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New methods to assess water diffusion in amorphous matrices: a critical comparison

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Interest of water diffusion

Water diffusion through solid food matrices is a **key parameter** for

Processing
(e.g. spray drying, belt drying, sintering…)

Storage and shelf-life
(low moisture products)

Optimization of drying rate
(falling rate period)

Avoid phase transitions, texture modifications, product degradation…

Water diffusion through an **amorphous matrix** can **plasticize it**
(changes in viscosity, mechanical and thermal properties, caking…)

In particular, **glass transition** might affect water diffusion

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How to assess water diffusion?

- **No standard method** is available
- Several experimental techniques, depending on the product/application
- Two main approaches:
  - ***pseudo steady*** *state diffusion* (diffusion cell)
  - ***unsteady state*** (based on drying kinetics)

Solid supported droplets

Thin layer of droplets

Filament technique

Droplets in aerodynamic field

Falling tower

Spray tower

Freely floating droplets

Acoustic levitation

Techniques differentiate for

- **Experimental design** (sample geometry, measurements…)
- **Data treatment** (analytical vs numerical solutions, statistics…)

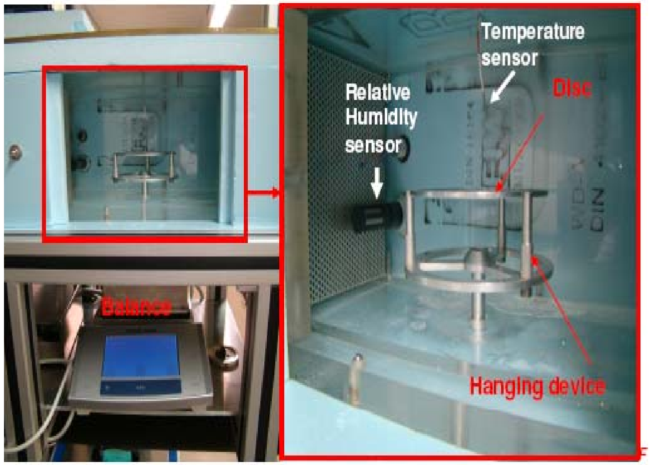
Need of a **mathematical model** adapted to the chosen experimental design

New techniques to measure water diffusion

Automatic sorption device (SPS-11)

*Water sorption/desorption behavior **from powders***

Thin Film Dryer (TFD)



*Drying of thin **liquid films***

Our study

Calculation of diffusion coefficients for different **Maltodextrins** (DE 6 to 47)

I. Automatic sorption device (SPS – 11)

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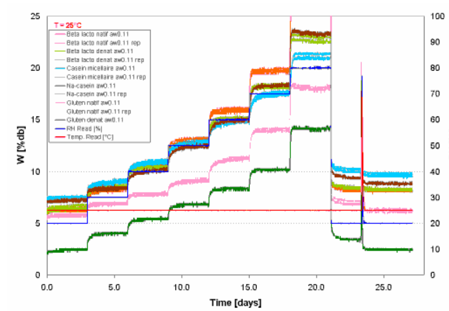
Principle of the SPS-11

Climatic chamber:

- controlled air **RH (0-100%)** and **T (20-90°C)**
- laminar air flow

Up to 12 powder samples with regular weighing



Experimental conditions

- **MD 21 and 47** pre-equilibrated in desiccators
- **Different shapes**: **powder** (not well defined shape) vs **cylinders**
- **50 mg** of each powder (2 replicates) put in the SPS-11 at **25°C**
- RH increased from **11% to 70% with 10% steps**

Mathematical models

Two models: **Crank** (Fick's law for spheres) and **Weibull distribution**

Assumptions

- Surface of the sample in equilibrium with surrounding air
- External resistance to mass transfer is negligible
- Initial moisture distribution is uniform
- **D is independent from water content**

$$W_{(t)} = W_{\infty} \cdot \left(1 - \frac{6}{\pi^2} \sum_{1}^{100} \frac{1}{n^2} \exp(-4n^2\pi^2 D t^k / d^2)\right)$$

Crank equations for spheres *(Crank, 1975)*

W_{∞} *equilibrium moisture content (%db)*; W_0 *initial moisture content (%db)*; t *drying time(s)*; r *sphere radius(m)*; D *water diffusion coefficient (m²/s)*

$$\frac{W_t - W_0}{W_{\infty} - W_0} = 1 - \exp\left(-\left(\frac{t}{\alpha}\right)^{\beta}\right)$$

$$\alpha = \frac{l^2}{D}$$

Weibull distribution *(Marabi et al., 2003)*

α *scale parameter (s)*; β*shape of the kinetic curve parameter (dimensionless)*; l *sample radius (m)*

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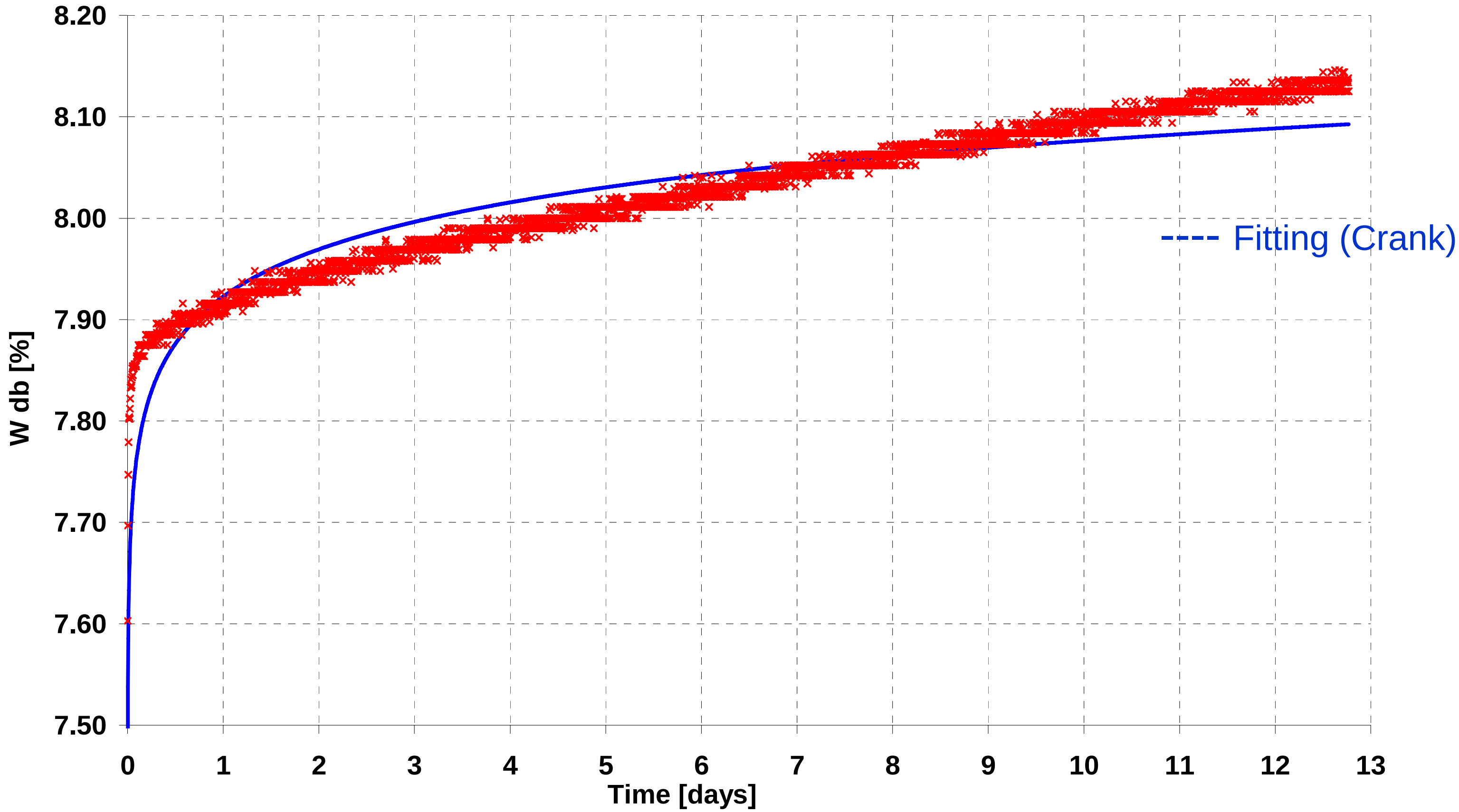
MD21 – 43% to 53% RH equilibration kinetics



SPS-11 can be used to build **sorption isotherms** and/or simulate **storage conditions**

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Water diffusion coefficients

- **Weibull** model better than Crank (lower residues)
- Models are adapted only for **well defined geometry**

	D (a_w 0.22) (m^2/s)		D (a_w 0.33) (m^2/s)		D (a_w 0.43) (m^2/s)		D (a_w 0.54) (m^2/s)	
	Crank	***Weibull***	*Crank*	***Weibull***	*Crank*	***Weibull***	*Crank*	***Weibull***
MD 21 Powder	$2.28\ 10^{-10}$	$3.81\ 10^{-13}$	$2.55\ 10^{-10}$	$5.27\ 10^{-15}$	$3.57\ 10^{-10}$	$6.95\ 10^{-19}$	//	//
MD 21 Cylinder	//	**$1.79\ 10^{-13}$**	//	**$3.25\ 10^{-13}$**	//	**$6.90\ 10^{-13}$**	//	cryst
MD 47 Powder	$1.65\ 10^{-10}$	$2.39\ 10^{-15}$	$1.67\ 10^{-10}$	$5.67\ 10^{-18}$	Through Tg	$8.89\ 10^{-16}$	cryst	cryst
MD 47 Cylinder	$2.23\ 10^{-08}$	**$6.21\ 10^{-13}$**	//	**$4.42\ 10^{-13}$**	Through Tg	**$7.03\ 10^{-14}$**	cryst	**$1.50\ 10^{-13}$**

- **Slow water diffusion** (**D ~ 10^{-13} m^2/s** for **3.9% < W_{db} < 10.9%**)
- **Models are not adapted to describe diffusion behavior through glass transition**

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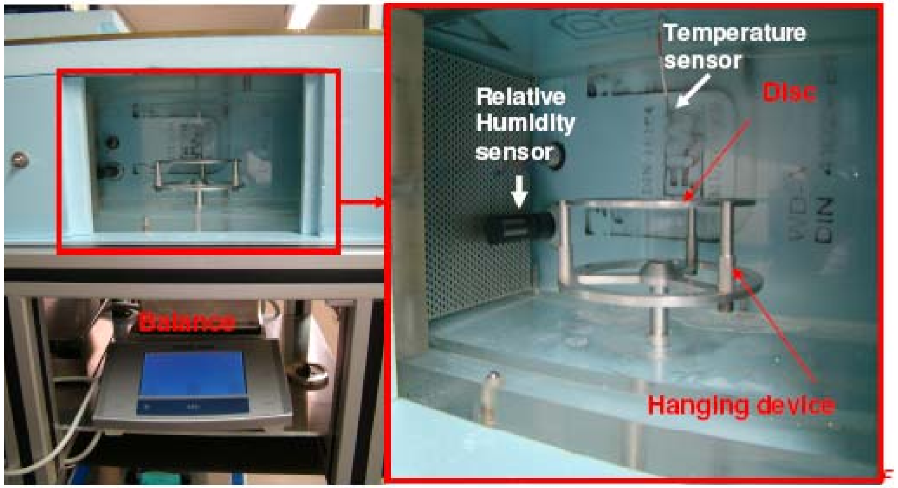
Principle of TFD

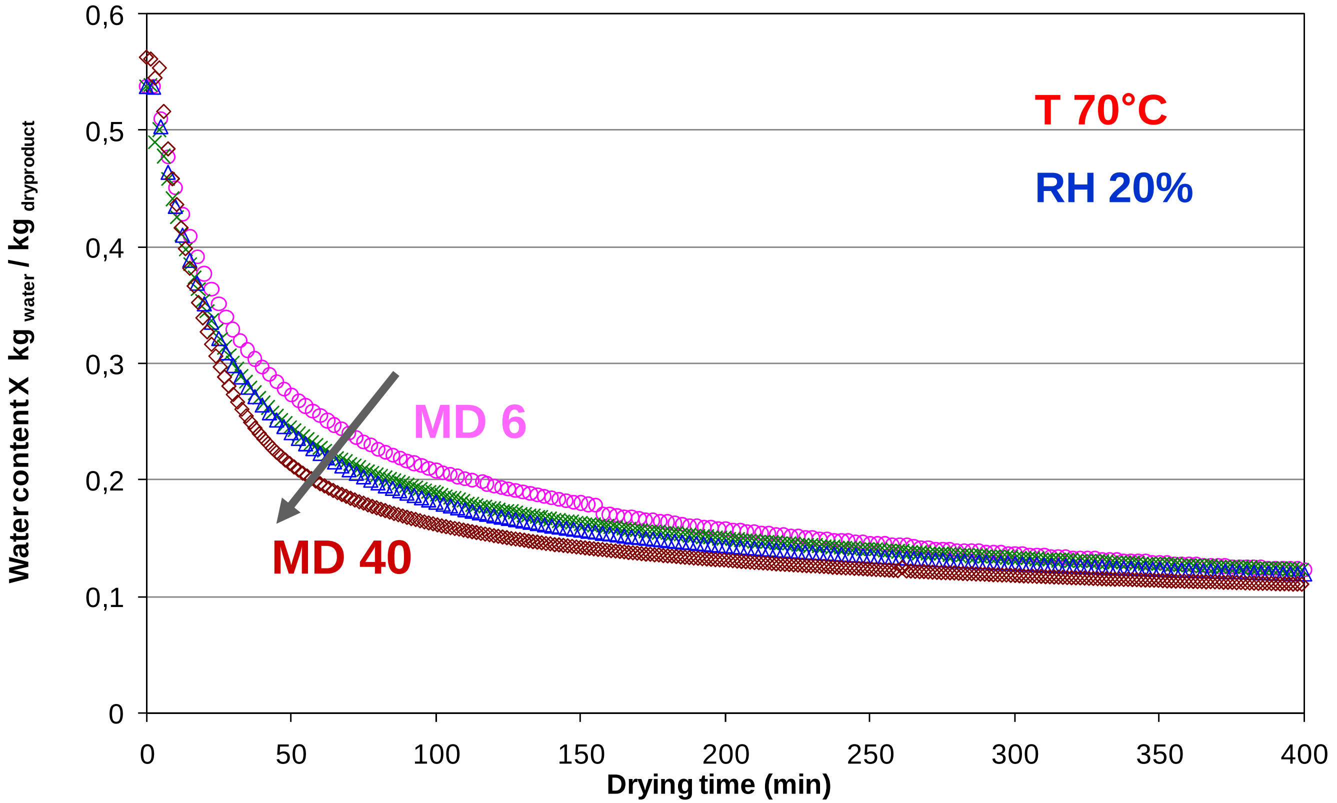
- **Liquid viscous film** spread on a plate (d =10 cm, thickness: 0.6 cm)
- Laminar air flow (0.6 m/s), controlled **air T (up to 70°C) and RH (10-100%)**
- Continuous sample weighing ➔ **drying kinetics**



Experimental conditions

- Drying of liquid solutions (**TS 65%**) of **Maltodextrins** (DE 6-12-21-29-40)
- Air T: 70 °C   Air RH: 20%

Drying kinetics of maltodextrin solutions



Diffusion limited drying
- The **higher** the **molecular weight** (lower DE) the **slower** the **drying rate**
- Difference in mass transfer resistance due to **viscosity** and **glass transition**

II. TFD – Drying kinetics and glass transition

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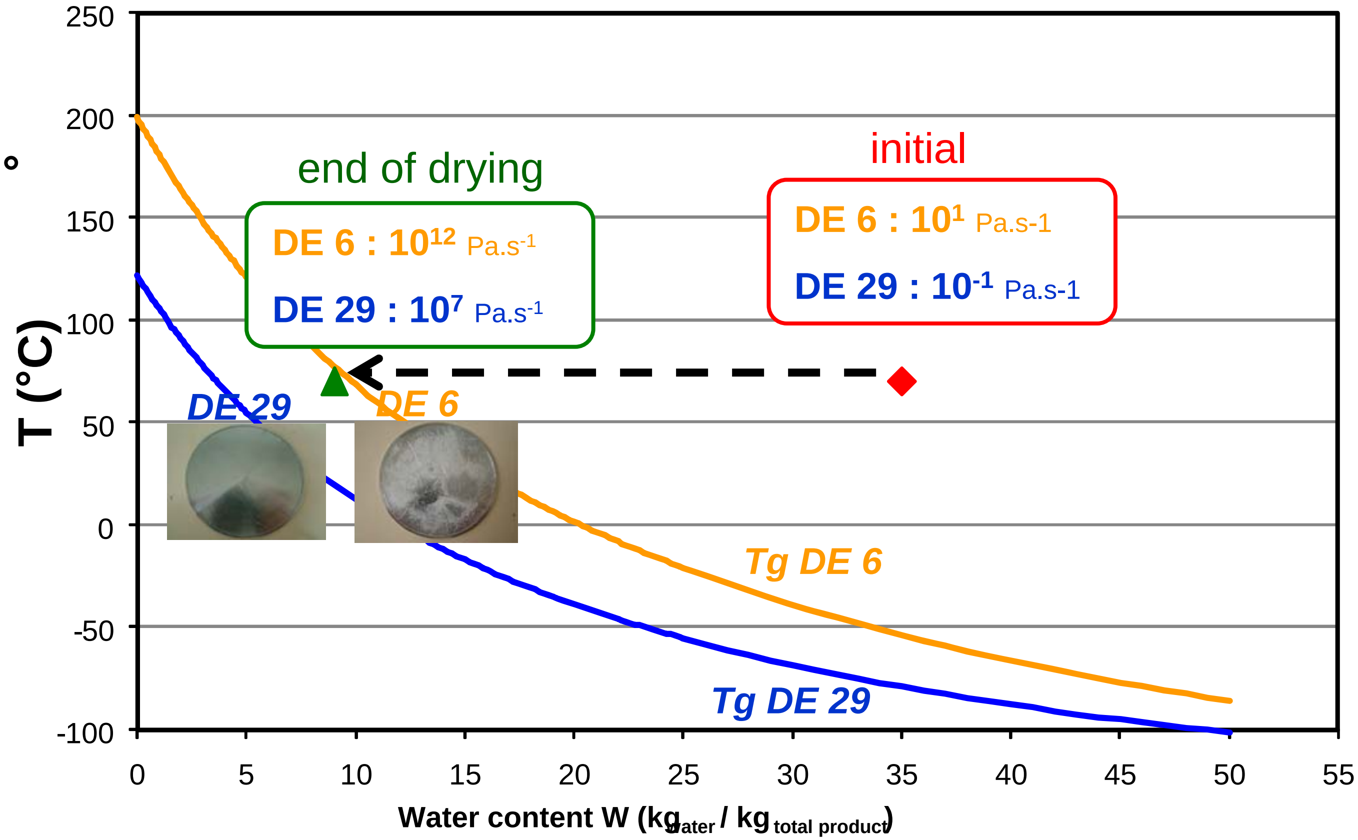
Effect of glass transition



Low DE Maltodextrins **cross the glass transition** curve during drying
➔ Much **higher viscosity** in the final steps of drying ➔ **slower diffusion**

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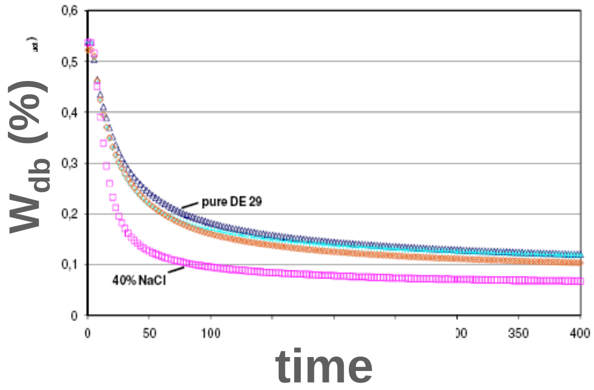
Mathematical models

Calculation of **diffusion coefficient** as a **function of water content**

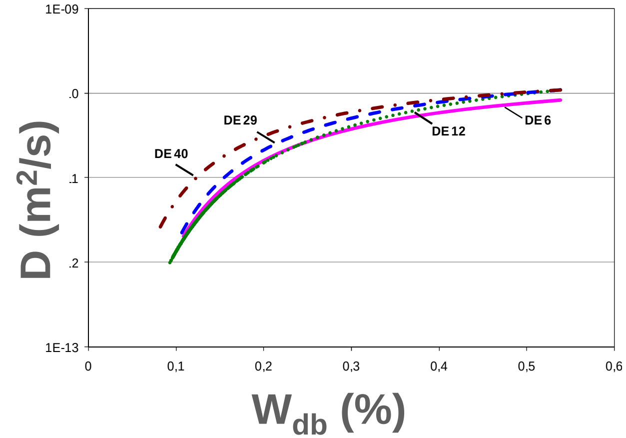
Assumption: regular regime approach

Drying kinetics



Choice of Model

Diffusion coefficient



Stokes-Einstein
Yamamoto method ***(Yamamoto et al., 1997)***
Maxwell-Stefan approach

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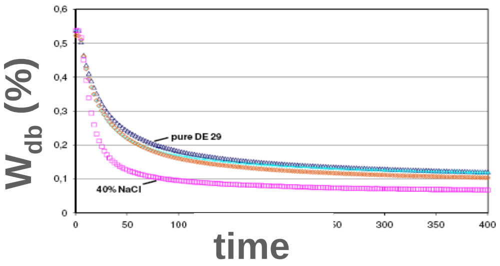
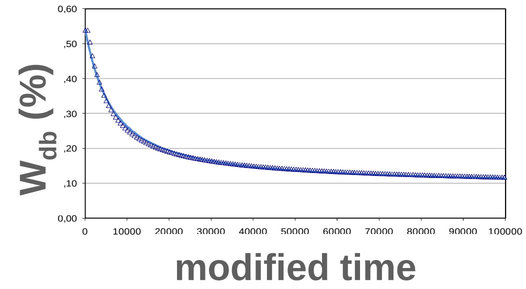
Yamamoto model



1 Convert time into modified time

$$\tau = (A_t / Ws)^2 t$$



2 Smooth curve

$$X = \exp\left(\frac{\ln(x'_0) + k \ln(x'_1)\tau'}{1 + k\tau'} \right)$$

3 Apparent diffusion coefficient

$$Da = \frac{4}{\pi^2} \frac{k(\ln x'_0 - \ln x'_1)}{(1 + k\tau')^2}$$

4 Parameter a

$$a = \frac{\ln(Da_1 / Da_2)}{\ln(x_1 / x_2)}$$

5 Diffusion coefficient

$$Dx_1 = \frac{(a+1)\pi Da_1}{2Sh(Qs_1)^2}$$

$$D_w = \exp\left(-\frac{a + b X_P}{1 + c X_P} \right) \exp\left(-\frac{10^6 (d + 190 X_P)}{8314 (1 + 10 X_P)} \right) \left(\frac{1}{T_P + 273} - \frac{1}{303} \right)$$

D_w = f(X,T) with **4 fitting parameters** (a,b,c,d)

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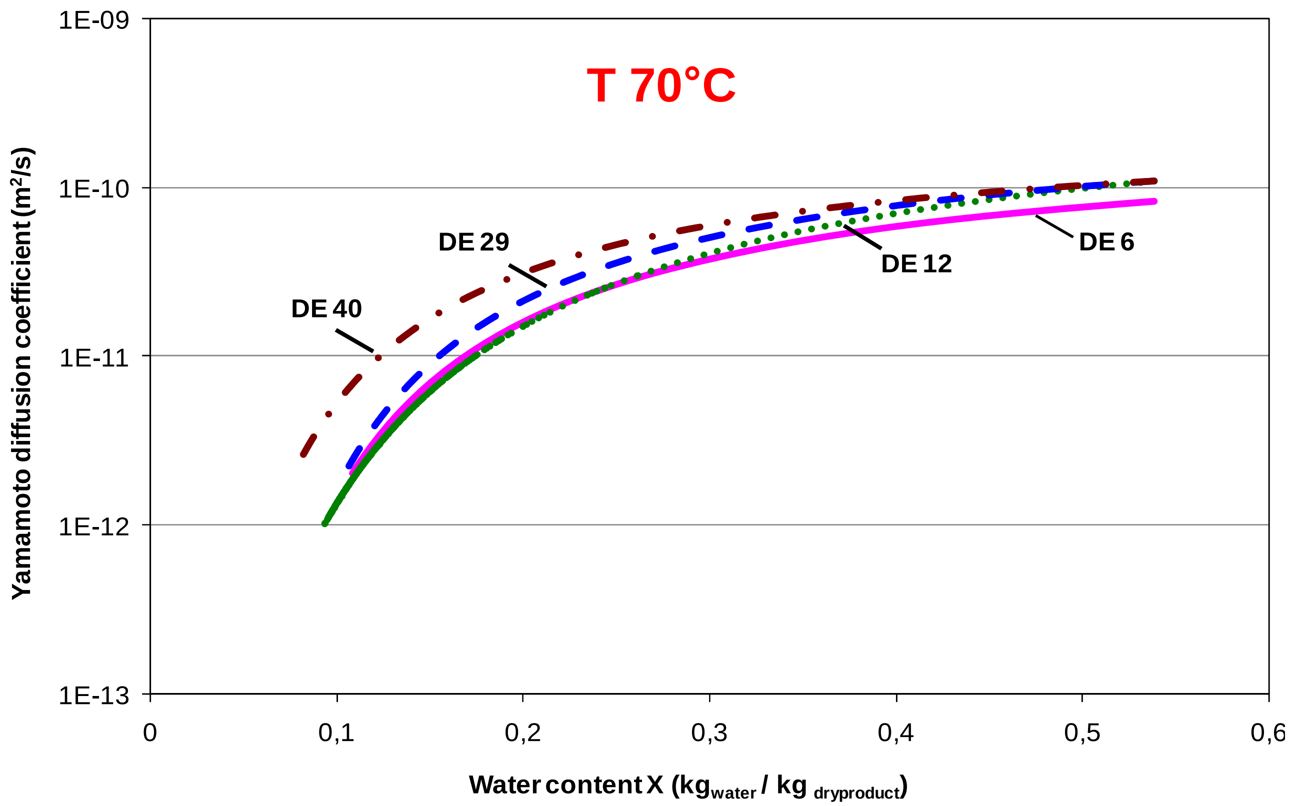
Diffusion coefficients of maltodextrins



Reflecting the drying kinetics ➔ **lower diffusion for low DE**

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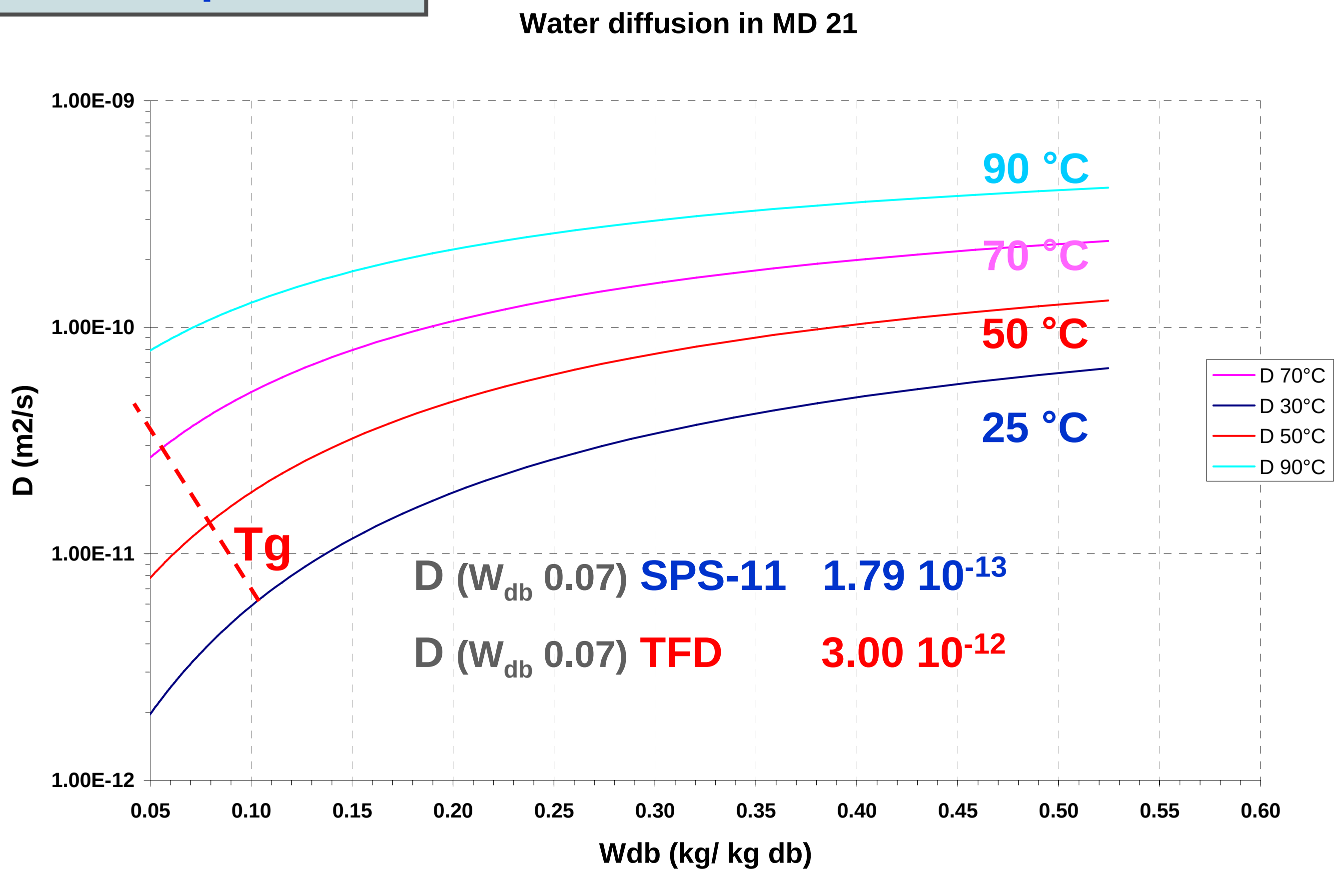
Effect of temperature



D decreases with increasing temperature
Sharper decrease below Tg
Similar order of magnitude for diffusion coefficient calculated with SPS-11 and TFD

Conclusions

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- **SPS-11** and **TFD** are **powerful tools** to investigate the **water diffusion behavior in amorphous food matrices**

- **Automatic sorption device (SPS-11)**
  - Adapted to simulate water diffusion during sorption/desorption of **powders**
  - Possibility to build **sorption isotherms**
  - Mathematical models work **only for well defined geometry**
  - Models are **not adapted** when powder is **close to glass transition**

- **Thin Film Dryer (TFD)**
  - Adapted to simulate water diffusion during **drying of viscous liquids**
  - Good to **simulate falling rate period** during drying
  - **Possible to obtain diffusion data above glass transition**

Thank you for your attention !!

Back slides

Outline

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1. Introduction
   - interest of water diffusion
   - methods to measure water diffusion
2. Automatic sorption device
   - Crank vs Weibull model
   - effect of shape
3. Thin film drying
   - drying of MD 6 to 40
   - Yamamoto and Maxwell-Stephan model
   - effect of Tg
4. Comparison between techniques

Plan (15 minutes!!)

- Interest of diffusion
- Difficulty of assessment
- Measure by SPS-11 → examples for « spaghetti », using Cranck equations. For particles, big differences in results, as not perfect spheres → no good mathematical modeling. Furthermore, no data when passing glass transition, and diffusion coefficient is supposed to be independent from water content
- Measure by TFD. Starting from a liquid, with well defined geometry ➔ application of Yamamoto model.

  Examples for maltodextrin, providing good data for drying simulations (e.g. Marc Räderer)

How diffusion of water evolves during drying?

Maxwell-Stefan approach

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Force balance between **friction force** and **driving force** inside the film

Velocity difference between the permeant and its environment

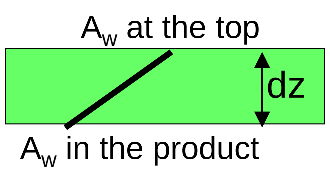
$$\zeta_{12} x_2 u_1 = -RT \frac{d \ln a_i}{dz}$$

Difference in chemical potential due to the location z

$$u_1 = -\frac{Đ}{x_2} \frac{d \ln a_1}{dz}$$

Expressed as a function of mass flux (TFD)

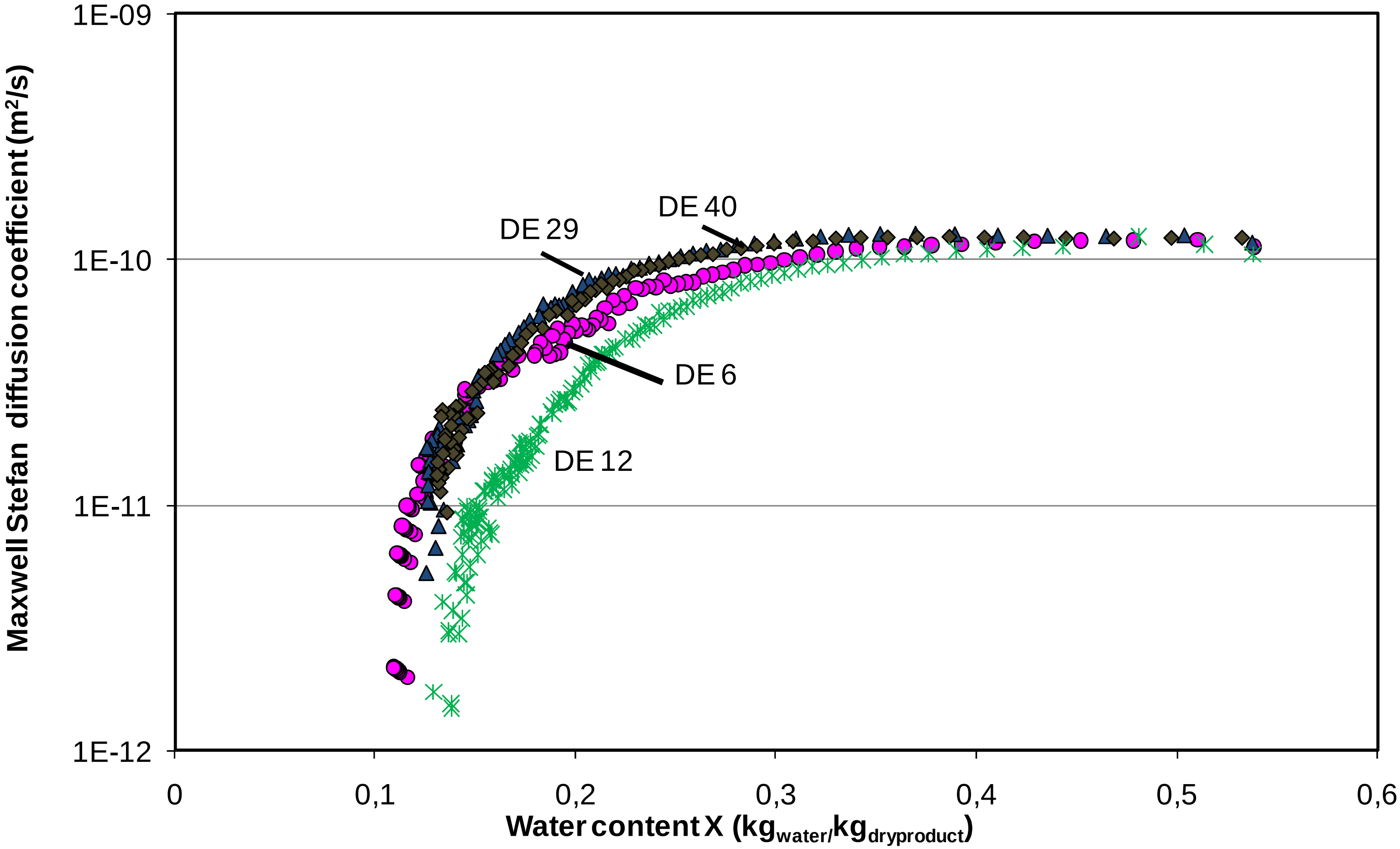
$$M_1 = -\rho w_1 \frac{Đ}{(x_2)} \frac{d \ln a_1}{dz}$$



- Based on physics → more reliable
- Signification of an inverse drag coefficient: mobility of component 1in 2

How diffusion of water evolves during drying?

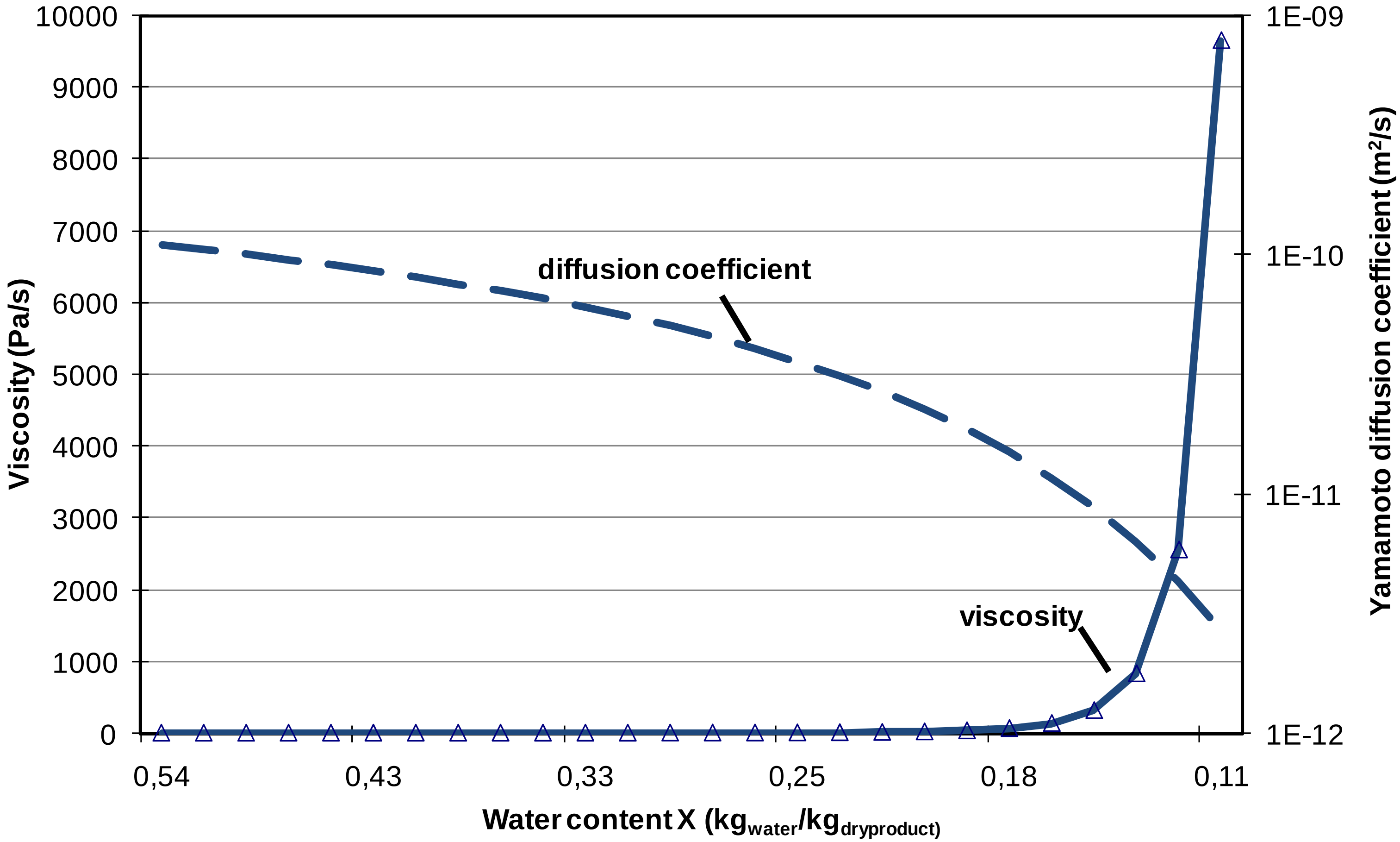
Maxwell-Stefan approach



- Water content and molecular weight dependence
- DE 6 has a strange behavior

How diffusion of water evolves during drying?

How can the diffusion difference be explained ?



- Diffusion drops when viscosity increase
- Not linear relation