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NMR Phase Noise in Bitter Magnets

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We have studied the temporal instability of a high field resistive Bitter magnet through nuclear magnetic resonance (NMR). This instability leads to transverse spin decoherence in repeated and accumulated NMR experiments as is normally performed during signal averaging. We demonstrate this effect via Hahn echo and Carr–Purcell–Meiboom–Gill (CPMG) transverse relaxation experiments in a 23-T resistive magnet. Quantitative analysis was found to be consistent with separate measurements of the magnetic field frequency fluctuation spectrum, as well as with independent NMR experiments performed in a magnetic field with a controlled instability. Finally, the CPMG sequence with short pulse delays is shown to be successful in recovering the intrinsic spin–spin relaxation even in the presence of magnetic field temporal instability. © 2001 Academic Press

Key Words: **bitter magnets; NMR; phase noise; spin decoherence.**

1. INTRODUCTION

Bitter magnets and their hybrid combination with superconducting magnets are the only source of continuously applied fields above 30 T. As such, they offer a unique environment for studying a wide range of effects whose field scales are inaccessible by other means. Along with these advantages, however, the Bitter magnets have the disadvantage of low inductance that leads to temporal fluctuations of the field from power supply ripple. This can have a surprisingly pronounced effect on measurements that depend on phase coherence such as spin–spin relaxation in nuclear magnetic resonance. We have studied this effect with the high field magnets at the National High Magnetic Field Laboratory in Tallahassee, Florida.

To produce fields in the 30-T range, currents on the order of 30 kA are generated in solenoidal geometries. This leads to several difficulties. Since the magnets are resistive ($R \approx 10$ mΩ) and have very low inductance ($L \approx 3.73$ mH), they are subject to the temporal instability of their power supplies. The Joule heating produced by the currents must be countered with a continuous cooling source which may fluctuate in time. Finally, large fields produce very substantial forces directed radially outward for a solenoidal magnet. A solution to some of these problems, first conceived by Francis Bitter and realized in 1939, is the construction of circular "Bitter plates" (*1*). Each of these plates is cut along a radius and connected together end-to-end in a "stack" that directs the current in a solenoidal path. A set of holes is carved out of the plates in specially chosen locations. These holes allow a continuous flow of cooling water around the entire stack and dissipate its Joule heat. According to the NHMFL modified design, the holes are carved in arc shapes so as to reduce the stresses produced by the Lorentz forces on the magnet currents. The maximum steady field achieved with these optimized hole patterns is 33 T (*2, 3*). However, inherent in the operation of Bitter magnets are temporal instabilities whose magnitude and source have been quantitatively identified in numerous studies to measure and suppress them (*4–7*). The cooling water's temperature varies with time, causing small thermal expansion and contraction of the Bitter plates, changing their current density and therefore the applied field. Nuclear magnetic resonance (NMR) measurements (*6, 7*) have demonstrated the connection between field drift and water temperature, showing variations in magnetic field with an amplitude of 17 parts per million (ppm) per degree centigrade (in agreement with the thermal expansion coefficient of copper), a period of 2 min (consistent with the temperature regulation cycle), and long-term stability of order 10 ppm. The power supplies themselves have been refurbished to suppress ripple effects, giving an observed reduction by 3 ppm in long-term variation. Switching from temperature-based to flow-based control in the water temperature regulation provided improved response time. A flux stabilization system, which includes pick-up coil feedback and a ^{2}H NMR lock for low frequencies, combined with a manually stabilized water temperature, has demonstrated temporal stability of better than 1 ppm over periods of approximately 10 min (*6, 7*). In addition, the power supply has significant short term instability (1–3 ppm) in the DC-audio range, particularly at integral multiples of 60 Hz, identified by measurement with a pick-up coil (*4, 7*). Such variations can have a pronounced effect on high resolution NMR measurements performed in the Bitter magnets where phase coherence is of great importance and are the subject of this paper. Experiments have been performed using copper shields to suppress field fluctuations in

Bitter magnets in order to control eddy current heating effects in a metallic sample (*5*) and have recently been applied by ourselves to control field fluctuations that affect NMR experiments (*8*). We have achieved a suppression factor of 100 at 30 Hz with this method.

We have performed nuclear magnetic resonance NMR spin–spin relaxation measurements over a wide time scale in a high-field resistive Bitter magnet. We determined the decay of the transverse magnetization in single or multiple pulsed spin-echo sequences. The nuclear spin decoherence in a time-stable magnetic field will be referred to here as the intrinsic spin–spin relaxation. Normally, successive signal accumulations are performed and averaged to improve signal-to-noise. However, if the magnetic field fluctuates in time on the time scale of the separation of the excitation pulse and the detected echo, the phase of the received signal will fluctuate on successive accumulations producing a serious degradation of the signal amplitude. We have studied a sample of known intrinsic spin–spin relaxation and characterized the field fluctuations through analysis of the NMR decay profiles using Hahn echo and Carr–Purcell–Meiboom–Gill (CPMG) NMR methods. We have shown that the CPMG short time-delay sequence recovers the intrinsic relaxation, even in the presence of field fluctuations.

2. EXPERIMENTAL TECHNIQUE

In order to study the Bitter magnet fluctuations through NMR, a sample is required whose intrinsic spin–spin relaxation is distinguishable from the extrinsic decoherence due to the applied field. This requirement precludes the use of most solids, whose intrinsic relaxation rates are too large and would dominate the effects from magnet fluctuations. Additionally, liquids with large diffusion coefficients exhibit dephasing from diffusion in a magnetic field gradient; this is 10 ppm/mm of sample size for the Bitter magnet we have used. The material we have chosen is a deuterated glycerol imbibed into the pores of a silica gel (Davisson 52) to restrict diffusion. We have checked that diffusive dephasing is negligible by repeating our measurements in a large field gradient produced by displacing the probe from the most homogeneous region of the magnet.

Two NMR pulse sequences have been used. The first is the Hahn spin-echo sequence. Two pulses are applied: a $\pi/2$ pulse to tip the magnetization into the observation plane and a π pulse to reverse the dephasing due to static field inhomogeneity. A single echo is formed in this sequence, at a time equal to twice the separation between the pulses: $t = 2\tau$. The second relaxation sequence applied in this study is the Carr–Purcell–Meiboom–Gill sequence (*9, 10*). In this experiment, a long train of π pulses is applied in regular intervals following the initial excitation, each one producing a spin echo. The RF phases of the inversion pulses in this sequence are all perpendicular to the first $\pi/2$ pulse. This has the effect of correcting for small errors in the pulse inversion angle rather than having them accumulate over the course of the sequence.

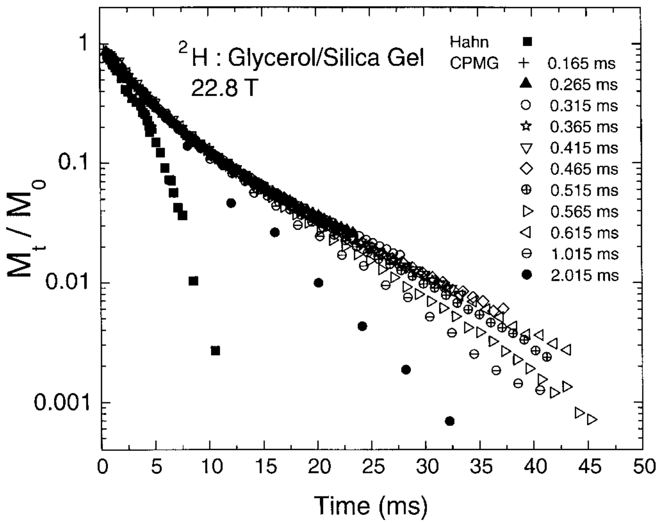

FIG. 1. Transverse magnetization relaxation profiles in a resistive Bitter magnet. CPMG profiles are labeled by the interval τ.

3. BITTER MAGNET DATA

High-field, $H = 22.8$ T, ^{2}H NMR experiments were performed at 148.7 MHz in the resistive magnet in Cell 7 of the National High Magnetic Field Laboratory in Tallahassee, Florida. The observed linewidth was approximately 60 ppm, attributable to inhomogeneous broadening due to applied field inhomogeneity. A $\pi/2$ RF pulse of 10 μs was used, sufficient to uniformly excite the resonance line. All experiments were repeated 256 times at a repetition time of 50 ms. The maximum duration of each CPMG experiment was 2 min, and that of the Hahn echo experiment, including all delays measured in the profile, was 5 min. With these sequences we have explored dephasing in transverse decay experiments with time delays from 0.165 (CPMG) to 10 ms (Hahn echo) as shown in Fig. 1. Each decay profile is the convolution of the intrinsic spin–spin relaxation and an additional dephasing contribution due to the unstable applied field. The intrinsic behavior was determined in an 8-T stable superconducting magnet with a Hahn echo sequence over the time scale shown in Fig. 1 and coincides with the short time delay CPMG pulse sequences in the figure. The Bitter magnet CPMG profiles with small interpulse delays tend to preserve the coherence of the magnetization from sweep to sweep and thus recover the intrinsic profile. As the delays between inversion pulses become longer, ultimately leading to the Hahn echo sequence with only one inversion pulse per excitation, the applied field's instability causes significant decoherence in the accumulated signal. This leads us to an important conclusion: the CPMG sequence is a viable method of recovering intrinsic NMR spin–spin relaxation countering the effect of applied field fluctuations. The multiexponential intrinsic decay determined in this way is faster than for bulk glycerol. We speculate that this intrinsic behavior is a characteristic of the inhomogeneous relaxation from the surface of the silica-gel, a phenomenon that is generally observed for liquids imbibed in porous media (*11*). It represents a distribution of surface interactions and/or a distribution of surface-to-volume ratios from different parts of the porous sample.

In order to analyze the transverse decays as a consequence of magnetic field fluctuations, we derive and show tests of a harmonic model for the applied field fluctuations. Taking the small delay CPMG profiles as a measure of the intrinsic relaxation, we divide out this decay from each profile in Fig. 1 and analyze the remaining dependence in terms of the model. This procedure allows us to extract the principal component of the Bitter magnet field ripple.

4. TRANSVERSE DECAY CALCULATIONS

We have calculated the expected transverse magnetization decay from a Hahn echo experiment performed repeatedly in an applied field with harmonic instability and also compared the calculations with NMR data acquired in an unstable field of this form, generated by superimposing a harmonic fluctuation to the field of a stable superconducting magnet. We have applied this understanding to the data acquired in the resistive Bitter magnet in order to extract both the principal frequency and the amplitude of the fluctuations of the field. The results are compared with an independent determination of the field instability obtained from a pickup coil.

In the special case of a harmonic field variation, we can find an exact form for the accumulated phase and consequently the degradation of the signal amplitude. We first assume that at the time of the first RF pulse the phase of the applied field is a random variable, i.e., all initial phases φ are equally probable.

$$H(t) = h\cos(\omega t + \varphi) \qquad [1]$$

We wish to calculate the echo height M/M_0 as a function of its delay time, twice the pulse separation 2τ. This requires summing the 2-dimensional projections of the nuclear spins onto the plane transverse to the applied field. In our case this sum corresponds to the accumulation of multiple acquisitions.

$$\frac{M_t}{M_0} = \sum_{n=1}^{N} e^{i\phi_n} \equiv \langle e^{i\phi}\rangle = \frac{1}{2\pi}\int_0^{2\pi} e^{i\phi} d\varphi \qquad [2]$$

We first calculate the phase of the magnetization for a single sweep in the presence of the sinusoidal applied field. The initial placement of a the magnetization after the first pulse is taken along the x-axis, and the second pulse's effect is to reverse whatever y-component it has developed, or equivalently, to invert the sign of its phase angle at $t = \tau$. The net phase for a single acquisition is thus,

$$\phi(2\tau) = \int_0^{\tau} \gamma H(t)dt - \int_{\tau}^{2\tau} \gamma H(t)dt. \qquad [3]$$

For the harmonic field this gives,

$$\phi(2\tau) = -\frac{\gamma h}{\omega}[\sin(2\omega\tau + \varphi) - 2\sin(\omega\tau + \varphi) + \sin\varphi]. \qquad [4]$$

Inserting this expression into Eq. [2] gives the following exact result for the magnitude of the transverse magnetization:

$$\left|\frac{M_t}{M_0}(2\tau)\right| = \left|\int_0^{2\pi}\frac{d\varphi}{2\pi} e^{i(4(\gamma h/\omega)\sin^2(\omega\tau/2))\sin(\omega\tau+\varphi)}\right| = \left|J_0\left(4\frac{\gamma h}{\omega}\sin^2\left(\frac{\omega\tau}{2}\right)\right)\right|, \qquad [5]$$

where J_0 is the zeroth-order Bessel function of the first kind. Since this function has nodes, we see that the effect on transverse NMR measurements of an unstable applied field can be quite pronounced. For small arguments, we can approximate the Bessel function by its first two terms:

$$J_0(x) \approx 1 - \frac{1}{4}x^2, \qquad [6]$$

which gives for the Hahn echo decay,

$$\left|\frac{M_t}{M_0}(2\tau)\right| \approx 1 - 4\left(\frac{\gamma h}{\omega}\right)^2 \sin^4\left(\frac{\omega\tau}{2}\right). \qquad [7]$$

In general the full time dependence of the field variation is required to determine the phase dispersion and hence calculate the Hahn echo. However, for small dispersion the gaussian phase approximation (GPA) can be used to approximate the Hahn echo decay. In this approach, the Hahn echo decay is given by,

$$\left|\frac{M_t}{M_0}\right| = \left|\sum_{n=1}^{N} e^{i\phi_n}\right| \approx e^{-\langle\phi^2\rangle/2}. \qquad [8]$$

To show the application of the GPA for the harmonically

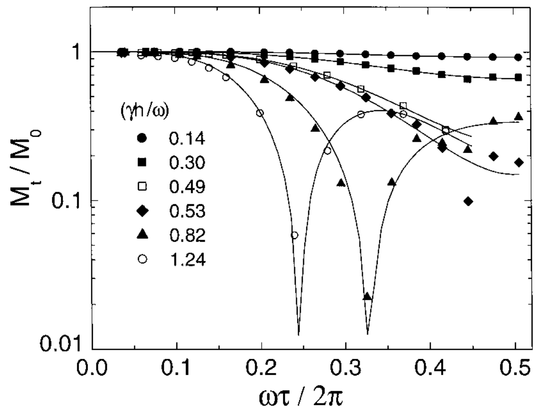

FIG. 2. Hahn echo NMR measurement of cumulative dephasing in a harmonically fluctuating applied field. Open symbols are ^{2}H in D_2O; closed symbols are ^{1}H in glycerol. Lines are fits to a harmonic fluctuation model (Eq. [5]).

fluctuating fields we perform the average of Eq. [8] over the random phase of the applied field, to obtain

$$\left|\frac{M_t}{M_0}\right|(2\tau) \approx e^{-4(\gamma h/\omega)^2 \sin^4(\omega\tau/2)}. \qquad [9]$$

For small times, this expression can be expanded as

$$\left|\frac{M_t}{M_0}\right|(2\tau) \approx 1 - 4\left(\frac{\gamma h}{\omega}\right)^2 \sin^4\left(\frac{\omega\tau}{2}\right), \qquad [10]$$

consistent with Eq. [7]. Finally, we note that the leading order term of the decay is quartic in the echo time:

$$\left|\frac{M_t}{M_0}(2\tau)\right| \approx \exp\left(-\frac{1}{4}(\gamma h\omega)^2(2\tau)^4\right). \qquad [11]$$

In the second pulse sequence, the CPMG sequence, inversion (π) pulses are applied at times τ, 3τ, 5τ, etc., so that a train of echoes is generated at times 2τ, 4τ, 6τ, etc. The peaks of these echoes define a dephasing profile. To calculate this profile in the presence of the unstable field, we must evolve the magnetization through each interpulse period, invert its phase at each pulse, and evaluate its magnitude midway between two pulses. In this case, an exact solution is not possible even for the harmonically varying field. We can, however, obtain a good approximation to the profile using the gaussian phase approximation (Eq. [8]). As in the Hahn echo case, for this scheme we must calculate the mean-square phase of the accumulated signal at each point in time. For the CPMG multiple-pulse sequence, the result of this calculation is shown below.

$$\begin{aligned}\langle\phi^2\rangle(2N\tau) = \left(\frac{\gamma h}{\omega}\right)^2 \Big[&1 + (-1)^{N+1}\cos(2N\omega\tau) \\ &+ 2\sum_{k=1}^{N}(-1)^{N+k+1}\cos((2(N-k)+1)\omega\tau) \\ &+ 2\sum_{k=1}^{N}(-1)^{k}\cos((2k-1)\omega\tau) \\ &+ 2\sum_{k,m=1}^{N}(-1)^{k+m}\cos(2(k-m)\omega\tau)\Big]. \qquad [12]\end{aligned}$$

One important feature here is that for small $\omega\tau$, i.e., for inversion pulses occurring rapidly compared to the applied field frequency, the leading order term is *quartic* in τ. This indicates a strong suppression of the dispersion for sufficiently low pulse interval, just as observed in our Bitter magnet CPMG data (Fig. 1).

To test the harmonic model, we have performed NMR transverse relaxation experiments on liquids in the presence of an applied sinusoidally varying field up to 20 ppm of the static Zeeman field from a superconducting magnet. Hahn echo transverse decays for both glycerol (^{1}H NMR, 1.0 T) and D_2O (^{2}H NMR, 3.2 T) are shown in Fig. 2. In each case the intrinsic spin–spin relaxation of the system has been measured without applied fluctuations and divided out of the measured decay. Each data set is labeled by the value extracted from a fit to the harmonic model (Eq. [5]). At a given harmonic field frequency, we find all curves to be completely determined by the current-to-field ratio of the harmonic field coil. With this one adjust-

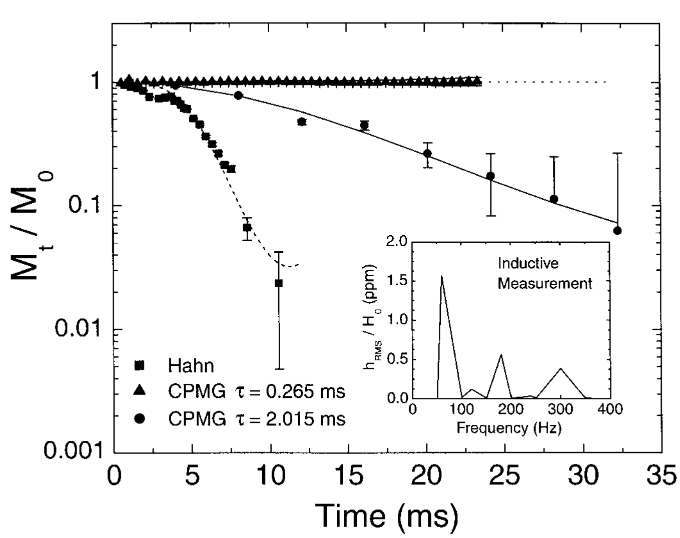

FIG. 3. Transverse magnetization residual profiles in the 23-T field of a Bitter magnet. Lines are fits to our calculation of a Hahn echo or CPMG relaxation from a harmonic model. Inset: Field fluctuations from an inductive measurement (*4*).

able parameter, the whole set of experiments are well described by the harmonic model in Eq. [5].

Having successfully tested this model by direct experiment, we apply it to the decoherence observed in the Bitter magnet experiments. The Hahn echo and CPMG decays shown in Fig. 3 are the "residual" decays, that is to say in addition to intrinsic relaxation. The Hahn echo data and the CPMG $\tau = 2.015$ ms data are significantly affected by the field fluctuations, but the short delay CPMG data ($\tau = 0.265$ ms) are not. Along with each data set we show a curve of the appropriate decay form (Hahn or CPMG) in the gaussian phase approximation to the harmonic model. The field parameters extracted from the fit of the Hahn echo data to the harmonic model are 0.4 rms ppm at 88 Hz. The curves for both CPMG experiments correspond to a ripple of 0.16 rms ppm at 113 Hz. In the inset are shown measurements of the field fluctuation spectrum acquired through an inductive pickup coil placed within the Cell 7 Bitter magnet (*4*). Both NMR experiment types, analyzed with the harmonic model, identify a weighted average of the field fluctuation components present in the magnet. There is qualitative but reasonable agreement of the two sequences' results with each other and with the pickup coil measurements. It is interesting to note, however, that both measurement techniques reveal significant ripple components well beyond the expected cutoff frequency scale of the magnet itself, given by $(R/L) \approx 3$ Hz.

Given the successful explanation of our ^{2}H NMR Bitter magnet experiments, we also point out how results might differ for other probe nuclei. From Eq. [10], we can estimate the time over which the decoherence due to the magnet has reduced the signal by 1%. This serves as an estimate for the period of time that would be roughly uncompromised by the unstable field and the upper limit of accessible intrinsic relaxation times by the Hahn echo method.

$$(2\tau)_{0.99} = \left(\frac{4 \ln\left(\frac{1}{0.99}\right)}{(\gamma h \omega)^2} \right)^{1/4} \qquad [13]$$

Taking the parameters inferred from the deuterium Hahn echo decay gives $(2\tau)_{0.99} = 1.7$ ms. The time expected for a proton NMR experiment under the same conditions would be smaller, $(2\tau)_{0.99} = 0.67$ ms. This smaller window of operability is consistent with proton NMR in a water–acetone solution done in the 25-T Keck resistive magnet at the NHMFL (*12*). Work is in progress in our group to combat this phase noise problem by two additional techniques (*8*, *13*). In one strategy, the NMR signal can be accumulated in the polar rather than cartesian domain to separate the phase noise from echo amplitude determinations. A second approach involves the use of a high-quality, helium-cooled, inductive shield sufficiently conductive to screen even the low-frequency magnetic field fluctuations of the Bitter magnets.

5. CONCLUSIONS

We have performed NMR spin–spin relaxation measurements in a 23-T resistive Bitter magnet. We have demonstrated the effect of the unstable applied field on the spin coherence observed in an NMR experiment performed in it, obtaining results in agreement with separate measurements of the magnets' instability. Finally, we show that the CPMG sequence is an effective tool in extracting intrinsic spin–spin relaxation even in the presence of an unstable applied field.

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