

THERMODYNAMICAL PROPERTIES OF NUCLEAR SPIN SYSTEMS WITH DIPOLAR INTERACTION IN SOLIDS. LOW-FIELD CASE. II

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The properties of spin systems subjected to dipolar interactions in thermodynamic equilibrium are considered for arbitrary and zero magnetic field. It has been shown that by converting spin operators to boson annihilation and creation operators and taking into account the complete dipolar Hamiltonian, it is possible to find a partition function and density operator in non-exponential form. The obtained results are valid in a wide region of spin temperatures without restriction to the high temperatures approximation. The exact properties of two spin systems in arbitrary spin temperatures are considered.

1. Introduction

The nonsecular parts of the dipolar coupling Hamiltonians play an essential role in processes equalizing temperatures between dipolar and any other subsystems in solids. These problems were discussed in several publications, which dealt with the perturbation theory, in the case of high temperatures approximation for the spin temperatures theory (Goldman 1970, Jeener 1968). In this paper spin systems in solids of which spins are subjected to dipolar interactions are considered. The thermodynamical properties of these systems in the case of pure dipolar interactions, as well as when a solid is found in a constant magnetic field, are discussed. Although obtained results are valid for arbitrary values of the external magnetic field, this particular attention, in numerical discussion, is devoted to systems in magnetic field which do not isolate a dipolar subsystem from Zeeman. Taking into account a complete dipolar coupling Hamiltonian all calculations are performed for spin systems in thermodynamic equilibrium.

In Section 2 the dipolar coupling Hamiltonian in terms of boson annihilation and creation operators have been noted. The partition function and density operator have been found based on the operator differential equation describing the temperature evolution

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of the non-normalized density operator in normal form. This equation, determining the properties of spin systems in a thermodynamic equilibrium state, was described in the previous paper I (Nosel 1976). It is shown here that in the considered cases of spin systems, the above mentioned density operator may be presented in the form of the sum of two operators, one of which describes purely Zeeman interactions, and the second one dipolar interactions as well as their mutual conjugation. We note, too, that another decomposition of the density operator is possible. For the Zeeman subsystem, a non-normalized density operator in normal form is described by a homogeneous differential equation which may be definitely solved. The remaining part of the total non-normalized density operator is determined by the linear inhomogeneous differential equation with constant coefficients. Because of the great number of interacting spins, solving this inhomogeneous equation exactly is rather difficult and therefore we find the solution in a special series form. This solution is presented in Section 3 where an approximation form of the density operator, having validity in a wide region of spin temperatures, has been found. On the basis of obtained results, the partition function, as well as the energy, the entropy, the specific heat and magnetization, have been calculated (Section 4).

In the last Section an exact description of two-spin systems in arbitrary and zero magnetic field is given.

2. Density operator

The temperature evolution of the non-normalized density operator in normal form in thermodynamic equilibrium is described by the equation (Nosel 1976)

$$\frac{\partial \sigma}{\partial \beta} + \mathcal{N}(\mathcal{H}(x^+, y) + \Lambda)\sigma = 0, \quad (2.1)$$

where $\beta = (kT)^{-1}$. The operator $\sigma(\beta)$ provides us with the possibility of immediately finding the partition function and, of course, the normalized density operator.

In considering this case, the total Hamiltonian is the sum of Hamiltonians describing interactions of N individual spins to external magnetic field $\mathbf{B} = B_0 \mathbf{k}$, where \mathbf{k} is the unit vector in the direction of the z axis, and internal interactions which are dipolar

$$\mathcal{H} = \sum_{i=1}^N \mathcal{H}_Z^{(i)} + \sum_{i < j}^N \mathcal{H}_D^{(ij)}. \quad (2.2)$$

The Hamiltonians of Zeeman interaction for (i) spin and of the dipolar interaction for (ij) pair spins, in terms of boson annihilation and creation operators, may be expressed in the following manner

$$\mathcal{H}_Z^{(i)} = -\frac{\hbar \omega_0}{2} (1 - \eta) b_i^+ b_i, \quad (2.3)$$

$$\mathcal{H}_D = -(A_{ij}^+ b_{ij} + B_{ij}^+ O_{ij}), \quad (2.4)$$

where

$$\begin{aligned}
 A_{ij}^+ &= A_1^{+(ij)} + A_2^{+(ij)}\eta, \\
 A_1^{+(ij)} &= f_0^{(ij)}b_{ij}^+ + f_1^{(ij)}O_{ij}^+ + f_2^{(ij)}c_{ij}^+, \\
 A_2^{+(ij)} &= f_{-2}^{(ij)}b_{ij}^+ - f_{-1}^{(ij)}O_{ij}^+ + f_0^{(ij)}c_{ij}^+, \\
 B_{ij}^+ &= f_{-1}^{(ij)}b_{ij}^+ - f_0^{(ij)}O_{ij}^+ - f_1^{(ij)}c_{ij}^+, \\
 b_{ij} &= b_i b_j, \\
 O_{ij} &= (1+\eta)b_i c_j, \\
 f_0^{(ij)} &= \frac{d_{ij}}{4}(3\cos^2\theta_{ij}-1) = \frac{d_{ij}}{4}F_0^{(ij)}, \\
 f_{\pm 1}^{(ij)} &= \frac{3}{4}d_{ij}\sin\theta_{ij}\cos\theta_{ij}e^{\pm i\phi_{ij}} = \frac{d_{ij}}{2}F_{\pm 1}^{(ij)}, \\
 f_{\pm 2}^{(ij)} &= \frac{3}{4}d_{ij}\sin^2\theta_{ij}e^{\pm i2\phi_{ij}} = d_{ij}F_{\pm 2}^{(ij)}, \\
 d_{ij} &= \hbar^2\gamma^2 r_{ij}^{-3}, \\
 \omega_0 &= \gamma B_0.
 \end{aligned}$$

The operators (2.3), (2.4) have the normal form. The differential operator Λ in equation (2.1) is given by

$$\Lambda = D_1^{(Z)} + D_1^{(D)} + D_2^{(D)}, \quad (2.5)$$

$$D_1^{(Z)} = -\frac{\hbar\omega_0}{2}(1-\eta) \sum_{i=1}^N b_i^+ \frac{\partial}{\partial b_i^+},$$

$$D_1^{(D)} = -\sum_{i<j}^N \left[(A_{ij}^+ b_j + B_1^{+(ij)} c_j) \frac{\partial}{\partial b_i^+} + (A_{ij}^+ b_i + B_1^{+(ij)} c_i) \frac{\partial}{\partial b_j^+} \right],$$

$$D_2^{(D)} = -\sum_{i<j}^N \left(A_{ij}^+ \frac{\partial^2}{\partial b_i^+ \partial b_j^+} + B_1^{+(ij)} \frac{\partial^2}{\partial b_i^+ \partial c_j^+} \right),$$

where

$$B_1^{+(ij)} = B_{ij}^+(1+\eta).$$

Introducing the following notations:

$$D_0^{(Z)} = \mathcal{H}_Z(x^+, y), \quad D_0^{(D)} = \mathcal{H}_D(x^+, y),$$

and

$$D = D_1^{(Z)} + D_2^{(D)}, \quad D_1 = D_0^{(Z)} + D_1^{(D)}, \quad D_2 = D_0^{(D)},$$

equation (2.1) may be rewritten as

$$\frac{\partial \sigma}{\partial \beta} + \mathcal{N}(D_0 + D_1 + D_2)\sigma = 0. \quad (2.6)$$

Introduction of operators D_0, D_1, D_2 is convenient because they have special properties. Let us consider a monomial which is product of k annihilation operators and k creation operators. Then the operator D_0 does not change the number k , operator D_1 increases k by 1 and operator D_2 increases k by 2.

Let us present the non-normalized density operator in the form of the product of two normal ordered operators $\sigma_Z(\beta)$ and $\sigma_{ZD}(\beta)$

$$\sigma = \mathcal{N}\sigma_Z\sigma_{ZD}. \quad (2.7)$$

The operator $\sigma_Z(\beta)$ describes the Zeeman subsystem without taking into account the internal interactions, and is determined by the equation (paper I)

$$\frac{\partial \sigma_Z}{\partial \beta} + \mathcal{N}(D_0^{(Z)} + D_1^{(Z)})\sigma_Z = 0, \quad (2.8)$$

the solution of which is

$$\sigma_Z(\beta) = \sum_{i=0}^N S_i^{(Z)} = \prod_{i=1}^N [1 + (A + B\eta)b_i^+ b_i], \quad (2.9)$$

where

$$S_0^{(Z)} = 1,$$

$$A(\omega_0) = B(-\omega_0) = \exp\left(\frac{\hbar\omega_0}{2}\beta\right) - 1.$$

The information about internal interactions between spins and their dependence on Zeeman interactions is contained in the operator $\sigma_{ZD}(\beta)$. Because the Hamiltonian describing dipolar interactions is rather complicated, therefore suggests, for the results of paper I, that the operator $\sigma_{ZD}(\beta)$ may be sought in the form of a series

$$\sigma_{ZD}(\beta) = \sum_{i=0}^N S_i^{(ZD)} \quad (2.10)$$

with

$$S_0^{(ZD)} = 1, \quad S_1^{(ZD)} = 0.$$

The $S_k^{(Z)}$ and $S_k^{(ZD)}$ are monomials in annihilation and creation operators. Every individual monomial consists of k annihilation operators. Now the $\sigma(\beta)$ may be otherwise expressed as

$$\sigma(\beta) = \sigma_Z + \sum_{i=2}^N \sum_{j=0}^N S_i^{(ZD)} S_j^{(Z)}. \quad (2.11)$$

Since the individual monomials of the type $S_i^{(ZD)}S_j^{(Z)}$ are composed of $i+j = k$ annihilation operators, they may therefore be replaced by a single symbol S_k . The last expansion can now be written in the form

$$\sigma(\beta) = \sigma_z(\beta) + \sigma'(\beta) \quad (2.12)$$

where

$$\sigma'(\beta) = \sum_{i=2}^N S_i. \quad (2.13)$$

The equation determining the operator $\sigma'(\beta)$ follows from Eq. (2.6). It is an inhomogeneous linear equation with constant coefficients which has the form

$$\frac{\partial \sigma'}{\partial \beta} + \mathcal{N}[\mathcal{H}(x^+, y) + A]\sigma' = -\mathcal{N}[\mathcal{H}_D(x^+, y) + A_D]\sigma_z. \quad (2.14)$$

From the above equation we get the following recurring form of equations, determining S_k operators

$$\frac{\partial S_k}{\partial \beta} + \mathcal{N} \sum_{i=0}^2 D_i S_{k-i} = -\mathcal{N} \sum_{i=0}^2 D_i^{(D)} S_{i+k-2}^{(Z)}, \quad (2.15)$$

with

$$S_0 = S_1 = 0, \quad S_0^{(Z)} = 1.$$

For $k = 2$ we obtain

$$\frac{\partial S_2}{\partial \beta} + \mathcal{N} D_0 S_2 = -\mathcal{N} \sum_{i=0}^2 D_i^{(D)} S_i^{(Z)}. \quad (2.16)$$

The form of this equation, which describes systems of N spins, is the same as in the case of the system consisting of two interacting spins. Further operators S_k for $k = 3, 4, \dots$ appear when the simultaneous interactions to the next spins are taken into account. These further corrections to the density operator are small, however, in comparison to S_2 , and therefore will not be considered here. They will be discussed in the next paper.

3. Solution of Eq. (2.16)

Since the form of the operator $\sigma_z(\beta)$, which describes the Zeeman interaction, is known exactly (2.9), the the right-hand side of Eq. (2.16) may be easily found with the help of relations (3.12)—(3.15) given in paper I. The obtained result is the following:

$$\mathcal{N} \sum_{i=0}^2 D_i^{(D)} S_i^{(Z)} = - \sum_{i < j}^N [(e^{k\omega_0\beta} A_1^{+(ij)} + e^{-k\omega_0\beta} A_2^{+(ij)} \eta) b_{ij} + B_{ij}^+ O_{ij}]. \quad (3.1)$$

Let the operator S_2 have the form

$$S_2 = \sum_{i < j}^N \{ [(E_{ij} + F_{ij}\eta)b_{ij}^+ + (G_{ij} - H_{ij}\eta)O_{ij}^+ + (I_{ij} + J_{ij}\eta)c_{ij}^+] b_{ij} + [(K_{ij} - M_{ij}\eta)b_{ij}^+ - L_{ij}O_{ij}^+] O_{ij} \}, \quad (3.2)$$

where $E_{ij}, F_{ij}, \dots, M_{ij}$ are unknown functions of β . The calculation $\mathcal{N}D_0S_2$ provides us with the following result:

$$\mathcal{N}D_0S_2 = - \sum_{i < j}^N \{ (\hbar\omega_0 b_{ij}^+ + A_1^{+(ij)}) [(E_{ij} + J_{ij}\eta)b_{ij} + K_{ij}O_{ij}] + (-\hbar\omega_0 c_{ij}^+ + A_2^{+(ij)}) [(I_{ij} + F_{ij}\eta)b_{ij} - M_{ij}O_{ij}] + 2B_{ij}^+ [(G_{ij} - H_{ij}\eta)b_{ij} - L_{ij}O_{ij}] \}. \quad (3.3)$$

From Eq. (2.16) result the three systems of differential equations determining unknown functions of the spin temperature. These systems of equations are:

$$\frac{\partial X}{\partial \beta} = A(\omega_0)X + B, \quad (3.4)$$

$$\frac{\partial Y}{\partial \beta} = A^*(-\omega_0)Y + B^*, \quad (3.5)$$

$$\frac{\partial Z}{\partial \beta} = A'Z + B', \quad X(0) = Y(0) = Z(0) = \mathbf{0}, \quad (3.6)$$

$$X = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}, \quad Y = \begin{pmatrix} y_1 \\ y_2 \\ y_3 \end{pmatrix}, \quad Z = \begin{pmatrix} K_{ij} \\ L_{ij} \\ M_{ij} \end{pmatrix},$$

$$(x_1, x_2, x_3) = (e^{-\hbar\omega_0\beta}E_{ij}, e^{-\hbar\omega_0\beta}G_{ij}, e^{-\hbar\omega_0\beta}I_{ij}),$$

$$(y_1, y_2, y_3) = (e^{\hbar\omega_0\beta}F_{ij}, e^{\hbar\omega_0\beta}H_{ij}, e^{\hbar\omega_0\beta}J_{ij}),$$

$$A(\omega_0) = \begin{pmatrix} f_0^{(ij)} & 2f_{-1}^{(ij)} & f_{-2}^{(ij)} \\ f_1^{(ij)} & -(\hbar\omega_0 + 2f_0^{(ij)}) & -f_{-1}^{(ij)} \\ f_2^{(ij)} & -2f_1^{(ij)} & -(2\hbar\omega_0 - f_0^{(ij)}) \end{pmatrix},$$

$$A' = \begin{pmatrix} \hbar\omega_0 + f_0^{(ij)} & -2f_{-1}^{(ij)} & -f_{-2}^{(ij)} \\ -f_1^{(ij)} & -2f_0^{(ij)} & -f_{-1}^{(ij)} \\ -f_2^{(ij)} & -2f_1^{(ij)} & -\hbar\omega_0 + f_0^{(ij)} \end{pmatrix},$$

$$B = \begin{pmatrix} f_0^{(ij)} \\ f_1^{(ij)} \\ f_2^{(ij)} \end{pmatrix}, \quad B' = \begin{pmatrix} f_{-1}^{(ij)} \\ f_0^{(ij)} \\ f_1^{(ij)} \end{pmatrix}.$$

It is seen from Eq. (3.5) that the solution of this equation will be obtained from Eq. (3.4) by the relation

$$Y(\omega_0) = X^*(-\omega_0). \quad (3.7)$$

We therefore have to solve only two systems of differential equations, namely systems (3.4) and (3.6). The above systems of equations have been solved using a Laplace transformation. The determinant of algebraic equations obtained after the Laplace transformation (Eqs. (3.4)) is

$$\begin{aligned} \Delta = & s^3 + 3\hbar\omega_0 s^2 + (2\hbar^2\omega_0^2 - \frac{3}{4}d_{ij}^2)s \\ & - \frac{3}{4}\hbar\omega_0 d_{ij}^2 - 2\hbar^2\omega_0^2 f_0^{(ij)} + \frac{d_{ij}^3}{4}. \end{aligned} \quad (3.8)$$

Substituting the expression " $r - \hbar\omega_0$ " for " s ", one obtains the characteristic equation

$$r^3 + pr + q = 0, \quad (3.9)$$

where

$$p = -d_{ij}^2(\varepsilon_{ij}^2 + \frac{3}{4}), \quad (3.9a)$$

$$q = \frac{d_{ij}^3}{2}(\frac{1}{2} - \varepsilon_{ij}^2 F_0^{(ij)}), \quad (3.9b)$$

$$\varepsilon_{ij} = \frac{\hbar\omega_0}{d_{ij}}. \quad (3.9c)$$

It is known from the theory of third order algebraic equations that if $\frac{q^2}{4} + \frac{p^3}{27}$ is negative, then the equation has three different real roots. It has been verified that this condition fulfilled in the case of interactions considered here. Therefore the solution of Eq. (3.9), in trigonometric form, may be written as

$$r_k^{(ij)} = d_{ij}\alpha_k^{(ij)} \quad (3.10)$$

where

$$\begin{aligned} \alpha_k^{(ij)} &= 2 \left(\frac{\varepsilon_{ij}^2}{3} + \frac{1}{4} \right)^{\frac{1}{2}} \cos \frac{\varphi_{ij} + 2(k-1)\pi}{3}, \\ \cos \varphi_{ij} &= -\frac{q}{2} \left(-\frac{p}{3} \right)^{-\frac{1}{3}}, \quad k = 1, 2, 3. \end{aligned}$$

Further calculations, involving an inverse Laplace transformation, yield the following results:

$$E_{ij} = \sum_{k=1}^3 a_k^{(ij)} e^{r_k^{(ij)}\beta} - a_0^{(ij)} e^{\hbar\omega_0\beta}, \quad (3.11)$$

$$I_{ij} = \frac{F_2^{(ij)}}{2} \sum_{k=1}^3 \frac{2\alpha_k^{(ij)} - 1}{(\alpha_k^{(ij)} - \alpha_l^{(ij)}) (\alpha_k^{(ij)} - \alpha_m^{(ij)})} e^{r_k^{(ij)\beta}}, \quad (3.12)$$

$$G_{ij} = \frac{F_1^{(ij)}}{4} \sum_{k=1}^3 \frac{2\alpha_k^{(ij)} + 2\varepsilon_{ij} - 1}{(\alpha_k^{(ij)} - \alpha_l^{(ij)}) (\alpha_k^{(ij)} - \alpha_m^{(ij)})} e^{r_k^{(ij)\beta}}, \quad (3.13)$$

where

$$a_0^{(ij)} = \frac{2\varepsilon_{ij}^2 F_0^{(ij)} + 3\varepsilon_{ij} - 1}{4(\alpha_1^{(ij)} - \varepsilon_{ij}) (\alpha_2^{(ij)} - \varepsilon_{ij}) (\alpha_3^{(ij)} - \varepsilon_{ij})}, \quad (3.13a)$$

$$a_k^{(ij)} = \frac{F_0^{(ij)} \alpha_k^{(ij)2} + (\varepsilon_{ij} F_0^{(ij)} - \frac{1}{2} F_0^{(ij)} + 2) \alpha_k^{(ij)} + \frac{1}{2} \varepsilon_{ij} (F_0^{(ij)} + 2) - 1}{4(\alpha_k^{(ij)} - \varepsilon_{ij}) (\alpha_k^{(ij)} - \alpha_l^{(ij)}) (\alpha_k^{(ij)} - \alpha_m^{(ij)})},$$

$$k \neq l \neq m.$$

The functions which satisfy Eq. (3.5) are

$$F_{ij}(\omega_0) = E_{ij}(-\omega_0), \quad (3.14)$$

$$H_{ij}(\omega_0) = G_{ij}^*(-\omega_0), \quad (3.15)$$

$$J_{ij}(\omega_0) = I_{ij}^*(-\omega_0). \quad (3.16)$$

Having solved equations (2.4) the system of equations (3.6) may now be easily solved. The characteristic equation of the system of algebraic equations, which arises from (3.6) after performing a Laplace transformation, is

$$s^3 + ps + q = 0 \quad (3.17)$$

where p and q are determined by (3.9a) and (3.9b). The roots of this equation are given by (3.10). However, the obtained values K_{ij} , L_{ij} , M_{ij} have the following form:

$$K_{ij} = \frac{F_{-1}^{(ij)}}{4} \sum_{k=1}^3 \frac{2\alpha_k^{(ij)} + 2\varepsilon_{ij} - 1}{(\alpha_k^{(ij)} - \alpha_l^{(ij)}) (\alpha_k^{(ij)} - \alpha_m^{(ij)})} e^{r_k^{(ij)\beta}}, \quad (3.18)$$

$$L_{ij} = \sum_{k=1}^3 \frac{a_k'^{(ij)}}{\alpha_k^{(ij)}} e^{r_k^{(ij)\beta}} + \frac{2\varepsilon_{ij}^2 F_0^{(ij)} - 1}{8\alpha_1^{(ij)} \alpha_2^{(ij)} \alpha_3^{(ij)}}, \quad (3.19)$$

$$M_{ij} = \frac{F_1^{(ij)}}{4} \sum_{k=1}^3 \frac{2\alpha_k^{(ij)} - 2\varepsilon_{ij} - 1}{(\alpha_k^{(ij)} - \alpha_l^{(ij)}) (\alpha_k^{(ij)} - \alpha_m^{(ij)})} e^{r_k^{(ij)\beta}}, \quad (3.20)$$

where

$$a_k'^{(ij)} = \frac{2F_0^{(ij)} \alpha_k^{(ij)2} - (F_0^{(ij)} + 2) \alpha_k^{(ij)} - 2\varepsilon_{ij}^2 F_0^{(ij)} + 1}{8(\alpha_k^{(ij)} - \alpha_l^{(ij)}) (\alpha_k^{(ij)} - \alpha_m^{(ij)})}, \quad k \neq l \neq m.$$

In the case when the external magnetic field is absent, the determinant (3.8) has the form

$$\Delta = s^3 - \frac{3}{4} d_{ij}^2 s + \frac{d_{ij}^3}{4}, \quad (3.21)$$

and characteristic equation has real roots, two of which are equal. These roots are

$$r_1^{(ij)} = r_3^{(ij)} = \frac{d_{ij}}{2}, \quad r_2^{(ij)} = -d_{ij}. \quad (3.22)$$

Now we have

$$E_{ij} = F_{ij} = \frac{2}{3} \left(\frac{F_0^{(ij)}}{4} + 1 \right) e^{\frac{d_{ij}}{2}\beta} - \frac{1}{3} \left(\frac{F_0^{(ij)}}{2} - 1 \right) e^{-d_{ij}\beta} - 1, \quad (3.23)$$

$$G_{ij} = H_{ij}^* = \frac{F_1^{(ij)}}{3} (e^{\frac{d_{ij}}{2}\beta} - e^{-d_{ij}\beta}), \quad (3.24)$$

$$I_{ij} = J_{ij}^* = \frac{2}{3} F_2^{(ij)} (e^{\frac{d_{ij}}{2}\beta} - e^{-d_{ij}\beta}). \quad (3.25)$$

Evidently the solution of Eq. (3.17), for $\omega_0 = 0$, is given by (3.22) too, and we obtain the following form of the functions K_{ij} , L_{ij} , M_{ij} :

$$K_{ij} = M_{ij}^* = H_{ij}, \quad (3.26)$$

$$L_{ij} = \frac{1}{3} \left(\frac{F_0^{(ij)}}{2} - 1 \right) e^{\frac{d_{ij}}{2}\beta} - \frac{1}{6} (F_0^{(ij)} + 1) e^{-d_{ij}\beta} + \frac{1}{2}. \quad (3.27)$$

In this way the exact form of the operator S_2 , as well as the exact form of the density operator for an arbitrary pair of interacting spins have been found. One can say, then, that the found density operator describes, in a general case, spin systems in approximation based on the exact form of the density operator describing the two-spin system. At the same time the simultaneous interaction of more than two spins is neglected.

4. Entropy, energy, specific heat, and magnetization

In this section we will calculate such quantities characterizing the considered system in thermodynamic equilibrium as the entropy, the internal energy, the specific heat and the magnetization. These quantities can be found from the partition function of the spin system. Let us calculate the matrix elements of the operator $\sigma(\beta)$ in the representation (see paper I)

$$|\alpha\rangle = |n_{\alpha 1} n_{\alpha 2} \dots n_{\alpha N}, n'_{\alpha 1} n'_{\alpha 2} \dots n'_{\alpha N}\rangle, \quad (4.1)$$

where $n_{\alpha i}$ and $n'_{\alpha i}$ refer to boson operators of type b and c , respectively. In the case of spins $I = \frac{1}{2}$, finding the matrix elements of the operator $\sigma(\beta)$ is not difficult. The diagonal

elements are (9.0) :

$$\sigma_{\alpha\alpha} \equiv \langle \alpha | \sigma | \alpha \rangle = \prod_{i=1}^N (1 + An_{\alpha i} + Bn'_{\alpha i}) + \sum_{i < j} [E_{ij}n_{\alpha i}n_{\alpha j} + F_{ij}n'_{\alpha i}n'_{\alpha j} - L_{ij}(n_{\alpha i}n'_{\alpha j} + n'_{\alpha i}n_{\alpha j})]. \quad (4.2)$$

The first and second derivatives of the matrix elements with respect to β are

$$R_{\alpha} \equiv \frac{\partial \sigma_{\alpha\alpha}}{\partial \beta} = \frac{\partial (\sigma_Z)_{\alpha\alpha}}{\partial \beta} + \sum_{i < j} \left[\sum_{k=1}^3 P_{\alpha k}^{(ij)} + \hbar \omega_0 (a_0^{(ij)}(-\omega_0) e^{-\hbar \omega_0 \beta} n'_{\alpha i} n'_{\alpha j} - a_0^{(ij)}(\omega_0) e^{\hbar \omega_0 \beta} n_{\alpha i} n_{\alpha j}) \right], \quad (4.3)$$

$$Q \equiv \frac{\partial R_{\alpha}}{\partial \beta} = \frac{\partial^2 (\sigma_Z)_{\alpha\alpha}}{\partial \beta^2} + \sum_{i < j} \left[\sum_{k=1}^3 r_k^{(ij)} P_{\alpha k}^{(ij)} - \hbar^2 \omega_0^2 (a_0^{(ij)}(\omega_0) e^{\hbar \omega_0 \beta} n_{\alpha i} n_{\alpha j} + a_0^{(ij)}(-\omega_0) e^{-\hbar \omega_0 \beta} n'_{\alpha i} n'_{\alpha j}) \right], \quad (4.4)$$

where

$$\begin{aligned} \frac{\partial (\sigma_Z)_{\alpha\alpha}}{\partial \beta} &= \frac{\hbar \omega_0}{2} \sum_{k=1}^N (e^{\frac{\hbar \omega_0}{2} \beta} n_{\alpha k} - e^{-\frac{\hbar \omega_0}{2} \beta} n'_{\alpha k}) \prod_{i \neq k} (1 + An_{\alpha i} + Bn'_{\alpha i}), \\ \frac{\partial^2 (\sigma_Z)_{\alpha\alpha}}{\partial \beta^2} &= \frac{\hbar^2 \omega_0^2}{4} \left\{ \sum_{k=1}^N \left[(e^{\frac{\hbar \omega_0}{2} \beta} n_{\alpha k} + e^{-\frac{\hbar \omega_0}{2} \beta} n'_{\alpha k}) \prod_{i \neq k} (1 + An_{\alpha i} + Bn'_{\alpha i}) \right. \right. \\ &+ \left. \sum_{i \neq k} (e^{\hbar \omega_0 \beta} n_{\alpha k} n_{\alpha i} + e^{-\hbar \omega_0 \beta} n'_{\alpha k} n'_{\alpha i} - n_{\alpha k} n'_{\alpha i} - n'_{\alpha k} n_{\alpha i}) \prod_{l \neq i} (1 + An_{\alpha l} + Bn'_{\alpha l}) \right] \Big\}, \\ P_{\alpha k}^{(ij)} &= r_k^{(ij)} \left[a_k^{(ij)}(\omega_0) n_{\alpha i} n_{\alpha j} + a_k^{(ij)}(-\omega_0) n'_{\alpha i} n'_{\alpha j} - \frac{a_k'^{(ij)}}{a_k^{(ij)}} (n_{\alpha i} n'_{\alpha j} + n'_{\alpha i} n_{\alpha j}) \right] e^{r_k^{(ij)} \beta}. \end{aligned}$$

Using thermodynamic dependences, one can now calculate interesting values. The internal energy of the spin system E , the entropy S , and the specific heat in a constant magnetic field C_B , can be expressed in the following manner:

$$Z = \text{Tr } \sigma(\beta), \quad (4.5)$$

$$E = -\frac{1}{Z} \sum_{\alpha} R_{\alpha}. \quad (4.6)$$

$$S = k(\ln Z + E\beta), \quad (4.7)$$

$$C_B = k\beta^2 \left(\frac{1}{Z} \sum_{\alpha} Q_{\alpha} - E^2 \right). \quad (4.8)$$

The expected values of the spin operators may be expressed by the matrix elements of the operator $\sigma(\beta)$. For the expected values of the I_z component of the spin we obtain the following expression:

$$\langle I_z \rangle = \frac{1}{2Z} \sum_{\alpha} \sum_{i=1}^N (n_{\alpha i} - n'_{\alpha i}) \sigma_{\alpha \alpha}. \quad (4.9)$$

In the formulas (4.5)—(4.9) the sum is taken over all states of the spin system.

5. Two-spin system

We will now consider, as a simplest case, a system of two identical spins in thermodynamic equilibrium. It follows, from the results of previous sections of this paper, that in the case of two spins $I = \frac{1}{2}$, subjected to constant magnetic field and dipolar interaction, we obtain the exact form of the partition function and of the density operator. Using representation (4.1) to calculate the matrix elements of the operator $\sigma(\beta)$, we find from (4.2) the partition function, which after respective transformations can be written as

$$Z = 2 + C_1 e^{k\omega_0\beta} + C_2 e^{-k\omega_0\beta} + \sum_{i=1}^3 a_i e^{r_i\beta} + b, \quad (5.1)$$

where

$$C_1(\omega_0) = C_2(-\omega_0) = 1 - a_0^{(12)}, \quad (5.1a)$$

$$a_i = \frac{6\alpha_i^3 + (2\varepsilon^2 F_0 - 1)(3\alpha_i^2 - \varepsilon^2)}{4\alpha_i(\alpha_i^2 - \varepsilon^2)(\alpha_i - \alpha_k)(\alpha_i - \alpha_l)}, \quad k \neq l \neq i,$$

$$b = \frac{1 - 2\varepsilon^2 F_0}{4\alpha_1\alpha_2\alpha_3}, \quad r_i \equiv r_i^{(12)}, \quad \alpha_i \equiv \alpha_i^{(12)}, \quad F_0 \equiv F_0^{(12)}, \quad \varepsilon \equiv \varepsilon_{12}.$$

The exact formulas for the energy, the entropy and the specific heat in the constant magnetic field are determined by (4.6)—(4.8) with first and second derivatives of the partition function given as

$$\sum_{\alpha} R_{\alpha} = d[\varepsilon(C_1 e^{k\omega_0\beta} - C_2 e^{-k\omega_0\beta}) + \sum_{k=1}^3 a_k \alpha_k e^{r_k\beta}], \quad (5.2)$$

$$\sum_{\alpha} Q_{\alpha} = d^2[\varepsilon^2(C_1 e^{k\omega_0\beta} + C_2 e^{-k\omega_0\beta}) + \sum_{k=1}^3 a_k \alpha_k^2 e^{r_k\beta}]. \quad (5.3)$$

The expected values of components of the spin operator are

$$\langle I_x \rangle = \frac{3\varepsilon}{Z} \sin \theta \cos \theta \cos \Phi \sum_{i=1}^3 \frac{e^{r_i \beta}}{(\alpha_i - \alpha_k)(\alpha_i - \alpha_l)}, \quad (5.4)$$

$$\langle I_y \rangle = \langle I_x \rangle \operatorname{tg} \Phi, \quad (5.5)$$

$$\begin{aligned} \langle I_z \rangle &= \frac{1}{Z} (e^{\hbar\omega_0\beta} - e^{-\hbar\omega_0\beta} + E_{12}(\beta) - F_{12}(\beta)) \\ &= \frac{1}{Z} (C_1 e^{\hbar\omega_0\beta} - C_2 e^{-\hbar\omega_0\beta} + \sum_{i=1}^3 a_i'' e^{r_i \beta}), \end{aligned} \quad (5.6)$$

where

$$a_i'' = \frac{\varepsilon(2F_0\alpha_i^2 + 3\alpha_i - 1)}{2(\alpha_i^2 - \varepsilon^2)(\alpha_i - \alpha_k)(\alpha_i - \alpha_l)}, \quad i \neq k \neq l. \quad (5.6a)$$

The components of magnetization perpendicular to the external magnetic field are, in general, different from zero. In the field $B_0 \neq 0$ all components are zero for temperatures $T = \pm\infty$ ($\beta = 0$), because then

$$\sum_{i=1}^3 \frac{1}{(\alpha_i - \alpha_k)(\alpha_i - \alpha_l)} = 0$$

and

$$E_{12}(0) = F_{12}(0) = 0.$$

However, when the temperature approaches ± 0 the magnetization approaches non-exponentially the respective maximal values. The transversal magnetization, for a given magnetic field and θ, Φ , shows the same dependence on temperature in region of positive and negative spin temperatures on the contrary to the longitudinal magnetization which changes sign when the temperature changes sign. Without an external magnetic field the spin system does not show the magnetization. It immediately follows from formulas (5.4—5.6a) and (3.13a), (5.1a). Substituting $\varepsilon = 0$ we get $\langle I_x \rangle = \langle I_y \rangle = 0$ and

$$\langle I_z \rangle = \frac{1}{Z} (C_1 - C_2) = 0$$

because $C_1 = C_2$. In this case the partition function, the energy, and specific heat may be written in a very simple form

$$Z = 1 + 2e^{\frac{d}{2}\beta} + e^{-d\beta}, \quad (5.7)$$

$$E = \frac{d}{Z} (e^{-d\beta} - e^{\frac{d}{2}\beta}), \quad (5.8)$$

$$C_B = \frac{kd^2\beta^2}{2Z^2} (e^{\frac{d}{2}\beta} + 9e^{-\frac{d}{2}\beta} + 2e^{-d\beta}). \quad (5.9)$$

The variation with $-1/T$ of the internal energy, the specific heat, and the entropy of the spin system, for the case $\varepsilon = 1$, are presented in the figures. Spin temperatures are measured in units of k/d . If we take into account, for instance, nuclei of fluorine with a near-neighbor separation of 2.725×10^{-10} m (as in CaF_2) and protons distant about 1.6×10^{-10} m (as

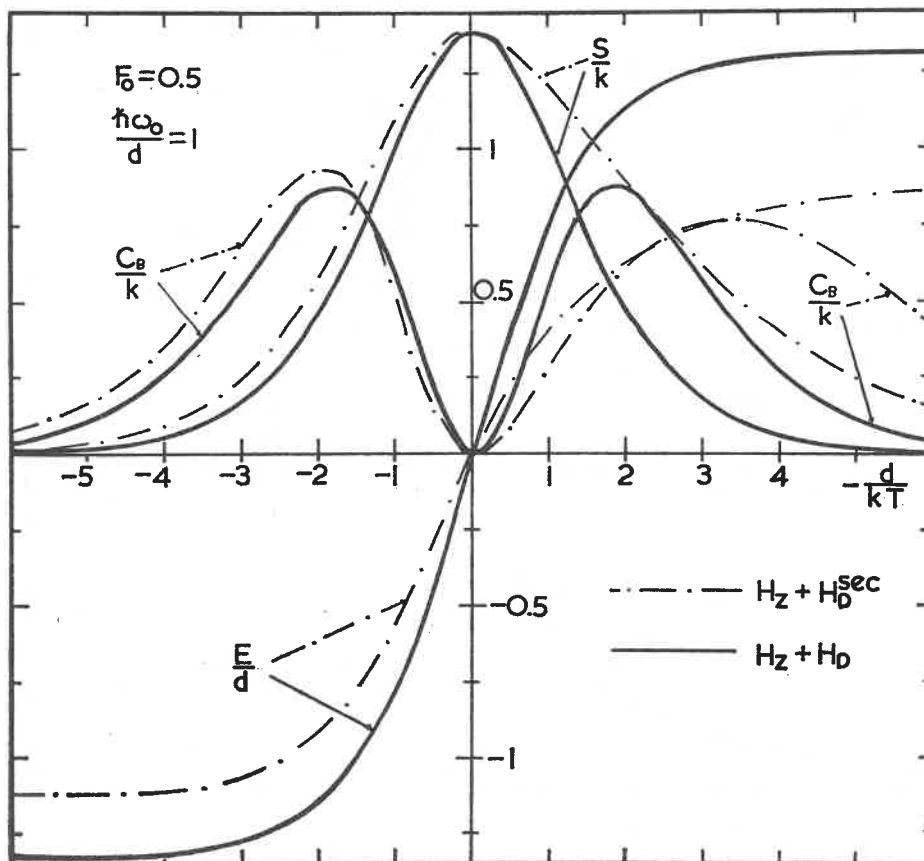


Fig. 1. Variation with inverse temperature of the entropy S , the energy E and the specific heat C_B of two-spin system as calculated for a low magnetic field ($\hbar\omega_0/d = 1$) and the angle $\pi/4$ between B_0 and r_{12} ($F_0 = 0.5$). The solid lines represent exact values (formulas (4.7), (5.7)–(5.9) of this paper) and dotted lines approximate ones obtained from the secular part of the dipolar Hamiltonian only

in water molecules) then the value ε will be equal to 1 in magnetic fields 1.31×10^{-4} T and 6.89×10^{-4} T, respectively. The graphs are made for two cases, namely when the direction of the vector B_0 is inclined at an angle $\pi/4$ to the internuclear displacement vector r ($F_0 = 0.5$), and when it is perpendicular to r ($F_0 = -1$). We see that variation with spin temperature of the discussed magnitudes for $F_0 = 0.5$ (Fig. 1) is identical in the regions of positive and negative temperatures. All terms of a dipolar coupling Hamiltonian are effective. Some asymmetry, with respect to infinite temperature, appears for $F_0 = -1$

(Fig. 2). Here the terms of Hamiltonian, which are responsible for transitions determined by quantum conditions $\Delta m = \pm 1$, are ineffective. Likely, though this asymmetry has another character, is in the case $F_0 = 2$ (B_0 is parallel to r) where nonsecular terms of the Hamiltonian are ineffective. The greater ε is, the better the internal dipolar coupling will

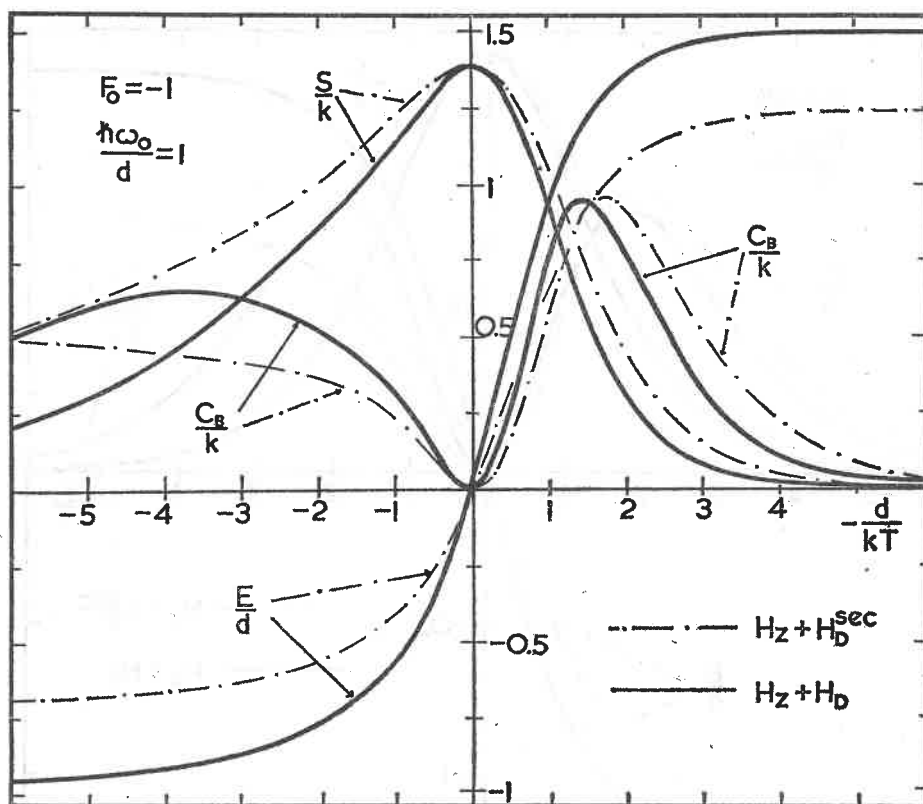


Fig. 2. Variation with inverse temperature of the entropy S , the energy E and the specific heat C_B of the two-spin system in a low magnetic field ($\hbar\omega_0/d = 1$). The angle between B_0 and r_{12} has been taken equal to $\pi/2$ ($F_0 = -1$). The full and dotted lines indicate the same as in Fig. 1

be described by the secular part of the Hamiltonian. It was calculated that for $\varepsilon = 10$ results are practically identical to those obtained from the secular part of the dipolar coupling Hamiltonian.

For comparison with exact results, in the figures are also additionally plotted the numerical values obtained, taking into consideration only the secular part of the dipolar Hamiltonian (dotted lines). For the above mentioned nuclei of fluorine the errors of this approximation for $F_0 = 0.5$ in the energy, the specific heat and the entropy at positive temperature 2.5×10^{-6} K ($d/kT = 0.1$) reaches 31.1%, 37.9% and 0.14%, respectively, however at the same negative temperature 41.2%, 42.2% and 0.14%, respectively. On the contrary, for the considered protons in an analogous situation ($F_0 = 0.5$, $d/kT = 0.1$)

the same values of errors appear at a temperature 1.4×10^{-5} K. These differences in temperatures result from a distinct dipolar constant. At still lower temperatures positive as well as negative, the errors are greater reaching at one point a maximum.

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REFERENCES

- Goldman, M., *Spin Temperature and Nuclear Magnetic Resonance in Solids*, Clarendon Press, Oxford 1970.
- Jeener, J., in *Advances in Magnetic Resonance*, 3, Academic Press, New York 1968, p. 206.
- Nosel, W., *Acta Phys. Pol.* A50, 433 (1976).