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Relation between a Transition in Molecular Mobility and Collapse Phenomena in Glucose–Water Systems

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In concentrated glucose glasses with water contents between 10 and 30 wt %, an indication for a transition in mobility of the sugar protons above the glass transition temperature is observed, using proton magnetic resonance techniques. The first transition in mobility is positioned at the glass transition temperature while the second is about 20–30 °C higher. The temperature of this second transition is found to depend on water content, resulting in a new line in the state diagram of glucose–water mixtures. In freeze-concentrated glucose glasses we find two similar transitions. We interpret the second transition as the so-called crossover temperature, where the dynamics changes from solid-like to liquid-like. In freeze-concentrated glasses an increase in the amount of ice melting per degree is observed just above the temperature of the second transition. We propose that both in concentrated and freeze-concentrated glucose glasses, this second transition relates to so-called collapse phenomena in glasses.

Introduction

Sugars in foods exist as crystals, in an amorphous state or in solution. The amorphous state of sugars can be formed during cooling from a melt or by rapid removal of the solute from the sugar solution by means of dehydration or the formation of ice. In these processes oversaturated sugar solutions are produced and if the sugar does not crystallize, an amorphous sugar matrix or so-called sugar glass is formed.¹ Bringing the temperature of the sugar glass above its so-called glass transition temperature, the sugar matrix shows macroscopically visible changes in physical properties compared to below the glass transition temperature (T_g). These changes are generally attributed to a reduction in viscosity upon increasing temperature above the glass transition temperature, such that flow on a practical time scale occurs. It is found that the time span that is required for the visible change in physical properties to occur depends on the temperature. In fact, this time span decreases with increasing temperature, above T_g . It is also found that this time span exhibits an abrupt decrease at a specific temperature. This temperature is usually referred to as the collapse temperature.^{2,3} For sugar glasses, collapse temperatures and the concomitant collapse phenomena occur in general 15–25 degrees above T_g .¹

Examples of collapse phenomena include (1) the stickiness and caking of powders; (2) plating of particles on amorphous granules; and (3) structural collapse of freeze-dried materials.⁴

The onset of collapse phenomena is still under debate. For example, collapse phenomena in glasses that are formed due to removal of water from the sugar solution by means of ice formation (i.e., freeze-concentrated glasses) have been related to the so-called onset of ice melting transition which can be observed using differential scanning calorimetry (DSC).^{5,6} This transition is observed in a DSC curve as a shoulder on the ice melting peak. It was suggested⁶ that collapse phenomena in other types of glasses, such as glasses obtained by drying, have the same origin as this onset in ice melting transition in freeze-concentrated systems.

In view of our interest in the onset of the above-described collapse phenomena we studied two types of glucose glasses from a molecular mobility point of view. One type of glass is the so-called freeze-concentrated glass, and the other type is obtained by cooling from the melt (i.e., concentrated glass). Specifically, we determined the molecular mobility of sugar and water using a proton nuclear magnetic resonance (¹H NMR) technique.^{7,8} In the freeze-concentrated glucose glasses we also used this technique to determine the glucose concentration in the solution phase during ice melting. In both types of glasses we observe a transition in molecular mobility at a temperature situated above the glass transition temperature and we propose that this transition in molecular mobility is related to the origin of collapse in both types of glucose glasses.

Materials and Methods

Preparation of Samples. Sugar glasses were prepared in two ways. (1) *Concentrated* glucose–water glasses were prepared by mixing the appropriate amounts of sugar and water, melting the mixture, and quickly cooling it below the glass transition temperature. Concentrated glasses prepared this way were compared with concentrated glasses prepared by freeze-drying and because no differences were found we used only glasses

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prepared from the melt. (2) *Freeze-concentrated* glucose glasses were prepared by freeze-concentrating a sugar solution along the following route. Upon cooling 20 wt % solutions of sugars, ice is formed. Due to this freezing out of water, the sugar concentration in the solution phase increases up to approximately 80 wt %. Upon further cooling, an 80 wt % sugar glass is formed. In this particular case of freeze-concentrated glucose glasses, the resulting material is heterogeneous as it contains small ice crystals dispersed in a sugar glass. This is in contrast to the concentrated glucose glasses under (1), which are homogeneous materials. Anhydrous glucose was obtained from Jansen Chimica, and glucose monohydrate from Merck. Glucose with deuterated hydroxyl groups was prepared by dissolving the monohydrate (1 g) in D₂O (5 mL) and subsequently freeze-drying before adjusting the water content with D₂O. For the NMR samples, appropriate amounts of sugar and water were mixed in 5 mm NMR tubes and sealed to prevent water evaporation.

¹H NMR Spectroscopy. ¹H NMR measurements were performed on a Bruker AMX 300 spectrometer equipped with a Bruker 5 mm proton probe operating at a resonance frequency of 300.13 MHz. The temperature was regulated with a nitrogen temperature controller. In this way, the temperature stability was within ± 0.5 K. A spectral width of 500 kHz was used. The duration of the 90° pulse was 4.5 μ s. The free induction decays (FID) are averages of 4–256 scans having 2048 data points. Using a repetition time of 10 s, the signal of ice is saturated. We estimate that the signal of ice contributes less than 15% to total amplitude of the FID by comparing the signal of ice (without sugar) with the signal of the freeze-concentrated glasses.

The NMR spectrum of the immobile proton fraction is assumed to be a rectangular line shape with a total width $2b$, convoluted with a Gaussian line shape with a standard deviation given by parameter a .^{9,10} Superimposed on this rectangular line shape is a Lorentzian line shape arising from the mobile protons. For the analysis of the NMR, the FIDs $F(t)$ were fitted by the following equation:⁸

$$F(t) = A \exp\left[\frac{-a^2 t^2}{2}\right] \frac{\sin bt}{bt} + B \exp\left[\frac{-t}{T_{2m}}\right] \quad (1)$$

where A and B denote the amplitudes originating from immobile and mobile protons, respectively, and T_{2m} is the spin–spin relaxation time of the mobile proton fraction. The lower limiting value of T_{2m} is 2×10^{-5} s, which is about $2b$,⁸ and corresponds to an upper limit of the rotation correlation time τ_R of 3×10^{-6} s calculated using the Bloembergen–Purcell–Pound theory.⁹ T_{2m} is proportional to τ_R if $1/\tau_R \ll$ than the Larmor frequency.⁹ Protons with τ_R values of 3×10^{-6} s will be called immobile. Upon decreasing temperatures, the values of T_{2m} and B decrease. However, if the T_{2m} value obtained by fitting to eq 1 becomes smaller than 2×10^{-5} s, which indicates that there is no longer a mobile proton fraction, the data are fitted to the first part of eq 1 only. The NMR signal arising from the ring and exocyclic protons in deuterated glucose samples is also fitted to the first part of eq 1. On increasing the temperature, the dipolar interactions start to average out and the broad component sharpens up. As long as the FIDs show oscillations, characteristic for the rectangular line shape of the immobile proton fraction, they are well-fitted with eq 1. Finally, the oscillatory character of the FID is lost and then the FIDs are fitted to a biexponential function.

The second moment (M_2) is calculated using $M_2 = a^2 + 1/3b^2$ where a and b are determined from fitting the FID with eq 1.⁹

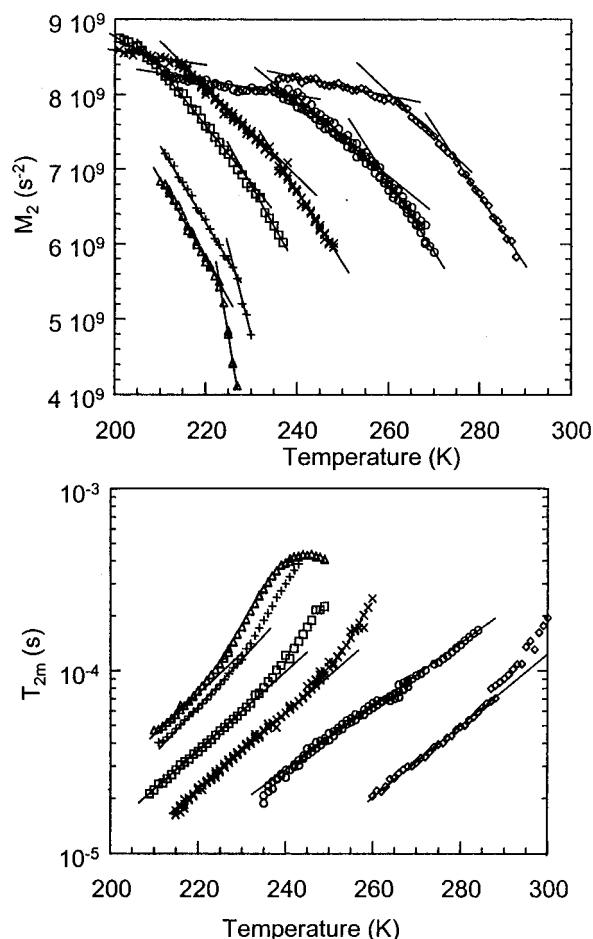


Figure 1. The second moment (M_2) of the immobile protons (Figure 1A) and the spin–spin relaxation time (T_{2m}) of the mobile protons (Figure 1B) versus temperature for 70 (Δ), 73 ($+$), 75 (\square), 80 (\times), 85 (\circ), and 90 wt % (\diamond) glucose solutions.

M_2 of the immobile protons is a measure of incompletely averaged dipolar interactions.^{8,10} In the analysis of M_2 of the immobile protons, the following points should be taken into account.⁸ A reduction of M_2 takes place if (1) the proton density is lowered (since the dipolar interactions decrease with the sixth power of the proton–proton distance), and/or if (2) anisotropic motions or very slow isotropic rotations increase, since both partly average out the dipolar interactions.

DSC. Samples with a weight between 10 and 20 mg were measured using a Pyris 1 DSC (Perkin–Elmer) at a cooling and heating rate of 80 and 10 K/min, respectively. The samples are always cooled to 190 K before reheating, until the temperature of annealing. After annealing, all samples are cooled to 190 K, which is the starting temperature for the heating scan, except for the ones annealed at 180 K. From the heating scans the onset of the glass transition T_g' and of the onset of ice melting (T_m') are determined.

Results

Concentrated Glucose–Water Mixtures. Upon warming concentrated glucose glasses with water contents between 10 and 30 wt %, we find indications for two transitions as observed in the slope of the second moment (M_2) of the immobile protons against temperature (Figure 1A). The first transition occurs at the glass transition temperature (T_g) (see Figure 2) and the second transition is observed at $T = T_{tr2}$ where T_{tr2} is 20–30 °C higher than T_g . Note that in solutions with a glucose content

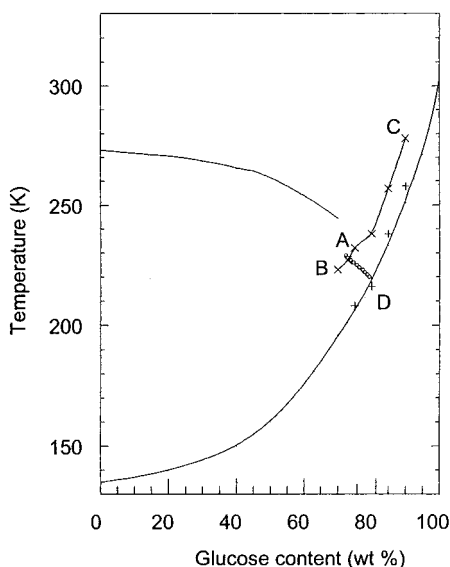


Figure 2. State diagram of glucose. The freezing point depression data are taken from Luyet²⁵ and Young.²⁶ The glass transition data are taken from Noel et al.¹² Line BAC represents the T_{ir2} temperature. Point D is T_g' of glucose.

of 70 and 73 wt %, T_g is too low to be measured and only T_{ir2} is observed. The indication for the second transition is also apparent as an increase in the slope of the spin–spin relaxation time (T_{2m}) against temperature (Figure 1B). Note that the glass transition will not appear in Figure 1B since there are too few mobile protons at T_g . The temperatures of the indicative second transition as a function of water content define the line BAC in the state diagram (Figure 2).

To exclude the possibility that the second transition in M_2 may be due to the fact that the fraction of immobile protons decreases we used partly deuterated glucose samples (such that all exchangeable protons are deuterated), ensuring that all protons would remain immobile in the temperature range studied. The same two transitions were observed (data not shown), leading to the conclusion that the second transition is related to changes in mobility of the immobile protons.

Freeze-Concentrated Glucose–Water Mixtures. In freeze-concentrated glucose glasses we also obtained two transitions in M_2 as a function of the temperature, similar to the ones as observed in concentrated glasses. The interpretation of these transitions in freeze-concentrated is, however, more elaborate than it is for concentrated glasses. Namely, the transitions in freeze-concentrated glasses could also be related to changes in the ice melting process, such as the rate of ice melting or the amount of ice that melts.

To exclude these possibilities we first studied the influence of the ice melting process on the molecular mobility. To avoid effects of delayed ice formation in the temperature range of interest we first identified the conditions to obtain freeze-concentrated glasses that are maximally concentrated. Subsequently, these maximally freeze-concentrated glasses were used to study the ice melting process. Finally, all these findings allow us to draw conclusions about the nature of the second transition.

First, the conditions to obtain freeze-concentrated glasses were investigated as follows. The process of freeze concentration was studied using DSC, following the annealing protocols of Ablett.¹¹ In the inset of Figure 3A, DSC heating traces of a freeze-concentrated glucose glass are shown as a function of temperature. The temperature range between 195 and 245 K is enlarged to show temperature shifts of the glass transition

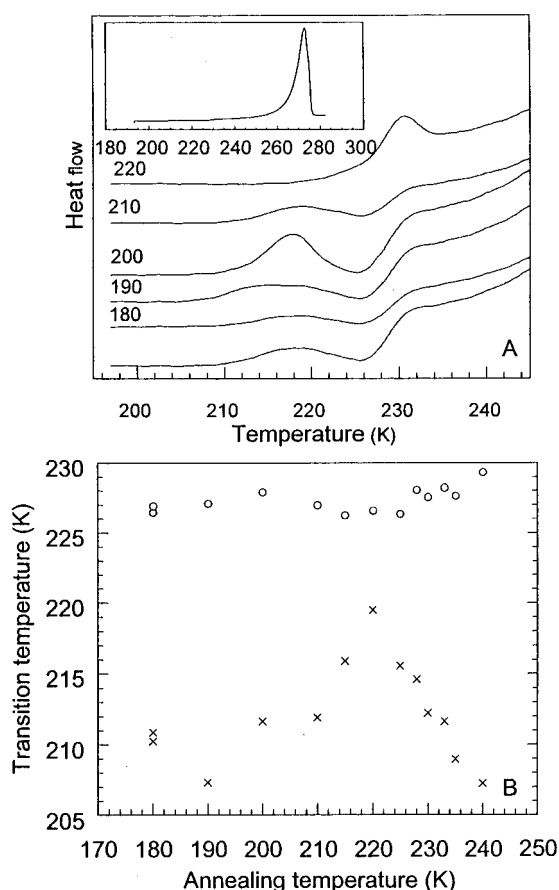


Figure 3. The inset of Figure 3A shows a DSC scan of 20 wt % glucose. For the samples annealed at temperatures indicated at each scan the temperature range from 195 to 245 K is enlarged, to show the effect of annealing on the transition temperatures. The scan without temperature is not annealed. In Figure 3B the onset temperatures of the glass transition (T_g') (x) and the second transition (T_{ir2}) (o) are shown as a function of annealing temperature.

temperature as a function of the annealing temperature (Figure 3A). In the DSC heating traces of freeze-concentrated glucose between 195 and 245 K two thermal transitions are observed, first the glass transition temperature, denoted by T_g' , and secondly, a second transition temperature $T_{m'}$, where the prime refers to the fact that the glass is freeze-concentrated. The onset temperatures of these transitions are shown in Figure 3B as a function of the annealing temperature.

A quench-cooled glucose glass has a T_g value of 210 K, and annealing above 210 K leads to ice formation. Formation of ice increases the glucose concentration and thus increases the glass transition temperature (Figure 3B). The maximum glass transition temperature occurs at 220 K. Taking into account that a T_g' value of 220 K corresponds to the T_g value of a concentrated 81 wt % glucose–water glass,¹² we deduce that the maximum freeze concentration should be 81 wt %. We note that Figure 3B also shows annealing temperatures below 210 K. If the glass is annealed below 210 K, overshoot peaks are observed at the glass transition temperature. This is, for example, clearly visible for an annealing temperature at 200 K (cf., Figure 3A). This overshoot slightly decreases the T_g' onset value. Therefore the decreases in T_g' at annealing temperatures below 210 K are artifacts, due to aging of the glass.

We note that the process of freeze concentration during annealing as studied by DSC could in principle also be followed by ¹H NMR (since the water mobility is decreased during this process, implying a decrease in the spin–spin relaxation time,

T_{2m} . However, the maximum cooling rate in a NMR experiment is relatively low, which causes the process of freeze concentration to be always completed during cooling. Therefore the resulting T_{2m} values as a function of annealing temperature remain constant (data not shown).

Using the findings above we concluded for our NMR experiments that annealing for 1 h at 220 K yielded maximally freeze-concentrated glucose glasses. These freeze-concentrated glucose glasses were subsequently used to study the influence of the ice melting process on the second transition.

The influence of the ice melting process on the molecular mobility in freeze-concentrated glucose glasses was studied by means of determining M_2 , T_{2m} , and the amount of mobile protons (B) as a function of temperature. The results are shown in Figure 4A, B, C, respectively. Immediately above the glass transition (220 K), ice starts to melt. This is observed as an increase in the amount of the mobile protons, which is due to an increase of the amount of water (Figure 4C). Around 235 K an increase in the amount of ice melting per degree is observed as an increase in the derivative of B toward temperature (Figure 4C). This increase in the amount of ice melted per degree will be referred to as an increase in the ice melting rate.

The mobility of the glucose protons shows indications for two transitions exhibited by abrupt changes in the temperature dependence of M_2 (Figure 4A). The first transition corresponds to the glass transition around 220 K as was observed with DSC for freeze-concentrated glucose glasses (Figure 3B). The temperature of the first transition is slightly influenced by the heating rate of the experiment (as expected for a glass transition). At 230 K, a second transition in the mobility of the solid protons is observed (Figure 4A). Note that at temperatures above the second transition the solid protons become so mobile that they belong to the mobile fraction and no longer are characterized by M_2 . Therefore only one data point of M_2 is reported above 230 K. The fact that the sugar protons become mobile within one degree indicates that the change in mobility at T_{ir2} is very abrupt.

T_{2m} above 220 K ($= T_g'$) shows a stronger increase with temperature in a freeze-concentrated glass than in an 80 wt % glucose solution (Figure 4B). This implies that the mobility of the water protons increases (due to ice melting). Namely, T_{2m} around T_g' is indicative for water rotational mobility because at T_g' all mobile protons are water protons. This follows from the fact that around T_g' the ratio of amplitudes of the mobile (B) and immobile (A) component in the FID (B/A) is smaller than the theoretical B/A value in the case of all water protons being mobile and all sugar protons being immobile in an 80 wt % system.⁸ Around 230 K, where the solid protons undergo a second transition (Figure 4A), the mobility of the mobile protons also increases, which follows from the increase in slope of T_{2m} against temperature (Figure 4B). T_{2m} no longer increases around 240 K, probably because the ring protons of glucose start to contribute to the mobile proton signal.

To interpret the above-described transitions in M_2 and T_{2m} in freeze-concentrated glasses similar to the transitions in concentrated glasses, we should exclude the possibility that an abrupt increase in ice melting rate would cause the second transition. Inspired by the idea of Franks that ice dissolution would be kinetically hindered just above T_g ⁶ and therefore would be dependent on the heating rate, we studied the water mobility and magnitude of the mobile fraction as a function of heating rate (Figure 4B,C). The highest heating rate in the NMR experiments is 0.6 K/min, which is 1 order of magnitude smaller than in the DSC experiments where the heating rate equals 10

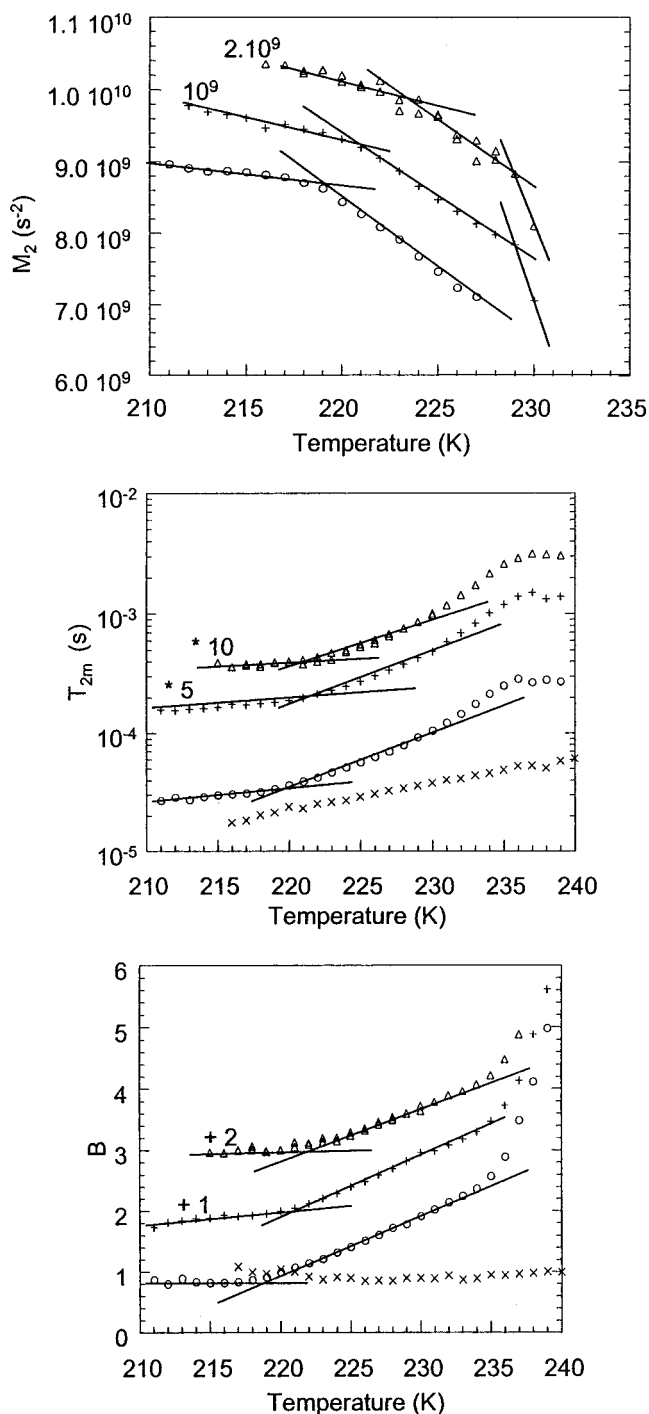


Figure 4. The second moment (M_2) of the immobile protons (Figure 4A), the spin–spin relaxation time (T_{2m}) of the mobile protons (Figure 4B), and the amplitude (B) of the mobile protons (Figure 4C) versus temperature for maximally freeze-concentrated glucose solutions heated with a rate of 100 (Δ), 380 ($+$), and 3600 (o) s per degree and for a 80 wt % glucose glass (x) heated with a rate of 100 s per degree. The amplitudes (B) are divided by the amplitude at 220 K to scale the results. The results in Figure 4A,B,C are shifted for clarity.

K/min. The lowest heating rate is 0.023 K/min (i.e., 1 K/h). This time scale of 1 K/h lies in the same range as that of ice formation and ice melting during annealing, as observed with DSC. We make two observations. (1) Both transitions, T_g' and T_{ir2} , are observed separately for various heating rates (Figure 4A,B). (2) From Figure 4C it follows that the slope of B versus T , indicative of increase of the mobile fraction, and thus of rate of ice melting, is independent of heating rate, between 220 and

235 K. Note that there is a slight decrease in T_g' with decreasing heating rate (as expected). These two observations lead us to conclusion that the second transition is not caused by a change in ice melting rate.

The state diagram of glucose around the intersection point of the freezing point depression line and the glass transition temperature line (Figure 2) was constructed as follows. The concentration of glucose at temperatures between 220 and 230 K is calculated from the amount of ice melted (this in turn can be calculated from the increase in amplitude B (Figure 4C)). For example, at 220 K where the sample is a 81 wt % glass, it is known what the value of B/A should be if all water protons are mobile and all sugar protons are immobile. This ratio is 0.39. The measured value of B/A , however, is 0.2 (data not shown). The percentage of mobile water protons turns out to be 60%. Taking a starting sample consisting of 20 g of glucose and 80 g of water, the resulting freeze-concentrated sample will consist of 20 g of glucose, 5.2 g of water, and 74.8 g of ice (using a glucose concentration of 81 wt %). The amplitude B at 220 K will be caused by $0.6 \times 5.2 \text{ g} = 3.1 \text{ g}$ of water. At 230 K, the signal B is 1.9 times larger. Thus, 2.8 g of ice has melted during heating from 220 to 230 K. The solution concentration is calculated to be 72 wt %.

This value for the glucose concentration can also be determined from values for T_{2m} by comparing the values of T_{2m} in freeze-concentrated glucose at 230 K with the T_{2m} values in concentrated glucose solutions at 230 K (Figure 1B). This yields a concentration of glucose of 73 wt %. Thus, the values of the glucose concentration at 220 and 230 K are 81 and 73 wt %, denoted by A and D in the state diagram, respectively (Figure 2). The low rate of ice melting between 220 and 230 K, which causes a linear increase in B , leads to the line AD in the state diagram (Figure 2).

Discussion

In this paper we have determined the molecular mobility in sugar–water systems in the temperature range around the glass transition temperature (T_g). Two types of glucose glasses have been investigated: (1) concentrated glucose glasses (prepared by mixing the appropriate amount of sugar and water, melting, and subsequently cooling below T_g), and (2) freeze-concentrated glucose glasses (prepared by cooling a 20 wt % glucose solution; due to ice formation during cooling, ultimately an 80 wt % glucose glass is formed). We will first discuss the results according to the division into these two types. Then we will discuss the similarity between the two types of glasses.

Concentrated Glucose–Water Mixtures. By using ^1H NMR, indications for two transitions in the mobility of the glucose protons in glucose glasses with a water content between 10 and 30 wt % have been observed. We propose that the second transition temperature may be identified as the so-called crossover temperature, where the dynamics of the system changes from liquid-like to solid-like upon cooling. This proposition is based on the following suggestive description on how the dynamics of a glass system may be related to changes in M_2 .

Below T_g , M_2 is only influenced by small angular anisotropic motion of the protons (i.e., β relaxation processes). Since the angle and rate of these anisotropic motions increases slightly with temperature below T_g ,¹³ the dipolar interactions will be averaged out, resulting in a decrease of M_2 with increasing temperature, below T_g . Above T_g , both diffusional motion (α relaxation) and small angular anisotropic motion (β relaxation) will partly average the dipolar interactions. This results in a

stronger decrease of M_2 with temperature above compared to below T_g . Therefore the glass transition is observed as the first change in the temperature dependence of M_2 . At the glass transition temperature all protons still belong to the immobile fraction. Since the activation energy of the β relaxation is 10-fold smaller than of the α relaxation,¹² the α and β relaxation processes will merge at some temperature upon heating above T_g .¹² The crossover temperature is characterized by the merging of the α relaxation and the slow β relaxation process.^{14,15} This is indeed observed as the second change in the temperature dependence of M_2 (at T_{tr2}). Above the crossover temperature diffusional motion dominates the liquid dynamics, leading to α relaxation. As long as the rotational motion has a τ_R value $> 3 \times 10^{-6} \text{ s}$ the dipolar interactions are not completely averaged out in the time scale of the NMR experiment and the motion is characterized by M_2 .

We add that we observed that at T_{tr2} the first sugar protons become mobile, corresponding to a $\tau_R > 3 \times 10^{-6} \text{ s}$. This may also indicate that the second transition signifies the crossover temperature. Namely, in general, the time scale associated with crossover temperatures lies between 10^{-8} s and 10^{-6} s .^{14,16,17} Our τ_R value is in the same range as observed at the crossover temperature in other glass formers such as sorbitol,^{18,19} polybutadiene,¹⁶ and *o*-terphenyl.¹⁶ We note that in a deuterium NMR study of 75 wt % glucose solutions a bifurcation of the α and β relaxation is shown around 240 K.²⁰ This is at a slightly higher temperature than the T_{tr2} transition we observe at 230 K (Figure 1A). The discrepancy may be due to uncertainties in the glucose concentration due to the presence of a small amount of ice.²⁰

Taking into account the above-described view on transitions in the dynamics of glass systems we may also relate the abrupt increase in mobility of the sugar at T_{tr2} to so-called collapse phenomena as follows. In general, collapse is attributed to a decrease in viscosity above T_g until a value of 10^8 Pa s , where flow on practical time scales is observed. This phenomena is usually observed as something that occurs suddenly. We suggest that an underlying transition in molecular mobility causes this sudden change in flow and that this transition occurs at $T = T_{tr2}$. We note that it was already shown for a number of glass formers that the temperature dependence of the viscosity changes at the crossover temperature.²¹ Furthermore, in bending experiments, also two transitions were observed for the loss and storage moduli as a function of temperature,^{22,23} one at T_g (where the storage modulus decreases slightly above T_g) and a second transition 15° above T_g (showing a stronger decrease in the storage modulus) This latter (second) transition was also related to collapse.²³

In short, we find indications for a transition in molecular mobility in concentrated glucose–water mixtures above T_g and propose that this transition can be interpreted as a crossover temperature, where the dynamics changes from solid like to liquid like. The temperature of T_{tr2} depends on water content, resulting in an extra line B–A–C in the state diagram (Figure 2). We suggest that the second transition in molecular mobility, above T_g , is the underlying cause of collapse phenomena in concentrated glucose–water glasses.

Freeze-Concentrated Glucose–Water Mixtures. Two transitions in molecular mobility are observed as changes in the derivatives of M_2 and T_{2m} with temperature (Figure 4A,B). Also the amount of mobile protons as a function of temperature shows two transitions (Figure 4C). The first transition occurs at the glass transition temperature and the second transition at 230 K. Both transitions are not affected by heating rate. Furthermore, the increase in the amount of mobile protons, indicative of the

amount of ice melting per degree, is not affected by the heating rate (slope of B versus T in Figure 4 C). This leads us to the conclusion that the second transition is not caused by a change in ice melting rate. The second transition is also not related to the onset of ice melting, since the amount of water in our experiments was found to increase immediately at the glass transition temperature, and not at a higher temperature.

We note that using DSC measurements, also two transitions can be observed. One at T_g' ($=220$ K) and the other at 227 K (Figure 3 B). It was suggested that the second transition is due the fact that ice melting would be kinetically hindered above T_g' .^{6,11,24} This, in turn, was proposed to be related to the fact that mixing of the meltwater with the glucose solution that is surrounding the ice crystals would be hindered by the high viscosity of the glucose solution. The second transition would then signify the transition from kinetically hindered to normal equilibrium ice melting.⁶ This reasoning would imply that at extremely low heating rates, where the diffusion of the melted ice into the sugar matrix would not be hindered, this second transition would have to coincide with T_g' .^{6,11,24} Our molecular mobility data suggest a different explanation for the occurrence of two transitions since they show that at lower heating rates both transition temperatures do not coincide. Hence, the second transition is not coupled to the onset of ice melting nor to the rate of ice melting within the temperature range between 220 and 230 K.

Similarities between Freeze-Concentrated and Concentrated Sugar Glasses. We propose that, analogous to concentrated sugar–water mixtures, the second transition in M_2 signifies the crossover temperature of the concentrated glucose–water mixture surrounding the ice where the dynamics of the glucose–water mixture changes from solid-like to liquid-like.

Although in concentrated glucose glasses the second transition occurs 20 – 30 degrees above T_g while in freeze-concentrated solutions a temperature difference of only 10° is observed, we propose that the origin of the second transition is the same in both systems. Namely, in freeze-concentrated glasses ice starts to melt immediately above T_g' , which decreases the glucose concentration and which thus leads to a lower second transition temperature.

This difference between the two systems can be explained quantitatively as follows. The glucose concentration in the freeze-concentrated phase at the second transition temperature, $T_{tr2} = 230$ K, is calculated to be 72 wt % (as obtained from the amplitude of the mobile component (Figure 4C)). This value for a freeze-concentrated system corresponds well to the value of 74 wt % at the crossover temperature of 230 K in a concentrated system (as determined from the line BAC in the state diagram). Hence the second transition temperature in a freeze-concentrated glucose systems is equal to the crossover temperature in a concentrated glucose system provided that its glucose concentration equals the concentration of glucose in the freeze-concentrated system at this temperature.

Thus the second transition in a concentrated system is similar to the second transition in a freeze-concentrated system.

In concentrated systems, the occurrence of a crossover temperature has been proposed in a previous section to form the underlying cause of collapse phenomena in concentrated glucose–water glasses. Taking into account our conclusion that the second transition in a concentrated system (i.e., crossover temperature) must be similar to the second transition in a freeze-concentrated system, we propose that this second transition in freeze-concentrated systems is related to collapse phenomena in these systems. This is observed as an increase in rate of ice

melting (Figure 4C). Furthermore, the modulus in freeze-concentrated glasses obtained in bending tests also decreases in two steps.^{22,23}

The state diagram of glucose water mixtures, as shown in Figure 2, summarizes all results. A maximally freeze-concentrated glucose–water glass (81 wt %) undergoes a glass transition at 220 K, i.e., point D in Figure 2. Immediately above T_g' ice starts to melt slowly and this corresponds to a steep freezing point depression line (line DA in Figure 2). At a temperature of 230 K, the line BAC, representing the crossover temperature line, crosses the freezing point depression line at point A. This implies that the molecular mobility in the glucose–water mixture progressively increases. This is accompanied by an increase in the amount of ice melting per degree (cf., Figure 4C). We first note that the line DA and the literature freezing point depression line (Figure 2), as obtained from DSC measurements do not connect since we cannot calculate the glucose concentration between 60 and 75 wt %. We note furthermore that the extrapolation of line DA does not connect with the freezing point depression line as obtained from DSC (i.e. literature freezing point depression line). This can be explained by taking into account that the literature freezing point depression line represents the peak temperatures of the melting process observed in the DSC curves²⁵ while the NMR line represents the ice melting process which starts immediately above T_g' , i.e., at a temperature below the peak temperature in the DSC curve. Thus, during the NMR experiments some ice already has melted before the peak temperature in the DSC experiments is reached. Therefore the peak temperature in the DSC experiment relates to the onset of ice melting temperature, as obtained by NMR, but at a concentration of glucose which is lower than the concentration of initial glucose. Hence, the literature freezing point depression line should be shifted to the left in order to be compared to the line DA as obtained from NMR.

Conclusion

An indication for a second transition in proton mobility is observed, above the glass transition temperature, which is interpreted as the crossover temperature. We propose that this second transition is the origin of collapse phenomena in both concentrated and freeze-concentrated sugar glasses, thereby marking their limit of mechanical stability.

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References and Notes

- (1) Roos, Y. *Phase Transitions in Foods*; Academic Press: San Diego, 1995.
- (2) Flink, J. M. In *Physical Properties of Foods*; Peleg, M., Bageley, E. B., Eds.; AVI publishing Co. Inc.: Westport, Ct, 1983; pp 473–521.
- (3) Tsourouflis, S.; Flink, J. M.; Karel, M. *J. Sci. Food Agric.* **1976**, *27*, 509–519.
- (4) Levine, H.; Slade, L. *Cryo-Lett.* **1988**, *9*, 21–63.
- (5) MacKenzie, A. P. *Philos. Trans. R. Soc. London* **1977**, *B*, 167–189.
- (6) Shalaev, E. Y.; Franks, F. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1511–1517.
- (7) Ablett, S.; Izzard, M. J.; Lillford, P. J.; Arvanitoyannis, I.; Blanshard, J. M. V. *Carbohydr. Res.* **1993**, *246*, 13–22.
- (8) van den Dries, I. J.; van Dusschoten, D.; Hemminga, M. A. *J. Phys. Chem.* **1998**, *102*, 10483–10489.
- (9) Abragam, A. *The principles of nuclear magnetism*; Clarendon Press: Oxford, 1961.

- (10) McBrierty, V. J.; Packer, K. J. *Nuclear magnetic resonance in solid polymers*; Cambridge University Press: Cambridge, 1995.
- (11) Ablett, S.; Izzard, M. J.; Lillford, P. J. *J. Chem. Soc. Faraday Trans.* **1992**, 88, 789–794.
- (12) Noel, T. R.; Parker, R.; Ring, S. G. *Carbohydr. Res.* **1996**, 282, 193–206.
- (13) Schnauss, W.; Fujara, F.; Sillescu, H. *J. Chem. Phys.* **1992**, 97, 1378–1389.
- (14) Sokolov, A. P. *Endeavour* **1997**, 21, 109–113.
- (15) Rössler, E.; Warschewske, U.; Eiermann, P.; Sokolov, A. P.; Quitmann, D. *J. Non-Cryst. Solids* **1994**, 172, 113–125.
- (16) Rössler, E.; Tauchert, J.; Eiermann, P. *J. Phys. Chem.* **1994**, 98, 8173–8180.
- (17) Sokolov, A. P. *J. Non-Cryst. Solids* **1998**, 235, 190–195.
- (18) Wagner, H.; Richert, R. *J. Non-Cryst. Solids* **1998**, 242, 19–24.
- (19) Wagner, H.; Richert, R. *J. Phys. Chem. B* **1999**, 103, 4071–4077.
- (20) Moran, G. R.; Jeffrey, K. R. *J. Chem. Phys.* **1999**, 110, 3472–3483.
- (21) Rossler, E.; Hess, K. U.; Novikov, V. N. *J. Non-Cryst. Solids* **1998**, 223, 207–222.
- (22) MacInnes, W. M. Dynamical Mechanical Thermal analysis of sucrose solutions. In *The glassy state in foods*; Blanshard, J. M. V., Lillford, P. J., Eds.; Nottingham University Press: Nottingham, 1993; pp 223–248.
- (23) MacInnes, W. M. “2nd year report of the FAIRCT961085 project Molecular Mobility in Foods,” 1999.
- (24) Roos, Y.; Karel, M. *Int. J. Food Sci. Technol.* **1991**, 26, 553–566.
- (25) Luyet, B.; Rasmussen, D. *Biodynamica* **1968**, 10, 167–191.
- (26) Young, F. E. *J. Phys. Chem.* **1957**, 61, 616.