コントラスト変調中性子小角散乱を用いたソフトマター多成分系の精密構造解析

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コントラスト変調
中性子小角散乱法

中性子散乱

高分子科学における中性子散乱の果たした功績

高分子溶融体中の一本鎖の広がりはガウス統計に従う.

- Paul J. Flory: 1974年ノーベル化学賞
- Peter Debye: 高分子におけるDebye関数

高分子溶融体のダイナミクス

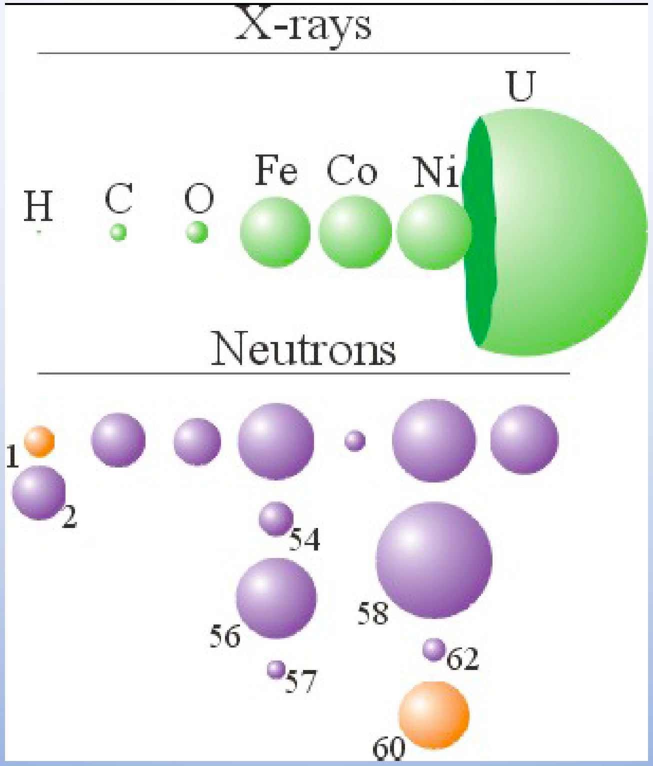
- deGennes, Doi & Edwards Model (Reptation Model)の検証.
  中性子スピンエコー法による直接検証（at ILL in 1980’s; Richter, Mezei, *etc.*）
- deGennes：1991年ノーベル物理学賞

高分子希薄溶液のダイナミクス

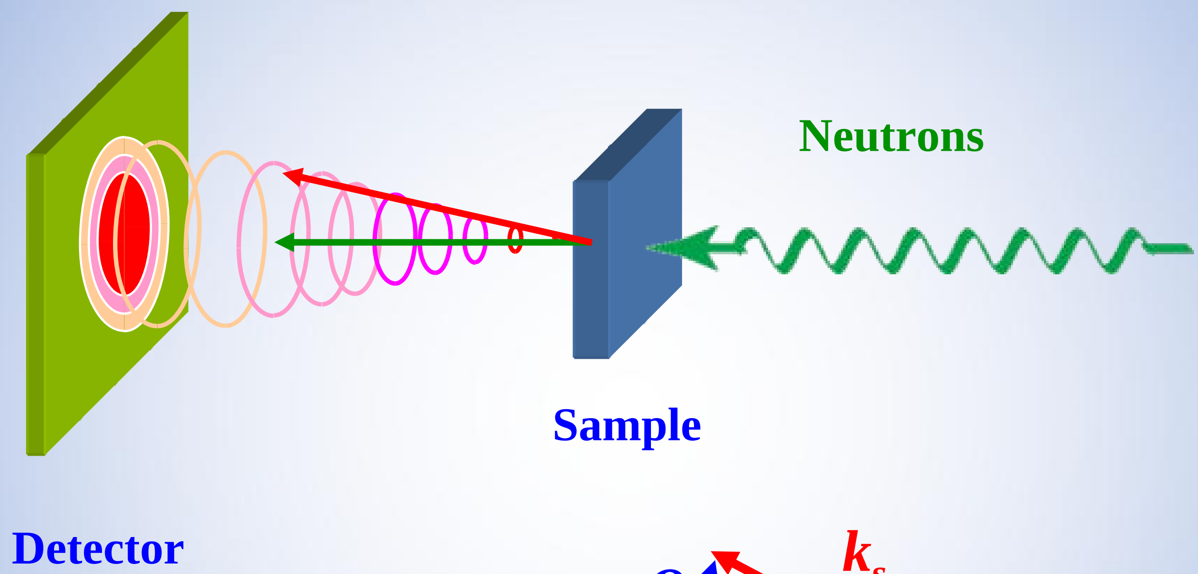
- 中性子スピンエコー法によるZimm Modelの直接検証（at ILL in 1980’s; Higgins, Richter, *etc.*）

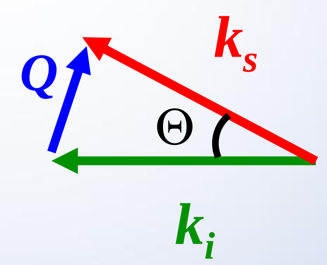
重水素標識

	b [×10^{12} cm]	σ_{coh} [×10^{24} cm]	σ_{inc} [×10^{24} cm]
^{1}H	-0.374	1.76	79.7
^{2}D	0.667	5.59	2



中性子小角散乱実験





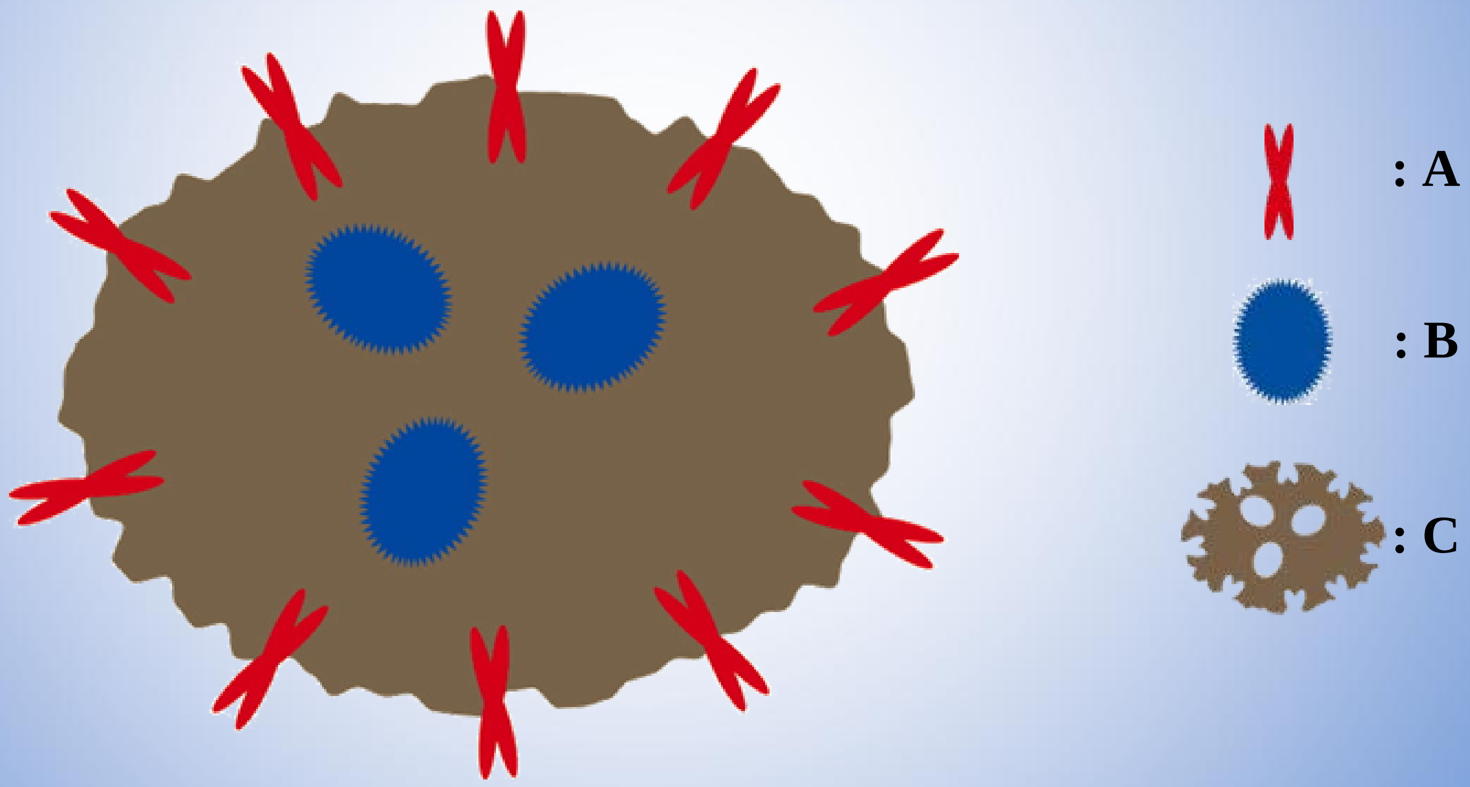
$$|\boldsymbol{k_i}| = |\boldsymbol{k_s}| = 2\pi / \lambda$$

$$|\boldsymbol{Q}| = |\boldsymbol{k_s} - \boldsymbol{k_i}| = \frac{4\pi}{\lambda}\sin\frac{\Theta}{2}$$

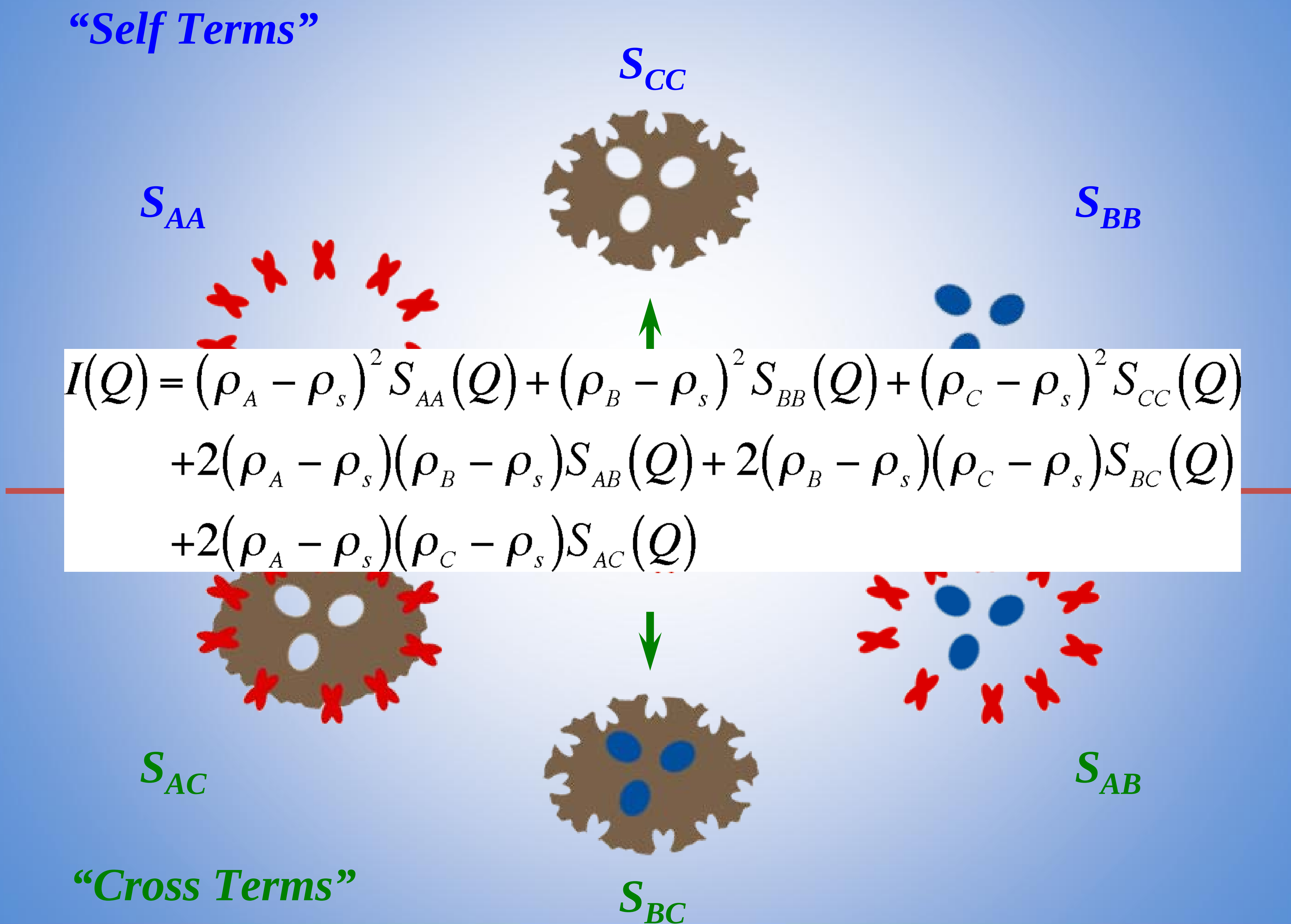
k_i : 入射波の波数ベクトル
k_s : 散乱波の波数ベクトル
Q : 散乱ベクトル

多成分系における中性子小角散乱実験

"どのように少量の小さい重要な成分を識別できるのか?"

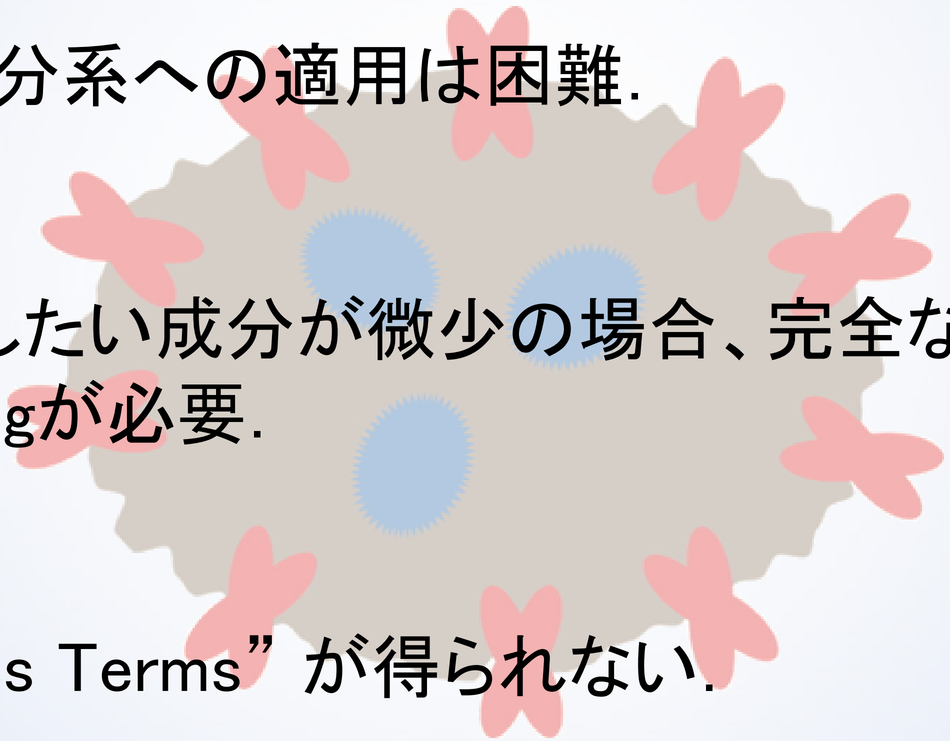


多成分系からの散乱



$$
\begin{aligned}
I(Q) = {} & (\rho_A - \rho_s)^2 S_{AA}(Q) + (\rho_B - \rho_s)^2 S_{BB}(Q) + (\rho_C - \rho_s)^2 S_{CC}(Q) \\
& + 2(\rho_A - \rho_s)(\rho_B - \rho_s) S_{AB}(Q) + 2(\rho_B - \rho_s)(\rho_C - \rho_s) S_{BC}(Q) \\
& + 2(\rho_A - \rho_s)(\rho_C - \rho_s) S_{AC}(Q)
\end{aligned}
$$

Contrast Matching



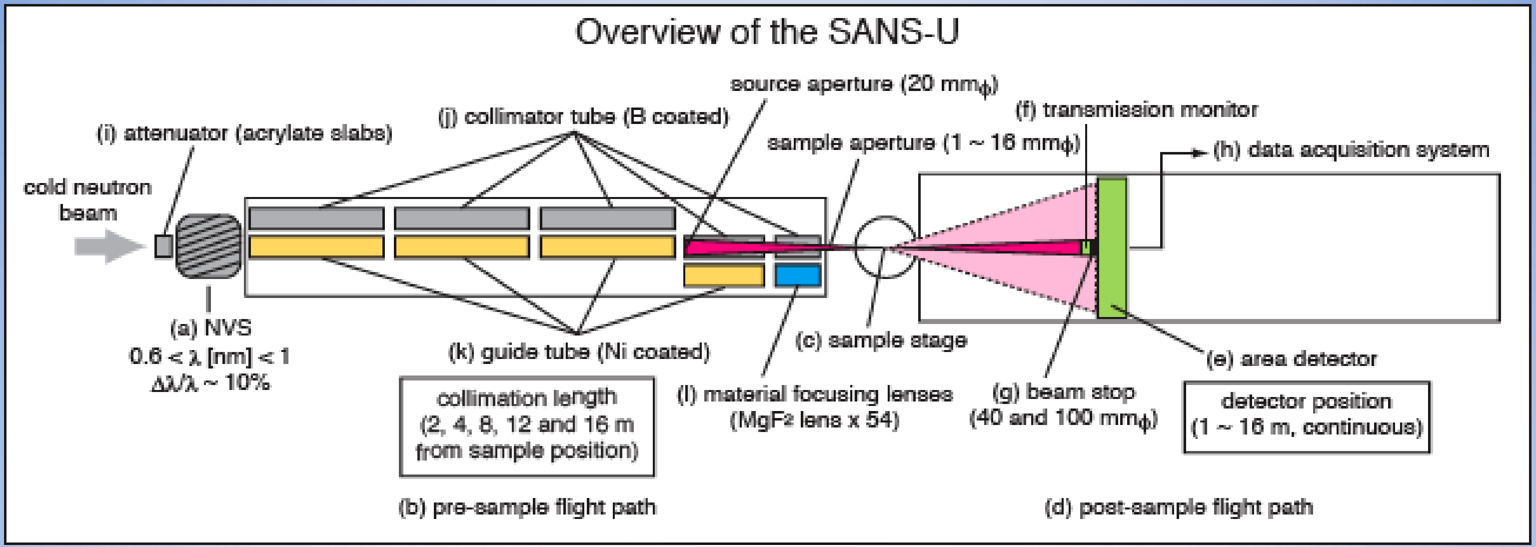
- 多成分系への適用は困難.
- 観測したい成分が微少の場合、完全なMatchingが必要.
- “Cross Terms” が得られない.

⇩

Contrast Variation

中性子小角散乱

Small-Angle Neutron Scattering (SANS)



SANS-U

(ISSP, U-Tokyo@JAEA.Tokai.JP)

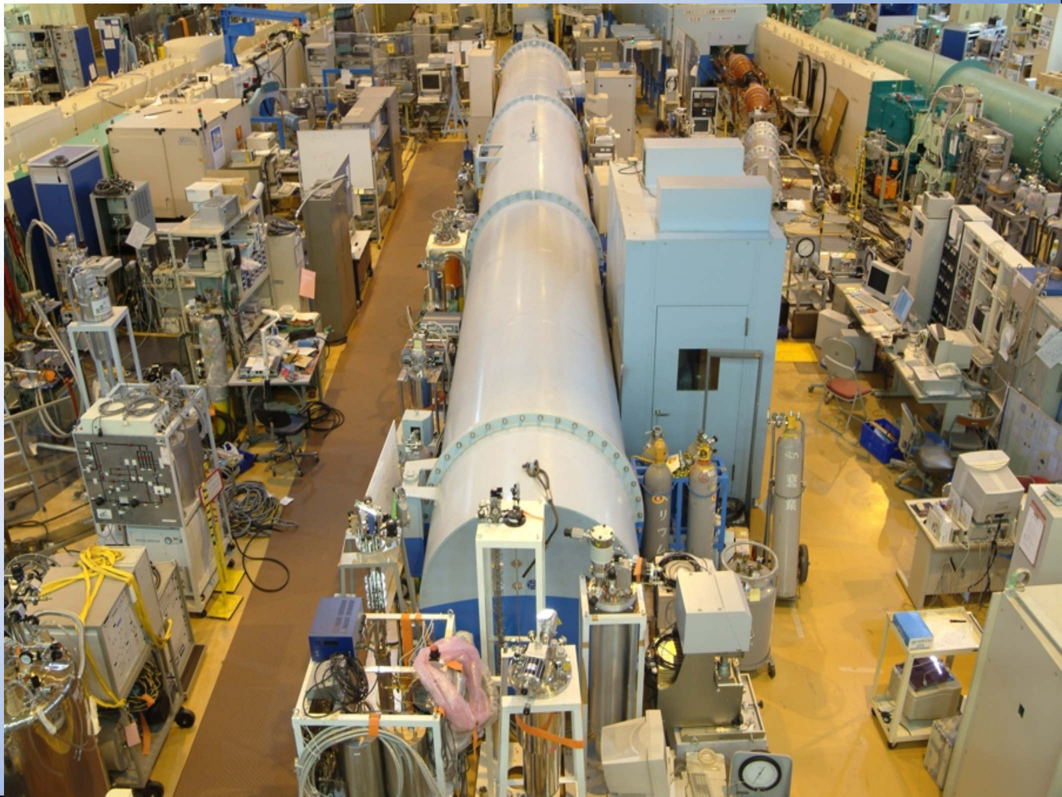
・wavelength; 7.0Å

($\Delta\lambda/\lambda = 0.10$)

・sample to detector distance;

1m〜16m

http://www.issp.u-tokyo.ac.jp/labs/neutron/

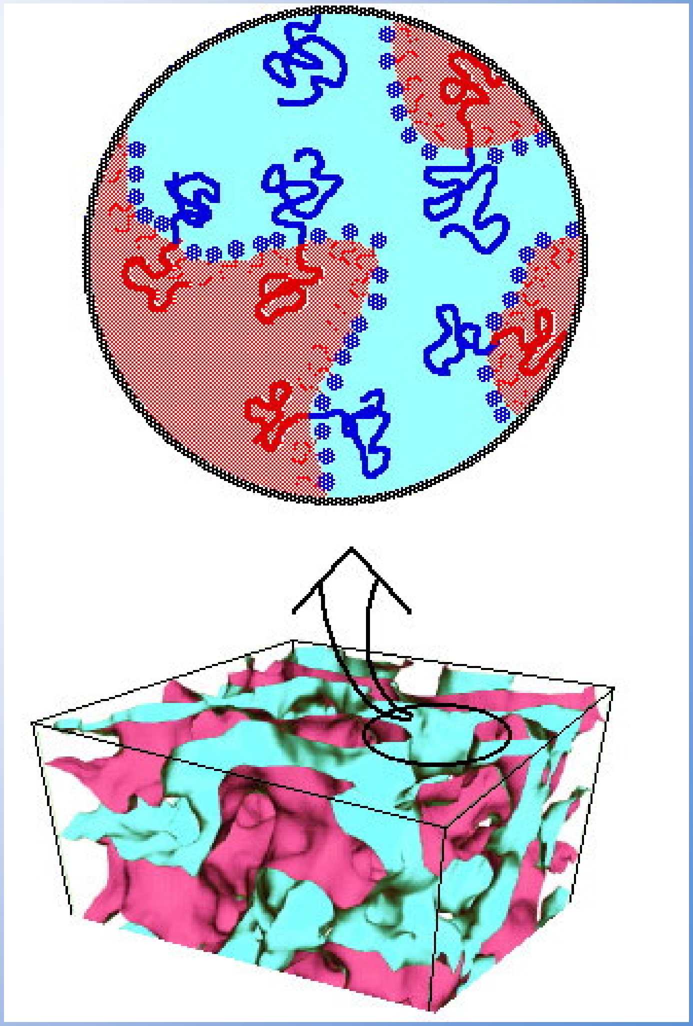


界面における高分子の微細構造解析1

マイクロエマルジョン中での両新媒性高分子

Effect of amphiphilic block copolymers on the structure and phase behavior of oil–water-surfactant mixtures

H. Endo, J. Allgaier, M. Monkenbusch,
D. Richter, G. Gompper
(*FZ-Jülich*)
B. Jacobs, Th. Sottmann, R. Strey
(*Universität zu Köln*)



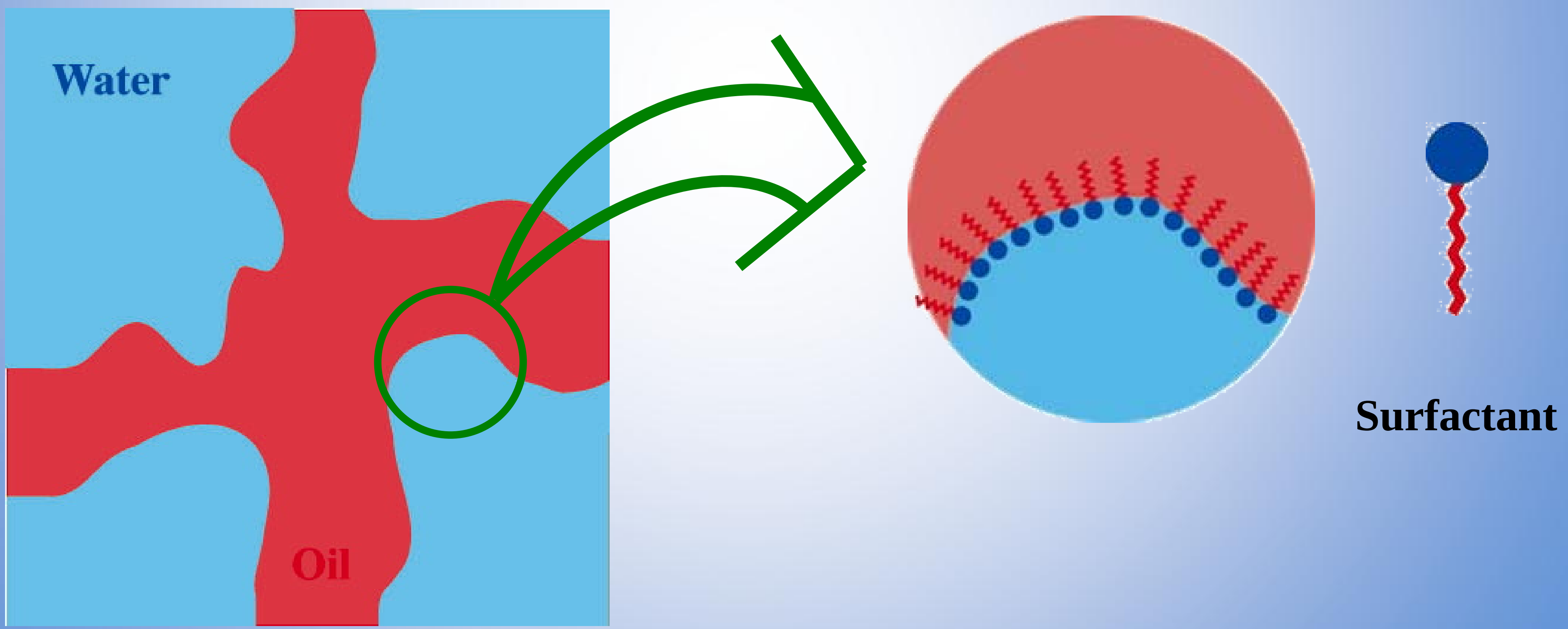
Phys. Rev. Lett. **85**, 102 (2000)

J. Chem. Phys. **115**, 580 (2001)

Eur. Phys. Lett. **56**, 683 (2001)

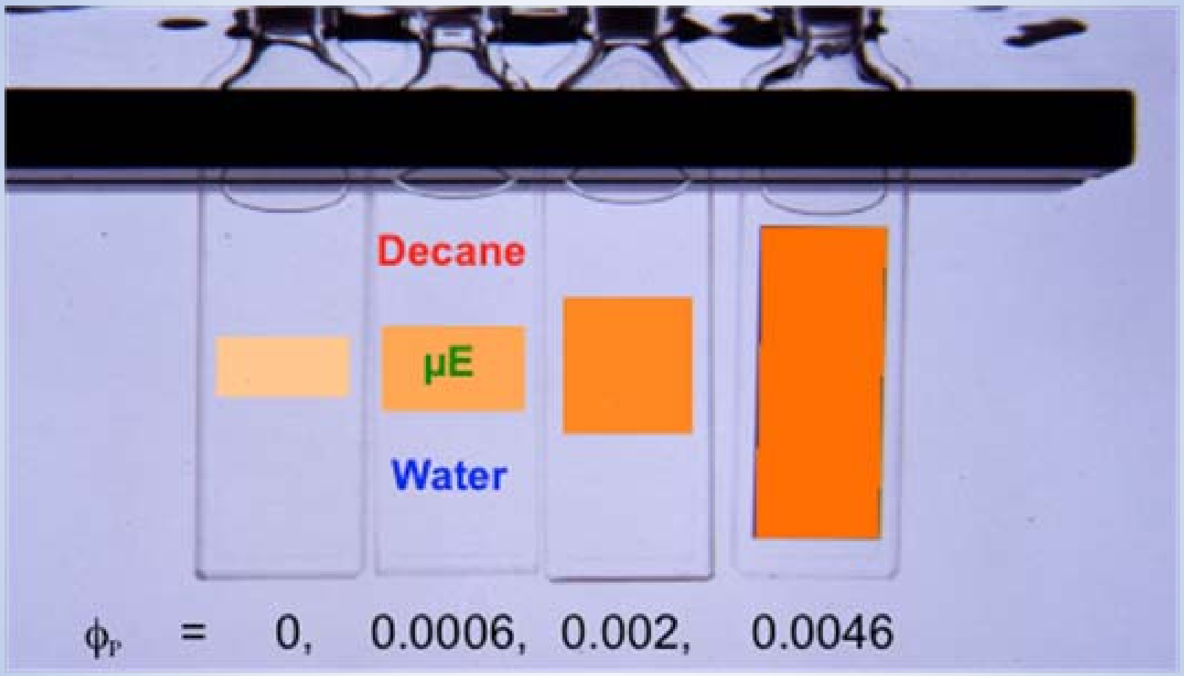
Microemulsion

Mixtures of **oil** and **water** mediated by surfactants



Polymer Boosting Effect

48% Oil, 48% Water, & 4% Surfactant



B. Jakobs et al., Langmuir **15**, (1999) 6707

Mw > 10 kg/mol

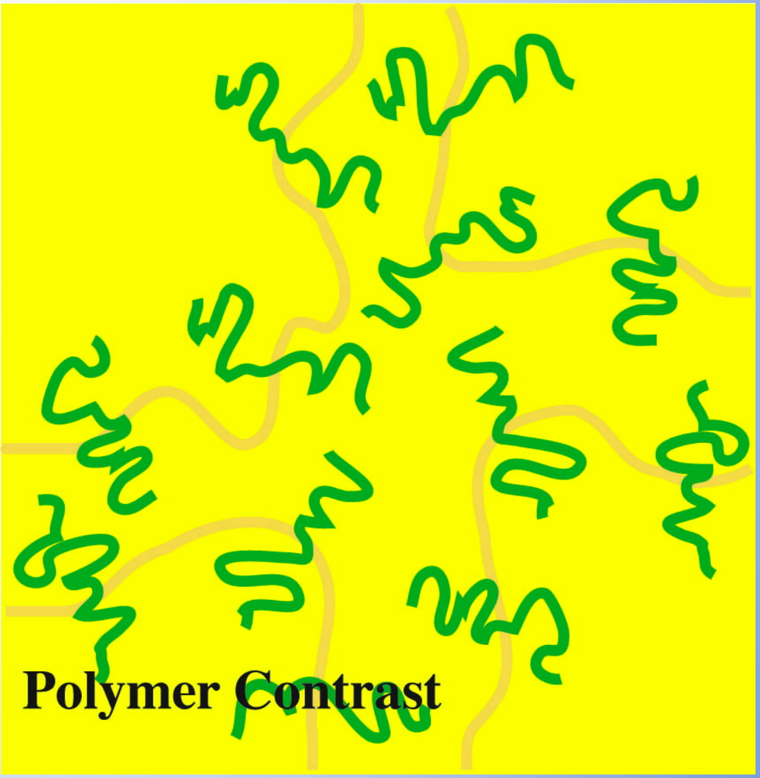
Mw = 0.335 kg/mol

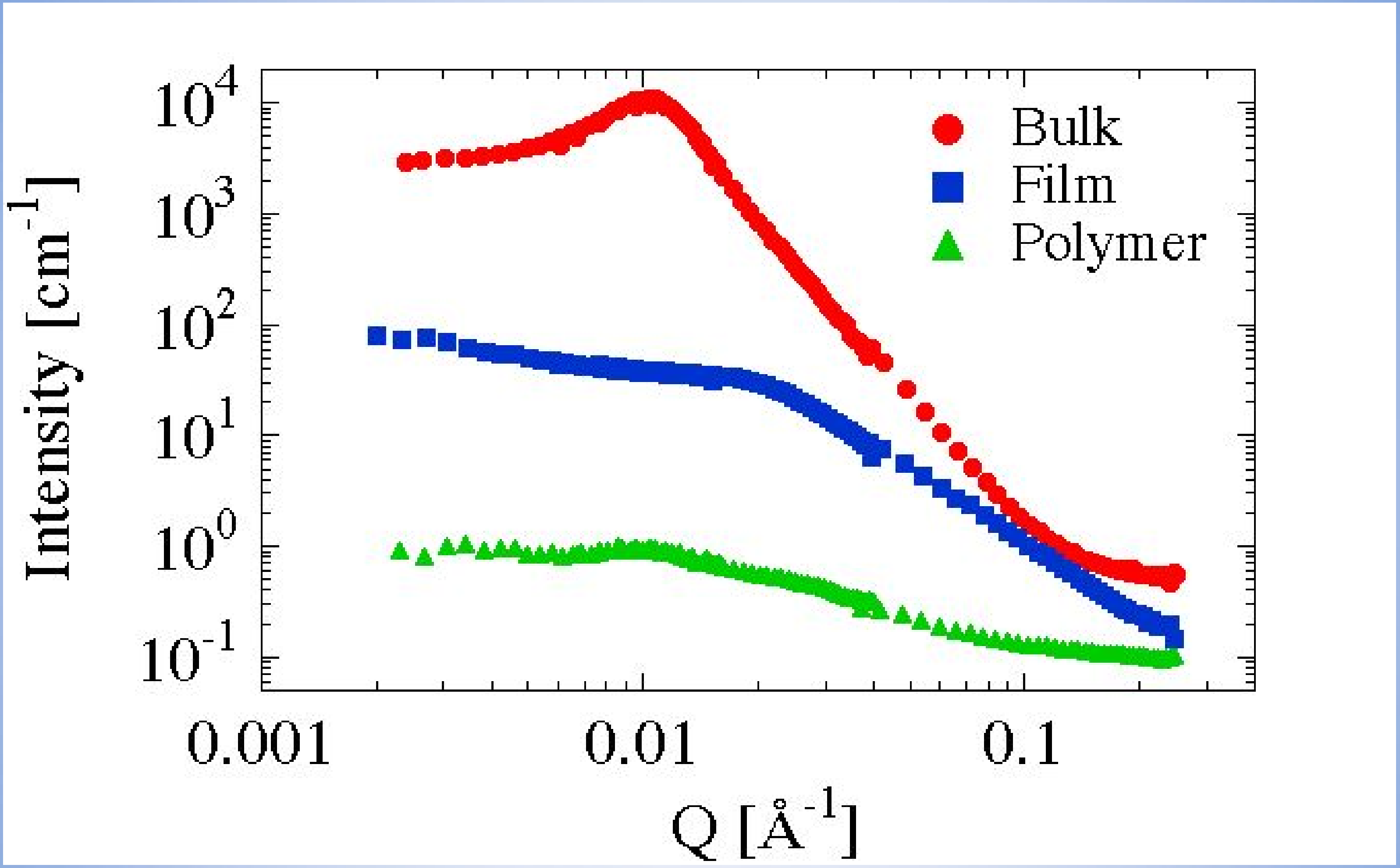
Contrast

d-Water and h-decane

d-Water, d-Decane and h-Surfactant

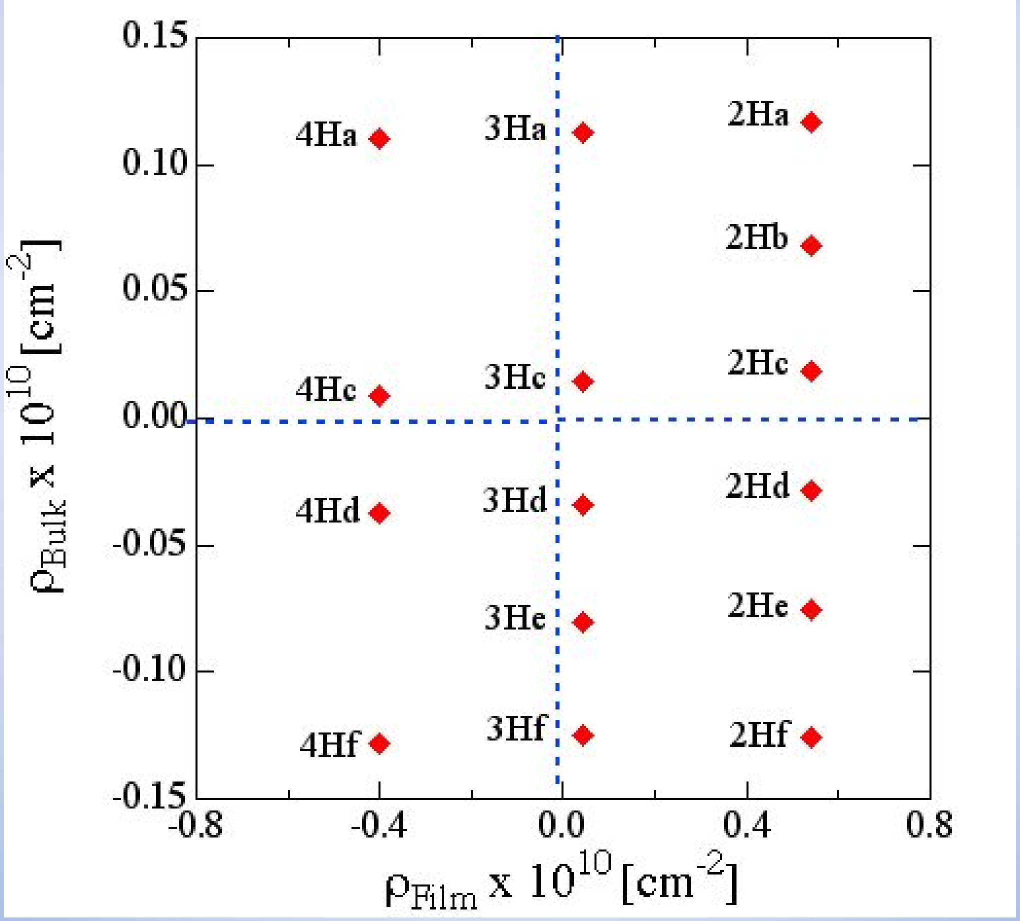
d-Water, d-Decane, d-Surfactant and h-Polymer

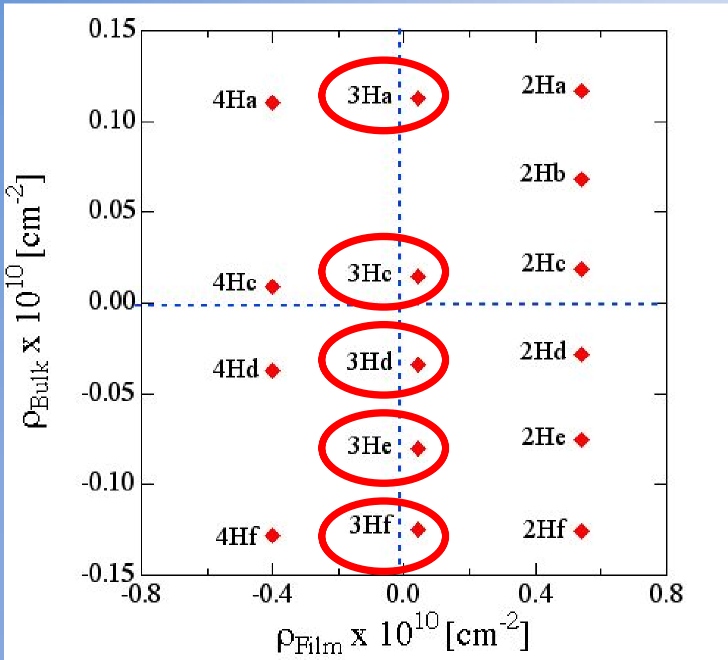




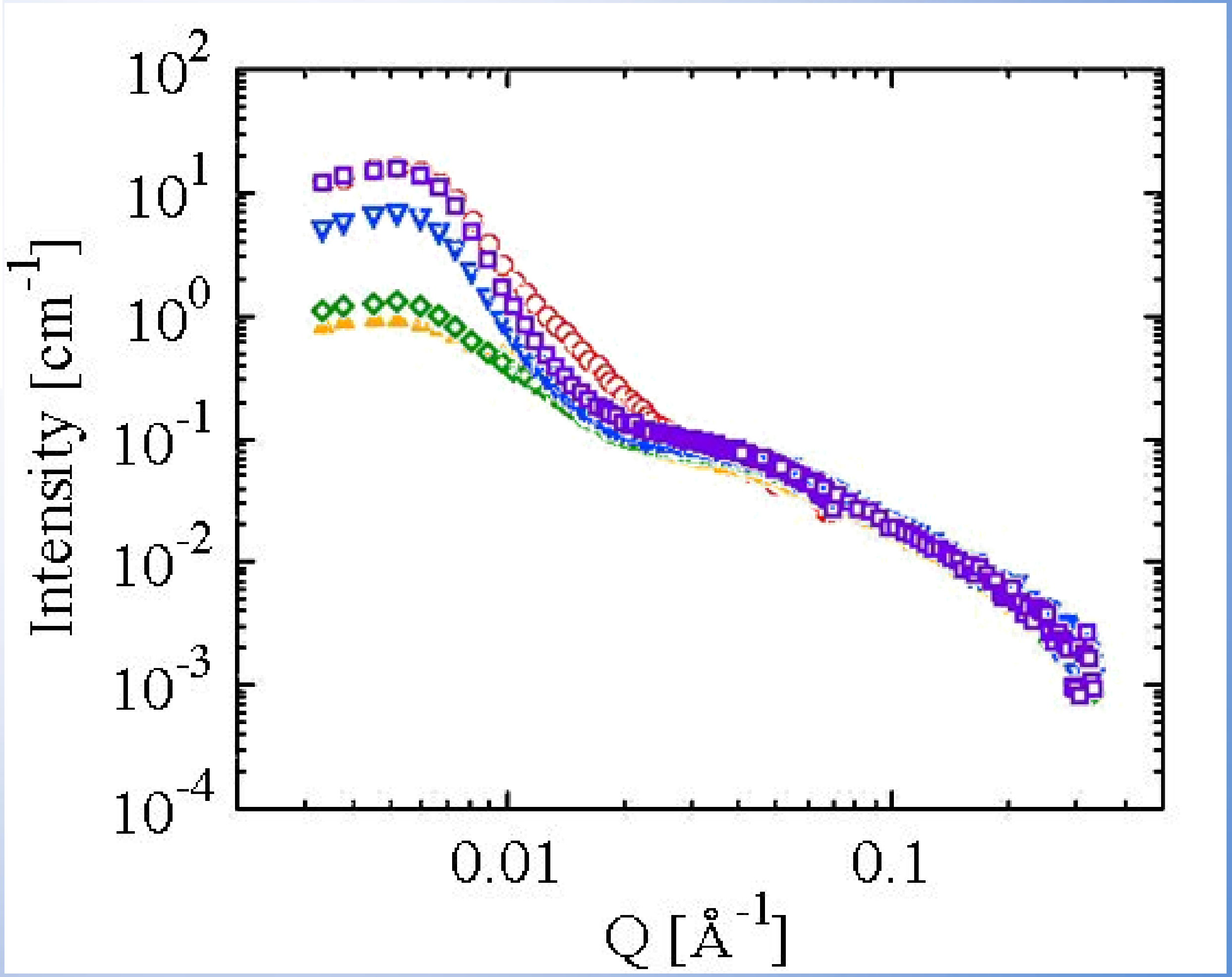
Difficulty : vastly different scattering intensities

Double Contrast Variation





$\rho_{Bulk} \times 10^{10}$ [cm^{-2}]
$\rho_{Film} \times 10^{10}$ [cm^{-2}]
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.8
-0.4
0.0
0.4
0.8
4Ha
3Ha
2Ha
2Hb
4Hc
3Hc
2Hc
4Hd
3Hd
2Hd
3He
2He
4Hf
3Hf
2Hf



Intensity [cm^{-1}]
Q [Å^{-1}]
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0.01
0.1

Evaluation of Partial Scattering Functions

$$\boxed{\begin{aligned} I(Q) = {} & (\rho_w - \rho_o)^2 S_{ww}(Q) + (\rho_f - \rho_o)^2 S_{ff}(Q) + (\rho_p - \rho_o)^2 S_{pp}(Q) \\ & +2(\rho_w - \rho_o)(\rho_f - \rho_o) S_{wf}(Q) + 2(\rho_f - \rho_o)(\rho_p - \rho_o) S_{fp}(Q) \\ & +2(\rho_p - \rho_o)(\rho_w - \rho_o) S_{pw}(Q) \end{aligned}}$$

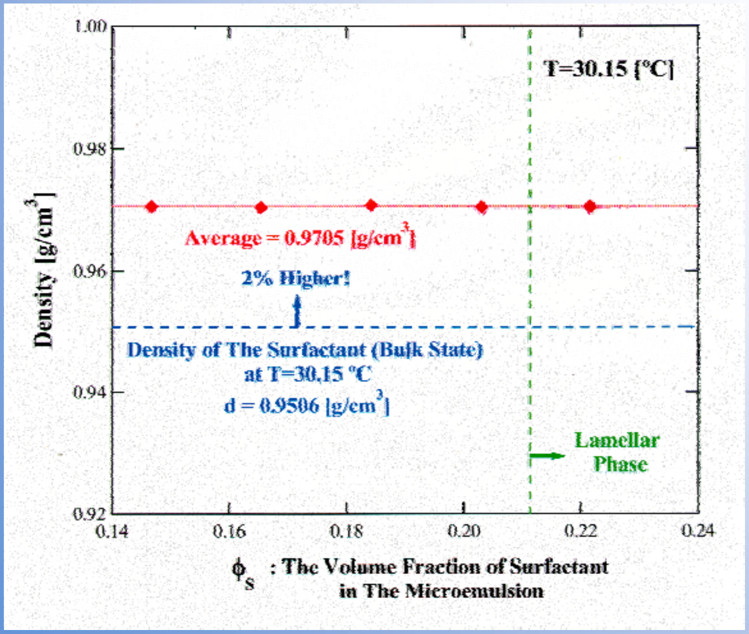
$$\begin{pmatrix} I_1(Q) \\ \vdots \\ I_i(Q) \end{pmatrix} = \begin{pmatrix} \Delta^1\rho_w{}^2 & \Delta^1\rho_f{}^2 & \Delta^1\rho_p{}^2 & \Delta^1\rho_w\Delta^1\rho_f & \Delta^1\rho_f\Delta^1\rho_p & \Delta^1\rho_p\Delta^1\rho_w \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \Delta^i\rho_w{}^2 & \Delta^i\rho_f{}^2 & \Delta^i\rho_p{}^2 & \Delta^i\rho_w\Delta^i\rho_f & \Delta^i\rho_f\Delta^i\rho_p & \Delta^i\rho_p\Delta^i\rho_w \end{pmatrix} \cdot \begin{pmatrix} S_{ww}(Q) \\ S_{ff}(Q) \\ S_{pp}(Q) \\ S_{wf}(Q) \\ S_{fp}(Q) \\ S_{pw}(Q) \end{pmatrix}$$

Contrasts must be known very precisely!

Determination of Scattering Length Densities

1. **Measurement of partial density by precise densimeter**

e.g. surfactant in microemulsion/ pure surfactant



2. **Determination of exact degree of deuteration**

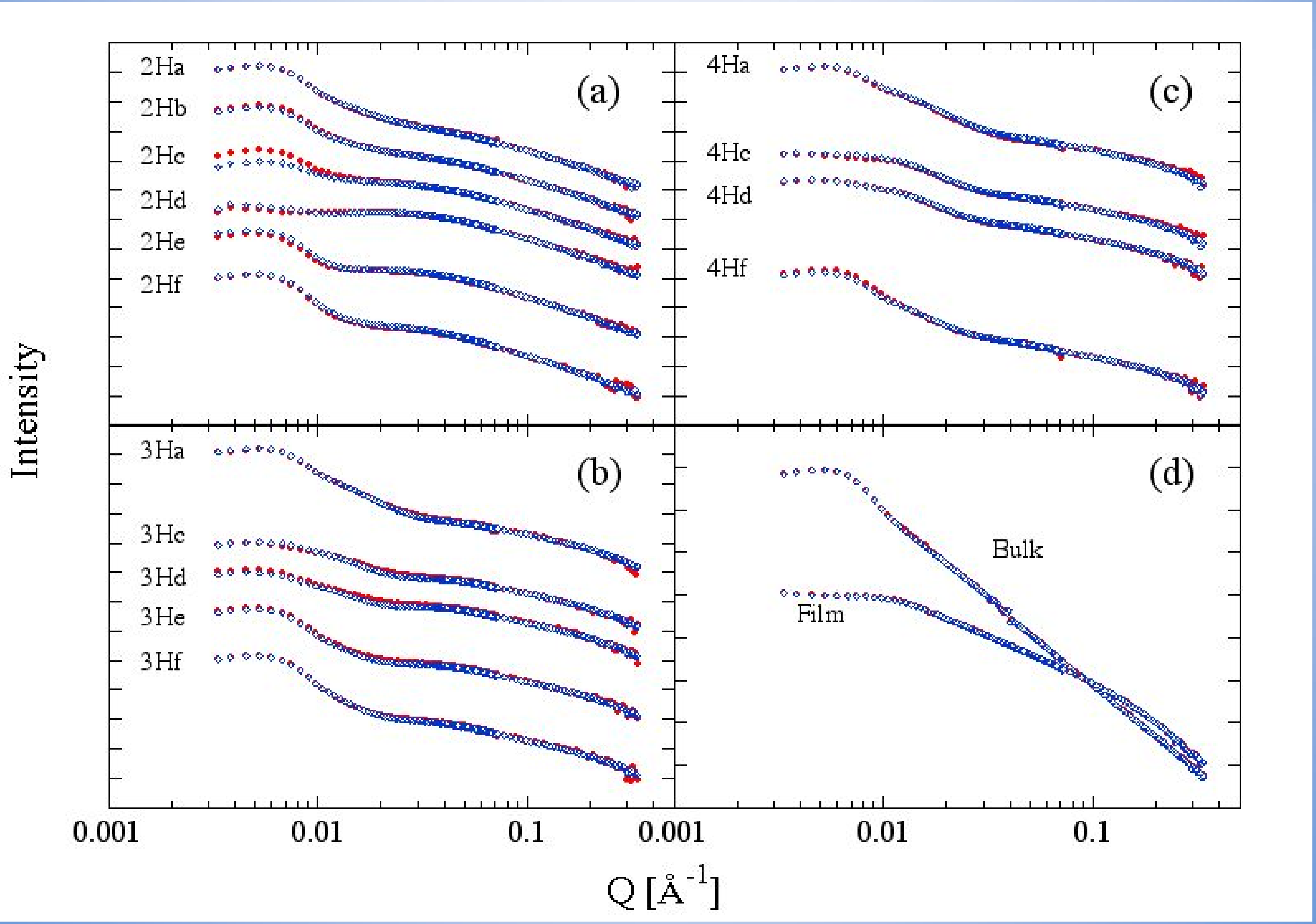
PEO/PEP : fully protonated

d-decane : 98.87% (NMR)

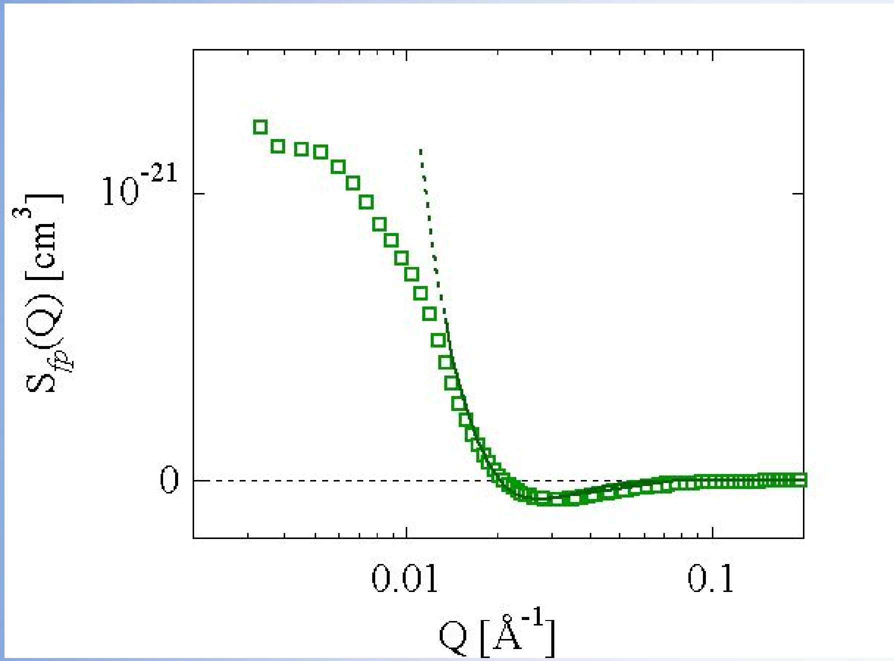
d-water : 98.96%
contrast variation

***d*-surfactant : 99.23% (NMR)**

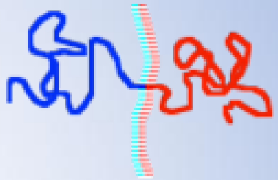
Experimental & Reconstructed Data

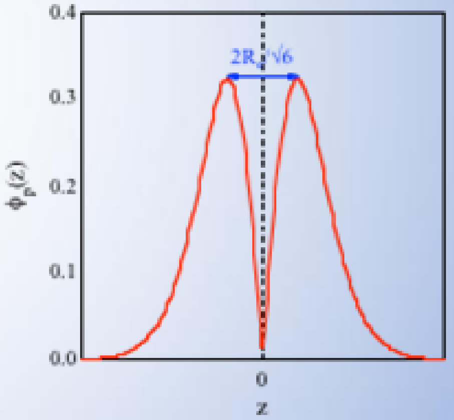


Partial Scattering Functions : S_{fp}



Mushroom conformation





$$S_{fp}(Q) = A_p(Q) \cdot A_f^*(Q)$$

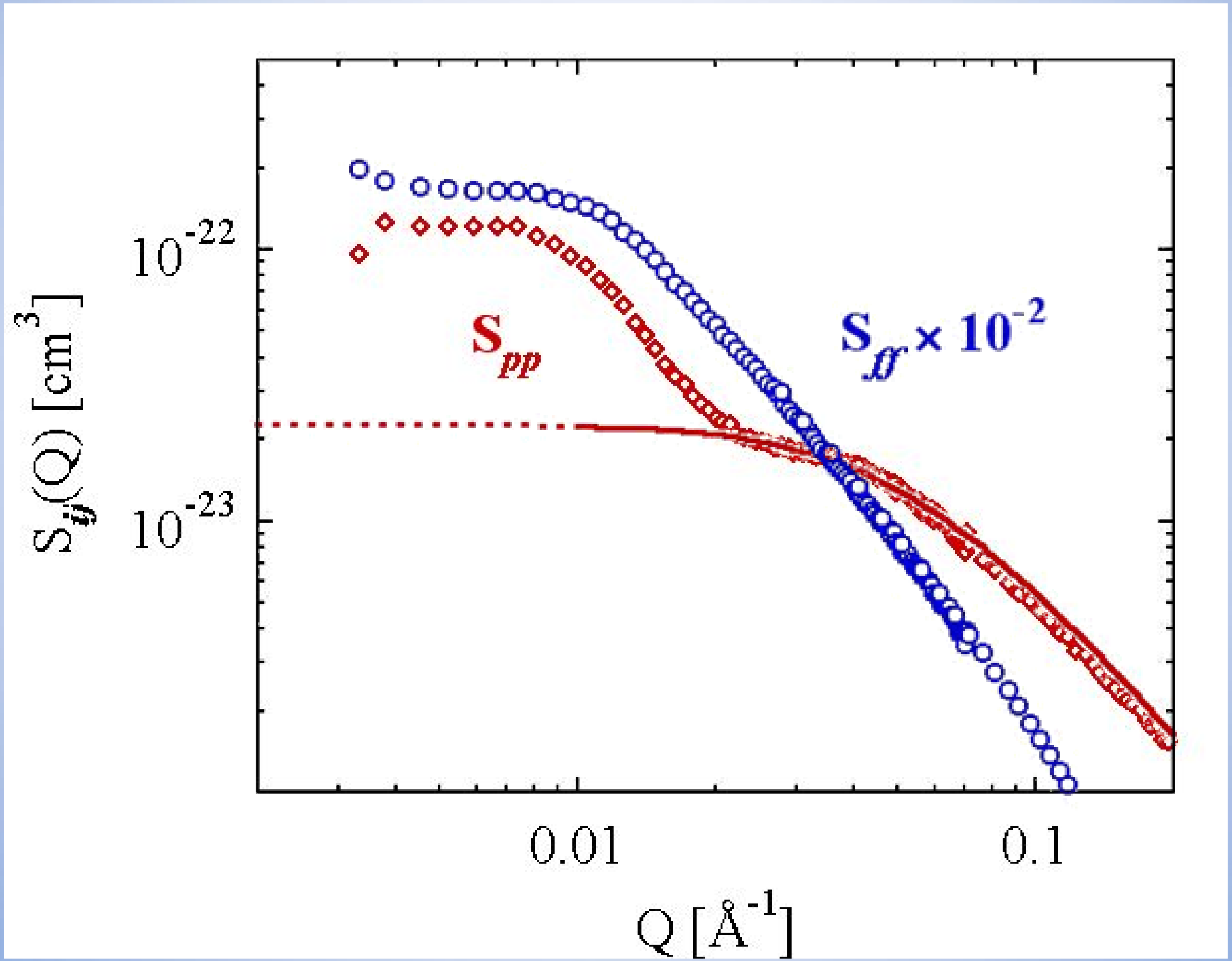
$$\approx \text{Fourier}[f_p(z)] \cdot 1/Q^2$$

$$\phi_p(z) = \frac{\sqrt{6\pi}}{R_e}\left[erfc\left(\frac{\sqrt{6}}{2}\frac{z}{R_e}\right) - erfc\left(\sqrt{6}\frac{z}{R_e}\right)\right]$$

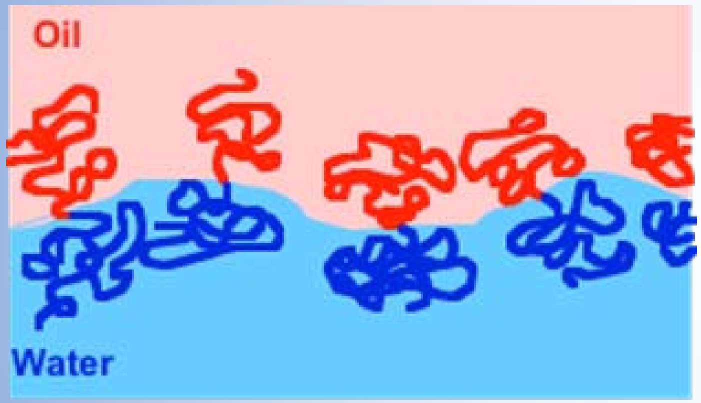
E. Eisenriegler et al., JCP **77**, (1982) 6296

Direct access to the polymer scattering amplitude!

Partial Scattering Functions : S_{pp}



How does the polymer work?



> The polymers keeps mushroom conformation

> Decoration of the film by the polymers

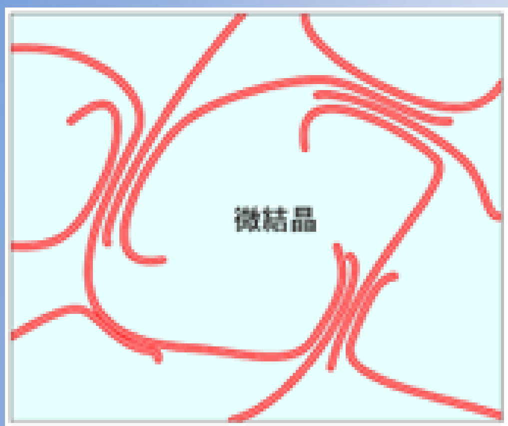
Stiffening of membrane by entropic springs makes large scale structure stable and thereby enhances the emulsification power

界面における高分子の微細構造解析２

ナノコンポジットゲル中の
高分子の吸着構造

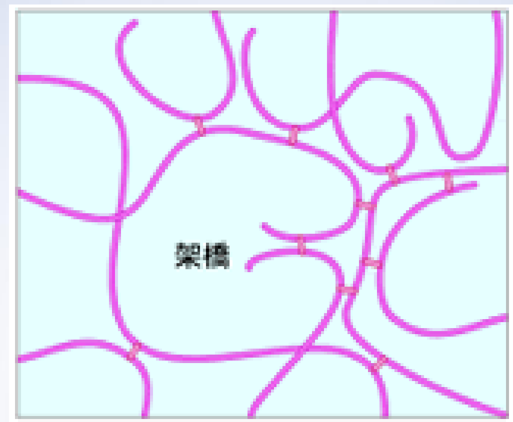
ゲルとは？

物理ゲル



物理的な力(水素結合・疎水性相互作用・ファンデルワールス力etc.)で架橋したゲル。

化学ゲル



化学結合で架橋したゲル。

水を良く吸うが，力学的に弱い

第3のゲル

?

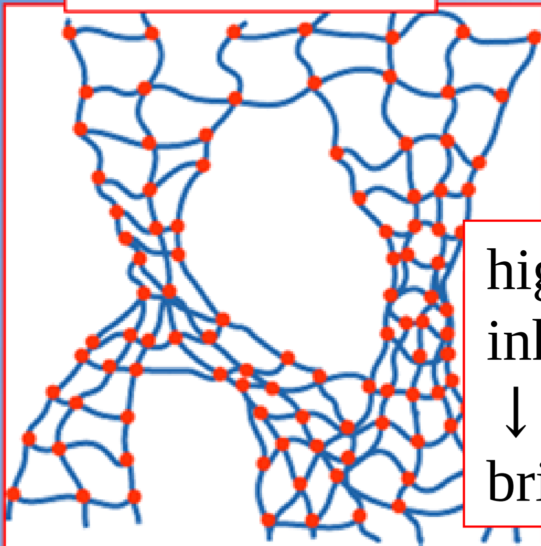
⇩

>>Slide-Ring Gel®
>>ダブルネットワークゲル
>>NCゲル
>>テトラPEGゲル

高強度・高圧縮・高延伸

What is NC gel?

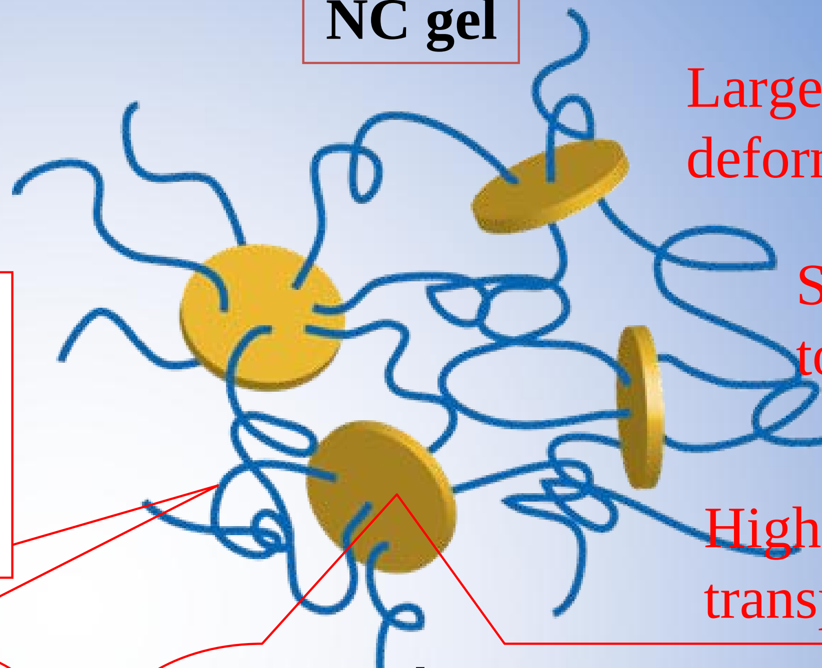
Chemical gel



3-D polymer network

high inhomogeneities
↓
brittleness

NC gel

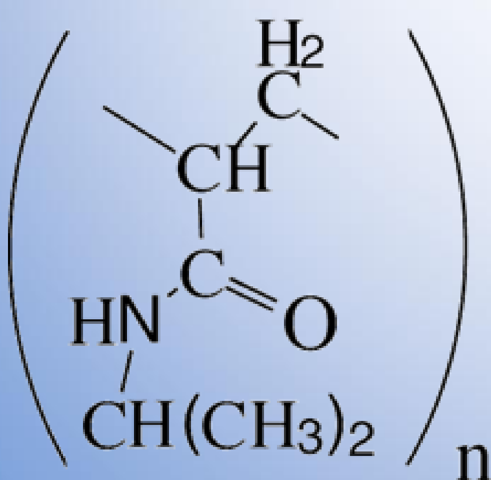


Large deformability

Strong toughness

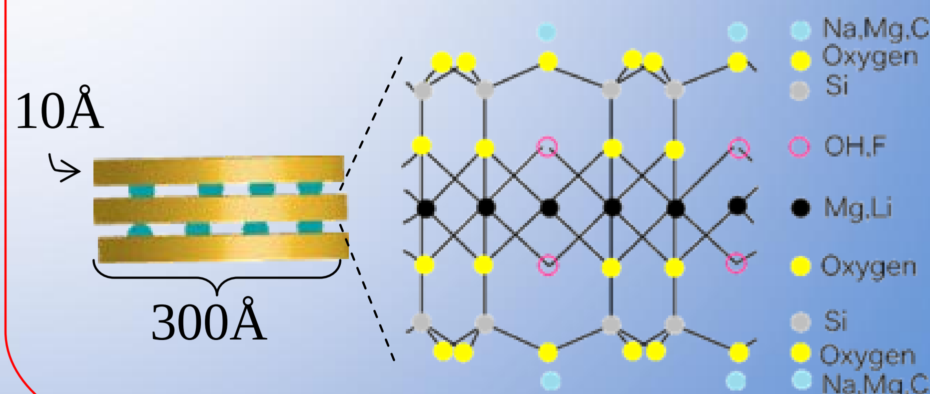
High transparency

Poly(N-isopropylacrylamide) (PNIPA)



clay;Laponite

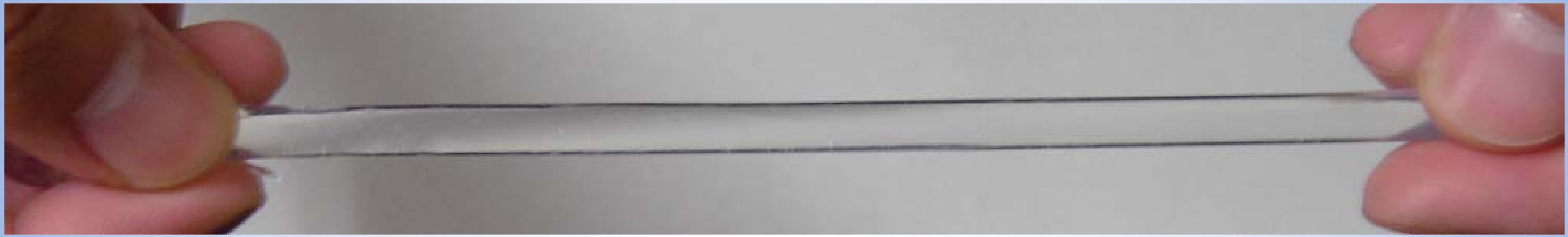
$Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$

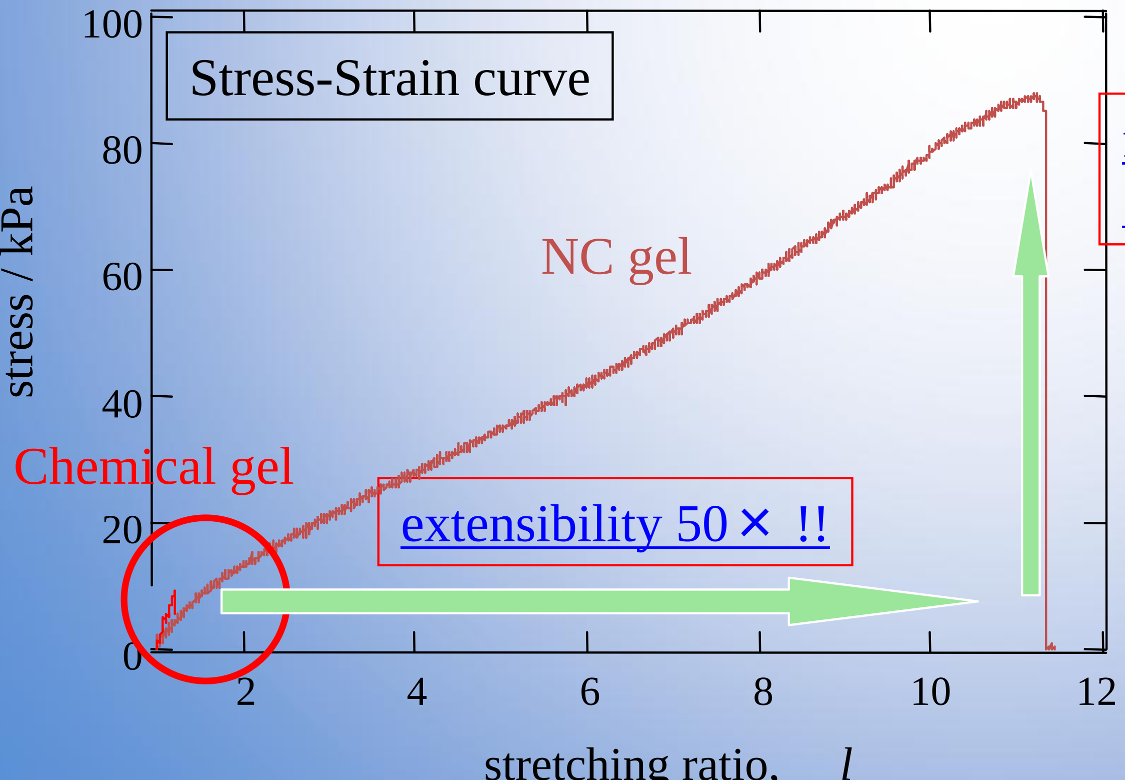


Haraguchi et al. *Macromolecules*, *2002*, **35**, 10162

Mechanical Property

High extensibility and high flexibility



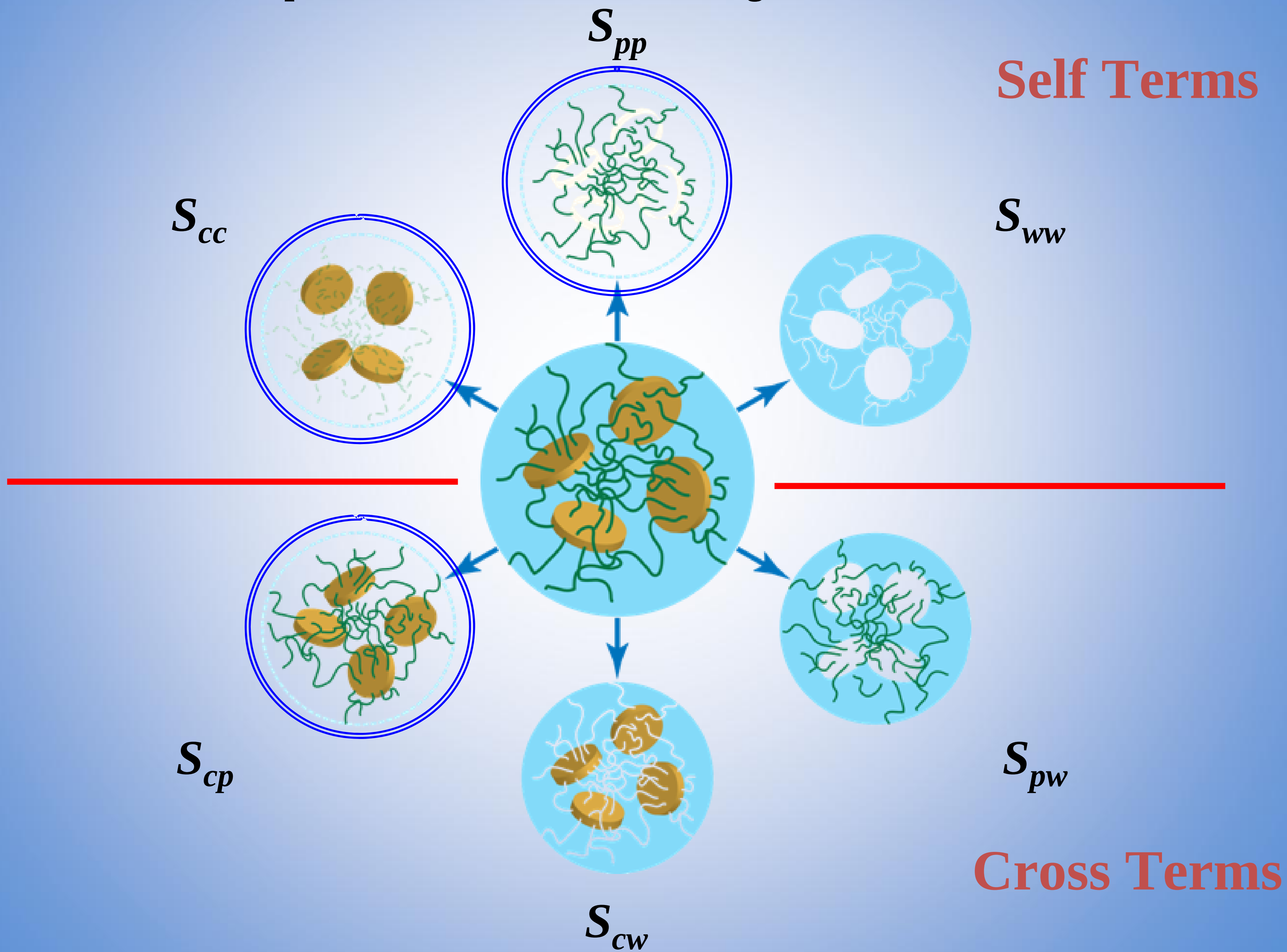


force-sustainability
10× !!

We investigated the microscopic structure of NC gel by SANS.

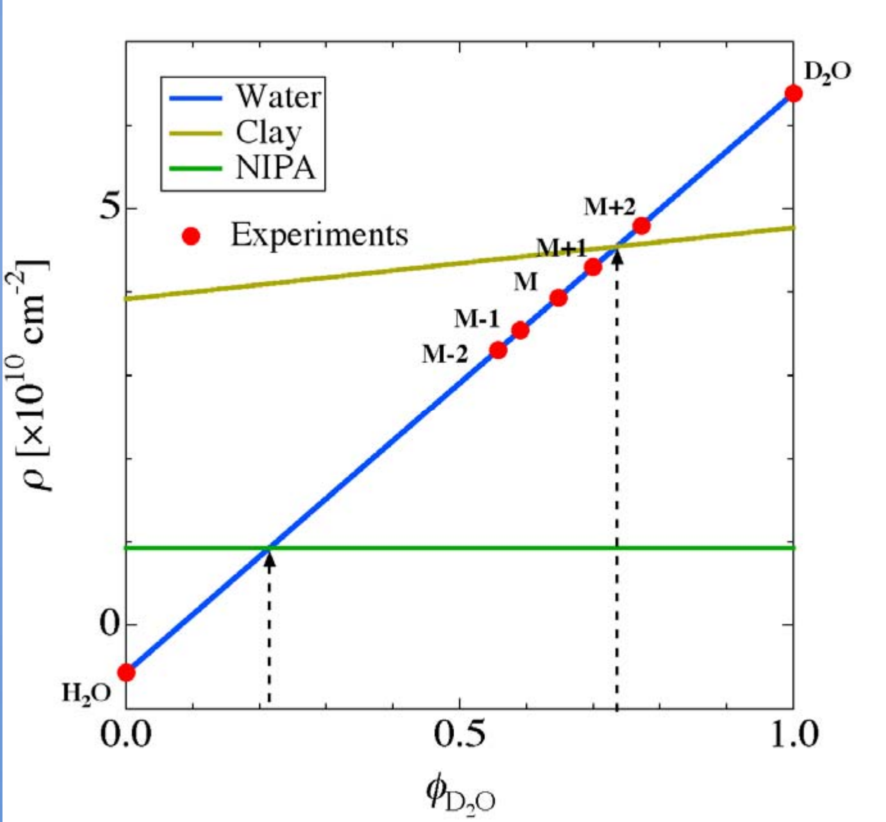
Contrast Variation

⇒ **Decomposition into Partial Scattering Functions**



Contrast Variation - Experiments

D_2O/H_2O Ratio and Scattering Contrast



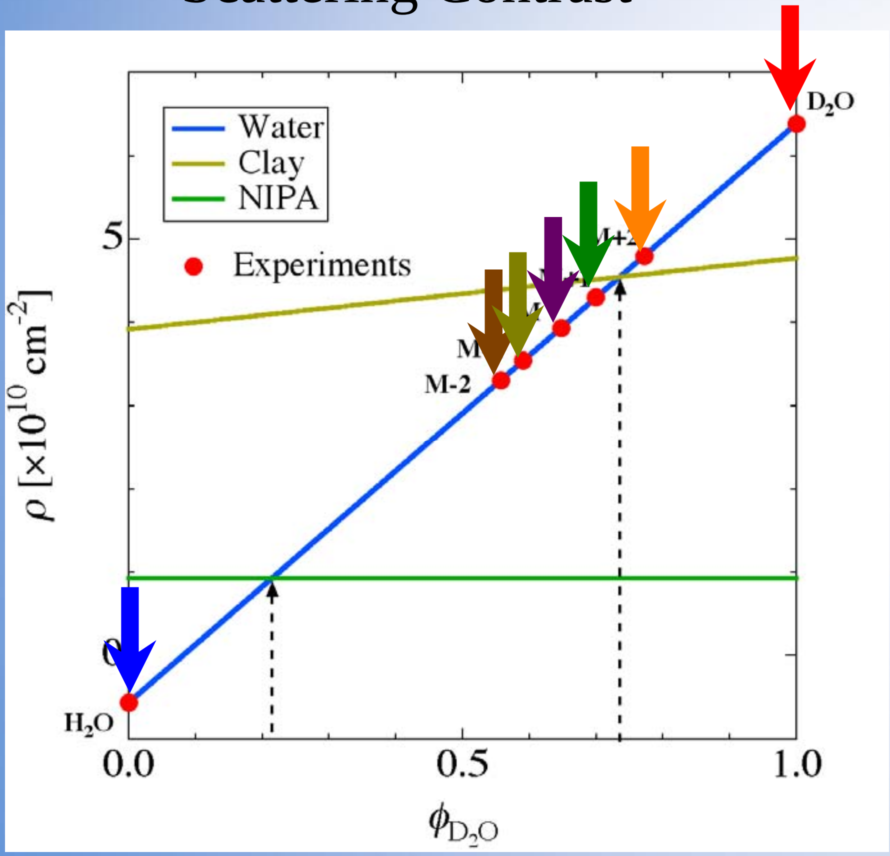
Nanocomposite Gel

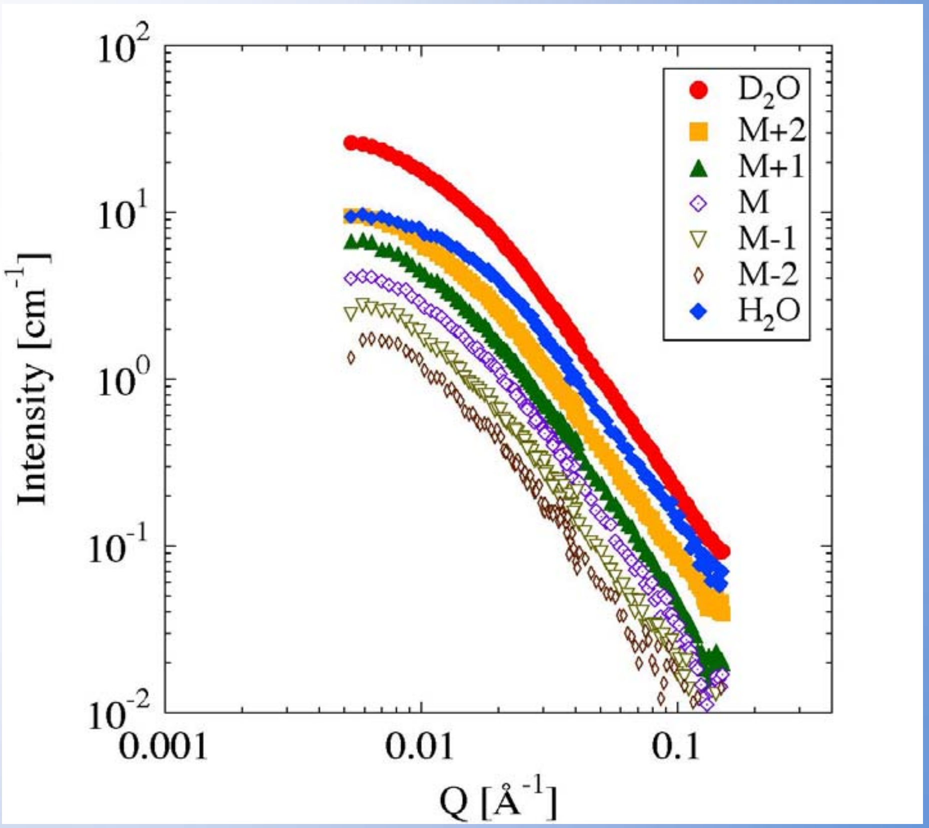
$\phi_{Clay} = 0.013$
$\phi_{Polymer} = 0.042$

Synthesized by means of Redox polymerization in aqua solution containing dispersion of the clay.

Contrast Variation - Experiments

D_2O/H_2O Ratio and
Scattering Contrast





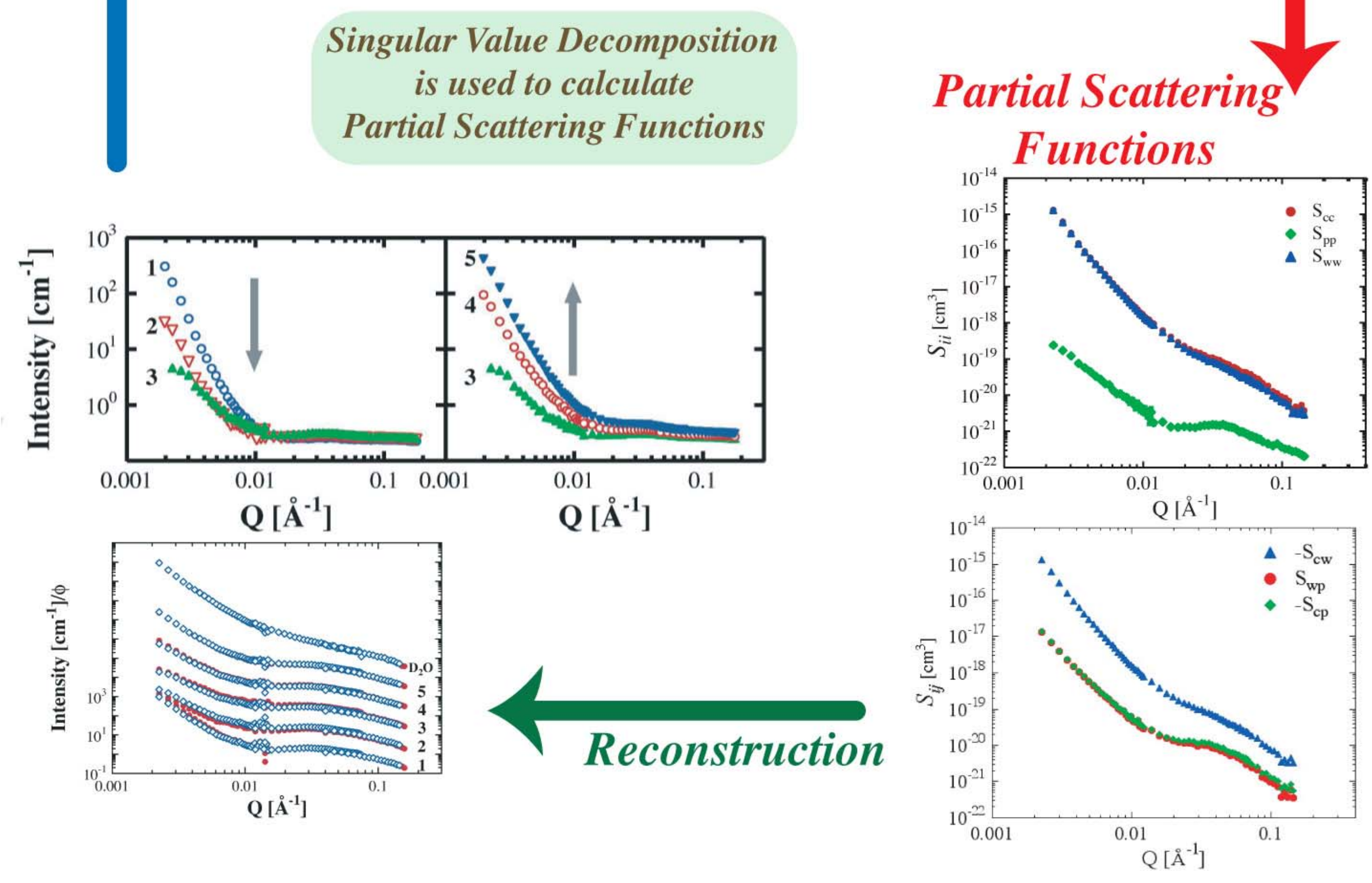
Scattering Intensities

Contrast Variation - Procedure

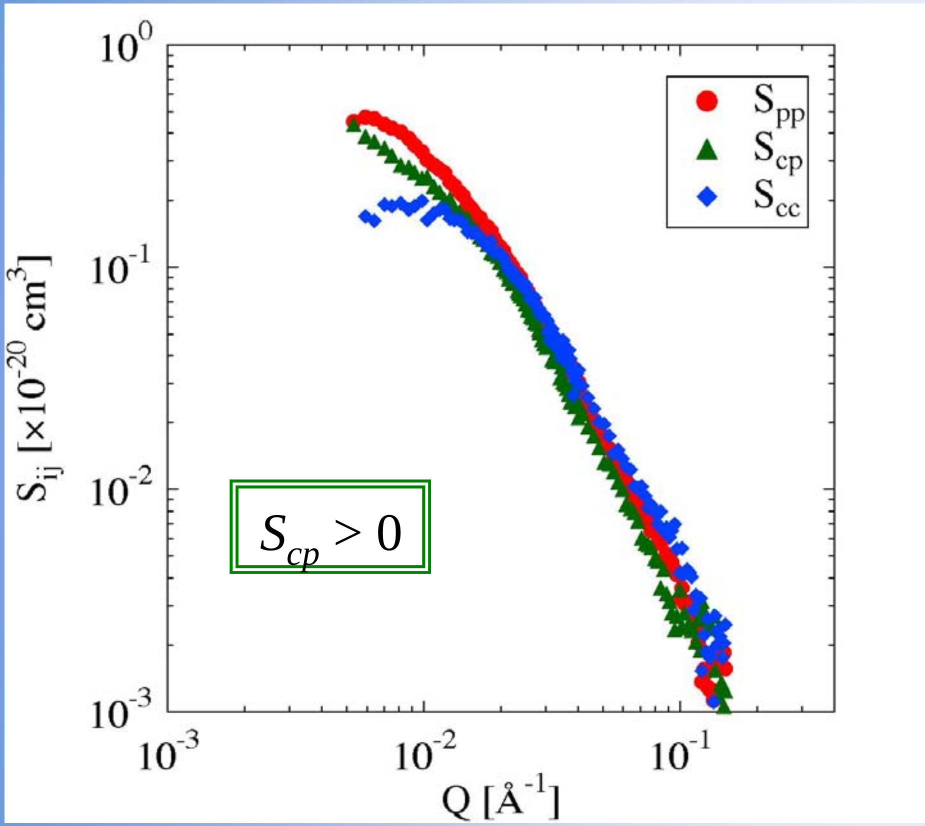
Input

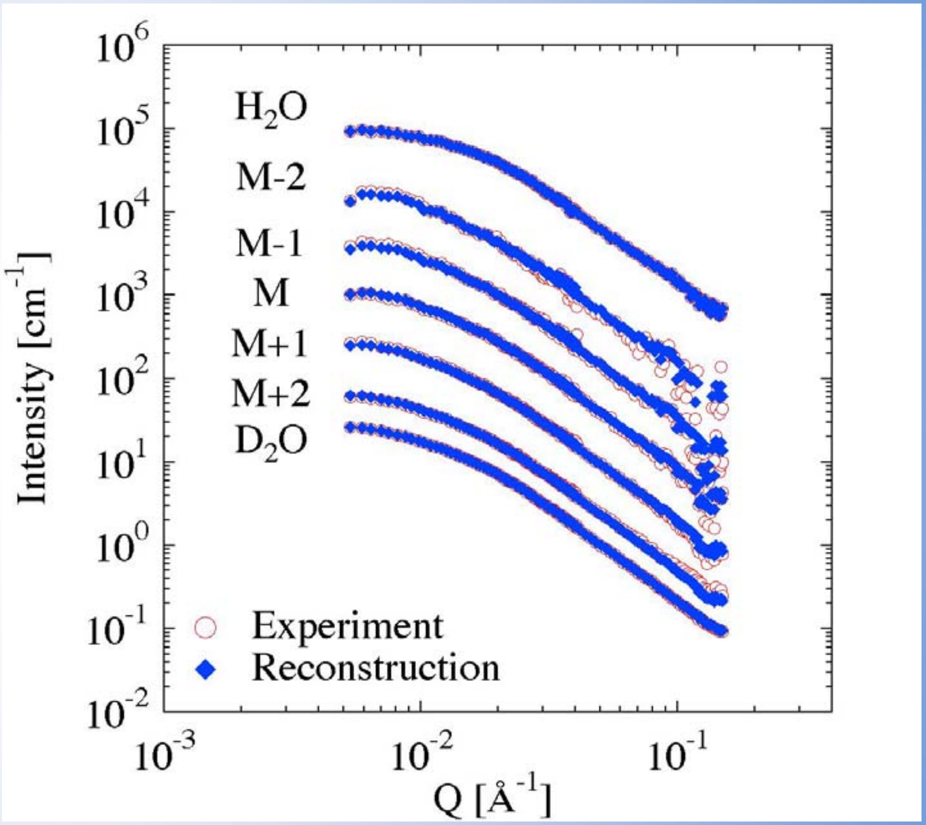
$$\begin{pmatrix} I_1(Q) \\ \vdots \\ I_n(Q) \end{pmatrix} = \begin{pmatrix} \Delta_1\rho_c^{\ 2} & 2\Delta_1\rho_c \cdot \Delta_1\rho_p & \Delta_1\rho_p^{\ 2} \\ \vdots & \vdots & \vdots \\ \Delta_n\rho_c^{\ 2} & 2\Delta_n\rho_c \cdot \Delta_n\rho_p & \Delta_n\rho_p^{\ 2} \end{pmatrix} \cdot \begin{pmatrix} S_{cc}(Q) \\ S_{cp}(Q) \\ S_{pp}(Q) \end{pmatrix}$$

Output



Contrast Variation - Decomposition & Reconstruction





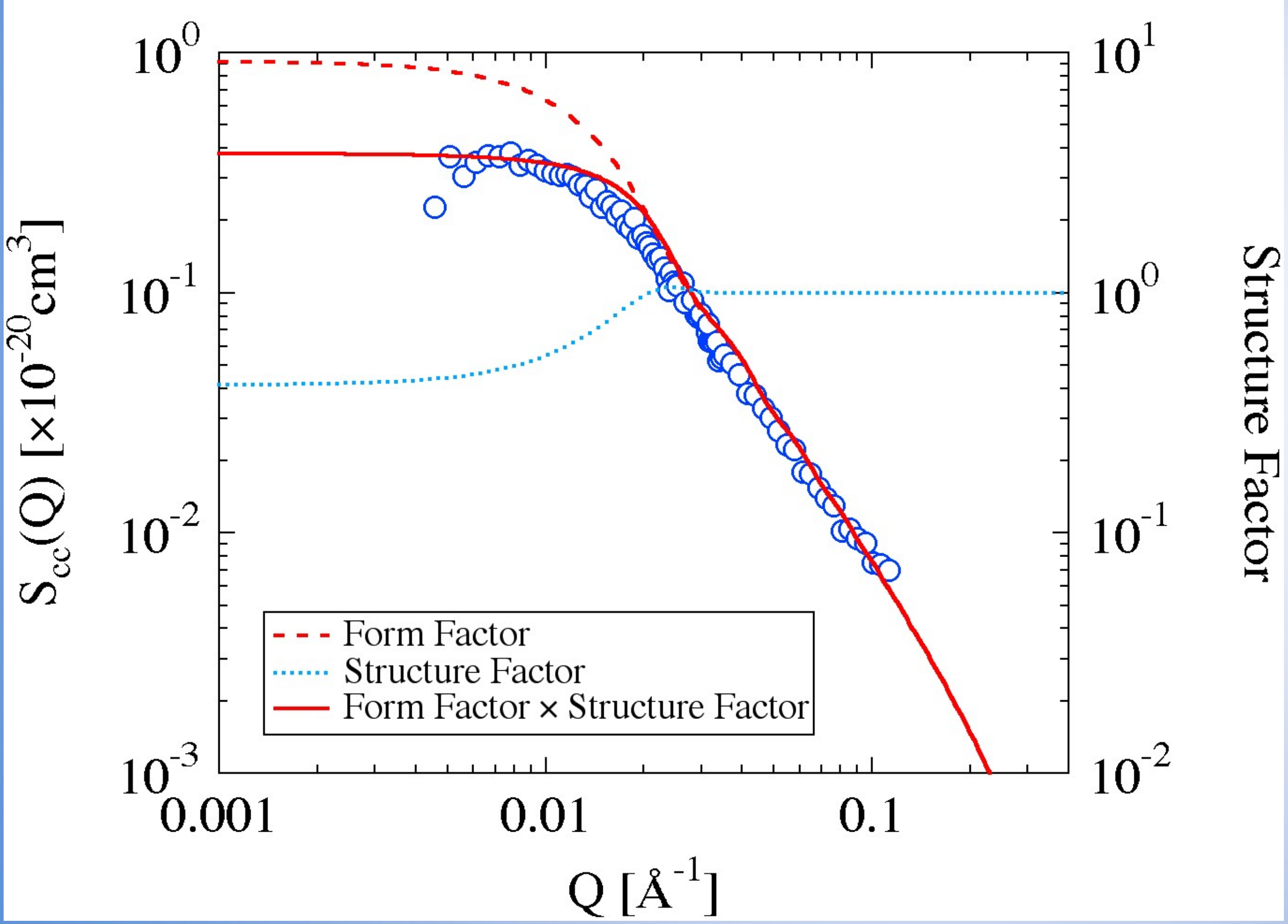
Decomposed Partial Scattering Functions

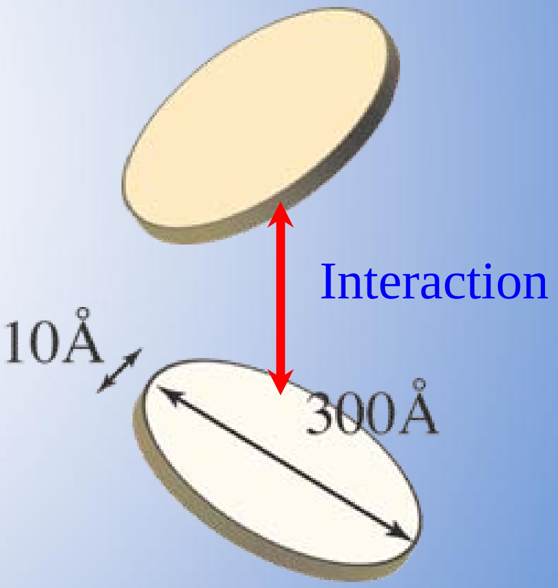
Comparison of Experimental Data with Reconstructed Data

Evaluation of
Partial Scattering Function - S_{cc}

$$S_{cc}$$

Evaluation of Partial Scattering Function - S_{cc}





Scattering Function: S_{cc}

$$S_{cc}(Q) = n_c \cdot S_c(Q) \cdot P_c(Q)$$

Form Factor

$$P_c(Q) = \int_0^{\pi/2} \{A_c(Q)\}^2 \sin\theta d\theta$$

$$A_c(Q) = V_c \frac{2J_1(QR_c \sin\theta)}{QR_c \sin\theta} \frac{\sin(Qd_c \cos\theta/2)}{Qd_c \cos\theta/2}$$

Structure Factor

$$S_c(Q) = 1 + \frac{\langle A_c(Q)\rangle^2}{P_c(Q)} \cdot S(Q)$$

where

$$\langle A_c(Q)\rangle = \int_0^{\pi/2} A_c(Q) \sin\theta d\theta$$

$S(Q)$: Percus-Yevic Equation

Parameters

Fixed

n_c : Number Density of Clay

V_c : Volume of a Clay Platelet

R_c : Radius of a Clay Platelet

d_c : Thickness of a Clay Platelet

Fitting

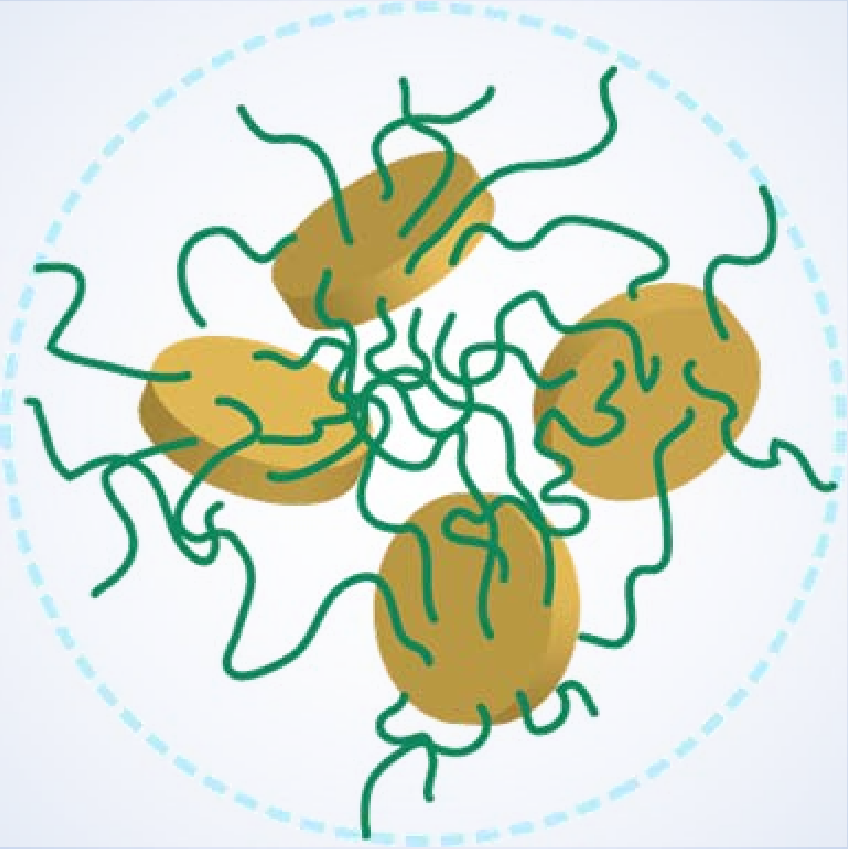
R_{PY} : Excluded Radius of a Clay Platelet determined by Percus-Yevick Eq.

(R_{PY} = 117Å was obtained.)

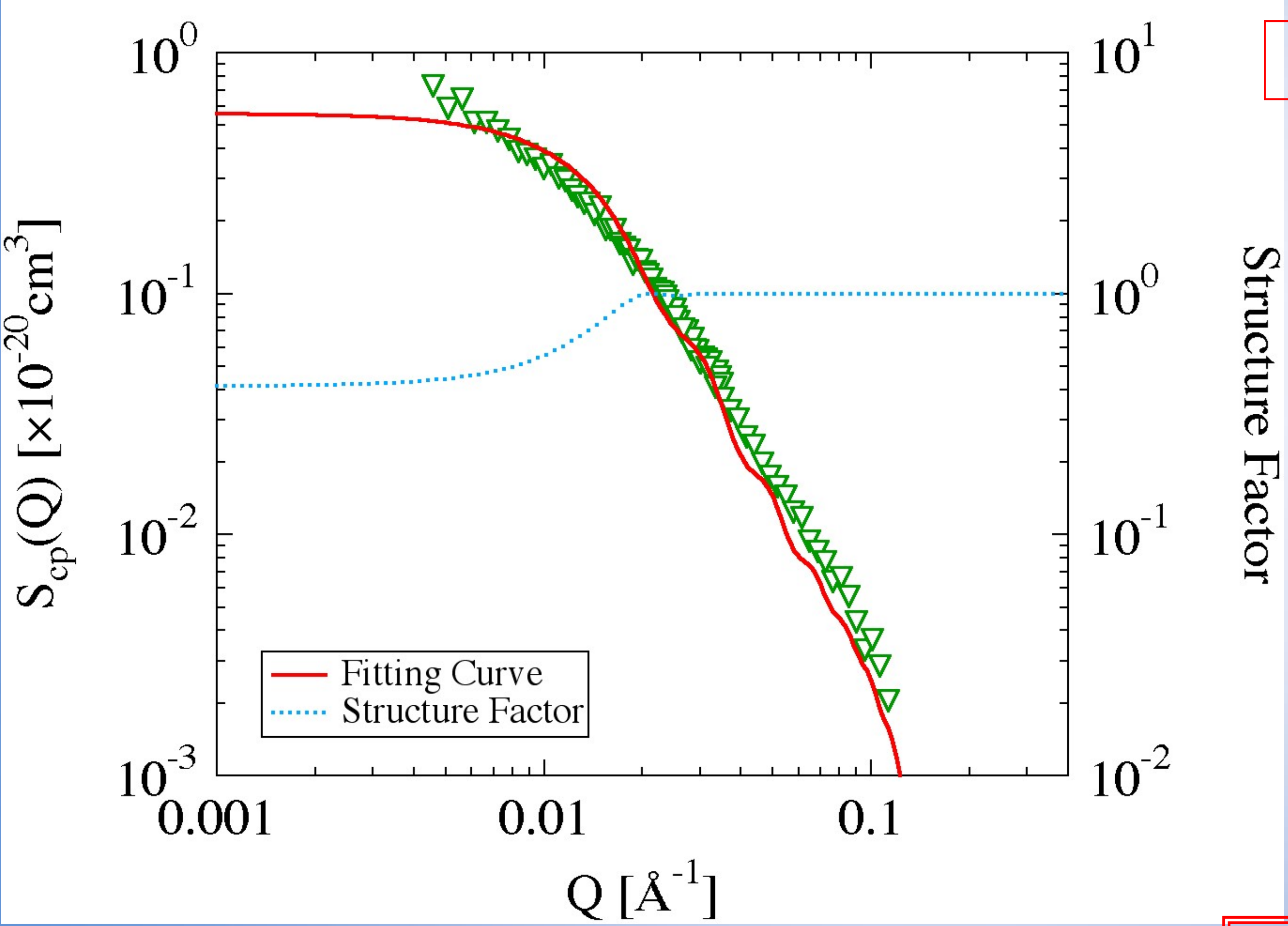
Evaluation of

Partial Scattering Function - S_{cp}

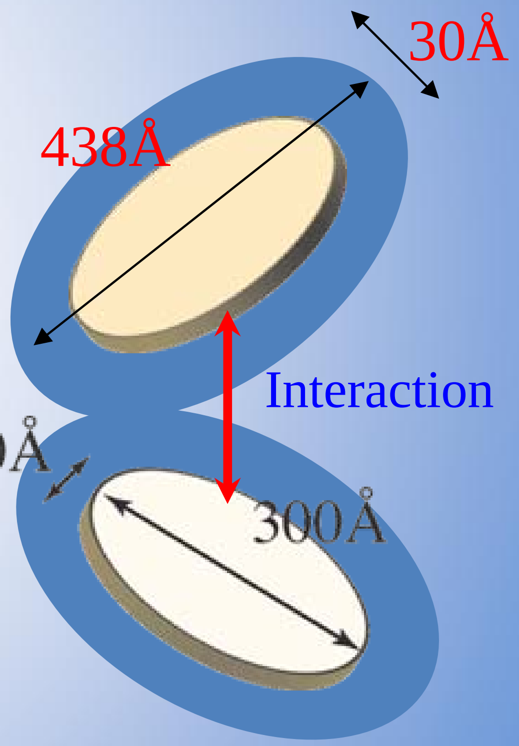
S_{cp}



Evaluation of Partial Scattering Function - S_{cp}



ϕ_{Water} = 0.65 (Local)



Φ_{Water} = 0.95 (Overall)

Scattering Function: S_{cp}

$$S_{cp}(Q) = n_c \cdot \left[\left\langle A_c(Q) \cdot A_p(Q) \right\rangle + \left\langle A_c(Q) \right\rangle \left\langle A_p(Q) \right\rangle \cdot \{ S(Q) - 1 \} \right]$$

where

$$\left\langle A_c(Q) \cdot A_p(Q) \right\rangle = \int_0^{\pi/2} A_c(Q) \cdot A_p(Q) \sin\theta d\theta$$

$$\left\langle A_p(Q) \right\rangle = \int_0^{\pi/2} A_p(Q) \sin\theta d\theta$$

Scattering Amplitude for Polymer Layer

$$A_p(Q) = \left(\phi_{pl} - \phi_{pex} \right) V_p \cdot A_{p//}(Q\sin\theta) \cdot A_{p\perp}(Q\cos\theta) - \phi_{pl} V_c \cdot A_c(Q)$$

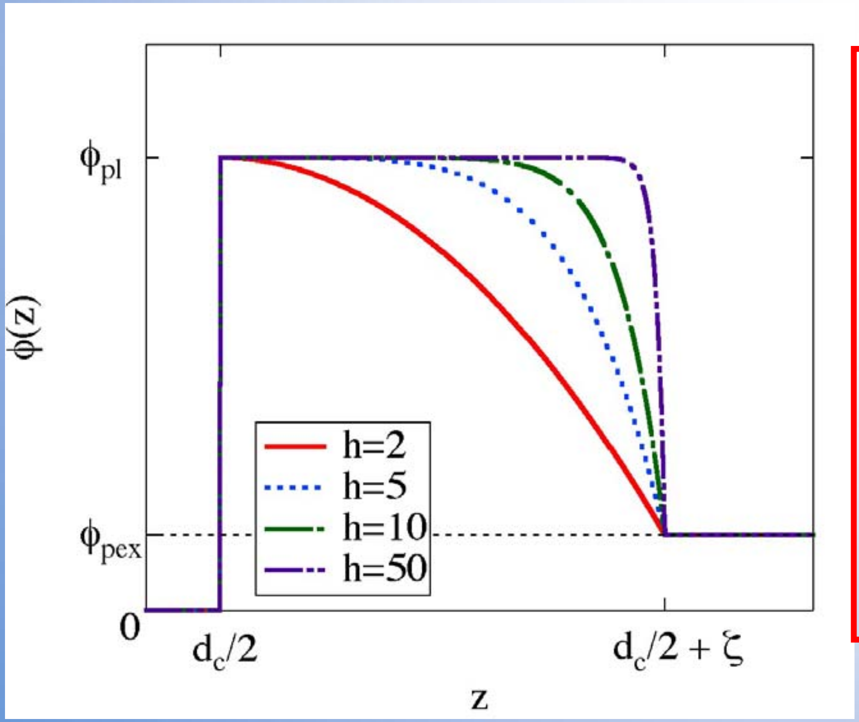
$$A_{p\perp}(Q) \propto \int_0^{\infty} \boxed{\phi_z(z)} \cos(Qz) dz$$

$$A_{p//}(Q) = \frac{2 J_1 \left(Q R_p \right)}{Q R_p}$$

Polymer Density Profile: $\phi_z(z)$

$$\phi_z(z) \propto 1 - \left(\frac{z}{\zeta}\right)^h \qquad (0 \le z \le \zeta,\ 1 \le h)$$

h=2 was predicted for end-grafted polymer chains by Milner et al. [*Macromolecules* **21**,2610-2619 (1988)]

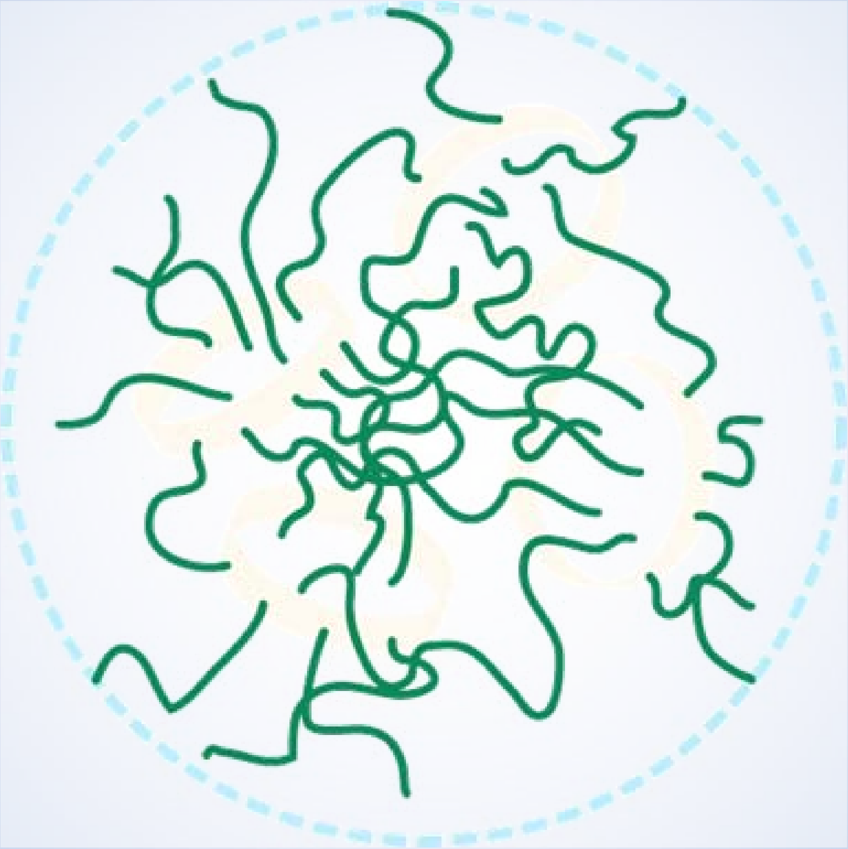


Parameters
Fitting
R_p = 219Å : Radius of a Polymer Layer
z = 10Å : Thickness of a Polymer Layer
***h* = 5.3** : Exponent for Polymer Density Profile
f_{pl} = 0.35 : Volume Fraction of Polymers in the Layer

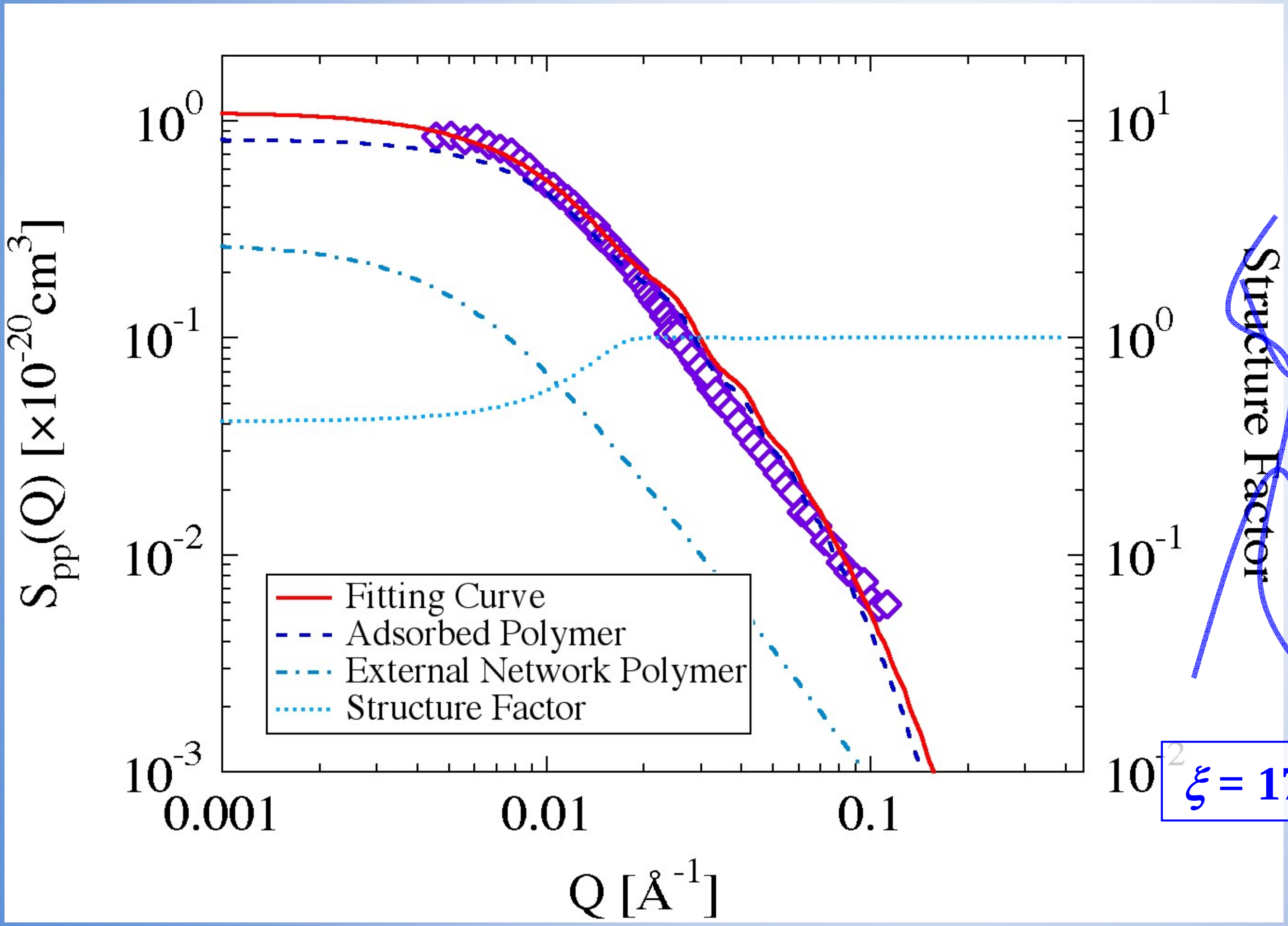
Evaluation of

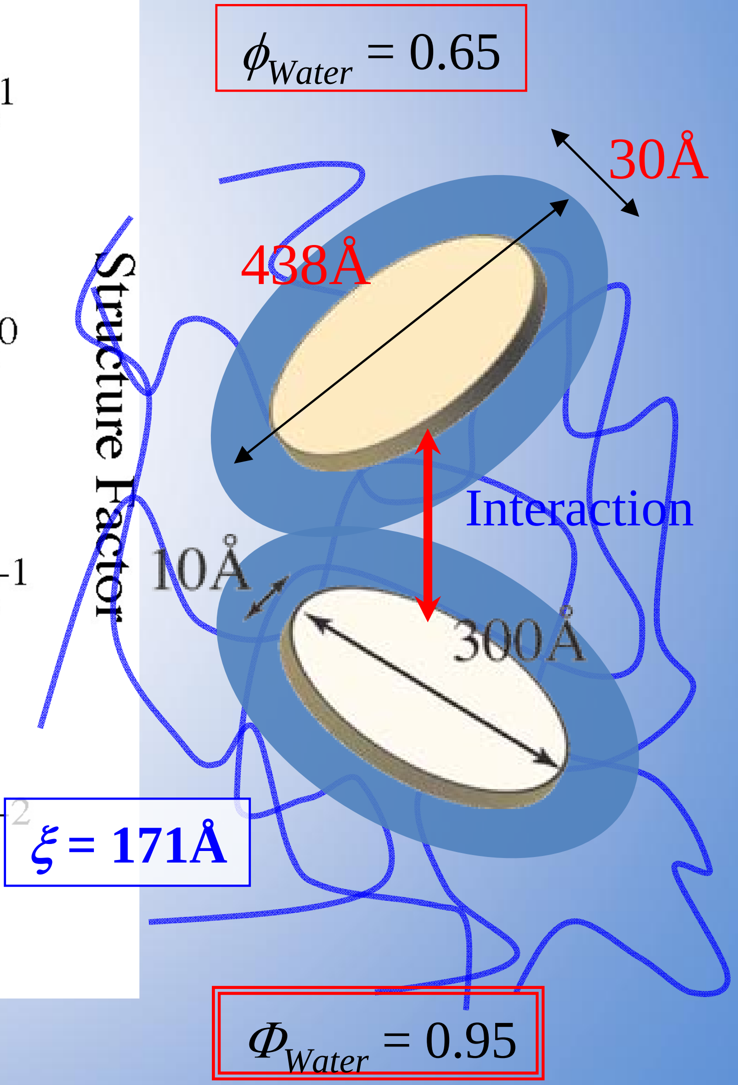
Partial Scattering Function - S_{pp}

S_{pp}



Evaluation of Partial Scattering Function - S_{pp}





Scattering Function: S_{pp}

$$S_{pp}(Q) = n_c \cdot \left[\left\langle \left\{ A_p(Q) \right\}^2 \right\rangle + \left\langle A_p(Q) \right\rangle^2 \cdot \left\{ S(Q) - 1 \right\} \right] + \boxed{\frac{S_0}{1 + Q^2 \xi^2}}$$

where

$$\left\langle \left\{ A_p(Q) \right\}^2 \right\rangle = \int_0^{\pi/2} \left\{ A_p(Q) \right\}^2 \sin\theta d\theta$$

無延伸状態のNCゲルのまとめ

>> S_{cc}からクレイナノ粒子が系内で均質に分散している事が確かめられた。

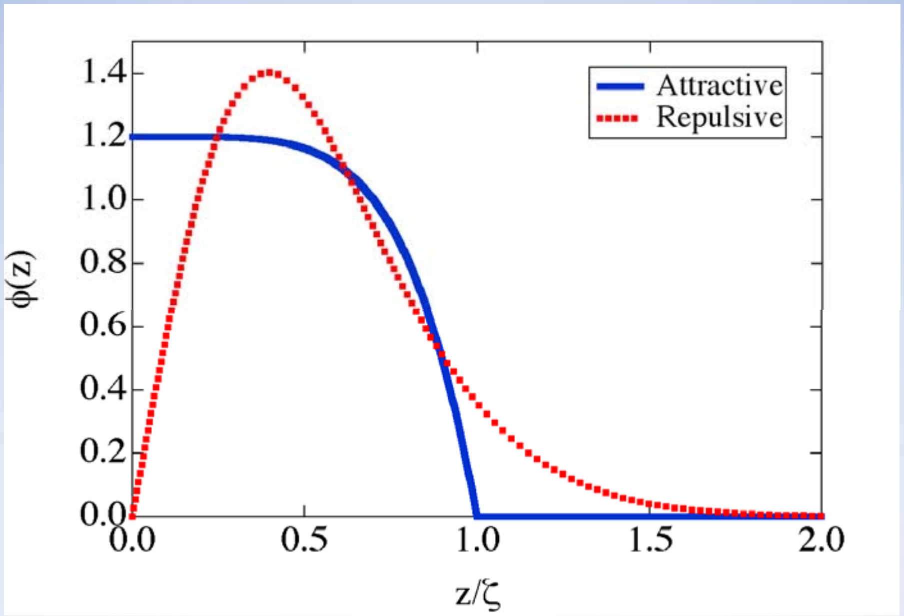
>> $S_{cp} > 0$であることから、クレイ粒子に高分子鎖が物理的(水素結合？)に吸着することで、クレイ粒子が二次元架橋剤として機能している事が実験的に確かめられた。

>> NCゲル中の高分子鎖ネットワークの広がりが特異的に大きい事がS_{pp}から明らかとなった。

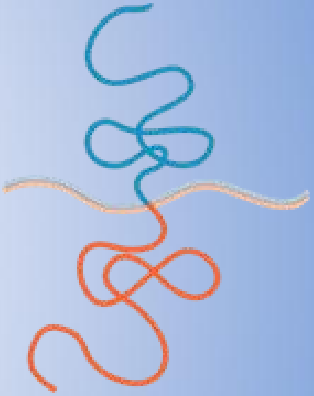
Published on *Macromolecules* 2008, **41**, 5406-5411

実空間プロファイル

Attractive

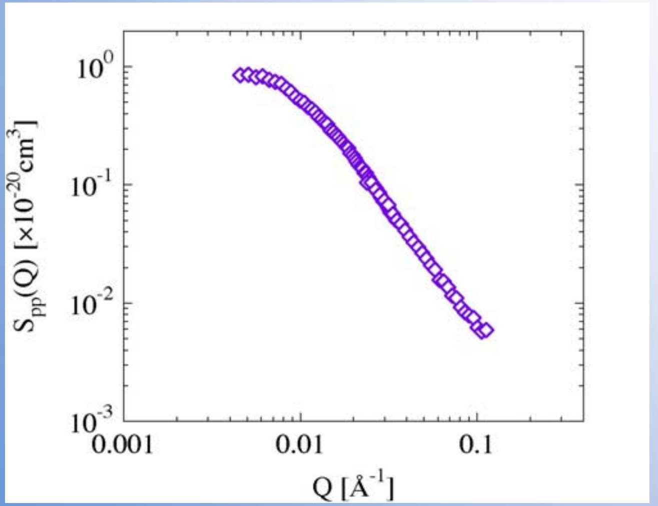


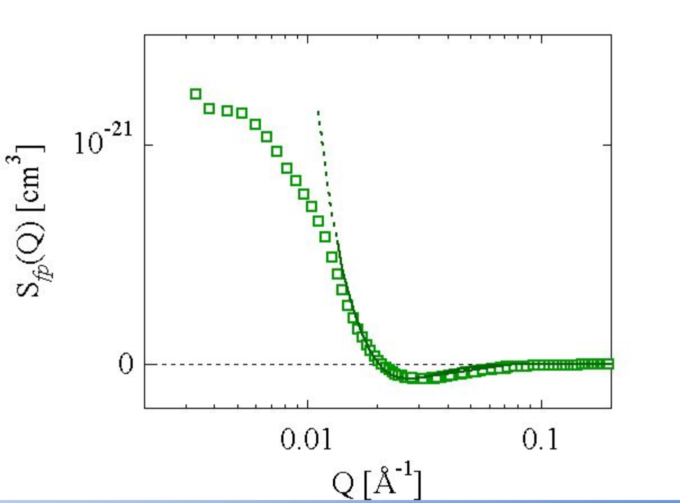
Repulsive



逆空間プロファイル

（Cross Terms）





Cross Termを得る事で決定出来る.

コントラスト変調中性子小角散乱を用いた その他の多成分系の実験例

「バイオミネラリゼーション」

タンパク質 – リン酸カルシウム複合系

"Structural dynamics of a colloidal protein-mineral complex bestowing on calcium phosphate a high solubility in biological fluids” *Biointerphases* **2**, 16-20 (2007).

高分子 – 炭酸カルシウム複合系

"On the role of block copolymer additives for calcium carbonate crystallization - SANS investigation by applying contrast variation” *Journal of Chemical Physics* **120**, 9410-9423 (2004).

「ナノコンポジット」

高分子 – シリカ粒子系

"Analysis of surface structure and hydrogen/deuterium exchange of colloidal silica suspension by contrast-variation small-angle neutron scattering” *Langmuir* **24**, 4537-4543 (2007).

「多成分系レオロジー」

ナノコンポジットゲルの延伸下におけるコントラスト変調実験

“Deformation mechanism of nanocomposite gels studied by contrast variation small-angle neutron scattering” *Physical Review E* **80**, 030801(R) 1-4 (2009).

「超分子構造」

ポリロタキサンの構造解析

"Mechanically Interlocked Structure of Polyrotaxane Investigated by Contrast Variation Small-Angle Neutron Scattering” *Macromolecules* **42**, 6327-6329 (2009).

謝辞

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