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Fundamentals of Fat Crystallisation

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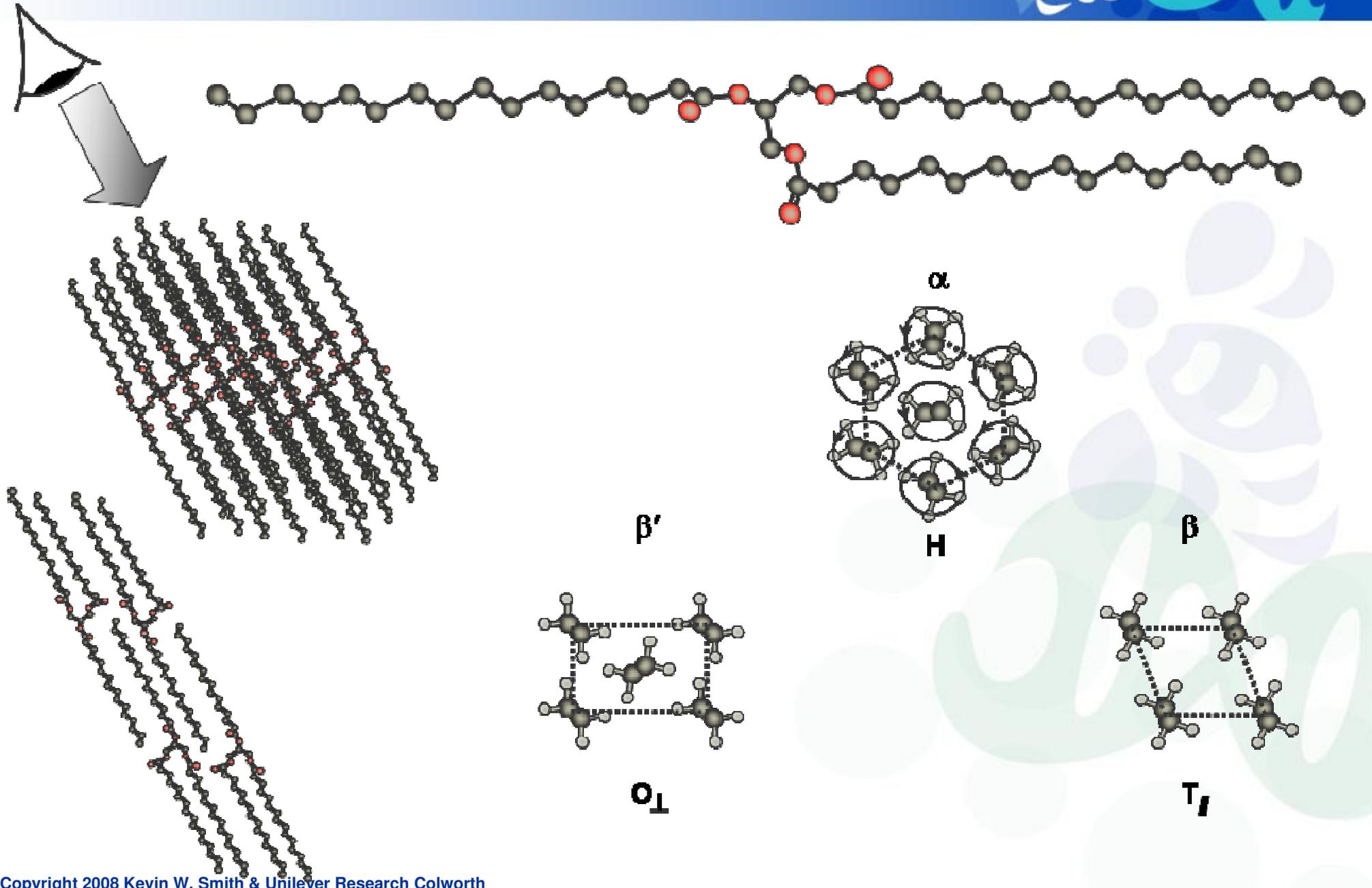




- Polymorphism
- Phase Behaviour
- Nucleation & Growth
- Crystal Morphology
- Minor Components & Additives



Fat Polymorphism

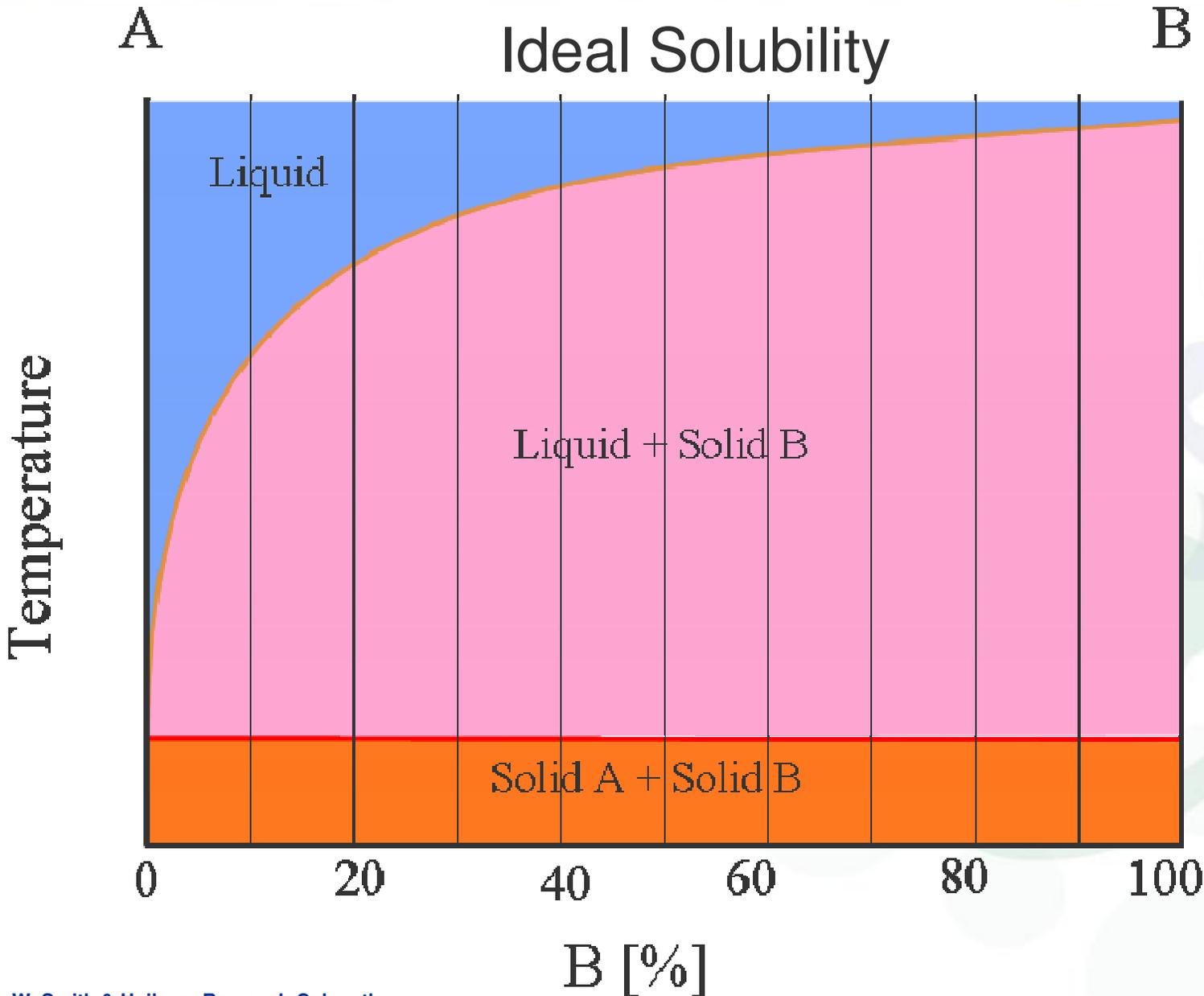


Fat Polymorphs

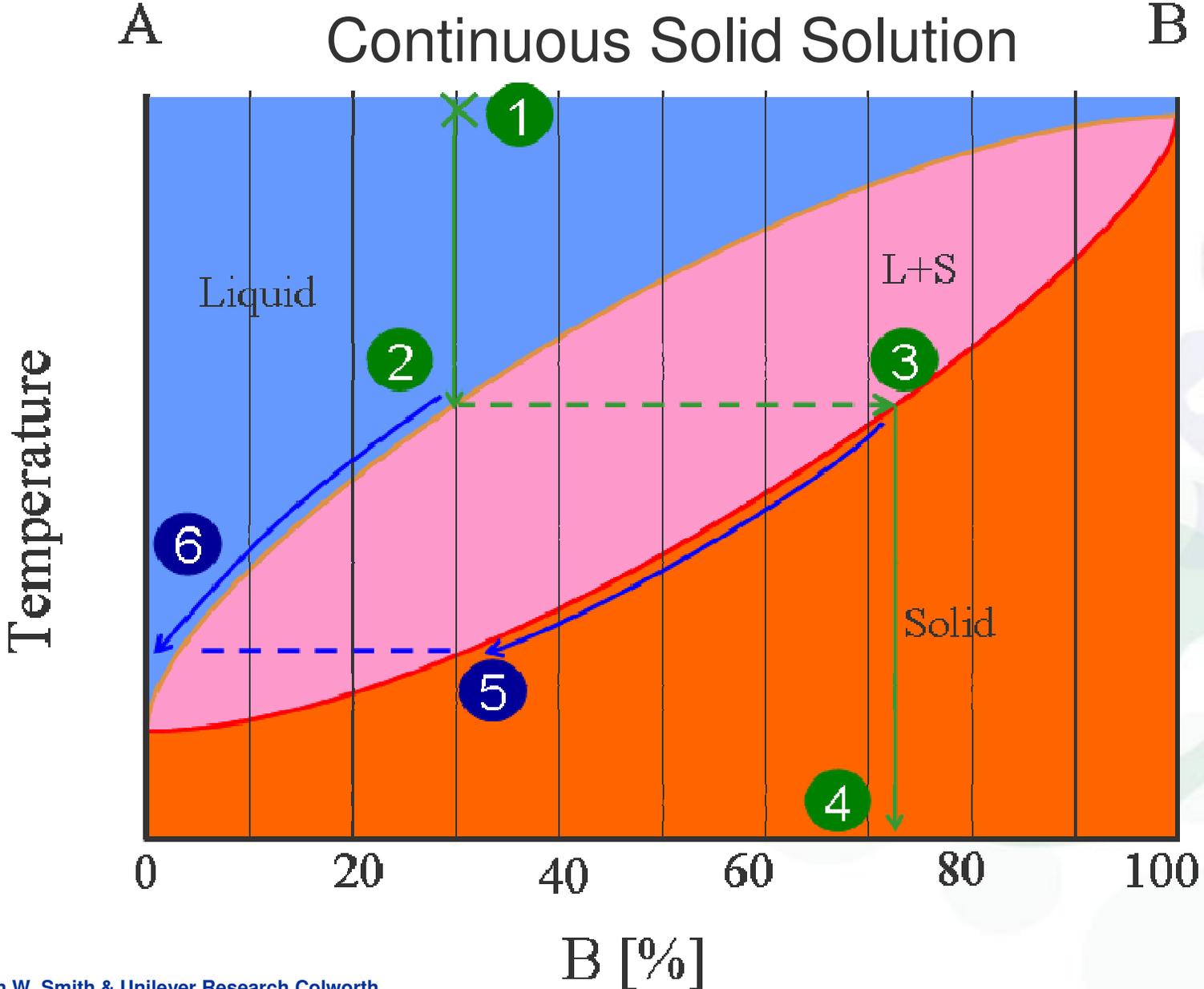


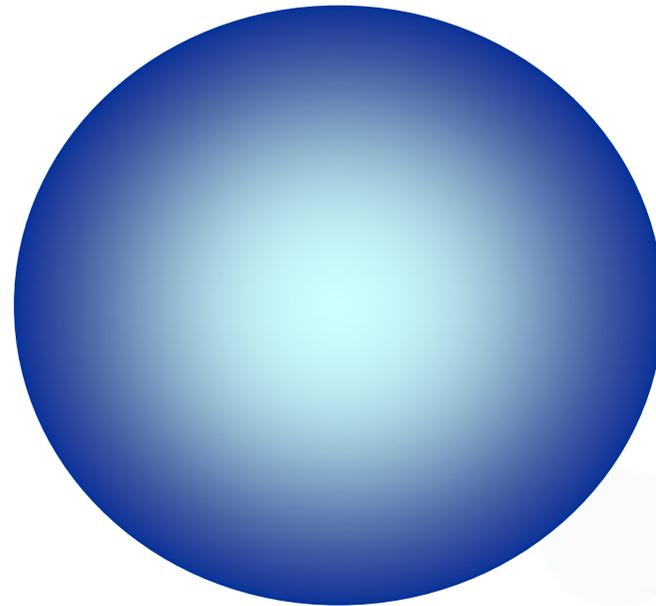
- Differ in
 - Crystal structure
 - Melting point
 - Melting enthalpy
 - Density
 - Stability
- Transform from less stable to more stable
 - Rate is temperature/time dependent
- Determined by process conditions

Phase Behaviour



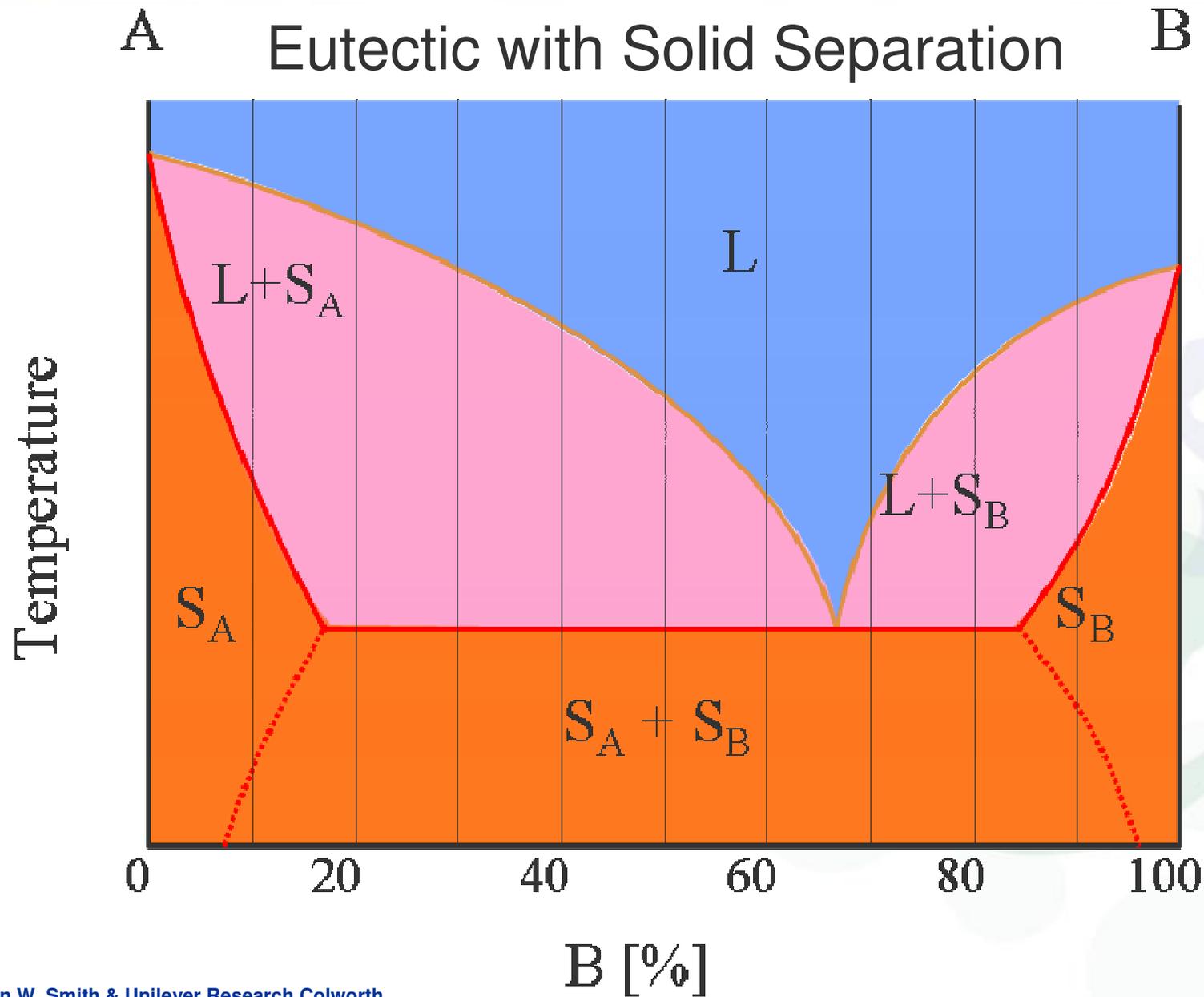
Phase Behaviour





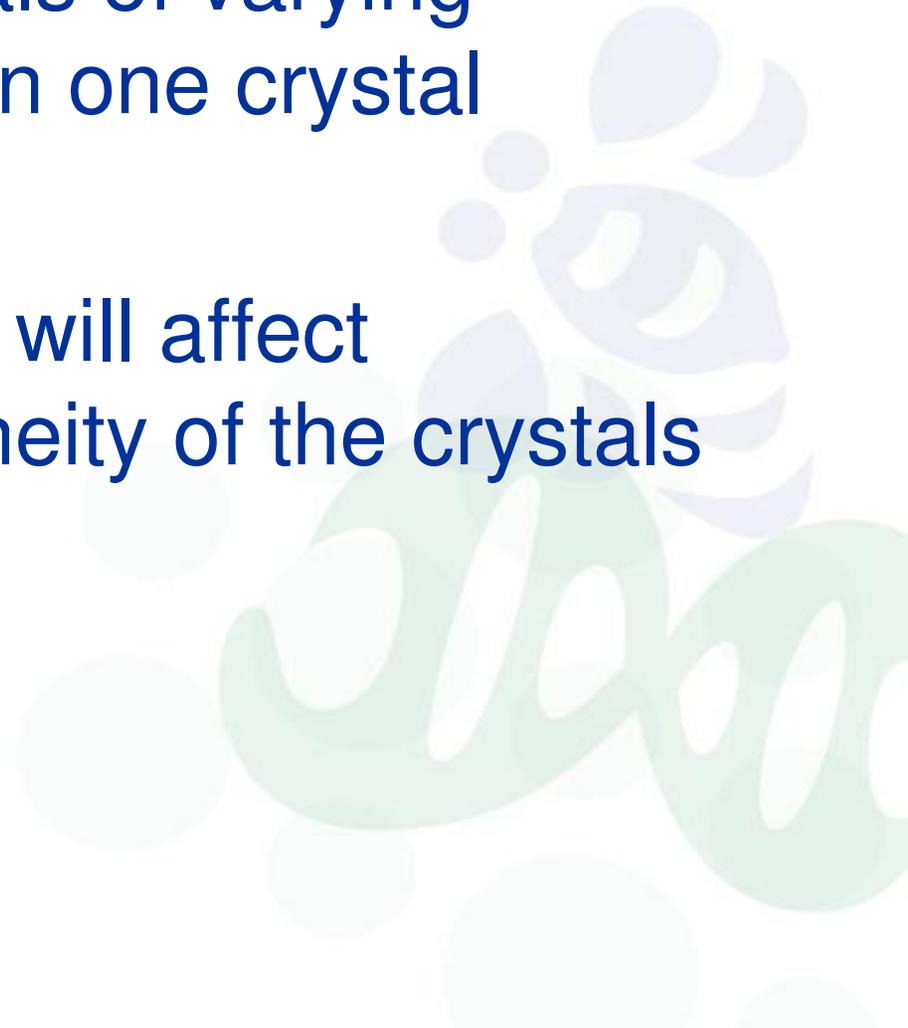
- Composition varies from centre to surface

Complex Phase Behaviour





- Complex phase behaviour of natural fats will lead to mixed crystals of varying composition, even within one crystal
- Speed of crystallisation will affect compositional homogeneity of the crystals

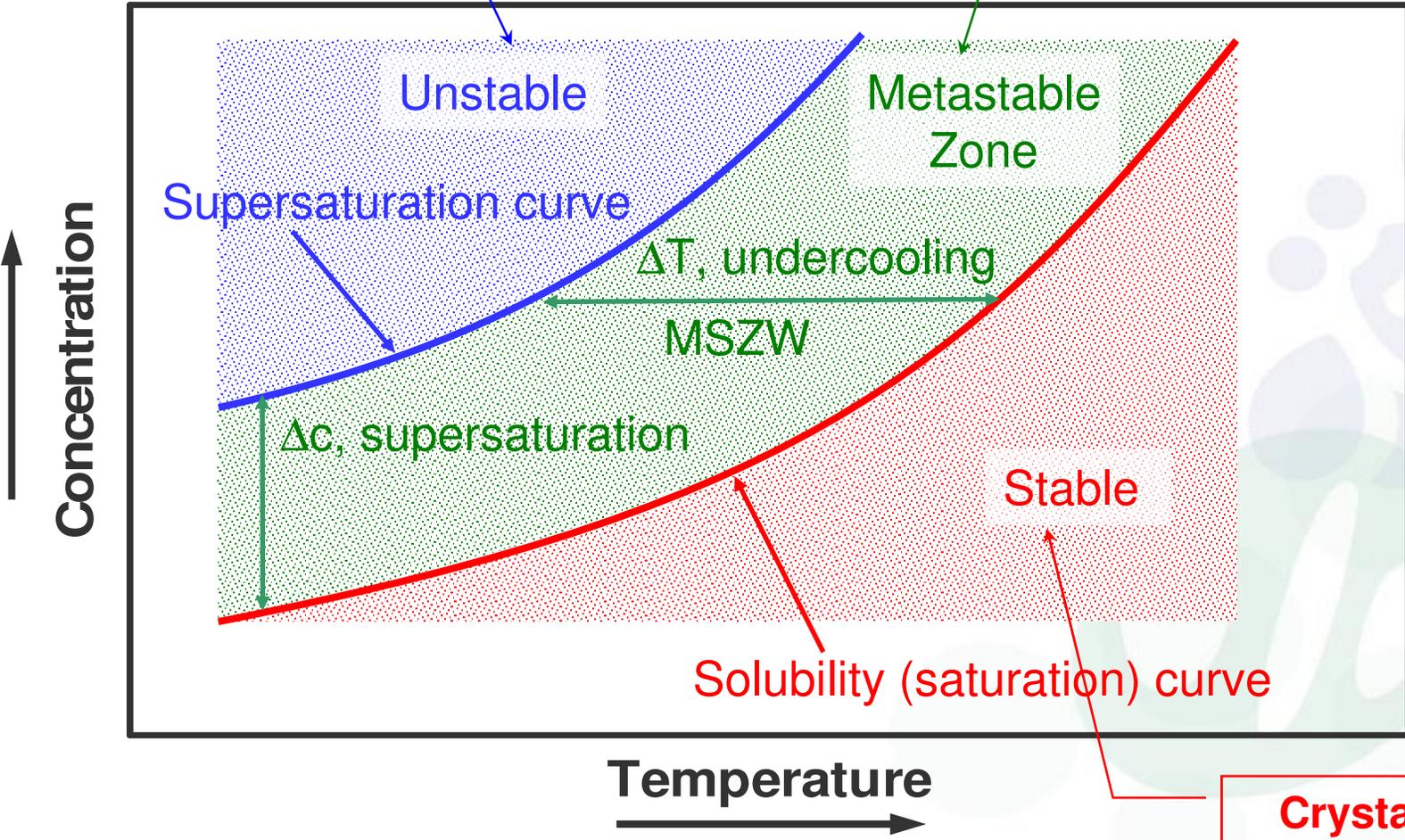


Supersaturation/Undercooling



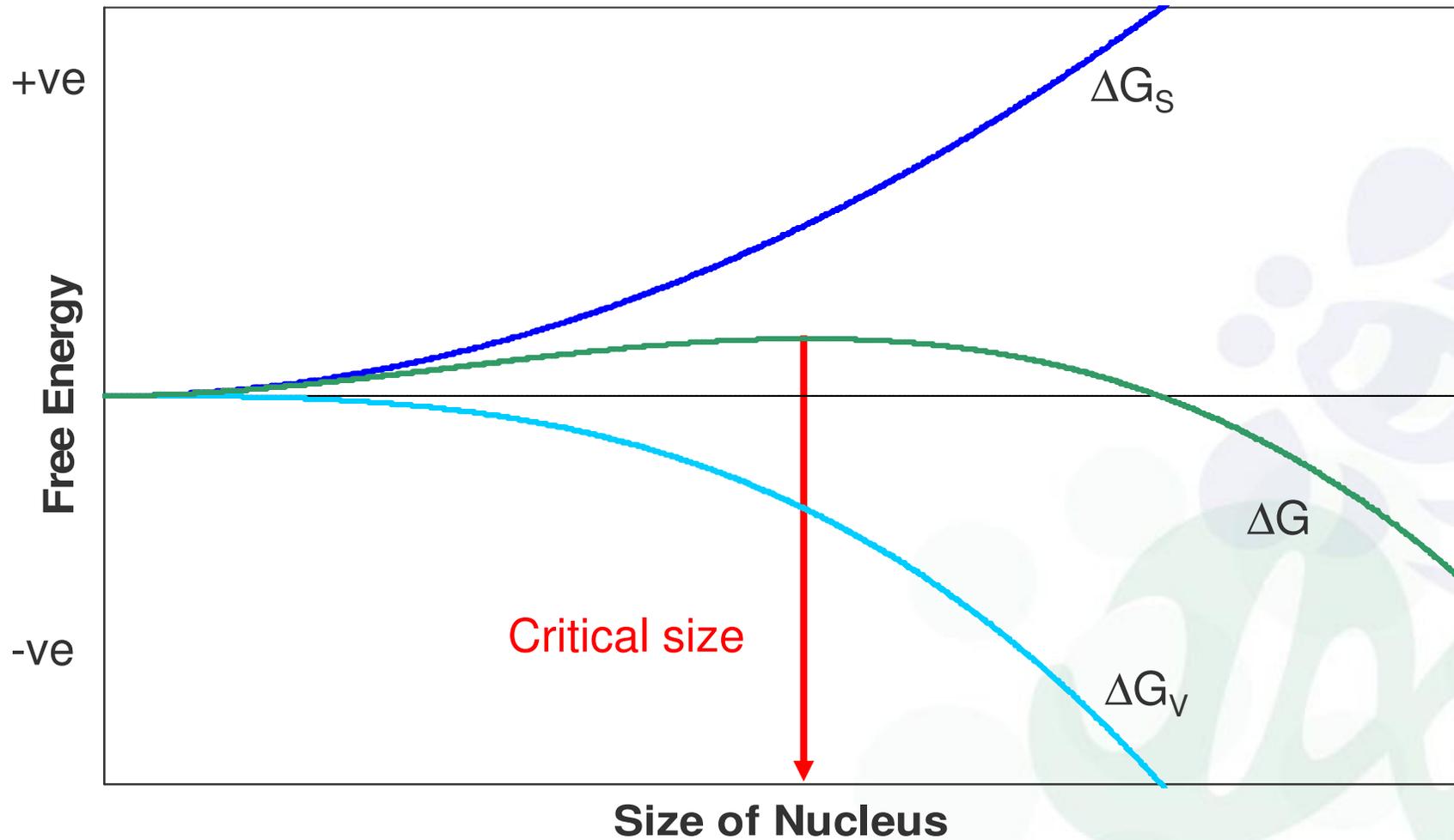
Crystallisation always occurs

Crystallisation possible

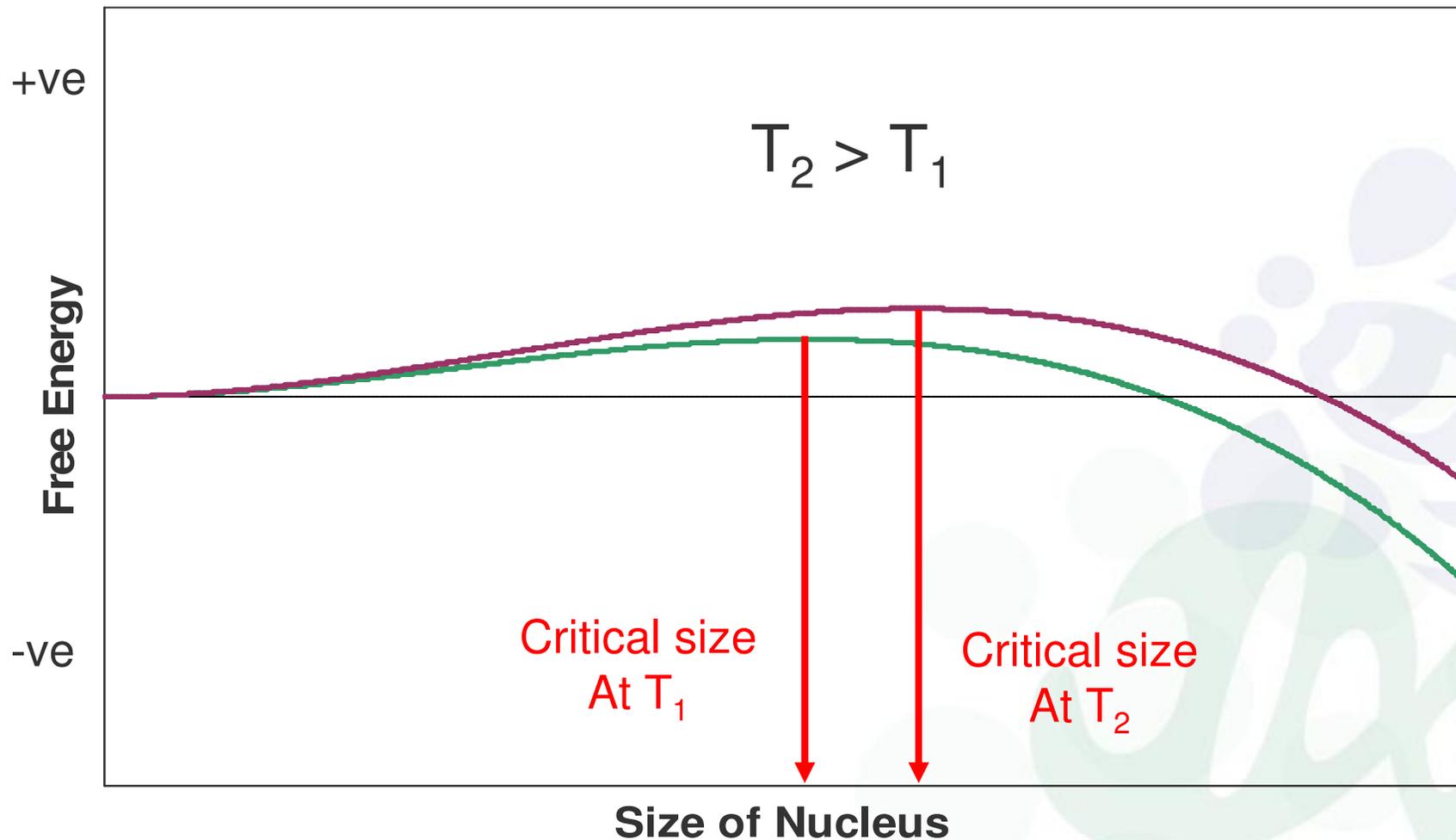


Crystallisation will not occur

Nucleus Formation



Critical Nucleus Size

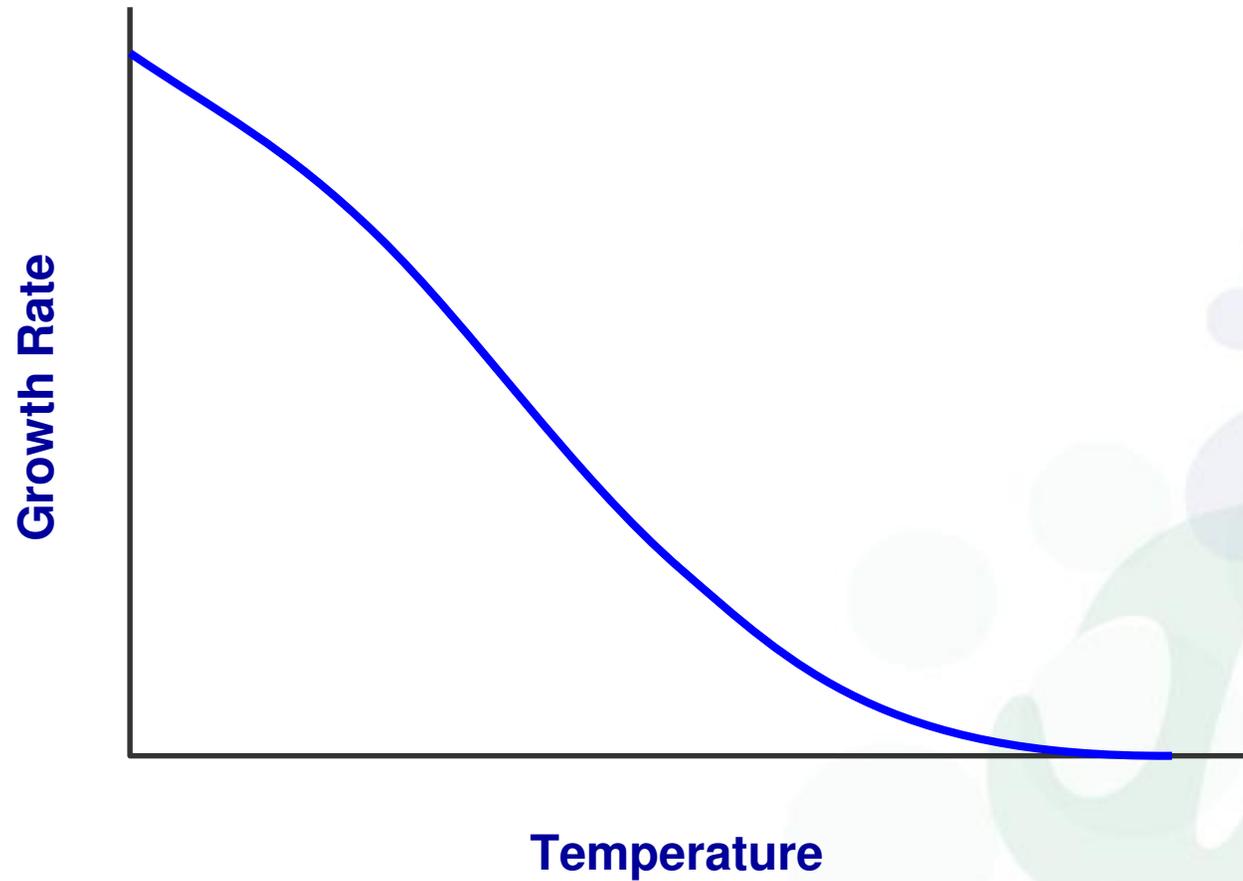


Nucleation



- Embryo formation
 - Continuously form and re-dissolve
- Critical size
 - Smallest crystal that can exist at given concentration and temperature
- Exponential temperature dependence
- Homogeneous
 - Occurs spontaneously in the liquid phase
 - Doesn't, usually, occur in fats
- Heterogeneous
 - Initiated by added seed crystals, non-fat particles (e.g. dust) or side of container
- Secondary nucleation
 - Existing crystals may break apart leading to pieces that can act as nuclei or seeds for further crystallisation
- Less stable polymorphs have lower heats of crystallisation
 - Nucleation rate is fastest for α and lowest for β

Growth Rate

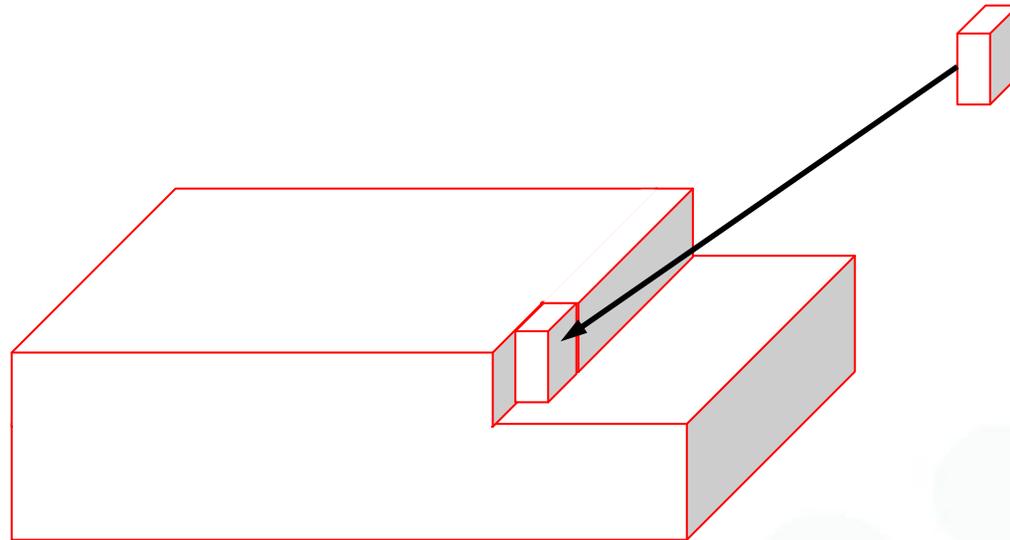


Crystal Growth



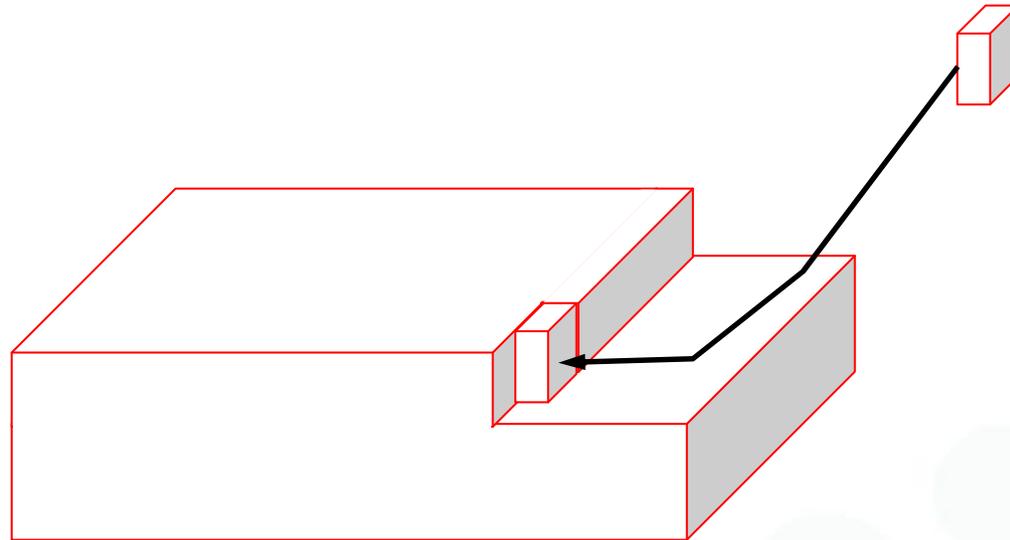
- Rate is proportional to degree of undercooling and inversely proportional to viscosity
 - i.e. faster at low temperatures, but slower if temperature is very low
- The most stable polymorph is least soluble
 - β has highest growth rate at a given degree of undercooling
- Rapid cooling below the melting point of all polymorphs almost always leads to crystallisation of the unstable form, α
 - Nucleation is exponentially dependent on temperature

Crystal Growth



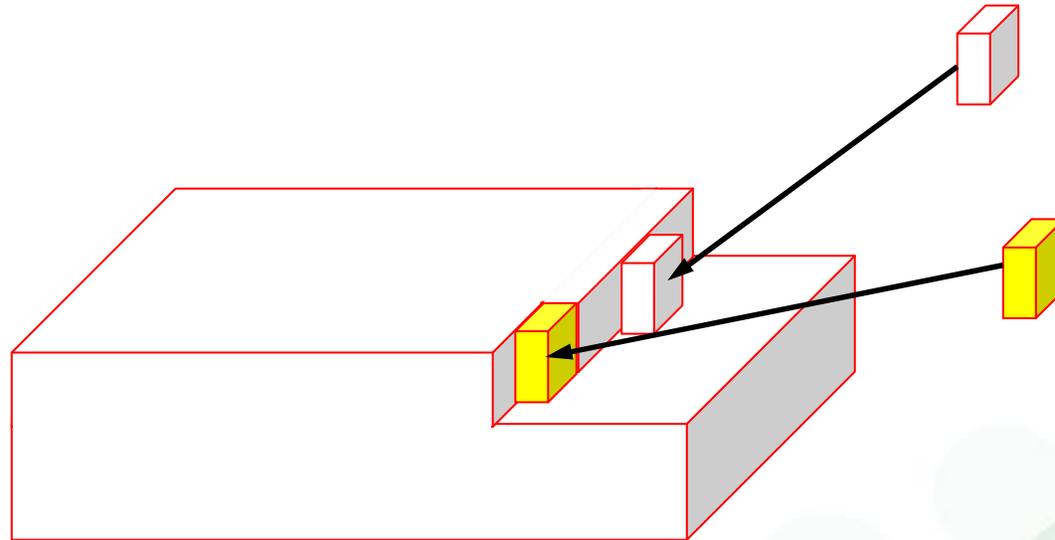
- **Growth may occur by simple addition at a kink**

Crystal Growth



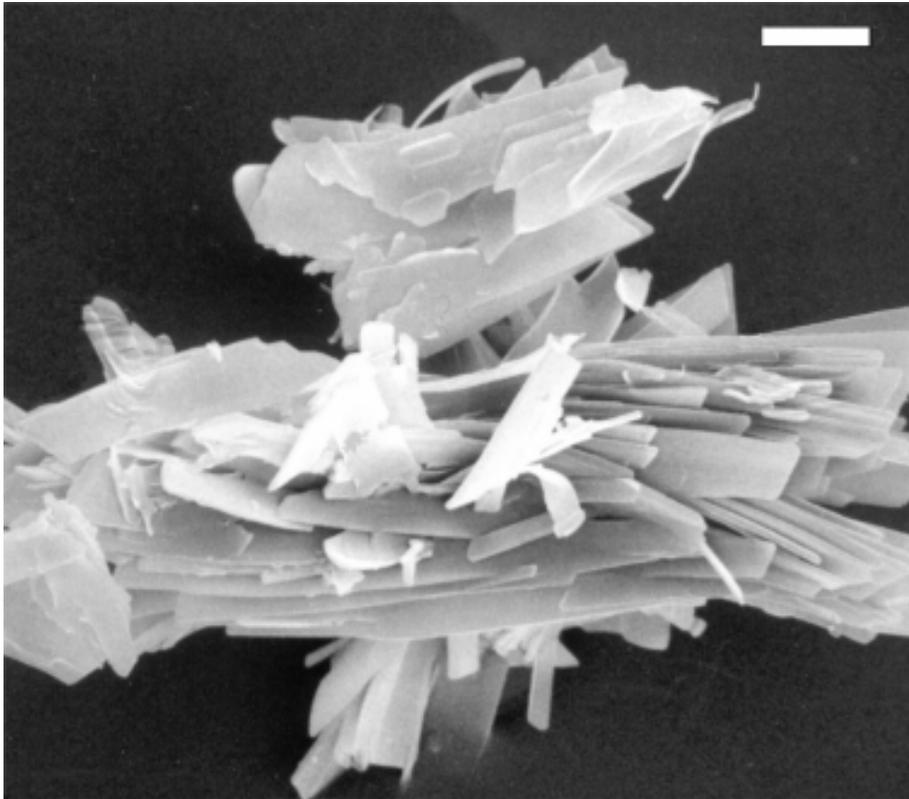
- Or by addition to the surface and migration to the 'kink'

Crystal Growth

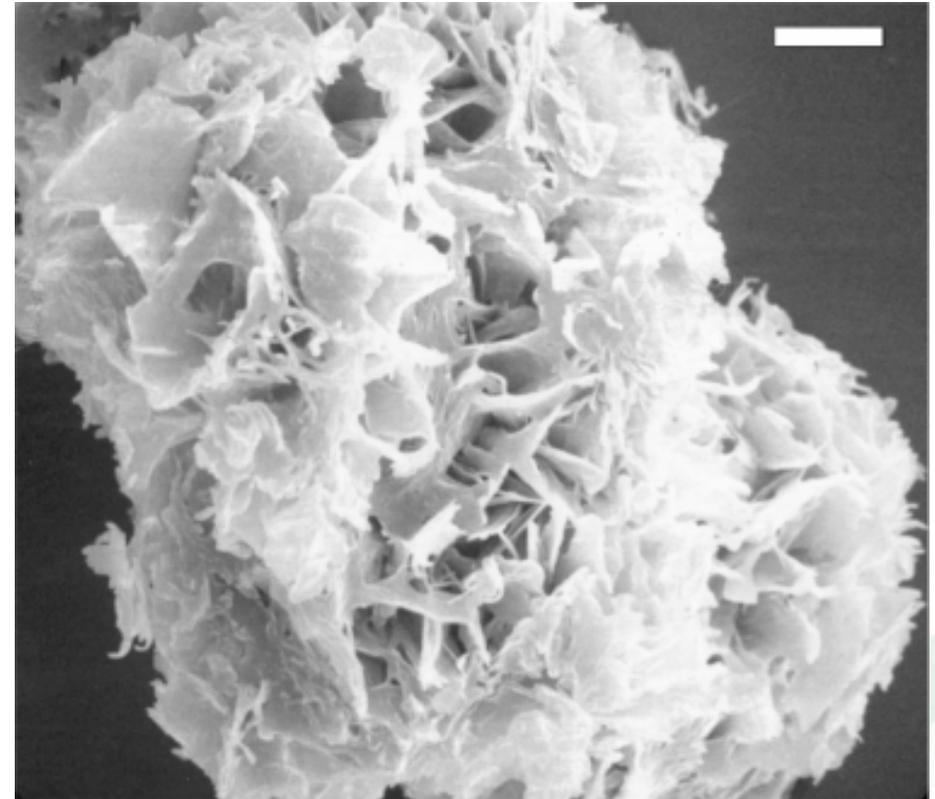


- **During rapid crystallisation, ‘foreign’ molecules may be incorporated and growth may occur at a ‘step’**

Crystal Morphology



PPP



POP

white bar = 20 μ m



Palm Oil

white bar = 20 μ m



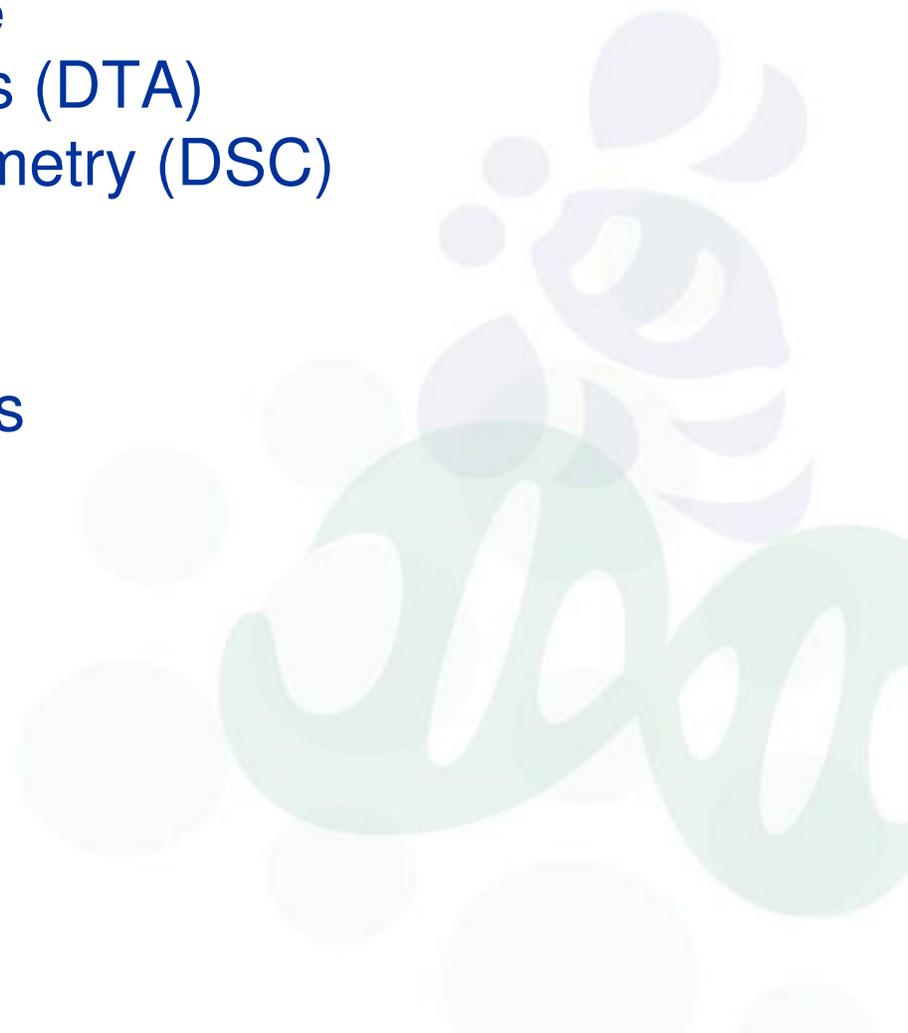
- Dependent on
 - Composition
 - Polymorphic form
 - Speed of crystallisation



Measurement of Crystallisation



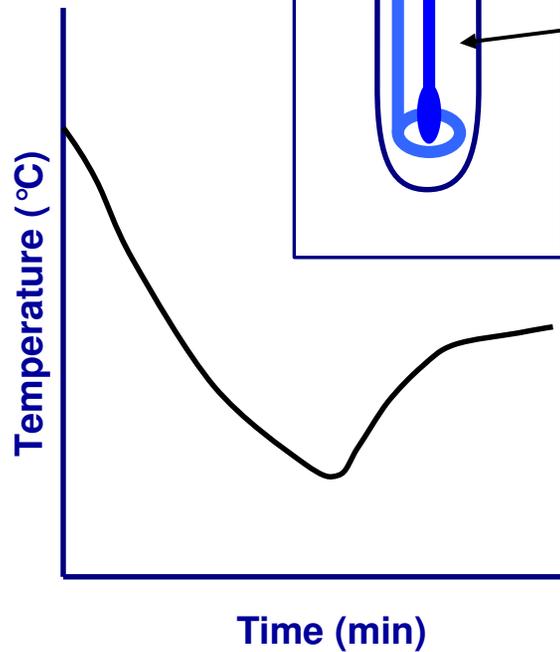
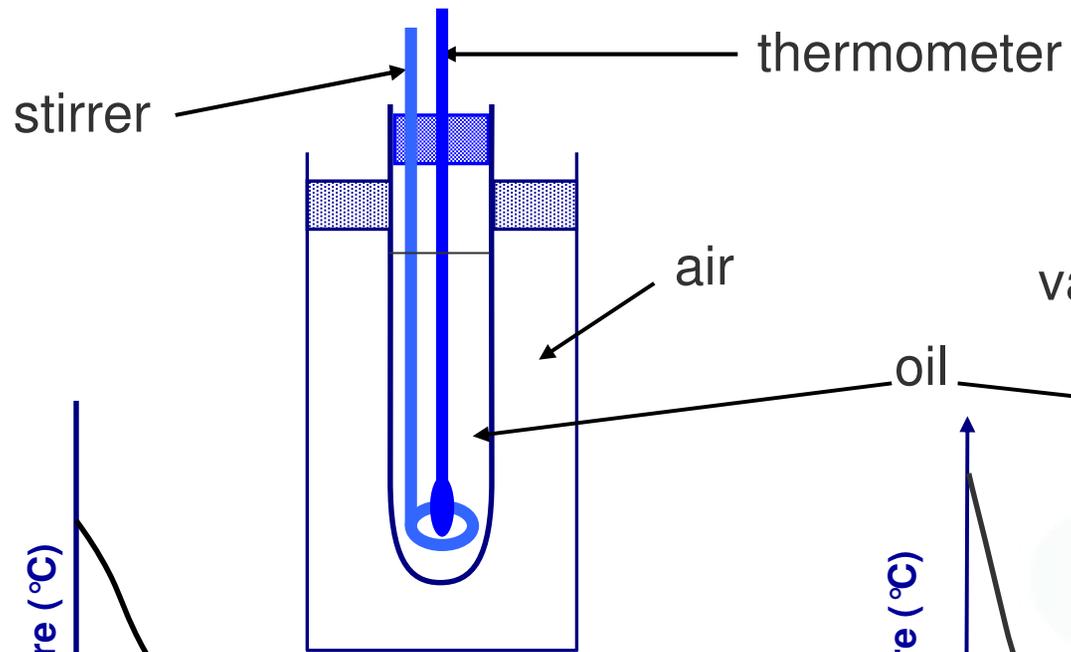
- Thermal methods
 - Cooling curves
 - Jensen, Shukoff, temper curve
 - Differential Thermal Analysis (DTA)
 - Differential Scanning Calorimetry (DSC)
- Optical methods
 - Microscopy & image analysis
 - Turbidimetry
- Other
 - NMR – solid fat content
 - X-ray diffraction



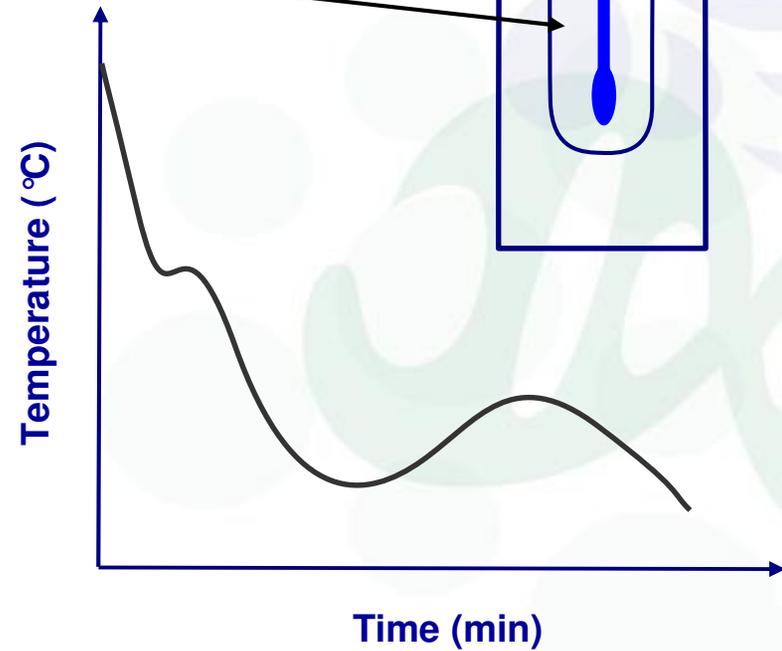
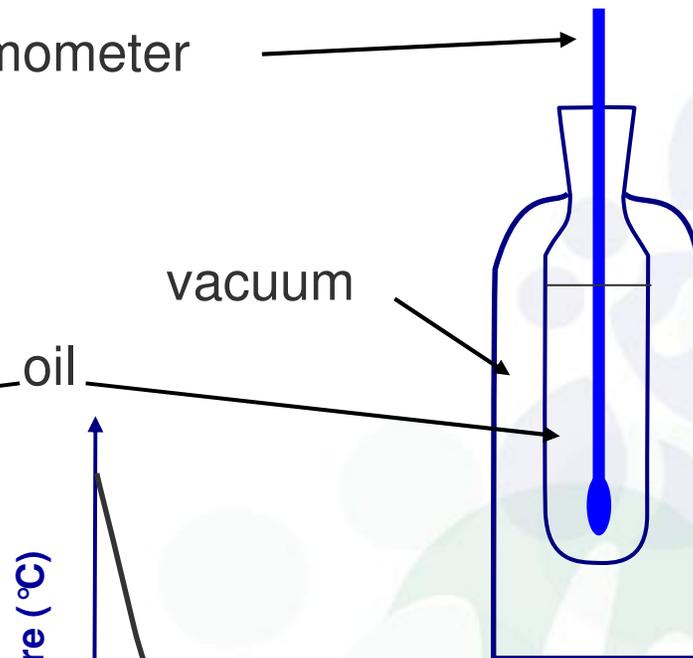
Cooling Curves



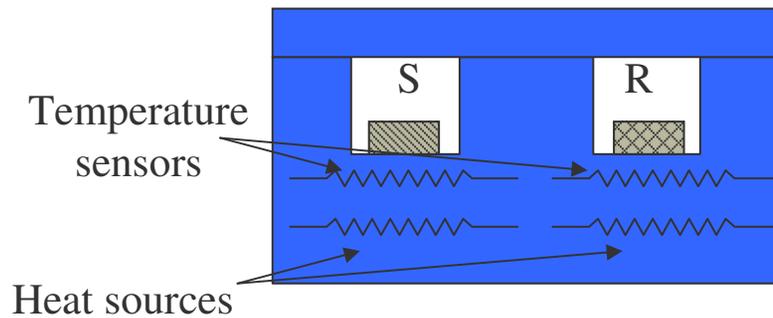
Jensen



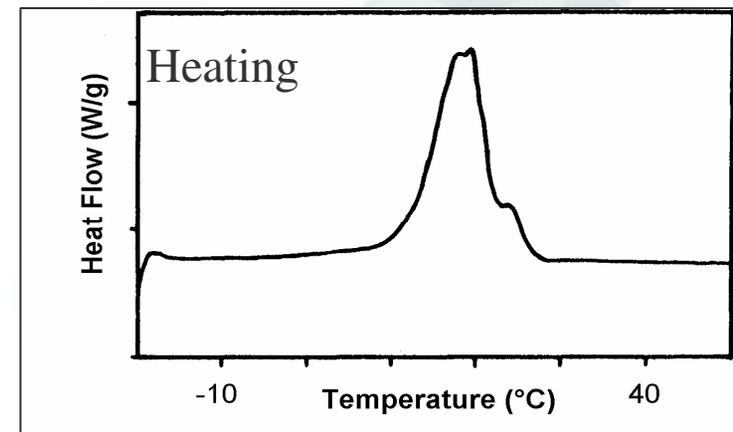
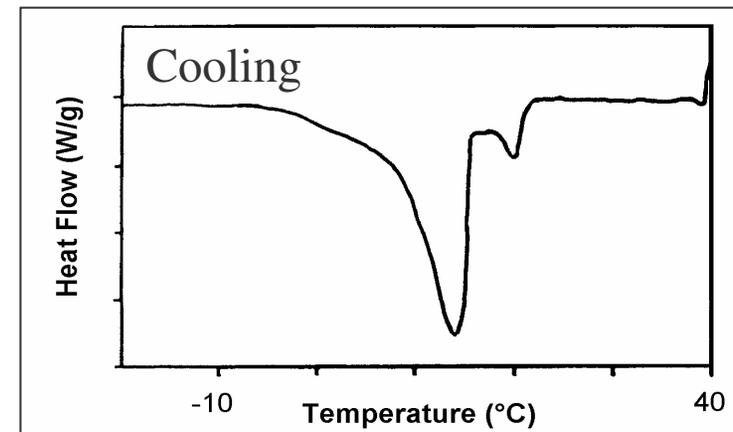
Shukoff



Differential Scanning Calorimetry

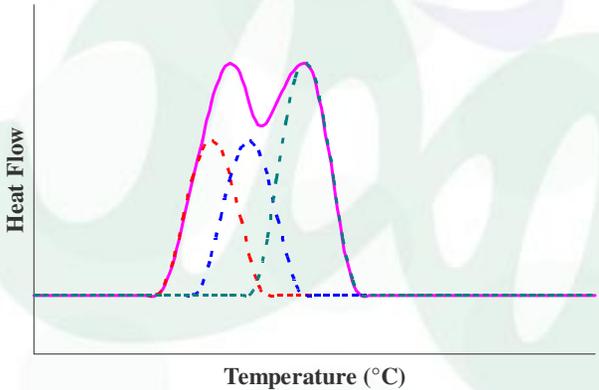
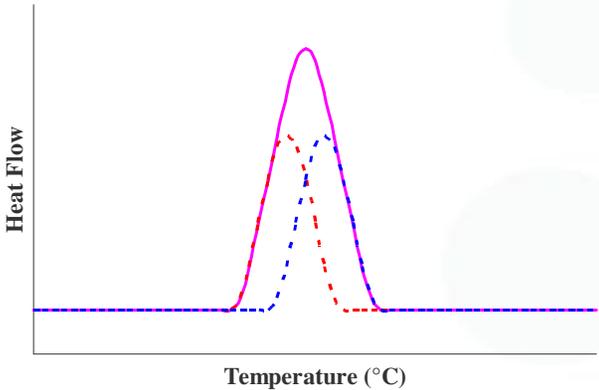
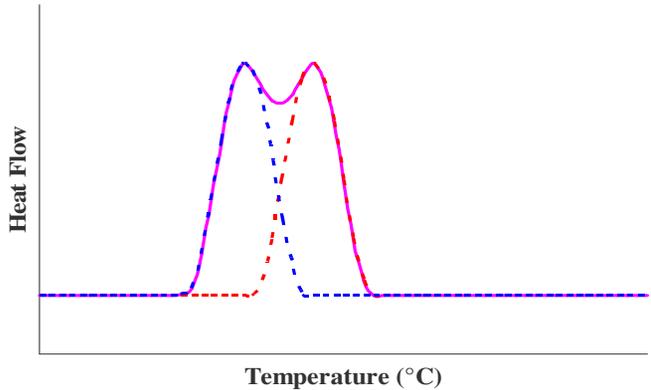
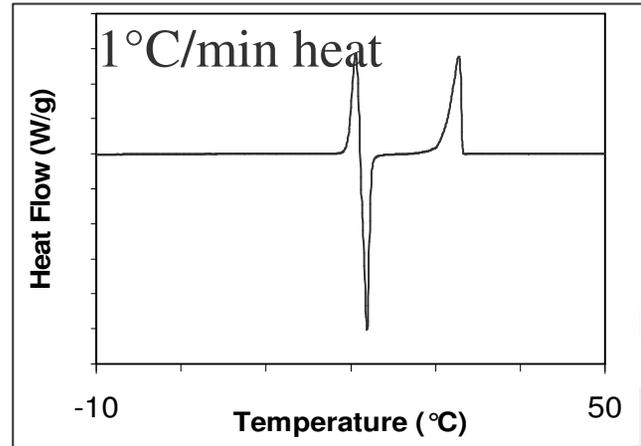
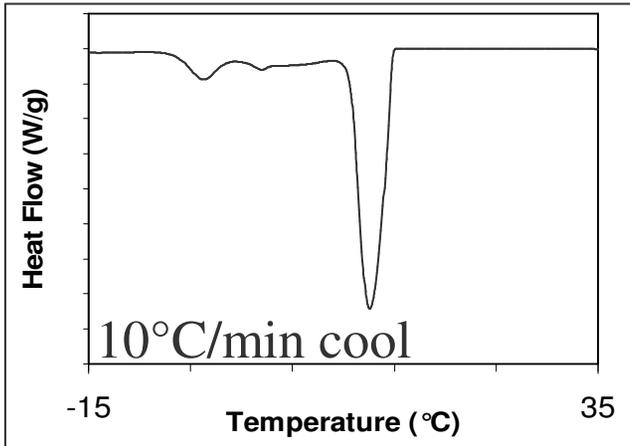


- Crystallisation evolves heat
- Melting absorbs heat
- Difference in heat flow from sample compared to (non-crystallising) reference

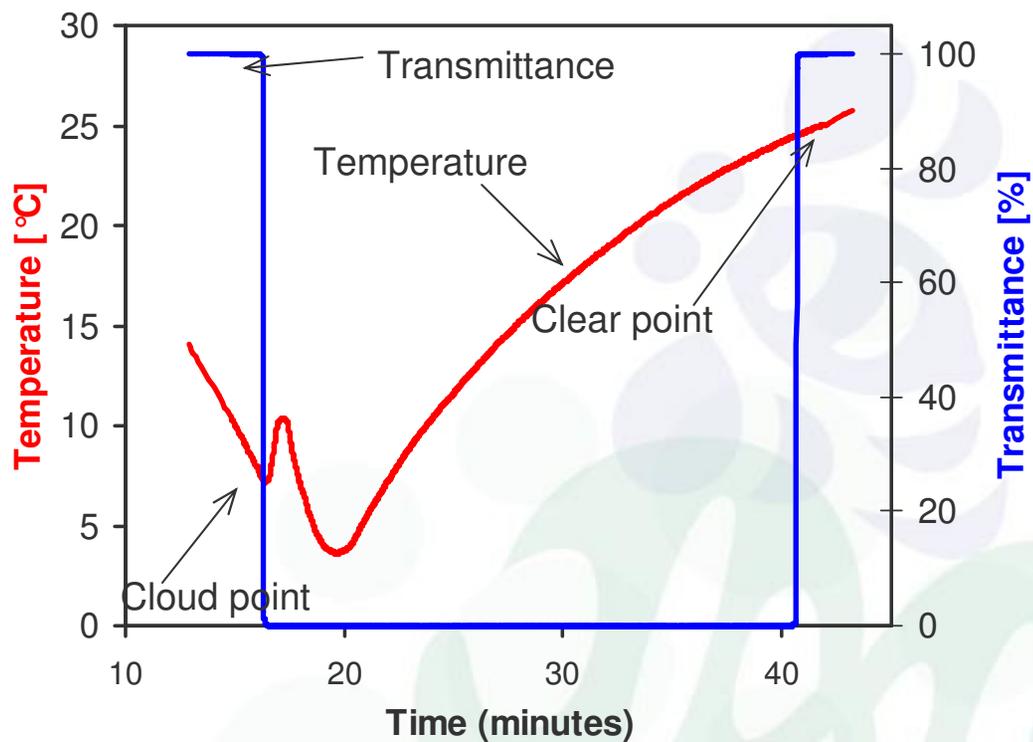
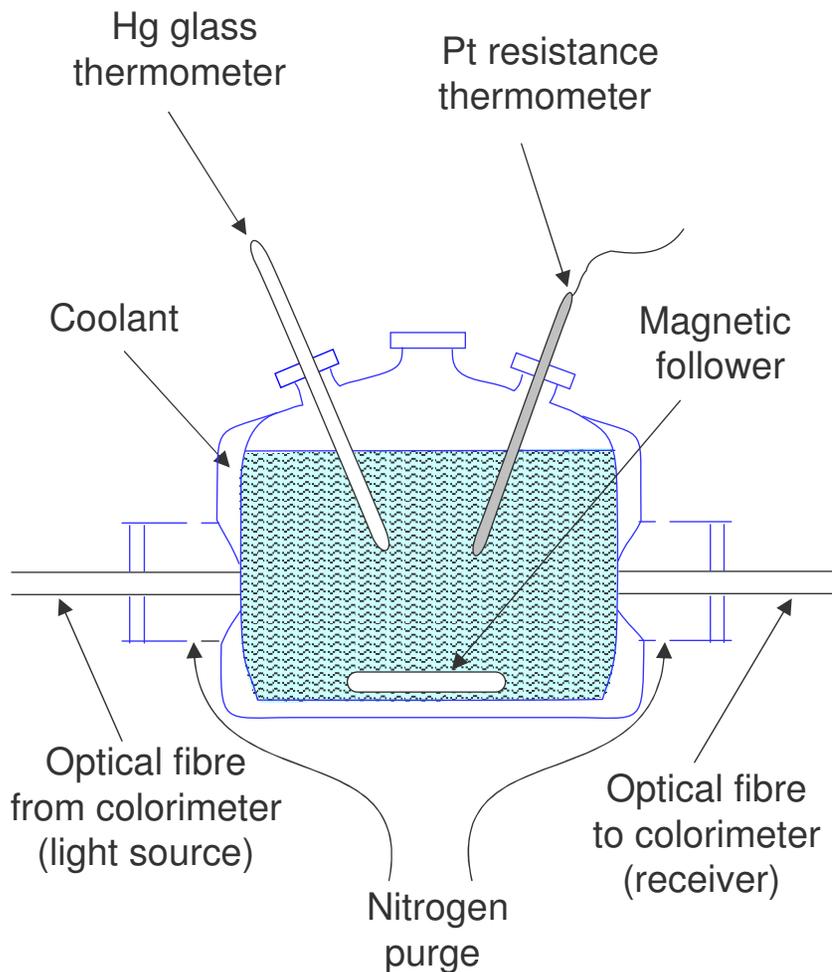




Pure POST



Turbidimetry





- Natural fats are complex
 - Polymorphism
 - Phase behaviour
- Crystallisation can be complex
 - Nucleation
 - Growth
 - Minor components/additives
 - Cooling rates
 - Temperature
- Measurement
 - Techniques can be complementary

