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Nonequilibrium statistical Zubarev's operator and Green's functions for an inhomogeneous electron gas

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Nonequilibrium properties of an inhomogeneous electron gas are studied using the method of the nonequilibrium statistical operator by D.N. Zubarev. Generalized transport equations for the mean values of inhomogeneous operators of the electron number density, momentum density, and total energy density for weakly and strongly nonequilibrium states are obtained. We derive a chain of equations for the Green's functions, which connects commutative time-dependent Green's functions "density-density", "momentum-momentum", "enthalpy-enthalpy" with reduced Green's functions of the generalized transport coefficients and with Green's functions for higher order memory kernels in the case of a weakly nonequilibrium spatially inhomogeneous electron gas.

Key words: *nonequilibrium statistical operator, Green's functions, generalized transport coefficients, inhomogeneous electron gas*

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1. Introduction

Investigations of the nonequilibrium properties of many-electron systems are a topical problem in modern nanotechnology [1,2]. Nonequilibrium properties of spatially inhomogeneous many-electron systems are of special importance both from theoretical and experimental points of view. They play a determining role in the processes of absorption, desorption, in catalytic reactions between atoms and molecules at the surfaces of transition metals [3–5], in carbon nanostructures [6,7], including the processes of excitation and ionization of gas atoms and molecules [8–10]. Nonequilibrium properties of many-electron systems were explored by means of various methods, in particular by the Green's functions method [11–17]. For further studies of the Green's function and for specific calculations, the time-dependent method of density functional [24–30] is developed [24–30] based on the Kohn-Sham ideas [18–20], with formulation based on the hydrodynamic approach [21,22] and Mori-like projection operators [23].

In the present paper the method of nonequilibrium statistical operator (NSO) [15] by D.N. Zubarev is applied to the description of nonequilibrium properties of an inhomogeneous electron gas at a metal surface. This method is based on N.N. Bogolyubov's ideas about the reduced description of nonequilibrium states of the system. In the second section the Hamiltonian of a spatially inhomogeneous electron gas, based on the generalized "jellium" model, is presented. Based on this the one- and two-electron distribution functions, free energy, surface energy, inhomogeneous electrical field of electrons of semi-infinity jellium are calculated in [31–34] using the method of dynamical collective variables and the functional representation with taking screening effects into account. These results of equilibrium theory are considered as basic ones for the development of nonequilibrium statistical theory of transport processes for a spatially inhomogeneous electron gas. In the third section, the NSO [15] for a nonequilibrium spatially inhomogeneous electron gas in the generalized "jellium" model is obtained with taking into account electric and magnetic fields, obeying averaged Maxwell equations. Mean values of the number density, momentum density, and total energy density operators, which satisfy the corresponding conservation laws, are chosen as the parameters of a reduced description. In the same section, by means of NSO with projection technique we obtain generalized transport equations for the reduced description parameters, which are applicable to the consideration of both weakly and strongly nonequilibrium processes of charge transfer, electric current, and the energy transport in the case of spatially inhomogeneous electron gas. In the fourth section the generalized transport equations for a weakly nonequilibrium spatially inhomogeneous electron gas are obtained. The chain of equations for Green's functions is constructed for the transport kernels (memory functions dealt with generalized coefficients of viscosity, heat conductivity etc.) within the framework of Tserkovnikov approach [35–37]. This chain of equations interrelates the commutative time-dependent Green's functions "density-density", "momentum-momentum", "enthalpy-enthalpy" with reduced (time evolution operator includes projection) Green's functions of the generalized transport coefficients and reduced Green's functions of higher-order memory functions for weakly nonequilibrium spatially inhomogeneous electron gas.

2. Hamiltonian of the equilibrium inhomogeneous electron gas within the "jellium" model

We consider a semi-restricted metal surface with an unlimited ionic subsystem in the OXY plane with "metal-vacuum" transitions in the direction, perpendicular to this plane. The Hamiltonian of this system is chosen to be the following:

$$H = T + V_{ee} + V_{ei} + V_{ii}, \tag{2.1}$$

where

$$T = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\Delta_i \tag{2.2}$$

is an operator of the kinetic energy of conductivity electrons, m denotes the electron mass, N stands for the number of electrons;

$$V_{ee} = \frac{1}{2}\sum_{i\neq j}^{N}\frac{\mathrm{e}^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{2.3}$$

is the potential energy of interaction between electrons, $\mathbf{r}_i$ denotes the radius-vector of i-th electron position;

$$V_{ii} = \frac{1}{2}\int \mathrm{d}\mathbf{R}_1 \int \mathrm{d}\mathbf{R}_2 \frac{\hat{\rho}_{\text{ion}}(\mathbf{R}_1)\,\hat{\rho}_{\text{ion}}(\mathbf{R}_2)}{|\mathbf{R}_1 - \mathbf{R}_2|} \tag{2.4}$$

is the potential energy of an ionic subsystem, $\hat{\rho}_{\text{ion}}(\mathbf{R}) = Z\mathrm{e}\sum_{i=1}^{N_{\text{ion}}}\delta(\mathbf{R} - \mathbf{R}_i)$ denotes a microscopic density of the ion charge distribution, $\mathbf{R}_i$ means the radius-vector of the ion position, Ze stands for the ion charge and N_{ion} is the number of ions.

$$V_{ie} = -\mathrm{e}\sum_{i=1}^{N}\int \mathrm{d}\mathbf{R}\frac{\hat{\rho}_{\text{ion}(\mathbf{R})}}{|\mathbf{r}_i - \mathbf{R}|} \tag{2.5}$$

denotes the energy of interaction between the conductivity electrons and the ionic subsystem. The system obeys electro-neutrality condition: $\int \mathrm{d}\mathbf{R}\hat{\rho}_{\text{ion}}(\mathbf{R}) = \mathrm{e}N$.

To specify the "jellium" subsystem, let us present the distribution function of the ion charge in the following form: $\hat{\rho}_{\text{ion}}(\mathbf{R}) = \hat{\rho}_{\text{jell}}(\mathbf{R}) + \delta\hat{\rho}_{\text{ion}}(\mathbf{R})$, where $\hat{\rho}_{\text{jell}}(\mathbf{R})$ stands for the distribution function of ion charge in the "jellium" model, $\delta\hat{\rho}_{\text{ion}}(\mathbf{R}) = \hat{\rho}_{\text{ion}}(\mathbf{R}) - \hat{\rho}_{\text{jell}}(\mathbf{R})$ is the difference between the charge distribution of the ionic subsystem and of the "jellium" model. The Hamiltonian of the "jellium" model could be presented as

$$H = H_{\text{jell}} - \mathrm{e}\sum_{i=1}^{N}\int \mathrm{d}\mathbf{R}\frac{\hat{\rho}_{\text{ion}(\mathbf{R})}}{|\mathbf{r}_i - \mathbf{R}|}\,, \tag{2.6}$$

where

$$H_{\text{jell}} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\Delta_i + \frac{1}{2}\sum_{i\neq j=1}^{N}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N}V\left(\mathbf{r}_i\right), \tag{2.7}$$

$$V(\mathbf{r}_i) = \int \mathrm{d}\mathbf{R}_1\mathrm{d}\mathbf{R}_2\left[\frac{1}{2N}\frac{\delta\hat{\rho}(\mathbf{R}_1)\delta\hat{\rho}(\mathbf{R}_2)}{|\mathbf{R}_1 - \mathbf{R}_2|} + \frac{1}{N}\frac{\delta\hat{\rho}(\mathbf{R}_1)\hat{\rho}_{\text{jell}}(\mathbf{R}_2)}{|\mathbf{R}_1 - \mathbf{R}_2|} - e\frac{\delta\hat{\rho}(\mathbf{R}_1)\delta\hat{\rho}(\mathbf{R}_2 - \mathbf{r}_i)}{|\mathbf{R}_1 - \mathbf{R}_2|}\right] \tag{2.8}$$

is the surface potential. In the second quantization representation, based on the wave functions formalism [31,32], Hamiltonian (2.6) can be written down as:

$$H = H_{\text{jell}} + \Delta H - \frac{H}{2S}\sum_{\mathbf{q}}{}'\upsilon(\mathbf{q}\,|0)\ , \tag{2.9}$$

where

$$H_{\text{jell}} = H_0 + \frac{1}{2SL}\sum_{k,\mathbf{q}}{}'\upsilon_{k(\mathbf{q})}\hat{\rho}_{k(\mathbf{q})}\hat{\rho}_{k(-\mathbf{q})} \tag{2.10}$$

is the Hamiltonian of a "jellium" model for the inhomogeneous electron gas [31,32] in the collective variables representation.

$$H_0 = \sum_{\mathbf{p},\alpha}E_\alpha\left(\mathbf{p}\right)a_\alpha^+\left(\mathbf{p}\right)a_\alpha\left(\mathbf{p}\right). \tag{2.11}$$

S is the OXY surface area; L determines the range of values of a coordinate $Z\{-\frac{L}{2},\frac{L}{2}\}$ in the surface, perpendicular to OXY; $\nu_k(\mathbf{q}) = 4\pi\frac{\mathrm{e}^2}{(q^2+k^2)}$ denotes the Fourier transform of Coulomb interaction, $k = 2\pi\frac{n}{L}$, $\quad n = 0, \pm1, \pm2, \ldots,\quad \mathbf{q} = (q_x, q_y) = 2\pi m_{x,y},\quad m_{x,y} = 0, \pm1, \pm2, \ldots,\quad \nu(\mathbf{q}\,|z) = 2\pi\mathrm{e}^2\exp\{-q\,|x|\}/q$ is the two-dimensional Fourier transform of Coulomb interaction. $E_\alpha(\mathbf{p})$ is the electron energy, while $a_\alpha^+(\mathbf{p})$, $a_\alpha(\mathbf{p})$ stand for the electron creation and annihilation operators with momentum $\mathbf{p}$ in the α-state, respectively.

$$\hat{\rho}_k(\mathbf{q}) = \sum_{\mathbf{p},\alpha,\alpha'}\langle\alpha|\exp(\mathrm{i}kz)\,|\alpha'\rangle a_\alpha^+(\mathbf{p})a_{\alpha'}(\mathbf{p}-\mathbf{q}) \tag{2.12}$$

is a mixed Fourier transform of the local density of electrons, $\langle\alpha|\ldots.|\alpha'\rangle = \int\mathrm{d}z\varphi_\alpha^*(z)\ldots\varphi_{\alpha'}(z)$, $\varphi_\alpha(z)$ is a wave function of an electron in the α-state in the direction, perpendicular to the "metal-vacuum" surface. The second term of (2.9) describes interaction between electronic and ionic subsystems:

$$\Delta H = \frac{N_{\text{ion}}}{2SL}\sum_{k,\mathbf{q}}{}'S_k(\mathbf{q})\omega_k(\mathbf{q})\hat{\rho}_{-k}(-\mathbf{q}), \tag{2.13}$$

where N_{ion} is the number of ions, $S_k(\mathbf{q}) = \frac{1}{N_{\text{ion}}}\sum\limits_{n=1}^{N_{\text{ion}}}\exp(\mathrm{i}\mathbf{q}\mathbf{R}_n)$ means an equilibrium structure factor of ions, $\mathbf{R}_n$ denotes the radius-vector of the ion in OXY plane, $\omega_k(\mathbf{q})$ stands for a form-factor of the ion-electron interaction.

The Hamiltonian (2.9) is a generalization of the "jellium" model because it takes into account the interaction between electronic and ionic subsystems via the form-factor of the ion-electron interaction in ΔH. The equilibrium state of the system can be completely described by the statistical operator

$$\rho_0 = \frac{1}{Q}\mathrm{e}^{-\beta(H-N\mu)}, \tag{2.14}$$

where

$$Q = \mathrm{Sp}\,\mathrm{e}^{-\beta(H-N\mu)} \tag{2.15}$$

is a partition function of the equilibrium statistical operator in the generalized "jellium" model. μ denotes a chemical potential of the electronic subsystem, $\beta = \frac{1}{k_{\mathrm{B}}T}$, k_{B} is the Boltzmann constant. T stands for an equilibrium value of the system temperature. The equilibrium mean value $\langle \hat{\rho}_k(\mathbf{q}) \rangle_0$ defines local electric field of the electronic subsystem at the metal surface,

$$\mathrm{i}k\mathbf{q}\mathbf{E}_k(\mathbf{q}) = 4\pi\mathrm{e}\,\langle \hat{\rho}_k(\mathbf{q}) \rangle_0 . \tag{2.16}$$

In [31–34] for the presented model there has been proposed a new approach to the calculation of thermodynamic potential, which consists in the reduction of the corresponding non-Gaussian integral to the Gaussian form with a renormalized correlation function "density-density". It was shown that an effective potential of the electron interaction completely defines the thermodynamic potential. By means of functional integration there has been evaluated the one-particle distribution function of the electrons for the "jellium" model of semi-infinite domain of the metal with consideration of exchange and correlation effects. One has also calculated an effective potential of the electron interaction and a two-particle correlation function "density-density" for a semi-restricted metal in the "jellium" model; their asymptotic behaviour has been studied at large distances between electrons in the plane of dividing surface. Such investigations of the equilibrium structure distribution functions and thermodynamic values form a good basis for the creation of a noneqiulibrium statistical theory of the spatially inhomogeneous electron gas.

3. Nonequilibrium statistical operator of an inhomogeneous electron gas

A Hamiltonian of the nonequilibrium inhomogeneous electron gas of the metal surface with taking into account the electromagnetic processes in the "jellium" model can be written as:

$$\tilde{H}(t) = \tilde{T}(t) + H_{ph} + V_{ee} + V_{ei} + V_{ii}, \tag{3.1}$$

where

$$\tilde{T}(t) = \frac{\hbar^2}{2m}\sum_{i=1}^{N}\left(\vec{\nabla}_i - \frac{\mathrm{e}}{c}\mathbf{a}(\mathbf{r};t)\right)^2 + \sum_{i=1}^{N}\mathrm{e}\varphi(\mathbf{r}_i;t), \tag{3.2}$$

c denotes the light velocity, $\mathbf{a}(\mathbf{r};t)$, $\varphi(\mathbf{r}_i;t)$ are, correspondingly, the vector and scalar potentials of the quantized electromagnetic field.

$$H_{ph} = \int_0^{\infty}\mathrm{d}w\hbar w\int \mathrm{d}\mathbf{r}\hat{\mathbf{f}}^{+}(\mathbf{r};w)\,\hat{\mathbf{f}}(\mathbf{r};w), \tag{3.3}$$

$\hbar w$ means the energy of a photon, $\hat{\mathbf{f}}^{+}(\mathbf{r};w)\,,\hat{\mathbf{f}}(\mathbf{r};w)$ are the boson field creation and annihilation operators of the electromagnetic field quantum in the space-frequency representation:

$$\begin{aligned}\left[\hat{\mathbf{f}}_i(\mathbf{r};w)\,\hat{\mathbf{f}}_j^{+}(\mathbf{r}';w)\right] &= \delta_{ij}\delta(\mathbf{r}-\mathbf{r}_j)\,\delta(w-w'),\\ \left[\hat{\mathbf{f}}_i(\mathbf{r};w)\,\hat{\mathbf{f}}_j(\mathbf{r}';w)\right] &= \left[\hat{\mathbf{f}}_i^{+}(\mathbf{r};w)\,\hat{\mathbf{f}}_j^{+}(\mathbf{r}';w)\right] = 0.\end{aligned} \tag{3.4}$$

$\mathbf{a}(\mathbf{r};t)$ corresponds to the microscopic value of the vector potential operator, expressed via the creation and annihilation operators of the photons of electromagnetic field [13]:

$$\hat{\mathbf{a}}(\mathbf{r}) = \sum_{\lambda\mathbf{k}}\left(\frac{2\pi\mathrm{e}^2}{V\omega_k}\right)^{\frac{1}{2}}\left[\mathrm{e}_{\mathbf{k}\lambda}\hat{f}_{\mathbf{k}\lambda}\mathrm{e}^{\mathrm{i}\mathbf{kr}} + \mathbf{e}^{*}_{\mathbf{k}\lambda}\hat{f}^{+}_{\mathbf{k}\lambda}\mathrm{e}^{-\mathrm{i}\mathbf{kr}}\right], \tag{3.5}$$

where $\mathbf{e}_{\mathbf{k}\lambda}$ is the photon polarization vectors, which satisfy orthogonality conditions:

$$\mathbf{e}_{\mathbf{k}\lambda}\mathbf{k} = 0, \quad \sum_{\lambda=1}^{2}\mathbf{e}_{\mathbf{k}\lambda_i}\mathbf{e}^{*}_{\mathbf{k}\lambda_j} = \delta_{ij} - \frac{k_ik_j}{k^2},$$

where $\lambda = 1,2$ is the photon polarization, V stands for a volume. $\hat{\mathbf{a}}(\mathbf{r})$ defines the quantized electrical and magnetic field operators

$$\begin{aligned} \hat{\mathbf{H}}(\mathbf{r}) &= \vec{\nabla} \times \hat{\mathbf{a}}(\mathbf{r}), \qquad \hat{\mathbf{E}}(\mathbf{r}) = \hat{\mathbf{E}}^t(\mathbf{r}) + \hat{\mathbf{E}}^l(\mathbf{r}), \\ \hat{\mathbf{E}}^t(\mathbf{r}) &= -\frac{1}{c}\frac{\partial}{\partial t}\hat{\mathbf{a}}(\mathbf{r}), \qquad \hat{\mathbf{E}}^l(\mathbf{r}) = -\vec{\nabla} \cdot \left(\int \mathrm{d}\mathbf{r}' \frac{\hat{\rho}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int \mathrm{d}\mathbf{R} \frac{\hat{\rho}_{\mathrm{ion}}(\mathbf{R})}{|\mathbf{r}-\mathbf{R}|} \right). \end{aligned} \tag{3.6}$$

$\hat{\mathbf{E}}^t(\mathbf{r})$ is the quantized transverse electrical field operator; $\hat{\mathbf{E}}^l(\mathbf{r})$ means the longitudinal Coulomb field, created by the electron subsystem in positively charged ion field with a fixed distribution $S_k(\mathbf{q})$ at the surface. $\hat{\mathbf{H}}(\mathbf{r})$ and $\hat{\mathbf{E}}(\mathbf{r})$ satisfy the corresponding microscopic Maxwell-Lorentz equations:

$$\vec{\nabla} \times \hat{\mathbf{E}}(\mathbf{r}) = -\frac{1}{c}\frac{\partial}{\partial t}\hat{\mathbf{H}}(\mathbf{r}), \qquad \vec{\nabla} \times \hat{\mathbf{H}}(\mathbf{r}) = \frac{1}{c}\frac{\partial}{\partial t}\hat{\mathbf{E}}(\mathbf{r}) + \frac{4\pi}{c}\hat{\mathbf{j}}_e(\mathbf{r}). \tag{3.7}$$

$$\vec{\nabla} \cdot \hat{\mathbf{H}}(\mathbf{r}) = 0, \qquad \vec{\nabla} \cdot \hat{\mathbf{E}}(\mathbf{r}) = 4\pi\left(e\hat{\rho}(\mathbf{r}) + Ze\hat{\rho}_{\mathrm{ion}}(\mathbf{R})\right), \tag{3.8}$$

where

$$\hat{\mathbf{j}}_e(\mathbf{r}) = \frac{\mathrm{i}e}{2m}\left\{ \left(\vec{\nabla} + \frac{\mathrm{i}e}{c}\mathbf{a}(\mathbf{r};t) \right) \psi^+(\mathbf{r})\,\psi(\mathbf{r}) - \text{her.con.} \right\} \tag{3.9}$$

denotes a current of the electron density operators without account of the spin degrees of freedom, which are taken into account, respectively, by the term $\vec{\nabla} \times \psi^+(\mathbf{r})\,\sigma\psi(\mathbf{r})$; σ is a matrix of the intrinsic magnetic momentum of electron; $\psi^+(\mathbf{r}), \psi(\mathbf{r})$ stand for the field creation and annihilation operators of the electrons: $\hat{\rho}(\mathbf{r}) = \psi^+(\mathbf{r})\,\psi(\mathbf{r})$. The vector and scalar potentials in the Hamiltonian (3.1) are determined from the averaged Maxwell-Lorentz equations:

$$\vec{\nabla} \times \left\langle \hat{\mathbf{E}}(\mathbf{r}) \right\rangle^t = -\frac{1}{c}\frac{\partial}{\partial t}\left\langle \hat{\mathbf{H}}(\mathbf{r}) \right\rangle^t, \qquad \vec{\nabla} \times \left\langle \hat{\mathbf{H}}(\mathbf{r}) \right\rangle^t = \frac{1}{c}\frac{\partial}{\partial t}\left\langle \hat{\mathbf{E}}(\mathbf{r}) \right\rangle^t + \frac{4\pi}{c}\left\langle \hat{\vec{j}}_e(\mathbf{r}) \right\rangle^t, \tag{3.10}$$

$$\vec{\nabla} \cdot \left\langle \hat{\mathbf{H}}(\mathbf{r}) \right\rangle^t = 0, \qquad \vec{\nabla} \cdot \left\langle \hat{\mathbf{E}}(\mathbf{r}) \right\rangle^t = 4\pi\left(\langle e\hat{\rho}(\mathbf{r})\rangle^t + \langle Ze\hat{\rho}_{\mathrm{ion}}(\mathbf{R})\rangle^t \right), \tag{3.11}$$

$$\begin{aligned} \left\langle \hat{\mathbf{H}}(\mathbf{r}) \right\rangle^t &= \vec{\nabla} \times \langle \hat{\mathbf{a}}(\mathbf{r}) \rangle^t = \vec{\nabla} \times \mathbf{a}(\mathbf{r};t), \\ \left\langle \hat{\mathbf{E}}(\mathbf{r}) \right\rangle^t &= \left\langle \hat{\mathbf{E}}^t(\mathbf{r}) \right\rangle^t + \left\langle \hat{\mathbf{E}}^l(\mathbf{r}) \right\rangle^t, \\ \left\langle \hat{\mathbf{E}}^t(\mathbf{r}) \right\rangle^t &= -\frac{1}{c}\frac{\partial}{\partial t}\langle \hat{\mathbf{a}}(\mathbf{r}) \rangle^t = -\frac{1}{c}\frac{\partial}{\partial t}\mathbf{a}(\mathbf{r};t), \\ \left\langle \hat{\mathbf{E}}^l(\mathbf{r}) \right\rangle^t &= -\vec{\nabla} \cdot \left(\int \mathrm{d}\mathbf{r}' \frac{\langle e\hat{\rho}(\mathbf{r}')\rangle^t}{|\mathbf{r}-\mathbf{r}'|} + \int \mathrm{d}\mathbf{R} \frac{\langle Ze\hat{\rho}_{\mathrm{ion}}(\mathbf{R})\rangle_0}{|\mathbf{r}-\mathbf{R}|} \right), \end{aligned} \tag{3.12}$$

where the mean values $\langle \ldots \rangle^t = \mathrm{Sp}\left(\ldots \rho(t)\right)$ are calculated with the NSO $\rho(t)$, obeying the Liouville equation:

$$\frac{\partial}{\partial t}\rho(t) + \mathrm{i}L(t)\,\rho(t) = 0, \tag{3.13}$$

with the normalization condition $\mathrm{Sp}\,\rho(t) = 1$. $\mathrm{i}L(t)$ is a Liouville operator, which corresponds to the Hamiltonian (3.1), so that $\mathrm{i}L(t)\rho(t) = \mathrm{i}/\hbar\left[\tilde{H}(t), \rho(t)\right]$.

The nonequilibrium statistical operator $\rho(t)$ as a solution of the Liouville equation has to be found using the method of NSO by D.N. Zubarev [15]. In this method the general solution for (3.13) with taking into account the Kawasaki-Gunton projection can be presented in the following form:

$$\rho(t) = \rho_q(t) - \int_{-\infty}^{t} \mathrm{e}^{\varepsilon(t'-t)} T_q(t,t')\left(1 - P_q(t')\right)\rho_q(t')\,\mathrm{d}t', \tag{3.14}$$

where transition $\varepsilon \to +0$ has to be performed after a thermodynamic limit $N \to \infty, \quad V \to \infty$ and selects retarded solutions of the Liouville equation (3.13) [15].

$$T_q(t,t') = \exp_+ \left\{ \int_t^{t'} (1 - P_q(\tau))\, \mathrm{i}L(\tau) \mathrm{d}\tau \right\}$$

is the evolution operator with taking into account the Kawasaki-Gunton projection operator $P_q(t)$. Its structure depends on the auxiliary statistical operator $\rho_q(t)$ in the formulation of the Cauchy problem for the Liouville equation with $t = t_0, \quad \rho(t_0) = \rho_q(t_0)$ [15].

In the NSO method [15] $\rho_q(t)$, according to the Gibbs' hypothesis, can be found from the extremum of the informational entropy with fixed parameters of the reduced description and obeying the normalization condition $\mathrm{Sp}\rho(t) = 1$. To describe nonequilibrium properties of spatially inhomogeneous electron gas at the metal surface with taking into account the electromagnetic processes, the mean nonequilibrium values of the number density of the electrons $\langle\hat{\rho}(\mathbf{r})\rangle^t$, momentum density $\langle\hat{\mathbf{p}}(\mathbf{r})\rangle^t$, and total energy density $\langle\hat{\varepsilon}(\mathbf{r})\rangle^t$, which satisfy the corresponding conservation laws, can be chosen as the parameters of the reduced description. $\langle\hat{\rho}(\mathbf{r})\rangle^t$ determines a nonequilibrium value of density of the electron charge $\langle\hat{\rho}_e(\mathbf{r})\rangle^t = \mathrm{e}\langle\hat{\rho}(\mathbf{r})\rangle^t$, $\left\langle\hat{\mathbf{j}}_\mathbf{e}(\mathbf{r})\right\rangle^t$ is a mean nonequilibrium value of the electric current of the electrons, $\left\langle\hat{\mathbf{j}}_e(\mathbf{r})\right\rangle^t = \mathrm{e}/m\,\langle\hat{\mathbf{p}}(\mathbf{r})\rangle^t$. At the same time, $\left\langle\hat{\mathbf{j}}_e(\mathbf{r})\right\rangle^t$, $\langle\hat{\rho}_e(\mathbf{r})\rangle^t$, according to (3.10)–(3.12), define the mean nonequilibrium values of the magnetic and electric fields and their potentials. With this choice of the parameters of reduced description, one can write down the following expression (in the nonrelativistic approximation) for $\rho_q(t)$ [15]:

$$\rho_q(t) = \exp\left\{ -\Phi(t) - \int \mathrm{d}\mathbf{r}\beta(\mathbf{r};t)\left(\hat{\varepsilon}'(\mathbf{r};t) - \mu_{\mathrm{el}}(\mathbf{r};t)\,\hat{\rho}(\mathbf{r})\right)\right\}, \tag{3.15}$$

where $\Phi(t)$ is the Massieu-Planck functional:

$$\Phi(t) = \ln \mathrm{Sp}\, \exp\left\{ - \int \mathrm{d}\mathbf{r}\beta(\mathbf{r};t)\left(\hat{\varepsilon}'(\mathbf{r}) - \mu_{\mathrm{el}}(\mathbf{r};t)\,\hat{\rho}(\mathbf{r})\right)\right\}, \tag{3.16}$$

$\beta(\mathbf{r};t)$ and $\mu_{\mathrm{el}}(\mathbf{r};t)$ denote the Lagrange multipliers, determined, respectively, from the self-consistency conditions

$$\left\langle \hat{\varepsilon}'(\mathbf{r})\right\rangle^t = \left\langle \hat{\varepsilon}'(\mathbf{r})\right\rangle^t_q, \tag{3.17}$$

$$\langle\hat{\rho}(\mathbf{r})\rangle^t = \langle\hat{\rho}(\mathbf{r})\rangle^t_q \tag{3.18}$$

and thermodynamic relations:

$$\frac{\delta\Phi(t)}{\delta\beta(\mathbf{r};t)} = -\left\langle\hat{\varepsilon}'(\mathbf{r})\right\rangle^t_q = -\left\langle\hat{\varepsilon}'(\mathbf{r})\right\rangle^t, \tag{3.19}$$

$$\frac{\delta\Phi(t)}{\delta\beta(\mathbf{r};t)\,\mu_{\mathrm{el}}(\mathbf{r};t)} = -\langle\hat{\rho}(\mathbf{r})\rangle^t_q = -\langle\hat{\rho}(\mathbf{r})\rangle^t, \tag{3.20}$$

$$\frac{\delta S(t)}{\delta\left\langle\hat{\varepsilon}'(\mathbf{r};t)\right\rangle^t} = \beta(\mathbf{r};t), \tag{3.21}$$

$$\frac{\delta S(t)}{\delta\langle\hat{\rho}(\mathbf{r};t)\rangle^t} = -\beta(\mathbf{r};t)\,\mu_{\mathrm{el}}(\mathbf{r};t), \tag{3.22}$$

and define the inverse nonequilibrium temperature $\beta^{-1}(\mathbf{r};t) = k_{\mathrm{B}}T(\mathbf{r};t)$ and the electrochemical potential of the electronic subsystem: $\mu_{\mathrm{el}}(\mathbf{r};t) = \mu(\mathbf{r};t) + \mathrm{e}\varphi(\mathbf{r};t)$. Here $\mu(\mathbf{r};t)$ is the local nonequilibrium chemical potential of the electrons, $\langle\ldots\rangle^t_q = \mathrm{Sp}(\ldots\rho_q(t))$. $\hat{\varepsilon}'(\mathbf{r})$ is the total energy density in the moving frame: $\hat{\varepsilon}'(\mathbf{r}) = \hat{\varepsilon}(\mathbf{r}) - (\mathbf{v}(\mathbf{r};t) + \mathrm{e}/c\cdot\mathbf{a}(\mathbf{r};t))\,\hat{\mathbf{p}}(\mathbf{r}) + m/2\cdot v^2(\mathbf{r};t)\,\hat{\rho}(\mathbf{r})$,

$\mathbf{v}(\mathbf{r};t)$ denotes a vector of mean velocity of the electrons. $S(t)$ is the nonequilibrium Gibbs' entropy defined as follows:

$$S(t) = -\langle \ln \rho_q(t) \rangle_q^t = \Phi(t) + \int d\mathbf{r}\beta(\mathbf{r};t)\left(\left\langle \hat{\varepsilon}'(\mathbf{r}) \right\rangle_q^t - \mu_{\text{el}}(\mathbf{r};t)\langle \hat{\rho}(\mathbf{r}) \rangle_q^t \right),$$

or, taking into account the self-consistency conditions (3.17)–(3.18), $S(t)$ could be rewritten as:

$$\begin{aligned} S(t) \;&=\; \Phi(t) + \int d\mathbf{r}\beta(\mathbf{r};t)(\langle \hat{\varepsilon}(\mathbf{r}) \rangle^t - \left(\mathbf{v}(\mathbf{r};t) + \frac{e}{c}\mathbf{a}(\mathbf{r};t)\right)\langle \hat{\mathbf{p}}(\mathbf{r}) \rangle^t \\ &\quad - \nu(\mathbf{r};t)\langle \hat{\rho}(\mathbf{r}) \rangle^t - e\varphi(\mathbf{r};t)\langle \hat{\rho}(\mathbf{r}) \rangle^t), \end{aligned} \tag{3.23}$$

where $\nu(\mathbf{r};t) = \mu(\mathbf{r};t) - m/2 \cdot v^2(\mathbf{r};t)$. The nonequilibrium entropy is a functional of the nonequilibrium average densities of the total energy, momentum and number of the electrons, conjugate thermodynamic parameters $\beta(\mathbf{r};t)$, $\mathbf{v}(\mathbf{r};t)$, $\mu(\mathbf{r};t)$, and the field potentials $\mathbf{a}(\mathbf{r};t)$, $\varphi(\mathbf{r};t)$. Taking into account the definition of $\hat{\varepsilon}'(\mathbf{r})$, one can present the statistical operator $\rho_q(t)$ in the following form:

$$\begin{aligned} \rho_q(t) \;&=\; \exp\left\{-\Phi(t) - \int d\mathbf{r}\beta(\mathbf{r};t)(\hat{\varepsilon}(\mathbf{r}) - \left(\mathbf{v}(\mathbf{r};t) + \frac{e}{c}\mathbf{a}(\mathbf{r};t)\right)\hat{\mathbf{p}}(\mathbf{r}) \right. \\ &\quad \left. -\nu(\mathbf{r};t)\hat{\rho}(\mathbf{r}) - \mathrm{e}\varphi(\mathbf{r};t)\hat{\rho}(\mathbf{r}))\right\}, \end{aligned} \tag{3.24}$$

where contributions of the quantized electromagnetic field are selected. According to the structure of the statistical operator (3.24), the Kawasaki-Gunton projection operators have the following form:

$$\begin{aligned} P_q(t)\rho' \;&=\; \rho_q(t) - \int d\mathbf{r}(\frac{\delta\rho_q(t)}{\delta\langle \hat{\varepsilon}(\mathbf{r}) \rangle^t}\langle \hat{\varepsilon}(\mathbf{r}) \rangle^t + \frac{\delta\rho_q(t)}{\delta\langle \hat{\mathbf{p}}(\mathbf{r}) \rangle^t}\langle \hat{\mathbf{p}}(\mathbf{r}) \rangle^t + \frac{\delta\rho_q(t)}{\delta\langle \hat{\rho}(\mathbf{r}) \rangle^t}\langle \hat{\rho}(\mathbf{r}) \rangle^t)\mathrm{Sp}\rho') \\ &\quad + \int d\mathbf{r}(\frac{\delta\rho_q(t)}{\delta\langle \hat{\varepsilon}(\mathbf{r}) \rangle^t}\mathrm{Sp}(\hat{\varepsilon}(\mathbf{r})\rho') + \frac{\delta\rho_q(t)}{\delta\langle \hat{\mathbf{p}}(\mathbf{r}) \rangle^t}\mathrm{Sp}(\hat{\mathbf{p}}(\mathbf{r})\rho') + \frac{\delta\rho_q(t)}{\delta\langle \hat{\rho}(\mathbf{r}) \rangle^t}\mathrm{Sp}(\hat{\rho}(\mathbf{r})\rho') \end{aligned}$$

with the operator properties: $P_q(t)P_q(t') = P_q(t)$, $P_q(t)\rho' = \rho_q(t)$, $P_q(t)\rho_q(t') = \rho_q(t)$. Specifying the action of the Liouville operator $\mathrm{i}L(t)$ and $(1 - P_q(t))$ on the quasi-equilibrium statistical operator $\rho_q(t)$ (3.24) according to (3.14), one can obtain, for the nonequilibrium statistical operator of the inhomogeneous electron gas, the following result:

$$\begin{aligned} \rho(t) \;&=\; \rho_q(t) + \int d\mathbf{r}\int_{-\infty}^{t} dt' e^{\varepsilon(t'-t)}T_q(t,t')\left\{\int_0^1 d\tau\rho_q^\tau(t')I_\varepsilon(\mathbf{r};t')\rho_q^{1-\tau}(t')\beta(\mathbf{r};t') \right. \\ &\quad \left. -\int_0^1 d\tau\rho_q^\tau(t')I_p(\mathbf{r};t')\rho_q^{1-\tau}(t')\beta(\mathbf{r};t')\left(\mathbf{v}(\mathbf{r};t') + \frac{e}{c}\mathbf{a}(\mathbf{r};t')\right)\right\}, \end{aligned} \tag{3.25}$$

where $I_\varepsilon(\mathbf{r};t')$, $I_p(\mathbf{r};t')$ are the generalized fluxes of energy and momentum:

$$\begin{aligned} I_\varepsilon(\mathbf{r};t') &= (1 - P(t))\,\mathrm{i}L(t)\,\hat{\varepsilon}(\mathbf{r}), \\ I_p(\mathbf{r};t') &= (1 - P(t))\,\mathrm{i}L(t)\,\hat{\mathbf{p}}(\mathbf{r}), \end{aligned} \tag{3.26}$$

$P(t)$ is a Mori-like projection operator. Its structure is related to the structure of the Kawasaki-Gunton operator and could be presented as

$$\begin{aligned} P(t)\hat{A} \;&=\; \left\langle \hat{A} \right\rangle_q^t + \int d\mathbf{r}\frac{\delta\left\langle \hat{A} \right\rangle_q^t}{\delta\langle \hat{\varepsilon}(\mathbf{r}) \rangle^t}\left(\hat{\varepsilon}(\mathbf{r}) - \langle \hat{\varepsilon}(\mathbf{r}) \rangle^t\right) \\ &\quad + \int d\mathbf{r}\frac{\delta\left\langle \hat{A} \right\rangle_q^t}{\delta\langle \hat{\mathbf{p}}(\mathbf{r}) \rangle^t}\left(\hat{\mathbf{p}}(\mathbf{r}) - \langle \hat{\mathbf{p}}(\mathbf{r}) \rangle^t\right) + \int d\mathbf{r}\frac{\delta\left\langle \hat{A} \right\rangle_q^t}{\delta\langle \hat{\rho}(\mathbf{r}) \rangle^t}\left(\hat{\rho}(\mathbf{r}) - \langle \hat{\rho}(\mathbf{r}) \rangle^t\right). \end{aligned}$$

$P(t)$ (unlike $P_q(t)$) acts on the dynamical values and possesses the properties of the projection on the space of reduced description parameters $\hat{\varepsilon}(\mathbf{r}), \hat{\mathbf{p}}(\mathbf{r}), \hat{\rho}(\mathbf{r})$: $P(t)P(t')=P(t)$, $P(t)\hat{\varepsilon}(\mathbf{r})=\hat{\varepsilon}(\mathbf{r})$, $P(t)\hat{\mathbf{p}}(\mathbf{r})=\hat{\mathbf{p}}(\mathbf{r})$, $P(t)\hat{\rho}(\mathbf{r})=\hat{\rho}(\mathbf{r})$. At that the equation $(1-P(t))\,\mathrm{i}L(t)\,\hat{\rho}(\mathbf{r})=0$ is satisfied.

Thus, we obtained the NSO of an inhomogeneous electron gas in the generalized “jellium” model based on the idea of a reduced description. The nonequilibrium statistical operator is a functional of dynamical quantities, whose mean values are observable quantities. It is also a functional of the generalized fluxes (3.26) that describe dissipative processes, related both to the motion of electrons and to the quantum electromagnetic field. Taking into account the identities,

$$\tfrac{\partial}{\partial t}\langle\hat{\rho}(\mathbf{r})\rangle^t=\langle \mathrm{i}L(t)\,\hat{\rho}(\mathbf{r})\rangle^t, \qquad \tfrac{\partial}{\partial t}\langle\hat{\mathbf{p}}(\mathbf{r})\rangle^t=\langle \mathrm{i}L(t)\,\hat{\mathbf{p}}(\mathbf{r})\rangle_q^t+\left\langle \hat{I}_p(\mathbf{r};t)\right\rangle^t,$$
$$\tfrac{\partial}{\partial t}\langle\hat{\varepsilon}(\mathbf{r})\rangle^t=\langle \mathrm{i}L(t)\,\hat{\varepsilon}(\mathbf{r})\rangle_q^t+\left\langle \hat{I}_\varepsilon(\mathbf{r};t)\right\rangle^t,$$

one can obtain generalized transport equations of the inhomogeneous electron gas at the metal surface in the following form:

$$\frac{\partial}{\partial t}\langle\hat{\rho}(\mathbf{r})\rangle^t = -\frac{1}{m}\frac{\partial}{\partial\mathbf{r}}\cdot\langle\hat{\mathbf{p}}(\mathbf{r})\rangle^t, \tag{3.27}$$

$$\begin{aligned}\frac{\partial}{\partial t}\langle\hat{\mathbf{p}}(\mathbf{r})\rangle^t &= \langle \mathrm{i}L(t)\,\hat{\mathbf{p}}(\mathbf{r})\rangle_q^t+\int \mathrm{d}\mathbf{r}'\int_{-\infty}^{t}\mathrm{d}t' e^{\varepsilon(t'-t)}\varphi_{I_pI_\varepsilon}(\mathbf{r},\mathbf{r}';t,t')\,\beta(\mathbf{r}';t')\\ &\quad -\int \mathrm{d}\mathbf{r}'\int_{-\infty}^{t}\mathrm{d}t' e^{\varepsilon(t'-t)}\varphi_{I_pI_p}(\mathbf{r},\mathbf{r}';t,t')\,\beta(\mathbf{r}';t')\left(\mathbf{v}(\mathbf{r}';t')+\frac{e}{c}\mathbf{a}(\mathbf{r}';t')\right),\end{aligned} \tag{3.28}$$

$$\begin{aligned}\frac{\partial}{\partial t}\langle\hat{\varepsilon}(\mathbf{r})\rangle^t &= \langle iL(t)\,\hat{\varepsilon}(\mathbf{r})\rangle_q^t+\int \mathrm{d}\mathbf{r}\int_{-\infty}^{t}\mathrm{d}t' e^{\varepsilon(t'-t)}\varphi_{I_\varepsilon I_\varepsilon}(\mathbf{r},\mathbf{r}';t,t')\,\beta(\mathbf{r}';t')\\ &\quad -\int \mathrm{d}\mathbf{r}'\int_{-\infty}^{t}\mathrm{d}t' e^{\varepsilon(t'-t)}\varphi_{I_\varepsilon I_p}(\mathbf{r},\mathbf{r}';t,t')\,\beta(\mathbf{r}';t')\left(\mathbf{v}(\mathbf{r}';t')+\frac{e}{c}\mathbf{a}(\mathbf{r}';t')\right),\end{aligned} \tag{3.29}$$

where $\varphi_{I_pI_p}(\mathbf{r},\mathbf{r}';t,t'), \varphi_{I_\varepsilon I_\varepsilon}(\mathbf{r},\mathbf{r}';t,t'), \varphi_{I_pI_\varepsilon}(\mathbf{r},\mathbf{r}';t,t'), \varphi_{I_\varepsilon I_p}(\mathbf{r},\mathbf{r}';t,t')$ denote spatially inhomogeneous generalized memory kernels related to the generalized viscosity and heat conductivity as well as to the coefficients that describe cross-correlations of viscous and heat processes of the electron gas. They have a structure of Kubo functions:

$$\varphi_{I_nI_m}(\mathbf{r},\mathbf{r}';t,t')=\mathrm{Sp}\left\{I_n(\mathbf{r};t)\,T_q(t,t')\int_0^1\mathrm{d}\tau\rho_q^\tau(t')\,I_m(\mathbf{r}';t')\rho_q^{1-\tau}(t')\right\}. \tag{3.30}$$

The system of equations (3.27)–(3.29) describes strongly nonlinear transport processes of the generalized “jellium” model. This system of equations is unclosed, because it contains (functionally) thermodynamic parameters $\beta(\mathbf{r};t), \mathbf{v}(\mathbf{r};t), \mu(\mathbf{r};t)$, determined by the self-consistency conditions (3.17), (3.18) as well as the vector and scalar potentials $\mathbf{a}(\mathbf{r};t)$, determining magnetic and electric fields, which obey the averaged Maxwell equations (3.10),(3.11). Thus, the generalized transport equations (3.27)–(3.29) should be considered self-consistently with the averaged Maxwell equations (3.10)–(3.11) for electromagnetic field. It is clear from the proposed approach that in the case of interaction of inhomogeneous electron gas of the metal surface with unbound atoms or molecules of gas (for instance, in catalysis processes), first of all the electromagnetic polarization of atoms and molecules takes place, and then the processes of their absorption, desorption and chemical reactions are possible.

The generalized transition kernels (3.30), dealing with the corresponding viscosity and heat conductivity, which describe many-electron dissipative processes, are a special problem in the transport equations (3.27)–(3.29). Calculation of their time-spatial dependences is one of the main tasks in the modern theory of nonequilibrium processes. To solve these problems for classical and quantum systems of interacting particles, the method of the Mori-like projection operators and the method of time-dependent Green's functions are used. For weakly nonequilibrium systems the chain of transport equations (3.27)–(3.29) is considerably simplified, and the NSO method makes it possible [36,37] to obtain the system of equations for time correlation functions or the corresponding "density-density", "momentum-momentum", "energy-energy" Green's functions. The same approach allowed us [36] to obtain the chain of equations for the time-dependent Green's functions related to generalized transport coefficients. A similar chain of equations for Green's functions was proposed by Tserkovnikov [35].

4. Time correlation functions and Green's functions of a weakly inhomogeneous electron gas

Let us consider the case of a nonequilibrium state of an inhomogeneous electron gas in the "jellium" model, when the parameters $\beta(\mathbf{r};t), \mu(\mathbf{r};t)$ weakly deviate from their equilibrium values β, μ, and the corresponding fields are small. Then expanding the quasi-equilibrium statistical operator (3.15) in a series in deviations of thermodynamic parameters and excluding them from $\rho_q(t)$ by means of self-consistency conditions (3.17), (3.18), one can obtain the following form for $\rho_q(t)$ in the linear approximation:

$$\begin{aligned} \tilde{\rho}_q(t) &= \rho_0 + \sum_{\mathbf{q}} \int \mathrm{d}z \int \mathrm{d}z' \left\langle \delta\hat{\rho}(\mathbf{q};z)\right\rangle^t \Phi^{-1}_{\rho\rho}(\mathbf{q};z,z')\,\hat{\rho}(\mathbf{q};z',\tau) \\ &\quad + \sum_{\mathbf{q}} \int \mathrm{d}z \int \mathrm{d}z' \left\langle \delta\hat{\mathbf{p}}(\mathbf{q};z)\right\rangle^t \Phi^{-1}_{pp}(\mathbf{q};z,z')\,\hat{\mathbf{p}}(\mathbf{q};z',\tau) \\ &\quad + \sum_{\mathbf{q}} \int \mathrm{d}z \int \mathrm{d}z' \left\langle \delta\hat{h}(\mathbf{q};z)\right\rangle^t \Phi^{-1}_{hh}(\mathbf{q};z,z')\,\hat{h}(\mathbf{q};z',\tau). \end{aligned} \tag{4.1}$$

We have used the $(\mathbf{q},z)$ representation of the functions; z denotes a coordinate in a normal direction $\mathbf{q}$ to the dividing surface, where $\delta\hat{\rho}(\mathbf{q};z) = \hat{\rho}(\mathbf{q};z) - \langle\hat{\rho}(\mathbf{q};z)\rangle_0$, $\delta\hat{\mathbf{p}}(\mathbf{q};z) = \hat{\mathbf{p}}(\mathbf{q};z) - \langle\hat{\mathbf{p}}(\mathbf{q};z)\rangle_0$ $\langle\hat{\mathbf{p}}(\mathbf{q};z)\rangle_0 = 0$, $\delta\hat{h}(\mathbf{q};z) = \hat{h}(\mathbf{q};z) - \left\langle\hat{h}(\mathbf{q};z)\right\rangle_0$, and $\langle\ldots\rangle_0 = \mathrm{Sp}(\ldots\rho_0)$ stands for the equilibrium averaging with operator (2.14). $\hat{h}(\mathbf{q};z)$ denotes the generalized enthalpy operator of the inhomogeneous electron gas:

$$\hat{h}(\mathbf{q};z) = \hat{\varepsilon}(\mathbf{q};z) - \int \mathrm{d}z' \int \mathrm{d}z'' \left\langle \hat{\varepsilon}(\mathbf{q};z)\,\hat{\rho}(\mathbf{q};z')\right\rangle_0 \Phi^{-1}_{\rho\rho}(\mathbf{q};z',z'')\,\hat{\rho}(\mathbf{q};z''), \tag{4.2}$$

where $\Phi^{-1}_{\rho\rho}(\mathbf{q};z',z'')$ is an equilibrium correlation function, defined from the condition

$$\sum_{\mathbf{q}\mathbf{q}'} \int \mathrm{d}z' \Phi_{\rho\rho}(\mathbf{q};z,z')\,\Phi^{-1}_{\rho\rho}(\mathbf{q}';z',z'') = \delta(z-z'')\,\delta_{\mathbf{q}\mathbf{q}'}, \tag{4.3}$$

$$\Phi_{\rho\rho}(\mathbf{q};z,z') = \langle\hat{\rho}(\mathbf{q};z)\,\hat{\rho}(\mathbf{q};z',\tau)\rangle_0 = \mathrm{Sp}\left(\hat{\rho}(\mathbf{q};z)\int_0^1 \mathrm{d}\tau\rho_0^{\tau}\hat{\rho}(\mathbf{q};z')\,\rho_0^{1-\tau}\right) \tag{4.4}$$

is the Kubo equilibrium "density-density" correlation function for the inhomogeneous electron gas. Functions $\Phi^{-1}_{pp}(\mathbf{q};z,z')$ and $\Phi^{-1}_{hh}(\mathbf{q};z,z')$ are determined from the following integral relations:

$$\sum_{\mathbf{q}\mathbf{q}'} \int \mathrm{d}z' \Phi^{-1}_{pp}(\mathbf{q};z,z')\,\Phi^{-1}_{pp}(\mathbf{q}';z',z'') = \delta(z-z'')\,\delta_{\mathbf{q}\mathbf{q}'},$$
$$\sum_{\mathbf{q}\mathbf{q}'} \int \mathrm{d}z' \Phi^{-1}_{hh}(\mathbf{q};z,z')\,\Phi^{-1}_{hh}(\mathbf{q}';z',z'') = \delta(z-z'')\,\delta_{\mathbf{q}\mathbf{q}'}.$$

In the quasi-equilibrium statistical operator (4.1) the quantities $\hat{\rho}(\mathbf{q};z)$, $\hat{\mathbf{p}}(\mathbf{q};z)$, $\hat{h}(\mathbf{q};z)$ $(\hat{\rho}(\mathbf{q};z,\tau)$, $\hat{\mathbf{p}}(\mathbf{q};z,\tau)$, $\hat{h}(\mathbf{q};z,\tau)$ have the following structure: $\hat{a}(\mathbf{q};z,\tau)=\int\limits_0^1 \mathrm{d}\tau\rho_0^{\tau}\hat{a}(\mathbf{q};z)\rho_0^{1-\tau})$ and are orthogonal in the average values sense: $\langle\hat{\rho}(\mathbf{q},z)\hat{\mathbf{p}}(\mathbf{q};z',\tau)\rangle_0=0$, $\left\langle\hat{\mathbf{p}}(\mathbf{q},z)\hat{h}(\mathbf{q};z',\tau)\right\rangle_0=0$, $\left\langle\hat{\rho}(\mathbf{q},z)\hat{h}(\mathbf{q};z',\tau)\right\rangle_0=0$.

In the approximation (4.1), the nonequilibrium statistical operator of the inhomogeneous electron gas has the form

$$\begin{aligned}\rho(t) &= \tilde{\rho}_q(t)-\sum_{\mathbf{q}}\int\mathrm{d}z\int\mathrm{d}z'\int\limits_{-\infty}^{t}\mathrm{d}t'e^{\varepsilon(t-t')}T_q^0(t,t')\left\{\tilde{I}_p(\mathbf{q};z',\tau)\Phi_{pp}^{-1}(\mathbf{q};z,z')\langle\delta\hat{\mathbf{p}}(\mathbf{q};z)\rangle^{t'}\right.\\ &\left.+\tilde{I}_h(\mathbf{q};z',\tau)\Phi_{hh}^{-1}(\mathbf{q};z,z')\left\langle\delta\hat{h}(\mathbf{q};z)\right\rangle^{t}\right\}. \end{aligned}\qquad(4.5)$$

where $T_q^0(t,t')$ is an evolution operator with the Kawasaki-Gunton projectors in the linear approximation (4.1),

$$\begin{aligned}\tilde{I}_p(\mathbf{q};z,\tau)&=\int\limits_0^1\mathrm{d}\tau\rho_0^{\tau}\tilde{I}_p(\mathbf{q};z)\rho_0^{1-\tau},\qquad \tilde{I}_h(\mathbf{q};z,\tau)=\int\limits_0^1\mathrm{d}\tau\rho_0^{\tau}\tilde{I}_h(\mathbf{q};z)\rho_0^{1-\tau},\\ \tilde{I}_p(\mathbf{q};z)&=(1-P)\mathrm{i}L(t)\hat{\mathbf{p}}(\mathbf{q};z),\qquad \tilde{I}_h(\mathbf{q};z)=(1-P)\mathrm{i}L(t)\hat{h}(\mathbf{q};z)\end{aligned}\qquad(4.6)$$

are the generalized fluxes in the linear approximation; P is the Mori-like operator, which has the following structure:

$$\begin{aligned}P\hat{A} &= \left\langle\hat{A}\right\rangle_0+\sum_{\mathbf{q}}\int\mathrm{d}z\int\mathrm{d}z'\left\{\left\langle\hat{A}\hat{\rho}(\mathbf{q};z)\right\rangle_0\Phi_{\rho\rho}^{-1}(\mathbf{q};z,z')\hat{\rho}(\mathbf{q};z')\right.\\ &\left.+\left\langle\hat{A}\hat{\mathbf{p}}(\mathbf{q};z)\right\rangle_0\Phi_{pp}^{-1}(\mathbf{q};z,z')\hat{\mathbf{p}}(\mathbf{q};z')+\left\langle\hat{A}\hat{h}(\mathbf{q};z)\right\rangle_0\Phi_{hh}^{-1}(\mathbf{q};z,z')\hat{h}(\mathbf{q};z')\right\}\end{aligned}\qquad(4.7)$$

with properties $P\hat{\rho}(\mathbf{q};z)=\hat{\rho}(\mathbf{q};z)$, $P\hat{\mathbf{p}}(\mathbf{q};z)=\hat{\mathbf{p}}(\mathbf{q};z)$, $P\hat{h}(\mathbf{q};z)=\hat{h}(\mathbf{q};z)$, $PP=P$, $P(1-P)=0$.

In the approximation (4.2), the generalized transport equations (3.27)–(3.29) have a closed structure:

$$\frac{\partial}{\partial t}\langle\delta\hat{\rho}(\mathbf{q};z)\rangle^t + \int\mathrm{d}z'\mathrm{i}\Omega_{\rho p}(\mathbf{q};z,z')\langle\delta\hat{\mathbf{p}}(\mathbf{q};z')\rangle^t=0,\qquad(4.8)$$

$$\begin{aligned}\frac{\partial}{\partial t}\langle\delta\hat{\mathbf{p}}(\mathbf{q};z)\rangle^t &+ \int\mathrm{d}z'\mathrm{i}\Omega_{ph}(\mathbf{q};z,z')\left\langle\delta\hat{h}(\mathbf{q};z')\right\rangle^t\\ &- \int\mathrm{d}z'\int\limits_{-\infty}^{t}\mathrm{d}t'e^{\varepsilon(t'-t)}\tilde{\varphi}_{ph}(\mathbf{q};z,z';t,t')\left\langle\delta\hat{h}(\mathbf{q};z')\right\rangle^{t'}\\ &- \int\mathrm{d}z'\int\limits_{-\infty}^{t}\mathrm{d}t'e^{\varepsilon(t'-t)}\tilde{\varphi}_{pp}(\mathbf{q};z,z';t,t')\langle\delta\hat{\mathbf{p}}(\mathbf{q};z')\rangle^{t'}=0,\end{aligned}\qquad(4.9)$$

$$\begin{aligned}\frac{\partial}{\partial t}\left\langle\delta\hat{h}(\mathbf{q};z')\right\rangle^t &+ \int\mathrm{d}z'\mathrm{i}\Omega_{hp}(\mathbf{q};z,z')\langle\delta\hat{\mathbf{p}}(\mathbf{q};z')\rangle^t\\ &- \int\mathrm{d}z'\int\limits_{-\infty}^{t}\mathrm{d}t'e^{\varepsilon(t'-t)}\tilde{\varphi}_{hp}(\mathbf{q};z,z';t,t')\langle\delta\hat{\mathbf{p}}(\mathbf{q};z')\rangle^{t'}\\ &- \int\mathrm{d}z'\int\limits_{-\infty}^{t}\mathrm{d}t'e^{\varepsilon(t'-t)}\tilde{\varphi}_{hh}(\mathbf{q};z,z';t,t')\left\langle\delta\hat{h}(\mathbf{q};z')\right\rangle^{t'}=0,\end{aligned}\qquad(4.10)$$

where $\mathrm{i}\Omega_{\rho p}(\mathbf{q};z,z'),\mathrm{i}\Omega_{ph}(\mathbf{q};z,z'),\mathrm{i}\Omega_{hp}(\mathbf{q};z,z')$ are normalized correlation functions:

$$\begin{aligned}
\mathrm{i}\Omega_{\rho p}(\mathbf{q};z,z') &= \int \mathrm{d}z'' \left\langle \dot{\hat{\rho}}(\mathbf{q};z)\,\hat{\mathbf{p}}(\mathbf{q};z'';\tau)\right\rangle_0 \Phi^{-1}_{pp}(\mathbf{q};z'',z'),\\
\mathrm{i}\Omega_{ph}(\mathbf{q};z,z') &= \int \mathrm{d}z'' \left\langle \dot{\hat{\mathbf{p}}}(\mathbf{q};z)\,\hat{h}(\mathbf{q};z'';\tau)\right\rangle_0 \Phi^{-1}_{hh}(\mathbf{q};z'',z'),\\
\mathrm{i}\Omega_{hp}(\mathbf{q};z,z') &= \int \mathrm{d}z'' \left\langle \dot{\hat{h}}(\mathbf{q};z)\,\hat{\mathbf{p}}(\mathbf{q};z'';\tau)\right\rangle_0 \Phi^{-1}_{pp}(\mathbf{q};z'',z'),
\end{aligned} \tag{4.11}$$

are the elements of the frequency matrix in the Mori theory of the projection operators, which describe non-dissipative processes. $\tilde{\varphi}_{hp}(\mathbf{q};z,z';t,t')$, $\tilde{\varphi}_{ph}(\mathbf{q};z,z';t,t')$ mean the generalized transport kernels that describe dynamical correlations between viscous and heat conduction processes for a weakly nonequilibrium inhomogeneous electron gas in the generalized "jellium" model. $\tilde{\varphi}_{pp}(\mathbf{q};z,z';t,t')$, $\tilde{\varphi}_{hh}(\mathbf{q};z,z';t,t')$ are the corresponding transport kernels related to the generalized viscosity and heat conductivity. According to (3.30), they have the following structure:

$$\begin{aligned}
\tilde{\varphi}_{\tilde{I}_n\tilde{I}_m}(\mathbf{q};z,z';t,t') &= \int \mathrm{d}z''\mathrm{Sp}(\tilde{I}_n(\mathbf{q};z)\,T^0_q(t,t')\int_0^1 \mathrm{d}\tau\rho_0^{\tau}\tilde{I}_m(\mathbf{q};z'')\,\rho_0^{1-\tau})\Phi_{mm}(\mathbf{q};z'',z'),\\
\tilde{I}_m(\mathbf{q};z'') &= \left(\tilde{I}_p(\mathbf{q};z''),\tilde{I}_h(\mathbf{q};z'')\right).
\end{aligned} \tag{4.12}$$

In the NSO method [37], the transport equations (4.8)–(4.10) make it possible to obtain a closed system for the time correlation functions of dynamical variables $\hat{\rho}(\mathbf{q};z),\hat{\mathbf{p}}(\mathbf{q};z),\hat{h}(\mathbf{q};z)$. In a matrix form it can be presented as:

$$\begin{aligned}
\frac{\partial}{\partial t}\bar{\Phi}(\mathbf{q};z,z';t) &+ \int \mathrm{d}z'' i\Omega(\mathbf{q};z,z'')\,\bar{\Phi}(\mathbf{q};z'',z';t)\\
&- \int \mathrm{d}z'' \int_{-\infty}^{t} \mathrm{d}t' e^{\varepsilon(t'-t)}\bar{\varphi}(\mathbf{q};z,z'';t,t')\,\bar{\Phi}(\mathbf{q};z'',z';t') = 0,
\end{aligned} \tag{4.13}$$

where

$$\bar{\Phi}(\mathbf{q};z,z';t) = \begin{bmatrix} \Phi_{\rho\rho} & \Phi_{\rho p} & \Phi_{\rho h}\\ \Phi_{p\rho} & \Phi_{pp} & \Phi_{ph}\\ \Phi_{h\rho} & \Phi_{hp} & \Phi_{hh} \end{bmatrix}_{(\mathbf{q};z,z';t)} \tag{4.14}$$

is a matrix of time correlation functions of the dynamical variables $\hat{\rho}(\mathbf{q};z),\hat{\mathbf{p}}(\mathbf{q};z),\hat{h}(\mathbf{q};z)$ for the inhomogeneous electron gas. They have the following structure:

$$\Phi_{nm}(\mathbf{q};z,z';t) = \langle \hat{a}(\mathbf{q};z;t)\,\hat{a}(\mathbf{q};z';\tau)\rangle_0\,,$$

where $\hat{a}(\mathbf{q};z;t) = \mathrm{e}^{iLt}\hat{a}(\mathbf{q};z)$.

$$i\bar{\Omega}(\mathbf{q};z,z') = \begin{bmatrix} 0 & i\Omega_{\rho p} & 0\\ i\Omega_{p\rho} & 0 & i\Omega_{ph}\\ 0 & i\Omega_{hp} & 0 \end{bmatrix}_{(\mathbf{q};z,z')} \tag{4.15}$$

is a frequency matrix, which describes non-dissipative correlations in the system,

$$\bar{\varphi}(\mathbf{q};z,z';t,t') = \begin{bmatrix} 0 & 0 & 0\\ 0 & \tilde{\varphi}_{pp} & \tilde{\varphi}_{ph}\\ 0 & \tilde{\varphi}_{hp} & \tilde{\varphi}_{hh} \end{bmatrix}_{(\mathbf{q};z,z';t,t')} \tag{4.16}$$

denotes a matrix of the memory functions (transport kernels) that describe dissipative processes in a spatially inhomogeneous electron gas. In the case of spatial homogeneity in the hydrodynamic limit $|\mathbf{k}| \to 0$, $\omega \to 0$ (here $\mathbf{k}$ stands for a three-dimensional wave vector, ω is the frequency)} $\tilde{\varphi}_{pp} \sim k^2\eta$, $\tilde{\varphi}_{hh} \sim k^2\lambda$, $\tilde{\varphi}_{ph} = \tilde{\varphi}_{hp} \sim 0$, where η is viscosity, λ means heat conductivity of the spatially homogeneous electron gas. It is important to note that omitting the energy fluctuations (or generalized enthalpy fluctuations) in the system of equations (4.10), i.e. with $i\Omega_{ph} = i\Omega_{hp} = 0$, $\tilde{\varphi}_{ph} = \tilde{\varphi}_{hp} = 0$, $\tilde{\varphi}_{hh} = 0$, we actually obtain the system of equations of [23], which has been obtained by means of projection operators and the method of dynamical variables $\hat{\rho}(\mathbf{q};z)$, $\hat{\mathbf{p}}(\mathbf{q};z)$ for the inhomogeneous electron gas in TDDFT formulation. Our approach generalizes the results of [23] by taking into account the enthalpy fluctuations. In the spatially inhomogeneous case, using Fourier transformation for the space coordinate z, Fourier and Laplace transformations for the time coordinate, defined by the relations,

$$\begin{aligned} f(\omega) &= \int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{\mathrm{i}\omega t} f(t), \qquad f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega \mathrm{e}^{-\mathrm{i}\omega t} f(\omega), \\ f(s) &= \int_{0}^{\infty} \mathrm{d}t \mathrm{e}^{ist} f(t),\ \mathrm{Im}s > 0, \qquad f(s) = \int_{-\infty}^{0} \mathrm{d}t \mathrm{e}^{-ist} f(t), \qquad \mathrm{Im}s < 0, s = \omega \pm \mathrm{i}\varepsilon \end{aligned}$$

one can present the system of equations (4.8)–(4.10) in the following form:

$$s\bar{\Phi}(\mathbf{q};k,k';s) + \sum_{k'} \mathrm{i}\bar{\Omega}(\mathbf{q};k,k'';s)\bar{\Phi}(\mathbf{q};k'',k';s)\sum_{k''}\bar{\varphi}(\mathbf{q};k,k'';s)\bar{\Phi}(\mathbf{q};k'',k';s) = \bar{\Phi}(\mathbf{q};k,k';0), \tag{4.17}$$

where $\tilde{\varphi}_{pp}(\mathbf{q};k,k'';s) = q^2 k\eta(\mathbf{q};k,k'';s)k''$, $\tilde{\varphi}_{hh}(\mathbf{q};k,k'';s) = q^2 k\lambda(\mathbf{q};k,k'';s)k'$. Here $\eta(\mathbf{q};k,k'';s)$, $\lambda(\mathbf{q};k,k'';s)$ are the generalized viscosity and heat conductivity for the inhomogeneous electron gas in the generalized "jellium" model. To evaluate these quantities, one can apply the method of Green's function, developed by Tserkovnikov [35], or, alternatively, the method of NSO [36,37]. For this purpose we introduce the matrix of the reduced Green's functions, related to the matrix of memory kernels

$$\mathrm{i}\bar{\varphi}(\mathbf{q};z,z';s) = \bar{G}^{(r)}(\mathbf{q};z,z';s) = -\mathrm{i}\int_{0}^{\infty} \mathrm{d}t \mathrm{e}^{ist}\bar{\varphi}(\mathbf{q};z,z';t),\ \mathrm{Im}s > 0, \tag{4.18}$$

$$\bar{G}^{(r)}(\mathbf{q};z,z';t) = -\frac{\mathrm{i}}{\hbar}\Theta(t)\bar{\varphi}(\mathbf{q};z,z';t). \tag{4.19}$$

In the presented equations $\bar{G}^{(r)}(\mathbf{q};z,z';t)$ are the retarded reduced Green's functions, $\Theta(t)$ denotes the Heviside's step function.

It is natural to introduce the piecewise-analytic functions, determined in a complex plane s with a cut along the real axis ($\mathrm{Im}\, s \neq 0$). Then

$$\bar{G}(\mathbf{q};z,z';s) = \int_{-\infty}^{\infty} \mathrm{d}\omega(\mathrm{e}^{\hbar\beta\omega} - 1)\frac{\bar{\varphi}(\mathbf{q};z,z';\omega)}{s-\omega} \tag{4.20}$$

with $\mathrm{Im}\, s > 0$, coincides with the analytic continuation of the Fourier transforms of the retarded reduced Green's functions $\bar{G}^{(r)}(\mathbf{q};z,z';s)$, and with $\mathrm{Im}\, s < 0$, coincides with the analytic continuation of the Fourier transformation of the advanced Green's functions $\bar{G}^{(a)}(\mathbf{q};z,z';s)$,

$$\bar{G}^{(a)}(\mathbf{q};z,z';t) = \frac{\mathrm{i}}{\hbar}\Theta(-t)\bar{\varphi}(\mathbf{q};z,z';t), \tag{4.21}$$

and

$$\bar{G}^{(a)}(\mathbf{q};z,z';s) = \mathrm{i}\int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{ist}\bar{\varphi}(\mathbf{q};z,z';t),\ \mathrm{Im}\, s < 0.$$

The quantities $\bar{\varphi}(\mathbf{q};z,z';\omega)$ can be calculated using discontinuous jump of Green's functions on the real axis, see equation (4.20), and can be presented as

$$\bar{G}(\mathbf{q};z,z';\omega+\mathrm{i}\varepsilon) - \bar{G}(\mathbf{q};z,z';\omega-\mathrm{i}\varepsilon) = \frac{2\pi}{\mathrm{i}\hbar}(\mathrm{e}^{\hbar\beta\omega} - 1)\bar{\varphi}(\mathbf{q};z,z';\omega). \tag{4.22}$$

Now, according to the Green's functions method, we obtain the equation for $\bar{G}(\mathbf{q};z,z';s)$ in the following form:

$$\begin{aligned} s\bar{G}(\mathbf{q};z,z';s) &+ \int \mathrm{d}z''\mathrm{i}\Omega^{(1)}(\mathbf{q};z,z'')\,\bar{G}(\mathbf{q};z'',z';s) \\ &- \int \mathrm{d}z''\bar{\varphi}^{(1)}(\mathbf{q};z,z'';s)\,\bar{G}(\mathbf{q};z'',z';s) = \bar{\varphi}(\mathbf{q};z,z';0)\,, \end{aligned} \tag{4.23}$$

where $\mathrm{i}\Omega^{(1)}(\mathbf{q};z,z'')$ denotes the frequency matrix and $\varphi^{(1)}(\mathbf{q};z,z'';s)$ is the matrix of memory functions, constructed on the operators of the generalized dissipative fluxes

$$\begin{aligned} \tilde{I}_a^{(1)}(\mathbf{q};z) &= \Big\{\tilde{I}_\rho^{(1)}(\mathbf{q};z)=0,\ \tilde{I}_p^{(1)}(\mathbf{q};z)=\Big(1-P^{(1)}\Big)\,\mathrm{i}L^{(1)}\tilde{I}_p^{(1)}(\mathbf{q};z)\,, \\ &\qquad \tilde{I}_h^{(1)}(\mathbf{q};z)=\Big(1-P^{(1)}\Big)\,\mathrm{i}L^{(1)}\tilde{I}_h^{(1)}(\mathbf{q};z)\Big\}\,, \\ \mathrm{i}L^{(1)} &= \Big(1-P^{(1)}\Big)\,\mathrm{i}L, \end{aligned}$$

where Mori-like projection operator $P^{(1)}$ is constructed on the generalized fluxes (4.6) $\tilde{I}_\rho(\mathbf{q};z)$, $\tilde{I}_p(\mathbf{q};z)$, $\tilde{I}_h(\mathbf{q};z)$ and has the following structure (in the matrix form):

$$P^{(1)}\cdots = \langle\cdots\rangle_0 + \int \mathrm{d}z\int \mathrm{d}z'\,\Big\langle\cdots\tilde{I}^{(+)}(\mathbf{q};z,\tau)\Big\rangle_0\Big\langle\tilde{I}(\mathbf{q};z)\cdot\tilde{I}^{(+)}(\mathbf{q};z')\Big\rangle_0^{-1}\tilde{I}(\mathbf{q};z') \tag{4.24}$$

with the corresponding properties of the projection operator $\mathcal{P}$. Here

$$\tilde{I}(\mathbf{q};z) = \mathrm{col}\Big(\tilde{I}_\rho(\mathbf{q};z)\,,\tilde{I}_p(\mathbf{q};z)\,,\tilde{I}_h(\mathbf{q};z)\Big)$$

denotes a column vector,

$$\tilde{I}^{(+)}(\mathbf{q};z) = \Big(\tilde{I}_\rho(\mathbf{q};z)\,,\tilde{I}_p(\mathbf{q};z)\,,\tilde{I}_h(\mathbf{q};z)\Big)$$

is a line vector. In the accepted notation, the matrix $\mathrm{i}\bar{\Omega}^{(1)}(\mathbf{q};z,z')$ has the structure

$$\mathrm{i}\bar{\Omega}^{(1)}(\mathbf{q};z,z') = \int \mathrm{d}z''\,\Big\langle\mathrm{i}L^{(1)}\tilde{I}(\mathbf{q};z)\cdot\tilde{I}^{(+)}(\mathbf{q};z'',\tau)\Big\rangle_0\Big\langle\tilde{I}(\mathbf{q};z'')\cdot\tilde{I}^{(+)}(\mathbf{q};z',\tau)\Big\rangle_0^{-1}, \tag{4.25}$$

and the matrix of higher memory functions has the following form:

$$\begin{aligned} \bar{\varphi}^{(1)}(\mathbf{q};z,z';t) &= \int \mathrm{d}z''\langle\Big(1-P^{(1)}\Big)\,\mathrm{i}L^{(1)}\tilde{I}(\mathbf{q};z)\,T_q^{(1)}(t)\int_0^1 \mathrm{d}\tau\rho_0^{-\tau}\Big(1-P^{(1)}\Big)\,\mathrm{i}L^{(1)}\tilde{I}^{(+)}(\mathbf{q};z'')\,\rho_0^{\tau}\rangle_0 \\ &\quad\times\Big\langle\tilde{I}(\mathbf{q};z'')\cdot\tilde{I}^{(+)}(\mathbf{q};z',\tau)\Big\rangle_0^{-1}, \end{aligned} \tag{4.26}$$

where $T_q^{(1)}(t)=\exp\big\{\big(1-P^{(1)}\big)\,\mathrm{i}L^{(1)}t\big\}$ is a reduced time evolution operator. At that, the following relation between the matrix of Green's functions $\bar{G}^{(1)}(\mathbf{q};z,z';s)$ and the matrix of Green's functions $\bar{G}(\mathbf{q};z,z';s)$ is valid:

$$\bar{G}^{(1)}(\mathbf{q};z,z';s) = \bar{G}(\mathbf{q};z,z';s) - \int \mathrm{d}z''\int \mathrm{d}z'''\bar{G}_{Ia}(\mathbf{q};z,z'';s)\bar{G}^{(0)}(\mathbf{q};z'',z''';s)^{-1}\,\bar{G}_{aI}(\mathbf{q};z''',z';s)\,, \tag{4.27}$$

where $\bar{G}^{(0)}(\mathbf{q};z'',z''';s)$ stands for the matrix of commutative Green's functions, constructed on the parameters $\hat{a}_m(\mathbf{q};z)=\Big\{\hat{\rho}(\mathbf{q};z)\,,\hat{\mathbf{p}}(\mathbf{q};z)\,,\hat{h}(\mathbf{q};z)\Big\}$ of the reduced description for inhomogeneous electron gas, and is defined by

$$G_{nm}^{(0)}(\mathbf{q};z',z'';s) = \frac{1}{\mathrm{i}\hbar}\int_0^\infty \mathrm{d}t\mathrm{e}^{ist}\,\langle[\hat{a}_n(\mathbf{q};z';t)\,,\hat{a}_m(\mathbf{q};z'')]\rangle_0\,. \tag{4.28}$$

Green's functions $\bar{G}_{Ia}\left(\mathbf{q}; z, z''; s\right)$, $\bar{G}_{aI}\left(\mathbf{q}; z''', z'; s\right)$ have a structure, similar to (4.28)

$$\bar{G}_{I_n m}\left(\mathbf{q}; z', z''; s\right) = \frac{1}{\mathrm{i}\hbar} \int\limits_0^\infty \mathrm{d}t e^{ist} \left\langle \left[\tilde{I}_n\left(\mathbf{q}; z'; t\right), \hat{a}_m\left(\mathbf{q}; z''\right) \right] \right\rangle_0, \tag{4.29}$$

where $\tilde{I}_n\left(\mathbf{q}; z'; t\right) = \exp\{(1-P)\mathrm{i}Lt\}\tilde{I}_n\left(\mathbf{q}; z'\right)$. The matrices of Green's functions (4.29), (4.28) obey the equations, similar to (4.23) with the corresponding matrices of memory functions. Then, taking into account the relations like (4.27) for higher memory functions, we obtain a chain of equations for the time correlation functions.

We have proposed one of the possible approaches to the description of nonequilibrium properties of spatially inhomogeneous electron gas in the generalized "jellium" model. To this end the method of nonequilibrium statistical operator by D.N. Zubarev has been used, based on the Bogolubov's ideas of the abbreviated description of the nonequilibrium states of the system. Our choice of the mean densities of particles number, momentum and total energy as the parameters of a reduced description of nonequilibrium properties of the spatially inhomogeneous electron gas provides realization of the conservation laws. In this approach we obtained the nonequilibrium statistical operator and the generalized transport equations for mean values of the number density, momentum density and total energy density, which are coupled with the averaged Maxwell equations for the electromagnetic field via equations for the mean vector and scalar potentials. The obtained generalized transport equations take into account the memory effects and many-electron viscous and heat processes. These equations can be applied to the description of both weakly and strongly nonequilibrium states and to the calculation of spatially inhomogeneous mean values $\langle\hat{\rho}\left(\mathbf{q}; z\right)\rangle^t$, $\langle\hat{\mathbf{p}}\left(\mathbf{q}; z\right)\rangle^t$ and $\langle\hat{\varepsilon}\left(\mathbf{q}; z\right)\rangle^t$.

The obtained chain of equations interrelates the commutative time-dependent "density-density", "momentum-momentum", "enthalpy-enthalpy" Green's function and the reduced Green's functions, constructed on the generalized transport kernels (dealing with viscosity, heat conductivity and cross-correlation coefficient) as well as reduced Green's function of the higher order memory functions for weakly nonequilibrium spatially inhomogeneous electron gas. The chain of equations for the Green's functions contains the elements of the frequency matrix (4.15) and equilibrium correlation functions (4.4), which could be expressed via interaction potentials and one- and two-electron distribution functions, calculated in [31–34].

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Нерівноважний статистичний оператор Зубарєва і функції Гріна для неоднорідного електронного газу

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Досліджуються нерівноважні властивості просторово неоднорідного електронного газу з використанням методу нерівноважного статистичного оператора Зубарєва. Отримано узагальнені рівняння переносу для середніх значень густин операторів числа електронів, їх імпульсів та повної енергії для опису як слабо, так і сильно нерівноважних станів системи. Отримано ланцюжок рівнянь функцій Гріна, який зв'язує комутаторні часові функції Гріна “густина-густина”, “імпульс-імпульс”, “ентальпія-ентальпія” із приведеними функціями Гріна узагальнених коефіцієнтів переносу в'язкості, теплопровідності (включаючи перехресні в'язко-теплові коефіцієнти переносу) та із приведеними функціями Гріна вищих функцій пам'яті для слабонерівноважного просторово неоднорідного електронного газу.

Ключові слова: *нерівноважний статистичний оператор, функції Гріна, узагальнені коефіцієнти переносу, неоднорідний електронний газ.*

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