

where $T_0 = (2S\hbar k_F/k_B)$, S is the velocity of sound, and k_F is the Fermi wave vector. If one used a velocity of sound of 3×10^5 cm/sec, T_0 from the data corresponds to $k_F \approx 2 \times 10^7$ cm $^{-1}$. The free-electron model of Nb $_3$ Sn, with the full valence of 4.75, would imply $k_F \approx 2 \times 10^8$ cm $^{-1}$, while a one-dimensional lattice would imply $k_F \approx 6 \times 10^7$ cm $^{-1}$, in fair agreement. Unfortunately, (3) would also imply a linear term too large compared to the exponential to fit the experimental resistivity.

Additional evidence for the source of the anomalous behavior of the resistivity of Nb $_3$ Sn is provided by Hall measurements made at 27, 78, and 300°K in fields up to 7600 G. The Hall voltage was positive, independent of temperature, and in terms of a one-carrier model, implied a hole density of 1.77×10^{22} holes/cc. The effective valence of Nb $_3$ Sn is thus 0.27 holes per atom, and the room temperature mobility is 4.3 cm 2 /Vsec. Although quantitative interpretation of this Hall constant is difficult since it undoubtedly arises from multiple band effects, the temperature independence is significant for the present paper. Since, from 300–27°K, the resistivity changes by a factor of 6, the constant Hall voltage supports the view that the scattering time rather than the effective number of carriers is changing

as the temperature is reduced, and would appear to rule out the Wilson-Mott model^{8,10} for Nb $_3$ Sn.

The present paper has shown the existence of a pronounced resistivity anomaly in Nb $_3$ Sn, and demonstrated that the temperature variation can be fit to an accuracy of 1% from 18–850°K, by a surprisingly simple expression. Moreover, Hall measurements support the view that the anomaly arises from an unexpected rapid temperature dependence of the scattering probability, below 200°K. Unfortunately, a more quantitative treatment requires a better knowledge of the band structure and bonding in Nb $_3$ Sn than is presently available, in particular, an analysis of the role played by the chains of strongly bonded niobium atoms. It is hoped that such a quantitative treatment of the structure of Nb $_3$ Sn and its transport behavior may also lead to an understanding of the intriguing fact that this material has the highest T_c of any known superconductor (18.3°K).

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¹⁰ M. B. Brodsky, Phys. Rev. **131**, 137 (1963).

Study of Oscillations and Correlations in the Relaxation of a Model Spin System*

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A detailed investigation is made of the approach to equilibrium of system of spins with $I=1/2$. The spin-spin interaction $\sum_k \sum_{j < k} B_{jk} \sigma_x^j \sigma_x^k$ with B_{jk} constant is treated exactly, while the additional interaction $\sum_k \sum_{j < k} L_{jk} \sigma_x^j \sigma_x^k$ with L_{jk} depending on lattice vibrations is treated by means of the assumption of sufficiently short correlation times for the L_{jk} operators. All correlations between the L_{jk} are included. The effect of the correlations usually neglected is expressed in terms of a sum over states somewhat resembling an Ising-model partition function with the time replacing interaction strength. The oscillatory relaxation via the B_{jk} and the monotonic relaxation via the phonons compete with each other; interference effects between the two relaxation modes also occur; the origin and nature of the irreversibility are very different for the two relaxation modes.

1. INTRODUCTION

THE problem of nuclear magnetic relaxation via the dipole-dipole interaction in a crystal lattice is a many-body problem in which the correlations between spins at different sites play a role. At temperatures sufficiently low, so that the lattice is effectively rigid, the system of spins is an isolated system with a discrete system of energy levels; the approach to equilibrium of an initial polarization transverse to an applied

static magnetic field is in this case oscillatory, as both the experiments and the explicit calculations of Lowe and Norberg have shown.¹ At high temperatures the dipole-dipole relaxation in solids is described by Bloch's general theory of relaxation,² in which the lattice vibrations play the role of a heat bath; the relaxation of an initial polarization transverse to the static magnetic field is in this case described by a sum of decaying exponentials. The occurrence of oscillations at low temperatures and their disappearance at high temperatures³

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¹ I. Lowe and R. Norberg, Phys. Rev. **107**, 46 (1957).

² F. Bloch, Phys. Rev. **105**, 1206 (1957).

³ Some discussion of this phenomenon is given by A. Sher and H. Primakoff, Phys. Rev. **119**, 178 (1960).

provided the stimulus for the present study. The oscillatory approach to equilibrium of other isolated systems with a discrete set of frequencies has been studied⁴ particularly by Mazur, Montroll, Hemmer, Van Hove, Prigogine, and Bingen. The more general relation of master equations to the occurrence of oscillation in the approach to equilibrium has been discussed by Zwanzig,⁵ by Van Hove and Verboven,⁶ and by Willis.⁷

Solution of the Bloch equations for the magnetic relaxation of identical spin- $\frac{1}{2}$ particles coupled by dipole-dipole interaction gives a single relaxation time (T_2) for the transverse relaxation. It has been particularly clearly pointed out by Hubbard⁸ that to obtain these solutions, correlations between the interactions of one pair of spins (i, j) and adjacent pairs (j, k) have to be neglected. Consequently,⁹ the solutions are not really applicable to solids.

The aim of the present paper is to study the extension of the theory by including all correlations between spins as well as the low-temperature oscillations for a rather simple model Hamiltonian for which the time-dependent density matrix can be evaluated completely by elementary methods. The Hamiltonian used is obtained by generalizing the Lowe-Norberg Hamiltonian to include spin-lattice interactions. The interaction Hamiltonian in this model commutes with the Zeeman term, so that only transverse relaxation can be studied; the longitudinal relaxation requires an exchange of energy between the Zeeman term and the lattice. It has been shown by Lowe and Norberg that in the rigid-lattice case the Hamiltonian used leads to qualitatively correct results. The features we have studied include: (A) the manner in which the correlations mentioned by Hubbard modify the transverse relaxation; (B) interference and competition of relaxation involving short correlation times with that involving long correlation times; (C) the nature of irreversibility in the two cases.

As is usual in the application of Bloch theory, we split the total Hamiltonian into a Hamiltonian for the spin system (\mathcal{H}_s), one for the lattice (\mathcal{H}_L) and spin-lattice coupling (G):

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_L + G. \quad (1)$$

All energies and Hamiltonians will in the following be expressed in units of \hbar . For \mathcal{H}_s take the Lowe-Norberg

model

$$\mathcal{H}_s = \sum_{j < k}^N B_{jk} \sigma_x^j \sigma_x^k - \gamma H \sum_j \sigma_x^j, \quad (2)$$

where B_{jk} are constants characterizing the rigid-lattice interaction, and the σ_x^j are Pauli spin matrices. The sum is over all pairs of spins in the crystal. This form of \mathcal{H}_s restricts consideration to spin- $\frac{1}{2}$ nuclei; it is, in fact, the Ising-model Hamiltonian with arbitrary range and strength of interaction. This Hamiltonian by itself gives rise to an oscillatory approach to equilibrium, arising from the superposition of the discrete set of frequencies of the spin system. We include the Zeeman term $-H\gamma \sum_i \sigma_x^i$ in the spin Hamiltonian, although such a term has little effect on the transverse relaxation, other than superimposing a Larmor precession on the spin motion. The lattice Hamiltonian \mathcal{H}_L depends only on lattice variables; at this point its explicit form is not needed.

The interaction term G is given by

$$G = \frac{1}{2} \sum_j \sum_k L_{jk} \sigma_x^j \sigma_x^k, \quad L_{jj} = 0, \quad (3)$$

where $L_{jk} = L_{kj}$ are operators depending on lattice variables. We require that the average of L_{jk} over an equilibrium distribution of lattice coordinates vanishes. This involves no loss of generality,⁷ as the B_{jk} can always be redefined in accordance with this requirement. Physically, one may think of the B_{jk} and L_{jk} in terms of an expansion of the lattice vibrations about their equilibrium position, the B_{jk} being a function only of the equilibrium positions, and the L_{jk} depending on deviations from equilibrium. We treat \mathcal{H}_s exactly, but in studying the time evolution due to G , we assume correlation times for the L_{jk} , which are short compared to relaxation times. The correlation times of the B_{jk} are, of course, infinite.

2. RELAXATION FOR NONRIGID LATTICE

The time evolution of the expectation of a spin operator θ can be given in terms of the time-dependent density matrix $\rho(t)$ of the total system:

$$\langle \theta \rangle_t = \text{Tr}^{(S,L)} \theta \rho(t); \quad \rho(t) = \exp(-i\mathcal{H}t) \rho(0) \exp(i\mathcal{H}t). \quad (4)$$

Here the (S, L) means the trace is to be over the states of the lattice as well as those of the spin system. Carrying out the trace over the lattice, noting that the commutators $[\mathcal{H}_s, G]$ and $[\mathcal{H}_s, \mathcal{H}_L]$ vanish, one obtains

$$\langle \theta \rangle_t = \text{Tr}^{(S)} \theta \rho_s(t), \quad (5)$$

with

$$\begin{aligned} \rho_s(t) &= \exp(-i\mathcal{H}_s t) \rho_s'(t) \exp(i\mathcal{H}_s t), \\ \rho_s'(t) &= \text{Tr}^{(L)} \exp[-i(G + \mathcal{H}_L)t] \rho(0) \\ &\quad \times \exp[i(G + \mathcal{H}_L)t]. \end{aligned} \quad (5a)$$

In the case of the rigid lattice, $G=0$, and consequently $\rho_s'(t) = \rho(0)$. For the nonrigid lattice⁸ Bloch's

⁴ The work on systems with discrete levels, particularly on assemblies of harmonic oscillators, is reviewed by E. Montroll in Lectures Theoret. Phys. 3, 221 (1960). Full references are given there.

⁵ R. Zwanzig, Lectures Theoret. Phys. 3, 106 (1960).

⁶ L. Van Hove and E. Verboven, Physica 27, 418 (1961).

⁷ C. R. Willis, Phys. Rev. 127, 1405 (1962).

⁸ P. Hubbard, Rev. Mod. Phys. 33, 249 (1961).

⁹ A. Yoshimori and J. Koringa, Phys. Rev. 128, 1059, 1061 (1962) have applied other methods (Green functions, stochastic variables in Hamiltonian) to study relaxation of a pair of dipoles; they obtain some features not contained in the usual solutions of the Bloch equation.

theory gives the following differential equation for $\rho_s'(t)$:

$$(d\rho_s'/dt) + i[N, \rho_s'(t)] = 2 \sum_{lk} K_{kl}(0) [[V^l, \rho_s'(t)], V^k], \quad (6)$$

with $N = \sum_{k,l} V^k V^l A_{kl}$, where the summation indices k and l each represent a pair of spins (q, q') and (p, p') , respectively, and $V^k \equiv \sigma_x^q \sigma_x^{q'}$;

$$A_{kl} \equiv \int_0^\infty \frac{d\omega}{\omega} \{K_{kl}(-\omega) - K_{kl}(\omega)\}.$$

The spectral density function is

$$K_{kl}(\omega) \equiv \frac{1}{4} \int_{-\infty}^\infty \langle L_{q,q'}(\tau) L_{p,p'} \rangle_\beta e^{i\omega\tau} d\tau. \quad (7)$$

The $L_{q,q'}$ are defined by (3), and the correlation functions are explicitly (with $\beta = \hbar/kT$)

$$\begin{aligned} & \langle L_{q,q'}(\tau) L_{p,p'} \rangle_\beta \\ & \equiv \text{Tr}[\exp(-\beta\mathcal{C}_L) \exp(i\mathcal{C}_L\tau) L_{q,q'} \exp(-i\mathcal{C}_L\tau) L_{p,p'}] / \\ & \quad \text{Tr} \exp(-\beta\mathcal{C}_L). \end{aligned} \quad (8)$$

The spectral density satisfies the symmetry relation

$$K_{lk}(-\omega) = e^{-\beta\omega} K_{kl}(\omega). \quad (9)$$

The assumptions required in deriving (6) are given carefully by Hubbard.⁸ They are: (i) that the lattice behaves like a heat bath, remaining in thermal equilibrium at a constant temperature while the spin system relaxes; (ii) that the correlation time of the lattice $\tau_c \ll 1/|N|, 1/|R|$, where R is the right-hand side of Eq. (6). The correlation time is defined as the reciprocal of a frequency ω^* , such that the spectral density functions change negligibly with any frequency change much less than ω^* . Consequently,

$$\langle L_{q,q'}(\tau) L_{p,p'} \rangle_\beta \approx 0, \quad \text{for } |\tau| \gg \tau_c. \quad (10)$$

The formal solution of (6) can be obtained by introducing an ordering parameter¹⁰ θ . Operators to the right-hand side of θ operate to the right of ρ_s' and operators on the left of θ operate on the left of ρ_s' . Then the solution to (6) in operator form is

$$\begin{aligned} \rho_s'(t) &= \exp\{it[\theta, N]\} \\ &+ 2t \sum_{lk} K_{kl}(0) [[V^l, \theta], V^k] \rho_s(0). \end{aligned} \quad (11)$$

To carry it further, introduce the representation in which all the σ_x^j are simultaneously diagonal, each having two eigenvalues $m_j = \pm 1$. The solution to (6) becomes in this representation

$$\langle m | \rho_s'(t) | n \rangle = \langle m | \rho_s(0) | n \rangle e^{-i\mu_{mn}t} e^{-\lambda_{mn}t}, \quad (12)$$

where $\langle m |$ stands for $\langle m_1 m_2 \cdots m_N |$, etc. We write in

¹⁰ U. Fano, Phys. Rev. **96**, 869 (1954).

more explicit notation $K_{q,q';p,p'}$ for K_{kl} , where, however, $K_{q,q';p,p'} = K_{q,q';p,p} \equiv 0$, and the order of subscript q, q' , as well as that of p, p' is irrelevant. Then, with use of (9),

$$\begin{aligned} \lambda_{mn} &= \sum_{q,q'} \sum_{p,p'} K_{q,q';p,p'}(0) (m_q m_{q'} - n_q n_{q'}) \\ & \quad \times (m_p m_{p'} - n_p n_{p'}), \end{aligned} \quad (13)$$

$$\mu_{mn} = \sum_{q,q'} \sum_{p,p'} A_{q,q';p,p'} (m_q m_{q'} m_p m_{p'} - n_q n_{q'} n_p n_{p'}). \quad (14)$$

It follows from the Definitions (7) and (8) that λ_{mn} and μ_{mn} are both real quantities. That λ_{mn} cannot be negative follows from the observation that the trace $\text{Tr} \rho_s'(t) = 1$ is a constant of the motion according to the Bloch equation: Remembering that ρ_s' is Hermitian with $0 \leq \langle n | \rho_s' | n \rangle \leq 1$, it is clear that

$$\text{Tr} \rho_s'^2 = \sum_{m,n} |\langle n | \rho_s' | m \rangle|^2 \leq 1;$$

consequently, no element of the density matrix can have a magnitude larger than unity, as would occur if λ_{mn} were negative. The property $\lambda_{mn} \geq 0$ can also be proved directly from the general properties of the correlation functions.

From (14) it is seen $\lambda_{nn} = \mu_{nn} = 0$; therefore

$$\langle n | \rho_s'(t) | n \rangle = \langle n | \rho_s(0) | n \rangle,$$

reflecting the fact that all the σ_x^j are constants of the motion. It may occur that some of the off-diagonal elements of matrix λ_{mn} vanish for particular values of the $K_{kl}(0)$ functions. If such $\lambda_{mn} = 0$ for $m \neq n$, it implies that $\langle m | \rho_s' | n \rangle$ does not decay, and it suggests that some other physical constant of the motion may exist, which prevents the density matrix from reaching the final distribution $\lim_{t \rightarrow \infty} \langle m | \rho_s'(t) | n \rangle = \langle m | \rho_s(0) | m \rangle \delta_{mn}$.

Let us transform to the laboratory frame for the case that the spin-spin coupling involves only short correlation times, so that $B_{jk} = 0$ in (2). From (5a) and (12) one has then

$$\langle m | \rho_s(t) | n \rangle = \langle m | \rho_s(0) | n \rangle e^{-i\omega_{mn}t} e^{-\lambda_{mn}t} \quad (15)$$

with

$$\omega_{mn} = \gamma H \sum_{j=1}^N (n_j - m_j) + \mu_{mn}. \quad (16)$$

In the solutions which have been given^{8,11} in the literature for the case of dipole-dipole relaxation, the quantity N in (6) is neglected. This neglect is usually justified by the statement that the term will give rise to only very small modifications of the Larmor precession, if the external field is sufficiently strong. From (16) the usual assumption as applied to the present example is $|\mu_{mn}| \ll |\omega_{mn} - \mu_{mn}|$ for $m \neq n$. An alternative assumption that justifies the neglect of the μ_{mn} is $|\mu_{mn}| \ll \lambda_{mn}$ for $m \neq n$. In the dipole-dipole solutions in the literature, it also has been assumed⁸ that $K_{kl}(\omega)$

¹¹ R. Kubo and K. Tomita, J. Phys. Soc. (Japan) **9**, 888 (1954).

$= \delta_{kl} K_{ll}(\omega)$. If this assumption is made, it is evident from (14) that $\mu_{mn} = 0$, and can be disregarded without the further assumption that μ_{mn} is small. As an application of (15) we calculate the transverse relaxation of a single spin component $I_z^\alpha = \frac{1}{2} \sigma_z^\alpha$. If the sample is regarded as infinite and no initial correlations exist between spins, all spins are equivalent in a simple lattice structure, so that the total spin is

$$\langle I_z \rangle_t = (N/2) \text{Tr} \sigma_z^\alpha \rho_s(t). \quad (17)$$

Terms in the sum for $\lambda_{m_1 m_2 \dots m_\alpha \dots m_N; m_1 m_2 \dots m_\alpha \dots m_N}$ vanish unless one of each pair (q, q') and (p, p') is the same as α . With this observation, (15) leads to

$$\begin{aligned} \text{Tr} \sigma_z^\alpha \rho_s(t) &= -i \sum_m m_\alpha e^{2im_\alpha \gamma H t} \\ &\times \exp[-16 \sum_q \sum_p K_{q\alpha p\alpha}(0) m_q m_{p'}] \\ &\times \langle m_1 m_2 \dots -m_\alpha \dots | \rho(0) | m_1 \dots m_\alpha \dots \rangle. \end{aligned} \quad (18)$$

A particular initial density matrix of physical interest is that for an ensemble with a given average polarization in the z direction,

$$\begin{aligned} \langle m | \rho(0) | n \rangle &= \frac{\langle m | \exp(a \sum_j \sigma_z^j) | n \rangle}{\text{Tr} \exp(a \sum_j \sigma_z^j)} \\ &= \frac{1}{2^N} \prod_{j=1}^N \langle m_j | 1 + \sigma_z^j \tanh a | n_j \rangle, \end{aligned} \quad (19)$$

where a is a constant, corresponding to $\beta \gamma H_z$, if the sample had come to thermal equilibrium in an effective field H_z prior to time $t=0$. The matrix elements of $\rho(0)$ required in (18) are equal to $i m_\alpha 2^{-N} \tanh a$, so that after summing over m_α , (18) becomes

$$\begin{aligned} \langle \sigma_z^\alpha \rangle_t &= 2^{-N+1} \tanh a \cos(2\gamma H t) \\ &\times \sum'_m \exp(-16 \sum_q \sum_p K_{q\alpha p\alpha}(0) m_q m_{p'}). \end{aligned} \quad (20)$$

The prime again denotes the sum is not over m_α .

The sum over states occurring in (20) is quite similar to the partition function of the Ising model. It is beyond the scope of the present investigation to attempt to evaluate this sum in general; possibly some of the methods which have been successful¹² in treating the Ising model may also be applied here. A very special case is one in which all the $K_{q\alpha p\alpha}^{(0)}$ are equal. Those terms corresponding to the absence of long-range order [$(1/N) \sum_{j=1}^N m_j = 0$], give no relaxation. Evidently then, this very special assumption about the $K_{q\alpha p\alpha}^{(0)}$ introduces constraints into the system, which prevent $\langle \sigma_z^\alpha \rangle$ from decaying to zero.

If the diagonal coefficients $K_{p\alpha p\alpha}(0)$ in the sums in (20) are factored out, one has

$$\langle \sigma_z^\alpha \rangle_t = 2^{-N+1} \tanh a \cos(2\gamma H t) e^{-t/T_2} Z(t), \quad (21)$$

¹² See G. Horwitz and H. Callen, Phys. Rev. 124, 1757 (1961), for a recent evaluation of the generalized Ising partition function.

with

$$1/T_2 \equiv 16 \sum_q K_{q\alpha q\alpha}(0), \quad (22)$$

$$Z(t) \equiv \sum'_m \exp(-16 \sum_{q \neq p} K_{q\alpha p\alpha}(0) m_q m_{p'}). \quad (23)$$

In the aforementioned usual approximation, $K_{q\alpha p\alpha} = \delta_{qp} K_{q\alpha q\alpha}$, the quantity $Z(t) = 2^{N-1}$ and $\langle \sigma_z^\alpha \rangle_t$ relaxes with the single relaxation time T_2 .

Equations (20) or (21) depend on the properties of the lattice only through the $K_{q\alpha p\alpha}^{(0)}$ functions. The form of these functions can be obtained in a straightforward way. If, in particular, the $L_{qq'}$ are expanded in terms of the displacement of nuclei from their equilibrium position, and these displacements are, in turn, expressed in terms of phonon creation and annihilation operators, one obtains in the harmonic approximation

$$\begin{aligned} K_{qq'; pp'}^{(0)} &= \sum_k B_{kk}^{qq'} B_{kk}^{pp'} \frac{e^{\beta \omega_k}}{(e^{\beta \omega_k} - 1)^2} \\ &+ \sum_{k \neq l} \sum \Delta_{kl} B_{kl}^{qq'} B_{kl}^{pp'} \left(\frac{3 - e^{-\beta \omega_k}}{e^{\beta \omega_k} - 1} \right)^2, \end{aligned} \quad (24)$$

where (k, l) designate phonon states. Δ_{kl} equals one, when $\omega_k = \omega_l$ and is zero otherwise. The $B_{kl}^{q, q'}$ are constants independent of temperature, but determined by the lattice structure. At very low temperatures ($\beta \rightarrow \infty$), the $K_{qq', pp'}^{(0)}$ evidently vanish; while at high temperatures they become large. The temperature dependence is a function of the number of phonons present, which is small at low temperature and large at high temperature.

3. RELAXATION OF THE ISOLATED SPIN SYSTEM

In the preceding section an irreversible relaxation process is described, in which the z component of magnetic moment of the spin system decays from its initial value to its thermal equilibrium value, namely, zero. The irreversibility has its origin in the coupling with the lattice vibrations, which are described at all times by a thermal equilibrium distribution. The continual averaging over the lattice coordinates introduces a loss of information and the associated irreversibility.

In describing the origin of the irreversibility for the rigid-lattice case, consider first quite generally an energetically isolated system with discrete energy levels E_n . From (4), the behavior of density matrix ρ_s and the expectation of a dynamical variable θ are given by

$$\langle m | \rho(t) | n \rangle = e^{-i\nu_{mn}t} \langle m | \rho_s(0) | n \rangle, \quad \nu_{mn} \equiv E_m - E_n; \quad (25)$$

$$\begin{aligned} \langle \theta(t) \rangle &= \sum_{nm} A(n, m) e^{-i\nu_{mn}t} = \int A(\omega) e^{-i\omega t} d\omega; \\ A(n, m) &\equiv \langle n | \theta | m \rangle \langle m | \rho(0) | n \rangle, \\ A(\omega) &\equiv \sum_{nm} A(n, m) \delta(\omega - \nu_{mn}). \end{aligned} \quad (26)$$

In sharp contrast to Eq. (15), the relation (25) shows that the elements of the density matrix for the isolated system are either constants or vary periodically with time. They do not approach an asymptotic value, although their time average value, $\delta_{E_m-E_n}\langle m|\rho(0)|n\rangle$ indicates a steady state about which the system oscillates. The expectation value $\langle\theta\rangle_t$ is a particular linear combination of oscillatory terms. Since ρ and θ are Hermitian, $A(m,n)=A^*(n,m)$, or $A(\omega)=A^*(-\omega)$.

To study how (26) may describe irreversibility, consider in particular an initial configuration with the property

$$A(m,n)=A(n,m)\geq 0 \quad (27)$$

so that (26) becomes

$$\langle\theta\rangle_t=\sum_{n<m}\sum A(mn)\cos\nu_{mn}t. \quad (28)$$

Note from (28) that $\langle\theta\rangle_t=\langle\theta\rangle_{-t}$. In most experiments the system is not isolated for $t<0$ and therefore not described by (28), for $t<0$. The general behavior described by (28) is as follows: At $t=0$, the $\langle\theta\rangle_t$ has its maximum value. Destructive interference reduces $\langle\theta\rangle_t$ so that after some characteristic coherence time t_c the time-average value

$$\langle\langle\theta\rangle_t\rangle_{av}=\sum_{n<m}\sum A(m,n)\delta_{E_m-E_n}$$

will have been reached. If the total number of levels of the system is finite, then the expression (28) is a finite sum of periodic terms, and the quantity $\langle\theta\rangle_t$ is periodic or almost periodic with a finite period, or recurrence time t_{rec} . If the energy spectrum of the system is continuous, and $A(\omega)=A(-\omega)$, the recurrence time is generally not finite. But an oscillatory approach to equilibrium is perfectly possible. For example a rectangular spectrum $A(\omega)$ of width $2\omega_0$ gives a $\sin\omega_0 t/t$ behavior for $\langle\theta\rangle_t$.

One observes an apparently irreversible process in the laboratory, if the duration of the experiments is of the order of t_c , but many orders of magnitude less than the recurrence time. The quantities t_{rec} and t_c refer to a specific initial density matrix $\rho(0)$ and to a particular dynamical variable θ . This may be contrasted to the situation with spin-lattice interaction. All the relaxation times of the system are in that case already contained in the time dependence of the density matrix (15), although the relaxation of a particular dynamical variable with a particular initial density matrix may involve only some of these times. The recurrence time is infinite in the spin-lattice case, as is evident from (15). The recurrence time for Eq. (28) has been studied in general by Kac, Slater, Montroll, and others.⁴

We investigate here only some physical features on which the presence of irreversibility depends for the particular example of the Hamiltonian (2), with mag-

netic field $H=0$. From the eigenvalues of (2),

$$\nu_{mn}=\frac{1}{2}\sum_{j\neq k}\sum B_{jk}(m_j m_k - n_j n_k), \quad B_{kj}=B_{jk}. \quad (29)$$

For $\theta=\sigma_z^\alpha$, (26) is

$$\begin{aligned} \langle\sigma_z^\alpha\rangle_t &= -i\sum_m m_\alpha \exp(-2itm_\alpha \sum_k B_{k\alpha} m_k) \\ &\times \langle m_1 m_2 \cdots m_\alpha \cdots m_N | \rho_s(0) | m_1 \cdots -m_\alpha \cdots m_N \rangle. \end{aligned} \quad (30)$$

With the initial state (19), the

$$A(mn)=\frac{\tanh a}{2^N} \prod_{j=1}^N \delta_{m_j n_j} \delta_{m_\alpha - n_\alpha} \quad (31)$$

satisfy (27). The prime indicates exclude $j=\alpha$.

The sum in (30) is readily carried out¹ to give with (31)

$$\langle\sigma_z^\alpha\rangle_t = \tanh a \prod_{j=1}^N \cos B_{\alpha j} t. \quad (32)$$

If B_0 is the largest of the $B_{\alpha j}$, then $t_c \cong \pi/2B_0$. Explicit evaluation of the behavior of $\langle\sigma_z^\alpha\rangle_t$ for the fluorine spin of a CaF_2 crystal according to Lowe and Norberg shows that (32) corresponds to an oscillatory decay of the initial polarization in a time of the order of 10^{-5} sec, and $t_{rec} \gg t_c$. The recurrence time depends strongly on the distribution of values $B_{K\alpha}$, and in particular¹³ on whether or not different values are commensurate. For a model considering nearest-neighbor interaction only ($B_{j\alpha}=B_0$ or 0), behavior is purely periodic with frequency B_0 . The opposite extreme occurs if the distribution of the $B_{j\alpha}$ is well approximated by a continuous Gaussian distribution, leading to an exponential decay to equilibrium without oscillations.

The particular initial density matrix (19) is one which also emphasizes the relaxation phenomenon because as we see from (30) and (31), it has the effect of giving each of the different frequencies exactly equal amplitudes. The density matrix (19) is a direct product of single-spin density matrices, in which all spin-spin correlations are neglected. The measured initial polarization does not require this. For example, one can suppose that the spin system is polarized initially in the z direction, in such a highly correlated way that all the matrix elements

$$\langle m_1 m_2 \cdots m_\alpha \cdots m_N | \rho_s(0) | m_1 \cdots -m_\alpha \cdots m_N \rangle$$

vanish, except those for one particular value of all the m_i other than m_α . Let these nonvanishing elements of $\rho_s(0)$ be equal to $(i/2)m_\alpha \tanh a$. It follows from (30) that the initial polarization is again $\tanh a$ and (27) is satisfied; but instead of (32) one obtains a simple

¹³ See E. Montroll, Ref. 4.

oscillation:

$$\langle \sigma_z^\alpha \rangle_t = \tanh a \cos(2t \sum_k B_{\alpha k} \mu_k), \quad (33)$$

where the μ_K are the above-mentioned particular values (± 1) of m_K . In this example the initial density matrix gives one frequency a large amplitude, and the others a zero amplitude, thus preventing all relaxation effects.

Next we wish to show the relation of the relaxation considered to the relaxation function employed in general theory of linear irreversible processes developed by Kubo.¹⁴ Consider the relaxation linear in H_z . From (30) and (31)

$$\langle I_z \rangle_t = \frac{1}{2} \sum_\alpha \langle \sigma_z^\alpha \rangle_t = H_z \phi_{\text{LN}}(t), \quad (34)$$

$$\phi_{\text{LN}}(t) = (\beta \gamma N / 2^{N+1}) \sum_m \cos(2t \sum_k B_{k\alpha} m_k).$$

The Lowe-Norberg function $\phi_{\text{LN}}(t)$ is based on the uncorrelated initial density matrix (19). However, Kubo's theory applies to an initial equilibrium density matrix, including correlations

$$\rho(0) = \exp(-\beta \mathcal{H}_s) / \text{Tr} \exp(-\beta \mathcal{H}_s) \quad (35)$$

with \mathcal{H}_s given by (2). The linear relaxation with initial density matrix (35) is found to be

$$\begin{aligned} \langle I_z \rangle_t &= H_z \phi(t) \\ \phi(t) &= (N/2) \sum_m A(m) \cos(2t \sum_k B_{k\alpha} m_k) \\ &= \frac{\gamma \exp(-\beta E_m') \sinh(\beta \sum_k B_{k\alpha} m_k)}{\sum_k \exp(-\beta E_k')} \frac{\sum_k B_{k\alpha} m_k}{\sum_k \exp(-\beta E_k')} \\ &\cong \beta \gamma \frac{\exp(-\beta E_m')}{\sum_k \exp(-\beta E_k')}, \end{aligned} \quad (36)$$

$$E_m' = \frac{1}{2} \sum_{j \neq k} \sum_j B_{jk} m_j m_k.$$

The prime again means exclude α or m_α in the sums. The expression (36) for the Kubo relaxation function $\phi(t)$ may be periodic or quasiperiodic and therefore not satisfy the condition $\lim_{t \rightarrow \infty} \phi(t) = 0$, on which many of the relations of the Kubo theory of irreversible proc-

$$\begin{aligned} \langle \sigma_z^\alpha \rangle_t &= \frac{\tanh a}{2^{N-1}} e^{-t/T_2} Z(t) \left[\prod_k \cos B_k t - \sum_{s < r=2} \sum_{N-1} \{m_s m_r\}_t \prod_{l=s,r} \sin B_l t \prod_{k \neq s,r} \cos B_k t \right. \\ &\quad \left. + \sum_{p < q < r < s=4} \sum_{N-1} \{m_p m_q m_r m_s\}_t \prod_{l=p,q,r,s} \sin B_l t \prod_{k \neq p,q,r,s} \cos B_k t - \dots + (i)^{N-1} \left\{ \prod_{l=1}^{N-1} m_l \right\}_t \prod_l \sin B_l t \right]. \end{aligned} \quad (39c)$$

The form of the last term is taken with N an odd number for the sake of being definite. In (39c) it is

¹⁴ R. Kubo, J. Phys. Soc. (Japan) 12, 570 (1957).

esses depend. The needed convergence factor is obtained, if one takes into account the fact that the interaction via the phonons is finite, however small. Treating that interaction in the usual approximation leads to

$$\phi(t) = e^{-t/T_2} \sum_m A(m) \cos(2t \sum_K B_{k\alpha} m_k).$$

4. RELAXATION IN THE PRESENCE OF SHORT AND VERY LONG CORRELATION TIMES

Having looked at the separate solutions for relaxation of the spin system in contact with a reservoir with short correlation times, and that for the spin system in contact only with coordinates having very long relaxation times, we study next the solution for the case where the two types of relaxation processes compete. The general solution for the density matrix follows from (5a), (15), and (25):

$$\langle m | \rho_s(t) | n \rangle = e^{-i(\omega_{mn} + \nu_{mn})t} e^{-\lambda_{mn}t} \langle m | \rho_s(0) | n \rangle. \quad (37)$$

For further discussion it will be convenient to put $\omega_{mn} = 0$, thus taking out the Larmor precession, which is irrelevant to the free relaxation, and neglecting the second-order perturbation corrections μ_{mn} to the dominant frequencies ν_{mn} . It is convenient to regard $Z(t)$, the quantity already introduced in Eq. (23), as an ordinary partition function. Then for any function $A(m)$ of the m_j , the corresponding expectation value is indicated by braces:

$$\{A\}_t \equiv \sum_m A(m) \exp(-16 \sum_{q \neq p} K_{p\alpha q} \alpha(0) m_q m_p t) / Z(t). \quad (38)$$

For the initial density matrix (19) one then finds

$$\langle \sigma_z^\alpha \rangle_t = (\tanh a / 2^{N-1}) e^{-t/T_2} Z(t) \{ \cos(t \sum_j B_{j\alpha} m_j) \}_t, \quad (39a)$$

where T_2 is defined by (22). An alternative form is

$$\langle \sigma_z^\alpha \rangle_t = (\tanh a / 2^{N-1}) e^{-t/T_2} Z(t) \text{Re} \left\{ \prod_{j=1}^N e^{im_j B_{j\alpha} t} \right\}_t, \quad (39b)$$

where Re means "the real part of." If in (39b) one writes $e^{im_j B_{j\alpha} t} = \cos B_{j\alpha} t + im_j \sin B_{j\alpha} t$, and carries out the indicated product, one obtains the series

understood that in all the sums and products the particular spin α is excluded; also the simplified notation $B_k \equiv B_{k\alpha}$ is used. The quantities $Z(t) \{ \dots \}_t$ occurring in (39c) can be expressed in terms of the deriva-

tives of the partition function. Let $\tau_{lk} \equiv -16tK_{ak\alpha}(0)$, then

$$Z(t)\{m_s m_r\}_t = \partial Z / \partial \tau_{sr},$$

$$Z(t)\{m_p m_q m_r m_s\}_t = \partial^2 Z / \partial \tau_{pq} \partial \tau_{rs}, \text{ etc.}$$

Just as in (21), the completely explicit calculation hinges on evaluating the partition function (38).

From Eqs. (39a)–(39c) the following is noted: (i) It is evident from (39a) that the earlier solution (21) with $H=0$ provides at all times an upper limit to the polarization $\langle \sigma_z^\alpha \rangle_t$. Evidently, the rigid-lattice interaction can hasten, but not retard, the approach to equilibrium. (ii) The first term in the $[\dots]$ in (39c) gives just the product of the short correlation time solution (21) with the long correlation time solution (32). All the other terms vanish unless there are pairs of spins (s,r) for which $B_{s\alpha} \neq 0$, $B_{r\alpha} \neq 0$, and simultaneously $K_{r\alpha, s\alpha}^{(0)} \neq 0$. They may thus be interpreted as interference terms between the two types of relaxation processes occurring simultaneously.¹⁵

The higher order terms of the form, e.g.,

$$\{m_p m_q m_r m_s m_u m_v\}_t \prod_{l=p,q,r,s,u,v} \sin B_{l\alpha} t$$

will contribute only if the nucleus α interacts directly with each of the nuclei (p,q,r,s,u,v) , and each of m_i in the $\{ \}$ is connected with at least one of the other m_j in the $\{ \}$ via a nonvanishing $K_{i\alpha j\alpha}(0)$. Otherwise the term will contain a factor $\{m_i\}_t$ which equals zero. If a nucleus in a solid or very large molecule is within range of the direct interaction of only very few other magnetic nuclei, the series in (39c) breaks off after a few terms. (iii) The initial state used in (39) is such that at $t=0$ all the interference terms vanish; both the $\sin B_k t$ factors, as well as the $\{ \dots \}$ coefficients vanish.

Which of the two competing relaxation processes described in (37) to (39) will predominate depends on the numerical magnitude of the $B_{j\alpha}$ and the $K_{q\alpha, p\alpha}(0)$. Of course, the limiting case $K_{q\alpha, p\alpha}(0) \rightarrow 0$ corresponds to the Lowe-Norberg oscillatory solution, and the opposite limit $B_{j\alpha} \rightarrow 0$ gives the exponentially decaying solution. Generally, the condition that the solution show no oscillations is a complicated one; but for the case $K_{q\alpha, p\alpha}(0) = \delta_{pq} K_{q\alpha, q\alpha}(0)$, no oscillations can occur if

$$B_0 T_2 \ll 1. \quad (40)$$

Here B_0 is the largest of all the $B_{j\alpha}$. Equation (40) states that the solution is strongly damped before oscillations have begun. A sufficient, but probably too stringent, condition in the general case is that

$$B_0 \ll 8\pi \sum_q \sum_p K_{p\alpha q\alpha}(0) m_p m_q \quad (41)$$

for all m_p and m_q .

¹⁵ Another interference effect between relaxation via two mechanisms has been noted by Yoshimori and Korrington, Ref. 9.

If the opposite conditions from (40) or (41) are satisfied (with \gg instead of \ll), the behavior of $\langle \sigma_z^\alpha \rangle_t$ is predominantly determined by the rigid-lattice solution, except for very long times.

5. REMARKS

We have shown that the transverse relaxation of an Ising (or truncated dipolar) spin system with lattice interaction can be solved by elementary means, provided it is possible to divide the coefficients of the interaction into those that are practically constant, and those having correlation times short compared to relaxation times. The result is not completely simplified, but involves a sum over states formally very similar to the sum over states in the corresponding thermal equilibrium problem. The particular simplifying feature in treating transverse relaxation is that the Zeeman energy of the system is a constant of the motion. In a corresponding treatment of longitudinal relaxation,¹⁶ and the interesting case of time dependence through a phase transition, this simplifying feature would have to be abandoned. However, the other simplifying feature, the possibility of separating correlation times into short ones and long ones, is a feature applicable to many physical relaxation problems. This separation is a useful one, because the mathematical methods suited to treating the two regimes are very different.

The present model yields a simple picture of the origin of oscillations in the approach to equilibrium: The subsystem involving long correlation times evolves in an oscillatory way; the dissipative effect of the subsystem with short correlation times acts too slowly to damp out the oscillations before several maxima and minima have occurred. This picture does not seem to depend on the particular model, except, again, the requirement that the "lattice" may be divided into one subsystem with short correlation times, and another with only long correlation times.

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¹⁶ A model for longitudinal relaxation in one dimension has been studied by R. Glauber, J. Math. Phys. 4, 294 (1963).