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Coaxial probe for nuclear magnetic resonance diffusion and relaxation correlation experiments

Yiqiao Tang, Martin Hürlimann, Soumyajit Mandal, Jeffrey Paulsen, and Yi-Qiao Song(a)
Schlumberger-Doll Research, 1 Hampshire Street, Cambridge, Massachusetts 02139, USA

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A coaxial nuclear magnetic resonance (NMR) probe is built to measure diffusion and relaxation properties of liquid samples. In particular, we demonstrate the acquisition of two-dimensional (2D) distribution functions ($T_1$, $T_2$, and diffusion–$T_2$), essential for fluids characterization. The compact design holds promise for miniaturization, thus enabling the measurement of molecular diffusion that is inaccessible to conventional micro-NMR setups. Potential applications range from crude oil characterization to biomolecular screening and detections. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4866363]

I. INTRODUCTION

Fluid analysis/typing plays a central role in characterizing a sample of interest and understanding the underpinning intermolecular interactions. In particular, nuclear magnetic resonance (NMR) is a powerful tool to characterize molecular structure and physical properties of a wide range of materials through both high-resolution NMR spectroscopy and low-resolution relaxation and diffusion methods. Conventional NMR systems require a permanent magnet to generate $B_0$ field for magnetizing spins in the sample, and a radio-frequency (RF) coil to generate $B_1$, an RF magnetic field for spin manipulation and signal detection. The standard approach of encoding diffusion information in NMR measurement is the so-called “pulsed field gradient” (PFG) technique. For PFG-NMR measurements, additional magnetic field coils and the associated electronics are needed to produce magnetic field gradients in order to encode spatial information and to measure diffusion. This hardware adds complexity and thus constrains the range of possible applications. For example, it is difficult to perform NMR under extreme conditions, such as high temperatures (up to 200 °C) and pressures (30,000 psi) and with limited space for instrumentation in geological exploration. Such needs pose a significant challenge to the mechanical and electrical design, equipment operation, and cost control of the functional devices.

In parallel to the PFG approach, an alternative technique of spatial encoding has emerged that is based on $B_1$ gradients. In early work, a single-turn coil was deployed to generate a non-uniform $B_1$ field. The sample was placed some distance away where the $B_1$ field gradient is approximately uniform. A separate pick-up coil was then used to detect the nuclear induction. It was demonstrated that with this $B_1$ gradient technique, the self-diffusion coefficient of the fluid could be well-determined. A particularly interesting follow-up was the development of the toroid based NMR probe at the Argonne National Laboratory and the University of Bonn. In this design, the RF field is well confined inside the metallic toroid container where the fluid sample is placed. The RF field is inhomogeneous with a substantial gradient.

Here, we have adapted this toroid-based design and elongated the dimension along the axial dimension, resulting in a structure resembling a coaxial cable with an outer shield and a center conductor as the RF probe. Tuning is achieved by adding an external capacitor between the center conductor and the outside shield. We name this structure tentatively a coaxial probe. The fluid sample is contained within the coaxial cavity between the center conductor and the shield where the RF field $B_1$ varies appreciably within the fluid sample. We show in this paper, both in theory and experiment, that the coaxial NMR probe is well suited to measure various fluid properties, including the $T_1$ and $T_2$ relaxation times, the diffusion coefficient ($D$), and corresponding multi-dimensional distribution functions. The coaxial NMR probe does not require the use of a PFG system for diffusion measurements, which is a significant simplification of hardware and electronics. Moreover, it eliminates complications due to eddy currents that often plague conventional diffusion measurements. The mechanical structure and the small dimensions will allow high pressure and temperature ratings, high values of gradient for diffusion measurements, and enhanced sensitivity.

II. SENSOR DESCRIPTION AND THEORY

The basic coaxial probe consists of three parts: the central conductor, the outer metallic vessel, and the sample space, shown in Figure 1(a). The inner conductor and outer metallic vessel were both made of high-purity copper (>99.0% purity), and electrically connected at one end. The inner wire is 0.1 cm in diameter, while the outer vessel is 1 cm in diameter. The wire is tightly fed through a Teflon insert, which insulates the central conductor and also serves as a spacer for the liquid sample. The fluid channel is located between the Teflon insert and the copper shield, with an inner and outer radius $r_0 = 0.25$ cm and $r_1 = 0.5$ cm, respectively. With a 4 cm chamber length, the total fluid volume is 2.36 cm³. The probe is connected to an electronic tuning circuit to ensure frequency tuning and 50-ohm impedance matching at 42.58 MHz, as shown in Figure 1. The tuning

(a)Author to whom correspondence should be addressed. Electronic mail: ysong@slb.com.

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and matching capacitors are adjustable from 130 to 190 pF, and from 20 to 45 pF, respectively. The overall probe Q is about 50. All experiments were conducted in the bore of a 1-T superconducting magnet (Oxford Instruments), with the central axis of the coaxial probe oriented parallel to the \( B_0 \) field. NMR experiments were performed using an AVANCE II spectrometer (Bruker Biospin).

The \( B_1 \) field is generated as an electrical current \( I \) is applied to the coaxial probe. Quantitatively, the RF field \( \vec{B}_1 \) and the gradient \( g_1 \) in the sample space are

\[
\vec{B}_1 = \frac{\mu_0 I}{2\pi r} \vec{e}_\theta, \tag{1}
\]

\[
g_1 = -\frac{\mu_0 I}{2\pi r^2} \vec{e}_r, \tag{2}
\]

where \( \mu_0 \) is the vacuum magnetic permeability, \( r \) is the radius, and \( \vec{e}_\theta \) and \( \vec{e}_r \) are the unit vectors in the azimuthal and radial direction of the wire, respectively. The RF field and its gradient, both varying considerably as a function of \( r \), are shown in Figure 1(b).

The local spin nutation frequency is defined as \( \omega_1 = \gamma B_1/2 \), where \( \gamma \) is the gyromagnetic ratio of the spin.

Pulse sequences used in this work are shown in Figure 2. Each RF pulse is defined by its duration \( t \) (relative to a nominal 90° pulse) and its phase \( \phi \). In these sequences, the amplitudes of all pulses were kept constant. Phase cycling schemes were designed to select the desired coherence pathways.

We employed the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence \(^{11,12} \) to determine \( T_2 \). We used refocusing pulses that were twice as long as the initial excitation pulse. Given the wide distribution of RF field strength \( \omega_1 \) within the sample volume, the amplitudes of the first few CPMG echoes show large variance that quickly average out before the echo amplitudes approach an asymptotic regime.\(^{16} \) The amplitudes in the asymptotic regime are given by

\[
M_{T_2,asy}(nt_E) = M_0 \int d\omega f(\omega_1) \omega_1 \sin(\omega_1 \tau_{90}) e^{-\frac{\gamma \tau_{90}}{T_2}}, \tag{3}
\]

where \( f(\omega_1) \) is the distribution function for \( \omega_1 \) that for the coaxial geometry is given by \( f(\omega_1) = 1/\omega_1^3 \), \( t_E \) is the echo spacing, and \( n \) is the echo number. Here, \( \tau_{90} \) is the duration of the nominal 90° pulse defined by \( \gamma (B_1) \tau_{90} = \frac{\pi}{2} \) with \( \gamma \) the spatial average of the \( B_1 \) field. At an RF power of 15 W, we performed a nutation experiment by varying the pulse length from 3 \( \mu \text{s} \) to 20 \( \mu \text{s} \), and recorded the free-induction-decay signal.\(^{5} \) Similar to Eq. (3), we used the formula \( M = M_0 \int d\omega_1 \sin(\omega_1 \tau_{90}) \omega_1 \) and probe parameters to determine that \( B_1 \) varied from 15.3 G to 76.5 G, and the field gradient \( g_1 \) accordingly ranged from 61.2 G/cm to 15.3 G/cm, as shown in Figure 1(b).

The measured relaxation time, \( T_{2,\text{eff}} \), has two contributions due to the intrinsic relaxation time \( T_2 \) and due to diffusion in the RF gradient.

\[
\frac{1}{T_{2,\text{eff}}} = \frac{1}{T_2} + \frac{1}{T_{2,\text{diff}}}. \tag{4}
\]

The RF gradient induces a spatial modulation of the magnetization within the sample space. In the limit of negligible \( B_0 \) inhomogeneity, the modulation is characterized by the local wave vector \( q(r) = \gamma g_1(r) \tau_{90} \). Diffusion in this modulation attenuates the signal with a decay rate of \( 1/T_{2,\text{diff}} = q^2 \bar{D} \). Given the expressions for the RF field, the gradient, and the pulse duration \( \tau_{90} \), this diffusion induced decay rate can be rewritten as \( 1/T_{2,\text{diff}} = D \bar{n}^2/(2r_\text{ave})^2 \), where \( r_\text{ave} \) is related to the average sample radius. Note that to first order, the diffusive contribution does not depend on the echo spacing. For
For practical purposes, we can set $T_d$ final. Following Ref. 16, it is useful to analyze the difference signal $M_{T_1}(\Delta) = M_{T_1}(\Delta \to \infty) - M_{T_1}(\Delta)$, which is given by

$$\delta M_{T_1}(\Delta) = M_0 \int_{t_0}^{\infty} dt_1 \sin(\omega_1 t_0) \cos(\omega_1 t_1) \left[ \cos(\omega_1 t_1) - 1 \right] e^{-\Delta/T_1}.$$  

This suggests that the $T_1$ kernel has the same simple form as the $T_2$ kernel in Eq. (5)

$$k_{T_1}(\Delta) = B e^{-\Delta/T_1}$$  

with the calibration constant given in this case by: $B = \int_{t_0}^{\infty} dt_1 \sin(\omega_1 t_0) \cos(\omega_1 t_1) \left[ \cos(\omega_1 t_1) - 1 \right]$. Diffusion measurements were performed by using the rotary-echo pulse sequence shown in Fig. 2(c). In these experiments, the duration $t_p$ of the first two pulses is systematically increased, which in turn increases the wave vector $q$ that controls the spatial modulation of the longitudinal magnetization during the interval $\Delta$

$$q = \gamma g_1 t_p = \frac{2 \pi}{\gamma \mu_0 D} \sin^2 t_p.$$  

The second pulse spatially demodulates the longitudinal magnetization and the third pulse is used to generate transverse magnetization for the detection of the signal. By increasing $t_p$ to values much larger than $\tau_0$, the wave vector can be made comparable and larger than the inverse of the diffusion length, $(DA)^{1/2}$. In this case, the attenuation of the signal due to diffusion in the interval $\Delta$, given by $\exp(-q^2 D \Delta)$, becomes appreciable. In the coaxial probe, the wave vector $q$, and therefore the attenuation, is not uniform across the sample. The magnetization close to the inner conductor, where $\omega_1$ and the $B_1$ gradient are large, decays faster than the magnetization close to the outer conductor. The resulting signal of the desired coherence pathway for the coaxial probe is given

$$M_D(t_p) = M_0 e^{-\Delta/T_1} \int_{t_0}^{\infty} dt_1 \sin(\omega_1 t_0) \cos^2(\omega_1 t_p) \times \exp \left\{ -4\pi^2 \omega_1^2 \frac{A}{\gamma^2 \mu_0^2 F} D t_p \right\}.$$  

For small values of $t_p$, the term $\cos^2(\omega_1 t_p)$ leads to rapid oscillations in the signal $M_D(t_p)$. To obtain sufficient diffusion sensitivity, it is necessary to use longer pulse durations, $t_p \gg \tau_0$. In this asymptotic case, the factor $\cos^2(\omega_1 t_p)$ may be replaced
by its average value of $1/2$. In addition, magnetization that recovers towards the thermal equilibrium during the interval \( \Delta \) can be spin-locked during the second pulse and introduces an offset \( a_1 \) into the detected signal, i.e., Eq. (10). This offset is independent of \( t_p \), but is proportional to \( 1 - e^{-2\pi} \). In the limit \( \Delta \ll T_1 \), \( a_1 \) scales as \( \Delta T_1 \). For sufficiently long pulse duration \( t_p \), the diffusion kernel is then given by

\[
k_D(t_p) = a_1 \left( \frac{\Delta}{T_1} \right) + e^{-\frac{\Delta}{T_1}} \int_0^{\omega_1} d\omega_2 \sin(\omega_1 \tau_{90}) \exp\left\{ -\frac{4\pi^2 \omega_1^2 \Delta}{\gamma^2 \mu_0^2 T_2^2} \right\}.
\]

(11)

Many fluids of interest have a complex composition and their NMR response cannot be described by a single relaxation time or diffusion coefficient. In such cases, it is necessary to use the one-dimensional distribution functions \( f(T_2) \), \( f(T_1) \), and \( f(T_{12}) \) to adequately capture the relaxation and diffusion behavior.

\[
M_{T_2,\text{asy}}(nt_E) = \int dt_2 f(T_2) k_{T_2}(nt_E),
\]

(12)

\[
\delta M_{T_2}(\Delta) = \int dt_2 f(T_1) k_{T_2}(\Delta),
\]

(13)

\[
M_{\text{D,asy}}(t_p) = \int dD f(D) k_D(t_p).
\]

(14)

Given the simple exponential kernels for the \( T_1 \) and \( T_2 \) measurements, the distribution functions \( f(T_2) \) and \( f(T_1) \) can be extracted from the measured data using Laplace inversion, \(^{14-16}\) while for the diffusion measurement, the inversion routine has to be extended to include the more complicated form of the diffusion kernel of Eq. (11).

For a more complete characterization of fluids and for understanding the intermolecular and interfacial interactions of molecules and substrates, it is essential to extend these basic NMR experiments and measure 2D distribution functions. The sequences in Figures 2(d) and 2(e) are used to measure \( D-T_2 \) and \( T_1-T_2 \) distribution functions, respectively. \(^{14-16}\) This is achieved by replacing the detection of free induction decays in Figs. 2(a) and 2(c) by a train of CPMG echoes. Similar to the standard CPMG sequence, the magnetization reaches quickly an asymptotic regime after the first few echoes and the responses are given by

\[
M_{D-T_2,\text{asy}}(t_p, nt_E) = \int dD dt_2 f(D, T_2) k_D(t_p) k_{T_2}(nt_E),
\]

(15)

\[
\delta M_{T_1-T_2,\text{asy}}(\Delta, nt_E) = \int dt_1 dt_2 f(T_1, T_2) k_{T_1}(\Delta) k_{T_2}(nt_E).
\]

(16)

We applied the 2D Fast Laplace Inversion algorithm \(^{14,15}\) to analyze the data obtained by the sequences in Figures 2(d) and 2(e) to extract the two-dimensional \( D-T_2 \) and \( T_1-T_2 \) distribution functions \( f(D, T_2) \) and \( f(T_1, T_2) \), respectively.

### III. EXPERIMENTAL RESULTS

The system was tested with different types of fluids and the results were interpreted using Eqs. (12) to (16). Figure 3 shows data on water with the sequences in Figure 2. In the \( T_1 \) measurement, we deployed the sequence in Figure 2(a) with \( \tau_{90} = 5.35 \mu s \) and \( \tau_{180} = 10.7 \mu s \), while \( \Delta \) varied from 0.001 s to 16 s in 22 steps with logarithmically spaced intervals. Free induction decays (FID) were recorded immediately after the nominal 90° pulse. In the data analysis, we subtracted from the measurement with \( \Delta = 16 \) s all the other data points to obtain \( \delta M_{T_1} (\Delta) \), and fitted the processed data with a single exponential decay. In the \( T_2 \) measurement, we set \( \tau_{90} = 5.35 \mu s \) and \( \tau_{180} = 10.7 \mu s \) and the echo spacing \( t_E = 4 \) ms. A total of 1024 echoes were recorded, and fitted by an exponential decay. \( T_1 \) and \( T_2 \) were determined to be 2.32 s and 1.93 s (The difference in \( T_1 \) and \( T_2 \) for water sample is likely due to an oxygen effect, respectively). Here, the interpulse spacing is much shorter than \( T_2 \) and diffusion effects have been ignored.

We also note the transient effect in the initial few echoes before the asymptotic regime is reached, shown in the inset of Figure 3(b), due to the inhomogeneity of the \( B_1 \) field.\(^{17}\)

In diffusion measurements, the delay \( \Delta \) was set to be a constant at 160 ms, while the duration of the pair of winding and unwinding pulses was varied from 0 to 4 ms. Using Eq. (11), \( D = 2.53 \times 10^{-7} \) m\(^2\)/s rendered an optimal fit (red curve) to the data, as shown in Figure 3(c). The measured value of \( D \) agreed to within 10% with the literature value \((2.32 \times 10^{-7} \) m\(^2\)/s at 25 °C)\(^{18}\). The initial oscillations in Figure 3(c) originate from the imperfect averaging of the squared cosine term in Eq. (10) when the pulse length is short,\(^{19}\) and is unrelated to molecular diffusion.

To test the form of the diffusion kernel in Eq. (11), we also performed a set of measurements using the \( D-T_2 \) sequence in Figure 2(d) with a fixed pulse duration of the first two pulses at 4 ms, while the delay \( \Delta \) was ramped up from 160 to 320 ms. With this value of \( t_p \), the second term in Eq. (11) becomes vanishingly small and the signal is directly given by the offset term \( a_1 \). Given that \( \Delta T_1 < 0.14 \), we expect a linear dependence of the echo strength on \( \Delta \). This is indeed the case as shown in the inset of Figure 3(c). Error bars in the plot are the standard error of means for the first twenty echoes at every value of \( \Delta \).

We also tested the system with n-decane (C\(_{10}\)H\(_{22}\)) and plotted the diffusion data of water and n-decane as a function of \( D_{T_2}^2 \), where \( D \) are the respective diffusion coefficients for the two species from literature (for water, \( D = 2.32 \times 10^{-7} \) m\(^2\)/s; and for n-decane, \( D = 1.39 \times 10^{-7} \) m\(^2\)/s). From Eq. (11), the plotted data should be independent of fluid type in the asymptotic regime and a function of the \( B_1 \) distribution in the cavity. This is confirmed by the results shown in Figure 3(d).

Subsequently, we tested the probe with an admixture of mineral oil (CVS mineral oil up) and water. Mineral oil largely consists of alkanes with carbon numbers ranging from 15 to 40. The pulse sequences in Figures 2(d) and 2(e) were deployed to generate 2D distribution functions suitable for fluid typing. A fast 2D Laplace inversion algorithm was used to interpret the data. In the algorithm,\(^{20}\) Tikhonov regularization was applied to counterbalance the residual fitting.
errors and the known noise amplitude. More specifically, a regularization term, \( \alpha \), is used to measure the desired smoothness in the distribution function and makes the inversion less ill-conditioned. An optimized \( \alpha \) is such that the fitting bias is minimized and the result is stable in the presence of noise. In plotting the data, we set \( \alpha = 1 \).

As can be seen in Figure 4, water and mineral oil are clearly separated in both \( T_1-T_2 \) and \( D-T_2 \) distribution functions. Strong correlations between \( T_1-T_2 \) and \( D-T_2 \) are evident. The diffusion coefficient and the \( T_1, \ T_2 \) relaxation times of water and mineral oil from 2D measurements are consistent with earlier 1D measurement on the respective samples. While the peak for water is narrow and circular in shape, the mineral oil peak is extended in both distribution functions reflecting its more complex composition.

IV. CONCLUSION

Overall, we have demonstrated the capability of the coaxial NMR probe in assessing relaxation and diffusion
properties of water, a pure alkane, and a mineral oil. $T_1$-$T_2$ and $D-T_2$ distribution functions were obtained to further distinguish species and consistency between theory and experimental data was observed. In addition, the probe design is well-suited for measuring many other properties of liquids. For example, the coaxial probe may be used to measure the density of hydrogen within the sample, which is one of the important parameters characterizing crude oils. The probe may also be used to measure flow rate through the probe cavity by replacing the cylindrical geometry with a funnel-shaped cavity. A funnel-shaped cavity will generate a $B_1$ gradient in the longitudinal direction, which may be used to encode the fluid movement along the coaxial cavity.

Recent advancements in microelectronics have enabled the miniaturization of NMR devices, e.g., a micro-NMR system for cancer profiling. The coaxial probe may be made much smaller than demonstrated here and further integrated with suitable microelectronics. Its capability to provide diffusion measurement without conventional pulsed field gradients significantly expands the range of measurements that are accessible to conventional NMR relaxometry. For these reasons, we expect many applications for the design, such as in oilfield exploration, food science, environmental monitoring, and biomolecular screening and detection.