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Chemical reactions on adsorbing surface: kinetic level of description

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Based on the effective Hubbard model we suggest a statistical description of reaction-diffusion processes for bimolecular chemical reactions of gas particles adsorbed on the metallic surface. The system of transport equations for description of particles diffusion as well as reactions is obtained. We carry out the analysis of the contributions of all physical processes to the formation of diffusion coefficients and chemical reactions constants.

Key words: *reaction-diffusion processes, adsorption, kinetic description*

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1. Introduction

Investigation of diffusion processes of atoms adsorbed on metallic surface, catalytic reactions between adsorbed particles, creation of nanostructures are the topical problems of modern surface physics [1–4]. Usually, these studies are carried out based on the reaction-diffusion type transport equations obtained semi-phenomenologically using various statistical approaches [4–5], with coefficients of adsorption, desorption, diffusion, chemical constant rates defined experimentally. However, these coefficients conceal the mechanisms of certain physical processes depending on atom-atom interaction, interaction between atoms and surface, its electron and polarization properties. In particular, the processes of CO oxidation on a platinum surface are described by chemical kinetics equations based on the ZGB model [6] and its generalizations [7–9]. These equations contain determined adsorption constants of CO and O particles and constant rates of CO_2 synthesis on the surface. Theoretical scheme for diffusion-reaction processes of gaseous mixture in the system "metal-adsorbate-gas" was presented in reference [10], where the authors considered both the kinetics of reacting atoms and the electron structure of surface.

To take into account specified processes on the surface of metal one has to work out in detail the basic model of the system. In references [11,12] such a model was based on the effective Hubbard Hamiltonian allowing particles tunnelling from one site of the lattice to another, oscillation between ground and excited states within quantum well created by surrounding atoms, and interaction with phonons of the surface. This model looks quite attractive for the study of catalytic processes after a minor generalization concerning complex creation. In our paper we proceed in the similar direction allowing bimolecular chemical reactions on the substrate sites. We consider them as instant processes, though being described in quantum statistics manner. It is worth noting that the obtained reaction-diffusion type transport equations possess the same basic property as chemical kinetics equations for classical systems [13–15]; namely, a coupling between diffusion coefficients and reaction rates due to renormalization of transport kernels. In our case this renormalization follows from the inclusion of the two-particle distribution function into the basic set of dynamic variables. We derived the system of kinetic equations using the method of nonequilibrium statistical operator (NSO) of D.N.Zubarev [16]. The formalism presented here resembles the projection operator technique used by the authors of references [13–15] in describing the bimolecular reactions in liquids, though the origin of dissipative processes is quite different. Constant rates have a more complicated form as well, involving all parameters of the initial Hamiltonian.

Our paper is organized as follows: in the second section we present the generalized Hubbard Hamiltonian with taking into consideration the term responsible for chemical reactions. In section 3 the set of kinetic equations for weakly nonequilibrium case is written down. Though being linear in fluctuations of dynamic variables, these equations possess “hidden” nonlinearity which is disclosed by introducing the two-particle correlation function in section 5 with subsequent renormalization of both diffusion coefficients and constant rates. In the preceding section 4 we perform the analysis of partial contributions of all processes into the formation of coherent and incoherent dynamics of the system. Finally, we supply the last section with some conclusions.

2. Effective Hubbard model

The subject of our interest is a four-sort system of adsorbed particles on the metallic surface which allows bimolecular chemical reactions. We picture this surface as a lattice of s sites where atoms are located within quantum wells. An adsorbed atom can tunnel from one site to another, transfer from the ground state to the excited one within the well, interact with phonons of the lattice and react with other atoms. To describe the kinetics of such reactions we use the effective Hubbard model with generalized Hamiltonian

$$H = H_{\mathrm{A}} + H_{\mathrm{ph}} + H_{\mathrm{int}} + H_{\mathrm{reac}}, \tag{2.1}$$

where H_{A} corresponds to the atoms adsorbed on the metal surface:

$$\begin{aligned} H_{\mathrm{A}} &= \sum_{f,f',\sigma}\sum_{\alpha}(-t_0^{\alpha}a^{\dagger}_{\alpha f0\sigma}a_{\alpha f'0\sigma}+t_1^{\alpha}a^{\dagger}_{\alpha f1\sigma}a_{\alpha f'1\sigma}) \\ &+\sum_{\alpha f}\frac{W_{\alpha}}{2}(n_{\alpha f1}-n_{\alpha f0})+\sum_{\alpha f}\frac{U_{\alpha}}{2}n_{\alpha f}(n_{\alpha f}-1); \end{aligned} \tag{2.2}$$

we use notations f, f' for numeration of adsorbing sites (AS) on which particles locate in the ground (0) and excited (1) states with corresponding tunnelling amplitudes $(t_0^{\alpha}, t_1^{\alpha})$ from one AS f to another f'; σ means spin label. W_{α} denotes vibrational frequency within a well between ground and excited states of the adsorbed atom; $a^{\dagger}_{\alpha fi\sigma}$, $a_{\alpha fi\sigma}$ are creation and annihilation Fermi operators for the atoms of sort α in AS f, vibrational state i and with spin σ,

$$f_{\alpha fi\sigma}=a^{\dagger}_{\alpha fi\sigma}a_{\alpha fi\sigma} \tag{2.3}$$

stands for the density operator for the atoms of sort α with quantum numbers f, i, σ; U_{α} denotes the intrasite repulsion energy. Besides,

$$f_{\alpha fi}=\sum_{\sigma}f_{\alpha fi\sigma},\quad f_{\alpha f}=f_{\alpha f0}+f_{\alpha f1}. \tag{2.4}$$

Hamiltonian of phonon subsystem which describes metallic surface has the form

$$H_{\mathrm{ph}}=\sum_{k}\hbar\omega_k\left(b^{\dagger}_k b_k+\frac{1}{2}\right)+H^{\mathrm{int}}_{\mathrm{ph}}, \tag{2.5}$$

where $b^{\dagger}_k$, b_k correspond to phonon creation and annihilation operators in normal modes k, while the second term $H^{\mathrm{int}}_{\mathrm{ph}}$ describes the coupling between phonons of substrate and gas particles:

$$H_{\mathrm{int}}=\sum_{\alpha,f}\left[f_{\alpha f}\sum_{k}\gamma^{\alpha}_{fk}(b_k+b^{\dagger}_k)+\sum_{\sigma}(a^{\dagger}_{\alpha f0\sigma}a_{\alpha f1\sigma}+a^{\dagger}_{\alpha f1\sigma}a_{\alpha f0\sigma})\sum_{k}\chi^{\alpha}_{fk}(b_k+b^{\dagger}_k\right], \tag{2.6}$$

with additional assumption that amplitudes of coupling between phonons and adsorbate density γ as well as between phonons and vibrational excitations within each well χ depend only on the sort of the particle and on its localization.

Hamiltonian responsible for chemical reactions between the adsorbed patricles in representation of secondary quantization has the following form:

$$H_{\mathrm{reac}}=\sum_{\bar{\alpha},\bar{\beta},\bar{\alpha}',\bar{\beta}'}\langle\bar{\alpha}',\bar{\beta}'|\Phi_{\mathrm{reac}}|\bar{\alpha},\bar{\beta}\rangle a^{\dagger}_{\bar{\alpha}'}a^{\dagger}_{\bar{\beta}'}a_{\bar{\alpha}}a_{\bar{\beta}}+\langle\bar{\alpha}',\bar{\beta}'|\Phi_{\mathrm{reac}}|\bar{\alpha},\bar{\beta}\rangle^{*}a^{\dagger}_{\bar{\beta}}a^{\dagger}_{\bar{\alpha}}a_{\bar{\beta}'}a_{\bar{\alpha}'}, \tag{2.7}$$

where indexes $\bar{\alpha}$, $\bar{\beta}$ denote the set of all quantum numbers $\{\alpha, f, i, \sigma\}$, $\{\beta, f', i', \sigma'\}$ (sort, number of AS, vibrational state, spin), while $\langle\bar{\alpha}',\bar{\beta}'|\Phi_{\mathrm{reac}}|\bar{\alpha},\bar{\beta}\rangle$ mean reaction amplitudes. One has to point out that Hamiltonian (2.7) describes bimolecular reactions A+B $\rightarrow$ C+D though its generalization to the case of reaction of synthesis A+B $\rightarrow$ AB is straightforward. However, the analysis of complex creation on the metallic surface is a rather complicated separate problem which lies beyond the scope of our investigation. Instead of this, we set our mind on studying the kinetics of chemical reactions. In the next section we present the chain of kinetic equations for unary and binary distribution functions of adsorbed particles in weakly nonequilibrium case.

3. Kinetics of chemically reacting adsorbed particles

To describe the kinetics of chemical reactions on the surface of substrate we introduce nonequilibrium one- and two-particle distribution functions

$$\begin{aligned} \langle f_{\bar\alpha\bar\alpha'}\rangle^t \equiv \langle f_{\alpha fi\sigma,\alpha' f' i'\sigma'}\rangle^t &= \mathrm{Sp}\left[a^{\dagger}_{\alpha' f' i'\sigma'} a_{\alpha fi\sigma}\rho(t)\right], && (3.1)\\ \langle G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\rangle^t &= \mathrm{Sp}\left[a^{\dagger}_{\alpha' f' i'\sigma'} a_{\alpha fi\sigma} a^{\dagger}_{\beta' s' j'\kappa'} a_{\beta sj\kappa}\rho(t)\right], && (3.2)\end{aligned}$$

where $\rho(t)$ denotes a nonequilibrium statistical operator obeying the quantum Liouville equation

$$\left(\frac{\partial}{\partial t}+\mathrm{i}L\right)\rho(t)=0. \qquad (3.3)$$

Here iL stands for Liouville operator defined via commutator with Hamiltonian

$$\mathrm{i}L\rho(t)\equiv\dot\rho(t)=\frac{\mathrm{i}}{\hbar}[H,\rho(t)]. \qquad (3.4)$$

Phonon subsystem (metal surface) will be considered to be equilibrium. However, if one is interested in surface reconstruction processes due to adsorption, chemical reaction, desorption, he needs to include a nonequilibrium phonon distribution function

$$\langle n_{\mathrm{ph}}(k)\rangle^t=\mathrm{Sp}[n_{\mathrm{ph}}(k)\rho(t)], \qquad n_{\mathrm{ph}}(k)=b^{\dagger}_k b_k \qquad (3.5)$$

into the initial basic set of dynamic variables (3.1)–(3.2).

To calculate averages (3.1)–(3.2) or to obtain transport equations one has to solve the quantum Liouville equations for $\rho(t)$. Using the method of nonequilibrium statistical operator, the retarded solutions for $\rho(t)$ could be expressed via a time integral with the relevant (quasiequilibrium) statistical operator $\rho_{\mathrm{rel}}(t)$, for which boundary condition $\rho(t)_{t=t_0}=\rho_{\mathrm{rel}}(t_0)$ is formulated. Relevant statistical operator is constructed from the entropy maximum principle under conditions of fixed parameters of abbreviated description (3.1), (3.2) and normalization to unity. It takes the usual exponential (quasi Gibbs) form

$$\rho_{\mathrm{rel}}(t)=\exp\{-\Phi(t)-\beta(H-\sum_{\bar\alpha\bar\alpha'}\mu_{\bar\alpha\bar\alpha'}(t)f_{\bar\alpha\bar\alpha'}-\sum_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\mu_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}(t)G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'})\}, \qquad (3.6)$$

where

$$\Phi(t)=\ln\mathrm{Sp}\exp\left\{-\beta(H-\sum_{\bar\alpha\bar\alpha'}\mu_{\bar\alpha\bar\alpha'}(t)f_{\bar\alpha\bar\alpha'}-\sum_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\mu_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}(t)G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'})\right\} \qquad (3.7)$$

is the Massier-Planck functional, $\beta=1/k_{\mathrm{B}}T$, (k_{B} denotes Boltzmann constant) while $\mu_{\bar\alpha\bar\alpha'}(t)$, $\mu_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}(t)$ mean Lagrange multipliers determined from self-consistency conditions

$$\begin{aligned} \langle f_{\bar\alpha\bar\alpha'}\rangle^t &= \langle f_{\bar\alpha\bar\alpha'}\rangle^t_{\mathrm{rel}}, && (3.8)\\ \langle G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\rangle^t &= \langle G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\rangle^t_{\mathrm{rel}}. && (3.9)\end{aligned}$$

Diagonal elements $\mu_{\bar{\alpha}\bar{\alpha}}(t)$ denote the time-dependent chemical potential of the particle in $\bar{\alpha}$ state. Diagonal elements of the other Lagrange multiplier sometimes are treated as a chemical potential of the complex on the metallic surface if one allows the synthesis reactions [17] but do not have transparent physical meaning in case of instant bimolecular chemical reactions.

In the framework of NSO method one can obtain the chain of integro-differential equations for averages (3.1)–(3.2). However, these equations in a general case are not closed and are very complicated for analysis. To overcome this complicity we will consider a weakly nonequilibrium approximation which is linear in fluctuations of generalized thermodynamic forces (or, which is the same, linear in fluctuations of dynamic variables), when deviations from corresponding equilibrium values are very small. On the other hand, since we deal with intrinsic nonlinear processes during chemical reactions, we have to exceed the limits of linear kinetics. Taking into consideration two-particle distribution functions, we can effectively proceed further (to quadratic fluctuations) and describe the reaction-diffusion processes on metallic surface. Limiting ourselves by linear approximation in $\delta\mu_{\bar{\gamma}\bar{\gamma}'}(t')$, $\delta\mu_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}(t')$, excluding them from statistical operator $\rho_{\mathrm{rel}}(t)$ due to self-consistency conditions (3.8)–(3.9), we can write down the following system of kinetic equations:

$$\begin{aligned}\frac{\partial}{\partial t}\langle\delta f_{\bar{\alpha}\bar{\alpha}'}\rangle^t \; = \; & \sum_{\bar{\gamma}\bar{\gamma}'}\Omega_{f_{\bar{\alpha}\bar{\alpha}}f_{\bar{\gamma}\bar{\gamma}'}}\langle\delta f_{\bar{\gamma}\bar{\gamma}'}\rangle^t - \sum_{\bar{\gamma}\bar{\gamma}'}\int\limits_{-\infty}^{t}\mathrm{e}^{\varepsilon(t'-t)}\phi_{f_{\bar{\alpha}\bar{\alpha}'}f_{\bar{\gamma}\bar{\gamma}'}}(t,t')\langle\delta f_{\bar{\gamma}\bar{\gamma}'}\rangle^{t'}\mathrm{d}t' \\ & + \sum_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}\Omega_{f_{\bar{\alpha}\bar{\alpha}'}\bar{G}_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}}\langle\delta\bar{G}_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}\rangle^t \\ & - \sum_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}\int\limits_{-\infty}^{t}\mathrm{e}^{\varepsilon(t'-t)}\phi_{f_{\bar{\alpha}\bar{\alpha}'}\bar{G}_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}}(t,t')\langle\delta\bar{G}_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}\rangle^{t'}\mathrm{d}t',\end{aligned} \tag{3.10}$$

$$\begin{aligned}\frac{\partial}{\partial t}\langle\delta\bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}\rangle^t \; = \; & \sum_{\bar{\gamma}\bar{\gamma}'}\Omega_{\bar{G}_{\bar{\alpha}\alpha'\bar{\beta}\bar{\beta}'}f_{\bar{\gamma}\bar{\gamma}'}}\langle\delta f_{\bar{\gamma}\bar{\gamma}'}\rangle^t + \sum_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}\Omega_{\bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}\bar{G}_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}}\langle\delta\bar{G}_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}\rangle^t \\ & - \sum_{\bar{\gamma}\bar{\gamma}'}\int\limits_{-\infty}^{t}\mathrm{e}^{\varepsilon(t'-t)}\phi_{\bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}f_{\bar{\gamma}\bar{\gamma}'}}(t,t')\langle\delta f_{\bar{\gamma}\bar{\gamma}'}\rangle^{t'}\mathrm{d}t' \\ & - \sum_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}\int\limits_{-\infty}^{t}\mathrm{e}^{\varepsilon(t'-t)}\phi_{\bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}\bar{G}_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}}(t,t')\langle\delta\bar{G}_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}\rangle^{t'}\mathrm{d}t',\end{aligned} \tag{3.11}$$

where one has to put $\varepsilon\to 0$ in thermodynamic limit [16], $\delta f_{\bar{\gamma}\bar{\gamma}'} = f_{\bar{\gamma}\bar{\gamma}'} - \langle\delta f_{\bar{\gamma}\bar{\gamma}'}\rangle_0$, $\delta\bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'} = \bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'} - \langle\bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}\rangle_0$ are fluctuations of dynamic variables near their equilibrium values determined by the equilibrium statistical operator ρ_0,

$$\bar{G}_{\bar{\gamma}\bar{\gamma}'\bar{\zeta}\bar{\zeta}'} = G_{\bar{\gamma}\bar{\gamma}'\bar{\zeta}\bar{\zeta}'} - \sum_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}\langle G_{\bar{\gamma}\bar{\gamma}'\bar{\zeta}\bar{\zeta}'}f_{\bar{\alpha}\bar{\alpha}'}\rangle_0\,[\Phi_{ff}]^{-1}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}\,f_{\bar{\beta}\bar{\beta}'}\,, \tag{3.12}$$

$[\Phi^{-1}_{ff}]_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}$ denotes the matrix inverse to the matrix of two-particle equilibrium correlation function $\Phi_{f_{\bar{\alpha}\bar{\alpha}'}f_{\bar{\beta}\bar{\beta}'}} = \langle f_{\bar{\alpha}\bar{\alpha}'}\int_0^1 d\tau\rho_0^{\tau}f_{\bar{\beta}\bar{\beta}'}\rho_0^{-\tau}\rangle_0$, which could be obtained from the relation

$$\sum_{\bar\gamma\bar\gamma'}[\Phi_{ff}]^{-1}_{\bar\alpha\bar\alpha'\bar\gamma\bar\gamma'}\,\Phi_{f_{\bar\gamma\bar\gamma'}f_{\bar\beta\bar\beta'}}=\delta_{\bar\alpha\bar\beta}\delta_{\bar\alpha'\bar\beta'}\,. \tag{3.13}$$

In transport equations (3.10)–(3.11) Ω denotes static correlation functions to be determined as follows:

$$\begin{aligned}
\Omega_{f_{\bar\alpha\bar\alpha'}f_{\bar\beta\bar\beta'}} &= \sum_{\bar\gamma\bar\gamma'}\langle\dot f_{\bar\alpha\bar\alpha'}\int_0^1 \mathrm{d}\tau\rho_0^\tau f_{\bar\gamma\bar\gamma'}\rho_0^{-\tau}\rangle_0\,[\Phi_{ff}]^{-1}_{\bar\gamma\bar\gamma'\bar\beta\bar\beta'}\,, &(3.14)\\
\Omega_{f_{\bar\alpha\bar\alpha'}G_{\bar\beta\bar\beta'\bar\gamma\bar\gamma'}} &= \sum_{\bar\zeta\bar\zeta'\bar\nu\bar\nu'}\langle\dot f_{\bar\alpha\bar\alpha'}\int_0^1 \mathrm{d}\tau\rho_0^\tau \bar G_{\bar\zeta\bar\zeta'\bar\nu\bar\nu'}\rho_0^{-\tau}\rangle_0\,[\Phi_{\bar G\bar G}]^{-1}_{\bar\zeta\bar\zeta'\bar\nu\bar\nu',\bar\beta\bar\beta'\bar\gamma\bar\gamma'}\,, &(3.15)\\
\Omega_{\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}f_{\bar\gamma\bar\gamma'}} &= \sum_{\bar\zeta\bar\zeta'}\langle\dot{\bar G}_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\int_0^1 \mathrm{d}\tau\rho_0^\tau f_{\bar\zeta\bar\zeta'}\rho_0^{-\tau}\rangle_0\,[\Phi_{ff}]^{-1}_{\bar\zeta\bar\zeta'\bar\gamma\bar\gamma'}\,, &(3.16)\\
\Omega_{\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\bar G_{\bar\gamma\bar\gamma'\bar\zeta\bar\zeta'}} &= \sum_{\bar\nu\bar\nu'\bar\kappa\bar\kappa'}\langle\dot{\bar G}_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\int_0^1 \mathrm{d}\tau\rho_0^\tau \bar G_{\bar\nu\bar\nu'\bar\kappa\bar\kappa'}\rho_0^{-\tau}\rangle_0\,[\Phi_{\bar G\bar G}]^{-1}_{\bar\nu\bar\nu'\bar\kappa\bar\kappa',\bar\gamma\bar\gamma'\bar\zeta\bar\zeta'}\,, &(3.17)
\end{aligned}$$

$[\Phi_{\bar G\bar G}]^{-1}$ denotes the matrix inverse to the fourth-order correlation function

$$\Phi_{\bar G_{\bar\gamma\bar\gamma'\bar\zeta\bar\zeta'}\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}}=\langle\bar G_{\bar\gamma\bar\gamma'\bar\zeta\bar\zeta'}\int_0^1 \mathrm{d}\tau\rho_0^\tau\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\rho_0^{-\tau}\rangle_0 \tag{3.18}$$

and is determined in the standard way as

$$\sum_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}[\Phi_{\bar G\bar G}]^{-1}_{\bar\nu\bar\nu'\bar\mu\bar\mu',\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\,\Phi_{\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\bar G_{\bar\gamma\bar\gamma'\bar\zeta\bar\zeta'}}=\delta_{\bar\nu\bar\gamma}\delta_{\bar\nu'\bar\gamma'}\delta_{\bar\mu\bar\zeta}\delta_{\bar\mu'\bar\zeta'}. \tag{3.19}$$

Functions (3.14)–(3.17) describe a non-dissipative dynamics and give coherent contribution to the motion of particles on the metallic surface [12].

In its turn, the dissipative dynamics (diffusion of the particles on substrate sites) is described via kinetic kernels ϕ_{ff} in equations (3.10)–(3.11), which possess the following structure:

$$\begin{aligned}
\phi_{f_{\bar\alpha\bar\alpha'}f_{\bar\beta\bar\beta'}}(t,t') &= \sum_{\bar\gamma\bar\gamma'}\langle\bar I_{f_{\bar\alpha\bar\alpha'}}T^0(t,t')\int_0^1 \mathrm{d}\tau\rho_0^\tau\bar I_{f_{\bar\gamma\bar\gamma'}}\rho_0^{-\tau}\rangle_0\,[\Phi_{ff}]^{-1}_{\bar\gamma\bar\gamma'\bar\beta\bar\beta'}\,, &(3.20)\\
\phi_{f_{\bar\alpha\bar\alpha'}\bar G_{\bar\beta\bar\beta'\bar\gamma\bar\gamma'}}(t,t') &= \sum_{\bar\mu\bar\mu'\bar\nu\bar\nu'}\langle\bar I_{f_{\bar\alpha\bar\alpha'}}T^0(t,t')\int_0^1 \mathrm{d}\tau\rho_0^\tau\bar I_{\bar G_{\bar\nu\bar\nu'\bar\mu\bar\mu'}}\rho_0^{-\tau}\rangle_0\,[\Phi_{\bar G\bar G}]^{-1}_{\bar\nu\bar\nu'\bar\mu\bar\mu',\bar\beta\bar\beta',\bar\gamma\bar\gamma'}\,, &(3.21)\\
\phi_{\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}f_{\bar\gamma\bar\gamma}}(t,t') &= \sum_{\bar\zeta\bar\zeta'}\langle\bar I_{\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}}T^0(t,t')\int_0^1 \mathrm{d}\tau\rho_0^\tau\bar I_{f_{\bar\zeta\bar\zeta'}}\rho_0^{-\tau}\rangle_0\,[\Phi_{ff}]^{-1}_{\bar\zeta\bar\zeta'\bar\gamma\bar\gamma'}\,, &(3.22)\\
\phi_{\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\bar G_{\bar\zeta\bar\zeta'\bar\gamma\bar\gamma'}}(t,t') &= \sum_{\bar\nu\bar\nu'\bar\mu\bar\mu'}\langle\bar I_{\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}}T^0(t,t')\int_0^1 \mathrm{d}\tau\rho_0^\tau\bar I_{\bar G_{\bar\nu\bar\nu'\bar\mu\bar\mu'}}\rho_0^{-\tau}\rangle_0\,[\Phi_{\bar G\bar G}]^{-1}_{\bar\nu\bar\nu'\bar\mu\bar\mu',\bar\zeta\bar\zeta',\bar\gamma\bar\gamma'}\,, &(3.23)
\end{aligned}$$

where $\bar{I}_{f_{\bar{\alpha}\bar{\alpha}'}}$, $\bar{I}_{\bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}}$ denote generalized dissipative fluxes in weakly nonequilibrium approximation defined as follows:

$$\bar{I}_{f_{\bar{\alpha}\bar{\alpha}'}} = (1-\mathcal{P}_0)\dot{f}_{\bar{\alpha}\bar{\alpha}'}, \qquad \bar{I}_{\bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}} = (1-\mathcal{P}_0)\dot{\bar{G}}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}, \tag{3.24}$$

where Mori projection operator $\mathcal{P}_0$ has the following structure:

$$\begin{aligned}\mathcal{P}_0 A \;=\;& \langle A\rangle_0 + \sum_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'} \langle A \int_0^1 \mathrm{d}\tau \rho_0^{\tau} f_{\bar{\alpha}\bar{\alpha}'} \rho_0^{-\tau}\rangle_0 \, [\Phi_{ff}]^{-1}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'} \, f_{\bar{\beta}\bar{\beta}'} \\ &+ \sum_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'} \sum_{\bar{\gamma}\bar{\gamma}'\bar{\zeta}\bar{\zeta}'} \langle A \int_0^1 \mathrm{d}\tau \rho_0^{\tau} \bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'} \rho_0^{-\tau}\rangle_0 \, [\Phi_{\bar{G}\bar{G}}]^{-1}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}',\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'} \, \bar{G}_{\bar{\zeta}\bar{\zeta}'\bar{\gamma}\bar{\gamma}'}\end{aligned} \tag{3.25}$$

and projects any variable A onto the space of dynamic variables f and $\bar{G}$, which are orthogonal to each other due to definition (3.12). $\mathcal{P}_0$ enters the evolution operator $T^0(t,t') = \exp\{(1-\mathcal{P}_0)\mathrm{i}L(t'-t)\}$ and because of its complicated structure render an exact calculation of kinetic kernels (3.20)–(3.23) practically impossible. In reference [12] the diffusion coefficients determined by ϕ_{ff} were calculated in assumption of the absence of cross-correlations between intrawell and interwell processes (as well as between intrawell processes changing the quantum state of the particle). Such diagonalization of the kinetic kernels allowed the authors to obtain the diffusion coefficients D in "neares-neighbours interaction" approximation and to show that D possess some additional, nongeometric, anisotropy due to the coupling of adsorbate motion to the lattice vibrations. Disclaiming any explicit calculation of coherent terms Ω and kinetic kernels ϕ, we perform the analysis of the contribution of each of the processes to the formation of diffusion coefficients. Some words will be said about the possibility of calculations of non-dissipative terms defining coherent motion of adsorbate on the lattice.

4. Partial contributions of various processes on the surface to the formation of coherent and incoherent motion of the adsorbate

Let us dwell our attention on the structure of dissipative fluxes (3.24) more in detail. Taking into account the equilibrium state of phonon subsystem and commutative relations for fermion operators $[a^{\dagger}_{\bar{\alpha}}, a_{\bar{\beta}}]_- = \delta_{\bar{\alpha}\bar{\beta}}$ one can write down the results of Liouville operator action on one-particle dynamic variable $f_{\bar{\alpha}\bar{\alpha}'} = a^{\dagger}_{\bar{\alpha}'}a_{\bar{\alpha}}$. For convenience of the analysis we present contributions from each part of Hamiltonian (2.1) separately. Besides, we note down explicitly the dependence of Fermi operators on the sorts of the particles, AS numbers, vibrational states and spins. We will also suppose that Hubbard repulsion constant U does not depend on the sort of the particles.[1]

[1]Taking the sort-dependent U_α into consideration leads to the 4-th power term in creation and annihilation operators which does not contribute to diffusion coefficients, see the next page.

As a result of the commutator of one-particle dynamic variable $a^{\dagger}_{\bar{\alpha}'}a_{\bar{\alpha}}$ with Hamiltonian of the adsorbed particles (2.2) we have got the following flux:

$$\begin{aligned}
I^{A}_{f_{\bar{\alpha}\bar{\alpha}'}} &= \frac{\mathrm{i}}{\hbar}\left[a^{\dagger}_{\alpha f i\sigma}a_{\alpha' f' i'\sigma'}, H_{\mathrm{A}}\right] \\
&= \frac{\mathrm{i}}{\hbar}\sum_{s'}\Big(-t_0^{\alpha'}a^{\dagger}_{\alpha f i\sigma}a_{\alpha' s' 0\sigma'}\delta_{i'0} + t_0^{\alpha}a^{\dagger}_{\alpha s' 0\sigma}a_{\alpha' f' i'\sigma'}\delta_{i0}\Big) - \Big(0\to 1\Big) \\
&\quad + \frac{\mathrm{i}}{2\hbar}\Big(W_{\alpha'}a^{\dagger}_{\alpha f i\sigma}a_{\alpha' f' 1\sigma'}\delta_{i'1} - W_{\alpha}a^{\dagger}_{\alpha f 1\sigma}a_{\alpha' f' i'\sigma'}\delta_{i1}\Big) - \Big(1\to 0\Big).
\end{aligned} \tag{4.1}$$

From the structure of expression (4.1) for the flux generated by the Hamiltonian of the adsorbed particles it is clear that its diagonal part consists only of the first term. The total number of particles of the sort α does not change due to tunnelling between different AS, oscillations between ground and excited states and Hubbard repulsion: $\sum_{si\sigma} I^{A}_{f_{\alpha si\sigma}f_{\alpha si\sigma}} = 0$. Another thing worth mentioning concerns the linear structure of the current in the combination $a^{\dagger}a$. Since Mori operator is defined on one- and two-particle dynamic variables, the action of $(1-\mathcal{P}_0)$ projects out the contribution (4.1) from the dissipative kernels. Hence, the purely coherent term associated with (2.1) does not contribute to the diffusion of the particles.

The next step is to analyze the contribution of interactive part of Hamiltonian (2.5) into the formation of incoherent dynamics of the system. The flux associated with H_{int} has the following form:

$$\begin{aligned}
I^{\mathrm{int}}_{f_{\bar{\alpha}\bar{\alpha}'}} &= \frac{\mathrm{i}}{\hbar}\left[a^{\dagger}_{\alpha f i\sigma}a_{\alpha' f' i'\sigma'}, H_{\mathrm{int}}\right] \\
&= \frac{\mathrm{i}}{\hbar}\sum_{k}\Big(\gamma^{\alpha'}_{f'k} - \gamma^{\alpha}_{fk}\Big)\Big(b^{\dagger}_{k} + b_{k}\Big)a^{\dagger}_{\alpha f i\sigma}a_{\alpha' f' i'\sigma'} \\
&\quad + \frac{\mathrm{i}}{\hbar}\sum_{k}\Big(b^{\dagger}_{k} + b_{k}\Big)\Big(\chi^{\alpha'}_{f'k}a^{\dagger}_{\alpha f i\sigma}a_{\alpha' f' 1\sigma'}\delta_{i'0} - \chi^{\alpha}_{fk}a^{\dagger}_{\alpha f 0\sigma}a_{\alpha' f' i'\sigma'}\delta_{i1}\Big) + \Big(0\leftrightarrow 1\Big).
\end{aligned} \tag{4.2}$$

Looking at the expression for $I^{\mathrm{int}}_{f_{\bar{\alpha}'}f_{\bar{\alpha}}}$ one can note that its diagonal part consists only of the term related to χ. However, it does not mean that the coupling with density modes can not contribute to diffusion coefficients. It gives contribution in indirect way: via tunnelling (or “jumping”) processes with change of quantum numbers $\alpha f i\sigma \to \alpha f' i'\sigma$. At the stage of calculation of diagonal elements, see equation (3.10), the transition probabilities $f_{\alpha f i\sigma,\alpha f' i'\sigma'}$ form the coefficients of diffusion in the same way as density fluctuations.

Nonlinear term $(b^{\dagger}_{k} + b_{k})a^{\dagger}a$ being not from the basic set of dynamic variables after the action of projection operator $(1-\mathcal{P}_0)$ determines the dissipative flux $\bar{I}_{f_{\bar{\alpha}}f_{\bar{\alpha}'}}$ (3.24) and diffusion coefficients of the particle on the lattice.

The last contribution to the formation of kinetic kernels comes from chemical reactions. Dynamic flux associated with the reactive part of Hamiltonian (2.1) has the following structure:

$$I^{\mathrm{reac}}_{f_{\bar{\alpha}\bar{\alpha}}} = \frac{\mathrm{i}}{\hbar}\sum_{\bar{\beta}\bar{\gamma}\bar{\zeta}}\Big\{\langle\bar{\gamma}\bar{\zeta}|\Phi_{\mathrm{reac}}|\bar{\alpha}\bar{\beta}\rangle a^{\dagger}_{\bar{\zeta}}a^{\dagger}_{\bar{\gamma}}a_{\bar{\alpha}}a_{\bar{\beta}} - \langle\bar{\gamma}\bar{\zeta}|\Phi_{\mathrm{reac}}|\bar{\alpha}\bar{\beta}\rangle^{*}a^{\dagger}_{\bar{\beta}}a^{\dagger}_{\bar{\alpha}}a_{\bar{\gamma}}a_{\bar{\zeta}}\Big\}. \tag{4.3}$$

In the latter equation for reasons of convenience we presented only the diagonal part. Again we see that (4.3) does not contribute to diffusion coefficients, being a linear combination of the basic dynamic variables and vanishing after the action of projection operator $(1-\mathcal{P}_0)$.

In the similar way one can perform the analysis of different processes contribution to the formation of dissipative flux $\bar{I}_{\bar{G}}$. It consists of the terms related to substrate-adsorbate interaction as well as to chemical reactions, while contribution from $I^A_{\bar{G}}$ vanishes after the projecting procedure $(1-\mathcal{P}_0)$.

If we suppose equilibrium correlations between phonons and particles to be small

$$\langle (b^\dagger + b)a^\dagger a\rangle_0 \approx \langle (b^\dagger + b)\rangle_0 \langle a^\dagger a\rangle_0\,, \tag{4.4}$$

(in general case it is not true a priori), then we can obtain dissipative flux $\bar{I}_f = (1-\mathcal{P})_0\dot{f}$ by simple change of variables $b^\dagger_k, b_k \to \delta b^\dagger_k, \delta b_k$, where $\delta b_k = b_k - \langle b_k\rangle_0$, $\delta b^\dagger_k = b^\dagger_k - \langle b^\dagger_k\rangle_0$. In reference [11] the initial Hamiltonian (2.1) without chemical reactions (2.7) by means of double unitary transformation was put into exponential form with respect to phonon-adsorbate interaction, $\exp[-\sum_k \Delta^{ss'}_k b_k - \text{h.c.}]$, where functions $\Delta^{ss'}_k$ were determined by corresponding coupling coefficients γ and χ whereas the terms linear in bosons were absent. In our case, the averaging procedure with non-transformed Hamiltonian (2.1) results in nonzero values $\langle b^\dagger_k\rangle_0$, $\langle b_k\rangle_0$. If we are interested in nonequilibrium dynamics of the substrate we have to add the one-particle phonon distribution function to the basic set (3.1)–(3.2) and construct the system of kinetic equations for different subsystems: adsorbate (distribution functions $f(t)$, $\bar{G}(t)$) and substrate (phonon distribution function $\langle n_{pk}(k)\rangle^t = \langle b^\dagger_k b_k\rangle^t$). [2]

In the end of the section we touch upon the evaluation of non-dissipative terms related to the coherent motion of the adsorbate. According to the definition of equilibrium correlation functions Ω (3.14)–(3.17) one has to calculate the action of equilibrium statistical operator ρ_0 on Bose and Fermi operators. This procedure is known to be satisfiable only in the limit of weak interaction and neglecting the non-linear term related to chemical reactions [11,16], when, on the one hand, explicit expressions could be obtained, and on the other hand – one can use Wick's decomposition. In any case, additional information is necessary about the exact quantum number dependence of tunnelling constants as well as the coupling amplitudes.

5. Contribution of chemical reactions to kinetic equations

In the previous section we obtained the closed system of kinetic equations for fluctuations of one- and two-particle distributions functions $\langle \delta f_{\bar{\alpha}\bar{\alpha}'}\rangle^t$, $\langle \delta \bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}\rangle^t$ around their equilibrium values. Let us remind that all these formulae were derived in the assumption of weakly nonequilibrium case. On the other hand, we intend to apply the obtained kinetic equations for such intrinsic nonlinear processes as bimolecular chemical reactions. However, there is no contradiction here: equations for $\langle \delta \bar{G}_{\bar{\alpha}\bar{\alpha}'\bar{\beta}\bar{\beta}'}\rangle^t$

[2]Dynamic correlation function between adsorbate and substrate should also be included into the basic set if one intends to advance deeper in the hierarchy of kinetic equations.

possess an implicit nonlinearity in fluctuations of one-particle distribution function. Indeed, introducing a two-particle correlation function $g_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}(t)$ in its usual way [16] one can write down the expression for dynamic variable $\langle\delta\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\rangle^t$ as follows:

$$\begin{aligned}\langle\delta\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}\rangle^t &= \delta g_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}(t)+\langle\delta f_{\bar\alpha\bar\alpha'}\rangle^t\langle\delta f_{\bar\beta\bar\beta'}\rangle^t+\langle\delta f_{\bar\beta\bar\beta'}\rangle^t\langle\delta f_{\bar\alpha\bar\alpha'}\rangle_0\\ &-\langle\delta f_{\bar\alpha\bar\beta'}\rangle^t\langle\delta f_{\bar\beta\bar\alpha'}\rangle^t-\langle\delta f_{\bar\beta\bar\alpha'}\rangle^t\langle\delta f_{\bar\alpha\bar\beta'}\rangle_0-\sum_{\bar\nu\bar\nu'}\chi_{\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}f_{\bar\nu\bar\nu'}}\langle\delta f_{\bar\nu\bar\nu'}\rangle^t. \quad (5.1)\end{aligned}$$

Here

$$\delta g_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}(t)=g_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}(t)-g^0_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}, \quad (5.2)$$

means fluctuation of correlation function and

$$\chi_{\bar G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}f_{\bar\nu\bar\nu'}}=\sum_{\bar\gamma\bar\gamma'}\langle G_{\bar\alpha\bar\alpha'\bar\beta\bar\beta'}f_{\bar\gamma\bar\gamma'}\rangle_0\,[\Phi_{ff}]^{-1}_{\bar\gamma\bar\gamma'\bar\nu\bar\nu'} \quad (5.3)$$

denotes static correlation function of adsorbed atoms. Further we will neglect permutations of quantum indexes related to Fermi statistics referring readers to reference [17] for their explicit expressions.

It is necessary to make the following remark. In principle, it is possible to proceed in a somewhat different way: to elaborate on nonlinear terms $\langle\delta f\rangle^t$ in original kinetic equations instead of taking two-particle distribution function into consideration. But in our opinion this line is less promising. On the one hand, it is necessary to use one of the nonlinear dynamics methods to exclude generalized thermodynamic forces in the relevant statistical operator; on the other hand, all the information about nonequilibrium correlations will be lost. For the reactions of synthesis to take into account the two-particle distribution functions is a principal question.

Thus, limiting ourselves by quadratic terms in fluctuations of dynamic variables, we write down kinetic equations for one-particle distribution functions and two particle correlation functions in the following matrix form:

$$\frac{\partial}{\partial t}\langle\delta f\rangle^t = M^{(1)}_{ff}(t)\cdot\langle\delta f\rangle^t+M_{f\bar G}(t)\cdot\left(\delta g(t)+\langle\delta f\rangle^t\otimes\langle\delta f\rangle^t\right), \quad (5.4)$$

$$\begin{aligned}\frac{\partial}{\partial t}\delta g(t) &= M_{\bar Gf}(t)\cdot\langle\delta f\rangle^t+M^{(1)}_{\bar G\bar G}(t)\cdot\langle\delta f\rangle^t\otimes\langle\delta f\rangle^t-M^{(1)}_{ff}(t)\otimes\langle\delta f\rangle^t\cdot\langle\delta f\rangle^t\\ &+M^{(2)}_{\bar G\bar G}(t)\cdot\delta g(t), \quad (5.5)\end{aligned}$$

where we denoted the scalar product of matrixes by symbol $\cdot$ and direct product by symbol $\otimes$. The other notations in equations (5.4)–(5.5) are as follows:

$$M_{f\bar G}(t) = \Omega^{(1)}_{f\bar G}-\int_{-\infty}^{t}\mathrm{e}^{\epsilon(t'-t)}\phi^{(1)}_{f\bar G}(t,t')\mathrm{d}t', \quad (5.6)$$

$$M_{\bar Gf}(t) = \Omega^{(2)}_{\bar Gf}-\int_{-\infty}^{t}\mathrm{e}^{\epsilon(t'-t)}\phi^{(2)}_{\bar Gf}(t,t')\mathrm{d}t', \quad (5.7)$$

$$M^{(1)}_{ff}(t) = \Omega^{(1)}_{ff}-\int_{-\infty}^{t}\mathrm{e}^{\epsilon(t'-t)}\phi^{(1)}_{ff}(t,t')\mathrm{d}t', \quad (5.8)$$

$$M^{(1)}_{\bar{G}\bar{G}}(t) = \Omega^{(1)}_{\bar{G}\bar{G}} - \int\limits_{-\infty}^{t} \mathrm{e}^{\epsilon(t'-t)}\phi^{(1)}_{\bar{G}\bar{G}}(t,t')\mathrm{d}t', \tag{5.9}$$

$$M^{(2)}_{\bar{G}\bar{G}}(t) = \Omega^{(2)}_{\bar{G}\bar{G}} - \int\limits_{-\infty}^{t} \mathrm{e}^{\epsilon(t'-t)}\phi^{(2)}_{\bar{G}\bar{G}}(t,t')\mathrm{d}t'. \tag{5.10}$$

In equations (5.6)–(5.10) we used the Markovian approximation for kinetic kernels [17]. We suppose the character evolution times of $\phi(t,t')$ are much smaller than those for distribution functions which allows us to take $\langle\delta f\rangle^t$, $\delta g(t)$ out from the integrals, though relaxation times for various kernels are different: decay of kernels (3.21)–(3.23) is much faster than that of (3.20) constructed exceptionally on one-particle distribution functions. Explicit expressions for renormalized Ω and ϕ functions entering the equations (5.6)–(5.10) could be found in appendix.

We constructed the closed system of kinetic equations for fluctuations of one-particle distribution function and two-particle correlation function. The next natural step is to solve it. However, because of its nonlinear structure, usual methods of linear kinetics like Laplace transformation [18] are not helpful. Formally one can carry the last term of equation (5.5) to its left hand side and find a solution for correlation function $\delta g(t)$ in an operator form with respect to $[\partial/\partial t - M^{(2)}_{\bar{G}\bar{G}}(t)]^{-1}$. This procedure again leads to the appearance of higher order fluctuations in $\langle\delta f\rangle^t$; therefore, we consider a steady state for the correlation function, when $\frac{\partial}{\partial t}\delta g(t) = 0$. In that case the solutions for fluctuations of the correlation function could be substituted to the first equation of the chain (5.4)–(5.5) and after some algebra the equations for one-particle functions take the form:

$$\frac{\partial}{\partial t}\langle\delta f\rangle^t = -\int\limits_{-\infty}^{t} \mathrm{e}^{\epsilon(t'-t)}\hat{\varphi}_{ff}(t,t')\mathrm{d}t'\cdot\langle\delta f\rangle^t + \hat{\Sigma}_{ff}(t)\cdot\langle\delta f\rangle^t - K(t)\cdot\langle\delta f\rangle^t\otimes\langle\delta f\rangle^t, \tag{5.11}$$

where

$$\hat{\Sigma}_{ff}(t) = \Omega^{(1)}_{ff} - \Omega_{f\bar{G}}(t)\cdot\left[\Omega^{(2)}_{\bar{G}\bar{G}}(t)\right]^{-1}\cdot\Omega_{\bar{G}f}(t), \tag{5.12}$$

and similar expression for the first term in (5.11) with substitution

$$\Omega \rightarrow -\int\limits_{-\infty}^{t} \mathrm{e}^{\epsilon(t'-t)}\phi(t,t')\mathrm{d}t',$$

$$K(t) = M_{f\bar{G}}(t)\cdot\left(\left[M^{(2)}_{\bar{G}\bar{G}}(t)\right]^{-1}\cdot M^{(1)}_{\bar{G}\bar{G}}(t) - \left[M^{(2)}_{\bar{G}\bar{G}}(t)\right]^{-1}\cdot M^{(1)}_{ff}(t)\otimes\mathcal{I}+\mathcal{I}\right). \tag{5.13}$$

Thus, we obtained a nonlinear kinetic equation for fluctuations of one-particle distribution functions of the atoms adsorbed on the surface of substrate. In equation (5.11) we separated a term dealing with transport kernel $\hat{\varphi}_{ff}$, which forms diffusion coefficients of adsorbed atoms. It has a usual renormalized form [18] being expressed via higher kinetic kernels in Markovian approximation. Such renormalization takes into account many-particle correlations on the lattice sites (up to the four-particle correlation in the present case). Functions $\hat{\Sigma}_{ff}(t)$ describe coherent (non-dissipative) motion of the adsorbate on the lattice sites and are related to static correlation functions of higher order, being expressed through matrix elements of the initial Hamiltonian (including chemical reactions) and structural distribution functions. Factor $K(t)$ in the last term of equation (5.11) is related to constant rates of chemical reactions.

The system (5.11) looks very similar to reaction-diffusion type equations [5] but in fact it is just a starting point to obtain them. All the time we call this system "*a chain of kinetic equations*" to stress the fact that we deal with essentially kinetic stage of evolution. All static correlation functions as well as kinetic kernels were dependent on the number of adsorbing site s and vibrational states of the particle i (we can neglect spin label σ because there is not any spin-site interaction in the initial Hamiltonian). In such a way we supply the dynamics of the "adsorbate-metal surface" system with some extra information, not relevant if one is going to describe chemical kinetics. One of the ways of passing to the chemical kinetic level consists in the averaging of all Ω and ϕ over all lattice sites s and states i. Then diffusion coefficients, functions Ω that describe a coherent motion of the adsorbate and values K associated with constant rates become only time-dependent; summing fluctuations of one-particle distribution functions over s and i one passes to number density (remind that $n_\alpha = \sum_{fi\sigma} f_{\alpha fi\sigma}$). The other way was proposed in reference [12] when diffusion coefficients were calculated as square mean displacements of gas particles in the nearest neighbour approximation. Here we face another kind of averaging typical of random walks processes. In any case, the question how to calculate dissipative and non-dissipative counterparts of kinetic equation (5.11) in a definite approximation remains open and has to be the subject of further investigations.

6. Conclusions

Using the effective Hubbard model within the framework of NSO method we obtained the equations of chemical kinetics for the description of reaction-diffusion processes of the atoms adsorbed on metallic surface. We started from the initial chain of equations for one- and two-particle distribution functions in weakly nonequilibrium form. The obtained kinetic equations consist of the terms responsible for coherent (non-dissipative) motion of adsorbate as well as incoherent summands dealing with diffusion of the particles on substrate sites. It was shown that in such a model there are contributions due to adsorbate-substrate interaction and chemical reactions into the formation of kinetic kernels.

The next step in our study was to pass from the weakly nonequilibrium case to nonlinear dynamics. We performed this step by introducing two-particle correlation functions and neglecting fluctuations higher than cubic. The obtained system of equations consists of the drift terms and kernels renormalized due to many-particle interactions. One can consider the obtained kinetic equations as a starting point for chemical kinetics.

To proceed further one has to get rid of redundant information connected with site-state dependence of kinetic kernels, averaging them over all sites of the surface. In practice it means that we have to evaluate non-dissipative and dissipative terms in a certain approximation neglecting extra information related to quantum states of every particle. In such a way one goes from the kinetic level of description of the processes on the surface to chemical kinetics equations. Though it is not the same as the ordinary transfer from kinetics to hydrodynamics [19], the main idea rests on excluding some additional "degrees of freedoms" (quantum number dependency of the kernels) from consideration. As a result one could obtain the system of equations where the only fluctuation of number densities (or concentrations) would be involved.

In any case, a natural question about evaluation of the drift terms and transport kernels arises every time one is going to perform a numerical analysis of chemical kinetics equations. However, we left aside the answer to this question considering it as a part of future studies.

Appendix

In appendix we present the renormalized correlation functions Ω and kinetic kernels ϕ which form the system of kinetic equations (5.4)–(5.5). As we have already said, permutation of quantum indexes related to Fermi statistics in the expressions for matrixes (5.6)–(5.10) is neglected. We can write down the following expressions for M:

$$\begin{aligned} M^{(1)}_{ff}(t) &= M_{ff}(t) + M_{f\bar{G}}(t)\cdot\langle f\rangle_0 - M_{f\bar{G}}(t)\cdot\chi_{Gf}, && \text{(A.1)}\\ M^{(2)}_{\bar{G}f}(t) &= M^{(1)}_{\bar{G}f}(t) - M^{(1)}_{ff}(t)\otimes\langle f\rangle_0 + \chi_{Gf}\cdot M^{(1)}_{ff}(t), && \text{(A.2)}\end{aligned}$$

at that

$$\begin{aligned} M^{(1)}_{\bar{G}f}(t) &= M_{\bar{G}f}(t) + M_{\bar{G}\bar{G}}(t)\cdot\langle f\rangle_0 - M_{\bar{G}\bar{G}}(t)\cdot\chi_{Gf}, && \text{(A.3)}\\ M^{(1)}_{\bar{G}\bar{G}}(t) &= M_{\bar{G}\bar{G}}(t) - M^{(1)}_{ff}(t)\mathcal{I}\otimes\mathcal{I} - M_{f\bar{G}}(t)\otimes\langle f\rangle_0 + \chi_{Gf}\cdot M_{f\bar{G}}(t), && \text{(A.4)}\\ M^{(2)}_{\bar{G}\bar{G}}(t) &= M_{\bar{G}\bar{G}}(t) - M_{f\bar{G}}(t)\otimes\langle f\rangle_0 + \chi_{Gf}\cdot M_{f\bar{G}}. && \text{(A.5)}\end{aligned}$$

In the expressions presented above we used Markovian approximation for kinetic kernels writing the sum of Ω and ϕ in the form

$$M_{AB}(t) = \Omega_{AB} - \int\limits_{-\infty}^{t} \mathrm{e}^{\epsilon(t'-t)}\phi_{AB}(t,t')\mathrm{d}t', \qquad \{A,B\} = \{f,\bar{G}\}. \qquad \text{(A.6)}$$

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Хімічні реакції на адсорбуючій поверхні: кінетичний рівень опису

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На основі ефективної моделі Хаббарда запропоновано статистичний опис реакційно-дифузійних процесів для бімолекулярних хімічних реакцій між частинками газу, адсорбованими на металічній поверхні. Отримано систему рівнянь переносу, що описують як дифузію частинок, так і хімічні реакції між ними. Проаналізовано вклади усіх фізичних процесів в формування коефіцієнтів дифузії та констант реакцій.

Ключові слова: *реакційно-дифузійні процеси, адсорбція, кінетичний опис*

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