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## Scientific School of Nonequilibrium Aeromechanics at St. Petersburg State University

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**Abstract**—The review describes the creation and development of the scientific school of Sergei Vasil'yevich Vallander at the Leningrad (now St. Petersburg) State University. We discuss the achievements of the scientific school in the development of methods of the kinetic theory of gases for the simulation of nonequilibrium flows, the construction of rigorous self-consistent mathematical models of varying complexity for strong and weak deviations from equilibrium, and the application of the developed models in solving modern problems of aerodynamics. Particular attention is paid to the study of non-equilibrium kinetics and transport processes in carbon dioxide, identifying the key relaxation mechanisms of polyatomic molecules, the development of physically reasonable reduced hybrid models, and the optimization of numerical simulation of flows using modern machine-learning methods. We discuss the problems of correctly accounting for electronic excitation in modeling the kinetics and transport processes, models of equilibrium gas flows with multiple ionization, and the peculiarities of simulating bulk viscosity in polyatomic gases.

**Keywords:** nonequilibrium aeromechanics, kinetic equations, physical–chemical processes, vibrational-chemical kinetics, transport processes

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### 1. ESTABLISHMENT OF VALLANDER'S SCIENTIFIC SCHOOL

The study and teaching of hydromechanics at St. Petersburg University began from the first years of the university foundation in 1724. The first lectures on hydromechanics were given to students of St. Petersburg University by Leonhard Euler (1707–1783) and Daniel Bernoulli (1700–1782), academicians of the Imperial Academy of Sciences. In 1929, the Department of Hydroaeromechanics was established, chaired by Professor Alexander Alexandrovich Satkevich (1869–1938) [1].

The scientific school of nonequilibrium aeromechanics was created in the 1950s by Sergei Vasilievich Vallander [2, 3], who headed the department of hydroaeromechanics for twenty-five years (1950–1975). In 1949 Vallander defended his habilitation thesis “Missiles and Wings in a Supersonic Flow.” The defense became a notable scientific event of the day. Academicians V. I. Smirnov, M. V. Keldysh, L. I. Sedov, S. A. Khristianovich, and A. A. Dorodnitsyn, present at the defense, highly appreciated the results of the thesis. Several results presented in Vallander's dissertation became a part of classical gas dynamics and are presented, in particular, in books [4] and [5]. One of these results is the tangent cone method for solving the problem of a supersonic gas flow around pointed bodies or bodies of revolution. Another important result of Vallander's dissertation is the principle of the stabilization of hypersonic inviscid-gas flows.

In the 1950s Vallander took charge of the intensive gas-dynamics research at the Department of Hydroaeromechanics based on the results obtained by him. He proposed a method for numerically determining the aerodynamic characteristics of wings of finite span [6]. Led by him in the 1950s, the department began research on fluid flows in turbines and lattices, which were commissioned by the Leningrad Metal Plant and the Central Boiler and Turbine Institute (CBTI). He proposed a method for calculating

the potential flow of an inviscid incompressible fluid around an infinite airfoil cascade [7], and obtained a solution to the spatial problem of fluid flow in a turbine [8]. His work [9] presented a mathematical apparatus necessary for applying the method of singularities to the calculation of flows in general radial-axial turbines, which made it possible to reduce the three-dimensional problem of simulating the flow in a central-axial turbine to two dimensions.

In the late 1950s Vallander turned to a new scientific direction: the dynamics of rarefied gases. His interest in this topic was due to the rapid development of cosmonautics and the need to model the processes occurring near the surfaces of spacecraft. At high altitudes under the conditions of aircraft entry into the atmospheres of planets, strong deviations from equilibrium occur in gas flows, so the methods of continuum mechanics based on introducing a physically infinitely small volume and the assumption of maintaining thermodynamic equilibrium are not suitable for determining the flow parameters. It is necessary to take into account the rarefaction of the gas and the kinetic processes that occur during particle collisions. Vallander was one of the first to understand the promise of using the kinetic approach to solving problems of gas dynamics. He wrote several papers on applying the theory of kinetic equations for this approach. He proposed new integral equations for the distribution functions of particles of a rarefied monatomic and polyatomic gas [10–12], which are valid under the same assumptions under which Boltzmann derived his famous integro-differential equation for the distribution function in 1872. The integral form for the Boltzmann equation was proposed earlier by Enskog [13] and Grad [14], and then by other authors. The Vallander equations fundamentally differ from previously existing integral forms of the Boltzmann equation. The main difference is that the Vallander equations describe not only the dynamics of rarefied-gas molecules and their collisions with each other, but also the interaction of gas particles with the surfaces of bodies within a flow or with the boundary of the considered region using functions called boundary transformants. In addition, the integral form of the equations made the method of successive approximations efficient for their numerical solution.

Vallander clearly understood that for the development of high-speed aviation and space technology, it is necessary to study the physical-chemical processes that occur in high-temperature gas flows. Under his leadership and with his direct participation, the department began research on flows of chemically reacting and relaxing mixtures of gases, and the initial stage already yielded new and interesting results. The new approach proposed in [15] to describe relaxation processes in gas flows, turned out to be promising; it was based on the joint solution of equations of gas dynamics and equations for the populations of energy levels of gas molecules. A method was proposed for calculating equilibrium distributions in chemically reacting mixtures of gases [16] and the Chapman–Enskog method was generalized for gases with internal degrees of freedom and chemical reactions [17]. Vallander's ideas significantly enriched the classical kinetic theory, filling it with new physical meaning.

Vallander's works on aerodynamics found practical application in the creation and development of rocket and space technology, which was an important industry for the USSR. As a result, he was awarded the State Prize of the USSR in 1973 as part of a team that included specialists from RSC Energia (currently the S. P. Korolev Rocket and Space Corporation Energia) and the Central Research Institute for Machine Building, which are the leading organizations in the rocket and space industry.

The development of orbital-satellite constellations, including space systems for socio-economic purposes, equipped with multichannel imaging equipment for remote sensing of the Earth in various spectral ranges, further expanded the range of problems for the students of Vallander to successfully participate in. The knowledge gained at the department allows graduates to work in various areas using satellite imagery data to solve such important economic and environmental problems as mapping land resources, monitoring forests, assessing the condition and use of agricultural land, inventorying crops, or identifying unused land in order to increase the economic efficiency of the use of the Russia's land.

The research team created by Vallander immediately made a name for itself with new results. Based on Vallander's ideas, intensive research began in the following areas: the interaction of rarefied gases with surfaces [18–25], the kinetic theory of gases and plasma [17, 26–29], the theory of nonequilibrium processes in gas flows (see monographs [28, 30] and numerous articles in journals in the 2000s–2020s). A number of works were carried out together with the Institute for Computer Aided Design, Russian Academy of Sciences [31–33]; with Novosibirsk State University and the Institute of Theoretical and Applied Mechanics, Siberian Branch, Russian Academy of Sciences [34–39]; as well as with the European Space Agency [40–43] and universities in Europe [44–58], the United States [59–63], and Brazil [64–66].

In this review, we focus in more detail on the results related to the development of rigorous self-consistent mathematical models of nonequilibrium flows and their application to specific problems of physical-chemical gas dynamics.

## 2. CHAPMAN–ENSKOG THEORY FOR STRONG DEVIATIONS FROM EQUILIBRIUM

One of the modern areas of research carried out by the department is the study of gas dynamics, non-equilibrium kinetics, and transport processes in gases under strong deviations from equilibrium. The results obtained in this direction are considered in detail in book [28] translated into English [30] and in many papers.

The original Chapman–Enskog theory [67–69] was constructed for weak deviations from equilibrium, when all physical-chemical processes proceed noticeably faster than the rate of change in the macroscopic state of the system. For strong deviations from equilibrium, some elementary processes proceed on a hydrodynamic time scale, and therefore, to describe the flow, it is necessary to take into account relaxation processes in the system of fluid-dynamic equations. The theory was modified for gases with fast and slow processes in [17, 28, 30].

The description is based on a system of kinetic equations for the distribution function of the reacting-gas mixture. In the absence of external body forces, the kinetic equations can be written in the form of the Boltzmann equation (for gases with internal degrees of freedom, we use the Wang-Chang–Uhlenbeck notation [70]):

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = J_{cij}, \quad (1)$$

here  $f_{cij}$  is the distribution function of particles of chemical species  $c$  at vibrational and rotational energy levels  $i$  and  $j$ ,  $\mathbf{u}_c$  is the velocity of particles of species  $c$ ,  $J_{cij}$  is an integral operator describing the change in the distribution function as a result of various collisions. If there are fast and slow processes in the system, Eq. (1) in the dimensionless form can be written as

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = \frac{1}{\epsilon} J_{cij}^{\text{rap}} + J_{cij}^{\text{sl}}, \quad (2)$$

where the small parameter  $\epsilon$  is determined by the ratio of the characteristic times of fast and slow processes,  $\epsilon = \frac{\tau_{\text{rap}}}{\tau_{\text{sl}}}$ , and the integral operators  $J_{cij}^{\text{rap}}$  and  $J_{cij}^{\text{sl}}$  correspond to processes occurring on microscopic and hydrodynamic time scales.

To solve Eqs. (2), the distribution function is expanded into a series in terms of the small parameter  $\epsilon$

$$f_{cij}(\mathbf{r}, \mathbf{u}, t) = \sum_n \epsilon^n f_{cij}^n(\mathbf{u}, \rho_\lambda(\mathbf{r}, t), \nabla \rho_\lambda(\mathbf{r}, t), \nabla^2 \rho_\lambda(\mathbf{r}, t), \dots). \quad (3)$$

In the Chapman–Enskog theory the distribution function depends on the coordinate  $\mathbf{r}$  and time  $t$  not explicitly, but via the macro parameters  $\rho_\lambda(\mathbf{r}, t)$  and their gradients of various orders.

Let us give a brief scheme of the modified Chapman–Enskog method, which can be used to construct a closed description of the gas flow for arbitrary deviations from equilibrium [28, 29].

1. Separation of collisional processes into fast and slow and determining the hierarchy of relaxation times and the small parameter as the ratio of the characteristic times of fast and slow processes. For different degrees of nonequilibrium, the hierarchy of characteristic times can differ significantly.

2. Writing the Boltzmann equation in the dimensionless form and selecting the integral operators of fast and slow processes.

3. Selecting the collision invariants of fast processes. This step is key for correct description of a strongly nonequilibrium flow, and also contains the main difference from the original Chapman–Enskog theory, which is based on the introduction of invariants of all collisional processes. The number of additional invariants determines the degree of detail of the gas description, as well as the number of macroparameters and transport equations for them.

4. Determination of the macro parameters corresponding to collision invariants of fast processes. This set of macroparameters provides a closed description of the flow under the considered nonequilibrium conditions.

5. Writing the normalization conditions for the distribution function. The distribution function is normalized with respect to the set of macro parameters selected at the previous step. The peculiarity of normalization is that the distribution function of the zero approximation completely determines the macroparameters, and the subsequent approximations do not contribute to the defining macroscopic variables.

6. Derivation of transport equations from the general Boltzmann equation and determination of the flow and relaxation terms.

7. Zero-order approximation of the generalized Chapman–Enskog theory:

(a) calculation of the zero-order distribution function from the condition that the integral operator of fast processes is equal to zero;

(b) using normalization conditions to determine the unknown coefficients in the expression for the distribution function;

(c) calculation of transport and relaxation terms and deriving the fluid-dynamic equations in the zero approximation; these equations correspond to the model of an inviscid non-heat-conducting fluid (the Euler equations), taking into account strong deviations from equilibrium.

8. First-order approximation:

(a) deriving an integral equation for the distribution function in the first-order approximation;

(b) calculation of the differential operator  $Df^{(0)}$ ;

(c) writing the structural form of the first-order correction to the distribution function as a linear combination of gradients of macroparameters;

(d) derivation of constitutive relations for transport and relaxation terms in the first-order approximation; the resulting fluid-dynamic equations correspond to the model of a viscous heat-conducting fluid (the Navier–Stokes equations) taking into account strong deviations from equilibrium;

(e) calculation of the transport coefficients included in the constitutive relations for the diffusion velocity, heat flux, stress tensor, and rate coefficients of physical and chemical processes.

9. If necessary, higher approximations can be considered (for example, the Burnett equations).

### 3. APPLYING THE GENERAL METHOD TO VARIOUS DEVIATIONS FROM EQUILIBRIUM

This general scheme was used to develop specific models of varying complexity for a closed description of flows with physical and chemical transformations and the numerical simulation of nonequilibrium flows based on the developed models. The state-to-state model was considered in [71–74]; the multitemperature approximation was developed in [44, 49, 75–79]; the one-temperature formulation is considered in [43, 44, 80–84]; and the problems of modeling locally equilibrium flows are discussed in [85–90]. The constructed mathematical models were generalized to the case of polyatomic gases with several vibrational modes in [45, 53, 57, 91–100].

#### 3.1. State-Resolved Model

The conditions for using this model assume fast translational-rotational and slow vibrational-chemical relaxation:

$$\tau_{tr} < \tau_{rot} \ll \tau_{vibr} \sim \tau_{react} \sim \theta. \quad (4)$$

Here  $\tau_{tr}$ ,  $\tau_{rot}$ ,  $\tau_{vibr}$  are the average times of translational, rotational, and vibrational relaxation;  $\tau_{react}$  is the characteristic time of chemical reactions; and  $\theta$  is the characteristic gas-dynamic time. Under these conditions, all transitions of the vibrational energy and chemical reactions are considered on the time scale of changes in the macroscopic variables of the flow, density, velocity, and temperature of the gas. It should be noted that at high temperatures and in an ionized gas, when the particles are in electronically excited states, transitions between the electronic levels of atoms and molecules may occur also considered as slow processes [50, 51, 101]. In this section we do not consider electronic excitation and ionization to simplify the description of the gas.

The small parameter in the state-to-state model is introduced based on Eq. (4),  $\epsilon = \tau_{tr}/\theta$ ; the integral operator of fast processes includes elastic collisions and transitions of rotational energy, while the operator of slow processes includes exchanges of vibrational energy and chemical reactions. The collision invariants of the fast process are the mass, momentum, and total energy of particles in a collision, as well as the set of variables  $a_{ci}$  ( $c = 1, \dots, l$ ,  $i = 0, \dots, l_c$ ,  $l$  is the number of chemical species of the mixture, and  $l_c$  is the number of excited vibrational levels of particles of species  $c$ ), independent of velocity and rotational state and arbitrarily dependent on chemical species  $c$  and vibrational level  $i$  [28, 44, 71]. These quantities are preserved, since all vibrational-chemical processes are frozen in the time scale  $\tau_{tr}$ . The set of macroparameters corresponding to these collision invariants includes the populations of the vibrational levels of mol-

ecules  $n_{ci}(\mathbf{r}, t)$ , the number densities of atoms  $n_a(\mathbf{r}, t)$ , the gas velocity  $\mathbf{v}(\mathbf{r}, t)$ , and the total energy per unit mass  $E(\mathbf{r}, t)$ .

The system of transport equations in the state-to-state approximation contains equations for the evolution of the populations of the vibrational levels of molecules and the number densities of atoms, and the equations for the conservation of momentum and energy of the mixture:

$$\frac{\partial n_{ci}}{\partial t} + \nabla \cdot (n_{ci}(\mathbf{v} + \mathbf{V}_{ci})) = R_{ci}^{\text{vibr}} + R_{ci}^{\text{react}}, \quad c = 1, \dots, l_m, \quad i = 0, \dots, l_c, \quad (5)$$

$$\frac{\partial n_a}{\partial t} + \nabla \cdot (n_a(\mathbf{v} + \mathbf{V}_a)) = R_a^{\text{react}}, \quad a = l_m + 1, \dots, l, \quad (6)$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{P}) = 0, \quad (7)$$

$$\frac{\partial \rho E}{\partial t} + \nabla \cdot (\rho E \mathbf{v} + \mathbf{P} \cdot \mathbf{v} + \mathbf{q}) = 0. \quad (8)$$

Here  $l_m$  is the number of molecular components of the mixture,  $\rho$  is the density of the mixture, and the total energy per unit mass  $E$  of the mixture is the sum of the internal and kinetic energies:

$$E = u + v^2/2, \quad (9)$$

where the internal energy of a unit mass of the mixture has the form

$$\rho u = e^{\text{tr}} + e^{\text{r}} + e^{\text{v}} + e^{\text{f}}, \quad (10)$$

and includes (per unit volume) the translational energy:

$$e^{\text{tr}} = \frac{3}{2} n k_{\text{B}} T, \quad (11)$$

the rotational energy and vibrational energy of the molecular components of the mixture

$$e^{\text{r}} = \sum_{c=1}^{l_m} n_c k_{\text{B}} T, \quad (12)$$

$$e^{\text{v}} = \sum_{c=1}^{l_m} \sum_{i=0}^{l_c} n_{ci} \varepsilon_i^c, \quad (13)$$

and the formation energy

$$e^{\text{f}} = \sum_{c=1}^l n_c \varepsilon_c. \quad (14)$$

In the relations above,  $n = \sum_c n_c$  is the number density of the mixture,  $n_c$  is the number density of the species  $c$ ,  $k_{\text{B}}$  is the Boltzmann constant,  $T$  is the mixture temperature,  $\varepsilon_i^c$  is the vibrational energy of the  $i$ th state of the  $c$ -type molecule, and  $\varepsilon_c$  is the formation energy of a  $c$ -type particle. In (12) and (13) it is assumed that the rotational and vibrational energies of the molecule are independent of each other, and the rotation of the molecule is described by the rigid rotator model [30].

The system of Eqs. (5)–(8) was obtained in general form in [28, 44, 71] and closed in the same papers. The transport and relaxation terms in the system (diffusion velocity for each vibrational and chemical species  $\mathbf{V}_{ci}$ , stress tensor  $\mathbf{P}$ , heat flux  $\mathbf{q}$ , source terms  $R_{ci}$ ,  $R_a$ ) are determined by the distribution function in each approximation of the method.

Let us first consider the right-hand sides of Eqs. (5) and (6), which are the sum of the source terms of the mixture components due to vibrational-energy transitions ( $R^{\text{vibr}}$ ) and chemical reactions ( $R^{\text{react}}$ ). The source terms describing any elementary process of type  $r$ :

$$\sum_{ci} v'_{ci,r} [A_c](i) \leftrightarrow \sum_{ci} v''_{ci,r} [A_c](i)$$

in which either a change in the internal energy of colliding particles or a chemical transformation occurs can be written in the general form:

$$R_{ci}^r = (v_{ci,r}'' - v_{ci,r}') \left( k_{fi}^r \prod_{ci} (n_{ci})^{v_{ci,r}'} - k_{bi}^r \prod_{ci} (n_{ci})^{v_{ci,r}''} \right). \quad (15)$$

Here  $v_{ci,r}'$  and  $v_{ci,r}''$  are stoichiometric coefficients of the process  $r$  in the forward and backward directions,  $[A_c]$  is the symbol of the chemical element, and  $k_{fi}^r$  and  $k_{bi}^r$  are state-to-state rate coefficients of the process  $r$  in the forward and backward directions, the relationship between which is determined by detailed-balance relations [30].

Then  $R^{\text{vibr}}$  and  $R^{\text{react}}$  have the form:

$$R_{ci}^{\text{vibr}} = \sum_{r \in \mathcal{V}} R_{ci}^r, \quad R_{ci}^{\text{react}} = \sum_{r \in \mathcal{R}} R_{ci}^r, \quad (16)$$

where  $\mathcal{V}$  and  $\mathcal{R}$  stand for the sets of energy-exchange processes and chemical reactions, respectively.

Let us proceed to closure of the system in various approximations of the generalized Chapman–Enskog theory. In the zero-order approximation, the distribution function has the form of a Maxwell–Boltzmann distribution over velocity and rotational energy [28]. In this regard, the diffusion velocities and heat flux are equal to zero  $\mathbf{V}_{ci} = \mathbf{V}_a = \mathbf{q} = 0$ , and the stress tensor has a diagonal form  $\mathbf{P} = p\mathbf{I}$  ( $p = nk_B T$  is the mixture pressure,  $\mathbf{I}$  is the unit tensor). The state-to-state rate coefficients of reactions and transitions of vibrational energy are functions of the gas temperature,  $k_{fi}^r = k_{fi}^r(T)$ , and expressions (15) are reduced to the law of mass action written in a state-to-state approximation (for the populations of all vibrational levels). In this case, the general system of fluid-dynamic Eqs. (5)–(8) is reduced to the equations of motion and energy of an inviscid, non-heat-conducting gas (the Euler equations), supplemented by the equations of detailed state-to-state vibrational-chemical kinetics.

In the first-order approximation of the theory, the distribution function contains a correction, which is a linear combination of gradients of macro parameters. The gradient coefficients are calculated from the integral equations defined by the linearized integral operator of fast processes [28]. In this case, the diffusion velocity has the form

$$\mathbf{V}_{ci} = -\sum_{dk} D_{cidk} \mathbf{d}_{dk} - D_{Tci} \nabla \ln T, \quad (17)$$

where  $D_{cidk}$  and  $D_{Tci}$  are the diffusion and thermal-diffusion coefficients for all chemical and vibrational species, and  $\mathbf{d}_{ci}$  are the corresponding diffusive driving forces:

$$\mathbf{d}_{ci} = \nabla \left( \frac{n_{ci}}{n} \right) + \left( \frac{n_{ci}}{n} - \frac{\rho_{ci}}{\rho} \right) \nabla \ln p. \quad (18)$$

The stress tensor is written in the form

$$\mathbf{P} = (p - p_{\text{rel}})\mathbf{I} - \zeta \nabla \cdot \mathbf{v} \mathbf{I} - 2\eta \left( \mathbf{S} - \frac{1}{3} \nabla \cdot \mathbf{v} \mathbf{I} \right), \quad (19)$$

$\eta$  and  $\zeta$  are coefficients of shear and bulk viscosity,  $p_{\text{rel}}$  is the relaxation pressure, and  $\mathbf{S} = (\nabla \mathbf{v} + \nabla \mathbf{v}^T)/2$  is the strain-rate tensor.

The total energy flux has the form

$$\mathbf{q} = -\lambda' \nabla T - p \sum_{ci} D_{Tci} \mathbf{d}_{ci} + \sum_{ci} \rho_{ci} h_{ci} \mathbf{V}_{ci}, \quad (20)$$

$\lambda'$  is the coefficient of thermal conductivity,  $\rho_{ci}$  and  $h_{ci}$  are the mass density and specific enthalpy of species  $c$  at the  $i$ -th level

$$h_{ci} = \frac{1}{m_c} \left( \frac{5}{2} k_B T + \langle \epsilon_{\text{rot}}^{ci} \rangle + \epsilon_i^c + \epsilon_c \right), \quad (21)$$

$m_c$  is the mass of a particle of type  $c$  and  $\langle \epsilon_{\text{rot}}^{ci} \rangle$  is the average rotational energy for species  $c$  and  $i$ .

The source terms in the first-order approximation can be formally represented in the form (15); however, the reaction-rate coefficients depend not only on temperature, but also on the populations of vibrational levels and gradients of macroparameters, in particular, on the velocity divergence and affinity of all chemical reactions and vibrational-energy exchanges [28, 43, 102]. Therefore, expression (15) no longer

corresponds to the law of mass action, but also characterizes the deviation from this law and the connection of the stress tensor and reaction rates.

The physical meaning of all state-to-state transport coefficients and the algorithms for their calculation are considered in detail in [28, 30, 71, 72, 101, 103, 104]. A specific feature of the state-to-state model is that the heat flux is determined not only by the process of heat conduction, but also by heat transfer due to mass diffusion, thermal diffusion, and the diffusion of vibrational energy [28, 73]. The contributions of these processes to heat transfer in various flows were studied in [61, 73, 92, 105, 106].

Over the past twenty years, the team of the scientific school has solved a number of modern problems of physical and chemical kinetics and nonequilibrium gas dynamics within the framework of the state-to-state model:

—A generalized Treanor–Marrone model was constructed for the state-to-state dissociation rate coefficients taking into account the dependence of the model parameters on the vibrational level [47, 107, 108]; a method for optimizing the parameters was proposed based on the results of semiclassical and quantum-mechanical-trajectory calculations [108–110]; a similar method has been developed for state-to-state exchange reactions, taking into account the vibrational and electronic excitation of reactants and reaction products [57, 109, 111].

—A technique was proposed for obtaining cross sections for state-to-state chemical reactions and vibrational–energy transitions using the inverse Laplace transform [35, 112–114]. The results were used in direct statistical modeling.

—Simplified techniques for calculating the state-to-state transport coefficients and rotational relaxation time have been proposed, which make it possible to take into account the dependence of collision cross sections on the vibrational and electronic levels of particles [65, 66, 72, 101, 115–117]. The models are implemented in the KAPPA [118] and PAINeT [119] software packages.

—The problem of spatially homogeneous relaxation in binary mixtures of oxygen and nitrogen [62, 120, 121], CO [122], air [63, 123], and carbon dioxide [94, 99] has been solved. The aim of the study was to validate the kinetic models, to determine the key mechanisms of relaxation in a polyatomic gas, and to develop a theoretical basis for constructing hybrid models. These issues are discussed in detail in the following sections.

—Flows behind shock waves in binary mixtures and CO [28, 36, 50, 51, 105, 124–127], air [126, 128–130], and carbon dioxide [131] have been studied in the state-to-state formulation. The models of kinetics were validated, compared with experimental data [132–135] and the results of other authors [136], and the contribution of various processes to the kinetics and heat fluxes was estimated. For the problem of a reflected shock wave, taking into account vibrational relaxation in the region between incident and reflected shock waves was shown to be important [127].

—The state-to-state kinetics and processes of heat transfer in nozzles have been studied [28, 30, 73, 137, 138]; the important role of vibrational deactivation and the recombination reaction in the formation of nonequilibrium distributions is shown; the role of thermal conductivity, mass diffusion, thermal diffusion, and the diffusion of vibrational energy in heat transfer has been studied.

—The one-dimensional problem of nonequilibrium flow in the boundary layer along the stagnation line in binary mixtures [48, 52, 139], air [140], and carbon dioxide [53, 55–57, 92] has been solved. Relaxation mechanisms, the influence of the catalytic properties of the surface on heat fluxes, and the distribution of macroparameters have been studied. A new kinetic model has been constructed to determine the boundary conditions on a partially catalytic surface in a rarefied gas [24, 25].

Examples of applying the state-to-state model for studying the kinetics of carbon dioxide are discussed in Section 4.

### 3.2. Multitemperature Model

Multitemperature models describe flows for which the following condition is satisfied for the characteristic times of the processes:

$$\tau_{tr} < \tau_{rot} < \tau_{VV} \ll \tau_{VV'} < \tau_{TRV} < \tau_{react} \sim \theta, \quad (22)$$

$\tau_{VV}$  and  $\tau_{VV'}$  are the average time between collisions of molecules of the same and different types, respectively, at which the exchange of vibrational energy occurs, and  $\tau_{TRV}$  is the time of vibrational–energy transitions to other forms.

Following the general outline of the method, we define a small parameter, integral operators of fast and slow processes, and collision invariants of a fast process. In this case, the number of invariants is notice-

ably smaller. In a fast process, in addition to the mass, momentum, and total energy of particles, a set of values  $a_c$  ( $c = 1, \dots, l$ ) is preserved under condition (22), depending arbitrarily on the chemical species  $c$  (the species does not change in a fast process), as well as the number of vibrational quanta  $i$  of each molecular species, which does not change during VV exchanges [28]. Such collision invariants correspond to the following set of macroparameters: the number density of particles of chemical species  $c$   $n_c(\mathbf{r}, t)$ , gas velocity  $\mathbf{v}(\mathbf{r}, t)$ , total specific energy  $E(\mathbf{r}, t)$ , and specific numbers of vibrational quanta of molecular components  $W_c(\mathbf{r}, t)$ . This set of macroparameters makes it possible to significantly reduce the number of equations describing the flow of the reacting mixture as compared to the state-to-state approach.

The closed system of equations includes equations for changing the composition of the mixture, equations for the conservation of momentum and total energy, and relaxation equations for the average numbers of vibrational quanta of molecular components:

$$\frac{\partial n_c}{\partial t} + \nabla \cdot (n_c(\mathbf{v} + \mathbf{V}_c)) = R_c^{\text{react}}, \quad c = 1, \dots, l, \quad (23)$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{P}) = 0, \quad (24)$$

$$\frac{\partial \rho E}{\partial t} + \nabla \cdot (\rho E \mathbf{v} + \mathbf{P} \cdot \mathbf{v} + \mathbf{q}) = 0, \quad (25)$$

$$\frac{\partial \rho_c W_c}{\partial t} + \nabla \cdot (\rho_c W_c \mathbf{v} + \mathbf{q}_c^w) = R_c^w, \quad c = 1, \dots, l_m. \quad (26)$$

Here

$$\rho_c W_c = \sum_{i=0}^{l_c} i n_{ci}, \quad (27)$$

$\mathbf{V}_c$  is the diffusion velocity of  $c$ -type chemical species,  $\mathbf{q}_c^w$  is the flux of the number of vibrational quanta,  $R_c^{\text{react}}$  is the rate of change in the number densities of chemical types due to chemical reactions, and  $R_c^w$  is the rate of change in the average number of quanta due to all slow processes.

The zero-order distribution function gives us expressions for the populations of vibrational levels and allows us to close the system of Eqs. (23)–(26) in the Euler approximation. For an anharmonic oscillator, the populations  $n_{ci}$  are described by the Treanor distribution [141]

$$n_{ci}(n_c, T, T_1^c) = \frac{n_c}{Z_c^v(T, T_1^c)} \exp\left(-\frac{\varepsilon_i^c - i\varepsilon_1^c}{k_B T} - \frac{i\varepsilon_1^c}{k_B T_1^c}\right), \quad (28)$$

and for a harmonic oscillator, they are described by the Boltzmann distribution

$$n_{ci}(n_c, T, T_v^c) = \frac{n_c}{Z_c^v(T_v^c)} \exp\left(-\frac{\varepsilon_i^c}{k_B T_v^c}\right), \quad (29)$$

where  $Z_c^v$  is the vibrational partition function,  $T_v^c$  is the vibrational temperature of the molecular species  $c$ , and  $T_1^c$  is the temperature of the first vibrational state of the given species. The temperature  $T_1^c$  is introduced for the anharmonic-oscillator model. In (28), the vibrational energy  $\varepsilon_i^c$  is measured from the energy of the zero state.

Expressions for the transport terms in the first-order approximation of the Chapman–Enskog theory were obtained in [28, 30, 44]. It is shown that, for an anharmonic oscillator, the fluxes of vibrational quanta and the total energy flux depend on the gradients of the gas temperature and the temperatures of the first level of all molecular components with the corresponding cross thermal conductivity coefficients. The stress tensor has the form (19), and the bulk viscosity coefficient is determined not only by rotational relaxation, as in the state-to-state model, but also by nonresonant VV exchange. Diffusion velocities are introduced for each chemical species and do not contain the vibrational-energy diffusion contribution. This process in the multitemperature model is described by gradients of vibrational temperatures, on which the quasi-stationary vibrational distributions depend. Algorithms for calculating transport coefficients in the multitemperature approximation are described in detail in [28, 30, 44, 75]. These algorithms were generalized for polyatomic gases with several vibrational modes in [45, 91, 142].



The right-hand sides in Eqs. (23) and (26) can be obtained by averaging the state-to-state relaxation terms:

$$E_c^{\text{react}} = \sum_r \sum_i R_{ci}^r, \quad r \in \mathcal{R}, \quad (30)$$

$$R_c^w = \sum_r \sum_i i R_{ci}^r, \quad r \in \mathcal{V}\mathcal{V}', \text{TRV}, \mathcal{R}. \quad (31)$$

The traditional and computationally less expensive approach is the multitemperature approach, where the calculation of  $R_c^{\text{react}} = \sum_r R_c^r$  uses a relation similar to (15), but without taking into account the vibrational state of molecules. In this case, the reaction rate coefficients  $k_f^r$  and  $k_b^r$  are functions of the parameters  $T$  and  $T_v^c$  (see, for example, [143, 144]). The use of the harmonic-oscillator model makes it possible to pass from Eq. (26) for the average number of vibrational quanta to the equations for the vibrational energy of the molecular components of the mixture:

$$\frac{\partial e_c^v}{\partial t} + \nabla \cdot (e_c^v \mathbf{v} + \mathbf{q}_c^v) = R_c^v, \quad c = 1, \dots, l_m, \quad (32)$$

where

$$e_c^v = \sum_i n_{ci} \varepsilon_i^c, \quad \mathbf{q}_c^v = \varepsilon_i^c \mathbf{q}_c^w, \quad R_c^v = \varepsilon_i^c R_c^w.$$

In computational fluid dynamics (CFD), the following relation is often used to determine the right-hand side of Eq. (32) [145]:

$$R_c^v = \sum_{r \in \mathcal{V}'} \frac{e_c^v(T) - e_c^v(T_v^c)}{\tau_r} + \frac{e_c^v(T_v^c)}{n_c} R_c^{\text{react}}, \quad (33)$$

where the first term is the relation of the approximate Landau–Teller theory [146] describing the change in the vibrational energy due to energy exchanges ( $\tau_r$  is the relaxation time for the  $r$ -th exchange), and the second term approximately takes into account the contribution of chemical reactions to vibrational relaxation.

The limitations of this approach are discussed in [77, 78, 96, 100, 147]. In [77, 78], rigorous models of the vibrational-relaxation rate and the cross effect of chemistry and relaxation in mixtures of diatomic gases were developed within the framework of the generalized Chapman–Enskog theory. It is shown that, if the vibrational-relaxation time  $\tau$  is determined correctly,  $\tau_{vT}$  depends on the translational and vibrational temperatures, and the Landau–Teller formula in the zero-order approximation of the theory contains the temperature ratio  $T/T_v^c$ . In the first-order approximation (in a viscous gas), the Landau–Teller formula is, strictly speaking, inapplicable, since the rate of vibrational relaxation depends on the divergence of the velocity and the affinity of chemical reactions and vibrational-energy transitions [77]. This also applies to the rate of chemical reactions. Estimates of first-order effects were carried out in [78] and conditions were found under which it is important to take into account the deviation of the relaxation rate from the Landau–Teller formula and the first-order terms in the rate of chemical reactions cannot be discarded. This approach was generalized to the case of polyatomic gases with several vibrational modes in [96, 148].

Modeling the mutual influence of vibrational relaxation and chemical reactions (CVCV) is also a non-trivial task with a number of works [28, 49, 145, 149, 150] focusing on it. To derive CVCV terms, the Boltzmann distribution is usually used with additional assumptions about the form of the chemical-reaction rate coefficients; a generalization of this approach to the case of the Treanor distribution was proposed in [49]. We note that formulas (31) have an advantage: for them the issue of calculating the CVCV relationship is solved automatically and does not require the use of a specific quasi-stationary distribution and additional simplifying assumptions.

The approach described in this section is rigorous and self-consistent; it makes it possible to construct the correct closure of system of Eqs. (23)–(26). Within the framework of this multitemperature model, the scientific school's team investigated the following problems:

—The problem of spatially homogeneous relaxation and one-dimensional flows of an inviscid, non-heat-conducting gas behind shock waves in binary mixtures of oxygen and nitrogen [79], air [49, 151], and carbon dioxide [95, 152–155]. The models of kinetics were validated and compared with experimental

data [134] and state-to-state simulation results. The influence of chemical reactions and their coupling to vibrational relaxation on the distribution of macroparameters behind the shock-wave front was estimated, and the role of the anharmonicity of vibrations was studied. It was shown that the presence of intermode exchanges in polyatomic gases narrows the applicability of the Landau–Teller theory for calculating the rate of vibrational relaxation.

—The multitemperature kinetics in nozzles has been studied [28, 30, 73, 76]; a significant difference was shown between the quasi-stationary and state-to-state distributions at the middle and upper vibrational levels in expanding flows. The Boltzmann (29) and Treanor (28) distributions do not describe the formation of a plateau-like region at medium vibrational levels; the best results are obtained by using the composite Gordiets distribution [73, 75, 156]. However, the flow macroparameters depend rather weakly on the distribution used.

—In collaboration with the Institute of Theoretical and Applied Mechanics, Siberian Branch, Russian Academy of Sciences, the developed multitemperature models were implemented into the ANSYS Fluent software package and used to model two-dimensional flows near the surface of a wedge, double wedge, and cone [34, 37]. A comparison with measured pressure and heat-flux profiles was carried out [157–159]. We note the important role of correct modeling of the rate of vibrational relaxation and chemical reactions in a high-enthalpy separated flow near the surface of a double wedge.

—Two-dimensional carbon-dioxide flows near the surface of the Mars Sample Return Orbiter (MSRO) descent spacecraft were studied within the framework of the viscous-shock-layer model [31–33], as well as flows along the stagnation line and on the surface of the Mars Pathfinder [54]. The correct modeling of vibrational relaxation in calculating the parameters in the shock layer is shown to be important; in this case, a simplified two-temperature model can be used near the surface of the MSRO spacecraft. Taking into account the bulk viscosity significantly affects the magnitude of the heat flux on the surface of the spacecraft. Using the model of transport processes developed in [91, 160] significantly improves the accuracy of calculating heating near the spacecraft surface and the agreement with experimental data on heat fluxes [161, 162].

—The problem of the shock-wave structure in a viscous nonequilibrium  $\text{CO}_2$  flow was solved [98, 163]. A comparison was made with the results of calculations in the one-temperature approximation and direct simulation Monte Carlo (DSMC). The profiles of the density, temperature, vibrational temperatures, stresses and heat fluxes are studied, and the role of bulk viscosity is discussed. The effects of heat-flux compensation due to transfer of the vibrational energy of different modes of carbon dioxide are clarified.

Sections 4 and 5 discuss the applications of multitemperature models to the study of the vibrational chemical kinetics of carbon dioxide, the applicability of reduced models, and possible ways of optimizing numerical simulation.

### 3.3. One-Temperature Model

This model assumes slow chemical reactions and fast relaxation of internal degrees of freedom. The relation for the characteristic times of processes has the form:

$$\tau_{\text{tr}} < \tau_{\text{int}} \ll \tau_{\text{react}} \sim \theta, \quad (34)$$

$\tau_{\text{int}}$  is the relaxation time of the internal energy.

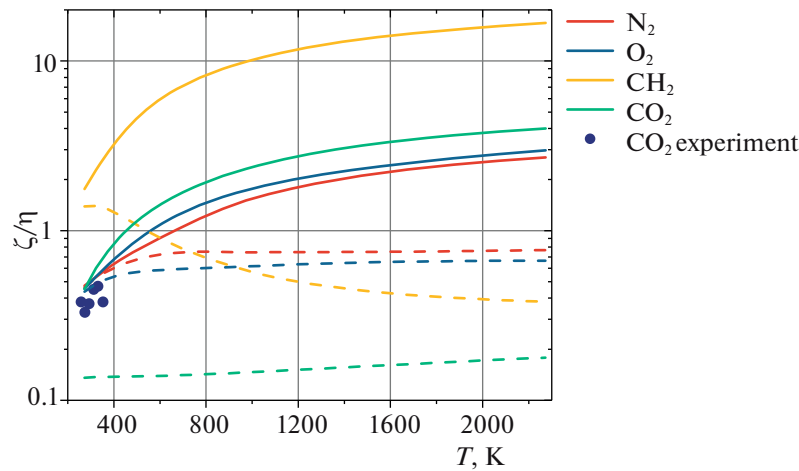
Under these conditions, the equilibrium Boltzmann distribution (29) is established with temperature  $T_v^c = T$ . The system of equations describing the one-temperature nonequilibrium chemical kinetics includes equations for the number densities of the mixture components, the momentum and total energy conservation equations:

$$\frac{\partial n_c}{\partial t} + \nabla \cdot (n_c(\mathbf{v} + \mathbf{V}_c)) = R_c^{\text{react}}, \quad (35)$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{P}) = 0, \quad (36)$$

$$\frac{\partial \rho E}{\partial t} + \nabla \cdot (\rho E \mathbf{v} + \mathbf{P} \cdot \mathbf{v} + \mathbf{q}) = 0. \quad (37)$$

The transport and relaxation terms in this system, as well as the algorithms for calculating transport coefficients, are discussed in detail in [28, 30, 69, 164].



**Fig. 1.** Ratio of the coefficients of bulk and shear viscosity for various gases. Solid lines:  $\zeta/\eta$ , dotted lines:  $\zeta_{\text{rot}}/\eta$ , points: experimental data [173] for  $\zeta/\eta$   $\text{CO}_2$ .

Although quite simple, the one-temperature model makes it possible to take into account strong deviations from equilibrium caused by chemical reactions, as well as weak deviations from thermal equilibrium due to introduction of the bulk viscosity coefficient, relaxation pressure, and thermal conductivity coefficients of internal degrees of freedom. Generally, transport processes in a one-temperature gas have been fairly widely studied. However, a number of problems still cause debate and have not been resolved entirely. Let us discuss in more detail two interesting problems: the phenomenon of bulk viscosity and the effect of electronic excitation.

The study of bulk viscosity and relaxation processes in molecular polyatomic gases and their mixtures is a challenging problem of gas dynamics. In the works of Leontovich and Mandelshtam in 1937 [165], and then by Tisza in 1941 [166], an additional mechanism for the damping of sound waves, i.e., molecular relaxation, was experimentally discovered. This served as the basis for introducing the bulk viscosity coefficient  $\zeta$ , which characterizes the final rate of energy redistribution between the translational and internal degrees of freedom and the subsequent additional compression/expansion of the gas volume after its initial compression or expansion. This effect violates the so-called Stokes relation  $3\eta_2 + 2\eta = 0$  ( $\eta_2 = \zeta - \frac{3}{2}\eta$  is the second viscosity coefficient) for gases with internal degrees of freedom.

Since its discovery, bulk viscosity has been widely discussed in publications (see the detailed review in [167, 168]) and even caused controversy [169, 170] due to inaccurate definitions. For example, Cramer [171] states that the ratio of the bulk and shear viscosity coefficients  $\zeta/\eta$  for polyatomic gases such as carbon dioxide and methane can reach several thousand at low temperatures. This statement inspired a lot of computational works, in which new hydrodynamic effects associated with bulk viscosity were numerically discovered.

In [93, 172] the possible reasons of high bulk viscosity were investigated and it was found that the results of [171] were obtained based on an incorrect assumption, namely, splitting the bulk viscosity coefficient into two independent terms related to rotational and vibrational relaxation

$$\zeta = \zeta_{\text{rot}} + \zeta_{\text{vibr}}. \quad (38)$$

Based on the rigorous approach of the kinetic theory, it was shown that such a division is incorrect, since the rotational and vibrational motion of molecules are interconnected. As a result, it was proved that the ratio  $\zeta/\eta$  in  $\text{CO}_2$  does not exceed 3–5, which is confirmed by experiment [173].

The  $\zeta/\eta$  ratio for different gases is shown in Fig. 1, the solid lines [168] and the dots show the experimental data [173]. The maximum  $\zeta/\eta$  ratio was obtained for methane, while the results for nitrogen, oxygen, and carbon dioxide are comparable. It is interesting to estimate the actual contribution of different degrees of freedom to the bulk viscosity. The dotted lines in Fig. 1 correspond to the  $\zeta_{\text{rot}}/\eta$  ratio calculated without vibrational degrees of freedom. This assumption is often made in relaxation hydrodynamics [171]. It can be seen that even at low temperatures, the contribution of vibrational degrees of freedom to the bulk viscosity of polyatomic gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ) is significant, and with increasing temperature it also increases

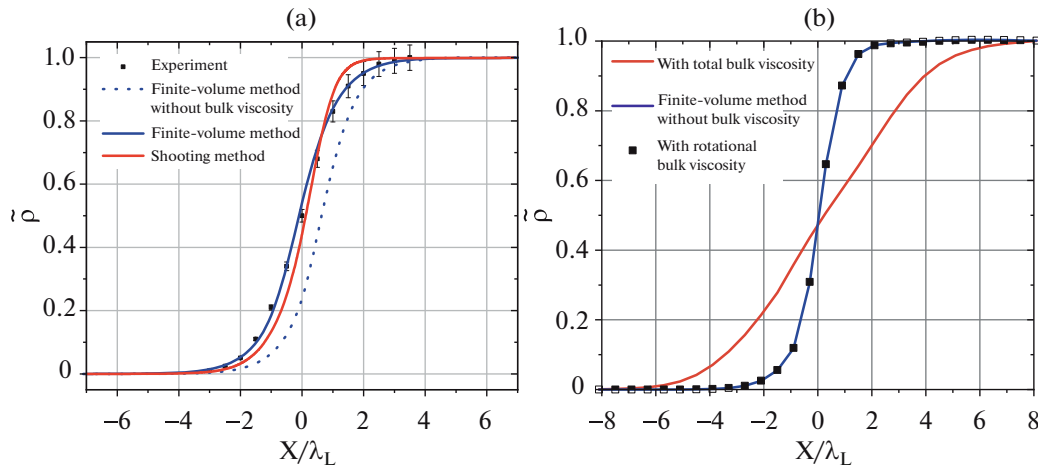


Fig. 2. Dimensionless density profiles as functions of  $x/\lambda_L$ .  $p_L = 6.66$  Pa,  $T_L = 300$  K. (a) is  $N_2$ ,  $M = 3.8$ ; (b)  $CO_2$ ,  $M = 5$ .

noticeably for diatomic gases. Thus, taking into account vibrational modes is important for the correct calculation of bulk viscosity.

An interesting topic for research is the role of bulk viscosity in the simulation of real gas flows. Since the bulk viscosity is multiplied by velocity divergence in the hydrodynamic equations, the resulting term in the Navier–Stokes equation has the form  $\nabla \cdot (\zeta \nabla \cdot \mathbf{v} I)$ . Under the condition  $\zeta/\eta \approx 1$ , this term turns out to be small in many flows [167]; in particular, in the boundary layer it has the second order of smallness. However, if, following [171], we assume  $\zeta/\eta \approx 10^3$ , then the bulk viscosity contribution would be dominant in many flows. This once again emphasizes the importance of accurately estimating this coefficient.

Under the realistic condition  $\zeta/\eta \approx 1$ , the contribution of bulk viscosity to hydrodynamics turns out to be significant only in flows with large gradients, for example, in a shock-wave front. The shock-wave structure was studied in [97, 98, 174–178] based on various models of bulk viscosity. It is shown that taking into account the bulk viscosity significantly improves the agreement between the calculated and experimental temperature profiles.

Figure 2 shows profiles of the dimensionless density  $\tilde{\rho}$  in the shock wave front as a function of the  $x$  coordinate relative to the mean free path in the undisturbed flow  $\lambda_L$ . Pressure and temperature of the undisturbed flow are:  $p_L = 6.66$  Pa,  $T_L = 300$  K, the Mach numbers varied. For nitrogen, the solutions obtained without and with bulk viscosity by the shooting and finite-volume methods [97, 177] are compared with the experimental results [179]. The inclusion of bulk viscosity in the stress tensor notably improves the calculated profile. For carbon dioxide, the role of vibrational degrees of freedom is also analyzed: the solutions obtained using  $\zeta$  and  $\zeta_{\text{rot}}$  are compared. It can be seen that taking into account rotational modes has practically no effect on the shape of the profile, and the main contribution comes from vibrational modes.

The role of the relaxation pressure in hydrodynamics is discussed in [147, 175, 180–182]. For a shock-heated gas, the contribution of  $p_{\text{rel}}$  to the stress tensor is negligible.

Until recently, in computational fluid dynamics, the transport coefficients were mostly calculated using approximate semiempirical formulas and mixing rules [183, 184]. Such an approach does not always correctly take into account the excitation of the internal degrees of freedom of molecules (electronic, vibrational, and rotational), which can significantly affect heat fluxes. For example, the discrepancy between the results obtained for heat fluxes and telemetry data can reach 100% or more [185], which calls for the further development of accurate theoretical methods. In high-temperature flows, it is especially important to take into account electronic excitation.

In most works of the twentieth century, atoms were assumed to be structureless particles, and the internal energy of molecules was calculated only taking into account vibrational and rotational degrees of freedom (with the exception of works [186, 187]). This was, among other reasons, due to the lack of data on the set of possible electronic levels of atoms, the number of which, up to the ionization energy, is, generally speaking, unlimited. Another reason was that calculation of partition functions and transport coefficients requires a large amount of computational resources.

Correctly taking into account electronic excitation began in the early 2000s in the works of our colleagues from the University of Bari Aldo Moro [188, 189] (for an equilibrium plasma) and in the works of the St. Petersburg School of Nonequilibrium Aeromechanics [80–83] (in the one-temperature approximation). One interesting result was the derivation of a correction to the Eucken formula, which makes it possible to take into account the effect of electronic excitation [83]:

$$f_{\text{int}} = \begin{cases} 1.328, & T < 3000 \text{ K} \\ 1.42, & 3000 < T < 25000 \text{ K}. \end{cases} \quad (39)$$

Here  $f_{\text{int}}$  is the Eucken factor [190], which takes into account the contribution of the internal degrees of freedom to the thermal conductivity coefficient. In the original paper by Eucken,  $f_{\text{int}} = 1$ . Hirschfelder [186] proposed a value of  $f_{\text{int}} = 1.328$ , which worked well for moderate temperatures. Formula (39) provides good agreement with exact calculation over a wide range of conditions.

The analysis of transport processes carried out in [80, 84, 191] showed that at high temperatures the contribution of electronic excitation to the heat capacities and thermal conductivities becomes significant. The next step was the construction of a state-to-state model that takes into account the electronic state of each component of the mixture [101]. A specific feature of the model is that it takes into account the fact that, for electronically excited particles, the linear size of the particle changes with an increase in the electron energy due to a growing radius of the orbit of the outer electron shell, [101], and that change is non-monotonic.

The developed theoretical models were used to simulate a plane shock wave under the conditions of the Fire II flight experiment [106]. It was shown that the flow parameters greatly depend both on the choice of the model of chemical processes and on the choice of the kinetic-theory approach: in contrast to the results obtained in the two-temperature approximation, the molar fractions of atoms calculated in the state-to-state model behind the shock-wave front demonstrated a monotonous behavior. It was shown that under these conditions two-temperature models cannot correctly predict radiative heating. The further adoption of exact models requires optimization and acceleration of numerical algorithms for calculating state-to-state transport coefficients.

### 3.4. Models of Locally Equilibrium Flows

Locally equilibrium flows exist under the condition

$$\tau_{\text{tr}} < \tau_{\text{int}} < \tau_{\text{react}} \ll \theta, \quad (40)$$

that is, when all physical and chemical processes occur on time scales much smaller than the hydrodynamic scale. Papers [85–90, 192] investigate equilibrium flows of reacting gases taking into account ionization.

Thermodynamic studies of the equilibrium composition of ionized-gas mixtures usually use algebraic systems, including the Saha equations [193], the conditions of electroneutrality and the conservation of nuclei. In many cases, these systems can only be solved using various simplifications and approximations. In this case, it is not always possible to determine the influence of the initial state of the mixture on its equilibrium composition. Statistical description of the equilibrium states makes it possible to considerably simplify the calculation of the equilibrium composition of the plasma.

Monograph [85] describes in detail statistical models that produce the equilibrium distribution functions of particles in ideal gases with physical-chemical processes even in cases where the results of their interaction during collisions require additional study.

Using these statistical models, it was possible to obtain the equilibrium distribution functions of micro-particles in mixtures of monatomic gases with multiple ionization (see [88]). These distributions correspond to the entropy maximum under the constraints of conservation of energy, the number of nuclei  $\tilde{n}_k$  of each chemical element present in the system, and all electrons (free and bound) per unit volume.

In [88], the distributions of the concentrations of free electrons  $n_{e^-}$  corresponding to these functions, as well as the concentrations of atoms and ions of various chemical species ( $k = 1, \dots, k_*$ ) with charges  $+c$ , were presented in the form

$$n_{e^-} = Z_{e^-}(T)y, \quad (41)$$

$$n_{kc} = Z_{kc}(T)x_k y^{N_k - c}, \quad k = 1, \dots, k_*, \quad c = 0, \dots, N_k, \quad (42)$$

where  $x_k > 0$  ( $k = 1, \dots, k_*$ ) and  $y > 0$ .

Here  $Z_{e^-}(T)$  and  $Z_{kc}(T)$  are partition functions of the corresponding particles at a certain temperature value. The factors  $x_k$  in formulas (42) indicate the nuclei of a certain chemical element in the corresponding particles. Different powers of the factor  $y$  in formulas (41) and (42) indicate the number of electrons in these particles. This takes into account that the number of electrons in neutral atoms of the  $k$ -th kind coincides with the number  $N_k$  of the corresponding element in the periodic table.

If the initial state of an ideal mixture of monatomic gases is known, relations (41) and (42) make it possible to reduce the problem of determining the equilibrium composition of the mixture at any temperature to solving the system of equations

$$\sum_{c=0}^{N_k} n_{kc}(T) = \tilde{n}_k^{(0)}, \quad k = 1, \dots, k_*, \quad (43)$$

$$\sum_{k=1}^{k_*} \sum_{c=0}^{N_k} n_{kc}(T)(N_k - c) + \tilde{n}_{e^-}(T) = \sum_{k=1}^{k_*} \tilde{n}_k^{(0)} N_k, \quad (44)$$

where  $\tilde{n}_k^{(0)}$  is the initial density of atoms of  $k$ -th type.

Substituting expressions (41) and (42) into Eqs. (43) and (44) gives us the expressions

$$x_k = \tilde{n}_k^{(0)} / \sum_{c=0}^{N_k} Z_{kc}(T) y^{N_k - c}, \quad (45)$$

and allows us to reduce the solution of the problem to determining factor  $y$  from the equation

$$f(T, y) = \sum_{k=1}^{k_*} \tilde{n}_k^{(0)} N_k, \quad (46)$$

the left-hand side of which is obtained by substituting formulas (41) and (42) into the left-hand side of Eq. (44) and replacing the parameter  $x_k$  by expression (45).

In [88] it was shown that Eq. (46) has a unique positive solution at any temperature  $T$ . In this case, it is possible to use the graphical method, which makes the study of the equilibrium composition of a multiply ionized mixture even easier.

The equilibrium statistical distributions discussed above can be used not only in a steady-state mixture of monatomic gases with multiple ionization, but also in locally equilibrium flows of such media (see, for example, [89, 90]).

These distributions can also be considered as the zero-order approximation of the Chapman–Enskog theory in describing nonequilibrium flows of ionizing gases [194].

#### 4. INVESTIGATION OF FLOWS OF MIXTURES WITH CARBON DIOXIDE

Since the 1960s, nonequilibrium processes in carbon dioxide have become more relevant, since it is key for laser technologies, thermal protection for spacecraft intended for descent in the Martian atmosphere, and environmental problems of the Earth. The kinetics of nonequilibrium  $\text{CO}_2$  is being studied by many scientific groups using different approaches. The main simulation difficulty lies in the structure of the  $\text{CO}_2$  molecule, which, on the one hand, is linear, but at the same time has three vibrational modes (symmetric, deformation, and asymmetric). This gives more than eight thousand vibrational states of the molecule and an even greater number of different types of vibrational-energy exchange.

State-to-state simulation is an accurate tool for the most detailed assessment of the influence of various kinetic processes. However, when studying the vibrational relaxation of  $\text{CO}_2$ , it is necessary to solve several thousand equations, which is computationally complex and limits the applicability of the approach to 0-dimensional (0D) and one-dimensional (1D) problems. To reduce computational costs, often not all vibrational states of  $\text{CO}_2$  are taken into account. Papers [53, 55, 56, 92] present studies of a one-dimensional  $\text{CO}_2$  flow along the stagnation line, where the vibrational energy was limited to 3 eV, which is much less than the dissociation energy. Paper [195] proposed a nonequilibrium plasma model with only 28 vibrational states of the  $\text{CO}_2$  molecule considered on the basis of the Fridman model [196]. Another way to reduce the number of equations, developed in [197, 198], is to group vibrational states into one

combined state using the two-mode approach, while the anharmonic terms in the expression for the vibrational energy are discarded.

Two-temperature models are widely used in CFD due to their computational efficiency. However, in the case of CO<sub>2</sub> they do not take into account different vibrational modes and different rates of vibrational-energy exchange between them [93]. More realistic multitemperature models that take into account the energy exchange between asymmetric and combined symmetric-deformation CO<sub>2</sub> modes were developed in [142, 199] using the generalized Chapman–Enskog theory and offer algorithms for calculating the transport coefficients. These models were used to simulate shock-heated flows in mixtures with CO<sub>2</sub> [200] and two-dimensional simulation of flows near the orbiter, cone, and sphere [31, 38]. One of the limitations of these models is that the relaxation term in the vibrational-energy equation is written in the simplified Landau–Teller form, which is not suitable for intermode vibrational exchange.

Despite the effectiveness of multitemperature models, they have to be carefully verified. In [94, 95, 99], two problems of 0D relaxation of an inviscid gas were considered: (1) pure CO<sub>2</sub> and (2) a mixture of CO<sub>2</sub>/CO/O<sub>2</sub>/C/O. The simulation results, obtained by the state-to-state approach, traditional multitemperature models, and a new hybrid multitemperature approach were compared for arbitrary initial deviations from equilibrium.

The main results of these works are presented below.

#### 4.1. State-to-State Model (STS)

We consider the problem of spatially homogeneous relaxation. As noted above, CO<sub>2</sub> molecules have three vibrational modes, which means that their vibrational energy depends on three quantum numbers  $i_1$ ,  $i_2$ , and  $i_3$ . For each set of quantum numbers, it is necessary to write its own equation for the populations:

$$\frac{\partial n_{i_1, i_2, i_3}}{\partial t} = R_{i_1, i_2, i_3}^{\text{vibr}} + R_{i_1, i_2, i_3}^{\text{react}} \quad (47)$$

This equation was supplemented with the total energy-conservation equation for pure gas and equations similar to (5) and (6) without spatial derivatives.

The complex structure of the CO<sub>2</sub> molecule induces a lot of different exchanges of vibrational energy, which can be divided into several main groups of energy-exchange processes and chemical reactions for mixtures with carbon dioxide:

**1. VT<sub>m</sub> and VT<sub>c</sub> exchanges** between translational and vibrational degrees of freedom of molecules as a result of a collision with a particle of type M, the internal state of which does not change. Only single-quantum transitions were taken into account as the most probable ones. Often, when modeling nonequilibrium CO<sub>2</sub> flows, only VT<sub>2</sub> transitions are considered [53, 91, 195], since their rates are much higher than the VT<sub>1</sub> and VT<sub>3</sub> exchange rates.

**2. Multiquantum intermode VV<sub>1-2</sub>, VV<sub>2-3</sub>, and VV<sub>1-2-3</sub> exchanges** within one CO<sub>2</sub> molecule. These processes were chosen on the basis of the smallest energy variation during the transition:  $\Delta\varepsilon_{\text{VV}_{1-2}} = 10.54 \text{ cm}^{-1}$ ;  $\Delta\varepsilon_{\text{VV}_{2-3}} = 359.96 \text{ cm}^{-1}$ ;  $\Delta\varepsilon_{\text{VV}_{1-2-3}} = 349.42 \text{ cm}^{-1}$ . While the VV<sub>1-2</sub> exchange is almost resonant, in other intermode transitions part of the energy is transferred to the translational mode, but the energy change is much smaller than in VT transitions (for example,  $\Delta\varepsilon_{\text{VT}_2} = 667.25 \text{ cm}^{-1}$ ). A small change in energy causes a high probability of these energy exchanges.

**3. Intramode VV<sub>m</sub> and VV<sub>c</sub> exchanges** of vibrational quanta in each  $m$ -th mode of a CO<sub>2</sub> molecule and in collisions of diatomic molecules of the same kind.

**4. Intermolecular transitions VV<sub>3-CO</sub>, VV<sub>1-2-CO</sub>, VV<sub>2-CO</sub>, and VV<sub>1-O<sub>2</sub></sub>** involving vibrational modes of CO<sub>2</sub> and diatomic particles, as well as vibrational energy exchanges in collisions of diatomic molecules of different VV<sub>c-d</sub> types.

**5. Chemical reactions** dissociation, recombination and exchange reactions.

The state-to-state coefficients of the rate of vibrational energy transitions were calculated using the Schwartz–Slawsky–Herzfeld model [201] with corrections introduced in [94]. In recent works [96, 100, 202], a more reliable FHO (Forced Harmonic Oscillator) model describing vibrational energy exchanges in diatomic molecules was generalized to the case of CO<sub>2</sub> molecules. Using this model in state-to-state calculations is extremely computationally expensive, but it is acceptable in multitemperature simulation. The rate coefficients for the dissociation of carbon dioxide molecules and exchange reactions were calculated using models [57, 109], which take into account the vibrational states of both reactants and reaction

**Table 1.** Kinetic scheme. Designations: STS is the state-to-state model, HMT is the hybrid multitemperature model, RMT I and RMT II are the reduced multitemperature models, SSH is a model for describing vibrational transitions [201], LT is the Landau–Teller equation, TM is the Treanor–Marrone model [149], STSa are averaged state-to-state relaxation terms, and AL is the Arrhenius law

Process	Equation*	STS	HMT	RMT I	RMT II
VT <sub>1</sub>	CO <sub>2</sub> (i <sub>1</sub> ) + M ↔ CO <sub>2</sub> (i <sub>1</sub> ± 1) + M	SSH	STSa	...	...
VT <sub>2</sub>	CO <sub>2</sub> (i <sub>2</sub> ) + M ↔ CO <sub>2</sub> (i <sub>2</sub> ± 1) + M	”	”	LT	LT
VT <sub>3</sub>	CO <sub>2</sub> (i <sub>3</sub> ) + M ↔ CO <sub>2</sub> (i <sub>3</sub> ± 1) + M	”	”	...	...
VT <sub>CO</sub>	CO(i) + M ↔ CO(i ± 1) + M	”	”	”	LT
VT <sub>O<sub>2</sub></sub>	O <sub>2</sub> (i) + M ↔ O <sub>2</sub> (i ± 1) + M	”	”	”	”
VV <sub>1-2</sub>	CO <sub>2</sub> (i <sub>1</sub> , i <sub>2</sub> ) + M ↔ CO <sub>2</sub> (i <sub>1</sub> ± 1, i <sub>2</sub> ∓ 2) + M	”	”	...	...
VV <sub>2-3</sub>	CO <sub>2</sub> (i <sub>2</sub> , i <sub>3</sub> ) + M ↔ CO <sub>2</sub> (i <sub>2</sub> ± 3, i <sub>3</sub> ∓ 1) + M	”	”	LT	...
VV <sub>1-2-3</sub>	CO <sub>2</sub> (i <sub>1</sub> , i <sub>2</sub> , i <sub>3</sub> ) + M ↔ CO <sub>2</sub> (i <sub>1</sub> ± 1, i <sub>2</sub> ± 1, i <sub>3</sub> ∓ 1) + M	”	”	”	...
VV <sub>1</sub>	CO <sub>2</sub> (i <sub>1</sub> ) + CO <sub>2</sub> (k <sub>1</sub> ) ↔ CO <sub>2</sub> (i <sub>1</sub> ± 1) + CO <sub>2</sub> (k <sub>1</sub> ∓ 1)	”	...	...	...
VV <sub>2</sub>	CO <sub>2</sub> (i <sub>2</sub> ) + CO <sub>2</sub> (k <sub>2</sub> ) ↔ CO <sub>2</sub> (i <sub>2</sub> ± 1) + CO <sub>2</sub> (k <sub>2</sub> ∓ 1)	”	...	...	...
VV <sub>3</sub>	CO <sub>2</sub> (i <sub>3</sub> ) + CO <sub>2</sub> (k <sub>3</sub> ) ↔ CO <sub>2</sub> (i <sub>3</sub> ± 1) + CO <sub>2</sub> (k <sub>3</sub> ∓ 1)	”	...	...	...
VV <sub>CO</sub>	CO(i) + CO(k) ↔ CO(i ± 1) + CO(k ∓ 1)	”	...	...	...
VV <sub>O<sub>2</sub></sub>	O <sub>2</sub> (i) + O <sub>2</sub> (k) ↔ O <sub>2</sub> (i ± 1) + O <sub>2</sub> (k ∓ 1)	”	...	...	...
VV <sub>CO-O<sub>2</sub></sub>	CO(i) + O <sub>2</sub> (k) ↔ CO(i ± 1) + O <sub>2</sub> (k ∓ 1)	”	STSa	LT	LT
VV <sub>3-CO</sub>	CO <sub>2</sub> (i <sub>3</sub> ) + CO(k) ↔ CO <sub>2</sub> (i <sub>3</sub> ± 1) + CO(k ∓ 1)	”	”	”	”
VV <sub>1-2-CO</sub>	CO <sub>2</sub> (i <sub>1</sub> , i <sub>2</sub> ) + CO(k) ↔ CO <sub>2</sub> (i <sub>1</sub> ± 1, i <sub>2</sub> ± 1) + CO(k ∓ 1)	”	”	”	”
VV <sub>2-CO</sub>	CO <sub>2</sub> (i <sub>2</sub> ) + CO(k) ↔ CO <sub>2</sub> (i <sub>2</sub> ± 3) + CO(k ∓ 1)	”	”	...	...
VV <sub>1-O<sub>2</sub></sub>	CO <sub>2</sub> (i <sub>1</sub> ) + O <sub>2</sub> (k) ↔ CO <sub>2</sub> (i <sub>1</sub> ± 1) + O <sub>2</sub> (k ∓ 1)	”	”	LT	LT
DR <sub>CO<sub>2</sub></sub>	CO <sub>2</sub> (i <sub>1</sub> , i <sub>2</sub> , i <sub>3</sub> ) + M ↔ CO(i) + O + M	[57]	”	MT	MT
DR <sub>CO</sub>	CO(i) + M ↔ C + O + M	MT	”	”	”
DR <sub>O<sub>2</sub></sub>	O <sub>2</sub> (i) + M ↔ O + O + M	”	”	”	”
ER <sub>1</sub>	CO <sub>2</sub> (i <sub>1</sub> , i <sub>2</sub> , i <sub>3</sub> ) + O ↔ CO(i) + O <sub>2</sub> (k)	[109]	”	AL	AL
ER <sub>2</sub>	CO(i) + O ↔ O <sub>2</sub> (k) + C	”	”	”	”
ER <sub>3</sub>	CO(i) + CO(k) ↔ CO <sub>2</sub> (i <sub>1</sub> , i <sub>2</sub> , i <sub>3</sub> ) + C	”	”	”	”

\*For CO<sub>2</sub> molecules, only quantum numbers are given, which change upon collision.

products. The popular Treanor–Marrone model [149] was used to describe the dissociation of diatomic molecules with equilibrium rate coefficients from [144, 203]. Table 1 shows the equations of all groups of processes and the corresponding models of the rate coefficients that were used in the calculations. We note that for a single-component gas, the kinetic scheme is limited by VT<sub>m</sub>, VV<sub>m</sub>, VV<sub>1-2</sub>, VV<sub>2-3</sub>, and VV<sub>1-2-3</sub> transitions.

#### 4.2. Hybrid Multitemperature Model (HMT)

Multitemperature models are usually based on the assumption of fast intramode VV exchanges [30]. If the exchanges VV<sub>1</sub>, VV<sub>2</sub>, VV<sub>3</sub>, VV<sub>CO</sub>, and VV<sub>O<sub>2</sub></sub> occur on the time scale of translational and rotational relaxation, then the following relation is valid for the characteristic times of the processes:

$$\begin{aligned}
 \tau_{tr} < \tau_{rot} < \tau_{VV_m} \ll \tau_{VV_{1-2}} \sim \tau_{VT_m} \sim \tau_{VV_{2-3}} \sim \tau_{VV_{1-2-3}} \sim \tau_{VV_{3-CO}} \\
 \sim \tau_{VV_{1-2-CO}} \sim \tau_{VV_{1-O_2}} \sim \tau_{VT_m} < \tau_{react} \sim \theta, \\
 m = 1, 2, 3, CO, O_2.
 \end{aligned}
 \tag{48}$$



Under this condition, the vibrational distribution of CO<sub>2</sub> molecules for the anharmonic-oscillator model is the four-temperature Treanor distribution [95]:

$$n_{i_1, i_2, i_3}(T, T_1, T_2, T_3) = \frac{n_{\text{CO}_2} s_{i_1, i_2, i_3}}{Z_{\text{CO}_2}^{\text{V}}(T, T_1, T_2, T_3)} \exp\left(-\frac{\varepsilon_{i_1, i_2, i_3} - (i_1 \varepsilon_{1,0,0} + i_2 \varepsilon_{0,1,0} + i_3 \varepsilon_{0,0,1})}{k_{\text{B}} T} - \frac{i_1 \varepsilon_{1,0,0}}{k_{\text{B}} T_1} - \frac{i_2 \varepsilon_{0,1,0}}{k_{\text{B}} T_2} - \frac{i_3 \varepsilon_{0,0,1}}{k_{\text{B}} T_3}\right), \quad (49)$$

here  $s_{i_1, i_2, i_3}$  is the statistical weight,  $Z_{\text{CO}_2}^{\text{V}}(T, T_1, T_2, T_3)$  is the multitemperature vibrational partition function [95],  $\varepsilon_{1,0,0}$ ,  $\varepsilon_{0,1,0}$ , and  $\varepsilon_{0,0,1}$  are the energies of the first vibrational levels of the corresponding mode with the unexcited levels of the remaining modes. We note that distribution (49) takes into account the difference between the vibrational-mode temperatures and makes it possible to include important relaxation mechanisms that are often discarded in traditional multitemperature models.

The basic system of equations is derived from (23)–(26) simplified for an inviscid gas and the zero dimensionality of the problem, but for each vibrational mode, its own equation for the number of vibrational quanta is written:

$$\frac{\partial \rho_{\text{CO}_2} W_m}{\partial t} = R_m^{\text{w}}, \quad m = 1, 2, 3, \quad (50)$$

where

$$\rho_{\text{CO}_2} W_m(T, T_1, T_2, T_3) = \sum_{i_1, i_2, i_3} i_m n_{i_1, i_2, i_3}, \quad m = 1, 2, 3. \quad (51)$$

The relaxation terms in the hybrid model are calculated according to (30) and (31) by averaging the state-to-state relaxation terms and excluding from them the fast processes  $\text{VV}_m$  and  $\text{VV}_c$ :

$$R_m^{\text{w}} = \sum_{i_1, i_2, i_3} i_m (R_{i_1, i_2, i_3}^{\text{vibr}} + R_{i_1, i_2, i_3}^{\text{react}}), \quad m = 1, 2, 3, \quad (52)$$

$$R_c^{\text{w}} = \sum_{i_c} i_c (R_{i_c}^{\text{vibr}} + R_{i_c}^{\text{react}}), \quad c = \text{CO}, \text{O}_2, \quad (53)$$

$$R_{\text{CO}_2}^{\text{react}} = \sum_{i_1, i_2, i_3} R_{i_1, i_2, i_3}^{\text{react}}, \quad (54)$$

$$R_c^{\text{react}} = \sum_{i_c} R_{i_c}^{\text{react}}, \quad c = \text{CO}, \text{O}_2. \quad (55)$$

The advantages of this model are discussed below in Section 4.4.

### 4.3. Simplified Multitemperature Models

Along with the hybrid multitemperature model we considered two simplified models. In commonly used multitemperature models, the  $\text{VT}_1$  and  $\text{VT}_3$  transitions in the symmetric and asymmetric modes are usually neglected due to the lack of experimental measurements of the corresponding relaxation times. In addition, assuming that the vibrational-energy transitions between the symmetric and deformation modes  $\text{VV}_{1-2}$  occur faster than other intermode processes  $\text{VV}_{m-k}$ , we can introduce  $T_{12}$ , i.e., the total vibrational temperature for the combined (symmetric deformation) CO<sub>2</sub> mode. In this case, the set of governing Eqs. (23)–(26) and (50) is reduced, since instead of two separate relaxation equations for  $W_1$  and  $W_2$ , we obtain one equation for the average number of vibrational quanta in the combined mode,  $W_{12}$  [91, 95]:

$$\rho_{\text{CO}_2} W_{12}(T, T_{12}, T_3) = \sum_{i_1, i_2, i_3} (2i_1 + i_2) n_{i_1, i_2, i_3}, \quad (56)$$

We shall call the above model RMT I (Reduced Multitemperature model) in the following discussion. For this model, the set of macroscopic variables includes:  $T$ ,  $T_{12}$ ,  $T_3$ ,  $T_v^c$  ( $c = \text{CO}, \text{O}_2$ ),  $n_c$  ( $c = \text{CO}_2, \text{CO}, \text{O}_2, \text{O}, \text{C}$ ). The relaxation terms in the conservation equations for vibrational quanta are calculated using the traditional Landau–Teller approach with relaxation times suggested in experimental studies [204]. The Treanor–Marrone model [149] was used to describe the dissociation of CO<sub>2</sub>, CO, and O<sub>2</sub> molecules with the parameter  $U = \infty$  and the equilibrium dissociation rate coefficients from [144, 203]. Chemical exchange reactions were simulated using the one-temperature Arrhenius law with parameters from the

same references, and the corresponding chemical reaction coupling terms were not included in the vibrational-energy relaxation equations.

We can further simplify the multitemperature model if we assume fast intermode exchanges in  $\text{CO}_2$  molecules. In this case, the vibrational modes of  $\text{CO}_2$  are not distinguished, and relaxation occurs mainly due to VT exchange and transitions between particles of different chemical types. This simplest multitemperature model with one common vibrational temperature  $T_v^{\text{CO}_2}$  for carbon-dioxide molecules will be referred to below as RMT II. This approach is similar to multitemperature models widely used in mixtures of diatomic gases [30, 145]. In RMT II, vibrational relaxation is described in terms of the Landau–Teller approach, while chemical reactions are modeled similarly to the case of RMT I. A summarized list of models used in the calculations is given in Table 1.

#### 4.4. Advantages and Disadvantages of the Theoretical Models

First of all, we note that the state-to-state model describes the vibrational chemical kinetics in most detail and makes it possible to reveal the key mechanisms of relaxation. Another advantage of the state-to-state approach is that the coupling between vibrational relaxation and chemical reactions (CVCV) is natural, without simplifying assumptions and phenomenological models. Thus, in the absence of experimental data, state-to-state simulation can be considered as a reference. The only drawback of the model is its low computational efficiency.

The traditional multitemperature models (RMT I and II) are much more numerically efficient, but have many limitations. First of all, they require data on the times of vibrational relaxation for all nonequilibrium processes. Although some experiments are available for  $\text{VT}_2$ ,  $\text{VV}_{2-3}$ ,  $\text{VV}_{1-2-3}$ , and some intermolecular transitions [204–207], there are no reliable data on  $\text{VT}_1$ ,  $\text{VT}_3$ , and  $\text{VV}_{1-2}$  transitions. In addition, the extrapolation of existing experimental results to a wider temperature range is not always justified. The next problem is that the applicability of the Landau–Teller (LT) approach to modeling intermode and intermolecular transitions requires careful assessment under conditions of a strong deviation from equilibrium [96]. Another problem concerns the exact simulation of the vibrational-chemical coupling. The applicability of known CVCV models [149, 150] to polyatomic gases with different temperatures of vibrational modes has not been discussed in publications and needs to be substantiated. Finally, the RMT-II model is generally unable to take into account any intermode vibrational transitions in  $\text{CO}_2$  and the excitation of individual  $\text{CO}_2$  modes.

The hybrid multitemperature model (HMT) with averaged relaxation terms based on state-to-state terms has many advantages over the STS and RMT models. In the HMT approach, gas dynamics is described in terms of a reduced set of governing equations compared to the state-to-state model.

That said, the state-to-state kinetics is reflected in the self-consistently derived relaxation terms; plus, there are no problems with vibrational-chemical coupling and missing relaxation times for various processes. Another advantage is the possibility of using HMT models with different vibrational distributions (Boltzmann [30, 145], Treanor [49, 141], and even more complex Gordiets distributions [75, 156]). In conclusion, we note that the hybrid approach combines the advantages of detailed and accurate STS modeling with the efficiency of multitemperature models. The results show that the HMT model can be very promising for the numerical simulation of two- and three-dimensional flows.

#### 4.5. Results of Studying the Zero-Dimensional Vibrational Relaxation of Single-Component $\text{CO}_2$ and Mixtures

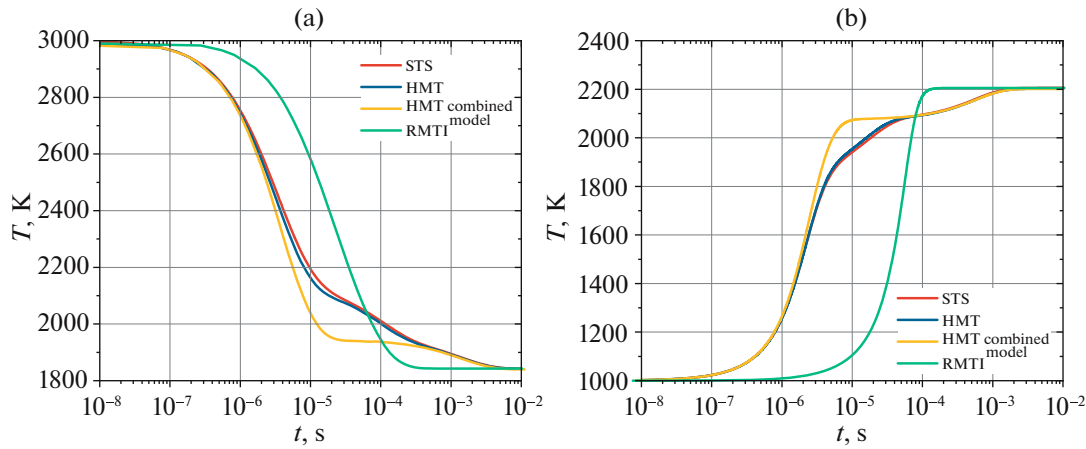
The first problem of the relaxation of single-component  $\text{CO}_2$  without chemical transformations was considered from different viewpoints [94, 95]:

—Two test cases were considered: when at the initial moment of time the gas temperature is higher than the vibrational temperature of the molecules and, conversely, when the gas is vibrationally excited, but has a low temperature. In this case, the initial vibrational temperature of the three modes was the same.

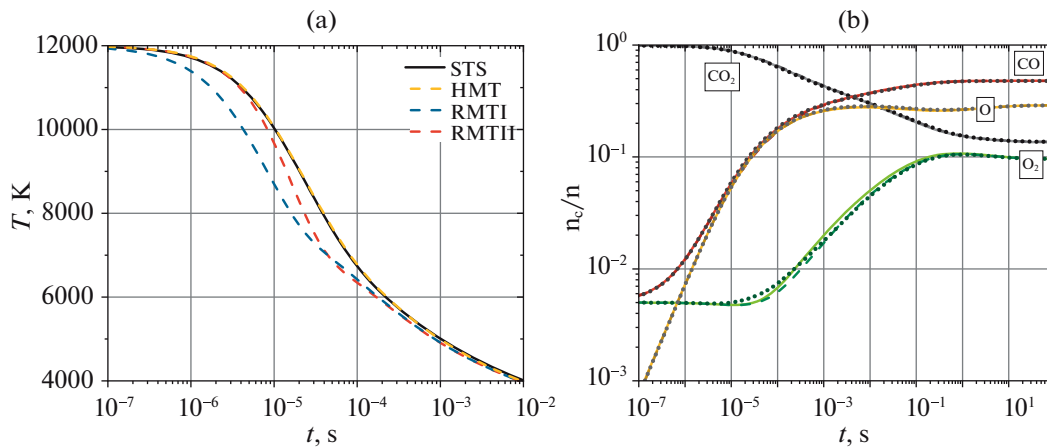
—In state-to-state simulation, various kinetic schemes were considered, and estimates were made of the contributions of energy exchanges to the relaxation process.

—The simulation results with the full vibrational spectrum and simplified spectra [53, 195] were compared.

—State-to-state and multitemperature calculations were compared.



**Fig. 3.** Evolution of the gas temperature for the initial temperature conditions: (a)  $T^{(0)} = 3000$  K,  $T_v^{(0)} = 1000$  K, anharmonic oscillator; (b)  $T^{(0)} = 1000$  K,  $T_v^{(0)} = 3000$  K, harmonic oscillator.

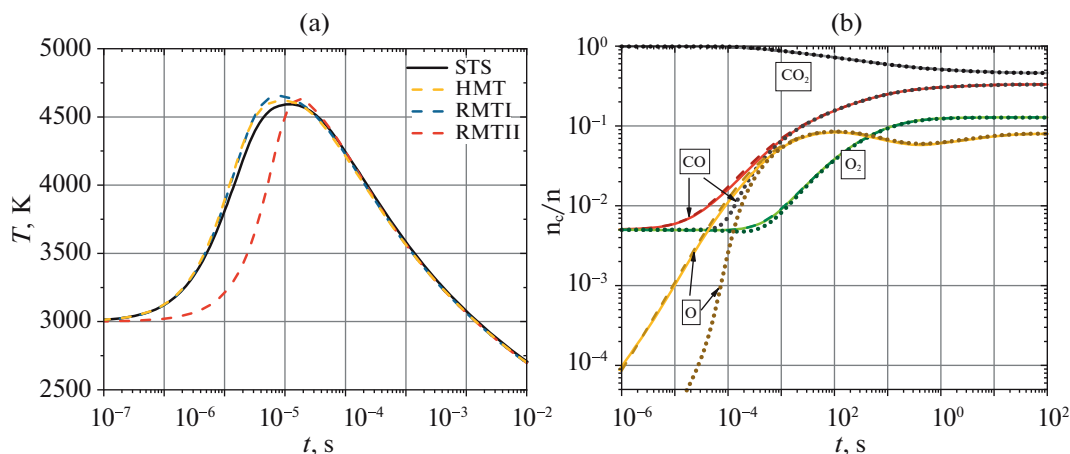


**Fig. 4.** Evolution of the gas temperature (a) and mixture composition (b) for the initial temperature conditions  $T^{(0)} = 12\,000$  K,  $T_v^{(0)} = 6000$  K, anharmonic oscillator. In (b): STS is solid lines, HMT is dashed lines, RMT II is dots.

For both temperature conditions, the dominant processes are  $VT_1$ ,  $VT_2$ ,  $VV_{1-2}$  and  $VV_{1-2-3}$  exchanges. An important result is that the contribution of intramode  $VV_m$  transitions can be disregarded. Calculation of these processes is the most resource heavy.

It was shown that, in the absence of chemical transformations, limiting the vibrational spectrum to a threshold of 3 eV does not affect the solution if all vibrational states below this energy are taken into account. This makes it possible to significantly reduce computational costs. The model [195] based on a set of isolated states cannot be applied for high-temperature regimes and can only be used under temperature conditions when the excitation of symmetric and deformation modes does not affect the thermodynamic functions.

Figure 3 shows the change in the gas temperature as a function of time for various approaches. The hybrid multitemperature model showed a temperature value close to the state-to-state approach (the difference is less than 3%). The use of a simpler multitemperature model with the Landau–Teller relation gives rather poor agreement with the STS solution over the entire computational domain. Calculations were also performed with a hybrid model with combined symmetric and deformation modes (yellow lines on the graphs), where  $T_1 = T_2 = T_{12}$ . Here we note a good agreement with the STS results in the initial and



**Fig. 5.** Evolution of the gas temperature (a) and mixture composition (b) for the initial temperature conditions  $T^{(0)} = 12000$  K,  $T_v^{(0)} = 6000$  K, harmonic oscillator. In (b): STS is solid lines, HMT is dashed lines, RMT II is dots.

final phases of relaxation, but in the middle part using this model yields a significant under- or overestimation of the gas temperature.

We note that the HMT model does not provide much advantage in terms of computational costs when solving a system of stiff ordinary equations. On the one hand, the Jacobi matrix is significantly easier to calculate in the HMT approach, since the system contains dozens of equations instead of several thousand. On the other hand, averaging of the state-to-state relaxation terms requires calculation of the rate coefficients for all energy transitions and reactions, which is quite time and resource consuming. Thus, for a single-component gas, the numerical costs of STS and HMT models are comparable.

The second considered problem is studying the vibrational and chemical relaxation of initially pure  $\text{CO}_2$  for various temperature conditions using different approaches. Figures 4 and 5 present the results of simulation: changes in the temperature and relative numerical densities of the mixture components. The comparison shows excellent agreement between the solutions obtained using the STS and HMT approaches. It can be noted that simplified RMT models can provide satisfactory accuracy only under certain conditions, while the HMT model can be considered universal, suitable for arbitrary deviation from thermochemical equilibrium.

The use of the cutoff vibrational spectrum of  $\text{CO}_2$  in the case of a mixture showed an increase in the error due to the significant influence of the upper vibrational states on chemical processes.

The calculation time for a five-component mixture, which is used to estimate the numerical efficiency of the hybrid approach in comparison with the simplified multitemperature models and the STS approach, is given in Table 2. In multicomponent mixtures, the number of vibrational transitions and chemical reactions is very high. This results in an unacceptably low efficiency of the STS model, which takes into account each vibrational state of molecules. The HMT approach provides a solution two orders of magnitude faster. Traditional multitemperature approaches (RMT) are about thirty times faster than HMT, but their accuracy is much lower. Therefore, the HMT approach can be recommended for simulating highly nonequilibrium  $\text{CO}_2$  flows in a wide range of conditions.

**Table 2.** Comparison of calculation times for various models

Model	Time, s	
	$T^{(0)} > T_v^{(0)}$	$T^{(0)} < T_v^{(0)}$
STS	556875	516735
HMT	6504	5766
RMT I	261	178
RMT II	215	116

**Table 3.** Time spent ( $T$ , s) solving the problem of spatially homogeneous relaxation (0D) and flow behind a shock wave (1D) in  $\text{CO}_2$ . Various approaches (state-to-state, hybrid multitemperature, neural network)

	0D	1D
State-to-state model	1507	2310
Hybrid 4-T model	982	1270
Neural network	148	190

## 5. DEVELOPMENT OF PROPRIETARY SOFTWARE AND SIMULATION OPTIMIZATION USING MACHINE LEARNING

To use the models developed by the research team in engineering calculations, the software packages KAPPA (Kinetic Approach to Physical Processes in Atmospheres) [118] and PAINeT (Planet Atmosphere Investigator of Nonequilibrium Thermodynamics) [119, 208] were developed to calculate the macroparameters, transport coefficients, and transport terms in various problems of gas dynamics, taking into account the influence of strong nonequilibrium, chemical reactions, ionization, and electronic excitation. The PAINeT software package includes a database of physical properties of 21 atoms and molecules, as well as their various electronic and electronic-vibrational states (more than twelve thousand in total); as well as a database of chemical reactions (more than 2200 in total, including state-to-state reactions depending on electronic, vibrational, and electronic-vibrational levels). To simulate the structure of a shock wave in viscous flows of polyatomic gases, the software package SW-NSF-Solver [97, 98] was developed, based on the finite-volume method and exact algorithms for calculating the transport coefficients in polyatomic gases. Over the past ten years, the team has registered over ten computer programs and databases. KAPPA and SW-NSF-Solver software are freely available and can be used by interested researchers to solve scientific problems.

Interdisciplinary studies of the possibilities of using artificial intelligence to optimize resource-intensive calculations of kinetics and transport processes have become a new direction for the scientific school. The study was supported by a grant from St. Petersburg State University “Machine learning in problems of nonequilibrium aeromechanics.” It was shown that machine learning can be used to speed up calculations of physical properties and transport coefficients of gas mixtures, taking into account electronic excitation. In this approach a trained neural network performs instant accurate calculations of the transport coefficients for mixtures with an arbitrarily set input vector of values consisting of molar fractions of the mixture components, gas temperature and pressure, and an output vector of the required transport coefficients and/or other physical parameters [209]. Based on the results of these studies, a software module is currently being developed that provides a convenient user interface for working with modern machine-learning libraries for use in modern problems of hydroaeromechanics.

The papers [210, 211] considered the applicability of various machine-learning methods for state-to-state simulation of the rate of vibrational relaxation in mixtures of air components. Various strategies were analyzed and recommendations were given on the choice of methods. Thus, one of the promising methods for calculating the relaxation rate in diatomic gases is the  $k$ -NN ( $k$  nearest neighbors) algorithm. However, the results obtained cannot be used for polyatomic gases due to the high dimensionality of the system.

To optimize the state-to-state simulation of carbon dioxide, efficient parallelization algorithms and regression methods were proposed for calculating the rate coefficients of vibrational-energy transitions [212, 213]. The neural-network approach proposed in [131] for calculating the rate of vibrational relaxation in hybrid models described in the previous section turned out to be the most promising. The speed of solving a spatially homogeneous problem and a one-dimensional problem of the flow behind a plane shock wave in  $\text{CO}_2$  with the help of a neural network increased by more than an order of magnitude, while the hybrid approach reduced the cost by about a factor of two (see Table 3) [131]. In this case, the error of the solution does not exceed 5%. It is expected that in two-dimensional and three-dimensional problems and in problems taking into account chemical reactions or using accurate but computationally complex models of reaction rate coefficients, the gain will be even more significant.

## 6. RECOGNITION OF THE SCIENTIFIC SCHOOL

The school of nonequilibrium aeromechanics of St. Petersburg University has received wide recognition in Russia and abroad. In 1973, Vallander and his team of scientists were awarded the State Prize of the USSR for their work on the dynamics of rarefied gases. For scientific merits and merits in the field of

education in the USSR, Vallander was awarded the Order of Lenin (1961). In 1976, for a series of works in the field of physical-chemical aerodynamics, Vallander was awarded the University Prize (posthumously). In 1977, the book by S.V. Vallander, E.A. Nagnibeda, and M.A. Rydalevskaya “Some Questions concerning the Kinetic Theory of a Chemically Reacting Gas Mixture” was published [17], claiming the University Prize. Later, two more series of papers received awards from St. Petersburg University: in 2005, a team of authors (E.V. Kustova, E.A. Nagnibeda, M.A. Rydalevskaya) was awarded the first prize of St. Petersburg State University “For Scientific Works,” and in 2021, A.A. Kosareva, O.V. Kunova, and M.A. Mekhonoshina received the prize “For Contribution to Science of Young Researchers.” Members of the scientific team were repeatedly invited as lecturers and researchers to the universities of France, Italy, Germany, Belgium, and Brazil. Among the employees of the scientific school are members of the editorial boards of well-known journals: Journal of Technical Physics, Fundamental and Applied Hydrophysics, Bulletin of St. Petersburg University. Mathematics. Mechanics. Astronomy, Physical-Chemical Kinetics in Gas Dynamics, Journal of Theoretical and Applied Mechanics, as well as guest editors of Plasma Source Science and Technology, Fluids, and Frontiers in Physics.

The team’s research has been supported by numerous grants (over the past ten years, work has been carried out under nine grants from the St. Petersburg Government, eleven grants from the Russian Foundation for Basic Research (RFBR) and four grants from the Russian Science Foundation (RSF), including RFBR and RSF grants for young scientists). Over ten years, more than 150 articles have been published in top scientific Russian and foreign journals and ten PhD theses have been defended. The team held two scientific schools for young scientists and one all-Russian and three international conferences. Students and graduate students of the department participate in scientific projects and work on grants, make presentations at all-Russian and international conferences, undergo internships in Russian and foreign research centers; many receive scholarships from the Government of the Russian Federation and the President of the Russian Federation (six personal scholarships over the past three years) and win competitions of the Committee for Science and Higher Education of the Government of St. Petersburg.

#### 7. ROLE OF THE “VESTNIK OF ST. PETERSBURG UNIVERSITY. MATHEMATICS. MECHANICS. ASTRONOMY” JOURNAL IN THE DEVELOPMENT OF THE SCIENTIFIC SCHOOL

We note the special role of the journal in the formation and development of the school of nonequilibrium aeromechanics of St. Petersburg State University. For more than 60 years, starting from the first works of S.V. Vallander [11, 15, 16] with colleagues and students, the scientific team has been invariably publishing their results in Vestnik. The first works of students and graduate students are approbated in the journal, the results of top scientists and biographical sketches of our colleagues are published. Over the past twenty years, the team of the scientific school has published more than 40 papers in Vestnik on studies of transport processes in strongly nonequilibrium media [24, 81, 82, 106, 115, 117, 147, 180, 214, 215], vibrational chemical kinetics [107, 112, 113, 120–124, 127, 128, 137, 216, 217], models of an equilibrium ionized and reacting gas [86, 87, 89, 192], model kinetic equations [218], kinetics of polyatomic molecules [97, 152, 153, 160, 177, 212, 213, 219, 220], and the development of machine-learning methods in nonequilibrium aeromechanics [131, 210]. Fruitful cooperation with the journal “Vestnik of St. Petersburg University. Mathematics. Mechanics. Astronomy” in many ways contributes to the success of the scientific school.

#### 8. CONCLUSIONS

The paper reviews the main areas of activity of the scientific school of nonequilibrium aeromechanics founded by S.V. Vallander in the 1950s. The results published in more than 200 articles, monographs, and textbooks are briefly discussed. Over the past years, the school has trained dozens of well-known scientists in the field of physical and chemical aerodynamics and has achieved great success in the development of rigorous mathematical methods for modeling nonequilibrium flows, applying new approaches to the study of modern problems of nonequilibrium aeromechanics, the development of software tools, and investigating new innovative directions. The staff of the scientific school is proud of its students, many of whom have made a significant contribution to the development of Russian science, use scientific knowledge in solving important applied problems, and also work in universities and educate new generations of specialists.

## FUNDING

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