SANS at interfaces and in bulk systems under shear

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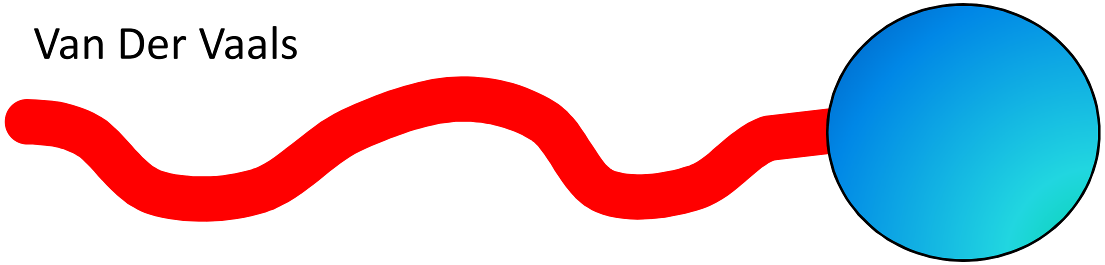
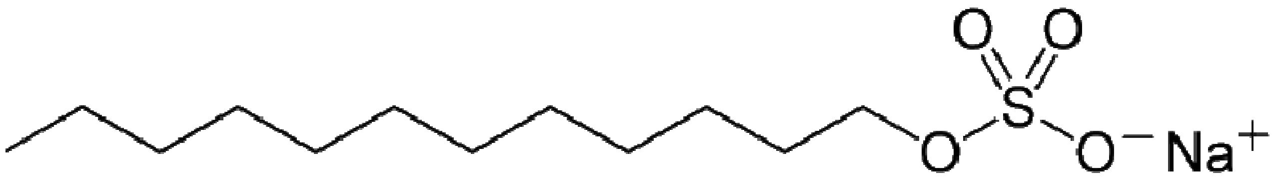
Surfactants

Ionic // Coulomb

Van Der Vaals





Hydrogen Bonds

Teflon / Flourinated Carbon Molecules

Applications of Surfactants

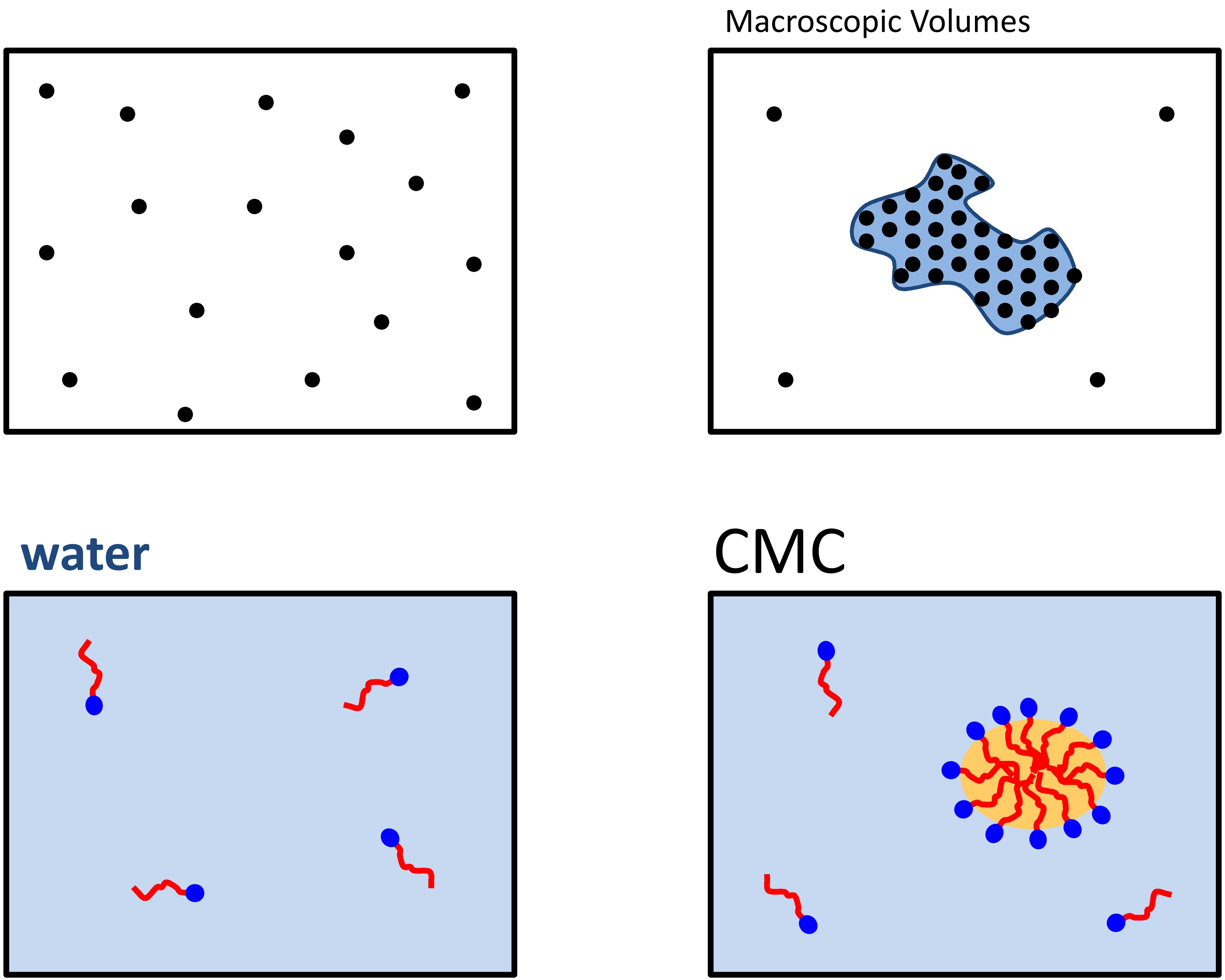
Hair care

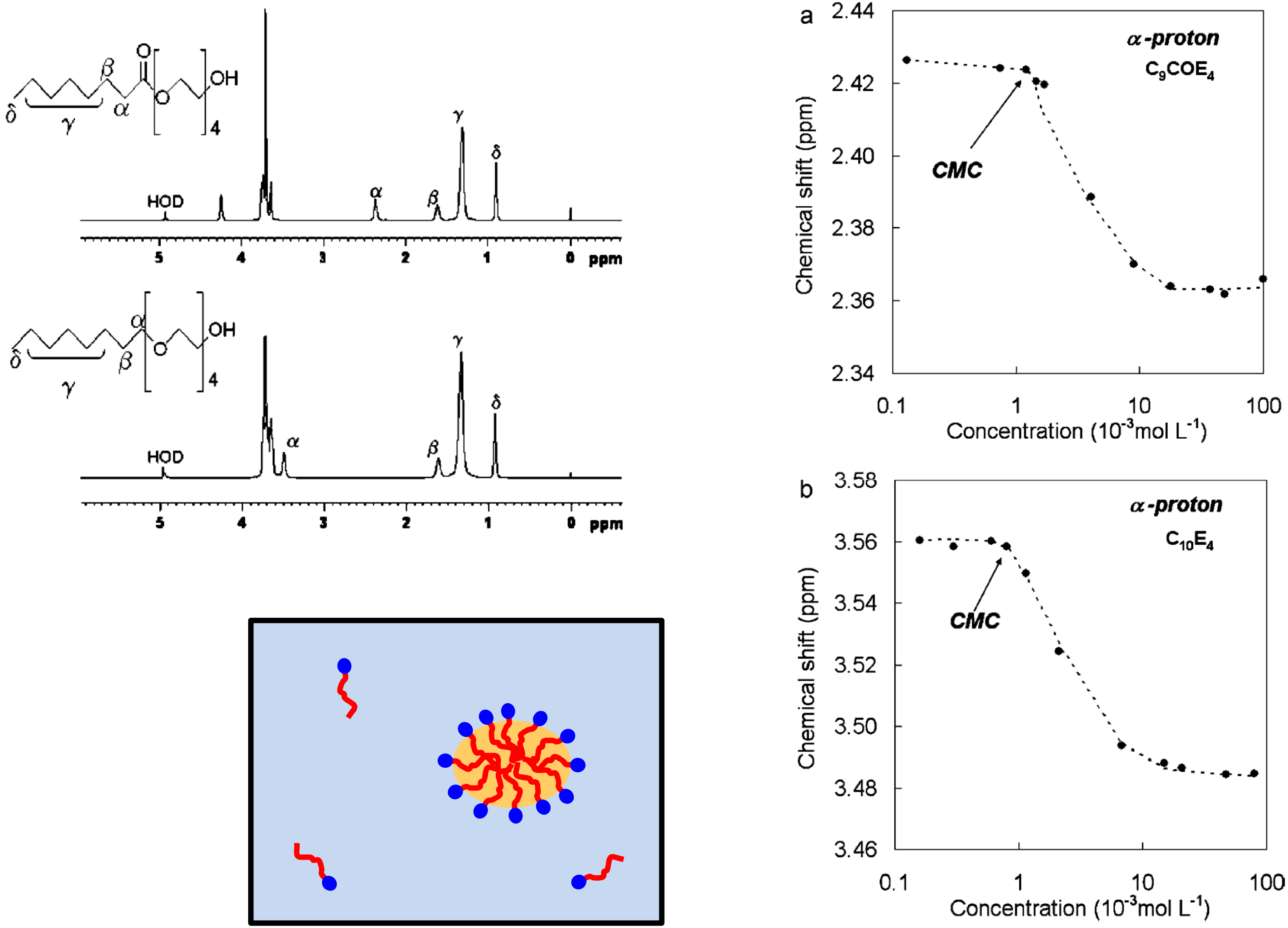
Cosmetics

Personal care

Detergents

Enhanced oil recovery


Macroscopic Volumes
water
CMC

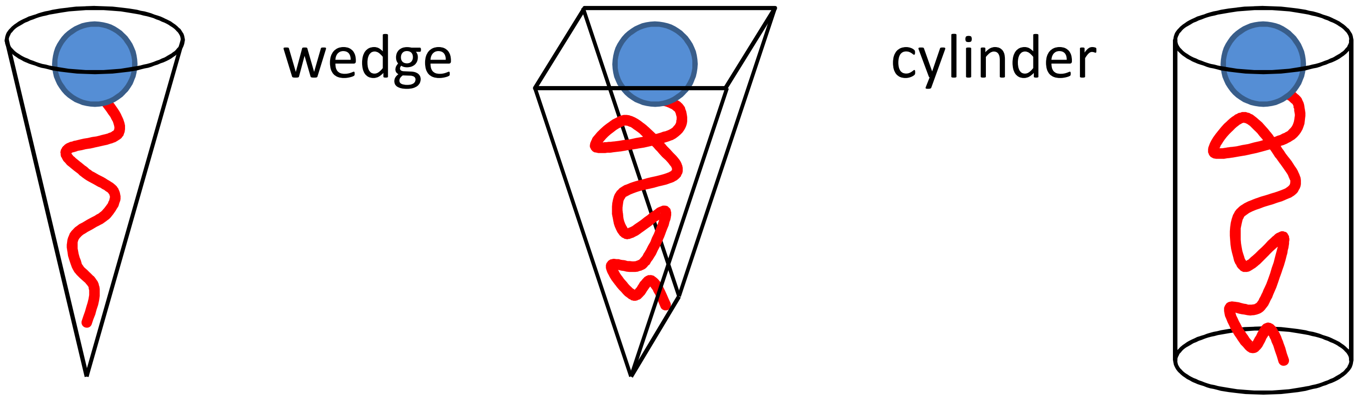


O
OH
4
δ
γ
β
α
HOD
α
β
γ
δ
5
4
3
2
1
0
ppm
OH
4
δ
γ
β
α
HOD
α
β
γ
δ
5
4
3
2
1
0
ppm
a
α-proton
C_9COE_4
CMC
Chemical shift (ppm)
2.44
2.42
2.40
2.38
2.36
2.34
0.1
1
10
100
Concentration (10^{-3}mol L^{-1})
b
α-proton
$C_{10}E_4$
CMC
Chemical shift (ppm)
3.58
3.56
3.54
3.52
3.50
3.48
3.46
0.1
1
10
100
Concentration (10^{-3}mol L^{-1})

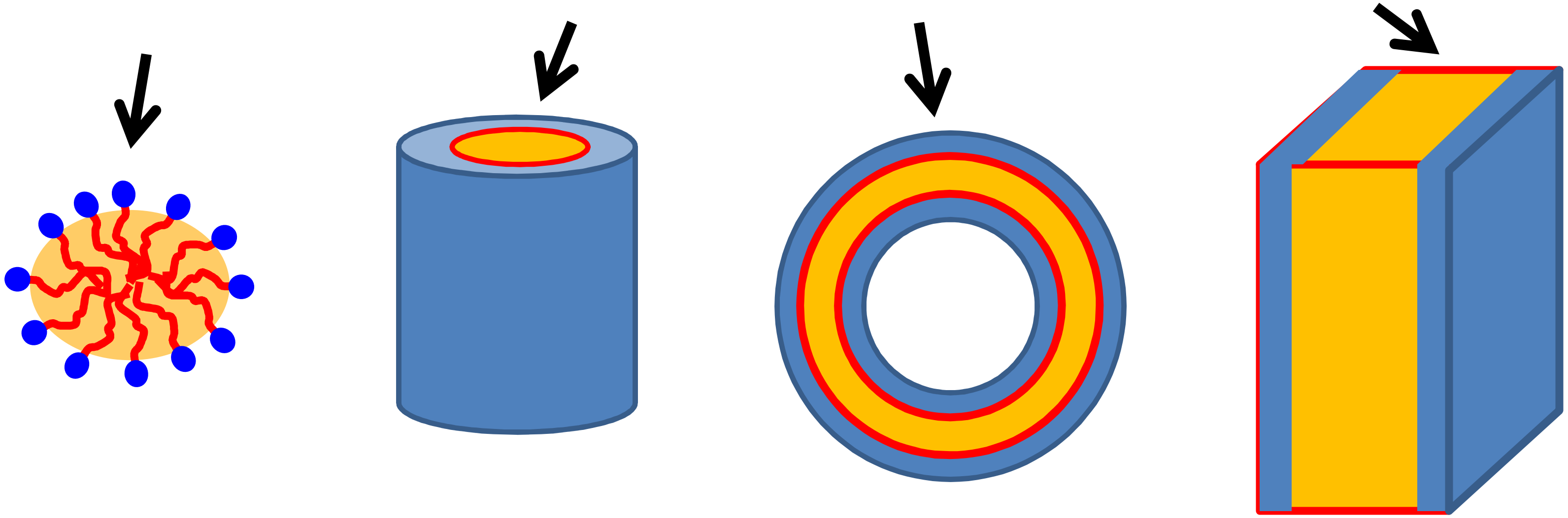
Packing Parameter

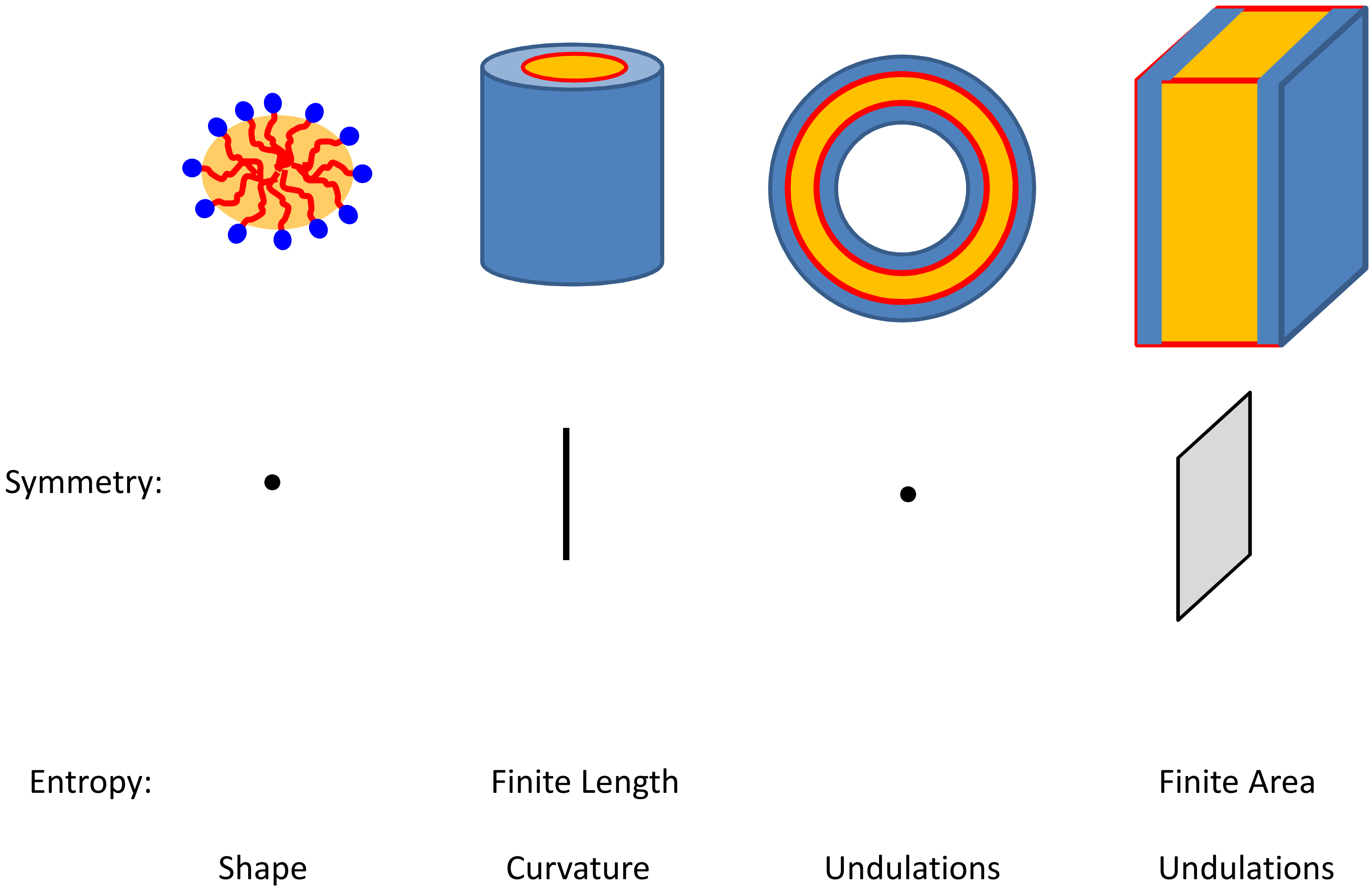
$$P = \frac{v}{a \cdot l}$$

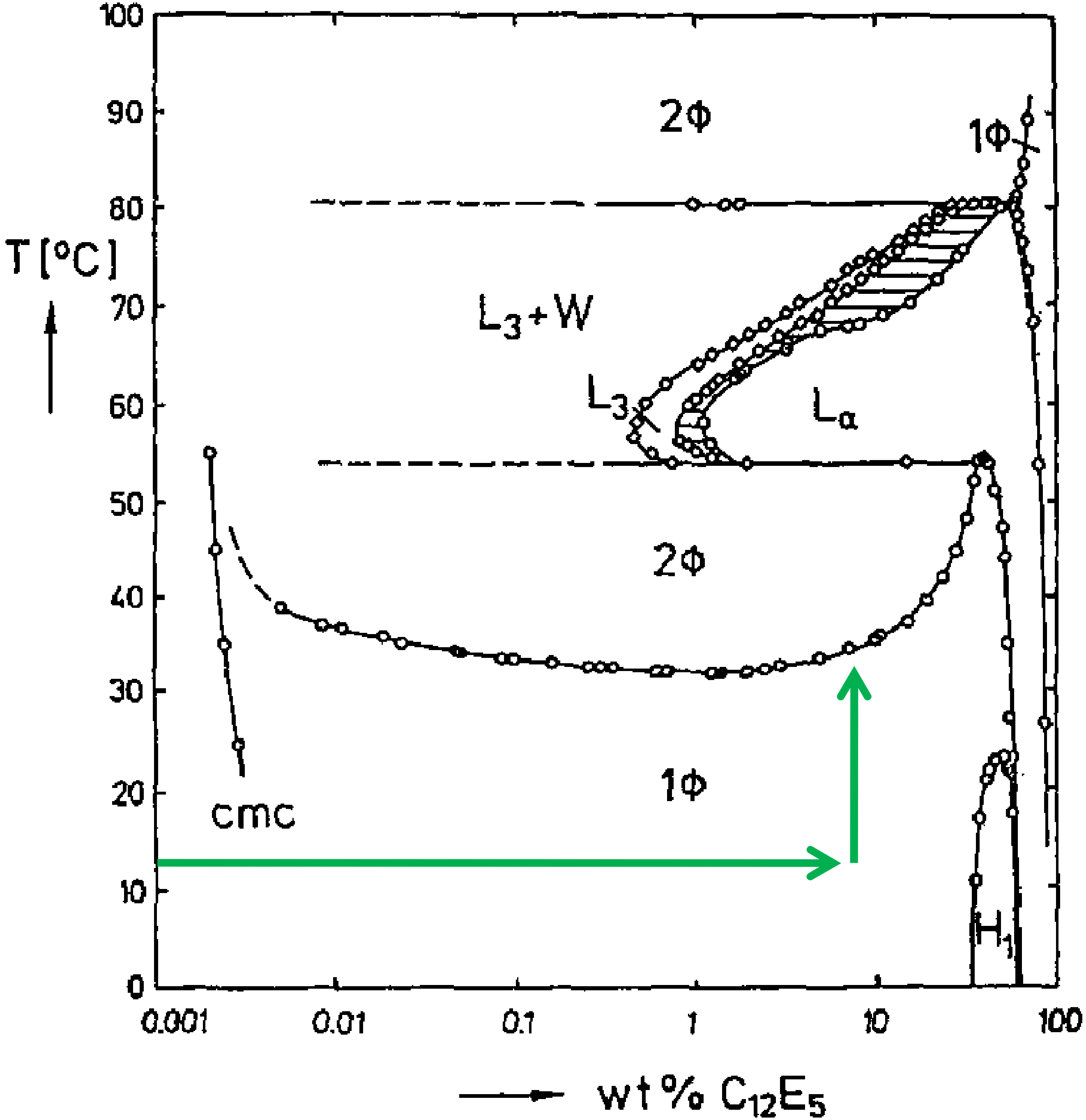
cone wedge cylinder



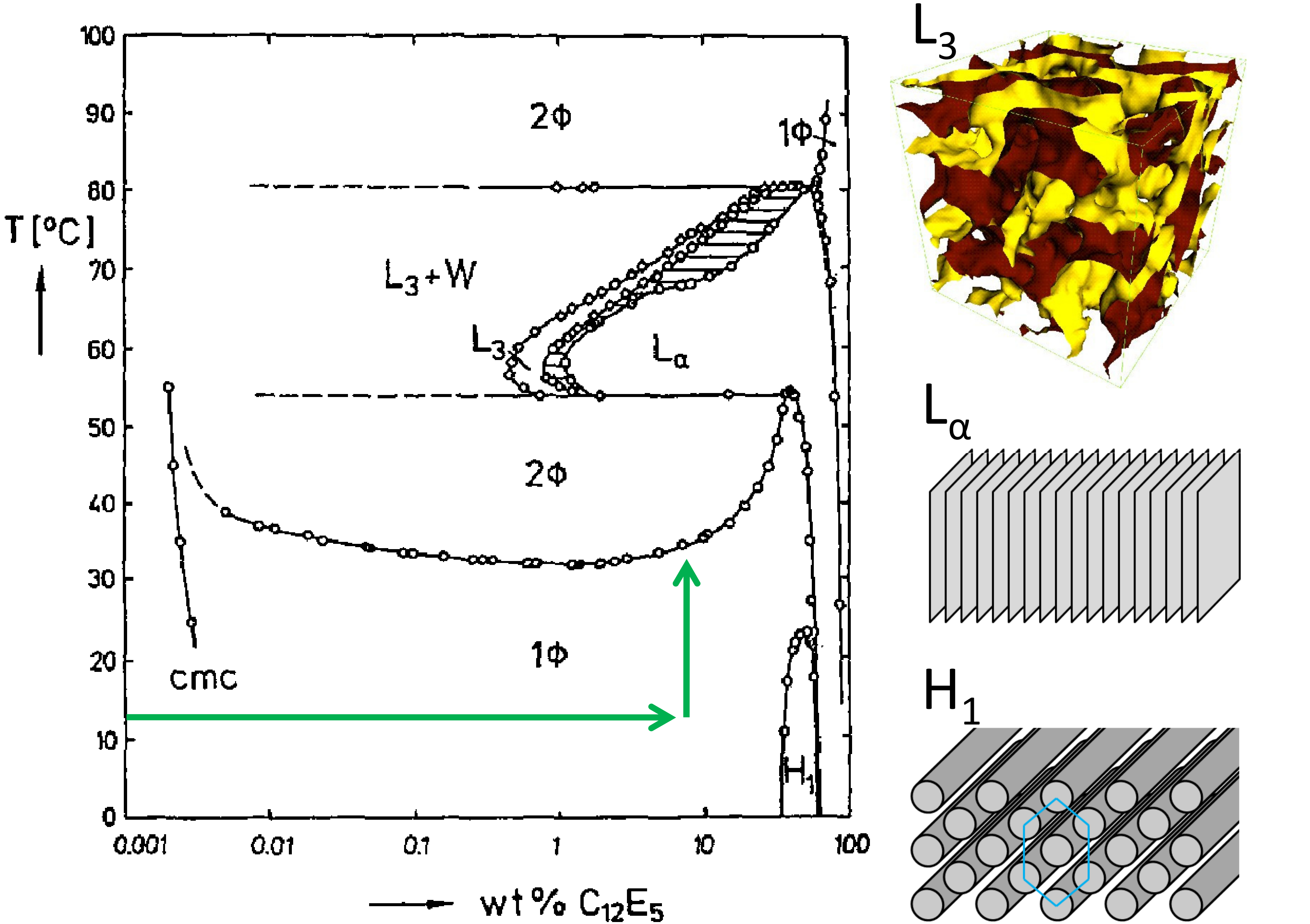
P = 0 .. 1/3, 1/3 .. 1/2, 1/2 .. 1, 1



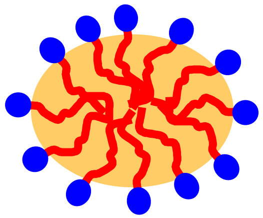

Symmetry:
Entropy:
Finite Length
Finite Area
Shape
Curvature
Undulations
Undulations



T [°C]
100
90
80
70
60
50
40
30
20
10
0
2Φ
1Φ
$L_3 + W$
L_3
L_α
2Φ
1Φ
cmc
H_1
0.001
0.01
0.1
1
10
100
wt % $C_{12}E_5$



100
90
80
70
60
50
40
30
20
10
0
T [°C]
2Φ
1Φ
$L_3 + W$
L_3
L_α
2Φ
1Φ
cmc
H_1
0.001
0.01
0.1
1
10
100
wt % $C_{12}E_5$
L_3
L_α
H_1

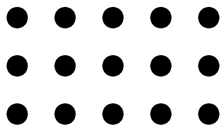


Interactions

Steric Repulsions

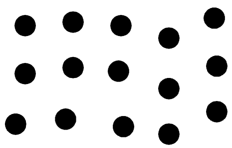
Coulomb Interactions

Symmetry:



Cubic, hexagonal, lamellar…

Entropy:

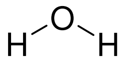


Distortions

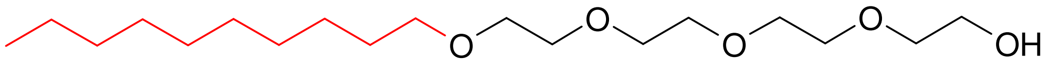
Soft Matter	**Classical Hard Matter**
Soft Potentials	Coulomb Potentials
High Entropy	Low Entropy

Microemulsions

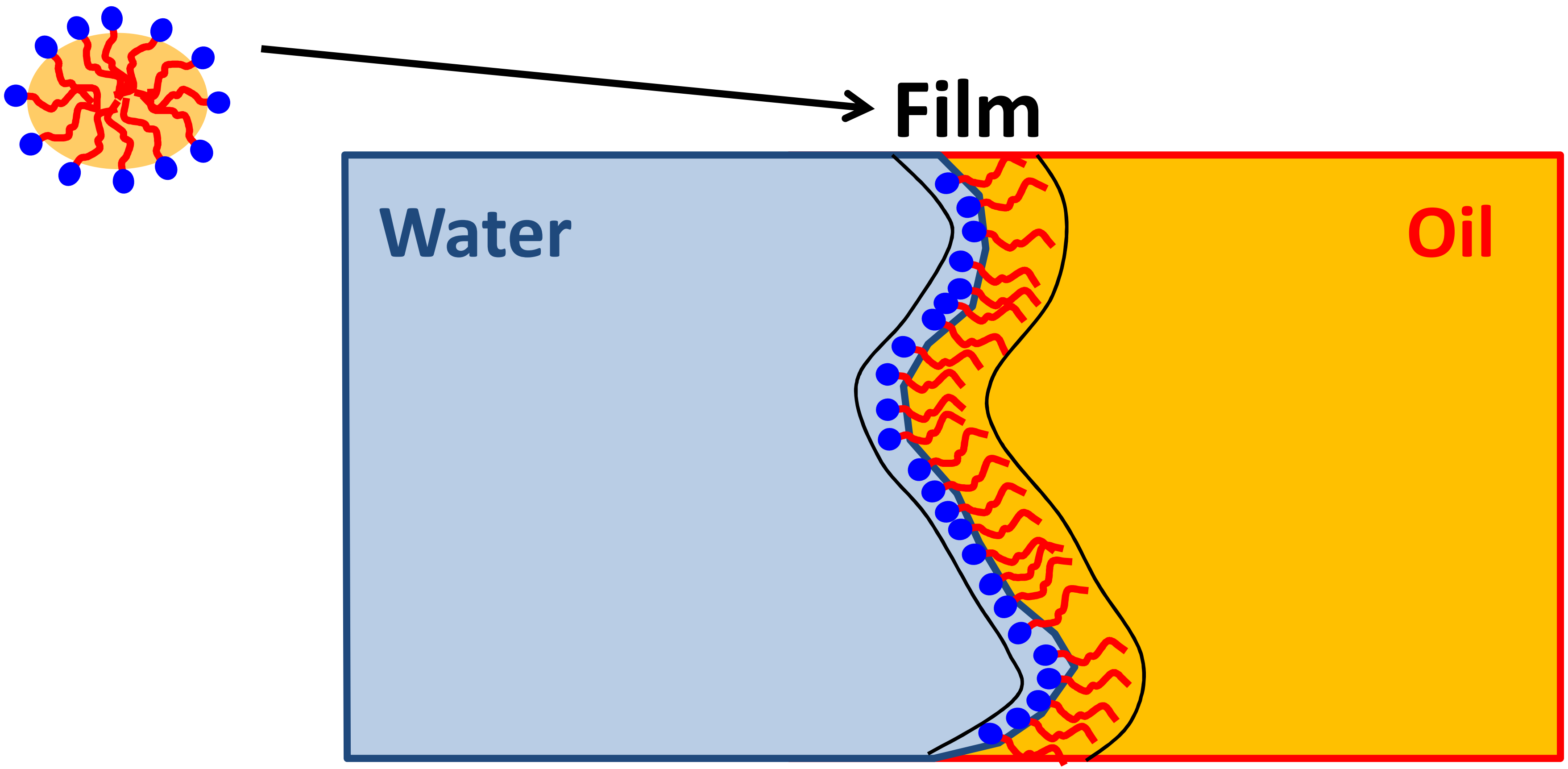
Stability !!!

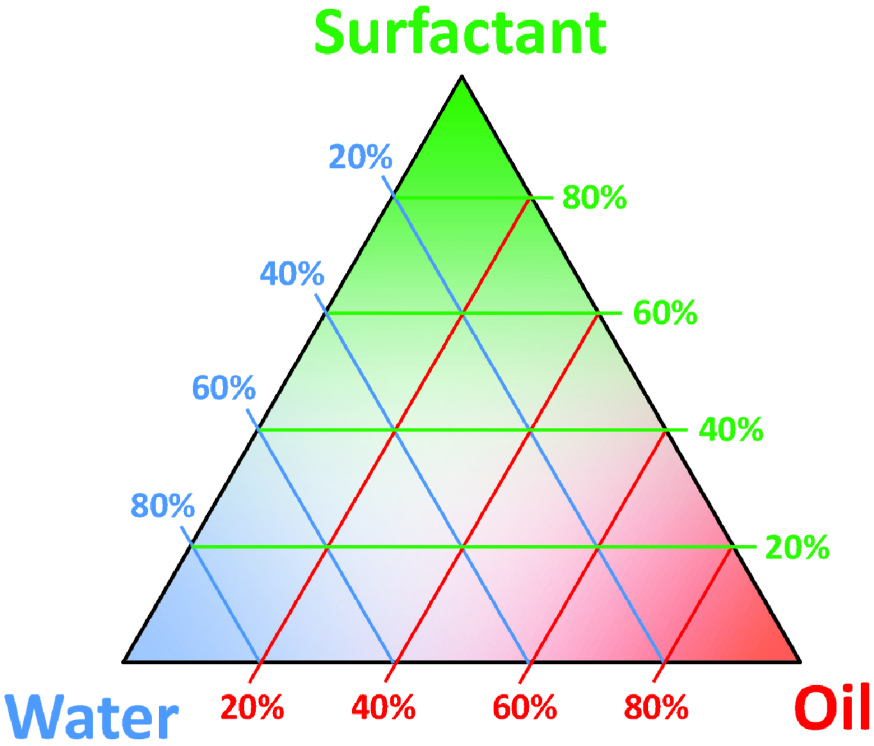
Water: H_2O 

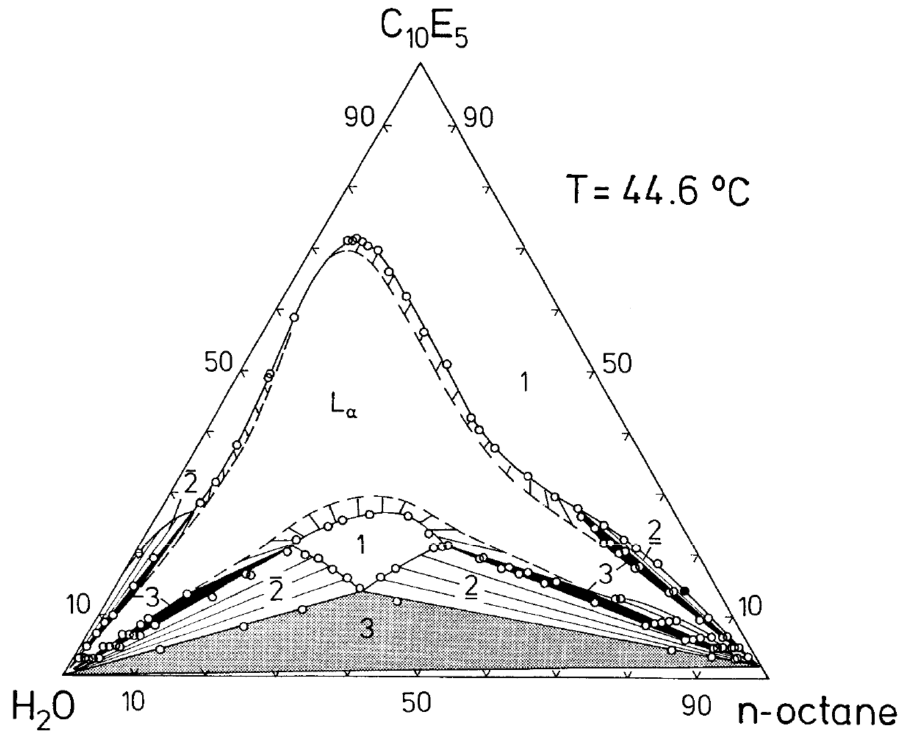
Oil: Decane 

Surfactant: $C_{10}E_4$ 

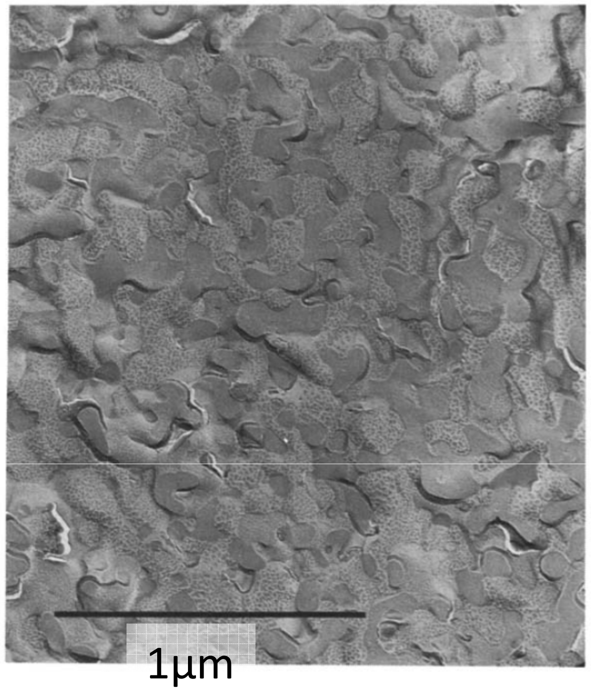
Micelles

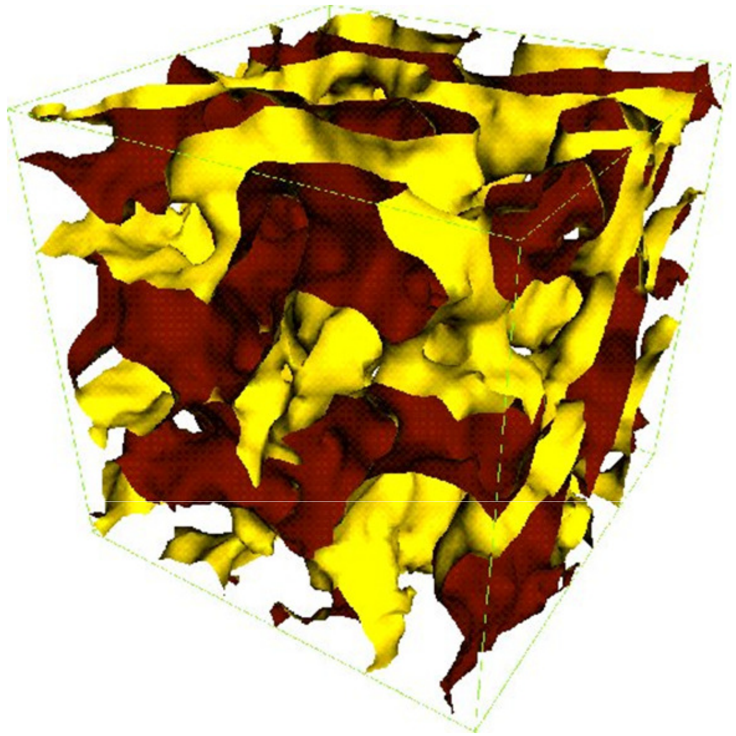



Surfactant
20%
40%
60%
80%
80%
60%
40%
20%
Water
20%
40%
60%
80%
Oil

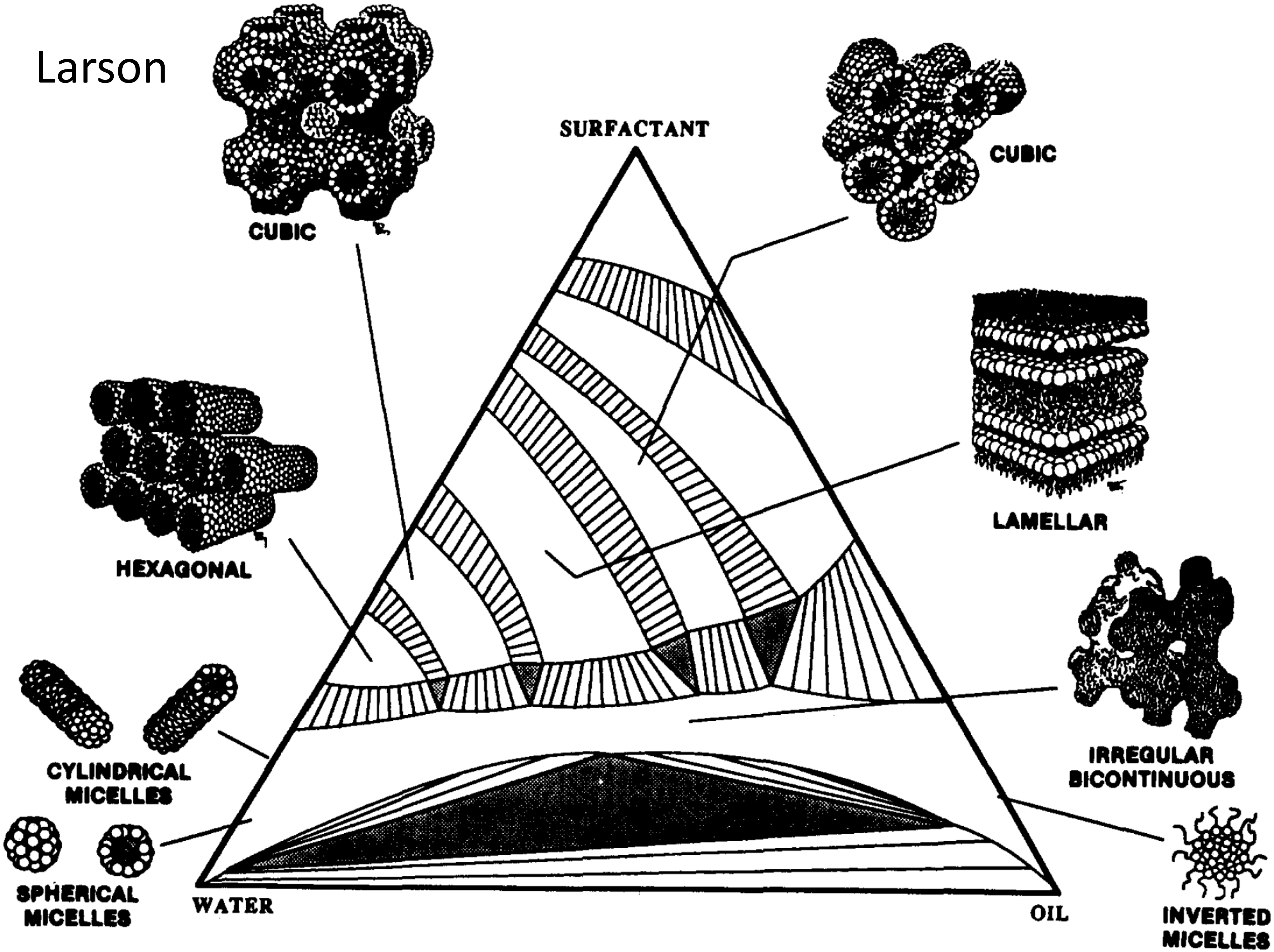

$C_{10}E_5$
90
90
T = 44.6 °C
50
50
L_α
10
10
H_2O
10
50
90
n-octane

Bicontinuous Microemulsion



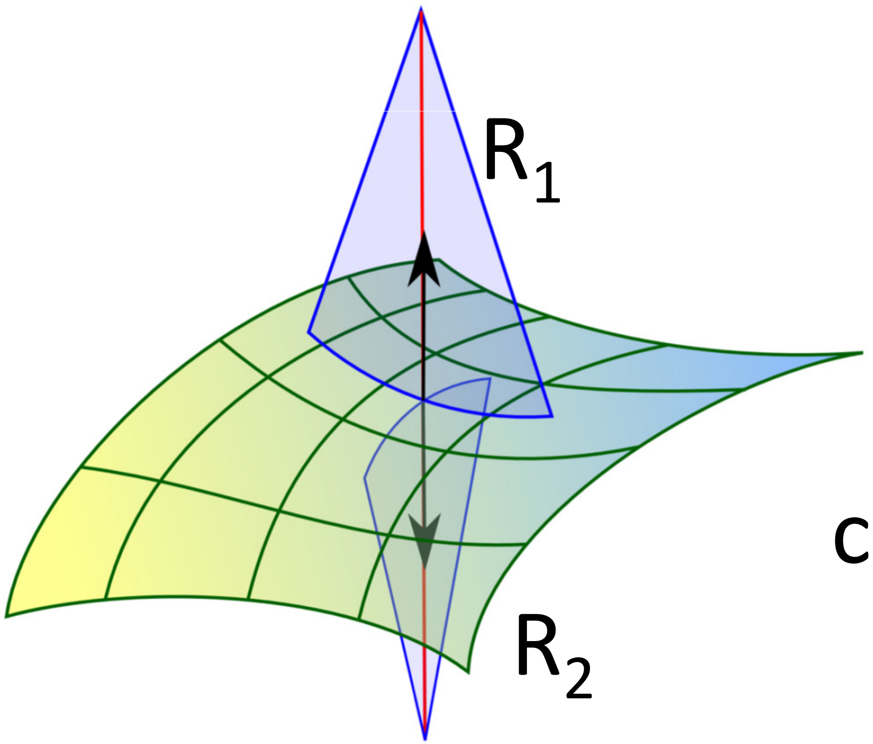


Larson


SURFACTANT
WATER
OIL
CUBIC
CUBIC
HEXAGONAL
LAMELLAR
IRREGULAR
BICONTINUOUS
CYLINDRICAL
MICELLES
SPHERICAL
MICELLES
INVERTED
MICELLES

Free Energy

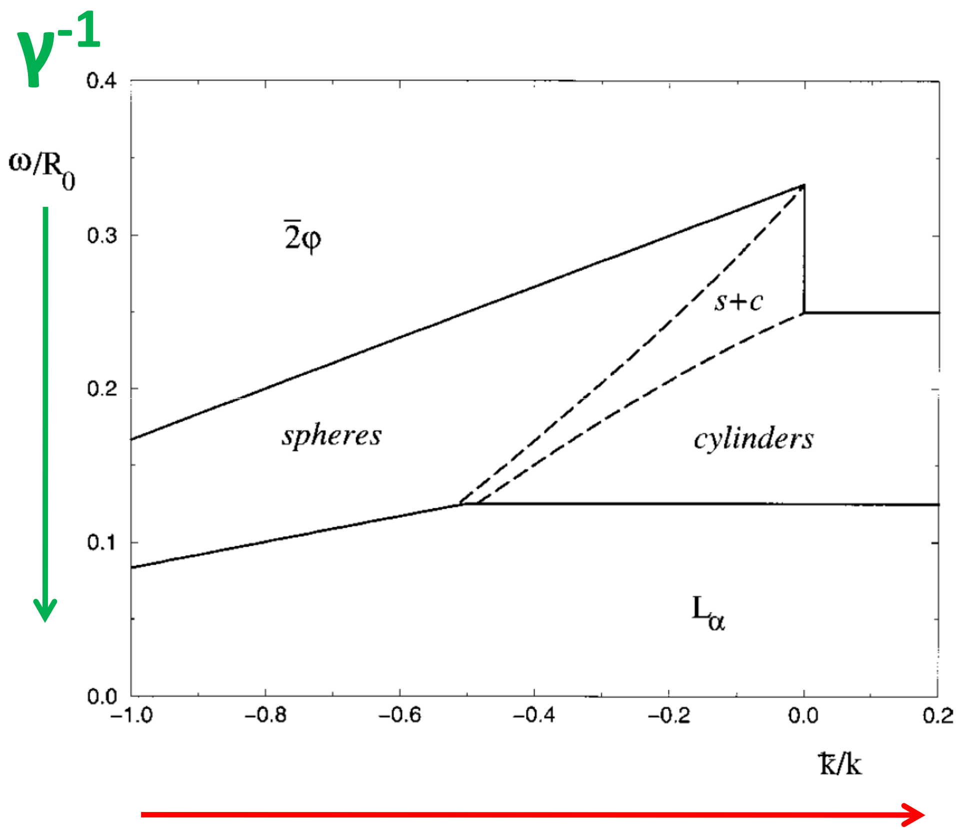
$$F = \int dS \left(\gamma + \frac{1}{2}\kappa(c_1 + c_2 - 2c_0)^2 + \bar{\kappa} c_1 c_2 \right)$$

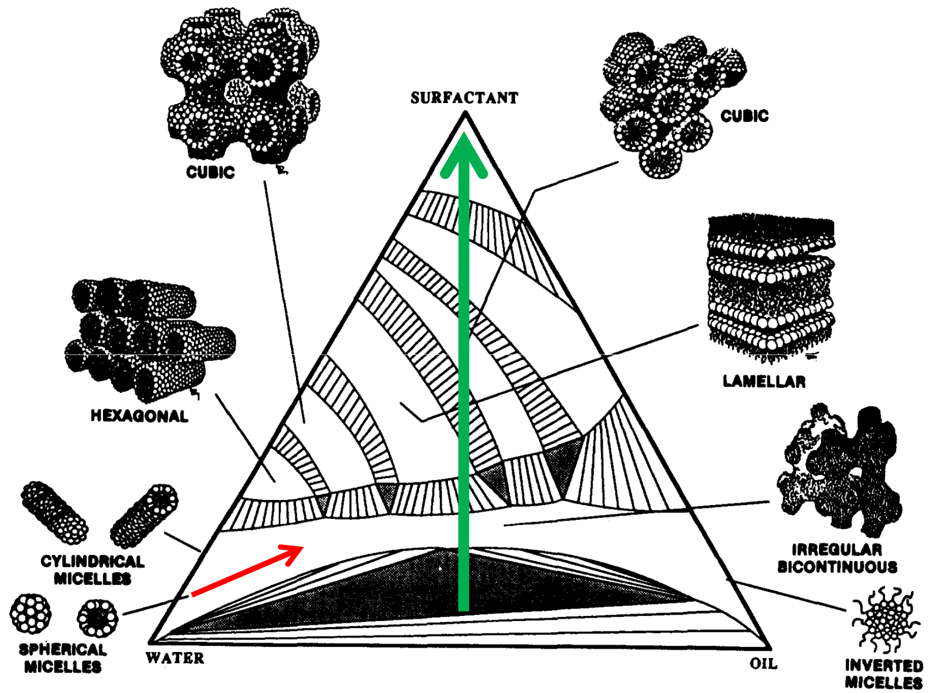


$c_1 = R_1^{-1}$

$c_2 = R_2^{-1}$

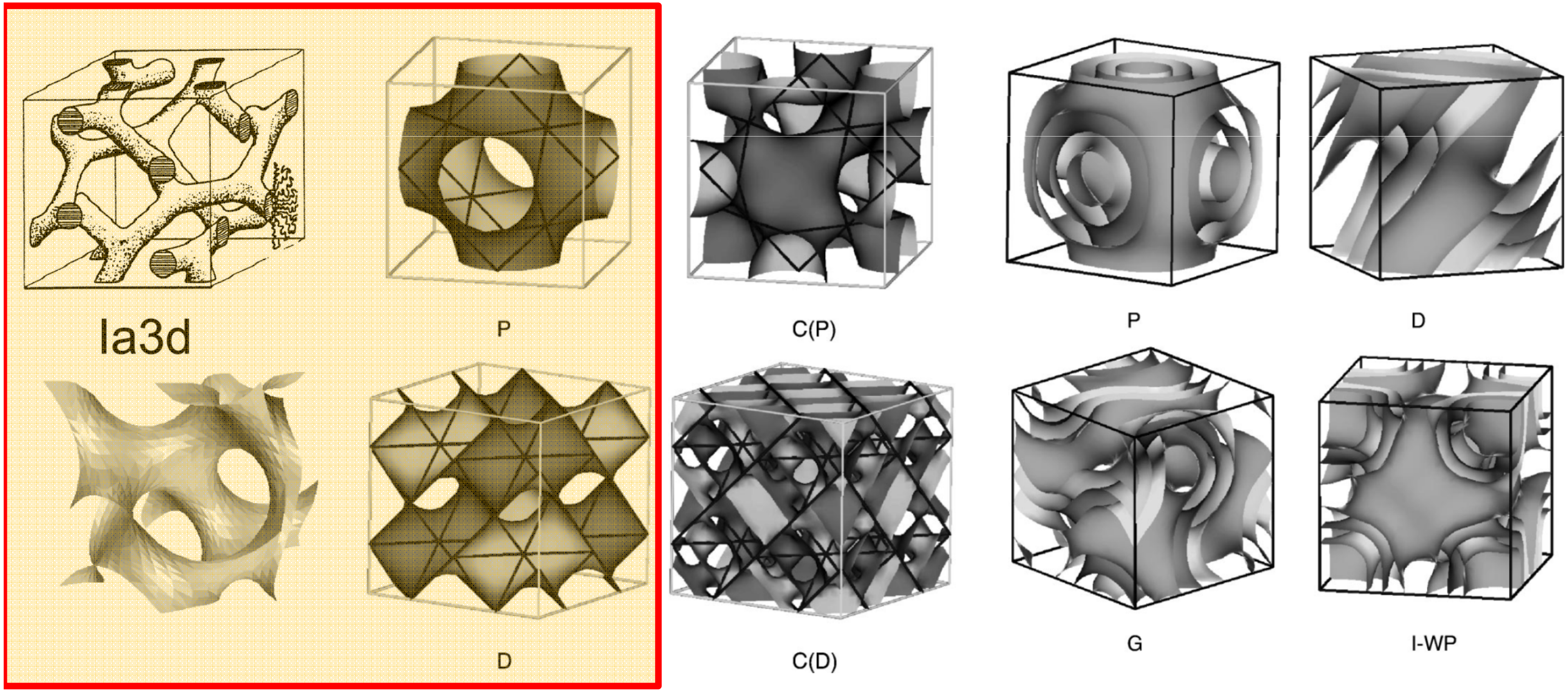
Phase Diagram f. Small Concentrations



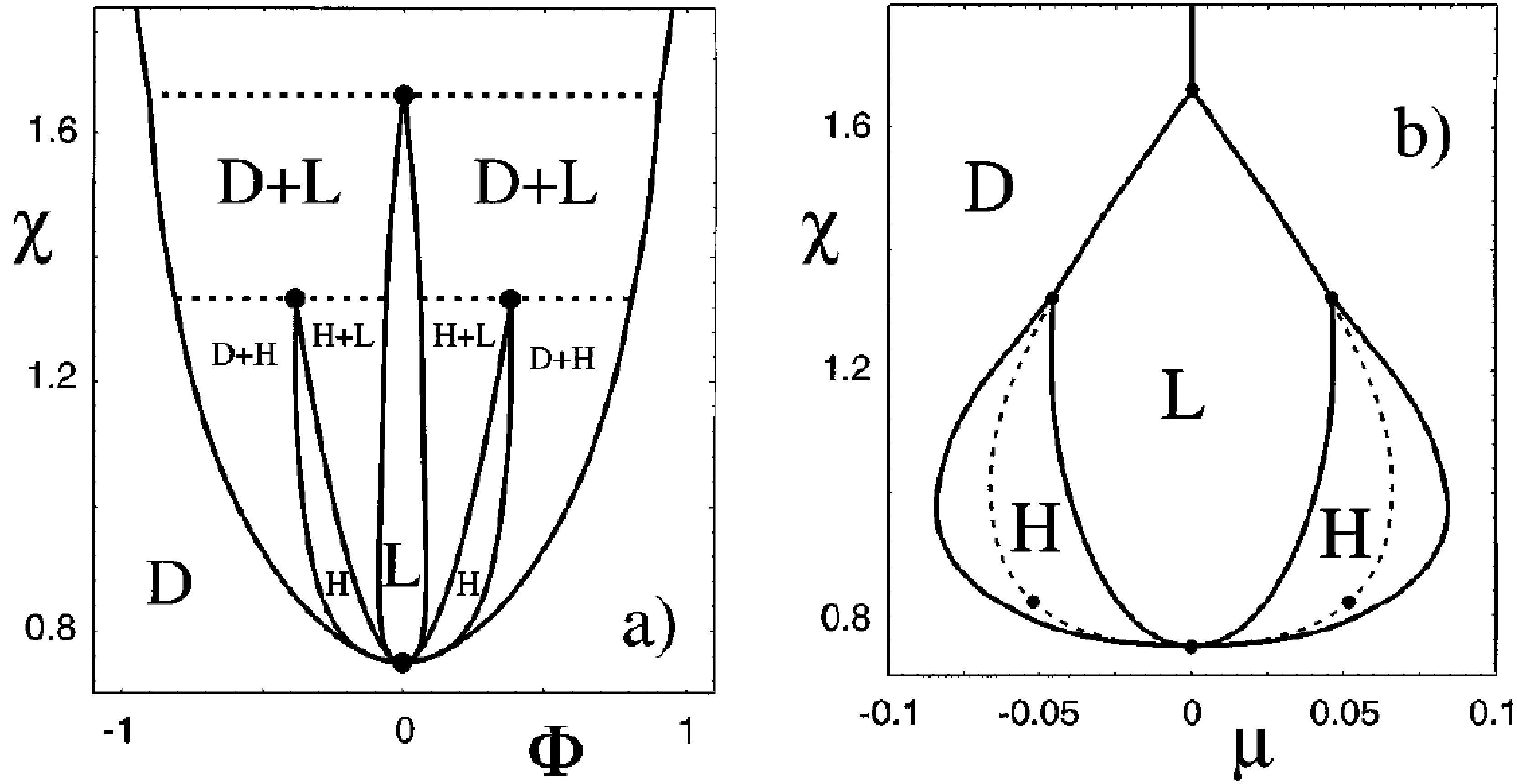


Interactions

$$F_{\text{steric}} \propto c_0^{-2} \left(\frac{k_B T}{\kappa} \right)^2 \frac{\phi_{\text{oil}}^3}{(1 - \phi_{\text{oil}})^2}$$

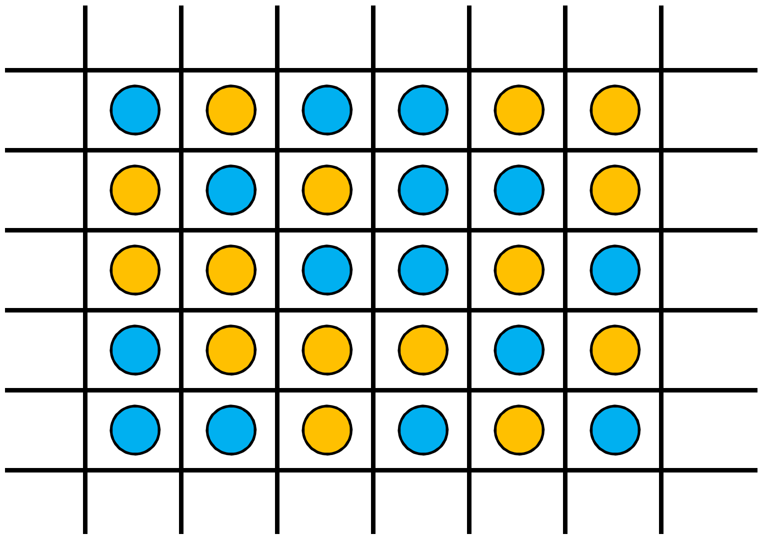


$$F[\Phi] = \int dV \left(-\frac{\chi}{2}\Phi^2 + \frac{1-\Phi}{2} \ln \frac{1-\Phi}{2} + \frac{1+\Phi}{2} \ln \frac{1+\Phi}{2} - \frac{1}{2}(\nabla\Phi)^2 + \frac{1}{2}(\nabla^2\Phi)^2 - \mu\Phi \right)$$



Oil **Surfactant** **Water**

Translational Entropy



N: lattice sites

k: species A
N-k: species B

$$\frac{S}{k_B} = -\ln(\Omega) = -\ln\left(\frac{N!}{k!\cdot(N-k)!}\right) = \phi_A \cdot \ln \phi_A + \phi_B \cdot \ln \phi_B$$

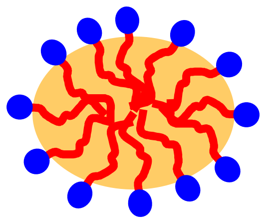
Summary: Microemulsions

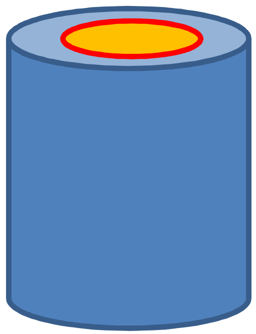
From Bulky Surfactant Molecules → Surfactant Film

* Packing Parameter

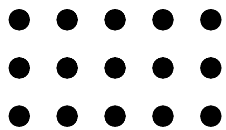
* Helfrich Energy

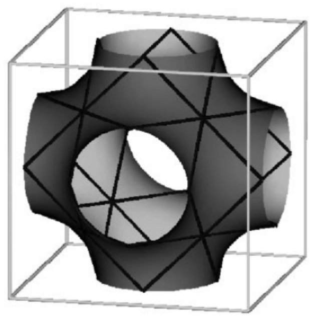
Simple Shapes (diluted system)





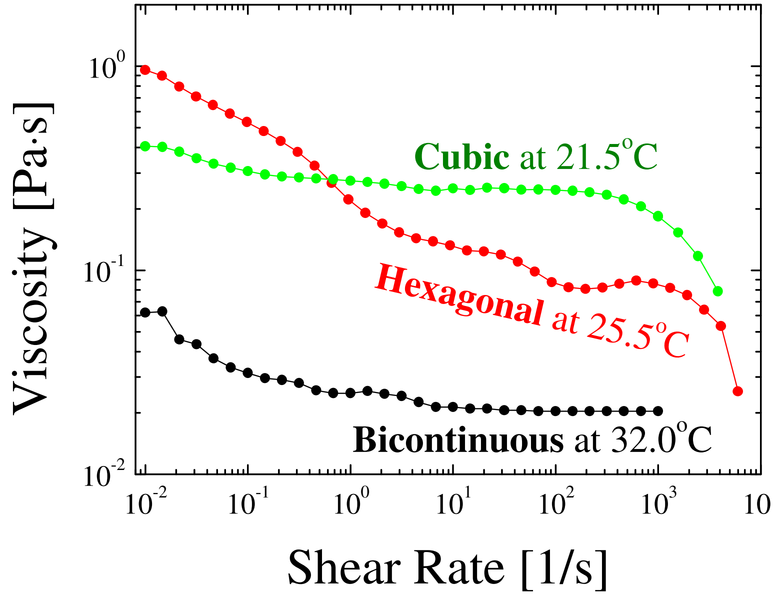
Liquid Crystalline Phases

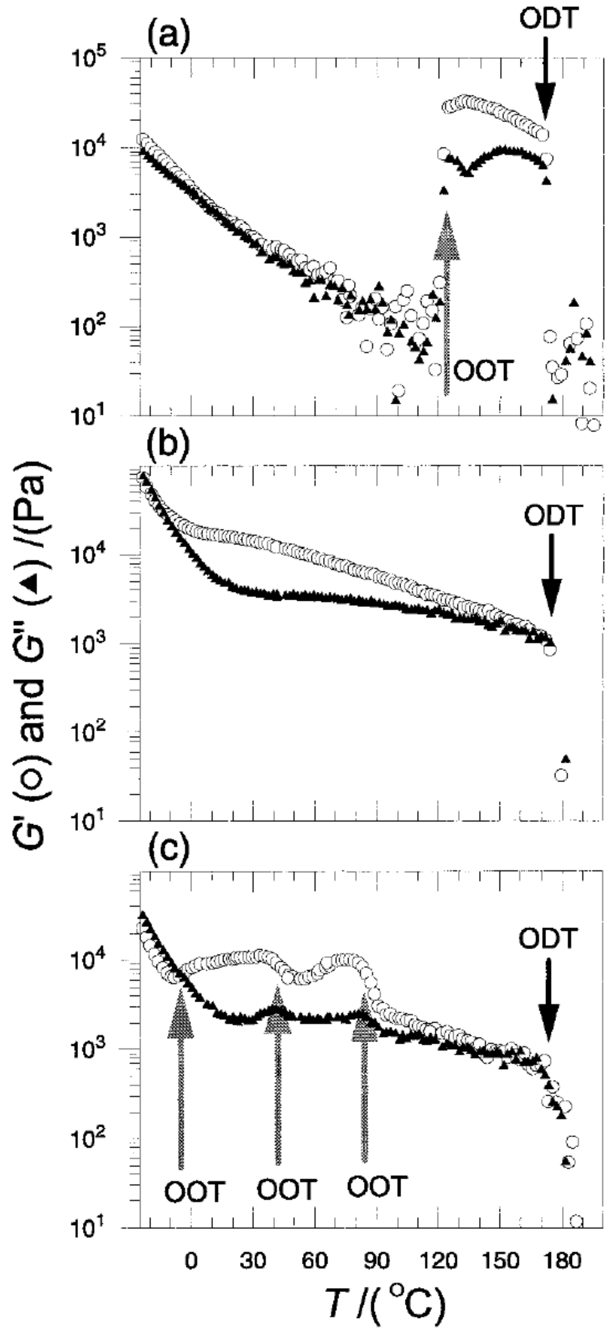




Measurements

Rheology



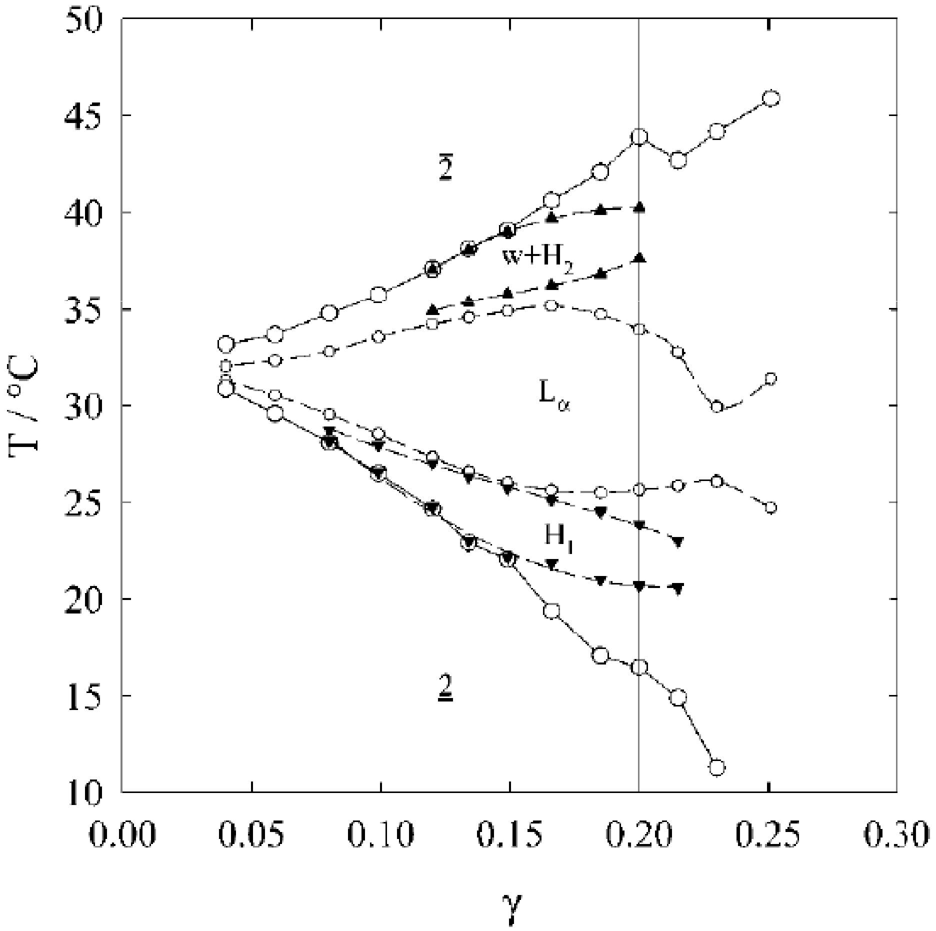


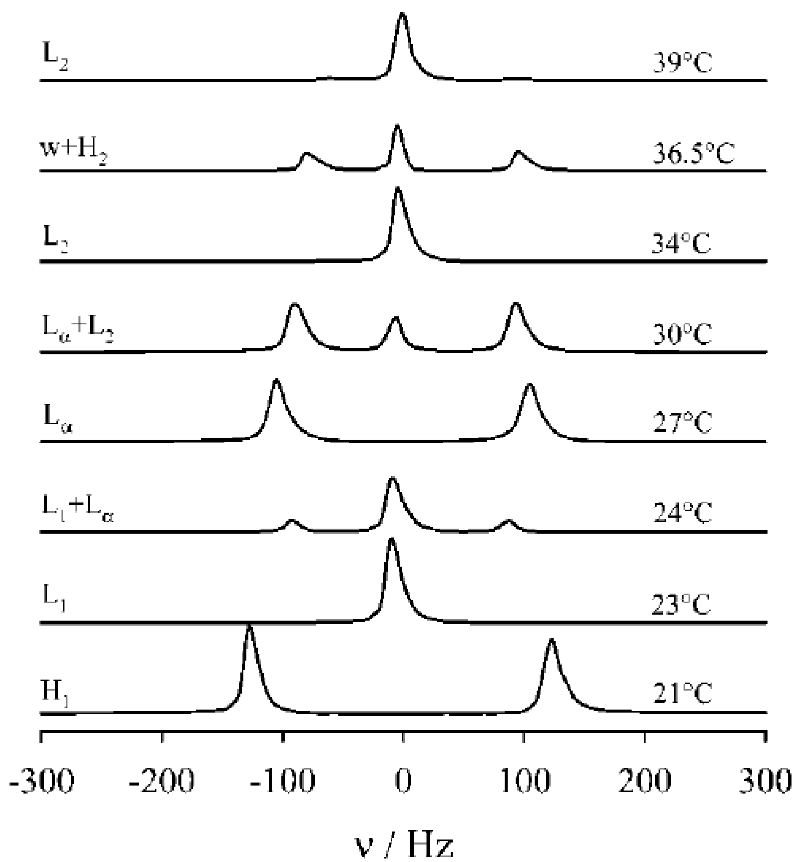
Optical Measurements

Crossed Polarizers

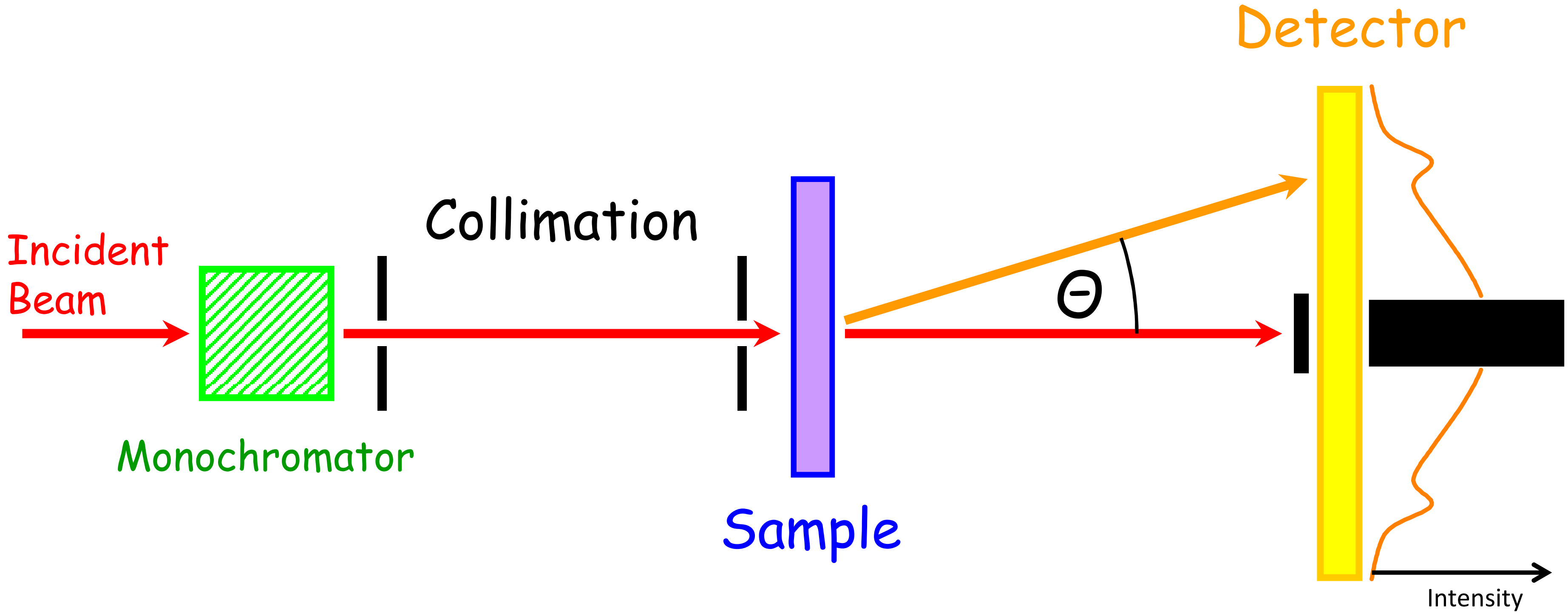
Anisotropic Domains

NMR - Microemulsion



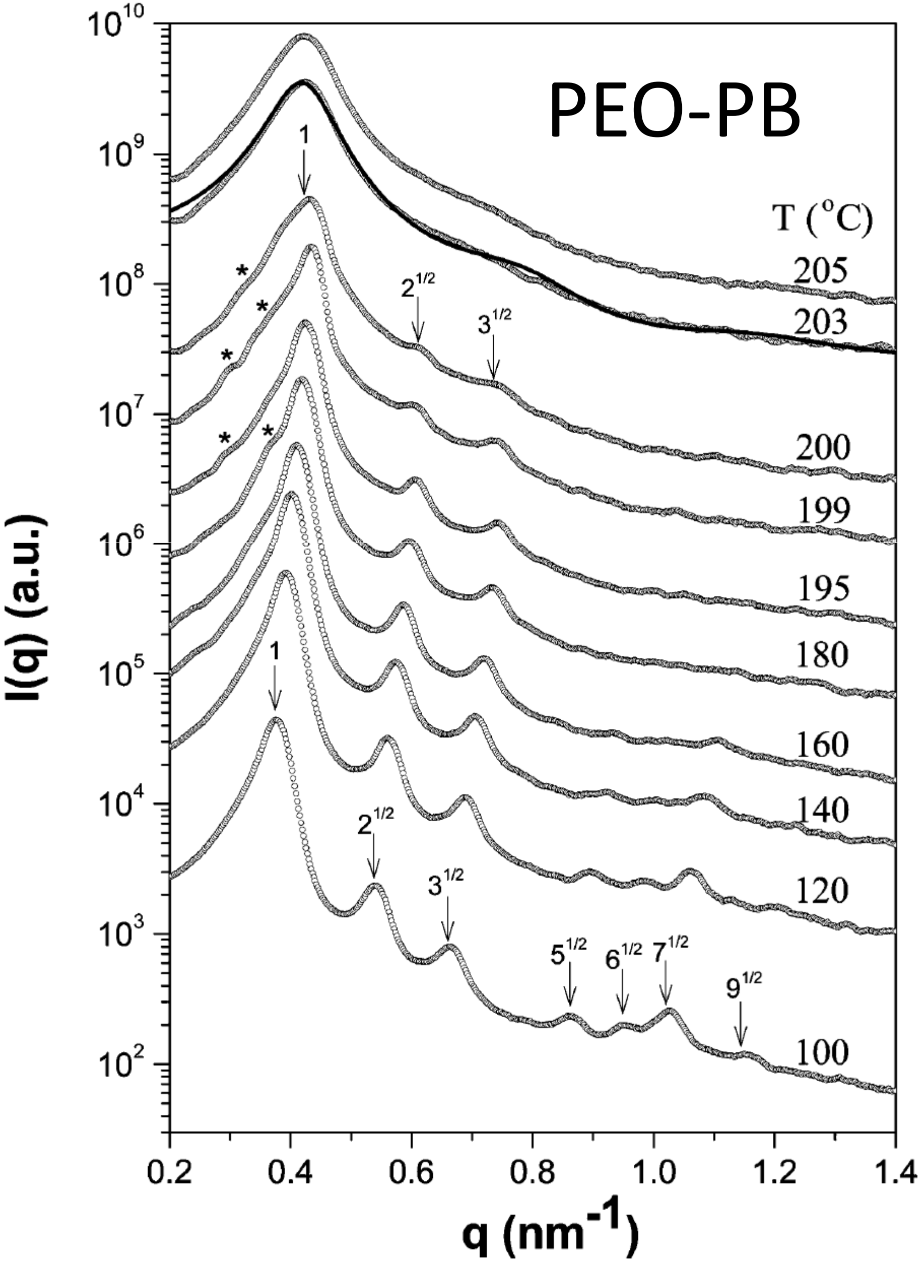


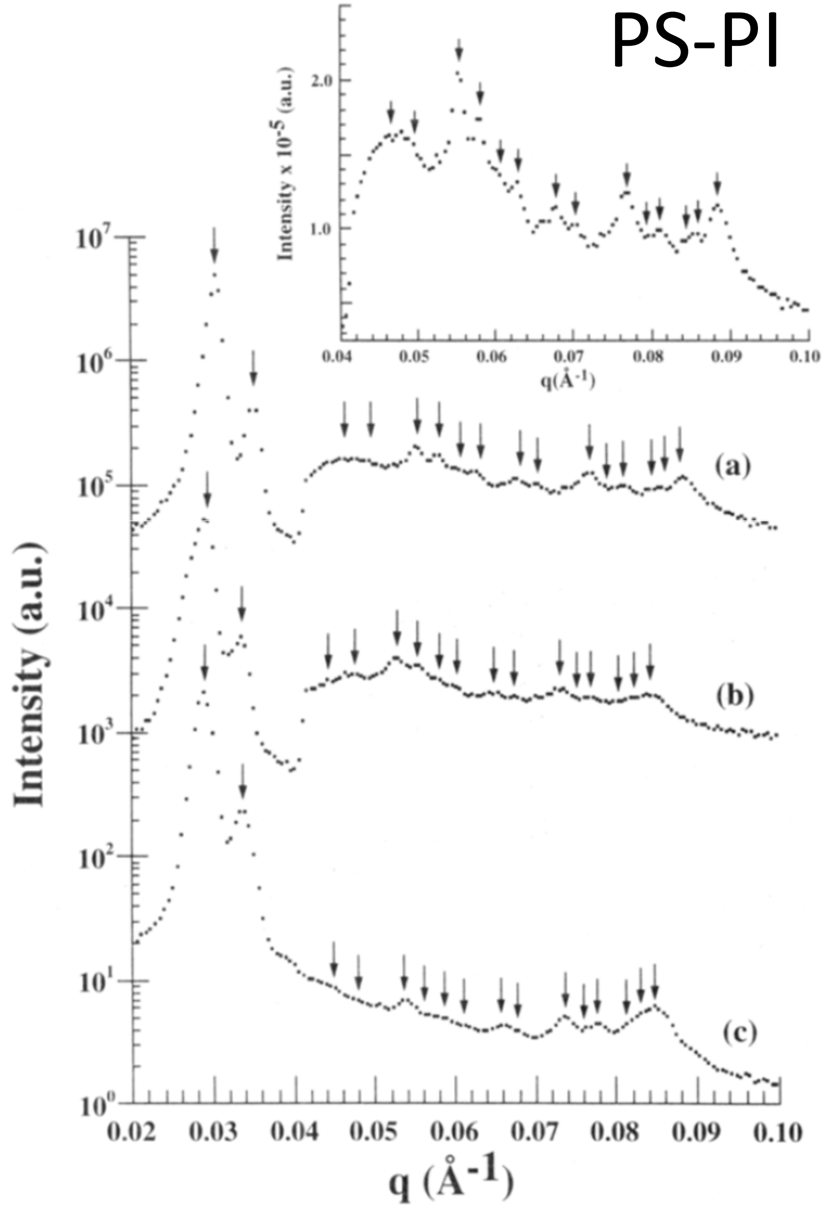
Small Angle Scattering:

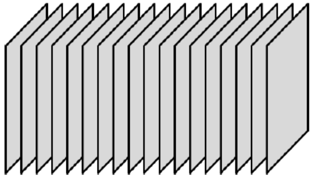
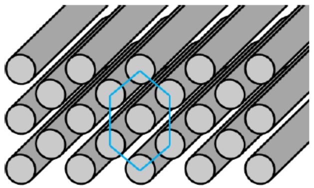
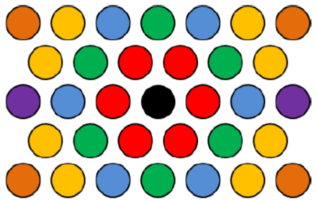
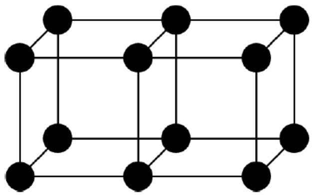
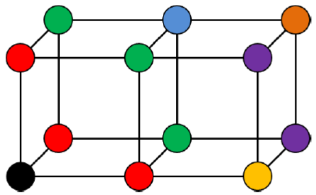
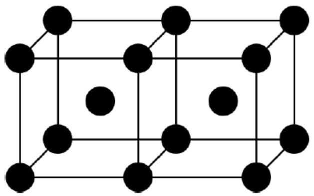
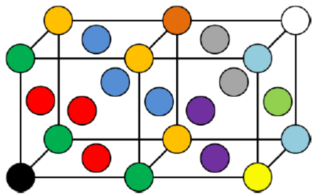


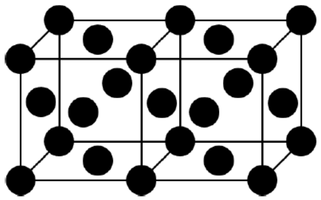
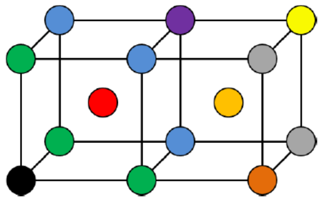
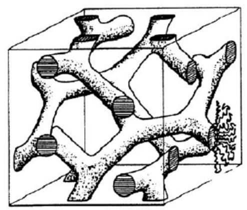
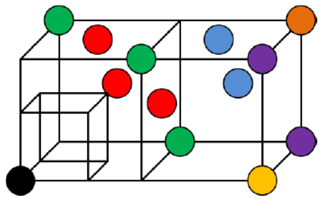
$$Q = \frac{4\pi}{\lambda}\sin\left(\frac{\Theta}{2}\right) \approx \frac{2\pi}{\lambda}\Theta \qquad Q \approx \frac{2\pi}{\ell}$$

SAS


PEO-PB
T (°C)
205
203
200
199
195
180
160
140
120
100
1
$2^{1/2}$
$3^{1/2}$
$5^{1/2}$
$6^{1/2}$
$7^{1/2}$
$9^{1/2}$
I(q) (a.u.)
q (nm^{-1})


PS-PI
(a)
(b)
(c)
Intensity (a.u.)
q (Å^{-1})
Intensity x 10^{-5} (a.u.)
q(Å^{-1})

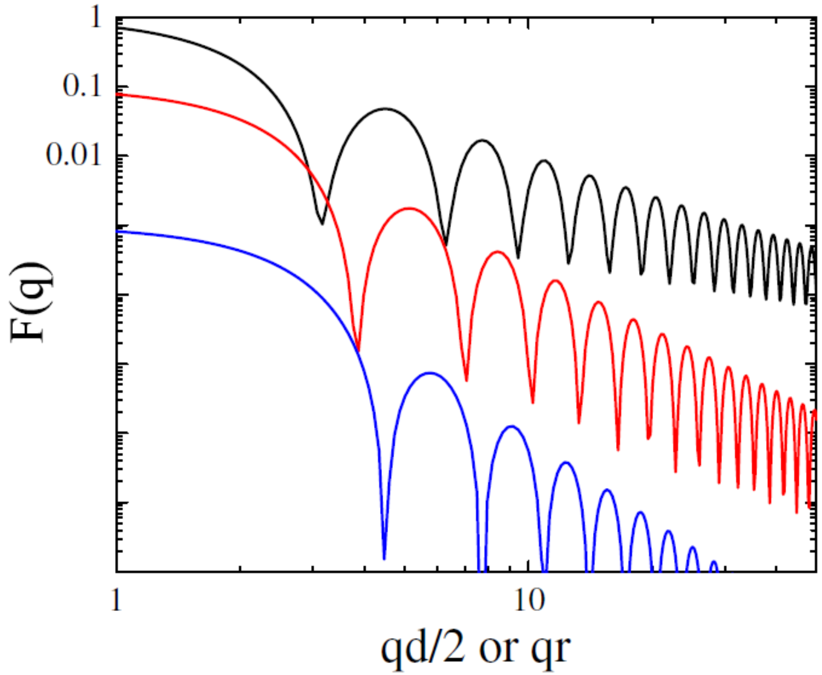
real space	reciprocal space	lattice points of reciprocal space (Miller indices)		
lamellar	(lamellar)	$(h,0,0)$		
		$(1,0,0)$ 1	$(5,0,0)$ 5	$(9,0,0)$ 9
		$(2,0,0)$ 2	$(6,0,0)$ 6	$(10,0,0)$ 10
		$(3,0,0)$ 3	$(7,0,0)$ 7	$(11,0,0)$ 11
		$(4,0,0)$ 4	$(8,0,0)$ 8	...
hexagonal	hexagonal	$(h,k,0)$		
		$(1,0,0)$ 1	$(2,2,0)$ $\sqrt{12}$	$(3,3,0)$ $\sqrt{21}$
		$(1,1,0)$ $\sqrt{3}$	$(3,1,0)$ $\sqrt{13}$	$(5,0,0)$ $\sqrt{25}$
		$(2,0,0)$ $\sqrt{4}$	$(4,0,0)$ $\sqrt{16}$	$(4,2,0)$ $\sqrt{28}$
		$(2,1,0)$ $\sqrt{7}$	$(3,2,0)$ $\sqrt{19}$	$(5,1,0)$ $\sqrt{31}$
		$(3,0,0)$ $\sqrt{9}$	$(4,1,0)$ $\sqrt{21}$	$(4,3,0)$ $\sqrt{31}$
sc	sc	(h,k,l)		
		$(1,0,0)$ 1	$(2,1,1)$ $\sqrt{6}$	$(3,1,1)$ $\sqrt{11}$
		$(1,1,0)$ $\sqrt{2}$	$(2,2,0)$ $\sqrt{8}$	$(2,2,2)$ $\sqrt{12}$
		$(1,1,1)$ $\sqrt{3}$	$(2,2,1)$ $\sqrt{9}$	$(3,2,0)$ $\sqrt{13}$
		$(2,0,0)$ $\sqrt{4}$	$(3,0,0)$ $\sqrt{9}$	...
		$(2,1,0)$ $\sqrt{5}$	$(3,1,0)$ $\sqrt{10}$	
bcc	fcc	(h,k,l) and $(h+\frac{1}{2},k+\frac{1}{2},l)$		
		$(\frac{1}{2},\frac{1}{2},0)$ $\sqrt{\frac{1}{2}}$	$(1,1,1)$ $\sqrt{3}$	$(2,1,0)$ $\sqrt{5}$
		$(1,0,0)$ $\sqrt{1}$	$(\frac{3}{2},1,\frac{1}{2})$ $\sqrt{\frac{7}{2}}$	$(2,\frac{3}{2},\frac{1}{2})$ $\sqrt{\frac{13}{2}}$
		$(1,\frac{1}{2},\frac{1}{2})$ $\sqrt{\frac{3}{2}}$	$(2,0,0)$ $\sqrt{4}$	$(\frac{5}{2},\frac{1}{2},0)$ $\sqrt{\frac{13}{2}}$
		$(1,1,0)$ $\sqrt{2}$	$(2,\frac{1}{2},\frac{1}{2})$ $\sqrt{\frac{9}{2}}$	...
		$(\frac{3}{2},\frac{1}{2},0)$ $\sqrt{\frac{5}{2}}$	$(\frac{3}{2},\frac{3}{2},0)$ $\sqrt{\frac{9}{2}}$	

fcc	bcc	(h,k,l) and $(h+\frac{1}{2},k+\frac{1}{2},l+\frac{1}{2})$		
		$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ $\sqrt{\frac{3}{4}}$ $(1,0,0)$ $\sqrt{1}$ $(1,1,0)$ $\sqrt{2}$ $(\frac{3}{2},\frac{1}{2},\frac{1}{2})$ $\sqrt{\frac{11}{4}}$ $(1,1,1)$ $\sqrt{3}$	$(2,0,0)$ $\sqrt{4}$ $(\frac{3}{2},\frac{3}{2},\frac{1}{2})$ $\sqrt{\frac{19}{4}}$ $(2,1,0)$ $\sqrt{5}$ $(2,1,1)$ $\sqrt{6}$ $(\frac{5}{2},\frac{1}{2},\frac{1}{2})$ $\sqrt{\frac{27}{4}}$	$(\frac{3}{2},\frac{3}{2},\frac{3}{2})$ $\sqrt{\frac{27}{4}}$ $(2,2,0)$ $\sqrt{8}$ $(\frac{5}{2},\frac{3}{2},\frac{1}{2})$ $\sqrt{\frac{35}{4}}$ ...
gyroid Ia$\bar{3}$d		$(h,k,0)$ with $h+k+l=2n$ and further restrictions		
		$(2,1,1)$ $\sqrt{6}$ $(2,2,0)$ $\sqrt{8}$ $(3,2,1)$ $\sqrt{14}$ $(4,0,0)$ $\sqrt{16}$ $(4,2,0)$ $\sqrt{20}$	$(3,3,2)$ $\sqrt{22}$ $(4,2,2)$ $\sqrt{24}$ $(4,3,1)$ $\sqrt{26}$ $(5,2,1)$ $\sqrt{30}$ $(4,4,0)$ $\sqrt{32}$	$(6,1,1)$ $\sqrt{38}$ $(5,3,2)$ $\sqrt{38}$ $(6,2,0)$ $\sqrt{40}$ $(5,4,1)$ $\sqrt{42}$ ...

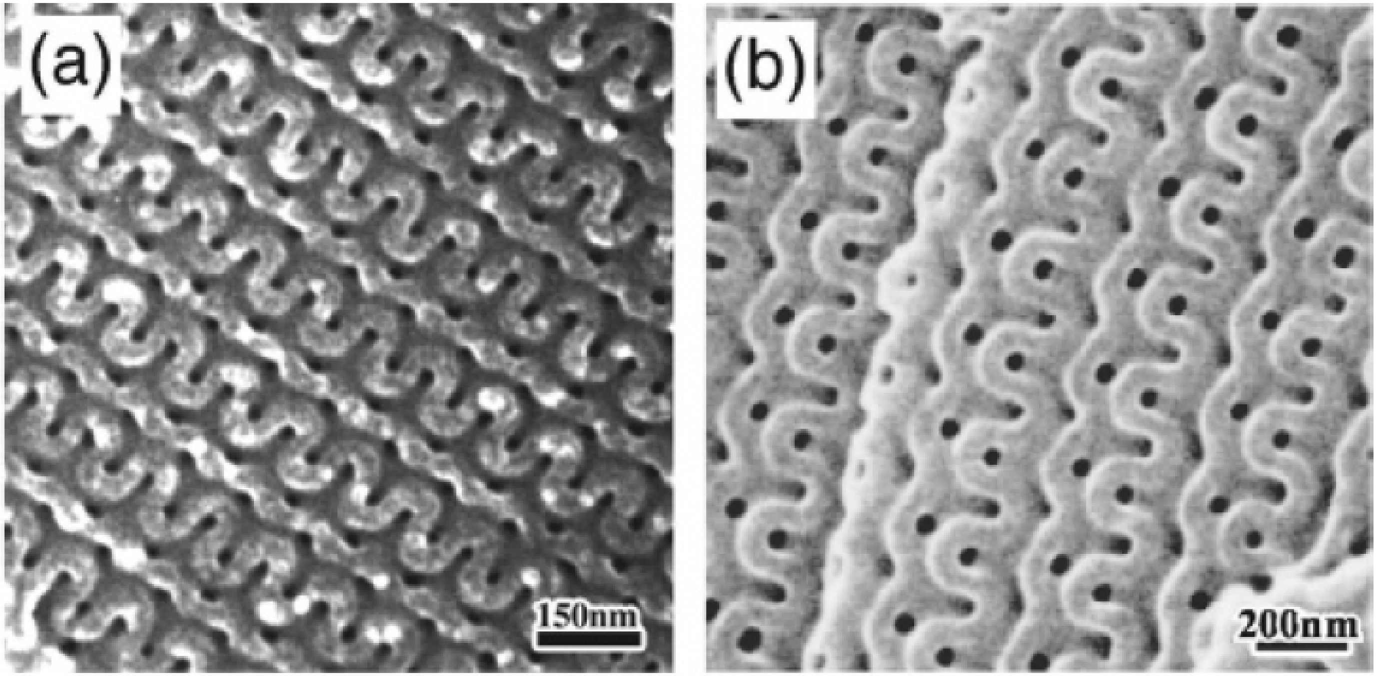
Formfactors

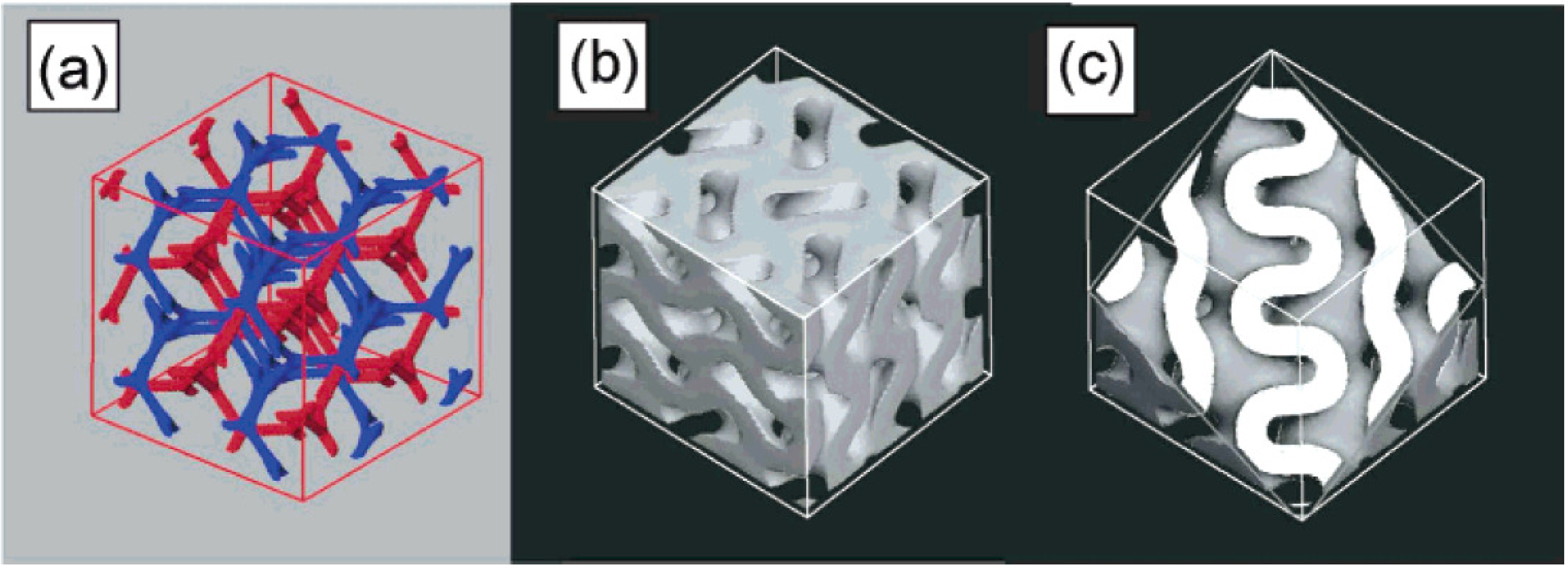
$$I(q_{h,k,l}) \propto S(q_{h,k,l}) \cdot F(q_{h,k,l})$$

lamellar	$F(q) = \left(\frac{\sin(qd/2)}{qd/2}\right)^2$
cylindrical	$F(q) = \left(2\frac{J_1(qr)}{qr}\right)^2$
spherical	$F(q) = \left(3\frac{\sin(qr) - qr\cos(qr)}{(qr)^3}\right)^2$



TEM





Summary Measurements

Optical

NMR

} isotropic / anisotropic

Rheology
- Relative Viscosities
- Frequency sweep

} quick and easy (Optical, NMR, Rheology)

Small Angle Scattering
- For many peaks: High accuracy
- For indistinguishable peaks: Esoteric

} powerful (single crystals) (Rheology, Small Angle Scattering)

⋮

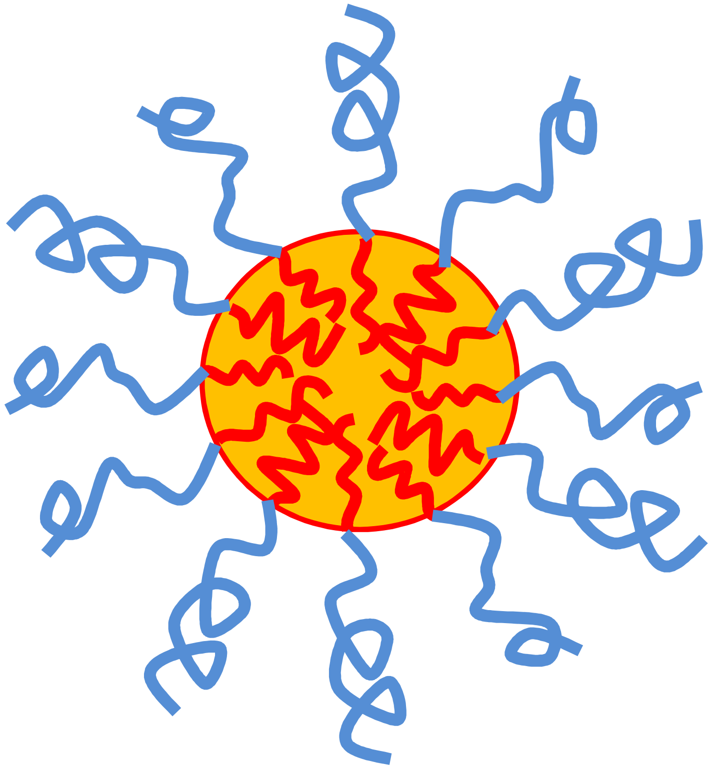
TEM
- Many cuts needed

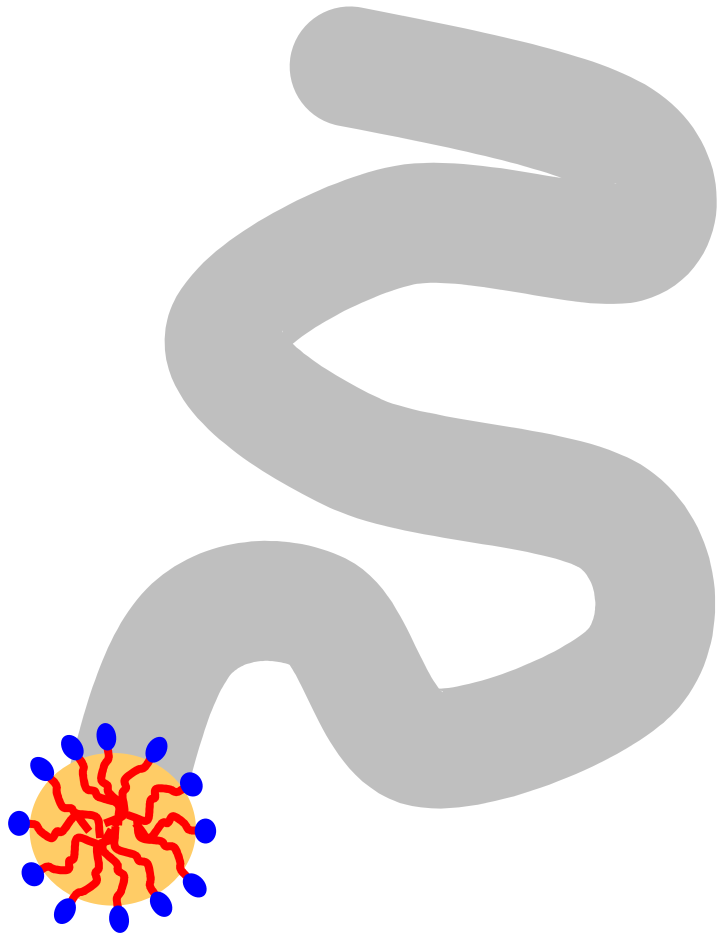
} further extension

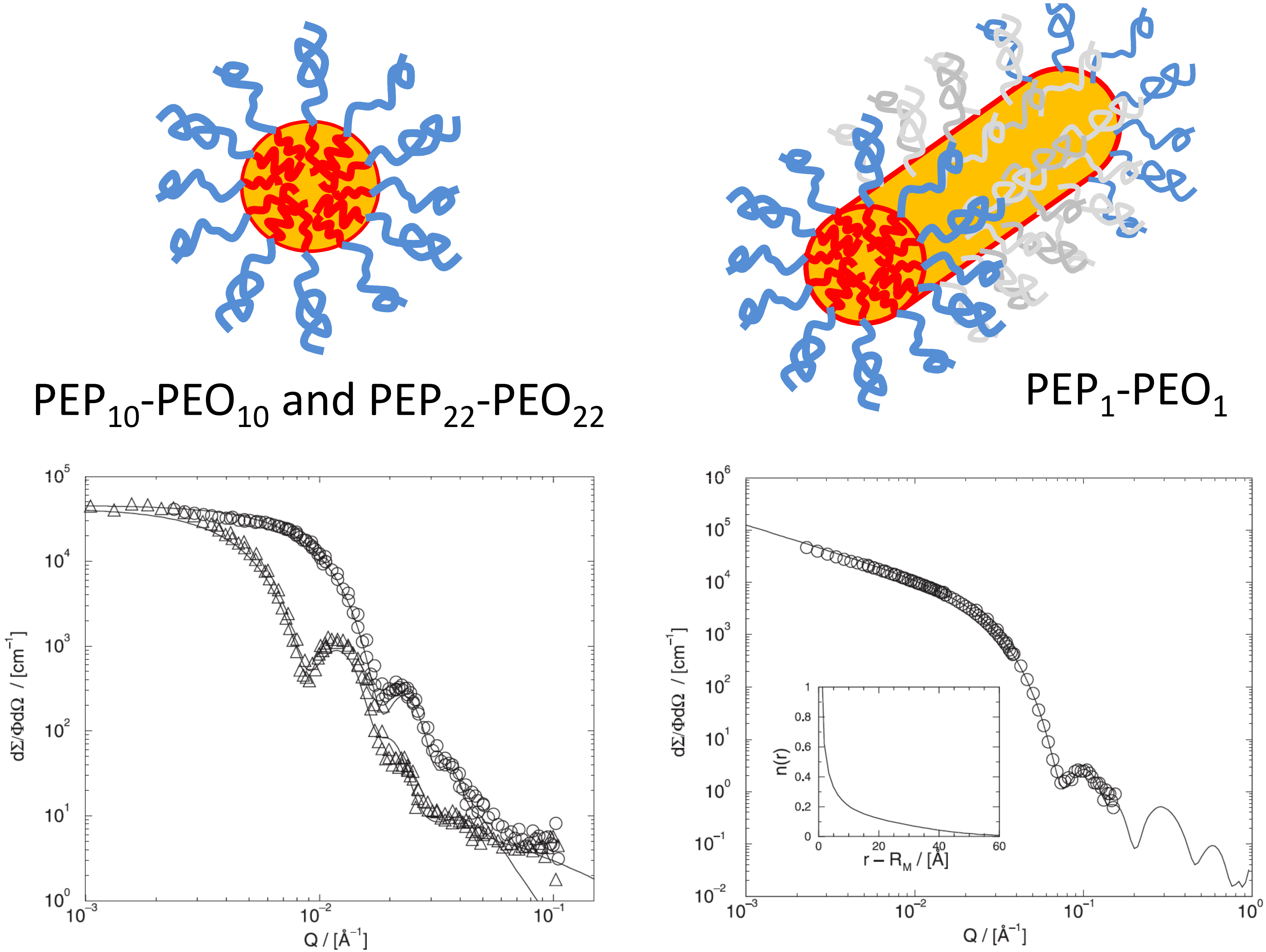
Scattering from polymeric systems

Wormlike Micelles

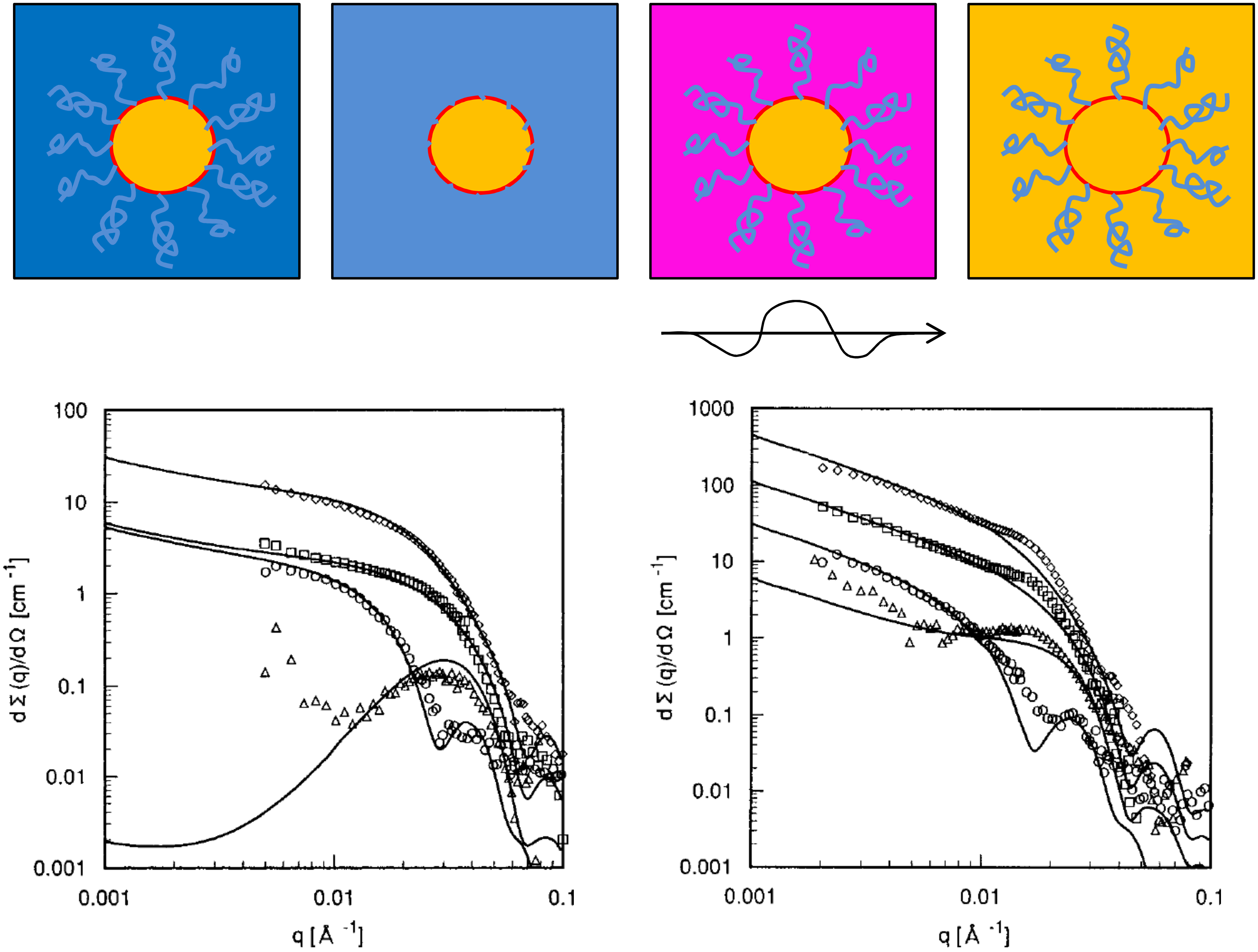
Polymer Micelles





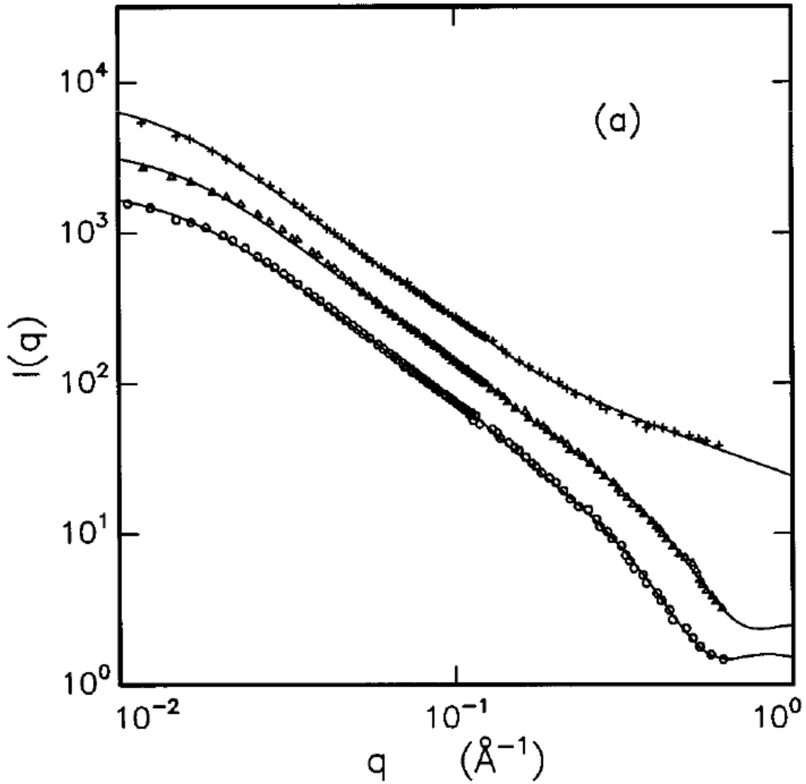


PEP10-PEO10 and PEP22-PEO22
PEP1-PEO1
dΣ/ΦdΩ / [cm⁻¹]
Q / [Å⁻¹]
n(r)
r − R_M / [Å]

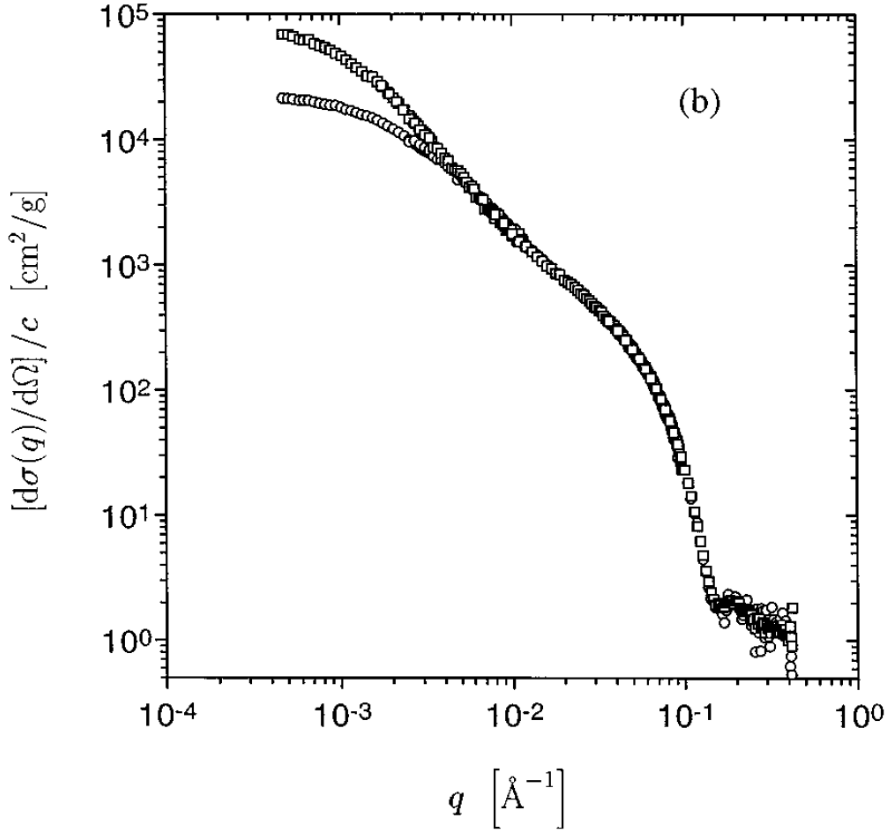

100
10
1
0.1
0.01
0.001
0.001
0.01
0.1
q [Å -1]
d Σ (q)/d Ω [cm -1]
1000
100
10
1
0.1
0.01
0.001
0.001
0.01
0.1
q [Å -1]
d Σ (q)/d Ω [cm -1]

Wormlike Micelles or Polymer

PS in CS_2



water/isooctane/lecitin

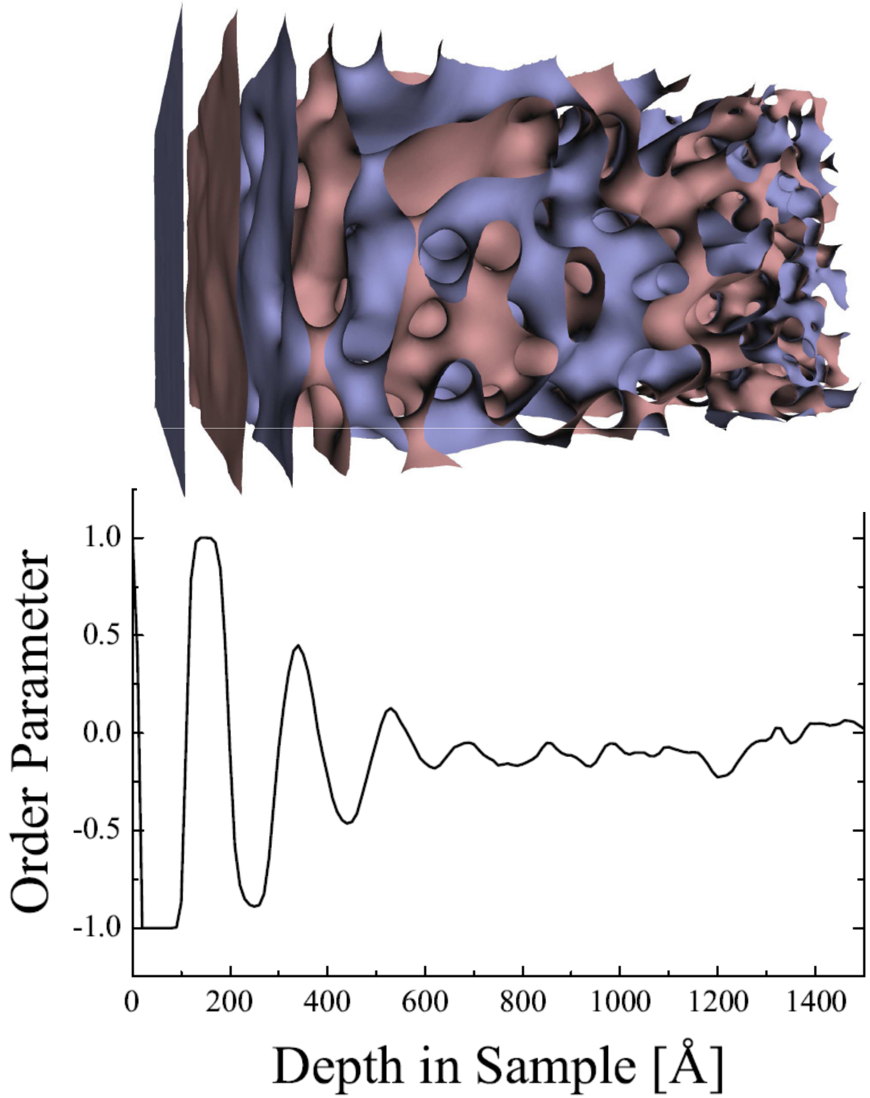


Oil Production

<u>Aqueous Surfactant Systems are used for:</u>

- Drilling Fluid
- Secondary/Tertiary Oil Production
- Fracturing Fluid

Simulations (M. Belushkin)



Single order parameter:

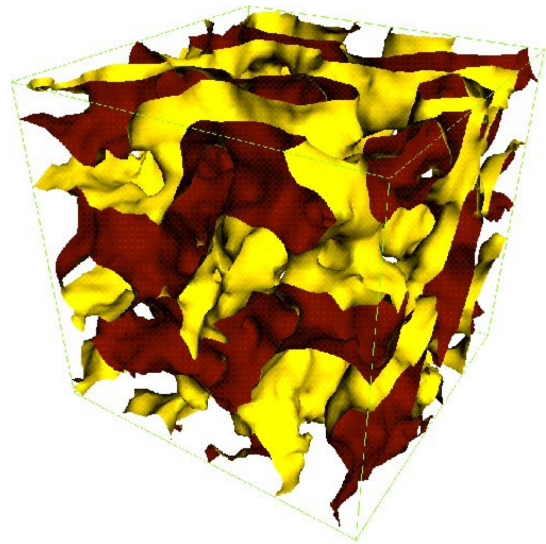
+1: Oil
-1: Water
0: Surfactant

Lamellar order decays !!!

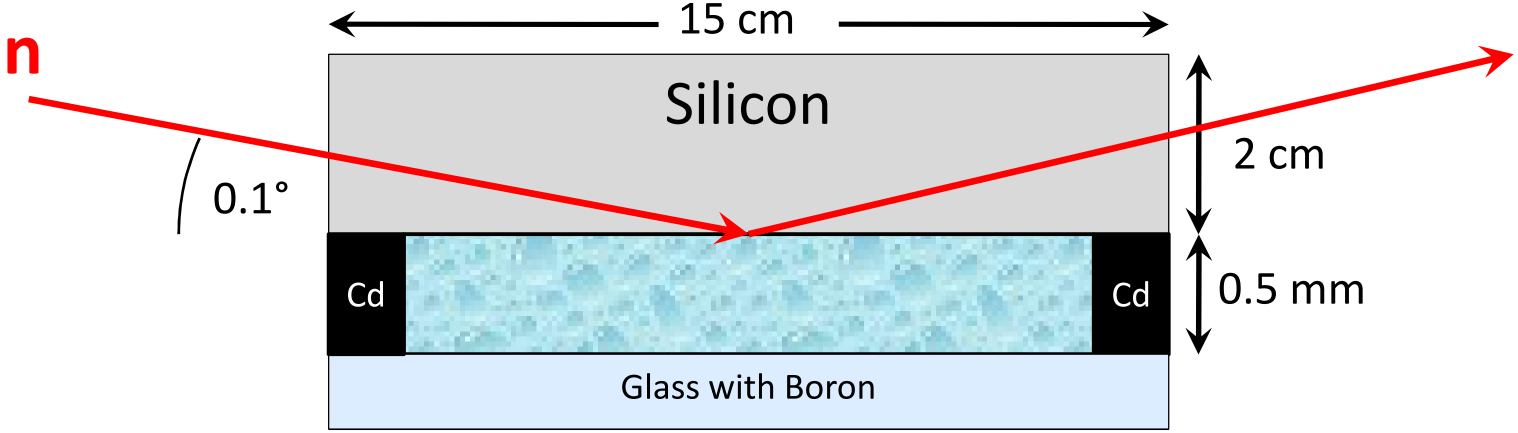
The System

Water: D_2O, H_2O (41.5%vol)
Oil: Decane (41.5%vol)
Surfactant: $C_{10}E_4$ (17.0%vol)

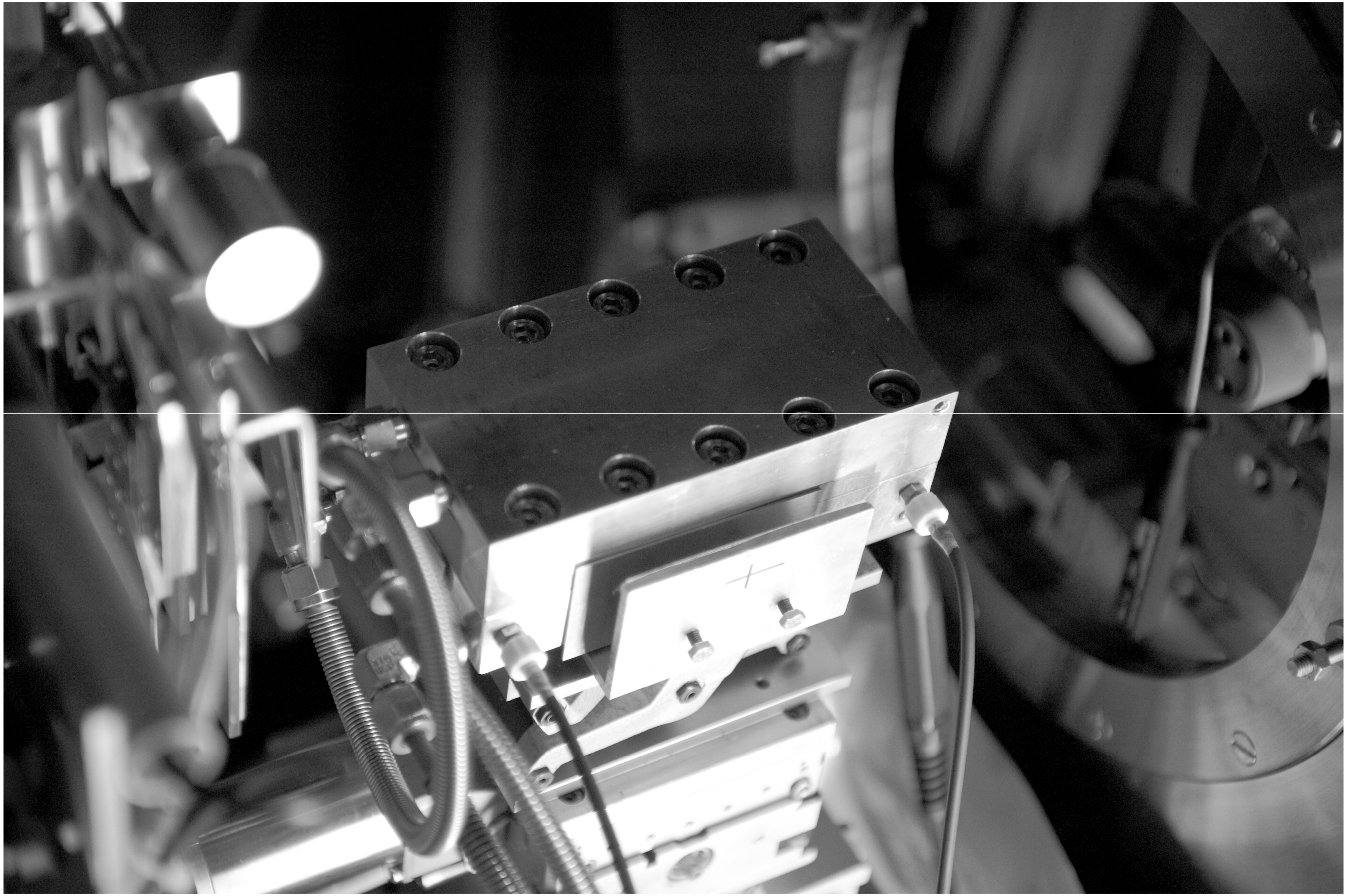
Temperature ca. 25°C

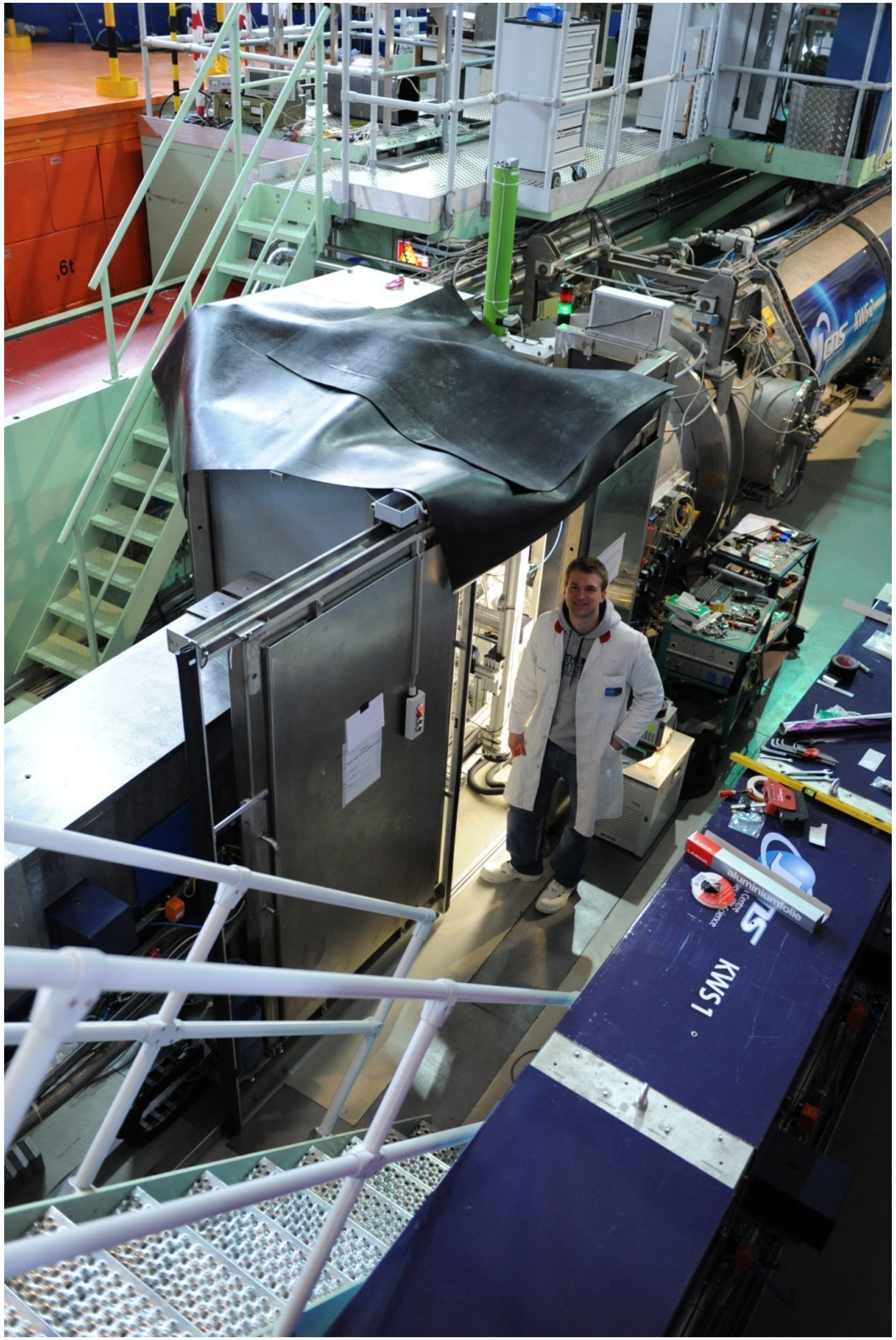


The Cell

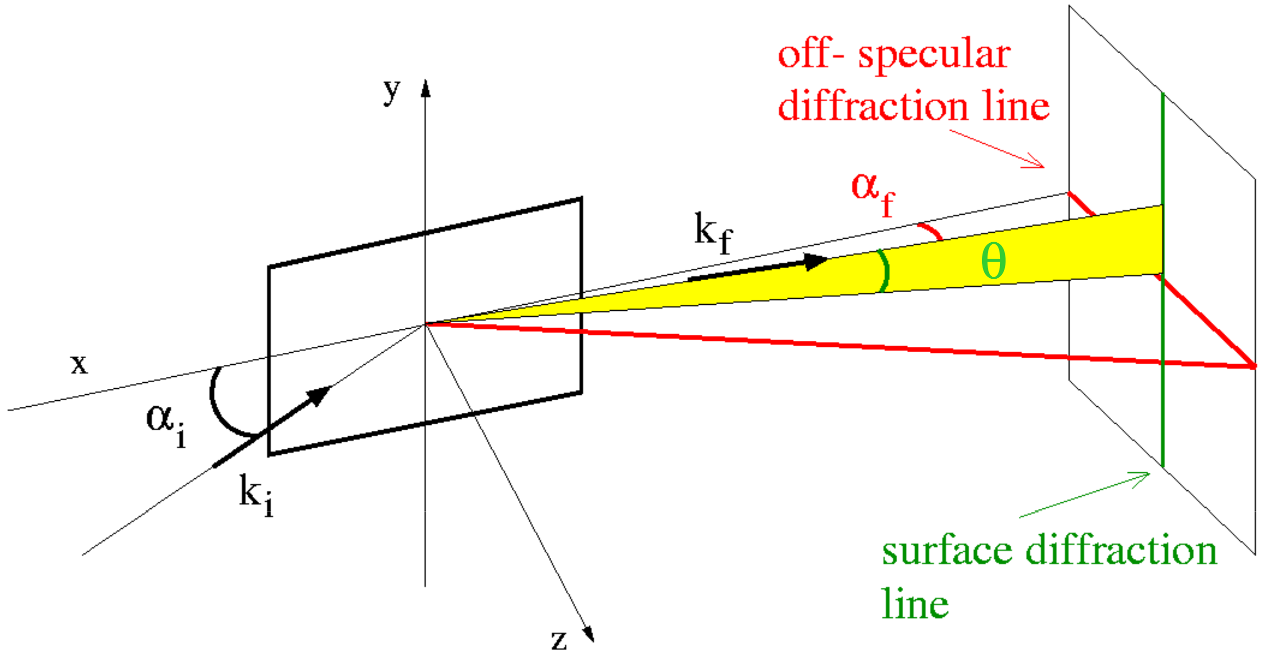


The Cell




KWS 1
aluminiumfolie

Grazing incidence:



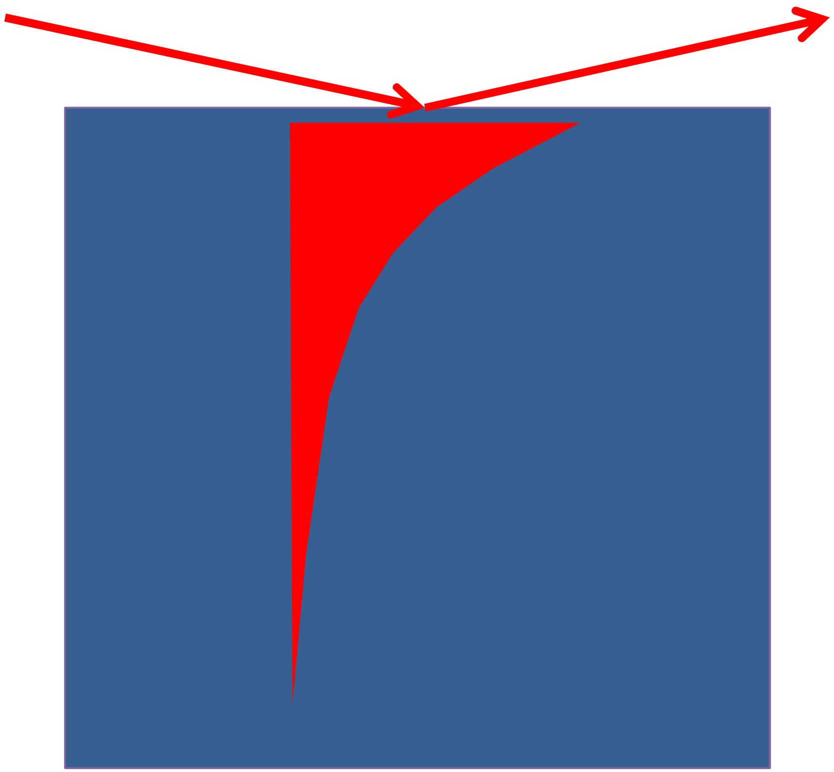
$$\begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} = \frac{2\pi}{\lambda} \cdot \begin{pmatrix} \frac{1}{2}(\alpha_i^2 - \alpha_f^2) - \frac{1}{2}\theta_y^2 \\ \theta_y \\ \alpha_i + \alpha_f \end{pmatrix}$$

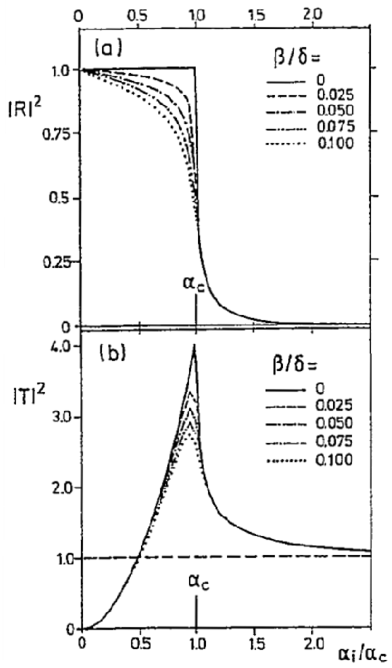
→ Reflect.: 1 µm < $\zeta_{//}$ < 20 µm

→ GISANS: 2 nm < $\zeta_{//}$ < 600 nm

(large θ_y, α critical angle)
α might be large...

Evanescent Wave: the depth information





◄ Fig. 2.2. (a) X-ray reflectivity $|R_i|^2$ and (b) transmissivity $|T_i|^2$ versus α_i for various β/δ

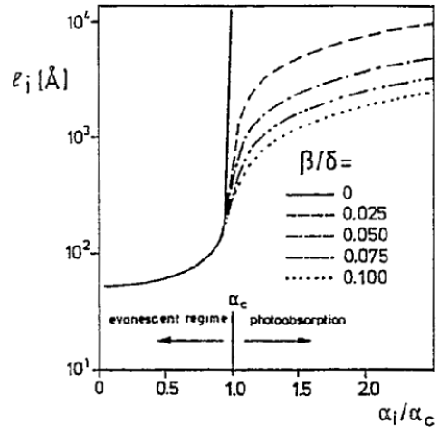
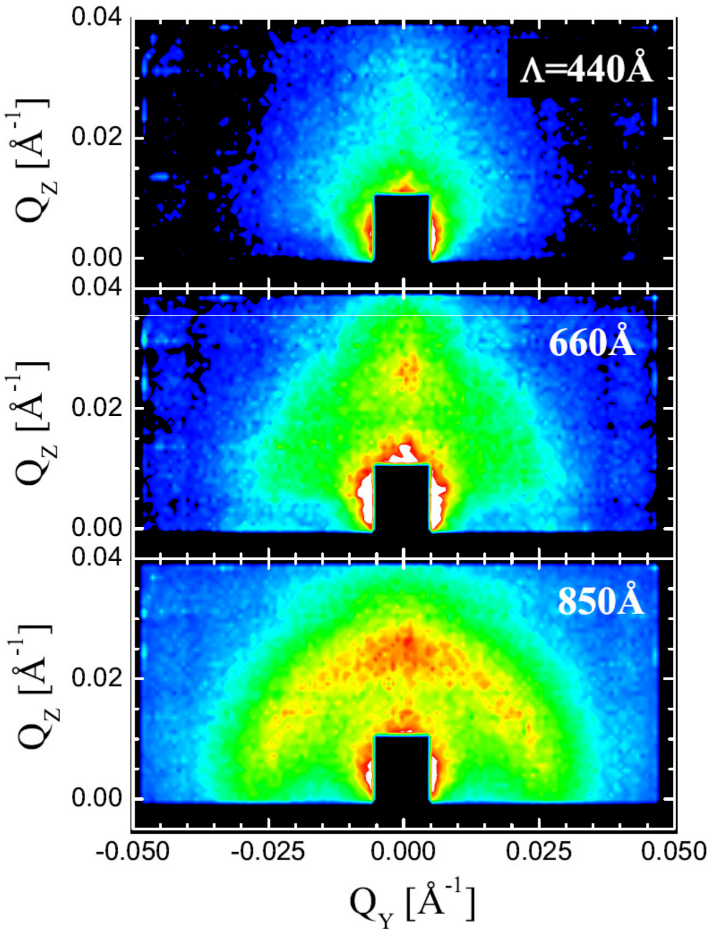
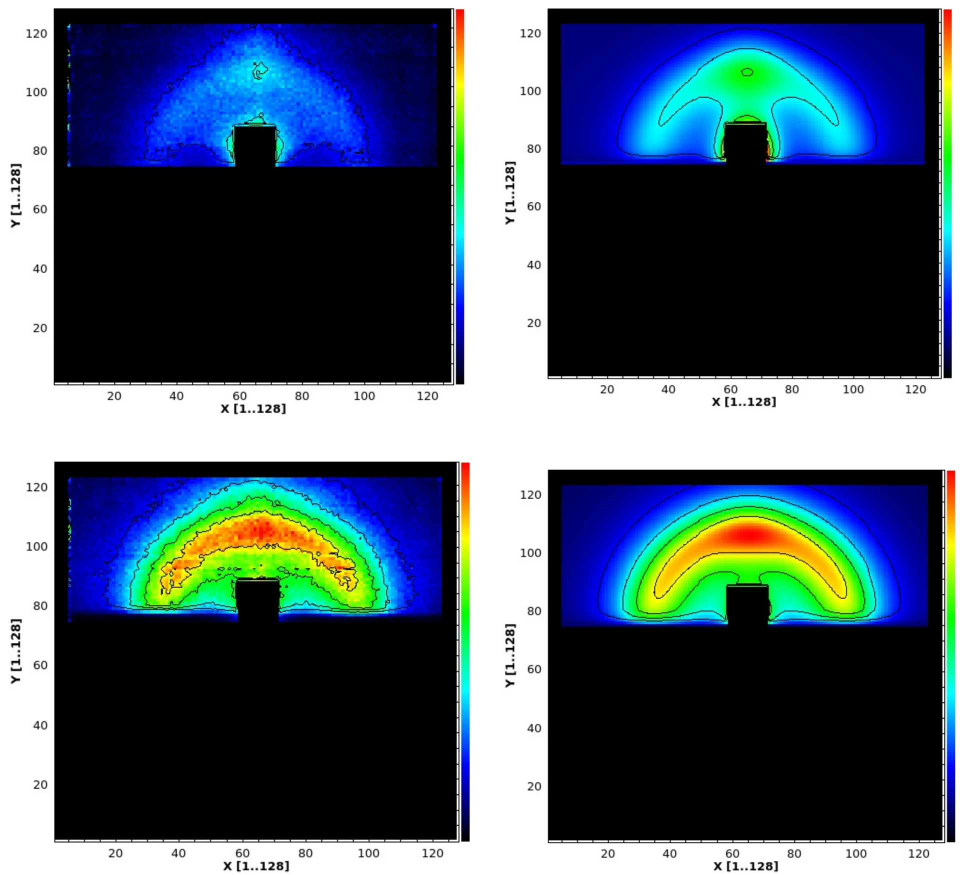


Fig. 2.3. Penetration depth ℓ_i of evanescent x-rays versus α_i/α_c for various β/δ

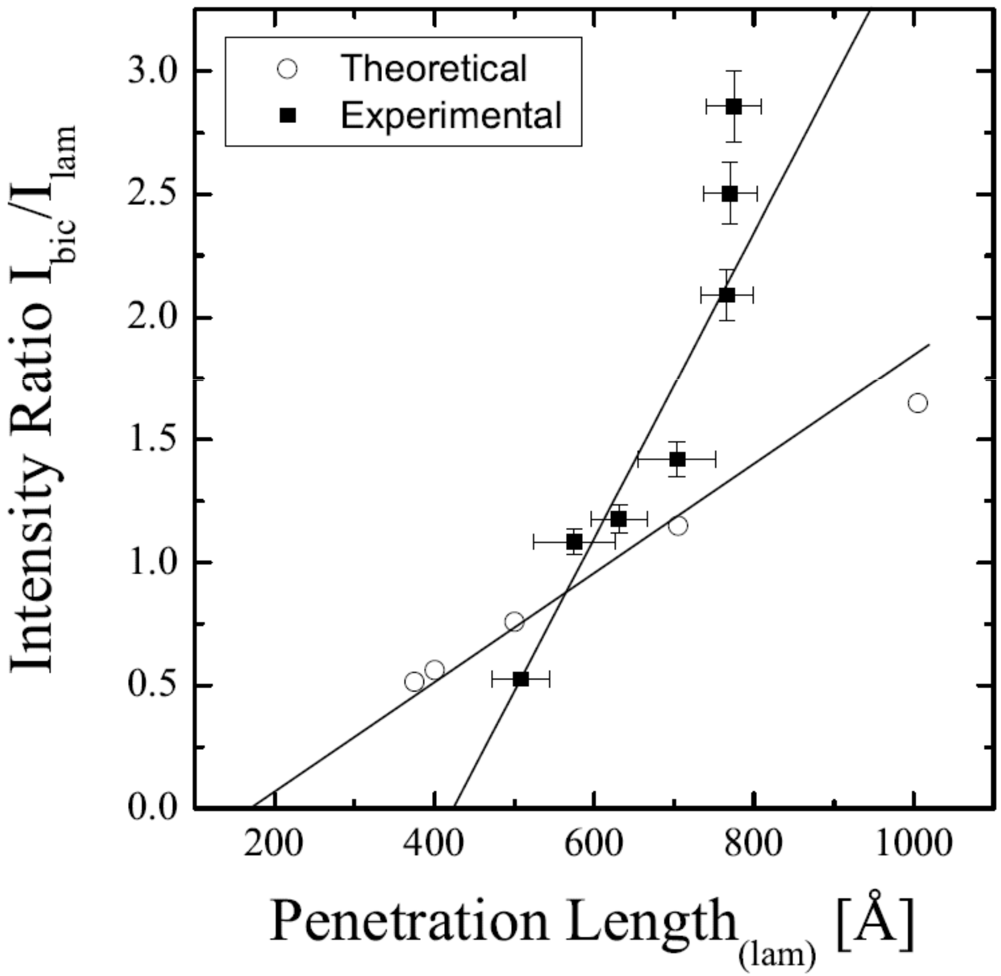
$$L_{i,0} \propto \Delta\rho^{-1/2}$$

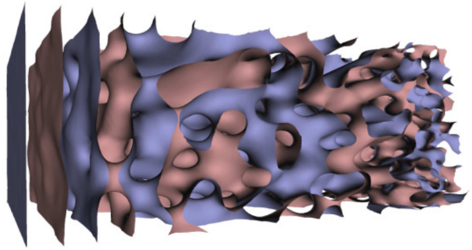
Measurements vs. Fits

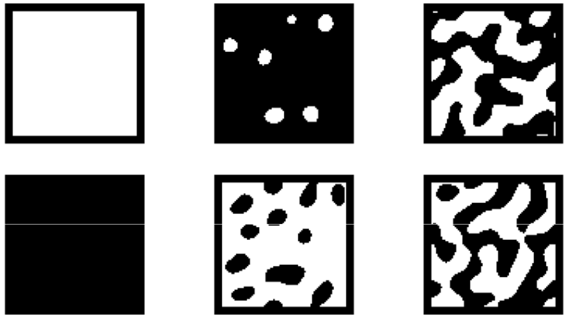




Results from GISANS

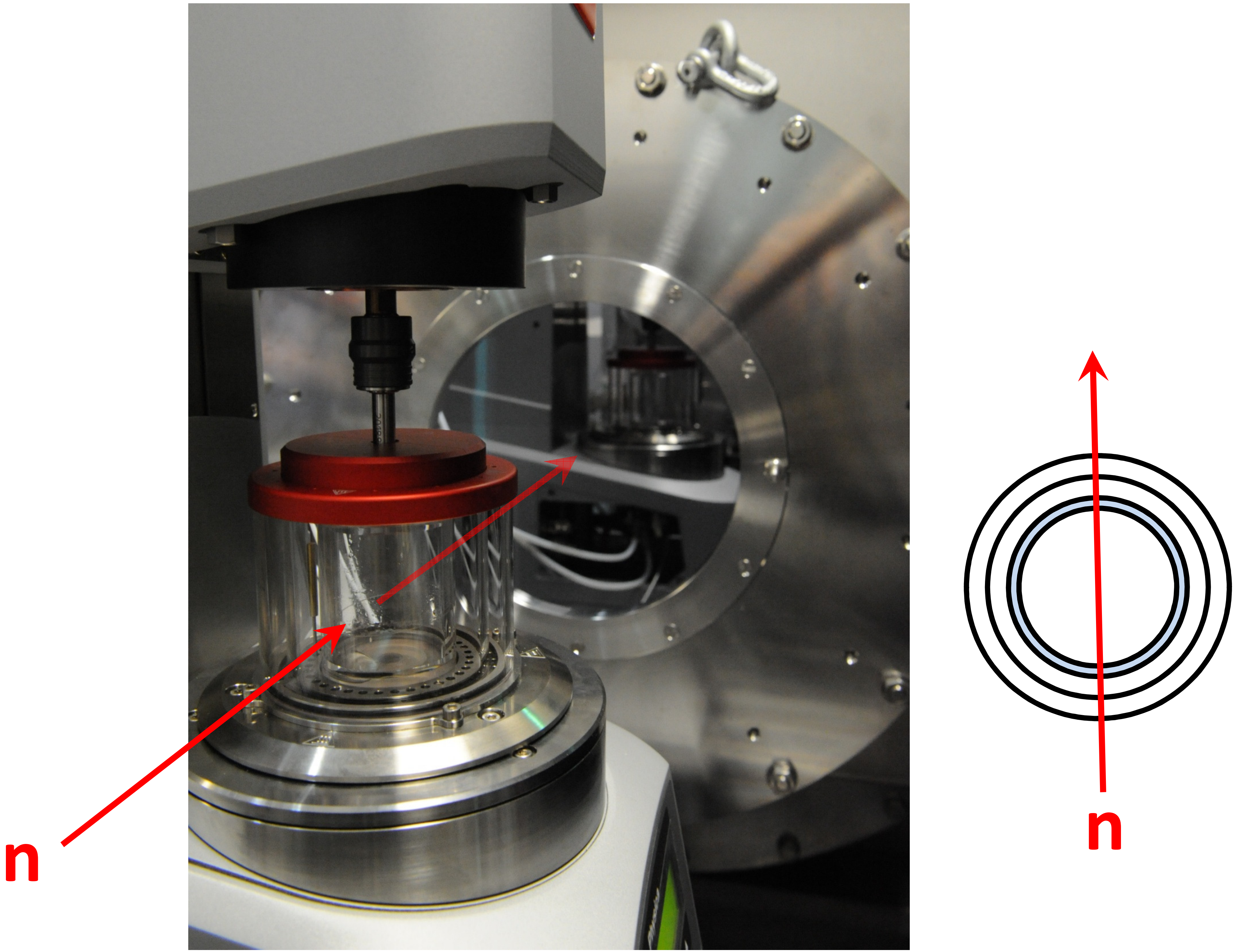




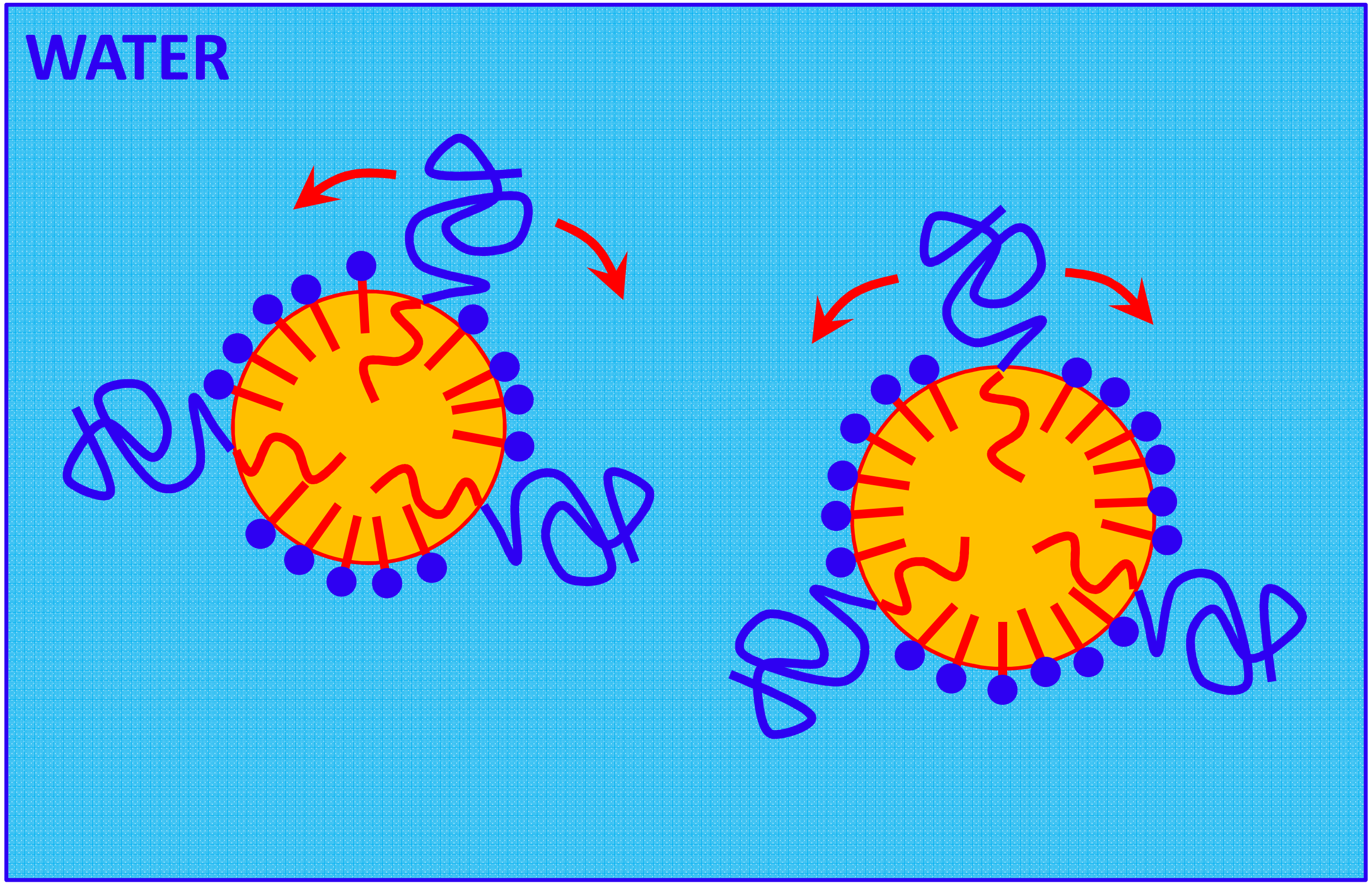


Lamellar: Peak

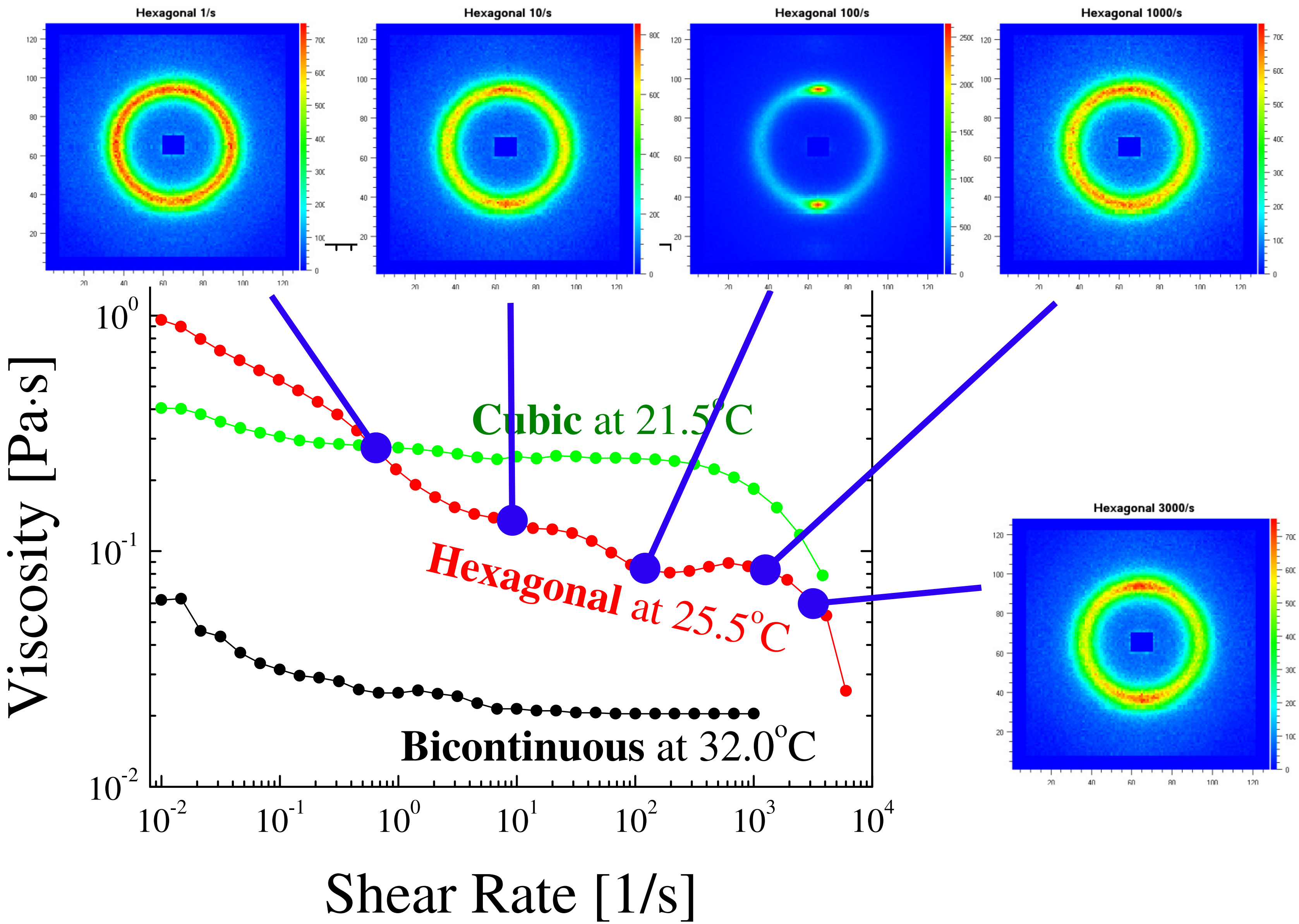
Isotropic: perforated lam.
+ bicontinuous


n
n

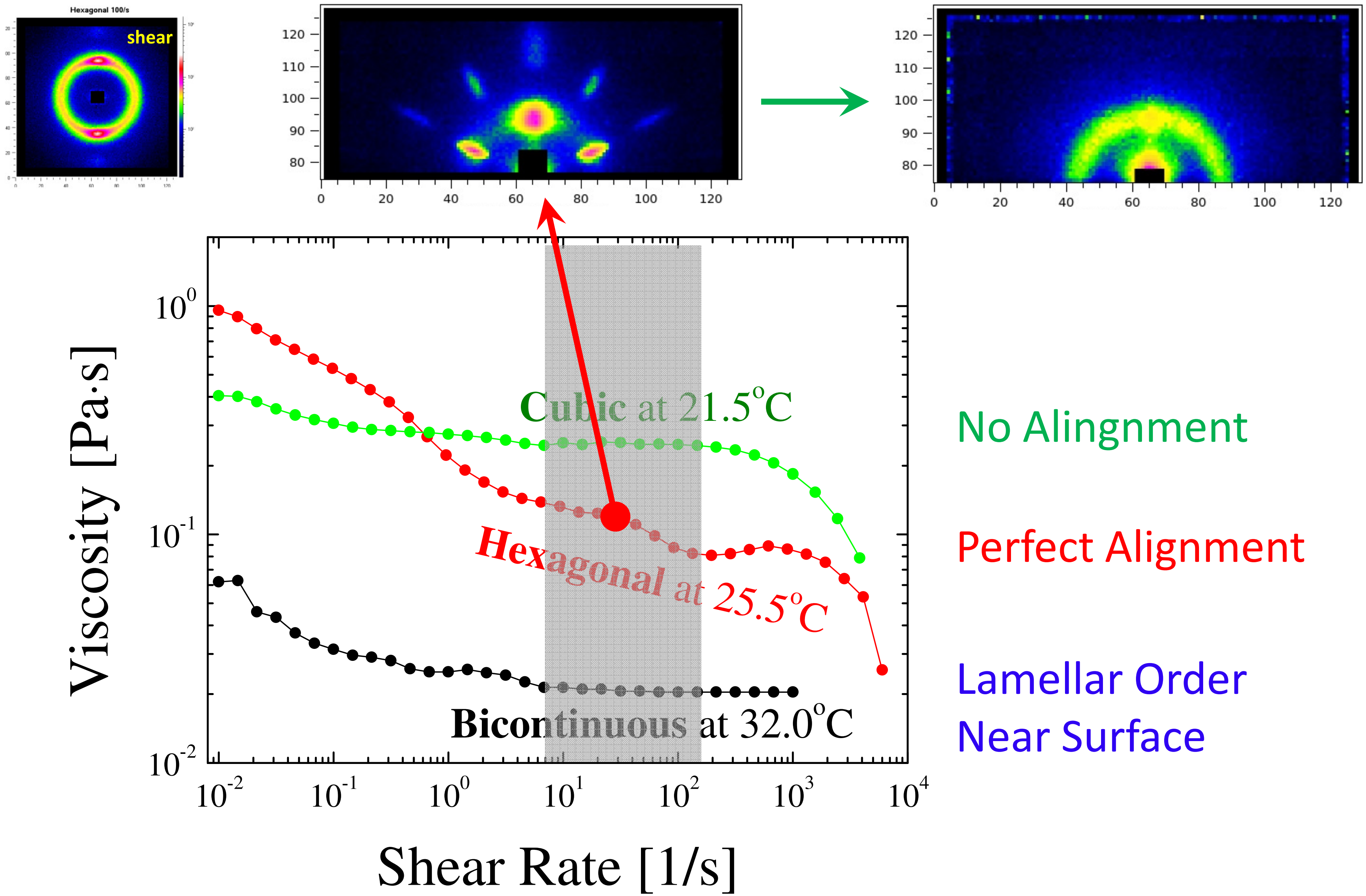
Microemulsion with Unsymmetric Polymer



Shear Scans with SANS hexagonal



Comparison to Injected Microemulsion in GISANS Cell

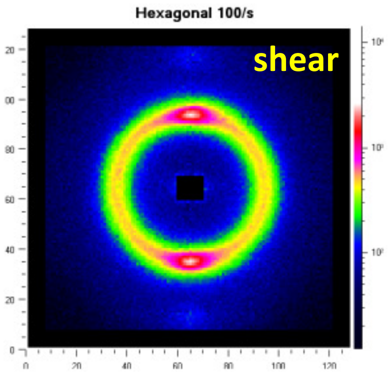


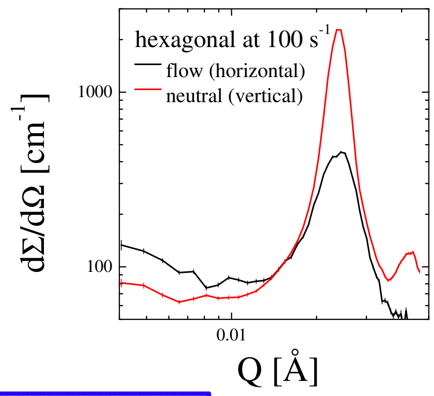
No Alingnment

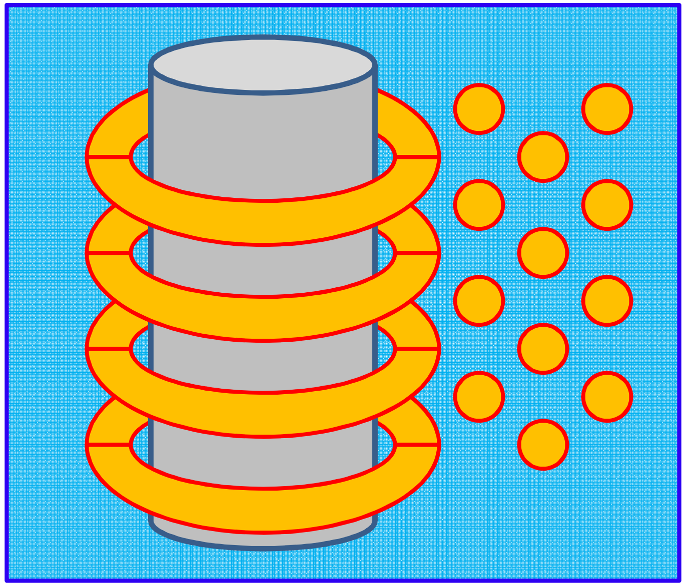
Perfect Alignment

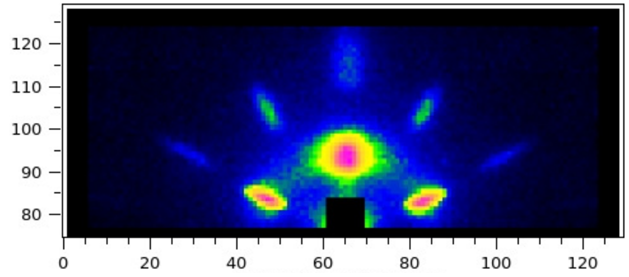
Lamellar Order
Near Surface

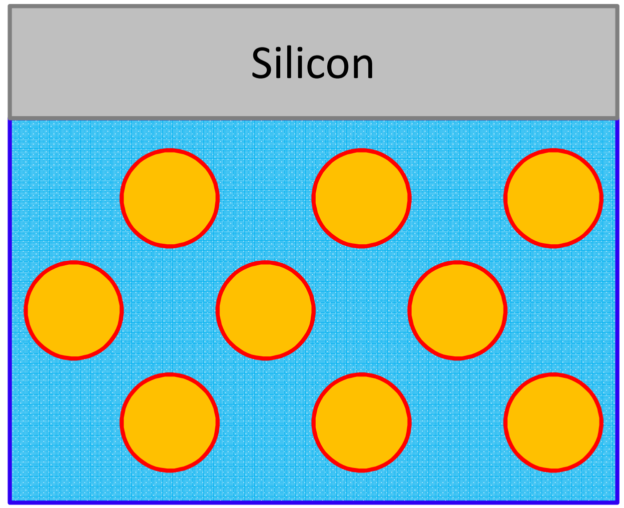
Comparison to Injected Microemulsion in GISANS Cell











Summary

Amphiphile
Condensation – Self Assembly
High Symmetry
Interactions

Concepts: * Aqueous Surfactant Systems
* Microemulsions
* (Polymeric Systems) not here
* (Mesoscopic Particles) (Ianus) not here

Actual research:
Surfaces
Mesoscopic Particles
Surfactants + Polymers