VIOLATION OF THE SPIN-TEMPERATURE HYPOTHESIS*

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A "Loschmidt demon" is exhibited which effectively reverses the spin-spin relaxation of a system of interacting magnetic dipoles in a strong external field, thereby demonstrating that this system does not approach internal thermodynamic equilibrium in a time T_2 as was implicitly recognized by Philippot.

The coupled nuclear spins in a solid with very slow spin-lattice relaxation comprise an isolated system which for many purposes can be treated by thermodynamic methods.[1] One begins with the system in equilibrium at the lattice temperature T, performs various manipulations on the spins, waits a time T_2 characteristic of the spin-spin coupling, during which the spin system is imagined to approach internal equilibrium, and calculates a final spin temperature T_s through conservation of energy or other constants of the motion. The purpose of this Letter is to report some experiments for which this simple spin-temperature picture is not valid.

Consider the common situation in which a single-species solid is first brought to equilibrium with the lattice in a magnetic field $H_0\vec{k}$. If H_0 is sufficiently strong compared with the dipolar local field $H_{\rm loc}$, one describes the spin-density matrix by the canonical distribution

$$\rho_{\rm eq}(T) = (1/Z)\exp(M_z H_0/kT), \qquad (1)$$

where $\vec{M} = \gamma\hbar\sum\vec{I}_i$ is the operator for the total magnetic moment. Now a very short $\frac{1}{2}\pi$ rf pulse is applied at resonance (or $\vec{H}_0$ is abruptly rotated through $\frac{1}{2}\pi$) converting the density matrix to an initial value $\rho(0)$ which is the same as (1) except that M_z is replaced by M_x. The magnetization $\langle\vec{M}\rangle = \langle M_x\rangle\vec{i}$ decays[2] in a time $T_2 \sim (\gamma H_{\rm loc})^{-1}$ under the influence of the truncated dipolar Hamiltonian

$$\mathcal{H}_d{}^0 = \sum_{i<j}\sum b_{ij}(\vec{I}_i\cdot\vec{I}_j - 3I_{zi}I_{zj}), \qquad (2)$$

the truncation being increasingly valid as $H_0/H_{\rm loc}$ is made large. At a time $t_1 > T_2$ one commonly assumes the system has undergone an irreversible approach to an internal equilibrium state. If so, conservation of energy requires that the appropriate microcanonical distribution be characterized by infinite spin temperature: $\rho(t_1) = \rho_{\rm eq}(\infty) = 1/Z$. The magnetization will never recur and cannot be recalled by applying any external fields, since their Hamiltonian commutes trivially with $\rho_{\rm eq}(\infty)$.

Figure 1 exhibits a striking contradiction of this line of thought. Following a Bloch decay in CaF_2 we apply a strong rf perturbation to be described presently, after which the magnetization $\langle M_x\rangle$ returns in the form of an echo. This echo is of a quite different nature from the superficially similar one produced by Hartmann and Hahn,[3] which depends on the inhomogeneous character of the dipolar interaction between unlike spins and throws no suspicion on any aspect of spin thermodynamics.

The contradiction just mentioned is an illustration of Loschmidt's paradox.[4] We remind the reader that the microcanonical distribution is an arbitrary one which is chosen for mathematical simplicity when one knows nothing about the detailed dynamical history of the system. Yet in fact we know a great deal: The actual density matrix at time t_1 (in the rotating reference frame) is in fact

$$\rho_R(t_1) = \exp\left(\frac{-i}{\hbar}\mathcal{H}_d{}^0 t_1\right)\rho(0)\exp\left(\frac{i}{\hbar}\mathcal{H}_d{}^0 t_1\right). \qquad (3)$$

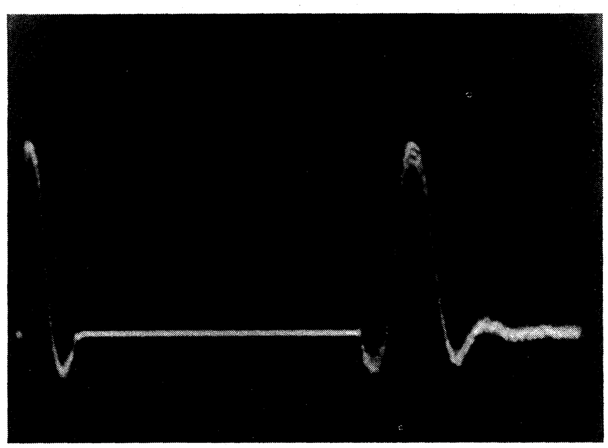

FIG. 1. Transient NMR of the ^{19}F nuclei in solid CaF_2. Following a normal Bloch decay, an rf burst of length 260 μsec with $H_1 = 95$ G (see text) was applied during the noise-free portion of the trace. Thereupon an echo occurs at a total delay of 365 μsec from the beginning of the experiment. In other experiments the initial decay was allowed to disappear fully before applying the burst.

While some phase functions, e.g., $\vec{M}(t_1)$, approach their equilibrium values for $t_1 > T_2$, it is not at all obvious that $\rho_R(t_1) \to \rho_{eq}(\infty)$ for any value of t_1.

The experiments are easily understood on the basis of equations of motion such as (3). Suppose that a strong resonant rf field H_1 is applied for a time t_B beginning at t_1. In the doubly (tilted) rotating reference frame[5] defined by

$$\rho_{DTR} = DT\rho_R T^{-1}D^{-1},$$
$$D = \exp(-i\gamma H_1 t I_z), \quad T = \exp(\tfrac{1}{2}i\pi I_y), \tag{4}$$

the system develops under an effective Hamiltonian[5]

$$\mathcal{H}_{DTR}(t) = -\tfrac{1}{2}\mathcal{H}_d{}^0 + \mathcal{H}'(t), \tag{5}$$
$$\mathcal{H}'(t) = -\tfrac{3}{4}\sum_{i<j}\sum b_{ij}[I_{+i}I_{+j}\exp(-zi\gamma H_1 t) + \text{c.c.}]. \tag{6}$$

Over an integral number of periods $\pi/\gamma H_1$ the effects of $\mathcal{H}_{DTR}(t)$ can be replaced by those of a time-independent average Hamiltonian[6]

$$\overline{\mathcal{H}}_{DTR} = \sum_{n=0}^{\infty}\overline{\mathcal{H}}_{DTR}{}^{(n)},$$

the importance of whose terms in general decreases approximately as $(H_{1oc}/H_1)^n$. In our experiments we have actually reversed the phase of the rf field (sign of H_1) at intervals of $\pi/\gamma H_1$, making $\overline{\mathcal{H}}_{DTR}{}^{(1)}$ vanish identically and leaving

$$\overline{\mathcal{H}}_{DTR} \approx -\tfrac{1}{2}\mathcal{H}_d{}^0 \tag{7}$$

as a very good approximation for times t_B such that

$$(H_{1oc}/H_1)^2\gamma H_{1oc}t_B \lesssim 1. \tag{8}$$

(The phase alternation is not essential to the general argument but makes the experiment work better in practice for a number of reasons.[6])

Equation (7) shows that the evolution of ρ_{DTR} may be regarded as proceeding backward in time,[7] at half the normal rate, a point which is central to this discussion.

But it is ρ_R we are interested in, so we transform back into the rotating frame, using the condition that t_B is an integral multiple of $\pi/\gamma H_1$, $\exp(2i\gamma H_1 t_B I_z) = 1$,

$$\rho_R(t_B + t_1) = T^{-1}\exp\left(\frac{-it_B}{\hbar}\overline{\mathcal{H}}_{DTR}\right)T\rho_R(t_1)T^{-1} \times\exp\left(\frac{it_B}{\hbar}\overline{\mathcal{H}}_{DTR}\right)T. \tag{9}$$

Now modify the experiment by initiating and terminating the burst with $\frac{1}{2}\pi$ pulses of opposing phases ($\pm y$ directions in the rotating frame). These pulses just cancel the transformations T, T^{-1} in (9). Now the state of the system, after a further unperturbed development for a time t_2, is

$$\rho_R(t_1 + t_B + t_2) = U\rho_R(0)U^{-1},$$
$$U = \exp\left(\frac{-it_2}{\hbar}\mathcal{H}_d{}^0\right)\exp\left(\frac{-it_B}{\hbar}\overline{\mathcal{H}}_{DTR}\right) \times\exp\left(\frac{-it_1}{\hbar}\mathcal{H}_d{}^0\right). \tag{10}$$

Inserting (8) into (10), we see that at the time which satisfies $t_1 + t_2 = \frac{1}{2}t_B$ one has $U = 1$; the original state returns, as signalled by the echo. This is the experiment of Fig. 1, the sequence of events being summarized by

$$(\tfrac{1}{2}\pi, x), t_1, (\tfrac{1}{2}\pi, -y), B_x(t_B), (\tfrac{1}{2}\pi, y), t_z, \text{ echo},$$

where B_x denotes the burst of phase-alternated 180° rotations about the x axis and (θ, μ) denotes a θ pulse about the μ axis.

The success of the experiment depends on the validity of approximation (8) which can be satisfied in our apparatus for t_B of several hundred μsec. But consider the interesting point that in principle a value of H_1 (with $H_0 > H_1$) can always be found which suffices to recover the initial state, to any desired accuracy after any desired time. In this sense it can be said that the system of dipoles does not behave irreversibly and never reaches equilibrium.

We have performed several other experiments which are understandable in the same way:

(2) $B_x(t_B), (\frac{1}{2}\pi, y), \frac{1}{2}t_B$, echo: During the burst, the original magnetization $M_0\vec{k}$ undergoes a Bloch decay in the rotating frame. Later, at $t = 3t_B/2$, an echo appears, showing that the system did not reach a spin temperature state in the rotating frame.

(3) $(\frac{1}{2}\pi, x), t_1, (\frac{1}{2}\pi, y), B_x(t_B)$, decay: A burst is applied following a Bloch decay in the laboratory frame. Another Bloch decay follows the burst and is maximized for $t_B = 2t_1$.

(4) $(\frac{1}{2}\pi, x), t_1, (\theta, y), t_2, (\frac{1}{2}\pi, -y), B_x(2t_2), (\theta, -y), B_x(4t_1), (\theta, y), B_x(2t_2), (\frac{1}{2}\pi, y), t_2, (\theta, -y), t_1$, echo: For $\theta = \frac{1}{4}\pi$, the experiment begins with Jeener's method[8] for producing a dipolar state. For $\theta = \frac{1}{2}\pi$ one has the "solid-echo" experiment.[9] The time-reversing bursts result in both cases in a full playback of the magnetization signal.

It is worth mentioning that the echo-forming $\frac{1}{2}\pi$ pulse in a solid-echo experiment can be regarded as reversing the effect of one part of

$\mathcal{H}_d{}^{0\,10}$: $\exp[i(\mathfrak{A}+\mathfrak{B})t] \to \exp[i(\mathfrak{A}-\mathfrak{B})t]$, which is not equivalent to a time reversal since $\mathfrak{A}$ is large. In the present experiments, the corresponding correction term $\overline{\mathcal{H}}_{\mathrm{DTR}}{}^{(2)}$ can be made as small as desired by a well-defined procedure. In this respect our experiments are closer to the inhomogeneous spin echo,[11] but succeed in reversing the dynamics of a system of interacting particles.

Our experiments show that the concepts of semiequilibrium and spin temperature in solids, while clearly of great value, must not be employed indiscriminately. We are of course only pointing out a special case of a general problem concerning criteria for irreversibility in isolated dynamical systems. We intend to discuss this matter more fully elsewhere, as well as extensions of the NMR experiment to repeated bursts and the problem of line narrowing in solids.

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PHONON DISPERSION AND THE PROPAGATION OF SOUND IN LIQUID HELIUM-4 BELOW 0.6°K†

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Recent experiments on the attenuation and velocity of sound in liquid He^4 at low temperatures are discussed in terms of the excitation model of liquid He^4. By assuming for the long-wavelength excitations the dispersion relation $\epsilon(p)=cp[1-\gamma p^2-\delta p^4\cdots]$ with γ *negative*, we are able to reconcile previous disagreements between theory and experiment.

In this Letter we make some general comments on the attenuation and velocity of sound in liquid helium-4 in the temperature range below 0.6°K where the only thermal excitations of importance are phonons. Despite considerable theoretical effort, the attenuation and velocity in this temperature range are not well understood. The theories of Pethick and ter Haar,[1] Kwok, Martin, and Miller,[2] Khalatnikov,[3] and Disatnik[4] give for the attenuation

$$\alpha=\frac{\pi^2}{30}\frac{(u+1)^2}{\rho\hbar^3}\frac{(kT)^4}{c^6}\omega \times[\arctan\omega\tau-\arctan(\tfrac{3}{2}\gamma\bar{p}^2\omega\tau)], \quad (1)$$

and for the change in velocity Δc,

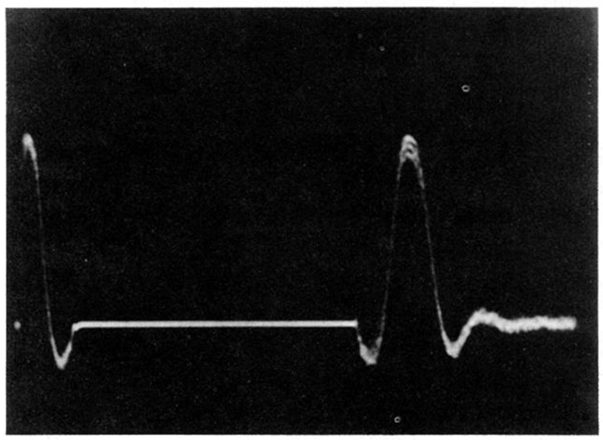
$$\Delta c=\frac{\pi^2}{60}\frac{(u+1)^2}{\rho\hbar^3}\left(\frac{kT}{c}\right)^4\ln\frac{1+(\omega\tau)^2}{1+(\frac{3}{2}\gamma\bar{p}^2\omega\tau)^2}, \quad (2)$$

where u is the Grüneisen constant $(\rho/c)\partial c/\partial\rho$, ρ the density, k Boltzmann's constant, c the velocity of sound, ω the frequency of the sound wave, τ the thermal phonon lifetime, $\bar{p}=3kT/c$, and γ is defined by the energy-momentum relation for low-momentum phonons,

$$\epsilon(p)=cp[1-\gamma p^2-\delta p^4\cdots]. \quad (3)$$

In the derivation of Eqs. (1) and (2) it is assumed that the γp^2 term dominates over the δp^4 term for most of the thermal phonons with which the sound wave interacts. We note the following:

(a) The experimental attenuation[5-7] is larger than predicted by Eq. (1) when the known value of u is used.[8] There is uncertainty regarding the correct values of γ and τ. γ has generally been assumed to be positive and of the order of 10^{35}



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