# Interpretation of the Magnetic Resonance Imaging Signal from a Foam

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Foams are important in a variety of industries including food, petroleum and chemical processing. Recently several research groups (Assink et al., 1988; German and McCarthy, 1989) have demonstrated the effectiveness of measuring vertical phase density in foams as a function of time by magnetic resonance imaging (MRI). The advantage of using MRI for studying the stability of such multiphase systems lies in the ability to uniquely determine the density as a function of position noninvasively. Data obtained from these experiments should prove to be a sensitive test of theoretical models of these systems. The objective of this communication is to describe difficulties associated with interpretation of the MRI signal from foams.

Nuclear magnetic resonance (NMR) spectroscopy is one of the premier methods for probing the chemical structure and identity of molecules. This spectroscopy is based on the interaction of the magnetic properties of nuclei with an applied external magnetic field. Nuclei which possess nuclear spin angular momenta are NMR-active. When these nuclei are placed in an external magnetic field, they precess as magnetic dipoles with a frequency given by the Larmor relationship:

$$\omega = -\gamma \boldsymbol{B}_o \tag{1}$$

where

$\omega$ = angular frequency of precession
$\gamma$ = gyromagnetic ratio
$\mathbf{B}_o$ = external magnetic field strength

Each nuclei's local external magnetic field is a combination of the external applied field and the sum of the magnetic field produced by nearby dipoles. Hence, the dispersion of the frequency response is sensitive to structural and chemical features of the sample. The dispersion in the frequency response for hydrogen is typically on the order of several ppm of the external field.

Magnetic resonance imaging is an extension of standard nuclear magnetic resonance spectroscopy. MRI was initially developed as a medical diagnostic probe. In addition to the application of a homogeneous external magnetic field, pulsed linear magnetic field gradients are applied to produce a frequency variation across the sample which can be converted into spatial coordinates. For instance, if we apply a gradient in the x direction, $\boldsymbol{G} = \partial \boldsymbol{B}/\partial x$, then the precessional frequency becomes a function of the sum of the homogeneous field and the linear gradient:

$$\omega = -\gamma(\boldsymbol{B}_o + \boldsymbol{G}x) \tag{2}$$

The frequency spectrum can be converted by using Eq. 2 into a position-dependent signal intensity. By the proper application of gradients, one-, two- or three-dimensional mappings of the NMR signal intensity can be recorded.

In nuclear magnetic resonance, there are two primary time constants which characterize the return of the experimental system to equilibrium: the spin-lattice relaxation time constant, $T_1$; and the spin-spin relaxation time constant, $T_2$. The spin-lattice time constant characterizes the exchange of energy between the excited nuclear spins and their surroundings (the lattice). Spin-lattice relaxation is typically described by an exponential decay in the signal strength. Spin-lattice relaxation time constants are usually between 0.1 and 1.5 s for hydrogen in aqueous biological solutions (Mansfield and Morris, 1982). Spin-spin relaxation describes the process of energy exchange between adjacent nuclear moments without the exchange of energy with the lattice (Gadian, 1982). This relaxation process normally is described well by an exponential decay with a time constant less than or equal to the spin-lattice relaxation time constant (Slichter, 1980).

For desired signal to noise ratios, the nuclear magnetic resonance experiments are generally repeated and the results added together. If the experiments are repeated faster than five times the spin-lattice time constant, the signal intensity becomes

weighted in a fashion similar to the saturation recovery experiment

$$S\alpha\rho[1 - \exp(-PD/T_1)] \tag{3}$$

where

$PD$ = delay between successive experiments
$\rho$ = nuclei density
$S$ = signal intensity in the saturation recovery experiment

This situation is complicated in imaging experiments where a spin echo is generally used to refocus the magnetization (this eliminates interference from gradient switching and r.f. pulses), and the signal intensity depends upon the specific experimental procedure (Morris, 1986). In the most basic Hahn spin echo experiment, the signal intensity after the spin echo is a function of the nuclei density, the experimental delay between excitation and refocusing pulses, $\tau$, and the spin-spin relaxation time constant

$$S\alpha\rho \exp(-2\tau/T_2) \tag{4}$$

The most general situation results, when the signal intensity depends on both time constants. For the MRI experiments used to date (Assink, et al., 1988; German and McCarthy, 1989) to measure foam drainage, Eq. 4 is a good first approximation of the signal intensity.

A one-dimensional mapping of the signal intensity is used in this study to follow the change in signal intensity and hence foam density with time. The influence of relaxation phenomena on the signal intensity is demonstrated and the procedure for correcting the signal is discussed.

## Experimental Method

For the fresh egg white foams, whites from Rhode Island Red hen eggs were used. The reconstituted egg white was made from dehydrated egg white (Henningsen Foods, Inc., Omaha, NE) and distilled water. The reconstituted egg white had a 12.5% solids content. The foam generation procedure was the same for both the fresh and reconstituted whites. 60 mL of the whites were whipped for 2 min with a hand-held mixer (Sunbeam). A portion of the resulting egg white foam was place in a 5-cm ID,, 5-cm-deep cylindrical sample cell. Within one minute of the completion of whipping, the foam sample was inserted into the spectrometer. $^1$H spectra were recorded with a birdcage coil (0.15 m ID) at 85.5 MHz on a two-tesla Oxford magnet and a CSI-II multinuclear spectrometer with imaging system (General Electric Medical Systems). A Fourier Imaging spin echo pulse sequence was used. One-dimensional projections were acquired by turning off the phase encode gradient. Spin-spin relaxation times were measured using a Hahn spin echo technique. Response of the receiver coil was found to be linear within experimental error.

## Results and Discussion

Shown in Figure 1 is a plot of the MRI signal intensity from an egg white foam as it drains. The MRI signal intensity is initially uniform and subsequently changes in time as the foam drains. The MRI signal intensity of the egg white foam is a function of both experimental parameters and time constants for relaxation.

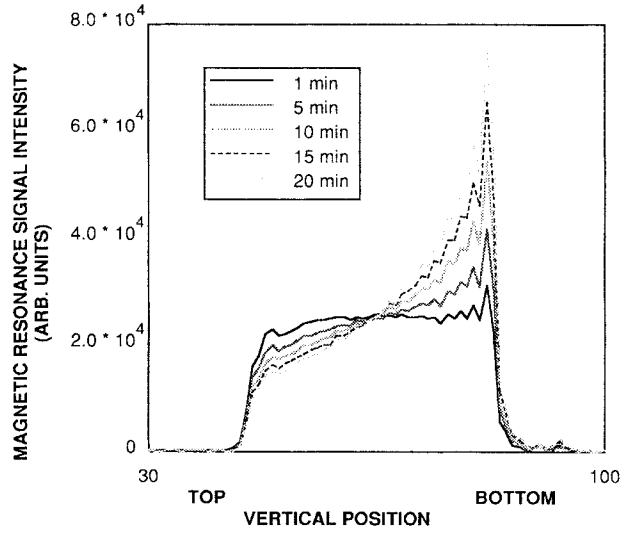


**Figure 1. Magnetic resonance signal intensity as a function of vertical position from a draining egg white foam for 1, 5, 10, 15 and 20 min.**

Assink et al. (1988) have previously shown that the response of the radio frequency coil needs to be calibrated. This can be accomplished by using a water-filled sample tube and mapping the response of the coil. Thus, the signal intensity from an unknown sample can be corrected for the nonlinear response of the receiver coil. In addition, the signal may need to be corrected for the effect of relaxation parameters. If the $T_2$ varies as a function of position within the sample and $\tau$ is not small compared to $T_2$, then the signal would need to be corrected to obtain accurate information.

In order to correctly determine the density of the egg white foam, the variation of the spin-spin relaxation time constant within the foam must be measured. The spin-spin relaxation time constant as measured by the Hahn spin echo technique varies as a function of time and position as shown in Figures 2 and Figure 3. Additionally the hydrogen spin-spin relaxation times within the foam are significantly different from those in the liquid, for instance, in the rehydrated egg white, the liquid spin-spin relaxation time is 120 ms, and the foam relaxation time is between 5 and 25 ms. In general, at each plane perpendicular to gravity within the foam, the spin-spin relaxation time increases with time and at each time interval the spin-spin relaxation time increases with density. Clearly, in order to quantitatively compare the drainage profiles in time we need to correct for relaxation effects when $T_2$ is not much greater than $2\tau$.

The recorded signal intensity and the signal intensity corrected for spin-spin relaxation effects are plotted in Figure 4. The corrected signal intensity is obtained by acquiring two one-dimensional projections with different echo delays (TE) and solving for the spin-spin relaxation time and the density at each spatial position using Eq. 4. This procedure has a significant limitation in that we assume only one time constant is needed to describe the initial spin echo decay of the signal. If the spin echo decay of the system cannot be initially described by a single exponential, then three or more spin echos would need to be

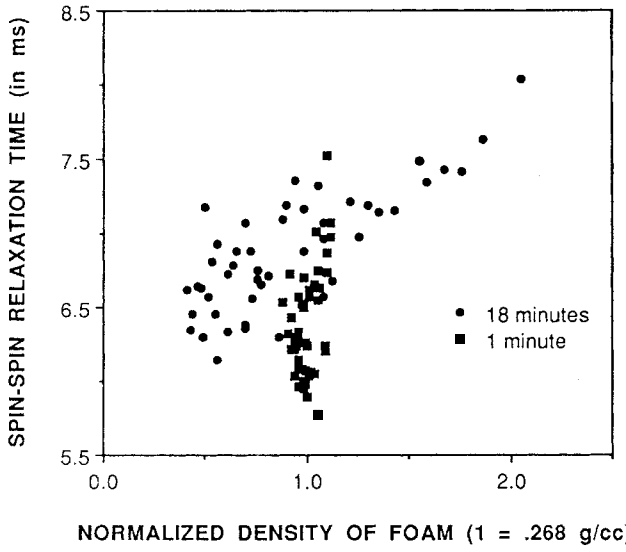


**Figure 2. Spin-spin relaxation time in a reconstituted egg white foam as a function of density of the foam.**

acquired to correct the signal relaxation effects during the experiment.

The differences in the density profile and the NMR signal intensity profile are somewhat significant for the egg white foam. Most importantly, the difference in relaxation times of the foam and the liquid could introduce large errors in predicting liquid density and drainage rates, if uncorrected signal intensities were used for analysis. The magnitude of the correction will depend upon both the experimental pulse sequence and the properties of the experimental system. For instance, the stabilized aqueous foam studied by Assink et al. (1988) did not exhibit a spin echo signal intensity that depended on differences in spin-spin relaxation between the foam and the liquid (Assink, 1989). This would occur in systems that had spin-spin relaxation times much greater than the time delays in the spin echo pulse sequence. For accurate interpretation of the MRI signal, both the spin-lattice and spin-spin relaxation time constants should be measured as well as the response of the receiver coil.

The signal intensity of a spin echo can be affected by relaxation, flow, diffusion and exchange processes. As the aqueous phase drains or the molecules diffuse in the foam, the nuclei will experience changing magnetic fields, since they are moving through an applied gradient. This results in a loss of phase coherence and hence a decrease in the signal amplitude. In rapidly draining foams, it is expected that flow effects would dominate the observed spin-spin relaxation behavior. An estimate of the influence of the diffusion and flow effects can be made by using the results of Carr and Purcell (1954) and estimating the field gradient experienced by the flowing liquid. The contribution from diffusion in a fresh egg white foam is about 5% of the spin-spin relaxation rate (rate = $1/T_2$) and the contribution due to flow is also approximately 5%. Thus, at most for the fresh egg white foams, these effects are not the major contributors to the difference between the bulk $T_2$ and the $T_2$ of the foam. The possibility of several different chemical environments is a probable cause.

The existence of two distinctly different environments for

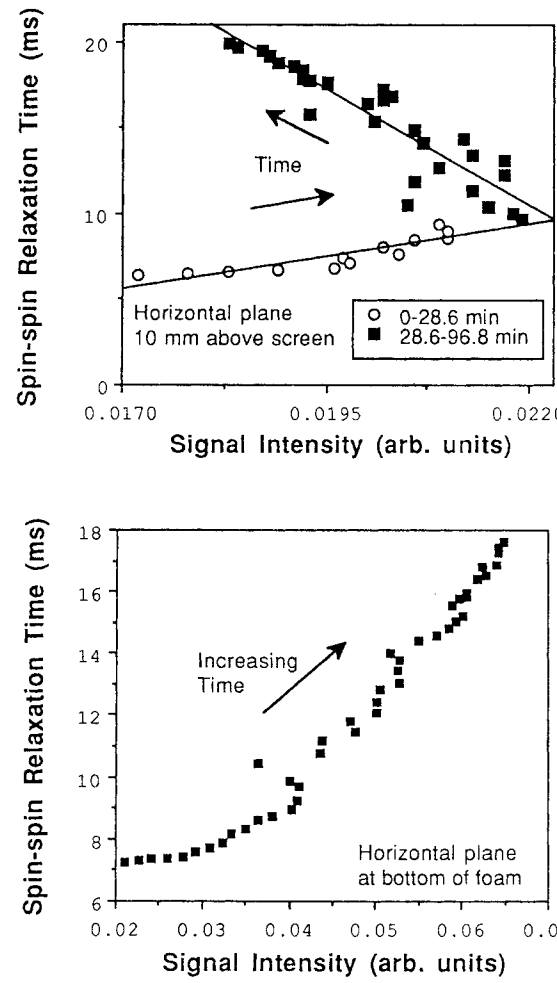


**Figure 3. Changes in the spin-spin relaxation time as a function of time, position and NMR signal intensity (corrected for spin-spin relaxation time variations) in a reconstituted egg white foam.**

Each data point represents a different time during a 90-min experiment; the data were acquired every two minutes. Each graph represents data from a horizontal plane at different heights within the foam column: a. 10 mm above the bottom of the foam; b. bottom of the foam.

hydrogen nuclei within a foam is easily justified (there most likely exists many different environments of molecular mobility). One environment would be similar to that of the bulk liquid and correspond to the majority of the liquid in the plateau borders and lamella. The second environment would be one in which the properties of the interface between the liquid and the bubble would govern the local relaxation processes. Thus, the relaxation rates of protons in a foam could be affected by both cross-relaxation and proton exchange (Richardson and Steinberg, 1987). In general, these effects will tend to reduce the absolute value of the measured relaxation time constants, and thus these effects are qualitatively consistent with the data.

The increase in the observed spin-spin relaxation times within the foam as a function of time is probably a result of an increase in bubble size. The bubbles in a foam will increase in size over time, since the thermodynamics of the system favors this increase. As a result of the increase in bubble size, the mass ratio

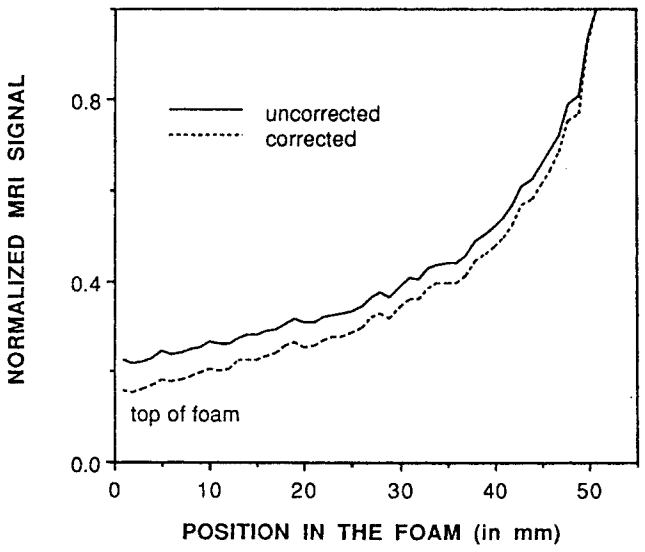


**Figure 4. Uncorrected magnetic resonance signal intensity and magnetic resonance signal intensity corrected for spin-spin relaxation effects.**

of the hydrogen in the restricted motion environment to that in the liquid-like environment probably decreases, resulting in an increase in the observed spin-spin relaxation time. Figure 3 shows the change in spin-spin relaxation time as a function of specific vertical positions within the foam and time of drainage. The data are generally consistent with a two state type of model in which the ratio of nuclei in a restricted motion environment to nuclei in a more mobile environment controls the observed relaxation time. In the upper portions of the foam, the density is decreasing in time, in the lower portions of the foam the density at first increases and then decreases. Throughout the entire foam, the average bubble size should be increasing with time. If the ratio of the restricted protons to mobile protons is decreasing with the increase in bubble size and increase in density, we should see an increase in the spin-spin relaxation times as the draining proceeds. The data in Figure 3 suggest that this is indeed what is occuring. Verification of a simple two-state fast-exchange model for relaxation in an egg white foam, is not possible from the data collected to date. Additional experiments quantifying the contributions of diffusion and flow to the spin-spin relaxation time and measurements of the bubble size distributions as a function of time and position would be necessary.

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