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BIOMATH
Department of Applied Mathematics, Biometrics and Process Control

Mathematical Modelling of the Crystallization Kinetics of Fats: A Methodological View

Peter A. Vanrolleghem, Imogen Foubert and Koen Dewettinck
BIOMATH Dept. Food Technology and Nutrition

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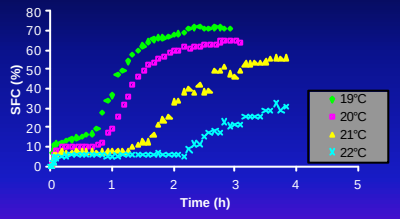
RUG-Biomath, Coupure 653, 9000 Gent, Belgium (e-mail Peter.Vanrolleghem@rug.ac.be)

Why model crystallization kinetics?

- To gain insight in/quantify/predict effects of
  - fat composition
  - differences in fat origin
  - processing conditions
  - temperature (profiles)
  - additives / minor components
- Our focus on:
  - milk fat
  - cocoa butter (Belgian chocolate)

Why model crystallization kinetics? (cont'd)

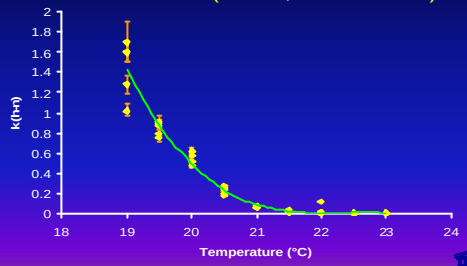
Typical NMR data set



Compare a (small) number of characteristic numbers: e.g. 3 Avrami model parameters (a, k, n)

Example of characteristic number

Temperature effect on crystallization rate constant (EAT-P, Foubert et al.)

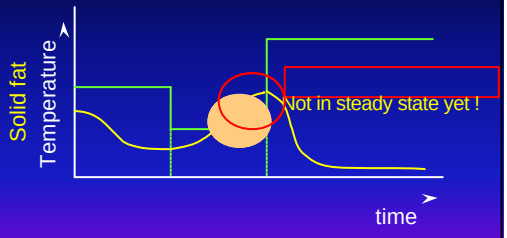


Modelling wish-list

- General:
  - Adequate model to describe/summarize data
  - Meaningful parameters --> physical interpretation
  - Accurate parameter values
  - Statistically correct procedures
  - Confidence information on parameter values
- Specific for our study:
  - Dynamic model for time-varying process conditions

Why a dynamic model ?

Dynamic behaviour is not a sequence of steady states



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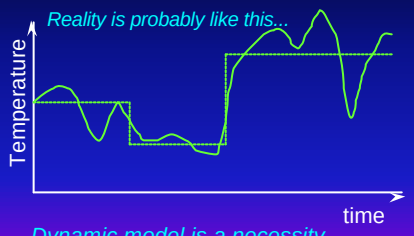

Dynamic model is a necessity
--> differential equation model

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Avrami model

- Algebraic equation form

$$f(t) = a * \left(1 - \exp(-k * t^n)\right)$$

- Differential equation form :

$$\frac{df}{dt} = n * k * t^{n-1} * (a - f)$$

$$\frac{df}{dt} = n(T) * k(T) * t^{n(T)-1} * (a(T) - f)$$

k,a = constant

n,k,a = not constant

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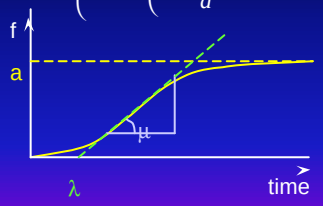
Gompertz model (Kloek et al., 2000)

- Algebraic equation form:

$$f(t) = a * \exp\left(-\exp\left(-\frac{m * e}{a} * (t - l) + 1\right)\right)$$



- Differential equation form exists too

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Foubert model (see EAT-P)

- Differential equation form:

$$\frac{dh}{dt} = K * \left(h^n - h\right) \qquad h(t) = \frac{a - f(t)}{f(t)}$$

- Algebraic equation form exists too

Purpose: - select adequate model
- get accurate parameter values

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Parameter estimation

- Minimise difference between:
  - data
  - model predictions
- Two approaches:
  - linear regression of transformed model
    - one-step method (on pocket calculator)
  - non-linear regression (with original model)
    - iterative method (e.g. with Excel, Origin, SigmaPlot, WEST)
- Underlying assumptions on measurement errors:
  - independent, normally distributed, constant variance

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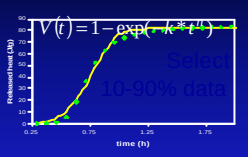
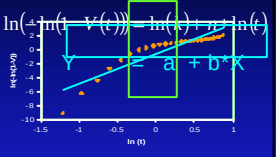
Linearization of Avrami model

Non-linear regression



Linear regression



Result
(95% confidence intervals)

k = [2.1 – 3.3]

n = [4.3 – 5.5]

Result
(95% confidence intervals)

k = [0.4 – 0.8]

n = [3.4 – 5.0]

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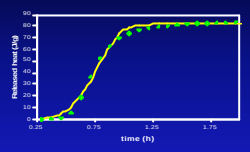
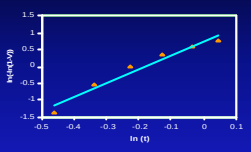
Linearization of Avrami model

Non-linear regression



Linear regression (10-90%)



Result
(95% confidence intervals)

k = [2.1 – 3.3]

n = [4.3 – 5.5]

Result
(95% confidence intervals)

k = [1.6 – 2.5]

n = [3.3 – 4.9]

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Problems with Linearization

- Data are transformed since the model is rewritten
  e.g V(t) --> ln(-ln(1-V))
- Errors no longer obey statistical requirements for proper linear regression (e.g. normality)

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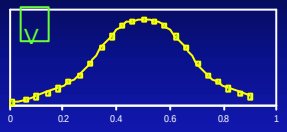
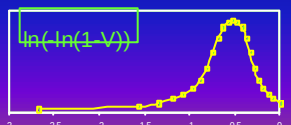
Problems with Linearization (cont'd)

Measurements of V with *normal* distribution



lead to a *non-normal* distribution of transformed data



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Problems with Linearization (cont'd)

- Data are transformed since the model is rewritten
  e.g V(t) --> ln(-ln(1-V))
- Errors no longer obey statistical requirements for proper linear regression (e.g. normality)

==> biased parameter values

i.e. true value differs from estimated value !

==> no more physical interpretation allowed !

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Problems with Linearization (cont'd)

- Calculation of confidence intervals
- Non-linear regression: $f(t) = a * \left(1 - \exp(-k * t^n)\right)$
  – confidence intervals directly on a,k,n
- linear regression: $\ln\left(-\ln\left(1 - V(t)\right)\right) = \ln(k) + n * \ln(t)$
  – confidence interval on n
  – confidence interval on ln(k) --> interval on k ?
  – no information on a because a is hidden in V: $V(t) = \frac{f(t)}{a}$

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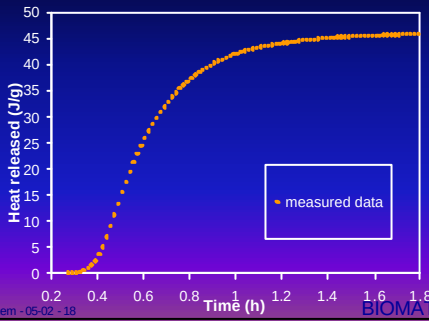
Model selection

Three models (Avrami, Gompertz, Foubert) are fitted



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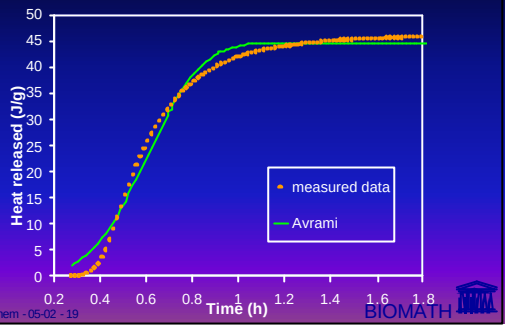

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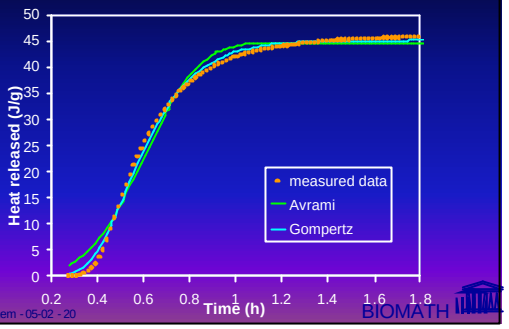

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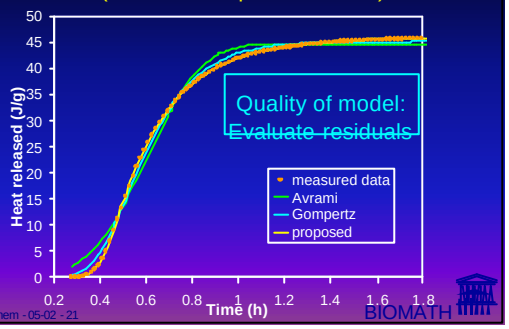
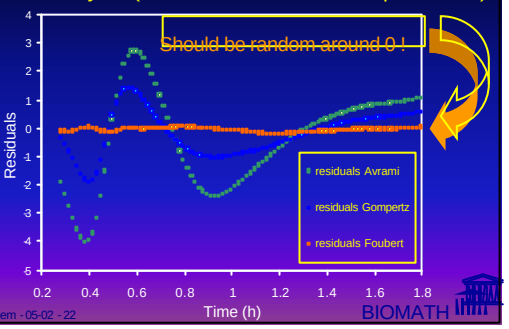


Model selection

Residuals analysis (Residual = data - model prediction)



Residuals analysis

Non-random residuals

⇓

Data are (auto)correlated

= no independent information
= no truly new information per data point

⇓

Calculated confidence limits are too optimistic !

Non-adequate model leads to non-random residuals

Take home

- Modellers wish-list
  - Adequate model to describe/summarize data
  - Meaningful parameters --> physical interpretation
  - Accurate parameter values
  - Confidence information on parameter values
- Linearization
  - biased parameter values
  - difficult to obtain confidence limits on parameters
- Residuals
  - too optimistic confidence limits
- New dynamic models (in differential equation form)