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Reciprocity relations for open nonlinear systems in variable fields

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A proof of reciprocity relations for nonlinear systems in inhomogeneous variable electric and magnetic fields in the presence of unsteady spin currents, thermodynamic flows and mechanical disturbances is obtained by the Kubo method in the approximation of Markov relaxation and locally quasi-equilibrium distribution.

Keywords: Nonlinear distributed systems, locally quasi-equilibrium distribution, Markov relaxation, spin current, reciprocity

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Introduction

The classical Onsager relations of symmetry of kinetic coefficients [1] were obtained in the linear approximation based on the invariance of macroscopic motion with respect to time inversion and on the assumption that the average relaxation of spontaneous fluctuations in the system proceeds in accordance with macroscopic laws. They were first applied to thermodynamic processes accompanied by entropy production. The linear relation between flows and gradients was introduced phenomenologically. The quantum substantiation of reciprocity relations was performed by Kubo [2] with the equilibrium density operator (i.e., in the linear approximation) and does not allow for the presence of temperature and concentration gradients and heat and matter flows in the system. Attempts to apply the Kubo method to thermodynamic processes did not yield meaningful results, not least because of the fact that the interactions involved in thermodynamic processes cannot be characterized by introducing additive components into the Hamiltonian [3].

The interest in generalizing the Onsager reciprocity relations to open nonlinear systems in the recent decade is largely stimulated by the progress in spintronics [4], straintronics [5], and spin caloritronics [6]. The observation of the anomalous Ettingshausen effect [7] and switching of the sign of the Peltier effect under a combined action of a magnetic field and mechanical stress [8,9] form the basis for efficient spin-thermal transport systems. Notably, significant violations of the reciprocity relations between spin-dependent Peltier and Seebeck effects, which are attributable to the nonlinearity of the voltage-current relationship at strong transport currents, were observed [10]. The reciprocity relations for nonlinear systems are satisfied only in particular cases (e.g., for closed systems in a constant and homogeneous magnetic field [11]). It was demonstrated experimentally that these relations are satisfied within the measurement accuracy [12]. Since spintronic and caloritronic components are open nonlinear systems functioning in inhomogeneous and nonstationary magnetic, electric, and temperature fields, general reciprocity relations for such systems are of interest.

The dynamics of open systems is characterized in modern quantum mechanics by the Lindblad equation for the density matrix of the system derived by eliminating the environment (reservoir) variables [13]. The operator in charge of the energy exchange with the reservoir has the form of the Lindblad superoperator. However, accurate derivation of such an operator preserving both the trace of the density matrix and its positive definiteness is extremely complex. Various approximations and phenomenological considerations are applied in practice. For example, it may be assumed that the superoperator for interacting subsystems is a sum of superoperators for noninteracting subsystems. It was demonstrated in [14] that this approach does not guarantee compliance with the laws of thermodynamics and that the average values of operators may differ in order of magnitude from the correct ones. An alternative way to analyze open systems is the quasi-equilibrium density operator method [15]. Thermodynamic processes are then regarded as perturbations of the quasi-equilibrium operator that are introduced additively into the von Neumann equation for the density operator. This approach is applicable to a nonlinear medium with spin currents and heat flows.

1. Locally quasi-equilibrium distribution

Let us consider an open system in inhomogeneous and varying magnetic and electric fields that consists of several types of interacting particles (components). The particles within each component are the same. The system exchanges energy and matter with thermostats and particle reservoirs through contacts (regions S_k of the system boundary surface S, where the system comes into contact with the environment). Let the Hamiltonian of the system ($\hat{H}$) and its observables ($\hat{D}_i$), which do not depend explicitly on time in the Schrödinger representation, be describable by quasilocal density operators

$$\hat{H}(t) = \int\limits_V \hat{h}(t, \mathbf{r}) d^3r + \hat{H}_r(t), \quad \hat{D}_i(t) = \int\limits_V \hat{d}_i(t, \mathbf{r}) d^3r, \tag{1}$$

where $\hat{H}_r$ is the relaxation system–environment interaction Hamiltonian and V is the system volume. Operator $\hat{d}(t, \mathbf{r})$ is quasilocal; its matrix element in the coordinate representation $d(t, \mathbf{r}, \mathbf{r}', \mathbf{r}'')$ decreases rapidly with distance from at least one of the points $\mathbf{r}'$ and $\mathbf{r}''$ to point $\mathbf{r}$ [16]. The interaction representation is used in (1) and below.

Let us designate the mass, the charge, the spin gyromagnetic ratio, and the spin of particles of the ith component as m_i, q_i, γ_i, and s_i, respectively. If particles are interacting via the Coulomb interaction, we may choose the following in the second quantization representation [15,16]:

$$\hat{h}(t, \mathbf{r}) = \frac{1}{2m_i} \left(\hat{\mathbf{p}}_i + \frac{q_i}{c} \hat{\mathbf{A}}(t, \mathbf{r}) \right) \hat{\Psi}^{+}_{i\sigma}(t, \mathbf{r}) \left(\hat{\mathbf{p}}_i - \frac{q_i}{c} \hat{\mathbf{A}}(t, \mathbf{r}) \right)$$
$$\times \hat{\Psi}_{i\sigma}(t, \mathbf{r}) - \hbar \gamma_i \Psi^{+}_{i\sigma}(t, \mathbf{r}) \mathbf{s}_{i\sigma\sigma'} \Psi_{i\sigma'}(t, \mathbf{r}) \mathbf{B}(r, \mathbf{r})$$
$$+ q_i \hat{\Psi}^{+}_{i\sigma}(t, \mathbf{r}) \hat{\Psi}_{i\sigma}(t, \mathbf{r}) \hat{\varphi}(t, \mathbf{r}) - \hat{d}_i(t, \mathbf{r}) f_i(t, \mathbf{r}). \tag{2}$$

Here, $\hat{\mathbf{A}}(t, \mathbf{r})$ is the operator of vector potential of the magnetic field;

$$\hat{\varphi}(t, \mathbf{r}) = \int \hat{\Psi}^{+}_{j\sigma}(t, \mathbf{r}') \frac{q_j}{|\mathbf{r} - \mathbf{r}'|} \hat{\Psi}_{j\sigma}(t, \mathbf{r}') d^3r' + \varphi(t, \mathbf{r}) \tag{3}$$

is the operator of potential of the electric field; $\varphi(t, r)$ is the potential of the electric field produced by sources external to the considered system; $f_i(t, \mathbf{r})$ are the distributions of the specified mechanical forces corresponding to observables D_i; $\hat{\Psi}_{i\sigma}(\mathbf{r})$ is the field operator of particles of the ith component; σ is the spin variable; and $\mathbf{s}_{i\sigma\sigma'}$ is the spin operator. A particle of the ith component is located at point $\mathbf{r}$, and a particle of the jth component is at point $\mathbf{r}'$. The operator representation of potentials is due to the fact that they are produced not only by external sources, but also by particles of the system. Therefore, they are not specified functions of time and coordinates and instead depend on operators of these particles.

Accordingly, in the interaction representation

$$\hat{c}_i(t, \mathbf{r}) = \hat{\Psi}^{+}_{i\sigma}(t, \mathbf{r}) \hat{\Psi}_{i\sigma}(t, \mathbf{r}),$$
$$\hat{s}_{i\alpha}(t, \mathbf{r}) = \hat{\Psi}_{i\sigma}(t, \mathbf{r}) s_{i\alpha\sigma\sigma'} \hat{\Psi}_{i\sigma'}(t, \mathbf{r}),$$
$$\hat{\pi}_{i\alpha}(t, \mathbf{r}) = -\frac{i\hbar}{2} \left(\frac{\partial \hat{\Psi}_{i\sigma}(t, \mathbf{r})}{\partial r_\alpha} \hat{\Psi}_{i\sigma}(t, \mathbf{r}) \right.$$
$$\left. - \hat{\Psi}^{+}_{i\sigma}(t, \mathbf{r}) \frac{\partial \hat{\Psi}_{i\sigma}(t, \mathbf{r})}{\partial r_\alpha} \right) \tag{4}$$

are the operators of particle densities and the αth projection of the spin and momentum of particles of the ith component (there is no summation over i in formulae (4)).

In order to switch to a continual description of the system, we average out the density of Hamiltonian (2) over a physically small volume $v \in V$ centered at point $\mathbf{r}$ that contains a sufficient number of particles for averaging. Let us expand the potentials into a Taylor series about point $\mathbf{r}$. Assuming that volume v is small, we limit ourselves to the second expansion term within it. The following is obtained in the Coulomb calibration and the dipole approximation:

$$\hat{\varphi}(t, \mathbf{r} + \mathbf{r}') = \hat{\varphi}(t, \mathbf{r}) + \mathbf{r}' \nabla \hat{\varphi}(t, \mathbf{r}), \quad \mathbf{r} \in v,$$
$$\hat{\mathbf{A}}(t, \mathbf{r} + \mathbf{r}') = \hat{\mathbf{A}}(t, \mathbf{r}) + (\mathbf{r}' \nabla) \hat{\mathbf{A}}(t, \mathbf{r})$$
$$= \hat{\mathbf{A}}(t, \mathbf{r}) + \left[\hat{\mathbf{B}}(t, \mathbf{r}) \times \mathbf{r}' \right] /2. \tag{5}$$

Let us insert expansion (5) into the right-hand part of formula (2). We neglect the quantities quadratic in magnetic field and add the total time derivative of $\hat{\mathbf{P}}(\mathbf{r}))\hat{\mathbf{A}}(t, \mathbf{r})$. Having performed standard transformations, we obtain the following for the sum of the first, the second, and the third terms:

$$-\frac{\hbar^2}{2m_i} \hat{\Psi}^{+}_{i\sigma}(\mathbf{r}) \Delta \hat{\Psi}_{i\sigma}(\mathbf{r}) - \hat{\mathbf{M}}(\mathbf{r}) \hat{\mathbf{B}}(t, \mathbf{r})$$
$$- \hat{\mathbf{P}}(\mathbf{r}) \hat{\mathbf{E}}(t, \mathbf{r}) - \hat{\rho}_e(t, \mathbf{r}) \hat{\varphi}(\mathbf{r}). \tag{6}$$

Here,

$$\frac{1}{v} \int\limits_v q_i \hat{\Psi}^{+}_{i\sigma}(t, \mathbf{r} + \mathbf{r}') \hat{\Psi}_{i\sigma}(t, \mathbf{r} + \mathbf{r}') d^3r' = \hat{\rho}_0(t, \mathbf{r}) + \hat{\rho}_e(t, \mathbf{r}),$$

$$\hat{\mathbf{P}}(t, \mathbf{r}) = \frac{1}{v} \int\limits_v q_i \hat{\Psi}^{+}_{i\sigma}(t, \mathbf{r} + \mathbf{r}') \mathbf{r}' \hat{\Psi}_{i\sigma}(t, \mathbf{r} + \mathbf{r}') d^3r',$$

$$\hat{\mathbf{M}}(t, \mathbf{r}) = \frac{1}{v} \int\limits_v \left\{ -\frac{i\hbar q_i}{2cm_i} \hat{\Psi}_{i\sigma}(t, \mathbf{r}+\mathbf{r}') \left[\mathbf{r}' \times \frac{\partial}{\partial \mathbf{r}} \right] \hat{\Psi}_{i\sigma}(t, \mathbf{r}+\mathbf{r}') \right.$$
$$\left. + \hbar \gamma_i \hat{\Psi}^{+}_{i\sigma}(t, \mathbf{r} + \mathbf{r}') \mathbf{s}_{i\sigma\sigma'} \hat{\Psi}_{i\sigma'}(t, \mathbf{r} + \mathbf{r}') \right\} d^3r' \tag{7}$$

are operators of the unperturbed charge density, perturbation of the charge density, polarization (i.e., the dipole-moment density), and magnetization (i.e., the magnetic-moment density), respectively. If the system in its unperturbed state is locally electrically neutral, $\hat{\rho}_0(t, \mathbf{r}) = 0$.

Assuming that averaging over volume v containing a large number of particles is equivalent to the quantum average, we substitute the volume-average operator of perturbation of the charge density (7) with its quantum average $\rho(t, \mathbf{r}) = \langle \hat{\rho}_e(t, \mathbf{r}) \rangle$, which is regarded as a specified classical function defined by the interaction between the system and thermostats. With relations (5) taken into account, formula (2) then takes the form

$$\hat{h}(t, \mathbf{r}) = \hat{h}_0(t, \mathbf{r}) - \hat{d}_i(t, \mathbf{r}) f_i(t, \mathbf{r}). \tag{8}$$

Here,

$$\hat{h}_0(t, \mathbf{r}) = -\frac{\hbar^2}{2m_i} \hat{\Psi}^{+}_{i\sigma}(t, \mathbf{r}) \Delta \hat{\Psi}_{i\sigma}(t, \mathbf{r}) \tag{9}$$

is the density operator of stationary unperturbed Hamiltonian $\hat{H}_0$.

Operators $\hat{\mathbf{E}}(t,\mathbf{r})$ and $\hat{\mathbf{B}}(t,\mathbf{r})$ in Eq. (6) are the operators of effective fields acting on a particle at point $\mathbf{r}$. They are the sums of fields produced by sources external to the system and fields produced by all particles of the system except the one under consideration. If the sources of particles are thermostats, it may be assumed that their state remains unchanged in interaction with the system. Fields $\mathbf{E}(t,\mathbf{r})$, $\mathbf{H}(t,\mathbf{r})$ produced by external sources and charge density $\rho(t,\mathbf{r})$ may then be regarded as specified classical functions. If the variation of polarization and magnetization within small volume v is negligible, it may be assumed that the effective field is a field in a small spherical cavity centered at point $\mathbf{r}$:

$$\hat{\mathbf{E}}(t,\mathbf{r}) = \mathbf{E}(t,\mathbf{r}) + 4\pi\hat{\mathbf{P}}(t,\mathbf{r})/3,$$

$$\hat{\mathbf{B}}(t,\mathbf{r}) = \mathbf{H}(t,\mathbf{r}) + 4\pi\hat{\mathbf{M}}(t,\mathbf{r})/3.$$

Term $-4\pi\hat{\mathbf{P}}^2(t,\mathbf{r})/3 - 4\pi\hat{\mathbf{M}}^2(t,\mathbf{r})/3$ may then be included into density (9) of the unperturbed Hamiltonian. It follows from the second and the third formulae (7) that it includes in this case the dipole Coulomb interaction of charges and the magnetodipole, spin-orbit, and spin-spin (exchange) interaction of all charged particles of the system. In accordance with (2), the Coulomb interaction between charges is represented by term $\hat{\varphi}(t,\mathbf{r})\rho(t,\mathbf{r})$, which is regarded as a perturbation. Among observables $\hat{d}_i(t,\mathbf{r})$ are potential $\hat{\varphi}(t,\mathbf{r})$ and projections of polarization $\hat{P}_\alpha(t,\mathbf{r})$ and magnetization $\hat{M}_\alpha(t,\mathbf{r})$. Specified mechanical forces $\rho(t,\mathbf{r})$, $E_\alpha(t,\mathbf{r})$, and $H_\alpha(t,\mathbf{r})$ correspond to them.

The number of degrees of freedom of the environment is much higher than that of the system, and the state of the environment remains unchanged in interaction with the system. It may then be assumed that the relaxation Hamiltonian of the system with the environment depends not on the environment operators, but on their quantum averages (i.e., classical quantities that are random functions of time). The relaxation Hamiltonian of the system with the environment may then also be regarded as a random function of time and observables of the system only. With Eqs. (1) and (8) taken into account, the dynamics of density operator $\hat{\rho}$ and observables of such a system is characterized by closed von Neumann equations

$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = -\int\limits_V f_i(t,\mathbf{r})\left[\hat{d}_i(t,\mathbf{r}),\hat{\rho}\right]d^3r + \left[\hat{H}_r,\hat{\rho}\right],$$

$$i\hbar\frac{\partial\hat{d}_i}{\partial t} = \left[\hat{d}_i(t,\mathbf{r},\hat{H}_0)\right], \quad \hat{H}_0 = \int\limits_V \hat{h}_0(t,\mathbf{r})d^3r. \tag{10}$$

If external mechanical inputs are lacking, a stationary locally quasi-equilibrium distribution is established in the system with density operator [15]

$$\hat{\rho}^q(t) = \exp\Bigg\{-\Phi(t) - \int\limits_V \theta(t,\mathbf{r})\big(\hat{h}_0(t,\mathbf{r})$$

$$- \mu_i(t,\mathbf{r})\hat{c}_i(t,\mathbf{r}) + \hbar\gamma_i\hat{s}_{i\alpha}(t,\mathbf{r})B_\alpha(t,\mathbf{r})\big)d^3r\Bigg\},$$

$$\Phi(t) = \ln\mathrm{Sp}\exp\Bigg\{-\int\limits_V \theta(t,\mathbf{r})\big(\hat{h}_0(t,\mathbf{r})$$

$$- \mu_i(t,\mathbf{r})\hat{c}_i(t,\mathbf{r}) + \hbar\gamma_i\hat{s}_{i\alpha}(t,\mathbf{r})B_\alpha(t,\mathbf{r})\big)d^3r\Bigg\}. \tag{11}$$

Here, Φ is the Massieu–Planck functional for a quasi-equilibrium system in external fields [17], $\theta(t,\mathbf{r}) = 1/(kT(t,\mathbf{r}))$, k is the Boltzmann constant, $T(t,\mathbf{r})$ is the local temperature, and $\mu_i(t,\mathbf{r})$ is the local chemical potential of particles of the ith component. An inhomogeneous and nonstationary distribution of functions and operators in (11) and (12) may be established if the system comes into contact with several different thermostats and reservoirs.

2. Thermodynamic forces and flows

In the second quantization representation, we introduce a complete orthonormal system of „single-particle“ functions $\Psi^i_p(\mathbf{r},t)$ with discrete index p for each component. In the space of the second quantization wave functions $\Phi(n^1_1,\ldots,n^i_p,\ldots)$, where n^i_p is the occupation number of the pth single-particle state of the ith component, we introduce the basis of eigenfunctions of unperturbed Hamiltonian $\hat{H}_0\Phi_k(\ldots n^i_p\ldots) = E_k\Phi_k(\ldots n^i_p\ldots)$.

The solution of the second von Neumann equation (10) takes the form

$$\hat{d}(t,\mathbf{r}) = \exp\left(i\hat{H}_0t/\hbar\right)\hat{d}(0,\mathbf{r})\exp\left(-i\hat{H}_0t/\hbar\right),$$

$$d_{km}(t,\mathbf{r}) = \exp(i\omega_{km}t')d_{km}(t-t'\mathbf{r}). \tag{12}$$

Here, $\omega_{km} = (E_k - E_m)/\hbar$. Therefore, in view of the Hermitian nature of observables,

$$\hat{d}_i(-t,\mathbf{r}) = \varepsilon_i\hat{d}^*_i(t,\mathbf{r}),$$

$$d_{ikm}(-t,\mathbf{r}) = \varepsilon_i d^*_{ikm}(t,\mathbf{r}) = \varepsilon_i d_{imk}(t,\mathbf{r}). \tag{13}$$

Here, $\varepsilon_i = 1$ if the ith observable does not change sign upon time inversion (as polarization) and its operator in the Schrödinger representation is real, and $\varepsilon_i = -1$ if the ith observable changes sign upon time inversion (as magnetization) and its operator in the Schrödinger representation is imaginary.

Let us introduce vectors $\mathbf{F}(t,\mathbf{r}) = \{\ldots f_i(t,\mathbf{r}),\ldots\} = \mathbf{F}(-t,\mathbf{r})$ and $\tilde{\mathbf{F}}(t,\mathbf{r} = \{\ldots\varepsilon_i f_i(t,\mathbf{r}),\ldots\}$. At this stage, we consider the components of magnetic induction on which quasi-equilibrium distribution (11) does depend explicitly as separate forces that are not included into vector $\mathbf{F}$ of mechanical forces. Quasi-equilibrium distribution (11) then does not depend explicitly on mechanical forces. Since $\hat{s}^*_{i\alpha}(t,\mathbf{r}) = -\hat{s}_{i\alpha}(t,\mathbf{r})$, we obtain the following from the first Eq. (11):

$$\hat{\rho}^{q*}(-\mathbf{B}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r})) = \hat{\rho}^q(\mathbf{B}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r})). \tag{14}$$

Here, $\mathbf{T}(t,\mathbf{r}) = \{T(t,\mathbf{r}), \mu_1(t,\mathbf{r}), \ldots\}$. The first Eq. (10) yields

$$\hat{\rho}(-t, \mathbf{F}(t,\mathbf{r})) = \hat{\rho}^*(t, \tilde{\mathbf{F}}(t,\mathbf{r})) \tag{15}$$

Let us perform time inversion in relation

$$d_i(t,\mathbf{r}) = \mathrm{Sp}\{\hat{\rho}(t, \mathbf{F}(t,\mathbf{r}))\hat{d_i}(t,\mathbf{r})\}$$

. Taking (13) and (15) into account, we obtain $\varepsilon_i d_i(t,\mathbf{r}) = \mathrm{S}p\{\hat{\rho}^*(t, \tilde{\mathbf{F}}(t,\mathbf{r}))\varepsilon_i \hat{d_i}^*(t,\mathbf{r})\}$. Since observable $d_i(t,\mathbf{r})$ is real, $d_i(t,\mathbf{r}) = \mathrm{Sp}\{\hat{\rho}(t, \tilde{\mathbf{F}}(t,\mathbf{r}))\hat{d_i}(t,\mathbf{r})\}$. Thus,

$$\hat{\rho}(t, \mathbf{F}(t,\mathbf{r})) = \hat{\rho}(t, \tilde{\mathbf{F}}(t,\mathbf{r})). \tag{16}$$

The first Eq. (10) in the Markovian relaxation approximation, which corresponds to the Onsager assumption [1], has the following matrix form:

$$\rho_{km}(t_0, \mathbf{F}, \mathbf{T}, \mathbf{B}) = \rho^0_{km}(\mathbf{F}, \mathbf{T}, \mathbf{B}),$$

$$\frac{\partial \rho_{km}(t, \mathbf{F}, \mathbf{T}, \mathbf{B})}{\partial t} = \frac{\rho^q_{km}(\mathbf{T}, \mathbf{B}) - \rho_{km}(t, \mathbf{F}, \mathbf{T}, \mathbf{B})}{\tau_{km}}$$

$$- \frac{i}{\hbar} \int\limits_V f_j(t,\mathbf{r})(\rho_{kl}(t, \mathbf{F}, \mathbf{T}, \mathbf{B}) d_{jlm}(t,\mathbf{r})$$

$$- d_{jkl}(t,\mathbf{r})\rho_{lm}(t, \mathbf{F}, \mathbf{T}, \mathbf{B}))d^3r. \tag{17}$$

Here, $\tau_{km} = \tau_{mk}$ are real positive relaxation times, and it is assumed that the system at time t_0 was in a quasi-equilibrium state with density matrix ρ^0_{km}. It is implied here and elsewhere that functions $\mathbf{F}, \mathbf{T}$ and $\mathbf{B}$ depend on time and coordinates.

We seek the solution of Eq. (17) in the form $\rho_{km}(t, \mathbf{F}, \mathbf{T}, \mathbf{B}) = \tilde{\rho}_{km}(t, \mathbf{F}, \mathbf{T}, \mathbf{B}) \exp(i\omega_{km}t)$. It follows from the second Eq. (13) that

$$\tilde{\rho}_{km}(t_0, \mathbf{F}, \mathbf{T}, \mathbf{B}) = \rho^0_{km}(t, \mathbf{T}, \mathbf{B}) \exp(-i\omega_{km}t_0),$$

$$\frac{\partial \tilde{\rho}_{km}(t, \mathbf{F}, \mathbf{T}, \mathbf{B})}{\partial t}$$

$$= \frac{\rho^q_{km}(\mathbf{T}, \mathbf{B}) \exp(-i\omega_{km}t_0) - \tilde{\rho}_{km}(t, \mathbf{F}, \mathbf{T}, \mathbf{B})}{\tau_{km}}$$

$$- i\omega_{km}\tilde{\rho}_{km}(t, \mathbf{F}, \mathbf{T}, \mathbf{B}) - \frac{i}{\hbar} \int\limits_V f_j(t,\mathbf{r})$$

$$\times (\tilde{\rho}_{kl}(t, \mathbf{F}, \mathbf{T}, \mathbf{B}) d_{jlm}(0,\mathbf{r})$$

$$- d_{jkl}(0,\mathbf{r})\tilde{\rho}_{lm}(t, \mathbf{F}, \mathbf{T}, \mathbf{B},))d^3r. \tag{18}$$

Let us perform complex conjugation in Eq. (18) by substituting $\mathbf{F}(t,\mathbf{r})$ with $-\tilde{\mathbf{F}}(t,\mathbf{r})$ and $\mathbf{B}(t,\mathbf{r})$ with $-\mathbf{B}(t,\mathbf{r})$. $\mathbf{T}(t,\mathbf{r})$ is left intact. Taking Eq. (14) into account, we obtain

$$\tilde{\rho}^*_{km}(t_0, -\tilde{\mathbf{F}}, \mathbf{T}, -\mathbf{B}) = \rho^q_{km}(\mathbf{T}, \mathbf{B}) \exp(-i\omega_{mk}t_0),$$

$$\frac{\partial \tilde{\rho}^*_{km}(t, -\tilde{\mathbf{F}}, \mathbf{T}, -\mathbf{B})}{\partial t}$$

$$= \frac{\tilde{\rho}^q_{km}(t, \mathbf{T}, \mathbf{B}) \exp(-i\omega_{mk}t_0) - \tilde{\rho}^*_{km}(t, -\tilde{\mathbf{F}}, \mathbf{T}, -\mathbf{B})}{\tau_{km}}$$

$$- i\omega_{mk}\tilde{\rho}^*_{km}(t, -\tilde{\mathbf{F}}, \mathbf{T}, -\mathbf{B}) - \frac{i}{\hbar} \int\limits_V \varepsilon_j f_j(t,\mathbf{r})$$

$$\times (\tilde{\rho}^*_{kl}(t, -\tilde{\mathbf{F}}, \mathbf{T}, -\mathbf{B}) d_{jlm}(0,\mathbf{r})$$

$$- d_{jkl}(0,\mathbf{r})\tilde{\rho}^*_{lm}(t, -\tilde{\mathbf{F}}, \mathbf{T}, -\mathbf{B},))d^3r. \tag{19}$$

With the second Eq. (13) taken into account, it follows from the uniqueness of solution of Cauchy problems (18) and (19) that $\tilde{\rho}_{km}(\mathbf{F}(t,\mathbf{r}), \mathbf{T}(t,\mathbf{r}), \mathbf{B}(t,\mathbf{r})) = \tilde{\rho}^*_{km}\left(-\tilde{\mathbf{F}}(t,\mathbf{r}), \mathbf{t}(t,\mathbf{r}) - \mathbf{B}(t,\mathbf{r})\right)$ under a simultaneous substitution of all frequencies ω_{km} with ω_{mk}. With condition (16) taken into account, we find $\tilde{\rho}_{km}(\mathbf{F}(t,\mathbf{r}), \mathbf{T}(t,\mathbf{r}), \mathbf{B}(t,\mathbf{r})) = \tilde{\rho}^*_{km}(-\mathbf{F}(t,\mathbf{r}), \mathbf{T}(t,\mathbf{r}), -\mathbf{B}(t,\mathbf{r}))$. Thus, magnetic field $\mathbf{B}$ on which quasi-equilibrium distribution (11) does depend explicitly may be regarded as a mechanical force and included into vector $\mathbf{F}$. With the Hermitian nature of the operator taken into account, we then obtain

$$\tilde{\rho}_{km}(\mathbf{F}(t,\mathbf{r}), \mathbf{T}(t,\mathbf{r})) = \tilde{\rho}_{mk}(-\mathbf{F}(t,\mathbf{r})\mathbf{T}(t,\mathbf{r})). \tag{20}$$

Equation (17) is equivalent to integral equation

$$\rho_{km}(t) = (\rho^0_{km} + \rho^q_{km}(t)) \exp\left(\frac{t_0 - t}{\tau_{km}}\right) - \rho^q_{km}(t)$$

$$+ \int\limits_{t_0}^{t} \exp\left(\frac{t_0 - t}{\tau_{km}}\right) \frac{d\rho^q_{km}(t')}{dt'} dt' + \frac{i}{\hbar} \int\limits_V \int\limits_{t_0}^{t} \exp\left(\frac{t' - t}{\tau_{km}}\right)$$

$$\times f_j(t',\mathbf{r}')(d_{jkl}(t',\mathbf{r}',)\rho_{lm}(t') - \rho_{kl} d_{jlm}(t',\mathbf{r}'))dt'd^3r'. \tag{21}$$

Integration by parts was performed here in the integral containing ρ^q_{km}. In accordance with Eq. (11),

$$\frac{d\hat{\rho}^q(t)}{dt} = \frac{1}{2}\left\{\hat{\rho}^q(t)\hat{A}(t) + \hat{A}(t)\hat{\rho}^q(t)\right\},$$

$$\hat{A}(t) = -\int\limits_V \theta(t,\mathbf{r})\left(\frac{\partial \hat{h}_0(t,\mathbf{r})}{\partial t} - \mu_i(t,\mathbf{r})\frac{\hat{c}_i(t,\mathbf{r})}{\partial t}\right.$$

$$\left. + \hbar\gamma_i B_\alpha(t,\mathbf{r})\frac{\partial \hat{s}_{\alpha i}(t,\mathbf{r})}{\partial t}\right)d^3r$$

$$-\int\limits_V \left(\frac{\partial \theta(t,\mathbf{r})}{\partial t}\hat{h}_0(t\mathbf{r}) - \frac{\partial \theta(t,\mathbf{r})\mu_i(t,\mathbf{r})}{\partial t}\hat{c}_i(t,\mathbf{r})\right.$$

$$\left. + \hbar\gamma_i \hat{s}_{\alpha i}(t,\mathbf{r})\frac{\partial \theta(t,\mathbf{r})B_\alpha(t,\mathbf{r})}{\partial t}\right)d^3r - \frac{d\Phi}{dt}. \tag{22}$$

The corresponding density operators of matter and energy flows and the spin current of the ith component, which satisfy the continuity equation, may be introduced for quasilocal density operators [16]:

$$\frac{\partial\hat{h}}{\partial t}=-\frac{\partial\hat{q}_\alpha}{\partial r_\alpha},\quad \frac{\partial\hat{c}_i}{\partial t}=-\frac{\partial\hat{j}_{i\alpha}}{\partial r_\alpha},$$

$$\frac{\partial\hat{s}_{i\alpha}}{\partial t}=-\frac{\partial\upsilon_{i\alpha\beta}}{\partial r_\beta},\qquad \alpha=1,2,3. \tag{23}$$

Relations (23) do not uniquely define the flow density operators. One may introduce an additional requirement in that the correct transformation properties should be maintained under Galilean transformation $r\to\mathbf{r}'=\mathbf{r}+\mathbf{v}t$

$$\hat{c}_i(\mathbf{r}')\to\hat{c}'_i(\mathbf{r}')=\hat{c}_i(\mathbf{r}'),\quad \hat{h}(\mathbf{r})\to\hat{h}'(\mathbf{r}')+\upsilon^2m_i\hat{c}_i(\mathbf{r}')/2,$$

$$\hat{\pi}_{i\alpha}(\mathbf{r})\to\hat{\pi}'_{i\alpha}(\mathbf{r}')=\hat{\pi}_{i\alpha}(\mathbf{r}')+\upsilon_\alpha m_i\hat{c}_i(\mathbf{r}'),$$

$$\hat{j}_{i\alpha}(\mathbf{r}')\to\hat{j}'_{i\alpha}(\mathbf{r}')=\hat{j}_{i\alpha}(\mathbf{r}')+\upsilon_\alpha\hat{c}_i(\mathbf{r}'),$$

$$\hat{q}_{i\alpha}(\mathbf{r})\to\hat{q}'_{i\alpha}(\mathbf{r}')=\hat{q}_{i\alpha}(\mathbf{r}')+\upsilon_\alpha\hat{h}(\mathbf{r}')$$

$$+\upsilon^2m_i\hat{j}'_{i\alpha}(\mathbf{r}')/2+\upsilon_\alpha\upsilon_\beta\hat{\pi}_\beta(\mathbf{r}'). \tag{24}$$

Density operator (2) of the following form satisfies conditions (23) and (24) [16]:

$$\hat{q}_\alpha(t,\mathbf{r})=\frac{i}{2\hbar}\int_V d^3r'r'_\alpha\int_0^1\left[\hat{h}_0(t,\mathbf{r}-(1-\xi)\mathbf{r}'),\hat{h}(t,\mathbf{r}+\xi\mathbf{r}')\right]d\xi.$$

Similar relations also hold true for density operators of the form (4). Here, the commutator in the inner integral is calculated with account for commutation relations

$$\Psi_{i\sigma'}(\mathbf{r}')\hat{\Psi}^+_{i\sigma}\pm\hat{\Psi}_{i\sigma}(\mathbf{r})\hat{\Psi}_{i\sigma'}(\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma\sigma'},$$

where the upper sign is for fermions and the lower one is for bosons. The other commutators and anticommutators are equal to zero. In addition, $\hat{\Psi}^+_{i\sigma'}(\mathbf{r}')\Delta_\mathbf{r}\hat{\Psi}_{is}(\mathbf{r})=\Delta_\mathbf{r}(\hat{\Psi}^+_{i\sigma'}(\mathbf{r}')\hat{\Psi}_{i\sigma}(\mathbf{r}))$. With (9) taken into account, we then obtain

$$\hat{j}_{i\alpha}=\frac{\hat{\pi}_{i\alpha}}{m_i},$$

$$\hat{\upsilon}_{i\alpha\beta}=\hat{\Psi}_{i\sigma}s_{i\alpha\sigma\sigma'}-\frac{\hat{p}_{i\beta}}{2m_i}\hat{\Psi}_{i\sigma'}-\frac{\hat{p}_{i\beta}}{2m_i}\hat{\Psi}^+_{i\sigma}s_{i\alpha\sigma\sigma'}\hat{\Psi}_{i\sigma'}. \tag{25}$$

Let us insert Eqs. (23) into the first integral in the right-hand part of the second Eq. (22) and integrate by parts:

$$\int_V\theta\left(\frac{\partial\hat{h}_0}{\partial t}-\mu_i\frac{\partial\hat{c}_i}{\partial t}+\hbar\gamma B_\alpha\frac{\partial\hat{s}_{\sigma i}}{\partial t}\right)d^3r$$

$$=-\theta_k\hat{Q}_k+\theta_k\mu_{ik}\hat{I}_{ik}-\hbar\gamma_i\theta_kB_{\alpha k}\hat{\Sigma}_{i\alpha k}$$

$$+\int_V\left(\hat{q}_\alpha\frac{\partial\theta}{\partial r_\alpha}-\hat{j}_{i\alpha}\frac{\partial(\theta\mu_i)}{\partial r_\alpha}+\hbar\gamma_i\hat{\upsilon}_{i\alpha\beta}\frac{\partial(\theta B_\alpha)}{\partial r_\beta}\right)d^3r. \tag{26}$$

Here,

$$\hat{Q}_k(t)=\int_{s_k}n_{k\beta}(\mathbf{r})\hat{q}_\beta(t,\mathbf{r})d^2r,$$

$$\hat{I}_{ik}(t)=\int_{s_k}n_{k\beta}(\mathbf{r})\hat{j}_{i\beta}(t,\mathbf{r})d^2r,$$

$$\Sigma_{i\alpha k}(t)=\int_{s_k}n_{k\beta}(\mathbf{r})\upsilon_{i\alpha\beta}(t,\mathbf{r})d^2r$$

are the operators of flows of energy, particles of the ith component, and the α-projection of the spin current of particles of the ith component through the kth contact, respectively; $\theta_k(t)=\theta(t,\mathbf{r}_k)$; $\mu_{ik}(t)=\mu_i(t,\mathbf{r}_k)$; $B_{\alpha k}(t)=B_\alpha(t,\mathbf{r}_k)$; $\mathbf{r}_k$ is the coordinate of the center of the kth contact; and $n_{k\beta}$ is the β-projection of the outward normal to the surface of the kth contact.

Alongside with mechanical observables $\hat{d}_i(\mathbf{r})$ and the corresponding mechanical forces $f_i(t,\mathbf{r})$, we introduce thermodynamic observables: densities of energy $\hat{h}_0(t,\mathbf{r})$, particles of the ith component $\hat{c}_i(t,\mathbf{r})$, and projection of their spin $\hat{s}_{i\alpha}(t,\mathbf{r})$, projections of the flow densities of energy $\hat{q}_\alpha(t,\mathbf{r})$ and particles of the ith component $\hat{j}_{i\alpha}(t,\mathbf{r})$, components of the spin-current density tensor of particles of the ith component $\hat{\upsilon}_{i\alpha\beta}(t,\mathbf{r})$, flows of energy $-\hat{Q}_k(t)$, particles of the ith component $\hat{I}_{ik}(t)$, and the α-projection of the spin current of particles of the ith component $\hat{\Sigma}_{i\alpha k}$ through the kth contact and the corresponding thermodynamic forces $\partial\theta/\partial t$, $-\partial(\theta\mu_i)\partial t$, $\partial\theta/\partial r_\alpha$, $-\partial(\theta\mu_i)/\partial r_\alpha$, $\hbar\gamma_i\partial(\theta B_\alpha)/\partial r_\beta$, $\theta_k(t)$, $\theta_k(t)\mu_{ik}(t)$, and $-\hbar\gamma_i\theta_kB_{\alpha k}$. We preserve common numeration and designations $\hat{d}_i(\mathbf{r})$ and $f_i(t,\mathbf{r})$ for all observables and forces, but include only mechanical forces into vector $\mathbf{F}(t,\mathbf{r})$. Thermodynamic forces are included into vector $\mathbf{T}(t,\mathbf{r})$.

3. Reciprocity relations

Let time t_0 in formula (21) tend to $-\infty$. The first term in the right-hand part is then equal to zero. Let us introduce new variable $\tau=t-t'$. With (22) and (26) taken into account, Eq. (21) takes the form

$$\rho_{km}(t)=\frac{i}{\hbar}\int_V\int_0^\infty\exp\left(\frac{-\tau}{\tau_{km}}\right)\left(d_{jkl}(t-\tau,\mathbf{r}')\rho_{kl}(t-\tau)\right.$$

$$\left.-\rho_{kl}(t-\tau)d_{jlm}(t',\mathbf{r}')\right)f_j(t-\tau\mathbf{r}')d\tau d^3r'$$

$$-\rho^q_{km}(t)-\int_0^\infty\exp\left(\frac{-\tau}{\tau_{km}}\right)\rho^q_{km}(t-\tau)\frac{d\Phi(t-\tau)}{dt}d\tau$$

$$-\frac{1}{2}\int_V\int_0^\infty\exp\left(\frac{-\tau}{\tau_{km}}\right)\left(d_{jkl}(t-\tau,\mathbf{r}')\rho^q_{kl}(t-\tau)\right.$$

$$\left.+\rho^q_{kl}(t-\tau)d_{jlm}(t',\mathbf{r}')\right)f_j(t-\tau\mathbf{r}')d\tau d^3r'. \tag{27}$$

The first integral incorporates mechanical quantities, while the third one incorporates thermodynamic quantities.

The following is obtained for the average value of observables from (27):

$$d_i(t,\mathbf{r},\mathbf{F},\mathbf{T}) = \rho_{km}(t,\mathbf{F},\mathbf{T})d_{imk}(t,\mathbf{r},\mathbf{F},\mathbf{T}) = d_i^q(t,\mathbf{r})$$

$$+\iint\limits_{V\ 0}^{\ \ \infty} \chi_{ij}(\tau,\mathbf{r},\mathbf{r}',\mathbf{F},\mathbf{T})f_j(t-\tau,\mathbf{r})d\tau d^3r'. \qquad (28)$$

The first term in the right-hand part of (28) takes the form

$$d_i^q(t,\mathbf{r},\mathbf{F},\mathbf{T}) = -\rho_{km}^q(t)d_{imk}(\mathbf{r},t)$$

$$-\int_0^\infty \exp\left(\frac{-\tau}{\tau_{km}}\right)\rho_{km}^q(t-\tau)d_{imk}(t,\mathbf{r})\frac{d\Phi(t-\tau)}{dt}d\tau \qquad (29)$$

and characterizes the quasi-equilibrium value of the observable.

The second term in (28) characterizes the response of a nonlinear system to mechanical and thermodynamic inputs. With the second Eq. (13) taken into account, the response function for a mechanical input at $t' = t - \tau/2$ has the form of the Kubo formula [2]

$$\chi\big(\tau,\mathbf{r},\mathbf{r}',\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r})\big) = \frac{i\rho_{km}(t-\tau,\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r}))}{\hbar\exp(\tau/\tau_{km})}$$

$$\times\left\{d_{iml}(t,\mathbf{r})d_{jlk}(t-\tau,\mathbf{r}') - d_{jml}(t-\tau,\mathbf{r}')d_{ilk}(t,\mathbf{r})\right\}$$

$$= \frac{i\tilde{\rho}_{km}(\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r}))}{\hbar\exp(\tau/\tau_{km})}\exp\left(i\omega_{mk}\frac{\tau}{2}\right)\left\{d_{iml}\left(\frac{\tau}{2},\mathbf{r}\right)\right.$$

$$\left.\times d_{jlk}\left(-\frac{\tau}{2},\mathbf{r}\right) - d_{jml}\left(-\frac{\tau}{2},\mathbf{r}'\right)d_{ilk}\left(\frac{\tau}{2},\mathbf{r}\right)\right\}. \qquad (30)$$

The following is obtained for a thermodynamic input:

$$\chi_{ij}(\tau,\mathbf{r},\mathbf{r}',\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r})) = -\frac{\tilde{\rho}_{km}^q(\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r}))}{2\exp(\tau/\tau_{km})}$$

$$\times\exp(i\omega_{mk}\tau/2)\left\{d_{iml}(\tau/2,\mathbf{r})d_{jlk}(-\tau/2,\mathbf{r}')\right.$$

$$\left.+\,d_{jml}(-\tau/2,\mathbf{r}')d_{ilk}(\tau/2,\mathbf{r})\right\}. \qquad (31)$$

If the thermodynamic response is a flow through the kth contact, $\mathbf{r} = \mathbf{r}_k$ is set in formulae (28)−(30). If the thermodynamic input is temperature and (or) chemical potential of the kth contact, $\mathbf{r}' = \mathbf{r}_k$ is set in formulae (28) and (31), and integration over $\mathbf{r}'$ is not performed in (28). With relations (20) taken into account, the following is obtained from formula (30) for a mechanical response to a mechanical input:

$$\chi_{ji}(\tau,\mathbf{r},\mathbf{r}',-\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r})) = \frac{i\tilde{\rho}_{mk}(\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r}))}{\hbar\exp(\tau/\tau_{km})}$$

$$\times\exp(i\omega_{km}\tau/2)\left\{d_{jml}(\tau/2,\mathbf{r})d_{ilk}(-\tau/2,\mathbf{r}')\right.$$

$$\left.-\,d_{iml}(-\tau/2\mathbf{r}')d_{jlk}(\tau/2,\mathbf{r})\right\}.$$

Substituting $k \leftrightarrow m$ with the second Eq. (14) and the symmetry of matrix τ_{km} taken into account, we find

$$\chi_{ji}(\tau,\mathbf{r},\mathbf{r}',-\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r})) = \frac{i\tilde{\rho}_{km}(\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r}))}{\hbar\exp(\tau/\tau_{km})}$$

$$\times\exp(i\omega_{km}\tau/2)\varepsilon_i\varepsilon_j\left\{d_{jik}(-\tau/2,\mathbf{r})d_{iml}(\tau/2,\mathbf{r}')\right.$$

$$\left.-\,d_{ilk}(\tau/2\mathbf{r}')d_{jml}(0,\mathbf{r})\right\}. \qquad (32)$$

In a similar fashion, we obtain the following for a thermodynamic response to thermodynamic inputs from formula (31):

$$\chi_{ji}(\tau,\mathbf{r},\mathbf{r}',-\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r})) = -\frac{\tilde{\rho}_{km}^q(\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r}))}{2\exp(\tau/\tau_{km})}$$

$$\times\exp(i\omega_{mk}\tau/2)\varepsilon_i\varepsilon_j\left\{d_{iml}(\tau/2,\mathbf{r})d_{jik}(-\tau/2,\mathbf{r}')\right.$$

$$\left.+\,d_{jml}(-\tau/2\mathbf{r}')d_{ilk}(\tau/2,\mathbf{r})\right\}. \qquad (33)$$

Comparing (30) with (32) and (31) with (33), we obtain the reciprocity relations for the function of mechanical response of an open nonlinear system to mechanical inputs and the function of thermodynamic response to thermodynamic inputs

$$\chi_{ij}(\tau,\mathbf{r},\mathbf{r}'\mathbf{F}(t,\mathbf{r})\mathbf{T}(t,\mathbf{r}))$$

$$= \varepsilon_i\varepsilon_j\chi_{ji}(\tau,\mathbf{r}',\mathbf{r},-\mathbf{F}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r})). \qquad (34)$$

In relations (30)−(34) an below, the argument of functions $\mathbf{F}(t,\mathbf{r})$ and $\mathbf{T}(t,\mathbf{r})$ implies that the response depends on the values of forces at all time points prior to t in the entire region V. Apparently, certain information regarding the structure of the system is needed to analyze the reciprocity relations between mechanical and thermodynamic quantities and quasi-equilibrium value (29).

If components of polarization $P_\alpha(t,\mathbf{r})$ are the mechanical response and components of electric field $E_\alpha(t,\mathbf{r})$ are the mechanical input, response function $\chi_{\alpha\beta}$ is the dielectric susceptibility tensor. If components of magnetization $M_\alpha(t,\mathbf{r})$ are the mechanical response and components of magnetic field $H_\alpha(t,\mathbf{r})$ are the mechanical input, response function $\chi_{\alpha\beta}$ is the magnetic susceptibility tensor. In both cases, it follows from formula (34) that

$$\chi_{\alpha\beta}(\tau,\mathbf{r},\mathbf{r}',\mathbf{E}(t,\mathbf{r}),\mathbf{H}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r}))$$

$$= \chi_{\beta\alpha}(\tau,\mathbf{r}',\mathbf{r},-\mathbf{E}(t,\mathbf{r}),-\mathbf{H}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r})).$$

The following is obtained for the response function of polarization to the magnetic field or magnetization to the electric field:

$$\chi_{\alpha\beta}(\tau,\mathbf{r},\mathbf{r}',\mathbf{E}(t,\mathbf{r}),\mathbf{H}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r}))$$

$$= -\chi_{\beta\alpha}(\tau,\mathbf{r}',\mathbf{r},-\mathbf{E}(t,\mathbf{r})-\mathbf{H}(t,\mathbf{r}),\mathbf{T}(t,\mathbf{r})).$$

4. Nonlinear system in external fields

Let us consider a system exchanging energy and charged zero-spin particles of one type through two contacts 1 and 2 with temperatures T_1 and T_2, respectively. The chemical potential and the flow of charged particles are proportional to the electric potential and the current, respectively. If the sources of particles are thermostats, it may be assumed that their state remains unchanged in interaction with the system. The currents through contacts may then be regarded as specified functions of time and as thermodynamic forces. Assuming in what follows that the current and the potential, which is taken to be equal to zero at infinity, are electric quantities, we choose the following numeration of thermodynamic quantities at contacts: $e\varphi_1$, $e\varphi_2$, Q_1, Q_2, where e is the particle charge. The corresponding thermodynamic forces are $\theta_1 I_1/e$, $\theta_2 I_2/e$, θ_1, θ_2. Let us write Eqs. (28) in the stationary mode without quasi-equilibrium components for contacts 1 and 2. Since $I_1 = -I_2 = I$ in the stationary mode, we obtain

$$e\varphi_1 = \kappa_{11} I/(T_1 e) - \kappa_{12} I/(T_2 e) + \kappa_{13}/T_1 + \kappa_{14}/T_2,$$

$$e\varphi_2 = \kappa_{21} I/(T_1 e) - \kappa_{22} I/(T_2 e) + \kappa_{23}/T_1 + \kappa_{24}/T_2,$$

$$Q_1 = \kappa_{31} I/(T_1 e) - \kappa_{32} I/(T_2 e) + \kappa_{33}/T_1 + \kappa_{34}/T_2,$$

$$Q_2 = \kappa_{41} I/(T_1 e) - \kappa_{42} I/(T_2 e) + \kappa_{43}/T_1 + \kappa_{44}/T_2. \quad (35)$$

$$\kappa_{ij}(\mathbf{F}, \mathbf{T}) = \frac{1}{k} \int\limits_0^\infty \chi_{ij}(\tau, \mathbf{r}'_j, \mathbf{r}''_j, \mathbf{F}, \mathbf{T}) d\tau,$$

$$\mathbf{r}'_1 = \mathbf{r}'_3 = \mathbf{r}''_1 = \mathbf{r}''_3 = \mathbf{r}_1,$$

$$\mathbf{r}'_2 = \mathbf{r}'_4 = \mathbf{r}''_2 = \mathbf{r}''_4 = \mathbf{r}_2. \quad (36)$$

It is assumed in (23), (35) and elsewhere that the thermodynamic flows and potentials do not change sign upon time inversion. This ensures the irreversibility of thermodynamic processes. It follows from relations (34) and (36) that

$$\kappa_{ij}(\mathbf{F}, \mathbf{T}) = \kappa_{ji}(-\mathbf{F}, \mathbf{T}), \qquad i,\ j = 1, 2, 3, 4. \quad (37)$$

The sources of particles are thermostats that are sufficiently large for their potential without perturbations to be equal to the potential at infinity (i.e., zero). If the magnetic field and mechanical forces at $I = 0$ and $\theta_1 = \theta_2 = \theta$ do not produce thermal flows and electric potentials, $\varphi_1 == \varphi_2 = 0$, $Q_1 = Q_2 = 0$; i.e.,

$$\kappa_{13}(\mathbf{F}, T, 0) = -\kappa_{14}(\mathbf{F}, T, 0),$$

$$\kappa_{23}(\mathbf{F}, T, 0) = -\kappa_{24}(\mathbf{F}, T, 0),$$

$$\kappa_{33}(\mathbf{F}, \mathbf{B}, T, 0) = -\kappa_{34}(\mathbf{F}, T, 0),$$

$$\kappa_{44}(\mathbf{F}, T, 0) = -\kappa_{43}(\mathbf{F}, T, 0). \quad (38)$$

Setting $T_1 = T - \Delta T/2$, $T_2 = T + \Delta T/2$, $U = \varphi_2 - \varphi_1$, we obtain

$$U = k\big\{\kappa_{12}(\mathbf{F}, T, I)/T_1 + \kappa_{21}(\mathbf{F}, \mathbf{T}, \mathbf{I})/T_2 - \kappa_{11}(\mathbf{F}, T, I)/T_1$$
$$- \kappa_{22}(\mathbf{F}, T, I)/T_2\big\} I/e + \big\{\kappa_{24}(\mathbf{F}, T, I) + \kappa_{23}(\mathbf{F}, T, I)$$
$$- \kappa_{13}(\mathbf{F}, T, I) - \kappa_{14}(\mathbf{F}, T, I)\big\}/(eT)$$
$$- \big\{\kappa_{14}(\mathbf{F}, T, I) + \kappa_{23}(\mathbf{F}, T, I)\big\}/\Delta T/(eT^2), \quad (39)$$

$$Q_1 = \frac{\kappa_{31}(\mathbf{F}, T, 0) - \kappa_{32}(\mathbf{F}, T, 0)}{eT} I$$
$$- \frac{\partial}{\partial T} \frac{\kappa_{31}(\mathbf{F}, T, I) - \kappa_{32}(\mathbf{F}, T, I)}{2eT} I \Delta T$$
$$+ \frac{\kappa_{31}(\mathbf{F}, T, I) - \kappa_{31}(\mathbf{F}, T, 0) - \kappa_{32}(\mathbf{F}, T, I) + \kappa_{32}(\mathbf{F}, T, 0)}{eIT} I^2$$
$$- \frac{\kappa_{34}(\mathbf{F}, T, I)}{T^2} \Delta T. \quad (40)$$

$$Q_2 = \frac{\kappa_{41}(\mathbf{F}, T, 0) - \kappa_{42}(\mathbf{F}, T, 0)}{eT} I$$
$$+ \frac{\partial}{\partial T} \frac{\kappa_{41}(\mathbf{F}, T, I) - \kappa_{42}(\mathbf{F}, T, I)}{2eT} I \Delta T$$
$$+ \frac{\kappa_{41}(\mathbf{F}, T, I) - \kappa_{41}(\mathbf{F}, T, 0) - \kappa_{42}(\mathbf{F}, T, I) + \kappa_{42}(\mathbf{F}, T, 0)}{eIT}$$
$$\times I^2 + \frac{\kappa_{43}(\mathbf{F}, T, I)}{T^2} \Delta T. \quad (41)$$

In view of (38), the first two terms in Eq. (39) at $I = 0$ are equal to zero. Therefore, the third term characterizes the Seebeck effect with coefficient

$$Z(\mathbf{F}, T, I) = \{\kappa_{14}(\mathbf{F}, T, I) + \kappa_{23}(\mathbf{F}, T, I)\}/(eT^2). \quad (42)$$

In view of (37) and (38), the first terms in (40) and (41) are equal in magnitude and differ in sign. They characterize the Peltier effect (linear in current) with coefficient

$$\Pi(\mathbf{F}, T) = \{\kappa_{41}(\mathbf{F}, T, 0) - \kappa_{42}(\mathbf{F}, T, 0)\}/(eT). \quad (43)$$

The last terms, which are equal in view of (37), characterize the thermal conductivity. Summing Eqs. (40) and (41), adding the work of a source against the thermal emf, and taking (37) and (38) into account, we obtain the following for the power released in the system:

$$W(\mathbf{F}, T, I) = K(\mathbf{F}, T) I \Delta T + R(\mathbf{F}, T, I) I^2 + D(\mathbf{F}, T, I) \Delta T. \quad (44)$$

The first term in (44) characterizes the Thompson effect with coefficient

$$K(\mathbf{F}, T) = \frac{\partial}{\partial T}$$
$$\times \frac{\kappa_{42}(\mathbf{F}, T, 0) - \kappa_{41}(\mathbf{F}, T, 0) - \kappa_{32}(\mathbf{F}, T, 0) - \kappa_{31}(\mathbf{F}, T, 0)}{2eT}$$
$$- \{\kappa_{14}(\mathbf{F}, T, 0) + \kappa_{23}(\mathbf{F}, T, 0)\}/(eT^2).$$

while the second term characterizes the Joule–Lenz heat release on the nonlinear resistance of the system

$$R(\mathbf{F},T,I)$$
$$=\frac{\kappa_{42}(\mathbf{F},T,I)-\kappa_{42}(\mathbf{F},T,0)+\kappa_{32}(\mathbf{F},T,I)-\kappa_{32}(\mathbf{F},T,0)}{eI}$$
$$-\frac{\kappa_{41}(\mathbf{F},T,I)-\kappa_{41}(\mathbf{F},T,0)+\kappa_{31}(\mathbf{F},T,I)-\kappa_{31}(\mathbf{F},T,0)}{eI}.$$

The Thompson relations for a nonlinear system follow from relations (37) and (38):

$$Z(\mathbf{F},T,0)=\Pi(-\mathbf{F},T)/T,$$
$$K(\mathbf{F},T)=d\Pi(\mathbf{F},T)dT+\Pi(-\mathbf{F},T)/T. \qquad (45)$$

At $F=0$ (i.e., for a linear system), we obtain classical relations [18]

$$Z(T)=\Pi(T)/T, \quad K(T)=(1/T)d(T\Pi(T))/dT.$$

The third term in (44) characterizes the Righi–Leduc effect and the piezocaloric effect (i.e., the influence of the magnetic field and mechanical stress on the thermal conductivity)

$$D(\mathbf{F},T,I)=k\frac{\kappa_{43}(\mathbf{F},T,I)-\kappa_{43}(-\mathbf{F},-T,I)}{T}$$
$$-\frac{\kappa_{14}(\mathbf{F},T,I)-\kappa_{14}(\mathbf{F},T,0)+\kappa_{23}(\mathbf{F},T,I)-\kappa_{23}(\mathbf{F},T,0)}{eT^2}$$
$$+\frac{\partial}{\partial T}\frac{\kappa_{42}(\mathbf{F},T,I)-\kappa_{42}(\mathbf{F},T,0)-\kappa_{41}(\mathbf{F},T,I)+\kappa_{41}(\mathbf{F},T,I)}{2eT}$$
$$-\frac{\partial}{\partial T}\frac{\kappa_{32}(\mathbf{F},T,I)-\kappa_{32}(\mathbf{F},T,0)-\kappa_{31}(\mathbf{F},T,I)+\kappa_{31}(\mathbf{F},T,0)}{2eT}.$$

The dependence of coefficient D on the magnetic field characterizes the Hall and magnetoresistive effects, and its dependence on mechanical stress characterizes the piezoresistive effect. The dependences of Seebeck (42) and Peltier (43) coefficients on the magnetic field characterize the Nernst and Ettingshausen effects, respectively. The dependences of these quantities on mechanical stress characterize the corresponding piezoeffects.

If the charged particles exchanged between the system and thermostats through contacts have an ordered spin, the potentials and heat flows are produced by both charge and spin currents. Three components of spin current Σ_α and magnetic field B_α are then added at each contact to the thermodynamic forces and the responses, respectively. Reciprocity conditions (37) are still satisfied, but indices i and j run through the values from 1 to 10. Accordingly, the number of equations of the form (35) increases to 10. In addition, the spin currents through contacts are not equal in magnitude even in the stationary mode. With Eqs. (2), (17), and (23) taken into account, the equation for the average components of spin moment density $s_\alpha(t,\mathbf{r})=\langle\hat{s}_{\alpha(t,\mathbf{r})}\rangle$ takes the form

$$\frac{\partial S_\alpha(t,\mathbf{r})}{\partial t}=\mathrm{Sp}\left(\hat{s}_\alpha(t,\mathbf{r})\frac{d\hat{\rho}}{dt}+\frac{\partial\hat{s}_\alpha(t,\mathbf{r})}{\partial t}\hat{\rho}\right)$$
$$=\frac{s^e_\alpha(t,\mathbf{r})-s_{\alpha(t,\mathbf{r})}}{T_\alpha}-\hbar\gamma\left[\mathbf{B}(t,\mathbf{r})\times\mathbf{s}(t,\mathbf{r})\right]_\alpha-\frac{\partial\upsilon_{\alpha\beta}(t,\mathbf{r})}{\partial r_\beta}. \qquad (46)$$

Here, $\upsilon_{\alpha\beta}(t,\mathbf{r})=\langle\hat{\upsilon}_{\alpha\beta}(t,\mathbf{r})\rangle$ is the spin current density tensor, and relaxation times τ_{mn} for each component of the spin density are substituted with averaged value T_α.

Let us integrate Eq. (46) over the volume of the medium assuming that the magnetic field is homogeneous:

$$\frac{dS_\alpha}{dt}+\frac{S_\alpha-S^e_\alpha}{T_\alpha}+\hbar\gamma\left[\mathbf{B}\times\mathbf{S}\right]_\alpha+\Sigma_{\alpha2}-\Sigma_{\alpha1}. \qquad (47)$$

Equation (47) should be used together with equations of the form (35). Therefore, relations (38) and relations (45) stemming from them have a more complex structure if spin currents are present.

The gradients of temperature and chemical potential are thermodynamic forces. If the chemical potential of particles of the ith component depends on the densities of particles of all components, the following is obtained from (28):

$$j_{i\alpha}(t,\mathbf{r},\mathbf{F},\mathbf{B})=\iint\limits_{V\,0}^{\quad\infty}\frac{\chi_{i\alpha j\beta}(\tau,\mathbf{r},\mathbf{r}',\mathbf{B},\mathbf{T})}{kT}\frac{d\mu_j(t-\tau,\mathbf{r}')}{dc_k}$$
$$\times\frac{\partial c_k(t-\tau,\mathbf{r}')}{\partial r_\beta}d\tau d^3r'+\iint\limits_{V\,0}^{\quad\infty}\xi_{i\alpha j\beta}(\tau,\mathbf{r},\mathbf{r}',\mathbf{F},\mathbf{B},\mathbf{T})$$
$$\times\mu_j(t-\tau,\mathbf{r}')\frac{\partial T(t-\tau,\mathbf{r}')}{\partial r_\beta}d\tau d^3r'. \qquad (48)$$

The first and the second terms in relation (48) are generalizations of the Fick diffusion law and the Ludwig–Soret law, respectively [18]. In accordance with (37),

$$\chi_{i\alpha j\beta}(\tau,\mathbf{r},\mathbf{r}',\mathbf{F},\mathbf{B},\mathbf{T})=\chi_{j\beta i\alpha}(\tau,\mathbf{r}'\mathbf{r},-\mathbf{F},-\mathbf{B},\mathbf{T}),$$
$$\xi_{i\alpha j\beta}(\tau,\mathbf{r},\mathbf{r}',\mathbf{F},\mathbf{B},\mathbf{T})=\xi_{j\beta i\alpha}(\tau,\mathbf{r}'\mathbf{r},-\mathbf{F},-\mathbf{B},\mathbf{T}).$$

Let us consider the reciprocity relations for the mechanical response to a mechanical input using the example of electric quantities in the absence of fields produced by external sources. The sole mechanical observable in the medium is then the $\varphi(t,\mathbf{r})$ potential distribution, and the corresponding mechanical force is density $\rho(t,\mathbf{r})$ of free charges involved in the exchange between the system and thermostats. Assuming that thermodynamic inputs are lacking, we obtain the following from Eq. (28) for the response induced by an electric input:

$$\varphi(t,\mathbf{r})=\int\limits_V\int\limits_0^\infty\chi_{11}(\tau,\mathbf{r},\mathbf{r}',\rho,\mathbf{B},\mathbf{T})\rho(t-\tau,\mathbf{r}')d\tau d^3r'. \qquad (49)$$

Dropping the indices of χ, we obtain the following from (34):

$$\chi(\tau, \mathbf{r}, \mathbf{r}', \rho(t, \mathbf{r}), \mathbf{B}(t, \mathbf{r}), \mathbf{T}(t, \mathbf{r}))$$
$$= \chi(\tau, \mathbf{r}', \mathbf{r}, -\rho(t, \mathbf{r}), -\mathbf{B}(t, \mathbf{r}), \mathbf{T}(t, \mathbf{r})). \qquad (50)$$

Let us introduce relaxation time τ_r of the system with the property that all $\chi_{ij}(\tau > \tau_r) \equiv 0$. With the exponential factor in formula (30) taken into account, we may assume that $\tau_r > \max(\tau_{nm})$. Let us expand the charge density in the expression under integral sign in formula (49) into a Taylor series about t. At $\tau \leq \tau_r$ in the quasi-stationary mode, when $\tau_r|d^3\rho/dt^3| \ll |d^2\rho/dt^2|$, we limit ourselves to the third term of the series and differentiate with respect to r_α with continuity equation (23) taken into account:

$$\frac{\partial\varphi(t, \mathbf{r})}{\partial r_\alpha} = \int\limits_V \int\limits_0^\infty \frac{\partial\chi(\tau, \mathbf{r}, \mathbf{r}', \rho, \mathbf{B}, \mathbf{T})}{\partial r_\alpha} \rho(t, \mathbf{r}') d\tau d^3r'$$
$$+ \int\limits_V \int\limits_0^\infty \tau \frac{\partial\chi(\tau, \mathbf{r}, \mathbf{r}', \rho, \mathbf{B}, \mathbf{T})}{\partial r_\alpha} \frac{\partial j_\beta(t\mathbf{r}')}{\partial r'_\beta} d\tau d^3r'$$
$$- \frac{\partial}{\partial t} \int\limits_V \int\limits_0^\infty \frac{\tau^2}{2} \frac{\partial\chi(\tau, \mathbf{r}, \mathbf{r}', \rho, \mathbf{B}, \mathbf{T})}{\partial r_\alpha} \frac{\partial j_\beta(t, \mathbf{r}')}{\partial r'_\beta} d\tau d^3r'.$$

Integrating the second and the third terms of this equation by parts considering that in the inner region for quasilocal function $\chi(\tau, \mathbf{r} \in V), \mathbf{r}' \in S, \rho, \mathbf{B}, \mathbf{T} = 0$, we find

$$\frac{\partial\varphi(t, \mathbf{r})}{\partial r_\alpha} = \int\limits_V \int\limits_0^\infty \frac{\partial\chi(\tau, \mathbf{r}, \mathbf{r}', \rho, \mathbf{B}, \mathbf{T})}{\partial r_\alpha} \rho(t, \mathbf{r}') d\tau d^3r'$$
$$- \int\limits_V \int\limits_0^\infty \tau \frac{\partial^2\chi(\tau, \mathbf{r}, \mathbf{r}', \rho, \mathbf{B}, \mathbf{T})}{\partial r_\alpha \partial r'_\beta} j_\beta(\tau\mathbf{r}') d\tau d^3r'$$
$$+ \frac{\partial}{\partial t} \int\limits_V \int\limits_0^\infty \frac{\tau^2}{2} \frac{\partial^2\chi(\tau, \mathbf{r}, \mathbf{r}', \rho, \mathbf{B}, \mathbf{T})}{\partial r_\alpha \partial r'_\beta} j_\beta(\tau\mathbf{r}') d\tau d^3r'.$$

With the Maxwell equation taken into account, we obtain

$$E_\alpha(t, \mathbf{r}) = \int\limits_V \xi_\alpha(\mathbf{r}, \mathbf{r}', \rho, \mathbf{B}, \mathbf{T}) \rho(t, \mathbf{r}') d^3r'$$
$$+ \int\limits_V \lambda_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \mathbf{j}, \mathbf{B}, \mathbf{T}) j_\beta(t, \mathbf{r}') d^3r', \qquad (51)$$

$$A_\alpha(t, \mathbf{r}) = \int\limits_V \zeta_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \mathbf{j}, \mathbf{A}, \mathbf{T}) j_\beta(t, \mathbf{r}') d^3r', \qquad (52)$$

$$\xi(\mathbf{r}, \mathbf{r}', \rho, \mathbf{B}, \mathbf{T}) = -\int\limits_0^\infty \frac{\partial\chi(\tau, \mathbf{r}, \mathbf{r}', \rho, \mathbf{B}, \mathbf{T})}{\partial r_\alpha} d\tau,$$

$$\lambda_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \mathbf{j}, \mathbf{B}, \mathbf{T}) = \int\limits_0^\infty \tau \frac{\partial^2\chi(\tau, \mathbf{r}, \mathbf{r}', \mathbf{j}, \mathbf{B}, \mathbf{T})}{\partial r_\alpha \partial r'_\beta} d\tau,$$

$$\zeta_{\alpha,\beta}(\mathbf{r}, \mathbf{r}', \mathbf{j}, \mathbf{A}, \mathbf{T}) = -c \int\limits_0^\infty \frac{\tau^2}{2} \frac{\partial^2\chi(\tau, \mathbf{r}, \mathbf{r}', \mathbf{j}, \mathbf{A}, \mathbf{T})}{\partial r_\alpha \partial r'_\beta} d\tau. \qquad (53)$$

It is taken into account in relations (52) and (53) that vector potential $\mathbf{A}$ defines uniquely magnetic field $\mathbf{B}$ and, in view of Eq. (23), the current density distribution defines the charge density. Vectors $\mathbf{A}$ and $\mathbf{j}$ change sign upon coordinate inversion. The second derivative of function χ does not change sign upon coordinate inversion. Assuming that function χ is doubly continuously differentiable and taking relations (50) and (52) into account, we obtain the following:

$$\lambda_{\alpha,\beta}(\mathbf{r}, \mathbf{r}/, \mathbf{j}, \mathbf{b}, \mathbf{T}) = \lambda_{\beta\alpha}(\mathbf{r}', \mathbf{r}, -\mathbf{j}, -\mathbf{B}, \mathbf{T}),$$

$$\zeta_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \mathbf{j}, \mathbf{A}, \mathbf{T}) = \zeta_{\beta,\alpha}(\mathbf{r}', \mathbf{r}, -\mathbf{j}, -\mathbf{A}, \mathbf{T})$$
$$= \zeta_{\beta\alpha}(\mathbf{r}', \mathbf{r}, \mathbf{j}, \mathbf{A}, \mathbf{T}). \qquad (54)$$

The first term in Eq. (51) is a Coulomb field produced by a distributed charge in an inhomogeneous anisotropic nonlinear medium with spatial dispersion. The second term in Eq. (51) is a generalization of the differential Ohm's law, and Eq. (52) is a version of the Biot–Savart law.

Let us examine the dynamics of the system energy under the influence of mechanical forces. It follows from Eqs. (1), (9), and (10) and the rule of permutation of operators under the spur sign that

$$\frac{dW}{dt} = \frac{d\langle\hat{H}\rangle}{dt} = \mathbf{Sp}\left(\frac{\partial\hat{\rho}}{\partial t}\hat{H}\right) - \int\limits_V f_i(t, \mathbf{r})$$
$$\times \mathbf{Sp}\left(\hat{\rho}\frac{\partial\hat{d}_i(t, \mathbf{r})}{\partial t}\right) d^3r + \mathbf{Sp}\left(\hat{\rho}\frac{\partial\hat{H}_r}{\partial t}\right)$$
$$- \int\limits_V \frac{\partial f_i(t, \mathbf{r})}{\partial t} \mathbf{Sp}\left(\hat{\rho}\hat{d}_i(t, \mathbf{r})\right) d^3r$$
$$= -\int\limits_V \frac{\partial f_i(t, \mathbf{r})}{\partial t} d_i(t, \mathbf{r}) d^3r + \left\langle\frac{\partial\hat{H}_r}{\partial t}\right\rangle. \qquad (55)$$

The second and the first terms in the right-hand part of (55) characterize the interaction with thermostats and the influence of mechanical forces, respectively. If Eq. (28)

is taken into account, the first term takes the form

$$-\int_V\int_V\int_0^\infty \chi_{ij}(\tau,\mathbf{r},\mathbf{r}',\mathbf{F},\mathbf{B},\mathbf{T})\frac{df_i(t,\mathbf{r})}{dt}$$
$$\times\frac{f_j(t+\tau,\mathbf{r}')+f_j(t-\tau,\mathbf{r}')}{2}d\tau d^3r d^3r'$$
$$+\int_V\int_V\int_0^\infty \chi_{ij}(\tau,\mathbf{r},\mathbf{r}',\mathbf{F},\mathbf{B},\mathbf{T})\frac{df_i(t,\mathbf{r})}{dt}$$
$$\times\frac{f_j(t+\tau,\mathbf{r}')-f_j(t-\tau,\mathbf{r}')}{2}d\tau d^3r d^3r'. \qquad (56)$$

The first term in formula (56) changes sign upon time inversion (i.e., characterizes the reversible energy exchange between the system and sources of mechanical forces **F**). It corresponds to the power of work P_F done by the sources of external forces on the system. The second term does not change sign upon time inversion (i.e., characterizes the irreversible energy exchange between the system and sources of forces **F**). It corresponds to heat power Q_F produced in the system under the influence of external mechanical forces. Let us expand the forces in the expression under integral sign in formula (56) into a Taylor series about t in the quasistationary mode:

$$Q_F(t)=\int_V\int_V\int_0^\infty \tau\chi_{ij}(\tau,\mathbf{r},\mathbf{r}',\mathbf{F},\mathbf{T})\frac{\partial f_i(t,\mathbf{r})}{\partial t}$$
$$\times\frac{\partial f_j(\mathbf{r}')}{\partial t}d\tau d^3r d^3r',$$
$$P_F(t)=-\int_V\int_V\int_0^\infty \chi_{ij}(\tau,\mathbf{r},\mathbf{r}',\mathbf{F},\mathbf{T})\frac{\partial f_i(t,\mathbf{r})}{\partial t}$$
$$\times\left\{f_j(t,\mathbf{r}')+\frac{\tau^2}{2}\frac{\partial^2 f_j(t,\mathbf{r}')}{\partial t^2}\right\}d\tau d^3r d^3r'. \qquad (57)$$

In the case of electrical input, we set $f(t,\mathbf{r})=\rho(t,\mathbf{r})$ in (55), use relations (23), and integrate by parts with respect to r and r' in the first equation. With formulae (52) and (54) taken into account, we obtain the following for the heat power density:

$$q_F(t,\mathbf{r})=j_\alpha(t,\mathbf{r})\int_V \lambda_{\alpha\beta}(\mathbf{r},\mathbf{r}',\mathbf{j},\mathbf{B},\mathbf{T})j_\beta(t,\mathbf{r}')d^3r',$$
$$\xi(\mathbf{r},\mathbf{r}',\rho,\mathbf{B},\mathbf{T})=-\int_0^\infty \chi(\tau,\mathbf{r},\mathbf{r}',\rho,\mathbf{B},\mathbf{T})d\tau,$$
$$p_F(t,\mathbf{r})=\frac{\partial\rho(t,\mathbf{r})}{\partial t}\int_V \xi(\mathbf{r},\mathbf{r}',\rho,\mathbf{B},\mathbf{T})\rho(t,\mathbf{r}')d^3r'$$
$$+\frac{j_\alpha(t,\mathbf{r})}{c}\int_V \zeta_{\alpha\beta}(\mathbf{r},\mathbf{r}',\mathbf{j},\mathbf{A},\mathbf{T})\frac{\partial j_\beta(t,\mathbf{r}')}{\partial t}d^3r'. \qquad (58)$$

With Eqs. (58) and (53) taken into account, it follows from (51) that

$$\mathbf{E}(t,\mathbf{r})\mathbf{j}(t,\mathbf{r})=q_F(t,\mathbf{r})+\mathbf{j}(t,\mathbf{r})\frac{\partial}{\partial\mathbf{r}}$$
$$\times\int_V \xi(\mathbf{r},\mathbf{r}',\rho,\mathbf{B},\mathbf{T})\rho(t,\mathbf{r}')d^3r'=q_F(t,\mathbf{r})$$
$$+\operatorname{div}\left\{\mathbf{j}(t,\mathbf{r})\int_V \xi(\mathbf{r},\mathbf{r}',\rho,\mathbf{B},\mathbf{T})\rho(t,\mathbf{r}')d^3r'\right\}$$
$$+\frac{\partial\rho(t,\mathbf{r})}{\partial t}\int_V \xi(\mathbf{r},\mathbf{r}'\rho,\mathbf{B},\mathbf{T})\rho(t,\mathbf{r}')d^3r'. \qquad (59)$$

If nonlocalities are insignificant, we set

$$\xi(\mathbf{r},\mathbf{r}',\rho,\mathbf{B},\mathbf{T})=\xi(\mathbf{r},\rho,\mathbf{B},\mathbf{T})\delta(\mathbf{r}-\mathbf{r}'),$$
$$\lambda_{ij}(\mathbf{r},\mathbf{r}',\mathbf{j},\mathbf{B},\mathbf{T})=\lambda(\mathbf{r},\mathbf{j},\mathbf{B},\mathbf{T})\delta(\mathbf{r}-\mathbf{r}'),$$
$$\zeta_{ij}(\mathbf{r},\mathbf{r}',\mathbf{j},\mathbf{A},\mathbf{T})=\zeta(\mathbf{r},\mathbf{j},\mathbf{A},\mathbf{T})\delta(\mathbf{r}-\mathbf{r}').$$

It then follows from Eq. (54) that

$$\lambda_{\beta\alpha}(\mathbf{r},-\mathbf{j},-\mathbf{B},\mathbf{T})=\lambda_{\alpha\beta}(\mathbf{r},\mathbf{j},\mathbf{B},\mathbf{T}),$$
$$\zeta_{\beta\alpha}(\mathbf{r},\mathbf{j},\mathbf{A},\mathbf{T})=\zeta_{\alpha\beta}(\mathbf{r},\mathbf{j},\mathbf{A},\mathbf{T}).$$

The first Eq. (58) then takes the form of the Joule–Lenz law for a nonlinear anisotropic inhomogeneous medium without dispersion

$$q_F(t,\mathbf{r},\mathbf{j},\mathbf{B},\mathbf{T})=\lambda_{ij}(\mathbf{r},\mathbf{j},\mathbf{B},\mathbf{T})j_i(t,\mathbf{r})j_j(t,\mathbf{r}),$$
$$q_F(t,\mathbf{r},-\mathbf{j},-\mathbf{B},\mathbf{T})=q_F(t,\mathbf{r},\mathbf{j},\mathbf{B},\mathbf{T}). \qquad (60)$$

The second Eq. (58) then takes the form

$$p_F(t,\mathbf{r})=\frac{\partial}{\partial t}\left\{\frac{\xi(\mathbf{r},\rho,\mathbf{B},\mathbf{T})\rho^2(t,\mathbf{r})}{2}\right.$$
$$\left.+\frac{\zeta_{\alpha\beta}(\mathbf{r},\mathbf{j},\mathbf{A},\mathbf{T})j_\alpha(t,\mathbf{r})j_\beta(t,\mathbf{r})}{2c}\right\}. \qquad (61)$$

When analyzing Eq. (56), we assumed that the first term (i.e., power P_F of the work of external forces) characterizes the reversible energy exchange between the system and sources of mechanical forces **F** (i.e., the maximum work done by the system on the environment under constant temperature with its sign reversed). Therefore, the expression in curly brackets in the right-hand part of Eq. (61) is the density of free energy $\phi(t,\mathbf{r})$ with the property that the Massieu–Planck functional in the second Eq. (11) takes the form $\Phi(t)=\int_V \phi(t,\mathbf{r})d^3r$. The first term in curly brackets in the right-hand part of Eq. (61) may be regarded as the electric component of the free energy density produced by distributed charges. The second term, which has the form of $\mathbf{j}(t,\mathbf{r})\mathbf{A}(t,\mathbf{r})/(2c)$ in accordance with (53), may be regarded as the magnetic component of the free energy density produced by distributed currents.

Equation (59), in turn, takes the form

$$\mathbf{E}(t,\mathbf{r})\mathbf{j}(t,\mathbf{r})=q_F(t,\mathbf{r},\mathbf{j},\mathbf{B},\mathbf{T})+\frac{\partial}{\partial t}\left\{\frac{\xi(\mathbf{r},\rho,\mathbf{B},\mathbf{T})\rho^2(t,\mathbf{r})}{2}\right\}$$
$$+\,\mathrm{div}\{\xi(\mathbf{r},\rho,\mathbf{B},\mathbf{T})\rho(t,\mathbf{r})\mathbf{j}(t,\mathbf{r})\}. \qquad (62)$$

The left-hand part of Eq. (62) is the work done in unit time by the electric field on charges in unit volume of the medium. It is spent on altering the electric component of the free energy density and producing the heat power density and the energy flow density. In an electrically locally neutral system $\mathbf{E}(t,\mathbf{r})\mathbf{j}(t,\mathbf{r})=q_F(t,\mathbf{r},\mathbf{j},\mathbf{B},\mathbf{T})$.

If laminar flows of components with velocities $\mathbf{v}_i(t,r)=\langle\hat{\mathbf{j}}_i(t,r)\rangle/\langle\hat{c}_i(t,r)\rangle$, are produced in the system under the influence of mechanical forces, the Hamiltonian density in locally quasi-equilibrium density operator (11) is transformed with transformation properties (24) taken into account [16]:

$$\hat{\rho}^q=\exp\left\{-\Phi(t)-\int\limits_V\theta(t,\mathbf{r})\big(\hat{h}_0(t,\mathbf{r})-(\mu_i(t,\mathbf{r})\right.$$
$$\left.-\,m_i v_i^2(t,\mathbf{r}))\hat{c}_i(t,\mathbf{r})-\mathbf{v}(t,\mathbf{r})\pi(t,\mathbf{r})\big)d^3r\right\}, \qquad (63)$$

while Massieu–Planck functional $\Phi(t)$ is, in accordance with (61), also dependent on mechanical forces. It follows from Eq. (11) that this dependence stems from the dependence of the local temperature on mechanical forces (e.g., due to the heat release in the system and the chemical potentials of components).

Conclusion

In this study, by a nonlinear system is meant a system the response of which to an external input does not satisfy the principle of superposition. Within the proposed approach, this nonlinearity emerges due to the deviation of the density operator from the locally quasi-equilibrium one under the influence of external inputs. This deviation is possible if the external input exceeds the level that depends on the system structure (e.g., on nonharmonic terms in the unperturbed Hamiltonian).

Kinetic coefficients (30) and (31) for the response to mechanical and thermodynamic inputs were determined sensu Kubo [2] formally (without specifying the physical mechanism of this response). The derivation of these relations and reciprocity relation (34) based on them is valid in the Markovian relaxation approximation if the unperturbed Hamiltonian is stationary and the unperturbed system is in a quasi-equilibrium state (11). In addition, the system remains stable under the influence of a perturbation that may be presented as a sum of products of a classical specified force by an operator corresponding to an external dynamic variable and an operator of Markovian relaxation to the quasi-equilibrium state. The applicability of Markovian relaxation and the locally quasi-equilibrium operator was examined in [14] and [15], respectively. The principle of weakening of Bogolubov correlations may be used here [19,20]. Nonmarkovian relaxation processes in open dissipative systems interacting with thermostats decay much faster than the primary Markovian relaxation. Therefore, it may be assumed that relation (30) and subsequent relations are valid at $\tau\geqslant\tau_m$, where τ_m is the characteristic time of transition of the system to Markovian relaxation. This time depends on the structure of the system.

The transformations of the Coulomb potential in (3) and subsequent relations correspond to the common multipole expansion and are needed to write Eq. (10) in the quasiclassical form with external inputs regarded as classical fields characterized by specified functions of time and coordinates and dynamic variables regarded as quantum quantities characterized by Hermitian operators. The assumptions made in this case are needed specifically to substantiate the applicability of the quasiclassical representation and limit rather severely the applicability of the theory. If external inputs are regarded as operator variables, the formalism of quantized fields may be used. However, the density matrix of an open system interacting with quantized fields has a complex multiindex structure, and calculations become rather cumbersome. The Kraus formalism [21] may probably allow one to derive a result in a closed form and determine whether the obtained reciprocity relations are exclusive for the quasiclassical approach or also remain valid for quantized fields. Presumably, one may also analyze the restrictions on the relaxation nature in the process.

Local temperatures and chemical potentials in Eq. (17) are regarded as specified classical parameters. Naturally, they are dynamic variables in real open systems interacting with thermostats (particle sources), and Hermitian operators dependent on coordinates and time should correspond to them. These operators need to be constructed in order to obtain self-consistent equations. Since the temperature and the chemical potential are extensive quantities, their local operators cannot be constructed in a standard way as density operators of certain additive quantities [16]. In order to relate them to the entropy density operator, one needs to construct it for a nonequilibrium system. This problem has not been solved yet.

In the recent decade, the interrelation between magnetic and electric properties of the form (50) has been noted at room temperature in multiferroics, which are promising materials for information and energy-saving technologies. The principal types of magnetoelectric interaction, their mechanisms, and the conditions for their emergence were discussed in [22]. The results presented in [23–25] verify the efficiency of control over the magnetization dynamics by mechanical stress and electric fields. It was demonstrated in [26,27] that mechanical stress acts as an „elastic gauge field“that interacts with fermions in a manner similar to the electromagnetic field. The studied Hall viscosity is characterized by relation (30) with components of the magnetic field and the stress tensor included into vector $\mathbf{F}(t, \mathbf{r})$ and components of magnetization and the deformation tensor regarded as the response. The magnitude of this gauge field may be characterized by the corresponding effective magnetic field. The theoretical estimate given in [28] is 10 T. Experimental estimates based on the Landau levels demonstrate that the stress-induced field may be stronger than 300 T [29]. This field may provide effective polarization of the spin current at room temperature.

The authors of [30] used the microscopic theory to demonstrate that the temperature gradient in ferromagnetic materials is equivalent to the effective electric field and produces spin current. Its dependence on the temperature gradient agrees with (48). The possibility of control over heat flows by the spin current was verified in [31]. This control is efficient at high influence densities when the system becomes substantially nonlinear. The proposed method for analysis of quantum transport effects resulting from polarization of the mechanically induced spin current forms the basis for design and optimization of parameters of efficient systems of heat transport.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] L. Onsager. Phys. Rev., **37**, 405 (1931).
[2] R. Kubo. J. Phys. Soc. Jpn., **12** (6), 570 (1957). doi.org/ 10.1143/JPSJ.12.570
[3] R. Kubo, M. Yokota, S. Nakajima. J. Phys. Soc. Jpn., **12** (11), 1203 (1957). DOI: 10.1143/JPSJ.12.1203
[4] A. Hirohata, K. Yamada, Y. Nakatani, I.-L. Prejbeanu, B. Dieny, P. Pirro, B. Hillebrands. JMMM, **509**, 166711 (2020). DOI: 10.1016/j.jmmm.2020.166711
[5] A.A. Bukharaev, A.K. Zvezdin, A.P. Pyatakov, Y.K. Fe ti sov. Physics-Uspekhi, **61** (12), 1175 (2018). DOI: 10.3367/UFNe.2018.01.038279
[6] G.E.W. Bauer, E. Saito, B.J. van Wees. Nature Mater., **11**, 391 (2012). DOI: 10.1038/NMAT3301
[7] A. Miura, H. Sepehri-Amin, K. Masuda, H. Tscuchira, V. Miura, R. Iguchi, Y. Sakuraba, J. Shiomi, K. Hono, K. Uchida. Appl. Phys. Lett., **115**, 222403 (2019). DOI: 10.1063/1.5131001
[8] S. Ota, K. Uchida, R. Iguchi, P. Van Thach, H. Awano, D. Chibal. Scientif. Repor., **9**, 13197 (2019). DOI: 10.1038/s41598-019-49567-2
[9] T. Hirai, H. Sepehri-Amin, K. Hasegavwa, T. Koyama, R. Iguchi, T. Ohkubo, D. Chiba, K. Uchida. Appl. Phys. Lett., **118**, 022403 (2021). DOI: 10.1063/5.0034858
[10] F.K. Dejene, J. Flipse, B.J. van Wees. Phys. Rev. B, **90**, 180402(R) (2014). DOI: 10.1103/PhysRevB.90.180402
[11] V.K. Ignat'ev. Tech. Phys. Lett., **45** (6), 563 (2019). DOI: 10.1134/S1063785019060075
[12] V.K. Ignatjev, S.V. Perchenko. Tech. Phys., **62** (6), 852 (2017). DOI: 10.1134/S1063784217060135
[13] A. Rivas. Phys. Rev. Lett., **124** (16), 0601 (2020). DOI: 10.1103/PhysRevLett.124.160601
[14] V.Yu. Shishkov, E.S. Andrianov, A.A. Pukhov, A.P. Vi no gra dov, A.A. Lisyansky. Physics-Uspekhi, **62** (5), 510 (2019). DOI: 10.3367/UFNe.2018.06.038359
[15] D. Zubarev, V. Morozov, G. Ropke. *Statistical Mechanics of Nonequilibrium Processes* (Akademie Verlag, 1997), v. 1.
[16] A.I. Akhieser, S.V. Peletminsky. *Methods of Statistical Physics* (Nauka, M., 1977)
[17] M.A. Leontovich. *An Introduction to Thermodynamics, Statistical Physics* (Nauka, M., 1983)
[18] S.R. de Groot, P. Mazur. *Non-Equilibrium Thermodynamics* (North-Holland Publishing Company, Amsterdam, 1962).
[19] N.N. Bogolubov. *Selected works in 3 volumes.* (Scientific Thought, Kiev, 1971), v. 3, p. 166–173.
[20] N.N. Bogolubov. *Selected University Lectures* (Moscow University Press, M., 2009), p. 338–352.
[21] K. Kraus. *States, Effects, and Operations: Fundamental Notions of Quantum Theory, ser. Lecture Notes in Physic* (Springer-Verlag, 1983), v. 190. *Lectures in Mathematical Physics at the University of Texas at Austin.* DOI: 10.1007/3-540-12732-1
[22] A.P. Pyatakov, A.K. Zvezdin. Physics-Uspekhi, **55** (6), 557 (2012). DOI: 10.3367/UFNr.0182.201206b.0593
[23] K. Roy, S. Bandyopadhyay, J. Atulasimha. Phys. Rev. B, **83** (22), 4412 (2011). DOI: 10.1103/PhysRevB.83.224412
[24] C.-Y. Liang, A. Sepulveda, S. Keller, G.P. Carman. J. Appl. Phys., **119** (11), 3903 (2016). DOI: http://dx.doi.org/10.1063/1.4944650
[25] A. Khan, D. Nikonov, S. Manipatruni, T. Ghani, I.A. Young. Appl. Phys. Lett., **104** (26), 2407 (2014). DOI: http://dx.doi.org/10.1063/1.4884419
[26] A. Cortijo, Y. Ferreirós, K. Landsteiner, M.A.H. Vozmediano. 2D Mater, **3** (1), 1002 (2016). DOI: 10.1088/2053-1583/3/1/011002
[27] V.K. Ignatiev, N.G. Lebedev, A.A. Orlov, S.V. Perchenko. JMMM, **494**, 165658 (2020). DOI: 10.1016/j.jmmm.2019.165658
[28] F. Guinea, M.I. Katsnelson, A.K. Geim. Nature Phys., **6**, 30 (2010). DOI: 10.1038/NPHYS1420
[29] N. Levy, S.A. Burke, K.L. Meaker, M. Panlasigui, A. Zettl, F. Guinea, A.H. Castro Neto, M.F. Crommie. Science, **329**, 544 (2010). DOI: 10.1126/science.1191700
[30] Y. Takezoe, K. Hosono, A. Takeuchi, G. Tatara. Phys. Rev. B, **82** (9), 094451 (2010). DOI: 10.1103/PhysRevB.82.094451
[31] I.A. Starkov, O.V. Pakhomov, A.S. Starkov. JMMM, **496**, 165949 (2020). DOI: 10.1016/j.jmmm.2019.165949