GENERAL QUESTIONS OF THERMODYNAMICS, STATISTICAL PHYSICS, AND QUANTUM MECHANICS

STATISTICAL THEORY OF ELECTRON DIFFUSION PROCESSES IN AN ELECTRON SUBSYSTEM WITHIN THE GENERALIZED “JELLIUM” MODEL

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A generalized approach, which takes into account the influence of the discreteness of an ionic subsystem for investigation of ionic and electronic structures of a semibounded metal is proposed. The generalized equation of electron diffusion for an inhomogeneous electron gas is obtained on the basis of the generalized “jellium” model. The calculation of quasiequilibrium partition function by the method of functional integration in the case of the local pseudopotential of the electron-ion interaction of a metal surface is presented. The connection of quasiequilibrium distribution functions of electrons with the electrochemical potential by proper cumulant averages of the “jellium” model is obtained. In the linear approximation by electrochemical potential, the relation with the time-dependent density functional theory (TDDFT) is obtained.

1. Introduction

Investigations of the structure and properties of metals’ surface and its reconstruction in various catalytic processes are a topical problem in the physics of surface. Atoms situated near a metal surface undergo the action of the other forces as compared with atoms in depth of a metal. In the processes of absorption, desorption, and surface diffusion, this fact results in the relaxation or reconstruction of a crystal lattice in a layer near to the surface. Changes of the atomic structure near the surface also results in changes of the electronic structure and forces between atoms. This means that, in the presence of the processes of absorption and surface diffusion, electronic and ionic structures should be calculated self-consistently. For this type of calculations, the method of density functional [1–3], the method of molecular orbitals [4], and the quantum Monte-Carlo methods [5] are the most convenient to be used. For the description of nonequilibrium characteristics of half-bounded electron systems and various condensed systems in the last ten years, TDDFT is actively developed and widely used [6–29]. The problems and tasks of quantum chemistry, the perspectives of development, and achievements of TDDFT are presented, for example, in [26]. TDDFT is based on the Kohn–Sham density functional theory (DFT) [1, 30–34]. In this theory with the use of the Runge–Gross theorem [6], the complicated time-dependent Schrödinger equation for many particles is transformed in a system of Kohn–Sham time-dependent one-particle equations that describe a system of N non-interacting particles, which are placed in external time-dependent potentials $v_s(\mathbf{r},t)$, produce the same density $\rho(\mathbf{r},t)$, and can be solved more faster. Almost in every time-dependent Kohn–Sham calculation for the approximation of the unknown time-dependent exchange-correlation potential, the adiabatic local density approximation (ALDA) is used. In [9], on the basis of the formulation of a time-dependent density current theory in the ALDA, a relation between the generalized viscosity coefficients and exchange-correlation functions is found. In [18] within TDDFT, a generalized hydrodynamic approach is used to obtain a relation of the exchange-correlation part of vector potential with the viscosity tensor, based on the Landau theory of the Fermi liquid. The description of memory effects in TDDFT, by considering initial states, is presented in [10, 14]. Simple approximated solutions of linear response equations in TDDFT are obtained in [35]. The problems concerning the formulation of Kohn–Sham time-dependent density function theory [6], radical Kohn–Sham formulation [20], and reformulation of TDDFT [36, 37] are critically analyzed in [29].

There are various theoretical approaches [38, 39] developed for the description of equilibrium characteristics and nonequilibrium processes (diffusion, absorption, desorption) for spatially inhomogeneous electron-atomic systems. It is important that both DFT and TDDFT are based on the Kohn–Sham's idea and they have an identical strategy of investigations, however, they meet some difficulties [29]. A self-consistent description of atomic and electron subsystems within the investigation of nonequilibrium processes is presented in [38], where the kinetic description of electron processes is carried out. It is obvious that, in the processes of absorption, desorption, and surface diffusion, a metal surface is reconstructed with changing the nonequilibrium properties of both electronic and ionic subsystems. Thus, electron diffusion, heat-viscosity, and electromagnetic properties of an electron subsystem are changed in the field of ions of a metal surface. A generalized approach, which takes the influence of discreteness of an ion subsystem into account and is based on the "jellium" model [41, 42], is proposed in [40] for the investigation of ionic and electron structures of a semibounded metal. The influence of the discreteness of the ion density on the characteristics of a semibounded "jellium" was developed by means of the construction of the perturbation theory with a pseudopotential of electron-ion interaction in [34, 43–45], where, however, a linear response of electron density to a lattice potential does not take the inhomogeneity of an electron subsystem into account. In our approach, we show how the surface potential is formed and present a calculation of the grand partition function for the generalized model with cumulant averages of the "jellium" model [41, 42]. In the present paper, the generalized equation of electron diffusion for an inhomogeneous electron gas, based on the "jellium" model, is obtained, and the calculation of the quasiequilibrium partition function by means of the functional integration method with a local pseudopotential of electron-ion interaction of a metal surface is presented. The relation of quasiequilibrium distribution functions of electrons with the electrochemical potential via the corresponding cumulant averages of the "jellium" model [41, 42] and the generalized equation of electron diffusion in the linear approximation with regard for a nonequilibrium electrochemical potential are obtained. In the same approximation, the equation for the time correlation function "density-density", which determines a dynamical structure factor of the electron subsystem of a semibounded metal, is presented. The relation of this electron diffusion model in the linear approximation to TDDFT [6–12] is shown.

2. Generalized "jellium" Model. Calculation of the Great Partition Function

2.1. Hamiltonian of the system

To take the influence of the discreteness of the ion subsystem of a semibounded metal into account, the Hamiltonian of the system should be written as

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

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

where the first and the second terms of the equation denote the kinetic energy and the potential energy of the interaction between electrons, respectively, the third term is the potential energy of the interaction between ions, and the last denotes the potential energy of the interaction between electrons and ions. Electrons with charge e, mass m, and coordinates $\mathbf{r}_i$ are in the field of ions, $i = 1, \ldots, N$, N_{ion} denotes the number of ions, $\mathcal{Z}e$ is the ion charge, and $\mathbf{R}_j$ ($-\infty < X_j, Y_j < +\infty$, $Z_j \leqslant z_0$, $Z_0 = \text{const}$, $z = Z_0$ is the dividing surface) stands for the radius-vector of the ion, $j = 1, \ldots, N_{\text{ion}}$. We consider ions as immobile in the volume of the system $V = SL$, where S denotes the square of the surface of the semibounded metal, L determines the range of change of an electron coordinate in the normal direction to the metal surface: $z \in (-L/2, +L/2)$, $S \to \infty$, $L \to \infty$. The system obeys the electro-neutrality condition

$$\mathcal{Z}N_{\text{ion}} = N. \tag{2}$$

Let us specify the Hamiltonian of the "jellium" model H_{jell} investigated in [41, 42]. This model is considered as the basic one for the description of thermodynamical and structure characteristics of a semibounded metal. The Hamiltonian of this system can be presented as

$$H = H_{\rm jell} + \sum_{i=1}^{N}\left(\sum_{j=1}^{N_{\rm ion}} e w_{\rm ps}(\mathbf{r}_i - \mathbf{R}_j) + \int d\mathbf{R}\frac{e\rho_{\rm jell}(\mathbf{R})}{|\mathbf{r}_i - \mathbf{R}|}\right) +$$

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

$$- \frac{(eN)^2}{2V^2}\int d\mathbf{R}\int d\mathbf{R}'\frac{1}{|\mathbf{R}-\mathbf{R}'|}, \tag{3}$$

where

$$H_{\rm jell} = H_{\rm jell}^{\rm unif} + \sum_{i=1}^{N} V_{\rm jell}(\mathbf{r}_i), \tag{4}$$

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

$$+ \frac{(eN)^2}{2V^2}\int d\mathbf{R}\int d\mathbf{R}'\frac{1}{|\mathbf{R}-\mathbf{R}'|} - \frac{e^2 N}{V}\sum_{i=1}^{N}\int d\mathbf{R}\frac{1}{|\mathbf{r}_i - \mathbf{R}|} \tag{5}$$

is the Hamiltonian of a homogeneous “jellium”,

$$V_{\rm jell}(\mathbf{r}_i) = e\int d\mathbf{R}\frac{eN/V - \rho_{\rm jell}(\mathbf{R})}{|\mathbf{r}_i - \mathbf{R}|} \tag{6}$$

means the term of the surface potential which is formed by the semibounded “jellium”;

$$\rho_{\rm jell}(\mathbf{R}) \equiv \rho_{\rm jell}(Z) = \rho_0\theta(-d - Z), \quad \rho_0 = \frac{eN}{SL/2} \tag{7}$$

denotes the distribution of the ion density in the “jellium” model, and parameter d is determined by the electro-neutrality condition.

Then the potential of the ion-electron interaction reads

$$w(\mathbf{r}_i, \mathbf{R}_j) = w_{\rm ps}(\mathbf{r}_i - \mathbf{R}_j) + \Delta w(\mathbf{r}_i, \mathbf{R}_j), \tag{8}$$

where $w_{\rm ps}(\mathbf{r}_i - \mathbf{R}_j)$ is the periodic potential of interaction between electrons in the case of a semibounded metal (pseudopotential), $\Delta w(\mathbf{r}_i, \mathbf{R}_j)$ denotes the deviation of the potential of the ion-electron interaction of the semibounded metal from the periodic potential. Then

$$V_{\rm ion}(\mathbf{r}_i) = \sum_{j=1}^{N_{\rm ion}} e\Delta w(\mathbf{r}_i, \mathbf{R}_j) \tag{9}$$

is the term of the surface potential which is formed with the deviation $\Delta w(\mathbf{r}_i, \mathbf{R}_j)$ of the real potential of the ion-electron interaction of the semibounded metal $w(\mathbf{r}_i, \mathbf{R}_j)$ from the potential of a nonbounded metal. As a result of the specifying of $H_{\rm jell}^{\rm unif}$, the Hamiltonian of the system can be written as

$$H = H_{\rm jell}^{\rm unif} + \sum_{i=1}^{N}\left(\sum_{j=1}^{N_{\rm ion}} e w_{\rm ps}(\mathbf{r}_i - \mathbf{R}_j) + \right.$$

$$\left. + \int d\mathbf{R}\frac{e\rho_{\rm jell}(\mathbf{R})}{|\mathbf{r}_i - \mathbf{R}|}\right) + \sum_{i=1}^{N} V(\mathbf{r}_i) +$$

$$+ \frac{1}{2}\sum_{i\neq j=1}^{N_{\rm ion}}\frac{(\mathcal{Z}e)^2}{|\mathbf{R}_i - \mathbf{R}_j|} - \frac{(eN)^2}{2V^2}\int d\mathbf{R}\int d\mathbf{R}'\frac{1}{|\mathbf{R}-\mathbf{R}'|}, \tag{10}$$

where

$$V(\mathbf{r}_i) = V_{\rm jell}(\mathbf{r}_i) + V_{\rm ion}(\mathbf{r}_i) \tag{11}$$

denotes the total surface potential which acts on electrons. The potential of the ion-electron interaction can be modeled by means of a local model pseudopotential

$$w(\mathbf{r}_i - \mathbf{R}_j) = -\frac{\mathcal{Z}e}{|\mathbf{r}_i - \mathbf{R}_j|} + f(\mathbf{r}_i - \mathbf{R}_j). \tag{12}$$

The obvious form of the functions $f(\mathbf{r}_i - \mathbf{R}_j)$ depends on the chosen local model pseudopotential. We consider that the surface potential $V(\mathbf{r})$ is the function of the electron coordinate in the direction normal to the dividing surface:

$$V(\mathbf{r}) = V(z).$$

Then, in the second-quantization representation based on the wave function formalism, we have

$$\Psi_{\mathbf{p},\alpha}(\mathbf{r}) = \frac{1}{\sqrt{S}}e^{i\mathbf{p}\mathbf{r}_{||}}\varphi_\alpha(z), \quad \mathbf{r} = (\mathbf{r}_{||}, z),$$

where $\varphi_\alpha(z)$ and ε_α denote eigenfunctions and eigenvalues of the Schrödinger equation

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

By performing the Fourier transformation of the electron density, we present Hamiltonian (10) as

$$H=\sum_{\mathbf{p},\alpha}E_\alpha(\mathbf{p})a^\dagger_\alpha(\mathbf{p})a_\alpha(\mathbf{p})+$$

$$+\frac{1}{2SL}\sum_{\mathbf{q}}{}'\sum_k\nu_k(\mathbf{q})\rho_k(\mathbf{q})\rho_{-k}(-\mathbf{q})-$$

$$-\frac{\mathcal{Z}N_{\text{ion}}}{SL}\sum_{\mathbf{q}}{}'\sum_k\nu_k(\mathbf{q})\mathrm{S}_k(\mathbf{q})\rho_k(\mathbf{q})+$$

$$+\frac{eN_{\text{ion}}}{SL}\sum_{\mathbf{q},k}\mathrm{S}_k(\mathbf{q})f_k(\mathbf{q})\rho_k(\mathbf{q})-\frac{N}{2S}\sum_{\mathbf{q}}{}'\nu(\mathbf{q}|0)+$$

$$+\frac{1}{2}\sum_{i\neq j=1}^{N_{\text{ion}}}\frac{1}{S}\sum_{\mathbf{q}}{}'\mathcal{Z}^2\nu(\mathbf{q}|Z_i-Z_j)\mathrm{e}^{\mathrm{i}\mathbf{q}(\mathbf{R}_{||i}-\mathbf{R}_{||j})},\qquad(13)$$

where the prime near the sum means, due to the electroneutrality condition (2), the absence of terms with $\mathbf{q}=0$, $\nu_k(\mathbf{q})=4\pi e^2/(q^2+k^2)$ and $f_k(\mathbf{q})$ are the three-dimensional Fourier transforms of the Coulomb potential and a local term of the pseudopotential (12):

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

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

$\mathbf{R}_{||j}=(X_j,Y_j),\mathbf{R}_{||j}=(X_j,Y_j);$

$\nu(\mathbf{q}|z)=2\pi e^2\mathrm{e}^{-q|z|}/q$ denote the two-dimensional Fourier transform of the Coulomb potential:

$$\frac{e^2}{r}=\frac{1}{S}\sum_{\mathbf{q}}\nu(\mathbf{q}|z)\mathrm{e}^{-\mathbf{q}\mathbf{r}_{||}},$$

$E_\alpha(\mathbf{p})=\dfrac{\hbar^2p^2}{2m}+\varepsilon_\alpha$ is the electron energy in a state $(\mathbf{p},\alpha)$,

$$\mathrm{S}_k(\mathbf{q})=\frac{1}{N_{\text{ion}}}\sum_{j=1}^{N_{\text{ion}}}\mathrm{e}^{-\mathrm{i}\mathbf{q}\mathbf{R}_{||j}-\mathrm{i}kZ_j}\qquad(14)$$

is the structure factor of the ion subsystem, and the Fourier transform of the electron density looks as

$$\rho_k(\mathbf{q})=\sum_{\mathbf{p},\alpha_1,\alpha_2}\langle\alpha_1|\mathrm{e}^{\mathrm{i}kz}|\alpha_2\rangle a^\dagger_{\alpha_1}(\mathbf{p})a_{\alpha_2}(\mathbf{p}-\mathbf{q}),\qquad(15)$$

where

$$\langle\alpha_1|\ldots|\alpha_2\rangle=\int\mathrm{d}z\,\varphi^*_{\alpha_1}(z)\ldots\varphi_{\alpha_2}(z).$$

In the calculation of thermodynamical potential for a spatially inhomogeneous electron gas in the generalized "jellium model (13), we present the great partition function as

$$\Xi=\mathrm{Sp}\,\mathrm{e}^{-\beta(H-\mu N)},\qquad(16)$$

where μ denotes the chemical potential of the electron subsystem. Considering (13), we obtain

$$\Xi=C\mathrm{e}^{-\beta H_{\text{ii}}}\mathrm{Sp}\,\mathrm{e}^{-\beta H_0'-\beta H_{\text{ee}}-\beta H_{\text{ei}}},\qquad(17)$$

where

$$C=\exp\left(\beta\frac{N}{2S}\sum_{\mathbf{q}}{}'\nu(\mathbf{q}|0)\right),$$

$$H_{\text{ii}}=\frac{1}{2}\sum_{i\neq j=1}^{N_{\text{ion}}}\frac{1}{S}\sum_{\mathbf{q}}{}'\mathcal{Z}^2\nu(\mathbf{q}|Z_i-Z_j)\mathrm{e}^{\mathrm{i}\mathbf{q}(\mathbf{R}_{||i}-\mathbf{R}_{||j})}$$

is the Hamiltonian of the ion-ion interaction,

$$H_0'=\sum_{\mathbf{p},\alpha}\left(E_\alpha(\mathbf{p})-\mu\right)a^\dagger_\alpha(\mathbf{p})a_\alpha(\mathbf{p})$$

is the kinetic part of the Hamiltonian of electrons;

$$H_{\text{ee}}=\frac{1}{2SL}\sum_{\mathbf{q}}{}'\sum_k\nu_k(\mathbf{q})\rho_k(\mathbf{q})\rho_{-k}(-\mathbf{q})$$

denotes the Hamiltonian of interaction between electrons in the representation of collective variables;

$$H_{\text{ei}}=-\frac{\mathcal{Z}N_{\text{ion}}}{SL}\sum_{\mathbf{q}}{}'\sum_k\nu_k(\mathbf{q})\mathrm{S}_k(\mathbf{q})\rho_k(\mathbf{q})+$$

$$+\frac{eN_{\rm ion}}{SL}\sum_{\mathbf{q},k}\mathrm{S}_k(\mathbf{q})f_k(\mathbf{q})\rho_k(\mathbf{q}) \tag{18}$$

is the Hamiltonian of the ion-electron interaction in the representation of collective variables with modulation of the ion-electron interaction by the local pseudopotential (12).

Then using the interaction representation, the great partition function can be written as

$$\Xi = C\mathrm{e}^{-\beta H_{\rm ii}}\Xi_0\langle \mathrm{T}S(\beta)\rangle_0, \tag{19}$$

where

$$\Xi_0 = \mathrm{Sp}\,\mathrm{e}^{-\beta H_0'} \tag{20}$$

denotes the partition function of the non-interacting semibounded "jellium", $\langle\dots\rangle_0 = \frac{1}{\Xi_0}\mathrm{Sp}\,(\mathrm{e}^{-\beta H_0'}\dots)$.

$$S(\beta) = S_1(\beta)S_2(\beta),$$

$$S_1(\beta) = \exp\Bigg[-\frac{1}{2SL}\int\limits_0^\beta \mathrm{d}\beta'\times$$

$$\times\sum_{\mathbf{q}}{}'\sum_{k}\nu_k(\mathbf{q})\rho_k(\mathbf{q}|\beta')\rho_{-k}(-\mathbf{q}|\beta')\Bigg] \tag{21}$$

is the contribution from the interaction between electrons;

$$S_2(\beta) = \exp\Bigg[\frac{\mathcal{Z}N_{\rm ion}}{SL}\int\limits_0^\beta \mathrm{d}\beta'\sum_{\mathbf{q}}{}'\sum_{k}\nu_k(\mathbf{q})\mathrm{S}_k(\mathbf{q})\rho_k(\mathbf{q}|\beta')-$$

$$-\frac{eN_{\rm ion}}{SL}\int\limits_0^\beta \mathrm{d}\beta'\sum_{\mathbf{q},k}\mathrm{S}_k(\mathbf{q})f_k(\mathbf{q})\rho_k(\mathbf{q}|\beta')\Bigg] \tag{22}$$

is the ion-electron contribution, where

$$\rho_k(\mathbf{q}|\beta') = \mathrm{e}^{\beta' H_0'}\rho_k(\mathbf{q})\mathrm{e}^{-\beta' H_0'}.$$

Taking $w_k(\mathbf{q}) = -\mathcal{Z}\nu_k(\mathbf{q}) + ef_k(\mathbf{q})$, for $S_2(\beta)$, we obtain

$$S_2(\beta) = \exp\left[-\frac{N_{\rm ion}}{SL}\int\limits_0^\beta \mathrm{d}\beta'\sum_{\mathbf{q},k}w_k(\mathbf{q})\mathrm{S}_k(\mathbf{q})\rho_k(\mathbf{q}|\beta')\right]. \tag{23}$$

By selecting the Hamiltonian of the interacting semibounded "jellium" from (19), its characteristics being considered in [41, 42], the great partition function (19) can be presented via averages of the selected Hamiltonian as

$$\Xi = C\mathrm{e}^{-\beta H_{\rm ii}}\Xi_{\rm jell}\langle S_2(\beta)\rangle_{\rm jell}, \tag{24}$$

where

$$\Xi_{\rm jell} = \mathrm{Sp}\,\left(\mathrm{e}^{-\beta H_0'}\mathrm{T}S_1(\beta)\right)$$

means the partition function of the "jellium",

$$\langle\dots\rangle_{\rm jell} = \frac{1}{\Xi_{\rm jell}}\mathrm{Sp}\,\left(\mathrm{e}^{-\beta H_0'}\mathrm{T}S_1(\beta)\dots\right). \tag{25}$$

Having passed from the temperature representation to the frequency representation, we have, according to the rule ($A=\rho$):

$$A_k(\mathbf{q}|\nu) = \frac{1}{\beta}\int\limits_0^\beta \mathrm{d}\beta'\mathrm{e}^{\mathrm{i}\nu\beta'}A_k(\mathbf{q}|\beta'),$$

$$A_k(\mathbf{q}|\beta') = \sum_\nu \mathrm{e}^{-\mathrm{i}\nu\beta'}A_k(\mathbf{q}|\nu),$$

where ν denotes the Bose frequency. For $\langle S_2(\beta)\rangle_{\rm jell}$, one can obtain

$$\langle S_2(\beta)\rangle_{\rm jell} = \exp\Bigg[\sum_{n=1}^{\infty}\left(\frac{\beta N_{\rm ion}}{SL}\right)^n\frac{\mathrm{i}^n}{n!}\times$$

$$\times\sum_{\mathbf{q}_1,\dots,\mathbf{q}_n}\sum_{k_1,\dots,k_n}\mathrm{S}_{k_1}(\mathbf{q}_1)w_{k_1}(\mathbf{q}_1)\dots\mathrm{S}_{k_n}(\mathbf{q}_n)w_{k_n}(\mathbf{q}_n)\times$$

$$\times\overline{\mathfrak{M}}_{k_1,\dots,k_n}(\mathbf{q}_1,\dots,\mathbf{q}_n)\Bigg], \tag{26}$$

where

$$\overline{\mathfrak{M}}_{k_1,\dots,k_n}(\mathbf{q}_1,\dots,\mathbf{q}_n) = \mathrm{i}^n\langle\rho_{k_1}(\mathbf{q}_1|0)\dots\rho_{k_n}(\mathbf{q}_n|0)\rangle_{{\rm jell},c}.$$

The irreducible averages are calculated by using the nonequilibrium statistical operator of the "jellium" model as a reference frame [40]. Analogously to [42], the s-particle distribution function of electrons can be presented in the form

$$F_s(\mathbf{r}_1,\dots,\mathbf{r}_n) = F_s(\mathbf{r}_1,\dots,\mathbf{r}_n)^{\rm jell}\exp\Bigg[\sum_{n\geqslant 1}\frac{i^n}{n!}\left(\frac{\beta N_i}{SL}\right)^n\times$$

$$\times \sum_{\mathbf{q}_1,\dots,\mathbf{q}_n}{}' \sum_{k_1,\dots,k_n} w_{k_1}(\mathbf{q}_1) S_{k_1}(\mathbf{q}_1) w_{k_n}(\mathbf{q}_n) S_{k_n}(\mathbf{q}_n) \times$$

$$\times \dots \Delta \mathfrak{M}^{(s)}_{-k_1,\dots,-k_n}(-\mathbf{q}_1,\dots,-\mathbf{q}_n)\Big], \tag{27}$$

where

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

$$-\mathfrak{M}_{k_1,\dots,k_n}(\mathbf{q}_1,\dots,\mathbf{q}_n), \tag{28}$$

the calculation of this type of averages is given in [41, 42, 46].

Thus, using the "jellium" model as a reference frame, we obtain a factorized representation (27) of the partition function and the distribution function of electrons. One of the multipliers corresponds to the "jellium" model and another one considers the discreteness of the ion subsystem.

3. Generalized Equation of Electron Diffusion of an Inhomogeneous Electron Gas of a Metal Surface

For the description of electron diffusion processes in the presented model, a mean value of the electron density operator related to the corresponding inhomogeneous electrical field can be chosen as the main parameter of the reduced description

$$\nabla \cdot \mathbf{E}(\mathbf{r};t) = e\langle \varrho(\mathbf{r})\rangle^t, \tag{29}$$

where $\langle(...)\rangle^t = \mathrm{Sp}\,(...)\rho(t)$, $\rho(t)$ denotes the nonequilibrium statistical operator of the generalized "jellium" model obeying the Liouville equation with Hamiltonian (13). Taking the chosen geometry of the model into account, a value of $\langle \varrho(\mathbf{r})\rangle^t$ corresponds to the mixed Fourier transform $\langle \rho_k(\mathbf{q})\rangle^t$. To found $\rho(t)$, the method of nonequilibrium statistical operator by Zubarev [47, 48] is applied to a solution of the Liouville equation with regard for the projection technique. In this approach, the solution of the equation can be presented in the general form as

$$\rho(t) = \rho_q(t) + \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} T_q(t,t') \times$$

$$\times (1 - \mathcal{P}_q(t')) iL_N \rho_q(t') \mathrm{d}t', \tag{30}$$

where

$$T_q(t,t') = \exp\left\{ -\int\limits_{t'}^{t} (1 - \mathcal{P}_q(t'')) iL_N \mathrm{d}t'' \right\} \tag{31}$$

is the generalized evolution operator within the projection technique. The quantity $\mathcal{P}_q(t)$ stands for the Kawasaki–Gunton projection operator which acts on statistical operators according to

$$\mathcal{P}_q(t)\rho' \;=\; \rho_q(t)\,\mathrm{Sp}\,(\rho') + \sum_n \Bigg(\mathrm{Sp}\,(\rho'\hat{P}_n) -$$

$$-\mathrm{Sp}\,(\rho')\langle \hat{P}_n\rangle^t \Bigg) \frac{\delta \rho_q(t)}{\delta \langle \hat{P}_n\rangle^t}, \tag{32}$$

and has the following properties:

$$\mathcal{P}_q(t)\rho(t') = \rho_q(t), \quad \mathcal{P}_q(t)\rho_q(t') = \rho_q(t),$$

$$\mathcal{P}_q(t)\mathcal{P}_q(t') = \mathcal{P}_q(t), \quad \mathcal{P}_q(t)\frac{\partial \rho(t)}{\partial t} = \frac{\partial \rho_q(t)}{\partial t}.$$

To found the proper form of the nonequilibrium statistical operator $\rho(t)$ of the inhomogeneous electron gas, we need to set the auxiliary statistical operator $\rho_q(t)$ which is determined by the Gibbs method with a fixed parameter of the reduced description $\langle \rho_k(\mathbf{q})\rangle^t$ and obeys the normalization condition $\mathrm{Sp}\,\rho_q(t) = 1$. In the case under consideration, the auxiliary statistical operator has the following form:

$$\rho_q(t) = \exp(-\Phi(t) - \beta(H - \frac{1}{SL}\sum_k \sum_{\mathbf{q}} \tilde{\mu}_k(\mathbf{q};t)\rho_k(\mathbf{q}))). \tag{33}$$

Here, $\Phi(t) = \ln Z(t)$ is the Massieu–Planck functional, and $Z(t)$ denotes the partition function of the quasiequilibrium statistical operator:

$$Z(t) = \mathrm{Sp}\,\exp\left(-\beta \left(H - \frac{1}{SL}\sum_k \sum_{\mathbf{q}} \tilde{\mu}_k(\mathbf{q};t)\rho_k(\mathbf{q}) \right) \right), \tag{34}$$

$\tilde{\mu}_k(\mathbf{q};t) = \mu_k(\mathbf{q};t) + e\varphi_k(\mathbf{q};t)$ stands for the Fourier transform of the electrochemical potential of electrons, $\mu_k(\mathbf{q};t)$ stands for the Fourier transform of the chemical potential of electrons, and $\varphi_k(\mathbf{q};t)$ denotes the Fourier transform of a local electric potential. The quantity $\tilde{\mu}_k(\mathbf{q};t)$ can be found from the self-consistency condition

$$\langle\rho_k(\mathbf{q})\rangle^t = \langle\rho_k(\mathbf{q})\rangle^t_q, \tag{35}$$

and the thermodynamical relations

$$\frac{\delta S(t)}{\delta\langle\rho_k(\mathbf{q})\rangle^t} = -\mu_k(\mathbf{q};t), \tag{36}$$

$$\frac{\delta S(t)}{\delta\langle e\rho_k(\mathbf{q})\rangle^t} = -\varphi_k(\mathbf{q};t), \tag{37}$$

where $S(t)$ is the nonequilibrium entropy determined according the Gibbs' hypothesis as

$$S(t) = -\mathrm{Sp}\,(\ln\rho_q(t))\rho_q(t) = \Phi(t) + \beta\Bigg(\langle H\rangle^t -$$

$$-\sum_k\sum_{\mathbf{q}}\tilde{\mu}_k(\mathbf{q};t)\langle\rho_k(\mathbf{q})\rangle^t\Bigg) =$$

$$= \ln Z(t) + \beta(\langle H\rangle^t - \sum_k\sum_{\mathbf{q}}\mu_k(\mathbf{q};t)\langle\rho_k(\mathbf{q})\rangle^t -$$

$$-\sum_k\sum_{\mathbf{q}}\varphi_k(\mathbf{q};t)\langle e\rho_k(\mathbf{q})\rangle^t), \tag{38}$$

and $\langle e\rho_k(\mathbf{q})\rangle^t = e\langle\rho_k(\mathbf{q})\rangle^t$ denotes the mean electron charge density. According to the structure of the nonequilibrium entropy, the transport processes in the system in the accepted model are predetermined by gradients of the local values of the chemical and electrical potentials. According to the structure of the quasiequilibrium statistical operator, the Kawasaki–Ganton projection operator has the structure

$$P_q(t)\rho' = (\rho_q(t) - \sum_k\sum_{\mathbf{q}}\frac{\delta\rho_q(t)}{\delta\langle\rho_k(\mathbf{q})\rangle^t}\langle\rho_k(\mathbf{q})\rangle^t\mathrm{Sp}\,(\rho'))+$$

$$+\sum_k\sum_{\mathbf{q}}\frac{\delta\rho_q(t)}{\delta\langle\rho_k(\mathbf{q})\rangle^t}\mathrm{Sp}\,(\rho_k(\mathbf{q})\rho').$$

This structure will be manifested also in the action of the operators

$$(1-\mathcal{P}_q(t))iL_N\rho_q(t') = \sum_k\sum_{\mathbf{q}}\int\limits_0^1 \mathrm{d}\tau\times$$

$$\times(\rho_q)^\tau(t')\mathcal{P}(t')iL_N\rho_k(\mathbf{q})\beta\tilde{\mu}_k(\mathbf{q};t')\rho_q(t')^{1-\tau} =$$

$$=\sum_k\sum_{\mathbf{q}}\int\limits_0^1\mathrm{d}\tau(\rho_q)^\tau(t')\mathcal{P}(t')iL_N\rho_k(\mathbf{q})\rho_q(t')^{1-\tau}\frac{\delta S(t')}{\delta\langle\rho_k(\mathbf{q})\rangle^{t'}},$$

where $\mathcal{P}(t)$ is a Mori-like projection operator which acts on the operators of dynamical quantities and can be written down as

$$\mathcal{P}(t')\hat{A} = \langle\hat{A}\rangle^t_q + \sum_k\sum_{\mathbf{q}}\frac{\delta\langle\hat{A}\rangle^t_q}{\delta\langle\rho_k(\mathbf{q})\rangle^{t'}}(\rho_k(\mathbf{q}) - \langle\rho_k(\mathbf{q})\rangle^{t'}).$$

As seen from its structure, it depends on a form of the quasiequilibrium statistical operator which includes the quasiequilibrium partition function $Z(t)$. By using the quasiequilibrium statistical operator $\rho(t)$ for the parameter of the reduced description $\langle\rho_k(\mathbf{q})\rangle^t$ with regard for the relation

$$\frac{\partial}{\partial t}\langle\rho_k(\mathbf{q})\rangle^t = \langle iL\rho_k(\mathbf{q})\rangle^t_q + \langle(1-P(t))iL\rho_k(\mathbf{q})\rangle^t,$$

we obtain the generalized quantum equation of electron diffusion

$$\frac{\partial}{\partial t}\langle\rho_k(\mathbf{q})\rangle^t = -\sum_{k'}\int\limits_{-\infty}^t e^{\varepsilon(t'-t)}kq^2D(k\mathbf{q};k',-\mathbf{q};t,t')k'\times$$

$$\times\beta(\mu_{k'}(-\mathbf{q};t') + e\varphi_{k'}(-\mathbf{q};t'))\mathrm{d}t', \tag{39}$$

where

$$kq^2D(k\mathbf{q};k',-\mathbf{q};t,t')k' = \mathrm{Sp}\Bigg\{(1-\mathcal{P}(t))iL\rho_k(\mathbf{q})\times$$

$$\times T_q(t,t')\int\limits_0^1\mathrm{d}\tau\rho_q^\tau(t')(1-\mathcal{P}(t'))iL\rho_{k'}(-\mathbf{q})\rho_q^{1-\tau}(t')\Bigg\}; \tag{40}$$

and $D(k\mathbf{q};k',-\mathbf{q};t,t')$ stands for the generalized coefficient of electron diffusion. For its calculation, we need to calculate the quasiequilibrium partition function (34) of distribution (33).

4. Calculation of Quasiequilibrium Partition Function for the Inhomogeneous Electron Gas within the Generalized "Jellium" Model

For the calculation of the quasiequilibrium partition function (34), we use the functional integration method developed for spatially inhomogeneous electron systems in [41, 42]. Specifying the contribution of the collective variables in Hamiltonian (13), $Z(t)$ can be presented in the particular case as a local potential:

$$Z(t)=\mathrm{Sp}\left\{\exp\biggl(-\beta\biggl(H_0-\frac{1}{2S}\sum_{\mathbf{q}}{}'\nu(\mathbf{q}|0)+\right.$$

$$+\frac{1}{2SL}\sum_{k,\mathbf{q}}\nu_k(\mathbf{q})\rho_k(\mathbf{q})\rho_{-k}(-\mathbf{q})+$$

$$\left.+\frac{1}{2SL}\sum_{k,\mathbf{q}}B(\mathbf{q},k;t)\rho_{-k}(-\mathbf{q})\biggr)\biggr)\right\}, \tag{41}$$

where $B(\mathbf{q},k;t)=N_{ion}S_k(\mathbf{q})\omega_k(\mathbf{q})-\bar{\mu}_k(\mathbf{q};t)$. Then, to calculate $Z(t)$, we specify the frame corresponding to the "jellium" model:

$$Z(t)=\exp\left\{\beta\frac{N}{2S}\sum_{\mathbf{q}}{}'\nu(\mathbf{q}|0)\right\}Z_{\mathrm{jell}}\Delta Z(t), \tag{42}$$

where

$$Z_{\mathrm{jell}}=\mathrm{Sp}\left\{\exp(-\beta H_{\mathrm{jell}})\right\} \tag{43}$$

is the partition function of the "jellium" model of inhomogeneous electron gas corresponding to the equilibrium state calculated in [41, 42].

$$\Delta Z(t)=\frac{1}{Z_{\mathrm{jell}}}\mathrm{Sp}\ \left\{\exp(-\beta H_{\mathrm{jell}})S(\beta;t)\right\}=\langle S(\beta;t)\rangle_{\mathrm{jell}}, \tag{44}$$

$$S(\beta;t)=T\exp\left[-\int\limits_0^\beta \mathrm{d}\beta'\frac{1}{SL}\sum_{k,\mathbf{q}}B(\mathbf{q},k;t)\rho_{-k}(-\mathbf{q};\beta')\right], \tag{45}$$

$$\rho_k(\mathbf{q};\beta')=e^{\beta' H_{\mathrm{jell}}}\rho_k(\mathbf{q})e^{-\beta' H_{\mathrm{jell}}}. \tag{46}$$

For the calculation of $\Delta Z(t)$, we use the cumulant representation

$$\Delta Z(t)=\exp\biggl[\sum_{n=1}\frac{i^n}{n!}\left(\frac{\beta}{SL}\right)^n\sum_{\mathbf{q}_1\cdots\mathbf{q}_n}\sum_{k_1\ldots.k_n}B(\mathbf{q}_1,k_1;t)\times$$

$$\times\ldots B(\mathbf{q}_n,k_n;t)M_{-k_1\ldots-k_n}(-\mathbf{q}_1\ldots.-\mathbf{q}_n)\biggr], \tag{47}$$

where

$$M_{k_1\ldots.k_n}(\mathbf{q}_1\ldots.\mathbf{q}_n)=i^n\langle T\rho_{k_1}(\mathbf{q}_1|0),\ldots.\rho_{k_n}(\mathbf{q}_n|0)\rangle^c_{\mathrm{jell}} \tag{48}$$

denotes the cumulant irreducible averages of fluctuations of the electron density calculated by using the equilibrium statistical operator of the "jellium" model. In particular, the second cumulant has the following structure:

$$M_{k_1,k_2}(\mathbf{q}_1,\mathbf{q}_2)=\langle\rho_{k_1}(\mathbf{q}_1)\rho_{k_2}(\mathbf{q}_2)\rangle_{\mathrm{jell}}-$$

$$-\langle\rho_{k_1}(\mathbf{q}_1)\rangle_{\mathrm{jell}}\langle\rho_{k_2}(\mathbf{q}_2)\rangle_{\mathrm{jell}}. \tag{49}$$

It is related to the static structure factor $S(k_1,\mathbf{q}_1;k_2,\mathbf{q}_2)=\langle\rho_{k_1}(\mathbf{q}_1)\rho_{k_2}(\mathbf{q}_2)\rangle_{\mathrm{jell}}$ of the inhomogeneous electron gas of the metal surface.

In the Gauss' approximation, $\Delta Z(t)$ has the form

$$\Delta Z^{\mathrm{G}}(t)=\exp\biggl[-\frac{1}{2}\left(\frac{\beta}{SL}\right)^2\sum_{\mathbf{q}_1\mathbf{q}_2}\sum_{k_1k_2}B(\mathbf{q}_1,k_1;t)\times$$

$$\times B(\mathbf{q}_2,k_2;t)M_{-k_1,-k_2}(-\mathbf{q}_1,-\mathbf{q}_2)\biggr], \tag{50}$$

and it is expressed via the second cumulant of the "jellium" model of inhomogeneous electron gas [41, 42]. According to the definition of the s-particle distribution function of electrons [41, 42], we get the quasiequilibrium s-particle distribution functions of electrons, whose structures are similar (27):

$$F_s(\mathbf{r}_1,\ldots,\mathbf{r}_n;t)=F_s(\mathbf{r}_1,\ldots,\mathbf{r}_n)^{\mathrm{jell}}\times$$

$$\times\exp\biggl[\sum_{n\geqslant 1}\frac{i^n}{n!}\left(\frac{\beta N_i}{SL}\right)^n\sum_{\mathbf{q}_1,\ldots,\mathbf{q}_n}{}'\sum_{k_1,\ldots,k_n}B(\mathbf{q}_1,k_1;t)\times$$

$$\times\ldots B(\mathbf{q}_n,k_n;t)\Delta\mathfrak{M}^{(s)}_{-k_1,\ldots,-k_n}(-\mathbf{q}_1,\ldots,-\mathbf{q}_n)\biggr], \tag{51}$$

where $\Delta\mathfrak{M}^{(s)}_{-k_1,\dots,-k_n}(-\mathbf{q}_1,\dots,-\mathbf{q}_n)$ coincides with (28). Equations (51) give the relation of the distribution functions to the electrochemical potential $\bar{\mu}_k(\mathbf{q};t)$. From this point of view, we obtain the self-consistent system of the coupled generalized equation of electron diffusion (39), the Maxwell equation (29), and Eq. (51). This enables, in particular, to set the inverse problem of calculation of the diffusion coefficients by using the relation of the unary quasiequilibrium distribution function (with regard for the self-consistency condition (35)) to a nonequilibrium electrochemical potential with corresponding relation (29). It is important that the relation of the quasiequilibrium distribution functions of electrons to the electrochemical potential in (51) is expressed via the corresponding cumulant averages of the “jellium” model. Thus, for the corresponding approximation of the quasiequilibrium distribution functions (51) related to the approximation of the quasiequilibrium partition function in the generalized “jellium” model [41, 42], by calculating the cumulant averages (49) and by performing the corresponding approximate calculation of the generalized diffusion coefficient (40), we obtain the self-consistent system of equations (39), (29), (51). The obtained system enables us to make calculation of a nonequilibrium profile of the electron density and a nonequilibrium value of the electrical field. This self-consistent system of equations generalizes the time-dependent density functional theory [6–10] with the corresponding approximations in finding the Kohn–Sham Hamiltonian in the TDDFT formulation. Indeed, the Kohn–Sham Hamiltonian in the TDDFT formulation has the form

$$\hat{H}_{\mathrm{KS}}(t) = \hat{H}^{\mathrm{DFT}}_{\mathrm{KS}} + \int \mathrm{d}\mathbf{r} v_1(\mathbf{r};t) +$$

$$+ v_{H,1}(\mathbf{r};t) + v_{xc,1}(\mathbf{r};t)]\hat{\rho}(\mathbf{r}), \qquad (52)$$

where $\hat{H}^{\mathrm{DFT}}_{\mathrm{KS}}$ denotes the Kohn–Sham Hamiltonian in the DFT formulation, $v_1(\mathbf{r};t)$ is the periodic potential related to the “density-density” function of a response $v_1(\mathbf{r};t)$:

$$\rho_1(\mathbf{r};\omega) = \int \mathrm{d}\mathbf{r}' \chi(\mathbf{r},\mathbf{r}';\omega) v_1(\mathbf{r}';\omega),$$

$$\rho(\mathbf{r};t) = \rho_{\mathrm{DFT}}(\mathbf{r}) + \rho_1(\mathbf{r};\omega)e^{-i\omega t} + \text{c.c.},$$

$$\rho(\mathbf{r};t) = \langle \rho(\mathbf{r};t)\rangle^t,$$

$$v_{\mathrm{H},1}(\mathbf{r};t) = e^2 \int \mathrm{d}\mathbf{r}' \frac{\rho(\mathbf{r}';t)}{|\mathbf{r}-\mathbf{r}'|}$$

is the Hartree potential, $\rho_{\mathrm{DFT}}(\mathbf{r})$ denotes a mean spatially inhomogeneous value of electron density in DFT,

$$v_{xc,1}(\mathbf{r};t) = v_{xc,\mathrm{DFT}}(\mathbf{r}) +$$

$$+ \int_{-\infty}^{t} \mathrm{d}t' \int \mathrm{d}\mathbf{r}' f_{xc}(\mathbf{r},\mathbf{r}';t-t')\rho_1(\mathbf{r}';t) \qquad (53)$$

is a time-dependent exchange-correlation potential related to the kernel of exchange-correlation dissipative processes:

$$f_{xc}(\mathbf{r},\mathbf{r}';t-t') = \frac{\delta v_{xc,1}[\rho](\mathbf{r};t)}{\delta\rho(\mathbf{r}';t')}|_{\rho_{\mathrm{DFT}}(\mathbf{r})},$$

where $v_{xc,\mathrm{DFT}}(\mathbf{r})$ denotes an exchange-correlation potential in DFT.

In a linear approximation for the generalized equation of electron diffusion, according to the deviation of the nonequilibrium electrochemical potential from its equilibrium value $\delta\tilde{\mu}_k(\mathbf{q};t) = \tilde{\mu}_k(\mathbf{q};t) - \tilde{\mu}_k(\mathbf{q})$, one can obtain, in the closed form,

$$\frac{\partial}{\partial t}\delta\langle\rho_k(\mathbf{q})\rangle^t = -\sum_{k'} \int_{-\infty}^{t} e^{\varepsilon(t'-t)} k q^2 \times$$

$$\times \tilde{D}(k\mathbf{q};k',-\mathbf{q};t,t')k'\delta\langle\rho_{k'}(\mathbf{q})\rangle^{t'}\mathrm{d}t', \qquad (54)$$

where $\delta\langle\rho_k(\mathbf{q})\rangle^t = \langle\rho_k(\mathbf{q})\rangle^t - \langle\rho_k(\mathbf{q})\rangle_0$, and $\langle\rho_k(\mathbf{q})\rangle_0$ means the spatially inhomogeneous value of electron density calculated by using the nonequilibrium statistical operator of the generalized “jellium” model and can be found in (27). In this case, $\delta\langle\rho_k(\mathbf{q})\rangle^t$ is related to $\delta\tilde{\mu}_k(\mathbf{q};t) = \tilde{\mu}_k(\mathbf{q};t) - \tilde{\mu}_k(\mathbf{q})$ by the expression

$$\delta\langle\rho_k(\mathbf{q})\rangle^t = -\sum_{k'} \chi(k,\mathbf{q},k',-\mathbf{q})\delta\tilde{\mu}_{k'}(\mathbf{q};t) \qquad (55)$$

which follows from the self-consistency condition (35) $\tilde{\mu}_k(\mathbf{q}) = \mu_k(\mathbf{q}) + e\varphi_k(\mathbf{q})$, where $\mu_k(\mathbf{q})$ and $\varphi_k(\mathbf{q})$ are the local equilibrium values of the electrochemical potential and the average scalar potential of the inhomogeneous electron gas,

$$\chi(k,\mathbf{q},k',-\mathbf{q}) = \langle\rho_k(\mathbf{q}) \int_0^1 \rho_0^{\xi}\rho_{k'}(-\mathbf{q})\rho_0^{-\xi}\rangle_0 \mathrm{d}\xi \qquad (56)$$

denotes the Kubo "density-density" correlation function,

$$kq^2\tilde{D}(k\mathbf{q};k',-\mathbf{q};t,t')k'=\sum_{k''}\mathrm{Sp}\,\{(1-\mathcal{P}_0)iL\rho_k(\mathbf{q})\times$$

$$\times T_0(t,t')\int\limits_0^1 \mathrm{d}\tau\rho_0^{\tau}(1-\mathcal{P}_0)iL\rho_{k''}(-\mathbf{q})\rho_0^{1-\tau}\}\times$$

$$\times\chi^{-1}(k'',\mathbf{q},k',-\mathbf{q})$$

is the renormalized spatially inhomogeneous diffusion coefficient, $\mathcal{P}_0$ stands for a Mori-like projection operator constructed on $\rho_k(\mathbf{q})$, and $T_0(t,t')$ denotes a time evolution operator with the corresponding Mori-like operator. Based on Eq. (54) and using the well-known method described in [49], one can obtain the equation for the time correlation function "density-density":

$$\Phi_{\rho\rho}(k,\mathbf{q},k',-\mathbf{q};t)=\langle\rho_k(\mathbf{q};t)\rho_{k'}(-\mathbf{q})\rangle_0, \qquad (57)$$

$$\frac{\partial}{\partial t}\Phi_{\rho\rho}(k,\mathbf{q},k',-\mathbf{q};t)=-\sum_{k''}\int\limits_{-\infty}^{t}e^{\varepsilon(t'-t)}kq^2\times$$

$$\times\tilde{D}(k\mathbf{q};k'',-\mathbf{q};t,t')k''\Phi_{\rho\rho}(k'',\mathbf{q},k',-\mathbf{q};t')\mathrm{d}t'. \qquad (58)$$

By separating the terms $\varphi_{1,k}(\mathbf{q})$, $\varphi_{1,k}(\mathbf{q};t)$, the Hartree terms $\varphi_{\mathrm{H},k}(\mathbf{q})$ and $\varphi_{\mathrm{H},k}(\mathbf{q};t)$, and the exchange-correlation terms $\varphi_{xc,k}(\mathbf{q})$ and $\varphi_{xc,k}(\mathbf{q};t)$, according to Eqs. (54), (55) and (52), (53) in the frequency representation in the Fourier transforms $\varphi_k(\mathbf{q})$ and $\varphi_k(\mathbf{q};t)$ of the corresponding scalar potentials ($v(\mathbf{r})$ (DFT) and $v(\mathbf{r};t)$ (TDDFT), one can establish the connection of the generalized diffusion coefficient with the kernel of exchange-correlation dissipative processes. Indeed, Eq. (53) can be represented as

$$\delta v_{xc,1}(\mathbf{r};t)=\int\limits_{-\infty}^{t}\mathrm{d}t'\int\mathrm{d}\mathbf{r}'f_{xc}(\mathbf{r},\mathbf{r}';t-t')\delta\rho_1(\mathbf{r}';t), \quad (59)$$

where $\delta v_{xc,1}(\mathbf{r};t)=v_{xc,1}(\mathbf{r};t)-v_{xc,DFT}(\mathbf{r})$ ч $\delta\rho_1(\mathbf{r}';t)=\rho_1(\mathbf{r}';t)-\rho_{DFT}(\mathbf{r})$. Then, by applying the time Fourier transformation to Eqs. (59) and (54) and the $(k,\mathbf{q})$ Fourier transformation to (59),

$$\delta v_{xc,k}(\mathbf{q};\omega)=\sum_{k'}f_{xc}(k,k'\mathbf{q},\omega)\delta\rho_{k'}(\mathbf{q};\omega), \qquad (60)$$

$$i\omega\delta\rho_k(\mathbf{q};\omega)=-\sum_{k'}kq^2\tilde{D}(k\mathbf{q};k',-\mathbf{q};\omega)k'\delta\rho_{k'}(\mathbf{q};\omega), \qquad (61)$$

we obtain the relation of $\delta v_{xc,k}(\mathbf{q};\omega)$ and $f_{xc}(k,k'\mathbf{q},\omega)$ to the generalized diffusion coefficient $\tilde{D}(k\mathbf{q};k',-\mathbf{q};\omega)$.

5. Conclusions

Thus, we have presented the statistical theory of the processes of electron diffusion for the electron subsystem on the basis of the generalized "jellium" model that considers the discreteness of the ion subsystem of a semibounded metal. In this approach, the calculation of the great partition function and the partition function of a quasiequilibrium distribution of the electron subsystem is executed by means of the functional integration method via the corresponding cumulant averages of the "jellium" model. Thus, this enables us to obtain the analytical relations for the spatially inhomogeneous equilibrium s-particle functions and their relation to the quasiequilibrium distribution functions for the electron subsystem. Moreover, using the pair-correlation approximation with $s=1$ in (51), one can obtain the relation

$$F_1(\mathbf{r}_1;t)=\rho(\mathbf{r}_1;t)=F_1(\mathbf{r}_1)^{\mathrm{jell}}\times$$

$$\times\exp[\frac{i}{1!}(\frac{\beta N_i}{SL})\sum_{\mathbf{q}_1}\sum_{k_1}B(\mathbf{q}_1,k_1;t)\Delta\mathfrak{M}^{(1)}_{-k_1}(-\mathbf{q}_1)], \quad (62)$$

between the nonequilibrium mean value of electron density of a semibounded metal and the electrochemical potential via the mean values $F_1(\mathbf{r}_1)^{\mathrm{jell}}=\rho^{\mathrm{jell}}(\mathbf{r}_1)$, $\Delta\mathfrak{M}^{(1)}_{-k_1}(-\mathbf{q}_1)$ which are calculated in [41, 42]. The electrochemical potential is related to $\rho(\mathbf{r}_1;t)$ by the generalized diffusion equation (39), which enables us to calculate the spatially inhomogeneous time-dependent diffusion coefficient of the electron subsystem. Furthermore, relations (51) enable one to calculate the binary and higher-order quasiequilibrium structure distribution functions as a function of the electrochemical potential related to $\rho(\mathbf{r}_1;t)$ by Eq. (39). Thus, we have obtained a self-consistent scheme of calculation of the time-dependent characteristics via the equilibrium structure distribution functions of a semibounded metal [41,42]. This approach enables one to describe only the electron diffusion processes caused by the gradients of the chemical potential of electrons and by the potential term of the electrical field related to the gradient of the scalar electrical potential. To describe the heat-viscosity and electromagnetic processes, we need to have a more general formulation of statistical theory based on the conservation laws of the number density of particles, momentum, and total energy.

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СТАТИСТИЧНА ТЕОРІЯ ЕЛЕКТРОДИФУЗІЙНИХ ПРОЦЕСІВ ЕЛЕКТРОННОЇ ПІДСИСТЕМИ В УЗАГАЛЬНЕНІЙ МОДЕЛІ “ЖЕЛЕ”

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Резюме

Для дослідження іонної та електронної структур напівобмеженого металу запропоновано узагальнений підхід, що враховує вплив дискретності іонної підсистеми, основою для якого є модель напівобмеженого “желе”. На основі такої моделі отримано узагальнене рівняння електродифузії для неоднорідного електронного газу та представлено розрахунок квазірівноважної статистичної суми методом функціонального інтегрування у випадку локального псевдопотенціалу електрон-іонної взаємодії поверхні металу. Отримано зв’язок квазірівноважних функцій розподілу електронів із електрохімічним потенціалом через відповідні кумулянтні середні моделі “желе”. У лінійному наближені за електрохімічним потенціалом отримано зв’язок із часозалежною теорією функціонала густини (TDDFT).