Neutrons in Soft Matter

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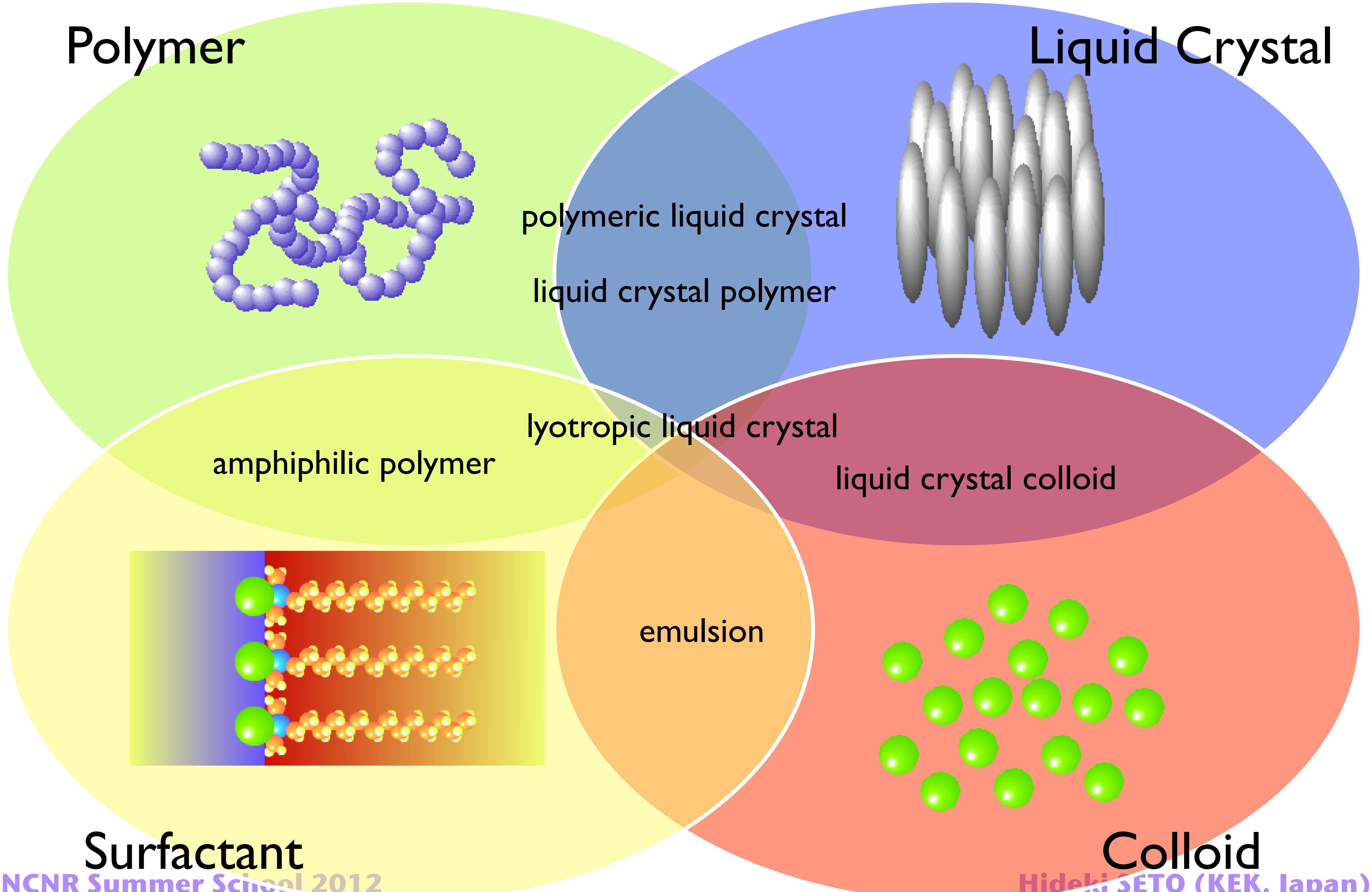
Self-introduction

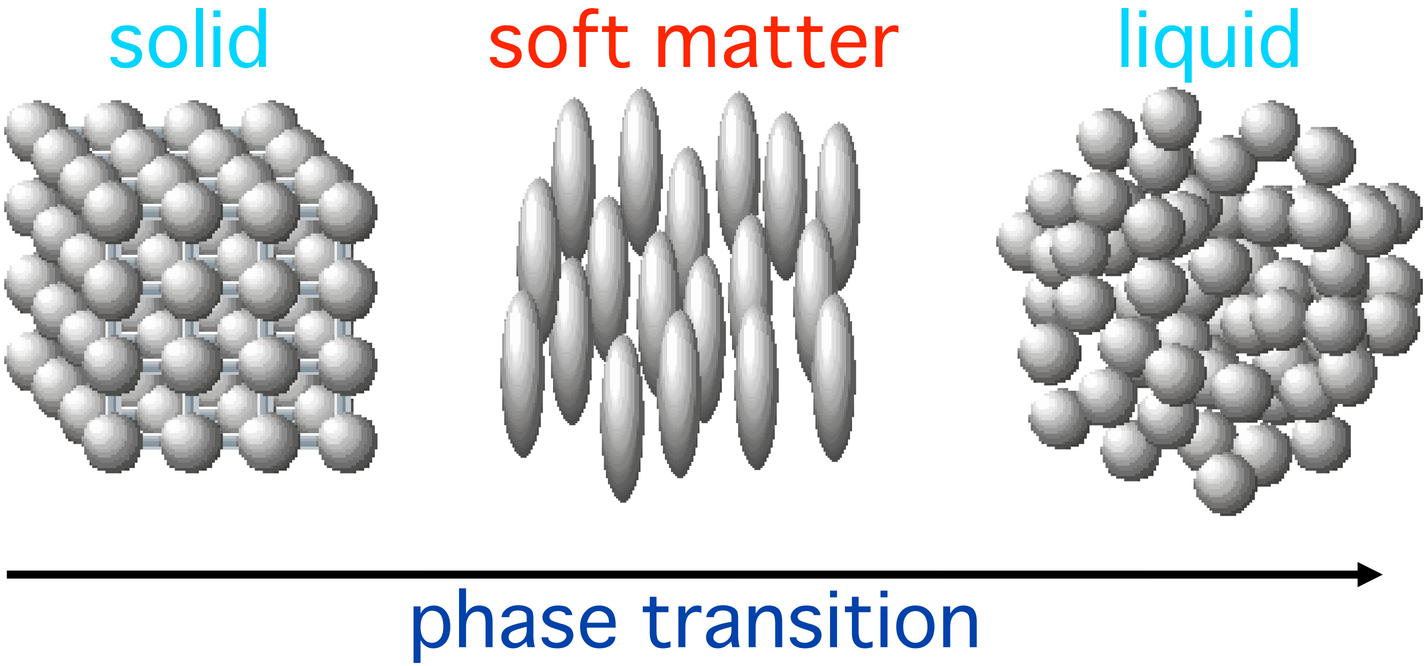
- Born in 1961 — Fukushima, Japan
- 1984 Graduated from Kyoto Univ.
- 1989 Ph. D from Osaka Univ. — Shape memory alloy; Single X’tal/X-ray, Neutron
- 1989-2002 Research Associate at Hiroshima Univ. — Microemulsion; SANS/NSE
- 2002-2008 Associate Prof. at Kyoto Univ. — Soft Matter Physics; Non-equilibrium phenomena
- 2008- Professor at KEK — J-PARC

Soft Matter

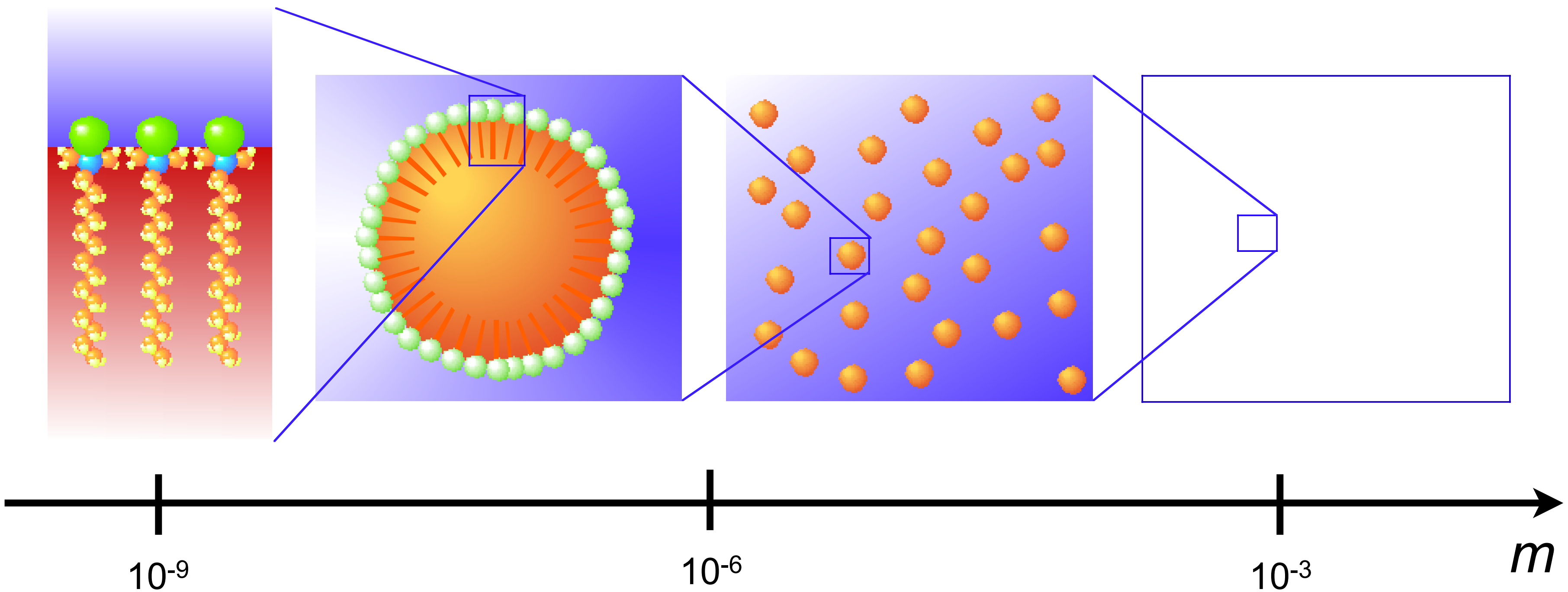

Polymer
Liquid Crystal
polymeric liquid crystal
liquid crystal polymer
lyotropic liquid crystal
amphiphilic polymer
liquid crystal colloid
emulsion
Surfactant
Colloid

Common properties

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



Hierarchical structure



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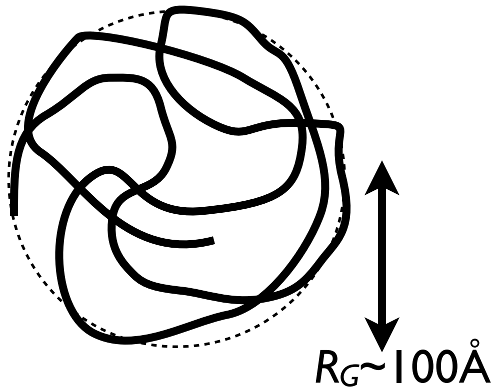
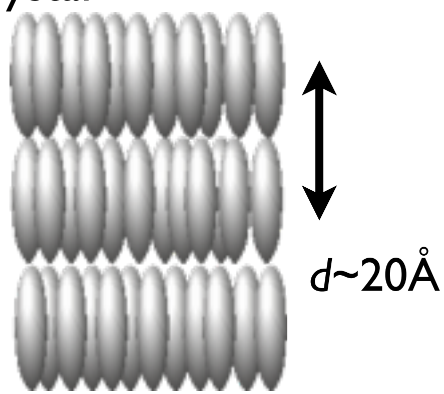
Nano-scale Structures in Soft Matter

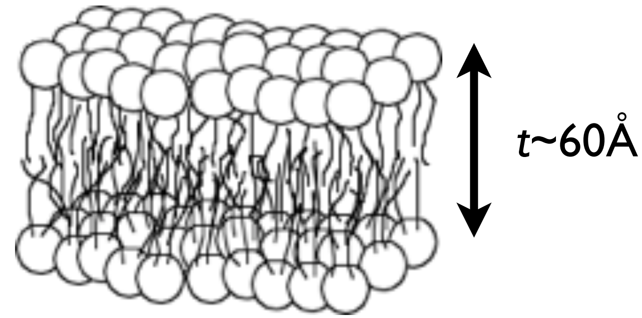
polymer



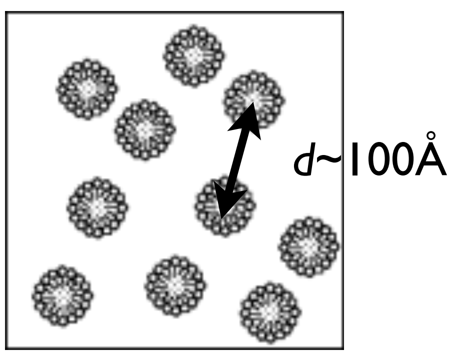
liquid crystal



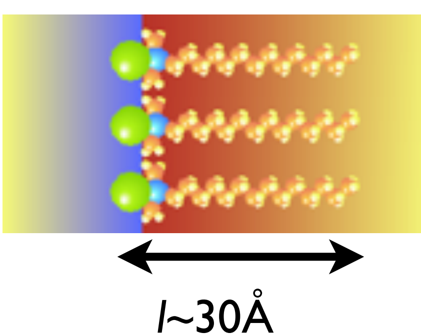
membrane



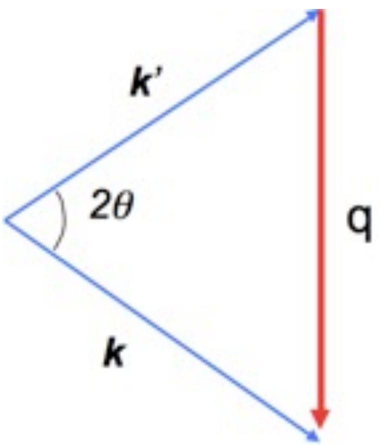
colloids



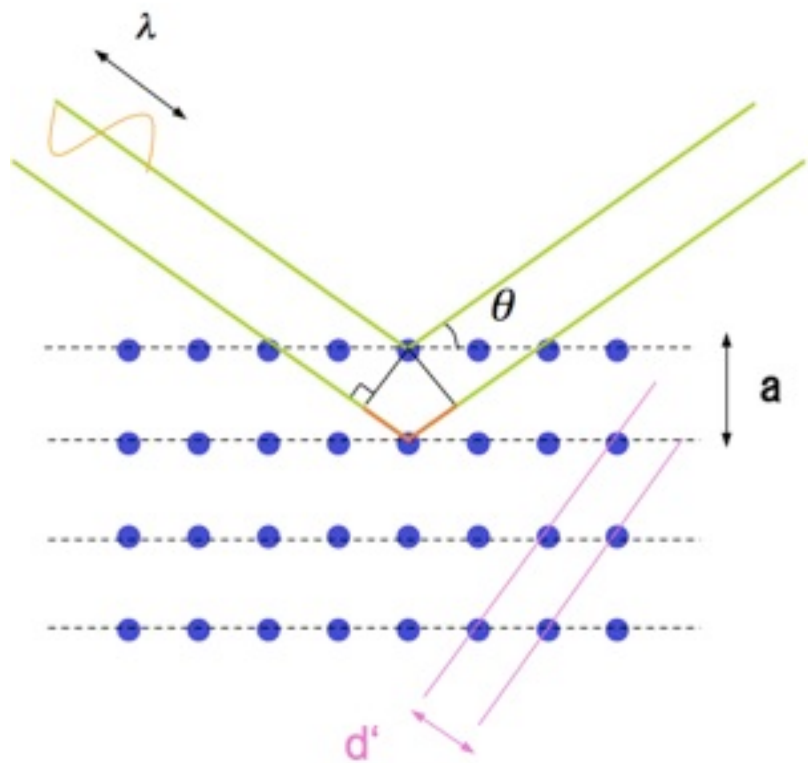
surfactant



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: $2a \sin\theta = n\lambda$

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

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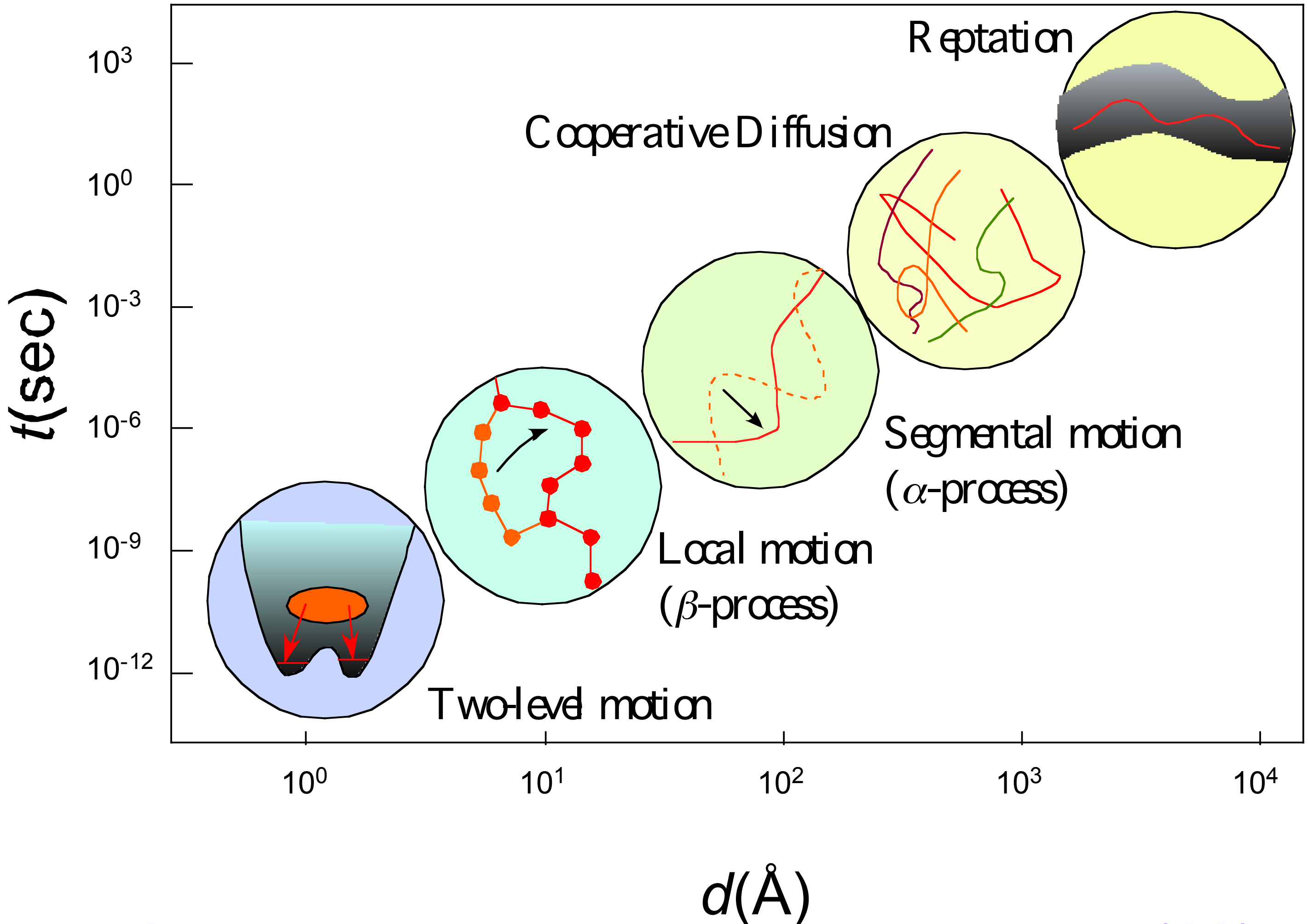
Hierarchical dynamics



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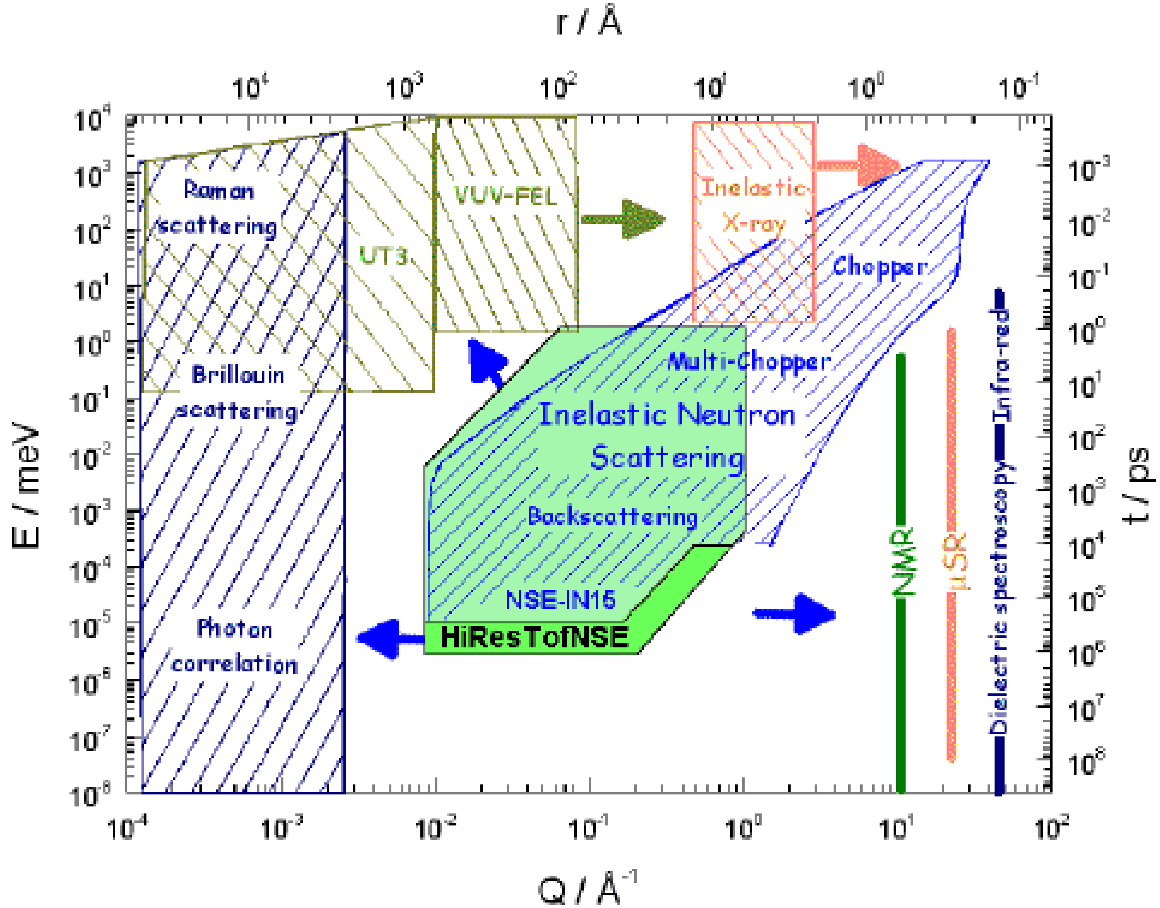
Inelastic/Quasi-elastic scattering

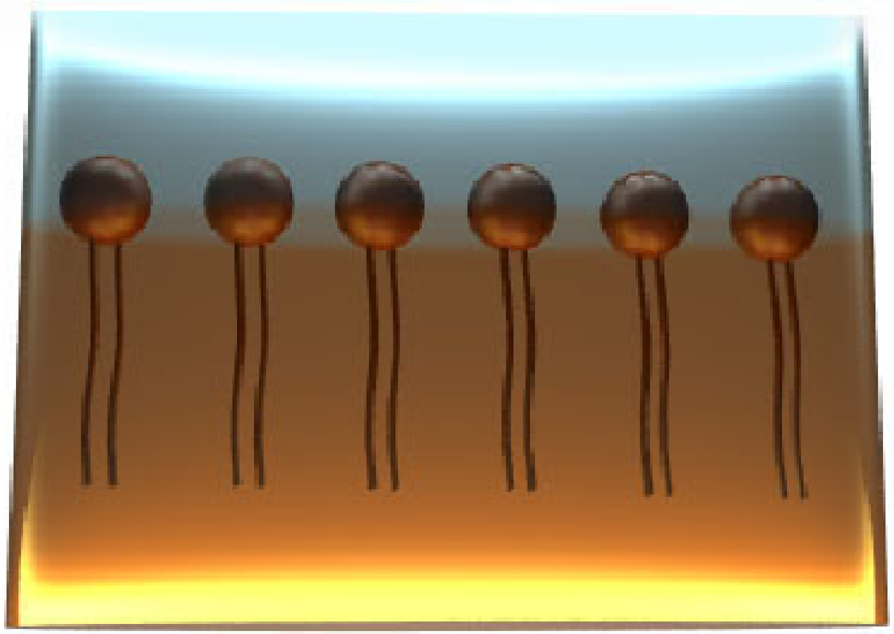


Surfactants

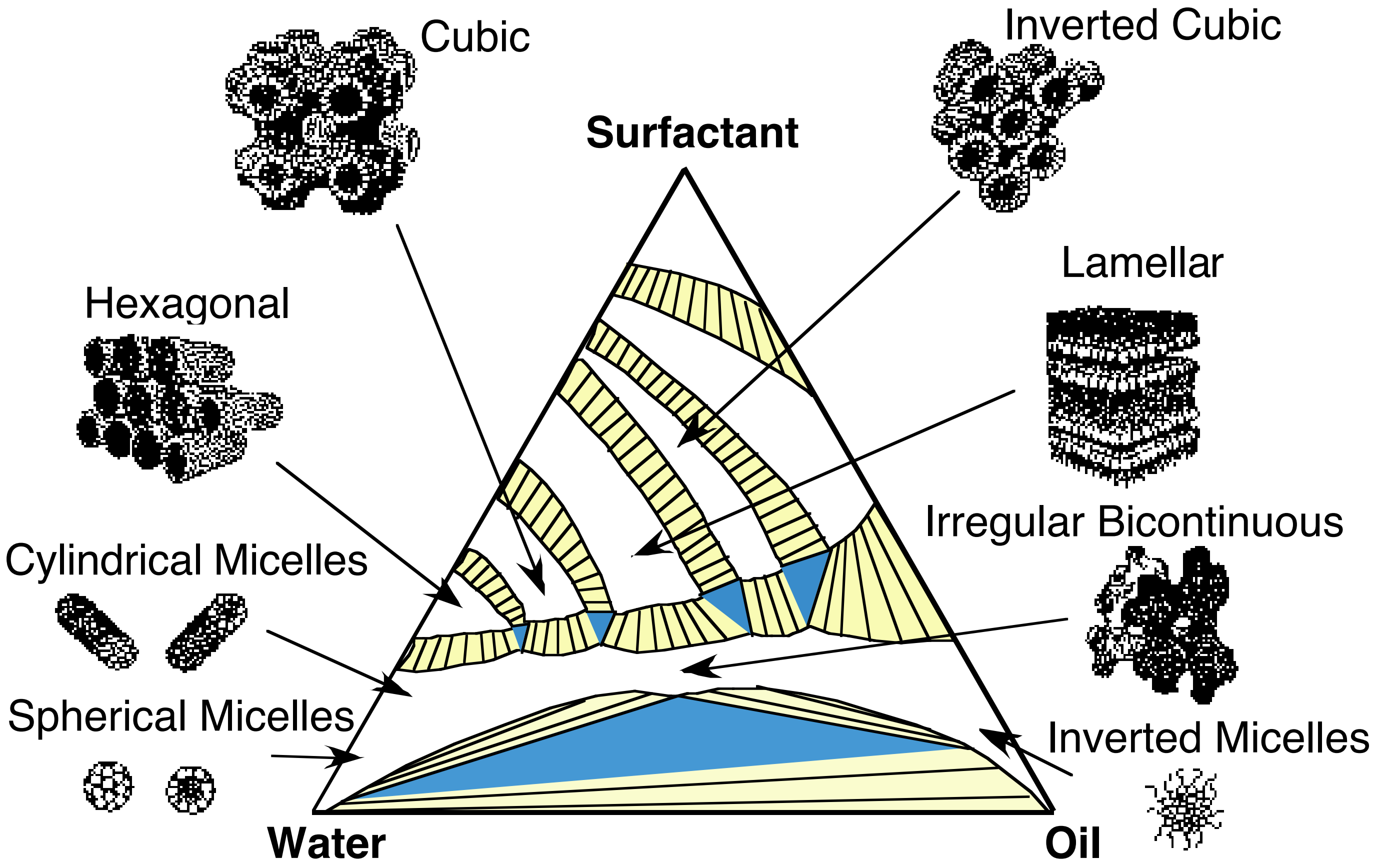
Amphiphilic property

hydrophilic

hydrophobic



Semi-microscopic structures



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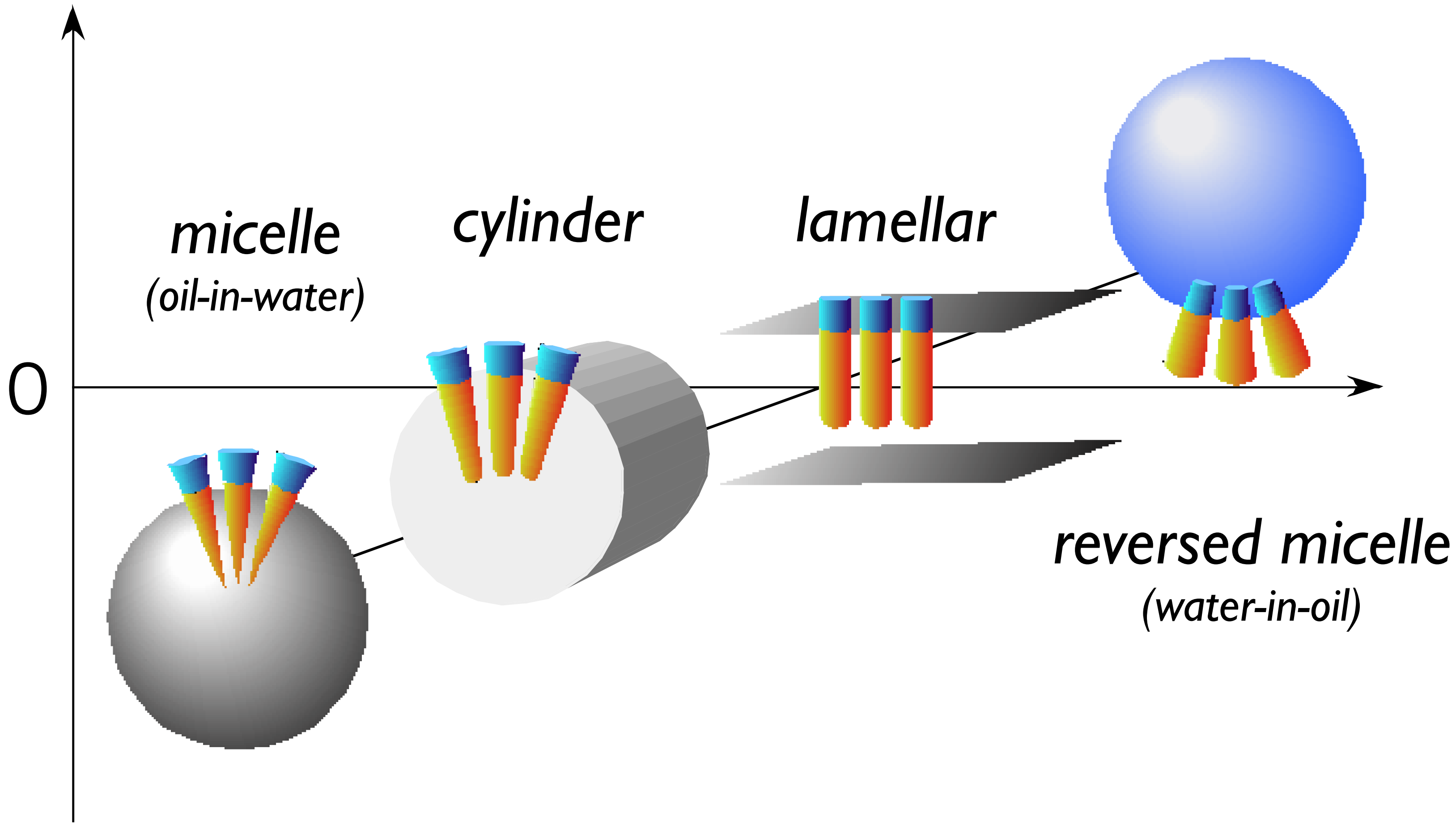
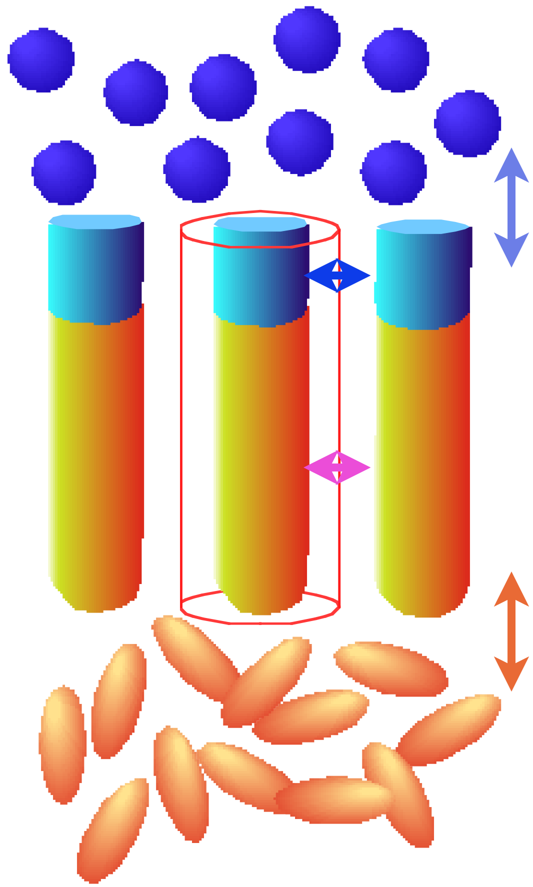
Spontaneous Curvature

depends on packing parameter

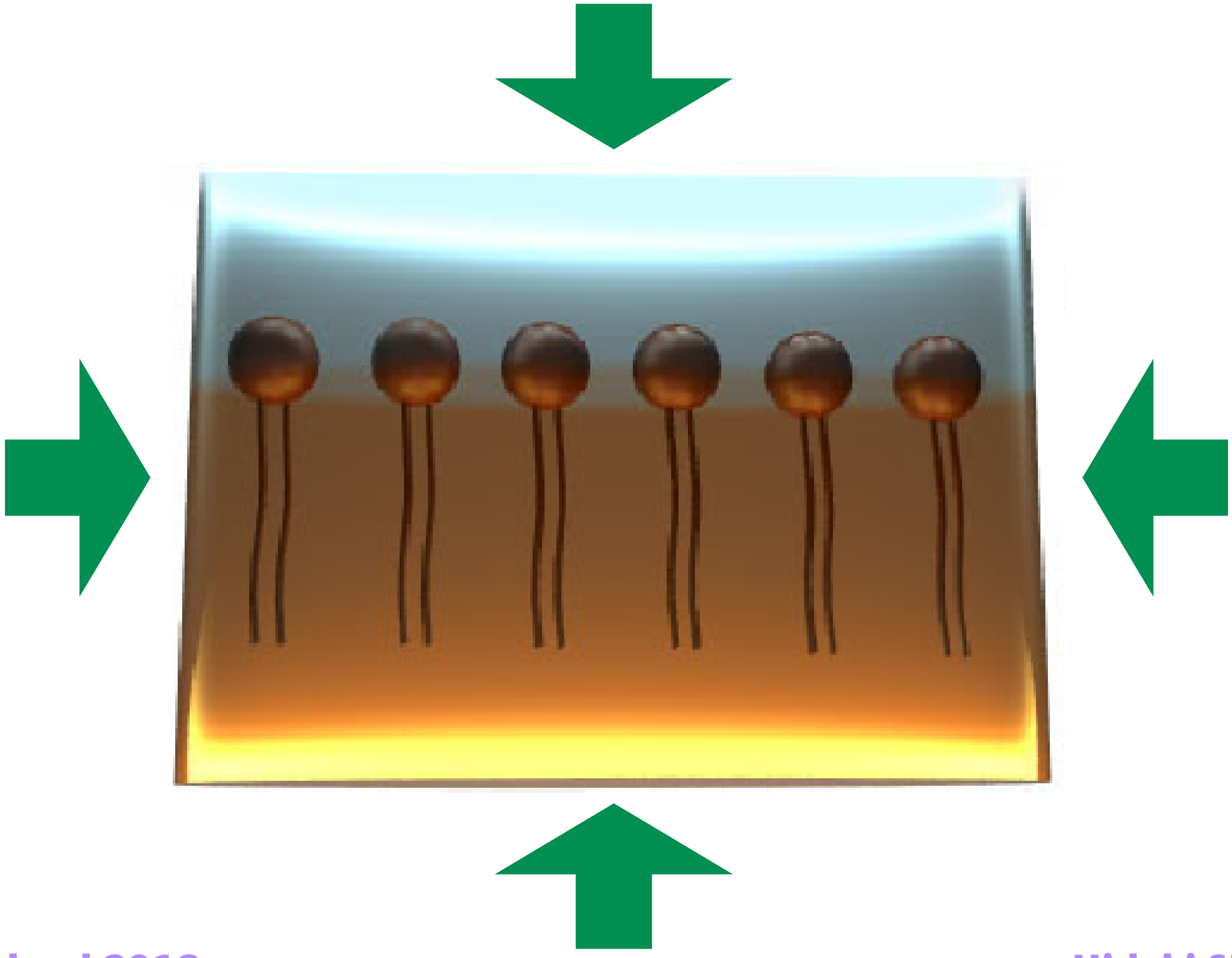


Packing parameter

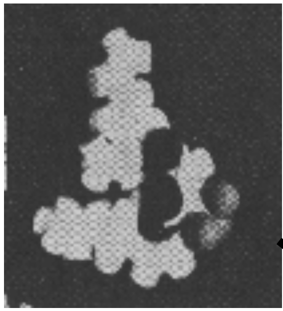


Pressure dependence

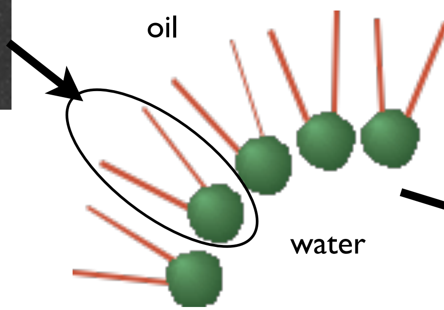
M. Nagao, HS, et al. 1999-2007



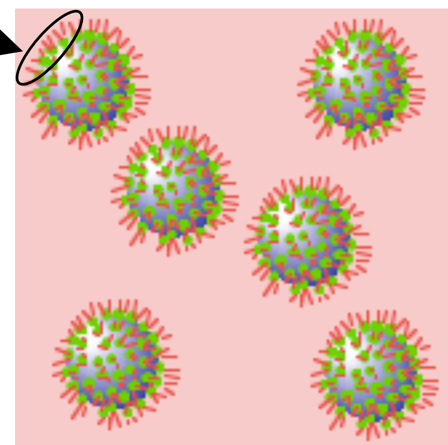
AOT + D_2O + *n*-decane



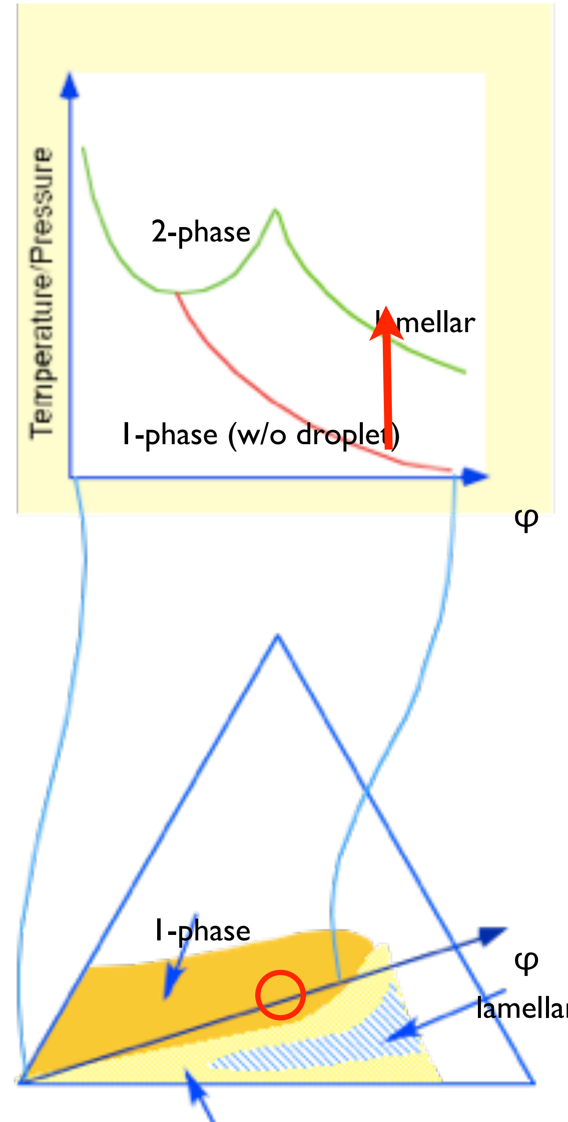
AOT molecule



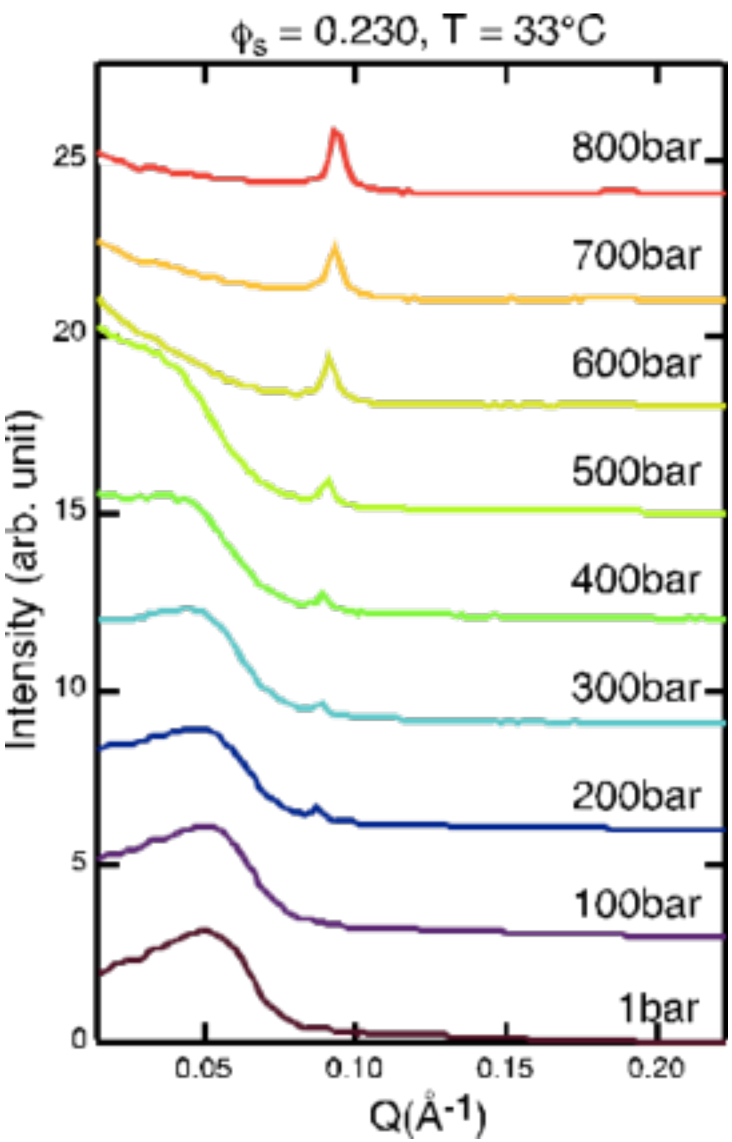
spontaneous curvature > 0



water-in-oil droplet

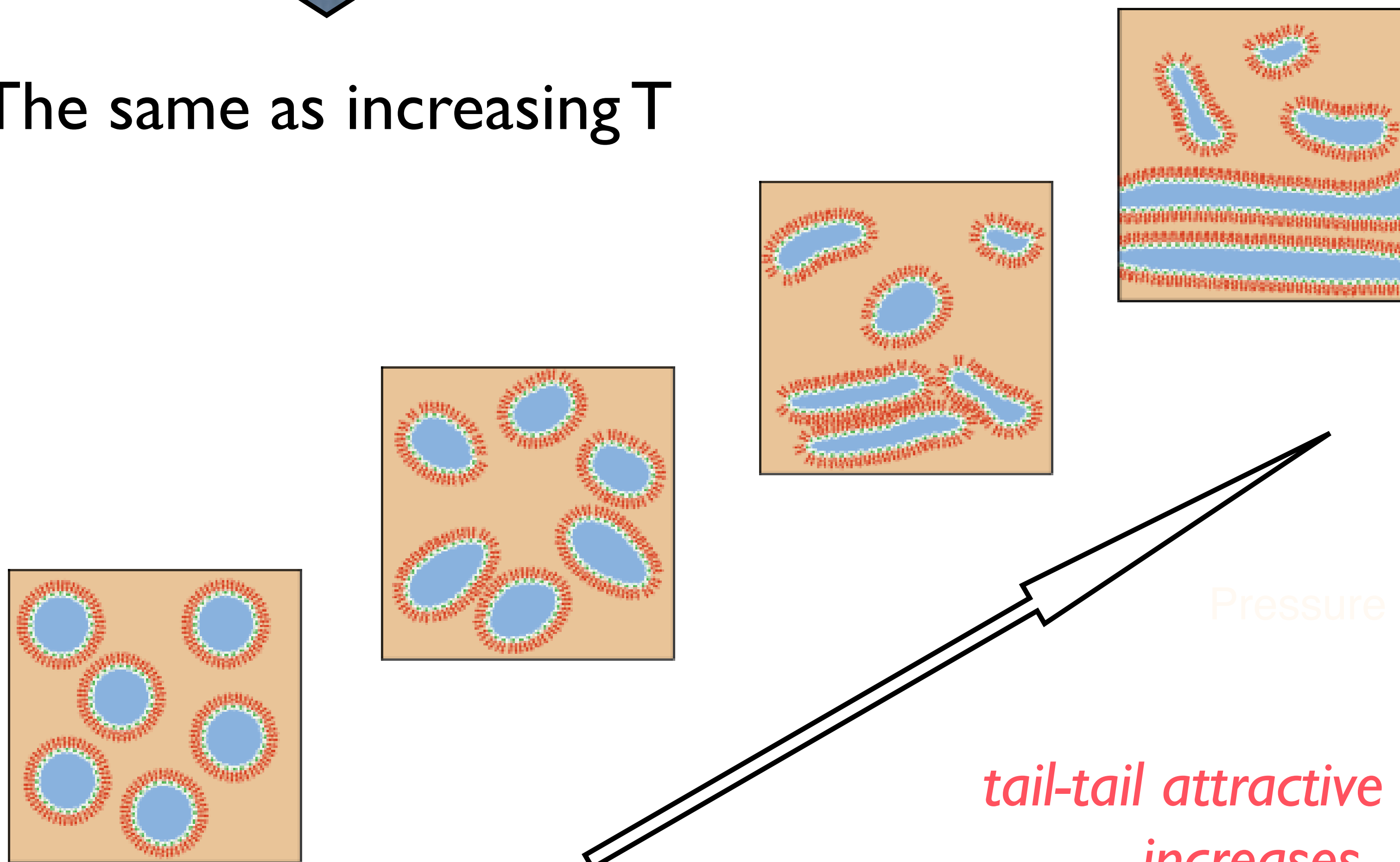


Pressure dependence of SAXS



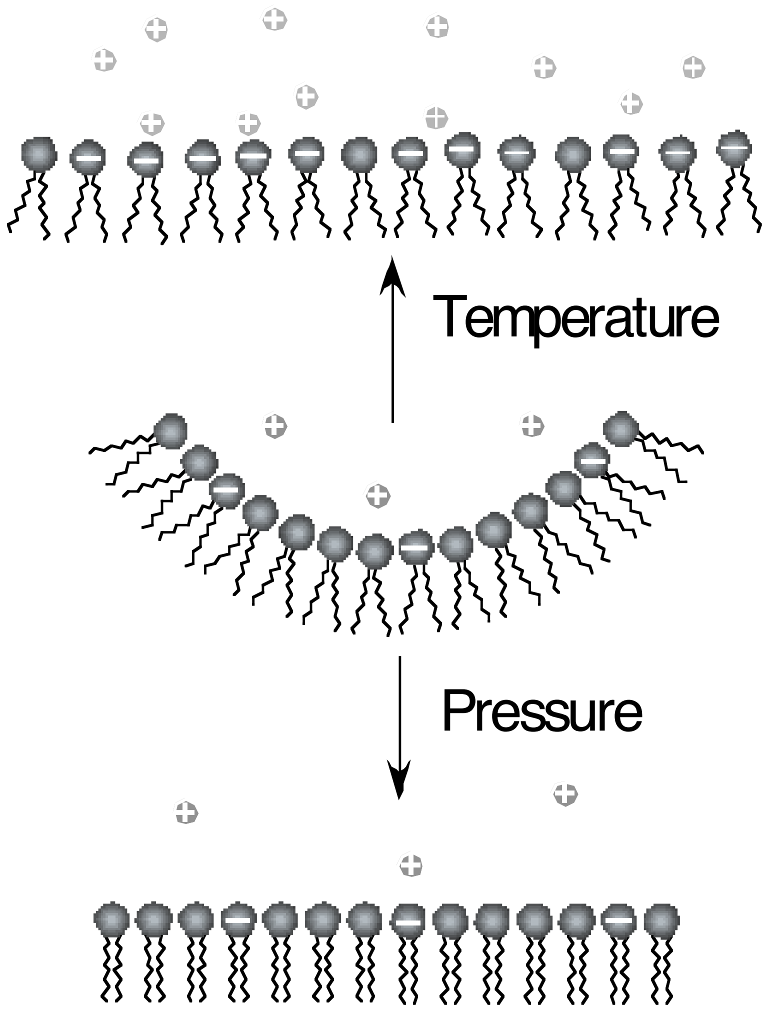
Structure change with P

The same as increasing T



tail-tail attractive force increases

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

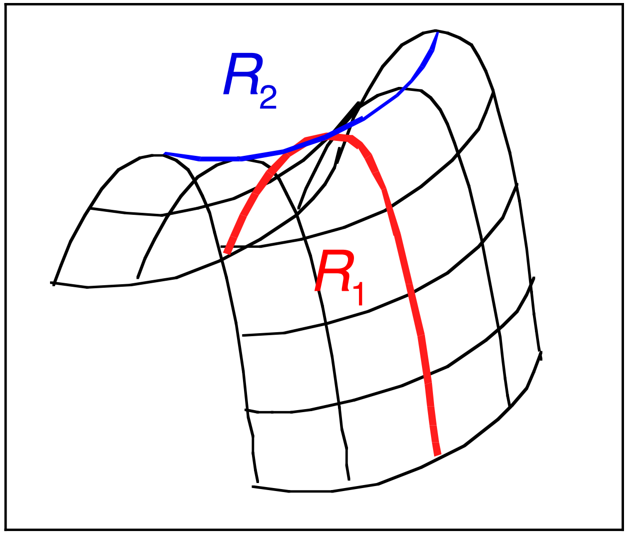


counter-ion dissociation

tail-tail interaction

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

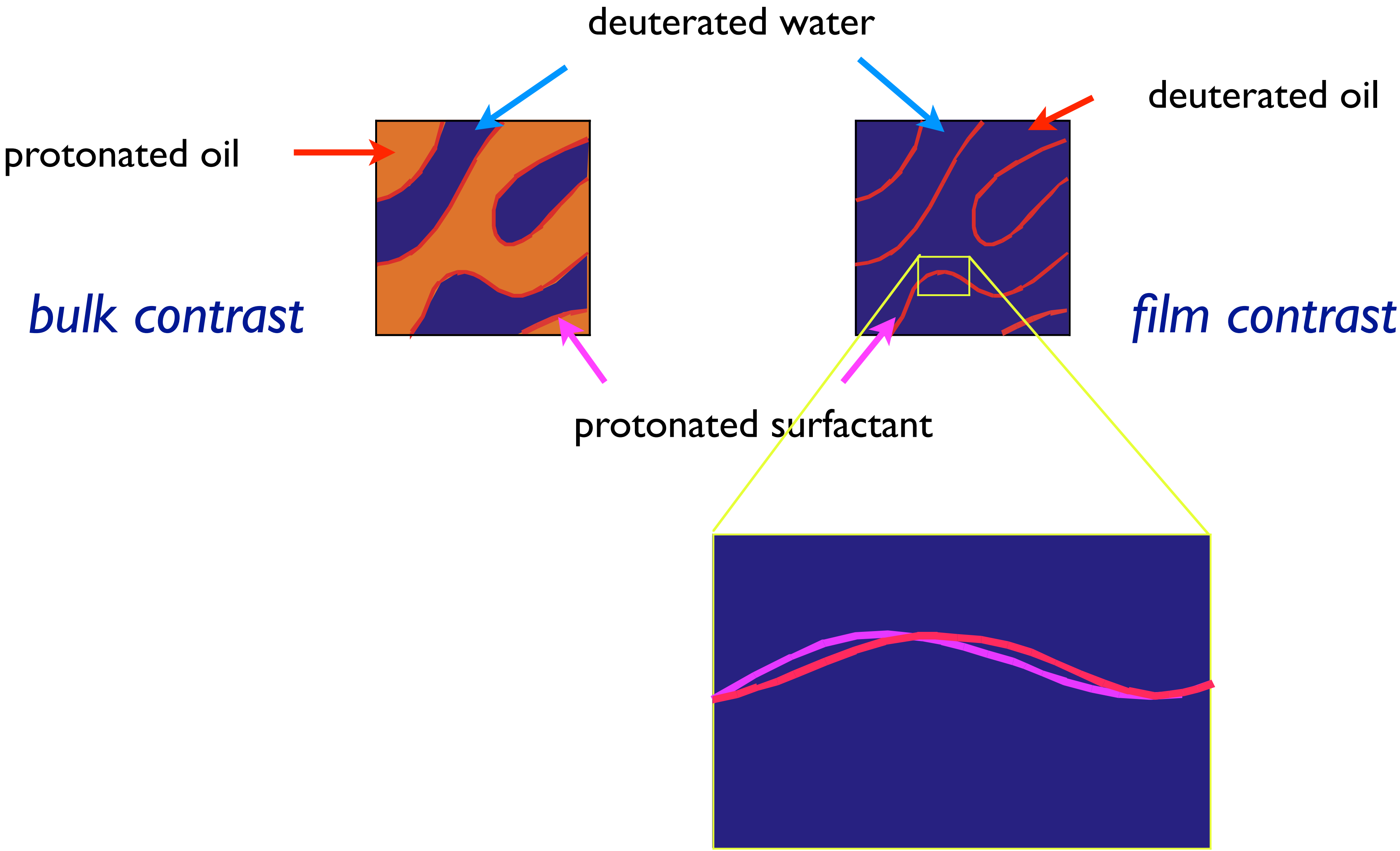
bending modulus

saddle-splay modulus

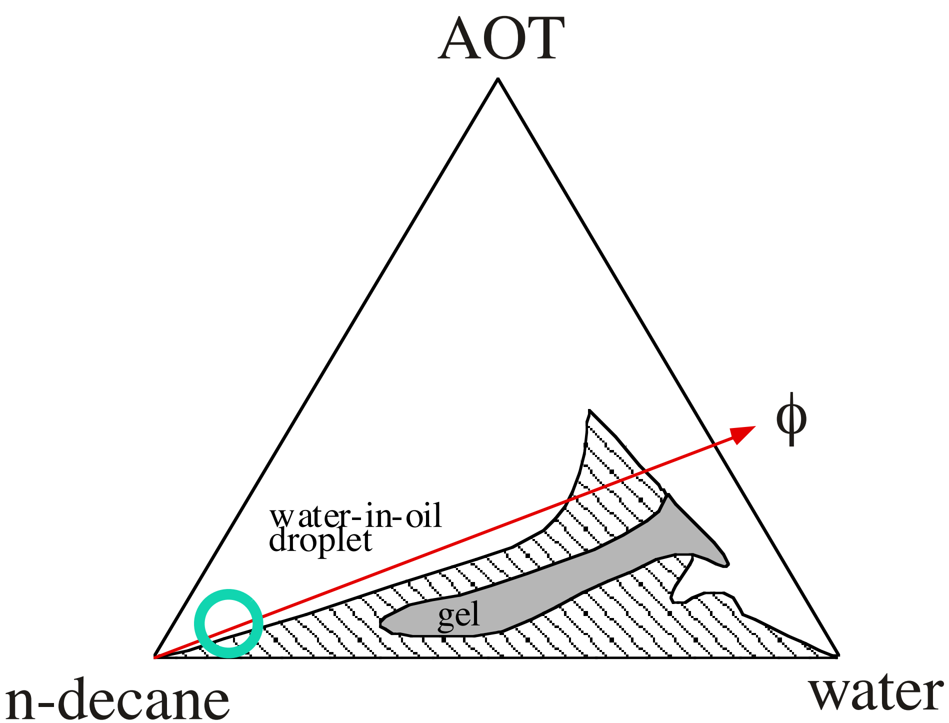
$$E_{bend} = \int \left[\kappa \left(H - \frac{1}{R_s}\right)^2 + \bar{\kappa} K \right] dS$$

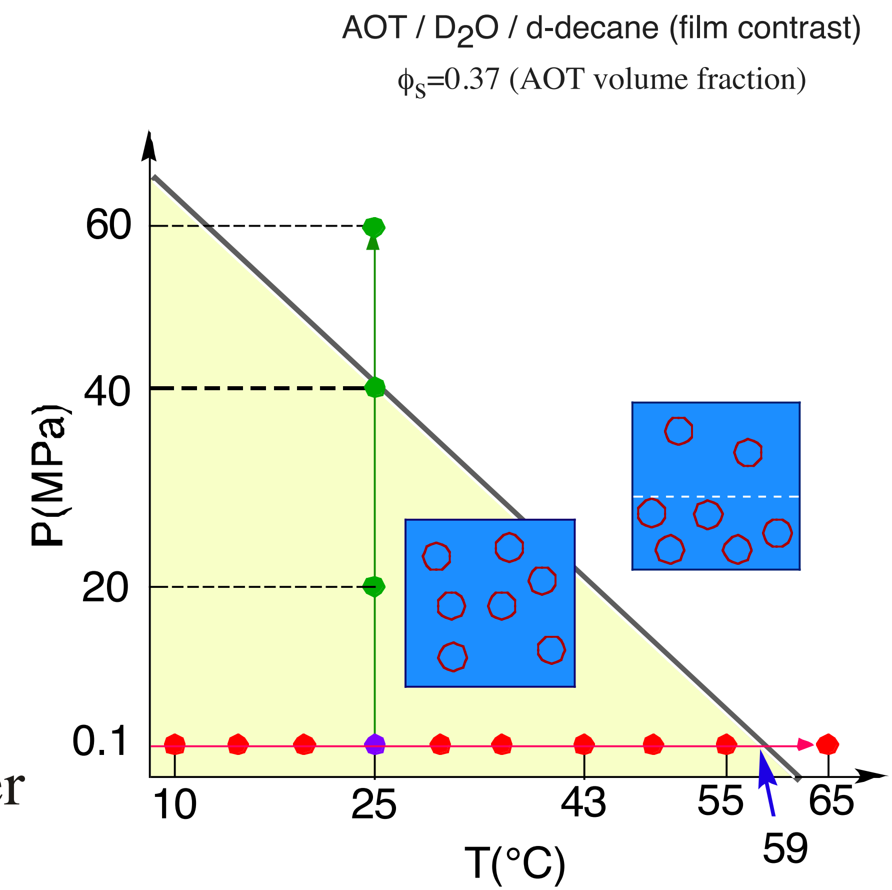
spontaneous curvature

Neutrons see...



Phase separation of a water-in droplet

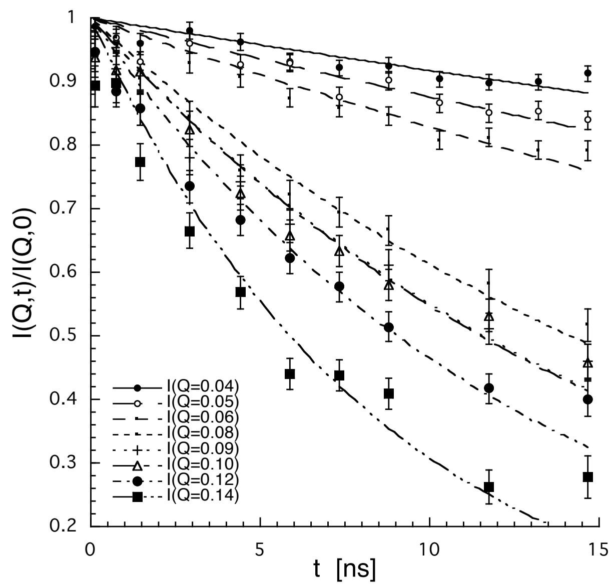




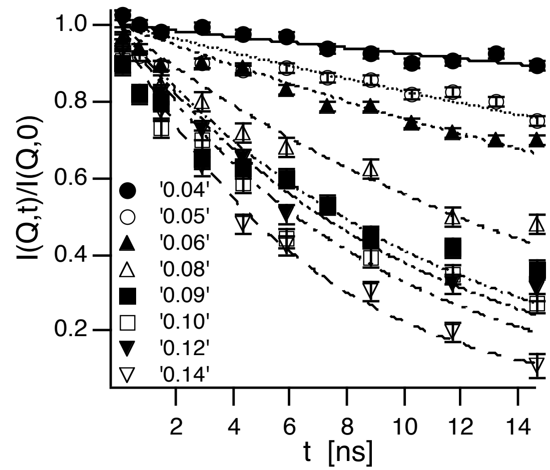
Kawabata et al., Phys. Rev. Lett. **92** (2004) 056103.

Results of NSE experiments

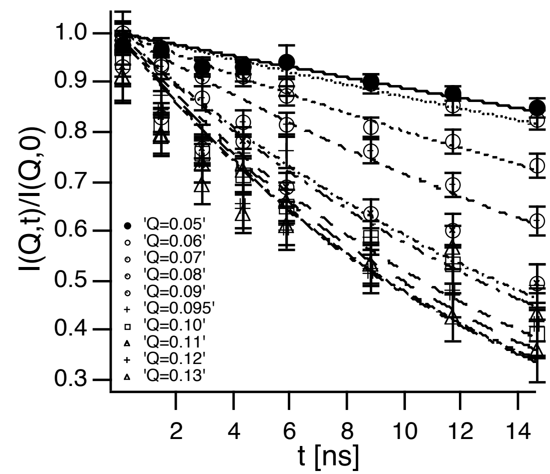
Room temperature/pressure
T=25°C/P=0.1MPa



T=43°C/P=0.1MPa



T=25°C/P=20MPa



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

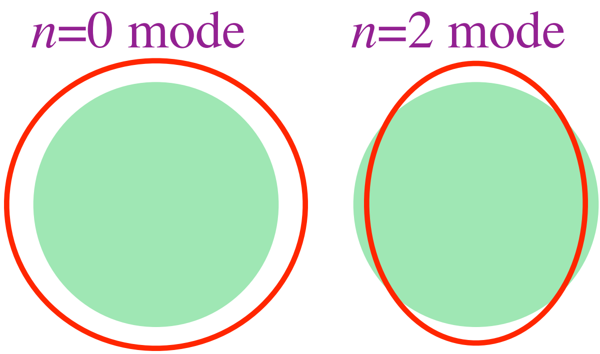
$$I(Q,t)/I(Q,0) = \exp[-D_{eff}Q^2 t]$$

damping frequency of the 2nd mode deformation

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

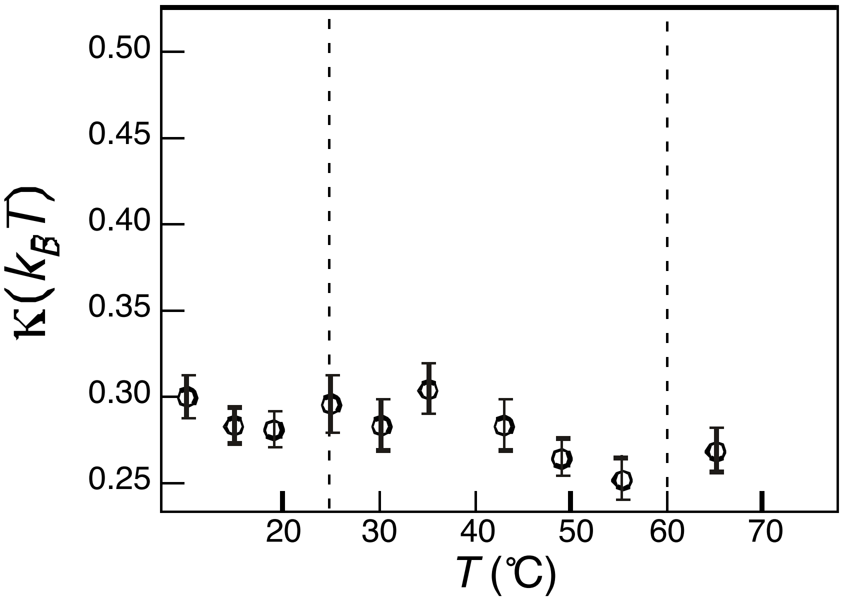


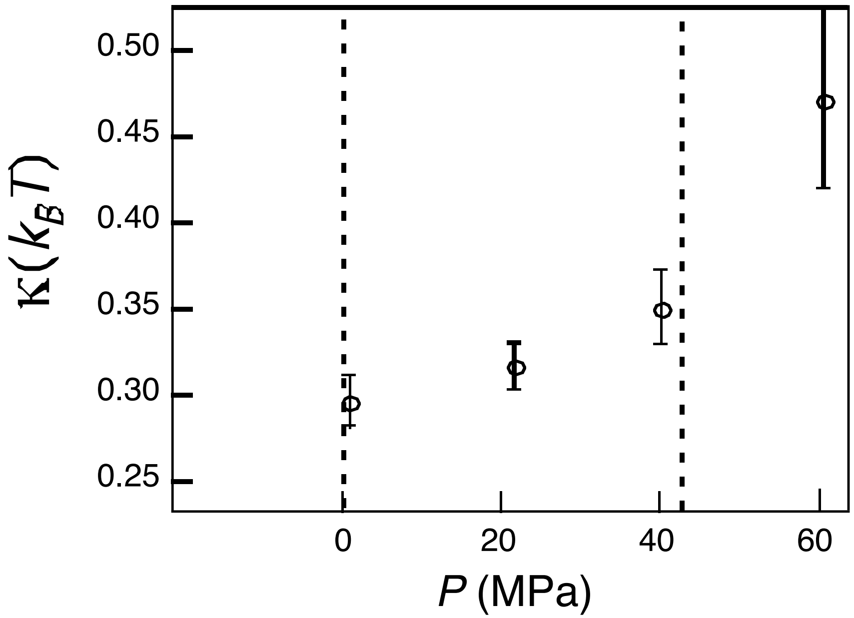
where

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

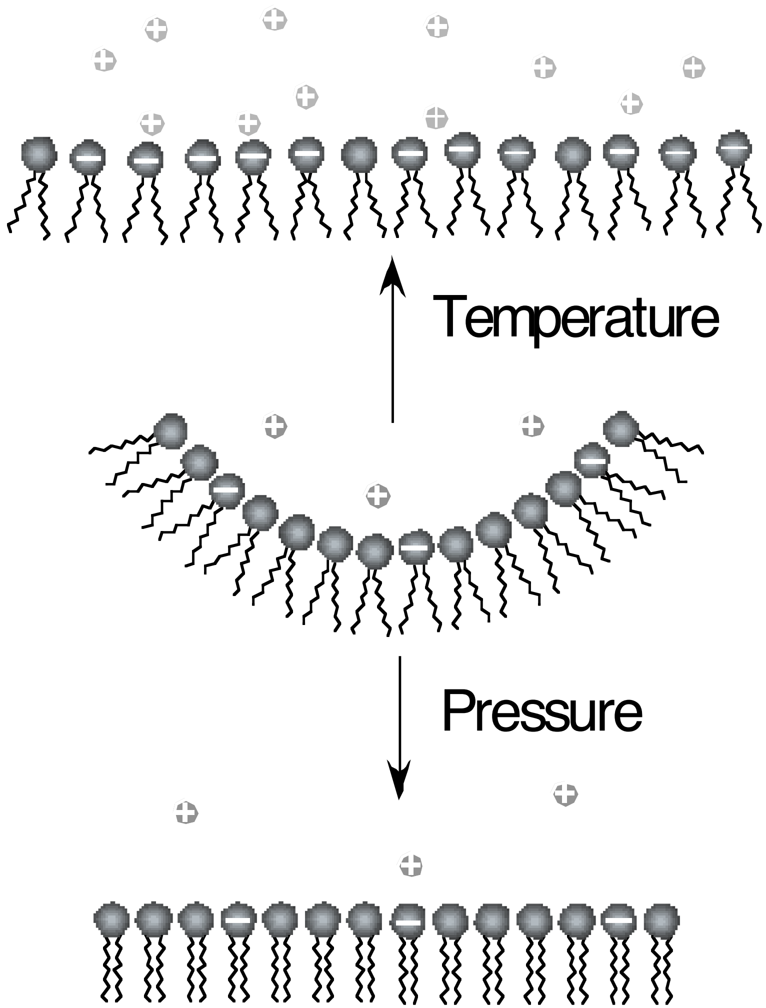
$$f_2(QR_0) = 5[4\,j_2(QR_0) - (QR_0)\,j_3(QR_0)]^2$$

T- and P- dependence of the bending modulus





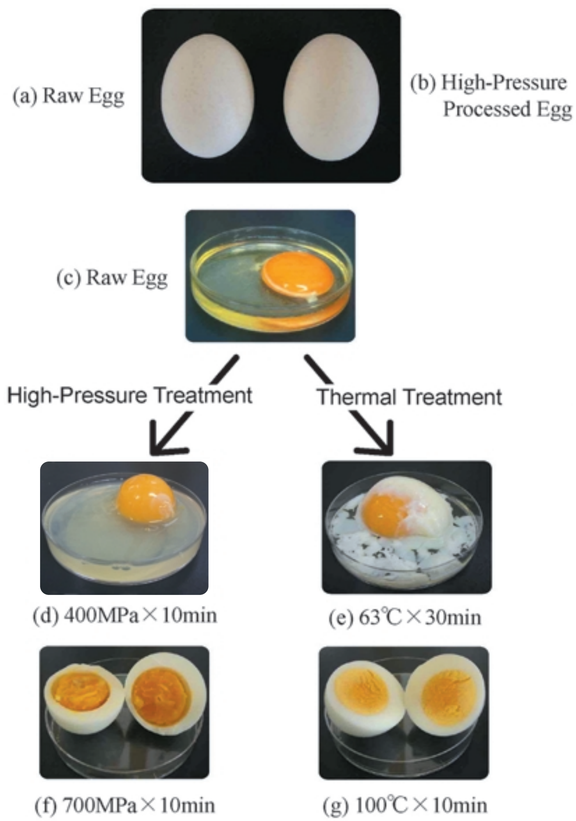
T- and P-effects on an ionic surfactant monolayer



	spontaneous curvature	bending modulus
Temperature	decrease	decrease
Pressure	decrease	increase

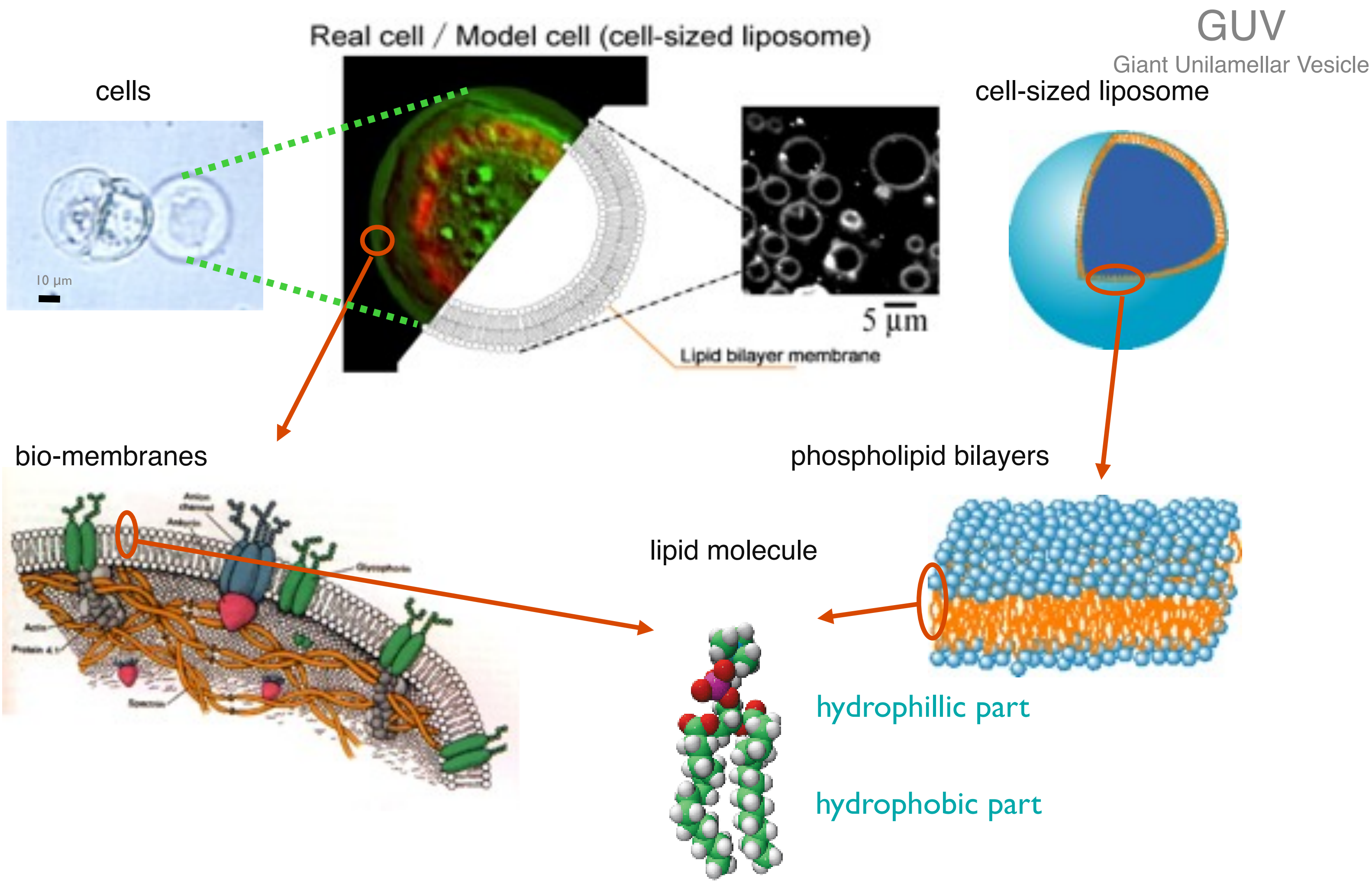
Possible application

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

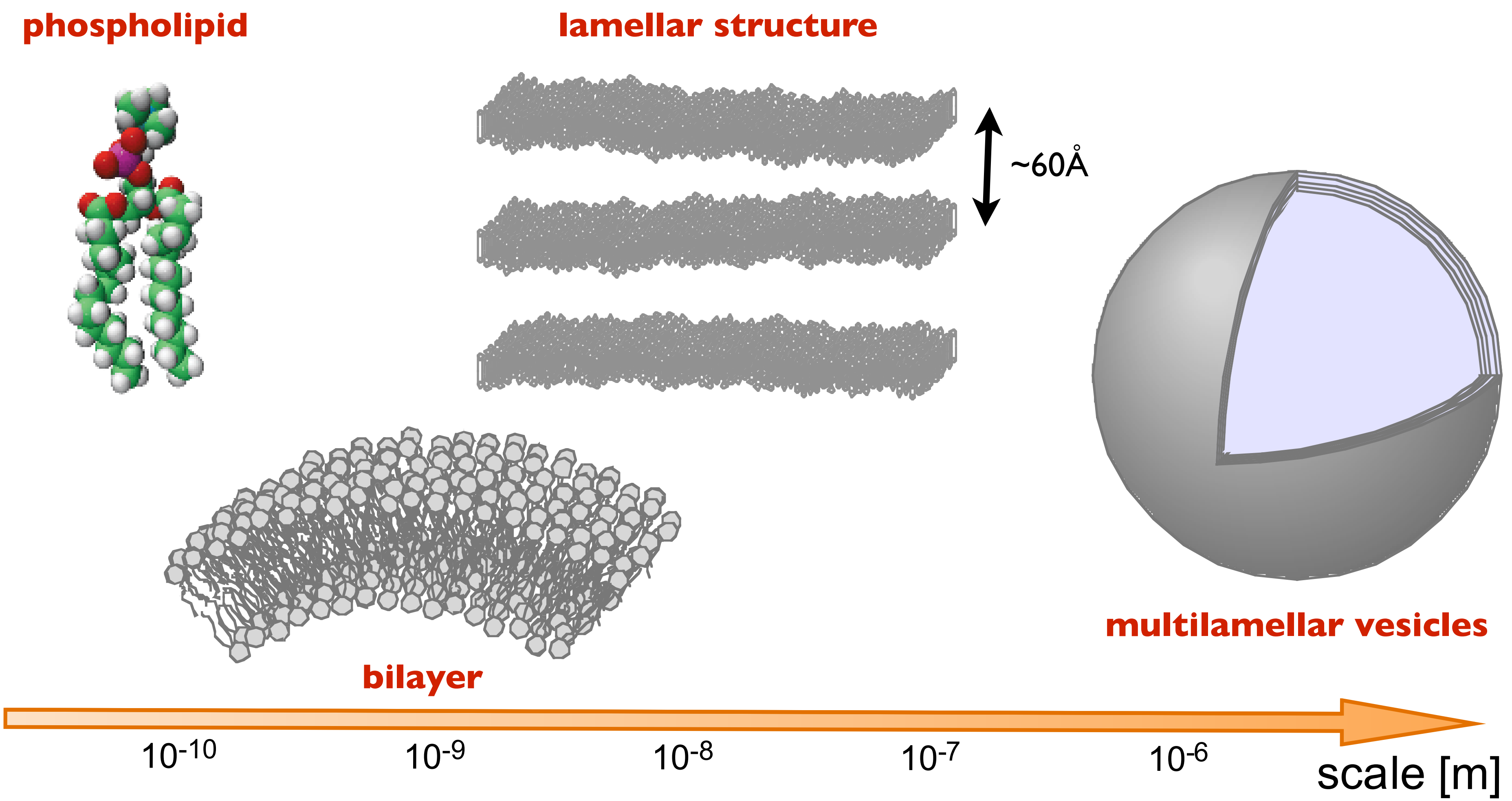


Lipids

Cells and Vesicles



Lamellar structure of lipid bilayers



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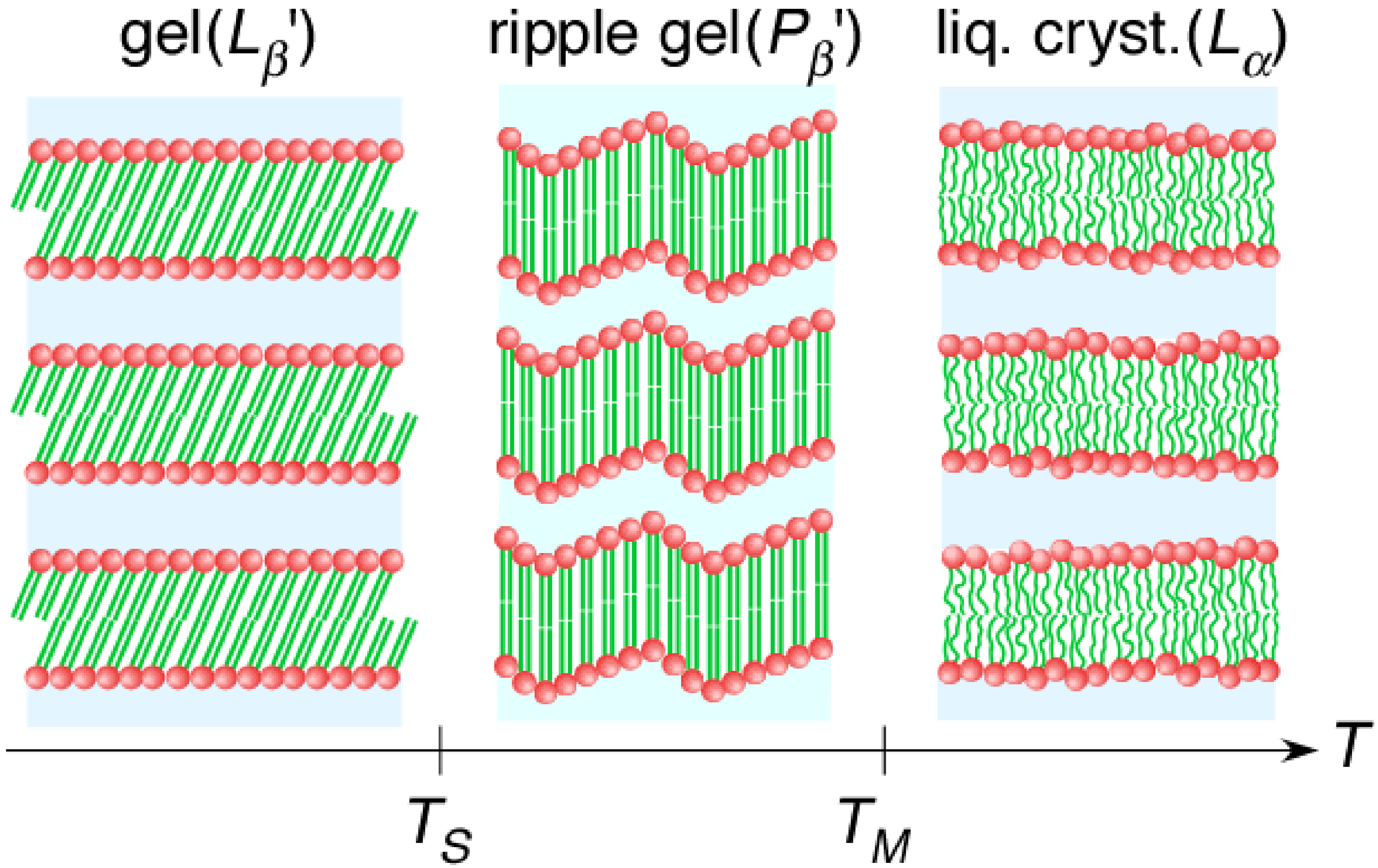
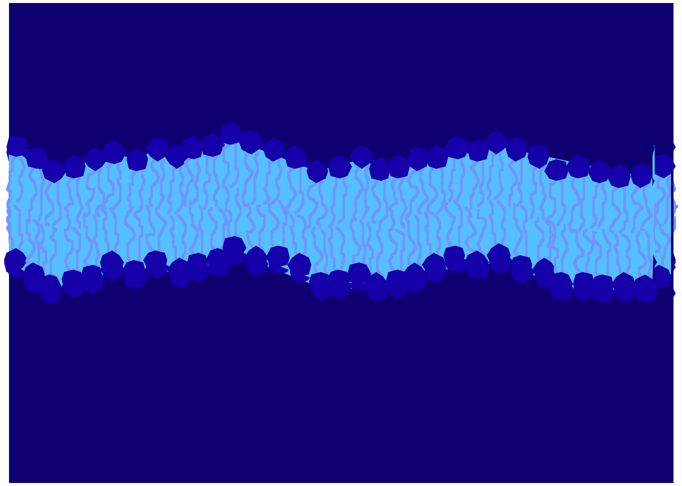
Phase transitions of lipid bilayers



Neutron vs X-ray

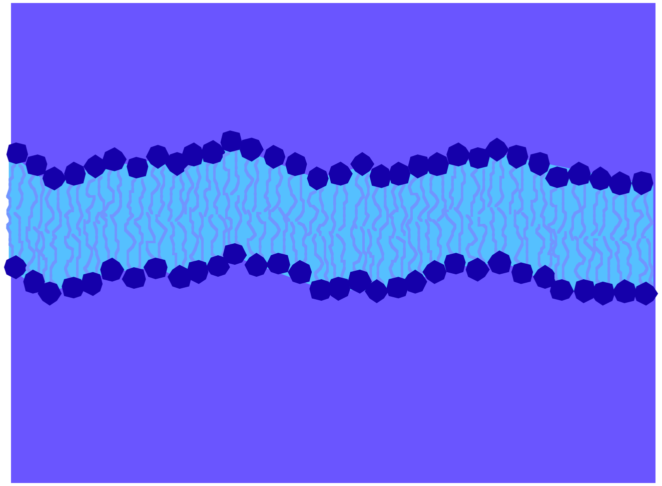
neutron



dynamical behavior

bending modulus

x-ray



static structure

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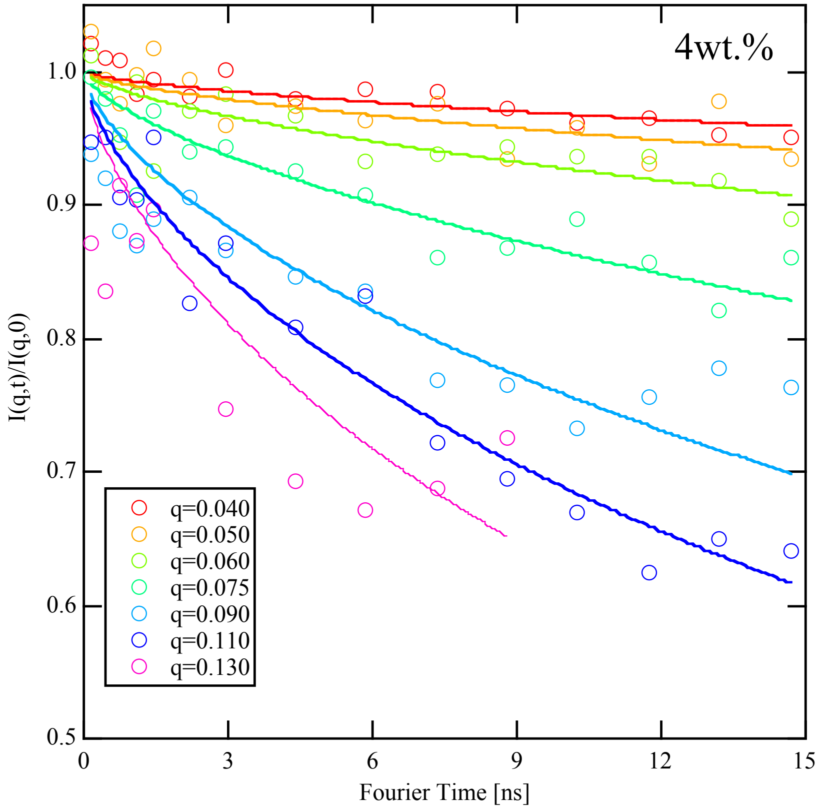
NSE measurements on lipid bilayers

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

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

d~1000Å

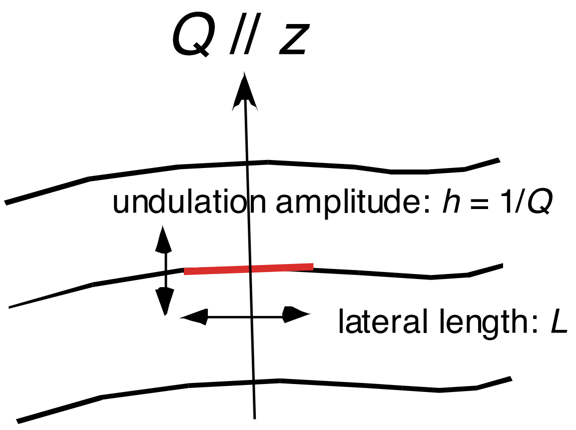
Considered as a single membrane fluctuation.



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

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

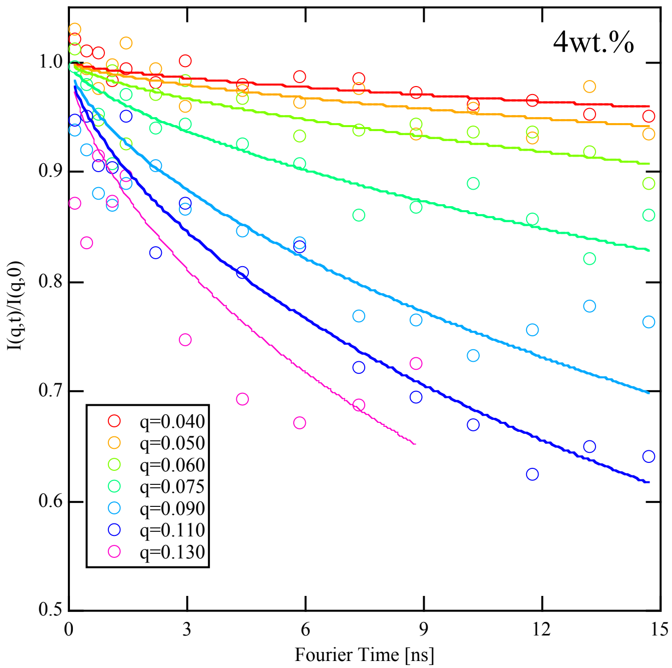
with

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

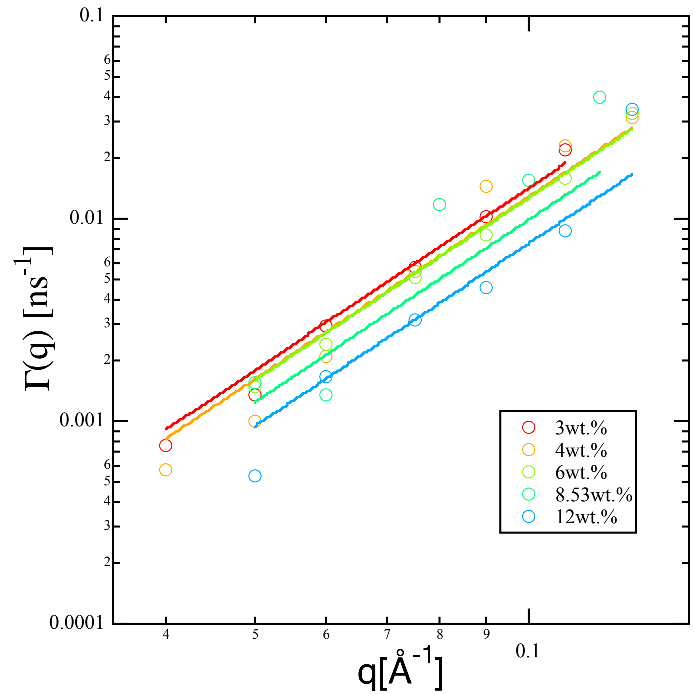
$\gamma_\alpha = 0.024$ (2D object)
$= 0.0056$ (1D object)

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

NSE results



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



$$\Gamma=Aq^3$$

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

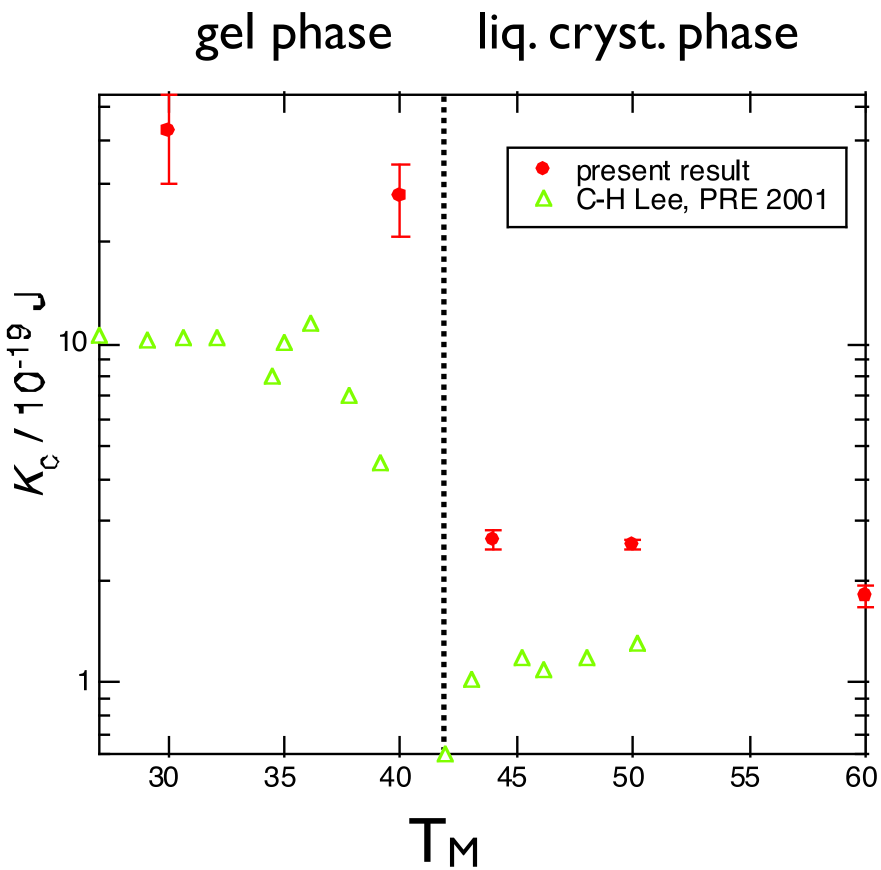
K_c:bending modulus

η: viscosity of D_2O

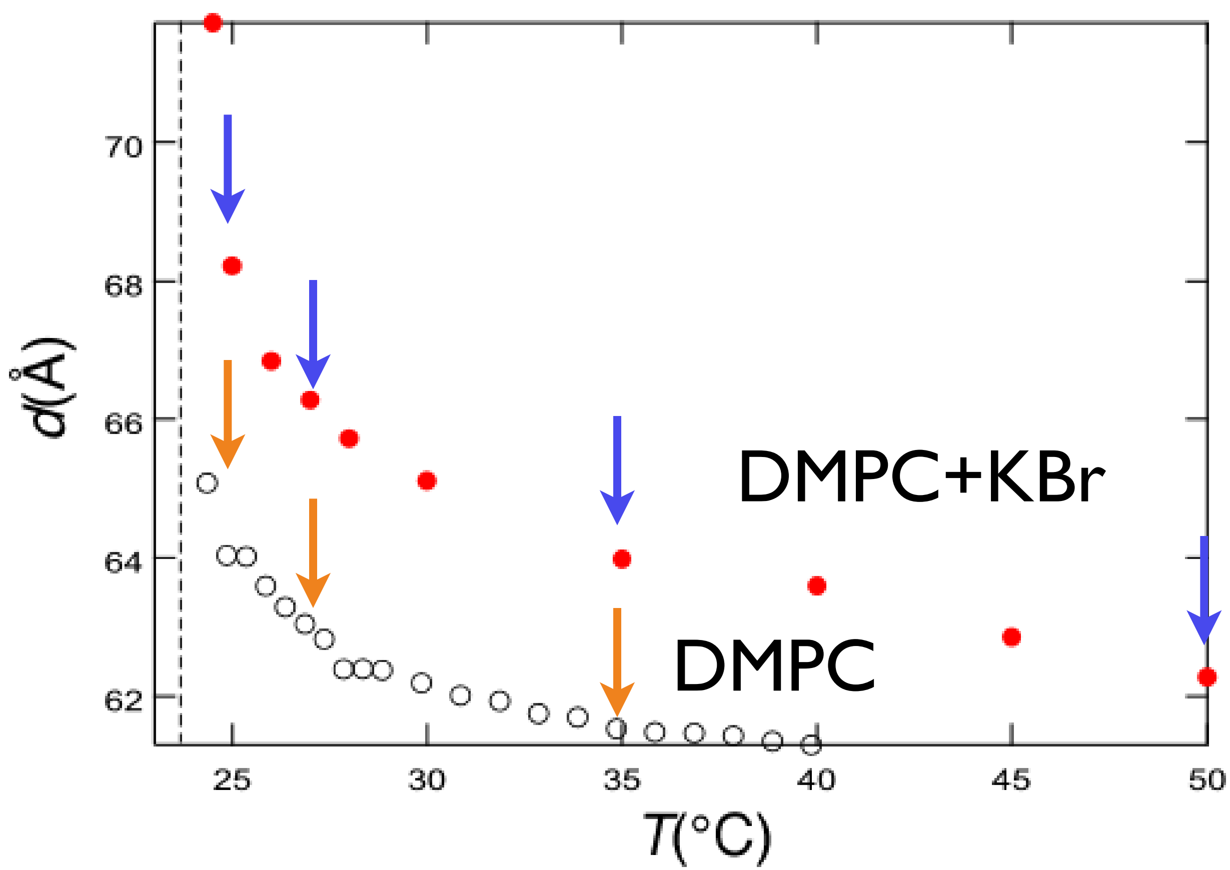
γ_α=0.025 : 2D membrane

γ_κ=1 : $K_c >> k_BT$

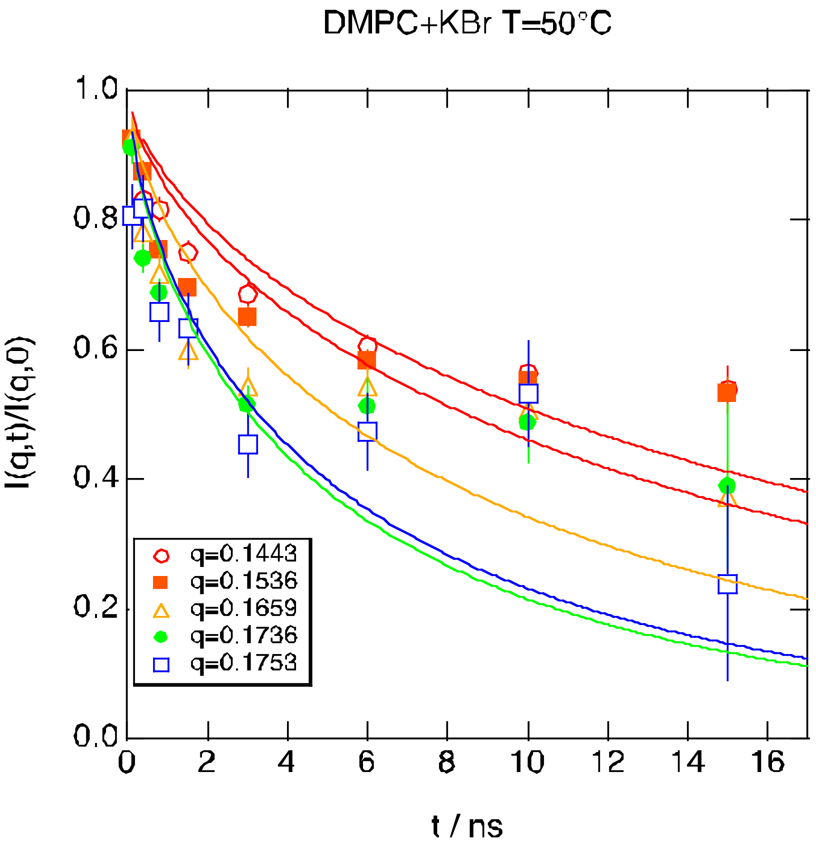
T-dependence of bending modulus

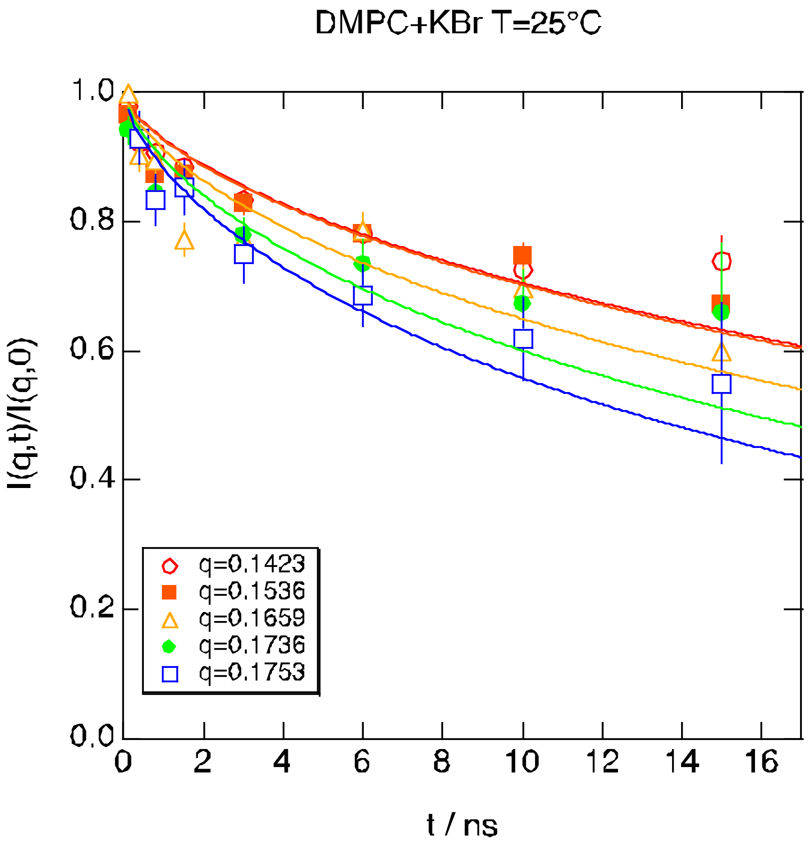


Anomalous swelling above T_M



NSE results

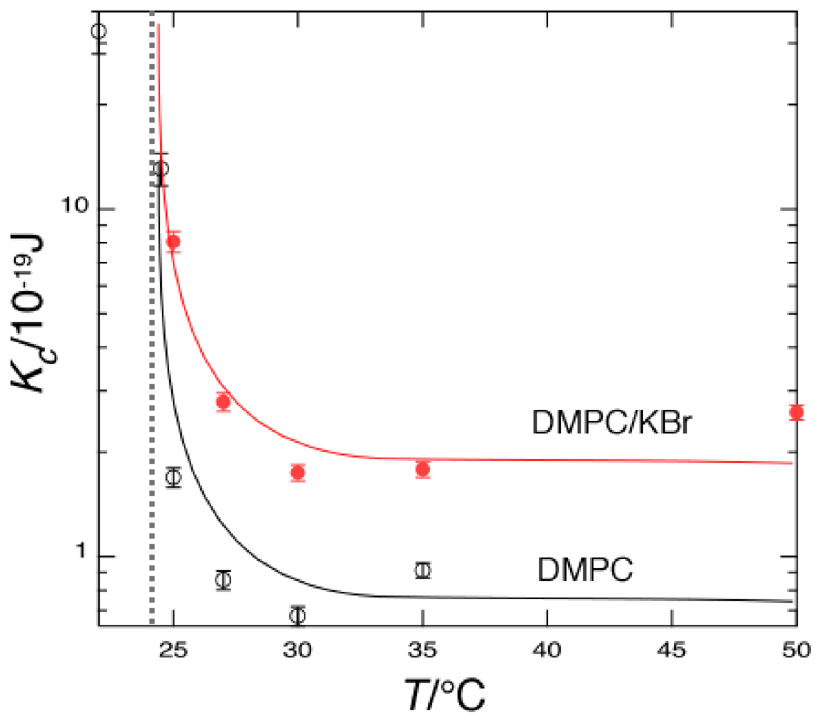




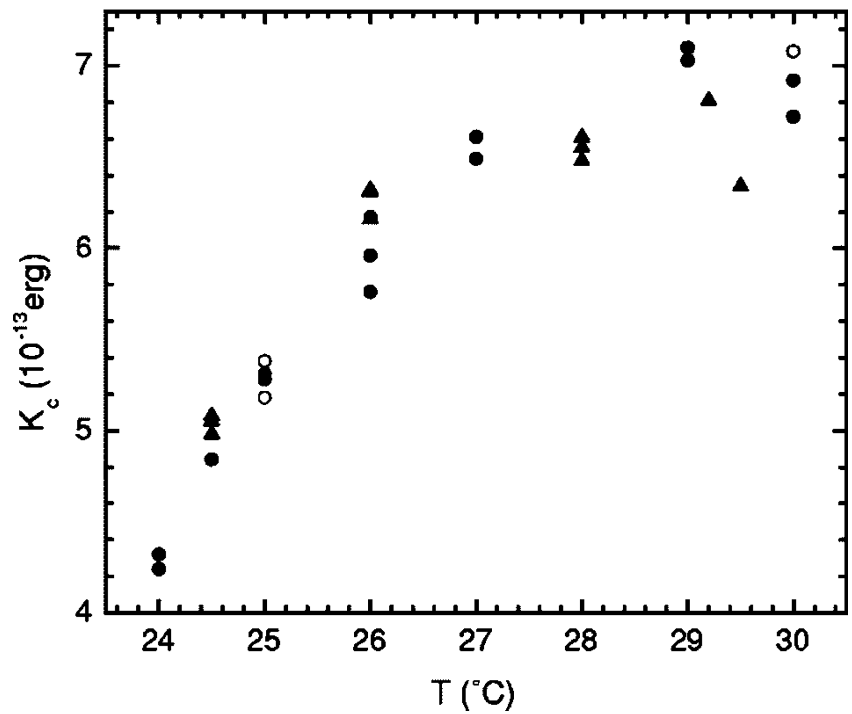
$$I(q,t)/I(q,0) = C\exp[-(\Gamma t)^{2/3}]$$

Bending modulus

NSE, 2007



SAXS, 2005



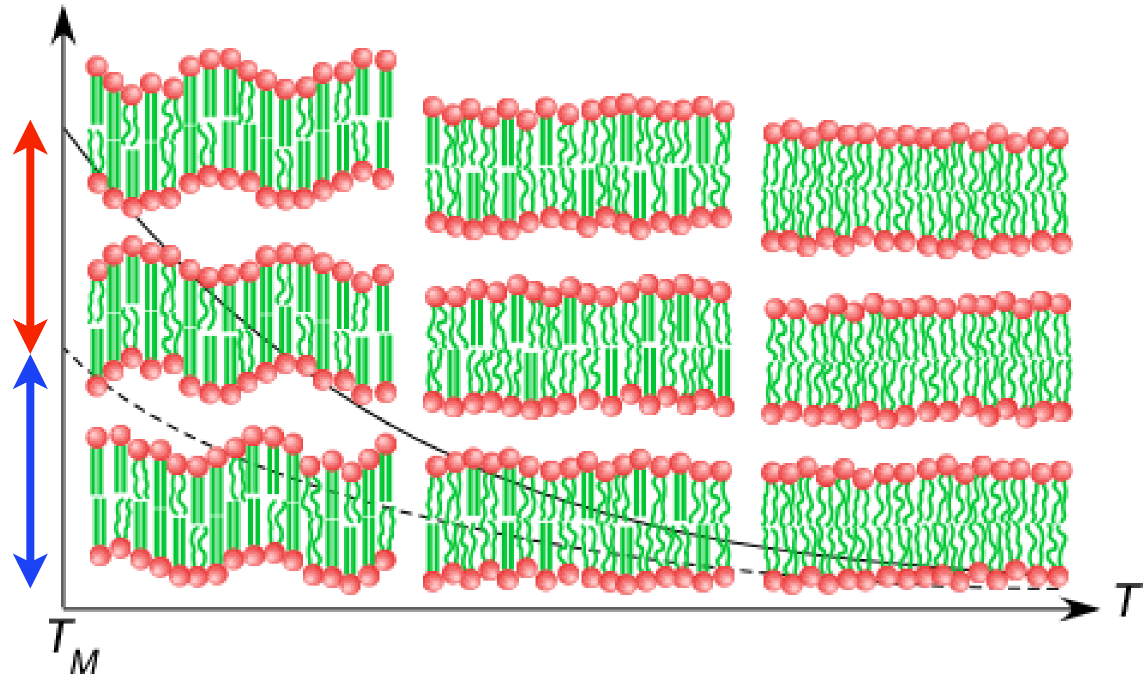
Softening ⇨ Thermal fluctuation increases

⇨ Repeat distance increases

Our interpretation

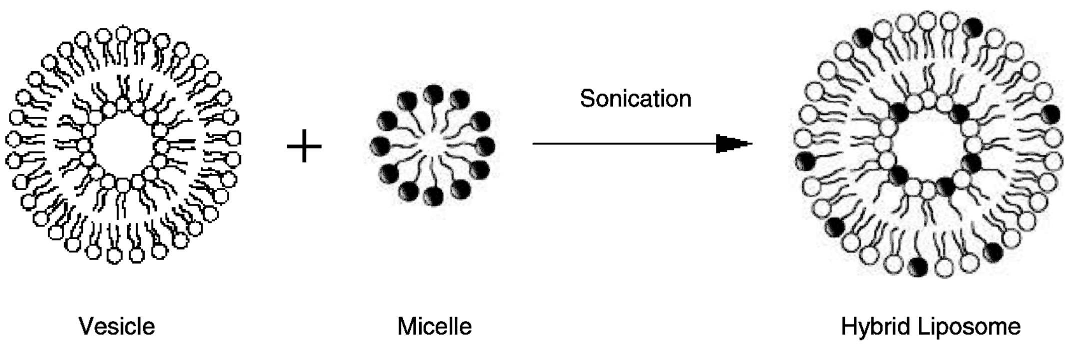
irregular stacking of bumpy layers

thickening & hardening

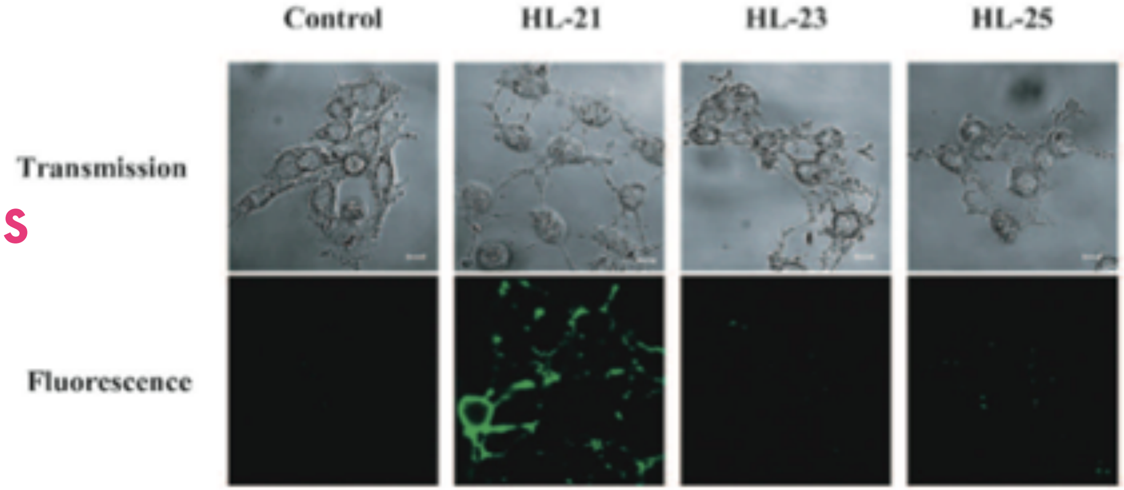


Possible application

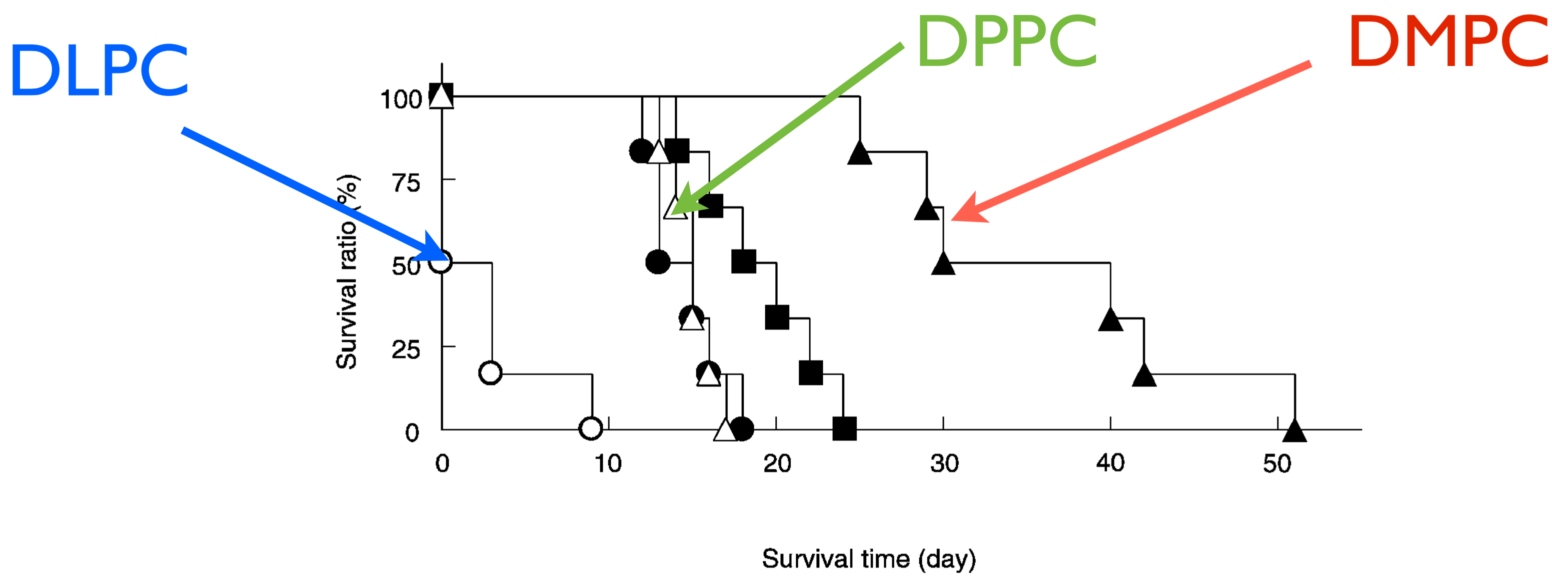
Inhibitory Effects of Hybrid Liposomes on the Growth of Tumor Cells



HL induces apoptosis of tumor cells



Survival ratio depends on lipids



DMPC(LC phase at RT) → compatible with tumor cells
Soft

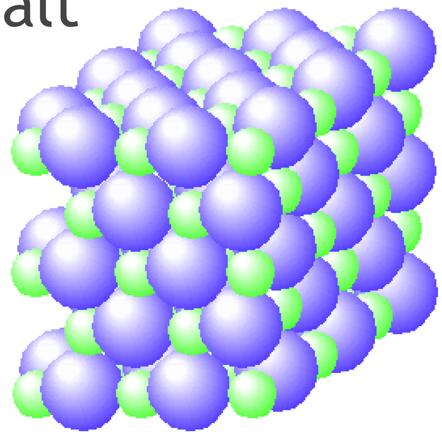
DPPC(Gel phase at RT) → no effect
Hard

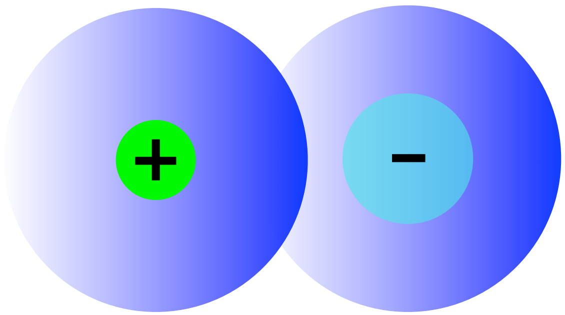
DLPC(LC phase at RT) → kills normal cells
Foreigner

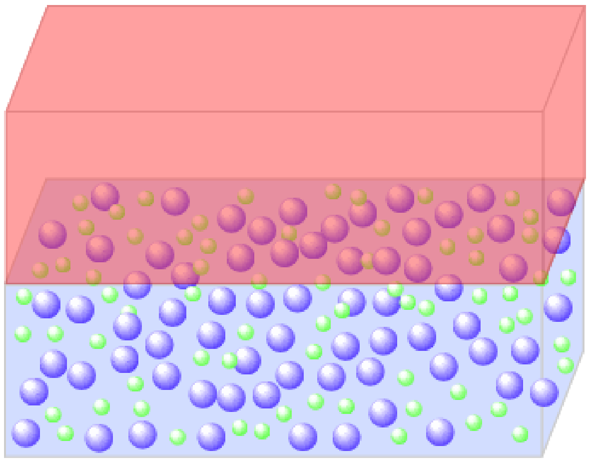
Salts

Salt vs Surfactant

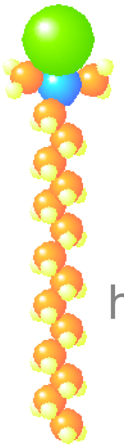
Salt

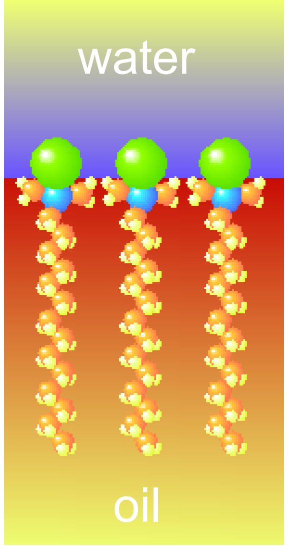


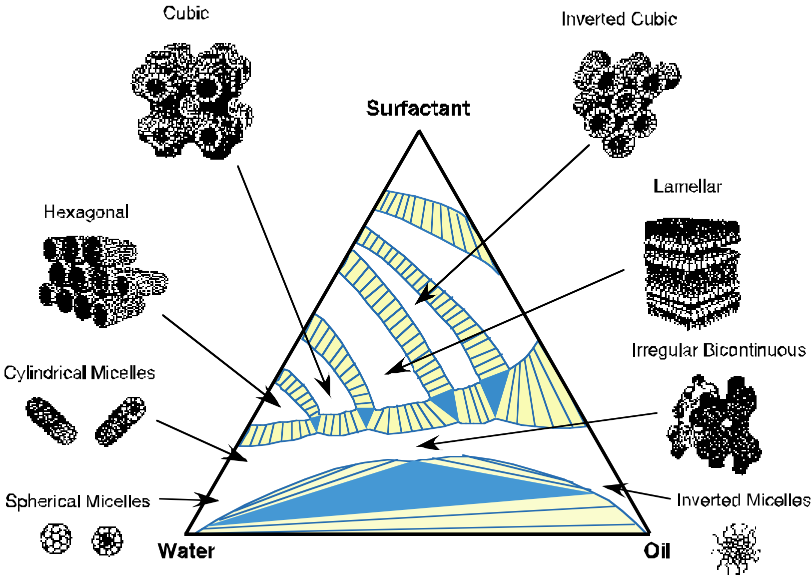




Surfactant







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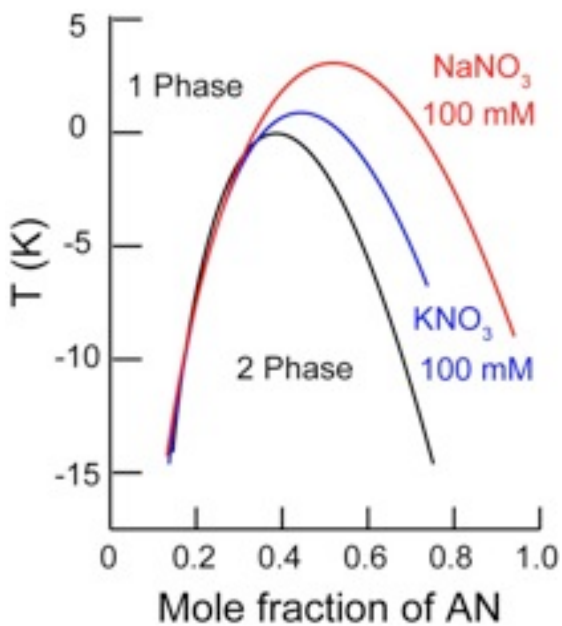
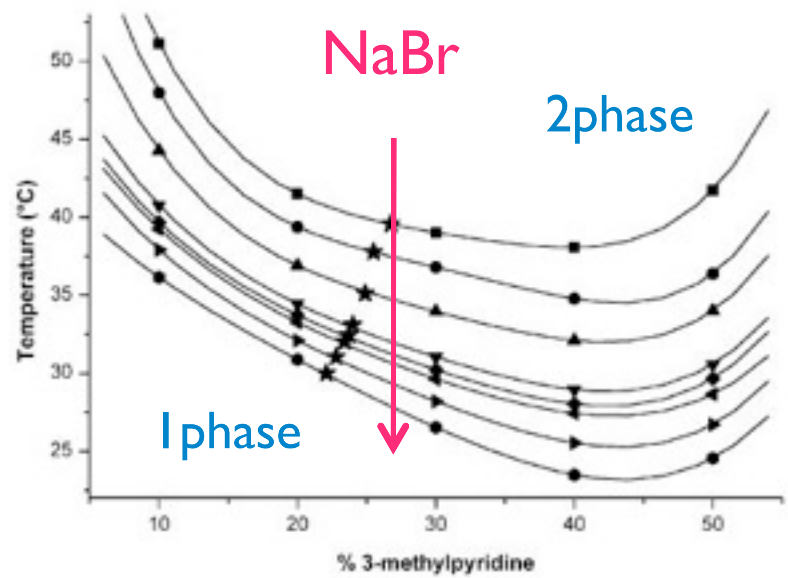
Water + Organic Solvent + Salt

water + acetonitrile (UCST)



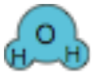
V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions", Plenum Press (1978).

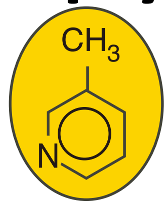
water + 3-methylpyridine (LCST)



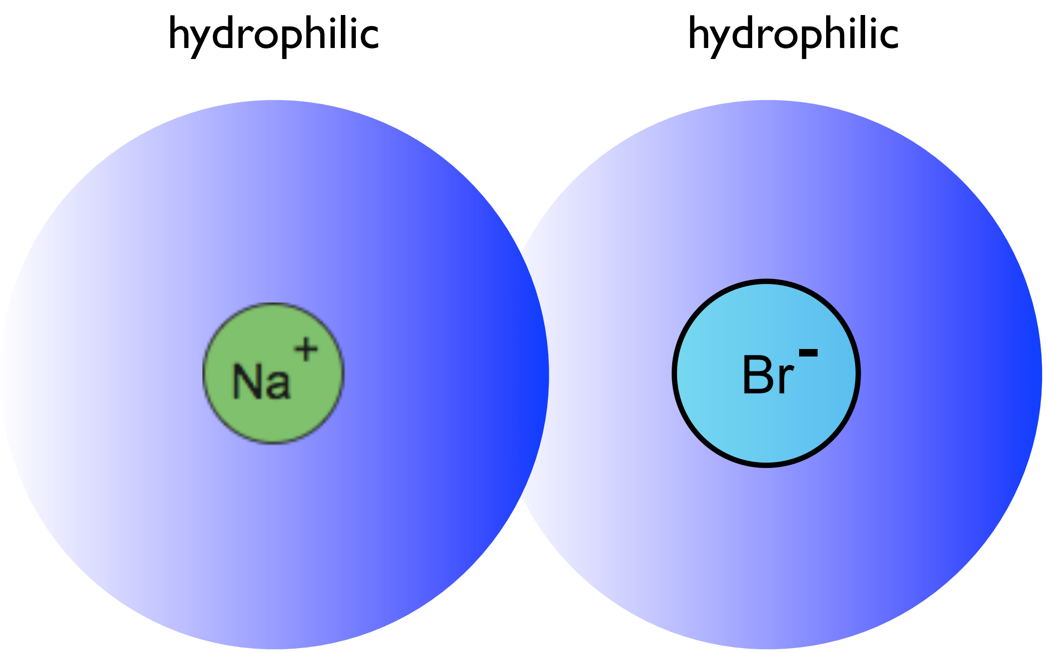
M. Wagner, et al., PCCP, **4**, 5330 (2002).

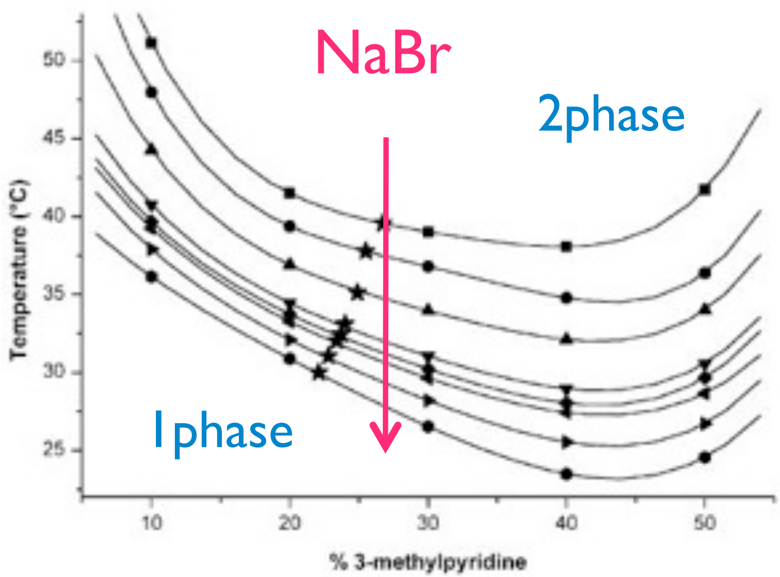
D_2O + 3-methylpyridine (3MP) + salt





normal salt



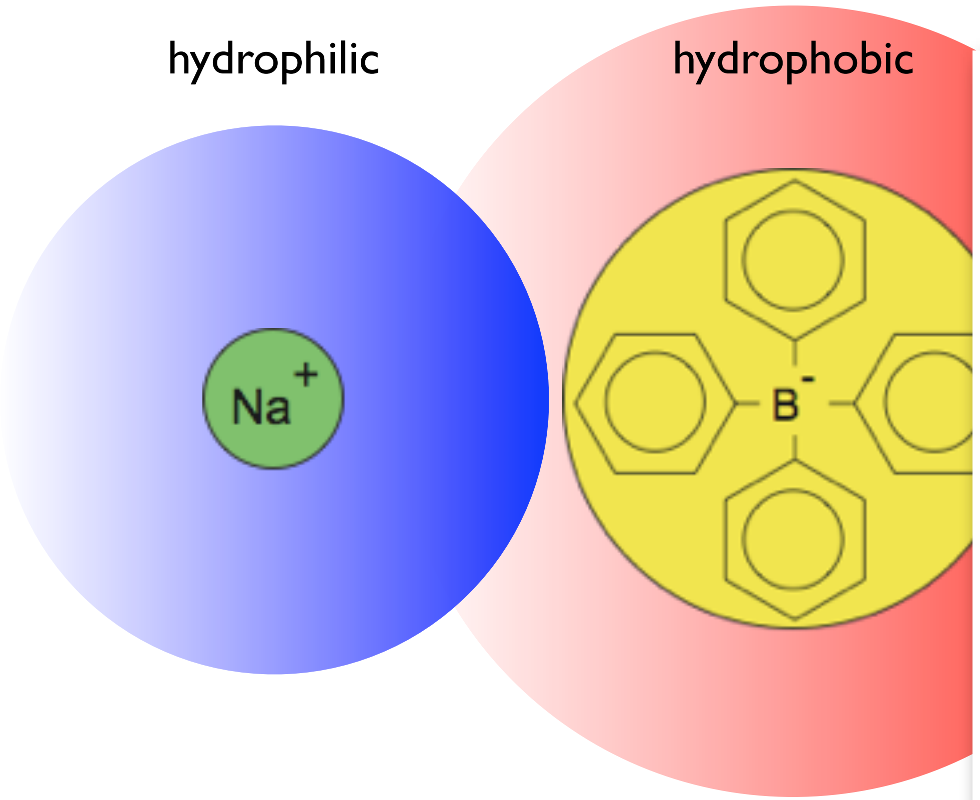


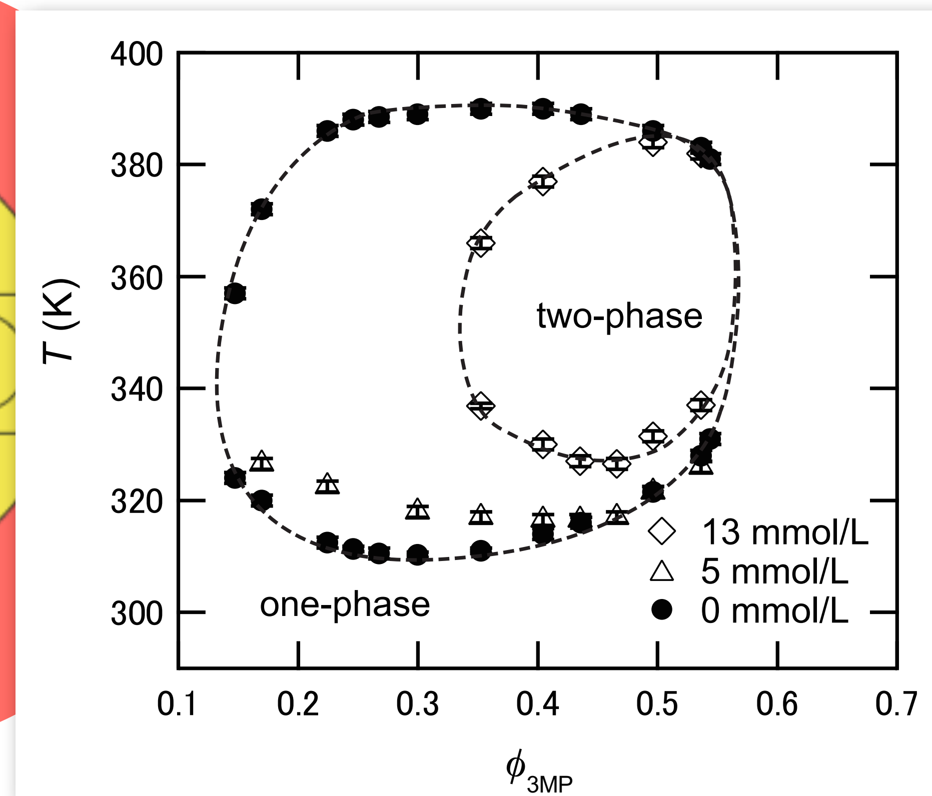
M. Wagner, et al., PCCP, **4**, 5330 (2002).

Antagonistic Salt

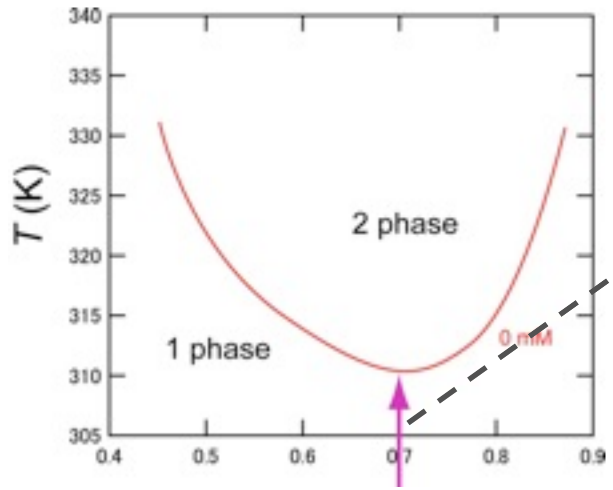
K. Sadakane, HS, et al. 2006-

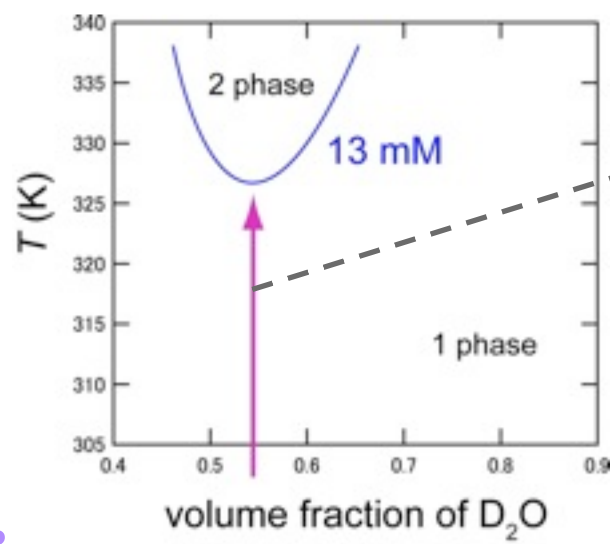
sodium tetraphenylborate ($NaBPh_4$)



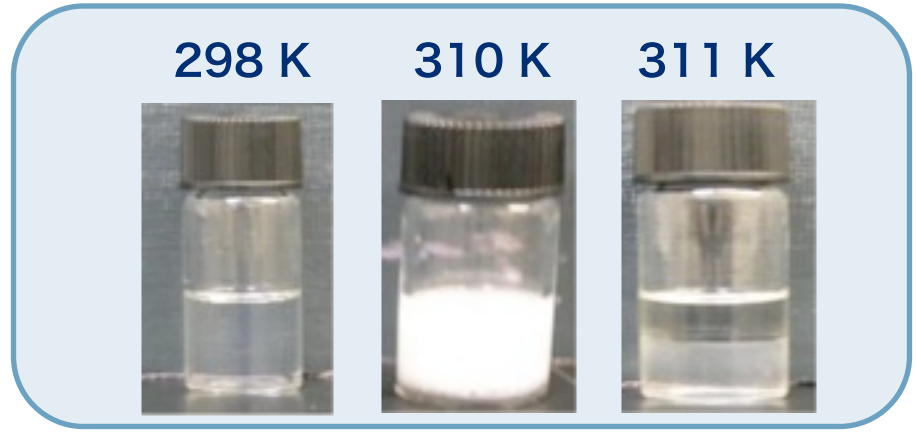


Visual inspection

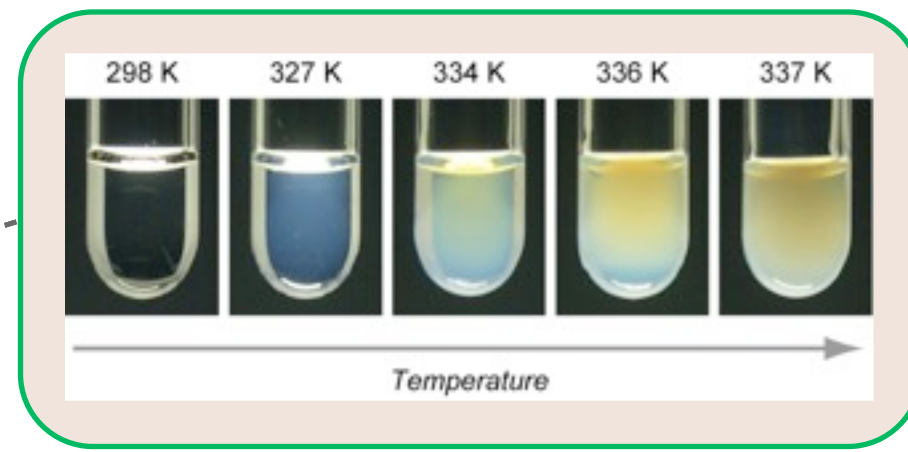




①



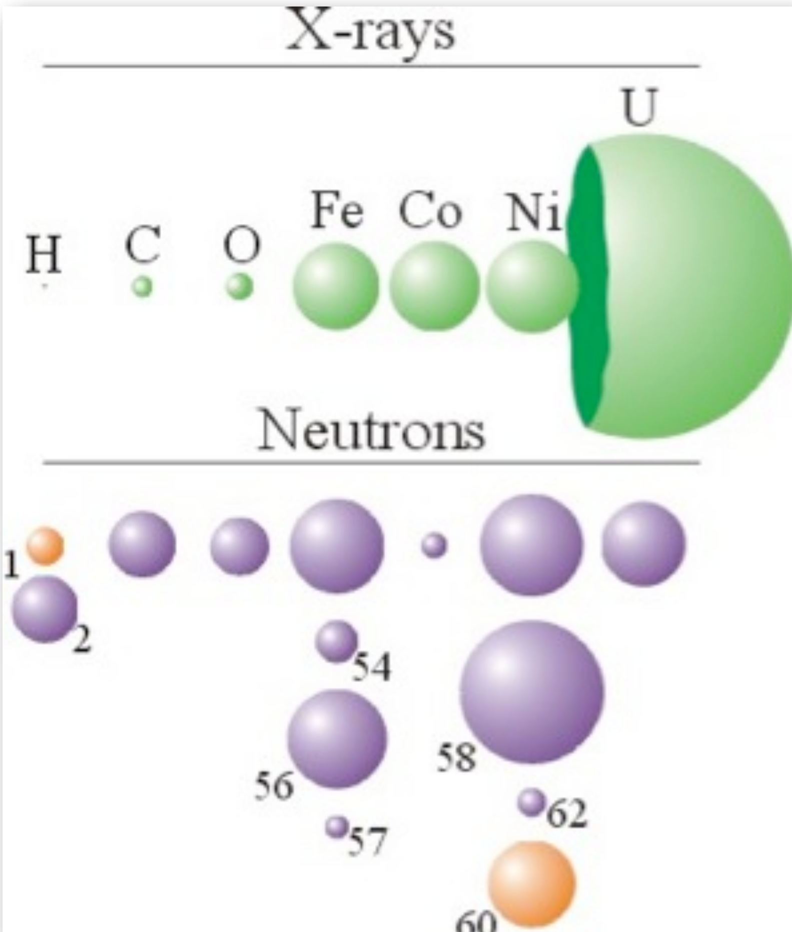
②



③

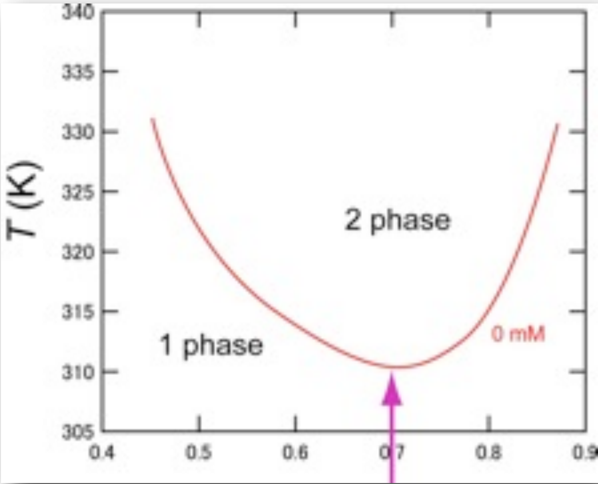
No phase separation is observed when $NaBPh_4$ > 15 mM

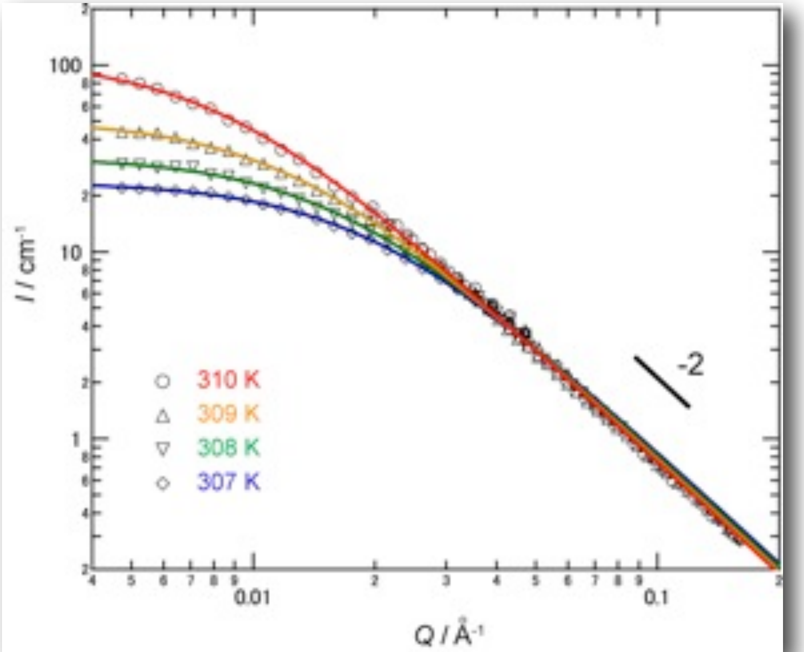
Scattering Length Densities



Small-Angle Neutron Scattering

① $NaBPh_4$ = 0 mM





298 K 310 K 311 K

Ornstein-Zernike equation

$$I(Q) = \frac{I_0}{1 + \xi^2 Q^2}$$

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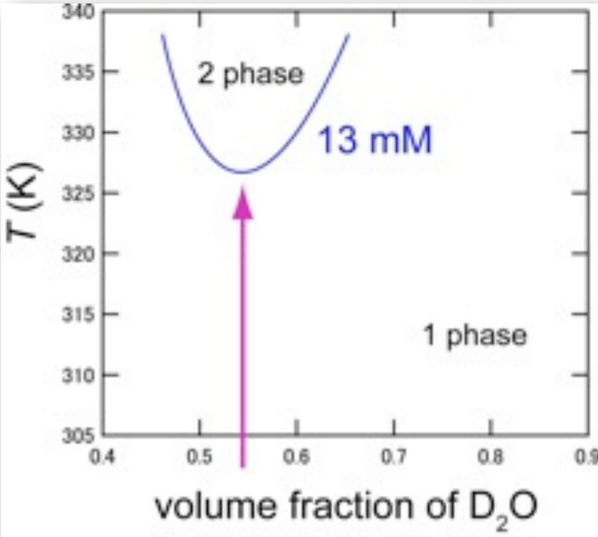
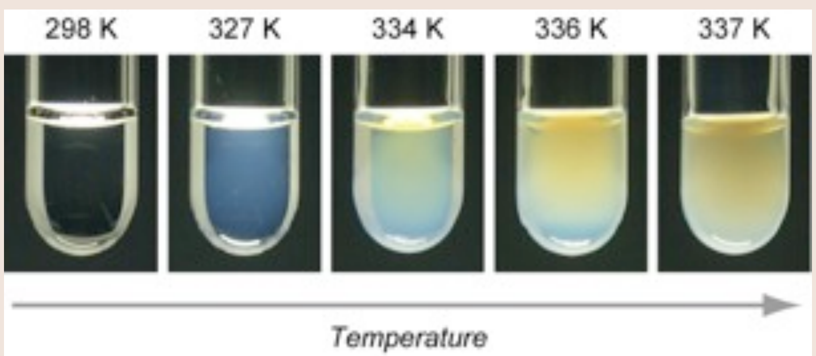
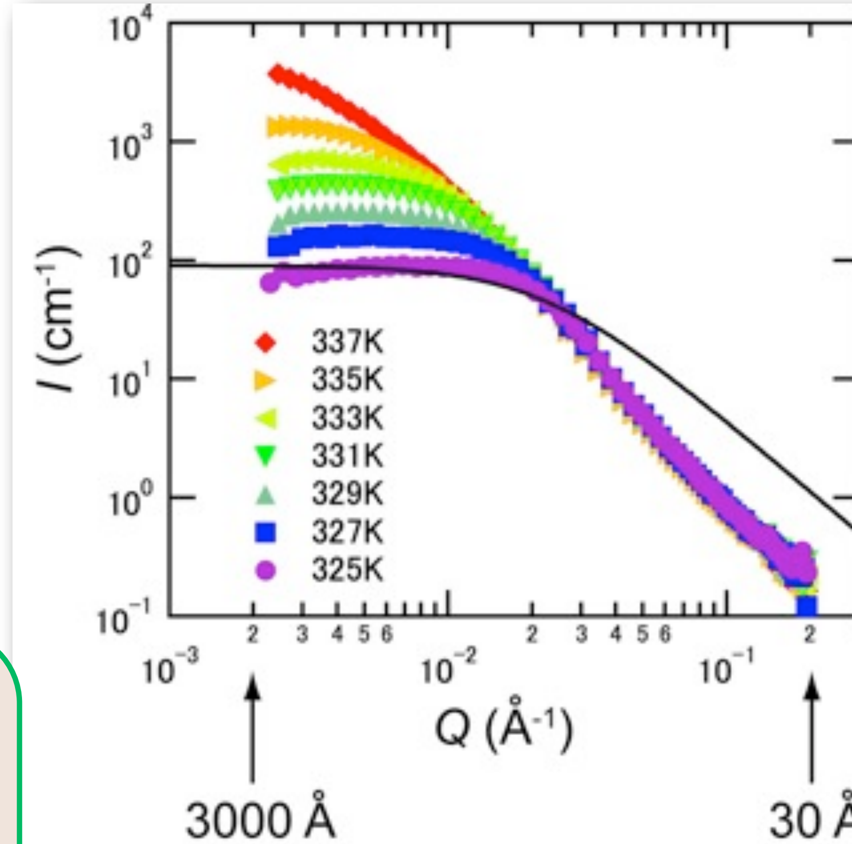
Deviation from O-Z

② $NaBPh_4$ = 13 mM



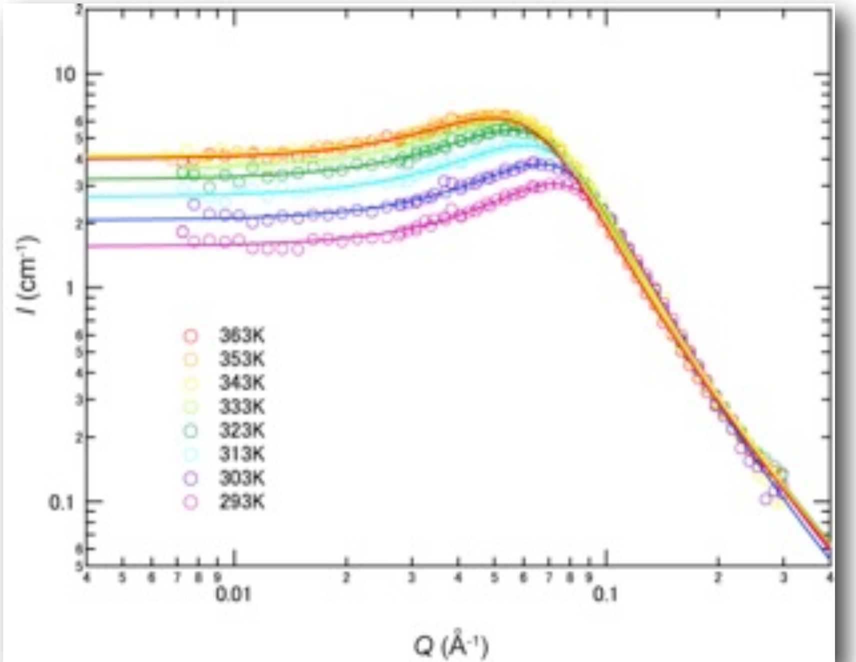


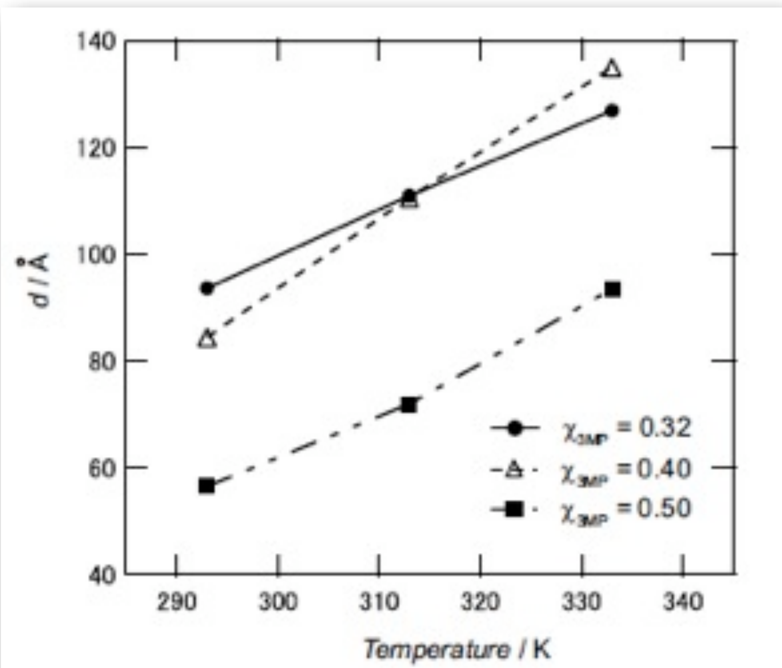


$$I(Q) = \frac{I_0}{1+\xi^2 Q^2}$$

Charge density wave model

③ $NaBPh_4$ = 85 mM

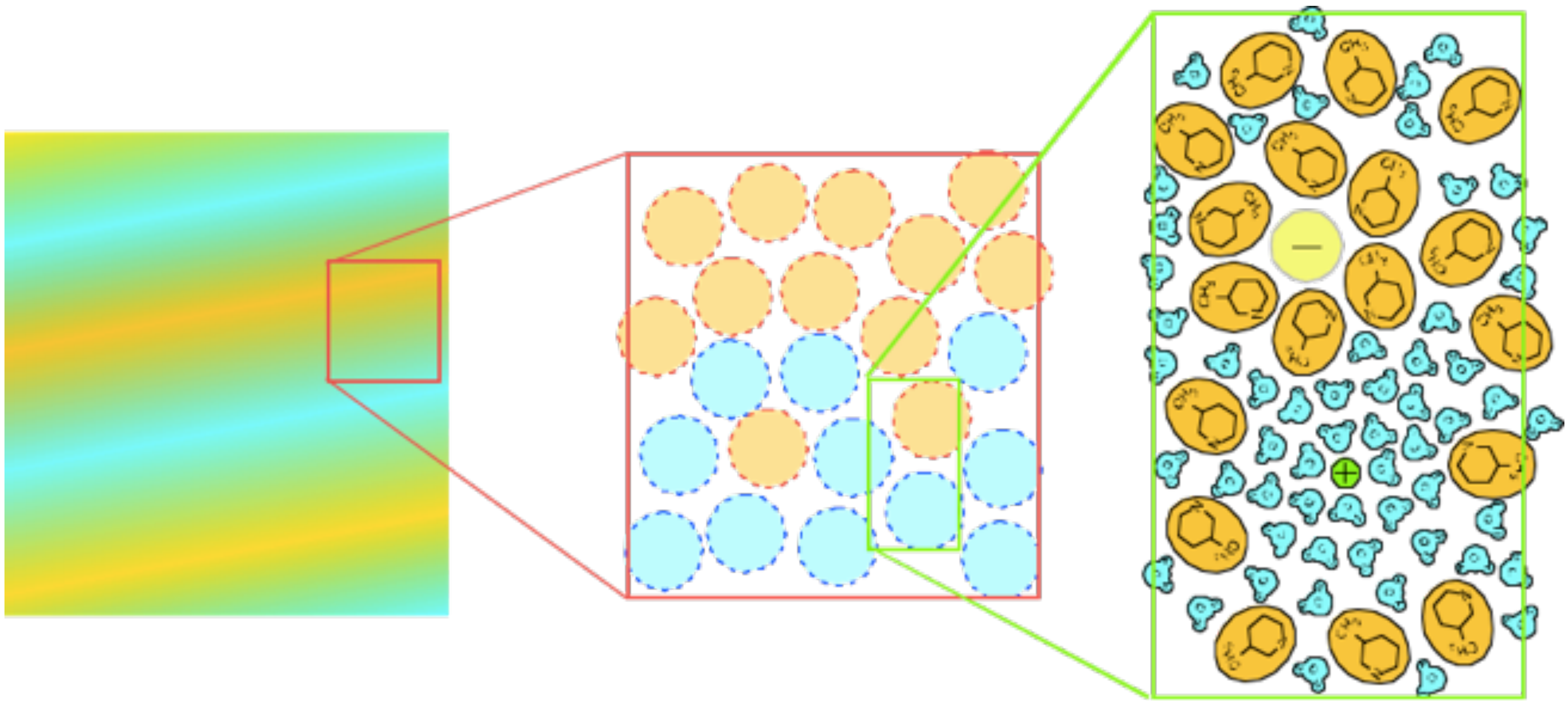




$$I_{\rm OK}(Q) = \frac{I_0}{1 + (1 - \gamma_p{}^2/(1 + \lambda^2 Q^2))\xi^2 Q^2}$$

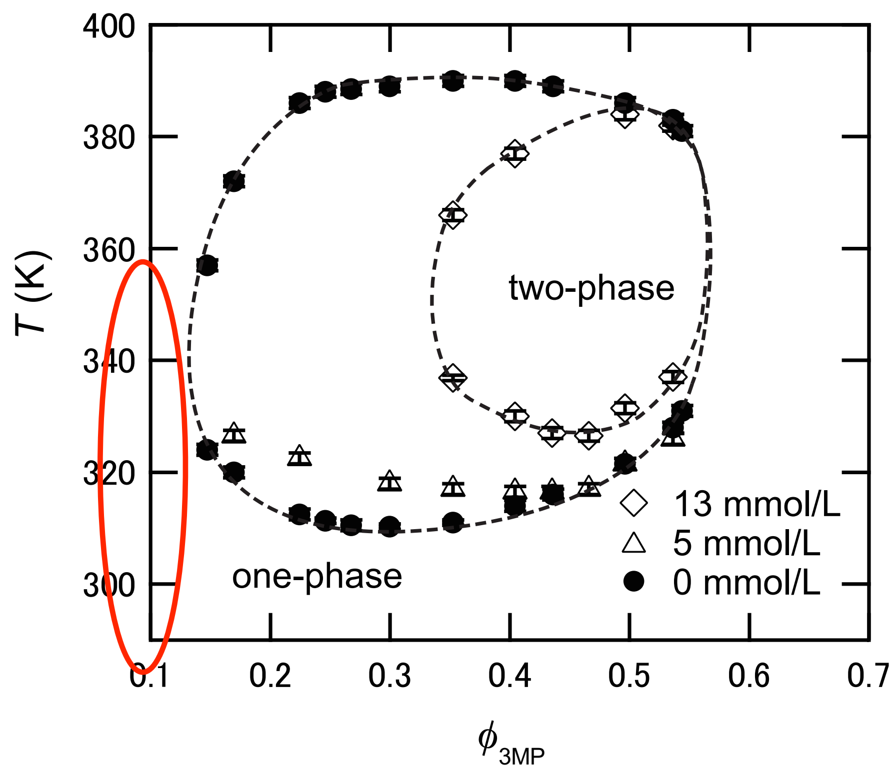
Onuki and Kitamura, JCP 2004

Schematic picture

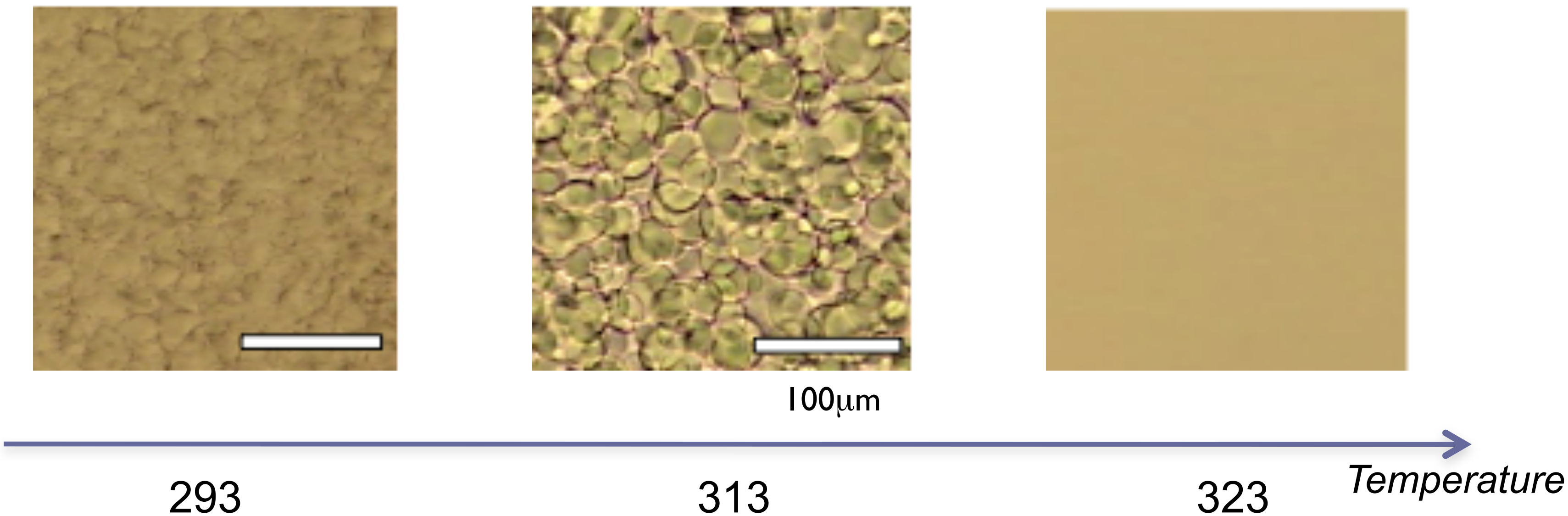


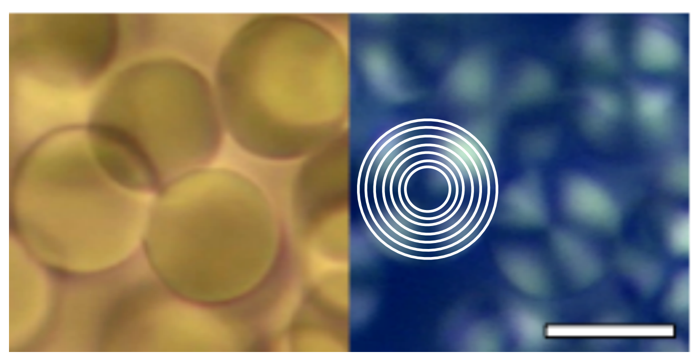
$NaBPh_4$ = 85 mM, water rich

K. Sadakane, HS, et al., Phys. Rev. Lett. **103**, 167803 (2009).



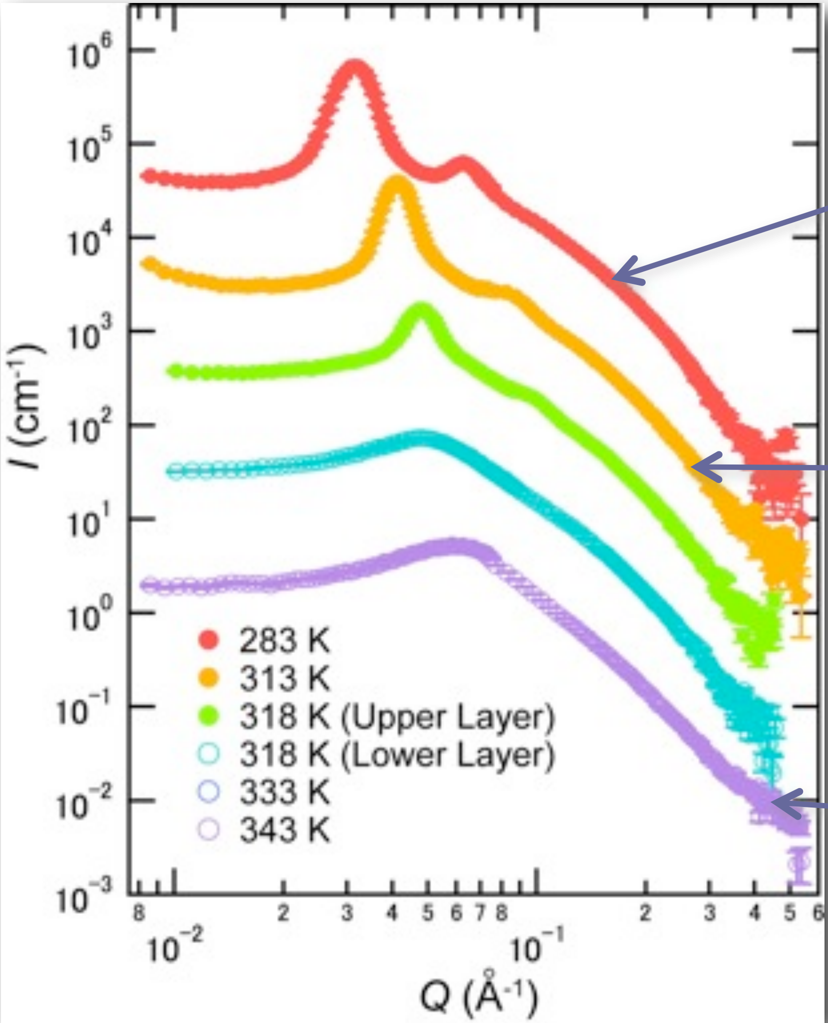
Optical Microscope

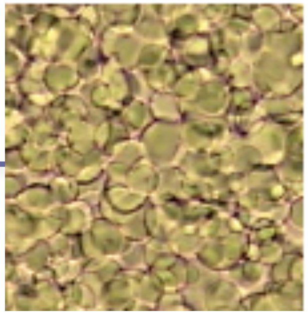




20μm

SANS results





Model analysis

Scattering Intensity: $I(Q) = P(Q) \times S(Q)$

$$I(Q) = \frac{2\pi P(Q) S(Q)}{dQ^2}$$

$P(Q)$: Form factor of membrane

$$P(Q) = \frac{2(\Delta\rho)^2}{Q^2}\left[1 - \cos(\delta Q)\, e^{-\sigma^2 Q^2/2}\right]$$

$S(Q)$: Structure factor of lamellar

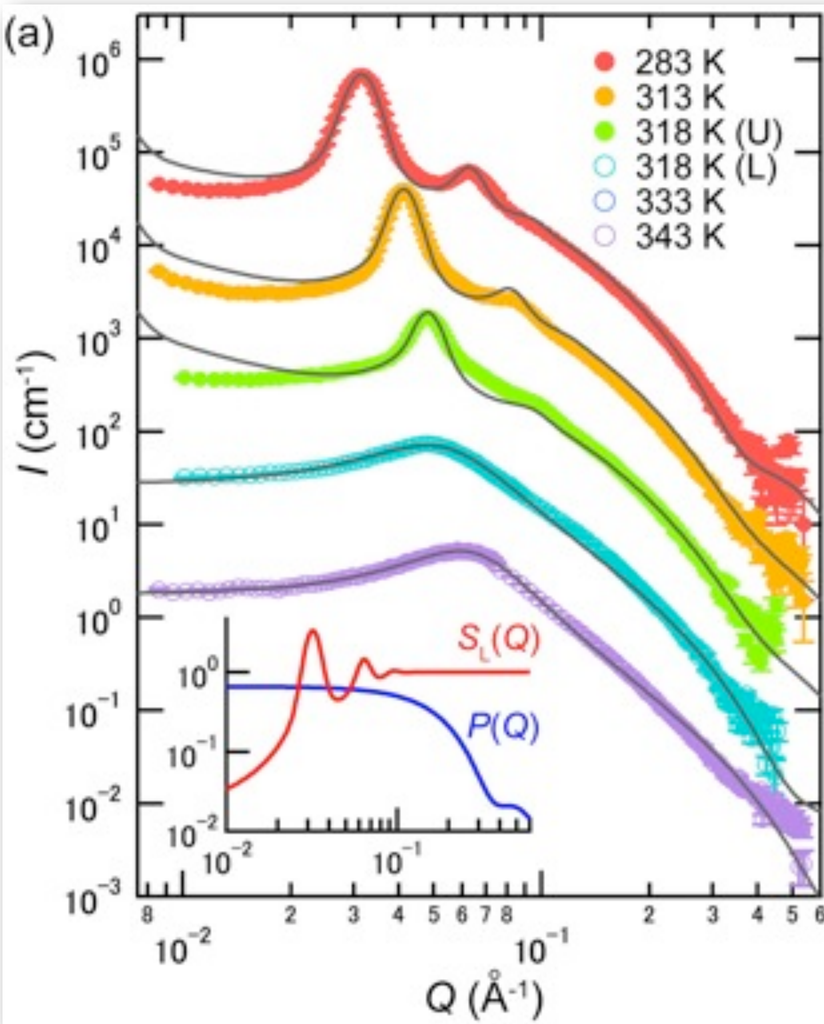
$$S(Q) = 1 + 2\sum_{n=1}^{N-1}\left(1 - \frac{n}{N}\right)\cos\left(\frac{dnQ}{1 + 2\Delta Q^2 d^2 \alpha(n)}\right) \times \exp\left[-\frac{\Delta Q^2 d^2 n + 2d^2 \alpha(n) Q^2}{2\left(1 + 2\Delta Q^2 d^2 \alpha(n)\right)}\right]\frac{1}{\sqrt{1 + 2\Delta Q^2 d^2 \alpha(n)}}$$

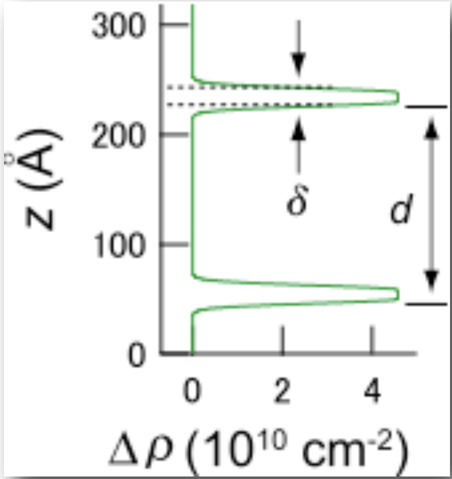
δ : thickness of membrane

d : repeat distance between each membrane

Δρ : scattering contrast between membrane and bulk solution

Result of the fitting



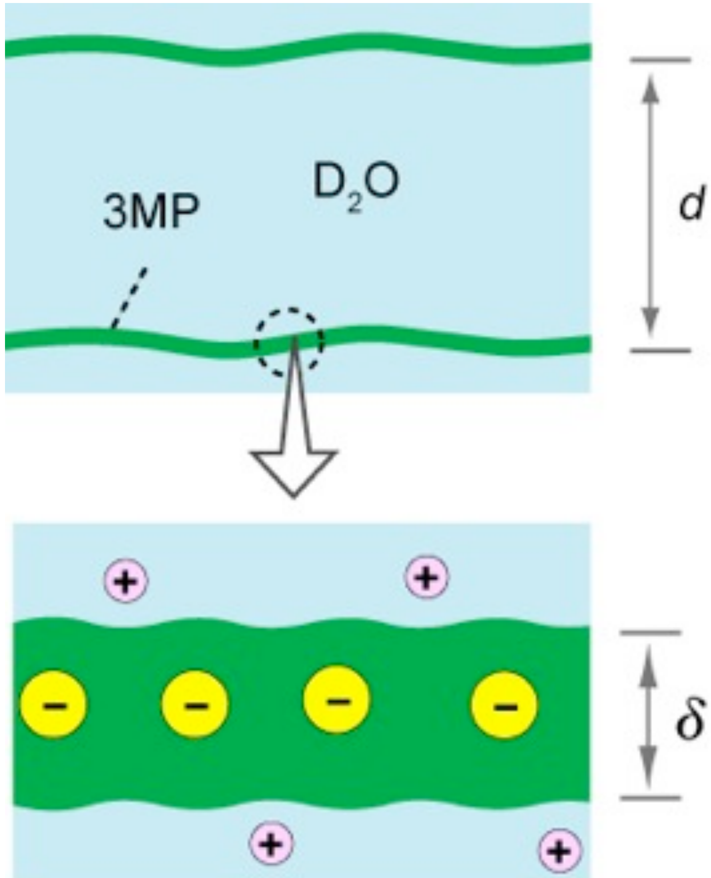


Fit parameters

δ = 13.9 ±0.1 (Å)

d = 149.7 ±0.6 (Å)

$\Delta\rho$ = 4.90 ±0.01 ($10^{10}cm^{-2}$)



Scattering length densities

D_2O : ρ = 6.39 ($10^{10}cm^{-2}$)

3MP : ρ = 1.42 ($10^{10}cm^{-2}$)

→ $\Delta\rho$= 4.97 ($10^{10}cm^{-2}$)

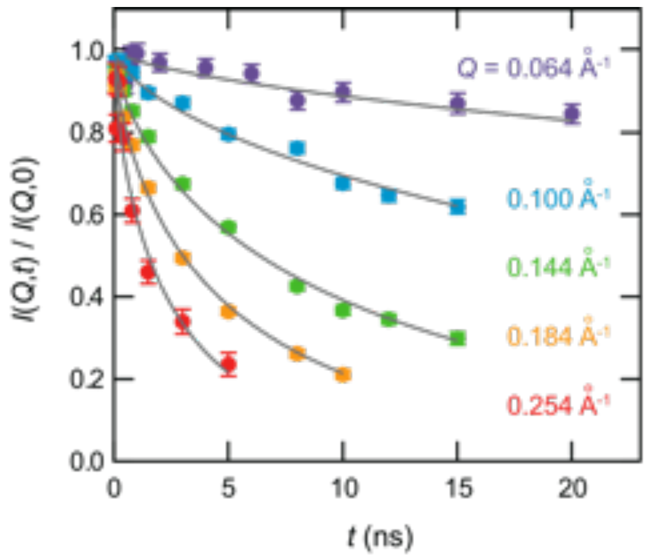
Estimation of the membrane thickness

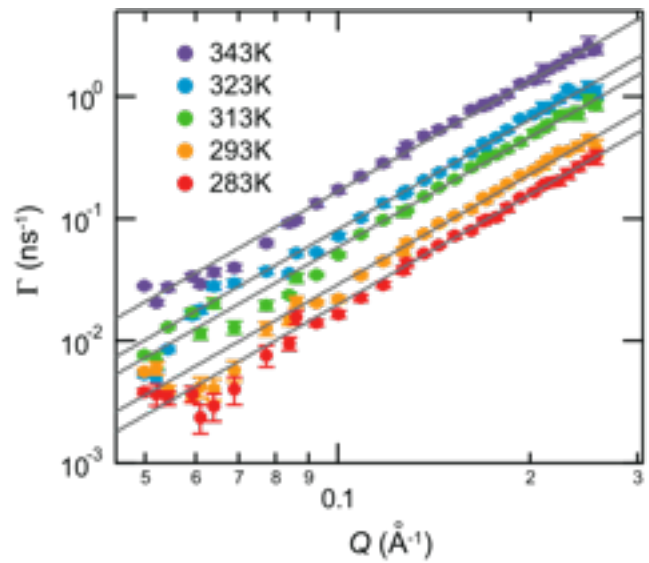
$\delta = \varphi_{3MP}\, d$ = 149.7 ×0.09 = 13.5 Å

→ This value is consistent with the fitting value, 13.9 Å.

NSE confirmed the membrane picture

ϕ_{3MP} =0.09, C_{salt}=85 mM
T=293.2K





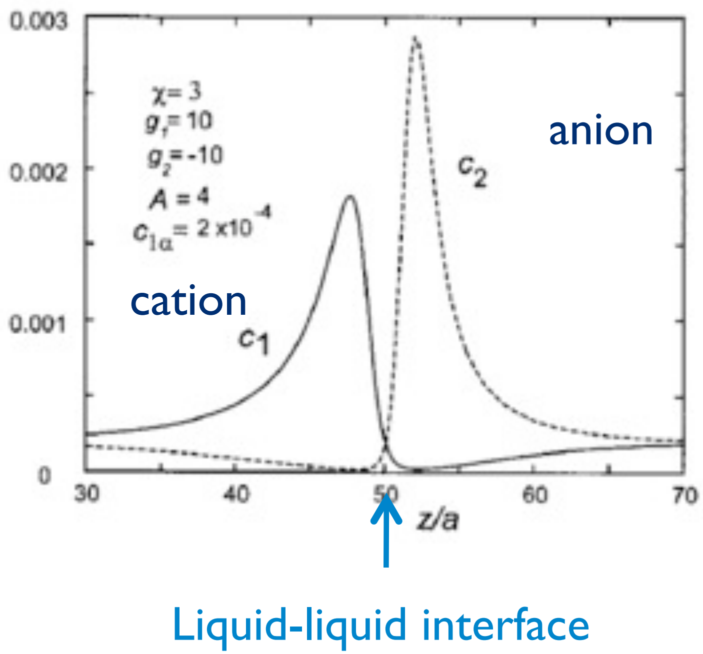
$I(Q,t)/I(Q,0)=\exp(-(\Gamma t)^{2/3})$

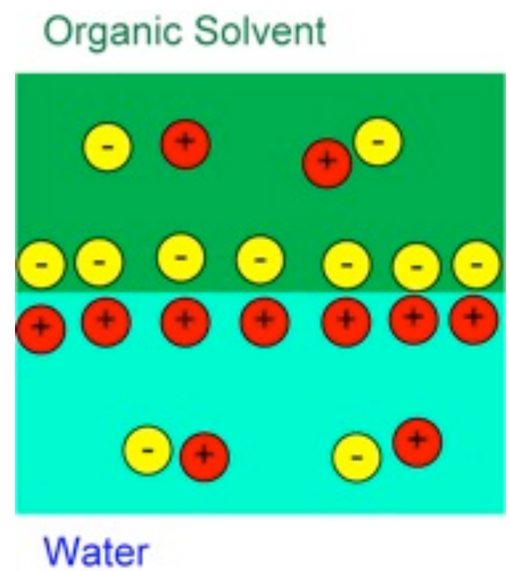
$\Gamma=0.025(k_BT/\kappa)^{1/2}(k_BT/\eta)Q^3$

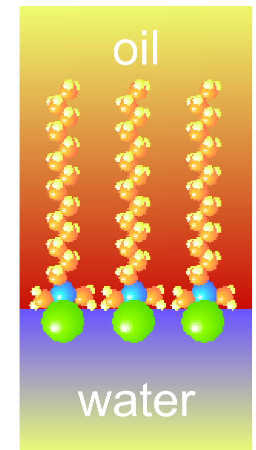
The single membrane fluctuation model (Zilman and Granek) explains well.

Behave as amphiphilic molecules

A. Onuki, J. Chem. Phys, 128, 224704 (2008).







Decreasing the interfacial energy in the presence of ions

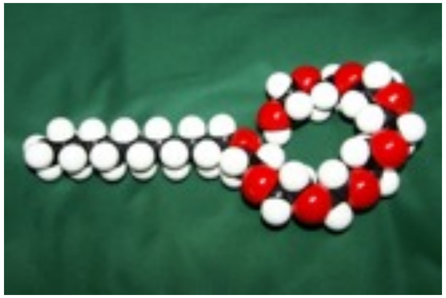
$$\Delta\gamma = -AT\sqrt{n_{\rm ion}/\ell_{\rm B}}$$

(n_{ion} : concentration of ion)

Possible application

detergent

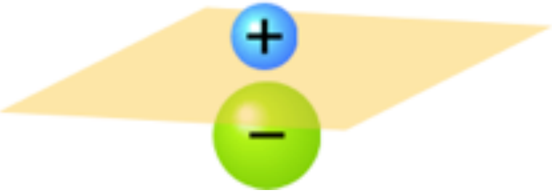
surfactant



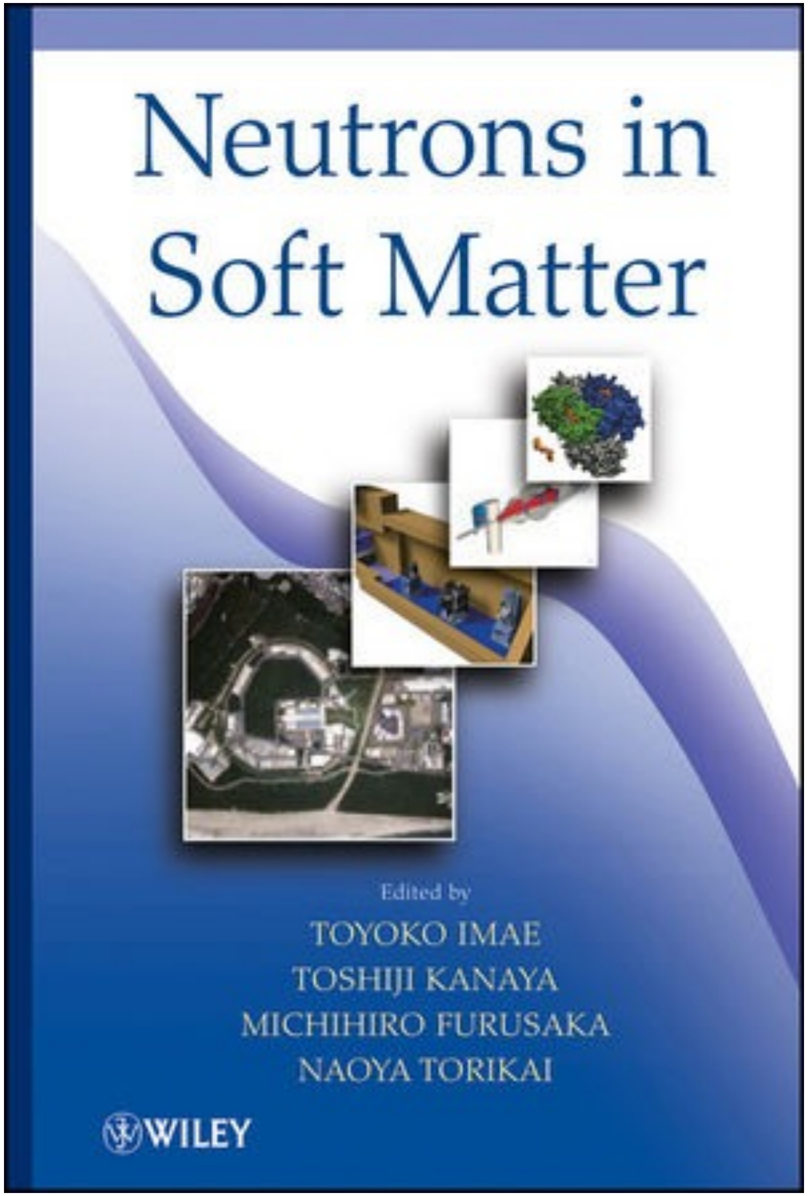
difficult to dissociate

salt

cation+anion



easy to dissociate


Neutrons in
Soft Matter
Edited by
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$158.00