Modelling the phase and crystallisation behaviour of fat mixtures

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- Introduction
- Equilibrium
- Kinetics
- The full works

Collaboration

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Unilever R&D, Vlaardingen

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- Eckhard Flöter

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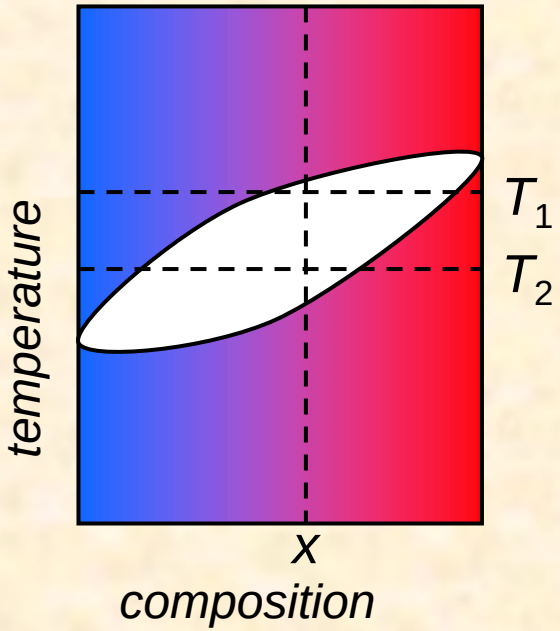
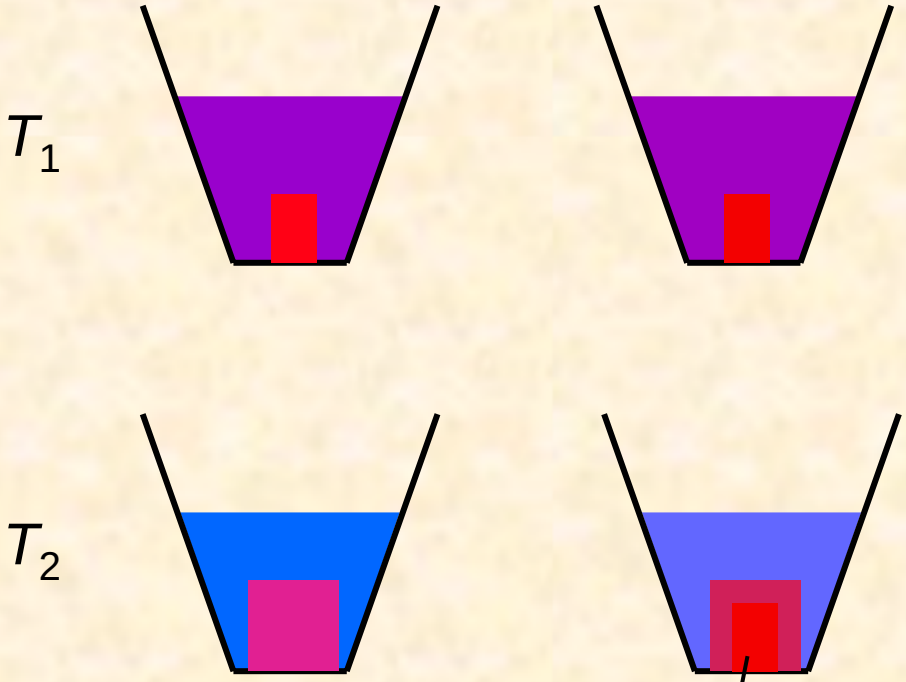
Thermodynamics & kinetics



equilibrium kinetics



composition gradient in solid

equilibrium description not good enough

Goal

- ‘Complete’ description of crystallisation behaviour of (fat) mixtures
  - segregation
    - undercooling
    - mass transport
    - heat transport

    } less important
  - nucleation
  - polymorphism (including metastable phases)
- Kinetics ***very*** important
- Ambitious…

What is needed?

- Equilibrium phase diagrams
  - often not available
- Kinetic parameters: kinetic phase diagrams
  - often not available
- Algorithm to deal with mixtures
  - MMCG (“Modelling Mixed Crystal Growth”) package

Equilibrium binary phase diagrams

- Requires set of thermodynamic parameters
- Ideal mixture of fraction *x* of B in (1-*x*) of A

$$G(T,x) = (1-x)G_A(T) + xG_B(T) + RT[(1-x)\ln x + x\ln x]$$

  - parameters of pure compounds are sufficient
- Deviations from ideal: excess functions

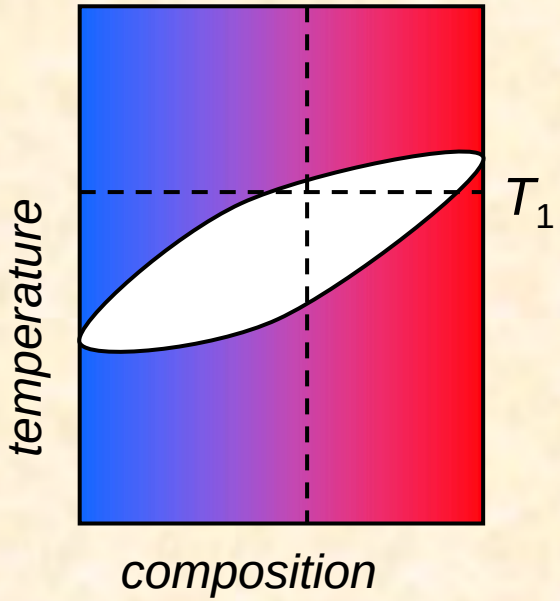
$$G(T,x) = (1-x)G_A(T) + xG_B(T) + RT[(1-x)\ln x + x\ln x] + G^E(T,x)$$

  - excess enthalpy (heat of mixing): H^E
  - excess entropy: S^E
  - e.g., regular solution: $H^E \neq 0$; $S^E = 0$
  - expressions of different sophistication possible for excess functions, e.g. a Redlich-Kister expansion

$$G^E(T,x) = Ax(1-x)\{1 + B(1-2x) + C(1-2x)^2 + \ldots\}$$

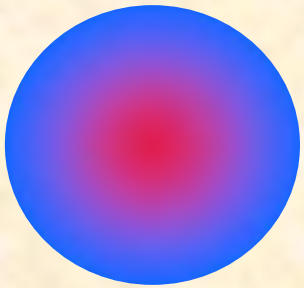
Equilibrium phase diagrams

- To do: determine thermodynamic parameters
- However: complicated by kinetics
  - less segregation than predicted from equilibrium
  - solid composition closer to liquid composition
  - happens in reality

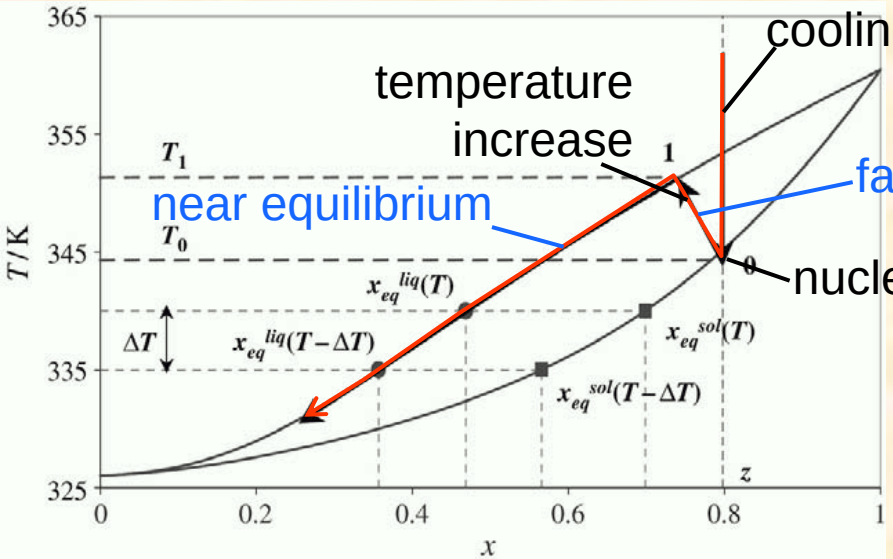


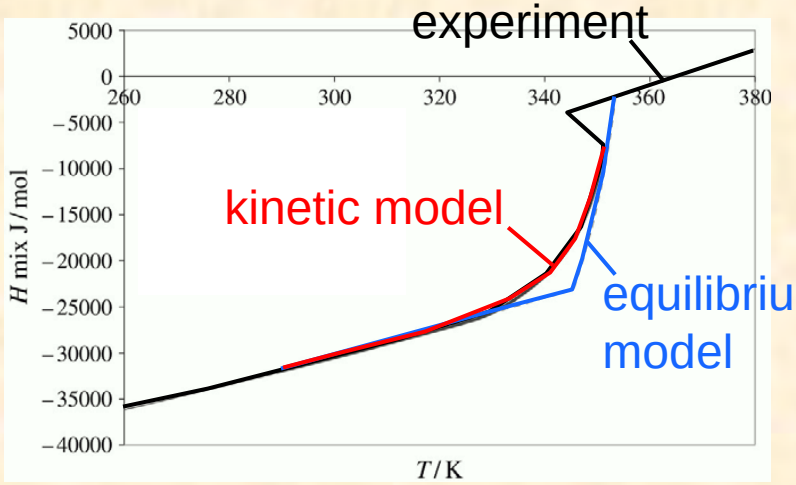
Low supersaturation

- Assumptions
  - no diffusion in solid
  - homogeneous liquid
  - crystallizing solid locally in equilibrium with liquid
- Then: concentration gradient in solid



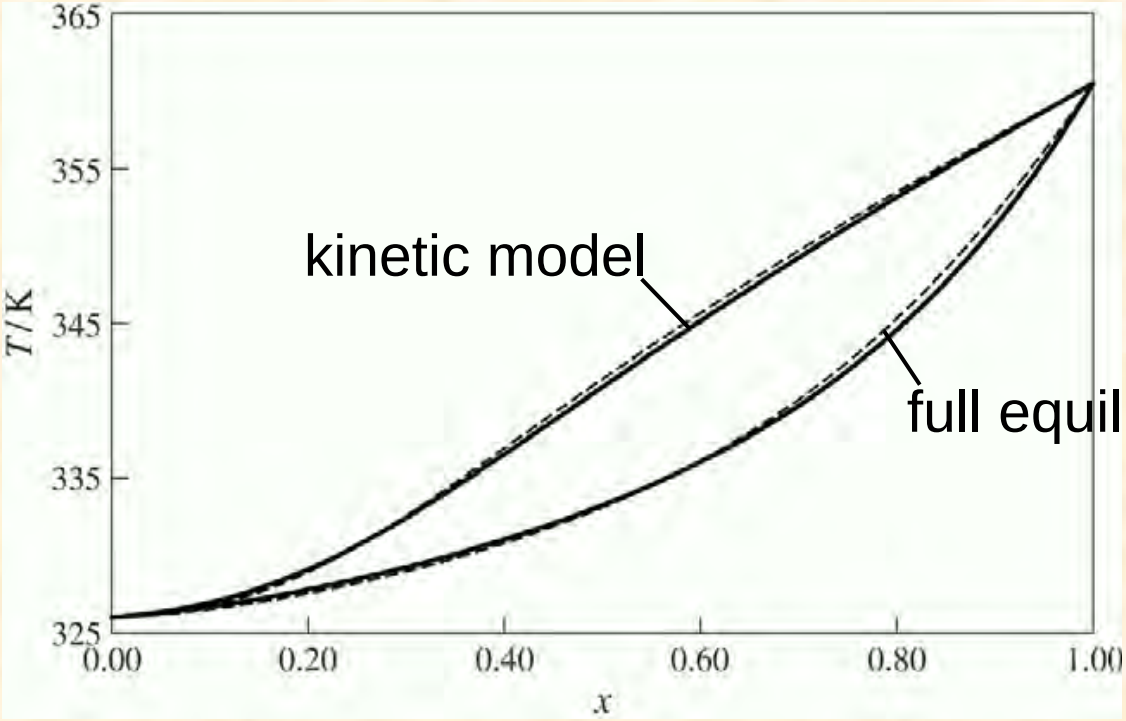
Determination of phase diagram





enthalpy
cooling path

Determination of phase diagram



Matovic et al., Calphad 30 (2006) 209.

- Kinetic model
  - derive excess enthalpy and entropy
  - fast way to find equilibrium phase diagram

Kinetic phase diagrams

- System typically does not follow equilibrium phase diagram: include kinetics
- Linear kinetic segregation model (LKS)
  - flux of component *i* to solid (J^+) and from solid (J^-) are related by

$$\frac{J_i^+}{J_i^-} = \exp\left(\frac{\Delta\mu_i}{RT}\right)$$

  - growth rate of component *i*

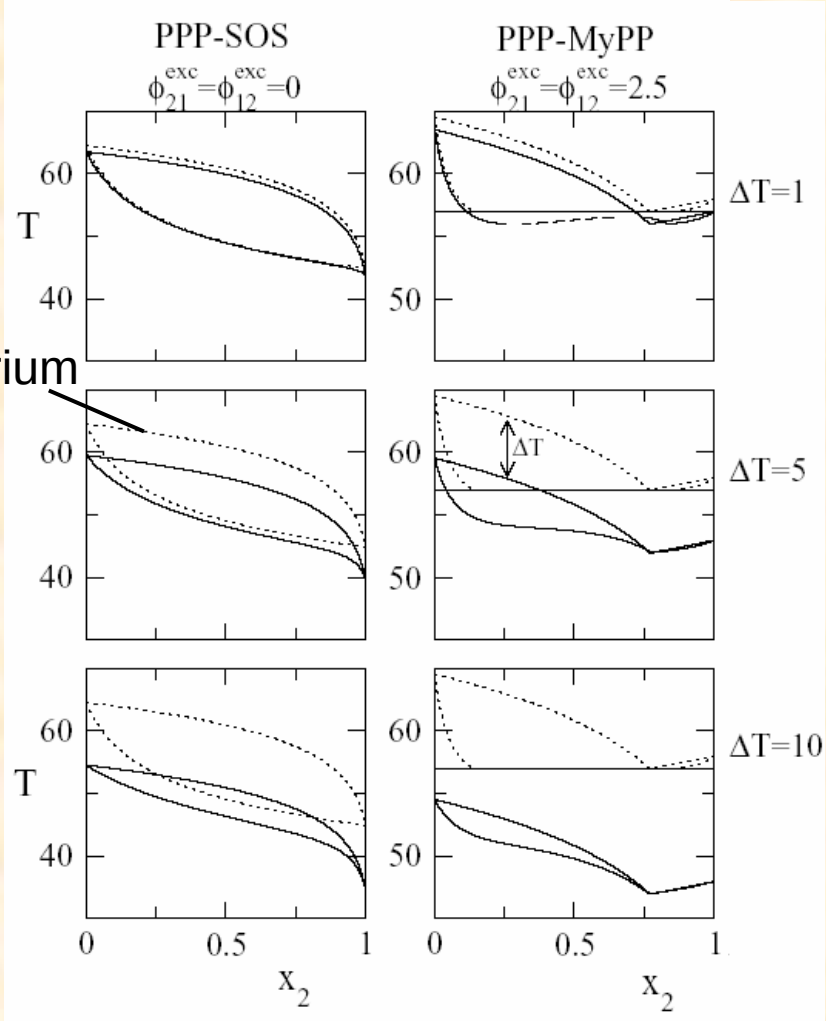
$$R_i = K_i \sigma_i$$

kinetic constant

supersaturation

  - yields net flux, dependent on supersaturation
  - (yields thermodynamic equilibrium for zero growth)

Examples



equilibrium

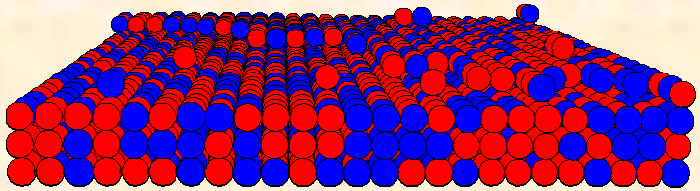
- less segregation due to kinetics
- larger effect for larger supersaturation

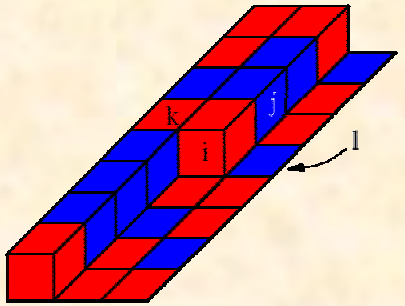
P = palmitic acid
S = stearic acid
O = oleic acid
My = myristic acid

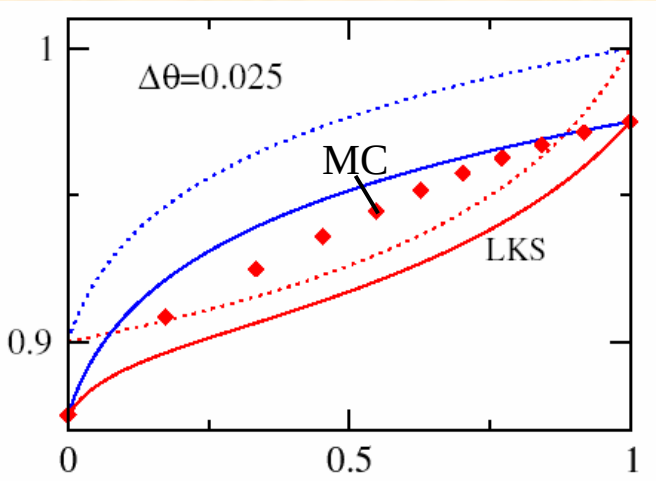
Los et al., J. Phys. Chem. B. 106 (2002) 7321.

Other kinetic models

- Monte Carlo simulation of binary Kossel model
  - few assumptions
- Mean field kink site kinetic segregation model (MFKKS)
  - moderate/large undercooling
- Combination of LKS with MFKKS yields best results
- LKS still good starting point

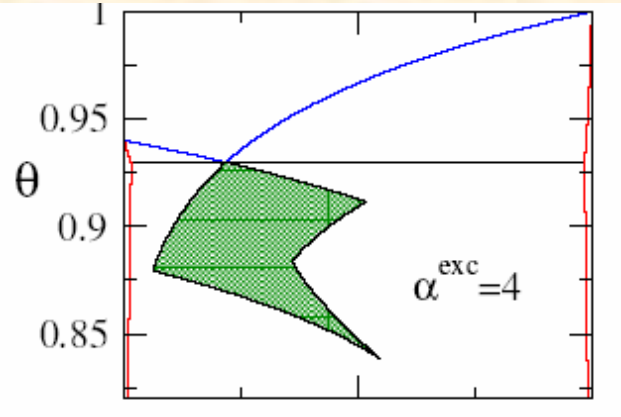


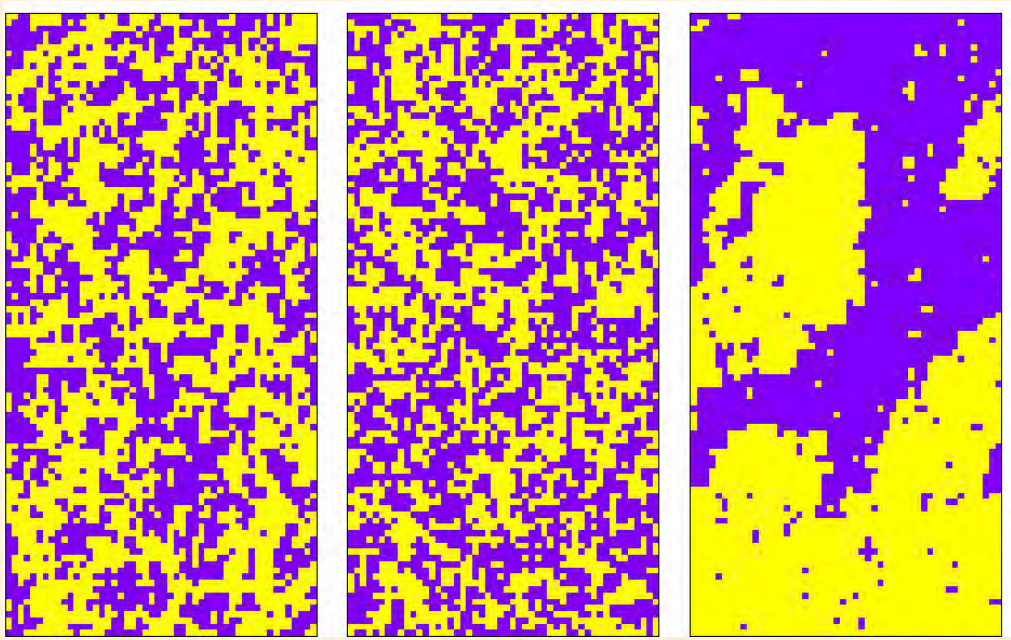




Kinetic phase separation domains

- Near eutectic point
  - simultaneous growth of solid phases with different (and non-equilibrium) composition

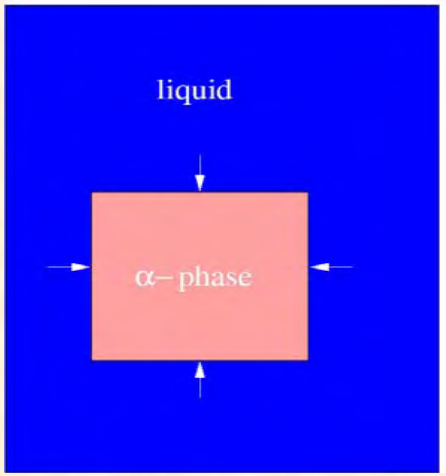


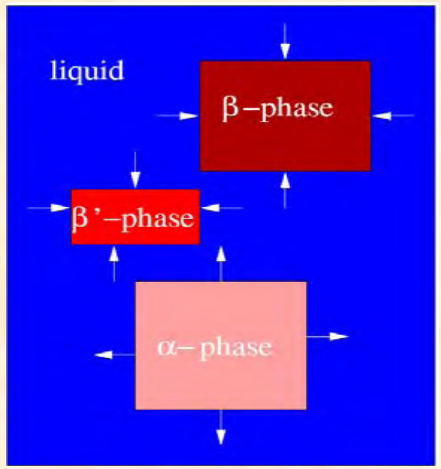


Los et al., Calphad 30 (2006) 216.

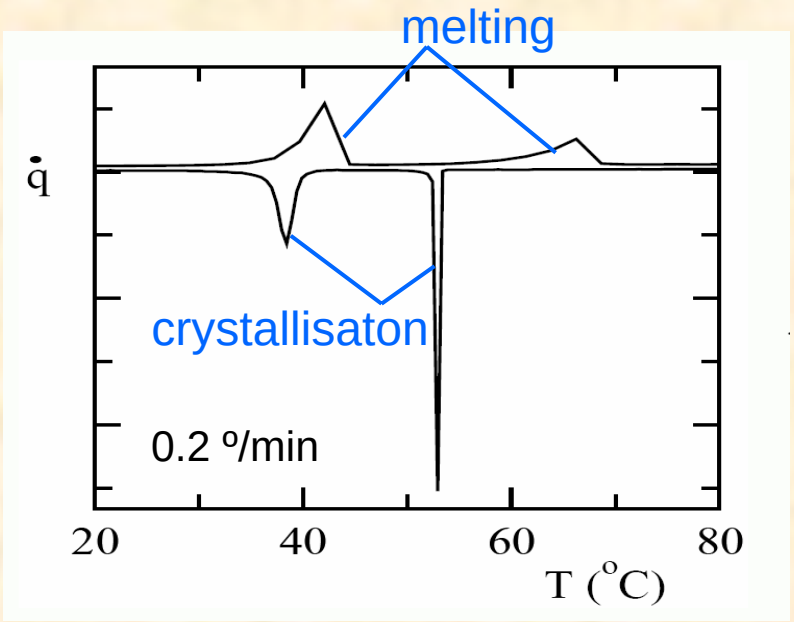
Combining everything (MMCG)

1. Equilibrium phase diagrams
2. Kinetic phase diagrams
3. Multi-component systems (equilibrium + kinetics)
   - parameters for every relevant phase/component
4. Time & temperature evolution ⟵ **NEW!**
   - growth
   - melting
   - nucleation
   - polymorphic transitions

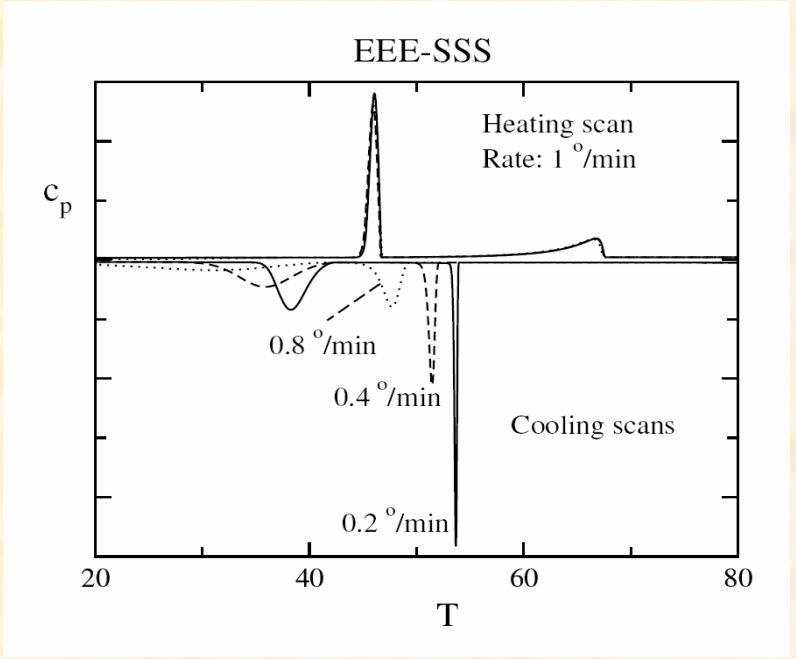




Differential scanning calorimetry (DSC)



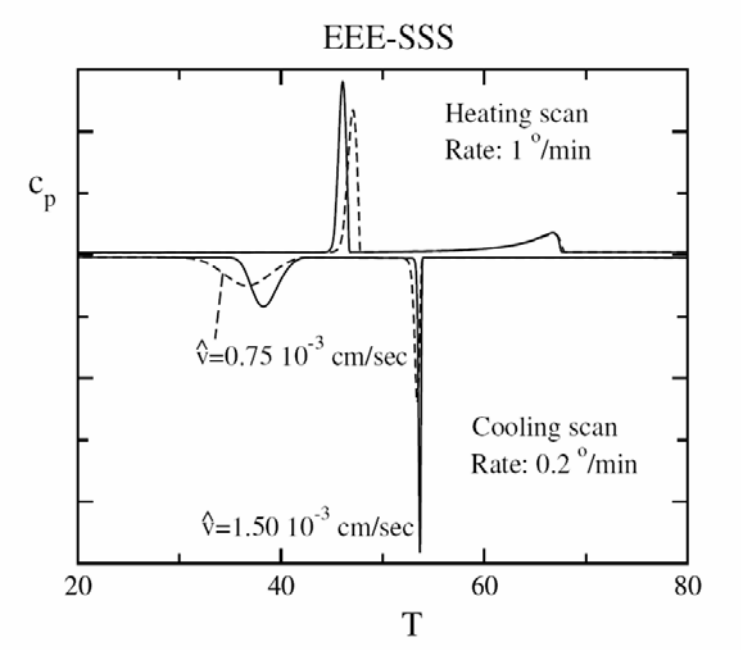
experiment



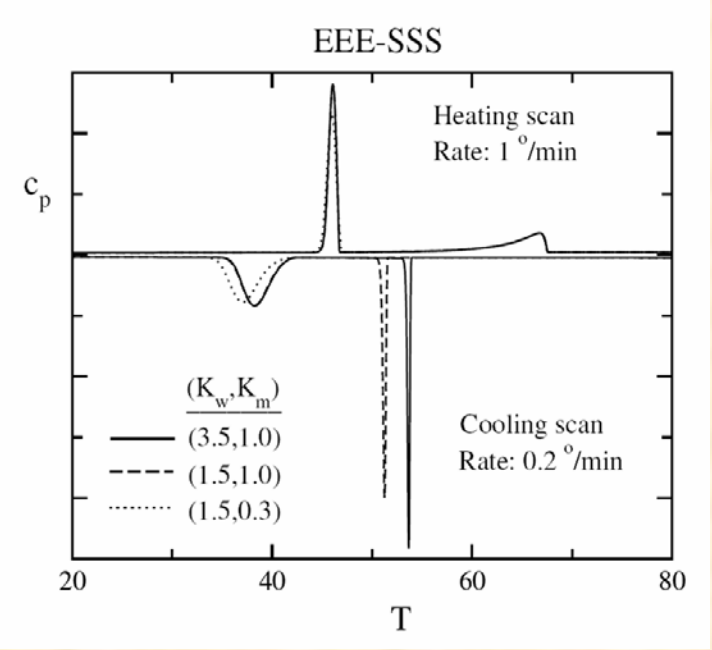
modelling for different cooling rates

- binary fat mixture
  - EEE & SSS (x_{SSS} = 0.32)
    - E = elaidic acid
    - S = stearic acid

DSC - effect of kinetic constants



growth velocity constant

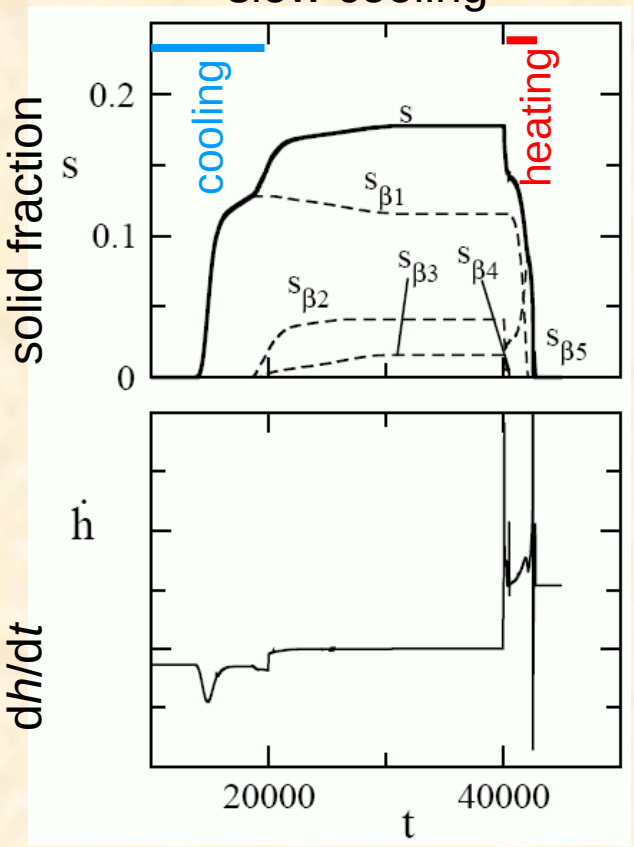


nucleation constant

Fat blend with 32 components

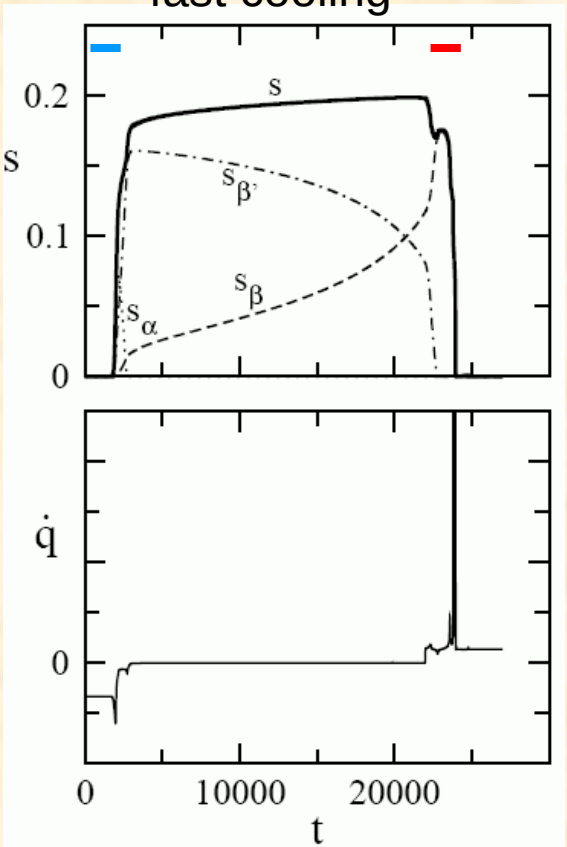
- Cool/isothermal/heating sequence 350 → 285 → 350°C

slow cooling



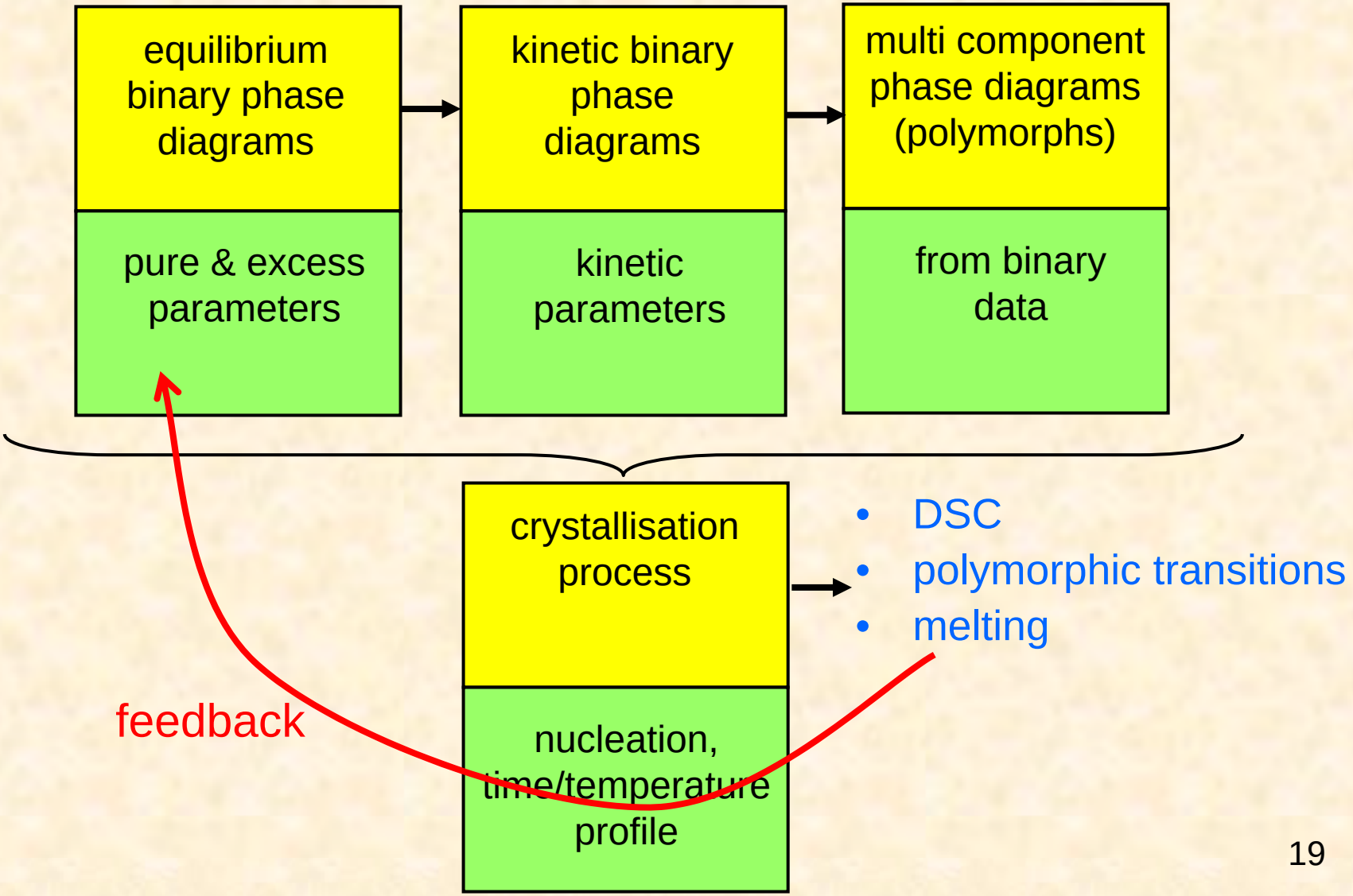
several β polymorphs

fast cooling



sequence α → β' → β

Summary


equilibrium binary phase diagrams
kinetic binary phase diagrams
multi component phase diagrams (polymorphs)
pure & excess parameters
kinetic parameters
from binary data
crystallisation process
nucleation, time/temperature profile
feedback
DSC
polymorphic transitions
melting

Conclusions and outlook

- Kinetics are crucial during crystallisation
  - crystallisation = kinetics
- Thermodynamic + kinetic parameters + models → ‘full’ description of crystallisation of mixtures
- Software available

- Derive efficient approximation for excess functions for wide range of fats
  - make use of modelling capabilities
  - make use of Monte Carlo simulations