complex systems

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outline

shape fluctuations of surfactant membrane in microemulsion

single membrane fluctuation in model biomembranes

evidence of sliding cyclodextrin along polymer chain

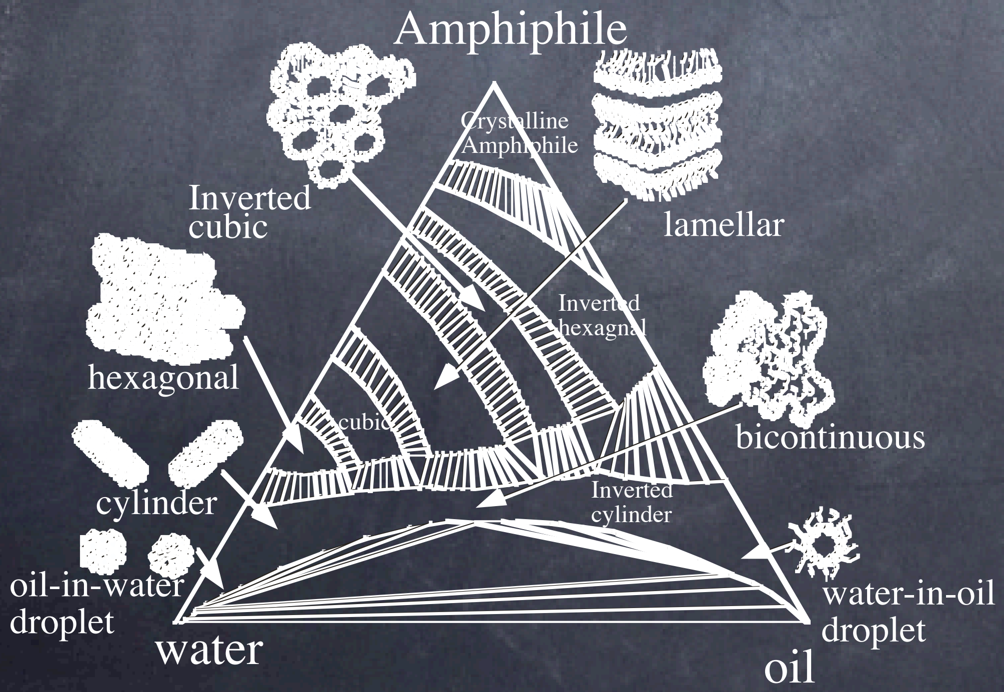
shape fluctuations of surfactant membrane in microemulsion

microemulsions

water, oil, surfactant

Surface active agent (surfactant) reduces surface energy between water and oil, so that water and oil can be mixed together.

In the nanometer length scale, however, water and oil domains are separated each other. Nono-scale structures are self-assembled.



various types of mesophase

surfactant membranes are thermally fluctuating

surfactant everywhere in our life


hydrophilic head group
hydrophobic tail group

two different physical properties are coexisting within a molecule

Surfactant

cell membranes

clothes dyeing

paint

manure
insecticide

chocolate
icecream

glasses
carpet

concrete

engine oils
brake oils
lubricating oils
antifreeze solutions

asphalt

cosmetics
dry cleaning

physics

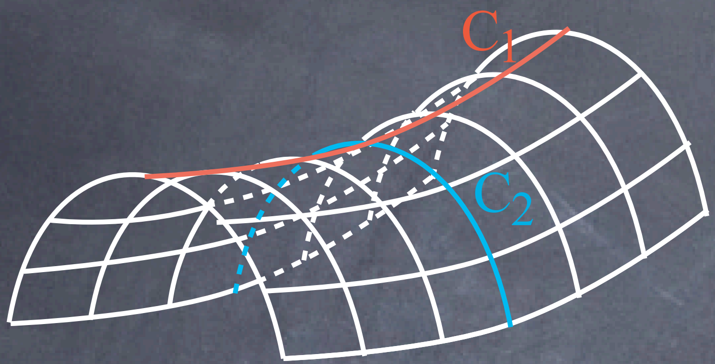
chemistry

industry

biology

...

physical properties of surfactant membranes



surface can be characterized by two principal curvatures C_1 and C_2.

structure and dynamics are predetermined by surface energy

bending free energy

W. Helfrich, *Z. Naturforsch. C* **28**, 693 (1973).

$$f_{bend} = 2\kappa\left(\frac{c_1 + c_2}{2} - c_0\right)^2 + \bar{\kappa} c_1 c_2$$

bending modulus

spontaneous curvature

saddle-splay modulus

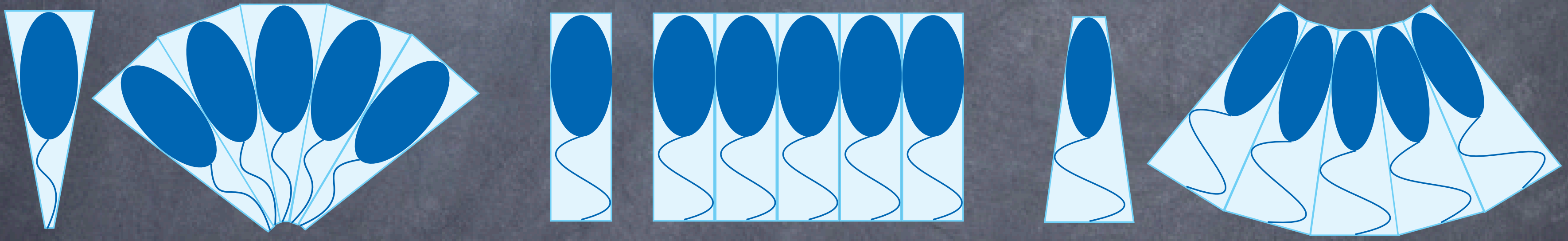
how to determine those parameters

$$f_{bend} = 2\kappa\left(\frac{c_1+c_2}{2} - c_0\right)^2 + \bar{\kappa} c_1 c_2$$

$\bar{\kappa}$ elastic modulus responding to shear deformation

thus, negligible for fluid membranes like microemulsions

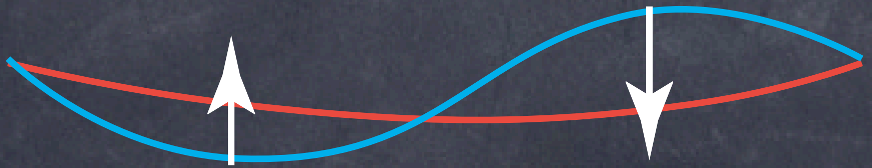
c_0 effective shape of surfactant molecule: static structure



micelles lamellae inverse micelles

interaction change around the molecules (T, P, ...)

κ relaxation of a membrane to have c_0: dynamic structure



NSE

how to study microemulsions I

static structure

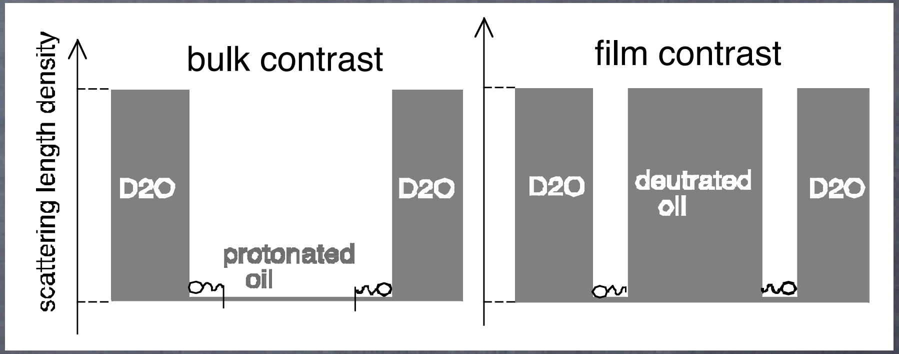
size of water droplet ~ nm

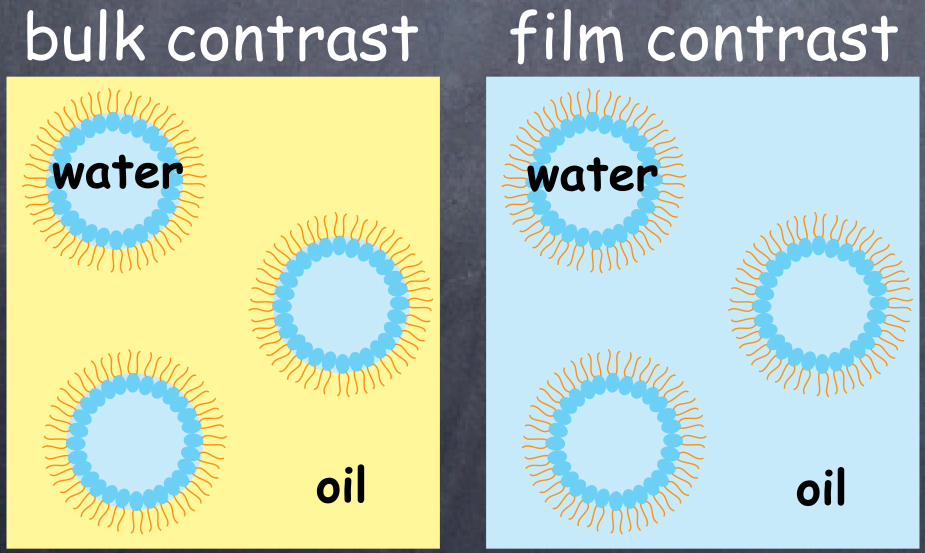
coherent small-angle scattering

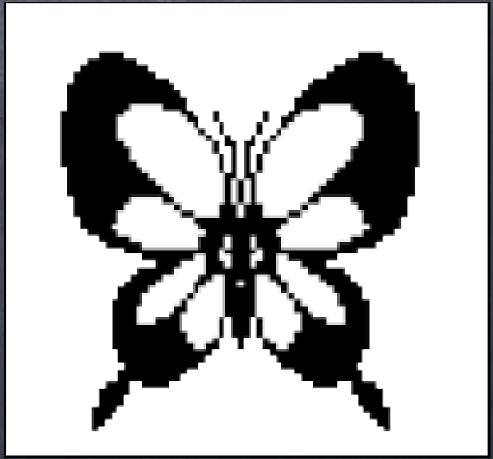
coherent SANS intensity (form factor): $I(q) = \int \Delta\rho(r)\exp[-iqr]dr$

$\Delta\rho(r)$: scattering length density difference

contrast variation technique

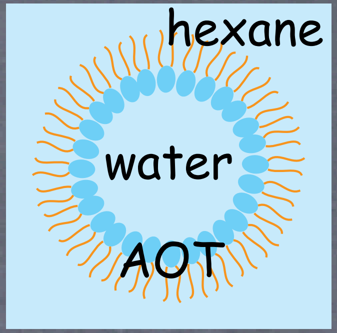


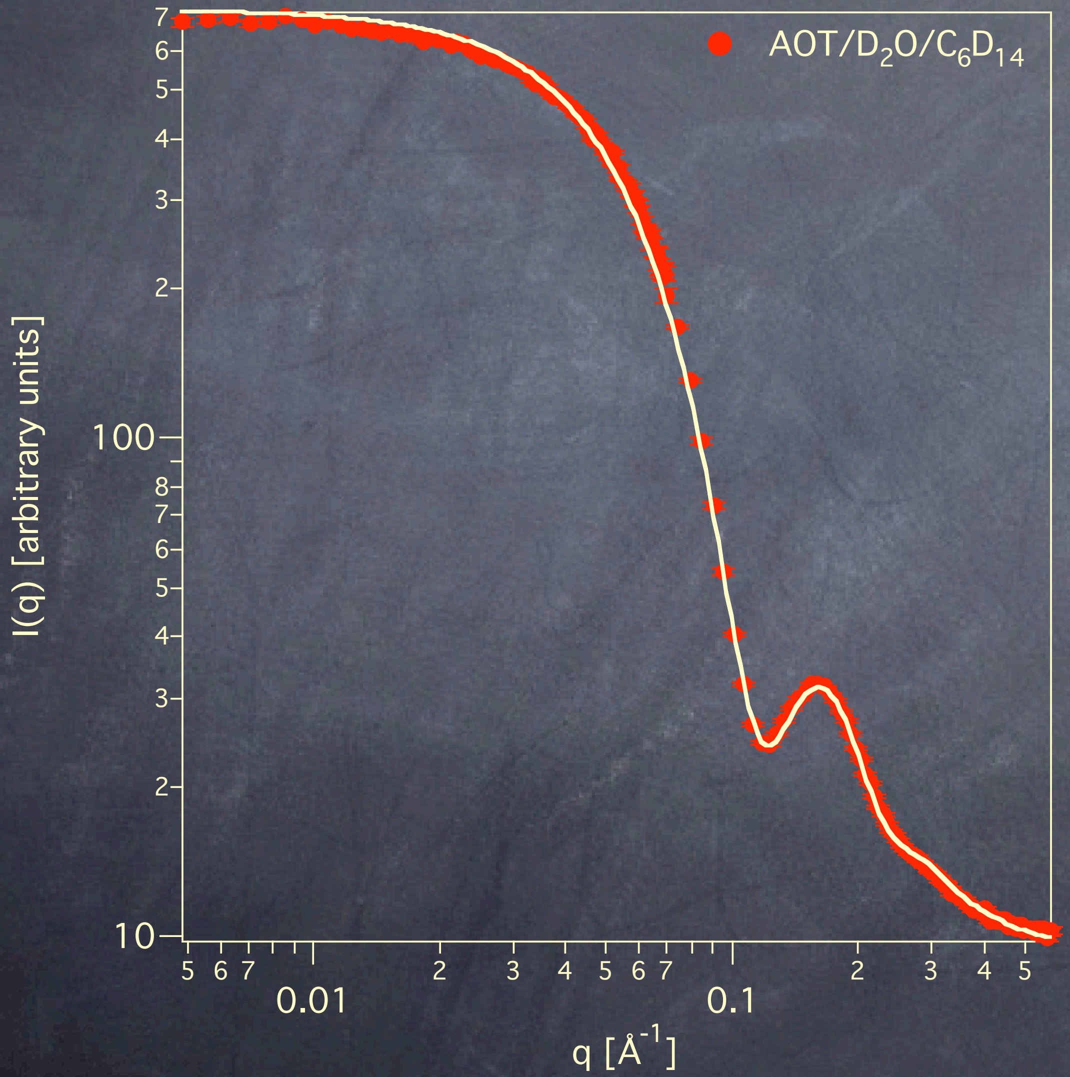




how to study microemulsions I

static structure: example





core-shell model form factor

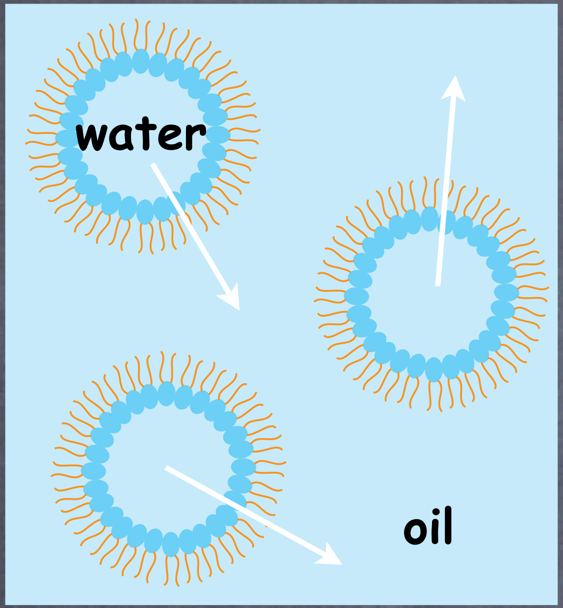
Gaussian distribution of radius of droplets

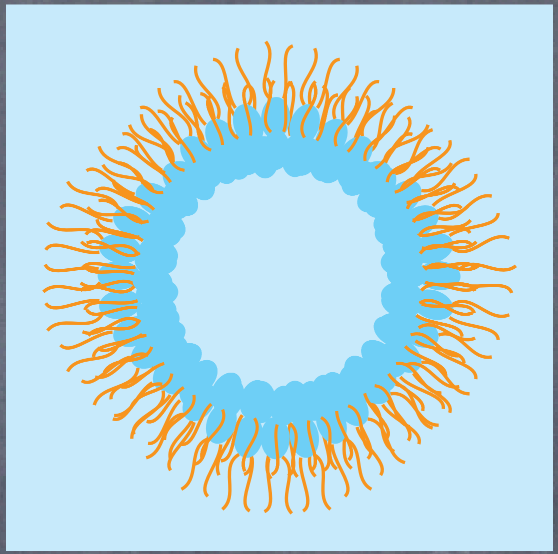
Instrumental smearing effect

Rcore=20.9Å
shell thickness=7.5Å
core polydispersity=0.19

how to study microemulsions II

dynamic structure





translational diffusion + shape fluctuation

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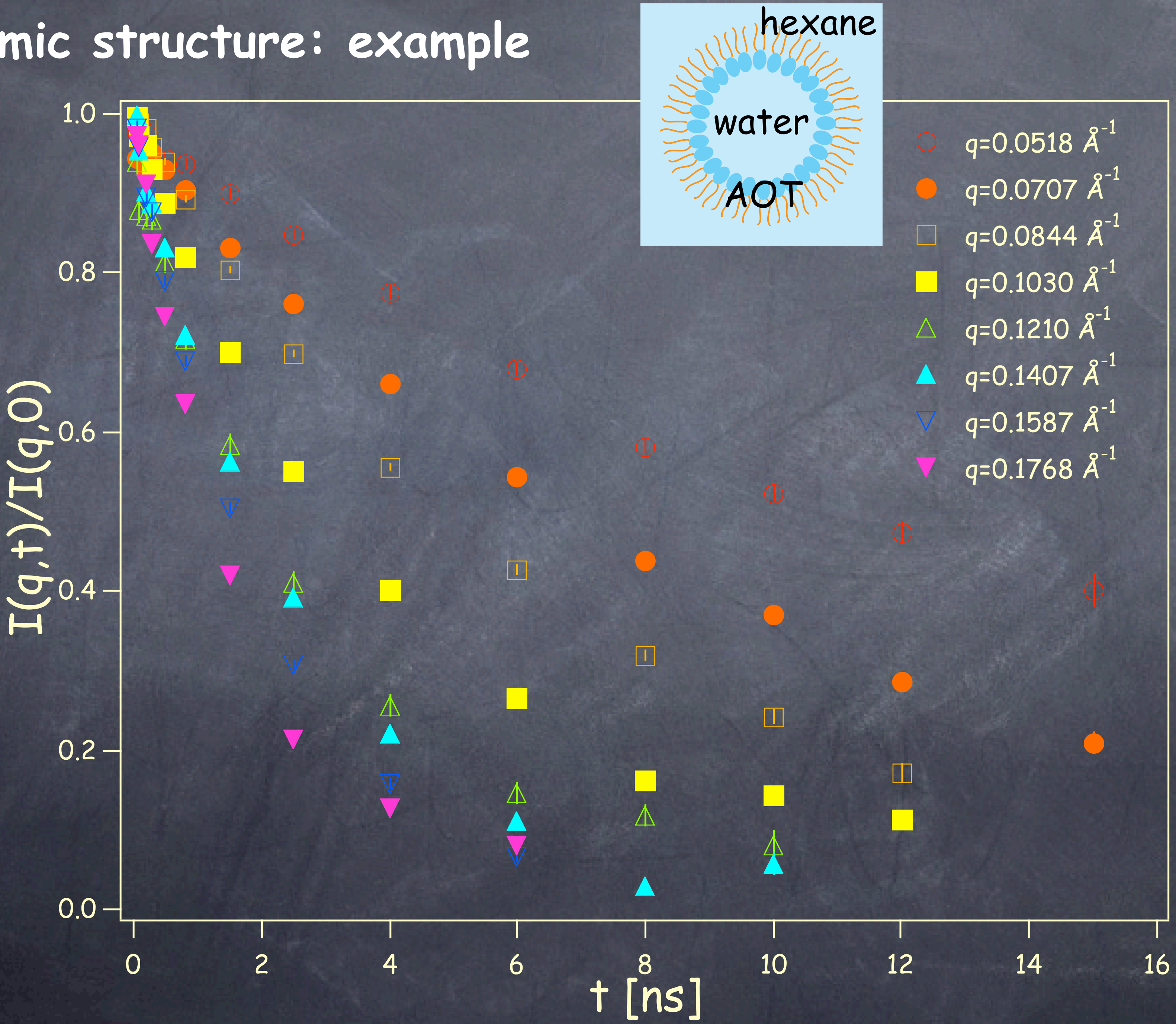
DLS, NMR, NSE, ... NSE

how to study microemulsions II

dynamic structure: example

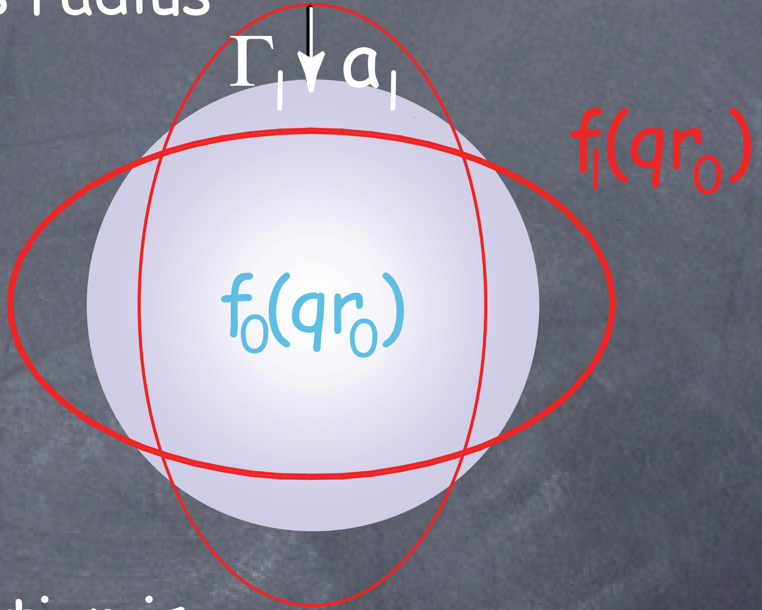


theory of shape fluctuation dynamics

$$f_{bend} = 2\kappa\left(\frac{1}{r_0} - \frac{1}{r_s}\right)^2$$

$\bar{\kappa}$ term is neglected

r_s: spontaneous radius



Expansion of r in spherical harmonics
with amplitude a

$$r(\Omega) = r_0\left(1 + \sum_{l,m} a_{lm} Y_{lm}(\Omega)\right)$$

In this case, intermediate scattering function is

$$I(q,t) = \left\langle V_s^2 (\Delta\rho)^2 \underbrace{\exp(-D_0 q^2 t)}_{\text{translational diffusion}} \times \left[\underbrace{f_0(qr) + \sum_{l \geq 2} \frac{2l+1}{4\pi} f_l(qr) \langle |a_l|^2 \rangle \exp(-\Gamma_l t)}_{\text{shape fluctuation}} \right] \right\rangle$$

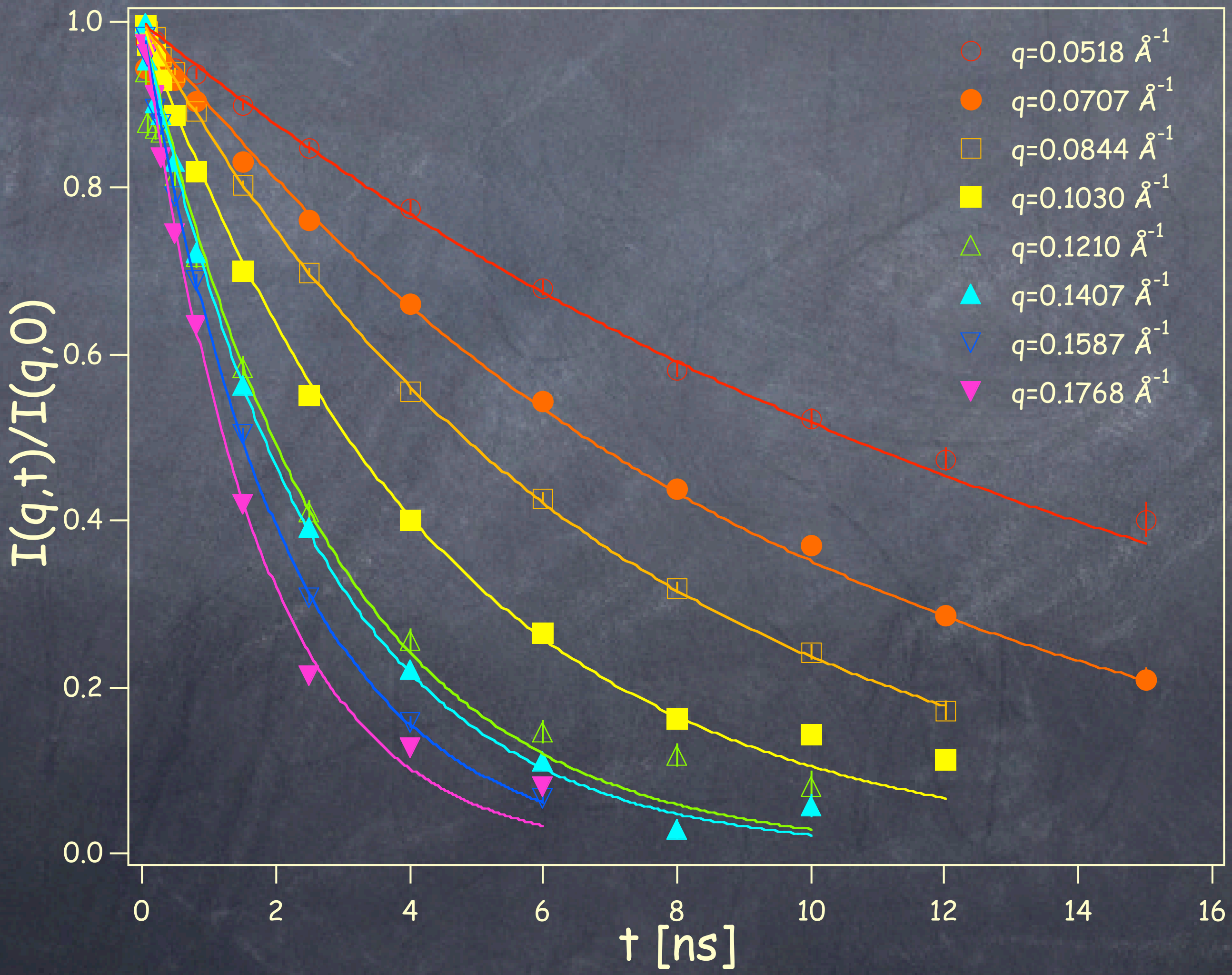
for simplicity, higher order term with l is neglected

S. T. Milner and S. A. Safran, *Phys. Rev. A* **36**, 4371 (1987).

to get bending modulus of surfactant film I

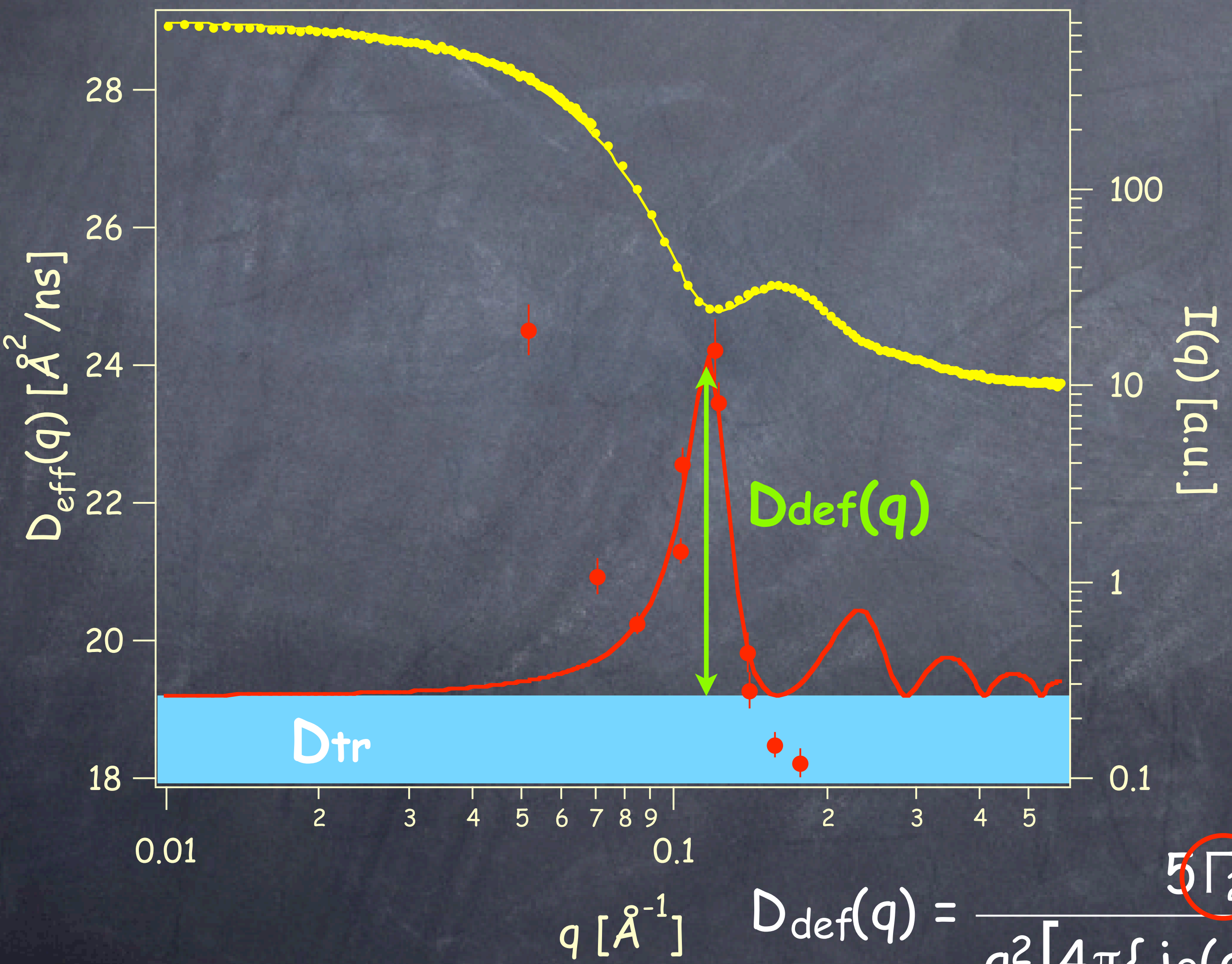
I(q,t) can be approximated as a single exponential decay function

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



to get bending modulus of surfactant film II

$$D_{eff}(q) = D_{tr} + D_{def}(q)$$



$$D_{def}(q) = \frac{5\Gamma_2 f_2(qr_0)\langle|a_2|^2\rangle}{q^2\left[4\pi\{j_0(qr)\}^2 + 5f_2(qr)\langle|a_2|^2\rangle\right]}$$

to get bending modulus of surfactant film III

now, we know dynamic parameters Γ_2 and a_2 as well as static structure parameters r_{core}, r_{shell}, and polydispersity

$$\Gamma_2 = \frac{\kappa}{\eta r_0^3}\left[4\frac{r_0}{r_s} - 3\frac{\bar{\kappa}}{\kappa} - \frac{3k_BT}{4\pi\kappa}f(\phi)\right]\frac{24\eta}{23\eta' + 32\eta}$$

2nd mode relaxation rate relates to the bending modulus

$$p^2 = \frac{\langle|a_0|^2\rangle}{4\pi} = \frac{\langle r^2\rangle}{\langle r\rangle^2} - 1 = \frac{k_BT}{4\pi}\left[6(2\kappa + \bar{\kappa}) - 8\kappa\frac{r_0}{r_s} + \frac{3k_BT}{2\pi}f(\phi)\right]^{-1}$$

polydispersity relates to the 0-th mode amplitude a_0

$$\kappa = \frac{1}{48}\left(\frac{k_BT}{\pi p^2} + \Gamma_2 r_0^3\frac{23\eta' + 32\eta}{3}\right) = 4.7\times10^{-21}\mathrm{J} = 1.2k_BT$$

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

bending modulus of surfactant membrane ~ thermal energy

→ thermal fluctuations of surfactant membrane affect self-assembly of the systems

QUESTIONS?

applications of shape fluctuation analysis

Droplet size effects on AOT microemulsion
by J. S. Huang et al., Phys. Rev. Lett. (1987).

Cosurfactant effects on AOT microemulsion
by B. Farago et al., Phys. Rev. Lett. (1990).

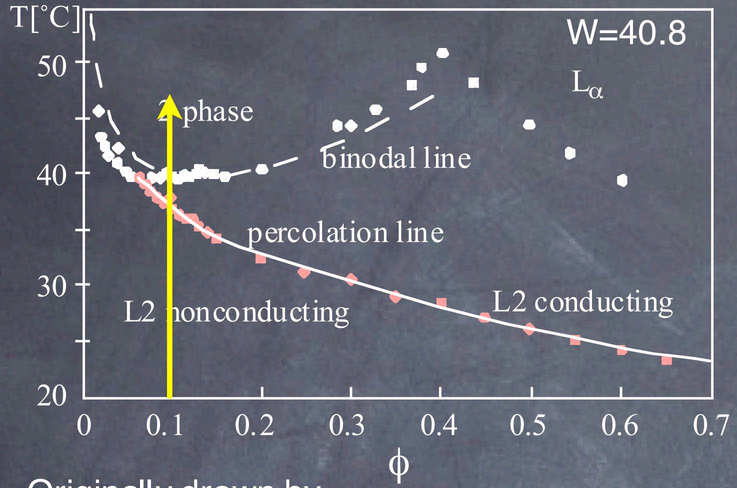
Charge density effects on AOT microemulsion
by B. Farago and M. Gradzielski, J. Chem. Phys. (2001).

Temperature and Pressure effects on AOT microemulsion
by Y. Kawabata et al., Phys. Rev. Lett. (2004).,
J. Chem. Phys. (2007).

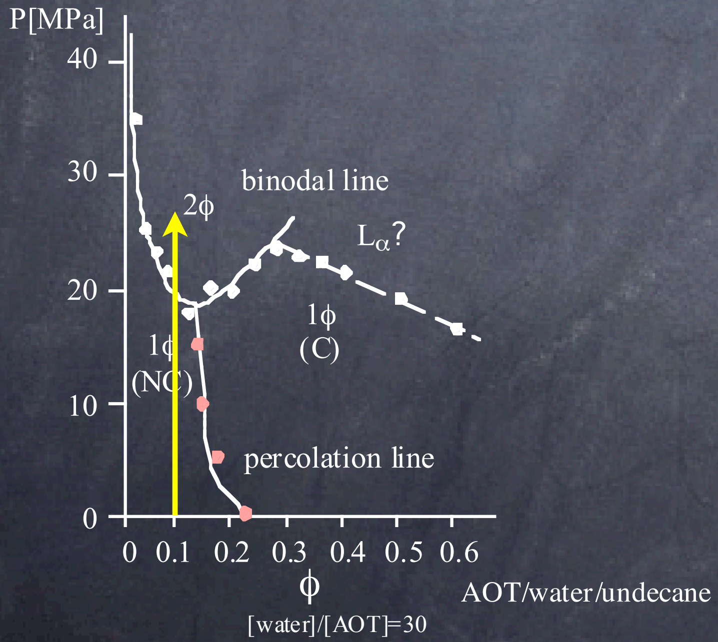
Solvent effects on AOT microemulsion
by C. Kitchens et al., J. Phys. Chem. B (2005).

Droplet concentration dependence on AOT microemulsion
by M. Nagao and H. Seto, Phys. Rev. E submitted.

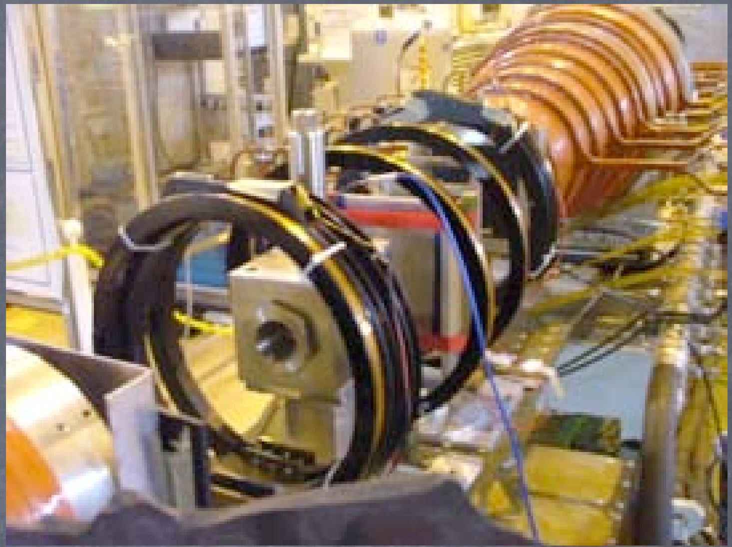
Pressure experiment using NSE



Originally drawn by
Cametti *et al. Phys. Rev. A* **45**, R5358 (1992).



Z. Saïdi, J. L. Daridon and C. Boned J. Phys. D: Appl. Phys. **28** (1995) 2108.

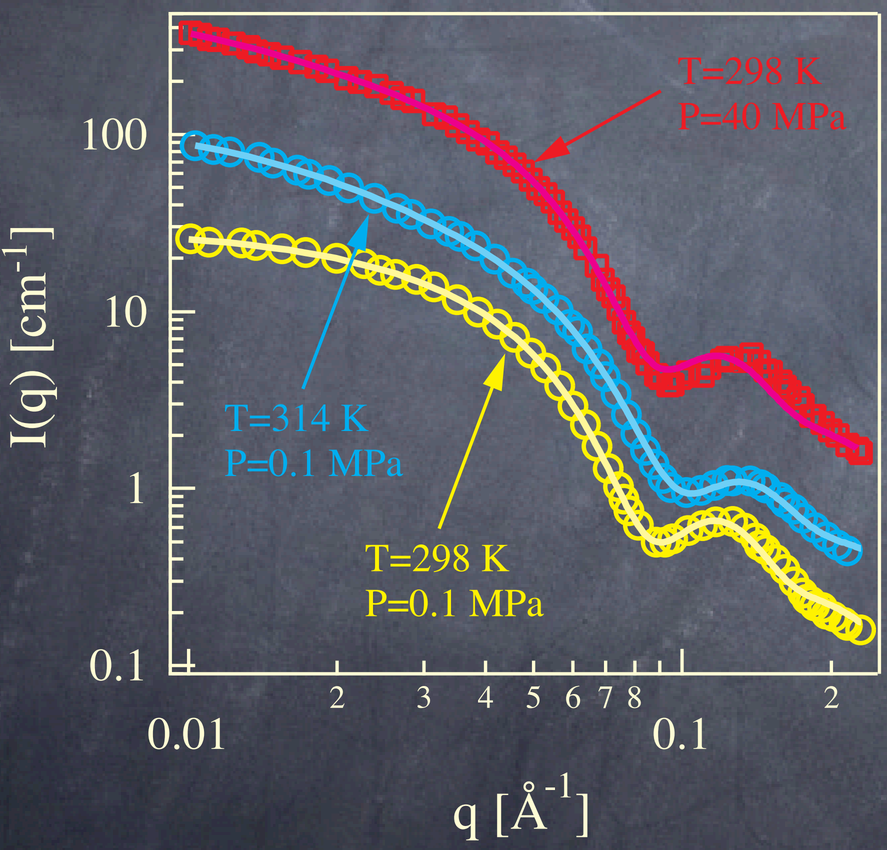


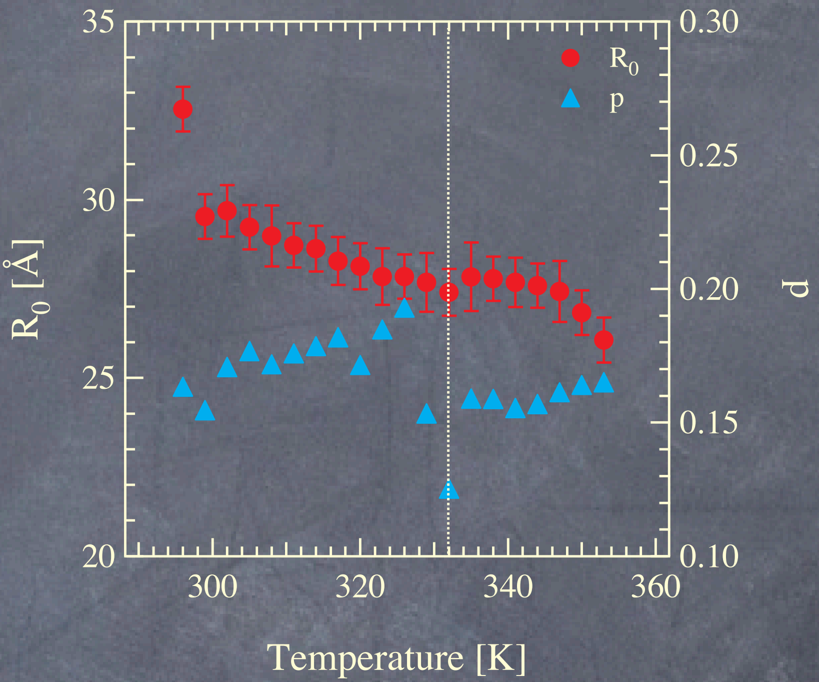
pressure set up at ISSP-NSE, Japan

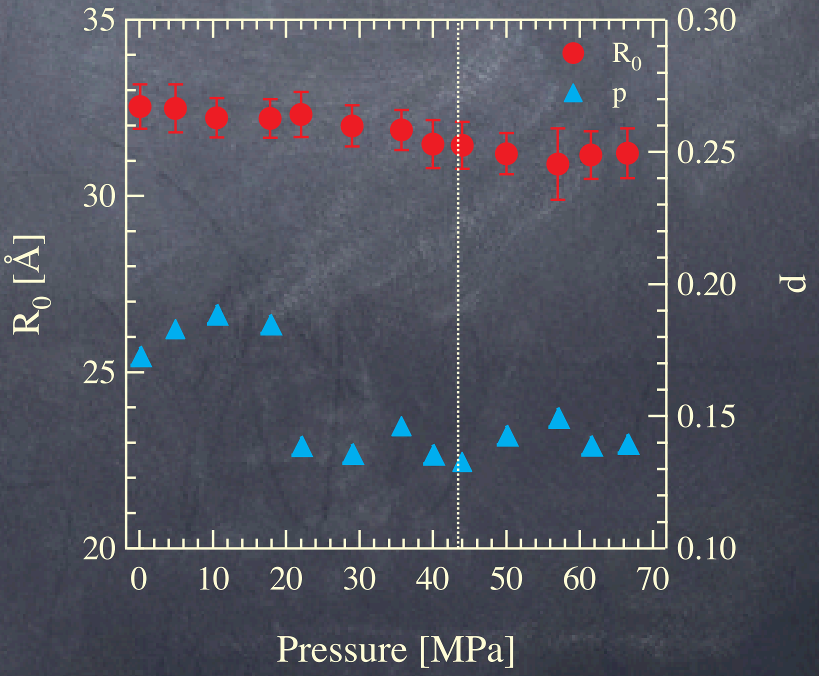
nonmagnetic stainless steel body,
sapphire windows
$0 \leq P \leq 100$ MPa, $20 \leq T \leq 70$ °C,
$0.01 \leq q \leq 0.15$ Å^{-1}

temperature and pressure variation I

SANS result



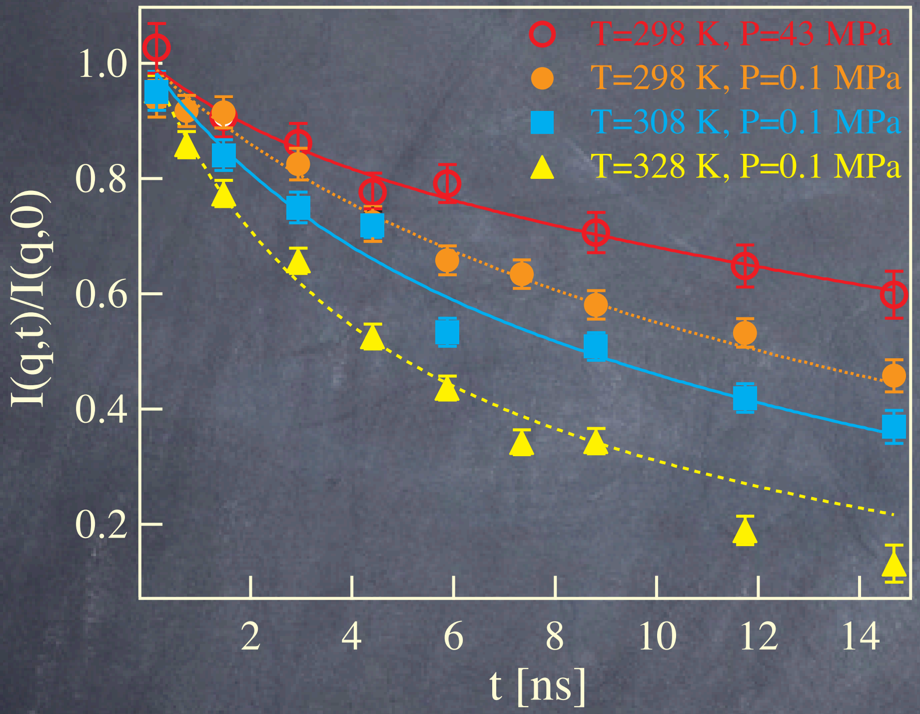




Y. Kawabata et al., *J. Chem. Phys.* **127**, 044705 (2007).

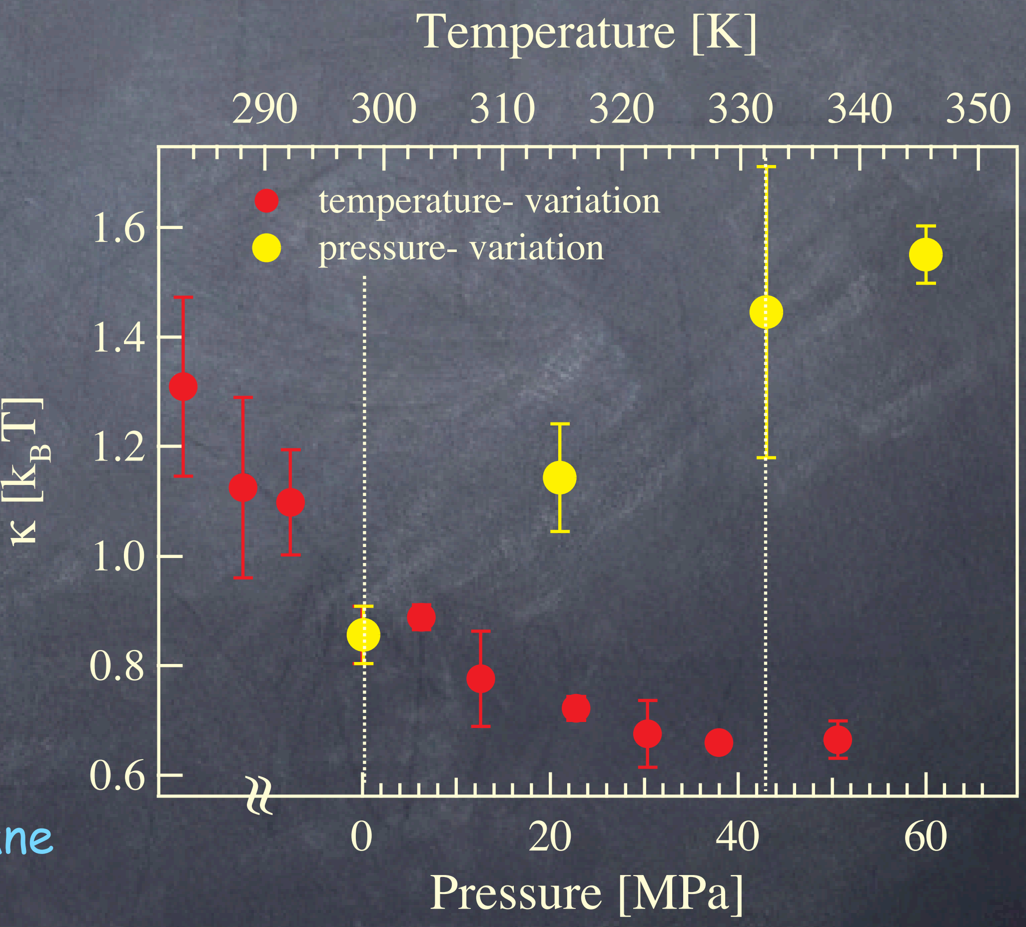
temperature and pressure variation II

NSE result



higher pressure; slower decay

higher temperature; faster decay

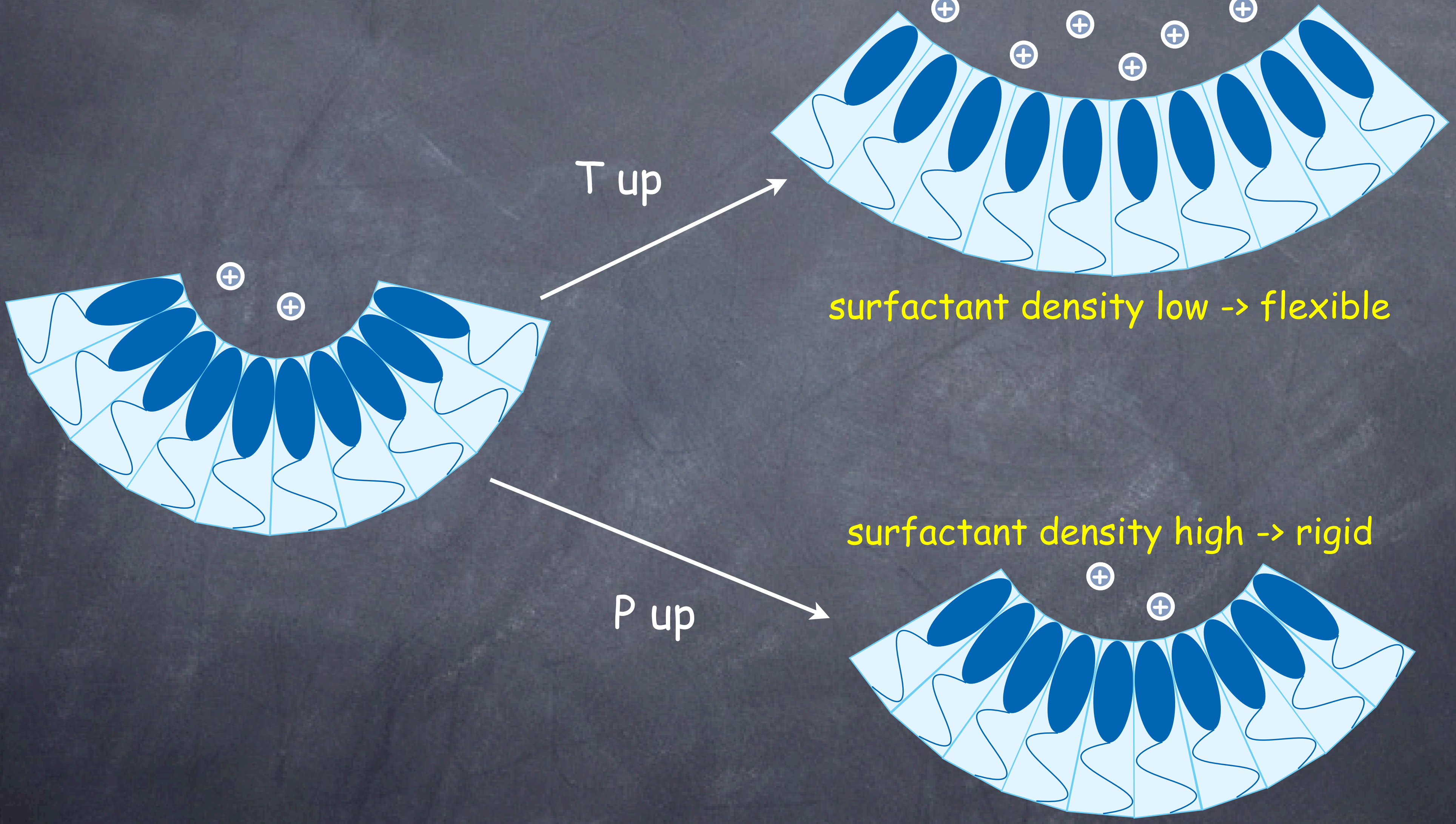


higher pressure: more rigid membrane

higher temperature: more flexible membrane

Y. Kawabata et al., *J. Chem. Phys.* **127**, 044705 (2007).

mechanisms



T up

head-head repulsion increase

surfactant density low -> flexible

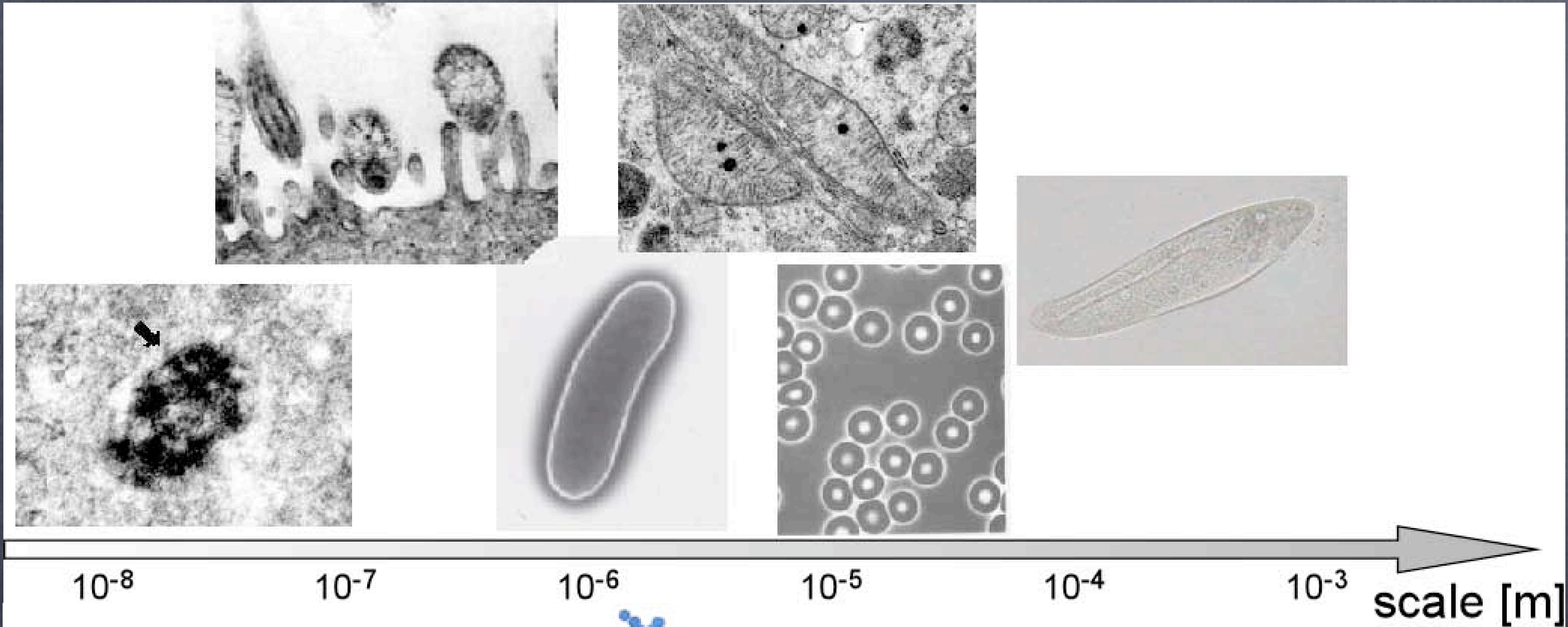
P up

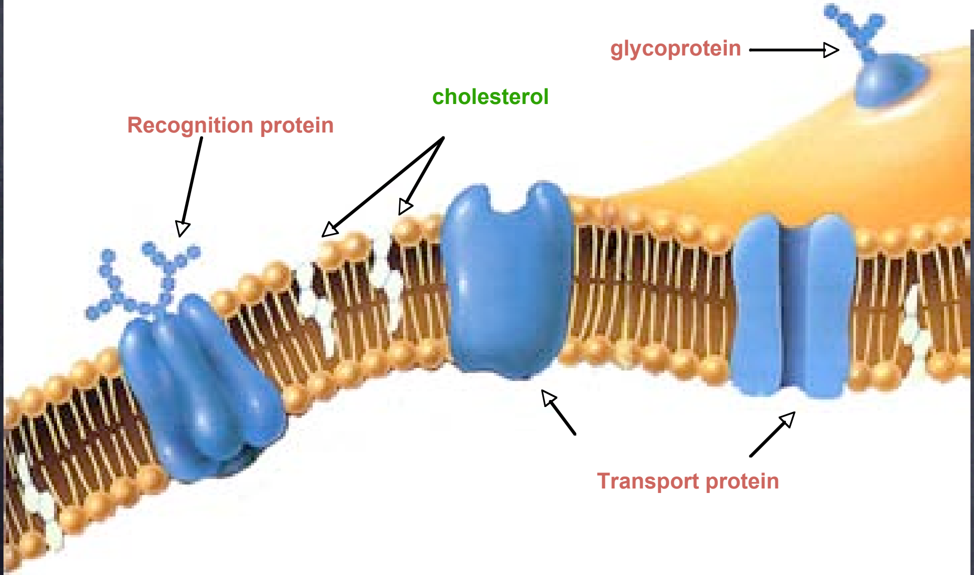
surfactant density high -> rigid

tail-tail attraction increase

single membrane fluctuations in model biomembranes

various structures of cell membrane

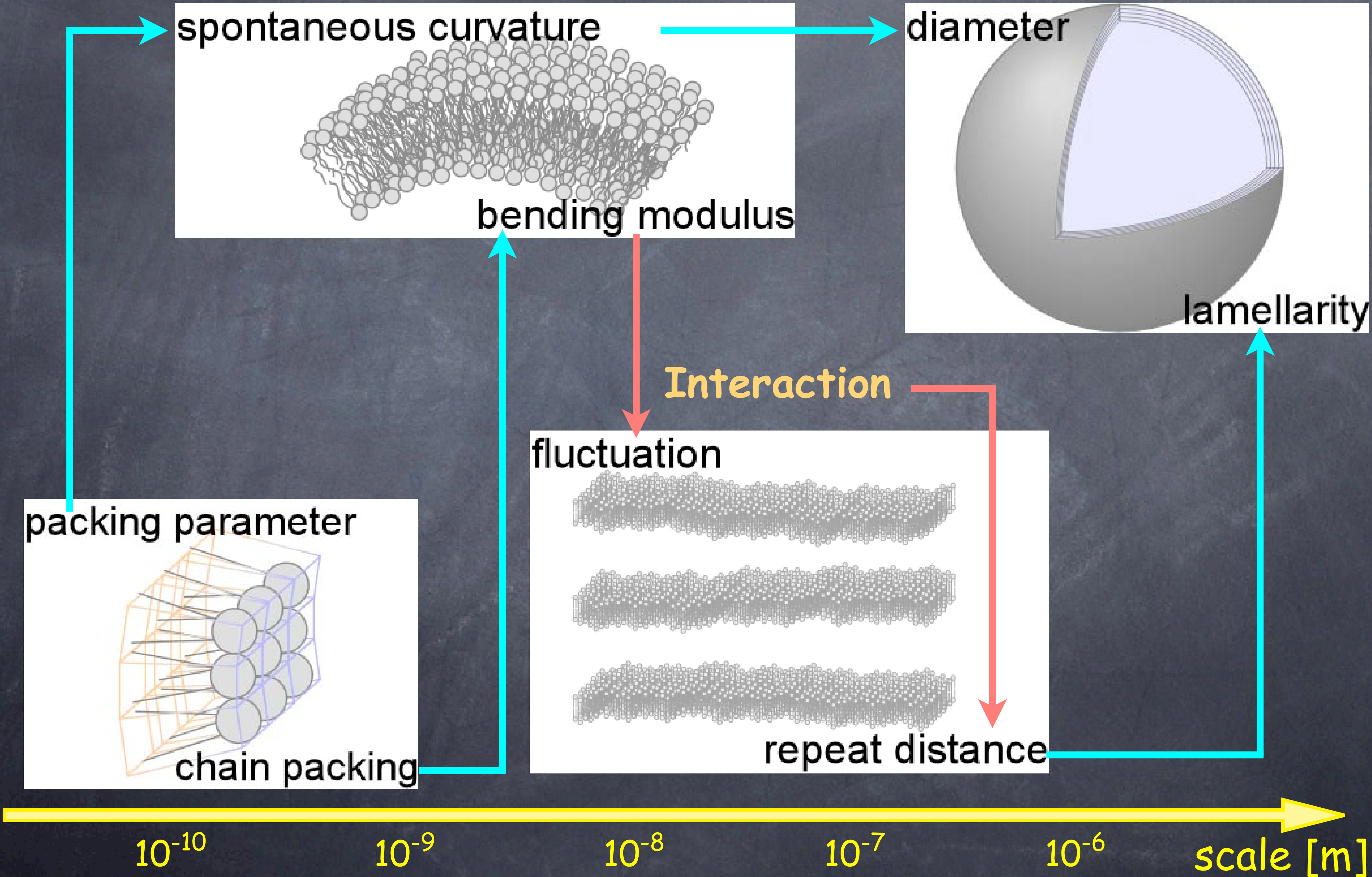




lipid bilayers are the basic structure of cell membranes

physical properties of cell membranes -> using model biomembranes (lipid bilayer)

hierarchical structure of lipid vesicles



packing parameter

chain packing

spontaneous curvature

bending modulus

Interaction

fluctuation

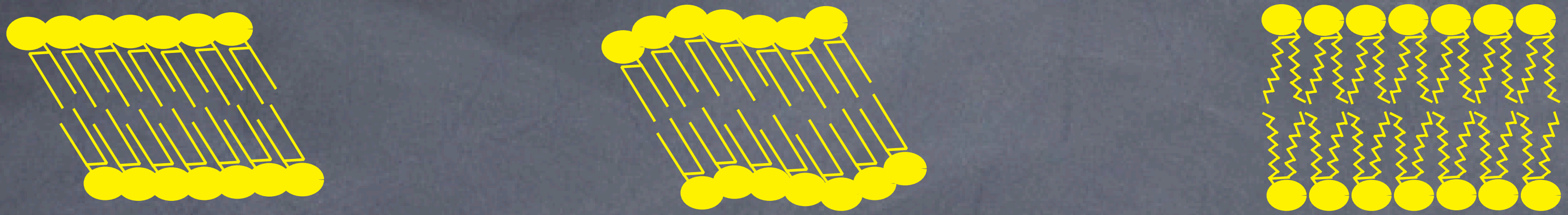
repeat distance

diameter

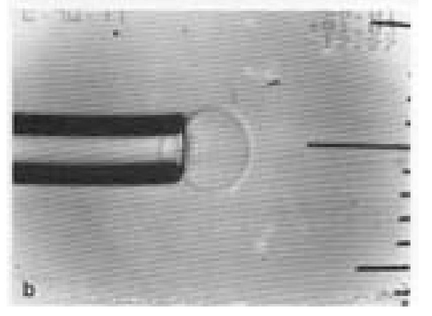
lamellarity

10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} scale [m]

phase diagram

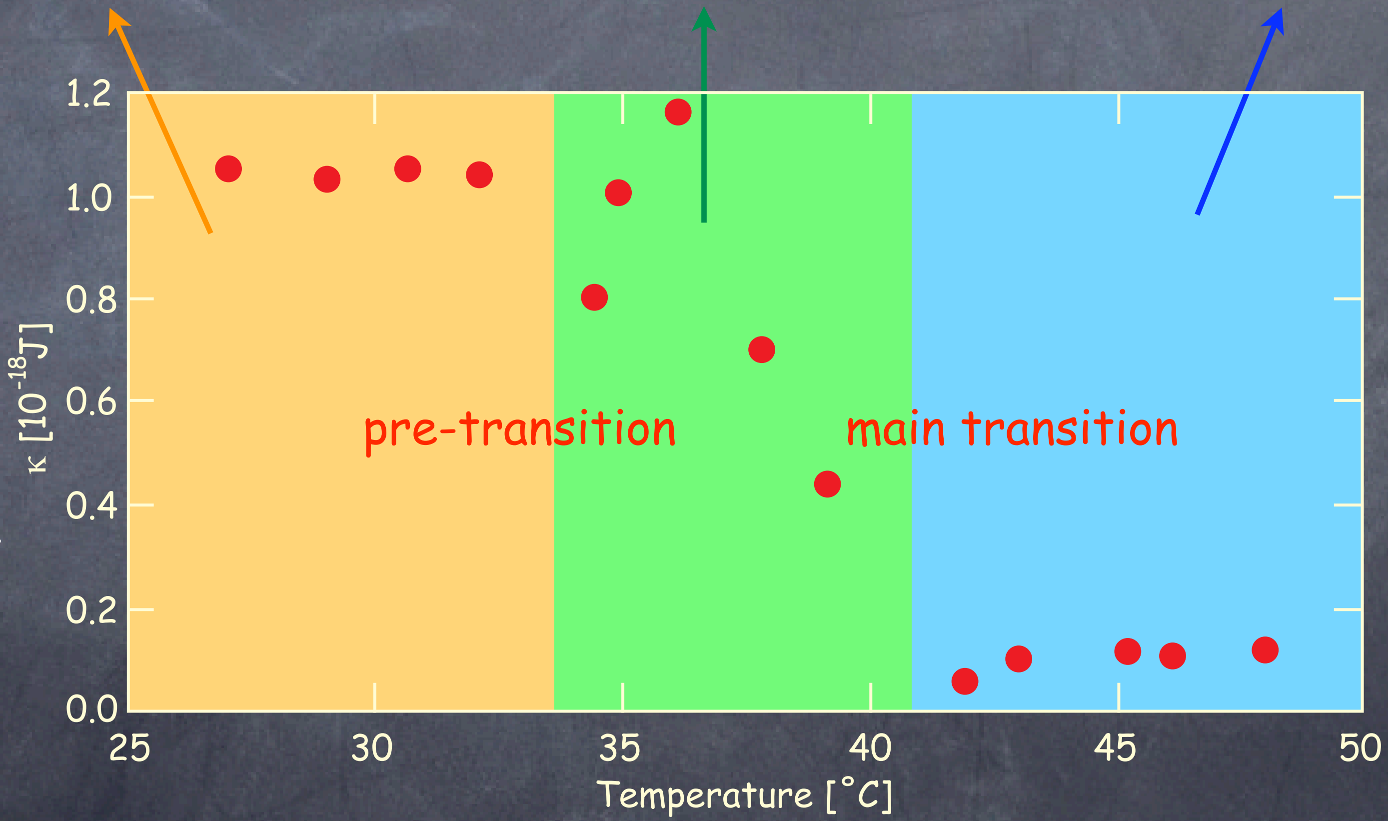


lamellar gel phase (Lβ′) ripple gel phase (Pβ′) liquid crystalline phase (Lα)



R. Kwolk and E. Evans, *Biophys. J* **35**, 637 (1981).

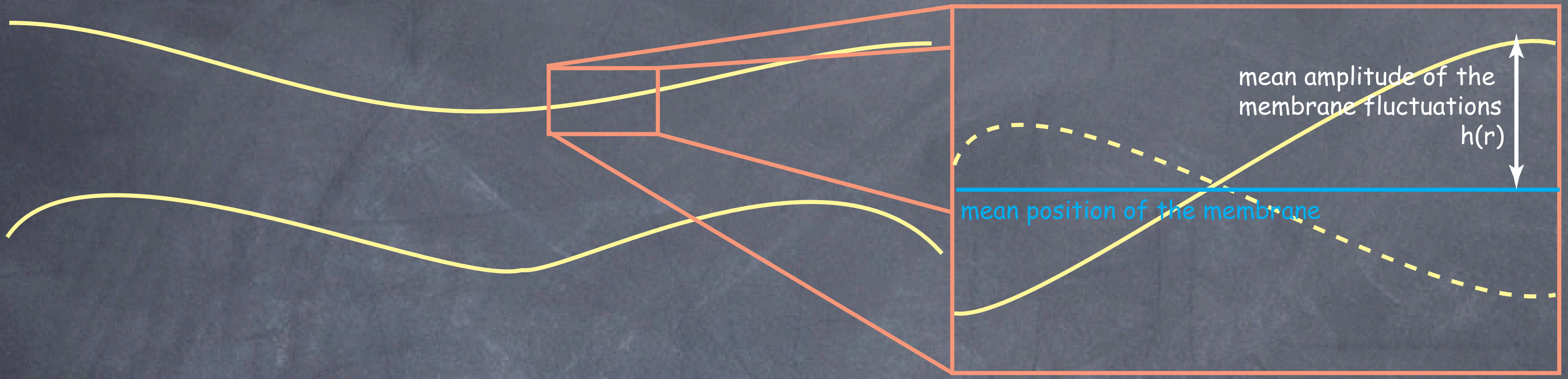
micropipetting



C. H. Lee et al, *Phys. Rev. E* **64**, 020901 (2001).

values of κ differ one order of magnitude between higher and lower temperatures than the main transition temperature

single membrane fluctuation model



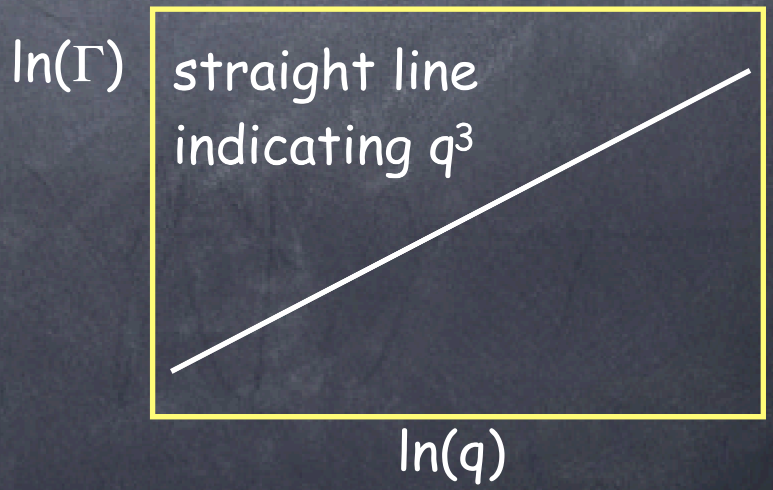
bending energy of the membrane

$$H = \frac{1}{2}\int \kappa[\nabla^2 h(\boldsymbol{r})]^2 d\boldsymbol{r}$$

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

in case of 2-D membranes, $\beta=2/3$

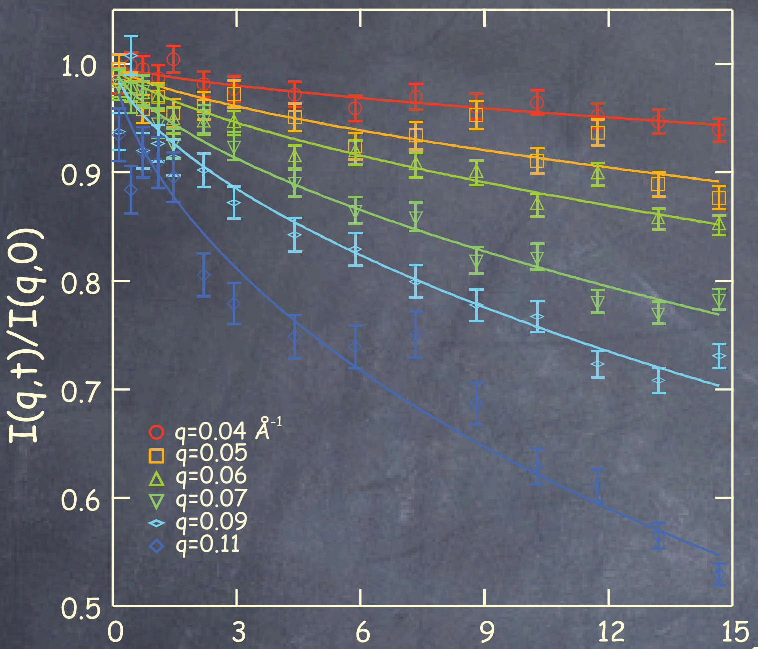
$$\Gamma(q) = 0.025\left(\frac{k_B T}{\kappa}\right)^{1/2}\frac{k_B T}{\eta}q^3$$



straight line indicating q^3

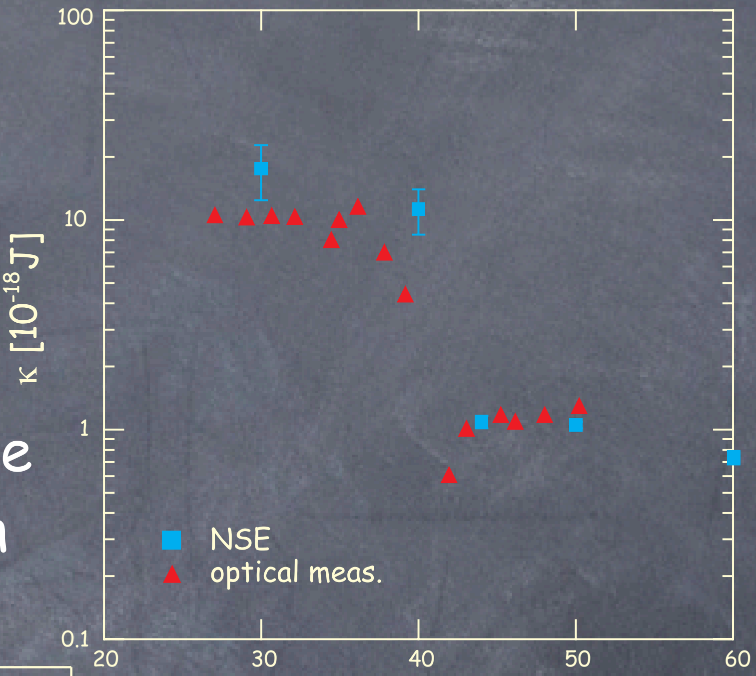
A. G. Zilman and R. Granek, *Phys. Rev. Lett.*, **77**, 4788 (1996).

NSE data

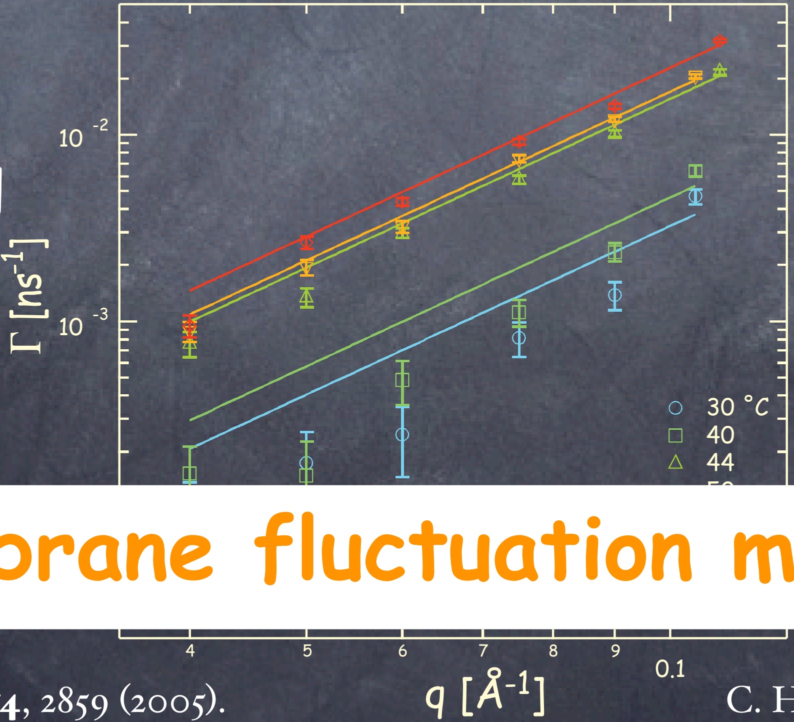


I(q,t) data follows stretched exponential decay with β=2/3

Γ follows q³, which is expected by the single membrane fluctuation model



estimated values of κ is consistent to the values in literature



single membrane fluctuation model is useful

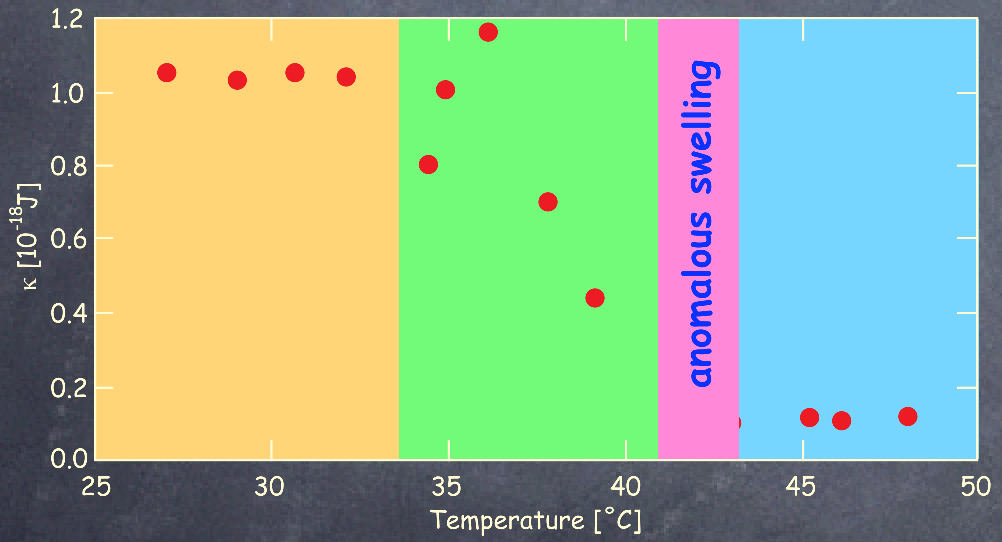
N. L. Yamada et al, *J. Phys. Soc. Jpn.* **74**, 2859 (2005).

H. Seto et al, submitted to *Euro. Phys. J. E.*

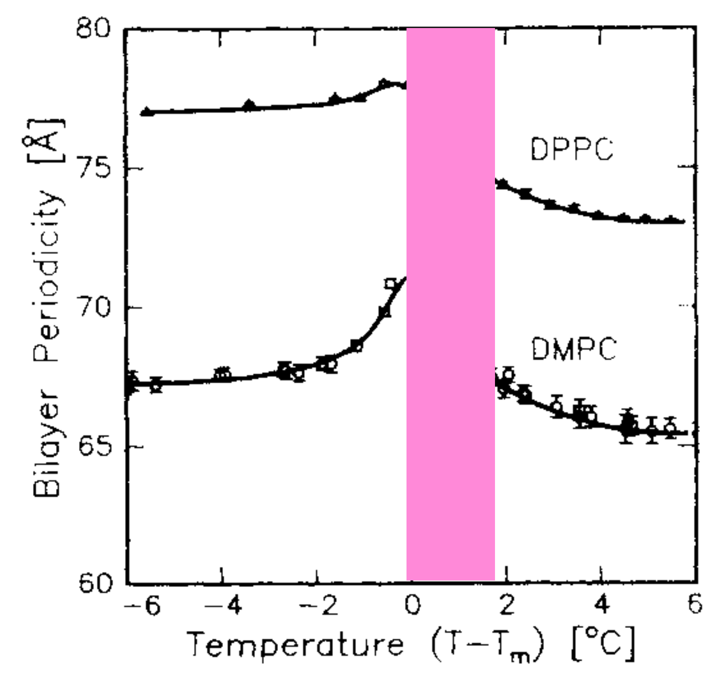
C. H. Lee et al, *Phys. Rev. E* **64**, 020901 (2001).

anomalous swelling

increase of the mean repeat distance between lipid bilayers with decreasing temperature to the main transition temperature

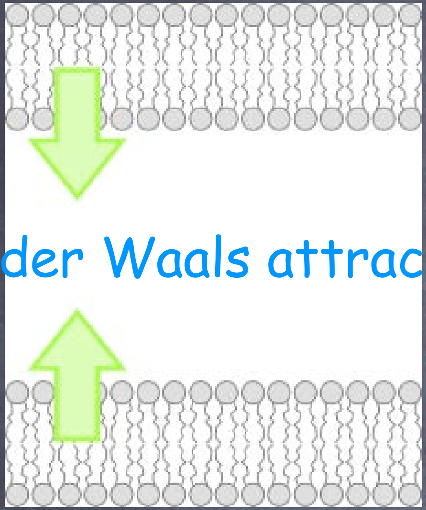


C. H. Lee et al, *Phys. Rev. E* **64**, 020901 (2001).

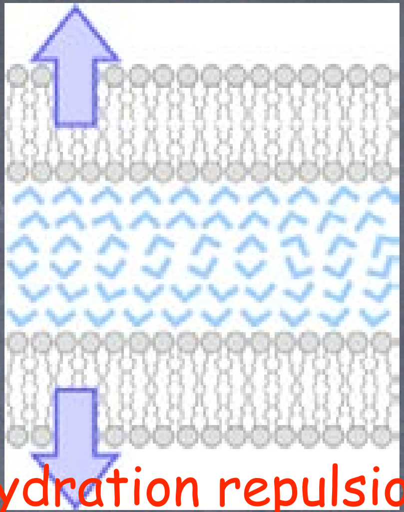


T. Hønger et al., *Phys. Rev. Lett*. **72**, 3911 (1994).

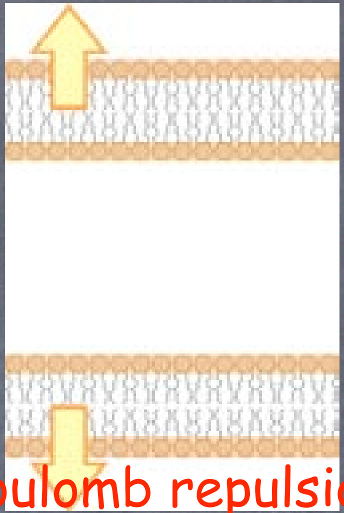
Interaction between membranes



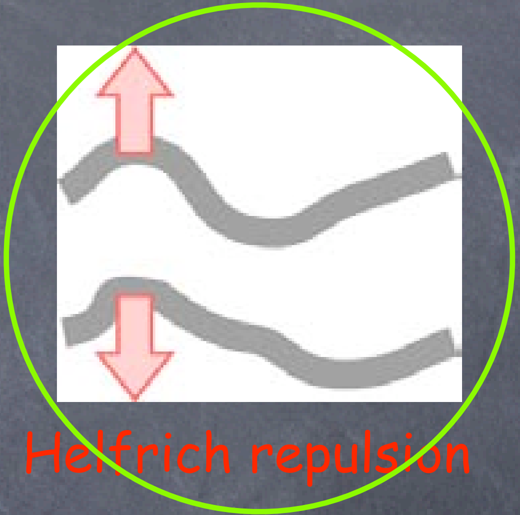
van der Waals attraction



hydration repulsion



Coulomb repulsion



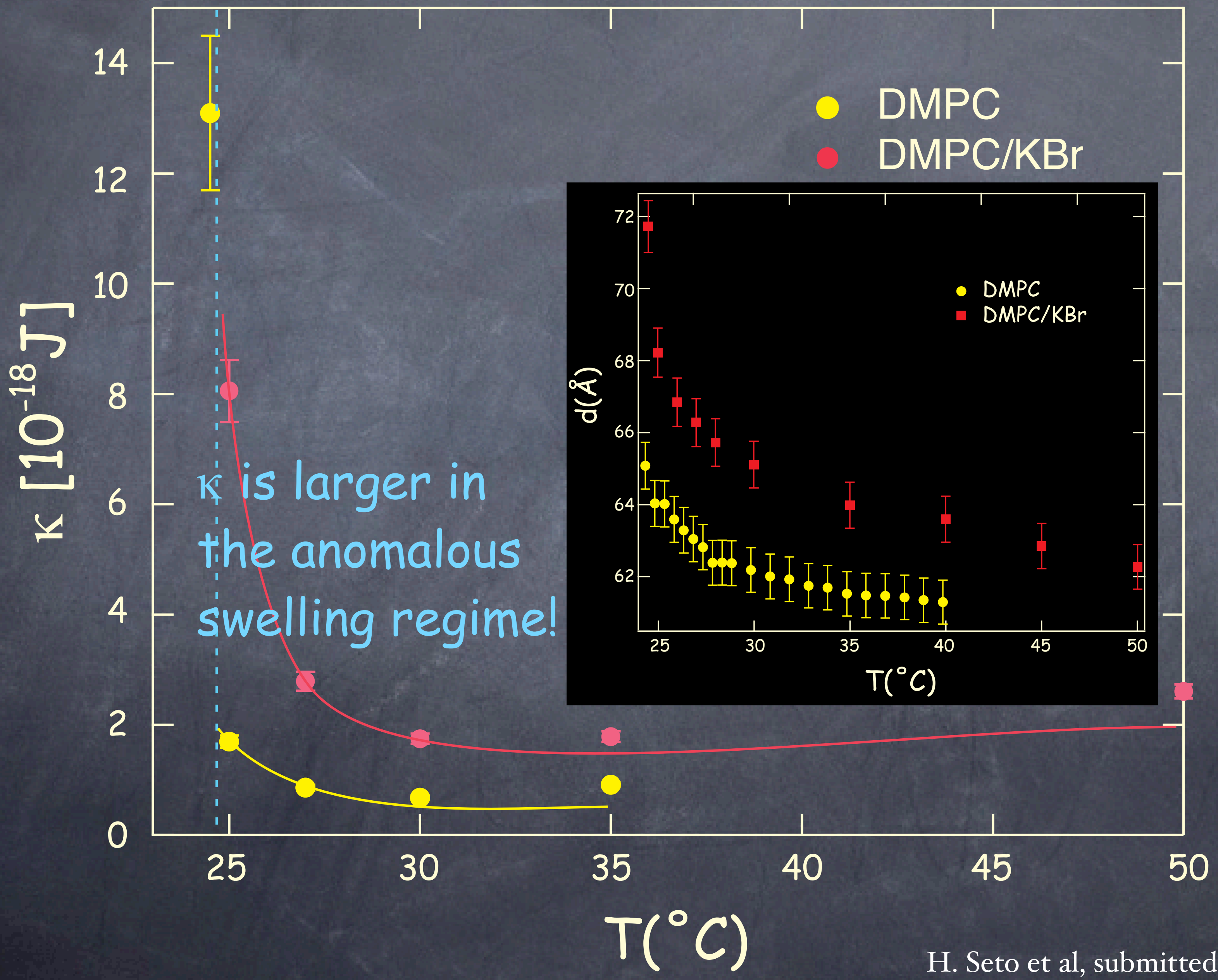
Helfrich repulsion

In the anomalous swelling regime, Helfrich repulsion can be larger to make the lamellar repeat distance longer.

softening of the layer can be the origin of the anomalous swelling.

Let's check this by NSE technique.

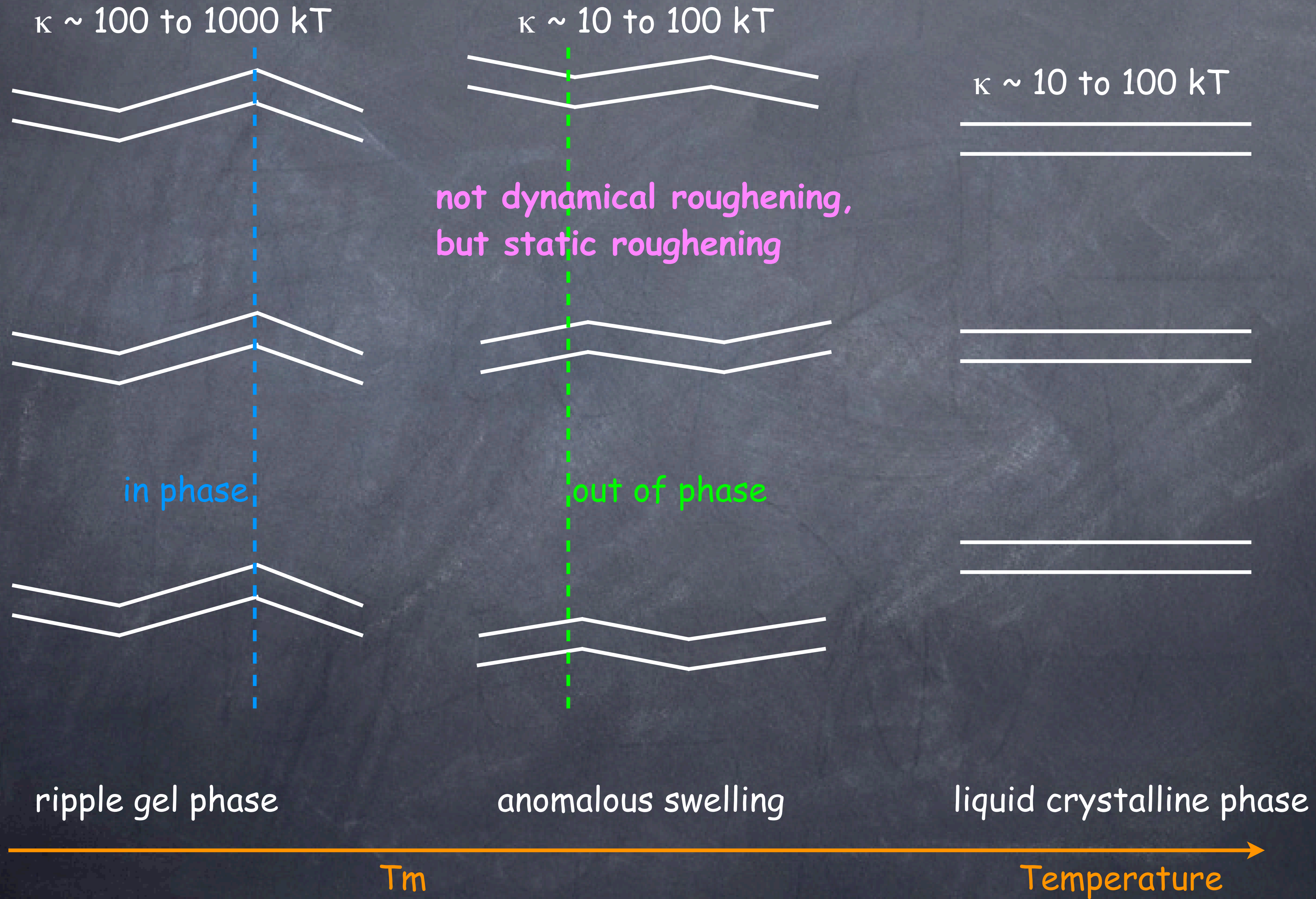
bending modulus in anomalous swelling



κ is larger in the anomalous swelling regime!

H. Seto et al, submitted to *Euro. Phys. J. E.*

origin of the anomalous swelling



κ ~ 100 to 1000 kT

κ ~ 10 to 100 kT

κ ~ 10 to 100 kT

not dynamical roughening,
but static roughening

in phase

out of phase

ripple gel phase

anomalous swelling

liquid crystalline phase

Tm

Temperature

summary of the talk

shape fluctuations of surfactant membrane in microemulsion

collaboration with Dr. Kawabata and Profs. Seto and Takeda

single membrane fluctuation in model biomembranes

collaboration with Dr. Yamada and Prof. Seto

messages

NSE can access collective dynamics of complex systems such as polymers, micelles, surfactants especially in the low-q region. NSE gives you unique opportunities to see dynamics in these fields. I hope you will come back to do your own science!

Thank you for your attention