

## The phase diagram of milk: a new tool for optimising the drying process

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**Abstract** – The spray-drying process of milk has been developed using an approach based more on empirical and technological concepts than on food material science. However, optimisation of the concentration and spray-drying steps require a detailed consideration of material phase transitions as well as the kinetics of possible chemical reactions and physical transformations. The phase diagram of milk, now completed by a description of glass transition, was found to be a very powerful tool for understanding the physical changes that may occur during milk dehydration. In this paper, the glass transition line versus the concentration and the sorption isotherm are presented for both whole milk and skimmilk and a universal relationship between the glass transition temperature and water activity is proposed. The phase transition lines as well as the kinetics of lactose crystallisation are also described here. In whole milk, depending on the concentration and the temperature, lactose may undergo at least two phase transitions: (1) nucleation of alpha hydrate lactose crystals in a supersaturated milk concentrate; and (2) nucleation of beta anhydrous crystals in a rubbery-glassy powder state. However, in skimmilk powders nucleation of a mixture of anhydrous beta and alpha lactose was identified.

**Phase diagram / lactose / glass transition / crystallisation / kinetics**

**Résumé** – **Le diagramme de phase du lait: un nouvel outil pour optimiser le procédé de séchage.**

Le procédé d'atomisation du lait a été développé selon une approche davantage fondée sur des concepts empiriques et technologiques que sur la science des matériaux alimentaires. L'optimisation des étapes de concentration et de séchage nécessite de considérer attentivement les transitions de phase ainsi que la cinétique des réactions chimiques et des transformations physiques envisageables. Le diagramme de phase du lait, maintenant complété avec la description de la transition vitreuse se trouve être un outil très puissant pour comprendre les changements physiques qui peuvent se produire durant la déshydratation du lait selon le chemin du procédé. Dans cet article la courbe de transition vitreuse en fonction de la concentration et l'isotherme de sorption sont établis aussi bien pour le lait entier que pour le lait écrémé, et une équation universelle reliant la transition vitreuse à l'activité de

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l'eau est proposée. Les courbes de changement de phase ainsi que la cinétique de cristallisation du lactose sont aussi décrites. Dans le lait entier, selon la concentration et la température, le lactose peut subir au moins deux transitions de phase : (1) la nucléation de cristaux de lactose alpha monohydrate dans un concentré de lait supersaturé et (2) la nucléation de cristaux de lactose beta anhydre dans l'état vitreux visco-élastique. Cependant, dans les poudres de lait écrémé, un mélange de lactose beta et alpha anhydre a été identifié.

## Diagramme de phase / lactose / transition vitreuse / cristallisation / cinétique

### 1. INTRODUCTION

The spray-drying process of milk has been developed using an approach based more on empirical and technological concepts than on food material science. However, optimisation of the concentration and the spray-drying steps require a detailed consideration of material phase transitions, especially concerning the state of lactose. Milk powder manufacture should preserve emulsion functionality throughout the process down to reconstitution. In particular, fat globules should be well covered with membranes and encapsulated in a fully amorphous matrix to limit free fat [5]. Therefore, lactose crystallisation, either during concentration or spray-drying, should be avoided [6]. Since 1990, due to meaningful use of the glass transition concept, exploitation of the state diagram has spread gradually [10] in various food processing applications. This paper deals with the phase diagram of milk, focusing on phase transitions of lactose, and includes some kinetic considerations. It is both a critical review of the literature and a summary of some personal results that will not be presented in detail. The main objective is to present and discuss a very powerful and robust tool for technologists: the state diagram of milk.

### 2. THE VARIOUS STATES OF LACTOSE IN MILK

Lactose is the major ingredient of milk. When it is dissolved in water or raw milk at

a pH between 2 and 7, lactose exists in two anomeric forms: alpha and beta. The beta:alpha ratio (governed by mutarotation) is not strongly dependent on temperature and concentration [1], but may be influenced by the presence of salts. Lactose is more stable in the crystalline alpha monohydrate form, containing 5.0% water chemically bound to the crystal lattice structure. Crystalline monohydrate alpha lactose is not very soluble (7.4% w/w water over total matter at 20 °C; 18.5% at 60 °C), compared to sucrose (66.7% at 20 °C; 74.3% at 60 °C). However, the beta form is more soluble (16.1% at 20 °C; 36.0% at 60 °C) and mutarotation of the alpha fraction into the beta form (equilibrated beta:alpha ratio is about 1.6 at 20 °C and 1.4 at 90 °C) increases the final solubility. When a non-crystallised milk concentrate is spray-dried, the lactose is rapidly solidified in an amorphous solid structure [6]. The beta:alpha ratio in this powdered glassy state (typically 1.2 to 1.4) is not thought to significantly change during the end of drying. In a glassy powder particle, the amorphous lactose coats milk proteins and fat globules. Amorphous lactose is metastable, and may undergo glass transition and crystallisation under certain conditions, e.g. water uptake or heat treatment.

#### 2.1. The glass transition in milk powders

The onset glass transition temperature ( $T_g$ ) of any milk powder, characterised by the water content (W) or the water activity ( $a_w$ ) is mainly an effect of the amorphous

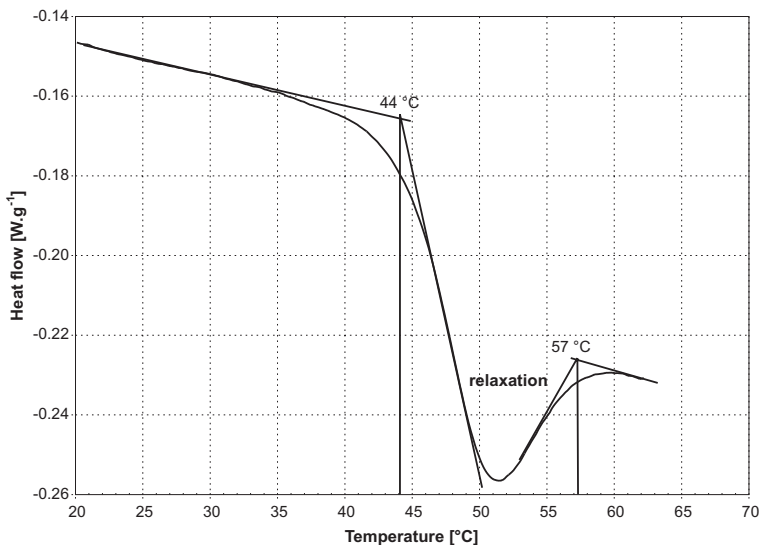
lactose. It can be determined by differential scanning calorimetry (DSC). However, in whole milk powders (WMP)  $T_g$  may be difficult to detect; depending on the  $W$ , the glass transition may more or less overlap the end point of fat melting. Therefore, DSC is easier to use in skimmilk powders (SMP). The procedure for determining the  $T_g$  and its relationship to  $W$  and  $a_w$  in WMP or SMP requires:

- The accurate determination of  $W$  and  $a_w$  (at a given temperature) of the sample. In the next examples,  $W$  values were determined in duplicate (difference  $< 0.1\%$ ) using a home-made method (2 h at  $102\text{ }^\circ\text{C}$  at 25 mbar initial pressure, in presence of  $\text{P}_2\text{O}_5$ ), which fully removes the water (proved by NIR) and gives results in very good agreement with Karl-Fischer. The  $a_w$  values were determined at  $25\text{ }^\circ\text{C}$  in duplicate (difference  $< 0.005$ ) using a Rotronic Hygroskop DT calibrated with saturated salts.
- Doing a first DSC scan to eliminate the relaxation of the matrix by heating to the

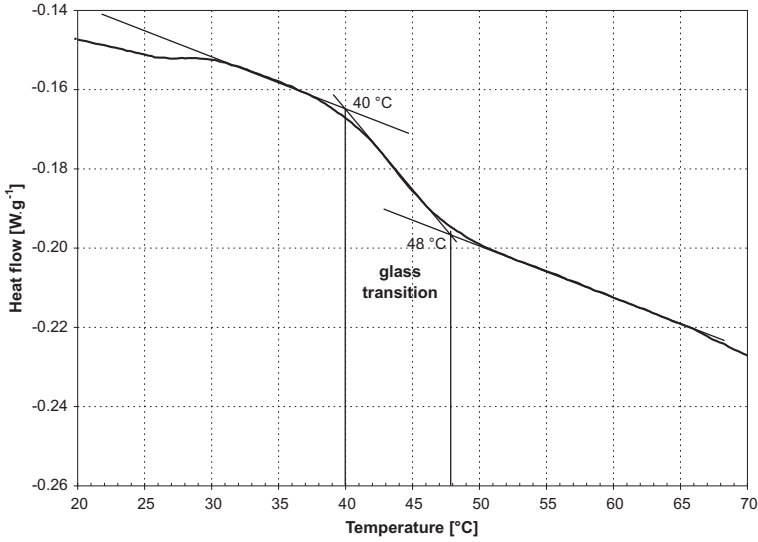
end of the relaxation mechanism (but avoiding any other physical or chemical reactions). Otherwise, the onset of the relaxation peak will dramatically affect determination of the onset  $T_g$ .

- The rapid cooling of the sample (at the rate of  $-25\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ ) in the glassy solid state, to typically  $50\text{ }^\circ\text{C}$  below the expected  $T_g$ , and then heating it a second time to a higher temperature, in order to detect successively the temperature of the true glass transition, lactose crystallisation and onset of non-enzymatic browning.  $T_g$  determinations were done in duplicate (differences  $< 2\text{ }^\circ\text{C}$ ).

The DSC procedure is illustrated (Figs. 1 and 2) for a typical industrial spray-dried SMP (canned at  $5.1\%$   $W$ ), using a Seiko 220C DSC instrument with heating at  $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . Onset with relaxation (1st scan) is at  $44\text{ }^\circ\text{C}$  and the true  $T_g$  (2nd scan) is  $4\text{ }^\circ\text{C}$  lower at  $40\text{ }^\circ\text{C}$ . The end point of relaxation is at  $57\text{ }^\circ\text{C}$ , but the end point of the glass transition is at  $48\text{ }^\circ\text{C}$ .



**Figure 1.** Matrix relaxation temperature as determined by 1st heating of SMP (5.1%  $W$ ) at  $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ .



**Figure 2.** Matrix  $T_g$  as determined by 2nd heating of SMP (5.1% W) at  $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ .

The relationship between  $T_g$  and  $W$  or  $a_w$  for both WMP and SMP will be examined later.

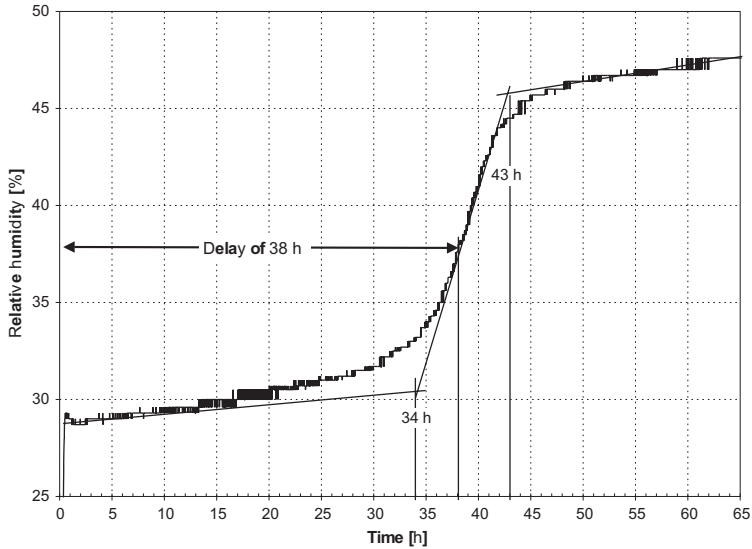
**2.2. Lactose crystallisation in milk powders**

Lactose crystallisation may occur in milk powders exposed to high relative humidities or submitted to heat treatments after a period of storage. However, the state of crystallisation seems to be different in SMP and WMP [1–3]. The storage period before significant nucleation is supposed to be  $(T - T_g)$  dependent, according to the glass transition theory. However, the kinetics of crystallisation is highly dependent on the experimental conditions [11].

**2.2.1. Isothermal heat treatment at constant water content**

A rather large amount of powder (e.g. a can or a tube) with a well-known  $W$  and  $T_g$  is exposed to a constant storage temperature above  $T_g$  (in an oven). If the packaging

material is not permeable to water, no water exchange with the outside environment is possible. Under such conditions, lactose crystallisation will induce a very significant increase in the  $a_w$  due to the release of water from the amorphous lactose during crystallisation (most often present in an anhydrous form). This water is available to the remaining amorphous ingredients (e.g. the proteins) and may provoke reactions such as Maillard browning. Figure 3 shows the profile of the relative humidity (RH) recorded by a sensor (Rologg Agent HT data logger; 36 seconds step, calibrated at  $65\text{ }^\circ\text{C}$  over saturated salts; typical sensor precision 2% RH) above an industrial spray-dried WMP (3.3% W;  $0.21\text{ }a_w$  at  $25\text{ }^\circ\text{C}$ ;  $47\text{ }^\circ\text{C } T_g$ ) stored at  $65\text{ }^\circ\text{C}$ . The RH first slightly increases due to relaxation of the amorphous matrix and the early stages of the Maillard reaction (no browning), which produce a small amount of water (max 0.1%). Then onset of lactose nucleation (after 34 h) provokes the first major water release, which plasticises the surrounding matrix, depresses the  $T_g$  and accelerates the propagation of

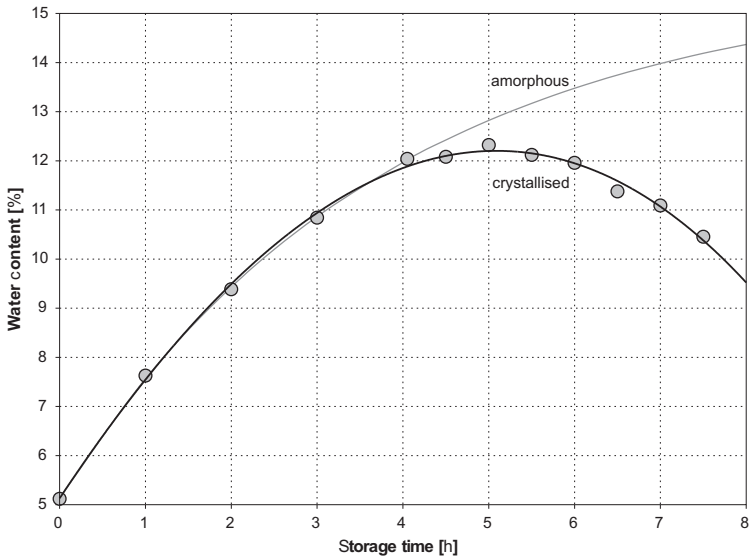


**Figure 3.** Increase in RH above a WMP (3.3% W) stored at 65 °C.

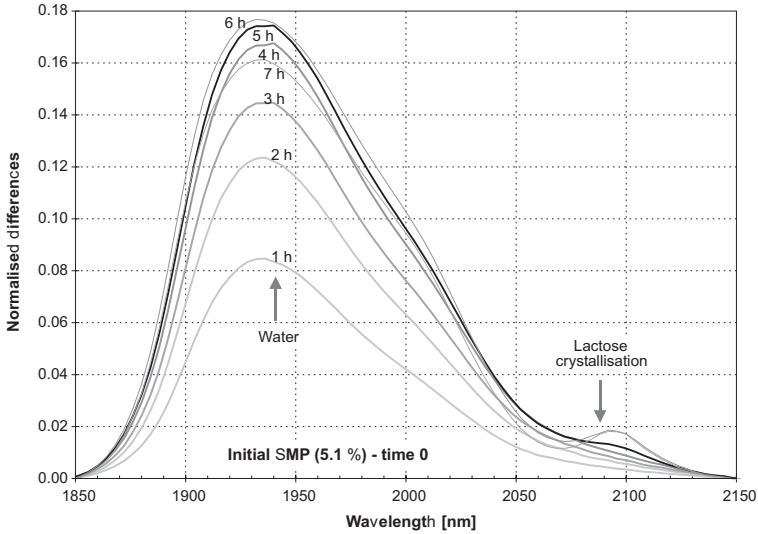
nucleation and crystal growth. Therefore, the maximum crystallisation level is reached in a rather short time (here within 9 h, between 34 and 43 h). It is suggested to use the midpoint of the RH step (here 38 h) to define the time required for crystallisation.

**2.2.2. Isothermal heat treatment at a constant relative humidity**

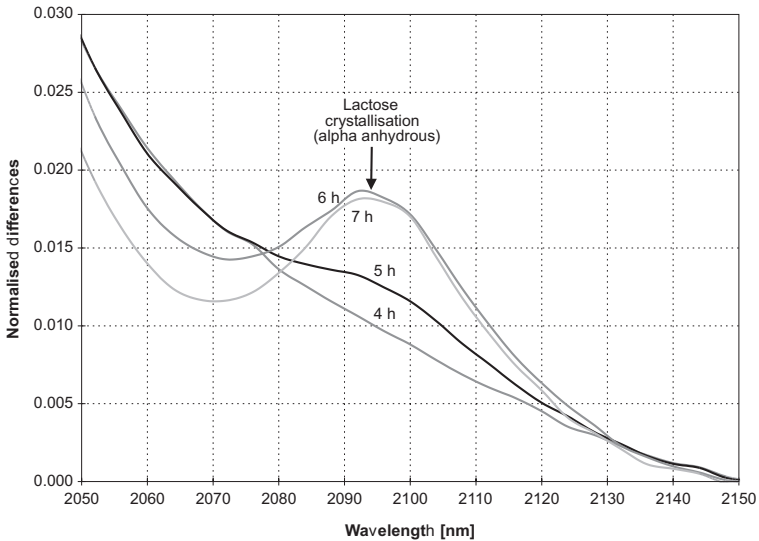
A rather small amount of powder of known initial W is evenly spread in a dish and exposed to a constant RH imposed by a saturated salt at a given temperature (most



**Figure 4.** Water exchange occurring in SMP (5.1%) exposed to 75% HR at 25 °C.



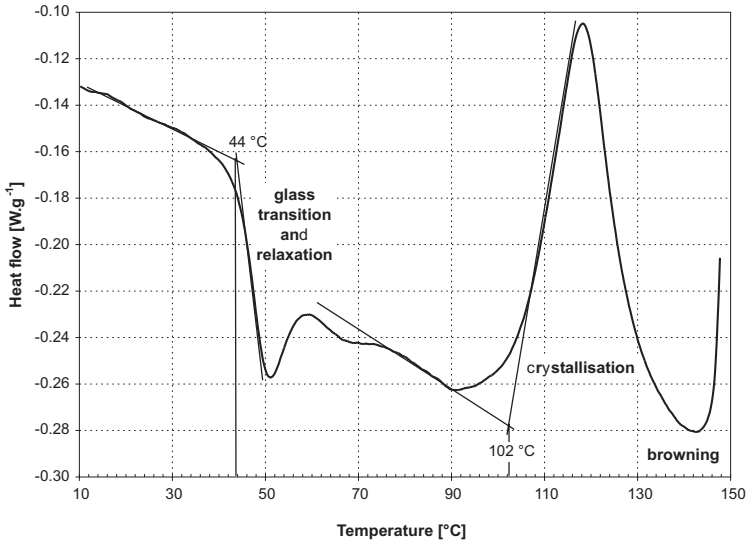
**Figure 5.** NIR normalised scan differences of SMP during sorption kinetics study at 75% RH and 25 °C.



**Figure 6.** NIR normalised scan differences of SMP after 4 to 7 h sorption at 75% RH and 25 °C.

often room temperature). The weight of the powder is recorded on a regular basis and the kinetics of water uptake and release (after the onset of crystallisation) with time follows. Figure 4 illustrates the water exchange between a SMP, initially at 5.1% W,

exposed for 8 h to humid air at 75% RH at 25 °C. Water uptake occurs during the first 4 h up to 12% W. Lactose nucleation occurs between 4 and 5 h. Then the W decreases to below 10% after 8 h. A Near Infrared Reflectance (NIR) fingerprint (InfraAlyzer



**Figure 7.** DSC at  $5^{\circ}\text{C}\cdot\text{min}^{-1}$  of SMP (5.1% W): 1st heating from 0 to 150 °C.

500, Bran and Luebbe) collected each hour allows the onset of crystallisation to be detected and the state of lactose to be predicted (Figs. 5 and 6).

### 2.2.3. Heating at a constant rate at a constant water content

This is the standard DSC procedure and it uses a very small sample (10 to 20 mg). Here, the onset crystallisation temperature is very dependent on the heating rate, and the initial W. Figure 7 shows the glass transition with the onset of the relaxation at 44 °C, the onset lactose crystallisation (102 °C), the full peak and the onset of Maillard browning for a SMP initially at 5.1% W heated at  $5^{\circ}\text{C}\cdot\text{min}^{-1}$ .

These different experiments allow data for modelling of the time period of lactose crystallisation to be collected.

## 3. THE PHASE DIAGRAM OF WHOLE MILK

The establishment of the milk state diagram, restricted to description of the state

of lactose, requires knowledge of three main lines described by the temperature versus the concentration in milk total solids (TS) at thermodynamical equilibrium:

- The freezing point depression line ( $T_f$ ): well known and described in the literature [7, 12], up to a certain TS.
- The solubility line ( $T_s$ ): established based on the solubility of lactose in water [12, 13], and according to the hypothesis on the partition of water to dissolve milk ingredients (mainly the proteins and the salts). The thermodynamical equilibrium requires a consideration of the mutarotation kinetics.
- The glass transition line ( $T_g$ ): consisting of a number of data points for milk at various TS, especially in the solid state zone. The reliability of the  $T_g$  line depends on the accuracy of the determination of the TS [0–100%] in milk solids and of the  $T_g$ . It also depends on the significance of the model used [9].

This paper focuses on the establishment of the glass transition line. The dynamic lines, which describe the time period of

crystallisation as a function of  $(T - T_g)$ , depend on the reliability of the  $T_g$ (TS) line. A procedure for obtaining a coherent model equation for both whole milk (WM) and skim milk (SM) will be presented.

### 3.1. The glass transition line of WM and SM

The Gordon and Taylor equation (1) may be applied to most amorphous soluble food products to describe the plasticising effect of water. This model requires adjustment of the three following constants:

- The glass transition  $T_{gw}$  of pure water.
- The glass transition  $T_{gm}$  of the fully dried material (influenced by the amorphous carbohydrates).
- A  $k$  coefficient, which express the non-linearity of the plasticising effect of water.

$$T_g(\text{TS}) = \frac{[\text{TS } T_{gm} + k (100 - \text{TS}) T_{gw}]}{[\text{TS} + k (100 - \text{TS})]} \quad (1)$$

As water is the solvent,  $T_{gw}$  may be considered as well defined (the reference value of  $-135^\circ\text{C}$  is commonly used [2]). Therefore, only the  $T_{gm}$  and  $k$  parameters need to be optimised experimentally. A small number of data points are sufficient for adjusting the coefficients. Here, the quality of the data is more important than their number. Two procedures may be considered:

- A first procedure consists of determining  $T_{gm}$  by measuring a fully dehydrated product, and then adjusting  $k$  by a curve fitting using the  $T_g$  of powders of known  $W$ . However, it is not easy to dehydrate an amorphous milk powder to 0.0%  $W$ . There is a risk of chemical change or partial recrystallisation by heating at too high a temperature, and diffusion of water throughout the matrix is slowed down as water is removed, thereby increasing the  $T_g$ . Moreover, it is difficult to prove that there is no residual water (NIR is an

option) and such a fully dehydrated amorphous powder will rapidly take up moisture from the environment during any manipulation. Therefore, procedures described in the literature [2] based on desiccation of freeze-dried samples over  $\text{P}_2\text{O}_5$  at room temperature for some days probably allow significant residual water content.

- Another procedure consists of adjusting both  $T_{gm}$  and  $k$  simultaneously by curve fitting (e.g. applying the Excel solver) using a set of experimental data. Most often in the literature, the TS are obtained by equilibrating dried powders at different RH (over saturated salts). The  $W$  reached after an arbitrary equilibration time is calculated based on the initial  $W$  and the weight exchange. Therefore, the initial  $W$  values will affect all other determinations. The powders are presumed to be in equilibrium at the  $a_w$  corresponding to the saturated salt solutions at the sorption temperature, and this is not necessarily true.

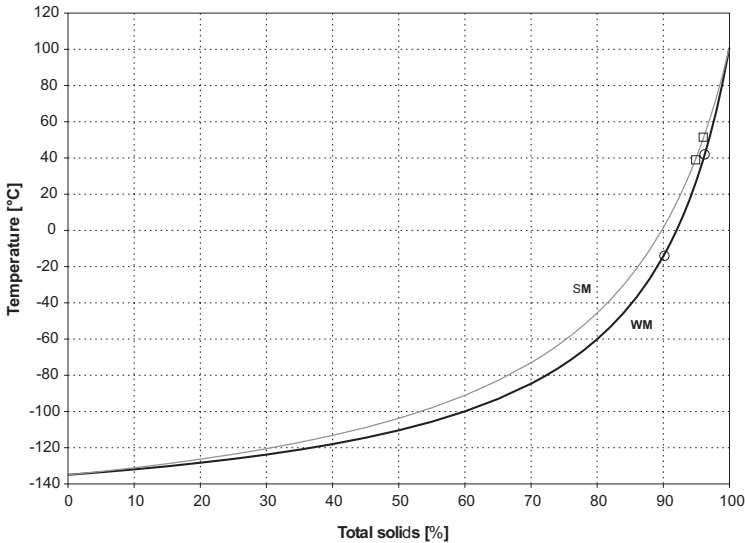
As already mentioned, the  $T_g$  may be difficult to detect for WMP between 4 and 8.5%  $W$ . The glass transition more or less overlaps fat melting (usually between  $-5$  and  $40^\circ\text{C}$ ). Consequently, determination of the onset  $T_g$  of WMP can only be done for powders with less than 4%, or more than 8.5%  $W$ . In any case, it is easier to determine onset  $T_g$  for SMP, and this implies a new adjustment of the  $k$  parameter for the Gordon and Taylor equation.

In this paper, the Gordon and Taylor equations for WM and SM will be established based on a minimum amount of data from four well-selected samples: two WMP (A and B) and two SMP (C and D). WMP-A (3.8%  $W$ ), SMP-C (4.0%) and SMP-D (5.1%) were obtained from conventional spray-drying by adapting after-drying fluidised bed parameters. These amorphous powders were canned and stored at room temperature for one month to allow water distribution and  $a_w$  equilibration. WMP-B



**Table I.** Analytical results for selected WMP and SMP.

	Water content W [%]	Total Solids TS [%]	$a_w$ @25 °C	Onset $T_g$ [°C] @5 °C·min <sup>-1</sup>
WMP-A	3.8	96.2	0.24	41
WMP-B	9.8	90.2	0.62	-13
SMP-C	4.0	96.0	0.20	52
SMP-D	5.1	94.9	0.27	39

**Figure 8.**  $T_g$  lines of WM and SM according to the Gordon-Taylor equation.

at 9.8% W was obtained directly from the output of the drying tower with extreme spray-drying conditions and a rapid cooling in liquid nitrogen to keep the powder fully amorphous. This frozen powder was stored at -40 °C for one month, and heated at 20 °C just before analysis. Table I summarises the results of W, TS,  $a_w$  and onset  $T_g$  (2nd scan) according to the reference methods for these four samples.

The first two  $T_g$ (TS) determinations of WMP-A and WMP-B allowed the exact calculation of both  $T_{gm}$  and  $k$  values of the Gordon and Taylor equation for WM. The fitted parameters are:  $T_{gm} = 100.6$  °C and

$k = 8.57$ . This  $T_{gm}$  value agrees with the value of 101 °C given in the literature for pure lactose [8, 9]. In the following sections, we will use the Gordon-Taylor equation for WM with the values  $T_{gm} = 101$  °C and  $k = 8.6$  (Fig. 8). The line for SM was obtained using a similar procedure with the second two  $T_g$ (TS) determinations, fixing  $T_{gm} = 101$  °C and optimising  $k = 6.5$  (Fig. 8). The same  $T_{gm}$  value was used for SM as the protein: lactose ratio of WM and SM are the same. Here the  $k$  value for SM agrees very well with the value of 6.7 obtained by Jouppila and Roos for skim milk powder [2].

### 3.2. The sorption isotherm of whole milk at 25 °C

Most sorption isotherms described in the literature are obtained by equilibrating a spray-dried amorphous powder over saturated salts at a range of RH at a fixed temperature. The  $W$  was either determined after sorption by a reference method, or calculated from weighing the water exchange and using the initial  $W$ . The powders are often equilibrated without recording the kinetics of sorption. In addition, the whole series of powders is supposed to be equilibrated after the same period of time. Then the data are used for fitting a mathematical model such as the Brunauer-Emmet-Teller (BET) or Guggenheim-Andersson-DeBoer (GAB), which is sometimes extrapolated.

However, the glass transition theory and the plasticising effect of water clarify the limits of this procedure:

- For samples with a low  $a_w$ , and especially in the case of desorption,  $T_g$  increases as water is removed from the surface of the particles. The matrix becomes more and more solid and the mobility of the molecules more and more difficult. Therefore, it may take weeks or months for dried particles to equilibrate at  $a_w$  below 0.2.
- For samples with a high  $a_w$ ,  $T_g$  decreases below the sorption temperature as water is adsorbed and diffuses into the matrix. The matrix is more and more rubbery and may collapse, often becoming like syrup. Then phase transitions and chemical reactions may occur rapidly, and the sample does not tend to the expected equilibrium.

The adjustment of the BET or GAB coefficient is very sensitive to such extreme data. In particular, the monolayer water content value ( $W_m$ ) is strongly influenced by non-equilibrated low  $a_w$  data.

Desorption samples may be advantageously obtained by directly spray-drying powders under various drying conditions

and immediately cooling the powders below their  $T_g$ . Those with  $W$  higher than 5% ( $T_g$  below 30 °C) must be frozen. The data may be treated either by the physical BET (2 parameters:  $C$  and  $W_m$ ) or the mathematical GAB (3 parameters) model. The GAB model is more flexible and fits the data better. However, it may diverge for high  $a_w$  values and does not necessarily fit the reality for low TS. Therefore, the physical BET model is preferred here, according to equation (2) with  $W_{db}$  expressed on a dry basis

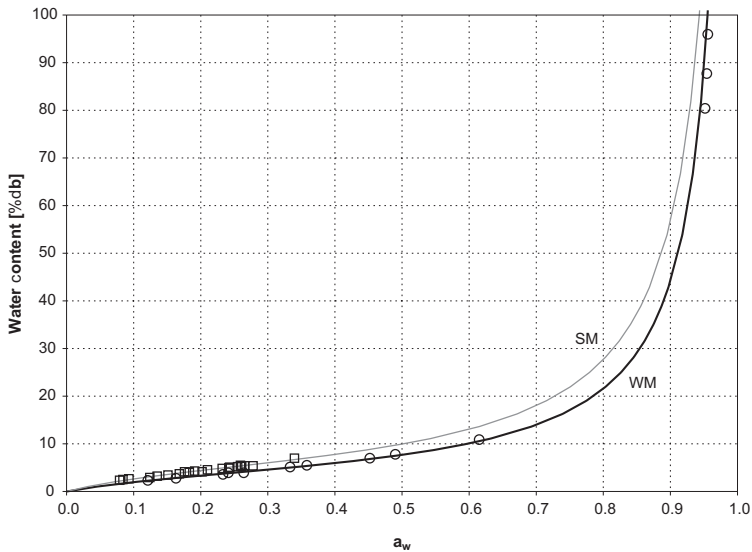
$$W_{db} / W_m = C a_w / [(1 - a_w)(1 - a_w + C a_w)]. \quad (2)$$

We collected such a spray-dried WMP (28% milk fat) up to about 10%  $W$ , as well as concentrated milk with TS between 45 and 55% total solids. The results that will be used for illustrating the procedure, grouped by series (spray-dried and concentrates) are given in Table II.

The BET parameters allow one to fit the low  $W$  values ( $W < 11\%$ ) very well. With  $C = 5.21$  and  $W_m = 4.69\%$  (dry basis), the residual standard deviation between the model and the first ten data points is 0.11%. However, the predicted data for the concentrate are systematically biased. By fitting all the data together the constants become  $C = 6.70$  and  $W_m = 4.28\%$ , but the model fits the low  $W$  data less well, especially the three data points ranged between 0.45 and 0.65  $a_w$ , which were the most difficult to establish (frozen samples which rapidly crystallise at room temperature). A compromise may be obtained by fixing the monolayer at the intermediate value  $W_m = 4.5\%$  and optimising  $C$  using the whole set of data. The best fit for WM is obtained for  $C = 5.79$  and the BET equation now fits all the data rather well, and may be used for the whole range of TS from liquid to solid. This BET desorption line of WM (28% fat) is shown in Figure 9. The BET line for SM (< 1% fat) was obtained by calculating  $W_m$  according to the solid not fat (SNF) and adjusting  $C$

**Table II.** Analytical results for WMP and concentrates.

	aw @25 °C	W ref [%]db	W BET [%]db	BET res [%]	(res/W) <sup>2</sup> [-]
spray-dried	0.121	2.33	2.27	0.06	0.001
spray-dried	0.163	2.79	2.85	-0.06	0.001
spray-dried	0.233	3.58	3.74	-0.16	0.002
spray-dried	0.264	3.94	4.13	-0.19	0.002
s-d & frozen	0.241	3.92	3.84	0.08	0.000
s-d & frozen	0.333	5.12	5.01	0.11	0.000
s-d & frozen	0.358	5.51	5.35	0.16	0.001
s-d & frozen	0.452	7.00	6.79	0.21	0.001
s-d & frozen	0.490	7.79	7.48	0.31	0.002
s-d & frozen	0.615	10.9	10.5	0.35	0.001
concentrate	0.954	87.7	97.6	-9.8	0.013
concentrate	0.956	96.0	100.9	-4.9	0.003
concentrate	0.961	102.9	113.1	-10.2	0.010
concentrate	0.961	111.3	115.3	-4.1	0.001
concentrate	0.964	116.2	125.1	-8.9	0.006
concentrate	0.966	120.6	130.6	-10.0	0.007



**Figure 9.** Desorption isotherm at 25 °C of WM (28% fat) and SM (< 1% fat).

for another series of SMP powders ranged between 0.08 and 0.34  $a_w$ . Thus the BET values for SM are  $W_m = 5.76\%$  and  $C = 6.344$ . The monolayer value of 5.76% for SM is a little higher than the value of 5.47% that can be calculated from the skim milk powder data obtained by Joupilla and Roos [2].

### 3.3. Glass transition and water activity

In a previous paper [12],  $T_g$  of skim, half skim and full cream milk powders versus the powder  $a_w$  measured at 25 °C were presented. It was shown that the relationship was linear in the range of  $a_w$  between 0.1 and 0.3, and a unique  $T_g(a_w)$  line allowed the description of the behaviour of the whole range of fat content, with the same lactose to protein ratio. Moreover, this line was rather similar to the line established for pure amorphous lactose [4] and for spray-dried whey powders with various degrees of lactose pre-crystallised in the alpha hydrate form. It was concluded that the  $a_w$  may be considered as the reference parameter for more generally describing the glass transition of any kind of amorphous

material that only contains lactose (no other low molecular weight carbohydrate). Similarly, a linear behaviour was also found for maltodextrins of various dextrose equivalents in a larger range of  $a_w$  between 0.2 and 0.75.

Now, the  $T_g(a_w)$  relationship of WM may be described over the full  $a_w$  range (0 to 1) by solving the  $T_g(TS)$  Gordon-Taylor relationship (1) and the robust BET description (2) of the sorption isotherm of WM. It may be done by reversing the BET equation in order to express  $a_w$  versus the  $W$  or the  $TS$ , then plotting  $T_g$  and  $a_w$  versus  $TS$ . The  $T_g(a_w)$  relationship of SM may be calculated using the Gordon-Taylor and the BET equations for SM and the same procedure. Both WM and SM related  $T_g(a_w)$  lines are plotted in Figure 10. It can be seen that the lines do not differ significantly.

By analysing the curvature we can see that the  $T_g(a_w)$  relationship is very linear between 0.12 and 0.65  $a_w$  and well predicted by the equation (3):

$$T_g[^\circ\text{C}] = -143.6 a_w + 77.8. \quad (3)$$

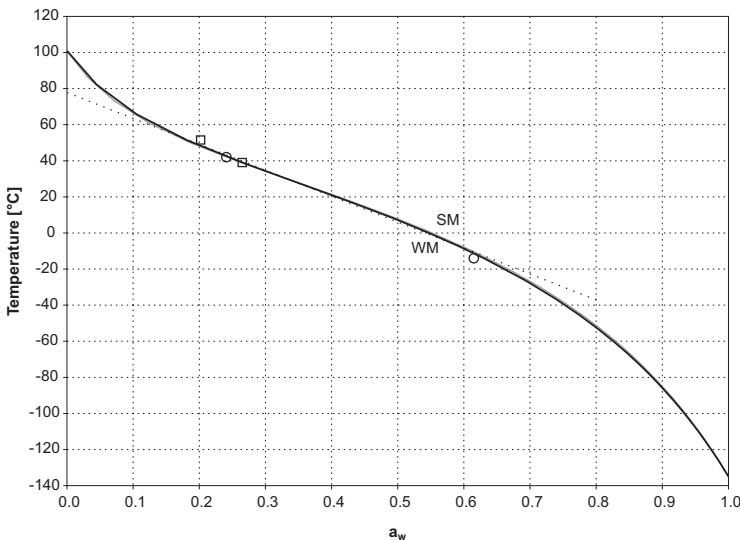
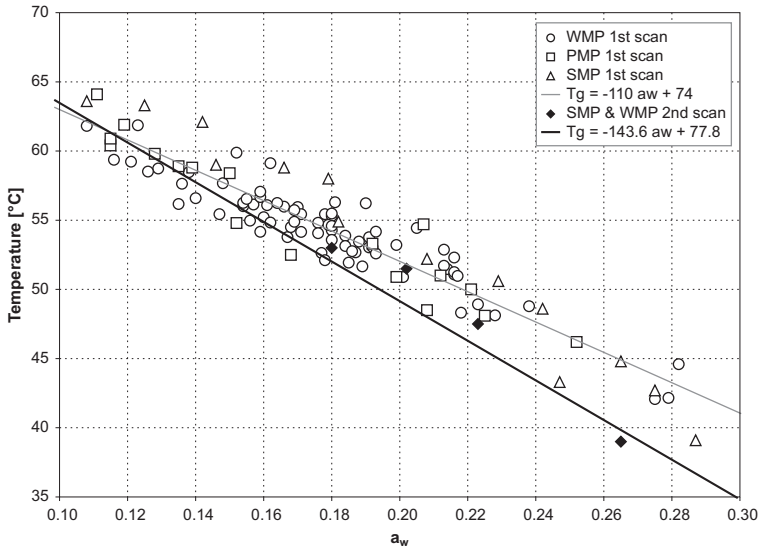


Figure 10. Glass transition versus  $a_w$  (at 25 °C) of milk-based products.



**Figure 11.** Linear  $T_g(a_w)$  behaviour of milk-based powders (1st scan and 2nd scan comparison).

Such a linear behaviour may be compared (see Fig. 11) to data for WMP, partially skimmed milk and SMP powders previously determined by DSC 1st scan at  $5\text{ °C}\cdot\text{min}^{-1}$  [12].

The following linear regression was calculated from these 1st scan data:  $T_g\text{ [°C]} = -110 a_w + 74$ . However, most data above  $0.2 a_w$  resulting from the 1st scan determinations averaged up to  $4\text{ °C}$  above the predicted line using the second scan. Therefore the slope of the linear regression should be lower. This is a typical effect of the relaxation using the onset  $T_g$  determination at the first scan. This very good fit between the new model and the previous data validates both equations (1) and (2) in the low  $a_w$  range between 0.1 and 0.3.

Finally, the full  $T_g(a_w)$  line, including the non-linearity in the very dry and wet regions, may be approximated well by a third degree polynomial:

$$T_g\text{ [°C]}(a_w) = -425 a_w^3 + 545 a_w^2 - 355 a_w + 101. \quad (4)$$

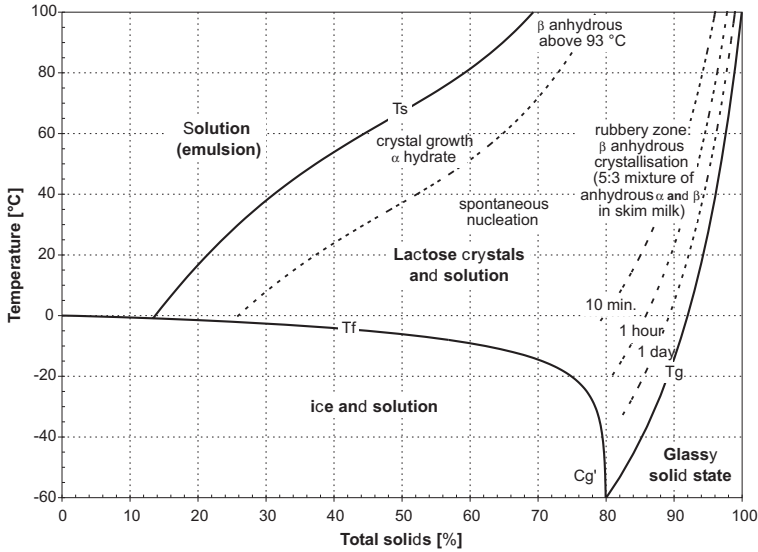
This “universal” equation may be very useful for estimating the  $T_g$  of any kind of milk (powder or concentrate with any fat content and any degree of lactose crystallisation) by determining only the  $a_w$  of the product at  $25\text{ °C}$ .

#### 4. LACTOSE CRYSTALLISATION IN THE RUBBERY REGION

The state diagram approach for WM (that may be adapted to SM), now completed with a robust glass transition line, allows the clarification of the regions (temperature and TS) where risk of lactose crystallisation exists (Fig. 12):

The state diagram may describe two situations where lactose crystallisation occurs:

- Cooling down a concentrate well below the solubility line (at least  $30\text{ °C}$  below) makes spontaneous nucleation of the less soluble form (the alpha monohydrate below  $93\text{ °C}$  and the beta anhydrous from above  $93\text{ °C}$ ) possible.



**Figure 12.** The state diagram of WM (lactose and water phase transitions).

– Heating an amorphous milk powder above the  $T_g$  line provokes lactose crystal nucleation. Here the delay is expected to be  $(T - T_g)$  dependent, and the crystal structure seems to be different for WMP and SMP.

The rubbery region with a high risk of crystallisation ( $TS > 90\%$ ) is shown in Figure 13. An attempt is made to describe the time period of lactose crystallisation (from 3 min to 1 day) using the William-Landel-Ferry (WLF) equation [9].

$$\text{Log } D_{cr} = \text{Log } D_g - C_1(T - T_g) / [C_2 + (T - T_g)] \quad (5)$$

with  $D_g$  expressed in seconds,  $\text{Log } D_g = 10$ ;  $C_1 = 8.93$  and  $C_2 = 14.4$ .

$\text{Log } D_g = 10$  is an arbitrary value. It means a period of crystallisation of  $10^{10}$  seconds (equal to more than 300 years!) at  $T = T_g$ .

The above WLF model was optimised using a pool of WM data (isothermic storage at different temperatures between 30 and 110 °C) and gave very good approximations

of the time period of lactose crystallisation for WM according to the Gordon-Taylor calculation of  $T_g$  based on reliable TS determinations. However, it was surprising to observe different states of crystallisation for SM and WM stored in cans at various temperatures.

#### 4.1. Lactose crystallisation forms in whole milk powders

WMP (2.5 to 4% W) stored under adverse conditions (some weeks at 40 °C or subjected to heat shocks of some hours at temperatures up to 70 °C) always exhibits a large amount of beta anhydrous crystals. This may be checked either by NIR or by capillary gas chromatography (CGC) analysis [14]. Short treatments (less than 1 h) at temperatures up to 100 °C give the same results. For instance, an initially fully amorphous WMP with 3.5% W ( $a_w = 0.24$ ) became very crystallised (and slightly yellow) in less than 1 h at 90 °C (but not at 80 °C): the total beta:alpha ratio increased from 1.32 to 4.2.

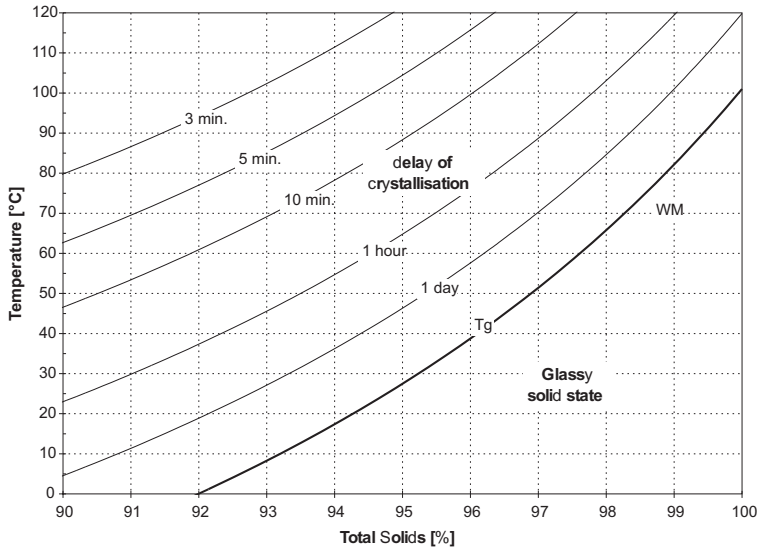


Figure 13. Detail of the dry region of the WM state diagram.

**4.2. Lactose crystallisation forms in skim milk powders**

The state of crystallisation was found to be rather different for SMP. After storing powders with a high W (5 to 6%) at 60 °C for some days, or with a lower W (3 to 4%) at 90 to 110 °C, a mixture of alpha and beta anhydrous crystals was found (detected by NIR and confirmed by CGC). As we can determine the beta/alpha ratio in the initial amorphous powder ( $R_a$ ) as well as in the final treated powder (R) by CGC, it is possible to calculate the degree of lactose crystallisation in any form if the crystalline ratio ( $R_c$ ) is known. The fraction of crystallised lactose  $F_{cr}$  (total of alpha and beta crystallised, referred to as total lactose) may be calculated by the following equation (6):

$$F_{cr} = (R_a - R) (1 + R_c) / [(R_a - R_c) (1 + R)]. \tag{6}$$

SMP with between 4 and 6.5% W and treated for between 30 min and 1 week at

temperatures between 60 and 110 °C was analysed by NIR and CGC. NIR shows crystallisation states, including both alpha and beta forms, but without crystallisation water. Coherent results on the fraction of crystallised lactose between 0 and 50% may be calculated using equation (6) by adjusting the crystalline beta: alpha ratio  $R_c$  to 0.6, which exactly confirms the 5:3 alpha:beta found elsewhere [3].

**5. CONCLUSION**

The  $T_g$  (2nd DSC scan) versus TS relationship may be described by the Gordon-Taylor equation. Simply changing the k value differentiates both WM and SM. The sorption isotherm BET equations were also adapted for WM and SM and may be applied in the whole TS range (0 to 100%). A universal description of  $T_g$  versus  $a_w$  (measured at 25 °C) was obtained. It is very linear between 0.12 and 0.65  $a_w$ . The non-linearity at low and very high TS is well predicted by a 3rd order polynomial.

The phase diagram of milk was therefore adapted to WM or SM. The WLF model allows the prediction of the kinetics of lactose crystallisation (from minutes to days) within the whole rubbery region ( $T_g + 100$  °C). Crystallisation in the beta anhydrous form was induced by subjecting WMP to heat shocks. A mixture of anhydrous alpha and beta lactose was found in SMP.

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