Ultralow magnetic fields elicit unexplained spin dynamics in water

Record-sensitive NMR measurements show that we still have more to learn about the most abundant liquid on the planet.

Placed in an external magnetic field, nuclear spins respond by dancing a two-step: They wobble, or precess, about the field axis, and polarize in the field direction. At room-temperature in a 100-μT field—comparable to that of an ordinary bar magnet—it takes water's spin-½ hydrogen nuclei about 10 seconds to relax, or achieve equilibrium polarization. In a 10-μT field, the spins relax in roughly ¾ the time.

The difference has to do with the protons' precession rate, or Larmor frequency, which is proportional to magnetic field intensity. As the Larmor frequency decreases, slower mechanisms can contribute to the relaxation process. At 100 μT, a proton's Larmor frequency is about 4 kHz, and spin relaxation is facilitated mostly by thermal fluctuations. At 10 μT the lower Larmor frequency of about 400 Hz allows proton exchange between H_3O^+ and H_2O and between H_2O and OH^- to help usher the system to equilibrium. The increase in the relaxation rate occurs around Larmor frequencies near 700 Hz (17 μT), roughly the same frequency with which protons hop between the various water complexes.

Aided by a superconducting quantum interference device (SQUID), low-field nuclear magnetic resonance experts at the National Metrology Institute in Berlin have now discovered yet another jump in water's spin-relaxation rate.[1] Led by Stefan Hartwig and Martin Burghoff, the team stumbled across the jump while probing relaxation at the ultralow Larmor frequencies produced by nanotesla fields, previously uncharted territory for NMR experiments.

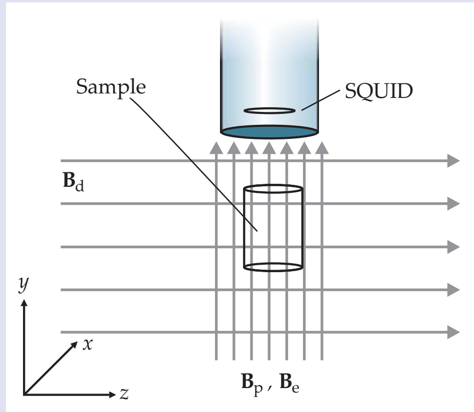

Figure 1. A water sample's ultralow-field spin dynamics are measured with a succession of three fields: a polarization field $\mathbf{B}_p$ that gives the sample its initial magnetization; an ultralow evolution field $\mathbf{B}_e$ that causes the magnetization decay; and a detection field $\mathbf{B}_d$ that induces precession about the z-axis. The resulting oscillating signal is detectable by a superconducting quantum interference device (SQUID). (Adapted from ref. 2.)

A slow precession

As sketched in figure 1, the Berlin group subjected a water sample to a succession of three static magnetic fields. To start, they generated a polarization field $\mathbf{B}_p$ in the vertical direction. That field, a few millitesla in intensity, induces a spin polarization of about ten parts per billion in the water sample—about a thousand times weaker than in conventional NMR, but still too strong to reveal new spin dynamics.

Next, they switched off $\mathbf{B}_p$ and switched on a much weaker, coaligned evolution field $\mathbf{B}_e$. Incorporating a feedback control scheme to counter field induction, they could achieve that switch in less than a millisecond. In $\mathbf{B}_e$, the precession of water's protons slows down, and the sample's magnetization begins to decay exponentially. Charting that decay over time gives what's known as the longitudinal relaxation rate R_1.

But the magnetic field generated by the faintly polarized water is minute, as small as a few picotesla. To accurately measure it, the researchers switched off $\mathbf{B}_e$ after some time τ and switched on the horizontally oriented detection field $\mathbf{B}_d$. At that instant, water's upward-pointing magnetization vector $\mathbf{M}$ begins to precess about the detection field, which causes the vertical component of its magnetic field, detected by a nearby SQUID magnetometer, to oscillate and decay. From that decay, the researchers could extract a reliable estimate of $\mathbf{M}$ at the moment $\mathbf{B}_e$ was turned off. By measuring $\mathbf{M}(\tau)$ for τ varying from 1 to 15 seconds and then successively repeating the procedure for $\mathbf{B}_e$ extending to less than 1 μT, the researchers pieced together R_1 values for Larmor frequencies as low as a few hertz.

The weakest fields the team probed were less than 1/500 the strength of Earth's geomagnetic field. At those intensities, even tiny fluctuations due to ambient RF waves would have foiled the experiment had the team not availed itself of the institute's state-of-the-art magnetically shielded room.

"They must have been extremely meticulous measurements," says Michelle Espy of Los Alamos National Laboratory, whose group also does ultralow-field NMR experiments. "At

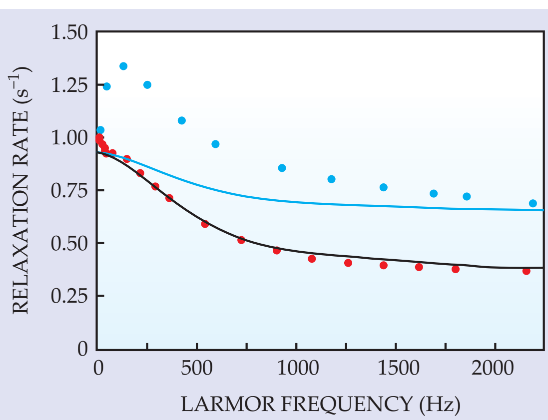

Figure 2. Water's longitudinal relaxation rate R_1 (red symbols), at which proton spins align with an external magnetic field, agrees with theory (black curve) when the protons' Larmor precession frequency is above 100 Hz. The deviation at lower frequencies suggests that in very weak fields, an as-yet-unknown mechanism aids spin relaxation. (The symbols intersect the vertical axis at about 1.0 s^{-1}; the curve intersects at about 0.9 s^{-1}.) The transverse relaxation rate R_2 (blue symbols), at which precessing spins decohere, exceeds theoretical predictions (blue curve) over a larger range. For both measurements, oxygen-17-enriched water was used, which enhanced spin–spin coupling. (Adapted from ref. 1.)

microtesla and below, magnetization from things that ordinarily are negligible can suddenly swamp what you're trying to measure."

A mystery mechanism

The Berlin team's low-field measurements weren't merely an exercise; they also revealed surprising physics. Apart from the expected rise due to proton exchange reactions, the measured R_1 values, shown in red in figure 2, also display an unexplained uptick as the Larmor frequency drops below 100 Hz.

Follow-up experiments suggest the rate increase has to do with coupling between H^+ nuclei and spin-5/2 ^{17}O nuclei. But as to the exact mechanism, Hartwig concedes, "We don't have a good explanation. Right now, we're hoping other theorists can offer some ideas."

Also sure to keep theorists busy are the team's measurements of water's transverse relaxation rate R_2, at which precessing nuclear spins decohere. The researchers obtained those measurements with the same experimental setup, except they bypassed the evolution field and switched directly from $\mathbf{B}_p$ to $\mathbf{B}_d$. The resulting oscillations in M_y have a Fourier peak corresponding to the Larmor frequency at $\mathbf{B}_d$. The width of that peak gives R_2.

The measured R_2 values, shown in blue in figure 2, exceed theoretical predictions and thus again implicate an as-yet-unknown relaxation mechanism. In a win for theory, however, the long-held principle that R_1 and R_2 should converge as the Larmor frequency approaches zero appears to hold true.

More surprises in store?

The usefulness of ultralow-field NMR extends beyond creating challenging theoretical puzzles. For example, experiments have hinted that healthy and cancerous tissues can be distinguished by their longitudinal relaxation times—a strategy known as T_1 contrasting—but only in microtesla fields and lower. Hartwig is not alone in suspecting that the same may be true of other materials; Espy, for one, hopes to use T_1 contrasting as a noninvasive way to identify explosive materials.

But as Espy puts it, for all the potential applications, "there's also real science to be discovered at low fields. We've thought for a long time that ultra-low-field NMR might reveal interesting molecular dynamics, but now the Berlin team has actually shown it—surprising things really do happen down there."

Ashley G. Smart

References

1. S. Hartwig et al., *J. Chem. Phys.* **135**, 054201 (2011).
2. M. Burghoff et al., *App. Phys. Lett.* **87**, 054103 (2005).

A belt of magnetically trapped antiprotons girdles Earth

An orbiting spectrometer has revealed the greatest concentration of antimatter yet seen—and it's only a few hundred kilometers away.

The satellite-borne spectrometer PAMELA, launched in 2006, is particularly good at detecting charged antimatter particles: positrons (e^+) and antiprotons ($\bar{p}$). Last year the PAMELA collaboration, led by Piergiorgio Picozza (University of Rome, Tor Vergata), reported a precision measurement of the minuscule $\bar{p}$ component of the spectrum of cosmic rays arriving at the top of the atmosphere. The measured $\bar{p}$ flux, the team found, could be explained by $\bar{p}$ production in high-energy collisions of cosmic-ray nuclei with ordinary interstellar matter.[1] So there was as yet no evidence of exotic sources of cosmic-ray antiprotons.

A similarly prosaic explanation holds for PAMELA's latest discovery: a significant $\bar{p}$ population magnetically trapped in Earth's inner Van Allen radiation belt.[2] The flux of trapped $\bar{p}$s spiraling around the belt's geomagnetic field lines turns out to be a thousand times greater than the flux of cosmic-ray $\bar{p}$s entering the atmosphere. That makes PAMELA's discovery the greatest concentration of antimatter yet observed. Even so, the team concludes that the trapped $\bar{p}$ population is readily explained by collisions in the atmosphere of cosmic-ray protons energetic enough to create neutron–antineutron pairs. In fact, the antiproton component of the Van Allen radiation belt had long been predicted and looked for, but only now has it been found.

Trapped in the inner belt

The inner Van Allen belt, characterized by its high concentration of trapped protons with kinetic energies up to a few GeV, does not extend down into the atmosphere. As shown in figure 1, it ranges in altitude from a few hundred kilometers near the magnetic poles to 10 000 km near the magnetic equator. Trapped protons spiral left-handedly around the lines of Earth's dipole field as they drift along them, bouncing back and forth between north and south magnetic-mirror points created by the field lines' convergence toward the poles.

Antiprotons entering the inner belt would become similarly trapped, if they arrived with sufficiently low energy and in a direction roughly orthogonal to the local magnetic field. But being negatively charged, they would spiral right-handedly. Annihilating encounters with resident protons would be rare in the relative vacuum of the belt. But where would a sufficient $\bar{p}$ influx come from to account for PAMELA's observation? The $\bar{p}$ component of the cosmic-ray spectrum is much too small.

Predictions of a trapped $\bar{p}$ population in the inner belt invoked the creation of antineutrons ($\bar{n}$) in the pair-production reaction

$$p + p \rightarrow p + p + \bar{n} + n,$$

instigated in atmospheric nuclei by cosmic-ray protons with energies above a threshold of about 7 GeV. Like a free neutron, an antineutron will beta decay into its charged partner with a half-life of 10 minutes. But why single out this circuitous route to the $\bar{p}$ when cosmic-ray collisions in the atmosphere also produce $p\bar{p}$ pairs directly? The reason is that as it plows through the atmosphere, a charged $\bar{p}$ loses energy faster than a neutral $\bar{n}$ and therefore is much less likely climb out to the inner belt before annihilating.

The trapped $\bar{p}$ population thus created would maintain a steady-state population—at least for a given phase in the 11-year solar cycle, which causes Earth's atmosphere to expand and contract—by continuous annihilation losses that equilibrate with the trapping of newly created low-energy $\bar{p}$s.

The orbiting spectrometer

PAMELA's principal component is a tracking magnetic spectrometer half a meter long (see PHYSICS TODAY, May 2011, page 10). An entering particle's curved path in the spectrometer's field measures its momentum per unit