Universal Long-Time Behavior of Nuclear Spin Decays in a Solid

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Magnetic resonance studies of nuclear spins in solids are exceptionally well suited to probe the limits of statistical physics. We report experimental results indicating that isolated macroscopic systems of interacting nuclear spins possess the following fundamental property: spin decays that start from different initial configurations quickly evolve towards the same long-time behavior. This long-time behavior is characterized by the shortest ballistic microscopic time scale of the system and therefore falls outside of the validity range for conventional approximations of statistical physics. We find that the nuclear free-induction decay and different solid echoes in hyperpolarized solid xenon all exhibit sinusoidally modulated exponential long-time behavior characterized by identical time constants. This universality was previously predicted on the basis of analogy with resonances in classical chaotic systems.

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The relationship between statistical physics and chaos is one of the most important and controversial problems in theoretical physics. Statistical physics is based on the assumption of some kind of randomness on the microscopic scale, yet the question of whether this randomness is at all related to the mathematical concept of chaos (well established for few-body classical systems) is not well understood [1,2]. In many-body systems, it is extremely difficult to separate the effects of randomness associated with true chaos from those associated with averaging over the macroscopic number of degrees of freedom [3–6]. The situation is further complicated by the lack of consensus on the universal definition of chaos in quantum systems [7]. In view of these complications, one approach is to proceed on the basis of conjectured parallels between the properties of mathematical chaotic systems and real many-body systems. The predicted consequences of these conjectures can then be tested numerically or experimentally. One such prediction about the universal long-time behavior of transient nuclear spin decays in solids has been made recently in Ref. [8]. The work presented here tested that prediction by measuring the transverse relaxation of ^{129}Xe nuclei (spin $= 1/2$) in solid xenon over 4 orders of magnitude using nuclear magnetic resonance (NMR). Such experiments are prohibitively challenging for conventional NMR due to the weak thermal magnetization achievable in even the strongest magnets. We have employed the technique of spin-exchange optical pumping [9] in order to achieve enhanced (hyperpolarized) magnetization required for this experiment.

In nearly perfect agreement with the prediction of Ref. [8], our experiments indicate that the long-time behavior of transverse nuclear spin decays in solids has the universal functional form

$$F(t) = Ae^{-\gamma t}\cos(\omega t + \phi), \tag{1}$$

where the decay coefficient γ and the beat frequency ω are *independent of the initially generated transverse spin configuration*. This long-time behavior sets in after only a few times T_2, where T_2 is the characteristic time scale for transverse decay determined by the interaction between nuclear spins [see Eq. (2)] and represents the shortest ballistic time scale in the system. The values of $1/\gamma$ and $1/\omega$ are also on the order of T_2. Hence, it cannot be that the spins are interacting with a fast-equilibrating heat bath, which would justify the exponential character of the decay, as for a common damped harmonic oscillator. Indeed, at 77 K in an applied magnetic field ≥ 1 T, the ^{129}Xe spins are well isolated from their environment. The longitudinal relaxation time $T_1 \approx 2.3$ h [10] while $T_2 \approx 1$ ms [11]; therefore, the decay cannot be attributed to spin-lattice relaxation. The oscillations in this decay, sometimes referred to as Lowe beats [12], constitute a correlation effect [13,14] induced by the spin-spin interaction and have

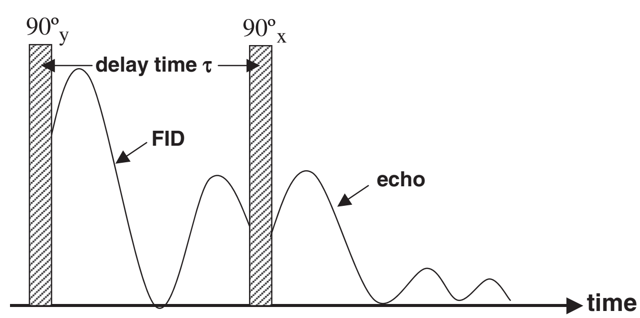

FIG. 1. The pulse sequence used to generate a solid echo. The magnitude of the free-induction decay (FID) including Lowe beats is shown schematically after the first pulse with the solid-echo response shown after the second pulse. The pulses are separated in phase by 90°: the first is along the rotating frame y axis, the second is along the rotating frame x axis. Unlike conventional Hahn echoes, the solid echo does not generally peak at time 2τ [7].

nothing to do with the Larmor frequency. We verified that the effects of radiation damping and inhomogeneities in the external field are also negligible on the time scale of T_2 [7]. The observed decay thus represents the approach of a closed quantum system to equilibrium.

We used the particular pulse sequence (see Fig. 1), known as a solid echo [7,15], which consists of two 90° pulses (the first along the y axis and the second along the x axis in the rotating frame) separated by a delay time τ. In contrast with the conventional Hahn spin echo [16] or the magic echo [17], the solid echo is not an amplitude-attenuated reproduction of the free-induction decay (FID) that peaks at time 2τ. Complete refocusing by solid echoes occurs only for isolated pairs of spins [15]. A deviation from complete refocusing is caused by higher-order correlations involving more than two spins. The solid-echo response depends on the spin configuration just after the second pulse, whereby different values of the delay time τ imply fundamentally different "after-pulse" configurations [7] that evolve from the uniformly polarized uncorrelated spin state at the beginning of the FID to highly correlated states induced by spin-spin interactions during the delay time [18]. Experimentally, these distinct after-pulse configurations are exactly what is required in order to clearly demonstrate the evolution to a universal long-time behavior.

On the time scale of our experiments, the system of interacting ^{129}Xe nuclei can be accurately described as isolated and governed by the Hamiltonian of the truncated magnetic dipolar interaction [19,20], which in the Larmor rotating reference frame has the form

$$\mathcal{H} = \sum_{k<n} [B_{kn}(I_k^x I_n^x + I_k^y I_n^y) + A_{kn} I_k^z I_n^z], \qquad (2)$$

where A_{kn} and B_{kn} are coupling constants and I_n^i are the spin operators representing the ith projection of the nth spin. The Hamiltonian in Eq. (2) is appropriate in the high-field limit where the Zeeman energy dominates dipolar couplings; hence, the shape and duration of the FID are independent of the applied field. The characteristic decay time scale T_2 is on the order of a few inverse nearest-neighbor coupling constants. Although the coupling constants in the Hamiltonian Eq. (2) can be very accurately determined from first principles, efforts over several decades [12,19–25] to predict the entire behavior of FIDs and spin echoes quantitatively have met only with limited success; direct calculations tend to lose predictive power in the long-time tail of the decay, where increasingly higher-order spin correlations become important [18]. Although methods have not yet been developed for the controllable calculation of ω and γ in Eq. (1), Ref. [8] predicted the quick onset [13] of the long-time behavior of Eq. (1) with the same values of ω and γ for all kinds of transverse decays in the same system. This prediction was based not on a conventional statistical theory but on a conjecture [13] that quantum spin dynamics generates extreme randomness analogous to classical chaos [7].

The long-time behavior of Eq. (1) for the FID alone has been previously observed in NMR experiments on ^{19}F in CaF_2 [26]. Analogous observations have also been made in numerical simulations of both classical [27] and quantum [28] spin lattices. Our experiment adds a new insight into this universality by demonstrating that the above long-time behavior is common to both FIDs and solid echoes in the same spin system. Since solid echoes initiated at different delay times τ start from distinct initial spin configurations, our findings suggest that the tails of transient nuclear spin signals are independent of initial conditions (apart from the oscillation phase and the overall amplitude).

For our experiments, both isotopically natural (26.4% ^{129}Xe, 21.29% ^{131}Xe) and enriched (86% ^{129}Xe, 0.13% ^{131}Xe) samples of solid polycrystalline xenon containing ^{129}Xe polarized to 5%–10% were prepared using spin-exchange convection cells [7,29]. FIDs and solid echoes were acquired at 77 K in an applied field of 1.5 T (^{129}Xe Larmor frequency of 17.6 MHz), well into the high-field limit of Eq. (2). The enormous dynamic range of these signals required a separate acquisition of the initial and long-time decays for each FID and echo using different gain settings for the NMR receiver [7].

In Fig. 2(a), representative decays of the signal magnitude for the FID and solid echoes with three different delay times τ are shown for enriched xenon on a semilog plot, with the time axis referenced to $\approx$100 μs (instrumental dead time) after the end of the first 90° pulse, i.e., at the start of the FID. The FID and each echo are acquired separately with the sample newly polarized, whereby the run-to-run variation in polarization prohibits a direct measurement of their relative amplitudes. Hence, the data for each echo are shown at the proper temporal location, starting $\approx$100 μs after the corresponding value of τ, and each echo is normalized to match the FID amplitude at $t = \tau$. Figure 2(b) shows the same four acquisitions time shifted and amplitude normalized relative to the FID to yield the best overlap at long times ($\approx$2.7 ms and later after the start of the FID or echo). The decay coefficient γ and beat frequency ω were obtained for each decay from a fit of the long-time signal magnitude to the absolute value of Eq. (1); a representative fit is shown in red. The results are summarized in Table I, where each entry represents the average of fits for six separate acquisitions of the FID or solid echo. For a given isotopic concentration of ^{129}Xe, the parameters γ and ω are the same for both the FID and all solid echoes independent of the delay time τ.

In contrast, there is no universal behavior in the initial portion of the transverse decays. This is connected to the theoretical expectation (discussed above) that the longer values of the delay time τ allow higher-order spin correlations that are not refocused by the solid echo to become stronger. As a result, the initial spin configurations for the FID and various solid echoes are different and not trivially related to one another [7].

In natural xenon, the long-time tails of the FID and the solid echo acquired with delay time $\tau = 0.56$ ms are also

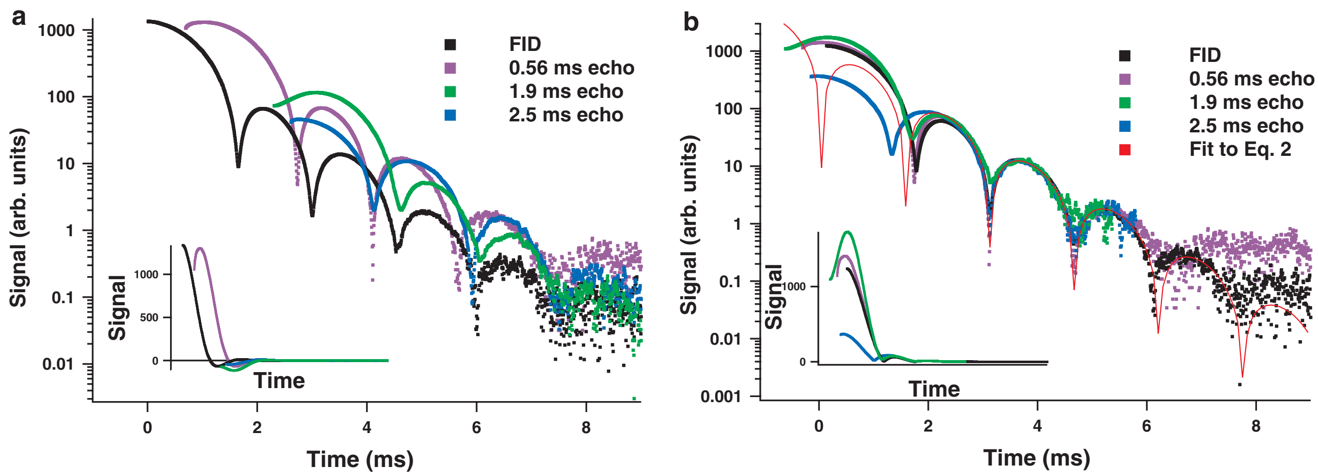

FIG. 2 (color). Representative acquisitions of FID and solid echoes (with three different delay times) recorded for ^{129}Xe in enriched polycrystalline xenon at 77 K. (a) The signal magnitudes are shown on a semilog plot (main) and exhibit characteristic beats. The actual signals plotted on a linear scale (inset) change sign, whereas the main plot has cusps at the zero-crossing points. The FID starts at $t = 0$ ms, and each echo starts at its respective delay time τ with its initial value normalized to the value of the FID at time τ. (b) The same data are shown again on a semilog plot (main) with the echoes both time shifted and amplitude normalized to illustrate the nearly perfect overlap of the long-time decays. For the 1.9 and 2.5 ms echoes, the noisiest data farthest out in time have been removed for clarity; this noisiness is evident for $t > 7$ ms in (a). The red line is a representative long-time fit to the absolute value of Eq. (1) with the decay coefficient $\gamma = 2.04\ \text{ms}^{-1}$ and the beat frequency $\omega = 1.25$ rad/ms. The distinct differences among the initial portions of the decays can be better appreciated in the linear absolute-value plot (inset).

nearly identical [7] and can be fit by Eq. (1) with parameters γ and ω given in Table I. The values of both of these parameters are smaller than in the enriched sample because in the natural sample the ^{129}Xe spins are more dilute, having been replaced with zero-spin species or with ^{131}Xe, for which the dipolar interaction has different coupling constants. The intrinsically weaker signal meant that the long-time tails of echoes with delay times $\tau \gtrsim 0.56$ ms could not be accurately measured.

The common quantitative long-time character of FIDs and spin echoes provides experimental support for the notion of eigenmodes of the time evolution operator $\hat{T}(t)$ in isolated many-body quantum systems. This operator is defined by the equation $\varrho(t, \mathbf{x}) = \hat{T}(t)\varrho(0, \mathbf{x})$, where $\varrho(0, \mathbf{x})$ is the many-body density matrix at some initial time $t = 0$, and $\mathbf{x}$ is the set of variables that describe the density matrix. It was conjectured [8,13] that in the observable long-time range, the nonequilibrium behavior of the density matrix for any small but macroscopic subsystem of the closed system is controlled by a complex-valued eigenmode having the form

$$\varrho_0(\mathbf{x})e^{(-\gamma+i\omega)t} + \varrho_0^*(\mathbf{x})e^{(-\gamma-i\omega)t}. \qquad (3)$$

If this conjecture is valid, then the long-time decay of Eq. (1) represents not just the property of one relaxation process, such as the FID, but rather an intrinsic property of the many-body dynamics of the system, and should manifest itself in numerous other relaxation processes, such as solid echoes with different delay times τ.

The eigenmodes of the time evolution operator as defined by Eq. (3) have no direct relation to the eigenvalues of the Hamiltonian of the many-body system, but rather they are expected to be counterparts of the Pollicott-Ruelle resonances [1,7,30] in classical hyperbolic chaotic systems. These resonances depend on the rate of probability loss from coarser to finer partitions of phase space [1,2]. In many-body quantum systems, there should exist an analogous transfer of spectral weight from lower to higher order quantum correlations [18].

Quantum analogs of Pollicott-Ruelle resonances have been observed numerically in kicked spin-1/2 chains [31], the kicked quantum top [32], Loschmidt echoes [33], and experimentally for the imitation of the single particle quantum problem in microwave billiards [34]. In all these cases, the quantum systems had one or several of the following features: (i) very few degrees of freedom,

TABLE I. The decay coefficient γ and beat frequency ω extracted from the fit of long-time data by Eq. (1) for FID and solid-echo experiments in both natural and ^{129}Xe-enriched solid xenon. Each entry represents an average of six separate experiments with the errors determined from the spread in the fit results. The delay time τ is the time between the 90° pulses in the solid-echo pulse sequence.

	γ (ms^{-1})	ω (rad/ms)
Enriched FIDs	1.25 ± 0.05	2.03 ± 0.04
Enriched echoes, $\tau = 0.56$ ms	1.25 ± 0.05	2.00 ± 0.03
Enriched echoes, $\tau = 1.9$ ms	1.22 ± 0.04	2.06 ± 0.03
Enriched echoes, $\tau = 2.5$ ms	1.25 ± 0.04	2.05 ± 0.04
Natural FIDs	1.04 ± 0.08	1.53 ± 0.08
Natural echoes, $\tau = 0.56$ ms	1.04 ± 0.12	1.52 ± 0.04

(ii) proximity to the classically chaotic limit, (iii) application of external time-dependent forces, removing the difficulty associated with the discrete frequency spectrum of an isolated quantum system. In contrast, we deal here with an essentially isolated system having a macroscopic number of maximally nonclassical components (spins $1/2$), i.e., no proximity to the classically chaotic limit, and no other precondition for chaos apart from the naturally occurring nonintegrable interaction between spins [7].

We note a remarkable fact revealed by Fig. 2(a): the phases of the long-time oscillations of the 1.9 and 2.5 ms echoes nearly coincide with each other and are shifted by π with respect to the FID phase. Indeed, one can observe that the zero crossings (cusps) of the FID and the two echoes coincide in the long-time regime. Given that these are the absolute-value plots, the above coincidences imply that the relative phases of the long-time signals are either zero or π. These two possibilities can be discriminated by keeping track of the successive sign changes at the zero-crossings for each signal. [The inset of Fig. 2(a) shows the sign of the FID and each echo.] This may be a fundamental phase relation associated with the fact that the 1.9 and 2.5 ms echoes start after the FID has begun to approach the asymptotic regime of Eq. (1). In contrast, the 0.56 ms echo starts well before the FID has reached that regime, and its phase has no particular relation to the other three signals.

We have observed a universal long-time behavior of ^{129}Xe FIDs and solid echoes in solid xenon. In all cases, a sinusoidally modulated exponential decay sets in after just a few times T_2. This behavior is universal in the sense that the two parameters characterizing the long-time decay are independent of the NMR pulse or delay sequence, even though each such sequence generates a different initial spin configuration. These findings reveal a fundamental property of nuclear spin dynamics. In addition, they also support the idea that the correspondence between classical and quantum chaotic properties of real many-body systems can be established at the level of Pollicott-Ruelle resonances. Further investigations, however, are required in order to clarify whether the eigenmodes of form (3) actually exist in many-spin density matrices and, if so, how far this correspondence can be taken [7].

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