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The Thermodynamic Theory of Magnetic Relaxation

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A thermodynamic consideration of magnetic relaxation is presented. With the aid of a symmetry principle of the kinetic coefficients, the time dependence of the magnetization and the internal temperature of the spin system has been found. Consideration is given to the conditions under which the internal spin-equilibrium is achieved far more rapidly than the equilibrium of the spin system with the lattice.

WE consider a condensed system (crystal, amorphous solid, liquid), which contains nuclei possessing spins. If initially the system of nuclear spins is not in thermal equilibrium with the other degrees of freedom of the body (with the "lattice"), then equilibrium is established within a certain length of time.

During the past few years, relaxation times of nuclear spins have been determined in various substances with the help of a study of nuclear magnetic resonance. We note that, in accord with experiment, the time path of approach to equilibrium has an exponential character (the law of the approach of nuclear magnetization to its equilibrium value has been determined in several experiments): The characteristic relaxation time is known as the relaxation time of the nuclear spins with the lattice.

In the case of paramagnetic relaxation the picture is much more complex: according to experiment, two relaxations occur, known as the spin-lattice and internal spin relaxations; the latter are observed only at high frequencies. Evidently two relaxations take place in the nuclear case also, but in the experiments which have been carried out at the present time, one of them (the internal spin) is not observed*.

Thermodynamic consideration of magnetic relaxation was first treated by Casimir and DuPre[1] under the assumption that internal equilibrium always exists in the spin system. A more general thermodynamic consideration was given in the researches of Shaposhnikov[2,3]. However, in these researches it was tacitly assumed that the internal relaxation time was much less than the time of spin-lattice relaxation. Although this is usually the case, it is nevertheless of interest to give a more general thermodynamic consideration of magnetic relaxation, making use of a basic principle of physical kinetics---the principle of the symmetry of the kinetic coefficients of Onsager. We also note that it is assumed in references 2,3 that the heat transferred from the lattice to the spin-system is proportional to the temperature difference which generally speaking, does not even occur (see below).

The consideration which we give is correct both for paramagnetic and for nuclear magnetic relaxation; in the latter case we shall assume that there is no strong electronic paramagnetism (i.e., our consideration will not be applicable to nuclear magnetic relaxations in paramagnetic salts and even less, to ferromagnetics).

We consider the case of a body which possesses magnetic isotropy; we shall consider the external magnetic field applied to the body to be homogeneous (the direction of the field we take to be the z direction) and constant in time. As a consequence of the fact that the direction of the external field is an axis of axial symmetry (thanks to the magnetic isotropy of the body), it is evident that the relaxation of the components of magnetization perpendicular to the field (in the case of nuclear magnetic relaxation, by magnetization we understand nuclear magnetization) M_x and M_y are independent of the relaxation of the longitudinal component M_z (which, for brevity, will be denoted by M) and the internal temperature of the spin system T.

In the present work we give the solution of the

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* To avoid misunderstanding we note that by internal spin relaxation time we mean the time of establishing the internal equilibrium in the spin system; in contradistinction, in some researches in nuclear magnetism there is introduced the spin-spin relaxation, which is the inverse of the absorption line width.

[1] H. B. G. Casimir and F. K. Du Pre, Physica 5, 507 (1938)

[2] I. G. Shaposhnikov, J. Exper. Theoret. Phys. USSR 18, 533 (1948)

[3] I. G. Shaposhnikov, J. Exper. Theoret. Phys. USSR 19, 225 (1949)

following problem: the initial state of the system is given with the aid of the initial values T_0 (the temperature of the lattice), T and M; it is required to find the time path of approach of these quantities to their equilibrium values. In this work we are not interested in the relaxations of the magnetization components perpendicular to the field.

We use a thermodynamic method; for its application it is necessary that the time required for the establishment of a state with definite T_0, T and M would be sufficiently small in comparison with the time of establishment of complete equilibrium (i.e., we assume that three time intervals are small: the time for the lattice to reach its equilibrium state, the time for the spins to reach equilibrium relative to the internal degrees of freedom, and the time for the spins to reach equilibrium relative to the Zeeman levels in the external field). We introduce the quantities m and τ

$$m = M - M_0, \quad \tau = \frac{1}{T} - \frac{1}{T_0}, \tag{1}$$

where M_0 is the equilibrium magnetization at temperature T_0. We decompose $\dot m$ and $\dot\tau$ (the dot denotes the time derivative) into powers of m and τ, and limit ourselves to linear terms:

$$\dot m = -\alpha m - \beta\tau, \quad \dot\tau = -\gamma m - \varepsilon\tau, \tag{2}$$

where the coefficients α, β, γ, and ϵ depend on the intensity of the external field and on the equilibrium temperature. With the substitutions $H \to -H$, $m \to -m$, $\tau \to \tau$ Eqs. (2) can be transformed into themselves; hence, we conclude that

$$\alpha(-H) = \alpha(H), \qquad \varepsilon(-H) = \varepsilon(H), \tag{3}$$
$$\beta(-H) = -\beta(H), \qquad \gamma(-H) = -\gamma(H).$$

We solve Eqs. (2) by taking m and τ proportional to $\exp(-\lambda t)$; for λ we obtain two values:

$$\lambda_\pm = {}^1\!/_2(\alpha + \varepsilon) \pm {}^1\!/_2\sqrt{(\alpha - \varepsilon)^2 + 4\beta\gamma}. \tag{4}$$

The real parts of λ_+ and λ_- must be positive; therefore,

$$\alpha + \varepsilon > 0, \quad \alpha\varepsilon - \beta\gamma > 0. \tag{5}$$

For m and τ we obtain solutions with two relaxations

$$m = C_+ \exp(-\lambda_+ t) + C_- \exp(-\lambda_- t), \tag{6}$$

$$\tau = \frac{1}{\beta}\{(\lambda_+ - \alpha) C_+ \exp(-\lambda_+ t) + (\lambda_- - \alpha) C_- \exp(-\lambda_- t)\}.$$

Among the quantities α, β, γ and ϵ there must be established one relation which makes use of the principle of the symmetry of kinetic coefficients[4,5]; for this purpose we introduce the equations (S = entropy of the entire system):

$$X_m = -\partial S / \partial m, \quad X_\tau = -\partial S / \partial\tau.$$

It is easy to obtain

$$\dot X_m = (\alpha S_{mm} + \gamma S_{m\tau}) m + (\beta S_{mm} + \varepsilon S_{m\tau})\tau, \tag{7}$$
$$\dot X_\tau = (\alpha S_{\tau m} + \gamma S_{\tau\tau}) m + (\beta S_{\tau m} + \varepsilon S_{\tau\tau})\tau.$$

The second derivatives of the entropy S_{mm}, $S_{m\tau}$, etc., in Eq. (7) are taken at full equilibrium.

Further, applying the principle of the symmetry of the kinetic coefficients, (assuming that m changes sign upon reversal of direction of the time, but τ does not change), we obtain

$$\beta S_{mm} - \gamma S_{\tau\tau} = (\alpha - \varepsilon) S_{\tau m}. \tag{8}$$

We shall assume that we are dealing with an ideal paramagnetic, so that we have for the heat capacity of the spin system (at constant magnetization) and for M_0

$$C = A / T^2, \tag{9}$$
$$M_0 = aH / T_0, \tag{10}$$

where A and a are constants (a = Curie's constant). Since we consider the case in which there is no spin system equilibrium between the internal and external (Zeeman) degrees of freedom, then, generally speaking,

$$M \neq aH / T.$$

In the work of Shaposhnikov[2] expression is found for the non-equilibrium thermodynamic potential of the spin system, in particular for an ideal paramagnetic substance,

$$\Phi = -\frac{A}{2T} - HM + \frac{TM^2}{2a}.$$

It is then easy to obtain the differential entropy of the spin system:

$$dS' = \frac{C}{T}\,dT - \frac{M}{a}\,dM.$$

Thus, for the entire system (lattice plus spin system), we obtain the second law of thermodynamics in the form (C_0 = heat capacity of the lattice):

$$dS = \frac{C_0}{T_0}\,dT_0 + \frac{C}{T}\,dT - \frac{M}{a}\,dM, \tag{11}$$

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[4] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, GITTL, Moscow, 1951

[5] S. R. deGroot, *Thermodynamics of Irreversible Processes*, North Holland Publishing Company, Amsterdam, 1952

according to the first law we have

$$C_0 dT_0 + C dT - H dM = 0 \tag{12}$$

For the m and τ derivatives of S we get

$$S_m = -\frac{1}{a}\frac{\partial M}{\partial m} m + C\frac{\partial T}{\partial m}\tau,$$

$$S_\tau = -\frac{1}{a}\frac{\partial M}{\partial \tau} m + C\frac{\partial T}{\partial \tau}\tau$$

(the coefficients of m and τ are evaluated at equilibrium). We therefore get for the second derivatives of the entropy, taken at complete equilibrium,

$$S_{mm} = -\frac{1}{a}\frac{\partial M}{\partial m}, \quad S_{\tau\tau} = C\frac{\partial T}{\partial \tau}, \tag{13}$$

$$S_{\tau m} = -\frac{1}{a}\frac{\partial M}{\partial \tau} = C\frac{\partial T}{\partial m}.$$

Making use of Eqs. (1) and (12), it is easy to obtain, after several transformations,

$$\frac{\partial M}{\partial m} = \frac{(C_0 + C)\,T^2}{G}, \quad \frac{\partial T}{\partial \tau} = -\frac{(C_0 T^2 + aH^2)\,T^2}{G}, \tag{14}$$

$$\frac{\partial M}{\partial \tau} = -aC\frac{\partial T}{\partial m} = -\frac{aCHT^2}{G},$$

where

$$G = (C_0 + C)\,T^2 + aH^2. \tag{15}$$

Thus, for an ideal paramagnetic substance, Eq. (8) takes the form

$$aC(C_0 T^2 + aH^2)\gamma - (C_0 + C)\beta = aCH(\alpha - \varepsilon). \tag{16}$$

Equations (4), (6) and (16) give the solution of the problem under discussion for an ideal paramagnetic which has magnetic isotropy.

In particular, we consider the case in which the interaction of the lattice with the internal degrees of freedom of the spin-system is much stronger than its interaction with the external degrees of freedom of the spin system; in such a case we can assume that the amount of heat dQ transferred from the lattice to the spin system in the time dt is

$$dQ = \varkappa(T_0 - T)\,dt, \tag{17}$$

where κ is the coefficient of thermal conduction between the lattice and the spin system]in the general case Eq. (17) would also contain terms proportional to $(M_0 - M)\,dt$]. According to Shaposhnikov[2] (who considered the case in which the departure from equilibrium is small), we then have

$$C\dot{T} - H\dot{M} = \varkappa T^2\tau.$$

Making use of Eqs. (2) and (14), and taking into account the fact that the latter equation must hold for the m and τ derivatives, it is easy to obtain

$$\gamma = -(H / CT^2)\alpha, \tag{18}$$

$$H\beta + CT^2\varepsilon = (G / C_0)\varkappa. \tag{19}$$

From (16), (18) and (19) we can easily obtain the relations

$$\beta = -aH\left(\alpha - \frac{\varkappa}{C_0}\right), \tag{20}$$

$$\varepsilon = \frac{aH^2}{CT^2}\alpha + \frac{C_0 + C}{C_0 C}\varkappa, \tag{21}$$

$$\alpha\varepsilon - \beta\gamma = \frac{G}{C_0 T^2}\frac{\varkappa}{C}\alpha. \tag{22}$$

It follows from Eqs. (5), (21) and (22) that the following inequalities must hold:

$$\alpha > 0, \quad \varepsilon > \frac{aH^2}{CT^2}\alpha, \quad \varepsilon > \frac{C_0 + C}{C_0 C}\varkappa. \tag{23}$$

Thus, to satisfy the condition (17) we have three independent relations among the coefficients α, β, γ, and ϵ [e.g., Eqs. (18), (19) and (21)]. Let

$$C_0 \gg C, \quad C_0 \gg aH^2 / T^2. \tag{24}$$

In the nuclear case, the conditions (24) prevail for all fields and temperatures currently attainable; in the paramagnetic case, (24) holds for temperatures above 1° K. In such a case, Eqs. (20), (21) and (22) take on the form

$$\beta = -aH\alpha, \tag{25}$$

$$\varepsilon = (aH^2 / CT^2)\alpha + (\varkappa / C), \tag{26}$$

$$\alpha\varepsilon - \beta\gamma = (\varkappa / C)\alpha. \tag{27}$$

Now suppose that the following condition is satisfied, in addition to (17) and (24):

$$\alpha + \varepsilon \gg \varkappa / C \tag{28}$$

or, what amounts to the same thing,

$$\alpha \gg (\varkappa T^2 / A)(1 - F), \tag{29}$$

where

$$F = aH^2 / (A + aH^2). \tag{30}$$

In this case, Eq. (4) takes the form

$$\lambda_+ = \alpha + \varepsilon; \tag{31}$$

$$\lambda_- = (\varkappa / C)\,\alpha / (\alpha + \varepsilon) \ll \lambda_+. \tag{32}$$

We thus obtain one fast relaxation time ($1/\lambda_+$) and one slow one ($1/\lambda_-$). According to Eq. (6), after a lapse of time much greater than $1/\lambda_+$,

$$m = C_- \exp(-\lambda_- t), \quad \tau = C_- \frac{\lambda_- - \alpha}{\beta} \exp(-\lambda_- t),$$

and we obtain [keeping in mind that, by (29) and (32), $\lambda_- \ll \alpha$]

$$m/\tau = -\beta/\alpha = aH. \tag{33}$$

On the other hand it is easy to see that the ratio m/τ must be just the same if $M = aH/T$ (i.e., if there is equilibrium between the internal and external degrees of freedom of the spin system).

We thus see that if the conditions (17), (24) and (28) are satisfied, then the picture of magnetic relaxation must be the following: first, after a short time [relaxation time $\rho_s = (1 - F)/\alpha$] internal equilibrium is achieved in the spin-system; the equilibrium of the spin-system with the lattice is achieved more slowly [relaxation time $\rho_l = A/(1 - F)\,\kappa T^2 = C/\kappa(1 - F)$]*. Since, by experiment, the picture of magnetic relaxation is in most cases exactly the same, we must conclude that the conditions (17) and (28) are ordinarily satisfied.

In conclusion, I wish to express my gratitude to Academician L. D. Landau for his constant interest in the present research.

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* If the weaker condition $(\kappa/C)\,\alpha \ll (\alpha + \epsilon)^2$ is satisfied rather than (28), then Eqs. (31) and (32) remain valid, but if $H > \sqrt{A/a}$, Eq. (33) is not obtained, since the inequality $\lambda_- \ll \alpha$ is not satisfied. In this case, we obtain one fast and one slow relaxation as before, but the internal spin equilibrium is achieved only along with the establishment of equilibrium of the spin system with the lattice.

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