

The background is an impressionistic painting of a mountain peak. The peak is dark and textured, with visible brushstrokes in shades of brown, black, and grey. The sky and surrounding landscape are rendered in soft, blended colors of yellow, orange, and blue, creating a hazy, atmospheric effect. The overall style is reminiscent of Impressionist art, emphasizing light and color over sharp lines and detail.

# Structure is the ultimate expression of the complexity of lipids: an impressionistic approach

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Department of Food Science

University of Guelph

Kaufmann Memorial Lecture, Rosario, Argentina, Nov. 2015

# *Thesis*

*Structure is the result of the interaction between molecular structure and external fields.*

*Macroscopic functionality is defined by this structure.*

# Lipid Structures discussed

- Fats and oils
- Oleogels
  - Self-assembled fibrillar networks
  - Polymer oleogels (ethylcellulose)
- Inverted Structured Emulsions



# What is fat?



## *To the chemist and chemical engineer:*

- a complex mixture of high melting point triacylglycerols in low melting point triacylglycerols with complex phase behavior – all can be explained from knowledge of molecular composition and phase behavior (SFC and phase diagrams are king...)

## *To the crystallographer:*

- a metastable polycrystalline material prone to recrystallization and fractionation – all can be explained from knowledge of polymorphism (XRD is king and DSC is queen...)

## *To the colloidal scientist:*

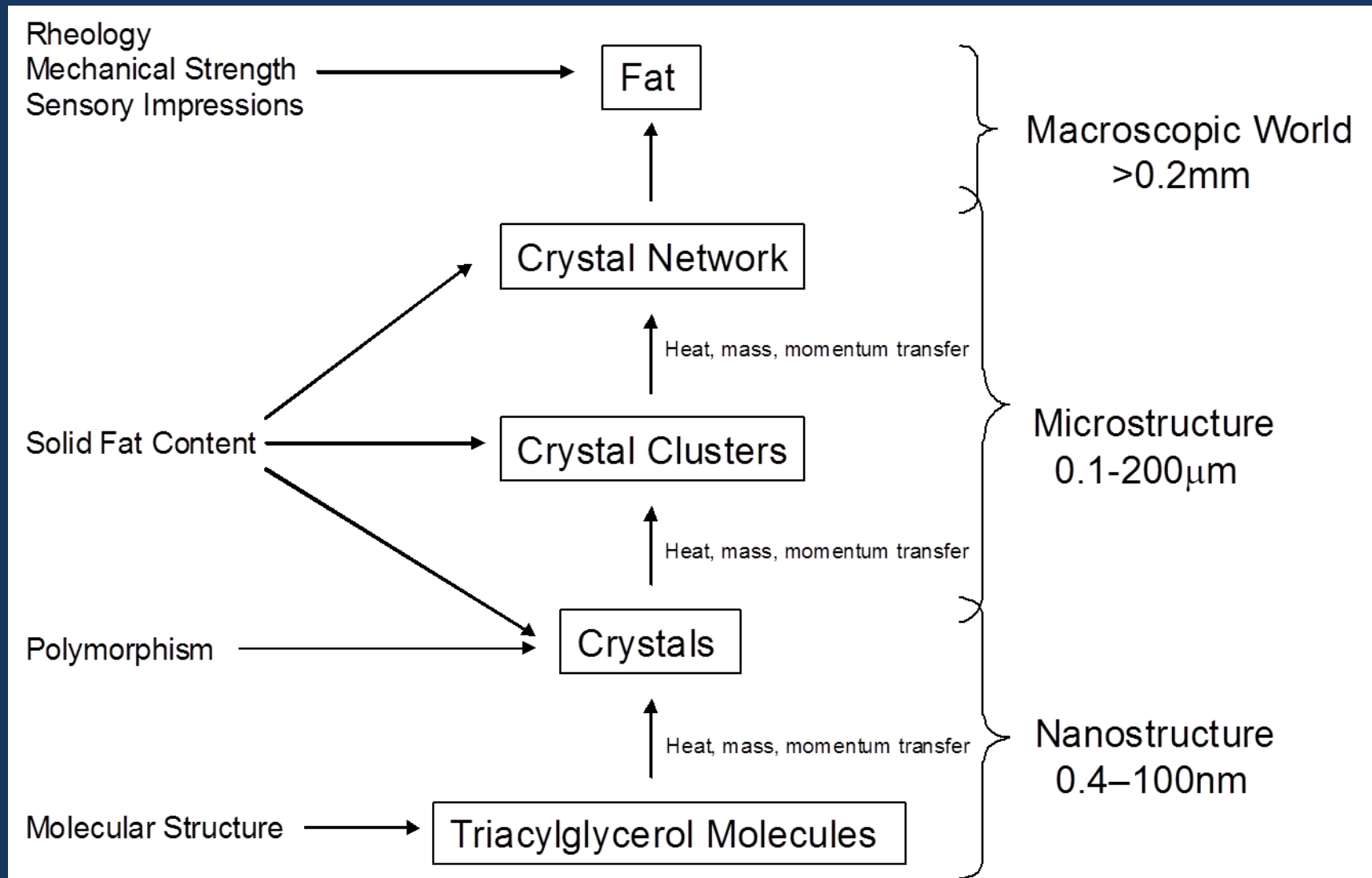
- a colloidal gel (or colloidal crystal) composed of a network of polycrystalline fat particles which trap liquid oil within – all can be explained from knowledge of the mesoscale structure, i.e., colloidal sizes, interactions, distribution (rheometer is king and microscope is queen...)

## *To the consumer:*

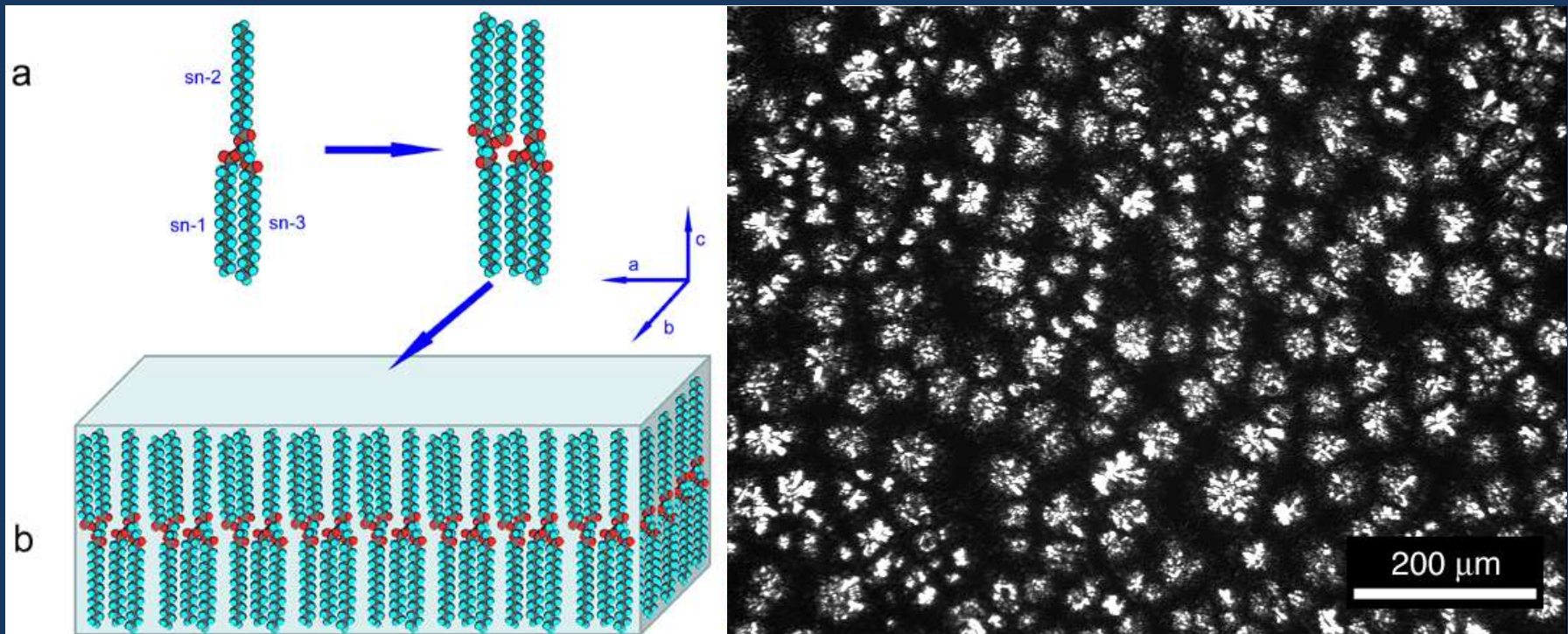
- something that makes you fat, but tastes good (cookies and chocolate rule...)



# Structural Hierarchy



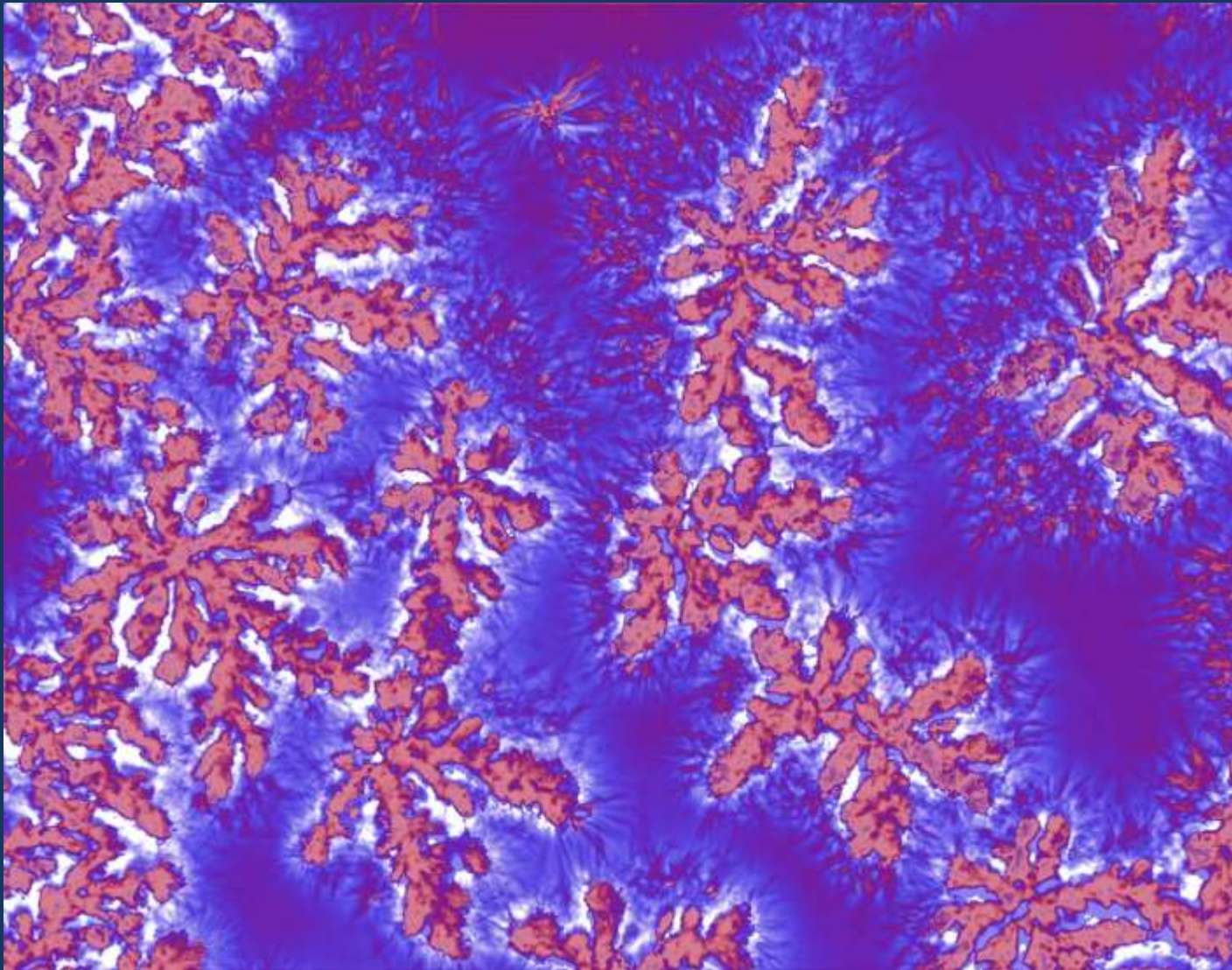
# Molecular and Meso Length Scales



# What is a crystal?

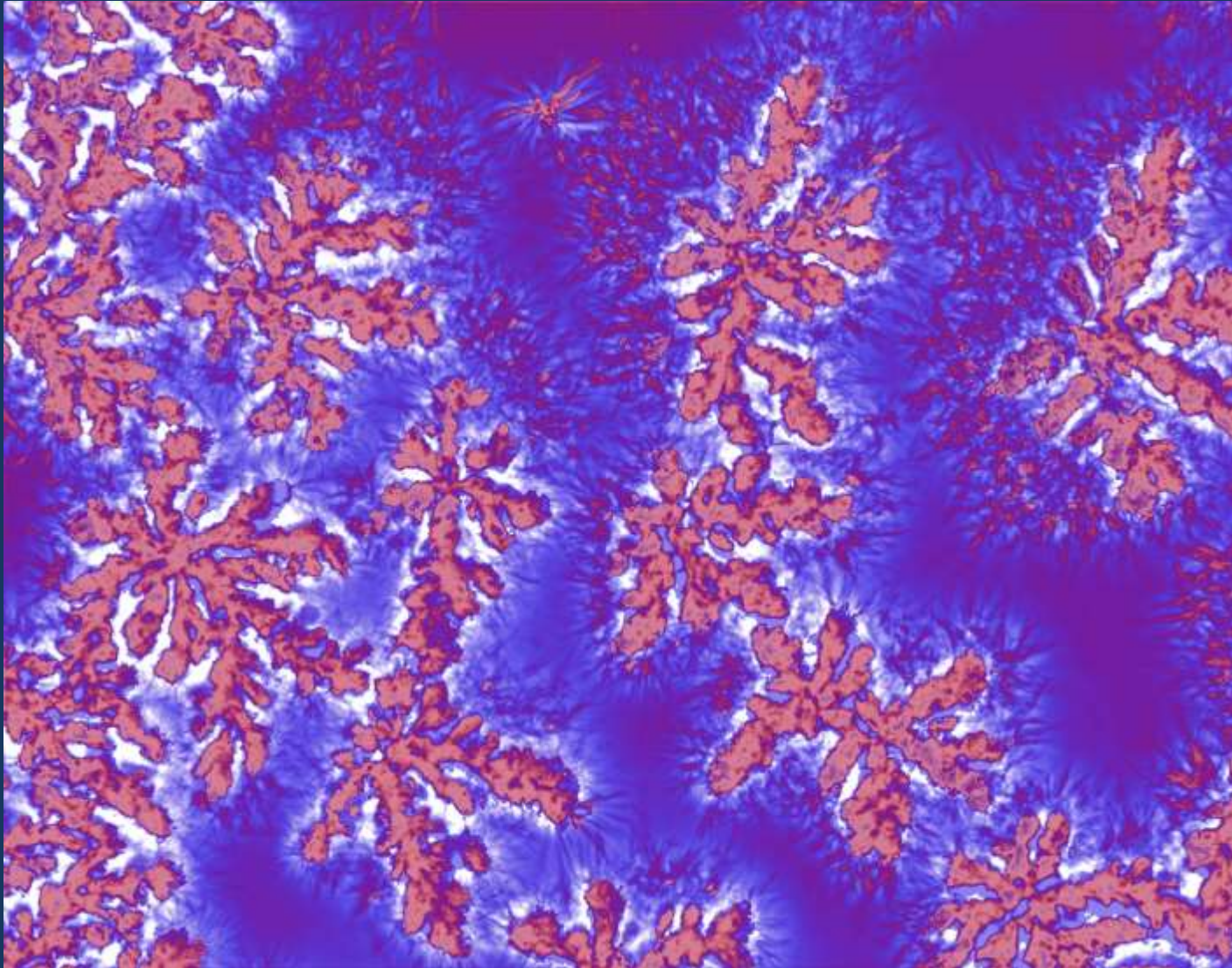




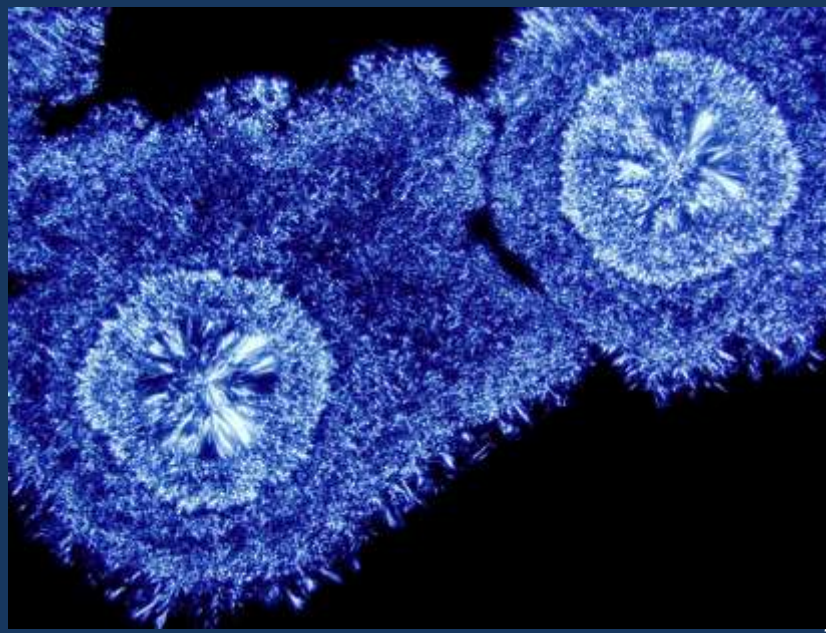
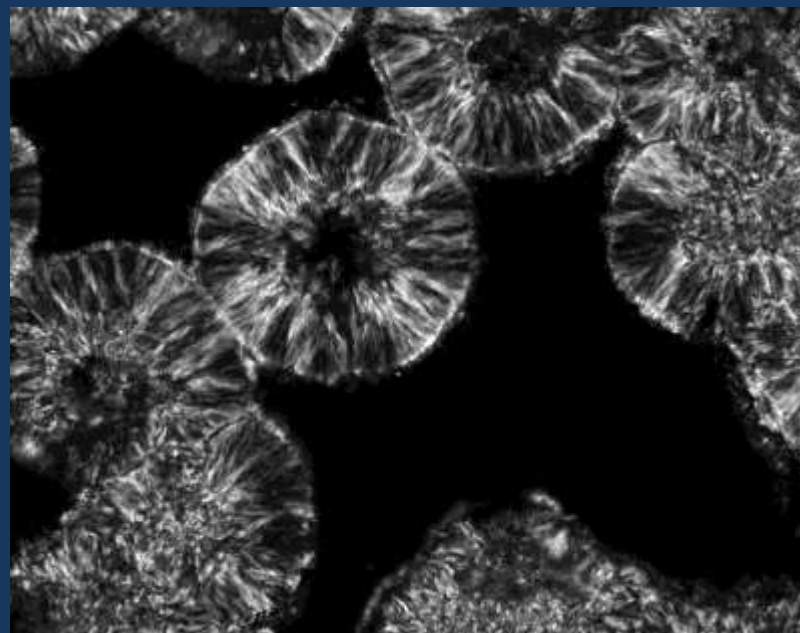
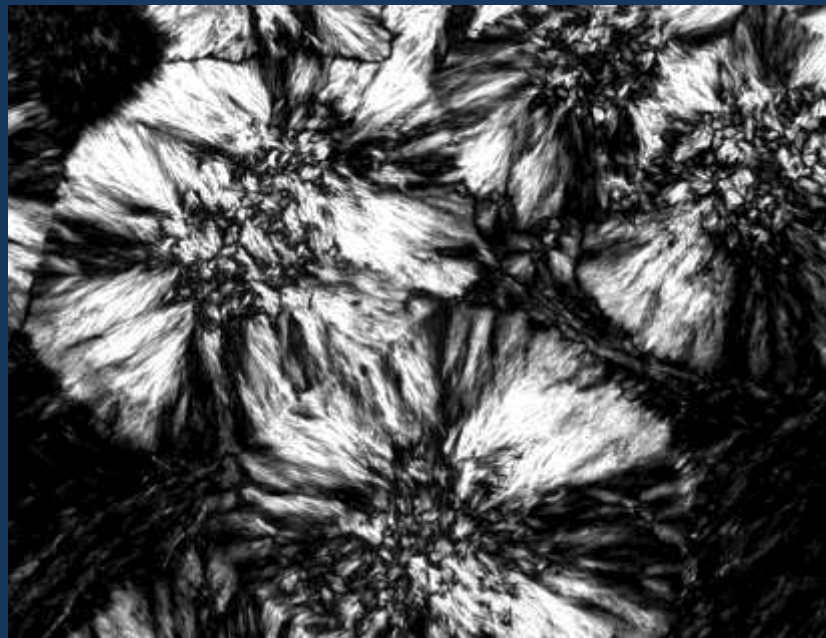
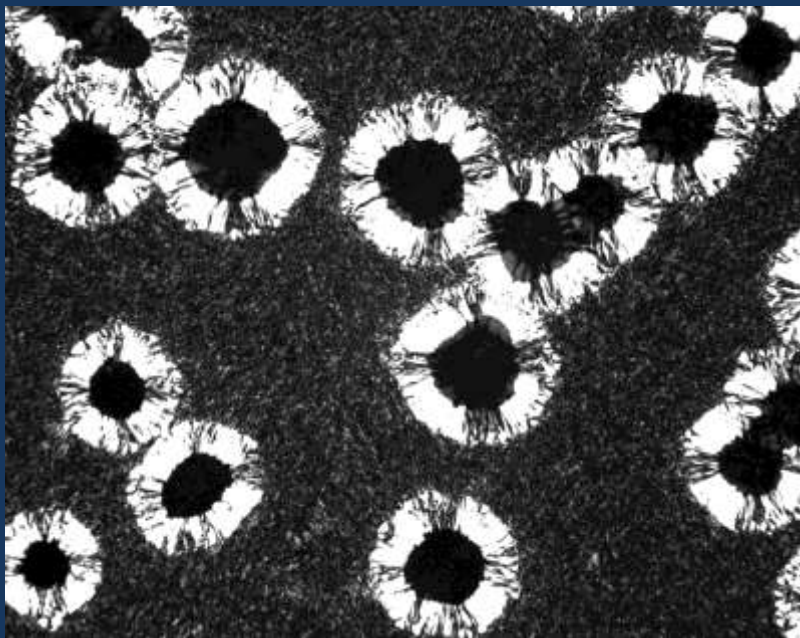




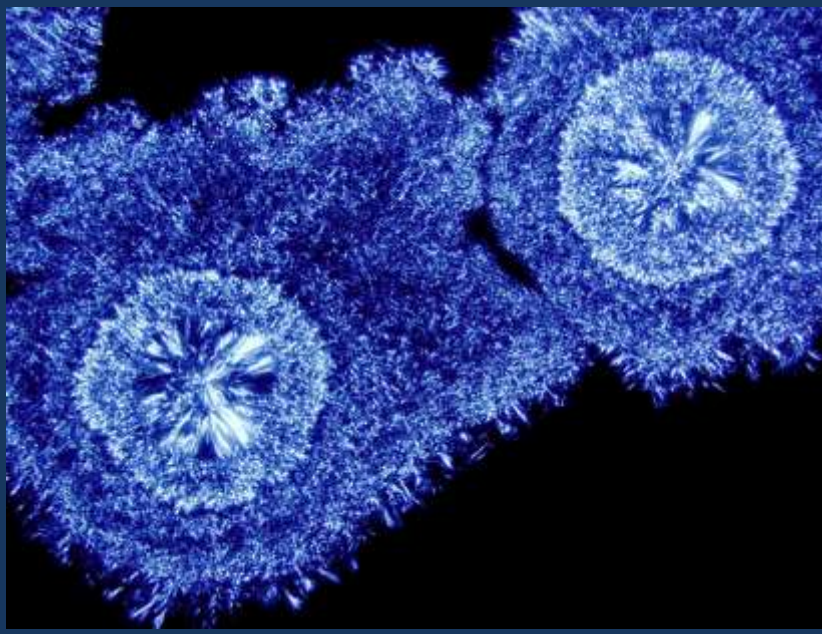
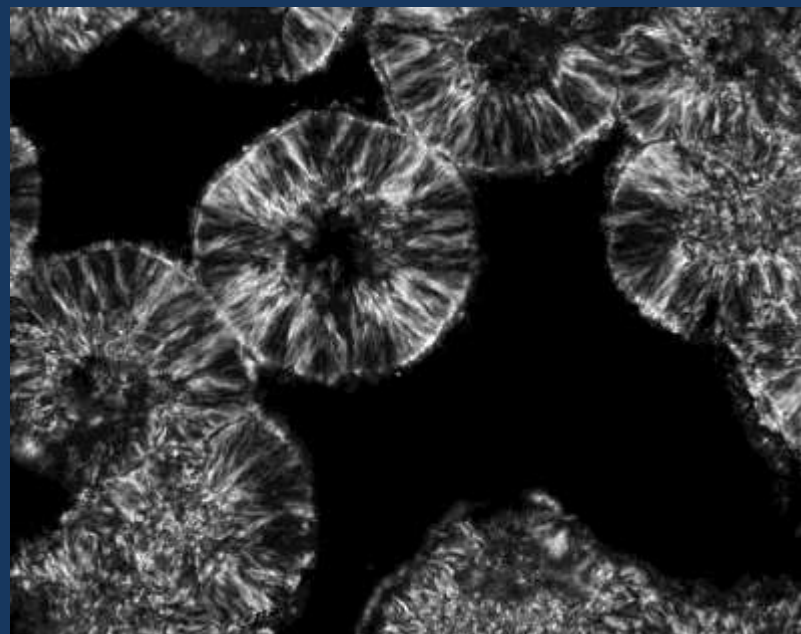
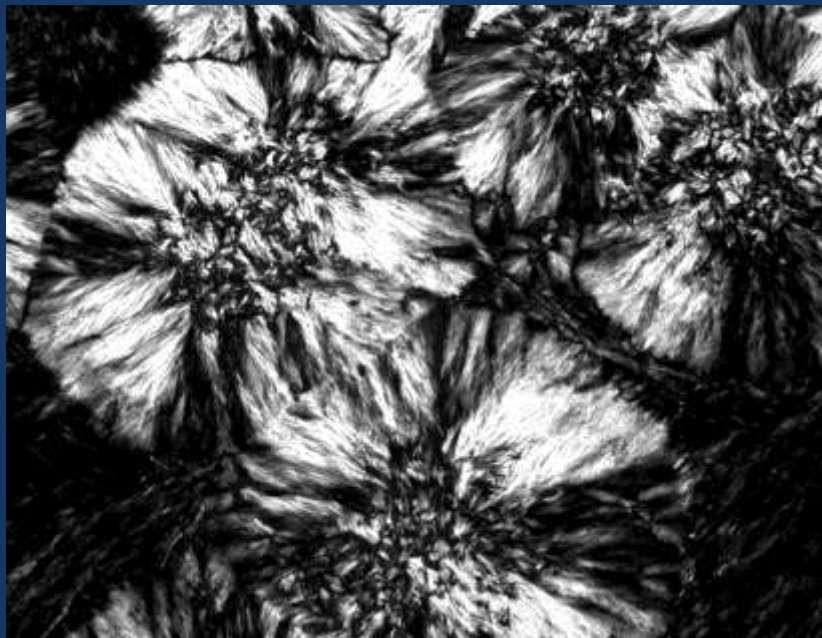
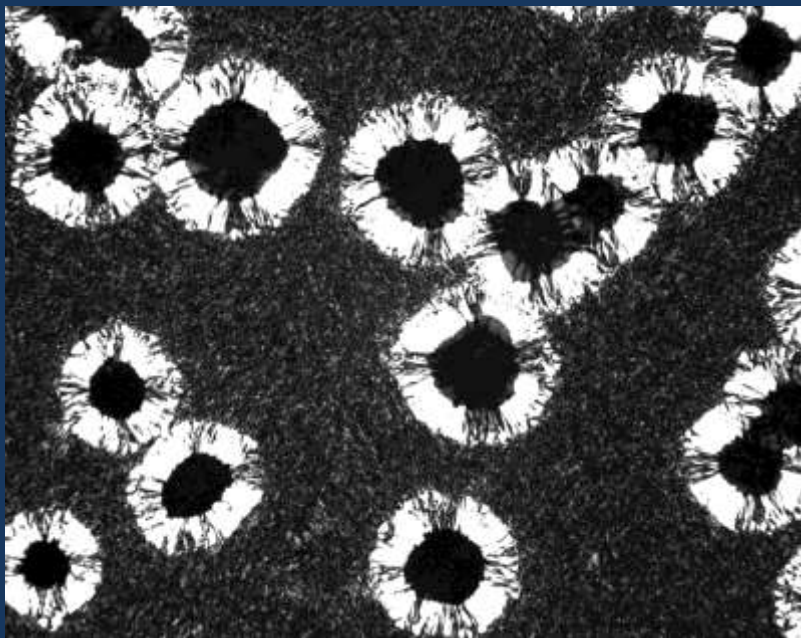
# What is a crystal?











# Early evidence of fat crystal nanostructure

# Jewel and Meara 1970

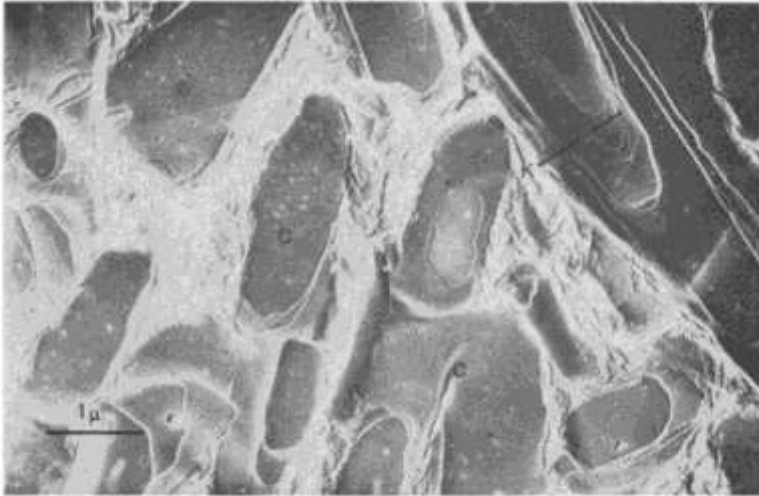


FIG. 9. A replica of a lard which had been treated with 35% aqueous Teepol, then rapidly cooled. Well defined crystals (C) are visible, each crystal being composed of a stack of crystallites (K). (Reduced approximately 45%)

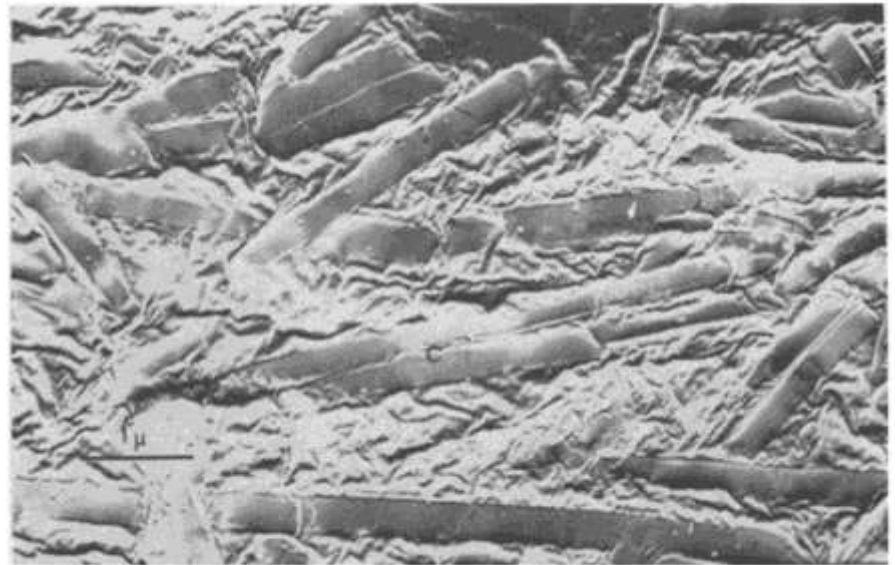


FIG. 4. A replica of a slowly cooled lard. Well defined crystals (C) can be seen. (Reduced approximately 45%)



# Poot et al. 1975

Poot's pimples

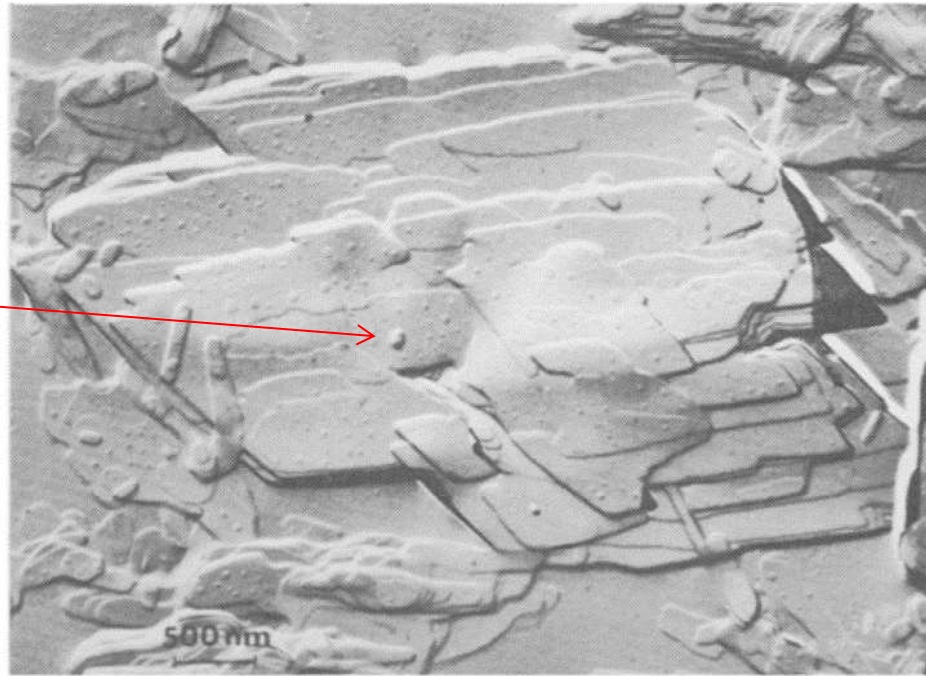
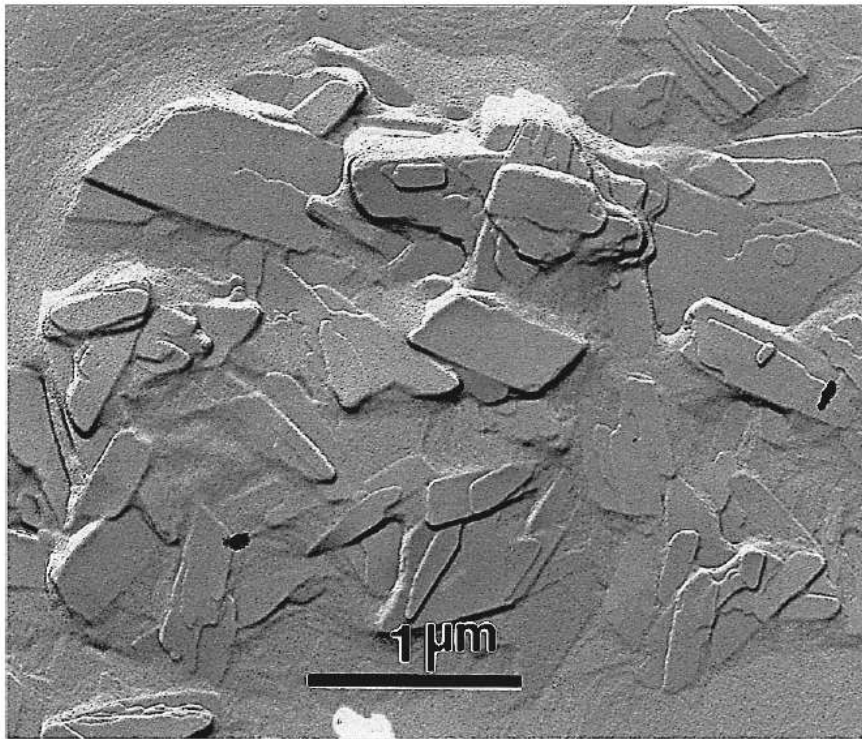


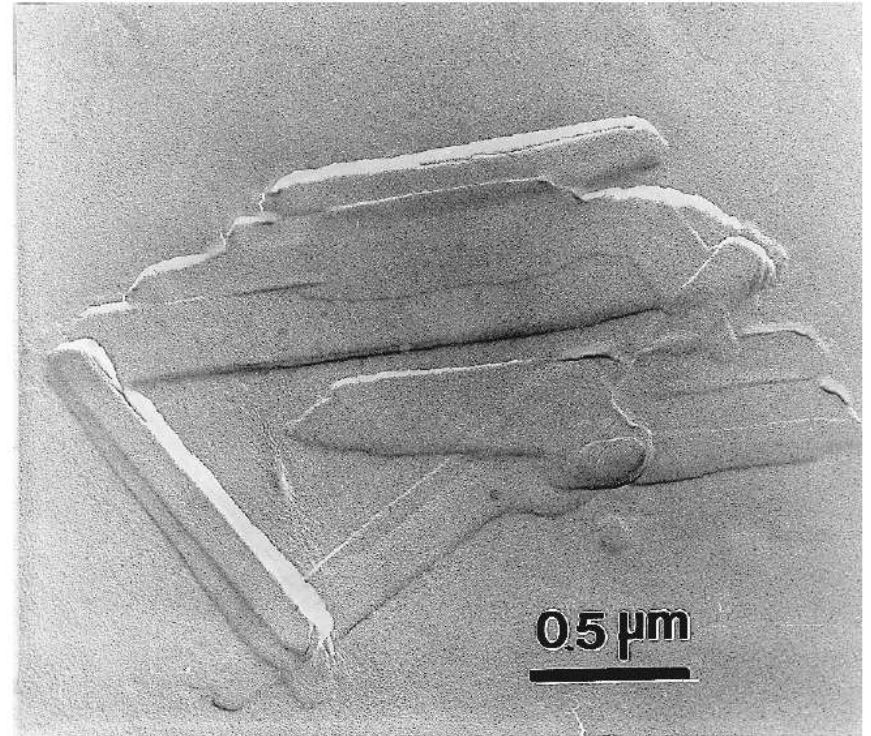
FIG. 7. Large fat crystal ( $\approx 5 \mu\text{m}$ ) from a margarine. The layered structure and "pimples" are easily distinguishable. Magnification used: 30,000.



# Heertje and Leunis, 1997....again

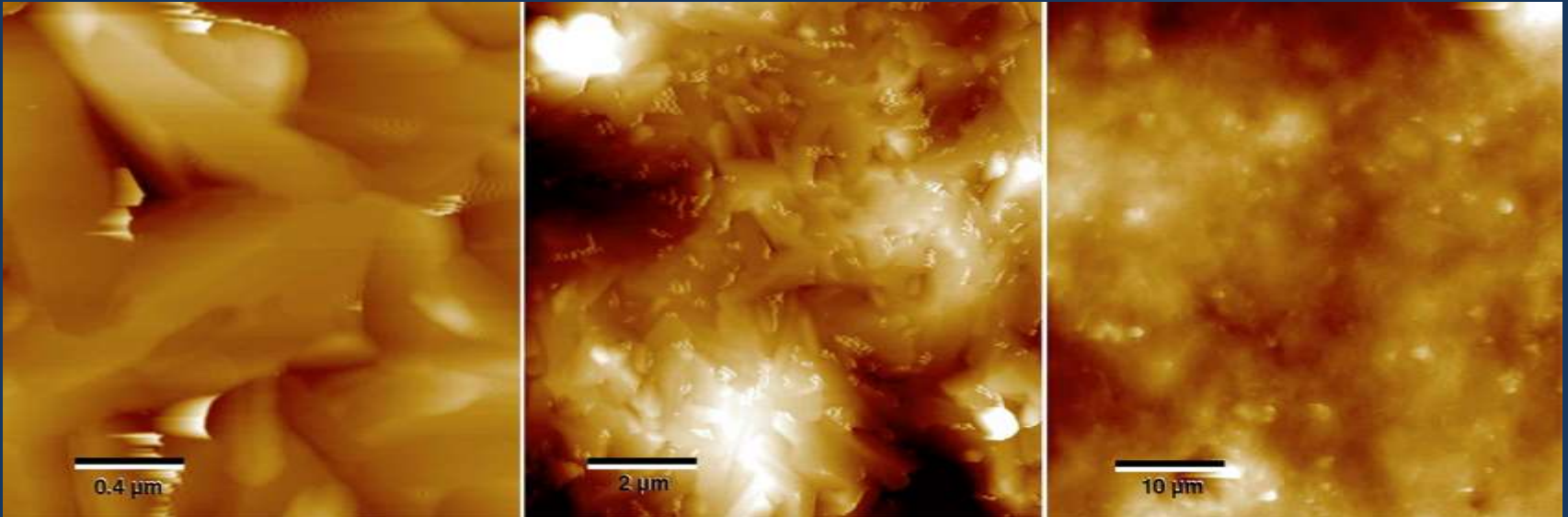


**Fig. 3** Example of the fat crystal habit for a sample cooled to 35 °C; detergent washing technique



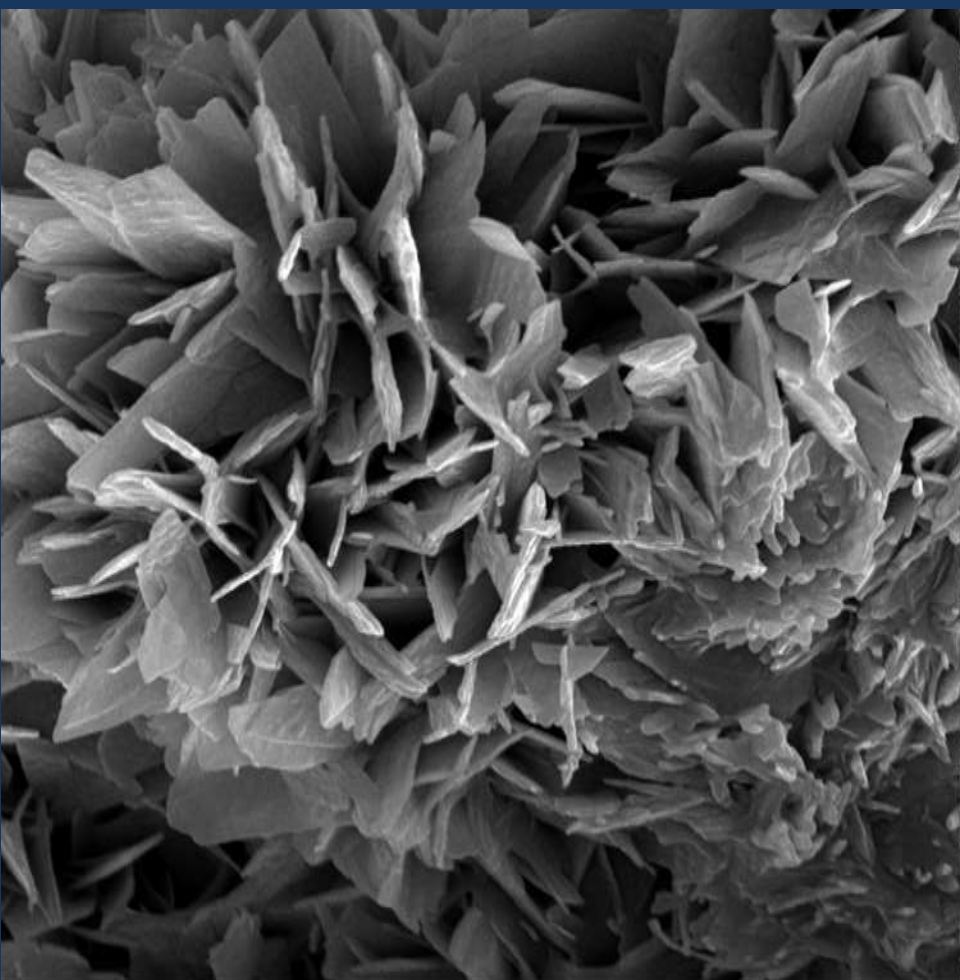
**Fig. 5** Example of the fat crystal habit for a sample cooled to 35 °C; carbon fixation technique

# AFM of cocoa butter

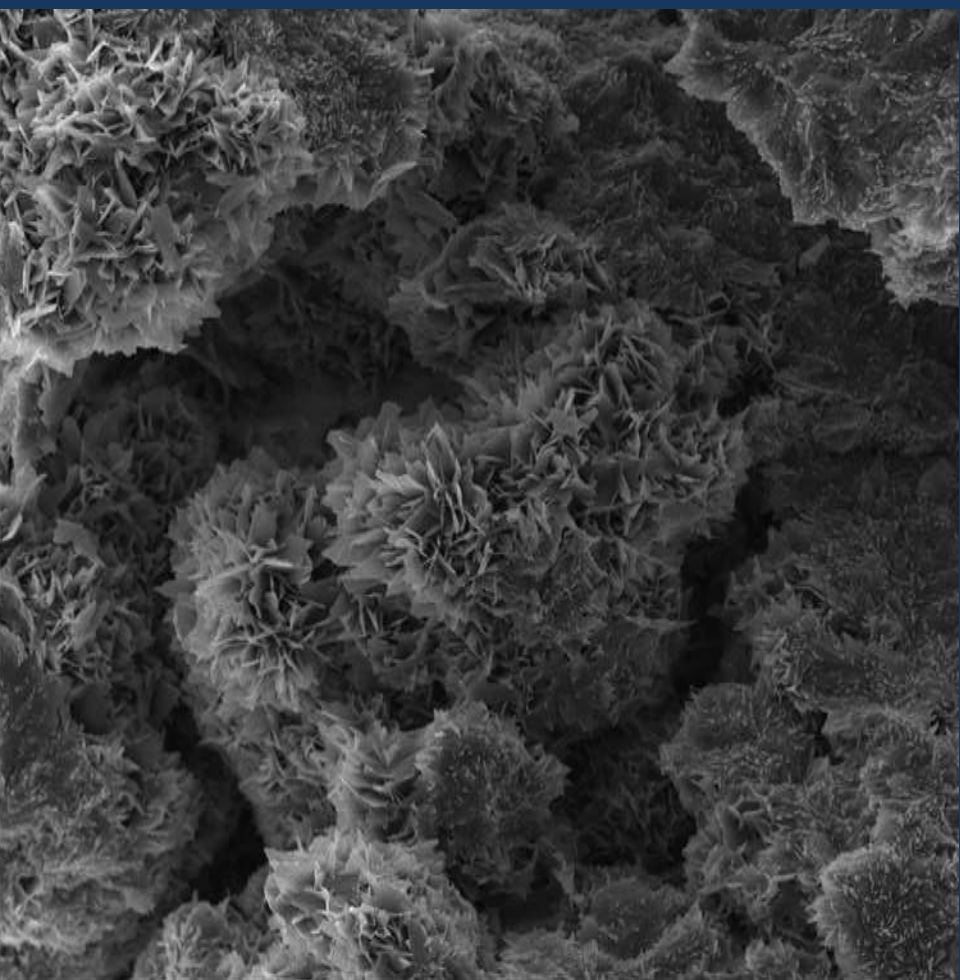


Cocoa butter crystallized at 22degC for 2 years, circa 1999



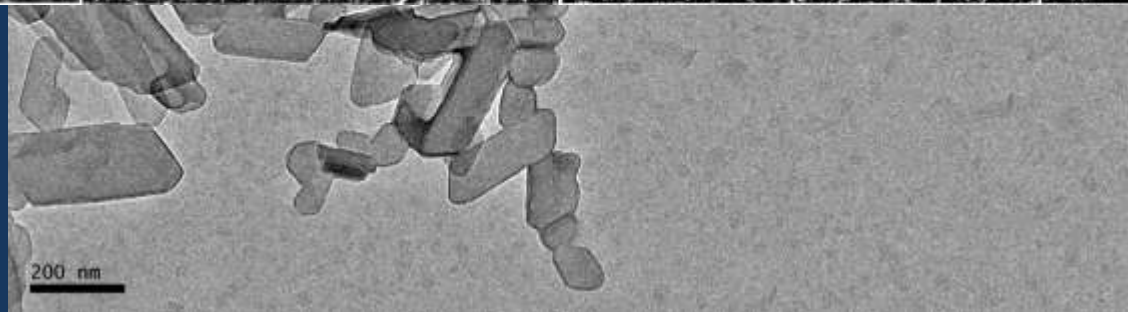
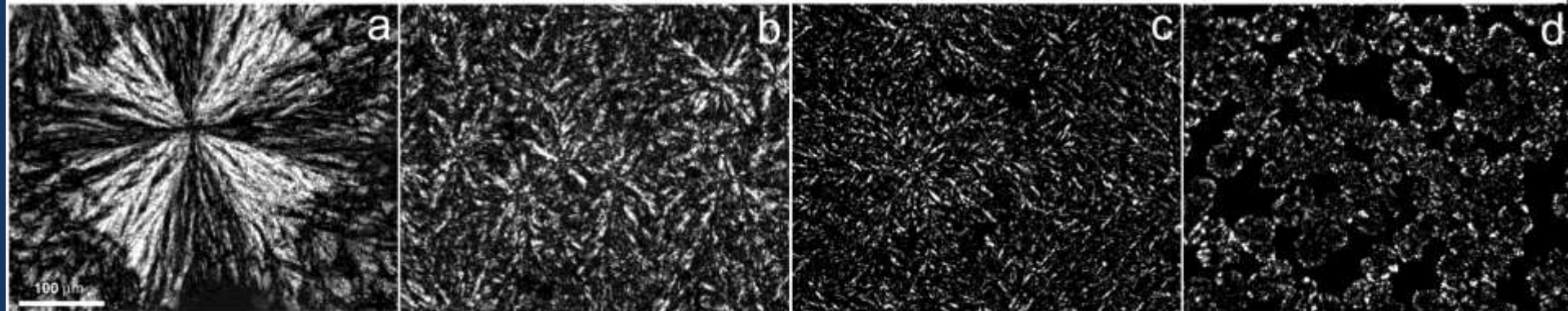


300808 10KV ..... 6.0um

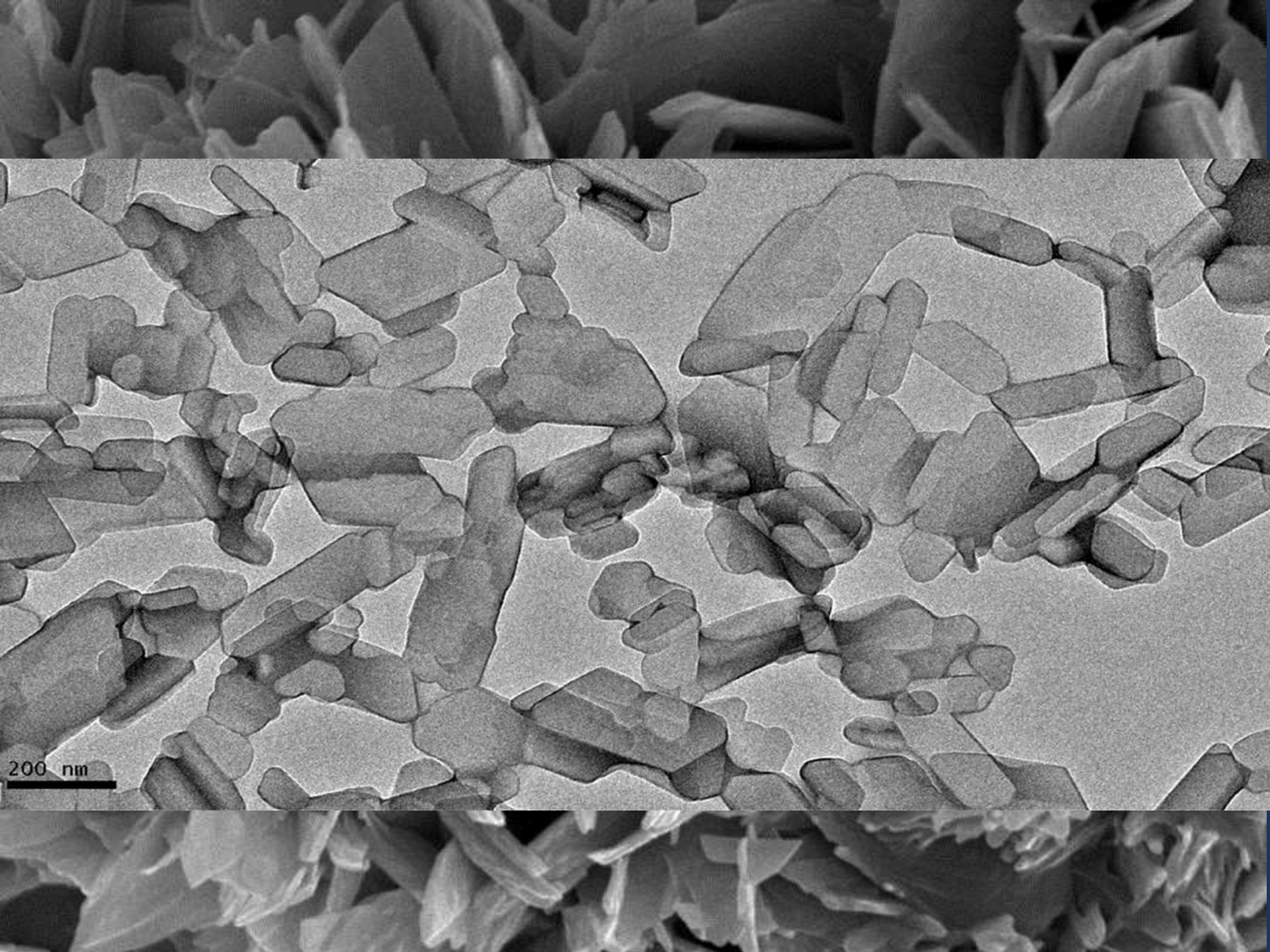


300809 10KV ..... 30um

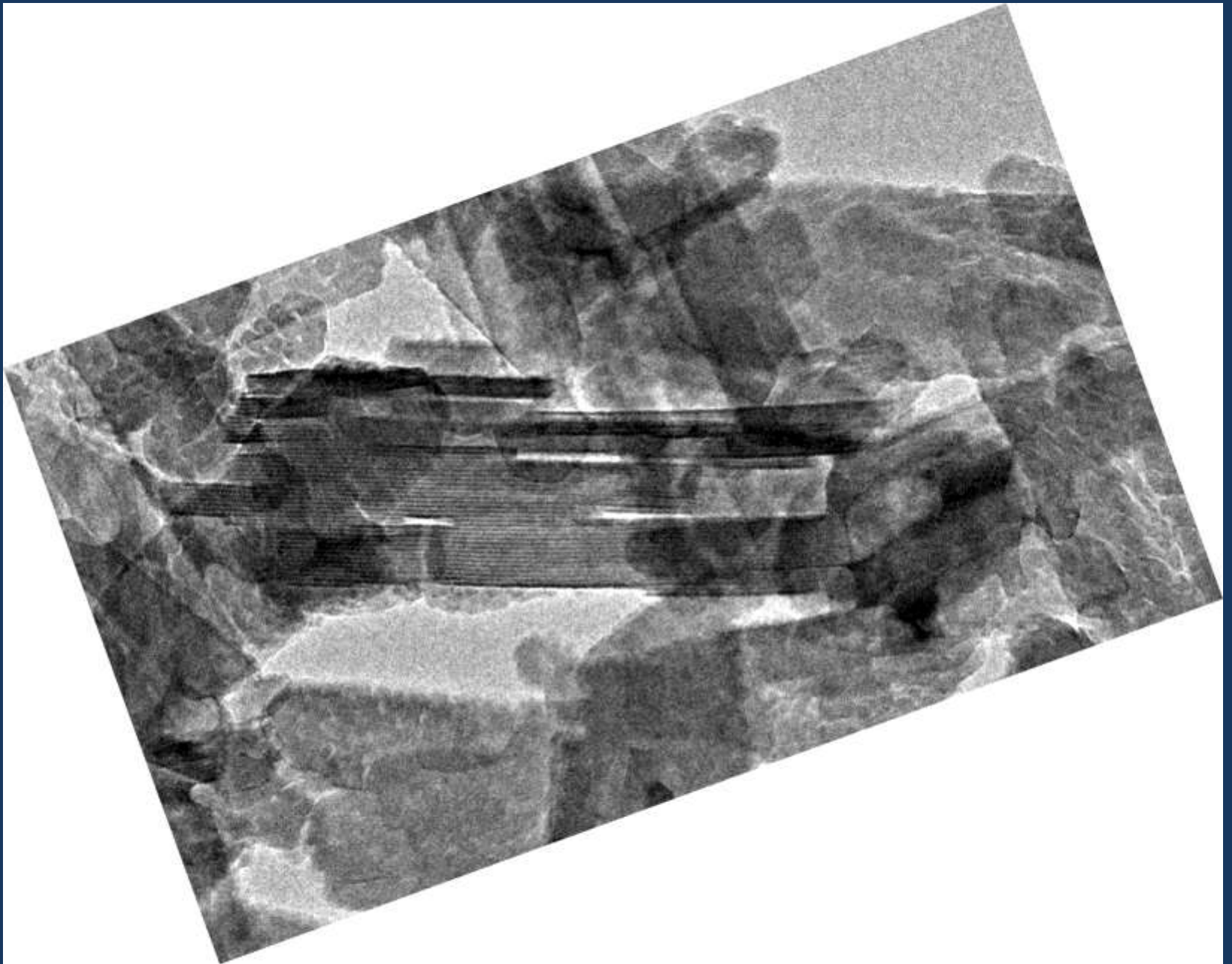
# PLM of fully hydrogenated soybean oil and dilutions in soybean oil, crystallized statically @ 30°C



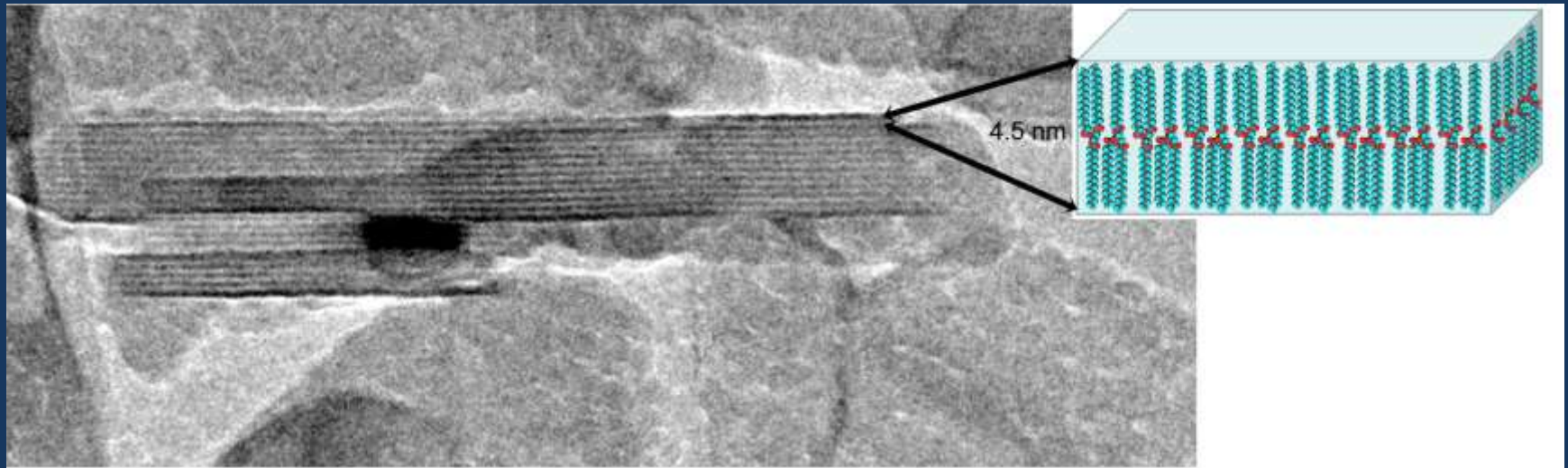


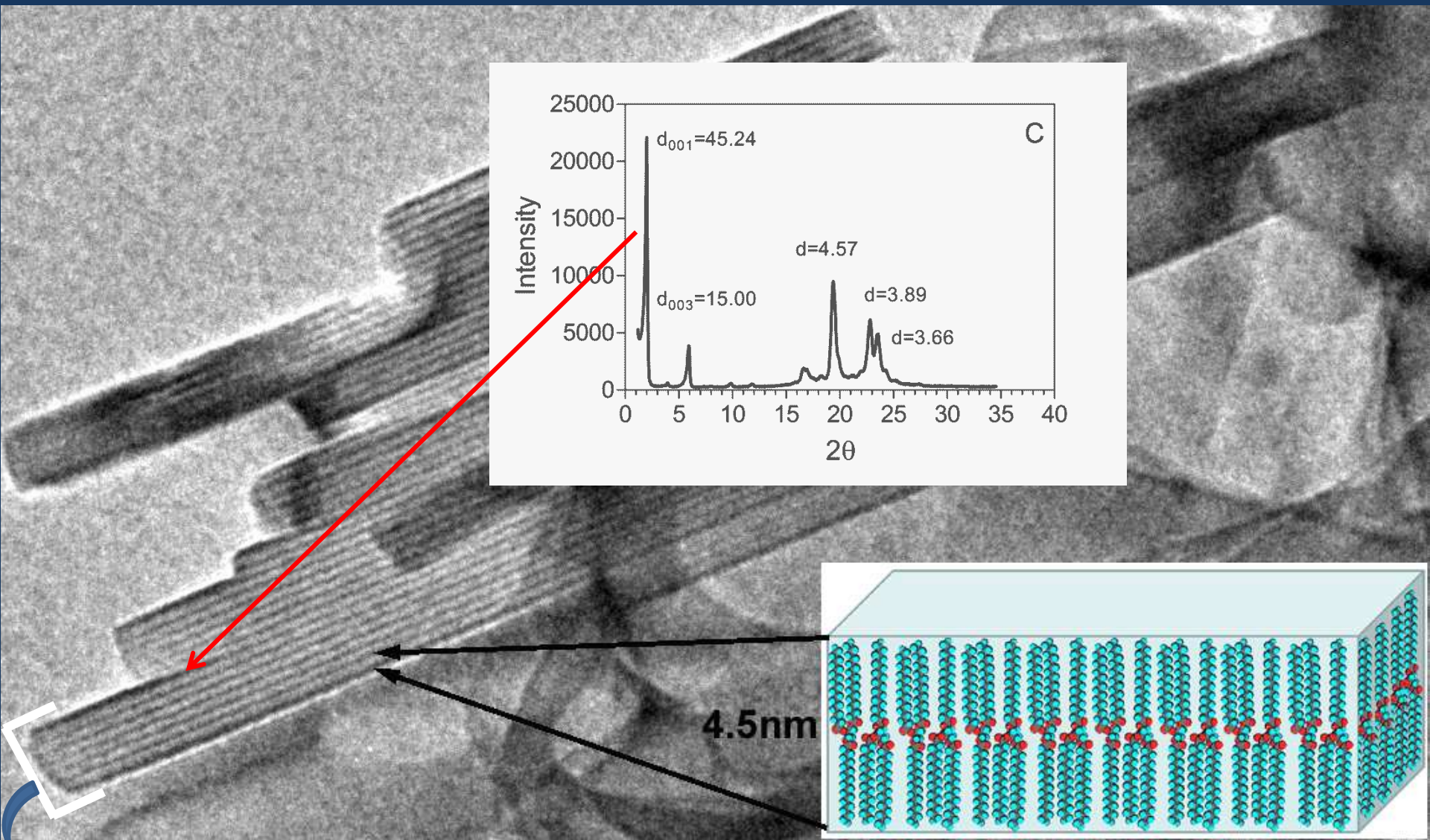






# Nanostructure of fats revealed by cryogenic Transmission Electron Microscopy of fully hydrogenated soybean oil after solvent removal



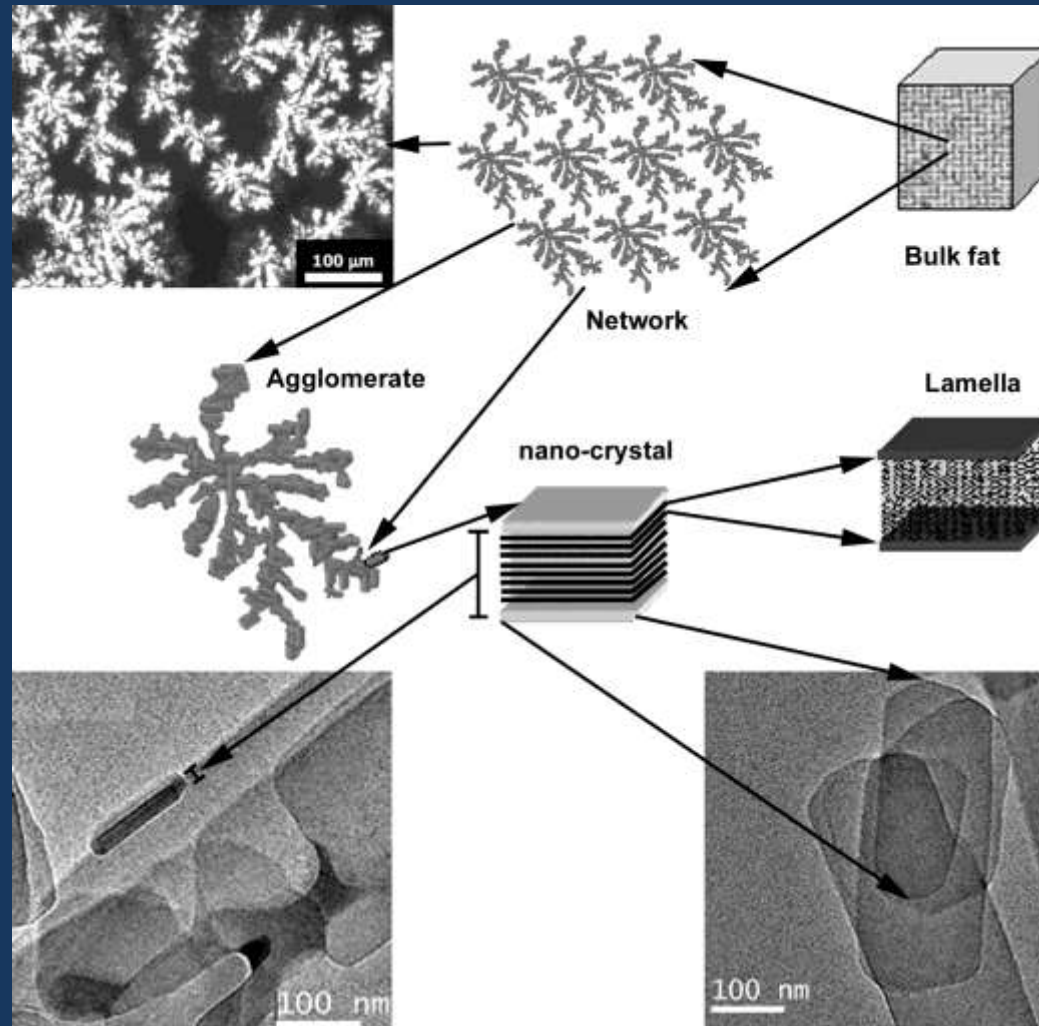


Platelet thickness

Cryo-TEM=  $4.23 \pm 0.76$  nm  
XRD= 4.5 nm



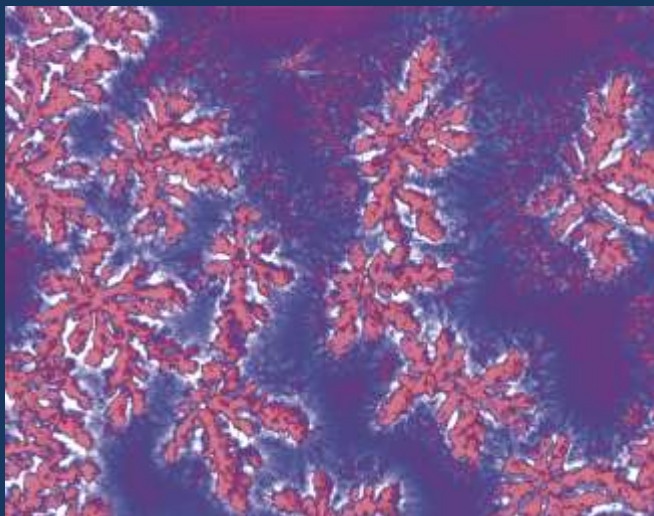
# Structural hierarchy in fats



= polycrystalline physical or chemical  
colloidal oleogel

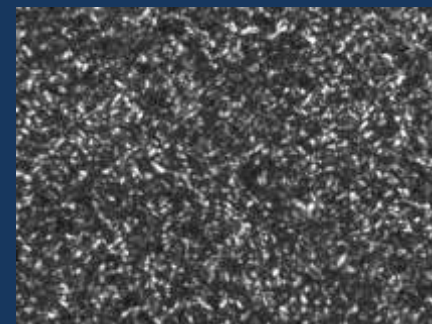
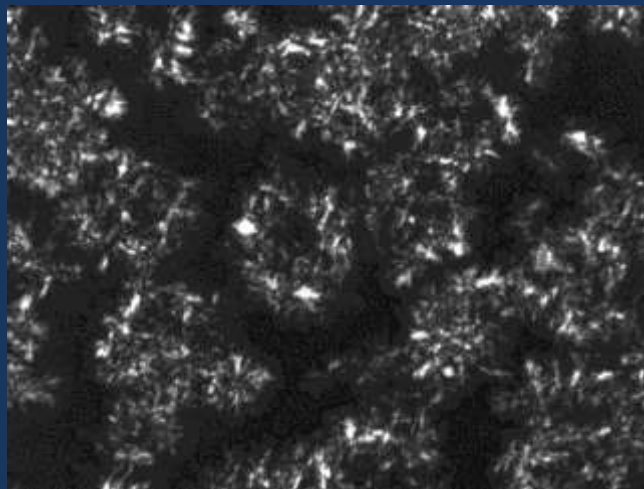




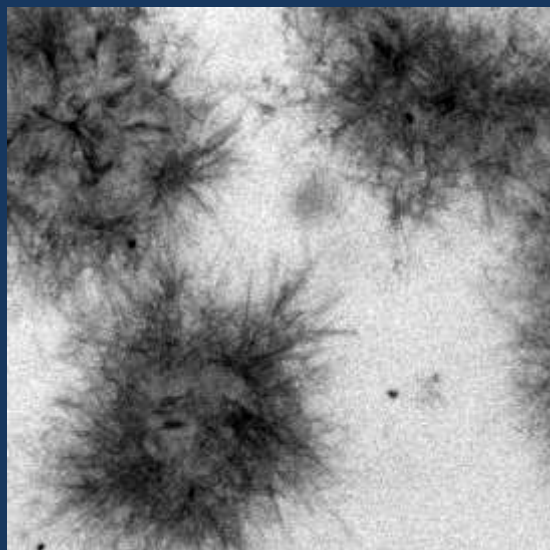


PLM-PhC of AMF HMF in triolein @22°C

PLM of CB @22°C

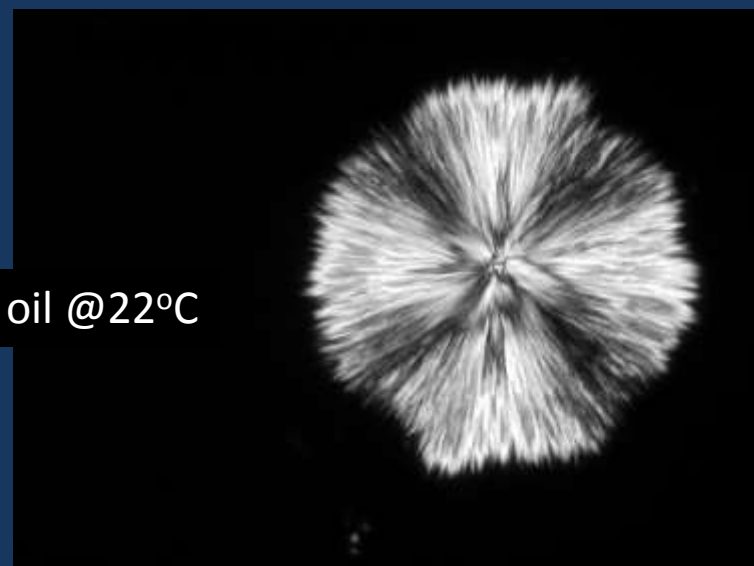


PLM of CB @10°C

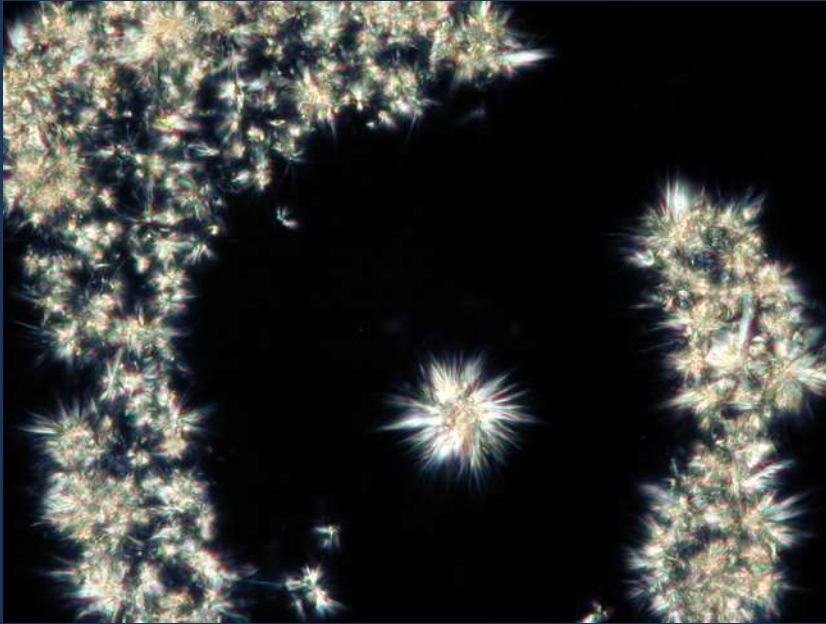


AMF CLSM using Nile Red @20°C

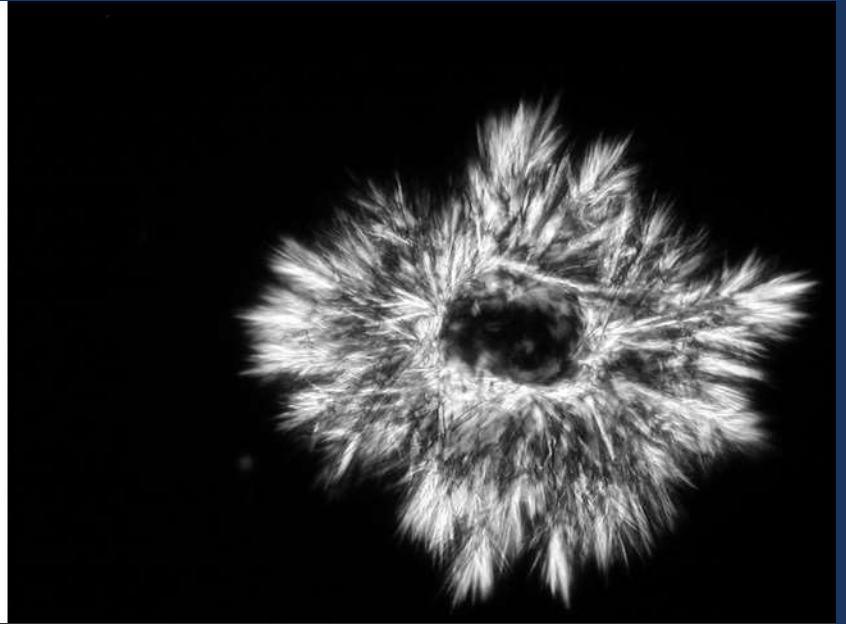
Palm oil @22°C



# Religious uncertainty in fat as demonstrated by palm oil crystals

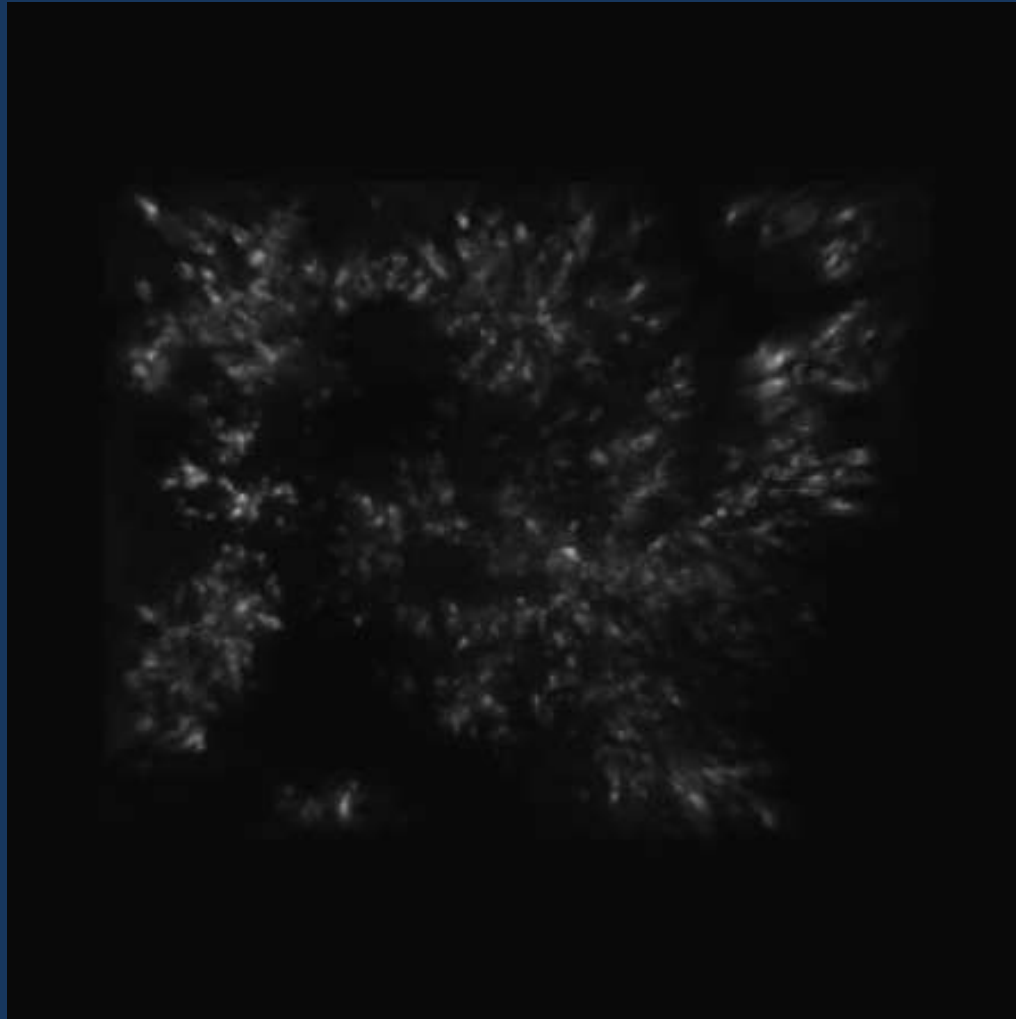


Muslim



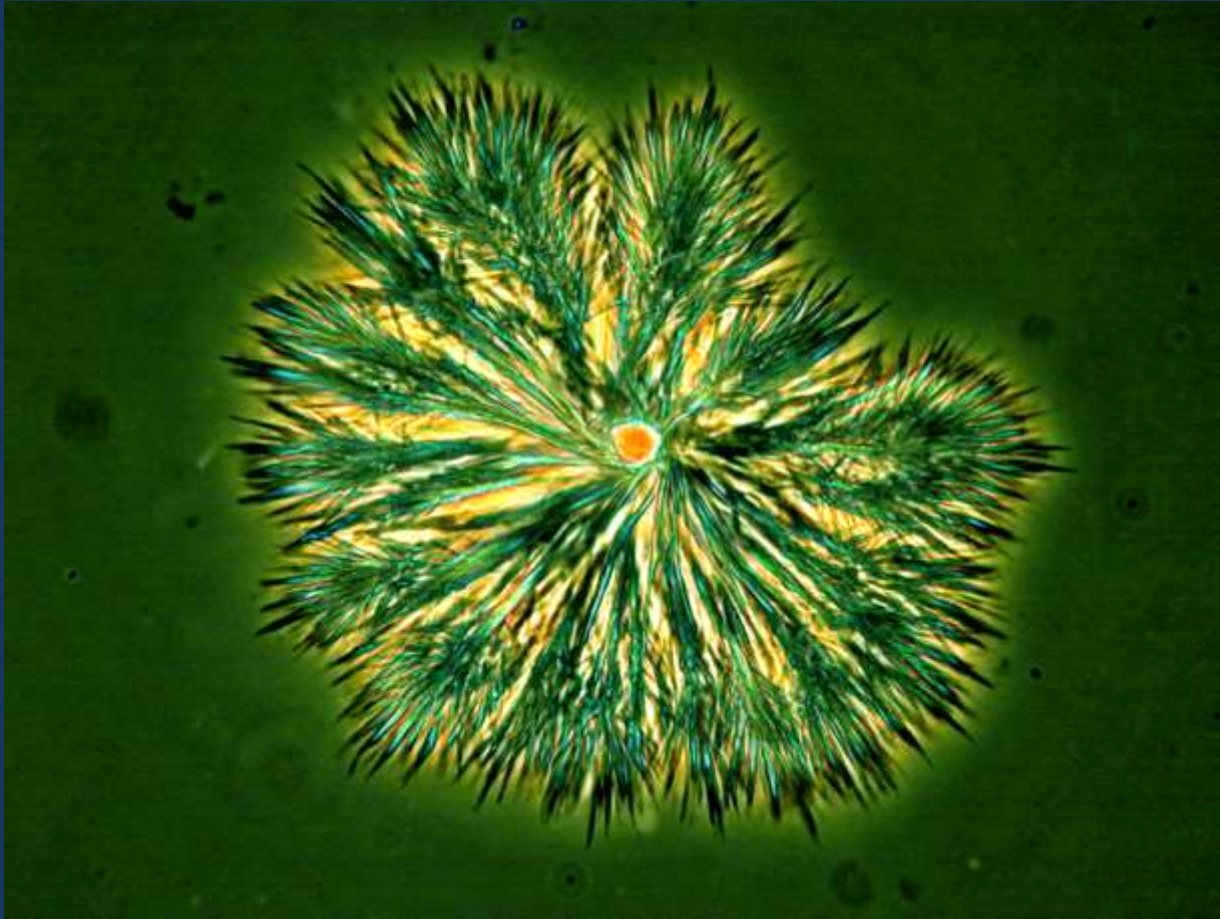
Christian

# 3-D network of a plastic fat revealed by wide-field blind deconvolution and z-slice reconstruction of PLM images

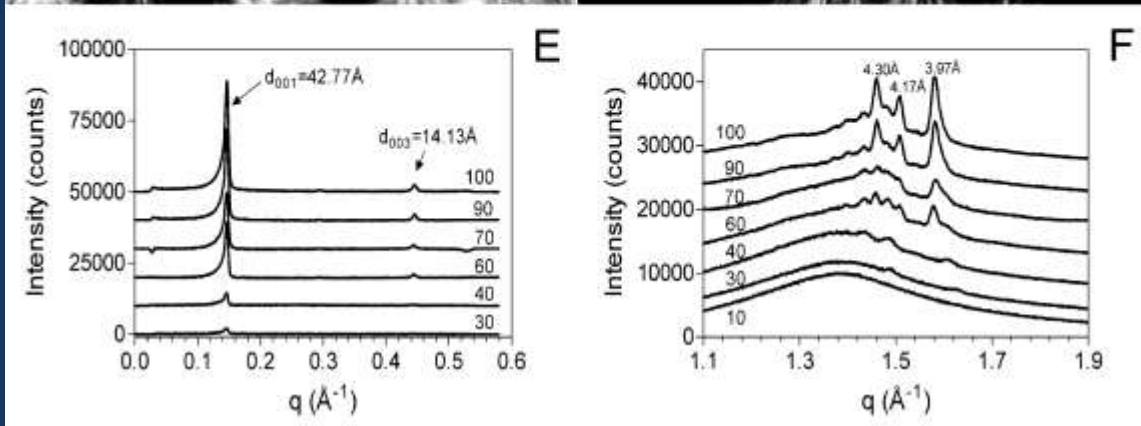
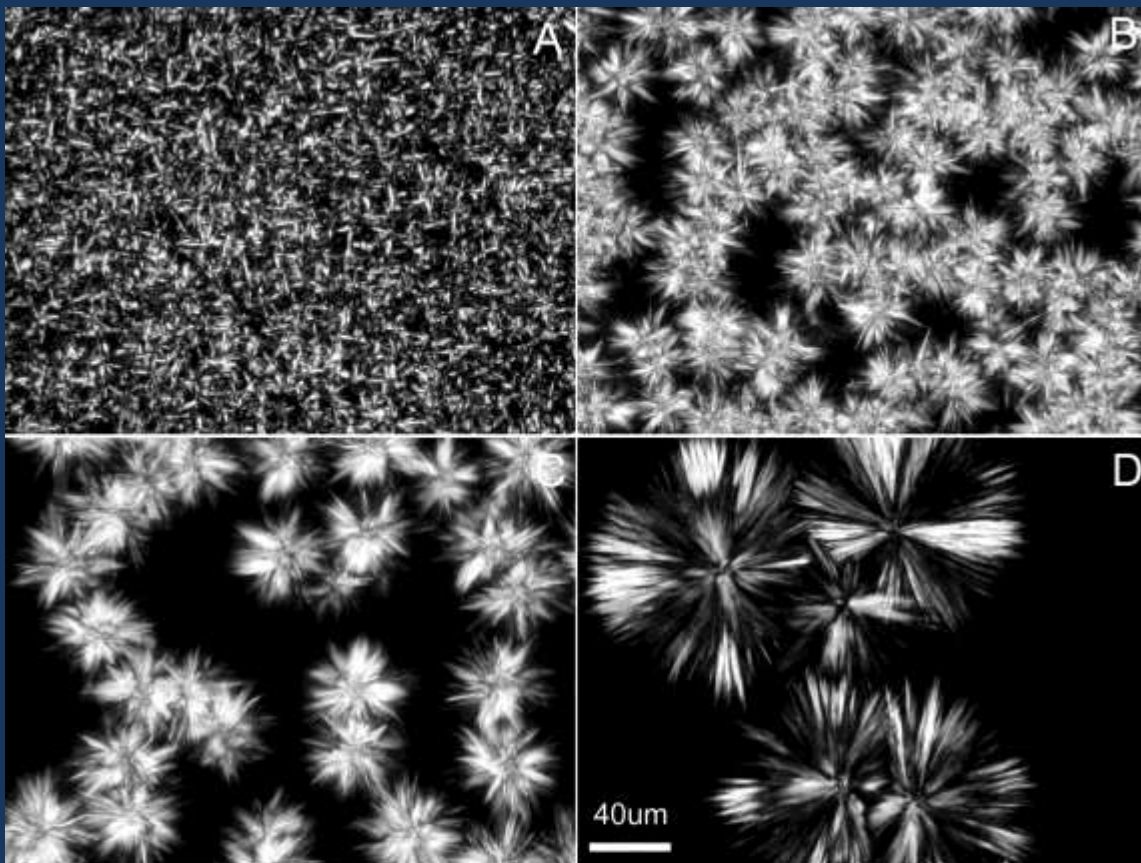


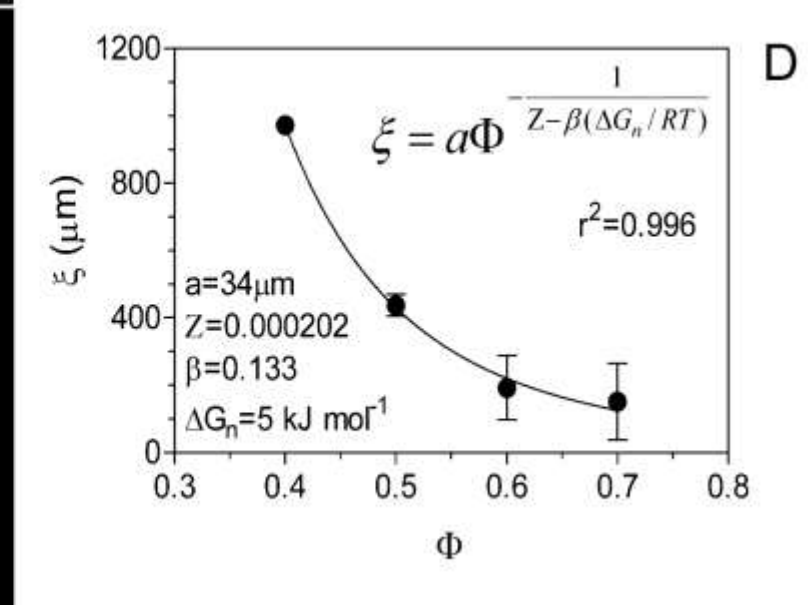
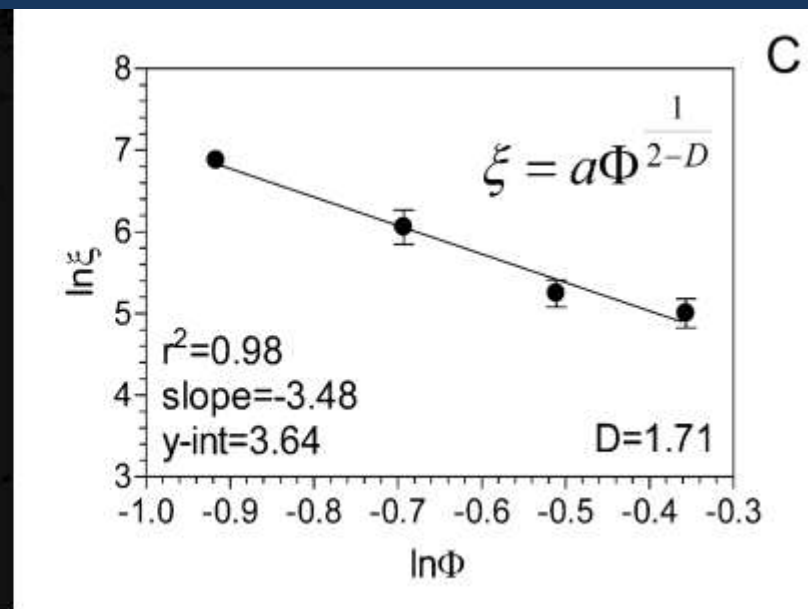
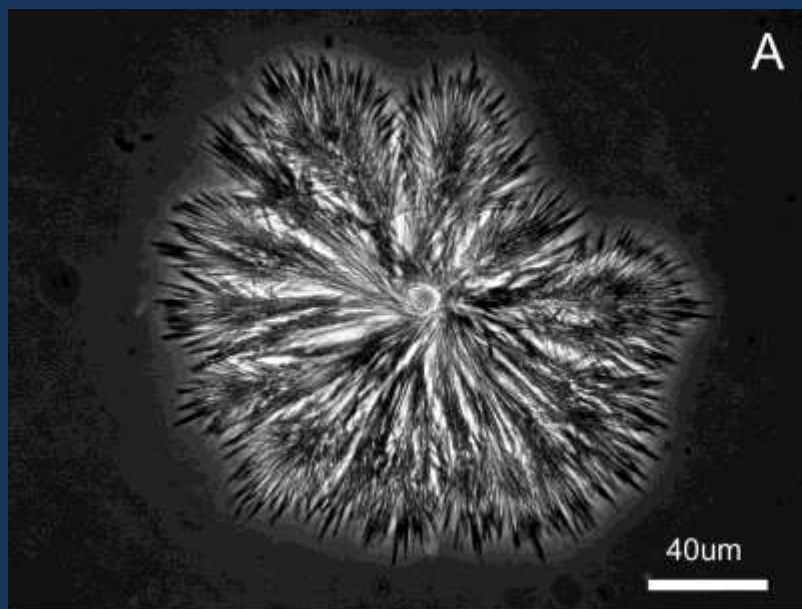


# Spherulites as fractal objects



Palm oil spherulite imaged using Phase Contrast light microscopy

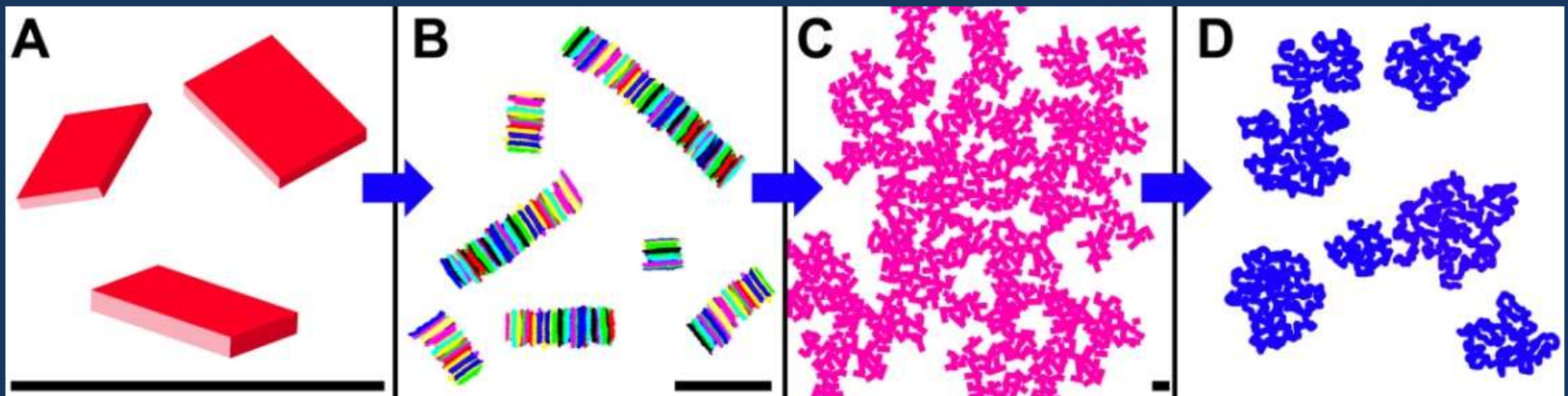






Nano to Meso???

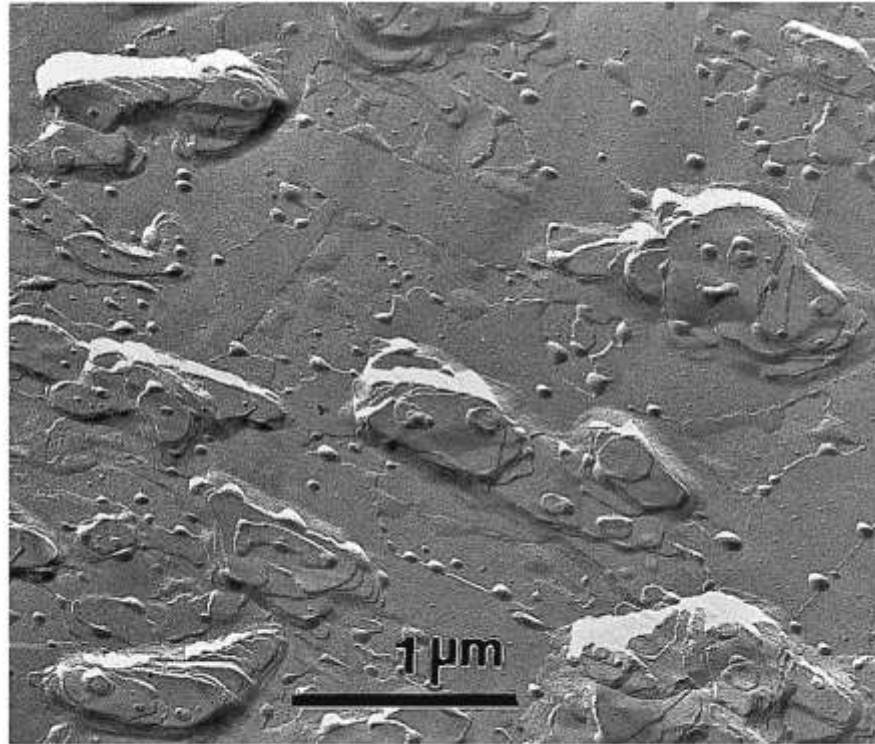
# Fat polycrystal formation is similar to a colloidal aggregation process



D.A. Pink et al., 2013, J. Applied Physics

Quinn, B. et al., 2014. J. Physics : Condensed Matter

# Crystal Clusters



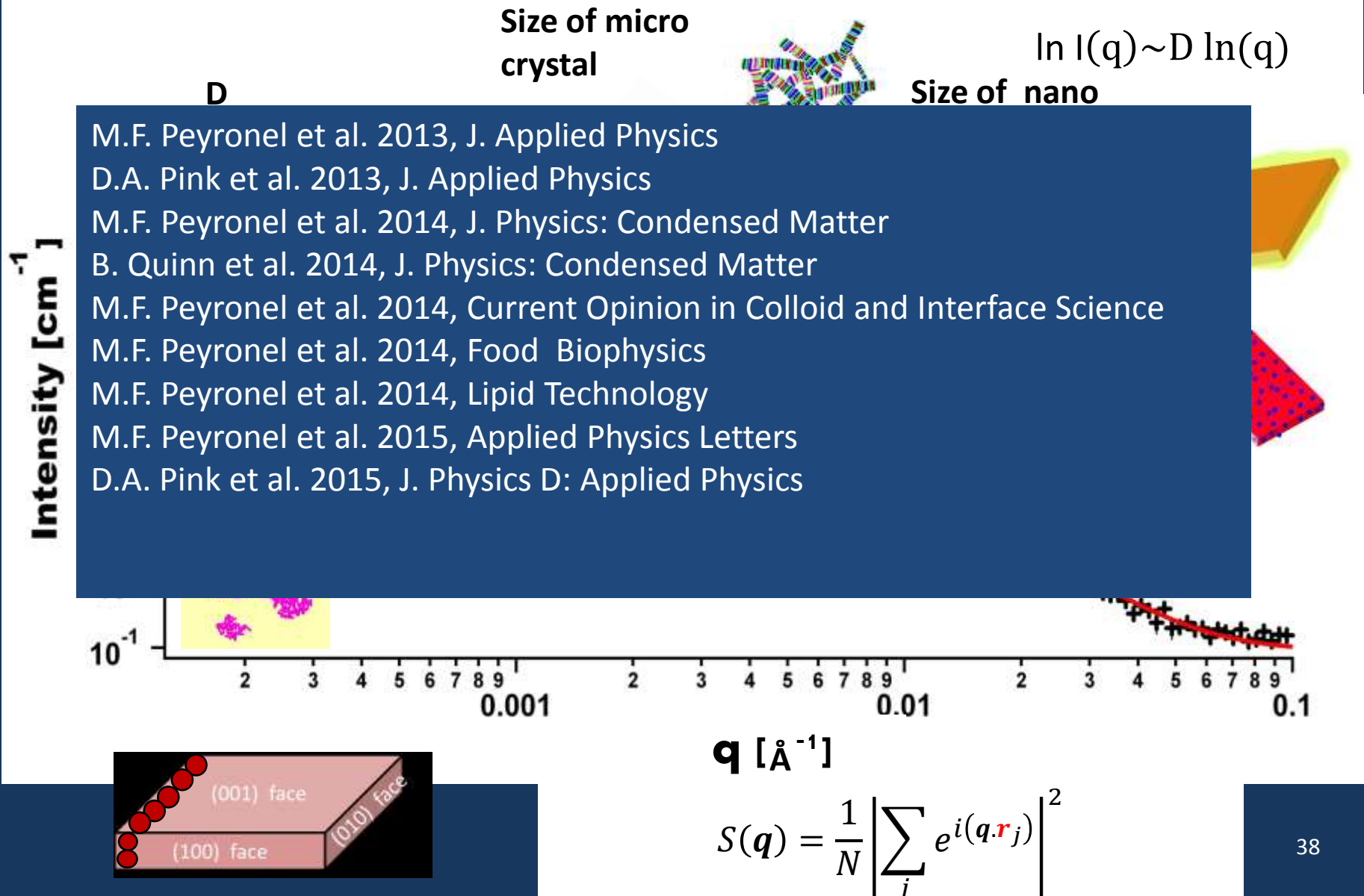
**Fig. 14** Well-separated crystal clusters from a commercial margarine; carbon fixation technique



# Physical Structural Levels

low to intermediate solid concentration

- The CNPs are the primary units that scatter
- CNPs aggregate
- Fractal interpretation



$$S(q) = \frac{1}{N} \left| \sum_i e^{i(q \cdot r_j)} \right|^2$$

# Oleogels!



← 0.5% 12-hydroxystearic acid in canola oil!



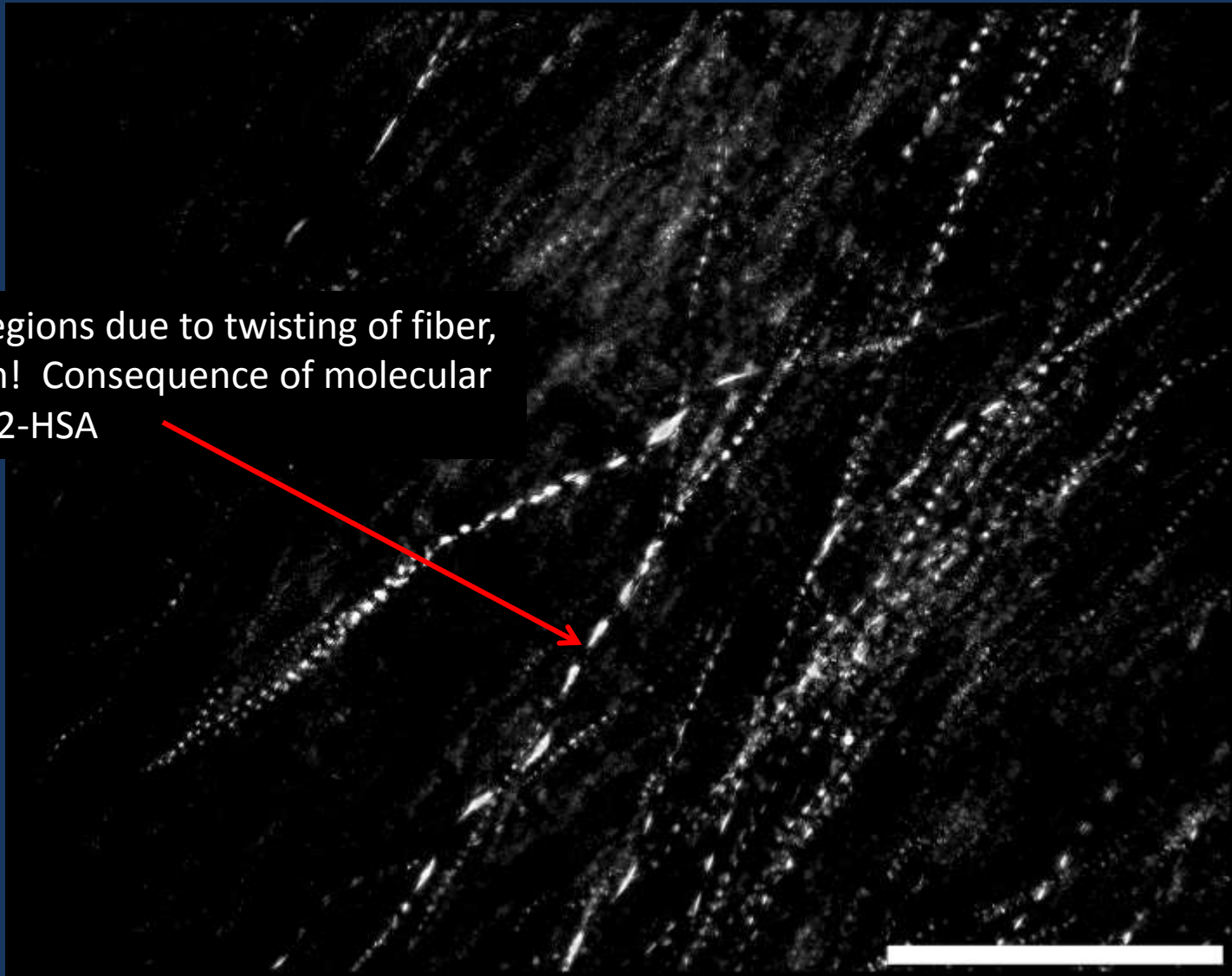
# 12-hydroxystearic acid oleogels formed at 0.5% levels in oil



This is called a SAFIN: self-assembled fibrilar network

Edmund Co



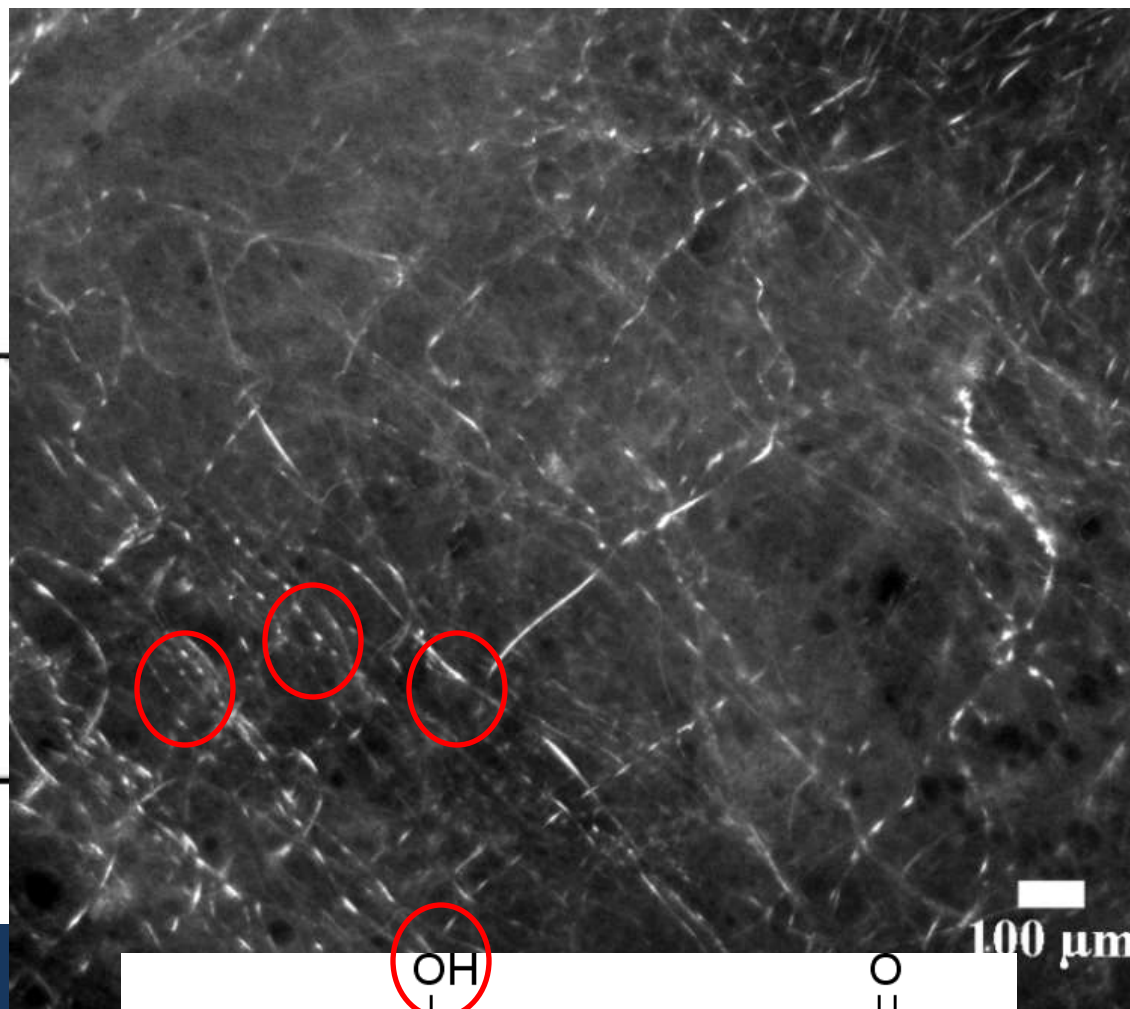


Dark/light regions due to twisting of fiber,  
Like a ribbon! Consequence of molecular  
Packing of 12-HSA

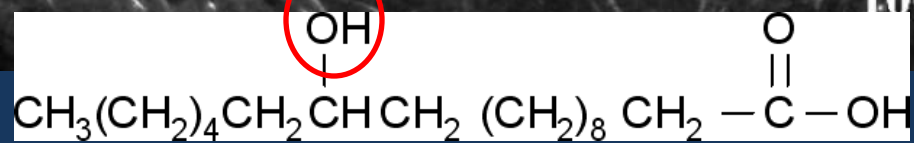
Deconvolved (wide-field, blind), PLM 2D projection of a 3D stack of z-slice of 12-hydroxystearic acid in canola oil. Mag bar is 100 $\mu$ m.

a

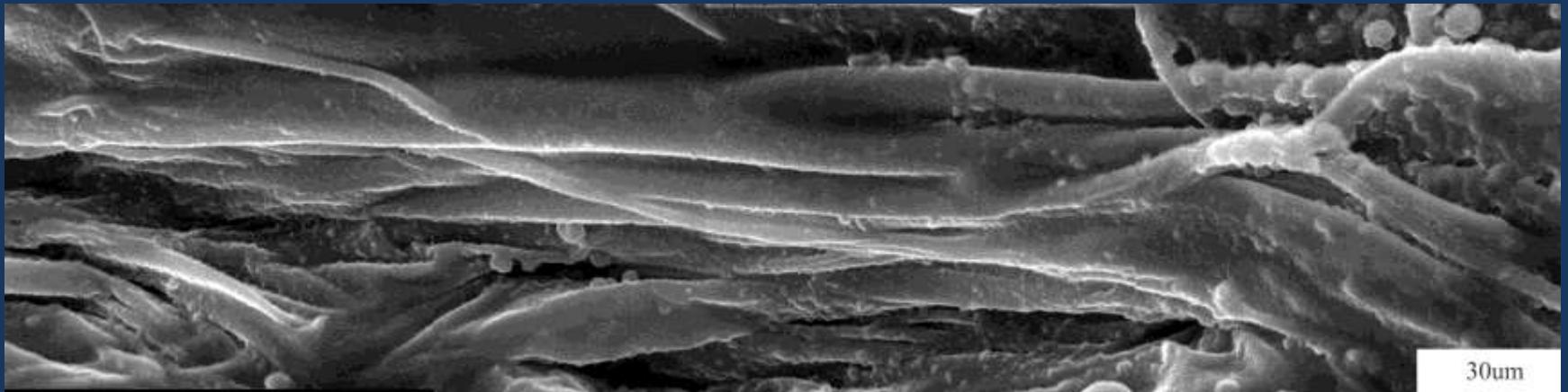
c



100  $\mu\text{m}$



# Cryo-SEM of 12-HSA oleogel after solvent removal



Michael Rogers



# Take home message

- SAFINs are just “frustrated” crystals – dimensionally restricted
- Need fibers ( $D=1$ ) or platelets ( $D=2$ ) for oleogel structuring at low mass fractions
- All of this from looking at images.....

# EC Edible-oil Based Oleogels

At the macroscopic level, gels behave similar to fat

→ Useful range 8-12% (w/w) in oil



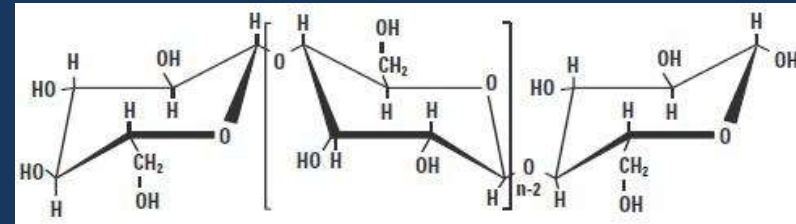
85% Canola oil  
15% EC<sup>10</sup>

80% Canola oil  
15% EC<sup>10</sup>, 5% SMS

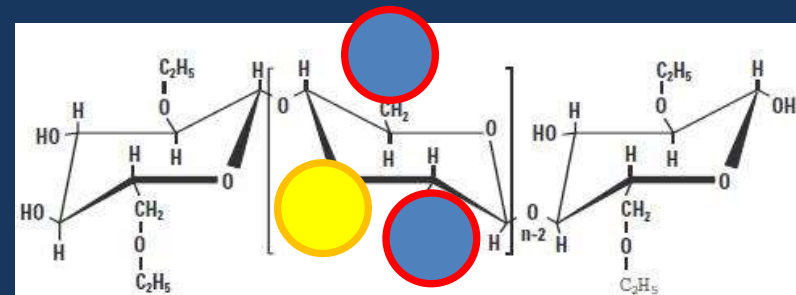
# Ethylcellulose (EC)

- 48% ethoxy content  
~2.5/3 hydroxyl groups
- Hydrophobic
- Film forming
- Available in a variety of different viscosities  
↳ EC<sup>10</sup>, EC<sup>20</sup>, EC<sup>45</sup>, ...

## Cellulose

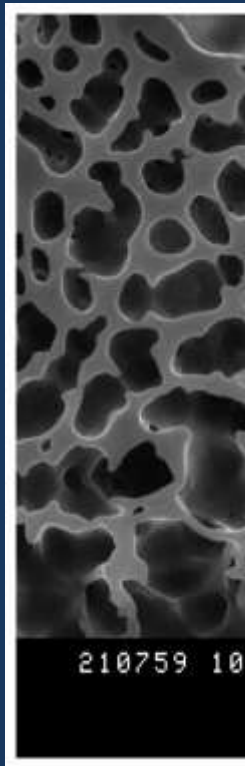


## Ethyl Cellulose

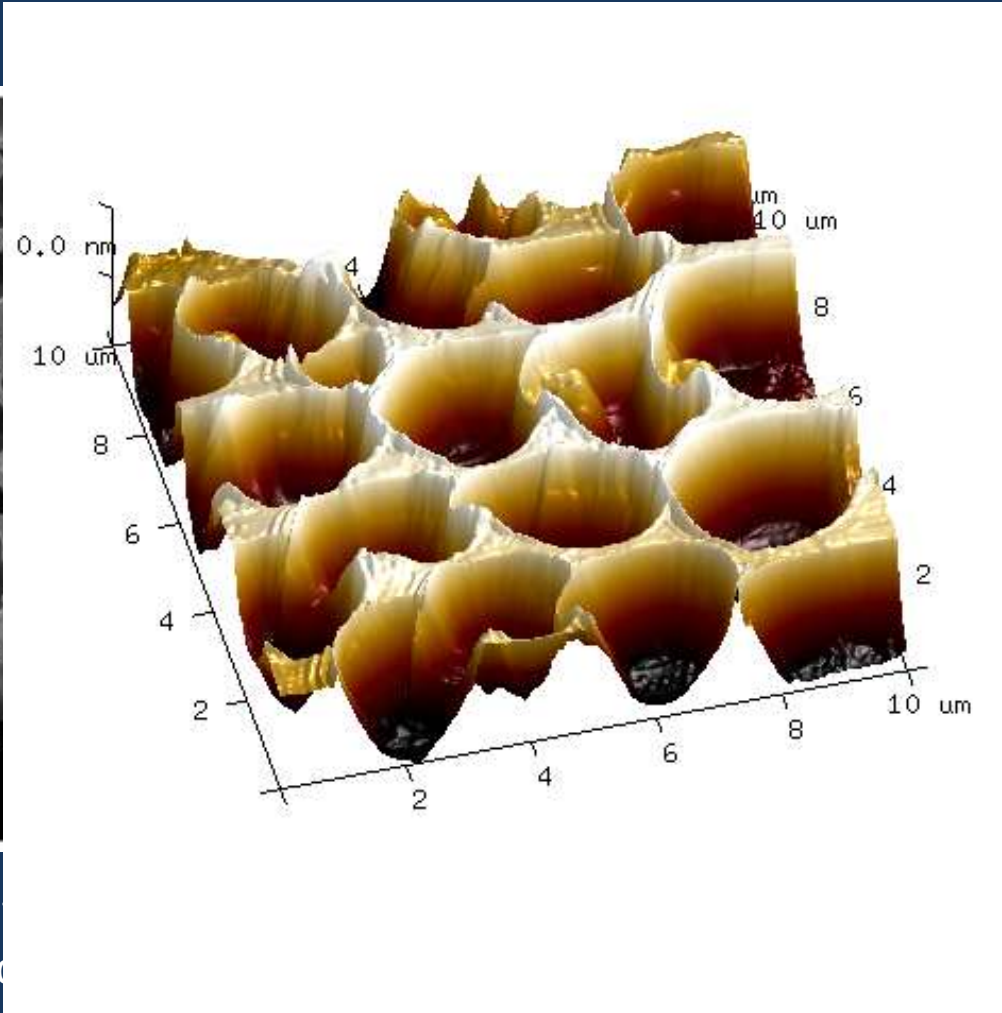




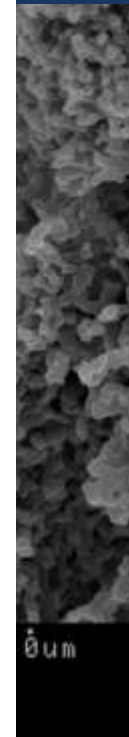
# Ethylcellulose Oleogel Microstructure



Cryo-SEM and  
color



AFM of native gel

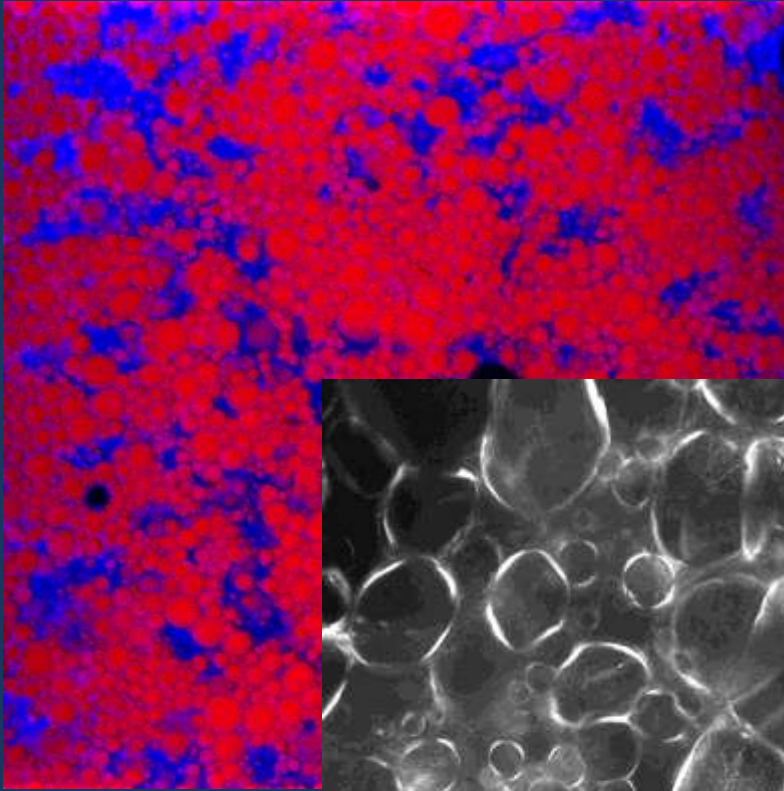


with ether

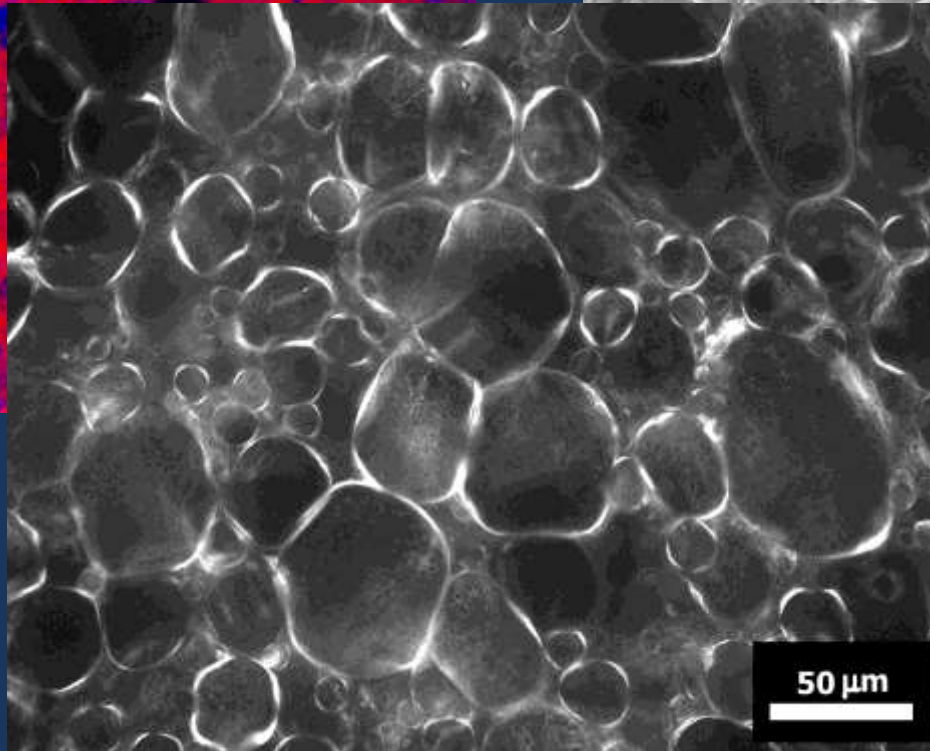
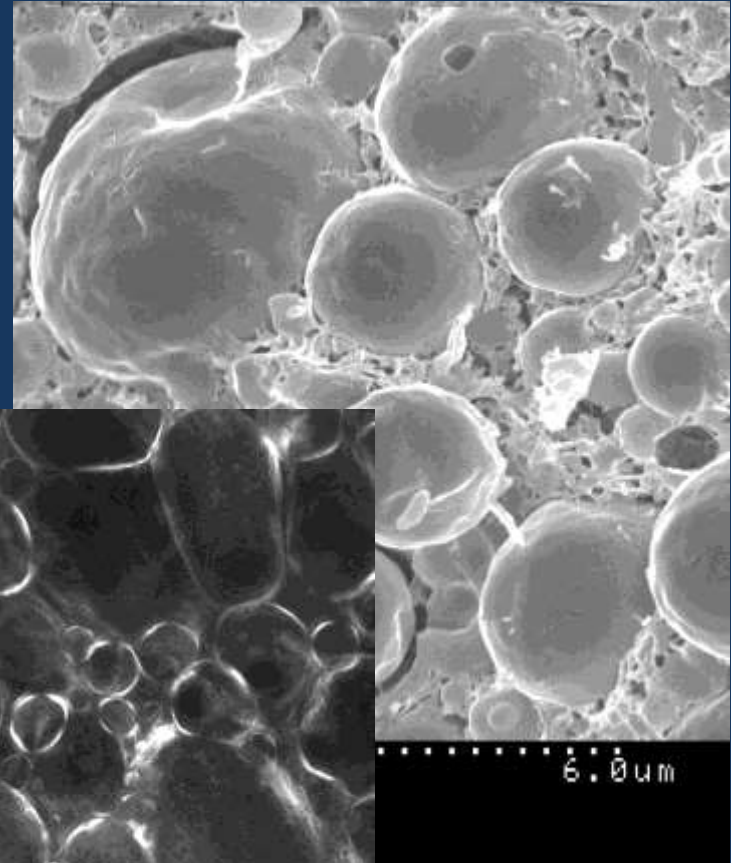
# Structured o/w Emulsions

Oil, water, saturated monoglyceride,  
co-surfactant

Nile red and coumarin stained CLSM



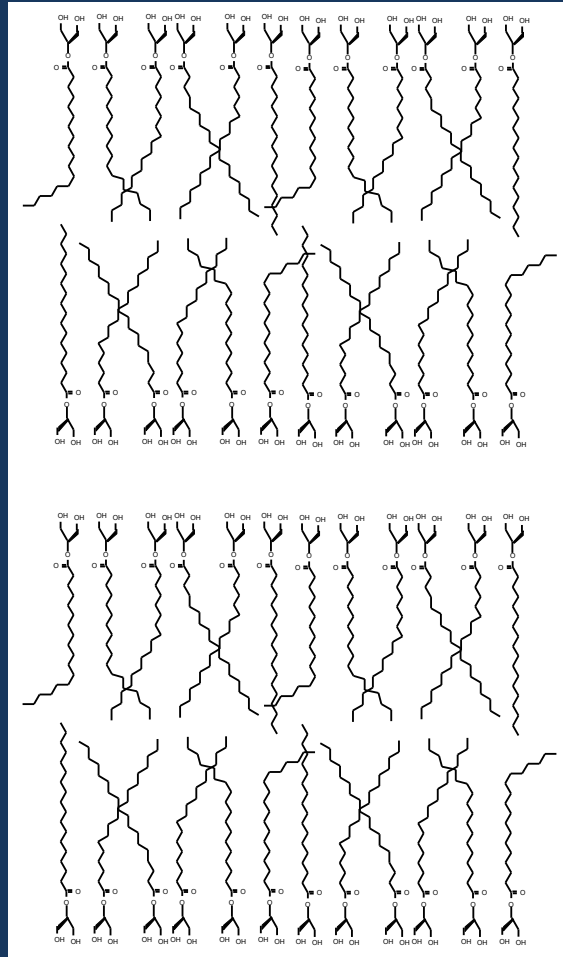
Freeze-fracture Cryo-SEM



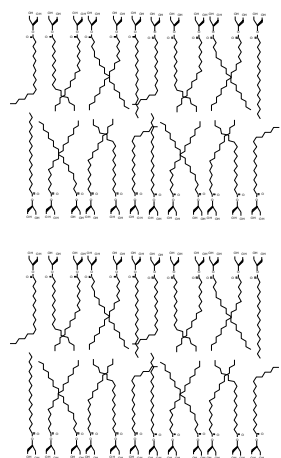
Polarized light micrograph



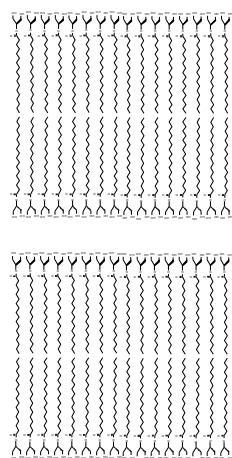
# Presence of liquid crystalline phases of monoglycerides are necessary for structure formation



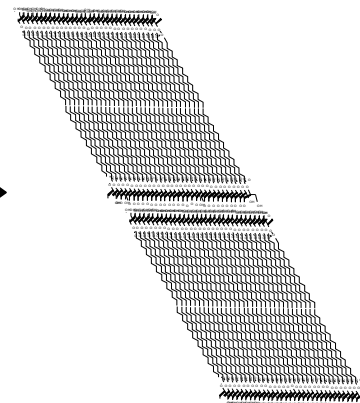
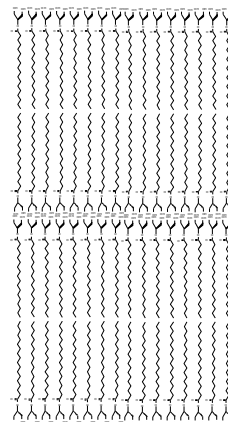
$L_{\alpha}$



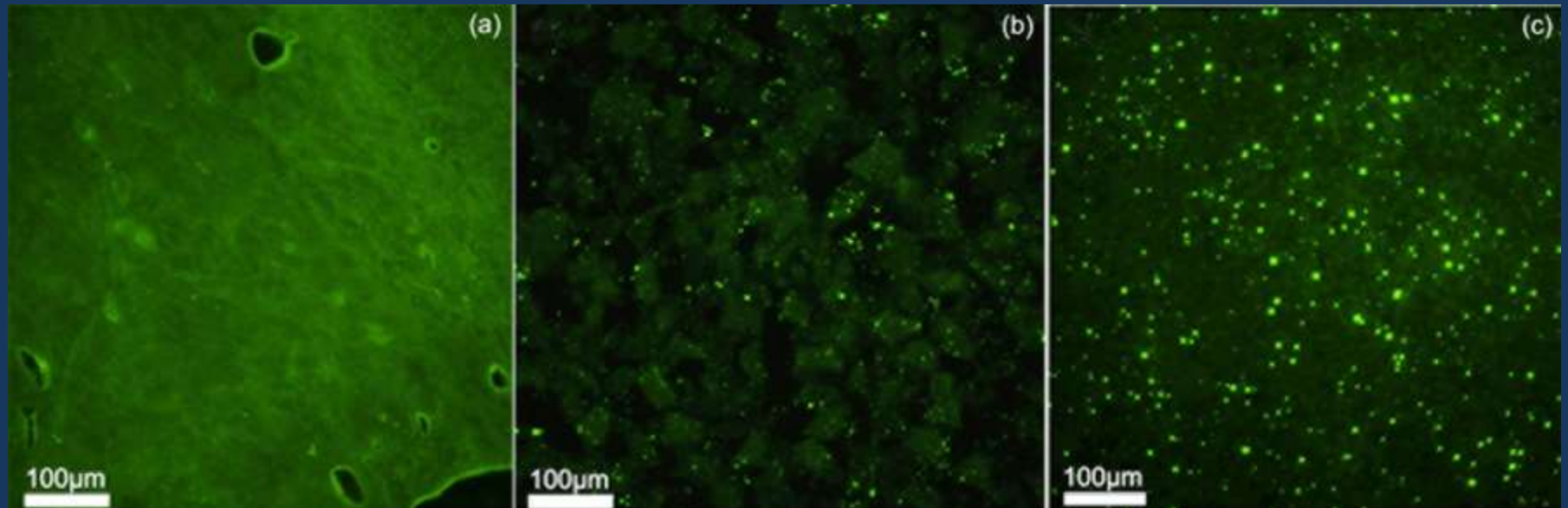
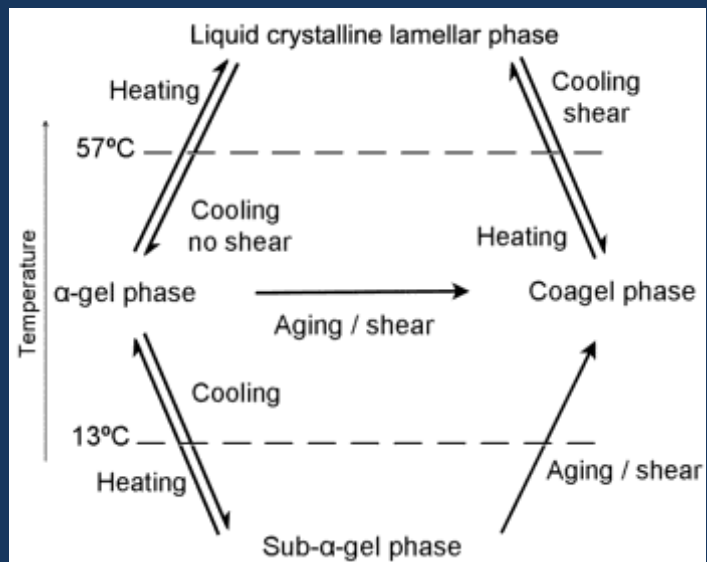
$L_{\alpha}$



$L_{\beta}$  ( $\alpha$ -gel)

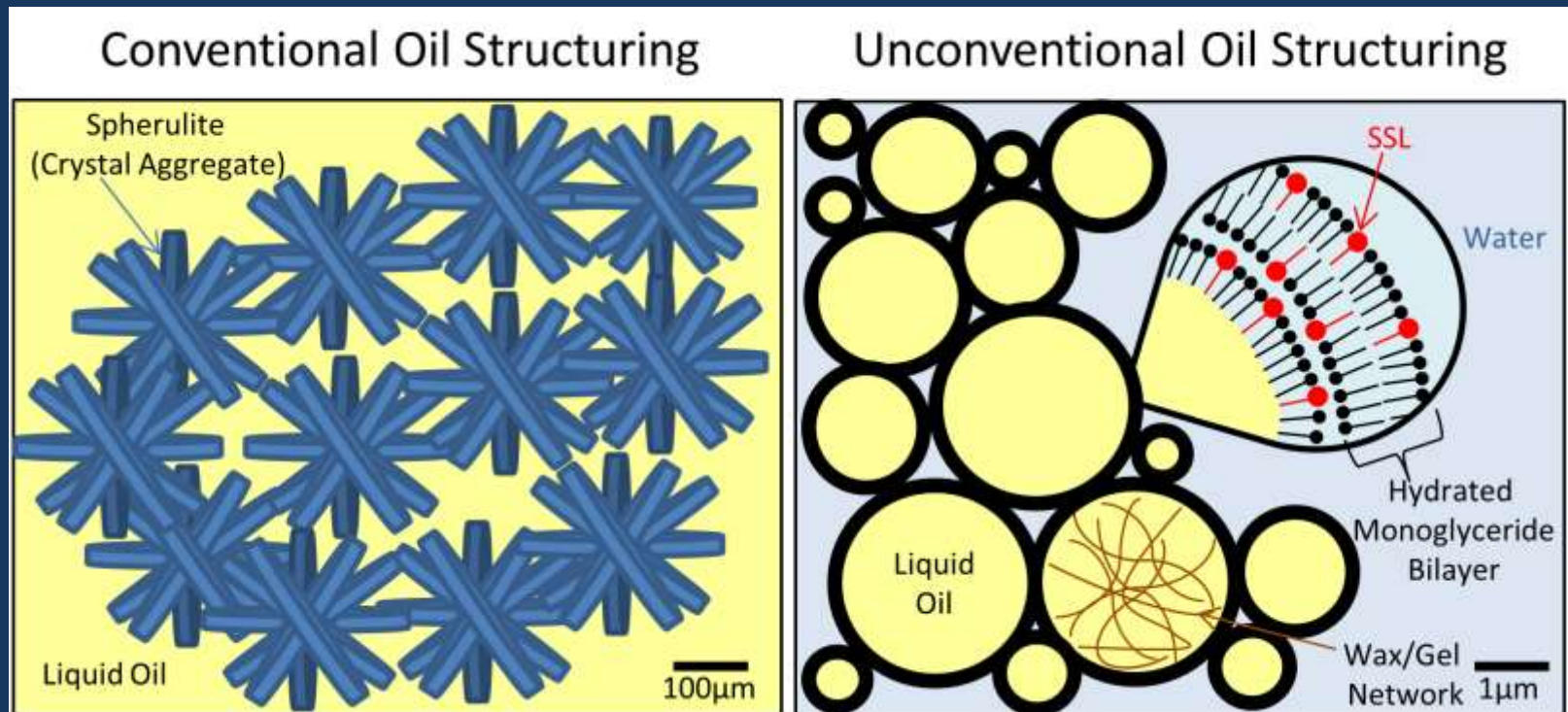


$\beta$ -gel  
(coagel)





# Unconventional Structuring requires unconventional thinking and visualization



# Impressionistic painting

- In impressionist painting, short, thick strokes of paint quickly capture the essence of the subject, rather than its details.
- Impressionists portrayed overall visual effects instead of details, and used short "broken" brush strokes of mixed and pure unmixed colour. Mixing takes place in the mind of the beholder.



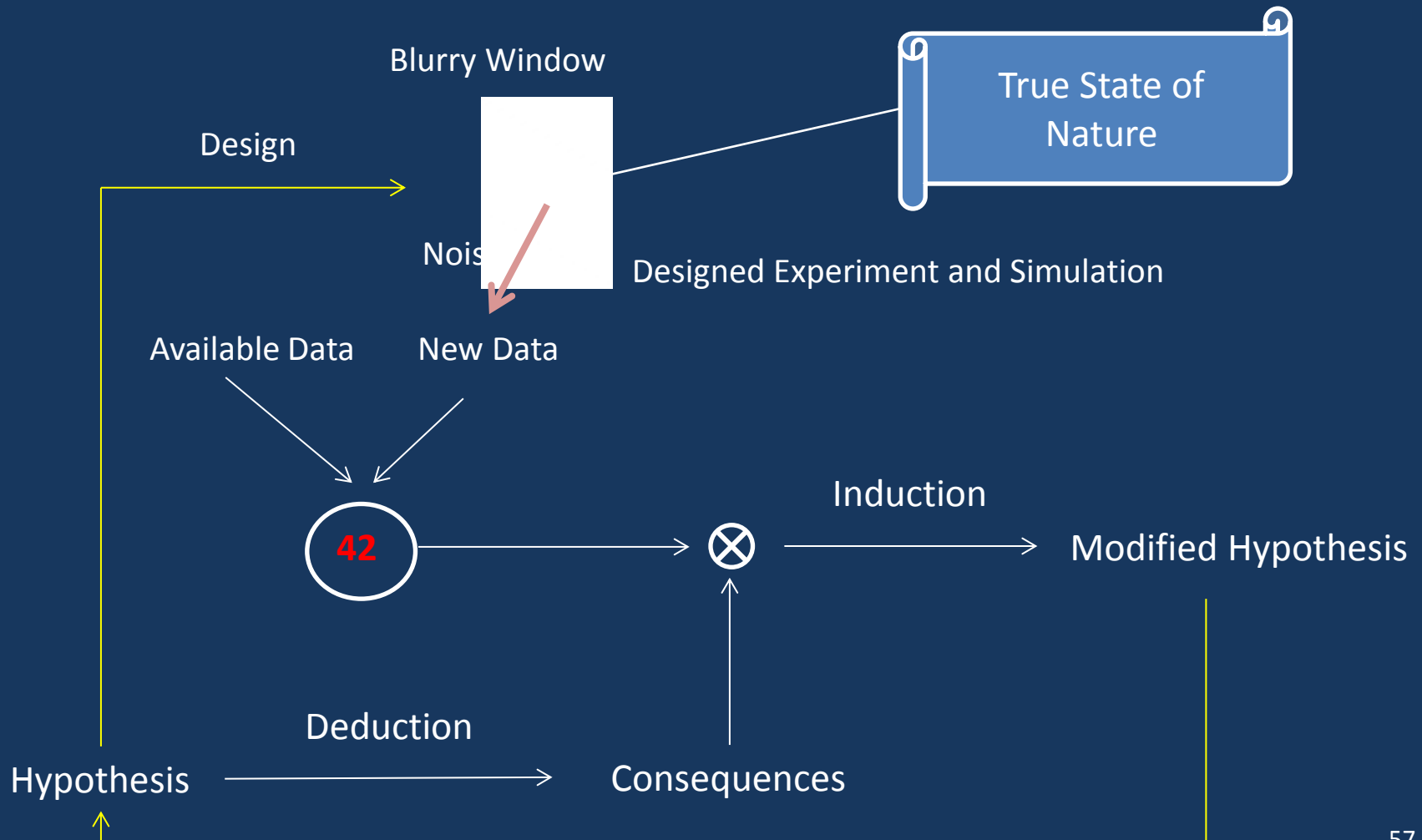
Claude Monet, 1872, Impression Sunrise



James Abbot McNeill Whistler, 1874 Night in Black and Gold, The Falling Rocket



# Attempting to pinpoint the true state of nature



# Scientific impressionism (hopefully not intentional!)

- Thick, short brush strokes in scientific research arise due to:
  - resolution limits of equipment
  - limited length scales accessible for investigation
  - environmental influences
  - inherent variability
  - sensitivity to initial and boundary conditions
  - limitations of operator/researcher/PI



Chance favors the prepared mind

Dans les champs de l'observation le hasard ne favorise que les esprits préparés  
*Louis Pasteur, 1854, University of Lille*

5  $\mu\text{m}$

# Funding Agencies

- Natural Sciences and Engineering Research Council
- Canada Research Chairs Program
- Ontario Ministry of Agriculture and Food
- Coasun Inc.
- Omnis Biotechnology Inc.
- Whistler Performance Lubricants Inc.
- Multinational Corporate Partners (5)







## Marangoni Lab

### Canada Research Chair in Food, Health and Aging

Food and Soft Materials Science Laboratory

University of Guelph

<http://www.crcfoodandhealth.com>

UNIVERSITY  
of GUELPH

CHANGING LIVES  
IMPROVING LIFE

<< 32 publications submitted in 2015 >>

#### Laboratory manager and Research Associate:

Fernanda Peyronel

#### Collaborators and their teams:

David Pink – theoretical physics, St. Francis Xavier

Stefan Idziak – experimental physics, Waterloo

Nuria Acevedo – nanotechnology, Iowa State

Shai Barbut – meat science, Guelph

Douglas Goff – dispersed and frozen systems, Guelph

#### Research Assistants:

Saeed Mirzaee Ghazani

Andrew Gravelle

Postdoctoral Fellows: none

Visiting Scientists/Students: 5

Undergraduate Researchers: 2

#### Graduate Students:

Fan Wang, Ph.D.

Braulio Macias, Ph.D.

Saeed Ghazani, Ph.D.

Pere Ramel, Ph.D.

Alexia Blake, M.Sc.

Chloe O'Sullivan, M.Sc.

Bethany Townsend, M.Sc.

Rachel Tanti, M.Sc.

\*Kristin Mattice, M.Sc.

\*Gayae Kim, M.Sc.

\*Brian Tienza, M.Sc.

#### Spin-off companies:

Coasun, Inc.

Omnis Biotechnology Inc.

Whistler Performance Lubricants



A black and white photograph of a textured surface, possibly a book cover, with a circular hole at the top center. The word "Gracias" is written in yellow.

**Gracias**