Transverse Spin Relaxation in Liquid ^{129}Xe in the Presence of Large Dipolar Fields

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Using spin-echo NMR techniques we study the transverse spin relaxation of hyperpolarized liquid ^{129}Xe in a spherical cell. We observe an instability of the transverse magnetization due to dipolar fields produced by liquid ^{129}Xe, and find that imperfections in the π pulses of the spin-echo sequence suppress this instability. A simple perturbative model of this effect is in good agreement with the data. We obtain a transverse spin relaxation time of 1300 sec in liquid ^{129}Xe, and discuss applications of hyperpolarized liquid ^{129}Xe as a sensitive magnetic gradiometer and for a permanent electric dipole moment search.

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Atomic magnetometers are widely used in precision measurements, such as searches for a permanent electric dipole moment (EDM) [1,2] and CPT violation [3]. The fundamental sensitivity limit of an atomic magnetometer is determined by the uncertainty in the measurement of the Zeeman precession frequency ω

$$\delta\omega = \frac{1}{\sqrt{NT_2 t}}, \quad (1)$$

where N is the number of atoms, T_2 is the transverse spin relaxation time, and t is the measurement time. Magnetometers using electron spin precession in Rb atoms [4] and nuclear spin precession in ^{199}Hg atoms [2] have approached this fundamental limit of sensitivity. Liquid ^{129}Xe is a very attractive substance for a magnetometer because of its high number density ($10^{22}/\mathrm{cm}^3$) and potentially long values of T_2. It also has a high electric field breakdown strength of 400 kV/cm [5], making it an excellent candidate for an EDM search. Large quantities of hyperpolarized liquid ^{129}Xe have recently been produced using spin exchange with optically pumped Rb atoms [6].

In this Letter we describe our experimental and theoretical studies of the transverse spin relaxation of liquid ^{129}Xe. We describe new nonlinear effects in the relaxation of the transverse magnetization due to large dipolar magnetic fields created by hyperpolarized ^{129}Xe. The effects of dipolar fields in NMR have recently attracted much attention. They have been studied using liquid ^{129}Xe [7] and ^{3}He [8] in a U-shaped sample tube. Theoretical models for these effects were considered in [9]. Unlike previous theoretical and experimental studies, we work in a spherical cell geometry and develop a simple perturbative model to describe the nonlinear effects in the regime of weak magnetic field gradients, when the magnetization of ^{129}Xe remains nearly the same everywhere in the cell. We find that under these conditions the transverse magnetization is unstable and small gradients of the external magnetic field are exponentially amplified. Similar behavior was observed in a simple numerical model consisting of eight spins located at the corners of a cube [9]. We also find that imperfections of π pulses in a standard Carr-Purcell-Meiboom-Gill (CPMG) spin-echo sequence [10] suppress the exponential growth of the magnetization gradients. Our experimental results are in good quantitative agreement with the perturbative model. After the instability is suppressed, we obtain $T_2 = 1300$ sec in liquid ^{129}Xe, which, we believe, is the longest transverse spin relaxation time measured in a liquid. We also discuss how the exponential amplification of the magnetic field gradients caused by dipolar interactions in liquid ^{129}Xe can be used to build a very sensitive magnetic gradiometer and to search for an EDM. For these applications it is convenient to use a SQUID magnetometer to detect ^{129}Xe magnetization with high signal-to-noise ratio in a very low magnetic field.

The longitudinal spin relaxation time T_1 of liquid ^{129}Xe has been investigated in [6,11]; at 180 K it is about 30 min. Spin relaxation in liquid ^{129}Xe is dominated by spin-rotation interactions, and an estimate of T_1 from the chemical shift of ^{129}Xe [12] is in good agreement with the experiment. In a liquid one might expect that the correlation time τ_c of the spin-rotation interaction would be very short, and in the regime of motional narrowing ($\tau_c\omega \ll 1$) T_2 should be equal to T_1. However, existence of long-lived Xe van der Waals molecules [13,14] could result in shorter values of T_2. In previous studies of the transverse relaxation in liquid ^{129}Xe [15,16] measured values of T_2 have been no longer than several seconds.

Our measurements are performed using ^{129}Xe polarized by spin-exchange optical pumping [17]. A schematic of the apparatus is shown in Fig. 1. A mixture of 2% Xe (in natural abundance), 2% N_2, and 96% ^{4}He flows at a pressure of 3 atm through an optical pumping cell containing Rb vapor at 155 °C. The Rb is optically pumped by a 40 W diode laser array whose spectrum is narrowed using an etalon [18]. Polarized ^{129}Xe gas freezes out of the mixture as it passes through a cold trap (77 K) in a magnetic field of 1.5 kG, where it has a longitudinal spin relaxation time of several hours. After 40 min of accumulation, approximately 7 g of Xe ice is collected in the cold trap. The trap is then warmed up and Xe gas flows to a 1.3 cm diam. spherical glass cell, where it liquefies at a temperature of 180 K maintained by a mixture of acetone ice and liquid.

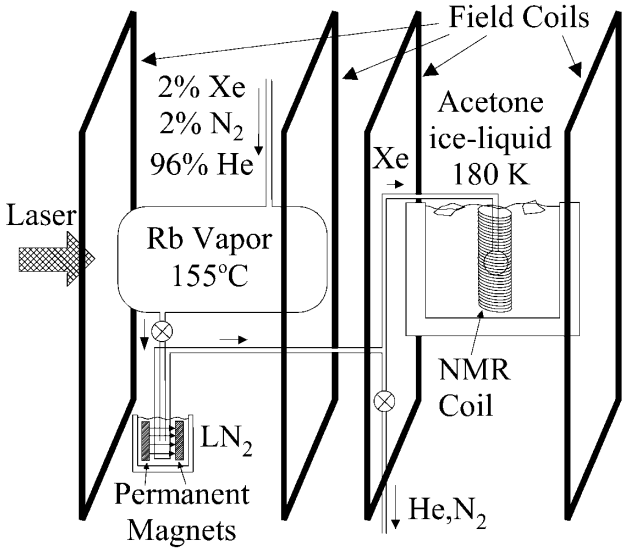

FIG. 1. Schematic of the apparatus. The magnetic field, created by four coils, has two uniform regions near the pumping cell and the liquid Xe cell.

The NMR measurements are performed in a magnetic field of 32 G ($\omega = 2\pi \times 37.5$ kHz). To eliminate radiation-damping effects the NMR coil is connected to a high-impedance amplifier without using a resonant circuit. The gradients of the external magnetic field are reduced to about 0.1 mG/cm by first-order gradient coils, so that the free-induction decay time due to dephasing of the spins is $T_2^* = 2$–3 sec. The timing of the RF pulses is controlled by an NMR pulser PC card [19], while the phases of the pulses are set with high precision using a DSP function generator that is controlled through serial interface commands also generated by the pulser card. Our measurements of T_1 are in agreement with [6].

To suppress spin dephasing due to residual external magnetic field gradients we use a standard CPMG spin-echo pulse sequence [10]. It consists of a $\pi/2$ pulse followed by a train of π pulses at times $\tau, 3\tau, 5\tau, \ldots$, whose phases are shifted by 90° from the phase of the $\pi/2$ pulse. The duration of the π pulses is about 1 msec. Typical values of τ are 30 to 100 msec, much shorter than T_2^*. The decay of the magnetization due to spin diffusion between π pulses is negligible.

The spin-echo technique does not prevent spin dephasing due to gradients created by the dipolar fields, since these gradients are reversed by π pulses together with the magnetization. For a uniform ^{129}Xe polarization in a spherical cell the dipolar field seen by ^{129}Xe atoms adds up to zero. However, in the presence of a small gradient of the external magnetic field the magnetization of ^{129}Xe will develop a helix which in turn produces a gradient of the magnetic field. We find that this positive feedback mechanism causes the gradients of the magnetic field and the magnetization to grow exponentially in time and results in a highly nonexponential decay of the transverse magnetization shown in Fig. 2.

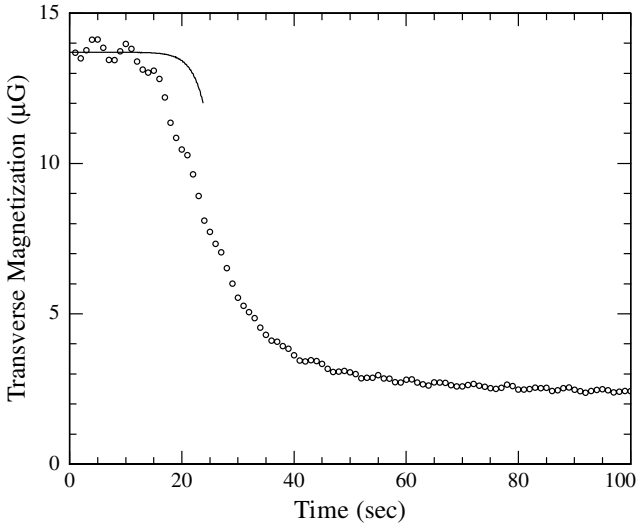

FIG. 2. Onset of nonexponential decay due to dipolar fields. Open circles: envelope of the transverse magnetization signal obtained with CPMG pulse sequence for $\tau = 100$ msec and an applied longitudinal field gradient $dH_{Ez}/dz = 1.4$ mG/cm. Solid line: model of the initial magnetization gradient growth with no free parameters.

We develop a simple model for a spherical cell to calculate the rate of exponential growth of the gradients and also incorporate into the model the effects of imperfect π pulses. The magnetic field felt by ^{129}Xe atoms is

$$\mathbf{B} = \mathbf{H}_E + \mathbf{H}_M + \frac{4\pi}{3}\mathbf{M}, \tag{2}$$

where $\mathbf{H}_E$ is the external magnetic field and $\mathbf{H}_M$ is the field created by ^{129}Xe magnetization [20]. This expression differs from the classical result $\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$ because two ^{129}Xe atoms cannot occupy the same space and the δ function part of the classical dipolar field does not contribute. If the initial $\pi/2$ pulse is applied along the $\hat{\mathbf{y}}$ direction in the rotating frame, the magnetization is rotated into the $\hat{\mathbf{x}}$ direction. Before the magnetization is significantly affected by the field gradients, only two terms of the Bloch equations are significant,

$$\frac{\partial M_y}{\partial t} = -\gamma M_0 B_z \quad \text{and} \quad \frac{\partial M_z}{\partial t} = \gamma M_0 B_y\,. \tag{3}$$

Only the gradients of H_{Ez} are important, since the gradients of H_{Ey} will average to zero in the rotating frame. We first consider the case when the longitudinal gradient of H_{Ez} dominates, $\mathbf{H}_E = gz\hat{\mathbf{z}}$. To first order the magnetization will also develop a linear gradient in the $\hat{z}$ direction, and we look for solutions in the form $M_y(\mathbf{r}, t) = m_y(t)\,(z/R)$, $M_z(\mathbf{r}, t) = m_z(t)\,(z/R)$, where R is the radius of the cell. The total magnetic field is

$$B_y = \frac{8\pi}{15}\,m_y(t)\,\frac{z}{R} \quad \text{and} \quad B_z = -\frac{16\pi}{15}\,m_z(t)\,\frac{z}{R} + gz\,. \tag{4}$$

In Eqs. (4) we omitted y gradients of the magnetic field because their effect averages to zero in the rotating frame. Equations (3) and (4) have a simple solution,

$$m_y(t) = -\gamma M_0 g R \frac{\sinh(\beta t)}{\beta}, \quad (5)$$

where $\beta = 8\pi\sqrt{2}\,\gamma M_0 \kappa/15$ and $\kappa = \kappa_L \equiv 1$ for the longitudinal gradient of H_{Ez}. For transverse gradients of H_{Ez} in the x or y direction of the lab frame the magnetization develops a gradient in the same direction. The solution is still given by Eq. (5) with $\kappa = \kappa_T \equiv 1/2$ for $\beta \ll \omega$. Thus, the gradients of the magnetization grow exponentially with a time constant that in our experiment is on the order of 2–20 sec. Even for a very small external magnetic field gradient, m_y/M_0 will quickly approach unity, at which point the transverse magnetization will dephase on a time scale of β^{-1} due to its own field gradients.

In the CPMG pulse sequence the magnetization and its gradients are reversed at times $\tau, 3\tau, 5\tau, \ldots$. This can be represented in Eqs. (4) by an alternating external field gradient g. In this case the differential equations (3) are solved numerically, but for $\tau\beta \ll 1$ and $t \gg \tau$ the numerical solution is well approximated by

$$m_y(t) = -\frac{2\sqrt{2}\,\pi\kappa}{15}\,\gamma^2 M_0^2 \tau^2 g R e^{\beta t}. \quad (6)$$

The gradient of the magnetization that appears before the first π pulse continues to grow exponentially and the spin-echo envelope starts to deviate from initial exponential decay at a time t_{ne} when $m_y(t_{ne}) \simeq M_0$. For parameters corresponding to the data shown in Fig. 2 we obtain $\beta^{-1} = 5$ sec, and $t_{\rm ne} \simeq 20$ sec, in good agreement with the data given exponential sensitivity to input parameters.

Equation (6) suggests that even for a very small magnetic field gradient and π pulse spacing the magnetization will eventually decay nonexponentially after a time on the order of several β^{-1}. However, as shown in Fig. 3, the growth of the magnetization gradients can be suppressed by imperfections in the π pulses of the CPMG sequence. Since the π pulses are applied along the $\hat{\mathbf{x}}$ direction in the rotating frame, the net effect of an inaccurate pulse length is to slowly rotate M_y and M_z components of the magnetization around the $\hat{\mathbf{x}}$ direction with an angular frequency $\omega_r = \phi/(4\pi\tau)$, where $\phi = \alpha - \pi$, and α is the true length of the "π" pulse. Adding this rotation to Eqs. (3), one finds

$$\beta = \left[\left(\frac{16\pi}{15}\,\kappa^2\gamma M_0 - \omega_r\right)\left(\frac{8\pi}{15}\,\gamma M_0 + \omega_r\right)\right]^{1/2}, \quad (7)$$

where κ is equal to κ_L or κ_T depending on the direction of the external field gradient. Thus, β is imaginary for $\omega_r > 16\pi/15\kappa^2\gamma M_0$ or $\omega_r < -8\pi/15\gamma M_0$ and the magnetization gradients do not grow exponentially. The solid points in Fig. 3 show the spin-echo envelope with π pulses intentionally shortened by 3%, which delays the onset of the nonexponential decay to about 250 sec. For the parameters corresponding to these data we find $\omega_r = -0.09$ sec^{-1} and $(8\pi/15)\gamma M_0 = 0.1$ sec^{-1}, so β given by Eq. (7) is close to zero within errors.

Figure 3 also shows the spin-echo envelope for a CPMG sequence with a smaller M_0 and a shorter π pulse spacing τ, which increases ω_r. In this case the transverse magnetization decays exponentially, with a time constant $T_2 = 1290$ sec. In other data sets we obtained values of T_2 up to 1360 sec. Most systematic effects would decrease the value of T_2, and we cannot exclude the possibility of an additional relaxation rate on the order of $1/T_2 - 1/T_1 = 2 \times 10^{-4}$ sec^{-1}. For example, it could be due to partial transverse spin relaxation on the walls of the cell. Note that if the walls of the cell were completely depolarizing, it would give a diffusion-limited relaxation rate of 1×10^{-3} sec^{-1}. Thus, our data are also consistent with intrinsic T_2 for liquid ^{129}Xe equal to $T_1 = 1800$ sec.

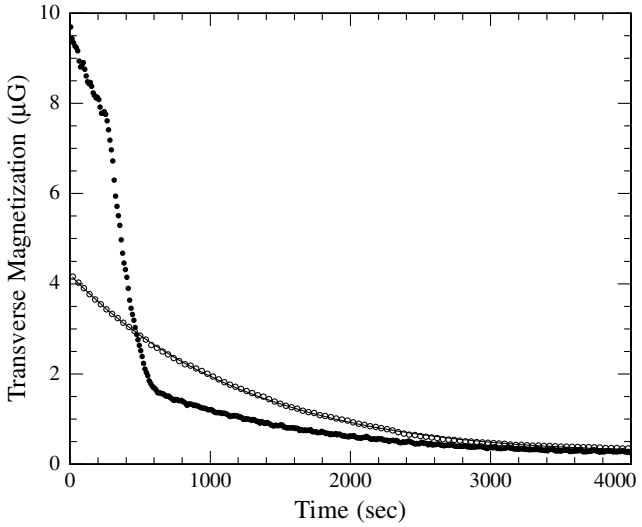

FIG. 3. Spin-echo envelope for CPMG sequence with $\tau = 100$ msec, $dH_{Ez}/dx = 1.4$ mG/cm, and the π pulse intentionally shortened by 3% (solid circles); with $\tau = 30$ msec and gradients reduced to about 0.1 mG/cm (open circles). An exponential fit to the latter gives $T_2 = 1290$ sec (solid line). Fits to the initial and final decay of the data shown with solid circles also give similar values of T_2.

Using our measurements of T_2, the fundamental limit on the sensitivity of a liquid ^{129}Xe magnetometer, given by Eq. (1), is estimated to be 3×10^{-17} G/$\sqrt{\rm Hz}$, 5 orders of magnitude better than the best SQUID magnetometers. However, to realize this sensitivity one needs an efficient way of detecting the frequency of precession of ^{129}Xe spins. A SQUID magnetometer can detect the precessing magnetic field created by polarized ^{129}Xe with a high signal-to-noise ratio. The magnetic field created by ^{129}Xe in natural abundance (26%) with 20% spin polarization contained in a 1 cm diameter cell is about 5 mG. For a SQUID sensitivity of 10^{-11} G/$\sqrt{\rm Hz}$ one would get a signal-to-noise ratio of $5 \times 10^8/\sqrt{\rm Hz}$. Such high signal-to-noise can be realized in SQUIDs using flux counting techniques [21].

The dipolar self-interaction effects discussed above also offer a very attractive technique for using liquid ^{129}Xe as a sensitive gradiometer. According to Eq. (5) the magnetization gradients produced by an external field gradient are exponentially amplified with a time constant β^{-1}. Liquid ^{129}Xe essentially acts as its own magnetometer, amplifying

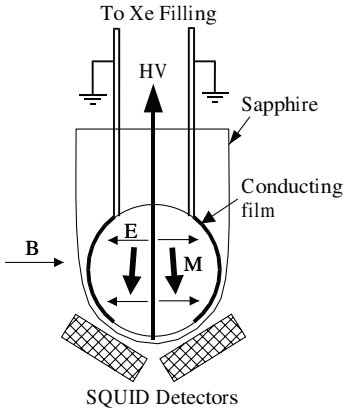

FIG. 4. Schematic of a liquid ^{129}Xe EDM experiment using high-T_c SQUID detectors.

the magnetization gradients until M_y becomes comparable to M_x. Thus, one does not need a very sensitive external magnetometer to detect the dephasing of the spins produced by a small gradient. One can merely wait until the gradients of the magnetization become large, measure M_y, M_x and β, and determine g from Eq. (5). Furthermore, by applying a magnetic field along the $\hat{\mathbf{x}}$ direction in the rotating frame, one can control the value of β through Eq. (7). In particular, by choosing a value of ω_r in the range $4\pi/15\gamma M_0 < \omega_r < 16\pi/15\gamma M_0$, one can suppress the exponential sensitivity to the transverse gradients of the magnetic field, but preserve the amplification of the longitudinal gradient of H_{Ez}. We have analyzed higher order gradients and found that they do not grow exponentially. We are presently setting up a SQUID in a low magnetic field shielded environment to investigate these effects in greater detail.

The long value of T_2 and exponential amplification of field gradients makes liquid ^{129}Xe particularly attractive for an EDM search. A limit on the EDM of ^{129}Xe would have similar implications as the limit on the ^{199}Hg EDM, which already sets some of the most stringent constraints on CP violation in supersymmetry and QCD [2]. The sensitivity of the ^{199}Hg EDM experiment is presently limited by statistics. Using liquid ^{129}Xe one can increase the number of atoms by a factor of 10^8, the electric field strength by at least a factor of 10, and T_2 by a factor of 10. Thus, limits on new sources of CP violation can be improved by several orders of magnitude even though ^{129}Xe is less sensitive by a factor of 10 to CP-violating effects than ^{199}Hg [22]. The exponential amplification of the magnetization gradients due to the dipolar fields will make the signal detection much easier. A schematic of a possible EDM experiment is shown in Fig. 4. The spherical cell containing liquid ^{129}Xe is divided into two parts by a thin conducting membrane. A high voltage applied to the membrane creates opposite electric fields in the two halves of the cell. For a finite EDM this would produce, to first order, a gradient of the Larmor precession frequency. Two SQUID magnetometers detect the oscillating magnetic field created by the precessing transverse magnetization of ^{129}Xe. A gradient of the magnetization would result in a phase shift between the signals recorded by the two magnetometers. As usual, by frequently reversing the polarity of high voltage one can separate the effects due to an EDM from spurious magnetic field gradients.

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[1] P. G. Harris *et al.,* Phys. Rev. Lett. **82**, 904 (1999).
[2] M. V. Romalis, W. C. Griffith, J. P. Jacobs, and E. N. Fortson, Phys. Rev. Lett. **86**, 2505 (2001).
[3] C. J. Berglund, L. R. Hunter, D. Krause, Jr., E. O. Prigge, M. S. Ronfeldt, and S. K. Lamoreaux, Phys. Rev. Lett. **75**, 1879 (1995).
[4] D. Budker, V. Yashchuk, and M. Zolotorev, Phys. Rev. Lett. **81**, 5788 (1998).
[5] S. E. Derenzo, T. S. Mast, H. Zaklad, and R. A. Muller, Phys. Rev. A **9**, 2582 (1974).
[6] K. L. Sauer, R. J. Fitzgerald, and W. Happer, Chem. Phys. Lett. **277**, 153 (1997); K. L. Sauer, Ph.D. thesis, Princeton University, 1998.
[7] K. L. Sauer, F. Marion, P. J. Nacher, and G. Tastevin, Phys. Rev. B **63**, 184427 (2001).
[8] E. Stoltz, J. Tannenhauser, and P. J. Nacher, J. Low Temp. Phys. **101**, 839 (1995).
[9] J. Jeener, Phys. Rev. Lett. **82**, 1772 (1999).
[10] S. Meiboom and D. Gill, Rev. Sci. Instrum. **29**, 688 (1958).
[11] E. R. Hunt and H. Y. Carr, Phys. Rev. **130**, 2302 (1963).
[12] H. C. Torrey, Phys. Rev. **130**, 2306 (1963).
[13] R. S. Mulliken, J. Chem. Phys. **52**, 5170 (1970).
[14] W. A. Herrebout, A. A. Stolov, E. J. Sluyts, and B. J. van der Veken, Chem. Phys. Lett. **295**, 223 (1998).
[15] W. M. Yen and R. E. Norberg, Phys. Rev. **131**, 269 (1963).
[16] C. H. Tseng, R. W. Mair, G. P. Wong, D. Williamson, D. G. Cory, and R. L. Walsworth, Phys. Rev. E **59**, 1785 (1999).
[17] B. Driehuys, G. D. Cates, E. Miron, K. Sauer, D. K. Walter, and W. Happer, Appl. Phys. Lett. **69**, 1668 (1996).
[18] M. V. Romalis, Appl. Phys. Lett. **77**, 1080 (2000).
[19] SpinCore Technologies Inc., Gainesville, FL 32653.
[20] M. V. Romalis and W. Happer, Phys. Rev. A **60**, 1385 (1999).
[21] J. T. Anderson and C. W. Everitt, IEEE Trans. Magn. **13**, 377 (1977).
[22] V. V. Flambaum, I. B. Khriplovich, and O. P. Sushkov, Phys. Lett. **162B**, 213 (1985).