

Zubarev nonequilibrium statistical operator method in Renyi statistics. Reaction-diffusion processes*

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The Zubarev nonequilibrium statistical operator (NSO) method in Renyi statistics is discussed. The solution of q -parametrized Liouville equation within the NSO method is obtained. A statistical approach for a consistent description of reaction-diffusion processes in "gas-adsorbate-metal" system is proposed using the NSO method in Renyi statistics.

Key words: *Renyi entropy, nonequilibrium statistical operator, chemical reaction*

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1. Introduction

Nowadays, investigating complex, self-organizing, fractal structures and various physical phenomena, such as subdiffusion, turbulence and chemical reactions, as well as various economical, social and biological systems, Tsallis [1], Renyi [2, 3], Sharma-Mittal [4, 5] statistics as well as superstatistics [6, 7] are extensively used along with the Gibbs one. A significant contribution to these investigations was made by A.I. Olemskoi [8–12] whose scientific activity we really lack. In particular, problems in synergetic description of self-organizing systems, description of the dynamics of phase transitions within the synergetic approach, the theory of stochastic systems with singular multiplicative noise are elegantly presented in the original work [9].

The Tsallis entropy is widely used in various directions of nonextensive statistical mechanics (for example, see [13–15] and references therein). Some examples are the phenomena of subdiffusion [16, 17] and turbulence [18, 19], and the investigations of transport coefficients in gases and plasma [20], as well as quantum dissipative systems [21]. The energy fluctuations [22], kinetics of nonequilibrium plasma [23], problems of self-gravitating systems [24] and complex systems [25, 26] were investigated within the Tsallis formalism. In references [27–29], Tsallis statistics was applied to a description of chemical reactions, in particular, nonlinear equations of reaction-diffusion processes were obtained in reference [27]. Despite the wide application of Tsallis entropy as a generalization of Gibbs-Shannon entropy, the Renyi entropy is of great interest as well [16, 30–37]. In particular, in this case it is possible to determine a connection between the parameter q and the heat capacity of the system [32]. It is important to note the papers [38, 39] by Luzzi et al., where the nonequilibrium statistical operator method and the Renyi entropy are used in describing the systems far from equilibrium. In particular, the nonequilibrium q -dependent Renyi ensemble as well as the generalized distribution functions of bosons and fermions were obtained in reference [38]. Therein the experiments on anomalous luminescence at nanometer quantum dots in semiconductor heterostructures were also described in this approach. A statistical approach for a description of fractal physical-chemical systems based on non-Fickian diffusion processes was proposed

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in reference [39]. Therein the investigations of anomalous diffusion in fractal-like electrodes in microbatteries were carried out. The nonextensive approach [40] as well as other ones [41, 42] leading to Lindblad equation was used to describe a decoherence in quantum mechanics. The references [43–45] are devoted to the investigation of nonlinear kinetics based on the Kramers, Boltzmann and Fokker-Planck equations within the framework of generalized statistics.

In the present paper, an approach to the formulation of extensive statistical mechanics of nonequilibrium processes [34] is considered, based on the Zubarev NSO method [46–48] and the maximum entropy principle for the Renyi entropy. This statistical approach is applied to a consistent description of reaction-diffusion processes in the “gas-adsorbate-metal” system. Reaction-diffusion and adsorption-desorption processes on the metal surface are nonlinear. They manifest an oscillation character, possess memory effects and are actual in terms of nanostructure formation on the surfaces occurring in catalytic phenomena [49–56].

2. Renyi entropy and nonequilibrium statistical operator method

The nonequilibrium state of a classical or quantum system of interacting particles is completely described by the nonequilibrium statistical operator $\varrho(x^N; t)$, which satisfies the classical or quantum Liouville (von Neumann) equation:

$$\frac{\partial}{\partial t}\varrho(x^N; t) + iL_N\varrho(x^N; t) = 0. \quad (2.1)$$

Here, iL_N is the Liouville operator of a system.

Within the NSO method framework, we will be looking for solutions of equation (2.1) which are independent of the initial conditions. The solutions will explicitly depend only on the observable quantities

$$\int d\Gamma_N \hat{P}_n \varrho(x^N; t) = \langle \hat{P}_n \rangle^t. \quad (2.2)$$

The nonequilibrium statistical operator has the following form:

$$\varrho(x^N; t) = \varrho_{\text{rel}}(x^N; t) - \int_{-\infty}^t e^{\varepsilon(t'-t)} T(t, t') [1 - P_{\text{rel}}(t')] iL_N \varrho_{\text{rel}}(x^N; t') dt', \quad (2.3)$$

where

$$T(t, t') = \exp_+ \left\{ - \int_{t'}^t [1 - P_{\text{rel}}(t')] iL_N dt' \right\}$$

is the evolution operator containing the projection (\exp_+ denotes ordered exponential). The relevant statistical operator (distribution function) $\varrho_{\text{rel}}(x^N; t)$ will be determined using the maximum entropy principle for the Renyi entropy

$$S^R(\varrho) = \frac{1}{1-q} \ln \int d\Gamma_N \varrho^q(t) \quad (2.4)$$

at fixed parameters of a reduced description, taking into account the normalization condition.

The relevant statistical operator corresponding to the Renyi entropy maximum has the following form:

$$\varrho_{\text{rel}}(t) = \frac{1}{Z_R} \left[1 - \frac{q-1}{q} \sum_n F_n(t) \delta \hat{P}_n \right]^{\frac{1}{q-1}}, \quad (2.5)$$

$$Z_R(t) = \int d\Gamma_N \left[1 - \frac{q-1}{q} \sum_n F_n(t) \delta \hat{P}_n \right]^{\frac{1}{q-1}}. \quad (2.6)$$

$Z_R(t)$ is the partition function of the relevant statistical operator, $\delta \hat{P}_n = \hat{P}_n - \langle \hat{P}_n \rangle^t$. The Lagrange multipliers $F_n(t)$ are defined from the self-consistency conditions:

$$\langle \hat{P}_n \rangle^t = \langle \hat{P}_n \rangle_{\text{rel}}^t, \quad (2.7)$$

where $\langle \dots \rangle_{\text{rel}}^t = \int d\Gamma_N \dots \varrho_{\text{rel}}(x^N; t)$.

In order to determine the generalized Kawasaki-Gunton projection operator entering (2.3)

$$P_{\text{rel}}(t)\varrho' = \left(\varrho_{\text{rel}}(t) - \sum_n \frac{\delta \varrho_{\text{rel}}(t)}{\delta \langle \hat{P}_n \rangle^t} \langle \hat{P}_n \rangle^t \right) \int d\Gamma_N \varrho' + \sum_n \frac{\delta \varrho_{\text{rel}}(t)}{\delta \langle \hat{P}_n \rangle^t} \int d\Gamma_N \hat{P}_n \varrho' \quad (2.8)$$

it is convenient to present the relevant statistical operator in a slightly different form:

$$\varrho_{\text{rel}}^*(t) = \frac{1}{Z_{\text{R}}^*} \left[1 - \frac{q-1}{q} \sum_n F_n^*(t) \hat{P}_n \right]^{\frac{1}{q-1}}, \quad (2.9)$$

with the partition function

$$Z_{\text{R}}^*(t) = \int d\Gamma_N \left[1 - \frac{q-1}{q} \sum_n F_n^*(t) \hat{P}_n \right]^{\frac{1}{q-1}} \quad (2.10)$$

and

$$F_n^*(t) = \frac{F_n(t)}{1 + \frac{q-1}{q} \sum_l F_l(t) \langle \hat{P}_l \rangle^t}. \quad (2.11)$$

An action of the operators $P_{\text{rel}}(t)iL_N$ on the relevant statistical operator can be presented as follows, by means of generalized projection which now acts on the dynamic variables, $P_{\text{rel}}(t)iL_N\varrho_{\text{rel}}(t) = P_{\text{rel}}(t)A(t)\varrho_{\text{rel}}(t) = [P(t)A(t)]\varrho_{\text{rel}}(t)$, where

$$P(t) \dots = \sum_{m,n} \langle \dots \hat{P}_m \rangle_{\text{rel}} \langle \hat{P}_m \delta \{ [q\psi(t)]^{-1} \hat{P}_n \}_{\text{rel}}^{-1} \delta \{ [q\psi(t)]^{-1} \hat{P}_n \}, \quad (2.12)$$

$$\psi(t) = 1 - \frac{q-1}{q} \sum_n F_n^*(t) \hat{P}_n.$$

Taking into account that $[1 - P_{\text{rel}}(t)]iL_N\varrho_{\text{rel}}(t) = -\sum_n I_n(t)F_n(t)\varrho_{\text{rel}}(t)$, where

$$I_n(t) = [1 - P(t)] \frac{1}{q} \psi^{-1}(t) \dot{\hat{P}}_n \quad (2.13)$$

are the generalized flows, we can now write down an explicit expression for the *nonequilibrium statistical operator*

$$\varrho(x^N; t) = \varrho_{\text{rel}}(x^N; t) + \sum_n \int_{-\infty}^t e^{\varepsilon(t-t')} T(t, t') I_n(t') F_n(t') \varrho_{\text{rel}}(x^N; t') dt'. \quad (2.14)$$

This allows us to obtain generalized *transport equations* for the reduced-description parameters. They can be presented in the form

$$\frac{\partial}{\partial t} \langle \hat{P}_m \rangle^t = \langle \dot{\hat{P}}_m \rangle_{\text{rel}}^t + \sum_n \int_{-\infty}^t e^{\varepsilon(t'-t)} \varphi_{mn}(t, t') F_n(t') dt', \quad (2.15)$$

with the generalized *transport kernels* (memory functions)

$$\varphi_{mn}(t, t') = \int d\Gamma_N \left\{ \dot{\hat{P}}_m T(t, t') I_n(t') \varrho_{\text{rel}}(t') \right\} \quad (2.16)$$

which describe the dissipative processes in the system.

3. q -generalization of Liouville equation

An interesting generalization of Liouville equation was proposed in [40], where the q -parametrized Liouville equation was obtained:

$$\frac{\partial}{\partial t} \rho(x^N; t) + i\tilde{L}_N(t) \rho(x^N; t) = 0, \quad (3.1)$$

where

$$i\tilde{L}_N(t) = \frac{iL_N}{1 + (1 - q)t iL_N} \quad (3.2)$$

is the q -parametrized Liouville operator. When $q = 1$ we have $i\tilde{L}_N(t) = iL_N$. For $|1 - q|\Omega t \ll 1$, where Ω is the characteristic frequency of the physical system considered, we may write [40] for (3.1):

$$\frac{\partial}{\partial t} \rho(x^N; t) + [iL_N - (1 - q)t(iL_N)^2] \rho(x^N; t) = 0. \quad (3.3)$$

This is the Lindblad type equation for nonequilibrium statistical operator $\rho(x^N; t)$. The Lindblad type equation within Renyi statistics was obtained in [21].

The solution of q -parametrized Liouville equation within the NSO method can be presented as follows:

$$\begin{aligned} \rho(x^N; t) &= -\varepsilon \int_{-\infty}^t e^{\varepsilon(t'-t)} T_q(t, t') \rho_{\text{rel}}(x^N; t') dt' \\ &= \rho_{\text{rel}}(x^N; t) - \int_{-\infty}^t e^{\varepsilon(t'-t)} \left\{ T_q(t, t') \frac{\partial}{\partial t'} \right. \\ &\quad \left. - \int_0^1 T_q^\tau(t, t') \frac{iL_N}{1 + (1 - q)(t' - t)iL_N} T_q^{1-\tau}(t, t') d\tau \right\} \rho_{\text{rel}}(x^N; t') dt', \end{aligned} \quad (3.4)$$

where

$$T_q(t, t') = \exp_+ \left\{ - \int_{t'}^t \frac{iL_N}{1 + (1 - q)t'' iL_N} dt'' \right\} \quad (3.5)$$

is the parametrized evolution operator. For $|1 - q|\Omega t \ll 1$ from (3.4) we obtain the solution of Lindblad type equation for $\rho(x^N; t)$.

It is important to note that, at $q \rightarrow t$, from (2.14) and (2.15) we reproduce the nonequilibrium statistical operator and the generalized transport equations for the reduced-description parameters within Gibbs statistics [46–48]. In the following section we apply the discussed approach to a description of reaction-diffusion processes, in particular, in catalytic processes.

4. Reaction-diffusion processes

Let us start with the Hamiltonian of the system of “gas-adsorbate-metal” in the following form $H = H' + H_{\text{reac}}$, $H' = H_a + H_a^{\text{int}}$. Here, H_a is the Hamiltonian of the gas subsystem considered according to the classical approach; H_a^{int} is the Hamiltonian describing the interaction between the gas atoms and the atoms adsorbed on the metal surface; H_{reac} is the Hamiltonian of interaction for chemical reactions between atoms or molecules adsorbed on the metal surface [49]

$$H_{\text{reac}} = \sum_{\bar{a}, \bar{b}, \bar{a}', \bar{b}'} \left(\langle \bar{a}', \bar{b}' | \Phi_{\text{reac}} | \bar{a}, \bar{b} \rangle \hat{q}_{\bar{a}'}^+ \hat{q}_{\bar{b}'}^+ \hat{q}_{\bar{a}} \hat{q}_{\bar{b}} + \langle \bar{a}', \bar{b}' | \Phi_{\text{reac}} | \bar{a}, \bar{b} \rangle^* \hat{q}_{\bar{a}}^+ \hat{q}_{\bar{b}}^+ \hat{q}_{\bar{a}'} \hat{q}_{\bar{b}'} \right), \quad (4.1)$$

where $\langle \bar{a}', \bar{b}' | \Phi_{\text{reac}} | \bar{a}, \bar{b} \rangle = \langle \bar{a}, \bar{b} | \Phi_{\text{reac}} | \bar{a}', \bar{b}' \rangle$ are the amplitudes of reaction between reagents A and B (supposed to be known from quantum mechanics). We introduce the notation \bar{a}, \bar{b} and \bar{a}', \bar{b}' for state of the reagents A, B (atoms or molecules) and for the state of atoms in the reaction products 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 operators of creation and annihilation of atomic states \bar{a}', \bar{b}' for molecule AB , and \bar{a}, \bar{b} for A and B , respectively.

Parameters of the reduced description are the averaged densities of gas atoms absorbed and not absorbed on the metal surface $\langle \hat{n}_{\bar{a}}(\vec{R}) \rangle^t = \text{Sp} \{ \hat{n}_{\bar{a}}(\vec{R}) \rho(t) \}$, $\langle \hat{n}_a(\vec{R}) \rangle^t = \text{Sp} \{ \hat{n}_a(\vec{R}) \rho(t) \}$. $\hat{n}_{\bar{a}}(\vec{R})$ is the density operator for gas atoms adsorbed on the metal surface in the state ν ; $\hat{n}_{\bar{a}}(\vec{R}) = \sum_j^{N_{\text{ad}}} \hat{\psi}_{\nu j}^+(\vec{R}) \hat{\psi}_{\nu j}(\vec{R})$; $\hat{\psi}_{\nu j}(\vec{R})$ are the creation and annihilation operators of gas atoms adsorbed in the state ν on the metal surface which satisfy the Bose-type commutation relations. Since we do not consider a catalyst surface explicitly in this model, the states ν and μ mean the adsorption centers, where atoms can be located. $\hat{n}_a(\vec{r}) = \sum_j^{N_{\text{ad}}} \delta(\vec{r} - \vec{r}_j)$ is the microscopic density of gas atoms, $\langle \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}') \rangle^t = \text{Sp} \{ \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}') \rho(t) \}$ is the nonequilibrium pair distribution function of the atoms or molecules adsorbed on the metal surface, and $\hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}') = \hat{n}_{\bar{a}}^{\nu}(\vec{R}) \hat{n}_{\bar{b}}^{\mu}(\vec{R}')$.

The relevant statistical operator has the form:

$$\begin{aligned} \rho_{\text{rel}} = \frac{1}{Z_{\text{R}}(t)} & \left\{ 1 - \frac{q-1}{q} \beta \left[\delta H(t) - \sum_a \int d\vec{r} \mu_a(\vec{r}; t) \delta \hat{n}_a(\vec{r}; t) \right. \right. \\ & \left. \left. - \sum_{\bar{a}} \sum_{\nu} \int d\vec{R} \mu_{\bar{a}}^{\nu}(\vec{R}; t) \delta \hat{n}_{\bar{a}}^{\nu}(\vec{R}; t) - \sum_{\bar{a}\bar{b}} \sum_{\nu\mu} \int d\vec{R} d\vec{R}' M_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}'; t) \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}'; t) \right] \right\}^{\frac{1}{q-1}}. \end{aligned} \quad (4.2)$$

The partition function of the relevant statistical operator is as follows

$$\begin{aligned} Z_{\text{R}}(t) = \text{Sp} & \left\{ 1 - \frac{q-1}{q} \beta \left[\delta H(t) - \sum_a \int d\vec{r} \mu_a(\vec{r}; t) \delta \hat{n}_a(\vec{r}; t) \right. \right. \\ & \left. \left. - \sum_{\bar{a}} \sum_{\nu} \int d\vec{R} \mu_{\bar{a}}^{\nu}(\vec{R}; t) \delta \hat{n}_{\bar{a}}^{\nu}(\vec{R}; t) - \sum_{\bar{a}\bar{b}} \sum_{\nu\mu} \int d\vec{R} d\vec{R}' M_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}'; t) \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}'; t) \right] \right\}^{\frac{1}{q-1}}. \end{aligned} \quad (4.3)$$

Here,

$$\text{Sp}\{\dots\} = \prod_{\alpha} \int \frac{(d\vec{r} d\vec{p})^{N_{\alpha}}}{N_{\alpha}!(2\pi\hbar)^{3N_{\alpha}}} \text{Sp}_{(v,\xi,\sigma)}\{\dots\},$$

$N_{\alpha} = \{N_a, N_{\bar{a}}\}$, $\text{Sp}_{(v,\xi,\sigma)}$ means the averaged summation over all values of spin and quantum numbers. The parameters $\mu_a(\vec{r}; t)$, $\mu_{\bar{a}}^{\nu}(\vec{R}; t)$, $M_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}'; t)$ should be determined from the corresponding self-consistency conditions

$$\langle \hat{n}_a(\vec{r}) \rangle^t = \langle \hat{n}_a(\vec{r}) \rangle_{\text{rel}}^t, \quad \langle \hat{n}_{\bar{a}}^{\nu}(\vec{R}) \rangle^t = \langle \hat{n}_{\bar{a}}^{\nu}(\vec{R}) \rangle_{\text{rel}}^t, \quad \langle \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}') \rangle^t = \langle \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}') \rangle_{\text{rel}}^t,$$

hence, we found that $\mu_a(\vec{r}; t)$ defines a local chemical potential of gas atoms; $\mu_{\bar{a}}^{\nu}(\vec{R}; t)$ is a local chemical potential of an atom adsorbed in a state ν on the metal surface. $\delta H(t) = H - \langle H \rangle^t$, $\delta \hat{n}_a(\vec{r}; t) = \hat{n}_a(\vec{r}) - \langle \hat{n}_a(\vec{r}) \rangle^t$, $\delta \hat{n}_{\bar{a}}^{\nu}(\vec{R}; t) = \hat{n}_{\bar{a}}^{\nu}(\vec{R}) - \langle \hat{n}_{\bar{a}}^{\nu}(\vec{R}) \rangle^t$, $\delta \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}'; t) = \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}') - \langle \hat{G}_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}') \rangle^t$.

According to (2.14), NSO of the system “gas-adsorbate-metal” has the following form

$$\begin{aligned} \rho(t) = \rho(t)_{\text{rel}} & + \sum_a \int d\vec{r} \int_{-\infty}^t e^{\varepsilon(t'-t)} T(t, t') \left[\int_0^1 d\tau \rho_{\text{rel}}^{\tau}(t') I_a(\vec{r}; t) \rho_{\text{rel}}^{1-\tau}(t') \beta \mu_a(\vec{r}; t') \right] dt' \\ & + \sum_{\bar{a}} \sum_{\nu} \int d\vec{R} \int_{-\infty}^t e^{\varepsilon(t'-t)} T(t, t') \left[\int_0^1 d\tau \rho_{\text{rel}}^{\tau}(t') I_{\bar{a}}^{\nu}(\vec{R}; t) \rho_{\text{rel}}^{1-\tau}(t') \beta \mu_{\bar{a}}^{\nu}(\vec{R}; t') \right] dt' \\ & + \sum_{\bar{a}, \bar{b}} \sum_{\nu, \mu} \int d\vec{R} d\vec{R}' \int_{-\infty}^t e^{\varepsilon(t'-t)} T(t, t') \left[\int_0^1 d\tau \rho_{\text{rel}}^{\tau}(t') I_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}'; t) \rho_{\text{rel}}^{1-\tau}(t') \beta M_{\bar{a}\bar{b}}^{\nu\mu}(\vec{R}, \vec{R}'; t') \right] dt'. \end{aligned} \quad (4.4)$$

$$\begin{aligned}
 I_a(\vec{r}; t) &= [1 - P(t)] \frac{1}{q} \psi^{-1}(t) \dot{n}_a(\vec{r}), & I_a^v(\vec{R}; t) &= [1 - P(t)] \frac{1}{q} \psi^{-1}(t) \dot{n}_a^v(\vec{R}), \\
 I_{G_{ab}}^{\nu\mu}(\vec{R}, \vec{R}'; t) &= [1 - P(t)] \frac{1}{q} \psi^{-1}(t) \dot{G}_{ab}^{\nu\mu}(\vec{R}, \vec{R}')
 \end{aligned} \tag{4.5}$$

are the generalized flows describing reaction-diffusion processes. The function $\psi(t)$ is defined by the relation

$$\begin{aligned}
 \psi(t) &= 1 - \frac{q-1}{q} \beta \left[\delta H(t) - \sum_a \int d\vec{r} \mu_a(\vec{r}; t) \delta \hat{n}_a(\vec{r}; t) \right. \\
 &\quad \left. - \sum_{\vec{a}} \sum_{\nu} \int d\vec{R} \mu_{\vec{a}}^{\nu}(\vec{R}; t) \delta \hat{n}_{\vec{a}}^{\nu}(\vec{R}; t) - \sum_{\vec{a}\vec{b}} \sum_{\nu\mu} \int d\vec{R} d\vec{R}' M_{\vec{a}\vec{b}}^{\nu\mu}(\vec{R}, \vec{R}'; t) \hat{G}_{\vec{a}\vec{b}}^{\nu\mu}(\vec{R}, \vec{R}'; t) \right].
 \end{aligned} \tag{4.6}$$

By means of NSO (4.4), we obtain the set of self-consistent generalized transport equations for averaged densities of adsorbed and non-absorbed atoms along with nonequilibrium pair distribution function of absorbed atoms (or molecules). It has the following form

$$\begin{aligned}
 \frac{\partial}{\partial t} \langle \hat{n}_a(\vec{r}) \rangle^t &= \langle \dot{\hat{n}}_a(\vec{r}) \rangle_{\text{rel}}^t + \sum_b \int d\vec{r}' \int_{-\infty}^t e^{\varepsilon(t'-t)} \varphi_{n_a n_b}(\vec{r}, \vec{r}'; t, t') \beta \mu_b(\vec{r}'; t') dt' \\
 &\quad + \sum_{\vec{b}} \sum_{\nu'} \int d\vec{R}' \int_{-\infty}^t e^{\varepsilon(t'-t)} \varphi_{n_a n_{\vec{b}}}^{\nu'}(\vec{r}, \vec{R}'; t, t') \beta \mu_{\vec{b}}^{\nu'}(\vec{R}'; t') dt' \\
 &\quad + \sum_{\vec{a}'\vec{b}'} \sum_{\nu'\mu'} \int d\vec{R}' d\vec{R}'' \int_{-\infty}^t e^{\varepsilon(t'-t)} \varphi_{n_a G_{\vec{a}'\vec{b}}}^{\nu'\mu'}(\vec{r}, \vec{R}', \vec{R}''; t, t') \beta M_{\vec{a}'\vec{b}}^{\nu'\mu'}(\vec{R}', \vec{R}''; t') dt',
 \end{aligned} \tag{4.7}$$

$$\begin{aligned}
 \frac{\partial}{\partial t} \langle \hat{n}_a^v(\vec{R}) \rangle^t &= \langle \frac{1}{i\hbar} [\hat{n}_a^v(\vec{R}), H'] \rangle_{\text{rel}}^t + \langle \frac{1}{i\hbar} [\hat{n}_a^v(\vec{R}), H_{\text{reac}}] \rangle_{\text{rel}}^t \\
 &\quad + \sum_b \int d\vec{r}' \int_{-\infty}^t e^{\varepsilon(t'-t)} \varphi_{n_a n_b}^v(\vec{R}, \vec{r}'; t, t') \beta \mu_b(\vec{r}'; t') dt' \\
 &\quad + \sum_{\vec{b}} \sum_{\nu'} \int d\vec{R}' \int_{-\infty}^t e^{\varepsilon(t'-t)} \varphi_{n_a n_{\vec{b}}}^{\nu\nu'}(\vec{R}, \vec{R}'; t, t') \beta \mu_{\vec{b}}^{\nu'}(\vec{R}'; t') dt' \\
 &\quad + \sum_{\vec{a}'\vec{b}'} \sum_{\nu'\mu'} \int d\vec{R}' d\vec{R}'' \int_{-\infty}^t e^{\varepsilon(t'-t)} \varphi_{n_a G_{\vec{a}'\vec{b}}}^{\nu'\mu'}(\vec{r}, \vec{R}', \vec{R}''; t, t') \beta M_{\vec{a}'\vec{b}}^{\nu'\mu'}(\vec{R}', \vec{R}''; t') dt',
 \end{aligned} \tag{4.8}$$

$$\begin{aligned}
 \frac{\partial}{\partial t} \langle \hat{G}_{ab}^{\nu\mu}(\vec{R}, \vec{R}') \rangle^t &= \langle \frac{1}{i\hbar} [\hat{G}_{ab}^{\nu\mu}(\vec{R}, \vec{R}'), H'] \rangle_{\text{rel}}^t + \langle \frac{1}{i\hbar} [\hat{G}_{ab}^{\nu\mu}(\vec{R}, \vec{R}'), H_{\text{reac}}] \rangle_{\text{rel}}^t \\
 &\quad + \sum_{b'} \int d\vec{r}' \int_{-\infty}^t e^{\varepsilon(t'-t)} \varphi_{G_{ab} n_{b'}}^{\nu\mu}(\vec{R}, \vec{R}'; t, t') \beta \mu_{b'}(\vec{r}'; t') dt' \\
 &\quad + \sum_{\vec{b}} \sum_{\nu'} \int d\vec{R}'' \int_{-\infty}^t e^{\varepsilon(t'-t)} \varphi_{G_{ab} n_{\vec{b}'}}^{\nu\mu\nu'}(\vec{R}, \vec{R}', \vec{R}''; t, t') \beta \mu_{\vec{b}'}^{\nu'}(\vec{R}''; t') dt' \\
 &\quad + \sum_{\vec{a}'\vec{b}'} \sum_{\nu'\mu'} \int d\vec{R}'' d\vec{R}''' \int_{-\infty}^t e^{\varepsilon(t'-t)} \varphi_{G_{ab} G_{\vec{a}'\vec{b}'}}^{\nu\mu\nu'\mu'}(\vec{r}, \vec{R}', \vec{R}'', \vec{R}'''; t, t') \beta M_{\vec{a}'\vec{b}'}^{\nu'\mu'}(\vec{R}'', \vec{R}'''; t') dt',
 \end{aligned} \tag{4.9}$$

where $\varphi_{n_a n_b}$, $\varphi_{n_a n_{\vec{b}}}$, $\varphi_{n_a n_{\vec{b}}}^{\nu\nu'}$, $\varphi_{G_{ab} G_{\vec{a}'\vec{b}'}}^{\nu\mu\nu'\mu'}$ are the generalized transport kernels. The second term in the right-hand side of (4.8), $\langle \frac{1}{i\hbar} [\hat{n}_a^v(\vec{R}), H_{\text{reac}}] \rangle_{\text{rel}}^t$, defines an averaged value of the operator of the rate of the reaction between adsorbed atoms on the metal surface. Transport kernels are built on the generalized

flows (4.5) taking into account the contributions of amplitudes of chemical reactions in the flows $I_a^v(\vec{R}; t')$ and $I_{G_{ab}}^{\nu\mu}(\vec{R}, \vec{R}'; t')$, and have the following form

$$\varphi_{BB'} = \text{Sp} \left\{ \dot{P}_B T(t, t') \int_0^1 d\tau \rho_{\text{rel}}^\tau(t') I_{B'}(t') \rho_{\text{rel}}^{1-\tau}(t') \right\}. \quad (4.10)$$

In particular, $\varphi_{n_a n_b}(\vec{r}, \vec{r}'; t, t')$ describes dynamical correlations of diffusive flows of gas atoms and is connected to the inhomogeneous diffusion coefficient of atoms (or molecules) $D_{ab}(\vec{r}, \vec{r}'; t)$. Similarly, the transport kernel $\varphi_{n_a n_b}^{\nu\nu'}(\vec{R}, \vec{R}'; t, t')$ describes dynamical dissipative correlations of diffusive flows of atoms adsorbed in the states ν and ν' on the metal surface and determines an inhomogeneous diffusion coefficient of the atoms adsorbed on the metal surface $D_{ab}^{\nu\nu'}(\vec{R}, \vec{R}'; t)$. Transport kernel $\varphi_{n_a n_b}^{\nu}(\vec{R}, \vec{r}'; t, t')$, $\varphi_{n_a n_b}^{\nu'}(\vec{r}, \vec{R}'; t, t')$ describes dynamical dissipative correlations between the flows of gas atoms and the atoms adsorbed on the metal surface, and determines the inhomogeneous coefficient of mutual diffusion “gas atom-adsorbed atom” $D_{ab}^{\nu\nu'}(\vec{r}, \vec{R}'; t)$. It is very important to investigate these diffusion coefficients. The transport kernel $\varphi_{G_{ab}p}^{\nu\mu}$ ($p = n, \bar{n}$) describes dissipative correlations of the flows and densities of adsorbed atoms with the flows of atoms, molecules and adsorbed atoms. Memory function $\varphi_{G_{ab}G_{a'b'}}^{\nu\mu\nu'\mu'}(\vec{R}, \vec{R}', \vec{R}'', \vec{R}'''; t, t')$ describes reaction-diffusion processes between the atoms adsorbed on the metal surface. They are higher memory functions with respect to dynamical variables $G_{ab}^{\nu\mu}$. We note here that at $q \rightarrow 1$, the generalized equations of reaction-diffusion processes correspond to the ones within the Gibbs statistics.

5. Conclusions

Summarizing, we proposed an approach to the formulation of extensive statistical mechanics of nonequilibrium processes based on the Zubarev NSO method and maximum entropy principle for Renyi entropy. We consider a q -parametrized Liouville equation which leads to Lindblad type equation at $|1 - q|\Omega t \ll 1$. The solution of this q -parametrized Liouville equation is obtained within the NSO method. The proposed approach is used to describe the reaction-diffusion processes which are relevant in catalytic nanotechnologies. Consequently, we obtain generalized transport equations (4.7)–(4.9) for the nonequilibrium averaged densities of adsorbed and non-adsorbed atoms of consistent description of the reaction-diffusion processes in the system “gas-adsorbate-metal” within Renyi statistics. At $q = 1$, these equations coincide with the equations of reaction-diffusion processes within Gibbs statistics [49]. As we can see, these equations are nonlinear and spatially inhomogeneous. They can describe strong as well as weak nonequilibrium processes in a system. The application of the obtained results to the consideration of a particular physical model will be done in our forthcoming works.

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Метод нерівноважного статистичного оператора Зубарєва у статистиці Рені. Реакційно-дифузійні процеси

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Обговорюється метод нерівноважного статистичного оператора (НСО) Зубарєва у статистиці Рені. Отримано розв'язок q -параметризованого рівняння Ліувілля в рамках методу НСО. Запропоновано статистичний підхід до узгодженого опису реакційно-дифузійних процесів у системі "газ-адсорбат-метал" методом НСО у статистиці Рені.

Ключові слова: ентропія Рені, нерівноважний статистичний оператор, хімічні реакції
