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# The dynamics of water in hydrated white bread investigated using quasielastic neutron scattering

**J Sjöström[1], F Kargl[2], F Fernandez-Alonso[3,4] and J Swenson[1]**

[1] Department of Applied Physics, Chalmers University of Technology, SE-41296 Göteborg, Sweden
[2] Institute of Mathematical and Physical Sciences, University of Wales, Aberystwyth SY23 3BZ, UK
[3] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK
[4] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

E-mail: johan.hedstrom@chalmers.se

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**Abstract**

The dynamics of water in fresh and in rehydrated white bread is studied using quasielastic neutron scattering (QENS). A diffusion constant for water in fresh bread, without temperature gradients and with the use of a non-destructive technique, is presented here for the first time. The self-diffusion constant for fresh bread is estimated to be $D_s = 3.8 \times 10^{-10}$ m$^2$ s$^{-1}$ and the result agrees well with previous findings for similar systems. It is also suggested that water exhibits a faster dynamics than previously reported in the literature using equilibration of a hydration-level gradient monitored by vibrational spectroscopy. The temperature dependence of the dynamics of low hydration bread is also investigated for $T = 280$–$350$ K. The average relaxation time at constant momentum transfer ($Q$) shows an Arrhenius behavior in the temperature range investigated.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Water is one of the primary ingredients in most food. It plays a fundamental role for the texture and taste of the product. Much research aims to understand the transport mechanisms in wheat-based food such as white bread [1]. When baking bread, water is transported through the dough and governs the degree of chemical changes, such as starch gelatinization [2], protein denaturation [3] and aroma-compound formation. Moreover, water is important for physical changes such as expansion of bubbles and the softness of the crumb [4]. After baking, the water content and its diffusion control the rate of ageing of the bread.

  

There have been many studies of the transport properties of water in bread and dough. The most direct approach is to measure the overall water content by weighing after heating [5, 6]. Measuring local water content in different regions of a loaf of bread enables one to create a moisture profile and estimate an effective diffusion rate by analysing moisture content over time. Experiments have shown [7, 8] that there is a net diffusion of water towards the inner part of the bread during heating. A direct measurement of this diffusion rate during heating was proposed [9] by the use of a fiber-optic near infrared reflectance (NIR) instrument inserted in the bread. The moisture content in different regions was measured using the absorption intensity of the first vibrational overtone of the water stretch mode at wavelength $\lambda = 1.45\ \mu$m as an indicator of the hydration level. It became evident [8, 10] that water migrates in its saturated gas phase towards the center of the dough when heated, and diffuses outwards in its liquid phase. In absence of direct observations of the dynamics, a model for the evolution of the moisture profile was developed and an effective diffusion constant derived [11]. The diffusion of water is much dependent on the heat conduction in the sample and vice versa. The interplay is very complex and the diffusion under baking is still an open subject.

To the best of the authors' knowledge no direct measurement of the overall water diffusion in already-baked bread has been published other than by magnetic resonance imaging (MRI) [12], in which the water content could not be satisfactorily determined [1]. In this study we probe the overall diffusion of water within a white bread at different hydration levels and temperatures. The sample geometry (20 mm × 20 mm × 1 mm) assures that the water diffusion is probed without the presence of temperature gradients within the sample. Thus, the problem of a complicated relation between heat and water diffusion does not apply to this study.

## 2. Material and experiment

The bread used in this study is a common commercially available toast bread[5] based on wheat. It consists of 46% carbohydrates (mainly starch), 8.5% proteins (mainly gluten proteins), 3.5% fat, and 4% food fibers according to the manufacturer [13]. Naturally, the result of the present study is specific to this particular composition. Even so, the choice of product is quite representative for (white) commercial wheat bread. Normal variations of carbohydrates and proteins are around 41–49% and 7–9% respectively (based on a survey of white bread from the largest bakeries in Europe and America).

The hydrated samples were prepared by cutting the crust of the bread and slicing approximately 20 mm × 20 mm × 2 mm large pieces of the bread. These were sandwiched between two glass discs in order to obtain a flat sample and dried in a vacuum oven for one week at 333 K. Even though there is some residual water left after this treatment (as shown by dielectric spectroscopy [14]) this sets the limit for 'dry' bread. After cooling to room temperature under vacuum the samples were carefully weighed and hydrated in 100% humidity to a hydration level $H = 3.3$ and 8.4 wt% (water mass/total mass). Each sample was placed in a flat Al container with an internal thickness of 1 mm. The fresh sample was simply cut from the fresh bread (baked within a couple of days before experiment) and placed it in the Al container.

The QENS measurements were performed on the high resolution inverted-geometry, time-of-flight spectrometer IRIS [15] at the pulsed neutron spallation source ISIS at the Rutherford Apppleton Laboratory, UK. With an incident neutron wavelength of 6.6 Å and the standard PG002 analysers, the instrument has an energy resolution of 17.5 $\mu$eV (FWHM), with a total

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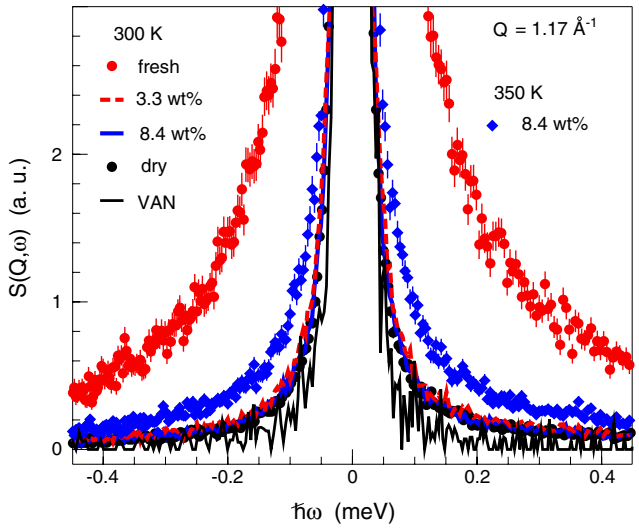


**Figure 1.** Quasielastic neutron scattering spectra of all samples at 300 K and $Q = 1.17$ Å$^{-1}$ in addition to $H = 8.4$ wt% also at 350 K. Each spectrum is normalized to unity at zero energy transfer. The vanadium spectrum recorded at 300 K determines the instrumental energy resolution function.

energy window of $\pm 0.5$ meV. The 51 detectors were grouped 3 by 3 resulting in a total of 17 individual spectra. To ensure good quality the spectra were analysed up to a scattering angle corresponding to $Q = 1.17$ Å$^{-1}$. Quasielastic measurements were performed at 300 K for all samples with additional measurements at 280, 320, 330 and 350 K for $H = 8.4$ wt%. The data were normalized to the elastic intensities measured at 130 K eliminating differences in detector efficiency and at the same time accounting for self-absorption of the sample.

It should be noted that corresponding measurements were carried out for samples hydrated with $D_2O$. The extent of H/D exchange in the samples was also monitored via optical measurements using a single-bounce attenuated-total-reflection FTIR spectrometer (Bruker Vertex 70 Specac Goldengate) with a constant resolution of 4 cm$^{-1}$ across the whole spectral range. Infrared data of the bending mode of water in the region 1000–2000 cm$^{-1}$ was used to determine the relative amounts of $H_2O$, $D_2O$ and HOD species in our sample upon deuteration. Unfortunately, the H–D exchange between the water and the hydroxyl groups, which are all over the starch polymers, was too large to justify a subtraction of the $D_2O$ spectra and thereby obtaining only the water dynamics. Therefore, in the present study we are not including any results from measurements on samples hydrated in $D_2O$.

The total scattering power of the samples is dominated by the large incoherent scattering of hydrogen nuclei. Hence, the neutrons essentially probe the self-dynamics of the hydrogen in the samples. This means that both the water (only $H_2O$) and the hydrogen containing entities of the biomolecules of the bread are investigated. Thus, the raw data is, to a good approximation, the incoherent dynamic structure factor of the hydrogens, $S_{\mathrm{inc}}(Q, \omega)$.

## 3. Results and discussion

Some typical QENS spectra taken at 300 K are shown in figure 1. A very pronounced quasielastic broadening occurs only for the fresh bread. The virtually dry bread, the bread

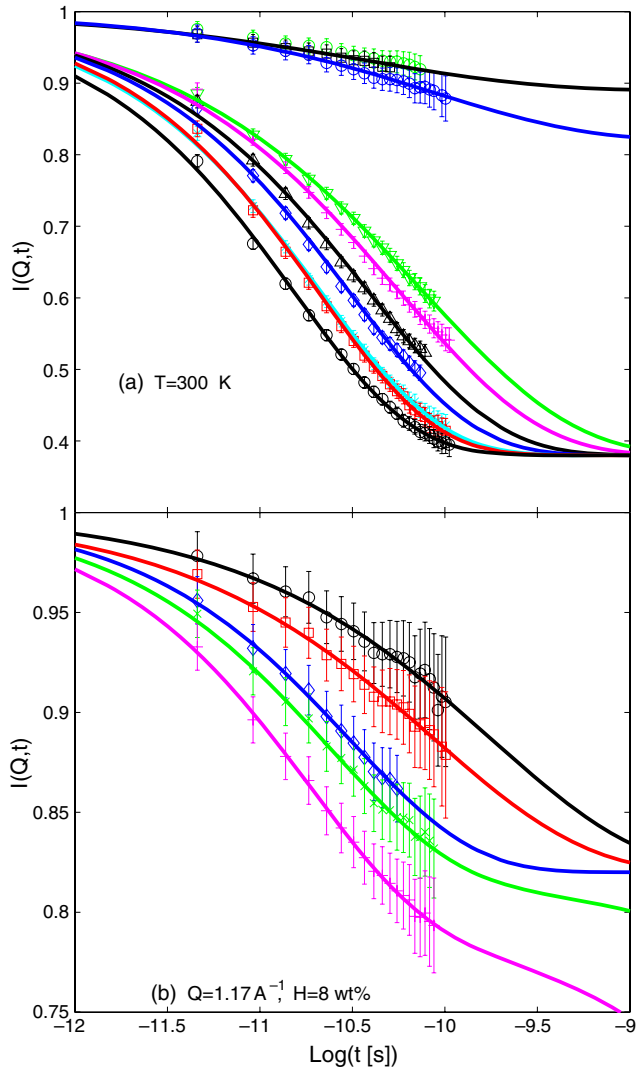


**Figure 2.** (a) The self-intermediate scattering function at $T = 300$ K and $Q = 1.17$ Å$^{-1}$ for the dry sample (green ○), $H = 3.3$ wt% (black □), $H = 8.4$ wt% (blue ○). The data for the fresh bread is also included for all $Q$ values: $Q = 0.46$ Å$^{-1}$ (green ∇), 0.59 Å$^{-1}$ (purple +), 0.72 Å$^{-1}$ (black △), 0.83 Å$^{-1}$ (blue ◇), 0.95 Å$^{-1}$ (light green ×), 1.06 Å$^{-1}$ (red □) and 1.17 Å$^{-1}$ (black ○). The solid lines are fits using equation (1). (b) The self-intermediate scattering function for the $H = 8.4$ wt% sample at $Q = 1.17$ Å$^{-1}$ and $T = 280$ K (black ○), 300 K (red □), 320 K (blue ◇), 330 K (green ×) and 350 K (purple +). The solid lines are fits with two KWW functions.

with $H = 3.3$ wt% and that with $H = 8.4$ wt% show almost the same, not very pronounced, broadening at 300 K, as can be seen by comparing these data with the resolution measurement (labelled VAN in figure 1). The broadening increases with increasing temperature, as is evident from a comparison of the spectra of the $H = 8.4$ wt% sample at 300 and 350 K.

The data for each temperature and $Q$ value were, after normalization, Fourier transformed to a self-intermediate scattering function $I(Q, t)$, shown in figure 2. It is evident that the data show both $Q$ and temperature dependences, as well as a dependence on $H$. In figure 2(a)

$I(Q = 1.17\ \text{Å}^{-1}, t)$ is shown for all hydration levels at $T = 300$ K in addition to $I(Q, t)$ for the fresh bread for all $Q$ values. The dry bread and the $H = 3.3$ wt% sample show a very weak relaxation, which is difficult to fit with high accuracy. It is however clear that the two curves are very similar and that increasing the water content to $H = 8.4$ wt% gives rise to a small but distinct relaxation. The fresh bread shows a very stretched relaxation in the experimental time window and is well described by a Kohlrausch–Williams–Watts (KWW) stretched exponential function [16, 17] plus a constant of the following form

$$I(Q, t) = (1 - I_\infty) \exp\left[-\left(\frac{t}{\tau}\right)^{\beta_{\text{KWW}}}\right] + I_\infty, \tag{1}$$

where $\beta_{\text{KWW}}$ is the stretching parameter ($0 \leqslant \beta_{\text{KWW}} \leqslant 1$), $\tau$ is a characteristic relaxation time and $I_\infty$ is the level at which the decay settles.

For the largest $Q$-value of the fresh bread the KWW function is almost fully relaxed to $I_\infty$ and the level at which it relaxes is fitted to $I_\infty = 0.38$. Assuming that the hydrogens of the biomolecules reflect mostly relaxations on timescales longer than 100 ps, we use the following ansatz: the relaxation seen up to 100 ps is due to dynamics of water in an otherwise (on this time scale) solid matrix of bread. As shown below this seems to be a reasonable assumption although local relaxation (e.g. methyl group rotations) in the bread matrix may give a slight contribution to the assumed water dynamics. The fraction of the total scattering cross section, $\sigma_{\text{tot}}$, originating from the hydrogens of the water molecules is thus $\sigma_w/\sigma_{\text{tot}} = 0.62$ in the fresh bread ($H = 41$ wt%). Even though $I(Q, t)$ is not fully relaxed for the smaller $Q$-values, it is likely that the contribution to the quasielastic broadening from the biomolecules of the bread is about the same or slightly less for smaller $Q$ due to the large size of the carbohydrates and proteins. For simplicity we have assumed that $I_\infty$ is $Q$ independent.

Since we know the mass fraction of hydrogen in water, $H_w = 11\%$, we can derive the mass fraction of hydrogen in the dry bread matrix, $H_{\text{dry}}$, using the empirical value for $I_\infty$ and the hydration level above. $H_{\text{dry}} = 5\%$ is so obtained. To verify that this is a reasonable estimation we consider the content of the bread. Carbohydrates, of which starch is the major contribution, constitute 75% of the dry material. Starch contains a mixture of two polysaccharides: amylose and amylopectin. Both of these are long polymers of glucose, linear and branched respectively. The repeating unit of such a polymer is $-[C_6H_{10}O_5]-$ which has a hydrogen mass fraction of roughly 6%. We can therefore rest assured that the approximation is reasonable.

Using the argument above the fraction of the scattering cross section due to water for the 8.4 wt% sample is estimated to $\sigma_w/\sigma_{\text{tot}} = 18\%$. In figure 2(b) $I(Q, t)$ of the $H = 8.4$ wt% sample is shown for $Q = 1.17\ \text{Å}^{-1}$ and all temperatures. The data are fitted with two KWW functions weighed by 0.18 and 0.82 respectively. For temperatures up to 320 K the larger of these functions is far out of the experimental time window and does not contribute to the probed relaxations. Thus, the fit describes one relaxation to a constant level of $I = 0.82$. Only for 330 and 350 K both relaxations are visible, even though the characteristic relaxation time of the bread is many orders of magnitude larger than the experimental time scale and the characteristic relaxation time for the water.

The $\beta_{\text{KWW}}$ parameter of the KWW fits is shown in figure 3. The value is almost constant within the error bars, but there is a slight trend of less stretching for higher temperatures and larger $Q$ values. From the characteristic relaxation time and $\beta_{\text{KWW}}$ value of the KWW fit it is also possible to deduce the average relaxation time according to the relation

$$\langle\tau\rangle = \frac{\tau}{\beta_{\text{KWW}}}\Gamma\left(\frac{1}{\beta_{\text{KWW}}}\right), \tag{2}$$

where $\Gamma$ is the gamma function. The $Q$ dependence of the average relaxation time is fitted by the Gaussian jump-length distribution model [18], which describes a translational jump

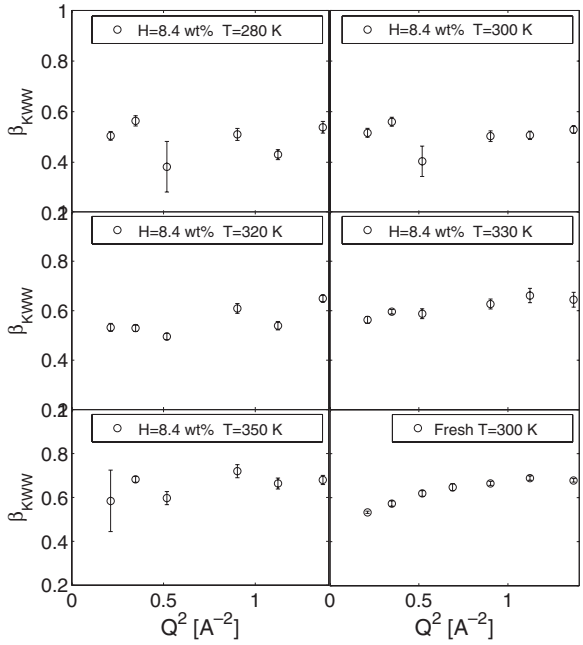


**Figure 3.** The KWW stretching parameter, $\beta_{\mathrm{KWW}}$ as a function of $Q^2$ obtained from the fits shown in figure 2.

diffusion process. The jump diffusion character of both bulk [19] and confined (hydrated protein [20]) water has previously been studied and is well established.

$$\frac{1}{\langle\tau\rangle} = \frac{1}{\tau_{\mathrm{res}}}\left[1 - \exp\left(-\frac{Q^2\langle r^2\rangle}{6}\right)\right], \tag{3}$$

where $\langle r^2\rangle^{0.5}$ is the mean jump length and $\tau_{\mathrm{res}}$ is the average residence time between two jumps. The fit is shown in figure 4. From the figure we see that the fresh sample follows more a $Q^2$ dependence of the relaxation rate, which describes a continuous translational diffusion. For the lower hydration level this seems not to be the case. This seems intuitive since motions should be more restricted by the macromolecules for low $H$. However, it should be noted that even bulk water exhibits translational diffusion with some jump diffusion character [19]. The temperature dependence for the 8.4 wt% sample is non-systematic due to large error bars that give quite uncertain fit parameters. It is evident however that the diffusion is of mainly translational character and that a self-diffusion constant therefore can be derived.

A self-diffusion constant ($D_{\mathrm{s}}$) can be derived from the fit parameters of equation (3) using [18]

$$D_{\mathrm{s}} = \langle r^2\rangle/6\tau_{\mathrm{res}}. \tag{4}$$

The results are shown in figure 5, where the increase in $D_{\mathrm{s}}$ with increasing temperature for the $H = 8.4$ wt% sample can be followed. The result for fresh bread at 300 K is also included in figure 5. This self-diffusion constant is in the vicinity of results found by QENS on water/carbohydrate (fructose and sucrose) solutions [21]. It is interesting to note that the enhancement of water mobility in fresh bread compared to $H = 8.4$ roughly corresponds to the difference in hydration level between these two samples. There is obviously not enough

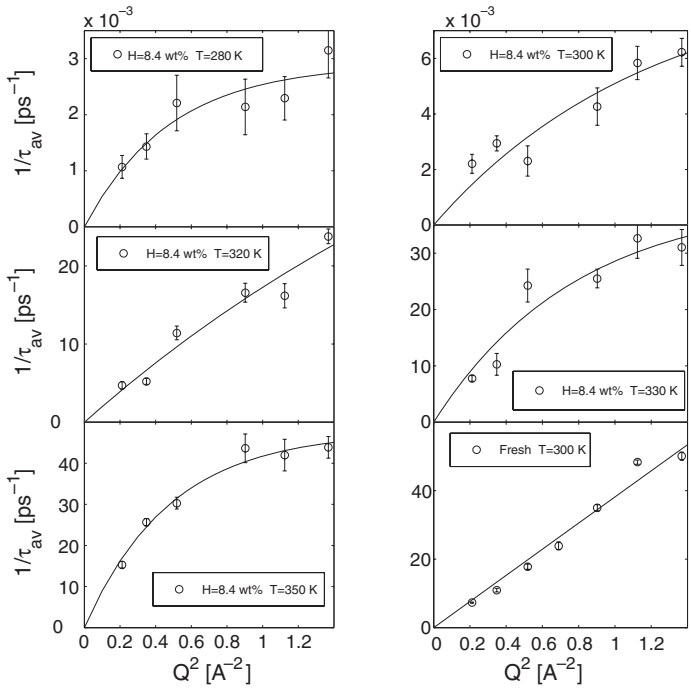


**Figure 4.** Average relaxation rate, $1/\tau_{\mathrm{av}}$, as a function of $Q^2$ for the $H = 8.4$ wt% sample at different temperatures and fresh bread at 300 K. The data for the $H = 8.4$ wt% sample is fitted by the Gaussian jump-length distribution model (equation (3)), whereas the data for the fresh bread is fitted by $\langle\tau\rangle^{-1} = DQ^2$.

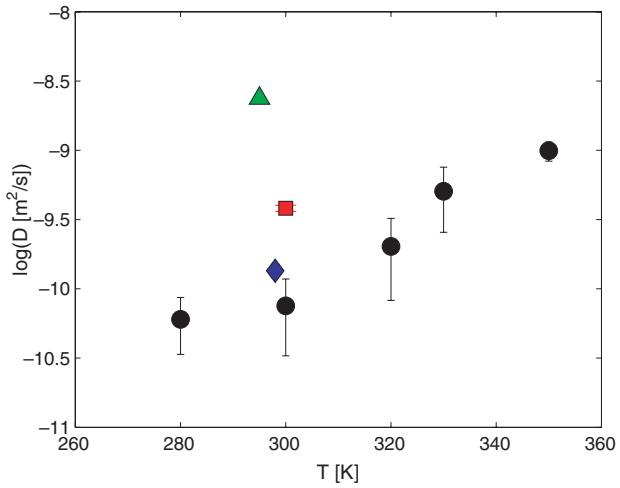


**Figure 5.** The self-diffusion coefficient for water in fresh bread at $T = 300$ K (closed square) and bread with $H = 8.4$ wt% (closed circles) derived from the fits shown in figure 4. A calculated result for water diffusion in white bread at $T = 298$ K (blue $\diamond$) is also included [11] as well as a QENS result for liquid water at $T = 295 \pm 4$ K (green $\triangle$) [18].

data to suggest that the diffusion constant scales linearly with hydration level but it is worth mentioning. For comparison, data of bulk water is included in figure 5 together with $D_{\mathrm{calc}}$ for

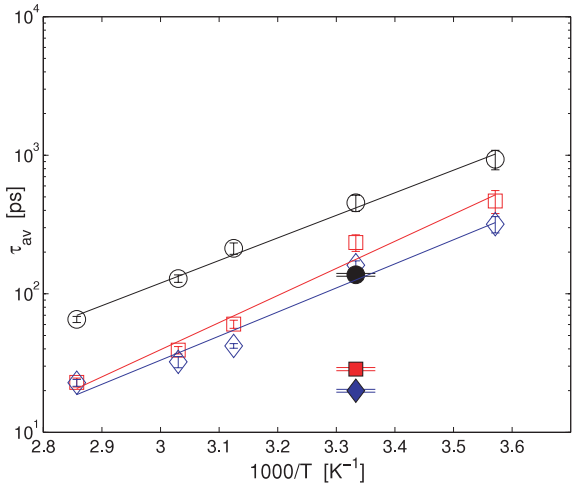


**Figure 6.** Arrhenius plot of the average relaxation time for the $H = 8.4$ wt% sample (open symbols) at the $Q$ equal to 0.49 Å$^{-1}$ (blue ◇), 0.95 Å$^{-1}$ (red □) and 1.17 Å$^{-1}$ (black ○) respectively. The relaxation times for fresh bread at 300 K are also shown (closed symbol) for the same $Q$ values. The full lines show fits by equation (5).

liquid water in bread crumb derived by the semi-empirical model in [11]. The present study gives $D_s = 2.8 \times D_{calc}$. It should be noted that the result of [11] is based on the evolution of the local hydration level at a number of different depths into the bread and does not exactly reflect the self-diffusion. This could indicate that a certain change in the water content by the NIR absorption technique of [11] does not exclude that the water molecules exhibit a faster random-walk-like dynamics. This could also imply that the structure of white bread has a larger fraction of closed pores than accounted for in present models.

In figure 6 an Arrhenius plot of the average relaxation times obtained at $Q = 0.46$, 0.95 and 1.17 Å$^{-1}$, respectively are shown for the $H = 8.4$ wt% sample.

The temperature dependence of $\langle\tau\rangle$ is fitted by the Arrhenius equation

$$\langle\tau\rangle = \tau_0 \exp\left(\frac{E_a}{k_B T}\right), \tag{5}$$

where $\tau_0$ describes the high temperature asymptote of the relaxation time and $E_a$ is the activation energy of the process. The mean value of the activation energy from the fitted data sets is $E_a = 14.8$ kJ mol$^{-1}$, which agrees with previous studies of confined water [22] but is about twice the activation energy for rotational relaxation of bulk water [19]. It is worth noting that water relaxations usually follow a non-Arrhenius behavior. However for narrow temperature ranges it is difficult to separate Arrhenius behavior from e.g. Vogel–Fulcher–Tammann behavior. Thus, whether the temperature dependence of the water dynamics in bread can be described by the Arrhenius law over a wider temperature range remains an open question.

## 4. Concluding remarks

This QENS study of water dynamics in low hydration and fresh white bread shows that the dynamics of water is well separated from the dynamics of the bread matrix. The water

relaxation is well described by a KWW function. From the analysis of the data a self-diffusion constant for water in fresh bread is obtained, $D_s = 3.8 \times 10^{-10}$ m$^2$ s$^{-1}$. This is the first time the self-diffusion constant of already-baked bread has been directly measured without destructive methods. The result is in agreement with findings from previous studies of similar systems but larger than previous models for water in bread suggest. This might indicate that the fraction of closed pores in the structure is somewhat larger than previously thought.

The different time scales of the water dynamics and the dynamics in the rest of the bread supports the conclusions of [14]. In that paper the same bread as is used in this study was investigated using broadband dielectric spectroscopy (BDS) and differential scanning calorimetry (DSC). It was shown that two relaxations of water were visible in the BDS spectra (though they become indistinguishable in the high temperature range of the present study) and that one of them coincided with a calorimetric glass transition observed for $H = 9$ wt% bread at $T \sim 175$ K. For low hydration levels ($H = 3.3$ wt%) no glass transition was detected and only one process was visible in the BDS spectra. It was concluded that the water clusters for those samples were too small for having any cooperative motions needed to produce a glass transition. The present study supports both that the dynamical processes in BDS spectra actually originates from water and that the dynamics of water for the lower hydration levels is very restricted. However, it should be noted that the water, even though being pure water, in these studies is strongly associated with the biopolymers of the bread and therefore exhibits properties far from those of bulk water.

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## References

[1] Wagner M, Lucas T, Le Ray D and Thyrstam G 2007 *J. Food Eng.* **78** 1167
[2] Noel T R and Ring S G 1992 *Carbohydr. Res.* **227** 203
[3] Tolstoguzov V 2002 *Crit. Rev. Biotechnol.* **22** 89
[4] Manley D 1998 *Manual 4 Baking and Cooling of Biscuits* (Cambridge: Woodhead Publishing, Abingdon)
[5] Hasatani M, Arani N, Harui H and Itaya Y 1992 *Dry. Technol.* **10** 623
[6] Lotsie M, Peczalski R, Andrieu J and Laurent M 2002 *J. Food Eng.* **51** 131
[7] Marston P E and Wannan T L 1976 *Bakers Dig.* **50** 24
[8] De Vries U, Sluimer P and Bloksma A H 1989 *Cereal Science and Technology in Sweden: Conf. Proc. (Lund)* p 174
[9] Thorvaldsson K and Skjöldebrand C 1996 *J. Food Eng.* **29** 1
[10] Thorvaldsson K and Skjöldebrand C 1998 *Lebensm.-Wiss. u.-Technol.* **31** 167
[11] Thorvaldsson K and Skjöldebrand C 1999 *J. Food Eng.* **40** 167
[12] Wagner M, Lucas T, Davenel A, Broyart B, Collewet G and Thyrstam G 2003 *Proc. ICEF9 (Montpellier, France)* p 469
[13] www.pagen.se
[14] Cerveny S, Schwartz G A, Bergman R and Swenson J 2004 *Phys. Rev. Lett.* **93** 245702
[15] Carlile C and Adams M 1992 *Physica* B **182** 431

[16] Kohlraush R 1847 *Ann. Phys.* **72** 393
[17] Williams G and Watts D 1970 *Trans. Faraday Soc.* **66** 80
[18] Tuck J, Hall P, Hayes M, Ross D and Poinsignon C 1984 *J. Chem. Soc., Faraday Trans.* I **80** 309
[19] Teixeira J, Bellisent-Funel M-C, Chen S H and Dianoux A J 1985 *Phys. Rev.* A **31** 1913
[20] Bellisent-Funel M-C, Teixeira J, Bradley K F and Chen S H 1992 *J. Physique* I **2** 995
[21] Smith L J, Price D L, Chowdhuri Z, Brady J W and Saboungi M L 2004 *J. Chem. Phys.* **120** 3527
[22] Takahara S, Nakano M, Kittaka S, Kuroda Y, Mori T, Hamano H and Yamaguchi T 1999 *J. Phys. Chem.* B **103** 5814