SPIN ECHOES AND LOSCHMIDT'S PARADOX

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ABSTRACT

Isolated systems of many particles often appear to behave irreversibly, though they are in principle dynamically reversible. In some cases this reversibility can be made evident in 'echo' phenomena, in which the system is literally restored to a dynamical state which existed in the past. Whether such echoes are in principle possible for all isolated systems is not known. However, they do not require the absence of interactions among the particles. Thus the inhomogeneous and 'magic sandwich' echoes are aspects of the same phenomenon.

I. INTRODUCTION

The spin echo[1] tends to astonish us when we first encounter it: a transverse magnetization seems to appear spontaneously 'out of nowhere' as if Maxwell's demon had been at work. Of course there is no cause for alarm; the phenomenon is fully and easily understood. However, the fact that the spins behave independently in this experiment, so that its analysis can be carried out in terms of the dynamical behaviour of a single representative spin, has suggested to some that this feature is indispensable to the production of echoes, which would then in principle be impossible in a 'genuine' many-body system of interacting particles. The fact that they are possible in both principle and practice is made clear by recent experiments[2, 3] on the dipole–dipole coupled nuclear spins in solids, based on special properties of coupled dipoles in strong external fields[4–6]. Therefore it is appropriate to discuss once again the role of echo phenomena *vis-à-vis* thermodynamics[7–9]. The problem is more than a century old, and we do not claim anything new in what follows. But the fact that it has been a subject of recurring discussion for such a long time shows that our intuitions about the behaviour of many-body systems have a persistent susceptibility to error, and that occasional pedagogical reexamination may be a good thing.

In the following section we discuss the essential general features of echo phenomena as a general way of conceptualizing the dynamical reversibility of isolated systems. The next section describes the technical features of the inhomogeneous spin echoes from this point of view. Applications of homogeneous echoes to solid state physics and chemistry are discussed by Pines *et al.*[10] in another paper in this Symposium.

II. LOSCHMIDT'S PARADOX AND LOSCHMIDT'S DEMON

A system of spins of long T_1 undergoing a Bloch decay is an example of an isolated system (fixed N, V, E). So is that favourite system of kinetic theorists, the gas in an insulating container with perfectly reflecting, rigid walls. Does such a system spontaneously move toward a condition of thermodynamic equilibrium? The answer depends largely on one's definition of equilibrium. In classical statistical thermodynamics one would associate the equilibrium system with a microcanonical ensemble made up of systems having the prescribed values of N, V, and E but otherwise being completely unbiased in their dynamical states $\{p_1 \ldots q_{3N}\}$. That is, the density ρ of representative points in the $6N$-dimensional Γ-space is uniform on the proper constant energy surface. Once such a situation exists it can never change, since the right hand side of the Liouville equation

$$\frac{\partial \rho}{\partial t} = \{\mathscr{H}, \rho\} \tag{1}$$

vanishes. A similar relation holds quantum-mechanically.

By the same token, that situation can never have been reached from a condition of nonequilibrium; the dynamical laws obeyed by the particles are inherently time-reversible. Properly, a system known to have been out of equilibrium should be discussed in terms of an ensemble constrained not only in (N, V, E) but also by whatever knowledge we have of the initial state. Such an ensemble also develops according to equation 1, but ρ never reaches exactly the microcanonical form. The additional constraints imposed necessarily mean that it occupies a smaller volume in Γ-space than the full microcanonical ensemble, and Liouville's theorem tells us that that volume does not change with time.

Does this mean that one cannot apply equilibrium thermodynamics to an isolated system? Not at all. Experience tells us that nearly all macroscopic properties of such systems approach the values that are calculated on the basis of the microcanonical ensemble. The ensemble density becomes uniform in a coarse-grained sense[11], and ordinary phase-space averages fail to detect its lack of complete uniformity. While the general question of *which* properties approach their equilibrium values at what rates is still an active subject of research, we know that a system which displays equilibrium values for several observables is extremely likely to do so for others as well, regardless of its previous history of nonequilibrium.

Yet this is not an absolute guarantee, and failure to keep this in mind can lead to the failures of intuition mentioned earlier. In fact the time-development of isolated systems obeys the reversible laws of classical or quantum mechanics, despite the almost overwhelming impression of irreversible approach to equilibrium they present to our senses. This confrontation has been called Loschmidt's paradox[9, 12], and is traditionally stated in the context of the kinetic theory of gases: a gas is known to expand irreversibly to fill its container; yet a simultaneous reversal of the velocities of all the molecules would result in a reversal of this process (*Umkehreinwand*) in equally good accord with mechanical laws as the expansion itself.

It is convenient to discuss such events in terms of a *Loschmidt demon*, named by analogy with Maxwell's but having quite fundamentally different powers. For our purposes we distinguish them as follows:

Maxwell's demon makes a series of choices *on a molecular level* which ultimately result in bringing the system into a desired state. For example he can observe molecules approaching an aperture between two halves of a container and, by operating a shutter, can eventually segregate all of the gas into one compartment. He can do so irrespective of the prior history of the system, even if it was initially in 'true' equilibrium†.

Loschmidt's demon, *by macroscopic manipulations alone*, returns the system to the same dynamical state $\{p_1 \ldots q_{3N}\}$ which it possessed a prescribed time T earlier. He need not know what that state was but must know the Hamiltonian of the system. Thereafter the system will of course spontaneously reenact its dynamical history. If at some time during the interval T the system had been recognizably out of equilibrium, the nonequilibrium behaviour will recur as an echo.

A single velocity reversal as envisioned by Loschmidt does not accomplish this, inasmuch as it results in a retracing of a configurational history with mirrored momenta. Loschmidt's demon must perform two such reversals. The chain of events is depicted in *Figure 1*, which shows a projection of the

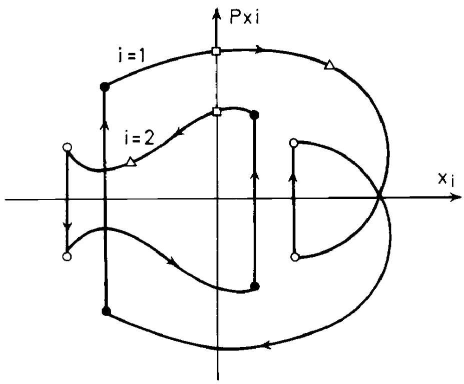

Figure 1. History of x and p_x for two of the molecules of a gas. Two successive velocity reversals (open circles) result in recovery of a dynamical state from the past.

full Γ space onto the x coordinate and its conjugate momentum for two of the molecules of a gas. The gas is imagined to begin condensed on the plane $x = 0$, symbolized by the squares for molecules 1 and 2. In the course of time the two points move along complicated paths under the influence of all the intermolecular forces, reaching the points denoted by open circles at the same instant. The velocities are then instantaneously reversed. Thereafter the gas develops backward in configuration space until a chosen instant denoted by the solid circles, whereupon the second velocity reversal

† Note that there is nothing physically impossible about this. In fact, if the demon has the same temperature as the gas, information theory shows that he must necessarily do as much work in decreasing the entropy of the gas as is required by the second law of thermodynamics. *cf.* L. Szilard. *Z. Physik* 53. 840 (1929). From this point of view the second law amounts to a forswearing of microscopic manipulations on systems to be described thermodynamically.

is performed. Shortly thereafter both points simultaneously reach the same locations they had at the beginning of the experiment. Note that the overall history involves one instant (squares) displaying nonequilibrium behaviour, as well as others (triangles) having no remarkable properties.

It might be imagined that Loschmidt's demon could never accomplish a reversal of velocities by macroscopic means alone, without knowledge of the microscopic state. Hahn[13] has suggested a thought experiment which shows how to do it for the special case of a gas of charged particles, all having the same value of $|e/m|$, in two dimensions. *Figure 2* shows the path

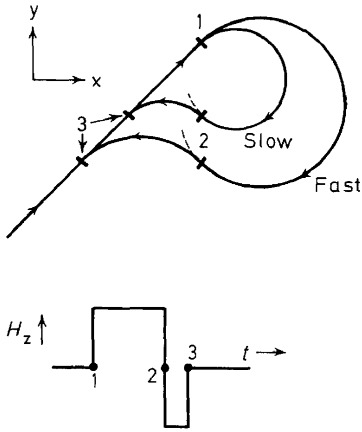

Figure 2. Proposed reversal of velocities in a two-dimensional electron gas.[13]

of a representative particle in the xy plane. At $t = 0$ a strong magnetic field is applied in the z direction, inducing a cyclotron precession whose frequency is $\omega_c = eH/2mc$ independent of particle velocity. (The trajectories of two particles of different speeds are shown.) At $t = 3\pi mc/eH$, when $\frac{3}{4}$ of a cyclotron orbit has been executed, the field is reversed for a further time $\pi mc/eH$, reversing the sense of the precession, and then shut off. The particles now retrace their original paths. Interactions among the particles will become unimportant if H is made sufficiently large. This experiment of course leaves open the interesting question of whether a Loschmidt demon is realizable for other kinds of systems, or of what conditions they must satisfy. As we shall see, he at least exists not only for the two-dimensional charged gas but for certain spin systems in strong external fields as well.

One could also ask whether more than one distinct Loschmidt demon exists for a given system, the differences being in the path in phase space by which the system is brought to an earlier dynamical state. In particular, consider a demon who is able instantaneously to reverse the sign of the Hamiltonian $\mathscr{H}$ (for example by changing the signs of the masses (!) and interaction potentials of all the particles). A system thus reversed would retrace exactly the path in phase space which it had followed before the reversal, since the phase space distribution obeys equation 1. Whether or not such a reversal of $\mathscr{H}$ is literally possible, it is often convenient to think of Loschmidt reversals in such terms. This can always be done by making a canonical transformation to a new phase space, moving with respect to the ordinary one, so that the representative point appears to move under the influence of a Hamiltonian $-\mathscr{H}$ when viewed in the moving phase space. In this restricted sense the Loschmidt reversal can always be said to accomplish $\mathscr{H} \to -\mathscr{H}$ and, therefore, a time reversal, viz. equation 1. Of course this is only a way of speaking and not a prescription for constructing a Loschmidt demon. Note that in a phase space moving according to the Heisenberg prescription

$$\rho^* = [\exp(i\mathscr{H}t)]\,\rho\exp(-i\mathscr{H}t) \tag{2}$$

the density is invariant and the question of approach to equilibrium (or any other condition) does not arise. If the notion of Hamiltonian-reversal or time-reversal is to be useful in discovering Loschmidt demons it must be by suggesting external forces which make the moving frame of reference somehow appropriate to the system.

III. LOSCHMIDT DEMONS FOR SPIN ECHOES

The relation of the point of view just expressed to the Hahn spin echo is easily expressed. For our purposes we will find it convenient first to discuss a segment of a Carr–Purcell train of type B[14] comprising an interval 4τ which begins just after one 180° pulse and ends just after the *second* succeeding pulse. In the rotating frame, the state vector develops according to

$$\psi_R(t_0 + 4\tau) = P\,e^{-2i\mathscr{H}\tau}P,\,e^{-2i\mathscr{H}\tau}\psi_R(t_0) \tag{3}$$

with

$$P = \exp(-i\pi I_x) \tag{4}$$

Insertion of the identity operator $P^{-1}P$ at the point marked by the comma in equation 3, and using the fact that $P^2 = 1$ for 180° pulses, one has

$$\psi_R(t_0 + 4\tau) = e^{-2i\tilde{\mathscr{H}}\tau}\,e^{-2i\mathscr{H}\tau}\psi_R(t_0) \tag{5}$$

where

$$\tilde{\mathscr{H}} = P\mathscr{H}P^{-1}. \tag{6}$$

For the usual inhomogeneous distribution of Larmor frequencies about some reference frequency the secular rotating frame Hamiltonian is

$$\mathscr{H} = \sum_{i=1}^{N} \delta_i I_{zi} \tag{7}$$

Whereupon equation 6 shows that

$$\tilde{\mathscr{H}} = -\mathscr{H};\ \psi_R(t_0 + 4\tau) = \psi_R(t_0) \tag{8}$$

The Loschmidt demon has restored the system to the same dynamical state it was in at time t_0. The passage from equations 3 to 5 embodies the introduction of an interaction representation from which the explicit rf pulse fields have been removed. In this (singularly) moving reference frame the Hamiltonian appears to have been reversed in sign during the second half of the

4τ interval, corresponding to a reversed time development. Naturally if a nonequilibrium magnetization $\langle \boldsymbol{M} \rangle$ existed at any time during the interval, it will be echoed at the corresponding moment in the next such interval.

The Hamiltonian (7) contains no interactions among the particles, as mentioned in Section I, and is thus analogous to the famous ideal gas of noncolliding particles which is incapable of reaching Maxwell–Boltzmann equilibrium. However, this point is peripheral to the discussion above, which centred on the symmetries of $\mathscr{H}$ under rotations in spin space. (Corresponding symmetries exist under rotations in laboratory space when the δ_i arise from an inhomogeneous magnet, and echo phenomena are known for spinning samples[15]). Even Hamiltonians describing interacting particles may possess symmetries which permit the construction of Loschmidt demons.

The 'magic sandwich' echoes[3] are a case in point. Here the relevant rotating-frame secular Hamiltonian is the truncated dipole–dipole interaction

$$\mathscr{H}_d^0 = \sum_{i<j}^{N}\sum b_{ij}(\boldsymbol{I}_i \cdot \boldsymbol{I}_j - 3I_{zi}I_{zj}) \tag{9}$$

which possesses all the requisite nonlocal features one is accustomed to associate with irreversibility. The manipulation to be performed, in its simplest[2, 3] but not most effective form, consists in applying a strong rf field of specified duration t_B in the x direction of the rotating frame, immediately preceded and followed by 90° pulses, one in the $+y$ and the other in the $-y$ direction. Omitting the effects of $\mathscr{H}_d^0$ during the brief 90° pulses (but not during the much longer interval t_B), one has

$$\psi_R(t_0 + t_B) = \exp\left(-i\frac{\pi}{2}I_y\right)\exp\{-it_B(\gamma H_1 I_x + \mathscr{H}_d^0)\}\exp\left(i\frac{\pi}{2}I_y\right) \tag{10}$$

Now if H_1 is much stronger than the dipolar local fields, $\mathscr{H}_d^0$ can be treated as a perturbation in equation 10. To first order we keep only that part of $\mathscr{H}_d^0$ which is diagonal in a representation which diagonalizes $\gamma H_1 I_x$. It (and its higher order corrections) are conveniently found by coherent averaging theory[16], the result being an operator

$$\mathscr{H}_d^x = \sum_{i<j}\sum -\frac{1}{2}b_{ij}(\boldsymbol{I}_i \cdot \boldsymbol{I}_j - 3I_{xi}I_{xj}) \tag{11}$$

Now the centre factor of equation 10 can be written as the product of two commuting exponentials, one of which is the identity operator *if the duration of the burst is adjusted so that* $\gamma H_1 t_B = 2n\pi$, *n* an integer:

$$\exp(-2in\pi I_x) = (1)^{I_x} = 1 \tag{12}$$

Now

$$\begin{aligned}\psi_R(t_0 + t_B) &= \left\{\exp\left(-i\frac{\pi}{2}I_y\right)\exp(-it_B\mathscr{H}_d^x)\exp\left(i\frac{\pi}{2}I_y\right)\right\}\psi_R(t_0)\\ &= \exp\{-it_B(-\tfrac{1}{2}\mathscr{H}_d^0)\}\psi_R(t_0)\\ &= \psi_R\left(t_0 - \frac{t_B}{2}\right)\end{aligned} \tag{13}$$

The state of the system is the same as it was a time $t_B/2$ before the beginning of the burst. Any decay of magnetization or any other property that might have occurred during that period is recovered.

A version of this experiment is shown in *Figure 3*. Here, instead of the steady rf field described above, a complex pulse train is based on a pulsed

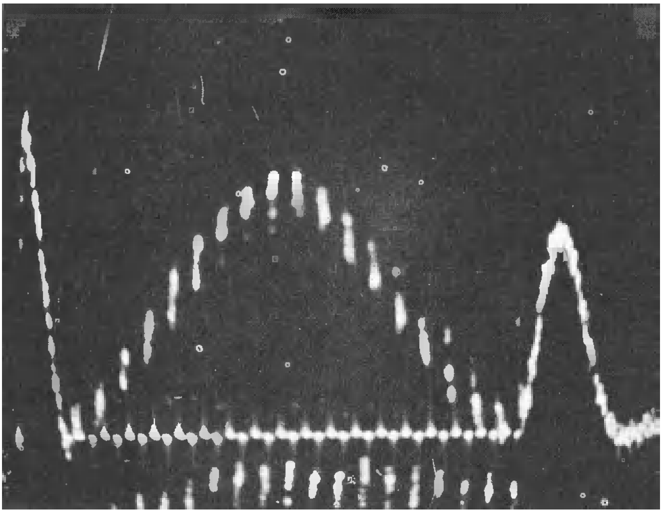

Figure 3. Dipolar echo in a CaF_2 crystal, using a pulse sequence for time reversal.[5]

line-narrowing method[17] according to the prescription of Schneider and Schmiedel[5]. A free induction decay is allowed to occur for a certain time, after which the time-reversing pulse sequence is applied. Through the windows in the sequence one can see a 'rotary echo' representing the retracing of the dynamical history of the system through $t = 0$ to the equivalent of a negative time. (In this case the reverse development is somewhat slower than the half-normal rate implied by equation 13). Upon termination of the sequence the system develops normally through $t = 0$, recovering and subsequently losing the original magnetization.

IV. CONCLUSION

The main point of the preceding discussion has been to emphasize the fact that isolated dynamical systems indeed do obey the (reversible) laws of mechanics, irrespective of the number of particles they contain or the apparent complexity of the interactions among them. In effect every such system possesses a set of perfect 'normal modes' to which the notion of damping is foreign, but we are not always able to see how to excite a single one of these modes in such a way as to make its coherence experimentally evident. The fact that we cannot usually do so deliberately implies that it is not likely to occur by accident. Thus experimental predictions based on a postulated equilibrium distribution of modes are nearly always in accord with ones based on the true distribution resulting from some previous history.

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