The University Of Sheffield.

Effect of Unsaturated Acyl Chains on Structural Transformations in Triacylglycerols

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Crystallisation and Physical Properties of Fat:
From Molecules to Market, 18-19 June 2008, Ghent University, Belgium

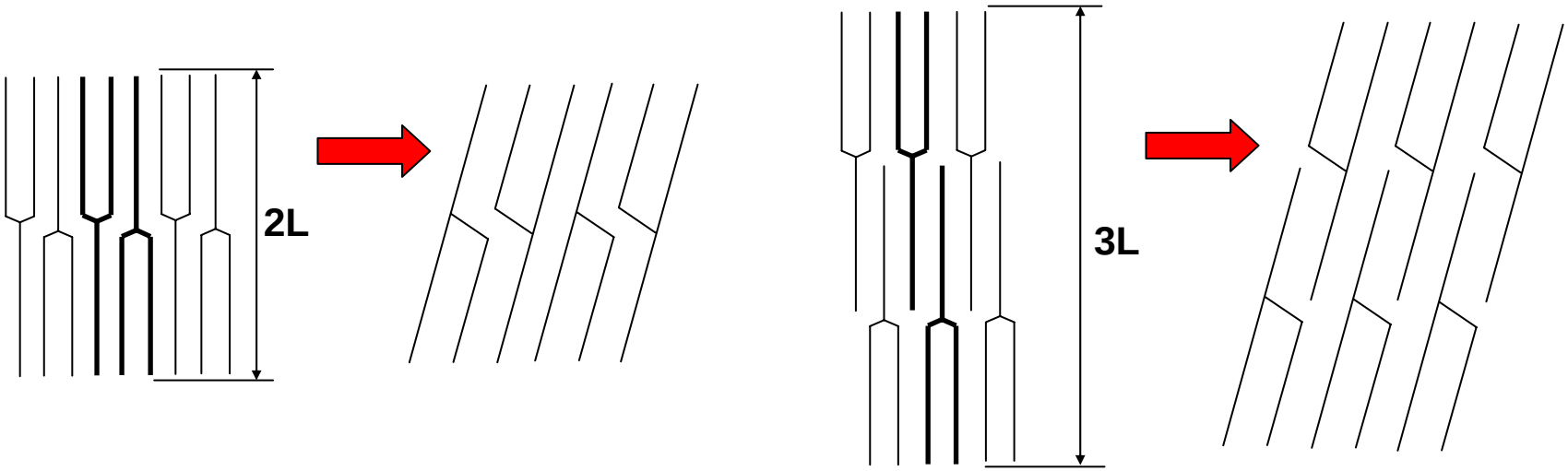
Motivation

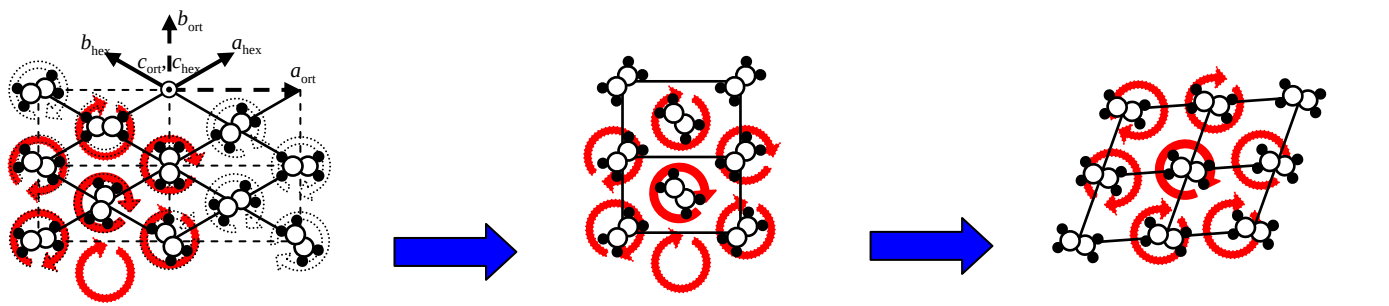
Apart from double and triple chain type of packing common in stable crystal structures of triacylglycerols there is an evidence for another organization of molecules occurring at the very beginning of crystallization from the melt before the formation of the stable crystal structures.

Outline

- Stable triacylglycerol phases
- Observations of transient phases of triacylglycerols
- Structure of the transient phases
- Transformation of the transient phases

Packing of alkane chains within a layer of triacylglycerols

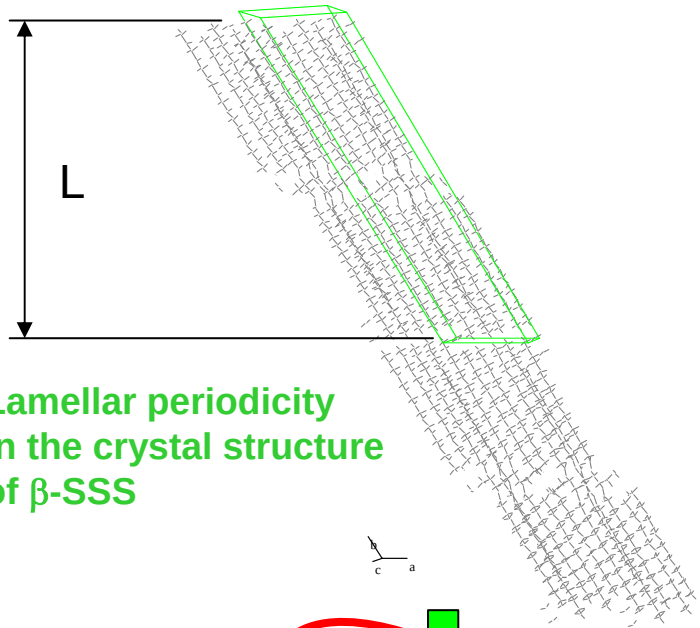




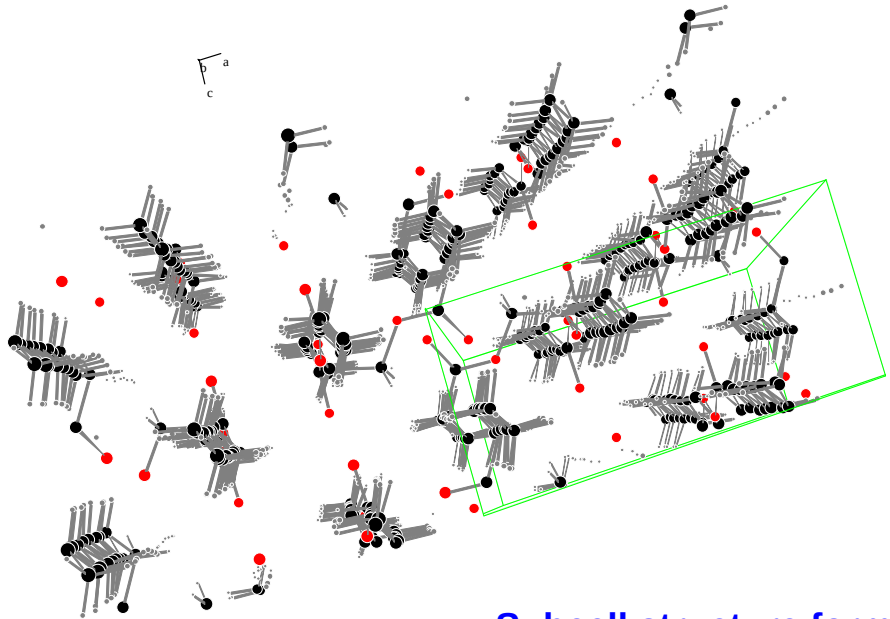
H $O_{\perp}$ $O_{//}$ $M_{//}$ $T_{//}$

sub-α ⇔ α β’ β

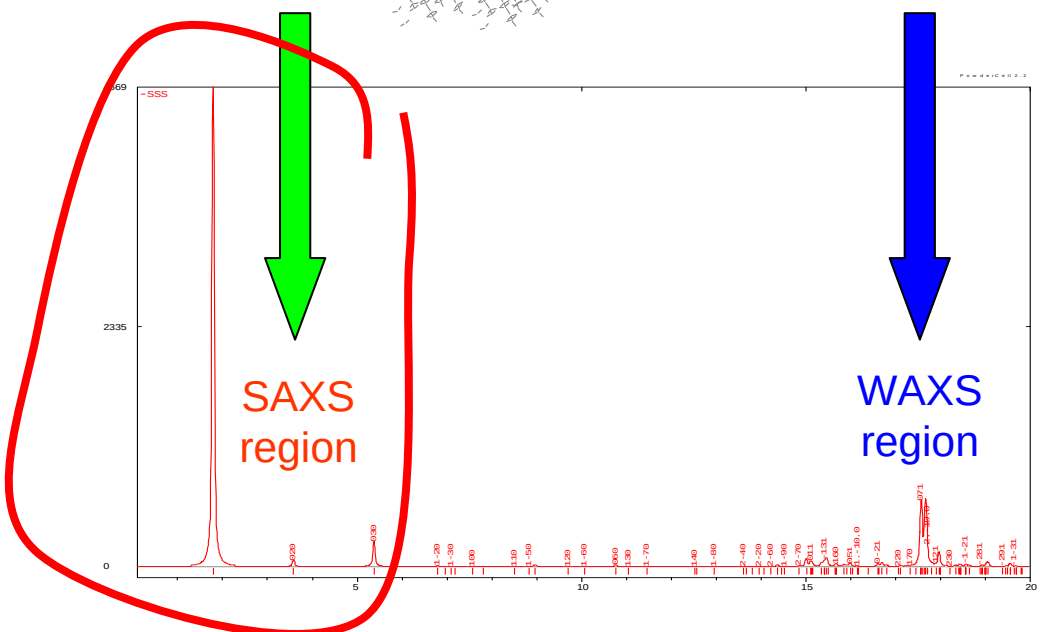
Crystal structure and X-ray powder diffraction pattern of β-tristearin (SSS)



Lamellar periodicity in the crystal structure of β-SSS



Subcell structure formed by packing of acyl chains in the crystal structure of β-SSS



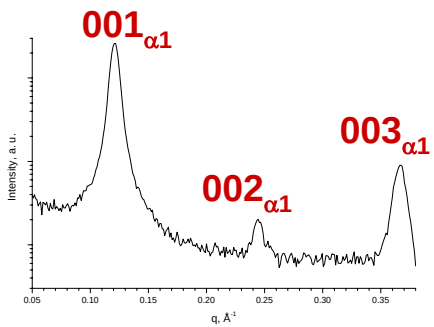
Notes. Structural data were taken from the Cambridge Crystallographic Database, published in A. van Langevelde et al., Acta Cryst. B57, 2001, p.372. Computer programme PowderCell 2.4 were used for the structural presentaton and calculations of the diffraction pattern (wavelength of X-ray radiation = 1.4Å).

Projection of the electron density along the layer normal reconstructed from X-ray scattering patterns

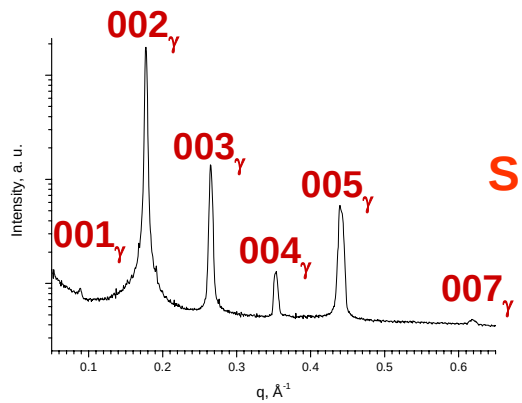
2-chain packing of triacylglycerols (2L)

3-chain packing of triacylglycerols (3L)

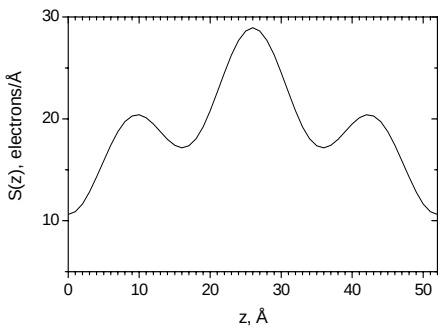
SSS



SLnS

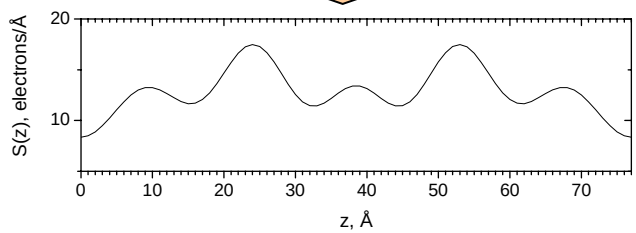


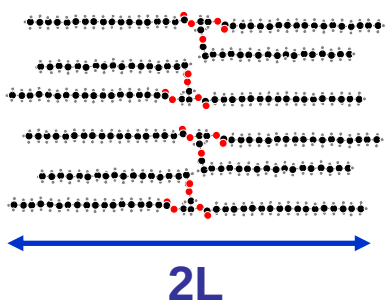
X-ray scattering pattern



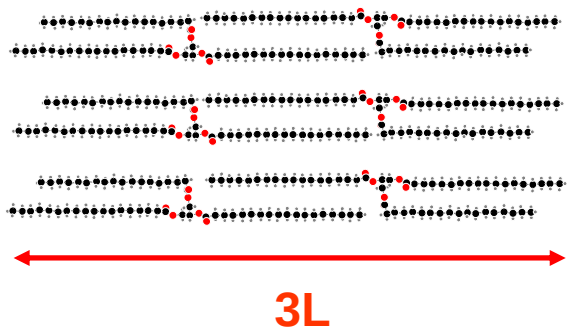
Projection of the electron density

$$S(z) = \frac{1}{L}\sum_{l=1}^{\infty} k(l)\cdot|F(l)|\cdot\cos\left(\frac{2\pi l z}{L}\right)$$

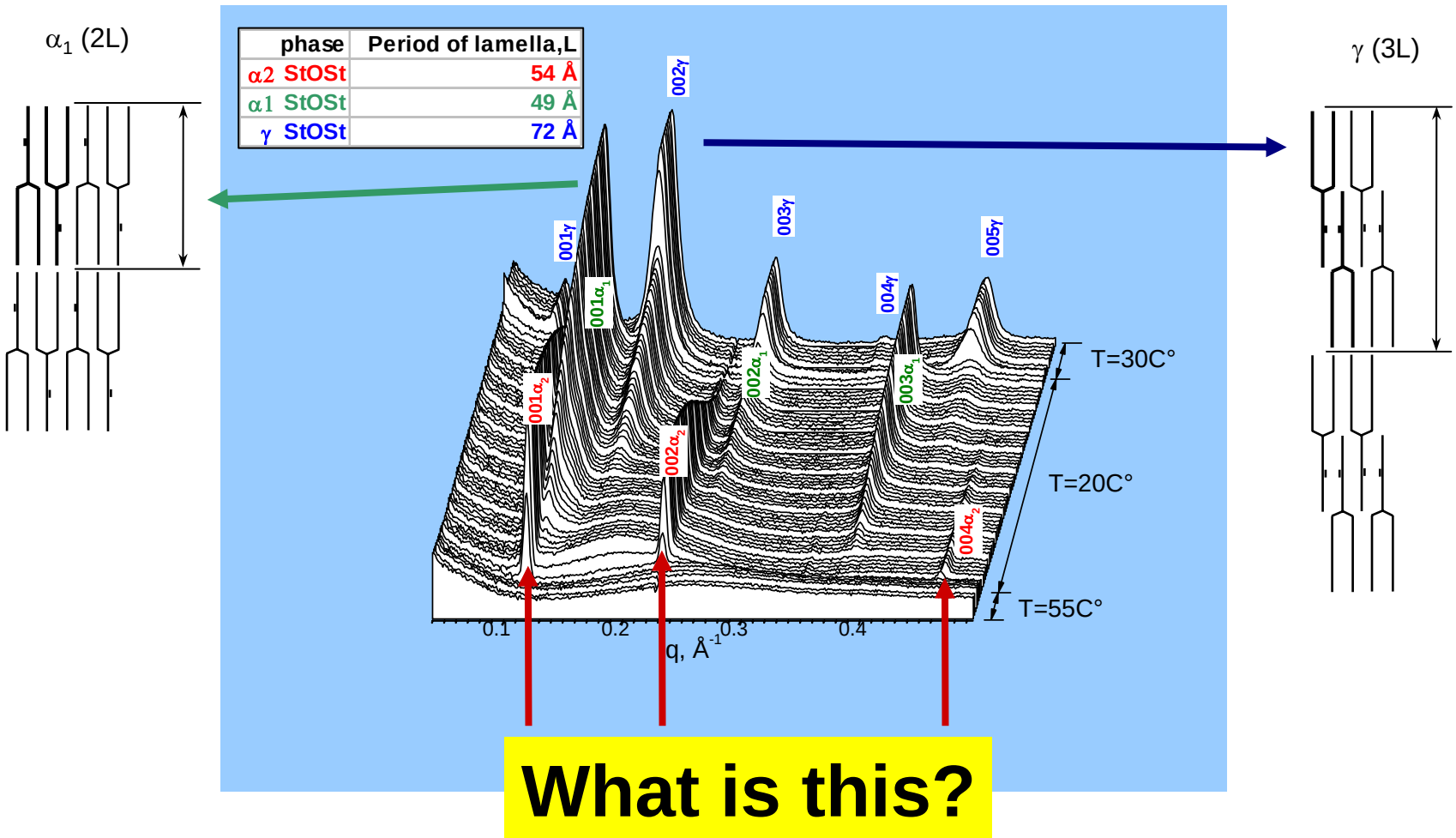




motif of packing (atomic positions)



Time resolved SAXS of isothermal crystallization of StOSt



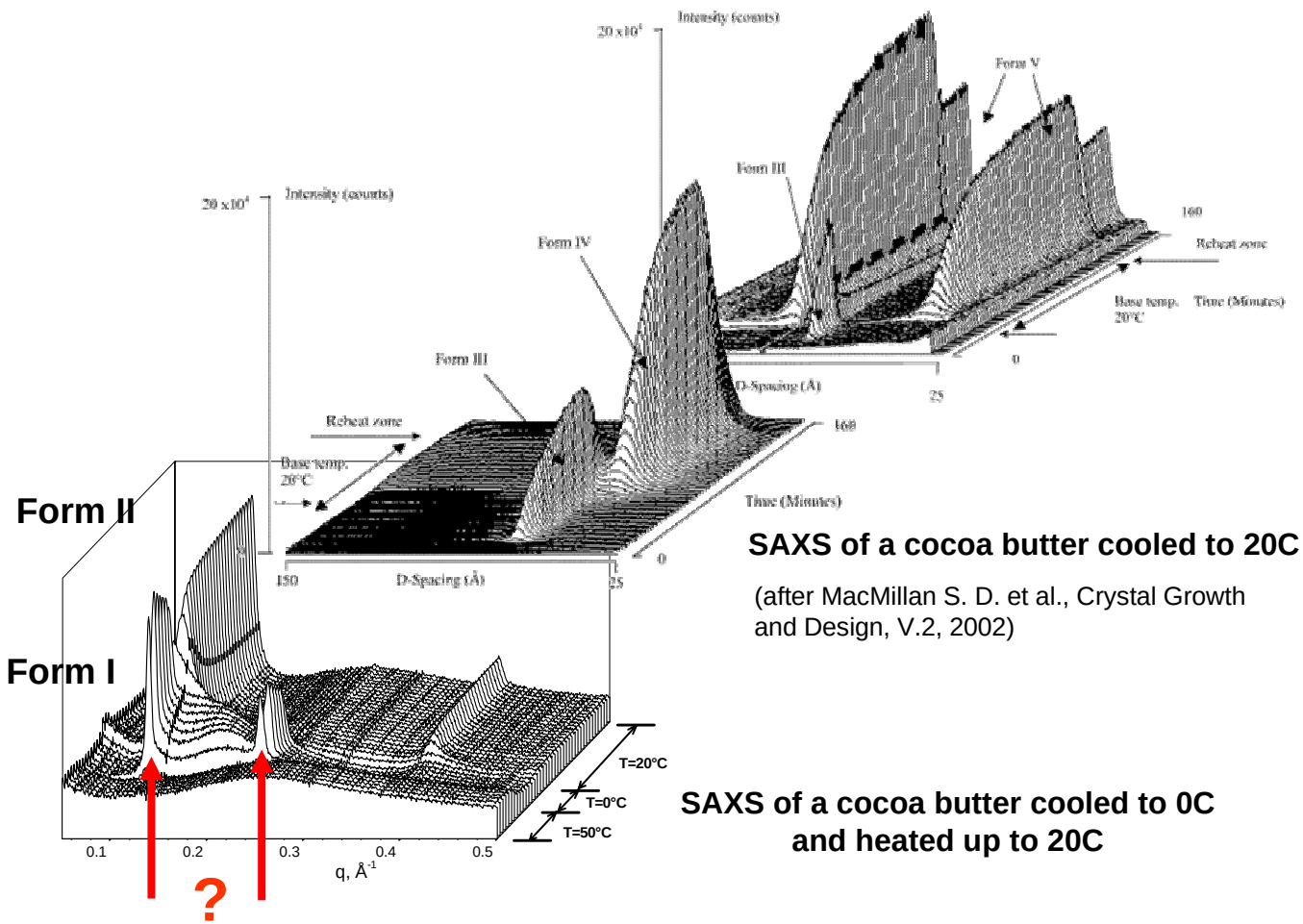
What is this?

Cocoa butter phase transitions

Cocoa butter composition

TAG	%
OLO	0.5
PLO	0.6
PLP	2.3
OOO	0.7
POO	2.5
PLSt	4.2
POP	16.3
StOO	3.4
StLSt	2.6
POSt	34.8
PPSt	1.4
StOSt	25.8
PStSt	1.3
StOAr	2.0
StStSt	0.9
Saturated TAG	3.6
Monounsaturated TAG	79.0
Polyunsaturated TAG	17.4
Total	100.0

SAXS of a cocoa butter cooled to 20C with a shear rate of 3 s^{-1}

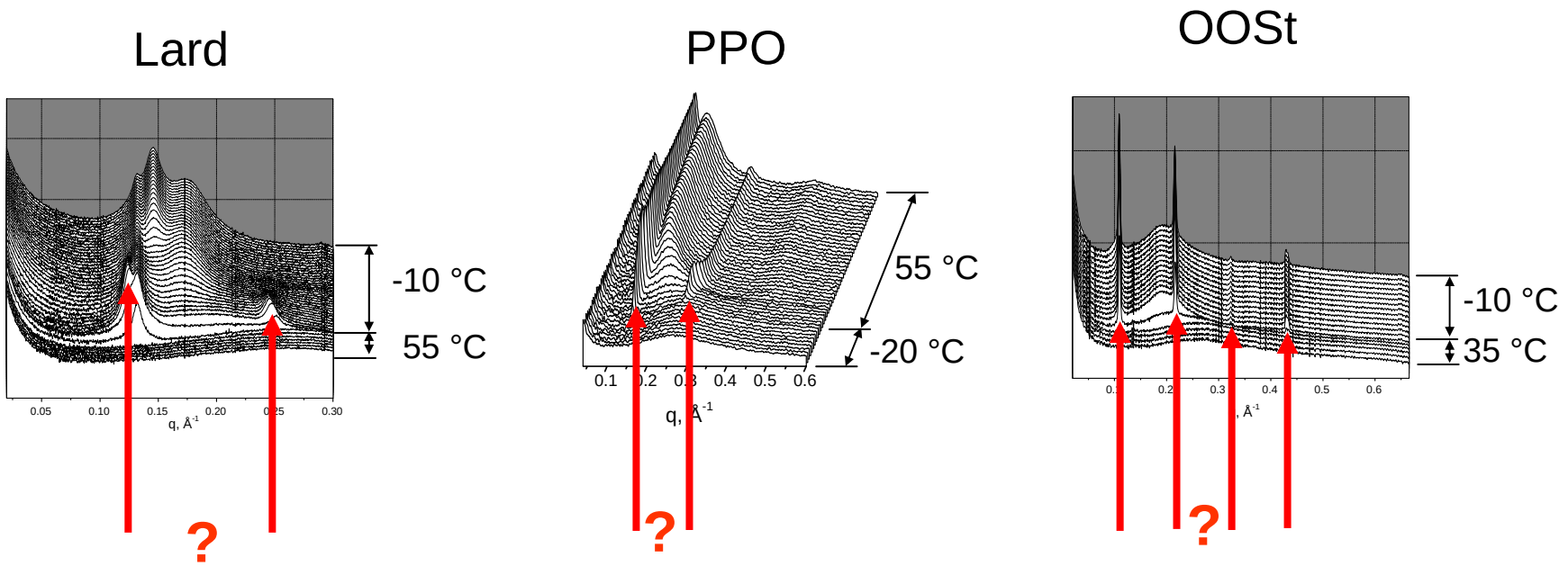


SAXS of a cocoa butter cooled to 20C

(after MacMillan S. D. et al., Crystal Growth and Design, V.2, 2002)

SAXS of a cocoa butter cooled to 0C and heated up to 20C

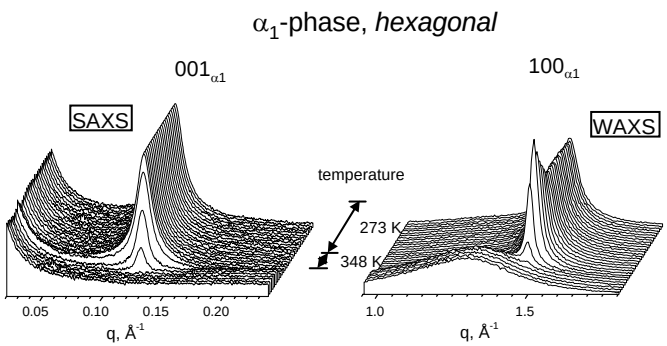
Isothermal crystallization of triacylglycerols (time resolved SAXS)



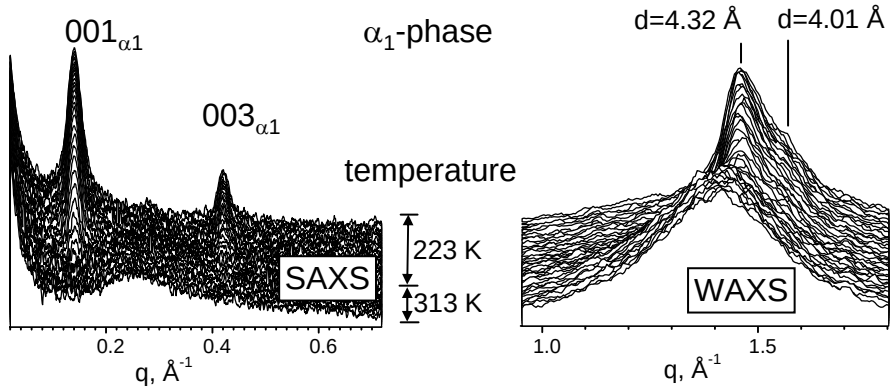
This phase are restricted to pure TAGs containing both saturated and unsaturated acyl chains or mixtures thereof including natural fats

Isothermal crystallization of triacylglycerols with C18 acyl chains (time resolved SAXS)

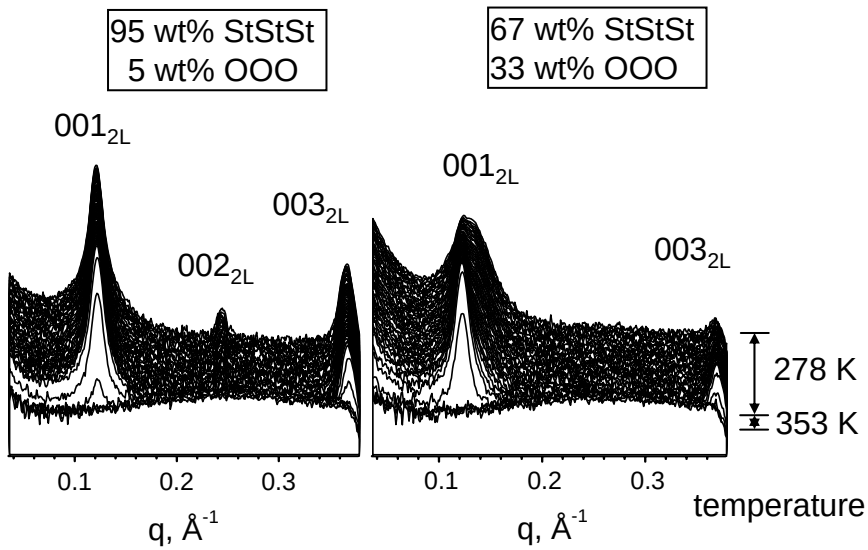
All chains are saturated: Tristearin (StStSt)



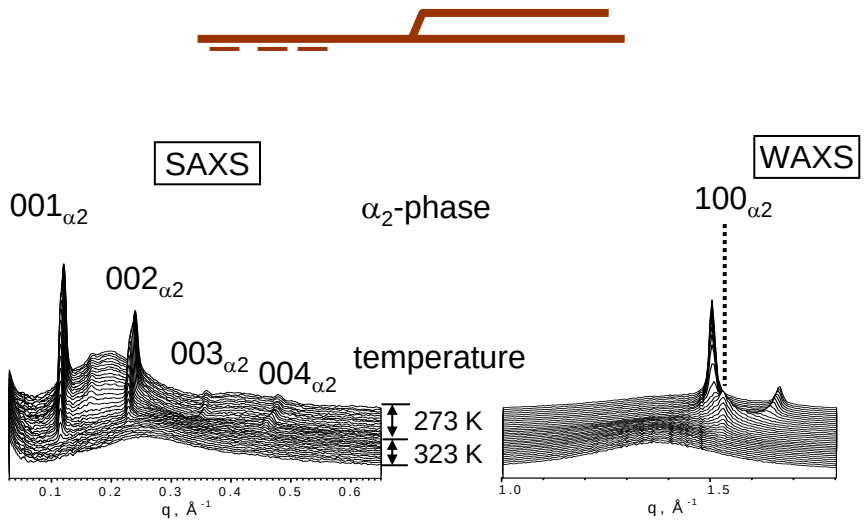
All chains are unsaturated: Triolein (OOO)



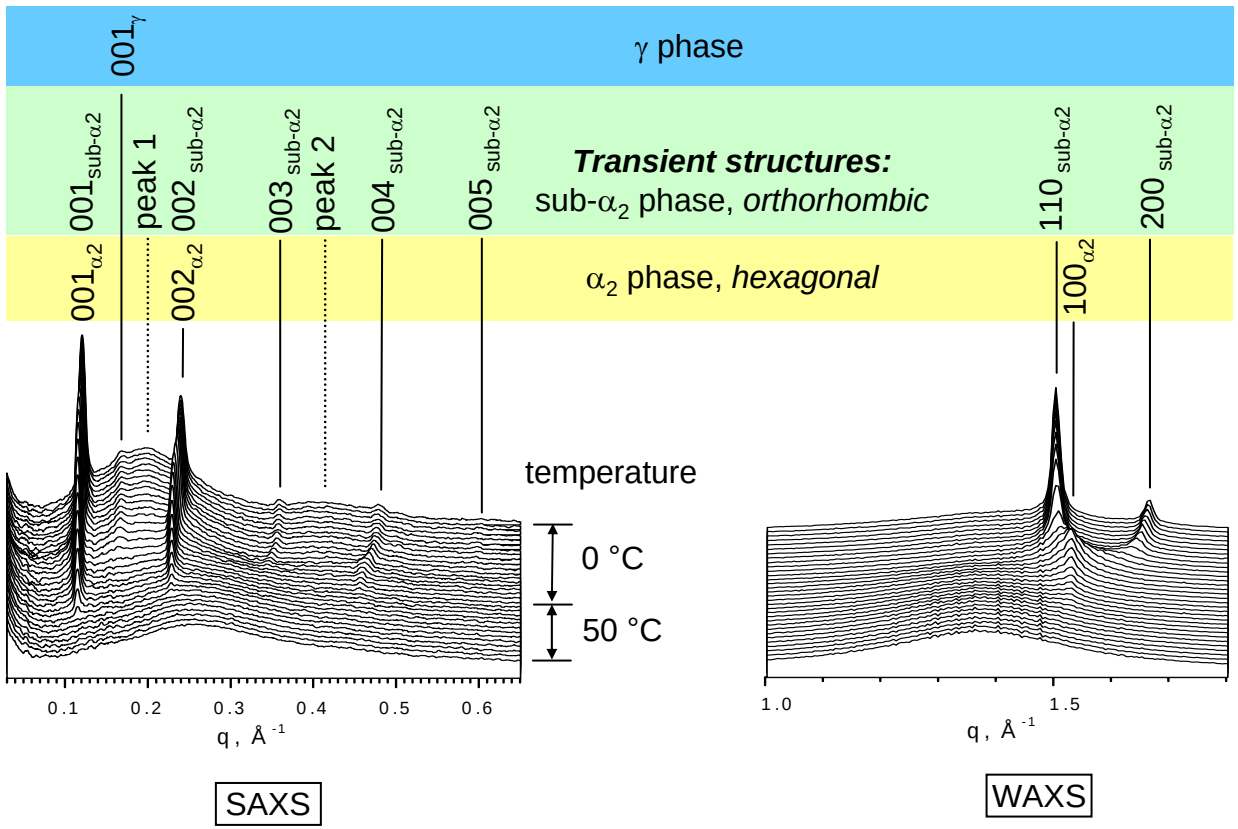
Blends StStSt + OOO



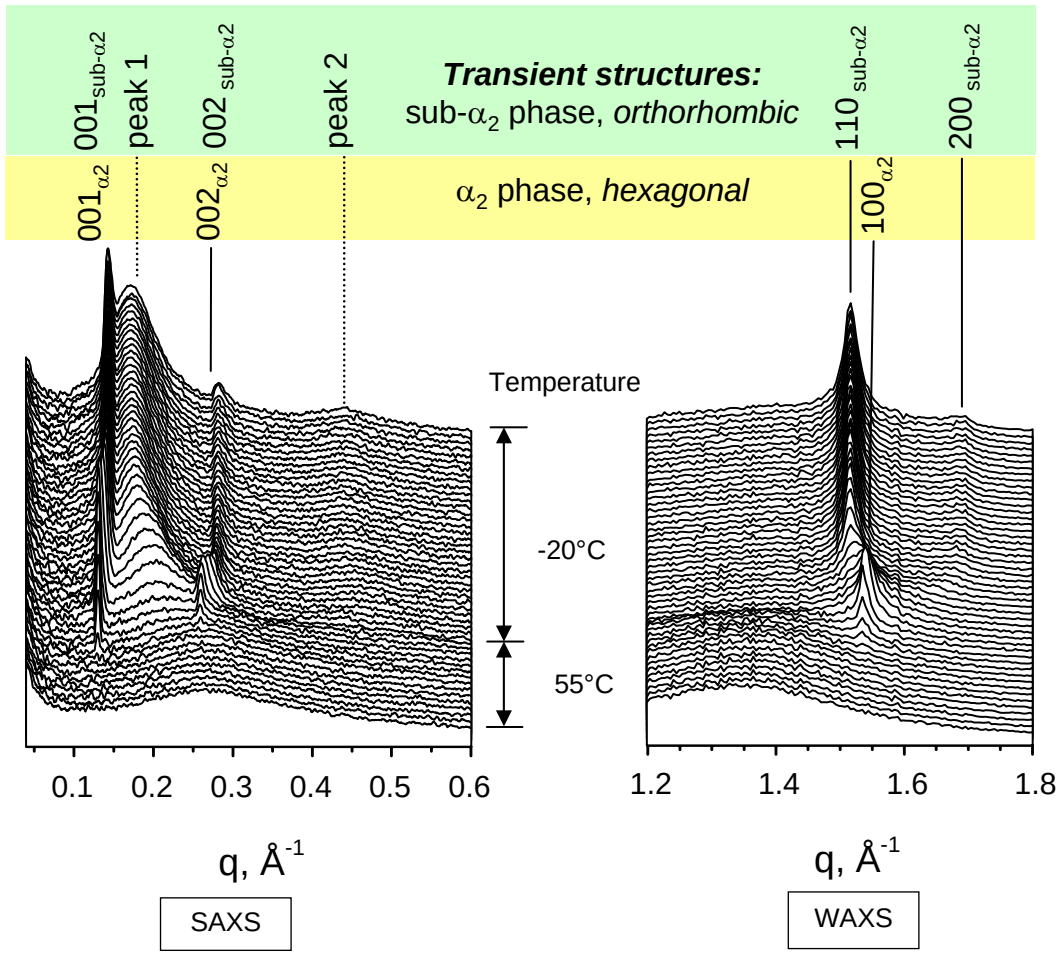
Saturated and unsaturated chains: StLnSt



Isothermal crystallization of StLnSt



Isothermal crystallization of PPO



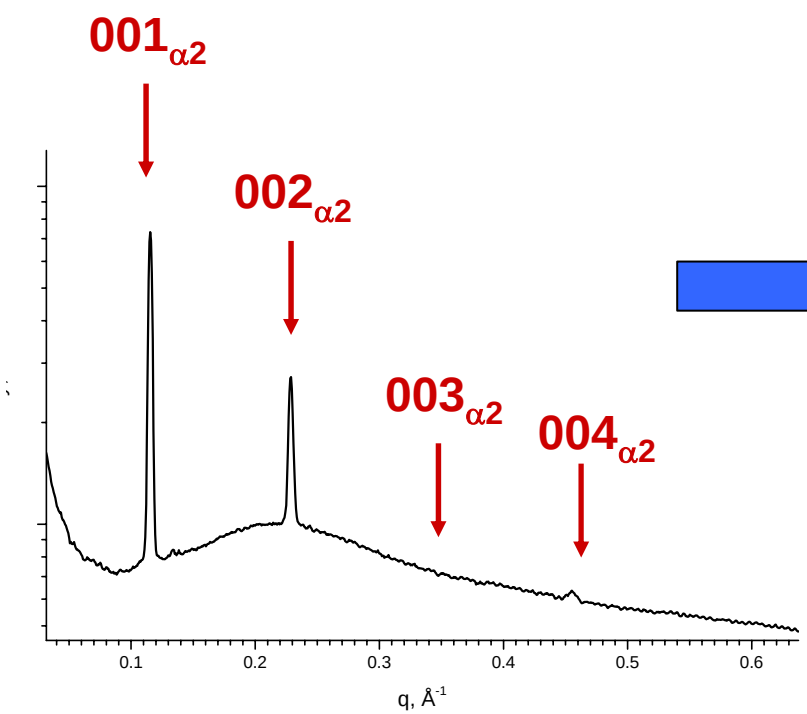
after Mykhaylyk et al, J. Appl. Cryst., 2007, p. s297.

The evolution of the structural characteristics of the α_2-phase

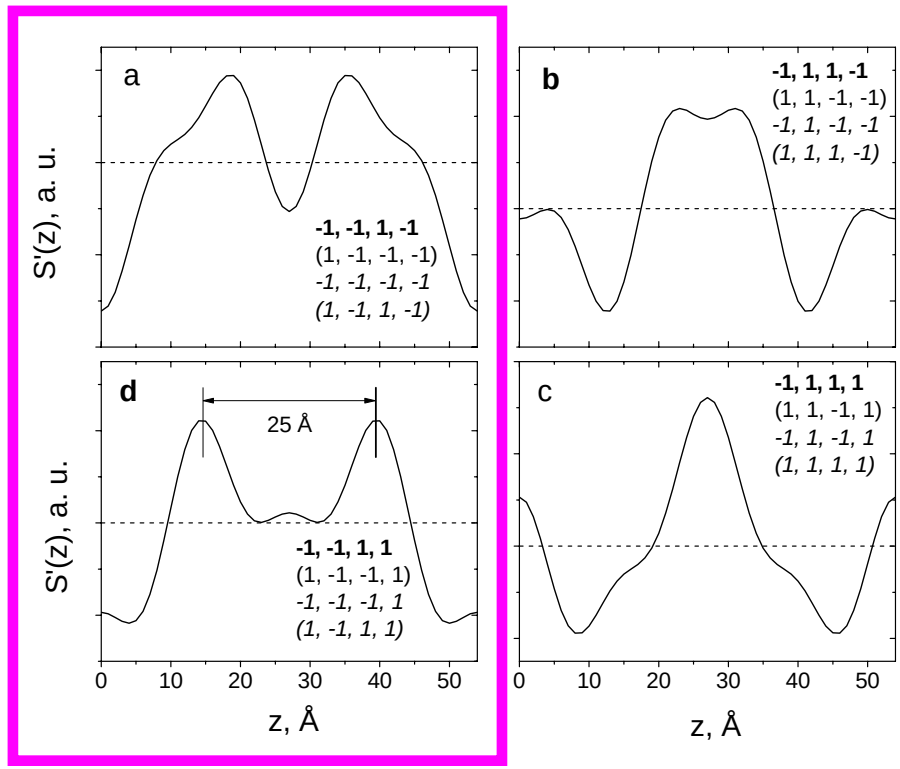
TAG	Initial stage		Final stage		Conditions of quenching
	L, Å	*d*, Å	*L*, Å	*d*, Å	
StOSt	54.3	4.09	51.5	4.20, 3.80	55 °C → 20 °C
POP	52.0	n/a	n/a	n/a	50 °C → -20 °C
StLnSt	54.4	4.11	52.5	4.13, 3.69	40 °C → -10 °C
PLnP	51.9	4.10	49.9	4.17, 3.76	60 °C → -5 °C
OOSt	57.4	4.11	57.4	4.11	35 °C → -10 °C
PPO	48.0	4.09	42.8	4.14, 3.72	55 °C → -20 °C

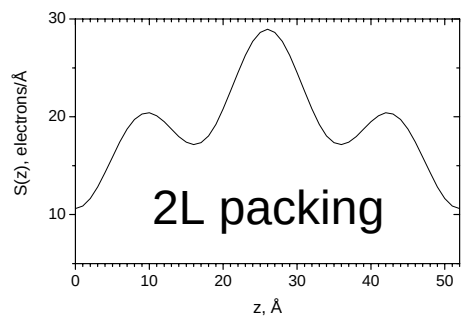
after Mykhaylyk et al, J. Appl. Cryst., 2007, p. s297.

Four groups of projections of the electron density profile on the layer normal



SAXS pattern of α_2-StOSt



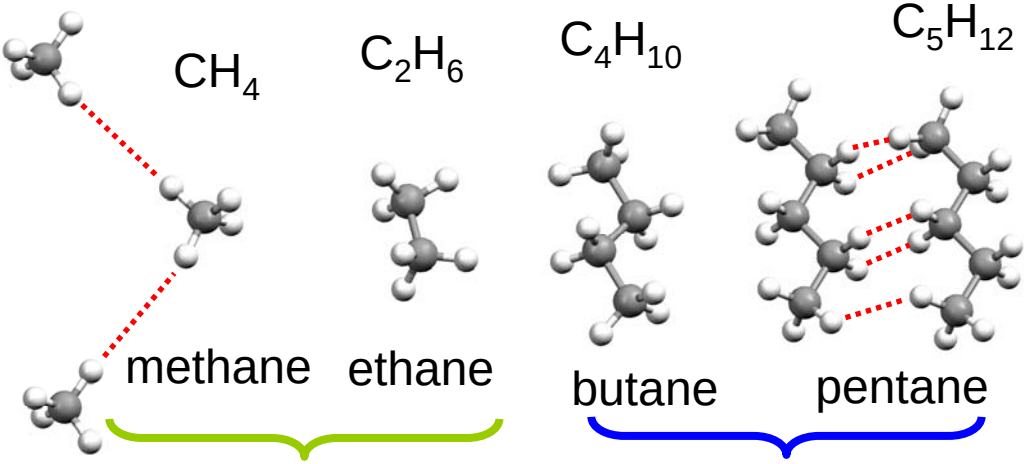


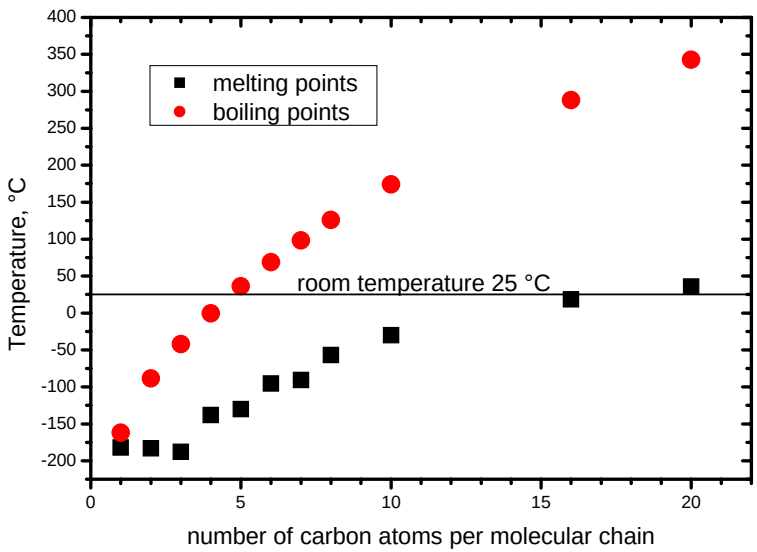
Two important observations!

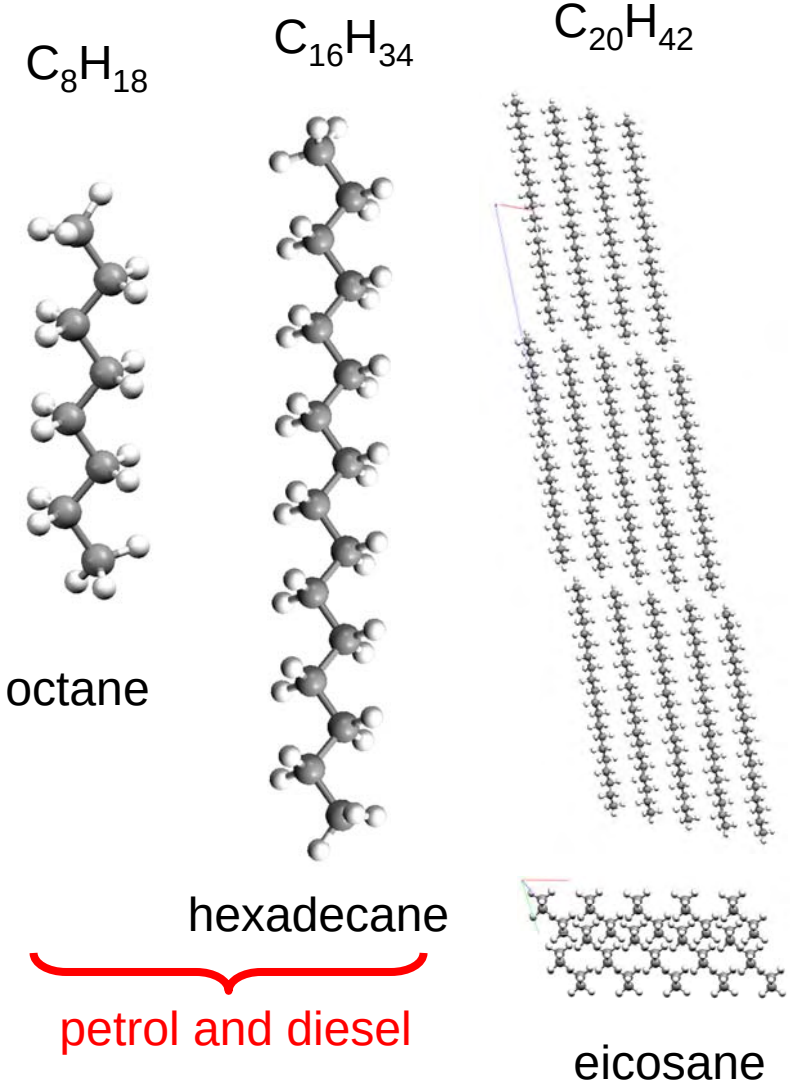
- The α_2-phase forms during quenching from the melt; therefore, the structural organization of this phase should resemble supramolecular ordering of triacylglycerols in the melt
- This phase is observed only in mixed saturated/unsaturated triacylglycerols

What do we know about liquid alkanes?

Alkane in gas, liquid and solid state



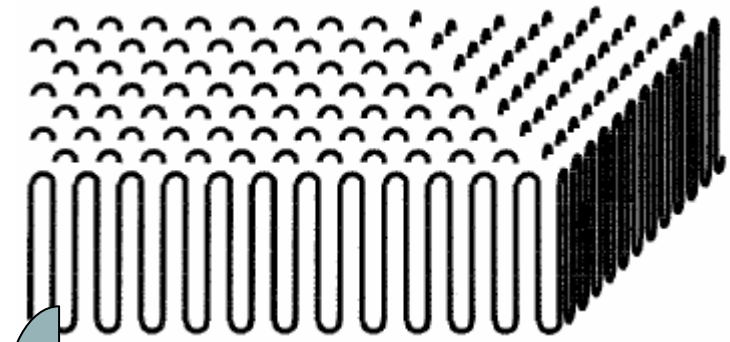


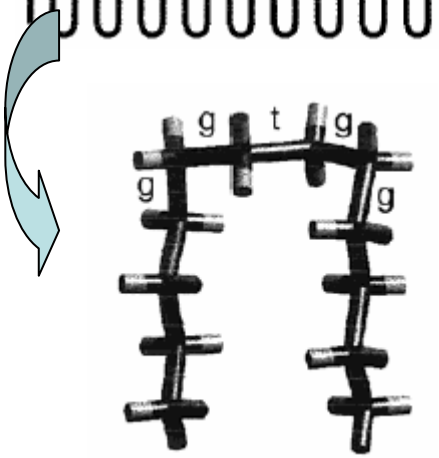


Alkanes are non-polar only weak intermolecular forces act between the alkane molecules

Folding of polymer chains

Schematic drawing of
a chain-folded polymer crystal
(after Ungar G. & Zeng X.,
Chemical Reviews, V. 101, 2001)





Chain conform. / Paraffin	E	F2	F3	F4	F5
C102	+				
C150	+	+			
C198	+	+	+		
C246	+	+	+	+	
C294	+	+	+	+	
C390	+	+	+	+	+

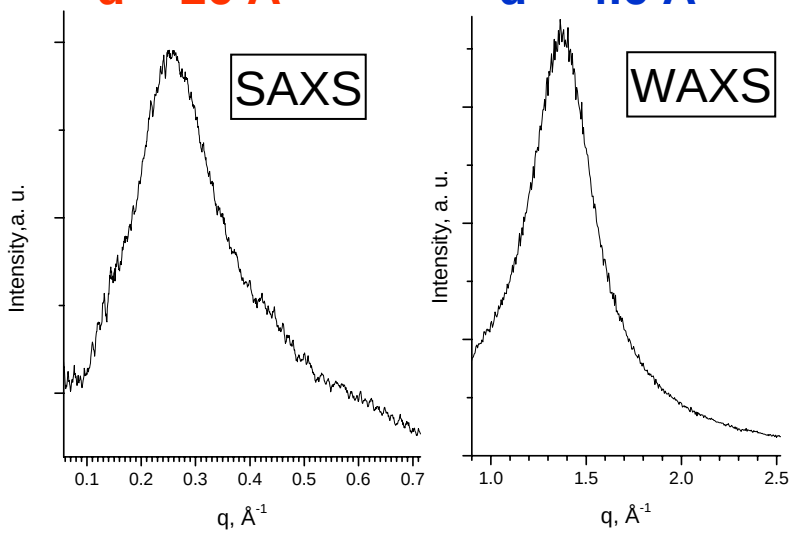
Integer folded forms observed in long *n*-alkanes, for a given alkane more folds per molecule can be obtained with increasing supercooling.

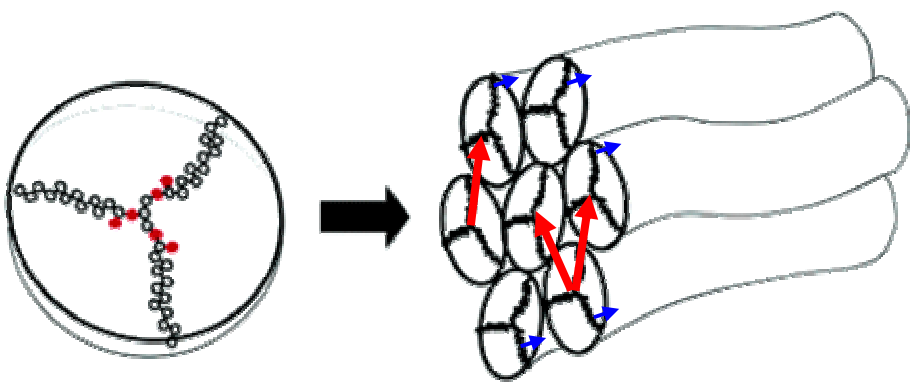
Structure of the chain fold in crystalline monoclinic cycloalkane *c*-(CH2)34
(after Kay H. F. & Newman B. A., Acta Cryst., B24, 1968)

Models for supramolecular ordering in liquid triacylglycerides

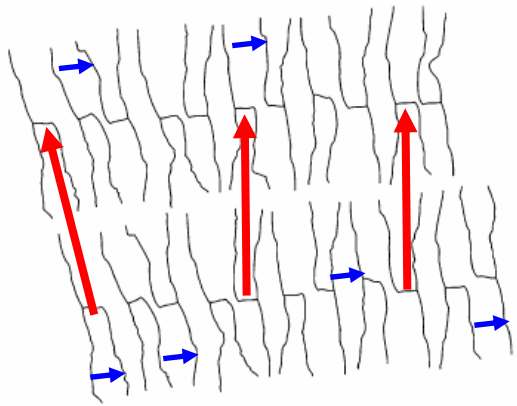
StLnSt in a liquid state at 50 °C

d ~ 26 Å **d ~ 4.6 Å**

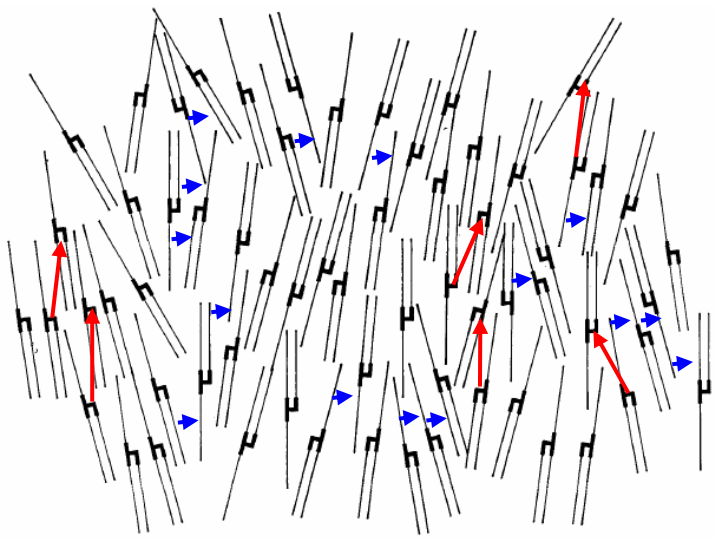




Discotic model by Corkery et al, 2007



Smectic model by Larson, 1972

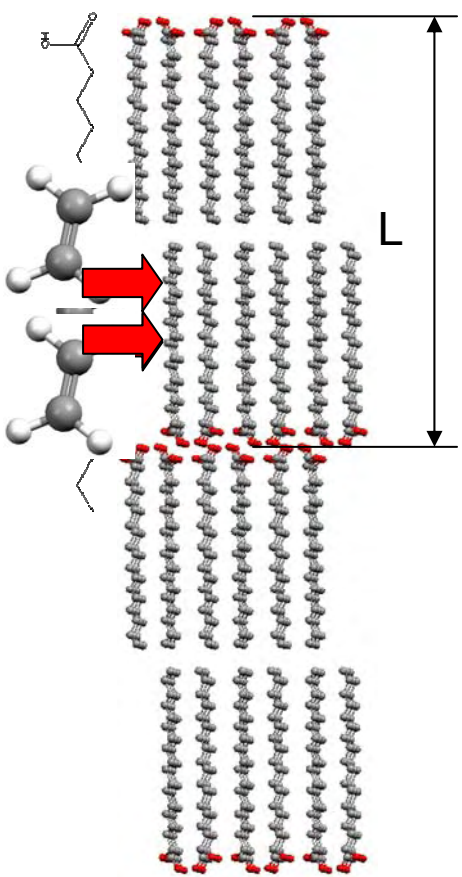


Nematic model by Cebula et al, 1992

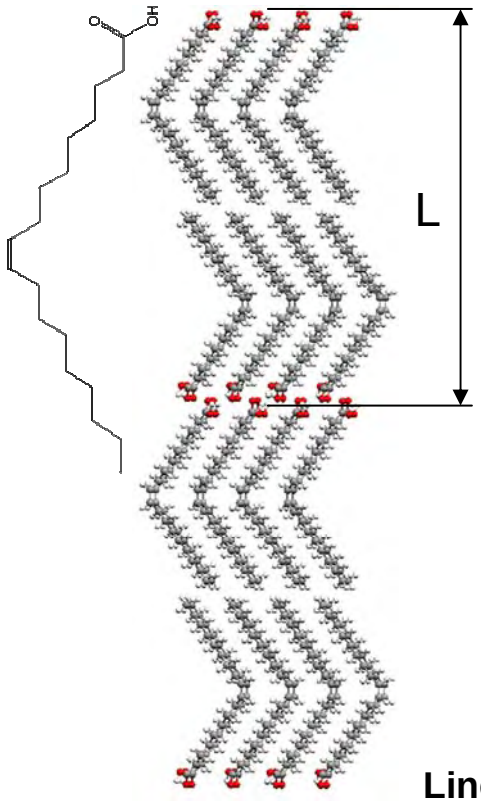
What do we know about unsaturated C–C bonds in alkyl chains?

Fatty acids

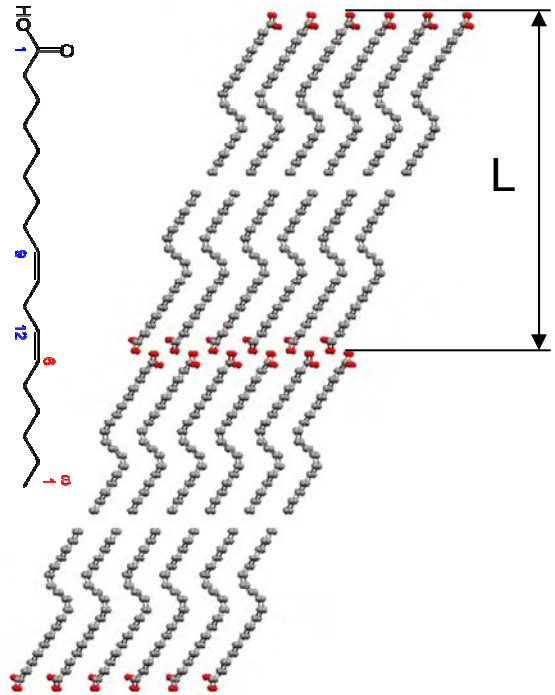
Stearic acid
$C_{18}H_{36}O_2$



Oleic acid
$C_{18}H_{34}O_2$



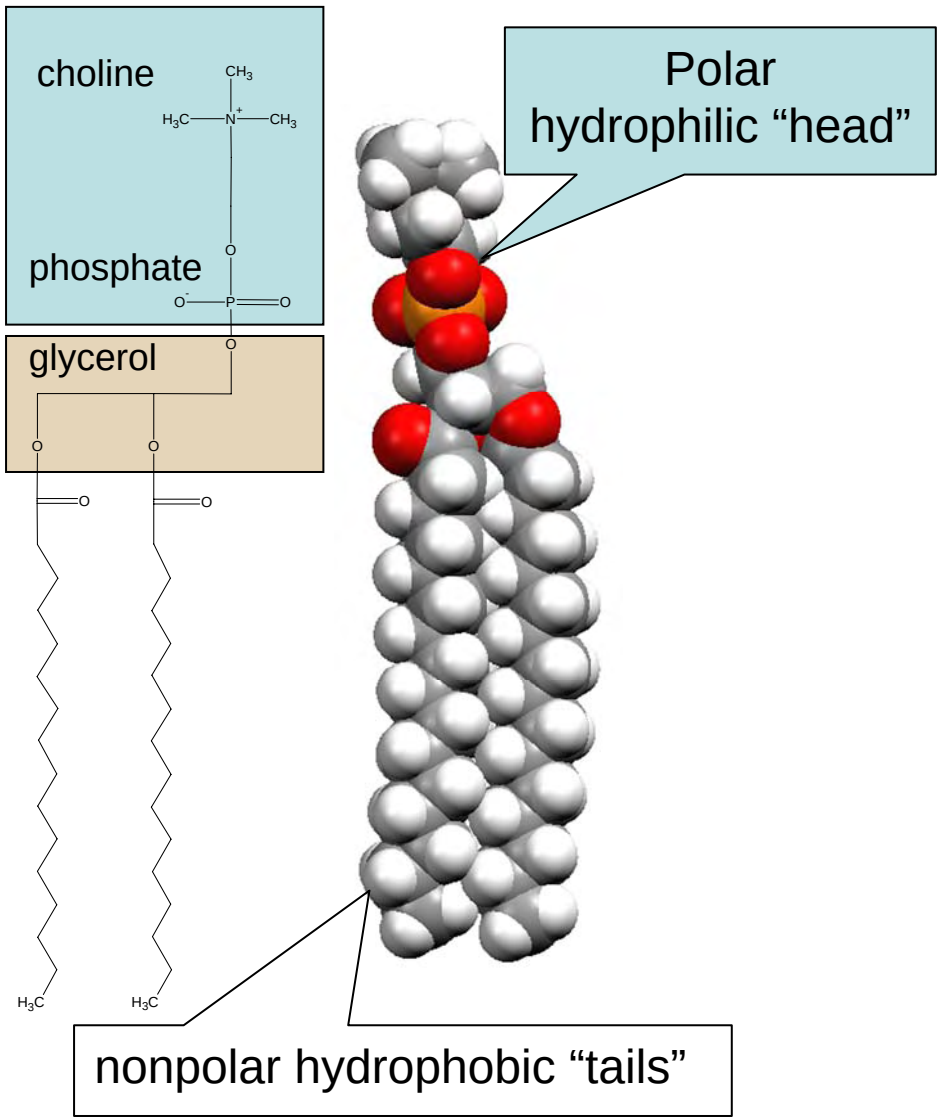
Linoleic acid (ω-6)
$C_{18}H_{32}O_2$

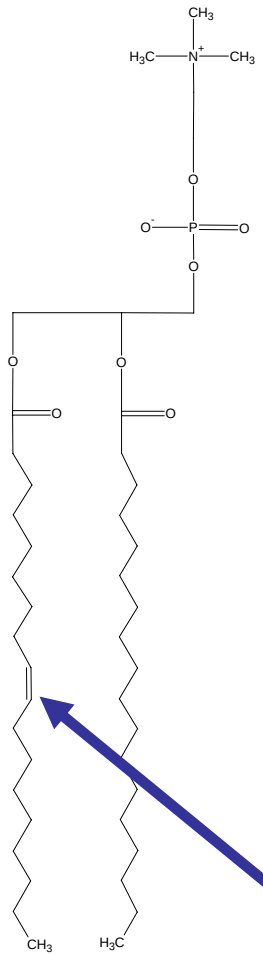


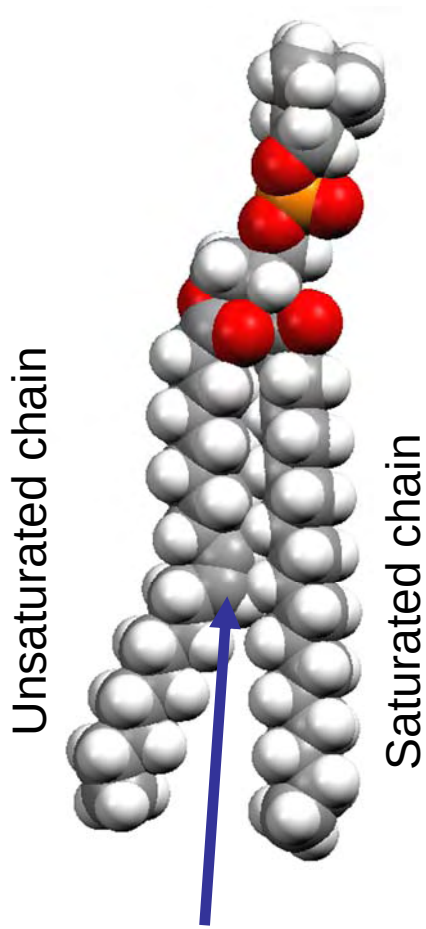
Linoleic acid (ω-6) is one of the two **essential fatty acids** (the other is **alpha-linolenic acid,** ω-3) that humans require. They are "essential" because they can not be produced by the human body.

Phospholipids

Phosphatidyl choline (lecithin)

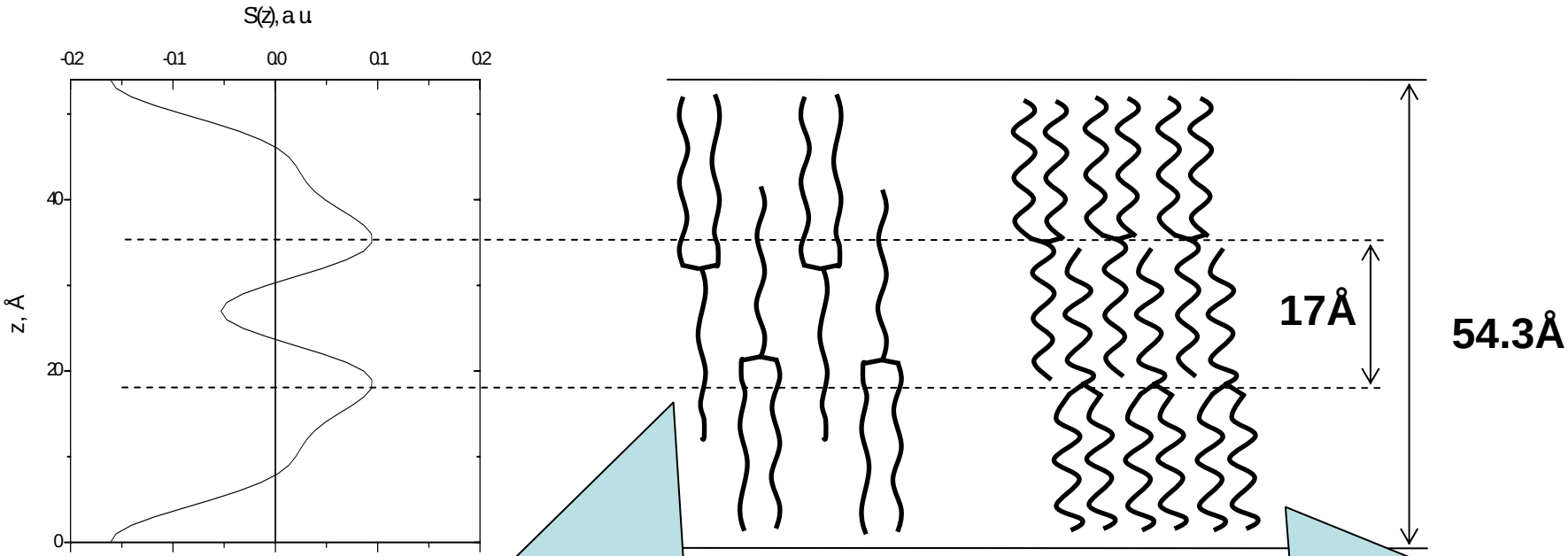






A double bond makes an unsaturated chain
The kink (or kinks) prevent close packing

Considering the group a)



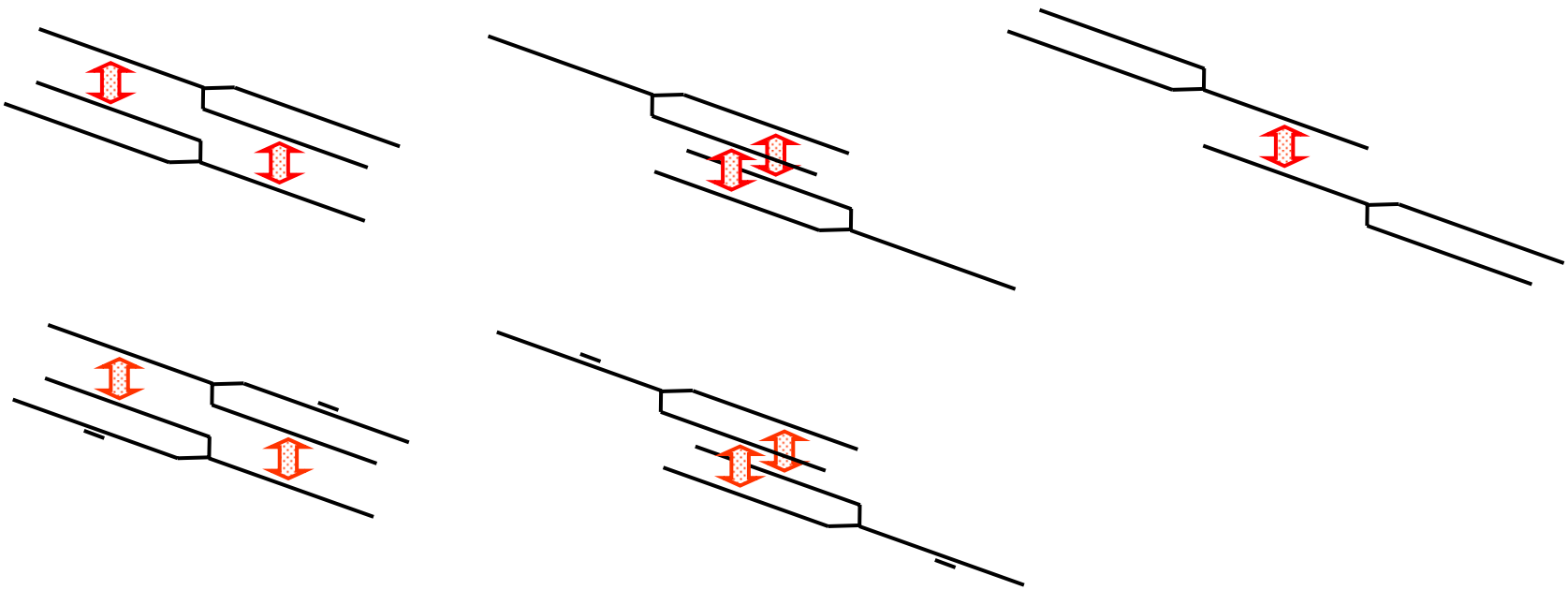
-The position of the glycerol residues does not match the distance measured from the electron density profile;
-The structure has the mass density far below the mass density of the liquid state

-The mass density of the structure is very large (~1.4 g/cm^3);
-Acyl chains are not straight;
-Hexagonal packing of the acyl chains within the layer is unlikely

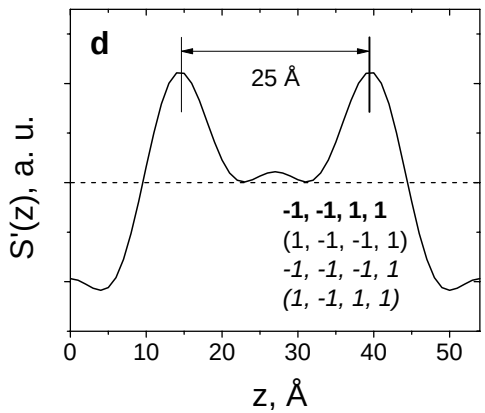
Possible dimeric units in liquid triacylglycerols

Four chains interaction

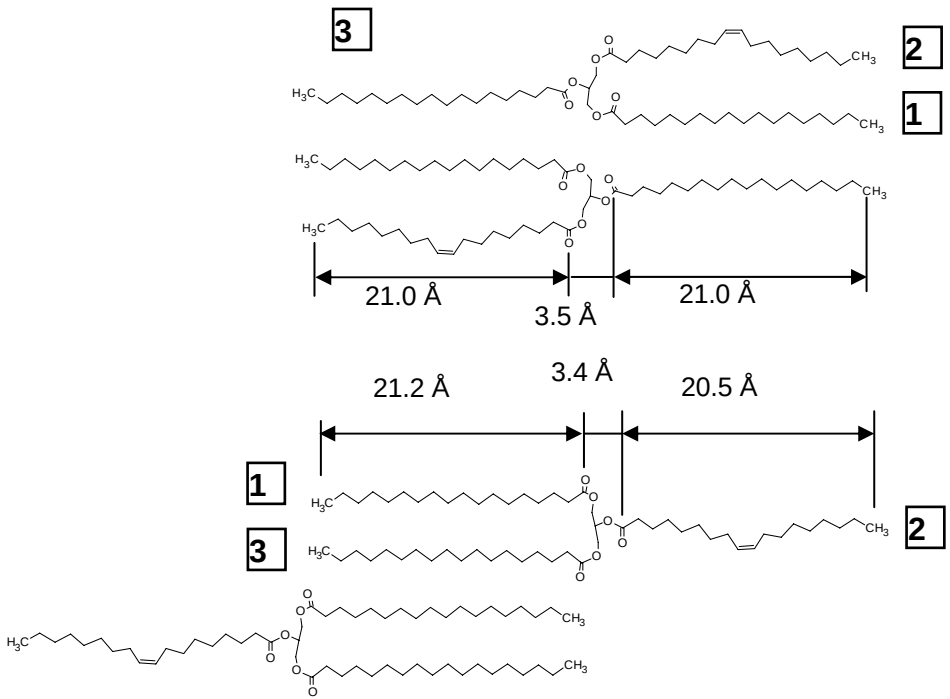
Two chains interaction



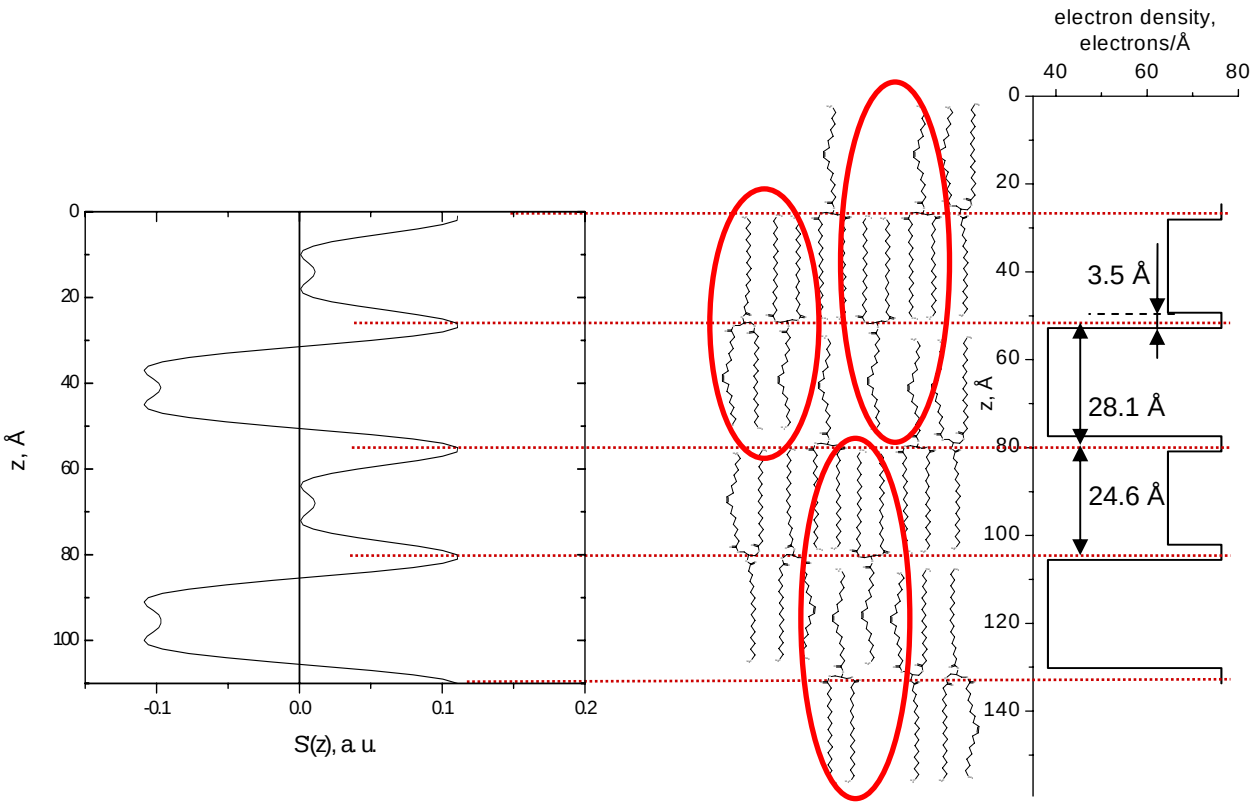
Considering the group d)



Representative models of packing of StOSt molecules in dimers (projections onto the slide plane), which is likely to be formed in the liquid state before the formation of the α_2-phase



A model of packing of the StOSt molecules in the layers of the α_2-phase



Scattering patterns of liquid crystals

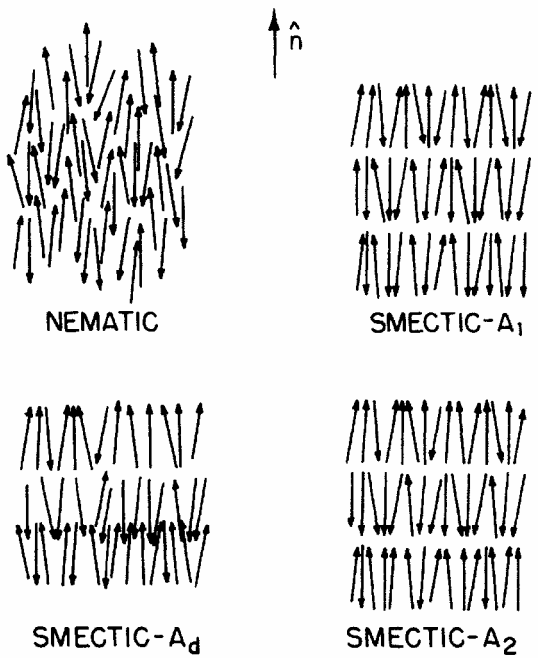


FIG. 1. Schematic representation of the polar nematic and smectic-A phases. The molecules are drawn as thin rods with an arrow on one end to denote the lack of inversion symmetry produced by an off-center dipole.

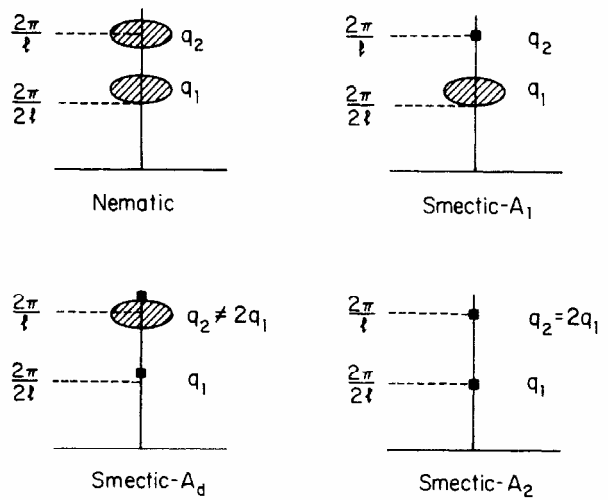
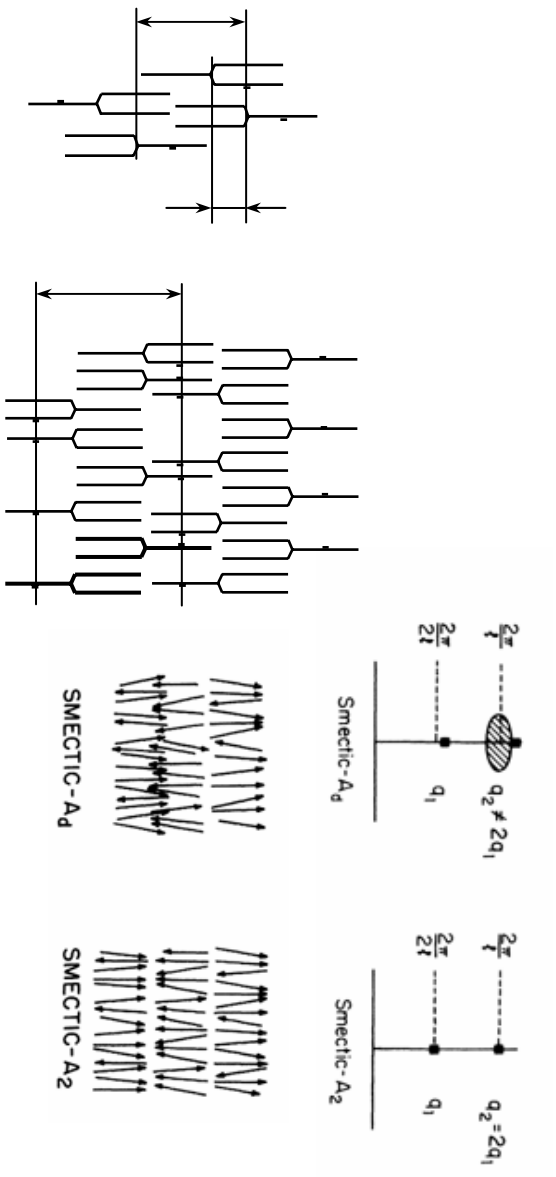
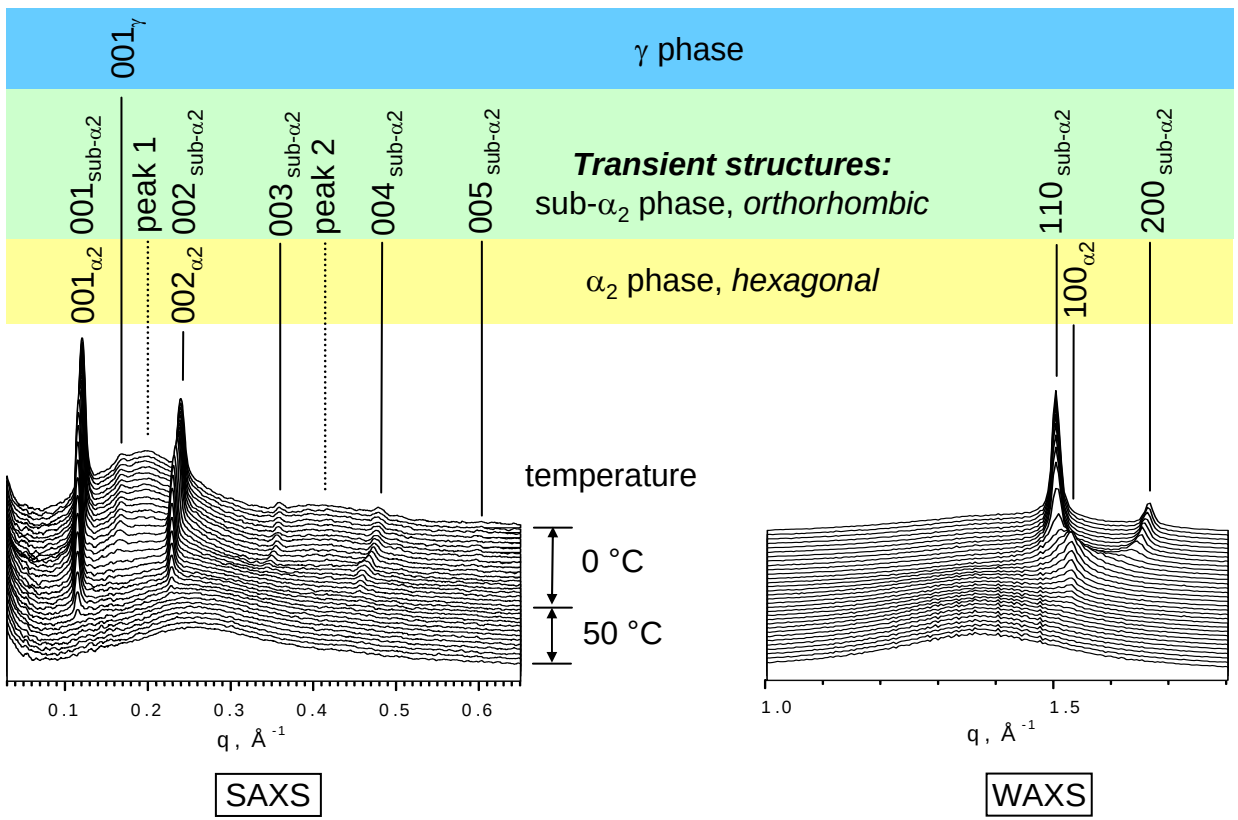


FIG. 2. Diffraction patterns of the polar nematic and smectic-A phases. The vertical axis indicates the q_z direction and the horizontal axis indicates the $q_x q_y$ plane. The small solid squares denote Bragg-like spots and the large ellipses denote diffuse spots. The monolayer ordering ($d = l$) produces the scattering at q_2 and the dipolar ordering ($l < d \leq 2l$) produces the scattering at q_1.

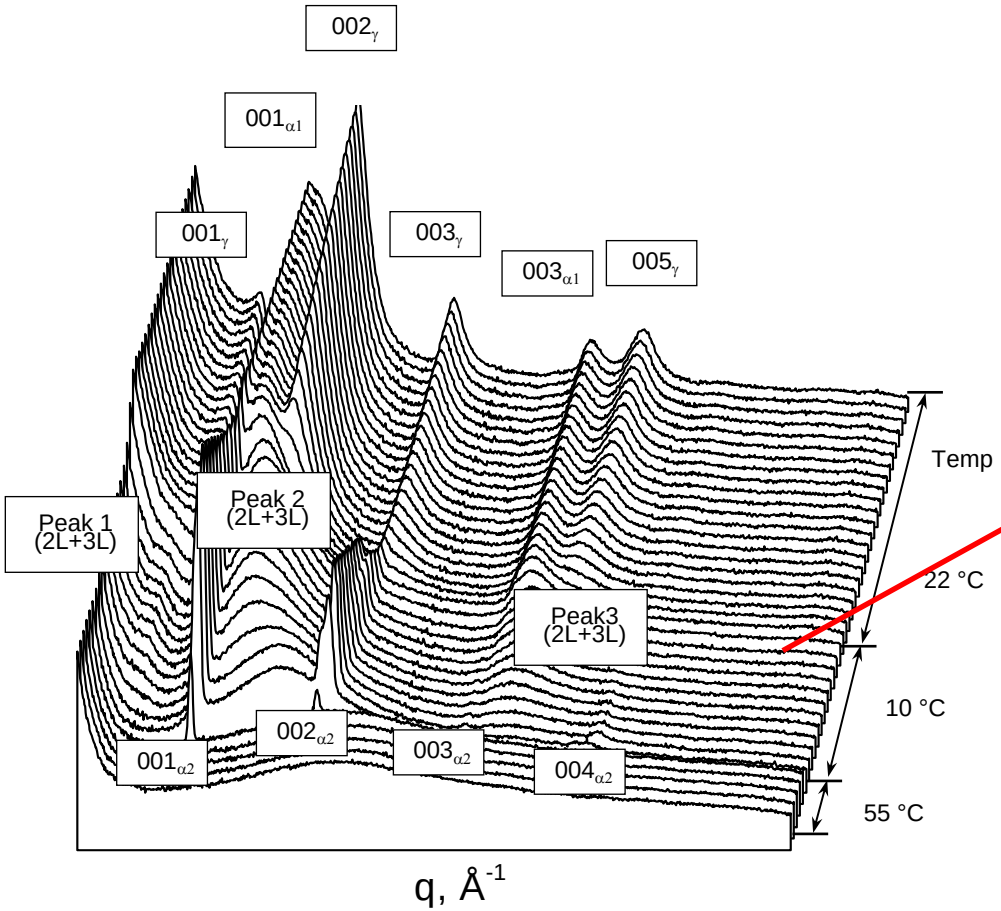
K. K. Chan et al, Phys. Rev A, V. 34, 1986, p. 1420

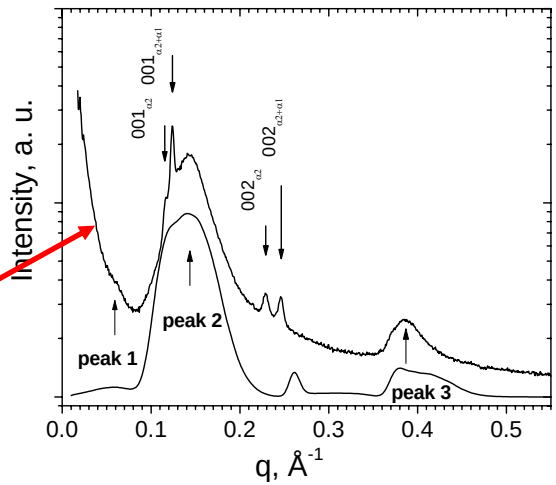
Isothermal crystallization of StLnSt



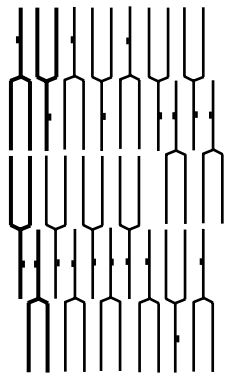


2L+3L transient structure





2L+3L



Simulated and experimental SAXS patterns of random 2L+3L StOSt structure

The experimental SAXS pattern of StOSt isothermal crystallization at 10 °C from the melt (55 °C)

after Mykhaylyk et al,
J. Appl. Cryst., 2007, p. s297

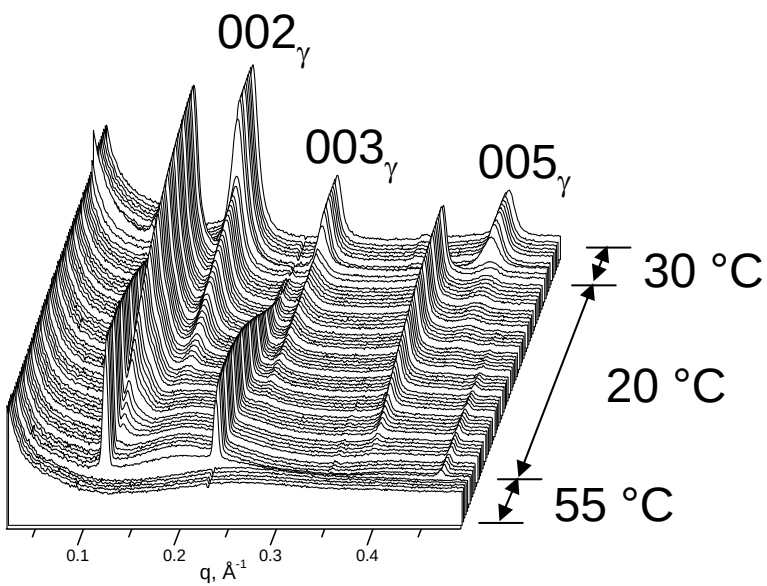
Can we make use of this finding about structural transformations in triacylglycerols?

α_2-phase is a distinctive property of mixed saturated/unsaturated triacylglycerols. It may be possible to find conditions when this property can be effectively used in fat fractionation.

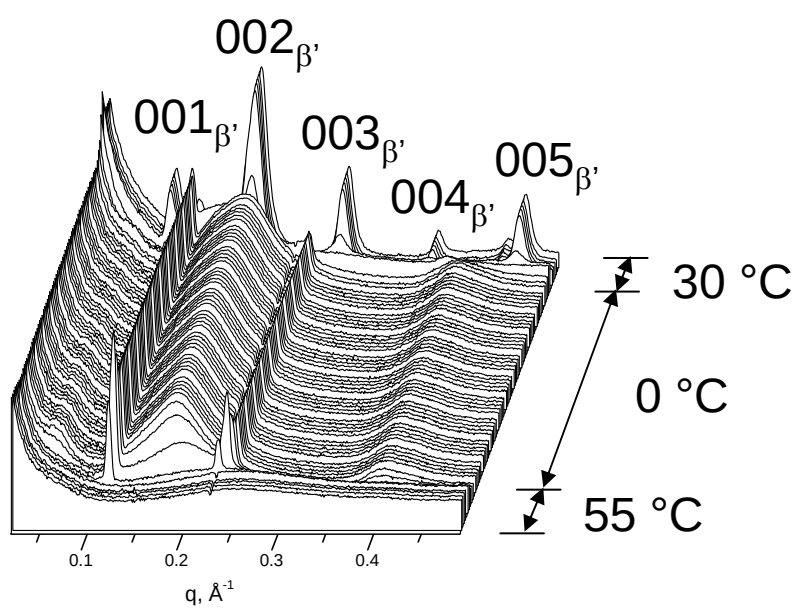
Transient structures of α_2-phase can be used to control polymorphic transformations of triacylglcerols.

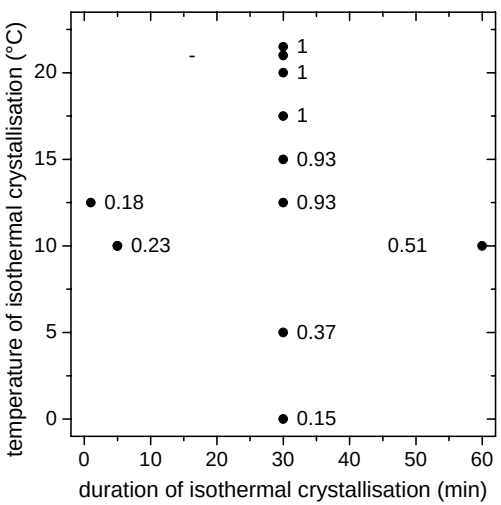
Polymorphic transformations of StOSt

Liquid → α_2 → α_1 + γ → γ



Liquid → α_2 → sub-α_2 → β' + γ





γ phase fraction in StOSt crystallized at 30 °C after isothermal crystallization at different temperatures for a certain duration.

after Mykhaylyk & Hamley, J. Phys. Chem., 2004, p. 8069

Conclusions

- Transient phases are identified in mixed saturated/unsaturated triacylglycerols or their mixtures. The transient phase formation is caused by a mismatch between saturated and unsaturated acyl chains followed by their separation in the melt
- These phases resembles smectic A_2 liquid crystal phases
- Reduction of the longitudinal diffusion of the molecules at low temperatures freezes the molecular motion and makes unsaturated bonds to be terminal points causing formation of interdigitated phases similar to smectic A_d liquid crystal phases
- At certain conditions dictated by molecular structure the transient phases can develop into other structures such as 2L+3L during StOSt isothermal crystallization
- The structural state of the transient phases effect further polymorphic transformations of triacylglycerols at high temperatures

Acknowledgements