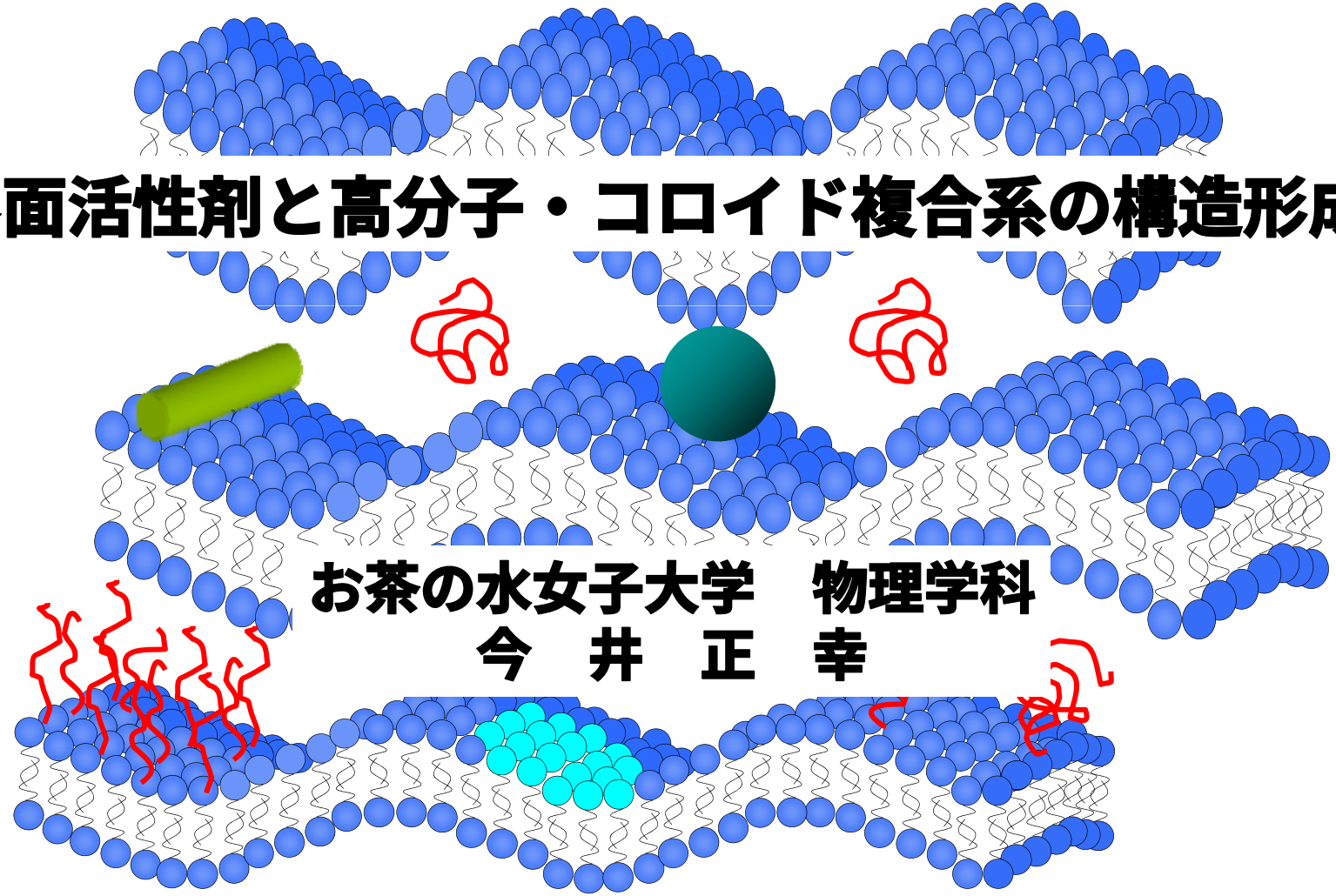
界面活性剤と高分子・コロイド複合系の構造形成



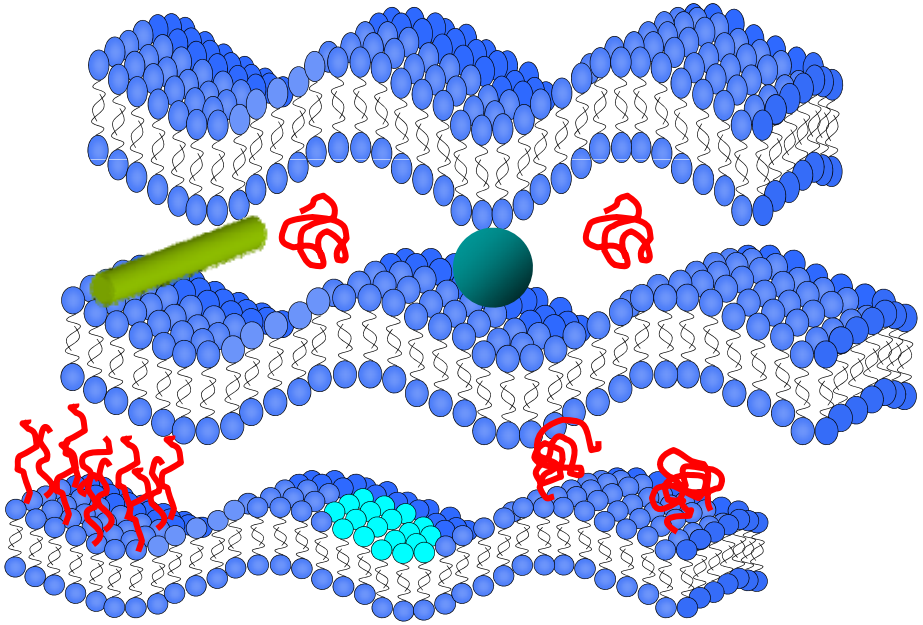
お茶の水女子大学　物理学科
今　井　正　幸

1. ソフトマター複合系

系の内部自由度が大きい為、その構造の安定性が
エントロピー的な要因に強く支配されている物質群

異種のソフトマターを複合させ、幾何学的に
エントロピーを競合させる事による構造形成

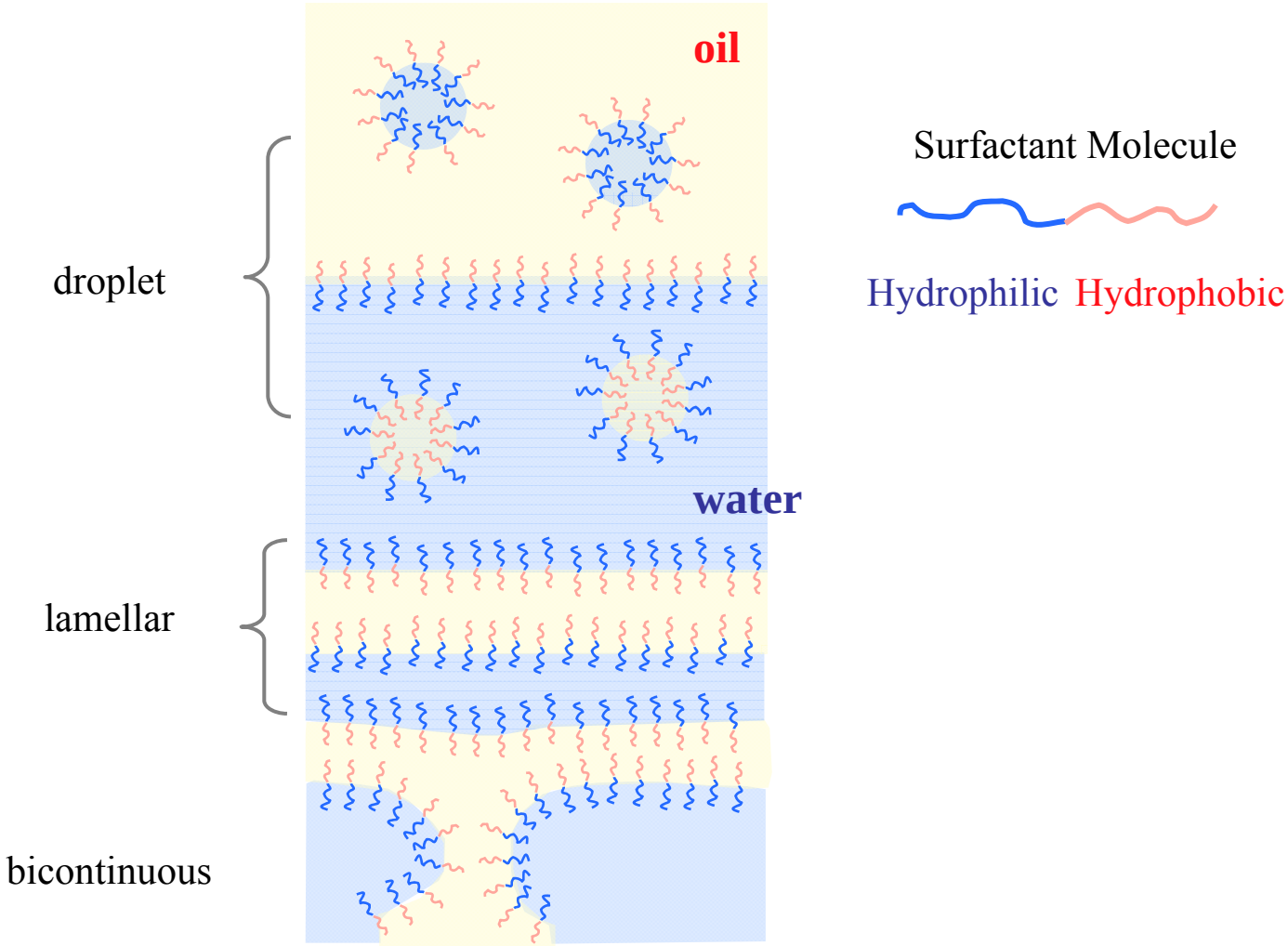
Membrane Based Soft Matter Complex System



- Membranes + Polymer
- Membranes + Colloids
- Membranes + Liquid Crystal
- Polymer Anchored Membrane

2. Nano-Droplets Confining Polymer Chains

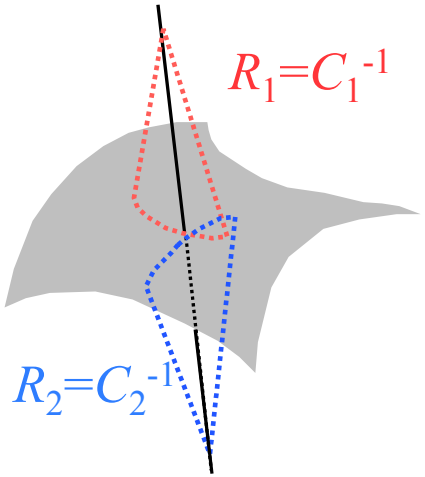
Microemulsion (surfactant/water/oil system)



Static Structure of Microemulsion

Bending Energy of surfactant mono-layer

$$f = \frac{1}{2}\kappa(2H - 2C_0)^2 + \bar{\kappa}K$$



Mean curvature : $H = \frac{C_1 + C_2}{2}$, Gaussian curvature : $K = C_1 \cdot C_2$

C_0: spontinuous curvature, κ: bending modulus, $\bar{\kappa}$: Gaussian modulus,

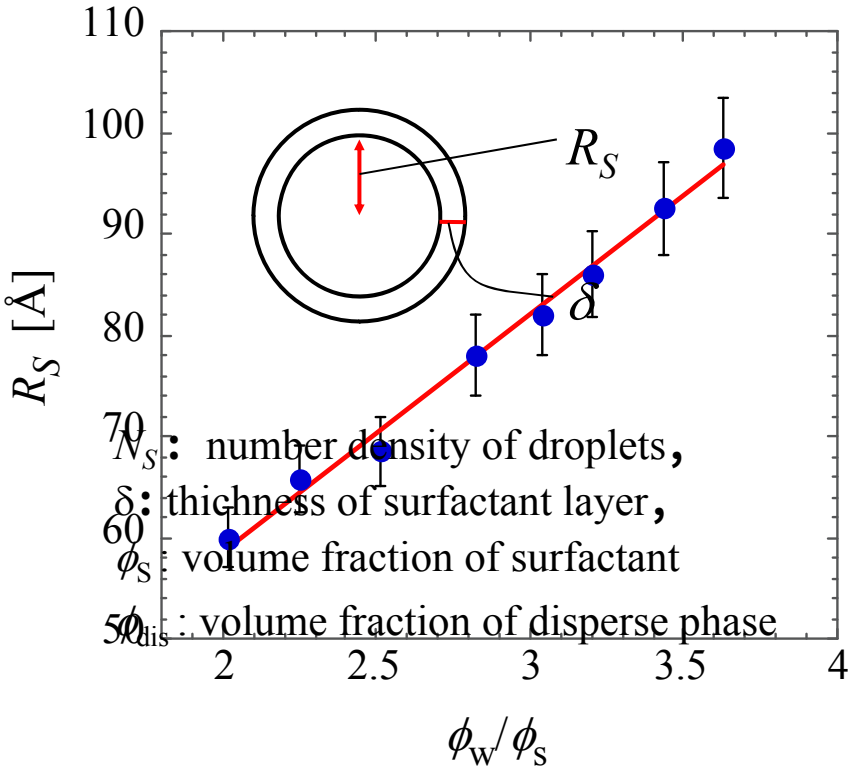
Constrain of incompressibility

In the case of sphere

$$N_S \cdot 4\pi R_S^2 \delta = \phi_S$$

$$N_S \cdot \frac{4}{3}\pi R_S^3 = \phi_{dis}$$

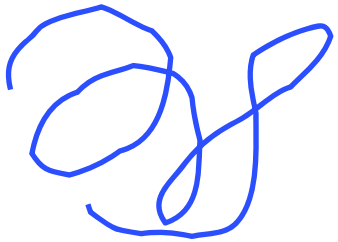
$$\therefore R_S = 3\delta \frac{\phi_{dis}}{\phi_S}$$



N_S: number density of droplets,
δ: thichness of surfactant layer,
ϕ_S: volume fraction of surfactant
ϕ_{dis} : volume fraction of disperse phase

Nano-Structures Confining Polymer Chains

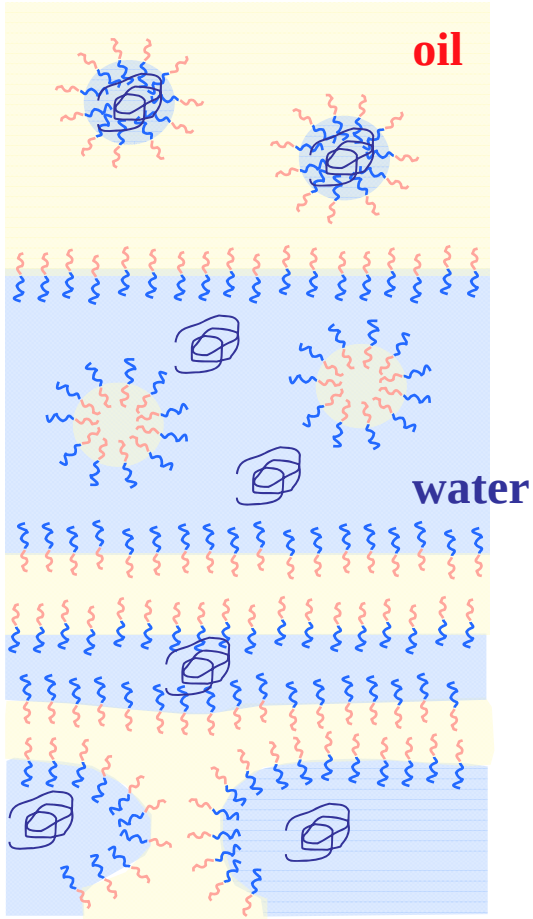
Polymer chain



$$F_{chain} = F_{conf} + F_{ex}$$

F_{conf}:conformational energy of polymer

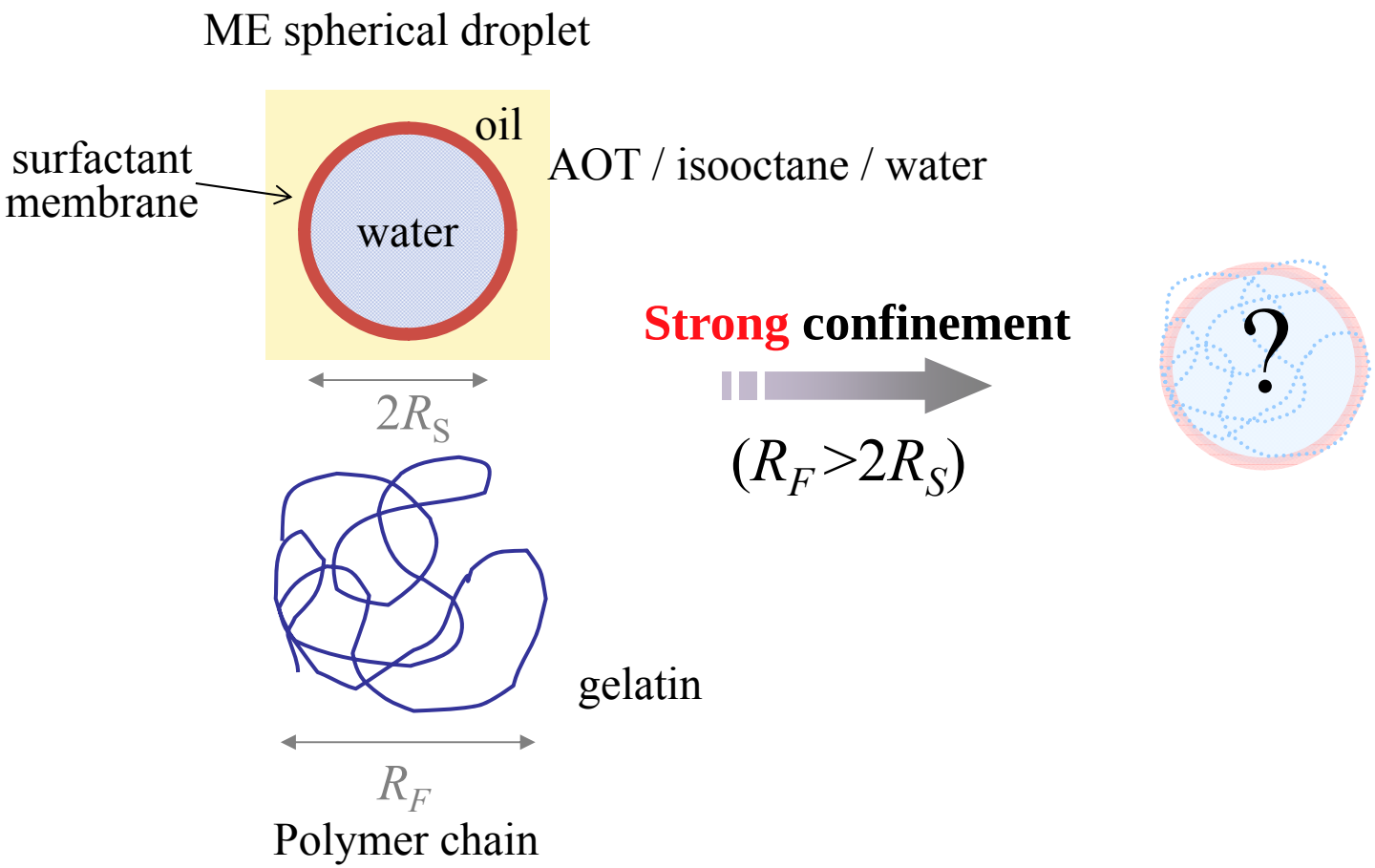
F_{ex} : excluded volume effect of segments



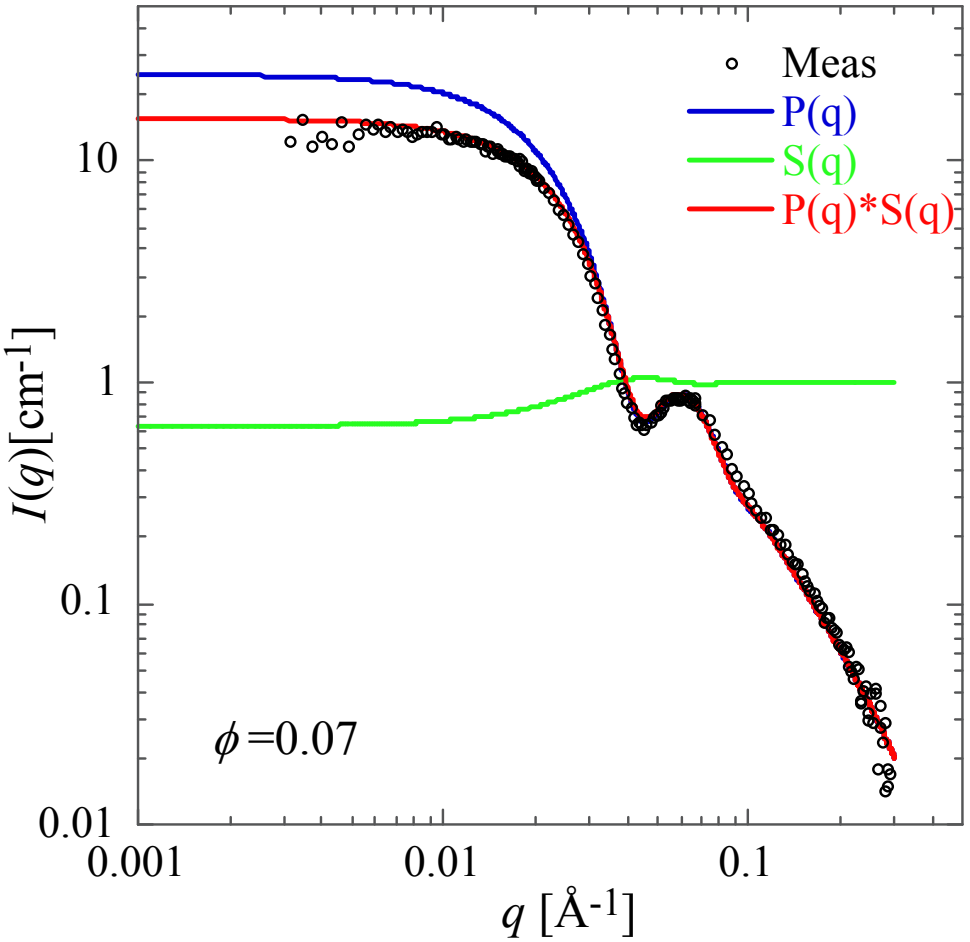
ME

good container for confining polymer chain

Nano-Droplets Confining Polymer Chains



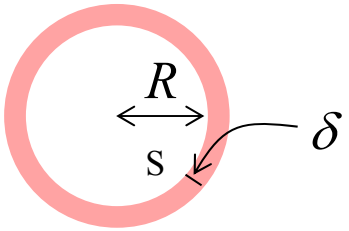
Nano-Droplets without Polymer Chains



Scattering function of the spherical model

$P(q)$: spherical shell model

$S(q)$: Percus-Yeivic potential model



Fitting results

R_S = 59.8Å

δ = 8.0Å

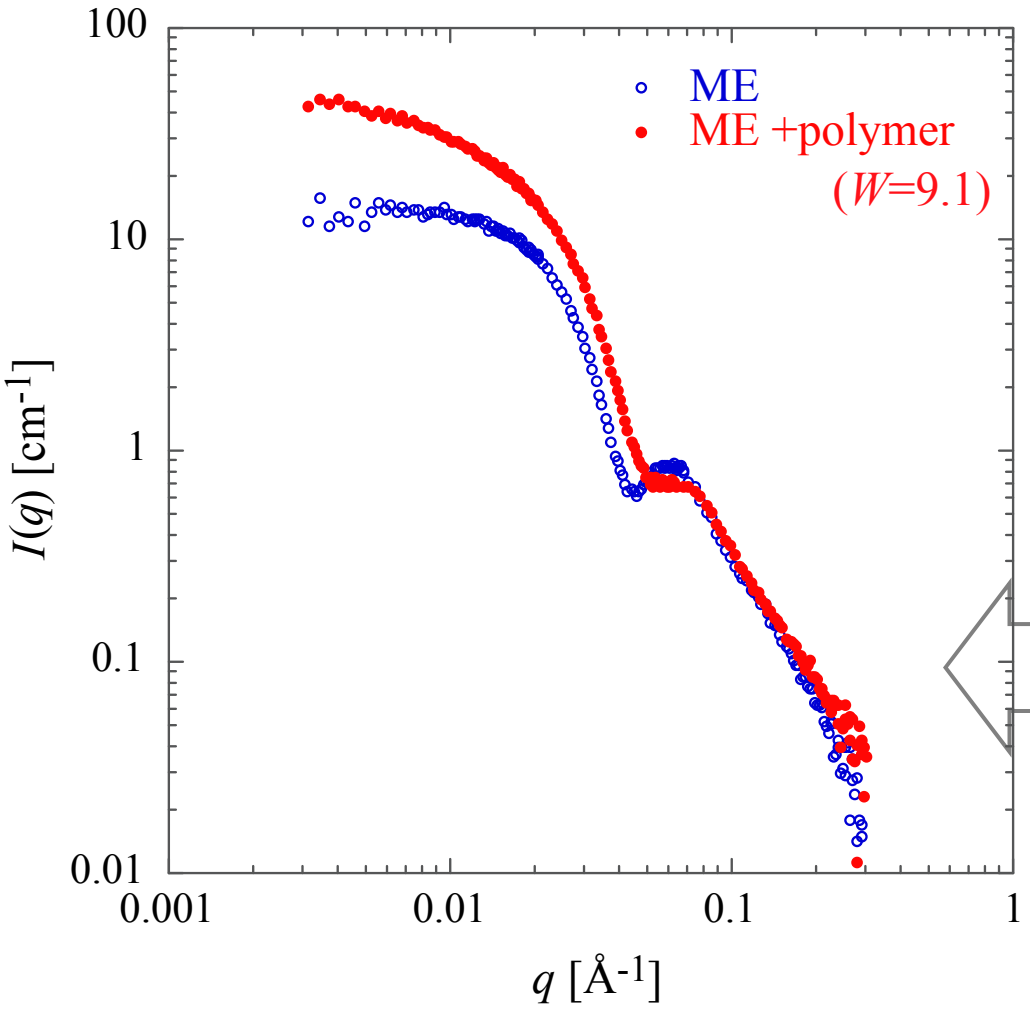
□ □ 0.141

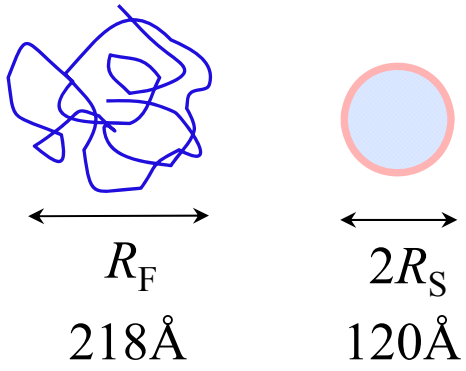
$N_S = 5.1 \times 10^{16}$[cm^{-3}]

ME droplet shape : **sphere**

SANS profiles of ME with strong confinement of polymer

Degree of confinement : $R_F/2R_S = 1.82$

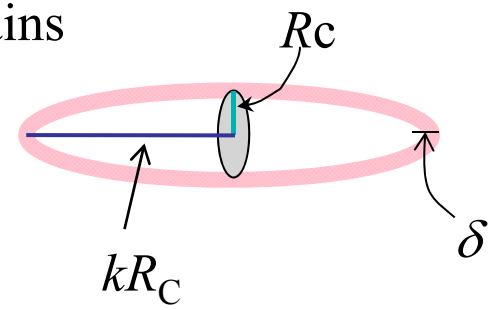


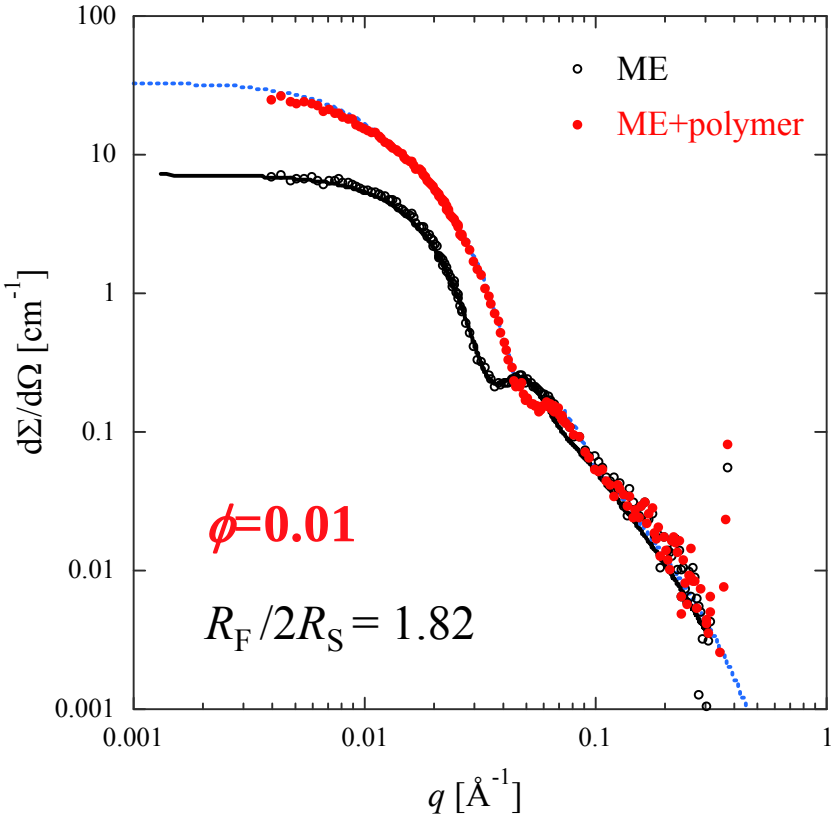


By confining the polymer chains strongly,

- peak position shifted to high q
- scattering intensity increased in the low q region

SANS Profile for Nano-Droplets Confining Polymer Chains





Scattering function of the rod model

$P(q)$: prolate core shell model

$S(q)$: Obtained by Monte Carlo simulation

Fitting results

$R_C = 45.3$Å

$\delta = 8$ Å

$k = 4$

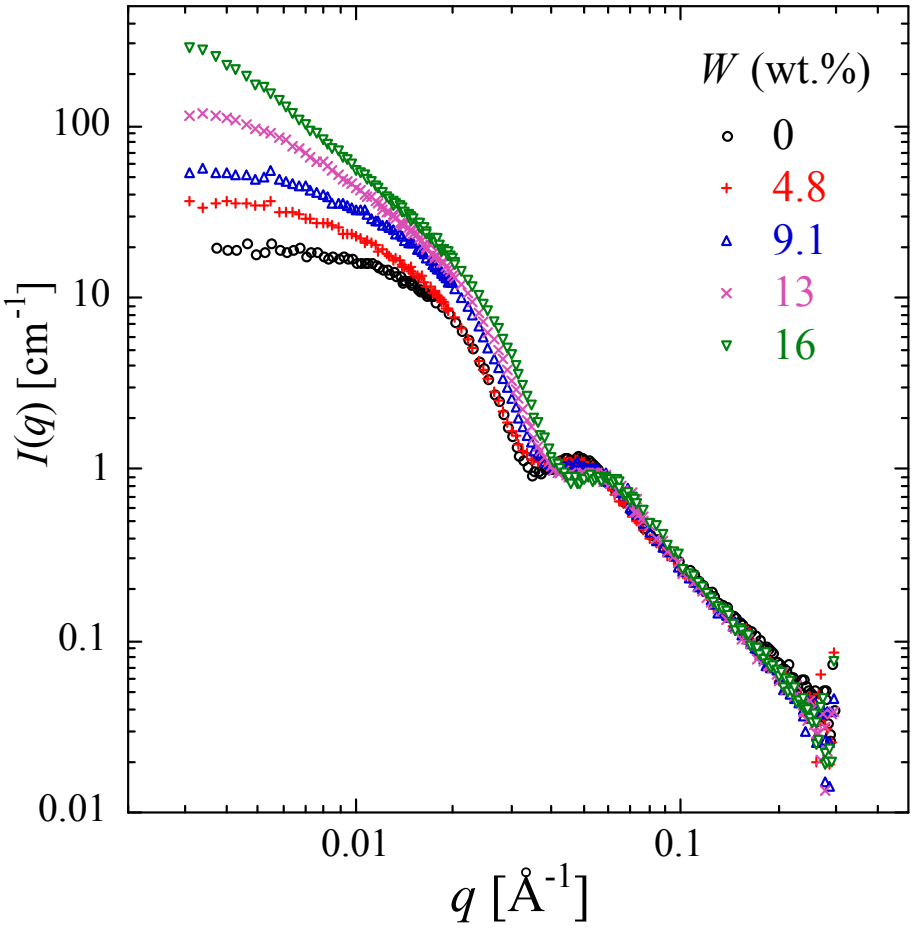
$N_C = 4.0 \times 10^{16}$[cm^{-3}]

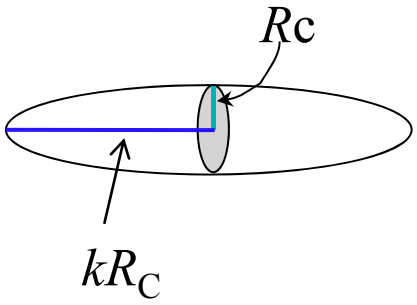
$n_p = 0.8$ chain per one rod-like droplet

Morphology of ME is **changed** from **sphere** to **prolate** by confining the polymer chains strongly.

SANS profiles of ME confining polymer chains at the different *W*

$R_F/2R_S = 1.43$, ϕ=0.07





Fitting results

W	R_C [Å]	k	n_p	$10^{16}N$ [cm^{-3}]
0	76	1	0	2.9
4.8	66	2	0.8	2.3
9.1	62	3	1.8	1.8
13	54.5	6	4.2	1.2
16	51.3	15?	----	----

n_p : average number of [illegible] per droplet

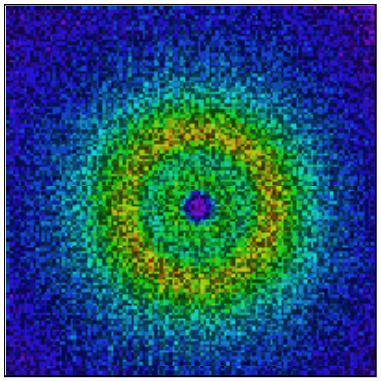
N: droplet density

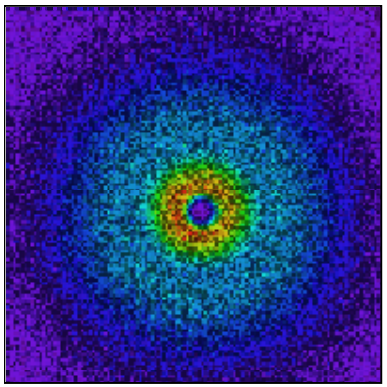
Number of droplets decreased

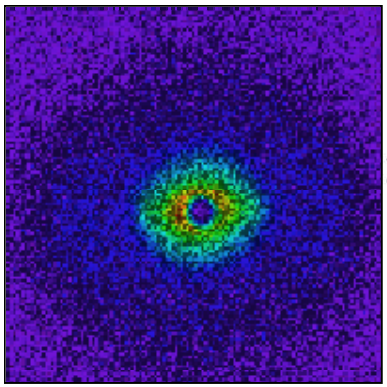
SANS patterns of dense ME droplets confining polymer chains

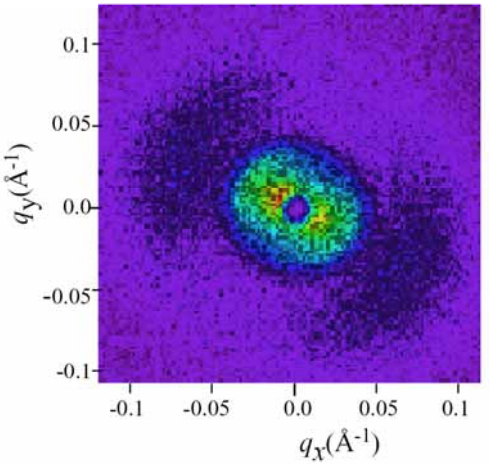
$R_F/2R_S = 1.43$, $\phi = 0.4$

degree of confinement



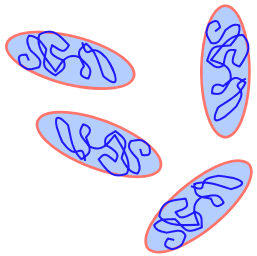




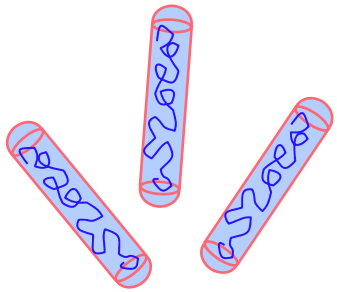


$W = 0$

$W = 13$



$W = 23$

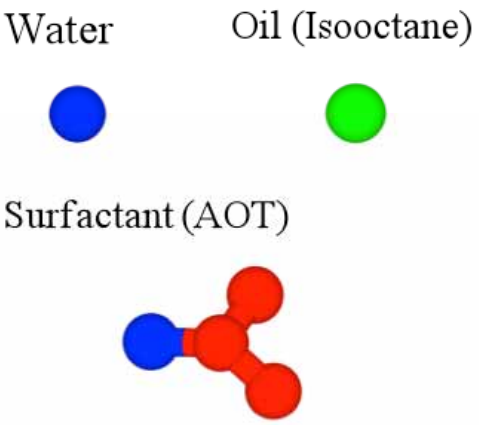


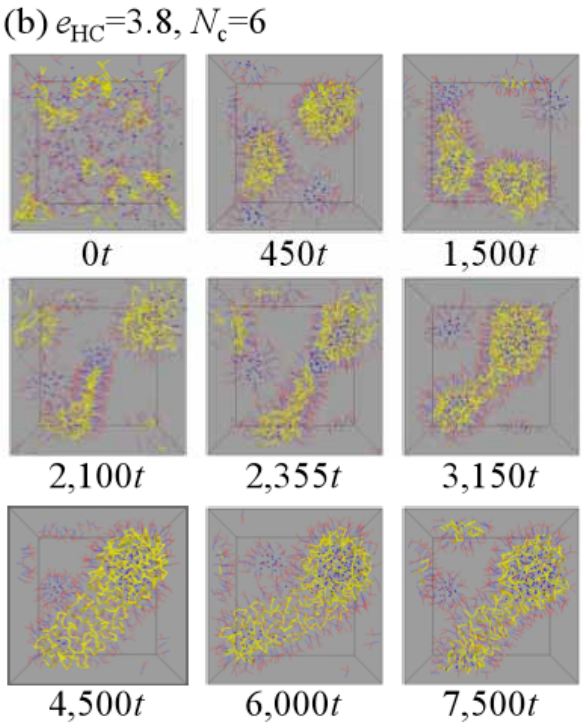
$W = 26$

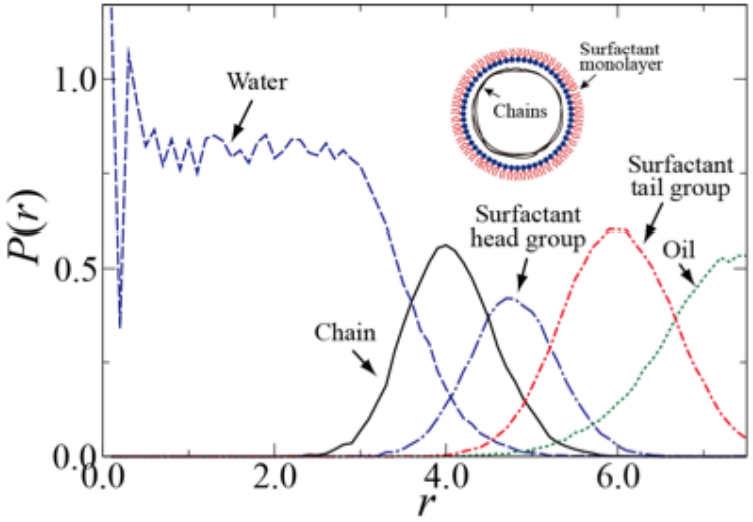
Orientational ordering by polymer confinement

Isotropic-Nematic transition

Molecular dynamics simulation

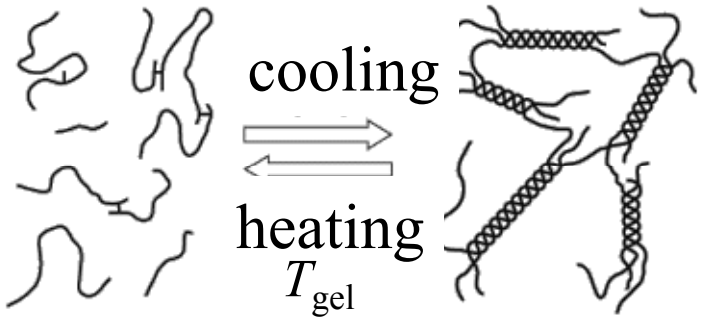




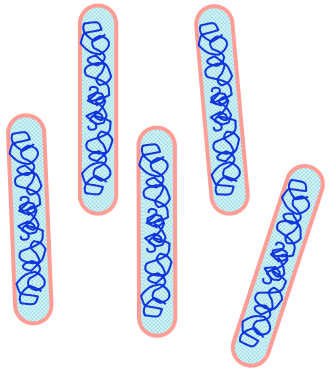


N. Urakami et al., Soft Matter (2011)

Gelatin：associated polymer by temperature



Prolate droplet



$T > T_{gel}$

T_{gel}

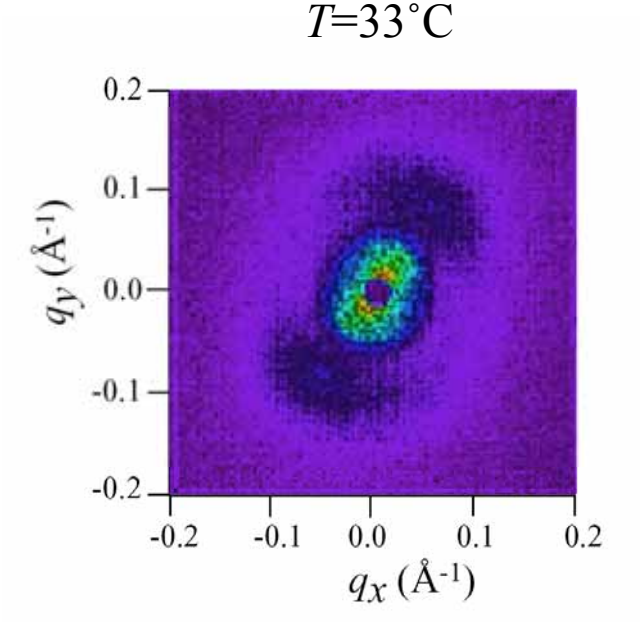
?

$T < T_{gel}$

In dence system

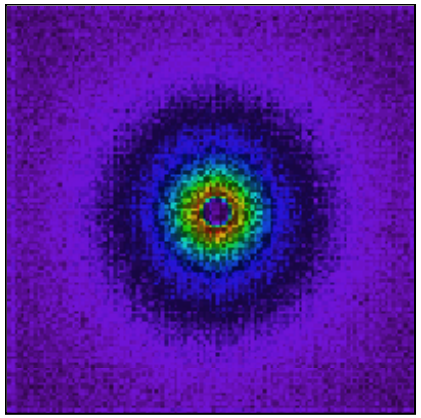
$R_F/2R_S$=1.43, ϕ = 0.4, W=26wt%

$T > T_{gel}$
T=33˚C

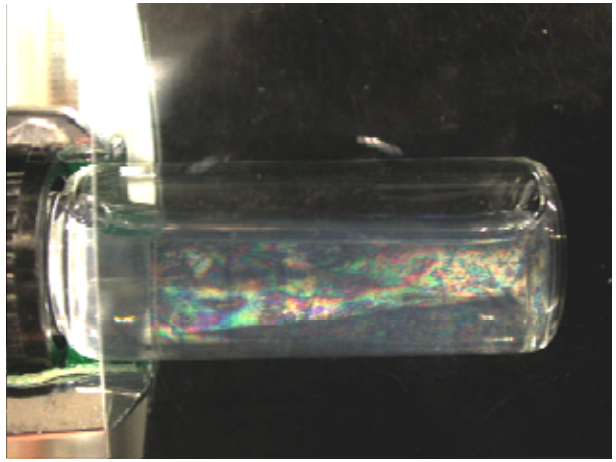


reversible

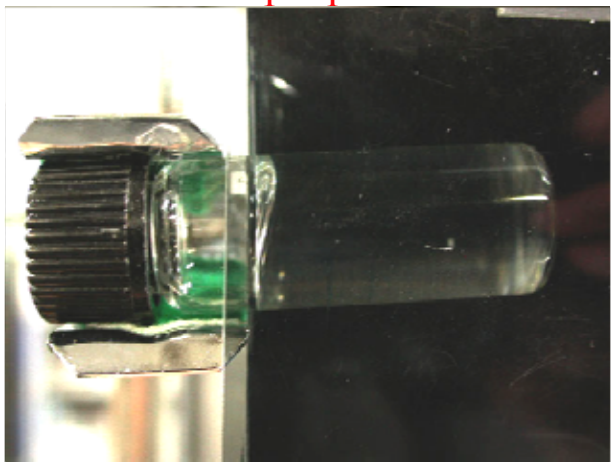
$T < T_{gel}$
T=22˚C



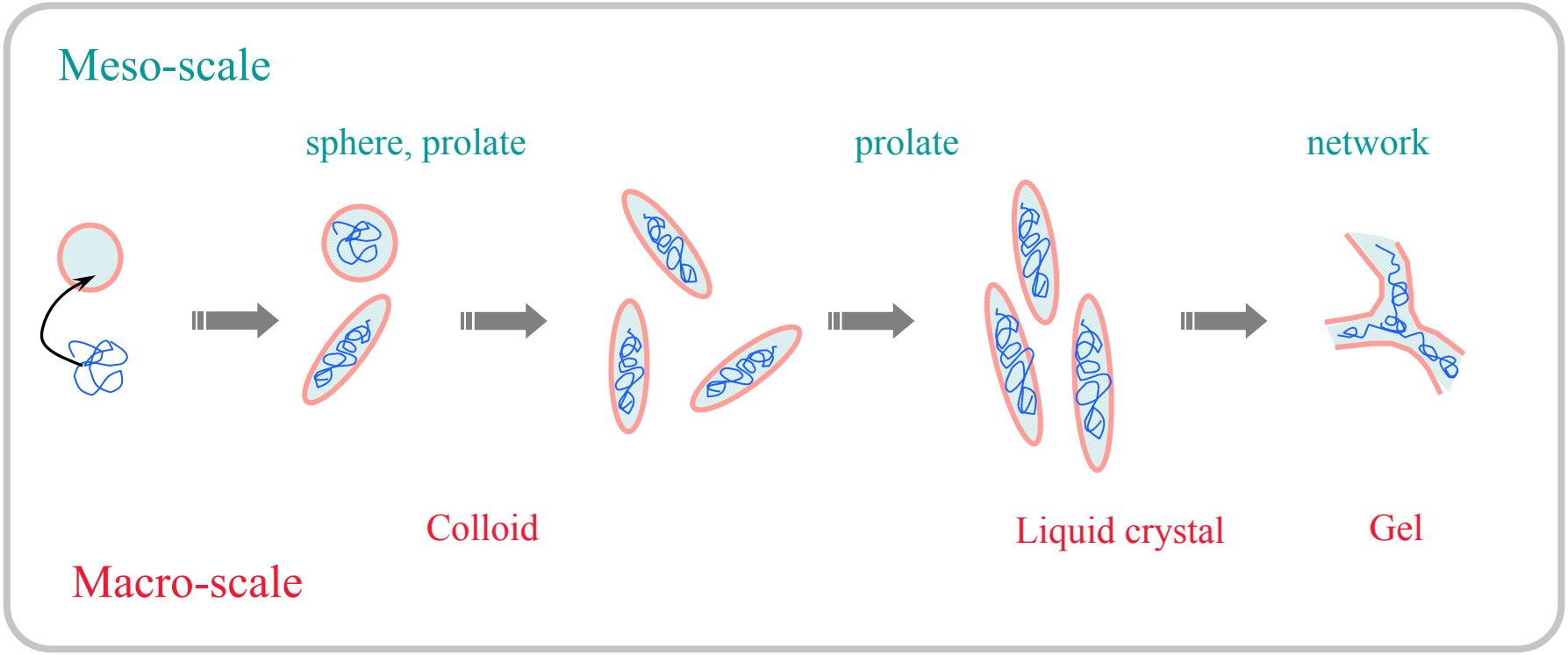
Anisotropic pattern



Isotropic pattern



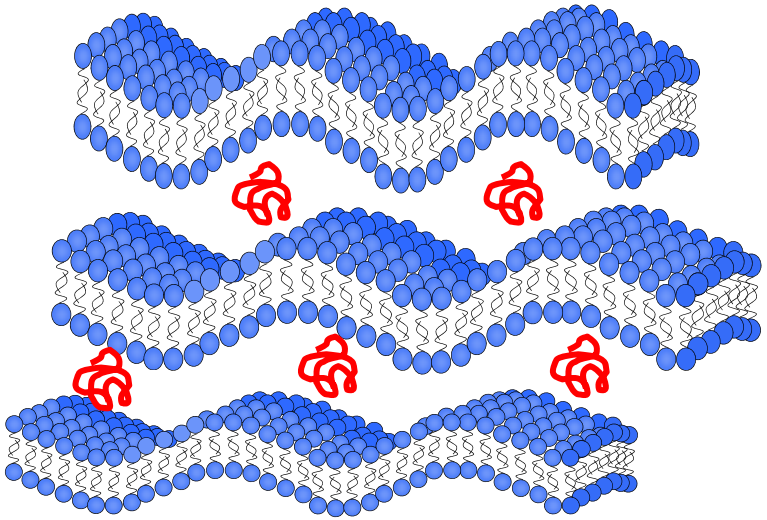
Morphology Transition Induced by Polymer Confinement



K. Nakaya, et al., Europhys. Lett. **71**, 494 (2005)

Lamellar Membranes Confining Guests

Membrane + Polymer

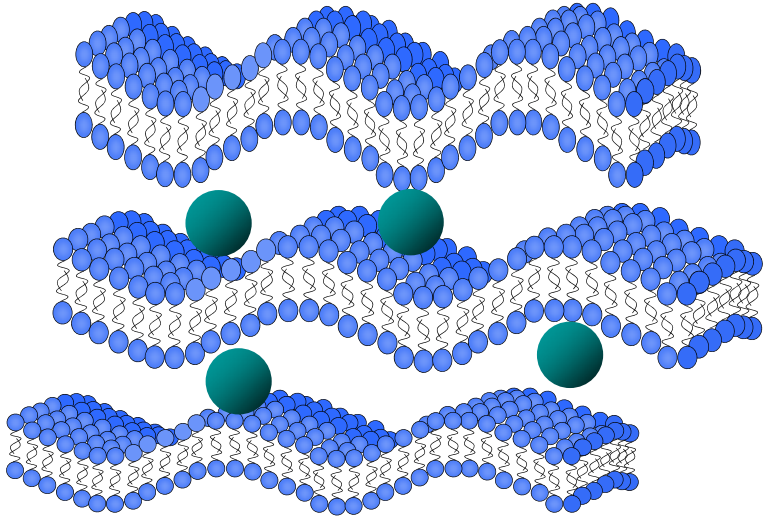


Surfactant : $C_{12}E_5$

$CH_3(CH_2)_{11}(OC_2H_4)_5OH$

Polymer :
Polyethylene Oxide (PEO)
*M*w=20,000 *R*g~100Å

Membrane + Colloid Particles

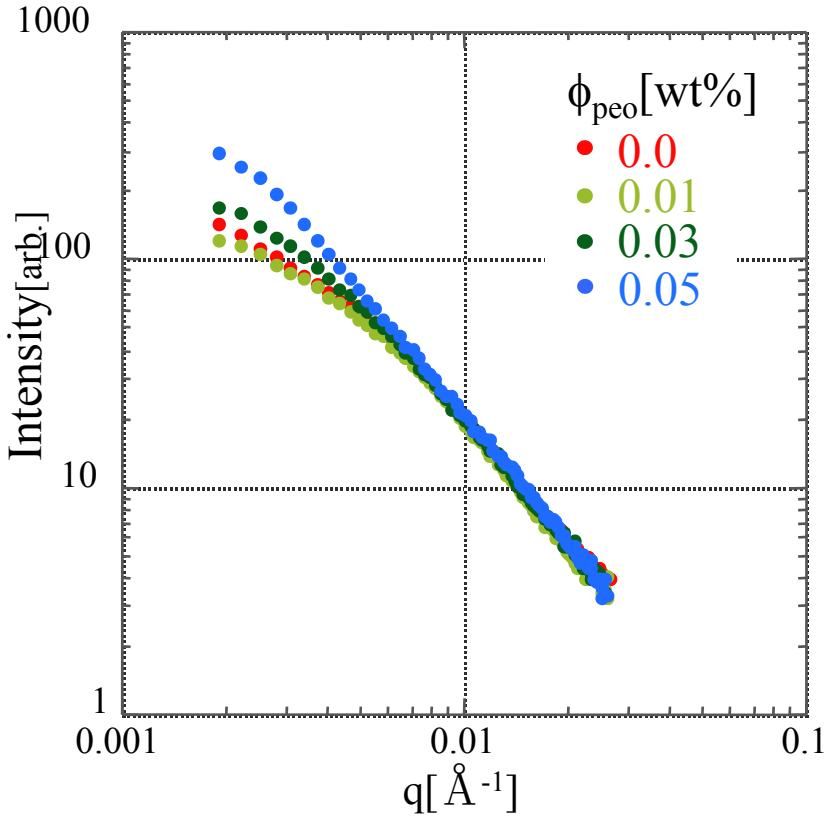


$\bar{d} \approx 800$ Å

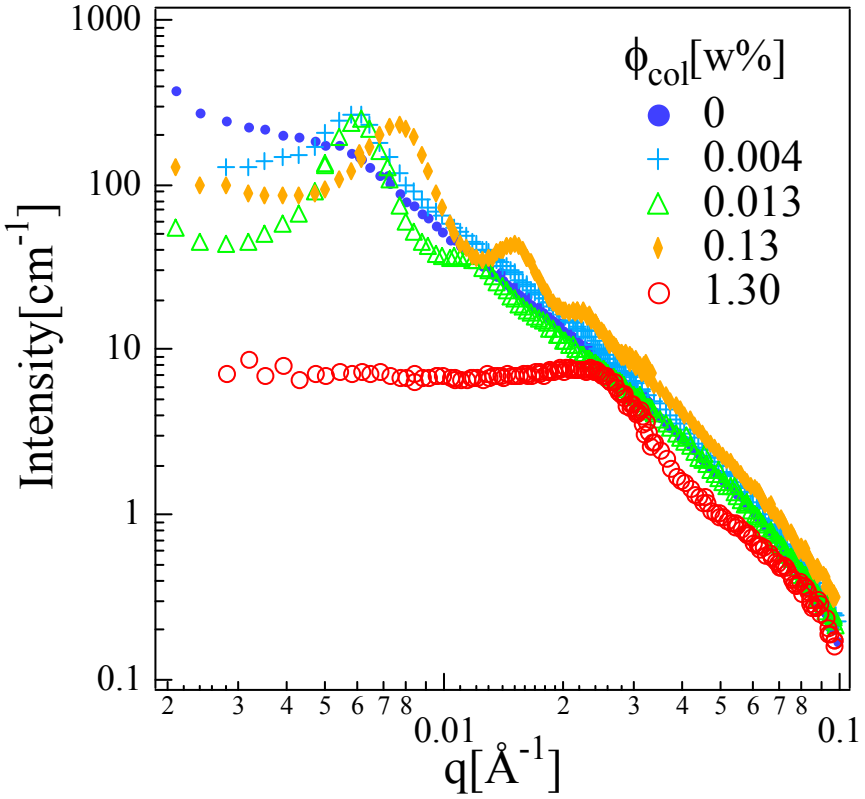
Colloid Particle:
Polystyrene Latex (*R*=100 Å)

Small Angle Neutron Scattering Profiles

$C_{12}E_5$ + Polymer System

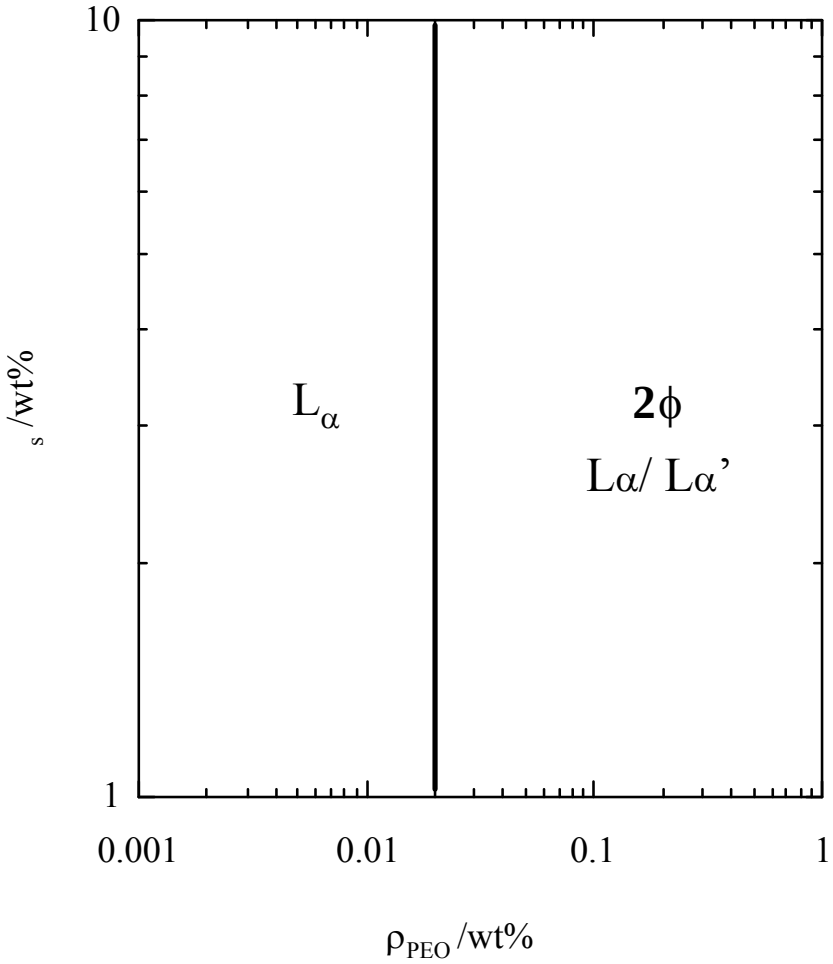


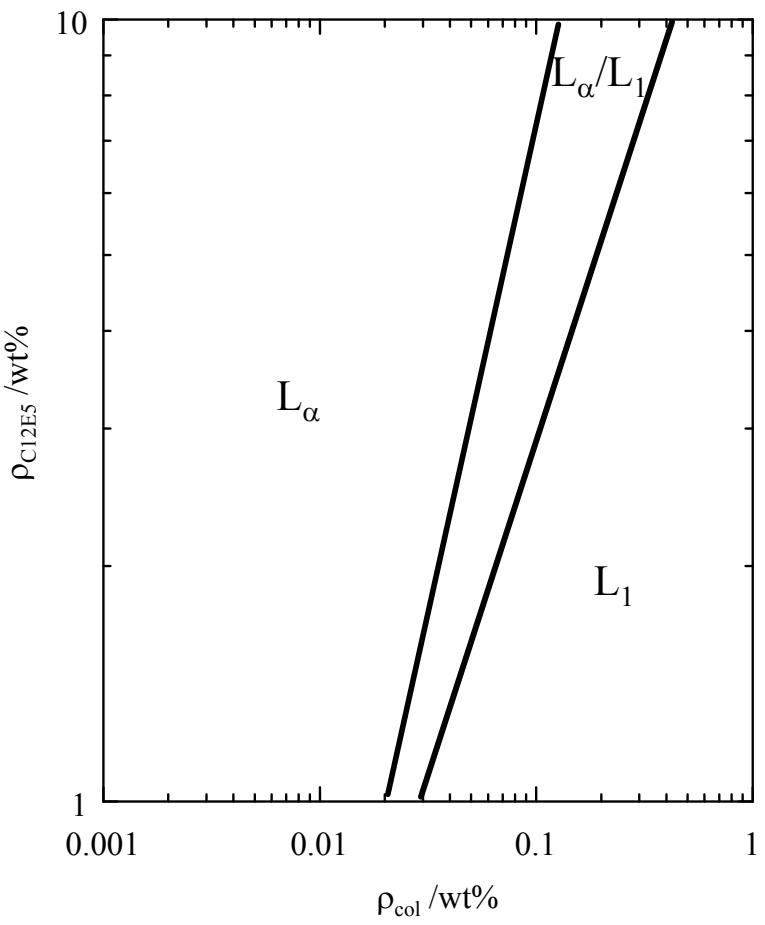
$C_{12}E_5$ + Colloidal Particle System



Phase Diagrams

Lα: Lamellar Phase, L1: Micelle Phase

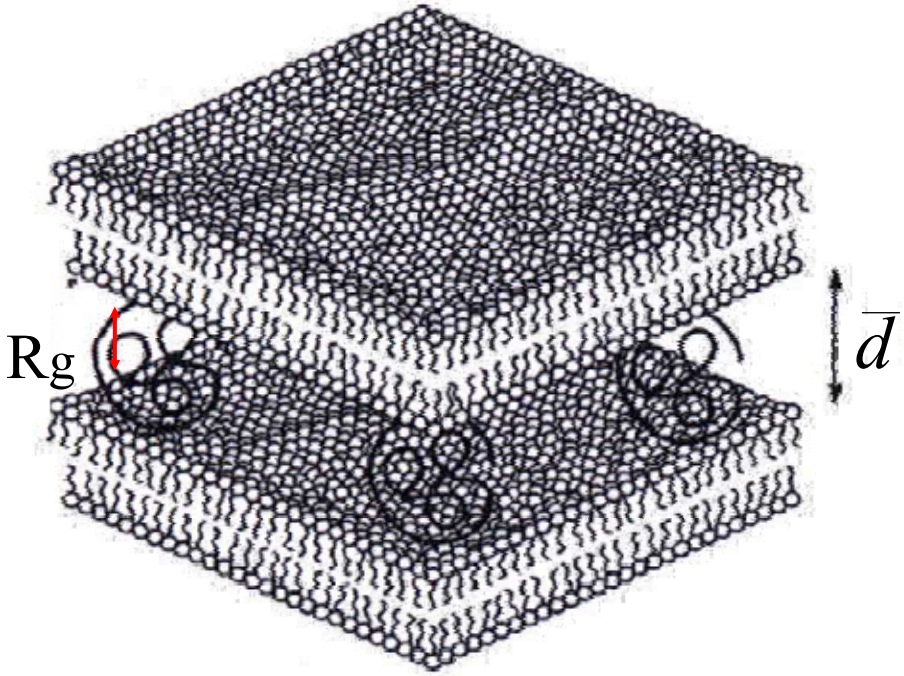




$C_{12}E_5$ + Polymer System

$C_{12}E_5$ + Colloidal Particle System

Lamellar Membrane Confining Polymer Chains



Potential Energy of
Polymer Confinement

$$f_{Poly} \cong \frac{k_B T}{a^3}\bar{d}\frac{\bar{\Phi}_{eff}}{N}\ln(\bar{\Phi}_{eff})$$

$$\bar{\Phi}_{eff} = \bar{\Phi}\frac{\bar{d}}{\bar{d}-2R_g}$$

$$R_g < \bar{d},\ \Phi < \Phi^*$$

Φ^*: Overlapping Concentration

M. Daoud and P.G. de Gennes, (1977).

J.T. Brooks and M.E. Cates, (1993).

Free Energy for Lamellar Membrane Confining Polymer Chain System

$$f_{total} = f_{und} + f_{poly}$$

$$\overline{B}_{\mu} = d\{\frac{\partial^2 f}{\partial \overline{d}^2} - \frac{[\frac{1}{\overline{d}}\frac{\partial f}{\partial \overline{\Phi}} - \frac{\partial^2 f}{\partial \overline{\Phi}\partial \overline{d}}]^2}{(\partial^2 f / \partial \overline{\Phi}^2)}\}$$

$$f_{und} = \frac{3\pi^2 (k_B T)^2}{256\kappa \overline{d}^2}$$

$$\overline{B}^{Hel} = \frac{9\pi^2 (k_B T)^2}{128\kappa \overline{d}^4} d$$

$$f_{poly} \cong \frac{k_B T}{a^3}\overline{d}\frac{\overline{\Phi}_{eff}}{N}\ln(\overline{\Phi}_{eff})$$

$$\overline{B}_{\mu}^{pol} = -\frac{4k_B T R_g^2 d\overline{\Phi}}{a^3 N \overline{d}^3}(1+\log[\frac{\overline{d}\,\overline{\Phi}}{\overline{d}-2R_g}])^2$$

$$\overline{B}_{total} = \overline{B}_{Hel} + \overline{B}_{\mu}^{pol}$$

Addition of polymer into lamellar membrane slit

Destabilized lamellar structure

Estimation of Membrane-Colloid Interaction Potential: f_{mc}

Layer compressibility: $\overline{B}_{\mu}$

$$\overline{B}_{\mu} = d\{\frac{\partial^2 f_{mc}}{\partial \overline{d}^2} - \frac{[\frac{1}{\overline{d}}\frac{\partial f_{mc}}{\partial \overline{\Phi}} - \frac{\partial^2 f_{mc}}{\partial \overline{\Phi}\partial \overline{d}}]^2}{\frac{\partial^2 f_{mc}}{\partial \overline{\Phi}^2}}\}$$

Static Structure Factor

$$S(q) = 1 + 2\sum_{1}^{N-1}(1-\frac{n}{N})\cos(\frac{qdn}{1+2\Delta q^2 d^2 \alpha(n)}) \times \exp[-\frac{2q_z^2 d^2 \alpha(n) + \Delta q^2 d^2 n^2}{2(1+2\Delta q^2 d^2 \alpha(n))}]\frac{1}{\sqrt{1+2\Delta q^2 d^2 \alpha(n)}}$$

$$\alpha(n) = \frac{\eta}{(2\pi)^2}[\ln(\pi n) + \gamma]$$

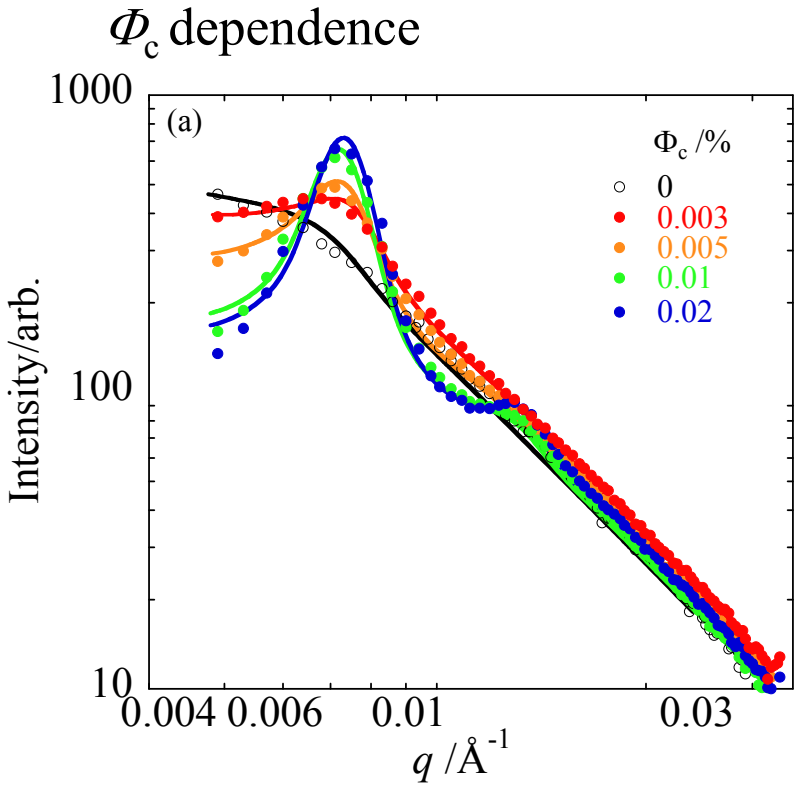
$$\eta = \frac{q_0^2 k_B T}{8\pi\sqrt{K\overline{B}}}$$

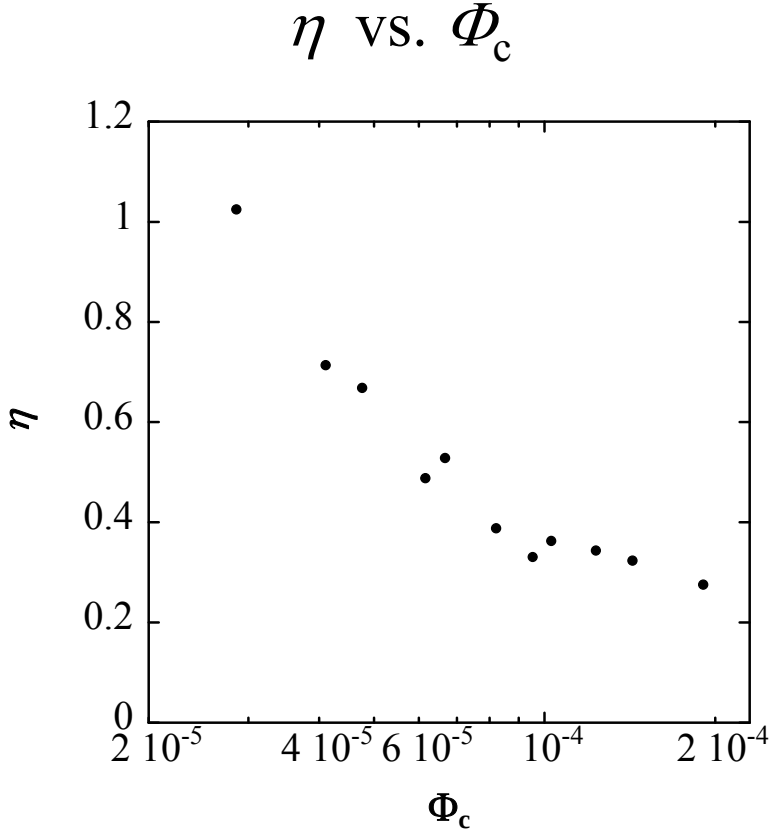
Dynamic Structure Factor

$$\frac{S(q,\tau)}{S(q,0)} = \exp[-(\Gamma\tau)^{2/3}]$$

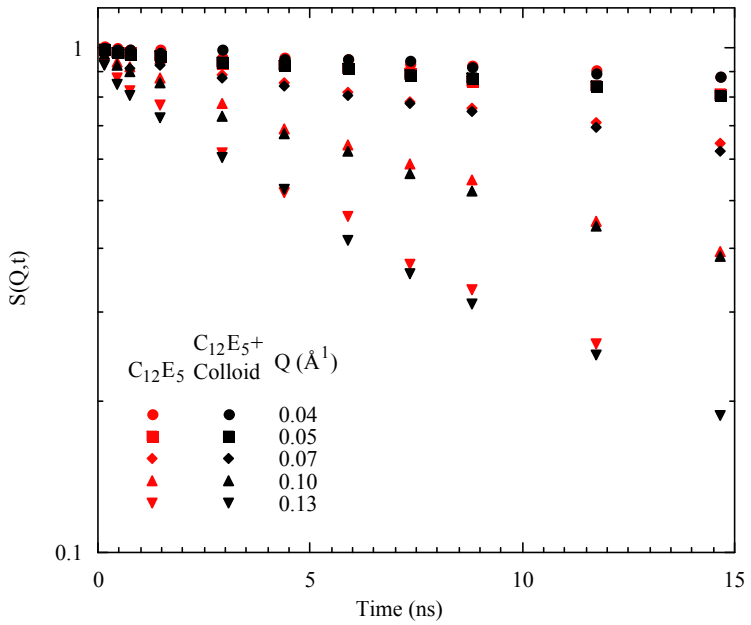
$$\Gamma_q = 0.025\gamma_k(\frac{k_B T}{\kappa})^{1/2}\frac{k_B T}{\eta_v}q^3$$

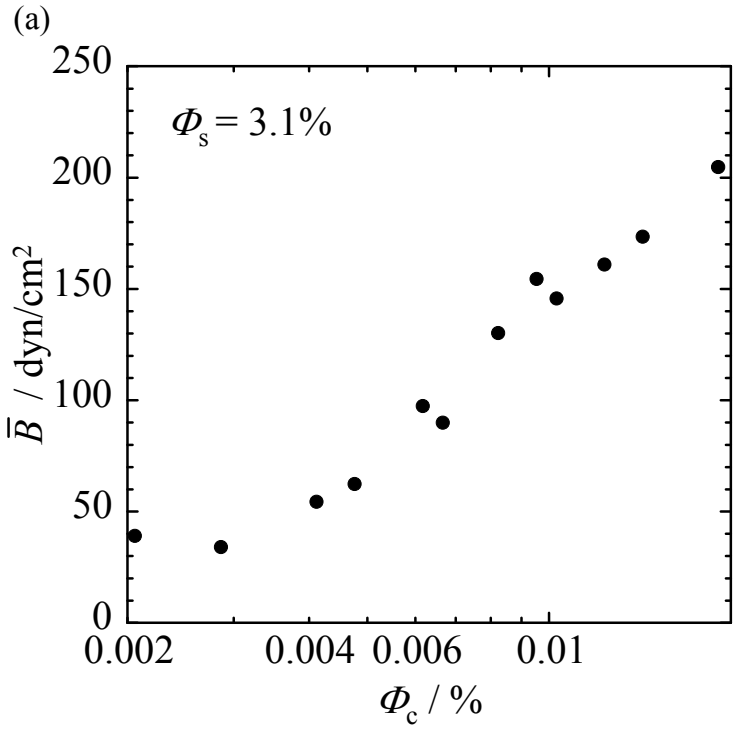
$$\gamma_k \cong 1 - 3\ln(q\xi)k_B T/4\pi\kappa$$


Φ_c dependence
(a)
Φ_c /%
0
0.003
0.005
0.01
0.02
Intensity/arb.
1000
100
10
0.004
0.006
0.01
0.03
q /Å^{-1}


η vs. Φ_c
η
1.2
1
0.8
0.6
0.4
0.2
0
2 10^{-5}
4 10^{-5}
6 10^{-5}
10^{-4}
2 10^{-4}
Φ_c

Estimation of bending modulus from NSE measurements





κ / k_BT

$C_{12}E_5$/water ~3.0

$C_{12}E_5$/water + colloidal particle ~2.8

Model for Membrane-Colloid Interaction Potential: f_{mc}

Suppression of Membrane Fluctuations by Confined Colloids

Effective Volume Fraction

$$\overline{\Phi}_c^{eff} = \overline{\Phi}_c \left(\frac{\overline{d}}{R_c}\right)^m$$

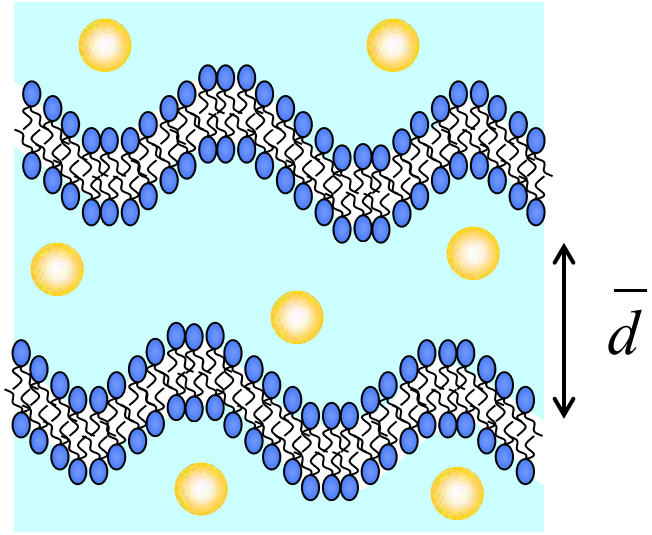
Restriction of membrane fluctuations

$$|u(r)| \leq \overline{d}\tanh^n(1/\alpha\overline{\Phi}_c^{eff})$$

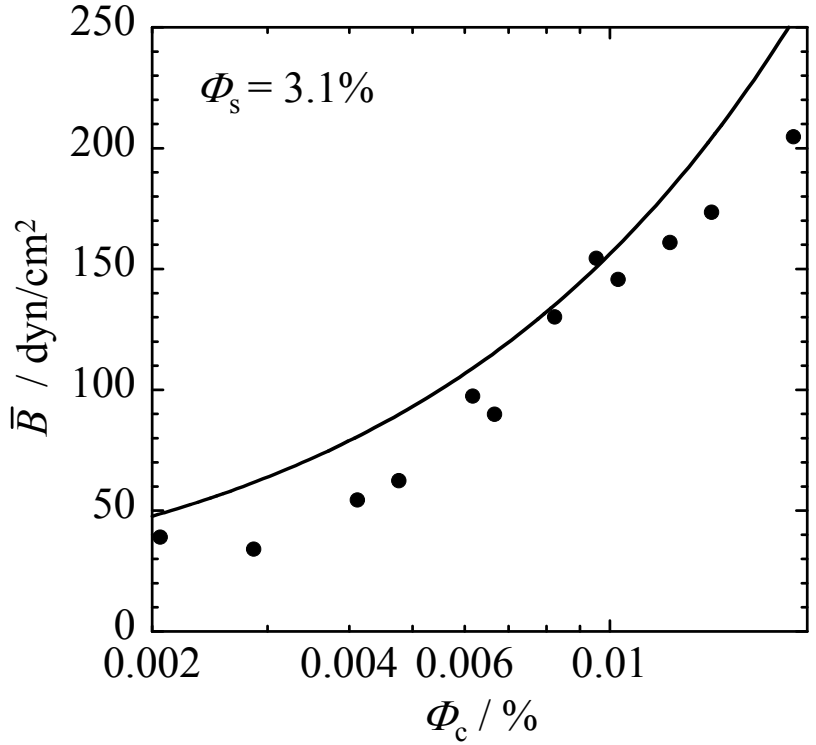
$$\overline{\Phi}_c^{eff} << 1 \quad |u(r)| \leq \overline{d}$$

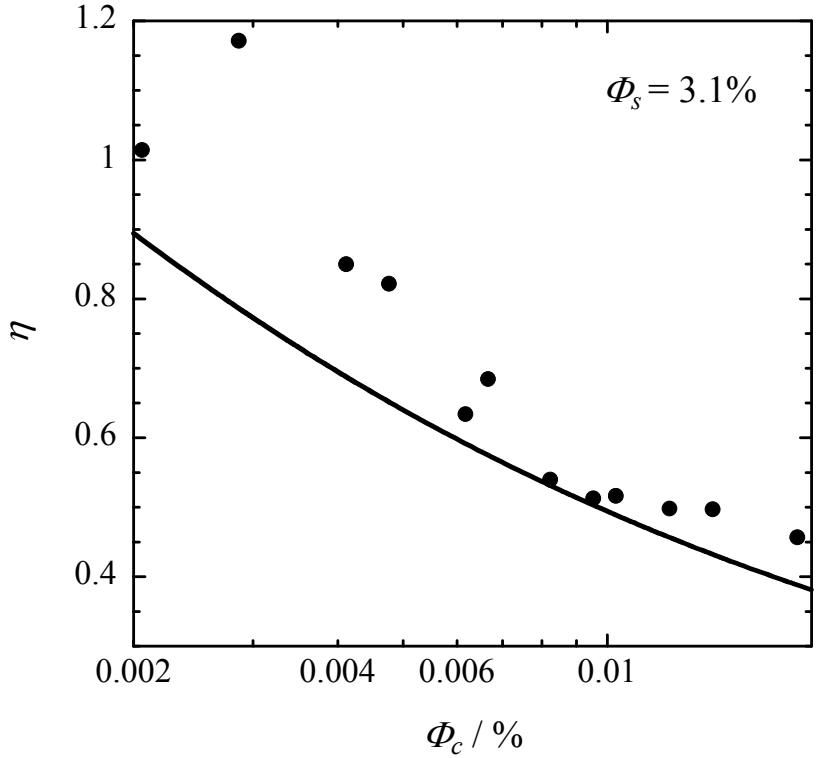
$$\overline{\Phi}_c^{eff} \sim 1 \quad |u(r)| \sim 0$$

$$R(q) = \frac{<|u_q|^2>_{restricted}}{<|u_q|^2>_{free}}$$

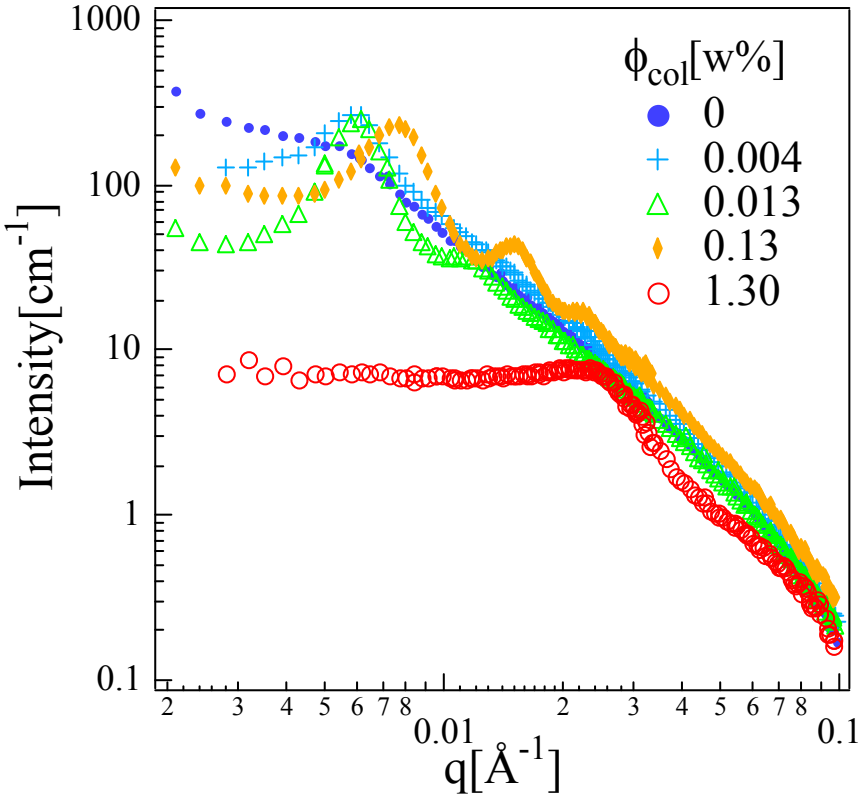


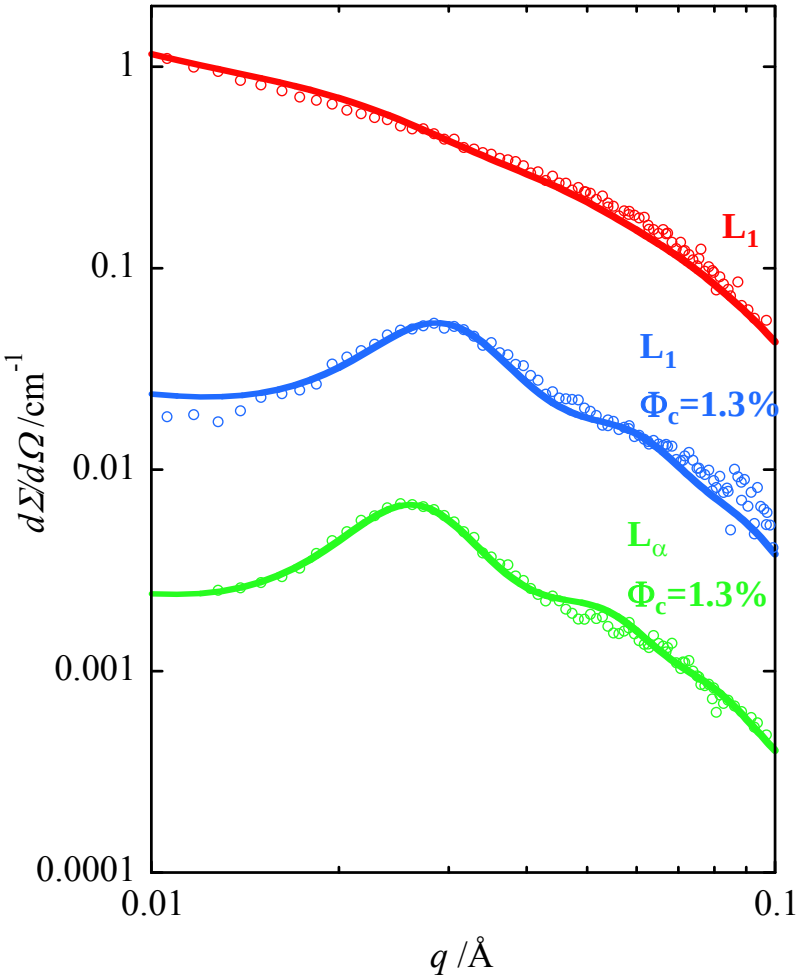
$$f_{mc} = -\frac{1}{2}k_B T \ln R(q) = \frac{(k_B T)^2}{32\mu\kappa}\frac{1}{\overline{d}^2\tanh^n(1/\alpha\overline{\Phi}_c^{eff})}$$


250
200
150
100
50
0
$\bar{B}$ / dyn/cm^2
$\Phi_s = 3.1\%$
0.002
0.004
0.006
0.01
Φ_c / %


1.2
1
0.8
0.6
0.4
η
$\Phi_s = 3.1\%$
0.002
0.004
0.006
0.01
Φ_c / %

コロイドからの散乱を消去





Polydisperse prolate core shell model

$$I(q) = N_m \int g(r) P_m(q,r)\, dr\, S_m'(q)$$

Form Factor

$$\left\langle P_m(q) \right\rangle \equiv \int_0^1 \left| H(q,x) \right|^2 dx$$

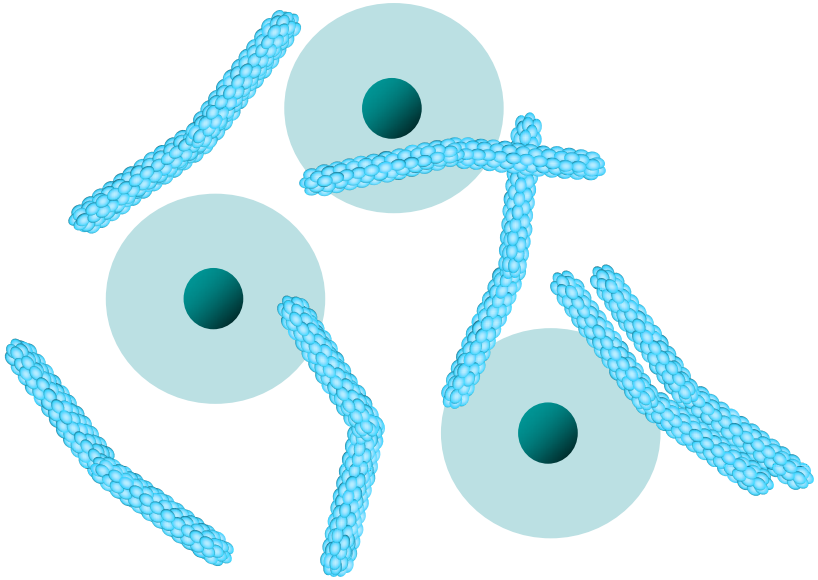
$$H(q,x) = (\rho_t - \rho_h)\frac{4}{3}\pi a_t R_t^3 \left[3\frac{j(u_t)}{u_t} \right] + (b_h - b_s)\frac{4}{3}\pi a R^3 \left[3\frac{j(u)}{u} \right]$$

$$u_t = qR_t\sqrt{a_t^2 x^2 + (1 - x^2)} \qquad u = qR\sqrt{a^2 x^2 + (1 - x^2)}$$

Structure Factor

$$S_m'(q) = 1 + \beta(q)[S_m(q) - 1]$$

$$\beta(q) = \left| < H(q) > \right|^2 / < \left| H(q) \right|^2 >$$



メッセージ

界面活性剤膜が形成するメソ構造に、
ゲスト成分として高分子・コロイドを添加

↓

膜とゲスト成分の
エネルギー的ないしはエントロピー的な相互作用
によるメソ構造の形態転移が生じる。

↓

この形態転移を利用して
膜系に新たな構造や物性や付与する事が可能

共同研究者

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