

THE PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 119, No. 6

SEPTEMBER 15, 1960

Irreversibility in Interacting Spin Systems*

J. PHILIPPOT†

Institute for Fluid Dynamics and Applied Mathematics, University of Maryland, College Park, Maryland

(Received May 11, 1960)

A system whose Hamiltonian is split into two terms $\mathcal{H}=\mathcal{H}_0+\lambda V$ exhibits two types of irreversible processes. The first processes are described by \mathcal{H}_0 alone; only the second processes, which result from the perturbation, lead to an increase of the entropy of the system. These processes are illustrated by the examples of free precession and cross-relaxation. General formulas are given for transition probabilities and the expressions, applied to cross-relaxation in LiF, agree with the results obtained by Bloembergen and Pershan.

1. INTRODUCTION

THE master equation describes the evolution of the populations of the eigenstates or group of eigenstates of an unperturbed Hamiltonian \mathcal{H}_0 under the influence of a small perturbation λV . The unperturbed Hamiltonian is separable and has a continuous energy spectrum. All the degrees of freedom are mixed in the perturbation λV which causes transitions between the eigenstates of \mathcal{H}_0 .

The theory of the master equation is based on the existence of a double time scale corresponding to the splitting of the Hamiltonian into a large \mathcal{H}_0 and a small perturbation λV . If we follow the evolution of the density matrix ρ , starting from any initial state, we may distinguish two different steps. In the first one, the unperturbed Hamiltonian alone, \mathcal{H}_0 , has a uniformization effect on the phases of the off-diagonal elements of ρ

$$\rho_{k,i}(t) = \rho_{k,i}(0) \exp[-i(E_k - E_i)t/\hbar]. \quad (1.1)$$

In the second step, as a result of the perturbation λV , and with a time scale depending on the magnitude of λ , the diagonal elements themselves will reach their equilibrium values. Thus, there are in fact two steps in the evolution of the system, and there are also two kinds of irreversible processes. The first class of processes is related to the action of \mathcal{H}_0 alone. The second class, which results from the effect of the perturbation, includes the

real irreversible processes, in the sense that they lead to an increase of the entropy of the system.

2. EFFECT OF THE UNPERTURBED HAMILTONIAN \mathcal{H}_0

A perfect gas without collisions, an harmonic solid, an assembly of independent spins in a constant magnetic field are all examples of systems with a separable Hamiltonian. Borel¹ was the first to study the evolution to homogeneity in space in terms of the velocity distribution in a perfect gas. The case of an harmonic solid has been studied in detail by several authors.^{2,3} But the simplest example of this class of irreversible processes is surely the one of an assembly of independent spins.

Consider a set of identical magnetic moments, initially all parallel to the x axis. They are placed in a constant slightly inhomogeneous magnetic field H in the z direction. All magnetic dipoles will precess with some angular velocity $\omega = \gamma H$, where H is the magnetic field at the position of the dipole. To make things simpler, let us suppose that we observe the phenomena in the rotating coordinate system or that the mean value of H over the sample is zero. As a result of the inhomogeneity of the field, there will be a distribution function $g(\omega)$ for the angular velocities ω . The system will thus become rapidly uniform in the angle space, that is the resultant magnetic moment will disappear according

* This research was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.

† On leave of absence from the University of Brussels, Brussels, Belgium.

¹ E. Borel, *Mécanique Statistique* (Gauthier Villars, Paris, 1925).

² G. Klein and I. Prigogine, *Physica* **19**, 1053 (1953).

³ P. Mazur and E. Montroll, *J. Math. Phys.* **1**, 70 (1960).

to the formula

$$M(t) \sim \int_{-\infty}^{+\infty} g(\omega) e^{i\omega t} d\omega, \quad (2.1)$$

if one introduces a complex x, y plane. The condition for $M(t)$ to vanish at $t = \infty$ is given by Riemann-Lebesgue theorem, that is, it is necessary that the integral

$$\int_{-\infty}^{+\infty} |g(\omega)| d\omega$$

exists.

The interest of this example is that it is so simple. It allows us to understand immediately that there is no contradiction between the reversibility of the equations of motion and the irreversibility of the behavior of certain quantities. Also, it permits us to clarify the meaning of the two paradoxes known as the recurrence paradox (Wiederkehrinwand) and the paradox of the inversion of the velocities (Umkehrinwand). If we wait a very long time, we know that according to Poincaré, the system will come back as near as we want to its initial state. This is of course true, but the corresponding time is so long⁴ that it has no physical meaning. Furthermore, it is clear that if we want to predict the evolution for such long times, we have to know exactly the initial positions and velocities, and then we don't have a continuous function $g(\omega)$ but rather a sum of δ functions for which the Riemann-Lebesgue theorem does not hold. On the other hand, if the velocities are reversed, as in spin echo experiments, we come back to the initial situation. It is easily seen that initial situations giving rise to an echo are characterized by the fact that there exists no initial distribution function in the corresponding μ space.⁵

We may summarize as follows the characteristics of this type of irreversible processes:

- (1) The system has a large number of degrees of freedom.
- (2) Its Hamiltonian is separable and has a continuous spectrum.
- (3) There exists no true relaxation time, nor any irreversible equation, but only a characteristic time.
- (4) There are as many analytical invariants as initial momenta.
- (5) The entropy remains constant.

3. FREE PRECESSION IN INTERACTING SPINS

We consider now a rigid lattice of spins, coupled by a dipole-dipole interaction. It is well known that a system containing a few down spins in an assembly of up spins is described by elementary excitations called spin waves. The interaction between spin waves may be treated in the same way as the interaction between

phonons in an anharmonic crystal. This problem shall not be considered here. We shall examine only the situation in which there are nearly as many up as down spins. As an illustration of the previous ideas, we shall study the problem of the free precession signal and the problem of cross-relaxation. We shall see that the first phenomenon, decay of the free precession signal, belongs to the first class of irreversible processes, whereas the second, cross-relaxation, corresponds to an increase of the entropy.

The free precession signal is the Fourier transform of the absorption curve $g(\omega)$. This means that everything happens as if we had an assembly of independent spins with frequency distribution $g(\omega)$. The Hamiltonian of the problem contains the Zeeman part and the dipole-dipole part:

$$\mathcal{H} = - \sum_k \gamma \hbar H_0 S_k^z + \sum_{k < l} v_{kl}, \quad (3.1)$$

where the external magnetic field H_0 is now homogeneous. If we had to deal with the Zeeman part alone, all magnetic moments would precess with the same angular velocity $\omega = \gamma H_0$. The behavior of the whole system would be periodic, with a period $2\pi\omega^{-1}$ equal to the Poincaré recurrence time. Now, the interaction v_{kl} contains a part

$$A_{kl} = (\gamma^2 \hbar^2 / r_{kl}^3) S_k^z S_l^z (1 - 3 \cos^2 \theta_{kl}), \quad (3.2)$$

which is diagonal in the representation in which the z component S_k^z of the individual spin of each nucleus k is diagonal. Let us imagine a model having the Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \sum_{k < l} A_{kl}$. We can easily understand the qualitative behavior of the precession signal on the basis of such a model. The precession signal is given by

$$G(t) = \text{Tr}[M_x(t) M_x], \quad (3.3)$$

where $M_x(t)$ is the value of the x component of the magnetic moment operator in the interaction representation

$$M_x(t) = \exp(iAt/\hbar) M_x \exp(-iAt/\hbar), \quad A = \sum_{k < l} A_{kl}. \quad (3.4)$$

Thus

$$G(t) = \sum_{nn'} |M_{xnn'}|^2 \exp[i(A_n - A_{n'})t/\hbar] \\ = \text{Tr}(M_x^2) \prod_k \cos(A_{jkl}/\hbar), \quad (3.5)$$

which is the Fourier transform of the absorption curve

$$g(\omega) = \sum_{nn'} |M_{xnn'}|^2 \delta(E_n - E_{n'} - \omega). \quad (3.6)$$

In this model, the precession signal goes to zero with oscillations, but is always positive if the magnetic field coincides with an axis of symmetry of order two of the crystal. We must of course remember that the effect of the flip-flop term B_{kl} has been neglected. Lowe and

⁴ P. C. Hemmer, L. C. Maximom, and H. Wergeland, Phys. Rev. **111**, 689 (1958).

⁵ J. Philippot, Bull. classe sci., acad. roy. Belg. **45**, 591 (1959).

Norberg⁶ have taken this into account using a power series development in time. The coefficients of t^2 and t^4 are then equal to the second and fourth moments of the absorption curve.

4. CROSS-RELAXATION^{7,8}

Let us first consider the transport properties in an assembly of identical spins. We shall admit that we have always nearly as many up as down spins and moreover we shall suppose that up and down spins are "well mixed." That means that we want to exclude very particular situations in which different spin states should be separated in space. In this case, as a result of the diagonal terms in the dipole-dipole interaction (the A_{kl} terms), the static part of the local field, although varying rapidly from one lattice point to another, has a continuous distribution function. This fact results from our assumption of randomness and from the r^{-3} behavior of dipole-dipole interaction. If we try to use the general method of integrating the equations of motion, retaining all terms which are powers of the combination $\lambda^2 t$,⁹ a difficulty appears immediately. The calculations are done in the representation where the z components of individual spins are diagonal. But, in order to perform the asymptotic integrations over long times, we have to introduce explicitly a continuous variable for the energy levels. The complexity of the relation between the two representations prevents an exact calculation of this type.

We may describe the processes of energy transfer in the following way. Energy exchange occurs during a time interval $(0, \Delta t)$ between the spins for which the resonance condition in the local field is satisfied. As a result, at time Δt , a new spatial distribution of the local fields is realized for which we shall again make an assumption of randomness. This hypothesis of the persistence of the chaos of the spins is here the analog of the "Stoszahlansatz." This physical situation is completely different from the one considered by Anderson¹⁰ in his paper on the absence of diffusion in certain random lattices. Anderson considers one up spin in an assembly of down spins, but a fixed energy is associated once and forever to each lattice point. This is the inhomogeneous broadening. Thus, if there is no possibility of conserving energy in a transition at the initial time, a transition shall never occur. When the broadening is of dipolar origin, the local field, or the energy of a spin is a fluctuating quantity as considered by Bloembergen.¹¹ One could also say that these two distinct situations are characterized by the fact that each spin fixed in space has a frequency distribution with a vanishing or nonvanishing dispersion in the corresponding Gibbs ensemble.

⁶ I. T. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

⁷ N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

⁸ A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

⁹ L. Van Hove, Physica **21**, 517 (1955).

¹⁰ P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

¹¹ N. Bloembergen, Physica **15**, 410 (1949).

An estimation of the relaxation time may be obtained in this way. Let us consider the pair of spins located at k and l . The probability of finding at k the frequency ω is $g(\omega)$. Assume that there are no correlations and that the probability of finding the frequency ω' at l is $g(\omega')$. The transition probability for a double flip becomes

$$W_{kl} = \frac{1}{4\hbar^2} \int g(\omega)g(\omega') e^{i(\omega-\omega')t} dt d\omega d\omega' |B_{kl}|^2 \quad (4.1)$$

(the temperature dependence has been neglected and I has been chosen $= \frac{1}{2}$). The total transition probability for the spin k is

$$W = \sum_l W_{kl} = \frac{2\pi}{4\hbar^2} \int g^2(\omega) d\omega \sum_l |B_{kl}|^2 \quad (4.2)$$

$(1/\hbar^2) \sum_l |B_{kl}|^2$ is precisely equal to $1/9$ of the second moment $M_2 = \int \omega^2 g(\omega) d\omega$. Thus we get for the mean lifetime of a Zeeman state the expression

$$T^{-1} = \frac{2\pi}{36} M_2 \int g^2(\omega) d\omega \quad (4.3)$$

If two species of spins with different gyromagnetic ratio γ are present, we have to introduce two distribution functions $g_1(\omega)$ and $g_2(\omega)$. The cross-relaxation time is then given by

$$\begin{aligned} & \frac{1}{4\hbar^2} \int g_1(\omega)g_2(\omega') e^{i(\omega-\omega')t} dt d\omega d\omega' \sum_l |B_{kl}^{(1,2)}|^2 \\ &= \frac{1}{4} M_2(1,2) \int g_1(\omega)g_2(\omega) d\omega, \end{aligned} \quad (4.4)$$

where $M_2(1,2)$ is precisely that contribution to the second moment M_2 which is dropped in the calculation of the line broadening by different spin species.¹² Let us introduce spin temperatures by writing the probability of finding a spin of species 1 with an energy $\pm \hbar\omega$ as

$$\begin{aligned} g_1^+(\omega) &= f_1(\omega) \exp(-\hbar\omega/2kT), \\ g_1^-(\omega) &= f_1(\omega) \exp(+\hbar\omega/2kT). \end{aligned} \quad (4.5)$$

We thus have for the total rate of energy transfer from system 1 to system 2

$$\begin{aligned} & \frac{dE}{dt}(1 \rightarrow 2) \\ &= \frac{2\pi}{36} N M_2(1,2) \int \hbar\omega f_1(\omega) f_2(\omega) \\ & \quad \times \left\{ \exp\left[\frac{\hbar\omega}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] - \exp\left[-\frac{\hbar\omega}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \right\} d\omega \\ &= \int \hbar^2 \omega^2 f_1(\omega) f_2(\omega) d\omega \frac{\pi N M_2(1,2)}{36k} \left(\frac{1}{T_1} - \frac{1}{T_2}\right), \end{aligned} \quad (4.6)$$

¹² T. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

where $N=N_1=N_2$ =number of spins of each species. Using the relations

$$\frac{d}{dt}\left(\frac{1}{T_1}\right)=\frac{dE_1}{dt}/\left(-T_1^2\frac{dE_1}{dT_1}\right), \quad (4.7)$$

$$\frac{dE_1}{dT_1}=\frac{1}{kT_1^2}\frac{\text{Tr}[\mathcal{H}\mathcal{C}_1^2]}{\mathcal{H}_1} \quad (4.8)$$

[the index 1 (or 2) refers to system 1 (or 2), \mathcal{H} is the total number of spin states, here 2^N], we find

$$\frac{d}{dt}\left(\frac{1}{T_1}\right)=-R_{12}\left(\frac{1}{T_1}-\frac{1}{T_2}\right), \quad (4.9)$$

$$\frac{d}{dt}\left(\frac{1}{T_2}\right)=-R_{21}\left(\frac{1}{T_1}-\frac{1}{T_2}\right), \quad (4.10)$$

with

$$R_{12}=\frac{\pi M_2(1,2)}{9\omega_0^2}\int\omega^2 f_1(\omega)f_2(\omega)d\omega, \quad (4.11)$$

and

$$\frac{R_{21}}{R_{12}}\simeq\left(\frac{\gamma_1}{\gamma_2}\right)^2,$$

where we have used the approximation $\mathcal{H}\mathcal{C}_1\simeq\gamma\hbar H_0\sum_k S_k^z=\hbar\omega_0\sum_k S_k^z$. This gives for this simple case an explicit formula for the coefficients introduced by Schumacher.¹³

5. EXTENSION TO HIGHER ORDERS IN THE PERTURBATION

It happens very often that the expression (4.4) for the transition probability of a cross-relaxation process is vanishingly small compared to higher order terms in the perturbation for which the resonance condition is much more easily satisfied. In other words, we have to calculate the terms which are proportional to the time t but of a higher order in the perturbation. In such processes, the system goes through intermediate states for which the energy is not conserved. We perform this calculation using the interaction representation of the density matrix. We have

$$\mathcal{H}=\mathcal{H}_0+\lambda V,$$

$$\rho_{\text{in}}(t)=\exp(-i\mathcal{H}_0 t/\hbar)\rho(0)\exp(i\mathcal{H}_0 t/\hbar), \quad (5.1)$$

$$V_{\text{in}}(t)=\exp(-i\mathcal{H}_0 t/\hbar)V\exp(i\mathcal{H}_0 t/\hbar). \quad (5.2)$$

The equation of motion is

$$i\hbar\partial\rho_{\text{in}}/\partial t=[\lambda V_{\text{in}},\rho_{\text{in}}], \quad (5.3)$$

the formal solution of which is

$$\rho_{\text{in}}(t)=\exp\left(-\frac{i\lambda}{\hbar}\int_0^t V(t')dt'\right)\rho\times\exp\left(+\frac{i\lambda}{\hbar}\int_0^t V(t')dt'\right). \quad (5.4)$$

The exponentials are defined by

$$\begin{aligned} &\exp\left(-\frac{i\lambda}{\hbar}\int_0^t V(t')dt'\right) \\ &\equiv 1-\frac{i\lambda}{\hbar}\int_0^t V(t')dt' \\ &+\left(-\frac{i\lambda}{\hbar}\right)^2\int_0^t dt'\int_0^{t'} dt'' V(t')V(t'')+\dots \end{aligned} \quad (5.5)$$

When this expression is substituted in (5.4), the terms of a given order in λ are of two types: those coming from the development of one exponential only and those in which the corresponding terms of both exponentials are matched in pairs. These last ones determine the transition probability. Thus the transition probability from state s to state r is given by the term proportional to t in

$$\begin{aligned} &\left[1-\frac{i\lambda}{\hbar}\int_0^t V_{rs}(t')dt'\right. \\ &+\left(-\frac{i\lambda}{\hbar}\right)^2\int_0^t dt'\int_0^{t'} dt'' V_{rk}(t')V_{ks}(t'')+\dots\left.]\rho_{ss}(0)\right. \\ &\times\left[1+\frac{i\lambda}{\hbar}\int_0^t V_{sr}(t')dt'\right. \\ &+\left(+\frac{i\lambda}{\hbar}\right)^2\int_0^t dt'\int_0^{t'} dt'' V_{sk}(t')V_{kr}(t'')+\dots\left.]. \end{aligned}$$

When the resonance condition for the λ^2 term is not satisfied, the first nonvanishing contribution is given by

$$\frac{2\pi t}{\hbar^2}\lambda^4\sum_k\left|\frac{V_{rk}V_{ks}}{E_k-E_s}\right|^2\delta\left(\frac{E_r-E_s}{\hbar}\right), \quad (5.7)$$

where the summation over k in the second term is to be

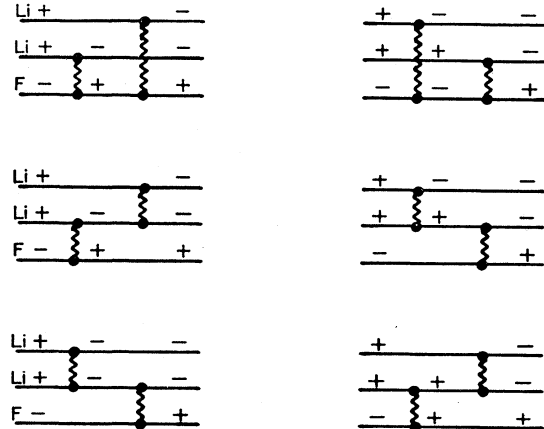


FIG. 1. Diagrams corresponding to the terms of (5.9).

¹³ R. T. Schumacher, Phys. Rev. **112**, 837 (1958).

performed over "linked clusters" or "connected diagrams" only. Let us illustrate this using the example of LiF. Pershan¹⁴ has recently shown that for fields of the order of 50 gauss the essential mechanism consists in two Li flips and one opposite F flip. Using Pershan's notations (S denotes a lithium spin operator, I a fluorine spin operator, no prime refers to an interaction between two Li, one prime refers to a LiF interaction, and two primes to two F), we have to evaluate the modulus of

$$\mathcal{V}_{rs} = \frac{1}{\hbar} \left\{ \left(\frac{B'C'}{\omega_{Li}} - \frac{C'B'}{\omega_F - \omega_{Li}} \right) + \left(\frac{B'C}{\omega_{Li}} - \frac{CB'}{\omega_F - \omega_{Li}} \right) + \left(\frac{D'E}{2\omega_{Li}} - \frac{ED'}{\omega_F} \right) \right\}. \quad (5.9)$$

A connected diagram is associated with each term as shown in Fig. 1.

Neglecting correlations and using the approximation of the overlap of two Gaussian line shapes, one gets for

¹⁴ P. S. Pershan, Phys. Rev. **117**, 109 (1960).

the transition probability

$$W_{rs} = (2\pi/\hbar^2) g_{12}(\omega_{12}) |\mathcal{V}_{rs}|^2, \quad (5.10)$$

where

$$g_{12}(\omega_{12}) = \frac{1}{\{2\pi[2(\Delta\omega)_{Li}^2 + (\Delta\omega)_F^2]\}^{\frac{1}{2}}} \times \exp\left(\frac{-(\omega_F - 2\omega_{Li})^2}{2[2(\Delta\omega)_{Li}^2 + (\Delta\omega)_F^2]}\right). \quad (5.11)$$

Using the approximation $\omega_F = 2\omega_{Li}$ in (5.9), which is justified if the Gaussian is very narrow, this result coincides with the expression given by Pershan.

The temperature variation is then obtained by replacing the expression for W_{rs} in Schumacher's formula for R_{12} .

ACKNOWLEDGMENTS

We want to express our gratitude to Professor Bloembergen and Professor Prigogine for their interest and to thank Dr. Jeener and Dr. Pershan for many stimulating discussions.

Induced and Spontaneous Emission in a Coherent Field. III

I. R. SENITZKY

U. S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey

(Received November 9, 1959)

The theory developed in the first two articles of this series, dealing with the interaction between the electromagnetic field in a cavity resonator and a number of two-level molecules, is generalized to include a Gaussian spread in the molecular frequency. The center of the molecular frequency distribution coincides with the cavity resonant frequency. There is a coherent driving field in the cavity at the same frequency, and cavity loss is taken into account.

Using the formalism previously developed for a quantum-mechanical field in a lossy cavity, expressions are obtained by means of second-order perturbation theory for the expectation values of the field strength and field energy in the cavity, and of the power loss by the molecules. It is shown that the parts of the field energy resulting from induced and spontaneous emission, respectively, initially increase as the square of the time and approach steady-state values after (different, in general) transient periods, each of which is determined by two time constants: cavity relaxation time and inverse molecular frequency spread.

INTRODUCTION

IN the first article of this series,¹ an analysis was made of the interaction between a number of two-level quantum-mechanical systems (hereafter referred to as molecules) and a coherent cavity field, the latter as well as the former being treated quantum-mechanically. The situation considered was that of a lossless cavity,

¹ I. R. Senitzky, Phys. Rev. **111**, 3 (1958), hereafter referred to as I.

It is also shown that both the induced and spontaneous emission power radiated by the molecules increase initially linearly with the time and approach steady-state values after transient periods. For the induced emission power, the transient period is determined by only one time constant, the inverse molecular frequency spread, while for the spontaneous emission power it is determined both by the inverse molecular frequency spread and the cavity relaxation time. The ratio of induced to spontaneous emission is initially n , and approaches a steady-state value

$$n[\exp(r^2)(1 - \operatorname{erf} r)]^{-1},$$

where n is the driving field energy in units of the photon energy, and r is the ratio of the cavity resonance width to molecular frequency spread. The seeming inconsistency of this value with the classical value of the ratio of the Einstein coefficients is discussed.

and the molecules were all in resonance with the cavity. Under these two idealizations, neither the induced nor the spontaneous emission approached a steady state. In the second article,² a quantum-mechanical formalism was developed for the field of a lossy cavity and applied to the interaction with the molecules. In this case the spontaneous emission approached a steady state after

² I. R. Senitzky, Phys. Rev. **115**, 227 (1959), hereafter referred to as II.