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Borckmans, P.
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ON THE SPIN-SPIN RELAXATION

by J. PHILIPPOT and P. BORCKMANS*)

Faculté des Sciences, Université Libre de Bruxelles, Belgique

Synopsis

A study of the origin of the disagreement between the expression of the spin-spin relaxation time give by Caspers and that of Anderson and Hartmann, and Tjon is presented. Tjon's integral equation is discussed.

I. *Introduction.* The problem of spin-spin relaxation in paramagnetic solids has been studied recently by several authors[1–8]). Many of them have been interested in the establishment of a Pauli equation in the limit of a high external magnetic field and of a high temperature:

$$H_0 \gg H_L \quad \text{and} \quad \hbar\omega_0/kT \ll 1$$

(where H_L is the local field and $\omega_0/2\pi$ the Larmor frequency in the field H_0). Caspers[1]) has followed an alternative method, evaluating directly the relaxation function. His result disagrees with that of Anderson and Hartmann[3]) based on the idea of Zeeman and dipole-dipole temperatures. However, it is clear that Caspers's direct evaluation of the autocorrelation function of the z component of the magnetic moment: $\mathrm{Tr}\{M_z M_z(t)\}$ and a calculation starting from the master equation must give the same final result. Tjon[7]) has used the master equation to evaluate the correlation function and he obtains a result in accordance with that of Hartmann and Anderson. The aim of this note is to clarify the disagreement existing between these authors, but first we shall recall briefly their theory.

II. *Caspers's theory.* When a sample is submitted to a constant external field $H_0 + h$ directed along the z axis of the reference frame and the small field h is suddenly switched off at $t = 0$, the linear response of the system is given by

$$\overline{M}_z(t) - \overline{M}_z^{(0)} = \phi_{zz}(t)\, h \tag{2.1}$$

where $\overline{M}_z(t)$ is the average magnetic momentum at time t and $\overline{M}_z^{(0)}$ the equilibrium magnetization in the presence of the external field H_0 alone.

*) Aspirant au Fonds National de la Recherche Scientifique.

The system being in equilibrium in a field $H_0 + h$ for $t < 0$ is described by a canonical density matrix

$$\rho_{(t<0)} = \exp\{-\beta[(H_0 + h)\, M_z + \sum_s V^{(s)}]\}/\mathrm{Tr}\,\{\ldots\}. \tag{2.2}$$

The Hamiltonian of the system is:

$$\begin{aligned}\mathscr{H} &= \mathscr{H}_{\text{Zeeman}} + \mathscr{H}_{\text{interaction}} \\ &= \mathscr{H}_Z + \sum_{s=0,\pm1,\pm2} V^{(s)}.\end{aligned} \tag{2.3}$$

The various terms of the interaction have been classified according to their commutation rules with the Zeeman Hamiltonian $\mathscr{H}_Z = -H_0 M_z = \omega_0 S_z$ (S_z is the z component of the total angular momentum). The following commutation rules are then valid:

$$[S_z, V^{(s)}] = s\hbar V^{(s)}. \tag{2.4}$$

Retaining only the first terms of the expansion in $\hbar\omega/kT$ (high temperature assumption), we find for $\phi_{zz}(t)$:

$$\phi_{zz}(t) = \beta\, \mathrm{Tr}\{M_z M_z(t)\}\, (\mathrm{Tr}\ 1)^{-1} \tag{2.5}$$

where $M_z(t)$ is the Heisenberg representation of M_z:

$$M_z(t) = \exp it\mathscr{H}/\hbar\, M_z \exp -it\mathscr{H}/\hbar. \tag{2.6}$$

To evaluate $\phi_{zz}(t)$, Caspers uses a representation in which the total Hamiltonian is diagonal.

At this point we would like to stress on a few remarks:

It is clear that a rate equation is valid only in a well chosen representation and for a Hamiltonian satisfying certain properties[9]). One usually uses a representation diagonalizing the unperturbed part of the Hamiltonian $\mathscr{H}_0$ (here $\mathscr{H}_Z + V^{(0)}$) which has a continuous spectrum in the limit of a large system ($N \to \infty$). The perturbation should of course not commute with $\mathscr{H}_0$ and should have matrix elements varying slowly with some continuous quantum number in order to make asymptotic time integrations possible. Caspers's choice of a representation not only renders any comparison with other theories difficult but also presents great risks as to the continuity properties of the matrix elements involved in his theory.

The next step in Caspers's calculation is to split the trace in the sum of the time independent diagonal elements and the sum of the nondiagonal elements

$$\mathrm{Tr}\{M_z M_z(t)\} = \sum_n |\langle n\, |M_z|\, n\rangle|^2 + \sum_{n \neq m} \langle n\, |M_z|\, m\rangle\langle m\, |M_z(t)|\, n\rangle. \tag{2.7}$$

Or also, after dividing by $N\ \mathrm{Tr}\ 1 = Np$,

$$N^{-1}\langle\langle M_z M_z(t)\rangle\rangle = \sum_n |\langle n\, |M_z|\, n\rangle|^2\, (pN)^{-1} + \Omega(t) \tag{2.8}$$

where the double bracket represents the normalized trace.

The matrix elements $\langle m\,|M_z(t)|\,n\rangle$ are then written, using the iteration solution of the motion equation:

$$M_z(t) = M_z + \sum_{l=1}^{\infty} (i\hbar)^{-l} \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{l-1}} \mathrm{d}t_l [M_z;\, V(t_1),\, V(t_2),\, \ldots,\, V(t_l)] \tag{2.9}$$

where $V = \sum_{s\neq 0} V^{(s)}$ and $V(t)$ is the interaction representation of V. The notation $[;\,,\ldots,\ldots]$ stands for the commutators of the commutators. The terms of the series (2.9) are expanded in orthogonal operators and Caspers retains only the part of $M_z(t)$ which is proportional to M_z; he therefore writes

$$(i\hbar)^{-l}[M_z;\, V(t_1),\, V(t_2),\, \ldots,\, V(t_l)] = \\ = -g_l(t_1 - t_2,\, t_2 - t_3,\, \ldots,\, t_{l-1} - t_l)\, M_z + T_l \tag{2.10}$$

and drops the T_l terms. He then obtains after some calculations an integral equation which in the limit of instantaneous collisions reduces to the following differential equation for $\Omega(t)$:

$$\frac{\mathrm{d}\Omega(t)}{\mathrm{d}t} = \frac{\int_0^\infty \mathrm{d}\tau \,\langle\!\langle [M_z;\, V(\tau),\, V]\, M_z \rangle\!\rangle}{(i\hbar)^{+2}\,\langle\!\langle M_z^2 \rangle\!\rangle}, \tag{2.11}$$

and thus the relaxation time is

$$\tau_{ss} = \frac{(i\hbar)^2\,\langle\!\langle M_z^2 \rangle\!\rangle}{\int_0^\infty \mathrm{d}\tau\,\langle\!\langle [M_z;\, V(\tau),\, V]\, M_z \rangle\!\rangle}. \tag{2.12}$$

III. *Comments on Caspers's theory.* The dropping of the T_l terms of (2.9) is justified in the calculation of $\mathrm{Tr}\{M_z M_z(t)\}$ since $\mathrm{Tr}\{M_z T_l\} = 0$ and as noted by Tjon in the calculation of $\mathrm{Tr}\{M_z M_z(t)\}$ one might as well keep the T_l terms since their contribution, in this case, is vanishing. One then finds that the magnetization decreases exponentially to zero. This indicates that Caspers's derivation is not correct*).

In fact, working in a representation where M_z and $V^{(0)}$ are diagonal, using standard methods and retaining only second order terms, one finds immediately for the diagonal elements of $\mathrm{d}M_z/\mathrm{d}t$ the analogue of a Pauli equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle k\,|M_z(t)|\,k\rangle = -\langle k\,|M_z(t)|\,k\rangle \sum_l |\langle k\,|V|\,l\rangle|^2 \frac{2\pi}{\hbar}\,\delta(E_k - E_l) + \\ + \sum_l \langle l\,|M_z(t)|\,l\rangle\,|\langle k\,|V|\,l\rangle|^2 \frac{2\pi}{\hbar}\,\delta(E_k - E_l) \tag{3.1}$$

*) Caspers's equation apparently results from a confusion between M_z and $M_z(t)$ in an intermediate step of the calculation.

where $|k\rangle$ are the eigenstates and E_k the eigenvalues of the unperturbed Hamiltonian $-H_0 M_z + V^{(0)}$.

From (3.1) we deduce

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathrm{Tr}\{M_z M_z(t)\} = \mathrm{Tr}\left\{\{(i\hbar)^{-2}\int_0^\infty \mathrm{d}\tau[M_z(t);\,V(\tau),\,V(0)]\,M_z\right\}. \tag{3.2}$$

One finds of course the same result by retaining the M_z component of the expansion of $\mathrm{d}M_z/\mathrm{d}t$ in orthogonal operators:

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathrm{Tr}\{M_z M_z(t)\} = \frac{\mathrm{Tr}\{(i\hbar)^{-2}\,\mathrm{Tr}[\int_0^\infty \mathrm{d}\tau[M_z(t);\,V(\tau),\,V(0)]\,M_z]\,M_z^2\}}{\mathrm{Tr}\,\{M_z^2\}}. \tag{3.3}$$

This last form is easily compared with Caspers's result (2.11). For long times, the matrix elements $\langle k\,|M_z(t)|\,k\rangle$ tend to the constant $\langle M_z\rangle_E$ over the corresponding microcanonical surface and $\langle\langle M_z M_z(t)\rangle\rangle$ tends towards $\langle\langle \langle M_z\rangle_E^2\rangle\rangle$ in agreement with Tjon's theory.

We therefore believe that Caspers's equation (2.11) is not correct. It is equivalent to a closed equation for the inverse of the Zeeman temperature T_Z

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{T_Z}-\frac{1}{T_Z^0}\right) = -\frac{1}{\tau_{ss}}\left(\frac{1}{T_Z}-\frac{1}{T_Z^0}\right). \tag{3.4}$$

However, since Hartmann and Anderson have shown that the system we are interested in presents two quasi invariants, the Zeeman and the dipole-dipole energies, it has become clear that the time evolution is governed by Hartmann and Anderson's coupled equations

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{T_Z}\right) &= \frac{1}{\tau_{12}}\left(\frac{1}{T_Z}-\frac{1}{T_D}\right)\\ \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{T_D}\right) &= \frac{1}{\tau_{21}}\left(\frac{1}{T_D}-\frac{1}{T_Z}\right)\end{aligned} \tag{3.5}$$

T_Z, T_D being respectively the Zeeman and the dipole-dipole temperatures. The true relaxation time is then

$$\tau_r = \frac{\frac{1}{2}H_{l,\mathrm{sec}}^2}{H^2+\frac{1}{2}H_{l,\mathrm{sec}}^2}\,\tau_{12} \tag{3.6}$$

where

$$H_{l,\mathrm{sec}}^2 = 2\,\frac{\mathrm{Tr}[(V^{(0)})^2]}{\mathrm{Tr}[\mathscr{H}_Z^2]}\,H^2 \tag{3.7}$$

and τ_{12} is equal to Caspers's relaxation time (2.12).

IV. *Integral equations for the magnetization.* The general formalism developed by Prigogine[10]) and Résibois[11]) allows to write down immediately an integral equation for the diagonal elements of $M_z(t)$:

$$\frac{\mathrm{d}}{\mathrm{d}t}[M^d_{z(t)}]_{kk} = \int_0^t \mathrm{d}\tau \left\{ \sum_{m=2}^{\infty} (i\hbar)^{-m} \int_0^\tau \mathrm{d}\tau_1 \ldots \int_0^{\tau_{m-3}} \mathrm{d}\tau_{m-2} \times \right.$$
$$\left. \times \langle k\,|[V(\tau), [V(\tau_1), \ldots, V(\tau_{m-2}), [V(0), M^d_{z(t-\tau)}]\ldots]\,|k\rangle_{\mathrm{d.i.}} \right\} \qquad (4.1)$$

where

$$M^d_z(t) = \sum_k |k\rangle\,\langle k\,|M_z(t)|\,k\rangle\,\langle k|.$$

The subscript d.i. indicates that one has to take the dynamical irreducible part of the commutator. This condition ensures that M_z is never represented by a diagonal matrix in the intermediate states. (cf. appendix and reference 11).

In contrast with Tjon's integral equation, the kernel of (4.1) is of infinite order. This property is not affected by the use of Van Hove's diagonal singularity condition (see appendix). Tjon's integral equation is only correct to the second order. However, it might be necessary to go to a higher order than the second to describe completely the physical processes responsible for the approach to equilibrium. It has been shown by one of us[6]) that the processes describing the evolution of the dipole-dipole subsystem to internal equilibrium are of the fourth order if one uses the representation where $-\mathrm{H}_0 M_z$ and $V^{(0)}$ are diagonal.

Caspers has also written an integral equation for $\Omega(t)$. The kernel of his equation is of infinite order and contains a condition of irreducibility analogous to that of Résibois[11]). We shall, however, not discuss it in detail since we have already seen that it does not reduce to the correct differential equation.

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APPENDIX

We treat in this appendix the problem of the introduction of Van Hove's δ-singularity in Tjon's theory.

As it was shown by one of us[12]), we can in fact consider two different types of δ-singularity. In the first one, there is no random element physically present in the problem and we cannot say, a priori, of which order the diagonal term is, compared to the sum of the non-diagonal terms (interference terms) (e.g. $\sum_l V_{kl}V_{lk}/\sum_l \sum_s V_{kl}V_{ls}$ = unknown), although the diagonal

term is greater than any nondiagonal term by a factor N. We must thus be careful when we use Van Hove's δ-singularity condition in the form

$$(V^2)_{ks} = F_1(k)\,\delta(k-s) + F_2(k, s)$$

because we do not know, at first, wether $F_2(k, s)$ may be neglected or not, compared to $F_1(k)$. In the other case, physically, there appears a "strong" δ-singularity in the problem. In the case of the scattering of an electron by randomly distributed centers, a real $\delta(k-k')$ appears in the space of the electron's wave vector, which expresses the randomness of the phases of the matrix elements of the perturbation and of the distribution of the scattering centers. Verboven[13]) also uses the same argument in his theory of electrical conductivity, as he considers a disordered alloy with the components randomly distributed.

But even if we should have, in the problem treated by Tjon, this "strong" type of δ-singularity, as we call it, it would not give us the result obtained by Tjon, whose theory is only valid up to the second order.

Effectively let us consider the fourth order term of Tjon's equations (4.3), (4.4) ((see 7(a)))

$$T_t^{(4)}(Es) = (i\hbar)^{-4}\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_3 \int_0^{t_3} \mathrm{d}t_4 \times$$
$$\times \sum_\alpha \langle Es\alpha|\,[S_z;\, V(t_1),\, V(t_2),\, V(t_3),\, V(t_4)]\,|Es\alpha\rangle. \qquad \text{(A.1)}$$

We recall that the representation used is defined by

$$\mathscr{H}_0\,|Es\alpha\rangle = E\,|Es\alpha\rangle$$
$$S_z\,|Es\alpha\rangle = s\,|Es\alpha\rangle \qquad \text{(A.2)}$$

where

$$\mathscr{H}_0 = \mathscr{H}_Z + V^{(0)}.$$

If we now develop the commutator we shall find sixteen terms to all of which we have to apply Van Hove's δ-singularity in all possible manners. After regrouping the different classes of terms we obtain

$$T_t^{(4)}(Es) = \left(\frac{1}{i\hbar}\right)^4 \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_3 \int_0^{t_3} \mathrm{d}t_4 \times$$

a) $\times \sum_\alpha \{\langle Es\alpha|[[S_z;\, V(t_1),\, V(t_2)]_d,\, V(t_3),\, V(t_4)]_d|\, Es\alpha\rangle$

b) $+ \langle Es\alpha\,|[[S_z,\, V(t_1)][V(t_2)\; V(t_3)]_d,\, V(t_4)]_d|\, Es\alpha\rangle$

c) $+ \langle Es\alpha\,|[[V(t_2)\; V(t_3)]_d\,[S_z,\, V(t_1)],\, V(t_4)]_d|\, Es\alpha\rangle$

d) $+ \langle Es\alpha\,|[V(t_4),\, V(t_2)[[S_z,\, V(t_1)]\; V(t_3)]_d]_d|\, Es\alpha\rangle$

$$\text{e)} \quad + \langle Es\alpha \,|[[V(t_3)[V(t_1), S_z]]_d \, V(t_2), V(t_4)]_d| \, Es\alpha\rangle$$

$$\text{f)} \quad + \langle Es\alpha \,|[S_z; V(t_1), V(t_2), V(t_3), V(t_4)]_d| \, Es\alpha\rangle \tag{A.3}$$

where the last term is the rest of the terms of that order and where the subscript "d" means that one has to take the diagonal elements. From all these terms, Tjon only keeps the first term of the r.h.s. of (A.3). We will now determine the contributions of all these terms. To do this we apply the techniques developed by Résibois in the general theory of irreversible processes, based on the dynamical irreducibility condition[12]). But we shall have to modify them slightly as we study here the time evolution of an operator and not of the density matrix.

We use the diagrams introduced by Fujita[14]), which we have modified to adapt them to our problem. We shall briefly expose how we proceed before giving the global results.

Let us consider one particular m^{th}-order term of

$$T_t^{(m)}(Es) = \left(\frac{1}{i\hbar}\right)^m \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^t \mathrm{d}t_m \times$$

$$\times \sum_\alpha \langle Es\alpha \,|[S_z; V(t_1), V(t_2), \ldots, V(t_m)]| \, Es\alpha\rangle_{\text{d.i.}}, \tag{A.4}$$

i.e. (to simplify the notation we use $|E_m s_m \alpha_m\rangle \equiv |n_m\rangle$)

$$\left(\frac{1}{i\hbar}\right)^m \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{m-1}} \mathrm{d}t_m \sum_{\{n_i\}} \{\langle n \,|V(t_i)|\, n_1\rangle\langle n_1 \,|V(t_j)|\, n_2\rangle \ldots$$

$$\ldots \langle n_{l-1} \,|V(t_l)|\, n_l\rangle\langle n_l \,|S_z|\, n_l\rangle\langle n_l \,|V(t_\alpha)|\, n_{l+1}\rangle \ldots \langle n_m \,|V(t_\delta)|\, n\rangle\}_{\text{d.i.}}, \tag{A.5}$$

to which we apply the d.i. condition (subscript!!)
with

$$t_i < t_j < \ldots < t_l$$

$$t_\alpha > t_\beta > \ldots > t_\delta$$

and $t_i, t_j, \ldots, t_\alpha, t_\beta, \ldots, t_\beta$ are the $t_m, t_{m-1}, \ldots, t_2, t_1$. At time t the system is in the diagonal state $\langle n_l \,\|\, n_l\rangle$ *). At this point we have to adapt the method to our problem. The technique was developed to study the contributions of the various terms of the time variation of the density matrix (Schrödinger representation), here we study the time variation of an operator (Heisenberg representation) and there is thus a time inversion in the sense that instead of working upward in the time scale, we work downward. Thus in the direction of decreasing time, a first transition, $V(t_1)$ brings the system to an

*) To avoid any confusion with the usual definition of a scalar product, use is made of a double bar.

intermediate state $\langle n_l \parallel n_{l+1}\rangle$, a second transition $V(t_2)$ to another intermediate state $\langle n_l \parallel n_{l+2}\rangle$, and so on until the system comes back finally to the diagonal state $\langle n \parallel n\rangle$ through the last interaction $V(t_m)$. The d.i. condition implies that no intermediate state $\langle n_i \parallel n_j\rangle$ is diagonal. This condition is easy to understand if we associate a graph with each term as (A.5). We take a horizontal line and we draw a dot for each interaction $V(t_i)$ ordered from right to left as time increases; all interactions appearing on the left of S_z are indicated above the horizontal line and the ones appearing on the right are drawn below this line. Under each vertical line we mark the state the system has reached after each interaction has occurred, e.g. (Fig. 1). To illustrate the technique, we shall now apply the method both a reducible and nonreducible fourth order term of (A.3).

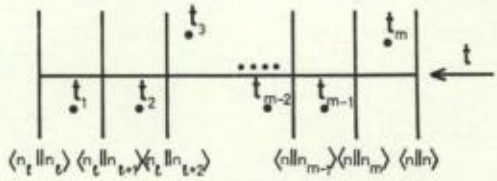

Fig. 1. Schematic description of one m^{th} order contribution.

a) *Reducible term*: $[V(t_1)\, M_z V(t_2)]_d\, V(t_3)\, V(t_4)]_d$

$$\langle n\,|V(t_1)|\,n'\rangle\langle n'\,|M_z|\,n'\rangle\langle n'\,|V(t_2)|\,n\rangle\langle n\,|V(t_3)|\,n''\rangle\langle n''\,|V(t_4)|\,n\rangle$$

The following diagram is associated to this term (Fig. 2).
We see that there is an intermediate diagonal state and thus the term is reducible and contributes to the second order.

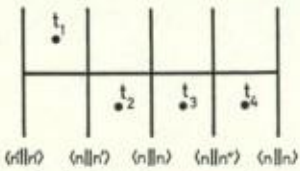

Fig. 2. Reducible fourth order term.

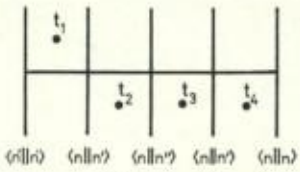

Fig. 3. Irreducible fourth order term.

b) *Nonreducible term*: $[V(t_1)\, M_z[V(t_2)\, V(t_3)]_d\, V(t_4)]_d$

$$\langle n\,|V(t_1)|\,n'\rangle\langle n'\,|M_z|\,n'\rangle\langle n'\,|V(t_2)|\,n''\rangle\langle n''\,|V(t_3)|\,n'\rangle\langle n'\,V(t_4|\,n\rangle$$

We then associate the other diagram (Fig. 3).

As there appears no intermediate diagonal state the term is not reducible and it contributes to the fourth order.

By the same way, we may test all terms appearing in (A.3). We find that:

a) is reducible and thus contributes to the second order
b), c), d), e), f) are irreducible and thus contribute to the fourth order. So we see that Tjon neglects the fourth order terms which have been proved to be important in spin-spin relaxation by Philippot[6]) as they describe the first step of this relaxation, namely the dipole-dipole relaxation.

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