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A Study of Entropy Change in a Spin Quantum System

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Abstract

The entropy change in a spin system coupled to a magnetic field is investigated by solving an evolution equation for a quantum spin system. Entropy of the system is discussed and the exchange of entropy between the spins and field can be studied. The full quantum treatment of spins and field shows that the coherent nature of this field is very important for reaching the spin echo.

Keywords

Spin, Field, Quantum, Entropy, Coherent, Integrable

1. Introduction

The investigation of the behavior of the entropy in a system that evolves through a well defined cycle can provide knowledge as to how quantum mechanics at a fundamental level enters into statistical physics and thermodynamics [1] [2] [3]. The second law of thermodynamics claims that disorder is generally as a result of the evolution. After its appearance, it is virtually impossible to eliminate. There are many systems which can be explored in terms of a mathematical model which produces predictions and also admit experimental study [4] [5]. An important and useful system to look at is one made up of a large number of spins which are initially aligned and precess in an inhomogeneous magnetic field until they point in various directions. The spins start in an ordered state and in time become disordered. The spins are subjected to a radio-frequency pulse of a particular frequency and direction. The subsequent evolution reverses the accumulated disorder causing the spins to return to their initial aligned state [6] [7]. The question of just how much disorder is created during this process and is this disorder effectively removed or to what extent is the original state recovered by the end of the process is certainly of great interest. The more general question, do evolutions take place at the quantum level for which the entropy does not change but remains constant throughout. This is the case studied here [8] [9] [10] [11]. It could be said that a proper thermodynamic treatment should take into account the correlations between the spin and translational degrees of freedom [12]. But it is worth proceeding as done here to provide a benchmark for different ways of looking at this. Also there is often a fuzzy region as to what is referred to as system and environment in quantum mechanics.

Classically the physical situation is constructed by subjecting a system of spins to a strong, stable magnetic magnetic field B which points along the z axis. Let μ be the magnetic moment of the nuclei in the macroscopic sample, then if $\mu B \gg k_B T$, at equilibrium, all spins except a small population will point up along the z-axis. A pulse from a radio-frequency field B, is directed along the x axis and oscillates at the spins average Larmor frequency $\omega = 2\mu B/\hbar$ with length $\pi/2\omega_1$, where $\omega_1 = \mu B/\hbar$. This is just the amount of time which is required for the Larmor procession around the field of the pulse to rotate all the spins to a common orientation perpendicular both to the z-axis and to the direction of the pulse in a co-rotating frame. The spins now precess freely about the z-axis.

Initially, all the spins are aligned. However, local inhomogeneities in the magnetic field give a different precession rate for the spins. Inhomogeneities of about one percent will cause the spins to unalign completely after 1000 revolutions, as an example. As long as the coupling between different spins and between spins and lattice is weak, the disorder is almost entirely due to the different rates of the Larmor precession. Between the start of the precession at $t = 0$ and the spin-spin or spin-lattice relaxation time, a second pulse can be applied, twice the length of the first pulse. This causes the spins to precess by an angle π about the rotating magnetic field of the pulse. In the co-rotating frame the effect of the precession is to take the i-th spin from angle γ_i to an angle $-\gamma_i$. So the second pulse conjugates the total phase that each spin has accumulated during the course of the precession.

As the spins precess, each in its own magnetic field, the precession of each spin undoes the phase that is accumulated before its phase was conjugated. At time t after the second pulse, the spins are lined up again along a direction 180 away from the original orientation. In terms of an experiment, the realignment of the spins induces a signal which can be detected. This signal is the echo of the signal that originally aligned the spins. If the pulse that conjugates the spin phases shows up after the spin-spin or spin-lattice relaxation time, the spins then fail to realign. The spins following their conjugation must undo or reverse their entire previous evolution, which includes significant interactions. It is found that a carefully selected sequence of pulses is sufficient to reverse not only the evolution of the spins, but their interaction with the other spins as well.

Once the system has been prepared so that there is complete knowledge of the state of the spins subject to the evolution, the spins precess, and knowledge about individual orientations is not preserved. Field inhomogeneities act in such a way as to cause the spins to reach a state of seemingly maximum entropy. Application of the second pulse causes the spins to quickly return to a state of zero entropy. It is desired to find out what this says about the second law of thermodynamics. It will be seen that, in fact, the second law of thermodynamics is preserved.

One way to account for this is that entropy collected by the spins during the evolution is transferred into the quantum state of the electromagnetic field pulse that causes this reversal. If this happened, it could be said the second law applies to the whole system of spins and field. This as the following results show is not what actually happens. The entropy of the spins does not go into the magnetic field. A second possibility is that the entropy of the spins does not increase and they are not disordered in an absolute sense, but appear to be as suggested already. To study this, the algorithmic entropy which is the length of the shortest algorithm that can reproduce the spin's configuration, is a good measure of this. The only difference between the algorithmic randomness of the spin-echo system and its statistical entropy is that while the entropy remains constant, the algorithmic complexity goes like $\log\left(t/\Delta t\right)$. The term that comes from specifying the amount of time that the system has evolved since the spins were aligned. This factor will be used as a benchmark later. There is a third explanation which is the one that does account for what is obtained by calculation and will become apparent in due course.

2. A Model System and Its Solution

The Hamiltonian for a spin-1/2 particle subject to a magnetic field with strength $B_0 = \omega_0/\gamma$ along the *z*-axis and to a radio frequency field with frequency ω along the *x*-axis is given in terms of creation and annihilation operators $b^\dagger, b$ and Pauli matrices as

$$\hat{H} = \frac{1}{2}\hbar\omega_0\sigma_z + \hbar\eta\left(\hat{b}\sigma_+ + \hat{b}^\dagger\sigma_-\right) + \hbar\Omega\hat{b}^\dagger\hat{b}, \quad \hat{b}^\dagger\hat{b}\left|n\right\rangle = n\left|n\right\rangle. \tag{2.1}$$

In (2.1) η and Ω are constants. Define the set of basis for the Hilbert space under consideration to be

$$\left|n,\uparrow\right\rangle = \left|n\right\rangle \otimes \left|\uparrow\right\rangle, \quad \left|n,\downarrow\right\rangle = \left|n\right\rangle \otimes \left|\downarrow\right\rangle. \tag{2.2}$$

Using the properties of the operators $\sigma_\pm$, we have $\sigma_+\left|\uparrow\right\rangle = 0$ and $\sigma_-\left|\downarrow\right\rangle = 0$, $\hat{H}$ can be applied to the basis states defined in (2.2)

$$\begin{aligned} \hat{H}\left|n,\uparrow\right\rangle &= \frac{1}{2}\hbar\omega_0\left|n,\uparrow\right\rangle + \hbar\eta\sqrt{n+1}\left|n+1,\downarrow\right\rangle + \hbar\Omega n\left|n,\uparrow\right\rangle \\ &= \hbar\left(\frac{1}{2}\omega_0 + n\Omega\right)\left|n,\uparrow\right\rangle + \hbar\eta\sqrt{n+1}\left|n+1,\downarrow\right\rangle, \end{aligned} \tag{2.3}$$

$$\begin{aligned} \hat{H}\left|n+1,\downarrow\right\rangle &= -\frac{1}{2}\hbar\omega_0\left|n+1,\downarrow\right\rangle + \hbar\eta\sqrt{n+1}\left|n,\uparrow\right\rangle + \hbar\Omega\left(n+1\right)\left|n+1,\downarrow\right\rangle \\ &= \hbar\left(-\frac{1}{2}\omega_0 + \left(n+1\right)\Omega\right)\left|n+1,\downarrow\right\rangle + \hbar\eta\sqrt{n+1}\left|n,\uparrow\right\rangle. \end{aligned} \tag{2.4}$$

The operator $\hat{H}$ has a 2×2 matrix representation as

$$\hat{H} = \hbar \begin{pmatrix} -\frac{1}{2}\omega_0 + (n+1)\Omega & \eta\sqrt{n+1} \\ \eta\sqrt{n+1} & \frac{1}{2}\omega_0 + n\Omega \end{pmatrix} \tag{2.5}$$

It is required to diagonalize this Hamiltonian operator (2.5). First the eigenvalues are found to be

$$E_{\pm} = \hbar\left(\Omega\left(n+\frac{1}{2}\right) \pm \sqrt{\left(\frac{\omega_0 - \Omega}{2}\right)^2 + \eta^2 (n+1)}\right) = \hbar\left(\Omega\left(n+\frac{1}{2}\right) \pm \lambda_n\right), \tag{2.6}$$

where the quantity λ_n is defined by

$$\lambda_n = \sqrt{\frac{1}{4}(\omega_0 - \Omega)^2 + \eta^2 (n+1)}. \tag{2.7}$$

The actual eigenstates are determined by solving

$$\begin{pmatrix} -\frac{1}{2}\omega_0 + (n+1)\Omega - \left(\Omega\left(n+\frac{1}{2}\right) \pm \lambda_n\right) & \eta\sqrt{n+1} \\ \eta\sqrt{n+1} & \frac{1}{2}\omega_0 + n\Omega - \left(\Omega\left(n+\frac{1}{2}\right) \pm \lambda_n\right) \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{2.8}$$

For the case with the upper sign in (2.8), setting $\alpha = \omega_0 - \Omega$ the eigenvector is

$$\begin{pmatrix} 1 \\ \dfrac{\frac{1}{2}\alpha + \lambda_n}{\eta\sqrt{n+1}} \end{pmatrix}. \tag{2.9}$$

Vector (2.9) can be normalized by dividing with $\mathcal{N} = \sqrt{\eta^2 (n+1) + \left(\frac{1}{2}\alpha + \lambda_n\right)^2}$ and the result is

$$\begin{pmatrix} \dfrac{\eta\sqrt{n+1}}{\mathcal{N}} \\ \dfrac{\frac{1}{2}\alpha + \lambda_n}{\mathcal{N}} \end{pmatrix} = \begin{pmatrix} \cos\vartheta_n \\ \sin\vartheta_n \end{pmatrix}. \tag{2.10}$$

For the lower sign, an eigenvector is

$$\begin{pmatrix} \dfrac{-\frac{1}{2}\alpha + \lambda_n}{\eta\sqrt{n+1}} \\ 1 \end{pmatrix}. \tag{2.11}$$

It has a normalized form as

$$\begin{pmatrix} -\dfrac{\frac{1}{2}\alpha + \lambda_n}{\mathcal{N}} \\ \dfrac{\eta(n+1)}{\mathcal{N}} \end{pmatrix} = \begin{pmatrix} -\sin\vartheta_n \\ \cos\vartheta_n \end{pmatrix}. \tag{2.12}$$

The normalized eigenstates can then be put together as follows

$$\begin{aligned} \left|\varphi_+(n)\right\rangle &= \cos\vartheta_n \left|n+1,\downarrow\right\rangle + \sin\vartheta_n \left|n,\uparrow\right\rangle, \\ \left|\varphi_-(n)\right\rangle &= -\sin\vartheta_n \left|n+1,\downarrow\right\rangle + \cos\vartheta_n \left|n,\uparrow\right\rangle. \end{aligned} \tag{2.13}$$

The original states can be expressed in terms of the eigenstates by solving (2.13),

$$\begin{aligned} \left|n,\uparrow\right\rangle &= \sin\vartheta_n \left|\varphi_+(n)\right\rangle + \cos\vartheta_n \left|\varphi_-(n)\right\rangle, \\ \left|n+1,\uparrow\right\rangle &= \cos\vartheta_n \left|\varphi_+(n)\right\rangle - \sin\vartheta_n \left|\varphi_-(n)\right\rangle. \end{aligned} \tag{2.14}$$

This solves the Hamiltonian eigenvalue problem.

A wave function $\psi(\boldsymbol{r},t)$, which at time $t=0$ is a linear superposition of stationary states $\sum_\alpha c_\alpha \psi_\alpha(\boldsymbol{r})$ evolves under the influence of a t-independent Hamiltonian as follows. If the energies of the levels are called E_α then from linearity of the Schrödinger equation, the evolution in time of this wavefunction follows from this

$$\sum_\alpha C_\alpha \mathrm{e}^{-iE_\alpha t/\hbar} \psi_\alpha(\boldsymbol{r}).$$

Initially for the situation discussed here, the spins are lined up along the x-axis, and the radio frequency field is off. The initial state of a typical spin is

$$\left|\psi(0)\right\rangle = \frac{1}{\sqrt{2}}\left(\left|0,\uparrow\right\rangle + \left|0,\downarrow\right\rangle\right). \tag{2.15}$$

The spin precesses around the magnetic field which is directed along the z-axis. Following the plan above, at time t, the state vector is given by

$$\left|\psi(t)\right\rangle = \frac{1}{\sqrt{2}}\left(\mathrm{e}^{-i\omega_0 t/2\hbar}\left|n,\uparrow\right\rangle + \mathrm{e}^{i\omega_0 t/2\hbar}\left|n,\downarrow\right\rangle\right). \tag{2.16}$$

This state can also be transformed into the eigenstate basis $\left|\varphi_\pm\right\rangle$ so that $\left|\psi(t)\right\rangle$ is expressed as

$$\begin{aligned} \left|\psi(t)\right\rangle = \frac{1}{\sqrt{2}}&\left(\mathrm{e}^{-i\omega_0 t/2\hbar}\left[\sin\vartheta_n \left|\varphi_+(n)\right\rangle + \cos\vartheta_n \left|\varphi_-(n)\right\rangle\right]\right) \\ &+ \mathrm{e}^{i\omega_0 t/2\hbar}\left[\cos\vartheta_{n-1}\left|\varphi_+(n-1)\right\rangle - \sin\vartheta_{n-1}\left|\varphi_-(n-1)\right\rangle\right]. \end{aligned} \tag{2.17}$$

To obtain the evolution of the state $\left|\psi(t)\right\rangle$ further along starting from (2.17), it should be recalled that both $\left|\varphi_\pm(n)\right\rangle$ are eigenstates of the total Hamiltonian $\hat{H}$ which has the eigenvalues $E_n = \hbar\left(\Omega(n+1/2) \pm \lambda_n\right)$. Therefore after a time $\tau = \Delta t$ further along, the state $\left|\psi(t)\right\rangle$ evolves to a new state $\left|\psi(t+\tau)\right\rangle$ under the influence of the evolution operator $\hat{H}$. To obtain this final state each of the eigenfunctions in (2.17) must be multiplied by the approximate imposed phase factor of

$$\mathrm{e}^{-iE_{n,\pm\tau}/\hbar}. \tag{2.18}$$

This will cause $\left|\psi(t)\right\rangle$ to evolve to the final state $\left|\psi(t+\tau)\right\rangle$ which is

$$\begin{aligned}\left|\psi(t+\tau)\right\rangle = \frac{1}{\sqrt{2}}\Big\{&\mathrm{e}^{-i\omega_0 t/2\hbar - i(\Omega(n+1/2)+\lambda_n)\tau}\sin\vartheta_n\left|\varphi_+\right\rangle \\ &+\mathrm{e}^{-i\omega_0 t/2\hbar - i(\Omega(n+1/2)-\lambda_n)\tau}\cos\vartheta_n\left|\varphi_-(n)\right\rangle \\ &+\mathrm{e}^{i\omega_0 t/2\hbar - i(\Omega(n-1/2)+\lambda_{n-1})\tau}\cos\vartheta_{n-1}\left|\varphi_+(n-1)\right\rangle \\ &-\mathrm{e}^{i\omega_0 t/2\hbar - i(\Omega(n-1/2)-\lambda_{n-1})\tau}\sin\vartheta_{n-1}\left|\varphi_-(n-1)\right\rangle\Big\}.\end{aligned} \tag{2.19}$$

The fact that $\left|\varphi_\pm(n)\right\rangle$ energy eigenstates of $\hat{H}$ has been used.

Suppose n is very large, then the λ_n can be approximated as follows

$$\lambda_n \approx \eta(n+1)^{1/2}, \quad \vartheta_n \approx \frac{\pi}{4},$$

$$\begin{aligned}\left|\psi(t+\tau)\right\rangle = \frac{1}{2}\Big\{&\mathrm{e}^{-i\omega_0 t/2\hbar - i(\Omega(n+1/2)+\lambda_n)\tau}\frac{1}{\sqrt{2}}\left(\left|n+1,\downarrow\right\rangle + \left|n,\uparrow\right\rangle\right) \\ &+\mathrm{e}^{-i\omega_0 t/2\hbar - i(\Omega(n+1/2)-\lambda_n)\tau}\frac{1}{\sqrt{2}}\left(-\left|n+1,\downarrow\right\rangle + \left|n,\uparrow\right\rangle\right) \\ &+\mathrm{e}^{i\omega_0 t/2\hbar - i(\Omega(n-1/2)+\lambda_{n-1})\tau}\frac{1}{\sqrt{2}}\left(\left|n,\downarrow\right\rangle + \left|n-1,\uparrow\right\rangle\right) \\ &-\mathrm{e}^{i\omega_0 t/2\hbar - i(\Omega(n-1/2)-\lambda_{n-1})\tau}\frac{1}{\sqrt{2}}\left(-\left|n,\downarrow\right\rangle + \left|n-1,\uparrow\right\rangle\right)\Big\}\end{aligned} \tag{2.20}$$

$$\begin{aligned}=\frac{1}{\sqrt{2}}\Big\{&-\mathrm{e}^{-i\omega_0 t/2\hbar - i(\Omega(n+1/2)\tau)}\sin(\lambda_{n-1}\tau)\left|n+1,\downarrow\right\rangle + \mathrm{e}^{-i\omega_0 t/2\hbar - i(\Omega(n+1/2)\tau)}\cos(\lambda_n\tau)\left|n,\uparrow\right\rangle \\ &+\mathrm{e}^{i\omega_0 t/2\hbar - i(\Omega(n-1/2)\tau)}\cos(\lambda_{n-1}\tau)\left|n,\downarrow\right\rangle - \mathrm{e}^{i\omega_0 t/2\hbar - i(\Omega(n-1/2)\tau)}\sin(\lambda_{n-1}\tau)\left|n-1,\uparrow\right\rangle\Big\}\end{aligned} \tag{2.21}$$

Following the experimental procedure for the maximum spin echo, a radio frequency pulse is applied for a time τ such that $\lambda_{n-1}\tau \approx \lambda_n\tau \approx \pi/2$, so that only the sine terms remain and the state vector simplifies to the form

$$\begin{aligned}\left|\psi(t+\tau)\right\rangle = &\frac{i}{\sqrt{2}}\mathrm{e}^{-i\Omega\tau}\left\{-\mathrm{e}^{-i\omega_0 t/2\hbar - i\Omega\tau/2}\left|n+1,\downarrow\right\rangle - \mathrm{e}^{i\omega_0 t/2\hbar + i\Omega\tau/2}\left|n-1,\uparrow\right\rangle\right\} \\ &-\frac{i}{\sqrt{2}}\mathrm{e}^{-i\Omega\tau}\left\{\mathrm{e}^{-i\omega_0 t/2\hbar - i\Omega\tau/2}\left|n+1,\downarrow\right\rangle + \mathrm{e}^{i\omega_0 t/2\hbar + i\Omega\tau/2}\left|n-1,\uparrow\right\rangle\right\}.\end{aligned} \tag{2.22}$$

If the radio frequency pulse is applied for an arbitrary length of time, after the pulse the system is in a superposition of states, namely, of a state that gives an echo and a state that does not.

At the time $t+\tau$, the radio frequency is turned off, so the Ω and η terms drop out of the Hamiltonian and so the two states $\left|\uparrow\right\rangle$, $\left|\downarrow\right\rangle$ are eigenstates of the remaining Hamiltonian. The evolution is then governed by multiplication with

$$\mathrm{e}^{\pm i\omega_0 t/2},$$

and so at time $2t+\tau$, the system's state vector is given by

$$\left|\psi(2t+\tau)\right\rangle = -\frac{i}{\sqrt{2}}\mathrm{e}^{-i\Omega\tau}\left\{\mathrm{e}^{-i\Omega\tau/2}\left|n+1,\downarrow\right\rangle + \mathrm{e}^{i\Omega\tau/2}\left|n-1,\uparrow\right\rangle\right\}. \tag{2.23}$$

This state is independent of ω_0, the radio pulse renders all the spins in the same state at time $2t+\tau$ regardless of any inhomogeneities in B that would lead to different frequencies of precession. This is the desired result. The spins do not communicate their phase $\omega_0 t$ to the radio frequency field at the time of reversal.

This is an unexpected result. The state $\left|\psi(2t+\tau)\right\rangle$ determined in the way described above for a pure state does not give a spin echo. Each spin taken on its own is in a mixture at time $2t+\tau$ and so the density matrix is

$$\rho_{spin}=\frac{1}{2}\left(\left|\uparrow\right\rangle\left\langle\uparrow\right|+\left|\downarrow\right\rangle\left\langle\downarrow\right|\right). \tag{2.24}$$

If the radio frequency field is in a number state, then the spins fail to realign.

Such fields in real life are generally superpositions of number states. These can be accurately approximated by a coherent state

$$\left|\psi_{rf}\right\rangle=\mathrm{e}^{-|\alpha|^2/2}\sum_n\frac{\alpha^n}{n!}\left|n\right\rangle. \tag{2.25}$$

If the radio frequency field is in a coherent state then,

$$\begin{aligned}\left|\psi(2t+\tau)\right\rangle_{coherent}&=-\frac{1}{\sqrt{2}}\mathrm{e}^{-|\alpha|^2/2}\sum_n\frac{\alpha^n}{n!}\left(\mathrm{e}^{-i\Omega\tau/2}\left|n+1,\downarrow\right\rangle+\mathrm{e}^{i\Omega\tau/2}\left|n-1,\uparrow\right\rangle\right)\\&=-\frac{1}{\sqrt{2}}\mathrm{e}^{-|\alpha|^2/2}\sum_n\left(\frac{\alpha^{n-1}}{(n-1)!}\mathrm{e}^{-i\Omega\tau/2}\left|n,\downarrow\right\rangle+\frac{\alpha^{n+1}}{(n+1)!}\mathrm{e}^{i\Omega\tau/2}\left|n,\uparrow\right\rangle\right)\\&=\left|\psi_{rf}\right\rangle\left(-\frac{1}{\sqrt{2}}\right)\left(\mathrm{e}^{-i\Omega\tau/2}\left|\downarrow\right\rangle+\mathrm{e}^{i\Omega\tau/2}\left|\uparrow\right\rangle\right).\end{aligned} \tag{2.26}$$

Both the radio frequency field and the spins are essentially in pure states at time $2t+\tau$. The entropy of the spins at the time of reversal is not transferred to the field. Near the peak of the coherent state, $n\approx\alpha$,

$$\frac{\alpha^{n-1}}{(n-1)!}\approx\frac{\alpha^{n+1}}{(n+1)!}, \tag{2.27}$$

Therefore, the interference necessary to bring about the spin echo happens.

If the field is in a coherent state, the spin echo takes place as usual. It the field is in a squeezed state which is sufficiently close to a number eigenstate, however, the $\left|\uparrow\right\rangle$ and $\left|\downarrow\right\rangle$ states of the spin cannot interfere and so the spin echo does not occur.

The situation is exactly analogous to the double-slit experiment. If the plane in which the slits are extracted, is in a squeezed state sufficiently close to a momentum eigenstate, then one can discover which slit a photon has gone through by measuring the plane's momentum after the photon has passed through. It is found that no interference pattern appears on the screen. The essential features of the spin-echo effect are preserved by the quantum mechanical treatment. The spins become realigned without transferring information to the electromagnetic field. Since Hamiltonian systems are nondissipative, it is in principle feasible to follow the progress of such a system up to a substantial fraction of its Poincaré time. A device to extract energy must devote more and more resources to this as time goes on to retrieve the same amount of work.

3. Statistical and Physical Entropy

That the spins become disordered and then ordered again is very interesting from the point of view of entropy. However, the overall disorder of spins and magnetic field only increases by a small amount. It is the structure of the magnetic field inhomogeneities which give the crucial data that allows the reversal to be accomplished at a relatively small cost.

With regard to statistical entropy of this kind of system, it can be shown that the normal statistical mechanical entropy of the spins increases. It then decreases during the cycle and the echo is produced. Since the spins and magnetic field constitute a Hamiltonian system, neglecting spin-spin and spin-lattice interaction, it must be that the overall statistical entropy of the spins and field remains constant, as well as the magnetic field on its own. Statistical entropy of the spins at time t can be determined as a function of the entropy of the field.

Let $p_t(\omega_i)\,\mathrm{d}\omega$ denote the probability that the Larmor frequency of spin i lies in the interval $[\omega_i, \omega_i + \mathrm{d}\omega)$, and $p_t(\gamma_i)\,\mathrm{d}\gamma$ the probability that γ_i resides in the set $[\gamma_i, \gamma_i + \mathrm{d}\gamma]$ at time t. Now $\gamma_i(t) = \omega_i t$ at time t, so $p_t(\gamma_i)\,\mathrm{d}\gamma = (1/t)\,p(\gamma_i(t))\,\mathrm{d}\gamma$. The entropies

$$S(\gamma_i(t)) = -\int_0^{2\pi} p_t(\gamma)\log p_t(\gamma/\Delta\gamma)\,\mathrm{d}\gamma, \quad S(\omega_t) = -\int_{-\infty}^{\infty} p(\omega)\log p\left(\frac{\omega}{\Delta\omega}\right)\mathrm{d}\omega. \tag{3.1}$$

are related for times less than $2\pi/\delta\omega$ as

$$S(\gamma_i(t)) = S(\omega_i) + \log\left(\frac{\Delta\omega t}{\Delta\gamma}\right). \tag{3.2}$$

Entropies or continuous probability distributions are used, so a normalization can be used so that distributions which have spread $\Delta\gamma$ and $\Delta\omega$ have zero entropy. Probability distributions with smaller spreads have negative entropies. However, since the course graining used permits accuracy greater than $\Delta\omega$, $\Delta\gamma$, such negative entropies never occur in practice. The orientation of the spins are defined $mod\, 2\pi$ whenever $S(\gamma_i(t)) > \log(2\pi/\Delta\gamma)$, the two are equated.

At $t = 0$ the statistical entropy of the spins is zero, and the entropy of spins and field taken together is just the entropy of the field. If the deviation of the Larmor frequency about their mean is uncorrelated, then the statistical entropy of all the spins is just N times the entropy for a single spin, and the mutual information between spins and field as a function of time is

$$\begin{aligned} I(\{\gamma_i(t)\},\{\omega_i\}) &= S(\{\gamma_i(t)\}) + S(\{\omega_i\}) - S(\{\gamma_i(t)\},\{\omega_i\}) \\ &= S(\{\omega_i\}) + N\log\left(\frac{\Delta\omega}{\Delta\gamma}t\right). \end{aligned} \tag{3.3}$$

Again the right-hand is set to be zero when (3.3) is negative. The statistical entropy of the spins rises as $N\log t$ and is equal to the mutual information between spins and magnetic field.

After the pulse has conjugated the phases, the entropy of the spins decreases just as rapidly. The natural evolution of the system uses the mutual information between spins and field to decrease the entropy of the spins. The quantity of mutual information available is exactly enough to reduce the entropy of the spins to zero without requiring an increase of entropy somewhere else. Spin-spin and spin-lattice relaxation times are much smaller than the Poincaré time for a macroscopic spin-echo system. Also the spins become thermally randomized long before $\log(t/\Delta t)$ is significant.

It is significant to realize that in fact any integrable Hamiltonian system is analogous to the spin-echo system. The phase space of an integrable system can be decomposed into action variables by means of a canonical transformation. This is similar to frequencies of precession, and angle variables analogous to the angles of the spins.

Since Hamiltonian systems are nondissipative, it is possible to follow, in principle, the evolution of such a system up to a large part of the Poincaré time. The term $\log(t/\Delta t)$ does make a difference in terms of the amount of energy that can be extracted from an integrable system as work. The device must devote more resources to do this as time increases in order to extract this energy and take out some amount of work. The physical entropy which puts limits how much entropy work can be extracted from a system changes as $\log(t/\Delta t)$.

Extracting the same amount of work from an integrable system takes more and more resources as time goes on. To understand this, the concept of physical entropy mentioned previously can be used to look at the idea of fully utilizing the energy in the induction signal from the spin echo. This could be done by storing physical electrical energy in a capacitor for example. This leads to the idea of a Maxwell's demon device that can capture and store it. As time goes on, it must either use more memory to perform the task, or dissipate more and more energy. The demon to be envisioned is just a device that opens a switch in the circuit between a coil and capacitor after the charge initiated by the pulse shows up. The result is that the capacitor receives the charge and stores the energy from the signal. To capture all of the energy in the signal, it has to hit the switch at precisely the right time. If it is too early charge does not build up on the capacitor, too late and all charge leaks away. The demon would have to know exactly the time of the arrival of the pulse to store all the pulses energy. Thus the apparatus has to commit $\log(t/\Delta t)$ of memory space. The quantity of resources needed to capture the pulse energy measured with respect to memory space grows as the logarithm of the time. In this event, the demon devotes only a small amount of resources to capturing the energy of the pulse. If the arrival time is more arbitrary, the chances of $S(t)$ differing significantly from $\log(t/\Delta t)$ are small. The requirement that the device is not triggered by a thermal fluctuation while waiting for the pulse puts a minimum value on the diverted energy.

The two extreme alternatives can be summarized now. The first, due to the demon, states the pulse is in a very definite state, arriving at a definite time. The demon can take advantage of the pulse energy, but it must allocate about

$S \sim \log(t/\Delta t)$ of space in memory to store the arrival time of the pulse. After arrival of the pulse the record is of no further use. However, there is a cost in terms of memory required to store the arrival time. After arrival the record is of no further use, but to pay for its erasure is not free. The second, the demon possesses no information about the time of arrival of the pulse. The pulse appears to the demon to possess an entropy $\log(t/\Delta t)$. Localizing the energy of the pulse to a definite state by storing it in the capacitor, entropy $\log(t/\Delta t)$ must be allotted somewhere, such as dissipation in the triggering mechanism. The total physical entropy $S_f = H + S$ is the same for both situations behaving like the logarithm of the time.

4. Conclusion

A decrease in disorder in this spin system does not violate the second law of thermodynamics since the state of the system is highly correlated with the state of the magnetic field entropy is not an extensive variable here. The fine-grained entropy of spins and field remains constant. When such correlations exist, the entropy of the whole is significantly less than the sum of the entropies of the parts. The interesting fact for this kind of system is that the apparatus uses the mutual information between field and spins to reduce the entropy of the spins without decreasing the entropy of the field and spins combined. The third possibility alluded to earlier is that although the entropy of the spins in fact increases then decreases during the spin-echo, the entropy of the total system-spins, lattice and magnetic field remains constant or almost so for times significantly less than the spin-spin, spin-lattice relaxation times. This model could lead to more insights into integrable systems in general [13] [14]. Any integrable Hamiltonian system is analogous to the spin-echo system. Using a canonical transformation the phase space of an integrable system can be broken up into action angle variables, similar to procession frequencies, and angle variables analogous to the angles of the spins.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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