Molecular dynamics in concentrated sugar solutions and glasses: an NMR field cycling study

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Molecular dynamics in concentrated sugar solutions and glasses: an NMR field cycling study

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The frequency dependence of the proton longitudinal relaxation time in concentrated sugar in water solutions and glasses is compared with various theoretical models and used to derive correlation times characterizing the dynamic state of the water and sugar. It is shown that the water retains a high degree of molecular mobility even in the 'sugar glass', while the spectral density of the 3-dimensional glass lattice shows no evidence for a distribution of correlation times.

1. Introduction

Sugar–water glasses are systems of great interest as potential encapsulating matrices for flavours and pharmaceutical products. A major limitation is their instability to slow changes whereby moisture uptake raises the glass transition temperature \( T_g \) above the storage temperature, leading to sugar crystallization. At temperatures above \( T_g \) there can also be collapse phenomena in which the sugar matrix undergoes a transition from solid-like to liquid-like mobility, resulting in flow on a practical timescale [1]. This is the probable origin of structural collapse in freeze-dried materials [2, 3] and stickiness and caking of powders. It is therefore important to understand the relationship between the molecular mobility of the constituent water and sugars and the moisture content and temperature above and below the glass transition temperature.

Although the reorientational motion of the sugar component is believed to be immeasurably slow below the glass transition temperature, this is not the case with the low molecular weight water component. Our earlier exploratory multinuclear NMR cross-relaxation studies of water dynamics in 10% maltose glasses confirmed that water retains a high degree of translational and rotational mobility, although reliable molecular correlation times could only be estimated with those techniques [4]. It is also obvious that, although the sugar matrix may be orientationally 'frozen' below the glass transition temperature, there are still other modes of motion to be considered, including the vibrational (phonon) modes of the 3-dimensional sugar lattice, plus the internal rotational modes of any sugar side chains. In amorphous glassy matrices there might also be a distribution of motional correlation times resulting from a distribution of local molecular environments. It is therefore important to understand how the more mobile water component affects these other low frequency modes of the sugar lattice and how these are related to \( T_g \), and the collapse phenomenon.

Finding suitable techniques to investigate these questions presents a continuing challenge. Several conventional macroscopic techniques have been applied to the problem, including low frequency mechanical spectroscopy, medium and high frequency dielectric spectroscopy and viscosity measurements [5]. These data are usually interpreted with linear response theory but, unfortunately, the relationship between the macroscopic response and the molecular and microscopic processes underlying it is far from trivial. The usual approach is to define various 'relaxation times', such as those for the so-called \( \alpha \) and \( \beta \) relaxation processes, and attempt to relate them to molecular properties [6]. Fortunately, NMR provides a far more direct handle on molecular motions in these systems. 2-Dimensional deuterium NMR has been used to probe the reorientational dynamics of glucose in glucose–water solutions just above the glass transition temperature [7]. Our earlier work using water oxygen-17 (\( \text{H}_2^{17}\text{O} \)) and deuterium (\( \text{D}_2\text{O} \)) relaxation measurements focused on the water dynamics in a saturated sucrose solution, and succeeded in measuring water reorientational correlation times in this system at 298 K, well above \( T_g \) [8, 9]. Unfortunately these multinuclear measurements could not be extended into the glassy state because the deuterium and oxygen-17 relaxation times became immeasurably short. It was
concluded that fast field cycling measurements of the frequency dispersion in the proton longitudinal relaxation time would probably be the method of choice for studying molecular dynamics in the glassy state, and this is the subject of the present paper. Attempts to extend these field cycling measurements using deuterium (or oxygen-17) NMR in sucrose solutions made up in D2O or H218O have, so far, failed due to the poor signal-to-noise at the low measurement frequencies available.

2. Experimental

The frequency dependence of the proton longitudinal relaxation time was measured using a Spinmaster-FFC fast field cycling relaxometer supplied by Stelar (info@stelar.it). A variable temperature probe was used, having a proton measurement frequency of 12 MHz with a frequency range down to 10 kHz and permitting measurements down to 223 K. The field switching time was 3 ms with a 5 μs 90° radiofrequency pulse and a deadtime of 14 μs. The signal was obtained by integrating the intensity of the first 16 μs of the FID after the deadtime delay. Additional higher frequency measurements were made on Bruker MSL100 and MSL300 spectrometers operating at proton frequencies of 100 MHz and 300 MHz respectively.

Glassy state samples were made by dissolving the sugar (either sucrose or xylose) in water at moderately high temperatures up to 373 K, followed by rapid temperature quenching. When measurements were made in D2O the sugar hydroxyl protons were first replaced by deuterium by repeat cycles of dissolution in excess D2O and freeze-drying.

3. Theory

3.1. Exchange Analysis

Before analysing the experimental data it is helpful to consider the theoretical form of the frequency dispersions expected for sugar–water systems above and below Tg. A sucrose solution has three distinct pools of protons, namely the non-exchanging CH protons of sucrose, the exchangeable sucrose hydroxyl protons and the pool of water protons. These three proton populations can exchange longitudinal magnetization by dipolar cross-relaxation and, in the case of the sucrose hydroxyl protons and water, by direct chemical exchange. In principle, the time evolution of the longitudinal magnetization for all three proton pools. We can therefore write:

$$R = P_w R_w + P_{CH} R_{CH} + P_{OH} R_{OH}, \quad (1)$$

where

$$P_w + P_{CH} + P_{OH} = 1. \quad (2)$$

Further simplification is possible if we note that the exchangeable and non-exchangeable protons on the sucrose are modulated by the same sucrose rotational and translational dynamics and that they are coupled by strong dipole–dipole interactions. Therefore it is reasonable to assume that all sucrose protons have essentially the same longitudinal relaxation rate, $R_s = R_{CH} = R_{OH}$.

Equation (1) therefore reduces to

$$R(\omega) = P_w R_w(\omega) + (1 - P_w) R_s(\omega), \quad (3)$$

where $P_w$ is the proton fraction of water. Therefore we need to consider the theory for the water dynamics, $R_w(\omega)$, and the sucrose dynamics, $R_s(\omega)$, separately.

3.2. The Water Dynamics

Well above the glass transition temperature we expect the water to contribute only a constant, frequency-independent, baseline term to our dispersion data. This can be understood if we assume, for simplicity, a single correlation time model for the water relaxation such that

$$R_w(\omega) = C_w [J(\omega_0, \tau_w) + 4J(2\omega_0, \tau_w)], \quad (4)$$

where $C_w$ is a constant proportional to the dipolar coupling constant and the spectral density, $J(\omega, \tau)$ is defined as

$$J(\omega, \tau) = \tau/(1 + n^2 \omega^2 \tau^2). \quad (5)$$

Here $\tau_w$ is the single correlation time characterizing the water dynamics. In writing equation (4) we have not invoked the conventional multi-state description of water, such that there are two or more exchanging populations of ‘hydration’ and ‘free’ water. At the high concentrations of sucrose used in these studies there is very little, if any, ‘free’ water that is not hydrogen bonding the sucrose hydroxyl groups. The order of magnitude of $\tau_w$ can be estimated from our earlier dispersion study of water dynamics in a saturated sucrose solution using water oxygen-17 relaxation. In that study the water reorientational was found to be characterized by two correlation times. The first, labelled $\tau_f$, corresponded to near-isotropic reorientation, and assumed a value of about 130 ps. The slower correlation time, labelled $\tau_r$, characterized the averaging of the residual oxygen-17 quadrupolar interaction, and was found to be about 5 ns and increasing with increasing viscosity.

We therefore expect that, well above $T_g$, the correlation time $\tau_w$ characterizing the dipolar interaction
dynamics in equation (4) will be very short, and of the order of a few nanoseconds at most. The midpoint of the $T_1$ dispersion is obtained when $\omega B = \tau_w$ is unity which, for a correlation time of 1 ns, occurs at a resonance frequency of about 160 MHz. Because the maximum frequency measured in our field cycling experiment is 10 MHz the water dynamics well above $T_g$ should contribute only a frequency-independent constant background term equal to $5C_w\tau_w$.

The situation below the glass transition temperature is less straightforward because it is difficult to know a priori the extent to which the water dynamics are slowed by interaction with the glassy matrix. Our previous proton and deuterium NMR studies of the dynamics of water in a 10% maltose glass showed that water retained a high degree of mobility, and this has since been confirmed in other independent studies [4]. It appears that when the system enters the glassy state the sugar molecules are irrotationally frozen in a rigid 3-dimensional matrix, while the smaller water molecules are dynamically uncoupled and continue to undergo rapid translational and rotational motion within the pores formed by the sugar matrix. The average lifetime of water at any particular site in the glass matrix was estimated to be of the order of $10^{-5}$ s [4], which would give a dispersion midpoint around 16 kHz. Therefore it is possible that in the glassy state the water will contribute a frequency dispersion having the form of equation (4), and we will show that this is indeed the case.

3.3. The sucrose dynamics

The dynamics of sucrose molecules in solution well above the glass transition temperature have been extensively studied by high resolution $^{13}$C NMR [11–14], and a number of facts have emerged. Across the concentration and temperature ranges for which separate $^{13}$C resonances can be resolved for the eight CHOH group carbons it is found that all eight carbons have identical longitudinal relaxation times. Because the CH vectors point in different directions, this implies that the sucrose molecule is undergoing near isotropic rotation as a rigid body. These $^{13}$C data also show that ring puckering does not contribute to the $^{13}$C relaxation, because the 5-membered fructose ring possesses a greater degree of conformational flexibility than the six-membered pyranose ring. Thus it is found that all eight carbons have identical longitudinal relaxation times. Because the CH vectors point in different directions, this implies that the sucrose molecule is undergoing near isotropic rotation as a rigid body. These $^{13}$C data also show that ring puckering does not contribute to the $^{13}$C relaxation, because the 5-membered fructose ring possesses a greater degree of conformational flexibility than the six-membered pyranose ring, yet all ring carbons have the same longitudinal $^{13}$C relaxation times. However, the data also show that the three exocyclic-CH$_2$OH groups undergo internal rotation. This follows because, if there were no internal rotation, the $^{13}$C longitudinal relaxation rate of these three groups should be exactly twice that of the ring carbons, because they are bonded to two CH protons.

In fact their relaxation rate is only about 1.7 times greater, indicating partial motional averaging through internal rotation.

To describe the sucrose dynamics above the glass transition temperature we will therefore invoke a model-independent spectral density function, $J(\omega)$, such that

$$J_{\text{CH}}(\omega) = S^2 \left[ \frac{\tau_c}{(1 + \omega^2 \tau_c^2)} + \frac{4\omega_c}{(1 + 4\omega^2 \tau_c^2)} \right]$$

$$+ (1 - S^2) \frac{\tau_{\text{eff}}}{(1 + \omega^2 \tau_{\text{eff}}^2)}$$

$$+ 4\frac{\tau_{\text{eff}}}{(1 + 4\omega^2 \tau_{\text{eff}}^2)},$$

(6)

where

$$1/\tau_{\text{eff}} = 1/\tau_c + 1/\tau_{\text{int}}$$

(7)

Here $\tau_c$ is the reorientational correlation time for overall tumbling of the sucrose molecule while $\tau_{\text{int}}$ is the correlation time characterizing the internal rotation of the three CH$_2$OH groups. $S$, which ranges between 0 and 1, is a generalized order parameter characterizing the degree of isotropy of the internal motion. Isotropic internal motion corresponds to $S = 0$ while internal motion oriented about only a single axis corresponds to $S = 1$.

The rotational correlation time $\tau_c$ can be estimated using the VTG relationship [15], according to which,

$$\tau_c = \tau_{\text{c}} \exp \left[ \frac{B}{(T - T_0)} \right]$$

(8)

The constants in this equation have been tabulated for sucrose–water systems [15]. For example, in an 80% w/w sucrose solution at 298 K, $\tau_{\text{c}}$ is $11.6 \times 10^{-13}$ s, $B$ is 1060 K and $T_0$ is 218 K, so that $\tau_c$ is calculated to be 66 ns, which gives a predicted dispersion midpoint at about 2.4 MHz, well within the observable frequency range. The correlation times for internal rotation of the CH$_2$OH groups are harder to estimate. The CH$_2$OH group reorientational correlation time in solid $\beta$-D-allose has been measured by NMR and can be described by

$$\tau_{\text{int}} = \tau_{\text{int}0} \exp \left[ \frac{E}{RT} \right],$$

(9)

with $\tau_{\text{int}0}$ equal to $5.2 \times 10^{-11}$ s and an activation energy $E$ of 33.5 kJ mol$^{-1}$. At 298 K this gives a correlation time of 38.8 $\mu$s. Whether this also applies to the solution state at 298 K is unknown. One can speculate that the barriers to internal rotation are mainly steric and involve internal hydrogen bonding, so should be independent of the overall tumbling of the molecule. If so, the internal rotation can be assumed to be slow, with a dispersion midpoint in the 1–10 kHz region, which is outside the experimental range that covers 10 kHz to 10 MHz. However, this conclusion is only provisional, because it assumes that the internal rotations of the three groups in sucrose have similar dynamics to those in $\beta$-D-allose, and are concentration-independent.
With these assumptions the sucrose dynamics well above the glass transition temperature can be obtained by assuming \( \tau_c < \tau_{\text{int}} \) so that \( \tau_{\text{eff}} = \tau_c \) and we have a single correlation time model where

\[
J_{\text{CH}}(\omega) = \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} \right] \frac{\omega}{\tau_c} + \frac{4\tau_c}{(1 + 4\omega^2 \tau_c^2)} \quad (T \gg T_g). \tag{10}
\]

The concentration dependence of the sucrose dynamics well above \( T_g \) can be formulated by assuming \( \tau_{\text{int}} \) is concentration independent and that the overall tumbling of the sucrose molecule above the glass transition temperature follows the Stokes–Einstein relationship, which predicts a linear relationship between \( \tau_c \) and solution shear viscosity \( \eta \). Obviously this relationship will break down as we approach the glass transition and the sucrose molecules become irrotationally bound in a 3-dimensional matrix. It is therefore of interest to investigate to what extent the experimental correlation times scale with solution shear viscosity.

Like the water, the sucrose dynamics below \( T_g \) is harder to formulate. If we assume the sucrose is irrotationally bound in the glass matrix then \( \tau_c \to \infty \), and we would expect that either internal rotation of the side chains or vibrational modes in the sucrose lattice provide the major relaxation pathway. In the former case we can put \( \tau_{\text{eff}} = \tau_{\text{int}} \) and write

\[
J_{\text{CH}}(\omega) = (1 - S^2) \left[ \frac{\tau_{\text{int}}}{1 + \omega^2 \tau_{\text{int}}^2} \right] \frac{\omega}{\tau_{\text{int}}} + 4\tau_{\text{int}}/(1 + 4\omega^2 \tau_{\text{int}}^2) \quad (T \ll T_g), \tag{11}
\]

which predicts a low frequency dispersion characterized by a single correlation time below \( T_g \). The possible contribution of lattice phonons is considered later.

### 3.4. Predicted overall dispersion behaviour

Having analysed the separate contributions of the water and sucrose above and below the glass transition temperature we are now in a position to predict the combined behaviour. Above \( T_g \) we expect that there will be a constant background term from the water and a dispersion characterized by a single rotational correlation time for the sucrose such that

\[
R(\omega) = P_w C_w \frac{\tau_w}{(1 + \omega^2 \tau_w^2)} + (1 - P_w) C_{\text{CH}} \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} \right] + 4\tau_c/(1 + 4\omega^2 \tau_c^2), \tag{12}
\]

where \( C_w \) and \( C_{\text{CH}} \) are constants proportional to the dipolar coupling constant for water and the sucrose protons, respectively.

Below \( T_g \), or in very concentrated solutions just above \( T_g \), we predict a slowing down of the water dynamics so that a double dispersion is observed. Assuming internal rotations provide the sucrose relaxation pathway we can therefore write

\[
R(\omega) = P_w C_w \frac{\tau_w}{(1 + \omega^2 \tau_w^2)} + 4\tau_w/(1 + 4\omega^2 \tau_w^2) + (1 - P_w)(1 - S^2) C_{\text{CH}} \left[ \frac{\tau_{\text{int}}}{1 + \omega^2 \tau_{\text{int}}^2} \right] + 4\tau_{\text{int}}/(1 + 4\omega^2 \tau_{\text{int}}^2). \tag{13}
\]

Besides the transition from a single to double dispersion, the validity of this analysis can be tested by replacing the water with D\(_2\)O. This can be modelled by setting \( P_w \) to zero in equations (9) and (13), although there may also be minor changes arising from the replacement of the sucrose hydroxyl protons by deuterons, which will alter the constant \( C_{\text{CH}} \) and slightly increase the rotational correlation time. In D\(_2\)O well above the glass transition temperature we therefore predict that the baseline term from the water should disappear, leaving only the rotational correlation time dispersion from the non-exchanging sucrose protons, characterized by a correlation time \( \tau_c \):

\[
R(\omega) = A C_{\text{CH}} \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} \right] + 4\tau_c/(1 + 4\omega^2 \tau_c^2). \tag{14}
\]

Here \( A \) is a constant to take account of the changed second moment (or, equivalently, dipolar coupling). Below \( T_g \), the contribution from the overall tumbling motion of the sucrose molecule will be eliminated because the sucrose forms an irrotational 3-dimensional matrix, so only side chain internal rotations remain together with possible phonon modes from the sucrose lattice. The double dispersion of equation (13) should therefore become a single dispersion arising only from the second term.

### 3.5. Predictions for the xylose–water system

The contribution from the internal rotation of the CH\(_2\)OH side chain can be eliminated by repeating the experiments with a pentose sugar such as D-xylose, which lacks the side chain. There are then two situations to consider, depending on whether the measurements are performed above or below \( T_g \).

*Xylose–water above \( T_g \).* If our analysis is correct, the xylose–water system well above \( T_g \) should be dominated by rotational motion of the xylose, characterized by a single rotational correlation time. In H\(_2\)O there will also be a constant baseline contribution which should vanish in D\(_2\)O.

*Xylose–water below \( T_g \).* The most interesting behaviour is expected below \( T_g \). A 100% xylose-OD glass can be made which lacks all water and where all xylose hydroxyl protons have been exchanged with deuterons, leaving only the xylose CH proton signal. Without side chain motions to provide a rapid relaxation sink the only remaining motions below the glass transition temperature should be those of the 3-dimensional amorphous glass xylose network itself. These motions would be expected to be irrotational and involve...
phonon modes of the 3-dimensional lattice itself. In addition there should be a relaxation peak from deuterium quadrupolar relaxation from the xylose-OD groups. This peak will be superimposed on the lattice dispersion. We therefore need to consider the form of the spectral density functions arising from the xylose lattice vibrations and the deuterium quadrupolar cross-relaxation.

3.6. Spectral densities of amorphous sugar–glass networks

Solid state spectral densities usually involve a distribution of correlation times and several models have been reviewed by Beckmann [16]. In the case of xylose glasses, the distribution of correlation times could arise because the amorphous lattice creates local domains each characterized by its own motional correlation time. In addition there may also be various degrees of correlated motion in the lattice. One particularly interesting distribution of correlation times gives rise to a simple ‘stretched’ spectral density [16]:

\[ J(\omega) = 2\beta/\omega[(\omega\tau)^{\beta}/1 + (\omega\tau)^{2\beta}], \]

where \(0 < \beta < 1\) is a parameter characterizing the width of the correlation time distribution. In the limit \(\beta = 1\) this reduces to the conventional single correlation time model.

A quite different form of spectral densities arises if the xylose glass matrix is viewed as a percolating, self-similar fractal 3-dimensional network. Blinc et al. [17] have deduced the form of the spectral densities expected for such networks by treating the dominant motion as slow transverse vibrational fluctuations of the chains forming the network, and characterized by a vibrational density of states. According to this model, the spin–lattice relaxation rate should have a power law dependence on frequency such that

\[ R_1 = B\omega^{-n} \]

where the exponent \(n\) is related to the fractal (Hausdorff) dimension \(d\), characterizing how the mass scales with length and also to \(D\) which is the spectral (fracton) dimension which determines the density of vibrational states on a fractal lattice. Three models were considered such that

\[ n = 1 - d/(5 - 3d) \quad \text{(fractal weak scattering model),} \]
\[ n = 1/(d + 1) \quad \text{(Rayleigh scattering model),} \]
\[ n = 1 - d/2D \quad \text{(heavy-damping model).} \]

Note that in the Euclidean limit that \(d = D = 1\) the relaxation rate is simply proportional to \(\omega^{-1/2}\).

3.7. Deuterium quadrupolar dips

As we shall demonstrate, a deuterated 100% xylose-OD solution gives rise to a pronounced deuterium quadrupolar ‘dip’ above, at and below the glass transition temperature. The conventional expression ‘quadrupolar dip’ refers, of course, to plots of \(T_1(\omega)\). In plots of \(R_1(\omega)\) the ‘dip’ appears as a peak superimposed on the dispersion curve. The origin of this peak is well known; it results from transfer of proton longitudinal magnetization to the deuterium pool that undergoes much faster relaxation by reorientational modulation of the electric-quadrupolar interaction. When fitting this deuterium peak we will assume a Gaussian lineshape of the form

\[ R_{\text{quad}}(\omega) = C[\exp(\omega - \omega_0)^2/M], \]

where \(\omega_0\) is the central peak frequency and \(M\) is the second moment characterizing the peak width.

4. Results

Having considered several theoretical models relating molecular dynamics to the frequency dispersion we are now in a position to compare theory with experiment.

4.1. Concentrated sucrose solutions well above \(T_g\)

Figure 1 shows the dispersion curves for 51% w/w sucrose solutions in both H\(_2\)O and D\(_2\)O at 273 K, which is well above the glass transition temperature. These data appear to conform quite well to the theoretical predictions, and can be fitted to a single dispersion with an adjustable baseline of the form of equation (12). Replacing water by D\(_2\)O still gives a clear dispersion.

Figure 1. Frequency dependence of the longitudinal proton relaxation rate \(R_1\) (in s\(^{-1}\)) for 51% w/w sucrose solutions in either water H\(_2\)O, or in D\(_2\)O at 273 K. Only the non-exchanging sucrose CH protons are observed in D\(_2\)O. The lines are the fits of equation (12).
Table 1. Concentration dependence of the sucrose and water correlation times at 298 K derived by fitting the sucrose–H2O dispersions with equation (12).

<table>
<thead>
<tr>
<th>Sucrose concentration in % w/w</th>
<th>51</th>
<th>59.5</th>
<th>72.8</th>
<th>84.7</th>
<th>90.1</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water proton fraction</td>
<td>0.624</td>
<td>0.541</td>
<td>0.392</td>
<td>0.238</td>
<td>0.160</td>
<td>0.083</td>
</tr>
<tr>
<td>Water/sucrose molar ratio</td>
<td>0.948</td>
<td>0.928</td>
<td>0.877</td>
<td>0.774</td>
<td>0.676</td>
<td>0.500</td>
</tr>
<tr>
<td>Sucrose correlation time in ns at 298 K</td>
<td>20</td>
<td>11</td>
<td>23</td>
<td>66</td>
<td>732</td>
<td>1940</td>
</tr>
<tr>
<td>Baseline/s−1</td>
<td>2.5</td>
<td>4.7</td>
<td>16.8</td>
<td>109</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Water correlation time in ns at 298 K</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>265±16</td>
<td>229±16</td>
</tr>
</tbody>
</table>

with an almost identical correlation time but with zero baseline, confirming that the main dispersion does not arise from the water but from either the overall sucrose reorientation or, conceivably, from the rotation of the CH2OH side chains or a combination of both. It is also interesting to note that the relaxation rate on the low frequency side of the dispersion for 51% sucrose at 273 K is actually greater in D2O than in water. There are three reasons for this. Equation (12) shows that merely putting \( P_w \) to zero will increase the magnitude of the second ‘sucrose tumbling’ term even if the dynamics are unchanged. The calculated increase in \( R \) at low frequencies is actually from 14.3 s\(^{-1}\) to 24 s\(^{-1}\) for a 51% sucrose solution, assuming that \( C_{CH} \) and \( \sigma \) are unchanged by the replacement. In fact the experimental dispersion curve shows that the correlation time at 273 K is increased slightly from \( 5.0 \times 10^{-9} \) s to \( 6.1 \times 10^{-9} \) s, presumably because of the increased mass resulting from the replacement of OH by OD groups and the slightly increased solution viscosity. The second moment \( C_{CH} \) also increases slightly from a calculated value of \( 0.96 \times 10^8 \) s\(^{-2}\) to \( 2.1 \times 10^8 \) s\(^{-2}\). Presumably this is because the CH protons have a slightly faster intrinsic dipolar relaxation mechanism than the sucrose OH protons. Table 1 lists the experimental best-fit parameters from equation (12) in both water and D2O for a range of sucrose concentrations up to 95% w/w, all well above \( T_g \).

Figure 2 compares the sucrose rotational correlation times with the solution shear viscosity as a function of increasing sucrose concentration at 298 K. It is clear that the two parameters are not well correlated and certainly do not obey the Stokes–Einstein relationship. This may reflect the increasing role of the internal rotational mode as the viscosity increases.

4.2. 90% and 95% sucrose–water systems

Figure 3 shows the dispersion for a 90.1% w/w sucrose solution in water (H2O) at a temperature of 230.9 K, well below the glass transition temperature of 261.5 K. These data conform very well with the double dispersion predicted by equation (13), strongly suggesting that there are separate dispersive contributions from the water and sucrose molecules. Because of the unknown magnitude of the order parameter in equation (13) both the amplitudes and correlation times of the two dispersions were treated as adjustable parameters when fitting the data. The most significant feature of the fit is undoubtedly the water and sucrose correlation times, which are listed in table 2. These show clearly that, even in the glass at 230.9 K, the water undergoes rapid reorientation with correlation times of 138 ns. Figure 4 shows the double dispersion fit for the even more concentrated 95% sucrose solution in water at 298 K, which is just above the glass transition temperature of 293 K [18].

To explore the effect of passage through the glass transition temperature on the water and sucrose correlation times the double dispersion of the 90.1% w/w sucrose sample was analysed as the temperature was...
lowered from 298 K, well above the glass transition temperature of 261.5 K, to one well below it, 230.9 K. The resulting correlation times are listed in Table 2 and display a number of surprising trends. First, the water correlation remains short, even in the glassy state. In fact there is even a systematic tendency for it to shorten, perhaps indicating increasing decoupling of the water and sucrose dynamics. Second, the effective sucrose correlation time shows a systematic increase, but no very obvious discontinuity at the glass transition temperature. This is surprising because the above analysis would lead one to expect a transition from rotational dynamics to one dominated by side chain rotation and vibrational (phonon) modes. To gain additional information and to confirm the double dispersion assignments, we therefore switched from sucrose to xylose that lacks the complication of reorienting side chains.

### 4.3. 95% xylose solutions in D2O

Figure 5 shows the dispersion observed at 298 K (i.e. well above $T_g$) for a 95% solution of xylose in D2O, where all exchangeable protons have been replaced with deuterons. In this system we expect to observe a single-correlation time dispersion of the form of equation (10) arising from the rotational tumbling of the xylose CH protons, and figure 5 shows that this model does provide an adequate fit to the data. There is a possible contribution from cross-relaxation onto the deuterium. Indeed, the fit can be slightly improved by including an additional Gaussian term of the form of equation (18), but this is a comparatively minor contribution in this system.

### 4.4. 100% xylose glasses in their protonated and deuterated forms

A glass can be made from pure xylose either in the protonated state or in the deuterated state where all xylose hydroxyl protons are exchanged for deuterons. According to the literature [18], the glass transition temperature for this system is 283 K. Molten xylose in its fully protonated form at 298 K is expected to give a single dispersion of the form of equation (10), where the correlation time characterizes the near-isotropic...
xylose reorientation. Figure 6 shows that this is the case, and provides additional proof that the dispersion observed in the sucrose solutions arises from the sucrose and not from water. The fit can be slightly improved by introducing a second dispersion (see figure 6), though this may simply be a consequence of greater mathematical flexibility, because there is no obvious physical justification for a second component in this case. The data for a molten deuterium-exchanged xylose at 298 K is shown in figure 7, and shows a pronounced deuterium quadrupolar peak along with a single dispersion which presumably arises from overall tumbling of the xylose molecules.

The data at and below $T_g$ for this sample is particularly interesting. Figure 8 shows that, besides the expected deuterium quadrupolar peak, a dispersion is still evident in the data. As there are no side chain contributions possible, and rotational degrees of freedom have, presumably, been frozen out in the glassy state, the observed dispersion must arise from low frequency vibrational modes in the 3-dimensional xylose lattice. These dispersion data were fitted with the 'stretched spectral density' function of equation (15) but the best fit value for the exponent $\beta$ was 0.99, showing that only a simple spectral density function with a single correlation time of 1.5 $\mu$s is required. Therefore it appears that the distribution of motional correlation times in the glassy sugar matrix is very narrow, and does not reflect the range of amorphous environments that might have been expected. This suggests that the motions are not localized rotations of xylose molecules which, in the glassy state would face a very high potential barrier anyway. Instead the dispersion must arise from vibra-
tional modes in the lattice, having a microsecond time-scale. Attempts to fit this dispersion with the power law expression in equation (16) were not particularly convincing (see figure 9) and gave an exponent \( n \) of 0.73. It is conceivable that the dispersive component in figure 8 has an additional term arising from relaxation in the dipolar field [19]. However the fact that the data can be fitted with a single dispersion argues against this possibility, though it has to be admitted that there is increasing experimental error at the lowest frequencies, so fits to alternative models cannot be precluded. The increasing experimental error at low frequencies is a feature of many of the data, and arises whenever the longitudinal relaxation time approaches the field switching time.

5. Conclusions

The results show that the combination of NMR field cycling and deuterium exchange is a powerful technique for investigating molecular dynamics both above and below the glass transition temperature. The sugar and water dynamics can be separated readily, and show that even in the sugar glass the water remains highly mobile. The observations conform reasonably well to the theoretical predictions. In particular, the transition from a single to a double dispersion in the sucrose-water system is confirmed, and demonstrates the slowing down of the water dynamics. The simple xylose dispersion in D2O below \( T_g \) also provides a nice experimental handle on the lattice dynamics in the sugar glass. Somewhat surprisingly, the results show that the sugar dynamics, even in the amorphous glass, can still be described with a single correlation time model, and there is no evidence for a distribution of correlation times. Even more surprising is the observation, in table 2, that the water correlation time shows no obvious break as the temperature is lowered through the glass transition, and even shows a slight tendency to shorten. This result confirms our earlier observation [4] of the decoupling of the water and sucrose dynamics in the glassy state.

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References