Magnetic resonance in magnetically dilute solids at low temperatures

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Paramagnetic resonance is considered in magnetically dilute systems of dipole-interacting spins for arbitrary polarization and under the condition $|\beta\overline{E}| \ll 1$, where β is the reciprocal temperature of the dipole subsystem and $\overline{E}$ is the spin interaction energy at average distance. Kinetic equations are formulated for the saturation theory. The thermodynamics of a quasi-equilibrium two-temperature system and the resonance-line shape are investigated for the first time ever for a real dipole–dipole interaction. The thermodynamic study is based on a concentration expansion of the thermodynamic potential. The resonance-line shape is analyzed by a concentration expansion of the memory function and by a cumulant expansion. The thermal mixing (in a rotating coordinate frame) is determined for a system with arbitrary initial Zeeman and high-dipole initial temperatures. Analytic expressions are obtained in some limiting cases, while the intermediate regions are investigated numerically. Cooling the dipole reservoir alters greatly both the thermodynamic and the dynamic properties of the disordered spin system.

1. INTRODUCTION

The study of quantities that describe magnetic resonance in a system of dipole-interacting spins is one of the most fundamental problems of microwave spectroscopy. The need for calculating or at least estimating the line shape, the thermodynamic properties, and the rate of magnetic relaxation is encountered in practically all theories aimed at the study of multiparticle systems. Two approaches have been used mainly to estimate the linewidth and line shape in magnetically dilute substances: the method of moments and Anderson's statistical method.[1,2] The former had been strongly criticized,[3,4] and the latter,[5] after a number of generalizations, is suitable for the description of the absorption of the energy of a high-frequency magnetic field by a weak-nonequilibrium spin system in the high-temperature approximation (HTA), when $T \gg \omega_0, \omega_L$ (ω_0 is the central frequency of the magnetic resonance and ω_L is the frequency of the local field due to the dipole–dipole interactions). The thermodynamic properties and the magnetic relaxation have been well investigated in the HTA.[1,2]

Of recent interest, however, is the study of the spin systems at low temperatures down to that of magnetic ordering.[8–10] Dynamic cooling of the spin–spin interaction reservoir is used and, in accord with Provotorov's theory, the system is in a two-temperature quasi-equilibrium state. This theory, however, holds for high temperatures of both the Zeeman subsystem and the spin–spin interaction subsystem. Development of a low-temperature theory of saturation calls therefore for corresponding theories of the line shape, of the magnetic relaxation, and of the thermodynamic properties.

The line-shape statistical theory was extended to include the case of a low Zeeman temperature for spins $S = 1/2$ in Ref. 11 and for $S = 3/2$ in Ref. 12. The influence of spin-polarization effects on the phase relaxation was studied in Ref. 13. A high-temperature interaction subsystem was implied in these studies. Steps towards the development of a low-temperature saturation theory were made in Refs. 14–16, but none include an analysis of the line shape and of the thermodynamic properties of regular as well as dilute systems. A rather effective method of allowing for nonlinear effects in low-temperature thermodynamics is given in Ref. 8 (Ch. 5). Nonlinear effects in the moments of the NMR line-shape function are considered in Ref. 17. For systems with low spin density, however, this method is much less useful, since it is valid only for $\beta E_0 < 1$, where E_0 is the interaction energy of two nearest spins and β is the reciprocal dipole temperature.

We have previously developed[18] a correlation-expansion method that makes it possible to construct, in the Anderson model (i.e., with account taken of only the anisotropic part of the dipole–dipole interaction), a statistical theory of the magnetic resonance line shape (RLS) in a magnetically dilute spin system, for arbitrary cooling of the Zeeman subsystem and during that stage of dipole-subsystem cooling for which $\beta\overline{E} < 1$, where $\overline{E}$ is the spin interaction energy at average distance. A direct extension of the method to include systems with a more realistic interaction encounters many mathematical difficulties.

We consider in the present paper the case of arbitrary temperatures of a Zeeman spin subsystem and of moderately low ($\beta\overline{E} < 1$) dipole temperatures, for disordered systems with secular spin–spin interaction. Starting from a concentration expansion of the observables,[3,7,18] we have obtained convenient expressions for the thermodynamic quantities, analyzed the RLS by two methods, and investigated the solution of the ensuing equations (that describe the mixing of Zeeman and dipole subsystems by an alternating field, i.e., establishment of a single spin temperature in a rotating coordinate frame).

In the actual calculations we have confined ourselves to a spin $S = 1/2$, to an ellipsoidal sample, and to an uncorrelated distribution of the spins over the lattice sites.

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2. ABSORPTION SIGNAL FOR TWO-TEMPERATURE QUASI-EQUILIBRIUM. SATURATION-THEORY EQUATIONS

The Hamiltonian of the system considered is

$$\mathscr{H}=\mathscr{H}_z+\mathscr{H}_d+2\omega_1 S_x\cos\omega t,\qquad \mathscr{H}_z=\omega_0 S_z, \tag{1}$$

where $\mathscr{H}_d$ is the secular part of the dipole–dipole interaction Hamiltonian, $\omega_1=\gamma H_1$ (H_1 is the amplitude of the field rotating around the z axis at a frequency ω). Under quasi-equilibrium conditions the density matrix is described by the expression

$$\rho=\exp(-\beta_z\mathscr{H}_z-\beta\mathscr{H}_d)/\mathrm{Sp}\exp(-\beta_z\mathscr{H}_z-\beta\mathscr{H}_d). \tag{2}$$

The general expression for the absorption signal under these conditions, at a distance Δ from the Larmor frequency ω_0, can be represented in the linear-response approximation in the form[8]

$$\langle S_y(\Delta)\rangle=-\frac{\omega_1}{4}\int_{-\infty}^{\infty}dt\,e^{i\Delta t}\langle[S_+(t),S_-]\rangle, \tag{3}$$

where the temporal evolution is determined by the operator $\mathscr{H}_d$, and

$$S_+(t)=\exp(i\mathscr{H}_d t)S_+\exp(-i\mathscr{H}_d t).$$

An essential role in what follows is played by a transition from the commutator mean value $C(t)=\langle[S_+(t),S_-]\rangle$ to the anticommutator mean $A(t)=\langle[S_+(t),S_-]_+\rangle$. We rewrite (2) in the form

$$\rho=\exp(-\beta\tilde{\mathscr{H}})/\mathrm{Sp}\exp(-\beta\tilde{\mathscr{H}}),$$

where

$$\tilde{\mathscr{H}}=\mathscr{H}_d+\beta_z\mathscr{H}_z/\beta.$$

We change over in $S_+(t)$ to the Hamiltonian $\tilde{\mathscr{H}}$:

$$S_+(t)=\exp(-i\beta_z\omega_0 t/\beta)\exp(i\tilde{\mathscr{H}}t)S_+\exp(-i\tilde{\mathscr{H}}t).$$

We have then

$$\langle S_y(\Delta)\rangle=-\frac{\omega_1}{4}\int_{-\infty}^{\infty}dt\,\tilde{C}(t)\exp[i(\Delta-\beta_z\omega_0/\beta)t], \tag{4}$$

where $\tilde{C}(t)$ corresponds formally to total equilibrium with a temperature β^{-1} and a Hamiltonian $\tilde{\mathscr{H}}$. Using the known connection[19] between the spectral representations of the equilibrium correlation functions $\tilde{C}(t)$ and $\tilde{A}(t)$ and changing next from $\tilde{\mathscr{H}}$ to the initial Hamiltonian, we get

$$\begin{gathered}\langle S_y(\Delta)\rangle=\frac{\pi}{2}\omega_1 A(0)\,\mathrm{th}\frac{\beta_z\omega_0-\beta\Delta}{2}g(\Delta),\\ g(\Delta)=\frac{1}{2\pi A(0)}\int_{-\infty}^{\infty}dt\,A(t)\exp(i\Delta t).\end{gathered} \tag{5}$$

These relations generalize the fluctuation–dissipation theorem to include the two-temperature case. The transition from (3) to (5) is important because the function $g(\Delta)$ is non-negative for all Δ. This is proved by expressing $g(\Delta)$ in the proper representation of the Hamiltonian $\mathscr{H}_z+\mathscr{H}_d$. Thus, the absorption signal vanishes, for arbitrary subsystem temperatures, at a single point $\Delta=\beta_z\omega_0/\beta$ (a property well known in the HTA). An approximate procedure of calculating $\langle S_y(\Delta)\rangle$ must not violate this important property. It leads, in particular, to the possibility of measuring for arbitrary ratio of β and β_z by recording the zero of the absorption signal.

Expression (5) can serve as a basis for deriving, for magnetic-resonance saturation in solids, equations that generalize the Provotorov equations that are valid in the HTA to include the case of arbitrary values of β and β_z. Using the exact relation[8]

$$\frac{d}{dt}\langle S_z\rangle=\omega_1\langle S_y\rangle,$$

calculating $\langle S_z\rangle$ with the aid of (2), and assuming that the temporal evolution of the system is described by the temporal evolution of the quantities $\beta(t)$ and $\beta_z(t)$, we obtain with the aid of (5)

$$C_{zz}\frac{d\beta_z}{dt}+C_{zd}\frac{d\beta}{dt}=-\frac{\pi}{2}\sigma\omega_1^2\omega_0\,\mathrm{th}\frac{\beta_z\omega_0-\beta\Delta}{2}g(\Delta), \tag{6}$$

where

$$C_{ab}=-\frac{1}{N}\frac{\partial\langle\mathscr{H}_a\rangle}{\partial\beta_b}$$

are the partial heat capacities of the subsystems ($\sigma=A(0)/N$), and N is the total number of spins ($\sigma=1$ for $S=1/2$). As the second equation, just as in the HTA, we can use the spin-system energy conservation law in a rotating coordinate frame (RCF). The Hamiltonian is then $\mathscr{H}_{\mathrm{RCF}}=\Delta S_z+\mathscr{H}_d$, and the density matrix expressed in terms of the Zeeman temperature in the laboratory frame has the form (2) as before (the dipole temperature is the same in both systems). The condition

$$\frac{d}{dt}\langle\mathscr{H}_{\mathrm{RCF}}\rangle=0$$

makes it possible to obtain

$$\left(C_{dd}+\frac{\Delta}{\omega_0}C_{zd}\right)\frac{d\beta}{dt}+\left(C_{dz}+\frac{\Delta}{\omega_0}C_{zz}\right)\frac{d\beta_z}{dt}=0. \tag{7}$$

From (6) and (7) we get

$$\begin{aligned}\frac{d\beta_z}{dt}&=-\frac{\sigma}{2}\frac{\omega_0 C_{dd}+\Delta C_{zd}}{C_{zz}C_{dd}-C_{zd}C_{dz}}\mathrm{th}\frac{\beta_z\omega_0-\beta\Delta}{2}\pi\omega_1^2 g(\Delta),\\ \frac{d\beta}{dt}&=\frac{\sigma}{2}\frac{\Delta C_{zz}+\omega_0 C_{dz}}{C_{zz}C_{dd}-C_{zd}C_{dz}}\mathrm{th}\frac{\beta_z\omega_0-\beta\Delta}{2}\pi\omega_1^2 g(\Delta).\end{aligned} \tag{8}$$

We have confined ourselves here to a relatively elementary derivation of these equations. Note, however, that this result is obtained also by a more consistent analysis on the basis of the Nakajima–Zwanzig projection by choosing the Kawasaki–Gunton projector[20] $\mathscr{P}$ in the form

$$\mathscr{P}X=\rho-\sum_{a=z,d}\frac{\partial\rho}{\partial\langle\mathscr{H}_a\rangle}[\langle\mathscr{H}_a\rangle\mathrm{Sp}\,X-\mathrm{Sp}\,\mathscr{H}_a X], \tag{9}$$

where X is an arbitrary operator, and $\langle\mathscr{H}_a\rangle=\mathrm{Sp}\,\mathscr{H}_a\rho$.

Equations (8) go over in the HTA into the Provotorov equations. They differ from the equations formulated in Ref. 16 in that the subsystems are not redefined, a procedure unnecessary in our opinion, particularly for magnetically dilute systems. In contrast to the HTA, C_{ab} and $g(\Delta)$ are functions of β and β_z, which cannot be determined explicitly in the general case.

3. CONCENTRATION EXPANSION OF THE CORRELATION FUNCTIONS

We examine most closely the correlation function

$$A(t)=\langle\langle[S_+(t),\,S_-]_+\rangle\rangle_c=A(0)G(t), \tag{10}$$

where the temporal evolution is governed by the secular part of the dipole–dipole interaction,

$$\mathscr{H}_d=\frac{1}{2}\sum_{x,q}n_xn_q\hat{B}_{xq},\qquad \hat{B}_{xq}=A_{xq}(S_x^zS_q^z-\alpha\mathbf{S}_x\mathbf{S}_q),$$
$$A_{xq}=\frac{3}{2}\frac{\gamma^2\hbar}{|\mathbf{x}-\mathbf{q}|^3}(1-3\cos^2\theta_{xq}). \tag{11}$$

In (11), n_x is the occupation number of site **x**, namely, $n_x=1$ if the site **x** is occupied by a spin and $n_x=0$ if it is not. In Eq. (10), $\langle\ldots\rangle_c$ denotes configuration averaging over all possible realizations of the spin distributions over the lattice site. Pure dipole–dipole interaction corresponds to $\alpha=1/3$. In the Anderson model $\alpha=0$. We assume further that $S=1/2$ and that the occupations of different sites do not correlate, i.e., $\langle n_x\rangle_c=f$, $\langle n_xn_q\rangle=f^2$ for $x\neq q$, etc. Here $f=N/N_{\text{site}}\ll 1$ is the density of the spins (of the occupied sites).

We change from averages over the density matrix (3) to averages over the "Zeeman" density matrix $\rho_0=\exp(-\beta_z\mathscr{H}_z)/\mathrm{Sp}\exp(-\beta_z\mathscr{H}_z)$:

$$\langle[S_+(t),S_-]_+\rangle=\sum_q n_q\langle[S_q^+(t),S_q^-]_+\exp(-\beta\mathscr{H}_d)\rangle_0\Big/\langle\exp(-\beta\mathscr{H}_d)\rangle_0$$
$$+\sum_{x\neq q}n_xn_q\langle[S_x^+(t),S_q^-]_+\exp(-\beta\mathscr{H}_d)\rangle_0/\langle\exp(-\beta\mathscr{H}_d)\rangle_0. \tag{12}$$

We have separated in (12) a single-index sum and took it into account that $n_x^2=n_x$. Not all the occupation numbers have been written out explicitly in (12), since $\mathscr{H}_d$ depends on them.

We shall use below expansions of the observables in terms of the occupation numbers and the concentrations. The methods are described in sufficient detail in Refs. 3 and 7 (see also Ref. 18 and the review paper[21]). We confine ourselves to high-symmetry (e.g., cubic) lattices and to ellipsoidal samples. The lattice sums of form $\Sigma_x\varphi(\mathbf{x}-\mathbf{q})$ given for them below are practically independent of **q**. Taking into account the self-averaging of $A(t)$ we have

$$G(t)=A(t)/A(0)=\langle A(t)\rangle_c/\langle A(0)\rangle_c.$$

In the leading order in the concentration f, we have

$$G(t)=1+f\sum_{x\neq 0}\langle[S_0^++S_x^+,\tilde{S}_0^-(-t)-S_0^-]_+\exp(-\beta\hat{B}_{0x})\rangle_0/$$
$$\langle\exp(-\beta\hat{B}_{0x})\rangle_0, \tag{13}$$

where $\tilde{\tilde{S}}_0^-(-t)=\exp(-i\hat{B}_{0x}t)S_0^-\exp(i\hat{B}_{0x}t)$. As usual, in this approximation everything is expressed in terms of solutions of two-spin problems. These solutions were obtained by using the identities

$$\varphi(S_k^z)=\frac{1}{2}\Big[\varphi\Big(\frac{1}{2}\Big)+\varphi\Big(-\frac{1}{2}\Big)\Big]+S_k^z\Big[\varphi\Big(\frac{1}{2}\Big)-\varphi\Big(-\frac{1}{2}\Big)\Big],$$

$$\langle\varphi(S_k^z,S_q^z)\rangle=\frac{(1+p)^2}{4}\varphi\Big(\frac{1}{2},\frac{1}{2}\Big)+\frac{(1-p)^2}{4}\varphi\Big(-\frac{1}{2},-\frac{1}{2}\Big)$$
$$+\frac{1-p^2}{4}\Big[\varphi\Big(\frac{1}{2},-\frac{1}{2}\Big)+\varphi\Big(-\frac{1}{2},\frac{1}{2}\Big)\Big],$$
$$\varphi(\mathbf{S}_x\mathbf{S}_q)=\frac{3}{4}\varphi\Big(\frac{1}{4}\Big)+\frac{1}{4}\varphi\Big(-\frac{3}{4}\Big)$$
$$+\mathbf{S}_x\mathbf{S}_q\Big[\varphi\Big(\frac{1}{4}\Big)-\varphi\Big(-\frac{3}{4}\Big)\Big], \tag{14}$$
$$S=\frac{1}{2},\qquad \mathbf{x}\neq\mathbf{q},$$

where φ is an arbitrary function, and $p=2\langle S_q^z\rangle_0=-\tanh(\beta_z\omega_0/2)$ is the polarization at $\beta=0$. We ultimately get

$$G(t)=1+m_0(t)+m_1(t), \tag{15}$$

$$m_0(t)=f\sum_x(\cos at-1+ip\sin at), \tag{16}$$

$$m_1(t)=f(1-p^2)\sum_x\frac{h(1+u)(\cos at-1)+ip(h-u-hu)\sin at}{1+h-hu+p^2(h-u-hu)}, \tag{17}$$

$$a={}^1/_2A_{0x},\quad h={}^1/_2\,\mathrm{th}(\alpha\beta a),\quad u=\mathrm{th}({}^1/_2\,\beta a). \tag{18}$$

Note that $m_1(t,\beta=0)=0$, and that m_0 is independent of β.

A direct calculation of the RLS $g(\Delta)$ on the basis of (5) is impossible. In fact, it is shown below [see (24)] that, for example, $m_0(E_0t\gg 1)=-D|t|+i\delta t$, i.e., individual terms of the terms of the series increase with time without limit. It is therefore necessary to rearrange the concentration expansion so as to have a satisfactory long-wave asymptote. There are two general methods for such a transformation. One is based on the construction of approximations for the memory function,[19,22] and the other on the use of cumulant expansions.[21,23] In both cases it is useful to compare the results with an exactly solvable model, whose role is assumed here by the Anderson model with $\beta=0$ (Refs. 18 and 24).

The memory function $K(t)$ corresponding to the correlation $G(t)$ is the kernel of the integrodifferential equation

$$\frac{dG(t)}{dt}=-\int_0^t d\tau K(\tau)G(t-\tau). \tag{19}$$

We know[8] that even simple approximations of $K(t)$ lead to good results for the RLS in systems with regular spin arrangement. The construction of $K(t)$ is based then on the first terms of its expansion in powers of t, determined from the first terms of the $G(t)$ expansion (i.e., from the moments of the corresponding Fourier transforms). It is shown in Ref. 7 that such a comparison of the concentration expansions of this function makes it possible to solve analogous problems for systems with low spin concentrations, without using any other approximations.

The Laplace transforms of the functions $G(t)$ and $K(t)$

$$G(\lambda)=\int_0^\infty dte^{-\lambda t}G(t),\qquad K(\lambda)=\int_0^\infty dte^{-\lambda t}K(t)$$

are connected by the relation $K(\lambda)=G(\lambda)^{-1}-\lambda$, while

$$g(\Delta)=g_m(\Delta)=\frac{1}{\pi}\frac{R(\Delta)}{R^2(\Delta)+[\Delta+I(\Delta)]^2},\tag{20}$$

where $R(\Delta)=\operatorname{Re}K(\lambda=\varepsilon-i\Delta)$, $I(\Delta)=-\operatorname{Im}K(\lambda=\varepsilon-i\Delta)$, $\varepsilon\to+0$.

In the leading order of the concentration expansion we have

$$K(\lambda)=-\lambda^2(m_0(\lambda)+m_1(\lambda))=K_0(\lambda)+K_1(\lambda),$$

$$K_0(\lambda)=f\lambda\sum_x\frac{a^2-ip\lambda a}{\lambda^2+a^2},\tag{21}$$

$$K_1(\lambda)=f\lambda(1-p^2)\sum_x\frac{h(1+u)a^2-ip\lambda a(h-u-hu)}{[1+h-hu+p^2(h-u-hu)](\lambda^2+a^2)}.$$

The use of cumulant expansions is based as a rule on the representation

$$G(t)=(1+G_2(t))\exp(-G_1(t))$$

with separation of the leading terms of $G_1(t)$. The general principles of the method of cumulant expansions are described in sufficient detail in Kubo's classical paper,[23] and examples demonstrating its efficacy in the physics of disordered systems are given in Refs. 21, 25, and 26. An effective representation in our case is

$$G(t)=(1+m_1(t))\exp(m_0(t)),\tag{22}$$

on the basis of which, with allowance for (5) and (10), we have

$$g(\Delta)=g_c(\Delta)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,(1+m_1(t))\exp(m_0(t)+i\Delta t).\tag{23}$$

In the Anderson model Eq. (22) coincides with the exact solution at $\beta=0$ (Ref. 24), while $m_1\exp m_0$ coincides with the first term of the correlation expansion for all β (Ref. 18).

To obtain quantitative results we must next specify the shape of the sample, the type of the crystal lattice, and the orientation of the external field. Substantial simplifications arise in the continuous-medium approximation (CMA), when the sums over **x** in (16), (17), and (21) are replaced by integrals. This is legitimate if in the region of its significant values the summed expression changes little on going to the nearest site, as is the case in (16) and (17) for $E_0t\gg1$ and in (21) for $|\lambda|\ll E_0$. Here $E_0=\gamma^2\hbar/r^3_{\min}$, while $r_{\min}$ is the shortest distance between the spins in the lattice. Note that the contribution of the region of small $|\mathbf{x}|\sim r_{\min}$ in (16) and (17) is insignificant if $E_0t\gg1$ both by virtue of the small volume of the region and as a result of the rapid oscillations of the summed expression when **x** is varied.

In the continuous-medium approximation we have

$$\begin{gathered}m_0(t)=-D|t|+i\delta t,\qquad D=\frac{2\pi^2}{3^{3/2}}c\gamma^2\hbar,\\ \delta=\left[\frac{2\pi}{3^{3/2}}\left(3^{1/2}-\ln\frac{3^{1/2}+1}{3^{1/2}-1}\right)+\pi\xi\right]pc\gamma^2\hbar.\end{gathered}\tag{24}$$

The volume density of the spins is here $c=f/\Omega$, and Ω is the volume of the unit cell. The parameter ξ depends on the orientation of the ellipsoidal sample relative to the external field and on the ratio of the ellipsoid axes, with $-1\leqslant\xi\leqslant2$; for a sphere we have $\xi=0$. Let us examine the calculation of δ in greater detail. Obviously,

$$\begin{gathered}\delta=\frac{1}{t}fp\sum_x\sin at=\delta_1+\delta_2+\delta_3,\\ \delta_1=\frac{fp}{t}\sum_{|x|<R}\left(\sin at-\frac{at}{1+|at|}\right),\\ \delta_2=\frac{fp}{t}\sum_{|x|<R}\left(\frac{at}{1+|at|}-at\right),\qquad\delta_3=\frac{fp}{t}\sum_x at=\pi\xi p\gamma^2\hbar c.\end{gathered}\tag{25}$$

Since δ_1 and δ_2 do not depend on the shape of the sample, they can be calculated by summation inside the sphere, followed by taking the limit as $R\to\infty$. The macroscopic shift δ_3 is determined by the mean-field contribution which is proportional to ξ (Ref. 8, Ch. 5). The contribution of the second term to the fluctuational shift δ_2 is zero. Therefore, using the CMA, we have

$$\begin{aligned}\delta_2&=\frac{fp}{t}\sum_{|x|<R}\frac{at}{1+|at|}=4\pi cp\int_0^1dy\int_0^R r^2\,dr\frac{\varkappa\chi(y)}{r^3+|\varkappa\chi(y)t|}\\&=-\pi cp\gamma^2\hbar\int_0^1dy\chi(y)\ln|\chi(y)|\\&=\frac{2\pi}{3^{3/2}}\left(3^{1/2}-\ln\frac{3^{1/2}+1}{3^{1/2}-1}\right)cp\gamma^2\hbar=0.502cp\gamma^2\hbar.\end{aligned}$$

Here $y=\cos\theta$, $r=|\mathbf{x}|$, $\varkappa=\frac{3}{4}\gamma^2\hbar$, $\chi(y)=1-3y^2$. Next,

$$\begin{aligned}\delta_1&=\frac{cp}{t}\int d^3x\left(\sin\frac{\varkappa\chi t}{r^3}-\frac{\varkappa\chi t}{1+|\varkappa\chi t|}\right)\\&=4\pi\varkappa cp\int_0^1dy\chi(y)\int_0^\infty r^2\,dr\left(\sin\frac{1}{r^3}-\frac{1}{r^3+1}\right)=0\end{aligned}$$

since the integral with respect to y vanishes.

Similarly

$$K_0(\lambda)=D-i\delta.\tag{26}$$

Equations (19) and (22) lead to the same result at $m_1=0$, i.e., at $\beta=0$:

$$G_0(t)=G(t,\ \beta=0)=\exp(-D|t|+i\delta t),\tag{27}$$

$$g_0(\Delta)=g(\Delta,\beta=0)=\frac{1}{\pi}\frac{D}{(\Delta+\delta)^2+D^2}.\tag{28}$$

We have no such simple equations for m_1 and K_1. In the case considered, however, when $\beta D\sim\beta\overline{E}\ll1$, we can obtain closed expressions for $g(\Delta)$. In fact, combining (17), (23), and (24) and using the CMA, we have

$$g_c(\Delta)=g_0(\Delta)+g_{1c}(\Delta),\tag{29}$$

$$\begin{aligned}g_{1c}(\Delta)&=c(1-p^2)\\&\times\int d^3x\frac{h(1+u)\varphi_c(\Delta,a)-p(h-u-hu)\varphi_s(\Delta,a)}{1+h-hu+p^2(h-u-hu)},\end{aligned}\tag{30}$$

where

$$\begin{gathered}\varphi_c(\Delta,a)={}^1/_2[g_0(\Delta+a)+g_0(\Delta-a)]-g_0(\Delta),\\ \varphi_s(\Delta,a)={}^1/_2[g_0(\Delta-a)-g_0(\Delta+a)].\end{gathered}$$

Note that the integral in (30) is independent of the shape of the sample and the integration limits are therefore infinite.

Replacing the integration with respect to $|\mathbf{x}|$ by integration with respect to $|a|$ and calculating next the integral over the angles, we get

$$g_{1c}(\Delta)=\frac{2}{\pi}D(1-p^2)$$
$$\times\int_0^\infty\frac{da}{a^2}\frac{(u-h-hu^2)[(1+p^2)\varphi_c h+p\varphi_s]}{1-p^4u^2-2(1-p^4)hu+(1+p^2)^2h^2(u^2-1)}\tag{31}$$

where

$$\varphi_c=\varphi_c(\Delta,a),\ \varphi_s=\varphi_s(\Delta,a),\ h=h(a)={}^1/_2\operatorname{th}\alpha\beta a,$$
$$u=u(a)=\operatorname{th}{}^1/_2\beta a.$$

The integrand in (31) can be written in the form

$$\chi_c(a,\Delta)\psi_c(a)+\chi_s(a,\Delta)\psi_s(a),$$

where $\chi_c(a,\Delta)=\varphi_c(a,\Delta)/a^2$, $\chi_s(a,\Delta)=\varphi_s(a,\Delta)/a$. Both χ_c and χ_s have for $a>0$ a resonance maximum at $a=|\Delta+\delta|$, with a width of order D. On the other hand, the functions $\psi_c(a)$ and $\psi_s(a)$, by virtue of the condition $\beta D\ll 1$, are practically constant near this maximum. Therefore in the leading order in βD we can make in (31) the substitutions $\psi_c(a)\rightarrow\psi_c(\Delta+\delta)$, $\psi_s(a)\rightarrow\psi_s(\Delta+\delta)$ and integrate next with respect to a. As a result,

$$\frac{g_{1c}(\Delta)}{g_0(\Delta)}=\Phi_0(\Delta,D)=(1-p^2)(u_0-h_0-u_0^2h_0)$$
$$\times\frac{p+[1-2\pi g_0(\Delta)D](1+p^2)h_0}{1-p^4u_0^2-2(1-p^4)h_0u_0+(1+p^2)^2h_0^2(u_0^2-1)},\tag{32}$$

where

$$h_0=h(\Delta+\delta)={}^1/_2\operatorname{th}(\alpha\beta(\Delta+\delta)),$$
$$u_0=u(\Delta+\delta)=\operatorname{th}({}^1/_2\beta(\Delta+\delta)).$$

In the Anderson model, $h=0$. Equation (32) for that case was obtained earlier in Ref. 18.

We consider now $g_m(\Delta)$. In the leading order in the concentration we have

$$R(\Delta)=\operatorname{Re}K(\varepsilon-i\Delta)=D+R_1(\Delta),$$
$$I(\Delta)=-\operatorname{Im}K(\varepsilon-i\Delta)=\delta+I_1(\Delta),\tag{33}$$
$$R_1(\Delta)=D\Phi_0(\Delta,0),\tag{34}$$

$$\frac{I_1(\Delta)}{D}=\Phi_1(\Delta\beta)=\frac{2(1-p^2)}{\pi}\Delta\beta\int_0^\infty\frac{da}{a(a^2-\Delta^2\beta^2)}\cdot$$
$$\cdot\frac{(u_1-h_1-h_1u_1^2)(ah_1(1+p^2)+\Delta\beta p)}{1-p^4u_1^2-2(1-p^4)h_1u_1+(1+p^2)^2(u_1^2-1)h_1^2}.\tag{35}$$

Here $h_1=\frac{1}{2}\tanh(\alpha a)$, $u_1=\tanh(a/2)$. An estimate of the asymptotes by standard methods[22] leads to the values .

$$\Phi_1(\Delta\beta\rightarrow 0)=\frac{2(1-p^2)}{\pi}\zeta_0(p^2)\Delta\beta,$$
$$\zeta_0(p^2)=\int_0^\infty\frac{da}{a^2}\frac{(u_1-h_1-h_1u_1)h_1(1+p^2)}{1-p^4u_1^2-2(1-p^4)h_1u_1+(1+p^2)^2(u_1^2-1)},\tag{36}$$

$$\Phi_1(\Delta\beta\rightarrow\infty)=-\frac{p}{2\pi(1+p^2)}\ln(\Delta\beta)^2,\tag{37}$$
$$\zeta_0(p^2\rightarrow 1)=\left[(1-p^2)\ln\frac{1}{1-p^2}\right]^{-1},$$
$$\zeta_0(p^2,\alpha\rightarrow 0)=\frac{\alpha\ln(1/\alpha)}{2(1-p^2)},\tag{38}$$
$$\zeta_0(p^2=0,\alpha\sim{}^1/_3)\approx[\alpha(1-\alpha)/2]^{1/2}.\tag{39}$$

Here $\alpha<1/2$ and Eq. (39) was estimated from the asymptotes of the integrand in (36) as $a\rightarrow\infty$ and $a\rightarrow 0$.

It follows from (35)–(39) that $I_1/\Delta\lesssim\beta D\ll 1$ for all $\Delta\beta$ and p. Therefore, with account taken of Eq. (20), we can neglect the contribution of I_1 in $g_m(\Delta)$. Note, however, that if $\Delta\lesssim D$ Eq. (36) defines a contribution proportional to β from I_1 to the resonance-frequency shift. To the same accuracy, we can neglect the terms R_1 in the denominator of $g_m(\Delta)$ in (20), and obtain ultimately

$$g_m(\Delta)=g_0(\Delta)+g_{1m}(\Delta),$$
$$g_{1m}(\Delta)=g_0(\Delta)\frac{(1-p^2)(u_0-h_0-u_0^2h_0)[p+(1+p^2)h_0]}{1-p^4u_0^2-2(1-p^4)h_0u_0+(1+p^2)^2h_0^2(u_0^2-1)}.\tag{40}$$

Attention is called to the fact that $g_c(\Delta)$ defined by Eqs. (29) and (32) and $g_m(\Delta)$ are practically equal. In fact, g_{1c} and g_{1m} differ only in the region where $\Delta\lesssim D$. In this region, however, we have $(g_{1c}-g_{1m})/g_0\lesssim(\beta D)^2$, which is much lower than the accuracy with which g_1 has been calculated. The contribution of g_1 becomes substantial only at $\beta\Delta\sim 1$.

Analysis of Eq. (17) shows that, in order of magnitude, $|m_1(t)|\lesssim D|\beta|$. Therefore, one of the conditions for the applicability of expressions (22) and (32) is $D|\beta|\ll 1$. The restrictions on the region of applicability of Eq. (22) in the HTA have been considereed in great detail in Ref. 7. Recall that this equation is accurate in the Anderson model, and that the deviations in real systems are of order not lower than c^2, increase with time, and are due to the presence of flip-flop processes. At lower temperatures, however, the spin flips are slowed down, and the region of applicability (with respect to t) of (22) should increase. It is important also that Eq. (22) is accurate in the Anderson model also if $p\neq 0$, but $\beta=0$ (Refs. 18 and 24).

The possible difference between the RLS functions $g(\Delta)$ and $g_0(\Delta)$ at $\beta=0$ and $p=0$ is not as strong as the difference between $G(t)$ and $\exp m_0(t)$. It is not qualitative but quantitative, is small, is concentrated in the region $|\Delta|\lesssim D$, and is determined by the contribution of the flip-flop processes.[7] Accordingly, the agreement between $g(\Delta,\beta=0)$ and $g_0(\Delta)$ should improve with increase of $|p|$. The influence of the dipole temperature β^{-1} is concentrated in $g_1(\Delta)$. The behavior of $g_1(\Delta\gg D)$ is due to the function $m_1(t\ll 1/D)$, which is determined accurately in our method. The practical equality of g_{1c} and g_{1m} at $\Delta\lesssim D$ means apparently that the equations obtained are reliable in this region.

4. CONCENTRATION EXPANSION OF THE THERMODYNAMIC QUANTITIES

The energies and the heat capacities can be expressed using the function

$$F(\beta,\beta_z)=-\langle\ln\operatorname{Sp}\exp(-\beta_z\mathscr{H}_z-\beta\mathscr{H}_d)\rangle_c =F_z-\langle\ln\langle\exp(-\beta\mathscr{H}_d)\rangle_0\rangle_c, \tag{41}$$

where

$$F_z=F(0,\beta_z)=-N\ln\operatorname{ch}\frac{\beta_z\omega_0}{2}.$$

Obviously,

$$\langle\mathscr{H}_a\rangle=\frac{\partial F}{\partial\beta_a},\qquad C_{ab}=-\frac{1}{N}\frac{\partial^2F}{\partial\beta_a\,\partial\beta_b}=C_{ba},\qquad(\beta_d=\beta). \tag{42}$$

Expanding F_c in terms of the occupation numbers from $\mathscr{H}_d$ and averaging we have, in the leading order in f,

$$F=F_z-\frac{fN}{2}\sum_x\ln\langle\exp(-\beta\hat{B}_{0x})\rangle_0=F_z+F_c. \tag{43}$$

Using (11) and (14), we find that

$$\begin{gathered}\langle\exp(-\beta\hat{B}_{0x})\rangle_0=L(h,u)\operatorname{ch}\frac{\beta a}{2}\exp(\alpha\beta a/2),\\ L(h,u)=\frac{1+p^2}{2}(1-u)+\frac{1-p^2}{2}\frac{1+u}{1+2h}.\end{gathered} \tag{44}$$

The notation here is the same as in Eq. (18). The succeeding transformations of (44) will be aimed at separating the singularities of this expression at large and small $|\mathbf{x}|$, after which a transition to the CMA becomes possible. For large $|\mathbf{x}|$, i.e., for small a, the following is valid:

$$L(h,u)=1-\frac{a\beta}{2}[\alpha+p^2(1-\alpha)].$$

To separate the contribution due to the shape of the sample, we introduce therefore

$$\ln\tilde{L}(h,u)=\ln L(h,u)+\frac{1}{2}[\alpha+p^2(1-\alpha)]\frac{a\beta}{1+|a\beta|}.$$

We have now

$$\begin{aligned}F_c&=-\frac{Nf}{2}\sum_x\left(\frac{\alpha\beta a}{2}+\ln\operatorname{ch}\frac{\beta a}{2}+\ln L\right)\\ &=-\frac{Nf}{2}\sum_x\left\{\frac{\alpha\beta a}{2}-\frac{1}{2}[\alpha+p^2(1-\alpha)]\frac{a\beta}{1+|a\beta|}\right.\\ &\qquad\left.+\ln\operatorname{ch}\frac{\beta a}{2}+\ln\tilde{L}\right\}=\sum_{i=0}^{3}\Phi_i,\end{aligned} \tag{45}$$

where

$$\begin{gathered}\Phi_0=\frac{Nf}{4}\sum_x p^2(1-\alpha)\beta a=\frac{Nc}{4}p^2(1-\alpha)\beta\pi\gamma^2\hbar\xi,\\ \Phi_1=\frac{Nf}{4}[\alpha+p^2(1-\alpha)]\sum_{|x|<R}\left(\frac{a\beta}{1+|a\beta|}-a\beta\right),\\ \Phi_2=-\frac{Nf}{2}\sum_{|x|<R}\ln\operatorname{ch}\frac{\beta a}{2},\qquad\Phi_3=-\frac{Nf}{2}\sum_{|x|<R}\ln\tilde{L}(h,u).\end{gathered} \tag{46}$$

Only Φ_0 depends here on the shape of the sample. In the remaining Φ_i we can sum inside the sphere and then let its radius R tend to infinity.

If the condition $E_0\beta\gg1$ is met, we can change over to the CMA. The contribution of the second term in Φ_1 is zero and the first is determined by an integral of the same type as for the shift δ_2 in (25). Taking this into account, we have

$$\Phi_1=N\frac{\beta\delta_2}{4p}[\alpha+p^2(1-\alpha)],\qquad\frac{\delta_2}{p}=0.502c\gamma^2\hbar. \tag{47}$$

It is convenient next to represent Φ_2 in the form $\Phi_2=\Phi_2^{(0)}+\Phi_2^{(1)}+\Phi_2^{(2)}$, where

$$\Phi_2^{(0)}=-\frac{Nf|\beta|}{4}\sum_{x<R}|a|=-\frac{3}{16}Nc|\beta|\gamma^2\hbar\left(\xi_1+\frac{16\pi}{3^{5/2}}\ln\frac{R^3}{\Omega}\right), \tag{48}$$

$$\Phi_2^{(1)}=\frac{Nf}{4}\sum_{x<R}\frac{|\beta a|}{1+|\beta a|/2}=-N\frac{D|\beta|}{2\pi}\left[\ln|\beta D|+\frac{3^{3/2}}{4}\int_0^1dy\,|\chi(y)|\ln|\chi(y)|-\ln\left(\frac{16\pi^2}{3^{5/2}}cR^3\right)\right], \tag{49}$$

$$\Phi_2^{(2)}=-\frac{Nf}{2}\sum_{x<R}\left[\ln\operatorname{ch}\frac{\beta a}{2}-\frac{(\beta a/2)^2}{1+|\beta a|/2}\right]=0.1812\frac{ND|\beta|}{2\pi}. \tag{50}$$

The constant ξ_1 in (48) depends on the type of the crystal lattice and on the orientation of the latter relative to the external magnetic field. For a simple cubic lattice we obtain

$$\xi_1[100]=5.821,\quad\xi_1[110]=2.110,\quad\xi_1[111]=-0.804. \tag{51}$$

In the presence of an exchange interaction exceeding the dipole interaction at distances $r<r_{\text{ex}}\ll\bar{r}=r_0/f^{1/3}$, it is useful to use an approximation in which it is assumed that $A_{r0}=0$ at $|\mathbf{r}|<r_{\text{ex}}$ (Ref. 27), i.e., the spins coupled by exchange interaction are disregarded in the usual spin dynamics, since they reach equilibrium with the bulk of the crystal spins too slowly. We use in this case the substitution

$$\sum_{0\neq|x|<R}\to\int_{r_{ex}}^{R}\frac{d^3x}{\Omega},\qquad\frac{4\pi}{3}r_{ex}^3=N_{ex}\Omega, \tag{52}$$

which leads to the value

$$\xi_1=\xi_{10}=\frac{16\pi}{3^{5/2}}\ln\frac{\Omega}{r_{ex}^3}=-\frac{16\pi}{3^{5/2}}\ln\frac{3N_{ex}}{4\pi}. \tag{53}$$

Here N_{ex} is the number of sites in the region covered by the exchange interaction. We obtain finally

$$\Phi_2=-N\frac{D|\beta|}{2\pi}\left[\ln\frac{|\beta D|}{f}+\frac{3^{5/2}}{16\pi}\xi_1-2.569\right]. \tag{54}$$

Similarly,

$$\begin{gathered}\Phi_3=-N\frac{D|\beta|}{2\pi}J_0(p^2),\\ J_0(p^2)=\int_0^\infty\frac{da}{a^2}\ln[L(h_1,u_1)L(-h_1,-u_1)].\end{gathered} \tag{55}$$

Here $h_1=\frac{1}{2}\tanh(\alpha a)$, $u_1=\tanh(a/2)$. We obtain thus

$$F_c=-N\left\{\frac{\alpha\beta\delta_3}{4p}-(\alpha+p^2(1-\alpha))\frac{\beta\delta}{4p}+\frac{D|\beta|}{2\pi}\left[\ln\frac{|\beta D|}{f}+\xi_1+J_0(p^2)\right]\right\}, \tag{56}$$

where $\tilde{\xi}_1 = 3^{5/2}\xi_1/16\pi - 2.569$.

In the case of pure dipole interaction ($\alpha = 1/3$) the function $J_0(p^2)$ is uniformly approximated (with relative accuracy not lower than 2%) by the expression

$$J_0(p^2)=-\left\{\frac{2}{15}(3+5p^2)(1-p^2)\right.$$
$$\left.+p^2\left[\ln\frac{1}{\mu}+\frac{1}{8}-\frac{\pi^2\mu^2}{6(1+\pi^2\mu^2/10)}\right]\right\}, \qquad (57)$$

where

$$\mu=\left[\ln\frac{4}{1-p^2}\right]^{-1}.$$

To derive it we took it into account that

$$J_0(p^2\to 0)=-0.395-0.156p^2+O(p^4), \quad \alpha={}^1/_3, \qquad (58)$$

$$J_0(p^2\to 1)=-\varphi(\mu)+o(\mu^4),$$
$$\varphi(\mu)=\ln\frac{1}{\mu}+C+\ln\frac{2}{\pi}-\frac{\pi^2\mu^2}{6(1+\pi^2\mu^2/10)}. \qquad (59)$$

(here C is the Euler constant), joined together these asymptotes choosing the coefficient k in the equation

$$J_0(p^2)=-(0.395+kp^2)(1-p^2)-p^2\varphi(\mu)$$

such that (58) could be expanded for small p^2, and rounded off slightly some of the coefficients, for example $C + \ln(2/\pi) = 0.12563 \to 1/8$.

Note that the expansion (59) is valid for all $\alpha < 1/2$, and its singular terms are determined by the contribution of large $a \sim 1/\mu$ in the integeral (55), i.e., by the contribution of relatively close spin pairs. Actually $a \lesssim |\beta E_0|$, so that the asymptote (59) is valid if $\mu \gtrsim 1/|\beta E_0|$.

It is important that the expansions (58) and (59) can be differentiated, since they are valid in the complex p^2 region near the real interval (0,1). Therefore all the thermodynamic characteristics can be obtained in the CMA directly from Eqs. (41), (42), (56), (57). In particular, the Zeeman and dipole energies are defined in the CMA by the relations

$$E_z=N\frac{\omega_0}{2}P,$$
$$P=2\langle S_x^z\rangle=p\left[1-(1-p^2)\left(\frac{1-\alpha}{2}\beta\frac{\delta}{p}-\frac{D|\beta|}{\pi}\frac{\partial J_0(p^2)}{\partial p^2}\right)\right],$$
$$E_d=N\varepsilon_d, \qquad (60)$$
$$\varepsilon_d=\frac{D}{2\pi}\left\{\frac{\beta}{|\beta|}\left[\ln\frac{f}{|\beta D|}-J_0(p^2)-\tilde{\xi}_1+1\right]\right.$$
$$\left.+\frac{\pi\delta}{2pD}[\alpha+p^2(1-\alpha)]-\frac{\pi\delta_3\alpha}{2pD}\right\},$$

and for the heat capacities we have

$$C_{dd}=\frac{D}{2\pi|\beta|},$$
$$C_{dz}=\omega_0(1-p^2)\left[\frac{1}{4}(1-\alpha)\delta-\frac{|\beta|}{\beta}\frac{Dp}{2\pi}\frac{\partial J_0(p^2)}{\partial p^2}\right],$$
$$C_{zz}=C_{zz}^{(0)}+C_{zz}^{(1)}, \qquad C_{zz}^{(0)}=\frac{\omega_0^2}{4}(1-p^2), \qquad (61)$$
$$C_{zz}^{(1)}=-\frac{\omega_0^2}{8}\frac{\beta\delta}{p}(1-p^2)(1-3p^2)(1-\alpha)$$
$$-\omega_0^2(1-p^2)\frac{D|\beta|}{2\pi}J_{zz}(p^2),$$
$$J_{zz}(p^2)=-\frac{1}{2}\left[2p^2(1-p^2)\frac{\partial}{\partial p^2}+1-3p^2\right]\frac{\partial}{\partial p^2}J_0(p^2).$$

In addition to the continuous-medium approximation considered above, interest attaches also to the dipole high-temperature limit (DHTL), when p is arbitrary ($p^2 < 1$) and $|\beta E_0| \ll 1$. In this case it follows directly from (44) that

$$F_c=-N\left\{-\frac{1}{4}\delta_3 p(1-\alpha)+\frac{1}{16}\beta^2 M_2(1-p^2)\right.$$
$$\left.\times[(1-\alpha)^2p^2+3\alpha^2-2\alpha+1]\right\}; \qquad (62)$$

$$P=p\left\{1-\frac{1-p^2}{4}[2(1-\alpha)\delta_3+M_2\beta^2(\alpha^2+(1-\alpha)^2p^2)]\right\}, \qquad (63)$$

$$\varepsilon_d=\frac{1}{4}\delta_3 p(1-\alpha)-\frac{\beta}{8}M_2(1-p^2)[(1-\alpha)^2p^2+3\alpha^2-2\alpha+1];$$
$$C_{zz}^{(1)}=\frac{\omega_0^2}{16}(1-p^2)\left\{\frac{2\delta_3}{p}\beta(1-\alpha)(3p^2-1)\right.$$
$$\left.-\beta^2M_2[\alpha^2+3p^2(1-2\alpha)-5p^4(1-\alpha)^2]\right\},$$
$$C_{dz}=\frac{\omega_0}{4}(1-p^2)[\delta_3(1-\alpha)+\beta M_2 p(\alpha^2+(1-\alpha)^2p^2)],$$
$$C_{dd}={}^1/_8 M_2(1-p^2)[(1-\alpha)^2p^2+3\alpha^2-2\alpha+1], \qquad (64)$$

where, just as in the CMA, $C_{zz} = C_{zz}^{(0)} + C_{zz}^{(1)}$, while $C_{zz}^{(0)}$ is defined in (61). In these equations

$$M_2=\frac{f}{4}\sum_x A_{x0}^2$$

is the second moment at $p = 0$. Recall that in a simple cubic lattice

$$M_2[100]=2DE_0, \quad M_2[110]=0.75DE_0,$$
$$M_2[111]=0.33DE_0, \quad E_0=\gamma^2\hbar/\Omega.$$

In the approximation (52) we have $M_2 = M_{20}(N_{\text{ex}}) = 2.1E_0D/N_{\text{ex}}$.

Concluding this section, we note that for a system of spins coupled by the RKKY interaction, the concentration expansion of the free energy and of certain thermodynamic quantities was carried out for the state of total thermodynamic equilibrium in Refs. 28 and 29. The RKKY interaction energy, just as the dipole–dipole energy, decreases in proportion to r^{-3}, and it is natural to expect a definite similarity of the results. Study of a two-temperature system, however, raises problems not encountered in equilibrium thermodynamics, some of which are solved in the present paper (see also Ref. 30).

5. KINETICS OF RESONANCE SATURATION AND THERMAL MIXING IN A ROTATING COORDINATE FRAME

Equations (8) and the equations for the heat capacities and the energies, obtained in the preceding section, are the general basis for the calculation of the saturation kinetics of magnetic resonance in disordered systems, and for further generalizations aimed at taking spin–lattice relaxation into account. If, however, the interaction with the lattice can be neglected, it is convenient to begin the description of the kinetics with the equations for the polarization P and for the dipole energy ε_d. Note that these are in fact the directly observable quantities.[8]

Recognizing that the left-hand side of Eq. (6) is simply $\dot{\varepsilon}_z = \omega_0 \dot{P}/2$ we find that

$$\dot{P}=W\,\mathrm{th}\,\frac{\beta_z\omega_0-\beta\Delta}{2}=-W\frac{p-q}{1-pq},$$
$$p=-\mathrm{th}\,\frac{\beta_z\omega_0}{2},\qquad q=-\mathrm{th}\,\frac{\beta\Delta}{2},\qquad W=\pi\omega_1{}^2 g(p,q,\Delta). \tag{65}$$

Recall that $P=2\langle S_x^z\rangle$ is the polarization of the system spins, and $p=2\langle S_x^z\rangle_0$ is the polarization at infinite dipole temperature. One more equation gives the law, already used in (7), of energy conservation in a rotating coordinate frame:

$$\frac{\Delta}{2}P+\varepsilon_d=\mathrm{const}. \tag{66}$$

The system of equations becomes closed when supplemented by the equations $P=P(p,q)$, $\varepsilon_d=\varepsilon_d(p,q)$, which we choose to be Eqs. (60) and (63) as well as the relation that follows from (65):

$$\beta=\frac{1}{\Delta}\ln\frac{1-q}{1+q}. \tag{67}$$

Let us consider the canonical resonance-saturation problem when the dipole system has initially a high temperature and its polarization is arbitrary. (Its high-temperature analog is considered in Ref. 31.) This is just the state realized in a number of EPR experiments at temperatures $T\sim 1$ K and at frequencies $\omega_0/2\pi\sim$ 10–40 GHz.[27,32] We confine ourselves henceforth to spherical samples, neglect the fluctuation shift δ_2, and consider the case of dipole–dipole interaction, when $\alpha=1/3$. The DHTL leads then to the expression

$$P=p\left[1-\frac{1}{36}(1-p^2)M_2\beta^2(1+4p^2)\right],$$
$$\varepsilon_d=-\frac{1}{12}\beta M_2\left(1+\frac{2}{3}p^2\right), \tag{68}$$

and in the CMA case we have

$$P=p\left[1+\frac{1}{\pi}D|\beta|(1-p^2)\frac{\partial J_0(p^2)}{\partial p^2}\right], \tag{69}$$

$$\varepsilon_d=\frac{\beta}{|\beta|}\frac{D}{2\pi}\left[\ln\frac{f}{|\beta D|}-J_0(p^2)-\tilde{\xi}_1-1\right]. \tag{70}$$

Neglecting $\varepsilon_d(t=0)$, we can rewrite (66) in the form

$$\varepsilon_d=\frac{\Delta}{2}(P_0-P). \tag{71}$$

We assume for the sake of argument that M_2 is defined by an equation that allows for the existence of exchange interactions. Following the established research practice, we confine ourselves to detunings $|\Delta|\lesssim M_2^{1/2}$.

It can be seen directly from (65) that P tends monotonically to an equilibrium in which $p=q$, and it follows from (71) that $\varepsilon_d(t)$ also varies monotonically.

Let the final state $p_f=q_f$ lie in the DHTL region. Obviously, the entire process likewise takes place in this region. The condition for the applicability of DHTL in the presence of exchange interactions is

$$|E_0\beta|/N_{ex}\ll 1. \tag{72}$$

For $\Delta^2\lesssim M_2$ we have

$$(\beta\Delta)^2\leqslant\beta^2M_2\approx 8\beta^2E_0{}^2/N_{ex}\ll 1.$$

Therefore $q=-\frac{1}{2}\beta\Delta$, $|q|\ll 1$, in the DHTL region, and at equilibrium $\beta_f=-2p_f/\Delta$. Substituting these relations in (68), using (71), and retaining terms of order not higher than first in $p_f\ll 1$, we obtain for the polarization

$$P_f=\frac{3\Delta^2}{3\Delta^2+M_2}P_0, \tag{73}$$

and the condition for applicability of the DHTL takes the form

$$2E_0|\Delta P_0|/(N_{ex}(\Delta^2+{}^1/_3M_2))\ll 1,$$

or, recognizing that $D\approx 4fE_0$,

$$D|P_0\Delta|/(2\Delta^2 fN_{ex}+{}^1/_3D^2)\ll 1. \tag{74}$$

Note the appearance of the characteristic parameter fN_{ex}, which has the meaning of the fraction of the spins subject to exchange interaction. Clearly, the theory considered is valid only if $fN_{\mathrm{ex}}\ll 1$, otherwise allowance must be made for the exchange narrowing of the line and an explicit account must be taken of the effect of the exchange dynamics on the thermodynamics. The condition (74) is quite stringent. For example, if $\Delta\sim D$ it goes over into $3|P_0\Delta|/D\lesssim 1$ regardless of the actual value of fN_{ex}, and it was patently violated in the experiments of Refs. 27 and 32.

If the final state lands in the CMA region, the analysis is somewhat more complicated. For $P_f\ll 1$ we can again confine ourselves to terms not higher than of first order in p_f, arriving then, after taking into account the asymptote (58), Eq. (53), and the relations $P_f=p_f$ and $\mathrm{sign}(\beta\Delta p)=-1$, at the equation

$$\pi|\Delta p_f|+D\ln|p_f|=\pi|\Delta p_0|-D\left(\ln\frac{D}{f|\Delta|N_{ex}}+0.15\right). \tag{75}$$

Its solution for $|\ln|p_f||\gg\pi|\Delta p_f/D|$ is

$$p_f=0.86fN_{ex}\left|\frac{\Delta}{D}\right|\exp\left(\pi\left|\frac{\Delta}{D}p_0\right|\right), \tag{76}$$

and for $|\ln|p_f||\ll\pi|\Delta p_f/D|$

$$|p_f|=|p_0|-\frac{D}{|\pi\Delta|}\left(\ln\frac{D|p_0|}{fN_{ex}|\Delta|}+0.15\right). \tag{77}$$

With increase of Δ, the second term of (77) reverses sign, but this takes place at $|\Delta|=\Delta_{\max}\approx E_0/N_{\mathrm{ex}}$, where the theory considered is no longer applicable. For $1-|p_f|\ll 1$, taking into account the relation $\mu=|\Delta\beta|^{-1}$, the expansion (59), and the conservation law (71), we get

$$|P_f|=|P_0|-\frac{D}{\pi|\Delta|}\left[\ln\frac{D}{fN_{ex}|\Delta|}-0.26+\frac{1}{6}\pi^2\mu^2\right]. \tag{78}$$

In the considered range of Δ (if $\Delta^2\lesssim M_2$), the logarithmic terms in (77) and (78) are estimated at

$$\ln(D/fN_{ex}|\Delta|)\geqslant|\ln(fN_{ex})^{1/2}|\gg 0.26.$$

Equations (77) and (78) can therefore be combined to form the expression

$$|P_f|=|P_0|-\frac{D}{\pi|\Delta|}\ln\frac{D|P_0|}{fN_{ex}|\Delta|}. \tag{79}$$

This solution is valid both for $|\ln|P_f||\ll\pi|\Delta P_f/D|$ and for $1-|P_f|\ll 1$.

Figure 1 shows P_f vs the detuning, calculated from the approximate equations (73), (76), and (79), the results of a numerical calculation using Eqs. (68)–(71), and the more exact values obtained in the region $|\beta E_0|/N_{\rm ex}\sim 1$ by direct application of Eqs. (45) and (46) in the approximation (52) (solid lines). It can be seen that the exact dependence is close to the line that can be obtained from plots of the functions (73), (76), and (79) joined together by tangents in the intermediate regions. A similar analysis for the dipole energy ε_d is shown in Fig. 2. Note the substantial difference between the plots of $P_f(P_0,\Delta)$ in the DHTL and CMA regions. In particular, in the CMA we get a nontrivial dependence of (76) on P_0, and the parameter $\Delta_{1/2}$, which is equal to half-width of the $P_0-P_f(\Delta)$ line at half maximum, amounts to

$$\Delta_{1/2}\sim(D/\pi P_0)\ln(P_0/fN_{ex}),$$

whereas in the DHTL we have

$$\Delta_{1/2}\sim M_2^{1/2}\sim D/(fN_{ex})^{1/2}.$$

Let us examine the evolution of the system with time. The dependence of the rate W on p and q is quite weak and is immaterial in the qualitative analysis. If $Wt\ll 1$ Eq. (65) is equivalent to $\dot{P}=-WP$, and when t increases the system goes over into an exponential reaxation near the stationary solution $p_f=q_f$ at a new rate w_f.

If the final state lands in the DHTL region, we have

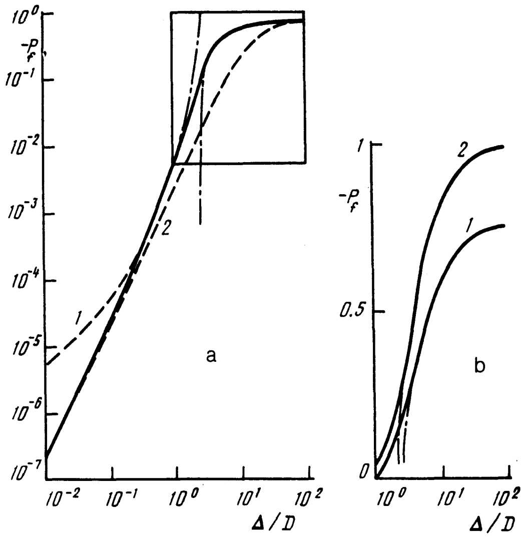

FIG. 1. Dependence of the quasistationary value of the polarization on the detuning $fN_{\rm ex}=5\times10^{-4}$; a: $P_0=0.76$, $(\beta_z\omega_0=2)$, curve *1*—extrapolation of values obtained from the equations for the CMA in the DHTL region; curve *2*—extrapolation of DHTL into the CMA region; the dash-dot line shows an extrapolation, according to Eqs. (76) and (79), into the region $1<\Delta/D<3$; b—separated $\Delta\gtrsim D$ detuning region; curve *1*—$P_0=0.76$, $(\beta_z\omega_0=2)$; curve *2*—$P_0=0.99$ $(\beta_z\omega_0=5)$.

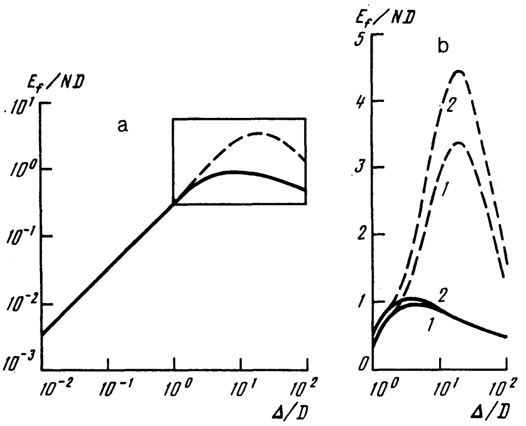

FIG. 2. Dependence of the quasi-stationary value of the dipole energy on the detuning; $fN_{\rm ex}=5\times10^{-4}$; a—$P_0=0.76$, $(\beta_z\omega_0=2)$; b—separated $\Delta\gtrsim D$ detuning region, curves *1*—$P_0=0.76$, $(\beta_z\omega_0=2)$, curves *2*—$P_0=0.99$, $(\beta_z\omega_0=5)$; dashed curves—DHTL results.

$q=(3\Delta^2/M_2)(P_0-P)$ for $p^2\ll 1$, as follows directly from the energy conservation in the RCF. Equation (65) takes then the form

$$\dot{P}=-W\left(1+\frac{3\Delta^2}{M_2}\right)(P-P_f),\qquad P_f=\frac{3\Delta^2}{3\Delta^2+M_2}P_0,$$

$$W=W(p=q=0).. \tag{80}$$

If the final state lands in the CMA region, then

$$\delta q=-\delta p\frac{1-p_f^2}{2}l\left.\frac{\pi\Delta/D+J_1l+J_2}{1+{}^1/_2lJ_2}\right|_{p=p_f},\qquad l=\ln\frac{1+|p_f|}{1-|p_f|}, \tag{81}$$

where

$$J_1=2|p|\frac{\partial}{\partial p^2}(1-p^2)\frac{\partial J_0}{\partial p^2},\qquad J_2=2|p|\frac{\partial J_0}{\partial p^2},$$

$$\delta q=q-q_f,\qquad \delta p=p-p_f.$$

This relation follows from Eq. (71) after substituting in it Eqs. (69), (70), and (67), taking the variation, and substituting $p=q=p_f$.

It is easy now to find that for small p_f the approach to equilibrium is described by the equation

$$\frac{d}{dt}\delta P=-W_f\left(1+\frac{\pi|\Delta P_f|}{D}\right)\delta P, \tag{82}$$

where $\delta P=P-P_f$, $W_f=W(p_f,q_f=p_f)$.

In the opposite case $1-P_f^2\ll 1$ it must be recognized that

$$\delta p=-\frac{\pi|\Delta|}{2D\mu}(1-p^2)\delta P.$$

It follows then from (81) and (59) that

$$\frac{d}{dt}\delta P=-W_f\left(1+\frac{\pi|\Delta|}{2D\mu_f}\right)\delta P. \tag{83}$$

This equation is strictly valid in the region of large $|\Delta|\sim E_0/N_{\rm ex}$ where

$$\mu_f=\frac{1}{\pi}\{6[\ln(D/fN_{ex}|\Delta|)-1.26]\}^{1/2}.$$

Comparison of (82) and (83), however, shows that it is natural to expect (83) to be valid also at small $|\Delta|$, when $P_f \approx p_f$, and it follows from (79) that

$$\mu_f = \left[\ln\frac{4}{1-p_f^2}\right]^{-1} = \left[\ln\frac{2\pi|\Delta|}{D\ln(D|P_0|/fN_{ex}|\Delta|)}\right]^{-1}. \qquad (84)$$

It follows from (80), (82), and (83) that the rates of approach to equilibrium differ quite strongly for DHTL and CMA.

We conclude by estimating the values of $|\beta D|$ reached in the processes considered above, and verify by the same token the condition $|\beta D| \ll 1$ of the validity of the formulated theory. The basis for this analysis are the relations (67), (76), and (79), with account taken of the fact that in the essential region of the values of Δ we have $q_f = p_f = P_f$. We confine ourselves next to the case $P_0^2 = 1$. It is easily seen that $\max|\beta D|$ is reached in the region where Eq. (79) is valid. In terms of the variables $b = |\beta D|$ and $x = |\Delta|/D$, and with allowance for Eq. (67), it reduces to

$$b = \frac{1}{x}\ln\left[\left(2\pi x - \ln\frac{1}{xfN_{ex}}\right) \Big/ \ln\frac{1}{xfN_{ex}}\right].$$

From this we get in the leading order in $\eta = \ln x/\ln(1/fN_{\text{ex}}) \ll 1$

$$b_{max} = |\beta D|_{max} = \frac{2\pi}{\ln(1/fN_{ex})}\frac{\ln\zeta}{\zeta+1} = \frac{1.75}{\ln(1/fN_{ex})}, \qquad (85)$$

where $\zeta = 3.591$ is the root of the equation $\zeta + 1 = \zeta\ln\zeta$. The maximum is reached at $x = [(\zeta+1)/2\pi] \times \ln(1/fN_{\text{ex}}) = 0.73\ln(1/fN_{\text{ex}})$. In this case $\ln x \approx \ln\ln(1/fN_{\text{ex}}) \ll \ln(1/fN_{\text{ex}})$, as was assumed in the derivation of (85). In the case $fN_{\text{ex}} = 5\times10^{-4}$ we obtain $b_{\max} = 0.23$. This value goes over into $b_{\max} = 0.29$ when the next term of the expansion in η is taken into account. Both values are substantially smaller than unity.

6. CONCLUSION

Thus, the concentration expansion of the thermodynamic quantities and of the line-shape function have enabled us to develop for the first time a consistent theory of magnetic-resonance saturation in magnetically dilute solids at arbitrary polarization and moderately low dipole temperature. Our solutions are valid up to the onset of spin–lattice relaxation; this stage is quite extensive at low temperatures.[2,8] Allowance for spin–lattice relaxation is related to no less important aspects of saturation theory.

Another object of future research is a generalization of the Provotorov two-temperature hypothesis to obtain a more detailed description of the slowest processes. These are the processes of establishment of quasi-equilibrium between small clusters of closely located spins and the remainder of the system.[27,32,33] It follows from thermodynamics alone that a self-consistent theory that permits CAM to be introduced in the DHTL region should consider separately at least clusters consisting of pairs and triplets. The first steps in this direction were made in Ref. 33. It appears that such an approach can lead to a theory that is valid at alternating-field amplitudes that satisfy the condition $W\tau_c \lesssim 1$, where τ_c is the time of the flip-flop processes in the main bulk of the spins.

The fact that the quantity $\beta D \sim \beta\overline{E}$ turned out to be the smallness parameter corresponding to concentration makes our results applicable to the study of a large group of phenomena connected with dynamic cooling of a subsystem of spin–spin interactions. In particular, a temperature region becomes accessible in which a transition of a system of dipole-interacting spins into a dipole-glass system sets in.[34] Analysis[8,17,35] of the results of the spin-temperature approximation of nonlinear effects shows that in the case of a strong separation the smallness parameter of this approximation is $\beta E_0 \simeq \beta\overline{E}/f$, i.e., the concentration expansion increases the range of dipole temperatures that lends itself to analysis by f^{-1} times.

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