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NMR Imaging in the Study of Diffusion of Water in Foods

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ABSTRACT

Most studies of moisture transport in foods and related polymeric materials have of necessity been integral experiments, for instance, the characterization of the drying of a food from the drying rate data only. Integral data are often insufficient to allow the investigation of the underlying physics of moisture transport, particularly in heterogeneous systems such as foods. Magnetic resonance imaging makes it possible to resolve spatially and temporally both moisture saturation and water self-diffusion coefficients. This information can then be used to determine effective transport coefficients, material structure, and material properties, and additionally to assist in the study of physicochemical processes.

Classical characterizations of moisture transport in food systems have employed integral techniques such as sorption–desorption or gravimetric analysis. These studies have proven useful for control of industrial processes, although they have failed to provide detailed insight or information on the role of material structure and properties in moisture transport. Magnetic resonance imaging is a new technology capable of providing measurements of component saturations and material properties on a spatially resolved basis. Through analysis and interpretation of

magnetic resonance imaging measurements it is possible to map internal structure, internal variations in transport rates, and internal variations in material properties such as membrane permeabilities. Nuclear magnetic resonance and magnetic resonance imaging can be utilized to measure the transport of mass by measuring molecular diffusion coefficients and/or by measuring internal gradients in component saturations. These two different data sets can then be applied to estimating the structure and properties of the material under study. This paper presents an introduction to magnetic resonance and outlines the strategy for characterizing moisture transport in food materials using magnetic resonance saturation profiles and self-diffusion measurements.

INTRODUCTION TO NMR IMAGING

The development of magnetic resonance spectroscopy began in the 1940s with nuclear magnetic resonance (NMR). NMR was independently discovered in the physics departments of Harvard University and Stanford University (Bloch, 1946), and is based on the interaction of a nuclear magnetic moment with an applied external magnetic field.

Many nuclei possess a nonzero angular momentum and therefore a magnetic moment. When these nuclei are placed in an external magnetic field, the magnetic moment is subjected to an applied torque which acts to align the magnetic moment with the applied external magnetic field. However, the resulting motion is a precession of the nuclear magnetic moment about the applied magnetic field. The frequency of the precessional motion is given by the Larmor equation:

$$\nu = \frac{\gamma}{2\pi} (1 + \chi)H \quad (1)$$

where ν is the frequency, γ is the gyromagnetic ratio, χ is the diamagnetic susceptibility of the material, and H is the applied external magnetic field strength. The Larmor equation provides the fundamental proportionality for NMR imaging; the frequency of precession is proportional to the applied magnetic field. The frequency can be controlled by controlling the spatial variations in the applied magnetic field. As the frequency is an observable in an NMR experiment, the spatial distribution of nuclear magnetic moments can be mapped through frequency variations:

$$\nu(\mathbf{r}) = \frac{\gamma}{2\pi} [(1 + \chi)H + \mathbf{G} \cdot \mathbf{r}] \quad (2)$$

where \mathbf{G} is the gradient and \mathbf{r} is position.

Bloch model

A complete description of the phenomena of magnetic resonance requires the use of quantum mechanics. However, for most applications of NMR imaging in water relationships in foods, the quantum mechanical model simplifies to a classical model first proposed by Bloch and thus called the Bloch model (Bloch, 1946). This model is the equation of motion for the nuclear magnetic moments, which is given as

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} \quad (3)$$

where \mathbf{M} is the net macroscopic magnetization in the sample and \mathbf{B} is the mean magnetic field within the sample ($\mathbf{B} = (1 + \chi)\mathbf{H}$). Solution of the Bloch equation predicts a precessional motion at the Larmor frequency for the nuclear magnetic moments. This equilibrium precessional motion can be disturbed by applying an oscillating orthogonal magnetic field at the Larmor frequency. After the oscillating field is turned off, the magnetic moments return to the equilibrium position. As the return to equilibrium is often exponential, Bloch added two time constants to his classical model to account for this:

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} - \frac{M_x \mathbf{i} + M_y \mathbf{j}}{T_2} - \frac{(M_z - M_0) \mathbf{k}}{T_1} \quad (4)$$

where T_1 is the spin-lattice or longitudinal relaxation time and T_2 is the spin-spin or transverse relaxation time.

The phenomenological Bloch model with relaxation assumes that the nuclei are stationary. The influence of diffusion or bulk flow of materials requires a modification of this basic model. The Bloch equations with diffusion terms were first derived by Torrey (1956):

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} - \frac{M_x \mathbf{i} + M_y \mathbf{j}}{T_2} - \frac{(M_z - M_0) \mathbf{k}}{T_1} + D \nabla \cdot \nabla \mathbf{M} \quad (5)$$

where D is the self-diffusion coefficient.

DIFFUSION MEASUREMENTS

NMR is one of the premier methods of measuring both the coherent and incoherent motion of matter. Coherent motion of a nuclear spin is governed by a deterministic velocity field. Both the laminar flow of fluids

and the plug flow of fluids are examples of coherent motion. Incoherent motion occurs when the movement of the spin is random and predictions of the movement are not precise. This occurs during diffusion. The NMR signal is influenced by both coherent and incoherent motion. Coherent motion is measured by its influence on the phase of the NMR signal and diffusive motion is measured through its attenuation of the NMR signal.

The typical method of measuring diffusion coefficients is to use pulsed-field-gradient (PFG) techniques (Stejskal & Tanner, 1965; Callaghan, 1984; Stilbs, 1987). Detailed analyses of this pulse sequence are available (Carr & Purcell, 1954; Woessner, 1961; Kärger *et al.*, 1988). For this paper, only the results of the analyses will be quoted. The spin echo intensity is attenuated by diffusion when the gradient has a nonzero value. The attenuation is generally recorded relative to the echo height when the gradient strength is zero. The ratio is a function of the diffusivity and pulse sequence parameters; for liquids, it is given by

$$R = \exp[-\gamma^2(\delta g)^2 D(\Delta - (\delta/3))] \quad (6)$$

The diffusivity, D , is calculated from the slope of a line through many data points generated by varying δ , Δ , or g^2 . The adjustable experimental parameters are: τ — the time between the 90° and 180° pulses, Δ — the time between the pulsed gradients, δ — the duration of the gradient pulses, and g — the strength of the gradient. If Δ is varied, care must be used to account for T_1 and T_2 relaxation.

Variations on this basic PFG experiment include using a stimulated echo for species with fast spin-spin relaxation rates and the use of echo attenuation to characterize sample microstructure. When molecules are restricted with regard to the extent of diffusive motion, the echo attenuation becomes independent of Δ ; this situation is called restricted diffusion.

In foods, the potential factors influencing diffusive measurements include impermeable boundaries (ice crystals, solids and droplet interfaces), permeable boundaries (membranes), and phase changes (vaporization during drying). The equations for describing some of these phenomena have been derived but some have not. Thus, care must be exercised when applying a solution to a case of restricted diffusion, to ensure that the correct mathematical description is applied. This is especially important in food systems, as the influence of food microstructure on diffusion should span the entire range from almost no influence to a complete restriction of the motion.

SATURATION MEASUREMENTS

NMR methods are sensitive to the density and state of NMR-active nuclei (protons, most commonly). Correct use of NMR data in the study of moisture transport requires a clear understanding of what is being measured. Two basic issues are considered in this section: what the signal means and what can it be used for.

Interpretation of the NMR Signal

The issue of the length scale of the measurement technique as compared with the length scale of the process itself is central to correct use and interpretation of measurements made in multiphase systems. In NMR, for example, routine imaging measurement of water content in cheese will not reveal significant variations in a cross-section (though relaxation-weighted images may). This is because the length scale over which significant changes in moisture content occur (the diameter of a cell) is much smaller than the length scale of the image (either the pixel size or the slice thickness). NMR imaging in this instance serves to smooth out local or small-scale variations in proton density and thereby reports averaged density profiles in the cheese. Though the cheese is microscopically heterogeneous, it appears to be macroscopically homogeneous as a result of the way in which the NMR images are made. The process of spatial smoothing is analogous to temporal smoothing (or averaging) in studies of turbulence and turbulent flow. Small-scale (rapid) fluctuations are filtered out so that the mean behavior of the flow field can be observed. Thus, NMR imaging acts as a spatial filter to even out the small-scale fluctuation in proton density. The physical basis, as well as in-depth analysis of spatial smoothing, has been the subject of intense development during the past 25 years (Whitaker, 1967; Marle, 1982; Baveye & Sposito, 1984). A spatially averaged quantity may be defined by

$$\langle \Psi_{\beta} \rangle = \frac{1}{V_{\beta}} \int_{V_{\beta}} \Psi_{\beta} dV \quad (7)$$

Physically, the averaging process given in eqn (7) corresponds to calculating the mean of a quantity $\langle \Psi_{\beta} \rangle$ (e.g. density, temperature or pressure) over the volume of the β -phase contained within the averaging volume, V . Central to this definition is the specification of the size of this averaging volume. Without such a specification, the averaged quantity is

somewhat fuzzily defined. An alternative definition can be given in terms of a weight function (Marle, 1982; Baveye & Sposito, 1984):

$$\langle \Psi_\beta \rangle = \int_{\mathbf{r}} \Psi(\mathbf{r}) I_\beta(\mathbf{r}) m(\mathbf{x} - \mathbf{r}) d^3\mathbf{r} \quad (8)$$

The weight-function approach to defining averaged quantities has been adopted by Baveye and Sposito in their proposal of the relativist view of multiphase transport. The relativist point of view attaches physical meaning to the weight function, $m(\mathbf{x})$, in that the weight function should represent the totality of the measurement. Finding an explicit expression for the weight function that characterizes an instrument used for multiphase measurements allows one to be specific about the length scale of the measurement (Cushman, 1986, 1987). In a sense, knowing the weight function is equivalent to knowing the size of the averaging volume in the definition in eqn (7).

The motivation that drives the intense scrutiny of the definition of a multiphase quantity is that the definitions given in eqns (7) and (8) can be used to derive rigorously transport equations for averaged quantities (Whitaker, 1980; Baveye & Sposito, 1984). The spirit of the relativist approach is that if transport equations are derived with the weight function(s) that characterize the instruments used to make experimental measurements, there is a solid base for comparing predictions of theories and the realities of experiments. Although useful in concept, there are still a number of issues to be resolved before a complete implementation of the relativist approach can be made routine. The primary results of this approach are a knowledge of the length scales involved in the measurement process. These scales are very helpful in identifying what is going on in an experiment with respect to what instrument is used for the observation. Additionally, a knowledge of the length scale of observation permits definition of the terms macroscopic, microscopic, homogeneous, and heterogeneous with respect to the instrument used for measurement. If a material is macroscopically homogeneous, there are no gradients in the macroscopic (or averaged) quantities that can be observed. Therefore, no macroscopic transport processes occur. Measurements on finely divided materials would probably qualify for this type of system. Though they may have small-scale structure, these materials are constructed so that they present no significant internal transport resistances (e.g. the Biot numbers are large) and they consequently appear uniform from a large-scale point of view. The usual experimental application of a macroscopically uniform specimen in drying studies is for equilibrium or

steady-state measurements (e.g. measurement of sorption isotherms). NMR imaging is not really needed in such a study (except, perhaps, to verify the assumption of uniformity), as the macroscopic profiles are not of interest. Because the sample is characterized everywhere by a single physical state, standard NMR spectroscopic measurements would suffice for the determination of relaxation times, diffusion coefficients (free or restricted), and density. However, it is of vital importance that the sample be macroscopically homogeneous for these measurements.

NMR imaging is most effective when used with macroscopically heterogeneous (non-uniform) samples. In such instances, the goal is to observe transport of averaged quantities and to identify large-scale transport mechanisms. For example, drying of thick specimens (wood, or large pieces of food) involves the existence of macroscopic moisture profiles in the material. As most NMR parameters depend to some extent on the moisture content, standard NMR measurements (without imaging) would lead to erroneous results if uniform specimens were assumed. A critical step in the use of an NMR imaging measurement is to verify that indeed the length scale on the measurement does exceed the local scale of the microstructure but does not exceed the length scale of the variation of large-scale quantities. Although the averaging of local fluctuations is a desirable process, if the averaging is carried too far, significant changes in the large-scale profile will be lost. On the other hand, if the instrument scale is too small, there will be excessive noise in the measurement that will require further filtering (smoothing).

The separation of scales in such measurements is not simple to determine, and the area is still evolving. However, separation in the scales by a factor of 10 should be sufficient unless there are countervailing circumstances. For example, if the heterogeneities in a sample are 50 μm , the imaging measurement should not attempt resolution smaller than 0.5 mm and the sample should be at least 5 mm. Problems can still occur if there are sharp gradients in the material. In such cases, length scale arguments are difficult to apply, so that strict adherence to such an approach may not be appropriate. Additionally, if the process does not have a well-separated length scale (e.g. it may be fractal-like), the spatial averaging approach becomes untenable. The determination of the scale on which a measurement has been made has thus been shown to be a critical factor in the use and interpretation of data in evaluating effective transport coefficients. For NMR, the length scale of the measurement can be evaluated with recourse to the Bloch equations and models of the pulse sequence used to generate the measurements. For spin-warp type sequences, this has been carried out (Maneval *et al.*, 1990a) with the

following final results:

$$\lambda_{sp} = \text{slice thickness} \quad (9a)$$

$$\lambda_{pe} = L/(N-1) \quad (9b)$$

$$\lambda_{fe} = 1/\gamma G_{fe} T_2 \quad (9c)$$

Two out of the three weight-function length scales are under the control of the experimenter. In the instance of the selective pulse (eqn (9a)), field gradient strength may be varied to change slice thicknesses, whereas in the case of phase encoding (eqn (9b)), the ability to acquire as many points in the allotted experiment time is the practical limit on what length scale is ultimately obtained. The length scale in the frequency-encoded direction (eqn (9c)) is controlled by sample characteristics in much the same way that the line width in a spectroscopy experiment is. Weight functions and length scales for other types of sequences (e.g. echo-planar techniques (Guilfoyle *et al.*, 1991)) can be found through suitable models of the respective pulse sequences. However, as phase- and frequency-encoding operations are common to most sequences, simple estimations based on the relevant encoding mechanism should be satisfactory.

Estimation of effective transport coefficients

Because NMR can directly measure translational motion, it has the capability of measuring diffusion coefficients *in situ* (see above section on diffusion measurements). Thus, the following discussion is divided into two parts: one part deals directly with the use of NMR imaging data to calculate effective diffusivity and the other considers the role of q-space techniques. If the goal of an experiment is to calculate the concentration dependence of a diffusivity, all that is needed is a well-defined measurement of the concentration profile and the mass flux for the profile. In view of the previous discussion, it should be clear that the calculated diffusivity is tied to the concentration and the length scale on which that concentration is measured. To produce data that are intrinsic to the physical process of interest (and not caused by an artifact of the experiment setup), it is important to ensure that the criteria with respect to length scales have been met. For example, if an experiment is constructed with a steady flux of moisture through a sample, measurement of the concentration profile through the specimen can be used to evaluate the concentration dependence of the diffusivity (Crank, 1983). Thus, if the flux (J_0) and the concentration profile ($C(x)$) are measured, the

diffusivity can be obtained through the following relationship:

$$D(x) = D[C(x)] = -J_0 / (dC/dx) \quad (10)$$

The work of Crank provides a good review of method that use measured profile data to estimate diffusivity in homogenized samples (i.e. samples in which the length-scale criteria are met). The use of NMR imaging measurements in this way generates diffusivities applicable to models of large-scale transport processes and is thereby of value in the engineering design of systems and equipment. Recently, another imaging approach, termed q-space imaging, has been proposed to measure diffusive motion in a sample. In q-space imaging, the NMR signal is made sensitive to spin displacements (such as might occur as a result of diffusion or convection) so that diffusion coefficients (both molecular and effective) can be 'imaged'. The q-space image provides another look at the dynamics of a specimen and may be used in tandem with standard spin-warp (also termed k-space techniques if the sample is macroscopically non-uniform). In such instances, data processing issues may limit the extent of the applications of the combined q-k space technique (Callaghan, 1991). When placed on the same spatial basis, it seems that there should be an interrelation of the diffusivity determined from the concentration profile (eqn (10)) and the information on the motional spectrum that is summarized in the q-space information at the same set of points. For example, in the development of models for predicting effective diffusivities in catalyst particles (Ryan *et al.*, 1982), it can be shown that the effective diffusivity tensor is determined by the molecular diffusivity (D) and the geometry of the particle,

$$\mathbf{D}_{\text{eff}} = D \left[\mathbf{I} + \frac{1}{V_\beta} \int_{A_{\beta k}} \mathbf{n}_{\beta k} \mathbf{f} dA \right] \quad (11)$$

where the vector, \mathbf{f} , is determined from models of the solid phase. As a paradigm, eqn (11) shows that the large-scale or effective diffusivity is determined by processes and structure on smaller scales. Thus, if there is information on both the large and small scale for the same material, the experimenter is potentially in a position to estimate both sides of eqn (11) and thereby provide a stringent test of the theory that led to eqn (11). With respect to measurements of transport phenomena in foods (and drying of foods, in particular), current efforts to produce the analog to eqn (11) are in only the preliminary phase. A major reason for this lies in the fact that there is a dearth of experimental techniques that can be used to help justify simplifying assumptions in the development of the

theory (Crapiste *et al.*, 1988). It appears that the coupling of NMR imaging measurements for generating large-scale diffusivities with q-space techniques that provide small-scale structural information will be a promising area of research in the future.

APPLICATIONS

Schmidt and Lai (1991) have recently reviewed applications of PFG diffusion measurements and NMR imaging saturation measurements in food systems. The applications discussed in this section will primarily be studies published since their review.

Diffusion measurements

Diffusion of water in foods and model food systems is influenced by the structure of the system and interaction of the water with macromolecules. For example, in macromolecular suspension, the diffusion of water is influenced by solvation and obstruction (Schmidt & Lai, 1991). The sensitivity of the diffusivity to structure has been used to explain the differences between the PFG determined diffusivity and the effective diffusivity calculated from gravimetric and sorption-desorption methods (Watanabe & Fukuoka, 1992; Watanabe & Yoshida, 1992; Weisser & Liebenspacher, 1992). In rehydration of soybeans, the length scale of the PFG study is 6 μm , whereas for gravimetric studies it is of the order of 270 μm (Watanabe & Fukuoka, 1992). Thus the influence of long-range structure is captured with the gravimetric measurements. Some of the variation in diffusivity values between methods may also be due to transient conditions occurring during adsorption processes (Weisser & Liebenspacher, 1992).

PFG measurements on moisture diffusion in soybeans have shown a curvature of the $\ln(R)$ plot, indicating restricted diffusion (Watanabe & Yoshida, 1992). Hills and Snaar (1992) have recently described an approach utilizing q-space microscopy to obtain both structural and dynamic information on moisture transport in cellular tissues. The q-space microscopy approach will be particularly important for testing theories of moisture transport in cellular systems.

Estimation of effective coefficients

Only a few studies have been performed to estimate effective diffusivities from NMR imaging saturation measurements (Maneval *et al.*,

1990*b*; McCarthy *et al.*, 1991; Ruan *et al.*, 1991; Schrader & Litchfield, 1992). Figures 1-3 are NMR imaging saturation profiles during drying in an unconsolidated bed of glass spheres during the constant-rate period, the falling-rate period and the receding-front period, respectively. The majority of these studies have applied Fick's second law and fit the saturation profiles, like those shown in Figs 1-3, to obtain an effective diffusivity. The work by Maneval *et al.*, 1990*b*) is the most extensive in terms of using MRI saturation measurements to test closure schemes proposed to explain drying. Results of this work indicated that the model

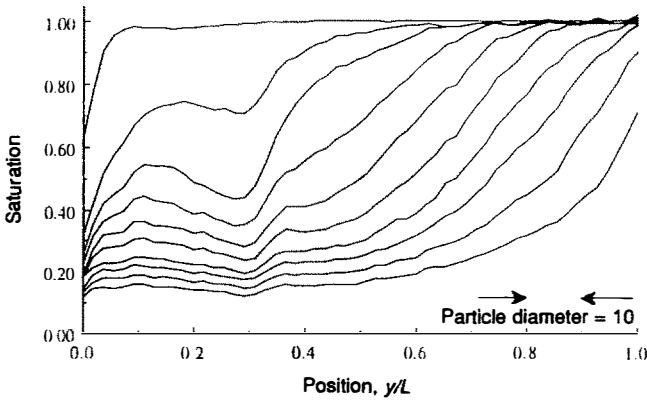


Fig. 1. MRI saturation profiles during the constant-rate period (particle size 0.45 mm, bed depth 45 mm). Profiles were measured every 90 min.

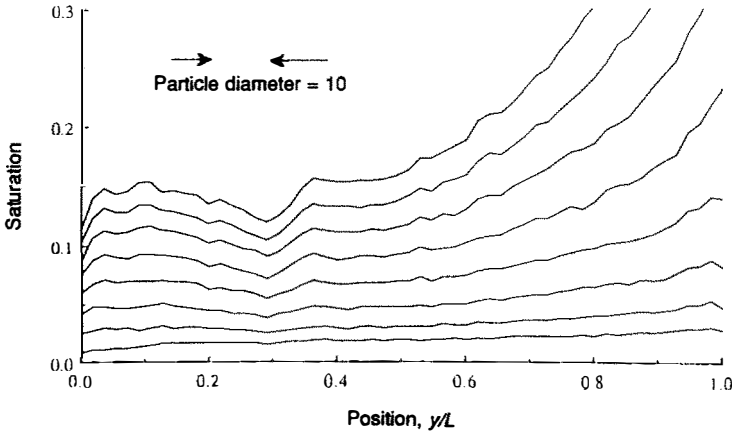


Fig. 2. NMR imaging saturation profiles during the falling-rate period (particle size 0.45 mm, bed depth 45 mm). Profiles were measured every 20 min.

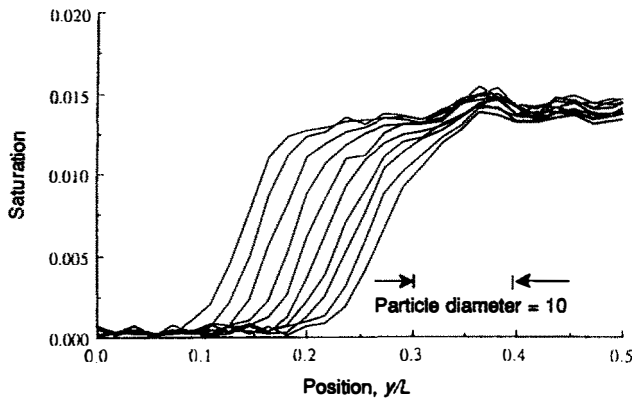


Fig. 3. NMR imaging saturation profiles during the receding-front period (particle size 0.45 mm, bed depth 45 mm). Profiles were measured every 50 min.

proposed by Schulünder (1988) provides a good description of the constant-rate period and the model by Maneval and Whitaker (1988) provides a good description of the first falling-rate period.

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