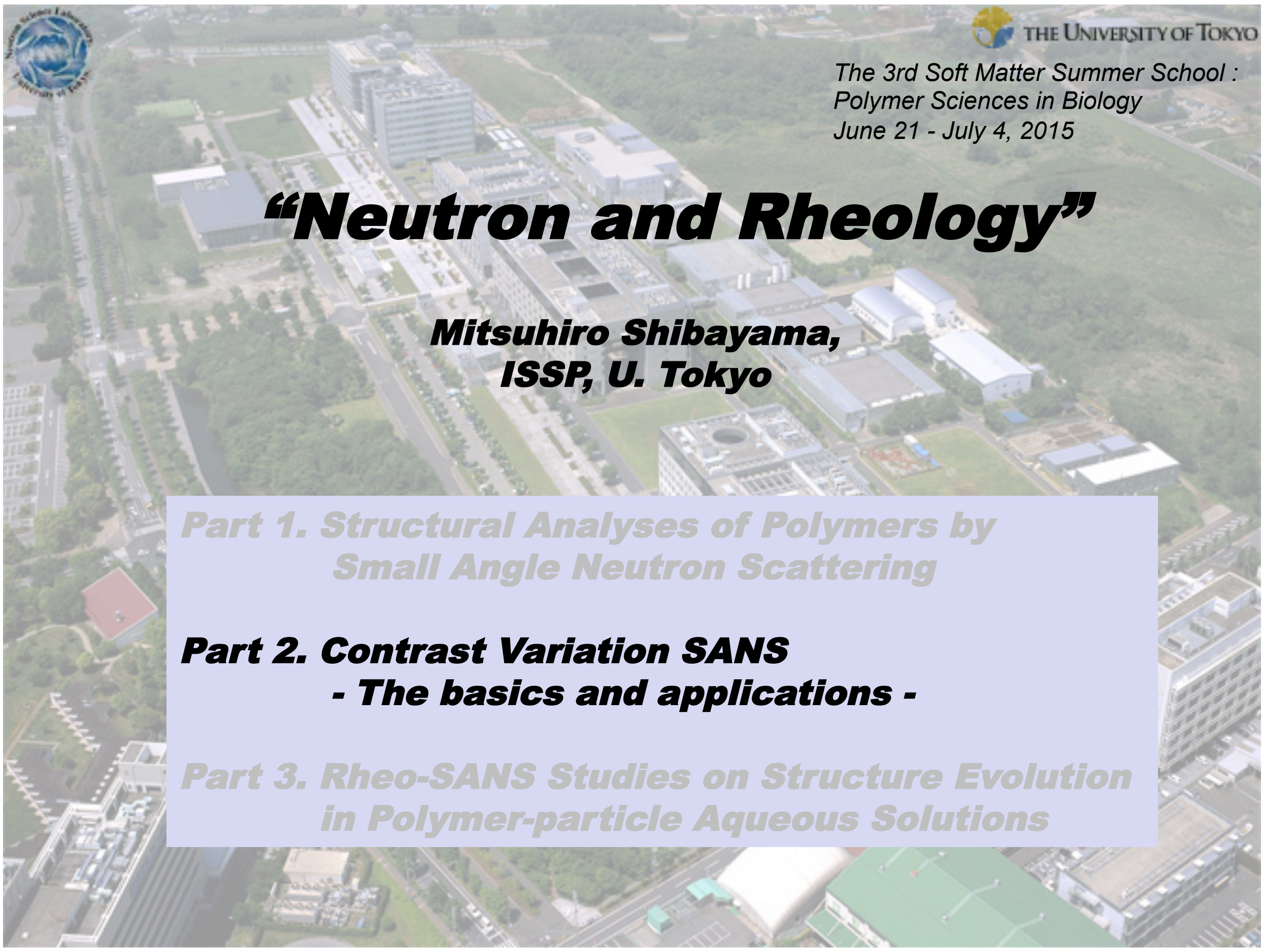

THE UNIVERSITY OF TOKYO

contents

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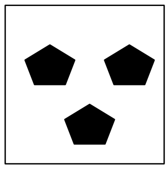
   - silica dispersions
   - polyrotaxane solutions

Contrast matching

two-component system (black and white)

$$I(q) = (\rho_1 - \rho_0)^2 S(Q) \qquad S_{11}(Q) = S_{00}(Q) = -S_{01}(Q) \equiv S(Q)$$

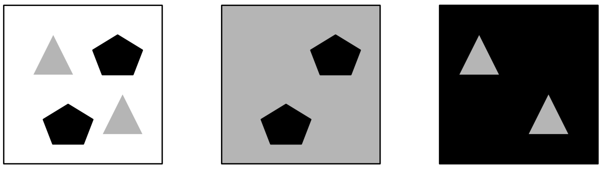


three-component system (black, white, and gray)

$$I(q) = (\rho_1 - \rho_0)^2 S_{11}(Q) + 2(\rho_1 - \rho_0)(\rho_2 - \rho_0) S_{12}(Q) + (\rho_2 - \rho_0)^2 S_{22}(Q)$$

$I(q) = (\rho_1 - \rho_0)^2 S_{11}(Q)$ *when* $\rho_0 = \rho_2$

$I(q) = (\rho_2 - \rho_0)^2 S_{22}(Q)$ *when* $\rho_0 = \rho_1$



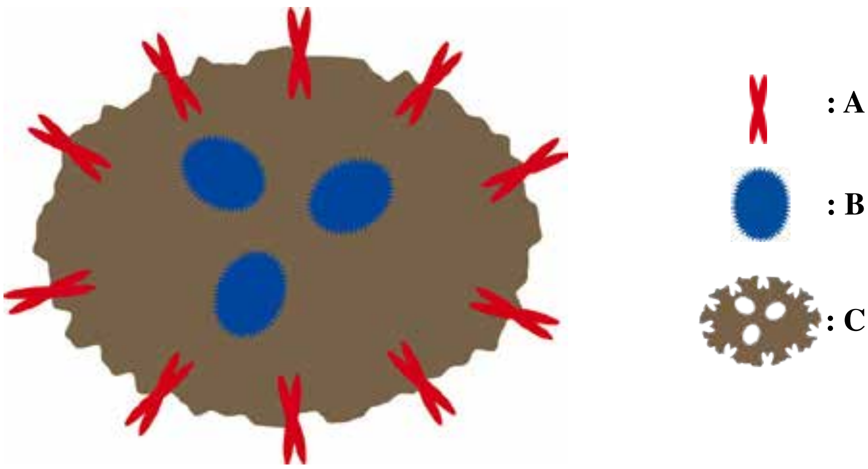
$\rho_0 = \rho_2$ $\rho_0 = \rho_1$

No information on $S_{12}(Q)$

Contrast variation

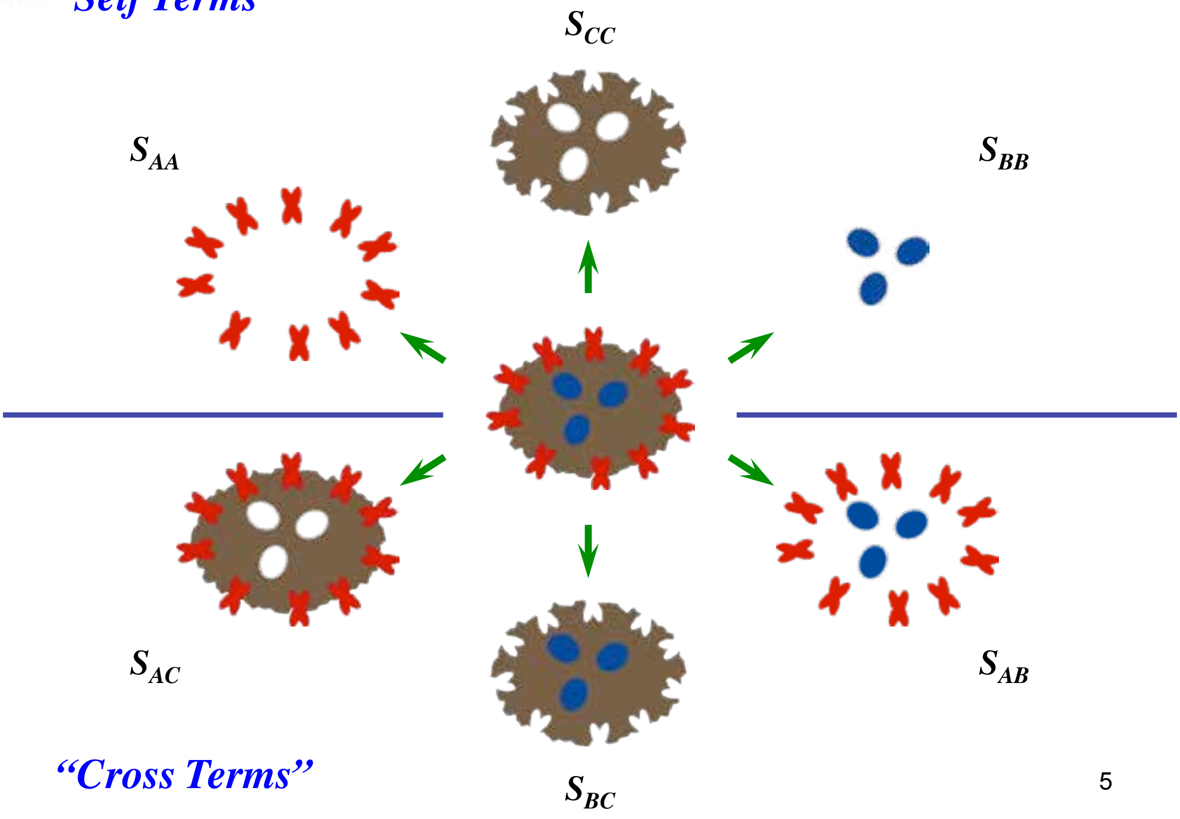
Scattering Analyses for Multi-Component System

"How can we extract the structure information?"

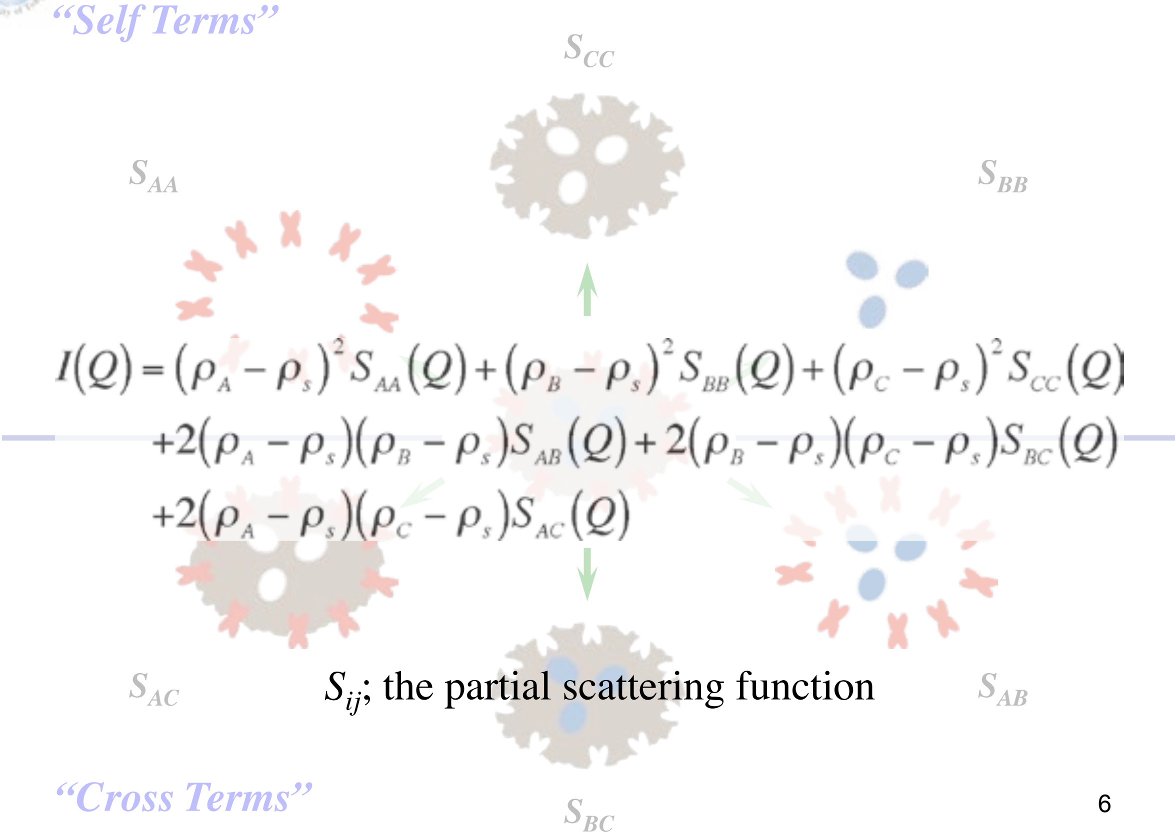


Courtesy of H. Endo (KEK)

“Self Terms”



“Cross Terms”



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

S_{ij}; the partial scattering function

Multicomponent BABINET principle

Endo, et al., J. Chem. Phys., 2004, 120, 9410.

the relationship between $S_{ij}(Q)$s

By assuming non-compressibility, one obtains

$$\sum_i F_i = 0$$

F_i; the scattering amplitude for component j

$$F_W = -F_C - F_P$$

$$S_{WW}(Q) = F_W^2 = (-F_C - F_P)^2 = S_{CC}(Q) + S_{PP}(Q) + 2S_{CP}(Q)$$

$$S_{CW}(Q) = F_C F_W = F_C(-F_C - F_P) = -S_{CC}(Q) - S_{CP}(Q)$$

$$S_{PW}(Q) = F_P F_W = F_P(-F_C - F_P) = -S_{CP}(Q) - S_{PP}(Q)$$

$$\left.\begin{matrix} S_{CC}(Q) \\ S_{CP}(Q) \\ S_{PP}(Q) \end{matrix}\right\} \Rightarrow \left\{\begin{matrix} S_{WW}(Q) \\ S_{CW}(Q) \\ S_{PW}(Q) \end{matrix}\right.$$

Multicomponent BABINET principle

Contrast variation SANS

Colloidal spheres

Duits, et al., J. Chem. Phys. 94, 4521(1991).
Bartlett, et al., J. Chem. Phys. 96, 3306 (1992).

Polymer aggregates or micelles

Richter, et al., Macromolecules, 30, 1053 (1997).
Poppe, et al., Macromolecules, 30, 7462 (1997).

Microemulsions

Endo, et al., PRL, 85, 102 (2000).
Pedersen, et al., PRE, 63, 061406 (2001).

Biological macromolecules

Willumeit, et al., J. Mol. Struct. 383, 201(1996).
Niimura, et al., J. Cryst. Growth, 200, 265 (1999)

contrast variation AND SANS
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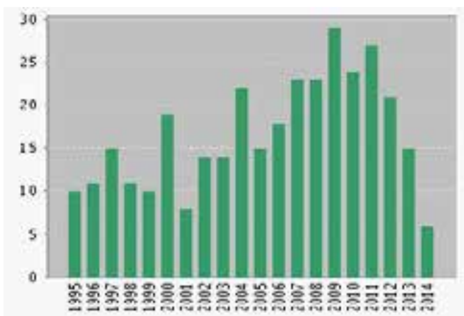


Problems (difficulties)
(1) highly model dependent
(2) accurate determination of the scattering length densities

Scattering intensity of multi-component systems

1. Derivation of the scattering function for a sphere

$$\rho(r) = \begin{cases} \Delta\rho_0 & |r| \le R \\ 0 & |r| > R \end{cases}$$

$$F(Q) = \int d^3\mathbf{r}\,\rho(\mathbf{r})\,e^{i\mathbf{Q}\cdot\mathbf{r}}$$

$$= \int_0^\infty dr \int_0^\pi d\alpha\,\rho(r)\,e^{iQr\cos\alpha}\left(2\pi r^2 \sin\alpha\right)$$

$$= 2\pi\Delta\rho_0 \int_0^R dr\,r^2 \int_0^\pi d\alpha \sin\alpha\, e^{iQr\cos\alpha}$$

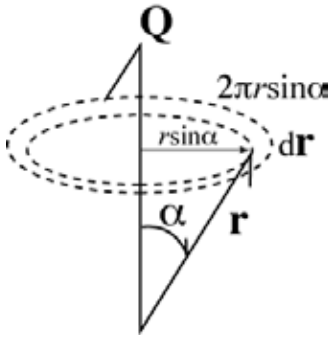
$$I_1(r) \equiv \int_0^\pi d\alpha \sin\alpha\, e^{iQr\cos\alpha}$$

$$F(Q) = 2\pi\Delta\rho_0 \int_0^R dr\,I_1(r)\,r^2$$

$$\cos\alpha \equiv t, \quad -\sin\alpha\, d\alpha = dt$$

$$I_1(r) \equiv \int_1^{-1} (-dt)\exp^{iQrt} = \left[\frac{e^{iQrt}}{iQr}\right]_{-1}^{1} = \frac{2\sin(Qr)}{Qr}$$

Orientation averaging



Volume element:

$$2\pi r \sin\alpha\, r dr = 2\pi r^2 \sin\alpha\, dr$$

$$\left\langle \exp[i\mathbf{Q}\cdot\mathbf{r}] \right\rangle_{orient} = \frac{\int_{\alpha=0}^{\pi} \exp[iQr\cos\alpha]\, 2\pi r^2 \sin\alpha\, d\alpha}{\int_{\alpha=0}^{\pi} 2\pi r^2 \sin\alpha\, d\alpha}$$

$$= \frac{\sin(Qr)}{Qr}$$

$$F(Q) = 2\pi\Delta\rho_0 \int_0^R dr I_1(r) r^2$$

$$= 4\pi\Delta\rho_0 \int_0^R dr \frac{\sin(Qr)}{Qr} r^2$$

$$Qr \equiv u, \quad dr \quad = du / Q$$

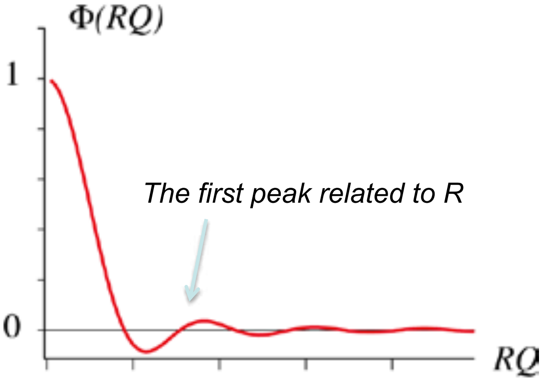
$$F(Q) = 4\pi\Delta\rho_0 \int_0^R dr \frac{\sin(Qr)}{Qr} r^2$$

$$= 4\pi\Delta\rho_0 \int_0^R \frac{du}{Q} \frac{\sin(u)}{u} \left(\frac{u}{Q}\right)^2$$

$$= \frac{4\pi\Delta\rho_0}{Q^3} \int_0^R du u \sin u = \frac{4\pi\Delta\rho_0}{Q^3} [\sin U - U \cos U]$$

$$= \frac{4\pi R^3 \Delta\rho_0}{3} \frac{3}{U^3} [\sin U - U \cos U] = V\Delta\rho_0 \Phi(U)$$

$$U \equiv QR, \quad \Phi(U) \equiv \frac{3}{U^3} [\sin U - U \cos U]$$



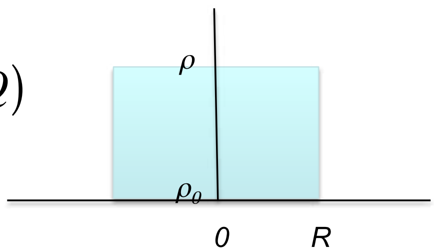
The scattering amplitude is proportional to the volume of the sphere V, and the scattering length density, $\Delta\rho_0$.

2. Scattering intensity from assembly of spherical objects

The scattering amplitude for a sphere

$$F(Q) = (\rho - \rho_0) \int_0^R e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} = (\rho - \rho_0) V_R \Phi_R(Q)$$

$$\Phi_R(Q) \equiv \frac{3[\sin(QR) - (QR)\cos(QR)]}{(QR)^3}, \quad V_R = \frac{4}{3}\pi R^3$$



ρ, ρ_0; the scattering densities of the sphere and the matrix [cm^{-2}]
R; the radius of the sphere

The scattering intensity from a sphere

$$I(Q) = (\rho - \rho_0)^2 V_R^2 \Phi_R^2(Q)$$

[cm^{-2}]^2 x [cm^3]^2 [-] = [cm^2]

The scattering intensity from an assembly of spheres

$$I(Q) = (\rho - \rho_0)^2 n V_R^2 \Phi_R^2(Q)$$

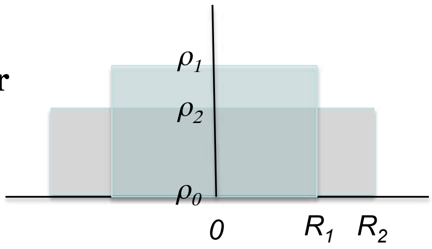
[cm^{-1}]

n; the number density of the sphere [cm^{-3}]

3. Scattering function for a spherical core-shell model

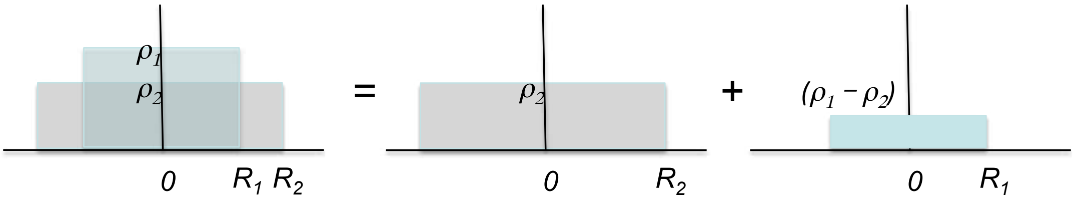
The scattering amplitude

$$F(Q)=(\rho_1-\rho_0)\int_0^{R_1} e^{i\mathbf{Q}\cdot\mathbf{r}}d\mathbf{r}+(\rho_2-\rho_0)\int_{R_1}^{R_2} e^{i\mathbf{Q}\cdot\mathbf{r}}d\mathbf{r}$$
$$=(\rho_1-\rho_0)\int_0^{R_1}\ +(\rho_2-\rho_0)\int_0^{R_2}\ -(\rho_2-\rho_0)\int_0^{R_1}$$
$$=(\rho_2-\rho_0)\int_0^{R_2}\ +(\rho_1-\rho_2)\int_0^{R_1}$$



The scattering intensity

$$I(q)=\left[(\rho_2-\rho_0)V_{R_2}\Phi_{R_2}(Q)+(\rho_1-\rho_2)V_{R_1}\Phi_{R_1}(Q)\right]^2$$



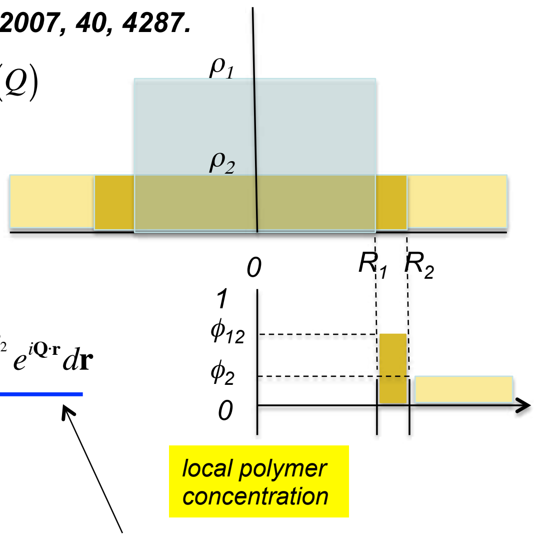
The scattering intensity

$$I(Q)=n\left[(\rho_2-\rho_0)V_{R_2}\Phi_{R_2}(Q)+(\rho_1-\rho_2)V_{R_1}\Phi_{R_1}(Q)\right]^2$$

4. Scattering function for a sphere and polymer matrix with an adsorbed layer

Miyazaki et al., Macromolecules, 2007, 40, 4287.

$$I(q)=(\rho_1-\rho_0)^2 S_{11}(Q)+2(\rho_1-\rho_0)(\rho_2-\rho_0)S_{12}(Q)$$
$$+(\rho_2-\rho_0)^2 S_{22}(Q)$$



$$F_1(q)=V_{R_1}\Phi_{R_1}(Q)$$

$$F_2(Q)=\phi_{12}\int_{R_1}^{R_2} e^{i\mathbf{Q}\cdot\mathbf{r}}d\mathbf{r}+\phi_2\int\eta(\mathbf{r})e^{i\mathbf{Q}\cdot\mathbf{r}}\,d\mathbf{r}-\phi_2\int_0^{R_2} e^{i\mathbf{Q}\cdot\mathbf{r}}d\mathbf{r}$$
$$=\phi_{12}\int_0^{R_2}\ -\phi_{12}\int_0^{R_1}\ +\phi_2\int\eta(\mathbf{r})e^{i\mathbf{Q}\cdot\mathbf{r}}\,d\mathbf{r}-\phi_2\int_0^{R_2}$$
$$=(\phi_{12}-\phi_2)\int_0^{R_2}\ -\phi_{12}\int_0^{R_1}\ +\phi_2\int\eta(\mathbf{r})e^{i\mathbf{Q}\cdot\mathbf{r}}\,d\mathbf{r}$$
$$=(\phi_{12}-\phi_2)V_{R_2}\Phi_{R_2}-\phi_{12}V_{R_1}\Phi_{R_1}+\phi_2\int\eta(\mathbf{r})e^{i\mathbf{Q}\cdot\mathbf{r}}\,d\mathbf{r}$$

Excluded volume occupied by the sphere

$\eta(r)$; a function representing the scattering amplitude of polymer solution which satisfies

$$\left[\int\eta(\mathbf{r})e^{i\mathbf{Q}\cdot\mathbf{r}}\,d\mathbf{r}\right]^2=\frac{I(0)}{1+\xi^2Q^2}$$

$$S_{11}(Q) = n_1 F_1^2 = n_1 V_{R_1}^2 \Phi_{R_1}^2(Q)$$

$$S_{22}(Q) = n_1 F_2^2$$

$$= n_1 \left[(\phi_{12} - \phi_2) \int_0^{R_2} \quad - \phi_{12} \int_0^{R_1} \quad + \phi_2 \int \eta(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} \right]^2$$

$$\approx n_1 \left[(\phi_{12} - \phi_2) \int_0^{R_2} \quad - \phi_{12} \int_0^{R_1} \quad \right]^2 + \frac{n_1 \phi_2^2 A}{1 + \xi^2 Q^2}$$

n_1; the number density of the sphere [cm^{-3}]
A; a constant with the dimension of [cm^3]^2

Here, we assumed no correlation between polymer and particle.

$$S_{12}(Q) = n_1 F_1 F_2$$

$$= n_1 \left[(\phi_{12} - \phi_2) \int_0^{R_2} \quad - \phi_{12} \int_0^{R_1} \quad + \phi_2 \int \eta(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} \right] V_{R_1} \Phi_{R_1}(Q)$$

$$= n_1 \left[(\phi_{12} - \phi_2) V_{R_2} \Phi_{R_2}(Q) - \phi_{12} V_{R_1} \Phi_{R_1}(Q) + \phi_2 \int \eta(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} \right] V_{R_1} \Phi_{R_1}(Q)$$

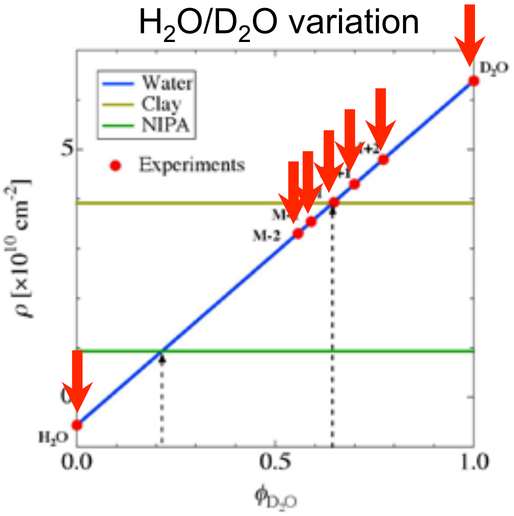
$$\approx n_1 (\phi_{12} - \phi_2) V_{R_2} \Phi_{R_2}(Q) V_{R_1} \Phi_{R_1}(Q) - n_1 \phi_{12} V_{R_1}^2 \Phi_{R_1}^2(Q)$$

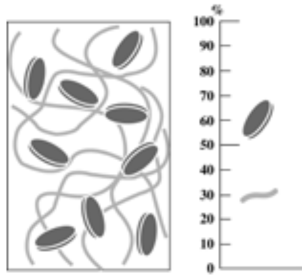
Contrast variation

Contrast variation

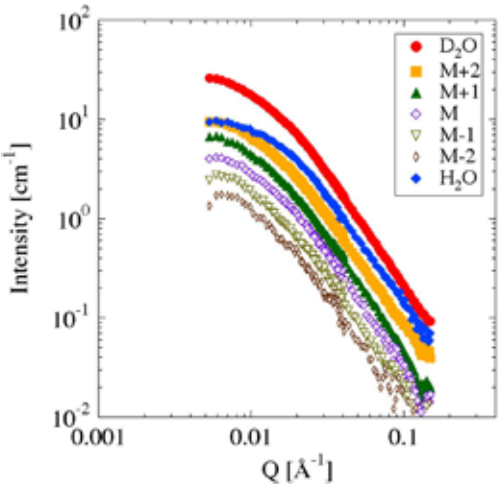
1. Design of the contrasts

H_2O/D_2O variation





2. SANS experiments



$I(q) \rightarrow S_{ij}(q)$

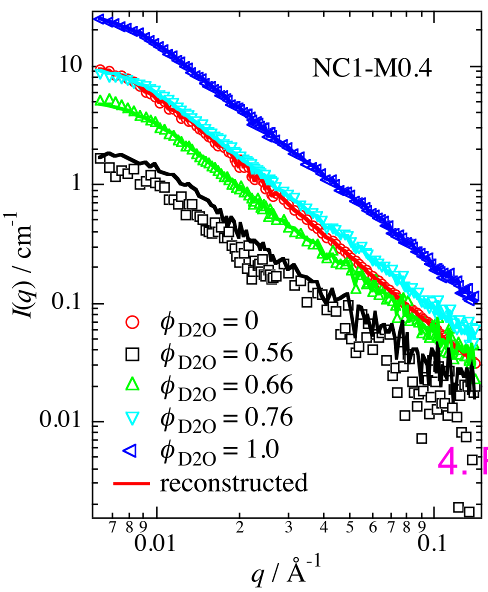
$$\begin{pmatrix}\Delta_1\rho_C^{\ 2} & \Delta_1\rho_P^{\ 2} & 2\Delta_1\rho_C\Delta_1\rho_P \\ \Delta_2\rho_C^{\ 2} & \Delta_2\rho_P^{\ 2} & 2\Delta_2\rho_C\Delta_2\rho_P \\ \Delta_3\rho_C^{\ 2} & \Delta_3\rho_P^{\ 2} & 2\Delta_3\rho_C\Delta_3\rho_P \\ & \vdots & \end{pmatrix}^{-1}\begin{pmatrix}I_1(q)\\ I_2(q)\\ I_3(q)\\ \vdots\end{pmatrix} = \begin{pmatrix}S_{CC}(q)\\ S_{PP}(q)\\ S_{CP}(q)\end{pmatrix}$$

2. $I(q) \rightarrow S_{ij}(q)$

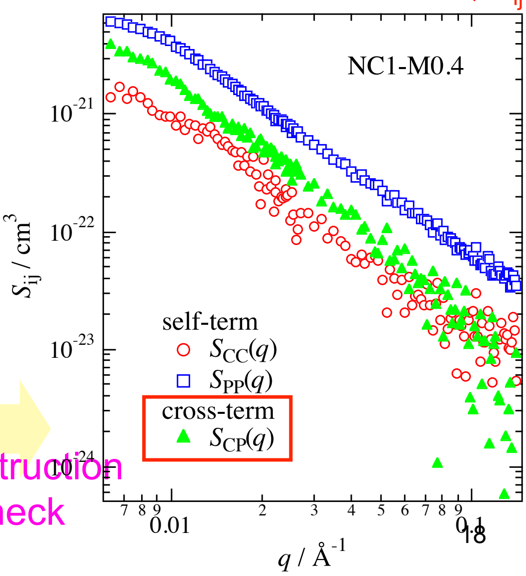
(singular value decomposition)

1. experiments

3. Partial scatt. fn ; $S_{ij}(q)$

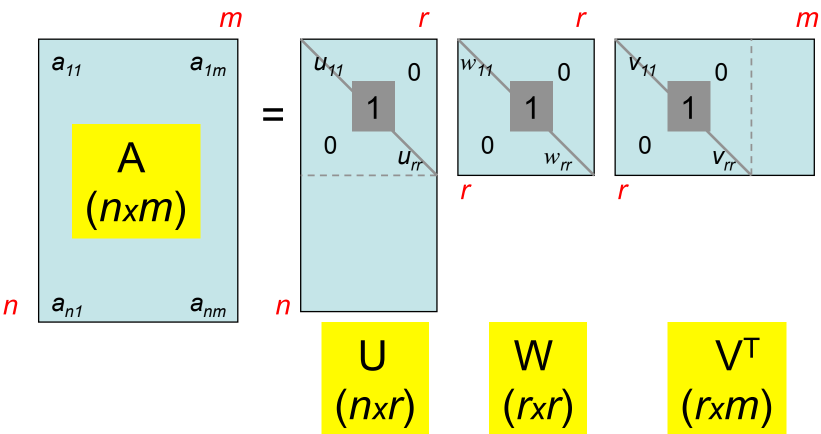


4. Reconstruction And check



Singular value decomposition

Singular value decomposition (1)



An arbitrary matrix A (*n*x*m*) can be decomposed to $UD_\lambda V^T$, where
U and V are (*n*x*r*) and (*m*x*r*) matrixes having orthonormal vectors of rank *r*. Hence,
$UU^T = VV^T = E$.

$$\mathbf{A} = \mathbf{U}\mathbf{D}_\lambda \mathbf{V}^T$$

$$\mathbf{A}^T\mathbf{A} = \left(\mathbf{U}\mathbf{D}_\lambda \mathbf{V}^T\right)^T\left(\mathbf{U}\mathbf{D}_\lambda \mathbf{V}^T\right) = \mathbf{V}\mathbf{D}_\lambda{}^T\mathbf{U}^T\mathbf{U}\mathbf{D}_\lambda\mathbf{V} = \mathbf{V}\mathbf{D}_{\lambda^2}\mathbf{V}^T$$

$$\mathbf{A}\mathbf{A}^T = \left(\mathbf{U}\mathbf{D}_\lambda\mathbf{V}\right)\left(\mathbf{U}\mathbf{D}_\lambda\mathbf{V}\right)^T = \mathbf{U}\mathbf{D}_{\lambda^2}\mathbf{U}^T$$

The eigenvector of A^TA is the row vector of V.

The eigenvector of AA^T is the row vector of U.

Singular value decomposition (2)

$$\mathbf{I} = \mathbf{CS}$$

No. of contrasts, *n*

$$\begin{pmatrix} I_1(q) \\ \\ \\ I_n(q) \end{pmatrix} = \begin{pmatrix} C_{11} & & C_{1m} \\ & & \\ & & \\ C_{n1} & & C_{nm} \end{pmatrix} \begin{pmatrix} S_1(q) \\ \\ \\ S_m(q) \end{pmatrix}$$

$$(n \times 1) \qquad (n \times m) \qquad (m \times 1)$$

No. of components, *m*

$$\mathbf{VW}^{-1}\mathbf{U}^{\mathrm{T}}$$

$$(m \times r) \quad (r \times r) \quad (r \times n) = \quad (m \times n)$$

Hence, $\mathbf{C}^{-1}$ is a (m x n) matrix.

$$\mathbf{C} = \mathbf{UWV}^{\mathrm{T}} \qquad m = {}_pC_2 = \frac{p(p-1)}{2}$$

$$\mathbf{U} = \begin{pmatrix} u_{11} & & \\ & & u_{rr} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \mathbf{W} = \begin{pmatrix} w_{11} & \\ & w_{rr} \end{pmatrix} \quad \mathbf{V} = \begin{pmatrix} v_{11} & & \\ & & v_{rr} \\ 0 & 0 & 0 \end{pmatrix}$$

$$(n \times r) \qquad (r \times r) \qquad (m \times r)$$

$$\mathbf{C}^{-1} \equiv \mathbf{c} = \left(\mathbf{UWV}^{\mathrm{T}}\right)^{-1} = \left(\mathbf{V}^{\mathrm{T}}\right)^{-1}\mathbf{W}^{-1}\mathbf{U}^{-1} = \mathbf{VW}^{-1}\mathbf{U}^{\mathrm{T}}$$

$$\because \mathbf{UU}^{\mathrm{T}} = \mathbf{VV}^{\mathrm{T}} = \mathbf{E}$$

$$\therefore \mathbf{U}^{\mathrm{T}} = \mathbf{U}^{-1}, \quad \mathbf{V}^{\mathrm{T}} = \mathbf{V}^{-1}$$

Singular value decomposition (3)

1. Define contrast matrixes and intensity vector

$$\mathbf{I} = \mathbf{CS}$$

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{1m} \\ & \\ C_{n1} & C_{nm} \end{pmatrix}$$

$$\mathbf{I} = \begin{pmatrix} I_1(q) \\ \\ I_n(q) \end{pmatrix}$$

2. Decompose C

$$\mathbf{C} = \mathbf{UWV}^{\mathrm{T}}$$

$$\mathbf{U} = \begin{pmatrix} u_{11} & & 0 \\ & u_{22} & \\ 0 & & u_{rr} \\ & & \\ 0 & & 0 \end{pmatrix} \quad V^{\mathrm{T}} = \begin{pmatrix} v_{11} & & 0 & 0 \\ & v_{11} & & \\ 0 & & v_{rr} & 0 \end{pmatrix} \quad w = \begin{pmatrix} w_{11} & w_{22} & .. & w_{rr} \end{pmatrix}$$

3. Calculate c

$$\mathbf{c} \equiv \mathbf{C}^{-1} = \left(\mathbf{UWV}^{\mathrm{T}}\right)^{-1} = \left(\mathbf{V}^{\mathrm{T}}\right)^{-1}\mathbf{W}^{-1}\mathbf{U}^{-1} = \mathbf{V}w_0\mathbf{U}^{\mathrm{T}}$$

4. Examine c

$$\mathbf{cC} = \mathbf{C}_{\mathrm{check}} \stackrel{?}{=} \begin{pmatrix} 1 & & 0 \\ & 1 & \\ 0 & & 1 \end{pmatrix}$$

$$\mathbf{c} = \begin{pmatrix} c_{11} & c_{1n} \\ & \\ c_{m1} & c_{mn} \end{pmatrix} \quad \mathbf{C} = \begin{pmatrix} C_{11} & C_{1m} \\ C_{n1} & C_{nm} \end{pmatrix}$$

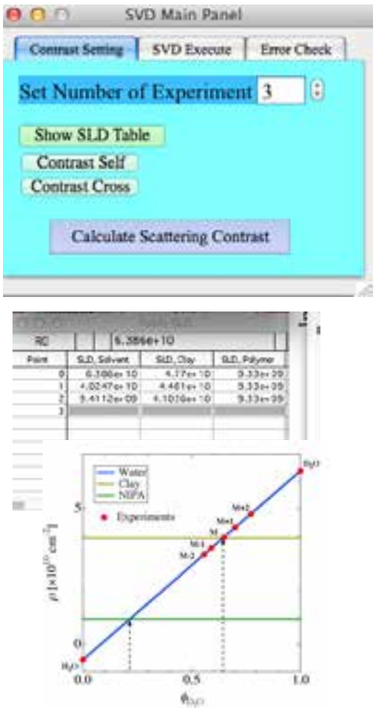
5. Obtain S

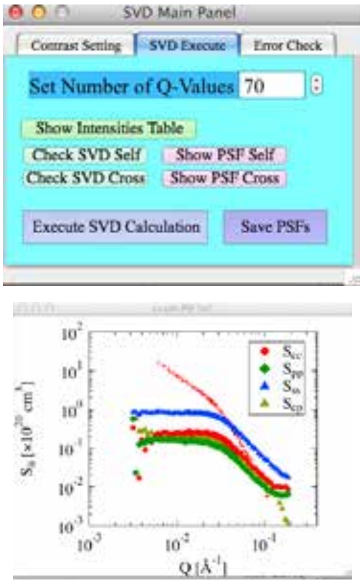
$$\mathbf{cI} = \mathbf{C}^{-1}\mathbf{I} = \mathbf{S}$$

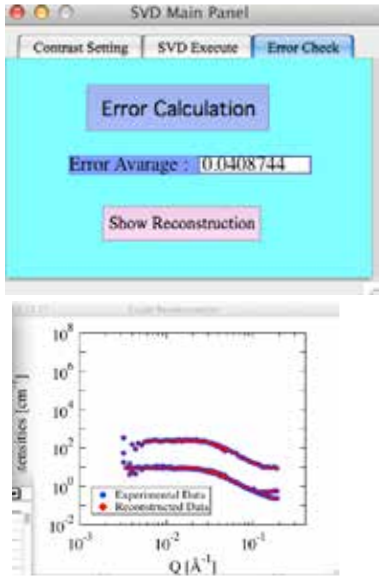
6. Reconstruct I

$$\mathbf{CS} = \mathbf{c}^{-1}\mathbf{S} = \mathbf{I}_{\mathrm{reconst}}$$

Igor program







contrast

Partial scattering functions

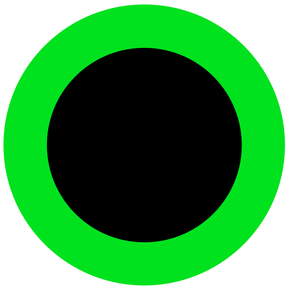
Re-constructed Scattered intensities

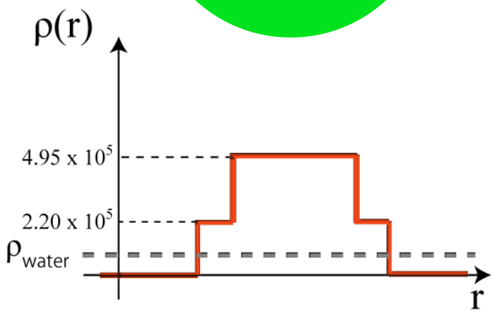
Igor matrix operation “MatrixSVD”

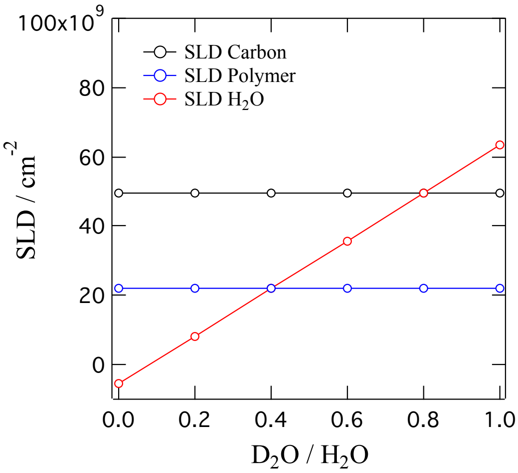
Simple models

- Core-shell model
- Sphere + polymer matrix (no correlation)
- Sphere + polymer matrix
  with excluded volume effect

Example 1. core-shell model



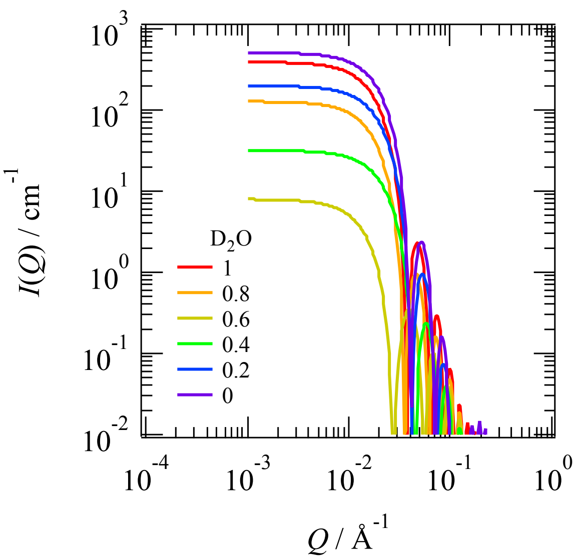


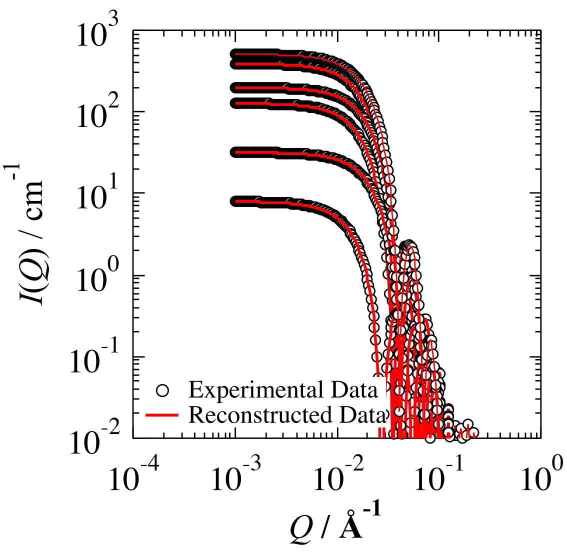


Core radius 100 Å
Shell thickness 26 Å
Conc of #1(carbon) 1 vol%
Conc of #2(polymer)1 vol%

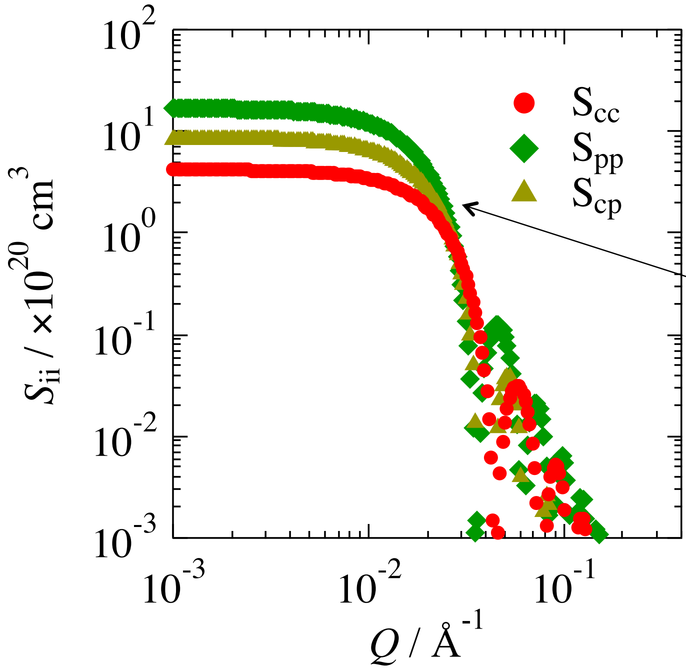
$$I(Q) = n\left[(\rho_2 - \rho_0)V_{R_2}\Phi_{R_2}(Q) + (\rho_1 - \rho_2)V_{R_1}\Phi_{R_1}(Q)\right]^2$$

CV SANS measurements (simulation and reconstruction)





Partial structure factors



The polymer scattering is very similar to that of spheres because the polymers are located only on the surface of spheres.

Examples 2 and 3

Ex.2 sph. + polymer (no correlation)

Ex.3 sph. + polymer (with excluded-vol. effect)

Rad. of sphere 100 Å
Rg of polymer 10 Å
Conc of #1(sphere) 1 vol%
Conc of #"(polymer) 1 vol%

Ex.2

$$I(q)=(\rho_C-\rho_S)^2 S_{CC}(Q)+(\rho_P-\rho_S)^2 S_{PP}(Q) \leftarrow$$

Simple addition of the partial scattering functions (“intensity”).

$$S_{CC}(Q)=n_C F_C^2=n_C V_R^2 \Phi_R^2(Q)$$

$$S_{PP}(Q)=n_C\left[\int \eta(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r}\right]^2 \approx \frac{n_C A}{1+\xi^2 Q^2}$$

Ex.3

$$I(q)=(\rho_C-\rho_S)^2 S_{CC}(Q)+2(\rho_C-\rho_S)(\rho_P-\rho_S)S_{CP}(Q)+(\rho_P-\rho_S)^2 S_{PP}(Q)$$

$$F_C(Q)=V_R\Phi_R(Q) \qquad F_P(Q)=\phi_P\int \eta(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r}-\phi_P\int_0^R e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r}=\underline{-\phi_P V_R \Phi_R+\phi_P\int \eta(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r}}$$

$$\left[\int \eta(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r}\right]^2=\frac{I(0)}{1+\xi^2 Q^2}$$

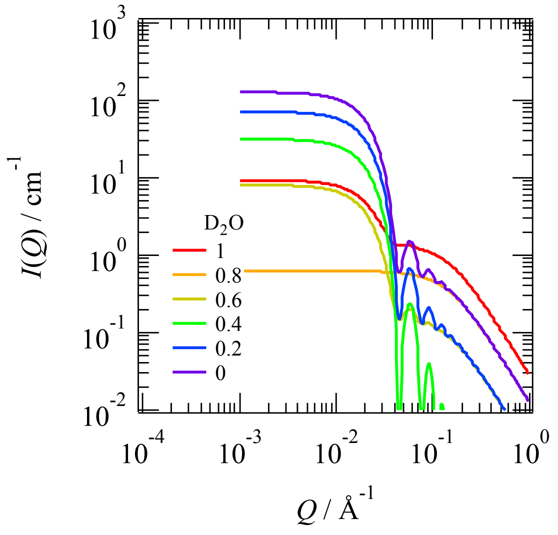
Babinet rule (in the “scattering amplitude”)

$$S_{CC}(Q)=n_C F_C^2=n_C V_R^2 \Phi_R^2(Q) \qquad S_{PP}(Q)=n_C\left[\phi_P\int \eta(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r}-\phi_P\int_0^R e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r}\right]^2 \approx n_C\phi_P^2 V_R^2 \Phi_R^2+\frac{n_C\phi_P^2 A}{1+\xi^2 Q^2}$$

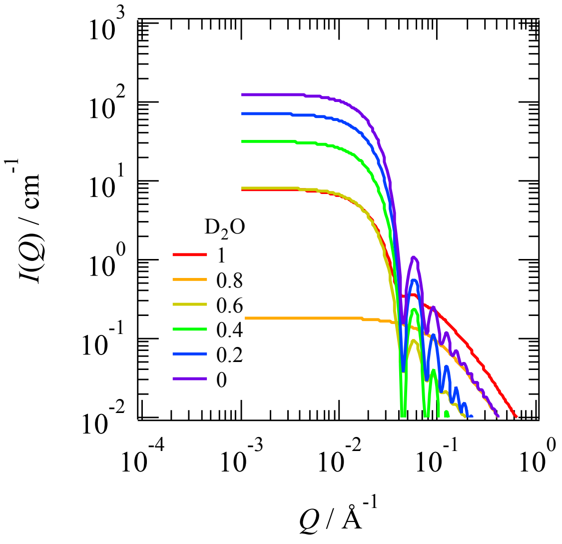
$$S_{CP}(Q)=n_C F_C F_P=n_C\left[-\phi_P V_R \Phi_R(Q)+\phi_P\int \eta(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r}\right]V_R\Phi_R(Q)\approx -n_C\phi_P V_R^2 \Phi_R^2(Q)$$

CV SANS measurements (simulation)

Ex.2

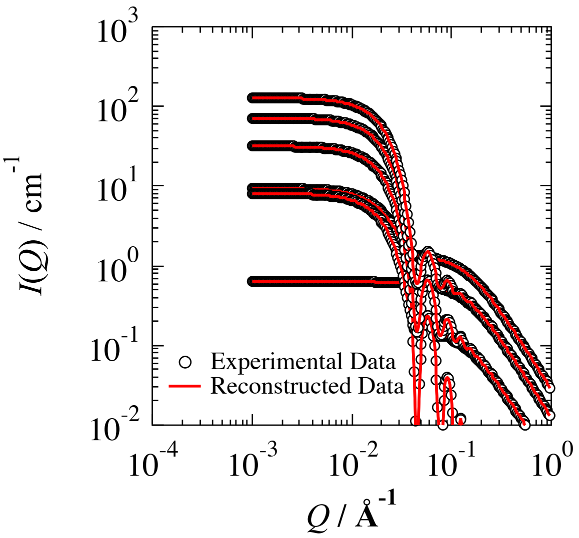


Ex.3

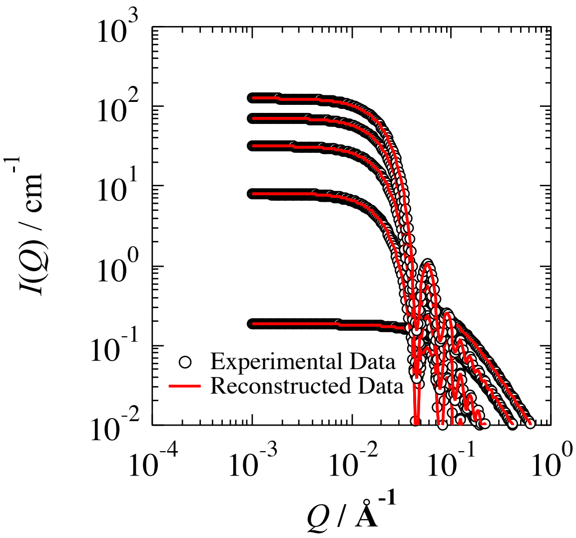


Re-construction

Ex.2

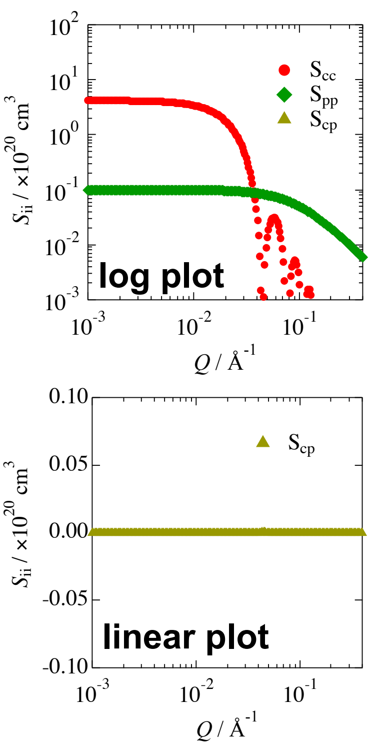


Ex.3

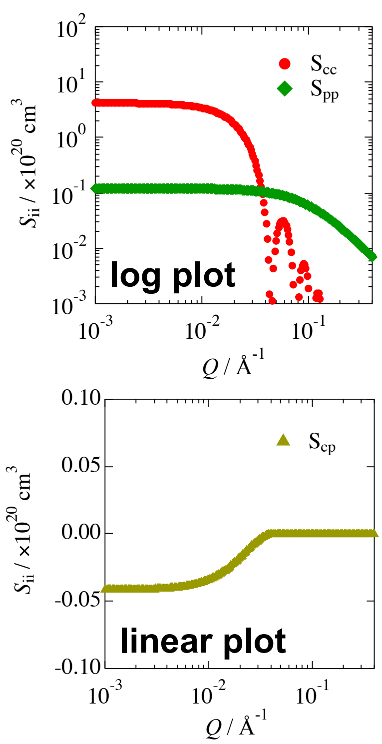


Partial structure factors

Ex.2



Ex.3



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applications

<Contrast matching>
Clay concentration dependence of microstructure in deformed poly(N-isopropylacrylamide)-clay nanocomposite gels
Miyazaki et al., Macromolecules, 2006, 39, 811.

<Contrast variation>
1. Gelation Mechanism of Poly(N-isopropylacrylamide)-Clay Nanocomposite Gels
Miyazaki et al., Macromolecules, 2007, 40, 4287.

Calc. of S_{PP}, S_{CC}, S_{CP}

2. Structure of nanocomposite hydrogel investigated by means of contrast variation small-angle neutron scattering
Endo et al., Macromolecules, 2008, 41, 5406.

Structure factor

3. Analysis of surface structure and hydrogen/deuterium exchange of colloidal silica suspension by contrast-variation small-angle neutron scattering
Suzuki et al., Langmuir, 2008, 24, 4537.

Gradual interface,
H/D substitution

4. Mechanically Interlocked Structure of Polyrotaxane Investigated by Contrast Variation Small-Angle Neutron Scattering
Mayumi et al., Macromolecules, 2009, 42, 6327.

$S_{CD} \approx S_{PED}$ ->
Mechanical interlock

5. Deformation mechanism of nanocomposite gels studied by contrast variation small-angle neutron scattering
Nishida et al., PRE, 2009, 80, 30801.

CV for anisotropic patterns
(elongation)

33

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<Contrast variation> (continued)

6. Nonuniformity in Cross-Linked Natural Rubber as Revealed by Contrast-Variation Small-Angle Neutron Scattering
Suzuki, et al., Macromolecules, 2010, 43, 1556.

CV for biological system
(natural rubber with
aminoic acid)

7. Microscopic Structure Analysis of Clay-Poly(ethylene oxide) Mixed Solution in a Flow Field by Contrast-Variation Small-Angle Neutron Scattering
Matsunaga et al., Macromolecules, 2010, 43, 5075.

8. Rheo-SANS Studies on Shear Thickening in Clay-Poly(ethylene oxide) Mixed Solutions
Takeda, et al., Macromolecules, 2010, 43, 7793.

9. The static structure of polyrotaxane in solution investigated by contrast variation small-angle neutron scattering
Endo, et al., Polym. J. 2011, 43, 155.

10. SANS Studies on Catalyst Ink of Fuel Cell
Shibayama, et al., J. Appl. Polym. Sci., 2014, 131, 39842.

Prague, July 8-12, 2007
46th Microsymposium of P.M., Prague
Nanosrucutred Polymers and Polymer Nanocomposites

Univ. Bayreuth Oct. 8, 2007

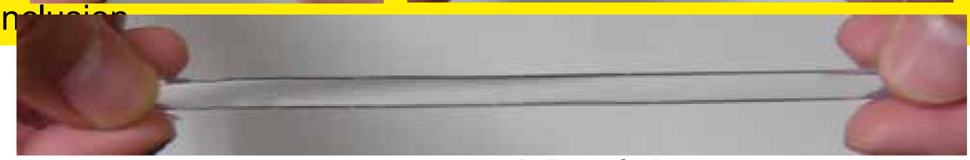
Small-angle Neutron Scattering and Dynamic Light Scattering Studies on High-Performance Polymer-Nanocomposite Hydrogels

Institute for Solid State Physics
The University of Tokyo

NC gels: High extensibility and high flexibility

1. Clay- ... te
2. SAN ... (
3. SAN ... (p
4. DLS:
5. Conclusion



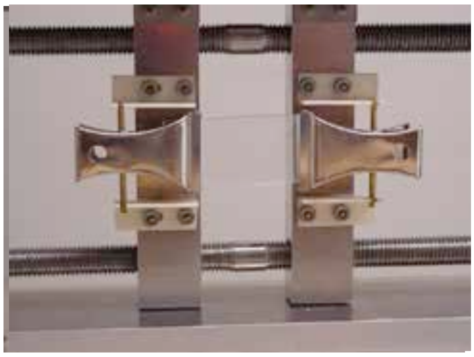


Acknowledgement:
Dr. K. Haraguchi, Kawamura Res. Inst.

Clay-polymer (straw) composite

mud wall

Instrument and samples: SANS



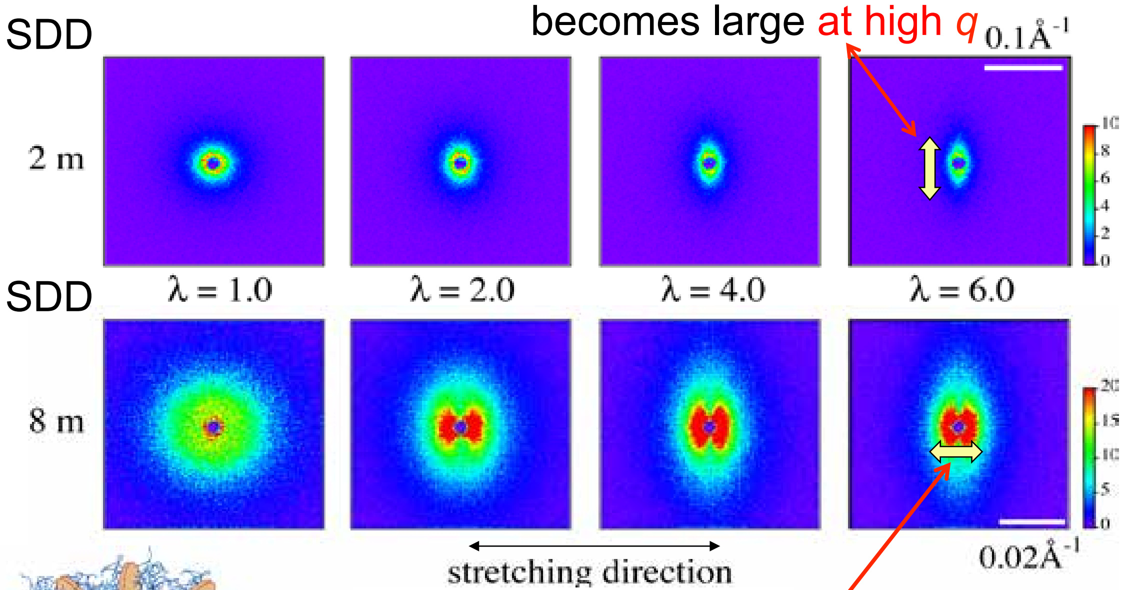
Stretching cell

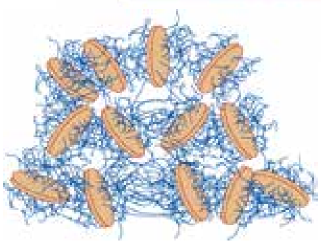
- SANS-U(ISSP, U-Tokyo@Tokai)
- wavelength; 7.0Å
- sample to detector distance; 2m,8m
- temperature; 20ºC
- stretching ratio $\lambda(\equiv l/l_o)$
  λ = 1.0, 1.2, 1.4, 1.6, 1.8,
  2.0, 2.5, 3.0, 4.0, 5.0, 6.0

- sample code; NC2, NC4, NC6
  (clay; 0.02, 0.04, 0.06 molL^{-1},
  NIPA; 7.8wt%)

SANS patterns in D_2O

Intensity for perpendicular direction
becomes large at high q





Intensity for parallel direction
becomes large at low q

Contrast matching

Scattering function of NC gel is obtained as below

clay(C), polymer(P), solvent(S)

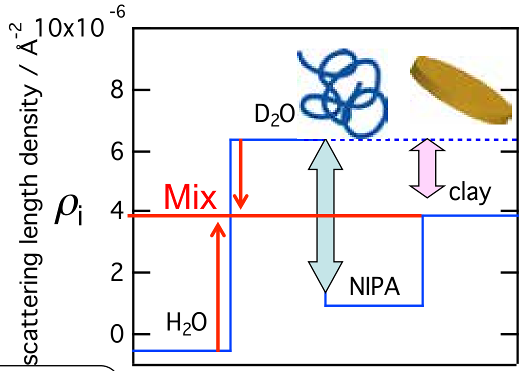
S_{ij} ; partial scattering function

$$I(q) = \phi_P\phi_S\boxed{(\rho_P-\rho_S)^2}S_{PP} + \phi_C\phi_S\boxed{(\rho_C-\rho_S)^2}S_{CC} + 2\phi_P\phi_C\boxed{(\rho_P-\rho_S)}\boxed{(\rho_C-\rho_S)}S_{PC}$$

if $\phi_{H2O} : \phi_{D2O} = 0.34 : 0.66$

$\rightarrow \boxed{\rho_S = \rho_C}$

$$I(q) = \phi_P\phi_S(\rho_P-\rho_S)^2 S_{PP}$$



Contrast matching enables us to **extract the polymer contribution(S_{PP})**.

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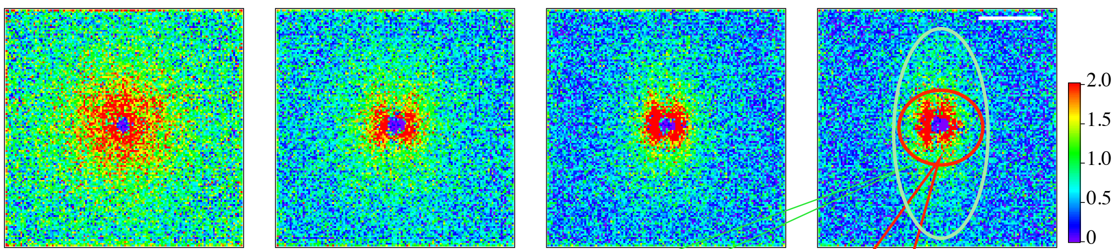
SANS patterns of NC4 with matching solvent

0.02Å^{-1}

SDD 8m

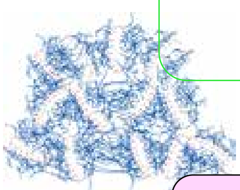


λ = 1.0 λ = 2.0 λ = 4.0 λ = 6.0

Stretching direction

Intensity for perpendicular direction increases in high-q region.

Intensity for parallel direction increases in low-q region.



Because of homogeneous dispersion of polymer!

Because of cross-link inhomogeneities (?)

Contrast variation method

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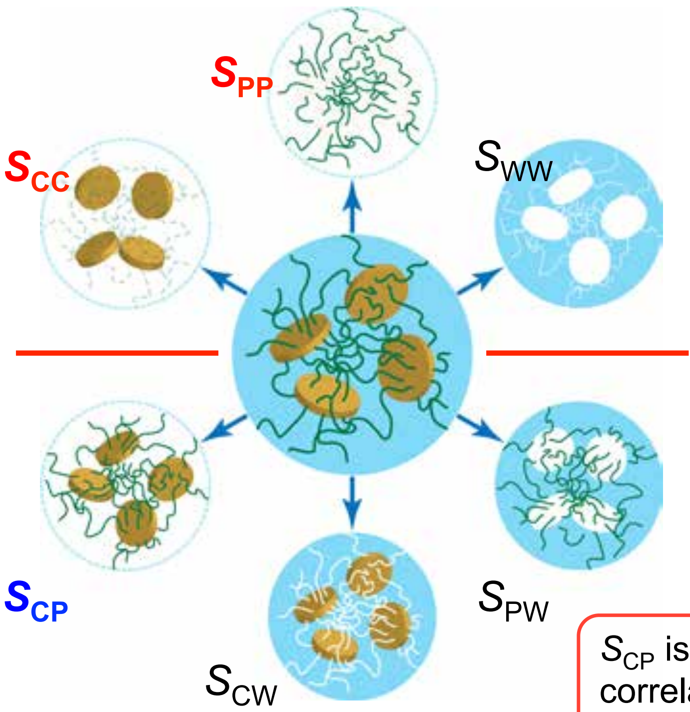
Self Terms



Cross Terms

Scatt. Intensity

$$I(q) = (\rho_C - \rho_S)^2 S_{CC}(q) + (\rho_P - \rho_S)^2 S_{PP}(q) + 2(\rho_C - \rho_S)(\rho_P - \rho_S) S_{CP}(q)$$

Contrast matching
→ one self term, S_{ii}

Contrast variation
→all terms, S_{ij}

S_{CP} is very important to study the correlation between polymer and clay.

Contrast variation

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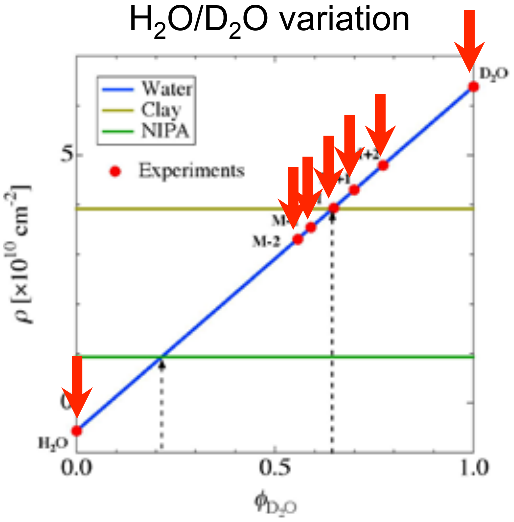
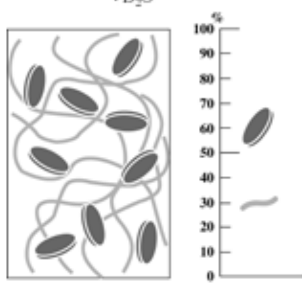
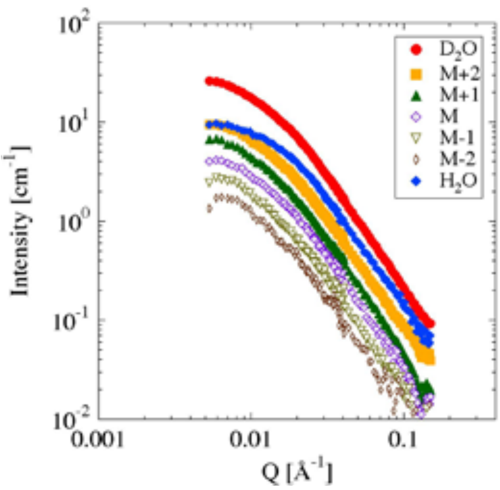
H_2O/D_2O variation







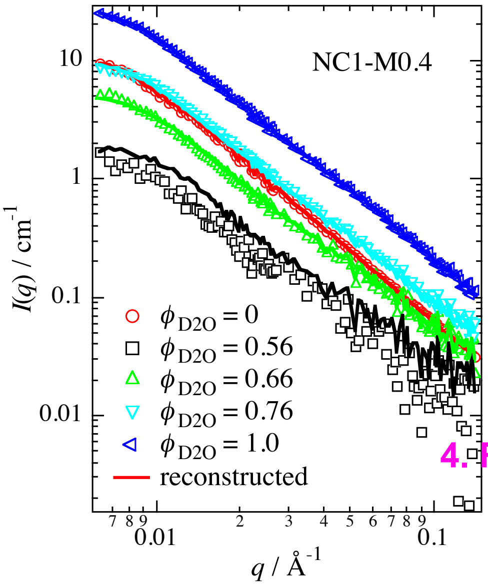
Scattering Intensities

$I(q) \rightarrow S_{ij}(q)$

$$\begin{pmatrix} \Delta_1\rho_C^{\ 2} & \Delta_1\rho_P^{\ 2} & 2\Delta_1\rho_C\Delta_1\rho_P \\ \Delta_2\rho_C^{\ 2} & \Delta_2\rho_P^{\ 2} & 2\Delta_2\rho_C\Delta_2\rho_P \\ \Delta_3\rho_C^{\ 2} & \Delta_3\rho_P^{\ 2} & 2\Delta_3\rho_C\Delta_3\rho_P \\ & \vdots & \end{pmatrix}^{-1} \begin{pmatrix} I_1(q) \\ I_2(q) \\ I_3(q) \\ \vdots \end{pmatrix} = \begin{pmatrix} S_{CC}(q) \\ S_{PP}(q) \\ S_{CP}(q) \end{pmatrix}$$

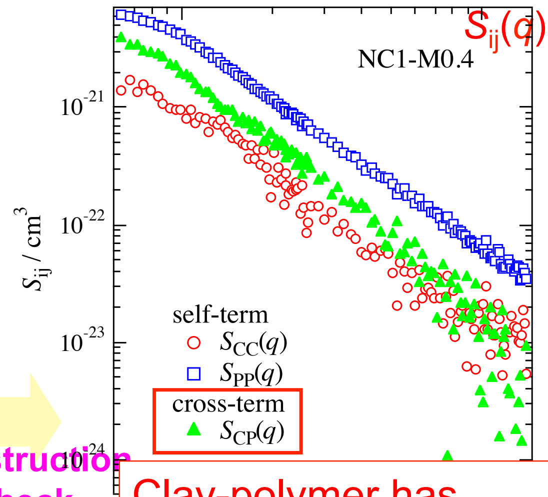
2. $I(q) \rightarrow S_{ij}(q)$
(singular value decomposition)

1. experiments



4. Reconstruction And check

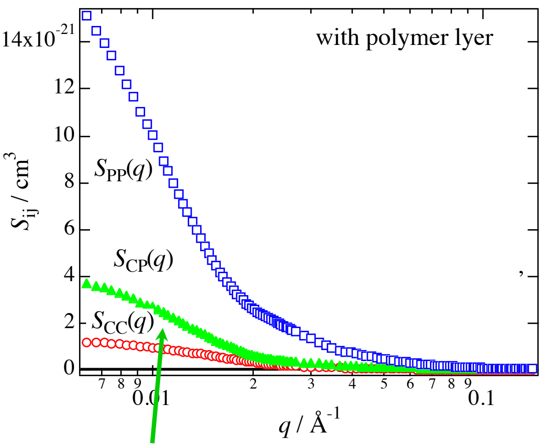
3. Partial scatt. fn ; $S_{ij}(q)$



Clay-polymer has strong correlation.

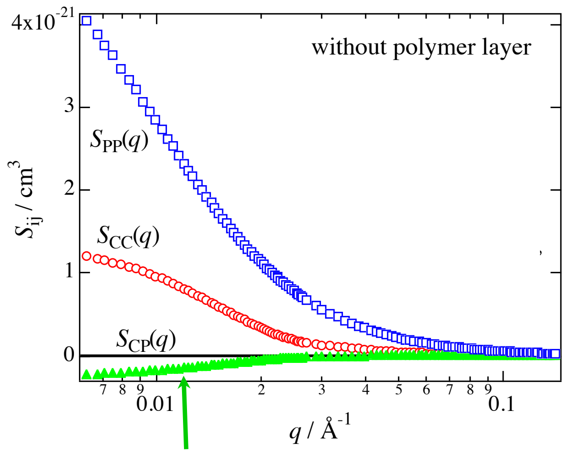
Cross-term

(a) Presence of correlation



$S_{CP} > 0$

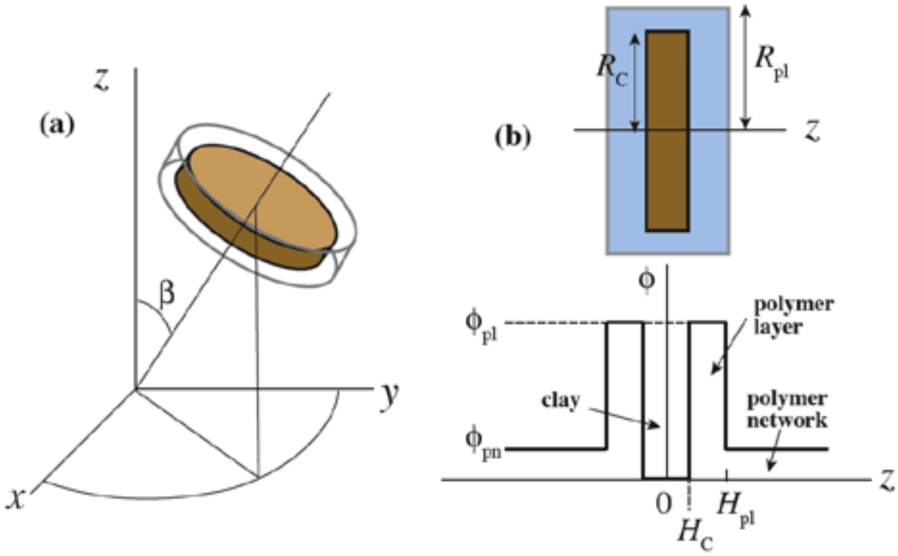
(b) No correlation



$S_{CP} < 0$

The sign of S_{CP} **indicates presence/absence of the correlation between clay and polymer.**

Evaluation of the scattering functions



Partial scattering functions

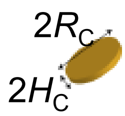
Cylinder: $F_{cyl}(R,H,\beta)$

$$F_{cyl}(R,H,\beta) = 2V \frac{\sin(qH\cos\beta)}{qH\cos\beta} \frac{J_1(qR\sin\beta)}{qR\sin\beta}$$

$V = 2\pi R^2 H$,
β ; azimuthal angle

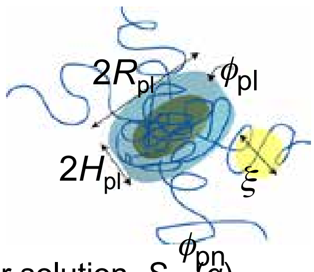
For a disc (R_C = 150Å, $2H_C$ = 10Å), S_{CC}(q)

$$S_{CC}(q) = \frac{N_C}{2}\int_{\beta=0}^{\pi} F_{cyl}(R_C,H_C,\beta)^2 \sin\beta d\beta$$



If a polymer layer is formed at the clay surface (R_{pl}, $2H_{pl}$, ϕ_{pl}), S_{CP}(q) reads

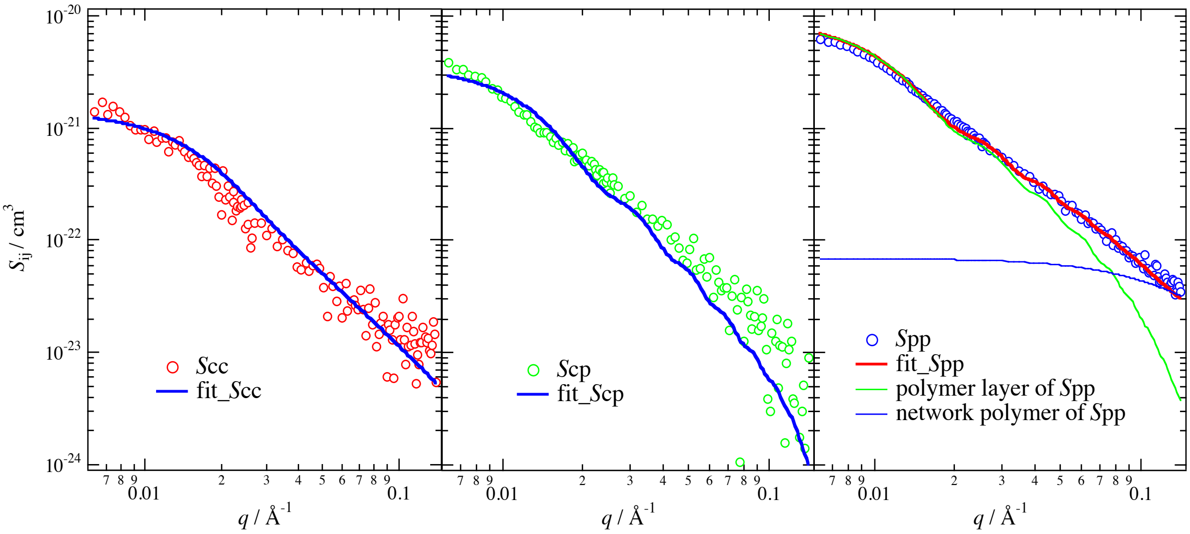
$$S_{CP}(q) = (\phi_{pl} - \phi_{pn})\frac{N_C}{2}\int_{\beta=0}^{\pi} F_{cyl}(R_{pl},H_{pl},\beta)F_{cyl}(R_C,H_C,\beta)\sin\beta d\beta - \phi_{pl}\frac{N_C}{2}\int_{\beta=0}^{\pi} F_{cyl}(R_C,H_C,\beta)^2 \sin\beta d\beta$$



Assuming the matrix scattering being equal to semi-dilute polymer solution, $S_{PP}(q)$

$$S_{PP}(q) = \frac{N_C}{2}\int_{\beta=0}^{\pi} [(\phi_{pl} - \phi_{pn})F_{cyl}(R_{pl},H_{pl},\beta) - \phi_{pl}F_{cyl}(R_C,H_C,\beta)]^2 \sin\beta d\beta + \frac{I(0)}{1+\xi^2 q^2}$$

Analysis of partial scattering functions



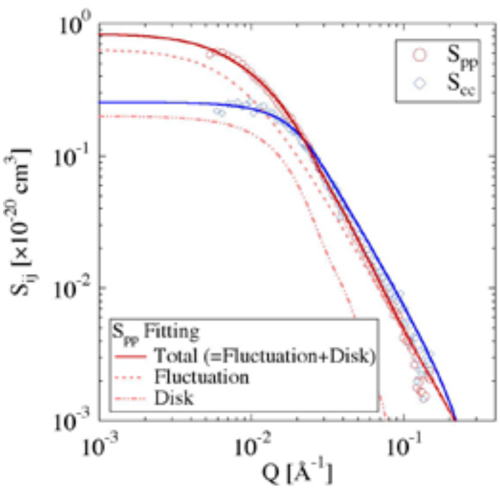
$S_{CC} \rightarrow N_C$

N_C:fixed
$S_{CP} \rightarrow R_P$, H_P, and ϕ_{pl}

N_C, R_P, H_P, ϕ_{pl}:fixed
$S_{PP} \rightarrow \xi$

The partial scattering functions are well reproduced.

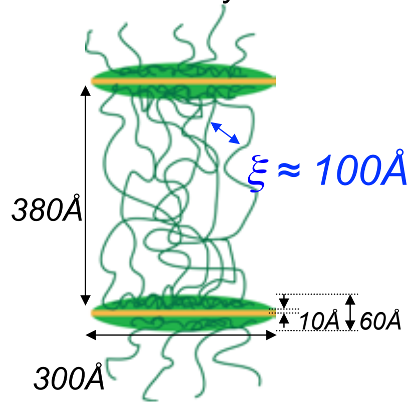
Evaluation of Partial Scattering Function



Fitting Results for ***S_{cc}*** *&* ***S_{pp}***

*>> **S_{cc}** can be fitted with a disk-model where the radius is 150Å and the thickness is 10Å.*

*>> **S_{pp}** consists of two parts; namely, approximately the half volume fraction of polymers is localized at the surface of the clays, and the other half of polymers crosslink between clays.*



Acknowledgement

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- **Neutron Scattering Program Committee (NSPAC), ISSP Proposal Nos. 5541, 6561**
- **JST (Japan Science and Technology Agency)**

Dr. K. Haraguchi
Kawamura Research Institute

Surface structure and Hydrogen/deuterium exchange of Colloidal silica suspension

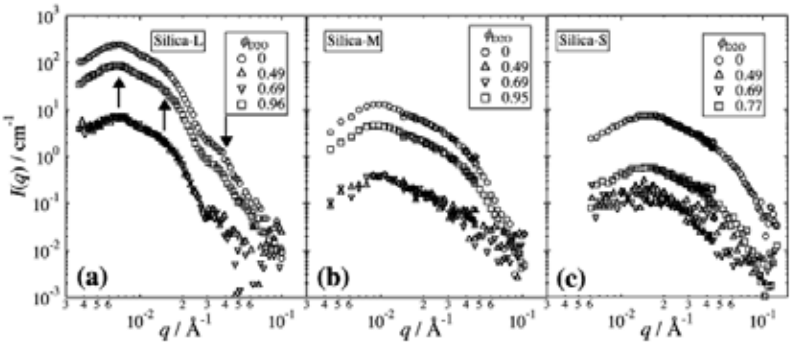
Suzuki et al., Langmuir, 2008, 24, 4537

Table 1. Sample Characteristics

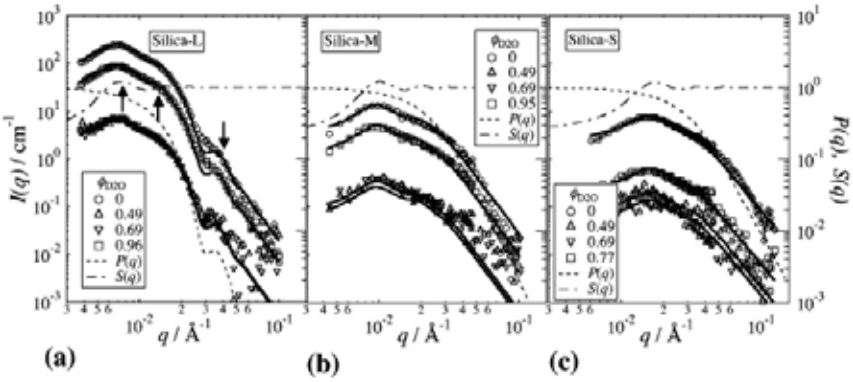
	$R_S{}^a$ (Å) as received	concentration as received (wt %)	d_{silica} (g/cm^3) as received	$A_S{}^a$ (m^2/g)	ϕ_S
Silica-L	100−150	40.7	2.26	120	0.012
Silica-M	40−55	20.3	2.21	290	0.006
Silica-S	20−30	10.6	2.23	540	0.012

[a] Provided by the manufacturer.

Topics:
Three kinds of silica particles, L, M, S
CV + Percus-Yevick analysis
Gradual interface ⟷ *Curve fitting*
H/D exchange ⟷ *I(0) intensity*



Observed SANS intensities



Simultaneous curve fitting with sphere and PY

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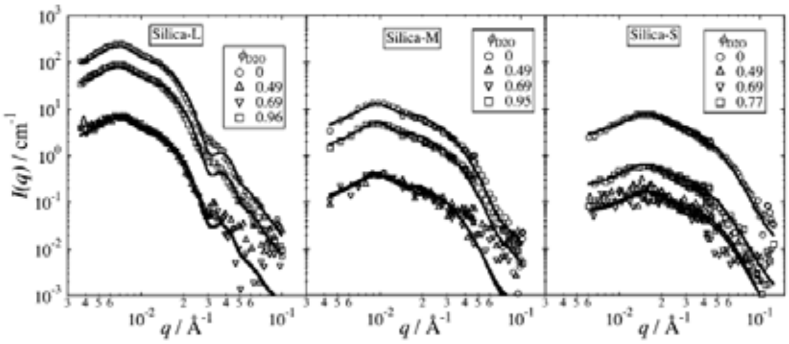
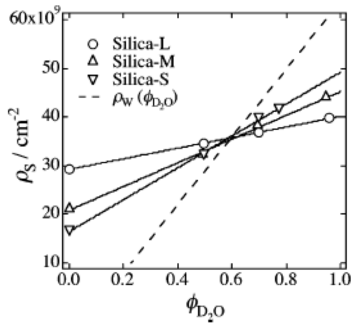


Results with a core-shell model:
Gradual interface and H/D exchange exclusively at the surface



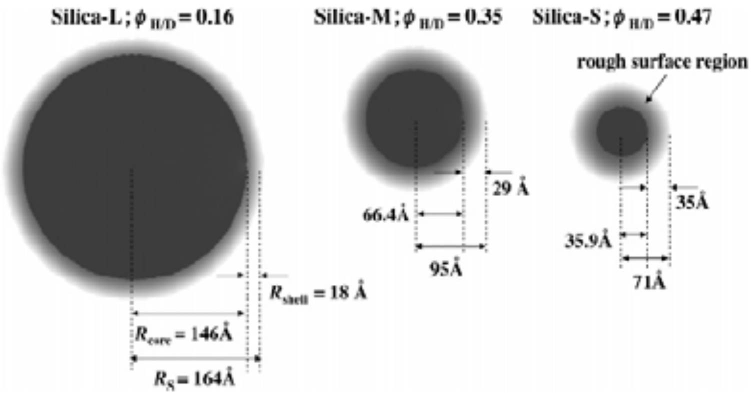
Size-dependent H/D exchange

Table 2. Structural Parameters Obtained by SANS

	R_S (Å)	R_{HS} (Å)	D (Å)	$n \times 10^9$ (Å^{-3})	$A_{S,0}$ (m^2/g)[a]	$A_S/A_{S,0}$
Silica-L	165 ± 0.2	414 ± 0.9	878	0.638	80.5	1.49
Silica-M	95.5 ± 0.4	303 ± 1.9	638	1.64	142	2.04
Silica-S	71.2 ± 0.2	173 ± 0.9	385	7.94	189	2.85

[a] Calculated with the structural parameters obtained by SANS by assuming a smooth surface.

New findings



Size-dependent H/D exchange

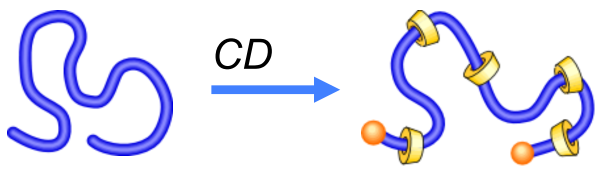
Size-dependent Surface thickness

Table 3. Fitting Parameters Used in Figure 9

	$\rho_{core} \times 10^{-10}$ (cm^{-2})	R_{core} (Å)	t (Å)
Silica-L	3.57 ± 0.01	146	18
Silica-M	3.52 ± 0.05	66.4	29
Silica-S	3.63 ± 0.04	35.9	35

Mechanically Interlocked Structure of Polyrotaxane Investigated by Contrast Variation Small-Angle Neutron Scattering

Mayumi et al., Macromolecules 2009, 42, 6327–6329



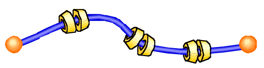
Sliding motion?
Topologically interlocked structure?

Flexible PEG chain

question:
How CDs are distributed on the PEG chains?

Sample Preparation

h-PR



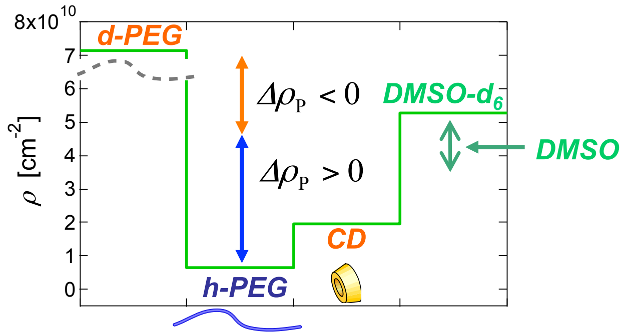
h-PEG + CD

$\Delta\rho_P > 0$

d-PR

d-PEG + CD

$\Delta\rho_P < 0$

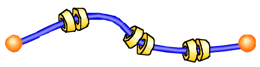


***M_w* of PEG : 35K**

Coverage of CDs : 25%

Solvent : DMSO and DMSO-d_6 mixture

h-PR

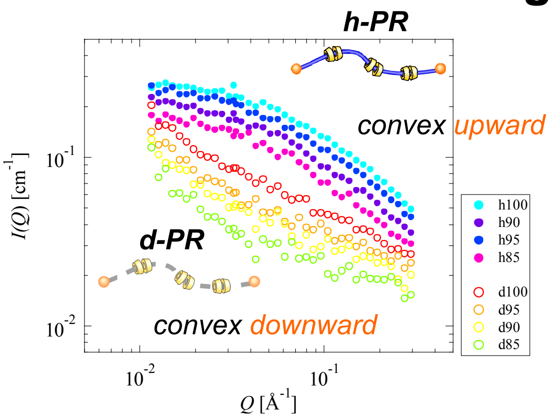


10 wt% (DMSO-d_6 fraction : 100, 95, 90, 85 %)

d-PR

10 wt% (DMSO-d_6 fraction : 100, 95, 90, 85 %)

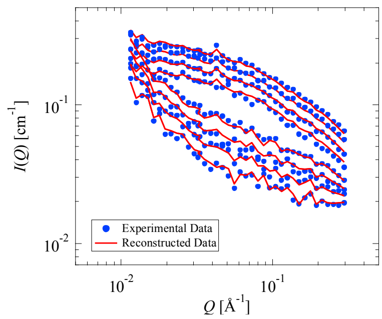
Decomposition and Reconstruction of Scattering Functions



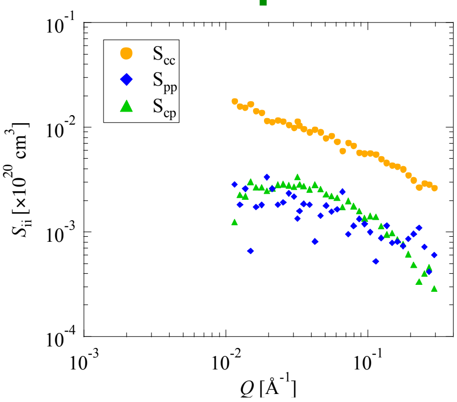
$$I(Q) = \Delta\rho_P^{\,2} S_{PP} + \Delta\rho_C^{\,2} S_{CC} + 2\Delta\rho_P \Delta\rho_C S_{CP}$$

Decomposition

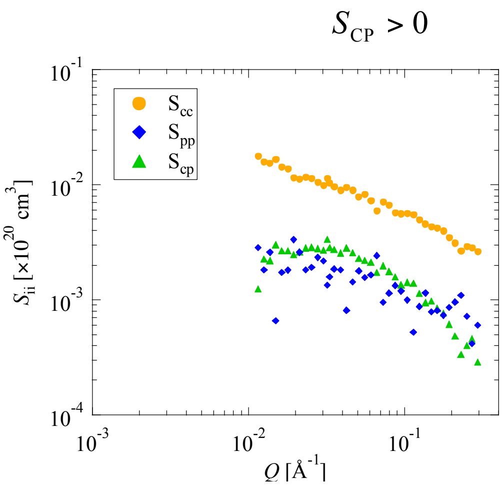
$$\begin{pmatrix} I_1 \\ I_2 \\ \vdots \\ I_n \end{pmatrix} = \begin{pmatrix} {}^1\Delta\rho_P^{\,2} & {}^1\Delta\rho_C^{\,2} & 2\,{}^1\Delta\rho_P\,{}^1\Delta\rho_C \\ {}^2\Delta\rho_P^{\,2} & {}^2\Delta\rho_C^{\,2} & 2\,{}^2\Delta\rho_P\,{}^2\Delta\rho_C \\ \vdots & \vdots & \vdots \\ {}^n\Delta\rho_P^{\,2} & {}^n\Delta\rho_C^{\,2} & 2\,{}^n\Delta\rho_P\,{}^n\Delta\rho_C \end{pmatrix} \begin{pmatrix} S_{PP} \\ S_{CC} \\ S_{CP} \end{pmatrix}$$

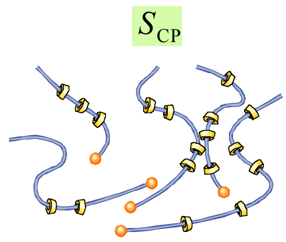


Reconstruction



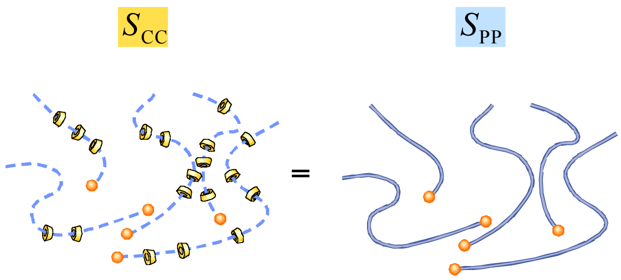
Obtained partial scattering functions



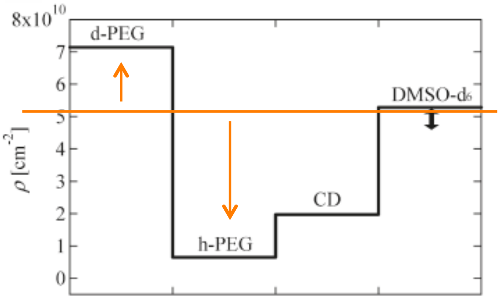


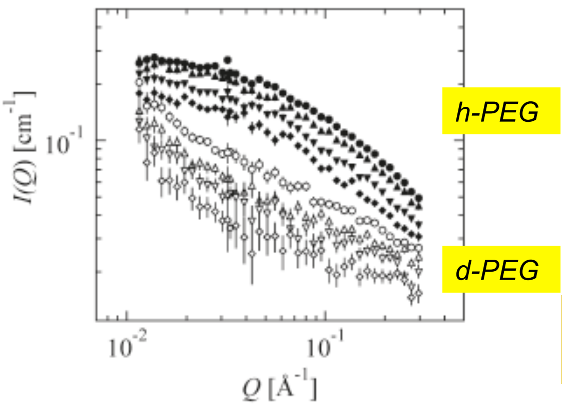
***Positive correlation* between CD and PEG**

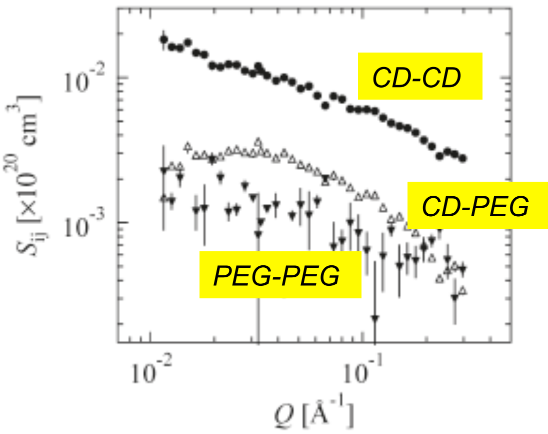
→ CD and PEG are *interlocked topologically*



CDs disperse randomly on the PEG chain







The CD-CD and CD-PEG partial scattering functions are similar to the PEG-PEG partical scattering function, indicating

CDs disperse randomly on the PEG chain, CD and PEG are interlocked topologically

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Concluding Remark

1. *CV SANS is a powerful technique for structural analysis of multicomponent systems.*
2. *CV SANS provides the information of the cross-correlation of the components, such as the interface, topological relationship of the components.*
3. *CV SANS is used to study colloidal spheres, polymer aggregates or micelles, microemulsions, biological macromolecules, etc.*
4. *Applications of CV SANS are demonstrated, namely, nanocomposite gels, silica nano-particle dispersions, and interlocked structure of polyrotaxane.*

Note: requirements (difficulties)
(1) Highly model dependent
(2) accurate determination of the scattering length densities