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Investigations of food colloids by NMR and MRI

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ABSTRACT

Since the publication of the ISO method for measurement of solid fat content using NMR relaxation at low field, the application of this technique to the characterisation of food composition and food structure on several length scales has expanded considerably. Improvements in the electronic and computational specifications of NMR spectrometers and the use of more sophisticated signal processing methods have led to several new applications, and NMR, previously recognized as a powerful technique to provide information regarding composition, is now widely used for microstructural investigations. Moreover, MRI applications have in recent years been extended from the medical field to food science and this has opened up new opportunities for the understanding of food. We examine here recent developments in these techniques, including NMR relaxation, multidimensional NMR relaxation, diffusion NMR and MRI.

Keyword: magnetic resonance imaging, NMR, relaxation, diffusion, food process, gel, emulsion

1 Introduction

The use of low field NMR spectrometers in the food industry began in the 70's with the commercial availability of the first benchtop NMR systems. Several applications were developed during the following years, but they were limited to the determination of water and fat content and measurement of the solid fat index. Surprisingly, the number of application did not increase much during the following twenty years. In 1992, the first International Conference on Applications of Magnetic Resonance in Food Science was organised, and since that time, with the improvements in benchtop NMR characteristics, new applications have been proposed. One of the most well-known is droplet size measurement. Moreover, the use of NMR relaxation time was proposed, not only for determination of water and fat content, but also for the investigation of food structure. Simultaneously, the use of magnetic resonance imaging techniques, in which the contrast in the image is governed by the NMR relaxation time, has emerged. MRI now is a powerful technique to monitor the composition and structural changes in foods during processing. This review focuses on the recent applications of low field NMR and MRI in food colloids and deals with recent advances such as multidimensional NMR relaxation and NMR diffusometry.

2 Solid and liquid-like relaxation

Most of the NMR relaxation studies on food colloids are performed with low magnetic field spectrometers typically operating at frequencies less than 25 MHz. Since the introduction of the benchtop low magnetic field NMR equipment in the 70s, the electronic and computational specifications have improved dramatically. Short, powerful excitation pulses now permit sampling of the relaxation decay curve from $11\mu s$ up to several seconds. The number of data points available (several hundred for Free Induction Decay (FID) and several thousand for the Carr Purcell Meiboom Gill sequence (CPMG)) and the fast sampling rate (20 MHz) are used for the simultaneous acquisition of the solid and liquid-like relaxation. Moreover, the use of continuous inverse Laplace transform methods has improved the understanding of relaxation behaviour in complex food products.

For T_2 relaxation, the signal is therefore directly fitted as a sum of Gaussian functions for the solid part and the sum of exponential functions for the liquid part:

$$Y(t) = \sum S_i \exp\left(-\left(\frac{t}{T_2}\right)^2\right) + \sum L_i \exp\left(-\frac{t}{T_2}\right) \quad \text{eq. 1}$$

However, the T_2 for the solid part is often very short (around 15 μ s) and the number of data available for the fitting is too small to allow multi-Gaussian fitting because of the limitation of the sampling rate of the acquisition board, so the solid part is mainly described by a single Gaussian function.

For a specific system with a highly structured solid phase such as lipid crystals in β polymorphic form, eq 1 becomes:

$$Y(t) = S \exp\left(-\frac{1}{2} a^2 t^2\right) \frac{\sin bt}{bt} + \sum L_i \exp\left(-\frac{t}{T_2}\right) \quad \text{eq. 2}$$

with the second moment M_2 calculated from the fitting parameters a and b with the following equation:

$$M_2 = a^2 + \frac{1}{3} b^2 \quad \text{eq. 3}$$

According to the chemical composition of the product, the signal for the Gaussian relaxation component can be attributed to non-exchangeable protons from solid fat, ice, protein and polysaccharides, whereas, the relaxation component from the liquid phase is generally attributed to protons from liquid water and liquid fat, and from exchangeable protons from biopolymers (proteins, carbohydrates or polysaccharides). The simultaneous acquisition of solid and liquid-like relaxation has been extensively used to improve significantly the accuracy of standard NMR applications such as solid fat content, and also to carry out quantitative analysis of NMR signals from complex products such as ice cream, cake, cheese, etc., leading to new NMR applications.

2.1 Solid and liquid fat relaxation

Determination of solid fat content is one of the most popular applications of NMR in the food industry. Nevertheless, this international reference method is based on very crude acquisition and data processing requiring the acquisition of a pair of data points (one at 11 μ s, which corresponds to both the solid and liquid part, and one at 70 μ s, which corresponds to the liquid part only). Following the work of Van Duynhoven et al. [1], Trezza et al. [2] recently, demonstrated that greater accuracy in the measurement of the solid fat content could be achieved from combined FID and CPMG acquisition and when the signal is analysed with semi-empirical mathematical functions for solid, semi-solid and liquid components. An extension of this method has also been proposed in order to adapt the method to non-

anhydrous fat products such as emulsions [3]. Indeed, in emulsions the contribution of non-fat solid-like protons such as non-exchangeable protein protons to the solid phase has to be taken into account. Moreover, this method (based on the fitting of both the FID and CPMG signal) which takes into account the relaxation time and the signal intensity can be used to assess the polymorphic composition of lipids. The free induction decay of the α polymorph was described by a monotonously decaying Gaussian function such as eq. 1, while for the β and β' polymorph an ‘Abragam sinc’ function was added (eq. 2). The results demonstrated that the NMR method was potentially the first technique to provide simultaneously the amount of the solid and liquid phase and the polymorphic state of the lipid. Parallel to the development of this T_2 -based approach, an investigation into the behaviour of the T_1 from the crystallised fat phase was carried out [4]. From an extended investigation of the effects of temperature and triacylglycerol chain lengths on the T_1 and the second moment M_2 , the authors proved the ability of NMR to determine the polymorphism of triacylglycerols regardless of temperature. For example, a ratio of 1.5 to 2 between the M_2 of the β form and the α form was observed whatever the triacylglycerol, while the T_1 values for the α polymorph were 15-25 times lower than for the β polymorph. The sensitivity of the T_1 relaxation time of the fat crystal organisation has previously been suggested in fat mixtures with added surfactant and in food emulsions. For example, wide variations in T_1 were observed according to the cooling rate of milk fat [5]. A shorter T_1 was observed for a faster cooling rate, and the T_1 was reduced when surfactants were added, compared to the T_1 from the dairy fat without surfactant. In dairy emulsions, a change in T_1 relaxation time of the fat crystal was observed according to the maturation temperature of the emulsion [6]. For a maturation temperature of 4°C a narrow T_1 distribution was obtained, whereas a bi-modal distribution was obtained for a maturation temperature of 12°C. Changes in the T_1 relaxation time of the crystallised phase of fat have been also reported in ice cream mix and ice cream [7]. The aim of the above study was to investigate the effects of the nature of fats, proteins and emulsifiers on the behaviour of the fats in the emulsion. Despite the high complexity of the composition and structure of ice cream and mixes, NMR relaxation times specific to fat protons have been extracted from the NMR signal. The results showed a decrease in the T_1 relaxation from the solid fat after emulsification according to the nature of the fat. Moreover, an effect of the nature of the emulsifiers and the protein on the relaxation time T_1 of the fat crystal was revealed. The authors suggested that the T_1 relaxation was explained by local disorder of the crystal

arrangement and by the size of the crystal and was related to the viscosity of the ice cream mixes.

Another improvement in the NMR relaxation method for the characterization of fat crystallisation has been proposed [8, 9]. Based on the Rheo-NMR method proposed by Callaghan for the measurement of a flow under shear, the authors showed that the NMR technique can be used for the *in situ* measurement of solid fat content under shear. A specific mini-Couette cell was developed to crystallise fat samples under shear. The cell was tested with blends of canola stearine and canola oil melted at 80°C, and then crystallised at 40°C under different shear rates inside the NMR spectrometer. This system should contribute to understanding of the effects of shear flow on the solid fat content of lipid systems.

Surprisingly, the behaviour of the signal from lipids in the liquid state has had little attention. In fact, the relaxation time of a mixture of lipids is often characterised by a wide continuous distribution of relaxation times both in T_2 and T_1 [10] and influenced by both the length of the carbon chain, and the amount of unsaturation [11] which complicates the interpretation of relaxation times of the lipid phase. Nevertheless, the use of chemometric methods has recently been proposed for the processing of T_2 relaxation decay of intact oilseeds instead of fitting methods [12]. The partial least square method was used directly on the CPMG data in order to predict the oil quality by its composition, cetane number, iodine value and kinematic viscosity. The use of NMR has therefore been proposed for the selection of high quality oils for biodiesel applications.

Lastly, the NMR solid fat method has also been extended to MRI to study lipid migration within chocolate [13-15]. In these experiments, only the liquid signal was recorded because of the limitations of echo times when using a spin echo technique. In fact, the T_2 from the solid phase (T_2 around 15 μ s) is too short to detect the solid phase. This limitation has recently been overcome by the use of a 1D centric SPRITE MRI method [16]. MR images from both the solid lipid and the liquid lipid can be acquired in a chocolate sample with this method. This new strategy will be very powerful to monitor the diffusion process of lipids in confectionery products.

2.2 *Ice relaxation*

The simultaneous acquisition of the solid and liquid-like relaxation decay signal has also been used to investigate the ice phase during freezing. For example, two components were identified in a binary sucrose solution for temperatures above -2°C [17]. The solid component was attributed to the non-exchangeable sucrose protons, and the liquid component was attributed to the water protons, the exchangeable sucrose protons and a fraction of the more mobile non-exchangeable sucrose protons. Below -2°C, which corresponds to the freezing temperature of water, the solid component described both the non-exchangeable sucrose protons and the ice protons. From acquisition of T_1 relaxation times, the authors demonstrated that the relaxation of ice protons can be distinguished from the sucrose protons. Variation in the ice T_1 relaxation time according to temperature exhibited the same behaviour as pure ice, whereas, the same authors demonstrated for the first time in a more complex product such as ice cream, that the ice relaxation time was affected by the protein types added to the formulation. The T_1 relaxation time of the ice was around 3600 ms for ice cream containing milk protein and between 1900 and 2200 ms for ice cream containing whey protein (Nollibel©). The difference was explained by the occurrence of defects in the ice crystal structure. These results open up new opportunities for the use of NMR in the characterisation of the ice in frozen food, which until now has been less fully investigated than the non-frozen water phase.

2.3 *Biopolymer relaxation*

The NMR relaxation behaviour of the solid components has also been investigated for biopolymers. For example, in milk protein mixture containing different amounts of lactose, two relaxation components were identified [18]. The short component was attributed to the non-exchangeable proton for the native protein casein, and the long component to the water proton and the lactose. Bi-exponential behaviour was also reported on T_2 for soy-protein isolate films. The short relaxation component with a solid-like behaviour was more sensitive to variations in water activity and glycerol content. The T_2 variations were related to the plasticizing effect on the biopolymer films [19]. The same solid-like behaviour was also reported in gelatine biopolymer films [20]. In these matrices two relaxation times were found for the biopolymer, one for the non-exchangeable protons and one for the exchangeable protons. However, the most fully studied system is still starch-based products. In the native state, the proton relaxation spectra of starch exhibit a complex multi-exponential behaviour

[21, 22]. In D₂O, the first relaxation peak at 10μs has been attributed to rigid amylopectin in the semi-crystalline lamellae, the relaxation peaks at 1 ms and 20 ms have been assigned to the mobile fraction of amylopectin in amorphous regions of the granule, and the longest relaxation time peak at 80 ms has been assigned to amylose. A decrease in the relative area of the semi-crystalline and the 1 ms amorphous amylopectin relaxation peaks was observed upon gelatinisation while an increase in the other two peaks was observed. In water, the starch protons exhibit a solid-like behaviour which becomes liquid-like after gelatinisation. NMR relaxation has therefore been extensively used to study the effects on the dynamic state of starch during processing such as the effects of storage temperature, water content and gluten content on starch retrogradation [23], and to investigate the gelatinisation process on rice starch [24]. The potential of NMR has recently been extended to the study of starch in complex systems containing fat and large amounts of sucrose such as cakes [25, 26]. For example, wide variations in the amount of gelatinised starch have been reported between the crust and the centre of madeleines [26]. The water gradient between the crust and the centre observed after cooking decreased during storage and was negligible after 15 days. Despite an increase in water content in the crust, no change in the starch relaxation time was observed for the solid-like component. However, an increase in the contribution of the solid starch component was observed in the centre and was related to the starch retrogradation. These results illustrated that careful analysis of the full NMR relaxation decay curves expands the potential of NMR, even in complex food system.

2.4 Water relaxation: a multiscale probe of food structure

The previous paragraphs have focused on improvements in NMR applications in analysis of the solid fraction of food colloids. However, the main NMR applications are based on the investigation of the water relaxation behaviour both from T₂ and T₁. Several studies have been undertaken to understand the mechanisms involved in the water relaxation rate. The main controversy concerns the relative importance of three mechanisms 1) the nature of the protein-associated water that contributes to the relaxation, 2) the contribution of the biopolymer protons exchanging with the water, and 3) the effects of the cross-relaxation between spin-lattice relaxation associated with water protons and biopolymer protons [27]. Using NMR CPMG T₂ dispersion [28-31] and quantitative analysis of the T₁ magnetic relaxation dispersion (MRD) [27, 32-36], it is now clear that the water relaxation can be explained by taking into account only two relaxation mechanisms, the protein-exchanging protons

relaxation and the relaxation from the internal water molecule. Moreover, analysis of ^1H , ^2H and ^{17}O MRD has demonstrated that the internal molecules involved in this mechanism are only marginally less mobile than the bulk water and should not be considered as “bound”, as they were for many years [33], and the number of water molecules is very small. For example, Venu et al [27] shown that a considerable difference in the MRD can be observed between a solution of pancreatic trypsin inhibitor and a mutant protein (G36S) lacking only one of the four internal water molecules. The water NMR relaxation in a biopolymer system has consequently to be interpreted as a probe of the biopolymer dynamics rather than a true measurement of water mobility.

Several applications have been proposed on the basis of the high sensitivity of the NMR water relaxation, i.e i) for measurement of water content with MRI, ii) for the investigation of changes in the food structure at a molecular level, iii) for the investigation of changes on a microscopic scale. Some aspects of these applications will be discussed and illustrated with some examples below.

2.4.1 Water relaxation and water content

The dependence of T_2 or T_1 on water content has been applied to determine oil and water content in fried food [37], to quantify the ice gradient in dough during freezing and thawing processes [38], to quantify water distribution during curd draining [39], and to monitor water ingress during rehydration of pasta [40, 41] and cereal-based products [42, 43], during drying of gelatine gels [44], and after cooking of pasta [45, 46]. An example of moisture loss during drying of gels is given in figures 1 and 2 [47]. The authors generated a simple calibration between solid content (expressed in °Brix) and the T_1 relaxation time (Figure 1) and a T_1 -null MRI sequence, which selectively nullifies the voxel with a specific T_1 value, and a specific solid content was used. In figure 2, the signal from regions with a specified solid content has been removed, clearly showing the concentration gradient across the sample.

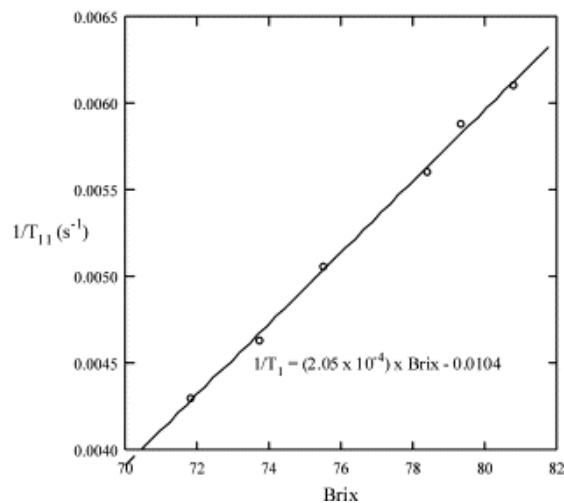


Figure 1 Calibration curve for ${}^{\circ}\text{Brix}$ and $1/\text{T}_1$ (data taken from [47]. Reprinted with permission).

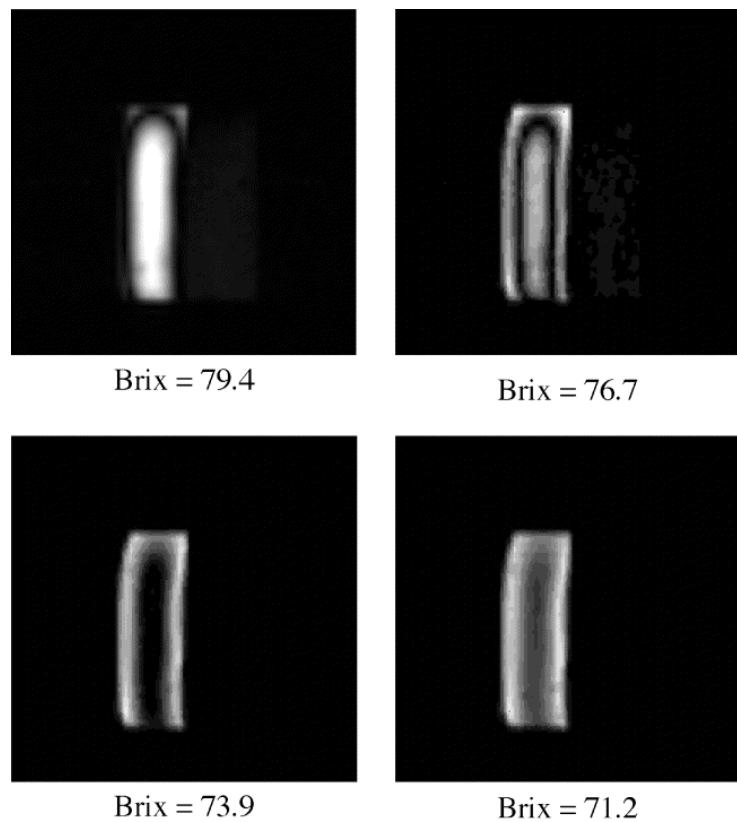


Figure 2 MRI transverse slice acquired with a T_1 -weighted sequence of a gel during drying. The parameters of the MRI sequence were chosen in such a way that a selective nulling of the signal within the gel was observed. The dark regions therefore correspond to systems having the solid content indicated. (data taken from [47]. Reprinted with permission)

2.4.2 Water relaxation and molecular structure

The dependence of relaxation on molecular structure has been extensively investigated in studies of changes in macromolecular food structure resulting from processing operations. The examples are numerous and have been extensively reviewed [48-50]. The water relaxation sensitivity to changes in the molecular dynamics of biopolymers has also been at the origin of MRI investigations into food processing operations. Consequently, if voxel intensity is T_2 value-weighted (T_2 -weighted images) information can be provided by MRI at a molecular level. However, since several processing operations induce concomitant changes in water content and molecular structure, which both affect the MRI images to a certain extent, care should be taken in the design of MRI protocols in order to provide correct interpretations of the grey level intensity of the images. It is nevertheless possible, using the appropriate MRI protocol to obtain spatial distributions on the scale defined by the voxel size (between 100 μm up to several millimetres) of structural changes on a molecular scale. This property has been widely exploited for the study of cheese ripening [51], potato frying [52], freezing-thawing effects in dairy gels [39], thermal coagulation of egg white [53] and egg quality [54, 55] and gelation of carbohydrate gels [56, 57], and during the evolution of the bread matrix during storage [58].

For such MRI applications, the results should be validated with specific NMR studies which provide clear descriptions of the variations in relaxation time parameters in relation to processing parameters [53]. For example, figure 3 describes the T_2 water relaxation time and the soluble protein concentrations in white egg according to temperature. Three phases can be distinguished to describe the T_2 variations. From 10 to 50°C, the increase in T_2 is related to temperature increase through an increase in the rotational mobility of both water molecules and protein molecules. From 50°C to 80°C the T_2 decreases. The decrease is explained by denaturation of the protein upon heating. Denaturation induces a decrease in rotational mobility probed by the T_2 relaxation. For this temperature range the T_2 evolution corresponds to changes in ovalbumin conformation, followed by its denaturation. Above 80°C, only temperature affects the T_2 values.

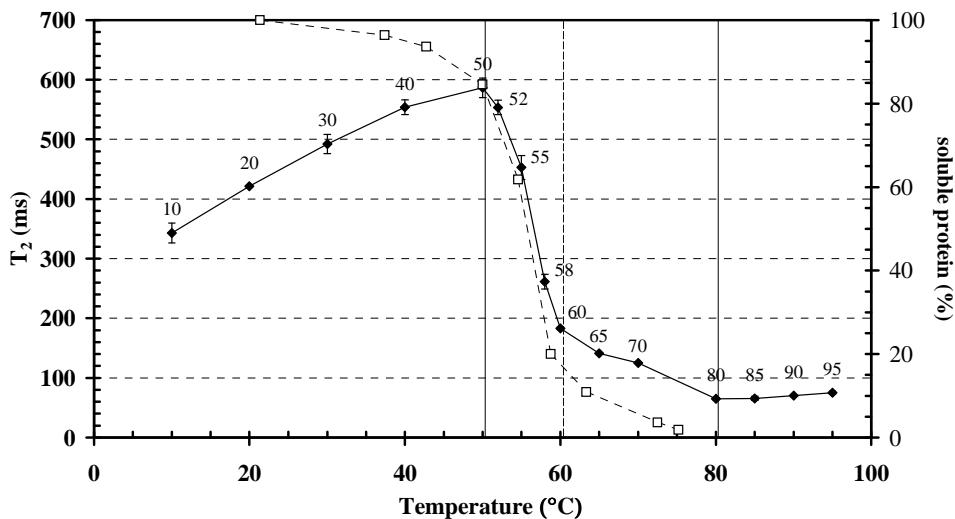


Figure 3 NMR T_2 relaxation and soluble protein concentration in egg white as according to temperature (data taken from [53]. Reprinted with permission)

A complete interpretation of the MRI T_2 cartography gradient observed during continuous heating of egg could therefore be proposed according to relaxation time behaviour upon changes in temperature (Figure 4). In this study the heating process was performed in one direction (from the top to the bottom), and the other walls of the container were insulated. At the beginning, uniform initial temperature (17°C) and T_2 values were observed. Eighteen minutes later, three areas could be distinguished, the first with T_2 from 450 to 550 ms which corresponded to an increase in T_2 because of the temperature. In this area the egg white was still liquid. The second area (from 550 to 250 ms) corresponded to the area where the egg white started to coagulate, and the third (with T_2 between 200 and 60 ms) was attributed to the cooked egg white with a temperature above 80°C . It should be pointed out that for a quantitative description of thermal processes, separate temperature mapping has to be performed in order to correct the T_2 value. This can be also achieved using MRI [59]

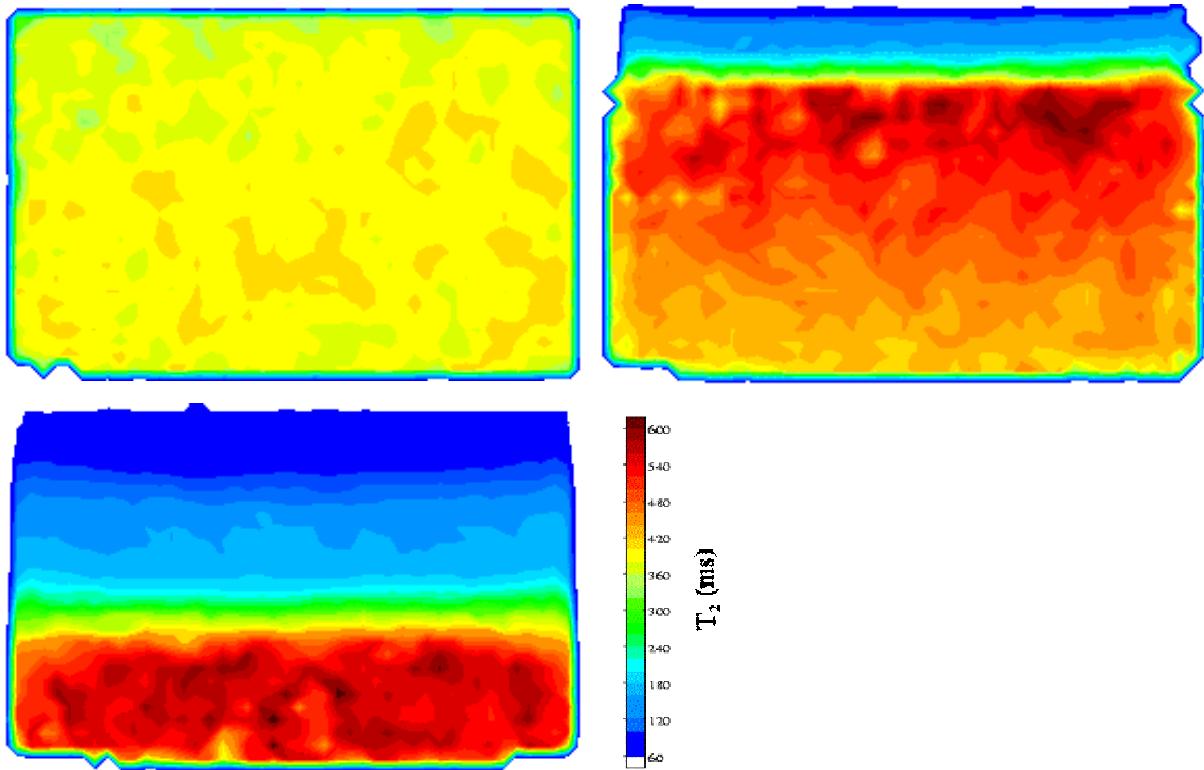


Figure 4 Transverse T_2 map of egg white during heating. All the surfaces of the beaker were insulated, and the heat exchanger was place on top of the beaker in order to limit convection flow. (data taken from [53]. Reprinted with permission)

2.4.3 Water relaxation and microscopic structure

The relaxation mechanism described above is only valid when the fast diffusive exchange limit is verified. In that case, because the exchange through thermal diffusion is fast, then the different water pool, the bulk and the hydration or internal water pool and the labile biopolymer are in exchange and the relaxation is the weight average of the three. Nevertheless, the T_2 from water can also be complicated by the effect of translational mobility characterised by the diffusion coefficient. If we consider two different environments (1 and 2) with a size a , where the NMR characteristics of water T_{21} and T_{22} are different, if the diffusion coefficient rate (D ($m^2 s^{-1}$)) is fast compared to the difference in relaxation rate ΔR_2 (with $R_2 = 1/T_2$), water relaxation will be average and a single mono-exponential signal will be measured. The NMR signal is given by :

$$Y(t) = A \exp\left(-\frac{t}{T_{2obs}}\right) \quad \text{eq. 4}$$

$$\text{with } \frac{1}{T_{2obs}} = \frac{P_1}{T_{21}} + \frac{P_2}{T_{22}}$$

On the other hand, if the diffusion coefficient is slow compared to the relaxation rate, then the water molecule will not be exchanged and the NMR signals will be characterised by several components, each with its own relaxation time. The NMR signal then becomes:

$$Y(t) = A_1 \exp\left(-\frac{t}{T_{21}}\right) + A_2 \exp\left(-\frac{t}{T_{22}}\right) \quad \text{eq. 5}$$

In this case each signal will be an NMR signature of the two local environments. The limit

between the fast and slow diffusion regimes is given by $\frac{a^2 \Delta R_2}{D} \ll 1$.

Multi-exponential behaviour has been reported in gels and emulsions when non-uniform water distribution was observed, and therefore water relaxation behaviour has been used as a probe of the microstructure or used to quantify the water holding capacity [60-62]. For example, in dairy products, changes in water distribution were observed during syneresis of a dairy gel [39]. A bi-exponential decay relaxation curve was observed and each component was attributed to the water expelled from the gel and to the water confined in the shrunk gel, respectively. Three water relaxation components have been identified in Mozzarella cheese, one for serum water, the water accumulated in the large open channels of the protein network, one for the water inside meshes of the casein gel-like network, and one for water trapped within the casein matrix [63]. A decrease in the T_2 from the serum was observed during aging, attributed to a change in the microstructure of the cheese, induced by the rearrangement of the protein network. In an imitation cheese matrix, the water relaxation was monitored at each stage of manufacture and the changes in water relaxation were described in a four-stage model of protein hydration/matrix development [64]. In rennet-derived retentates, the effects of the composition of the fat globule surface on water holding capacity have been studied [65]. Reconstituted fatty retentates were prepared from a fat-free retentate mixed with different fat-in-water emulsions stabilized with native phosphocaseinates (NPCs) or sodium caseinates. Coagulation of retentate reconstituted with native fat globules (fresh cream) and industrial fatty retentate was also investigated. The results showed that fatty products reconstituted from fresh cream and the industrial retentate presented lower water holding

capacity than that obtained with native phosphocaseinates (NPCs) or sodium caseinate emulsions.

A multiexponential relaxation behaviour for water has consistently been reported in native starch-water systems because of slow diffusive exchange [21, 22, 24, 66-70]. Four water populations have been identified in native starch, assigned to “channel water”, only observed in the B-type amylopectin crystal with a T_2 around 200 μ s, to water in the amorphous growth rings with a T_2 around 1 ms, to water in the semi-crystalline lamellae with a T_2 around 8ms, and to the extra-granular water with a T_2 longer than 30 ms [22]. Raising the temperature to 27°C causes merging of the two middle water relaxation components because of the fast diffusion of water between the amorphous growth rings and semi-crystalline lamellae. At higher temperatures, the relative intensity of this water population increases and the relaxation time decreases. This effect is explained by the swelling of the granules. Above the melting transition, the relative intensity of this component decreases considerably because of diffusion of the amylose out of the granule. Consequently, the effects of diffusive exchange between microscopic water compartments on NMR water relaxation provide a way to investigate changes during the processing of starch-based products such as non-enzymatic browning in dehydrated potatoes [71], the effects of gluten on recrystallisation kinetics [72], the effects of gluten on gelatinisation in white bread [73], the effects of storage on cooked rice grain [74] and the effects of water content and amylopectin crystallinity pattern on polymorphic gelatinisation [75], and during rehydration of breakfast cereals [76].

The multiexponential analysis of MRI liquid relaxation has not to our knowledge been carried out on food colloids. However, examples have been proposed for in vivo medical applications showing that bi-exponential fitting of the T_2 decay map improved the ability of MRI for quantitative measurements. This approach would be valuable for the characterisation of food products since most of them exhibit multiexponential relaxation behaviour.

3 Multidimensional NMR relaxation

The NMR applications described above are all based on the analysis of 1-dimensional conventional relaxation spectra. Although T_1 -filtered T_2 or T_2 -filtered acquisition has been performed for some specific applications, the data have always been processed with a 1-

dimensional Laplace inversion [77, 78]. The advent of a fast algorithm for 2-dimensional Laplace inversion [79] has recently led to the development of “multidimensional” NMR relaxometry. These types of measurement are valuable to improve the assignment of multi-exponential relaxation behaviour, and to study dynamic processes such as chemical exchange or diffusive exchange. For example, T₂-T₁ correlation and D-T₂ correlation experiments were performed on dairy products such as milk, yoghurt, cream and cheese [80]. For milk samples, a single peak was observed for both experiments and in that case the 2-D relaxation approach did not provide more information than a 1-D relaxation experiment. However, for the other samples a bi-modal distribution was observed for both experiments. The first peak was assigned to the water fraction and the second peak to the fat fraction. In T₁-T₂ correlation experiments the separation between the two relaxation components was still difficult and affected by the water content of the sample. Indeed, the results showed that the fat relaxation did not change with the chemical composition of the dairy sample, while the water relaxation associated with the water phase varied from sample to sample. Consequently, for a few samples an equal relaxation time value was observed for the two fractions thus preventing any separation of the two compounds. In contrast, the D-T₂ distribution functions improved separation of the water and fat features and, because of the large difference between the water diffusion and fat diffusion coefficients, this separation was independent of the chemical composition. This approach has been proposed for robust water and fat determination in dairy products. T₁-T₂ correlation spectroscopy has also been used to monitor the effects of high pressure and microwave processing on the microscopic water distribution and chain dynamics in starch-water systems and potato tissue [81]. This approach showed that high pressure-induced gels were radically different from the corresponding microwave heating-induced gels. For example, the T₂-T₁ correlation spectra for waxy maize starch showed only a shift for the two water peaks and for the mobile starch non-exchangeable proton after high pressure treatment. Whereas after microwave heating, the three peaks were similar to those of the untreated starch-water system, but in addition three new peaks emerged. Such methods present many opportunities for sample characterisation, but it is necessary to step back from the complexities of real food systems in order to assign the peaks to particular proton pools. As demonstrated by Marigheto et al [82], even in simple sucrose water solutions where complex T₁-T₂ spectra were observed, the assignment of the four peaks remained uncertain. The authors suggested that T₁-T₂ spectra can be used empirically as a “finger-print” for monitoring the complex changes associated with phase transformations.

4 Diffusion

We explained above how translational mobility can modify the relaxation decay curve from mono- to multi-exponential behaviour. Nevertheless, quantification of the diffusion coefficient from relaxation time experiments is still a challenge since the physical models used require several assumptions which often cannot be verified [83]. Consequently, other NMR and MRI techniques based on the use of an external magnetic field gradient are preferred because they do not require knowledge of the mechanism involved in the relaxation behaviour. These techniques are all based on the use of well-defined linear gradient pulses which change the strength of the magnetic field probed by the molecule's protons locally. Consequently, if a molecule diffuses spatially in this magnetic field gradient, the NMR signal is reduced: the faster the diffusion rate the higher the NMR signal reduction. A detailed description of this method, called pulsed field gradient NMR (PFG-NMR), q-NMR for NMR, and diffusion weighted MRI or diffusion tensor imaging (DTI) when using an MRI scanner, is provided by Price [83, 84]. The great advantage of MR diffusion spectroscopy and imaging is that quantitative measurement of the diffusion of water and metabolites can be performed non-invasively on a microscopic scale and in any direction of displacement. PFG-NMR is widely recognized as a powerful method to obtain microstructural information in emulsions [85, 86] and porous materials [87]. A routine PFG-NMR method has been proposed for the measurement of droplet size distribution in water/oil or oil/water emulsions [88-90]. The accuracy of the method has been widely debated for water droplet and oil droplet size determination in food emulsions such as butter, margarine and dressings [91-94]. Some extension of the method has recently been proposed for spatial determination of droplet size distribution from MRI data in emulsions [95] and to provide both real-time dispersion and spatially-resolved velocity measurements in a frozen drop of sucrose solution and emulsion [96]. However, the latter method requires the use of high field NMR spectrometers.

The PFG-NMR technique has also been used to study water mobility in different protein and polysaccharide systems. The water dependence on the protein concentration has been reported in casein and whey protein solution and gels [97, 98]. In both systems the water diffusion was reduced with increased protein concentrations in solutions and gels. The obstruction effect of the protein was explained by taking into account two self-diffusion flows: a water flow close to the protein backbone and a water flow around the casein micelle or globular whey proteins.

The effect of the change in network structure on the water diffusion coefficient was also investigated for casein gels. Independently of the method of preparing the gel, i.e acid or renneted gel, no difference in water diffusion was observed. However, heat treatment of the whey protein solution induced a slight reduction in the water diffusion. This was explained by a change in the accessibility of the whey protein aggregates to water. For casein, it was recognised that the overall accessibility to water was not significantly affected by the formation of a gel. The author concluded that water diffusion in protein systems follows a general trend whatever the protein system studied. The specific effects of casein and fat content on water diffusion have been outlined in a cheese model, and a general model describing the effects of water content on water self-diffusion has been proposed [65, 99]. This model includes the effects of aqueous phase composition, and the obstruction effects of casein and fat droplets on water diffusion. This model requires no structural information on the gel network since no effect of the structure has been observed, except when the water distribution inside the gel becomes heterogeneous and when the serum phase starts to release. A reduction in the water diffusion was observed in soya protein suspensions, according to the protein concentration. Moreover, the range of reductions observed was the same as that previously reported for whey protein suspension, which confirmed a general tendency to a obstruction effect induced by protein. After addition of calcium, the reduction in water self-diffusion measured in the precipitated of soy protein isolate was greater. The author suggested that in a suspension only the hydration and hydrodynamic interactions explained the change in the self-diffusion, while in the precipitate the obstruction effect of the protein particle has to be considered and included. Nevertheless, the author did not mention whether the water content was still the same in the precipitate and in the suspension. A slight difference in water content could explain difference in the water self-diffusion between the two systems.

In contrast to protein systems where slight effects of the protein structure on the water self-diffusion have been recorded, wide variations in water self-diffusion have been reported in starch suspensions according to the granule structure [100]. Anomalous water diffusion behaviour was found in the case of native starch. When the internal granule structure was destroyed by gelatinisation, the water diffusion conformed to simple unrestricted diffusion in 3D space. Moreover, a similar linear variation in the water self-diffusion related to the water content was observed for a fully heated wheat starch/water system, a fully heated wheat flour/water system and a fully heated rice starch/water system [101]. This suggests that the difference in microstructure after gelatinisation has little effect on the water diffusion. The

same tendency was recently reported during retrogradation of wheat starch gel [102]. The water self-diffusion of heat-gelatinised starch and ultrahigh pressured gelatinised starch stayed constant during storage despite retrogradation. Moreover, the change in water self-diffusion during storage of white bread crumb is mainly explained by moisture loss [103].

5 The future

Several studies are still in progress to improve the applications of NMR and MRI techniques to food colloids. Some of these, such as the use of multi-dimensional NMR relaxation are directly related to ways of manipulating the spin magnetisation , some involve the design of new magnet geometry such as the NMR-Mouse [104, 105], or open access systems such as the Halbach magnet [106], others involve the development of techniques to measure non-NMR parameters such as flow and rheological properties, referred to as velocimetry MRI or Rheo-NMR [107, 108], and others have proposed multi-sensor technology when NMR is associated simultaneously with other spectroscopy techniques such as NIR, impedance and ultrasound or scattering techniques [106]. Despite the development of MRI applications for food science, extrapolations to medical applications have been few, mainly because of the specificity of the different domains. However, some studies have demonstrated that in the future we will see greater levels of connection between food science and medical science and pharmaceutical applications. For example, a connection between the rehydration/dehydration processes for a food gel can be made with the monitoring of the controlled release and hydrogel volume erosion of an implant *in vivo* [109]. Other applications involve characterisation of food in the gastro-intestinal tract in humans and animals. Marciani et al. have used MRI to investigate the behaviour of lipid emulsions in the human stomach [110, 111]. Moreover, in order to improve the understanding of the relationship between meal viscosity and satiety, the T2 relaxation rate has been used to observe *in vivo* gelling of biopolymers in the stomach over time [112]. These recent studies demonstrate that promising new results can be expected from food MRI applications in the near future.

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** to date, the first in vivo investigation of gelation of polysaccharide in the stomach

* Of special interest.

** Of outstanding interest