Fat Crystallisation: mechanism and methods for studying

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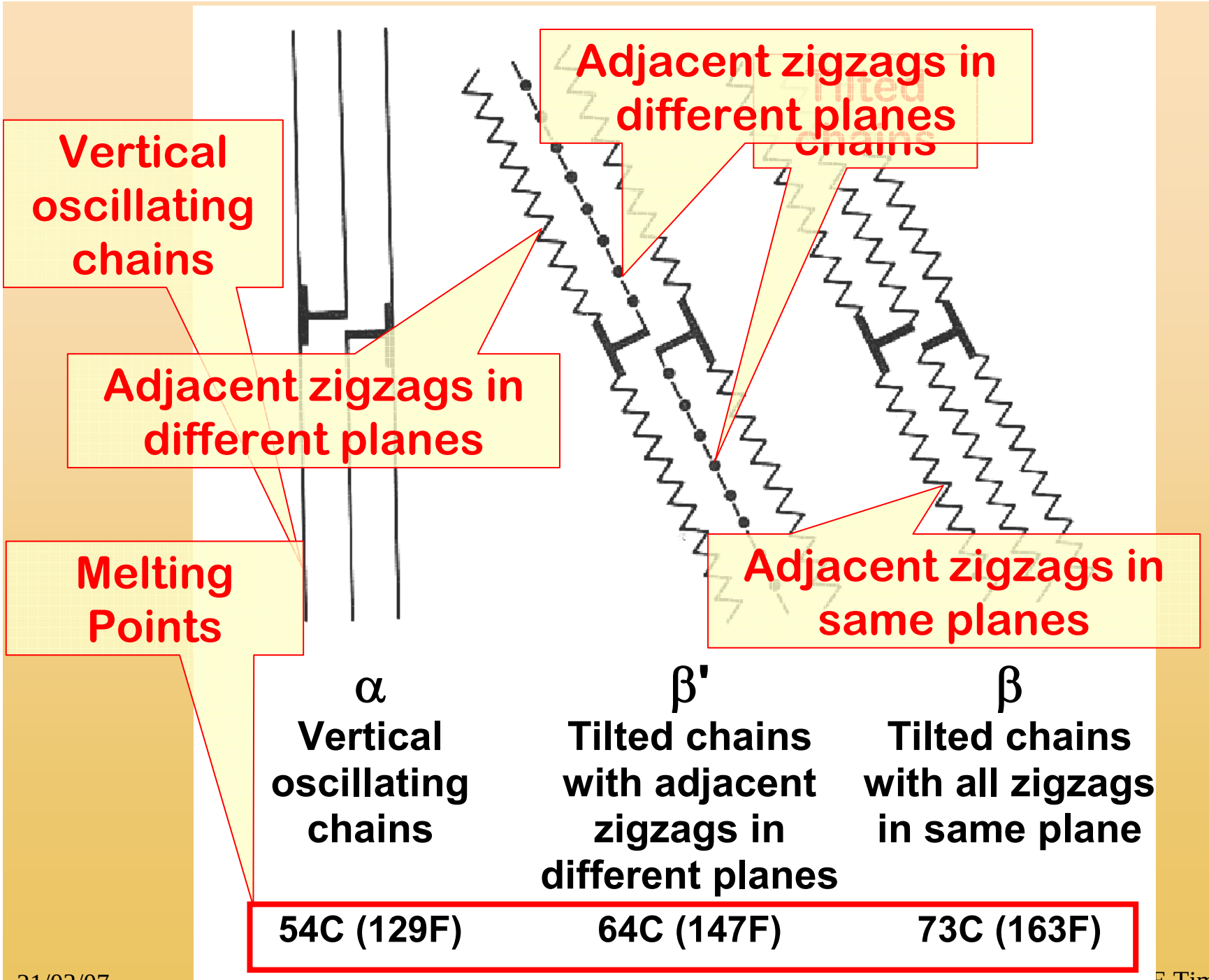
Ralph E Timms
Tel & Fax: +44 1526 322 515
Email: ralph@timms1.net

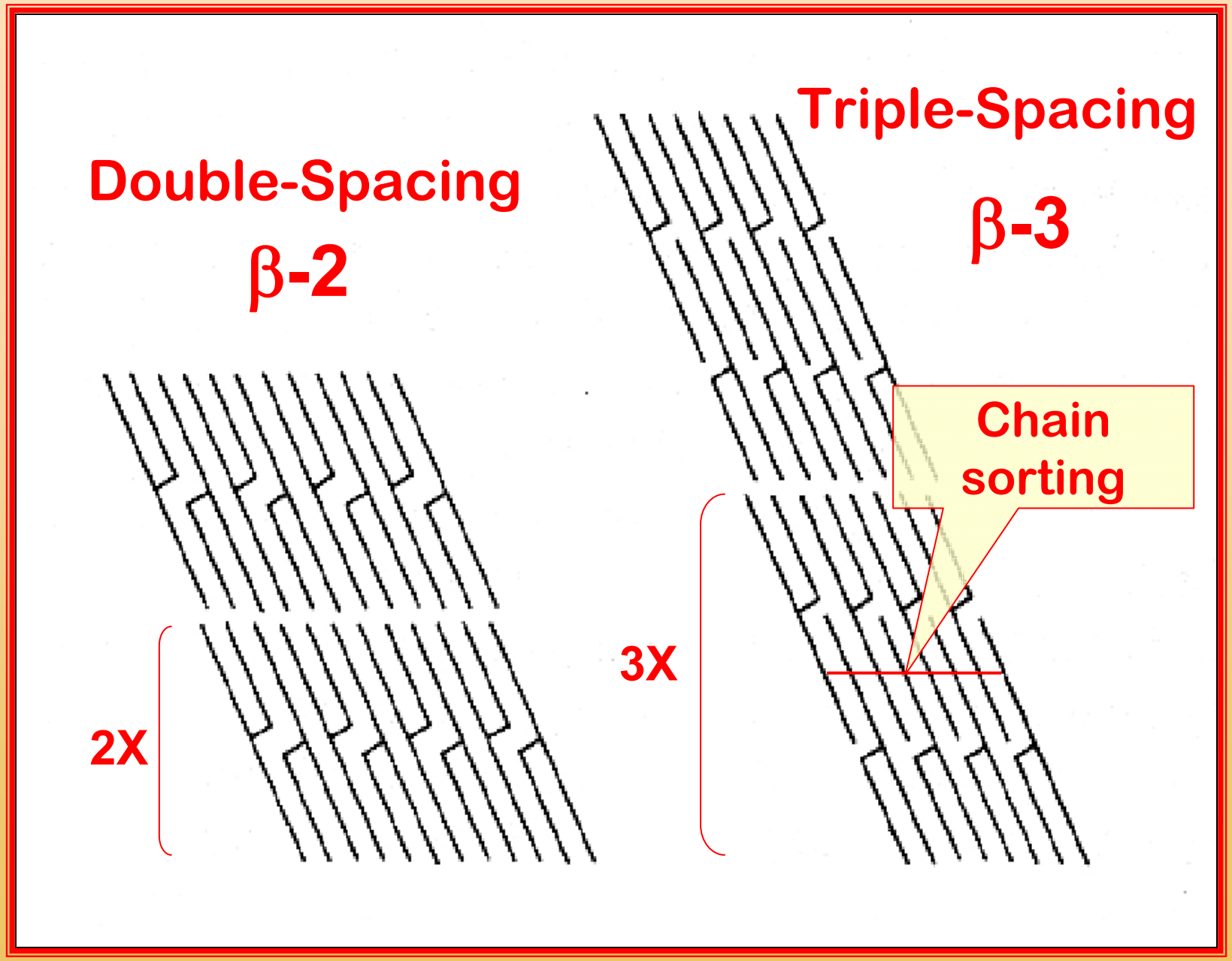
Fat Crystallisation: mechanism and methods for studying

- **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

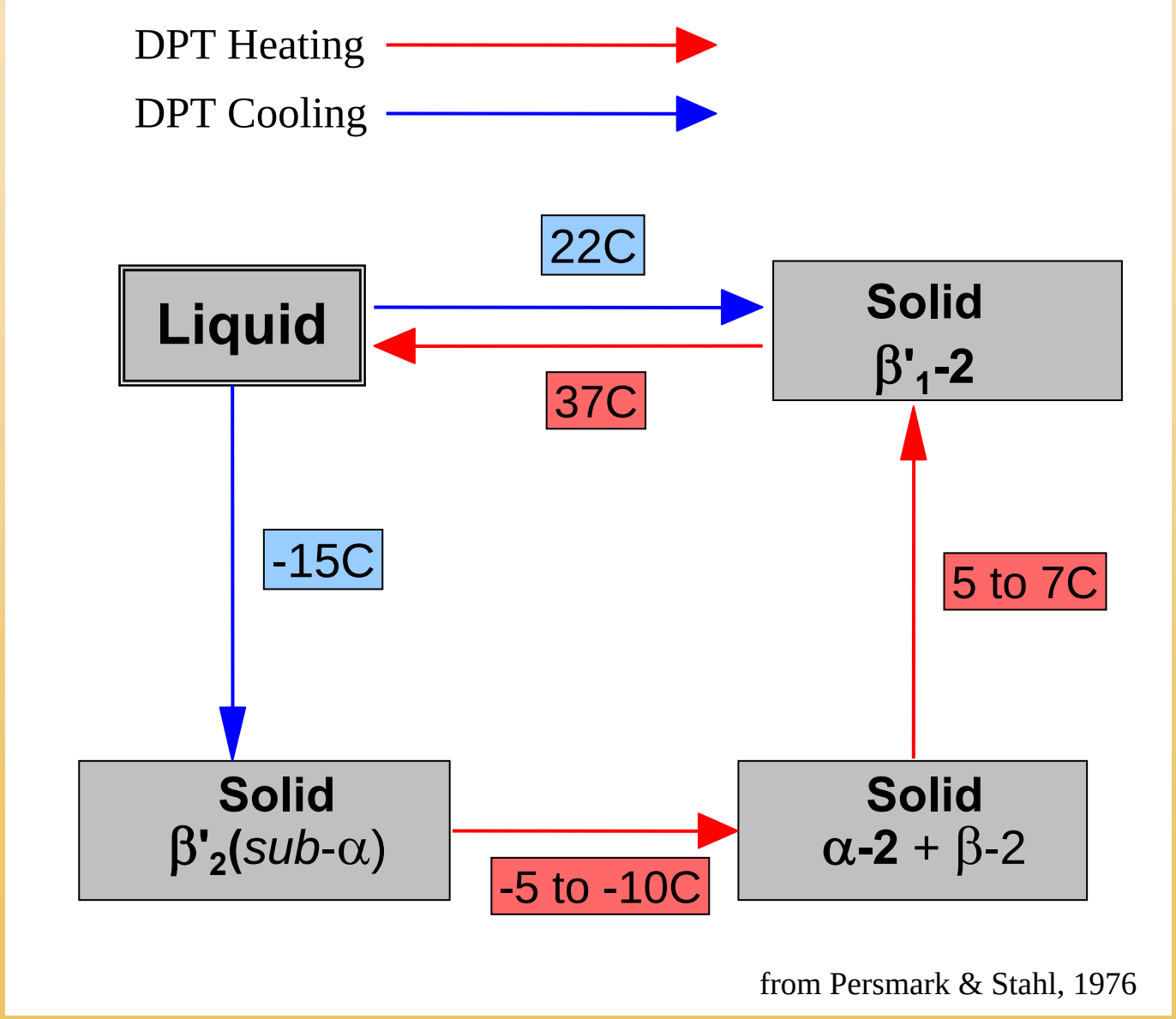
Polymorphism

- 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.


Vertical oscillating chains
Adjacent zigzags in different planes
Adjacent zigzags in different planes
Adjacent zigzags in same planes
Melting Points
α
Vertical oscillating chains
β'
Tilted chains with adjacent zigzags in different planes
β
Tilted chains with all zigzags in same plane
54C (129F)
64C (147F)
73C (163F)


Double-Spacing
β-2
2X
Triple-Spacing
β-3
3X
Chain
sorting

Polymorphism of Palm Oil & Fractions

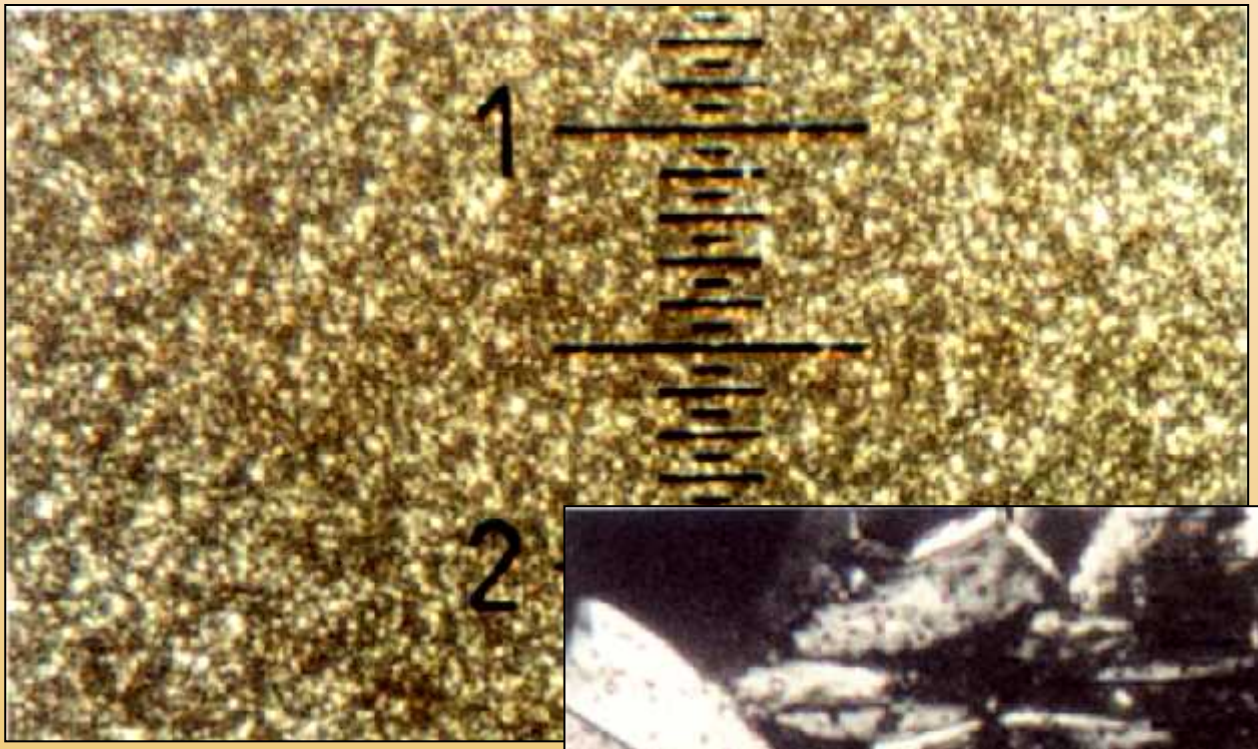


from Persmark & Stahl, 1976

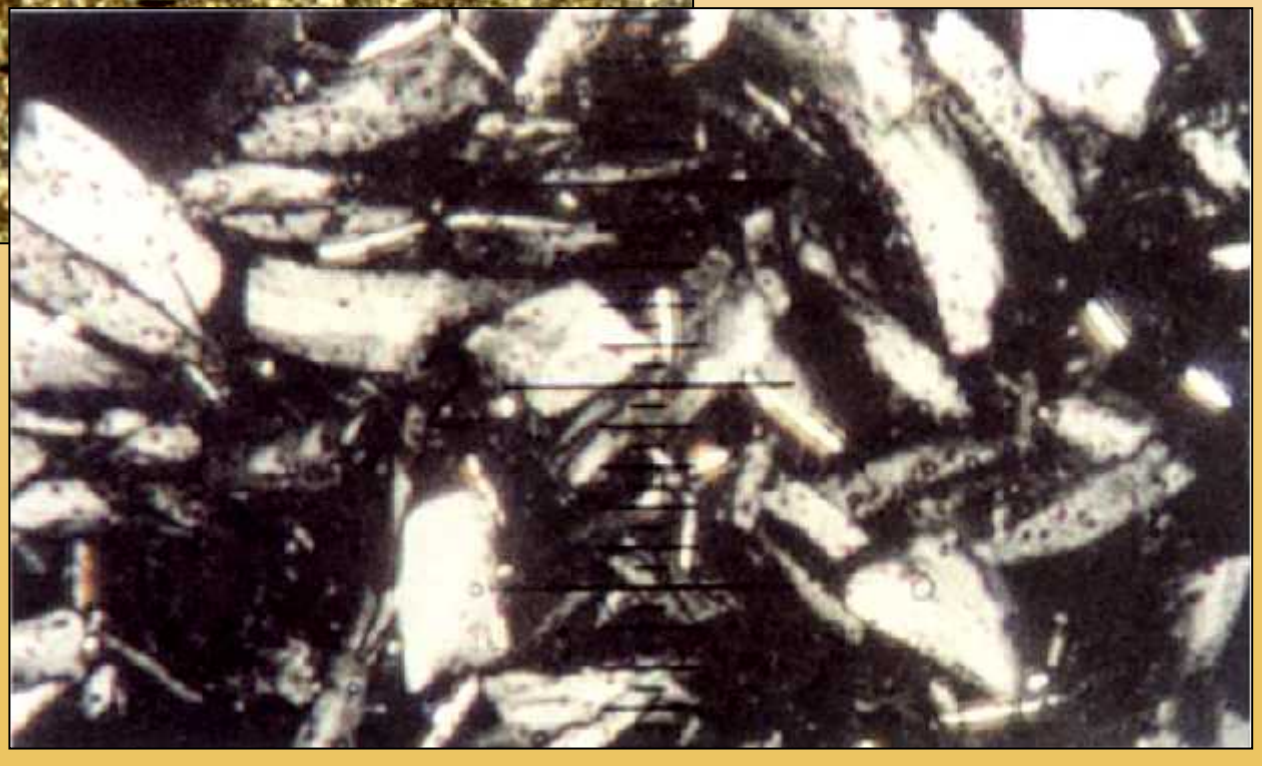
Stable/Typical Polymorphs of common fats

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')



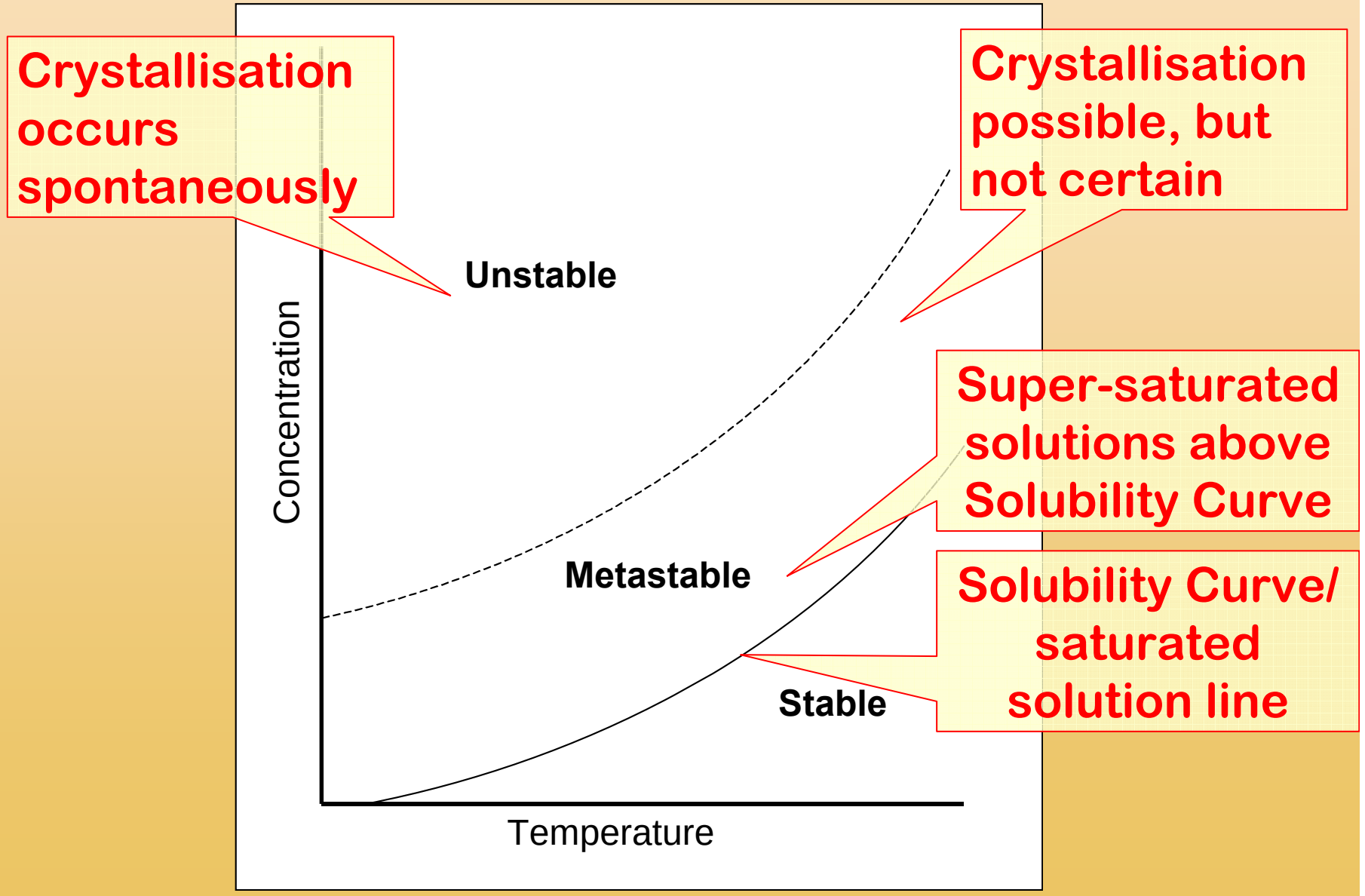
Sandy (β)

1 scale unit = 100µ
(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

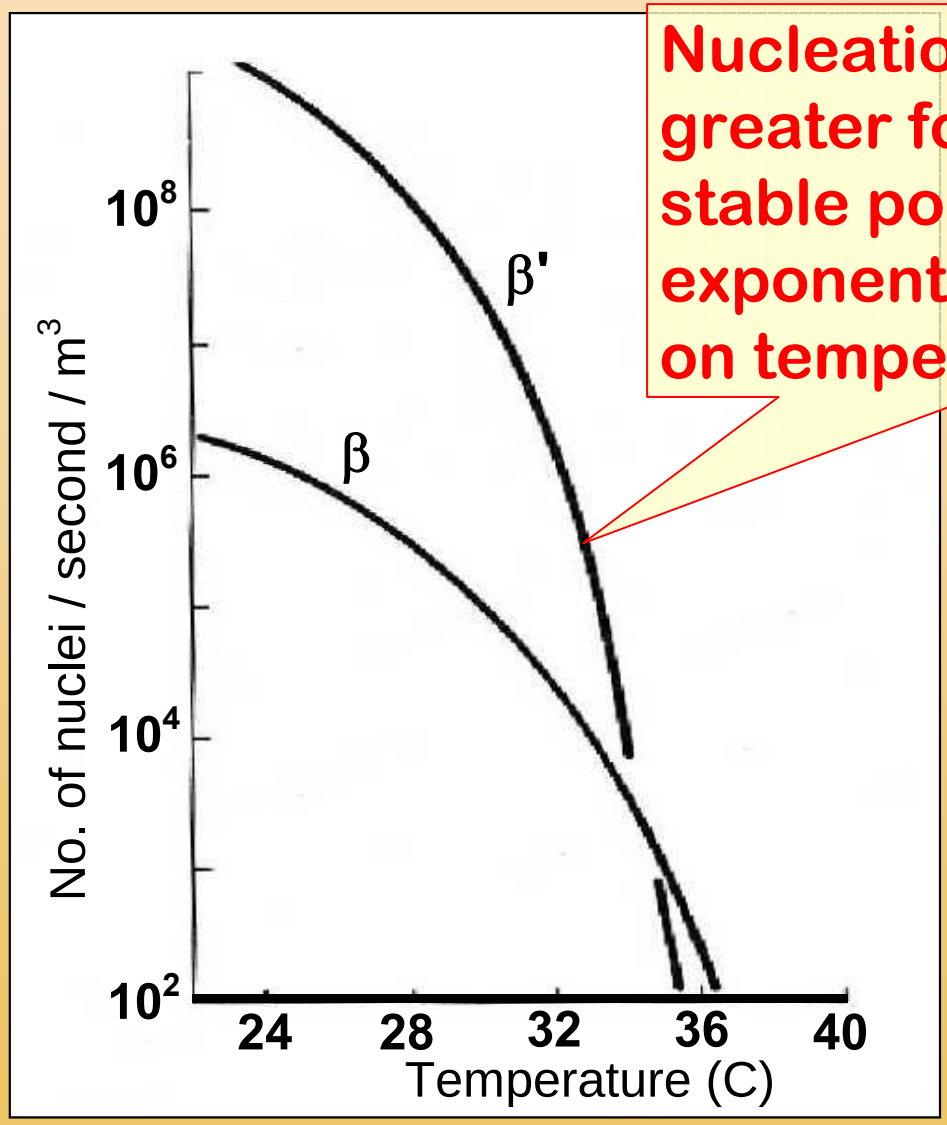
- **Homogeneous Nucleation** takes place spontaneously in the bulk of the liquid, but does not occur in fats in practice
- Instead, **Heterogeneous Nucleation** takes place and is initiated by solid particles such as dust, container wall or seed crystals
- This is why emulsions are difficult to crystallise - 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



Nucleation rate is greater for the less stable polymorph and is exponentially dependent on temperature

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 <u>exponentially</u> related to temperature

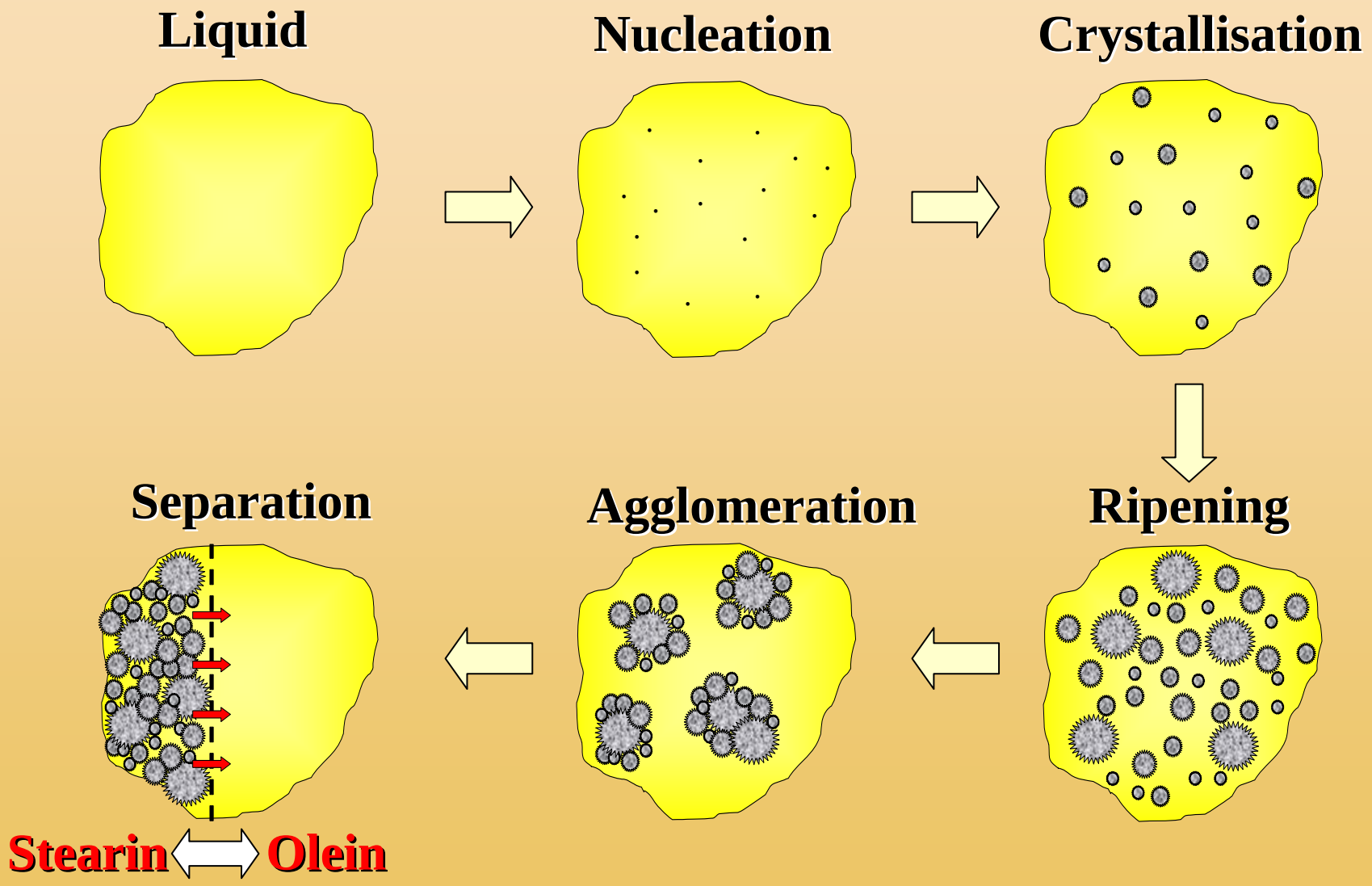
Crystallisation: Post-growth events - 1

- 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 10μm, the thermodynamic driving force is small

Crystallisation: Summary



Adapted from: desmet ballestra

Methods for studying

Measure:

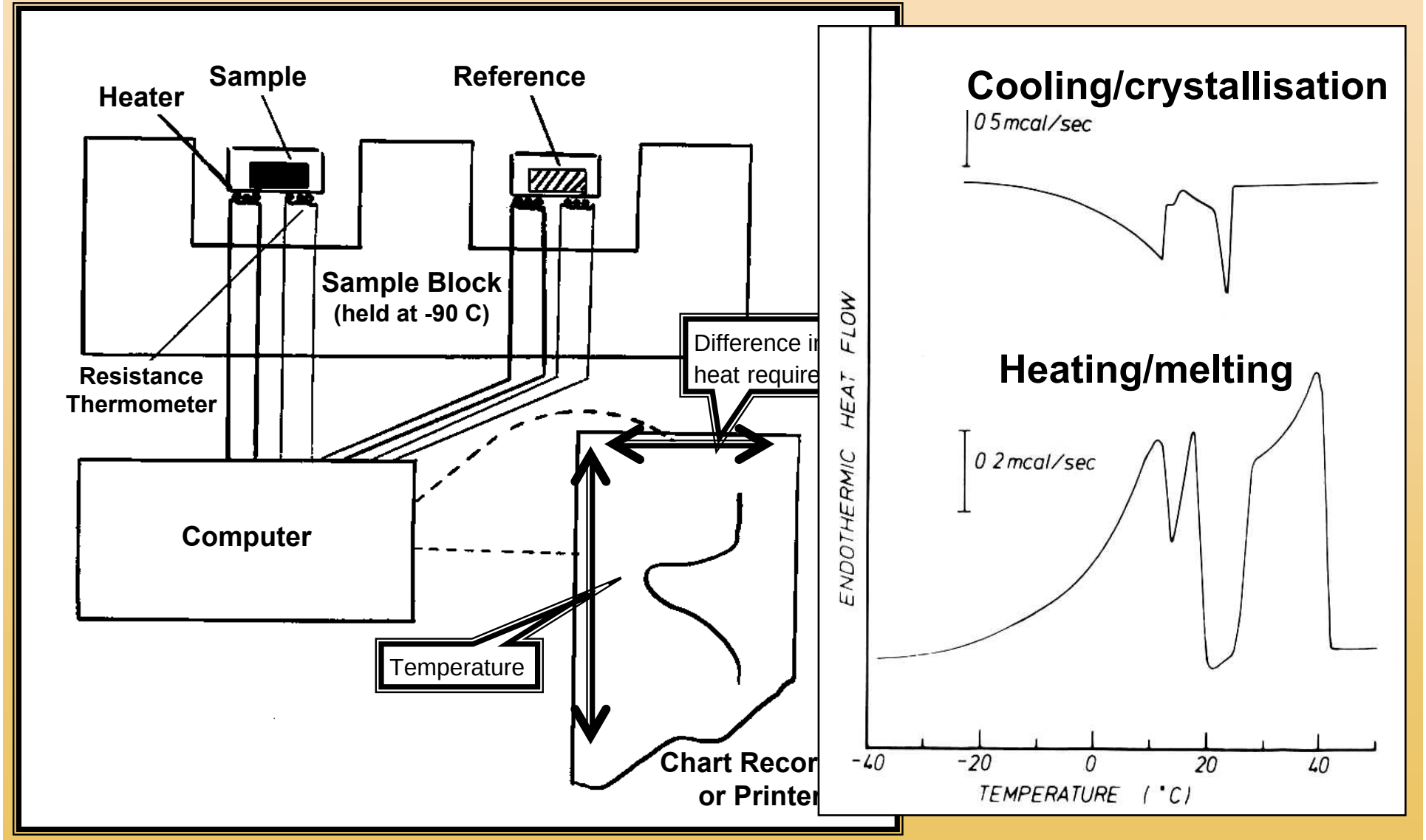
1. Heat evolved during crystallisation

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

2. Increase in amount of fat crystals

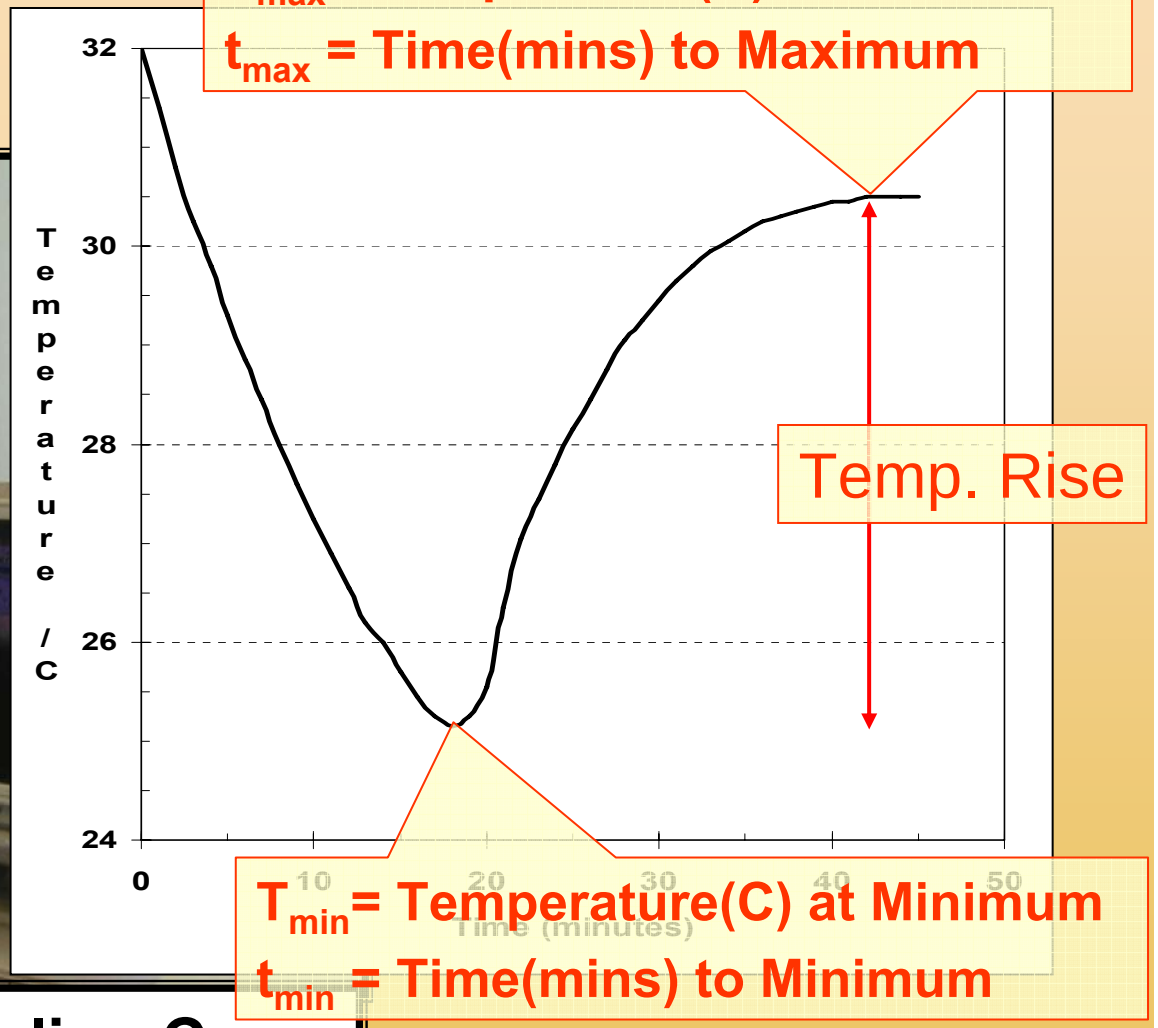
- Solid Fat Content by NMR
- Turbidity using light-scattering

Crystallisation of milk fat – DSC cooling & heating curves



Crystallisation of cocoa butter – Jensen Cooling Curve

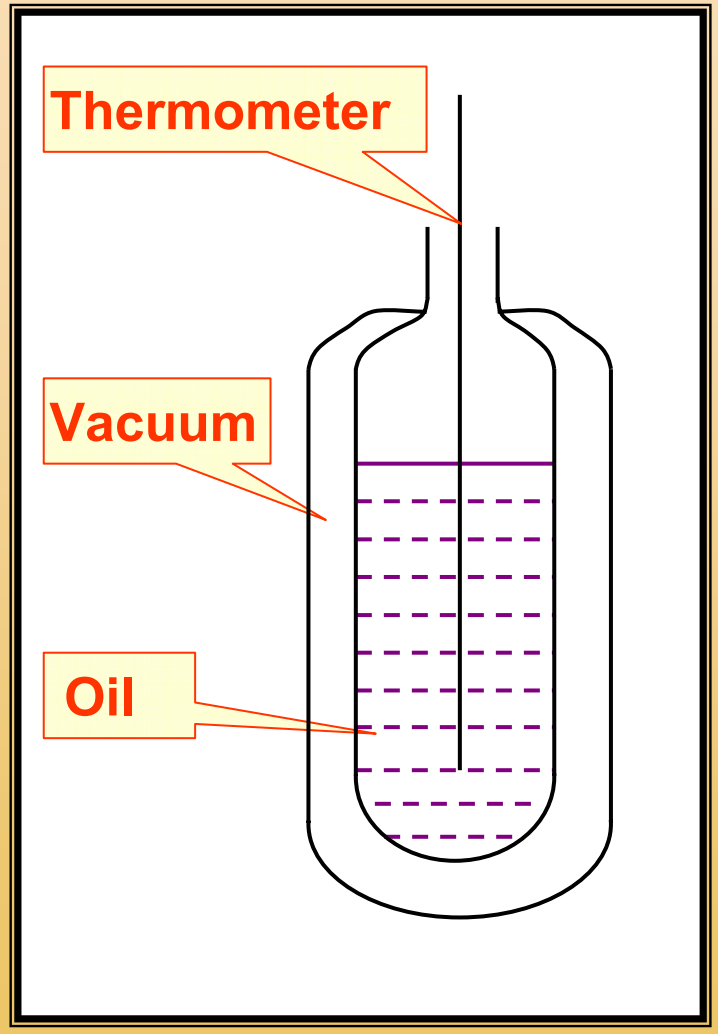
BSI Method 684:1.13

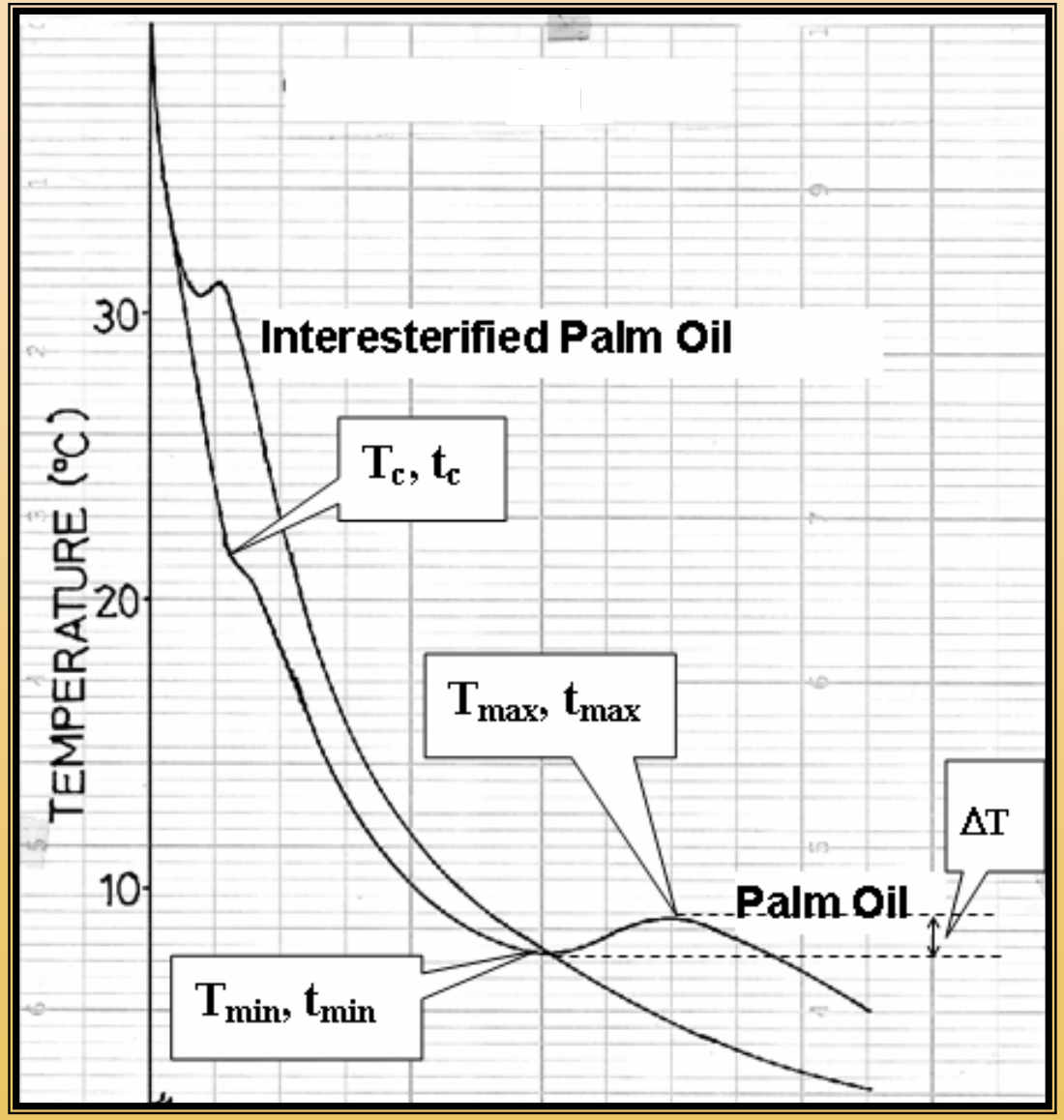


Automated Jensen Cooling Curve

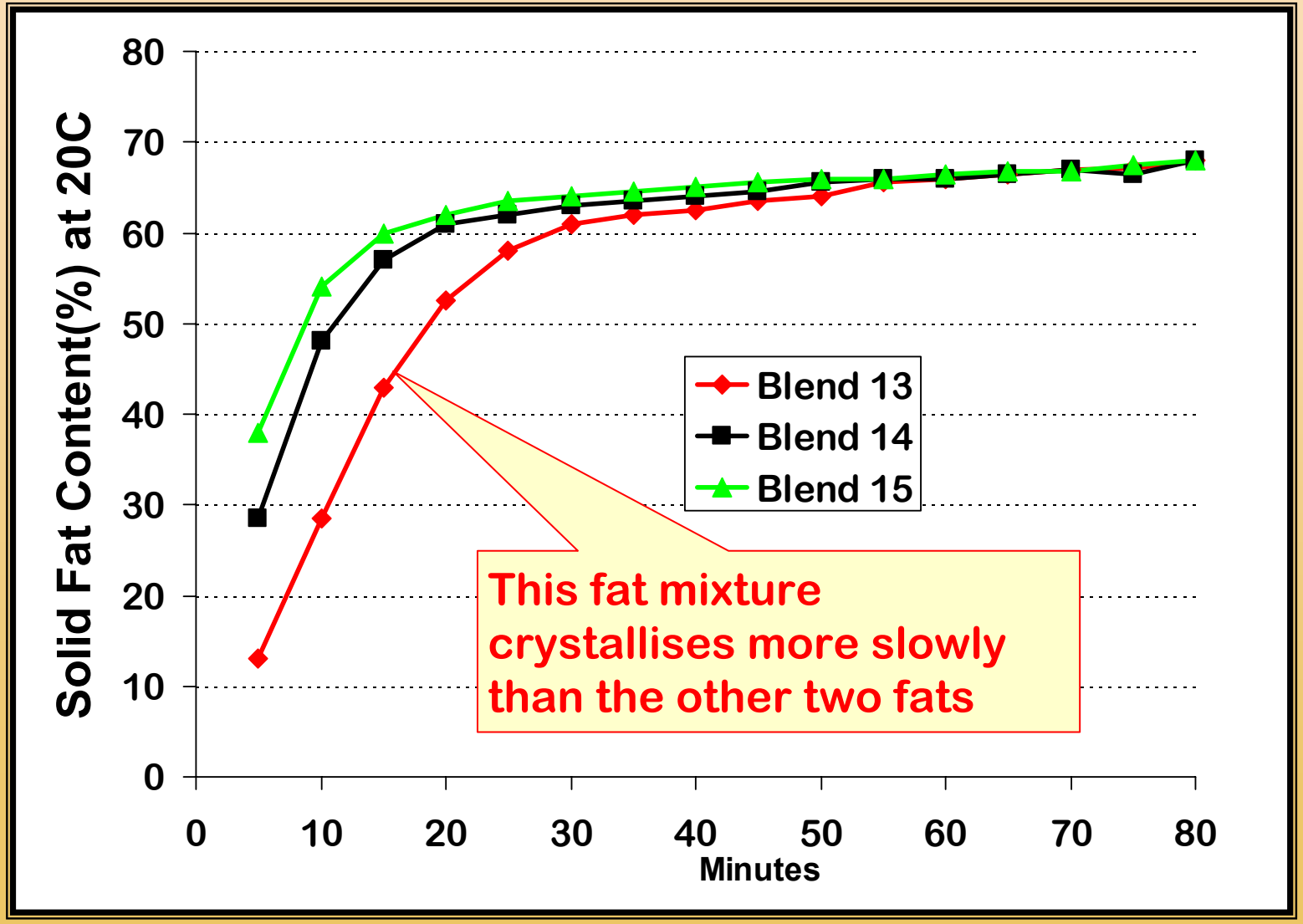
Crystallisation of palm oil – Shukoff Cooling Curve

IUPAC Method 2.132

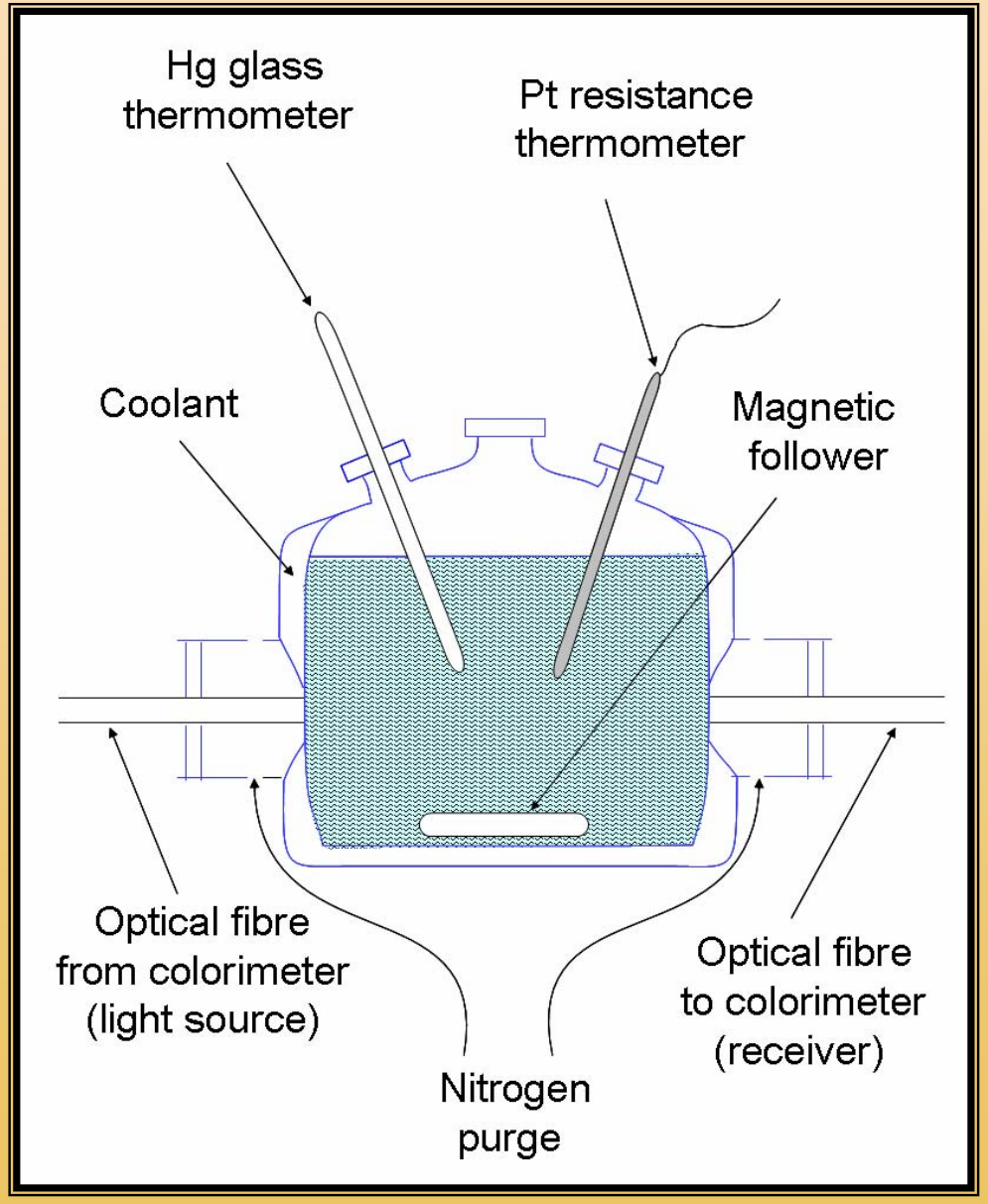




Crystallisation of 3 Fats - SFC Determination
(30C for 1 h tempering before measurement at 20C)

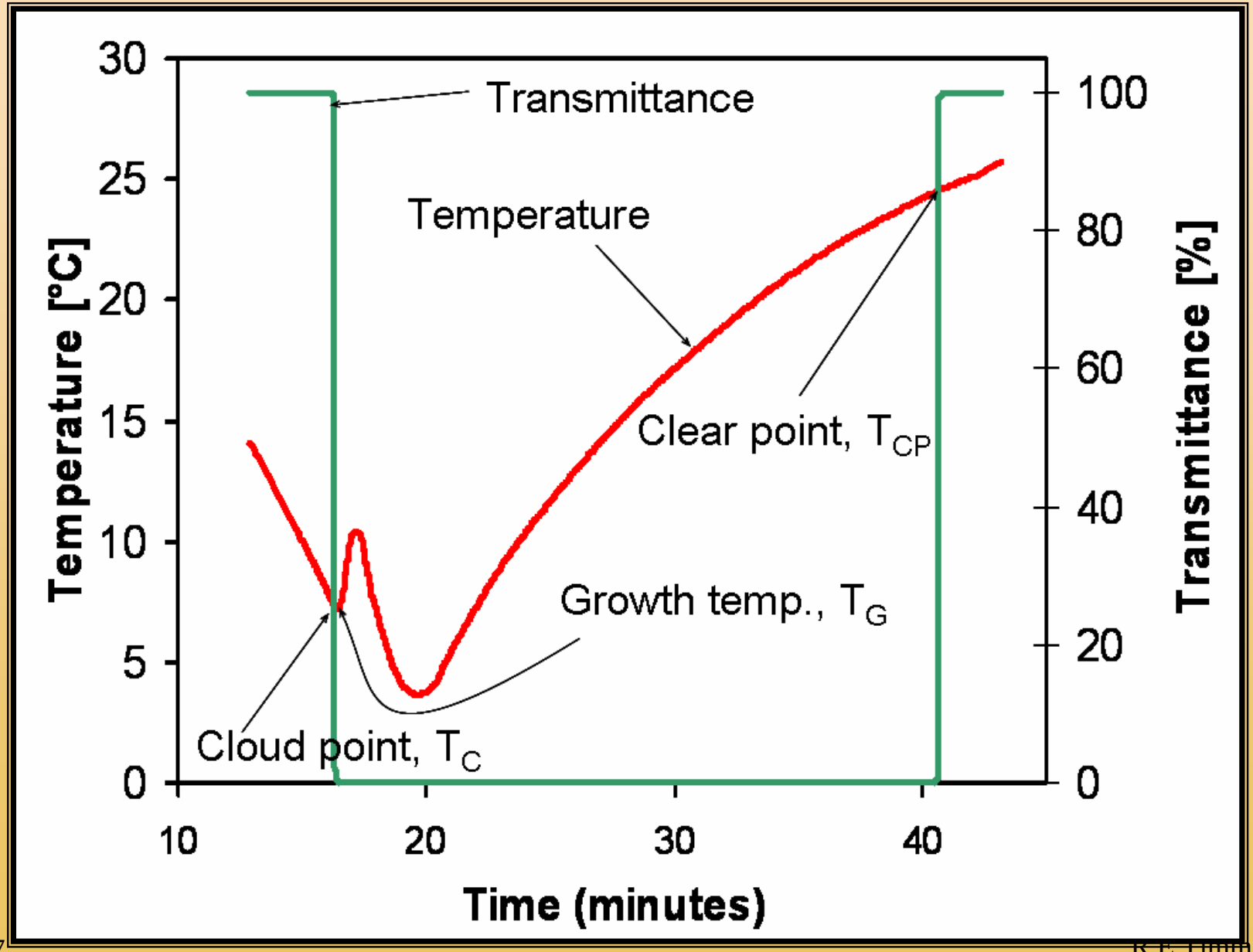


Turbidity using light-scattering - 1



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?