N W 37

PR–3–10—36 Gal. 1 8 on 10 No. 31EFG Spickie

Irreversibility in Paramagnetic Spin Systems: Free Induction Decay and Spin Diffusion

P. BORCKMANS* AND D. WALGRAEF†
Université Libre, Brussels, Belgium

(Received 20 September 1967)

In a recent work, the authors derived kinetic equations for the spin autocorrelation function for a paramagnetic spin system using the resummation procedure introduced by Résibois and De Leener in the framework of the statistical mechanics of irreversible processes due to Prigogine and co-workers. These equations are non-Markovian and nonlinear in the high-field, high-temperature, and Weiss-limit approximations. In the present paper, methods of approximation are given to solve such kinetic equations and are applied to the study of two important NMR problems, namely, free induction decay (FID) and spin diffuison. The general characteristics of the FID are obtained even in the lowest order of approximation owing to the resummation procedure, whereas the next higher-order correction leads to very good agreement with the experimental results given by Barnaal and Lowe. The following asymptotic form is also derived:

$$\Gamma(t) = (a\cos\alpha t + b\sin\alpha t)e^{-\beta t}.$$

A diffusion equation is obtained for the magnetization. From this the diffusion coefficient is computed and is found to be in agreement with that proposed by several authors. However, consideration of higher-order corrections does not seem to explain the strong dependence on the orientation of the external magnetic field which was observed experimentally by Leppelmeier.

* Aspirant au Fonds National Belge de la Recherche Scientifique.

† Aspirant au Fonds National Belge de la Recherche Scientifique.

[1] P. Borckmans and D. Walgraef, Physica **35**, 80 (1967).

[2] P. Resibois and M. De Leener, Phys. Rev. **151**, 305 (1966).

[3] M. De Leener and P. Resibois, Phys. Rev. **151**, 318 (1966).

[4] I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962).

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

[6] N. Bloembergen, Physica **15**, 386 (1949).

[7] S. Gade and I. J. Lowe, Phys. Rev. **156**, 817 (1967).

[8] G. W. Leppelmeier, Proceedings of the International Conference on Magnetic Resonance and Relaxation (Fourteenth Colloque Ampere, held in Ljubljana, 1966) (to be published).

[9] I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

[10] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England 1960), Chap. 4, p. 119.

[11] S. Clough and I. R. McDonald, Proc. Phys. Soc. (London) **86**, 833 (1965).

[12] W. A. B. Evans and J. G. Powles, Phys. Letters **24A**, 218 (1967).

[13] A. J. Tjon, Phys. Rev. **143**, 259 (1966).

[14] P. Mansfield, Phys. Rev. **151**, 199 (1966).

[15] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

[16] In the case of an additional strongly coupled perturbation term, such a procedure leads to an exponential decay because of the appearance of a second characteristic time in the problem which permits the definition of a Markovian domain. An example is the strong exchange term in the Hamiltonian of several metals (Pt^{195}, Na^{23},...). P. Resibois, P. Borckmans, and D. Walgraef, Phys. Rev. Letters **17**, 1290 (1966).

[17] M. Abramovitz and J. A. Stegun, *Handbook of Mathematical Functions* (Dover Publications, Inc., New York, 1965).

[18] D. E. Barnaal and I. J. Lowe, Phys. Rev. **148**, 328 (1966).

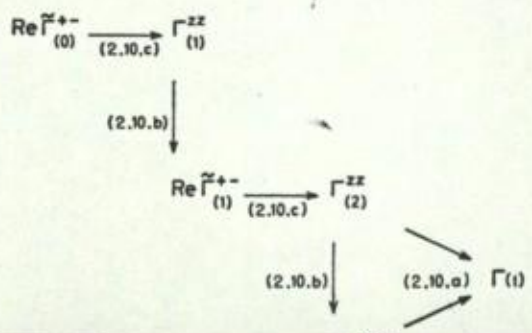
[19] L. L. Buishvili and D. N. Zubarev, Fiz. Trevd. Tela **7**, 722 (1965) [English transl.: Soviet Phys.—Solid State **7**, 580 (1965)].

TABLE I. Second-order diffusion constants. $D_{||}$: parallel to the external magnetic field (h); $D_{\perp}$: perpendicular to the external magnetic field; $D_{eff}=\frac{1}{3}(D_{xx}+D_{yy}+D_{zz})$. Units are 10^{-13} cm²/sec)

h	$D_{||}^{(2)}$	$D_{\perp}^{(2)}$	$D_{eff}^{(2)}$
[100]	6.98	2.38	3.93
[110]	4.52	3.36	3.75
[111]	4.98	3.59	3.86

TABLE II. Lattice sums.

	[100]	[110]	[111]
$\Sigma_j a_{ij}^3$	13.356	5.062	2.287
$\Sigma_j a_{ij}^4$	36.081	2.797	0.235
$\Sigma_j a_{ij}^3 x_{ij}^3$	10.486	3.472	2.583
$\Sigma_j a_{ij}^3 y_{ij}^3$	3.584	3.472	2.583
$\Sigma_j a_{ij}^3 z_{ij}^3$	3.584	3.275	2.583
$\Sigma_j a_{ij}^4 x_{ij}^3$	32.048	0.675	0.174
$\Sigma_j a_{ij}^4 y_{ij}^3$	2.071	0.675	0.174
$\Sigma_j a_{ij}^4 z_{ij}^3$	2.071	2.015	0.174
$\Sigma_j a_{ij}^3 x_{ij} y_{ij}$	0	1.275	0.580
$\Sigma_j a_{ij}^3 y_{ij} z_{ij}$	0	0	0.580
$\Sigma_j a_{ij}^3 z_{ij} x_{ij}$	0	0	0.580
$\Sigma_j a_{ij}^4 x_{ij} y_{ij}$	0	0.475	0.045
$\Sigma_j a_{ij}^4 y_{ij} z_{ij}$	0	0	0.045
$\Sigma_j a_{ij}^4 z_{ij} x_{ij}$	0	0	0.045



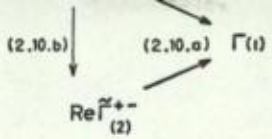


FIG. 1. The iteration process.

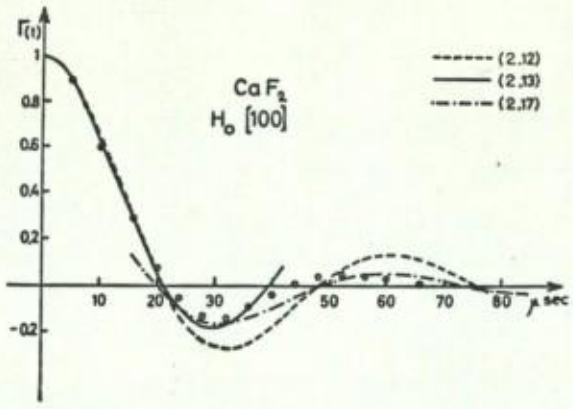


FIG. 2. The free induction decay in CaF_2 as given by the theory. The circles represent the experimental results of Narnaal and Lowe (Ref. 18).

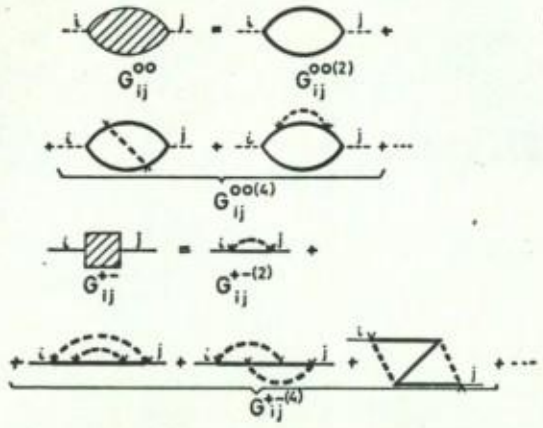


FIG. 3. Graphical representation of the kernels up to fourth order. The V signs represent either longitudinal or transverse vertices, but the "self-energy" type of contrigutiohs must be discarded because they are already included through the resummation procedure (heavy lines).

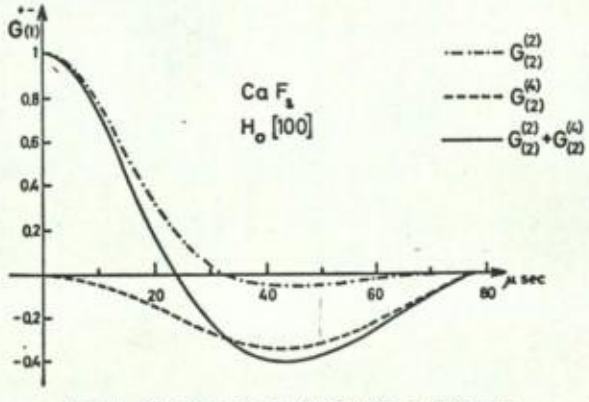


FIG. 4. The Kernels $G_{(1)}{}^{(2)}$, $G_{(1)}{}^{(4)}$ and their sum.

1. INTRODUCTION

IN a recent work[1] (hereafter I), the authors derived kinetic equations for the two-spin autocorrelation functions in the case of paramagnetism in the high-field, high-temperature approximations. The method used was an extension of that of Résibois and De Leener[2,3] (hereafter RDL), based on the general theory of non-equilibrium statistical mechanics developed by Prigogine and co-workers.[4] They treated the case of a Heisenberg spin system by reorganizing the perturbation expansion of the spin autocorrelation function so that the final equations involve only quantities which are meaningful for all times, short and long. In the case of paramagnetism, the equations obtained are (with the notation of I)

$$\partial_t \Gamma_{ab}{}^{zz}(t) = \int_0^t dt' \sum G_{aj}{}^{00}(t-t' \mid \{\Gamma^{\alpha\beta}\})\, \Gamma_{jb}{}^{zz}(t'), \quad (1.1)$$

$$\partial_t \Gamma_{ab}{}^{+-}(t) = \int_0^t dt' \sum G_{aj}{}^{+-}(t-t' \mid \{\Gamma^{\alpha\beta}\})\, \Gamma_{jb}{}^{+-}(t')$$

$$+ \int_0^t dt' \sum_j F_{aj}{}^{+-}(t-t', \tau \mid \{\Gamma^{\alpha\beta}\})\ \mathrm{Re}\Gamma_{jb}{}^{+-}(t')$$

$$(\alpha, \beta = z, +, -) \quad (1.2)$$

The aim of the present work is to give a scheme for the solution of these equations and to thus treat two major problems in nuclear magnetic resonance, that of the shape of the free induction decay (FID) and that of spin diffusion. But let us first make the following remarks about these equations:

(1) They are non-Markovian, and there is no Markovian limit because only one characteristic time (τ_d) appears in the problem $\tau_d \simeq \omega_l^{-1}$, where ω_l is the Larmor frequency of the spins in the local field.

(2) They are nonlinear because of the functional dependence of the kernels in the $\{\Gamma^{\alpha\beta}\}$. This dependence ensures that

$$\lim_{t\to\infty} G_{ij}{}^{\alpha\beta}(t \mid \{\Gamma^{\alpha\beta}\}) \to 0,$$

since the $\{\Gamma^{\alpha\beta}\}$ themselves tend to zero for long times.

(3) Applying the rules of I, the kernels may be written formally as

$$G_{ij}{}^{\alpha\beta}(t \mid \{\Gamma^{\alpha\beta}\}) = \sum_{n=1}^{\infty} \lambda^{2n} G_{ij}{}^{\alpha\beta(2n)}(t \mid \{\Gamma^{\alpha\beta}\}), \quad (1.3)$$

which is an expansion in the number n of the λ factors (measuring the strength of the dipole-dipole interaction) that appear *explicitly* in (1.3). However, we must remark that the *implicit* λ behavior due to the functional dependence in the $\{\Gamma^{\alpha\beta}\}$ is complicated. The successive terms in (1.3) correspond respectively to the renormalized two-, three-, $\cdots$, n-spins problems. Although there exist numerous intuitive arguments for it, the convergence of the problem has not yet been rigorously proved. The kernels calculated using the rules given in I consist of an infinite series of terms. We thus need approximations in order to get explicit expressions for the autocorrelation functions. In the short-time approximation, the functions are expanded in powers of the time, and they are given by their first few derivatives at $t=0$. In order to obtain a result valid for short and long times, the systems of Eqs. (1.1) and (1.2) can be solved numerically. This has been done with an approximate kernel containing the first two terms of the series

N-E-58

mation, the functions are expanded in powers of the time, and they are given by their first few derivatives at $t=0$. In order to obtain a result valid for short and long times, the systems of Eqs. (1.1) and (1.2) can be solved numerically. This has been done with an approximate kernel containing the first two terms of the series (1.3). The asymptotic solution can be obtained to the same approximation by using the Laplace transforms of the equations and the properties of the poles of the transformed autocorrelation functions. These methods give the time dependence of the autocorrelation functions from time $t=0$ to long times.

In the case of the free induction decay, the signal is proportional to $\Gamma(t)=\sum_{ij}\mathrm{Re}\Gamma_{ij}^{+-}(t)$, and the theory gives satisfactory results: (a) The second and the fourth moments are the same as those calculated by Van Vleck (in the Weiss limit).[5] (b) The damped oscillations of the signal are obtained even in the lowest order of approximation. This fact is due to the resummation of the perturbation scheme. (c) The predicted asymptotic form of the signal is given by

$$(a\cos\alpha t+b\sin\alpha t)e^{-\beta t} \qquad (\beta>0), \qquad (1.4)$$

where α, β, a, and b are constants that have been computed. (d) The agreement between the theoretical curve and the experimental one is good.

The part of the spin autocorrelation function which gives the hydrodynamical ($t\to\infty$, $r\to\infty$) behavior of the system leads to a description of spin diffusion. However, in this situation, if we speak in terms of conventional perturbation theory, the behavior of the system is dominated by frequent collisions, and to describe this we must make an extensive resummation of diagrams, and this is precisely the essence of the method we use. This resummation, at any rate, is necessary in a spin system in order to obtain a dissipation process. As pointed out by RDL, the Fourier transform $\Gamma_q(t)$ of $\Gamma_{ab}^{zz}(t)$ obeys a diffusion equation for $t\to\infty$ and $q\to\infty$. In our case, this allows us to calculate a diffusion coefficient for the magnetization of the system. This coefficient is in the lowest order of approximation, in good agreement with that calculated by several authors,[6-8] but the corrections due to higher orders of approximation do not yet seem to give a good agreement with the experimental results of Leppelmeier.[8]

In Sec. 2, the problem of free induction decay is treated, and the time dependence of the signal is given, both for short and long times. We compare our results with experimental data. In Sec. 3, the calculation of the diffusion coefficient for the magnetization is given to the second order of approximation. Fourth-order corrections are considered. The numerical calculations were made for a crystal of CaF_2, with the external field applied along the [100] direction. The kernels we use and the various lattice sums that have been calculated are given in the Appendix.

2. FREE INDUCTION DECAY

A. Statement of the Problem

An important problem in the theory of nuclear magnetic resonance in solids is the theoretical predic-

tion of the relaxation function $\Gamma(t)$, which describes the decay of the transverse magnetization. Although many authors have proposed solutions to this problem, none seems completely satisfactory. The first contribution was that of Van Vleck,[8] who calculated the lowest-order moments and showed that in the high-temperatrue approximation the odd moments vanish. However, the convergence of such a procedure is very slow, and the theory applies only near time zero. Lowe and Norberg[9] based theory theory and calculations on a series expansion of the form

$$\Gamma(t)=\sum_{n=0}^{\infty}\frac{t^n}{n!}\Gamma_n(t), \tag{2.1}$$

which is obtained by splitting the secular part of the dipolar Hamiltonian into two parts, one of which (the Ising part) is dominant for short times and can be treated exactly. Their theory describes the beats observed experimentally, and, up to fourth order, the agreement with the experimental curve is quite remarkable. Note that there are no physically clear arguments for neglecting higher-order terms, especially as their expansion diverges for long times. Abragam[10] has pointed out that such series expansion are not unique. This fact is clarified by Clough and MacDonald,[11] who obtained slightly better convergence using another expansion which generalized that of Lowe and Norberg. Very recently, Evans and Powles,[12] using a Dyson-type expansion, have also obtained good agreement with experiment.

Other theories have been developed and are based on the quantum statistical mechanics of nonequilibrium. Tjon,[13] who also split up the Hamiltonian, obtained an integro-differential equation

$$\partial_t\Gamma(t)=\int_0^t d\tau\,\alpha(\tau)\,\Gamma(-\tau), \tag{2.2}$$

where $\alpha(\tau)$ is an infinite-order series. But in order to solve this equation, he introduced the standard Gaussian approximation into the kernel, so that $\alpha(\tau)=A\exp(-B\tau^2)$, where the constants A and B can be so adjusted as to give very good agreement with experiment. On the other hand, Mansfield,[14] using the retarded Green's-function method[15] and a frequency-dependent decoupling approximation based on a physically intuitive approach, has also obtained satisfactory agreement with experiment.

In the present work, we do not, as most authors did, separate the secular dipolar Hamiltonian into two parts. The reason for this is that, although such a separation is formally possible, it may not serve as a basis for a perturbation calculation (because both parts are of the same order of magnitude), unless one retains all the terms of the expansion.[16] So, in order to obtain a meaningful result for long times, we are led to introduce a resummation procedure. We then obtain, even in the lowest order of approximation, the principal features of the line shape (damped oscillations).

B. Calculation of the Free-Induction-Decay Shape

The form of the signal is given by

$$\mathrm{Tr}\{S_x(t)\,S_x(0)\} \tag{2.3}$$

or

$$\Gamma(t)\tfrac{1}{2}(N\cos\omega_0 t), \tag{2.4}$$

where

$$\Gamma(t)=[\mathrm{Re}\Gamma_{++}(t)+\sum\mathrm{Re}\Gamma_{+-}(t)] \tag{2.5}$$

WG 26

$$\Gamma(t)=\lfloor \mathrm{Re}\,\Gamma^{+-}(t)+\sum_{j\neq i}\mathrm{Re}\,\Gamma_{ij}^{+-}(t)\rfloor_{T=\infty}. \quad (2.5)$$

The time evolution of the envelope $\Gamma(t)$ is given by the equation

$$\partial_t\Gamma(t)=\int_0^t dt'\sum_k G_{ik}^{+-}(t-t'\mid\{\Gamma^{\alpha\beta}\})\Gamma(t'), \quad (2.6)$$

with

$$\partial_t\,\mathrm{Re}\Gamma^{+-}(t)=\int_0^t dt'\,G_{ii}^{+-}(t-t'\mid\{\Gamma^{\alpha\beta}\})\,\mathrm{Re}\Gamma^{+-}(t')\Big| \quad (2.7a)$$

and

$$\partial_t\Gamma^{zz}(t)=\int_0^t dt'\,G_{ii}^{00}(t-t'\mid\{\Gamma^{\alpha\beta}\})\Gamma^{zz}(t'), \quad (2.7b)$$

where Γ and the $\{\Gamma^{\alpha\beta}\}$ are normalized. The kernels in the second and fourth order of approximation are given in the Appendix.

Short-Time Behavior

In this case, the curve is given by its moments, the first of which are calculated to be

$$M_2=-\tfrac{9}{16}\sum_j A_{ij}^2,$$

$$M_4=81/(16)^2$$
$$\times[3(\sum_j A_{ij}^2)^2-(3N)^{-1}\sum_{ijk\neq} A_{ij}^2(A_{jk}-A_{ik})^2-\sum_j A_{ij}^4]. \quad (2.8)$$

Comparison with Van Vleck's results shows that, whereas the second moments are identical, the fourth moments differ only by terms of the order of N_{eff}^{-1} (where N_{eff} is the number of effectively interacting spins; we recall that the terms of this order are neglected in this theory).

Long-Time Behavior

In order to solve the system (2.6), (2.7), where (a) and (b) are coupled nonlinear and non-Markovian integro-differential equations, we use a numerical method, because analytical forms of these functions cannot be obtained. This method is based on an iterative process and a Runge-Kutta type of solution.

In the second-order approximation, the system (2.6), (2.7) becomes

$$\partial_t\Gamma(t)=-\tfrac{9}{16}\sum_j A_{ij}^2\int_0^t dt'\,\Gamma^{zz}(t-t')\,\mathrm{Re}\Gamma^{+-}(t-t')\Gamma(t'),$$

$$\partial_t\,\mathrm{Re}\Gamma^{+-}(t)=-\tfrac{5}{16}\sum_j A_{ij}^2\int_0^t dt'\,\Gamma^{zz}(t-t')\,\mathrm{Re}\Gamma^{+-}(t-t')\,\mathrm{Re}\Gamma^{+-}(t'),$$

$$\partial_t\Gamma^{zz}(t)=-\tfrac{1}{8}\sum_j A_{ij}^2\int_0^t dt'\,[\mathrm{Re}\Gamma^{+-}(t-t')]^2\Gamma^{zz}(t'). \quad (2.9)$$

To solve this system, we use an iteration process (see Fig. 1). The successive linear approximations of (2.9) are the following:

$$\partial_t\Gamma_{(n)}(t)=-\tfrac{9}{16}\sum_j A_{ij}^2\int_0^t dt'\,\Gamma_{(n)}^{zz}(t-t')\,\mathrm{Re}\Gamma_{(n)}^{+-}(t-t')\Gamma_{(n)}(t'), \quad (2.10a)$$

$$\partial_t\,\mathrm{Re}\Gamma_{(n)}^{+-}(t)=-\tfrac{5}{16}\sum_j A_{ij}^2\int_0^t dt'\,\Gamma_{(n)}^{zz}(t-t')\,\mathrm{Re}\Gamma_{(n-1)}^{+-}(t-t')\,\mathrm{Re}\Gamma_{(n)}^{+-}(t'), \quad (2.10b)$$

$$\partial_t\Gamma_{(n)}^{zz}(t)=-\tfrac{1}{8}\sum A_{ij}^2\int^t dt'\,[\mathrm{Re}\Gamma_{(n-1)}^{+-}(t-t')]^2\Gamma_{(n)}^{zz}(t'), \quad (2.10c)$$

and for $n\to\infty$, the solutions of (2.9) and (2.10) are the same. In order to start the iteration process, we choose $\mathrm{Re}\tilde{\Gamma}_{(0)}{}^{+-}(t)$. This choice is of course arbitrary, but we take a function which already possesses the characteristics of $\mathrm{Re}\tilde{\Gamma}^{+-}(t)$ itself, in order to obtain a good approximation even if we iterate only to small n. The calculation of the moments of $\mathrm{Re}\tilde{\Gamma}^{+-}(t)$ gives

$$M_4/3M_2{}^2=1.23.$$

It thus appears that the usual Gaussian assumption is not appropriate, and we use the empirical form which takes into account the Gaussian decrease and the oscillations of the curve[11]:

$$\mathrm{Re}\tilde{\Gamma}_{(0)}{}^{+-}(t)=\exp(-a^2t^2)\,(\sin bt/bt), \quad (2.11)$$

where $a^2=3.801$ and $b=3.195$, a and b being calculated by fitting the second and fourth moments of $\mathrm{Re}\tilde{\Gamma}^{+-}(t)$ to (2.11). With this function we perform the iteration process up to $n=2$, and the solution of the equation

$$\partial_t\Gamma(t) = -\tfrac{9}{16}\sum_j A_{ij}{}^2\int_0^t dt'\;\Gamma_{(2)}{}^{zz}(t-t')\;\mathrm{Re}\tilde{\Gamma}_{(2)}{}^{+-}(t-t')\,\Gamma(t'), \quad (2.12)$$

obtained on an IBM 7040 computer, is given in Fig. 2. We have also computed a fourth-order correction by taking into account the equation

$$\partial_t\Gamma(t) = -\tfrac{9}{16}\sum_j A_{ij}{}^2 \times\int_0^t dt'\;\Gamma_{(2)}{}^{zz}(t-t')\;\mathrm{Re}\tilde{\Gamma}_{(2)}{}^{+-}(t-t')\,\Gamma(t') + \int_0^t dt'\;G_{(2)}{}^{(4)}(t-t')\,\Gamma(t'), \quad (2.13)$$

where $G_{(2)}{}^{(4)}$ is given in the Appendix and consists of double integrals over the products of $\Gamma_{(2)}{}^{zz}$ and $\mathrm{Re}\tilde{\Gamma}_{(2)}{}^{+-}$ The solution of (2.13) is also plotted in Fig. 2.

Asymptotic Behavior

It is also possible to obtain $\Gamma(t)$ for very long times by taking the Laplace transform of (2.6):

$$\tilde{\Gamma}(S)=\Gamma(0)/[S+G(S)], \quad (2.14)$$

where $G(S)$ is the transform of the kernel. With the usual Gaussian approximation, we obtain

$$G(S)=5.12w(iS/4.49), \quad (2.15)$$

where

$$w(z)=e^{-z^2}\,\mathrm{erfc}(iz). \quad (2.16)$$

The inversion of (2.14) for very long times can be obtained by determining numerically the poles of $\tilde{\Gamma}(S)$ closest to the imaginary axis. Using tables for the complex error function[17] and taking into account the properties of $w(z)$, we find

$$S_\pm=-S'\pm iS'',$$

with $S'=1.40\pm0.01$ and $S''=4.53\pm0.01$.

Applying the residue theorem, and because the next poles are sufficiently far from the imaginary axis ($S'>2\pi$) to be neglected for $t\to\infty$, we have by Laplace inversion

$$\Gamma_{t\to\infty}(t)=[0.388\cos0.113t+0.314\sin0.113t]e^{-0.035t},$$

N-E-59

inversion

$$\Gamma_{t\to\infty}(t)=[0.388\cos 0.113t+0.314\sin 0.113t]e^{-0.035t}, \tag{2.17}$$

where t is in microseconds. This result is also drawn in Fig. 2. It should be noted that the Gaussian assumption was made in order to simplify the calculations, and that another type of approximation would not destroy the oscillations or the exponential decrease of the curve.

C. Conclusions

It can be seen from Fig. 2 that the second-order approximation gives the main features of the curve and that it is qualitatively correct. The fourth order, as expected, changes the behavior for longer times and is in good agreement with the experimental curve[18] up to the second zero. For still longer times, the numerical method we have used becomes innacurate, so that results are no longer significant. It is believed that an equation of the form

$$\partial_t\Gamma(t)=\int_0^t dt'\,[G^{(2)}(t-t')+G^{(4)}(t-t')]\Gamma(t'), \tag{2.18}$$

with renormalizations calculated from (2.7) by taking the fourth-order kernels into account, would give better agreement. We feel confident about the convergence of the expansion, even though there exists no mathematical proof; the next-higher contribution behaves like t^6 for short times and will thus not influence the preceding terms, while for long times, the higher-order terms of the kernels will depend on more and more $\{\Gamma^{\alpha\beta}\}$ factors and will thus decrease very rapidly. To conclude, let us recall that our theory is able to predict the asymptotic form of $\Gamma(t)$.

3. SPIN DIFFUSION

Spin diffusion is the transport of Zeeman energy or magnetization via the dipole-dipole interactions and has been proved important both theoretically and experimentally in the establishment of a spin equilibrium in many relaxation processes. The first to recognize the importance of such processes was Bloembergen, who was also the first to propose a simple model to compute a diffusion coefficient.[6] Using first-order perturbation theory, he obtained a diffusion equation for the magnetization. However, his arguments are mainly phenomenological. Important steps towards a more sophisticated theory were made by Leppelmeier[8] and by Gade and Lowe,[9] who considered an inhomogeneous distribution of magnetization, but who had to introduce an important hypothesis about the time evolution of the density matrix of the system. Buishvili and Zubarev[19] obtained a diffusion equation for the magnetization by means of the statistical theory of irreversible processes. All these authors have obtained similar expressions for the diffusion coefficient, differing only by numerical constants; but no one has been able to explain the strong dependence of this constant on the orientation of the magnetic field relative to the crystal axis which was experimentally observed by Leppelmeier.[8]

It has been shown in I that the Fourier transform of the magnetization correlation function obeys the following equations:

$$\partial_t \Gamma_0(t) = -\int_0^t dt' \, \tilde{G}_0^{00}(t' \mid \{\Gamma^{\alpha\beta}\}) \, \Gamma_0(t-t'),$$

$$\partial_t \Gamma_q(t) = \int_0^t dt' \, [\tilde{G}_q^{00}(t' \mid \{\Gamma^{\alpha\beta}\}) - \tilde{G}_0^{00}(t' \mid \{\Gamma^{\alpha\beta}\})] \Gamma_q(t-t'), \tag{3.1}$$

where

$$\Gamma_q(t) = \sum_j \Gamma_{ij}^{zz} \exp(i_q \cdot r_{ij}), \tag{3.2}$$

and

$$\tilde{G}_q^{00} = \sum_{j(\neq i)} G_{ij}^{00} \exp(iq \cdot r_{ij}). \tag{3.3}$$

It can easily be shown that

$$\lim_{|q| \to 0} [G_q^{00}(t \mid \{\Gamma^{\alpha\beta}\}) - G_0^{00}(t \mid \{\Gamma^{\alpha\beta}\})] \sim - \mid q \mid^2. \tag{3.4}$$

In the limit $\mid q \mid \to 0$, we recover a relaxation time $\tau_d \mid q \mid^{-2}$, which is much longer than the dissipation time τ_d. We may then write

$$\partial_t \Gamma_q(t) \simeq \left\{ \int_0^\infty dt' \, [G_q^{00}(t' \mid \{\Gamma^{\alpha\beta}\}) - \tilde{G}_0^{00}(t' \mid \{\Gamma^{\alpha\beta}\})] \Gamma_q(t) \right\}. + O(q^4), \tag{3.5}$$

which is a diffusion equation

$$\partial_t \Gamma_q(t) = -\sum_{\alpha\alpha'} q_\alpha q_{\alpha'} D_{\alpha\alpha'} \Gamma_q(t), \quad (\alpha, \alpha' = x, y, z) \tag{3.6}$$

where

$$D_{\alpha\alpha'} = -\frac{1}{2} \left[\frac{\partial^2}{\partial q_\alpha \partial q_{\alpha'}} \int_0^\infty dt' \, \tilde{G}_q^{00}(t \mid \{\Gamma^{\alpha\beta}\}) \right]_{|q| \to 0}. \tag{3.7}$$

Again using the Gaussian assumption in order to simplify the calculations, we obtain in the second-order approximation

$$D_{\alpha\alpha'} = \tfrac{1}{8} (\pi / 5 \sum_{j \neq i} A_{ij}^2)^{1/2} \sum_{j(\neq i)} A_{ij}^2 (r_\alpha)_{ij} (r_{\alpha'})_{ij}. \tag{3.8}$$

This result is similar to the ones obtained by different authors.[6–8,19] The first steps toward the evaluation of the fourth-order correction have been taken, and it may easily be seen that the terms are of the type

$$\sum_j A_{ij}^4 (r_\alpha)_{ij} (r_{\alpha'})_{ij},$$

$$\sum_j \sum_s A_{ij}^2 A_{is} A_{js} (r_\alpha)_{ij} (r_{\alpha'})_{ij},$$

and

$$\sum_j \sum_s A_{ij}^2 A_{is}^2 (r_\alpha)_{ij} (r_{\alpha'})_{ij}.$$

A first evaluation of this correction does not seem to give the important variation with orientation which was experimentally observed by Leppelmeier.[8] Nevertheless, no definite conclusions can be drawn, and complementary calculations have been undertaken. Numerical results are given in Table I.

ACKNOWLEDGMENTS

We wish to thank Professor J. Philippot for his constant cooperation, Professor I. Prigogine for his en-

NE-60

We wish to thank Professor J. Philippot for his constant cooperation, Professor I. Prigogine for his encouragement, and Professor J. Jeener and Professor P. Résibois for many fruitful discussions. We would also like to thank Mrs. M. Delchambre for introducing us to computer work.

APPENDIX: KERNELS AND LATTICE SUMS

The kernels $G_{ij}^{\alpha\beta}(t\,|\,\{\Gamma^{\alpha\beta}\})$ are given by an infinite series of terms, these terms being associated with the so-called "renormalized basic irreducible skeleton graphs." The first graphs of this series are given in Fig. 3.

Using the calculation rules given in I, we obtain in the infinite temperature approximation

$$G_{ij}^{00(2)}=\tfrac{1}{8}A_{ij}^2\,\mathrm{Re}\Gamma^{+-}-\mathrm{Re}\Gamma^{+-}, \tag{A1}$$

$$G_{ij}^{00(4)}=-1/(2\times 4^3)\Big[\sum_s A_{is}^2A_{js}^2-8\sum_s A_{ij}^2A_{is}A_{js}\Big]\phi_s, \tag{A2}$$

$$G_{ii}^{00}=-\sum_{j(\neq i)}G_{ij}^{00}, \tag{A3}$$

$$G_{ij}^{+-(2)}=-\tfrac{1}{4}A_{ij}^2\,\mathrm{Re}\Gamma^{+-}\Gamma^{zz}, \tag{A4}'$$

$$G_{ii}^{+-(2)}=-\tfrac{5}{16}\sum_j A_{ij}^2\,\mathrm{Re}\Gamma^{+-}\Gamma^{zz}, \tag{A5}$$

$$\begin{aligned}G^{+-(4)}&=\sum_j G_{ij}^{+-(4)}\\&=\Big[18\sum_{j,k}A_{ij}^2A_{jk}^2+(37/2)\sum_{j,k}A_{ij}^2A_{ik}A_{kj}\Big]\phi_A\\&\quad+18\sum_{j,k}A_{ij}^2A_{jk}A_{ik}\phi_B\\&\quad+\Big[\tfrac{1}{2}\sum_{j,k}A_{ik}^2A_{ij}^2-(19/2)\sum_{j,k}A_{ij}^2A_{ik}A_{kj}\Big]\phi_C,\end{aligned} \tag{A6}$$

where

$$\begin{aligned}\phi_S(t)&=(1/64)\int_0^t dt'\int_0^{t'}dt''\,\mathrm{Re}\Gamma^{+-}(t-t')\\&\quad\times\mathrm{Re}\Gamma^{+-}(t-t'')\,\mathrm{Re}\Gamma^{+-}(t')\,\mathrm{Re}\Gamma^{+-}(t'')\Gamma^{zz}(t-t''),\\\phi_A(t)&=(1/128)\int_0^t dt'\int_0^{t'}dt''\,\mathrm{Re}\Gamma^{+-}(t-t')\\&\quad\times\mathrm{Re}\Gamma^{+-}(t'-t'')\,\mathrm{Re}\Gamma^{+-}(t'')\Gamma^{zz}(t')\Gamma^{zz}(t'-t''),\\\phi_B(t)&=(1/128)\int_0^t dt'\int_0^{t'}dt''\,\mathrm{Re}\Gamma^{+-}(t-t')\\&\quad\times\mathrm{Re}\Gamma^{+-}(t'-t'')\,\mathrm{Re}\Gamma^{+-}(t')'\Gamma^{zz}(t)\Gamma^{zz}(t-t''),\\\phi_C(t)&=(1/128)\int_0^t dt'\int_0^{t'}dt''\,\mathrm{Re}\Gamma^{+-}(t-t')\\&\quad\times\mathrm{Re}\Gamma^{+-}(t'-t'')\,\mathrm{Re}\Gamma^{+-}(t'')\Gamma^{zz}(t)\Gamma^{zz}(t'').\end{aligned} \tag{A7}$$

In Sec. 2, we have used the notation $G_{(2)}{}^{+-(2)}$ and $G_{(2)}{}^{+-(4)}$, which respectively represent $G^{+-(2)}$ and $G^{+-(4)}$ renormalized by $\Gamma_{(2)}{}^{zz}$ and $\mathrm{Re}\Gamma_{(2)}{}^{+-}$. The two two former kernels are given in Fig. 4 with their sum. We have also computed various lattice sums in the three orientations [100], [110], and [111] for CaF_2; they are given in Table II. It should be noted that

$$\theta_{ij}=(1-3\cos^2\theta_{ij})/|\,r_{ij}\,|^3,$$

where θ_{ij} is the angle between r_{ij} and the external field, and a_{ij} is dimensionless ($|\,r_{ij}\,|$ is given in the reduced units of the lattice). The sums are computed over the 1330 first neighbors.