Lipid Structuring and Soft Materials

Michael Rappolt

The Polymorphism of Soft Materials: Lyotropic Liquid Crystals

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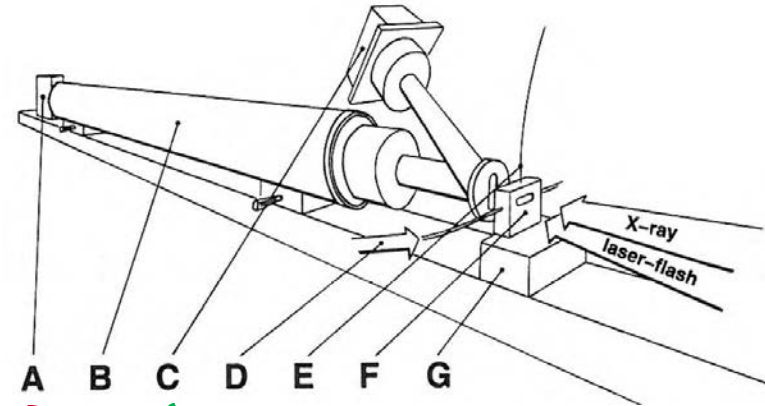
Useful Tools and Principles
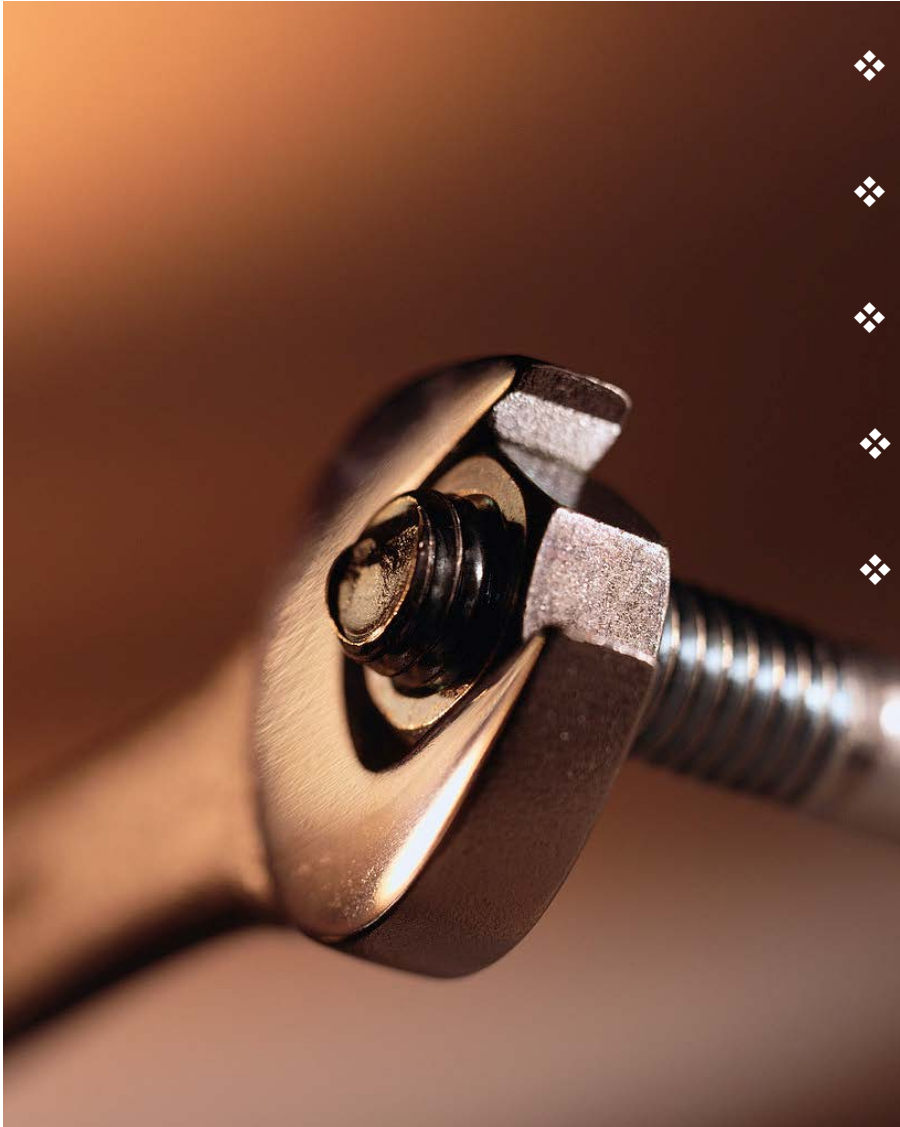
❖   SAXS/WAXS

❖   Classical Fourier Transform

❖   Modeling

❖   Membrane Curvature

❖   Packing Frustration

SAXS and WAXS
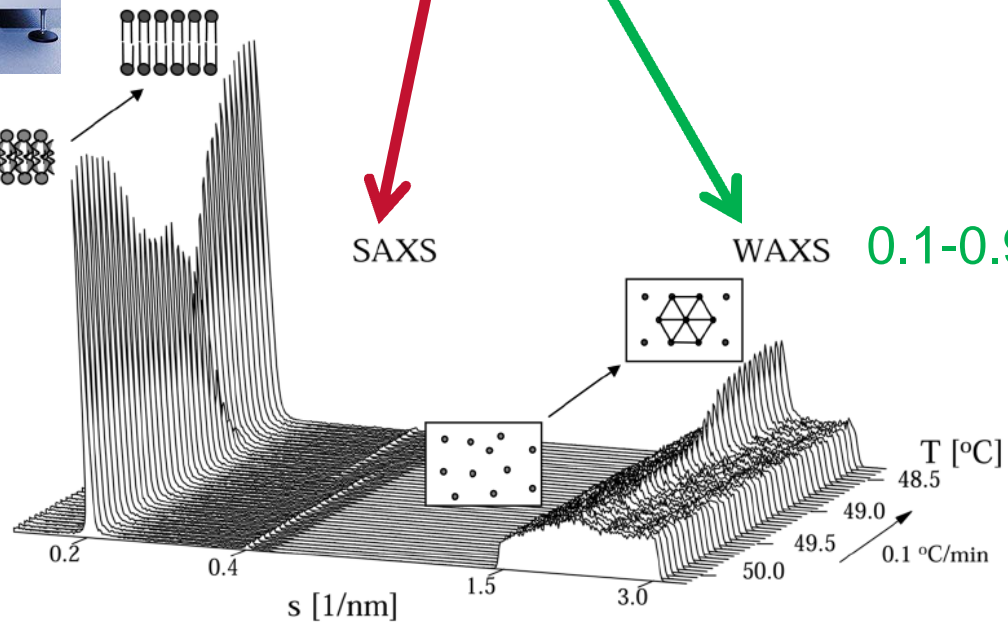

1-100 nm
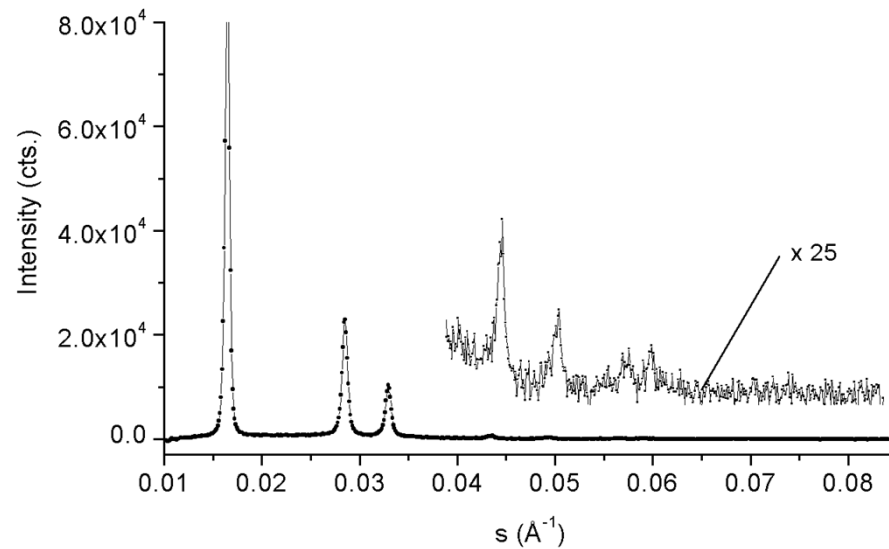
SAXS

WAXS 0.1-0.9 nm

A B C D E F G

X-ray
laser-flash

T [°C]
48.5
49.0
49.5   0.1 °C/min
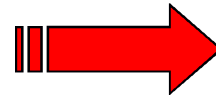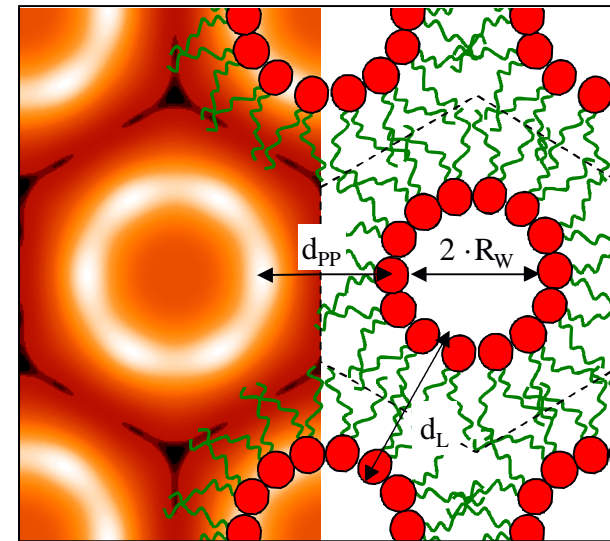50.0

s [1/nm]
0.2   0.4   1.5   3.0

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Classical Fourier Transform

SAXD

electron density map

$$\tilde{\rho}(\overrightarrow{r}) = \sum_{hkl}^{max} \alpha_{hkl} |F_{hkl}| \cos(\overrightarrow{q}_{hkl} \cdot \overrightarrow{r})$$
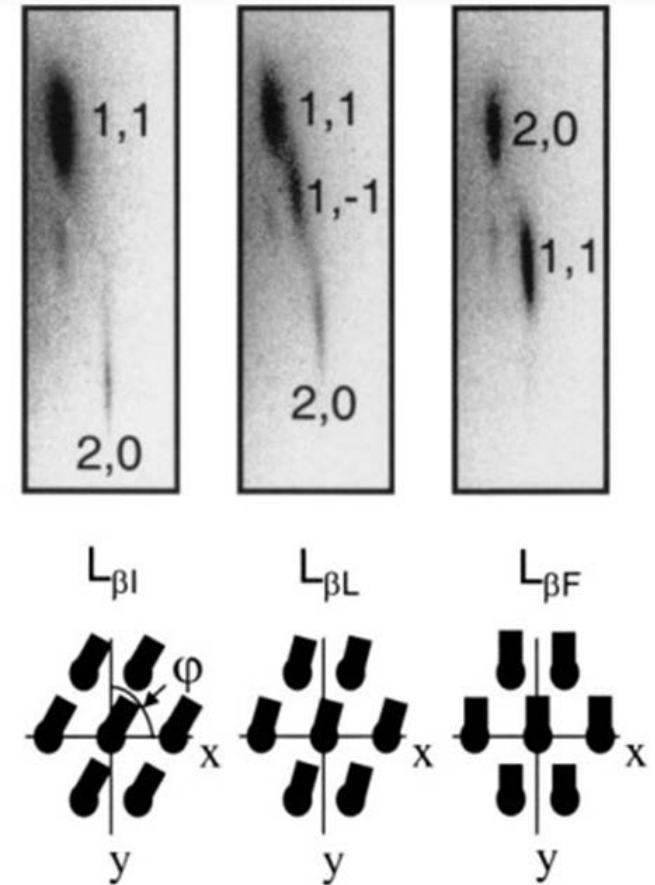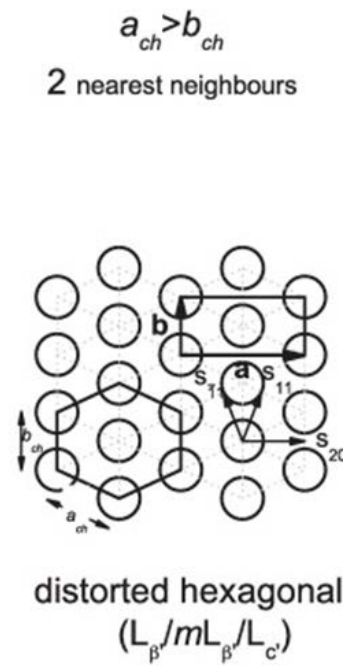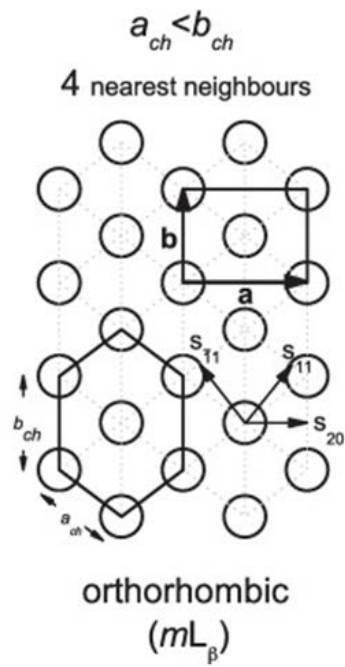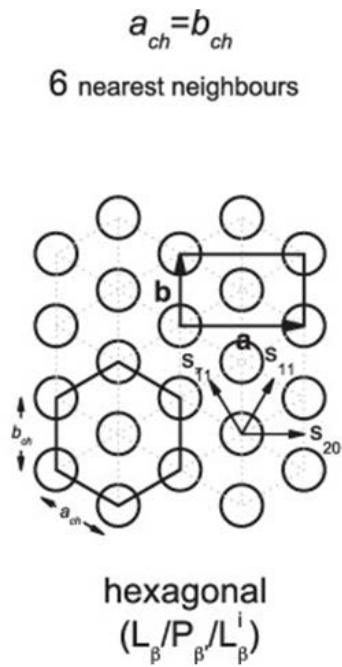
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The Global Model for Fluid Lamellar Phases

DAPC
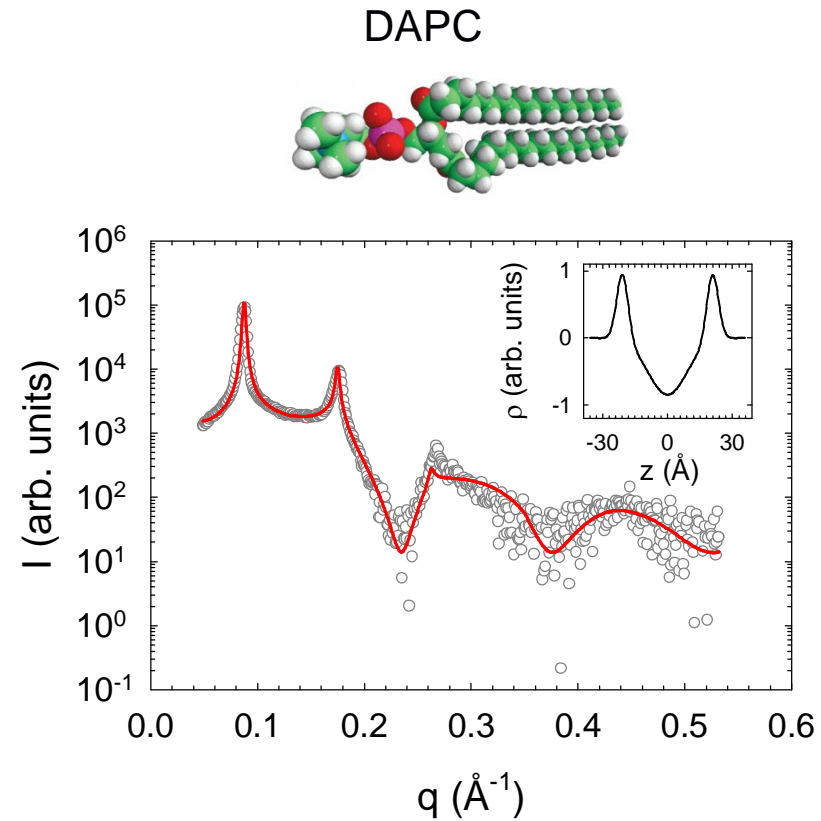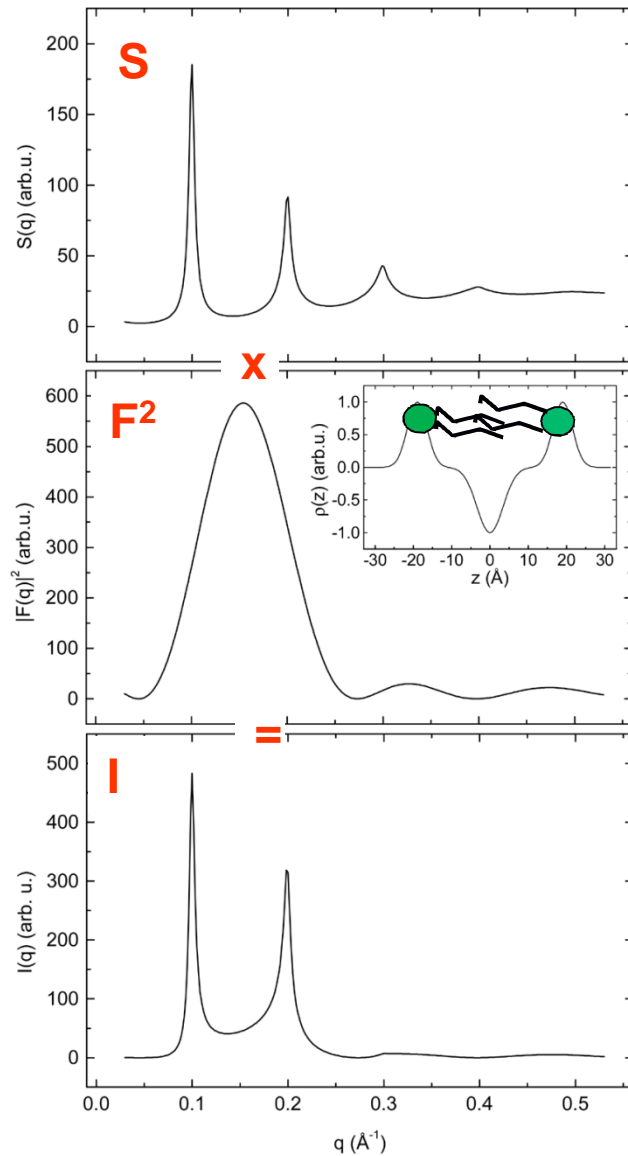
G. Pabst, M. Rappolt, H. Amenitsch and P. Laggner **2000** *Phys. Rev. E* 62, 4000

M. Rappolt, P. Laggner, and G. Pabst, *Recent Res. Devel.* **2004** Biophys. 3, 363
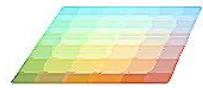
WAXD: Chain Packing

D. Marsh, Chem Phys Lipids 165:59-78 (2012)
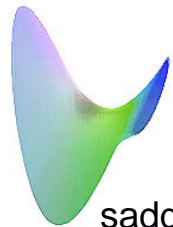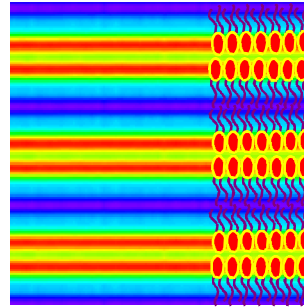
S. Tristram-Nagle et al.,Biophys J 83: 3324-3335 (2002)

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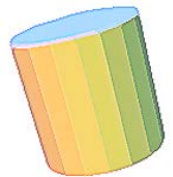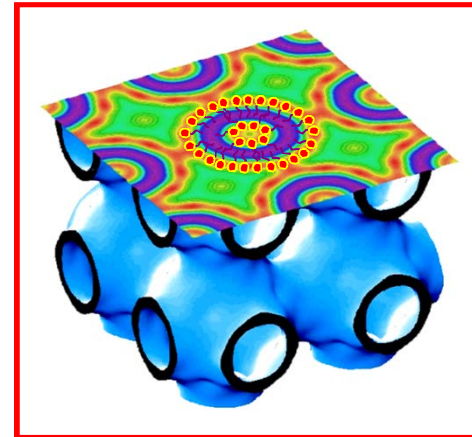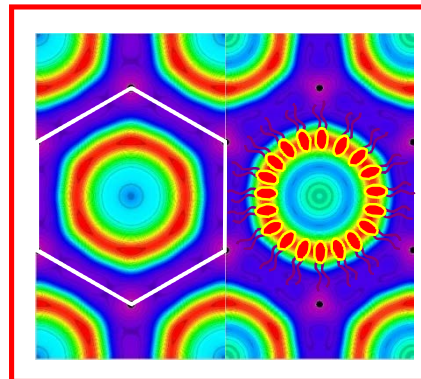# Curvature of Membranes

plane

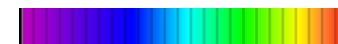c_1 c_2 H K D

0 0 0 0 0

saddle

+ - 0 - +

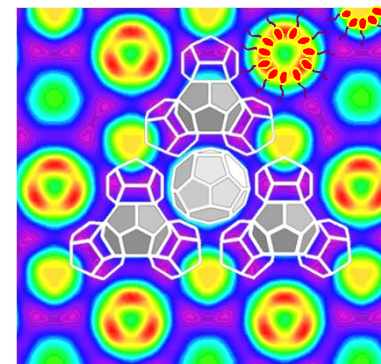cylinder

0 - - 0 +

sphere
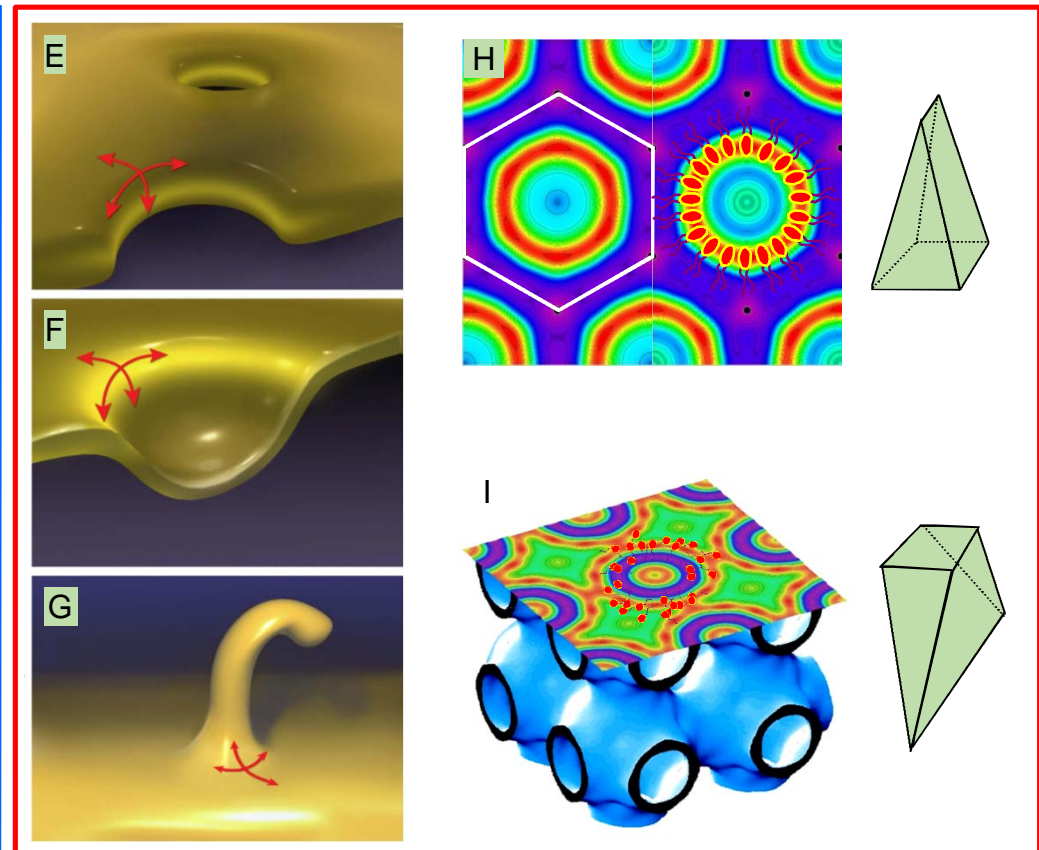
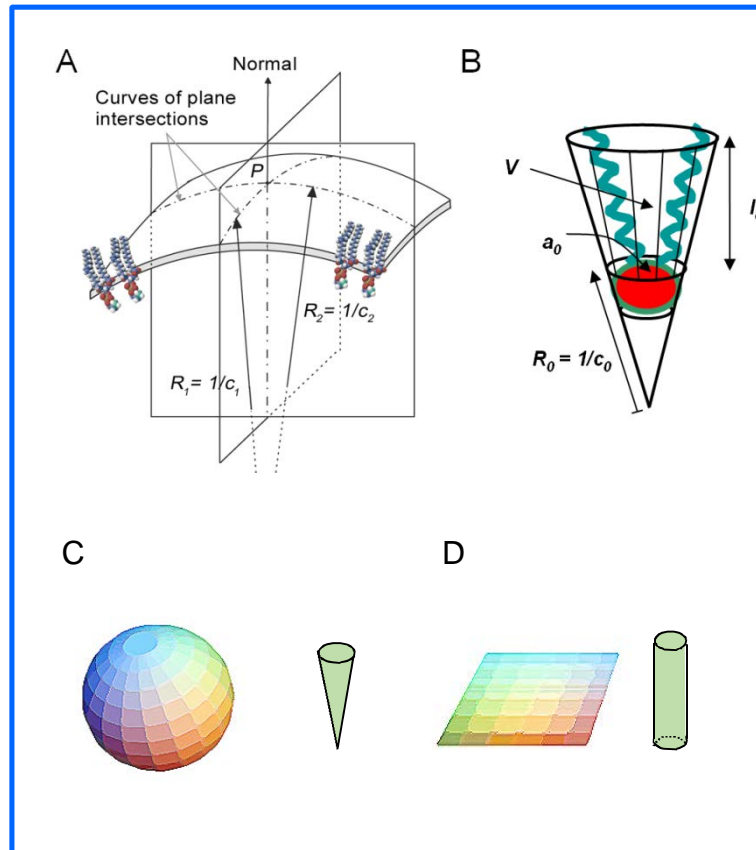- - - + 0

low   high

Molecular Shape

Packing and Curvature Frustration

water in oil

oil in water
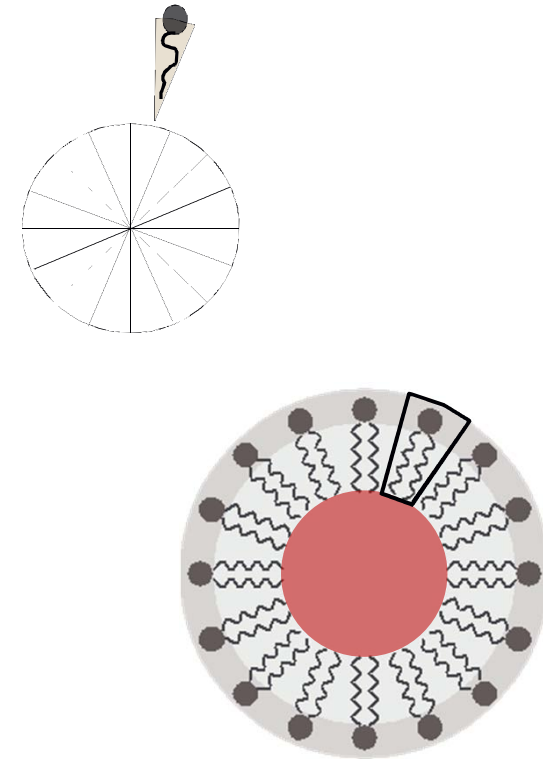
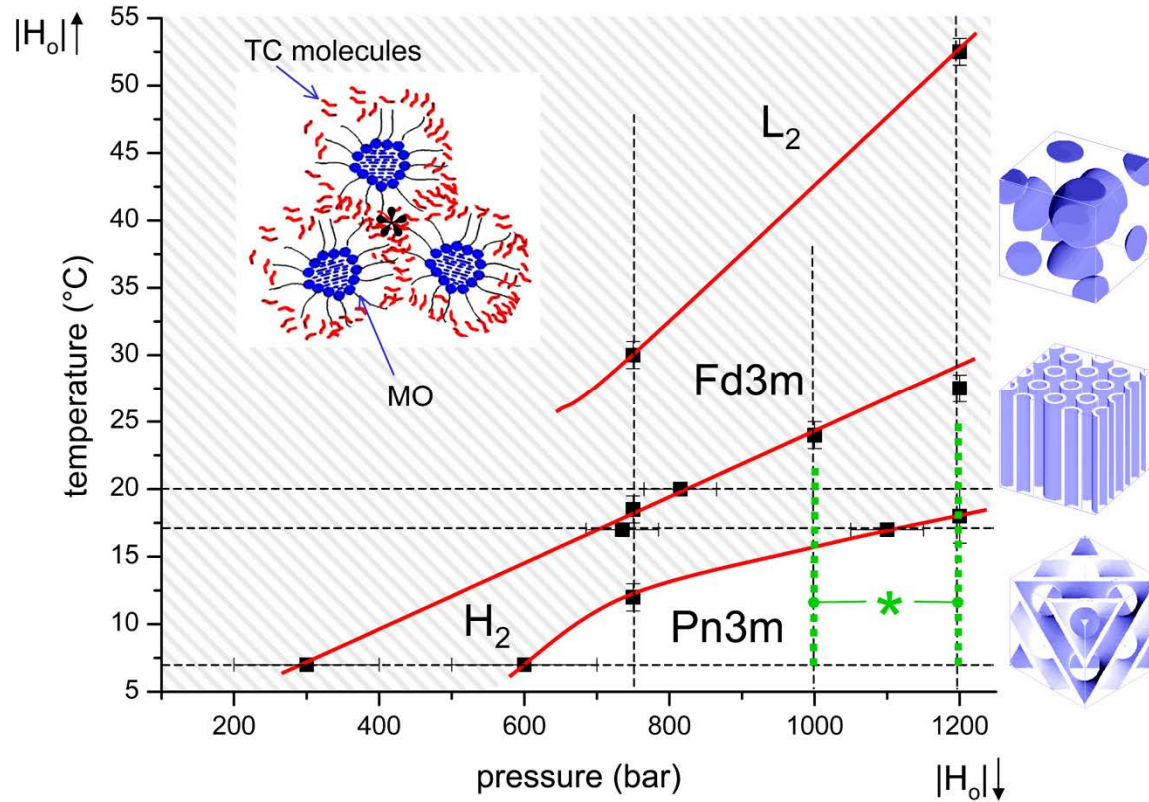Perutková, S., Daniel, M., Dolinar, G., Rappolt, M., Kralj-Iglic, V., and Iglic, A. (2009) In Advances in Planar Lipid Bilayers and Liposomes, Vol. 9, Burlington: Academic Press, pp. 237-278.

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Overcoming Packing Limitations

Tetradecane loaded monoolein/water system:

A. Yaghmur, M. Kriechbaum, H. Amenitsch, M. Steinhart, P. Laggner & M. Rappolt Langmuir 26, 1177-1185 (2010)

Working with Additives
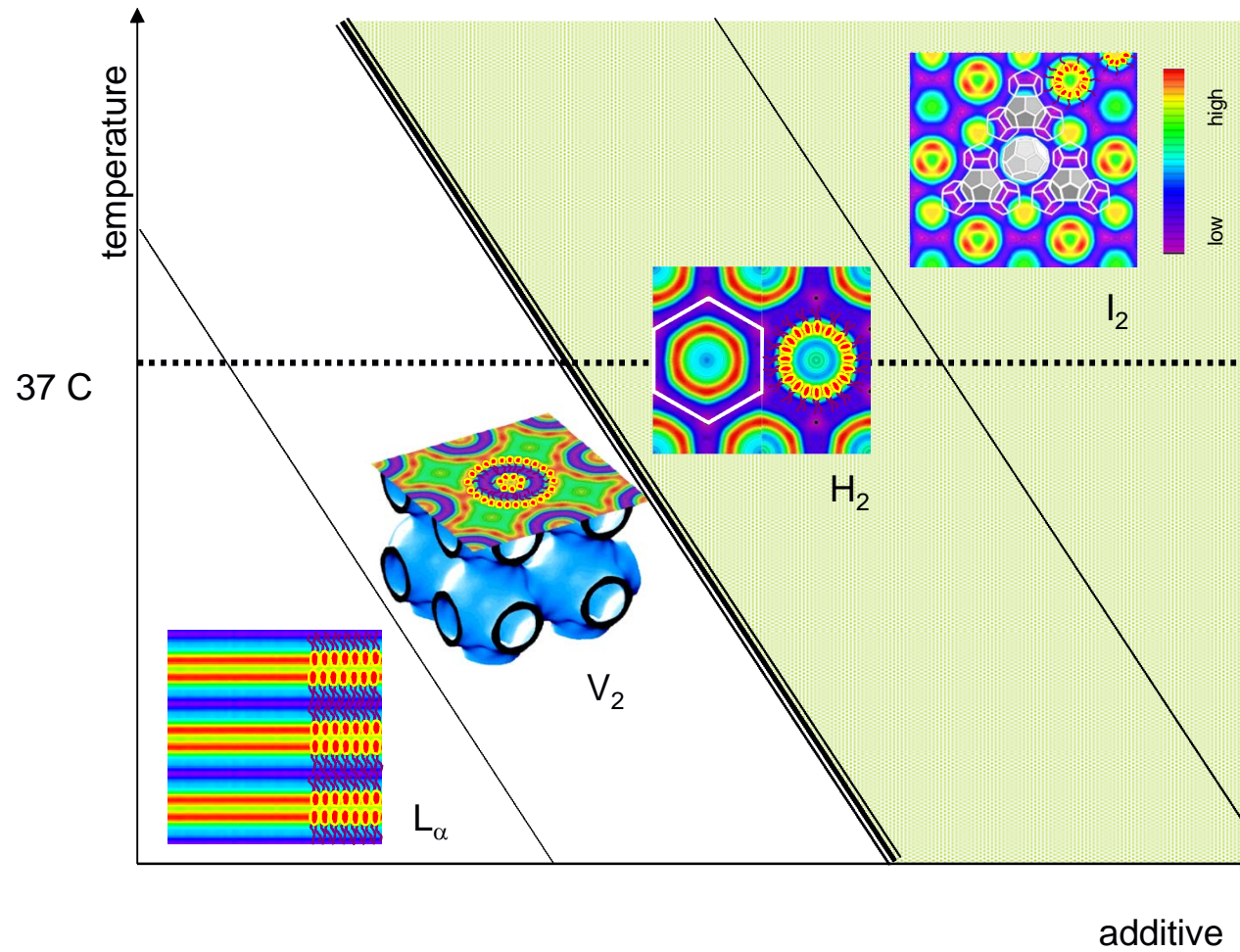
A. Yaghmur and M. Rappolt: Recent Advances in the Characterization of Lipid-Based Nanocarriers. In:Nano-architectures for solubilization and delivery in food, cosmetic and pharma applications" (eds. Nissim Garti & Idit Yuli-Amar), in press
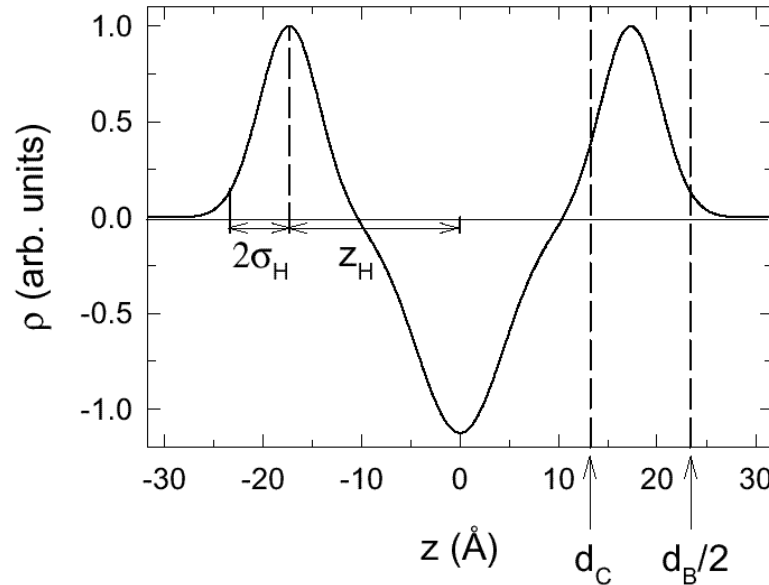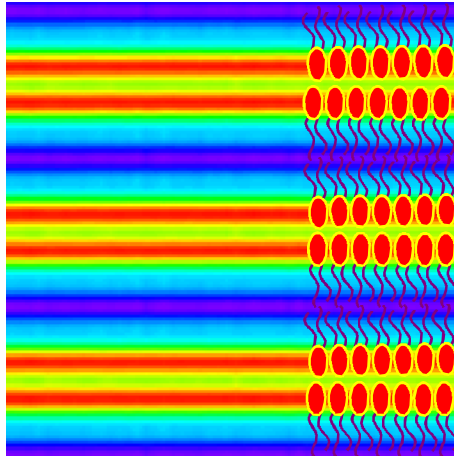
Polymorphism

❖ Lamellar Phases

❖ Bicontinuous Cubic Phases

❖ Tubellar Phases

❖ Micellar Phases

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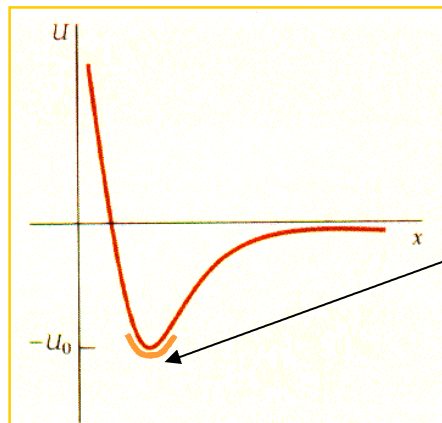
The Lamellar Phase

$d_B = 2 (z_H + 2\sigma_H)$
$d_W = d - d_B$
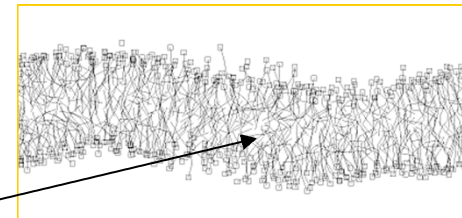
$d_C = d_B/2 - d_H$
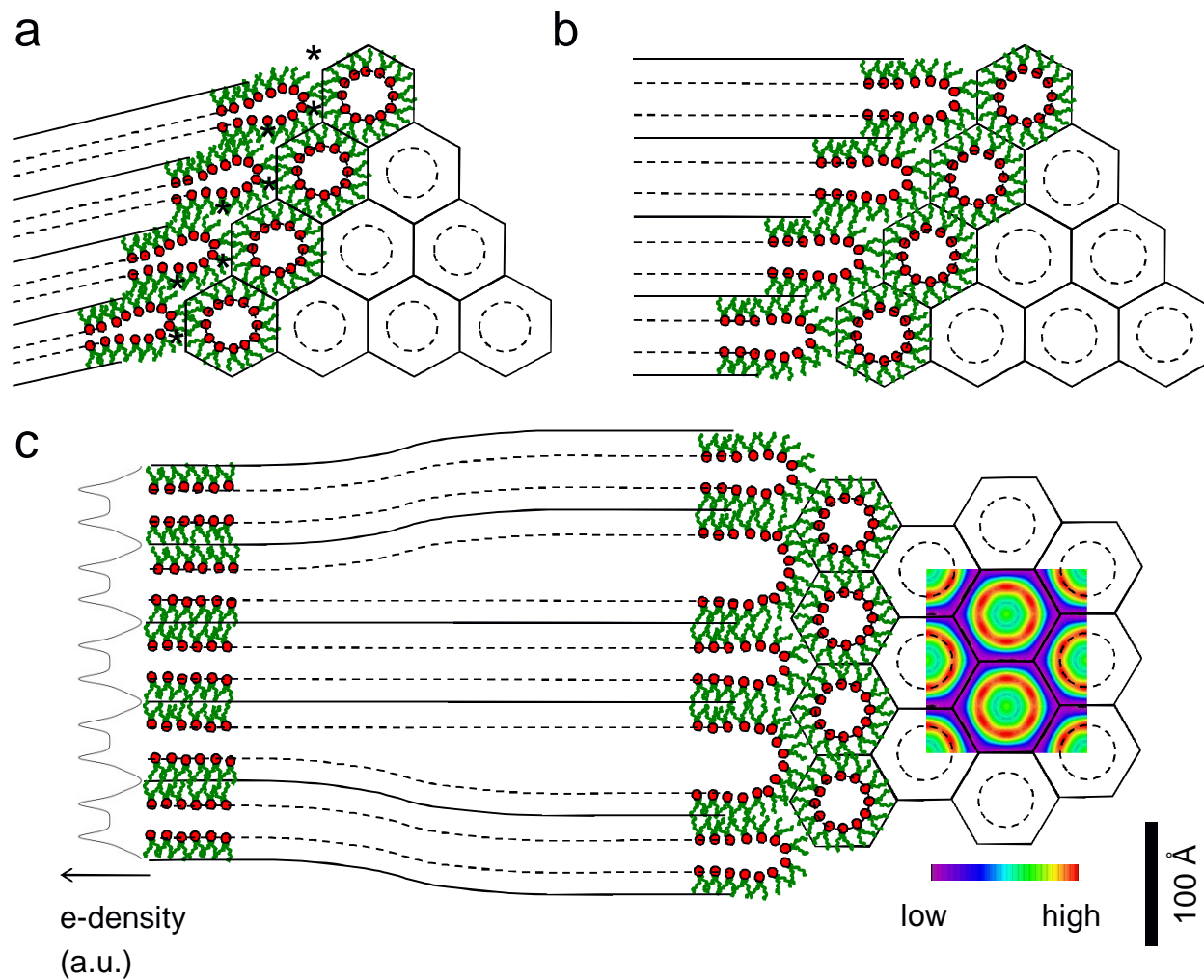$d_C = z_H - 4.1 \text{ Å}$

$A = (V_L + V_H)/d_C$
Geometrical method

$\eta \propto 1/\sqrt{(B\, K_c)}$

B: bulk compression modulus
K_c: bilayer bending modulus
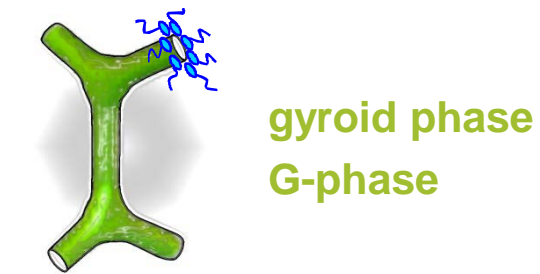
The Hexagonal Phase Formation

a

b

c

e-density
(a.u.)

low   high

100 Å

M. Rappolt et al., *Biophys. J.* 84 **2003 (a)**

A. Yaghmur, L. Paasonen, M. Yliperttula, A. Urtti, and M. Rappolt *J. Phys. Chem. Lett.*1 **2010 (b,c)**
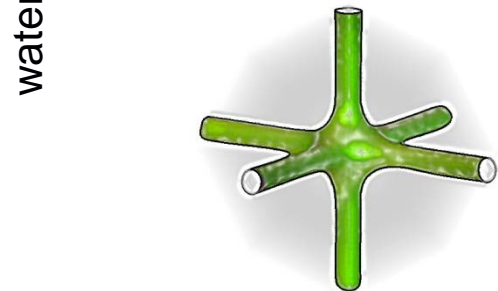
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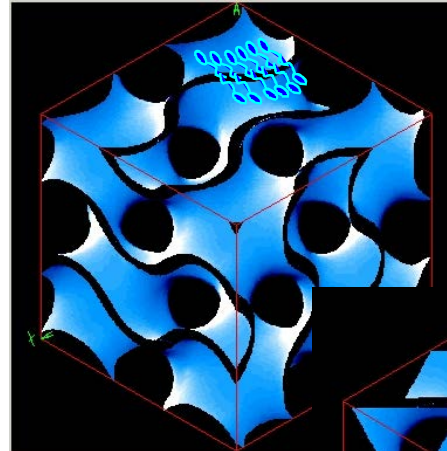# Density Maps of 3D Cubic Liquid Crystals

gyroid phase
G-phase

diamond phase
D-phase
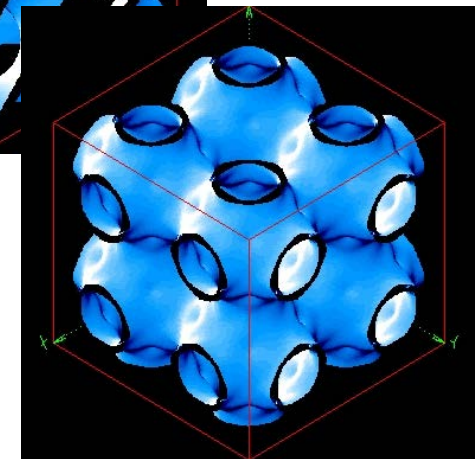
primitive phase
P-phase

water channel network

the bilayer mid-plane
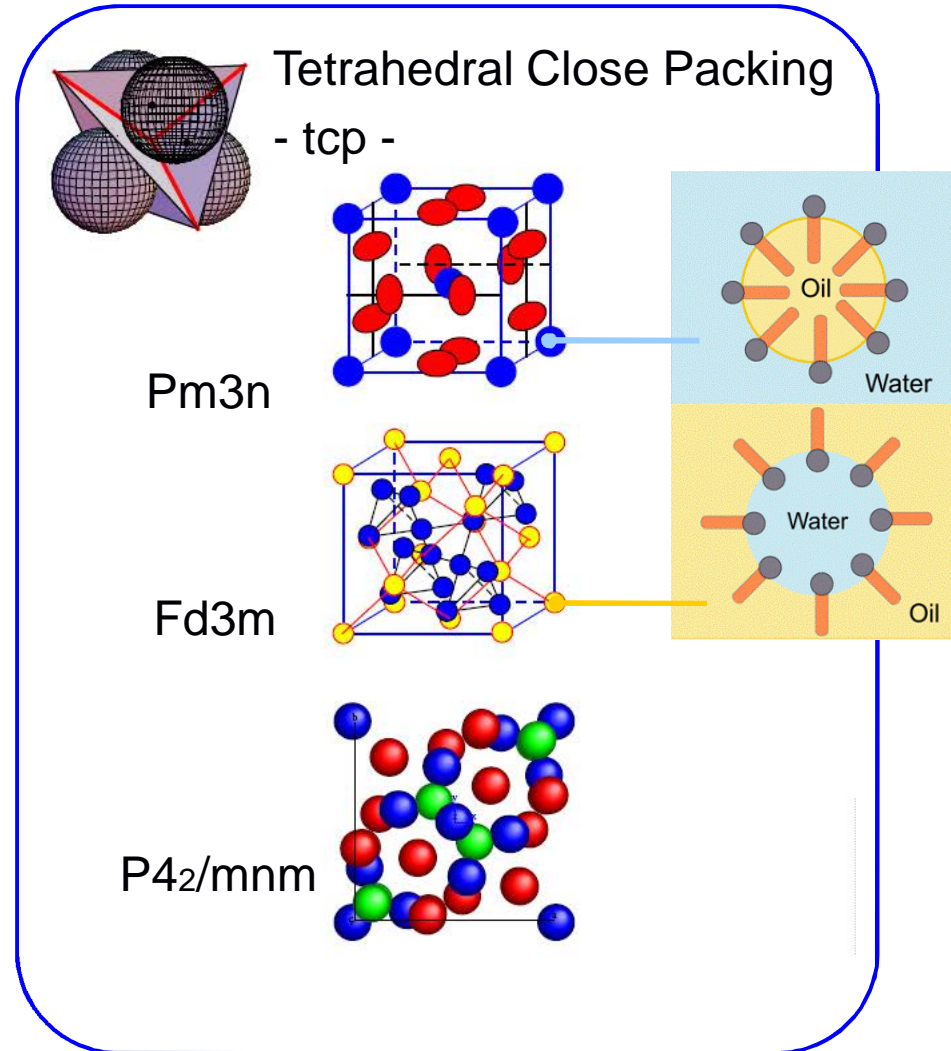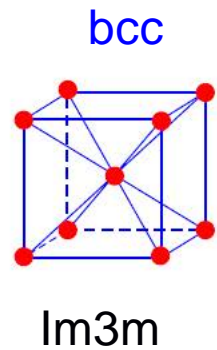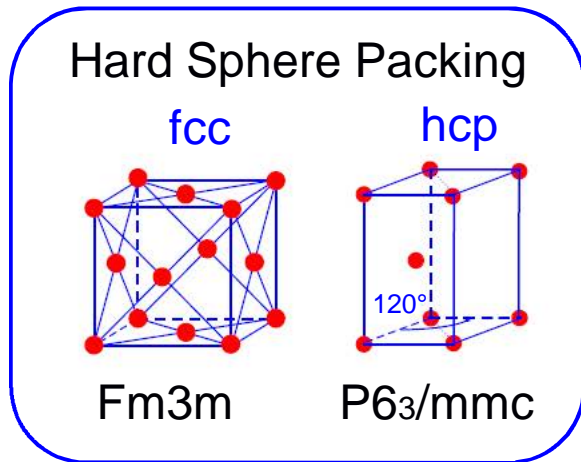
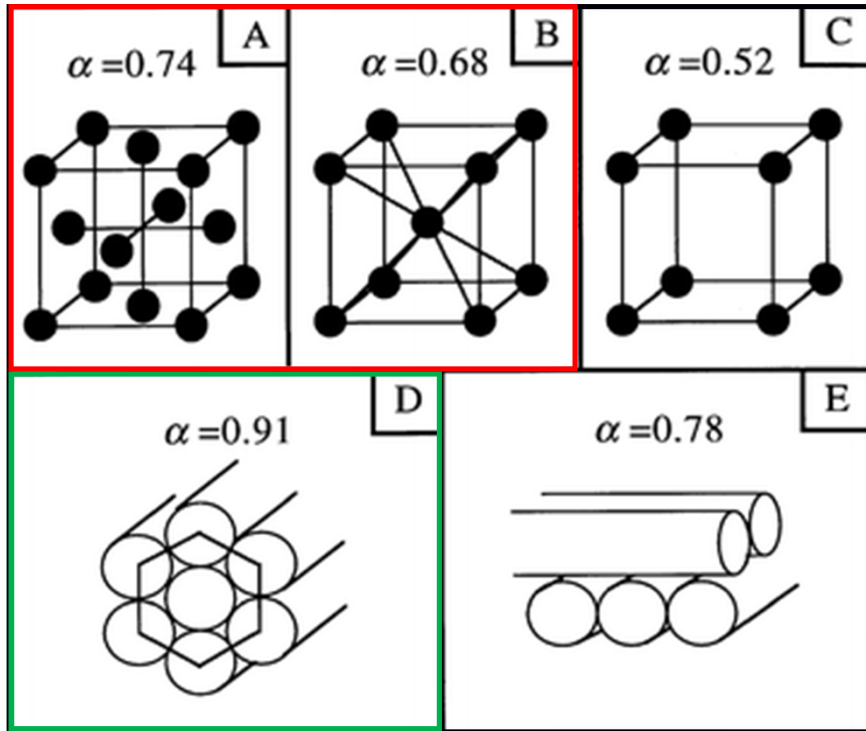# Overview on Micellar Phases

Hard Sphere Packing

fcc   hcp

120°

Fm3m   P6$_3$/mmc

bcc

Im3m

Tetrahedral Close Packing
- tcp -
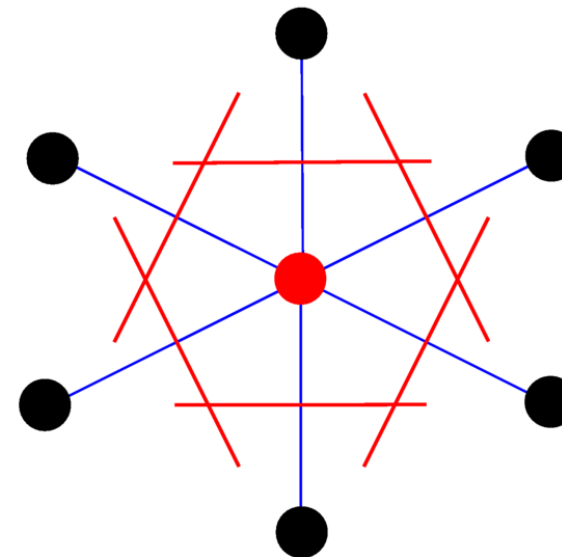
Pm3n

Fd3m

P4$_2$/mnm

Oil

Water

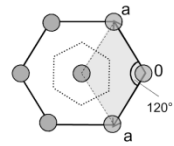Water

Oil

Packing Fraction & Wigner Seitz Cell

A: fcc, B: bcc , C: primitive cubic

Nature does not like loose packing!

Space Filling Polyhedron

A
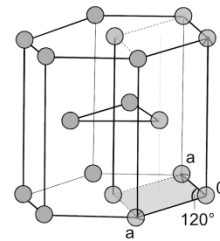
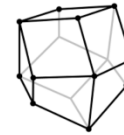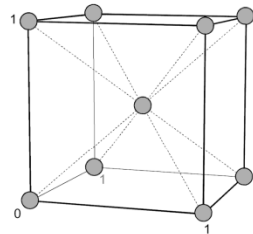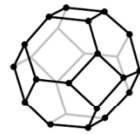p6m (2D-hcp)

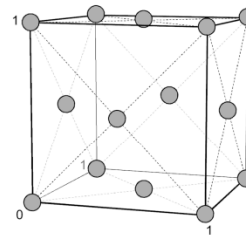Hexagon

B

P6₃/mmc (3D-hcp)

Trapezoid-
rhombic
dodecahedron

C

I_m3m (bcc)

Truncated
octahedron

D

F_m3m (fcc)

Rhombic
dodecahedron

E
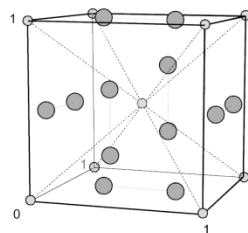
P_m3n
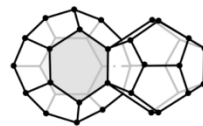
5¹²6² & 5¹²
cages

F

F_d3m

5¹² & 5¹²6⁴
cages
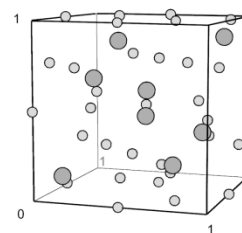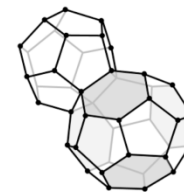
Yaghmur & Rappolt, AdvPLBL, 2013 in press

Further Packing Examples: C12EO12

bcc

fcc

- tcp -
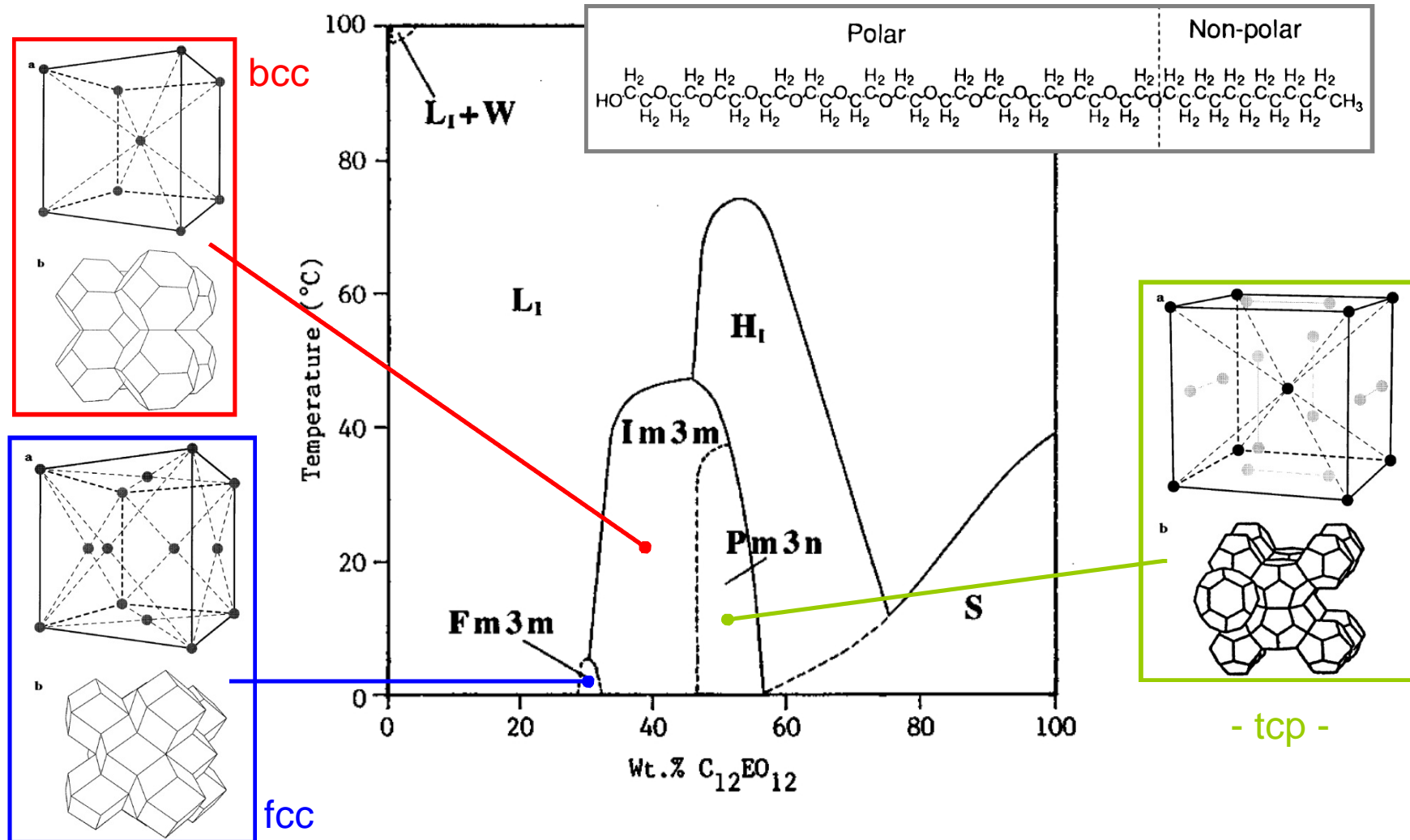
P. Sakya, J. M. Seddon, R. H. Templer, R. J. Mirkin, and G. J. T. Tiddy. Micellar Cubic Phases and Their Structural Relationships: The Nonionic Surfactant System C12EO12/Water. Langmuir 13, 3706-3714 (**1997**)

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The Fd3m Phase: Packing of „Mandarins & Oranges"
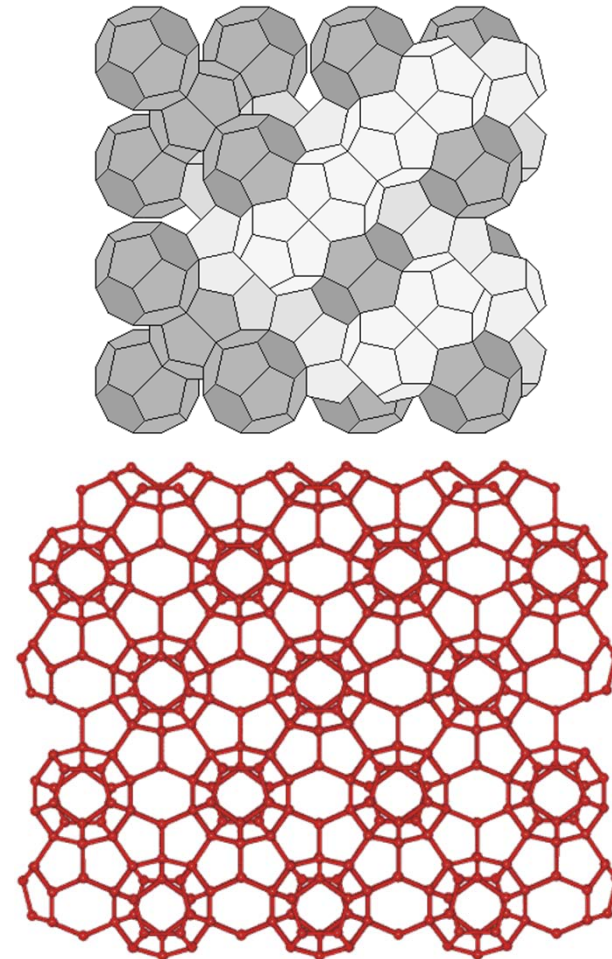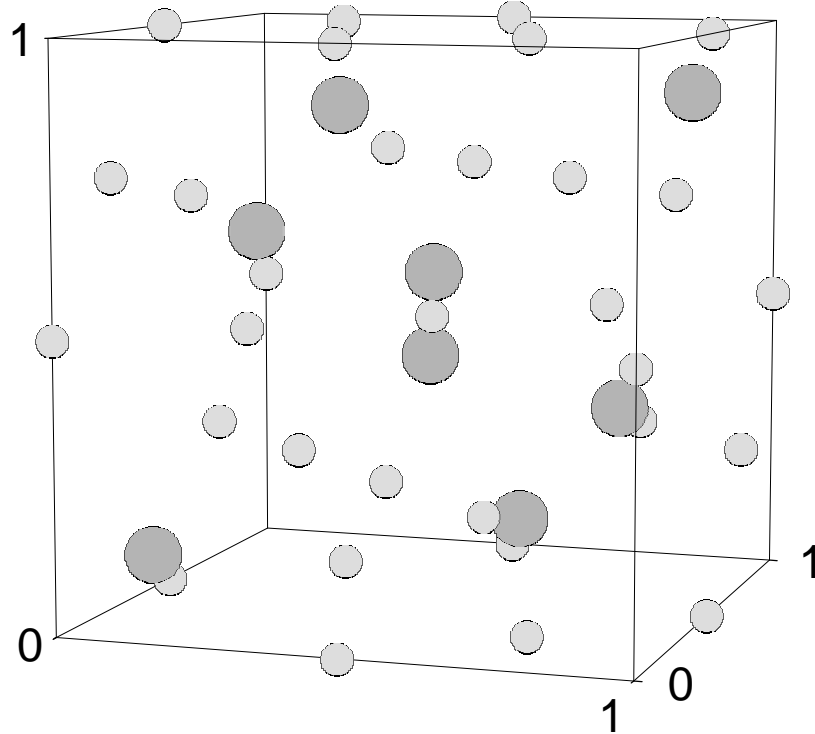
Another tcp - packing:

- sixteen 5^{12} (dodecaeder): Mandarins
- and eight $5^{12}6^4$ cages: Oranges

Prominent example: clathrate II water

H. Delacroix, T. Gulik-Krzywicky and J.M. Seddon. J. Mol. Biol. 258:88-103 (**1996**)

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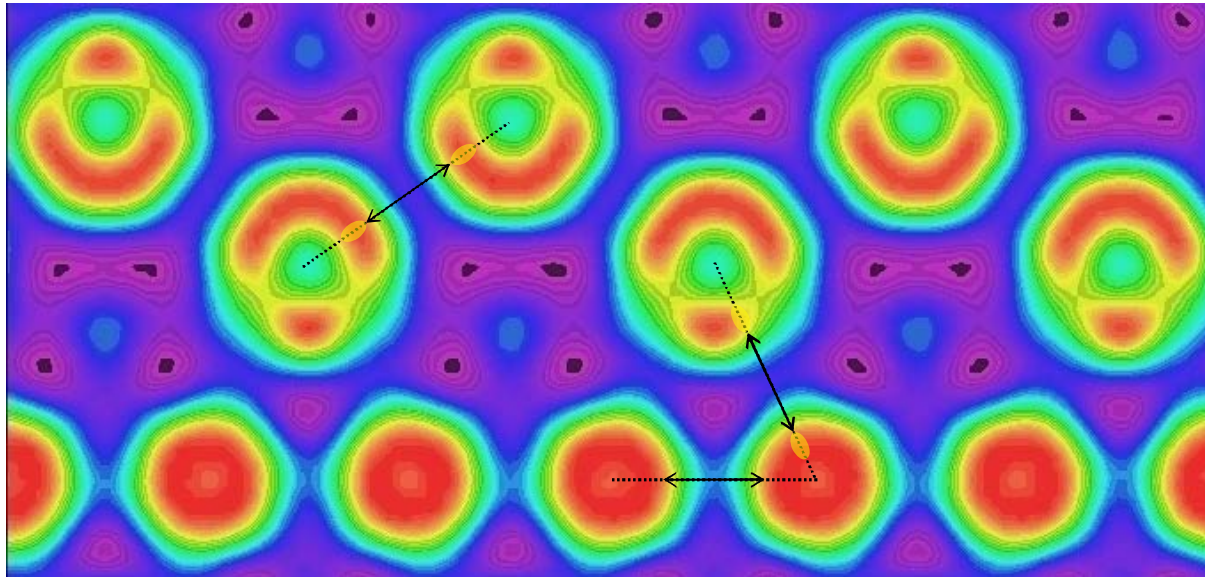# Micellar Shape and Lipid Chain Configuration

MO/OA

Monoolein (MO)
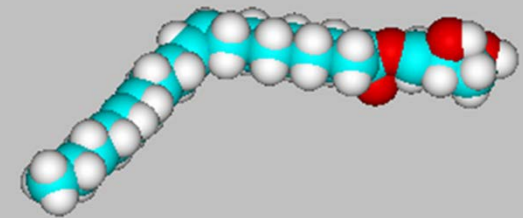
Monoelaidin (ME)

ME/EA

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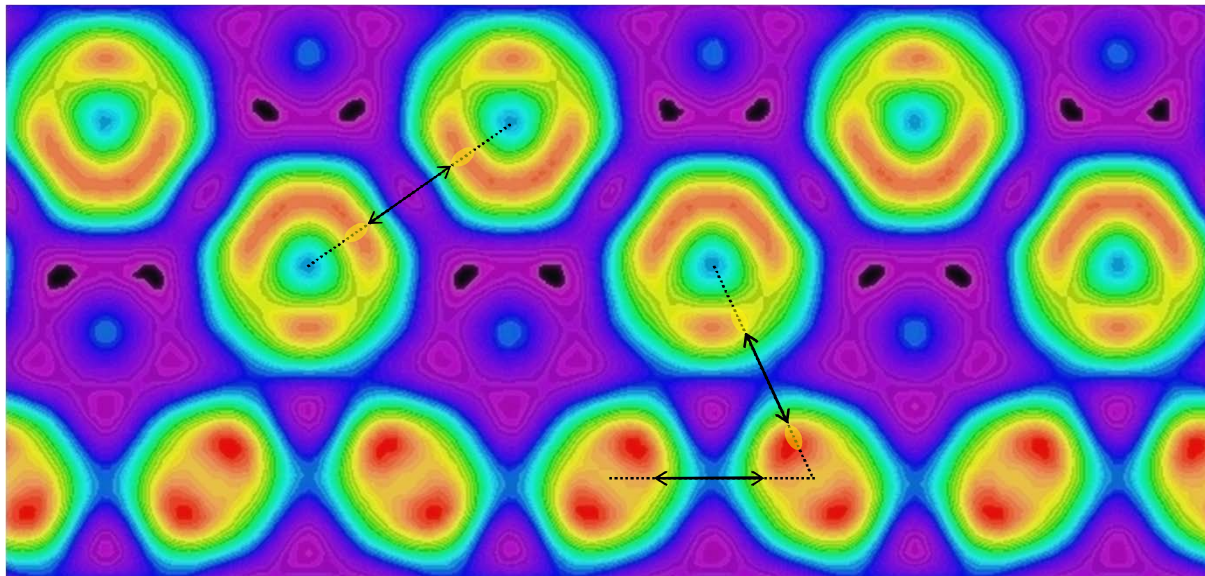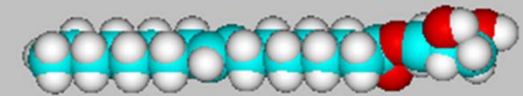
Shape of the Big Micelle

low high

A

B

-110   11-2

111
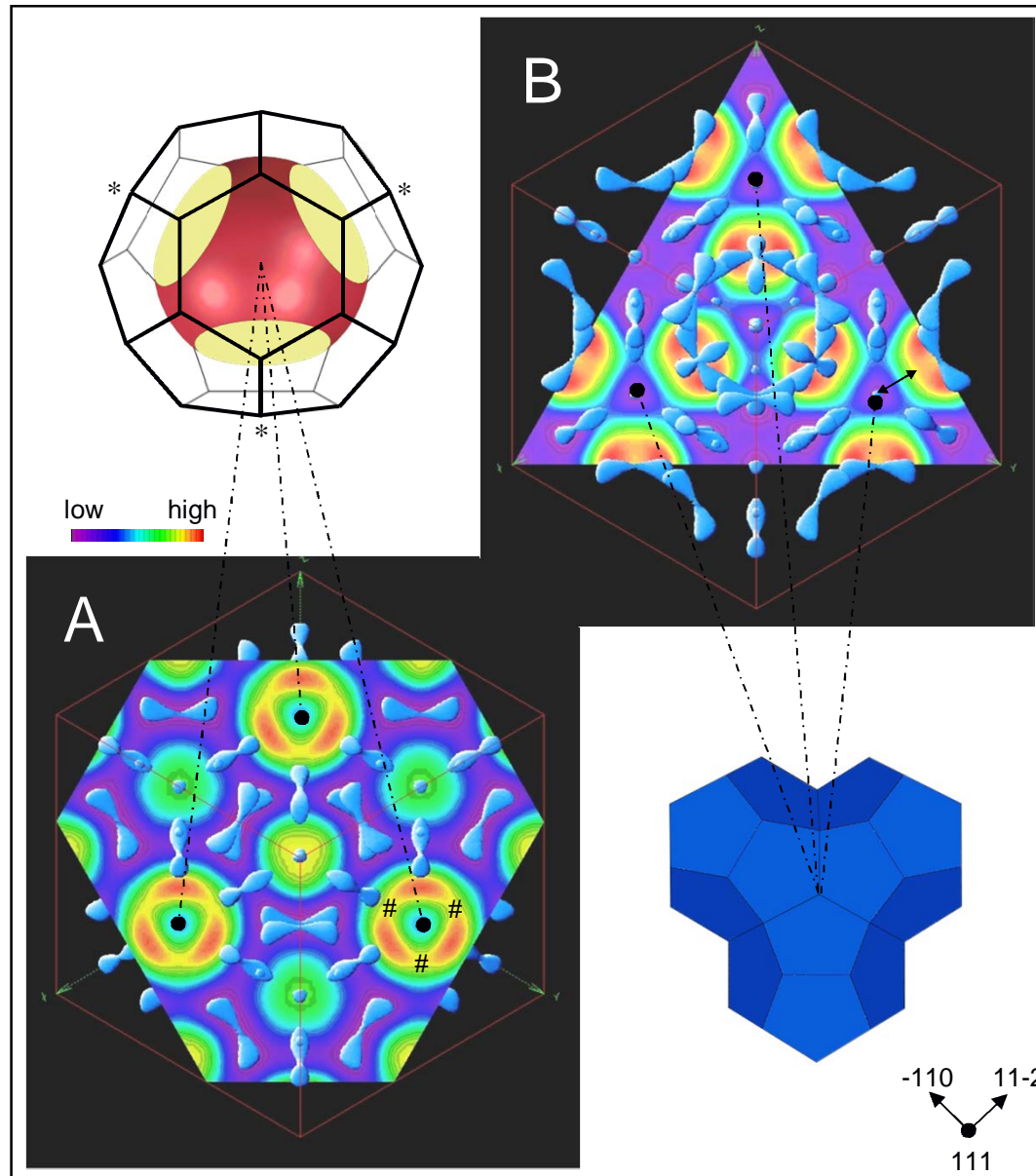
Rappolt et al., Soft Matter, 2013

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The Role of *Trans* Fatty Acids
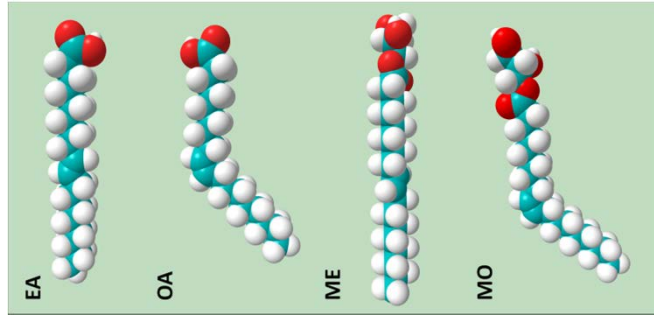
Yaghmur, A., Sartori, B., and Rappolt, M. (2012): Self-Assembled Nanostructures of Fully Hydrated Monoelaidin-Elaidic Acid and Monoelaidin-Oleic Acid Systems. Langmuir 28: 10105-10119.

Thank You!
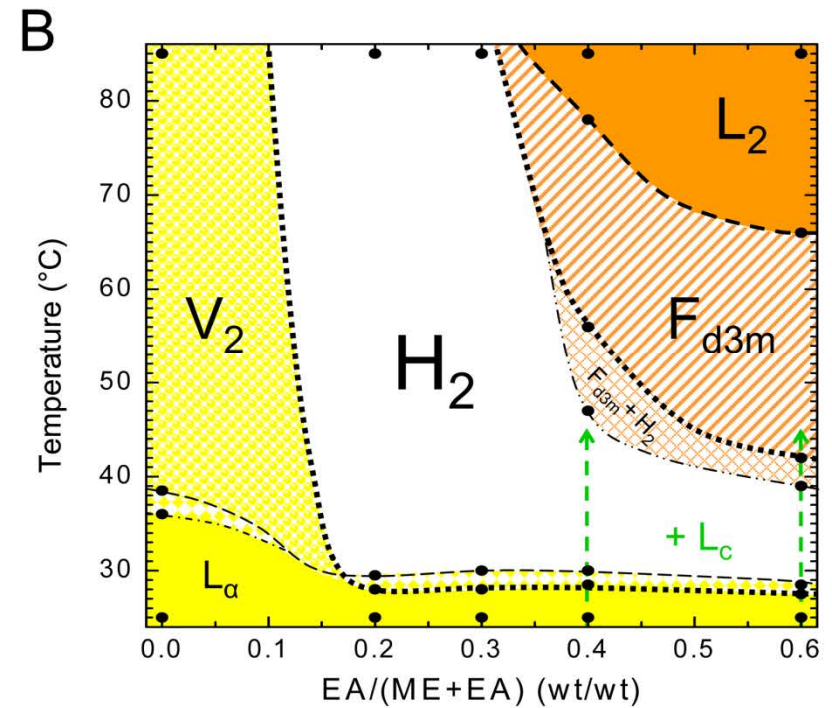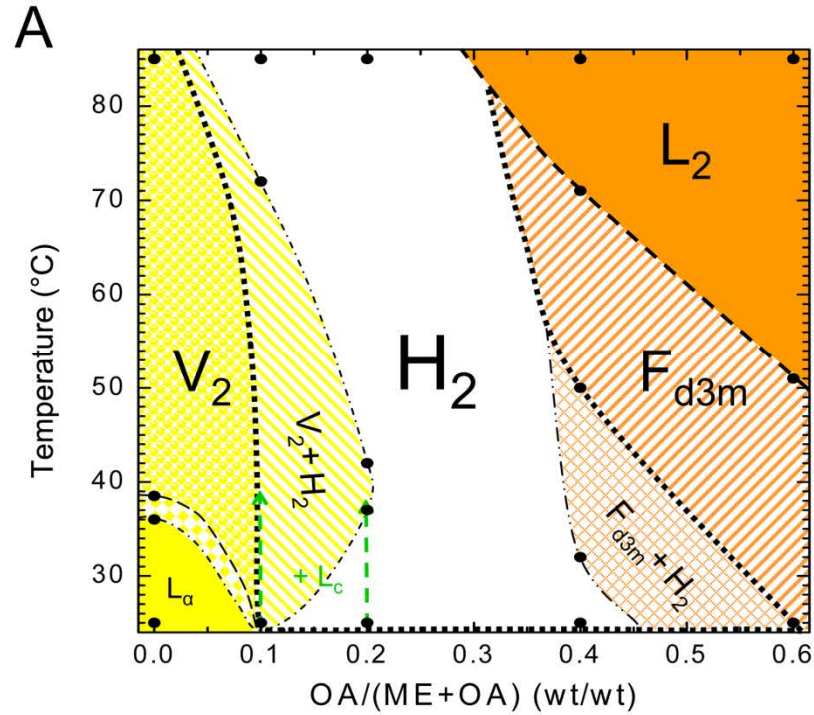
My special thanks go to:

*Water ballet explaining
a normal micelle ...*

Heinz Amenitsch*, Barbara Sartori*, Karl
Lohner, Georg Pabst and Peter Laggner

Austrian Academy of Sciences, IBN, Graz, Austria

*working at the Austrian SAXS Beamline Trieste

Anan Yaghmur

*Faculty of Pharmaceutical Sciences, University of
Copenhagen, Denmark*

Mike Morgan and Malcolm Povey

*School of Food Science & Nutrition, University of
Leeds, UK*

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