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"metal-adsorbate-gas"

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Statistical theory of diffusion - reaction processes in the system "metal-adsorbate-gas"

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Abstract. We present a statistical theory for diffusion - reaction processes of gaseous mixture in the system "metal - adsorbate - gas". The theory is based on equivalent taking into account of electron - electron, electron - atom and atom - atom interactions between adsorbed, non-adsorbed atoms and atoms of metal surface. On metal surface the bimolecular reactions of the kind $A + B \leftrightarrow AB$ are possible to occur between adsorbed atoms that is typical of catalytic processes. By means of Zubarev nonequilibrium statistical operator there is obtained the system of transport equations for the consistent description of electronic kinetic and diffusion - reaction atomic processes.

Статистична теорія дифузійно-реакційних процесів у системі "метал-адсорбат-газ"

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Анотація. Ми представляємо статистичну теорію дифузійно - реакційних процесів для газових сумішей в системі "метал - адсорбат - газ". Теорія базується на рівноправному врахуванні електрон - електронних, електрон - атомних та атом - атомних взаємодій між адсорбованими та неадсорбованими і атомами поверхні металу. На поверхні металу між адсорбованими атомами можуть проходити бімолекулярні реакції $A + B \leftrightarrow AB$. Застосувавши метод нерівноважного статистичного оператора Зубарєва, ми отримали систему рівнянь переносу для узгодженого опису кінетики електронів та дифузійно - реакційних атомних процесів.

1. Introduction

Processes of adsorbtion, desorbtion, diffusion of atoms, ions, polar and magnetic molecules or clusters on surfaces of metals, insulators, semiconductors play one of central roles in the development of nanostructural thin film technologies for micro and optoelectronics. Diffusion processes, adsorbtion and desorbtion mechanisms are decisive also in catalytic reactions on active surfaces which structure and electron structure have in these reactions a central role. Electronic processes on the metal surface, which create local electric fields in catalysis reactions also are the promoters of dissociation - association processes of gas molecules. All these phenomena sufficiently complicate the study of mechanics of different catalysis reactions. Besides, to understand them, a rigorous and detailed study of electronic kinetic and diffusion - reaction atom - molecular processes must be carried out. Such processes and phenomena are subject for an intensive experimental and theoretical study in solid state physics. Nowadays experimental methods of investigation such as scanning - tunnelling - microscopy (STM), scanning - tunnelling - spectroscopy (STS), field - ion - microscopy (FIM), and their modifications give each time a more detailed information about the electronic structure, diffusion processes, structural transformations on surfaces of metals, insulators, semiconductors, high temperature superconductor [1-7]. A more sequential theory of atom transport at scanning by tunnelling electrons with taking into account mechanisms of atoms heat oscillations and substrate phonon oscillations with the use of transfer Hamiltonian "substrate - adsorbate - tip" was presented and development in papers [8-11]. Of course, the processes of atoms and molecules transport on surface of a solid state, no matter whether the STM investigations are pursued or not, critically depend on both the nature of interactions between of them, which can be dipole or magnetic, and a state of substrate: paramagnetic, ferromagnetic, ferrimagnetic, etc. Furthermore, for such a spatially inhomogeneous systems one has another topical problem: the description of quantum transport processes on small times with taking account initial states and non-Markovian memory effects; the description of chemical catalitic reactions on a metal surface. One approach for the construction of quantum kinetic equations with taking account initial states and non-Markovian memory effects was suggested recently on the basis of the of mixed Green functions [12,13]. Processes of atoms and molecules transport on surface of solid states can be described here on the basis of the theory of surface diffusion [14,15], or kinetic equations [16,17].

In the present paper, we present generalized transport equations of a consistent description of electron kinetic and atomic diffusion - reaction of processes in a system "metal - adsorbate - gas". To this end we use the nonequilibrium statistical operator (NSO) method by D.N.Zubarev [12,18] and obtain a kinetic equation for one-electron density matrix and connected with this relation diffusion - reaction equations for adsorbed and nonadsorbed gas atoms on a metal surface.

2. Nonequilibrium statistical operator and transport equations of electrons and atoms of a system "metal - adsorbate - gas"

For the consistent description of electron kinetic of processes on a metal surface with adsorbed gas atoms or molecules one needs to take into account many peculiarities which are connected with screening effects and surface diffusion. We will consider the system "metal - adsorbate - gas". Gas molecules become polarized and can dissociate near the metal surface in nonhomogeneus electric field, which is produced by conduction electrons and localized electrons (for example d - electrons of transition metals) as well as by metal surface ions. Finally, due to the interaction, the dissociation products are adsorbed on the metal surface. This is the dissociation mechanism of gas molecules in numerous catalitic reactions (especially, ammiak catalysis). Then, the dissciation products of different molecules, which are adsorbed on metal surface, join the chemical reactions with energy threshold, which is sufficiently lower, than for reactionsin volume condition without catalizer. After that it is more preferable energetically for the reaction products to leave the surface. Modern catalitic reacrions of the surface are mainly bimolecular

$$A + B \leftrightarrow AB,$$
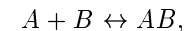
though metal surface atoms actively participate in them. This is displayed though the electron - ion - molecular interactions.

Let us suppose that after interaction of gas atoms or molecules with surface, some part of them is adsorbed. Let N_a be the total number of nonadsorbed atoms, whereas $N_{\bar{a}}$ be the number of atoms adsorbed on a metal surface, N_e be the total number of electrons, and N_s be the number of ions of a metal. The total Hamiltonian of such a system reads:

$$H = H_e + H_i^{int} + H_a + H_a^{int} + \sum_{\substack{\alpha = a, s, \bar{a} \\ 1 \leq f \leq N_\alpha}} U_\alpha(z_f) + H_{reac}, \qquad (2.1)$$

where H_a is the Hamiltonian of a gas subsystem. It is considered to be classical one. H_a^{int} is the Hamiltonian which describes interactions between gas atoms and electrons, metal surface ions and adsorbed atoms or molecules. H_i^{int} - is the Hamiltonian which describes the interactions between adsorbed gas atoms and metal surface ions; $U_\alpha(z_f)$ is an inhomogeneous effective potential of a surface which is assembled by collective effects in semilimited space, in our case in metal; H_e is the Hamiltonian of electron subsystem; H_{reac} is the interaction Hamiltonian for the chemical reaction between adsorbed atoms or molecules on a metal surface:

$$H_{reac} = \sum_{\bar{a},\bar{b},\bar{a}',\bar{b}'} (\langle \bar{a}',\bar{b}'|\Phi_{reac}|\bar{a},\bar{b}\rangle \hat{q}_{\bar{a}'}^+ \hat{q}_{\bar{b}'}^+ \hat{q}_{\bar{a}} \hat{q}_{\bar{b}} +$$

$$\langle \bar{a}',\bar{b}'|\Phi_{reac}|\bar{a},\bar{b}\rangle^* \hat{q}_{\bar{a}}^+ \hat{q}_{\bar{b}}^+ \hat{q}_{\bar{a}'} \hat{q}_{\bar{b}'})$$

with the amplitude $\langle \bar{a}',\bar{b}'|\Phi_{reac}|\bar{a},\bar{b}\rangle = \langle \bar{a},\bar{b}|\Phi_{reac}|\bar{a}',\bar{b}'\rangle$ of reaction between of reagents A, B and of the reaction products AB (we shall use the indices $\bar{a}$, $\bar{b}$ and $\bar{a}'\bar{b}'$ for the states of reagents A, B (atoms or molecules) and for the states an atoms in the reaction product AB). Here $\hat{q}_{\bar{a}'}^+$, $\hat{q}_{\bar{b}'}^+$, $\hat{q}_{\bar{a}}^+$, $\hat{q}_{\bar{b}}^+$ and $\hat{q}_{\bar{a}'}$, $\hat{q}_{\bar{b}'}$, $\hat{q}_{\bar{a}}$, $\hat{q}_{\bar{b}}$ are the atom creation and annihilation operators for the states $\bar{a}',\bar{b}'$, $\bar{a}$ and $\bar{b}$ of molecules AB, A and B, correspondingly. We will study the kinetics of an electron subsystem on a metal surface and diffusion - reaction processes of adsorbed and nonadsorbed gas atoms or molecules. In view of this, it is convenient to use the second quantization for electron subsystem in Hamiltonian (2.1) accordingly to Ref. [19]. To this end one needs to chose a proper basis of wave functions. Let us suppose that we know the solution to the Shrödinger equation for an electron

$$\left[-\frac{\hbar^2}{2m_e}\Delta + V_{e\alpha}(\mathbf{r} - \mathbf{X}_\alpha) \right] \psi_{\nu\alpha}(\mathbf{r} - \mathbf{X}_\alpha) = \varepsilon_{\nu\alpha}\psi_{\nu\alpha}(\mathbf{r} - \mathbf{X}_\alpha), \quad (2.2)$$

in potential fields of surface atom, nonadsorbed and adsorbed gas atoms. Here $\mathbf{X}_\alpha = (\mathbf{r}_\alpha, \mathbf{R}_\alpha)$ are Cartesian coordinates of particles. Eigen functions of equation (2.2) satisfy the conditions of orthogonality and completeness

$$\int d\mathbf{R}\psi_\nu^*(\mathbf{r} - \mathbf{R}_j)\psi_\mu(\mathbf{r}' - \mathbf{R}_j) = \delta_{\nu\mu},$$

$$\sum_\nu \psi_\nu^*(\mathbf{r} - \mathbf{R}_j)\psi_\nu(\mathbf{r}' - \mathbf{R}_j) = \delta(\mathbf{r} - \mathbf{r}')$$

for any $j = 1,\ldots N_b$, $\{\nu,\mu,\xi\}$ are quantum numbers and $\varepsilon_{\nu\alpha} = (E_\mu, \varepsilon_\nu, E_\xi^{ad})$ are eigen - values of electron energies. Let us use the set of

functions $\psi_{\nu\alpha}(\mathbf{r} - \mathbf{X}_\alpha) = (\psi_v(\mathbf{r} - \mathbf{R}_f), \varphi_\mu(\mathbf{r} - \mathbf{r}_l), \varphi_\xi^{ad}(\mathbf{r} - \mathbf{R}_l))$ as a basis for expansion of electron field operators:

$$
\begin{aligned}
\hat{\psi}(\mathbf{r},\mathbf{s}) \;=\; & \sum_{f=1}^{N_+}\sum_\nu\sum_{\sigma=\pm\hbar/2} \psi_\nu(\mathbf{r} - \mathbf{R}_f)\chi_\sigma(s)\hat{a}_{f\nu\sigma} + \quad (2.3) \\
& \sum_{l=1}^{N_a}\sum_\mu\sum_{\sigma=\pm\hbar/2} \varphi_\mu(\mathbf{r} - \mathbf{r}_l)\xi_\sigma(s)\hat{c}_{l\mu\sigma} +
\end{aligned}
$$

$$\sum_{l=1}^{N_{\bar{a}}}\sum_\xi\sum_{\sigma=\hbar/2} \varphi_\xi^{ad}(\mathbf{r} - \mathbf{R}_l)\chi_\sigma(s)\hat{c}_{l\xi\sigma}^{ad},$$

where $\chi_\sigma(s)$ are wave functions of an electron spin operator, $\sigma = \pm\hbar/2$ are the electron spin projections on a quantization axis, $\mathbf{s}$ is a spin coordinate. $\hat{a}_{f\nu\sigma}$, $\hat{c}_{l\mu\sigma}$, $\hat{c}_{l\xi\sigma}^{ad}$ end $\hat{a}_{f\nu\sigma}^+$, $\hat{c}_{l\mu\sigma}^+$, $\hat{c}_{l\xi\sigma}^{(ad)+}$ are electron annihilation and creation operators, $\mathbf{R}_f$ surface atom, $\mathbf{r}_l$ gas atom, $\mathbf{R}_l$ adsorbed atom on a metal surface, respectively. Then, the Hamiltonian of electron subsystem taking into account (2.3) in the second quantization representation, reads:

$$H_e = \sum_{\alpha,\nu,\sigma} \varepsilon_\nu^\alpha \hat{n}_{\nu,\sigma}^\alpha +$$

$$
\begin{aligned}
& \sum_{\alpha,\beta}\sum_{\sigma,\mu,\nu} t_{\mu\nu}^{\alpha\beta} \left(\hat{A}_{\nu\sigma}^{+\alpha}\hat{A}_{\mu\sigma}^\beta + \hat{A}_{\mu\sigma}^{+\beta}\hat{A}_{\nu\sigma}^\alpha \right) + \quad (2.4) \\
& \sum_{\substack{\alpha,\beta\\\alpha',\beta'}}\sum_{\nu\omega\sigma\mu\lambda\sigma'} W_{\omega\lambda}^{\nu\mu}(\alpha,\beta;\alpha',\beta')\hat{A}_{\nu\sigma}^{+\alpha}\hat{A}_{\mu\sigma'}^{+\beta}\hat{A}_{\lambda\sigma}^{\alpha'}\hat{A}_{\omega\sigma'}^{\beta'},
\end{aligned}
$$

where ε_ν^α is one-electron energy in a field of corresponding atom (surface, adsorbate, not adsorbate, tip). Operators $\hat{A}_{j\nu\sigma}^{+\alpha}$ vary from the set $\hat{a}_{f\nu\sigma}^+$, $\hat{c}_{l\mu\sigma}^+$, $\hat{c}_{l\xi\sigma}^{(ad)+}$, whereas operators $\hat{A}_{j\mu\sigma}^\alpha$ vary from the set $\hat{a}_{f\nu\sigma}$, $\hat{c}_{l\mu\sigma}$, $\hat{c}_{l\xi\sigma}^{ad}$ and are the electron creation and annihilation operators on $\mathbf{R}_f$ surface atom, $\mathbf{R}_l$ gas atom, $\mathbf{R}_l$ adsorbed atom on a metal surface, correspondingly.

$$\hat{n}_{\nu\sigma}^\alpha = \sum_{j=1} \hat{A}_{j\nu\sigma}^{+\alpha}\hat{A}_{j\mu\sigma}^\alpha$$

is the density operator of electrons in field of corresponding atoms.

$$\varepsilon_v^\alpha = \int d\mathbf{r}\psi_\nu^\alpha(\mathbf{r}) \left(-\frac{\hbar^2}{2m_e}\Delta + U_\alpha(z) + V_{\alpha\alpha}(\mathbf{r}) \right) \psi_\nu^\alpha(\mathbf{r}),$$

where $V_{\alpha\alpha}(\mathbf{r})$ are corresponding potentials of electrons in field of metal ions adsorbed, nonadsorbed gas atoms or molecules.

$$t_{\nu\mu}^{\alpha\beta} = \int \psi_\nu^\alpha(\mathbf{r})(-\frac{\hbar^2}{2m_e}\Delta + V_{\alpha\beta}(\mathbf{r}) + U_\alpha(z))\psi_\mu^\beta(\mathbf{r})d\mathbf{r}$$

are matrix elements of the Hamiltonian. They describe processes of electron transitions in field of corresponding atoms and ions.

$$W_{\omega\lambda}^{\nu\mu}(\alpha\beta;\alpha'\beta') = \frac{1}{2}\int\int \psi_\nu^\alpha(\mathbf{r})\psi_\omega^{\beta'}(\mathbf{r})\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_\mu^\beta(\mathbf{r}')\psi_\lambda^{\alpha'}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

is some Coulomb repulsive integral of electrons, which are connected with corresponding atoms in accordance with (2.3). Analysis of the total Hamiltonian (2.4) of the electron subsystem can be made in detail in view of the hybridization processes between electron states of a surface and atoms as well as effects of interaction between electrons. Such an analysis should be made on expansions on overlap integrals of orbitals of corresponding atoms similarly to [20]. The current of electrons between positions l and j in a system can be evaluated from the equation

$$J_{lj} = \int Sp(\hat{t}_{lj}(\hat{G}_{lj}^{+-} - \hat{G}_{jl}^{+-}))dE,$$

where $\hat{G}_{lj}^{+-}$, $\hat{G}_{jl}^{+-}$ are the spectral functions of time one-electron Green functions. These functions can be rewritten in the matrix form like this:

$$\hat{G}_{lj}(1,1') = \left[\begin{array}{cc} \hat{G}_{lj}^{++}(1,1') & \hat{G}_{lj}^{+-}(1,1') \\ \hat{G}_{lj}^{-+}(1,1') & \hat{G}_{lj}^{--}(1,1') \end{array}\right] =$$

$$\left[\begin{array}{cc} \hat{g}_{lj}^c(1,1') & \hat{g}_{lj}^<(1,1') \\ \hat{g}_{lj}^>(1,1') & \hat{g}_{lj}^a(1,1') \end{array}\right],$$

where $\hat{g}_{lj}^c$ are causal, $\hat{g}_{lj}^a$ anticausal and $\hat{g}_{lj}^<$, $\hat{g}_{lj}^>$ correlation Green functions for electrons:

$$\hat{g}_{lj}^{c,a}(1,1';t_0) = (i\hbar)^{-1}\langle T^{c,a}[\hat{\psi}_{lH}(1),\hat{\psi}_{jH}^+(1')]\rangle^{t_0},$$

$$\hat{g}_{lj}^>(1,1';t_0) = (i\hbar)^{-1}\langle\hat{\psi}_{lH}(1)\hat{\psi}_{jH}^+(1')\rangle^{t_0},$$

$$\hat{g}_{jl}^<(1,1';t_0) = -(i\hbar)^{-1}\langle\hat{\psi}_{jH}^+(1')\hat{\psi}_{lH}(1)\rangle^{t_0},$$

where $(1) = (\mathbf{r}_1,\mathbf{s}_1,t_1)$, $(1') = (\mathbf{r}'_1,\mathbf{s}'_1,t'_1)$. $\hat{\psi}_{lH}(1)$, $\hat{\psi}_{jH}^+(1')$ are field operators of electron in Heisenberg representation

$$\hat{\psi}_{lH}(1) = U(t_0,t)\hat{\psi}_l(\mathbf{r}_1,\mathbf{s}_1)U(t,t_0),$$

$$U(t,t_0) = e^{-i/\hbar(t-t_0)H}.$$

$T^{c,a}$ are direct and reverse time ordering operators. $\hat{g}_{lj}^c$, $\hat{g}_{lj}^a$, $\hat{g}_{lj}^<$, $\hat{g}_{lj}^>$ define retarded and advanced Green functions $\hat{g}_{lj}^R$, $\hat{g}_{lj}^A$, by the relations $\hat{g}_{lj}^R = \hat{g}_{lj}^c - \hat{g}_{lj}^< = \hat{g}_{lj}^> - \hat{g}_{lj}^a$, $\hat{g}_{lj}^A = \hat{g}_{lj}^c - \hat{g}_{lj}^> = \hat{g}_{lj}^< - \hat{g}_{lj}^a$. Functions

$$\hat{G}_{lj}(1,1';t_0) = (i\hbar)^{-1}\langle T_C[\hat{\psi}_{lH}(1),\hat{\psi}_{jH}^+(1')]\rangle^{t_0},$$

satisfy the equation of Dyson type in Keldysh formalism [21], [12,13,22]. T_C is an operator of time ordering on a Keldysh contour C [21]. Calculation of averages $\langle\cdots\rangle^{t_0}$ in Green functions is made with the help of nonequilibrium statistical operator $\rho(t)|_{t=t_0}$ in the initial time which should be defined from the solution to the quantum Liouville equation for our system " metal-adsorbate-gas". Problems of averaging on initial nonequilibrium states in Green functions have been analysed in detail in papers [21,13,22], where a mixed Green functions formalism as a generalization of the Keldysh-Schwinger one is proposed. Such an approach in our case could give a possibility to take into account an influence of diffusion - reaction gas processes on a surface on electron processes via averaging in corresponding Green function with the help of the nonequilibrium statistical operator of gas subsystem in initial time. In particular, it can be shown on the basis of [22], that the correlation Green function $\hat{g}_{jl}^<(1,1';t_0)$ in limit $t_0 \to -\infty$ and $t_1 = t'_1$ is equal to one-particle density matrix in r-representation

$$f_{lj}(\mathbf{r}_1,\mathbf{s}_1,\mathbf{r}'_1,\mathbf{s}'_1,t_1) = -i\hbar\lim_{t_0\to-\infty}\hat{g}_{jl}^<(1,1';t_0)|_{t_1=t'_1}.$$

It gives the connection of $\hat{g}_{jl}^<(1,1';t_0)$ with the electron current.

For a consistent description of both electron kinetic and diffusion - reaction processes of adsorbed and nonadsorbed gas atoms in a system "metal - adsorbate - gas" we will use the method of nonequilibrium statistical operator (NSO) by D.N.Zubarev [12]. This method is based on Bogolubov's ideas of a shortened description of nonequilibrium state of a system using the set of observed parameters. Such parameters of the shortened description can be nonequilibrium mean values of the electron subsystem:

$$\langle\hat{A}_{j\nu\sigma}^{+\alpha}\hat{A}_{l\xi\sigma'}^\beta\rangle^t = Sp\left(\hat{A}_{j\nu\sigma}^{+\alpha}\hat{A}_{l\xi\sigma'}^\beta\rho(t)\right) \qquad (2.5)$$

is the nonequilibrium one-electron density matrix; mean densities of adsorbed and nonadsorbed gas atoms or molecules on a metal surface are:

$$\langle\hat{n}_{\bar{a}}^\nu(\mathbf{R})\rangle^t = Sp\left(\hat{n}_{\bar{a}}^\nu(\mathbf{R})\rho(t)\right), \langle\hat{n}_a(\mathbf{r})\rangle^t = Sp\left(\hat{n}_a(\mathbf{r})\rho(t)\right), \qquad (2.6)$$

and

$$\langle \hat{\mathbf{d}}_a(\mathbf{r})\rangle^t = \mathrm{Sp}\left(\hat{\mathbf{d}}_a(\mathbf{r})\rho(t)\right) \qquad (2.7)$$

is the mean polarization of density of gas atoms or molecules,

$$\hat{\mathbf{d}}_a(\mathbf{r}) = \sum_{j=1}^{N_a} \mathbf{d}_j \delta(\mathbf{r}-\mathbf{r}_j)$$

is the microscopic polarization of density of gas atoms or molecules, $\mathbf{d}_j$ is dipole moment of particle j;

$$\langle \hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}')\rangle^t = \mathrm{Sp}\left(\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}')\rho(t)\right) \qquad (2.8)$$

is the nonequilibrium pair of the distribution function of adsorbed atoms or molecules on the metal surface. Here $\hat{n}_{\bar{a}}^{\nu}(\mathbf{R})$ is the density operator of gas atoms which are adsorbed in a ν- state on the metal surface; $\hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) = \sum_j^{N_a^{ad}} \hat{\psi}_{\nu j}^+(\mathbf{R})\hat{\psi}_{\nu j}(\mathbf{R})$, $\hat{\psi}_{\nu j}^+(\mathbf{R})$, $\hat{\psi}_{\nu j}(\mathbf{R})$ are the creation and annihilation operators in a ν- state of adsorbed gas atom on a metal surface.

$$\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}') = \hat{n}_{\bar{a}}^{\nu}(\mathbf{R})\hat{n}_{\bar{b}}^{\mu}(\mathbf{R}'),$$

$$\hat{n}_a(\mathbf{r}) = \sum_{j=1}^{N_a} \delta(\mathbf{r}-\mathbf{r}_j)$$

is the microscopic density of gas atoms or molecules. If the chemical bond, stimulated by the metal surface between adsorbed atoms appears, then the coordinate $L_{\bar{a}\bar{b}}$ molecule (cluster), consisting of the two atoms in states μ and ν, can be found, with the help of transition from individual reference systems for each atom $\hat{n}_{\bar{a}}^{\nu}(\mathbf{R})$, $\hat{n}_{\bar{b}}^{\mu}(\mathbf{R}')$ to their mass center reference system. Then $\langle \hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}')\rangle^t$ is a mean density of molecules, created in the chemical reaction between adsorbed atoms on metal surface. On the contrary, molecules, consisting of two atoms in states μ and ν, under the influence of nonhomogeneus magnetc field, can at first be dissociated to atoms and then be adsorbed by the metal surface. In this case, $\langle \hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}')\rangle^t$ is the nonequilibrium quantum distribution function of atoms on metal surface. Mean values of parameters of shortened description are calculated with the help of $\rho(t)$ -NSO of electrons and atoms of our system. This operator satisfies the Liouville equation

$$\frac{\partial}{\partial t}\rho(t) + iL_N\rho(t) = 0, \qquad (2.9)$$

where iL_N is the Liouville operator which corresponds to the total Hamiltonian (2.1). One can distinguish in the structure of the operator iL_N some classical and some quantum parts:

$$iL_N = iL_N^{cl} + iL_N^{qun},$$

$$iL_N^{cl} = \sum_{j=1}^{N_a} \frac{\mathbf{p}_j}{m_a}\frac{\partial}{\partial \mathbf{r}_j} - \frac{1}{2}\sum_{j\neq j'}^{N_a} \frac{\partial}{\partial \mathbf{r}_j}V_{aa}(|\mathbf{r}_j-\mathbf{r}_{j'}|)\left(\frac{\partial}{\partial \mathbf{p}_j}-\frac{\partial}{\partial \mathbf{p}_{j'}}\right) -$$

$$\sum_{j,\beta,f}^{N_a,N_\beta} \frac{\partial}{\partial \mathbf{r}_j}\left(V_{a\beta}(\mathbf{r}_j,\mathbf{R}_f)+U_a(z_j)\right)\frac{\partial}{\partial \mathbf{p}_j}$$

is thr classical part that corresponds to an interacting gas. $V_{a\beta}(\mathbf{r}_j,\mathbf{R}_f)$ are interaction potentials of gas atoms with other atoms of a system.

$$i\hat{L}_N^{qun}\hat{A} = \frac{1}{i\hbar}\left[\hat{A},H_e+H_i^{int}+H_a^{int}+U+H_{reac}\right]$$

is the quantum part of the total Liouville operator. The nonequilibrium statistical operator of electrons, atoms of a "metal - adsorbate - gas " is normalized as

$$\mathrm{Sp}\rho(t) = 1,$$

where $\mathrm{Sp}(\ldots) = \prod_\alpha \int \frac{(dx)^{N_\alpha}}{N_\alpha!(2\pi\hbar)^{3N_\alpha}}\mathrm{Sp}_{(\nu,\xi,\sigma)}(\ldots)$, $dx = d\mathbf{r}d\mathbf{p}$, $N_\alpha = \{N_a,N_{\bar{a}},N_e,N_s\}$, $\mathrm{Sp}_{(\nu,\xi,\sigma)}$ means summation on all values of spin and other quantum numbers. To find nonequilibrium statistical operator $\rho(t)$ one needs a boundary condition. Using the NSO method by D.N.Zubarev [12,18], we will looking for the solution to equation (2.9) in such a form, where time dependency is included indirectly via mean values of the set of the shortened description. To this end let us introduce into right hand side of the Liouville equation (2.9) some infinitely small source which destroys its symmetry on time inversion and selects needed retarded solutions [12,18]. Thus, we will start further from the equation

$$\left(\frac{\partial}{\partial t}+iL_N\right)\rho(t) = -\varepsilon\left(\rho(t)-\rho_q(t)\right), \qquad (2.10)$$

where $\varepsilon \to +0$ after thermodynamic limiting transition. Auxiliary quasiequilibrium statistical operator $\rho_q(t)$ is defined from the condition of extremum of information entropy of a system and conservation of normalization $\mathrm{Sp}\rho_q(t) = 1$ and fixed values of parameters of the shortened

description. In our case these parameters are defined by relations (2.5)-(2.8). Then, going by the standard way [12,18] one obtains the expression for quasiequilibrium statistical operator:

$$\rho_q(t) = \exp\{-\Phi(t) - \beta(H - \sum_{l,l'} b(l,l';t)\hat{N}_{ll'} - \qquad (2.11)$$

$$\sum_a \int d\mathbf{r}\mu_a(\mathbf{r};t)\hat{n}_a(\mathbf{r}) -$$

$$\sum_{\bar{a}} \sum_{\nu} \int d\mathbf{R}\mu_{\bar{a}}^{\nu}(\mathbf{R};t)\hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) - \sum_a \int d\mathbf{r}e(\mathbf{r};t)\hat{\mathbf{d}}_a(\mathbf{r}) -$$

$$\sum_{\bar{a}\bar{b}} \sum_{\nu\mu} \int d\mathbf{R}d\mathbf{R}' M_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}';t)\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}'))\},$$

where

$$\Phi(t) = \ln \mathrm{Sp}\exp\{-\beta(H - \sum_{l,l'} b(l,l';t)\hat{N}_{ll'} -$$

$$\sum_a \int d\mathbf{r}\mu_a(\mathbf{r};t)\hat{n}_a(\mathbf{r}) -$$

$$\sum_{\bar{a}} \sum_{\nu} \int d\mathbf{R}\mu_{\bar{a}}^{\nu}(\mathbf{R};t)\hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) - \sum_a \int d\mathbf{r}e(\mathbf{r};t)\hat{\mathbf{d}}_a(\mathbf{r}) -$$

$$\sum_{\bar{a}\bar{b}} \sum_{\nu\mu} \int d\mathbf{R}d\mathbf{R}' M_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}';t)\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}'))\},$$

is the Massieu-Planck functional. It is defined from the normalization condition $\rho_q(t)$. Parameters $b(l,l';t)$, $\mu_a(\mathbf{r};t)$, $\mu_{\bar{a}}^{\nu}(\mathbf{R};t)$, $\mathbf{e}(\mathbf{r};t)$, $M_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}';t)$ are defined from the self - consistency conditions

$$\langle\hat{N}_{ll'}\rangle^t = \langle\hat{N}_{ll'}\rangle_q^t, \quad \langle\hat{n}_a(\mathbf{r})\rangle^t = \langle\hat{n}_a(\mathbf{r})\rangle_q^t, \qquad (2.12)$$

$$\langle\hat{n}_{\bar{a}}^{\nu}(\mathbf{R})\rangle^t = \langle\hat{n}_{\bar{a}}^{\nu}(\mathbf{R})\rangle_q^t, \quad \langle\hat{\mathbf{d}}_a(\mathbf{r})\rangle^t = \langle\hat{\mathbf{d}}_a(\mathbf{r})\rangle_q^t,$$

$$\langle\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}')\rangle^t = \langle\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}')\rangle_q^t,$$

and denote, that $\mu_a(\mathbf{r};t)$ is the local chemical potential of a gas atom; $\mu_{\bar{a}}^{\nu}(\mathbf{R};t)$ is the local chemical potential of an adsorbed atom in a state ν on a metal surface; $\mathbf{e}(\mathbf{r};t)$ is the local electric field, which is made up by electron and ion subsystem on metal surface, and is defined by the Maxwellian equation:

$$\nabla\mathbf{e}(\mathbf{R};t) = 4\pi(\langle\hat{\rho}_e(\mathbf{R})\rangle^t + \langle\sum_f Z_f e\hat{n}_f(\mathbf{R})\rangle^t), \qquad (2.13)$$

where $\hat{n}_e(\mathbf{R}){=}\sum_\mathbf{s}\hat{\psi}^+(\mathbf{R},\mathbf{s})\hat{\psi}(\mathbf{R},\mathbf{s})$ is the density operator of the electron subsystem on metal surface, $\hat{\rho}_e(\mathbf{R}){=}e\hat{n}_e(\mathbf{R})$ is the density operator charge of electrons, e is the charge of electron and $\hat{n}_f(\mathbf{R}){=}\sum_{\mathbf{s}'}\hat{\psi}_f^+(\mathbf{R},\mathbf{s}')\hat{\psi}_f(\mathbf{R},\mathbf{s}')$ is the density operator of the ion subsystem on the metal surface, $\mathbf{s}'$ is a spin coordinate and Z_f is valence of ion on metal surface. $M_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}';t)$ is the local chemical potential of an adsorbed complex atoms $\bar{a}$, $\bar{b}$ in a states ν and μ on a metal surface; $\beta = \frac{1}{k_\mathrm{B}T}$, k_B is the Boltzmann constant, T is the equilibrium value of temperature. Here $\hat{N}_{ll'} = \hat{A}_l^+ \hat{A}_{l'}$, l, l' indicate the set of indices $\{\alpha, j\nu\sigma\}$; $\langle(\ldots)\rangle_q^t = \mathrm{Sp}(\ldots)\rho_q(t)$. Using the standard NSO procedure with taking account projection [12,18] and structure of $\rho_q(t)$ (2.11) one obtains from (2.10) the expression for nonequilibrium statistical operator:

$$\rho(t) = \rho_q(t) + \sum_{ll'}\int_{-\infty}^t e^{\epsilon(t'-t)}T(t,t')\int_0^1 d\tau\rho_q^\tau(t')$$

$$I_N(l,l';t')\rho_q^{1-\tau}(t')\beta b(l,l';t')dt'+$$

$$\sum_a\int d\mathbf{r}\int_{-\infty}^t e^{\epsilon(t'-t)}T(t,t')\int_0^1 d\tau\rho_q^\tau(t') \qquad (2.14)$$

$$I_a(\mathbf{r};t')\rho_q^{1-\tau}(t')\beta\mu_a(\mathbf{r};t')dt'+$$

$$\sum_{\bar{a}}\sum_\nu\int d\mathbf{R}\int_{-\infty}^t e^{\epsilon(t'-t)}T(t,t')\int_0^1 d\tau\rho_q^\tau(t')$$

$$I_{\bar{a}}^\nu(\mathbf{R};t')\rho_q^{1-\tau}(t')\beta\mu_{\bar{a}}^\nu(\mathbf{R};t')dt'+$$

$$\sum_a\int d\mathbf{r}\int_{-\infty}^t e^{\epsilon(t'-t)}T(t,t')\int_0^1 d\tau\rho_q^\tau(t')$$

$$I_d^a(\mathbf{r};t')\rho_q^{1-\tau}(t')\beta\mathbf{e}(\mathbf{r};t')dt'+$$

$$\sum_{\bar{a},\bar{b}}\sum_{\nu,\mu}\int d\mathbf{R}\int d\mathbf{R}'\int_{-\infty}^t e^{\epsilon(t'-t)}T(t,t')\int_0^1 d\tau\rho_q^\tau(t')$$

$$I_{G_{\bar{a}\bar{b}}}^{\nu\mu}(\mathbf{R}\mathbf{R}';t')\rho_q^{1-\tau}(t')\beta M_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}\mathbf{R}';t')dt',$$

where

$$T(t,t') = \exp\left\{-\int_{t'}^{t}(1-\mathcal{P}_q(t''))iL_N dt''\right\}$$

is an evolution operator with taking account projection. $\mathcal{P}_q(t)$ – is the Kawasaki-Gunton projection operator. It acts on statistical operator and has properties like this:

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

$$\mathcal{P}_q(t)\mathcal{P}_q(t') = \mathcal{P}_q(t).$$

It is connected with Mori projection operator $\mathcal{P}(t)$ by the relation:

$$\mathcal{P}_q(t)\hat{A}\rho_q(t) = \int_0^1 d\tau(\rho_q)^\tau \mathcal{P}(t)\hat{A}\rho'_q(t)^{1-\tau}.$$

$$\mathcal{P}(t)\hat{A} = \langle\hat{A}\rangle_q^t + \sum_{l,l'}\frac{\delta\langle\hat{A}\rangle_q^t}{\delta\langle\hat{N}_{ll'}\rangle^t}(\hat{N}_{ll'} - \langle\hat{N}_{ll'}\rangle^t) +$$

$$\sum_a \int d\mathbf{r}\frac{\delta\langle\hat{A}\rangle_q^t}{\delta\langle\hat{n}_a(\mathbf{r})\rangle^t}(\hat{n}_a(\mathbf{r}) - \langle\hat{n}_a(\mathbf{r})\rangle^t)$$

$$+\sum_{\bar{a}}\sum_\nu \int d\mathbf{R}\frac{\delta\langle\hat{A}\rangle_q^t}{\delta\langle\hat{n}_{\bar{a}}^\nu(\mathbf{R})\rangle^t}(\hat{n}_{\bar{a}}^\nu(\mathbf{R}) - \langle\hat{n}_{\bar{a}}^\nu(\mathbf{R})\rangle^t).$$

$$+\sum_a \int d\mathbf{r}\frac{\delta\langle\hat{A}\rangle_q^t}{\delta\langle\hat{\mathbf{d}}_a(\mathbf{r})\rangle^t}(\hat{\mathbf{d}}_a(\mathbf{r}) - \langle\hat{\mathbf{d}}_a(\mathbf{r})\rangle^t)$$

$$+\sum_{\bar{a}\bar{b}}\sum_{\nu\mu}\int d\mathbf{R}\int d\mathbf{R}'\frac{\delta\langle\hat{A}\rangle_q^t}{\delta\langle\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}')\rangle^t}(\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}') -$$

$$\langle\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}')\rangle^t).$$

$\mathcal{P}(t)$ acts on operators and has properties of a projection operator:

$$\mathcal{P}(t)\hat{n}_a(\mathbf{r}) = \hat{n}_a(\mathbf{r}), \quad \mathcal{P}(t)\hat{N}_{ll'} = \hat{N}_{ll'},$$

$$\mathcal{P}(t)\hat{n}_{\bar{a}}(\mathbf{R}) = \hat{n}_{\bar{a}}(\mathbf{R}), \quad \mathcal{P}(t)\hat{\mathbf{d}}_a(\mathbf{r}) = \hat{\mathbf{d}}_a(\mathbf{r}),$$

$$\mathcal{P}(t)\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}') = \hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}'),$$

$$\mathcal{P}(t)\mathcal{P}(t') = \mathcal{P}(t), \quad \mathcal{P}(t)(1-\mathcal{P}(t)) = 0.$$

$$I_N(l,l';t') = (1-\mathcal{P}(t'))\dot{\hat{N}}_{ll'}, I_a(\mathbf{r};t') = (1-\mathcal{P}(t'))\dot{\hat{n}}_a(\mathbf{r}),$$

$$I_{\bar{a}}^\nu(\mathbf{R};t') = (1-\mathcal{P}(t'))\dot{\hat{n}}_{\bar{a}}^\nu(\mathbf{R}), \tag{2.15}$$

$$I_d^a(\mathbf{r};t') = (1-\mathcal{P}(t'))\dot{\hat{\mathbf{d}}}_a(\mathbf{r}),$$

$$I_{G_{\bar{a}\bar{b}}}^{\nu,\mu}(\mathbf{R}\mathbf{R}';t') = (1-\mathcal{P}(t'))\dot{\hat{G}}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}')$$

are generalized flows, $\dot{\hat{N}}_{ll'} = \frac{1}{i\hbar}[\hat{N}_{ll'},H]$, $\dot{\hat{n}}_a(\mathbf{r}) = iL_N^{cl}\hat{n}_a(\mathbf{r}) = \frac{1}{m_a}\boldsymbol{\nabla}\cdot\hat{\mathbf{p}}_a(\mathbf{r})$, $\hat{\mathbf{p}}_a(\mathbf{r}) = \sum_{j=1}^{N_a}\mathbf{p}_j\delta(\mathbf{r}-\mathbf{r}_j)$ is the microscopic momentum density of gas atoms, $\dot{\hat{n}}_{\bar{a}}^\nu(\mathbf{R}) = \frac{1}{i\hbar}[\hat{n}_{\bar{a}}^\nu(\mathbf{R}),H]$; $\dot{\hat{\mathbf{d}}}_a(\mathbf{r}) = iL_N^{cl}\hat{\mathbf{d}}_a(\mathbf{r})$; $\dot{\hat{G}}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}') = \frac{1}{i\hbar}[\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}'),H]$. In such a way, we obtained a general expression for nonequilibrium statistical operator $\rho(t)$ of electrons and gas atoms in a system "metal - adsorbate - gas " for specific set of parameters of shortened description (2.5)–(2.8). It depends on generalized flows (2.14) which describe dissipative transport processes in a system. As far as under the principle of shortened description $\rho(t)$ is a functional of parameters $\langle\hat{N}_{ll'}\rangle^t$, $\langle\hat{n}_a(\mathbf{r})\rangle^t$, $\langle\hat{n}_{\bar{a}}^\nu(\mathbf{R})\rangle^t$, $\langle\hat{\mathbf{d}}_a(\mathbf{r})\rangle^t$, $\langle\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}')\rangle^t$ correspondingly to the self-consistency conditions (2.12), to have a complete description of nonequilibrium processes one needs to construct transport equations. To obtain them let us use the equality:

$$\frac{\partial}{\partial t}\langle\hat{B}_n\rangle^t = \langle iL_N\hat{B}_n\rangle^t = \langle iL_N\hat{B}_n\rangle_q^t + \langle I_B(t)\rangle^t,$$

where $\hat{B}_n = (\hat{N}_{ll'},\hat{n}_a(\mathbf{r}),\hat{n}_{\bar{a}}^\nu(\mathbf{R}),\hat{\mathbf{d}}_a(\mathbf{r}),\hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R},\mathbf{R}'))$ and

$$I_B(t) = (I_N(l,l';t),I_a(\mathbf{r};t),I_{\bar{a}}^\nu(\mathbf{R};t),I_d^a(\mathbf{r};t'),I_{G_{\bar{a}\bar{b}}}^{\nu\mu}(\mathbf{R}\mathbf{R}';t').$$

Averaging the right hand parts of these equalities with the help of NSO (2.14) one obtains generalized transport equations for one-electron density matrix and mean values of densities of adsorbed and nonadsorbed gas atoms:

$$\frac{\partial}{\partial t}\langle\hat{N}_{ll'}\rangle^t = \langle\dot{\hat{N}}_{ll'}\rangle_q^t + \sum_{j,j'}\int_{-\infty}^t e^{\epsilon(t'-t)}\varphi_{NN}(ll',jj';t,t')$$

$$\beta b(j,j';t')dt' +$$

$$\sum_a\int d\mathbf{r}'\int_{-\infty}^t e^{\epsilon(t'-t)}\varphi_{Nn_a}(ll',\mathbf{r};t,t')\beta\mu_a(\mathbf{r}';t')dt' + \tag{2.16}$$

$$\sum_{\bar{a}} \sum_{\nu'} \int d\mathbf{R}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{N n_{\bar{a}}}^{\nu'}(ll', \mathbf{R}; t, t') \beta \mu_{\bar{a}}^{\nu'}(\mathbf{R}'; t') dt' +$$

$$\sum_{a} \int d\mathbf{r}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{N d_a}(ll', \mathbf{r}'; t, t') \beta \mathbf{e}(\mathbf{r}'; t') dt' +$$

$$\sum_{\bar{a}\bar{b}} \sum_{\nu'\mu'} \int d\mathbf{R}' \int d\mathbf{R}'' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{N G_{\bar{a}\bar{b}}}^{\nu'\mu'}(ll', \mathbf{R}'\mathbf{R}''; t, t')$$

$$\beta M_{\bar{a}\bar{b}}^{\nu'\mu'}(\mathbf{R}'\mathbf{R}''; t') dt',$$

$$\frac{\partial}{\partial t} \langle \hat{n}_a(\mathbf{r}) \rangle^t = \langle \dot{\hat{n}}_a(\mathbf{r}) \rangle_q^t + \sum_{j,j'} \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{n_a, N}(\mathbf{r}; j, j'; t, t')$$

$$\beta b(j, j'; t') dt' +$$

$$\sum_{b} \int d\mathbf{r}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{n_a n_b}(\mathbf{r}, \mathbf{r}'; t, t') \beta \mu_b(\mathbf{r}'; t') dt' + \qquad (2.17)$$

$$\sum_{\bar{b}} \sum_{\nu'} \int d\mathbf{R}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{n_a n_{\bar{b}}}^{\nu'}(\mathbf{r}, \mathbf{R}'; t, t') \beta \mu_{\bar{b}}^{\nu'}(\mathbf{R}'; t') dt' +$$

$$\sum_{b} \int d\mathbf{r}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{n_a d_b}(\mathbf{r}, \mathbf{r}'; t, t') \beta \mathbf{e}(\mathbf{r}'; t') dt' +$$

$$\sum_{\bar{a}'\bar{b}} \sum_{\nu'\mu'} \int d\mathbf{R}' \int d\mathbf{R}'' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{n_a G_{\bar{a}'\bar{b}}}^{\nu'\mu'}(\mathbf{r}, \mathbf{R}'\mathbf{R}''; t, t')$$

$$\beta M_{\bar{a}'\bar{b}}^{\nu'\mu'}(\mathbf{R}'\mathbf{R}''; t') dt',$$

$$\frac{\partial}{\partial t} \langle \hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) \rangle^t = \langle \dot{\hat{n}}_{\bar{a}}^{\nu}(\mathbf{R}) \rangle_q^t + \sum_{j,j'} \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{n_{\bar{a}}, N}(\mathbf{R}; j, j'; t, t')$$

$$\beta b(j, j'; t') dt' +$$

$$\sum_{b} \int d\mathbf{r}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{n_{\bar{a}} n_b}^{\nu}(\mathbf{R}, \mathbf{r}'; t, t') \beta \mu_b(\mathbf{r}'; t') dt' + \qquad (2.18)$$

$$\sum_{\bar{b}} \sum_{\nu'} \int d\mathbf{R}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{n_{\bar{a}} n_{\bar{b}}}^{\nu\nu'}(\mathbf{R}, \mathbf{R}'; t, t') \beta \mu_{\bar{b}}^{\nu'}(\mathbf{R}'; t') dt' +$$

$$\sum_{b} \int d\mathbf{r}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{n_{\bar{a}} d_b}(\mathbf{r}, \mathbf{r}'; t, t') \beta \mathbf{e}(\mathbf{r}'; t') dt' +$$

$$\sum_{\bar{a}\bar{b}} \sum_{\nu'\mu'} \int d\mathbf{R}' \int d\mathbf{R}'' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{n_{\bar{a}} G_{\bar{a}'\bar{b}}}^{\nu'\mu'}(\mathbf{r}, \mathbf{R}'\mathbf{R}''; t, t')$$

$$\beta M_{\bar{a}'\bar{b}}^{\nu'\mu'}(\mathbf{R}'\mathbf{R}''; t') dt',$$

$$\frac{\partial}{\partial t} \langle \hat{\mathbf{d}}_a(\mathbf{r}) \rangle^t = \langle \dot{\hat{\mathbf{d}}}_a(\mathbf{r}) \rangle_q^t + \sum_{j,j'} \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{d_a, N}(\mathbf{r}; j, j'; t, t')$$

$$\beta b(j, j'; t') dt' +$$

$$\sum_{b} \int d\mathbf{r}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{d_a n_b}(\mathbf{r}, \mathbf{r}'; t, t') \beta \mu_b(\mathbf{r}'; t') dt' + \qquad (2.19)$$

$$\sum_{\bar{b}} \sum_{\nu'} \int d\mathbf{R}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{d_a n_{\bar{b}}}^{\nu'}(\mathbf{r}, \mathbf{R}'; t, t') \beta \mu_{\bar{b}}^{\nu'}(\mathbf{R}'; t') dt' +$$

$$\sum_{b} \int d\mathbf{r}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{d_a d_b}(\mathbf{r}, \mathbf{r}'; t, t') \beta \mathbf{e}(\mathbf{r}'; t') dt' +$$

$$\sum_{\bar{a}'\bar{b}} \sum_{\nu'\mu'} \int d\mathbf{R}' \int d\mathbf{R}'' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{d_a G_{\bar{a}'\bar{b}}}^{\nu'\mu'}(\mathbf{r}, \mathbf{R}'\mathbf{R}''; t, t')$$

$$\beta M_{\bar{a}'\bar{b}}^{\nu'\mu'}(\mathbf{R}'\mathbf{R}''; t') dt',$$

$$\frac{\partial}{\partial t} \langle \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') \rangle^t = \langle \dot{\hat{G}}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') \rangle_q^t + \sum_{j,j'} \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}$$

$$\varphi_{G_{\bar{a}\bar{b}}, N}(\mathbf{R}\mathbf{R}'; j, j'; t, t') \beta b(j, j'; t') dt' +$$

$$\sum_{b'} \int d\mathbf{r}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)} \varphi_{G_{\bar{a}\bar{b}} n_{b'}}^{\nu\mu}(\mathbf{R}\mathbf{R}', \mathbf{r}'; t, t') \beta \mu_{b'}(\mathbf{r}'; t') dt' + \qquad (2.20)$$

$$\sum_{\bar{b}'}\sum_{\nu'}\int d\mathbf{R}''\int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}\varphi^{\nu\mu\nu'}_{G_{\bar{a}\bar{b}}n_{\bar{b}'}}(\mathbf{R}\mathbf{R}',\mathbf{R}'';t,t')\beta\mu^{\nu'}_{\bar{b}'}(\mathbf{R}';t')dt'+$$

$$\sum_{b'}\int d\mathbf{r}'\int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}\varphi_{G_{\bar{a}\bar{b}}d_{b'}}(\mathbf{R}\mathbf{R}',\mathbf{r}';t,t')\beta\mathbf{e}(\mathbf{r}';t')dt'+$$

$$\sum_{\bar{a}'\bar{b}'}\sum_{\nu'\mu'}\int d\mathbf{R}''\int d\mathbf{R}'''\int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}\varphi^{\nu\mu\nu'\mu'}_{G_{\bar{a}\bar{b}}G_{\bar{a}'\bar{b}'}}(\mathbf{R}\mathbf{R}',\mathbf{R}''\mathbf{R}''';t,t')$$

$$\beta M^{\nu'\mu'}_{\bar{a}'\bar{b}'}(\mathbf{R}''\mathbf{R}''';t')dt',$$

where φ_{NN}, $\varphi_{n_a n_b}$, $\varphi^{\nu\nu'}_{n_{\bar{a}}n_{\bar{a}}}$, φ_{Nn_a}, $\varphi^{\nu'}_{Nn_{\bar{a}}}$, $\varphi^{\nu'}_{n_a n_{\bar{a}}}$, $\varphi_{d_a d_b}$, $\varphi^{\nu\mu\nu'\mu'}_{G_{\bar{a}\bar{b}}G_{\bar{a}'\bar{b}}}$ are generalized transport cores which describe dissipative processes in the system. Transport cores are built in the generalized flows (2.15) and have the following structure:

$$\varphi_{BB'}(t,t') = \mathrm{Sp}\left(I_B(t)T(t,t')\int\limits_{0}^{1}d\tau\rho^\tau_q(t')I_{B'}(t')\rho^{1-\tau}_q(t')\right), \quad (2.21)$$

In particular, the transport core $\varphi_{NN}(ll',jj';t,t')$ describes dynamical dissipative interelectron flows correlations, $\varphi_{n_a n_b}(\mathbf{r},\mathbf{r}';t,t')$ describes dynamical correlations of diffusion flows of gas atoms and, as it will be shown below, is connected with the nonuniform diffusion coefficient $D_{ab}(\mathbf{r},\mathbf{r}';t)$ of gas atoms or molecules. Similarly, the transport core $\varphi^{\nu\nu'}_{n_{\bar{a}}n_{\bar{b}}}(\mathbf{R},\mathbf{R}';t,t')$ describes dynamical dissipative correlations of diffusion flows of gas atoms in states ν and ν' on a metal surface and defines nonuniform diffusion coefficient $D^{\nu\nu'}_{\bar{a}\bar{b}}(\mathbf{R},\mathbf{R}';t)$ of adsorbed atoms on a metal surface. Another transport core describes dynamical dissipative correlations between generalized electron flow $I_N(l,l';t)$, gas atoms $I_{n_a}(\mathbf{r};t)$ and adsorbed atoms $I^\nu_{n_{\bar{a}}}(\mathbf{R};t)$. In particular, transport cores $\varphi^\nu_{n_{\bar{a}}n_b}(\mathbf{R};\mathbf{r}';t,t')$, $\varphi^{\nu'}_{n_a n_{\bar{b}}}(\mathbf{r};\mathbf{R};t,t')$ describe dissipative correlations between flows of gas atoms and adsorbed atoms and define nonuniform coefficients of mutual diffusion $D^{\nu'}_{a\bar{b}}(\mathbf{r},\mathbf{R}';t)$ "gas atom - adsorbed atom". Study of these diffusion coefficients in adsorption processes is very important.

$\varphi_{d_a d_b}(\mathbf{r},\mathbf{r}';t,t')$ are responsible for the polarization effects in molecules which are induced by dynamic electric field of the metal surface. Transport cores $\varphi^{\nu\mu}_{G_{\bar{a}\bar{b}}p}(\mathbf{R}\mathbf{R}';t,t')$ $\{p=N,n,\bar{n},d\}$ describe dissipative correlations between flows and adsorbed atoms density, electrons,

atoms, molecular flow densities, molecules polarization, and adsorbed atoms. $\varphi^{\nu\mu\nu'\mu'}_{G_{\bar{a}\bar{b}}G_{\bar{a}'\bar{b}}}(\mathbf{R}\mathbf{R}',\mathbf{R}''\mathbf{R}''';t,t')$ describe diffusion - reaction processes between adsorbed atoms on the metal surface. They are higher memory functions with respect to dynamical variables $G^{\nu\mu}_{\bar{a}\bar{b}}$. Calculation of these transport cores consists a well - known problem of nonequilibrium statistical mechanics. Thus, we obtained generalized transport equations (2.16)–(2.20) for one-electron density matrix, average nonequilibrium densities of adsorbed and nonadsorbed gas atoms for the consistent study of kinetic electron and atomic diffusion - reaction processes in a system "metal - adsorbate - gas". It can be seen, these equations have nonlinear and nonuniform structure, they can describe both strongly and weakly nonequilibrium processes. In further consideration our prime interest will be with the weakly nonequilibrium case.

3. Weakly nonequilibrium processes

In such a case one should suppose that one-electron density matrix $\langle\hat{N}_{ll'}\rangle^t$, average nonequilibrium densities of adsorbed and nonadsorbed gas atoms $\langle\hat{n}^\nu_{\bar{a}}(\mathbf{R})\rangle^t$, $\langle\hat{n}_a(\mathbf{r})\rangle^t$ and $\langle\hat{\mathbf{d}}_a(\mathbf{r})\rangle^t$, $\langle\hat{G}^{\nu,\mu}_{\bar{a}\bar{b}}(\mathbf{R},\mathbf{R}')\rangle^t$ correspondingly, reciprocal thermodynamic parameters $b(l,l';t)$, $\mu^\nu_{\bar{a}}(\mathbf{R};t)$, $\mu_a(\mathbf{r};t)$, $\mathbf{e}(\mathbf{r};t)$, $M^{\nu\mu}_{\bar{a}\bar{b}}(\mathbf{R},\mathbf{R}';t)$ deviate slightly from their equilibrium values. Then one can expand guasiequilibrium statistical operator (2.11) on deviations of parameters $b(l,l';t)$, $\mu^\nu_{\bar{a}}(\mathbf{R};t)$, $\mu_a(\mathbf{r};t)$, $\mathbf{e}(\mathbf{r};t)$, $M^{\nu\mu}_{\bar{a}\bar{b}}(\mathbf{R},\mathbf{R}';t)$ from their equilibrium values $b_0(l,l')$, $\mu^\nu_{\bar{a}}(\mathbf{R})$, $\mu_a(\mathbf{r})$, $M^{\nu\mu}_{\bar{a}\bar{b}}(\mathbf{R},\mathbf{R}')$ and restrict our expansion by the liner approximation. Then from (2.16)-(2.20) one obtains a transport equation in the linear approximation, using the Laplace transformation for time $t>0$,

$$\langle\hat{A}\rangle_z = i\int\limits_{0}^{\infty}e^{izt}\hat{A}(t)dt, z=\omega+i\varepsilon, \quad (3.1)$$

$$z\langle\delta\hat{p}_n\rangle_z - \sum_{j,j'}\Omega_{p_n N}(j,j';z)\langle\delta\hat{N}_{j,j'}\rangle_z -$$

$$\sum_b\int d\mathbf{r}'\Omega_{p_n n_b}(\mathbf{r}';z)\langle\delta\bar{n}_b(\mathbf{r}')\rangle_z - \quad (3.2)$$

$$\sum_{\bar{b}}\sum_{\nu'}\int d\mathbf{R}'\Omega^{\nu'}_{p_n n_{\bar{b}}}(\mathbf{R}';z)\langle\delta\bar{n}^{\nu'}_{\bar{b}}(\mathbf{R}')\rangle_z -$$

$$\sum_b \int d\mathbf{r}' \Omega_{p_n d_b}(\mathbf{r}'; z) \langle \delta \bar{\mathbf{d}}_b(\mathbf{r}') \rangle_z -$$

$$\sum_{\bar{a}\bar{b}} \sum_{\nu'\mu'} \int d\mathbf{R}'' \int d\mathbf{R}''' \Omega_{p_n G_{\bar{a}\bar{b}}^{\nu'\mu'}}(\mathbf{R}'', \mathbf{R}'''; z) \langle \delta \bar{G}_{\bar{a}\bar{b}}^{\nu'\mu'}(\mathbf{R}'', \mathbf{R}''') \rangle_z =$$

$$\langle \delta \hat{p}_n \rangle^{t=0},$$

where $\delta \hat{p}_n = (\delta \hat{N}_{l,l'}, \delta \bar{n}_a(\mathbf{r}), \delta \bar{n}_{\bar{a}}^{\nu}(\mathbf{R}), \delta \bar{\mathbf{d}}_a(\mathbf{r}), \delta \bar{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}'))$.
Here $\delta \hat{N}_{ll'} = \hat{N}_{ll'} - \langle \hat{N}_{ll'} \rangle_0$, $\delta \bar{n}_a(\mathbf{r}) = \bar{n}_a(\mathbf{r}) - \langle \bar{n}_a(\mathbf{r}) \rangle_0$,
$\delta \bar{n}_{\bar{a}}^{\nu}(\mathbf{R}) = \bar{n}_{\bar{a}}^{\nu}(\mathbf{R}) - \langle \bar{n}_{\bar{a}}^{\nu}(\mathbf{R}) \rangle_0$, $\delta \bar{\mathbf{d}}_a(\mathbf{r}) = \bar{\mathbf{d}}_a(\mathbf{r}) - \langle \bar{\mathbf{d}}_a(\mathbf{r}) \rangle_0$,
$\delta \bar{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') = \bar{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') - \langle \bar{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') \rangle_0$ where average values are
calculated with the use of equilibrium statistical operator

$$\rho_0 = Z^{-1} \exp\{-\beta(H - \sum_{ll'} b_0(l, l') \hat{N}_{ll'} - \tag{3.3}$$

$$\sum_a \int d\mathbf{r} \mu_a(\mathbf{r}) \hat{n}_a(\mathbf{r}) - \sum_{\bar{a}} \sum_{\nu} \int d\mathbf{R} \mu_{\bar{a}}^{\nu}(\mathbf{R}) \hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) -$$

$$\sum_{\bar{a}\bar{b}} \sum_{\nu\mu} \int d\mathbf{R} d\mathbf{R}' M_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R}, \mathbf{R}') \hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R}, \mathbf{R}'))\},$$

$$Z = \mathrm{Sp}\, \exp\{-\beta(H - \sum_{ll'} b_0(l, l') \hat{N}_{ll'} - \tag{3.4}$$

$$\sum_a \int d\mathbf{r} \mu_a(\mathbf{r}) \hat{n}_a(\mathbf{r}) - \sum_a \sum_{\nu} \int d\mathbf{R} \mu_{\bar{a}}^{\nu}(\mathbf{R}) \hat{n}_{\bar{a}}^{\nu}(\mathbf{R})) -$$

$$\sum_{\bar{a}\bar{b}} \sum_{\nu\mu} \int d\mathbf{R} d\mathbf{R}' M_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R}, \mathbf{R}') \hat{G}_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R}, \mathbf{R}')\}$$

is the grand partition sum of the system "metal - adsorbate - gas". $\mu_a(\mathbf{r})$, $\mu_{\bar{a}}^{\nu}(\mathbf{R})$ are local equilibrium values chemical potentials of nonadsorbed and adsorbed gas atoms. $\langle \ldots \rangle_0 = \mathrm{Sp}(\ldots \rho_0)$. Exclusion of parameters $\beta \delta b(l, l'; t)$, $\beta \delta \mu_a(\mathbf{r}; t)$, $\beta \delta \mu_{\bar{a}}^{\nu}(\mathbf{R}; t)$ and $M_{\bar{a}\bar{b}}^{\nu,\mu}(\mathbf{R}, \mathbf{R}')$ in $\rho_q(t)'$ with the help of self-consistency conditions (2.12) results in appearing of corresponding orthogonal variables

$$\bar{n}_a(\mathbf{r}) = \hat{n}_a(\mathbf{r}) - \sum_{\substack{l,l' \\ j,j'}} \langle \hat{n}_a(\mathbf{r}) \hat{N}_{ll'} \rangle_0 \Phi_{NN}^{-1}(l, l'; j, j') \hat{N}_{jj'},$$

$$\bar{n}_{\bar{a}}^{\nu}(\mathbf{R}) = \hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) - \sum_{\substack{l,l' \\ j,j'}} \langle \hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) \hat{N}_{ll'} \rangle_0 \Phi_{NN}^{-1}(l, l'; j, j') \hat{N}_{jj'} -$$

$$\sum_{ab} \int d\mathbf{r} \int d\mathbf{r}' \langle \hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) \bar{n}_a(\mathbf{r}) \rangle_0 [\Phi_{nn}^{-1}(\mathbf{r}\mathbf{r}')]_{ab} \bar{n}_b(\mathbf{r}')$$

$$\bar{\mathbf{d}}_a(\mathbf{r}) = \hat{\mathbf{d}}_a(\mathbf{r}) - \sum_{\substack{l,l' \\ j,j'}} \langle \hat{\mathbf{d}}_a(\mathbf{r}) \hat{N}_{ll'} \rangle_0 \Phi_{NN}^{-1}(l, l'; j, j') \hat{N}_{jj'} -$$

$$\sum_{a'b} \int d\mathbf{r}' \int d\mathbf{r}'' \langle \hat{\mathbf{d}}_a(\mathbf{r}) \bar{n}_{a'}(\mathbf{r}') \rangle_0 [\Phi_{nn}^{-1}(\mathbf{r}'\mathbf{r}'')]_{a'b} \bar{n}_b(\mathbf{r}'') -$$

$$\sum_{\bar{a}\bar{b}} \sum_{\nu'\mu'} \int d\mathbf{R}' \int d\mathbf{R}'' \langle \hat{\mathbf{d}}_a(\mathbf{r}) \bar{n}_{\bar{a}}^{\nu'} \mathbf{R}') \rangle_0$$

$$[\Phi_{nn}^{-1}(\mathbf{R}'\mathbf{R}'')]_{\bar{a}\bar{b}}^{\nu'\mu'} \bar{n}_{\bar{b}}^{\mu'}(\mathbf{R}''),$$

$$\bar{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') = \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') - \sum_{\substack{l,l' \\ j,j'}} \langle \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') \hat{N}_{ll'} \rangle_0$$

$$\Phi_{NN}^{-1}(l, l'; j, j') \hat{N}_{jj'} -$$

$$\sum_{a'b} \int d\mathbf{r}' \int d\mathbf{r}'' \langle \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') \bar{n}_{a'}(\mathbf{r}') \rangle_0$$

$$[\Phi_{nn}^{-1}(\mathbf{r}'\mathbf{r}'')]_{a'b} \bar{n}_b(\mathbf{r}'') -$$

$$\sum_{\bar{a}'\bar{b}'} \sum_{\nu'\mu'} \int d\mathbf{R}'' \int d\mathbf{R}''' \langle \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') \bar{n}_{\bar{a}}^{\nu'} \mathbf{R}'') \rangle_0$$

$$[\Phi_{nn}^{-1}(\mathbf{R}''\mathbf{R}''')]_{\bar{a}'\bar{b}'}^{\nu'\mu'} \bar{n}_b^{\mu'}(\mathbf{R}''')$$

$$\sum_{a'b} \int d\mathbf{r}' \int d\mathbf{r}'' \langle \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') \bar{\mathbf{d}}_{a'}(\mathbf{r}') \rangle_0$$

$$[\Phi_{dd}^{-1}(\mathbf{r}'\mathbf{r}'')]_{a'b} \bar{\mathbf{d}}_b(\mathbf{r}'')$$

Conditions of orthogonality for these variables are valid: $\langle \bar{n}_a(\mathbf{r}) \hat{N}_{jj'} \rangle_0 = 0$, $\langle \bar{n}_{\bar{a}}^{\nu}(\mathbf{R}) \hat{N}_{jj'} \rangle_0 = 0$, $\langle \bar{n}_a(\mathbf{r}) \bar{n}_{\bar{a}}^{\nu}(\mathbf{R}) \rangle_0 = 0$, $\langle \bar{n}_a(\mathbf{r}) \bar{\mathbf{d}}_{a'}(\mathbf{r}') \rangle_0 = 0$, $\langle \bar{n}_a(\mathbf{r}) \bar{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') \rangle_0 = 0$. Functions $\Phi_{NN}^{-1}(l, l'; j, j')$, $[\Phi_{nn}^{-1}(\mathbf{r}, \mathbf{r}')]_{ab}$ i $[\Phi_{nn}^{-1}(\mathbf{R}, \mathbf{R}')]_{\bar{a}\bar{b}}^{\nu\mu}$ are inversed to corresponding equilibrium correlation functions:

$$\Phi(ll', jj') = \langle \hat{N}_{ll'} \hat{N}_{jj'} \rangle_0, \tag{3.5}$$

for electron and gas subsystems

$$\Phi_{ab}(\mathbf{r}, \mathbf{r}') = \langle \bar{n}_a(\mathbf{r}) \bar{n}_b(\mathbf{r}') \rangle_0, \tag{3.6}$$

$$\Phi_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R},\mathbf{R}') = \langle \bar{n}_{\bar{a}}^{\nu}(\mathbf{R})\bar{n}_{\bar{b}}^{\mu}(\mathbf{R}')\rangle_0 \qquad (3.7)$$

and defined from corresponding integral relations [19].

$$\Omega_{AB}(z) = i\Omega_{AB} - \varphi_{AB}(z), \qquad (3.8)$$

$i\Omega_{AB}$ are normalized static correlation functions, they read:

$$i\Omega_{AB} = \langle \dot{\hat{A}}\hat{B}\rangle_0 \Phi_{BB}^{-1}, \qquad (3.9)$$

where $\hat{B}, \hat{A} = \left\{ \hat{N}_{ll'}, \bar{n}_a(\mathbf{r}), \bar{n}_{\bar{a}}(\mathbf{R})\right\}$, $\bar{\mathbf{d}}_{a'}(\mathbf{r}')$, $\bar{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R},\mathbf{R}')$, $\dot{\hat{A}} = iL_N\hat{A}$. $\varphi_{AB}(t,t')$ are normalized transport cores with the structure like this

$$\bar{\varphi}_{AB}(t,t') = \langle \bar{I}_A T_0(t,t')\bar{I}_B\rangle_0 \Phi_{AB}^{-1}, \qquad (3.10)$$

$$\bar{I}_A, \bar{I}_B = \left\{ \bar{I}_N(l,l'), \bar{I}_a(\mathbf{r}), \bar{I}_{\bar{a}}^{\nu}(\mathbf{R})\bar{I}_d^a(\mathbf{r}), \bar{I}_{G_{\bar{a}\bar{b}}}^{\nu\mu}(\mathbf{R}\mathbf{R}')\right\}.$$

where

$$T_0(t,t') = \exp\left\{-(t'-t)(1-\mathcal{P}_0)iL_N\right\}$$

is the evolution operator in the linear approximation;

$$\bar{I}_N(l,l') = (1-\mathcal{P}_0)\dot{\hat{N}}_{ll'},$$

$$\bar{I}_a(\mathbf{r}) = (1-\mathcal{P}_0)\dot{\bar{n}}_a(\mathbf{r}),$$

$$\bar{I}_{\bar{a}}^{\nu}(\mathbf{R}) = (1-\mathcal{P}_0)\dot{\bar{n}}_{\bar{a}}^{\nu}(\mathbf{R})$$

$$\bar{I}_d^a(\mathbf{r}) = (1-\mathcal{P}_0)\dot{\bar{\mathbf{d}}}_{a'}(\mathbf{r}'),$$

$$\bar{I}_{G_{\bar{a}\bar{b}}}^{\nu\mu}(\mathbf{R}\mathbf{R}') = (1-\mathcal{P}_0)\dot{\bar{G}}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R},\mathbf{R}')$$

are generalized flows in the linear approximation, where Mori projection operator $\mathcal{P}_0$ has the following structure

$$\mathcal{P}_0(\dots) = \langle\dots\rangle_0 + \sum_{\substack{l,l'\\j,j'}}\langle\dots\hat{N}_{ll'}\rangle_0\Phi^{-1}(l,l';j,j')\hat{N}_{jj'}+$$

$$\sum_{ab}\int d\mathbf{r}\int d\mathbf{r}'\langle\dots\bar{n}_a(\mathbf{r})\rangle_0[\Phi_{nn}^{-1}(\mathbf{r},\mathbf{r}')]_{ab}\bar{n}_b(\mathbf{r}')+$$

$$\sum_{\bar{a}\bar{b}}\sum_{\nu\nu'}\int d\mathbf{R}\int d\mathbf{R}'\langle\dots\bar{n}_{\bar{a}}^{\nu}(\mathbf{R})\rangle_0\left[\Phi_{nn}^{-1}(\mathbf{R},\mathbf{R}')\right]_{\bar{a}\bar{b}}^{\nu\nu'}\bar{n}_{\bar{b}}^{\nu'}(\mathbf{R}')+$$

$$\sum_{a'b}\int d\mathbf{r}'\int d\mathbf{r}''\langle\dots\bar{\mathbf{d}}_{a'}(\mathbf{r}')\rangle_0[\Phi_{dd}^{-1}(\mathbf{r}'\mathbf{r}'')]_{a'b}\bar{\mathbf{d}}_b(\mathbf{r}'')+$$

$$\sum_{\bar{a}\bar{b}}\sum_{\bar{a}'\bar{b}'}\sum_{\nu\nu'}\sum_{\mu\mu'}\int d\mathbf{R}\int d\mathbf{R}'\int d\mathbf{R}''\int d\mathbf{R}'''\langle\dots\bar{G}_{\bar{a}\bar{b}}^{\nu\nu'}(\mathbf{R},\mathbf{R}')\rangle_0$$

$$[\Phi_{GG}(\mathbf{R},\mathbf{R}',\mathbf{R}'',\mathbf{R}''')]_{\bar{a}\bar{b}\bar{a}'\bar{b}'}^{\nu\nu'\mu\mu'}\bar{G}_{\bar{a}'\bar{b}'}^{\mu\mu'}(\mathbf{R}'',\mathbf{R}''').$$

Its operator properties are as usual: $\mathcal{P}_0\mathcal{P}_0 = \mathcal{P}_0$, $\mathcal{P}_0(1-\mathcal{P}_0) = 0$, $\mathcal{P}_0\hat{N}_{ll'} = \hat{N}_{ll'}$, $\mathcal{P}_0\bar{n}_a(\mathbf{r}) = \bar{n}_a(\mathbf{r})$, $\mathcal{P}_0\bar{n}_{\bar{a}}^{\nu}(\mathbf{R}) = \bar{n}_{\bar{a}}^{\nu}(\mathbf{R})$, $\mathcal{P}_0\bar{\mathbf{d}}_a(\mathbf{r}) = \bar{\mathbf{d}}_a(\mathbf{r})$, $\mathcal{P}_0\bar{G}_{\bar{a}\bar{b}}^{\nu\nu'}(\mathbf{R},\mathbf{R}') = \bar{G}_{\bar{a}\bar{b}}^{\nu\nu'}(\mathbf{R},\mathbf{R}')$.

The set of transport equations for weakly nonequilibrium case is linear, closed and describes kinetic electron and atomic diffusion - reaction processes consistently. Functions $i\Omega_{AB}$ (2.22) are static correlation functions and can be expressed via the corresponding interparticle potentials of interactions and structural equilibrium distribution functions of electrons and atoms of our system. $\bar{\varphi}_{AB}(t,t')$ are time correlation functions which are built on generalized flows and describe dissipative processes in a system. In particular, $\bar{\varphi}_{NN}(l,l';j,j';t,t')$ describe interelectron dissipative processes, $\bar{\varphi}_{aa}(\mathbf{r},\mathbf{r}';t,t')$, $\bar{\varphi}_{\bar{a}\bar{a}}^{\nu\nu'}(\mathbf{R},\mathbf{R}';t,t')$ describe nonuniform diffusion processes of adsorbed and nonadsorbed gas atoms. All others memory functions describe cross dissipative correlations of flows of electrons and atoms in spatially inhomogeneous system "metal - adsorbate - gas". Set of transport equations (2.22) allows limiting cases. In particular, if formally one neglects of diffusion - reaction processes of adsorbed and nonadsorbed gas atoms, then electron kinetics in a system of metal surface is described by an equation for nonequilibrium one-electron density matrix. Using the propertis $\delta\hat{p}_n = \delta\hat{N}_{l,l'}$ in the (2.22), such an equation can be represented in a form

$$z\langle\delta\hat{N}_{ll'}\rangle_z - \sum_{j,j'}\Omega_{NN}(l,l';j,j';z)\langle\delta\hat{N}_{j,j'}\rangle_z = \langle\delta\hat{N}_{ll'}\rangle^{t=0}, \qquad (3.11)$$

where

$$\Omega_{NN}(l,l';j,j';z) = i\Omega_{NN}(l,l';j,j') - \bar{\varphi}_{NN}(l,l';j,j';z)$$

is the mass operator of an electron subsystem. This set of equations allows to define elements of one-electron density matrix $\langle\hat{a}_{f\nu\sigma}^{+}\hat{p}_{l\xi\sigma'}\rangle^t$. Electron tunnelling current between positions f and l on a metal surface is then expressed via these elements. Another limiting case can be obtained if one formally does not take into consideration the electron kinetic processes, whereas the interaction of adsorbed atoms and substrate considers to be classical only. Then the set (2.22) transfers to a set of nonuniform diffusion - reaction equations of adsorbed and nonadsorbed

gas atoms:

$$\frac{\partial}{\partial t}\langle\delta\hat{n}_a(\mathbf{r})\rangle^t = -\sum_b \int d\mathbf{r}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}\frac{\partial}{\partial \mathbf{r}}D_{ab}(\mathbf{r},\mathbf{r}';t,t')$$

$$\frac{\partial}{\partial \mathbf{r}'}\langle\delta\hat{n}_b(\mathbf{r}')\rangle^{t'}dt'$$

$$+\sum_{\bar{b}}\sum_{\nu'}\int d\mathbf{R}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}\frac{\partial}{\partial \mathbf{r}}D_{a\bar{b}}^{\nu'}(\mathbf{r},\mathbf{R}';t,t') \qquad (3.12)$$

$$\frac{\partial}{\partial \mathbf{R}'}\langle\delta\bar{n}_{\bar{b}}^{\nu'}(\mathbf{R}')\rangle^{t'}dt'-$$

$$+\sum_{\bar{a}\bar{b}}\sum_{\nu'\mu'}\int d\mathbf{R}'' \int d\mathbf{R}''' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}\frac{\partial}{\partial \mathbf{r}}K_{n_a G_{\bar{a}\bar{b}}}^{\nu'\mu'}(\mathbf{r};\mathbf{R}'',\mathbf{R}''';t,t')$$

$$\langle\delta\bar{G}_{\bar{a}\bar{b}}^{\nu'\mu'}(\mathbf{R}'',\mathbf{R}''')\rangle^{t'}dt',$$

$$\frac{\partial}{\partial t}\langle\delta\bar{n}_{\bar{a}}^{\nu}(\mathbf{R})\rangle^t = -\sum_{\bar{b}}\sum_{\nu'}\int d\mathbf{R}'\frac{\partial}{\partial \mathbf{R}}D_{\bar{a}\bar{b}}^{\nu\nu'}(\mathbf{R},\mathbf{R}';t,t')$$

$$\frac{\partial}{\partial \mathbf{R}'}\langle\delta\bar{n}_{\bar{b}}^{\nu'}(\mathbf{R}')\rangle^{t'}dt'$$

$$-\sum_b \int d\mathbf{r}'\frac{\partial}{\partial \mathbf{R}}D_{\bar{a}b}^{\nu}(\mathbf{R},\mathbf{r}';t,t') \qquad (3.13)$$

$$\frac{\partial}{\partial \mathbf{r}'}\langle\delta\hat{n}_b(\mathbf{r})\rangle^{t'}dt'+$$

$$+\sum_{\bar{a}'\bar{b}}\sum_{\nu'\mu'}\int d\mathbf{R}'' \int d\mathbf{R}''' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}\frac{\partial}{\partial \mathbf{R}}K_{n_{\bar{a}}G_{\bar{a}'\bar{b}}}^{\nu,\nu'\mu'}(\mathbf{R};\mathbf{R}'',\mathbf{R}''';t,t')$$

$$\langle\delta\bar{G}_{\bar{a}'\bar{b}}^{\nu'\mu'}(\mathbf{R}'',\mathbf{R}''')\rangle^{t'}dt',$$

$$\frac{\partial}{\partial t}\langle\delta\bar{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R},\mathbf{R}')\rangle^t = \sum_b \int d\mathbf{r}' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}K_{G_{\bar{a}\bar{b}}n_b}^{\nu\mu}(\mathbf{R},\mathbf{R}';\mathbf{r}';t,t')$$

$$\frac{\partial}{\partial \mathbf{r}'}\langle\delta\hat{n}_b(\mathbf{r}')\rangle^{t'}dt'$$

$$+\sum_{\bar{b}'}\sum_{\nu'}\int d\mathbf{R}'' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}K_{G_{\bar{a}\bar{b}}n_{\bar{b}'}}^{\nu\mu,\nu'}(\mathbf{R},\mathbf{R}';\mathbf{R}'';t,t') \qquad (3.14)$$

$$\frac{\partial}{\partial \mathbf{R}'}\langle\delta\bar{n}_{\bar{b}'}^{\nu'}(\mathbf{R}'')\rangle^{t'}dt'$$

$$-\sum_{\bar{a}'\bar{b}'}\sum_{\nu'\mu'}\int d\mathbf{R}'' \int d\mathbf{R}''' \int\limits_{-\infty}^{t} e^{\epsilon(t'-t)}K_{G_{\bar{a}\bar{b}}G_{\bar{a}'\bar{b}'}}^{\nu\mu,\nu'\mu'}(\mathbf{R},\mathbf{R}';\mathbf{R}'',\mathbf{R}''';t,t')$$

$$\langle\delta\bar{G}_{\bar{a}'\bar{b}}^{\nu'\mu'}(\mathbf{R}'',\mathbf{R}''')\rangle^{t'}dt',$$

where

$$\bar{n}_{\bar{a}}^{\nu}(\mathbf{R}) = \hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) - \sum_{ab}\int d\mathbf{r}d\mathbf{r}'\langle\hat{n}_{\bar{a}}^{\nu}(\mathbf{R})\hat{n}_a(\mathbf{r})\rangle_0[\Phi_{nn}^{-1}]_{ab}(\mathbf{r},\mathbf{r}')\hat{n}_b(\mathbf{r}')$$

$$\bar{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R},\mathbf{R}') = \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R},\mathbf{R}') - \sum_{a'b}\int d\mathbf{r}' \int d\mathbf{r}''\langle\hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R},\mathbf{R}')\hat{n}_{a'}(\mathbf{r}')\rangle_0$$

$$[\Phi_{nn}^{-1}(\mathbf{r}'\mathbf{r}'')]_{a'b}\hat{n}_b(\mathbf{r}'')-$$

$$\sum_{\bar{a}'\bar{b}'}\sum_{\nu'\mu'}\int d\mathbf{R}'' \int d\mathbf{R}'''\langle\hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\mathbf{R},\mathbf{R}')\bar{n}_{\bar{a}'}^{\nu'}(\mathbf{R}'')\rangle_0$$

$$[\Phi_{nn}^{-1}(\mathbf{R}''\mathbf{R}''')]_{\bar{a}'\bar{b}'}^{\nu'\mu'}\bar{n}_{\bar{b}}^{\mu'}(\mathbf{R}''')$$

and $D_{aa}(\mathbf{r},\mathbf{r}';t,t')$, $D_{a\bar{a}}^{\nu'}(\mathbf{r},\mathbf{R}';t,t')$, $D_{\bar{a}a}^{\nu}(\mathbf{R},\mathbf{r}';t,t')$, $D_{\bar{a}\bar{a}}^{\nu\nu'}(\mathbf{R},\mathbf{R}';t,t')$ are generalized nonuniform diffusion coefficients of non-adsorbed and adsorbed gas atoms on metal surface. In particular, coefficient $D_{ab}(\mathbf{r},\mathbf{r}';t,t')$ reads:

$$D_{ab}(\mathbf{r},\mathbf{r}';t,t') = \sum_{b'}\int d\mathbf{r}''\langle(1-\mathcal{P}_0)\hat{\mathbf{I}}_a(\mathbf{r})T_0(t,t')(1-\mathcal{P}_0)\hat{\mathbf{I}}_{b'}(\mathbf{r}'')\rangle_0 \quad (3.15)$$

$$[\Phi_{nn}^{-1}(\mathbf{r}'',\mathbf{r}')]_{b'b},$$

$\hat{\mathbf{I}}_a(\mathbf{r}) = \frac{1}{m_a}\hat{\mathbf{p}}_a(\mathbf{r})$ is the density of a gas atoms flow. Functions $[\Phi_{nn}^{-1}(\mathbf{r}'',\mathbf{r}')]_{ab}$ are defined from the integral equation

$$\sum_{b'}\int d\mathbf{r}''\Phi_{ab'}(\mathbf{r},\mathbf{r}'')[\Phi_{nn}^{-1}(\mathbf{r}'',\mathbf{r}')]_{b'b} = \delta(\mathbf{r}-\mathbf{r}')\delta_{ab},$$

where

$$\Phi_{ab}(\mathbf{r},\mathbf{r}') = \langle\hat{n}_a(\mathbf{r})\hat{n}_b(\mathbf{r}')\rangle_0$$

is the equilibrium pair distribution of gas atoms. Then, from the integral equation like above one can obtain the relation:

$$[\Phi_{nn}^{-1}(\mathbf{r}'', \mathbf{r}')]_{ab} = \frac{\delta(\mathbf{r} - \mathbf{r}')}{\langle \hat{n}_a(\mathbf{r}')\rangle_0} \delta_{ab} - c_2^{ab}(\mathbf{r}, \mathbf{r}'),$$

$\langle \hat{n}_a(\mathbf{r}')\rangle_0$ is unary distribution function, whereas $c_2^{ab}(\mathbf{r}, \mathbf{r}')$ is direct distribution function of gas atoms. Diffusion coefficients $D_{a\bar{a}}^{\nu'}(\mathbf{r}, \mathbf{R}'; t, t')$, $D_{\bar{a}a}^{\nu}(\mathbf{R}, \mathbf{r}'; t, t')$, $D_{\bar{a}\bar{a}}^{\nu\nu'}(\mathbf{R}, \mathbf{R}'; t, t')$ have structure similar to D_{aa} and are a generalization of Green-Kubo formulae for diffusion in spatially inhomogeneous systems. Their calculations depend on processes under consideration: long-time or short-time.

Transport core

$$K_{G_{\bar{a}\bar{b}} n_b}^{\nu\mu}(\mathbf{R}, \mathbf{R}'; \mathbf{r}'; t, t'),$$

$$K_{n_{\bar{a}} G_{\bar{a}'\bar{b}}}^{\nu, \nu'\mu'}(\mathbf{R}; \mathbf{R}'', \mathbf{R}'''; t, t'),$$

$$K_{G_{\bar{a}\bar{b}} G_{\bar{a}'\bar{b}'}}^{\nu\mu, \nu'\mu'}(\mathbf{R}, \mathbf{R}'; \mathbf{R}'', \mathbf{R}'''; t, t')$$

are higher memory functions and describe duffusion - reaction processes un the system.They have the following structure:

$$K_{G_{\bar{a}\bar{b}} n_b}^{\nu\mu}(\mathbf{R}, \mathbf{R}'; \mathbf{r}'; t, t') = \qquad (3.16)$$

$$\sum_{b'} \int d\mathbf{r}'' \langle \bar{I}_{G_{\bar{a}\bar{b}}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') T_0(t, t') \bar{I}_{b'}(\mathbf{r}'')\rangle_0 [\Phi_{nn}^{-1}(\mathbf{r}'', \mathbf{r}')]_{b'b},$$

$$K_{G_{\bar{a}\bar{b}} n_{\bar{a}}'}^{\nu, \mu\nu'}(\mathbf{R}; \mathbf{R}', \mathbf{R}''; t, t') = \qquad (3.17)$$

$$\sum_{\mu'\bar{b}'} \int d\mathbf{R}''' \langle \bar{I}_{G_{\bar{a}\bar{b}}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') T_0(t, t') \bar{I}_{\bar{b}'}^{\mu'}(\mathbf{R}''')\rangle_0 [\Phi_{nn}^{-1}(\mathbf{R}''', \mathbf{R}'')]_{\bar{b}'\bar{a}'}^{\nu, \mu},$$

$$K_{G_{\bar{a}\bar{b}} G_{\bar{a}'\bar{b}'}}^{\nu, \mu\nu'\mu'}(\mathbf{R}; \mathbf{R}', \mathbf{R}'', \mathbf{R}'''; t, t') = \qquad (3.18)$$

$$\sum_{\gamma\gamma'} \sum_{\bar{c}\bar{c}'} \int d\mathbf{R}_4 \int d\mathbf{R}_5 \langle \bar{I}_{G_{\bar{a}\bar{b}}}^{\nu\mu}(\mathbf{R}, \mathbf{R}') T_0(t, t') \bar{I}_{G_{\bar{c}\bar{c}'}}^{\gamma\gamma'}(\mathbf{R}_4, \mathbf{R}_5)\rangle_0$$

$$[\Phi_{GG}^{-1}(\mathbf{R}_4, \mathbf{R}_5 \mathbf{R}'', \mathbf{R}''')]_{\bar{c}\bar{c}'\bar{a}'\bar{b}'}^{\gamma\gamma'\nu',\mu'},$$

where $[\Phi_{GG}^{-1}(\mathbf{R}_4, \mathbf{R}_5 \mathbf{R}'', \mathbf{R}''')]_{\bar{c}\bar{c}'\bar{a}'\bar{b}'}^{\gamma\gamma'\nu',\mu'}$ are the elements of inverse matrice (can be found with the help of integral relations of type (2.32)) to the matrices, the elements of which are the equilibrium quantum correlation functions

$$\Phi_{\bar{c}\bar{c}'\bar{a}'\bar{b}'}^{\gamma\gamma'\nu',\mu'}(\mathbf{R}_4, \mathbf{R}_5 \mathbf{R}'', \mathbf{R}''') = \langle \bar{G}_{\bar{c}\bar{c}'}^{\gamma\gamma'}(\mathbf{R}_4, \mathbf{R}_5) G_{\bar{a}'\bar{b}'}^{\nu',\mu'}(\mathbf{R}'', \mathbf{R}''')\rangle_0 \qquad (3.19)$$

for the adsorbed atoms in corresponding states on the metal surface.

Correlation functions (3.26)-(3.28) are expressed via the four- three- two- and one- paricle quantum distribution functions. Problems of thier calculation is one of the most important in equilibrium statistical mechanics. For our case an additional complication arises due to the complexity of "metal - adsorbate - gas" system. The mentioned above correlation functions can be calculated as the functional derivatives of equilibrium Massie - Planck functional value, i.e. grand statistical sum: $\Phi = \ln Z$. In particular, the equilibrium correlation functions (3.26) - (3.28), (3.40) are expressed via the equilibrium functions:

$$\langle \hat{n}_a(\mathbf{r}) \hat{n}_b(\mathbf{r}')\rangle_0, \quad \langle \hat{N}_{ll'} \hat{N}_{jj'}\rangle_0,$$

$$\langle \hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) \hat{n}_{\bar{b}}^{\mu}(\mathbf{R}')\rangle_0, \quad \langle \hat{G}_{\bar{c}\bar{c}'}^{\gamma\gamma'}(\mathbf{R}_4, \mathbf{R}_5) \hat{G}_{\bar{a}'\bar{b}'}^{\nu'\mu'}(\mathbf{R}'', \mathbf{R}''')\rangle_0$$

$$\langle \hat{n}_a(\mathbf{r}) \hat{n}_{\bar{b}}^{\mu}(\mathbf{R}')\rangle_0, \quad \langle \hat{G}_{\bar{c}\bar{c}'}^{\gamma\gamma'}(\mathbf{R}_4, \mathbf{R}_5) \hat{n}_{\bar{b}}^{\mu}(\mathbf{R}')\rangle_0,$$

which are calculated for the equilibrium statistical operator ρ_0 (3.24). As it follows from its structure, the averages, given above, can be expressed via the Massie - Planck functional:

$$\langle \hat{n}_a(\mathbf{r}) \hat{n}_b(\mathbf{r}')\rangle_0 = \frac{\delta^2}{\delta\mu_a(\mathbf{r})\delta\mu_\mathbf{b}(\mathbf{r}')} \ln Z - \frac{\delta}{\delta\mu_a(\mathbf{r})} \ln Z \frac{\delta}{\delta\mu_b(\mathbf{r}')} \ln Z,$$

$$\langle \hat{n}_{\bar{a}}^{\nu}(\mathbf{R}) \hat{n}_{\bar{b}}^{\mu}(\mathbf{R}')\rangle_0 = \frac{\delta^2}{\delta\mu_{\bar{a}}^{\nu}(\mathbf{R})\delta\mu_{\bar{\mathbf{b}}}^{\mu}(\mathbf{R}')} \ln Z -$$

$$\frac{\delta}{\delta\mu_{\bar{a}}^{\nu}(\mathbf{R})} \ln Z \frac{\delta}{\delta\mu_{\bar{b}}^{\mu}(\mathbf{R}')} \ln Z,$$

$$\langle \hat{G}_{\bar{c}\bar{c}'}^{\gamma\gamma'}(\mathbf{R}_4, \mathbf{R}_5) \hat{G}_{\bar{a}'\bar{b}'}^{\nu'\mu'}(\mathbf{R}'', \mathbf{R}''')\rangle_0 =$$

$$\frac{\delta^2}{\delta M_{\bar{c}\bar{c}'}^{\gamma\gamma'}(\mathbf{R}_4, \mathbf{R}_5)\delta M_{\bar{a}'\bar{b}'}^{\nu'\mu'}(\mathbf{R}'', \mathbf{R}''')} \ln Z -$$

$$\frac{\delta}{\delta\delta M_{\bar{c}\bar{c}'}^{\gamma\gamma'}(\mathbf{R}_4, \mathbf{R}_5)} \ln Z \frac{\delta}{\delta M_{\bar{a}'\bar{b}'}^{\nu'\mu'}(\mathbf{R}'', \mathbf{R}''')} \ln Z,$$

$$\langle \hat{N}_{ll'} \hat{N}_{jj'}\rangle_0 = \frac{\delta^2}{\delta b_0(ll')\delta b_0(jj')} \ln Z - \frac{\delta}{\delta b_0(ll')} \ln Z \frac{\delta}{\delta b_0(jj')} \ln Z.$$

Other cross equilibrium function can be obtained from $\ln Z$ in the same way. So, the $\ln Z$, or grand statistical sum (3.25) should be calculated for the "metal - adsorbate - gas" system. This calculation depends much on the choice of the statistical model and can be performed with the help of collective variables method [25], which takes into account the screening effects.

Thus, using the NSO method by D.N.Zubarev, we have obtained generalized transport equations of consistent description of kinetic electron and diffusion- reaction atomic processes in a system "metal-adsorbate-gas". These equations are valid for both strongly and weakly nonequilibrium processes. They can be used for the calculation of one-electron density matrix and, in such a way, for electron currents and nonuniform diffusion and chemical reactions coefficients of adsorbed and non-adsorbed gas atoms on a metal surface. This is very important for the investigation of surface phenomena, in particular, in electron tunnelling scanning and in catalysis processes. It is important to take into consideration phonon oscillations of substrate atoms and study their affection on electron tunnelling processes and diffusion - reaction processes of adsorbed atoms.

It is important to role of local magnetic field, or, more generally, of electromagnetic field of electron - ion metal surface subsystem. Such magnetic feilds effect on ion, electron spin subsystems, and thus can induce local magnetization phenomenon, which together with polarization phenomenon cause the reconstruction of surface, increasing its catalytic activity. Certainly, these electromagnetic processes should be taken into account in catalytic syntesis on nanostructure.

A consideration of these problems in our approach will be the subject of our future work.

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