Contribution to the theory of nonequilibrium statistical operators

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(Submitted June 6, 1976)
Zh. Eksp. Teor. Fiz. **71**, 2330–2337 (December 1976)

A scheme is proposed for deriving the exact equations of motion of macroscopic quantities that characterize nonequilibrium processes in a large system. It is shown that in the high-temperature approximation this scheme yields linear differential equations. To illustrate the application of the proposed scheme, longitudinal relaxation in a nuclear spin system isolated from the lattice is analyzed.

1. We consider in this paper a quantumwise large physical system described in the most general fashion with the aid of a statistical operator $\rho(t)$ that satisfies the Newmann equation

$$\dot{\rho}(t) = -iL(t)\rho(t), \tag{1}$$

where $L(t)$ is the Liouville operator and we put $\hbar = 1$ (we shall use the same notation for operators of abstract Hilbert space and for the operators on them). Many macroscopic processes that take place in a large system can be characterized by the time dependences of macroscopic quantities $F_m(t)$, which are mean values $\bar{f}_m$ of microscopic quantities f_m pertaining to the considered system and having time-independent operators

$$F_m(t) = \bar{f}_m = \mathrm{Sp}\,\rho(t)f_m \tag{2}$$

(the same symbols will be used for the physical quantities and for their operators); here m denotes in the general case an aggregate of discrete and continuous indices j and ν. In the case of equilibrium processes, $\rho(t)$ is given at each instant of time (and possibly at each point of space) by a Gibbs expression with the values of all the quantities contained in it corresponding to this instant (and to this point) (in this case one speaks of local equilibrium). In the case of nonequivalent processes, it is customary to call $\rho(t)$ the nonequilibrium statistical operator (NSO).

There exist various schemes for constructing the NSO and for using it to obtain equations of motion from which to determine the quantities $F_m(t)$. A widely used scheme was proposed by Zubarev (see[1] and the literature cited therein). In this scheme, the equations of motion used to determine the quantities $F_m(t)$ are integro-differential, and remain such even in the high-temperature approximation; their approximate replacement by differential equations, which is employed in applications, is justified by a very special choice of the quantities f_m, namely, these quantities are chosen to be quasi-integrals of the motion (it is sometimes even stated[2] that the choice of the quantities f_m is the only one possible within the framework of the method of[1]). Yet the NSO can be constructed in a way that leads to exact equations of motion for the determination of $F_m(t)$, which turn out to be linear differential equations in the high-temperature approxi-

mation, without the aforementioned restriction on the choice of the values of f_m. We formulate below this method of constructing the NSO and obtain the corresponding exact equations of motion for macroscopic quantities (Secs. 2–4), which are subsequently adapted to the high-temperature approximation (Sec. 5). To illustrate the proposed general scheme, the obtained equations are used to solve one concrete problem of magnetic relaxation, which is also of independent interest, namely the problem of the longitudinal relaxation of the macroscopic magnetization of a nuclear spin system insulated from the lattice (Secs. 6 and 7).

2. The methods mentioned in Sec. 1 are characterized by the use of a certain operator $\sigma(t)$ and of certain macroscopic quantities $\beta_m(t)$, which are in a definite sense conjugated with the quantities $F_m(t)$. The aggregate of the quantities $\beta_m(t)$ is the solution of the following system of equations:

$$\mathrm{Sp}\,\sigma(t)f_m = F_m(t), \tag{3}$$

where

$$\sigma(t) = \left\{ \mathrm{Sp}\,\exp\left[-\sum \beta_m(t)f_m\right]\right\}^{-1} \exp\left[-\sum \beta_m(t)f_m\right], \tag{4}$$

and the meaning of the symbol $\sum$ depends on which indices are designated by m (see Sec. 1); it is assumed that the solutions exist and are unique. Thus, the quantities $\beta_m(t)$ and the operator $\sigma(t)$ are introduced jointly by relations (3) and (4). In the general case, which we presently have in mind, $\sigma(t)$ is not a statistical operator and its subsequent use does not mean that the present analysis is restricted to the case of local equilibrium or proximity to this equilibrium.

From (2)–(4) follows directly a relation that will play an important role later on. This relation was used by Robertson in his theory of nonequilibrium processes[3]

$$\dot{\sigma}(t) = P(t)\dot{\rho}(t), \tag{5}$$

where $P(t)$ is an operator whose action on the operator of any microscopic quantity pertaining to the considered system is determined by the rule

$$P(t)g = \sum \frac{\partial \sigma(t)}{\partial F_m(t)}\,\mathrm{Sp}\,f_m g, \tag{6}$$

where the meanings of the signs ∂ and $\sum$ are determined by the character of the indices designated by m (see Sec. 1); $\sigma(t)$ can be regarded as a function of the quantities $F_m(t)$ because they are connected with the quantities $\beta_m(t)$ by relation (3).

3. The proposed method of constructing and using the NSO is based on relation (5). It calls to invoking the formal integral of Eq. (1):

$$\rho(t) = \mathcal{L}(t)\rho(0), \tag{7}$$

where the operator $\mathcal{L}(t)$ is determined by the equation of motion and by the initial condition

$$\dot{\mathcal{L}}(t) = -iL(t)\mathcal{L}(t), \quad \mathcal{L}(0) = 1. \tag{8}$$

4. We integrate (5) with respect to time from 0 to t. The result includes the initial value $\sigma(0)$ of the operator $\sigma(t)$. We assume that

$$\sigma(0) = \rho(0), \tag{9}$$

i.e., that the statistical operator of the considered system is of the form (4) at the initial instant. The meaning of this initial condition lies in the fact that at the initial instant of time the state of the system is macroscopically specified (see also[4] concerning this question); in particular, when the f_m are additive quasi-integrals (or integrals) of the motion, Eq. (9) is valid if the system is in local equilibrium (or in equilibrium) at the initial instant; this corresponds to a large number of real situations of physical interest. Using (9) and (7), we can write down the result of the aforementioned integration of (5) in the form

$$\rho(t) = \mathcal{L}(t)\mathcal{N}(t)\sigma(t), \tag{10}$$

$$\mathcal{N}(t) = \sum_{n=0}^{\infty} \left[-\int_0^t dt' P(t')\mathcal{L}(t') \right]^n. \tag{11}$$

Finally, differentiating (10) with respect to time with allowance for (7) and using (2), we obtain the equations

$$\dot{F}_m(t) = \mathrm{Sp}\, f_m \dot{\mathcal{L}}(t)\mathcal{N}(t)\sigma(t), \tag{12}$$

which, after using the relations (3) between the $\beta_m(t)$ and $F_m(t)$, constitute a new set of equations of motion with which to find the quantities $F_m(t)$ (these relations elucidate also the auxiliary character of the quantities $\beta_m(t)$). If $\rho(0)$ is assumed to be arbitrary, then we obtain for $F_m(t)$ equations of motion that differ from (12) only in that the right-hand side will contain not $\sigma(t)$ but $\sigma(t) + [\rho(0) - \sigma(0)]$.

In the derivation of (12) we used only the Neumann equation (1) and the initial condition (9), and made no approximations whatever. Nor did we impose any restrictions on the choice of the quantities f_m. It is clear that within each concrete group of problems these quantities must be chosen such that the corresponding quantities $F_m(t)$ can be taken to be the internal macroscopic parameters of the considered system, i.e., that they comprise besides the external macroscopic parameters of the system also its macroscopic coordinates (the

complete set of mutually independent macroscopic quantities needed for the analysis). This choice always means assumption of one hypothesis or another. It makes it possible to assume (9) without loss of generality (cf. [4]). In practice it usually turns out that the operators of the so-chosen quantities f_m enter in the following manner in the Hamiltonian of the considered system:

$$\mathcal{H}(t) = \sum \alpha_m(t) f_m, \tag{13}$$

where those among the macroscopic quantities $\alpha_m(t)$ which are specified functions of the time and differ from unity characterize the external actions on the system; such a breakdown of the Hamiltonian into parts is referred to as a breakdown of the system into subsystems j with Hamiltonians $\int d\nu\, \alpha_{j\nu}(t) f_{j\nu}$. If this is the case, then the quantities $\alpha_m^{-1}(t)\beta_m(t)$ are the reciprocal temperatures of the subsystems determined by the breakdown (13)[3,5]; we emphasize that the concept of temperature is used here in its general sense, meaning that it characterizes both equilibrium and non-equilibrium states.

5. The equations of the system (12) (as well as all other exact equations of motion obtained for the macroscopic quantities by the molecular approach) can be used in practice only in one approximation or another. We consider now one such approximation which is frequently convenient.

Let the quantities f_m correspond to parts of the Hamiltonian of the considered system in the sense (13), and assume that in this system we can separate one part $(m = 0)$, which is the thermostat for the aggregate of the remaining parts $(m \neq 0)$ in which the processes are of interest to us. Let the quantities $\beta_{m\neq0}(t)$ be small in the sense that we can confine ourselves to terms of zeroth and first order in the expansion of the operator $\sigma(t)$ in powers of these quantities (high-temperature approximation). Let also the quantities $f_{m\neq0}$ be such that their operators satisfy the relations

$$\langle f_m \rangle_0 = 0, \quad \langle f_m \tilde{f}_{m'} \rangle_0 = \langle f_m f_{m'} \rangle_0 \delta_{mm'}, \tag{14}$$

$$\langle g_0 \rangle \equiv \mathrm{Sp}\, \sigma_0 g, \tag{15}$$

where σ_0 is the equilibrium statistical operator of the thermostat

$$\sigma_0 = [\mathrm{Sp}\, \exp(-\beta_0 f_0)]^{-1} \exp(-\beta_0 f_0), \tag{16}$$

$$\tilde{f}_m = \int_0^1 dx\, \sigma_0^x f_m \sigma_0^{-x}. \tag{17}$$

If f_m is chosen in correspondence with (13), satisfaction of (15) is ensured by the Hamiltonians of many actual problems. On the other hand, if relations (15) do not hold for some choice of f_m, it is possible, by appropriate origin shifts and orthogonalization, to obtain new f_m for which these relations are satisfied.

The aforementioned expansion of the operator $\sigma(t)$ yields in the high-temperature approximation

$$\sigma(t) = \left[1 - \sum_{m\neq0} \beta_m(t) \tilde{f}_m \right] \sigma_0. \tag{18}$$

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By virtue of (18), the connections given by (3) between the quantities $F_{m \neq 0}(t)$ and $\beta_{m \neq 0}(t)$ assume the simple form

$$F_m(t) = -\langle f_m \bar{f}_m \rangle_0 \beta_m(t), \tag{19}$$

and the operator P, now defined by the rule

$$Pg = \sum_{m \neq 0} \frac{\bar{f}_m \sigma_0}{\langle f_m \bar{f}_m \rangle_0} \operatorname{Sp} f_m g, \tag{20}$$

ceases to depend on the time. Accordingly, the equations of motion (12) become linear differential equations.

6. By way of a concrete application of the general scheme described in Secs. 2–5, we consider the relaxation in a homogeneous constant applied magnetic field **H** of the component longitudinal with respect to this field of the macroscopic magnetic moment **M** of a system, insulated from the lattice, of identical nuclear spins of an isotropic sample (in the absence of an applied field). Assume that at the initial instant, taken to be zero, there is no equilibrium, but **M** and **H** are directed along the same straight line; then **M** has no tranverse components also when $t > 0$. We write down the Hamiltonian of the system in the form

$$\mathscr{H} = f_1 + f_2, \quad f_1 = -H\mathscr{M}, \tag{21}$$

where $\mathscr{M}$ is the operator of the longitudinal component of the total microscopic magnetic moment and f_2 characterizes the interactions between the spins.

We assume the quantities $F_1 = \bar{f}_1 = -HM$ and $F_2 = f_2 \equiv U$ to be the internal macroscopic parameters of the system and write down for them the equations of motions in accordance with the scheme of Secs. 2–5. It is easy to verify that under the assumptions of Sec. 5, at $f_0 = 0$ ("cut-off" lattice) we have

$$\operatorname{Sp} f_{1,2} LPg = 0, \quad L\sigma(t) = (\operatorname{Sp} 1)^{-1} [\beta_2(t) - \beta_1(t)] [f_2, f_1], \tag{22}$$

where the square brackets at the end of the right-hand side of the second relation denote the commutator.

Taking (22) into account, equations (12) can be written in the form

$$\dot{F}_{1,2}(t) = \pm \varkappa(t) [\beta_1(t) - \beta_2(t)], \tag{23}$$

$$\varkappa(t) \equiv (\operatorname{Sp} 1)^{-1} \operatorname{Sp} [f_1, f_2] A(t) B(t) [f_2, f_1], \tag{24}$$

$$A(t) \equiv \int_0^t dt' \mathscr{L}(t'), \quad B(t) \equiv \sum_{n=0}^{\infty} [iLPA(t)]^n. \tag{25}$$

According to (19)

$$M = CH\beta_1, \quad C \equiv (\operatorname{Sp} 1)^{-1} \operatorname{Sp} \mathscr{M}^2, \tag{26}$$

$$U = -b\beta_2, \quad b \equiv (\operatorname{Sp} 1)^{-1} \operatorname{Sp} f_2^2, \tag{27}$$

where C and b denote respectively the Curie and the Van Vleck constants.

With the aid of (26) and (27) we obtain from (23) in final form the equations of motion for the solution of our problem:

$$\dot{M}(t) = -\varkappa_1(t) [M(t) - CH\beta(t)], \tag{28}$$

$$\dot{\beta}(t) = qC^{-1}H^{-1}\varkappa_1(t) [M(t) - CH\beta(t)], \tag{29}$$

where

$$\varkappa_1(t) \equiv C^{-1}H^{-2}\varkappa(t), \quad q \equiv H^2 H_i^{-2}, \quad H_i^2 \equiv bC^{-1}$$

is the constant of the internal field of the spin system, and we use a new symbol $\beta(t)$ for the reciprocal temperature $\beta_2(t)$ of the interaction subsystem.

We note that the interactions in the spin system are completely contained in Eqs. (28) and (29), and smallness of their non-secular parts was not assumed in the derivation of these equations. If it can be assumed that $\varkappa_1 = \mathrm{const}(t)$, then Eqs. (28) and (29) coincide with those obtained and used earlier (see[6]) for the longitudinal relaxation in a constant field.

7. Our purpose was to illustrate, with a concrete example, the general scheme described in Secs. 2–5 for obtaining equations of motions for macroscopic quantities. We turn now to the question of solving the obtained equations. From (28) and (29) we obtain an equation for the auxiliary quantities

$$m(t) = M(t) - CH\beta(t), \tag{30}$$

namely

$$\dot{m}(t) = -(1+q)\varkappa_1(t) m(t). \tag{31}$$

Equation (31) can be solved directly

$$m(t) = m(0) \exp\left[-(1+q) \int_0^t dt' \varkappa_1(t')\right]. \tag{32}$$

If the form of the function $\varkappa_1(t)$ is known, then by substituting (32) in the right-hand side of (28) we reduce the solution of our problem to integration of (28) with respect to time from 0 to t, which yields

$$M(t) = M(0) + [M(0) - CH\beta(0)](1+q)^{-1}$$
$$\times \left\{ \exp\left[-(1+q) \int_0^t dt' \varkappa_1(t')\right] - 1 \right\}. \tag{33}$$

For an approximate determination of $\varkappa_1(t)$, we can propose the following perturbation-theory scheme: For all the known spin–spin interactions we have

$$f_2 = \sum_{\alpha=-a}^{a} V^\alpha, \quad [I^0, V^\alpha] = \alpha V^\alpha, \tag{34}$$

where a is a non-negative number that determines the region of values of the summation index α, and $I^{(0)}$ is the longitudinal component of the total spin. We write down the Hamiltonian (21) in the form

$$\mathscr{H} = \mathscr{H}_0 + V, \quad \mathscr{H}_0 = f_1 + V^0, \quad V = \sum_{\alpha \neq 0} V^\alpha \tag{35}$$

and construct a perturbation theory with respect to V. In the first nonvanishing approximation we have

$$\varkappa_1(t) = \int_0^t dt \sum_{\alpha \neq 0} \alpha^2 \langle (I^0)^2 \rangle_0^{-1} \langle V^{-\alpha} \mathscr{L}_0(t') V^\alpha \rangle_0,$$

$$\mathscr{L}_0(t) \equiv [\mathscr{L}(t)]_{V=0}. \tag{36}$$

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We confine ourselves in (36) to terms with $a = 2$ (for example, bearing in mind the dipole spin–spin interaction). Then (34) is satisfied if

$$V^{\pm 1} = \frac{1}{2} \sum_{j,k} V^{\mp}(\mathbf{r}_j - \mathbf{r}_k) I_j^{\pm} I_k^0,$$

$$V^{\pm 2} = \frac{1}{2} \sum_{j,k} V^{\mp\mp}(\mathbf{r}_j - \mathbf{r}_k) I_j^{\pm} I_k^{\pm}, \qquad (37)$$

where the lower indices number the spins, the form of the lattice factors $V(\mathbf{r}_j - \mathbf{r}_k)$ is determined by the type of the interaction, and $I_n^{\alpha} \equiv I_{xn} + i\alpha I_{yn}$, $I_n^0 \equiv I_{zn}$, and I_{xn}, I_{yn}, I_{zn} are the components of the n-th spin.

Substitution of (37) in (36) yields correlation functions which we write down, confining ourselves to the pair-correlation approximation, in the form

$$\langle (I^0)^2 \rangle_0^{-1} \langle I_j^{\mp} I_k^0 \mathscr{L}_0(t) I_l^{\pm} I_m^0 \rangle_0 \approx \frac{2}{N} \langle I_k^0 \mathscr{L}_0(t) I_m^0 \rangle_0 G^{\pm}(t) \delta_{jl}, \qquad (38)$$

$$\langle (I^0)^2 \rangle_0^{-1} \langle I_j^{\mp} I_k^{\mp} \mathscr{L}_0(t) I_l^{\pm} I_m^{\pm} \rangle_0 \approx \frac{4}{3N} I(I+1) [G^{\pm}(t)]^2 \delta_{jl} \delta_{km}, \qquad (39)$$

Here N is the number of the spins and I is the value of the spin

$$G^{\pm}(t) \equiv \langle I^+ I^- \rangle_0^{-1} \langle I^{\mp} \mathscr{L}_0(t) I^{\pm} \rangle_0, \qquad (40)$$

where $I^{\alpha} \equiv \sum_j I_j^{\alpha}$.

At this choice of $\mathscr{H}_0$ (see (36)), we can approximately neglect the t-dependence of the first factor in the right-hand side of (38), after which we obtain for it

$$\langle I_k^0 \mathscr{L}_0(t) I_m^0 \rangle \approx \tfrac{1}{3} I(I+1) \delta_{km}. \qquad (41)$$

Indeed, when this factor is made less exact by substituting $N I_n^0$ for I^0, its dependence on the time vanishes, while the time dependence of the second factor remains the same. With the aid of (38)–(41) we obtain from (36)

$$\varkappa_1(t) = \omega_1^2 \int_0^t dt' G(t') + \frac{1}{2} \omega_2^2 \int_0^t dt' [(G^+(t'))^2 + (G^-(t'))^2], \qquad (42)$$

$$\qquad (43)$$

$$\omega_1^2 = \tfrac{1}{3} I(I+1) \sum_j V^-(\mathbf{r}_j) V^+(\mathbf{r}_j), \quad \omega_2^2 = \tfrac{8}{3} I(I+1) \sum_j V^{--}(\mathbf{r}_j) V^{++}(\mathbf{r}_j),$$

$$G(t) = \tfrac{1}{2} [G^+(t) + G^-(t)]. \qquad (44)$$

Now, as is customarily done in similar cases, we might have attempted to assume some more or less likely expressions for the correlation functions $G^{\pm}(t)$. In our

case, however, a physically more justified analysis is possible, because the Fourier transform of $G(t)$ yields the line-shape function of the transverse magnetic resonance in the linear-response approximation (see, e.g., [7]). By determining this function experimentally, we can easily solve our problem. We confine ourselves to the case when the aforementioned line can be regarded with sufficient approximation as Lorentzian. Then, as is well known (see, e.g., [7]), we have

$$G^{\pm}(t) = \exp(-t/\tau_c) \exp(\pm i\omega_0 t), \qquad (45)$$

where $\omega_0 \equiv \gamma H$ and τ_c is the correlation function, which enters in the Lorentz function. Substitution of (45) in (42) yields

$$\qquad (46)$$

$$\varkappa_1(t) = \sum_{\lambda=1}^{2} \left(\frac{\omega_{\lambda}}{\lambda\omega_0} \right)^2 \frac{\lambda\omega_0^2 \tau_c}{1 + (\omega_0\tau_c)^2} \left[1 + (\omega_0\tau_c \sin\lambda\omega_0 t - \cos\lambda\omega_0 t) \exp\left(-\frac{\lambda t}{\tau_c} \right) \right],$$

and from (33) we obtain ultimately

$$M(t) = M(0) + [M(0) - C H\beta(0)](1+q)^{-1}\varphi(t), \qquad (47)$$

$$\varphi(t) \equiv \exp\left\{ -(1+q) \sum_{\lambda=1}^{2} \left(\frac{\omega_{\lambda}}{\lambda\omega_0} \right)^2 \frac{\omega_0\tau_c}{1 + (\omega_0\tau_c)^2} \left[\lambda\omega_0 t + \frac{1 - (\omega_0\tau_c)^2}{1 + (\omega_0\tau_c)^2} \omega_0\tau_c \right. \right.$$

$$\qquad (48)$$

$$\times \left. \left. \left(\exp\left(-\frac{\lambda t}{\tau_c} \right) \cos\lambda\omega_0 t - 1 \right) - \frac{2(\omega_0\tau_c)^2}{1 + (\omega_0\tau_c)^2} \exp\left(-\frac{\lambda t}{\tau_c} \right) \sin\lambda\omega_0 t \right] \right\} - 1.$$

Thus, our problem has been solved completely. According to (48), the relaxation is accompanied by complicated oscillations to $t \ll \tau_c$ and becomes monotonic for $t \gg \tau_c$. The conclusion that an oscillating longitudinal relaxation of nuclear magnetization is possible agrees with the experimental results (see e.g., [8]).

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Translated by J. G. Adashko