The Role of Physical Properties Data in Product Development

From Molecules to Market

Gent June 18th and 19th 2008

Eckhard Flöter Unilever R&D Vlaardingen

Physical Properties Data

- Melting point, heat of fusion, solubility
- Crystallization behaviour characeristics
  - Kinetics
  - Polymorphic form
  - Habit, seize and shape
- Mixing behaviour, molecular interactions

- Purity
- Others: specific heat, density, diffusivity, ...

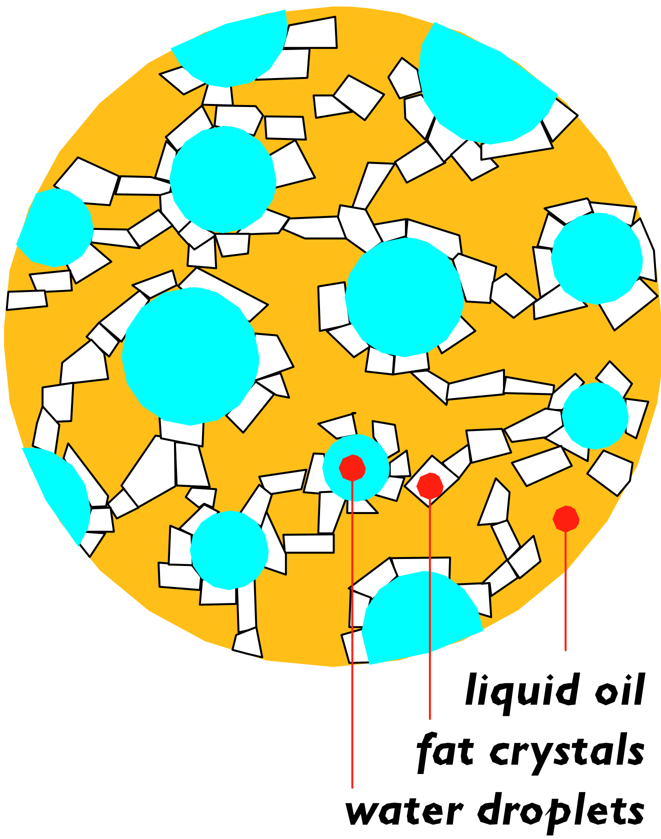
- We have little and no overall compilation

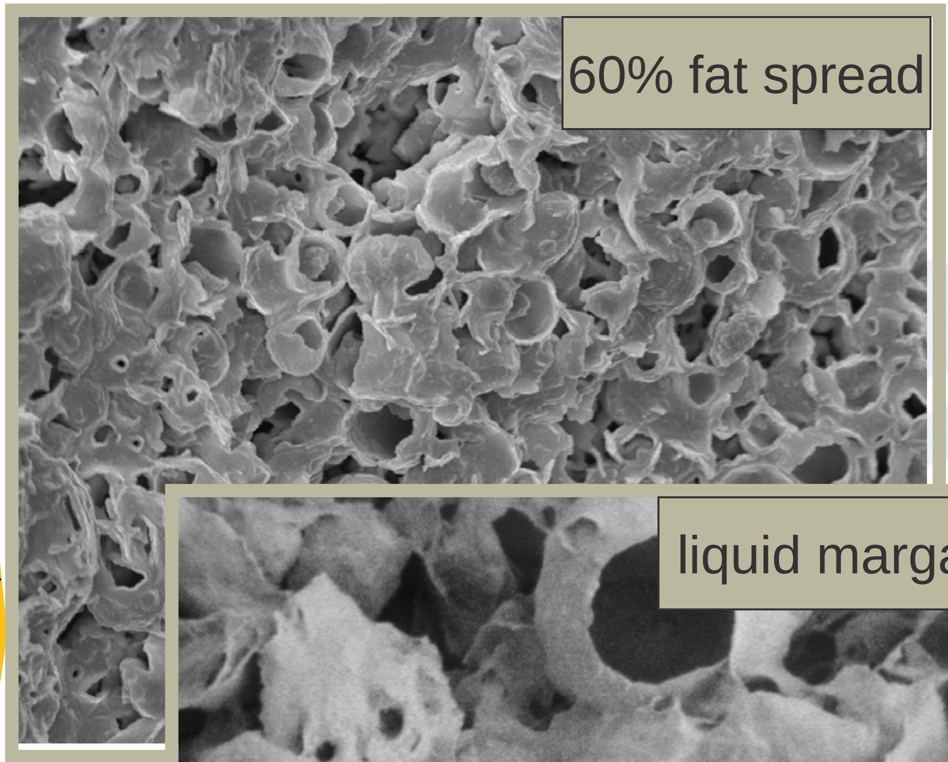
Intro

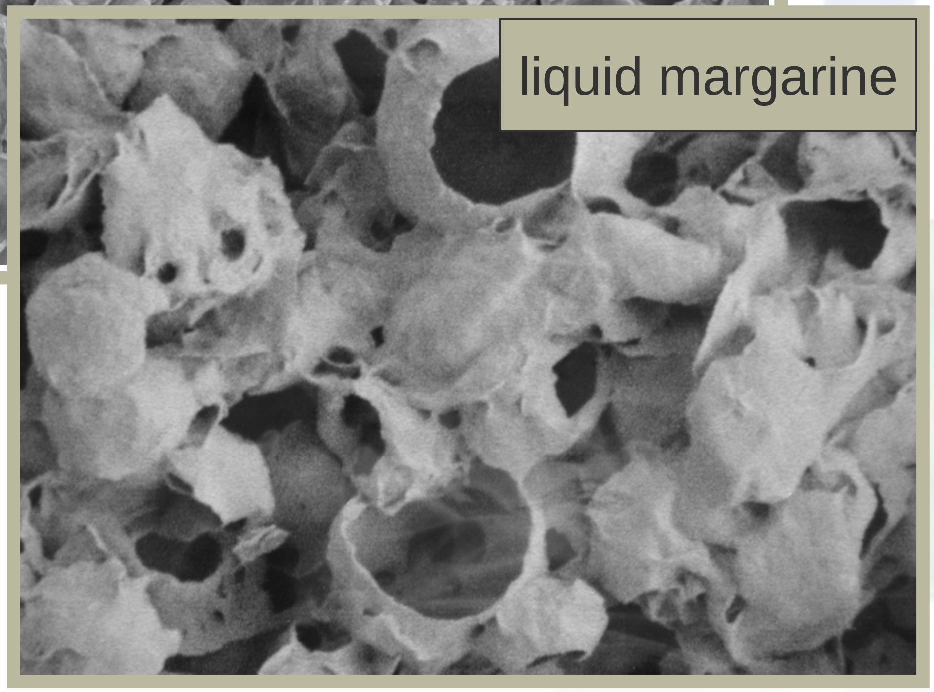
- Less answers, more questions
- Current reality of product development
  - Rules of thumb versus first principles
- Do we understand what we do ?
- Stimulate to think about the way to bridge the gap

Role of Fat Crystals

- emulsion stabilisation
- oil binding
- bulk hardness

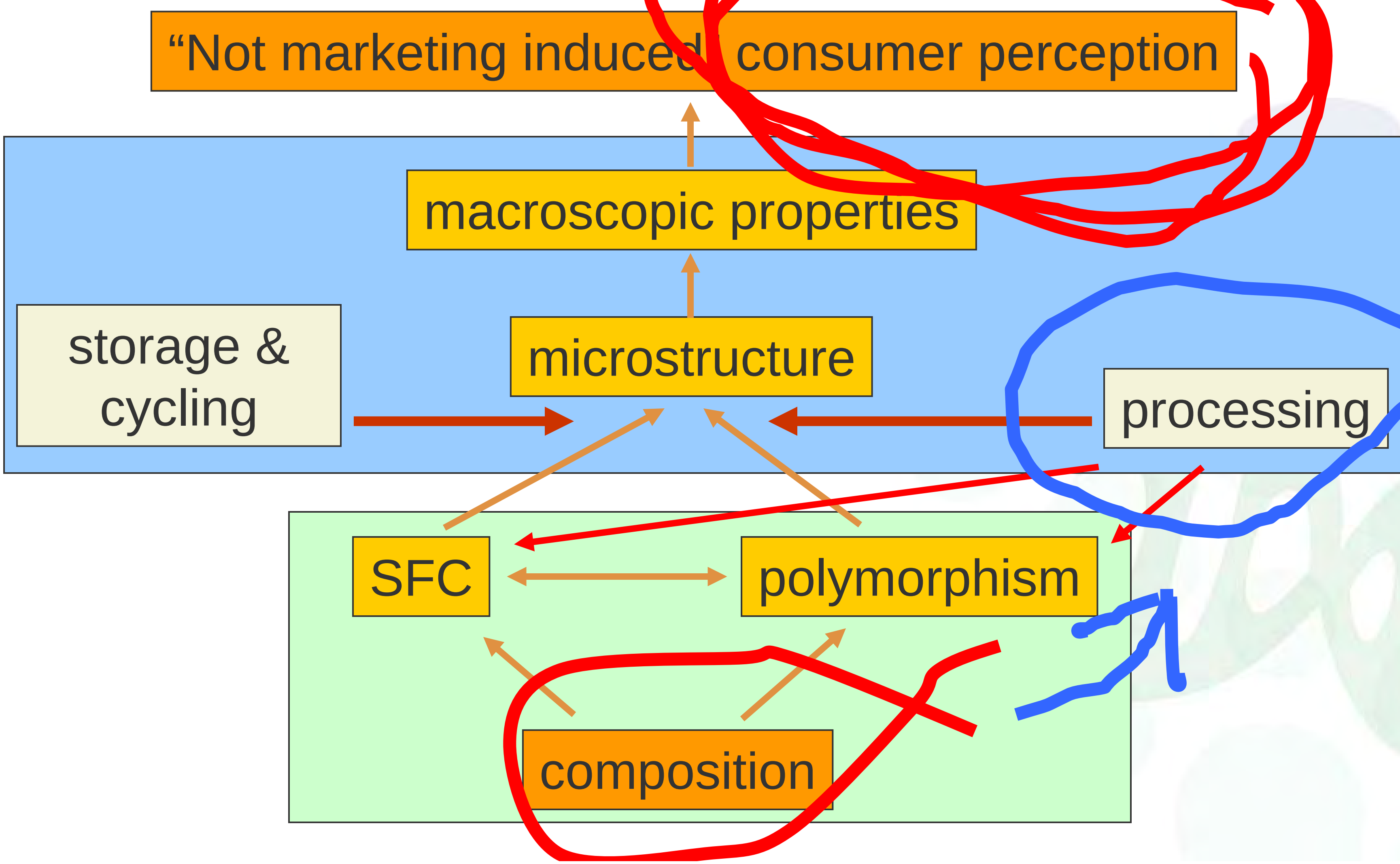






Hirachy of Product Structure

"Building the perfect sponge"



The old story of the SFC, first approximation

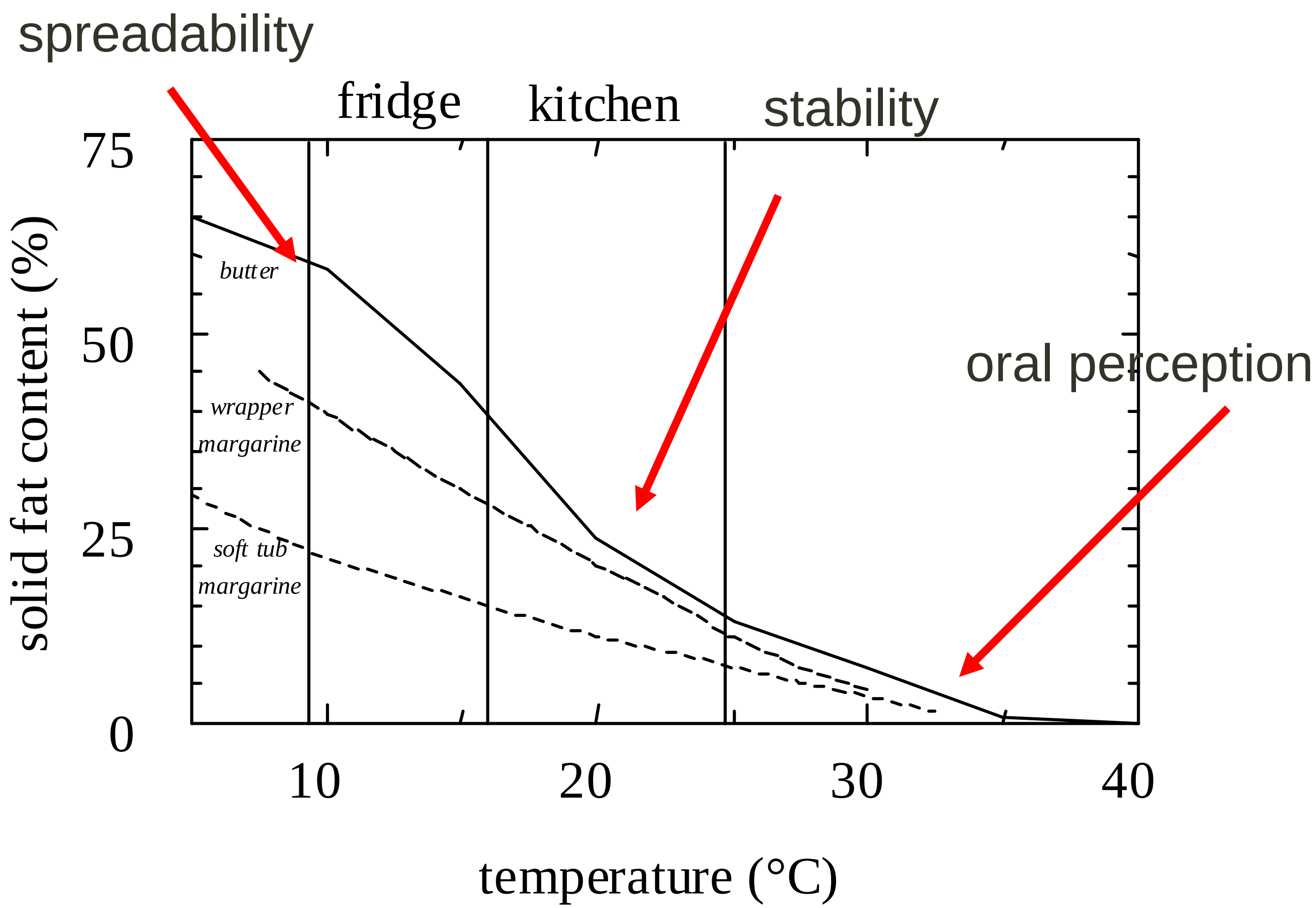
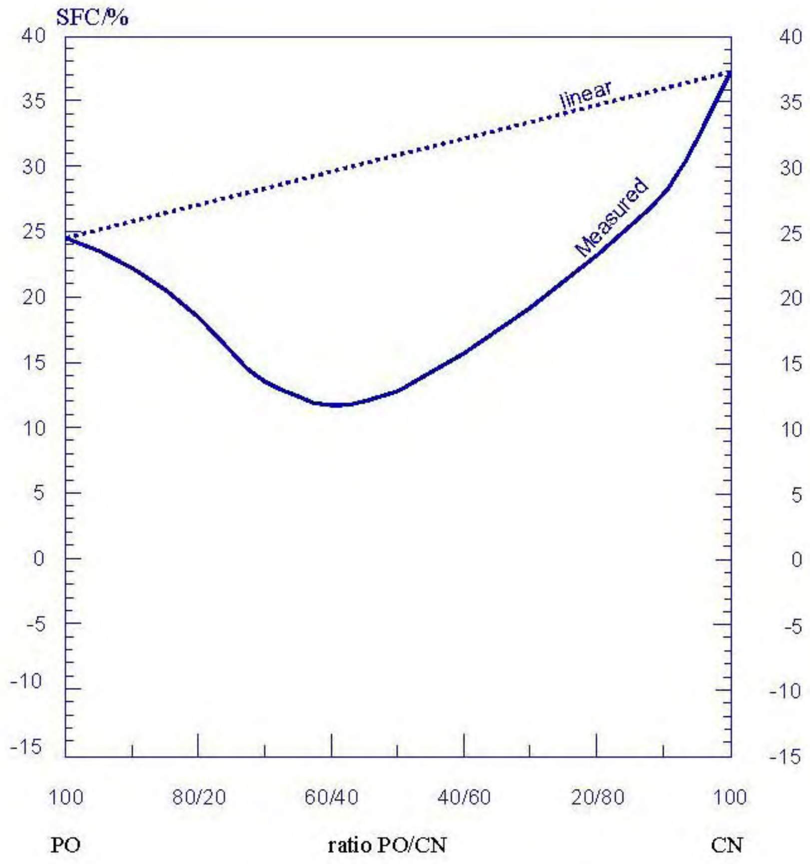
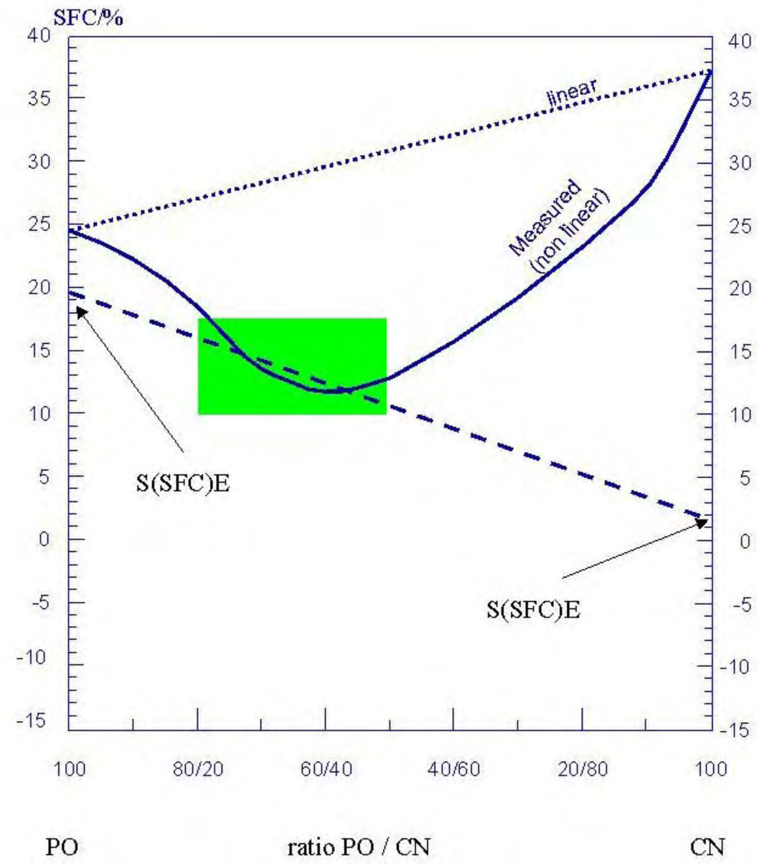


Figure 4

Linear Programming, old but still most practical





Applicability in field of operation,

meaningless but advanced rule of thumb

Equilibrium Modelling

Advanced approach presented by Elias today

Physical properties of pure TAGs components (dH$_{fus}$ and T$_m$)

Non-ideality mixed solid phases via standard Gex -model

choice of model and derivation of interaction parameters

large number of species, necessity for lumping (oil and gas industry)

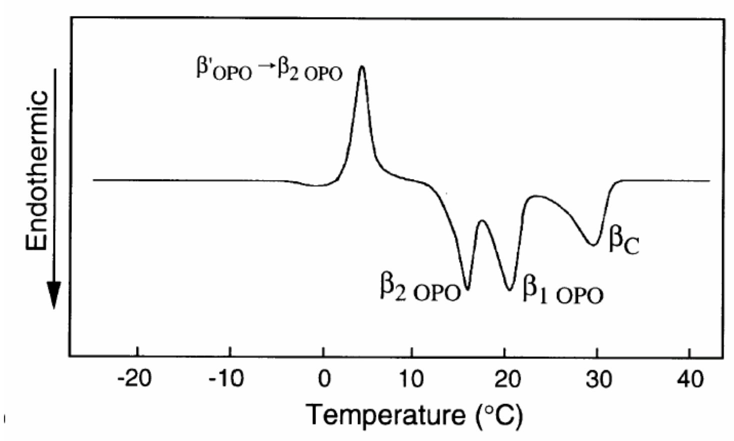
assumption of ideally mixed liquid phase

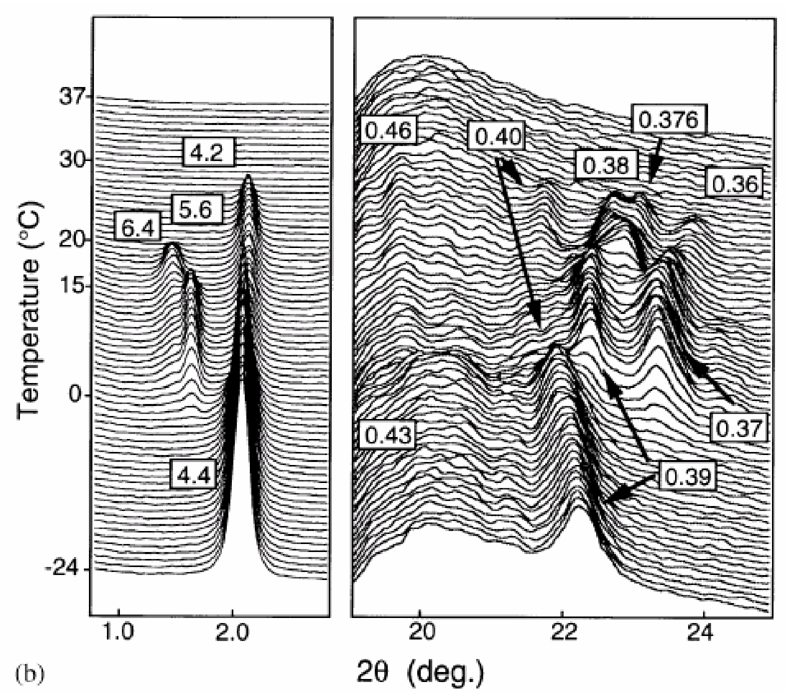
$$\ln\left(\frac{x_{i,eq}^{liq}}{\gamma_i^{sj} x_i^{sj}}\right) = -\frac{\Delta H_{fus,i}^{sj}}{R}\left(\frac{1}{T} - \frac{1}{T_i^{sj}}\right)$$

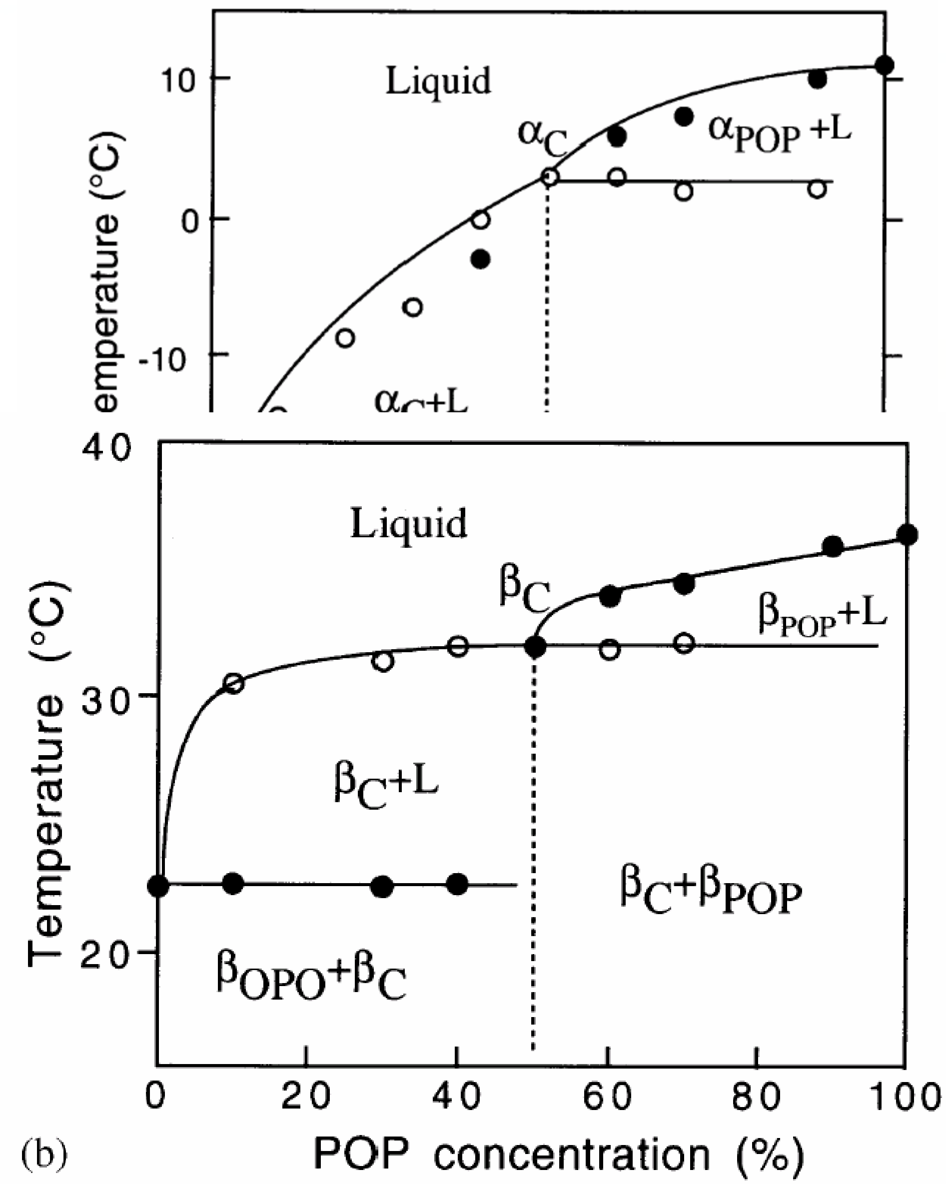
Minimisation of the total Gibbs free energy, => SFC + composition

Simple pure systems already give us a headache

DSC





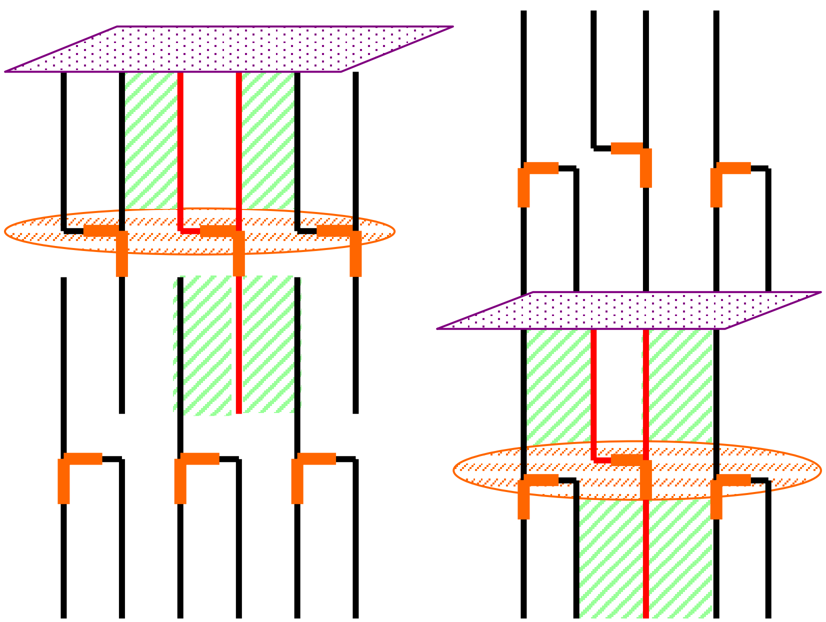


Need of comprehensive good input

Initial Group Contribution Method

$$\Delta H_f = H_{\text{int}} + H_{gly} + H_{mep} \qquad \Delta S_f = S_{\text{int}} + S_{gly} + S_{mep}$$

$$T_m = \frac{\Delta H_f}{\Delta S_f}$$



Triple CLS   Double CLS

H_{int} lateral interaction energy

H_{gly} glycerol energy

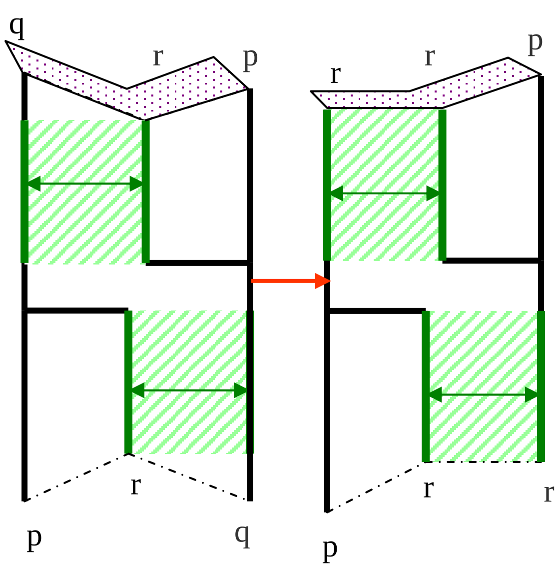
H_{mep} methyl end plane (**MEP**) energy

“Arbitrary” Choices, any better than LP ?

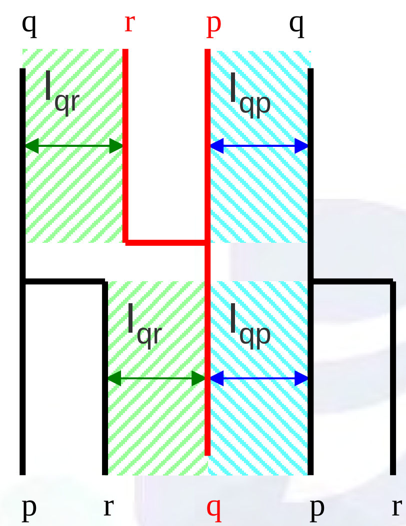
1. The lateral interaction energy

A) Double CLS

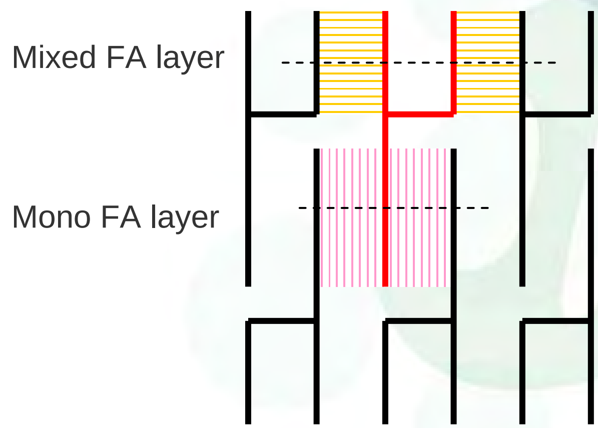
$$H_{qp} = H_{\min(p,q)\min(p,q)}$$



$$H_{\text{int}} = H_{qp} + H_{qr}$$



B) Triple CLS



*** Same lateral interaction energy**

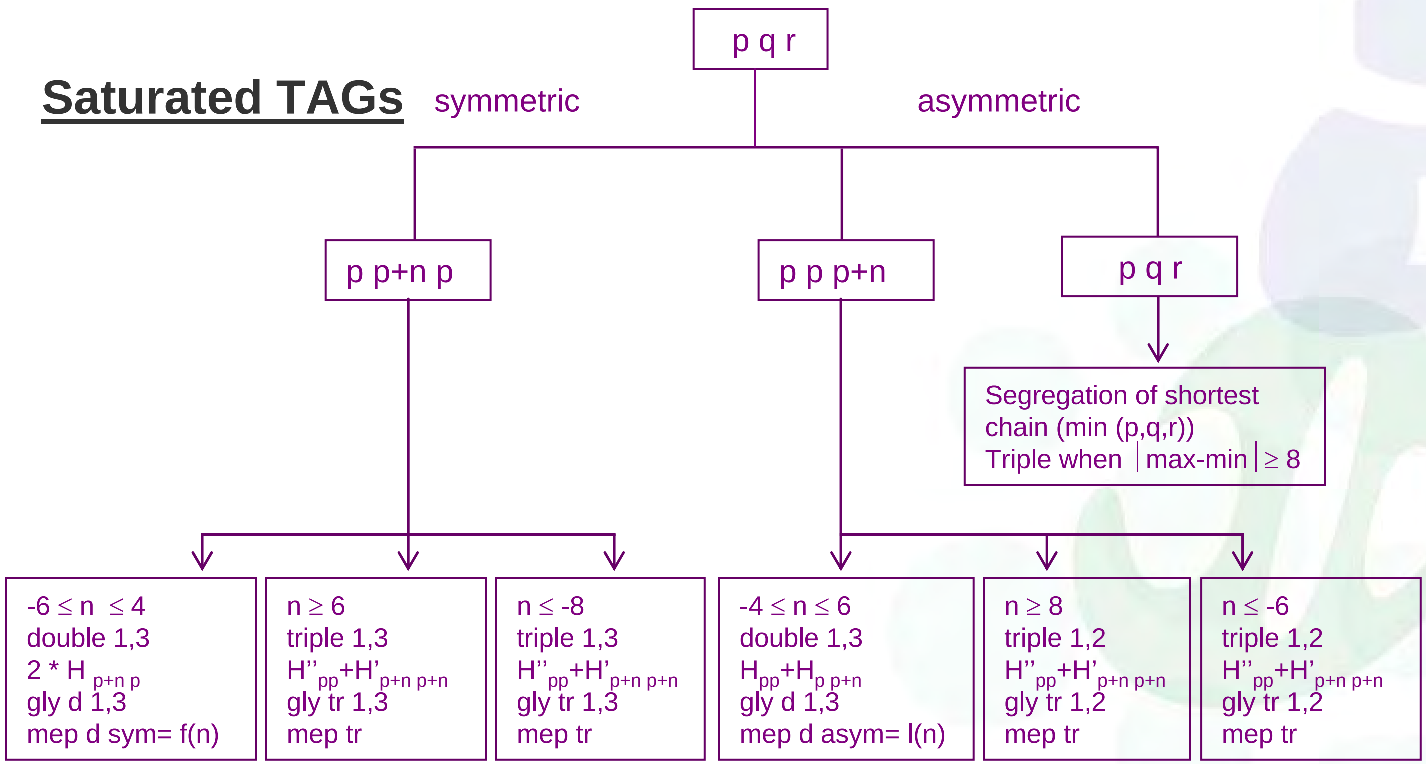
*** Different MEP**

*** Differentiation of the two layers**

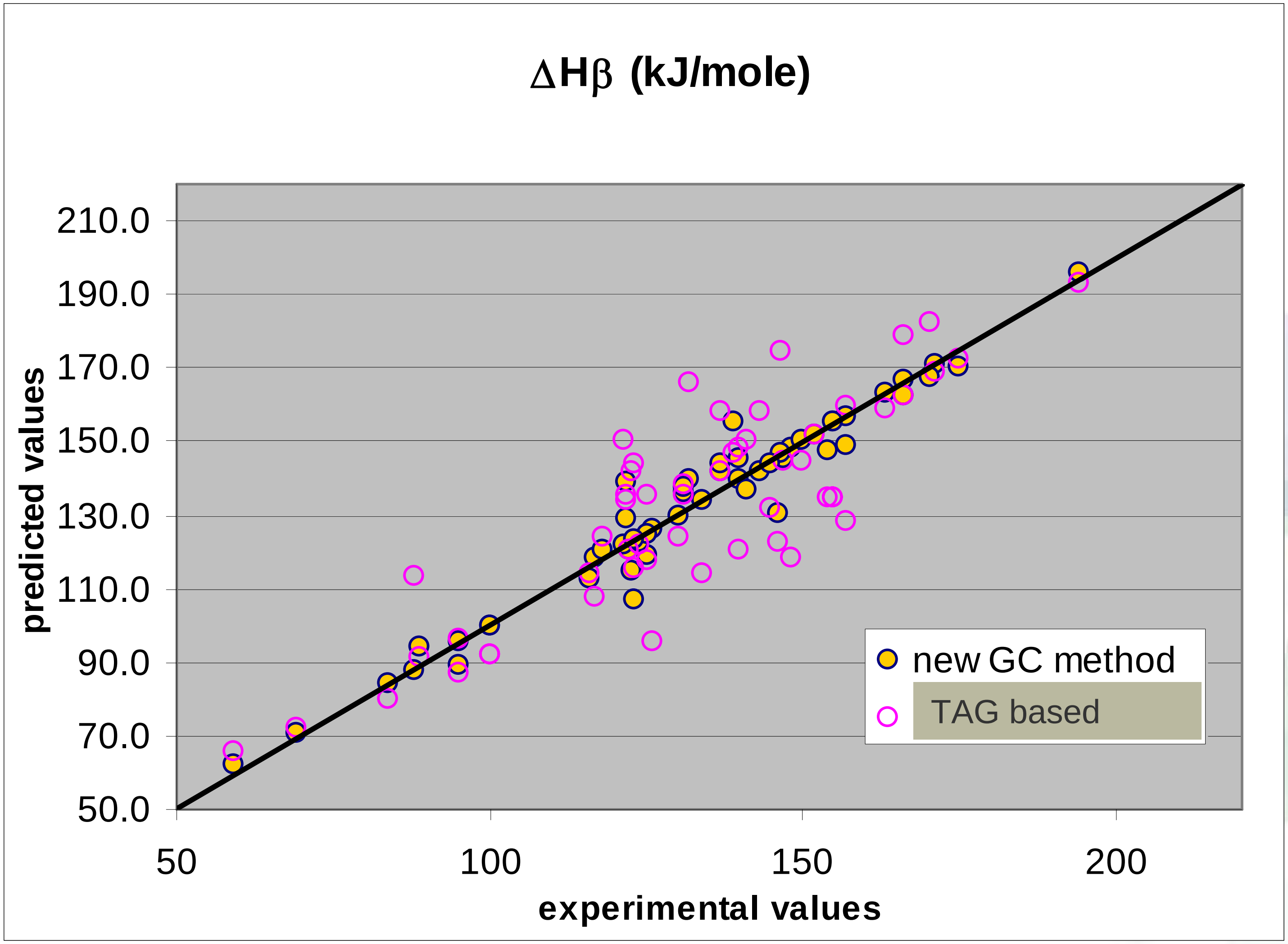
Analysis of limited available data
Rules of thumb

Structure Prediction Tree for Calculations

Saturated TAGs



Significant Improvement for dH, dS and T
With good results

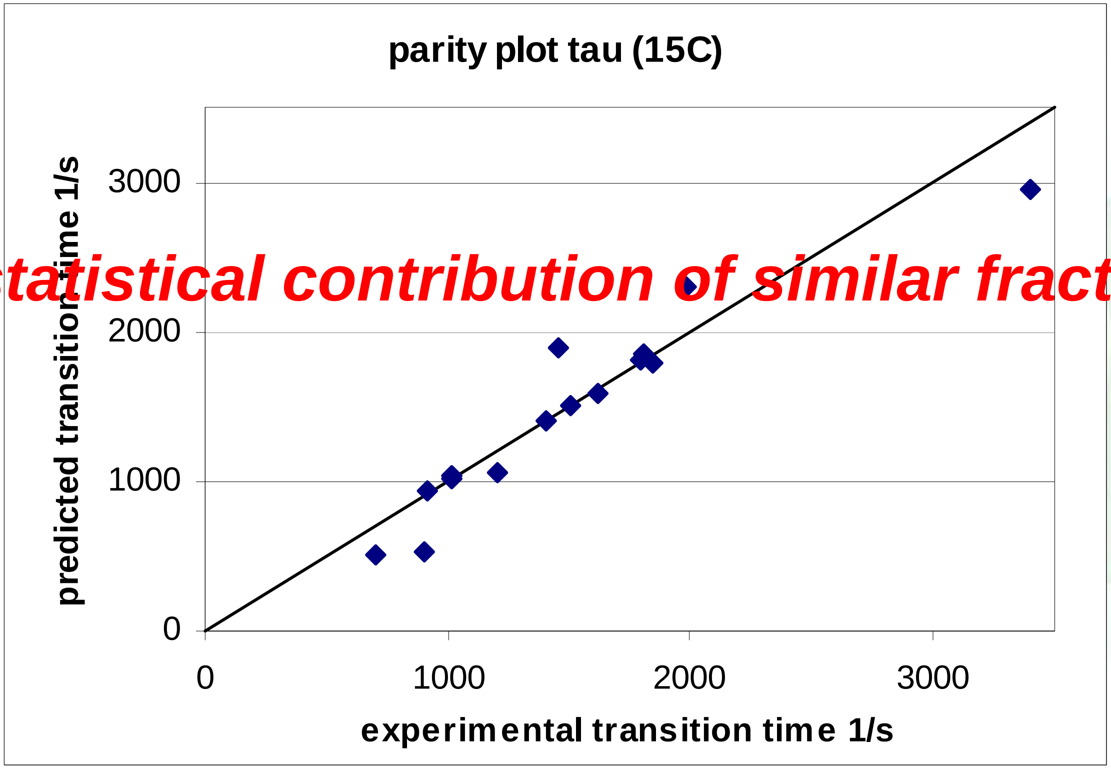


Good results, with doubts

Description of Polymorphic Transition kinetics of milk fat

Correlation of transition times of milk fat containing compositions

- -set of 6 milk fats & fractions and vegatable oil, 150 blends
- -isothermal stagnant crystallisation at 5 temperatures
- -identification of transition time as maximum rate dSFC/dT



But statistical contribution of similar fractions differs !!

Rules of thumb often, often not good enough

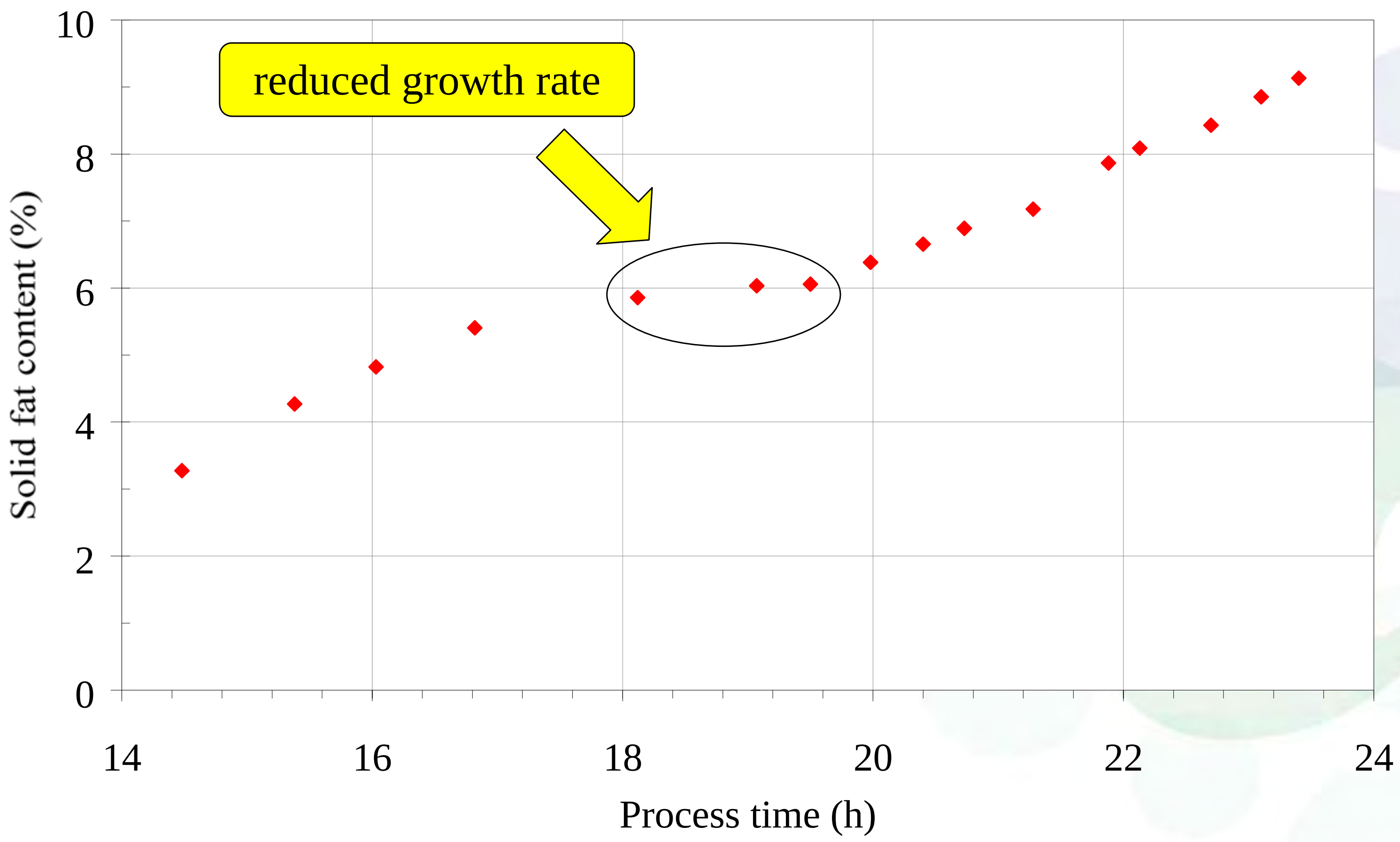
- Plenty of examples of surprises

- Milk fat often successfully treated as ternary system
  - High melting
  - Middle melting
  - Low melting fraction

- HOWEVER

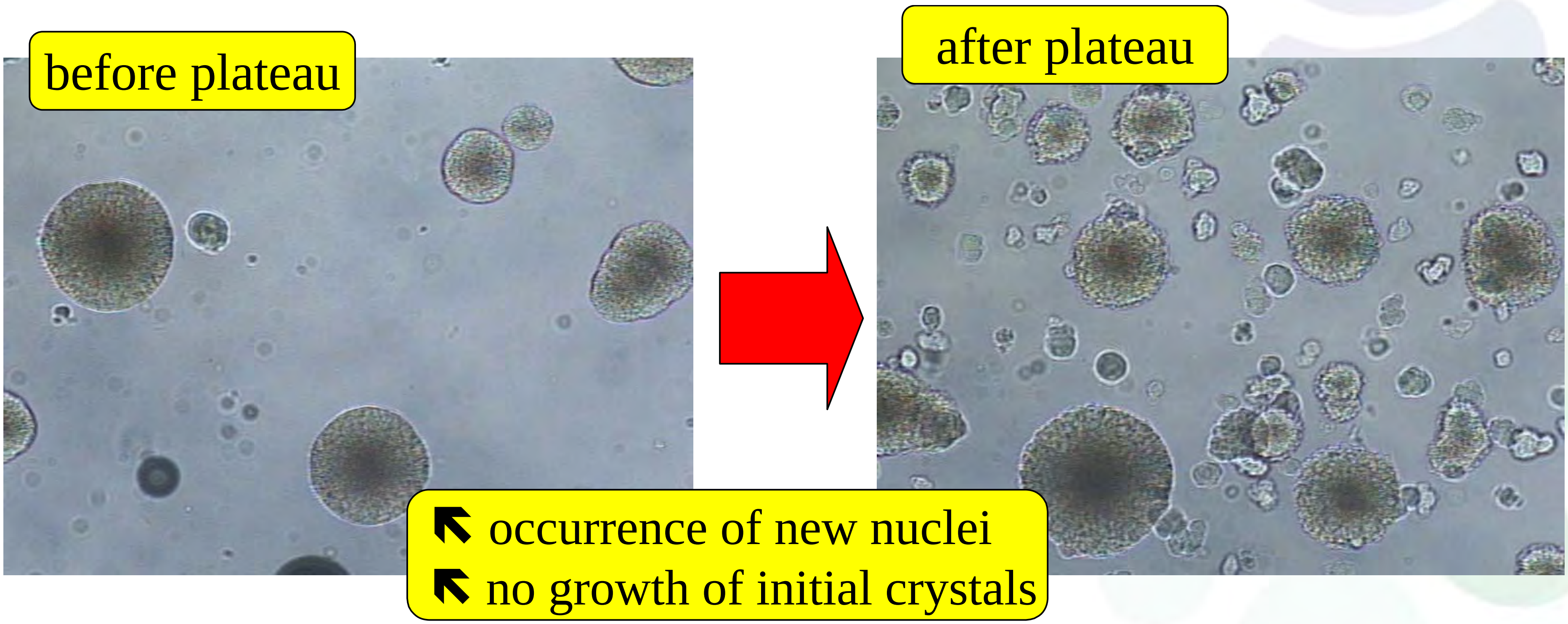
Crystallisation in Batch

Solid fat content as a function of time during crystallisation of milk fat olein at θ_c=18°C.

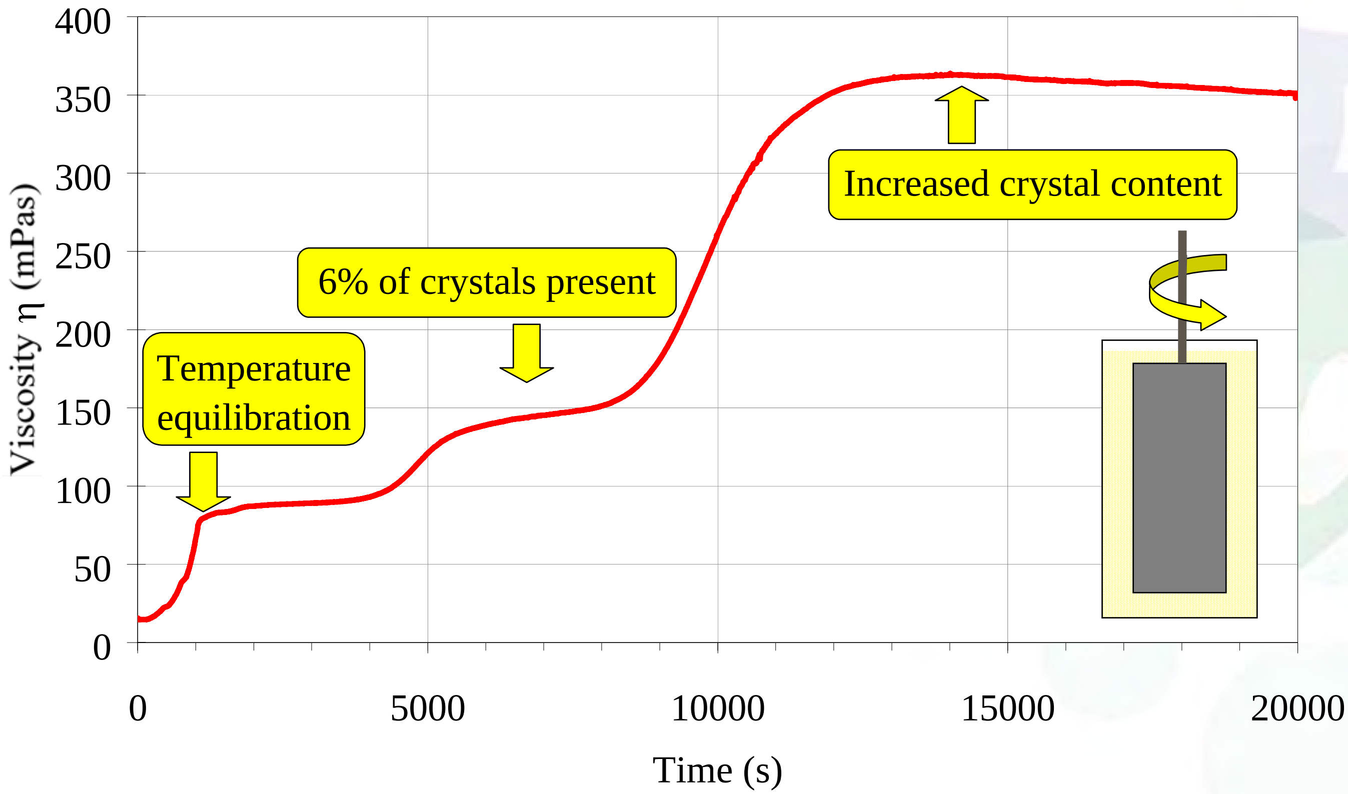


Crystallisation in Batch

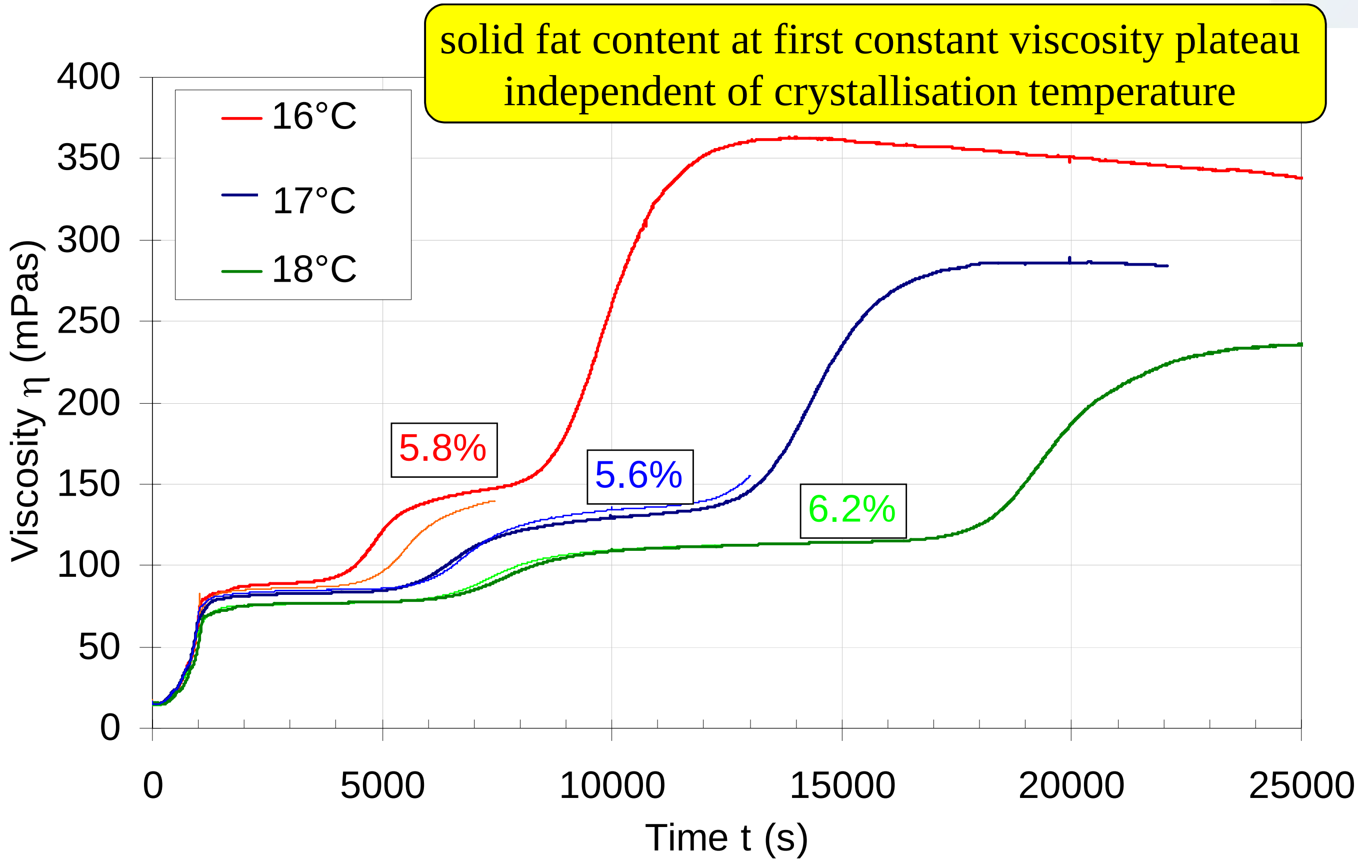
Microscopic pictures after 17h (left) and 22h (right) of milk fat olein crystallisation at θ_c=18°C (see). Image width 745μmC



- milk fat olein at a constant temperature of 18°C
- viscosity as a function of time (shear rate 1000rpm).
- melt inserted into rheometer 50°C (Haake RN3.1, concentric cylinder H1)

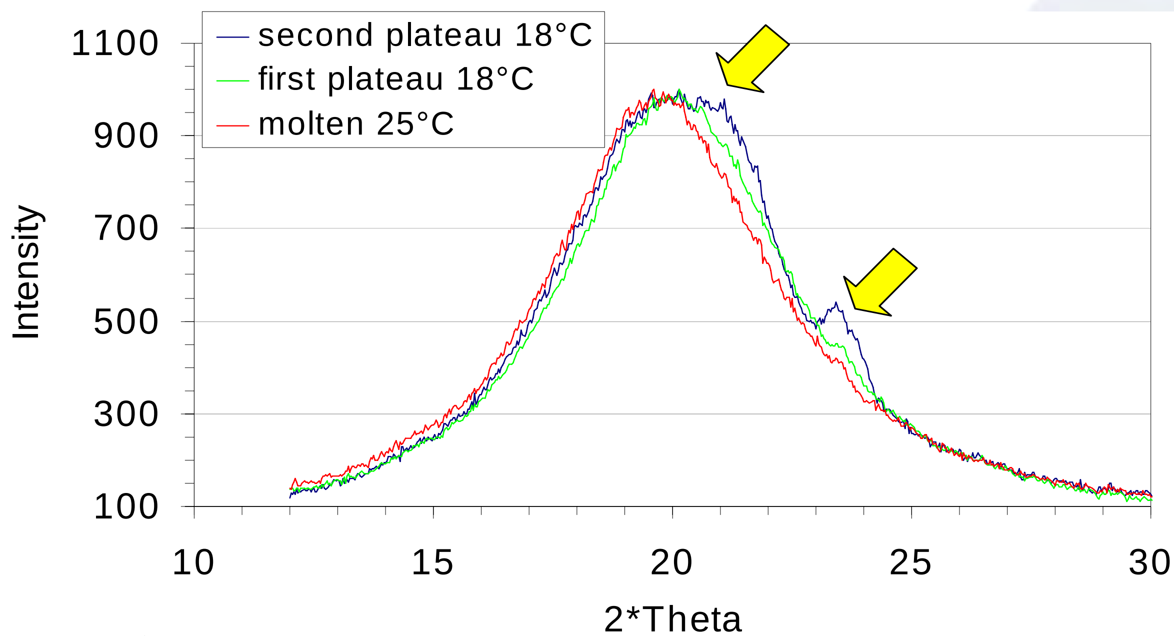


- Isothermal crystallisation at different temperatures
- value (6%) in agreement with batch crystalliser plateau



X-ray diffraction at intermediate and final plateau

- Both plateaus same polymorph β'
- nucleation of the separate second group of TAG's independent (induction time and dSFC) Not shown
- second step is no polymorphic transition



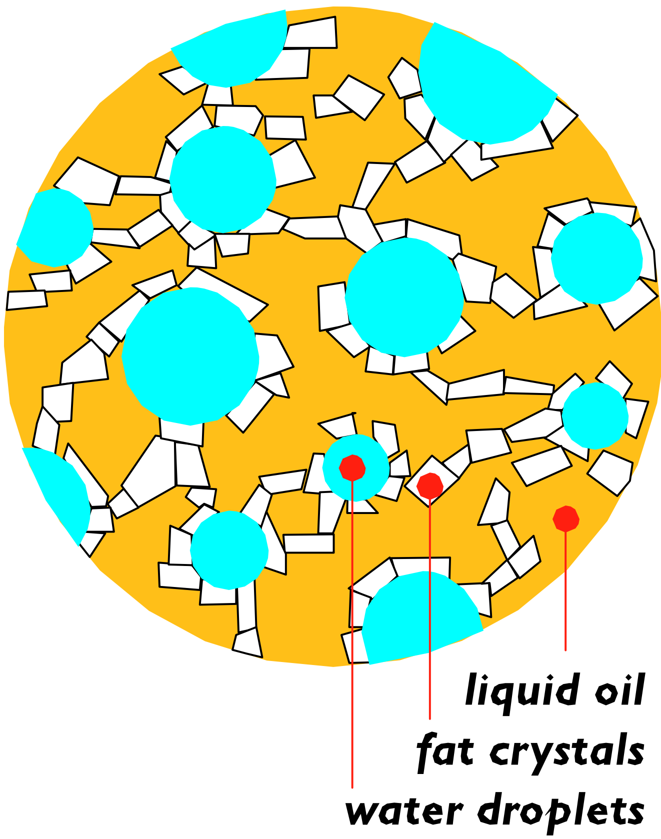
Both in the β' form (4.24 Å and 3.80 Å)

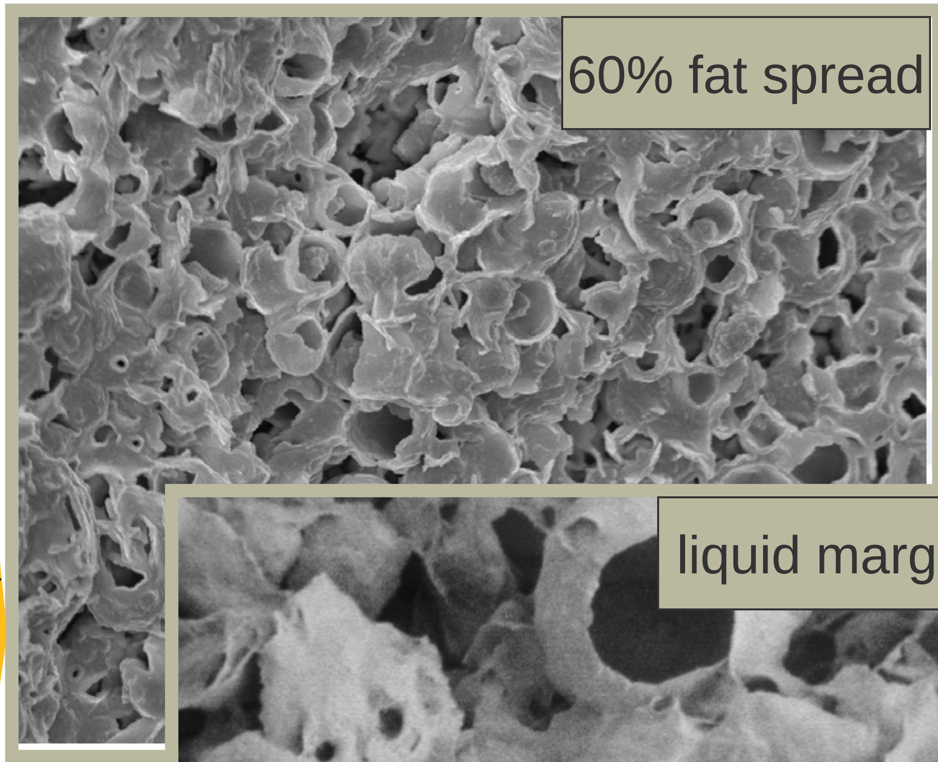
Conclusions and Recommendations

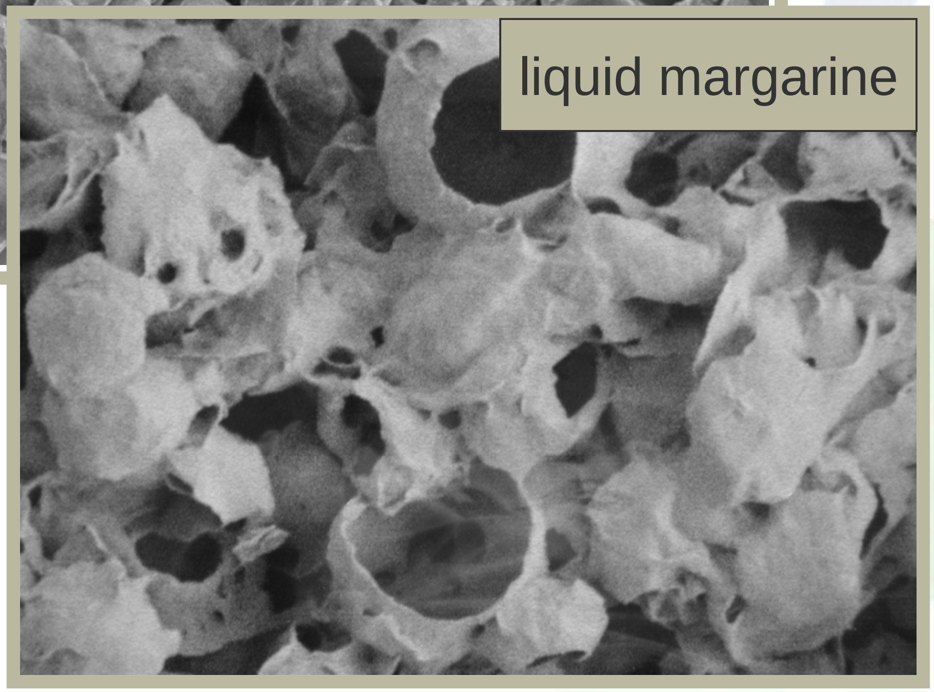
- **Stepwise crystallisation process <u>is no</u> polymorphic transition**
- **Solid immiscibility of TAG groups of milk fat olein identified**
- **Separate primary nucleation steps in various milk fat fractions**
- **Phenomenon is more pronounced in low-melting fractions.**
- **Viscosity good measure for nucleation process**
- **Even though milk fat is so complicated that it almost behaves as an ideal mixture it remains much more complicated if we take a closer look**

Emulsion stability, break up other ingredients

- emulsion stabilisation
- oil binding
- bulk hardness







Solubility and dissolving

Simple first approximation

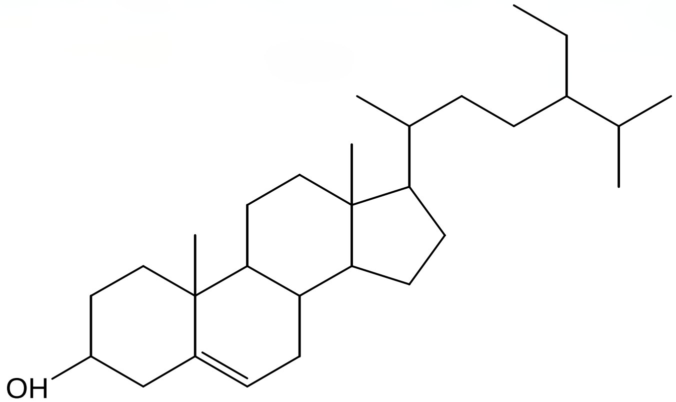
- knowledge of basic physical properties
  heat of fusion, melting point
- assume natural mixed system behaves
  as pure component

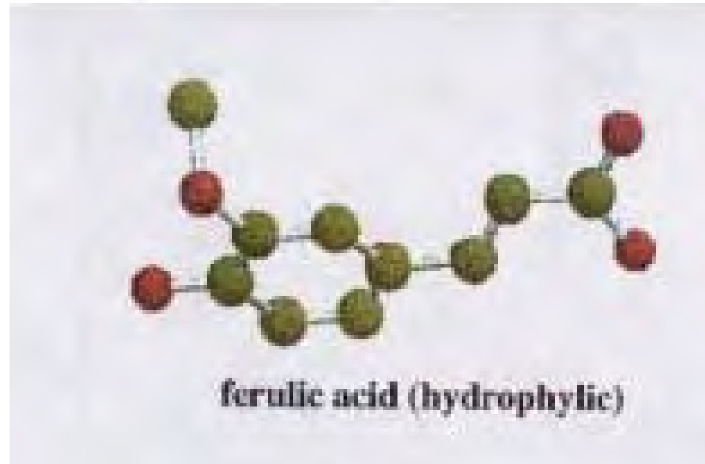
$$\ln\left(\frac{x_{i,eq}^{liq}}{\gamma_i^{sj} x_i^{sj}}\right) = -\frac{\Delta H_{fus,i}^{sj}}{R}\left(\frac{1}{T} - \frac{1}{T_i^{sj}}\right)$$

OR a few simple measurements

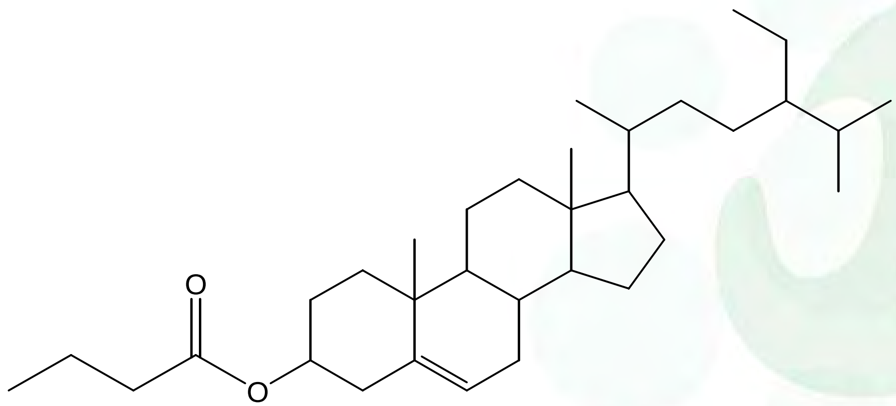
Sterols - Basic structure / Properties

- β-sitosterol

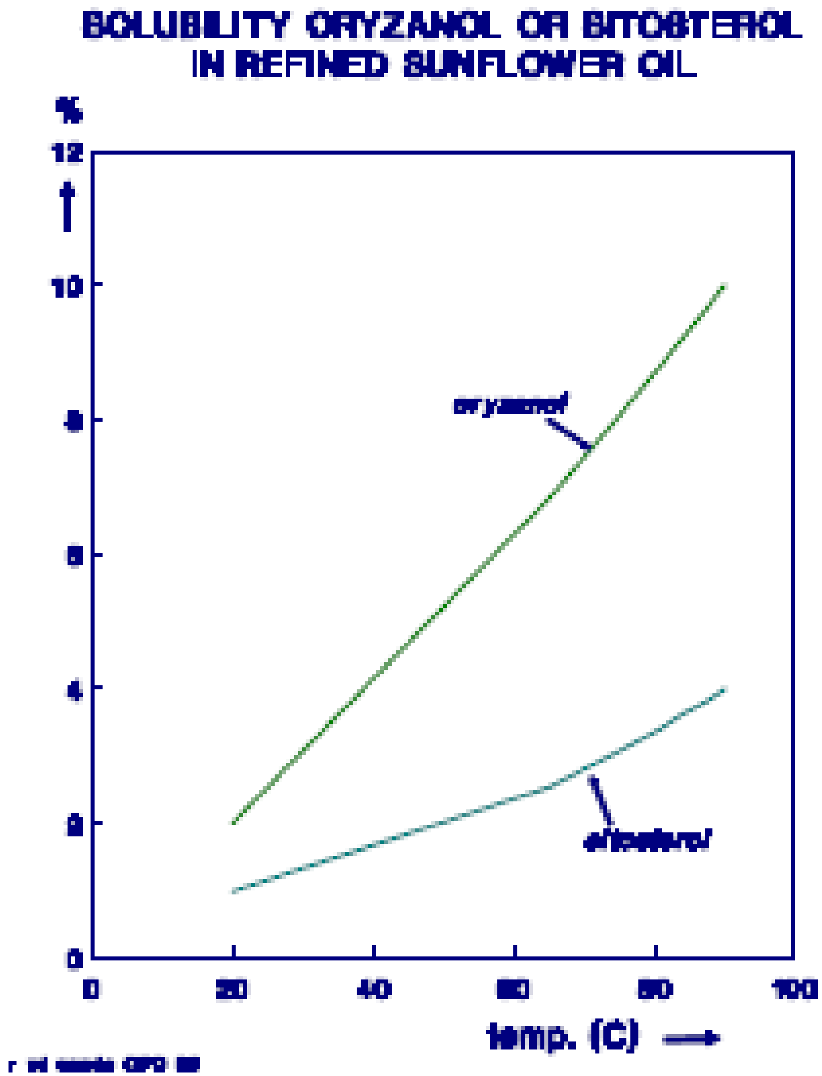


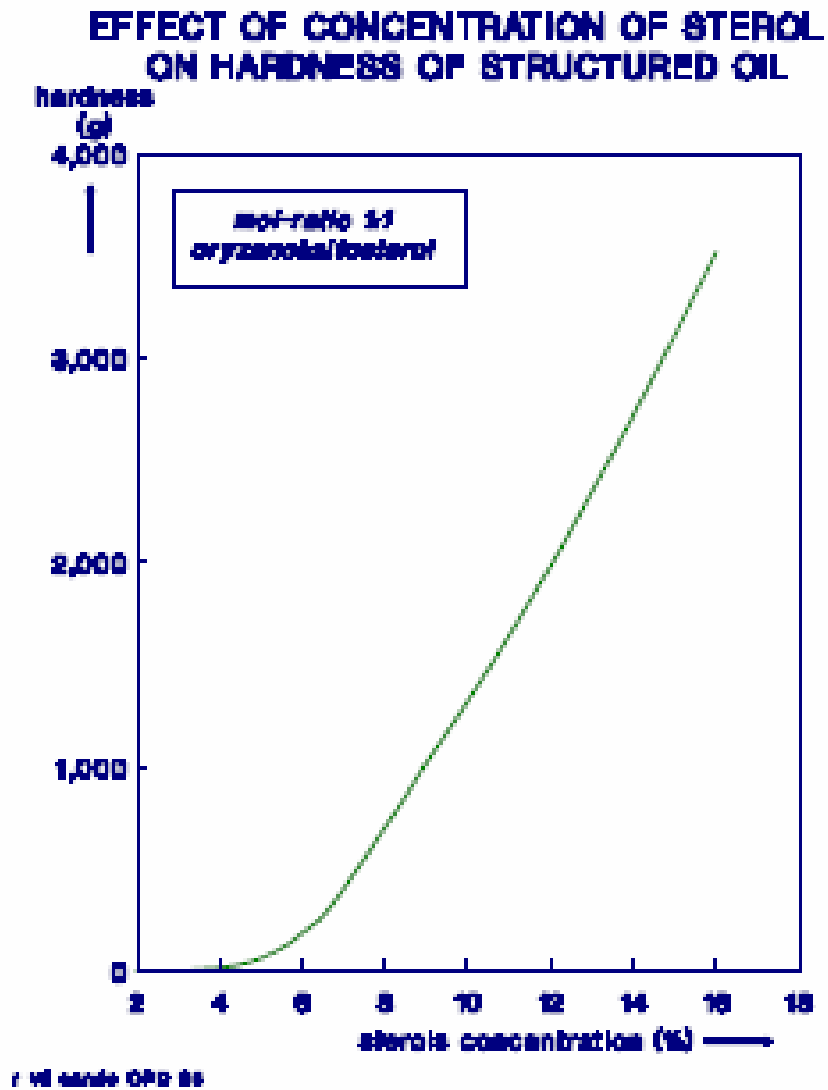


- β-sitosterol ester



Adding sterols

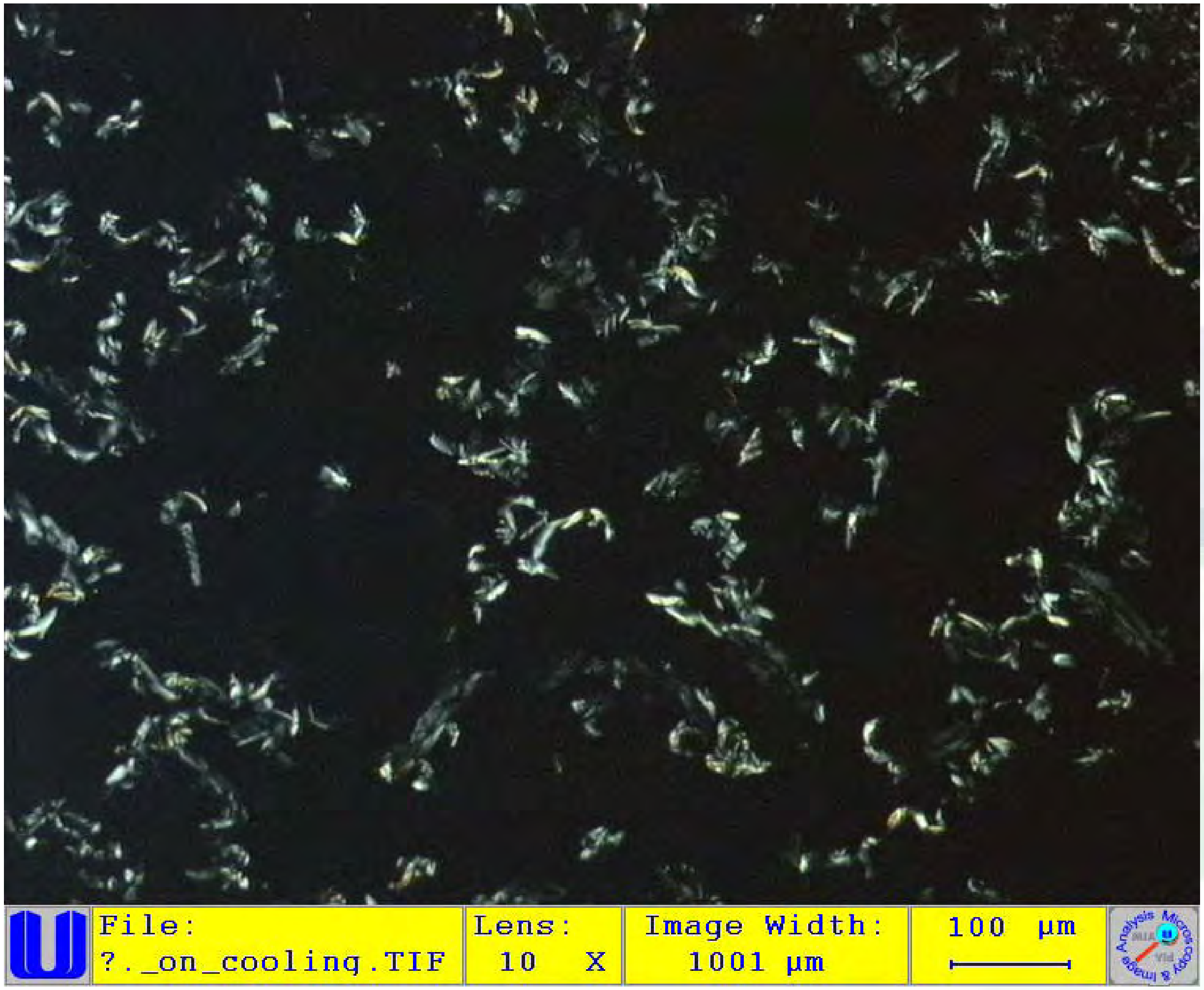




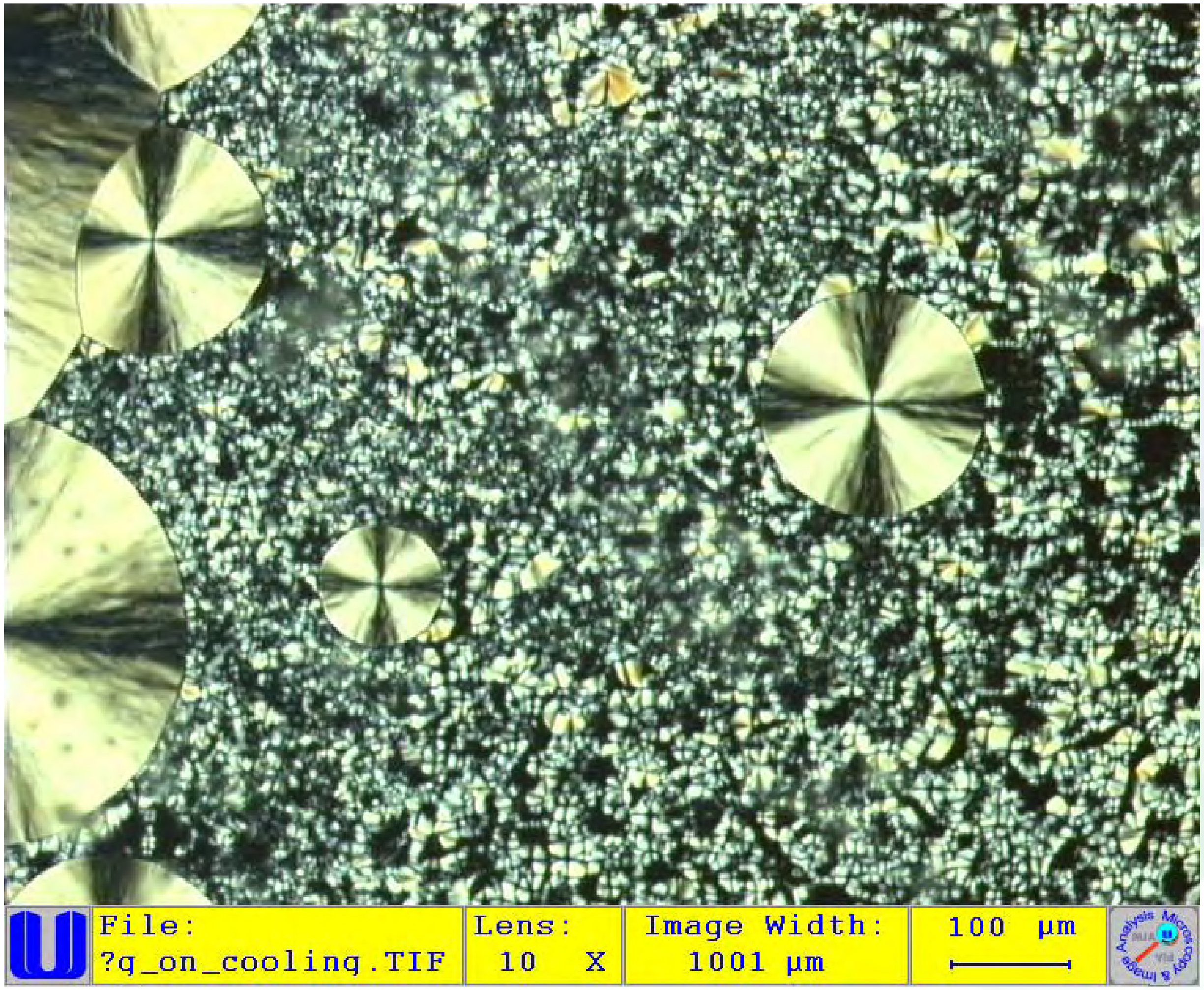
Storage at 5C, 3 days

Characterization of sterol C_{12}-SE at 80 °C on cooling

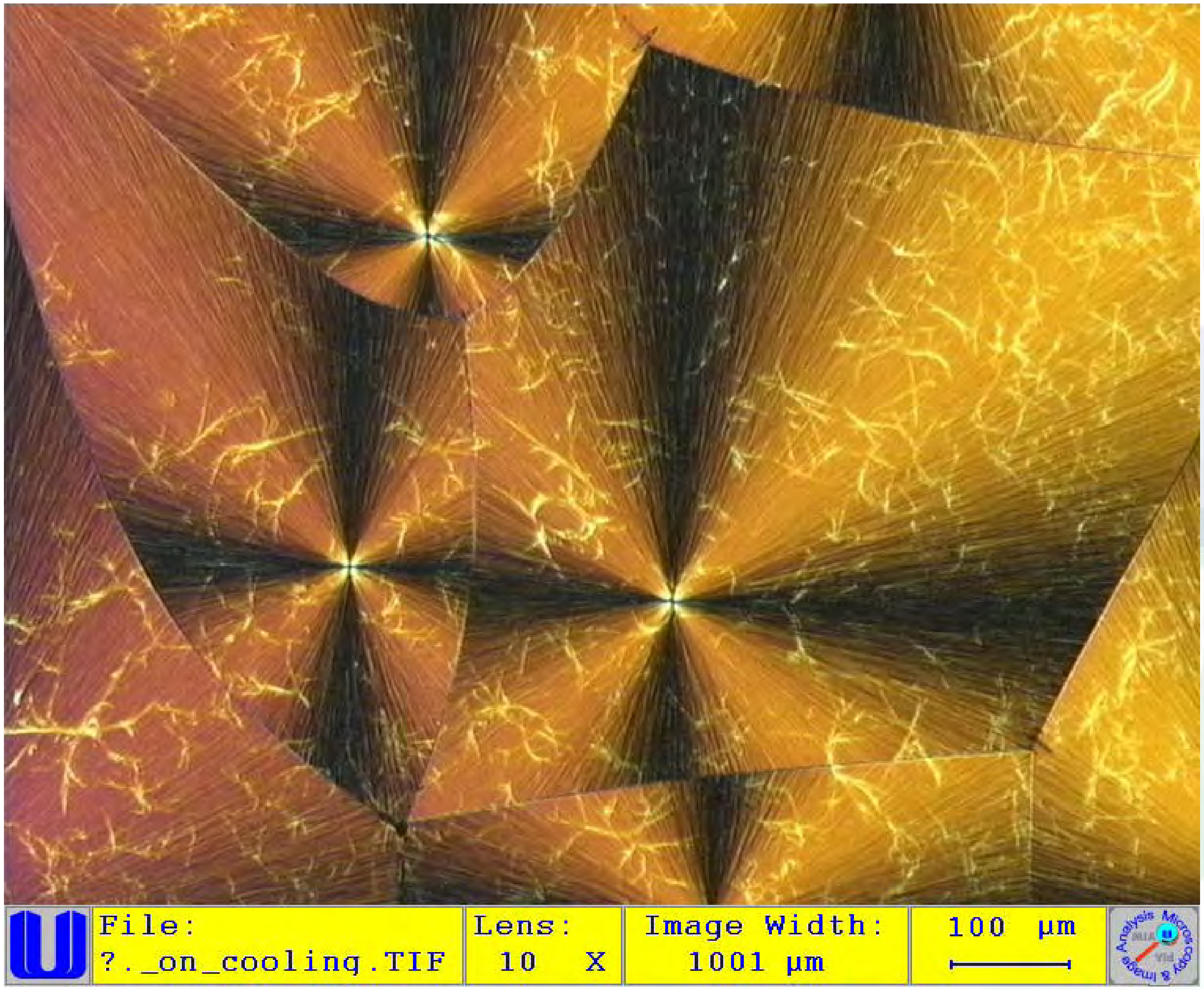
- Linkam Optical Microscopy - C_{12} sterol ester



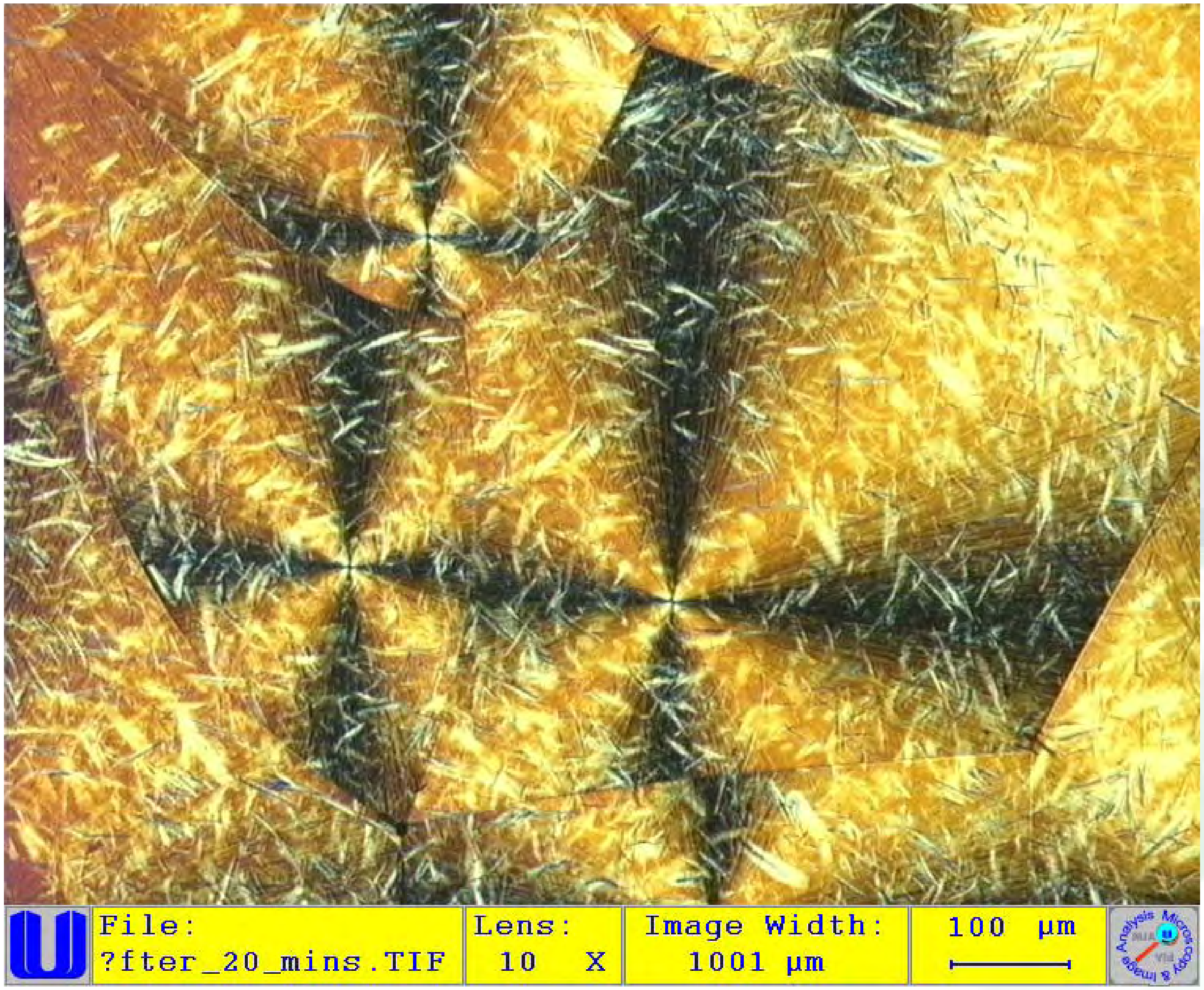
C_{12}-SE at 61 °C on cooling



C_{12}-SE at 55 °C on cooling



C_{12}-SE at 55 °C after 20 minutes



Conclusions Sterol Esters

- Structuring/gelling combinations can be found
  - Mechanism not yet understood

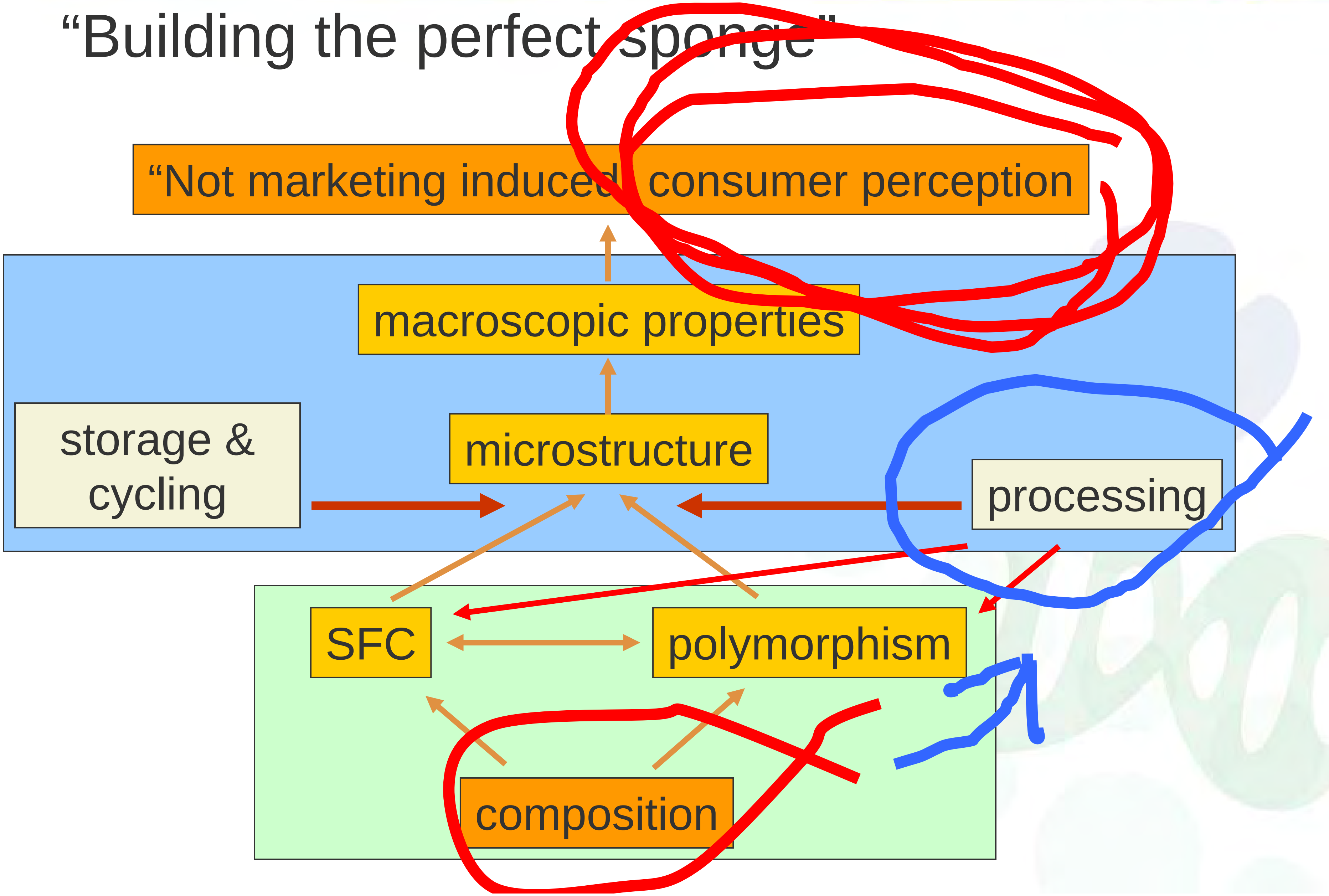
- Sterol ester characterization of pure SE
  - Complex crystallization behaviour
  - Real systems highly mixed, less problematic

The role of emulsifiers and how much we do not know

- Mainly HLB value as initial yard stick
- Dissolution behaviour
  - Monoglycerides in miix with lecithins
  - Kinetics of dissolution
- Competition at the interface
  - emulsifier/emulsifier
  - Emulsifier and Pickering stabilization through solid fat

Hirachy of Product Structure

"Building the perfect sponge"



Finally

Products going to market are complex systems full of surprises

- The link between “academic systems” and these real systems is far from trivial

However

- Study of understandable systems helps us to interpret and sharpen our insights
- Needed to formulate hypothesis explaining observations
- Guidance to more sound “quick and dirty” improvement strategies supported by rules of thumb and experience