Principle of symmetry of kinetic coefficients for systems with dragging

L. É. Gurevich and E. T. Krylov

A. F. Ioffe Physicotechnical Institute, USSR Academy of Sciences
(Submitted July 14, 1976)
Zh. Eksp. Teor. Fiz. **72**, 692–698 (February 1977)

We consider the kinetic-coefficient symmetry derived from the system of kinetic equations for a multicomponent system in which the components can drag one another. The self-adjoint character of the collision operator is utilized. We indicate for a multicomponent system a variational principle that makes it possible to determine, the solution of the kinetic equations without any supplementary conditions.

PACS numbers: 05.20.Dd

1. INTRODUCTION

The general derivation of the Onsager principle has a number of shortcomings: first, in the existing derivations[1,2] no account is taken of the dragging phenomenon in multicomponent systems; second, different components can have unequal temperatures and non-equilibrium concentration, leading to energy exchange between the components and to creation and annihilation of quasiparticles (for example, photons); finally, third, these derivations encounter certain formal difficulties which can be circumvented by more or less artificial stratagems.[3]

The main purpose of the present paper is to generalize the Onsager symmetry relations to include systems with dragging. The stratagem employed by us makes it possible to eliminate also the remaining indicated difficulties. It makes use of a system of kinetic equations under the most general assumptions concerning the collision operator, based (just as the Onsager principle) on the reversibility of microscopic processes. This method leads, for example, to a relation between the electron thermal conductivity due to their dragging by phonons, and to the phonon thermal conductivity due to their dragging by electrons. Another example is the connection between the phonon heat flux due to the electric field, and the electric current due to the flux of the electron-dragging phonons.

All the kinetic coefficients are expressed explicitly in terms of the collision operator. Finally, we indicate in the article a variational principle for an arbitrary multicomponent system. This system has the advantage over the Kohler principle in that when the solutions of the kinetic equation are substituted, the variational functional assumes a minimum value without any additional conditions.

2. SYSTEM OF KINETIC EQUATIONS "THERMODYNAMIC FORCES."

We consider a system consisting of several components, which we shall label by the symbol i. The kinetic equation for the component i is of the form

$$\frac{\partial}{\partial t} f_i + D_i = L_i^{\,j}(f_i, f_j), \tag{1}$$

where $f_i(\mathbf{p}_i)$ is the distribution function of the component i, the expression for D_i is

$$D_i = \frac{\partial \varepsilon_i}{\partial \mathbf{p}_i}\frac{\partial f_i}{\partial \mathbf{r}} - \frac{\partial \varepsilon_i}{\partial \mathbf{r}}\frac{\partial f_i}{\partial \mathbf{p}_i}, \tag{2}$$

L_{ij} is the collision integral of the components i and j; ε_i and $\mathbf{p}_i$ are the energy and momentum of particle of the ith component; raising the index j means summation over this index. In the linear approximation, to which we confine ourselves henceforth, we put

$$f_i = f_{0i} + \frac{\partial f_{0i}}{\partial \eta_i}\varphi_i, \quad \eta_i = \frac{\varepsilon_i - \mu_i}{T_i}, \tag{3}$$

where f_{0i} is a local-equilibrium Fermi or Bose distributions function, $\mu_i = \mu_{0i} + e_i\Phi$ is the electrochemical potential and the temperature of the component, e_i is the charge of its particle, and Φ is the electric potential.

We confine ourselves to an approximation linear in the deviation from equilibrium, in which the quantities $|\nabla\Phi|$, $|T_i - T_j|$, and the gradients are small quantities. The electrochemical potential μ_i will also be assumed to deviate little from its equilibrium value, and $\nabla\mu_i$ may not be equal to zero. In this little approximation we have

$$D_i = \frac{\partial f_{0i}}{\partial \eta_i}(\mathbf{v}_i, \nabla\eta_i), \quad \mathbf{v}_i \equiv \frac{\partial \varepsilon_i}{\partial \mathbf{p}_i}, \tag{4}$$

and the collision integral is

$$L_i^{\,j}(f_i, f_j) = L_i^{0j}(f_{0i}, f_{0j}) + L_i^{\,j}\varphi_j.$$

The first term on the right is connected with the difference between the temperatures of the components and the deviation of the chemical potentials from their equilibrium values. The second term is the linearized collision integral. The first index of L_{ij} indicates the number of the component in the equation in which this integral enters, while the second index shows which component in this expression is assumed to be in disequilibrium. For example, the diagonal element of the operator L_{ij}, if $i=j$ pertains to electrons, describes the scattering of non-equilibrium electrons by the equilibrium part of the system (equilibrium electrons, phonons, defects, etc.). If i pertains to electrons and j pertains to phonons, then $L_{ij}\varphi_j$ describes the dragging of the electrons by the non-equilibrium phonons, while $L_{ji}\varphi_i$ describes

0038-5646/77/4502-0363$02.40

the dragging of the phonons by the non-equilibrium electrons.

The system of kinetic equations (1) breaks up in this approximation into two coupled systems:

$$\frac{\partial f_{0i}}{\partial t}=\frac{\partial f_{0i}}{\partial \eta_i}\frac{\partial \eta_i}{\partial t}=L_i^{0j}(f_{0i},f_{0j}), \tag{5}$$

$$\frac{\partial f_{0i}}{\partial \eta_i}\frac{\partial}{\partial t}\varphi_i+D_i=L_i^j\varphi_j. \tag{6}$$

Equations (5) constitute a system for the quasi-equilibrium parameters T_i and μ_i, and the number of unknowns in this system is generally speaking larger than the number of equations. We supplement them by taking into account the energy and particle-number conservation laws. We confine ourselves to the case $\partial/\partial t=0$, and then the usual procedure for integrating (1) yields

$$\begin{gathered}\operatorname{div}\mathbf{j}_i^n=\int(d\mathbf{p}_i)L_i^{0j}(f_{0i},f_{0j}),\\ \operatorname{div}\mathbf{j}_i^\xi=\int(d\mathbf{p}_i)\xi_iL_i^0\,(f_{0i},f_{0j}),\quad (d\mathbf{p}_i)=\frac{d^3p_i}{(2\pi\hbar)^3},\end{gathered} \tag{7}$$

where $\xi_i=\varepsilon_i-\mu_i$, and the particle-number and energy flux densities are

$$\mathbf{j}_i^n=\int(d\mathbf{p}_i)\mathbf{v}_if_i,\quad \mathbf{j}_i^\xi=\int(d\mathbf{p}_i)\mathbf{v}_i\xi_if_i. \tag{8}$$

The systems (6) and (7) now comprise a complete system of equations for the parameters T_i and μ_i and for the functions φ_i, with T_i and μ_i entering in the equations for φ_i as parameters.

The integral operator L_{ij} is self-adjoint in the sense that

$$\langle\varphi_iL_{ij}\varphi_j\rangle=\langle\varphi_jL_{ji}\varphi_i\rangle;$$

the angle brackets denote here integration over the momenta of the component whose number coincides with the first index. The self-adjoint character of the operator L was considered in detail in[5] for cases of interest. It is obvious that if L_{ij} is an Hermitian operator, then the operator L_{ij}^{-1} is also Hermitian.

If the distribution function takes the form (3), then the rate of change of the entropy of the component i is equal to

$$\partial S_i/\partial t=\int(d\mathbf{p}_i)\{-\eta_iL_i^0\,(f_{0i},f_{0j})+D_i\eta_i+\varphi_iL_i^j\varphi_j-D_i\varphi_i\}. \tag{9}$$

We introduce the entropy flux density of the component i:

$$\begin{gathered}\mathbf{j}_i^s=\int(d\mathbf{p}_i)\mathbf{v}_i\sigma_i,\\ \sigma_i=f_i\ln f_i\pm(1\mp f_i)\ln\,(1\mp f_i),\end{gathered} \tag{10}$$

where the minus and plus signs correspond to Fermi and Bose statistics; then, as can be easily established,

$$\operatorname{div}\mathbf{j}_i^s=-\langle D_i\eta_i\rangle+\langle D_i\varphi_i\rangle, \tag{11}$$

and we obtain an equation for the change of the entropy in the following form:

$$\frac{\partial S_i}{\partial t}+\operatorname{div}\mathbf{j}_i^s=\left(\frac{\partial S_i}{\partial t}\right)_{\text{cт}}=\int(d\mathbf{p}_i)\{\eta_iL_i^{0j}(f_{0i},f_{0j})+\varphi_iL_i^j\varphi_j\}. \tag{12}$$

Simple calculations yield

$$\langle D_i\eta_i\rangle=\frac{1}{T_i}\operatorname{div}\mathbf{j}_i^\xi-\frac{\mu_i}{T_i}\operatorname{div}\mathbf{j}_i^n; \tag{13}$$

By virtue of (7), the first two terms in the right-hand side of (9) add up to zero, so that

$$\partial S_i/\partial t=-\langle D_i\varphi_i\rangle+\langle\varphi_iL_i^j\varphi_j\rangle. \tag{14}$$

In the stationary case, when $\partial S_i/\partial t=0$, we can write

$$\langle D_i\varphi_i\rangle=\langle\varphi_iL_i^j\varphi_j\rangle. \tag{15}$$

The expression $\langle D_i\varphi_i\rangle$ reduces to a form analogous to (13):

$$\langle D_i\varphi_i\rangle=(\mathbf{j}_i^\xi,\ \nabla T_i^{-1})-(\mathbf{j}_i^n,\ T_i^{-1}\nabla\mu_i). \tag{16}$$

The expressions ∇T_i^{-1} and $T_i^{-1}\nabla\mu_i$ assume the role of "thermodynamic forces," which we shall designate by the symbols $\mathbf{X}_{i\alpha}$ (i denotes the number of the component on which the force acts, and α is used to distinguish between the forces acting on one component). The number and form of the thermodynamic forces is determined by the macroscopic parameters on which the equilibrium or local-equilibrium distribution function depends. The forces that enter in (16) are a result of the fact that we have immediately specified the form of the local-equilibrium distribution functions. Were they to contain besides T and μ some other macroscopic parameters, then the number of the thermodynamic forces could increase.

3. SYMMETRY OF KINETIC COEFFICIENTS

The solutions φ_i of Eqs. (6) can be formally written in the form

$$\varphi_i=L_i^{-1j}D_j. \tag{17}$$

The flux densities are then

$$\begin{gathered}\mathbf{j}_i^n=\int(dp_i)\mathbf{v}_i\frac{\partial f_{0i}}{\partial\eta_i}L_i^{-1j}D_j,\\ \mathbf{j}_i^\xi=\int(dp_i)\mathbf{v}_i\xi_i\frac{\partial f_{0i}}{\partial\eta_i}L_i^{-1j}D_j.\end{gathered} \tag{18}$$

Substituting here the expressions for D_j, we obtain

$$\begin{gathered}\mathbf{j}_i^n=\int(dp_i)\mathbf{v}_i\frac{\partial f_{0i}}{\partial\eta_i}L_i^{-1j}\left(\mathbf{v}_j,\frac{\partial f_{0j}}{\partial\eta_j}\left(\xi_j\nabla\frac{1}{T_j}-\frac{\nabla\mu_j}{T_j}\right)\right),\\ \mathbf{j}_i^\xi=\int(dp_i)\mathbf{v}_i\xi_i\frac{\partial f_{0i}}{\partial\eta_i}L_i^{-1j}\left(\mathbf{v}_j,\frac{\partial f_{0j}}{\partial\eta_j}\left(\xi_j\nabla\frac{1}{T_j}-\frac{\nabla\mu_j}{T_j}\right)\right).\end{gathered} \tag{19}$$

If we write the expressions for the fluxes in the form

$$j_i^n=\alpha_i^j\nabla\mu_j+\beta_i^j\nabla T_j, \tag{20}$$

$$j_i^\xi=\gamma_i^j\nabla\mu_i+\delta_i^j\nabla T_j, \tag{21}$$

then, as seen from (19), (20), and (21), the following symmetry relations hold:

$$\alpha_{ij}T_j=\alpha_{ji}T_i, \tag{22a}$$

$$\beta_{ij}T_j^2=\gamma_{ji}T_i, \tag{22b}$$

$$\delta_{ij}T_j^2=\delta_{ji}T_i^2. \tag{22c}$$

If $i=j$ and this symbol pertains to electrons, then (22b) leads to the well-known relation between the thermoelectric coefficients. The coefficients α_{ij} can be called the mutual-diffusion coefficients. Finally, the symmetry properties of the matrix δ_{ij} denote that, for example, the thermal conductivity of the electrons, due to their dragging by phonons (at identical subsystem temperatures), is equal to the phonon thermal conductivity due to their dragging by the electrons. (Of course, it is assumed here that the dragging flux of the latter is determined only by T, and the thermoelectric field produced thereby is disregarded; this situation is realized in pure form in superconductors.[6])

In the foregoing derivation we have assumed the subsystem temperatures to be different. Under these conditions, energy should be exchanged between them. If an experimental situation is possible in which the subsystem temperatures and the temperature gradients are maintained constant, then the presence of this exchange does not change our derivations in any way. However, after having established relations (22) we can go to the limit of identical temperatures. A situation is also possible in which the temperature differences are so small that energy exchange between the subsystems is negligibly small, and the nonstationary behavior of the system, due to this exchange, can be neglected.

Relations (22) are based on the self-adjoint property of the operator L with respect to the functions φ. It is obvious that this self-adjoint property is closely connected with the invariance of the microscopic equations of motion relative to time reversal. The actual calculation of the kinetic coefficients by means of formulas (22) is made difficult by the presence in them of a reversible operator L^{-1}. However, the expressions for the kinetic coefficients can be easily reduced to a form in which they no longer contain this operator.

By virtue of the linearity of the kinetic equations

$$D_i = L_i^j \varphi_j$$

the function φ_i can be represented as a linear combination of terms proportional to the corresponding forces (since all the components interact with one another, it follows that φ_i depends on all the forces, and not only on the forces acting on the component i):

$$\varphi_i = \varphi_{i,\,j\alpha} X^{j\alpha}. \tag{23}$$

Since the forces are arbitrary and the theory is linear, the stationarity condition (16) takes in this case the form

$$\langle D_{i,\,i\alpha} \varphi_{l,\,j\beta} \rangle = \langle \varphi_{l,\,j\beta} L_i^k \varphi_{k,\,i\alpha} \rangle. \tag{24}$$

In analogy with (17) we can write in general form:

$$\langle D_i \varphi_i \rangle = (\mathbf{j}_{i\alpha}, \mathbf{X}^{i\alpha}), \tag{25}$$

where $\mathbf{j}_{i\alpha}$ has the meaning of the flux corresponding to the force $\mathbf{X}_{i\alpha}$. In turn, $\mathbf{j}_{i\alpha}$ depends linear on the forces:

$$\mathbf{j}_{i\alpha} = \varkappa_{i\alpha,\,j\beta} \mathbf{X}^{j\beta}. \tag{26}$$

Comparing (26), (25), and (24), we obtain

$$\varkappa_{i\alpha,\,j\beta} = \langle \varphi_{i,\,j\beta} L_i^k \varphi_{k,\,i\alpha} \rangle. \tag{27}$$

We note a circumstance of importance in what follows: From the fact that $D_{i,\,j\beta} \equiv 0$, it follows in the case $j \neq i$, by virtue of the kinetic equations, that

$$L_i^j \varphi_{j,\,k\alpha} = 0, \quad \text{if} \quad i \neq k, \tag{28a}$$

or

$$\langle \varphi_{i,\,j\alpha} L_i^k \varphi_{k,\,l\beta} \rangle = 0, \quad \text{if} \quad l \neq i. \tag{28b}$$

We shall now prove the symmetry properties of the kinetic coefficients written in this new form. (We note that the kinetic coefficients $\varkappa$ introduced here differ somewhat from the conventional ones [(4) and (6)], since they represent the coefficients of the linear coupling of the fluxes with the thermodynamic forces, and not with quantities of the type ∇T and $\nabla \mu$.)

The proof of the symmetry of the kinetic coefficients, based on the property (28) and on the self-adjoint character of the operator L, is obtained in the following manner:

$$\begin{aligned} \langle D^i{}_{,j\alpha} \varphi_{i,k\beta} \rangle &\equiv \langle D_{j,j\alpha} \varphi_{j,k\beta} \rangle = \langle \varphi_{i,k\beta} L^{il} \varphi_{l,j\alpha} \rangle \\ &= \langle \varphi_{l,j\alpha} L^{li} \varphi_{i,k\beta} \rangle = \langle \varphi^l{}_{,j\alpha} D_{l,k\beta} \rangle \equiv \langle \varphi_{k,j\alpha} D_{k,k\beta} \rangle, \end{aligned} \tag{29}$$

or

$$\langle D_{j,\,j\alpha} \varphi_{j,\,k\beta} \rangle = \langle D_{k,\,k\beta} \varphi_{k,\,j\alpha} \rangle, \tag{30}$$

whence it follows by virtue of (24) that

$$\varkappa_{i\alpha,\,j\beta} = \varkappa_{j\beta,\,i\alpha}; \tag{31}$$

indeed,

$$\begin{aligned} \langle D_{j,\,j\alpha} \varphi_{j,\,k\beta} \rangle &= \langle \varphi_{j,\,k\beta} L_j^i \varphi_{i,\,j\alpha} \rangle = \varkappa_{j\alpha,\,k\beta}, \\ \langle D_{k,\,k\beta} \varphi_{k,\,j\alpha} \rangle &= \langle \varphi_{k,\,j\alpha} L_k^i \varphi_{i,\,k\beta} \rangle = \varkappa_{k\beta,\,j\alpha}. \end{aligned}$$

To avoid misunderstandings, we note that the kinetic coefficients expressed by formula (27) do not satisfy formally the symmetry principle, but they can be easily reduced to the required form with the aid of the conditions (28). We demonstrate this using as the simplest example a two-component system, with each component acted upon by a single force, X_1 and X_2 respectively (the meaning of the simplified symbols is obvious); then

$$\begin{aligned} \varkappa_{1,2} &= \langle \varphi_{1,2} L_{11} \varphi_{1,1} \rangle + \langle \varphi_{1,2} L_{12} \varphi_{2,1} \rangle, \\ \varkappa_{2,1} &= \langle \varphi_{2,1} L_{21} \varphi_{1,2} \rangle + \langle \varphi_{2,1} L_{22} \varphi_{2,2} \rangle, \end{aligned}$$

But by virtue of (28) we have

$$L_{11} \varphi_{1,2} + L_{12} \varphi_{2,2} = 0, \quad L_{21} \varphi_{1,1} + L_{22} \varphi_{2,1} = 0;$$

whence

$$\langle \varphi_{1,1} L_{11} \varphi_{1,2} \rangle = -\langle \varphi_{1,1} L_{12} \varphi_{2,2} \rangle, \quad \langle \varphi_{2,2} L_{21} \varphi_{1,1} \rangle = -\langle \varphi_{2,2} L_{22} \varphi_{2,1} \rangle.$$

Taking the last equations into account we get

$$\varkappa_{1,2}=\langle\varphi_{1,2}L_{12}\varphi_{2,1}\rangle-\langle\varphi_{1,1}L_{12}\varphi_{2,2}\rangle,\ \varkappa_{2,1}=\langle\varphi_{2,1}L_{21}\varphi_{1,2}\rangle-\langle\varphi_{2,2}L_{21}\varphi_{1,1}\rangle.$$

When the symmetry of the operator L_{ij} is taken into account, the symmetry of the coefficients $\varkappa$ becomes obvious. A similar procedure can be employed also in more complicated cases.

The explicit expressions obtained by us for the kinetic coefficients are convenient for the use of the variational method with a variable functional

$$I={}^1/_2\langle\varphi_i L^{ij}\varphi_j\rangle-\langle D_i\varphi^i\rangle. \tag{32}$$

The solution of the kinetic equations (6) corresponds to a minimum of this functional without any additional conditions. Indeed, let φ_i be the solutions of Eqs. (6), and let $(\varphi=\psi)_i$ be a certain trial function. Then

$$\begin{aligned}I(\varphi-\psi)&={}^1/_2\langle(\varphi-\psi)_i L^{ij}(\varphi-\psi)_j\rangle-\langle D_i,(\varphi-\psi)^i\rangle\\&={}^1/_2\langle\varphi_i L^{ij}\varphi_j\rangle+{}^1/_2\langle\psi_i L^{ij}\psi_j\rangle-\langle\psi_i L^{ij}\varphi_j\rangle-\langle D_i\varphi^i\rangle\\&\quad+\langle D_i\psi^i\rangle={}^1/_2\langle\varphi_i L^{ij}\varphi_j\rangle+{}^1/_2\langle\psi_i L^{ij}\psi_j\rangle-\langle D_i\varphi^i\rangle\\&=I(\varphi)+{}^1/_2\langle\psi_i L^{ij}\psi_j\rangle.\end{aligned}$$

By virtue of the self-adjoint character of L

$$\langle\psi_i L^{ij}\psi_j\rangle\geqslant 0,$$

and consequently the functional is minimal at $\psi=0$. The absence of any additional conditions when this functional is used constitutes its substantial advantage over the functional proposed by Kohler.[4]

The connection of the functional I with the Kohler functional $\Phi=\langle\varphi_i L^{ij}\varphi_j\rangle$, which was introduced by him for the case of a single-component system, lies in the fact that variation of the latter subject to the additional condition $\langle D_i\varphi^i\rangle=\langle\varphi_i L^{ij}\varphi_j\rangle$, which is taken into account with the aid of Lagrange method, leads precisely to the functional I.

[1] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Fizmatgiz, 1962 [Pergamon, 1965].

[2] S. R. de Groot and P. Mazur, Nonequilibrium Thermodynamics, Wiley, 1962.

[3] R. Fisci, transl. in: Termodinamika neobratimykh protsessov (Thermodynamics of irreversible processes), IIL 1962, p. 178.

[4] J. M. Ziman, Electrons and Phonons, Oxford, 1959.

[5] B. T. Geĭlikman, Fiz. Nizkikh Temp. 2, 350 (1976) [Sov. J. Low Temp. Phys. 2, (1976)].

[6] L. E. Gurevich and E. T. Krylov, Zh. Eksp. Teor. Fiz. 68, 1337 (1975) [Sov. Phys. JETP 41, 686 (1975)]; Pis'ma Zh. Eksp. Teor. Fiz. 22, 467 (1975) [JETP Lett. 22, 226 (1975)].

Translated by J. G. Adashko

Magneto-optical spectra of 3*d* ions in spinel ferrites and weak ferromagnets

G. S. Krinchik, A. P. Khrebtov, A. A. Askochenskiĭ, E. M. Speranskaya, and S. A. Belyaev

Moscow State University

(Submitted July 15, 1976)
Zh. Eksp. Teor. Fiz. 72, 699–711 (February 1977)

The equatorial Kerr effect method was used to investigate the magneto-optical reflection spectra ($\delta(\omega)$ in weak ferromagnets—orthoferrites and hematite—and ferrimagnets—spinel ferrites and chromite ferrites—in the range from 1 to 5.4 eV. It is shown that the threshold of intense absorption in magnetically ordered crystals occurs in the region of the first two-exciton transition $2\times T_{1g}$. As a result of measurements of the chromite ferrites $CoCr_xFe_{2-x}O_4$ and $NiCr_xFe_{2-x}O_4$, in which the Fe^{3+} ions were located either in octahedral or tetrahedral positions, it is revealed that the decisive role is played by optical transitions with participation of ions from both sublattices. In spinel ferrites, optical transitions were observed in the divalent ions Ni^{2+} and Co^{2+}. In the region of the transition ${}^4A_2({}^4F)\rightarrow{}^4T_1({}^4P)$ in the CO^{2+} ions, values $\sim 10\%$ were obtained for the equatorial Kerr effect at room temperature.

PACS numbers: 78.20.Ls

INTRODUCTION

The magneto-optical properties of spinel ferrites, garnet ferrites, and certain weak ferromagnets in the infrared and visible regions of the spectrum are determined mainly by the character of the optical transitions, the frequencies of which lie in the near ultraviolet region. The reason is that the first intense optical transitions in the Fe^{3+} ions lie in this band, whereas the visible and infrared regions of the spectrum contain spin-forbidden, and frequently additionally parity-forbidden transitions between the levels of the 3*d* ions in the internal crystal field (crystalline transitions). Ultraviolet optical and magneto-optical spectra of iron garnets have been under intensive study in recent years because new crystals with high magneto-optical quality factors were found, containing bismuth, praseodymium, and neodymium.[1–4] It was established that in the region 2.8–3.3 eV, as well as weak crystalline transitions, there are two or three intense transitions, the origin of which was not finally determined, although it is precisely their enhancement under the influence of bismuth which causes