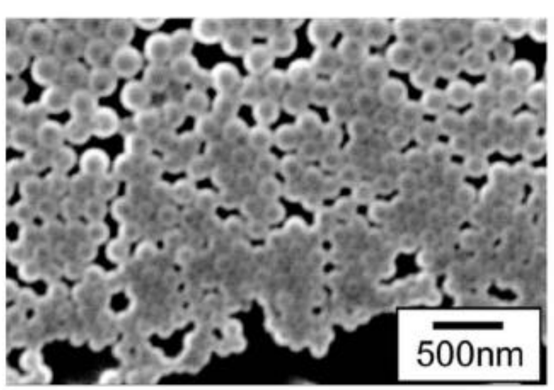
Self-ORganized Precipitation method (SORP)



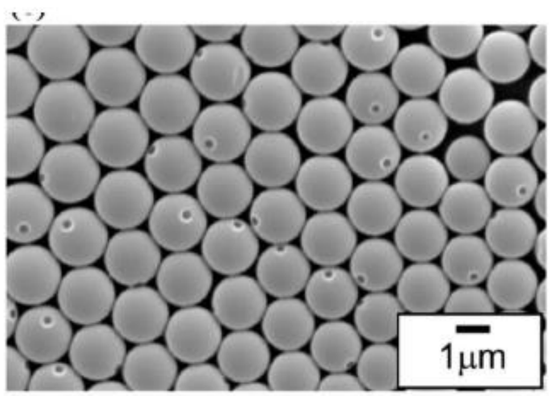
Self-
ORganized
Precipitation
(SORP) method

Possible to make sub-micron particles

サブミクロンサイズの
微粒子を作製可能



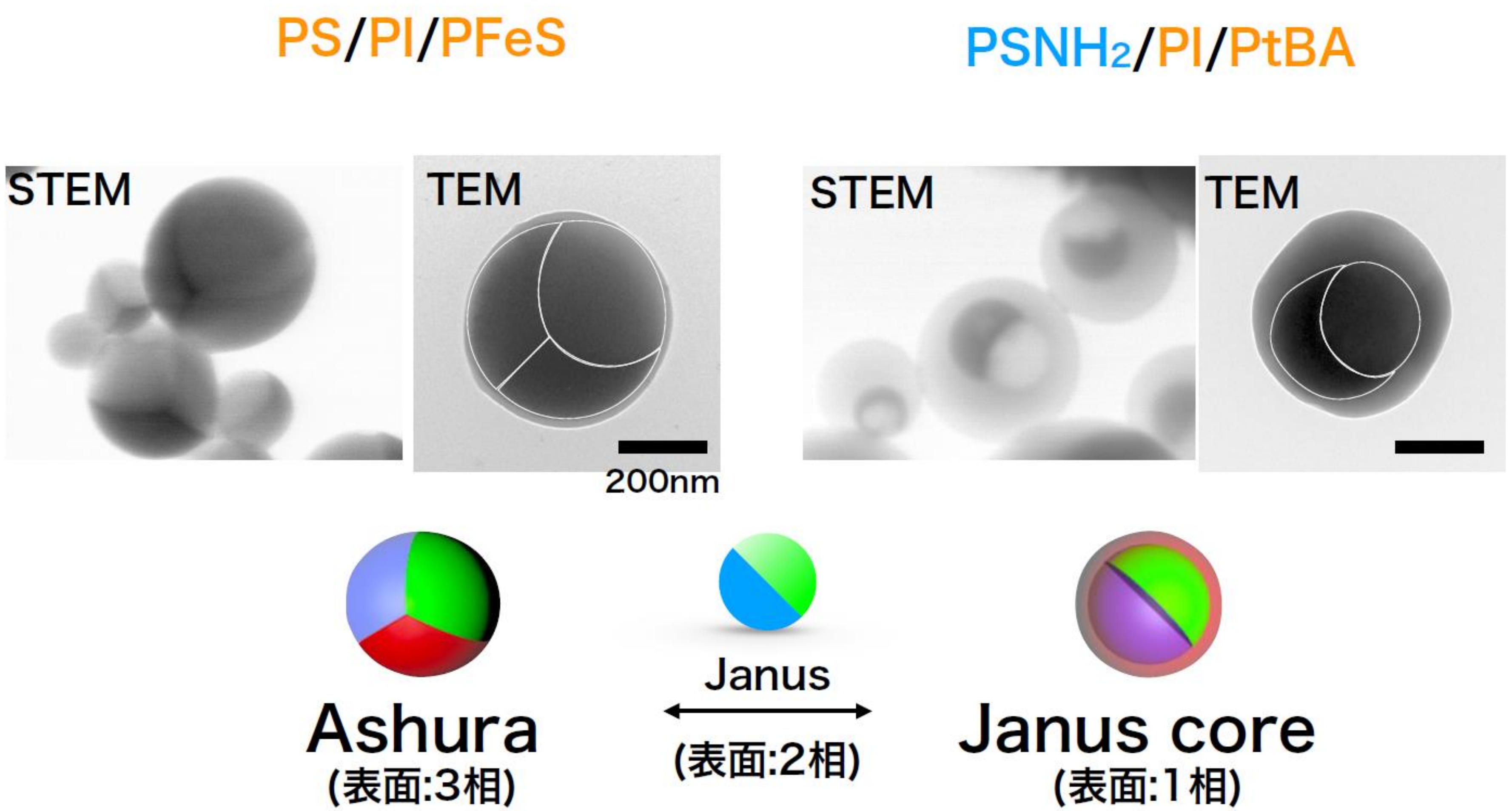
diameter : 200~300nm



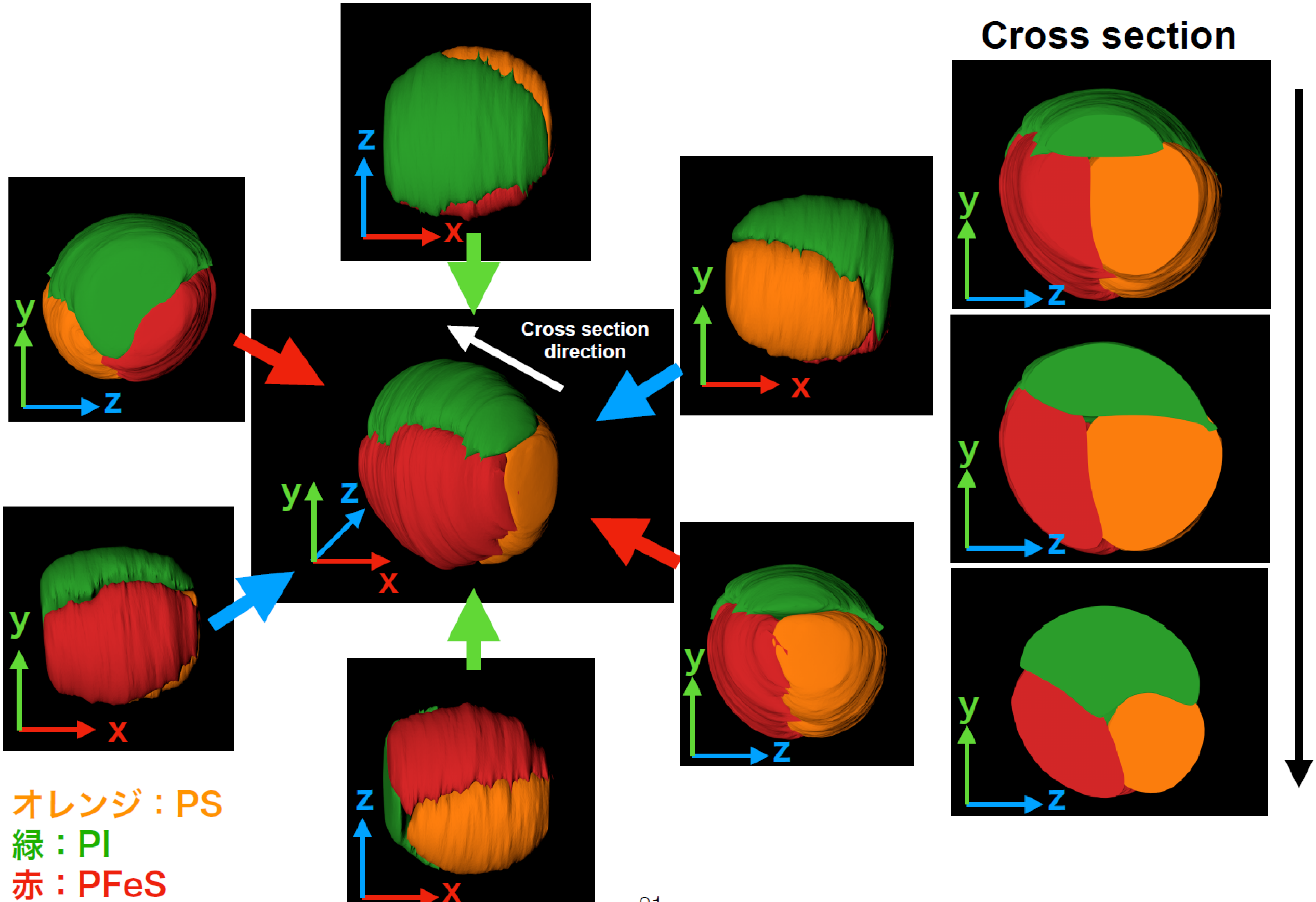
diameter : ~1.5μm

H.Yabu et al., Chaos 2005, 15, 047505

3 homopolymer blends

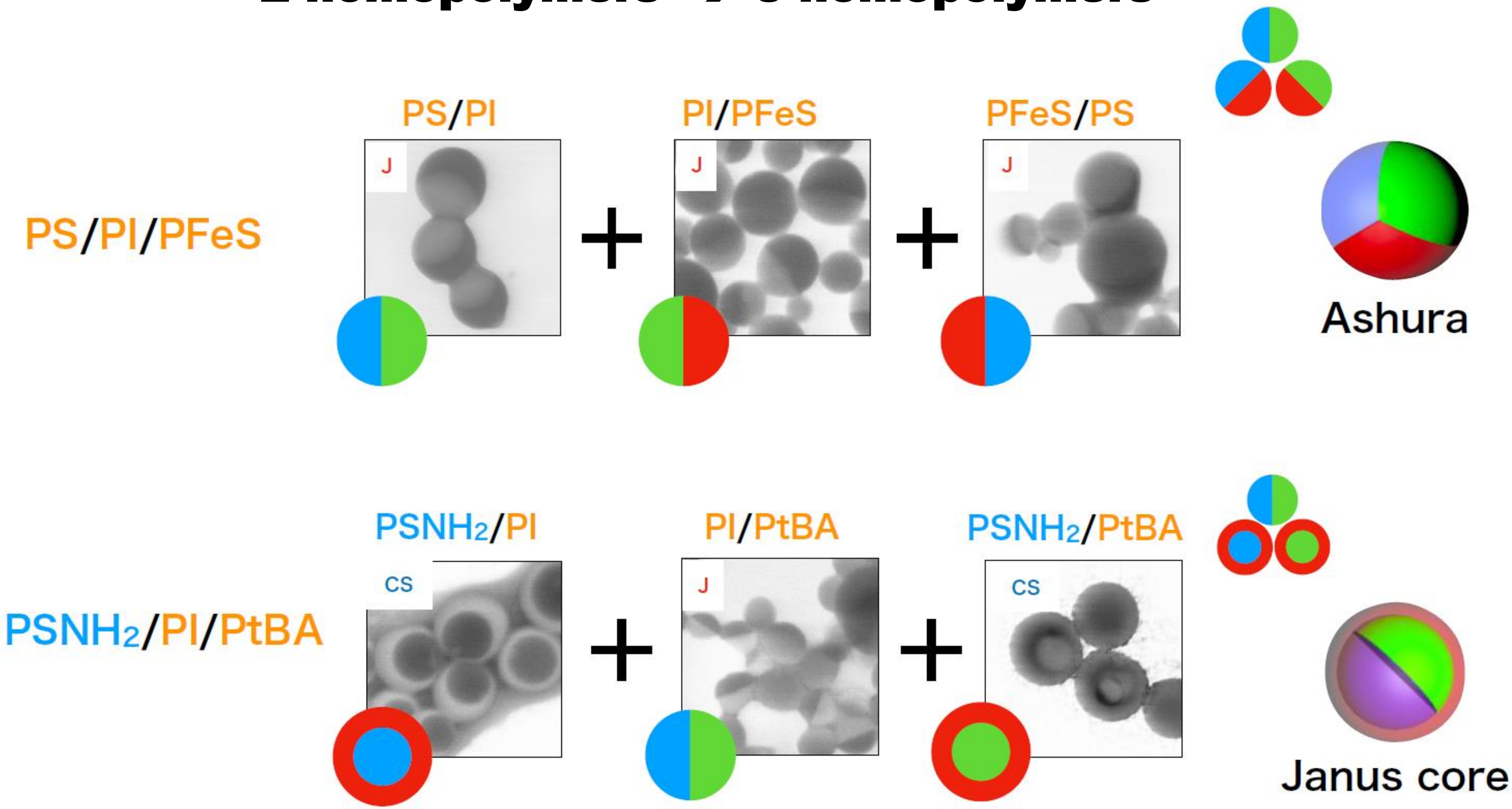


Electron Tomograpy of Asyura particles



オレンジ：PS
緑：PI
赤：PFeS

2 homopolymers → 3 homopolymers



Free energy for Ashura

Ashura Particles: Experimental and Theoretical Approaches for Creating Phase-Separated Structures of Ternary Blended Polymers in Three-Dimensionally Confined Spaces, ACS-omega (in press),
Yutaro Hirai, Edgar Avalos, Takashi Teramoto, Yasumasa Nishiura and Hiroshi Yabu

4-component model
3 homopolymers (v,w,z)+shape u

$$F \equiv F_{\epsilon_u,\epsilon_v,\epsilon_w,\epsilon_z}(u,v,w,z) = \int_\Omega \left\{ \frac{\epsilon_u^2}{2}|\nabla u|^2 + \frac{\epsilon_v^2}{2}|\nabla v|^2 + \frac{\epsilon_w^2}{2}|\nabla w|^2 + \frac{\epsilon_z^2}{2}|\nabla z|^2 + W(u,v,w,z) \right\} dr,$$

$$W = \frac{(u^2-1)^2}{4} + \frac{(v^2-1)^2}{4} + \frac{(w^2-1)^2}{4} + \frac{(z^2-1)^2}{4} + \underbrace{b_{10}\, u * v + b_{12}\, u * w +}_{\text{Affinity to solvent}}$$

$$b_{13}\, u * z + \underbrace{b_2 \left(u * v^2 + u * w^2 + u * z^2\right)}_{\text{Shape}} + \underbrace{b_3 (v * w + v * z + w * z)}_{\text{Interaction}} + \boxed{b_4\, v * w * z}$$

Triple junction

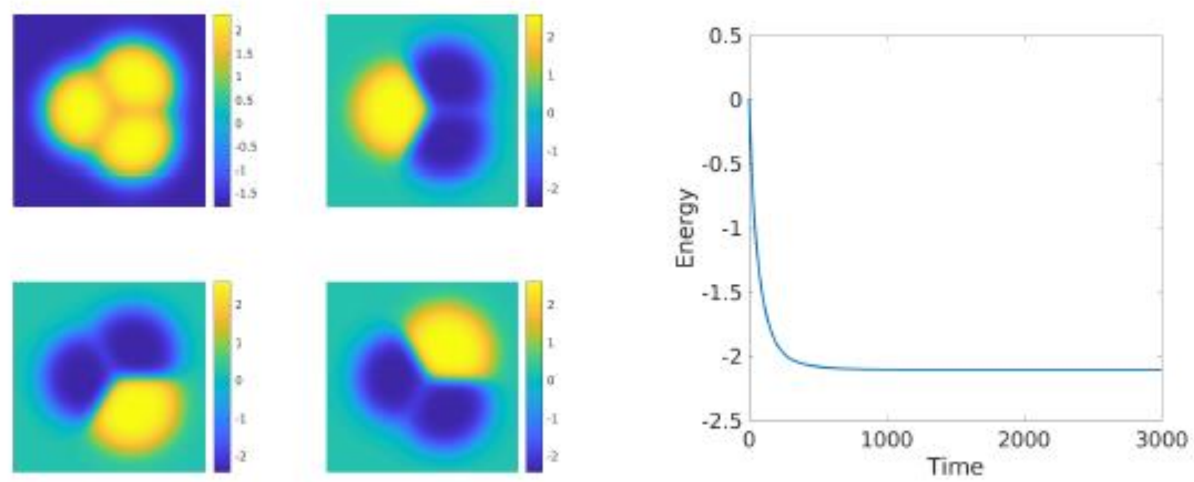
Listing 1: Parameters of simulation of Ashura particle

```
dx  =0.02;          % cell size
dt  =0.00004;       % time step
epsu=0.08;
epsv=0.04;
epsw=0.04;
epsz=0.04;
b10=-0.08;
b12=-0.08;
b13=-0.08;
b2=-0.8;
b3=0.4;
b4=-0.5             % b4<0 for ashura
tauU=1.0;
tauV=1.0;
tauW=1.0;
tauZ=1.0;
a=3.0;              % stability parameter
nsteps=4000;
L=0.8;              %system size
```

b3 is positive, b4 is negative

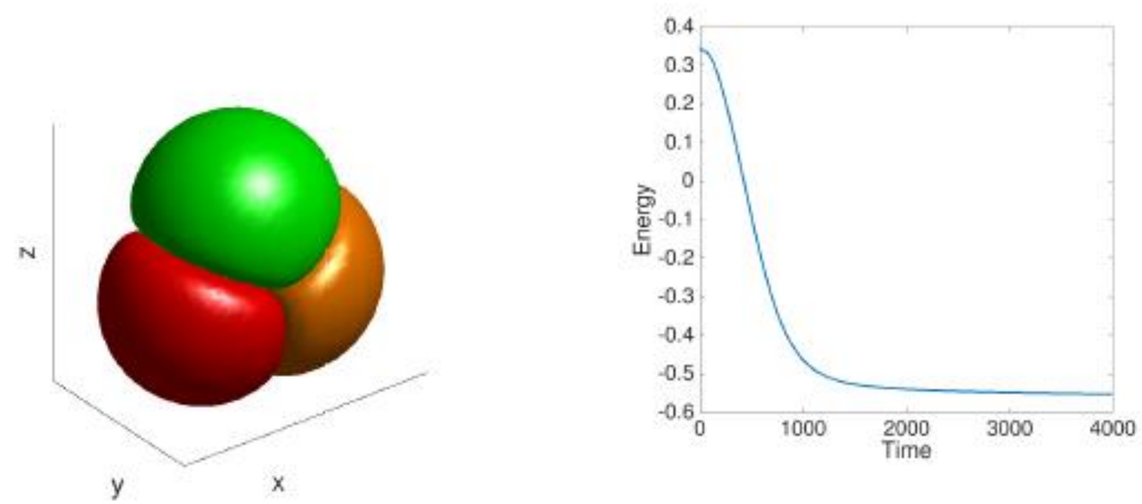
Symmetric for three polymers,
but
we also need cubic term v w z
to keep mutual exclusiveness.

2D・3D Asyura and the energy decay



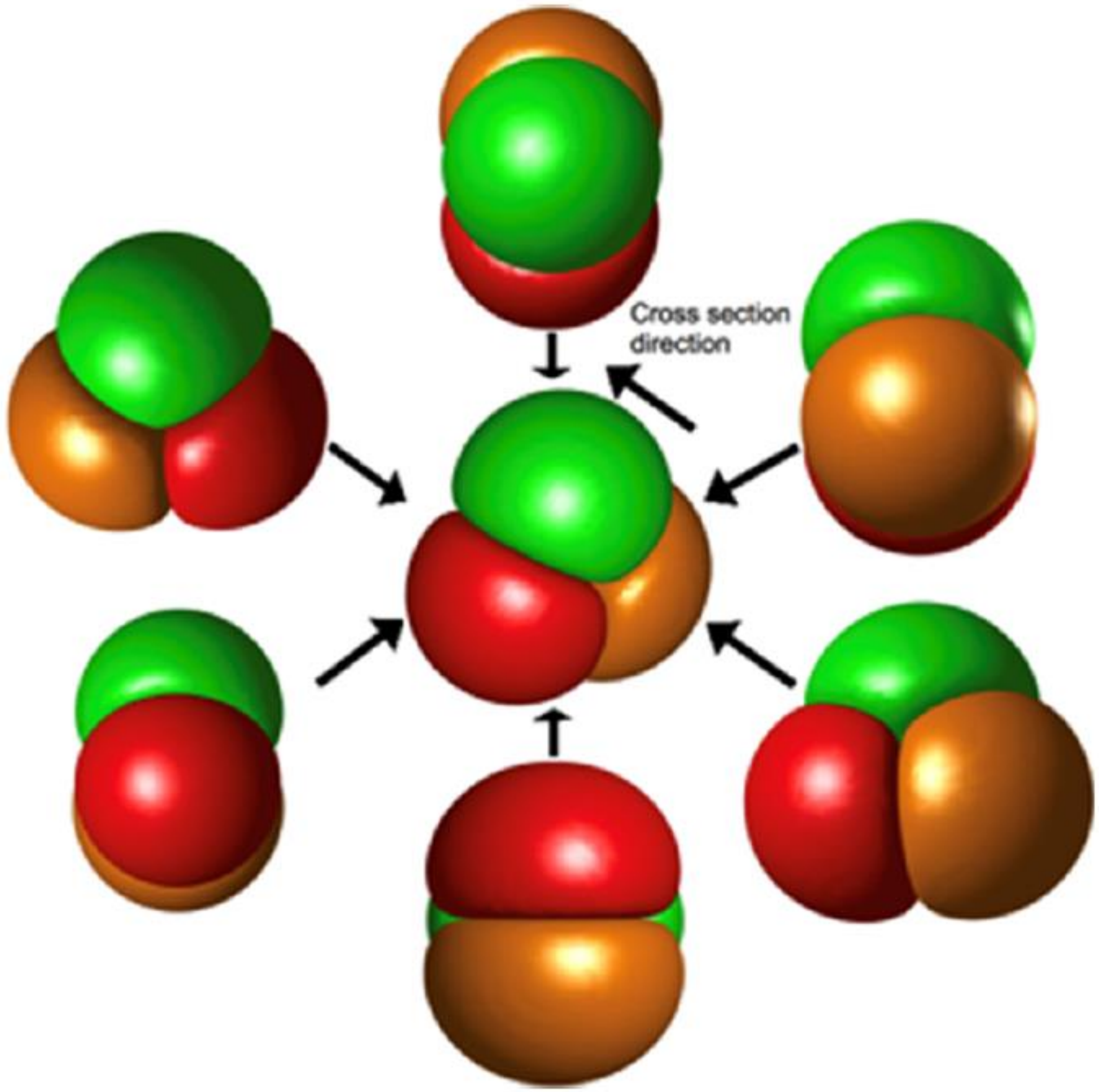
(a) (b)

Figure 1: (a) Steady morphology of Ashura particle in two dimensions with components u, v, w, and z. (b) The energy as function of time resulting of adding the terms in eq. 1.



(a) (b)

Figure 2: (a) Steady morphology of Ashura particle in three dimensions with components u, v, w, and z. (b) The energy as function of time resulting of adding the terms in eq. 1.

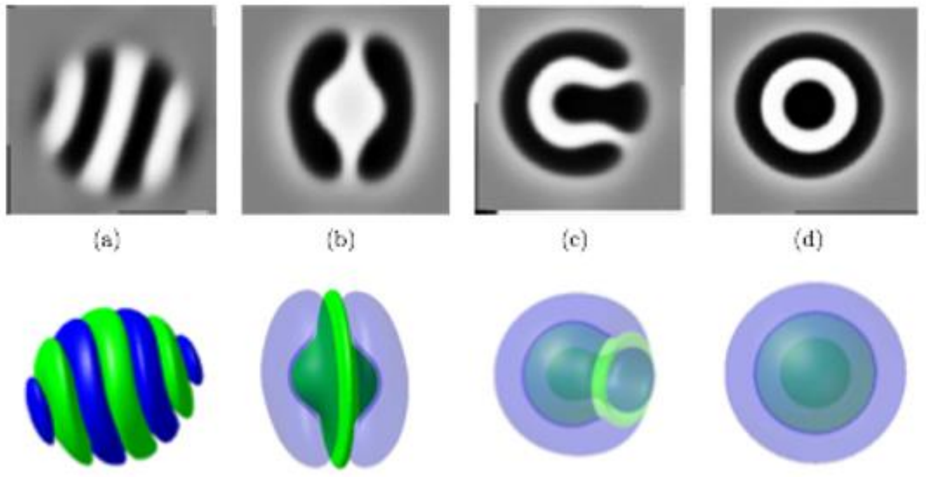


Parameters: $\epsilon_u = 0.08$, $\epsilon_v = \epsilon_w = \epsilon_z = 0.04$, $b_1 = -0.08$, $b_2 = -0.8$, $b_3 = -0.4$, $b_4 = -0.5$, $b_5 = 0.0$, $\tau_u = \tau_v = \tau_w = \tau_z = 1.0$.

.

Summary

- Control of shape and phase separation
  - Confinement dynamics: u-dynamics
  - Micro-phase separation: v-dynamics
  - Metamorphose when temperature is changed.



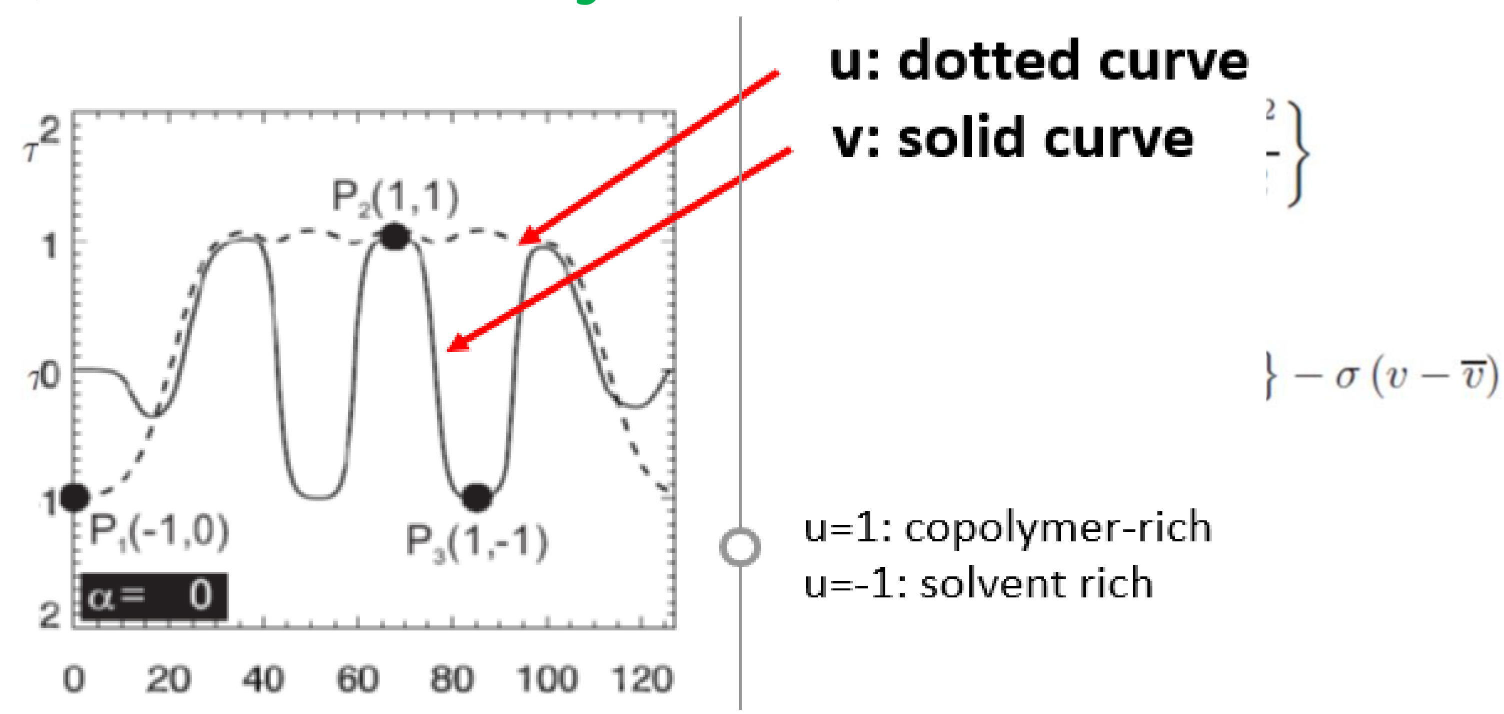
- Ashura particles (confined three polymers) can be produced both in experiments and simulations.
  - Cubic term vwz is necessary!

For reference: http://www.wpi-aimr.tohoku.ac.jp/nishiura_labo/index-e.html

Mathematical challenge

- Variational problem
  - Rugged landscape $$F_{\epsilon,\sigma}(u,v) = \int_{\Omega} \left\{ \frac{\epsilon_u^2}{2} |\nabla u|^2 + \frac{\epsilon_v^2}{2} |\nabla v|^2 + W(u,v) + \frac{\sigma}{2} \left| (-\triangle)^{-1/2} (v - \overline{v}) \right|^2 \right\} dr$$
  - Atlas for meta-stable patterns
- Singular Perturbation (Slow-Fast system) for 1D
  - 8d ODE problem

  for stationary patterns



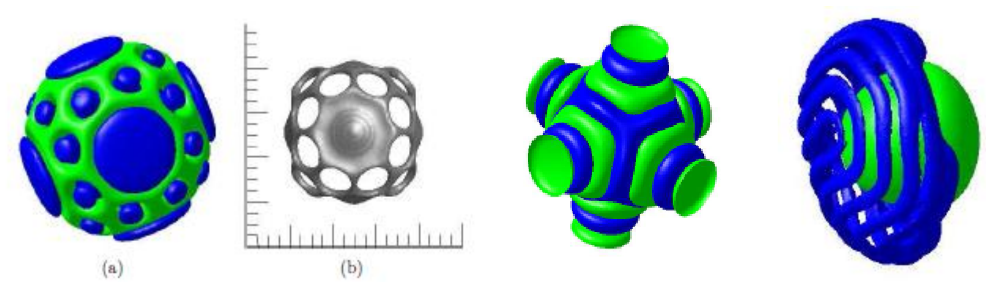
Thank you for listening!

Modeling and Computation

Edgar Avalos Takashi Teramoto

Experiments

Hiroshi Yabu



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