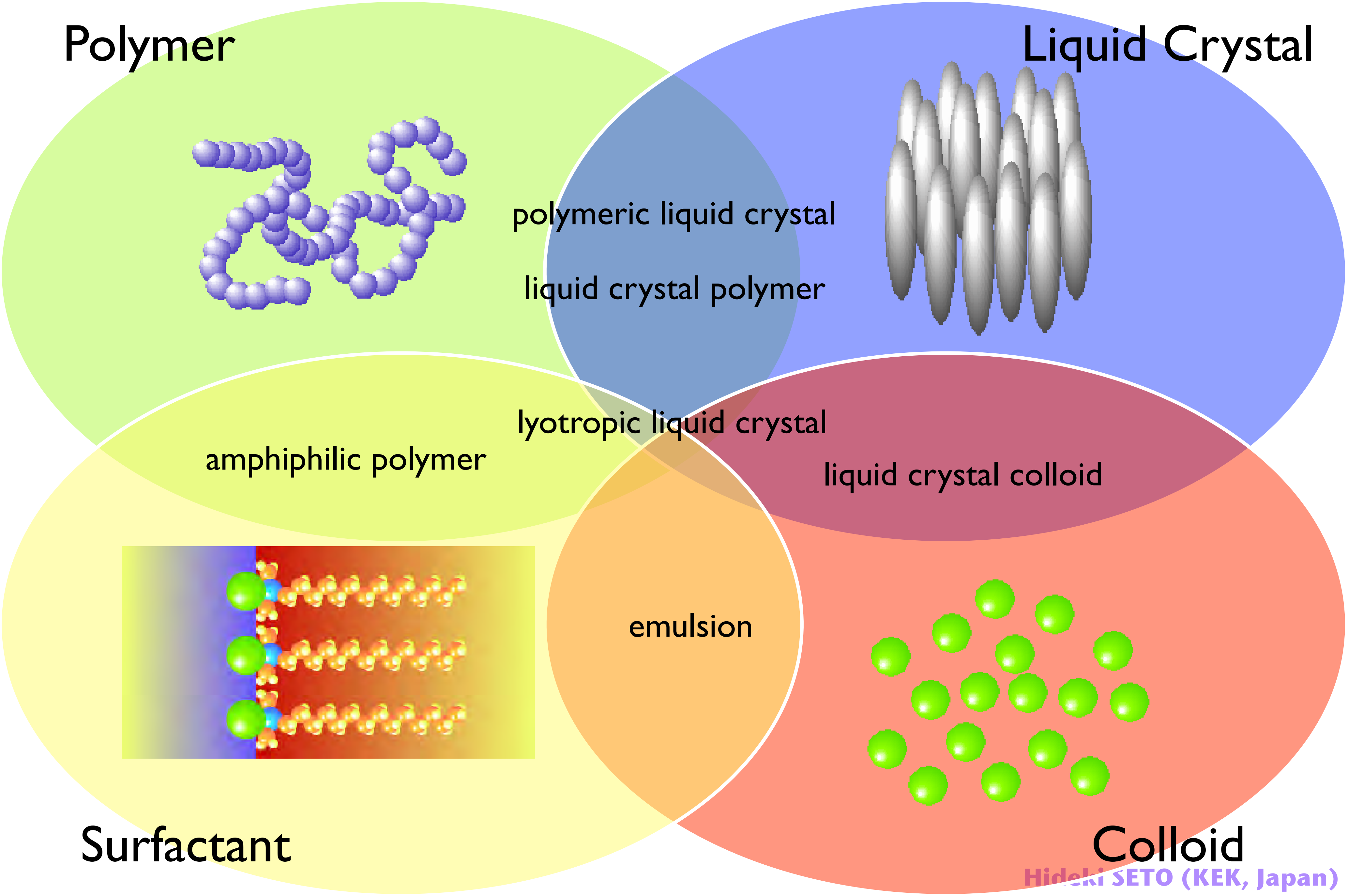
Neutron and Softmatter

Hideki Seto

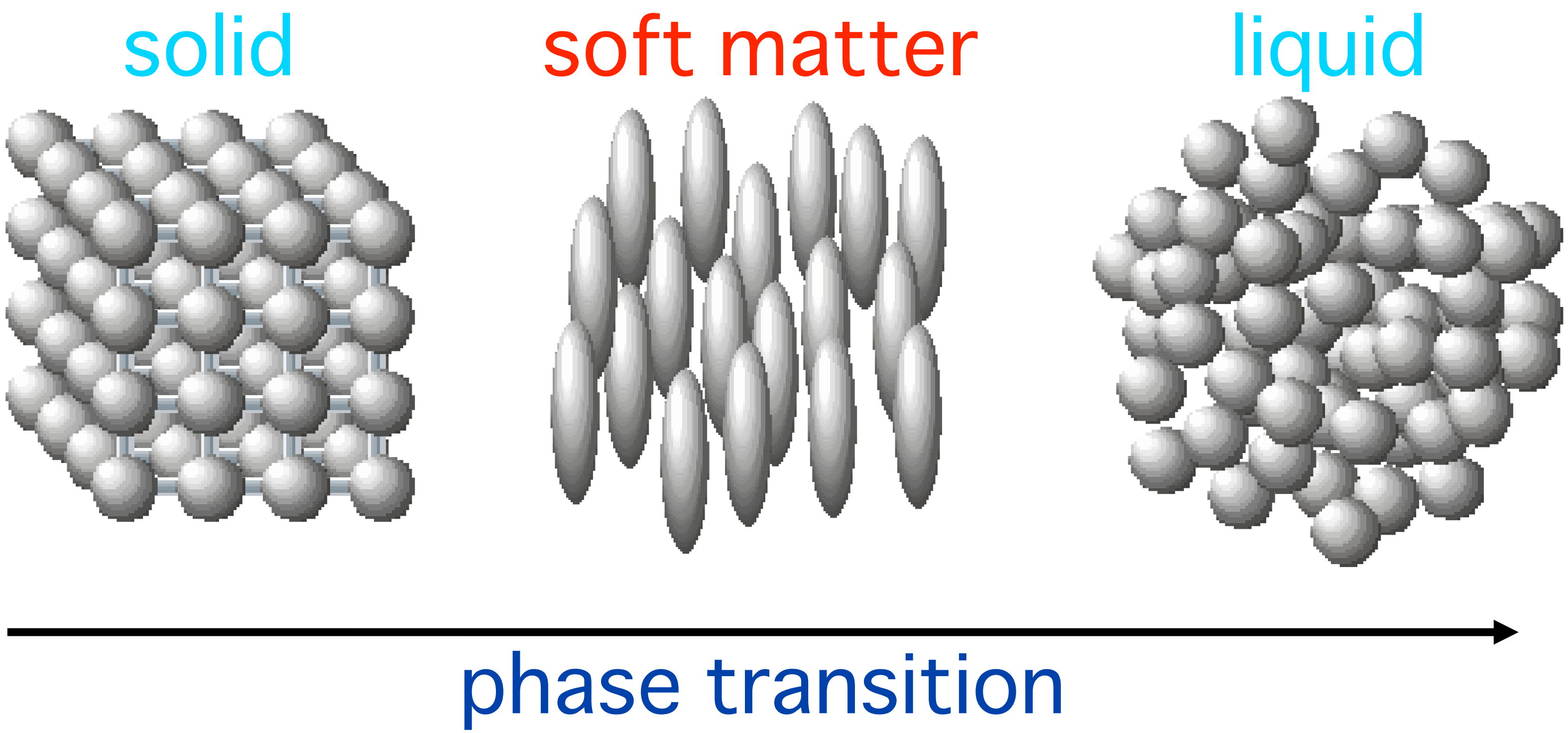
IMSS/J-PARC Center, KEK
SOKENDAI

Soft Matter


Polymer
Liquid Crystal
polymeric liquid crystal
liquid crystal polymer
lyotropic liquid crystal
amphiphilic polymer
liquid crystal colloid
emulsion
Surfactant
Colloid
Hideki SETO (KEK, Japan)

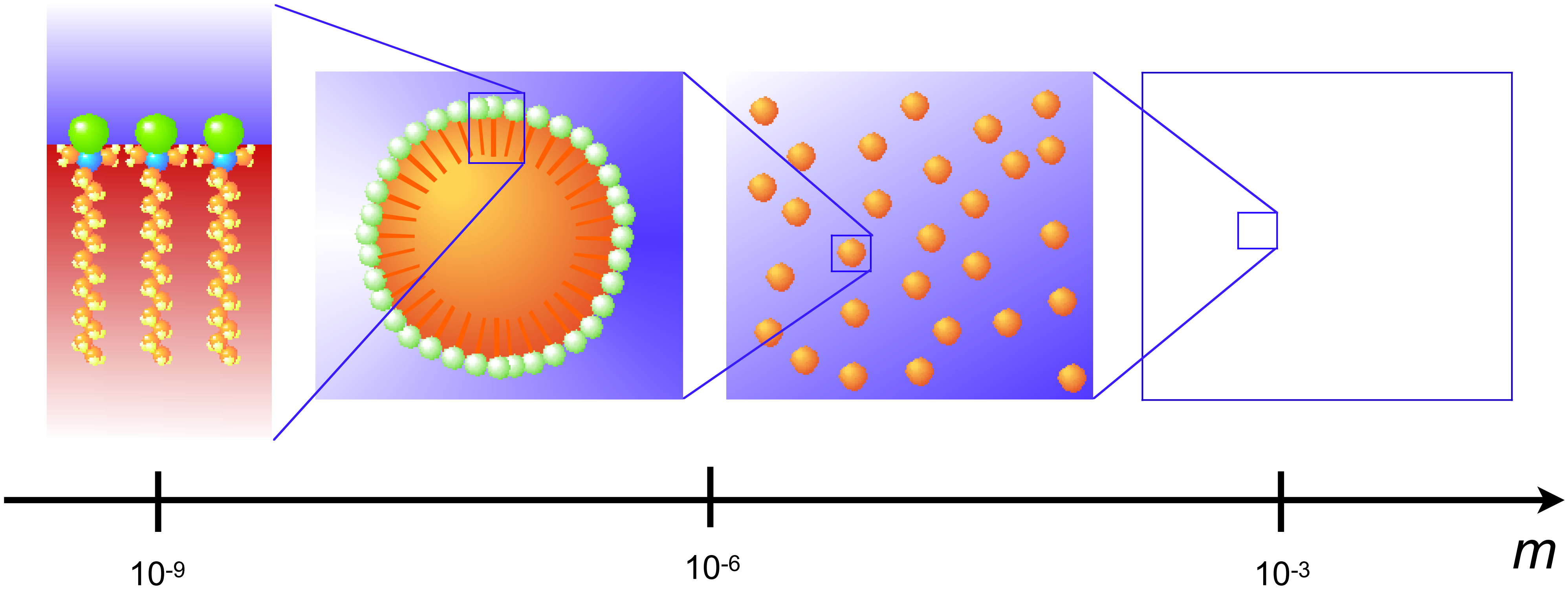
Common properties

- large number of internal degree of freedom
- weak interaction between structure unit
- delicate balance of entropy and enthalpy



Hideki SETO (KEK, Japan)

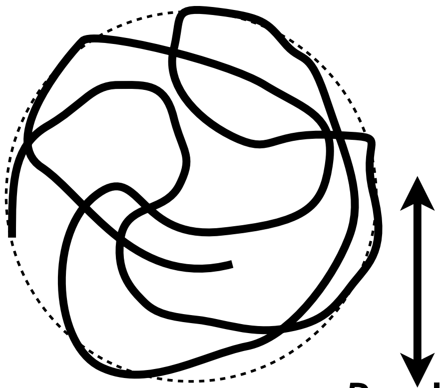
Hierarchical structure



Hideki SETO (KEK, Japan)

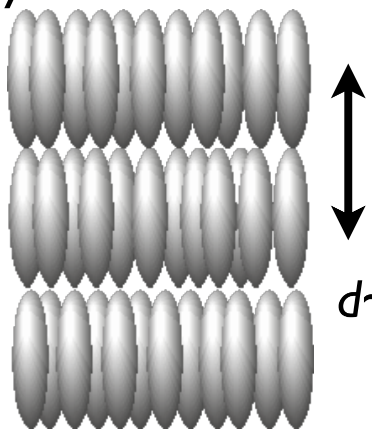
Nano-scale Structures in Soft Matter

polymer



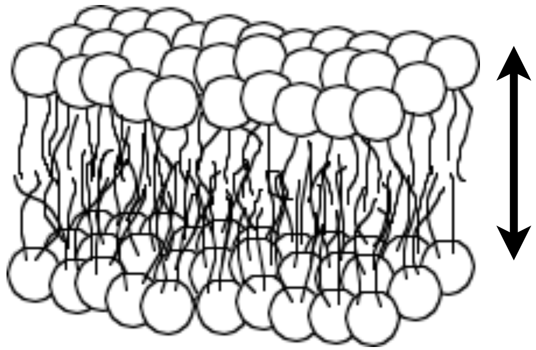
R_G~100Å

liquid crystal



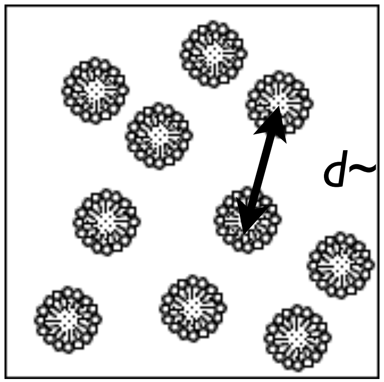
d~20Å

membrane



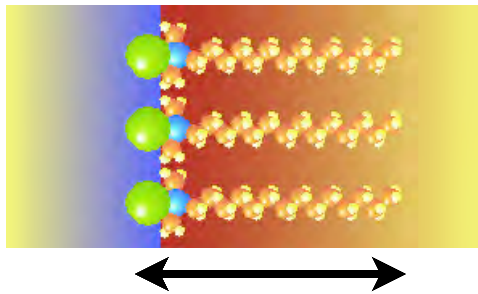
t~60Å

colloids



d~100Å

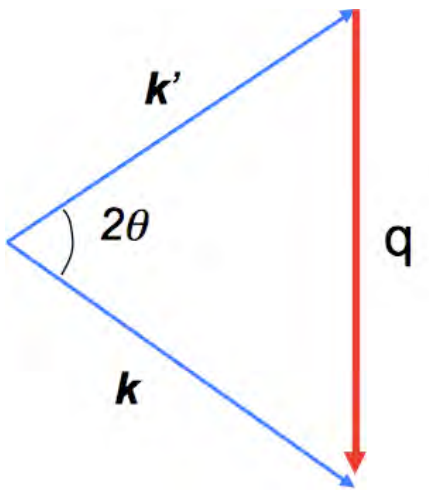
surfactant



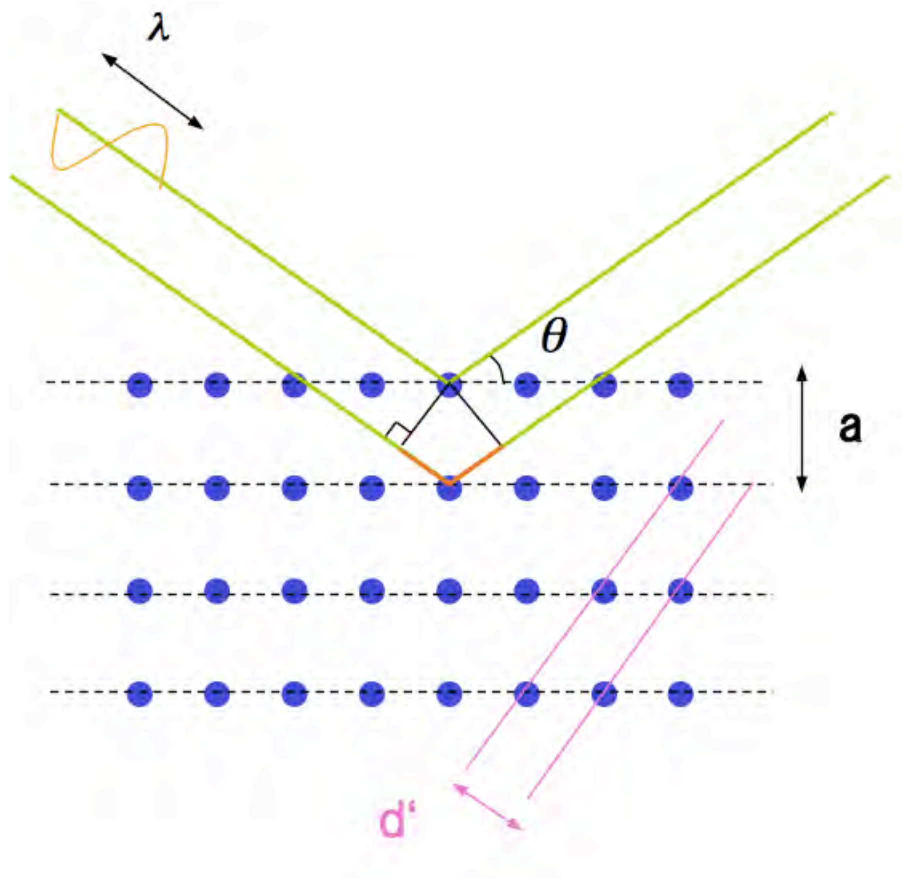
l~30Å

Hideki SETO (KEK, Japan)

Small-Angle Scattering



$$+\ \begin{array}{c} qa/2 = n\pi \\ q = 2\pi n/a \end{array}$$



$$\mathbf{q} = \mathbf{k} - \mathbf{k}'$$

$$q = 2k \sin\theta$$

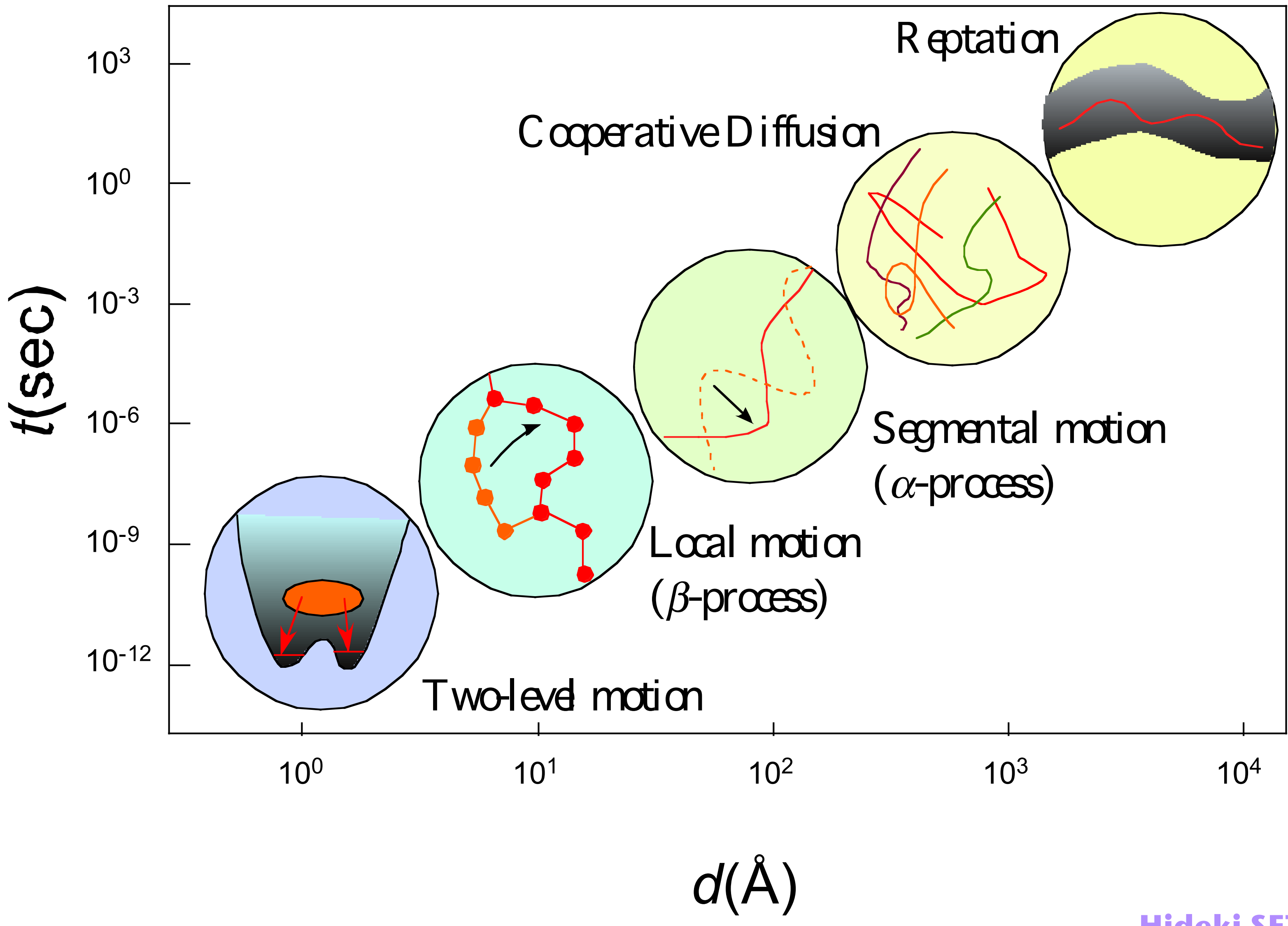
$$= 2(2\pi/\lambda)\sin\theta$$

Bragg's Law: $2a \sin \theta = n\lambda$

$\lambda \sim 5$Å, $a \sim 100$Å $\rightarrow$ $\theta \sim 1.4°$

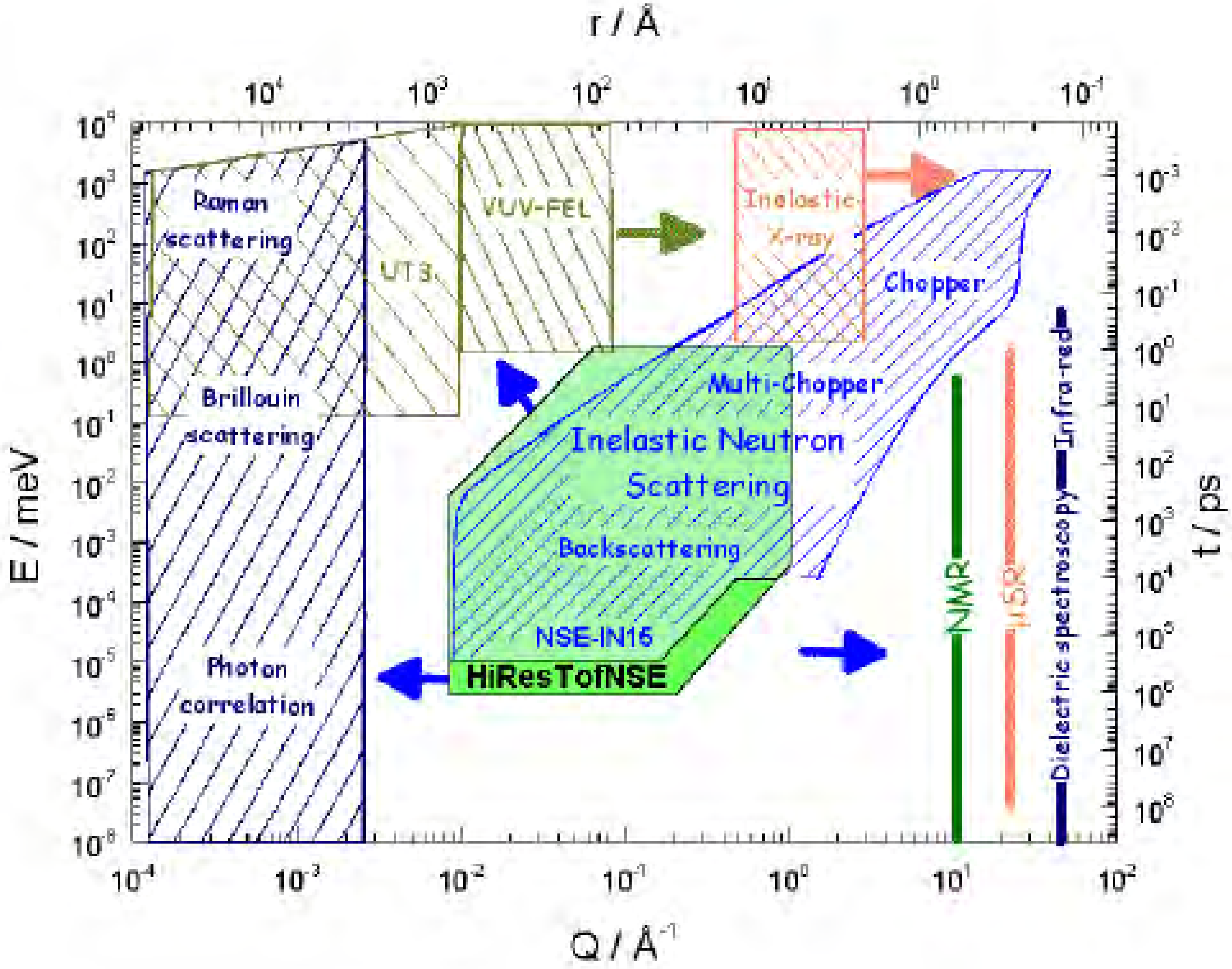
Hideki SETO (KEK, Japan)

Hierarchical dynamics



Hideki SETO (KEK, Japan)

Inelastic/Quasi-elastic scattering



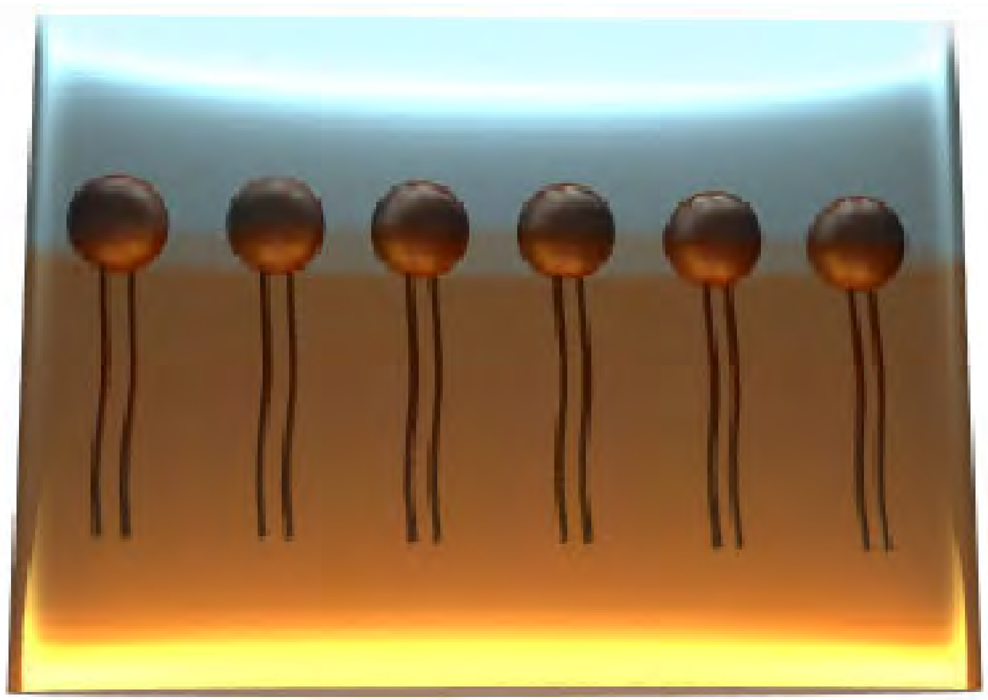
Hideki SETO (KEK, Japan)

Surfactants

Amphiphilic property

hydrophilic

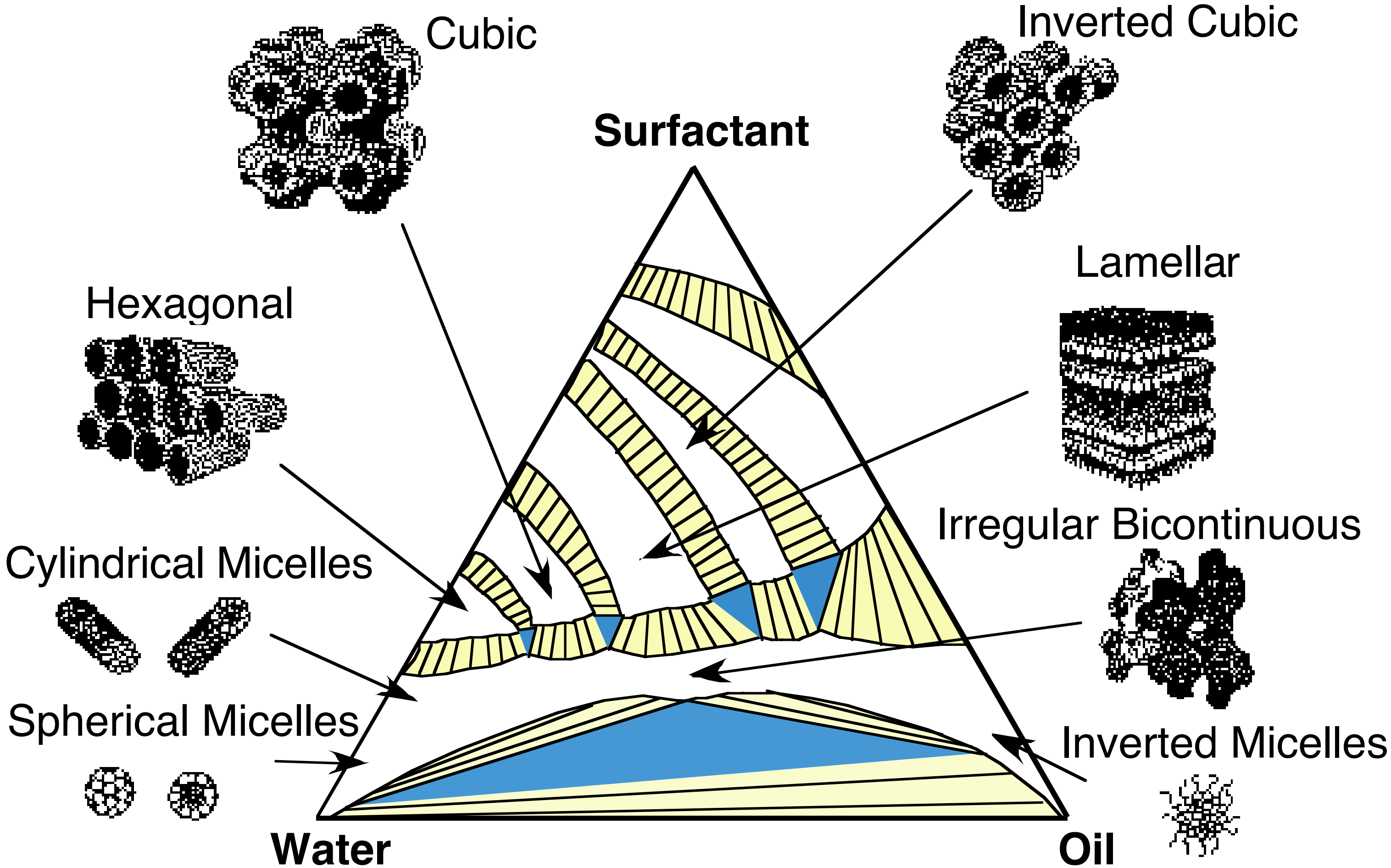
hydrophobic



water

oil

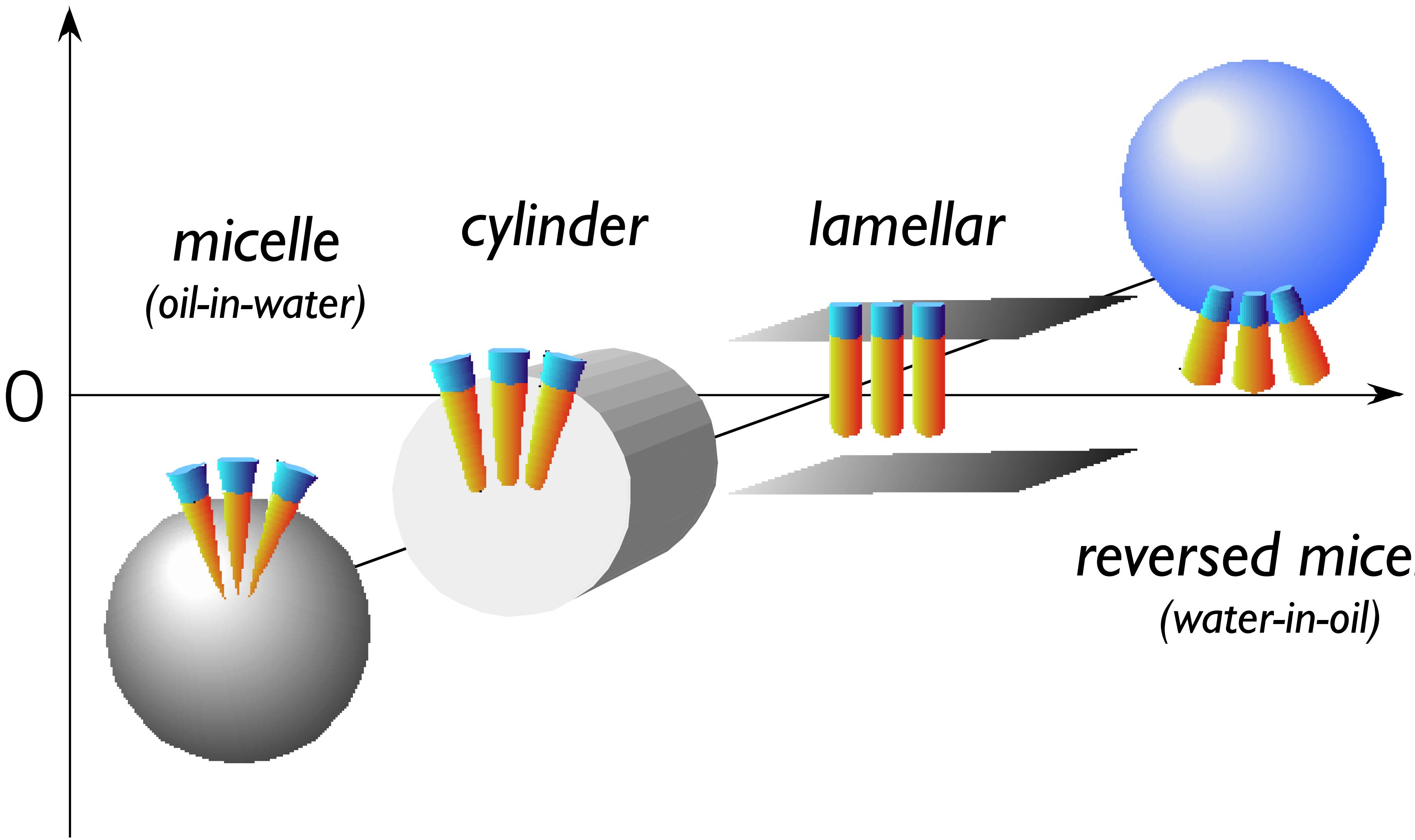
Semi-microscopic structures



Hideki SETO (KEK, Japan)

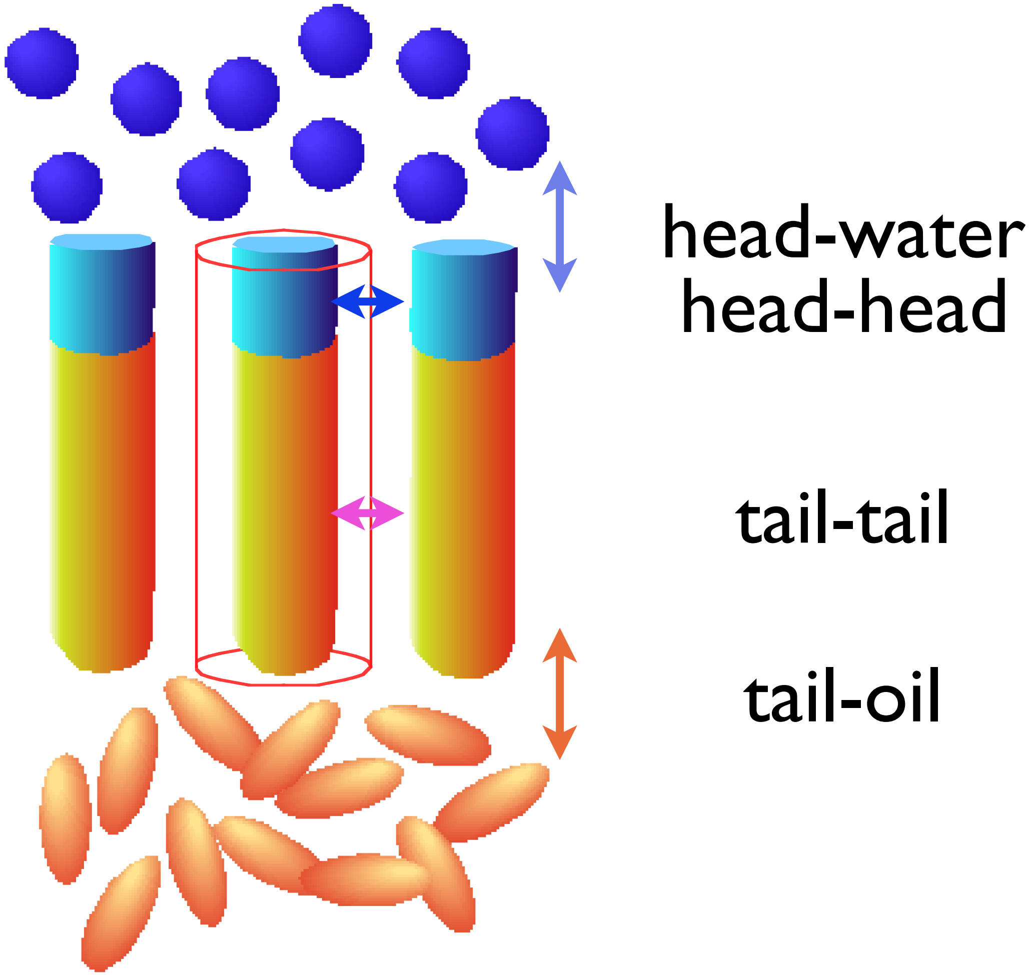
Spontaneous Curvature

depends on packing parameter



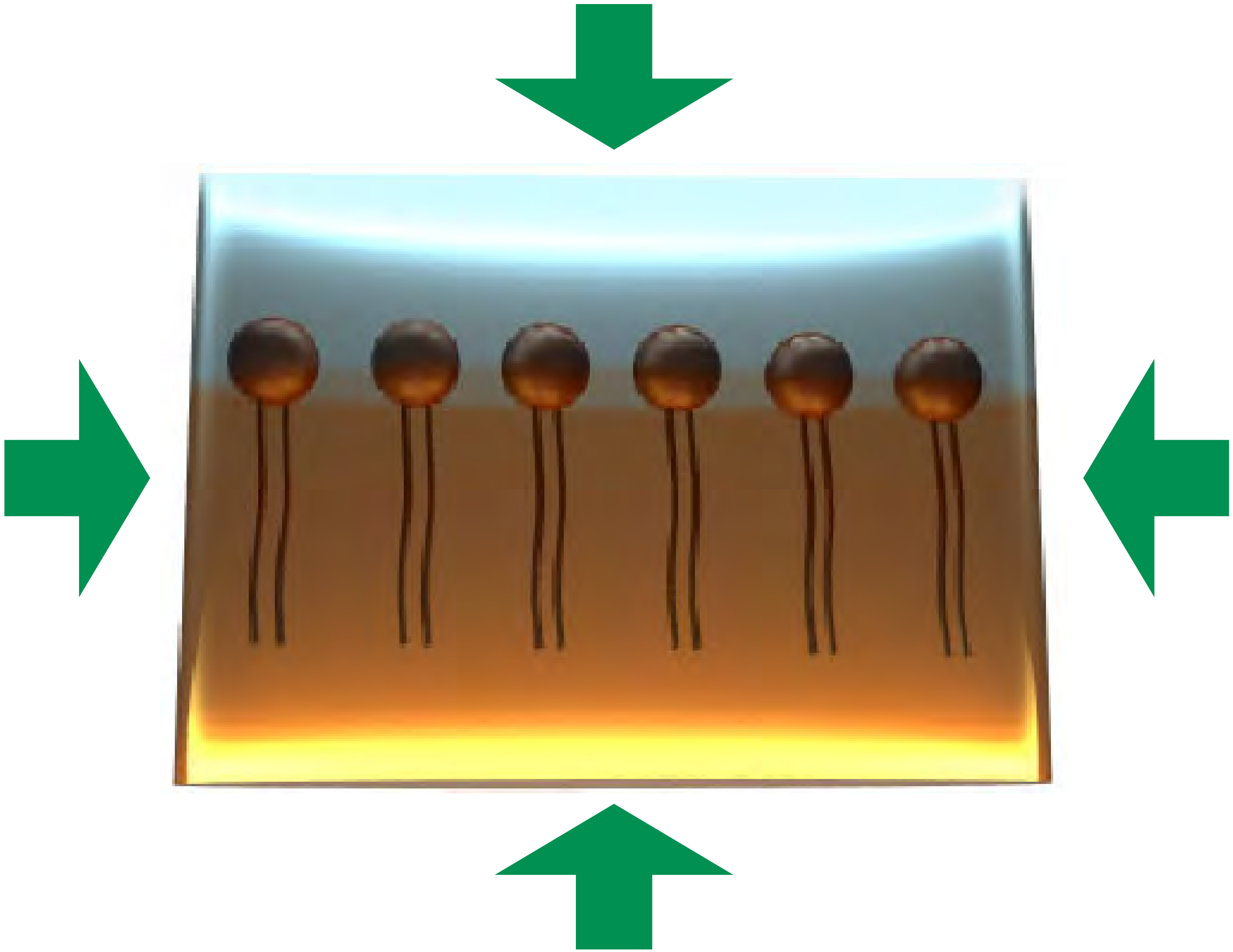
Hideki SETO (KEK, Japan)

Packing parameter

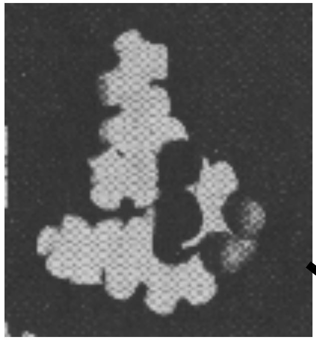


Pressure dependence

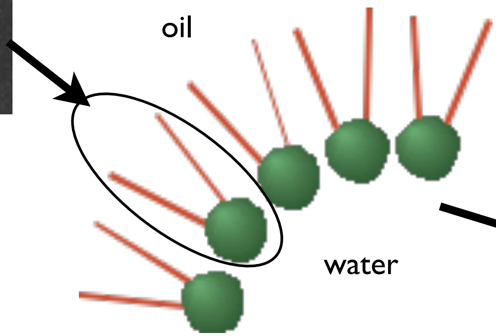
M. Nagao, HS, et al. 1999-2007



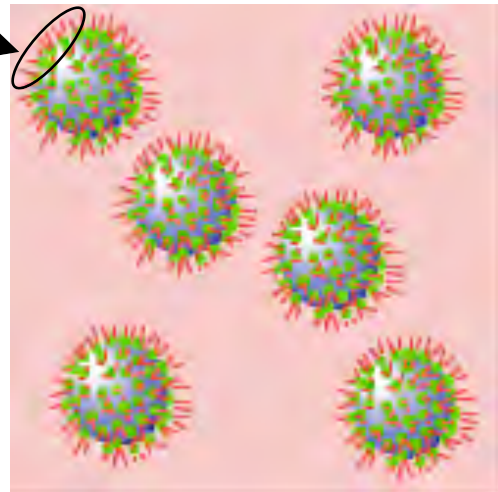
AOT + D_2O + *n*-decane



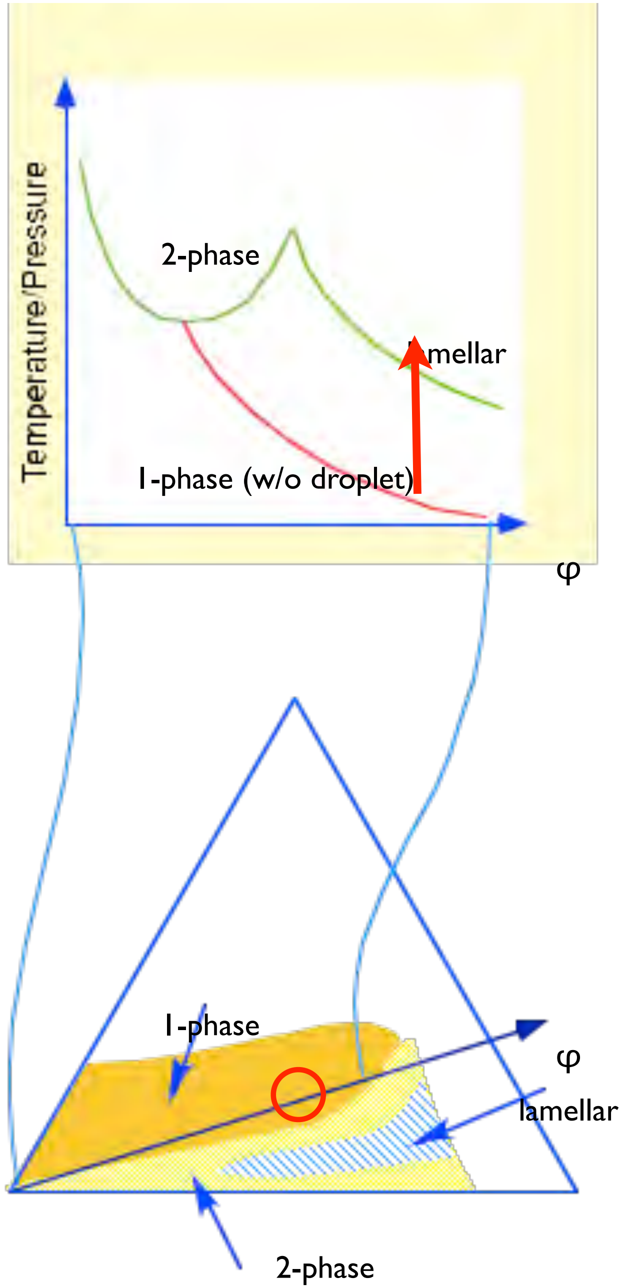
AOT molecule



spontaneous curvature > 0

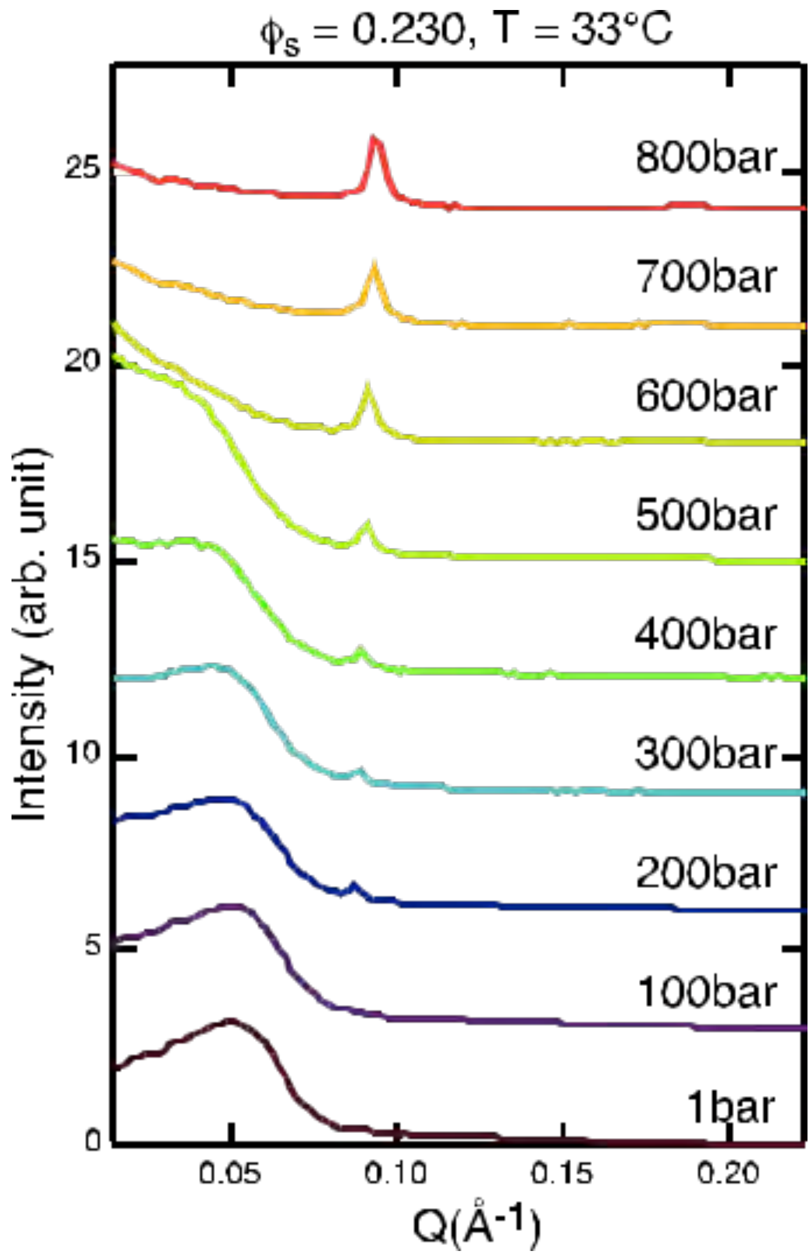


water-in-oil droplet



Hideki SETO (KEK, Japan)

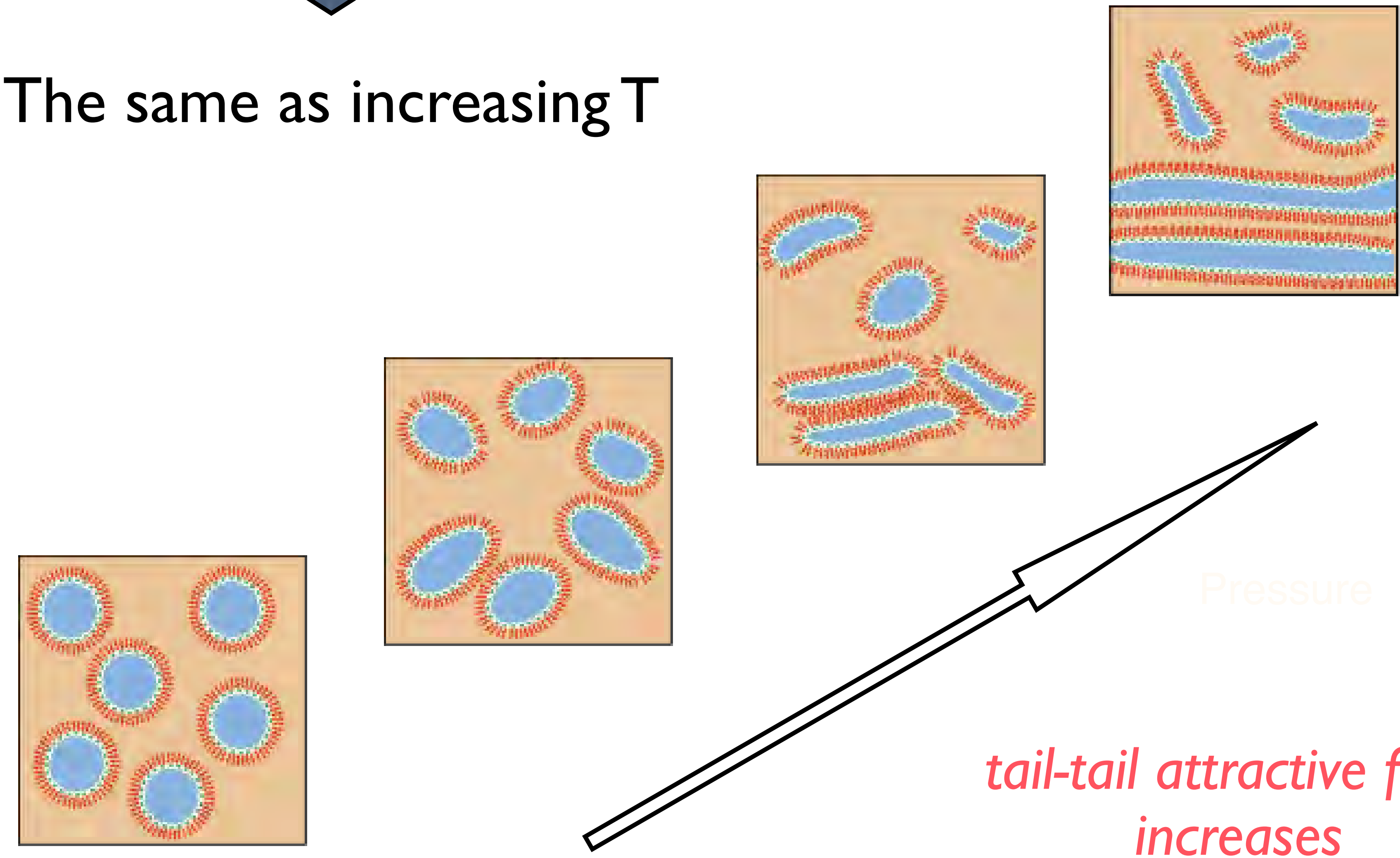
Pressure dependence of SAXS



Hideki SETO (KEK, Japan)

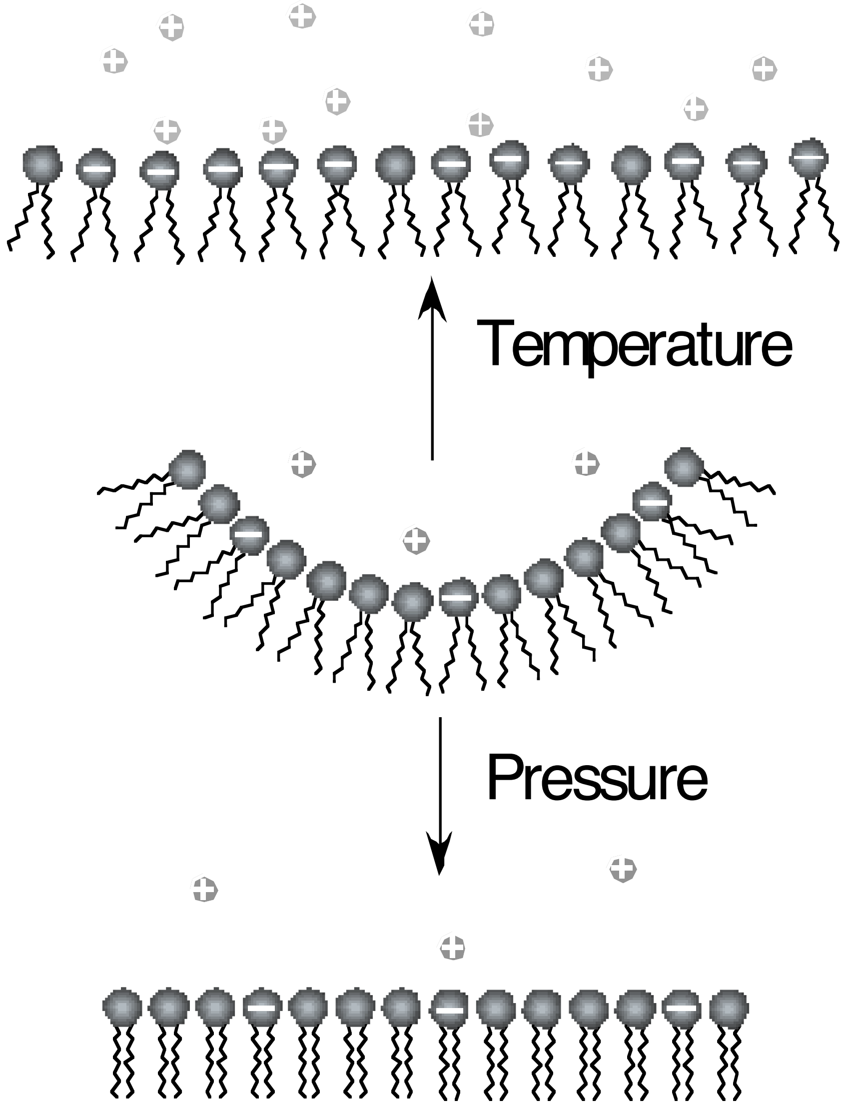
Structure change with P

The same as increasing T



tail-tail attractive force increases

Why T-effect and P-effect seems to be the same?



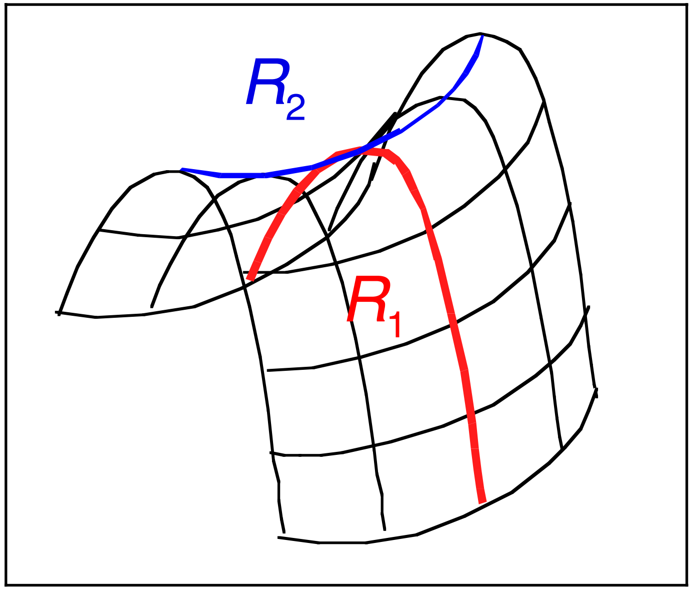
counter-ion dissociation

tail-tail interaction

Hideki SETO (KEK, Japan)

Bending energy of surfactant layers

W. Helfrich, Z. Naturforsch. C28 (1973) 693



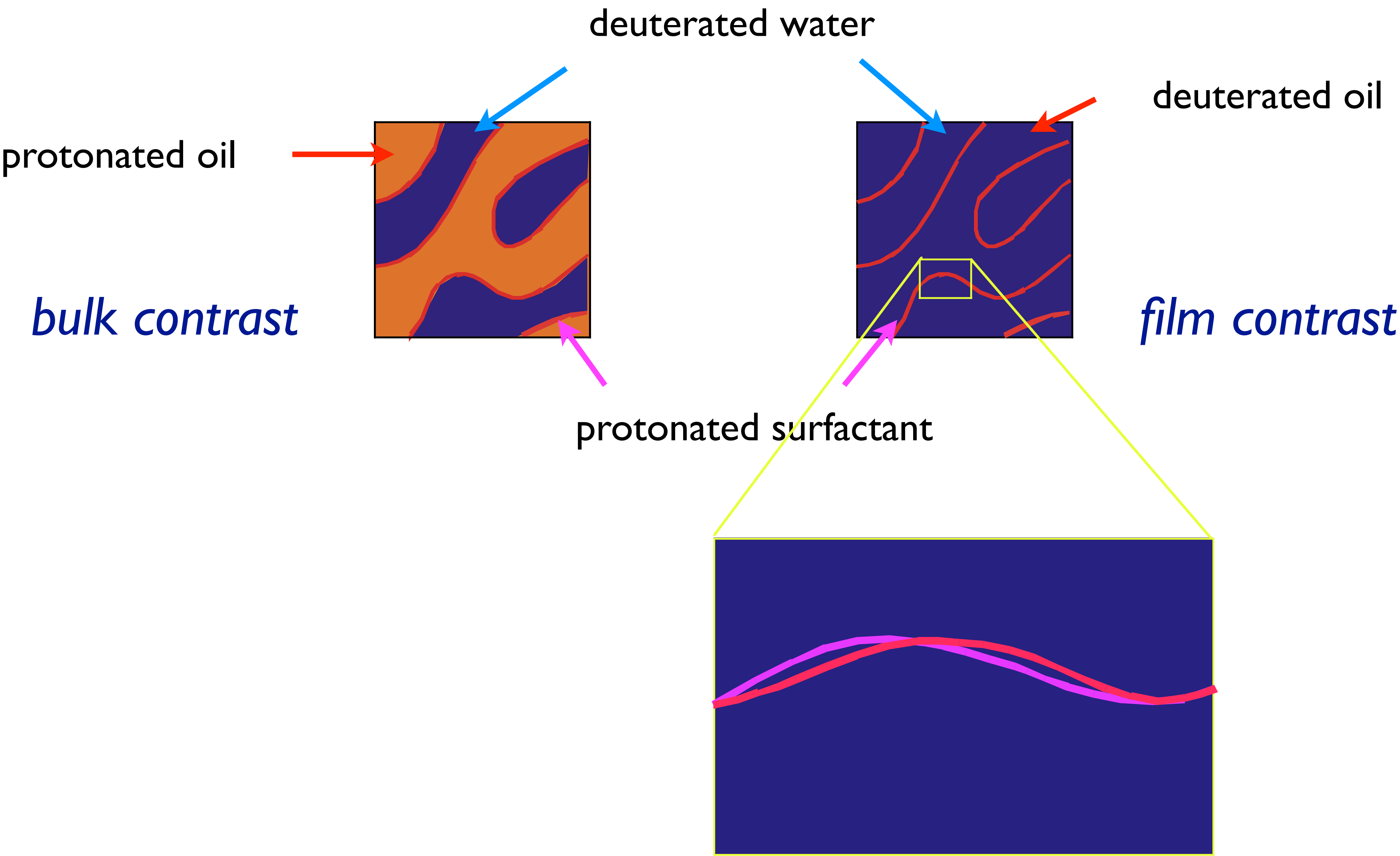
mean curvature $H = \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$

Gaussian curvature $K = \frac{1}{R_1}\frac{1}{R_2}$

$$E_{bend} = \int \left[\underbrace{\kappa}_{\text{bending modulus}} \Big(H - \frac{1}{\underbrace{R_s}_{\text{spontaneous curvature}}}\Big)^2 + \underbrace{\bar{\kappa}}_{\text{saddle-splay modulus}} K \right] dS$$

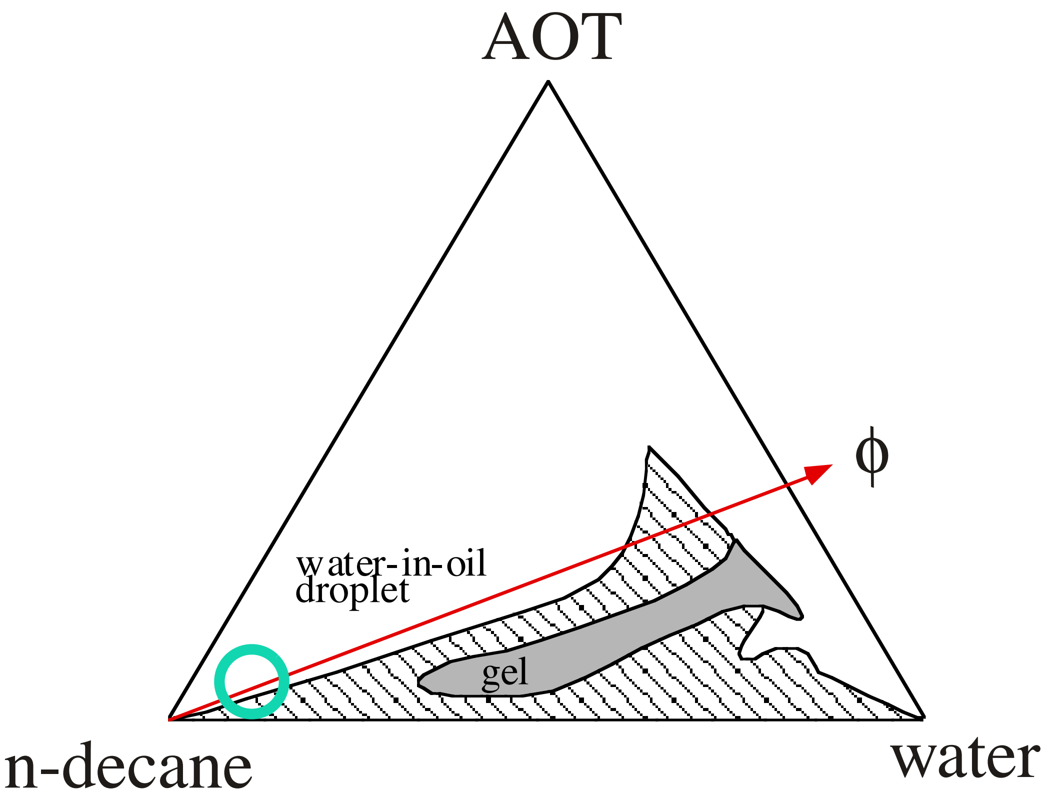
Hideki SETO (KEK, Japan)

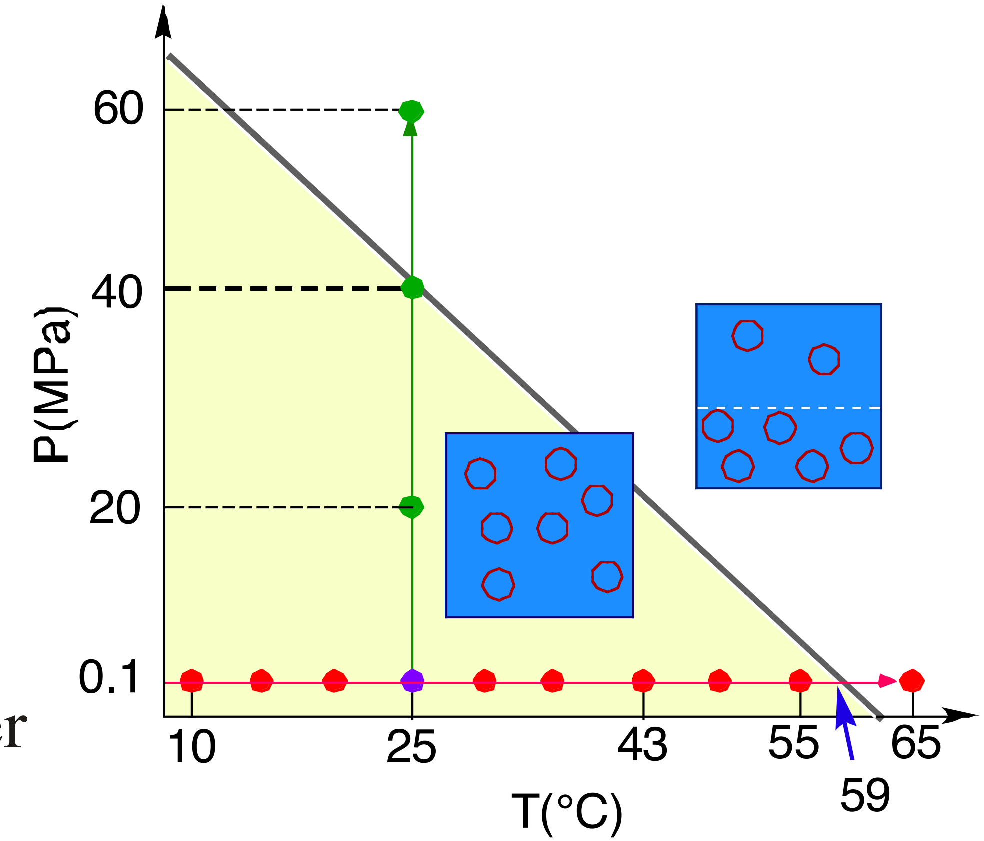
Neutrons see...



Hideki SETO (KEK, Japan)

Phase separation of a water-in droplet



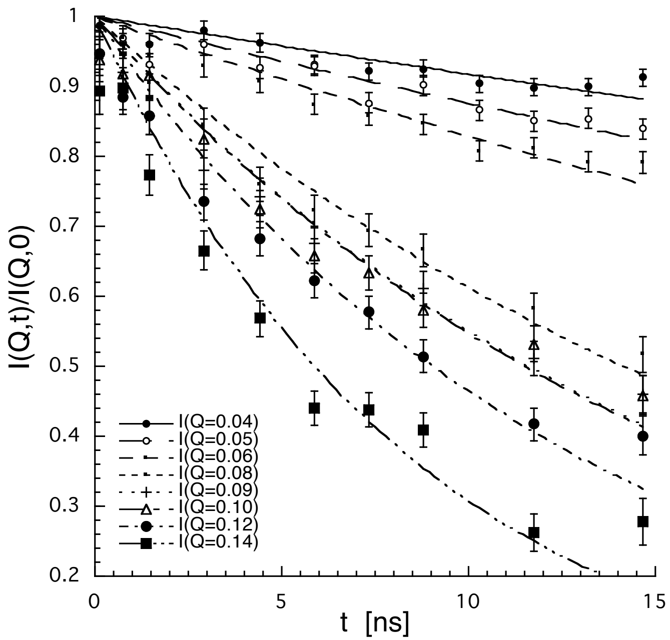


Kawabata et al., Phys. Rev. Lett. **92** (2004) 056103.

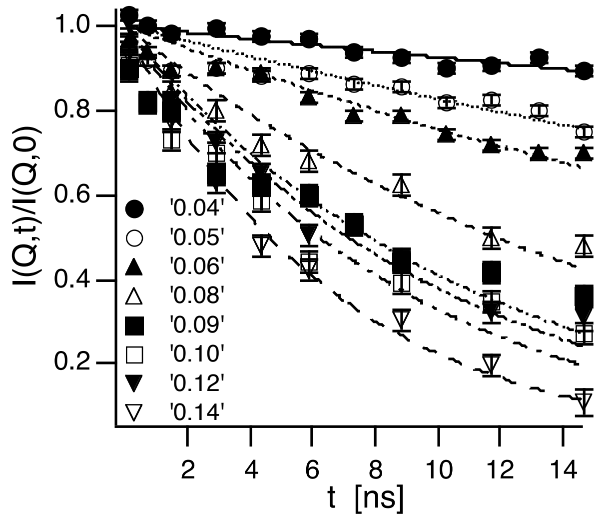
Hideki SETO (KEK, Japan)

Results of NSE experiments

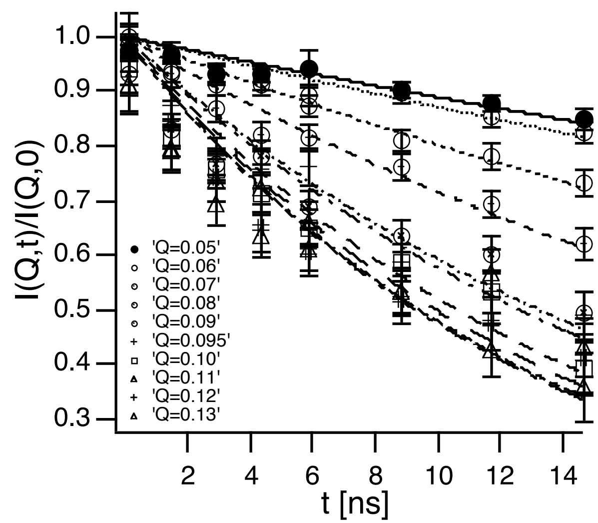
Room temperature/pressure
T=25°C/P=0.1MPa



T=43°C/P=0.1MPa



T=25°C/P=20MPa



Hideki SETO (KEK, Japan)

Scattering from a shell

Huang et al. PRL 59 (1987) 2600.
Farago et al. PRL **65** (1990) 3348.

Expansion of the shape fluctuation into spherical harmonics

$$R(\theta\ \phi, t) = R_0\{1 + \sum_{nm} a_{nm}(t) Y_{nm}(\theta\ \phi)\}$$

up to n=2 mode gives

damping frequency of the 2nd mode deformation

$$I(Q, t)/I(Q, 0) = \exp[-D_{eff} Q^2 t]$$

mean-square displacement of the 2nd mode deformation

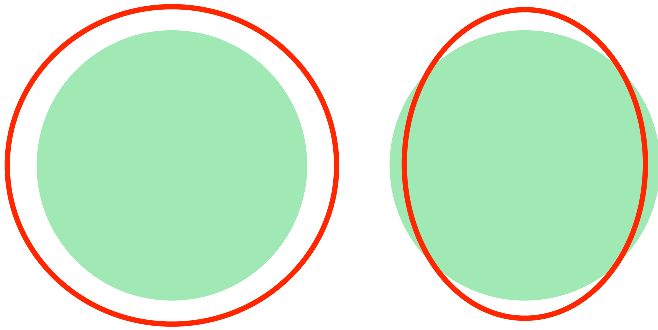
$$D_{eff} = D_{tr} + \frac{5\lambda_2 f_2(QR_0)\langle |a_2|^2 \rangle}{Q^2[4\pi f_0(QR_0) + 5 f_2(QR_0)\langle |a_2|^2 \rangle]}$$

translational diffusion

shape deformation

n=0 mode

n=2 mode



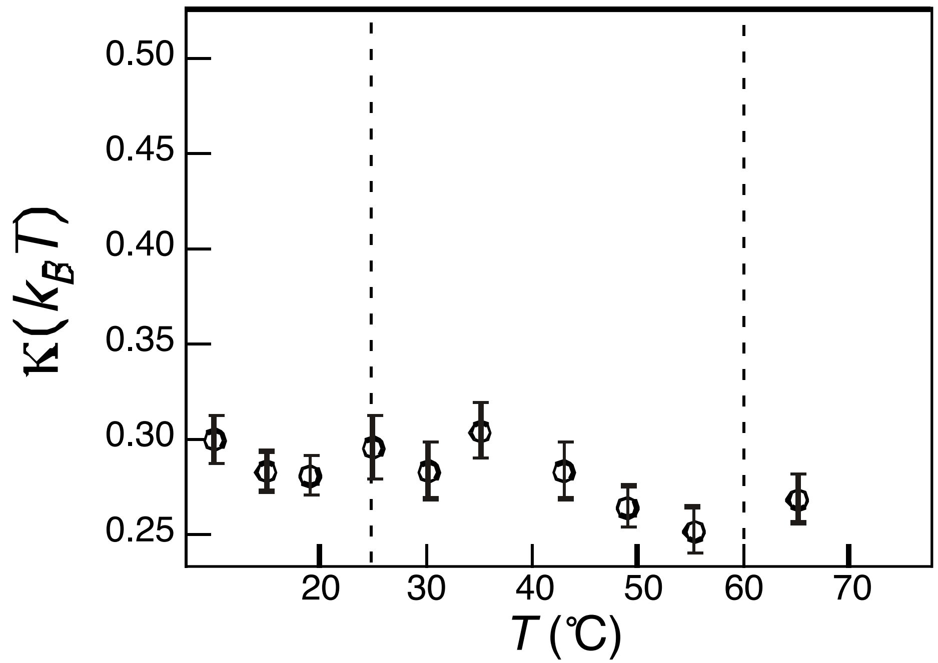
where

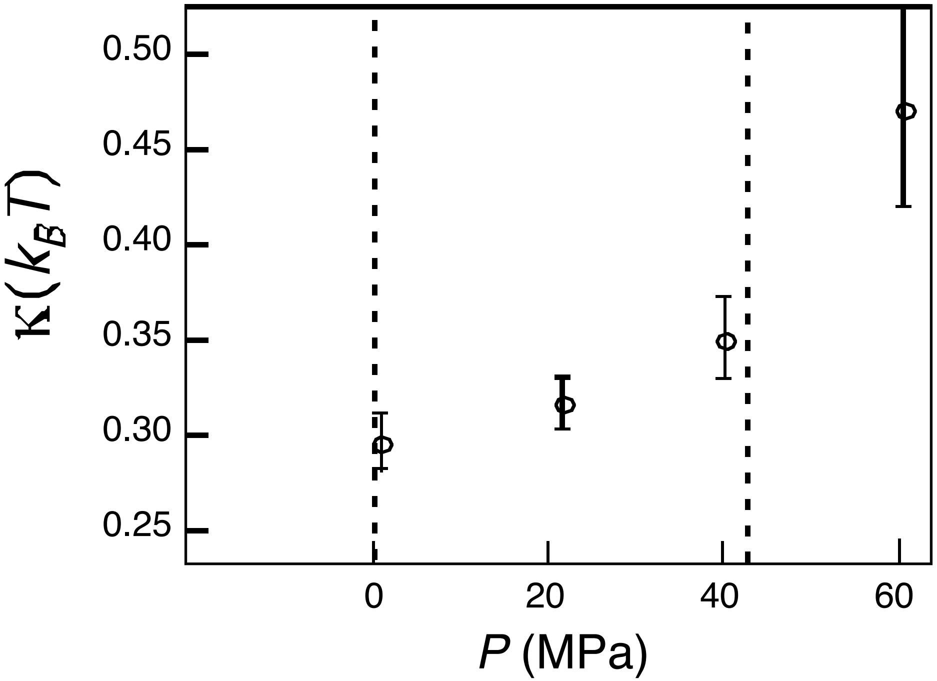
$$f_0(QR_0) = [\, j_0(QR_0)]^2$$

$$f_2(QR_0) = 5[4\, j_2(QR_0) - (QR_0)\, j_3(QR_0)]^2$$

Hideki SETO (KEK, Japan)

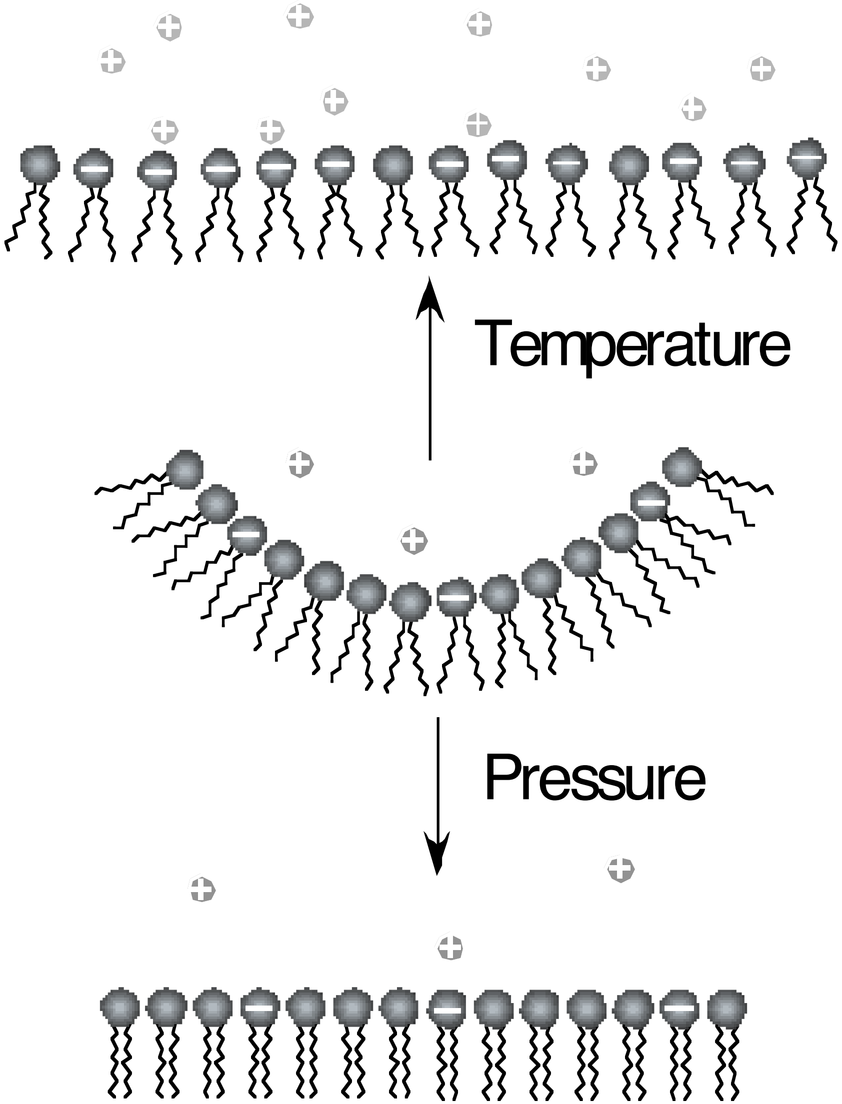
T- and P- dependence of the bending modulus





Hideki SETO (KEK, Japan)

T- and P-effects on an ionic surfactant monolayer

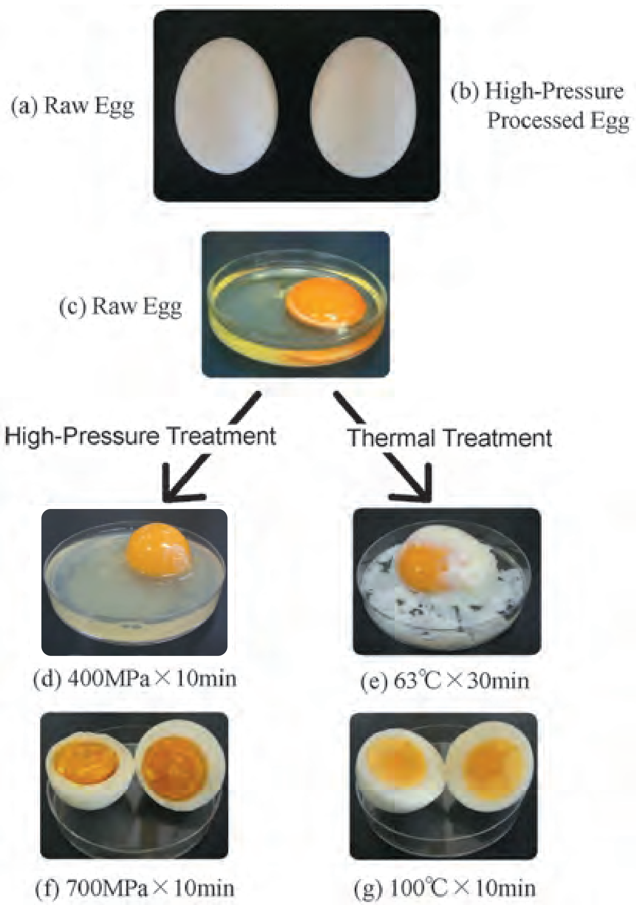


	spontaneous curvature	bending modulus
Temperature	decrease	decrease
Pressure	decrease	increase

Hideki SETO (KEK, Japan)

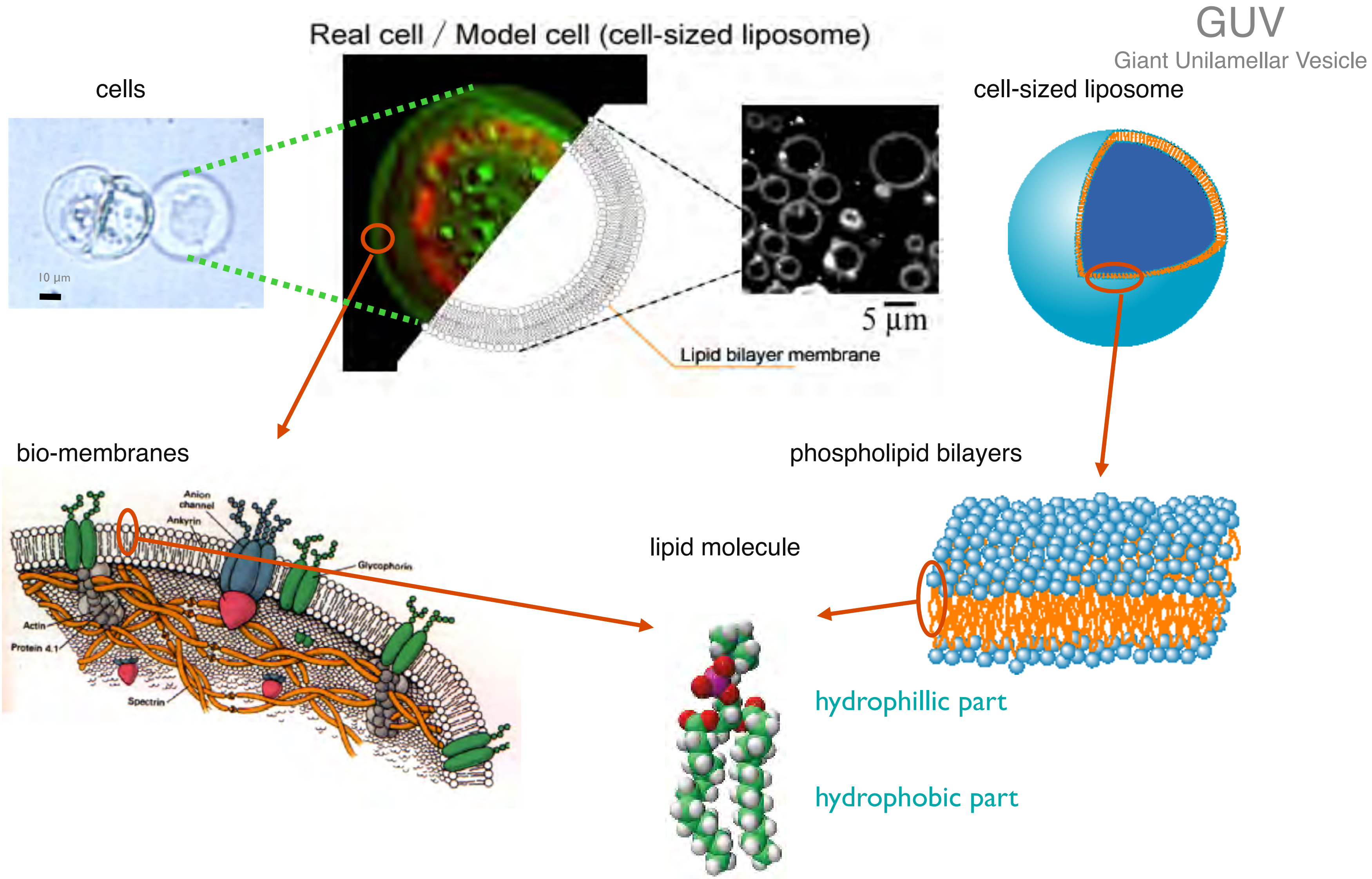
Possible application

-pressure antagonism of anesthesia
-deep sea organisms
-food processing



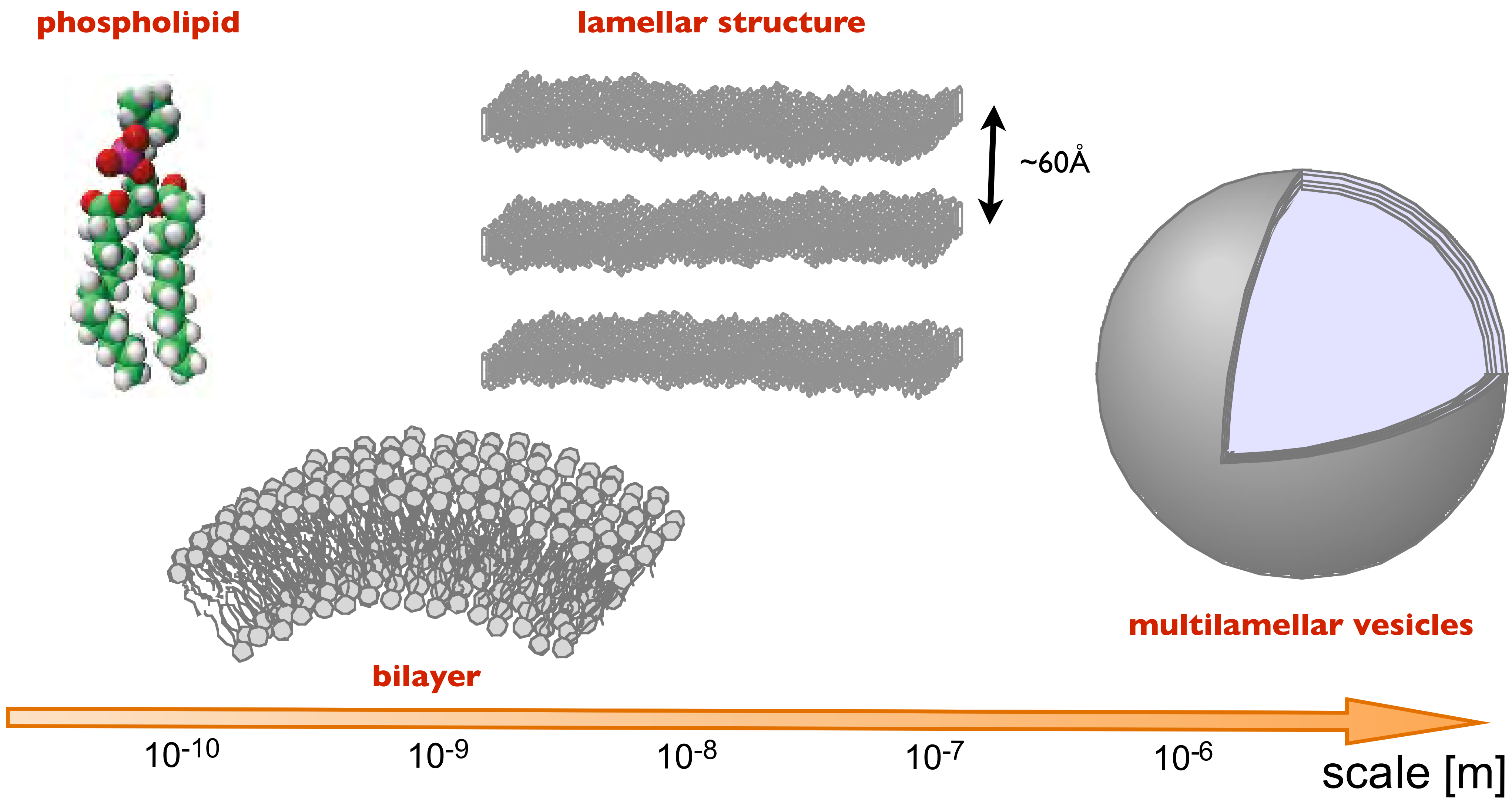
Lipids

Cells and Vesicles



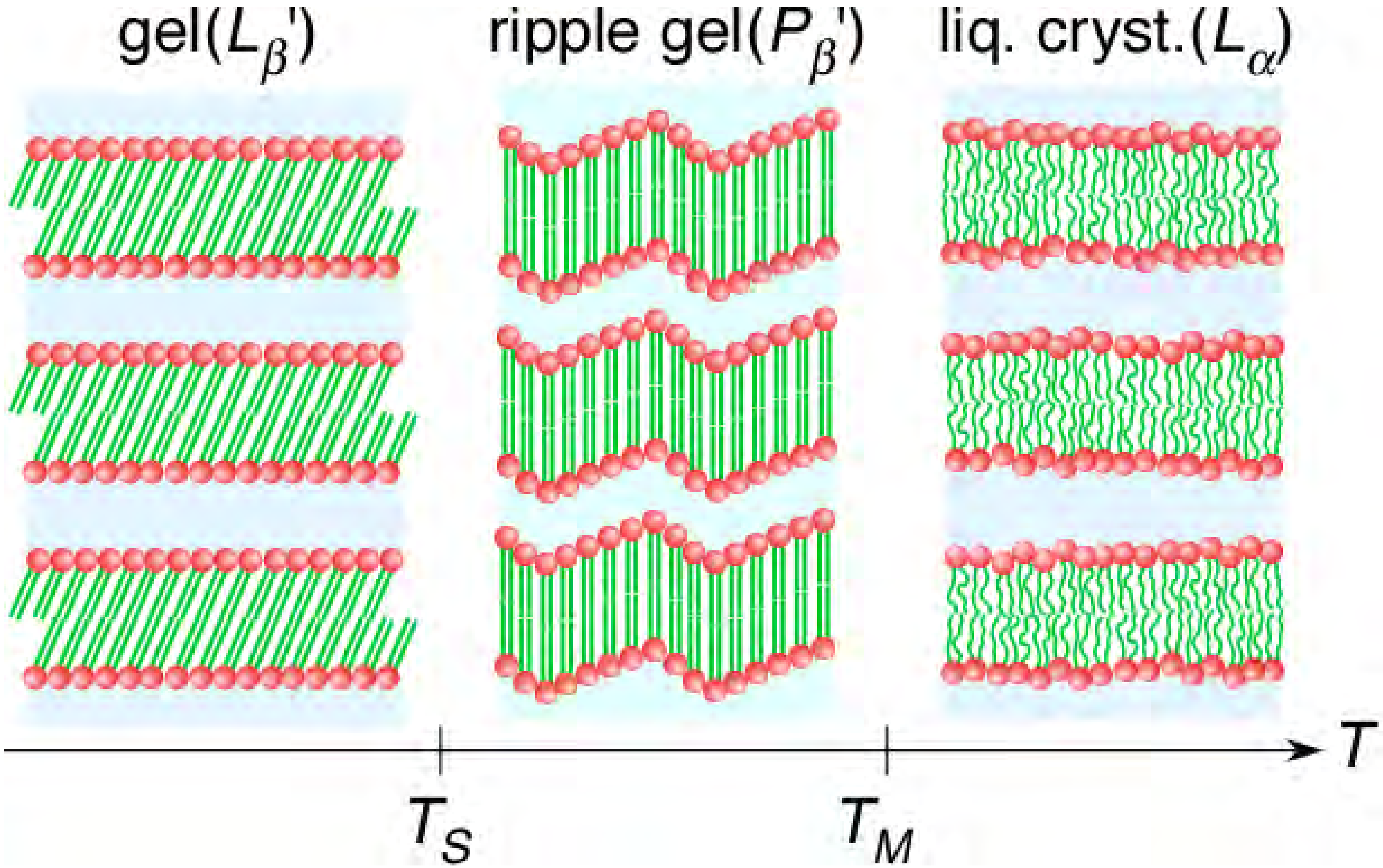
Hideki SETO (KEK, Japan)

Lamellar structure of lipid bilayers



Hideki SETO (KEK, Japan)

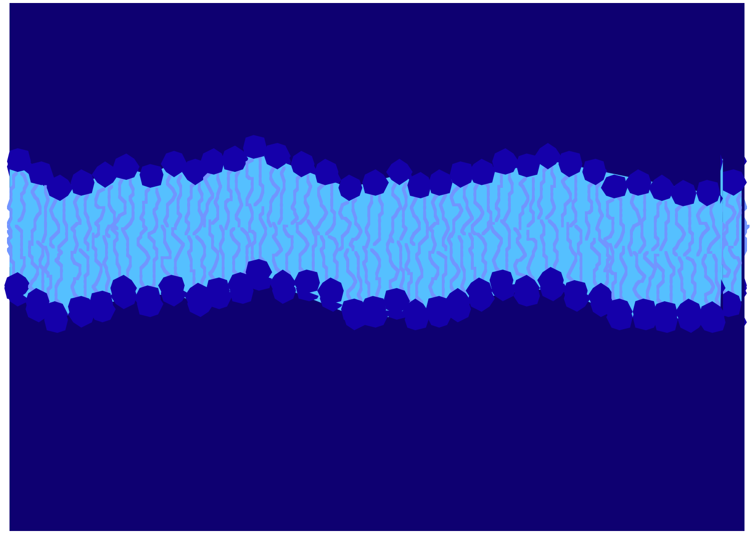
Phase transitions of lipid bilayers



Hideki SETO (KEK, Japan)

Neutron vs X-ray

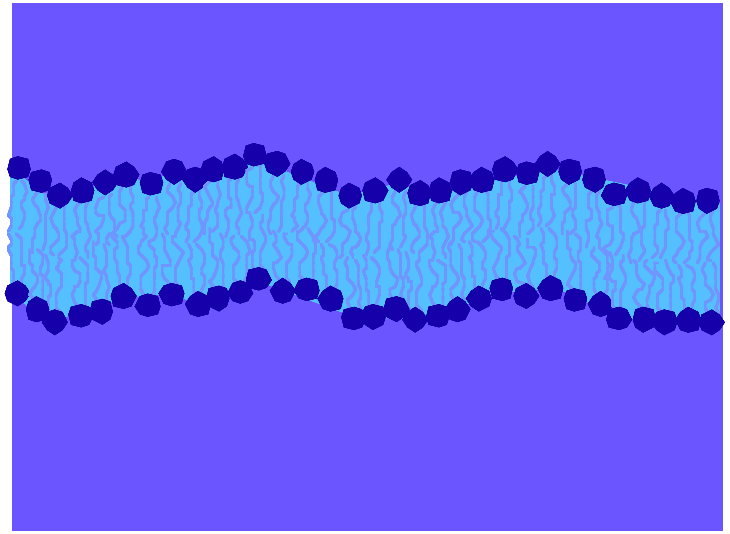
neutron



dynamical behavior

bending modulus

x-ray



static structure

Hideki SETO (KEK, Japan)

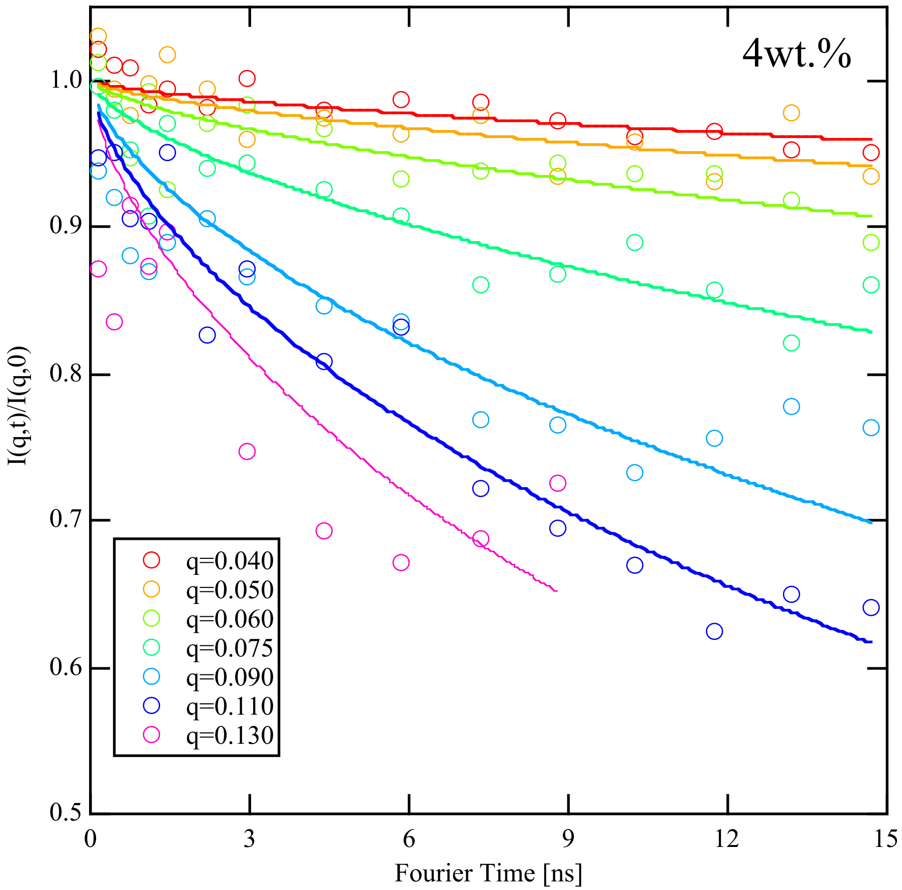
NSE measurements on lipid bilayers

N. L. Yamada, HS, et al. 2005-2008

DPPC/$CaCl_2$/D_2O
(DPPC: 4wt%, $CaCl_2$: 7mM)

d~1000Å

Considered as a single membrane fluctuation.



Hideki SETO (KEK, Japan)

Single membrane fluctuation

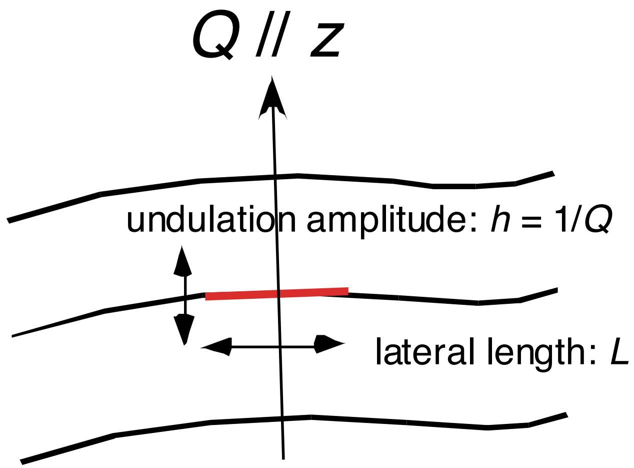
Zilman and Granek

A lateral length L along the membrane flat surface is perturbed in some way, because they are 2D connected object.

$$h \simeq (k_B T/\kappa)^{1/2}\ L^{\zeta}$$

roughness exponent: $\zeta = 1$ (2D object)
$= 3/2$ (1D object)

$$L \simeq (\kappa/k_B T)^{1/2\zeta}\ Q^{-1/\zeta}$$



The Stokes-Einstein diffusion coefficient is,

$$D(Q) \simeq (k_B T/\eta L) \simeq (k_B T/\eta)(k_B T/\kappa)^{1/2\zeta}\ Q^{1/\zeta}$$

The relaxation rate is,

$$\Gamma(Q) \simeq D(Q)Q^2 \simeq (k_B T/\eta)(k_B T/\kappa)^{1/2\zeta}\ Q^{2+(1/\zeta)}$$

Thus they obtained the stretched exponential form of the relaxation function as,

$$I(Q,\ t) = \exp[-(\Gamma(Q)t)^{\beta}]$$

where

$$\Gamma(Q) = \gamma_\alpha \gamma_\kappa\ (k_B T)^{1/\beta} \kappa^{1-(1/\beta)} \eta^{-1} Q^{2/\beta}$$

with

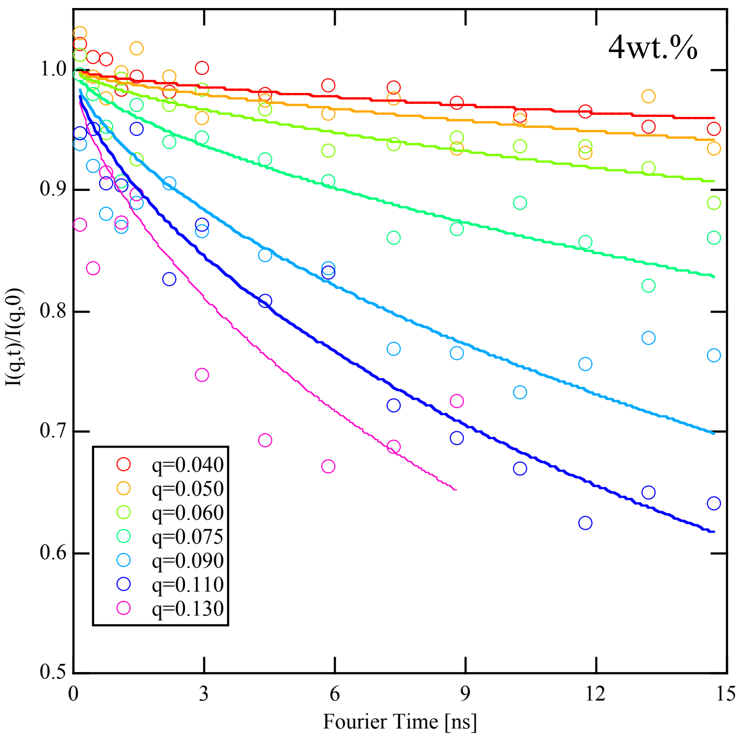
$\beta = \ 2 / (2+1/\zeta)\ = 2/3$ (2D object)
$= 3/4$ (1D object)

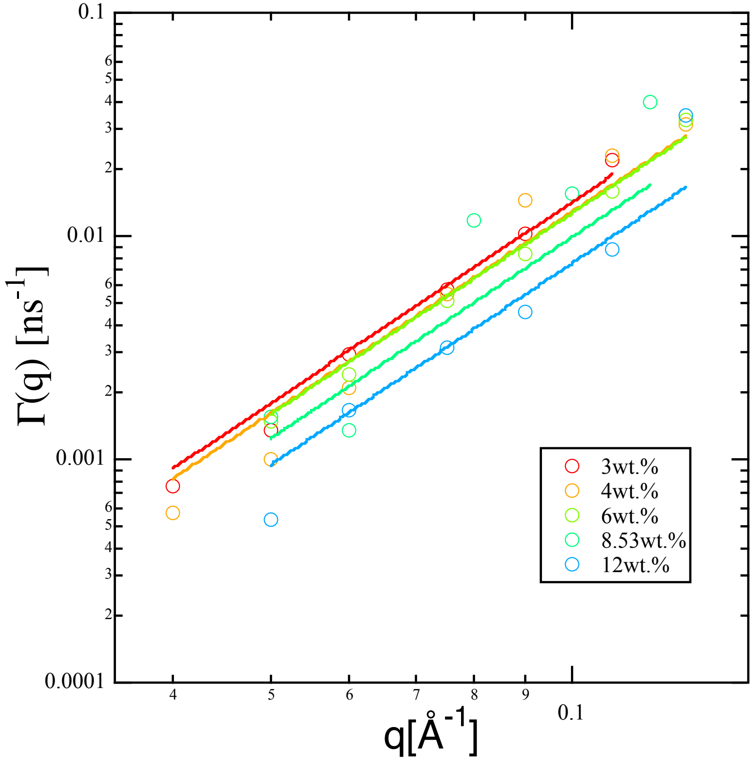
$\gamma_\alpha = 0.024$ (2D object)
$= 0.0056$ (1D object)

$\gamma_\kappa = 1 - 3\ \ln(\xi / l(t))\ k_B T / (4\pi\kappa)$

Hideki SETO (KEK, Japan)

NSE results





$$I(q,t)=I(q,0)\exp(-(\Gamma t)^{2/3})$$

$$\Gamma=Aq^3$$

$$K_c=(\gamma_\alpha\gamma_\kappa(k_BT)^{3/2}/A\eta)^2$$

K_c:bending modulus

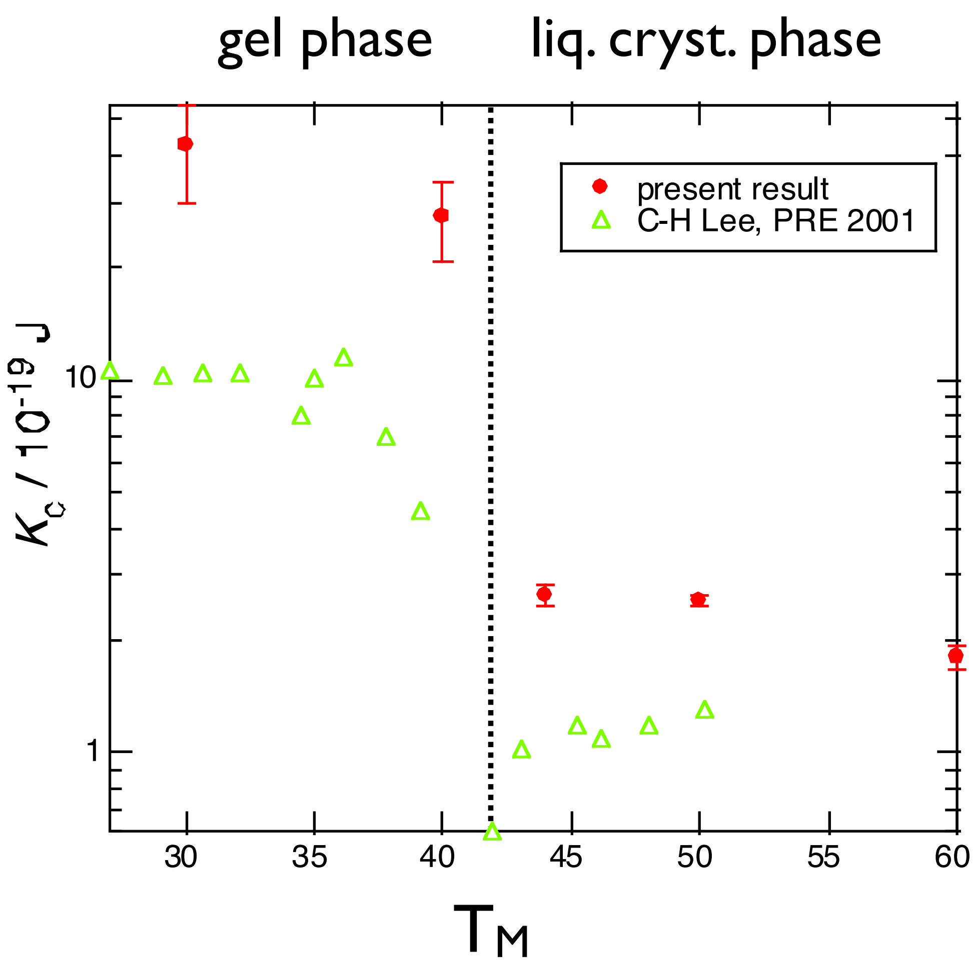
γ_α=0.025 : 2D membrane

η: viscosity of D_2O

γ_κ=1 : $K_c >> k_BT$

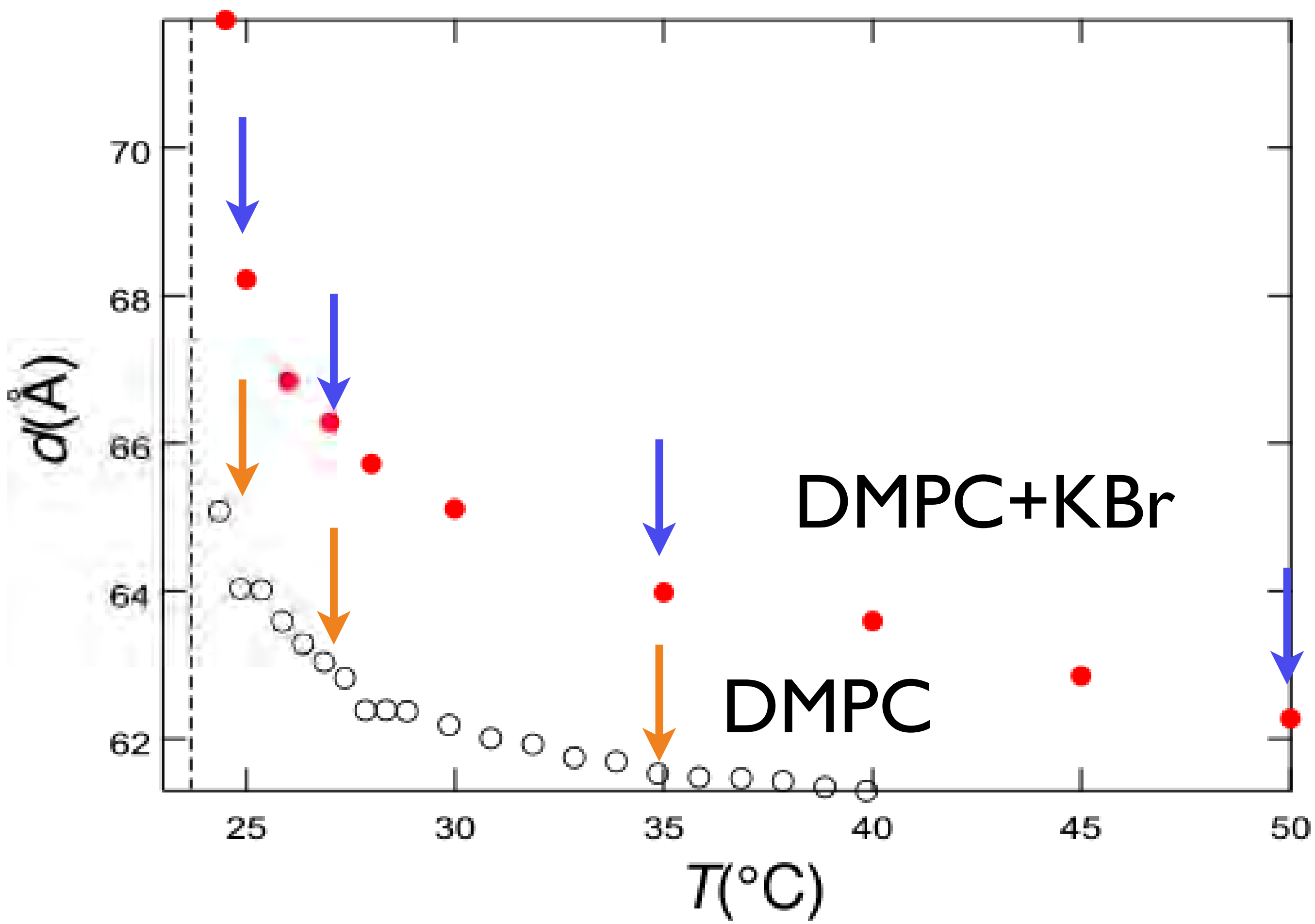
Hideki SETO (KEK, Japan)

T-dependence of bending modulus



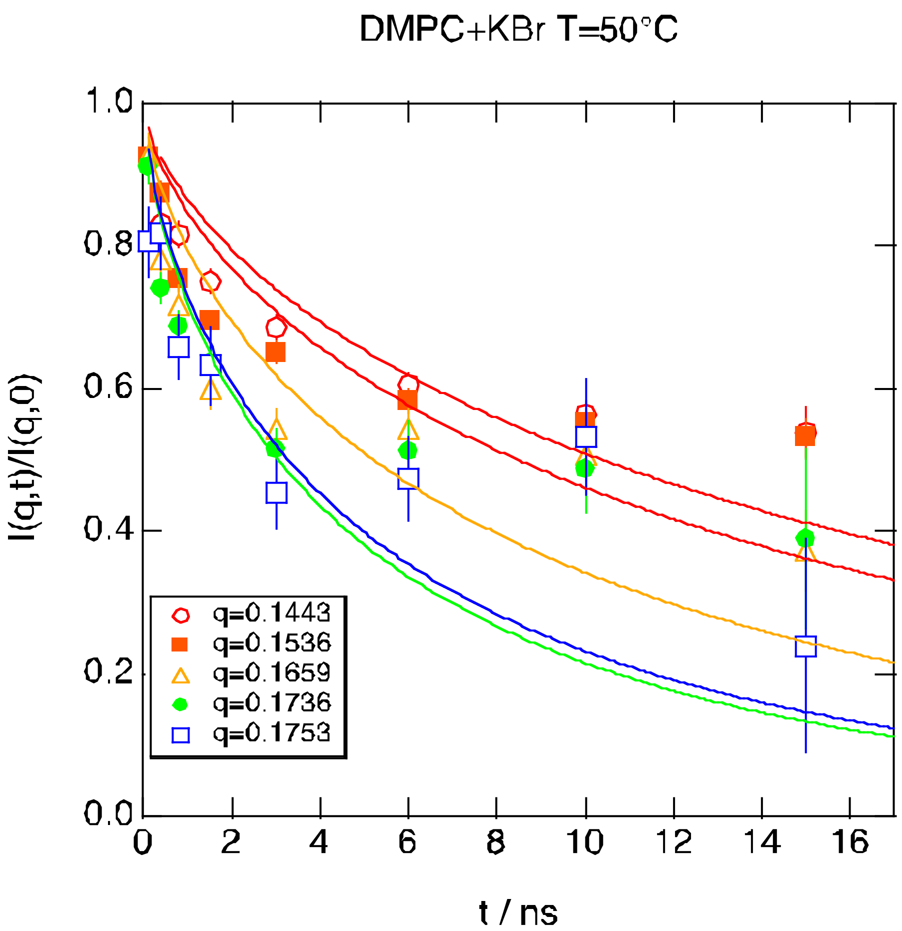
Hideki SETO (KEK, Japan)

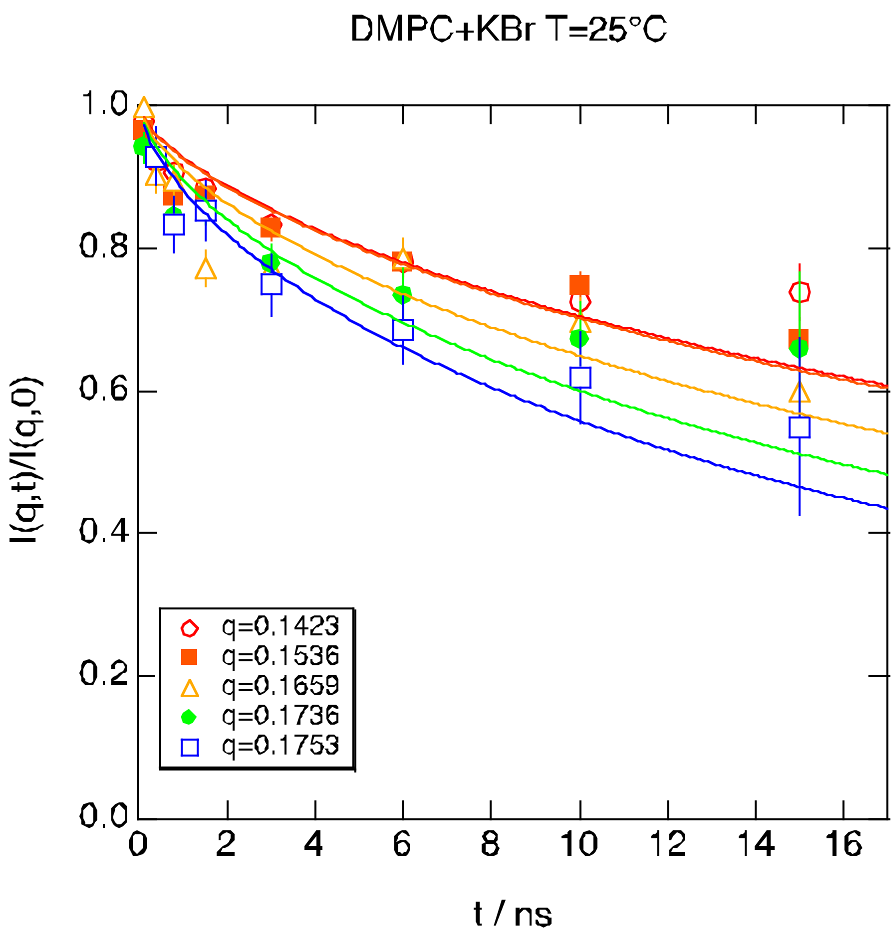
Anomalous swelling above T_M



Hideki SETO (KEK, Japan)

NSE results



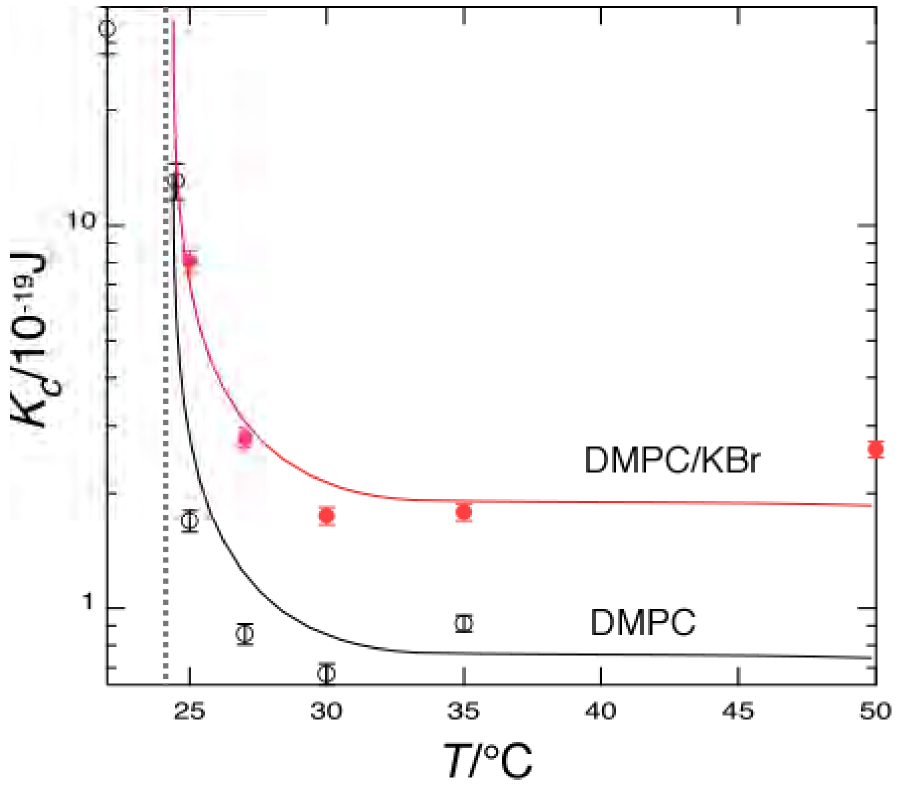


$$I\,(q,t)/I\,(q,0)=C\,\exp[-(\Gamma t)^{\,2/3}]$$

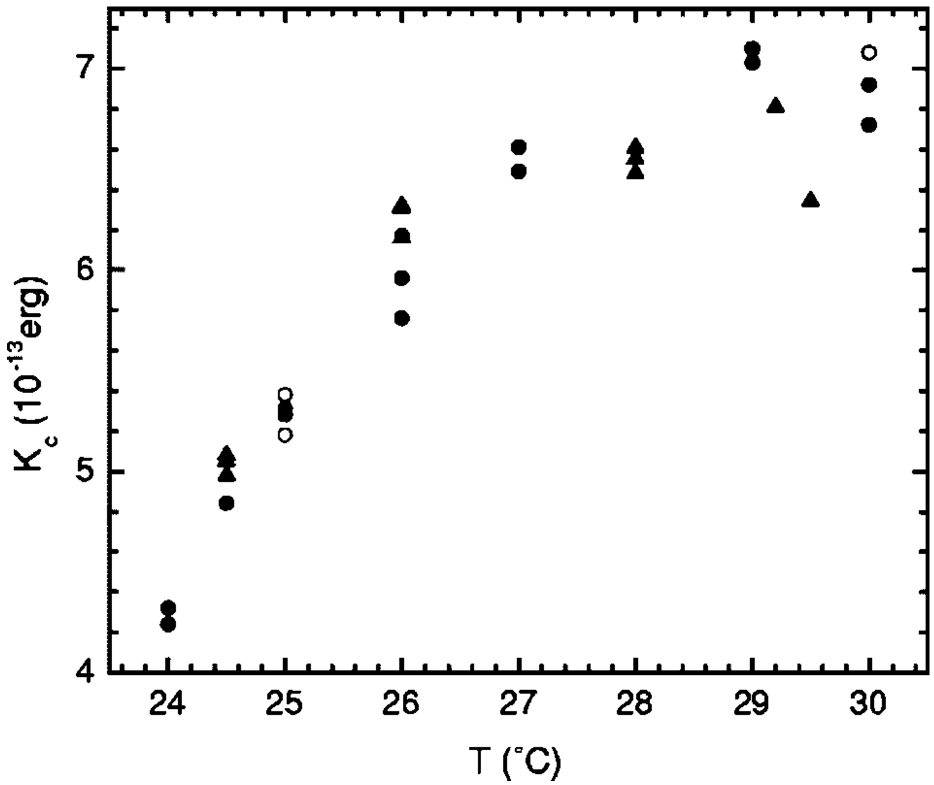
Hideki SETO (KEK, Japan)

Bending modulus

NSE, 2007



SAXS, 2005



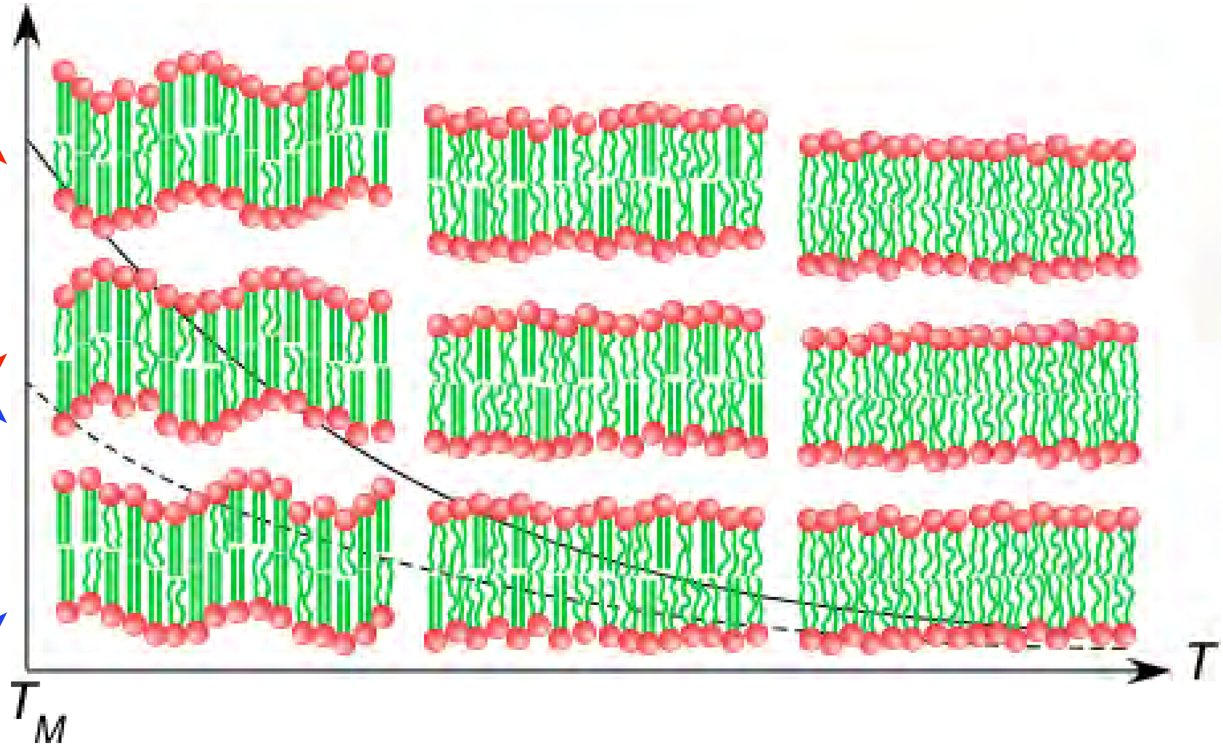
Softening ⇨ Thermal fluctuation increases

⇨ Repeat distance increases

Our interpretation

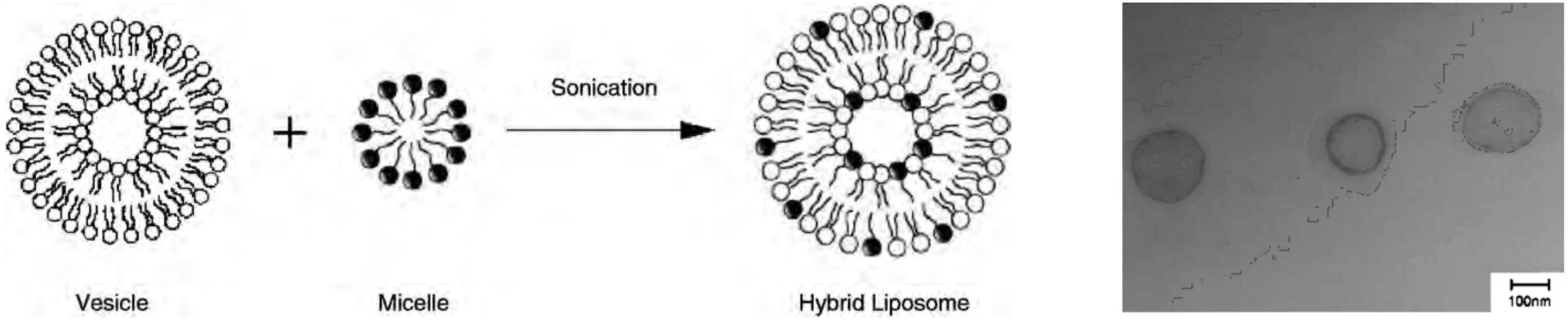
irregular stacking of bumpy layers

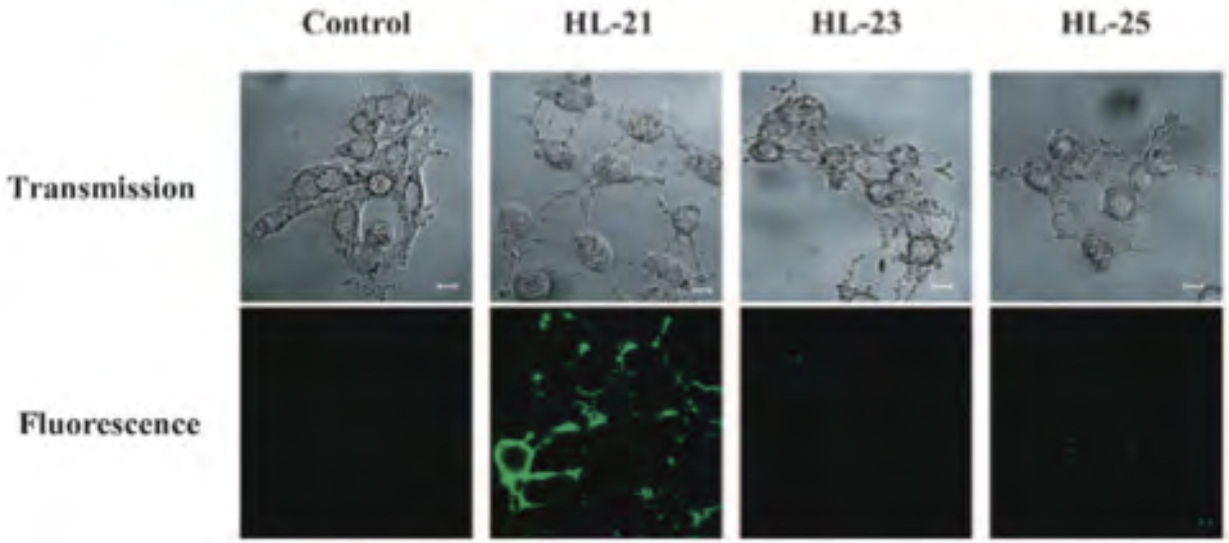
thickening & hardening



Possible application

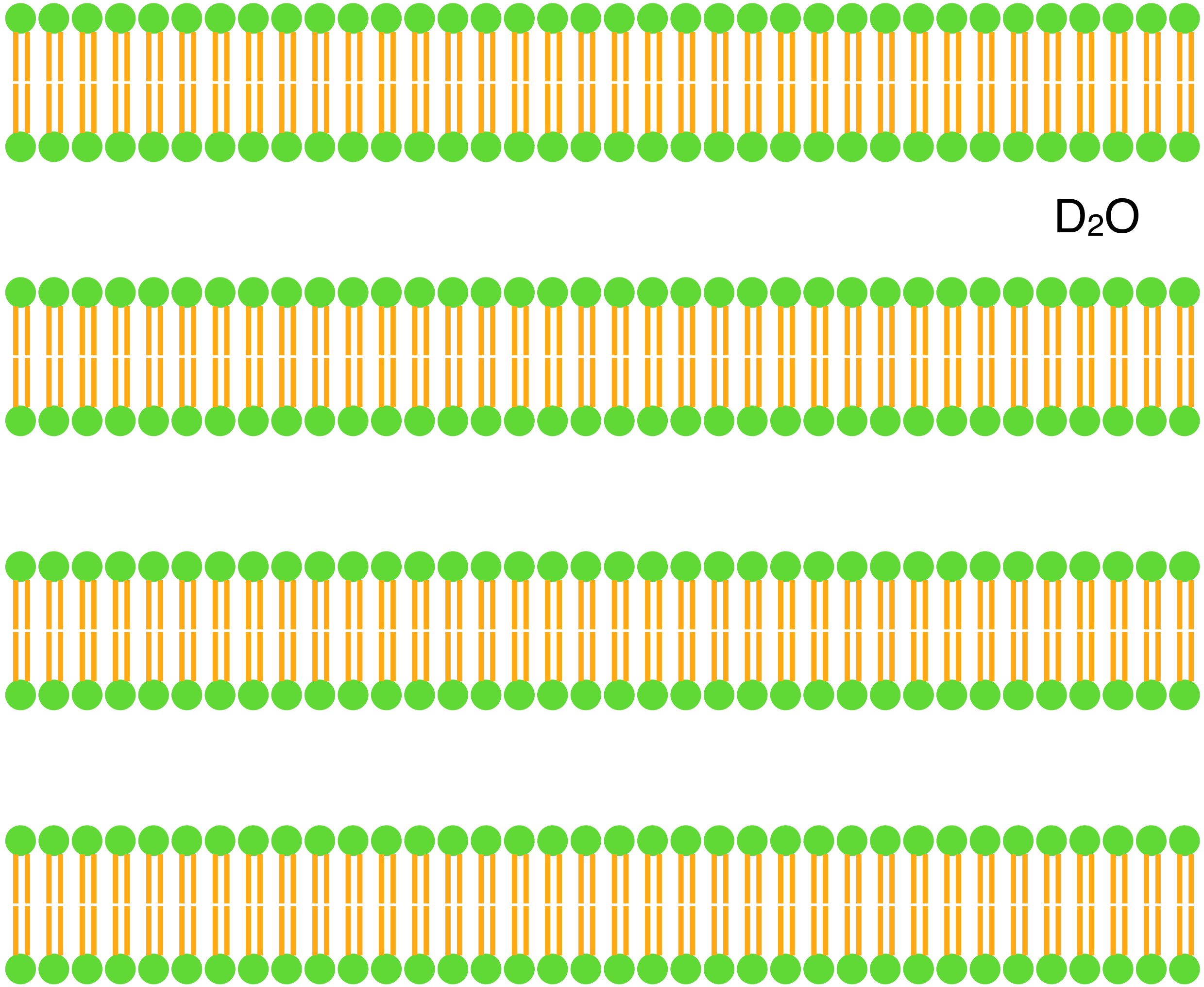
Inhibitory Effects of Hybrid Liposomes on the Growth of Tumor Cells





HL induces apoptosis of tumor cells

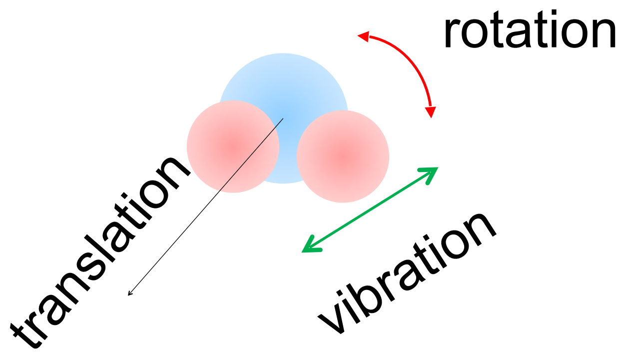
Lipid membrane & water

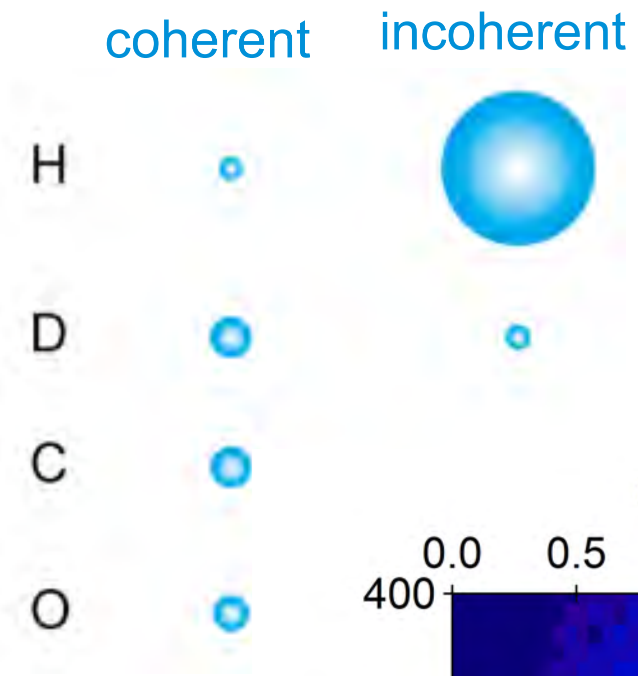


Lipid membrane & water

water

QENS with Incoherent Scattering



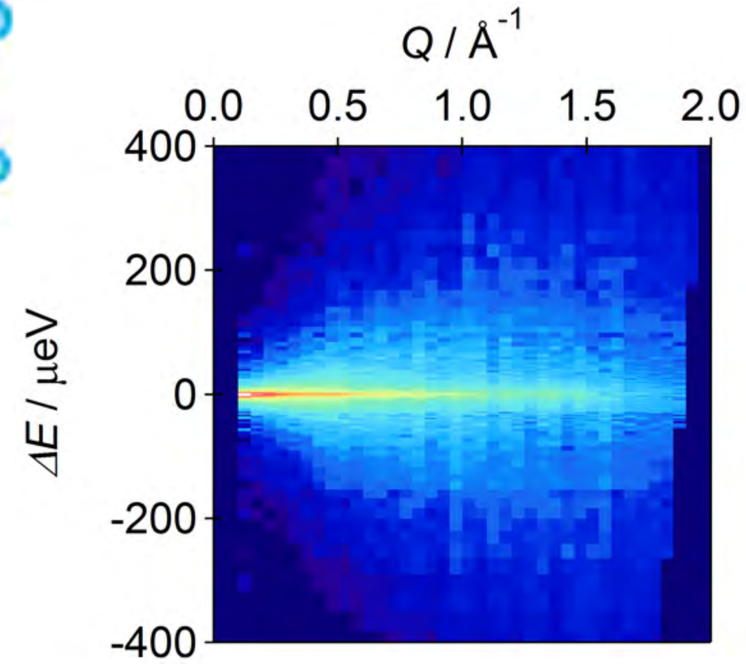


van Hove function

$$G(r,t) = \frac{1}{N}\sum_{j}\sum_{j'}\int\langle\delta[r - r' + r_j(0)]$$
$$\delta[r' - r_{j'}(t)]\rangle dr' \quad \text{(mutual correlation)}$$

$$G_s(r,t) = \frac{1}{N}\sum_{j}\int\langle\delta[r - r' + r_j(0)]$$
$$\delta[r' - r_{j'}(t)]\rangle dr' \quad \text{(self correlation)}$$

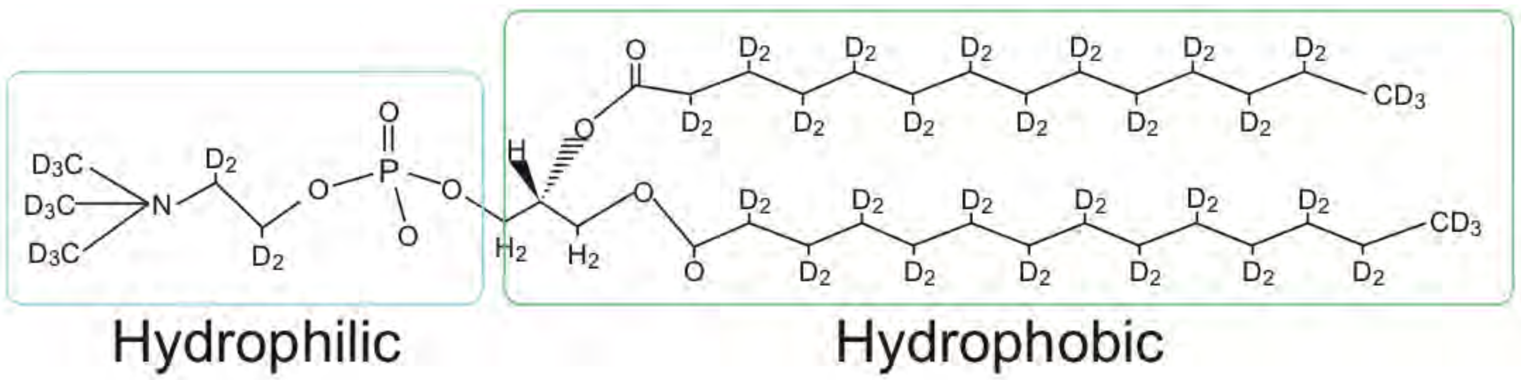
Fourier trans.



Purpose of this study

- Dynamical behavior of water molecules is investigated with QENS
  - Wide energy range / high energy resolution
    - Available to measure from free water to hydrated water
  - Fully deuterated phospholipid
    - QENS signal from hydrophlic part could be neglected and the dynamical behavior of water molecules can be estimated

Sample: d_{67}DMPC + H_2O



Samples

d_{67}DMPC-37H_2O

	Coherent scatt.	Incoherent scatt.
d_{67}DMPC	631.4 barn (8.5%)	631.4 barn (7.3%)
37H_2O	286.6 barn (3.9%)	5939.2 barn (80.3%)

DMPC-35D_2O

	Coherent scatt.	Incoherent scatt.
DMPC	374.5 barn (5.5%)	5779.3 barn (84.5%)
35D_2O	535.6 barn (7.9%)	143.5 barn (2.1%)

Sample can：14mm-φ / 40mm-h / 0.5mm-t (double cylinder)

Experimental

– Elastic Scan （50 ～ 320 K, 1 $Kmin^{-1}$)

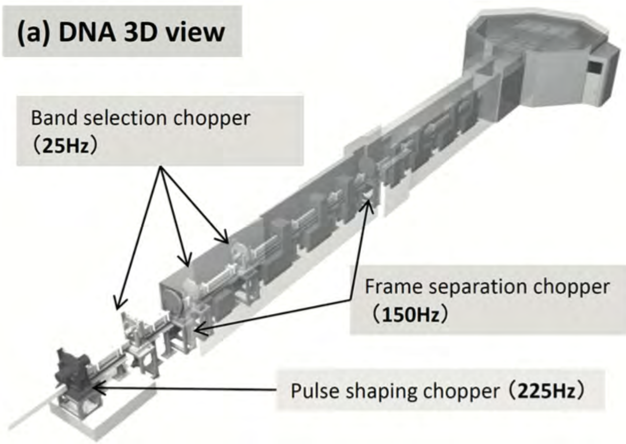
– Quasi-Elastic Neutron Scattering

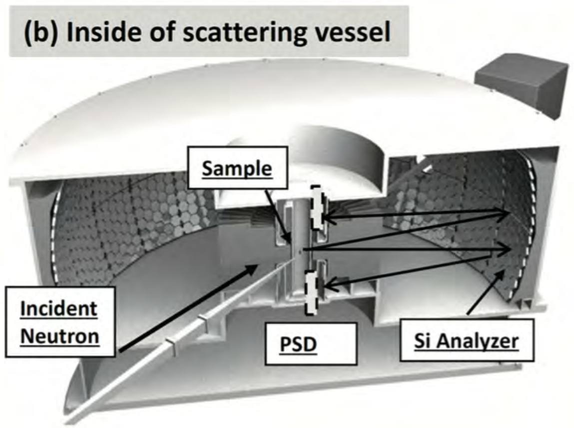
- d_{67}DMPC-37H_2O: 316, 305, 295, 285, 275 K (12h / Temp)

  $-0.5 \leq \Delta E \leq 0.5$ (meV) , δE_{Reso}= 3.6 μeV, at 3 chopper settings

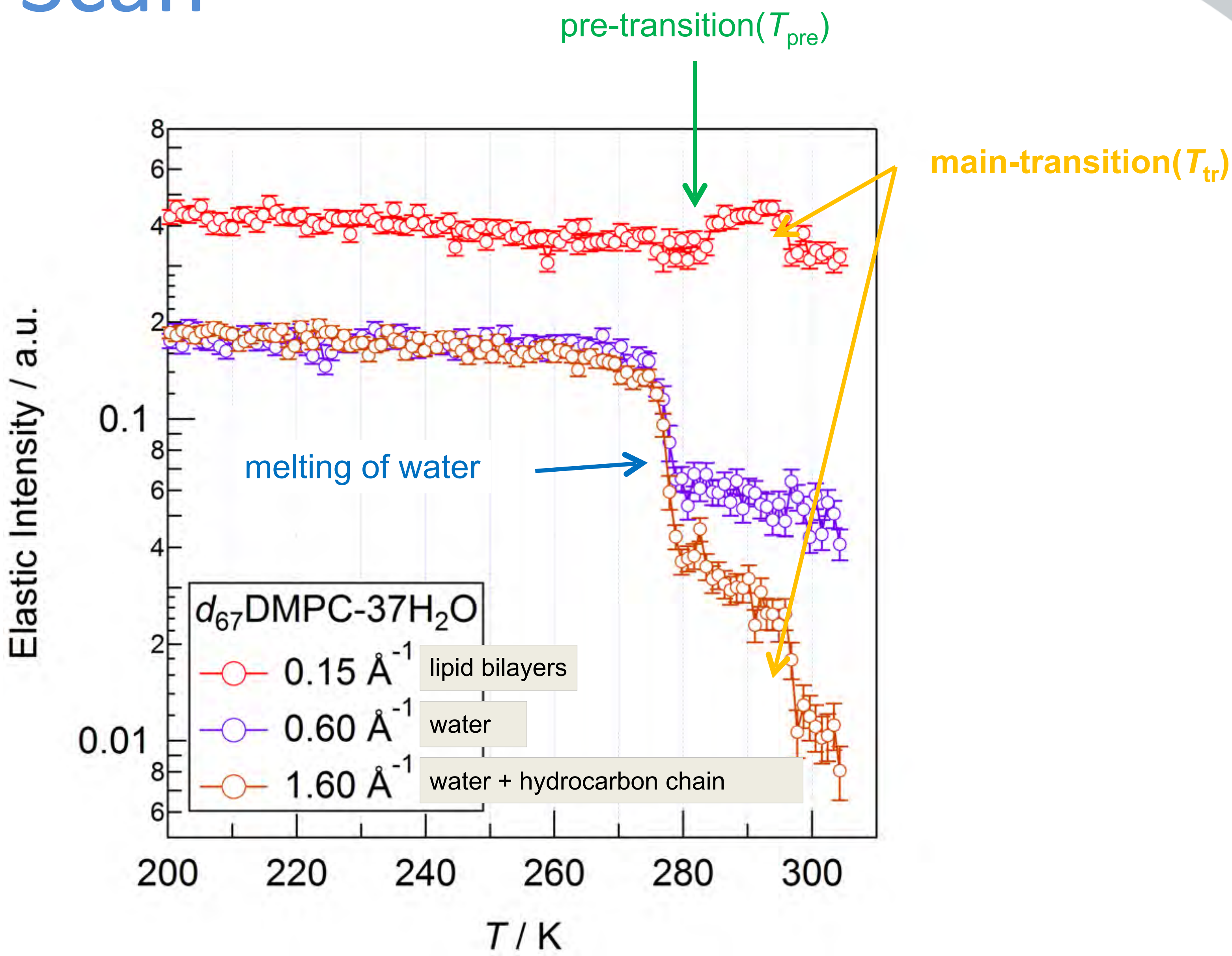
- DMPC-35D_2O: 306 K

  $-0.04 \leq \Delta E \leq 0.1$ (meV), at 1 chopper settings





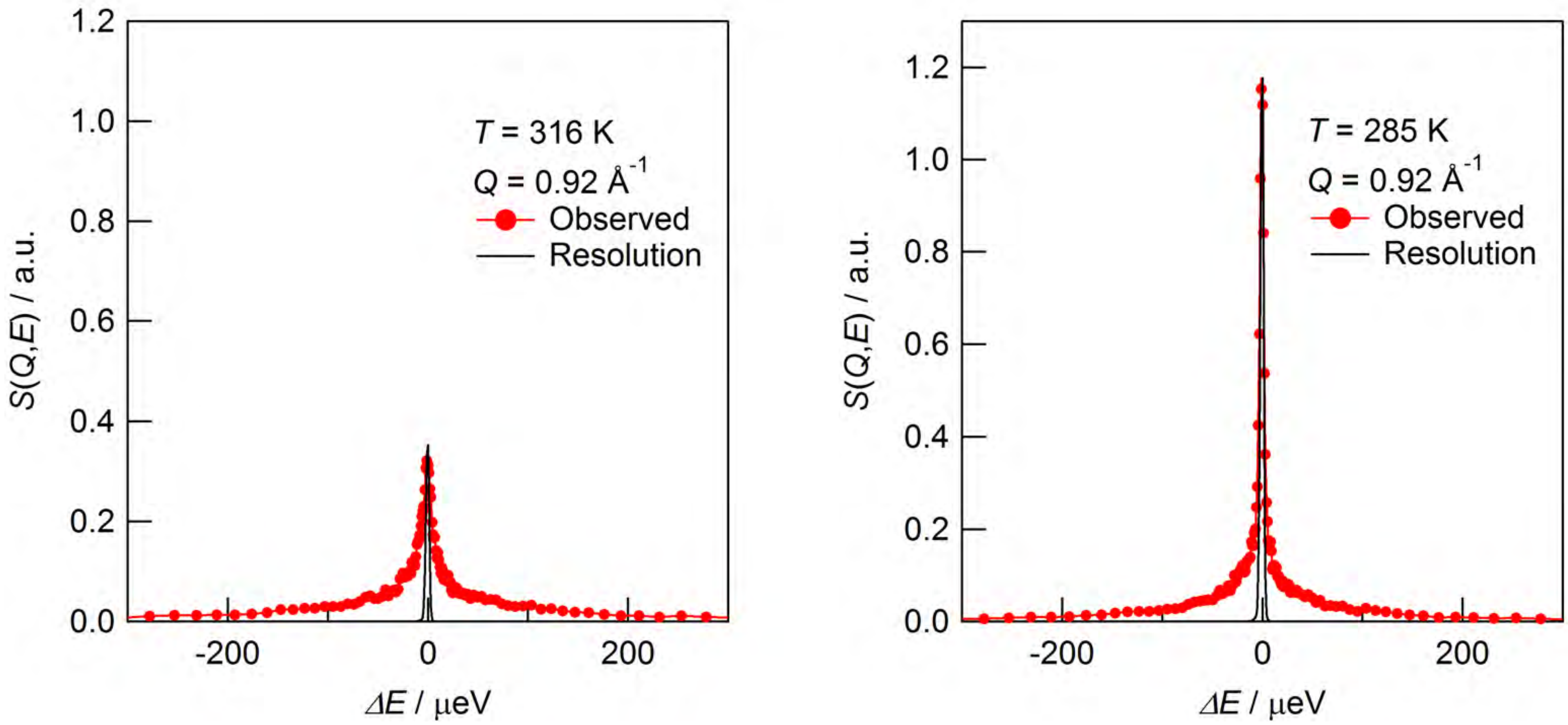
Elastic Scan



IMSS 物質構造科学研究所

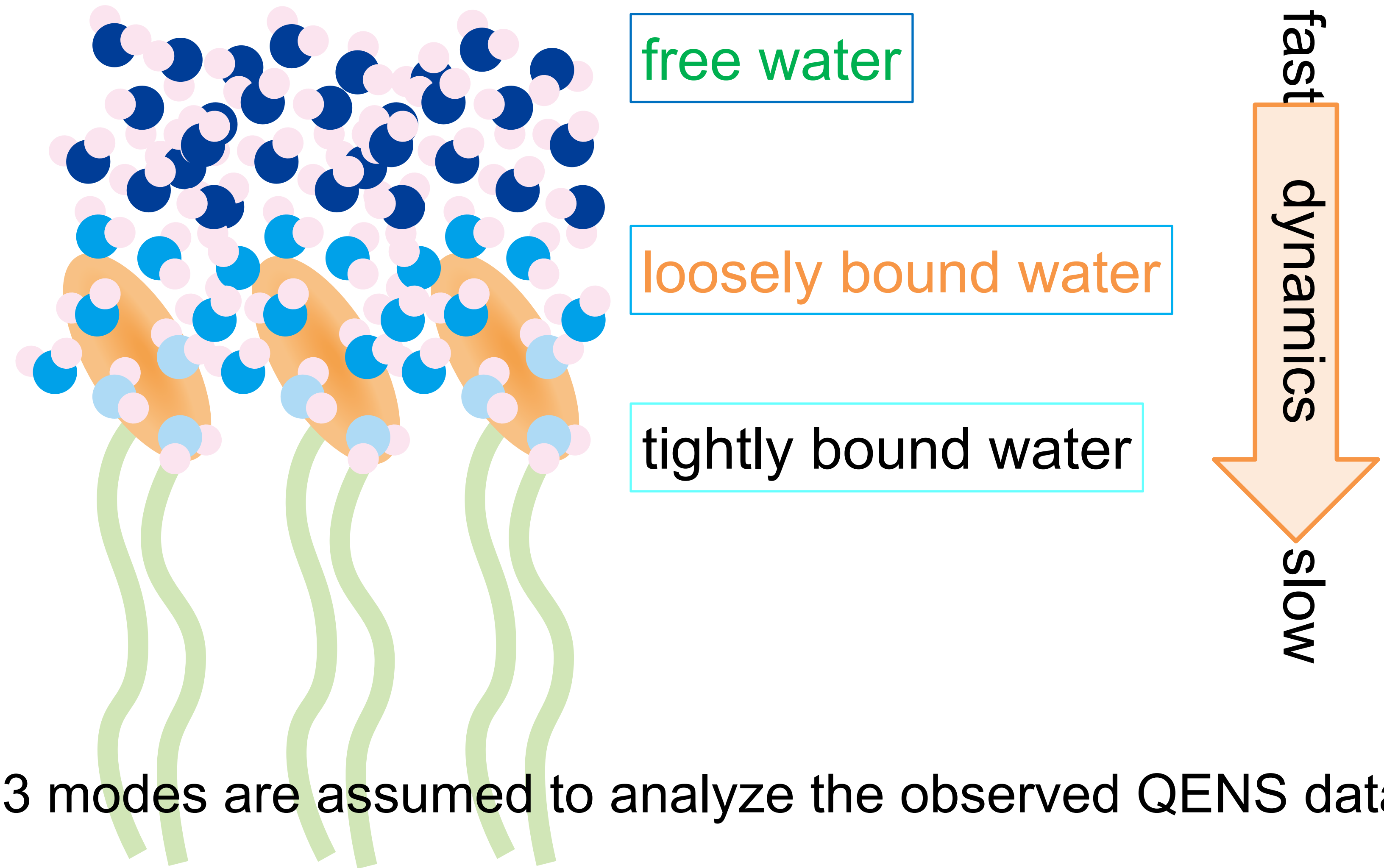
QENS data of $d_{67}DMPC\text{-}37H_2O$

dynamics of water molecules



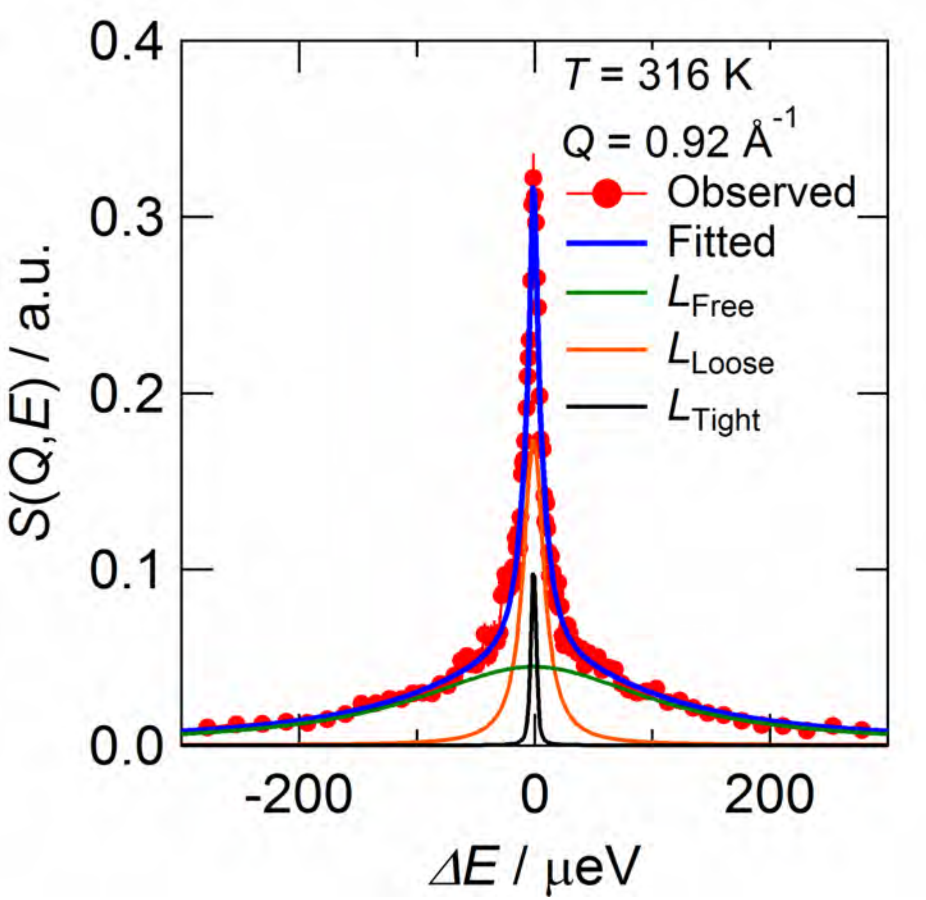
Quasi-Elastic Neutron Scattering was observed and its width increased with increasing temperature.

Model Analysis



3 modes are assumed to analyze the observed QENS data

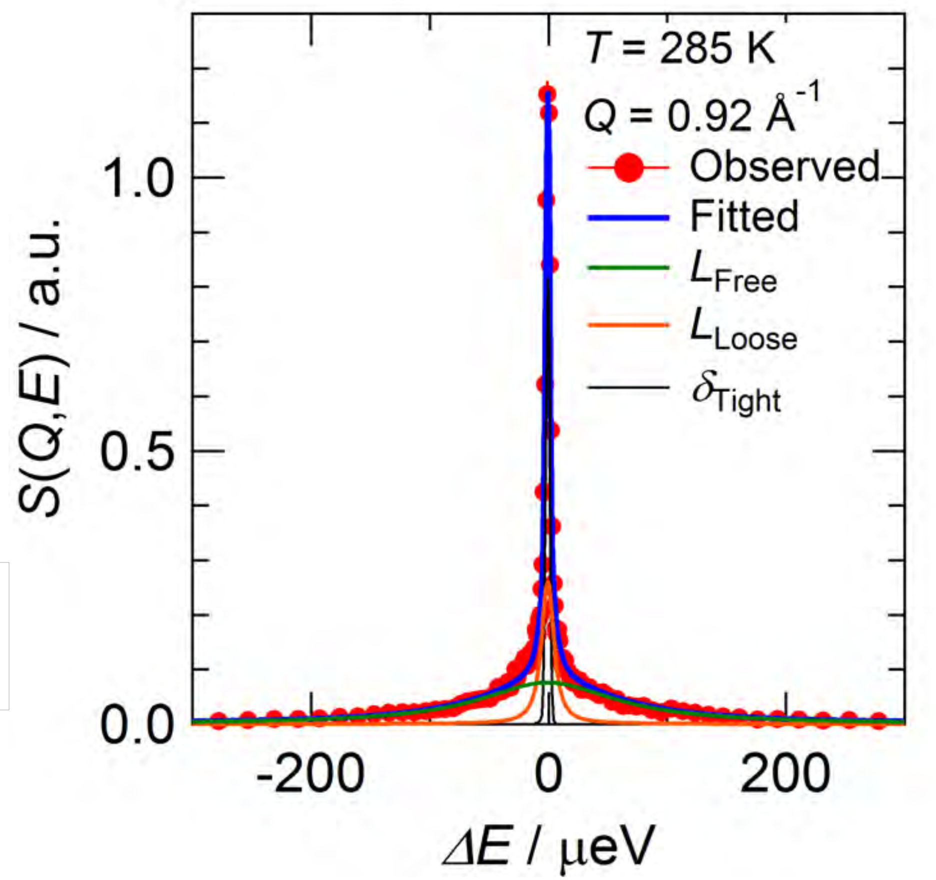
Liquid Crystalline Phase
(T = 316, 305, 295)



$$S(Q,E) = \{A_{\text{Tight}} L_{\text{Tight}} (\Gamma_{\text{Tight}}, E) + A_{\text{Loose}} L_{\text{Loose}} (\Gamma_{\text{Loosely}}, E) + A_{\text{Free}} L_{\text{Free}} (\Gamma_{\text{Free}}, Q)\} \otimes R(Q,E) + BG$$

IMSS
物質構造科学研究所

Ripple Gel Phase & Gel Phase
(T = 285, 275 K)

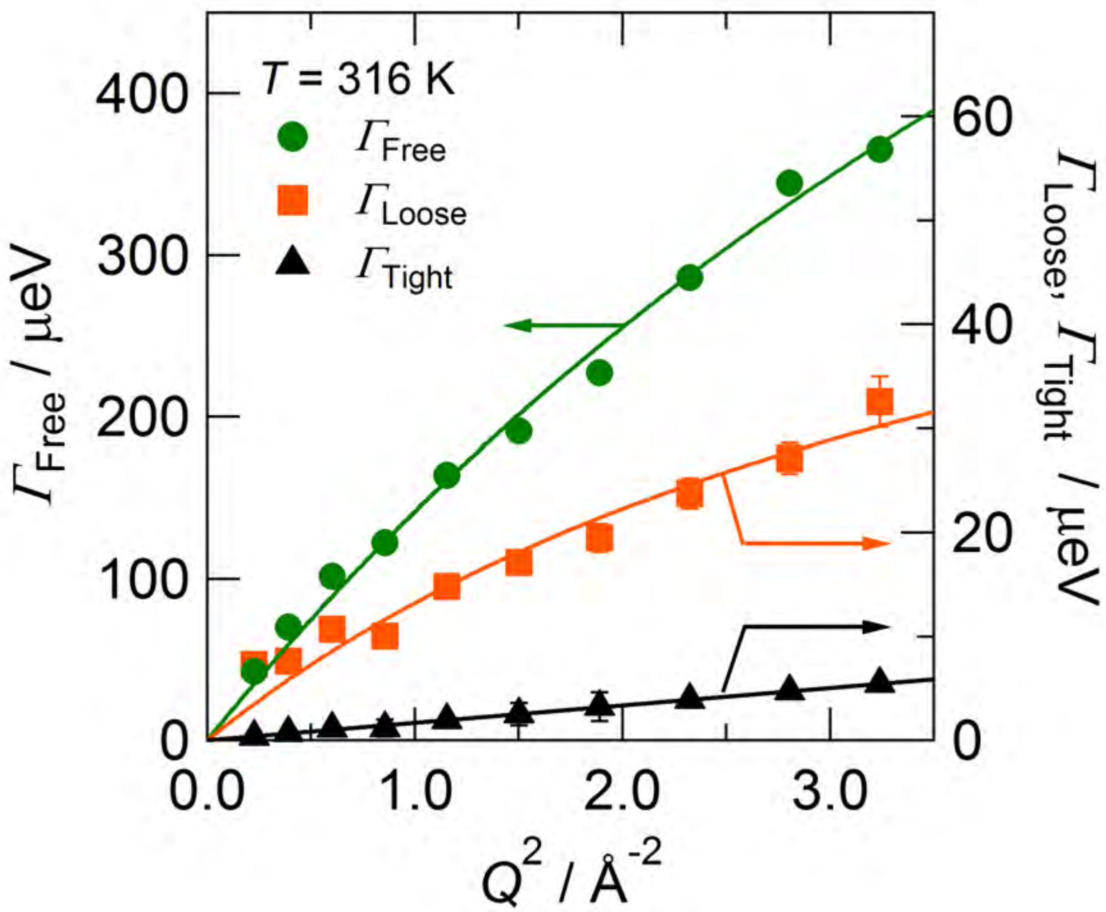


Tightly bound water is too fast to observe (the width is less than the resolution function).

$$S(Q,E) = \left\{A_{\mathrm{Tight}}\delta_{\mathrm{Tight}}(E) + A_{\mathrm{Loose}}L_{\mathrm{Loose}}(\Gamma_{\mathrm{Loosely}}, E) + A_{\mathrm{Free}}L_{\mathrm{Free}}(\Gamma_{\mathrm{Free}}, Q)\right\} \otimes R(Q,E) + BG$$

IMSS 物質構造科学研究所

Q^2 dependence of HWHM



Tightly bound water

Simple diffusion model (Fick's law)

$\Gamma_{\mathrm{Tight}} = DQ^2$

Loosely bound water

Free water

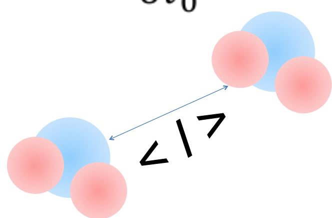
Jump diffusion modelo

$$\Gamma = \frac{DQ^2}{1 + DQ^2\tau_0}$$

τ_0 : mean residence time

D : diffusion constant ($D = \frac{\langle l \rangle^2}{6\tau_0}$)

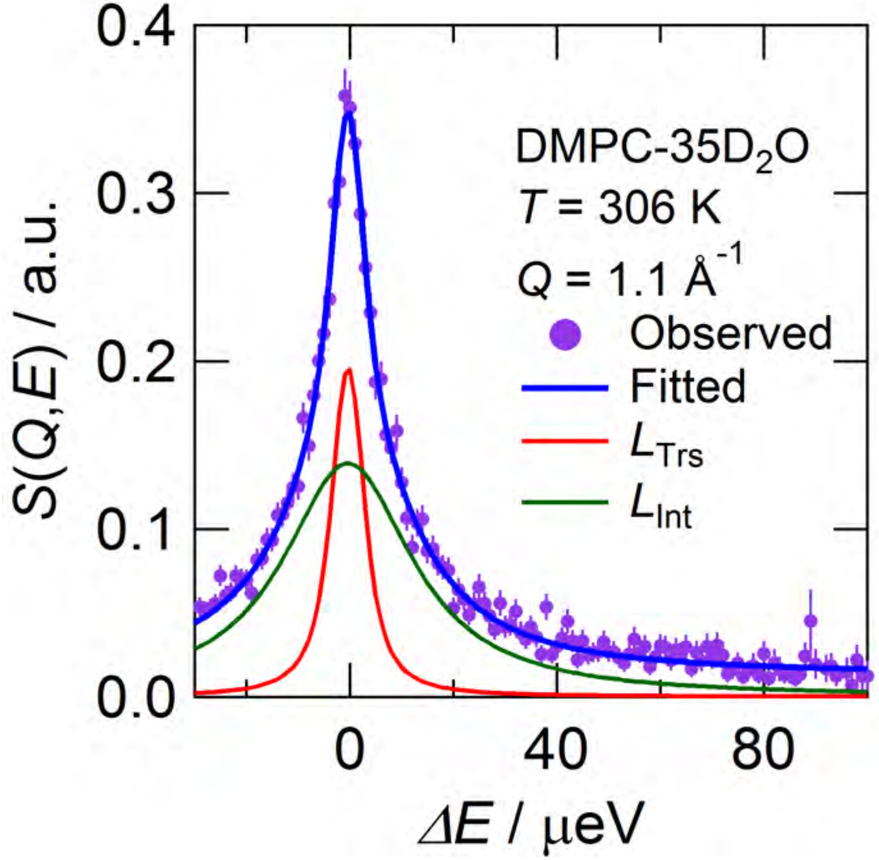
< l >: jump distance

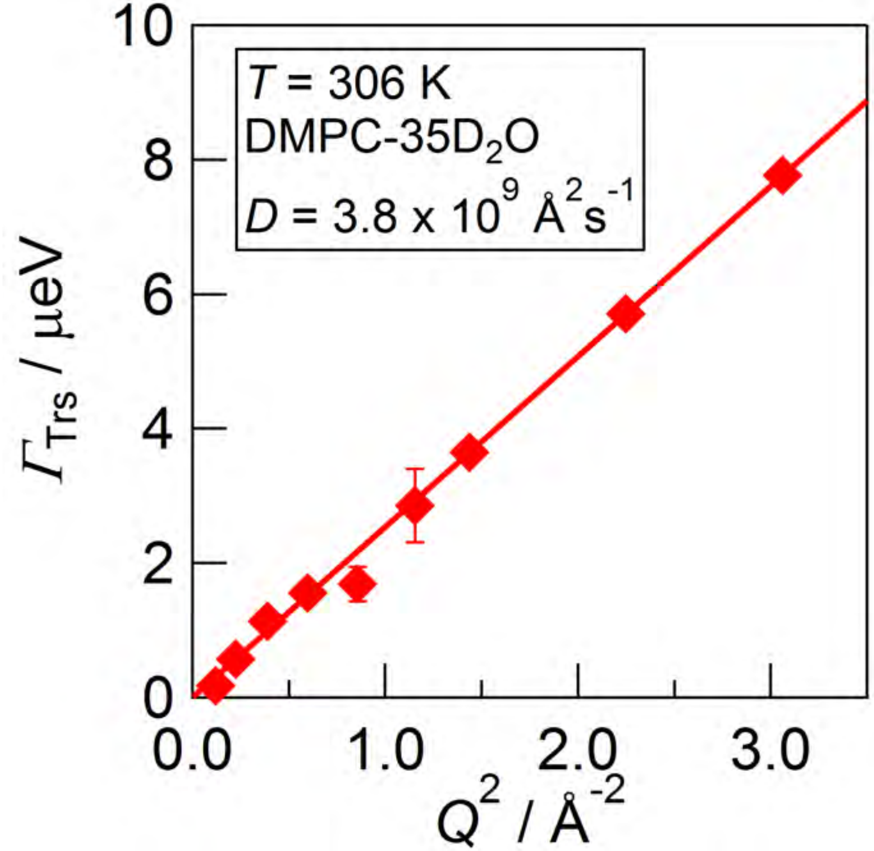


IMSS 物質構造科学研究所

QENS data of DMPC-35D_2O

Dynamics of lipid molecules





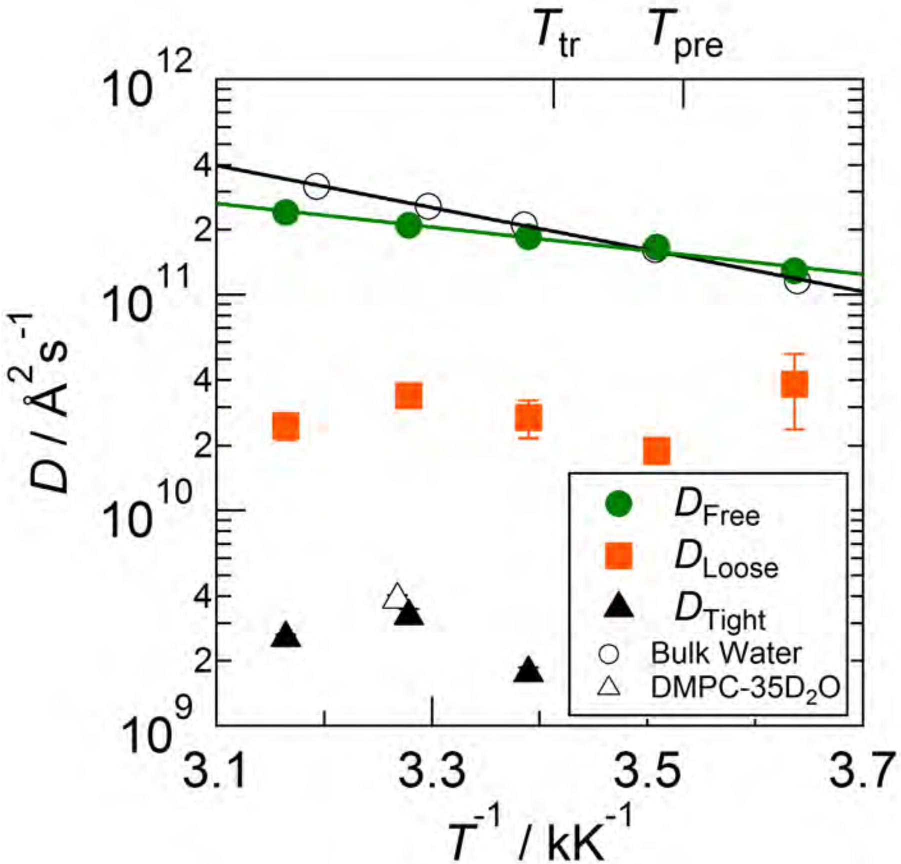
$$S(Q,E) = \{A_{\mathrm{Trs}}(Q)L_{\mathrm{Trs}}(\Gamma_{\mathrm{Trs}}, E) + A_{\mathrm{Int}}(Q)L_{\mathrm{Int}}((\Gamma_{\mathrm{Lat}} + \Gamma_{\mathrm{Int}}), E)\} \otimes R(Q,E) + BG$$

A model assuming lateral diffusion of lipid molecules within bilayer and internal mode of a lipid※

IMSS 物質構造科学研究所

※V. Sharma, et. al, *J. Chem. Phys. B*, **119** (2015), 4460.

Arrhenius plot of diffusion const.



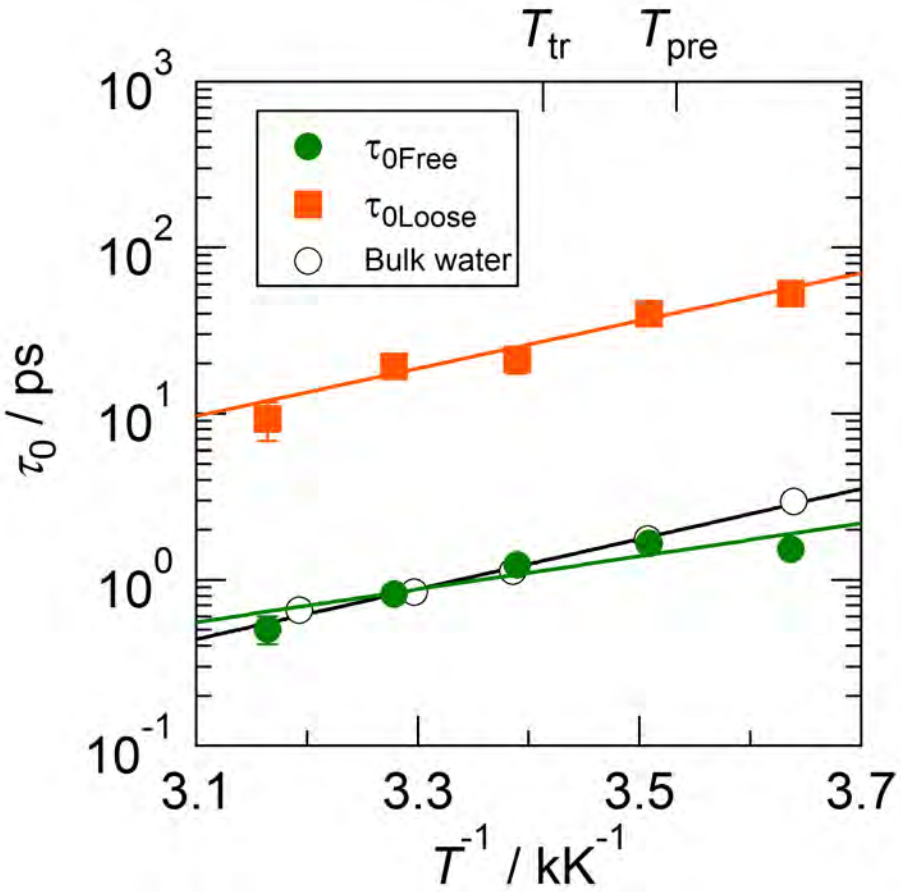
	Activation energy [$kJmol^{-1}$]
Free water	10.5 ± 1.2
Bulk water	18.6 ± 0.3

Activation energy of “Free water” is less than that of bulk water

Free water: diffusion constant is the same order as that of bulk water
Loosely bound water: 1 order less diffusion constant than that of free water
Tightly bound water: the same diffusion constant as that of DMPC

IMSS 物質構造科学研究所

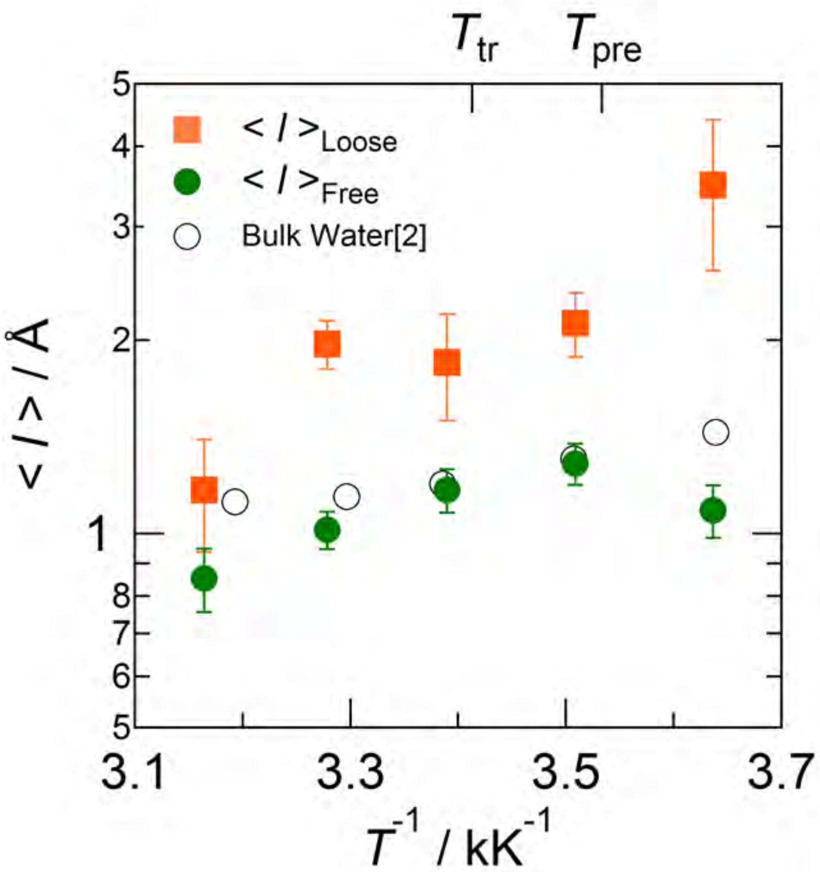
Arrhenius plot of mean res. time



	Activation Energy [kJmol^{-1}]
Free water	19.0 ± 2.5
Bulk water	28.9 ± 1.0
Loosely bound water	27.5 ± 3.2

Free water: mean residence time is the same as that of bulk water
Loosely bound water: 1 order of magnitude more than that of bulk water

Arrhenius plot of jump distance

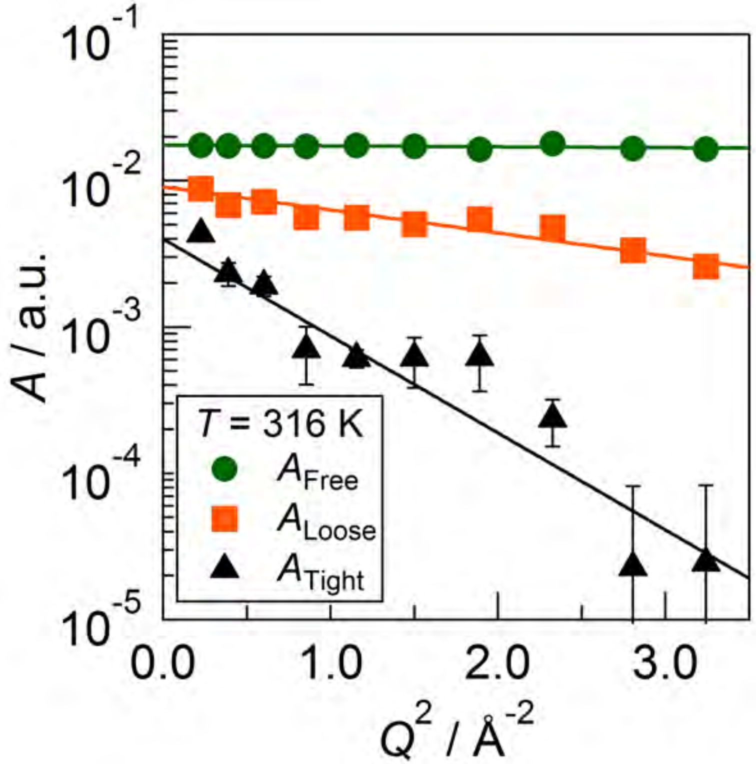


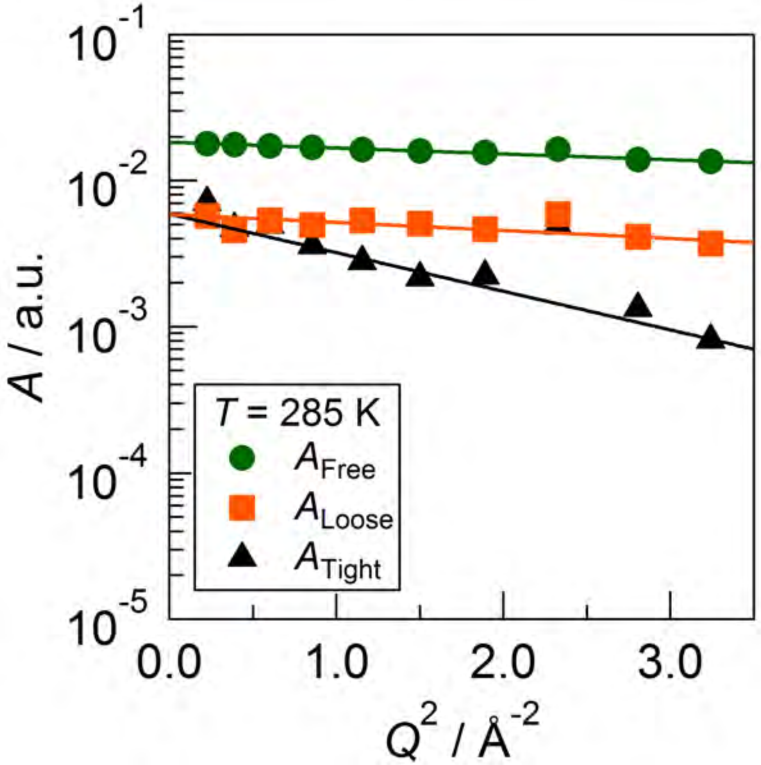
$$D = \frac{\langle l \rangle^2}{6\tau_0}$$

Jump distance of the loosely bound water is longer than that of bulk water
→hydrogen bonding distorts from the normal water structure

IMSS 物質構造科学研究所

Coefficients of 3 components

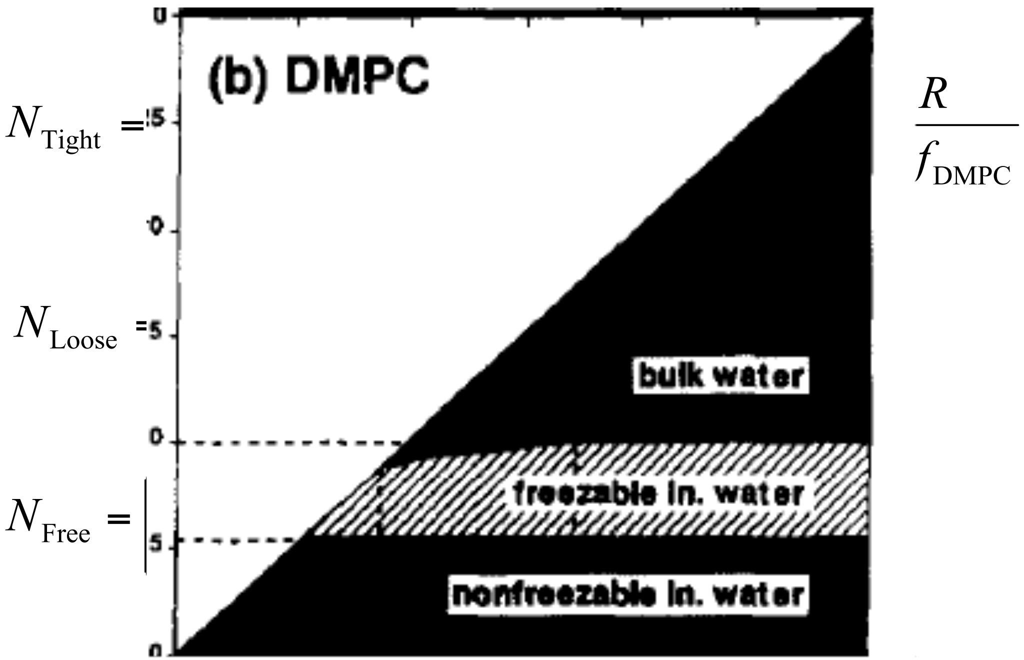


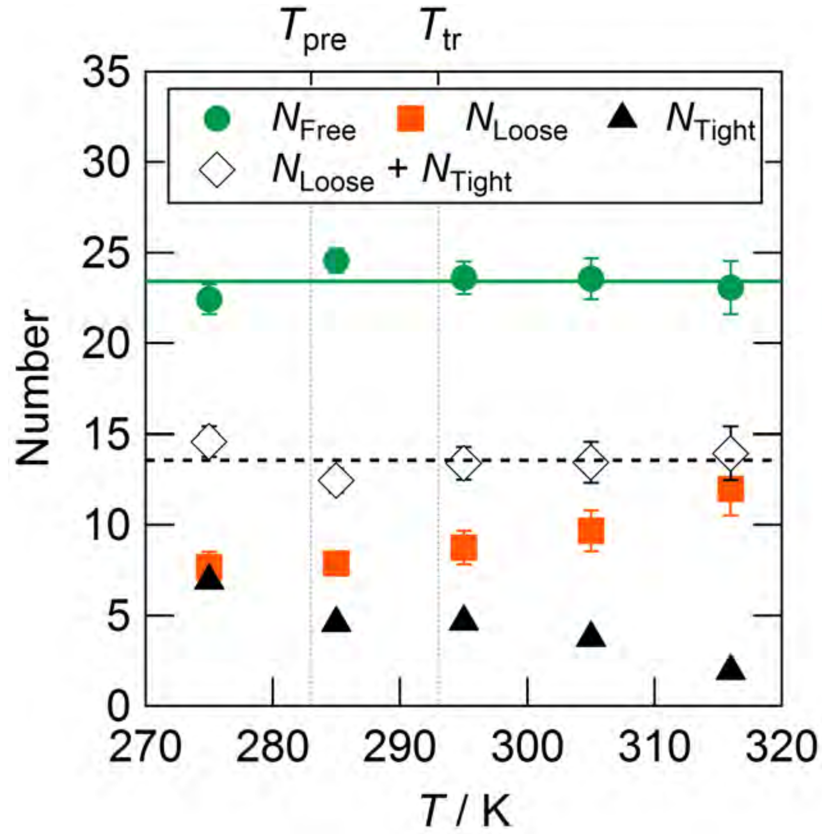


$$A = A_0 \exp\left(-\frac{\langle u \rangle^2 Q^2}{3}\right)$$

A_0's are proportional to the number of atoms.

Number of water molecules

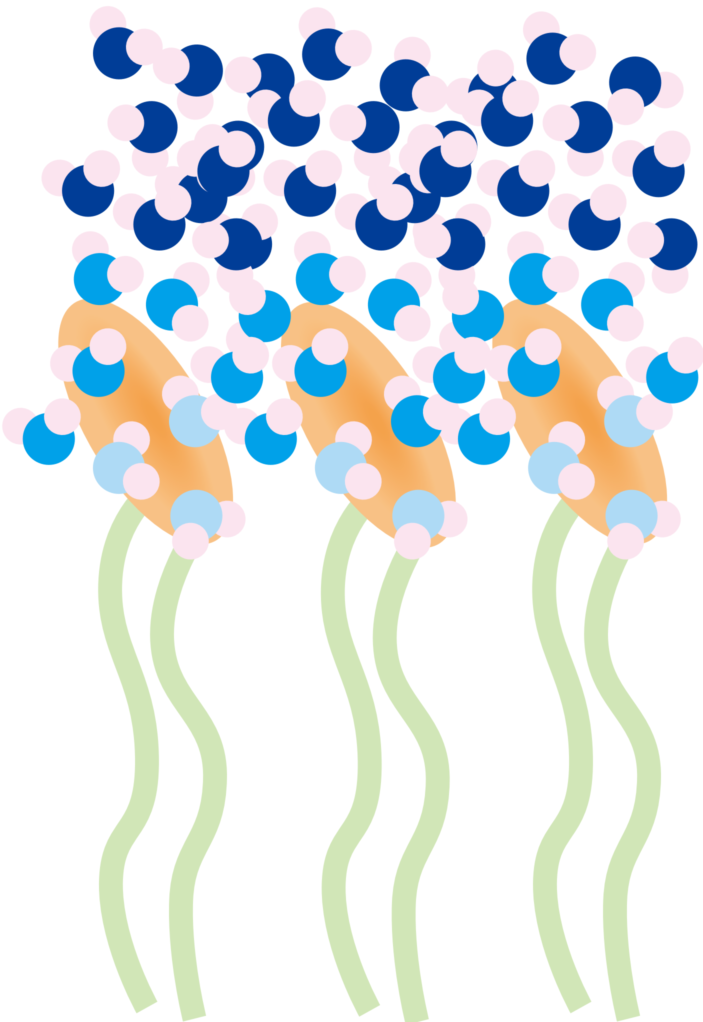




R = 37 (water molecules/lipid molecule)
f_{DMPC} = 0.083
(Incoherent scatt. fraction of DMPC)

Free water: almost constant
Loosely bound water: increase with increasing temperature
Tightly bound water: decrease with increasing temperature

Summary



free water

24 molecules: no T dependence
nearly bulk water, but confinement effect

loosely bound water

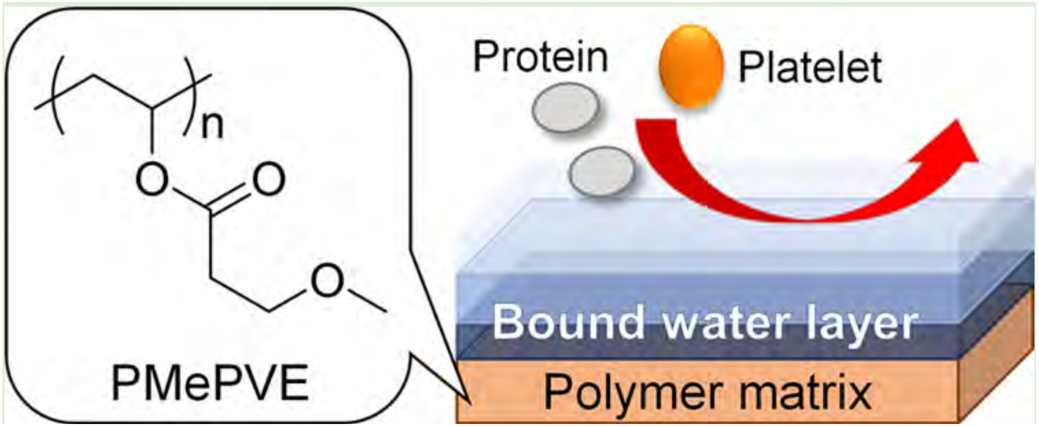
8-12 molecules: increase with T
slow dynamics: 1/10 of free water

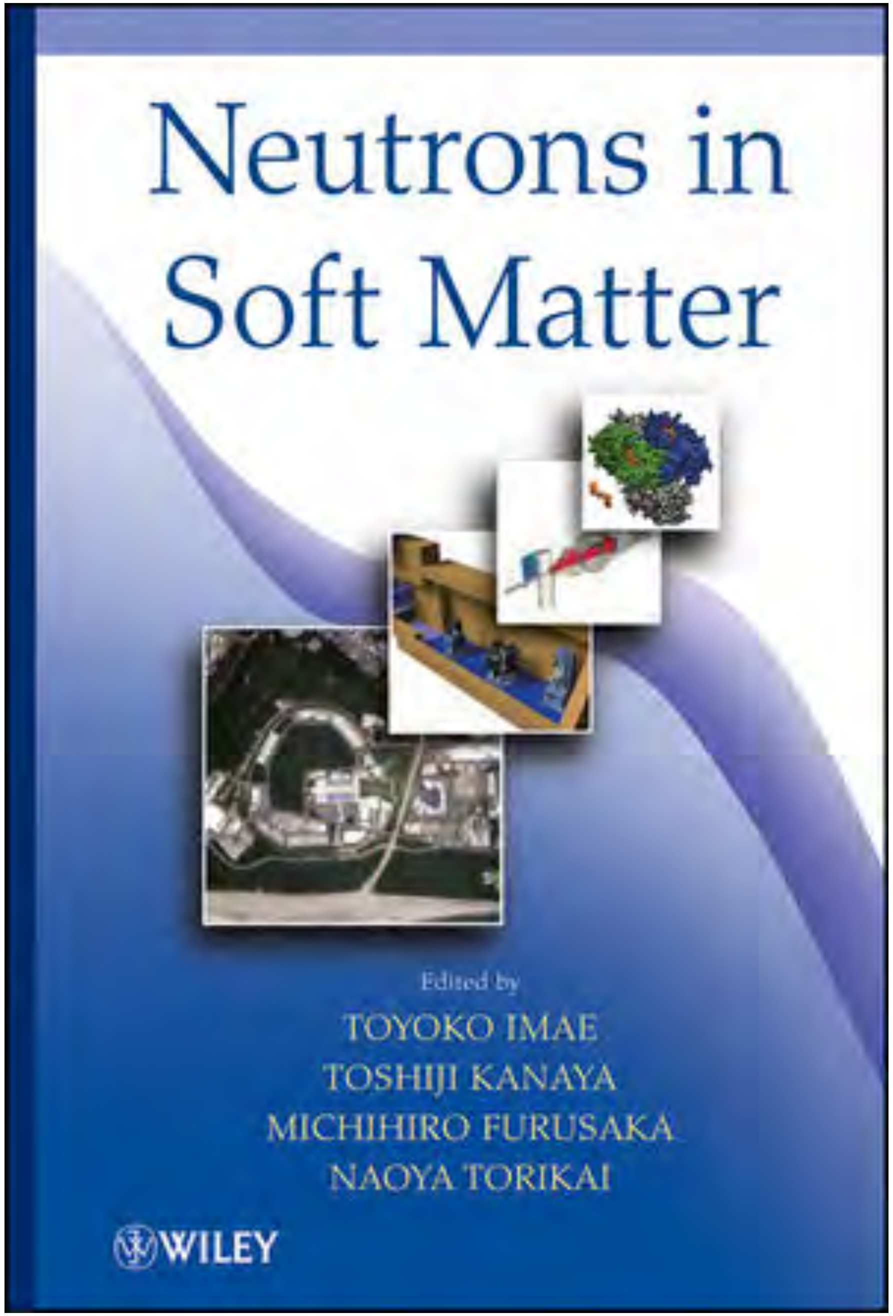
tightly bound water

7-2 molecules: decrease with T
move with lipid molecules

Possible application

bio-compatibility and bound water layer





Hardcover: $182.00
E-Book: $145.99