



Fat Crystallisation: mechanism and methods for studying

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Edible Oils and Fats - Trends in Raw Materials,
Processing and Applications
20–21 March 2007, Cairo**

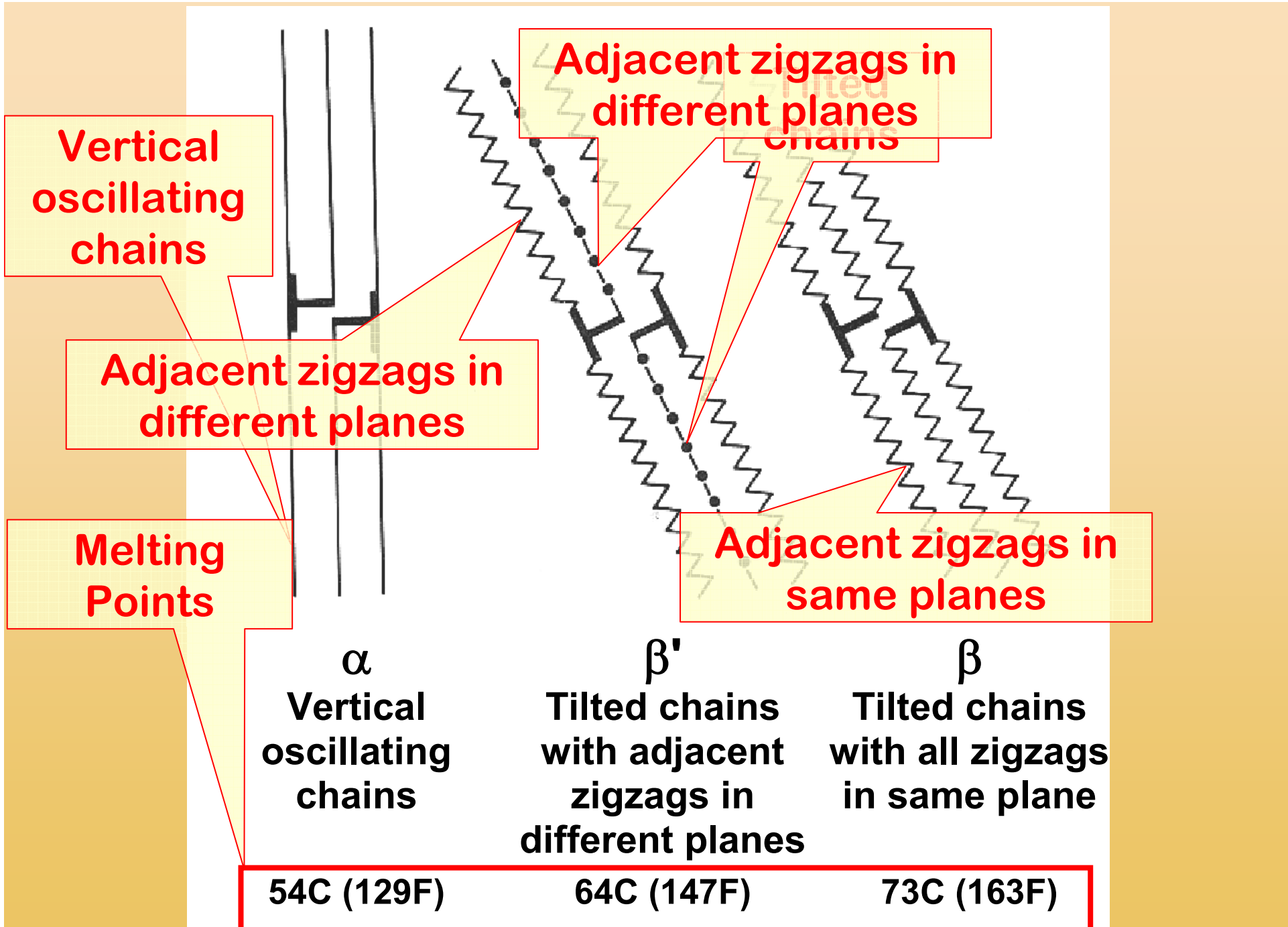
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Fat Crystallisation: mechanism and methods for studying

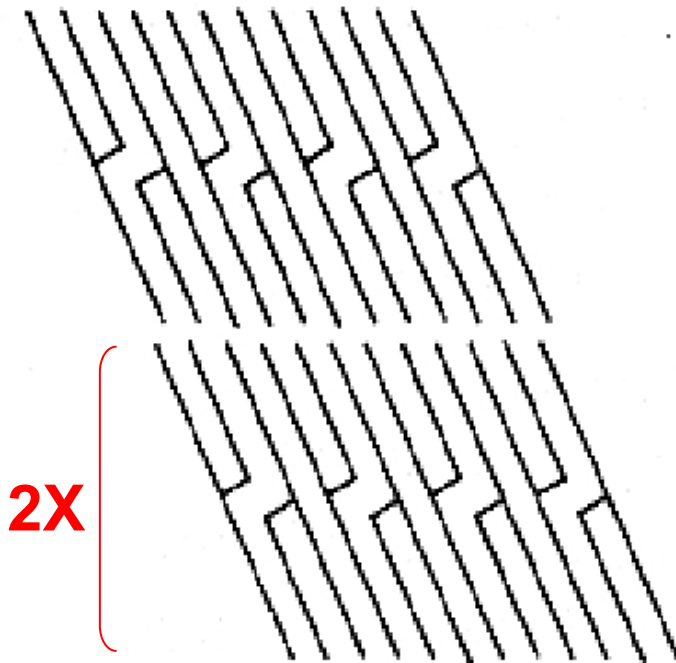
- **Polymorphism**
 - Basics
- **Crystallisation**
 - Nucleation, Growth and Supercooling
 - Post growth events, crystal ripening
- **Methods for studying**
 - Differential Scanning Calorimetry
 - Differential Thermal Analysis
 - Cooling Curves – Jensen & Shukoff
 - Solid Fat Content by NMR
 - Turbidity using light-scattering

Polymorphism

- Fats and triglycerides have different forms with different melting points
- Each form is called a **polymorph** and the phenomenon is called **polymorphism**: Greek 'many forms'
- Fats & triglycerides occur in any one of three basic types: α (alpha), β' (beta prime) and β (beta)
- All fats have an α polymorph; some are β' stable; some are β stable
- Transitions go from α to β' to β , in that order, which is the order of increasing stability.

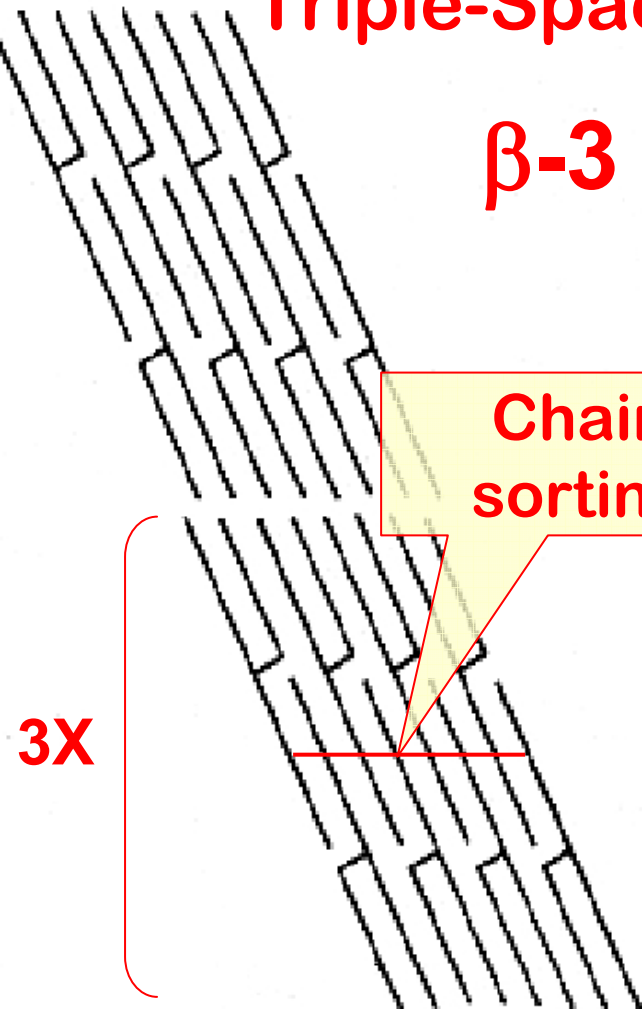


Double-Spacing
 $\beta-2$

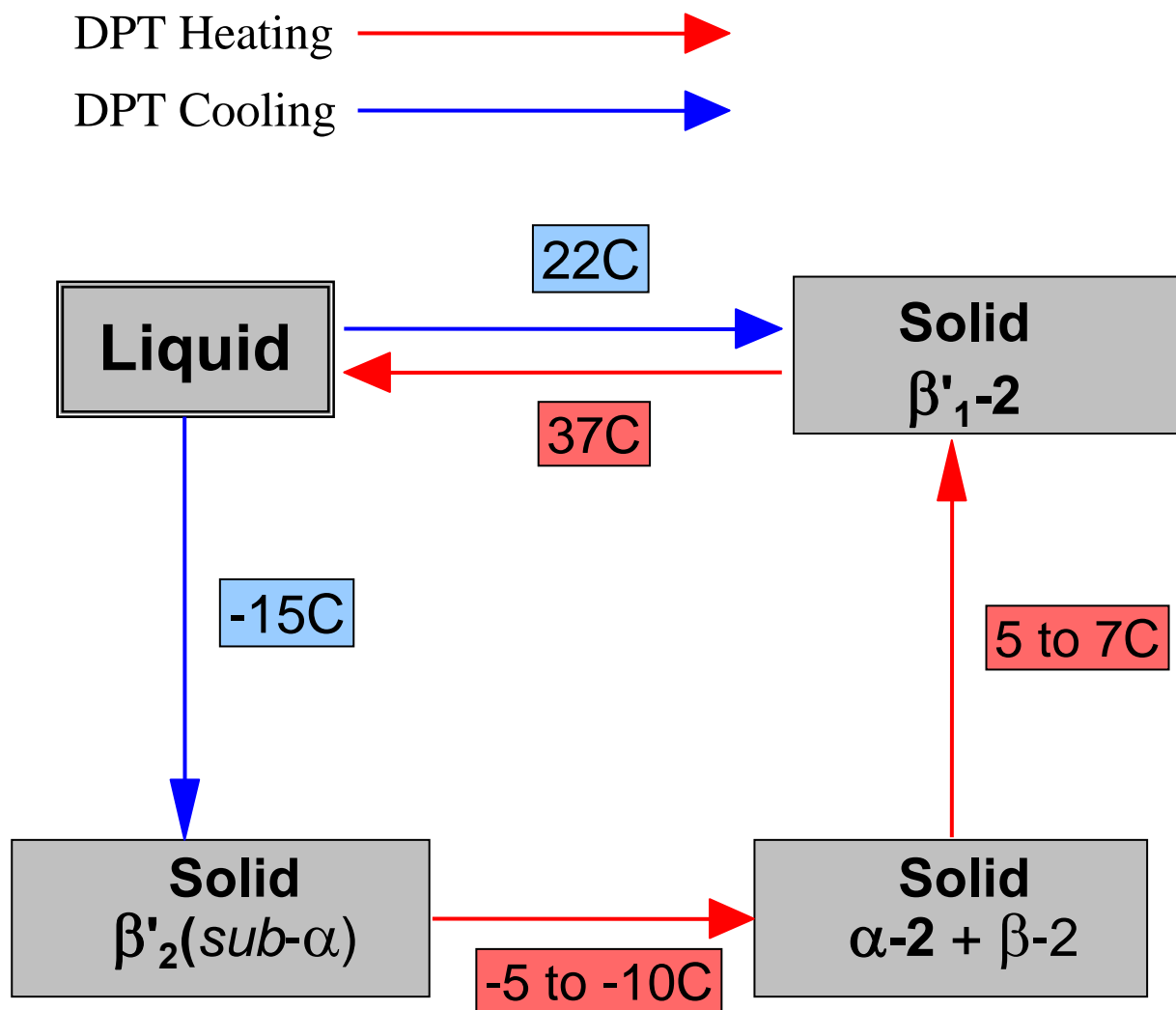


Triple-Spacing

$\beta-3$



Polymorphism of Palm Oil & Fractions

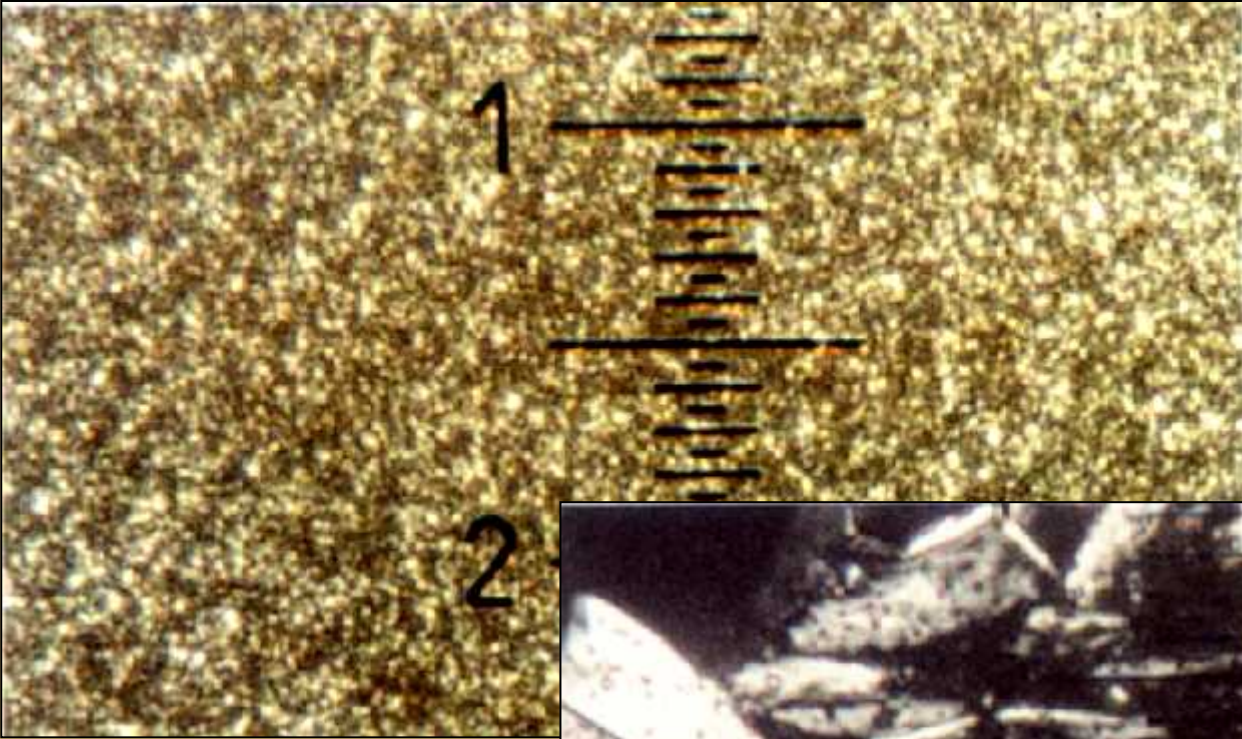


from Persmark & Stahl, 1976

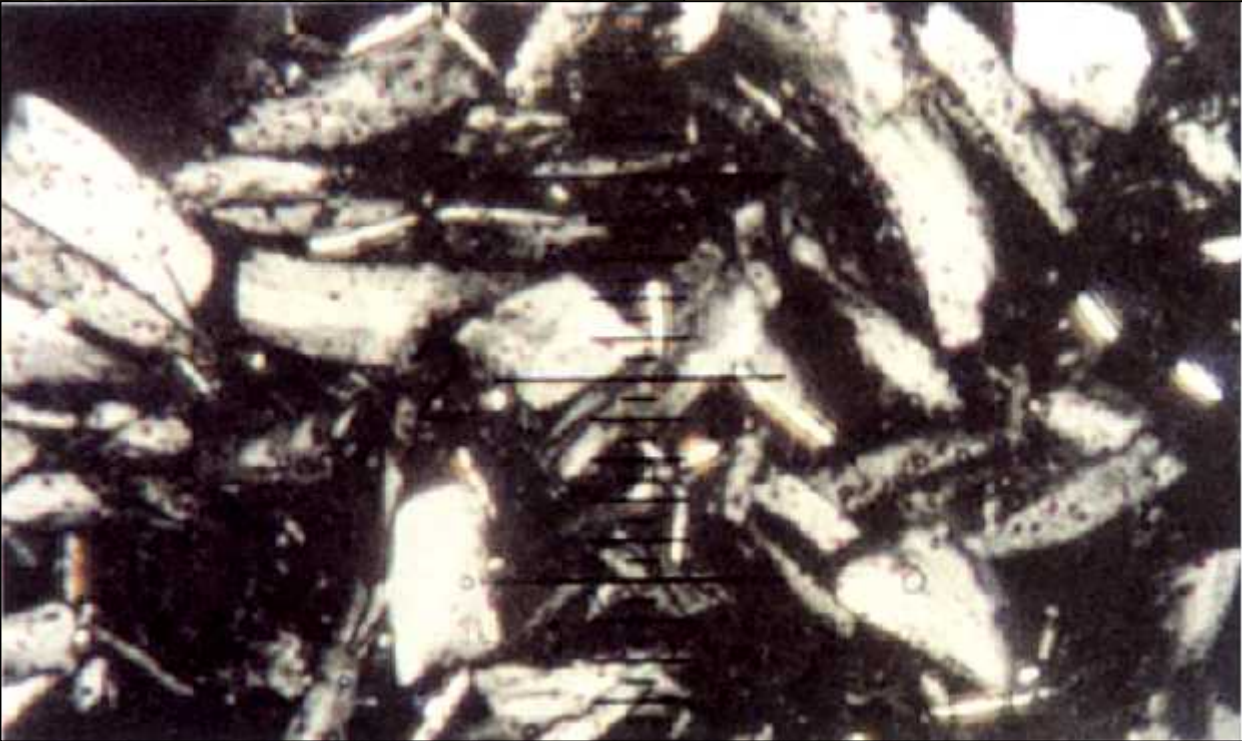
Stable/Typical Polymorphs of common fats

| Fat | Polymorph | Comment |
|-------------------------------------|-------------|---|
| Cocoa Butter | β -3 | Simple TAG mixture, mainly SOS type |
| Fully Hydrogenated Oils | β -2 | Simple TAG mixture, mainly SSS type. Except hydrogenated PO is β' -2. |
| Milk Fat | β' -2 | Complex TAG mixture |
| Lauric Oils (Palm Kernel & Coconut) | β' -2 | Complex TAG mixture |
| Partially Hydrogenated Oils | β' -2 | Complex TAG mixture |
| Interesterified Oils | β' -2 | Complex TAG mixture |
| Palm Oil | β' -2 | Moderately simple TAG mixture, diacylglycerols important |
| Lard | β' -3 | Moderately simple TAG mixture, mainly SSO type |

Polymorphism: Margarine & shortenings



Normal (β')



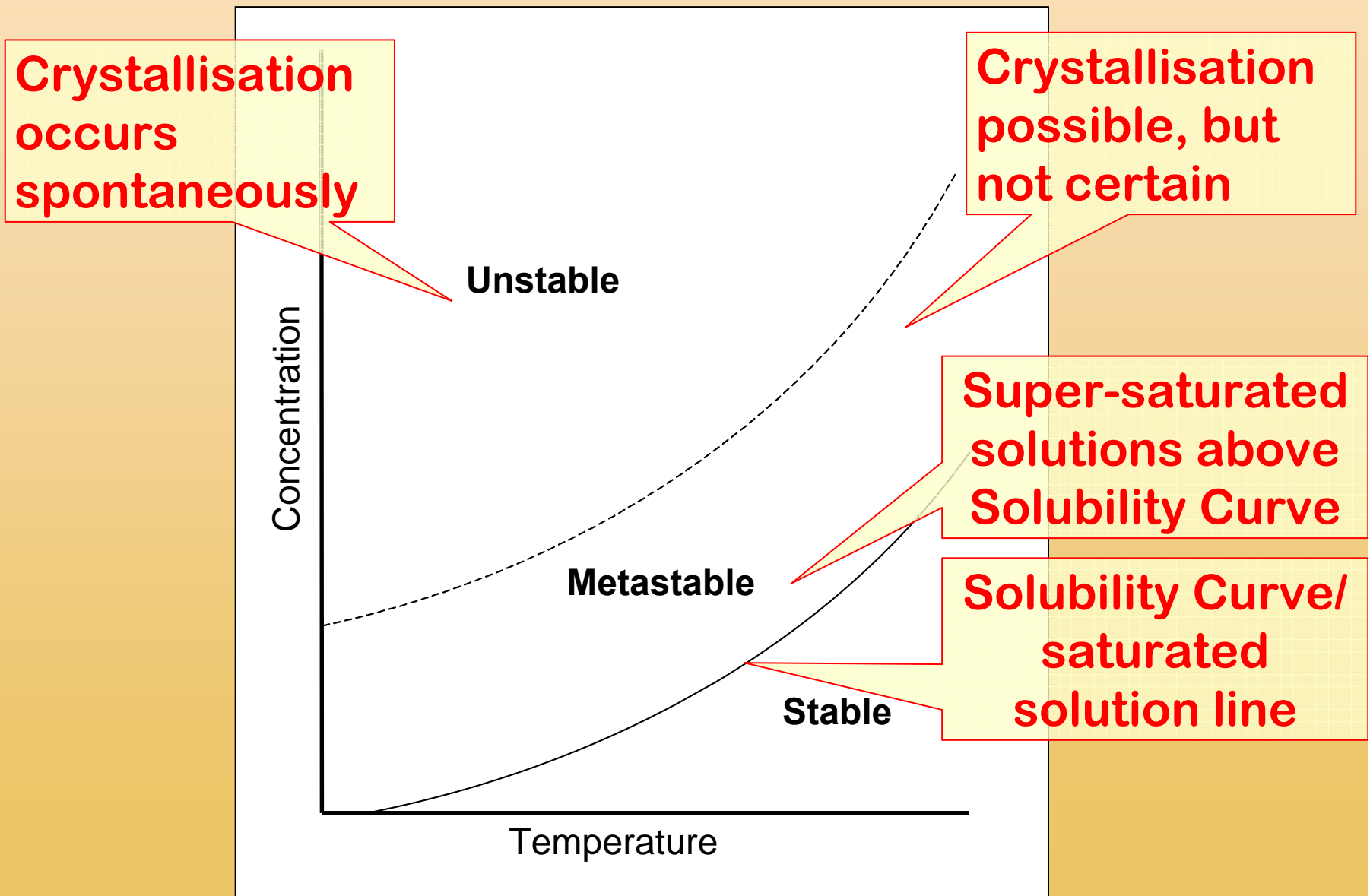
Sandy (β)

1 scale unit = 100 μ
(Danisco TP 1504-2e)

Crystallisation

- **Nucleation, Growth and Supercooling**
- **Post growth events, crystal ripening**

Crystallisation: Supercooling & Supersaturation



Crystallisation: Nucleation - 1

- A crystal nucleus is the smallest crystal that can exist in a triglyceride mixture of a certain concentration and temperature
- Aggregates of molecules smaller than a nucleus are called embryos and will redissolve if formed
- A stable crystal will form only when the energy gain due to the heat of crystallisation exceeds that required to overcome the surface energy required to increase the surface

Crystallisation: Nucleation - 2

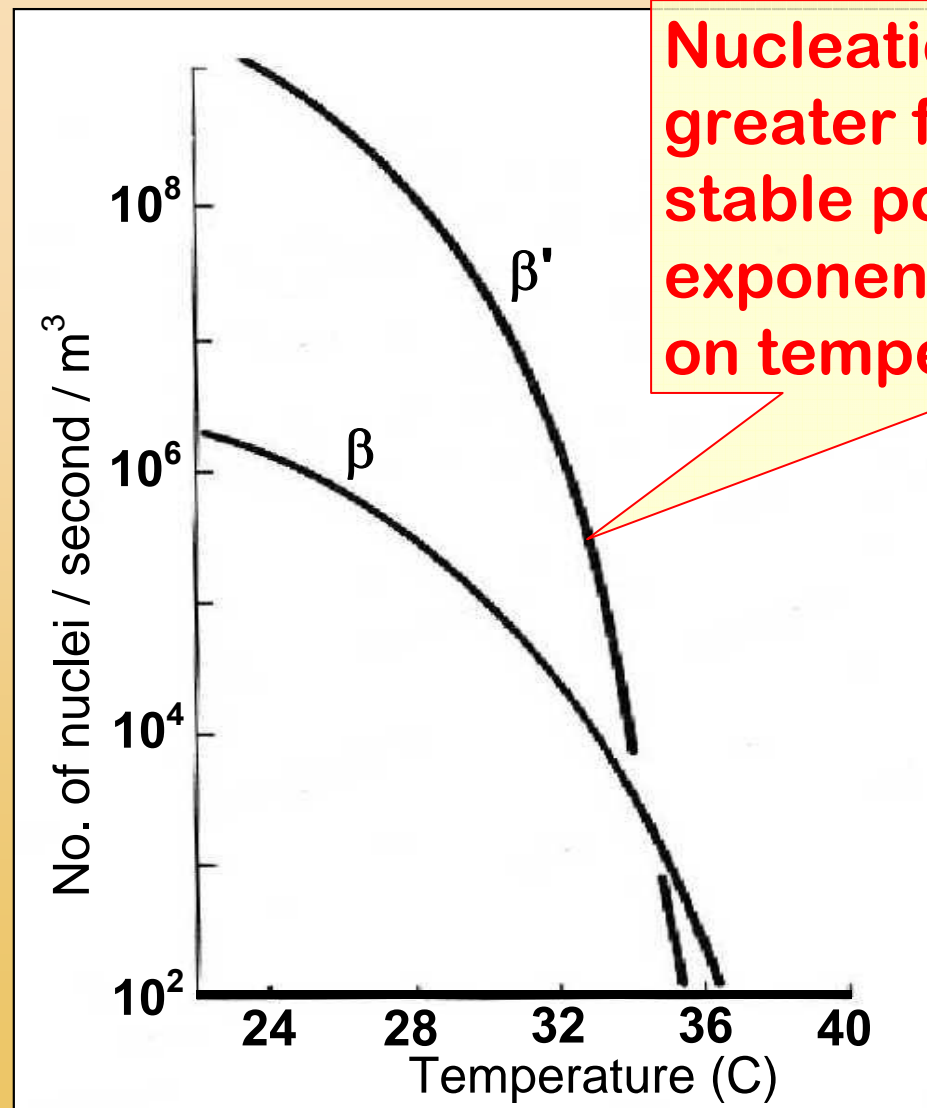
- **Homogeneous Nucleation** takes place spontaneously in the bulk of the liquid, but does not occur in fats in practice
- **Instead, Heterogeneous Nucleation** takes place and is initiated by solid particles such as dust, container wall or seed crystals
- This is why emulsions are difficult to crystallise - each droplet is isolated from the others so that seeds cannot propagate
- **Secondary Nucleation** occurs when small pieces break from existing crystals and act as nuclei for further crystallisation

Crystallisation: Nucleation - 3

- The least stable, α , polymorph has the lowest surface energy, as well as the lowest heat of crystallisation
- Small differences in surface energy produce large differences in nucleation rate
- Thus nucleation rates are in the order:

$$\alpha > \beta' > \beta$$

Crystallisation: Nucleation - 4



From van Putte & Bakker, 1987

Crystallisation: Growth

- Once a nucleus has formed, it starts to grow
- The growth rate is proportional to the degree of supercooling, i.e. lower temperature, and inversely proportional to the viscosity
- Like the nucleation rate, the growth rate depends on the polymorph crystallised
- The more stable the polymorph the less soluble it is and therefore the higher the growth rate, i.e.:

$$\beta > \beta' > \alpha$$

- But, rapid cooling of a fat always leads to the initial formation of unstable α (or β') crystals because nucleation is exponentially related to temperature

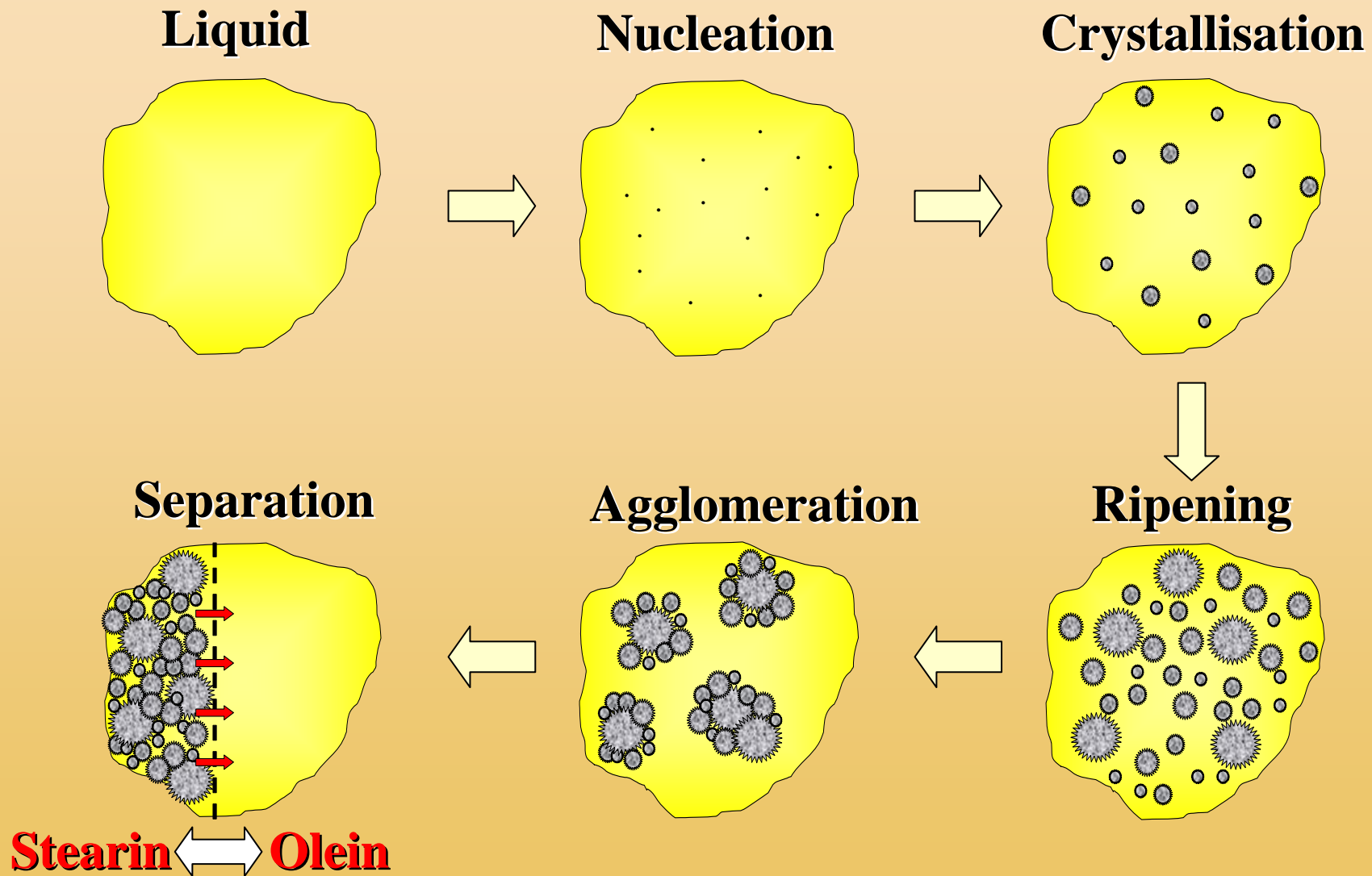
Crystallisation: Post-growth events - 1

- **Contraction**: Solid fat occupies about 90% of the volume of liquid fat
- The amount of contraction depends on the SFC of the fat (the amount of fat crystallised) and the polymorph - more stable polymorphs are denser
- **Agglomeration**: Crystals form agglomerates of spherulitic crystals with particle sizes of several hundred μm

Crystallisation: Post-growth events - 2

- (Ostwald) Ripening: As nucleation, growth and agglomeration proceed, the overall supersaturation decreases and the critical size for a stable crystal or nucleus increases.
- Smaller crystals, which were stable at lower levels of supersaturation, now become unstable and redissolve.
- In theory, the process would continue indefinitely until eventually only one large crystal was left in the presence of a slightly supersaturated liquid.
- In practice, once crystals grow to about $10\mu\text{m}$, the thermodynamic driving force is small

Crystallisation: Summary



Adapted from: desmet ballestra

Methods for studying

Measure:

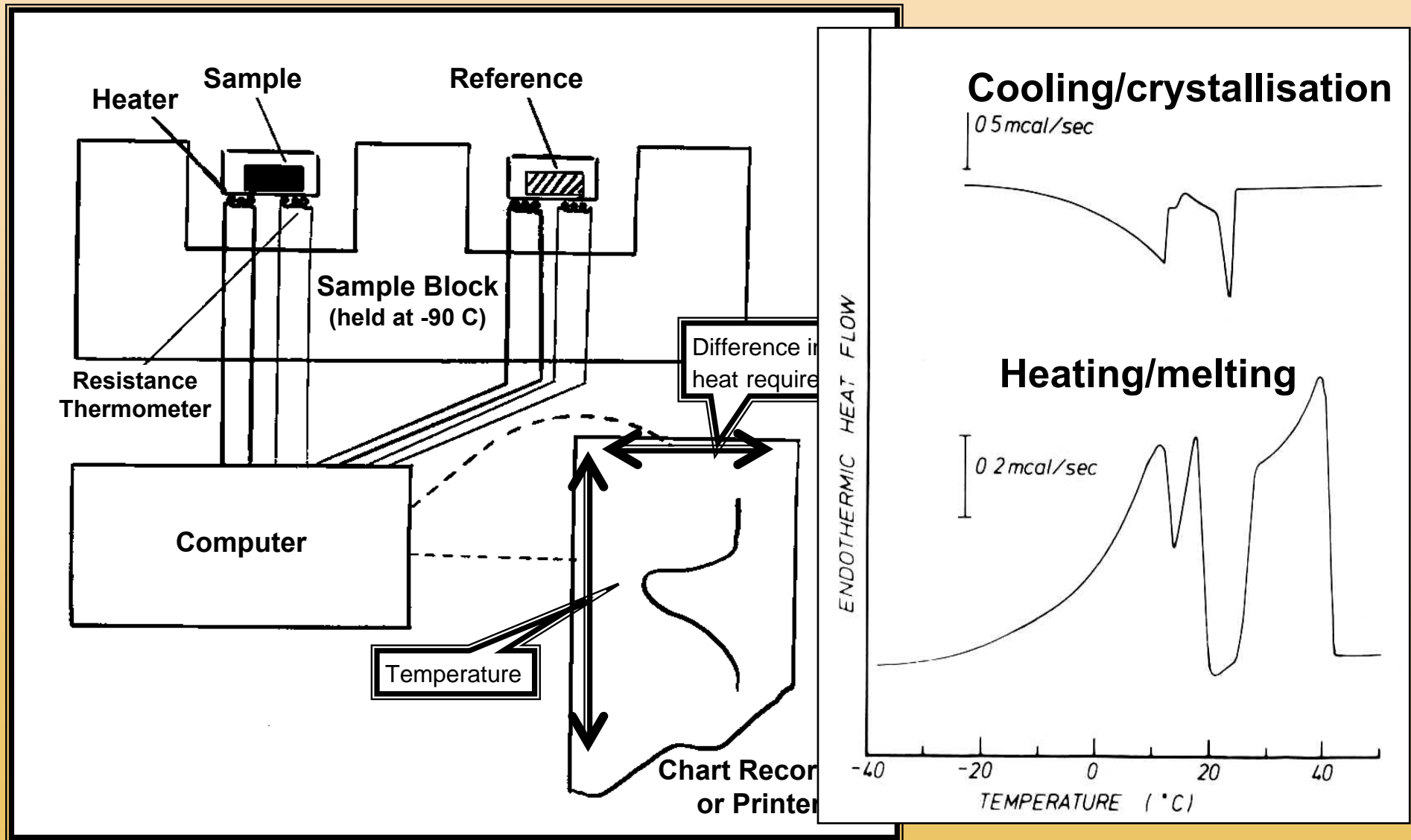
1. Heat evolved during crystallisation

- Differential Scanning Calorimetry
- Differential Thermal Analysis
- Cooling Curves – Jensen & Shukoff

2. Increase in amount of fat crystals

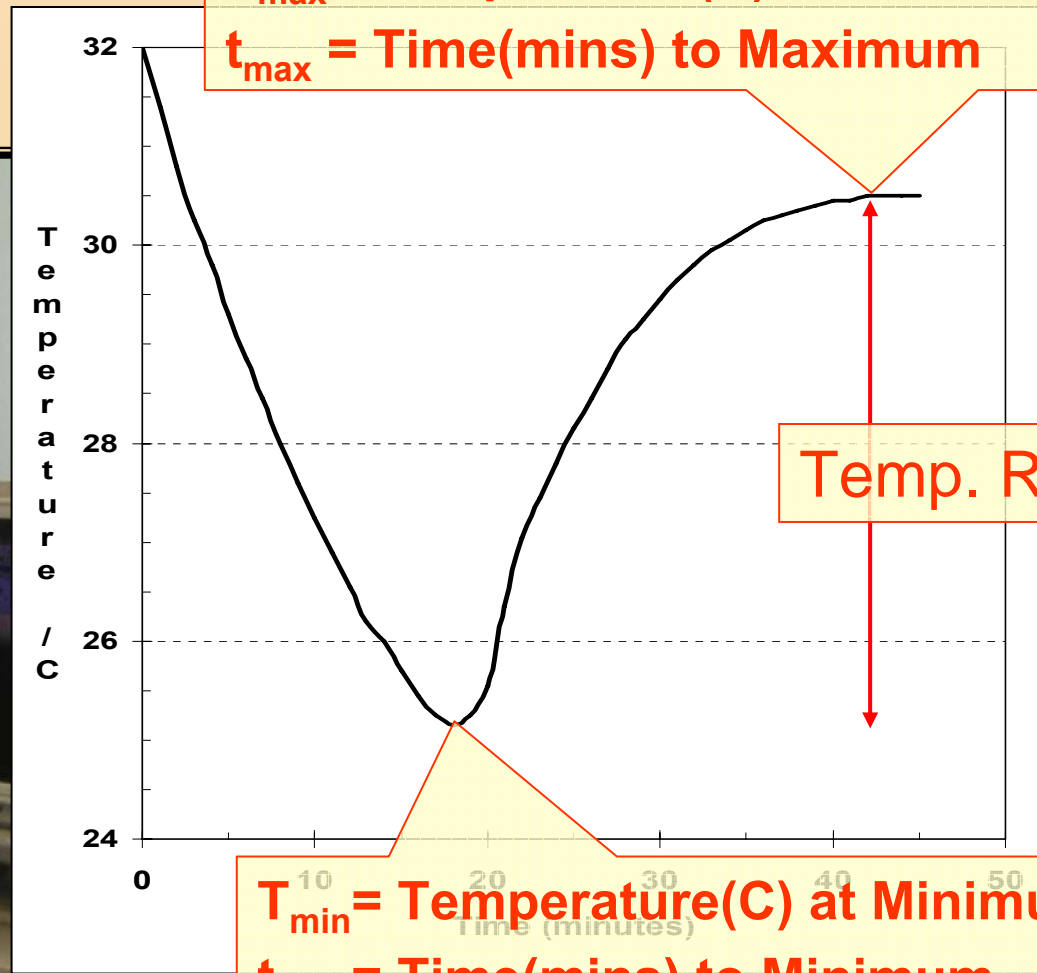
- Solid Fat Content by NMR
- Turbidity using light-scattering

Crystallisation of milk fat – DSC cooling & heating curves



Crystallisation of cocoa butter – Jensen Cooling Curve

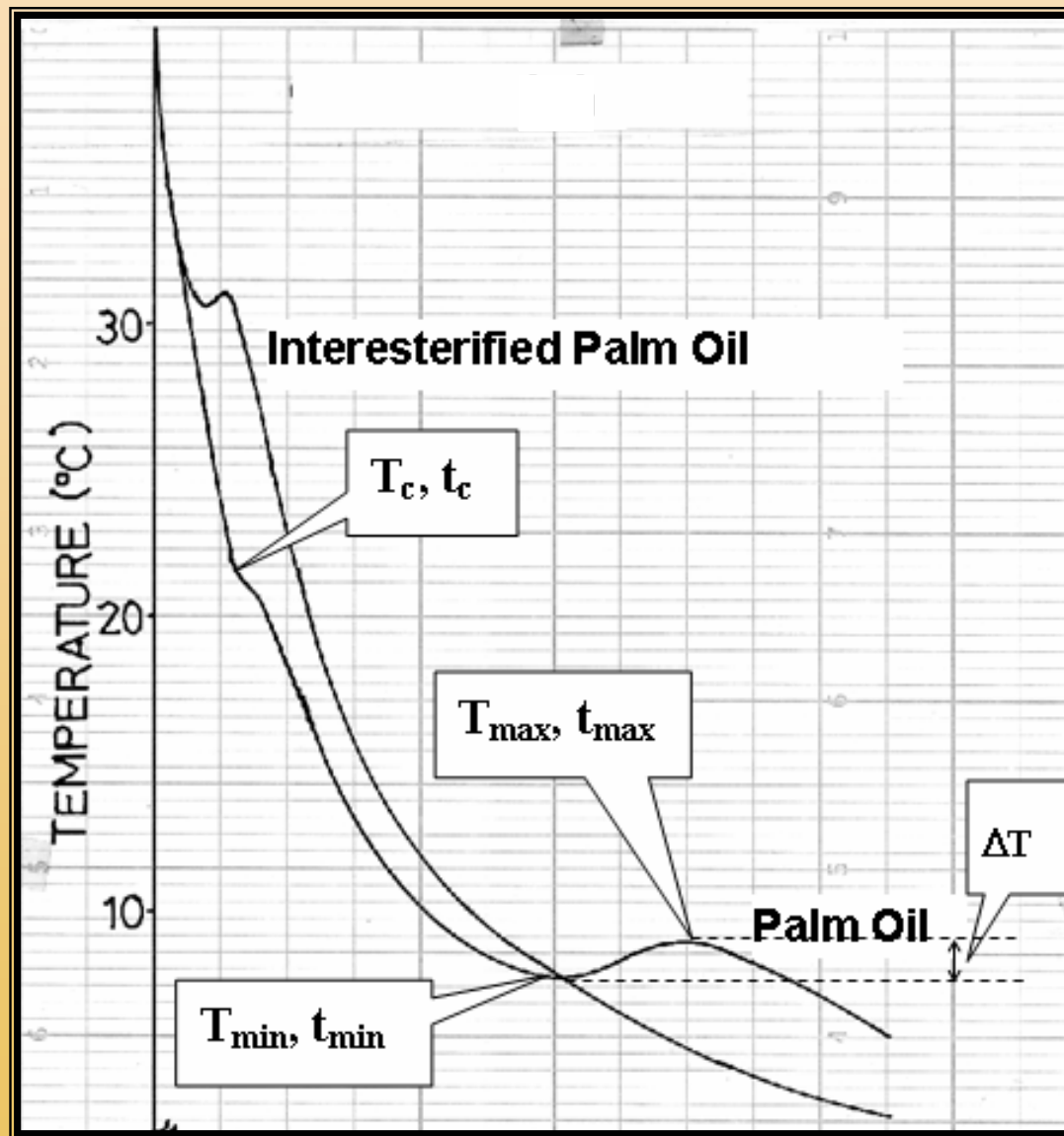
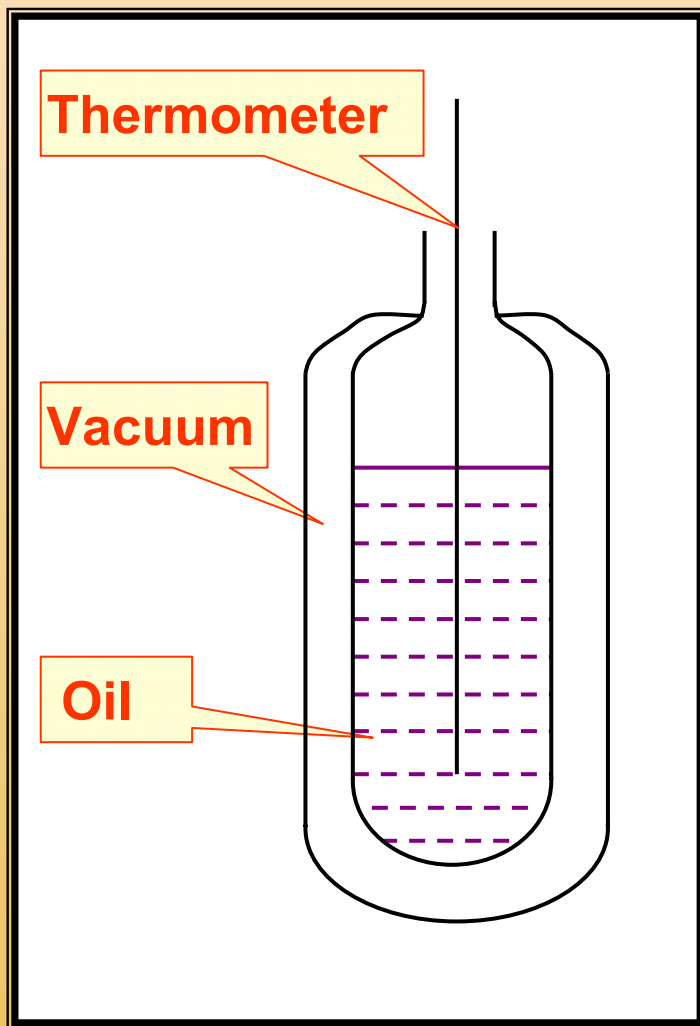
BSI Method 684:1.13



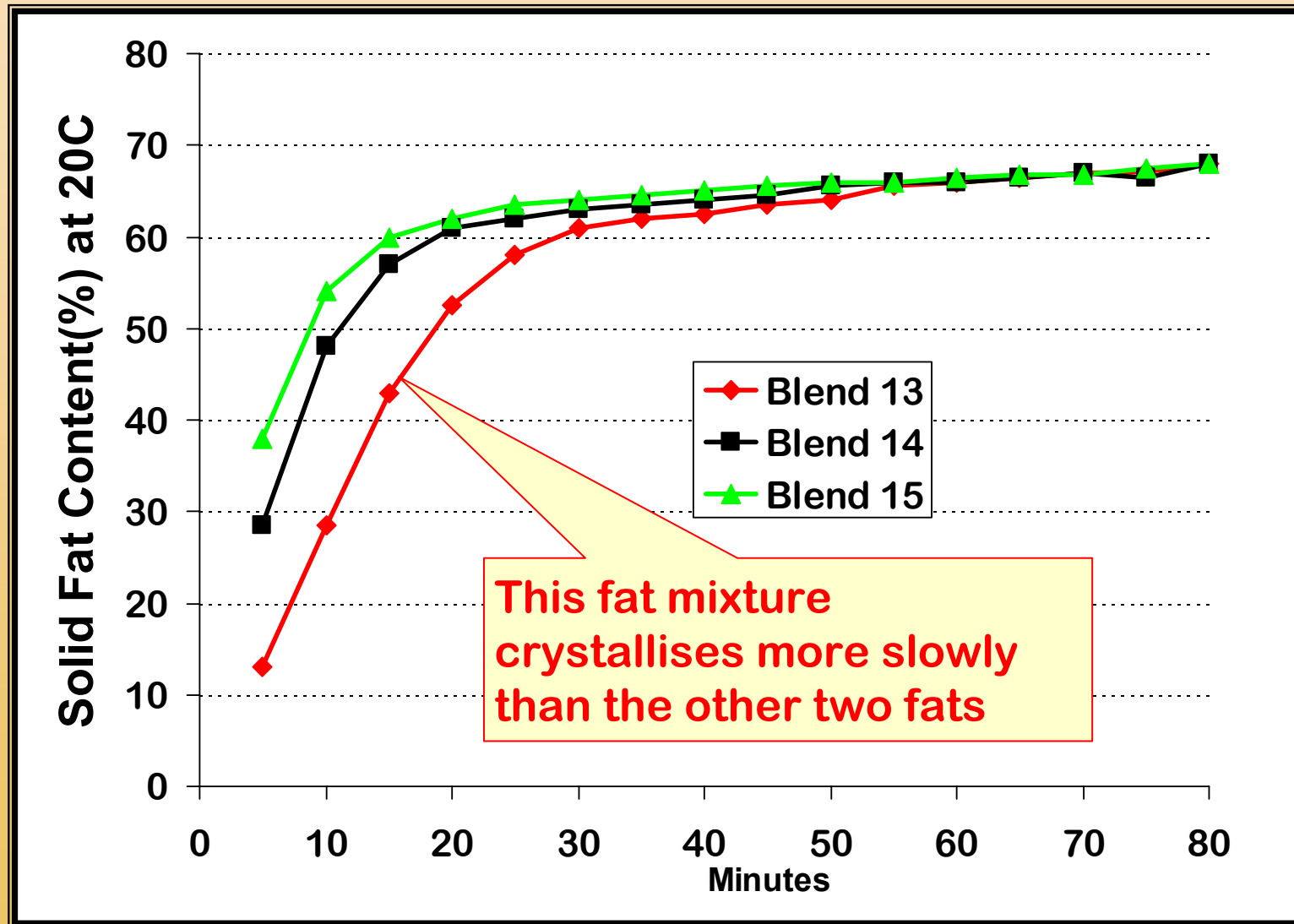
Automated Jensen Cooling Curve

Crystallisation of palm oil – Shukoff Cooling Curve

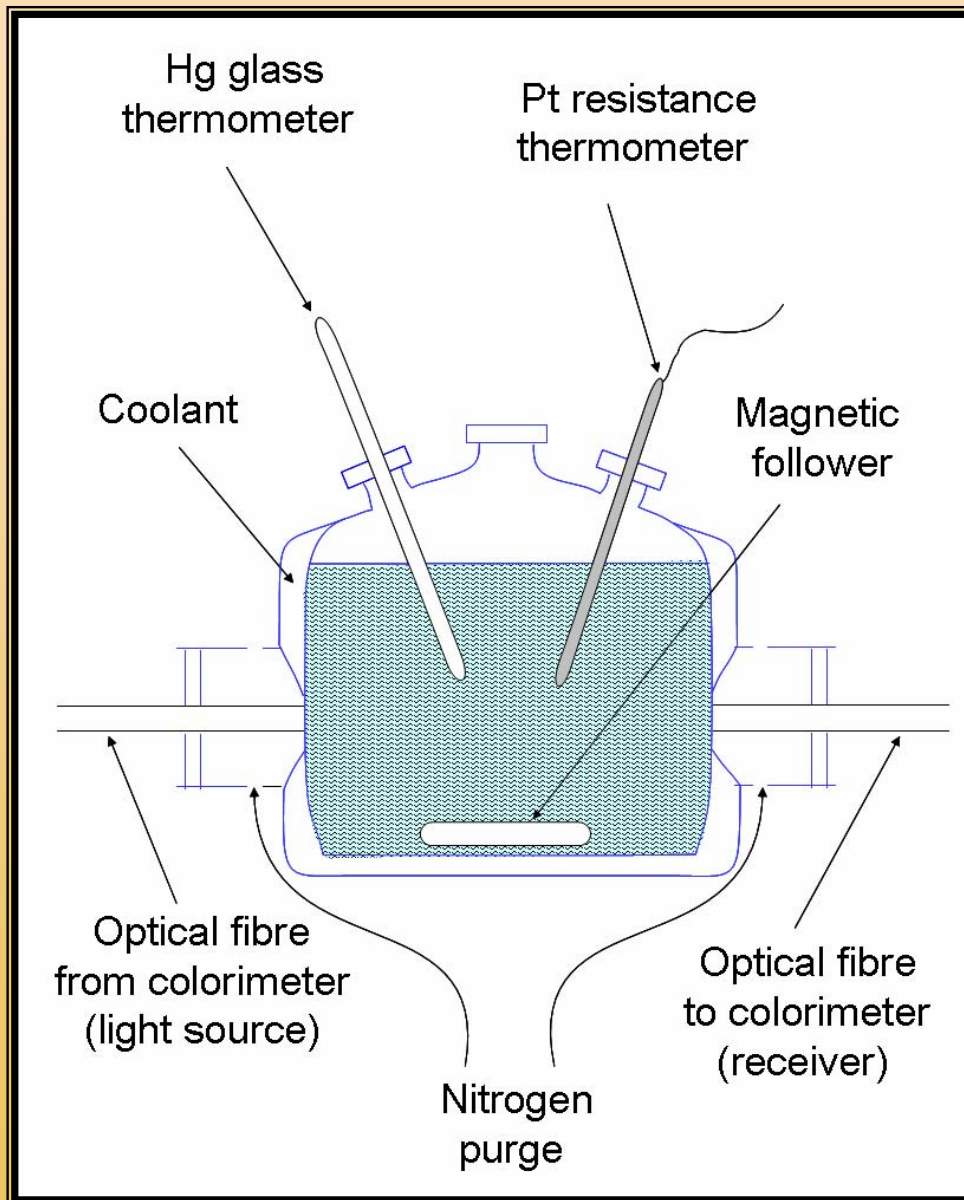
IUPAC Method 2.132



Crystallisation of 3 Fats - SFC Determination (30C for 1 h tempering before measurement at 20C)

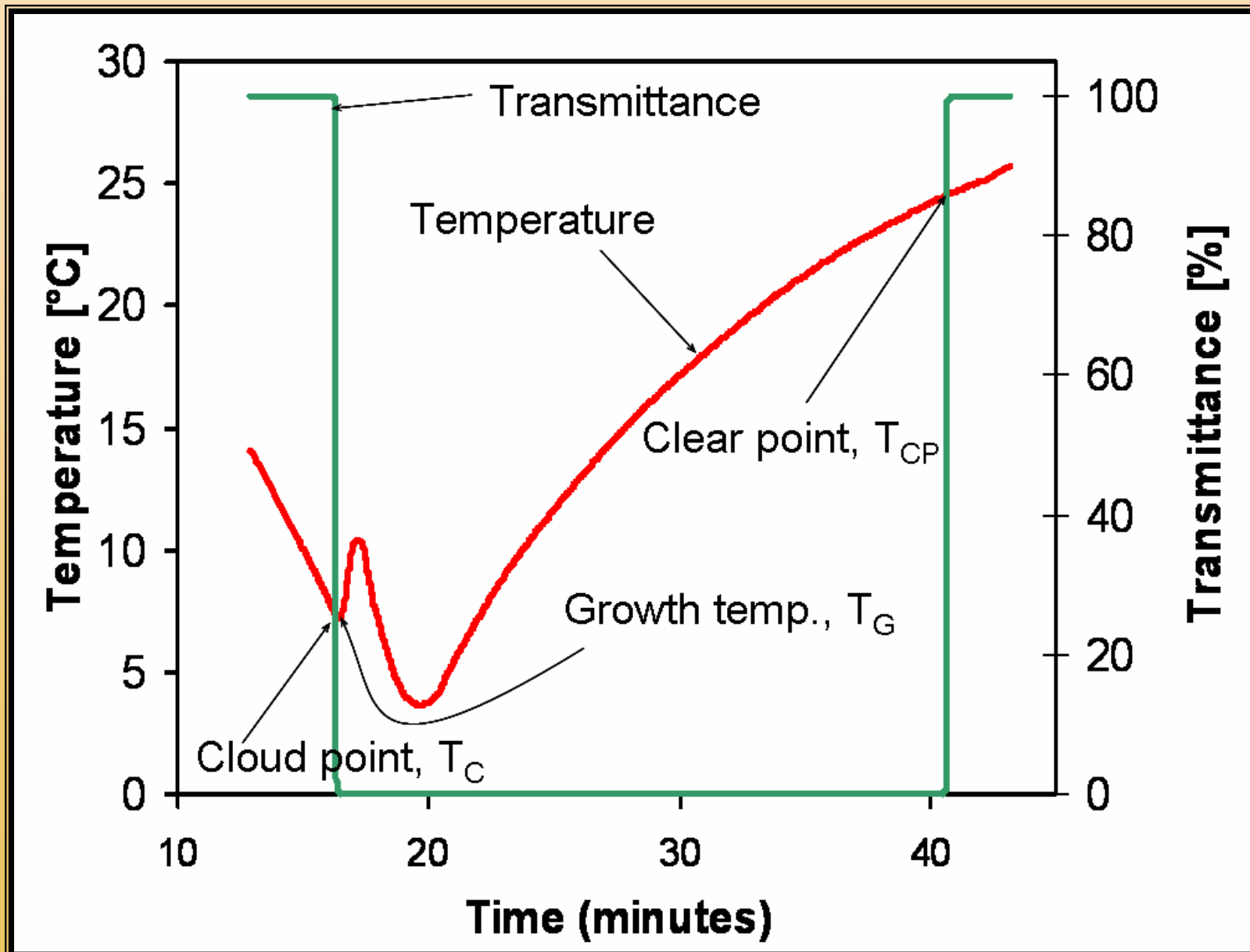


Turbidity using light-scattering - 1




From Smith, Cain & Talbot,
2005

Turbidity using light-scattering - 2



Fat Crystallisation: Summary

- **Polymorphism**
 - α , β' and β in order of increasing stability
 - double and triple spacing
 - β' preferred for many food fats
- **Crystallisation**
 - Nucleation followed Growth
 - α forms first
- **Methods for studying**
 - Heat evolved during crystallisation:
 - DSC, DTA, Cooling Curves
 - Increase in amount of fat crystals:
 - SFC, Turbidity



Thank you!
Any Questions?

