量子ビームでさぐるソフトマターの物性

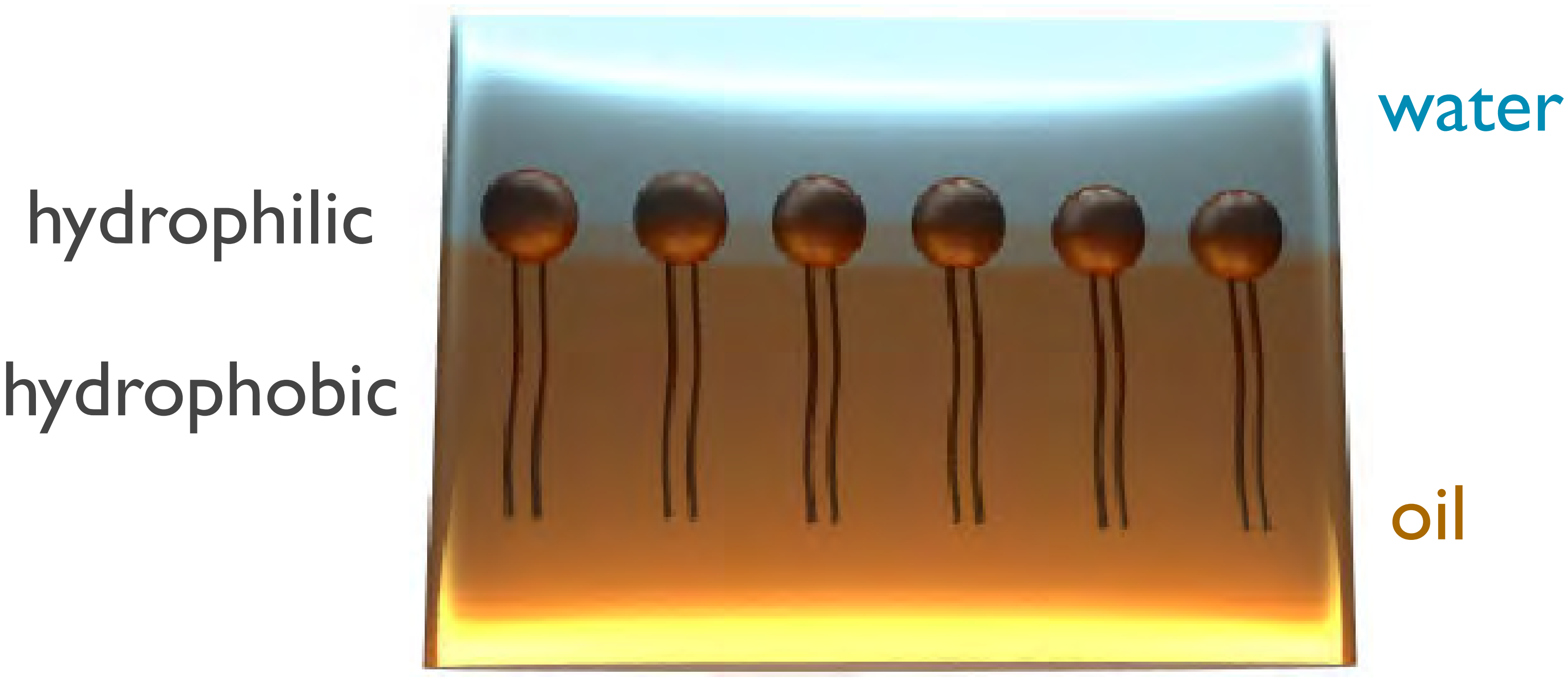
Membrane Dynamics

瀬戸秀紀

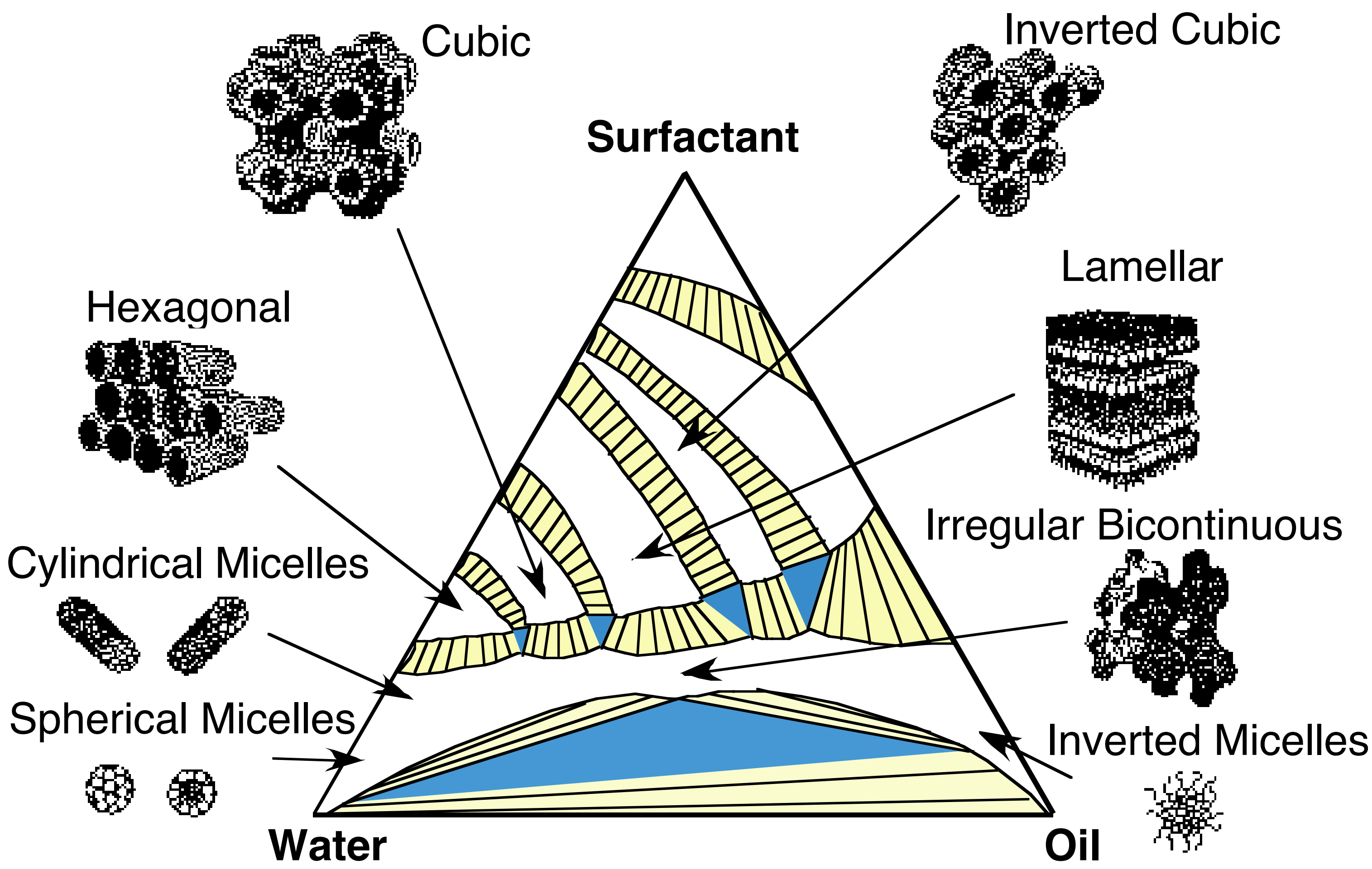
CROSS

High Energy Accelerator Research Organization

両親媒性分子系

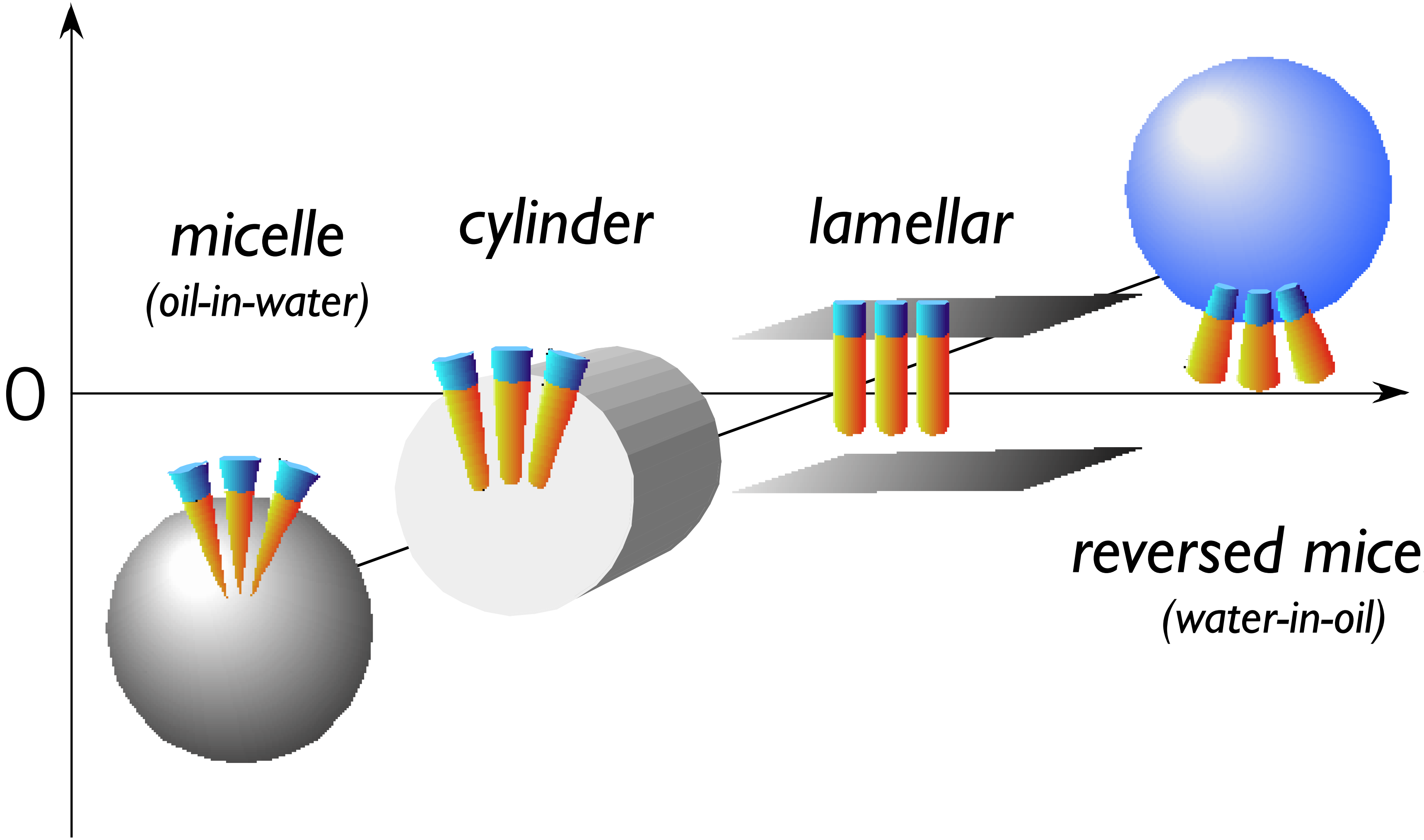


マイクロエマルションの構造

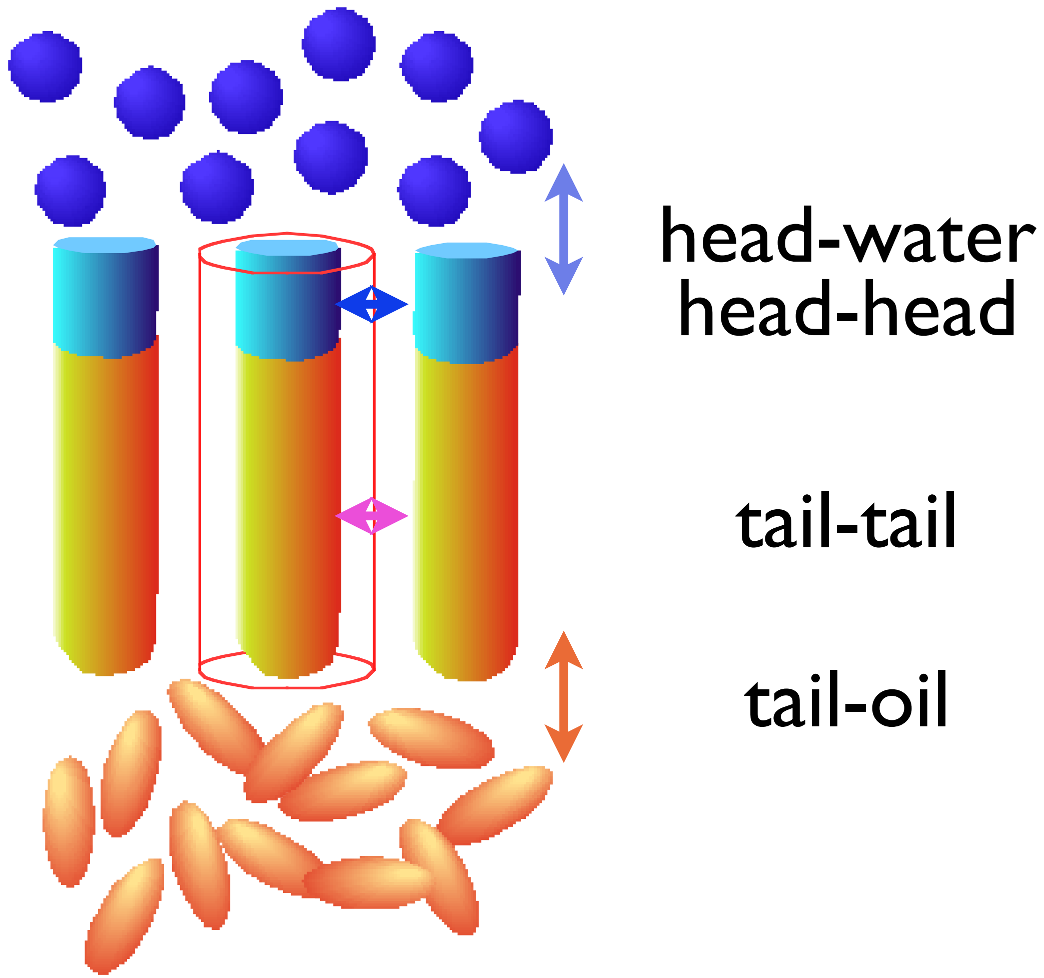


自発曲率

packing parameterに依存する

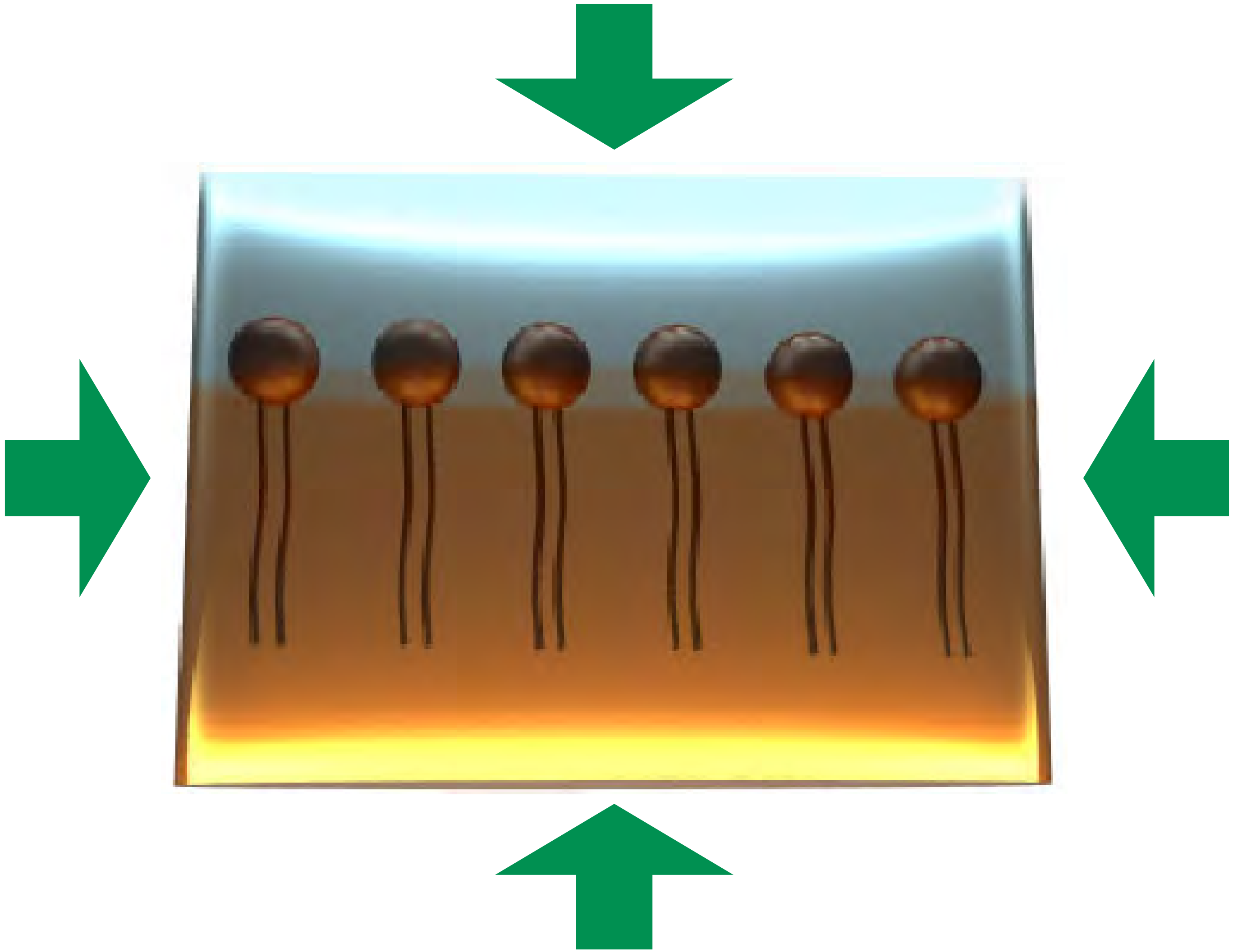


Packing parameter

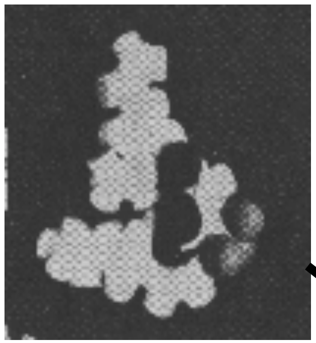


Pressure dependence

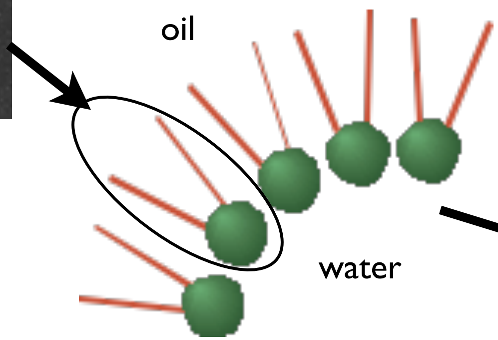
M. Nagao, HS, et al. 1999-2007



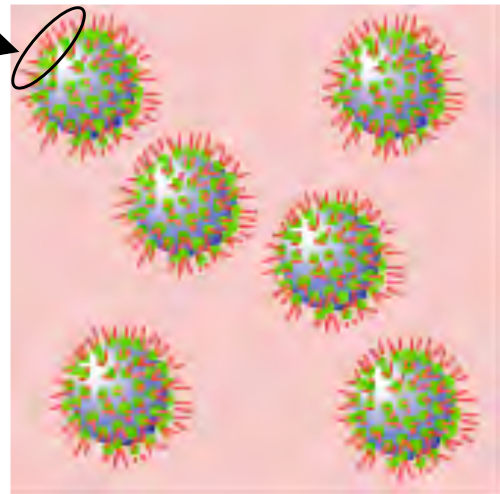
AOT + D_2O + *n*-decane



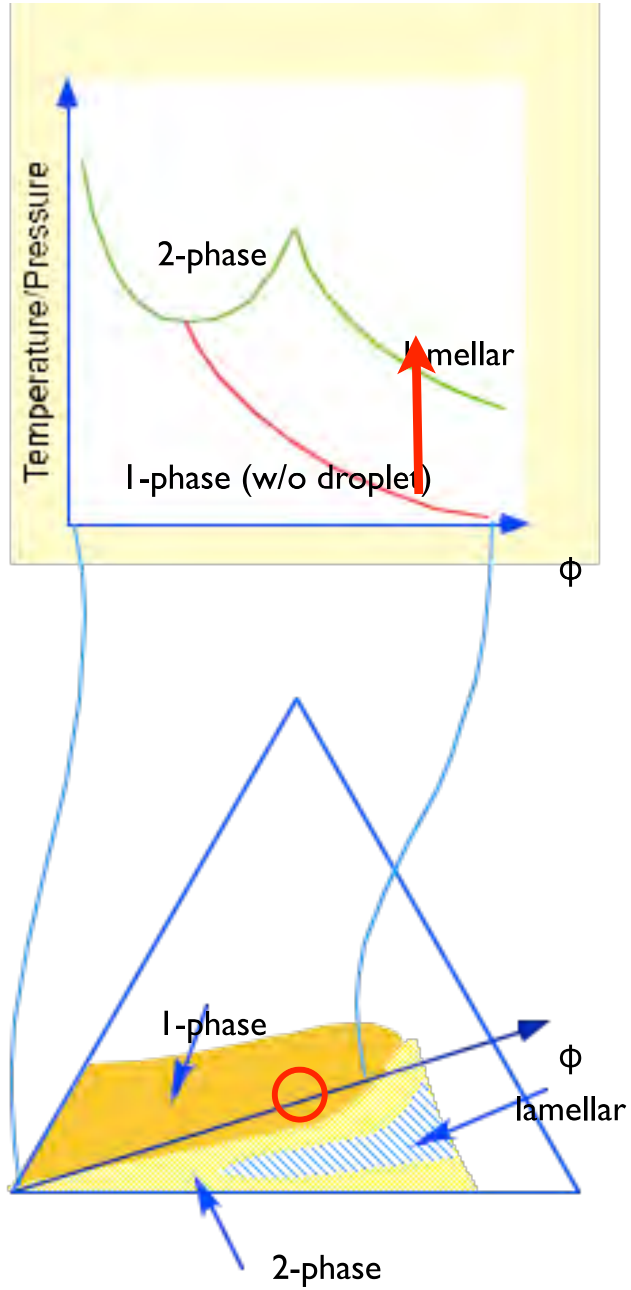
AOT molecule



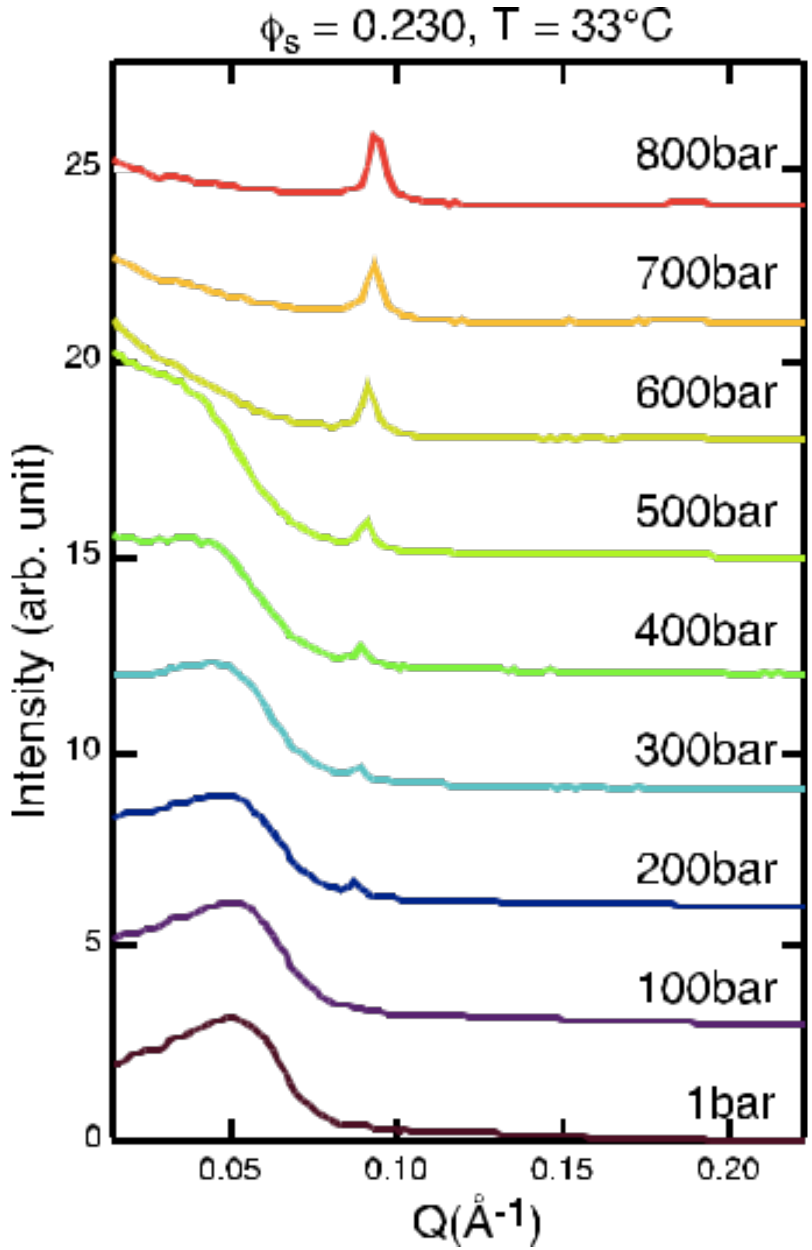
spontaneous curvature > 0



water-in-oil droplet

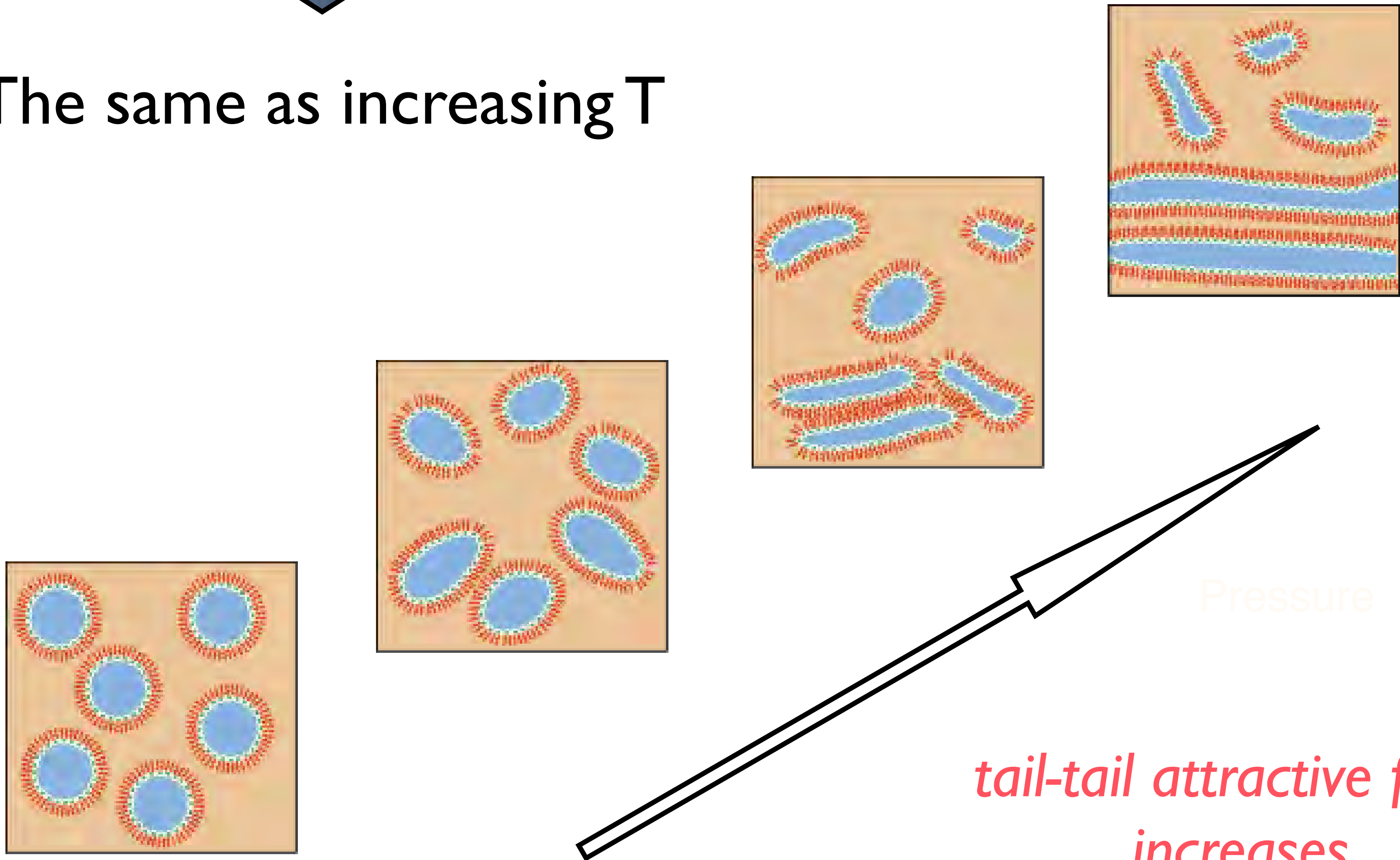


Pressure dependence of SAXS



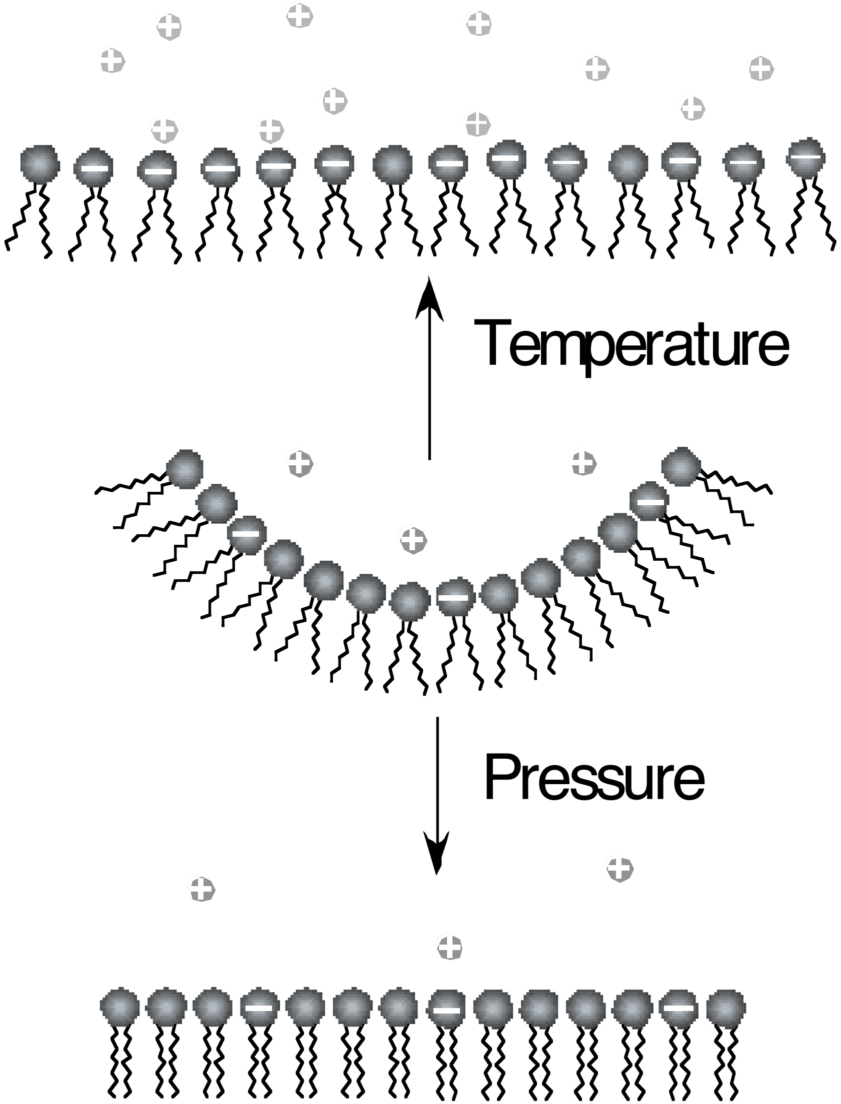
Structure change with P

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

温度変化と圧力変化の比較

ミクロな要因は違う

圧力変化：疎水基間相互作用

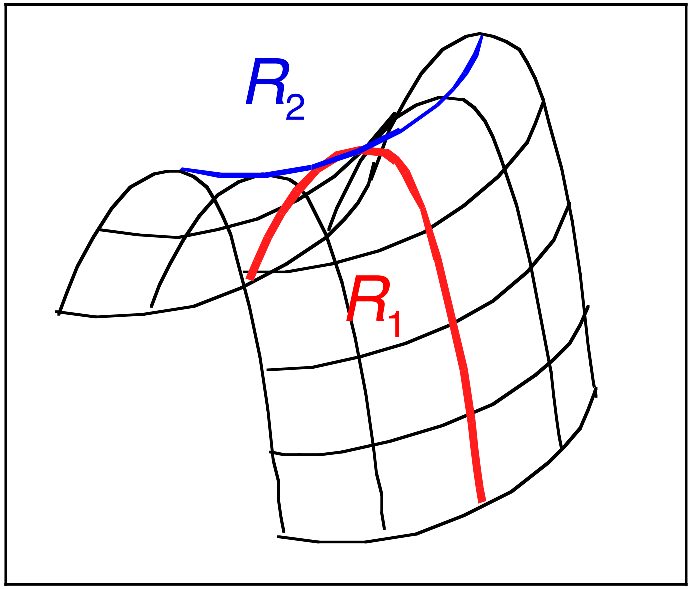
温度変化：親水基間相互作用

自発曲率の変化が影響？

膜の曲げ弾性係数は？

界面活性剤膜の曲げ弾性

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

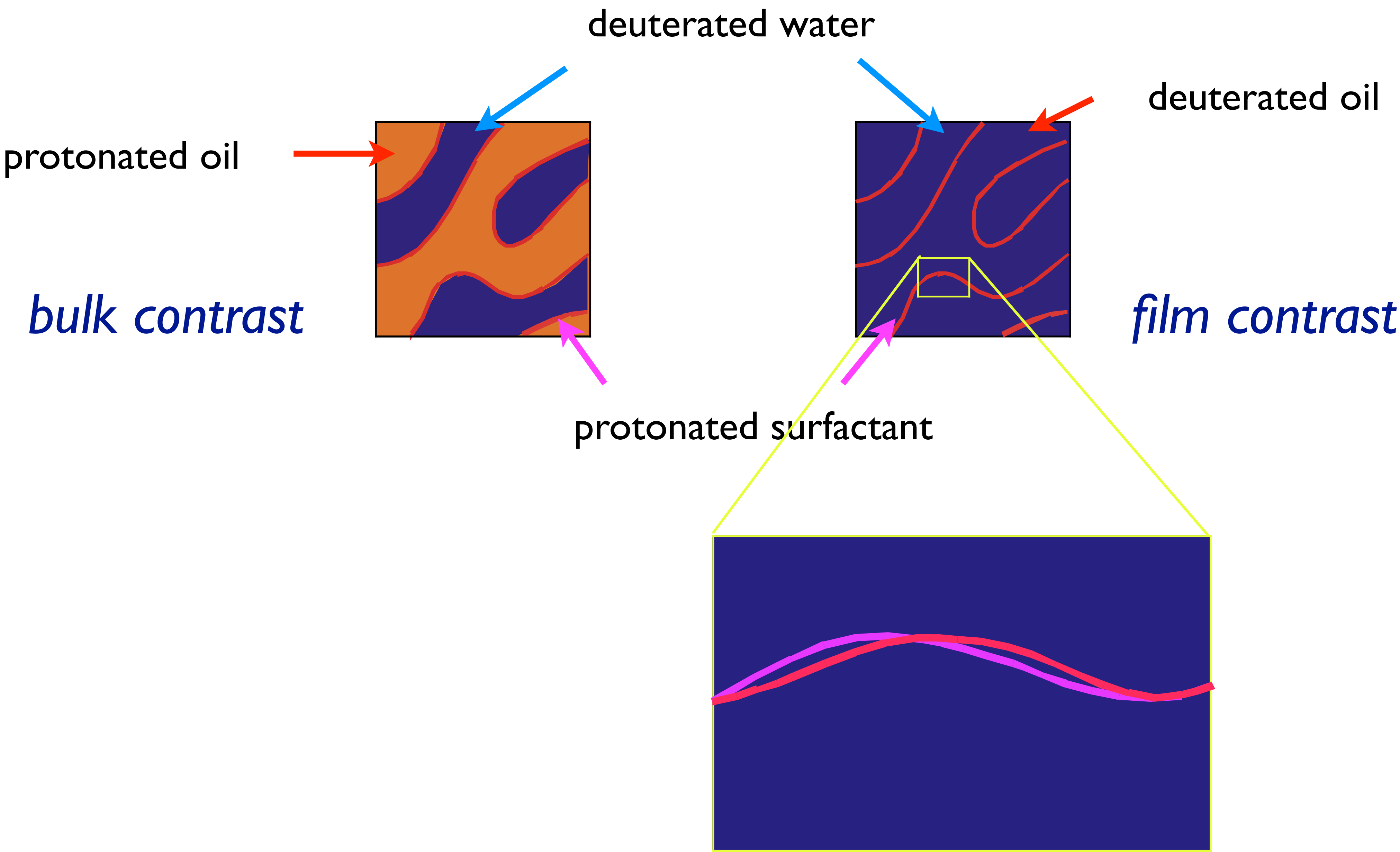
bending modulus

saddle-splay modulus

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

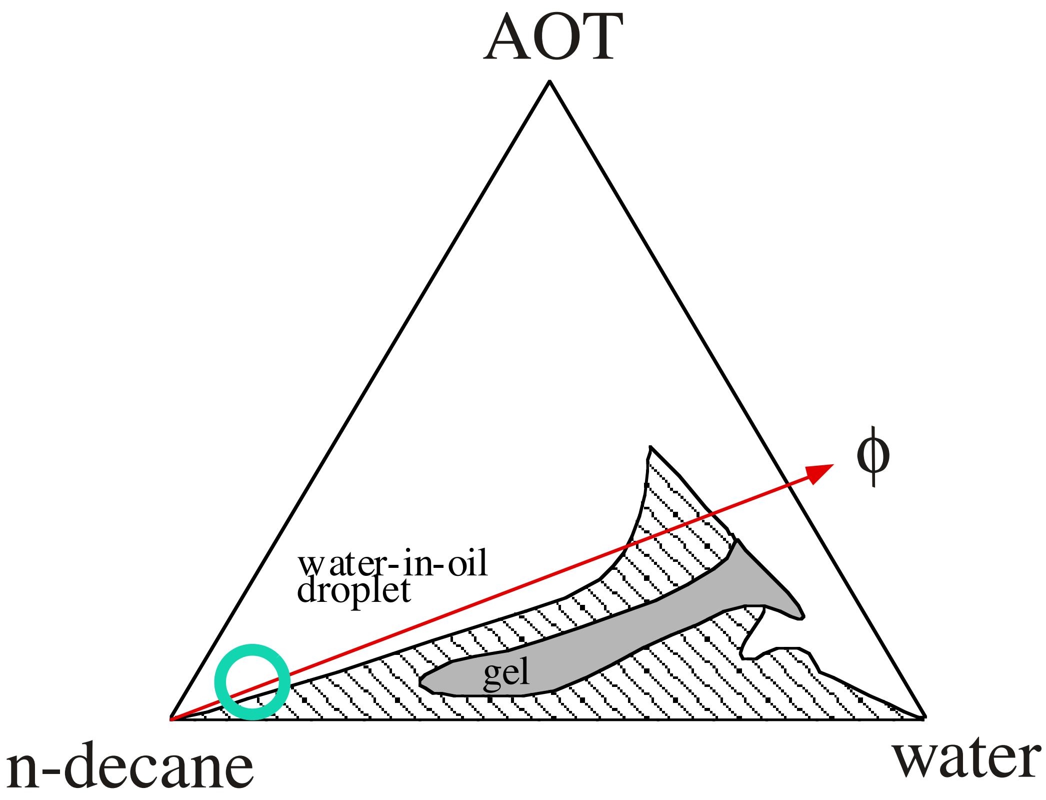
spontaneous curvature

膜だけを観る



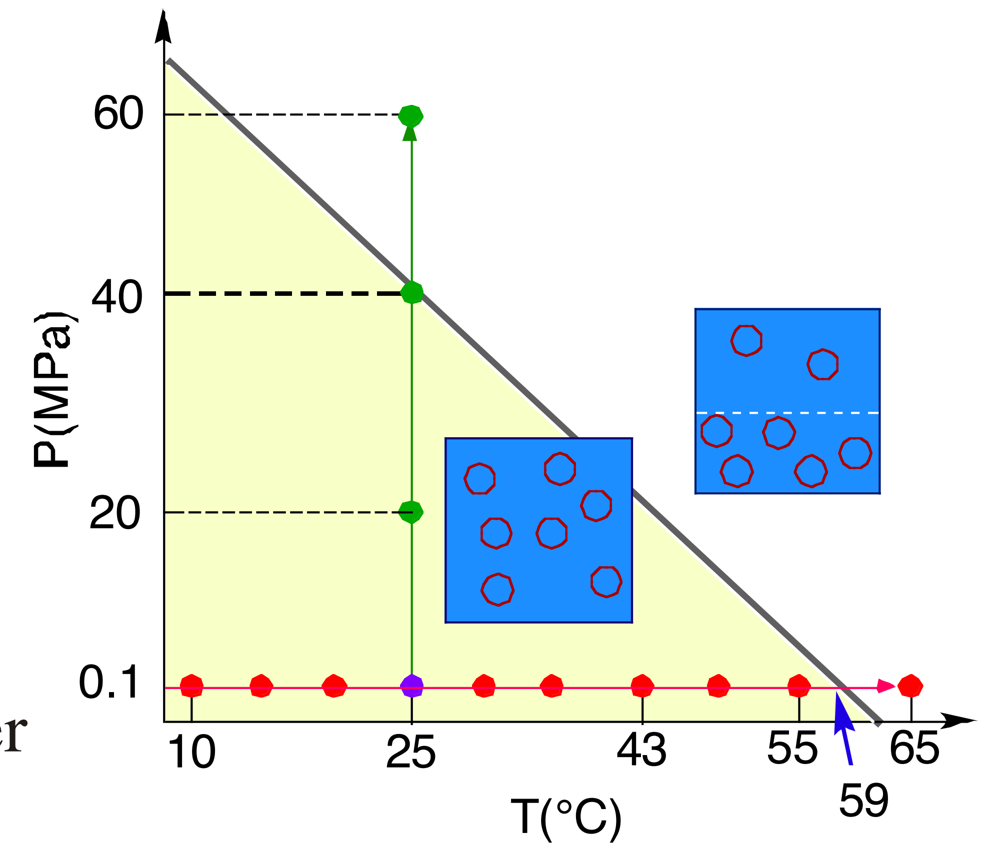
deuterated water
deuterated oil
protonated oil
bulk contrast
film contrast
protonated surfactant

油中水滴構造の相分離



AOT / D$_2$O / d-decane (film contrast)

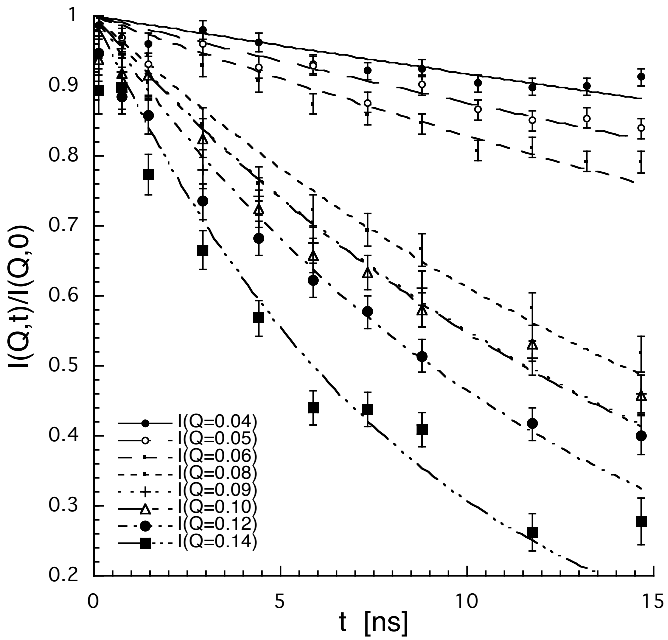
ϕ_S=0.37 (AOT volume fraction)



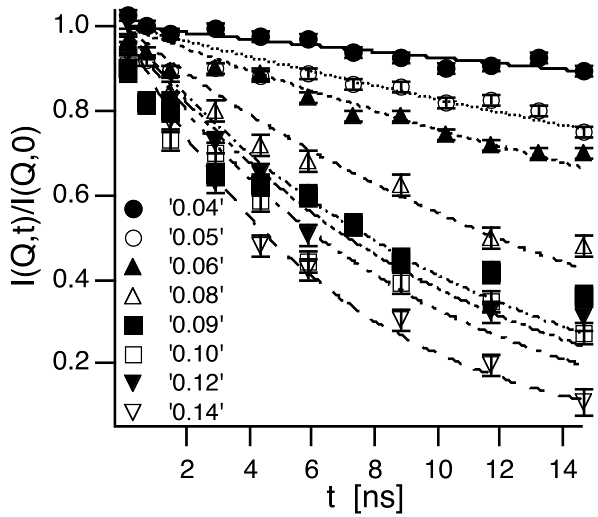
Kawabata et al., Phys. Rev. Lett. **92** (2004) 056103.

NSEの実験結果

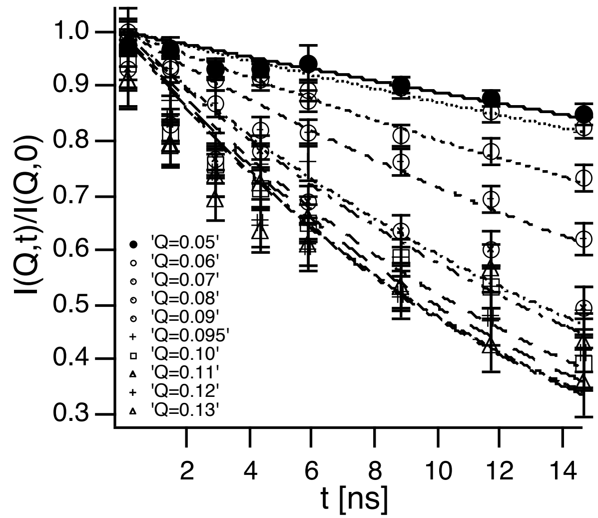
Room temperature/pressure
T=25°C/P=0.1MPa



T=43°C/P=0.1MPa



T=25°C/P=20MPa



球殻からの散乱

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

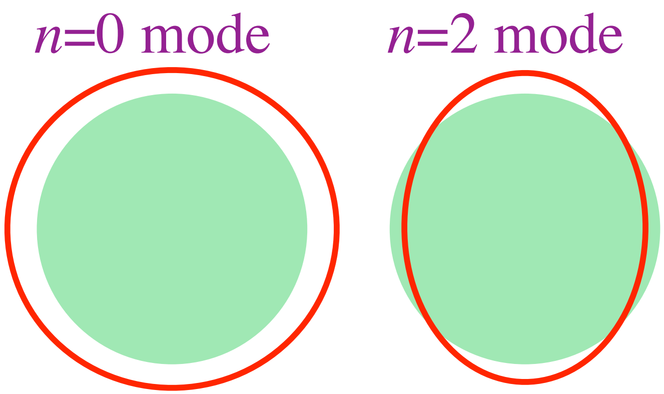
damping frequency of the 2nd mode deformation

mean-square displacement of the 2nd mode deformation

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

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

translational diffusion　　shape deformation

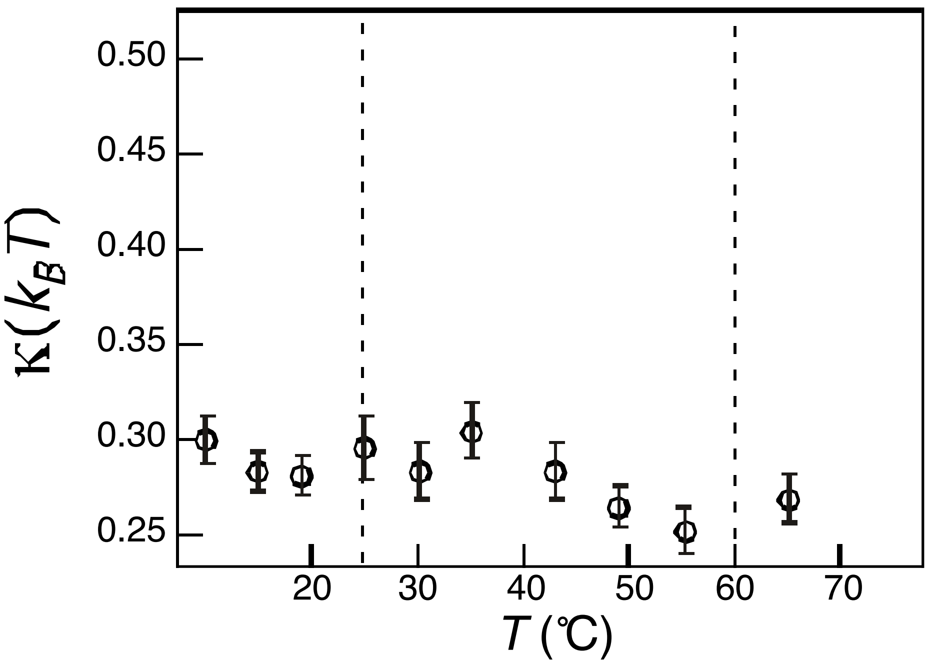


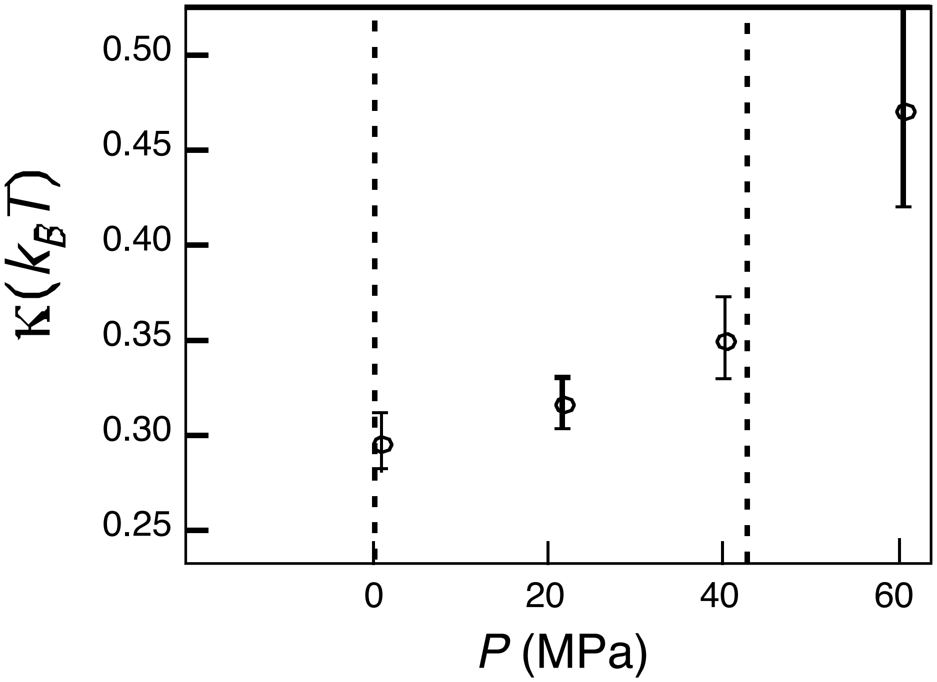
where

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

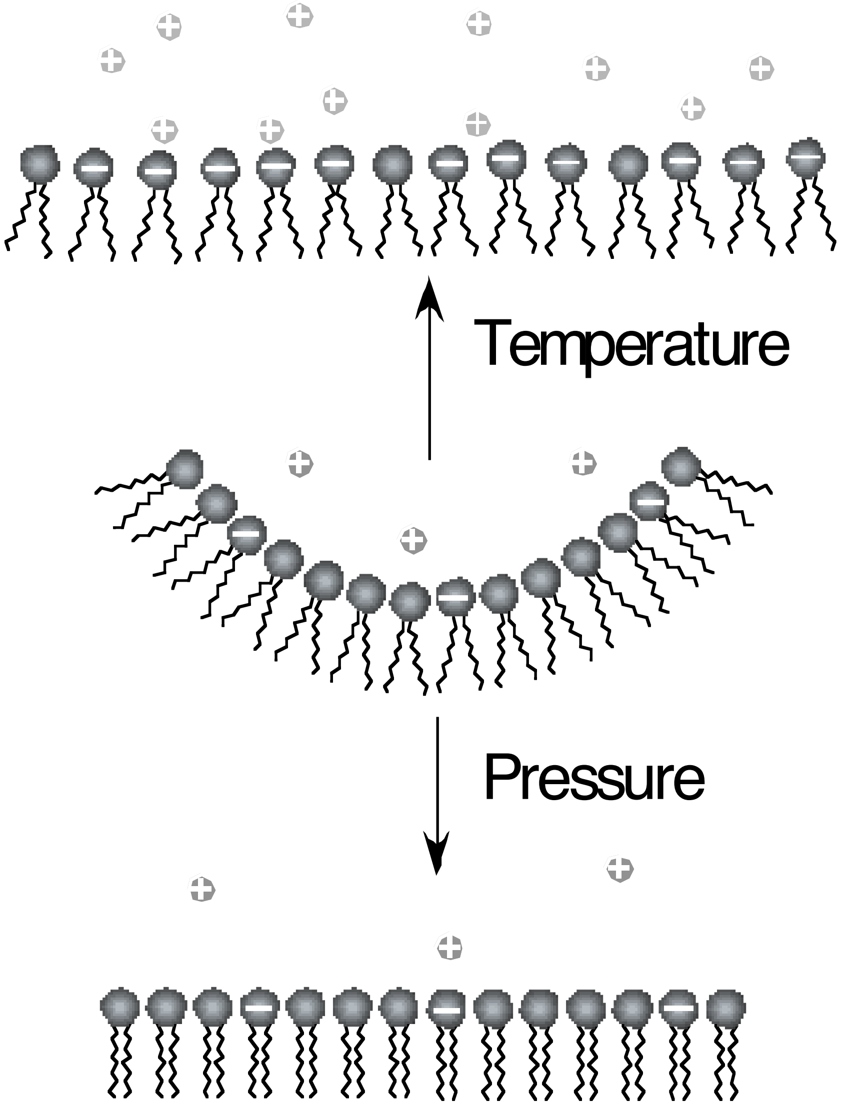
$$f_2(QR_0) = 5[4\, j_2(QR_0) - (QR_0)\, j_3(QR_0)]^2$$

曲げ弾性係数の温度変化と圧力変化



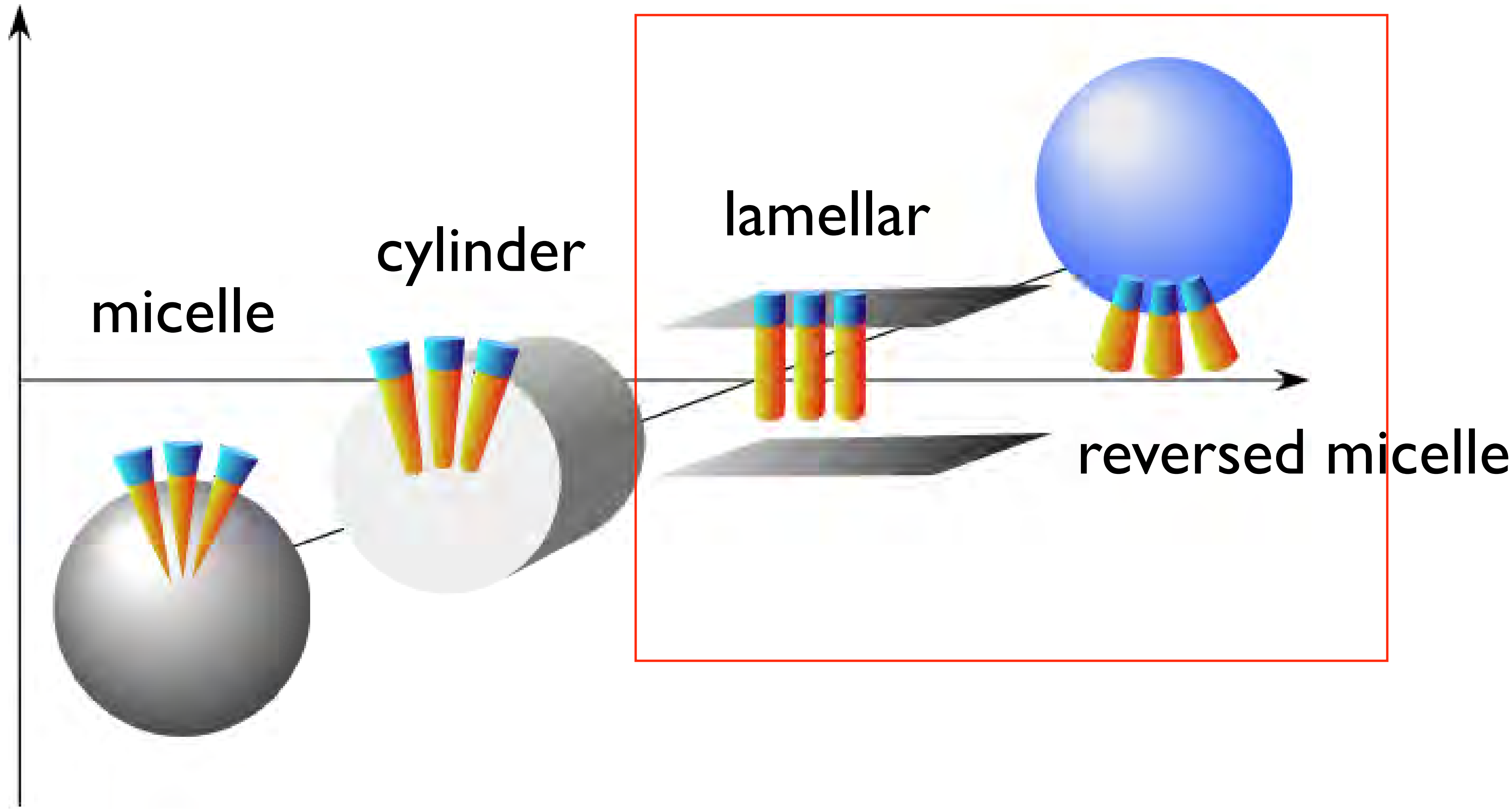


イオン性界面活性剤膜の温度効果と圧力効果



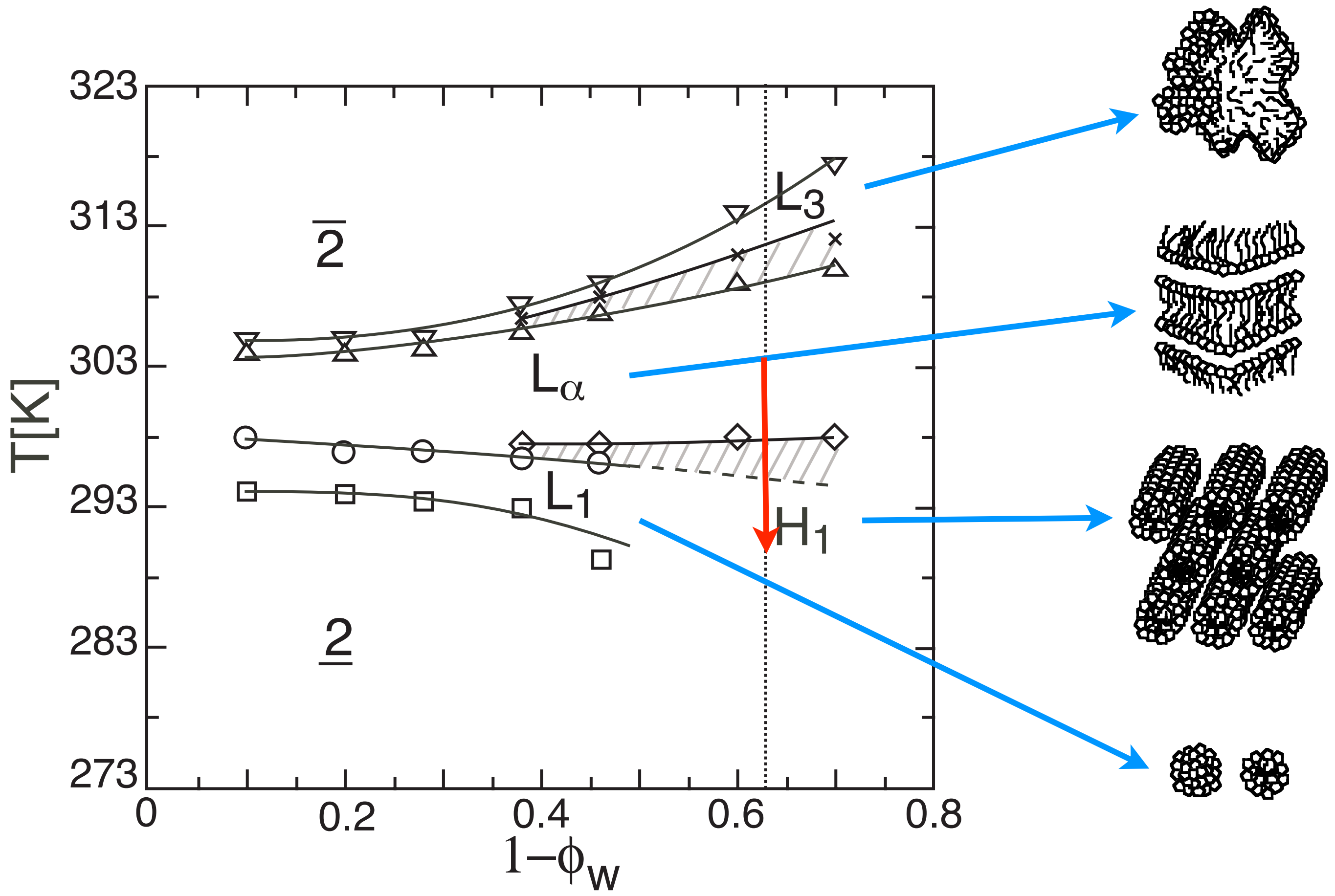
	spontaneous curvature	bending modulus
Temperature	decrease	decrease
Pressure	decrease	increase

AOT系のまとめ

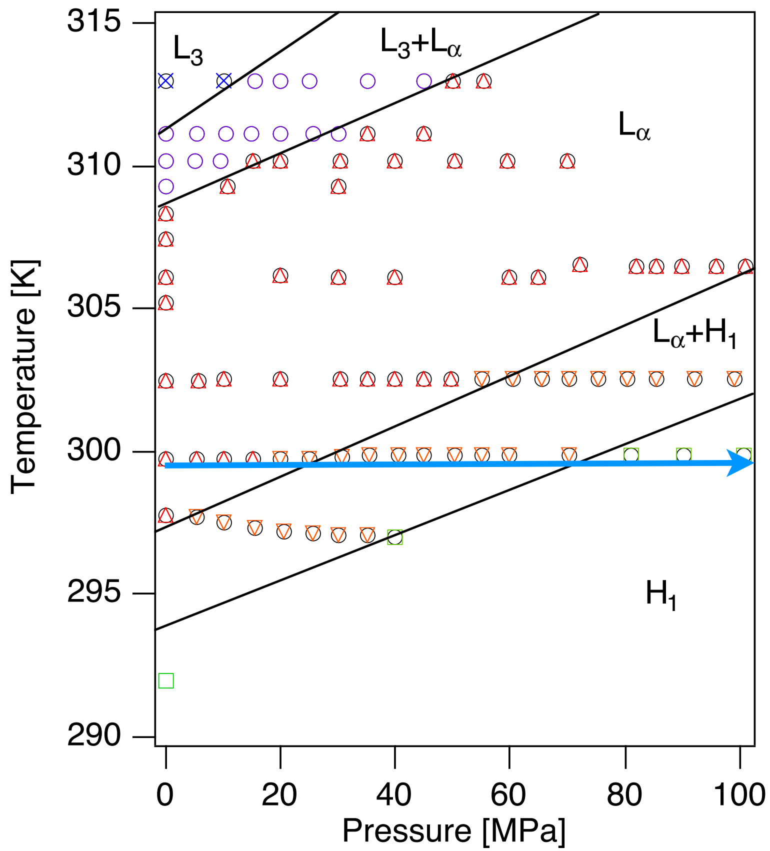


非イオン性界面活性剤$C_{12}E_5$ / D_2O / octane

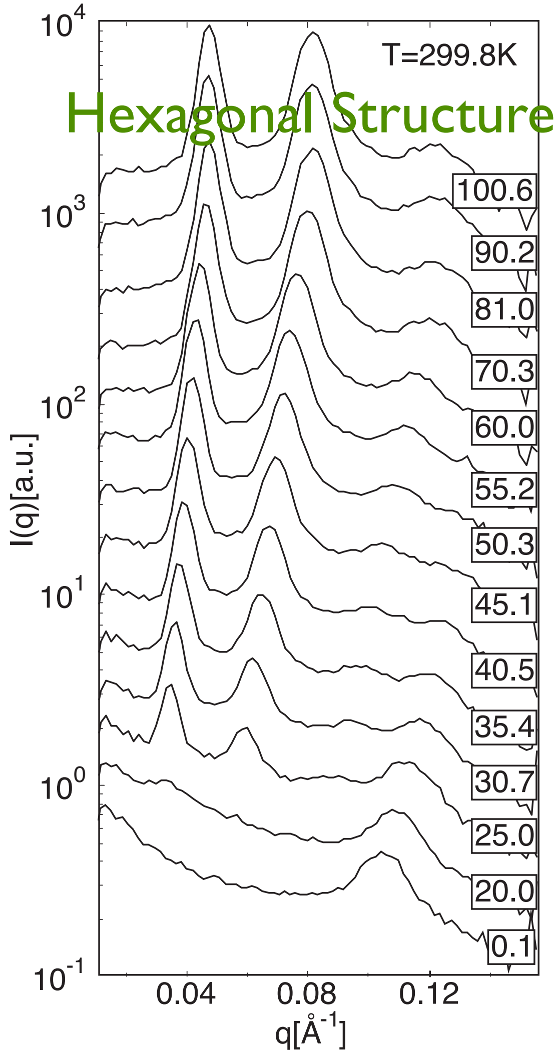
Nagao et al., J.Chem. Phys.,123 (2005) 054705.



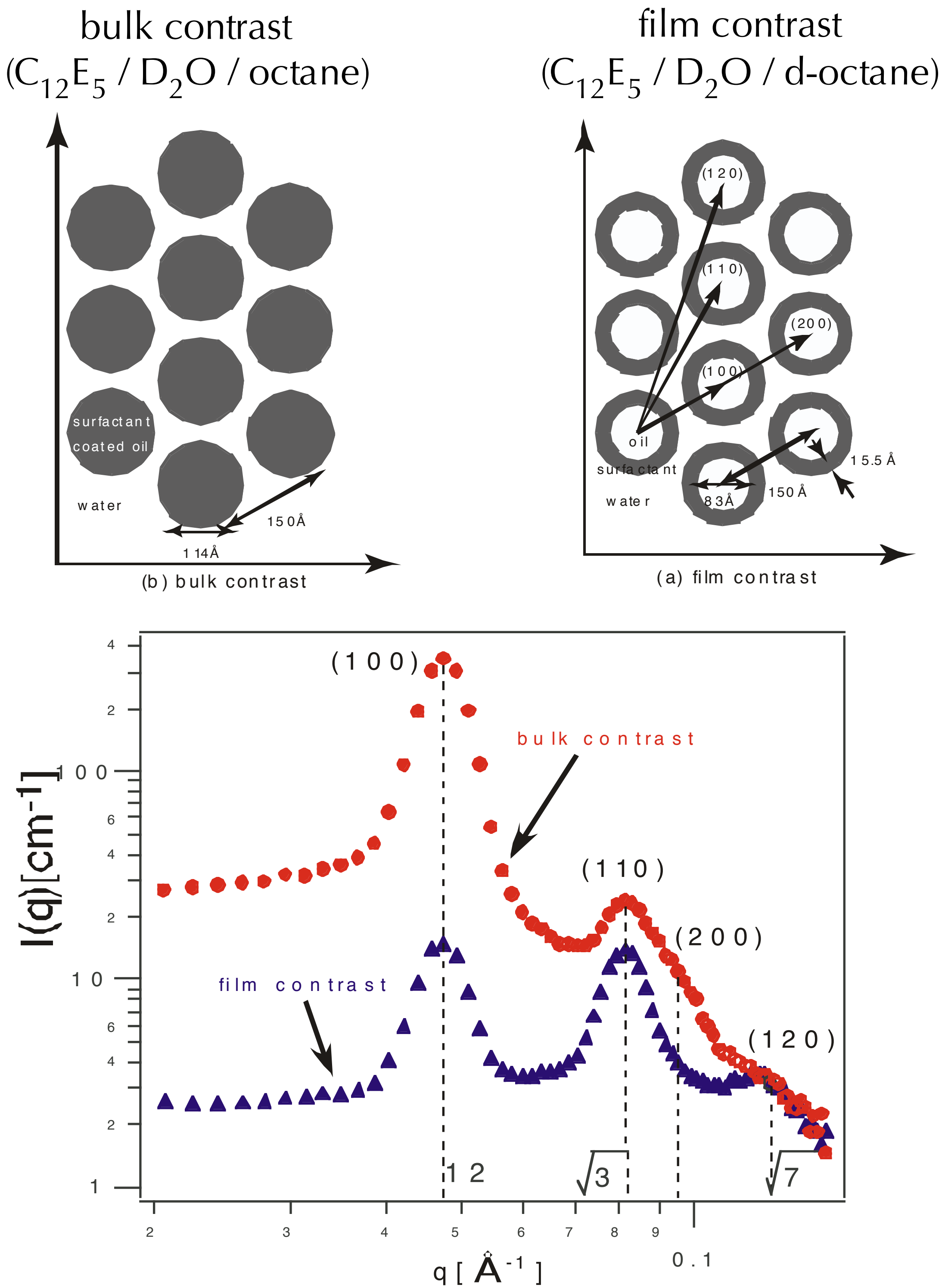
温度降下＝圧力上昇



315
310
305
300
295
290
0
20
40
60
80
100
Pressure [MPa]
Temperature [K]
L_3
L_3+L_α
L_α
$L_\alpha+H_1$
H_1

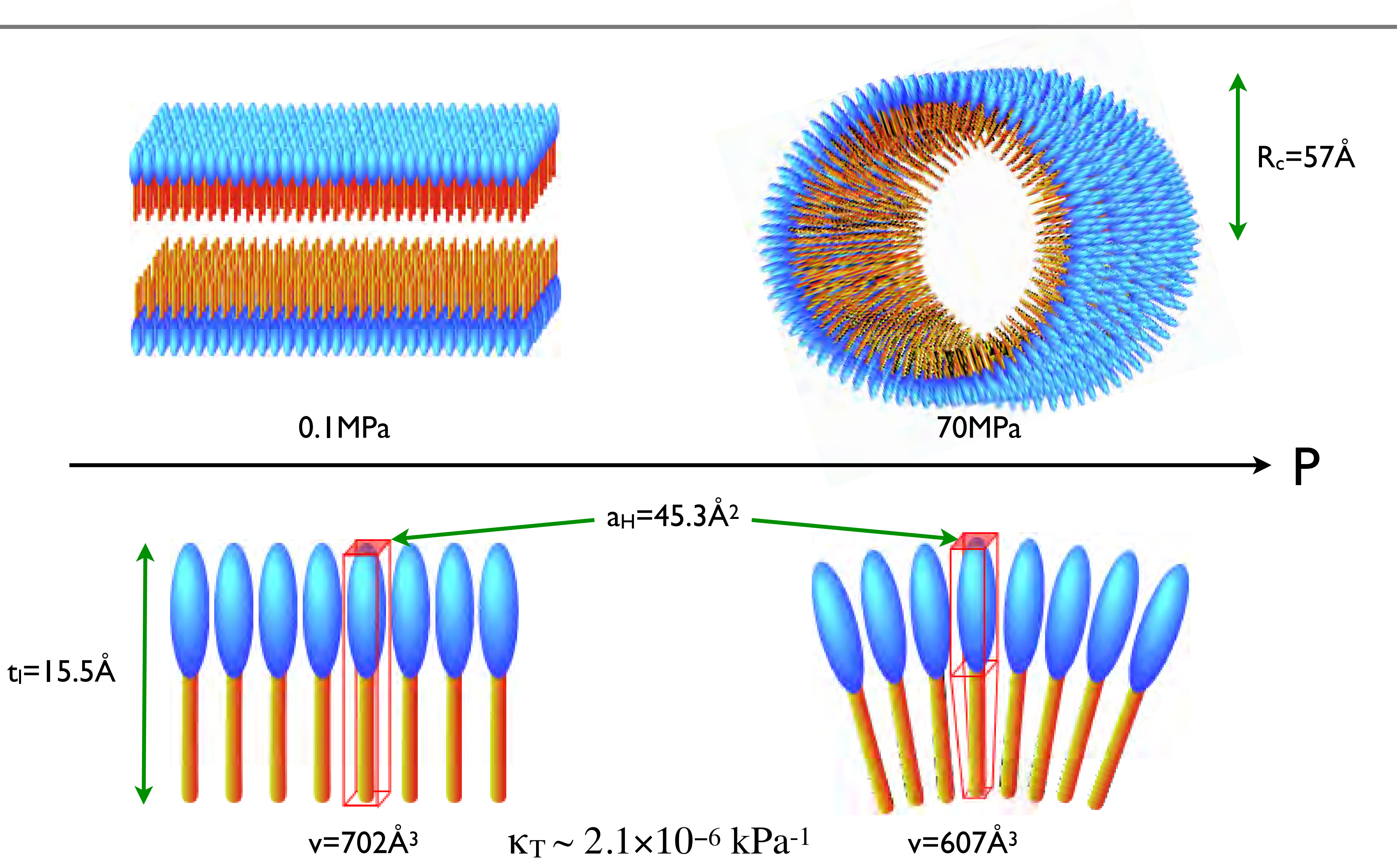


T=299.8K
Hexagonal Structure
100.6
90.2
81.0
70.3
60.0
55.2
50.3
45.1
40.5
35.4
30.7
25.0
20.0
0.1
10^4
10^3
10^2
10^1
10^0
10^{-1}
I(q)[a.u.]
0.04
0.08
0.12
q[Å^{-1}]



bulk contrast
($C_{12}E_5$ / D_2O / octane)
film contrast
($C_{12}E_5$ / D_2O / d-octane)
surfactant
coated oil
water
150Å
114Å
(b) bulk contrast
(120)
(110)
(200)
(100)
oil
surfactant
water
15.5 Å
150 Å
83Å
(a) film contrast
(100)
bulk contrast
(110)
(200)
(120)
film contrast
I(q)[cm-1]
q [Å-1]
1 2
√3
√7
0.1

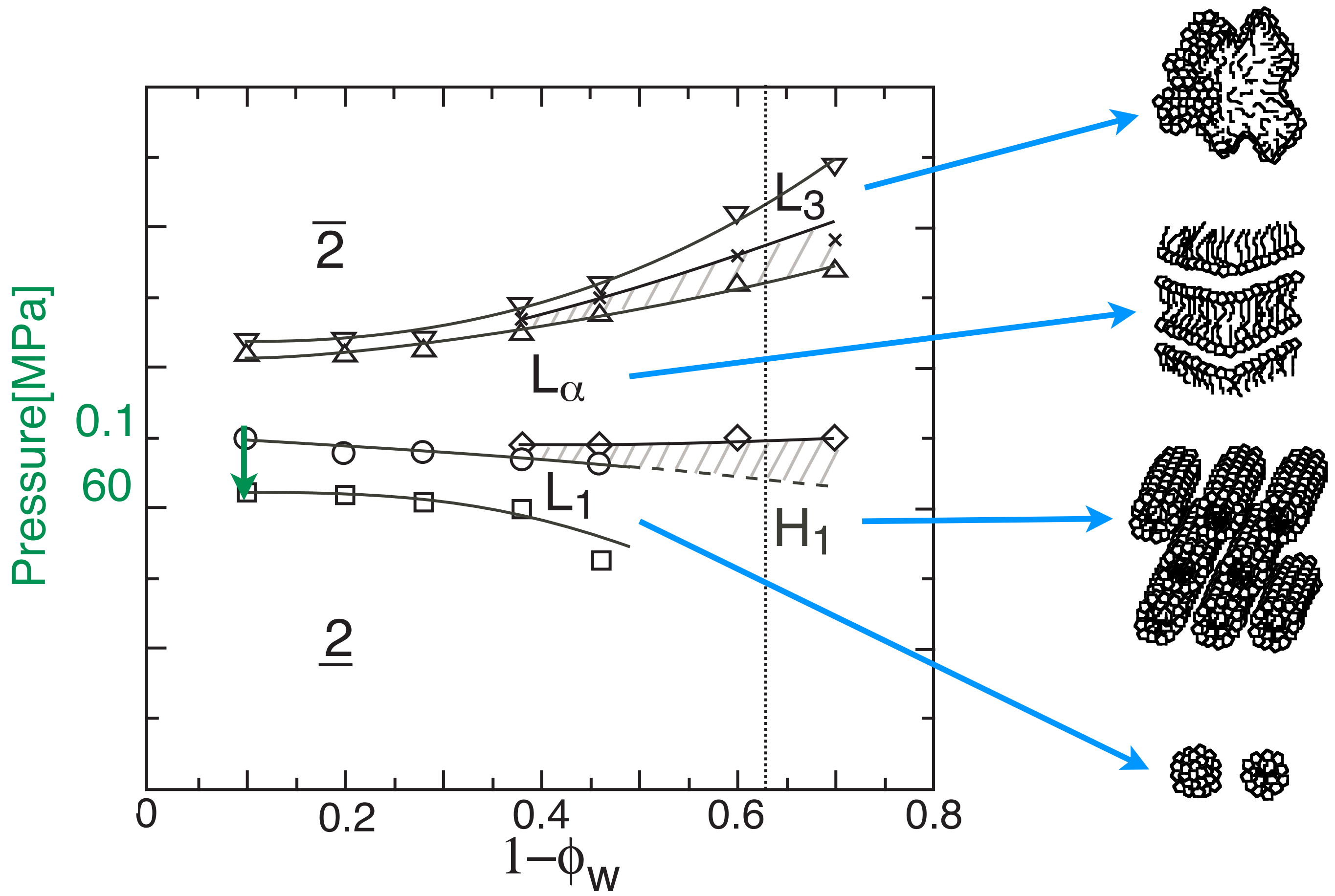
両親媒性分子の疎水基の圧縮



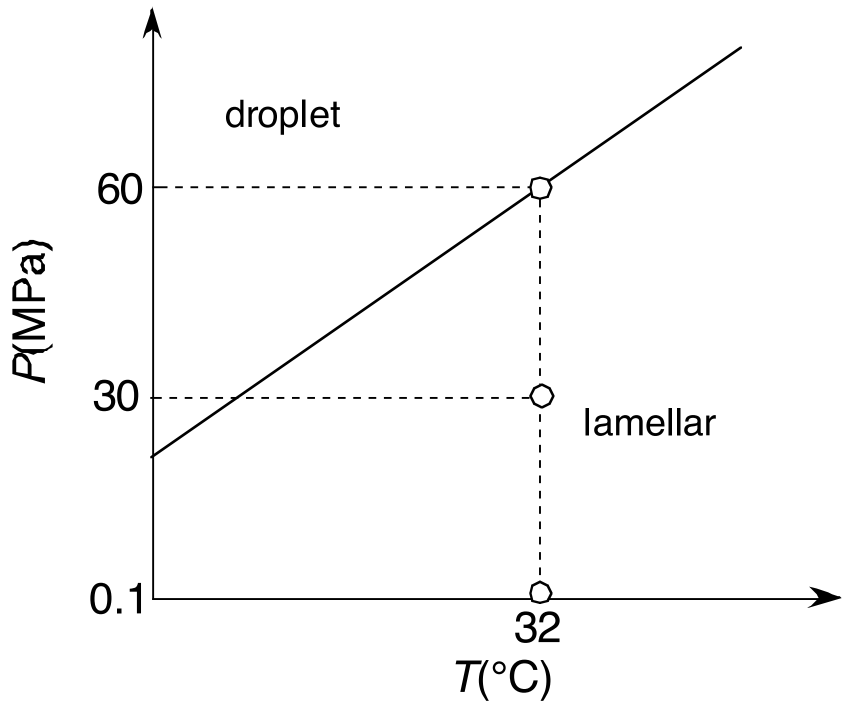
$\kappa_T \sim 2.1\times10^{-6}$ kPa^{-1}

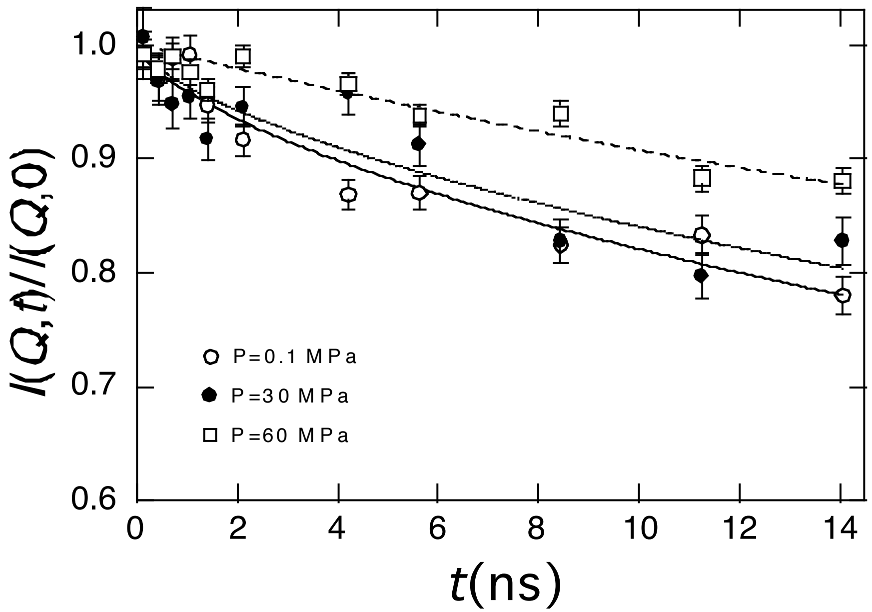
dodecane: 0.99×10^{-6} kPa^{-1}

曲げ弾性係数の圧力依存性



中性子スピンエコー実験の結果





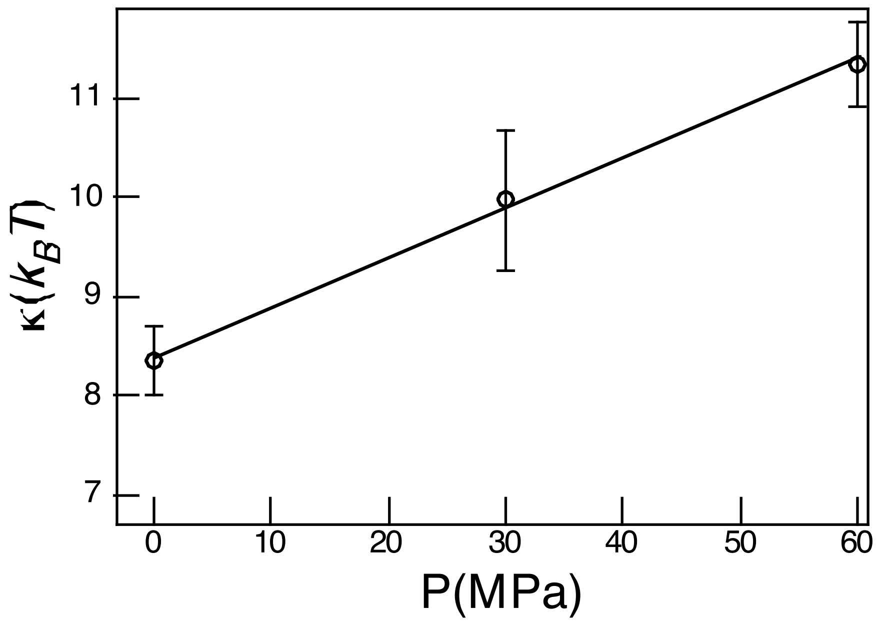
JRR-3M/iNSE

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

$$\Gamma = CQ^3$$

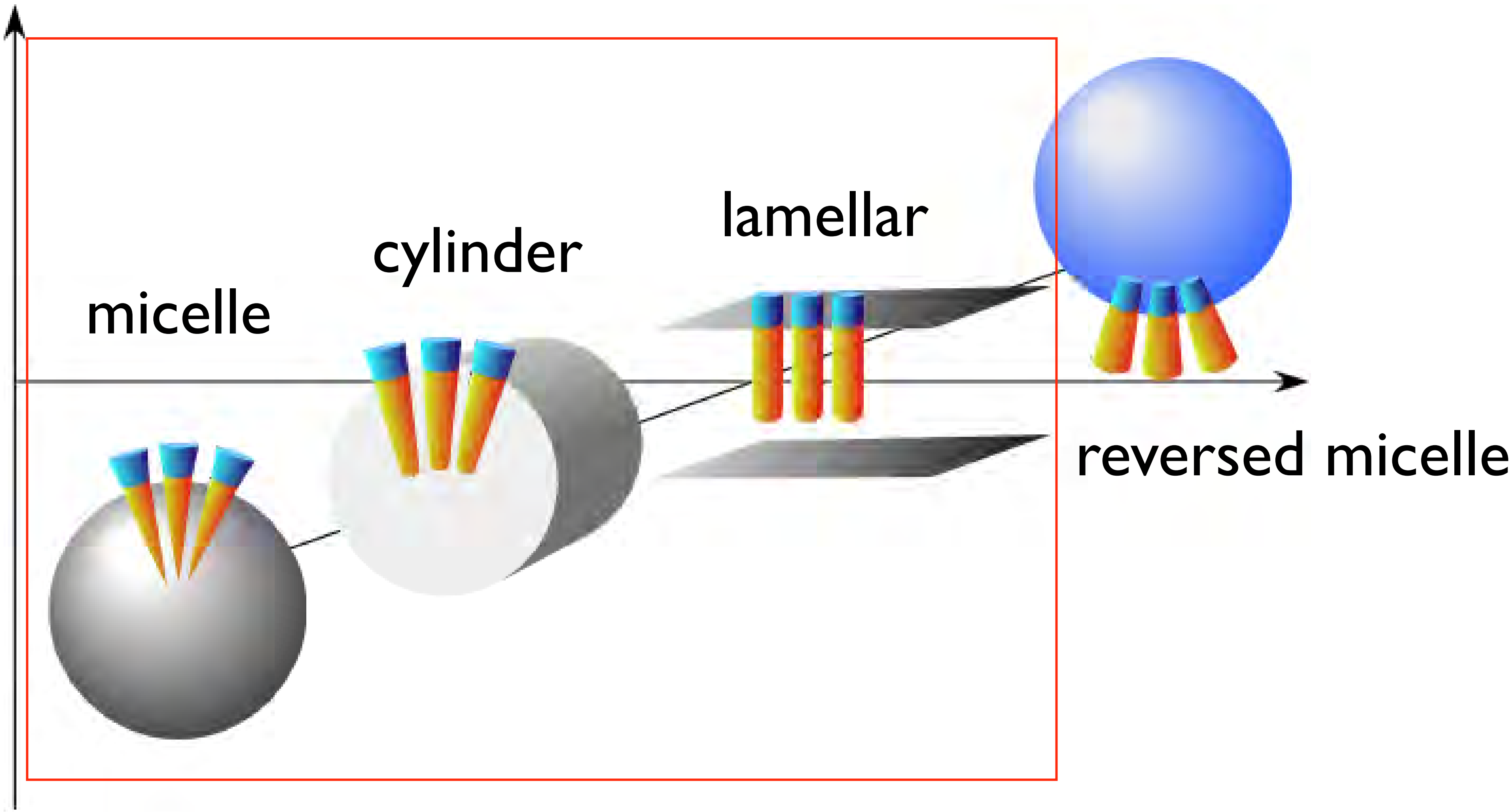
$$\kappa = \left(C^{-1}\gamma_\alpha\gamma_\kappa\left(k_BT\right)^{3/2}\eta^{-1}\right)^2$$

曲げ弾性係数の圧力依存性

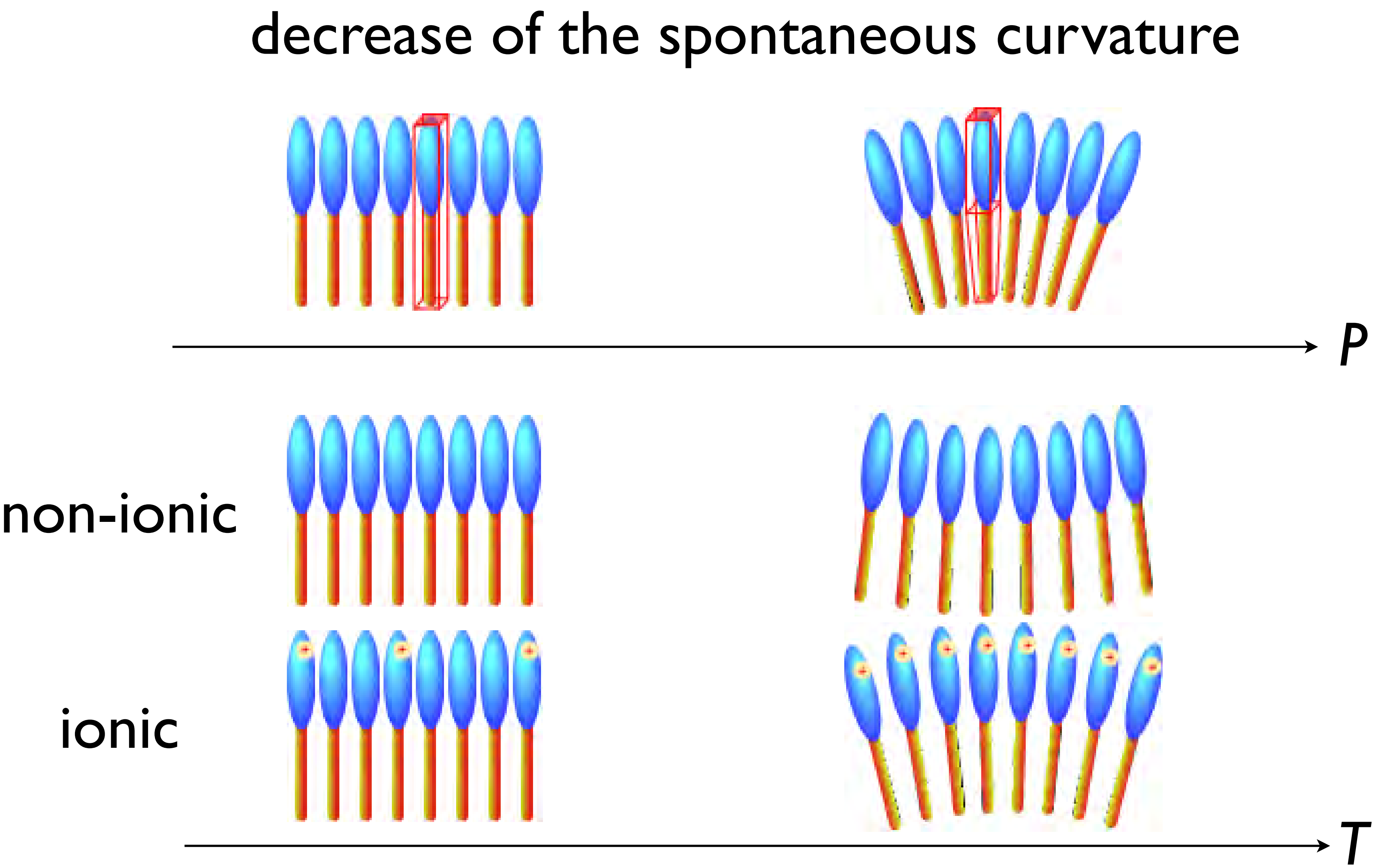


圧力により膜は硬くなる（AOTと同じ）

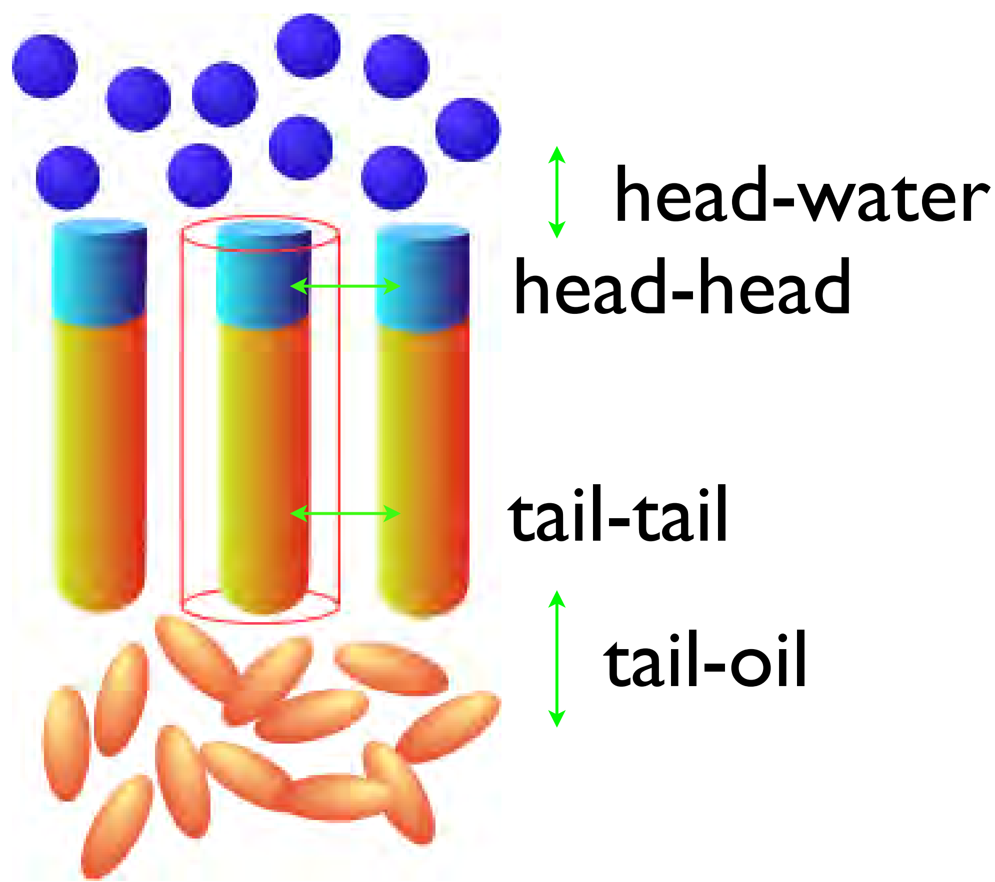
$C_{12}E_5$系のまとめ



両親媒性分子膜の温度・圧力変化



自発曲率←packing parameter



マイクロエマルションの構造変化

温度による変化

イオン性界面活性剤：親水基からの電離による反発
非イオン性界面活性剤：疎水基の運動状態の変化

圧力による変化

イオン性界面活性剤：疎水基同士or油との相互作用
非イオン性界面活性剤： 疎水基同士or油との相互作用

ナノスケールの構造のミクロな構造形成要因