THE NONEQUILIBRIUM STATISTICAL OPERATOR IN THE KINETICS OF IRREVERSIBLE PROCESSES WITH SMALL ENERGY TRANSFER

PHYSICS

1969

SovietRxiv

Abstract

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UDC 530.145:539.2.01

PHYSICS

V. P. KALASHNIKOV

THE NONEQUILIBRIUM STATISTICAL OPERATOR IN THE KINETICS OF IRREVERSIBLE PROCESSES WITH SMALL ENERGY TRANSFER

(Presented by Academician N. N. Bogolyubov, 3 X 1968)

1. In macroscopic kinetics one usually considers two types of slow irreversible processes (s.i.p.) (^{1}). The first type of s.i.p. applies to cases of spatial transfer of locally conserved quantities (processes of diffusion, heat conduction, internal friction). The second type of s.i.p. consists of processes in which the exchange of energy between interacting subsystems is impeded. This type includes, for example, the kinetics of the establishment of equilibrium in a system of electrons that do not interact with one another, through collisions with heavy ions or through scattering by photons (phonons) in a plasma and in a solid; relaxation of the energy of heavy Brownian particles; energy exchange in a system of electrons interacting by means of long-range forces; etc. In the works of D. N. Zubarev (^{2}) a very general method was proposed for the theoretical consideration of the kinetics of s.i.p., based on the use of invariants of operator equations of motion. In this approach, systems close to a state of local equilibrium were considered, when the nonequilibrium of the system can be described by a set of thermodynamic variables depending on the coordinates. In this way equations were obtained for the mean values of the densities of mechanical quantities and of the rates of their change in time.

In the present work this method is applied to s.i.p. of the second type. Slow energy exchange means that the phase trajectory of a nonequilibrium subsystem lies mainly on isoenergetic surfaces, shifting only weakly owing to interaction with other subsystems. It may therefore be assumed that in the vicinity of each isoenergetic surface the statistical distribution is close to the Gibbs distribution, with the parameters of this distribution depending on the value of the energy ζ that determines the position of the surface.

2. Let a nonequilibrium system with Hamiltonian H be characterized by a set of operators P_{km} (m is the number of the subsystem, k is an index

numbering the operators of the m-th subsystem). We introduce the densities $P_{km}(\zeta)$ of these quantities in energy space (with $P_{km} = \int d\zeta\, P_{km}(\zeta)$) and the corresponding set of macroscopic functions $F_{km}(\zeta, t)$, which describe the nonequilibrium of the system. The operators P_{km} may include the operators of energy, momentum, number of particles, etc. According to D. N. Zubarev (^{2}), the quantity

$$\widetilde{S}(t,0) = S(t,0) - \int_{-\infty}^{0} dt'\, e^{\varepsilon t'}\, \dot{S}(t+t', t'), \tag{1}$$

where

$$S(t,0) = \Phi + \sum_{km} \int d\zeta\, P_{km}(\zeta) F_{km}(\zeta, t);$$

$$\Phi = \ln \operatorname{Sp} \exp\left\{ -\sum_{km} \int d\zeta\, P_{km} F_{km}(\zeta, t) \right\}, \tag{2}$$

$$\dot{S}(t,0) = \frac{\partial S(t,0)}{\partial t} + (i\hbar)^{-1}[S(t,0), H]; \qquad \dot{S}(t,t') = e^{it'H/\hbar} \dot{S}(t,0) e^{-it'H/\hbar}$$

is an integral of the equation of motion as $\varepsilon \to 0$. The statistical operator ρ, constructed by analogy with the grand Gibbs ensemble in the form $\rho = \exp\{-S(t,0)\}$, will therefore, as $\varepsilon \to 0$, be an integral of the Liouville equation; moreover, this limit should be evaluated after letting the volume of the system tend to infinity. The expressions $S(t,0)$ and $\dot{S}(t,0)$ play the role of the entropy operator and the entropy-production operator, respectively. The functions $F_{km}(\xi, t)$ can be related to the mean values of the operators $P_{km}(\xi)$. We shall seek this relation from the equations

$$\operatorname{Sp}\{P_{km}(\xi)\rho\} \equiv \langle P_{km}(\xi)\rangle^t = \langle P_{km}(\xi)\rangle_L^t = \operatorname{Sp}\{P_{km}(\xi) e^{-S(t,0)}\}.$$

In this case

$$\langle P_{km}(\xi)\rangle^t = -\frac{\delta \Phi}{\delta F_{km}(\xi, t)}; \qquad F_{km}(\xi, t) = \frac{\delta \langle S(t,0)\rangle^t}{\delta \langle P_{km}(\xi)\rangle^t}. \tag{3}$$

The integral term in the right-hand side of formula (1) is determined by the interaction of the subsystems. Considering this interaction to be small, we expand ρ in powers of the entropy-production operator up to terms of first order inclusive. If we now write the equations of motion, averaged over the distribution ρ, for the operators $P_{km}(\xi)$, then, taking (3) into account, we obtain

$$-\sum_{k'm'}\int_0 d\xi'\,\left(P_{km}(\xi);P_{k'm'}(\xi')\right)^t\frac{\partial F_{k'm'}(\xi',t)}{\partial t}=$$

$$=\langle\dot{P}_{km}(\xi)\rangle_L^t+\int_{-\infty}^0 dt'\,e^{\varepsilon t'}\sum_{k'm'}\int d\xi'\,\Big\{\left(\dot{P}_{km}(\xi);\dot{P}_{k'm'}(\xi',t')\right)^t F_{k'm'}(\xi',t+t')+$$

$$+\left(\dot{P}_{km}(\xi);P_{k'm'}(\xi',t')\right)^t\frac{\partial}{\partial t'}F_{k'm'}(\xi',t+t')\Big\}, \qquad (4)$$

where the brackets $(\ldots;\ldots)^t$ denote correlation functions of the form

$$(A;B)^t=\mathrm{Sp}\int_0^1 d\tau\,\{A;e^{-\tau S(t,0)}(B-\langle B\rangle_L^t)e^{(\tau-1)S(t,0)}\}. \qquad (5)$$

The observed rate of increase of the entropy is then written in the form

$$\langle\dot{S}(t,0)\rangle^t=\int_{-\infty}^0 dt'\,e^{\varepsilon t'}\left(\dot{S}(t,0);\dot{S}(t+t',t')\right)^t. \qquad (6)$$

Formulas (3), (4) in principle solve the problem of computing the functions $F_{km}(\xi,t)$. Usually, in the theory of M.E.P. of the second type one uses differential Fokker-Planck equations in energy space. Equations of this type can be obtained from (4) by expanding the functions $F_{km}(\xi',t+t')$ in powers of the difference $\xi'-\xi$.

3. Let us consider, as an example, the kinetics of hot electrons in a semiconductor in crossed electric E and magnetic H fields. The Hamiltonian of the system has the form

$$H=\sum_p\varepsilon_p a_p^+a_p-eE^\alpha\sum_{pp'}x^\alpha_{pp'}a^+_{p'}a_p+H_{el}+H_l$$

where a_p^+,a_p are the Fermi operators of electrons with kinetic momentum p and energy ε_p; x^α is the one-electron coordinate; H_l is the lattice Hamiltonian; $H_{el}=\sum_{pp'}U_{pp'}a^+_{p'}a_p$ is the energy of interaction of electrons with the lattice.

If the proper frequencies of the scatterers are equal to Ω_M, then, neglecting the interaction with the electrons,

$$U_{p'p}(t)=\sum_M U^{(M)}_{p'p}e^{i\Omega_M t}.$$

We shall assume that electron scattering is nearly elastic, i.e., $\hbar\Omega_M$ is much smaller than the mean energy of the electrons. As the operators $P_{km}(\xi)$ we take the quantities $n(\xi)$; $H(\xi) = \xi n(\xi)$; $p^\alpha(\xi)$; $H_l + H_{el}$, satisfying the equations of motion

$$\dot{n}(\xi) = -\frac{\partial}{\partial\xi}\frac{eE^\alpha p^\alpha(\xi)}{m} + \dot{n}_{(l)}(\xi); \qquad \dot{H}(\xi) = \xi\dot{n}(\xi);$$

$$\dot{H}_l + \dot{H}_{el} = -\int d\xi\,\xi\dot{n}_{(l)}(\xi),$$

$$\dot{p}^\alpha(\xi) = e\left\{E^\alpha n(\xi) + \frac{1}{mc}\varepsilon_{\alpha\beta\gamma}p^\beta(\xi)H^\gamma\right\} - \frac{\partial}{\partial\xi}\frac{eE^\beta}{m}T^{\alpha\beta}(\xi) + \dot{p}^\alpha_{(l)}(\xi); \qquad (7)$$

here

$$n(\xi) = \sum_p \delta(\varepsilon_p - \xi)a_p^\dagger a_p; \qquad p^\alpha(\xi) = \sum_p p^\alpha\delta(\varepsilon_p - \xi)a_p^\dagger a_p;$$

$$T^{\alpha\beta}(\xi) = \sum_p p^\alpha p^\beta\delta(\varepsilon_p - \xi)a_p^\dagger a_p$$

are, respectively, the densities of particle number, momentum, and of the momentum-flux tensor, defined on the isoenergetic surface ξ;

$$\dot{n}^\xi_{(l)} = (i\hbar)^{-1}[n(\xi), H_{el}]; \qquad \dot{p}^\alpha_{(l)}(\xi) = (i\hbar)^{-1}[p^\alpha(\xi), H_{el}].$$

Since the equation of motion for $H(\xi)$ is a consequence of the equation for $n(\xi)$, the four operators considered correspond to three functions $F_{km}(\xi, t)$, which we denote by $\varphi(\xi, t)$; $-\chi^\alpha(\xi, t)$; β (it is assumed that the lattice is in equilibrium at temperature $1/\beta$). Thus the entropy operator $S(t, 0)$ has the form

$$S(t, 0) = \int d\xi(n(\xi)\varphi(\xi, t) - p^\alpha(\xi)\chi^\beta(\xi, t)) + \beta(H_l + H_{el}). \qquad (8)$$

In the zeroth approximation in the interaction, the mean values of the operators $n(\xi)$, $p^\alpha(\xi)$, and $T^{\alpha\beta}(\xi)$ are equal to

$$\langle n(\xi)\rangle^t = e^{-\varphi(\xi,t)}g(\xi); \qquad \langle p^\alpha(\xi)\rangle^t = \frac{2m\xi}{3}\chi^\alpha(\xi, t)e^{-\varphi(\xi,t)}g(\xi);$$

$$\langle T^{\alpha\beta}(\xi)\rangle^t_L = \delta_{\alpha\beta}\frac{2m\xi}{3}e^{-\varphi(\xi,t)}g(\xi); \qquad (9)$$

$$g(\xi) = \sum_p \delta(\varepsilon_p - \xi)$$

is the electron density of states. It follows from this that

$$-\int d\xi' \, (n(\xi); n(\xi'))^t \, \dot{\varphi}(\xi', t) = \langle \dot{n}(\xi) \rangle^t;$$

$$\int d\xi' \, (p^\alpha(\xi); p^\beta(\xi'))^t \, \dot{\chi}^\beta(\xi', t) = \langle \dot{p}^\alpha(\xi) \rangle^t, \tag{10}$$

where the correlation functions in these formulas are readily calculated:

$$(n(\xi); n(\xi'))^t = \delta(\xi - \xi') e^{-\varphi(\xi,t)} g(\xi);$$

$$(p^\alpha(\xi); p^\beta(\xi'))^t = \delta_{\alpha\beta} \delta(\xi - \xi') \frac{2m\xi}{3} e^{-\varphi(\xi,t)} g(\xi). \tag{11}$$

Formulas (10) and (11) make it possible to eliminate the time derivatives $\dot{\chi}^\alpha(\xi, t)$ and $\dot{\varphi}(\xi, t)$ from the expression for $\dot{S}(t+t', t')$. Equations (4) now take the form

$$-\dot{\varphi}(\xi, t) e^{-\varphi(\xi,t)} g(\xi) = -\frac{\partial}{\partial \xi} \frac{2eE^\alpha \chi^\alpha(\xi, t)}{3} \, \xi e^{-\varphi(\xi,t)} g(\xi) +$$

$$+ \int_{-\infty}^0 dt' \, e^{\varepsilon t'} \int d\xi' \, (\dot{n}_{(l)}(\xi); (\varphi(\xi', t+t') - \xi' \beta) \dot{n}_{(l)}(\xi', t') - \chi^\alpha(\xi', t+t') \dot{p}^\alpha_{(l)}(\xi', t'))^t; \tag{12}$$

$$\dot{\chi}^\alpha(\xi, t) \frac{2m\xi}{3} e^{-\varphi(\xi,t)} g(\xi) = e \left\{ E^\alpha + \frac{2\xi}{3c} \varepsilon_{\alpha\beta\gamma} \chi^\beta(\xi, t) H^\gamma \right\} e^{-\varphi(\xi,t)} g(\xi) -$$

$$-\frac{\partial}{\partial \xi} \frac{2e\xi}{3} E^\alpha e^{-\varphi(\xi,t)} g(\xi) +$$

$$+ \int_{-\infty}^0 dt' \, e^{\varepsilon t'} \int d\zeta' \, (\dot{p}^a_{(l)}(\zeta); \; (\varphi(\zeta', t+t') - \zeta' \beta) \dot{n}_{(l)}(\zeta', t') -$$

$$-\chi^\beta(\zeta', t+t') \dot{p}^a_{(l)}(\zeta', t') \big)^t. \tag{13}$$

We shall restrict ourselves to consideration of stationary solutions of equations (12) and (13). In the nonvanishing approximation in the inelasticity of scattering, the integral terms in these formulas take, respectively, the form

$$\frac{\partial}{\partial\zeta}\left\{\frac{2\xi^2}{3}e^{-\varphi(\zeta)}g(\zeta)\tau^{-1}(\zeta)\right\}\frac{\partial}{\partial\zeta}(\varphi(\zeta)-\zeta\beta); \qquad \frac{2m\xi}{3}e^{-\varphi(\zeta)}g(\zeta)\chi^a(\zeta)\omega(\zeta). \tag{14}$$

Thus, we have passed from integral equations for the functions $\varphi(\zeta)$ and $\chi^a(\zeta)$ to differential equations of the Fokker–Planck type in energy space. Here $\tau^{-1}(\zeta)$ and $\omega(\zeta)$ are the relaxation frequencies of the energy and momentum of an electron with energy ζ,

$$\tau^{-1}(\zeta)=\frac{3\pi}{2\hbar\xi^2 g(\zeta)}\sum_{p'\mathbf{p}M}(\hbar\Omega_M)^2\langle|U^{(M)}_{p'\mathbf{p}}|^2\rangle_L\delta(\varepsilon_p-\zeta)\delta(\varepsilon_{p'}-\zeta-\hbar\Omega_M),$$

$$\omega(\zeta)=\frac{\pi}{2\hbar m\xi g(\zeta)}\sum_{p'\mathbf{p}M}(\mathbf{p}'-\mathbf{p})^2\langle|U^{(M)}_{p'\mathbf{p}}|^2\rangle_L\delta(\varepsilon_p-\zeta)\delta(\varepsilon_{p'}-\zeta-\hbar\Omega_M). \tag{15}$$

In fact, these expressions contain sums of the quantities $\tau^{-1}(\zeta)$ and $\omega(\zeta)$ corresponding to different scattering mechanisms. Now equations (12) and (13) are readily solved:

$$\chi^{\pm}(\zeta)=\chi^x(\zeta)\pm i\chi^y(\zeta)=-\frac{\omega(\zeta)\pm i\omega_0}{\omega^2(\zeta)+\omega_0^2}\frac{\partial\varphi(\zeta)}{\partial\zeta}\frac{eE^{\pm}}{m};$$

$$\chi^z(\zeta)=-\frac{1}{\omega(\zeta)}\frac{\partial\varphi(\zeta)}{\partial\zeta}\frac{eE^z}{m}; \qquad \omega_0=\frac{eH}{mc}; \tag{16}$$

$$\varphi(\zeta)=\beta\int_0^{\zeta}d\zeta'\left\{1+\frac{e^2E^2}{m\xi}\tau(\zeta')\left[\frac{\cos^2\vartheta}{\omega(\zeta')}+\frac{\sin^2\vartheta\,\omega(\zeta')}{\omega^2(\zeta')+\omega_0^2}\right]\right\}^{-1}+C.$$

The constant C is determined from the normalization condition; ϑ is the angle between the electric and magnetic fields. The solutions obtained make it possible to compute all characteristics of hot electrons that interest us. Namely, the mean electron energy, the current density, and the entropy production are, respectively, equal to

$$\bar{\varepsilon}=\int d\zeta\,\zeta e^{-\varphi(\zeta)}g(\zeta); \qquad j^a=-\frac{2e}{3}\int d\zeta\,\xi\chi^a(\zeta)e^{-\varphi(\zeta)}g(\zeta);$$

$$\langle \dot{S}(t,0)\rangle = \frac{2\beta e E^a}{3}\int d\zeta\,\xi\chi^a(\zeta)e^{-\varphi(\zeta)}g(\zeta) = \beta j^{aE^a}. \tag{17}$$

All results obtained by the method of the kinetic equation for concrete combinations of mechanisms of scattering of the energy and momentum of electrons under the conditions considered are special cases of formulas (16) (see, for example, works (3)). In an analogous way one can also consider other nonequilibrium processes with small energy transfer.

Institute of Metal Physics
Academy of Sciences of the USSR
Sverdlovsk

Received
20 IX 1968

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Note: Figure translations are in progress. See original paper for figures.