
**STATISTICAL DESCRIPTION
OF ELECTRODIFFUSION PROCESSES
IN THE ELECTRON SUBSYSTEM OF A SEMIBOUNDED
METAL WITHIN THE GENERALIZED “JELLIUM” MODEL****P.P. KOSTROBIJ,¹ B.M. MARKOVYCH,¹ A.I. VASYLENKO,²
M.V. TOKARCHUK²**¹**Lviv Polytechnic National University***(12, Bandera Str., Lviv 79013, Ukraine; e-mail: bogdan_markovych@yahoo.com)*²**Institute of Physics of Condensed Systems, Nat. Acad. of Sci. of Ukraine***(1, Svientsytskyi Str., Lviv 79011, Ukraine)*PACS 05.60.Gg, 05.70.Np,
63.10.+a, 68.43, 82.20.Xr
©2011

Based on the calculation of the quasiequilibrium statistical sum by means of the functional integration method, we obtained a nonequilibrium statistical operator for the electron subsystem of a semibounded metal in the framework of the generalized “jellium” model in the Gaussian and higher approximations with respect to the dynamic electron correlations. This approach allows one to go beyond the linear approximation with respect to the gradient of the electrochemical potential corresponding to weakly nonequilibrium processes and to obtain generalized transport equations that describe nonlinear processes.

1. Introduction

Equilibrium characteristics and nonequilibrium processes of diffusion, adsorption, and desorption for spatially inhomogeneous electron-atom systems are described with the help of various theoretical approaches, both available and being developed ones. In particular, one widely uses the time-dependent density functional theory (TDDFT) [1–13]. During the years of its development, the TDDFT has demonstrated significant achievements and still extends its limits of application [13] though with certain problems [14]. The basis of the TDDFT is the Kohn–Sham density functional theory [15–19]. Another theoretical approach is related to the hydrodynamic model of surface plasmons for a spatially inhomogeneous electron gas proposed in [20–22] with the use of the response theory [23] based on the Boltzmann

kinetic equation. The quantum statistical theory for the description of nonequilibrium processes in “metal–adsorbate–gas” systems was developed in works [24–26] using Zubarev’s method of nonequilibrium statistical operator (NSO) [27, 28]. In particular, a self-consistent description of nonequilibrium processes in the atomic and electron subsystems was presented in [24] on the kinetic level of the description of electron processes. In the processes of adsorption, desorption, and surface diffusion, a metal surface undergoes a reconstruction accompanied by a variation of nonequilibrium properties of both electron and ion subsystems. In this case, the electrodiffusion, viscothermal, and electromagnetic properties of the electron subsystem change in the field of metal surface ions. To study the ion and electron structures of a semibounded metal, a generalized approach that takes the effect of discreteness of the ion subsystem into account and is based upon the model of semibounded “jellium” [29, 30] was proposed in [25, 26]. It is worth noting that the influence of the discreteness of an ion density on the characteristics of a semibounded “jellium” was considered in [19, 31–33] by means of constructing a perturbation theory with respect to the electron-ion interaction pseudopotential. However, the linear response of the electron subsystem to the lattice potential did not take the effects of inhomogeneity of the electron subsystem into account. The approach described in [25, 29, 30] allows one to model the formation of a surface potential and to calculate a large statistical sum for the generalized

model in terms of the cumulant averages of the “jellium” model. In [25], the generalized “jellium” model served as a basis for the statistical description of electrodiffusion processes for the electron subsystem of a semibounded metal with the use of the NSO method, where the only parameter of the reduced description was the nonequilibrium average value of the electron density. For such a system, the quasiequilibrium statistical sum was calculated by means of the functional integration method for the case of the local electron-ion interaction pseudopotential of the metal surface. In principle, it allowed one to obtain expressions for the nonequilibrium statistical operator in the Gaussian and higher approximations with respect to the dynamic electron correlations. In [25], the nonequilibrium statistical operator and the generalized transport equation of inhomogeneous diffusion were obtained for weakly nonequilibrium processes (linear approximation with respect to the gradient of the electrochemical potential). The same approximation was used to deduce an equation for the “density-density” time correlation function that determines the dynamic structural factor of the electron subsystem of a semibounded metal and to demonstrate the connection of this electrodiffusion model in the linear approximation with the TDDFT [1–4].

The given study represents the continuation of work [25]. We will obtain expressions for the nonequilibrium statistical operator in the Gaussian and higher approximations with respect to the dynamic electron correlations, by calculating the quasiequilibrium statistical sum by means of the functional integration method. This approach allowed us to go beyond the linear approximation with respect to the electrochemical potential. For the nonequilibrium statistical operator in the corresponding approximations, we will obtain generalized transport equations for the nonequilibrium average value of the electron density for strongly nonequilibrium processes for the electron subsystem of a semibounded metal.

2. Generalized “Jellium” Model. Nonequilibrium Statistical Operator

2.1. Hamiltonian of the system

Consider an electron-ion system that describes a semibounded metal with regard for the influence of the discreteness of the ion subsystem. We present the Hamiltonian of the system in the form

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_i + \frac{1}{2} \sum_{i \neq j=1}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} +$$

$$+ \frac{1}{2} \sum_{i \neq j=1}^{N_{\text{ion}}} \frac{(\mathcal{Z}e)^2}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_{i=1}^N \sum_{j=1}^{N_{\text{ion}}} e w(\mathbf{r}_i, \mathbf{R}_j), \quad (1)$$

where the first two terms represent the electron kinetic energy and the potential energy of electron-electron interaction, respectively, the third term stands for the potential energy of ion-ion interaction, and the last one is the energy of electron-ion interaction. Electrons in the ion field have the charge e , the mass m , and the coordinates \mathbf{r}_i , $i = 1, \dots, N$. By N_{ion} , we denote the number of metal ions with the charge $\mathcal{Z}e$ and the coordinates \mathbf{R}_j ($-\infty < X_j, Y_j < +\infty$, $Z_j \leq z_0$, $Z_0 = \text{const}$, $z = Z_0$ is the division plane), $j = 1, \dots, N_{\text{ion}}$. We suppose that ions are immobile in the system volume $V = SL$, where S is the surface area of the semibounded metal, and L determines the region of variation of the electron coordinate normal to the metal surface: $z \in (-L/2, +L/2)$, $S \rightarrow \infty$, $L \rightarrow \infty$. We consider that the system is electroneutral, i.e.

$$\mathcal{Z}N_{\text{ion}} = N. \quad (2)$$

In [25], Hamiltonian (1) was presented in terms of the collective variables of the electron subsystem of a semibounded metal specifying the Hamiltonian of the “jellium” model as a reference system:

$$\begin{aligned} H = & \sum_{\mathbf{p}, \alpha} E_{\alpha}(\mathbf{p}) a_{\alpha}^{\dagger}(\mathbf{p}) a_{\alpha}(\mathbf{p}) + \\ & + \frac{1}{2SL} \sum_{\mathbf{q}}' \sum_k \nu_k(\mathbf{q}) \rho_k(\mathbf{q}) \rho_{-k}(-\mathbf{q}) - \\ & - \frac{\mathcal{Z}N_{\text{ion}}}{SL} \sum_{\mathbf{q}}' \sum_k \nu_k(\mathbf{q}) S_k(\mathbf{q}) \rho_k(\mathbf{q}) + \\ & + \frac{eN_{\text{ion}}}{SL} \sum_{\mathbf{q}, k} S_k(\mathbf{q}) f_k(\mathbf{q}) \rho_k(\mathbf{q}) - \frac{N}{2S} \sum_{\mathbf{q}}' \nu(\mathbf{q}|0) + \\ & + \frac{1}{2} \sum_{i \neq j=1}^{N_{\text{ion}}} \frac{1}{S} \sum_{\mathbf{q}}' \mathcal{Z}^2 \nu(\mathbf{q}|Z_i - Z_j) e^{i\mathbf{q}(\mathbf{R}_{||i} - \mathbf{R}_{||j})}, \quad (3) \end{aligned}$$

where the primed sums mean the absence of terms with $\mathbf{q} = 0$ due to the electroneutrality condition (2), $\nu_k(\mathbf{q}) = 4\pi e^2/(q^2 + k^2)$ and $f_k(\mathbf{q})$ are the three-dimensional

Fourier transforms of the Coulomb potential and the local part of pseudopotential (4):

$$\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} = \frac{1}{SL} \sum_{\mathbf{q}, k} \nu_k(\mathbf{q}) e^{i\mathbf{q}(\mathbf{r}_{\parallel i} - \mathbf{r}_{\parallel j}) + ik(z_i - z_j)},$$

$$w(\mathbf{r}_i - \mathbf{R}_j) = -\frac{Ze}{|\mathbf{r}_i - \mathbf{R}_j|} + f(\mathbf{r}_i - \mathbf{R}_j), \quad (4)$$

$$f(\mathbf{r}_i - \mathbf{R}_j) = \frac{1}{SL} \sum_{\mathbf{q}, k} f_k(\mathbf{q}) e^{i\mathbf{q}(\mathbf{r}_{\parallel i} - \mathbf{R}_{\parallel j}) + ik(z_i - Z_j)},$$

$\mathbf{R}_{\parallel j} = (X_j, Y_j)$, $\nu(\mathbf{q}|z) = 2\pi e^2 e^{-q|z|}/q$ is the two-dimensional Fourier transform of the Coulomb potential: $\frac{e^2}{r} = \frac{1}{S} \sum_{\mathbf{q}} \nu(\mathbf{q}|z) e^{-\mathbf{q}\mathbf{r}_{\parallel}}$, $E_{\alpha}(\mathbf{p}) = \frac{\hbar^2 p^2}{2m} + \varepsilon_{\alpha}$ is the energy of an electron in the state (\mathbf{p}, α) ,

$$S_k(\mathbf{q}) = \frac{1}{N_{\text{ion}}} \sum_{j=1}^{N_{\text{ion}}} e^{-i\mathbf{q}\mathbf{R}_{\parallel j} - ikZ_j} \quad (5)$$

stands for the structural factor of the ion subsystem and the Fourier transform of the electron density:

$$\rho_k(\mathbf{q}) = \sum_{\mathbf{p}, \alpha_1, \alpha_2} \langle \alpha_1 | e^{ikz} | \alpha_2 \rangle a_{\alpha_1}^{\dagger}(\mathbf{p}) a_{\alpha_2}(\mathbf{p} - \mathbf{q}), \quad (6)$$

where $\langle \alpha_1 | \dots | \alpha_2 \rangle = \int dz \varphi_{\alpha_1}^*(z) \dots \varphi_{\alpha_2}(z)$. $\varphi_{\alpha}(z)$ and ε_{α} are the eigenfunctions and eigenvalues of the Schrödinger equation, respectively,

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V(z) \right] \varphi_{\alpha}(z) = \varepsilon_{\alpha} \varphi_{\alpha}(z),$$

$V(\mathbf{r}) = V(z)$ is the surface potential depending only on the electron coordinate normal to the division plane.

The same way as in [25], the electrodiffusion processes in the formulated model are described choosing the average value of the electron density operator as the main parameter of the reduced description of nonequilibrium processes in the electron subsystem of a semibounded metal. It is connected with the corresponding inhomogeneous electric field,

$$\nabla \cdot \mathbf{E}(\mathbf{r}; t) = e \langle \rho(\mathbf{r}) \rangle^t, \quad (7)$$

where $\langle (\dots)^t \rangle = \text{Sp}(\dots)\rho(t)$, $\rho(t)$ denotes the nonequilibrium statistical operator of the generalized ‘‘jellium’’ model that satisfies the Liouville equation with the

Hamilton operator (3). With regard for the chosen geometry of the model, the value of $\langle \rho(\mathbf{r}) \rangle^t$ will correspond to the mixed Fourier representation $\langle \rho_k(\mathbf{q}) \rangle^t$. To find $\rho(t)$ (the solution of the Liouville equation), we employ Zubarev’s NSO method [27, 28] and obtain, in the general case,

$$\rho(t) = \varepsilon \int_{-\infty}^t e^{\varepsilon(t'-t)} e^{iL_N(t'-t)} \rho_q(t') dt', \quad (8)$$

where $\varepsilon \rightarrow +0$ after passing to the thermodynamic limit, and iL_N is the Liouville operator corresponding to Hamilton operator (3). The quantity $\rho_q(t)$ denotes the quasiequilibrium statistical operator determined by the Gibbs method at fixed values of the parameter of the reduced description $\langle \rho_k(\mathbf{q}) \rangle^t$, and the normalization condition $\text{Sp} \rho_q(t) = 1$ hold. In our case, it has the following form [25]:

$$\rho_q(t) = \exp \left[-\Phi(t) - \beta \left(H - \frac{1}{SL} \sum_k \sum_{\mathbf{q}} \tilde{\mu}_k(\mathbf{q}; t) \rho_k(\mathbf{q}) \right) \right], \quad (9)$$

where $\Phi(t) = \ln Z(t)$ is the Massieu–Planck functional, and $Z(t)$ is the statistical sum of the quasiequilibrium statistical operator,

$$Z(t) = \text{Sp} \exp \left[-\beta \left(H - \frac{1}{SL} \sum_k \sum_{\mathbf{q}} \tilde{\mu}_k(\mathbf{q}; t) \rho_k(\mathbf{q}) \right) \right], \quad (10)$$

$\tilde{\mu}_k(\mathbf{q}; t) = \mu_k(\mathbf{q}; t) + e\varphi_k(\mathbf{q}; t)$ denotes the Fourier transform of the electron electrochemical potential, $\mu_k(\mathbf{q}; t)$ is the Fourier transform of the electron chemical potential, and $\varphi_k(\mathbf{q}; t)$ is the Fourier transform of the local electric potential. The quantity $\tilde{\mu}_k(\mathbf{q}; t)$ is determined from the self-consistency condition

$$\langle \rho_k(\mathbf{q}) \rangle^t = \langle \rho_k(\mathbf{q}) \rangle_q^t \quad (11)$$

and the thermodynamic relations

$$\frac{\delta \Phi(t)}{\delta \frac{\beta}{SL} \tilde{\mu}_k(\mathbf{q}; t)} = \langle \rho_k(\mathbf{q}) \rangle^t, \quad (12)$$

$$\frac{\delta S(t)}{\delta \langle \rho_k(\mathbf{q}) \rangle^t} = -\frac{\beta}{SL} \mu_k(\mathbf{q}; t), \quad (13)$$

$$\frac{\delta S(t)}{\delta \langle e\rho_k(\mathbf{q}) \rangle^t} = -\frac{\beta}{SL} \varphi_k(\mathbf{q}; t),$$

where $S(t)$ is the Gibbs nonequilibrium entropy,

$$\begin{aligned} S(t) &= -\text{Sp}(\ln \rho_q(t))\rho_q(t) = \\ &= \Phi(t) + \beta \left(\langle H \rangle^t - \frac{1}{SL} \sum_k \sum_{\mathbf{q}} \tilde{\mu}_k(\mathbf{q}; t) \langle \rho_k(\mathbf{q}) \rangle^t \right) = \\ &= \ln Z(t) + \beta \left(\langle H \rangle^t - \frac{1}{SL} \sum_k \sum_{\mathbf{q}} \mu_k(\mathbf{q}; t) \langle \rho_k(\mathbf{q}) \rangle^t - \right. \\ &\quad \left. - \frac{1}{SL} \sum_k \sum_{\mathbf{q}} \varphi_k(\mathbf{q}; t) \langle e\rho_k(\mathbf{q}) \rangle^t \right), \end{aligned} \quad (14)$$

$\langle e\rho_k(\mathbf{q}) \rangle^t = e\langle \rho_k(\mathbf{q}) \rangle^t$ is the average electron charge density. As follows from the structure of the nonequilibrium entropy, the transport processes in the system within the used model are caused by the gradients of the local chemical and electrochemical potentials.

With regard for the structure of $\rho_q(t)$, the nonequilibrium statistical operator can be presented in the form

$$\begin{aligned} \rho(t) &= \varepsilon \int_{-\infty}^t e^{\varepsilon(t'-t)} e^{iL_N(t'-t)} e^{-\hat{S}(t')} dt' = \\ &= \rho_q(t) + \int_{-\infty}^t e^{\varepsilon(t'-t)} e^{iL_N(t'-t)} \times \\ &\quad \times \int_0^1 d\tau \rho_q^\tau(t') \left(\frac{\partial}{\partial t'} + iL_N \right) \hat{S}(t') \rho_q^{1-\tau}(t') dt', \end{aligned} \quad (15)$$

where

$$\hat{S}(t') = \ln Z(t) + \beta \left(H - \frac{1}{SL} \sum_k \sum_{\mathbf{q}} \tilde{\mu}_k(\mathbf{q}; t) \rho_k(\mathbf{q}) \right) \quad (16)$$

is the entropy operator. In order to reveal the structure of the entropy operator, it is necessary to calculate the statistical sum $Z(t)$ of the quasiequilibrium statistical operator. With regard for the structure of Hamiltonian (3), $Z(t)$ can be put down as follows: [25]:

$$Z(t) = \text{Sp} \left\{ \exp(-\beta(H_0 - \frac{1}{2S} \sum_{\mathbf{q}} \nu(\mathbf{q}|0) + \right.$$

$$\left. + \frac{1}{2SL} \sum_{k, \mathbf{q}} \nu_k(\mathbf{q}) \rho_k(\mathbf{q}) \rho_{-k}(-\mathbf{q}) + \frac{1}{2SL} \sum_{k, \mathbf{q}} B(\mathbf{q}, k; t) \rho_{-k}(-\mathbf{q}) \right\}, \quad (17)$$

where $B(\mathbf{q}, k; t) = N_{\text{ion}} S_k(\mathbf{q}) \omega_k(\mathbf{q}) - \bar{\mu}_k(\mathbf{q}; t)$, $w_k(\mathbf{q}) = -Z\nu_k(\mathbf{q}) + ef_k(\mathbf{q})$, $H'_0 = \sum_{\mathbf{p}, \alpha} E_\alpha(\mathbf{p}) a_\alpha^\dagger(\mathbf{p}) a_\alpha(\mathbf{p})$ is the kinetic part of the Hamiltonian of the electron subsystem.

Applying the functional integration method and considering the “jellium” model as a reference system, $Z(t)$ can be written down as [25]

$$Z(t) = \exp \left\{ \beta \frac{N}{2S} \sum_{\mathbf{q}} \nu(\mathbf{q}|0) \right\} Z_{\text{jell}} \Delta Z(t), \quad (18)$$

where

$$Z_{\text{jell}} = \text{Sp} \{ \exp(-\beta H_0) T S_1(\beta) \} \quad (19)$$

is the statistical sum of the “jellium” model of the electron subsystem of a semibounded metal that corresponds to the equilibrium state calculated in [29, 30];

$$\begin{aligned} S_1(\beta) &= \exp \left[- \frac{1}{2SL} \int_0^\beta d\beta' \sum_{\mathbf{q}} \sum_k \nu_k(\mathbf{q}) \times \right. \\ &\quad \left. \times \rho_k(\mathbf{q}|\beta') \rho_{-k}(-\mathbf{q}|\beta') \right] \end{aligned} \quad (20)$$

is the contribution of the electron interaction, where $\rho_k(\mathbf{q}|\beta') = e^{\beta' H_0} \rho_k(\mathbf{q}) e^{-\beta' H_0}$,

$$\begin{aligned} \Delta Z(t) &= \frac{1}{Z_{\text{jell}}} \text{Sp} \left\{ \exp(-\beta H_0) T S_1(\beta) S_2(\beta; t) \right\} = \\ &= \langle S_2(\beta; t) \rangle_{\text{jell}}, \end{aligned} \quad (21)$$

where $\langle (\dots) \rangle_{\text{jell}} = \frac{1}{Z_{\text{jell}}} \text{Sp} \left\{ \exp(-\beta H_0) T S_1(\beta) (\dots) \right\}$;

$$\begin{aligned} S_2(\beta; t) &= \\ &= T \exp \left\{ - \int_0^\beta d\beta' \frac{1}{SL} \sum_{k, \mathbf{q}} B(\mathbf{q}, k; t) \rho_{-k}(-\mathbf{q}; \beta') \right\}. \end{aligned} \quad (22)$$

Using the cumulant representation, $\Delta Z(t)$ can be presented in the form

$$\Delta Z(t) = \exp \left[\sum_{n=1} \frac{i^n}{n!} \left(\frac{\beta}{SL} \right)^n \sum_{\mathbf{q}_1 \dots \mathbf{q}_n} \sum_{k_1 \dots k_n} B(\mathbf{q}_1, k_1; t) \dots \times \right. \\ \left. \times B(\mathbf{q}_n, k_n; t) \mathfrak{M}_{-k_1 \dots -k_n}(-\mathbf{q}_1 \dots -\mathbf{q}_n) \right], \quad (23)$$

where

$$\mathfrak{M}_{k_1 \dots k_n}(\mathbf{q}_1 \dots \mathbf{q}_n) = \\ = i^n \langle \Gamma \rho_{k_1}(\mathbf{q}_1 | 0), \dots, \rho_{k_n}(\mathbf{q}_n | 0) \rangle_{\text{jell}}^c \quad (24)$$

are the cumulant irreducible average values of the electron density fluctuations calculated with the help of the equilibrium statistical operator of the ‘‘jellium’’ model of the electron subsystem of a semibounded metal [29, 30]. In particular, the second cumulant has the structure

$$\mathfrak{M}_{k_1, k_2}(\mathbf{q}_1, \mathbf{q}_2) = \langle \rho_{k_1}(\mathbf{q}_1) \rho_{k_2}(\mathbf{q}_2) \rangle_{\text{jell}} - \\ - \langle \rho_{k_1}(\mathbf{q}_1) \rangle_{\text{jell}} \langle \rho_{k_2}(\mathbf{q}_2) \rangle_{\text{jell}} \quad (25)$$

and is connected with the static structural factor $S(k_1, \mathbf{q}_1; k_2, \mathbf{q}_2) = \langle \rho_{k_1}(\mathbf{q}_1) \rho_{k_2}(\mathbf{q}_2) \rangle_{\text{jell}}$ of the electron subsystem of a semibounded metal. In the Gaussian approximation, we obtain

$$\Delta Z^G(t) = \exp \left[-\frac{1}{2} \left(\frac{\beta}{SL} \right)^2 \sum_{\mathbf{q}_1 \mathbf{q}_2} \sum_{k_1 k_2} B(\mathbf{q}_1, k_1; t) \times \right. \\ \left. \times B(\mathbf{q}_2, k_2; t) \mathfrak{M}_{-k_1, -k_2}(-\mathbf{q}_1, -\mathbf{q}_2) \right] \quad (26)$$

is expressed in terms of the second cumulant of the ‘‘jellium’’ model of inhomogeneous electron gas [29, 30]. According to the definition of s -particle electron distribution functions [25, 29, 30], we obtain the quasiequilibrium s -particle electron distribution functions in the form

$$F_s(\mathbf{r}_1, \dots, \mathbf{r}_n; t) = F_s(\mathbf{r}_1, \dots, \mathbf{r}_n)^{\text{jell}} \times \\ \times \exp \left[\sum_{n \geq 1} \frac{i^n}{n!} \left(\frac{\beta N_{\text{ion}}}{SL} \right)^n \sum' \sum_{\mathbf{q}_1, \dots, \mathbf{q}_n k_1, \dots, k_n} B(\mathbf{q}_1, k_1; t) \dots \times \right.$$

$$\left. \times B(\mathbf{q}_n, k_n; t) \Delta \mathfrak{M}_{-k_1, \dots, -k_n}(-\mathbf{q}_1, \dots, -\mathbf{q}_n) \right], \quad (27)$$

where

$$\Delta \mathfrak{M}_{-k_1, \dots, -k_n}(-\mathbf{q}_1, \dots, -\mathbf{q}_n) = \\ = \mathfrak{M}_{-k_1, \dots, -k_n}(-\mathbf{q}_1, \dots, -\mathbf{q}_n) - \\ - \mathfrak{M}_{-k_1, \dots, -k_n}(-\mathbf{q}_1, \dots, -\mathbf{q}_n).$$

Relations (27) link the quasiequilibrium distribution functions with the electrochemical potential $\bar{\mu}_k(\mathbf{q}; t)$ through the corresponding cumulant averages of the ‘‘jellium’’ model. In view of the structure of $\Delta Z(t)$ (26), $\ln Z(t)$ can be written as

$$\ln Z(t) = \beta \frac{N}{2S} \sum_{\mathbf{q}}' \nu(\mathbf{q} | 0) + \ln Z_{\text{jell}} + \\ + \sum_{n=1} \frac{i^n}{n!} \left(\frac{\beta}{SL} \right)^n \sum_{\mathbf{q}_1 \dots \mathbf{q}_n} \sum_{k_1 \dots k_n} B(\mathbf{q}_1, k_1; t) \dots \times \\ \times B(\mathbf{q}_n, k_n; t) \mathfrak{M}_{-k_1 \dots -k_n}(-\mathbf{q}_1 \dots -\mathbf{q}_n), \quad (28)$$

where $\ln Z_{\text{jell}}$ can be calculated in various approximations with respect to the electron correlations [29, 30]. Based on (28) and (16), we obtain the expression for the nonequilibrium statistical operator in the general form:

$$\rho(t) = \rho_q(t) + \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} e^{iL_N(t'-t)} \left\{ \frac{i^n}{n!} \left(\frac{\beta}{SL} \right)^n \times \right. \\ \times \sum_{\mathbf{q}_1 \dots \mathbf{q}_n} \sum_{k_1 \dots k_n} \frac{\partial}{\partial t'} \left(B(\mathbf{q}_1, k_1; t') \dots B(\mathbf{q}_n, k_n; t') \right) \times \\ \left. \times \mathfrak{M}_{-k_1 \dots -k_n}(-\mathbf{q}_1 \dots -\mathbf{q}_n) \right\} \rho_q(t') -$$

$$- \frac{1}{SL} \sum_k \sum_{\mathbf{q}} \int_{-\infty}^t e^{\varepsilon(t'-t)} e^{iL_N(t'-t)}$$

$$\times \int_0^1 d\tau \rho_q^\tau(t') \dot{\rho}_k(\mathbf{q}) \rho_q^{1-\tau}(t') \tilde{\mu}_k(\mathbf{q}; t') dt', \quad (29)$$

where $\dot{\rho}_k(\mathbf{q}) = iL_N \rho_k(\mathbf{q}) = -k\mathbf{q} \cdot \mathbf{J}_k(\mathbf{q})$, and $\mathbf{J}_k(\mathbf{q})$ is the Fourier transform of the microscopic electron flux. The obtained expression represents a sum of the non-dissipative and dissipative parts. The first one corresponds to the operator $\rho_q(t)$, while the second one is described by the terms that contain the time derivatives of the functions $B(\mathbf{q}, k; t')$ and the microscopic fluxes $\dot{\rho}_k(\mathbf{q})$. Moreover, the derivative $\frac{\partial}{\partial t'} B(\mathbf{q}, k; t')$ can be presented as

$$\begin{aligned} \frac{\partial}{\partial t'} B(\mathbf{q}, k; t') &= \frac{\partial}{\partial t'} \left(N_{\text{ion}} S_k(\mathbf{q}) \omega_k(\mathbf{q}) - \tilde{\mu}_k(\mathbf{q}; t') \right) = \\ &= -\frac{\partial}{\partial t'} \tilde{\mu}_k(\mathbf{q}; t') = -\frac{\delta \tilde{\mu}_k(\mathbf{q}; t')}{\delta \langle \rho_k(\mathbf{q}) \rangle^{t'}} \frac{\partial}{\partial t'} \langle \rho_k(\mathbf{q}) \rangle^{t'}, \end{aligned}$$

where

$$\frac{\delta \tilde{\mu}_k(\mathbf{q}; t')}{\delta \langle \rho_k(\mathbf{q}) \rangle^{t'}} = -(\rho_k(\mathbf{q}) | \rho_{-k}(-\mathbf{q})_q^{-1}, \quad (30)$$

$$\begin{aligned} (\rho_k(\mathbf{q}) | \rho_{-k}(-\mathbf{q})_q^{-1} &= \int_0^1 \left\langle \left(\rho_k(\mathbf{q}) - \langle \rho_k(\mathbf{q}) \rangle_q^{t'} \right) \times \right. \\ &\times \left. \left(\rho_{-k}(-\mathbf{q}; \tau) - \langle \rho_{-k}(-\mathbf{q}) \rangle_q^{t'} \right) \right\rangle^{t'} d\tau, \quad (31) \end{aligned}$$

is the quantum quasiequilibrium correlation function,

$$\rho_k(\mathbf{q}; \tau) = \rho_q^\tau(t') \rho_k(\mathbf{q}) \rho_q^{-\tau}(t').$$

With regard for (30), the time derivative of $B(\mathbf{q}, k; t')$ can be presented in the form

$$\begin{aligned} \frac{\partial}{\partial t'} B(\mathbf{q}, k; t') &= (\rho_k(\mathbf{q}) | \rho_{-k}(-\mathbf{q})_q^{-1} \frac{\partial}{\partial t'} \langle \rho_k(\mathbf{q}) \rangle^{t'} = \\ &= (\rho_k(\mathbf{q}) | \rho_{-k}(-\mathbf{q})_q^{-1} \langle \dot{\rho}_k(\mathbf{q}) \rangle^{t'}. \quad (32) \end{aligned}$$

Thus, the nonequilibrium statistical operator (29) is a functional of the pair quasiequilibrium correlation functions (31), equilibrium correlation functions (24), average values of parameters of the reduced description

$\langle \rho_k(\mathbf{q}) \rangle^t$, and microscopic fluxes $\dot{\rho}(\mathbf{q})$ of the electron subsystem of a semibounded metal. To make the description complete, it is necessary to obtain the transport equation for $\langle \rho_k(\mathbf{q}) \rangle^t$ with the help of the non-equilibrium statistical operator (29). Based on the structure of $\rho(t)$, one can state that these equations will be nonlinear. The parameters $\tilde{\mu}_k(\mathbf{q}; t)$ in these equations should be found with the use of the self-consistency conditions (11). The obtained expression for the quasiequilibrium statistical operator with the Massieu–Planck functional (28) allows one to find the nonequilibrium statistical operator in the corresponding approximations, particularly in the Gaussian one.

3. Gaussian Approximation

Here, we will consider approximation (26), in which the nonequilibrium statistical operator and the transport equation for $\langle \rho_k(\mathbf{q}) \rangle^t$ will be obtained. The index G in all cases means the description of a function in the Gaussian approximation.

With regard for the structure of (26), we obtain the entropy operator (14) in the form

$$\begin{aligned} \hat{S}^{(G)}(t) &= \beta \frac{N}{2S} \sum_{\mathbf{q}}' \nu(\mathbf{q}|0) + \ln Z_{\text{jell}} - \\ &- \frac{1}{2} \left(\frac{\beta}{SL} \right)^2 \sum_{k_1, k_2} \sum_{\mathbf{q}_1, \mathbf{q}_2} \left(N_{\text{ion}} S_{k_1}(\mathbf{q}_1) \omega_{k_1}(\mathbf{q}_2) - \tilde{\mu}_{k_1}(\mathbf{q}_1; t) \right) \times \\ &\times \left(N_{\text{ion}} S_{k_2}(\mathbf{q}_2) \omega_{k_2}(\mathbf{q}_2) - \tilde{\mu}_{k_2}(\mathbf{q}_2; t) \right) \times \\ &\times \mathfrak{M}_{-k_1, -k_2}(-\mathbf{q}_1, -\mathbf{q}_2) + \\ &+ \beta \left(H - \frac{1}{SL} \sum_{k, \mathbf{q}} \tilde{\mu}_k(\mathbf{q}; t) \rho_k(\mathbf{q}) \right). \quad (33) \end{aligned}$$

In order to eliminate the parameters $\tilde{\mu}_k(\mathbf{q}; t)$ from this formula, we use the thermodynamic relation (12)

$$\frac{\delta \Phi^{(G)}(t)}{\delta \frac{\beta}{SL} \tilde{\mu}_k(\mathbf{q}; t)} = \langle \rho_k(\mathbf{q}) \rangle^t$$

which yields

$$\langle \rho_k(\mathbf{q}) \rangle^t = \frac{\beta}{SL} \times$$

$$\times \sum_{k', \mathbf{q}} (\bar{S}_{k'}(\mathbf{q}') - \bar{\mu}_{k'}(\mathbf{q}; t)) \mathfrak{M}_{-k', -k}^{-1}(-\mathbf{q}, -\mathbf{q}) \bar{S}_k(\mathbf{q}), \quad (34)$$

where

$$\bar{S}_k(\mathbf{q}) = N_{\text{ion}} S_k(\mathbf{q}) \omega_k(\mathbf{q}).$$

Defining the function $\mathfrak{M}_{-k, -k'}^{-1}(-\mathbf{q}, -\mathbf{q}')$ inverse to $\mathfrak{M}_{-k, -k'}(-\mathbf{q}, -\mathbf{q})$ by the relation

$$\sum_{k'', \mathbf{q}'} \mathfrak{M}_{k, k''}^{-1}(\mathbf{q}, \mathbf{q}'') \mathfrak{M}_{k'', k'}(\mathbf{q}'', \mathbf{q}') = \delta_{k, k'} \delta_{\mathbf{q}, \mathbf{q}'}$$

and using (34), we obtain the Fourier transform of the electron electrochemical potential as follows:

$$\bar{\mu}_k(\mathbf{q}; t) = \bar{S}_k(\mathbf{q}) - \left(\frac{\beta}{SL} \right)^{-1} \times \sum_{k', \mathbf{q}'} \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{S}_{k'}^{-1}(\mathbf{q}') \mathfrak{M}_{-k', -k}^{-1}(-\mathbf{q}', -\mathbf{q}). \quad (35)$$

One can see that the Fourier transform of the electrochemical potential in the Gaussian approximation is expressed in terms of the structural factor of the ion subsystem and the Fourier transform of the local part of the electron-ion interaction pseudopotential. The time dependence is described by the average nonequilibrium value of the electron density renormalized through the structural factor of the ion subsystem, the pseudopotential $\omega_k(\mathbf{q})$, and the function $\mathfrak{M}_{-k', -k}^{-1}(-\mathbf{q}', -\mathbf{q})$ inverse to the pair irreducible cumulant average value of the electron density fluctuation. Substituting (35) into the expression for the Massieu–Planck functional, we obtain

$$\begin{aligned} \Phi^{(G)}(t) &= \ln Z^G(t) = \beta \frac{N}{2S} \sum_{\mathbf{q}} \nu(\mathbf{q}|0) + \ln Z_{\text{jell}} - \\ &- \frac{1}{2} \sum_{k_1, k_2} \sum_{\mathbf{q}_1, \mathbf{q}_2} \langle \rho_{k_1}(\mathbf{q}_1) \rangle^t \bar{S}_{k_1}^{-1}(\mathbf{q}_1) \times \\ &\times \mathfrak{M}_{-k_1, -k_2}^{-1}(-\mathbf{q}_1, -\mathbf{q}_2) \bar{S}_{k_2}^{-1}(\mathbf{q}_2) \langle \rho_{k_2}(\mathbf{q}_2) \rangle^t. \end{aligned} \quad (36)$$

In this case, the entropy operator (33) takes the form

$$\hat{S}^{(G)}(t) = \beta \frac{N}{2S} \sum_{\mathbf{q}} \nu(\mathbf{q}|0) + \ln Z_{\text{jell}} -$$

$$\begin{aligned} &- \frac{1}{2} \sum_{k_1, k_2} \sum_{\mathbf{q}_1, \mathbf{q}_2} \langle \rho_{k_1}(\mathbf{q}_1) \rangle^t \bar{S}_{k_1}^{-1}(\mathbf{q}_1) \mathfrak{M}_{-k_1, -k_2}^{-1}(-\mathbf{q}_1, -\mathbf{q}_2) \times \\ &\times \bar{S}_{k_2}^{-1}(\mathbf{q}_2) \langle \rho_{k_2}(\mathbf{q}_2) \rangle^t + \beta \left(H - \frac{1}{SL} \sum_{k, \mathbf{q}} \left\{ \bar{S}_k(\mathbf{q}) - \left(\frac{\beta}{SL} \right)^{-1} \times \right. \right. \\ &\left. \left. \times \sum_{k', \mathbf{q}'} \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{S}_{k'}^{-1}(\mathbf{q}') \mathfrak{M}_{-k', -k}^{-1}(-\mathbf{q}', -\mathbf{q}) \right\} \rho_k(\mathbf{q}) \right). \end{aligned} \quad (37)$$

Instead of using the nonequilibrium statistical operator in the form (29) to obtain the transport equations for $\langle \rho_k(\mathbf{q}) \rangle^t$, we apply the nonequilibrium statistical operator with regard for the projection, which allows us to eliminate the time derivatives of thermodynamic parameters [25, 27, 28]. We obtain

$$\begin{aligned} \rho(t) &= \rho_q(t) - \\ &- \int_{-\infty}^t e^{\varepsilon(t-t')} T_q(t; t') (1 - P_q(t')) i L_N \rho(t') dt', \end{aligned} \quad (38)$$

where

$$T_q(t, t') = \exp_+ \left\{ - \int_{t'}^t (1 - P_q(t'')) i L_N dt'' \right\}$$

denotes the generalized evolution operator with regard for projection and $P_q(t')$ is the generalized Kawasaki–Gunton projection operator, whose structure depends on the quasiequilibrium statistical operator $\rho_q(t)$. In our case, $P_q(t)$ has the form

$$\begin{aligned} P_q(t) \rho' &= \left(\rho_q(t) - \sum_{k, \mathbf{q}} \frac{\delta \rho_q(t)}{\delta \langle \rho_k(\mathbf{q}) \rangle^t} \langle \rho_k(\mathbf{q}) \rangle^t \right) \text{Sp} \rho' + \\ &+ \sum_{k, \mathbf{q}} \frac{\delta \rho_q(t)}{\delta \langle \rho_k(\mathbf{q}) \rangle^t} \text{Sp}(\rho_k(\mathbf{q}) \rho') \end{aligned} \quad (39)$$

and the operator properties: $P_q(t) \rho(t) = \rho_q(t)$, $P_q(t) \rho_q(t) = \rho_q(t)$, $P_q(t) P_q(t') = P_q(t)$. In order to calculate the nonequilibrium statistical operator according to (38) in the Gaussian approximation for $\rho_q^{(G)}(t)$, we

must find, first of all, the Kawasaki–Gunton projection operator. Taking into account that

$$\begin{aligned} \rho_q^{(G)}(t) = \exp \left\{ - \left(\beta \frac{N}{2S} \sum_{\mathbf{q}} \nu(\mathbf{q}|0) + \ln Z_{\text{jell}} - \right. \right. \\ \left. - \frac{1}{2} \sum_{k_1, k_2} \sum_{\mathbf{q}_1, \mathbf{q}_2} \langle \rho_{k_1}(\mathbf{q}_1) \rangle^t \bar{S}_{k_1}^{-1}(\mathbf{q}_1) \times \right. \\ \left. \times \mathfrak{M}_{-k_1, -k_2}^{-1}(-\mathbf{q}_1, -\mathbf{q}_2) \bar{S}_{k_2}^{-1}(\mathbf{q}_2) \langle \rho_{k_2}(\mathbf{q}_2) \rangle^t + \right. \\ \left. + \beta \left(H - \frac{1}{SL} \sum_{k, \mathbf{q}} \left\{ \bar{S}_k(\mathbf{q}) - \left(\frac{\beta}{SL} \right)^{-1} \sum_{k', \mathbf{q}'} \langle \rho_{k'}(\mathbf{q}') \rangle^t \times \right. \right. \right. \\ \left. \left. \left. \times \bar{S}_{k'}^{-1}(\mathbf{q}) \mathfrak{M}_{-k', -k}^{-1}(-\mathbf{q}', -\mathbf{q}) \right\} \rho_k(\mathbf{q}) \right) \right\} \end{aligned} \quad (40)$$

and

$$\begin{aligned} \frac{\delta \rho_q^{(G)}(t)}{\delta \langle \rho_k(\mathbf{q}) \rangle^t} = - \sum_{k', \mathbf{q}'} (\rho_{k'}(\mathbf{q}', \tau) - \\ - \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{S}_{k'}^{-1}(\mathbf{q}')) \mathfrak{M}_{-k', -k}^{-1}(-\mathbf{q}', -\mathbf{q}) \bar{S}_k^{-1}(\mathbf{q}) \rho_q^{(G)}(t), \\ \text{we obtain the following expression for the Kawasaki–} \\ \text{Gunton projection operator:} \\ P_q^{(G)}(t) \rho' = (\rho_q^{(G)}(t) + \\ + \sum_{k, \mathbf{q}} \sum_{k', \mathbf{q}'} (\rho_{k'}(\mathbf{q}', \tau) - \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{S}_{k'}^{-1}(\mathbf{q}')) \times \\ \times \mathfrak{M}_{-k', -k}^{-1}(-\mathbf{q}', -\mathbf{q}) \bar{S}_k^{-1}(\mathbf{q}) \langle \rho_k(\mathbf{q}) \rangle^t \rho_q^{(G)}(t) \text{Sp} \rho' - \\ - \sum_{k, \mathbf{q}} \sum_{k', \mathbf{q}'} (\rho_{k'}(\mathbf{q}', \tau) - \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{S}_{k'}^{-1}(\mathbf{q}')) \times \\ \times \mathfrak{M}_{-k', -k}^{-1}(-\mathbf{q}', -\mathbf{q}) \bar{S}_k^{-1}(\mathbf{q}) \text{Sp}(\rho_k(\mathbf{q}) \rho') \rho_q^{(G)}(t). \end{aligned} \quad (41)$$

With regard for (41) and the relation

$$iL_N \rho_q(t) = \sum_{k, \mathbf{q}} W^{(G)}(k, \mathbf{q}; t) \times$$

$$\times \int_0^1 (\rho_q^{(G)})^\tau(t) \dot{\rho}_k(\mathbf{q}) (\rho_q^{(G)})^{1-\tau}(t) d\tau, \quad (42)$$

where

$$\begin{aligned} W^{(G)}(k, \mathbf{q}; t) = \frac{\beta}{SL} \bar{\mu}_k(\mathbf{q}; t) = \frac{\beta}{SL} \left\{ \bar{S}_k(\mathbf{q}) - \right. \\ \left. - \left(\frac{\beta}{SL} \right)^{-1} \sum_{k', \mathbf{q}'} \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{S}_{k'}^{-1}(\mathbf{q}) \mathfrak{M}_{-k', -k}^{-1}(-\mathbf{q}, -\mathbf{q}) \right\}, \end{aligned} \quad (43)$$

the nonequilibrium statistical operator can be written down in the form

$$\begin{aligned} \rho(t) = \rho_q^{(G)}(t) - \sum_{k, \bar{q}} \int_{-\infty}^t e^{\varepsilon(t'-t)} T_q^G(t, t') \times \\ \times \int_0^1 d\tau (\rho_q^{(G)}(t'))^\tau I_\rho(k, \mathbf{q}; t') \times \\ \times (\rho_q^{(G)}(t'))^{1-\tau} W^{(G)}(k, \mathbf{q}; t') dt', \end{aligned} \quad (44)$$

where

$$I_\rho(k, \mathbf{q}; t') = (1 - \mathcal{P}^{(G)}(t')) iL_N \rho_k(\mathbf{q}) \quad (45)$$

is generalized diffusion flow, $\mathcal{P}^{(G)}(t)$ is projection operator acting on the operator

$$\mathcal{P}^{(G)}(t) \hat{A} = \sum_{k', \mathbf{q}'} \sum_{k'', \mathbf{q}''} \delta \rho_{k'}(\mathbf{q}'; t) \times \quad (46)$$

$$\times \mathfrak{M}_{-k', -k''}^{-1}(-\mathbf{q}', -\mathbf{q}'') \bar{S}_{k''}^{-1}(\mathbf{q}'') \langle \rho_{k''}(\mathbf{q}'') \rangle_{\hat{A}}^t,$$

where $\delta \rho_{k'}(\mathbf{q}'; t) = \rho_{k'}(\mathbf{q}') - \langle \rho_{k'}(\mathbf{q}') \rangle^t \left(\frac{\beta}{SL} \right)^{-1} \bar{S}_{k'}^{-1}(\mathbf{q}')$, $\langle \dots \rangle_{(G)}^{t'} = \text{Sp}(\dots \rho_q^{(G)}(t'))$ is the averaging with the quasiequilibrium statistical operator in the Gaussian approximation. In its structure, the nonequilibrium statistical operator is a functional of the microscopic fluxes $\dot{\rho}_k(\mathbf{q})$, the observable quantities $\langle \rho_k(\mathbf{q}) \rangle^t$, and the quasiequilibrium and equilibrium correlation functions of the electron subsystem of a semibounded metal. With

its help, we obtain the transport equation for $\langle \rho_k(\mathbf{q}) \rangle^t$ in the form

$$\begin{aligned} \frac{\partial}{\partial t} \langle \rho_k(\mathbf{q}) \rangle^t &= \langle \dot{\rho}_k(\mathbf{q}) \rangle^t = \\ &= - \sum_{k', \mathbf{q}'} \int_{-\infty}^t e^{\varepsilon(t'-t)} D_{JJ}^{(G)}(k, \mathbf{q}; k', \mathbf{q}'; t, t') W^{(G)}(k', \mathbf{q}; t') dt', \end{aligned} \quad (47)$$

where

$$\begin{aligned} D_{JJ}^{(G)}(k, \mathbf{q}; k', \mathbf{q}'; t, t') &= \\ &= \langle I_\rho(k, \mathbf{q}) T_q^G(t, t') I_\rho(k', \mathbf{q}'; \tau) \rangle_{(G)}^{t'} = \\ &= k \mathbf{q} \cdot \left\langle \vec{J}_k(\mathbf{q}) T_q^G(t, t') \mathbf{J}_{k'}(\mathbf{q}'; \tau) \right\rangle_{(G)}^{t'} \cdot \mathbf{q}' k' = \\ &= k \mathbf{q} \cdot \tilde{D}_{JJ}^{(G)}(k, \mathbf{q}; k', \mathbf{q}'; t, t') \cdot \mathbf{q}' k', \end{aligned} \quad (48)$$

$\tilde{D}_{JJ}^{(G)}(k, \mathbf{q}; k', \mathbf{q}'; t, t')$ is the generalized diffusion coefficient of electrons in a semibounded metal calculated using the quasiequilibrium statistical operator in the Gaussian approximation.

4. Approximation $B_k(\mathbf{q}; t) B_{k'}(\mathbf{q}'; t) B_{k''}(\mathbf{q}''; t)$

Let us consider the next approximation after the Gaussian one for the quasiequilibrium statistical sum or the Massieu–Planck functional (28). In this case, we obtain the following expression for the entropy operator:

$$\begin{aligned} \hat{S}'(t) &= \beta \frac{N}{2S} \sum_{\mathbf{q}} \nu(\mathbf{q}|0) + \ln Z_{\text{jell}} - \\ &- \frac{1}{2} \left(\frac{\beta}{SL} \right)^2 \sum_{\mathbf{q}_1, \mathbf{q}_2} \sum_{k_1, k_2} B(\mathbf{q}_1, k_1; t) B(\mathbf{q}_2, k_2; t) \times \\ &\times \mathfrak{M}_{-k_1, -k_2}(-\mathbf{q}_1, -\mathbf{q}_2) + \\ &+ \frac{i}{3!} \left(\frac{\beta}{SL} \right)^3 \sum_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3} \sum_{k_1, k_2, k_3} B(\mathbf{q}_1, k_1; t) B(\mathbf{q}_2, k_2; t) \times \end{aligned}$$

$$\begin{aligned} &\times B(\mathbf{q}_3, k_3; t) \mathfrak{M}_{-k_1, -k_2, -k_3}(-\mathbf{q}_1, -\mathbf{q}_2, -\mathbf{q}_3) + \\ &+ \beta \left(H - \frac{1}{SL} \sum_{\mathbf{q}, k} \bar{\mu}_k(\mathbf{q}; t) \rho_k(\mathbf{q}) \right). \end{aligned} \quad (49)$$

In order to eliminate the parameters $\bar{\mu}_k(\mathbf{q}; t)$ from this formula, the thermodynamic relation (12) will be applied once again:

$$\frac{\delta \Phi(t)}{\delta \frac{\beta}{SL} \bar{\mu}_k(\mathbf{q}; t)} = \langle \rho_k(\mathbf{q}) \rangle^t.$$

From here, we derive the equation for $\bar{\mu}_{k_i}(\mathbf{q}_i; t)$:

$$\begin{aligned} \langle \rho_k(\mathbf{q}) \rangle^t &= - \frac{\beta}{SL} \sum_{\mathbf{q}_1, \mathbf{q}_2} \sum_{k_1, k_2} \left(\hat{S}_{k_1}(\mathbf{q}_1) - \bar{\mu}_{k_1}(\mathbf{q}_1; t) \right) \times \\ &\times \hat{S}_{k_2}(\mathbf{q}_2) \mathfrak{M}_{-k_1, -k_2}(-\mathbf{q}_1, -\mathbf{q}_2) - \\ &- \frac{i}{3!} \left(\frac{\beta}{SL} \right)^2 \sum_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3} \sum_{k_1, k_2, k_3} \left(\hat{S}_{k_1}(\mathbf{q}_1) - \bar{\mu}_{k_1}(\mathbf{q}_1; t) \right) \times \\ &\times \left(\hat{S}_{k_2}(\mathbf{q}_2) - \bar{\mu}_{k_2}(\mathbf{q}_2; t) \right) \hat{S}_{k_3}(\mathbf{q}_3) \times \\ &\times \mathfrak{M}_{-k_1, -k_2, -k_3}(-\mathbf{q}_1, -\mathbf{q}_2, -\mathbf{q}_3). \end{aligned} \quad (50)$$

In its structure, this equation is square with respect to the functions $\bar{\mu}_{k_i}(\mathbf{q}_i; t)$. To solve it approximately, we replace one of the quantities $\bar{\mu}_{k_i}(\mathbf{q}_i; t)$ on the right-hand side of the quadratic form by its value found in the Gaussian approximation (35). Then we obtain a linear equation for the function $\bar{\mu}_k(\mathbf{q}; t)$:

$$\begin{aligned} \langle \rho_k(\mathbf{q}) \rangle^t &= - \frac{\beta}{SL} \sum_{k', \mathbf{q}} \left(\bar{S}_{k'}(\mathbf{q}) - \bar{\mu}_{k'}(\mathbf{q}'; t) \right) \times \\ &\times G_{-k', -k}(-\mathbf{q}, -\mathbf{q}; t), \end{aligned} \quad (51)$$

where

$$\begin{aligned} G_{-k_1, -k_2}(-\mathbf{q}_1, -\mathbf{q}_2; t) &= \\ &= \bar{S}_{k_2}(\mathbf{q}_2) \mathfrak{M}_{-k_1, -k_2}(-\mathbf{q}_1, -\mathbf{q}_2) + \end{aligned}$$

$$\begin{aligned}
 & + \frac{i}{2} \frac{\beta}{SL} \sum_{\mathbf{q}', \mathbf{q}_3} \sum_{k', k_3} \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{S}_{k'}^{-1}(\mathbf{q}') \times \\
 & \times \mathfrak{M}_{-k', -k_2}^{-1}(-\mathbf{q}', -\mathbf{q}_2) \times \\
 & \times \bar{S}_{k_3}(\mathbf{q}_3) \mathfrak{M}_{-k_1, -k_2, -k_3}(-\mathbf{q}_1, -\mathbf{q}_2, -\mathbf{q}_3). \quad (52)
 \end{aligned}$$

As is seen, the function $G_{-k_1, -k_2}(-\mathbf{q}_1, -\mathbf{q}_2; t)$ depends on time through the observable quantities $\langle \rho_{k'}(\mathbf{q}) \rangle^t$. It also depends on the structural factor of the ion subsystem $S_{k'}(\mathbf{q})$, the Fourier transform of the local part of the electron-ion interaction pseudopotential $\omega_k(\mathbf{q})$, and the cumulant irreducible average values of the electron density fluctuations: pair $\mathfrak{M}_{-k', -k_2}(-\mathbf{q}, -\mathbf{q}_2)$ and triple ones $\mathfrak{M}_{-k_1, -k_2, -k_3}(-\mathbf{q}_1, -\mathbf{q}_2, -\mathbf{q}_3)$. The second term on the right-hand side of Eq. (52) involves the renormalization of the triple electron correlations through the pair ones that make the dominant contribution in the Gaussian approximation (see the previous section).

Defining $G_{-k_1, -k_2}^{-1}(-\mathbf{q}_1, -\mathbf{q}_2; t)$ as a function inverse to $G_{-k_1, -k_2}(-\mathbf{q}_1, -\mathbf{q}_2; t)$ by the relation

$$\begin{aligned}
 & \sum_{k'', \mathbf{q}''} G_{-k_1, -k_2}^{-1}(-\mathbf{q}_1, -\mathbf{q}_2; t) G_{-k'', -k_2}(-\mathbf{q}'', -\mathbf{q}_2; t) = \\
 & = \delta_{k_1, k_2} \delta_{\mathbf{q}_1, \mathbf{q}_2}
 \end{aligned}$$

and using Eq.(51), we derive the following expression for the Fourier transform of the electron electrochemical potential:

$$\begin{aligned}
 \bar{\mu}_k(\mathbf{q}; t) & = \bar{S}_k(\mathbf{q}) - \\
 & - \left(\frac{\beta}{SL} \right)^{-1} \sum_{k', \mathbf{q}} \langle \rho_{k'}(\mathbf{q}') \rangle^t G_{-k', -k}^{-1}(-\mathbf{q}', -\mathbf{q}; t). \quad (53)
 \end{aligned}$$

Now, with regard for (53), the entropy operator (49) can be presented in the form

$$\begin{aligned}
 \hat{S}'(t) & = \beta \frac{N}{2S} \sum_q \nu(q|0) + \ln Z_{\text{jell}} - \\
 & - \frac{1}{2} \sum_{k', k''} \sum_{\mathbf{q}', \mathbf{q}''} \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{G}_{k', k''}^{(2)}(\mathbf{q}', \mathbf{q}''; t) \langle \rho_{k''}(\mathbf{q}'') \rangle^t + \\
 & + \frac{i}{3!} \sum_{k', k'', k'''} \sum_{\mathbf{q}', \mathbf{q}'', \mathbf{q}'''} \bar{G}_{k', k'', k'''}^{(3)}(\mathbf{q}', \mathbf{q}'', \mathbf{q}'''; t) \times
 \end{aligned}$$

$$\begin{aligned}
 & \times \langle \rho_{k'}(\mathbf{q}') \rangle^t \langle \rho_{k''}(\mathbf{q}'') \rangle^t \langle \rho_{k'''}(\mathbf{q}''') \rangle^t + \\
 & + \beta \left(H - \frac{1}{SL} \sum_{k, \mathbf{q}} \left(\bar{S}_k(\mathbf{q}) - \left(\frac{\beta}{SL} \right)^{-1} \sum_{k', \mathbf{q}'} \langle \rho_{k'}(\mathbf{q}') \rangle^t \times \right. \right. \\
 & \left. \left. \times G_{k'k}^{-1}(\mathbf{q}, \mathbf{q}'; t) \right) \rho_k(\mathbf{q}) \right), \quad (54)
 \end{aligned}$$

where

$$\begin{aligned}
 \bar{G}_{k', k''}^{(2)}(\mathbf{q}', \mathbf{q}''; t) & = \sum_{k_1, k_2} \sum_{\mathbf{q}_1, \mathbf{q}_2} G_{k', k_1}^{-1}(\mathbf{q}', \mathbf{q}_1; t) \times \\
 & \times \mathfrak{M}_{-k_1, -k_2}(-\mathbf{q}_1, -\mathbf{q}_2) G_{k_2, k''}^{-1}(\mathbf{q}_2, \mathbf{q}''; t), \\
 \bar{G}_{k', k'', k'''}^{(3)}(\mathbf{q}', \mathbf{q}'', \mathbf{q}'''; t) & = \\
 & = \sum_{k_1, k_2, k_3} \sum_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3} G_{k', k_1}^{-1}(\mathbf{q}', \mathbf{q}_1; t) \times \\
 & \times G_{k'', k_2}^{-1}(\mathbf{q}'', \mathbf{q}_2; t) G_{k''', k_3}^{-1}(\mathbf{q}''', \mathbf{q}_3; t) \times \\
 & \times \mathfrak{M}_{-k_1, -k_2, -k_3}(-\mathbf{q}_1, -\mathbf{q}_2, -\mathbf{q}_3).
 \end{aligned}$$

These functions involve the dynamic renormalization of the cumulant irreducible average values of the electron density fluctuations: pair $\mathfrak{M}_{-k', -k_2}(-\mathbf{q}, -\mathbf{q}_2)$ and triple ones $\mathfrak{M}_{-k_1, -k_2, -k_3}(-\mathbf{q}_1, -\mathbf{q}_2, -\mathbf{q}_3)$ through functions (52). With regard for the entropy operator (49), the quasiequilibrium statistical operator reads

$$\begin{aligned}
 \rho_q^{(G+1)}(t) & = \exp \left(- \left(\beta \frac{N}{2S} \sum_{\mathbf{q}} \nu(\mathbf{q}|0) + \ln Z_{\text{jell}} - \right. \right. \\
 & - \frac{1}{2} \sum_{k', k''} \sum_{\mathbf{q}', \mathbf{q}''} \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{G}_{k', k''}^{(2)}(\mathbf{q}', \mathbf{q}''; t) \times \\
 & \times \langle \rho_{k''}(\mathbf{q}'') \rangle^t + \\
 & + \frac{i}{3!} \sum_{k', k'', k'''} \sum_{\mathbf{q}', \mathbf{q}'', \mathbf{q}'''} \bar{G}_{k', k'', k'''}^{(3)}(\mathbf{q}', \mathbf{q}'', \mathbf{q}'''; t) \times \\
 & \left. \left. \times \langle \rho_{k'}(\mathbf{q}') \rangle^t \langle \rho_{k''}(\mathbf{q}'') \rangle^t \langle \rho_{k'''}(\mathbf{q}''') \rangle^t + \right)
 \end{aligned}$$

$$\begin{aligned}
 & +\beta \left(H - \frac{1}{SL} \sum_{k, \mathbf{q}} \left(\bar{S}_k(\mathbf{q}) - \left(\frac{\beta}{SL} \right)^{-1} \sum_{k', \mathbf{q}'} \langle \rho_{k'}(\mathbf{q}') \rangle^t \times \right. \right. \\
 & \left. \left. \times G_{k'k}^{-1}(\mathbf{q}, \mathbf{q}'; t) \rho_k(\mathbf{q}) \right) \right), \quad (55)
 \end{aligned}$$

where the index “ $(G+1)$ ” denotes the third order with respect to the observable parameters in the quasiequilibrium statistical operator. In addition to the pair (Gaussian) one, it also allows for the cubic dependence on the parameters of the reduced description $\langle \rho_k(\mathbf{q}) \rangle^t$ with dynamic renormalizations in the functions $\bar{G}_{k', k''}^{(2)}(\mathbf{q}', \mathbf{q}''; t)$ and $\bar{G}_{k', k'', k'''}^{(3)}(\mathbf{q}', \mathbf{q}'', \mathbf{q}'''; t)$. Since

$$\begin{aligned}
 iL_N \rho_q^{(G+1)}(t) & = \sum_{k, \mathbf{q}} W^{(G+1)}(k, \mathbf{q}; t) \times \\
 & \times \int_0^1 (\rho_q^{(G+1)})^\tau(t) \dot{\rho}_k(\mathbf{q}) (\rho_q^{(G+1)})^{1-\tau}(t) d\tau, \quad (56)
 \end{aligned}$$

where

$$\begin{aligned}
 W^{(G+1)}(k, \mathbf{q}; t) & = \frac{\beta}{SL} \bar{\mu}_k(\mathbf{q}; t) = \frac{\beta}{SL} \left\{ \bar{S}_k(\mathbf{q}) - \right. \\
 & \left. - \left(\frac{\beta}{SL} \right)^{-1} \sum_{k' \mathbf{q}'} \langle \rho_{k'}(\mathbf{q}') \rangle^t G_{-k', -k}^{-1}(-\mathbf{q}', -\mathbf{q}; t) \right\}, \quad (57)
 \end{aligned}$$

we obtain the following expression for the nonequilibrium statistical operator in approximation (55):

$$\begin{aligned}
 \rho(t) & = \rho_q^{(G+1)}(t) - \sum_{k, \mathbf{q}} \int_{-\infty}^t e^{\varepsilon(t-t')} T_q^{(G+1)}(t, t') \times \\
 & \times (1 - P_q^{(G+1)}(t')) \int_0^1 (\rho_q^{(G+1)})^\tau(t') \dot{\rho}_k(\mathbf{q}) (\rho_q^{(G+1)})^{1-\tau}(t') \times \\
 & \times W^{(G+1)}(k, \mathbf{q}; t') dt', \quad (58)
 \end{aligned}$$

where the Kawasaki–Gunton projection operator $P_q^{(G+1)}(t')$ and the respective evolution operator $T_q^{(G+1)}(t, t')$ are calculated with the quasiequilibrium

statistical operator in approximation (55). Moreover, $P_q^{(G+1)}(t')$ has the following structure:

$$\begin{aligned}
 P_q^{(G+1)}(t) \rho' & = \left(\rho_q^{(G+1)}(t) - \right. \\
 & - \sum_{k, \mathbf{q}} \left\{ \left(\beta \rho_{k'}(\mathbf{q}', \tau) G_{k'k}^{-1}(\mathbf{q}, \mathbf{q}'; t) - \right. \right. \\
 & \left. \left. - \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{G}_{k', k}^{(2)}(\mathbf{q}', \mathbf{q}; t) \right) \times \right. \\
 & \times \frac{i}{2} \sum_{k', k''} \sum_{\mathbf{q}', \mathbf{q}''} \langle \rho_{k'}(\mathbf{q}') \rangle^t \langle \rho_{k''}(\mathbf{q}'') \rangle^t \times \\
 & \times \bar{G}_{k', k'', k}^{(3)}(\mathbf{q}', \mathbf{q}'', \mathbf{q}; t) \left. \right\} \langle \rho_k(\mathbf{q}) \rangle^t \rho_q^{(G+1)}(t) \text{Sp}(\rho') \times \\
 & + \sum_{k, \mathbf{q}} \left\{ \left(\beta \rho_{k'}(\mathbf{q}', \tau) G_{k'k}^{-1}(\mathbf{q}, \mathbf{q}'; t) - \right. \right. \\
 & \left. \left. - \langle \rho_{k'}(\mathbf{q}') \rangle^t \bar{G}_{k', k}^{(2)}(\mathbf{q}', \mathbf{q}; t) \right) \times \right. \\
 & \times \frac{i}{2} \sum_{k', k''} \sum_{\mathbf{q}', \mathbf{q}''} \langle \rho_{k'}(\mathbf{q}') \rangle^t \langle \rho_{k''}(\mathbf{q}'') \rangle^t \times \\
 & \left. \left. \times \bar{G}_{k', k'', k}^{(3)}(\mathbf{q}', \mathbf{q}'', \mathbf{q}; t) \right\} \text{Sp}(\rho_k(\mathbf{q}) \rho') \rho_q^{(G+1)}(t). \quad (59)
 \end{aligned}$$

As compared to the result of action of the operator $P_q^{(G)}(t)$ in the Gaussian approximation, it already includes the third order with respect to the parameters of the reduced description. With the help of the nonequilibrium statistical operator (55), we obtain the transport equation for $\langle \rho_k(\mathbf{q}) \rangle^t$ in the form

$$\begin{aligned}
 \frac{\partial}{\partial t} \langle \rho_k(\mathbf{q}) \rangle^t & = \langle \dot{\rho}_k(\mathbf{q}) \rangle_{(G+1)}^t - \\
 & - \sum_{k', \mathbf{q}'} \int_{-\infty}^t e^{\varepsilon(t-t')} D_{JJ}^{(G+1)}(k, \mathbf{q}; k', \mathbf{q}'; t, t') \times \\
 & \times W^{(G+1)}(k', \mathbf{q}; t') dt' +
 \end{aligned}$$

$$\begin{aligned}
& + \sum_{k', \mathbf{q}' - \infty}^t e^{\varepsilon(t'-t)} \langle \dot{\rho}_k(\mathbf{q}) T_q^{(G)}(t, t') P_q^{(G+1)}(t') \rangle \times \\
& \times \dot{\rho}_{k'}(\mathbf{q}'; \tau)_{(G+1)}^{t'} W^{(G+1)}(k', \mathbf{q}'; t') dt', \quad (60)
\end{aligned}$$

where

$$\begin{aligned}
& D_{JJ}^{(G+1)}(k, \mathbf{q}; k', \mathbf{q}'; t, t') = \\
& = \langle \dot{\rho}_k(\mathbf{q}) T_q^G(t, t') \dot{\rho}_{k'}(\mathbf{q}', \tau) \rangle_{(G+1)}^{t'} = \\
& = k \mathbf{q} \langle \mathbf{J}_k(\mathbf{q}) T_q^G(t, t') \mathbf{J}_{k'}(\mathbf{q}'; \tau) \rangle_{(G+1)}^{t'} \mathbf{q}' k' = \\
& = k \mathbf{q} \tilde{D}_{JJ}^{(G+1)}(k, \mathbf{q}; k', \mathbf{q}'; t, t') \mathbf{q}' k', \quad (61)
\end{aligned}$$

$\tilde{D}_{JJ}^{(G+1)}(k, \mathbf{q}; k', \mathbf{q}'; t, t')$ is the generalized diffusion coefficient of electrons in a semibounded metal calculated with the quasiequilibrium statistical operator in approximation (55). With regard for the structure of functions (52) and (57) and the Kawasaki–Gunton projection operator (59), we can conclude that Eq. (60) is nonlinear with respect to $\langle \rho_k(\mathbf{q}) \rangle^t$.

5. Conclusions

Electrodifusion processes in the electron subsystem of a semibounded metal are described on the basis of the generalized “jellium” model with the use of the NSO method, where the only parameter of the reduced description is the nonequilibrium average value of the electron density. Applying the functional integration technique, we have calculated the quasiequilibrium statistical sum for such a system in the case of the local pseudopotential of electron-ion interaction in a metal in the Gaussian and higher approximations with respect to the dynamic electron correlations. They are used to obtain expressions for the nonequilibrium statistical operator in the Gaussian and higher approximations with respect to the dynamic electron correlations, which makes it possible to go beyond the linear approximation with respect to the electrochemical potential. In the respective approximations for the nonequilibrium statistical operator, we have derived the generalized transport equations (generalized diffusion equations) for the nonequilibrium average value of the electron density that can be applied to the description of strongly nonequilibrium processes for the electron

subsystem of a semibounded metal. The generalized diffusion coefficients for electrons in a semibounded metal that enter the corresponding transport equations are calculated with the quasiequilibrium statistical operator in the respective approximations: Gaussian one (40) and approximation (55). An important point in such an approach is that the time correlation functions and the generalized diffusion coefficients are calculated with the quasiequilibrium statistical operator in the corresponding approximation and represent functionals of the observable quantities $\langle \rho_k(\mathbf{q}) \rangle^t$ of a certain order. Of special interest in this approach are the investigations of the dynamic structural factor for the nonequilibrium electron subsystem of a semibounded metal.

1. E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
2. C.A. Ullrich, U.I. Grossmann, and E.K.U. Gross, Phys. Rev. Lett. **74**, 872 (1995).
3. G. Vignale and W. Kohn, Phys. Rev. Lett. **77**, 2037 (1996).
4. G. Vignale and C.A. Ullrich, Phys. Rev. Lett. **79**, 4878 (1997).
5. N.T. Maitra, K. Burke, H. Appel, E.K.U. Gross and R. van Leeuwen, in *Reviews in Modern Quantum Chemistry: A Celebration of the Contributions of R.G. Parr*, edited by K.D. Sen (World Scientific, Singapore, 2001).
6. C.A. Ullrich and G. Vignale, arXiv: 0201483 v1 (2002).
7. N.T. Maitra, K. Burke, and C. Woodward, Phys. Rev. Lett. **89**, 023002 (2002).
8. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).
9. I.V. Tokatly and O. Pankratov, arXiv: 0209617 (2003).
10. M.A.L. Marques and E.K.U. Gross, Annu. Rev. Phys. Chem. **55**, 427 (2004).
11. S. Botti, F. Sottile, N. Vast et al., Phys. Rev. B. **69**, 155112 (2004).
12. M. Dion and K. Burke, Phys. Rev. A **72**, 020502(R) (2005).
13. J. Werschnik, E.K.U. Gross, and K. Burke, arXiv: 0410362 v2 (2005).
14. J. Schirmer and A. Dreuw, arXiv: 0602020, v1 (2006).
15. P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
16. R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).
17. R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).
18. W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
19. N.D. Lang and W. Kohn, Phys. Rev. B. **1**, 4555 (1970).

20. A. Equiluz, S.C. Ying, and J.J. Quinn, *Phys. Rev. B* **11**, 2118 (1975).
21. A. Equiluz and J.J. Quinn, *Phys. Rev. B* **14**, 1347 (1978).
22. A. Equiluz, *Phys. Rev. B* **19**, 1689 (1979).
23. A. Griffin and E. Zaremba, *Phys. Rev. A* **8**, 486 (1973).
24. P.P. Kostrobii, B.M. Markovych, Yu.K. Rudavskii, and M.V. Tokarchuk, *Condens. Matter Phys.* **4**, 407 (2001).
25. P.P. Kostrobii, B.M. Markovych, A.I. Vasilenko, and M.V. Tokarchuk, *Ukr. J. Phys.* **52**, 1096 (2007).
26. P.P. Kostrobii, M.V. Tokarchuk, B.M. Markovych, V.V. Ignatyuk, and B.V. Gnativ, *Reaction-Diffusion Processes in "Metal-Gas" Systems* (Lviv Polytechnic National University, Lviv, 2009) (in Ukrainian).
27. D.N. Zubarev, in *Reviews of Science and Technology. Modern Problems of Mathematics* **15**, 131 (VINITI, Moscow, 1980) (in Russian).
28. D. Zubarev, V. Morozov, and G. Röpke, *Statistical Mechanics of Nonequilibrium Processes* (Akademie-Verlag, Berlin, 1996).
29. P.P. Kostrobii and B.M. Markovych, *Zh. Fiz. Dosl.* **7**, 195 (2003).
30. P.P. Kostrobii and B.M. Markovych, *Zh. Fiz. Dosl.* **7**, 298 (2003).
31. N.D. Lang and W. Kohn, *Phys. Rev. B* **3**, 1215 (1971).
32. C. Fiolhais, C. Henriques, I. Sarria, and J.M. Pitarke, *Prog. Surf. Sci.* **67**, 285 (2001).
33. J.H. Rose and J.F. Dobson, *Solid State Comm.* **37**, 91 (1981).

Received 22.06.10.

Translated from Ukrainian by H.G. Kalyuzhna

ДО СТАТИСТИЧНОГО ОПИСУ ЕЛЕКТРОДИФУЗІЙНИХ
ПРОЦЕСІВ ЕЛЕКТРОННОЇ ПІДСИСТЕМИ
НАПІВОБМЕЖЕНОГО МЕТАЛУ
В УЗАГАЛЬНЕНІЙ МОДЕЛІ "ЖЕЛЕ"

П.П. Костробій, Б.М. Маркович, А.І. Василенко,
М.В. Токарчук

Резюме

За допомогою методу функціонального інтегрування отримано нерівноважний статистичний оператор для електронної підсистеми напівобмеженого металу в узагальненій моделі "желе" у гаусовому та вищих наближеннях за динамічними електронними кореляціями при розрахунку квазірівноважної статистичної суми. Такий підхід дає можливість вийти за межі лінійного наближення за градієнтом електрохімічного потенціалу, яке відповідає слабо нерівноважним процесам, та отримати узагальнені рівняння переносу, які описують нелінійні процеси.