

Soft Matter Complex System

A single component system:

The structures of soft matter are determined by their free volume that is restricted by the geometries.

Colloid : spherical excluded volume → close-packed crystal

Liquid crystal : rod-like excluded volume → nematic interaction

Polymer : segment excluded volume → self-avoiding chain

Membrane : 2D sheet → membrane fluctuations

Mixture of soft matter :

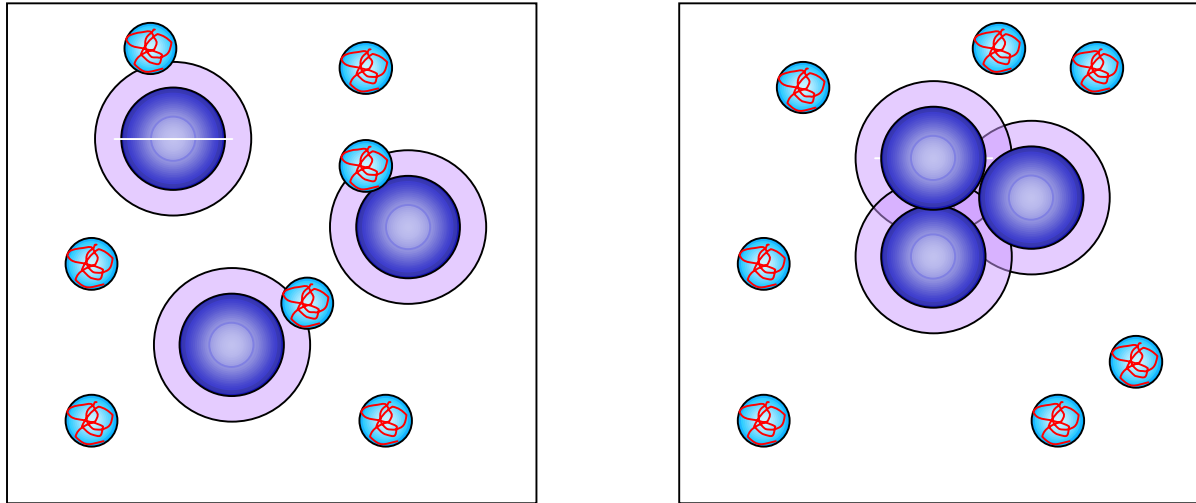
Competition of the free volume brings phase transition.

Depletion interaction

colloid and polymer mixture

colloid and liquid crystal mixture

Depletion Interaction



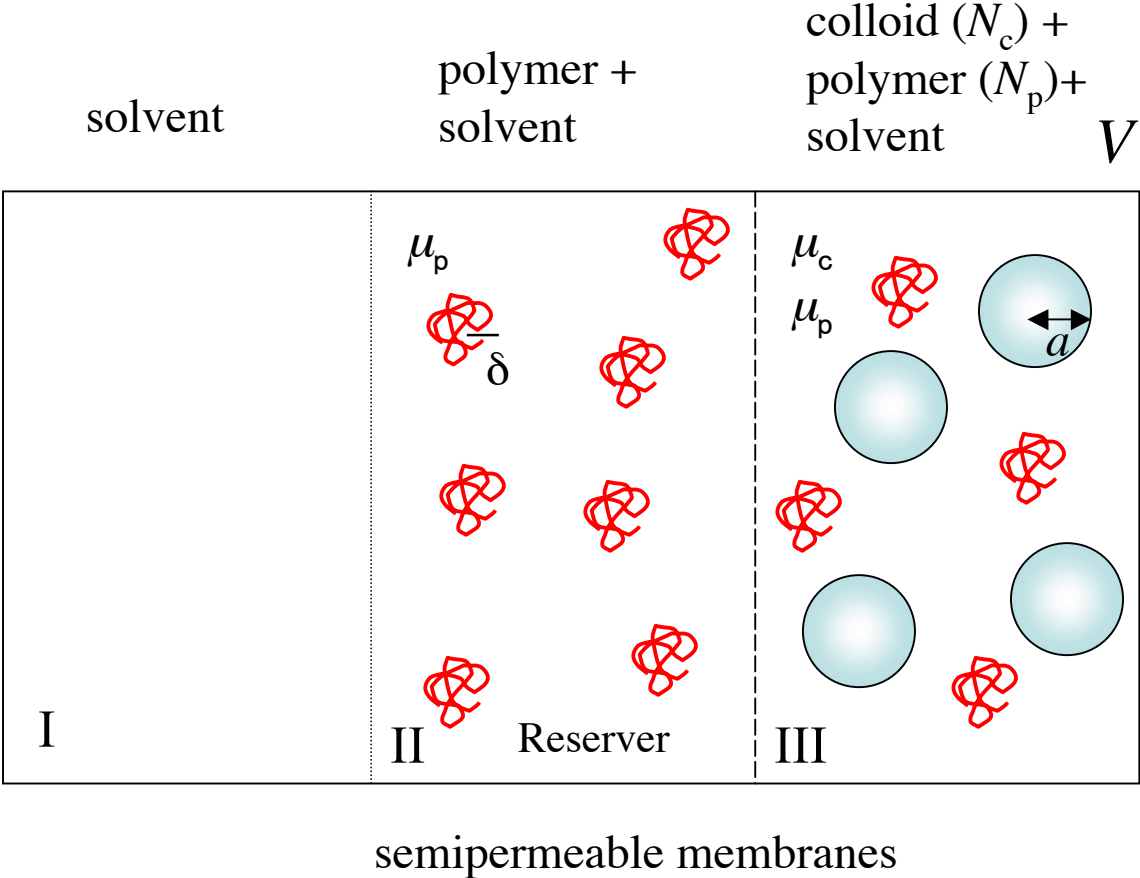
Depletion zone surrounding spherical colloid particle

Competition between
mixing entropy S_m and translational entropy S_t

$S_m > S_t$ Miscible

$S_m < S_t$ Aggregation

Thermodynamics of spherical colloid particles + polymer system



H.N.W. Lekkerkerker et al., Europhys. Lett. **20**, 559 (1992)

Ground Canonical Potential of the system III: Ω

$$\Omega = F - N_p \mu_p$$

F : Helmholtz Free Energy of System

N_p : Number of Polymer Chains

μ_p : Chemical Potential of Polymer

Grand Potential has the standard relationship

$$\Omega = -k_B T \ln \Xi$$

$$\Xi(N_c, \mu_p, V) = \sum_{N_p=0}^{\infty} z_p^{N_p} Z(N_c, N_p, V)$$

$Z(N_c, N_p, V)$: Canonical partition function

z_p : Activity of polymer chains

$$z_p = \exp(\mu_p / k_B T)$$

In this system, number of polymer chain, N_p , is variable, but determined by the chemical potential μ_p . Then we can deal with the system as canonical ensemble of colloids.

$$\Xi(N_c, \mu_p, V) = \frac{1}{N_c!} \int d\mathbf{r}^{N_c} \exp[-W(\mathbf{r}^{N_c}; \mu_p) / k_B T]$$

$W(\mathbf{r}^{N_c}; \mu_p)$ is the interaction potential of colloids depending on the configuration of colloids and chemical potential of polymers.

$$W = U_c - \Pi_p(\mu_p)V_{free}(\mathbf{r}^{N_c})$$

U_c : Inter-colloids potential without polymer

Π_p : Osmotic pressure of the reservoir (polymer solution)

V_{free} : Free volume of polymer chains

$$V_{free} = \alpha V$$

$\alpha(\phi_c, \delta/a)$: Free volume fraction

$$\begin{aligned} \Xi(N_c, \mu_p, V) &= \frac{1}{N_c!} \int d\mathbf{r}^{N_c} \exp[-(U_c - \Pi_p \alpha V) / k_B T] \\ &\sim \frac{1}{N_c!} \exp[-(U_c - \Pi_p \alpha V) / k_B T] \end{aligned}$$

$$\Omega = U_c - k_B T(N_c \ln N_c - N_c) - \Pi_p \alpha V = F_c(N_c, V) - \Pi_p \alpha V$$

$F_c(N_c, V)$: Helmholtz free energy for pure colloidal system

Helmholtz free energy of the system is given by

$$\begin{aligned} F &= \Omega + N_p \mu_p \\ &= F_c(N_c, V) + N_p \mu_p - \Pi_p \alpha V \\ &= F_c(N_c, V) + F_p(N_p, \alpha V) \end{aligned}$$

Helmholtz Free energy of pure polymer solution

$$\begin{aligned} F_p(N_p, \alpha V) &\cong k_B T n V \ln \frac{n}{\alpha} \\ n &= N_p / V \end{aligned}$$

Helmholtz Free energy of pure colloidal suspension

$$F_c(N_c, V) = -\int \Pi_c dV$$

Π_c is the osmotic pressure of pure colloidal solution.

Using hard-sphere compressibility $\xi = \frac{\Pi_c V}{N_c k_B T}$

$$F_c(N_c, V) = \frac{3k_B T}{4\pi\alpha^3} V \phi_c \int \frac{\xi}{\phi_c} d\phi_c$$

For fluid phase

$$\zeta(\text{fluid}) = \frac{1 + \phi_c + \phi_c^2 - \phi_c^3}{(1 - \phi_c)^3}$$

For crystal phase (FCC)

$$\zeta(\text{solid}) = \frac{1 + \phi_c + \phi_c^2 - 0.67825\phi_c^3 - \phi_c^4 - 0.5\phi_c^5 - 6.028e^{\xi(7.9-3.9\xi)}\phi_c^6}{1 - 3\phi_c + 3\phi_c^2 - 1.04305\phi_c^3}$$

In order to determine the coexistence of phase 1 and phase 2, we have to solve the following equations,

$$\mu_C(\phi_c^1, n_R) = \mu_C(\phi_c^2, n_R)$$

$$\Pi(\phi_c^1, n_R) = \Pi(\phi_c^2, n_R)$$

volume fraction of colloids : $\phi_c^1 \quad \phi_c^2$

number density of polymer chain : $n_R = n / \alpha = N_p / \alpha V$

In order to calculate the phase diagram, we must obtain the chemical potentials of the colloid and polymer (μ_c, μ_p) $\mu_i = (\partial \Omega / \partial N_i)_{V, N_{j(j \neq i)}}$,
and the total osmotic pressure $\Pi = -(\partial \Omega / \partial V)_{N_c, \mu_p}$.

$$(\mu_c - \mu_c^0) / k_B T = \int \frac{Z}{\phi_c} d\phi_c + Z - \frac{4}{3} \pi a^3 \frac{n}{\alpha} \frac{d\alpha}{d\phi_c}$$

$$(\mu_p - \mu_p^0) / k_B T = \ln\left(\frac{n}{\alpha}\right)$$

$$\frac{4\pi a^3 \Pi}{3k_B T} = \phi_c Z + \frac{4}{3} \pi a^3 \frac{n}{\alpha} \left(\alpha - \phi_c \frac{d\alpha}{d\phi}\right)$$

Next, we need the free volume fraction $\alpha(\phi)$.

$$\alpha = (1 - \phi_c) \exp[-A\gamma - B\gamma^2 - C\gamma^3]$$

$$\gamma = \phi_c / (1 - \phi_c) \quad A = 3\xi + 3\xi^2 + \xi^3 \quad B = \frac{9}{2} \xi^2 + 3\xi^3 \quad C = 3\xi^3 \quad \xi = \delta / a$$

Here we introduce the effective polymer number density $n_R = n / \alpha = N_p / \alpha V$,

$$n_R = \exp[(\mu_p - \mu_p^0) / k_B T]$$

Then we obtain expressions for μ_c and Π which are functions of ϕ and n_R .

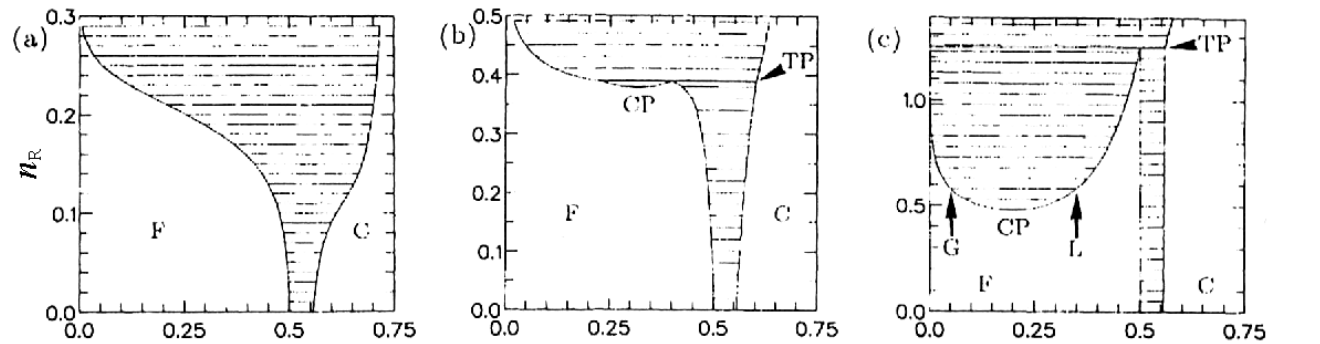
In order to calculate the phase diagram, we only need to solve

$$\mu_c(\phi_c^1, n_R) = \mu_c(\phi_c^2, n_R) \quad \Pi(\phi_c^1, n_R) = \Pi(\phi_c^2, n_R)$$

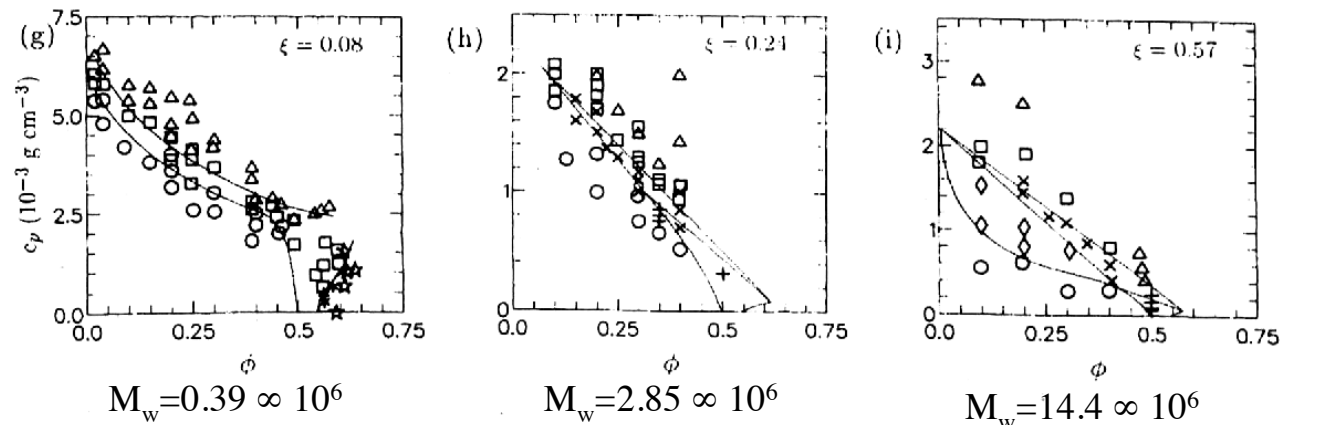
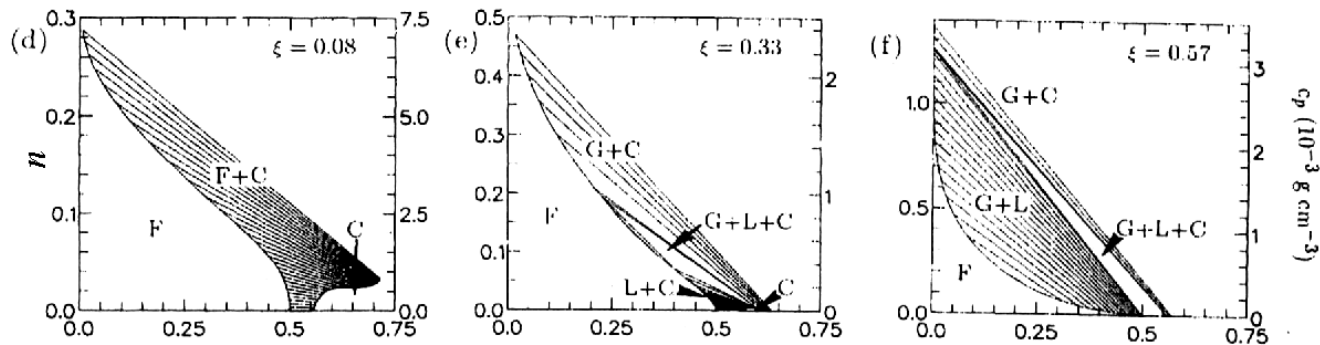
at given n_R . The polymer concentrations in these phases are then found from

$$n_1 = \alpha(\phi_c^1) n_R \quad n_2 = \alpha(\phi_c^2) n_R$$

Comparison between Theoretical Prediction and Experiments



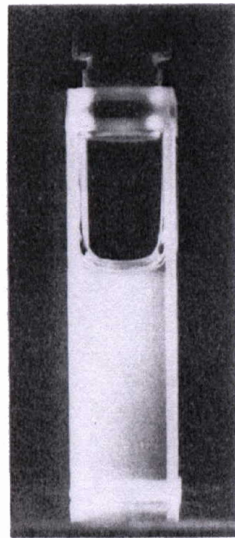
PMMA($a = 220$ nm)
+PS



○:fluid, ◇: gas+liquid
 ×:gas+liquid+crystal
 +:liquid+crystal,
 □:gas+crystal
 △:gel, ☆:glass

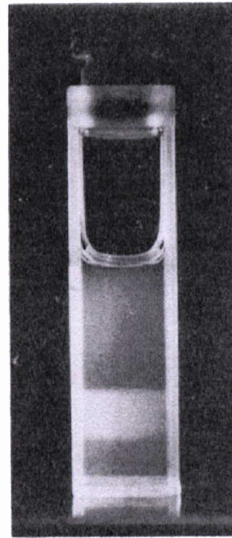
Phase behavior of PMMA colloidal particles (220 nm) + PS ($R_g=54$ nm) system

$$\phi_c=0.2$$



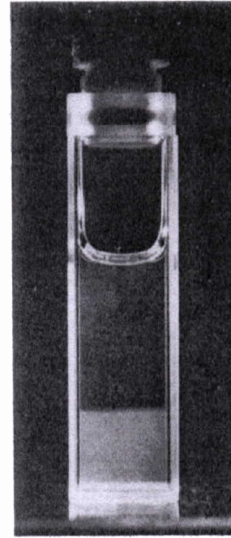
(a)

One Phase Region
fluid



(b)

Three Phase Region
crystal(bottom)
liquid (middle)
gas (top)

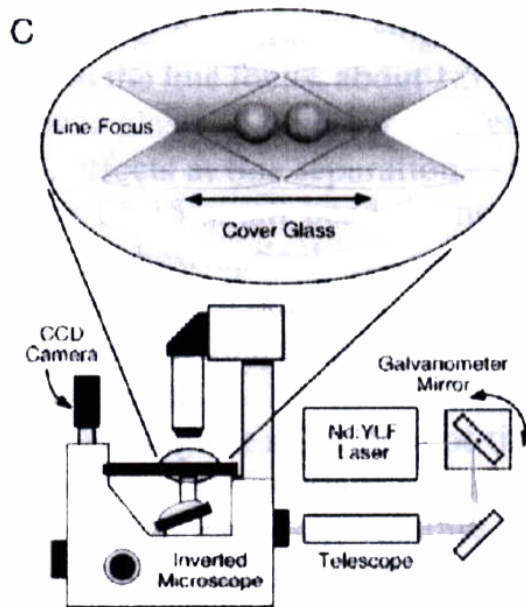


(c)

Two Phase Region
crystal (bottom)
gas (top)

Depletion Interaction Probed with a Line Optical Tweezers

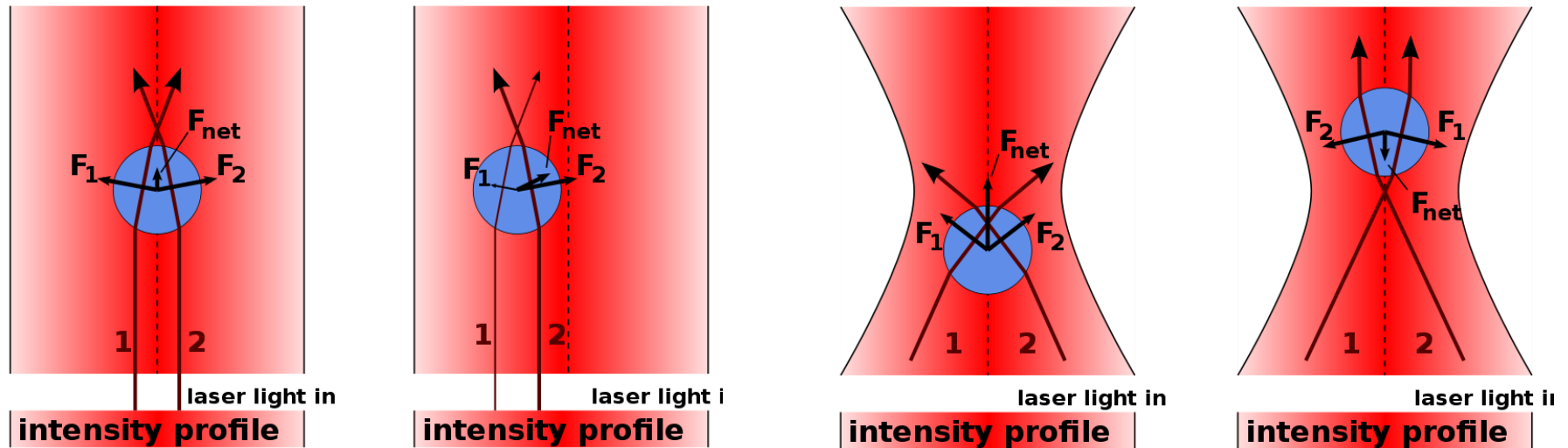
The laser focus is scanned back and forth along a line in the focal plane of the objective at 180 Hz. Under the such optical field, the colloidal particles freely diffuse along the line while is strongly confined in other two directions.



The effective interaction potential between the two particles is related to the probability, $P(r)$, of finding the two spheres with centers separated by r through the Boltzmann relation

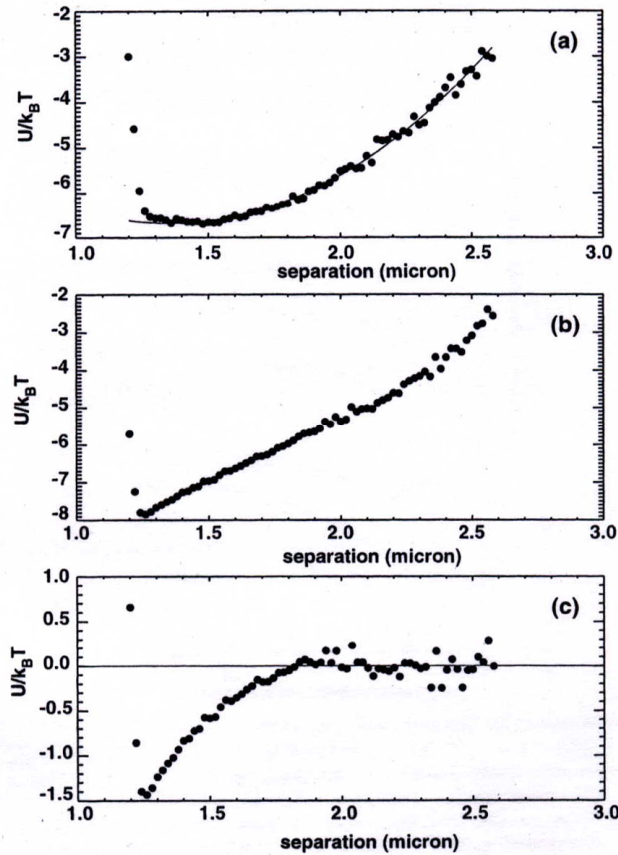
$$P(r) \propto \exp(-U(r)/k_B T)$$

Optical tweezers

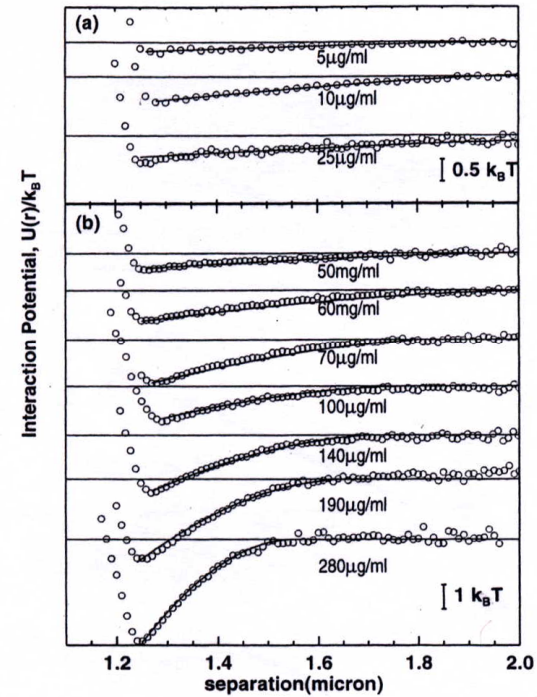


Individual rays of light emitted from the laser will be refracted as it enters and exits the dielectric bead. As a result, the ray will exit in a direction different from which it originated. Since light has a momentum associated with it, this change in direction indicates that its momentum has changed. Due to Newton's third law, there should be an equal and opposite momentum change on the particle.

1.25 μm silica spheres in DNA solutions



- (a) colloid particles in buffer solution
- (b) colloid particles + polymer
- (c) depletion interaction



Direct Observation of Aggregation in a Phase-Separating Colloid-Polymer Suspension

PMMA-latex in poly(styrene) solutions

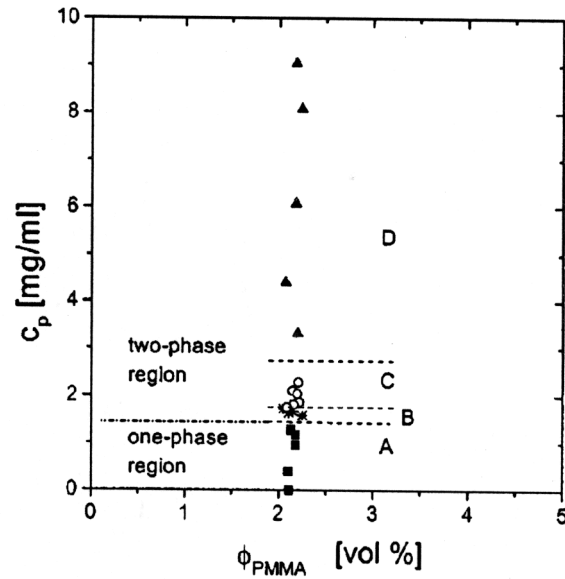
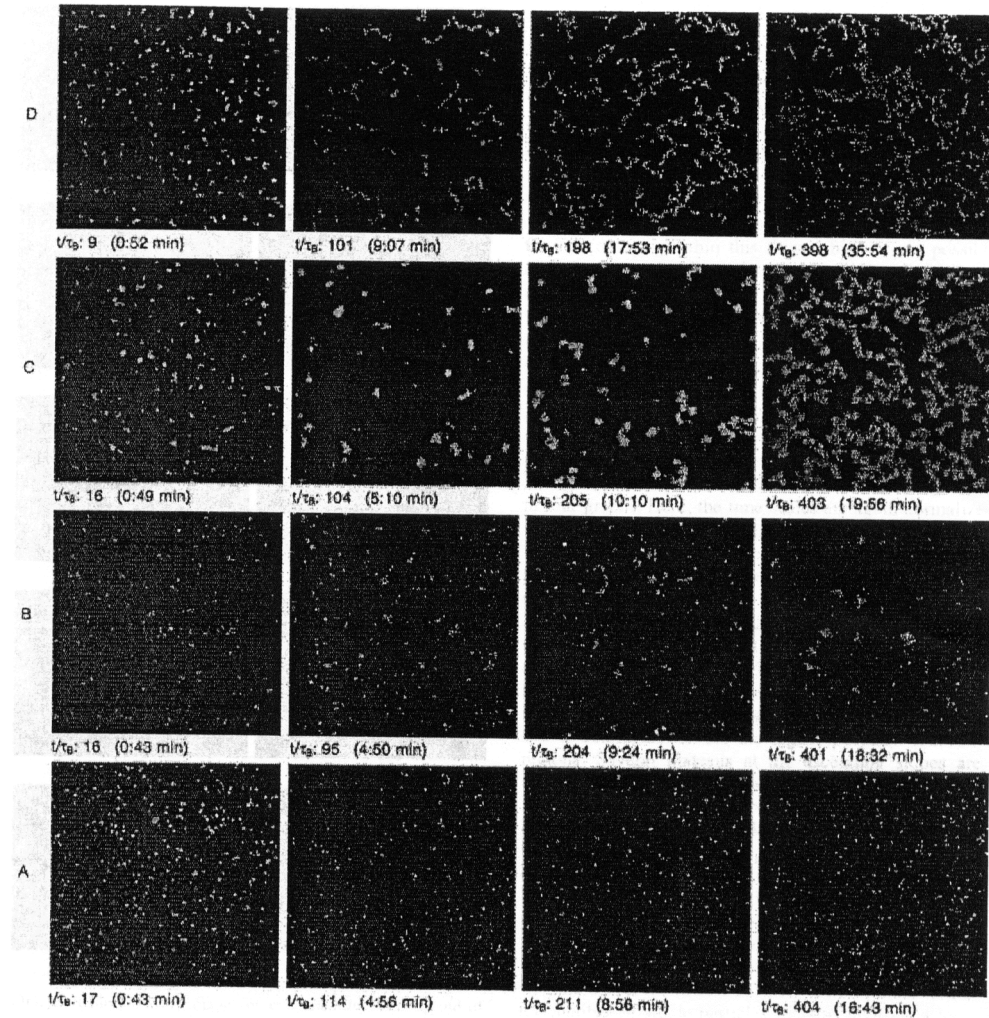
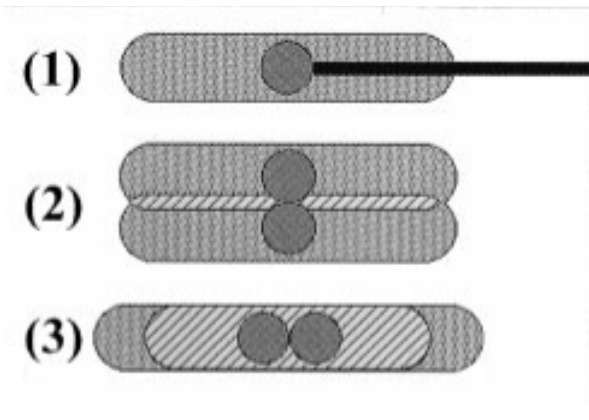


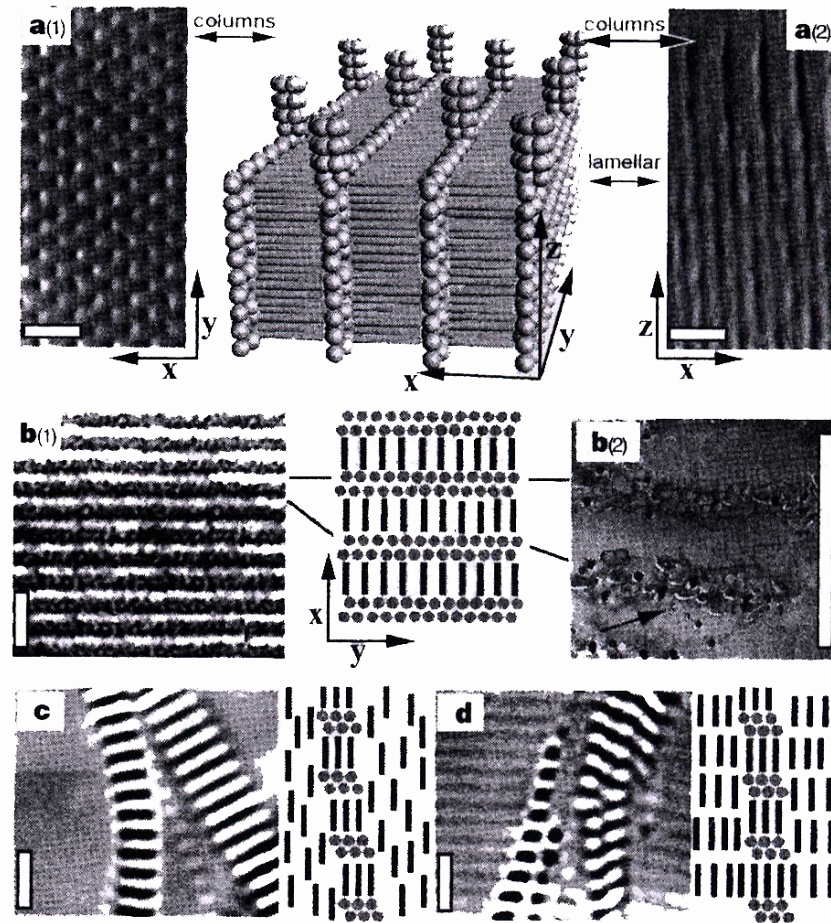
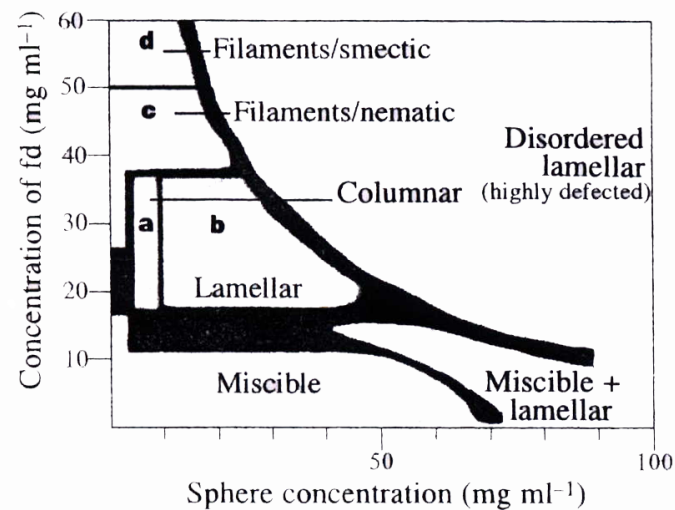
FIG. 3. Phase diagram of the colloid-polymer suspension with the four regimes indicated.



Depletion Interaction in Liquid Crystal (Rod-like Particle) + Polymer System



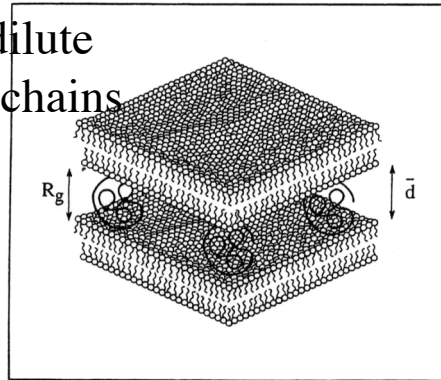
Overlapping of depletion zone for sphere + rod
 fd virus ($d=6.6$ nm, $l=880$ nm) + PS latex ($D=100$ nm)



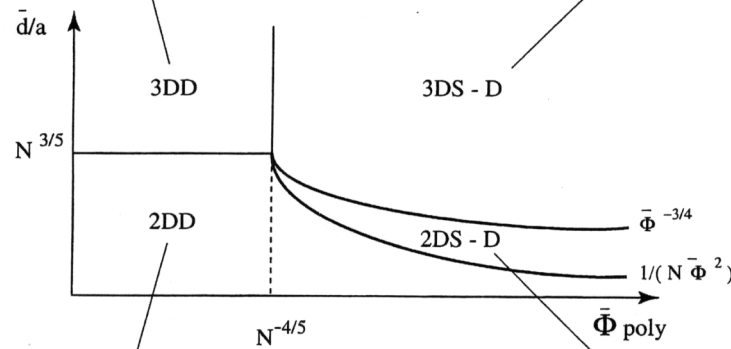
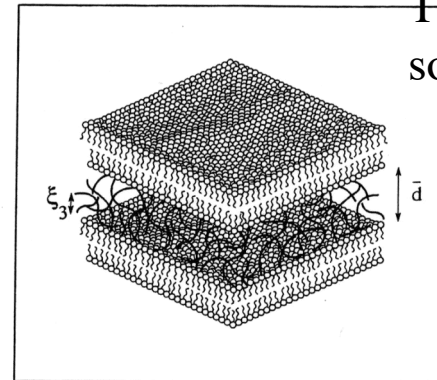
M. Adams, et al., Nature 393, 349 (1998).

Polymer chains confined into lamellar membrane slit

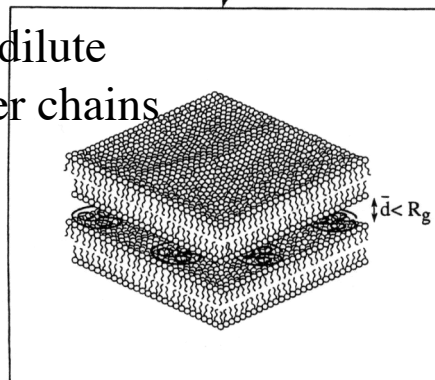
Three-dimensional dilute solution of polymer chains



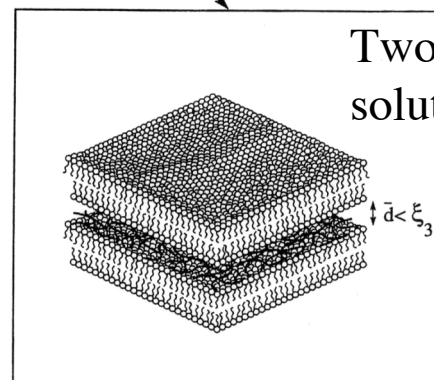
Three-dimensional semi-dilute solution of polymer chains



Two-dimensional dilute solution of polymer chains



Two-dimensional semi-dilute solution of polymer chains



Polymer size in bulk state

$$R_{F3} \cong aN^{\nu} = aN^{3/5} \quad \text{generally,} \quad \nu = \frac{3}{d_i + 2}$$

This polymer chain is confined into lamellar slit

$$\bar{d} \gg R_{F3}$$

$$R_{F3} \cong aN^{3/5}$$

$$\bar{d} < R_{F3}$$

$$R_{F2} = R_{F3} f\left(\frac{R_{F3}}{\bar{d}}\right) = R_{F3} f(x)$$

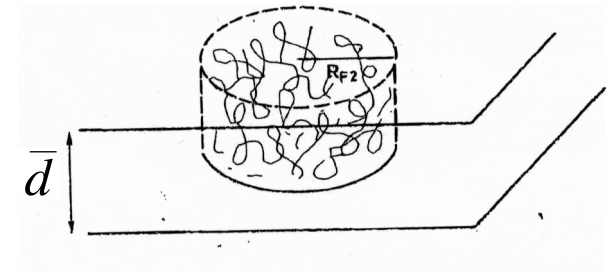
Scaling function $f(x)$ has the following nature

$$f(x \rightarrow 0) = 1$$

$$f(x \gg 1) \cong x^m$$

$$R_{F2} \sim R_{F3}^{m+1} \bar{d}^{-m} \sim N^{\frac{3}{5}(m+1)} a^{m+1} \bar{d}^{-m} \sim N^{3/4} \quad \Rightarrow \quad m=1/4$$

$$R_{F2} \cong aN^{3/4} \left(\frac{a}{\bar{d}}\right)^{1/4}$$



Scaling law in polymer chain

A Gaussian chain is described by the segment length b and the number of segments N . We introduce a coarse grained parameter set. A new segment is composed of λ segments. In this case,

$$N \rightarrow \lambda^{-1}N \quad b \rightarrow \lambda^{1/2}b$$

For $N \gg 1$, the macroscopic nature, such as mean square end-to-end distance, is invariant against this transformation.

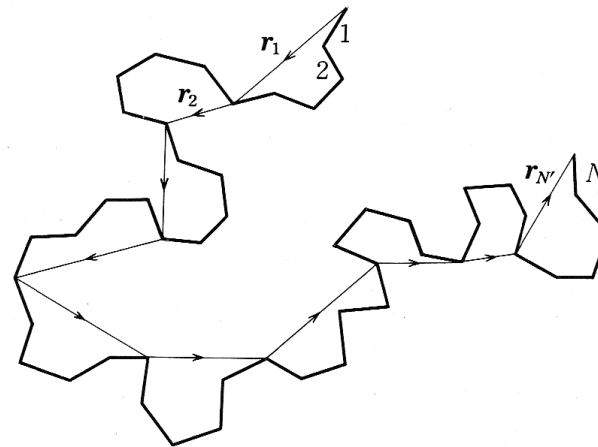
$$f(\lambda^{-1}N, \lambda^{1/2}b) = f(N, b)$$

For excluded volume chain

$$f(\lambda^{-1}N, \lambda^{\nu}b) = f(N, b) \quad \nu = 3/5$$

Generally,

$$A(\lambda^{-1}N, \lambda^{\nu}b) = \lambda^x A(N, b)$$



Overlap concentration of polymer chains (dilute - semi-dilute boundary)

3 D case Overlap concentration ρ_3^* is expressed by

$$\rho_3^* \cong \frac{N}{R_{F3}^3} \cong \frac{N}{(aN^{3/5})^3} \cong a^{-3} N^{-4/5} \quad \bar{\Phi}_{poly} = Na^3 / R_{F3}^3 = a^3 \rho_3$$

$${}^3\bar{\Phi}_{poly}^* = N^{-4/5}$$

2 D case Overlap concentration ρ_2^* is expressed by

$$\rho_2^*(x) \cong \frac{N}{\bar{d}R_{F2}^2} = \frac{N}{\bar{d}(R_{F3}(\frac{R_{F3}}{\bar{d}})^{1/4})^2} = \frac{R_{F3}}{\bar{d}} \frac{N}{R_{F3}^3(\frac{R_{F3}}{\bar{d}})^{1/2}}$$

$$\cong \rho_3^* x^{1/2}$$

$${}^2\bar{\Phi}_{poly}^* \cong a^3 \rho_2^* = a^3 (a^{-3} N^{-4/5}) (R_{F3} / \bar{d})^{1/2} = a^{1/2} / (\bar{d}^{1/2} N^{1/2})$$

$$\frac{\bar{d}}{a} \sim \frac{1}{N \bar{\Phi}_{poly}^2}$$

Semi-dilute solution of polymer chains

Blob model

$$3D \quad \xi(\bar{\Phi}_{poly}) = R_{F3} \left(\frac{{}^3\bar{\Phi}_{poly}^*}{\bar{\Phi}_{poly}} \right)^{m_{\xi 3}} \quad R_{F3} \cong aN^{3/5}$$

$${}^3\bar{\Phi}_{poly}^* = N^{-4/5}$$

Exponent $m_{\xi 3}$ should be independent of N .

$$m_{\xi 3} = 3/4$$

$$\xi_3 \cong a\bar{\Phi}_{poly}^{-3/4}$$

$$\bar{d} = \xi_3 \cong a\bar{\Phi}_{poly}^{-3/4}$$

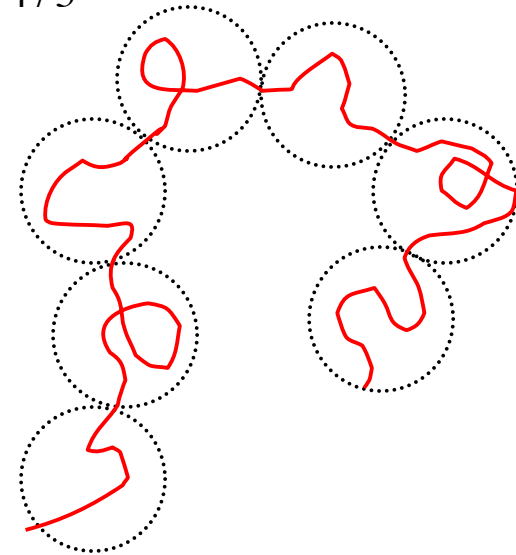
$$\frac{\bar{d}}{a} \cong \bar{\Phi}_{poly}^{-3/4}$$

2D

$$\xi(\bar{\Phi}_{poly}) = R_{F2} \left(\frac{{}^2\bar{\Phi}_{poly}^*}{\bar{\Phi}_{poly}} \right)^{m_{\xi 2}}$$

$$R_{F2} \cong aN^{3/4} \left(\frac{a}{\bar{d}} \right)^{1/4} \quad {}^2\bar{\Phi}_{poly}^* \cong a^{1/2} / (\bar{d}^{1/2} N^{1/2})$$

$$\xi_2 \cong \left(\frac{a^2}{\bar{d}} \right) \bar{\Phi}_{poly}^{-3/2}$$



Polymer contribution to the free energy per unit bilayer area

1) 3DD regime $\bar{d} \gg R_{F3}$ and $\bar{\Phi}_{poly} \ll \bar{\Phi}_{poly}^*$

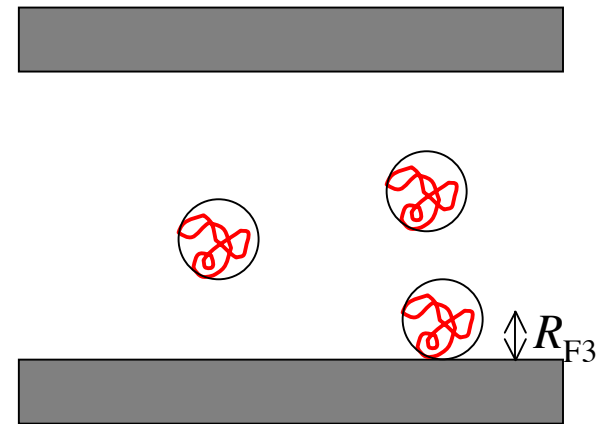
In this regime, the solution consists of a dilute solution of swollen polymer coil of radius R_{F3}

Depletion contribution

$$\bar{\Phi}_{poly}^{eff} \cong \bar{\Phi}_{poly} \frac{\bar{d}}{\bar{d} - 2R_{F3}}$$

Perfect gas contribution corrected for the depletion effect

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



2) 3D S-D regime $\bar{d} > a\bar{\Phi}_{poly}^{-3/4}$ and $\bar{\Phi}_{poly} > {}^3\bar{\Phi}_{poly}^*$

In this regime the chains overlap but still remain unsqueezed. The free energy consists of “bulk” semi-dilute polymer solution term and the depletion effect term (thickness of the depletion layer $\sim \xi_3$)

Bulk energy $\sim k_B T / \xi_3^3$

Depletion effect term

$$\text{Osmotic pressure} \quad \Pi \cong \frac{1}{\xi_3^3} k_B T$$

$$f_{3DSD}^{osm} = \Pi \xi_3 = \frac{k_B T}{\xi_3^2}$$

$$f_{3DSD} = \beta \frac{k_B T}{a^3} \bar{\Phi}_{poly}^{9/4} \bar{d} + 2\gamma \frac{k_B T}{a^2} \bar{\Phi}_{poly}^{3/2}$$

3) 2DSD regime $a/(N\bar{\Phi}_{poly}^2) < \bar{d} < a\bar{\Phi}_{poly}^{-3/4}$ and $\bar{\Phi}_{poly} > {}^3\bar{\Phi}_{poly}^*$

In this regime, the chains are strongly compressed and the solution behaves as an effective two-dimensional semi-dilute solution.

Osmotic pressure contribution

$$f_{2DSD}^{osmo} \sim \frac{k_B T}{\xi_2^2}$$

Entropic confinement contribution

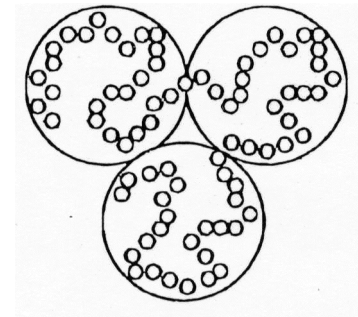
No. of blobs per pancake

$$\xi_2 \cong \bar{d} N_{pan}^{3/4} \quad \longrightarrow \quad N_{pan} \cong (\xi_2 / \bar{d})^{4/3}$$

No. of pancake blob per unit area $1/\xi_2^2$

$$f_{2DSD}^{conf} \sim \frac{k_B T}{\xi_2^2} \left(\frac{\xi_2}{\bar{d}}\right)^{4/3}$$

$$f_{2DSD} = \delta \frac{k_B T}{a^2} \left(\frac{a}{\bar{d}}\right)^{2/3} \bar{\Phi}_{poly} + \eta \frac{k_B T}{a^2} \left(\frac{\bar{d}}{a}\right)^2 \bar{\Phi}_{poly}^3 \quad \delta \cong 2.22, \eta \cong 1.72$$



4) 2DD regime

$$\bar{d} < R_F \quad \text{and} \quad \bar{\Phi}_{poly} <^3 \bar{\Phi}_{poly}^* \quad \text{or} \quad \bar{d} \ll a / (N \bar{\Phi}_{poly}^2) \quad \text{and} \quad \bar{\Phi}_{poly} \gg^3 \bar{\Phi}_{poly}^*$$

In this regime the polymer solution consists of a two-dimensional dilute gas of compressed polymer pancakes.

Entropic confinement contribution

No. of blobs per pancake

$$\xi_2 \cong \bar{d} N_{pan}^{3/4} \quad \longrightarrow \quad N_{pan} \cong (\xi_2 / \bar{d})^{4/3}$$

No. of pancake blob per unit area $1 / \xi_2^2$

$$f_{2DD}^{conf} \sim \frac{k_B T}{\xi_2^2} \left(\frac{\xi_2}{\bar{d}} \right)^{4/3}$$

Two-dimensional dilute gas

$$f_{2DD}^{gas} = k_B T \frac{\bar{d} \bar{\Phi}_{poly}}{Na^3} \ln \left(\frac{\bar{d} \bar{\Phi}_{poly}}{Na} \right)$$

$$f_{2DD} = \frac{k_B T}{a^2} \left[\frac{\bar{d} \bar{\Phi}_{poly}}{Na} \ln \left(\frac{\bar{d} \bar{\Phi}_{poly}}{Na} \right) + \alpha \left(\frac{a}{\bar{d}} \right)^{2/3} \bar{\Phi}_{poly} \right]$$

Layer compression modulus of a doped-solvent lamellar phase

σ : surface fraction of guest component molecules per unit bilayer area

$$\tilde{f} = f - \mu\sigma$$

μ : chemical potential of the guest component (conjugate to σ)

$$\bar{B}_\mu = d \frac{\partial^2 \tilde{f}}{\partial \bar{d}^2} \quad \bar{B}_\mu^{poly} = d \left\{ \frac{\partial^2 f}{\partial \bar{d}^2} - \frac{\left[\frac{1}{\bar{d}} \frac{\partial f}{\partial \bar{\Phi}_{poly}} - \frac{\partial^2 f}{\partial \bar{\Phi}_{poly} \partial \bar{d}} \right]^2}{\frac{\partial^2 f}{\partial \bar{\Phi}_{poly}^2}} \right\}$$

1) 3DD regime

$$\begin{aligned} \bar{B}_\mu^{3DD} &= - \frac{4k_B T R_F^2 d \bar{\Phi}_{poly}}{a^3 N \bar{d}^3} \left(1 + \ln \left[\frac{\bar{\Phi}_{poly}}{1 - 2(R_{F3}/\bar{d})} \right] \right)^2 \\ &\cong -4 \frac{k_B T N^{1/5} d \bar{\Phi}_{poly}}{a \bar{d}^3} \end{aligned}$$

2) 3DSD regime

$$\begin{aligned}\bar{B}_\mu^{3DSD} &= -d \frac{k_B T}{a \bar{d}^3} \frac{9 \rho^2 \bar{\Phi}_{poly}}{\frac{45}{16} \beta \bar{\Phi}_{poly}^{1/4} + \frac{3}{2} \rho \frac{a}{\bar{d}} \bar{\Phi}_{poly}^{-1/2}} \\ &\cong -\frac{16 \rho^2 k_B T}{5 \beta a} \frac{d}{\bar{d}^3} \bar{\Phi}_{poly}^{3/4}\end{aligned}$$

3) 2DSD regime

$$\begin{aligned}\bar{B}_\mu^{2DSD} &= d \left[\frac{25 \delta k_B T}{9 a^4} \left(\frac{a}{\bar{d}}\right)^{8/3} \bar{\Phi}_{poly} + \frac{\eta k_B T \bar{\Phi}_{poly}^3}{2 a^4} - \frac{25 k_B T}{54 a^4 \eta} \left(\frac{a}{\bar{d}}\right)^{16/3} \bar{\Phi}_{poly}^{-1} \right] \\ &\cong -\frac{25 \delta^2 k_B T}{54 \eta} \frac{d}{a^4} \left(\frac{a}{\bar{d}}\right)^{16/3} \bar{\Phi}_{poly}^{-1}\end{aligned}$$

4) 2DD regime

$$\begin{aligned}\bar{B}_\mu^{2DD} &= d \frac{5 \alpha k_B T}{9 \bar{d}^4} \left(\frac{a}{\bar{d}}\right)^{1/3} \bar{\Phi}_{poly} \left(-5 \alpha N + 8 \left(\frac{\bar{d}}{a}\right)^{5/3}\right) \\ &\cong -\frac{25 \alpha^2 k_B T}{9} N \bar{\Phi}_{poly} \left(\frac{a}{\bar{d}}\right)^{1/3} \frac{d}{\bar{d}^4}\end{aligned}$$

In all four regimes, the polymer confinement contribution is negative.

Layer compression modulus contributed from other inter-membrane interactions

$$\bar{B}_{mem} = d \frac{\partial^2 V}{\partial \bar{d}^2}$$

van der Waals interaction

$$\bar{B}_{vdW} = -\frac{dk_B T}{12} \left(\frac{6}{(d-\delta)^4} - \frac{12}{d^4} + \frac{6}{(d+\delta)^4} \right)$$

Hydration interaction

$$\bar{B}_{hyd} = \frac{dH_0}{\lambda^2} e^{-\bar{d}/\lambda}$$

Electrostatic interaction

$$\bar{B}_{ele} = \frac{4k_B T d}{\pi \lambda_D^3 l_B} \gamma^2 e^{-\bar{d}/\lambda_D} \quad \text{if } [\text{NaCl}] \neq 0 \text{ and } \bar{d}/\lambda_D \gg 1$$

Helfrich interaction

$$\bar{B}_{und} = \frac{3(k_B T)^2 d}{16\mu_{Hel} \kappa \bar{d}^4}$$

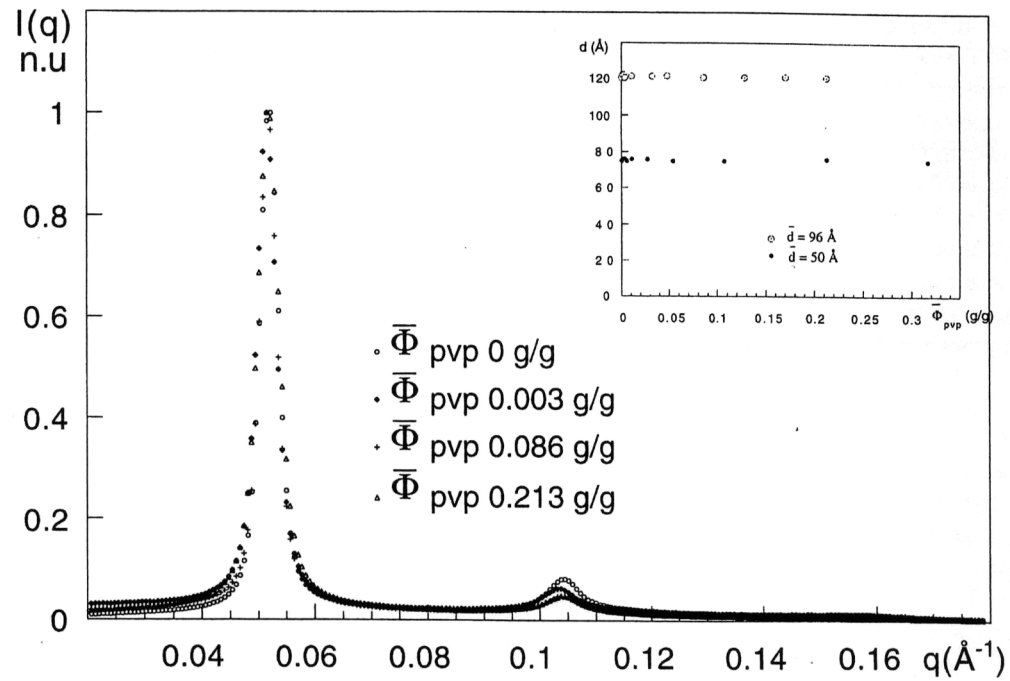
Total layer compression modulus

$$\bar{B} = \bar{B}_{mem} + \bar{B}_{\mu}^{poly}$$

Experiments

C. Ligoure, G. Bouglet, G. Porte, O. Diat, J. Phys. II (1997)

Sample: CPCI(cetylpyridinium chloride)/hexanol/water + Polyvinylpyrrolidone



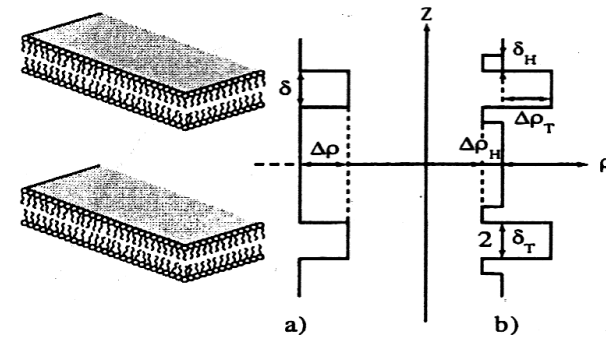
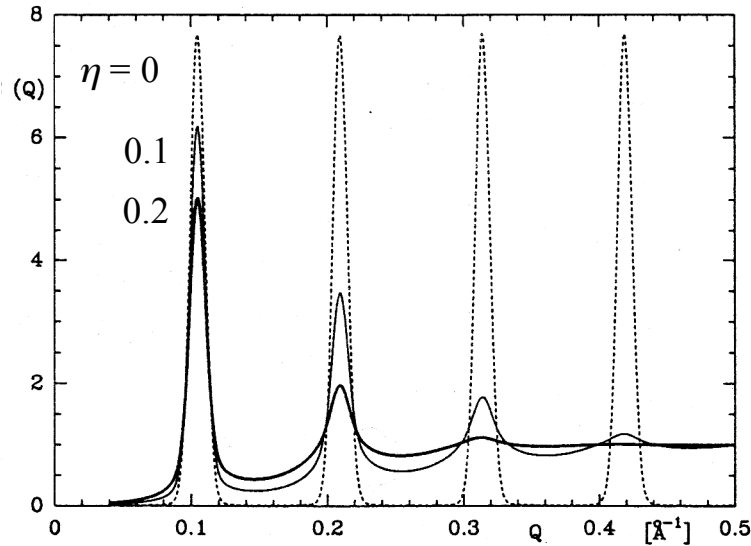
Scattering Profile Analysis

$$I(q) = 2\pi \frac{V}{d} \frac{P(q)S(q)}{q^2}$$

Structure Factor

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

$$\alpha(n) = \frac{\eta}{4\pi^2} [\ln(\pi n) + \gamma] \quad \eta = \frac{q_0^2 k_B T}{8\pi \sqrt{KB}}$$

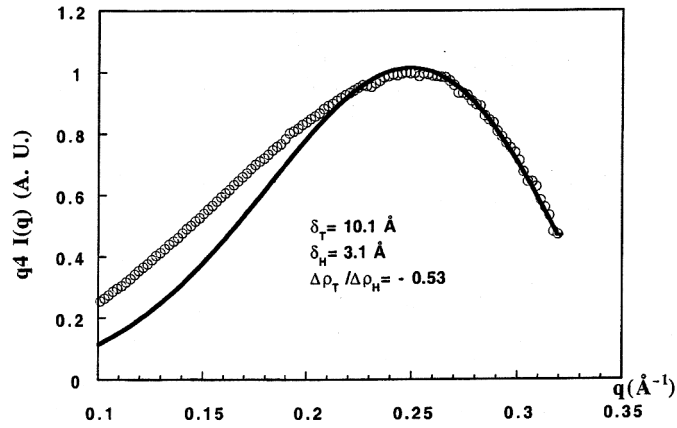


Form factor

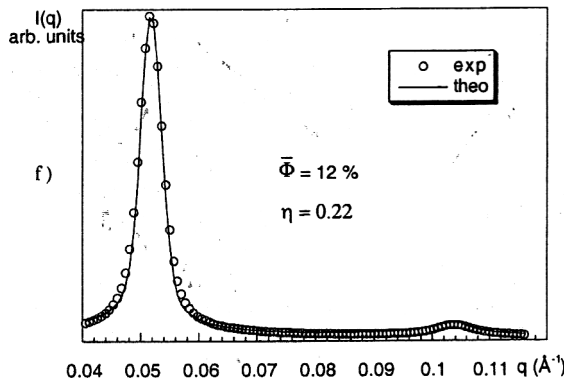
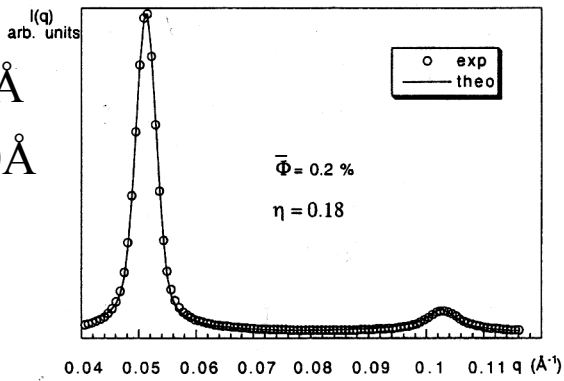
$$P_{neut}(q) = \frac{2\Delta\rho^2}{q^2} [1 - \cos(q\delta_{neut}) e^{-q^2\sigma^2/2}]$$

$$P_{X-ray}(q) = \frac{4}{q^2} \{ \Delta\rho_H [\sin[q(\delta_H + \delta_T)] - \sin(q\delta_T)] + \Delta\rho_T \sin(q\delta_T) \}^2$$

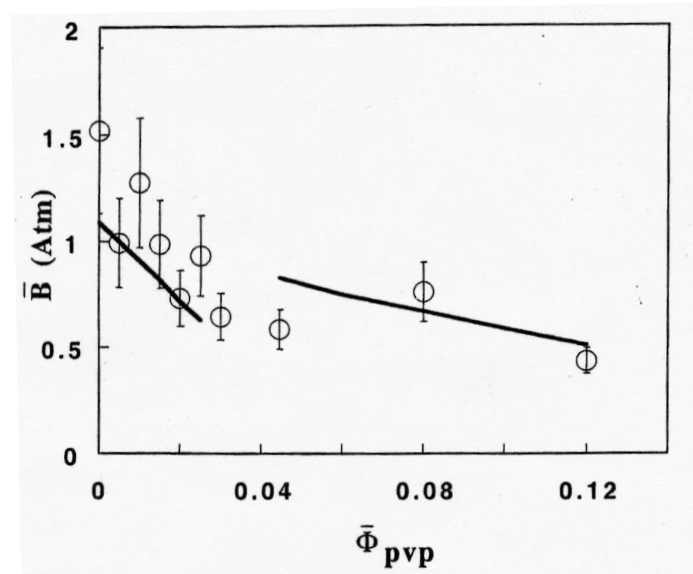
Dilute lamellar Sample : $P(q)$



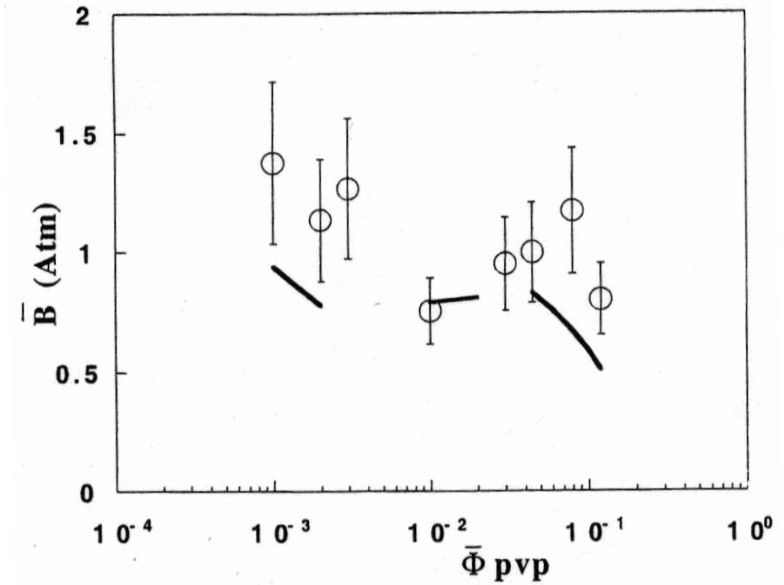
$\bar{d} = 100 \text{ \AA}$
 $R_g = 600 \text{ \AA}$



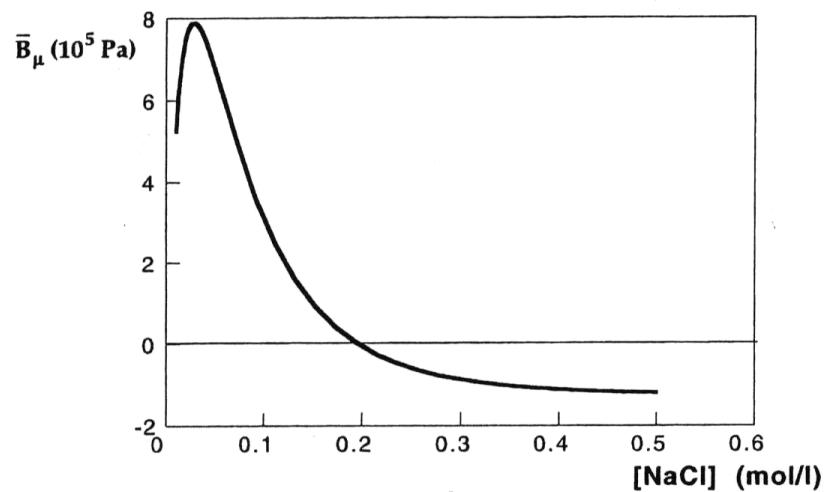
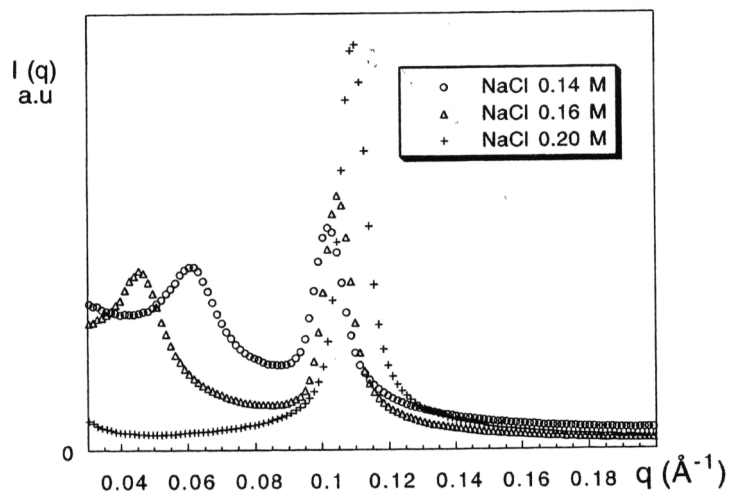
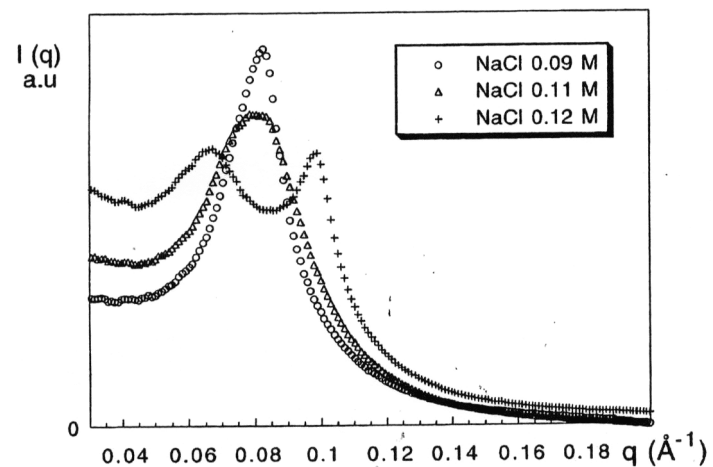
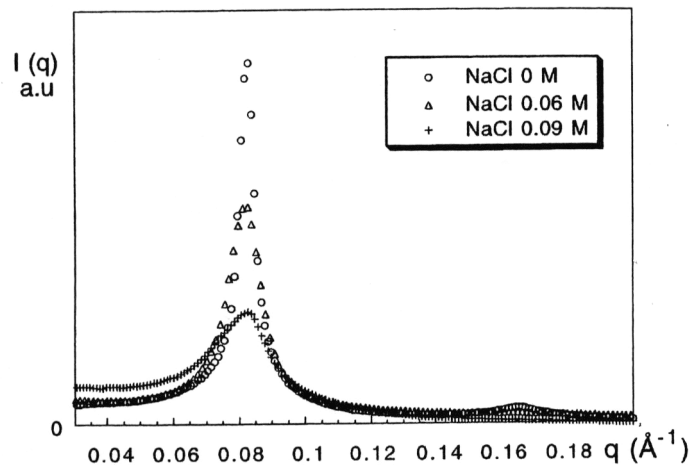
3DD - 3DSD



2DD - 2SDSD - 3DSD



Electrostatic interaction - Helfrich interaction



Confinement of colloids in lamellar slits

Samples:

Surfactant : $C_{12}E_5$

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

At 5 wt% $\bar{d} \approx 80$ nm

Colloidal Particle:

Polystyrene Latex ($a = 8$ nm)

- Counter experiment

Polymer :

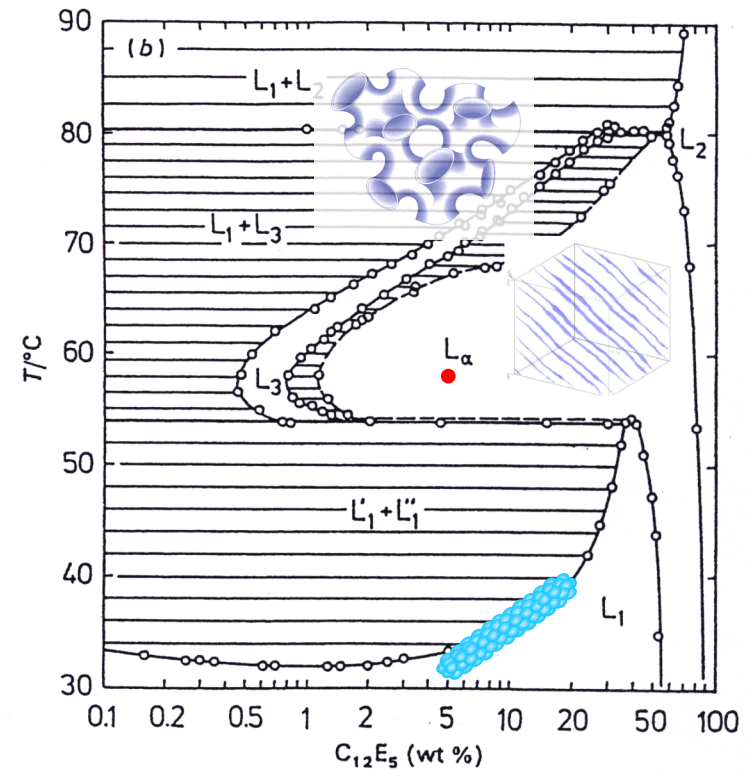
Polyethylene Oxide (PEO)

$M_w=20,000$ $R_g \sim 10$ nm

Neutron Scattering Experiments

Small Angle Neutron Scattering (SANS)

Neutron Spin Echo (NSE)



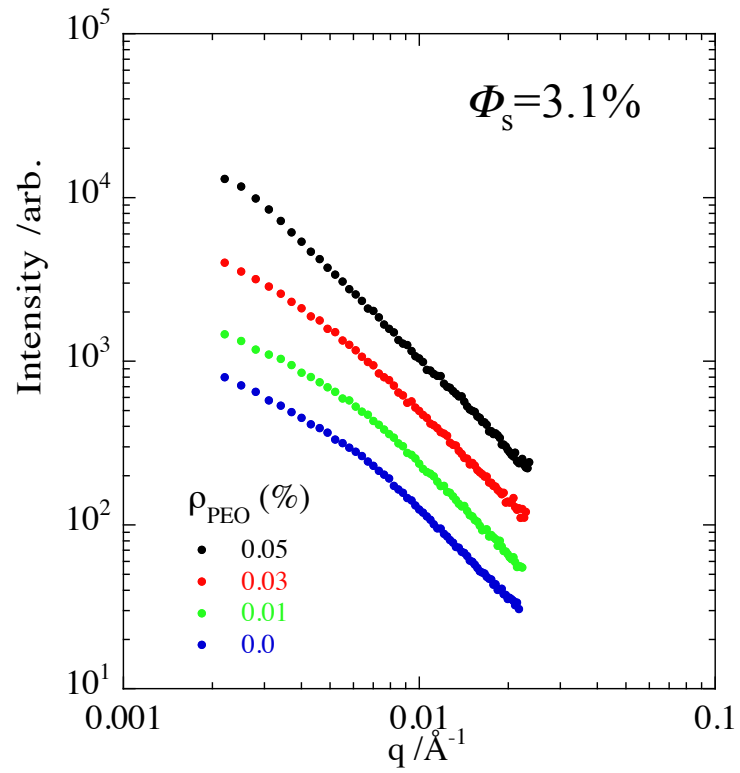
Phase Diagram of $C_{12}E_5$ System

Neutron Scattering Facility at Tokai

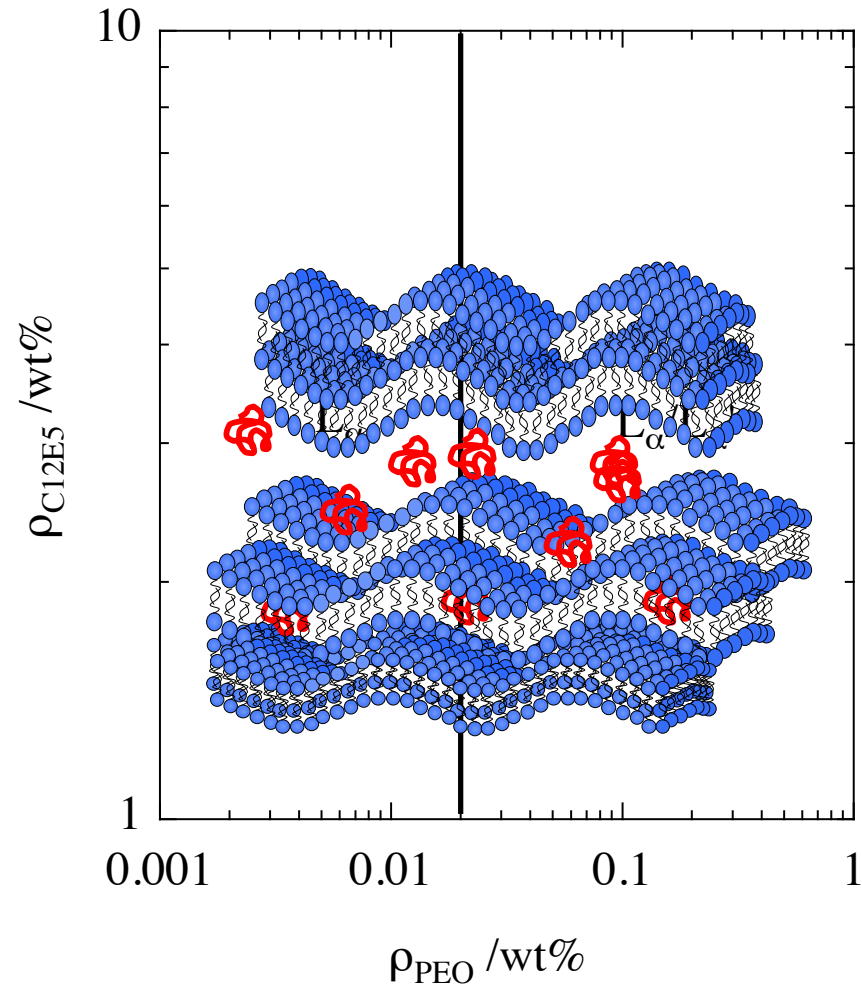


Lamellar Membrane + Polymer System

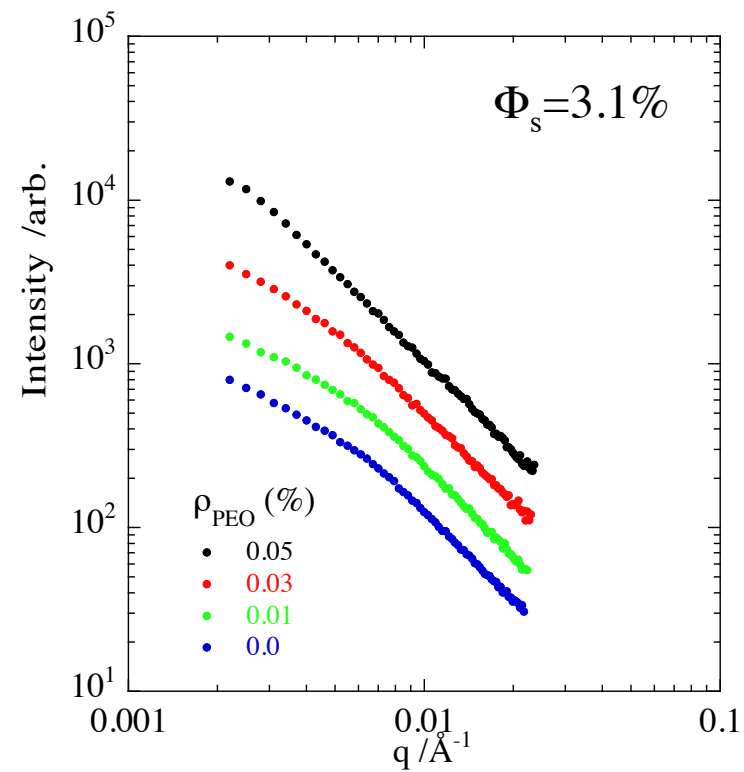
SANS Profiles



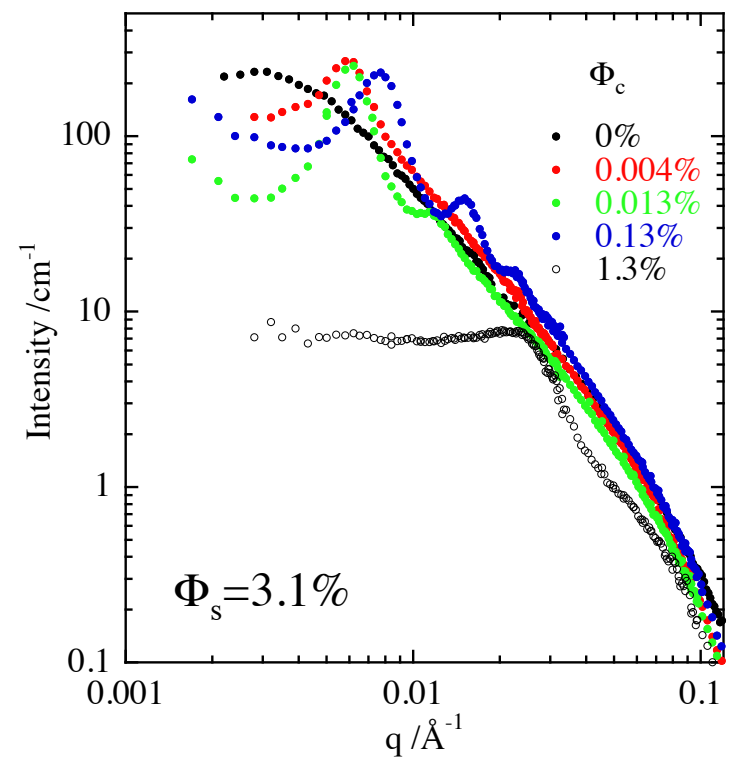
Phase Diagram



Membrane + Polymer System



Membrane + Colloids System



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

Layer compressibility: \bar{B}_μ

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

Static Structure Factor

$$S(q) = 1 + 2 \sum_1^{N-1} \left(1 - \frac{n}{N}\right) \cos\left(\frac{qdn}{1 + 2\Delta q^2 d^2 \alpha(n)}\right) \times \exp\left[-\frac{2q_z^2 d^2 \alpha(n) + \Delta q^2 d^2 n^2}{2(1 + 2\Delta q^2 d^2 \alpha(n))}\right] \frac{1}{\sqrt{1 + 2\Delta q^2 d^2 \alpha(n)}}$$

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

$$\eta = \frac{q_0^2 k_B T}{8\pi \sqrt{KB}}$$

Dynamic Structure Factor

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

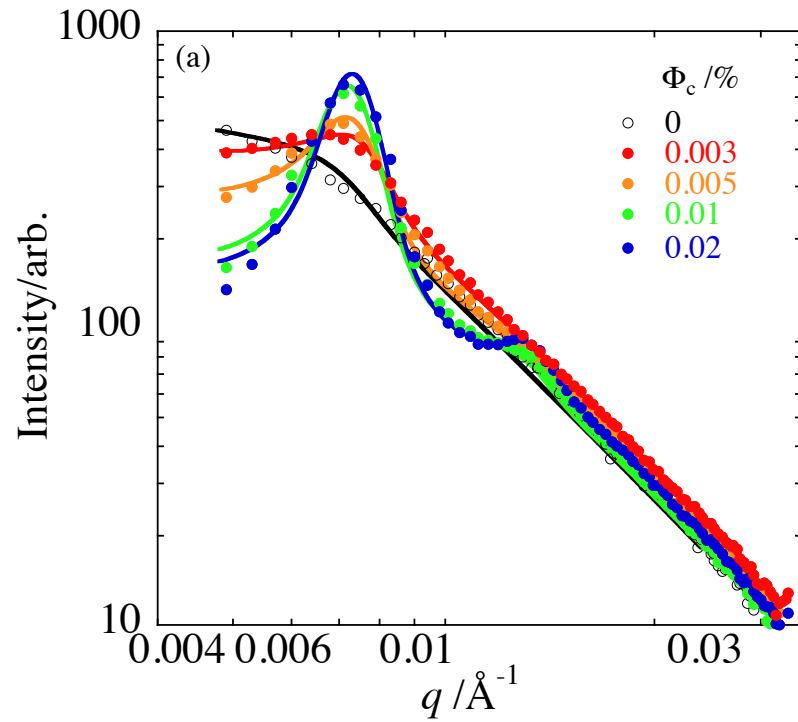
$$\Gamma_q = 0.025 \gamma_k \left(\frac{k_B T}{\kappa}\right)^{1/2} \frac{k_B T}{\eta_v} q^3$$

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

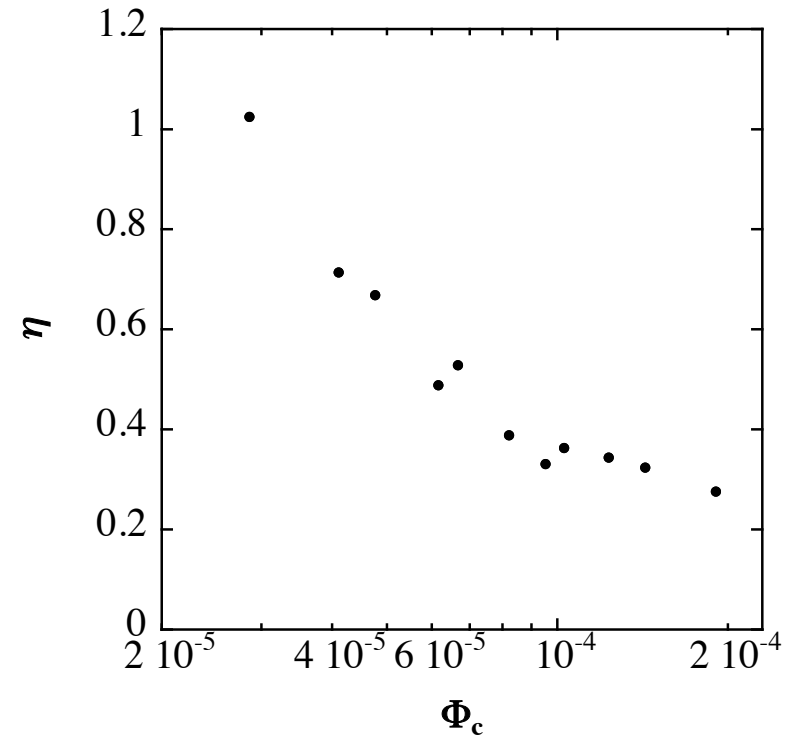
Compression modulus B

Estimation of Caillé parameter η

Fitting of SANS profile

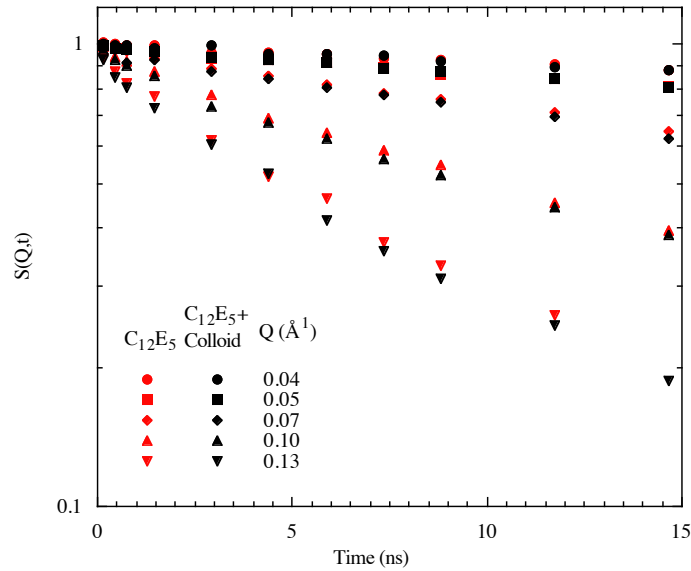


Caillé parameter η v.s. colloid concentration Φ_c



$$\eta = \frac{q_0^2 k_B T}{8\pi \sqrt{KB}}$$

Estimation of bending modulus from NSE measurements



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

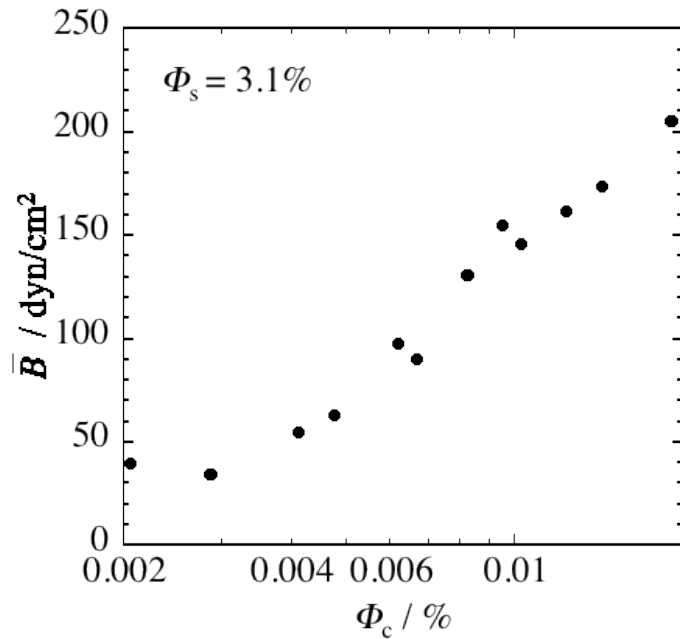
$$\Gamma_q = 0.025\gamma_k \left(\frac{k_B T}{\kappa}\right)^{1/2} \frac{k_B T}{\eta_v} q^3$$

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

$$\kappa / k_B T$$

$$C_{12}E_5/\text{water} \quad \sim 3.0$$

$$C_{12}E_5/\text{water} + \text{colloidal particle} \quad \sim 2.8$$



Bending modulus is independent of addition of colloidal particles.

Layer Compressibility



$$\eta = \frac{q_0^2 k_B T}{8\pi\sqrt{KB}}$$

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

Suppression of Membrane Fluctuations by Confined Colloids

Effective volume fraction of confined colloids

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

Restriction of membrane fluctuations

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

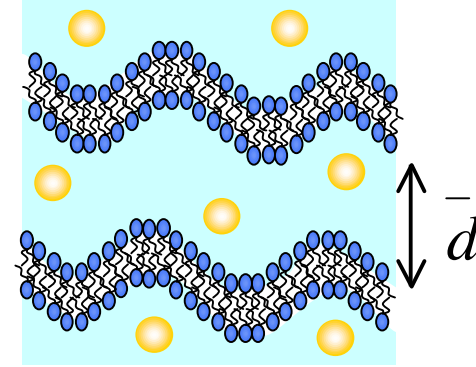
$$\bar{\Phi}_c^{eff} \ll 1 \quad |u(r)| \leq \bar{d}$$

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

$$R(q) = \frac{\langle |u_q|^2 \rangle_{restricted}}{\langle |u_q|^2 \rangle_{free}}$$

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

$$\bar{B}_{mc} = \frac{d}{32\mu} \frac{(k_B T)^2}{\kappa \bar{d}^4} \frac{g(\bar{\Phi}_c^{eff})}{h(\bar{\Phi}_c^{eff})}$$

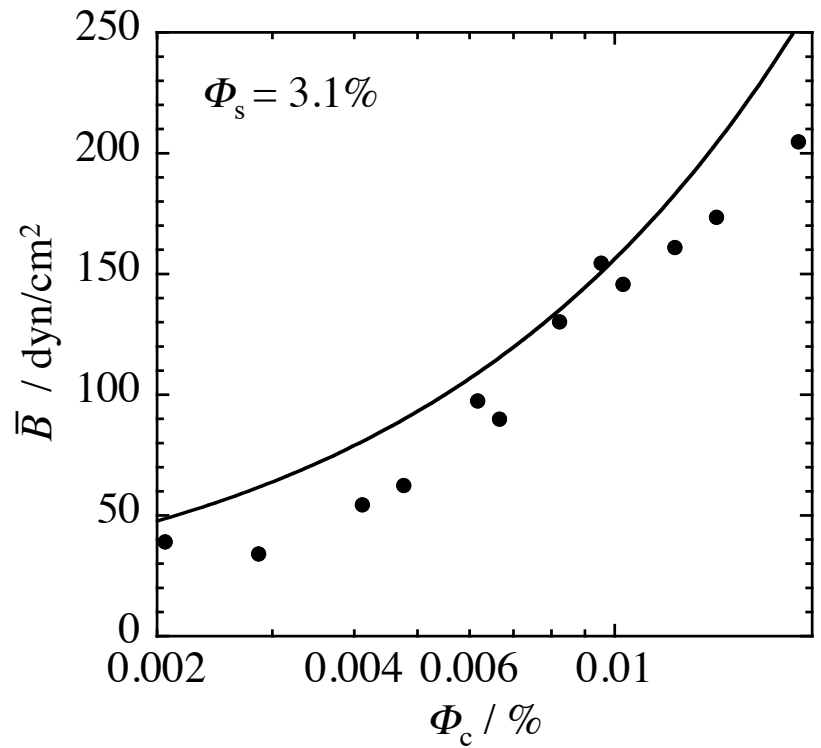


$$\begin{aligned} g(\bar{\Phi}_c^{eff}) = & -3\bar{d}^2 \bar{\Phi}_c^2 - 2mn^2 \left(\frac{R_c^m}{w} \right)^2 + 2m^2 n^2 \left(\frac{R_c^m}{w} \right) + 2(m-1)mn \frac{2R_c^m}{w} \cosh\left(\frac{2}{w\bar{\Phi}_c^{eff}} \right) \\ & + n \left(\frac{R_c^m}{w} \right) \bar{d}^m \bar{\Phi}_c \sinh\left(\frac{2}{w\bar{\Phi}_c^{eff}} \right) (3-4m-m^2) - 3 \left(\frac{R_c^m}{w} \right) \bar{d}^m \bar{\Phi}_c \sinh\left(\frac{4}{w\bar{\Phi}_c^{eff}} \right) \\ & + 3\bar{d}^{2m} \bar{\Phi}_c^2 \cosh\left(\frac{4}{w\bar{\Phi}_c^{eff}} \right) \end{aligned}$$

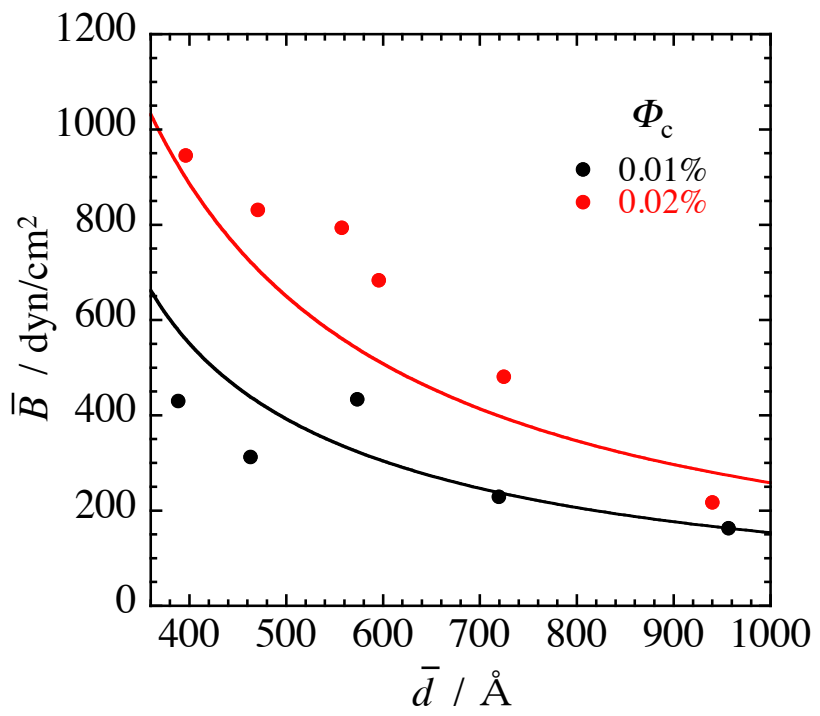
$$\begin{aligned} h(\bar{\Phi}_c^{eff}) = & 2\bar{d}^m \bar{\Phi}_c \sinh\left(\frac{1}{w\bar{\Phi}_c^{eff}} \right) \cosh\left(\frac{1}{w\bar{\Phi}_c^{eff}} \right) \tanh^{-n}\left(\frac{1}{w\bar{\Phi}_c^{eff}} \right) \times \\ & \left[-n \left(\frac{R_c^m}{w} \right) - \left(\frac{R_c^m}{w} \right) \cosh\left(\frac{2}{w\bar{\Phi}_c^{eff}} \right) + \bar{d}^m \bar{\Phi}_c \sinh\left(\frac{2}{w\bar{\Phi}_c^{eff}} \right) \right] \end{aligned}$$

Comparison between experiments and theory

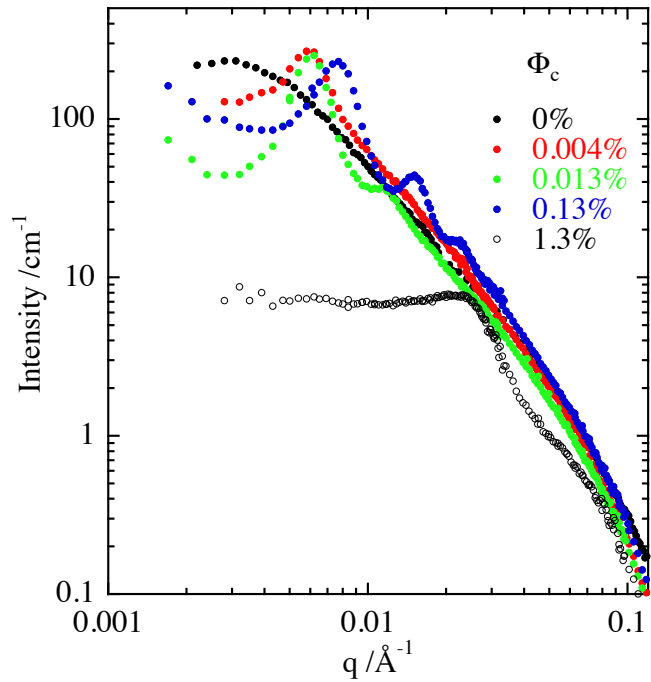
Φ_c dependence



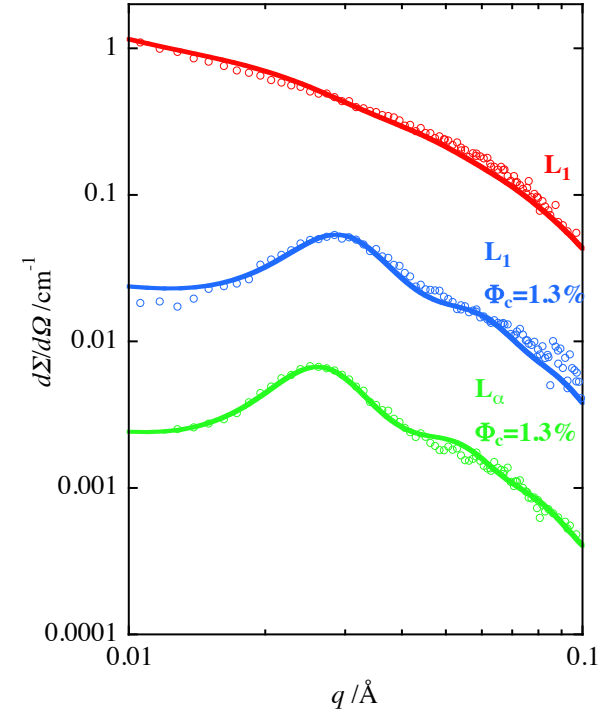
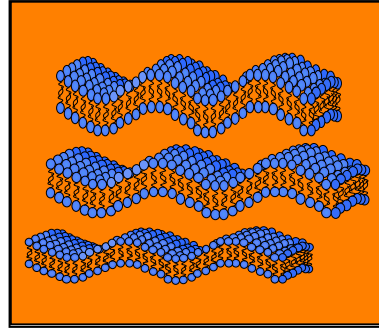
Φ_s dependence



Morphology transition induced by colloids



contrast matching experiment



Polydisperse prolate core shell model

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

Form Factor

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

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

$$u_t = q R_t \sqrt{a_t^2 x^2 + (1 - x^2)}$$

$$u = q R \sqrt{a^2 x^2 + (1 - x^2)}$$

