

Nonequilibrium statistical operator method: Generalized transport equations of diffusion-reaction processes

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Received 4 September 2003

Published online 30 January 2004 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2004

Abstract. Generalized transport equations for description of diffusion-reaction processes in chemically active mixtures are obtained. The nonequilibrium statistical operator method by Zubarev is used and both strong and weak nonequilibrium processes are analyzed. In the approximation of the second order in fluctuations we get generalized equations of chemical kinetics for bimolecular reactions with generalized rate constants. In the case of spatial uniformity the integro-differential equation for the matrix of partial scattering functions is received, which are related to partial dynamic structure factors of chemically reactive system by the time Fourier transformation.

PACS. 05.60.Cd Classical transport – 05.70.Ln Nonequilibrium and irreversible thermodynamics – 82.20.Mj Nonequilibrium kinetics

1 Introduction

Development of statistical theory of reaction-diffusion processes in classical and quantum systems is an important field of research in the modern nonequilibrium statistical physics. In particular, this concerns theoretical investigations of processes with the presence of catalytic reactions in bulk and on a surface, particularly on a metal one. Such studies are caused on the one hand, by radically new catalytic processes based on nanotechnologies and on the other hand by attempts to clear up of mechanisms of catalytic reactions. It is obvious that our knowledge of such mechanisms substantially depends on the choice of the level of description.

The fundamentally important problem in the theory of kinetic equations of chemical reactions is the question of their statistical substantiation [1]. Determination of chemical reaction rate constants for such processes as hydrolysis, dissociation and association of molecules, catalytic synthesis of ammonia on active surfaces, and others is concerned to the mentioned problem. These reactions are predominantly bimolecular and in order to elucidate their mechanisms one should take into account structural and dynamical transformations for neighbouring particles. The environment state in which chemical reactions occur can be characterized as kinetic or hydrodynamic, steady or unsteady nonequilibrium one. In each case the state influences the running of reactions. Thus a fundamentally complicated problem arises and lies in a self-consistent description of chemical reaction kinetics with nonequilib-

rium processes in surroundings. In order to solve such a problem it is necessary to apply methods of nonequilibrium statistical mechanics.

By now, some progress has been attained in the statistical substantiation of kinetics of reversible and irreversible chemical reactions in gases and liquids. In particular, the Enskog theory for chemically reacting liquids was developed in references [2,3]. The Smoluchowski's theory [4] and its modifications [5–8] were applied to the classical description of diffusion-controlled reactions. J. Keizer proposed an alternative approach [1,9,10] based on the nonequilibrium statistical thermodynamics and on calculation of the nonequilibrium radial distribution functions of reacting species through the correlation functions “density – density”. The fully renormalized kinetic theory by Mazenko [11–13] was applied for the first time to describe reversible chemical reactions $A+B \rightleftharpoons C+D$ in papers [14,15] and found subsequent advancement in works [16–18], where bimolecular reactions were considered. Felderhof with co-workers [19–22] used generalized transport equations and detailed balance equation with Mori's projection operator formalism.

In this direction of investigations one should also note the modified collision theory [23], the kinetic theory [24,25] which has been actively developing on the Bogoliubov's method [26], the nonequilibrium statistical theory of chemical reactions [27] based on the nonequilibrium statistical operator method by Zubarev [28,29]. One of important questions of these works is to receive microscopic expressions for reaction rate constants for dissociation or association of molecules including chemical

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reactions both in the volume phase and adsorption or desorption of atoms and molecules and catalytic phenomena on a surface of solids. In reference [27] generalized reaction-diffusion transport equations for many-component mixture of interacting atoms and molecules were obtained. In the accordance with reference [9,10] the nonequilibrium one- and two-particle distribution functions of chemically reacting atoms were taken as parameters of reduced description, see [24,25]. Really the creating for example of a two-atomic molecule AB from atoms A and B is described by the mean potential energy of a chemical bond which can be estimated with the help of experimental methods. Theoretically, this energy reads in the classical case:

$$E_{AB}^{\text{reac}}(t) = \int d\mathbf{r} \int d\mathbf{r}' \Phi_{AB}^{\text{reac}}(\mathbf{r}, \mathbf{r}') f_{AB}^m(\mathbf{r}, \mathbf{r}'; t),$$

where $\Phi_{AB}^{\text{reac}}(\mathbf{r}, \mathbf{r}')$ is the pair attractive potential modelling the chemical bond, $f_{AB}^m(\mathbf{r}, \mathbf{r}'; t)$ is a nonequilibrium internal molecular two-body distribution function of atoms A and B which generate the molecule AB. It is a special term in the mean potential energy of interacting atoms

$$\sum_{AB} E_{AB}^{\text{int}}(t) = \sum_{AB} (E_{AB}^{\text{short}}(t) + E_{AB}^{\text{reac}}(t) + E_{AB}^{\text{long}}(t)),$$

which together with the kinetic energy part form the full mean energy; $E_{AB}^{\text{short}}(t)$ and $E_{AB}^{\text{long}}(t)$ are respectively the short- and long-ranged parts of the full potential energy. The full mean energy is an observed parameter of the system and it satisfies the energy conservation law. Only the term $E_{AB}^{\text{reac}}(t)$ in the full potential energy of interacting atoms is connected with the nonequilibrium internal molecular distribution function $f_{AB}^m(\mathbf{r}, \mathbf{r}'; t)$. That is why if the kinetics of chemical reactions is described the quantity $E_{AB}^{\text{reac}}(t)$ can be chosen as one of characteristic parameters of molecule creation or dissociation. But in our approach [27] the function $f_{AB}^m(\mathbf{r}, \mathbf{r}'; t)$ is included in the system of the reaction-diffusion transport equations and thus it is necessary to distinguish in the generalized transport kernels the contribution of the pair attractive potential $\Phi_{AB}^{\text{reac}}(\mathbf{r}, \mathbf{r}')$ describing a chemical bond between atoms A and B.

In our treatment we will use the nonequilibrium statistical operator method developed by Zubarev. In the next sections we derive the generalized transport equations for the description of reaction-diffusion processes in chemically reacting classical mixtures. Microscopic expressions for the generalized transport coefficients are also received. In Section 3 in the case of weakly nonequilibrium processes we obtain reaction-diffusion transport equations for fluctuations of number densities and pair irreducible correlation functions which appear to be of the third order in the fluctuations. In the approximation of the second order in fluctuations we get generalized equations of chemical kinetics for bimolecular reactions with generalized rate constants. In the case of spatial uniformity the integro-differential equation for the matrix of partial scattering functions is received, which are related to partial dynamic structure factors of chemically reactive system by the time Fourier transformation.

2 Nonequilibrium statistical operator of chemically reacting mixtures. The classical description

We consider a many-component mixture of interacting atoms and molecules and suppose that reversible bimolecular chemical reactions as well as dissociation-association ones can occur between particles:



The Hamiltonian of the system can be written in the form:

$$H = \sum_{\alpha} \sum_{j=1}^{N_{\alpha}} \frac{p_j^2}{2m_{\alpha}} + \frac{1}{2} \sum_{\alpha\gamma} \sum_{j \neq l}^{N_{\alpha}, N_{\gamma}} \Phi_{\alpha\gamma}(\mathbf{r}_j, \mathbf{r}_l), \quad (2.2)$$

where \mathbf{p}_j is a momentum of the j th atom or molecule (which are assumed to be structureless for the simplicity), $\Phi_{\alpha\gamma}(\mathbf{r}_j, \mathbf{r}_l)$ denotes pair interaction potentials between particles of species α and γ . We suppose that the potential $\Phi_{\alpha\gamma}(\mathbf{r}_j, \mathbf{r}_l)$ consists of a short-range part (with a contribution describing a chemical bond between particles) and a long-range one.

A nonequilibrium state of the system is fully described by a nonequilibrium distribution function $\rho(x^N; t)$ which obeys the Liouville equation:

$$\frac{\partial}{\partial t} \rho(x^N; t) + iL_N \rho(x^N; t) = 0, \quad (2.3)$$

where iL_N is the Liouville operator corresponding to the Hamiltonian (2.2). The nonequilibrium distribution function $\rho(x^N; t)$ is normalized:

$$\int d\Gamma_N \rho(x^N; t) = 1, \quad d\Gamma_N = \prod_{\alpha} \frac{(dx)^{N_{\alpha}}}{N_{\alpha}! h^{3N_{\alpha}}}, \quad (2.4)$$

with $x^N = (x_1, x_2, \dots, x_N)$, $x_j = \{\mathbf{p}_j, \mathbf{r}_j\}$, $dx_j = d\mathbf{p}_j d\mathbf{r}_j$. In order to find the full nonequilibrium distribution function let us use the nonequilibrium statistical operator method by Zubarev [28]. It is based on ideas of the reduced description of the nonequilibrium state by means of a fixed set of observable parameters. Since our goal is to describe diffusion-reaction processes, one can choose averages of the following dynamical quantities as the parameters of the reduced description:

$$\langle \hat{n}_{\alpha}(\mathbf{r}) \rangle^t, \quad \langle \hat{n}_{\alpha}(\mathbf{r}) \hat{n}_{\gamma}(\mathbf{r}_1) \rangle^t. \quad (2.5)$$

These are nonequilibrium one-particle and pair distribution functions of particles of species α and γ . The averaging means $\langle \dots \rangle^t = \int d\Gamma_N \dots \rho(x^N; t)$. The quantity

$$\hat{n}_{\alpha}(\mathbf{r}) = \sum_{j=1}^{N_{\alpha}} \delta(\mathbf{r} - \mathbf{r}_j) \quad (2.6)$$

is a microscopic number density of particles of species α .

It is important to emphasize the particular role of the pair distribution function $\langle \hat{n}_{\alpha}(\mathbf{r}) \hat{n}_{\gamma}(\mathbf{r}_1) \rangle^t$. It can describe

both a nonequilibrium distribution of two atoms before a chemical reaction and a distribution of atoms which form a two-atomic molecule due to a chemical bond. In the last case $\langle \hat{n}_\alpha(\mathbf{r})\hat{n}_\gamma(\mathbf{r}_1) \rangle^t$ are internal molecular nonequilibrium distribution functions for atoms α and γ in the molecule. By the transition to the centre of masses coordinate system we obtain the number density average for molecules arising as a result of biatomic reactions. It is evident that if the atoms α and γ belong to two different molecules, then $\langle \hat{n}_\alpha(\mathbf{r})\hat{n}_\gamma(\mathbf{r}_1) \rangle^t$ is the pair intermolecular nonequilibrium distribution function of the corresponding atoms.

On the basis of the nonequilibrium statistical operator method by Zubarev [28,29], we seek the solution to the Liouville equation (2.3) with an infinitesimal source in the right-hand side:

$$\left[\frac{\partial}{\partial t} + iL_N \right] \rho(x^N; t) = -\varepsilon [\rho(x^N; t) - \rho_q(x^N; t)]. \quad (2.7)$$

The infinitesimal source breaks the symmetry of the equation in regard to time inversion and selects retarded solutions in the limit $\varepsilon \rightarrow +0$ after the thermodynamic limit. $\rho_q(x^N; t)$ is the relevant statistical distribution function to be determined from the extreme condition for the informational entropy of the system, if the parameters of the reduced description of the nonequilibrium state are fixed. In our case these parameters are averages (2.5). Thus, in accordance with works [27,28] we define $\rho_q(x^N; t)$ in the Gibbs form:

$$\rho_q(x^N; t) = \exp \left\{ -\Phi(t) - \beta \left(H - \sum_{\alpha} \int d\mathbf{r} \mu_{\alpha}(\mathbf{r}; t) \hat{n}_{\alpha}(\mathbf{r}) - \sum_{\alpha\gamma} \int d\mathbf{r} \int d\mathbf{r}_1 \mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) \hat{n}_{\alpha}(\mathbf{r}) \hat{n}_{\gamma}(\mathbf{r}_1) \right) \right\}, \quad (2.8)$$

where

$$\Phi(t) = \ln \int d\Gamma_N \exp \left\{ -\beta \left(H - \sum_{\alpha} \int d\mathbf{r} \mu_{\alpha}(\mathbf{r}; t) \hat{n}_{\alpha}(\mathbf{r}) - \sum_{\alpha\gamma} \int d\mathbf{r} \int d\mathbf{r}_1 \mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) \hat{n}_{\alpha}(\mathbf{r}) \hat{n}_{\gamma}(\mathbf{r}_1) \right) \right\} \quad (2.9)$$

is the Massieu-Planck functional determined from the normalization condition

$$\int d\Gamma_N \rho_q(x^N; t) = 1. \quad (2.10)$$

Lagrange parameters $\mu_{\alpha}(\mathbf{r}; t)$, $\mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t)$ are determined from the following conditions of the self-consistency:

$$\begin{aligned} \langle \hat{n}_{\alpha}(\mathbf{r}) \rangle^t &= \langle \hat{n}_{\alpha}(\mathbf{r}) \rangle_q^t, \\ \langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t &= \langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle_q^t, \end{aligned} \quad (2.11)$$

where $\langle \dots \rangle_q^t = \int d\Gamma_N \dots \rho_q(x^N; t)$ and the following notation $\hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) = \hat{n}_{\alpha}(\mathbf{r})\hat{n}_{\gamma}(\mathbf{r}_1)$ is used. Specifically, among the pair nonequilibrium distribution functions $\langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t = f_{\alpha\gamma}^m(\mathbf{r}, \mathbf{r}_1; t)$ there are internal molecular nonequilibrium ones $f_{\alpha\gamma}^m(\mathbf{r}, \mathbf{r}_1; t)$, which determine the

mean energy of a chemical bond $E_{\alpha\gamma}^{\text{reac}}(t)$ if a molecule is created from atoms of species α and γ . The physical meaning of the thermodynamical parameters $\mu_{\alpha}(\mathbf{r}; t)$ and $\mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t)$ can be obtained from the generalized thermodynamical relations, which associate these parameters with the Massieu-Planck functional (2.9), the reduced description parameters (2.5), and the Gibbs entropy functional. The last one reads:

$$\begin{aligned} S(t) &= -\langle \ln \rho_q(t) \rangle_q^t \\ &= \Phi(t) + \beta \langle H \rangle^t - \sum_{\alpha} \int d\mathbf{r} \beta \mu_{\alpha}(\mathbf{r}; t) \langle \hat{n}_{\alpha}(\mathbf{r}) \rangle^t \\ &\quad - \sum_{\alpha\gamma} \int d\mathbf{r} \int d\mathbf{r}_1 \beta \mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) \langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t, \end{aligned} \quad (2.12)$$

$\beta = 1/k_B T$, k_B is the Boltzmann constant, T is the equilibrium thermodynamic temperature. We can find from the generalized thermodynamic relations:

$$\frac{\delta \Phi(t)}{\delta \beta \mu_{\alpha}(\mathbf{r}; t)} = \langle \hat{n}_{\alpha}(\mathbf{r}) \rangle_q^t = \langle \hat{n}_{\alpha}(\mathbf{r}) \rangle^t, \quad (2.13)$$

$$\frac{\delta \Phi(t)}{\delta \beta \mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t)} = \langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle_q^t = \langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t, \quad (2.14)$$

where the conditions of the self-consistency (2.11) were taken into account. Equations (2.13, 2.14) show that the parameters μ_{α} and $\mu_{\alpha\gamma}$ are conjugated to the corresponding meanings of the nonequilibrium one-particle and pair distribution functions. From the next set of thermodynamic relations

$$\frac{\delta S(t)}{\delta \langle \hat{n}_{\alpha}(\mathbf{r}) \rangle^t} = -\beta \mu_{\alpha}(\mathbf{r}; t), \quad (2.15)$$

$$\frac{\delta S(t)}{\delta \langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t} = -\beta \mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t), \quad (2.16)$$

it follows that $\mu_{\alpha}(\mathbf{r}; t)$ is a nonequilibrium local chemical potential of species α , $\mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t)$ is a chemical potential of a two-atomic cluster or dimer which potentially form a molecule if a chemical bond arises between the atoms of species α and γ .

Using the NSO method [27,28] we can write the solution to equation (2.7) as follows

$$\begin{aligned} \rho(x^N; t) &= \rho_q(x^N; t) - \sum_{\alpha} \int d\mathbf{r}_1 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \\ &\quad \times T_q(t, t') I_n^{\alpha}(\mathbf{r}_1; t') \beta \mu_{\alpha}(\mathbf{r}_1; t') \rho_q(x^N; t') \\ &\quad - \sum_{\alpha\gamma} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} T_q(t, t') I_G^{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2; t') \\ &\quad \times \beta \mu_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2; t') \rho_q(x^N; t'), \end{aligned} \quad (2.17)$$

where

$$T_q(t, t') = \exp \left\{ - \int_{t'}^t dt'' [1 - \wp_q(t'')] iL_N \right\} \quad (2.18)$$

is the generalized evolution operator with allowance for the projection operation. The quantities

$$\begin{aligned} I_n^\alpha(\mathbf{r}_1; t') &= [1 - \varphi(t')] iL_N \hat{n}_\alpha(\mathbf{r}_1), \\ I_G^{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2; t') &= [1 - \varphi(t')] iL_N \hat{G}_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2) \end{aligned} \quad (2.19)$$

are the generalized fluxes of reaction-diffusion transport processes. $\varphi(t')$ is the Mori's projection operator. It acts on dynamical variables and has the following structure:

$$\begin{aligned} \varphi(t) \hat{A}(\mathbf{r}) &= \langle \hat{A}(\mathbf{r}) \rangle_q^t \\ &+ \sum_\alpha \int d\mathbf{r}_1 \frac{\delta \langle \hat{A}(\mathbf{r}) \rangle_q^t}{\delta \langle \hat{n}_\alpha(\mathbf{r}_1) \rangle^t} (\hat{n}_\alpha(\mathbf{r}_1) - \langle \hat{n}_\alpha(\mathbf{r}_1) \rangle^t) \\ &+ \sum_{\alpha\gamma} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\delta \langle \hat{A}(\mathbf{r}) \rangle_q^t}{\delta \langle \hat{G}_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2) \rangle^t} \\ &\times (\hat{G}_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2) - \langle \hat{G}_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2) \rangle^t). \end{aligned} \quad (2.20)$$

The properties of this operator are

$$\varphi(t)\varphi(t') = \varphi(t), \quad \varphi(t)(1 - \varphi(t)) = 0.$$

The projection operator $\varphi_q(t')$ in equation (2.18) is determined through the Mori's projector by the relation

$$\varphi_q(t') \rho' \hat{A}(\mathbf{r}) = \rho' \varphi(t) \hat{A}(\mathbf{r}).$$

We have obtained a general expression for the nonequilibrium distribution function presented by formula (2.17) which describes diffusion-reaction processes. It depends on the chosen set of parameters of reduced description (2.5) and on the generalized fluxes (2.19) which correspond for dissipative transport processes in the system. Since in accordance with the principle of reduced description the nonequilibrium distribution function $\rho(x^N; t)$ is a functional of parameters $\langle \hat{n}_\alpha(\mathbf{r}) \rangle^t$, $\langle \hat{n}_\alpha(\mathbf{r}) \hat{n}_\gamma(\mathbf{r}_1) \rangle^t$, corresponding to the conditions of self-consistency, it is necessary for the completeness of description of reaction-diffusion processes to construct the transport equations for these parameters.

In order to obtain such transport equations for the quantities $\langle \hat{n}_\alpha(\mathbf{r}) \rangle^t$, $\langle \hat{n}_\alpha(\mathbf{r}) \hat{n}_\gamma(\mathbf{r}_1) \rangle^t$, let us use the following identities:

$$\begin{aligned} \frac{\partial}{\partial t} \langle \hat{n}_\alpha(\mathbf{r}) \rangle^t &= \langle iL_N \hat{n}_\alpha(\mathbf{r}) \rangle^t \\ &= \langle iL_N \hat{n}_\alpha(\mathbf{r}) \rangle_q^t + \langle I_n^\alpha(\mathbf{r}; t) \rangle^t, \end{aligned} \quad (2.21)$$

$$\begin{aligned} \frac{\partial}{\partial t} \langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t &= \langle iL_N \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t \\ &= \langle iL_N \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle_q^t + \langle I_G^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) \rangle^t. \end{aligned} \quad (2.22)$$

After carrying out averaging in the right-hand sides of equations (2.21) and (2.22) with the help of the nonequilibrium distribution function (2.17) we receive the generalized transport equations for the reduced description

parameters [27]:

$$\begin{aligned} \frac{\partial}{\partial t} \langle \hat{n}_\alpha(\mathbf{r}) \rangle^t &= - \sum_{\alpha_1} \int d\mathbf{r}_1 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \\ &\times \frac{\partial}{\partial \mathbf{r}} D_{JJ}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1; t, t') \cdot \frac{\partial}{\partial \mathbf{r}_1} \beta \mu_{\alpha_1}(\mathbf{r}_1; t') \\ &- \sum_{\alpha_1 \gamma_1} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \\ &\times \left\{ \frac{\partial}{\partial \mathbf{r}} D_{JJn}^{\alpha\alpha_1 \gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \cdot \frac{\partial}{\partial \mathbf{r}_1} \beta \mu_{\alpha_1 \gamma_1}(\mathbf{r}_1, \mathbf{r}_2; t') \right. \\ &\left. + \frac{\partial}{\partial \mathbf{r}} D_{JnJ}^{\alpha\alpha_1 \gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \cdot \frac{\partial}{\partial \mathbf{r}_2} \beta \mu_{\alpha_1 \gamma_1}(\mathbf{r}_1, \mathbf{r}_2; t') \right\}, \end{aligned} \quad (2.23)$$

$$\begin{aligned} \frac{\partial}{\partial t} \langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t &= \langle \dot{\hat{G}}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle_q^t - \sum_{\alpha_1} \int d\mathbf{r}_2 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \\ &\times \left\{ \frac{\partial}{\partial \mathbf{r}} D_{JnJ}^{\alpha\gamma \alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \cdot \frac{\partial}{\partial \mathbf{r}_2} \beta \mu_{\alpha_1}(\mathbf{r}_2; t') \right. \\ &\left. + \frac{\partial}{\partial \mathbf{r}_1} D_{nJJ}^{\alpha\gamma \alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \cdot \frac{\partial}{\partial \mathbf{r}_2} \beta \mu_{\alpha_1}(\mathbf{r}_2; t') \right\} \\ &- \sum_{\alpha_1 \gamma_1} \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \\ &\times \left\{ \left[\frac{\partial}{\partial \mathbf{r}} D_{JnJn}^{\alpha\gamma \alpha_1 \gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \right. \right. \\ &\left. + \frac{\partial}{\partial \mathbf{r}_1} D_{nJJn}^{\alpha\gamma \alpha_1 \gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \right] \cdot \frac{\partial}{\partial \mathbf{r}_2} \beta \mu_{\alpha_1 \gamma_1}(\mathbf{r}_2, \mathbf{r}_3; t') \\ &\left. + \left[\frac{\partial}{\partial \mathbf{r}} D_{JnnJ}^{\alpha\gamma \alpha_1 \gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \right. \right. \\ &\left. \left. + \frac{\partial}{\partial \mathbf{r}_1} D_{nJJn}^{\alpha\gamma \alpha_1 \gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \right] \cdot \frac{\partial}{\partial \mathbf{r}_3} \beta \mu_{\alpha_1 \gamma_1}(\mathbf{r}_2, \mathbf{r}_3; t') \right\}, \end{aligned} \quad (2.24)$$

where

$$\begin{aligned} D_{JJ}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1; t, t') &= \int d\Gamma_N \left\{ (1 - \varphi(t)) \frac{1}{m_\alpha} \hat{\mathbf{p}}_\alpha(\mathbf{r}) \right. \\ &\left. \times T_q(t, t') (1 - \varphi(t')) \frac{1}{m_{\alpha_1}} \hat{\mathbf{p}}_{\alpha_1}(\mathbf{r}_1) \right\} \rho_q(x^N; t') \end{aligned} \quad (2.25)$$

is the generalized diffusion coefficient,

$$\hat{\mathbf{p}}_\alpha(\mathbf{r}) = \sum_{j=1}^{N_\alpha} \mathbf{p}_j \delta(\mathbf{r} - \mathbf{r}_j) \quad (2.26)$$

is a microscopic momentum density of α species. The functions $D_{JJn}^{\alpha\alpha_1 \gamma_1}$, $D_{JnJ}^{\alpha\alpha_1 \gamma_1}$, $D_{JnJ}^{\alpha\gamma \alpha_1}$, $D_{nJJ}^{\alpha\gamma \alpha_1}$ in equations (2.23, 2.24) are the generalized cross transport coefficients. They have a similar structure [27], for example:

$$\begin{aligned} D_{JJn}^{\alpha\alpha_1 \gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') &= \int d\Gamma_N \left\{ (1 - \varphi(t)) \frac{1}{m_\alpha} \hat{\mathbf{p}}_\alpha(\mathbf{r}) \right. \\ &\left. \times T_q(t, t') (1 - \varphi(t')) \frac{1}{m_{\alpha_1}} \hat{\mathbf{p}}_{\alpha_1}(\mathbf{r}_1) \hat{n}_{\gamma_1}(\mathbf{r}_2) \right\} \rho_q(x^N; t'). \end{aligned} \quad (2.27)$$

Functions $D_{JnJn}^{\alpha\gamma\alpha_1\gamma_1}$, $D_{nJJn}^{\alpha\gamma\alpha_1\gamma_1}$, $D_{JnnJ}^{\alpha\gamma\alpha_1\gamma_1}$, $D_{nJnJ}^{\alpha\gamma\alpha_1\gamma_1}$ are the generalized cross transport coefficients of the higher order in the dynamical variables $\hat{\mathbf{p}}_{\alpha_1}(\mathbf{r}_2)$, $\hat{n}_{\gamma_1}(\mathbf{r}_3)$. They also have analogous structure, for example:

$$D_{JnJn}^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') = \int d\Gamma_N \left\{ (1 - \wp(t)) \frac{1}{m_\alpha} \hat{\mathbf{p}}_\alpha(\mathbf{r}) \hat{n}_\gamma(\mathbf{r}_1) T_q(t, t') \right. \\ \left. \times (1 - \wp(t')) \frac{1}{m_{\alpha_1}} \hat{\mathbf{p}}_{\alpha_1}(\mathbf{r}_2) \hat{n}_{\gamma_1}(\mathbf{r}_3) \right\} \rho_q(x^N; t'). \quad (2.28)$$

The obtained transport equations (2.23, 2.24) are strongly nonlinear, non-Markovian and can describe both strongly and weakly nonequilibrium diffusion-reaction processes. They express the nonequilibrium one-particle and binary distribution functions through the generalized diffusion coefficients and cross transport coefficients, which are a generalization of functions of reactions. In the case of weakly nonequilibrium processes these equations become closed. In the next section we will consider such processes in details.

3 Weakly nonequilibrium diffusion-reaction processes

Let weakly nonequilibrium processes be characterized by small deviations of the parameters $\mu_\alpha(\mathbf{r}; t)$, $\mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t)$ from their corresponding equilibrium values $\mu_\alpha(\mathbf{r})$, $\mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1)$. This means that the reduced description parameters, namely, $\langle \hat{n}_\alpha(\mathbf{r}) \rangle^t$, $\langle \hat{n}_\alpha(\mathbf{r}) \hat{n}_\gamma(\mathbf{r}_1) \rangle^t$ differ little from their equilibrium values $\langle \hat{n}_\alpha(\mathbf{r}) \rangle_0 = f_1^\alpha(\mathbf{r})$, $\langle \hat{n}_\alpha(\mathbf{r}) \hat{n}_\gamma(\mathbf{r}_1) \rangle_0 = f_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1)$, where $f_1^\alpha(\mathbf{r})$ and $f_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1)$ are the one-particle and pair equilibrium distribution functions of particles. Brackets mean $\langle \dots \rangle_0 = \int d\Gamma_N \dots \rho_0(x^N)$ and function

$$\rho_0(x^N) = \frac{1}{Q} \exp \left\{ -\beta \left(H - \sum_\alpha \int d\mathbf{r} \mu_\alpha(\mathbf{r}) \hat{n}_\alpha(\mathbf{r}) - \sum_{\alpha\gamma} \int d\mathbf{r} \int d\mathbf{r}_1 \mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \hat{n}_\alpha(\mathbf{r}) \hat{n}_\gamma(\mathbf{r}_1) \right) \right\} \quad (3.1)$$

is the grand canonical Gibbs distribution for a chemically reacting mixture.

$$Q = \int d\Gamma_N \exp \left\{ -\beta \left(H - \sum_\alpha \int d\mathbf{r} \mu_\alpha(\mathbf{r}) \hat{n}_\alpha(\mathbf{r}) - \sum_{\alpha\gamma} \int d\mathbf{r} \int d\mathbf{r}_1 \mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \hat{n}_\alpha(\mathbf{r}) \hat{n}_\gamma(\mathbf{r}_1) \right) \right\} \quad (3.2)$$

is the corresponding grand partition function.

Let us expand the relevant distribution function (2.8) in the deviations $\delta\mu_\alpha(\mathbf{r}; t) = \mu_\alpha(\mathbf{r}; t) - \mu_\alpha(\mathbf{r})$, $\delta\mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) = \mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) - \mu_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1)$ and restrict our-

selves to the linear approximation:

$$\rho_q(x^N; t) = \rho_0(x^N) \left(1 + \sum_{\alpha_1} \int d\mathbf{r}_1 \delta\mu_{\alpha_1}(\mathbf{r}_1; t) \hat{n}_{\alpha_1}(\mathbf{r}_1) + \sum_{\alpha_1\gamma_1} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \delta\mu_{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2; t) \hat{G}_{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2) \right). \quad (3.3)$$

The parameters $\delta\mu_{\alpha_1}(\mathbf{r}_1; t)$, $\delta\mu_{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2; t)$ should be determined from the conditions of self-consistency (2.11). The relevant distribution function $\rho_q(x^N; t)$ becomes as follows:

$$\rho_q(x^N; t) = \rho_0(x^N) \left(1 + \sum_{\alpha_1\gamma_1} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \delta n_{\gamma_1}(\mathbf{r}_2; t) \xi_2^{\gamma_1\alpha_1}(\mathbf{r}_2, \mathbf{r}_1) \hat{n}_{\alpha_1}(\mathbf{r}_1) + \sum_{\alpha\gamma\alpha_1\gamma_1} \int d\mathbf{r} \int d\mathbf{r}_3 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \delta \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_3; t) \times \xi_4^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_3; \mathbf{r}_1, \mathbf{r}_2) \bar{G}_{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2) \right), \quad (3.4)$$

where

$$\delta n_\alpha(\mathbf{r}; t) = \langle \hat{n}_\alpha(\mathbf{r}) \rangle^t - \langle \hat{n}_\alpha(\mathbf{r}) \rangle_0, \\ \delta \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_3; t) = \langle \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_3) \rangle^t - \langle \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_3) \rangle_0, \quad (3.5)$$

$$\bar{G}_{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2) = \hat{G}_{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2) - \sum_\alpha \int d\mathbf{r} \chi_{\alpha\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) \hat{n}_\alpha(\mathbf{r}), \quad (3.6)$$

$$\chi_{\alpha\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) = \sum_{\alpha_2} \int d\mathbf{r}_3 \xi_2^{\alpha\alpha_2}(\mathbf{r}_3, \mathbf{r}) f_3^{\alpha_2\alpha_1\gamma_1}(\mathbf{r}_3, \mathbf{r}_1, \mathbf{r}_2),$$

and the function

$$f_3^{\alpha\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) = \langle \hat{n}_\alpha(\mathbf{r}) \hat{G}_{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2) \rangle_0 = \langle \hat{n}_\alpha(\mathbf{r}) \hat{n}_{\alpha_1}(\mathbf{r}_1) \hat{n}_{\gamma_1}(\mathbf{r}_2) \rangle_0 \quad (3.7)$$

is the three-particle equilibrium distribution function. One can show with the aid of equation (3.9) that

$$\langle \bar{G}_{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2) \hat{n}_{\gamma_2}(\mathbf{r}_3) \rangle_0 = 0. \quad (3.8)$$

This points to the fact of orthogonality of dynamical variables $\hat{n}_{\gamma_2}(\mathbf{r}_3)$ and $\bar{G}_{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2)$.

Functions $\xi_2^{\alpha\gamma_1}(\mathbf{r}, \mathbf{r}_2)$ and $\xi_4^{\alpha_1\gamma_1\alpha_2\gamma_2}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_4, \mathbf{r}_5)$ are determined from the following integral relations:

$$\sum_{\gamma_1} \int d\mathbf{r}_2 \xi_2^{\alpha\gamma_1}(\mathbf{r}, \mathbf{r}_2) f_2^{\gamma_1\alpha_1}(\mathbf{r}_2, \mathbf{r}_1) = \delta_{\alpha\alpha_1} \delta(\mathbf{r} - \mathbf{r}_1), \quad (3.9)$$

$$\sum_{\alpha_2\gamma_2} \int d\mathbf{r}_4 \int d\mathbf{r}_5 \xi_4^{\alpha_1\gamma_1\alpha_2\gamma_2}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_4, \mathbf{r}_5) \times f_4^{\alpha_2\gamma_2\alpha\gamma}(\mathbf{r}_4, \mathbf{r}_5; \mathbf{r}, \mathbf{r}_3) = \delta_{\alpha_1\gamma_1, \alpha\gamma} \delta(\mathbf{r}_1 - \mathbf{r}) \delta(\mathbf{r}_2 - \mathbf{r}_3), \quad (3.10)$$

where

$$f_4^{\alpha_2\gamma_2\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}, \mathbf{r}_3) = \langle \bar{G}_{\alpha_2\gamma_2}(\mathbf{r}_1, \mathbf{r}_2) \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_3) \rangle_0 \quad (3.11)$$

is the equilibrium four-particle distribution function.

Within the linear approximation for the quasiequilibrium distribution function $\rho_q(x^N; t)$ the transport equations (2.23, 2.24) take the following form:

$$\begin{aligned} \frac{\partial}{\partial t} \delta n_\alpha(\mathbf{r}; t) = & \\ & - \sum_{\alpha_1} \int d\mathbf{r}_1 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \bar{\varphi}_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1; t, t') \delta n_{\alpha_1}(\mathbf{r}_1; t') \\ & - \sum_{\alpha_1\gamma_1} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \bar{\varphi}_{nG}^{\alpha\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \\ & \times \delta \bar{G}_{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2; t'), \end{aligned} \quad (3.12)$$

$$\begin{aligned} \frac{\partial}{\partial t} \delta \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) = & \\ & - \sum_{\alpha_1} \int d\mathbf{r}_2 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \bar{\varphi}_{Gn}^{\alpha\gamma\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \delta n_{\alpha_1}(\mathbf{r}_2; t') \\ & - \sum_{\alpha_1\gamma_1} \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \bar{\varphi}_{GG}^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \\ & \times \delta \bar{G}_{\alpha_1\gamma_1}(\mathbf{r}_2, \mathbf{r}_3; t'), \end{aligned} \quad (3.13)$$

In the transport equations (3.12, 3.13) the generalized transport kernels which describe dissipative processes in the system read:

$$\begin{aligned} \bar{\varphi}_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1; t, t') = & \sum_{\alpha_2} \int d\mathbf{r}_2 \langle I_n^\alpha(\mathbf{r}) T_0(t, t') \\ & \times I_n^{\alpha_2}(\mathbf{r}_2) \rangle_0 \xi_2^{\alpha_2\alpha_1}(\mathbf{r}_2, \mathbf{r}_1), \end{aligned} \quad (3.14)$$

$$\begin{aligned} \bar{\varphi}_{nG}^{\alpha\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') = & \sum_{\alpha_2\gamma_2} \int d\mathbf{r}_3 \int d\mathbf{r}_4 \langle I_n^\alpha(\mathbf{r}) \\ & \times T_0(t, t') I_G^{\alpha_2\gamma_2}(\mathbf{r}_3, \mathbf{r}_4) \rangle_0 \xi_4^{\alpha_2\gamma_2\alpha_1\gamma_1}(\mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_1, \mathbf{r}_2), \end{aligned} \quad (3.15)$$

$$\begin{aligned} \bar{\varphi}_{Gn}^{\alpha\gamma\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') = & \sum_{\alpha_2} \int d\mathbf{r}_3 \langle I_G^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \\ & \times T_0(t, t') I_n^{\alpha_2}(\mathbf{r}_3) \rangle_0 \xi_2^{\alpha_2\alpha_1}(\mathbf{r}_3, \mathbf{r}_2), \end{aligned} \quad (3.16)$$

$$\begin{aligned} \bar{\varphi}_{GG}^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') = & \sum_{\alpha_2\gamma_2} \int d\mathbf{r}_4 \int d\mathbf{r}_5 \\ & \times \langle I_G^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) T_0(t, t') I_G^{\alpha_2\gamma_2}(\mathbf{r}_4, \mathbf{r}_5) \rangle_0 \\ & \times \xi_4^{\alpha_2\gamma_2\alpha_1\gamma_1}(\mathbf{r}_4, \mathbf{r}_5, \mathbf{r}_2, \mathbf{r}_3), \end{aligned} \quad (3.17)$$

where

$$\begin{aligned} I_n^\alpha(\mathbf{r}) = & (1 - \wp_0) iL_N \hat{n}_\alpha(\mathbf{r}) = -\frac{\partial}{\partial \mathbf{r}} \frac{1}{m_\alpha} \hat{\mathbf{p}}_\alpha(\mathbf{r}), \\ I_G^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) = & (1 - \wp_0) iL_N \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \end{aligned} \quad (3.18)$$

are generalized fluxes, \wp_0 is the Mori's projection operator. It has the following structure:

$$\begin{aligned} \wp_0 \hat{A}(\mathbf{r}) = & \langle \hat{A}(\mathbf{r}) \rangle_0 \\ & + \sum_{\alpha_1\gamma_1} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \langle \hat{A}(\mathbf{r}) \hat{n}_{\alpha_1}(\mathbf{r}_1) \rangle_0 \xi_2^{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2) \hat{n}_{\gamma_1}(\mathbf{r}_2) \\ & + \sum_{\alpha\gamma\alpha_1\gamma_1} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int d\mathbf{r}_4 \langle \hat{A}(\mathbf{r}) \bar{G}_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2) \rangle_0 \\ & \times \xi_4^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_3, \mathbf{r}_4) \bar{G}_{\alpha_1\gamma_1}(\mathbf{r}_3, \mathbf{r}_4), \end{aligned} \quad (3.19)$$

and properties: $\wp_0 \wp_0 = \wp_0$, $\wp_0 \hat{n}_\gamma(\mathbf{r}) = \hat{n}_\gamma(\mathbf{r})$, $\wp_0 \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) = \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1)$, $\wp_0 \hat{\mathbf{p}}_\alpha(\mathbf{r}) = 0$.

$$T_0(t, t') = \exp(-(1 - \wp_0) iL_N (t' - t))$$

is the propagator with the Mori projection operator in the linear approximation that corresponds to the standard Mori projection theory.

$$iL_N \hat{n}_\alpha(\mathbf{r}) = -\frac{\partial}{\partial \mathbf{r}} \frac{1}{m_\alpha} \hat{\mathbf{p}}_\alpha(\mathbf{r}),$$

$$\begin{aligned} iL_N \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) = & \\ & - \frac{\partial}{\partial \mathbf{r}} \frac{1}{m_\alpha} \hat{\mathbf{p}}_\alpha(\mathbf{r}) \hat{n}_\gamma(\mathbf{r}_1) - \hat{n}_\alpha(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}_1} \frac{1}{m_\gamma} \hat{\mathbf{p}}_\gamma(\mathbf{r}_1) \\ & + \sum_{\alpha_2} \int d\mathbf{r}_2 \chi_{\alpha_2\alpha\gamma}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) \frac{\partial}{\partial \mathbf{r}_2} \frac{1}{m_{\alpha_2}} \hat{\mathbf{p}}_{\alpha_2}(\mathbf{r}_2). \end{aligned}$$

It follows from the structure of the generalized fluxes (3.18) that the generalized transport kernels $\bar{\varphi}_{nn}^{\alpha\alpha_1}$, $\bar{\varphi}_{nG}^{\alpha\alpha_1\gamma_1}$, $\bar{\varphi}_{GG}^{\alpha\gamma\alpha_1\gamma_1}$ have the second, third, and fourth orders in dynamical variables $\hat{\mathbf{p}}_\alpha$, $\hat{\mathbf{p}}_{\alpha_1}$; $\hat{\mathbf{p}}_\alpha$, \hat{n}_γ , $\hat{\mathbf{p}}_{\alpha_1}$ and $\hat{\mathbf{p}}_\alpha$, \hat{n}_γ , \hat{n}_{γ_1} , $\hat{\mathbf{p}}_{\alpha_1}$. For example, one can show that the transport kernel $\bar{\varphi}_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1; t, t')$ is related to the generalized diffusion coefficient $D_{JJ}^{\alpha\gamma}$ by

$$\begin{aligned} \varphi_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1; t', t) = & \\ & \sum_{\gamma} \int d\mathbf{r}_2 \frac{\partial}{\partial \mathbf{r}} D_{JJ}^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_2; t, t') \frac{\partial}{\partial \mathbf{r}_2} \xi_2^{\alpha\gamma_1}(\mathbf{r}_2, \mathbf{r}_1) \end{aligned}$$

where

$$\begin{aligned} D_{JJ}^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_2; t', t) = & \langle I_n^\alpha(\mathbf{r}) T_0(t', t) I_n^\gamma(\mathbf{r}_2) \rangle_0 \\ = & \langle \frac{1}{m_\gamma} \hat{\mathbf{p}}_\gamma(\mathbf{r}) T_0(t', t) \frac{1}{m_\gamma} \hat{\mathbf{p}}_\gamma(\mathbf{r}_2) \rangle_0. \end{aligned}$$

These quantities can be expressed through the time correlation functions ‘‘momentum density-momentum density’’. The obtained system of equations (3.12, 3.13)

for reaction-diffusion processes includes hidden nonlinearities because

$$\langle \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t = \langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t - \sum_{\gamma_1} \int d\mathbf{r}_2 \chi_{\alpha\gamma\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) \langle \hat{n}_\gamma(\mathbf{r}_2) \rangle^t, \quad (3.20)$$

where $\langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle^t = f_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t)$ is the nonequilibrium two-particle distribution function of molecules of species α and γ . It satisfies the relation:

$$f_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) = g_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) + \langle \hat{n}_\alpha(\mathbf{r}) \rangle^t \langle \hat{n}_\gamma(\mathbf{r}_1) \rangle^t. \quad (3.21)$$

The same relation can be written for the equilibrium case:

$$\langle \hat{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) \rangle_0 = g_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) + \langle \hat{n}_\alpha(\mathbf{r}) \rangle_0 \langle \hat{n}_\gamma(\mathbf{r}_1) \rangle_0, \quad (3.22)$$

where, respectively, $g_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t)$ is the nonequilibrium pair correlation (irreducible) function for species α and γ and $g_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1)$ is its equilibrium counterpart. With the help of equations (3.20–3.22) and taking into account that $\delta n_\alpha(\mathbf{r}; t) = \langle \hat{n}_\alpha(\mathbf{r}) \rangle^t - \langle \hat{n}_\alpha(\mathbf{r}) \rangle_0$ we present the deviation $\delta \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t)$ in the form:

$$\begin{aligned} \delta \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) &= \delta g_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) + \delta n_\alpha(\mathbf{r}; t) \delta n_\gamma(\mathbf{r}_1; t) \\ &+ \delta n_\alpha(\mathbf{r}; t) \langle \hat{n}_\gamma(\mathbf{r}_1) \rangle_0 + \langle \hat{n}_\gamma(\mathbf{r}) \rangle_0 \delta n_\gamma(\mathbf{r}_1; t) \\ &- \sum_{\gamma_1} \int d\mathbf{r}_2 \chi_{\alpha\gamma\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) \delta n_{\gamma_1}(\mathbf{r}_2; t), \end{aligned} \quad (3.23)$$

where $\delta g_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) = g_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) - g_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1)$.

It can be easily seen that $\delta \bar{G}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t)$ is a quadratic function with respect to fluctuation δn . In order to eliminate this nonlinearity in the system of equations (3.12, 3.13) we introduce fluctuations of the irreducible pair correlation function $\delta g_2^{\alpha\gamma}$. After some manipulations one can obtain the following system of equations describing reaction-diffusion processes:

$$\begin{aligned} \frac{\partial}{\partial t} \delta n_\alpha(\mathbf{r}; t) &= - \sum_{\alpha_1} \int d\mathbf{r}_1 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \\ &\times [\bar{\varphi}_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1; t, t') + \Sigma_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1; t, t')] \delta n_{\alpha_1}(\mathbf{r}_1; t') \\ &- \sum_{\alpha_1\gamma_1} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \bar{\varphi}_{nG}^{\alpha\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \\ &\times [\delta g_2^{\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2; t') + \delta n_{\alpha_1}(\mathbf{r}_1; t') \delta n_{\gamma_1}(\mathbf{r}_2; t')], \end{aligned} \quad (3.24)$$

$$\begin{aligned} \frac{\partial}{\partial t} \delta g_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) &= \\ &- \sum_{\alpha_1} \int d\mathbf{r}_2 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \tilde{\Sigma}_{Gn}^{\alpha\gamma\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \delta n_{\alpha_1}(\mathbf{r}_2; t') \\ &- \sum_{\alpha_1\gamma_1} \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \Sigma_{GG}^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \\ &\times \delta n_{\alpha_1}(\mathbf{r}_2; t') \delta n_{\gamma_1}(\mathbf{r}_3; t') \\ &+ \sum_{\alpha_1} \int d\mathbf{r}_2 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \Sigma_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_2; t, t') \\ &\times \delta n_{\alpha_1}(\mathbf{r}_2; t') \delta n_\gamma(\mathbf{r}_1; t') \\ &+ \sum_{\alpha_1} \int d\mathbf{r}_2 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \Sigma_{nn}^{\gamma\alpha_1}(\mathbf{r}_1, \mathbf{r}_2; t, t') \\ &\times \delta n_{\alpha_1}(\mathbf{r}_2; t') \delta n_\alpha(\mathbf{r}; t') \\ &+ \sum_{\alpha_1\gamma_1} \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \\ &\times \left\{ [\varphi_{nG}^{\alpha\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \delta n_\gamma(\mathbf{r}_1; t') \right. \\ &+ \varphi_{nG}^{\alpha\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \delta n_\alpha(\mathbf{r}; t') \delta n_{\alpha_1}(\mathbf{r}_2; t') \delta n_{\gamma_1}(\mathbf{r}_3; t') \\ &- \Sigma_{GG}^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \delta g_2^{\alpha_1\gamma_1}(\mathbf{r}_2, \mathbf{r}_3; t') \\ &+ \varphi_{nG}^{\alpha\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3; t, t') \delta g_2^{\alpha_1\gamma_1}(\mathbf{r}_2, \mathbf{r}_3; t') \delta n_\gamma(\mathbf{r}; t') \\ &+ \varphi_{nG}^{\gamma\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \delta g_2^{\alpha_1\gamma_1} \\ &\left. \times (\mathbf{r}_2, \mathbf{r}_3; t') \delta n_\alpha(\mathbf{r}; t') \right\}, \end{aligned} \quad (3.25)$$

where functions $\Sigma_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1; t, t')$, $\tilde{\Sigma}_{Gn}^{\alpha\gamma\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t')$, $\Sigma_{GG}^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t')$ are connected with the generalized transport kernels (3.14–3.17). Their structure is presented in the appendix.

It follows from the structure of the transport equations (3.24, 3.25) that they and the system of equations (3.12, 3.13) as well, are nonlinear, namely, of the third order in fluctuations $\delta n_\gamma(\mathbf{r}_1; t') \delta n_\alpha(\mathbf{r}; t') \delta n_{\alpha_2}(\mathbf{r}_2; t')$. The generalized transport equations take also into account non-Markovian processes and spatial inhomogeneity. Thus it is very important to analyze them in simple approximations.

We shall consider the case of Markovian processes. Then one can suggest for the transport kernels (3.14–3.17) the following dependence on time:

$$\varphi_{AB}(t; t') \sim \varphi_{AB}(t) \delta(t - t').$$

Besides, we take into account fluctuations not higher than of the second order $\delta n_\alpha(\mathbf{r}; t') \delta n_\gamma(\mathbf{r}_1; t')$. Then, in the case of a stationary solution to equation (3.25)

$\frac{\partial}{\partial t} \delta g_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1; t) = 0$, we obtain equation (3.24) in the form:

$$\begin{aligned} \frac{\partial}{\partial t} \delta n_{\alpha}(\mathbf{r}; t) = & \\ & - \sum_{\alpha_1} \int d\mathbf{r}_1 [\varphi_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1) + \tilde{\Sigma}_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1)] \delta n_{\alpha_1}(\mathbf{r}_1; t) \\ & - \sum_{\alpha_1 \gamma_1} \int d\mathbf{r}_1 \int d\mathbf{r}_2 [K_{nG}^{\alpha\alpha_1 \gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) \\ & + K_{nG}^{\alpha\gamma_1 \alpha_1}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_1)] \delta n_{\alpha_1}(\mathbf{r}_1; t) \delta n_{\gamma_1}(\mathbf{r}_2; t), \end{aligned} \quad (3.26)$$

where

$$\begin{aligned} \tilde{\Sigma}_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1) = & \Sigma_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1) \\ & + \sum_{\gamma_1 \alpha_2} \int d\mathbf{r}_2 \int d\mathbf{r}_3 \bar{\varphi}_{nG}^{\alpha\alpha_2 \gamma_1}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3) \Omega_{Gn}^{\alpha_2 \gamma_1 \alpha_1}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_1), \end{aligned} \quad (3.27)$$

$$\begin{aligned} K_{nG}^{\alpha\alpha_1 \gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) = & \sum_{\alpha_2} \int d\mathbf{r}_3 \bar{\varphi}_{nG}^{\alpha\alpha_1 \alpha_2}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_3) \\ & \times \bar{\Omega}_{Gn}^{\alpha_1 \alpha_2 \gamma_1}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2). \end{aligned} \quad (3.28)$$

The expressions for the functions Ω are presented in the appendix. All these functions (3.27, 3.28), and (A.1–A.6) are expressed through the generalized transport kernels (3.14–3.17) taken in the Markovian approximation and through the equilibrium structural distribution functions $f_1^{\alpha}(\mathbf{r}) = \langle \hat{n}_{\alpha}(\mathbf{r}) \rangle_0$, $f_2^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1)$, $f_3^{\alpha\gamma\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2)$, $f_4^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, and $\chi_{\alpha\gamma\xi}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2)$.

In equation (3.26) we have distinguished a contribution of diffusion nature which is connected with the transport kernels $\varphi_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1)$ by the formula:

$$\varphi_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1) = \sum_{\gamma} \int d\mathbf{r}_2 \frac{\partial}{\partial \mathbf{r}} D^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_2) \frac{\partial}{\partial \mathbf{r}_2} \xi_2^{\gamma\alpha_1}(\mathbf{r}_2, \mathbf{r}_1), \quad (3.29)$$

where

$$D_{JJ}^{\alpha\gamma}(\mathbf{r}, \mathbf{r}_2) = \int_{-\infty}^0 dt e^{\varepsilon t} \langle I_n^{\alpha}(\mathbf{r}) T_0(t) I_n^{\gamma}(\mathbf{r}_2) \rangle_0 \quad (3.30)$$

is the generalized diffusion coefficient dependent on spatial coordinates written in the form of the Green-Kubo expression.

Let us consider the structure of system of equations (3.26) for reactions of the type $A + B \rightleftharpoons AB$ neglecting the higher-order dissipative correlation contributions for atoms of the same species,

$$\begin{aligned} & K_{nG}^{AAA}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_1) \delta n_A(\mathbf{r}_1; t) \delta n_A(\mathbf{r}_2; t), \\ & K_{nG}^{BBB}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_1) \delta n_B(\mathbf{r}_1; t) \delta n_B(\mathbf{r}_2; t), \end{aligned} \quad (3.31)$$

and higher-order dissipative correlation contributions for atoms of different species,

$$\begin{aligned} & K_{nG}^{A\alpha_1 A}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_1) \delta n_A(\mathbf{r}_1; t) \delta n_{\alpha_1}(\mathbf{r}_2; t), \\ & K_{nG}^{A\alpha_1 B}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_1) \delta n_B(\mathbf{r}_1; t) \delta n_{\alpha_1}(\mathbf{r}_2; t), \\ & K_{nG}^{A\alpha_2 \alpha_1}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_1) \delta n_{\alpha_1}(\mathbf{r}_1; t) \delta n_{\alpha_2}(\mathbf{r}_2; t). \end{aligned} \quad (3.32)$$

(For instance, α_1 can be a species of molecules AB which have been created due to the chemical reaction between atoms A and B or it can be a species of particles of the environment in which the chemical reactions take place):

$$\begin{aligned} \frac{\partial}{\partial t} \delta n_A(\mathbf{r}; t) = & \\ & - \int d\mathbf{r}_1 [\varphi_{nn}^{AA}(\mathbf{r}, \mathbf{r}_1) + \tilde{\Sigma}_{nn}^{AA}(\mathbf{r}, \mathbf{r}_1)] \delta n_A(\mathbf{r}_1; t) \\ & - \int d\mathbf{r}_1 [\varphi_{nn}^{AB}(\mathbf{r}, \mathbf{r}_1) + \tilde{\Sigma}_{nn}^{AB}(\mathbf{r}, \mathbf{r}_1)] \delta n_B(\mathbf{r}_1; t) \\ & - \int d\mathbf{r}_1 \int d\mathbf{r}_2 [K_{nG}^{AAB}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) + K_{nG}^{ABA}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_1)] \\ & \times \delta n_A(\mathbf{r}_1; t) \delta n_B(\mathbf{r}_2; t) \\ & - \int d\mathbf{r}_1 \int d\mathbf{r}_2 [K_{nG}^{ABA}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) + K_{nG}^{AAB}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_1)] \\ & \times \delta n_B(\mathbf{r}_1; t) \delta n_A(\mathbf{r}_2; t) \end{aligned} \quad (3.33)$$

$$\begin{aligned} \frac{\partial}{\partial t} \delta n_B(\mathbf{r}; t) = & \\ & - \int d\mathbf{r}_1 [\varphi_{nn}^{BA}(\mathbf{r}, \mathbf{r}_1) + \tilde{\Sigma}_{nn}^{BA}(\mathbf{r}, \mathbf{r}_1)] \delta n_A(\mathbf{r}_1; t) \\ & - \int d\mathbf{r}_1 [\varphi_{nn}^{BB}(\mathbf{r}, \mathbf{r}_1) + \tilde{\Sigma}_{nn}^{BB}(\mathbf{r}, \mathbf{r}_1)] \delta n_B(\mathbf{r}_1; t) \\ & - \int d\mathbf{r}_1 \int d\mathbf{r}_2 [K_{nG}^{BAB}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) + K_{nG}^{BBA}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_1)] \\ & \times \delta n_A(\mathbf{r}_1; t) \delta n_B(\mathbf{r}_2; t) \\ & - \int d\mathbf{r}_1 \int d\mathbf{r}_2 [K_{nG}^{BBA}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) + K_{nG}^{BAB}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_1)] \\ & \times \delta n_B(\mathbf{r}_1; t) \delta n_A(\mathbf{r}_2; t). \end{aligned} \quad (3.34)$$

Such the system of equations is a generalization of chemical kinetic equations [1], where only diffusion-reaction processes between reactants A and B are taken into account. The system of equations for diffusion-reaction processes, which includes higher-order dissipative correlation contributions for atoms of the same species (3.31) and higher-order dissipative correlation contributions (3.32) was presented in reference [27]. Besides the equations for density fluctuations of species A and B , between which chemical bonds may arise and molecule AB may be created, we take also into account equations for density fluctuations of species which do not directly take part in chemical reactions but may essentially influence the running of chemical processes through appropriate character of the interaction with A and B and through transport kernels, for example $K_{nG}^{\alpha_1 AB}$ or $K_{nG}^{\alpha_1 BA}$. Moreover, the molecule AB can play the role of α_1 , which has been formed on a certain stage of the time evolution of the system. But this aspect requires to consider non-Markovian processes. As a rule, the equations for number density fluctuations of particles which do not participate in the reaction are not taken into account in the chemical kinetics.

The system of equations (3.33, 3.34) is strongly nonlinear. For the specific chemical processes and transport

kernels (A.2–A.7), it should be solved together with certain initial conditions for fluctuations $\delta n_A(\mathbf{r}; t = t_0)$, $\delta n_B(\mathbf{r}; t = t_0)$, $\delta n_{\alpha_1}(\mathbf{r}; t = t_0)$.

Thus, in the case of weakly nonlinear processes in chemically reacting mixtures we have obtained a system of transport equations of reaction-diffusion type for fluctuations of number densities of each species and for those of pair correlation functions of particles. These equations turn out to be of the third order in fluctuations. In the second order approximations with respect to fluctuations the obtained system of equations can be reduced to that of chemical kinetics type for fluctuations of the average number densities with generalized reaction rate constants. This system of equations has been analyzed in the case of the Markovian approximation for the generalized transport kernels. An example of “association – dissociation” reactions has been considered.

4 Dynamic structure factors of chemically reactive systems

Dynamic structure factors of gaseous or fluid mixtures, both chemically active or not, give important information about heat, sound, diffusion and thermal diffusion processes. Therefore, these quantities are under intensive experimental investigations (neutron and light scattering) as well as theoretical treatment and computer simulations [1, 30, 31]. Generalized transport equations (2.23, 2.24) or their linearized counterparts (3.12, 3.13) permit us to find the dynamic structure factors for chemically reacting mixtures. Let us consider generalized transport equations (3.12, 3.13) in the case of spatial uniformity. After the spatial Fourier transformation we can write them in a matrix form:

$$\begin{aligned} \frac{\partial}{\partial t} \tilde{n}(\mathbf{k}; t) &= - \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} k^2 \tilde{\mathcal{D}}_{JJ}(\mathbf{k}; t, t') \tilde{n}(\mathbf{k}; t') \\ &- \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} k^2 \tilde{K}_{JnJ}^{(1)}(\mathbf{k}; t, t') \\ &\times [\tilde{G}(\mathbf{k}; t') - \tilde{S}(\mathbf{k}) - \tilde{\chi}(\mathbf{k}) \tilde{n}(\mathbf{k}; t')], \end{aligned} \quad (4.1)$$

$$\begin{aligned} \frac{\partial}{\partial t} [\tilde{G}(\mathbf{k}; t) - \tilde{\chi}(\mathbf{k}) \tilde{n}(\mathbf{k}; t)] &= - \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} k^2 \tilde{K}_{JnJ}^{(2)}(\mathbf{k}; t, t') \tilde{n}(\mathbf{k}; t') \\ &- \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} k^2 \tilde{T}_{JnJn}(\mathbf{k}; t, t') \\ &\times [\tilde{G}(\mathbf{k}; t') - \tilde{S}(\mathbf{k}) - \tilde{\chi}(\mathbf{k}) \tilde{n}(\mathbf{k}; t')], \end{aligned} \quad (4.2)$$

where

$$\tilde{K}_{JnJ}^{(1)}(\mathbf{k}; t, t') = \tilde{D}_{JnJ}(\mathbf{k}; t, t') + \tilde{D}_{JJn}(\mathbf{k}; t, t'), \quad (4.3)$$

$$\tilde{K}_{JnJ}^{(2)}(\mathbf{k}; t, t') = \tilde{D}_{JnJ}(\mathbf{k}; t, t') + \tilde{D}_{nJJ}(\mathbf{k}; t, t'), \quad (4.4)$$

$$\begin{aligned} \tilde{T}_{JnJn}(\mathbf{k}; t, t') &= \tilde{D}_{JnJn}(\mathbf{k}; t, t') + \tilde{D}_{nJJn}(\mathbf{k}; t, t') \\ &+ \tilde{D}_{JnnJ}(\mathbf{k}; t, t') + \tilde{D}_{nJnJ}(\mathbf{k}; t, t'), \end{aligned} \quad (4.5)$$

$\tilde{n}(\mathbf{k}; t)$ is a vector column with elements being the Fourier transforms of density fluctuations $n_\alpha(\mathbf{k}; t) = \langle \hat{n}_\alpha(\mathbf{k}) \rangle^t$, $\hat{n}_\alpha(\mathbf{k}) = \sum_{j=1}^{N_\alpha} e^{-i\mathbf{k}\cdot\mathbf{r}_j}$ is the Fourier transform of the microscopic density of atoms of species α , and $\langle \hat{n}_\alpha(\mathbf{k}) \rangle_0 = 0$ at $\mathbf{k} \neq 0$. $\tilde{G}(\mathbf{k}; t)$ is a matrix with elements $G_{\alpha\gamma}(\mathbf{k}; t) = \langle \hat{G}_{\alpha\gamma}(\mathbf{k}) \rangle^t = \langle \sum_{j,l=1}^{N_\alpha, N_\gamma} e^{-i\mathbf{k}\cdot(\mathbf{r}_j - \mathbf{r}_l)} \rangle^t$. The Fourier transforms of the partial scattering functions, which are related to the partial dynamic structure factors by the Fourier transformation: $S_{\alpha\gamma}(\mathbf{k}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} G_{\alpha\gamma}(\mathbf{k}; t)$, ω is a real number. $\tilde{S}(\mathbf{k}) = \tilde{G}(\mathbf{k})$ is a matrix with elements $S_{\alpha\gamma}(\mathbf{k})$, partial static structure factors of atoms of species α , γ .

Moreover, if a chemical bond arises between atoms α and γ , then $S_{\alpha\gamma}(\mathbf{k}, \omega)$ and $S_{\alpha\gamma}(\mathbf{k})$ can be interpreted as the intermolecular structure factors. That is, the matrix $\tilde{S}(\mathbf{k}, \omega)$ and $\tilde{S}(\mathbf{k})$ consist of elements which are the partial structure factors of atoms belonging to the same molecule or to different molecules that have been created due to the chemical reaction. $\tilde{D}_{JJ}(\mathbf{k}; t, t')$, $\tilde{D}_{JnJ}(\mathbf{k}; t, t')$, and $\tilde{D}_{JnJn}(\mathbf{k}; t, t')$ are matrices with elements being the Fourier transforms of generalized transport kernels (2.25, 2.27, 2.28), which are calculated in the linear approximation. That is to say, these are averaged with the equilibrium statistical operator, but not with $\rho_q(x^N; t)$.

After eliminating $\tilde{n}(\mathbf{k}; t)$ from equations (4.1, 4.2) we get an equation for $\tilde{G}(\mathbf{k}; t)$. This can be performed with the help of the Laplace transformation

$$A(\mathbf{k}; z) = i \int_0^{\infty} dt e^{izt} A(\mathbf{k}; t),$$

($\text{Im } z > 0$, $z = \omega + i\varepsilon$, $\varepsilon \rightarrow +0$) with respect to equations (4.1, 4.2). Taking into account that $\tilde{n}(\mathbf{k}; t = 0) = 0$, we receive the equation for $\tilde{G}(\mathbf{k}; t)$ in the following matrix form:

$$\begin{aligned} \frac{\partial}{\partial t} \tilde{G}(\mathbf{k}; t) &= - k^2 \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \tilde{\Omega}_{JnJn}(\mathbf{k}; t, t') [\tilde{G}(\mathbf{k}; t') - \tilde{S}(\mathbf{k})], \end{aligned} \quad (4.6)$$

where $\tilde{\Omega}_{JnJn}(\mathbf{k}; t, t')$ is a matrix of renormalized transport kernels. It has the following structure:

$$\tilde{\Omega}_{JnJn}(\mathbf{k}; t, t') = \tilde{T}_{JnJn}(\mathbf{k}; t, t') + \tilde{T}_{JnJn}^{(1)}(\mathbf{k}; t, t'). \quad (4.7)$$

The function $\tilde{T}_{J_n J_n}^{(1)}(\mathbf{k}; t, t')$ can be obtained by the reverse Laplace transformation of the quantity:

$$\begin{aligned} \tilde{T}_{J_n J_n}^{(1)}(\mathbf{k}; z) &= [z\tilde{\chi}(\mathbf{k}) - k^2(\tilde{K}_{J_n J_n}^{(2)}(\mathbf{k}; z) - \tilde{T}_{J_n J_n}(\mathbf{k}; z)\tilde{\chi}(\mathbf{k}))] \\ &\times [z\tilde{I} + k^2(\tilde{\mathcal{D}}_{JJ}(\mathbf{k}; z) - \tilde{K}_{J_n J_n}^{(1)}(\mathbf{k}; z)\tilde{\chi}(\mathbf{k}))]^{-1} \tilde{K}_{J_n J_n}^{(1)}(\mathbf{k}; z) \end{aligned} \quad (4.8)$$

with renormalization due to eliminating of $\tilde{n}(\mathbf{k}; z)$ from the system of equations (4.1), (4.2).

In order to obtain the partial dynamic structure factors of chemically reacting mixtures we can use the matrix equation (4.6). But then we meet the well-known problem connected with calculation of the generalized transport kernels (4.7) in the matrix $\tilde{\Omega}_{J_n J_n}(\mathbf{k}; t, t')$. One may investigate high- ($\omega \rightarrow \infty$) or low-frequency ($\omega \rightarrow 0$) limits (small ($t \rightarrow 0$) or long ($t \rightarrow \infty$) time intervals, respectively) for these kernels in specific cases. With accordance of the mode-coupling theory [30,32,33], in the limit ($\omega \rightarrow 0$) the generalized memory functions in equation (4.5) $\tilde{D}_{J_n J_n}$, $\tilde{D}_{n J_n J_n}$, $\tilde{D}_{J_n n J_n}$, $\tilde{D}_{n J_n J_n}$ can be approximately expressed through the generalized diffusion coefficients:

$$\begin{aligned} \tilde{D}_{J_n J_n}^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{k}; t) &\approx \sum_{\alpha_2\gamma_2} \left\{ D_{JJ}^{\alpha\alpha_2}(\mathbf{k}; t) G_{nn}^{\gamma\gamma_2}(\mathbf{k}; t) \right. \\ &\left. + \Phi_{J_n}^{\alpha\gamma_2}(\mathbf{k}; t) \Phi_{nJ}^{\alpha_2\gamma}(\mathbf{k}; t) \right\} \xi_4^{\alpha_2\gamma_2\alpha_1\gamma_1}(\mathbf{k}), \end{aligned} \quad (4.9)$$

where

$$\begin{aligned} \Phi_{J_n}^{\alpha\gamma_2}(\mathbf{k}; t) &= \left\langle \frac{1}{m_\alpha} \hat{\mathbf{p}}_\alpha(\mathbf{k}) e^{iL_N t} \hat{n}_{\gamma_2}(-\mathbf{k}) \right\rangle_0, \\ \Phi_{nJ}^{\alpha_2\gamma}(\mathbf{k}; t) &= \left\langle \hat{n}_{\alpha_2}(\mathbf{k}) e^{iL_N t} \frac{1}{m_\gamma} \hat{\mathbf{p}}_\gamma(-\mathbf{k}) \right\rangle_0 \end{aligned}$$

are the time correlation functions.

Insertion equation (4.9) into equation (4.6) with neglecting of $\tilde{T}_{J_n J_n}^{(1)}$ gives in the Fourier presentation an analogous nonlinear integral equation for $S_{\alpha\gamma}(\mathbf{k}, \omega)$ as in the mode-coupling theory. The term related to $\tilde{T}_{J_n J_n}^{(1)}$ includes $\tilde{T}_{J_n J_n}$ as well as third-order transport kernels, and generalized diffusion coefficients $D_{JJ}^{\alpha\gamma}$. It can be estimated in both ($\omega \rightarrow 0$) and ($\omega \rightarrow \infty$) limits.

5 Conclusions

Application of the nonequilibrium statistical operator method by Zubarev in the kinetics of chemically reacting mixtures has allowed us to obtain the generalized transport equations for the parameters of reduced description, namely, the nonequilibrium one-particle and pair distribution functions taking into account the Kawasaki-Mori projection technique. The transport kernels of these non-Markovian equations describe diffusional and many-particle dynamic correlations in which the projection operators separate slow and fast dynamical processes. Their behaviour can be studied in small and large time scales.

The nonequilibrium pair distribution function can be used to calculate $E_{AB}^{\text{reac}}(t)$, the mean energy of chemical bond for molecule AB, which has been created from atoms A and B. Our analysis of the generalized equations of chemical kinetics for weakly nonequilibrium processes reveals that these equations are of the third order with respect to the number density fluctuations. The equations can be important in exploration of nonequilibrium stationary microstructures due to chemical reactions on the surfaces [34].

In the approximation of the second order in the number density fluctuations we have obtained (in the Markovian approximation) such a system of equations which can be regarded as an analogue of the equations of chemical kinetics [1] for chemically reacting mixture with the generalized reaction rate constants expressed through the corresponding transport kernels (memory functions).

In the case of spatial uniformity we have received the system of integro-differential equations for the partial scattering functions, related to the partial dynamic structure factors by the Fourier transformation. Among these, there are a) inner molecular structure factors as a result of the creation of a molecule AB from atoms A and B; b) intermolecular atomic dynamic structure factors related to atoms A and B which belong to different molecules; c) and also, partial ones related to single atoms A and B.

It is worth to notice that our equations of chemical kinetics as well as the equations for the partial structure factors include the same transport kernels. These kernels can be approximately calculated in small and long time limits through equilibrium partial distribution functions, structure factors, and potential of interaction including the model potential of chemical reaction $\Phi_{AB}^{\text{reac}}(\mathbf{r}, \mathbf{r}')$. Such investigation is an objective of our next works.

Financial supports of this work by the National Academy of Sciences of Ukraine (project No 0102U000216) and by INTAS (project UA 95-0186) are gratefully acknowledged.

Appendix A

$$\begin{aligned} \Sigma_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1; t, t') &= 2 \sum_{\gamma_1} \int d\mathbf{r}_2 \varphi_{nG}^{\alpha\gamma_1\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \langle \hat{n}_{\gamma_1}(\mathbf{r}_2) \rangle_0 \\ &- \sum_{\gamma_1\alpha_2} \int d\mathbf{r}_2 \int d\mathbf{r}_3 \varphi_{nG}^{\alpha\gamma_1\alpha_2}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3; t, t') \chi_{\gamma_1\alpha_2\alpha_1}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_1), \end{aligned} \quad (A.1)$$

$$\begin{aligned} \tilde{\Sigma}_{Gn}^{\alpha\gamma\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') &= \Sigma_{Gn}^{\alpha\gamma\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \\ &+ \sum_{\alpha_2} \int d\mathbf{r}_3 \chi_{\alpha\gamma\alpha_2}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_3) \Sigma_{nn}^{\alpha_2\alpha_1}(\mathbf{r}_3, \mathbf{r}_2; t, t') \\ &- \Sigma_{nn}^{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_2; t, t') \langle \hat{n}_\gamma(\mathbf{r}_1) \rangle_0 - \Sigma_{nn}^{\gamma\alpha_1}(\mathbf{r}_1, \mathbf{r}_2; t, t') \langle \hat{n}_\alpha(\mathbf{r}) \rangle_0, \end{aligned} \quad (A.2)$$

$$\begin{aligned} \Sigma_{Gn}^{\alpha\gamma\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') &= \varphi_{Gn}^{\alpha\gamma\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t, t') \\ &+ 2 \sum_{\gamma_1} \int d\mathbf{r}_3 \varphi_{GG}^{\alpha\gamma\gamma_1\alpha_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2; t, t') \langle \hat{n}_{\gamma_1}(\mathbf{r}_3) \rangle_0 \\ &- \sum_{\gamma_1\alpha_2} \int d\mathbf{r}_3 \int d\mathbf{r}_4 \varphi_{GG}^{\alpha\gamma\gamma_1\alpha_2}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4; t, t') \\ &\times \chi_{\gamma_1\alpha_2\alpha_1}(\mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_2), \end{aligned} \quad (\text{A.3})$$

$$\begin{aligned} \Sigma_{GG}^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') &= \varphi_{GG}^{\alpha\gamma\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \\ &+ \sum_{\alpha_2} \int d\mathbf{r}_4 \chi_{\alpha\gamma\alpha_2}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_4) \varphi_{nG}^{\alpha_2\alpha_1\gamma_1}(\mathbf{r}_4, \mathbf{r}_2, \mathbf{r}_3; t, t') \\ &- \varphi_{nG}^{\alpha\alpha_1\gamma_1}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3; t, t') \langle \hat{n}_{\gamma}(\mathbf{r}_1) \rangle_0 \\ &- \varphi_{nG}^{\gamma\alpha_1\gamma_1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; t, t') \langle \hat{n}_{\alpha}(\mathbf{r}) \rangle_0. \end{aligned} \quad (\text{A.4})$$

$$\begin{aligned} \Omega_{Gn}^{\alpha_2\gamma_1\alpha_1}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_1) &= \sum_{\alpha_3\gamma_3} \int d\mathbf{r}_4 \int d\mathbf{r}_5 \\ &\times W_{GG}^{\alpha_2\gamma_1\alpha_3\gamma_3}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5) \tilde{\Sigma}_{Gn}^{\alpha_3\gamma_3\alpha_1}(\mathbf{r}_4, \mathbf{r}_5, \mathbf{r}_1), \end{aligned} \quad (\text{A.5})$$

$$\begin{aligned} \tilde{\Omega}_{Gn}^{\alpha_1\alpha_2\gamma_1}(\mathbf{r}, \mathbf{r}_3, \mathbf{r}_2) &= \\ &\sum_{\alpha_3\gamma_3} \int d\mathbf{r}_4 \int d\mathbf{r}_5 W_{GG}^{\alpha_2\gamma_1\alpha_3\gamma_3}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5) \Sigma_{nn}^{\gamma_3\alpha_1}(\mathbf{r}_5, \mathbf{r}), \end{aligned} \quad (\text{A.6})$$

where the function $W_{GG}^{\alpha_2\gamma_1\alpha_3\gamma_3}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5)$ obeys the relation:

$$\begin{aligned} \sum_{\alpha\gamma} \int d\mathbf{r} \int d\mathbf{r}' W_{GG}^{\alpha_1\gamma_1\alpha\gamma}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}, \mathbf{r}') \Sigma_{GG}^{\alpha\gamma\alpha_2\gamma_2}(\mathbf{r}, \mathbf{r}', \mathbf{r}_4, \mathbf{r}_5) = \\ \delta_{\alpha_1\alpha_2} \delta_{\gamma_1\gamma_2} \delta(\mathbf{r}_2 - \mathbf{r}_4) \delta(\mathbf{r}_3 - \mathbf{r}_5). \end{aligned} \quad (\text{A.7})$$

References

1. J. Keizer, *Statistical thermodynamics of nonequilibrium processes* (Springer-Verlag, Berlin-Heidelberg-New York-Tokyo, 1987)
2. N. Xystris, J.S. Dahler, *J. Chem. Phys.* **68**, 374 (1978)
3. N. Xystris, J.S. Dahler, *J. Chem. Phys.* **68**, 387 (1978)
4. M. von Smoluchowski, *Z. Phys. Chem.* **92**, 129 (1917)
5. S.A. Rice, in *Diffusion-Limited Reactions* (Elsevier, Amsterdam, 1985)
6. N. Agmon, A. Szabo, *J. Chem. Phys.* **92**, 5270 (1990)
7. A. Szabo, *J. Chem. Phys.* **95**, 2481 (1991)
8. W. Naumann, A. Szabo, *J. Chem. Phys.* **107**, 402 (1997)
9. J. Keizer, E. Peacock-Lopez, *Physica A* **147**, 61 (1987)
10. A. Molski, J. Keizer, *J. Chem. Phys.* **104**, 3567 (1996)
11. G.F. Mazenko, *Phys. Rev. A* **7**, 209 (1973)
12. G.F. Mazenko, *Phys. Rev. A* **7**, 222 (1973)
13. G.F. Mazenko, *Phys. Rev. A* **9**, 360 (1974)
14. R.I. Cukier, R. Kapral, J.R. Mehafeff, K.J. Shin, *J. Chem. Phys.* **72**, 1830 (1980)
15. R.I. Cukier, R. Kapral, J.R. Mehafeff, K.J. Shin, *J. Chem. Phys.* **72**, 1844 (1980)
16. M. Yang, S. Lee, K.J. Shin, *J. Chem. Phys.* **108**, 117 (1998)
17. M. Yang, S. Lee, K.J. Shin, *J. Chem. Phys.* **108**, 8557 (1998)
18. M. Yang, S. Lee, K.J. Shin, *J. Chem. Phys.* **108**, 9069 (1998)
19. B.U. Felderhof, R.B. Jones, *J. Chem. Phys.* **103**, 10201 (1995)
20. B.U. Felderhof, R.B. Jones, *J. Chem. Phys.* **106**, 954 (1997)
21. B.U. Felderhof, R.B. Jones, *J. Chem. Phys.* **106**, 967 (1997)
22. B.U. Felderhof, R.B. Jones, *J. Chem. Phys.* **106**, 5006 (1997)
23. I.V. Gopich, A.B. Doktorov, *J. Chem. Phys.* **105**, 2320 (1996)
24. A.B. Doktorov, A.A. Kipriyanov, *Physica A* **317**, 41 (2003)
25. A.A. Kipriyanov, A.B. Doktorov, *Physica A* **317**, 63 (2003)
26. N.N. Bogolubov, N.N. Bogolubov (Jr), *Introduction to Quantum Statistical Mechanics* (World Scien., Singapore, 1982)
27. M.V. Tokarchuk, P.P. Kostrobii, Y.A. Humenyuk, *J. Phys. Studies* **5**, 111 (2001) (in Ukrainian)
28. D. Zubarev, V. Morozov, G. Röpke, *Statistical Mechanics of Nonequilibrium Processes* (Akad. Verl. GmbH, Berlin, 1996)
29. D. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Plenum, New York, 1974)
30. J.P. Boon, S. Yip, *Molecular hydrodynamics* (Dover, New York, 1980)
31. U. Balucani, M. Zoppi, *Dynamics of the liquid state* (Clarendon Press, Oxford, 1994)
32. W. Götze, in *Liquids, Freezing and Glass Transitions*, edited by J.-P. Hansen, D. Levesque, J. Zinn-Justin, (North-Holland, Amsterdam, 1991)
33. J. Bosse, W. Götze, M. Lücke, *Phys. Rev. A* **17**, 434 (1978)
34. M. Hildebrand, A.S. Mikhailov, G. Ertl, *Phys. Rev. E* **58**, 5483 (1998)