model that does not contradict the results. For sapphire this could be the 3-level system given in Fig. 7.

At room temperature, both the ordinary as well as the photoconductivity result from electrons lifted from the occupied impurity level to the empty conduction band. This would explain why the light had no influence on the mobility measured in the Hall experiment.

Low mobilities are expected in ionic crystals,[6] but the measured 0.05 cm^2 V sec is quite low.

The large gap distance in the model is given in the literature[7] and the 0.85 to 1.1 eV gap comes from photoconductivity measurements as a function of light frequency. To have enough intensity we had to use broad-band infrared filters resulting of course in loss of structure details if present.

To check these gap values we plotted $\ln\sigma$ versus T^{-1}. For this we used ordinary high-temperature conductivity values of sapphire published by the Linde Company completed with the room-temperature value of our sample. The high-temperature slope of the curve leads to a gap of 7 eV; the low-temperature slope to a gap of 0.6 to 1.2 eV in fairly good agreement with the value given before. The spread depends on the kind of model assumed.[8]

ACKNOWLEDGMENTS

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[6] R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960), p. 256.

[7] N. B. Hannay, *Semiconductors* (Reinhold Publishing Corporation, New York, 1959), p. 54.

[8] A. J. Dekker, *Solid State Physics* (Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1959), p. 314.

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Spin-Spin Relaxation and Spin Temperatures

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The equilibrium and nonequilibrium properties of an assembly of interacting spins are analyzed in the case of paramagnetism (nuclear). The evolution towards equilibrium is described by a generalized Pauli equation. This equation contains two relaxation times: a first one characterizing the evolution of the dipole-dipole system to equilibrium and a second one describing the energy exchange between the dipole-dipole and the Zeeman system. The real temperature of the system is the dipole-dipole one whereas the state of the Zeeman system is given by a "chemical potential" fixing the mean magnetic moment. It is shown that the Zeeman dipole-dipole relaxation may also be considered as a kind of Brownian motion problem of a collective Zeeman coordinate in the "dipole-dipole heat bath."

INTRODUCTION

IN contrast with the rich development of the theory of irreversible processes in many body systems[1–3] (gases, plasmas, solids) there is a relative paucity of fundamental work in the field of spin-spin relaxation of paramagnetic substances. The difficulties in this domain follow from the peculiar structure of the Hamiltonian. The results of the general theory cannot directly be applied to this particular problem because one does not know the properties of the unperturbed Hamiltonian. One has to go formally ahead, working in an unknown representation. If the final expression can be written as traces, they may then be evaluated following Van Vleck. Let us also note that in many situations, series expansions may be used in the powers of the ratios of local magnetic field over external field H_l/H_0 and $\hbar\omega/kT$, a level splitting over the thermal energy. These expansions greatly simplify the problems. A general treatment has been given by Caspers,[4] starting from the expressions given by Kubo and Tomita to calculate the spin-spin relaxation time. An important progress in understanding the spin-spin relaxation mechanism has recently been made with the introduction of the notion of Zeeman and dipole-dipole temperatures by Anderson, Hartmann,[5] and Provotoroff.[6] As shown by Jeener[7] several problems are then easily handled using thermodynamical methods. However, a justification of these notions from first principle has not yet been given. In

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[1] I. Prigogine, *Nonequilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962).

[2] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[3] L. Van Hove, Physica **21**, 512 (1955); **23**, 441 (1957).

[4] W. J. Caspers, Physica **26**, 778 (1960).

[5] A. G. Anderson and S. R. Hartmann, *Magnetic and Electric Resonance and Relaxation*, edited by J. Smidt (North-Holland Publishing Company, Amsterdam, 1963).

[6] B. N. Provotoroff, Zh. Eksperim. i Teor. Fiz. **42**, 882 (1962) [translation: Soviet Phys.—JETP **15**, 611 (1962)].

[7] J. Jeener, following paper, Phys. Rev. **133**, A478 (1964).

this note we show that whereas the state of the dipole-dipole system is described by a true temperature, the state of the Zeeman system, i.e., the macroscopic magnetic moment, is given by the value of a quantity having the properties of a chemical potential. The dynamics of the evolution towards equilibrium is governed by a generalized Pauli equation. Four characteristic times appear in the phenomena: the "collision time" of the order of the inverse of the linewidth, the dipole-dipole, the Zeeman dipole-dipole, and the spin lattice relaxation time. Here, the last one is supposed to be much larger than all the others. It is also shown that the total magnetic moment plays the role of a collective coordinate coupled with the dipole-dipole system and that the Zeeman dipole-dipole relaxation may be considered as a kind of Brownian motion problem for which equations related to the Bloch equation[8] are set up.

A. EQUILIBRIUM PROPERTIES

Hamiltonian

The Hamiltonian of a rigid lattice of interacting spins, placed in a large constant external field H_0 directed along z, may be written as

$$\mathcal{H}=\mathcal{H}_{\text{Zeeman}}+\mathcal{H}_{\text{interaction}}, \tag{A1}$$

with

$$\mathcal{H}_Z=-H_0M_z=-(\omega_0/\gamma)M_z, \tag{A2}$$

where H_0 is the constant external field along z, ω_0 the Larmor frequency, γ the gyromagnetic ratio, M_z the z component of the total magnetic moment, and S_z the z component of the total angular moment. We denote by $\mathbf{I}_j$ the spin vector of the particle located at $\mathbf{r}_j$ and use the operators

$$I_j^0=(\mathbf{I}_j)_z,\quad I_j^{\pm1}=(\mathbf{I}_j)_x\pm i(\mathbf{I}_j)_y. \tag{A3}$$

They satisfy the commutation rules

$$[I_j^\lambda,I_k^\tau]=(-1)^{\lambda+\tau}(\lambda-\tau)I_j^{\lambda+\tau}\delta_{jk},\quad(\lambda,\tau=0,\pm1). \tag{A4}$$

We choose an interaction Hamiltonian of the form

$$\mathcal{H}_i=\sum_{j<k}\sum_{\lambda,\tau}C_{jk}^{\lambda\tau}I_j^\lambda I_k^\tau. \tag{A5}$$

A particular example is given by the dipole-dipole coupling, then

$$\mathcal{H}_i=\sum_{j<k}\hbar^2\gamma^2[r_{jk}^{-3}(\mathbf{I}_j\cdot\mathbf{I}_k)-3r_{jk}^{-5}(\mathbf{r}_{jk}\cdot\mathbf{I}_j)(\mathbf{r}_{jk}\cdot\mathbf{I}_k)]. \tag{A6}$$

We shall introduce also the operators

$$V^{(s)}=\sum_{j<k}\sum_{\lambda,\tau}C_{jk}^{\lambda\tau}I_j^\lambda I_k^\tau\delta_{\lambda+\tau,s}. \tag{A7}$$

They obey the following commutation rules

$$[S_z,V^{(s)}]=s\hbar V^{(s)}. \tag{A8}$$

Thus $V^{(s)}$ acting on an eigenstate of $\mathcal{H}_Z$ with total angular moment $M\hbar$ gives a new eigenstate with moment $(M+s)\hbar$. The total Hamiltonian is

$$\mathcal{H}=\mathcal{H}_Z+\sum_{s=0,\pm1,\pm2}V^{(s)}. \tag{A9}$$

Since the Zeeman Hamiltonian $\mathcal{H}_Z$ commutes with $V^{(0)}$ these two operators may be simultaneously diagonalized. We, therefore, introduce as basis vectors the eigenstates $|M,n\rangle$ satisfying the equations

$$\begin{aligned}\mathcal{H}_Z|M,n\rangle&=M\hbar\omega_0|M,n\rangle,\\ V^{(0)}|M,n\rangle&=E_{M,n}|M,n\rangle.\end{aligned} \tag{A10}$$

M is either an integer or a half integer, n stands for all the quantum numbers needed to define the corresponding eigenstate.

Zeeman and Dipole Temperatures, the Total Magnetic Moment as a Collective Coordinate

Anderson and Hartmann have shown that several experiments could be interpreted if one admits that the system is represented by a density matrix of the form

$$\rho=[\exp(-\beta_Z\mathcal{H}_Z-\beta_DV^{(0)})]/\alpha. \tag{A11}$$

This raises two questions. The first one concerns the stationarity of such states. We shall see in Part B that these states are metastable because the $V^{(s)}$ terms of the Hamiltonian induce transitions between the eigenstates of $\mathcal{H}_Z+V^{(0)}$ with the consequence that the Zeeman energy is no longer an invariant of the motion. The second question concerns the separation of the unperturbed Hamiltonian $\mathcal{H}_Z+V^{(0)}$ in two parts and the interpretation of $k\beta_Z^{-1}$ and $k\beta_D^{-1}$ as temperatures of two subsystems. This last problem shall be analyzed presently. Under what conditions is it justified to speak of two temperatures, a Zeeman temperature and a dipole-dipole temperature to characterize such a metastable state? Generally speaking, the commutability condition of $\mathcal{H}_Z$ and $V^{(0)}$ is not a sufficient one. It is furthermore necessary that the two Hamiltonians should be independent, that is, the same variables may not appear in both. The two Hilbert spaces spanned by the eigenvectors should be different. The eigenstates are then characterized by different quantum numbers so that it becomes possible to define reduced density matrices by taking partial traces over one of the subsystems. The situation is here analogous to the one studied by Tomonaga[9] for collective coordinates. Adopting this viewpoint, one sees that the total magnetic moment is a collective coordinate. However, this coordinate cannot be disentangled from the other internal ones which appear in the dipole-dipole Hamiltonian. Let us clarify this by writing the Fourier transformation that is performed to introduce a spin wave

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[8] F. Bloch, Phys. Rev. **102**, 104 (1956); **105**, 1206 (1957).

[9] S. Tomonaga, Progr. Theoret. Phys. (Kyoto) **13**, 467 (1955).

description if the spins are localized on a regular lattice.

$$I_{\mathbf{q}}{}^{\lambda}=N^{-1/2}\sum_{j} e^{i\mathbf{q}\cdot\mathbf{r}_j}I_j{}^{\lambda}. \tag{A12}$$

The $\mathbf{q}$ runs over the first Brillouin zone of crystal. The $I_{\mathbf{q}}{}^{\lambda}$ forms a complete set of commuting operators associated with collective coordinates. With this new system we can easily study the interdependence of the spin-spin and Zeeman systems. The total angular moment is, then, $I_0{}^0(N)^{1/2}$. On the other hand, the operator $V^{(0)}$ may be expressed as a function of the complete set $\{I_{\mathbf{q}}{}^{\lambda}\}$ including $I_0{}^0$. The problem is then to study under what conditions the terms in $I_0{}^0$ of the dipole-dipole Hamiltonian $V^{(0)}$ may be neglected, or when the subspaces $|M,n\rangle$ with different given M may be considered identical. Therefore, we express a typical term of $V^{(0)}$ as a function of the $I_{\mathbf{q}}{}^{\lambda}$

$$\sum_{k<l} I_k{}^{\lambda}I_l{}^{\tau}C_{kl}{}^{\lambda\tau}(\mathbf{r}_k-\mathbf{r}_l) =\sum_{\alpha}\sum_{\mathbf{q}} I_{\mathbf{q}}{}^{\lambda}I_{-\mathbf{q}}{}^{\tau}\exp(i\mathbf{q}\cdot\mathbf{r}_{\alpha})C^{\lambda\tau}(\mathbf{r}_{\alpha}). \tag{A13}$$

$\mathbf{r}_k$, $\mathbf{r}_l$ are the position vectors of spins k and l, and $\mathbf{r}_{\alpha}=\mathbf{r}_k-\mathbf{r}_l$. The eigenvalues of the $I_l{}^{\lambda}$ are of order one and, therefore, in the absence of very special phase correlations the $I_{\mathbf{q}}{}^{\lambda}$ are also of order one, except $I_0{}^0$ which is of order $N^+/(N)^{1/2}$, N^+ being the excess of up spins. The relative contribution of the collective Zeeman coordinate in $V^{(0)}$ is thus $(N^+/N)^2$, and may be neglected in the determination of thermodynamical properties when $(N^+/N)^2\ll 1$. This is the usual situation in paramagnetism, it supposes that $\hbar\omega_0/kT\ll 1$. This approximation is, therefore, typical of high temperatures. The energy is, thus, the sum of two quasi-independent contributions, the Zeeman energy and the dipole-dipole energy. We may also say that the separation of the Zeeman collective coordinate from the other degrees of freedom of the dipole-dipole system applies when $N^+/N\ll 1$, because then most of the dipole-dipole energy is in fluctuations. It does not apply when $N^+/N=0(1)$ because most of the dipole-dipole energy is then in the Weiss field. However, let us remark that the partition function (we now consider the case $\beta_Z=\beta_D=\beta$)

$$Z=\sum_{M}\exp(-\beta\mathcal{H}_Z)\sum_{n}\exp(-\beta V^{(0)})$$

does not factorize because the number of terms in the summation over n still depends on M. As a result, the thermodynamical quantities, for instance the entropy and the energy, are in general not sums of independent contributions coming from two subsystems. This is a first aspect of the problem where we emphasized the role of the total magnetization as a collective coordinate. In the following section we shall develop another aspect of the same problem: when a system has several invariants of the motion, how can we know whether they are independent or not?

Thermodynamical Aspect

The problem is to develop the statistical thermodynamics of systems with two invariants of the motion: the total energy and the total magnetic moment. A first method consists in starting from the relation $F=-kT\ln Z$, where the sum over states is restricted to the subspace of given M. To avoid the difficulty of taking partial traces we note that the situation is completely similar to that of a system with a given number of particles. The total number of particles and the total magnetic moment are operators with a discret spectrum playing the same role. We shall, therefore, use a method analogous to that of the grand canonical ensemble and consider a Gibbs ensemble of systems characterized by the density matrix

$$\rho_{M,n;M,n}=\exp(-q+\nu M-\beta E_{M,n}). \tag{A14}$$

The multiplier ν is fixed by the condition that $\bar{M}$ the mean value of M, is given. The normalization determines the potential

$$q=\ln\operatorname{Tr}\exp(\nu M-\beta V^{(0)}). \tag{A15}$$

Our ensemble is thus representative of a metastable system. Such a system will evolve to the complete equilibrium only when the effect of the perturbation terms $V^{(s)}$, $(s\neq 0)$ becomes important. The mean angular moment (in units $\hbar$) and the mean dipole-dipole energy are given by

$$\bar{M}=\partial q/\partial\nu,\quad \bar{E}_D=-(\partial q/\partial\beta). \tag{A16}$$

In the high-temperature, low-magnetic-moment limit, one gets for the q potential the expression

$$q=\operatorname{Tr}[\tfrac{1}{2}\beta^2V^{(0)2}+\tfrac{1}{2}\nu^2M^2+\cdots]/\operatorname{Tr}1. \tag{A17}$$

Dipole-dipole energy and angular moment are given by

$$\begin{aligned}\bar{E}_D&=-(\partial q/\partial\beta)=-\beta\operatorname{Tr}(V^{(0)2})/\operatorname{Tr}1,\\ \bar{M}&=\partial q/\partial\nu=\nu\operatorname{Tr}(M^2)/\operatorname{Tr}1.\end{aligned} \tag{A18}$$

It is only in this limiting case that $\bar{E}_D$ is a linear function of β and $\bar{M}$ a linear function of ν. The easiest way of seeing that β and ν are independent in this case consists in remarking that the first terms of the Taylor expansion of (A14) are also the first terms of an expansion of ρ in orthogonal operators as used by Fano,[10] since $\operatorname{Tr}[V^0M]=0$. β and ν are coefficients of this expansion and may therefore be chosen independently. The total energy is

$$\bar{E}_t=\bar{E}_D+\bar{E}_Z =[-\beta\operatorname{Tr}(V^{(0)2})-\nu\hbar\omega_0\operatorname{Tr}(M^2)]/\operatorname{Tr}1, \tag{A19}$$

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[10] U. Fano, Rev. Mod. Phys. **111**, 689 (1958).

and the entropy is (for spins I)

$$S=-k\,\mathrm{Tr}(\rho\ln\rho)=S_{\max}+S_D+S_Z$$
$$=Nk\ln(2I+1)$$
$$-k[\beta^2\,\mathrm{Tr}(V^{(0)2})+\nu^2\,\mathrm{Tr}(M^2)]/2\,\mathrm{Tr}1. \quad \text{(A20)}$$

From this, we can evaluate the potential

$$\mu=(\partial\bar{E}_t/\partial\bar{M})_S=\hbar\omega_0-\nu/\beta. \quad \text{(A21)}$$

The fact that energy and entropy are sums allows us, in this high-temperature low-magnetic-moment limit, to define a Zeeman temperature. One has

$$\begin{gathered}(\partial S/\partial\bar{E}_D)=(\partial S/\partial\bar{E}_t)_{\bar{M}}=1/T=1/T_D,\\ \partial S/\partial\bar{E}_Z=1/T_Z=k\nu/\hbar\omega_0.\end{gathered} \quad \text{(A22)}$$

There is, thus, a simple relation between ν and the "Zeeman temperature"

$$\nu=\hbar\omega_0/kT_Z=\bar{M}\,\mathrm{Tr}(1)/\mathrm{Tr}(M^2). \quad \text{(A23)}$$

In conclusion one may say that there is only one temperature, which is the dipole-dipole one, whereas the state of the Zeeman system is described by a multiplier ν related to a chemical potential.[11] However, it is possible to replace this quantity by a Zeeman temperature in the limit considered and as a result of the peculiar properties of the Hamiltonian. This is actually a simple illustration of the fact that equilibrium conditions between subsystems are given by an equality of temperature when the Hamiltonian is the only invariant. Whenever, besides the Hamiltonian, there exists another analytical invariant, the equilibrium is determined by a relation between the corresponding Lagrange multipliers. We shall see in Sec. B that the cross-relaxation phenomena furnish a beautiful example of this rule.

B. DYNAMICS OF THE EVOLUTION TOWARDS EQUILIBRIUM

We now take into account the $V^{(s)}$ terms ($s\neq0$), which cause, besides a shift of the levels, a coupling of the collective coordinate $I_0{}^0$ with the dipole-dipole system. This plays the role of heat bath, (in the sense that it is a many-body system rapidly reaching its equilibrium state) with the peculiar situation that the largest part of the specific heat is carried by the single Zeeman collective coordinate. As a result, the temperature of the "dipole-dipole heat bath" varies when brought in thermal contact with the Zeeman system. For initial distributions of the types (A14) the destruction of the magnetic moment as analytical invariant may be described in the high-temperature limit as an evolution of two subsystems to a common thermal equilibrium. We shall first set up a Pauli equation for the complete system in order to study the approach towards equilibrium. The treatment we present here differs from previous ones by the explicit introduction of the representation with basis vectors $|M,n\rangle$. It gives, therefore, a deeper physical understanding of the time evolution mechanism. It shows the necessity of extending the calculations to the fourth order in the perturbation and introduces the concept of a dipole-dipole relaxation time, which is the basis of the dynamical justification of the equilibrium considerations of Sec. A.

Master Equation for Interacting Spins Systems

It has been established, that under very general conditions, the time evolution of a large system with a continuous energy spectrum is governed by a non-Markovian master equation.[1,12] Neglecting temporarily the contribution from the nondiagonal elements of ρ at time zero, the diagonal elements of ρ satisfy[13]

$$\partial_t\langle k|\rho(t)|k\rangle=\int_0^t d\tau\Big\{\sum_{m=2}^{\infty}\Big(\frac{\lambda}{i\hbar}\Big)^m\int_0^\tau d\tau_1\cdots\int_0^{\tau_{m-3}}d\tau_{m-2}$$
$$\times\langle k|[V(\tau),[V(\tau_1),[\cdots[V(\tau_{m-2}),[V(0),\rho^d(t-\tau)]\cdots]|k\rangle_{d\,i}\Big\}, \quad \text{(B1)}$$

where $\rho^d(t)$ is the diagonal part of the density matrix

$$\rho^d(t)=\sum_k|k\rangle\langle k|\rho(t)|k\rangle\langle k|. \quad \text{(B2)}$$

The Hamiltonian has been written $\mathcal{H}=\mathcal{H}_0+\lambda V$, the $|k\rangle$ are the eigenstates of $\mathcal{H}_0$ and $V(t)$ is the interaction representation of V,

$$V(t)=\exp(i\mathcal{H}_0t/\hbar)V\exp(-i\mathcal{H}_0t/\hbar). \quad \text{(B3)}$$

The subscript $d\,i$ indicates that no intermediate states should be represented by a diagonal element of ρ. This is precisely the condition to be fulfilled in order to get one and one single t factor in the formal solution for $\rho(t)$.[14] One then recognizes in the right-hand side the time derivative of this formal solution. In applying this

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[11] The chemical potentials introduced by E. A. Desloge and W. A. Barker [Phys. Rev. **108**, 924 (1957)] correspond to a description in terms of the Zeeman states of individual spins and these authors introduce only one temperature which is the lattice temperature. In the case of the solids with spin-spin interaction considered here, the spin system has a continuous energy spectrum and the state of individual spins are not invariants of the motion with our unperturbed Hamiltonian. One has a chemical potential not for each Zeeman state of a single spin, but for each spin species. The temperature introduced here is that of the spin system.

[12] P. Résibois, Physica **29**, 721 (1963).

[13] We use the two notations $\rho_{k;k}=\langle k|\rho|k\rangle$.

[14] For further details concerning the general theory of irreversible processes, see Refs. 1 and 12.

general formalism to our problem we put

$$\mathcal{H}_0=\mathcal{H}_Z+V^{(0)},\quad \lambda V=\sum_{s\neq 0} V^{(s)}. \tag{B4}$$

The eigenstates of the unperturbed Hamiltonian are denoted by $|M,n\rangle$. We do not know these eigenstates. Nevertheless, we shall perform the calculations formally, assuming that an occupation number representation with continuous wave vectors exists. This hypothesis which is already implicitly assumed in Van Vleck's work,[15] is necessary for any theory of this kind. The expressions we obtain may afterwards be used to calculate traces which can be evaluated in any representation.

We now proceed to evaluate the kernel of this integral equation up to the terms in λ^4. Going then to the limit $t \gg \tau_C$, that is, considering the collisions as instantaneous, we derive a generalized Pauli equation. The collision time τ_C which appears here is of the order of the inverse of the linewidth $\Delta\omega$. This follows from the fact that the usual asymptotic formula,

$$\lim_{T\to\infty}\int d\omega \int_{-T}^{T} f(\omega)e^{i\omega t}dt=2\pi T f(0), \tag{B5}$$

may be applied as soon as $T \gg (\Delta\omega)^{-1}$, $\Delta\omega$ being the frequency interval over which $f(\omega)$ varies appreciably.

Collision Operator

(a) *Terms in* λ^2: They correspond to transitions $M \rightleftarrows M\pm 1$ and $M \rightleftarrows M\pm 2$. These are the usual second-order transition probabilities. They describe an energy transfer between the Zeeman coordinate and the dipole-dipole system and become more and more important for low fields. They are

$$\frac{2\pi}{\hbar}\Big|\Big(\sum_s V^{(s)}\Big)_{M,n;M',n'}\Big|^2 \times\delta[E_{M,n}-E_{M',n'}+(M'-M)\hbar\omega_0]. \tag{B6}$$

(b) *Terms in* λ^3: They also correspond to an energy exchange between the Zeeman and the dipole-dipole system. Since they are in a higher order in λ and describing the same processes as the previous terms, we shall neglect them.

(c) *Terms in* λ^4: There are two types of such terms. Those describing an energy exchange between the two subsystems and those bringing the dipole-dipole system towards equilibrium. The first class of processes is neglected for the same reason as in (b) and we proceed to calculate the second class. The different contributions may be classified using the diagrams introduced by Fujita.[16] However, it turns out that in the case of high fields one may simply take the square of the S matrix

$$\frac{2\pi}{\hbar}\delta(E_{M,n}-E_{M,n'})\Big|\sum_s\sum_{n''}\langle M,n'| \times V^{(s)}(E_{M,n}-E_{M-s,n''}-s\hbar\omega_0+i\epsilon)^{-1}V^{(-s)}|M,n\rangle\Big|^2. \tag{B7}$$

Using the formula

$$\lim_{\epsilon\to 0}(x+i\epsilon)^{-1}=P(1/x)-i\pi\delta(x),$$

and dropping the δ terms (high field approximation), one gets

$$\frac{2\pi}{\hbar}\delta(E_{M,n}-E_{M;n'})\Big|\sum_s[V^{(s)},V^{(-s)}]_{M,n;Mn'}/s\hbar\omega_0\Big|^2. \tag{B8}$$

Finally, the Pauli equation takes the form:

$$\begin{aligned}\partial_t\rho_{M,n;M,n} &=\frac{2\pi}{\hbar}\sum_{n'}\Big|\Big(\sum_s V^{(s)}\Big)_{M,n;M',n'}\Big|^2(\rho_{M',n';M',n'}-\rho_{M,n;Mn})\\ &\quad\times\delta[(M'-M)\hbar\omega_0+E_{M,n}-E_{M',n'}]\\ &\quad+\frac{2\pi}{\hbar}\sum_{n'}\Big|\sum_s[V^{(s)},V^{(-s)}]_{M,n;M,n'}/s\hbar\omega_0\Big|^2\\ &\quad\times(\rho_{M,n';M,n'}-\rho_{M,n;M,n})\delta(E_{M,n}-E_{M,n'}).\end{aligned} \tag{B9}$$

One easily sees that in this approximation and in the absence of special initial phase correlations one may neglect the contribution of the nondiagonal elements of ρ at time zero, since they always contain at least one factor λ more then the retained terms. Our equation is thus valid when the relations

$$\tau_{\text{collision}} \ll \tau_{\text{dipole-dipole}} < \tau_{\text{dipole Zeeman}} \ll \tau_{\text{spin-lattice}}$$

hold.

Discussion of the Maser Equation

The rate of the transitions is determined by the order in the perturbation but also by the possibility of conserving energy. The eigenvalues of $\mathcal{H}_Z+V^{(0)}$ form a band spectrum, one band for each M. The overlap between the different bands depends on the magnitude of the external field. For a weak overlap, transitions from one band to another ($\Delta M=s\neq 0$) are highly improbable because the relevant density of states becomes extremely low. On the other hand, the conditions of conservation of energy is easily fulfilled for transitions within the same band ($\Delta M=0$). As a result, the relation $\lambda^2/\tau_{DZ} \ll \lambda^4/\tau_{DD}$ holds for high fields.

Dipole-Dipole Relaxation

Let us suppose that the external field H_0 is such that the dipole-dipole relaxation time is much shorter than

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[15] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

[16] S. Fujita, Physica 28, 281 (1962).

the Zeeman dipole-dipole relaxation time. In the master equation, (B9), one may then neglect the terms in V^2 describing an energy exchange between the two subsystems, getting a set of separated equations for each M:

$$\partial_t\rho_{M,n;M,n}=2\pi/\hbar\sum_{n''}\Big|\sum_{s}\,[V^{(s)},V^{(-s)}]_{M,n'';M,n}\Big|^2$$
$$\times(\rho_{M,n'';M,n''}-\rho_{M,n;M,n})\delta(E_{M,n}-E_{M,n''})\,. \qquad \text{(B10)}$$

The system reaches its equilibrium in two steps. The first one is governed by the Eqs. (B10) which describe the evolution of the dipole-dipole system to internal equilibrium. The characteristic time of these processes is in λ^{-4}. However, as long as the eigenfunctions and eigenvalues of $V^{(0)}$ remain unknown, it is not possible to go from (B10) to a Boltzmann-like equation which should give us explicitly the dipole-dipole relaxation time. One expects that this time is of the order of $(\Delta\omega)^{-1}(H_0/H_l)^2$. It would be most interesting to measure this time, setting up experiments in which the distribution of the dipole-dipole energy is not a canonical one and to study its relation with diffusion processes.[17,18] The second step in the evolution towards equilibrium is characterized by an energy between the Zeeman and dipole-dipole subsystem, it brings the whole spin system to equilibrium, this is the Zeeman dipole-dipole relaxation.

Zeeman Dipole-Dipole Relaxation

The basic equation describing the variation of the Zeeman energy is

$$\partial_t(\mathrm{Tr}\rho\mathcal{H}_Z)$$
$$=\hbar\omega_0\sum_{M,n,n',s}MV_{M,n;M-s,n'}{}^{(s)}V_{M-s,n';M,n}{}^{(-s)}$$
$$\times(2\pi/\hbar)\delta(E_{M,n}-E_{M-s,n'})$$
$$\times(\rho_{M,n;M,n}-\rho_{M-s,n';M-s,n'})\,. \qquad \text{(B11)}$$

An estimation of the Zeeman dipole-dipole relaxation time has been given by Hartmann and Anderson[5] using the hypothesis that ρ is at any time of the form (A11). We treat this problem as some kind of Brownian motion of the collective Zeeman coordinate in the "dipole-dipole heat bath." Taking the trace of the master equation over the dipole-dipole system we obtain equations closely related to the usual Bloch equations, with the peculiarity that the temperature of the heat bath varies during the process. Let us assume that the diagonal elements of ρ have the form

$$\rho_{M,n;M,n}=\sigma_{M;M}\exp(-\beta_D E_n)/\mathrm{Tr}_{(n)}1$$
$$=\sigma_{M;M}\exp(-\beta_D E_n)/g(M)\,, \qquad \text{(B12)}$$

with the normalization

$$\sum_{M,n}\rho_{M,n;M,n}=\sum_{M}\sigma_{M;M}=1\,, \qquad \text{(B13)}$$

and the equilibrium distribution

$$\sigma_{M;M}=g(M)\exp(\beta_D M\hbar\omega_0)/$$
$$\sum_{M}g(M)\exp(\beta_D M\hbar\omega_0)\,. \qquad \text{(B14)}$$

One gets

$$\partial_t\sigma_{M;M}=-\sum_{s}\{2\Gamma_{MM}{}^{s}[\sigma_{M;M}-\exp(-\beta_D s\hbar\omega_0)$$
$$\times\sigma_{M+s;M+s}g(M)/g(M+s)]\}\,, \qquad \text{(B15)}$$

with

$$\Gamma_{MM}{}^{s}=\sum_{n,n'}V_{M,n;M+s,n'}{}^{(-s)}V_{M+s,n';M,n}{}^{(s)}\exp(-\beta_D E_n)$$
$$\times[\pi/\hbar g(M)]\delta(E_{M,n}-E_{M+s,n'}+s\hbar\omega_0)\,. \qquad \text{(B16)}$$

In (B15), β_D is still a function of time which is determined by the conservation of the total energy

$$(d/dt)\,\mathrm{Tr}[\rho(\mathcal{H}_Z+V^{(0)})]=0\,. \qquad \text{(B17)}$$

In the case of small deviations from equilibrium one may look for a solution of the form

$$\sigma_{M;M}(t)=g(M)\exp[\beta_D(t)M\hbar\omega_0]/\mathrm{Tr}1\,. \qquad \text{(B18)}$$

(B15) then gives the equations

$$(d/dt)\beta_Z=\sum_{s}2\Gamma_{MM}{}^{s}M^{-1}(\beta_D-\beta_Z)\,. \qquad \text{(B19)}$$

Remembering that M is very large, that $\Gamma_{MM}{}^{s}$ varies slowly with M, and that the relevant values of M are practically equal to $\bar{M}$, the set (B19) may then be replaced by a single equation which is the equation written by Hartmann, Anderson,[5] and Provotorov.[6]

$$(d/dt)\beta_Z=\sum_{s}\mathrm{Tr}[V^{(s)}V^{(-s)}\pi\hbar\delta(E_{M,n}-E_{M+s,n'}+s\hbar\omega_0)]$$
$$\times(\beta_D-\beta_Z)/\mathrm{Tr}(S_z{}^2)\,. \qquad \text{(B20)}$$

Let us remark that a large external rotating field can always be included in a new unperturbed Hamiltonian by means of a unitary transformation. As a result the spin systems evolves then towards a canonical distribution in the rotating frame as assumed by Redfield.[19] This problem shows the importance of the interference between external force and collision processes in a Boltzmann-like equation.

Cross Relaxation

The formalism may easily be extended to treat the problem of two or more spin species.[20,21] Let us, for instance, consider the case of two spin species. The Hamiltonian is

$$\mathcal{H}=\mathcal{H}_Z(1)+\mathcal{H}_Z(2)+V^{(0)}(1)+V^{(0)}(2)$$
$$+V^{(0)}(1,2)+\cdots\,. \qquad \text{(B21)}$$

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[17] P. G. de Gennes, J. Phys. Chem. Solids 4, 223 (1958).

[18] A. G. Redfield, Phys. Rev. 116, 315 (1959).

[19] A. G. Redfield, Phys. Rev. 98, 1787 (1955).

[20] N. Bloembergen, S. Shapiro, P. S. Pershan, and I. O. Artman, Phys. Rev. 114, 445 (1959).

[21] P. S. Pershan, Phys. Rev. 117, 109 (1960).

As in (A9), the sum of the Zeeman terms and of that part of the interaction which commutes with them is taken as unperturbed Hamiltonian. The basis vectors satisfy

$$[\mathcal{H}_Z(1)+\mathcal{H}_Z(2)]|M_1,M_2,n\rangle = \hbar(M_1\omega_1+M_2\omega_2)|M_1,M_2,n\rangle\,, \quad \text{(B22)}$$

$$[V^{(0)}(1)+V^{(0)}(2)+V^{(0)}(1,2)]|M_1,M_2,n\rangle = E_{M_1,M_2,n}|M_1,M_2,n\rangle\,.$$

The equilibrium properties of such systems are characterized by three invariants: the total energy (or the dipole-dipole energy) and two magnetic moments (or Zeeman energies). The density matrix representing an ensemble of such systems is

$$\rho_{M_1,M_2,n;\,M_1,M_2,n} = \exp(-q+\nu_1M_1+\nu_2M_2-\beta E_{M_1,M_2,n})\,, \quad \text{(B23)}$$

where the potential q is given by

$$q=\ln \operatorname{Tr} \exp\{\nu_1M_1+\nu_2M_2 -\beta[V^{(0)}(1)+V^{(0)}(2)+V^{(0)}(1,2)]\}\,. \quad \text{(B24)}$$

The mean angular moments (in units $\hbar$) are given by

$$\bar{M}_i=\partial q/\partial\nu_i \quad \text{(B25)}$$

and the chemical potentials by

$$\mu_i=(\partial\bar{E}_t/\partial\bar{M}_i)_S=-T(\partial S/\partial\bar{M}_i)_{\bar{E}_t}\,. \quad \text{(B26)}$$

When the difference of the Larmor frequencies becomes of the order of the linewidth, or more generally when $\alpha_1\omega_1+\alpha_2\omega_2\simeq\Delta\omega$ (α_i being integers close to one) one of the invariants is destroyed by the transition caused by the $V^{(s)}(1,2)$ terms of the Hamiltonian. In the situation just considered, the two angular momenta are replaced by the single invariant combination $M_1/\alpha_1-M_2/\alpha_2$. The usefulness of a thermodynamical approach to cross relaxation has recently been shown by Jeener.[7] This process is analogous to a chemical reaction in which chemical species are destroyed but where the total quantity of matter remains constant. Let us introduce as in chemical thermodynamics[22] the reaction coordinate ξ and write

$$\begin{aligned} \bar{M}_1(t)&=\bar{M}_1(0)+\alpha_1d\xi\,,\\ \bar{M}_2(t)&=\bar{M}_2(0)+\alpha_2d\xi\,, \quad \text{(B27)}\\ d\bar{M}_1/\alpha_1&=d\bar{M}_2/\alpha_2=d\xi\,. \end{aligned}$$

At equilibrium the entropy is maximum and the affinity of the reaction is equal to zero: $A=\alpha_1\mu_1+\alpha_2\mu_2=0$. The final values of β, $\bar{M}_1$, $\bar{M}_2$ are determined by the equations

$$\begin{aligned} &\beta(\alpha_1\hbar\omega_1+\alpha_2\hbar\omega_2)\\ &\quad-\bar{M}_1\alpha_1 \operatorname{Tr}1/\operatorname{Tr}(M_1^2)-\bar{M}_2\alpha_2\operatorname{Tr}1/\operatorname{Tr}(M_2^2)=0\,, \quad \text{(B28)}\\ &\quad\bar{M}_1/\alpha_1+\bar{M}_2/\alpha_2=C\,,\ \bar{E}_D+\bar{M}_1\hbar\omega_1+\bar{M}_2\hbar\omega_2=\bar{E}_t\,, \end{aligned}$$

expressing, respectively, the conditions of chemical equilibrium, the condition already expressed by (B27), and the conservation of energy. An alternative treatment consists in remarking that we now have two Zeeman collective coordinates, a linear combination of which being coupled to the dipole-dipole system through the $V^{(s)}$ terms. This is most easily seen if one rewrites the Zeeman Hamiltonian in the form

$$\begin{aligned} \mathcal{H}_Z=&\tfrac{1}{2}[S_z(1)/\alpha_1+S_z(2)/\alpha_2](\alpha_1\omega_1+\alpha_2\omega_2)\\ &+\tfrac{1}{2}[S_z(1)/\alpha_1-S_z(2)/\alpha_2](\alpha_1\omega_1-\alpha_2\omega_2)\,, \quad \text{(B29)} \end{aligned}$$

where that part of the Zeeman Hamiltonian that becomes coupled to the dipole-dipole system has been separated. The problem is now completely analogous to the Zeeman dipole-dipole relaxation already studied before. One could also say that the collective coordinate, $S_z(1)/\alpha_1+S_z(2)/\alpha_2$, should now be considered as being part of the dipole-dipole heat bath. Let us show that the condition of equal temperature for this coordinate and the dipole-dipole system is equivalent to the condition of chemical equilibrium. Noting that

$$\begin{aligned} &\beta_1S_z(1)\omega_1+\beta_2S_z(2)\omega_2\\ &=\left(\frac{\beta_1\alpha_1\omega_1+\beta_2\alpha_2\omega_2}{\alpha_1\omega_1+\alpha_2\omega_2}\right)\left(\frac{S_z(1)}{\alpha_1}+\frac{S_z(2)}{\alpha_2}\right)\\ &\quad\times\left(\frac{\alpha_1\omega_1+\alpha_2\omega_2}{2}\right)+\left(\frac{\beta_1\alpha_1\omega_1-\beta_2\alpha_2\omega_2}{\alpha_1\omega_1-\alpha_2\omega_2}\right)\\ &\quad\times\left(\frac{S_z(1)}{\alpha_1}+\frac{S_z(2)}{\alpha_2}\right)\left(\frac{\alpha_1\omega_1-\alpha_2\omega_2}{2}\right), \quad \text{(B30)} \end{aligned}$$

this condition is

$$(\beta_1\alpha_1\omega_1+\beta_2\alpha_2\omega_2)/(\alpha_1\omega_1+\alpha_2\omega_2)=\beta\,. \quad \text{(B31)}$$

Using (A21), $\beta_i=\bar{M}_i\operatorname{Tr}1/\hbar\omega_i\operatorname{Tr}(M_i^2)$, (B31) becomes equivalent to (B28).

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[22] I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longmans Green and Company, Inc., New York, 1954).