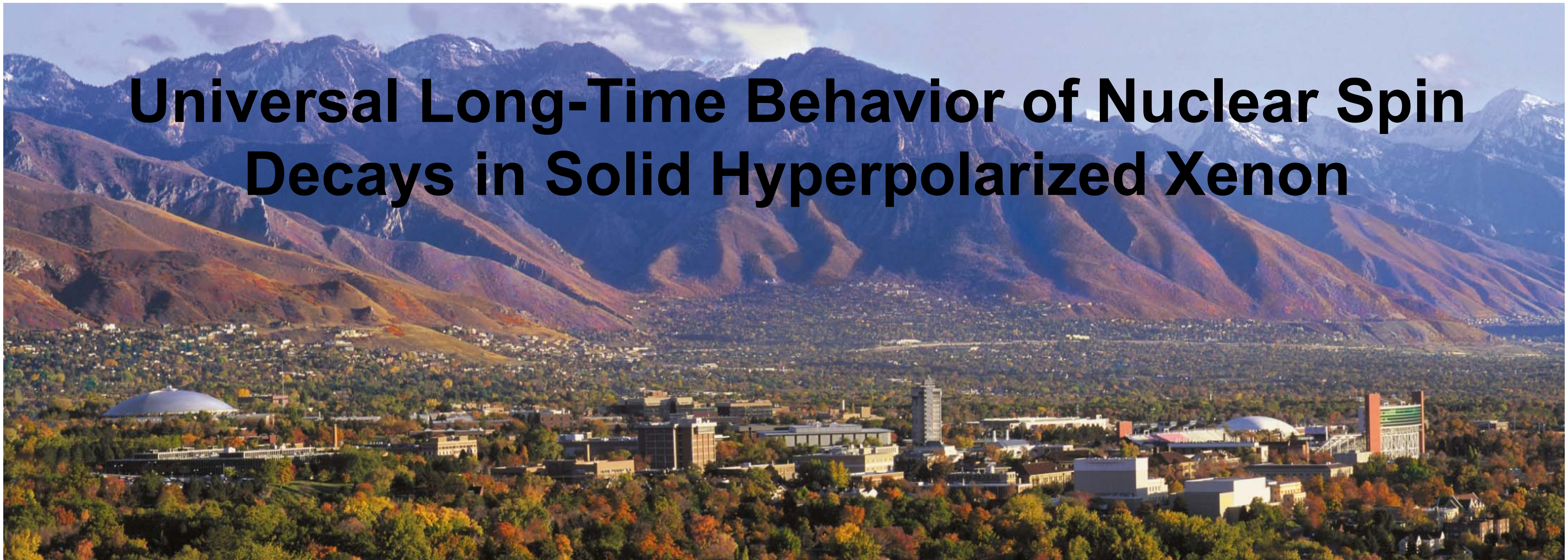
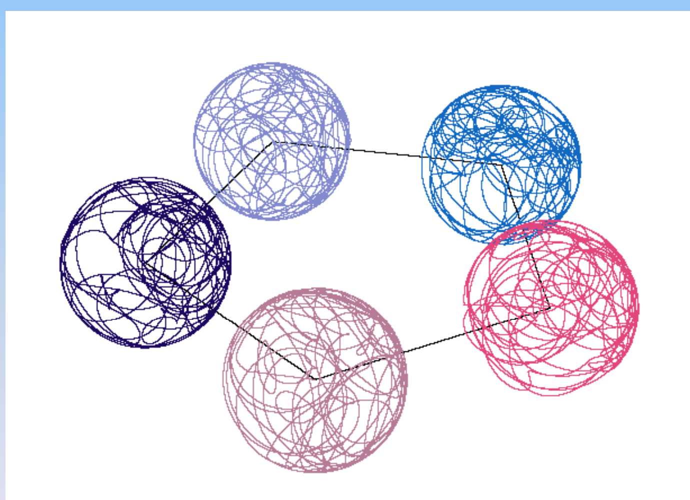
Universal Long-Time Behavior of Nuclear Spin Decays in Solid Hyperpolarized Xenon





THE UNIVERSITY OF UTAH

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DAMOP Session B4, Charlottesville, VA, 20 May 2009

Collaborators

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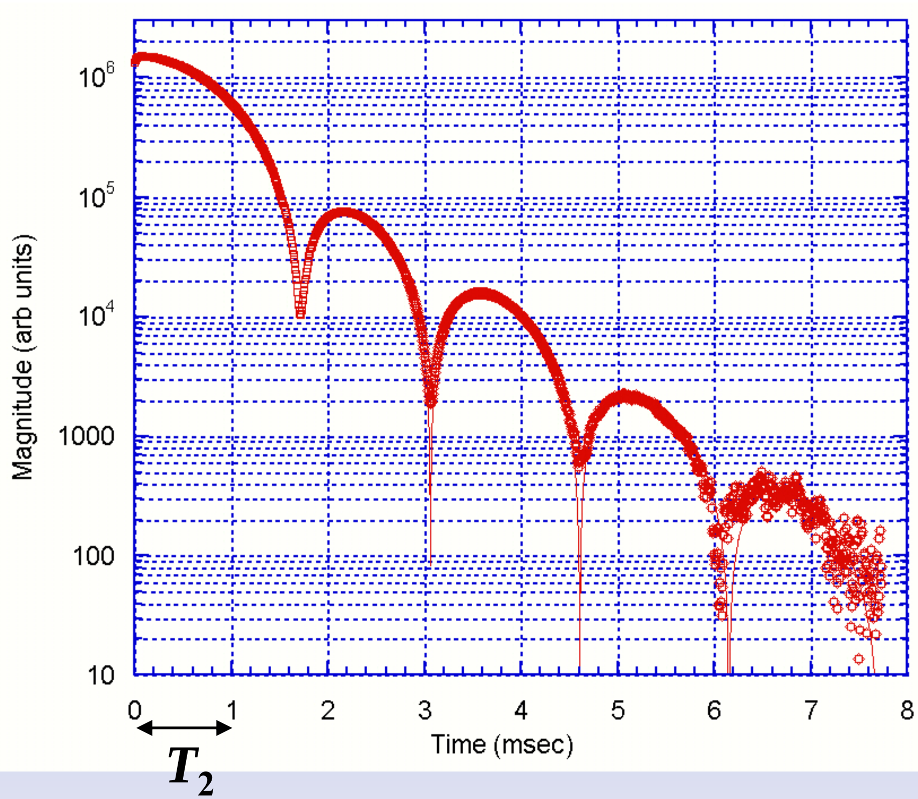
Boris V. Fine (Univ. Tennessee/Oak Ridge NL).

B.V. Fine, "Long-Time Behavior of Spin Echo," Phys. Rev. Lett. **94**, 247601 (2005).

- Makes prediction about universal "long-time" (after a few times T_2) behavior of transverse NMR decays in solids (FIDs and solid echoes).
- Better SNR $\Rightarrow$ hyperpolarized ^{129}Xe.

Extreme SNR NMR

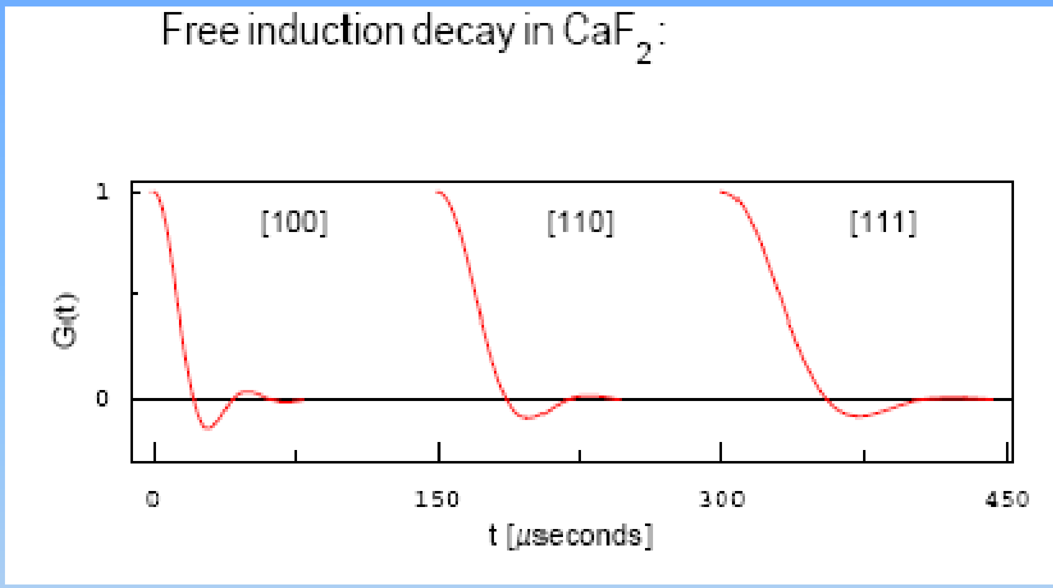
Magnitude of free-induction decay of ^{129}Xe in solid polycrystalline xenon at 77 K, 1.5 Tesla.



- **Use isotopically enriched Xe (86% ^{129}Xe)**
- **Hyperpolarize ≈ 1 mM Xe by SEOP to ≈ 10%.**
- **Freeze it as polycrystalline solid at 77 K. (Hyperpolarization survives phase transition!)**
- **Apply a 90° pulse.**
- **BIG signal (1-10 mV) before pre-amplification .**

Transverse coherence time $T_2 \approx$ 1 ms for ^{129}Xe, which comes from dipole-dipole interactions with near neighbors.

Why study transverse decays in a solid?

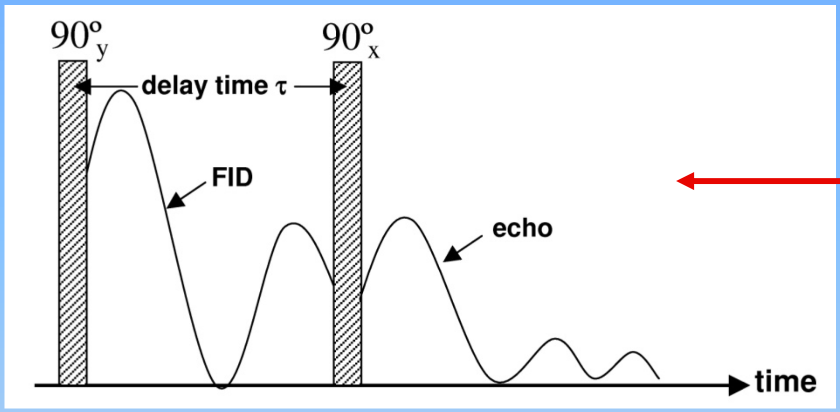


M. Engelsberg and I.J. Lowe, Phys. Rev. B 10, 822 (1974).

$$\mathcal{H} = \sum_{k<n} J_{kn}^z S_k^z S_n^z + \frac{1}{4}(J_{kn}^x - J_{kn}^y)(S_k^+ S_n^+ + S_k^- S_n^-) + \frac{1}{4}(J_{kn}^x + J_{kn}^y)(S_k^+ S_n^- + S_k^- S_n^+),$$

- **Spins interact by dipole-dipole interactions with MANY degrees of freedom.**
- **Details of transverse-decay spectrum can yield important information about the microscopic nature of these interactions. BUT…**
- **The theoretical shape is non-trivial and *exceedingly difficult* to calculate, particularly in the long-time regime ($t > T_2$).**

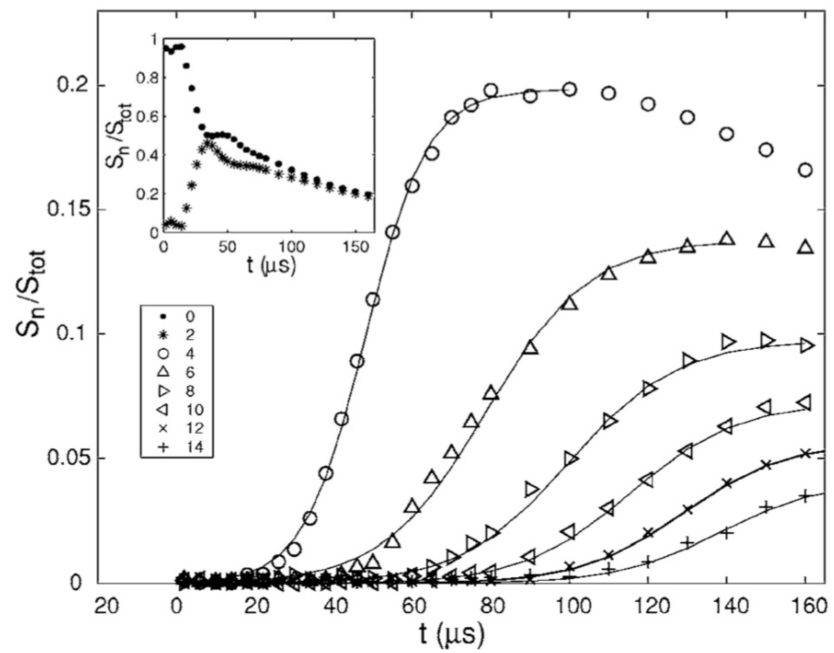
Spin Echoes in Solids



Showing the decay envelopes.

- A conventional 90-180 spin echo CANNOT refocus dipole-dipole dephasing.
- Solid echoes (Powles and Mansfield 1962): 90°_x - τ - 90°_y - detect
- Solid echoes only PARTIALLY refocus spins that are dephased by dipole-dipole interactions and do not generally peak at time 2τ.
- Degree of refocusing depends on τ.

Multiple-spin correlations in FID & echoes



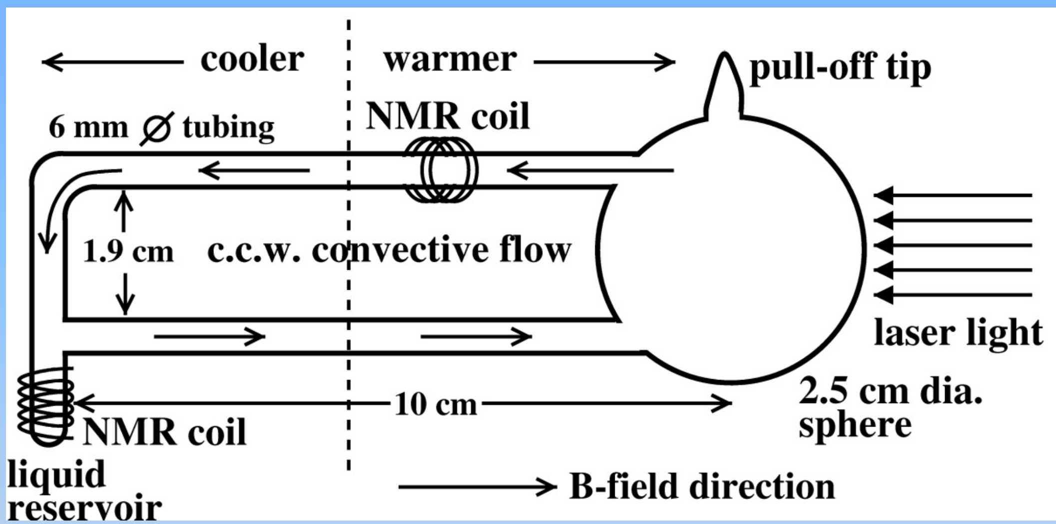
Growth of multiple-spin correlations in CaF_2 FID.
H. Cho, et al., Phys. Rev. B **72**, 054427 (2005).

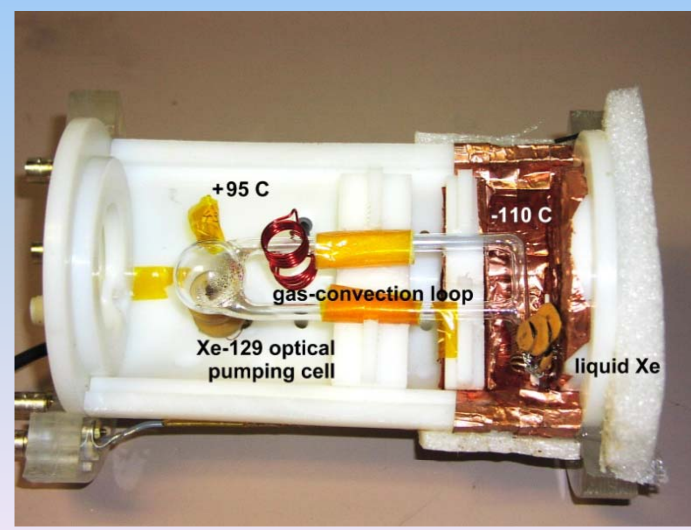
- **Solid echo works "perfectly" for spins 1/2 taken as pairs.**
- **In a real system, 3-spin, 4-spin, *etc.* interactions affect the evolution of coherence for longer and longer times τ.**

➢ **Bottom line: FID and solid echoes with different echo times τ create distinctly different collective transverse spin configurations at the end of the final pulse.**

Liquid hyperpolarized ^{129}Xe

Produced by phase exchange in a convection cell.





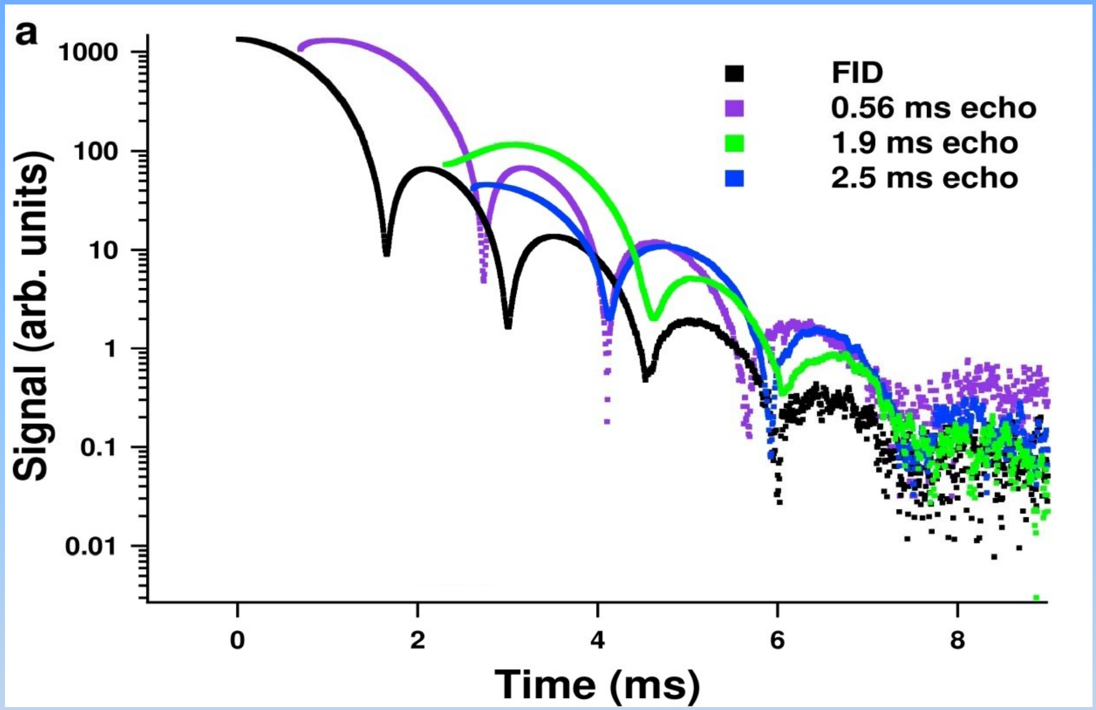
*T. Su, G.L. Samuelson, S.W. Morgan, G. Laicher, and B. Saam, App. Phys. Lett. **85**, 2429 (2004).

A Simple Experiment

Acquire FID and several solid echoes with different interpulse delay times τ and compare the behavior of the transverse NMR decays at times > T_2.

- **Huge signals from hyperpolarization allow examination of long-time behavior with high precision.**
- **Spin system is thermally isolated from environment (long T_1).**
- **As far from classical limit as possible (spins-1/2).**

Results in enriched solid ^{129}Xe*

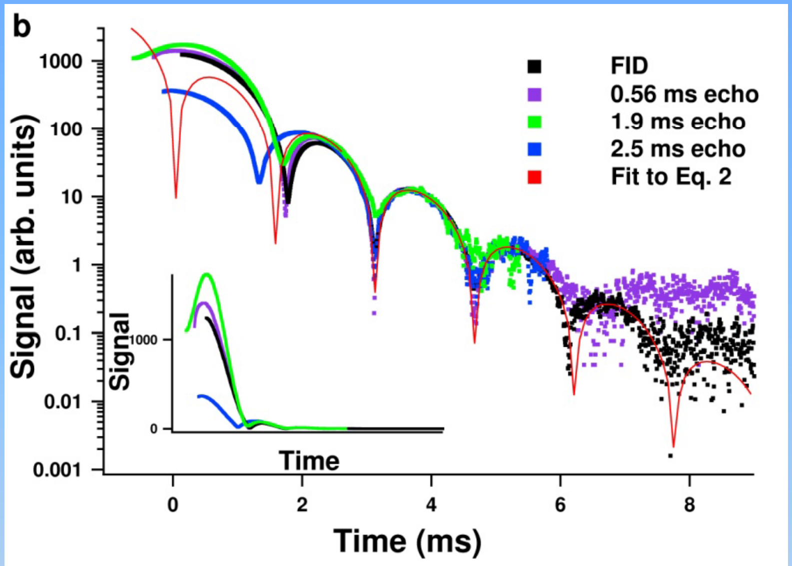


FID (in black) and solid echoes with 3 different values of τ.

- **Echoes shown starting at delay time τ from start of FID.**
- **Each FID/echo represents a distinct initial transverse spin state. (4 different initial configurations.)**

*S.W. Morgan, B.V. Fine, and B. Saam, Phys. Rev. Lett. **101**, 067601 (2008).

Universal Long-Time Behavior



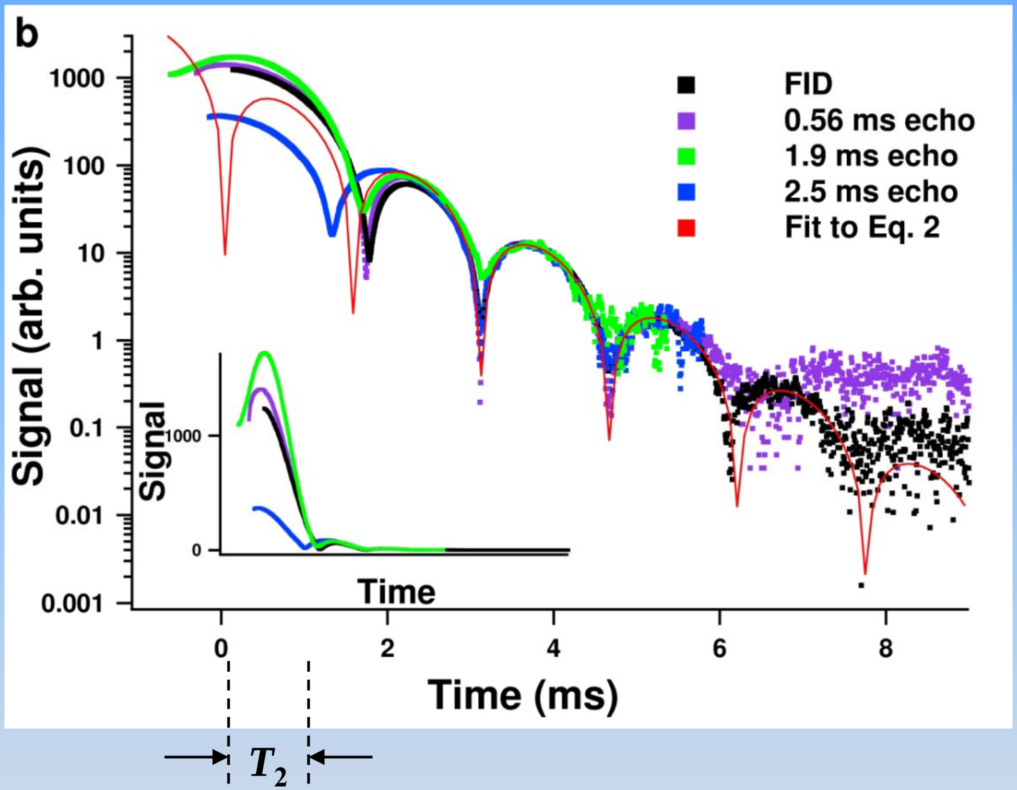
	γ (ms^{-1})	ω (rad/ms)
Enriched FIDs	1.25 ± 0.05	2.03 ± 0.04
Enriched echoes, $\tau = 0.56$ ms	1.25 ± 0.05	2.00 ± 0.03
Enriched echoes, $\tau = 1.9$ ms	1.22 ± 0.04	2.06 ± 0.03
Enriched echoes, $\tau = 2.5$ ms	1.25 ± 0.04	2.05 ± 0.04

Amplitude-normalized; time shifted.

Data are fit (red line) to: $$S(t) = \left|S_0 e^{-\gamma t} \cos(\omega t + \phi)\right|$$

- **Universal long-time behavior: γ and ω have same value for all 4 initial spin configurations; compare to initial behavior.**

An Interesting Time Scale



- Conventional long-time exponential behavior requires that "long times" be >> T_2, the "shortest ballistic microscopic time scale" in the system. (Think motional narrowing.)
- Here, γ^{-1} and ω^{-1} are both on the order of T_2; behavior appears to be outside the realm of conventional statistical physics.

A Specific Prediction

Earlier prediction from B.V. Fine* for the late-time behavior of the NMR free-induction decay and solid echo:

$$S(t) \sim e^{-\gamma t}\cos(\omega t + \phi)$$

where echoes (of all kinds and for different interpulse-delay times τ) should have the *same* ω and γ as the FID.

- **Motivated our experimental study.**
- **Based on a correspondence between many-particle quantum dynamics and the dynamics of classically chaotic systems.**

*B. V. Fine, Phys. Rev. Lett. **94**, 247601 (2005).

The Time-Evolution Operator

We normally think in terms of the eigenvalues and eigenfuctions of the Hamiltonian, but we can also formulate the problem in terms of the time evolution operator:

$$\rho(t,\mathbf{x}) = \hat{\mathrm{T}}(t)\rho(0,\mathbf{x})$$

Conjecture of B.V. Fine* is essentially that under the right conditions, solutions to this equation (eigenmodes of $\hat{\mathrm{T}}$) look like:

$$\rho_0(t,\mathbf{x}) = \rho_0(\mathbf{x})e^{-(\gamma-i\omega)t} + \rho^*(\mathbf{x})e^{-(\gamma+i\omega)t}$$

This is analagous to a formalism used in classical chaos theory, where the eigenmodes are known as Pollicott-Ruelle resonances.

*B. V. Fine, Phys. Rev. Lett. **94**, 247601 (2005).

Summary

Fundamental property of nuclear spin dynamics is revealed in long-time behavior of ^{129}Xe transverse decays in polycrystalline HP xenon.

- Solid hyperpolarized xenon is ideal system: thermally isolated, purely quantum-mechanical many-body system, maximally far from classical limit (spins-1/2).
- Large hyperpolarized signal allows precise characterization of decay over 4 orders of magnitude.
- Is it chaos? Explanation for universal behavior is beyond scope of conventional statistical physics. Chaos-based explanation previously predicted by B.V. Fine is compelling.

Hyperpolarized Gas Research Group

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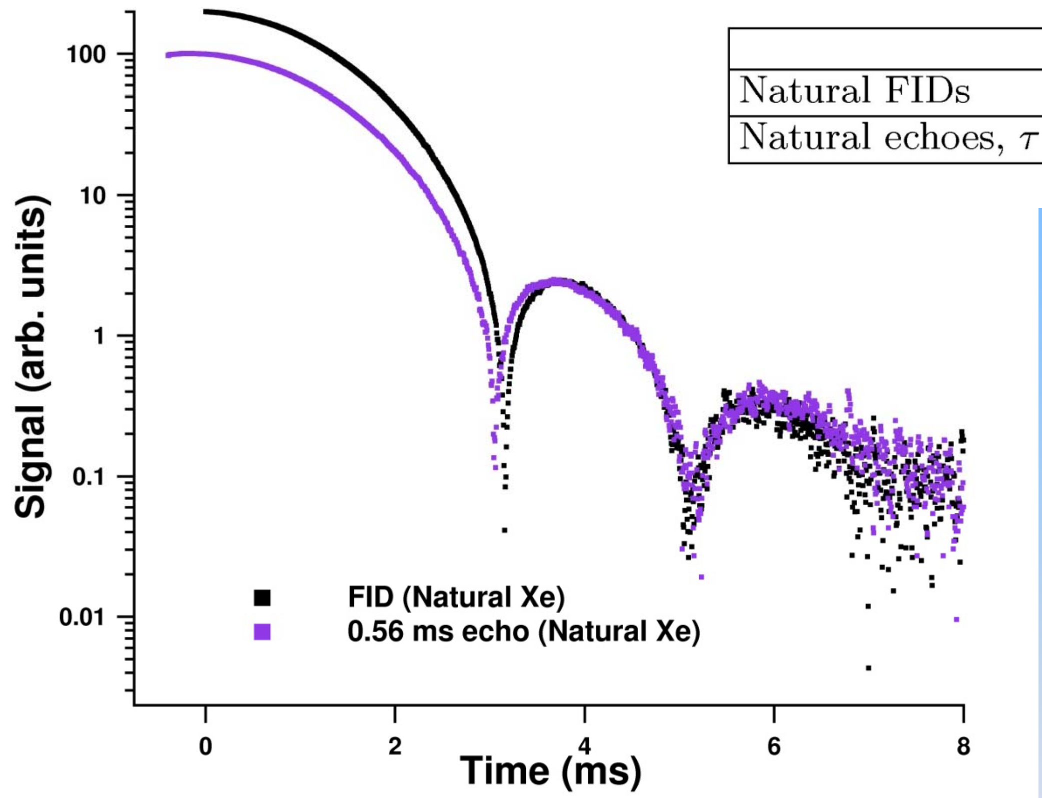
Zayd Ma

Undergraduates
Allison Schoeck
Laurel Hales
Oliver Jeong (HS student)

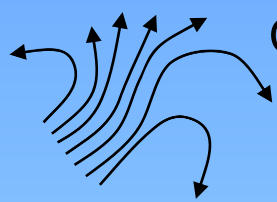
Similar Results for Natural Xenon



	γ (ms^{-1})	ω (rad/ms)
Natural FIDs	1.04 ± 0.08	1.53 ± 0.08
Natural echoes, $\tau = 0.56$ ms	1.04 ± 0.12	1.52 ± 0.04

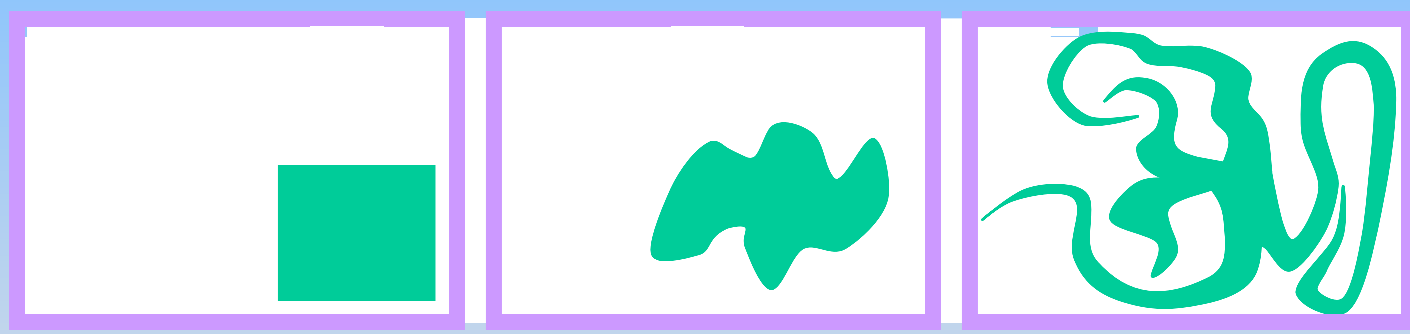
- Only one echo (with relatively short τ) could be acquired to compare to FID; SNR issues for larger τ.

Pollicott-Ruelle Resonances*



Chaotic mixing + Conservation of phase space volume (Liouville theorem)

Expansion-contraction picture in phase space



<u>Why are P.-R. resonances relevant?</u>

1. P.-R. resonances are the manifestations of extreme randomness, which has **no small scale bound**.

2. P.-R. resonance is <u>not</u> a property of one observable quantity. It is an **eigenmode** of the time evolution operator, which manifests itself in the behavior of **all** observable quantities having compatible symmetry.

*D. Ruelle, Phys. Rev. Lett. **56**, 405 (1986).

Incomplete History of FID Theories

1946	F. Bloch	Bloch equations, T_1, T_2
1948	N. Bloembergen, E. M. Purcell, and R.V. Pound	qualitative factors
1948	**J. H. Van Vleck**	**moments, Hamiltonian truncation**
1953	P. W. Anderson and P. R. Weiss	exchange narrowing
1957	**I. J. Lowe and R. E. Norberg (ISMAR Prize, 2004)**	**introduced free induction decay experimentally and theoretically**
1968	P. Borckmans and D. Walgraef	diagram technique
1973	G. W. Parker and F. Lado	memory functions
1975	M. Engelsberg and N.-C. Chao	continued fractions
1995	J. Jensen	
1972	C. W. Canters and C.S. Johnson	maximum entropy method
1985	P. A. Fedders and A. E. Carlsson	
1976	K. W. Becker, T. Plefka, and G. Sauermann	original physical models
1976	A. A. Lundin et al.	
1991	R. N. Shakhmuratov	
1997	B.V. Fine	spin problem is mapped onto a problem of coupled harmonic oscillators with several exact limits preserved.

Van Vleck:
“ *It is prohibitively difficult to determine the precise shape of the absorption line theoretically …*”