Ekaterina Nagnibeda

Elena Kustova

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Springer

# Heat and Mass Transfer

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Ekaterina Nagnibeda · Elena Kustova

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## Kinetic Theory of Transport and Relaxation Processes

Prof. Ekaterina Nagnibeda
St. Petersburg State University
Dept. of Mathematics and Mechanics
Universitetski prospect 28
St. Petersburg
Russia 198504
E-mail: e_nagnibeda@mail.ru

Prof. Elena Kustova
St. Petersburg State University
Dept. of Mathematics and Mechanics
Universitetski prospect 28
St. Petersburg
Russia 198504
E-mail: Elena_kustova@mail.ru

*The book is dedicated to the memory of our teacher Professor Sergey V. Vallander, one of the originators of non-equilibrium aerodynamics in Russia*

# Preface

In this book, we consider the kinetic theory of transport and relaxation processes in reacting gas flows strongly deviating from thermal and chemical equilibrium. In contrast to existing monographs on the kinetic theory of reacting systems, here we place the primary emphasis on the study for non-equilibrium distributions of gas molecules over velocity and internal energy and their effect on gas-dynamic parameters and dissipative properties of flows.

The development of the kinetic theory for multi-component mixtures of reacting gases under the conditions far from the equilibrium is essential to reach a solution for a number of current scientific and technical problems, such as modeling for the reentry of space vehicles into atmospheres of planets, studies for flows in high-enthalpy facilities and processes in active media of molecular lasers, discharges, combustion, cleaning of polluted atmosphere, etc.

Initially, the basic principles of the kinetic theory based on the Boltzmann equation were derived for the monoatomic gas. As a result, the classical transport theory in monoatomic gases and their mixtures was created. The generalization of the Boltzmann equation for gases with internal degrees of freedom and chemical reactions made in studies of L. Waldmann, Wang Chang and J. Uhlenbeck, S.V. Vallander determined a new stage of development of the kinetic theory and substantially contributed in its physical content. In Russia, further studies in this area were appreciably affected by S.V. Vallander concepts on the application of the kinetic approach to problems of aerodynamics and to the description of relaxation processes in gases.

In the 60–80-ies of the last century, numerous scientists and teams were involved into the development of the kinetic theory of molecular gases. These studies resulted in the formulation of the theory of transport processes and the development of calculation techniques for the kinetic coefficients for weakly non-equilibrium gas and under the conditions of existence of non-equilibrium Boltzmann distributions over particles internal energy.

At the present stage, there is a need for the kinetic theory of gases to take into account strong deviations from equilibrium and non-Boltzmann distributions arising in gas flows. In strongly non-equilibrium flows, characteristic times for gas-dynamic and relaxation processes become comparable, and therefore the equa-

tions for macroscopic parameters of the flow should be coupled to the equations of physical-chemical kinetics. The transport coefficients, heat fluxes, diffusion velocities directly depend on non-equilibrium distributions, which may differ substantially from the Boltzmann distribution. In this situation, the estimate for the impact of non-equilibrium kinetics on gas-dynamic parameters of a flow and its dissipative properties becomes especially important. In recent years, these problems receive much attention, and many new results have been published in a number of papers. However, still no monograph exists in which strongly non-equilibrium kinetics in gas flows and its influence on gas dynamics and heat- and mass transfer would be considered from a unified point of view. We hope that in this book we have been able to fill this gap to some extent.

Here, for the first time we present the kinetic theory for transport processes, taking into account state-to-state vibrational and chemical kinetics. Along with this new and the most rigorous approach, we also consider in detail kinetic models for transport and relaxation processes based on quasi-stationary non-Boltzmann distributions.

The contents of the book may be thematically divided into three parts. The first four Chapters concern construction of theoretical models for the dynamics of strongly non-equilibrium gases. On the basis of the generalized Chapman–Enskog method for gases with rapid and slow processes, we derive from kinetic equations the closed systems of equations for a flow of a mixture of reacting gases for different conditions of the non-equilibrium state. We present formulae for transport and relaxation terms in these equations, and construct algorithms for kinetic coefficients calculation.

The authors aimed not only at derivation and justification for mathematical models from the first principles of the kinetic theory of gases, but also at obtaining final calculation formulae for transport coefficients and rates of physical and chemical processes. These issues are considered in Chapters 5, 6. In Chapter 5, new calculation procedures for transport coefficients in the state-to-state kinetics approach and in quasi-stationary multi-temperature approximations are given, analyzed in detail, and compared with the calculation technique for the kinetic coefficients used in the one-temperature approximation. We suggest several simplifications for these procedures, which make their use substantially easier. The classical Eucken formula for the thermal conductivity coefficient is generalized for the case of strong deviations from equilibrium; also, an efficient calculation technique for diffusion coefficients in strongly non-equilibrium reacting gas is proposed. In Chapter 6, the calculation pattern is developed for the rate coefficients of different energy exchanges and reactions included in the equations for the kinetics of non-equilibrium gas mixtures.

Chapters 7–9 describe applications of the created models to simulations of some specific flows. In Chapter 7, we consider state-to-state vibrational and chemical kinetics in the relaxation zone behind strong shock waves in hypersonic gas flows, and show its impact on gas-dynamic parameters, diffusion, and heat transfer. In Chapter 8 we study non-equilibrium distributions in a boundary layer close to the surface of a space vehicle entering the Earth atmosphere. The effect of non-equilibrium kinetics in the gas phase and on the surface on macroscopic parameters and the heat

flux is discussed. In Chapter 9, we study non-equilibrium flows in nozzles in various approximations: taking into account state-to-state kinetics and on the basis of quasi-stationary distributions. Comparison between solutions for these problems, obtained in different approximations, made it possible to estimate the influence of non-equilibrium distributions on gas-dynamic parameters and transport properties of a flow, to establish the applicability limits for quasi-stationary approximations, and to formulate the conditions in which the more rigorous state-to-state description for non-equilibrium kinetics yields substantially different results.

Our work reflects the results we published in several cycles of studies, as well as lecture courses "The kinetic theory for non-equilibrium gas mixtures", "Physical gas dynamics", "Up-to-date methods in problems of non-equilibrium gas dynamics", we delivered for students of the Department of Mathematics and Mechanics of Saint-Petersburg State University.

The authors enjoyed fruitful collaboration with Mario Capitelli and his colleagues from the Plasma Chemistry Center in the University of Bari (Italy) with reference to problems considered in Chapters 6, 8, 9. In Chapter 8 we present results of some joint studies performed during 1998–2002. Some aspects of the theory of quasi-stationary approximations and their applications were developed by the authors during their work in the University of Provence in Marseilles (France) in 1995–2002. The results of these studies have been published in a series of papers written in collaboration with Aziz Chikhaoui; some part of these results is discussed in Chapters 3, 7 and 9.

The book was published first in 2003 in Russian by the Saint Petersburg University Press. The authors are grateful to the referees of the Russian edition of the book, A.A. Pyarnpuu and V.N. Uskov who made useful comments while reading the work. We also thank M.A. Rydalevskaya for useful discussions and advices.

# Contents

# Introduction

For the recent decades, the kinetic theory of gases has encountered a necessity to solve some new physical problems. One of them is modeling of gas flows under the conditions of strong deviations from thermodynamic equilibrium. Such conditions occur, for example, near surfaces of nonexpendable space vehicles in their reentry into the Earth atmosphere, in experiments carried out with high-enthalpy facilities, in supersonic gas flows in nozzles and jets, for various types of energy pumping into vibrational and electronic degrees of freedom.

In high-temperature and hypersonic flows of gas mixtures, the energy exchange between translational and internal degrees of freedom, chemical reactions, ionization and radiation may result in noticeable violation of thermodynamic equilibrium. In particular, it was found that a large section of descending trajectory of modern space vehicles in the course of their reentry into the Earth atmosphere lies at large heights (60 to 70 km), where the gas is substantially rarefied (its pressure there is of the order of $10^{-2}$ atm) and the characteristic times of kinetic and gas-dynamic processes are comparable. Therefore the non-equilibrium effects become of importance for a hypersonic flow and should be taken into account for the prediction of the flow parameters.

The non-equilibrium conditions in high-enthalpy flows in nozzles, jets, expanding tubes, originate as a result of rapid cooling of the flow, due to which the internal energy of gas appreciably exceeds the translational, and is not described by the gas temperature. Deviations from equilibrium distributions occur also as a result of chemical reactions of dissociation, recombination, and exchange both in the gas phase and on the surface of streamlined bodies; in the electrical discharges and due to the use of other ways of energy pumping into internal degrees of freedom of gas molecules. In many cases, the relaxation time for some degrees of freedom appears to be comparable with the characteristic time for the variation of basic gas-dynamic parameters of a flow. Therefore, in mathematical modeling of the flow, the equations of gas dynamics and kinetics of non-equilibrium processes should be considered jointly.

The kinetic theory of gases makes it possible to develop mathematical models of a flow under different conditions of its non-equilibrium state, i.e. to obtain closed

systems of equations of physical gas dynamics and to elaborate calculation procedures for kinetic coefficients included to these equations.

The derivation of macroscopic transport equations from the kinetic equations is of vital importance for the kinetic theory of gases. The foundations of the transport theory in gases were laid by J. Maxwell, L. Boltzmann, S. Chapman, D. Enskog. J. Maxwell was the first who using the statistical approach derived in 1867 the transport equation for an averaged molecular property [182]. L. Boltzmann in his famous study of 1872 [26] showed that the equations of hydrodynamics, which may be treated as transport equations for the mass, momentum, and energy, follow from the kinetic equations for the velocity distribution of gas molecules.

The problem of closing the transport equations was first considered by S. Chapman and D. Enskog. One of the important achievements of the method derived from their studies [55, 56, 75] was that the stress tensor and the energy flux included in the transport equation were expressed via gradients of hydro-dynamic parameters, while for the viscosity and thermal conductivity coefficients justified formulae were derived; thereby, the system of the transport equations was closed. These fundamental results were obtained without taking into account the excitation of molecular internal degrees of freedom, though L. Boltzmann in his book "The Lectures on Theory of Gases" [27] already stressed the importance of consideration of complex molecules and of taking their dissociation into account.

The first attempt to take into account the excitation of internal degrees of freedom in calculations for the transport coefficients was made in 1913 by E. Eucken [81], who introduced a phenomenological correction into the formula for the thermal conductivity coefficient. Later on, stricter analysis for the excitation of internal degrees of freedom of molecules, and then also chemical reactions occurring in collisions, resulted in the generalization for both the Boltzmann equation itself and the methods for its solution. The Wang Chang and Uhlenbeck equation [257, 258] was obtained as a result of generalization of the Boltzmann equation taking into account the internal energy of gas molecules; J. Ludwig and M. Heil [171] in their formulation for kinetic equations considered processes of dissociation and recombination; in the studies of L. Waldmann [254, 253, 255], rotational degrees of freedom were considered in detail.

One of the originators of the rarefied gas dynamics in Russia was S.V. Vallander who one of the first understood the prospects of application of molecular approach to the solution of problems of aerodynamics. In 1963 S.V. Vallander derived integral and integral-differential kinetic equations for distribution functions [243], generalized them for reacting gases with internal degrees of freedom [245], and suggested the molecular approach to the description of relaxation processes in gas flows [248].

In the following years, numerous studies were devoted to the development of kinetic theory for transport in gases with internal degrees of freedom and chemical reactions. Among the first were works by E. Mason, L. Monchik and their co-authors [179, 180, 189], in which Wang Chang and Uhlenbeck equations were used and efficient procedures for calculations of transport coefficient in gas mixtures were developed. In the same years, on the basis of S.V. Vallander equations, in the studies [246, 247] particular features of kinetic theory of gases with bimolecular chemical

reactions were analyzed and the Chapman–Enskog method was generalized; later, the study [226, 198] involved dissociation and recombination into consideration. Results obtained in the transport theory in the 60–80-ies are reflected in monographs [57, 112, 124, 82, 249, 7, 34, 262, 183, 76][1] and in a vast number of papers.

In the papers of the 60–70-ies concerning the theory of transport properties, mainly minor deviations from the local thermodynamic equilibrium were considered. Non-equilibrium effects were taken into account in transport equations by introducing supplementary kinetic coefficients: the coefficient of volume viscosity and corrections to the thermal conductivity coefficient. Such a description of the real gas effects becomes insufficient under the conditions of finite (not weak) deviations from the equilibrium, in which the energy exchange between some degrees of freedom and some part of chemical reactions proceed simultaneously with the variation of gas-dynamic parameters.

Allowing for different rates of non-equilibrium processes in the formulation of kinetic equations and the development of asymptotic methods for their solution [191, 86, 87] made it possible to construct and justify kinetic models for strongly non-equilibrium flows. This approach appeared to be extremely productive and later led to new important results in the kinetic theory, in particular, in the theory of transport processes [161, 162, 263, 249, 198, 181, 163, 35, 131, 139, 140, 60]. Thus as a result of the generalization of the Chapman–Enskog method it was shown that under strong deviations from the equilibrium, transport equations are to be considered jointly with the relaxation equations. Understanding of this feature of modeling of gas flows with rapid and slow processes resulted in substantial convergence of ideas and techniques of kinetic theory and of physical kinetics. The latter studies strongly non-equilibrium processes; however, until recently their kinetics was considered in spatially homogeneous gases without any connection with gas dynamics. Methods of kinetic theory made it possible to take into account the experience accumulated by physical kinetics in the solution of problems of non-equilibrium gas dynamics. At this way, further advancement was achieved in the theory of quasi-stationary distributions, which were used in simulations of non-equilibrium gas flows and the transport processes.

The first models that took into account strong non-equilibrium state with respect to vibrational degrees of freedom were two-temperature and multi-temperature models for transport and relaxation based on the non-equilibrium Boltzmann distribution over the molecular vibrational energy levels with the vibrational temperature different from that of the gas [265, 161, 170, 160, 34, 131]. However, this distribution is justified only under the condition that the systems of translational and vibrational degrees of freedom are totally isolated. The quasi-stationary distribution, which takes into account real characteristics of molecules and energy exchange between translational and vibrational degrees of freedom, was for the first time obtained in the study [242] on the basis of the solution of the equations for vibrational level populations. The Treanor distribution [242] and its generalization for strongly

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[1] From now on, studies are referred in chronological order.

excited gas suggested in [99], were important for the theory of vibrational relaxation [100, 101].

Taking into account non-Boltzmann distributions also led to new results in the transport theory [71, 138, 139, 140, 143]. Multi-temperature non-Boltzmann distributions were derived from kinetic equations for the distribution functions in a single-component gas [138, 140, 143], and then generalized for reacting mixtures [60, 59]. On the basis of these distributions, the theory for transport processes was developed and algorithms for calculations of non-equilibrium heat capacity and kinetic coefficients under the conditions of strong vibrational excitation were suggested. The Eucken correction to the thermal conductivity coefficient for a strongly non-equilibrium gas was generalized [140, 143]. This theory was applied to the simulation of heat transfer and diffusion behind strong shock waves [59] and in supersonic expanding flows [151]. These results made it possible to estimate the real gas effects and the impact of non-Boltzmann distributions on dissipative properties of strongly non-equilibrium gases not only qualitatively, but also quantitatively.

Simultaneous processes of vibrational relaxation and chemical reactions frequently lead to substantial violations in quasi-stationary distributions. This is distinctly manifested in recombination of atoms at the surface of a body moving with a hypersonic velocity. Simulations performed in Ref. [16] showed that the distribution of vibrationally excited molecules formed as a result of recombination both in the gas phase and on the surface strongly differs from quasi-stationary Boltzmann or Treanor distributions. A similar situation occurs in expanding flows in nozzles. Experimental studies for detailed vibrational kinetics in media whose equilibrium was disturbed by pumping energy into vibrational degrees of freedom also provide evidence for non-Boltzmann type of the population of vibrational levels [67, 84, 256, 214]. Under such conditions, a detailed description for the non-equilibrium kinetics based on the solution of equations for the vibrational level populations of gas molecules is needed. In a moving gas, these equations should be coupled to the equations of gas dynamics. Currently, the approach of state-to-state kinetics receives much attention in the studies for various gas flows, such as those behind strong shock waves [128, 169], in non-equilibrium boundary layers [14], in nozzles [233], in a shock layer close to a blunt body [45]. The solution for problems of gas dynamics taking into account the detailed state-to-state vibrational and chemical kinetics is extremely computationally consuming and has become possible due to intense development of numerical methods and to the substantial increase in the capacity of modern computers. Different models for physical and chemical processes from the standpoint of potentials of computational techniques of the fluid dynamics were discussed in the study [44].

The necessity for the analysis of heat and mass transfer in strongly non-equilibrium gas flows resulted in the development of the transport kinetic theory taking into account state-to-state vibrational and chemical kinetics. For the first time, the transport theory in the approximation of state-to-state kinetics was developed in the studies [141, 145, 147]. The method suggested there made it possible to reveal some specific features of diffusion and heat transfer in a strongly non-equilibrium gas flow, which cannot be described within the framework of multi-temperature or

near-equilibrium approximations. This technique was applied to study kinetics and heat and mass transfer in flows of reacting gases in the relaxation zone behind shock waves [141, 147], at the surfaces of space vehicles [12, 17, 153], in expanding flows [49]. The results obtained on the basis of this new approach showed the influence of non-equilibrium distributions formed in different flows on gas-dynamic parameters and transport properties, and were useful in establishing applicability limits for simpler multi-temperature models.

In addition to already indicated problems of physical gas dynamics, important up-to-date applications of simulation techniques of non-equilibrium vibrational and chemical kinetics in gas flows include, for example, solutions for environmental problems (see, for example, [252]), problems of astrophysics [222, 223], modeling of planet atmospheres [209, 211, 88], study for ejections from space vehicles close to their surfaces [221], combustion processes [126, 89, 187], applications of chemical kinetics in technological processes [200, 201].

In the present monograph, we develop mathematical models for transport and relaxation processes on the basis of kinetic equations. We place primary emphasis on the consideration for the conditions of a strongly vibrational and chemical non-equilibrium state and on the development of methods of the kinetic theory in the approximation of the state-to-state kinetics, and also on the basis of non-Boltzmann quasi-stationary distributions. This makes our study different from existing monographs on the kinetic theory of gases, which basically consider weak deviations from equilibrium distributions with respect to internal degrees of freedom, or multi-temperature Boltzmann distributions. We suggest practical procedures for calculations of transport coefficients, energy fluxes and diffusion velocities in the approximations of state-to-state and multi-temperature non-Boltzmann kinetics. In particular, we have obtained simplified expressions for coefficients of viscosity, thermal conductivity, and diffusion of a strongly non-equilibrium gas, which allows one to apply the developed theory to numerical simulations of various non-equilibrium flows. We present the results of applications of the elaborated models to specific reacting gas flows. These methods make it possible to estimate the effect of strongly non-equilibrium vibrational and chemical kinetics on gas dynamics and heat and mass transfer.

# Chapter 1
# Kinetic Equations and Method of Small Parameter

In the present monograph, on the basis of the methods of kinetic theory, we study non-equilibrium flows of multi-component mixtures consisted of molecular gases with translational, rotational, and vibrational degrees of freedom. Collisions between particles can result in the translational energy exchange, internal energy transitions, bimolecular chemical reactions, dissociation, and recombination. Our consideration is restricted by the conditions when electronic excitation, ionization, and radiation can be neglected. A quasi-classical approach is applied. In the framework of this approach, the translational degrees of freedom of gas particles are treated classically whereas the rotational and vibrational energy spectra are assumed to be quantized; the pure quantum effects of the diffraction and particles collective are neglected. The gas description is based on one-particle distribution functions of molecules over the velocity, internal energy and chemical species. The quasi-classical method is well suited for the solution of molecular supersonic aerodynamic problems in a wide temperature and pressure range. The quantum description becomes necessary for low temperatures and rapid processes in strong fields, as well as for light gases. Such conditions are not considered in the monograph.

In Chapter 1, a brief description of molecular spectra and specific heats is given, the main macroscopic parameters characterizing a non-equilibrium reacting gas mixture flow are defined on the basis of the distribution functions, and the kinetic equations for the distribution functions are derived. Further on, small parameters are introduced to the kinetic equations, the features of the small parameter method under the strongly non-equilibrium conditions are discussed, and the main ideas of the Chapman–Enskog method generalized for reacting gases with both rapid and slow processes in them are formulated.

## 1.1 Energy of Internal Degrees of Freedom: Macroscopic Gas Parameters

### 1.1.1 Rotational and Vibrational Energy of Molecules

Let us consider a gas mixture of various chemical species $c = 1, ..., L$. The internal energy $\varepsilon_{ij}^c$ of a molecule of $c$ species on the vibrational ($i$) and rotational ($j$) levels, is given by the formula:

$$\varepsilon_{ij}^c = \varepsilon_{ij}^{\mathrm{vibr},c} + \varepsilon_{ij}^{\mathrm{rot},c},$$

where $\varepsilon_{ij}^{\mathrm{vibr},c}$, $\varepsilon_{ij}^{\mathrm{rot},c}$ is the vibrational and rotational energy, respectively.

The internal energy spectrum is specified as a set of eigenvalues of the Schrödinger equation for a given intramolecular interaction potential. Detailed information on the molecular spectra can be found, for instance, in Refs. [110, 109]. A simplest model of the rotational motion of a diatomic molecule is that of the rigid rotator, assuming the rotational and vibrational energy to be independent. For this model, the following rotational levels are assigned to a molecule by quantum mechanics:

$$\varepsilon_{ij}^{\mathrm{rot},c} = \varepsilon_j^c = \frac{j(j+1)h^2}{8\pi^2 I_c}, \qquad j = 0, 1, \dots . \tag{1.1}$$

Here, $h$ is the Planck constant ($h = 6,6261 \cdot 10^{-34}$ J·s), $I_c$ is the moment of inertia of a molecule of $c$ species with respect to its rotation axis.

A more rigorous model takes into account the dependence of the rotational energy on the vibrational energy level of a rotating molecule (hereafter we use the notation $\varepsilon_{ij}^{\mathrm{rot},c} = \varepsilon_j^{ci}$) [63]:

$$\frac{\varepsilon_j^{ci}}{hc} = B_i^c j(j+1) - D_i^c j^2 (j+1)^2 + \dots , \tag{1.2}$$

where $c$ is the speed of light;

$$B_i^c = B_{\mathrm{e}}^c - \alpha_{\mathrm{e}}^c \left( i + \frac{1}{2} \right) + \dots ; \qquad D_i^c = D_{\mathrm{e}}^c - \beta_{\mathrm{e}}^c \left( i + \frac{1}{2} \right) + \dots ;$$

$B_{\mathrm{e}}^c$, $D_{\mathrm{e}}^c$, $\alpha_{\mathrm{e}}^c$, and $\beta_{\mathrm{e}}^c$ are the spectroscopic constants, the subscript "e" denotes the equilibrium internuclear distance of a diatomic molecule. Sometimes, in the formula (1.2) only the first term is retained, and $B_i^c$ is chosen as an average value, the same for all $i$.

The vibrational energy of a molecule is commonly assumed to be independent from the rotational level $\varepsilon_{ij}^{\mathrm{vibr},c} = \varepsilon_i^c$, and is simulated on the basis of the exponential interaction potential (the harmonic oscillator model) or the Morse potential (the anharmonic oscillator model). The Morse potential makes it possible to write the following expression for the vibrational energy of a diatomic molecule:

$$\frac{\varepsilon_i^c}{hc} = \omega_{\mathrm{e}}^c \left( i + \frac{1}{2} \right) - \omega_{\mathrm{e}}^c x_{\mathrm{e}}^c \left( i + \frac{1}{2} \right)^2 + \omega_{\mathrm{e}}^c y_{\mathrm{e}}^c \left( i + \frac{1}{2} \right)^3 + \dots , \tag{1.3}$$

where $\omega_{\mathrm{e}}^c$, $\omega_{\mathrm{e}}^c x_{\mathrm{e}}^c$, and $\omega_{\mathrm{e}}^c y_{\mathrm{e}}^c$ are the spectroscopic constants characterizing the frequency of vibrations and their anharmonicity.

Neglecting in the formula (1.3) the terms $\omega_{\mathrm{e}}^c x_{\mathrm{e}}^c$, $\omega_{\mathrm{e}}^c y_{\mathrm{e}}^c$, we obtain the harmonic oscillator spectrum:

$$\frac{\varepsilon_i^c}{hc} = \omega_{\mathrm{e}}^c \left( i + \frac{1}{2} \right). \tag{1.4}$$

The latter model does not describe correctly the energy of highly excited states. In particular, since the value $\Delta\varepsilon = \varepsilon_i^c - \varepsilon_{i-1}^c$ remains constant for all $i$, the vibrational energy $\varepsilon_i^c$ increases unrestrictedly with the vibrational level number. The anharmonic oscillator model provides a more precise approximation for the real molecular spectra as it takes into account their refinement for high vibrational levels, as well as the existence of the dissociation threshold. Usually in the expansion (1.3), only the first and the second terms are kept since the value $\omega_e^c y_e^c$ is much smaller than $\omega_e^c x_e^c$.

The most reliable data on the spectroscopic constants of diatomic molecules, obtained during the recent decades, are collected in Ref. [115]. The constants $\omega_e^c$, $\omega_e^c x_e^c$, $B_e^c$, and $\alpha_e^c$ for several diatomic molecules in the ground electronic state are presented in Table 1.1, along with the dissociation energy.

**Table 1.1** Spectroscopic constants for some diatomic molecules in the ground electronic state [115]

| Molecule | $\omega_e^c$, cm$^{-1}$ | $\omega_e^c x_e^c$, cm$^{-1}$ | $B_e^c$, cm$^{-1}$ | $\alpha_e^c$, $10^{-3}$cm$^{-1}$ | $D_c$, $10^4$cm$^{-1}$ |
|---|---|---|---|---|---|
| $H_2$ | 4401,21 | 121,34 | 60,853 | 3062 | 3,6118 |
| $N_2$ | 2358,57 | 14,32 | 1,998 | 17,3 | 7,871 |
| $O_2$ | 1580,19 | 11,98 | 1,4377 | 15,9 | 4,126 |
| NO | 1904,20 | 14,075 | 1,6720 | 17,1 | 5,240 |
| CO | 2169,81 | 13,29 | 1,93128 | 17,5 | 8,946 |

In Fig. 1.1, the energy of vibrational levels for molecular nitrogen, obtained on the basis of the accurate quasi-classical methods [79], is compared to that calculated for the harmonic and anharmonic oscillator models. We can see that for low levels, all models provide similar results whereas with the increase in the vibrational level, the harmonic oscillator model considerably overestimates the vibrational energy. The anharmonic oscillator model gives a satisfactory description for the vibrational levels up to $i = 30$ (with the accuracy within 5%), however, the discrepancy increases with the quantum number, and for $i > 55$, the error exceeds 10%.

Introducing the energy of the zero vibrational level $\varepsilon_0^c$, we can rewrite the value $\varepsilon_i^c$ in the form [100]:

$$\varepsilon_i^c = \varepsilon_0^c + hc\left(\omega_0^c i - \omega_0^c x_0^c i^2\right),$$

where

$$\frac{\varepsilon_0^c}{hc} = \frac{1}{2}\omega_e^c - \frac{1}{4}\omega_e^c x_e^c; \quad \omega_0^c = \omega_e^c - \omega_e^c x_e^c; \quad \omega_0^c x_0^c = \omega_e^c x_e^c.$$

If the energy is counted from that of the zero vibrational level rather than from its minimum value (as in the formulae (1.3) and (1.4)), then we have

$$\varepsilon_i^c = hc\left(\omega_0^c i - \omega_0^c x_0^c i^2\right) = \varepsilon_1^c i - hc\,\omega_0^c x_0^c i(i-1), \tag{1.5}$$

where

$$\varepsilon_1^c = hc\left(\omega_0^c - \omega_0^c x_0^c\right) = hc\left(\omega_e^c - 2\,\omega_e^c x_e^c\right) \tag{1.6}$$
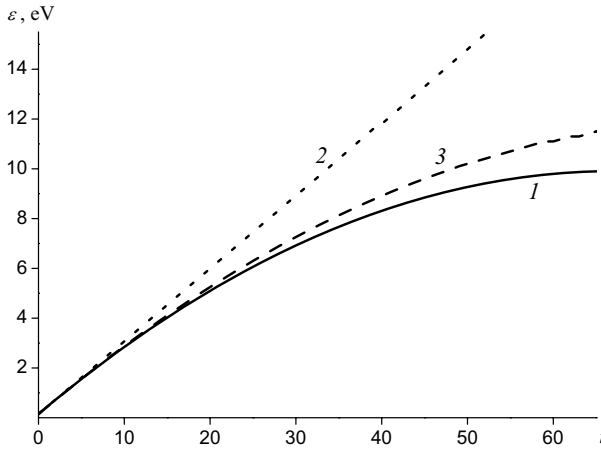
**Fig. 1.1** The energy of vibrational levels for $N_2$ as a function of $i$ for $j = 0$. Curve *1* — accurate calculations [79]; *2* — harmonic oscillators; *3* — anharmonic oscillators

is the energy of the first level counted from that of the zero level.

In some studies (see, for instance, Ref. [100, 63]), the coefficient of anharmonic-ity is introduced as $\alpha_c = \omega_e^c x_e^c / \omega_e^c$. Then

$$\varepsilon_1^c = hc\,\omega_e^c (1 - 2\alpha_c),$$

$$\varepsilon_i^c = hc\,\omega_e^c\,(1 - \alpha_c)\,i - hc\,\omega_e^c\,\alpha_c\,i^2 = h\nu_c\,(1 - \alpha_c)\,i - h\nu_c\,\alpha_c\,i^2,$$

where $\nu_c = c\,\omega_e^c$ is the frequency of vibrations. Using the frequency definition, the characteristic vibrational temperature of a diatomic gas can be defined: $\vartheta_{vibr}^c = h\nu_c/k$ ($k$ is the Boltzmann constant).

An important characteristics of a particle of the species $c$ is its energy of for-mation $\varepsilon_c$. In chemical kinetics [125], the energy of formation $\varepsilon_{AB}$ for a diatomic molecule AB is often defined using the energy of formation for atoms constituting the molecule $\varepsilon_A$ and $\varepsilon_B$, and that of dissociation (binding energy) $D_{AB}$:

$$\varepsilon_{AB} = \varepsilon_A + \varepsilon_B - D_{AB}.$$

The energy of atom formation $\varepsilon_A$ is specified by the dissociation energy $D_{A_2}$ of a corresponding homo-nuclear diatomic molecule $A_2$: $\varepsilon_A = D_{A_2}/2$.

## 1.1.2 Distribution Function and Macroscopic Parameters

The kinetic theory describes the fluid dynamics and kinetics of processes in gases on the basis of distribution functions. Let $f_{cij}(\mathbf{r}, \mathbf{u}, t)$ be a one-particle distribution function for mixture molecules over the chemical species $c$, vibrational $i$, and rota-tional $j$ energy levels in the phase space of the velocity $\mathbf{u}$, coordinates $\mathbf{r}$, and time

$t$. The function $f_{cij}(\mathbf{r},\mathbf{u},t)$ is introduced as the density of the mathematical expectation for the number of particles of species $c$, $i$, and $j$ in an element of the phase space $(\mathbf{r}, \mathbf{r}+d\mathbf{r})$, $(\mathbf{u}, \mathbf{u}+d\mathbf{u})$ for a time moment $t$.

An important objective of the kinetic theory is to establish the connection between the kinetic gas description and the gas-dynamic formulation, when the gas flow is characterized by the macroscopic parameters depending only on the spatial and time coordinates. The macroscopic gas parameters are specified as the moments of the distribution function. Let us introduce the main macroscopic parameters required for the description of a non-equilibrium reacting gas flow.

The population of molecular species $c$ for the vibrational level $i$ per unit volume (or the number density of molecules of $c$ species at the vibrational level $i$) is given by the expression

$$n_{ci}(\mathbf{r},t) = \sum_j \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c,$$

whereas the number density of molecular species $c$ is

$$n_c(\mathbf{r},t) = \sum_{ij} \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c = \sum_i n_{ci},$$

the number density of atoms $c$ is

$$n_{c,\mathrm{a}}(\mathbf{r},t) = \int f_c(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c,$$

and the number density of a gas mixture is given by

$$n(\mathbf{r},t) = \sum_{cij} \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c = \sum_c n_c.$$

From here on, the summation over $c$ means the summation over all molecular and atomic species.

The mass density of molecular species $c$ on the vibrational level $i$ ($m_c$ is the particle mass) is specified as

$$\rho_{ci}(\mathbf{r},t) = \sum_j m_c \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c = m_c n_{ci},$$

whereas the mass density of chemical species $c$ takes the form

$$\rho_c(\mathbf{r},t) = \sum_{ij} m_c \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c = m_c n_c,$$

and the mixture mass density is expressed as

$$\rho(\mathbf{r},t) = \sum_{cij} m_c \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c = \sum_c \rho_c.$$

The velocity of the macroscopic gas flow $\mathbf{v}(\mathbf{r},t)$ is introduced in the form

$$\rho\mathbf{v}(\mathbf{r},t) = \sum_{cij} m_c \int \mathbf{u}_c f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c.$$

The total energy of the mixture particles per unit mass $U$ is given by the formula

$$U(\mathbf{r},t) = E_{\text{tr}} + E_{\text{rot}} + E_{\text{vibr}} + E_{\text{f}},$$

where $E_{\text{tr}}$, $E_{\text{rot}}$, $E_{\text{vibr}}$, and $E_{\text{f}}$ are the specific translational, rotational, vibrational energy, and that of formation specified by the expressions

$$\rho E_{\text{tr}} = \sum_{cij} \int \frac{m_c c_c^2}{2} f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c, \tag{1.7}$$

$$\rho E_{\text{rot}} = \sum_{cij} \varepsilon_j^{ci} \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c, \tag{1.8}$$

$$\rho E_{\text{vibr}} = \sum_{cij} \varepsilon_i^c \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c = \sum_{ci} \varepsilon_i^c n_{ci}, \tag{1.9}$$

$$\rho E_{\text{f}} = \sum_{cij} \varepsilon_c \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c = \sum_{c} \varepsilon_c n_c. \tag{1.10}$$

The rotational and vibrational energies $\varepsilon_j^{ci}$ and $\varepsilon_i^c$ are counted from their zero values.

It should be noted that the values $\rho E_{\text{tr}}$, $\rho E_{\text{rot}}$, $\rho E_{\text{vibr}}$, and $\rho E_{\text{f}}$ represent the corresponding energy per unit volume. In addition to that, the specific internal energies $E_{\text{tr},c}$, $E_{\text{rot},c}$, $E_{\text{vibr},c}$, and $E_{\text{f},c}$ for a given chemical species $c$ are often introduced:

$$\rho_c E_{\text{tr},c} = \sum_{ij} \int \frac{m_c c_c^2}{2} f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c, \quad \rho E_{\text{tr}} = \sum_{c} \rho_c E_{\text{tr},c},$$

$$\rho_c E_{\text{rot},c} = \sum_{ij} \varepsilon_j^{ci} \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c, \quad \rho E_{\text{rot}} = \sum_{c} \rho_c E_{\text{rot},c},$$

$$\rho_c E_{\text{vibr},c} = \sum_{ij} \varepsilon_i^c \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c, \quad \rho E_{\text{vibr}} = \sum_{c} \rho_c E_{\text{vibr},c},$$

$$\rho_c E_{\text{f},c} = \sum_{ij} \varepsilon_c \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c, \quad \rho E_{\text{f}} = \sum_{c} \rho_c E_{\text{f},c}.$$

For the state-to-state gas description, it is also necessary to introduce the specific rotational energy $E_{\text{rot},ci}$ for molecular species $c$ at the vibrational level $i$:

$$\rho_{ci} E_{\text{rot},ci} = \sum_{j} \varepsilon_j^{ci} \int f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c.$$

Let us consider now the macroscopic parameters characterizing the transport of mass, momentum and energy in multi-component mixtures.

The diffusion velocity $\mathbf{V}_c$ of particles $c$ is specified as

$$n_c \mathbf{V}_c(\mathbf{r},t) = \sum_{ij} \int \mathbf{c}_c f_{cij}(\mathbf{r},\mathbf{u},t) \, d\mathbf{u}_c, \tag{1.11}$$

where $\mathbf{c}_c = \mathbf{u}_c - \mathbf{v}$ is the particle peculiar velocity.

The diffusion velocity $\mathbf{V}_{ci}$ of molecular species $c$ on the vibrational level $i$ has the form

$$n_{ci} \mathbf{V}_{ci}(\mathbf{r},t) = \sum_{j} \int \mathbf{c}_c f_{cij}(\mathbf{r},\mathbf{u},t) \, d\mathbf{u}_c. \tag{1.12}$$

The stress tensor $P$ is given by the formula

$$P(\mathbf{r},t) = \sum_{cij} \int m_c \mathbf{c}_c \mathbf{c}_c f_{cij}(\mathbf{r},\mathbf{u},t) \, d\mathbf{u}_c, \tag{1.13}$$

where $\mathbf{c}_c \mathbf{c}_c$ is the second rank tensor constituted of the products of the peculiar velocity components $\mathbf{c}_c$ ($c_x c_x$, $c_x c_y$, ...).

The total energy flux $\mathbf{q}$ is expressed as follows

$$\mathbf{q}(\mathbf{r},t) = \sum_{cij} \int \left( \frac{m_c c_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon_c \right) \mathbf{c}_c f_{cij}(\mathbf{r},\mathbf{u},t) \, d\mathbf{u}_c. \tag{1.14}$$

The total energy flux can be written as a sum of fluxes of the translational, rotational, and vibrational energy, as well as that of the formation energy $\varepsilon_c$:

$$\mathbf{q} = \mathbf{q}_{tr} + \mathbf{q}_{rot} + \mathbf{q}_{vibr} + \mathbf{q}_{f},$$

where

$$\mathbf{q}_{tr}(\mathbf{r},t) = \sum_{cij} \int \frac{m_c c_c^2}{2} \mathbf{c}_c f_{cij}(\mathbf{r},\mathbf{u},t) \, d\mathbf{u}_c;$$

$$\mathbf{q}_{rot}(\mathbf{r},t) = \sum_{cij} \varepsilon_j^{ci} \int \mathbf{c}_c f_{cij}(\mathbf{r},\mathbf{u},t) \, d\mathbf{u}_c;$$

$$\mathbf{q}_{vibr}(\mathbf{r},t) = \sum_{cij} \varepsilon_i^c \int \mathbf{c}_c f_{cij}(\mathbf{r},\mathbf{u},t) \, d\mathbf{u}_c;$$

$$\mathbf{q}_{f}(\mathbf{r},t) = \sum_{cij} \varepsilon_c \int \mathbf{c}_c f_{cij}(\mathbf{r},\mathbf{u},t) \, d\mathbf{u}_c.$$

### 1.1.3 Specific Heats

The energies of translational and internal degrees of freedom (1.7)–(1.10) specify such an important thermodynamic gas characteristics as the specific heat. The heat capacity per unit mass (specific heat) at constant volume is given by the formula

$$c_V = \left(\frac{\partial U}{\partial T}\right)_V = c_{V,\mathrm{tr}} + c_{V,\mathrm{rot}} + c_{V,\mathrm{vibr}} + c_{V,\mathrm{f}}, \qquad (1.15)$$

where $T$ is the gas temperature, $c_{V,\mathrm{tr}}$, $c_{V,\mathrm{rot}}$, and $c_{V,\mathrm{vibr}}$ are the contributions of the translational, rotational, and vibrational degrees of freedom to the constant volume specific heat, $c_{V,\mathrm{f}}$ is the part of the specific heat related to the energy of formation:

$$c_{V,\mathrm{tr}} = \left(\frac{\partial E_{\mathrm{tr}}}{\partial T}\right)_V, \qquad (1.16)$$

$$c_{V,\mathrm{rot}} = \left(\frac{\partial E_{\mathrm{rot}}}{\partial T}\right)_V, \qquad (1.17)$$

$$c_{V,\mathrm{vibr}} = \left(\frac{\partial E_{\mathrm{vibr}}}{\partial T}\right)_V, \qquad (1.18)$$

$$c_{V,\mathrm{f}} = \left(\frac{\partial E_{\mathrm{f}}}{\partial T}\right)_V. \qquad (1.19)$$

Substituting the distribution functions corresponding to the conditions of thermodynamic equilibrium into the formulae (1.7)–(1.10), we can obtain the relations connecting the equilibrium gas energy with the temperature, and using the expressions (1.16)–(1.19) with the equilibrium distribution functions, we can calculate the equilibrium heat capacities. If we substitute into the formulae (1.7)–(1.10) and (1.16)–(1.19) the distribution functions found from the kinetic equations for the non-equilibrium conditions, we can calculate the energy and the specific heats for a non-equilibrium gas. Note that the specific heat $c_{V,\mathrm{f}}$ is of importance for the conditions of chemical equilibrium or for weak deviations from it [78], whereas in the case of slow chemical reactions, this value is commonly neglected. In addition to that, the total energy under the non-equilibrium conditions is specified not only by the gas temperature but also by other macroscopic parameters such as the non-equilibrium vibrational level populations, species concentrations, and vibrational temperatures. Under the non-equilibrium conditions, some additional constituents of the heat capacity can be introduced (see, for instance, Chapter 3 devoted to multi-temperature models).

The specific heat of a gas at constant pressure is equal to

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p,$$

where $h$ is the specific gas enthalpy

$$h = \frac{p}{\rho} + U;$$

$p$ is the hydrostatic pressure. The pressure is related to the temperature via the equation of state, which for an ideal gas, takes the form

$$p = nkT = \rho \frac{R}{\mu} T. \tag{1.20}$$

Here, $k$ is the Boltzmann constant ($k = 1,3807 \cdot 10^{-23}$ J·K$^{-1}$), $R$ is the universal gas constant, $R = k \mathcal{N}_A$, $\mathcal{N}_A$ is the Avogadro number ($\mathcal{N}_A = 6,0221 \cdot 10^{23}$ mole$^{-1}$, $R = 8,3145$ J·mole$^{-1}$·K$^{-1}$), $\mu$ is the molar mass. For a mixture of ideal gases, the molar mass is determined as

$$\frac{1}{\mu} = \sum_c \frac{\rho_c}{\rho} \frac{1}{\mu_c},$$

and the equation of state can be rewritten in the form:

$$p = \rho \frac{R}{\mu} T = \sum_c \rho_c \frac{R}{\mu_c} T.$$

One can introduce the specific gas constant $\hat{R}_c = R/\mu_c$ of species $c$ or the mixture constant $\hat{R} = R/\mu$. Thus for air at the normal pressure and temperature, $\hat{R} = 287$ J·kg$^{-1}$·K$^{-1}$.

Taking into account the equation of state, we can reduce the specific heat at constant pressure to the form

$$c_p = \hat{R} + c_V.$$

In the present study, the constant volume specific heat is mainly used. Therefore, for the sake of the notation simplicity, the subscript "$V$" at the specific heat of translational and internal degrees of freedom is hereafter omitted: $c_{V,\text{tr}} = c_{\text{tr}}$, $c_{V,\text{rot}} = c_{\text{rot}}$, $c_{V,\text{vibr}} = c_{\text{vibr}}$, and $c_{V,\text{f}} = c_{\text{f}}$.

For the practical calculations, it is convenient to introduce the specific heat at constant volume for each chemical species $c$:

$$c_{\text{tr},c} = \left( \frac{\partial E_{\text{tr},c}}{\partial T} \right)_V, \qquad c_{\text{rot},c} = \left( \frac{\partial E_{\text{rot},c}}{\partial T} \right)_V,$$

$$c_{\text{vibr},c} = \left( \frac{\partial E_{\text{vibr},c}}{\partial T} \right)_V, \qquad c_{\text{f},c} = \left( \frac{\partial E_{\text{f},c}}{\partial T} \right)_V.$$

These values are related to the constituents of the total specific heat (1.16)–(1.19) by the expressions:

$$c_{\text{tr}} = \sum_c \frac{\rho_c}{\rho} c_{\text{tr},c}, \qquad c_{\text{rot}} = \sum_c \frac{\rho_c}{\rho} c_{\text{rot},c},$$

$$c_{\text{vibr}} = \sum_c \frac{\rho_c}{\rho} c_{\text{vibr},c}, \qquad c_{\text{f}} = \sum_c \frac{\rho_c}{\rho} c_{\text{f},c}.$$

Moreover, it is useful to define the constituent of the specific heat associated with the specific rotational energy of $c$ species on the vibrational level $i$:

$$c_{\text{rot},ci} = \left( \frac{\partial E_{\text{rot},ci}}{\partial T} \right)_V, \tag{1.21}$$

For this specific heat, the following relation is fulfilled:

$$c_{\text{rot}} = \sum_{ci} \frac{\rho_{ci}}{\rho} c_{\text{rot},ci}. \qquad (1.22)$$

In the case of the Maxwell velocity distribution, the energy of translational degrees of freedom takes the form

$$\rho E_{\text{tr}} = \frac{3}{2} nkT,$$

and therefore,

$$c_{\text{tr}} = \frac{3}{2} \frac{kn}{\rho} = \frac{3}{2} \frac{k}{\sum_c m_c \frac{n_c}{n}} = \frac{3}{2} \hat{R}. \qquad (1.23)$$

If the distribution of molecules over the rotational energy is Boltzmann's with the gas temperature $T$, then, for the rigid rotator model (1.1) under the condition $kT \gg h^2/(8\pi^2 I_c)$, the specific rotational energy of chemical species $c$ is given by the expression

$$\rho_c E_{\text{rot},c} = n_c kT,$$

and the specific heat of the rotational degrees of freedom satisfies the relation

$$c_{\text{rot},c} = \frac{k}{m_c}. \qquad (1.24)$$

In the limit case of low temperatures ($kT \ll h^2/(8\pi^2 I_c)$), $c_{\text{rot},c}$ is given by the formula [262]

$$c_{\text{rot},c} = \frac{3k}{m_c} \left( \frac{h^2}{4\pi^2 I_c kT} \right)^2 \exp\left( -\frac{h^2}{4\pi^2 I_c kT} \right).$$

Note that for the most gases (excepting $H_2$ and $D_2$), at the room temperatures, the condition $kT \gg h^2/(8\pi^2 I_c)$ is valid, and one can use the formula (1.24).

In the case of the equilibrium Boltzmann distribution over the vibrational energy levels, for the harmonic oscillator model with the infinite number of the levels, the specific vibrational energy of $c$ species is calculated as follows

$$E_{\text{vibr},c} = \frac{1}{m_c} \frac{h\nu_c}{\exp\left( \dfrac{h\nu_c}{kT} \right) - 1}, \qquad (1.25)$$

and the expression for the specific heat of the vibrational degrees of freedom takes the form [262]

$$c_{\text{vibr},c} = \frac{k}{m_c} \left( \frac{h\nu_c}{kT} \right)^2 \frac{\exp\left( \dfrac{h\nu_c}{kT} \right)}{\left[ \exp\left( \dfrac{h\nu_c}{kT} \right) - 1 \right]^2}. \qquad (1.26)$$

For high temperatures ($kT \gg h\nu_c$), the vibrational constituent of the specific heat is given by

$$c_{\text{vibr},c} = \frac{k}{m_c},$$

whereas for low temperatures ($kT \ll h\nu_c$), it is written as follows:

$$c_{\text{vibr},c} = \frac{k}{m_c} \left( \frac{h\nu_c}{kT} \right)^2 \exp\left( -\frac{h\nu_c}{kT} \right).$$

For the anharmonic oscillator model, the specific vibrational energy, as well as the corresponding heat capacity are given by more complex expressions even if the gas displays the equilibrium distribution over the vibrational energy. The vibrational constituents of the specific heats under the non-equilibrium conditions are studied in Chapter 3.

The existing calculations for the specific heats in molecular gases are mostly based on the assumption about the total thermodynamic equilibrium over all degrees of freedom. The comprehensive information on the specific heats in various temperature intervals is collected in the tables of the thermodynamic properties of materials (see Refs. [107, 235]). The most up-to-date data on the equilibrium specific heats for eighteen air components at temperatures 50–100000 K are given in Refs. [50, 94].

## 1.2 Kinetic Equations for Distribution Functions in Reacting Gas Mixtures

Following the studies [258, 253, 82, 249, 130, 78], let us write the kinetic equations for the distribution functions $f_{cij}(\mathbf{r}, \mathbf{u}, t)$ in a gas mixture with internal degrees of freedom and chemical reactions. We suppose that all assumptions, necessary for the derivation of the Boltzmann equation, are valid: particles interact only in the instant of a collision; between the collisions, particles move freely; the collisions occur instantaneously and in a point. Moreover, we neglect the influence of mass and electromagnetic forces on the variation of the distribution function.

The set of generalized kinetic equations for a reacting gas mixture can be written in the form

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = J_{cij}, \tag{1.27}$$

$$c = 1, ..., L, \quad i = 0, ..., L_c, \quad j = 0, ..., L_{ci}.$$

Here, $\nabla = \partial/\partial \mathbf{r}$; $L$ is the number of chemical species in a mixture, $L_c$ is the number of excited vibrational levels in molecular species $c$; $L_{ci}$ is the number of rotational levels of molecules $c$ on the vibrational level $i$, and $J_{cij}$ is the integral operator responsible for the variation of the distribution function resulted from collisions:

$$J_{cij} = J_{cij}^{\text{el}} + J_{cij}^{\text{int}} + J_{cij}^{\text{react}},$$

$$J_{cij}^{\text{react}} = J_{cij}^{2\rightleftharpoons2} + J_{cij}^{2\rightleftharpoons3},$$

$J_{cij}^{\text{el}}$, $J_{cij}^{\text{int}}$, $J_{cij}^{2\rightleftharpoons2}$, and $J_{cij}^{2\rightleftharpoons3}$ are, respectively, the collision operators for elastic collisions, in which only the translational energy varies, and those for inelastic collisions leading to the internal energy variation, bimolecular chemical reactions, and dissociation–recombination reactions.

In contrast to the classical Boltzmann equation which describes only binary collisions leading to the formation of two particles, in the kinetic equations (1.27), collisions resulting in dissociation as well as reverse triple collisions with recombination are taken into account (triple collisions which do not result in recombination are neglected since they are less probable). Such an approach for modeling of dissociation and recombination is applied in the studies [171, 226, 198, 130, 78]. The generalized Boltzmann equation for gas mixtures with internal degrees of freedom and bimolecular chemical reactions can be found, for instance, in Refs. [28, 249, 76, 8]. The kinetic equations for the distribution function over the velocity and internal energy levels in a single-component gas with one internal degree of freedom are derived in [258]. In Ref. [253], the rotational and vibrational degrees of freedom are taken into account in the kinetic equations, in [189] the kinetic equations for non-reacting multi-component mixtures with internal degrees of freedom are obtained.

Let us write the integral operators for various collision types. Suppose that particles $A_c(\mathbf{u}_c, i, j)$ and $A_d(\mathbf{u}_d, k, l)$ with the velocities $\mathbf{u}_c$, $\mathbf{u}_d$, on the vibrational levels $i$ and $k$, and rotational levels $j$ and $l$, collide. First, collisions without chemical reactions are considered, resulting in the energy exchange and the formation of particles with the velocities $\mathbf{u}'_c$, $\mathbf{u}'_d$, on the vibrational and rotational levels $i'$, $k'$, and $j'$, $l'$, respectively:

$$A_c(\mathbf{u}_c, i, j) + A_d(\mathbf{u}_d, k, l) \rightleftharpoons A_c(\mathbf{u}'_c, i', j') + A_d(\mathbf{u}'_d, k', l'). \qquad (1.28)$$

Here, the prime denotes the velocities and energy levels of particles after a collision. The integral operator $J_{cij}^{\text{int}}$ associated with the collisions (1.28) has the form [249]

$$J_{cij}^{\text{int}} = \sum_d \sum_{ki'k'} \sum_{lj'l'} \int \left( f_{ci'j'} f_{dk'l'} \frac{s_{ij}^c s_{kl}^d}{s_{i'j'}^c s_{k'l'}^d} - f_{cij} f_{dkl} \right) g \sigma_{cd,ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u}_d. \qquad (1.29)$$

In this expression, $s_{ij}^c$ is the statistical weight characterizing the degeneracy of the molecular state with the internal energy $\varepsilon_{ij}^c$. The differential cross section $\sigma_{cd,ijkl}^{i'j'k'l'}$ corresponds to a collision of particles of species $c$ and $d$, on the $i^{th}$ and $k^{th}$ vibrational and $j^{th}$ and $l^{th}$ rotational levels, moving with the relative velocity $\mathbf{g} = \mathbf{u}_c - \mathbf{u}_d$, which results in the transition of molecules to the vibrational levels $i'$ and $k'$, and rotational levels $j'$ and $l'$, whereas the relative velocity vector after the collision appears within the solid angle $d^2\Omega$. The following notations for the distribution functions before and after the collision are used:

$$f_{cij} = f_{cij}(\mathbf{r}, \mathbf{u}_c, t), \quad f_{ci'j'} = f_{ci'j'}(\mathbf{r}, \mathbf{u}'_c, t),$$

$$f_{dkl} = f_{dkl}(\mathbf{r}, \mathbf{u}_d, t), \quad f_{dk'l'} = f_{dk'l'}(\mathbf{r}, \mathbf{u}'_d, t).$$

The integral operator for elastic collisions $J_{cij}^{\text{el}}$ is obtained from Eq. (1.29) at $i' = i$, $j' = j$, $k' = k$, and $l' = l$.

The integral operator $J_{cij}^{2 \rightleftharpoons 2}$ for exchange chemical reactions

$$A_c(\mathbf{u}_c, i, j) + A_d(\mathbf{u}_d, k, l) \rightleftharpoons A_{c'}(\mathbf{u}_{c'}, i', j') + A_{d'}(\mathbf{u}_{d'}, k', l')$$

has the form [249, 76]

$$J_{cij}^{2 \rightleftharpoons 2} = \sum_{dc'd'} \sum_{ki'k'} \sum_{lj'l'} \int \left[ f_{c'i'j'} f_{d'k'l'} \frac{s_{ij}^c s_{kl}^d}{s_{i'j'}^{c'} s_{k'l'}^{d'}} \left( \frac{m_c m_d}{m_{c'} m_{d'}} \right)^3 - f_{cij} f_{dkl} \right] \times$$

$$\times g \sigma_{cd, ijkl}^{c'd', i'j'k'l'} d^2 \Omega d\mathbf{u}_d,$$

where $\sigma_{cd, ijkl}^{c'd', i'j'k'l'}$ is the differential cross section of collisions resulting in bimolecular chemical reactions. The distribution functions after the collision are denoted as $f_{c'i'j'} = f_{c'i'j'}(\mathbf{r}, \mathbf{u}_{c'}, t)$, $f_{d'k'l'} = f_{d'k'l'}(\mathbf{r}, \mathbf{u}_{d'}, t)$.

When one of the colliding particles is an atom, then in the formulae for the collision operators, the subscripts designating the rotational and vibrational quantum number of the corresponding particle in the expressions for the distribution functions and cross sections are omitted.

The integral operator for collisions with dissociation and recombination $J_{cij}^{2 \rightleftharpoons 3}$ can be written in the simplified form for the case of diatomic molecules, when dissociation results in the formation of only atomic species, and only atoms participate in the recombination reaction. In addition to this, we take into account the common assumption that the dissociation cross section does not depend on the internal state of a reaction partner (if the partner is a molecule), and this state does not vary as a result of dissociation or recombination:

$$A_c(\mathbf{u}_c, i, j) + A_d(\mathbf{u}_d, k, l) \rightleftharpoons A_{c'}(\mathbf{u}_{c'}) + A_{f'}(\mathbf{u}_{f'}) + A_d(\mathbf{u}_d', k, l), \tag{1.30}$$

$c'$, $f'$ are the atomic species of the dissociation products, $\mathbf{u}_{c'}$, $\mathbf{u}_{f'}$, $\mathbf{u}_d'$ are the particle velocities after the collision. Then the collision operator $J_{cij}^{2 \rightleftharpoons 3}$ for the reaction (1.30) can be written in the form [171, 198, 130, 78, 154]

$$J_{cij}^{2 \rightleftharpoons 3} = \sum_d \sum_k \sum_l \int \left[ f_{dkl}' f_{c'} f_{f'} h^3 s_{ij}^c \left( \frac{m_c}{m_{c'} m_{f'}} \right)^3 - f_{cij} f_{dkl} \right] \times$$

$$\times g \sigma_{cij, d}^{\text{diss}} d\mathbf{u}_d d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}_d',$$

$\sigma_{cij, d}^{\text{diss}}(\mathbf{u}_c, \mathbf{u}_d, \mathbf{u}_{c'}, \mathbf{u}_{f'}, \mathbf{u}_d')$ is the formal cross section of a collision resulting in the dissociation reaction, $f_{c'} = f_{c'}(\mathbf{r}, \mathbf{u}_{c'}, t)$, $f_{f'} = f_{f'}(\mathbf{r}, \mathbf{u}_{f'}, t)$ are the distribution functions of atoms formed during the dissociation reaction, $f_{dkl}' = f_{dkl}(\mathbf{r}, \mathbf{u}_d', t)$.

While writing the expressions for the collision integrals, we used the detailed balance relations for the cross sections of forward and backward bimolecular processes [254, 249, 76]:

$$s^c_{i'j'}s^d_{k'l'}g'^2\sigma^{ijkl}_{cd,i'j'k'l'}(\mathbf{g}',\Omega) = s^c_{ij}s^d_{kl}g^2\sigma^{i'j'k'l'}_{cd,ijkl}(\mathbf{g},\Omega'), \qquad (1.31)$$

$$s^{c'}_{i'j'}s^{d'}_{k'l'}m^2_{c'}m^2_{d'}g'^2\sigma^{cd,ijkl}_{c'd',i'j'k'l'}(\mathbf{g}',\Omega) = s^c_{ij}s^d_{kl}m^2_c m^2_d g^2\sigma^{c'd',i'j'k'l'}_{cd,ijkl}(\mathbf{g},\Omega') \qquad (1.32)$$

and dissociation-recombination [171, 226, 130, 8, 78]:

$$\frac{m^3_{c'}m^3_{f'}}{h^3}\sigma^{\mathrm{rec},cij}_{c'f'd}(\mathbf{u}_{c'},\mathbf{u}_{f'},\mathbf{u}'_d,\mathbf{u}_c,\mathbf{u}_d) = s^c_{ij}m^3_c g\sigma^{\mathrm{diss}}_{cij,d}(\mathbf{u}_c,\mathbf{u}_d,\mathbf{u}_{c'},\mathbf{u}_{f'},\mathbf{u}'_d), \qquad (1.33)$$

$\sigma^{\mathrm{rec},cij}_{c'f'd}(\mathbf{u}_{c'},\mathbf{u}_{f'},\mathbf{u}'_d,\mathbf{u}_c,\mathbf{u}_d)$ is the probability density of triple collisions resulting in dissociation (1.30).

The latter relation means the equal probability for forward and backward reactions (1.30). The relations connecting the probabilities of chemically reactive collisions with the differential cross sections are given in Refs. [197, 249] for exchange chemical reactions, and in Ref. [130] for dissociation-recombination reactions.

Taking into account the relations following from the microscopic conservation laws for binary collisions [249, 76]

$$m_c m_d\, d\mathbf{u}_c d\mathbf{u}_d/g = m_{c'} m_{d'}\, d\mathbf{u}_{c'} d\mathbf{u}_{d'}/g',$$

we can rewrite the equations (1.31), (1.32) in the alternative form:

$$s^c_{i'j'}s^d_{k'l'}g'\sigma^{ijkl}_{cd,i'j'k'l'}(\mathbf{g}',\Omega)\,d\mathbf{u}'_c d\mathbf{u}'_d = s^c_{ij}s^d_{kl}g\sigma^{i'j'k'l'}_{cd,ijkl}(\mathbf{g},\Omega')\,d\mathbf{u}_c d\mathbf{u}_d,$$

$$s^{c'}_{i'j'}s^{d'}_{k'l'}m^3_{c'}m^3_{d'}g'\sigma^{cd,ijkl}_{c'd',i'j'k'l'}(\mathbf{g}',\Omega)\,d\mathbf{u}_{c'} d\mathbf{u}_{d'} =$$
$$= s^c_{ij}s^d_{kl}m^3_c m^3_d g\sigma^{c'd',i'j'k'l'}_{cd,ijkl}(\mathbf{g},\Omega')\,d\mathbf{u}_c d\mathbf{u}_d.$$

The statistical weight $s^c_{ij}$ can be expressed in the general case as the product: $s^c_{ij} = s^c_i s^{ci}_j$, where $s^c_i$ is the statistical weight of the vibrational state $i$ of the molecular species $c$, whereas $s^{ci}_j$ is that of its rotational state $j$. The vibrational levels of a diatomic molecule are not degenerated, and $s^c_i = 1$. The rotational statistical weight is usually supposed to be equal to $s^{ci}_j = 2j+1$, which corresponds to the assumption of equiprobable distribution of the directions of the internal momentum for the molecules.

## 1.3 Small Parameters in Kinetic Equations and the Method of Different Scales

Introducing the characteristic times $\tau_\gamma$ of microscopic processes and the mean time of the variation of the macroscopic parameters $\theta$, we can rewrite the kinetic equations (1.27) in the dimensionless form:

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = \sum_\gamma \frac{1}{\varepsilon_\gamma}J^{(\gamma)}_{cij}. \qquad (1.34)$$

Here, the distribution functions are related to $n_* u_*^{-3}$, the time and the coordinates are divided by $\theta$ and $\theta u_*$, respectively, the components of the molecular velocity are related to $u_*$; $n_*, u_*$ are the characteristic values of the number density and molecular velocity (one can also choose $u_*$ as the mean thermal velocity $u_* = (2kT_*/m_*)^{1/2}$, where $T_*$ is the characteristic gas temperature; $m_* = \rho_*/n_*$; $\rho_*$ is the characteristic gas density); $J_{cij}^{(\gamma)}$ are the dimensionless integral operators associated with various processes, the cross sections of the processes $\gamma$ are related to the corresponding average values. The parameters $\varepsilon_\gamma$ are given by the ratios $\varepsilon_\gamma = \tau_\gamma/\theta$ and represent the analogues of the Knudsen numbers for collisions of different types.

The relations between $\tau_\gamma$ and $\theta$ make it possible to proceed from the kinetic description to the macroscopic approach, and justify the choice of an adequate mathematical model for the hydro-dynamic description of the gas. The characteristic times $\tau_\gamma$ of various processes often differ by the orders of magnitude. This difference is not essential if all $\tau_\gamma$ are substantially smaller compared to $\theta$:

$$\tau_\gamma \ll \theta \quad \forall \gamma. \tag{1.35}$$

Under this condition, in each small volume of the medium, the processes occurring in collisions between particles are substantially more rapid than the variation of the gas-dynamic parameters. Therefore, on the macroscopic time scale $\theta$, the gas state is equilibrium or weakly non-equilibrium. Under the condition (1.35), the kinetic equations (1.34) can be written in the form

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = \frac{1}{\varepsilon} J_{cij}, \tag{1.36}$$

where $\varepsilon = \tau/\theta \ll 1$; $\tau \sim \tau_\gamma$.

Under the strong non-equilibrium conditions, the discrepancy between the characteristic rates of physical-chemical processes plays the principal role. Let us divide the considered processes into two groups: while the first includes rapid processes with the characteristic times $\tau_{\mathrm{rap}}$ much smaller than $\theta$ ($\tau_{\mathrm{rap}} \ll \theta$), the second group contains slow processes with the times $\tau_{\mathrm{sl}}$ comparable to $\theta$ ($\tau_{\mathrm{sl}} \sim \theta$). On the time scale $\theta$, the processes of the latter type appear to be essentially non-equilibrium. Moreover, the quasi-stationary distributions established on the microscopic time scale $\tau_{\mathrm{rap}}$ as a result of rapid processes, are conserved on the time scale $\theta$. Slow processes make an important contribution to the variation of the main macroscopic parameters of a moving gas.

Processes with the characteristic time much greater than $\theta$, can be assumed frozen while studying a gas flow on the time scale $\theta$.

A mathematical consequence of the existence of rapid and slow processes in real gas flows, is that the small parameter $\varepsilon$ in the kinetic equations appears in both the differential operator and the integral operator for slow processes [191]. Indeed, under the condition

$$\tau_{\mathrm{rap}} \ll \tau_{\mathrm{sl}} \sim \theta \tag{1.37}$$

the kinetic equations (1.34) take the form

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = \frac{1}{\varepsilon} J_{cij}^{\text{rap}} + J_{cij}^{\text{sl}}, \tag{1.38}$$

$\varepsilon = \tau_{\text{rap}}/\tau_{\text{sl}} \sim \tau_{\text{rap}}/\theta \ll 1$ is the small parameter, and $J_{cij}^{\text{rap}}$, $J_{cij}^{\text{sl}}$ are the collision operators for rapid and slow processes, respectively.

For low values of the parameter $\varepsilon$, the equations (1.36) and (1.38) are those with a singular perturbation, and their solution beyond the vicinity of the initial point and thin layers near the boundary, can be found as a series in the integer powers of the small parameter. An important difference between Eqs. (1.36) and (1.38) is that in the former case, the equations for the zero-order approximation include the total integral operator $J_{cij}$ and have the form

$$J_{cij}^{(0)} = 0. \tag{1.39}$$

The superscript (0) indicates that the zero-order distribution function is substituted into the collision operator:

$$J_{cij}^{(0)} = J_{cij}(f^{(0)}, f^{(0)}) \tag{1.40}$$

for binary collisions, and

$$J_{cij}^{(0)} = J_{cij}(f^{(0)}, f^{(0)}, f^{(0)}) \tag{1.41}$$

for triple collisions with recombination. While considering the solution of the equations (1.38) in the zero-order approximation, one should take into account that, in contrast to the case of Eq. (1.36), only the integral operator of rapid processes turns to zero in the latter case:

$$J_{cij}^{\text{rap}\,(0)} = 0. \tag{1.42}$$

The equations (1.39) provide the description of a considered reacting gas mixture in the local thermodynamic equilibrium state. Such a state is established as a result of chemical reactions and all kinds of energy transitions during the interaction of various degrees of freedom. The equations (1.42) describe the quasi-stationary distributions which are established only due to rapid processes, whereas the distributions for the slowly relaxing degrees of freedom can be strongly non-equilibrium. Such conditions are typical for the non-equilibrium kinetics, when the connection between some degrees of freedom is broken. From the above discussion, an important feature of the asymptotic representation for the solution of the kinetic equations follows: the distribution function is non-equilibrium already in the zero-order approximation. In the higher-order approximations, the distribution function $f_{cij}^{(r)}$ is found from the linear integral equations including the linearized integral operator for rapid processes $J_{cij}^{\text{rap}}(f^{(0)}, f^{(r)})$, whereas the operator for slow processes appears only in the free terms of the integral equations. In the present monograph, the strongly non-equilibrium conditions (1.37) are studied, and gas flows are considered on the

time scale $\theta$. Consequently, the kinetic equations are written in the form (1.38). The characteristic features of the obtained solutions are compared to those for the kinetic equations (1.36) under the weak non-equilibrium conditions (1.35).

The operators $J_{cij}^{\text{rap}}$ and $J_{cij}^{\text{sl}}$ can be different for the numerous non-equilibrium situations since the classification of rapid and slow processes is different under the specific flow conditions. This is connected to the dependence of the rates of physical-chemical processes on the gas temperature. The review of experimental results concerning the measurements of the relaxation times and probabilities for various kinds of energy transitions can be found in the studies [236, 100, 58, 51].

Let us consider several typical cases. It is well known from experiments [236], that at the high temperature conditions which are typical for the supersonic and hypersonic aerodynamics, the equilibrium over the translational and rotational degrees of freedom is established for a substantially shorter time than that of vibrational relaxation and chemical reactions, and therefore the following relation takes place

$$\tau_{\text{el}} \lesssim \tau_{\text{rot}} \ll \tau_{\text{vibr}} < \tau_{\text{react}} \sim \theta. \tag{1.43}$$

Here, $\tau_{\text{el}}$, $\tau_{\text{rot}}$, $\tau_{\text{vibr}}$, and $\tau_{\text{react}}$ are, respectively, the relaxation times for the translational, rotational and vibrational degrees of freedom, and the characteristic time for chemical reactions. Under this condition, on the time scale $\theta$, the equilibrium or weakly non-equilibrium distributions over the velocity and rotational energy maintain during the macroscopic processes of vibrational relaxation and chemical reactions. For the description of non-equilibrium vibrational and chemical kinetics, it is necessary to consider the equations for the vibrational level populations and atomic species concentrations (the model of state-to-state kinetics). In a moving gas, these equations should be coupled to the fluid dynamic equations. In the present study, the main attention is focused on the state-to-state approach and its applications to particular gas flows. (see Chapters 2, 5–9).

In high enthalpy flows, for strong excitation of the vibrational degrees of freedom and moderate temperatures, the vibrational energy exchanges between molecules of the same chemical species occur much more frequently compared to the transitions of vibrational energy into translational and rotational [236, 100]:

$$\tau_{\text{el}} \lesssim \tau_{\text{rot}} < \tau_{\text{VV}} \ll \tau_{\text{TRV}} < \tau_{\text{react}} \sim \theta, \tag{1.44}$$

$\tau_{\text{VV}}$, $\tau_{\text{TRV}}$ are, respectively, the mean times for the VV vibrational energy exchange and TRV transitions of the vibrational energy into other modes.

Under the condition (1.44), on the time scale $\tau_{\text{VV}}$, quasi-stationary (multi-temperature) distributions over the vibrational levels establish, which then maintain during non-equilibrium chemical reactions (the model of non-equilibrium multi-temperature kinetics). Such conditions are studied in Chapter 3.

In the case of high-threshold or slow chemical reactions, with the rate considerably lower than that for the internal energy relaxation caused by the energy exchanges during collisions, we have the following characteristic time relation

$$\tau_{\text{el}} < \tau_{\text{int}} \ll \tau_{\text{react}} \sim \theta, \tag{1.45}$$

$\tau_{int}$ is the mean time for the internal energy relaxation. Under this condition, the non-equilibrium chemical kinetics can be considered on the basis of the maintaining one-temperature Boltzmann distributions over the internal energy levels of molecular species (the model of one-temperature chemical kinetics [126]). This case is considered in Chapter 4.

Finally, if chemical reactions also proceed much more rapidly than the gas-dynamic parameters vary,

$$\tau_{el} < \tau_{int} \lesssim \tau_{react} \ll \theta,$$

then, as is mentioned above, on the time scale $\theta$ the distribution of molecules over the energy levels and chemical species can be assumed equilibrium or near-equilibrium (the model of equilibrium chemical kinetics [39, 32, 33, 247, 249, 226, 46, 78]). The macroscopic flow parameters evolve with the maintaining thermally and chemically equilibrium distributions or weak deviations from these distributions.

Up to this point, we discussed the conditions when all parameters $\varepsilon_\gamma$ or at least one of them are smaller than unity. In these cases, the presence of the small parameter in the kinetic equations (1.34) makes it possible to proceed to various models for gas dynamics taking into account, with any given accuracy, the kinetics of physical-chemical processes occurring in a gas flow. Such a transition to the macroscopic description is impossible if either all $\varepsilon_\gamma$ are comparable to unity or some of them are much greater than unity ($\varepsilon_\gamma \gtrsim 1$). In these cases, the processes with $\varepsilon_\gamma \sim 1$ have the rates comparable to that of the macroscopic parameters variation. Under such a condition, on the time scale $\theta$ the macroscopic parameters should be found directly on the basis of the distribution functions obtained by the integration of the kinetic equations rather than from the equations of non-equilibrium gas dynamics.

Processes with the characteristic times $\tau_{fr}$ exceeding $\theta$ and, respectively, $\varepsilon_{fr} = \tau_{fr}/\theta \gg 1$, can be considered as frozen or near-frozen on the gas-dynamic time scale. These processes weakly influence the macroscopic parameters variation. In this case, the kinetic equations also contain the small parameter:

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = \sum_\gamma J_{cij}^{(\gamma)} + \frac{1}{\varepsilon_{fr}} J_{cij}^{fr}, \quad \frac{1}{\varepsilon_{fr}} \ll 1. \tag{1.46}$$

This case is similar to that of large Knudsen numbers in the Boltzmann equations, however, in Eq. (1.46), the small parameter $1/\varepsilon_{fr}$ appears in the integral operator of the slowest processes rather than in all collision operators.

The solution of the equations (1.46) can also be expressed as a series in the small parameter $1/\varepsilon_{fr}$. This does not make it possible to proceed to the macroscopic gas description (since the small parameter does not appear in the differential part), however, the simplified kinetic equations may be considered. In the zero-order approximation, the operator $J_{cij}^{fr}$ does not appear in Eqs. (1.46) (since slow processes are frozen), whereas in the higher-order approximations, the equations (1.46) are reduced to the linear integral-differential equations containing $J_{cij}^{fr}$ only in the free terms.

As an example, a gas flow within a strong shock wave front may be considered, where the macroscopic parameters vary very rapidly. Methods of non-equilibrium gas dynamics are inapplicable in such a situation, and the kinetic approach is required. However, within a thin layer (the shock wave front), the kinetic equations can be simplified since the characteristic times of vibrational relaxation and chemical reactions may sometimes exceed $\theta$:

$$\tau_{el} \lesssim \tau_{rot} \sim \theta \ll \tau_{vibr} < \tau_{react}.$$

Under this condition, in the zero-order approximation, vibrational relaxation and chemical reactions can be assumed to be frozen in the shock front, and the process of establishing the Maxwell velocity distribution and the Boltzmann distribution over the rotational energy levels dominates. Furthermore, the kinetic equations describing the process at this stage, include the integral operator of only elastic collisions and of those resulting in the rotational energy transitions (the non-linear operator in the zero-order approximation, and the linearized one in the higher order approximations).

In a gas with rapid and slow processes, a situation may occur when the characteristic time of only the part of slow processes $\tau_{sl,1}$ is of the same order of magnitude as $\theta$, whereas the characteristic times of the remaining processes $\tau_{sl,2}$ substantially exceed $\theta$:

$$\tau_{rap} \ll \tau_{sl,1} \sim \theta \ll \tau_{sl,2}. \tag{1.47}$$

Under the condition (1.47), the kinetic equations (1.38) contain two small parameters and take the form

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = \frac{1}{\varepsilon} J_{cij}^{rap} + J_{cij}^{sl,1} + \alpha J_{cij}^{sl,2}.$$

Here, $J_{cij}^{sl,1}, J_{cij}^{sl,2}$ are the collision operators for slow processes with the characteristic times $\tau_{sl,1}$ and $\tau_{sl,2}$, whereas the parameters $\varepsilon$ and $\alpha$ are given by the relations:

$$\varepsilon = \frac{\tau_{rap}}{\tau_{sl,1}} \sim \frac{\tau_{rap}}{\theta} \ll 1, \qquad \alpha = \frac{\theta}{\tau_{sl,2}} \sim \frac{\tau_{sl,1}}{\tau_{sl,2}} \ll 1.$$

While looking for the solution for Eqs. (1.47) as a power series in the small parameters, we obtain Eqs. (1.42) in the zero-order approximation, whereas in the first-order approximation for the power series in the parameter $\varepsilon$, we obtain the equations containing the linearized operator of rapid processes $J_{cij}^{rap}(f^{(0)}, f^{(1)})$. The free terms include the part of the operator of slow processes $J_{cij}^{sl,1}(f^{(0)}, f^{(0)})$ rather than the total operator. The operator $J_{cij}^{sl,2}(f^{(0)}, f^{(0)})$ does not enter into the equations of the first-order approximation in the parameter $\varepsilon$, and, therefore, the processes described by this operator do not affect the macroscopic parameters and flow-dissipative properties in the first-order approximation. This is clear since the condition (1.47) itself means the freezing of most slow processes (with the characteristic time $\tau_{sl,2}$) on the time scale $\theta$.

In order to find the distribution function and the governing equations for the macroscopic parameters in the higher-order approximations, it is necessary to estimate the orders of magnitude for $\varepsilon$ and $\alpha$. In particular, if $\varepsilon$ and $\alpha$ are of the same order, then the slowest processes with the characteristic time $\tau_{\mathrm{sl},2}$ should be taken into account in the second-order approximation (i.e., in the Burnett approximation generalized for gases with rapid and slow processes). Various modifications of the Chapman–Enskog method under the conditions when the kinetic equations include several small parameters, are considered, for instance, in the studies [191, 249, 86, 87, 8].

## 1.4  Modification of the Chapman–Enskog Method for Gases with Rapid and Slow Processes

Let us focus on the main aspects of the Chapman–Enskog method generalized for strongly non-equilibrium gases, in which physical-chemical processes can be divided into rapid and slow, and the characteristic time of slow processes is comparable to the macroscopic time. In this case, the kinetic equations take the form (1.38). The separation of the processes into rapid and slow, as well as the modification of the Chapman–Enskog method make it possible to pass from the kinetic equations to those of the non-equilibrium gas dynamics. Moreover, in contrast to the classical Chapman–Enskog method, the set of governing equations for the macroscopic flow parameters includes, in addition to the conservation equations, the relaxation equations.

The approximate solution of the equations (1.38) is sought as the generalized Chapman–Enskog series in the small parameter $\varepsilon$:

$$f_{cij}(\mathbf{r},\mathbf{u},t) = \sum_r \varepsilon^r f_{cij}^{(r)}(\mathbf{u},\rho_\lambda,\nabla\rho_\lambda,\nabla^2\rho_\lambda,...). \tag{1.48}$$

The spatial and time dependence of the series coefficients $f_{cij}^{(r)}$ is specified by the macroscopic gas parameters $\rho_\lambda(\mathbf{r},t)$, as well as their gradients of all orders: $\nabla\rho_\lambda,\nabla^2\rho_\lambda,....$ It is obvious that the representation of the distribution function in the form (1.48) imposes the restrictions on the values of gradients $\rho_\lambda$.

An important aspect of the method is the choice of the basic macroscopic parameters, for which a closed set of equations of non-equilibrium hydrodynamics and transport can be derived and justified. In the method proposed here, the macroscopic parameters $\rho_\lambda(\mathbf{r},t)$ are selected in accordance with the summational invariants of the most frequent collisions corresponding to rapid processes. In the kinetic theory, the collision invariants are defined as the values satisfying the microscopic conservation laws during collisions. The collision invariants are the independent eigenfunctions of the linearized collision operator corresponding to the zero eigenvalue. The set of collision invariants includes values conserved at any collision, such as the momentum $\psi_{cij}^{(1,2,3)} = m_c u_{cx}, m_c u_{cy}, m_c u_{cz}$ and total energy $\psi_{cij}^{(4)} = m_c u_c^2/2 + \varepsilon_{ij}^c + \varepsilon_c$, as well as the additional invariants of the most frequent collisions $\widetilde{\psi}_{cij}^{(\mu)}$ ($\mu = 1,2,...,M$).

The basic macroscopic parameters are introduced by the formulae

$$\rho_\lambda(\mathbf{r},t) = \sum_{cij} \int \psi_{cij}^{(\lambda)} f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c, \qquad \lambda = 1,2,3,4,$$

$$\widetilde{\rho}_\mu(\mathbf{r},t) = \sum_{cij} \int \widetilde{\psi}_{cij}^{(\mu)} f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c, \qquad \mu = 1,...,M.$$

Taking into account the definitions of the macroscopic parameters given in Section 1.1, one can see that $\rho_\lambda$ ($\lambda = 1,...,4$) are connected to the macroscopic velocity and total specific energy. The functions $\widetilde{\rho}_\mu$ are the additional macroscopic parameters. The governing transport equations for $\rho_\lambda(\mathbf{r},t)$, $\widetilde{\rho}_\mu(\mathbf{r},t)$ follow from the kinetic equations (1.38), after multiplying them by the collision invariants, integrating over the velocity and summing over $c$, $i$, $j$:

$$\frac{\partial \rho_\lambda}{\partial t} + \sum_{cij} \int \psi_{cij}^{(\lambda)} \mathbf{u}_c \cdot \nabla f_{cij}\,d\mathbf{u}_c = 0, \qquad \lambda = 1,2,3,4,$$

$$\frac{\partial \widetilde{\rho}_\mu}{\partial t} + \sum_{cij} \int \widetilde{\psi}_{cij}^{(\mu)} \mathbf{u}_c \cdot \nabla f_{cij}\,d\mathbf{u}_c = \sum_{cij} \int \widetilde{\psi}_{cij}^{(\mu)} J_{cij}^{\mathrm{sl}}\,d\mathbf{u}_c, \qquad \mu = 1,...,M.$$

The first four equations are those for the conservation of the momentum and total specific energy, whereas the equations for $\widetilde{\rho}_\mu$ are the additional relaxation equations:

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \boldsymbol{P} = 0, \tag{1.49}$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \boldsymbol{P} : \nabla \mathbf{v} = 0, \tag{1.50}$$

$$\frac{d\widetilde{\rho}_\mu}{dt} + \widetilde{\rho}_\mu \nabla \cdot \mathbf{v} + \nabla \cdot \widetilde{\mathbf{q}}_\mu = R_\mu, \qquad \mu = 1,...,M, \tag{1.51}$$

where

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u}_c \cdot \nabla.$$

The fluxes of the additional invariants are defined by the relations

$$\widetilde{\mathbf{q}}_\mu = \sum_{cij} \widetilde{\psi}_{cij}^{(\mu)} \int \mathbf{c}_c f_{cij}(\mathbf{r},\mathbf{u},t)\,d\mathbf{u}_c. \tag{1.52}$$

Note that we consider the invariants $\widetilde{\psi}_{cij}^{(\mu)}$ independent of the velocity.

The relaxation terms $R_\mu$ are expressed as functions of the collision operator for slow processes:

$$R_\mu = \sum_{cij} \widetilde{\psi}_{cij}^{(\mu)} \int J_{cij}^{\mathrm{sl}}\,d\mathbf{u}_c.$$

The additional equations (1.51) describe relaxation processes with the rates comparable to that of the macroscopic parameters $\rho_\lambda$ variation (i. e., on the macroscopic time scale $\tau_{sl} \sim \theta$). In a weakly non-equilibrium gas, all inelastic processes display much higher rates than that of the variation of the macroscopic parameters, and therefore can be classified as rapid processes. Furthermore, the set of governing equations for the macroscopic parameters includes only the conservation equations for the mass, momentum and energy (as well as the atomic composition of the reacting gases) and does not contain the additional relaxation equations.

The proposed principle for the choice of the macroscopic parameters provides the closure of the set of equations (1.49)–(1.51) in each approximation, and gives the possibility to express the transport and relaxation terms in these equations as functions of $\rho_\lambda$, $\widetilde{\rho}_\mu$ and their gradients.

Let us consider the distribution functions and governing equations for the macroscopic parameters keeping the zero-order and first-order terms in the series (1.48).

In the zero-order approximation, we have the equations (1.42) for the distribution function $f_{cij}^{(0)}$. The integrals entering into Eq. (1.42), can be written in the symmetrized form. Thus for collisions with bimolecular chemical reactions,

$$
J_{cij}^{2 \rightleftharpoons 2\,(0)} = \sum_{dc'd'} \sum_{ki'k'} \sum_{lj'l'} \int \left( \frac{f_{c'i'j'}^{(0)}}{a_{c'i'j'}} \frac{f_{d'k'l'}^{(0)}}{a_{d'k'l'}} - \frac{f_{cij}^{(0)}}{a_{cij}} \frac{f_{dkl}^{(0)}}{a_{dkl}} \right) \times
$$

$$
\times g\,\sigma_{cd,ijkl}^{c'd',i'j'k'l'}\,a_{cij}a_{dkl}\,d^2\Omega d\mathbf{u}_d, \tag{1.53}
$$

where $a_{cij} = m_c^3 s_{ij}^c$. For elastic collisions, $a_{cij} = 1$, whereas for the inelastic energy exchanges, $a_{cij} = s_{ij}^c$. Collisions with dissociation and recombination are commonly classified as slow processes.

From Eqs. (1.42), (1.53) it follows that the value $\ln f_{cij}^{(0)}/a_{cij}$ is conserved in any collision corresponding to rapid processes, and, therefore, can be expressed as the linear combination of the independent collision invariants of rapid processes. As a result, we obtain

$$
f_{cij}^{(0)} = a_{cij} \exp \left( - \sum_{\lambda=1}^{4} \beta_\lambda \psi_{cij}^{(\lambda)} - \sum_{\mu=1}^{M} \widetilde{\beta}_\mu \widetilde{\psi}_{cij}^{(\mu)} \right). \tag{1.54}
$$

The parameters $\beta_\lambda$, $\widetilde{\beta}_\mu$ are specified by $\rho_\lambda(\mathbf{r},t)$, $\widetilde{\rho}_\mu(\mathbf{r},t)$ and are found from the conditions of normalization:

$$
\sum_{cij} \int \psi_{cij}^{(\lambda)} f_{cij}^{(0)} \, d\mathbf{u}_c = \rho_\lambda, \qquad \lambda = 1,...,4, \tag{1.55}
$$

$$
\sum_{cij} \int \psi_{cij}^{(\lambda)} f_{cij}^{(r)} \, d\mathbf{u}_c = 0, \qquad r \geq 1, \qquad \lambda = 1,...,4, \tag{1.56}
$$

$$\sum_{cij} \int \widetilde{\psi}_{cij}^{(\mu)} f_{cij}^{(0)} \, d\mathbf{u}_c = \widetilde{\rho}_\mu, \qquad \mu = 1, ..., M, \tag{1.57}$$

$$\sum_{cij} \int \widetilde{\psi}_{cij}^{(\mu)} f_{cij}^{(r)} \, d\mathbf{u}_c = 0, \qquad r \geq 1, \qquad \mu = 1, ..., M. \tag{1.58}$$

Let us emphasize two important features of the normalizing conditions for the distribution functions in the Chapman–Enskog method generalized for the case of rapid and slow processes. First, the distribution function is normalized to the macroscopic parameters associated with the collision invariants of the most frequent collisions. Second, similarly to the classical Chapman–Enskog method, already the zero-order distribution function provides the full macroscopic parameters, whereas the higher-order distribution function approximations do not contribute to the values of the basic macroscopic parameters. It is, however, clear that the equations for the macroscopic parameters are different for various approximations.

The gas temperature definition is also connected to the conditions of normalization. In a gas with rapid and slow processes, the temperature is specified by the energy conserved in rapid processes. This feature is discussed in following Chapters while considering various non-equilibrium conditions. Thus, in the state-to-state approach, $T$ is specified by the energy of translational and rotational degrees of freedom, in the quasi-stationary models for slow chemical reactions, the temperature is determined by the total energy of translational and internal modes, whereas in a near-equilibrium reacting gas it is given by the overall internal energy including that of formation.

Taking into account the conditions (1.55), (1.57), after some transformations (see, for instance, [82]), we can represent the distribution function (1.54) as a product of the Maxwell–Boltzmann velocity and energy distribution for rapidly relaxing internal modes, and a factor taking into account non-equilibrium effects. For such a function, only a part of the collision operator turns into zero.

Substituting the distribution function $f_{cij}^{(0)}$ into the definitions (1.13), (1.14), and (1.52) of the transport terms, we can show that in the zero-order approximation, the stress tensor takes the diagonal form, whereas the vectors $\mathbf{q}$ and $\widetilde{\mathbf{q}}_\mu$ are equal to zero:

$$\boldsymbol{P}^{(0)} = nkT\boldsymbol{I} = p\boldsymbol{I}, \qquad \mathbf{q}^{(0)} = 0, \qquad \widetilde{\mathbf{q}}_\mu^{(0)} = 0 \;\; \forall \mu. \tag{1.59}$$

Here, $\boldsymbol{I}$ is the unity tensor. The expression for the pressure $p = nkT$ coincides with the ideal gas state equation (1.20).

The set of governing equations for the macroscopic parameters in the zero-order approximation describes an inviscid non-conducting relaxing gas flow, and taking into account Eq. (1.59), it can be written in the form

$$\rho \frac{d\mathbf{v}}{dt} + \nabla p = 0, \tag{1.60}$$

$$\rho \frac{dU}{dt} + p \nabla \cdot \mathbf{v} = 0, \tag{1.61}$$

$$\frac{d\widetilde{\rho}_\mu}{dt} + \widetilde{\rho}_\mu \nabla \cdot \mathbf{v} = R_\mu^{(0)}, \qquad \mu = 1, ..., M. \tag{1.62}$$

In the zero-order approximation, the right-hand sides $R_\mu$ of the relaxation equations are given by the relations

$$R_\mu^{(0)} = \sum_{cij} \widetilde{\psi}_{cij}^{(\mu)} \int J_{cij}^{\mathrm{sl}\,(0)} \, d\mathbf{u}_c.$$

The operator $J_{cij}^{\mathrm{sl}\,(0)}$ is specified by the expressions (1.40), (1.41).

In the higher-order approximations, for $r \geq 1$, the equations (1.38) turn into the linear integral equations for $f_{cij}^{(r)}$. These equations include the linearized collision operator for rapid processes $J_{cij}^{\mathrm{rap}}$. The operator for slow processes $J_{cij}^{\mathrm{sl}}$ appears only in the free terms of the integral equations (with the distribution functions known from the previous approximations). The functions $f_{cij}^{(r)}$ at $r \geq 1$ satisfy the normalizing conditions of the generalized Chapman–Enskog method (1.56), (1.58).

Let us consider the first-order distribution function:

$$f_{cij} = f_{cij}^{(0)} + f_{cij}^{(1)}, \qquad f_{cij}^{(1)} = f_{cij}^{(0)} \varphi_{cij}. \tag{1.63}$$

The first-order correction $\varphi_{cij}$ in Eq. (1.63) includes the small parameter $\varepsilon$ and is found from the equations

$$J_{cij}^{\mathrm{rap}}(\varphi) = -J_{cij}^{\mathrm{sl}\,(0)} + D f_{cij}^{(0)}. \tag{1.64}$$

Here,

$$D f_{cij}^{(0)} = \frac{\partial f_{cij}^{(0)}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij}^{(0)},$$

and $J_{cij}(\varphi)$ is the linearized (with the zero-order distribution function) operator of the most frequent collisions

$$J_{cij}^{\mathrm{rap}}(\varphi) = J_{cij}^{\mathrm{rap}}\left( f^{(0)}, f^{(0)} \varphi \right).$$

Switching from $\mathbf{u}_c$ to the peculiar velocity $\mathbf{c}_c$, we obtain

$$D f_{cij}^{(0)} = f_{cij}^{(0)}(\mathbf{r}, \mathbf{c}, t) \left( \frac{d \ln f_{cij}^{(0)}(\mathbf{r}, \mathbf{c}, t)}{dt} + \mathbf{c}_c \cdot \nabla \ln f_{cij}^{(0)}(\mathbf{r}, \mathbf{c}, t) - \right.$$

$$\left. - \frac{d\mathbf{v}}{dt} \cdot \nabla_{\mathbf{c}_c} \ln f_{cij}^{(0)}(\mathbf{r}, \mathbf{c}, t) - \left( \nabla_{\mathbf{c}_c} \ln f_{cij}^{(0)}(\mathbf{r}, \mathbf{c}, t) \right) \mathbf{c}_c : \nabla \mathbf{v} \right). \tag{1.65}$$

Here, the operator $\nabla_{\mathbf{c}_c}$ supposes differentiation with respect to the peculiar velocity $\mathbf{c}_c$: $\nabla_{\mathbf{c}_c} = \partial/\partial \mathbf{c}_c$. A characteristic feature of Eqs. (1.64) is that they include only the integral operator for rapid processes, whereas the operator for slow processes in the zero-order approximation $J_{cij}^{\mathrm{sl}\,(0)}$ appears in the free terms. Substituting $f_{cij}^{(0)}(\mathbf{r}, \mathbf{c}, t)$ into (1.65) and expressing the time derivatives of the macroscopic

parameters in terms of the spatial derivatives using the zero-order governing equations (1.60)–(1.62), we can obtain, after some transformation of Eqs. (1.64), the structural form of their solution:

$$\varphi_{cij} = -\mathbf{A}_{cij} \cdot \nabla \ln T - \boldsymbol{B}_{cij} : \nabla \mathbf{v} - F_{cij} \nabla \cdot \mathbf{v} - \sum_{\mu} \mathbf{X}_{cij}^{(\mu)} \cdot \nabla \ln \widetilde{\rho}_{\mu} - G_{cij}, \qquad (1.66)$$

where the functions $\mathbf{A}_{cij}$, $\boldsymbol{B}_{cij}$, $F_{cij}$, $\mathbf{X}_{cij}^{(\mu)}$, and $G_{cij}$ depend on the peculiar velocity and are found from the linear integral equations containing the linearized operator for the most frequent collisions.

Substituting the functions (1.63), (1.66) into the formulae for the transport and production terms appearing in Eqs. (1.49)–(1.51), we obtain the expressions for the stress tensor, heat flux, fluxes $\widetilde{\mathbf{q}}_{\mu}$, and relaxation terms $R_{\mu}$ in the first-order approximation. The expression for the stress tensor takes the form:

$$\boldsymbol{P}^{(1)} = (p - p_{\text{rel}})\boldsymbol{I} - 2\eta \boldsymbol{S} - \zeta \nabla \cdot \mathbf{v}\boldsymbol{I}. \qquad (1.67)$$

Here, $\boldsymbol{S}$ is the deformation rate tensor, $\eta$, $\zeta$ are the coefficients of shear and bulk viscosity, and $p_{\text{rel}}$ is the relaxation pressure .

Note that in Eq. (1.67), for the sake of convenience, the small parameter $\varepsilon$ is included into the expressions for $p_{\text{rel}}$ and viscosity coefficients. The transport coefficients, as well as the relaxation pressure are specified by the functions $\boldsymbol{B}_{cij}$, $F_{cij}$, and $G_{cij}$, which are found from the integral equations. Methods for the solution of these equations are discussed in Chapter 5 for various ways to divide processes into rapid and slow.

Additional terms in the diagonal elements of the stress tensor, containing the bulk viscosity and relaxation pressure, arise as a direct consequence of the non-equilibrium. The bulk viscosity exists under the conditions of both weak and strong deviations from the equilibrium. The bulk viscosity coefficient $\zeta$ turns to zero if all non-equilibrium processes occur on the gas-dynamic time scale $\theta$; the coefficient $\zeta$ differs from zero if at least one inelastic non-resonant process displays the rate exceeding that of the variations of macroscopic parameters (i.e. the process is rapid). In other words, the bulk viscosity appears in the case when among the rapid processes, there is a non-resonant exchange of the translational and internal energy, and disappears if the systems of translational and internal degrees of freedom are isolated. The relaxation pressure arises as a consequence of slow inelastic processes on the gas-dynamic time scale. The value $p_{\text{rel}}$ differs from zero, if both rapid and slow inelastic processes occur in the gas. The relaxation pressure turns to zero if all inelastic processes are rapid, or all inelastic processes proceed on the gas-dynamic time scale whereas the rapid processes include only elastic collisions.

The nature of bulk viscosity (the viscosity of volume expansion both in dense and rarefied gases with internal degrees of freedom) was discussed previously in the studies [162, 124, 82, 114, 183, 73, 74, 77]. It is interesting to mention, that in some papers, absolutely contradictory points of view are asserted [184]. In the

monograph [82], the effect of bulk viscosity is illustrated by the example of fast compression of an elementary gas volume. In this case, due to the difference between the relaxation times, all the energy transmitted into a system goes first to the translational mode, and is later redistributed between the internal degrees of freedom. Consequently, the hydrostatic pressure specified only by the translational motion of particles, at the beginning appears to be higher than it could be in the case of instantaneous exchange of the translational and internal energy. Thus the effect of bulk viscosity is similar to the excessive hydrostatic pressure in a compressed gas ($\nabla \cdot \mathbf{v} < 0$) and the reduced pressure in an expanding gas ($\nabla \cdot \mathbf{v} > 0$). Some experimental data on the bulk viscosity are given in Refs. [218, 108], the results of theoretical calculations can be found in the studies [194, 213, 139].

The effect of the relaxation pressure was mentioned for the first time in the study of L. I. Mandelshtam and M. A. Leontovich [175], and later on, in Refs. [124, 162, 249, 129]. This effect manifests itself as the decrease of the excessive pressure, caused by the rapid gas compression, due to slow inelastic processes. Calculations of $p_{\mathrm{rel}}$ in a diatomic gas [37, 36] demonstrated that it is much smaller than the hydrostatic pressure. It can be explained by low values of the cross sections for slow inelastic processes which specify the relaxation pressure.

The expressions for the heat flux $\mathbf{q}$ and additional fluxes $\widetilde{\mathbf{q}}_\mu$ include the gradients of temperature and macroscopic parameters $\widetilde{\rho}_\mu$:

$$\mathbf{q}^{(1)} = -\lambda_t \nabla T - \sum_\mu \lambda_\mu \nabla \widetilde{\rho}_\mu, \tag{1.68}$$

$$\widetilde{\mathbf{q}}_\mu^{(1)} = -\lambda_t^\mu \nabla T - \sum_\nu \lambda_\mu^\nu \nabla \widetilde{\rho}_\mu, \tag{1.69}$$

$\lambda_t$ is the thermal conductivity coefficient. The expression for the heat flux (1.68) depends not only on the temperature gradient but also on the gradients of the macroscopic parameters $\widetilde{\rho}_\mu$ with the corresponding coefficients $\lambda_\mu$. In Eq. (1.69), $\lambda_t^\mu$ and $\lambda_\mu^\nu$ are the additional coefficients describing the transport of the macroscopic property $\widetilde{\rho}_\mu$. These coefficients, in the same way as in the case of the viscosity coefficients, are found from the integral equations containing the linearized operator for the most frequent collisions. Similarly to Eq. (1.67), in the relations (1.68) and (1.69), the small parameter $\varepsilon$ is included into the transport coefficients.

Thus the existence of rapid and slow processes in a real gas flow and, respectively, the appearance of the additional collision invariants for rapid processes lead to the deformation of the distribution function already in the zero-order approximation of the generalized Chapman-Enskog method, as well as to the occurrence of additional relaxation equations in the system of governing equations. The stress tensor contains in the diagonal elements the bulk viscosity coefficient and relaxation pressure, whereas the heat flux is specified by the gradients of both gas temperature and additional macroscopic parameters. It is important to emphasize that in order to calculate the transport coefficients in a gas with rapid and slow

processes, one should solve the linear integral equations containing the integral operator of only rapid processes. As is already mentioned, in a weakly non-equilibrium gas, the rates for all internal energy transitions and chemical reactions substantially exceed that of the variation of macroscopic parameters (see the condition (1.35)), therefore, the additional invariants of rapid processes and the macroscopic parameters associated with them are absent. Furthermore, the expression for the heat flux contains only one thermal conductivity coefficient which includes the corrections connected to inelastic processes. These corrections as well as the bulk viscosity coefficient are specified by the cross sections of all processes occurring in the mixture. The relaxation pressure in a weakly non-equilibrium gas is equal to zero.

# Chapter 2
# State-to-State Approach

In this chapter, multi-component reacting gas mixture flows are studied under the conditions of strong vibrational and chemical non-equilibrium. For such flows, the zero-order and first-order distribution functions are derived in the frame of the modified Chapman–Enskog method. A set of macroscopic equations is obtained including the conservation equations coupled to the equations for the vibrational level populations and number densities of atomic species. The proposed approach makes it possible to develop the most detailed model of physical gas dynamics taking into account state-to-state vibrational and chemical kinetics. On the basis of the first-order distribution function, the kinetic theory of transport processes accounting for detailed non-equilibrium kinetics is established, and the features of dissipative processes under the conditions of strong deviations from the thermal and chemical equilibrium are discussed.

## 2.1  Zero-Order Distribution Function

Experimental results on the relaxation times of various processes demonstrate that, in a wide temperature range, the equilibration of translational and vibrational degrees of freedom proceeds much faster compared to the vibrational relaxation and chemical reactions. The characteristic relaxation times satisfy the relation (1.43). Under such conditions, the kinetic equations for the distribution functions take the form (1.38), where the integral operator of rapid processes $J_{cij}^{\mathrm{rap}}$ describes elastic collisions and rotational energy exchange:

$$J_{cij}^{\mathrm{rap}} = J_{cij}^{\mathrm{el}} + J_{cij}^{\mathrm{rot}}, \tag{2.1}$$

whereas the integral operator of slow processes $J_{cij}^{\mathrm{sl}}$ depends on the cross sections of vibrational energy exchange and chemical reactions:

$$J_{cij}^{\mathrm{sl}} = J_{cij}^{\mathrm{vibr}} + J_{cij}^{\mathrm{react}}. \tag{2.2}$$

The parameter $\varepsilon$ in Eqs. (1.38) represents the ratio of the characteristic times: $\varepsilon = \tau_{rap}/\tau_{sl}$, $\tau_{rap} \sim \tau_{el\text{-}rot}$, $\tau_{sl} \sim \theta$.

In order to solve the kinetic equations (1.38) with the integral operators (2.1), (2.2), we apply the Chapman–Enskog method modified for non-equilibrium gas flows with rapid and slow processes. Basic ideas of the method are given in 1.4. The modification of the Chapman–Enskog procedure for the conditions (1.43) was proposed in [60, 145], where the distribution functions and governing equations were derived in the zero- and first-order approximations, the expressions for the transport and relaxation terms were obtained, and the algorithm for the calculation of the transport coefficients was developed. The distribution function is expanded into the series (1.48) in the small parameter $\varepsilon$.

Let us consider the solution of the kinetic equations for the distribution functions in the zero-order approximation:

$$J_{cij}^{el(0)} + J_{cij}^{rot(0)} = 0. \tag{2.3}$$

As is demonstrated in the previous chapter, the zero-order solution is specified by the independent collision invariants of the most frequent collisions. First of all, in any collision, the momentum and particle total energy are conserved:

$$\psi_{cij}^{(v)} = m_c u_{cv}, \quad v = 1,2,3, \qquad \psi_{cij}^{(4)} = \frac{m_c u_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon_c.$$

Moreover, the additional invariants of the most frequent collisions are given by any value independent of the velocity and rotational level $j$ and depending arbitrarily on the vibrational level $i$ and chemical species $c$:

$$\psi_{cij}^{(\mu+4)} = a_{ci}, \quad c = 1,...,L, \quad i = 0,...,L_c, \quad \mu = 1,...,N,$$

where $N = \sum_{c=1}^{L_m} L_c$, $L$ is the number of chemical species, $L_m$ is the number of molecular species, and $L_c$ is the number of vibrationally excited levels for the chemical species $c$. These additional invariants appear due to the fact that vibrational energy exchange and chemical reactions are supposed to be frozen in rapid processes. Since along with the total energy, the sum of translational and rotational energy of interacting particles is also conserved in the most frequent collisions, the value

$$\psi_{cij}^{(4)} = m_c u_c^2/2 + \varepsilon_j^{ci}$$

can also be chosen as the invariant $\psi_{cij}^{(4)}$.

Based on the above set of the collision invariants, the solution of Eqs. (2.3) takes the form

$$f_{cij}^{(0)} = \left(\frac{m_c}{2\pi kT}\right)^{3/2} s_j^{ci} \frac{n_{ci}}{Z_{ci}^{rot}(T)} \exp\left(-\frac{m_c c_c^2}{2kT} - \frac{\varepsilon_j^{ci}}{kT}\right) \tag{2.4}$$

for molecular species, and

$$f_c^{(0)} = \left(\frac{m_c}{2\pi kT}\right)^{3/2} n_{c,\mathrm{a}} \exp\left(-\frac{m_c c_c^2}{2kT}\right) \tag{2.5}$$

for atomic species. Here, $n_{c,\mathrm{a}}$ is the number density of atoms $c$. The normalizing factors in Eqs. (2.4), (2.5) are calculated using the partition functions of translational $Z_c^{\mathrm{tr}}$ and rotational $Z_{ci}^{\mathrm{rot}}$ degrees of freedom defined in the statistical thermodynamics in the form

$$Z_c^{\mathrm{tr}}(T) = (2\pi kTm_c)^{3/2}\frac{V}{h^3},$$

where $V$ is the gas volume, and

$$Z_{ci}^{\mathrm{rot}}(T) = \sum_j s_j^{ci} \exp\left(-\frac{\varepsilon_j^{ci}}{kT}\right). \tag{2.6}$$

For diatomic molecules simulated by the rigid rotator model, the rotational energy given by the formula (2.6) does not depend on the vibrational level, and, therefore, the rotational partition function can be calculated using the simple expression

$$Z_{ci}^{\mathrm{rot}} = Z_c^{\mathrm{rot}} = \frac{8\pi^2 I_c kT}{\sigma h^2}, \tag{2.7}$$

where $\sigma$ denotes the symmetry factor, $\sigma = 2$ for homonuclear molecules, and $\sigma = 1$ for heteronuclear molecules.

The solution (2.4) represents the local equilibrium Maxwell–Boltzmann distribution over the velocity and rotational energy levels with the temperature $T$ and strongly non-equilibrium distribution over chemical species and vibrational energy levels. For atomic species, the solution (2.5) is the Maxwell distribution over the velocity and non-equilibrium distribution over chemical species. The distribution functions (2.4), (2.5) are completely specified by the macroscopic gas parameters $n_{ci}(\mathbf{r},t)$ $(c = 1,...,L, i = 0,1,...,L_c)$, $T(\mathbf{r},t)$, and $\mathbf{v}(\mathbf{r},t)$. These macroscopic parameters correspond to the set of the collision invariants of rapid processes.

The distribution functions satisfy the following conditions of normalization:

$$\sum_j \int f_{cij}^{(0)} d\mathbf{u}_c = n_{ci}, \quad c = 1,2,...,L, \ i = 0,...,L_c, \tag{2.8}$$

$$\sum_j \int f_{cij}^{(r)} d\mathbf{u}_c = 0, \quad r \geq 1, \quad c = 1,2,...,L, \ i = 0,1,...,L_c \tag{2.9}$$

(for atomic species, $n_{ci}$ is replaced with $n_{c,\mathrm{a}}$, the summation over $j$ in Eqs. (2.8), (2.9) is omitted, and the distribution function does not depend on $i$ and $j$. In these expressions and hereafter, the summation over $c$ means the summation over all molecular and atomic species),

$$\sum_{cij} m_c \int \mathbf{u}_c f_{cij}^{(0)} d\mathbf{u}_c = \rho \mathbf{v}, \tag{2.10}$$

$$\sum_{cij} m_c \int \mathbf{u}_c f_{cij}^{(r)} d\mathbf{u}_c = 0, \qquad r \geq 1, \tag{2.11}$$

$$\sum_{cij} \int \left( \frac{m_c c_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon_c \right) f_{cij}^{(0)} d\mathbf{u}_c = \frac{3}{2} nkT + \rho E_{\text{rot}} + \rho E_{\text{vibr}} + \rho E_{\text{f}}, \tag{2.12}$$

$$\sum_{cij} \int \left( \frac{m_c c_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon_c \right) f_{cij}^{(r)} d\mathbf{u}_c = 0, \qquad r \geq 1. \tag{2.13}$$

It is obvious that taking into account the definitions of the mean vibrational and formation energy (1.9), (1.10), as well as the relations (2.8), (2.9), we can rewrite the conditions (2.12) and (2.13) as follows:

$$\sum_{cij} \int \left( \frac{m_c c_c^2}{2} + \varepsilon_j^{ci} \right) f_{cij}^{(0)} d\mathbf{u}_c = \frac{3}{2} nkT + \rho E_{\text{rot}}, \tag{2.14}$$

$$\sum_{cij} \int \left( \frac{m_c c_c^2}{2} + \varepsilon_j^{ci} \right) f_{cij}^{(r)} d\mathbf{u}_c = 0, \qquad r \geq 1. \tag{2.15}$$

In the equations (2.12), (2.14) it is taken into account that the equilibrium translational energy per unit volume is defined as $\rho E_{\text{tr}} = \frac{3}{2} nkT$, whereas the rotational energy is given by

$$\rho E_{\text{rot}} = \sum_{c=1}^{L_{\text{m}}} \rho_c E_{\text{rot},c}(T).$$

For the majority of gas mixtures, at temperatures higher than the room temperature,

$$\rho_c E_{\text{rot},c}(T) = n_c kT.$$

The vibrational energy is expressed by

$$\rho E_{\text{vibr}} = \sum_{c=1}^{L_{\text{m}}} \sum_{i=0}^{L_c} \varepsilon_i^c n_{ci}.$$

The normalizing condition (2.14) makes it possible to introduce a single temperature of the translational and rotational degrees of freedom. Moreover, it is consistent with the well known rule of thermodynamics about the energy equipartition between thermal equilibrium modes. It is seen from Eq. (2.14) that the energy of translational and rotational degrees of freedom specifies the gas temperature in the present case.

The normalizing conditions (2.8)–(2.13) completely specify the macroscopic gas parameters (molecular vibrational level populations, atomic number densities, gas velocity, and temperature) in terms of the zero-order distribution functions. The higher order distribution functions do not contribute to the macroscopic parameters, this constitutes an important feature of the Chapman–Enskog formalism.

## 2.2   Closed Set of Governing Equations

The set of equations for the macroscopic parameters $n_{ci}(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$, and $T(\mathbf{r},t)$ is derived from Eq. (1.38). Integrating Eq. (1.38) over the velocity and summing over the rotational levels we obtain the equations for variables $n_{ci}(\mathbf{r},t)$, which correspond to the vibrational level populations for molecular species and atomic number densities for atomic components. Multiplying Eq. (1.38) by the collision invariants $\psi_{cij}^{(1,2,3)}$ and $\psi_{cij}^{(4)}$, integrating over the velocity and summing over the rotational and vibrational states, we obtain the conservation equations of the momentum and total energy. Finally, the set of governing equations for the macroscopic parameters $n_{ci}(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$, and $T(\mathbf{r},t)$ is found in the form:

$$\frac{dn_{ci}}{dt} + n_{ci}\nabla\cdot\mathbf{v} + \nabla\cdot(n_{ci}\mathbf{V}_{ci}) = R_{ci}, \tag{2.16}$$

$$c = 1,...,L, \ \ i = 0,...,L_c,$$

$$\rho\frac{d\mathbf{v}}{dt} + \nabla\cdot\boldsymbol{P} = 0, \tag{2.17}$$

$$\rho\frac{dU}{dt} + \nabla\cdot\mathbf{q} + \boldsymbol{P}:\nabla\mathbf{v} = 0. \tag{2.18}$$

In accordance with the relations (2.12), (2.14), the total energy per unit mass $U$ is specified by the zero-order distribution function:

$$\rho U = \frac{3}{2}nkT + \rho E_{\rm rot} + \sum_{ci}\varepsilon_i^c n_{ci} + \sum_c \varepsilon_c n_c.$$

The transport terms in Eqs. (2.16)–(2.18) are given by the formulae (1.12)–(1.14). In contrast to the macroscopic parameters, the transport terms in each approximation of the Chapman–Enskog method are specified by the corresponding distribution function.

The equations (2.16) describe non-equilibrium vibrational and chemical kinetics in a gas flow. The source terms in these equations are expressed via the integral operators of slow processes proceeding on the gas-dynamic time scale:

$$R_{ci} = \sum_j \int J_{cij}^{\rm sl} d\,\mathbf{u}_c = R_{ci}^{\rm vibr} + R_{ci}^{\rm react}. \tag{2.19}$$

The production terms $R_{ci}$ characterize the variation of the vibrational level populations and atomic number densities caused by different vibrational energy exchanges and chemical reactions. The expressions for $R_{ci}$ in the zero-order and first-order approximations, as well as the transport terms are considered below in the present Chapter.

The equations (2.16)–(2.18) provide a detailed description of vibrational and chemical kinetics and flow dynamics for weak deviations from the equilibrium distributions over the velocity and rotational energy levels and arbitrary deviations from the equilibrium for the vibrational degrees of freedom and chemical species. Let us

emphasize that for such an approach, the vibrational level populations are included to the set of main macroscopic parameters, and the equations for their calculation are coupled to the equations of gas dynamics. Particles of various chemical species in different vibrational states represent the mixture components, and the corresponding equations contain the diffusion velocities $\mathbf{V}_{ci}$ of molecules at different vibrational states.

The Chapman–Enskog method generalized for the conditions (1.43) gives the possibility to express, in any approximation, the transport and relaxation terms in Eqs. (2.16)–(2.18) as functions of the main macroscopic parameters $n_{ci}(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$, and $T(\mathbf{r},t)$ and thus to close completely the set of governing equations.

In the zero-order approximation (2.4), (2.5),

$$\boldsymbol{P}^{(0)} = nkT\boldsymbol{I}, \qquad \mathbf{q}^{(0)} = 0, \qquad \mathbf{V}_{ci}^{(0)} = 0 \quad \forall\, c,i, \tag{2.20}$$

and the set of governing equations takes the form

$$\frac{dn_{ci}}{dt} + n_{ci}\nabla\cdot\mathbf{v} = R_{ci}^{(0)}, \tag{2.21}$$

$$c = 1,...,L, \ \ i = 0,...,L_c,$$

$$\rho\frac{d\mathbf{v}}{dt} + \nabla p = 0, \tag{2.22}$$

$$\rho\frac{dU}{dt} + p\nabla\cdot\mathbf{v} = 0. \tag{2.23}$$

The right-hand sides of Eqs. (2.21) $R_{ci}^{(0)}$ are specified by the zero-order distribution function:

$$R_{ci}^{(0)} = \sum_j \int \left( J_{cij}^{\text{vibr}(0)} + J_{cij}^{\text{react}(0)} \right) d\,\mathbf{u}_c.$$

The expressions for $R_{ci}^{(0)}$ contain the microscopic rate coefficients for vibrational energy exchanges and chemical reactions averaged with the Maxwell–Boltzmann distribution over the velocity and rotational energy levels and depending on the vibrational states and chemical species of interacting particles. The definition of these coefficients is given in Section 2.5, and the algorithms for their calculation are discussed in Chapter 6.

The equations (2.21)–(2.23) describe detailed state-to-state vibrational and chemical kinetics in an inviscid non-conductive gas mixture flow in the Euler approximation.

The study of state-to-state vibrational kinetics started in the 50-ies on the basis of the phenomenological master equations for the vibrational level populations. In the paper of Montrol and Shuler [190], a single-component spatially homogeneous gas was considered, molecular spectra were simulated using the harmonic oscillator model. Under such assumptions, for an isolated system of diatomic molecules, and also in the case of small admixture of a diatomic gas in a noble gas, the exact analytical solutions of the equations for the vibrational level populations were obtained under various initial conditions. Based on these solutions, for a system

of harmonic oscillators the property of canonical invariance was proved. It consists in the conservation, during the relaxation process, of the initial form of the Boltzmann distribution over the vibrational levels with the vibrational temperature $T_v$ different from the gas temperature. This result gave a possibility to justify the transition from the equations for the vibrational level populations to a single equation for the vibrational temperature in a spatially homogeneous gas of harmonic oscillators. Much later, only in the 80-ies, the investigation of state-to-state vibrational and then chemical kinetics in specific gas flows was started, in particular, behind shock waves [128, 97, 2, 169, 192, 251, 141, 147], in a boundary layer [174, 15, 14, 48, 16], in the vicinity of the stagnation point of a blunt body [202, 45], in nozzles [225, 233, 65, 62, 64, 151], in electrical discharges [103, 47], in optically pumped systems [68, 84, 256, 214, 215]. Such a detailed approach makes it possible not only to find the distributions of particles over the vibrational and chemical species strongly deviating from the equilibrium, but also to estimate their influence on the gas-dynamic parameters and dissipative flow properties, in particular, on such important functions as the temperature and energy fluxes. Some results obtained by the application of the state-to-state approach to the specific reacting gas flows, as well as the comparison with the results found on the basis of simpler models are discussed in Chapters 7–9.

## 2.3 First-Order Distribution Function

Let us consider the linear integral equations for the distribution function in the first-order approximation of the modified Chapman–Enskog method: $f_{cij}^{(1)} = f_{cij}^{(0)} \varphi_{cij}$. These equations follow from the kinetic equations (1.38) and (1.64). In the equation (1.64), the linearized operator of the most frequent collisions can be written in the form similar to that introduced in [82] for non-reacting mixtures and in [60] for a gas mixture with chemical reactions:

$$J_{cij}^{\text{rap}}(\varphi) = -\sum_{dk} n_{ci} n_{dk} I_{cijdk}(\varphi).$$

Here,

$$I_{cijdk}(\varphi) = \frac{1}{n_{ci} n_{dk}} \sum_{l j' l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} \left( \varphi_{cij} + \varphi_{dkl} - \varphi_{cij'} - \varphi_{dkl'} \right) \times$$

$$\times g \sigma_{cd, ijkl}^{j' l'} d^2 \Omega \, d\mathbf{u}_d, \tag{2.24}$$

where $\sigma_{cd, ijkl}^{j' l'}$ is the differential cross section of elastic collisions (for $j = j'$ and $l = l'$) and collisions leading to the rotational energy exchange. Then the equation for the first-order correction $\varphi_{cij}$ can be obtained in the form

$$-\sum_{dk} n_{ci} n_{dk} I_{cijdk}(\varphi) = D f_{cij}^{(0)} - J_{cij}^{\text{sl}(0)}. \tag{2.25}$$

The expression for $Df_{cij}^{(0)}$ in Eq. (2.25) is found after the differentiation of the zero-order distribution functions (2.4), (2.5) and taking into account the zero-order governing equations (2.21)–(2.23):

$$
Df_{cij}^{(0)} = f_{cij}^{(0)} \left\{ \left( \frac{m_c c_c^2}{2kT} - \frac{5}{2} + \frac{\varepsilon_j^{ci} - \langle \varepsilon^{ci} \rangle_{\mathrm{rot}}}{kT} \right) \mathbf{c}_c \cdot \nabla \ln T + \right.
$$

$$
+ \frac{n}{n_{ci}} \mathbf{c}_c \cdot \mathbf{d}_{ci} + \frac{m_c}{kT} \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I} \right) : \nabla \mathbf{v} + \frac{R_{ci}^{(0)}}{n_{ci}} +
$$

$$
+ \left[ \frac{m_c c_c^2}{3kT} - 1 - \frac{p}{\rho T (c_{\mathrm{tr}} + c_{\mathrm{rot}})} \left( \frac{m_c c_c^2}{2kT} - \frac{3}{2} + \frac{\varepsilon_j^{ci} - \langle \varepsilon^{ci} \rangle_{\mathrm{rot}}}{kT} \right) \right] \nabla \cdot \mathbf{v} -
$$

$$
\left. - \frac{\sum_{ci} R_{ci}^{(0)} \left( \frac{3}{2} kT + \langle \varepsilon_j^{ci} \rangle_{\mathrm{rot}} + \varepsilon_i^c + \varepsilon_c \right)}{\rho T (c_{\mathrm{tr}} + c_{\mathrm{rot}})} \left( \frac{m_c c_c^2}{2kT} - \frac{3}{2} + \frac{\varepsilon_j^{ci} - \langle \varepsilon^{ci} \rangle_{\mathrm{rot}}}{kT} \right) \right\}.
$$

$$
(2.26)
$$

Here, $\mathbf{d}_{ci}$ is the diffusive driving force for molecules of $c$ chemical species at the vibrational level $i$:

$$
\mathbf{d}_{ci} = \nabla \left( \frac{n_{ci}}{n} \right) + \left( \frac{n_{ci}}{n} - \frac{\rho_{ci}}{\rho} \right) \nabla \ln p. \tag{2.27}
$$

One should keep in mind that $n_{ci} = n_{c,\mathrm{a}}$ for atomic species. The specific heats of translational and rotational degrees of freedom $c_{\mathrm{tr}}$ and $c_{\mathrm{rot}}$ are given by the expressions (1.23), (1.22). The mean rotational energy $\langle \varepsilon^{ci} \rangle_{\mathrm{rot}}$ appearing in Eq. (2.26) is defined as

$$
\langle \varepsilon^{ci} \rangle_{\mathrm{rot}} = \frac{1}{Z_{ci}^{\mathrm{rot}}} \sum_j s_j^{ci} \varepsilon_j^{ci} \exp \left( - \frac{\varepsilon_j^{ci}}{kT} \right) \tag{2.28}
$$

and is associated with the specific rotational energy of $c$ molecular species at the vibrational state $i$:

$$
\langle \varepsilon^{ci} \rangle_{\mathrm{rot}} = m_c E_{\mathrm{rot},ci}. \tag{2.29}
$$

Analyzing the expression (2.26) for the differential part of Eq. (2.25), we can represent its solutions in the following structural form:

$$
f_{cij}^{(1)} = f_{cij}^{(0)} \left( - \frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_{dk} \mathbf{D}_{cij}^{dk} \cdot \mathbf{d}_{dk} - \frac{1}{n} \mathbf{B}_{cij} : \nabla \mathbf{v} - \right.
$$

$$
\left. - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right). \tag{2.30}
$$

The first-order distribution function $f_{cij}^{(1)}$ depends on the derivatives of all macroscopic parameters: temperature $T$, velocity $\mathbf{v}$, vibrational level populations $n_{ci}$, and

atomic number densities $n_{c,a}$ which appear in the expression (2.27) for the diffusive driving force $\mathbf{d}_{ci}$. The free term $G_{cij}$ in Eq. (2.30) is connected to the slow relaxation processes: non-equilibrium chemical reactions and vibrational energy exchange.

The functions $\mathbf{A}_{cij}$ and $\mathbf{D}_{cij}^{dk}$ are vector functions of the peculiar velocity $\mathbf{c}_c$, the functions $\boldsymbol{B}_{cij}$ are tensor functions of $\mathbf{c}_c$, and $F_{cij}$ and $G_{cij}$ are scalar functions. All these functions depend also on the flow parameters, and, therefore, depend implicitly on $\mathbf{r}$ and $t$. Similarly to [82], we can rewrite the functions $\mathbf{A}_{cij}$ and $\mathbf{D}_{cij}^{dk}$ in the form

$$\mathbf{A}_{cij} \equiv A_{cij}(c_c)\mathbf{c}_c, \qquad \mathbf{D}_{cij}^{dk} \equiv D_{cij}^{dk}(c_c)\mathbf{c}_c,$$

and express the function $\boldsymbol{B}_{cij}$ as

$$\boldsymbol{B}_{cij} \equiv B_{cij}(c_c)\left(\mathbf{c}_c\mathbf{c}_c - \frac{1}{3}c_c^2\boldsymbol{I}\right),$$

where $A_{cij}$, $D_{cij}^{dk}$, and $B_{cij}$ are scalar functions of the absolute value of the peculiar velocity $c_c$.

Substituting the expression (2.30) into the integral equations (2.25) and comparing the coefficients at the gradients of the same macroscopic parameters, we obtain the linear integral equations for the functions $\mathbf{A}_{cij}$, $\mathbf{D}_{cij}^{dk}$, $\boldsymbol{B}_{cij}$, $F_{cij}$, and $G_{cij}$ ($c = 1, ..., L$, $i = 0, ..., L_c$, $j = 0, 1, ..., L_{ci}$, and $L_{ci}$ is the number of rotational levels in a molecule of species $c$ in the vibrational state $i$) [145]:

$$\sum_{dk} \frac{n_{ci}n_{dk}}{n^2} I_{cijdk}(\mathbf{A}) = \frac{1}{n}f_{cij}^{(0)}\left(\frac{m_c c_c^2}{2kT} - \frac{5}{2} + \frac{\varepsilon_j^{ci} - \langle\varepsilon^{ci}\rangle_{\text{rot}}}{kT}\right)\mathbf{c}_c, \tag{2.31}$$

$$\sum_{dk} \frac{n_{ci}n_{dk}}{n^2} I_{cijdk}(\mathbf{D}^{bn}) = \frac{1}{n_{ci}}f_{cij}^{(0)}\left(\delta_{cb}\delta_{in} - \frac{\rho_{ci}}{\rho}\right)\mathbf{c}_c, \tag{2.32}$$

$$b = 1, ..., L, \quad n = 0, 1, ..., L_c,$$

$$\sum_{dk} \frac{n_{ci}n_{dk}}{n^2} I_{cijdk}(\boldsymbol{B}) = \frac{m_c}{nkT}f_{cij}^{(0)}\left(\mathbf{c}_c\mathbf{c}_c - \frac{1}{3}c_c^2\boldsymbol{I}\right), \tag{2.33}$$

$$\sum_{dk} \frac{n_{ci}n_{dk}}{n^2} I_{cijdk}(F) = \frac{1}{n}f_{cij}^{(0)}\left[\frac{m_c c_c^2}{3kT} - 1 - \right.$$

$$\left. - \frac{p}{\rho T(c_{\text{tr}} + c_{\text{rot}})}\left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \frac{\varepsilon_j^{ci} - \langle\varepsilon^{ci}\rangle_{\text{rot}}}{kT}\right)\right], \tag{2.34}$$

$$\sum_{dk} \frac{n_{ci}n_{dk}}{n^2} I_{cijdk}(G) = -\frac{1}{n}J_{cij}^{\text{sl}(0)} + \frac{1}{n}f_{cij}^{(0)}\left[\frac{R_{ci}^{(0)}}{n_{ci}} - \right.$$

$$\left. - \frac{\sum_{ci} R_{ci}^{(0)}\left(\frac{3}{2}kT + \langle\varepsilon_j^{ci}\rangle_{\text{rot}} + \varepsilon_i^c + \varepsilon_c\right)}{\rho T(c_{\text{tr}} + c_{\text{rot}})}\left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + + \frac{\varepsilon_j^{ci} - \langle\varepsilon^{ci}\rangle_{\text{rot}}}{kT}\right)\right]. \tag{2.35}$$

While the equations for the functions $\mathbf{A}_{cij}$, $\boldsymbol{B}_{cij}$, $\mathbf{D}_{cij}^{dk}$, and $F_{cij}$ depend only on the linear integral operator of the most frequent collisions, the free terms of the equations for the function $G_{cij}$ include also the operator of slow processes in the zero-order approximation.

The uniqueness of the solutions of the integral equations (2.31)–(2.35) is provided by the additional constraints following from the normalizing conditions (2.8)–(2.11), (2.14), and (2.15) for the distribution functions [145]:

$$\sum_{cij} m_c \int f_{cij}^{(0)} A_{cij} c_c^2 d\mathbf{u}_c = 0, \tag{2.36}$$

$$\sum_{cij} m_c \int f_{cij}^{(0)} D_{cij}^{dk} c_c^2 d\mathbf{u}_c = 0, \quad d = 1,...,L, \ k = 0,...,L_d, \tag{2.37}$$

$$\sum_{j} \int f_{cij}^{(0)} F_{cij} d\mathbf{u}_c = 0, \quad c = 1,...,L, \ i = 0,...,L_c, \tag{2.38}$$

$$\sum_{j} \int f_{cij}^{(0)} G_{cij} d\mathbf{u}_c = 0, \quad c = 1,...,L, \ i = 0,...,L_c, \tag{2.39}$$

$$\sum_{cij} \int f_{cij}^{(0)} \left( \frac{m_c c_c^2}{2} + \varepsilon_j^{ci} \right) F_{cij} d\mathbf{u}_c = 0, \tag{2.40}$$

$$\sum_{cij} \int f_{cij}^{(0)} \left( \frac{m_c c_c^2}{2} + \varepsilon_j^{ci} \right) G_{cij} d\mathbf{u}_c = 0. \tag{2.41}$$

Moreover, the diffusive thermodynamic forces are not linearly independent:

$$\sum_{ci} \mathbf{d}_{ci} = 0$$

due to the relations

$$\sum_{ci} n_{ci}/n = 1, \quad \sum_{ci} \rho_{ci}/\rho = 1.$$

Therefore, Eq. (2.37) should be complemented by another constraint [60, 145]:

$$\sum_{dk} \frac{\rho_{dk}}{\rho} \mathbf{D}_{cij}^{dk} = 0. \tag{2.42}$$

Finally, the equations (2.31)–(2.35) complemented with the additional conditions (2.36)–(2.42) have unique solutions.

## 2.4　Transport Terms

Let us express the transport terms in Eqs. (2.16)–(2.18) as functions of the gradients of the main macroscopic parameters. Substituting the first-order distribution function (2.30) into the viscous stress tensor definition (1.13), we obtain

$$\boldsymbol{P} = (p - p_{\text{rel}})\boldsymbol{I} - 2\eta\boldsymbol{S} - \zeta\,\nabla\cdot\mathbf{v}\boldsymbol{I}. \tag{2.43}$$

Here, $p_{\text{rel}}$ is the relaxation pressure, $\eta$ and $\zeta$ are the coefficients of shear and bulk viscosity. In the state-to-state approach considered in this Chapter, the additional terms connected to the bulk viscosity and relaxation pressure appear in the diagonal terms of the stress tensor due to rapid inelastic TR energy exchange between the translational and rotational degrees of freedom. The existence of the relaxation pressure is caused also by slow processes of vibrational and chemical relaxation proceeding on the gas-dynamic time scale. If all slow relaxation processes in a system disappear, then $p_{\text{rel}} = 0$. The transport coefficients in the expression (2.43) can be written in terms of functions $\boldsymbol{B}_{cij}$, $F_{cij}$, and $G_{cij}$:

$$\eta = \frac{kT}{10}\,[\boldsymbol{B},\boldsymbol{B}], \qquad \zeta = kT\,[F,F], \qquad p_{\text{rel}} = kT\,[F,G]. \tag{2.44}$$

In these formulae, $[A,B]$ (where $A$, $B$ are arbitrary functions of molecular velocities) denotes a bilinear form depending on the linearized integral collision operator. In the kinetic theory, such bilinear forms are basically called bracket integrals. The bracket integrals in the expressions (2.44) are introduced similarly to those defined in [82] for a non-reacting gas mixture under the conditions of weak deviations from the equilibrium. However, in the case of the state-to-state model, the bracket integrals are associated only with the linearized operator of rapid processes.

Let us introduce first the partial bracket integrals

$$[A,B]'_{cidk} = \frac{1}{2n_{ci}n_{dk}} \sum_{jlj'l'} \int f^{(0)}_{cij} f^{(0)}_{dkl} \left(B_{cij} - B_{cij'}\right) \times$$

$$\times \left(A_{cij} - A_{cij'}\right) g\sigma^{j'l'}_{cd,ijkl} d^2\Omega\, d\mathbf{u}_c d\mathbf{u}_d, \tag{2.45}$$

$$[A,B]''_{cidk} = \frac{1}{2n_{ci}n_{dk}} \sum_{jlj'l'} \int f^{(0)}_{cij} f^{(0)}_{dkl} \left(B_{cij} - B_{cij'}\right) \times$$

$$\times \left(A_{dkl} - A_{dkl'}\right) g\sigma^{j'l'}_{cd,ijkl} d^2\Omega\, d\mathbf{u}_c d\mathbf{u}_d. \tag{2.46}$$

Subscripts "$cidk$" mean that the bracket integrals are calculated for collisions between particles of $c$ and $d$ chemical species in the vibrational states $i$ and $k$, respectively.

The full bracket integrals $[A,B]$ are obtained from (2.45), (2.46) carrying out the summation over the chemical species and vibrational states of interacting particles:

$$[A,B] = \sum_{cidk} \frac{n_{ci}n_{dk}}{n^2} \left([A,B]'_{cidk} + [A,B]''_{cidk}\right). \tag{2.47}$$

Notice once again that the bracket integrals are specified by the cross sections of the most probable collisions. Under the condition (1.43), the most frequent

collisions are the elastic collisions and those resulting in the exchange of translational and rotational energy. In the case of the weak non-equilibrium conditions considered for instance in [82], the bracket integrals depend on the cross sections of all microscopic processes.

The diffusion velocity $\mathbf{V}_{ci}$ of molecular components $c$ at the vibrational level $i$ is specified in the state-to-state approach by the first-order distribution function (2.30) [60, 145]:

$$\mathbf{V}_{ci} = -\sum_{dk} D_{cidk}\mathbf{d}_{dk} - D_{Tci}\nabla\ln T, \qquad (2.48)$$

where $D_{cidk}$ and $D_{Tci}$ are the multi-component diffusion and thermal diffusion coefficients for each chemical and vibrational species:

$$D_{cidk} = \frac{1}{3n}\left[\mathbf{D}^{ci}, \mathbf{D}^{dk}\right], \qquad D_{Tci} = \frac{1}{3n}\left[\mathbf{D}^{ci}, \mathbf{A}\right]. \qquad (2.49)$$

The total energy flux in the first-order approximation of the Chapman–Enskog method is found by substituting the expression (2.30) into the formula (1.14):

$$\mathbf{q} = -\lambda'\nabla T - p\sum_{ci} D_{Tci}\mathbf{d}_{ci} + \sum_{ci}\left(\frac{5}{2}kT + \langle\varepsilon^{ci}\rangle_{\rm rot} + \varepsilon_i^c + \varepsilon_c\right)n_{ci}\mathbf{V}_{ci}, \qquad (2.50)$$

where

$$\lambda' = \lambda_{\rm tr} + \lambda_{\rm rot} = \frac{k}{3}[\mathbf{A}, \mathbf{A}] \qquad (2.51)$$

is the thermal conductivity coefficient. The coefficients $\lambda_{\rm tr}$ and $\lambda_{\rm rot}$ are responsible for the energy transfer associated with the most probable processes which, in the present case, are the elastic collisions and inelastic TR- and RR rotational energy exchanges. In the state-to-state approach, the transport of the vibrational energy is described by the diffusion of vibrationally excited molecules rather than the thermal conductivity. In particular, the diffusion of the vibrational energy is simulated by introducing the independent diffusion coefficients for each vibrational state. It should be noted that all transport coefficients are specified by the cross sections of rapid processes excepting the relaxation pressure depending also on the cross sections of slow processes of vibrational relaxation and chemical reactions.

Analyzing the expressions (2.48), (2.50), and (2.27), we can notice that the energy flux and diffusion velocities include along with the gradients of temperature and atomic number densities also the gradients of all vibrational level populations. This constitutes the main feature of the heat transfer and diffusion in the state-to-state approach and the fundamental difference between $\mathbf{V}_{ci}$ and $\mathbf{q}$ and the heat flux and diffusion velocities obtained on the basis of all known in the literature models such as one-temperature or multi-temperature ones for both reacting and non-reacting mixtures. The comparison of the transport terms found in various quasi-stationary approaches (both chemically equilibrium and non-equilibrium) with the state-to-state transport terms defined by the formulae (2.48), (2.50) is performed in Chapters 3, 4.

Thus in the state-to-state approach, the distribution function in each approximation is determined by the vibrational level populations, atomic number densities, gas velocity, and temperature. The zero- and first-order distribution functions (2.4) and (2.30) describe, respectively, the local equilibrium and weakly non-equilibrium distributions over the velocity and rotational energy, whereas the distributions over the vibrational states and chemical species can be essentially non-equilibrium. The governing equations for the macroscopic parameters $n_{ci}(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$, and $T(\mathbf{r},t)$ in the zero- and first-order approaches represent the conservation equations of the momentum and total energy coupled to the equations of the state-to-state vibrational and chemical kinetics in the inviscid and viscous gas approximations, respectively. The transport terms in the governing equations are expressed as functions of the gradients of temperature, vibrational level populations, and number densities of atoms. The transport coefficients can be found solving the linear integral equations containing the linearized integral operator of the most frequent collisions. Algorithms for the transport coefficients calculation are given in Chapter 5.

Chapters 7–9 are devoted to the results obtained applying the proposed approach to the specific problems of non-equilibrium gas dynamics.

## 2.5 Production Terms

For a final closure of the equations (2.16)–(2.18), it is necessary to express the source terms $R_{ci}$ in Eqs. (2.16) as functions of the macroscopic parameters. Similarly to the case of the transport terms, we restrict our consideration to the zero-order and first-order distribution functions. Substituting the first-order distribution function $f_{cij} = f_{cij}^{(0)}(1 + \varphi_{cij})$ into the expression (2.19) for the relaxation terms $R_{ci}$ and taking into account the expressions (2.4), (2.5), and (2.30) for $f_{cij}^{(0)}$ and $f_{cij}^{(1)}$ yield the following form for $R_{ci}$:

$$R_{ci}^{\text{vibr}} = \sum_{dki'k'} \left( n_{ci'}n_{dk'}k_{c,i'i}^{d,k'k} - n_{ci}n_{dk}k_{c,ii'}^{d,kk'} \right), \tag{2.52}$$

$$R_{ci}^{\text{react}} = R_{ci}^{2\rightleftharpoons2} + R_{ci}^{2\rightleftharpoons3},$$

$$R_{ci}^{2\rightleftharpoons2} = \sum_{dc'd'}\sum_{ki'k'} \left( n_{c'i'}n_{d'k'}k_{c'i',ci}^{d'k',dk} - n_{ci}n_{dk}k_{ci,c'i'}^{dk,d'k'} \right), \tag{2.53}$$

$$R_{ci}^{2\rightleftharpoons3} = \sum_{dk}n_{dk} \left( n_{c'}n_{f'}k_{\text{rec},ci}^{dk} - n_{ci}k_{ci,\text{diss}}^{dk} \right). \tag{2.54}$$
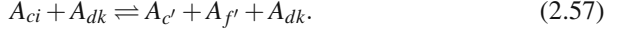
Here, the rate coefficients are introduced for the energy exchange:

$$A_{ci} + A_{dk} \rightleftharpoons A_{ci'} + A_{dk'}, \tag{2.55}$$

exchange chemical reactions:

$$A_{ci} + A_{dk} \rightleftharpoons A_{c'i'} + A_{d'k'} \tag{2.56}$$

and dissociation-recombination reactions:

$$A_{ci} + A_{dk} \rightleftharpoons A_{c'} + A_{f'} + A_{dk}. \tag{2.57}$$

The rate coefficients for the forward reactions (2.55)–(2.57) (for collisions of particles $A_{ci}$ and $A_{dk}$) are introduced, respectively, as $k_{c,ii'}^{d,kk'}$, $k_{ci,c'i'}^{dk,d'k'}$, and $k_{ci,\text{diss}}^{dk}$, the recombination rate coefficient is denoted as $k_{\text{rec},ci}^{dk}$. Note that if $k' = k$, then Eq. (2.55) describes VT(TV) transitions for a molecule $A_{ci}$ during the collision with a molecule $A_{dk}$

$$A_{ci} + A_{dk} \rightleftharpoons A_{ci'} + A_{dk},$$
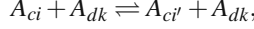
with the rate coefficient $k_{c,ii'}^{dk}$ of the forward transition. If $d$ is an atom, then the reaction (2.55) takes the form

$$A_{ci} + A_{d} \rightleftharpoons A_{ci'} + A_{d},$$
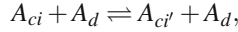
and the corresponding rate coefficient of the forward transition is $k_{c,ii'}^{d}$.

If $k \neq k'$ then the reaction (2.55) describes either $VV_1$ exchange of the vibrational energy between molecules of the same chemical species (for $c = d$) or $VV_2$ transitions between molecules of different chemical species (for $c \neq d$). Note that $VV_1$ and $VV_2$ transitions of the vibrational energy are almost always accompanied with the transfer of the part of vibrational energy into the translational or rotational modes, therefore these kinds of transitions are often called VVT- and VVR exchanges, respectively. As is mentioned above, the probability of a simultaneous exchange between three and more energy modes during one collision is rather low, consequently, these exchanges are usually omitted in the production terms of the kinetic equations.

In the dissociation and recombination reactions (2.57), the particle $A_{dk}$ can also be either a molecule or an atom. Therefore, different dissociation rate coefficients should be introduced: $k_{\text{rec},ci}^{dk}$, $k_{\text{rec},ci}^{d}$. Let us remind that we consider dissociation of only diatomic molecules, therefore only atoms can be dissociation products, and only atoms can recombine into a molecule. Moreover, it is assumed that the internal state of a molecular partner in the reaction (2.57) does not change during the collision.

The rate coefficients of the above processes depend on the order of the distribution function approximation. In the first-order approximation, the rate coefficient of the vibrational energy exchange (2.55) reads:

$$k_{c,ii'}^{d,kk'} = \sum_{jlj'l'} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci}n_{dk}} [1 + (\varphi_{cij} + \varphi_{dkl})] g\sigma_{cd,ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u}_d d\mathbf{u}_c. \tag{2.58}$$

Substituting the expressions (2.4) and (2.30) for $f_{cij}^{(0)}$ and $\varphi_{cij}$ into the definition (2.58) and taking into account that the integrals of odd functions over a symmetric interval vanish, we ensure that the coefficients $k_{c,ii'}^{d,kk'}$ depend only on the functions

$F_{cij}$ and $G_{cij}$ entering to Eq. (2.30) for $f_{cij}^{(1)} = f_{cij}^{(0)} \varphi_{cij}$. As a result, the following formulae for $k_{c,\,ii'}^{d,\,kk'}$ are obtained:

$$k_{c,\,ii'}^{d,\,kk'} = k_{c,\,ii'}^{d,\,kk'\,(0)}(T) + k_{c,\,ii'}^{d,\,kk'\,(1)}(n_{ci}, T) + k_{c,\,ii'}^{d,\,kk'\,(2)}(n_{ci}, T, \nabla \cdot \mathbf{v}). \qquad (2.59)$$

In the last formula

$$k_{c,\,ii'}^{d,\,kk'\,(0)} = \frac{4\pi}{Z_{ci}^{\mathrm{rot}} Z_{dk}^{\mathrm{rot}}} \left(\frac{m_{cd}}{2\pi kT}\right)^{3/2} \sum_{jlj'l'} \int \exp\left(-\frac{m_{cd}g^2}{2kT}\right) \times$$

$$\times s_j^{ci} s_l^{dk} \exp\left(-\frac{\varepsilon_j^{ci} + \varepsilon_l^{dk}}{kT}\right) g^3 \tilde{\sigma}_{cd,\,ijkl}^{i'j'k'l'} dg, \qquad (2.60)$$

$m_{cd}$ is the reduced mass of colliding particles, $\tilde{\sigma}_{cd,\,ijkl}^{i'j'k'l'}$ is the integral cross section of inelastic collisions obtained integrating the corresponding differential cross section over the solid angles, in which the relative velocity vector before and after collisions appears:

$$\tilde{\sigma}_{cd,\,ijkl}^{i'j'k'l'}(g) = \frac{1}{4\pi} \int \sigma_{cd,\,ijkl}^{i'j'k'l'}(\mathbf{g}, \Omega) d^2\Omega d^2\Omega'.$$

It is commonly supposed that the cross section depends on the absolute value $g$ of the relative velocity rather than the vector $\mathbf{g}$. Then

$$\tilde{\sigma}_{cd,\,ijkl}^{i'j'k'l'}(g) = \int \sigma_{cd,\,ijkl}^{i'j'k'l'}(g, \Omega) d^2\Omega.$$

The coefficients $k_{c,\,ii'}^{d,\,kk'\,(1)}$, $k_{c,\,ii'}^{d,\,kk'\,(2)}$ are found as

$$k_{c,\,ii'}^{d,\,kk'\,(1)} = -\frac{1}{n} \sum_{jlj'l'} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} (G_{cij} + G_{dkl}) g\sigma_{cd,\,ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u}_d d\mathbf{u}_c, \qquad (2.61)$$

$$k_{c,\,ii'}^{d,\,kk'\,(2)} = -\nabla \cdot \mathbf{v} \frac{1}{n} \sum_{jlj'l'} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} (F_{cij} + F_{dkl}) g\sigma_{cd,\,ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u}_d d\mathbf{u}_c. \qquad (2.62)$$

The coefficients $k_{c,\,ii'}^{d,\,kk'\,(0)}$ are associated with the local equilibrium Maxwell–Boltzmann distributions over the velocity and rotational energy whereas the remaining coefficients $k_{c,\,ii'}^{d,\,kk'\,(1)}$ and $k_{c,\,ii'}^{d,\,kk'\,(2)}$ take into account deviations from these distributions.

From the above expressions it is seen that in the zero-order approximation, the rate coefficients of vibrational transitions depend on the gas temperature and coincide with the phenomenological rate coefficients of corresponding transitions [236, 100]. These coefficients are interpreted as a number of transitions per unit time and can be connected to the transition probability in a single collision. For VT transitions ($k = k'$ or $d$ is an atom),

$$k_{c,ii'}^{d\,(0)} = \frac{Z_d}{n_d} P_{c,ii'}^{(d)},$$

where $P_{c,ii'}^{(d)}$ is the probability, for a molecule of $c$ species, of a VT transition from the vibrational state $i$ to $i'$ as a result of the collision with a particle $d$; $Z_d$ is a number of collisions between particles $c$ and $d$ per unit time.

For VV exchanges,

$$k_{c,ii'}^{d\,kk'\,(0)} = \frac{Z_d}{n_d} Q_{c,ii'}^{d,kk'},$$

$Q_{c,ii'}^{d,kk'}$ is the probability of a VV transition (2.55).

In the theory for relaxation processes, as well as for the solution of non-equilibrium gas-dynamic problems, the zero-order rate coefficients of energy transitions and chemical reactions corresponding to the Maxwell–Boltzmann distribution over the velocity and rotational states are commonly used. Analytical methods for the calculation of the vibrational transition probabilities in the zero-order approximation are discussed in detail in Refs. [236, 100]. Approximate formulae fitting the numerical results of trajectory calculations for air species are given in Ref. [51]. A review of different models for the transition probabilities including expressions for the rate coefficients can be found in [58]. Various forms for the rate coefficients of vibrational energy exchange recommended in the literature are summarized in Chapter 6.

The first-order rate coefficients of energy transitions depend not only on the temperature but also on the vibrational level populations. Moreover, they include the term proportional to the velocity divergence $\nabla \cdot \mathbf{v}$. It is obvious that in a spatially homogeneous gas with rapid and slow processes, the first-order correction to the rate coefficients contains only the first term given by Eq. (2.61). It can be also noted that the term depending on $\nabla \cdot \mathbf{v}$ disappears under the conditions when all inelastic non-equilibrium processes in a gas flow proceed on the gas-dynamic time scale $\theta$, and only elastic and strictly resonant collisions belong to the most frequent collisions. Such a situation takes place in the case of slow rotational relaxation, for instance, in a mixture of light molecules.

It is clear that the formulae (2.60)–(2.62) can be simplified for VT transitions when the particle $A_{dk}$ is an atom or $k' = k$. In particular, for a collision with an atom

$$k_{c,ii'}^{d\,(0)} = \frac{4\pi}{Z_{ci}^{\text{rot}}} \left( \frac{m_{cd}}{2\pi kT} \right)^{3/2} \sum_{jj'} \int \exp \left( -\frac{m_{cd}g^2}{2kT} \right) \times$$

$$\times\, s_j^{ci} \exp \left( -\frac{\varepsilon_j^{ci}}{kT} \right) g^3 \tilde{\sigma}_{cd,ij}^{i'j'} dg, \tag{2.63}$$

$$k_{c,ii'}^{d\,(1)} = -\frac{1}{n} \sum_{jj'} \int \frac{f_{cij}^{(0)} f_d^{(0)}}{n_{ci} n_d} \left( G_{cij} + G_d \right) g \sigma_{cd,ij}^{i'j'} d^2\Omega d\mathbf{u}_d d\mathbf{u}_c,$$

$$k_{c,ii'}^{d\,(2)} = -\nabla \cdot \mathbf{v} \frac{1}{n} \sum_{jj'} \int \frac{f_{cij}^{(0)} f_d^{(0)}}{n_{ci} n_d} \left( F_{cij} + F_d \right) g \sigma_{cd,ij}^{i'j'} d^2 \Omega d\mathbf{u}_d d\mathbf{u}_c.$$

The expressions for the rate coefficients of chemical reactions are written similarly:

$$k_{(\gamma)} = k_{(\gamma)}^{(0)}(T) + k_{(\gamma)}^{(1)}(n_{ci}, T) + k_{(\gamma)}^{(2)}(n_{ci}, T, \nabla \cdot \mathbf{v}), \tag{2.64}$$

where $k_{(\gamma)}$ for $\gamma = 1, 2, 3$ correspond to the rate coefficients of exchange reactions $k_{ci,c'i'}^{dk,d'k'}$, recombination $k_{\text{rec},ci}^{dk}$, and dissociation $k_{ci,\text{diss}}^{dk}$, respectively.

Let us now consider the rate coefficients of chemical reactions in the zero-order and first-order approximations. For exchange reactions we have

$$k_{ci,c'i'}^{dk,d'k'\,(0)} = \frac{4\pi}{Z_{ci}^{\text{rot}} Z_{dk}^{\text{rot}}} \left( \frac{m_{cd}}{2\pi kT} \right)^{3/2} \sum_{jlj'l'} \int \exp\left( -\frac{m_{cd}g^2}{2kT} \right) \times$$

$$\times s_j^{ci} s_l^{dk} \exp\left( -\frac{\varepsilon_j^{ci} + \varepsilon_l^{dk}}{kT} \right) g^3 \tilde{\sigma}_{cd,ijkl}^{c'd',i'j'k'l'} dg, \tag{2.65}$$

$$k_{ci,c'i'}^{dk,d'k'\,(1)} = -\frac{1}{n} \sum_{jlj'l'} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} \left( G_{cij} + G_{dkl} \right) g \sigma_{cd,ijkl}^{c'd',i'j'k'l'} d^2 \Omega d\mathbf{u}_d d\mathbf{u}_c, \tag{2.66}$$

$$k_{ci,c'i'}^{dk,d'k'\,(2)} = -\nabla \cdot \mathbf{v} \frac{1}{n} \sum_{jlj'l'} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} \left( F_{cij} + F_{dkl} \right) g \sigma_{cd,ijkl}^{c'd',i'j'k'l'} d^2 \Omega d\mathbf{u}_d d\mathbf{u}_c. \tag{2.67}$$

with $\tilde{\sigma}_{cd,ijkl}^{c'd',i'j'k'l'}$ designating the integral cross section of a collision resulting in a bimolecular reaction.

The recombination rate coefficients in the zero-order approximation can be represented in the form

$$k_{\text{rec},ci}^{dk\,(0)} = k_{\text{rec},ci}^{d\,(0)} = \frac{(m_{c'} m_{f'} m_d)^{3/2}}{(2\pi kT)^{9/2}} \sum_j \int \sigma_{c'f'd}^{\text{rec},cij}(\mathbf{u}_{c'}, \mathbf{u}_{f'}, \mathbf{u}_d', \mathbf{u}_c, \mathbf{u}_d) \times$$

$$\times \exp\left( -\frac{m_{c'} u_{c'}^2 + m_{f'} u_{f'}^2 + m_d u_d'^2}{2kT} \right) d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}_d' d\mathbf{u}_c d\mathbf{u}_d. \tag{2.68}$$

In the first-order approximation, the recombination rate coefficients read

$$k_{\text{rec},ci}^{dk\,(1)} = -\frac{1}{n} \sum_{jl} \int \frac{f_{c'}^{(0)} f_{f'}^{(0)} f_{dkl}^{(0)}}{n_{c'} n_{f'} n_{dk}} \left( G_{c'} + G_{f'} + G_{dkl} \right) \times$$

$$\times \sigma_{c'f'd}^{\text{rec},cij} d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}_d' d\mathbf{u}_c d\mathbf{u}_d, \tag{2.69}$$

$$k_{\text{rec},ci}^{dk\,(2)} = -\nabla \cdot \mathbf{v} \frac{1}{n} \sum_{jl} \int \frac{f_{c'}^{(0)} f_{f'}^{(0)} f_{dkl}^{(0)}}{n_{c'} n_{f'} n_{dk}} \left( F_{c'} + F_{f'} + F_{dkl} \right) \times$$

$$\times \sigma_{c'f'd}^{\text{rec},cij} d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}_d' d\mathbf{u}_c d\mathbf{u}_d. \qquad (2.70)$$

The zero-order dissociation rate coefficients take the form [171, 130]

$$k_{ci,\text{diss}}^{dk\,(0)} = k_{ci,\text{diss}}^{d\,(0)} = \frac{4\pi}{Z_{ci}^{\text{rot}}} \left( \frac{m_{cd}}{2\pi kT} \right)^{3/2} \sum_j \int \exp\left( -\frac{m_{cd} g^2}{2kT} \right) \times$$

$$\times s_j^{ci} \exp\left( -\frac{\varepsilon_j^{ci}}{kT} \right) g^3 \tilde{\sigma}_{cij,d}^{\text{diss}} dg, \qquad (2.71)$$

the integral dissociation reaction cross section is introduced by the formula

$$\tilde{\sigma}_{cij,d}^{\text{diss}} = \int \sigma_{cij,d}^{\text{diss}}(g, \mathbf{u}_{c'}, \mathbf{u}_{f'}, \mathbf{u}_d') d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}_d'.$$

In the first-order approximation,

$$k_{ci,\text{diss}}^{dk\,(1)} = -\frac{1}{n} \sum_{jl} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} \left( G_{cij} + G_{dkl} \right) \sigma_{cij,d}^{\text{diss}} d\mathbf{u}_c d\mathbf{u}_d d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}_d', \qquad (2.72)$$

$$k_{ci,\text{diss}}^{dk\,(2)} = -\nabla \cdot \mathbf{v} \frac{1}{n} \sum_{jl} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} \left( F_{cij} + F_{dkl} \right) \sigma_{cij,d}^{\text{diss}} d\mathbf{u}_c d\mathbf{u}_d d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}_d'. \qquad (2.73)$$

Since it is supposed that the cross sections of dissociation $\sigma_{cij,d}^{\text{diss}}$ and recombination $\sigma_{c'f'd}^{\text{rec},cij}$ do not depend on the vibrational state $k$ of the partner $A_{dk}$ in the reaction (2.57), the rate coefficients of dissociation and recombination in the zero-order approximation are also independent of $k$:

$$k_{ci,\text{diss}}^{dk\,(0)} = k_{ci,\text{diss}}^{d\,(0)}, \qquad k_{\text{rec},ci}^{dk\,(0)} = k_{\text{rec},ci}^{d\,(0)}.$$

The relations connecting the rate coefficients of forward and backward collisional processes follow from the microscopic detailed balance relations (1.31)–(1.33) after averaging them with the Maxwell–Boltzmann distribution over the velocity and rotational energy [197, 76, 130, 78]. Thus the rate coefficients of forward and backward vibrational energy transitions satisfy the relation

$$k_{c,i'i}^{d,k'k\,(0)} = k_{c,ii'}^{d,kk'\,(0)} \frac{s_i^c s_k^d}{s_{i'}^c s_{k'}^d} \frac{Z_{ci}^{\text{rot}} Z_{dk}^{\text{rot}}}{Z_{ci'}^{\text{rot}} Z_{dk'}^{\text{rot}}} \exp\left( \frac{\varepsilon_{i'}^c + \varepsilon_{k'}^d - \varepsilon_i^c - \varepsilon_k^d}{kT} \right), \qquad (2.74)$$

$s_i^c$ is the vibrational statistical weight. Similarly, for the chemically reactive collisions (2.56) and (2.57) we obtain

$$k_{c'i',ci}^{d'k',dk(0)} = k_{ci,c'i'}^{dk,d'k'(0)} \frac{s_i^c s_k^d}{s_{i'}^{c'} s_{k'}^{d'}} \left( \frac{m_c m_d}{m_{c'} m_{d'}} \right)^{3/2} \frac{Z_{ci}^{\text{rot}} Z_{dk}^{\text{rot}}}{Z_{c'i'}^{\text{rot}} Z_{d'k'}^{\text{rot}}} \times$$

$$\times \exp \left( \frac{\varepsilon_{i'}^{c'} + \varepsilon_{k'}^{d'} - \varepsilon_i^c - \varepsilon_k^d}{kT} \right) \exp \left( \frac{D_c + D_d - D_{c'} - D_{d'}}{kT} \right), \qquad (2.75)$$

$$k_{\text{rec},ci}^{d(0)} = k_{ci,\text{diss}}^{d(0)} s_i^c \left( \frac{m_c}{m_{c'} m_{f'}} \right)^{3/2} h^3 (2\pi kT)^{-3/2} Z_{ci}^{\text{rot}} \exp \left( -\frac{\varepsilon_i^c - D_c}{kT} \right). \qquad (2.76)$$

In the last formula, $m_c = m_{c'} + m_{f'}$.

For diatomic gases, the vibrational statistical weight $s_i^c = 1$. Moreover, for the rigid rotator model, the rotational partition function is independent of the vibrational state $Z_{ci}^{\text{rot}} = Z_c^{\text{rot}}$. In this case, the ratio of the backward and forward reaction rate coefficients takes the reduced form

$$K_{c,i'i}^{d,k'k(0)} = \frac{k_{c,i'i}^{d,k'k(0)}}{k_{c,ii'}^{d,kk'(0)}} = \exp \left( \frac{\varepsilon_{i'}^c + \varepsilon_{k'}^d - \varepsilon_i^c - \varepsilon_k^d}{kT} \right), \qquad (2.77)$$

$$K_{c'i',ci}^{d'k',dk(0)} = \frac{k_{c'i',ci}^{d'k',dk(0)}}{k_{ci,c'i'}^{dk,d'k'(0)}} = \left( \frac{m_c m_d}{m_{c'} m_{d'}} \right)^{3/2} \frac{Z_c^{\text{rot}} Z_d^{\text{rot}}}{Z_{c'}^{\text{rot}} Z_{d'}^{\text{rot}}} \times$$

$$\times \exp \left( \frac{\varepsilon_{i'}^{c'} + \varepsilon_{k'}^{d'} - \varepsilon_i^c - \varepsilon_k^d}{kT} \right) \exp \left( \frac{D_c + D_d - D_{c'} - D_{d'}}{kT} \right), \qquad (2.78)$$

$$K_{\text{rec-diss},ci}^{d(0)} = \frac{k_{\text{rec},ci}^{d(0)}}{k_{ci,\text{diss}}^{d(0)}} = \left( \frac{m_c}{m_{c'} m_{f'}} \right)^{3/2} h^3 (2\pi kT)^{-3/2} \times$$

$$\times Z_c^{\text{rot}} \exp \left( -\frac{\varepsilon_i^c - D_c}{kT} \right). \qquad (2.79)$$

The expressions (2.74), (2.75) and, respectively, (2.77) and (2.78) can be simplified if the collision partner is an atom. The expressions (2.74) and (2.77) also take a simplified form if the internal state of the collision partner-molecule remains unchanged during the collision.

# Chapter 3
# Multi-Temperature Models in Transport and Relaxation Theory

The approach proposed in the previous Chapter makes it possible to develop the most rigorous model of reacting gas mixture dynamics under the conditions of strong vibrational and chemical non-equilibrium, since it takes into account the detailed state-to-state vibrational and chemical kinetics for the definition of the gas flow parameters. However, practical implementation of this method leads to serious difficulties. The first important problem encountered in the realization of the state-to-state model is its computational cost. Indeed, the solution of the fluid dynamics equations coupled to the equations of the state-to-state vibrational and chemical kinetics requires numerical simulation of a great number of equations for the vibrational level populations of all molecular species. Moreover, in the viscous gas approximation, numerical simulations require the calculation of a large number of transport coefficients, particularly, diffusion coefficients in each space cell and at each time step, which significantly complicates the study of specific flows.

The second fundamental problem is that the closed system of macroscopic equations in the state-to-state approach includes the rate coefficients of all vibrational energy transitions and state-dependent rate coefficients of chemical reactions depending on the gas temperature and vibrational states of reaction reagents and products. Experimental and theoretical data on these rate coefficients and especially on the cross sections of inelastic processes are rather scanty.

Due to the above problems, simpler models based on quasi-stationary vibrational distributions are rather attractive for practical applications. In quasi-stationary approaches, the vibrational level populations are expressed in terms of a few macroscopic parameters, consequently, non-equilibrium kinetics can be described by a considerably reduced set of governing equations. Commonly used models are based on the Boltzmann distribution with the vibrational temperature different from the gas temperature. However, such a distribution appears not to be justified under the conditions of strong vibrational excitation, since it is valid solely for the harmonic oscillator model, which describes adequately only the low vibrational states. In the present Chapter, the non-Boltzmann vibrational distributions taking into account anharmonic vibrations and high vibrational excitation are derived starting from the kinetic equations. Based on these distributions, the kinetic theory of transport and relaxation processes is developed.

## 3.1   Generalized Treanor Distribution for a Gas Mixture

It is known from experiments [100] that in a vibrationally excited gas, near-resonant vibrational energy exchanges between molecules of the same chemical species proceed much faster than non-resonant transitions between different molecules, as well as transfers of vibrational energy to other modes and chemical reactions. Therefore the following relation between the characteristic relaxation times is fulfilled:

$$\tau_{\text{el}} \lesssim \tau_{\text{rot}} < \tau_{\text{VV}_1} \ll \tau_{\text{VV}_2} < \tau_{\text{TRV}} < \tau_{\text{react}} \sim \theta, \tag{3.1}$$

$\tau_{\text{VV}_1}$ is the mean time between the collisions of the same species resulting in the near-resonant vibrational energy exchange; $\tau_{\text{VV}_2}$ is the characteristic time of the vibrational energy exchange between different molecules.

Let us consider a multi-component reacting gas mixture flow under the condition (3.1). In this case, the integral operator of the most frequent collisions in the kinetic equations (1.38) for distribution functions includes the operator of $\text{VV}_1$ vibrational energy transitions between molecules of the same species along with the operators of elastic collisions and collisions with rotational energy exchanges:

$$J_{cij}^{\text{rap}} = J_{cij}^{\text{el}} + J_{cij}^{\text{rot}} + J_{cij}^{\text{VV}_1}. \tag{3.2}$$

The operator of slow processes $J_{cij}^{\text{sl}}$ consists of the operator of $\text{VV}_2$ vibrational transitions between molecules of different species, the operator describing the transfer of vibrational energy into rotational and translational modes $J_{cij}^{\text{TRV}}$, as well as the operator of chemical reactions $J_{cij}^{\text{react}}$:

$$J_{cij}^{\text{sl}} = J_{cij}^{\text{VV}_2} + J_{cij}^{\text{TRV}} + J_{cij}^{\text{react}}. \tag{3.3}$$

For the solution of Eqs. (1.38) with the collisional operators (3.2) and (3.3), the distribution function is expanded into the generalized Chapman–Enskog series in the small parameter $\varepsilon = \tau_{\text{VV}_1}/\theta$. In the zero-order approximation, the following equation for the distribution function is deduced:

$$J_{cij}^{\text{el}(0)} + J_{cij}^{\text{rot}(0)} + J_{cij}^{\text{VV}_1(0)} = 0. \tag{3.4}$$

The solution of these equations is specified by the invariants of the most frequent collisions. In addition to the invariants

$$\psi_{cij}^{(v)} = m_c u_{cv}, \quad v = 1,2,3, \qquad \psi_{cij}^{(4)} = m_c u_c^2/2 + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon_c,$$

which are conserved in any collision, under the condition (3.1) there are additional independent invariants of rapid processes:

$$\psi_{cij}^{(\mu+4)} = i_c, \quad \mu = 1,...,L_{\text{m}},$$

where $L_m$ is the number of molecular species, $i_c$ the number of the vibrational quanta in a molecular species $c$, and

$$\psi_{cij}^{(\lambda+L_m+4)} = a_c, \quad \lambda = 1,...,L,$$

where $a_c$ is an arbitrary value independent of the velocity, vibrational $i$ and rotational $j$ quantum numbers and depending arbitrarily on the particle chemical species $c$.

Invariants $\psi_{cij} = i_c$ present an important feature of collisions resulting in the $VV_1$ vibrational energy exchange between the molecules of the same species: during such collisions, the total number of vibrational quanta in a system of colliding particles is maintained. The existence of a similar invariant for VV transitions in a single-component gas was found for the first time in Ref. [242]. The analysis for the data for the probabilities of vibrational energy transitions showed that in a single-component gas, the most probable collisions are those resulting in the near-resonant vibrational energy exchange. In such a collision, the vibrational energy is not conserved because of the resonance defect arising due to the non-equidistant location of vibrational levels in real molecules:

$$\varepsilon_i + \varepsilon_k = \varepsilon_{i'} + \varepsilon_{k'} + \Delta\varepsilon,$$

where $\Delta\varepsilon$ is the resonance defect. Nevertheless, since the probability of single-quantum transitions appears to be very high, the total number of vibrational quanta of interacting molecules is kept constant during such collisions:

$$\varepsilon_i + \varepsilon_k = \varepsilon_{i\pm1} + \varepsilon_{k\mp1} + \Delta\varepsilon.$$

In this connection

$$i+k = (i\pm1)+(k\mp1). \tag{3.5}$$

The number of quanta also maintains for multi-quantum transitions:

$$i+k = (i\pm m)+(k\mp m), \quad m > 1. \tag{3.6}$$

Taking into account the conservation of the number of the quanta during VV transitions, a non-equilibrium quasi-stationary solution of balance equations for the vibrational level populations was found in Ref. [242]. This solution is now called the Treanor distribution. If we restrict our consideration with the harmonic oscillator spectrum, then it can be readily shown that the resonance defect during VV transitions vanishes, and the vibrational energy $\varepsilon_i^c$ is the additional collisional invariant of rapid processes. In this case, the Treanor distribution is reduced to the Boltzmann distribution with the vibrational temperature different from the gas temperature.

In a gas mixture, during $VV_1$ vibrational energy exchange between molecules of the same species, the number of vibrational quanta in a given species keeps constant, and for any chemical species $c$, the conditions (3.5), (3.6) are:

$$i_c + k_c = (i_c \pm m_c)+(k_c \mp m_c), \quad m_c \geq 1.$$

The existence of the other additional invariants $\psi_{cij} = a_c$ is explained by the fact that under the condition (3.1), slow chemical reactions remain frozen in the most frequent collisions.

Writing Eqs. (3.4) in the form (1.53) and taking into account the system of collision invariants we obtain the solution for these equations as

$$f_{cij}^{(0)} = \left(\frac{m_c}{2\pi kT}\right)^{3/2} \frac{n_c}{Z_c^{\text{int}}} s_{ij}^c \exp\left(-\frac{m_c c_c^2}{2kT} - \frac{\varepsilon_j^{ci}}{kT} - \frac{\varepsilon_i^c}{kT} - \vartheta_c i_c\right). \qquad (3.7)$$

Here, $Z_c^{\text{int}}$ is the non-equilibrium partition function of internal degrees of freedom:

$$Z_c^{\text{int}} = \sum_{ij} s_{ij}^c \exp\left(-\frac{\varepsilon_{ij}^c}{kT} - \vartheta_c i_c\right),$$

$\vartheta_c$ is a parameter.

If it is assumed that the rotational energy is independent of the molecular vibrational state (the rigid rotator model), then $s_{ij}^c = s_i^c s_j^c$, and the partition function is multiplicative:

$$Z_c^{\text{int}} = Z_c^{\text{rot}} Z_c^{\text{vibr}}, \qquad (3.8)$$

where $Z_c^{\text{rot}}$ is given by the formula (2.7), and $Z_c^{\text{vibr}}$ is the non-equilibrium vibrational partition function for molecular species $c$:

$$Z_c^{\text{vibr}} = \sum_i s_i^c \exp\left(-\frac{\varepsilon_i^c}{kT} - \vartheta_c i_c\right). \qquad (3.9)$$

The functions (3.7) represent the local equilibrium Maxwell-Boltzmann distribution of molecules over the velocity and rotational energy levels and the non-equilibrium distribution over the vibrational states and chemical species. For the vibrational level populations, from Eq. (3.7) it follows:

$$n_{ci} = \frac{n_c}{Z_c^{\text{vibr}}} s_i^c \exp\left(-\frac{\varepsilon_i^c}{kT} - \vartheta_c i_c\right), \qquad (3.10)$$

or

$$n_{ci} = n_{c0} \frac{s_i^c}{s_0^c} \exp\left(-\frac{\varepsilon_i^c - \varepsilon_0^c}{kT} - \vartheta_c i_c\right). \qquad (3.11)$$

The distribution function is specified by the macroscopic parameters $n_c$, $\mathbf{v}$, $T$, and $\vartheta_c$. The additional parameter $\vartheta_c$ is associated to the additional collision invariant $i_c$ and is introduced in terms of the mean specific number of vibrational quanta $W_c$ in molecular species $c$:

$$\rho_c W_c = \sum_{ij} i_c \int f_{cij} d\mathbf{u}_c.$$

For the sake of simplicity, the subscript "$c$" at the vibrational quantum number $i_c$ is hereafter omitted. Similarly to a single-component gas [242], we can define

the temperature $T_1^c$ of the first vibrational level for each molecular species $c$ by the expression

$$\frac{n_{c1}}{n_{c0}} = \frac{s_1^c}{s_0^c} \exp\left(-\frac{\varepsilon_1^c - \varepsilon_0^c}{kT_1^c}\right).$$

Writing Eq. (3.11) for $i = 1$ and comparing to the last expression, we obtain

$$\vartheta_c = \frac{\varepsilon_1^c - \varepsilon_0^c}{k}\left(\frac{1}{T_1^c} - \frac{1}{T}\right). \tag{3.12}$$

Below, the vibrational energy $\varepsilon_i^c$ and the energy of the first level $\varepsilon_1^c$ for species $c$ are counted from the energy of the zero level using the formulae (1.5), (1.6). Taking into account the relations (1.5), (3.12) we can modify the expression (3.9) for the vibrational partition function $Z_c^{\text{vibr}}$ as follows:

$$Z_c^{\text{vibr}} = Z_c^{\text{vibr}}(T, T_1^c) = \sum_i s_i^c \exp\left(-\frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} - \frac{i\varepsilon_1^c}{kT_1^c}\right). \tag{3.13}$$

Then the expression (3.10) for the vibrational level populations of species $c$ can be rewritten in the form

$$n_{ci} = \frac{n_c}{Z_c^{\text{vibr}}(T, T_1^c)} s_i^c \exp\left(-\frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} - \frac{i\varepsilon_1^c}{kT_1^c}\right). \tag{3.14}$$

It should be emphasized that $n_{ci}$ depends on two temperatures ($T$ and $T_1^c$) since the translational-rotational and vibrational degrees of freedom are not isolated in the most frequent collisions as a consequence of the non-resonant character of the VV$_1$ exchange.

The expression (3.14) yields the non-equilibrium quasi-stationary Treanor distribution [242] in a multi-component gas mixture. Note that similarly to a single-component gas, the distribution (3.14) describes adequately only the populations of low vibrational levels $i_c \leq i_{c*}$, where $i_{c*}$ corresponds to the minimum of the function $n_{ci}$. It is explained by the fact that the additional collision invariant $\psi_{cij} = i_c$ exists only at low levels $i_c \leq i_{c*}$. For the collisions of molecules at higher vibrational states $i_c > i_{c*}$, the probability of VV$_1$ transitions becomes comparable to that of VV$_2$ and VT vibrational energy exchanges. The value $i_{c*}$ is found from the relation

$$\left.\frac{\partial n_{ci}}{\partial i}\right|_{i_{c*}} = 0.$$

It is equal to [100]

$$i_{c*} = \frac{\varepsilon_1^c}{2\alpha_c h \nu_c}\frac{T}{T_1^c} + \frac{1}{2}. \tag{3.15}$$

In the high gas temperature range, if $T \gg T_1^c$, the level $i_{c*}$ appears to be close to the last vibrational level $i_c = L_c$, which can be found equalizing the vibrational energy $\varepsilon_{L_c}^c$ to the molecular dissociation energy $D_c$. Therefore, for $T \gg T_1^c$, the Treanor distribution is valid for the entire range of vibrational states.

For a strongly excited gas with a high vibrational energy supply ($T_1^c \gg T$), the minimum of the Treanor distribution is located rather low, and the increasing branch of the distribution is not physically consistent. In this case it is necessary to account for various relaxation channels at different groups of vibrational levels. Nonequilibrium vibrational distributions taking into account this effect was obtained for a one-component gas in Refs. [99, 100, 101, 138, 133, 143] and will be discussed in Section 3.7.

Under the conditions when the anharmonic effects can be neglected, the distribution (3.14) is reduced to the non-equilibrium Boltzmann distribution with the vibrational temperature of molecular components $T_v^c = T_1^c$ different from $T$:

$$n_{ci} = \frac{n_c}{Z_c^{\text{vibr}}} s_i^c \exp\left(-\frac{\varepsilon_i^c}{kT_1^c}\right), \tag{3.16}$$

where the vibrational partition function takes the form

$$Z_c^{\text{vibr}} = Z_c^{\text{vibr}}(T_1^c) = \sum_i s_i^c \exp\left(-\frac{\varepsilon_i^c}{kT_1^c}\right). \tag{3.17}$$

In the formulae (3.16), (3.17), $\varepsilon_i^c = i\varepsilon_1^c = ihc\omega_e^c = ih\nu_c$. If the infinite number of vibrational states is considered, then the specific vibrational energy $E_{\text{vibr},c}$ is obtained by the formula (1.25), in which instead of the gas temperature $T$ the vibrational temperature of the component $c$ $T_v^c$ appears.

In the case of the local thermal equilibrium, the vibrational temperatures of all molecular species are equal to the gas temperature $T_1^c = T$, and the Treanor distribution (3.14) is reduced to the one-temperature Boltzmann distribution:

$$n_{ci} = \frac{n_c}{Z_c^{\text{vibr}}} s_i^c \exp\left(-\frac{\varepsilon_i^c}{kT}\right), \tag{3.18}$$

$$Z_c^{\text{vibr}} = Z_c^{\text{vibr}}(T) = \sum_i s_i^c \exp\left(-\frac{\varepsilon_i^c}{kT}\right). \tag{3.19}$$

Fig. 3.1 presents the Treanor distribution (3.14) (*1*), which is compared to the non-equilibrium Boltzmann distribution (3.16) with the vibrational temperature $T_1$ (*2*) and thermal equilibrium Boltzmann distribution (3.18) with the temperature $T$ (*3*). The distributions are calculated for molecular nitrogen at the temperatures $T = 4000$, $T_1 = 1000$ K (Fig. 3.1,*a*) and $T = 1000$, $T_1 = 4000$ K (Fig. 3.1,*b*). In both cases, the thermal equilibrium Boltzmann distribution significantly deviates from the non-equilibrium ones, for $T_1/T < 1$ it is noticeably higher, and for $T_1/T > 1$ it is considerably lower compared to the non-equilibrium distributions. In the case $T_1/T < 1$, when the vibrational energy is less than translational, the non-equilibrium Treanor and Boltzmann distributions are close to each other, and for the case of high vibrational energy supply ($T_1/T > 1$), the Treanor distribution is significantly higher than the Boltzmann distribution in the entire range of vibrational numbers $i$.
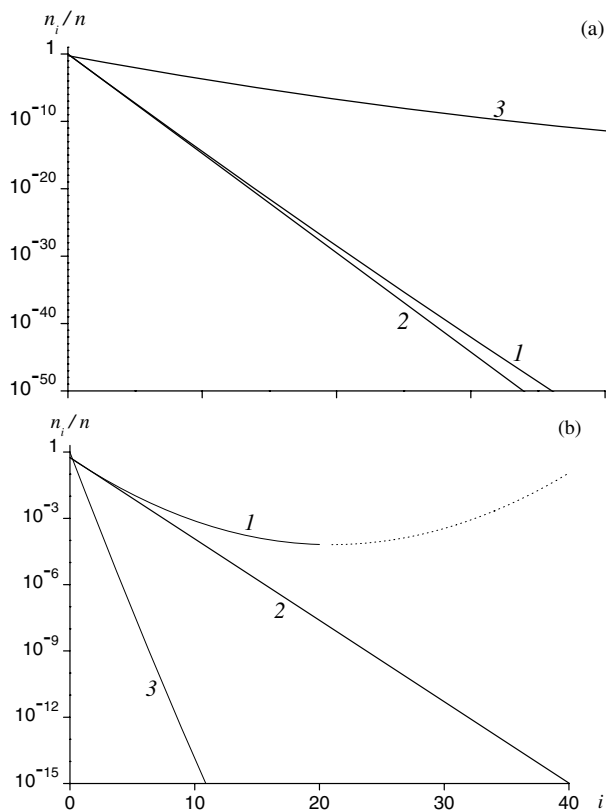
**Fig. 3.1** Dimensionless vibrational level populations in $N_2$

The increasing branch of the Treanor distribution, which is not physically realized, is indicated by the dotted line.

In some mixtures, vibrational quanta of all or several molecular species differ only slightly. In such a case, for these species the following relation is valid

$$\tau_{VV_1} \sim \tau_{VV_2} \ll \tau_{TRV}. \tag{3.20}$$

Under this condition, the corresponding parameters $\vartheta_c$ in Eq. (3.7) take close values. Then the vibrational temperatures are no longer independent functions and satisfy the relations following from the equality of parameters $\vartheta_c$. In a system of harmonic oscillators, if the condition (3.20) is valid for all species, a two-temperature quasi-stationary distribution is established, with a single vibrational temperature $T_v^c = T_v \; \forall c$. The assumption of equal vibrational temperatures of various components is rather attractive for practical applications, but its validity is limited. An empirical two-temperature model for a reacting gas mixture is proposed in [210, 211].

## 3.2   Macroscopic Parameters and Specific Heats

The distribution functions (3.7) depend on the macroscopic parameters $n_c(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$, $T(\mathbf{r},t)$, and $T_1^c(\mathbf{r},t)$. In the present case, in contrast to the state-to-state model, the number of main macroscopic parameters is reduced, and instead of the level populations of all vibrational states $n_{ci}$ it includes the vibrational temperatures $T_1^c$ and number densities $n_c$ of chemical species.

Let us write the normalizing conditions for the distribution function in the considered approach. In the formalism of the Chapman–Enskog method generalized for the case of rapid and slow processes (see Sections 1.4 and 2.1), the distribution function is normalized to the macroscopic parameters associated to the collision invariants of the most frequent collisions. Moreover, like in the classical Chapman–Enskog method, the main macroscopic parameters are not expanded into the series over the small parameter but are completely determined by the zero-order distribution functions.

Keeping in mind the above discussion, we obtain the conditions of normalization in the form:

$$\sum_{ij} \int f_{cij} d\mathbf{u}_c = \sum_{ij} \int f_{cij}^{(0)} d\mathbf{u}_c = n_c, \qquad c = 1, ..., L, \tag{3.21}$$

$$\sum_{cij} m_c \int \mathbf{u}_c f_{cij} d\mathbf{u}_c = \sum_{cij} m_c \int \mathbf{u}_c f_{cij}^{(0)} d\mathbf{u}_c = \rho \mathbf{v}, \tag{3.22}$$

$$\sum_{cij} \int \left( \frac{m_c c_c^2}{2} + \varepsilon_j^c + \varepsilon_i^c \right) f_{cij} d\mathbf{u}_c = \sum_{cij} \int \left( \frac{m_c c_c^2}{2} + \varepsilon_j^c + \varepsilon_i^c \right) f_{cij}^{(0)} d\mathbf{u}_c =$$

$$= \frac{3}{2} nkT + \sum_{c=1}^{L_m} \rho_c E_{\mathrm{rot},c}(T) + \sum_{c=1}^{L_m} \rho_c E_{\mathrm{vibr},c}(T, T_1^c), \tag{3.23}$$

$$\sum_{ij} i \int f_{cij} d\mathbf{u}_c = \sum_{ij} i \int f_{cij}^{(0)} d\mathbf{u}_c = \rho_c W_c(T, T_1^c), \qquad c = 1, ..., L_m. \tag{3.24}$$

The condition (3.23) is written taking into account the formula (1.10) for the formation energy and the condition (3.21).

The conditions (3.23), (3.24) differ from the normalizing conditions (2.8)–(2.11), (2.14), (2.15) derived in the state-to-state approach. In accordance with the conditions (2.12) and (2.14), the distribution function in the state-to-state model is normalized not only to the total energy, but also to the translational-rotational energy (and therefore to the vibrational energy). This is explained by the fact that under the condition (1.43), the translational-rotational and vibrational energies in a rapid process are conserved independently, and the transfer between the translational-rotational and vibrational modes occurs only in slow processes. In the generalized multi-temperature approach (3.7), translational-rotational and vibrational energies vary simultaneously during the most frequent collisions, as $VV_1$ transitions with non-vanishing resonance defect represent one of the rapid processes. As a consequence, the distribution

function is normalized to the total energy of translational, rotational and vibrational modes, and, besides that, to the total number of vibrational quanta in each molecular species.

The gas temperature in the state-to-state approach, as is mentioned above, is specified by the equilibrium energy of the translational and rotational degrees of freedom. In the generalized multi-temperature approach, as it follows from the normalizing conditions (3.23), (3.24), the gas temperature $T$ and the temperatures of the first vibrational levels of molecular components $T_1^c$ are defined jointly by the total energy of translational, rotational and vibrational modes, as well as by the number of vibrational quanta in molecular species.

In a system of harmonic oscillators, the normalizing conditions are also different from (3.23), (3.24). In this case, the $VV_1$ exchange is strictly resonant, and, therefore, in the rapid processes the translational-rotational and vibrational energies are conserved independently. The gas temperature is specified by the translational-rotational energy, whereas the vibrational temperature $T_v^c$ by the vibrational energy.

For the anharmonic oscillator model, the specific vibrational energy of molecular species $c$ depends on two temperatures $(T, T_1^c)$ and is introduced by the expression

$$\rho_c E_{\text{vibr},c}(T, T_1^c) = \sum_i \varepsilon_i^c n_{ci}(T, T_1^c).$$

Keeping in mind the Treanor distribution (3.14), we obtain

$$E_{\text{vibr},c}(T, T_1^c) = \frac{1}{m_c Z_c^{\text{vibr}}(T, T_1^c)} \sum_i s_i^c \varepsilon_i^c \exp\left(-\frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} - \frac{i\varepsilon_1^c}{kT_1^c}\right). \tag{3.25}$$

Similarly, the expression for the specific number of vibrational quanta of $c$ species takes the form

$$W_c(T, T_1^c) = \frac{1}{m_c Z_c^{\text{vibr}}(T, T_1^c)} \sum_i s_i^c i \exp\left(-\frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} - \frac{i\varepsilon_1^c}{kT_1^c}\right). \tag{3.26}$$

Since under non-equilibrium conditions the total specific energy of a system depends on two temperatures $(T, T_1^c)$, for the description of the system thermodynamic properties it is relevant to introduce two components of the vibrational specific heat, defining them as partial derivatives of the vibrational energy with respect to corresponding temperatures $T$ and $T_1^c$:

$$c_{\text{v},c}^T(T, T_1^c) = \frac{\partial E_{\text{vibr},c}}{\partial T}, \tag{3.27}$$

$$c_{\text{v},c}^{T_1}(T, T_1^c) = \frac{\partial E_{\text{vibr},c}}{\partial T_1^c}, \tag{3.28}$$

where the vibrational energy is given by (3.25). Hereafter, $c_{\text{v},c}^T$, $c_{\text{v},c}^{T_1}$ will be called the non-equilibrium modified specific heats of vibrational degrees of freedom. In order

to simplify the notations, the subscript "v" instead of "vibr" is used in the definitions for the modified specific heats $c_{v,c}^T$, $c_{v,c}^{T_1}$.

In addition to that, similar coefficients associated to the specific number of vibrational quanta (3.26) can be introduced:

$$c_{w,c}^T(T,T_1^c) = \frac{\varepsilon_1^c \partial W_c}{\partial T}, \tag{3.29}$$

$$c_{w,c}^{T_1}(T,T_1^c) = \frac{\varepsilon_1^c \partial W_c}{\partial T_1^c}. \tag{3.30}$$

These values can be treated as partial vibrational specific heats, since they are defined as derivatives with respect to the temperatures $T$ and $T_1^c$ of the part of vibrational energy equal to $\varepsilon_1^c W_c$ rather than the total vibrational energy. The partial specific heats (3.29), (3.30), unlike the specific heats (3.27), (3.28), are designated by the subscript "w". Below, the parameters associated to the specific number of vibrational quanta have the subscript "w".

The modified vibrational specific heats calculated on the basis of the definitions (3.27)–(3.30) depend on two temperatures $(T, T_1^c)$ and significantly differ from both the thermal equilibrium specific heat and the vibrational specific heat introduced for harmonic oscillators. For the harmonic oscillator model, the specific vibrational energy of $c$ species does not depend on the gas temperature $T$. Moreover, the specific vibrational energy $E_{\text{vibr},c}$ and the specific number of vibrational quanta $W_c$ are connected by the simple relation

$$E_{\text{vibr},c}(T_v^c) = \varepsilon_1^c W_c(T_v^c) = \frac{1}{m_c Z_c^{\text{vibr}}(T_v^c)} \sum_i s_i^c \varepsilon_i^c \exp\left(-\frac{\varepsilon_i^c}{kT_v^c}\right). \tag{3.31}$$

This relation makes it possible to treat the value $\varepsilon_1^c W_c$ as a harmonic component of the total vibrational energy $E_{\text{vibr},c}$ for a system of anharmonic oscillators.

It follows from Eq. (3.31) that in a system of harmonic oscillators, there is the only vibrational specific heat $c_{v,c}^{T_v}$ for each molecular species, and it is totally specified by the vibrational temperature $T_v^c$:

$$c_{v,c}^{T_v}(T_v^c) = \frac{\partial E_{\text{vibr},c}}{\partial T_v^c}, \tag{3.32}$$

$$c_{v,c}^T = c_{w,c}^T = 0, \qquad c_{w,c}^{T_v} = c_{v,c}^{T_v}.$$

When the infinite number of vibrational levels is taken into account, the final expression for $c_{v,c}^{T_v}(T_v^c)$ coincides with the expression (1.26) for the equilibrium specific heat of vibrational degrees of freedom, keeping in mind that in Eq. (1.26), the gas temperature $T$ should be replaced with the vibrational temperature $T_v^c$. Some results for the non-equilibrium specific heats in a single-component gas are discussed in Section 3.7.

## 3.3 Governing Equations in the Multi-Temperature Approach

The governing equations for the macroscopic parameters $n_c(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$, $T(\mathbf{r},t)$, and $T_1^c(\mathbf{r},t)$ were derived in [60, 59]. A closed system of reacting multi-component mixture dynamics consists of the equations of the multi-temperature chemical kinetics for the species number densities, conservation equations for the momentum and the total energy, and additional relaxation equations for the specific numbers of vibrational quanta $W_c$ in each molecular species $c$:

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c^{\text{react}}, \quad c = 1,...,L, \tag{3.33}$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \boldsymbol{P} = 0, \tag{3.34}$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \boldsymbol{P} : \nabla \mathbf{v} = 0, \tag{3.35}$$

$$\rho_c \frac{dW_c}{dt} + \nabla \cdot \mathbf{q}_{\text{w},c} = R_c^{\text{w}} - W_c m_c R_c^{\text{react}} + W_c \nabla \cdot (\rho_c \mathbf{V}_c), \tag{3.36}$$

$$c = 1,...,L_{\text{m}}.$$

The conservation equations for the momentum and total energy (3.34) and (3.35) formally coincide with the corresponding equations (2.17) and (2.18) obtained in the state-to-state approach. One should however bear in mind that in the multi-temperature approach, the total energy is a function of $T$, $T_1^c$, and $n_c$ and the transport terms are expressed as functions of the same set of macroscopic parameters (see Section 3.5). The diffusion velocity $\mathbf{V}_c$ in the equations of multi-temperature chemical kinetics (3.33) is introduced by the formula (1.11). The source terms in Eqs. (3.33) are determined by the collision operator of chemical reactions

$$R_c^{\text{react}} = \sum_{ij} \int J_{cij}^{\text{react}} d\mathbf{u}_c. \tag{3.37}$$

The production terms in the relaxation equations (3.36) for the specific numbers of vibrational quanta are expressed as functions of collision operators of all slow processes: $VV_2$ and TRV vibrational energy transfers and chemical reactions,

$$R_c^{\text{w}} = \sum_{ij} i \int J_{cij}^{\text{sl}} d\mathbf{u}_c = R_c^{\text{w},VV_2} + R_c^{\text{w},\text{TRV}} + R_c^{\text{w},\text{react}}. \tag{3.38}$$

The value $\mathbf{q}_{\text{w},c}$ in Eq. (3.36) has the physical meaning of the vibrational quanta flux of $c$ molecular species and is introduced on the basis of the additional collision invariant of the most frequent collisions $i_c$:

$$\mathbf{q}_{\text{w},c} = \sum_{ij} i \int \mathbf{c}_c f_{cij} d\mathbf{u}_c.$$

Thus the equations of non-equilibrium chemical kinetics (3.33) coupled to the conservation equations of the momentum and the total energy (3.34), (3.35), as well as to the relaxation equations (3.36) for the specific numbers of vibrational quanta in molecular components $W_c$ (3.36) form a closed system of governing equations for the macroscopic parameters of a reacting gas mixture flow in the generalized multi-temperature approach. It is obvious that the system (3.33)–(3.36) is considerably simpler than the corresponding system (2.16)–(2.18) in the state-to-state approach, as it contains much fewer equations. Indeed, instead of $\sum_c L_c$ ($c = 1, 2, ..., L_m$ stands for the molecular species) equations for the vibrational level populations, one should solve $L_m$ equations for the numbers of quanta and $L_m$ equations for the number densities of the chemical components ($L_c$ is the number of vibrational levels in the molecular species $c$, $L_m$ is the number of the molecular species in a mixture). Consequently, for a two-component mixture containing nitrogen molecules and atoms, one relaxation equation for $W_{N_2}$ and one equation for the number density of $N_2$ molecules should be solved instead of 46 equations for the level populations. While studying the important for practical applications five-component air mixture $N_2$, $O_2$, NO, N, O in the state-to-state approach, one should solve $L_{N_2} + L_{O_2} + L_{NO} = 114$ equations for the vibrational level populations. In the multi-temperature approach, they are reduced to six equations: three for the molecular number densities and three for $T_1^{N_2}$, $T_1^{O_2}$, and $T_1^{NO}$.

In a system of harmonic oscillators, the relaxation equations for the specific numbers of vibrational quanta $W_c$ (3.36) are transformed into those for the specific vibrational energy (see the relation (3.31)):

$$\rho_c \frac{dE_{\mathrm{vibr},c}}{dt} + \nabla \cdot \mathbf{q}_{\mathrm{vibr},c} = R_c^{\mathrm{vibr}} - E_{\mathrm{vibr},c} m_c R_c^{\mathrm{react}} + E_{\mathrm{vibr},c} \nabla \cdot (\rho_c \mathbf{V}_c),$$

$$c = 1, 2, ..., L_{\mathrm{m}},$$

with

$$\mathbf{q}_{\mathrm{vibr},c} = \varepsilon_1^c \mathbf{q}_{\mathrm{w},c}, \qquad R_c^{\mathrm{vibr}} = \varepsilon_1^c R_c^{\mathrm{w}}.$$

In the zero-order approximation of the Chapman–Enskog method, the transport terms are found taking into account the distribution function (3.7):

$$\mathbf{q}^{(0)} = \mathbf{q}_{\mathrm{w},c}^{(0)} = 0, \quad \mathbf{V}_c^{(0)} = 0, \quad \mathbf{P}^{(0)} = p\mathbf{I},$$

and the system (3.33)–(3.36) takes the form typical for inviscid non-conductive flows

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} = R_c^{\mathrm{react}(0)}, \qquad c = 1, ..., L, \tag{3.39}$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla p = 0, \tag{3.40}$$

$$\rho \frac{dU}{dt} + p \nabla \cdot \mathbf{v} = 0, \tag{3.41}$$

$$\rho_c \frac{dW_c}{dt} = R_c^{\mathrm{w}(0)} - m_c W_c R_c^{\mathrm{react}(0)}, \quad c = 1, ..., L_{\mathrm{m}}. \tag{3.42}$$

The production terms in equations (3.39), (3.42) are given by the formulae

$$R_c^{\text{react}(0)} = \sum_{ij} \int J_{cij}^{\text{react}(0)} d\mathbf{u}_c,$$

$$R_c^{\text{w}(0)} = \sum_{ij} \int i J_{cij}^{\text{sl}(0)} d\mathbf{u}_c$$

and contain the zero-order operators of VV$_2$ and TRV vibrational energy exchanges and chemical reactions.

## 3.4 First-Order Distribution Function

In the generalized multi-temperature approach, the linear integral equations for the first-order distribution functions take the form:

$$-\sum_d n_c n_d I_{cijd}(\varphi) = D f_{cij}^{(0)} - J_{cij}^{\text{sl}(0)}, \tag{3.43}$$

where the linearized integral operator of the most frequent collisions $I_{cijd}(\varphi)$ is introduced by the formula

$$I_{cijd}(\varphi) = \frac{1}{n_c n_d} \sum_{kli'j'k'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} \left( \varphi_{cij} + \varphi_{dkl} - \varphi_{ci'j'} - \varphi_{dk'l'} \right) \times$$

$$\times g \sigma_{cd,ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u}_d. \tag{3.44}$$

The expression (2.26) for the derivative of the distribution function $D f_{cij}^{(0)}$ in the multi-temperature approach can be written using the multi-temperature zero-order distribution function and the macroscopic equations corresponding to the zero-order approximation:

$$D f_{cij}^{(0)} = f_{cij}^{(0)} \left\{ \left( \frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[ \frac{\varepsilon_j^c}{kT} \right]_{\text{rot}}' + \left[ \frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} \right]_{\text{vibr}}' \right) \mathbf{c}_c \cdot \nabla \ln T + \right.$$

$$+ \left[ \frac{i\varepsilon_1^c}{kT_1^c} \right]_{\text{vibr}}' !\mathbf{c}_c \cdot \nabla \ln T_1^c + \frac{n}{n_c} \mathbf{c}_c \cdot \mathbf{d}_c + \frac{m_c}{kT} \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I} \right) : \nabla \mathbf{v} +$$

$$+ \left( \frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[ \frac{\varepsilon_j^c}{kT} \right]_{\text{rot}}' + \left[ \frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} \right]_{\text{vibr}}' \right) \frac{1}{T} \frac{dT}{dt} +$$

$$+ \frac{1}{T_1^c} \frac{dT_1^c}{dt} \left[ \frac{i\varepsilon_1^c}{kT_1^c} \right]_{\text{vibr}}' + \left( \frac{m_c c_c^2}{3kT} - 1 \right) \nabla \cdot \mathbf{v} + \frac{R_c^{\text{react}(0)}}{n_c} \right\}. \tag{3.45}$$

Here, the diffusive driving force $\mathbf{d}_c$ for particles $c$ is defined in the classical way [82]

$$\mathbf{d}_c = \nabla \left( \frac{n_c}{n} \right) + \left( \frac{n_c}{n} - \frac{\rho_c}{\rho} \right) \nabla \ln p, \tag{3.46}$$

notations $[\zeta_i]'_{\text{vibr}} = \zeta_i - \langle \zeta_i \rangle_{\text{vibr}}$ and $[\zeta_j]'_{\text{rot}} = \zeta_j - \langle \zeta_j \rangle_{\text{rot}}$ are introduced to simplify the representation of equations. The definition of the averaging operation over the rotational spectrum is given by the expression (2.28). Averaging over the vibrational spectrum is performed on the basis of the non-equilibrium quasi-stationary Treanor distribution (3.14):

$$\langle \zeta_i \rangle_{\text{vibr}} = \frac{\sum\limits_i s_i^c \zeta_i \exp \left( -\frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} - \frac{i\varepsilon_1^c}{kT_1^c} \right)}{\sum\limits_i s_i^c \exp \left( -\frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} - \frac{i\varepsilon_1^c}{kT_1^c} \right)}. \tag{3.47}$$

The equations for the calculation of $dT/dt$ and $dT_1^c/dt$ follow from the transport equations in the zero-order approximation (3.39)–(3.42):

$$\rho c_{\text{u}} \frac{dT}{dt} + \sum_c \rho_c c_{\text{v},c}^{T_1} \frac{dT_1^c}{dt} = -p \nabla \cdot \mathbf{v} - \sum_c R_c^{\text{react}(0)} U_c, \tag{3.48}$$

$$\rho_c c_{\text{w},c}^T \frac{dT}{dt} + \rho_c c_{\text{w},c}^{T_1} \frac{dT_1^c}{dt} = R_c^{\varepsilon(0)}, \quad c = 1, ..., L_{\text{m}}, \tag{3.49}$$

here, the following notations are introduced:

$$U_c = \frac{3}{2} kT + \langle \varepsilon_j^c \rangle_{\text{rot}} + \langle \varepsilon_i^c \rangle_{\text{vibr}} + \varepsilon_c;$$

$$R_c^{\varepsilon(0)} = \varepsilon_1^c R_c^{\text{w}(0)} - R_c^{\text{react}(0)} \langle i\varepsilon_1^c \rangle_{\text{vibr}};$$

$$c_{\text{u}} = \frac{\partial U}{\partial T} = c_{\text{tr}} + c_{\text{rot}} + \sum_c \frac{\rho_c}{\rho} c_{\text{v},c}^T + c_{\text{f}}. \tag{3.50}$$

The modified specific heat (3.50) differs from the equilibrium specific heat defined by Eq. (1.15) since the total specific energy $U$ under the non-equilibrium conditions depends not only on the temperature $T$, but also on the temperatures of the first vibrational levels $T_1^c$. Let us remind that the specific heats $c_{\text{tr}}$, $c_{\text{rot}}$, $c_{\text{v},c}^T$, $c_{\text{v},c}^{T_1}$, $c_{\text{w},c}^T$, and $c_{\text{w},c}^{T_1}$ are calculated on the basis of Eqs. (1.23), (1.22), (3.27)–(3.30).
    The determinant $\Delta$ of the linear system (3.48), (3.49) for the derivatives $dT/dt$, $dT_1^c/dt$ is equal to

$$\Delta = \rho_c c_{\text{w},c}^{T_1} \left( \rho c_{\text{u}} - \sum_c \rho_c c_{\text{w},c}^T \frac{c_{\text{v},c}^{T_1}}{c_{\text{w},c}^{T_1}} \right). \tag{3.51}$$

It is not equal to zero due to the properties of the specific heats calculated on the basis of the Treanor distribution (3.14): the second term in brackets in Eq. (3.51) is always negative, since the coefficients $c_{v,c}^{T_1}$, $c_{w,c}^{T_1}$ are always positive, and $c_{w,c}^{T}$ are always negative. The first term in brackets in Eq. (3.51) includes small negative anharmonic corrections $c_{v,c}^{T}$; in the range of validity of the Treanor distribution, the absolute values of these corrections are considerably smaller than always positive values $c_{tr}$ and $c_{rot}$. Thus $\Delta$ appears to be a positive value.

The derivatives $dT/dt$ and $dT_1^c/dt$ can be found from Eqs. (3.48), (3.49) in the explicit form:

$$\frac{dT}{dt} = \frac{-p\nabla \cdot \mathbf{v} - \sum_c R_c^{react(0)} U_c - \sum_c \frac{c_{v,c}^{T_1}}{c_{w,c}^{T_1}} R_c^{\varepsilon(0)}}{\rho c_u - \sum_c \rho_c c_{w,c}^{T} \frac{c_{v,c}^{T_1}}{c_{w,c}^{T_1}}},$$

$$\frac{dT_1^c}{dt} = \left[\rho_c c_{w,c}^{T_1}\left(\rho c_u - \sum_b \rho_b c_{w,b}^{T} \frac{c_{v,b}^{T_1}}{c_{w,b}^{T_1}}\right)\right]^{-1}\left[\rho_c c_{w,c}^{T}\sum_b R_b^{\varepsilon(0)}\frac{c_{v,b}^{T_1}}{c_{w,b}^{T_1}} + \right.$$

$$\left. +\rho_c c_{w,c}^{T}\left(p\nabla \cdot \mathbf{v} + \sum_b R_b^{react(0)} U_b\right) + \rho c_u R_c^{\varepsilon(0)} - R_c^{\varepsilon(0)}\sum_b \rho_b c_{w,b}^{T}\frac{c_{v,b}^{T_1}}{c_{w,b}^{T_1}}\right],$$

$$c = 1, 2, ..., L_m.$$

From the last expressions we can notice that $dT/dt$, $dT_1^c/dt$ depend linearly on $\nabla \cdot \mathbf{v}$, $R_c^{w(0)}$, and $R_c^{react(0)}$. Let us introduce some notations:

$$\Phi_0 = \rho c_u - \sum_c \rho_c c_{w,c}^{T}\frac{c_{v,c}^{T_1}}{c_{w,c}^{T_1}}, \tag{3.52}$$

$$\Phi_1 = -\sum_c R_c^{react(0)} U_c - \sum_c \frac{c_{v,c}^{T_1}}{c_{w,c}^{T_1}} R_c^{\varepsilon(0)}, \tag{3.53}$$

$$\Phi_2^c = \rho_c c_{w,c}^{T}\sum_b R_b^{\varepsilon(0)}\frac{c_{v,b}^{T_1}}{c_{w,b}^{T_1}} + \rho_c c_{w,c}^{T}\sum_b R_b^{react(0)} U_b + \rho c_u R_c^{\varepsilon(0)} -$$

$$-R_c^{\varepsilon(0)}\sum_b \rho_b c_{w,b}^{T}\frac{c_{v,b}^{T_1}}{c_{w,b}^{T_1}}, \qquad c = 1, 2, ..., L_m. \tag{3.54}$$

Then

$$\frac{dT}{dt} = \frac{-p\nabla \cdot \mathbf{v} + \Phi_1}{\Phi_0}, \tag{3.55}$$

$$\frac{dT_1^c}{dt} = \frac{\rho_c c_{w,c}^{T} p\nabla \cdot \mathbf{v} + \Phi_2^c}{\rho_c c_{w,c}^{T_1}\Phi_0}, \qquad c = 1, 2, ..., L_m. \tag{3.56}$$

Substituting Eqs. (3.55), (3.56) into the right-hand side of Eq. (3.45), we can ensure that the first-order distribution function can be written in the following structural form:

$$f_{cij}^{(1)} = f_{cij}^{(0)} \left( -\frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_d \mathbf{A}_{cij}^{d(1)} \cdot \nabla \ln T_1^d - \frac{1}{n} \sum_d \mathbf{D}_{cij}^d \cdot \mathbf{d}_d - \right.$$

$$\left. -\frac{1}{n} \mathbf{B}_{cij} : \nabla \mathbf{v} - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right). \tag{3.57}$$

The coefficients $\mathbf{A}_{cij}$, $\mathbf{A}_{cij}^{d(1)}$, $\mathbf{B}_{cij}$, $\mathbf{D}_{cij}^d$, $F_{cij}$, and $G_{cij}$ are functions of the peculiar velocity and macroscopic parameters of the particles. The integral equations for them can be derived substituting Eq. (3.45) into (3.43) and comparing the coefficients at the gradients of the same macroscopic parameters:

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}(\mathbf{A}) = \frac{1}{n} f_{cij}^{(0)} \left( \frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[ \frac{\varepsilon_j^c}{kT} \right]_{\text{rot}}' + \left[ \frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} \right]_{\text{vibr}}' \right) \mathbf{c}_c, \tag{3.58}$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}\left(\mathbf{A}^{b(1)}\right) = \frac{1}{n} f_{cij}^{(0)} \left[ \frac{i\varepsilon_1^c}{kT_1^c} \right]_{\text{vibr}}' \mathbf{c}_c, \quad b = 1,...,L_{\text{m}}, \tag{3.59}$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}\left(\mathbf{D}^b\right) = \frac{1}{n_c} f_{cij}^{(0)} \left( \delta_{cb} - \frac{\rho_c}{\rho} \right) \mathbf{c}_c, \quad b = 1,...,L, \tag{3.60}$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}(\mathbf{B}) = \frac{m_c}{nkT} f_{cij}^{(0)} \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I} \right), \tag{3.61}$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}(F) = \frac{1}{n} f_{cij}^{(0)} \left( \frac{m_c c_c^2}{3kT} - 1 + \frac{p}{T_1^c \Phi_0} \frac{c_{\text{w},c}^T}{c_{\text{w},c}^{T_1}} \left[ \frac{i\varepsilon_1^c}{kT_1^c} \right]_{\text{vibr}}' - \right.$$

$$\left. -\frac{p}{T\Phi_0} \left( \frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[ \frac{\varepsilon_j^c}{kT} \right]_{\text{rot}}' + \left[ \frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} \right]_{\text{vibr}}' \right) \right), \tag{3.62}$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}(G) = -\frac{1}{n} J_{cij}^{\text{sl}(0)} + \frac{1}{n} f_{cij}^{(0)} \left( \frac{\Phi_2^c}{\rho_c c_{\text{w},c}^{T_1} T_1^c \Phi_0} \left[ \frac{i\varepsilon_1^c}{kT_1^c} \right]_{\text{vibr}}' + \right.$$

$$\left. +\frac{\Phi_1}{T\Phi_0} \left( \frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[ \frac{\varepsilon_j^c}{kT} \right]_{\text{rot}}' + \left[ \frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} \right]_{\text{vibr}}' \right) + \frac{R_c^{\text{react}(0)}}{n_c} \right), \tag{3.63}$$

quantities $\Phi_0$, $\Phi_1$, $\Phi_2^c$ are introduced in Eqs. (3.52)–(3.54).

The linear integral operators in the equations (3.58)–(3.63) depend on the differential cross sections of the most frequent collisions. In the multi-temperature approach developed in the present Chapter, the most frequent collisions include elastic collisions, as well as those resulting in the rotational energy exchange and $VV_1$ vibrational energy transitions.

The normalizing conditions (3.21)–(3.24) impose the following additional constraints on the functions $\mathbf{A}_{cij}$, $\mathbf{A}_{cij}^{d(1)}$, $\boldsymbol{B}_{cij}$, $\mathbf{D}_{cij}^d$, $F_{cij}$, and $G_{cij}$:

$$\sum_{cij} m_c \int f_{cij}^{(0)} A_{cij} c_c^2 d\mathbf{u}_c = 0, \tag{3.64}$$

$$\sum_{cij} m_c \int f_{cij}^{(0)} A_{cij}^{d(1)} c_c^2 d\mathbf{u}_c = 0, \quad d = 1, ..., L_{\mathrm{m}}, \tag{3.65}$$

$$\sum_{cij} m_c \int f_{cij}^{(0)} D_{cij}^d c_c^2 d\mathbf{u}_c = 0, \quad d = 1, ..., L, \tag{3.66}$$

$$\sum_{ij} \int f_{cij}^{(0)} F_{cij} d\mathbf{u}_c = 0, \quad c = 1, ..., L, \tag{3.67}$$

$$\sum_{ij} \int f_{cij}^{(0)} G_{cij} d\mathbf{u}_c = 0, \quad c = 1, ..., L, \tag{3.68}$$

$$\sum_{cij} \int f_{cij}^{(0)} \left( \frac{m_c c_c^2}{2} + \varepsilon_j^c + \varepsilon_i^c \right) F_{cij} d\mathbf{u}_c = 0, \tag{3.69}$$

$$\sum_{cij} \int f_{cij}^{(0)} \left( \frac{m_c c_c^2}{2} + \varepsilon_j^c + \varepsilon_i^c \right) G_{cij} d\mathbf{u}_c = 0, \tag{3.70}$$

$$\sum_{ij} i \int f_{cij}^{(0)} F_{cij} d\mathbf{u}_c = 0, \quad c = 1, ..., L_{\mathrm{m}}, \tag{3.71}$$

$$\sum_{ij} i \int f_{cij}^{(0)} G_{cij} d\mathbf{u}_c = 0, \quad c = 1, ..., L_{\mathrm{m}}. \tag{3.72}$$

The diffusive thermodynamic forces $\mathbf{d}_c$ are not linearly independent due to the relation

$$\sum_c \mathbf{d}_c = 0.$$

Therefore, the constraint (3.66) is to be complemented by another one

$$\sum_d \frac{\rho_d}{\rho} \mathbf{D}_{cij}^d = 0. \tag{3.73}$$

The equations (3.58)–(3.63) together with the constraints (3.64)–(3.73) provide the unique solutions for the functions $\mathbf{A}_{cij}$, $\mathbf{A}_{cij}^{d(1)}$, $\boldsymbol{B}_{cij}$, $\mathbf{D}_{cij}^d$, $F_{cij}$, and $G_{cij}$.

## 3.5 First-Order Transport Terms

In this section, the transport terms in Eqs. (3.33)–(3.36) are considered on the basis of the first-order distribution function (3.57). The expression for the viscous stress tensor formally coincides with Eq. (2.43), the shear and bulk viscosity coefficients, as well as the relaxation pressure, are specified in terms of bracket integrals by the formulae (2.44). However, in the multi-temperature approach, the bracket integrals $[A, B]$ themselves are introduced differently compared to the state-to-state model:

$$[A, B] = \sum_{cd} \frac{n_c n_d}{n^2} \left( [A, B]'_{cd} + [A, B]''_{cd} \right), \tag{3.74}$$

$$[A, B]'_{cd} = \frac{1}{2 n_c n_d} \sum_{ijkli'j'k'l'} \int f^{(0)}_{cij} f^{(0)}_{dkl} \left( B_{cij} - B_{ci'j'} \right) \times$$

$$\times \left( A_{cij} - A_{ci'j'} \right) g \sigma^{i'j'k'l'}_{cd,ijkl} d^2 \Omega d\mathbf{u}_c d\mathbf{u}_d, \tag{3.75}$$

$$[A, B]''_{cd} = \frac{1}{2 n_c n_d} \sum_{ijkli'j'k'l'} \int f^{(0)}_{cij} f^{(0)}_{dkl} \left( B_{cij} - B_{ci'j'} \right) \times$$

$$\times \left( A_{dkl} - A_{dk'l'} \right) g \sigma^{i'j'k'l'}_{cd,ijkl} d^2 \Omega d\mathbf{u}_c d\mathbf{u}_d. \tag{3.76}$$

The partial bracket integrals $[A, B]'_{cd}$ and $[A, B]''_{cd}$ depend on the cross sections of elastic collisions and collisions resulting in the RT and VV$_1$ energy exchanges, i.e. on the cross sections of the most probable processes according to the relation (3.1) for the characteristic relaxation times.

Moreover, the linear integral equations (3.61)–(3.63) for the functions $\boldsymbol{B}_{cij}$, $F_{cij}$, and $G_{cij}$ defining the coefficients $\eta$, $\zeta$, and $p_{\mathrm{rel}}$ differ from the corresponding equations (2.33)–(2.35) in the state-to-state approach. First, the linear integral operators in the left-hand sides depend on the cross sections of collisions of different types. Second, the zero-order distribution functions $f^{(0)}_{cij}$ in the multi-temperature and state-to-state approaches are different from each other. In addition, the right-hand sides of the integral equations for the scalar functions $F_{cij}$ and $G_{cij}$ are not the same in the two considered approaches.

In the multi-temperature approach, the relaxation pressure $p_{\mathrm{rel}}$ and bulk viscosity coefficient $\zeta$ can be presented as sums of two terms:

$$\zeta = \zeta_{\mathrm{rot}} + \zeta_{\mathrm{vibr}}, \qquad p_{\mathrm{rel}} = p_{\mathrm{rel}}^{\mathrm{rot}} + p_{\mathrm{rel}}^{\mathrm{vibr}}, \tag{3.77}$$

where the first term is due to inelastic RT rotational energy exchange, whereas the second is connected to the $VV_1$ transitions in each vibrational mode.

The diffusion velocity in the first-order approximation takes the form

$$\mathbf{V}_c = -\sum_d D_{cd} \mathbf{d}_d - D_{Tc} \nabla \ln T - \sum_d D_{Tc}^{d(1)} \nabla \ln T_1^d, \tag{3.78}$$

and the diffusion and thermal diffusion coefficients $D_{cd}$ and $D_{Tc}$ for the particles of each chemical species are given by the formulae

$$D_{cd} = \frac{1}{3n}\left[\mathbf{D}^c, \mathbf{D}^d\right], \qquad D_{Tc} = \frac{1}{3n}\left[\mathbf{D}^c, \mathbf{A}\right]. \tag{3.79}$$

In addition to that, the formal derivation for the expression (3.78) leads to the appearance of additional thermal diffusion coefficients $D_{Tc}^{d(1)}$ associated with the gradients of temperatures of the first level in each vibrational mode:

$$D_{Tc}^{d(1)} = \frac{1}{3n}\left[\mathbf{D}^c, \mathbf{A}^{d(1)}\right]. \tag{3.80}$$

The total energy flux and the fluxes of vibrational quanta depend on the gradients of the gas temperature $T$, the temperatures of the first vibrational level $T_1^c$, and the molar fractions of chemical species $n_c/n$:

$$\mathbf{q} = -\left(\lambda' + \sum_c \lambda_{\text{vt},c}\right)\nabla T - \sum_c \left(\lambda_{\text{tv},c}\nabla T_1^c + \sum_d \lambda_{\text{vv},cd}\nabla T_1^d\right) -$$

$$-p\sum_c D_{Tc}\mathbf{d}_c - p\sum_c \frac{T_1^c}{T}\sum_d D_{Tc}^{d(1)}\mathbf{d}_d +$$

$$+\sum_c \left(\frac{5}{2}kT + \langle \varepsilon_j^c\rangle_{\text{rot}} + \langle \varepsilon_i^c\rangle_{\text{vibr}} + \varepsilon_c\right)n_c\mathbf{V}_c, \tag{3.81}$$

$$\varepsilon_1^c\mathbf{q}_{\text{w},c} = -\lambda_{\text{vt},c}\nabla T - \sum_d \lambda_{\text{vv},cd}\nabla T_1^d - p\frac{T_1^c}{T}\varepsilon_1^c\sum_d D_{Tc}^{d(1)}\mathbf{d}_d. \tag{3.82}$$

The heat conductivity coefficients in the expressions (3.81), (3.82) are also introduced on the basis of the bracket integrals:

$$\lambda' = \frac{k}{3}\left[\mathbf{A}, \mathbf{A}\right], \qquad \lambda_{\text{vt},c} = \frac{kT_1^c}{3T}\left[\mathbf{A}^{c(1)}, \mathbf{A}\right],$$

$$\lambda_{\text{tv},c} = \frac{kT}{3T_1^c}\left[\mathbf{A}, \mathbf{A}^{c(1)}\right], \qquad \lambda_{\text{vv},cd} = \frac{k}{3}\left[\mathbf{A}^{d(1)}, \mathbf{A}^{c(1)}\right]. \tag{3.83}$$

The coefficient $\lambda'$ describes the transport of the translational and rotational energy, as well as of a small part of the vibrational energy, which is transferred to the translational mode as a result of the non-resonant $VV_1$ transitions between molecules simulated by anharmonic oscillators. Hence the coefficient $\lambda'$ can be represented as a sum of three corresponding terms: $\lambda' = \lambda_{\text{tr}} + \lambda_{\text{rot}} + \lambda_{\text{anh}}$. The coefficients $\lambda_{\text{vv},cd}$ are associated with the transport of vibrational quanta in each molecular species and thus describe the transport of the main part of vibrational energy $\varepsilon_1^c W_c$. The cross coefficients $\lambda_{\text{vt},c}$, $\lambda_{\text{tv},c}$ are specified by both the transport of vibrational quanta and the vibrational energy loss (or gain) as a result of non-resonant $VV_1$ transitions. For

low values of the ratio $T_1^c/T$, the coefficients $\lambda_{\text{anh}}$, $\lambda_{\text{vt},c}$, and $\lambda_{\text{tv},c}$ are much smaller compared to $\lambda_{\text{vv},cd}$, and for the harmonic oscillator model $\lambda_{\text{vt},c} = \lambda_{\text{tv},c} = \lambda_{\text{anh}} = 0$ since $VV_1$ transitions appear to be strictly resonant. For the same reason, the coefficients $\zeta_{\text{vibr}}$ and $p_{\text{rel}}^{\text{vibr}}$ disappear in a system of harmonic oscillators.

It should be noted that the expressions (3.78), (3.81), and (3.82) are written formally on the basis of the first-order distribution function (3.57). In Refs. [60, 59], it is shown that some of the heat conductivity and thermal diffusion coefficients disappear because of the orthogonality of the polynomials used for the expansion of the functions $\mathbf{A}_{cij}$ and $\mathbf{A}_{cij}^{d(1)}$. This problem is discussed in Chapter 5 in more detail. In particular, $\lambda_{\text{vv},cd} = 0$ for $c \neq d$, and $D_{Tc}^{d(1)} = 0$ for any $d$. This makes it possible to simplify the expressions for the diffusion velocity and the heat flux:

$$\mathbf{V}_c = -\sum_d D_{cd}\mathbf{d}_d - D_{Tc}\nabla \ln T, \tag{3.84}$$

$$\mathbf{q} = -\left(\lambda' + \sum_c \lambda_{\text{vt},c}\right)\nabla T - \sum_c (\lambda_{\text{tv},c} + \lambda_{\text{vv},cc})\nabla T_1^c -$$

$$-p\sum_c D_{Tc}\mathbf{d}_c + \sum_c \rho_c h_c \mathbf{V}_c, \tag{3.85}$$

$$\varepsilon_1^c \mathbf{q}_{\text{w},c} = -\lambda_{\text{vt},c}\nabla T - \lambda_{\text{vv},cc}\nabla T_1^c.$$

Hereafter, the simplified expressions for $\mathbf{V}_c$, $\mathbf{q}$ and $\mathbf{q}_{\text{w},c}$ are used.

While writing Eq. (3.85) we take into account the relation $\langle \varepsilon_i^c \rangle_{\text{vibr}} = m_c E_{\text{vibr},c}$, the relation (2.29), as well as the definition for the specific enthalpy of $c$ particles

$$h_c = \frac{5}{2}\frac{kT}{m_c} + E_{\text{rot},c} + E_{\text{vibr},c} + \frac{\varepsilon_c}{m_c}, \qquad h = \sum_c \frac{\rho_c}{\rho} h_c.$$

The expressions for the diffusion velocity and heat flux in the multi-temperature approach are significantly different from the corresponding expressions in the state-to-state approach. Within the framework of the state-to-state model, the diffusion velocities and heat flux are determined by the gradients of temperature and all vibrational level populations, in the quasi-stationary approach $\mathbf{V}_c$ and $\mathbf{q}$ depend on the gradients of chemical species concentrations, the gas temperature and the temperatures of the first vibrational levels (or, for harmonic oscillators, vibrational temperatures) of molecular species. The number of independent diffusion coefficients in the multi-temperature model is considerably smaller than that in the approach accounting for the detailed vibrational kinetics. Therefore the use of the quasi-stationary vibrational distributions noticeably facilitates the heat fluxes calculation in a multi-component reacting gas mixture.

The proposed kinetic theory was applied in Ref. [59] for the simulation of gas-dynamic parameters, transport coefficients and heat fluxes in non-equilibrium reacting air flows behind strong shock waves.

## 3.6 Production Terms

In Section 3.3, the closed set of governing equations of a reacting gas mixture flow is derived in the generalized multi-temperature approach. The equations of the non-equilibrium kinetics (3.33), (3.36) contain the production terms $R_c^{\text{react}}$ and $R_c^{\text{w}}$. The chemical production term $R_c^{\text{react}}$ describes the variation of the particle $c$ number density due to chemical reactions, whereas the term $R_c^{\text{w}}$ characterizes the variation of the specific number of vibrational quanta $W_c$ in molecular species $c$ due to both slow vibrational energy exchanges and chemical reactions. To close the set of equations (3.33)–(3.36) it is necessary to express the production terms $R_c^{\text{react}}$ and $R_c^{\text{w}}$ as functions of the main macroscopic parameters. For this purpose, the expansion of the distribution function into the generalized Chapman–Enskog series over the small parameter $\varepsilon = \tau_{\text{VV}_1}/\theta$ is applied. Substituting the distribution function into Eq. (3.37) for $R_c^{\text{react}}$, we obtain the formulae for the calculation of $R_c^{2\rightleftharpoons 2}$ and $R_c^{2\rightleftharpoons 3}$:

$$R_c^{2\rightleftharpoons 2} = \sum_{dc'd'} \left( n_{c'} n_{d'} k_{c'c}^{d'd} - n_c n_d k_{cc'}^{dd'} \right), \tag{3.86}$$

$$R_c^{2\rightleftharpoons 3} = \sum_{d} n_d \left( n_{c'} n_{f'} k_{\text{rec},c}^{d} - n_c k_{c,\text{diss}}^{d} \right). \tag{3.87}$$

Here, $k_{cc'}^{dd'}$ is the multi-temperature rate coefficient of the reaction (2.56) (during a collision of two molecules or a molecule and an atom $A_d$). The coefficients $k_{c,\text{diss}}^{d}$, $k_{\text{rec},c}^{d}$ are the rate coefficients of dissociation and recombination reactions.

Restricting the consideration by the zero-order and first-order terms and writing $f_{cij}$ in the form $f_{cij} = f_{cij}^{(0)}(1 + \varphi_{cij})$, we obtain the expressions for the exchange reaction rate coefficients in the first-order approximation

$$k_{cc'}^{dd'} = \sum_{iki'k'} \sum_{jlj'l'} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_c n_d} \left[ 1 + (\varphi_{cij} + \varphi_{dkl}) \right] g \sigma_{cd,ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u}_d d\mathbf{u}_c. \tag{3.88}$$

The dissociation rate coefficient is found in the similar form, with the exception that instead of the cross section of the exchange reaction, the dissociation cross section appears in the last formula.

Taking into account the form (3.57) of the distribution function $f_{cij}^{(1)} = f_{cij}^{(0)} \varphi_{cij}$ and the fact that the integrals of odd functions over the velocity disappear, we can write:

$$k_{cc'}^{dd'} = k_{cc'}^{dd'(0)} \left( T, T_1^c, T_1^d \right) + k_{cc'}^{dd'(1)} \left( n_1, ..., n_L, T, T_1^c, T_1^d \right) +$$

$$+ k_{cc'}^{dd'(2)} \left( n_1, ..., n_L, T, T_1^c, T_1^d, \nabla \cdot \mathbf{v} \right). \tag{3.89}$$

A similar formula is also found for $k_{c,\text{diss}}^{d}$. The coefficients $k_\gamma^{(0)}$, $k_\gamma^{(1)}$, and $k_\gamma^{(2)}$ depend on the gas temperature, temperatures of the first vibrational levels of colliding particles $T_1^c$ and $T_1^d$ (in the case of the reaction in a collision with an atom, the only vibrational temperature $T_1^c$ appears in the formula); in addition to that, the

coefficients $k_\gamma^{(1)}$, $k_\gamma^{(2)}$ depend on the component number densities, and the coefficient $k_\gamma^{(2)}$ on the velocity divergence. While the coefficients $k_\gamma^{(0)}$ are obtained averaging the corresponding reaction cross sections with the zero-order distribution function (3.7), the coefficients $k_\gamma^{(1)}$, $k_\gamma^{(2)}$ are connected to the deviations from this distribution function.

In the zero-order approximation, the multi-temperature rate coefficients of exchange and dissociation reactions can be expressed in terms of the state-specific rate coefficients:

$$k_{cc'}^{dd'(0)} = \frac{1}{n_c n_d} \sum_{iki'k'} n_{ci} n_{dk}\, k_{ci,c'i'}^{dk,d'k'(0)}(T), \tag{3.90}$$

$$k_{c,\text{diss}}^{d(0)} = \frac{1}{n_c} \sum_i n_{ci}\, k_{ci,\text{diss}}^{d(0)}(T), \tag{3.91}$$

where $n_{ci}$ denotes some non-equilibrium quasi-stationary distribution. The coefficients $k_{ci,c'i'}^{dk,d'k'(0)}(T)$, $k_{ci,\text{diss}}^{d(0)}(T)$ are the state-to-state rate coefficients of bimolecular reactions and dissociation introduced in Section 2.5.

For the generalized Treanor distribution (3.14), the multi-temperature rate coefficients of exchange reactions occurring as a result of collisions of two molecules take the form

$$k_{cc'}^{dd'(0)}(T, T_1^c, T_1^d) = \frac{1}{Z_c^{\text{vibr}}(T, T_1^c) Z_d^{\text{vibr}}(T, T_1^d)} \sum_{iki'k'} s_i^c s_k^d \exp\left(-\frac{\varepsilon_i^c - i_c \varepsilon_1^c}{kT} - \right.$$

$$\left. -\frac{\varepsilon_k^d - k_d \varepsilon_1^d}{kT} - \frac{i_c \varepsilon_1^c}{kT_1^c} - \frac{k_d \varepsilon_1^d}{kT_1^d}\right) k_{ci,c'i'}^{dk,d'k'(0)}(T). \tag{3.92}$$

The rate coefficient for the exchange reaction in a collision of a diatomic molecule and an atom, as well as the dissociation rate coefficient, depends on two temperatures ($T$ and $T_1^c$):

$$k_{cc'}^{dd'(0)}(T, T_1^c) = \frac{1}{Z_c^{\text{vibr}}(T, T_1^c)} \sum_{ii'} s_i^c \exp\left(-\frac{\varepsilon_i^c - i_c \varepsilon_1^c}{kT} - \frac{i_c \varepsilon_1^c}{kT_1^c}\right) k_{ci,c'i'}^{dd'(0)}(T), \tag{3.93}$$

$$k_{c,\text{diss}}^{d(0)}(T, T_1^c) = \frac{1}{Z_c^{\text{vibr}}(T, T_1^c)} \sum_i s_i^c \exp\left(-\frac{\varepsilon_i^c - i_c \varepsilon_1^c}{kT} - \frac{i_c \varepsilon_1^c}{kT_1^c}\right) k_{ci,\text{diss}}^{d(0)}(T). \tag{3.94}$$

The total recombination rate coefficient $k_{\text{rec},c}^{d(0)}$ is defined in terms of the state-specific rate coefficients as follows

$$k_{\text{rec},c}^{d(0)}(T) = \sum_i k_{\text{rec},ci}^{d(0)}(T) \tag{3.95}$$

and depends on the gas temperature $T$ only. One should keep in mind that the superscript "0" in the notations for the state-to-state rate coefficients indicates that they are calculated by averaging the corresponding inelastic collision cross sections with

the Maxwell-Boltzmann distribution over the velocity and rotational energy. The dimension of the multi-temperature exchange and dissociation rate coefficients $k_{cc'}^{dd'}$, $k_{c'c}^{d'd}$ and $k_{c,\text{diss}}^{d}$ is $\text{m}^3 \cdot \text{s}^{-1}$, whereas that of the recombination rate coefficient $k_{\text{rec},c}^{d}$ is $\text{m}^6 \cdot \text{s}^{-1}$.

For the coefficients $k_{cc'}^{dd'\,(1)}$, $k_{cc'}^{dd'\,(2)}$ defining the rates of exchange reactions in the first-order approximation, the following relations are fulfilled

$$k_{cc'}^{dd'\,(1)} = -\frac{1}{n} \sum_{iki'k'} \sum_{jlj'l'} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_c n_d} \left(G_{cij} + G_{dkl}\right) g\sigma_{cd,ijkl}^{c'd',i'j'k'l'} d^2\Omega d\mathbf{u}_d d\mathbf{u}_c, \quad (3.96)$$

$$k_{cc'}^{dd'\,(2)} = -\nabla \cdot \mathbf{v} \frac{1}{n} \sum_{iki'k'} \sum_{jlj'l'} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_c n_d} \left(F_{cij} + F_{dkl}\right) g\sigma_{cd,ijkl}^{c'd',i'j'k'l'} d^2\Omega d\mathbf{u}_d d\mathbf{u}_c, \quad (3.97)$$

where the scalar functions $F_{cij}$ and $G_{cij}$ are the solutions for the linear integral equations (3.62), (3.63) with the additional constraints (3.67)–(3.72). The coefficients $k_{c,\text{diss}}^{d\,(1)}$, $k_{c,\text{diss}}^{d\,(2)}$ are given by similar expressions, with the exception that they contain the dissociation cross sections instead of the bimolecular reaction cross sections.

The relations connecting the multi-temperature rate coefficients of forward and backward reactions can be obtained applying the microscopic detailed balance relations for the collision cross sections. In the zero-order approximation, the connecting relations are derived from Eqs. (2.75), (2.76) or (2.78), (2.79) taking into account the vibrational distribution (3.14). As a result, the multi-temperature rate coefficients of backward reactions are expressed in terms of the state-specific rate coefficients of forward reactions and the ratios of the state-to-state rate coefficients of forward and backward reactions. Thus for bimolecular reactions we find

$$k_{c'c}^{d'd\,(0)}(T, T_1^{c'}, T_1^{d'}) = \frac{1}{Z_{c'}^{\text{vibr}}(T, T_1^{c'}) Z_{d'}^{\text{vibr}}(T, T_1^{d'})} \sum_{iki'k'} s_{i'}^{c'} s_{k'}^{d'} \exp\left(-\frac{i_{c'}'\varepsilon_1^{c'}}{kT_1^{c'}} - \right.$$

$$\left. -\frac{k_{d'}'\varepsilon_1^{d'}}{kT_1^{d'}} - \frac{\varepsilon_{i'}^{c'} - i_{c'}'\varepsilon_1^{c'}}{kT} - \frac{\varepsilon_{k'}^{d'} - k_{d'}'\varepsilon_1^{d'}}{kT}\right) k_{ci,c'i'}^{dk,d'k'\,(0)} K_{c'i',ci}^{d'k',dk\,(0)}(T), \quad (3.98)$$

whereas for dissociation-recombination we obtain

$$k_{\text{rec},c}^{d\,(0)}(T) = \sum_i k_{\text{rec},ci}^{d\,(0)}(T) = \sum_i k_{ci,\text{diss}}^{d\,(0)}(T) K_{\text{rec}-\text{diss},ci}^{d\,(0)}(T). \quad (3.99)$$

In these formulae, the ratios for the state-to-state rate coefficients $K_{c'i',ci}^{d'k',dk\,(0)}(T)$, $K_{\text{rec}-\text{diss},ci}^{d\,(0)}(T)$ are defined in (2.75), (2.76) or (2.78), (2.79).

The production term $R_c^{\text{w}}$ in the relaxation equations for $W_c$ can be expressed in terms of macroscopic parameters substituting the zero-order or the first-order distribution functions into the formulae (3.38). In the zero-order approximation, $R_c^{\text{w}(0)}$ includes the vibrational distributions (3.14) and the state-to-state rate coefficients of $VV_2$, $VT$ vibrational energy transitions and chemical reactions. Thus

$$R_c^{\text{w,VV}_2(0)} = \sum_d \sum_{iki'k'} i_c \left( n_{ci'} n_{dk'} k_{c,i'i}^{d,k'k\,(0)} - n_{ci} n_{dk} k_{c,ii'}^{d,kk'\,(0)} \right), \tag{3.100}$$

$$R_c^{\text{w,VT}(0)} = \sum_d n_d \sum_{ii'} i_c \left( n_{ci'} k_{c,i'i}^{d\,(0)} - n_{ci} k_{c,ii'}^{d\,(0)} \right), \tag{3.101}$$

$$R_c^{\text{w,react}} = R_c^{\text{w},2\rightleftharpoons2} + R_c^{\text{w},2\rightleftharpoons3},$$

$$R_c^{\text{w},2\rightleftharpoons2(0)} = \sum_{dc'd'} \sum_{iki'k'} i_c \left( n_{c'i'} n_{d'k'} k_{c'i',ci}^{d'k',dk\,(0)} - n_{ci} n_{dk} k_{ci,c'i'}^{dk,d'k'\,(0)} \right),$$

$$R_c^{\text{w},2\rightleftharpoons3(0)} = \sum_d n_d \sum_i i_c \left( n_{c'} n_{f'} k_{\text{rec},ci}^{d\,(0)} - n_{ci} k_{ci,\text{diss}}^{d\,(0)} \right).$$

In the expressions (3.100) and (3.101) $k_{c,ii'}^{d,kk'\,(0)}$ and $k_{c,ii'}^{d\,(0)}$ are the state-to-state rate coefficients of VV$_2$ and VT exchanges.

If anharmonic effects are neglected then the Boltzmann vibrational distributions (3.16) are valid, and the multi-temperature rate coefficients of the reactions (3.92)–(3.94) depend on $T$, $T_v^c$, and $T_v^d$ and take the form

$$k_{cc'}^{dd'\,(0)}(T,T_v^c,T_v^d) = \frac{1}{Z_c^{\text{vibr}}(T_v^c) Z_d^{\text{vibr}}(T_v^d)} \times$$

$$\times \sum_{iki'k'} s_i^c s_k^d \exp\left( -\frac{\varepsilon_i^c}{kT_v^c} - \frac{\varepsilon_k^d}{kT_v^d} \right) k_{ci,c'i'}^{dk,d'k'\,(0)}(T), \tag{3.102}$$

if $d$ is a molecule,

$$k_{cc'}^{dd'\,(0)}(T,T_v^c) = \frac{1}{Z_c^{\text{vibr}}(T_v^c)} \sum_{ii'} s_i^c \exp\left( -\frac{\varepsilon_i^c}{kT_v^c} \right) k_{ci,c'i'}^{dd'\,(0)}(T), \tag{3.103}$$

if $d$ is an atom, and

$$k_{c,\text{diss}}^d(T,T_v^c) = \frac{1}{Z_c^{\text{vibr}}(T_v^c)} \sum_i s_i^c \exp\left( -\frac{\varepsilon_i^c}{kT_v^c} \right) k_{ci,\text{diss}}^{d\,(0)}(T). \tag{3.104}$$

The expression for $R_c^{\text{w}}$ can be also simplified if the non-equilibrium Boltzmann distribution (3.16) instead of the Treanor distribution is used.

Under the thermal equilibrium conditions ($T_1^c = T$), the reaction rate coefficients depend solely on the gas temperature. The relations (3.98), (3.99) in this case are appreciably simplified, and the ratios of the one-temperature rate coefficients of forward and backward reactions are equal to the ratios of the partition functions of the reaction products and reagents.

Finally, the right-hand sides of Eqs. (3.33), (3.36) in the zero-order approximation of the generalized Chapman–Enskog method are expressed in terms of the macroscopic flow parameters $n_c$, $T$, and $T_1^c$. For the calculation of the multi-temperature reaction rate coefficients and functions $R_c^{\text{react}}$, $R_c^{\text{w}}$ in the zero-order approximation, the calculation of the state-to-state reaction rate coefficients is

required. In the first-order approximation, the multi-temperature reaction rate coefficients are found averaging the corresponding cross sections with the first-order distribution function (3.57).

In chemical kinetics, instead of the equations for particle number densities $n_c$, those for volumetric molar concentrations $\xi_c = n_c/\mathcal{N}_A$ ($\mathcal{N}_A$ is the Avogadro number) are often used. In this case, the right-hand sides of the equations (3.86), (3.87) should be written in the modified form. Summation is carried out over the reaction numbers rather than the chemical species of the reaction products and reagents. Then the chemical production term $R_c^{react}$ can be rewritten in the following form

$$R_c^{react} = \mathcal{N}_A \sum_r (v_{c,r}'' - v_{c,r}') \left( k_{f,r} \prod_s \xi_s^{v_{s,r}'} - k_{b,r} \prod_s \xi_s^{v_{s,r}''} \right). \tag{3.105}$$

Here, the stoichiometric coefficients $v_{c,r}'$ and $v_{c,r}''$ for each $r$th forward and backward reaction are introduced

$$\sum_{c=1}^L v_{c,r}' A_c \underset{b}{\overset{f}{\rightleftharpoons}} \sum_{c=1}^L v_{c,r}'' A_c$$

as well as the rate coefficients of forward and backward reactions $k_{f,r}$ and $k_{b,r}$, respectively. The summation in Eq. (3.105) is performed over all reactions $r$ ($r = 1,...,R$) taking place in a mixture, and the production is carried out over all chemical species $s$. The rate coefficients of forward and backward reactions $k_{f,r}$ and $k_{b,r}$ in Eq. (3.105) are connected with the coefficients $k_{cc'}^{dd'}$, $k_{c,diss}^d$, $k_{rec,c}^d$ defined in Eqs (3.92), (3.94) by the following relations:

$$k_{f,r} = -\frac{\mathcal{N}_A}{v_{c,r}'' - v_{c,r}'} k_{cc'}^{dd'}, \qquad k_{b,r} = -\frac{\mathcal{N}_A}{v_{c,r}'' - v_{c,r}'} k_{c'c}^{d'd} \tag{3.106}$$

for exchange reactions, and

$$k_{f,r} = -\frac{\mathcal{N}_A}{v_{c,r}'' - v_{c,r}'} k_{c,diss}^d, \qquad k_{b,r} = -\frac{\mathcal{N}_A^2}{v_{c,r}'' - v_{c,r}'} k_{rec,c}^d \tag{3.107}$$

for dissociation and recombination reactions.

The dimension of the coefficients $k_{f,r}$ and $k_{b,r}$ is $mole^{-1} \cdot m^3 \cdot s^{-1}$ for the exchange reactions and dissociation, and $mole^{-2} \cdot m^6 \cdot s^{-1}$ for the recombination reaction.

The equations (3.105) are written taking into account the following representation for the reaction rate $w_{f,r}$ [126]

$$w_{f,r} = k_{f,r} \prod_s \xi_s^{v_{s,r}'}. \tag{3.108}$$

The coefficient $k_{f,r}$ is often called the reaction rate constant, or specific reaction rate, i.e. the reaction rate under the condition when the concentration of each reagent is equal to unity.

The expression for $R_c^{\mathrm{w,react}}$ can also be written using the coefficients introduced above:

$$R_c^{\mathrm{w,react}} = \mathscr{N}_{\mathrm{A}} \sum_{r,\, v''_{c,r} > v'_{c,r}} (v''_{c,r} - v'_{c,r}) \times$$

$$\times \left( k_{\mathrm{f},r} \prod_s \xi_s^{v'_{s,r}} G_{\mathrm{app,f},r,c} - k_{\mathrm{b},r} \prod_s \xi_s^{v''_{s,r}} G_{\mathrm{va,b},r,c} \right) +$$

$$+ \mathscr{N}_{\mathrm{A}} \sum_{r,\, v''_{c,r} < v'_{c,r}} (v''_{c,r} - v'_{c,r}) \left( k_{\mathrm{f},r} \prod_s \xi_s^{v'_{s,r}} G_{\mathrm{va,f},r,c} - k_{\mathrm{b},r} \prod_s \xi_s^{v''_{s,r}} G_{\mathrm{app,b},r,c} \right),$$

where $G_{\mathrm{app,f},r,c}$ and $G_{\mathrm{va,b},r,c}$ are the numbers of vibrational quanta of $c$ molecules gained or lost by a system as a result of a forward and backward reaction $r$. The explicit formulae for these values are given in Ref. [59].

## 3.7 Strongly Non-equilibrium Quasi-stationary Distribution in a Pure Gas

### 3.7.1 Zero-Order Distribution Function

In the previous sections, the distribution functions and equations of non-equilibrium gas dynamics in gas mixtures are considered under the conditions when the probability of near-resonant $VV_1$ exchange between similar molecules considerably exceeds the probabilities of VT and VRT vibrational energy transfers into other modes.

Under the conditions of strong vibrational excitation, when the vibrational energy is noticeably higher than the translational and rotational ones, such a relation between transition probabilities is not valid for the entire set of vibrational levels. One of the characteristic features of vibrational kinetics in a highly excited gas is that various relaxation mechanisms prevail at different groups of vibrational levels [100]. At low levels, the most probable among all possible vibrational energy transfers is the near-resonant $VV'$ exchange of vibrational quanta:

$$i + k = i' + k' = (i \pm m) + (k \mp m)$$

(the non-resonant relaxation model [100]).

At intermediate levels, the probability of resonant $VV''$ transitions between the neighboring states appears to be higher than that for the other vibrational energy exchanges:

$$i + (i \pm 1) = (i \pm 1) + i \tag{3.109}$$

(resonant relaxation model [100]).

At high levels, the probabilities of all VV exchanges become comparable to that of VT transitions. Since the probability of VRT transitions is rather low compared to that of the other collisions, this process is usually neglected. The rate coefficients of VV and VT transitions calculated for different temperatures in the molecular nitrogen are presented in Fig. 3.2. The approximate expressions given in [48] are applied
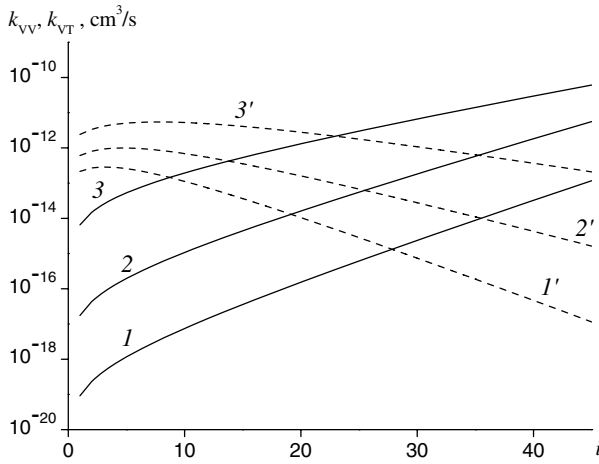
**Fig. 3.2** The rate coefficients of VV and VT transitions in nitrogen as functions of $i$ at different temperatures. Solid lines are the rate coefficients $k_{i,i-1}$ of VT transitions, dashed lines are $k_{i,i-1}^{01}$ of VV exchange. Curves *1,1'* — $T = 500$; *2,2'* — $T = 1000$; *3,3'* — $T = 2500$ K

to the rate coefficients calculation. In the latter paper, the fitting of the accurate results obtained in [21, 22] using a quasi-classical method was performed in a wide temperature range. As a result, the rate coefficients of vibrational energy transitions are represented in a simple analytical form.

From the above discussion it follows that at different levels, the characteristic times of vibrational relaxation adhere to different conditions:

$$\tau_{VV'} \ll \tau_{VT} \sim \theta, \ 0 \le i \le i_*,$$

$$\tau_{VV''} \ll \tau_{VT} \sim \theta, \ i_* \le i \le i_{**}, \qquad (3.110)$$

$$\tau_{VV} \sim \tau_{VT} \ll \theta, \ \ i_{**} \le i \le L.$$

The level $i_*$ corresponds to the minimum of the Treanor distribution (3.15), the level $i_{**}$ is found approximately from the ratio of VV and VT transition probabilities, and $L$ is the last vibrational level of a molecule.

Let us consider the kinetic equations (1.38) for the distribution function $f_{ij}(\mathbf{r}, \mathbf{u}, t)$ in a single-component gas with rapid and slow processes:

$$\frac{\partial f_{ij}}{\partial t} + \mathbf{u} \cdot \nabla f_{ij} = \frac{1}{\varepsilon} J_{ij}^{\mathrm{rap}} + J_{ij}^{\mathrm{sl}}.$$

Under the condition (3.110), the integral operators of rapid and slow processes appear to be different for various intervals of the vibrational spectrum:

$$J_{ij}^{\mathrm{rap}} = \begin{cases} J_{ij}^{\mathrm{el}} + J_{ij}^{\mathrm{rot}} + J_{ij}^{\mathrm{VV'}}, & 0 \le i < i_*, \\[2mm] J_{ij}^{\mathrm{el}} + J_{ij}^{\mathrm{rot}} + J_{ij}^{\mathrm{VV''}}, & i_* \le i \le i_{**}, \\[2mm] J_{ij}, & i_{**} \le i \le L, \end{cases}$$

$$J_{ij}^{\mathrm{sl}} = \begin{cases} J_{ij}^{\mathrm{VT}}, & 0 \le i < i_{**}, \\[2mm] 0, & i_{**} \le i \le L. \end{cases}$$

Here, $J_{ij}$ is the integral operator of all collisions.

Following the formalism of the generalized Chapman–Enskog method, we expand the distribution function into the series in the small parameter $\varepsilon = \tau_{\mathrm{rap}}/\tau_{\mathrm{sl}}$ and obtain the integral equations in the zero-order approximation:

$$J_{ij}^{\mathrm{rap}(0)} = 0.$$

One should bear in mind that the operator $J_{ij}^{\mathrm{rap}}$ varies for different groups of vibrational states. Therefore, the sets of invariants of the most frequent collisions, which specify the zero-order distribution function, are also different for various levels. For the entire range of the vibrational states, the collision invariants are represented by the mass $\psi_{ij}^{(1)} = m$, momentum $\psi_{ij}^{(v)} = mu_v$ ($v = 2, 3, 4$), and the total energy of a particle $\psi_{ij}^{(5)} = mu^2/2 + \varepsilon_{ij}$. For low and intermediate levels, additional collision invariants exist. At low levels ($0 \le i < i_*$), the number of vibrational quanta remains constant, and $\psi_{ij}^{(6)} = i$. At intermediate levels ($i_* \le i \le i_{**}$), in a transition between the adjacent states (3.109), any value $a_i$ independent of the velocity and the rotational state and depending arbitrarily on the vibrational level $i$ is conserved: $a_i + a_{i\pm1} = a_{i\pm1} + a_i$. Hence $\psi_{ij}^{(\mu+6)} = a_i$ ($\mu = i_*, ..., i_{**}$).

Taking into account that $\ln f_{ij}^{(0)}/s_{ij}$ is a linear combination of the invariants of the most frequent collisions, we find the representation of the zero-order distribution function which appears to be non-uniform with respect to the energy spectrum:

$$f_{ij}^{(0)} = \begin{cases} \left(\dfrac{m}{2\pi kT}\right)^{3/2} \dfrac{N_1}{Z^{\mathrm{rot}}Z^{\mathrm{vibr},1}} s_{ij} \exp\left(-\dfrac{mc^2}{2kT} - \dfrac{\varepsilon_i + \varepsilon_j}{kT} - \vartheta i\right), \\ \hspace{6cm} 0 \le i \le i_*, \\[3mm] \left(\dfrac{m}{2\pi kT}\right)^{3/2} \dfrac{n_i}{Z^{\mathrm{rot}}} s_j \exp\left(-\dfrac{mc^2}{2kT} - \dfrac{\varepsilon_j}{kT}\right), \hspace{1cm} i_* \le i \le i_{**}, \hspace{1cm} (3.111) \\[3mm] \left(\dfrac{m}{2\pi kT}\right)^{3/2} \dfrac{N_3}{Z^{\mathrm{rot}}Z^{\mathrm{vibr},3}} s_{ij} \exp\left(-\dfrac{mc^2}{2kT} - \dfrac{\varepsilon_i + \varepsilon_j}{kT}\right) i_{**} \le i \le L. \end{cases}$$

Here, $N_1, N_3$ are the numbers of molecules at low and high vibrational levels per unit volume. While writing (3.111), it is supposed that rotational and vibrational energies are independent, and the rotational partition function $Z^{\mathrm{rot}}$ is given by Eq. (2.7). $Z^{\mathrm{vibr},1}$ and $Z^{\mathrm{vibr},3}$ are the truncated vibrational partition functions:

$$Z^{\text{vibr},1} = \sum_{i=0}^{i_*} s_i \exp\left(-\frac{\varepsilon_i}{kT} - \vartheta i\right),$$

$$Z^{\text{vibr},3} = \sum_{i=i_{**}}^{L} s_i \exp\left(-\frac{\varepsilon_i}{kT}\right).$$

The parameter $\vartheta$ is connected to the total number of vibrational quanta at low levels:

$$\rho W = \sum_{i=0}^{i_*} \sum_j i \int f_{ij}^{(0)} d\mathbf{u}$$

and can be expressed in terms of the temperature of the first vibrational level $T_1$ introduced in Ref. [242]:

$$\vartheta = \frac{\varepsilon_1}{k}\left(\frac{1}{T_1} - \frac{1}{T}\right).$$

The populations $n_i$ of intermediate levels should be found from the corresponding balance equations. A close inspection of the analytical and numerical solutions for the equations for $n_i$ in spatially homogeneous gases, as well as experimental studies for vibrational level populations, show that the dependence of $n_i$ on the quantum number $i$ for intermediate levels takes the form of a sloping plateau.

The approximate expression for $n_i$ at intermediate levels is found in Refs. [100, 99, 101] in the form

$$\frac{n_i}{n} = \frac{\Gamma}{i+1} - \frac{P_{10}}{Q_{10}}\frac{kT}{12hc\omega_e x_e}\frac{\delta_{\text{VV}}^3}{\delta_{\text{VT}}}\frac{\exp(\delta_{\text{VT}}i)}{i+1}, \tag{3.112}$$

$P_{10}, Q_{10}$ are the probabilities of VT and VV transitions between the first and the zero level, $\delta_{\text{VT}}$, $\delta_{\text{VV}}$ are the temperature functions representing anharmonic corrections to the VT and VV transition probabilities, $\Gamma$ is a parameter. Here, as before, the Morse anharmonic oscillator model is applied.

In Ref. [100] it is shown that the main contribution to the level populations $n_i$ at intermediate levels is given by the first term in Eq. (3.112), while the second term defines only the length of the plateau section. Therefore we can approximate $n_i$ as

$$\frac{n_i}{n} = \frac{\Gamma}{i+1}, \quad i_* \le i \le i_{**}.$$

Substituting the latter relation into the formula (3.111) and writing the parameter $\vartheta$ in terms of $T_1$, we find

$$f_{ij}^{(0)} = \begin{cases} \left(\dfrac{m}{2\pi kT}\right)^{3/2} \dfrac{N_1}{Z^{\text{rot}}Z^{\text{vibr},1}} s_{ij}\exp\left(-\dfrac{mc^2}{2kT} - \dfrac{\varepsilon_j + \varepsilon_i - i\varepsilon_1}{kT} - \dfrac{i\varepsilon_1}{kT_1}\right), \\ \hspace{9cm} 0 \le i \le i_*, \\[2mm] \left(\dfrac{m}{2\pi kT}\right)^{3/2} \dfrac{\Gamma}{i+1}\dfrac{n}{Z^{\text{rot}}} s_j \exp\left(-\dfrac{mc^2}{2kT} - \dfrac{\varepsilon_j}{kT}\right), \qquad i_* \le i \le i_{**}, \\[2mm] \left(\dfrac{m}{2\pi kT}\right)^{3/2} \dfrac{N_3}{Z^{\text{rot}}Z^{\text{vibr},3}} s_{ij}\exp\left(-\dfrac{mc^2}{2kT} - \dfrac{\varepsilon_i + \varepsilon_j}{kT}\right), \quad i_{**} \le i \le L. \end{cases} \tag{3.113}$$

Parameters $N_1$, $N_3$, and $\Gamma$ are expressed in terms of $T$, $T_1$, and $n$ using the distribution function continuity at $i = i_*$, $i = i_{**}$ and the normalizing condition for the distribution function with respect to the total number density $n$.

As is already mentioned above, $i_*$ is found from the formula (3.15) written for a single-component gas. At $i = i_*$, the Treanor part of the distribution function achieves its minimum. The value $i_{**}$ is chosen in accordance with the requirement that at $i > i_{**}$, the probabilities of VV and VT transitions acquire the same order of magnitude. In Ref. [100] the following expression for the quantum number $i_{**}$ is proposed:

$$ i_{**} = i_* + \frac{\varepsilon_1}{\delta_{VT} + \delta_{VV}} \left( \frac{1}{kT} - \frac{1}{kT_1} \right). $$

Another way to find $i_{**}$ is to set the distribution (3.112) equal to zero. Indeed, this distribution loses its physical meaning while becomes negative. It is due to the fact that for the derivation of Eq. (3.112), the following assumption is applied in Ref. [100]:

$$ \left| \frac{d^2 \ln(n_i/n)}{di^2} \right| \ll \frac{2hc\omega_e x_e}{kT}. $$

The above assumption is not fulfilled if $i > i_{**}$. In this case

$$ i_{**} = \frac{1}{\delta_{VT}} \ln \left( \Gamma \frac{Q_{10}}{P_{10}} \frac{12hc\omega_e x_e}{kT} \frac{\delta_{VT}}{\delta_{VV}^3} \right). \tag{3.114} $$

The zero-order distribution function (3.113) depends on the macroscopic parameters $n$, $\mathbf{v}$, $T$, and $T_1$ and represents the Maxwell-Boltzmann distribution over the velocity and rotational energy, and a combined distribution over the vibrational energy: the Treanor distribution at low levels, the plateau distribution at intermediate levels, and the Boltzmann distribution at high levels with the corresponding normalizing coefficients. The distribution function (3.113) is derived from the kinetic equations in Refs. [138, 139].

Integrating Eq. (3.113) over the velocities and carrying out the summation over $j$, we obtain the representation for the vibrational level populations:

$$ n_i = \begin{cases} \dfrac{N_1}{Z^{\text{vibr},1}} s_i \exp \left( -\dfrac{\varepsilon_i - i\varepsilon_1}{kT} - \dfrac{i\varepsilon_1}{kT_1} \right), & 0 \leq i \leq i_*, \\[2ex] n \dfrac{\Gamma}{i+1}, & i_* \leq i \leq i_{**}, \\[2ex] \dfrac{N_3}{Z^{\text{vibr},3}} s_i \exp \left( -\dfrac{\varepsilon_i}{kT} \right), & i_{**} \leq i \leq L. \end{cases} \tag{3.115} $$

For practical calculations it is convenient to use the unique representation for the distribution function derived in [133]:

$$ f_{ij}^{(0)} = \left( \frac{m}{2\pi kT} \right)^{3/2} \frac{n s_{ij}}{Z^{\text{int}}} \exp \left( -\frac{mc^2}{2kT} - \frac{\varepsilon_j}{kT} - \frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} - \right. $$

$$ \left. - \frac{\beta\varepsilon_1}{kT_1} + \ln \frac{i_* + 1}{\gamma + 1} \right), \tag{3.116} $$
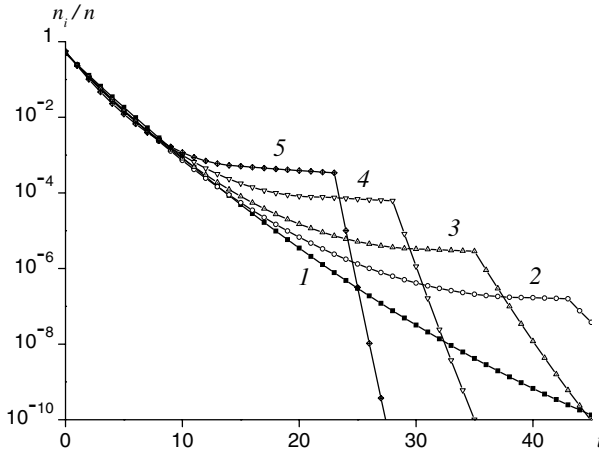
**Fig. 3.3** Vibrational distributions (3.115) in molecular nitrogen for different temperature ratios. Curve $1$ — $T = T_1 = 5000$; $2$ — $T = 2172$, $T_1 = 4580$; $3$ — $T = 1664$, $T_1 = 4435$; $4$ — $T = 1088$, $T_1 = 4205$; $5$ — $T = 680$, $T_1 = 3774$ K

here, $Z^{\text{int}} = Z^{\text{rot}}Z^{\text{vibr}}$, and $Z^{\text{vibr}}$ is the total non-equilibrium vibrational partition function

$$Z^{\text{vibr}} = \sum_i s_i \exp\left(-\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} - \frac{\beta\varepsilon_1}{kT_1} + \ln\frac{i_* + 1}{\gamma + 1}\right), \qquad (3.117)$$

$$\alpha = \begin{cases} i_{**}, & 0 \le i < i_{**}, \\ i, & i_{**} \le i < L, \end{cases} \qquad \beta = \begin{cases} i, & 0 \le i < i_*, \\ i_*, & i_* \le i < L, \end{cases}$$

$$\gamma = \begin{cases} i_*, & 0 \le i < i_*, \\ i, & i_* \le i < i_{**}, \\ i_{**}, & i_{**} \le i < L. \end{cases}$$

Fig. 3.3[1] presents the vibrational level populations (3.115) in molecular nitrogen for different temperature ratios $T_1/T$. It is seen that the distribution depends strongly on the non-equilibrium parameter $T_1/T$. The length of the plateau increases considerably with the increase of $T_1/T$. For $T_1/T < 4$, the plateau section is practically absent, and the vibrational level populations represent the combination of the Treanor and Boltzmann distributions. When $T_1/T < 1$, the distribution (3.115) turns into the Treanor distribution in the entire range of vibrational states, since $i_*$ is approximately equal to $i_{**}$ and coincides with the maximum possible number of excited states of the Morse oscillator. If anharmonic effects are neglected then (3.115) reduces to the non-equilibrium Boltzmann distribution with vibrational temperature $T_v = T_1$. If $T = T_1$, the distribution (3.115) turns into the local equilibrium one-temperature Boltzmann distribution over the vibrational levels.

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[1] The authors are grateful to Dr. T.Yu. Alexandrova for providing the data for Fig. 3.3, as well as for some figures in Chapters 6 and 9.

The conditions of normalization for the distribution function are written in the form:

$$\sum_{ij} \int f_{ij} d\mathbf{u} = \sum_{ij} \int f_{ij}^{(0)} d\mathbf{u} = n, \qquad (3.118)$$

$$\sum_{ij} m \int \mathbf{u} f_{ij} d\mathbf{u} = \sum_{ij} m \int \mathbf{u} f_{ij}^{(0)} d\mathbf{u} = \rho \mathbf{v}, \qquad (3.119)$$

$$\sum_{ij} \int \left( \frac{mc^2}{2} + \varepsilon_i + \varepsilon_j \right) f_{ij} d\mathbf{u} = \sum_{ij} \int \left( \frac{mc^2}{2} + \varepsilon_i + \varepsilon_j \right) f_{ij}^{(0)} d\mathbf{u} =$$

$$= \frac{3}{2} nkT + \rho E_{\text{rot}}(T) + \rho E_{\text{vibr}}(T, T_1), \qquad (3.120)$$

$$\sum_{i=0}^{i_*} \sum_{j} i \int f_{ij} d\mathbf{u} = \sum_{i=0}^{i_*} \sum_{j} i \int f_{ij}^{(0)} d\mathbf{u} = \rho W(T, T_1). \qquad (3.121)$$

It is seen from Eqs. (3.118)–(3.121) that the distribution function is normalized to the particles number density, macroscopic momentum, total energy and the number of quanta at low vibrational levels. The gas temperature $T$ and the temperature $T_1$ of the first vibrational level are specified by the total internal energy and the number of quanta $W$ at low states.

An alternative form of the quasi-stationary distribution in a strongly excited one-component gas was derived in Ref. [227] by introducing an approximate additional collision invariant for all vibrational levels.

### 3.7.2  Equations for Macroscopic Parameters

The governing equations for the macroscopic parameters $n$, $\mathbf{v}$, $T$, and $T_1$ are derived from the kinetic equations multiplying them by the invariants of the most frequent collisions, integrating over the velocity and performing the summation over $i$ and $j$. Since the invariant $\psi_{ij}^{(6)} = i$ remains constant only at low levels, in the equation associated with this invariant, the summation is carried out only over low states. Finally, the following set of equations is obtained for the macroscopic parameters:

$$\frac{dn}{dt} + n\nabla \cdot \mathbf{v} = 0, \qquad (3.122)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \boldsymbol{P} = 0, \qquad (3.123)$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \boldsymbol{P} : \nabla \mathbf{v} = 0, \qquad (3.124)$$

$$\rho \frac{dW}{dt} + \nabla \cdot \mathbf{q}_{\text{w}} = R^{\text{w}}. \qquad (3.125)$$

This system is much simpler compared to that (3.33)–(3.36) obtained in the multi-temperature approach for a gas mixture, since $L$ equations of chemical kinetics (3.33) are replaced by the sole, namely, the continuity equation (3.122). Moreover, the equation (3.125) for the specific number of vibrational quanta does not include the integral operator of non-equilibrium chemical reactions. On the other hand, the vibrational energy and the number of quanta are calculated in accordance with the more complex combined vibrational distribution (3.115). Taking into account the uniform representation (3.116), these values can be written in the form

$$E_{\mathrm{vibr}}(T,T_1) = \frac{1}{mZ^{\mathrm{vibr}}} \sum_i s_i \varepsilon_i \exp\left(-\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} - \frac{\beta\varepsilon_1}{kT_1} + \ln\frac{i_* + 1}{\gamma + 1}\right), \quad (3.126)$$

$$W(T,T_1) = \frac{1}{mZ^{\mathrm{vibr}}} \sum_{i=0}^{i_*} s_i i \exp\left(-\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} - \frac{\beta\varepsilon_1}{kT_1} + \ln\frac{i_* + 1}{\gamma + 1}\right). \quad (3.127)$$

The right-hand side of Eq. (3.125) is

$$R^{\mathrm{w}} = \sum_j \sum_{i=0}^{i_*} i \int J_{ij}^{\mathrm{sl}}\, d\mathbf{u}.$$

In the zero-order approximation, $\mathbf{P}^{(0)} = p\mathbf{I}$, $\mathbf{q}^{(0)} = 0$, and $\mathbf{q}_{\mathrm{w}}^{(0)} = 0$ and the equations (3.122)–(3.125) turn into the equations of an inviscid non-conductive gas flow in the generalized two-temperature approach. In Ref. [193], these equations are used for the simulation of non-equilibrium supersonic gas flows in nozzles, and the influence of the distribution shape on the gas-dynamic parameters is estimated.

### 3.7.3  Vibrational Relaxation Time and Specific Heats

Based on the proposed approach, the vibrational relaxation time in a flow of a gas consisted of anharmonic oscillators can be calculated. The relaxation time $\tau_{\mathrm{vibr}}$ can be introduced by the formula

$$\frac{1}{\tau_{\mathrm{vibr}}} = \frac{R^{\mathrm{w}(0)}}{\rho W^{\mathrm{eq}} - \rho W}, \quad (3.128)$$

where $R^{\mathrm{w}(0)}$ is determined by the zero-order distribution function, and the specific number of vibrational quanta $W^{\mathrm{eq}}$ is calculated on the basis of the local equilibrium Boltzmann distribution:

$$W^{\mathrm{eq}} = \frac{\displaystyle\sum_{i=0}^{i_*} i s_i \exp\left(-\frac{\varepsilon_i}{kT}\right)}{\displaystyle\sum_i s_i \exp\left(-\frac{\varepsilon_i}{kT}\right)}.$$
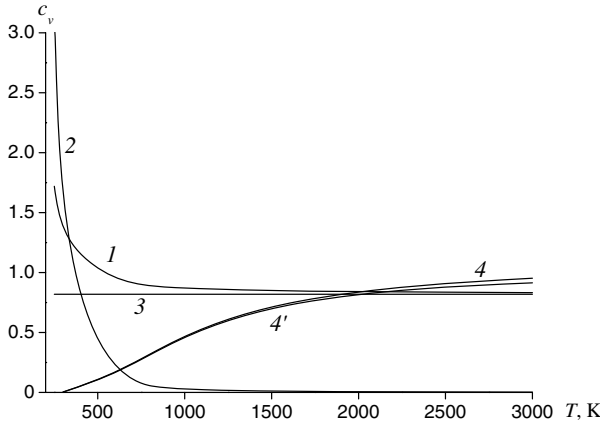
**Fig. 3.4** Dimensionless vibrational specific heats of $N_2$ as functions of $T$ at $T_1 = 2000$ K. Curve $1$ — $c_v^{T_1}$; $2$ — $-c_v^T$; $3$ — $c_v^{T_v}$ for harmonic oscillators; $4, 4'$ — the equilibrium specific heat $c_v^{eq}$ for harmonic and anharmonic oscillators
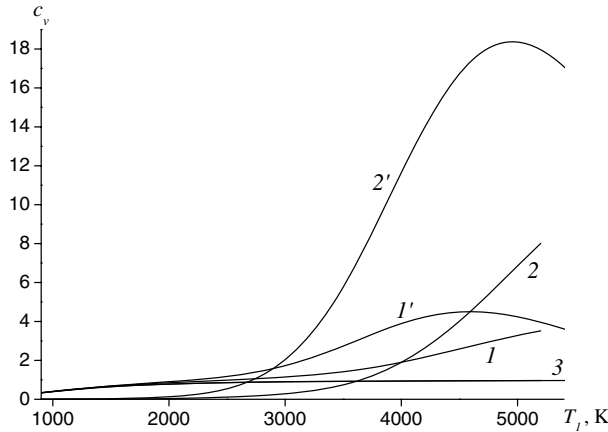


**Fig. 3.5** Dimensionless vibrational specific heats of $N_2$ as functions of $T_1$ at different $T$. Curves $1, 2$ — $T = 800$; $1', 2'$ — $T = 500$ K. $1, 1'$ — $c_v^{T_1}$; $2, 2'$ — $-c_v^T$; $3$ — $c_v^{T_v}$ for harmonic oscillators

Similar definitions of the relaxation time for the harmonic oscillator model are often introduced in the literature (see [100, 236]). In this case, the number of vibrational quanta in Eq. (3.128) is replaced by the specific vibrational energy of harmonic oscillators calculated using the formula (3.31).

Let us consider now in more detail the specific heats of the vibrational degrees of freedom. The modified specific heats are introduced by the formulae (3.27)–(3.30), however in the present approach, the specific vibrational energy and specific number
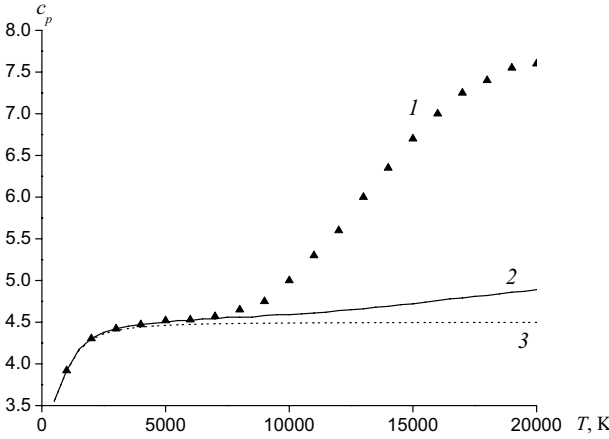
**Fig. 3.6** Dimensionless equilibrium constant pressure specific heats $c_p^{\mathrm{eq}}$ in $N_2$ as functions of $T$. Curve $1$ — the data given in Ref. [50]; $2,3$ — $c_p^{\mathrm{eq}}$ for anharmonic and harmonic oscillators, respectively

of quanta are associated to the combined distribution (3.115) and computed on the basis of the expressions (3.126), (3.127). Calculating the derivatives of (3.126) and (3.127) with respect to $T$ and $T_1$, we find the final expressions for the specific heats of a strongly non-equilibrium gas.

In Figs. 3.4, 3.5 the dimensionless (divided by $k/m$) specific heats $c_{\mathrm{v}}^T$ and $c_{\mathrm{v}}^{T_1}$ for molecular nitrogen are given as functions of $T$ and $T_1$. In addition to that, the vibrational specific heat $c_{\mathrm{v}}^{T_{\mathrm{v}}}$ calculated for the harmonic oscillator model (3.32), as well as the equilibrium specific heat $c_{\mathrm{v}}^{\mathrm{eq}}$ calculated at $T = T_1$ for both harmonic and anharmonic oscillators, are presented. One can notice that under the conditions of weak deviations from the equilibrium ($T_1 \approx T$) and for $T_1 < T$, the absolute value for $c_{\mathrm{v}}^T$ is negligibly small. The reason for such behavior is that under above conditions, the distribution (3.115) is close to the Boltzmann's with the vibrational temperature $T_1$ valid for harmonic oscillators, and for the harmonic vibrations $c_{\mathrm{v}}^T = 0$. When the non-equilibrium ratio $T_1/T$ increases, the absolute value of $c_{\mathrm{v}}^T$ also rises and at $T_1/T > 4$ exceeds $c_{\mathrm{v}}^{T_1}$. Note that $c_{\mathrm{v}}^{T_1} > c_{\mathrm{v}}^{\mathrm{eq}}$ for $T_1 > T$, and $c_{\mathrm{v}}^{T_1} < c_{\mathrm{v}}^{\mathrm{eq}}$ for $T_1 < T$. The non-equilibrium specific heat of harmonic oscillators increases monotonically with the vibrational temperature. For anharmonic oscillators, the dependence of the specific heat on $T$ or $T_1$ is non-monotonic, and at some values for the $T_1/T$ ratio we observe a peak of the specific heats explained by the non-uniform dependence of the vibrational energy of anharmonic oscillators on the temperatures $T$ and $T_1$.

The equilibrium specific heat $c_{\mathrm{v}}^{\mathrm{eq}}$ increases with the temperature, the discrepancy between the equilibrium specific heats of harmonic and anharmonic oscillators also rises with the temperature $T$. Consequently, we conclude that the anharmonicity of molecular vibrations is of particular importance under the non-equilibrium

conditions with $T_1 > T$, whereas in the case of equilibrium gases, its contribution becomes noticeable only at high temperatures.

Moreover, with the increase of the temperature, the influence of high vibrational levels on the specific heat turns to be important. Thus for moderate temperatures (for nitrogen, $T < 2000$ K) the high levels practically do not contribute to the specific heat even if the vibrational energy supply is large (the $T_1/T$ ratio is high). However, for temperatures about 6000–8000 K neglecting the upper vibrational states leads to underestimation for the specific heats.

Fig. 3.6 shows the dimensionless equilibrium constant pressure specific heats $c_p^{\mathrm{eq}}$ for harmonic and anharmonic oscillators. The effect of anharmonic vibrations is rather low for $T < 2000$ K. In the same Figure, $c_p^{\mathrm{eq}}$ calculated in Ref. [50] taking into account electronic excitation are also reproduced. It is seen that for $T > 8000$ K the electronic degrees of freedom significantly contribute to the specific heats.

In conclusion, let us note that the non-equilibrium specific heats are determined mainly by the shape of molecular distributions over the vibrational levels. Therefore, the specific heat is the main value affected by strong excitation of vibrational degrees of freedom. Deviations of the zero-order distribution functions from the Boltzmann's significantly influence the specific heat and consequently the coefficients of heat conductivity and bulk viscosity. This feature of the specific heat is important for the analysis of transport processes in a strongly non-equilibrium gas.

## 3.8 Transport Processes in a Gas with Strong Vibrational Excitation

### 3.8.1 First-Order Distribution Function

The first-order distribution function is found as the solution for the integral equation

$$-n^2 I_{ij}(\varphi) = D f_{ij}^{(0)} - J_{ij}^{\mathrm{sl}(0)}. \tag{3.129}$$

The linearized operator of rapid processes in a single-component gas $I_{ij}(\varphi)$ is given by

$$I_{ij}(\varphi) = \frac{1}{n^2} \sum_{kl i' j' k' l'} \int f_{ij}^{(0)} f_{kl}^{(0)} \left( \varphi_{ij} + \varphi_{kl} - \varphi_{i'j'} - \varphi_{k'l'} \right) \times$$

$$\times g \sigma_{ijkl}^{i'j'k'l'} d^2 \Omega d\mathbf{u}. \tag{3.130}$$

Note that the operator $I_{ij}(\varphi)$ is specified by the cross sections of various processes at different groups of energy levels thus being non-uniform over the vibrational spectrum.

The expression for $Df_{ij}^{(0)}$ in the generalized two-temperature approach is obtained in the form

$$
Df_{ij}^{(0)} = f_{ij}^{(0)} \left\{ \left( \frac{mc^2}{2kT} - \frac{5}{2} + \left[ \frac{\varepsilon_j}{kT} \right]_{\text{rot}}' + \left[ \frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} \right]_{\text{vibr}}' \right) \mathbf{c} \cdot \nabla \ln T + \right.
$$

$$
+ \left[ \frac{\beta\varepsilon_1}{kT_1} \right]_{\text{vibr}}' \mathbf{c} \cdot \nabla \ln T_1 + \frac{m}{kT} \left( \mathbf{cc} - \frac{1}{3}c^2\mathbf{I} \right) : \nabla\mathbf{v} +
$$

$$
+ \left( \frac{mc^2}{2kT} - \frac{3}{2} + \left[ \frac{\varepsilon_j}{kT} \right]_{\text{rot}}' + \left[ \frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} \right]_{\text{vibr}}' \right) \frac{1}{T}\frac{dT}{dt} +
$$

$$
\left. + \frac{1}{T_1}\frac{dT_1}{dt} \left[ \frac{\beta\varepsilon_1}{kT_1} \right]_{\text{vibr}}' + \left( \frac{mc^2}{3kT} - 1 \right) \nabla \cdot \mathbf{v} \right\}. \tag{3.131}
$$

Here, averaging over the vibrational spectrum is carried out using the non-equilibrium combined distribution (3.115):

$$
\langle \alpha \rangle_{\text{vibr}} = \frac{\displaystyle\sum_i \alpha_i s_i \exp\left( -\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} - \frac{\beta\varepsilon_1}{kT_1} + \ln\frac{i_* + 1}{\gamma + 1} \right)}{\displaystyle\sum_i s_i \exp\left( -\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} - \frac{\beta\varepsilon_1}{kT_1} + \ln\frac{i_* + 1}{\gamma + 1} \right)}.
$$

The derivatives $dT/dt$ and $dT_1/dt$ can be found from the energy conservation equation (3.124) and the equation for the specific number of vibrational quanta (3.125) in the zero-order approximation:

$$
\frac{dT}{dt} = -\frac{c_{\text{w}}^{T_1} p\nabla \cdot \mathbf{v} + c_{\text{v}}^{T_1} \varepsilon_1 R^{\text{w}(0)}}{\rho \left( c_{\text{u}} c_{\text{w}}^{T_1} - c_{\text{w}}^{T} c_{\text{v}}^{T_1} \right)}, \tag{3.132}
$$

$$
\frac{dT_1}{dt} = \frac{c_{\text{w}}^{T} p\nabla \cdot \mathbf{v} + c_{\text{u}} \varepsilon_1 R^{\text{w}(0)}}{\rho \left( c_{\text{u}} c_{\text{w}}^{T_1} - c_{\text{w}}^{T} c_{\text{v}}^{T_1} \right)}. \tag{3.133}
$$

Substituting the expressions (3.132) and (3.133) into Eq. (3.131) after some transformations we obtain the following structural form of the first-order distribution function $f_{ij}^{(1)}$:

$$f_{ij}^{(1)} = f_{ij}^{(0)} \left( -\frac{1}{n}\mathbf{A}_{ij} \cdot \nabla \ln T - \frac{1}{n}\mathbf{A}_{ij}^{(1)} \cdot \nabla \ln T_1 - \right.$$

$$\left. -\frac{1}{n}\mathbf{B}_{ij} : \nabla \mathbf{v} - \frac{1}{n}F_{ij}\nabla \cdot \mathbf{v} - \frac{1}{n}G_{ij} \right). \tag{3.134}$$

The functions $\mathbf{A}_{ij}$, $\mathbf{A}_{ij}^{(1)}$, $\mathbf{B}_{ij}$, $F_{ij}$, and $G_{ij}$ are found from the linear integral equations:

$$nI_{ij}(\mathbf{A}) = f_{ij}^{(0)}\mathbf{c}\left( \frac{mc^2}{2kT} - \frac{5}{2} + \left[\frac{\varepsilon_j}{kT}\right]'_{\text{rot}} + \left[\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT}\right]'_{\text{vibr}} \right), \tag{3.135}$$

$$nI_{ij}(\mathbf{A}^{(1)}) = f_{ij}^{(0)}\mathbf{c}\left[\frac{\beta\varepsilon_1}{kT_1}\right]'_{\text{vibr}}, \tag{3.136}$$

$$nI_{ij}(\mathbf{B}) = \frac{m}{2kT}f_{ij}^{(0)}\left( \mathbf{cc} - \frac{1}{3}c^2\mathbf{I} \right), \tag{3.137}$$

$$nI_{ij}(F) = f_{ij}^{(0)}\left\{ -\frac{nkT}{\rho(c_u c_{\text{w}}^{T_1} - c_{\text{w}}^T c_{\text{v}}^{T_1})} \frac{c_{\text{w}}^{T_1}}{T}\left( \frac{mc^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j}{kT}\right]'_{\text{rot}} + \right. \right.$$

$$\left. \left. + \left[\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT}\right]'_{\text{vibr}} \right) - \frac{c_{\text{w}}^T}{T_1}\left[\frac{\beta\varepsilon_1}{kT_1}\right]'_{\text{vibr}} + \frac{mc^2}{3kT} - 1 \right\}, \tag{3.138}$$

$$nI_{ij}(G) = -f_{ij}^{(0)}\left\{ \frac{\varepsilon_1 R^{\text{w}(0)}}{\rho(c_u c_{\text{w}}^{T_1} - c_{\text{w}}^T c_{\text{v}}^{T_1})} \frac{c_{\text{v}}^{T_1}}{T}\left( \frac{mc^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j}{kT}\right]'_{\text{rot}} + \right. \right.$$

$$\left. \left. + \left[\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT}\right]'_{\text{vibr}} \right) - \frac{c_u}{T_1}\left[\frac{\beta\varepsilon_1}{kT_1}\right]'_{\text{vibr}} \right\} - J_{ij}^{\text{sl}(0)}. \tag{3.139}$$

The uniqueness of the solutions for these equations is provided by the additional constraints following from the normalizing conditions for the distribution function (3.118)–(3.121):

$$\sum_{ij} m \int f_{ij}^{(0)} A_{ij} c^2 d\mathbf{u} = 0,$$

$$\sum_{ij} m \int f_{ij}^{(0)} A_{ij}^{(1)} c^2 d\mathbf{u} = 0,$$

$$\sum_{ij} \int f_{ij}^{(0)} F_{ij} d\mathbf{u} = 0,$$

$$\sum_{ij} \int f_{ij}^{(0)} G_{ij} d\mathbf{u} = 0,$$

$$\sum_{ij} \int f_{ij}^{(0)} \left( \frac{mc^2}{2} + \varepsilon_j + \varepsilon_i \right) F_{ij} d\mathbf{u} = 0,$$

$$\sum_{ij} \int f_{ij}^{(0)} \left( \frac{mc^2}{2} + \varepsilon_j + \varepsilon_i \right) G_{ij} d\mathbf{u} = 0,$$

$$\sum_{i=0}^{i_*} \sum_j i \int f_{ij}^{(0)} F_{ij} d\mathbf{u} = 0,$$

$$\sum_{i=0}^{i_*} \sum_j i \int f_{ij}^{(0)} G_{ij} d\mathbf{u} = 0.$$

### 3.8.2 Transport Terms

Now let us consider the first-order transport terms in Eqs. (3.122)–(3.125). The viscous stress tensor is given by the formula (2.43), the coefficients of shear and bulk viscosity and relaxation pressure in this relation are expressed in terms of bracket integrals by Eq. (2.44). For a single-component gas, the bracket integrals are given by the expression:

$$[A, B] = \sum_{ij} \int I_{ij}(A) B_{ij} \, d\mathbf{u}.$$

The linear integral operator $I_{ij}(A)$ is defined by Eq. (3.130) and contains the cross sections of various processes at different groups of vibrational levels.

The bulk viscosity coefficient and the relaxation pressure are related to the rapid inelastic processes and in the considered approach can be represented as a sum of two terms (see Eq. (3.77)). The first term is connected to the RT energy transitions, whereas the second is associated to the non-resonant vibrational energy exchanges. The relaxation pressure depends not only on the energy defect in rapid inelastic processes but is also specified by the cross sections of slow processes.

The diffusion velocity in a single-component gas disappears, and the heat flux includes only the gradients of $T$ and $T_1$

$$\mathbf{q} = - \left( \lambda' + \lambda_{vt} \right) \nabla T - \left( \lambda_{tv} + \lambda_{vv} \right) \nabla T_1, \qquad (3.140)$$

$$\lambda' = \frac{k}{3} [\mathbf{A}, \mathbf{A}], \qquad \lambda_{vt} = \frac{kT_1}{3T} \left[ \mathbf{A}^{(1)}, \mathbf{A} \right],$$

$$\lambda_{tv} = \frac{kT}{3T_1} \left[ \mathbf{A}, \mathbf{A}^{(1)} \right], \qquad \lambda_{vv} = \frac{k}{3} \left[ \mathbf{A}^{(1)}, \mathbf{A}^{(1)} \right].$$

The physical meaning of various heat conductivity coefficients in Eq. (3.140) is discussed in Section 3.5. For the harmonic oscillator model, the cross coefficients $\lambda_{vt}$ and $\lambda_{tv}$ are equal to zero.

The flux associated with the transport of vibrational quanta at low levels is found in the form

$$\varepsilon_1 \mathbf{q}_w = -\lambda_{vt} \nabla T - \lambda_{vv} \nabla T_1.$$

For harmonic oscillators,

$$\varepsilon_1 \mathbf{q}_w = \mathbf{q}_{vibr} = -\lambda_{vv} \nabla T_v,$$

and the vibrational energy flux is determined by the vibrational temperature gradient only. From the physical point of view, it is explained by the fact that during VV transitions, the resonance defect is equal to zero due to the equidistant location of the harmonic oscillator vibrational levels. Therefore the exchange of vibrational quanta between harmonic oscillators is resonant and no transfer of vibrational energy into the translational mode occurs during VV transitions.

Along with (3.140), the total energy flux $\mathbf{q}$ can be written alternatively as a sum of three terms related to the fluxes of translational, rotational and vibrational energy [71, 139, 140]:

$$\mathbf{q} = \mathbf{q}_{tr} + \mathbf{q}_{rot} + \mathbf{q}_{vibr},$$

where

$$\mathbf{q}_{tr} = -\lambda_{tr} \nabla T; \quad \mathbf{q}_{rot} = -\lambda_{rot} \nabla T; \quad \mathbf{q}_{vibr} = -\lambda'_{vt} \nabla T - \lambda_v \nabla T_1. \qquad (3.141)$$

In this case, for the heat conductivity coefficients in Eq. (3.141) we obtain

$$\lambda_{tr} = \frac{k}{3} \left[ \sqrt{\frac{m}{2kT}} \mathbf{c} \left( \frac{mc^2}{2kT} - \frac{5}{2} \right), \mathbf{A}_{ij} \right],$$

$$\lambda_{rot} = \frac{k}{3} \left[ \sqrt{\frac{m}{2kT}} \mathbf{c} \left( \frac{\varepsilon_j}{kT} - \left\langle \frac{\varepsilon_j}{kT} \right\rangle_{rot} \right), \mathbf{A}_{ij} \right],$$

$$\lambda'_{vt} = \frac{k}{3} \left[ \sqrt{\frac{m}{2kT}} \mathbf{c} \left( \frac{\varepsilon_i}{kT} - \left\langle \frac{\varepsilon_i}{kT} \right\rangle_{vibr} \right), \mathbf{A}_{ij} \right],$$

$$\lambda_v = \frac{k}{3} \left[ \sqrt{\frac{m}{2kT}} \mathbf{c} \left( \frac{\varepsilon_i}{kT} - \left\langle \frac{\varepsilon_i}{kT} \right\rangle_{vibr} \right), \mathbf{A}_{ij}^{(1)} \right].$$

The coefficients $\lambda'_{vt}$, $\lambda_v$ represent the sum of two terms:

$$\lambda'_{vt} = \lambda_{anh} + \lambda_{vt}, \qquad \lambda_v = \lambda_{tv} + \lambda_{vv},$$

the physical sense of these coefficients was discussed above (see Section 3.5).

Some results for the viscosity and heat conductivity coefficients in a single-component gas under the conditions of strong vibrational excitation are discussed below in Section 5.7.

The distribution function similar to (3.113) can be obtained also for a chemically reacting gas if the relations (3.110) are fulfilled for the molecules of each chemical species and the characteristic time of chemical reactions is of the same order of magnitude as the macroscopic time $\theta$. Such a distribution was derived in Ref. [61] for a binary mixture of atoms and molecules with dissociation and recombination and then applied to the numerical simulation of non-equilibrium nozzle flows. In Chapter 9, the results concerning non-equilibrium reacting mixture flows in nozzles obtained on the basis of various quasi-stationary models and within the frame of the state-to-state approach are analyzed.

# Chapter 4
# One-Temperature Model for Chemically Non-equilibrium Gas Mixtures

In the present Chapter, we consider a chemically reacting gas mixture flow under the condition (1.45), which suggests that the characteristic time for the relaxation of all internal energy modes is considerably smaller than that for chemical reactions. Such conditions often provide a subject for chemical kinetics studies [126], when non-equilibrium chemical reactions are simulated on the basis of the maintaining thermal equilibrium distributions over the internal energy. A kinetic description for the tempered reaction regime can be found in Refs. [249, 76, 60]. Thus, in the monograph [76], mathematical aspects of transport theory in reacting mixtures with slow chemical reactions are considered in detail, and efficient algorithms for the solution for linear transport systems are developed. In this Chapter, we briefly discuss the zero- and first-order distribution functions, governing equations, and the structure of transport and production terms in the one-temperature approach.

## 4.1 Zero-Order Distribution Function, Macroscopic Parameters and Set of Governing Equations

We consider the kinetic equations (1.38) for the distribution function of a multi-component gas mixture under the condition (1.45). In this case, the integral operator of rapid processes includes the operators of all collisions resulting in the internal energy variation:

$$J_{cij}^{\text{rap}} = J_{cij}^{\text{el}} + J_{cij}^{\text{rot}} + J_{cij}^{\text{vibr}} = J_{cij}^{\text{el}} + J_{cij}^{\text{int}}, \tag{4.1}$$

whereas the integral operator of slow processes is associated only with chemically reactive collisions:

$$J_{cij}^{\text{sl}} = J_{cij}^{\text{react}}. \tag{4.2}$$

The small parameter in Eq. (1.38) is the ratio of characteristic times for rapid and slow processes: $\varepsilon = \tau_{\text{int}} / \tau_{\text{react}} \sim \tau_{\text{int}} / \theta$. In the zero-order approximation, the equations (1.38) with the collision operators (4.1) and (4.2) are reduced to the equation:

$$J_{cij}^{\text{el}(0)} + J_{cij}^{\text{int}(0)} = 0. \tag{4.3}$$

The set of the collision invariants of rapid processes includes the invariants of any collision: $\psi_{cij}^{(\nu)} = m_c u_{c\nu}$ ($\nu = 1, 2, 3$), $\psi_{cij}^{(4)} = m_c u_c^2/2 + \varepsilon_{ij}^c + \varepsilon_c$, and, besides, the additional invariants of the most frequent collisions: $\psi_{cij}^{(\lambda+4)} = a_c$ ($\lambda = 1, ..., L$), where $a_c$ is any value independent of the velocity, vibrational and rotational levels $i$ and $j$, and arbitrarily depending on the chemical species $c$. The existence of the invariants $\psi_{cij}^{(\lambda+4)}$ is provided by the fact that under the condition (1.45), chemical reactions remain frozen in rapid processes.

Based on this set of collision invariants, the zero-order distribution function is found in the form

$$f_{cij}^{(0)} = \left( \frac{m_c}{2\pi kT} \right)^{3/2} \frac{n_c}{Z_c^{\text{int}}(T)} s_{ij}^c \exp \left( -\frac{m_c c_c^2}{2kT} - \frac{\varepsilon_{ij}^c}{kT} \right), \qquad (4.4)$$

while the internal partition function $Z_c^{\text{int}}(T)$ depends on the gas temperature $T$:

$$Z_c^{\text{int}}(T) = \sum_{ij} s_{ij}^c \exp \left( -\frac{\varepsilon_{ij}^c}{kT} \right).$$

We can also write

$$Z_c^{\text{int}}(T) = \sum_i s_i^c \exp \left( -\frac{\varepsilon_i^c}{kT} \right) Z_{ci}^{\text{rot}},$$

where $Z_{ci}^{\text{rot}}$ is given by Eq. (2.6).

In the given approach, the most frequent collisions include not only those with vibrational energy transitions between molecules of the same chemical species responsible for the formation of multi-temperature vibrational distributions, but also collisions with all other kinds of vibrational energy exchanges. Therefore, already on the microscopic time scale $\tau_{\text{rap}}$, rapid VV$_2$ vibrational energy exchange between unlike molecules leads to equalizing of the vibrational temperatures, and further on, VT transitions result in the equilibration of the vibrational and gas temperatures. Consequently, the distribution function takes the form of the thermal equilibrium Maxwell-Boltzmann distribution (4.4) with the gas temperature $T$. From Eq. (4.4) it follows that the vibrational level populations are described by the one-temperature Boltzmann distribution (3.18). A non-equilibrium regime of chemical reactions is taken into account in Eq. (4.4) through the dependence of $f_{cij}^{(0)}$ on the non-equilibrium number densities of chemical species $n_c$ found from the equations of chemical kinetics.

In this case, the distribution function is normalized to the number densities of chemical species, momentum and total energy. The conditions of normalization are given by the equations similar to Eqs. (3.21)–(3.23):

$$\sum_{ij} \int f_{cij} d\mathbf{u}_c = \sum_{ij} \int f_{cij}^{(0)} d\mathbf{u}_c = n_c, \qquad c = 1, ..., L, \qquad (4.5)$$

$$\sum_{cij} m_c \int \mathbf{u}_c f_{cij} d\mathbf{u}_c = \sum_{cij} m_c \int \mathbf{u}_c f_{cij}^{(0)} d\mathbf{u}_c = \rho \mathbf{v}, \qquad (4.6)$$

$$\sum_{cij} \int \left( \frac{m_c c_c^2}{2} + \varepsilon_{ij}^c \right) f_{cij} d\mathbf{u}_c = \sum_{cij} \int \left( \frac{m_c c_c^2}{2} + \varepsilon_{ij}^c \right) f_{cij}^{(0)} d\mathbf{u}_c =$$

$$= \frac{3}{2} nkT + \rho E_{\text{rot}} + \rho E_{\text{vibr}}. \qquad (4.7)$$

In contrast to the multi-temperature approach, the vibrational energy in Eq. (4.7) depends only on the gas temperature $T$ and the species number densities $n_c$:

$$\rho E_{\text{vibr}} = \sum_{c=1}^{L_{\text{m}}} \rho_c E_{\text{vibr},c} = \sum_{c=1}^{L_{\text{m}}} \frac{n_c}{Z_c^{\text{vibr}}(T)} \sum_i s_i^c \varepsilon_i^c \exp\left( -\frac{\varepsilon_i^c}{kT} \right), \qquad (4.8)$$

while the equilibrium vibrational partition function $Z_c^{\text{vibr}}(T)$ is given by the formula (3.19). The gas temperature in the one-temperature approach is specified by the total equilibrium energy.

The governing equations for the macroscopic parameters $n_c(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$, and $T(\mathbf{r},t)$, which specify the distribution function, include the equations of the one-temperature non-equilibrium chemical kinetics coupled to the conservation equations for the momentum and total energy:

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c^{\text{react}}, \quad c = 1, .., L, \qquad (4.9)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \qquad (4.10)$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v} = 0. \qquad (4.11)$$

Note that the total energy $U$ in Eq. (4.11) is a function of temperature and species number densities since the vibrational energy is given by Eq. (4.8). The production terms in Eqs. (4.9) take the form similar to (3.86), (3.87) but depend on the one-temperature rate coefficients of chemical reactions.

The distribution function (4.4), as well as the conditions of normalization (4.5)–(4.7) formally coincide with those obtained in Ref. [82] for the case of a non-reacting multi-component gas mixture under the conditions of weak deviations from the local thermodynamic equilibrium. In the latter case, the unknown parameters $n_c$ are found from the diffusion equations (Eqs. (4.9) with the zero right-hand sides). In the case of a reacting gas mixture considered here, the values $n_c$ are found from Eqs. (4.9), which describe both the diffusion processes and non-equilibrium chemical kinetics. This constitutes the fundamental difference between the two mentioned cases and leads to essentially different results in the zero-order approximation and, especially, in the first-order solution. The transition to the total (thermal and chemical) equilibrium is discussed briefly in Section 4.3.

Let us write the zero-order governing equations for the macroscopic parameters. Since $\mathbf{V}_c^{(0)} = 0$, $\mathbf{P}^{(0)} = p\mathbf{I}$, and $\mathbf{q}^{(0)} = 0$, we obtain

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} = R_c^{\text{react}(0)}, \qquad c = 1,..,L, \tag{4.12}$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla p = 0, \tag{4.13}$$

$$\rho \frac{dU}{dt} + p \nabla \cdot \mathbf{v} = 0. \tag{4.14}$$

The right-hand sides of the equations of chemical kinetics (4.12) take the form (3.86), (3.87). In the approximation of an inviscid non-conductive gas flow, the rate coefficients for exchange reactions, dissociation and recombination involved in the production terms depend only on the gas temperature $T$:

$$k_{cc'}^{dd'(0)}(T) = \frac{1}{Z_c^{\text{vibr}}(T)Z_d^{\text{vibr}}(T)} \sum_{iki'k'} s_i^c s_k^d \exp\left(-\frac{\varepsilon_i^c + \varepsilon_k^d}{kT}\right) k_{ci,c'i'}^{dk,d'k'(0)}(T), \tag{4.15}$$

when $d$ is a molecule,

$$k_{cc'}^{dd'(0)}(T) = \frac{1}{Z_c^{\text{vibr}}(T)} \sum_{ii'} s_i^c \exp\left(-\frac{\varepsilon_i^c}{kT}\right) k_{ci,c'i'}^{dd'(0)}(T), \tag{4.16}$$

if $d$ is an atom,

$$k_{c,\text{diss}}^{d(0)}(T) = \frac{1}{Z_c^{\text{vibr}}(T)} \sum_i s_i^c \exp\left(-\frac{\varepsilon_i^c}{kT}\right) k_{ci,\text{diss}}^{d(0)}(T). \tag{4.17}$$

In a thermally equilibrium gas, the ratio of the forward and backward reaction rate coefficients is also determined only by the gas temperature and is equal to the equilibrium constant for a given reaction:

$$K_{c'c}^{d'd(0)}(T) = \frac{k_{c'c}^{d'd(0)}(T)}{k_{cc'}^{dd'(0)}(T)} = \left(\frac{m_c m_d}{m_{c'} m_{d'}}\right)^{3/2} \frac{Z_c^{\text{int}}(T)Z_d^{\text{int}}(T)}{Z_{c'}^{\text{int}}(T)Z_{d'}^{\text{int}}(T)} \times$$

$$\times \exp\left(\frac{D_c + D_d - D_{c'} - D_{d'}}{kT}\right), \tag{4.18}$$

$$K_{\text{rec-diss}}^{(0)}(T) = \frac{k_{\text{rec},c}^{d(0)}}{k_{c,\text{diss}}^{d(0)}} = \left(\frac{m_c}{m_{c'} m_{f'}}\right)^{3/2} h^3 (2\pi kT)^{-3/2} Z_c^{\text{int}}(T) \exp\left(\frac{D_c}{kT}\right). \tag{4.19}$$

The expressions (4.18), (4.19) are often written as the ratios of the partition functions of the reaction products $Z_c$, $Z_d$ and reagents $Z_{c'}$, $Z_{d'}$ for bi-molecular reactions, or $Z_c$ and $Z_{c'}$, $Z_{f'}$ for dissociation-recombination reactions:

$$K_{c'c}^{d'd\,(0)}(T) = \frac{Z_c(T)Z_d(T)}{Z_{c'}(T)Z_{d'}(T)} \exp\left(\frac{Q}{kT}\right), \qquad (4.20)$$

$$K_{\text{rec–diss}}^{(0)}(T) = \frac{Z_c(T)/V}{Z_{c'}(T)/V \, Z_{f'}(T)/V} \exp\left(\frac{D_c}{kT}\right), \qquad (4.21)$$

where $Q$ is the reaction heat effect

$$Q = D_c + D_d - D_{c'} - D_{d'},$$

$Z_c$ is the total partition function:

$$Z_c = Z_c^{\text{tr}} Z_c^{\text{int}}.$$

The partition function $Z_c^{\text{tr}}$ for the translational degrees of freedom was introduced before in Section 2.1.

Rewriting the equations of non-equilibrium kinetics (4.12) in the form (3.105), we obtain for the thermal equilibrium rate coefficients $k_{f,r}$, $k_{b,r}$ for a given reaction $r$, the relations commonly used in chemical kinetics and identical to the relations (4.20), (4.21):

$$K_r(T) = \frac{k_{b,r}(T)}{k_{f,r}(T)} = \frac{\prod_c Z_c^{v'_{c,r}}/V}{\prod_c Z_c^{v''_{c,r}}/V} \exp\left(\frac{Q_r}{kT}\right).$$

The coefficients $k_{f,r}$, $k_{b,r}$ are connected with (4.15)–(4.17) by the relations (3.106), (3.107).

In chemical thermodynamics, the equilibrium constant $K_r(T)$ is usually expressed in terms of partial pressures $p_c$ related to the chemical equilibrium state:

$$K_r(T) = (RT)^{\tilde{v}_r} \frac{\prod_c p_c^{v'_{c,r}}}{\prod_c p_c^{v''_{c,r}}}, \qquad (4.22)$$

where $\tilde{v}_r = \sum_c (v''_{c,r} - v'_{c,r})$ represents the difference of the backward and forward reaction orders, or in terms of the equilibrium volumetric concentrations $\xi_c = n_c/\mathcal{N}_A$ of chemical species:

$$K_r(T) = \frac{\prod_c \xi_c^{v'_{c,r}}}{\prod_c \xi_c^{v''_{c,r}}}. \qquad (4.23)$$

The equilibrium constant $K_r(T)$ does not depend on the initial amounts of the reagents, and relations (4.22), (4.23) express another form of the mass action law [167]. The equilibrium constants $K_r(T)$ for many chemical reactions in wide temperature ranges are given in a number of handbooks and tables (see, for instance, [96, 107, 211]).

## 4.2   First-Order Distribution Function: Transport and Production Terms

In the approach of the thermal equilibrium gas mixture, the equations for the first-order distribution function have the form (3.43). The linearized operator of the most frequent collisions is formally given by Eq. (3.44). One should, however, keep in mind that in the one-temperature approach, the operator $I_{cijd}(\varphi)$ includes the cross sections of all collisions leading to the variation of the internal energy rather than only the cross sections of elastic, RT and VV transitions as occurs in the multi-temperature model.

The expression for $Df_{cij}^{(0)}$ in Eq. (3.43) obtained taking into account the zero-order governing equations (4.12)–(4.14) is:

$$
Df_{cij}^{(0)} = f_{cij}^{(0)} \left\{ \left( \frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[ \frac{\varepsilon_{ij}^c}{kT} \right]' \right) \mathbf{c}_c \cdot \nabla \ln T + \right.
$$

$$
+ \frac{n}{n_c} \mathbf{c}_c \cdot \mathbf{d}_c + \frac{m_c}{kT} \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I} \right) : \nabla \mathbf{v} + \frac{R_c^{\mathrm{react}(0)}}{n_c} +
$$

$$
+ \left( \frac{m_c c_c^2}{3kT} - 1 - \frac{p}{\rho T c_V} \left( \frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[ \frac{\varepsilon_{ij}^c}{kT} \right]' \right) \right) \nabla \cdot \mathbf{v} -
$$

$$
\left. - \frac{\sum_c R_c^{\mathrm{react}(0)} \left( \frac{3}{2} kT + \langle \varepsilon_{ij}^c \rangle + \varepsilon_c \right)}{\rho T c_V} \left( \frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[ \frac{\varepsilon_{ij}^c}{kT} \right]' \right) \right\}. \tag{4.24}
$$

Here, $c_V$ is the total constant volume specific heat given by the formula (1.15), $[\zeta_{ij}]' = \zeta_{ij} - \langle \zeta_{ij} \rangle$, and averaging is carried out with the thermal equilibrium Boltzmann distribution over the total internal energy $\varepsilon_{ij}^c$:

$$
\langle \zeta_{ij} \rangle = \frac{1}{Z_c^{\mathrm{int}}(T)} \sum_{ij} s_{ij}^c \zeta_{ij} \exp \left( -\frac{\varepsilon_{ij}^c}{kT} \right). \tag{4.25}
$$

Starting from Eq. (4.24), the first-order distribution function $f_{cij}^{(1)} = f_{cij}^{(0)} \varphi_{cij}$ can be written in the form:

$$
f_{cij}^{(1)} = f_{cij}^{(0)} \left( -\frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_d \mathbf{D}_{cij}^d \cdot \mathbf{d}_d - \frac{1}{n} \mathbf{B}_{cij} : \nabla \mathbf{v} - \right.
$$

$$
\left. - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right). \tag{4.26}
$$

The functions $\mathbf{A}_{cij}$, $\boldsymbol{B}_{cij}$, $\mathbf{D}_{cij}^d$, $F_{cij}$, and $G_{cij}$ are found as the solutions for the corresponding integral equations obtained by substituting the expression (4.24) into Eq. (3.43) and comparing the coefficients at the gradients of the same macroscopic variables:

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}(\mathbf{A}) = \frac{1}{n} f_{cij}^{(0)} \left( \frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[ \frac{\varepsilon_{ij}^c}{kT} \right]' \right) \mathbf{c}_c, \tag{4.27}$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}\left(\mathbf{D}^b\right) = \frac{1}{n_c} f_{cij}^{(0)} \left( \delta_{cb} - \frac{\rho_c}{\rho} \right) \mathbf{c}_c, \quad b = 1, ..., L, \tag{4.28}$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}(\boldsymbol{B}) = \frac{m_c}{nkT} f_{cij}^{(0)} \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \boldsymbol{I} \right), \tag{4.29}$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}(F) = \frac{1}{n} f_{cij}^{(0)} \left( \frac{2}{3} \frac{c_{\text{int}}}{c_V} \left( \frac{m_c c_c^2}{2kT} - \frac{3}{2} \right) - \frac{\hat{R}}{c_V} \left[ \frac{\varepsilon_{ij}^c}{kT} \right]' \right), \tag{4.30}$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}(G) = -\frac{1}{n} J_{cij}^{\text{react}(0)} + \frac{1}{n} f_{cij}^{(0)} \left( \frac{R_c^{\text{react}(0)}}{n_c} - \right.$$

$$\left. -\frac{\sum_c R_c^{\text{react}(0)} \left( \frac{3}{2} kT + \langle \varepsilon_{ij}^c \rangle + \varepsilon_c \right)}{\rho T c_V} \left( \frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[ \frac{\varepsilon_{ij}^c}{kT} \right]' \right) \right). \tag{4.31}$$

Here, $c_{\text{int}}$ is the specific heat of internal degrees of freedom

$$c_{\text{int}} = \left( \frac{\partial E_{\text{int}}}{\partial T} \right)_V = \sum_{c=1}^{L_{\text{m}}} \frac{\rho_c}{\rho} c_{\text{int},c}, \quad c_{\text{int},c} = \left( \frac{\partial E_{\text{int},c}}{\partial T} \right)_V,$$

where $E_{\text{int},c}$ is the specific internal energy of chemical species $c$, while $E_{\text{int}}$ is the total specific energy of a mixture. Since $E_{\text{int}} = E_{\text{rot}} + E_{\text{vibr}} + E_{\text{f}}$, then

$$c_{\text{int}} = c_V - c_{\text{tr}} = c_V - \frac{3}{2} \hat{R}.$$

The linear integral equations (4.27)–(4.31) contain the operator (4.1) of elastic collisions and those resulting in all kinds of inelastic energy exchange, linearized with the distribution function (4.4).

Additional constraints for the functions $\mathbf{A}_{cij}$, $\boldsymbol{B}_{cij}$, $\mathbf{D}_{cij}^d$, $F_{cij}$, and $G_{cij}$ follow from the conditions of normalization (4.5)–(4.7) and appear to be similar to the constraints (3.64), (3.66)–(3.70) derived in the multi-temperature approach:

$$\sum_{cij} m_c \int f_{cij}^{(0)} A_{cij} c_c^2 d\mathbf{u}_c = 0, \tag{4.32}$$

$$\sum_{cij} m_c \int f_{cij}^{(0)} D_{cij}^d c_c^2 d\mathbf{u}_c = 0, \qquad d = 1, ..., L, \tag{4.33}$$

$$\sum_{ij} \int f_{cij}^{(0)} F_{cij} d\mathbf{u}_c = 0, \qquad c = 1, ..., L, \tag{4.34}$$

$$\sum_{ij} \int f_{cij}^{(0)} G_{cij} d\mathbf{u}_c = 0, \qquad c = 1, ..., L, \tag{4.35}$$

$$\sum_{cij} \int f_{cij}^{(0)} \left( \frac{m_c c_c^2}{2} + \varepsilon_{ij}^c \right) F_{cij} d\mathbf{u}_c = 0, \tag{4.36}$$

$$\sum_{cij} \int f_{cij}^{(0)} \left( \frac{m_c c_c^2}{2} + \varepsilon_{ij}^c \right) G_{cij} d\mathbf{u}_c = 0. \tag{4.37}$$

These constraints should be complemented by the condition (3.73).

Comparing the structure of the first-order distribution functions obtained in the frame of the one-temperature (4.26) and multi-temperature (3.57) approaches, we notice that the expression (4.26) does not include the vibrational temperature gradients. On the other hand, in contrast to the case of a non-reacting mixture considered in [82], the first-order distribution function (4.26) contains the scalar term $G_{cij}$ related to non-equilibrium chemical reactions. Indeed, the integral equations (4.31) for the function $G_{cij}$ depend on the collision operator of slow chemical reactions.

The viscous stress tensor in the one-temperature approach is again expressed by the formula (2.43), however, the functions $B_{cij}$, $F_{cij}$, and $G_{cij}$ are found from other integral equations (4.29)–(4.31). The latter differ from the corresponding equations obtained both in the state-to-state and multi-temperature approaches. The coefficients of shear and bulk viscosity, as well as the relaxation pressure are calculated using Eq. (2.44), the bracket integrals in the latter formulae are defined by (3.74). Nevertheless, in the one-temperature approach, the bracket integrals related to the viscosity coefficients and relaxation pressure include the cross sections of elastic and all inelastic collisions which do not lead to chemical reactions. This is different from the multi-temperature model defining the corresponding bracket integrals as functions of the cross sections of only elastic, RT and VV exchanges. Moreover, the bracket integrals in the two approaches contain various zero-order distribution functions $f_{cij}^{(0)}$. The viscosity coefficients are determined by the cross sections of all kinds of energy transitions. The relaxation pressure depends on the same cross sections and, in addition, on the cross sections of chemically reactive collisions. The bulk viscosity coefficient in the one-temperature approach is associated to the inelastic RT and VT transitions, as well as to the non-resonant VV vibrational energy exchange.

The diffusion velocity in a gas mixture weakly deviating from the thermal equilibrium is specified by Eq. (3.84), where the diffusive driving forces $\mathbf{d}_c$ are given by the formula (3.46), and the multi-component diffusion and thermal diffusion coefficients are expressed in terms of bracket integrals via Eqs. (3.79). Similarly to the situation mentioned above with respect to the viscous stress tensor, one should bear

in mind that, although the bracket integrals specifying the diffusion and thermal diffusion coefficients in the one-temperature and multi-temperature approaches are introduced by the same formulae (3.74)–(3.76), they differ due to the cross sections of various collisional processes and also due to the different form of the zero-order distribution functions $f_{cij}^{(0)}$.

The total energy flux in the considered approach is associated with thermal conductivity, diffusion and thermal diffusion:

$$\mathbf{q} = -\lambda'\nabla T - p\sum_c D_{Tc}\mathbf{d}_c + \sum_c \rho_c h_c \mathbf{V}_c, \tag{4.38}$$

the partial thermal conductivity coefficient is defined as follows

$$\lambda' = \frac{k}{3}[\mathbf{A}, \mathbf{A}].$$

In the one-temperature approach, unlike the state-to-state and multi-temperature models, the heat conductivity coefficient $\lambda'$ describes the transport of all kinds of internal energy: $\lambda' = \lambda_{\mathrm{tr}} + \lambda_{\mathrm{int}} = \lambda_{\mathrm{tr}} + \lambda_{\mathrm{rot}} + \lambda_{\mathrm{vibr}}$ ($\lambda_{\mathrm{vibr}}$ is the vibrational thermal conductivity coefficient). The thermal conductivity coefficient depends on the cross sections of elastic and all inelastic collisions excepting those chemically reactive.

It is obvious that in the given case, the heat flux (4.38) takes the simplest form compared to that found in the framework of the state-to-state and multi-temperature approaches since it is determined only by the gradients of the gas temperature and molar fractions of the chemical species.

The thermal conductivity coefficient $\lambda'$ cannot be measured experimentally since there is a thermal diffusion phenomenon also related to the temperature gradient. For this reason, instead of the coefficient $\lambda'$, another heat conductivity coefficient is often introduced:

$$\lambda = \lambda' - nk\sum_c k_{Tc}D_{Tc},$$

where $k_{Tc}$ are the thermal diffusion ratios [255, 82]:

$$\sum_d D_{cd}k_{Td} = D_{Tc}, \quad c = 1, ..., L.$$

In this case, the total energy flux can be rewritten as

$$\mathbf{q} = -\lambda\nabla T + p\sum_c \left[k_{Tc} + \left(\frac{5}{2} + \left\langle\frac{\varepsilon_{ij}^c}{kT}\right\rangle + \frac{\varepsilon_c}{kT}\right)\frac{n_c}{n}\right]\mathbf{V}_c.$$

The coefficient $\lambda$ can be measured experimentally in a gas mixture under the steady-state conditions. For a single-component gas, since diffusion and thermal diffusion processes are absent, the coefficients $\lambda$ and $\lambda'$ coincide.

The mathematical properties of transport coefficients in both tempered and fast reaction regimes for a gas under weak deviations from the thermal equilibrium are discussed in Refs. [76, 78]. In particular, it is shown that due to the properties of

bracket integrals, the transport coefficients have some important features: the thermal conductivity coefficient $\lambda'$ is always positive, and so is the shear viscosity coefficient $\eta$; the bulk viscosity coefficient $\zeta$ is non-negative (and disappears only in the absence of polyatomic molecules in a mixture); the matrix of multi-component diffusion coefficients is symmetric and positive semi-definite. Similar properties can be established for the transport coefficients in the state-to-state and multi-temperature kinetic approaches. Some particular features of thermal conductivity in a strongly vibrationally excited gas are indicated in Section 5.7.

Let us now consider the chemical reaction rate coefficients contributing to the production terms $R_c^{\text{react}}$ in the equations (4.9) in the first-order approximation. Substituting the first-order distribution function (4.26) into Eq. (3.37) we can find $R_c^{\text{react}}$ in the form:

$$R_c^{\text{react}} = R_c^{2 \rightleftarrows 2} + R_c^{2 \rightleftarrows 3},$$

where the formulae for $R_c^{2 \rightleftarrows 2}$ and $R_c^{2 \rightleftarrows 3}$ formally coincide with (3.86), (3.87). The reaction rate coefficients in Eqs. (3.86), (3.87) are found from the relations similar to (3.88). The difference from the multi-temperature case is that the zero-order distribution function $f_{cij}^{(0)}$ and the first-order correction $\varphi_{cij}$ now take the form (4.4) and (4.26), respectively. Substituting the distribution functions (4.4) and (4.26) into (3.88) yields the expression (3.89). In this case, however, the coefficients $k_\gamma^{(0)}$, $k_\gamma^{(1)}$, $k_\gamma^{(2)}$ depend only on the gas temperature $T$ and species number densities $n_c$ (and $\nabla \cdot \mathbf{v}$ for the coefficient $k_\gamma^{(2)}$). The coefficients $k_\gamma^{(0)}$ correspond to the thermal equilibrium Maxwell-Boltzmann distribution over the velocity and internal energy levels; they are given by the formulae (4.15)–(4.17). The coefficients $k_\gamma^{(1)}$ and $k_\gamma^{(2)}$ account for weak deviations from the thermal equilibrium distribution (4.4). The expressions for their calculation coincide with Eqs. (3.96) and (3.97). The scalar functions $F_{cij}$ and $G_{cij}$ in the latest formulae are the solutions of the one-temperature integral equations (4.30), (4.31) complemented by the additional constraints (4.34)–(4.37).

The methods for the solution of the integral equations (4.27)–(4.31) for the functions $\mathbf{A}_{cij}$, $\mathbf{B}_{cij}$, $\mathbf{D}_{cij}^d$, $F_{cij}$, and $G_{cij}$, which specify the transport and reaction rate coefficients in the one-temperature approach, as well as the comparison of numerical algorithms for all kinetic coefficients in the state-to-state, multi-temperature, and one-temperature approaches, are considered in the next Chapter.

## 4.3  Transition to Chemical Equilibrium Regime

Modifications of the Chapman–Enskog method for reacting gas mixtures under the conditions of weak deviations from the total thermochemical equilibrium are proposed in Refs. [246, 247, 226, 249, 78]. In these studies, the zero-order and first-order distribution functions are obtained, and the transport theory based on these distributions is developed.

Under the conditions of chemical equilibrium, the zero-order distribution functions nullify the total collision operator including the operator of chemically reactive collisions:

$$J_{cij}^{\text{react}(0)} = 0.$$

In all approaches developed above, chemical reactions are assumed to be slow processes, therefore the integral equations for the determination of the distribution functions do not include $J_{cij}^{\text{react}}$ (this operator appears only in the free terms).

Under the conditions of weak deviations from the total equilibrium considered in this Section, all microscopic processes are supposed to be rapid, and the distribution function is found on the basis of the invariants of all types of collisions. In reacting gas mixtures, the set of collision invariants consists not only of the momentum and total energy (including the energy of formation), but contains also additional invariants related to chemical reactions. Such invariants are represented by the numbers of elements (atoms or other non-separable elements), which either exist in the free state or form molecules: $\psi_c^{(\lambda)} = k_{\lambda c}$ is the number of elements of the type $\lambda$ ($\lambda = 1, ..., \Lambda$) in a particle of chemical species $c$ (for atomic species, $k_{\lambda\lambda} = 1$). The zero-order distribution function corresponding to the local thermal and chemical equilibrium can be written in the form (4.4) where the number densities of chemical species $n_c$ are expressed by the relation

$$n_c = \frac{1}{h^3} (2\pi kTm_c)^{3/2} Z_c^{\text{int}}(T) \exp\left(\sum_\lambda \gamma_\lambda k_{\lambda c}\right) \exp\left(\frac{D_c}{kT}\right) \qquad (4.39)$$

and can be rewritten in the form [227]

$$n_c = \frac{Z_c(T)}{V} \exp\left(\sum_\lambda \gamma_\lambda k_{\lambda c}\right) \exp\left(\frac{D_c}{kT}\right), \qquad (4.40)$$

while $Z_c^{\text{int}}(T)$ and the total partition function $Z_c(T)$ are introduced in Section 4.1.

The parameters $\gamma_\lambda(\mathbf{r}, t)$ are connected to $\widetilde{n}_\lambda$, which represent the numbers of atoms $\lambda$ per unit volume:

$$\sum_c k_{\lambda c} n_c = \widetilde{n}_\lambda. \qquad (4.41)$$

Note that the number densities of species $n_c$ satisfy the equations of chemical equilibrium

$$R_c^{\text{react}(0)} = 0$$

and can be derived in the form (4.39), (4.40) directly from the above equations.

The normalizing conditions for the distribution function in the considered approach are written taking into account the conservation of the momentum, the total internal energy, including the energy of formation $\varepsilon_c$, and the numbers of elements of each type. These conditions contain Eqs. (2.10)–(2.13) (keep, however, in mind that, in Eq. (2.12), $E_{\text{vibr}} = E_{\text{vibr}}(n_1, ..., n_{L_m}, T)$ is the vibrational energy of a thermally and chemically equilibrium gas), as well as the additional conditions following from Eq. (4.41). The gas temperature is determined by the total specific internal energy including the energy of formation $E_{\text{f}}$.

In each approximation, the sets of governing equations for the macroscopic parameters $\mathbf{v}(\mathbf{r},t)$, $T(\mathbf{r},t)$, and $\widetilde{n}_\lambda(\mathbf{r},t)$ ($\lambda = 1,...,\Lambda$) are obtained from the kinetic equations. These governing equations for inviscid and viscous gas flows, as well as the expressions for the transport terms and transport coefficients are studied in detail in Refs. [226, 78].

In the case of non-equilibrium chemical reactions considered above in Sections 4.1, 4.2, the set of independent macroscopic parameters includes $\mathbf{v}(\mathbf{r},t)$, $T(\mathbf{r},t)$, and the number densities of various species $n_c(\mathbf{r},t)$ ($c = 1,...,L$), satisfying Eqs. (4.9). In the present case, the number densities $n_c$ are the solutions of the equations of chemical equilibrium and can be expressed in terms of parameters $\gamma_\lambda$, related to $\widetilde{n}_\lambda$. Note that the total number of elements $\Lambda$ is often smaller than that of chemical species $L$ in a mixture. For instance, in a five-component air mixture, $\Lambda = 2$, $L = 5$, and in a binary mixture $A_2/A$, $\Lambda = 1$, $L = 2$.

In the first-order approximation, the distribution function is expressed via the gradients of macroscopic parameters; the expression for $f_{cij}^{(1)}$ in the near-equilibrium case does not involve the scalar free term $G_{cij}$. The linear integral equations for the first-order correction $\varphi_{cij}$ depend on all collision operators including those of chemical reactions. The stress tensor in the viscous gas approximation can be obtained in the form (2.43), but in the considered case, the relaxation pressure disappears ($p_{\text{rel}} = 0$ since slow kinetic processes are absent). The bulk viscosity coefficient is defined by the cross sections of all inelastic processes including chemical reactions.

In Refs. [248, 247, 249, 226, 78], the heat flux in the case of weak deviations from the chemical equilibrium is expressed in terms of $\nabla T$, the gradients of macroscopic parameters $\gamma_\lambda$ and element diffusion velocities. As is emphasized in Ref. [78], it is more convenient to use the heat flux formula written in the conventional form as a function of the gas temperature gradient, species diffusive driving forces and species diffusion velocities. For a mixture with bimolecular reactions, such a transition is carried out in Ref. [249], whereas for gases with dissociation and recombination in Ref. [78]. The conventional form of the heat flux is useful for practical calculations and for a comparison with experimentally measured coefficients, as well as for the estimate of the contribution of chemical reactions to the total energy flux.

One should bear in mind that in the general case, the rigorous transition between the heat flux calculated in a chemically non-equilibrium one-temperature gas flow to the energy flux in the regime of weak deviations from the chemical equilibrium is prohibited even if the fluxes are expressed in terms of the same macroscopic parameters $n_c$, $p$, and $T$. This problem is discussed in detail in Section 5.6, while comparing the state-to-state and multi-temperature solutions. The impossibility of the transition is connected to the fact that the transport coefficients in the two approaches are found from different equations and depend on the cross sections of different processes: while in the case of weak chemical non-equilibrium, the transport coefficients depend on the cross sections of all energy exchanges and chemical reactions, in the one-temperature approach for a strongly chemically non-equilibrium gas, they are specified only by the cross sections of energy exchange. Nevertheless, if one assumes that the cross sections of chemically reactive collisions weakly contribute to the thermal conductivity and multi-component diffusion coefficients, one

can derive the expression for **q** in the regime of weak deviations from the chemical equilibrium from the Eq. (4.38) obtained in the one-temperature approach, simply substituting chemically equilibrium distributions (4.39), (4.40) into the latter formula. Then the thermal conductivity coefficient $\lambda'$ can be represented by the expression suggested in the studies of R. Brokaw and J. Butler [39, 32, 33]:

$$\lambda = \lambda_{tr} + \lambda_{int} + \lambda_{react},$$

where $\lambda_{react}$ is associated with the contribution of equilibrium chemical reactions to the thermal conductivity. The coefficient $\lambda_{react}$ can be easily calculated on the basis of equilibrium distributions.

In a more rigorous approach, the heat flux in a particular weakly chemically non-equilibrium flow should be found solving the Navier–Stokes transport equations coupled to the diffusion equations for the number densities of elements.

# Chapter 5
# Algorithms for the Calculation of Transport Coefficients

In order to define transport terms in the governing equations, it is necessary to calculate the coefficients of viscosity, thermal conductivity, diffusion, and relaxation pressure. In the present Chapter, algorithms for the calculation of transport coefficients are considered for different levels of accuracy of the description of non-equilibrium flows: in the state-to-state and quasi-stationary approaches. In contrast to weak non-equilibrium gases, the transport coefficients under the strong non-equilibrium conditions depend not only on the gas temperature but also on other parameters of the flow, which characterize the deviation from equilibrium, namely, on the vibrational level populations in the state-to-state approach and on the temperature of non-equilibrium modes in the quasi-stationary approximations. This results in some peculiarities in the transport coefficients discussed in this Chapter.

In Sections 5.1, 5.2, the computational formulae for all transport coefficients are derived using the solutions of the linear algebraic equations. The coefficients of the algebraic equations are expressed in terms of the bracket integrals introduced in the previous Chapters for various approaches. The calculation procedure for the bracket integrals is considered in detail, the ways for their simplification based on several assumptions are proposed, and the influence of the intermolecular interaction potential on the integrals for elastic collisions and, respectively, on the transport coefficients is discussed. In Section 5.5, a simplified scheme for the computation of the state-to-state transport coefficients is proposed. Taking into account these simplifications, in Section 5.6, a limit transition between the transport terms found in the state-to-state and quasi-stationary approaches is justified. Finally, a strongly non-equilibrium single-component gas is studied, and the generalization for the Eucken correction to the thermal conductivity coefficient is obtained for this case.

## 5.1 State-to-State Approach

Let us consider the transport terms in the equations (2.16)–(2.18) for $n_{ci}(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$, and $T(\mathbf{r},t)$ in the first-order approximation of the modified Chapman–Enskog method. The expressions (2.43), (2.48), and (2.50) for the stress tensor $\mathbf{P}$, diffusion velocity $\mathbf{V}_{ci}$ of molecular species $c$ on the vibrational level $i$, and heat flux $\mathbf{q}$,

obtained in Section 2.4, contain the coefficients of shear $\eta$ and bulk viscosity $\zeta$, relaxation pressure $p_{\mathrm{rel}}$, multi-component diffusion $D_{cidk}$ and thermal diffusion $D_{Tci}$ coefficients for molecules of species $c$ and $d$ on the vibrational levels $i$ and $k$, and the thermal conductivity coefficient $\lambda'$ associated with the energy transfer in elastic collisions and RT-transitions. All coefficients are expressed in terms of bracket integrals (2.47) (bilinear forms containing the linearized integral operators for the most frequent collisions) related to the functions $\mathbf{A}_{cij}$, $\boldsymbol{B}_{cij}$, $\mathbf{D}_{cij}^{dk}$, $F_{cij}$, and $G_{cij}$. These functions are solutions of the integral equations (2.31)–(2.35); the uniqueness of the solutions is guaranteed by the additional constraints (2.36)–(2.41), (2.42).

### 5.1.1 Expansions in the Sonine and Waldmann-Trübenbacher Polynomials

For the solution of the integral equations (2.31)–(2.35), the functions $\mathbf{A}_{cij}$, $\boldsymbol{B}_{cij}$, $\mathbf{D}_{cij}^{dk}$, $F_{cij}$, and $G_{cij}$ can be expanded into either infinite or finite series in terms of the systems of orthogonal Sonine and Waldmann-Trübenbacher polynomials. The Sonine polynomials are introduced as follows [57, 112, 82]:

$$S_{\nu}^{(n)}(x) = \sum_{p=0}^{n} \frac{\Gamma(\nu+n+1)}{(n-p)!\,p!\,\Gamma(\nu+p)}(-x)^{p}.$$

The polynomials satisfy the conditions of normalization and orthogonality

$$\int_{0}^{\infty} x^{\nu} e^{-x} S_{\nu}^{(p)}(x) S_{\nu}^{(q)}(x)\,dx = \frac{\Gamma(\nu+p+1)}{p!}\,\delta_{pq}.$$

In particular, for any $\nu$,

$$S_{\nu}^{(0)}(x) = 1, \qquad S_{\nu}^{(1)}(x) = \nu + 1 - x.$$

The Waldmann-Trübenbacher polynomials for the discrete energy levels are defined by the recurrent formula [258, 255]

$$P_{ij}^{(p)}\left(\frac{\varepsilon_{ij}^{c}}{kT}\right) = -\frac{\varepsilon_{ij}^{c}}{kT}P_{ij}^{(p-1)} + \sum_{q=0}^{p-1}\frac{\left\langle\frac{\varepsilon_{ij}^{c}}{kT}P_{ij}^{(p-1)}P_{ij}^{(q)}\right\rangle}{\left\langle P_{ij}^{(q)2}\right\rangle}P_{ij}^{(q)},$$

where the angle brackets denote the averaging operation. In the kinetic theory, averaging is usually carried out over the internal energy taking into account the zero-order distribution function. Thus in the case of weak deviations from the thermal equilibrium, the averaging is performed over the total internal energy (see also (4.25)):

$$\langle\zeta_{ij}^{c}\rangle = \frac{\displaystyle\sum_{ij}\zeta_{ij}^{c}s_{ij}^{c}\exp\left(-\frac{\varepsilon_{ij}^{c}}{kT}\right)}{\displaystyle\sum_{ij}s_{ij}^{c}\exp\left(-\frac{\varepsilon_{ij}^{c}}{kT}\right)}. \tag{5.1}$$

In a strongly non-equilibrium gas with rapid and slow processes, the zero-order distribution function corresponds to the equilibrium distribution over some degrees of freedom rather than to the total internal energy. This fact results in a modification of the averaging operation (5.1). Thus, in the state-to-state approach, the zero-order distribution function (2.4) describes the equilibrium distribution over the velocity and rotational energy levels, whereas the distribution over the vibrational levels is non-equilibrium and is related to the vibrational level populations. The right-hand sides of the integral equations (2.31)–(2.35) include only the rotational energy in the explicit form. Therefore, in the state-to-state approach, it is convenient to choose the Waldmann-Trübenbacher polynomials in the discrete rotational energy levels $P_j^{(p)}(\varepsilon_j^{ci}/(kT))$, defined using the averaging operation over the rotational spectrum (similarly to (2.28)):

$$
\langle \zeta_j^{ci} \rangle_{\text{rot}} = \frac{\sum_j \zeta_j^{ci} s_j^{ci} \exp\left(-\dfrac{\varepsilon_j^{ci}}{kT}\right)}{\sum_j s_j^{ci} \exp\left(-\dfrac{\varepsilon_j^{ci}}{kT}\right)}.
$$

The zero- and first-order polynomials in the state-to-state approach take the form

$$
P_j^{(0)} = 1, \qquad P_j^{(1)} = \left\langle \frac{\varepsilon_j^{ci}}{kT} \right\rangle_{\text{rot}} - \frac{\varepsilon_j^{ci}}{kT}.
$$

It can be easily shown that the Waldmann-Trübenbacher polynomials also satisfy the orthogonality condition. In particular, for the polynomials in the rotational energy, it is given by

$$
\left\langle P_j^{(p)} P_j^{(q)} \right\rangle_{\text{rot}} = \left\langle P_j^{(p)\,2} \right\rangle_{\text{rot}} \delta_{pq}.
$$

The choice of the polynomial system and its trial functions is an important and non-trivial problem. On the one hand, the appropriate choice of the trial functions can yield the simplest systems of algebraic equations for the definition of transport coefficients. On the other hand, one should keep in mind the convergence of the polynomials and, therefore, the number of expansion terms required for the transport coefficients calculation. The analysis of the Sonine and Waldmann-Trübenbacher polynomials convergence performed in Refs. [238, 203, 76], demonstrated that, in the case of weak deviations from the thermal equilibrium (in the one-temperature approach), although the expansion in the rotational and vibrational energy makes it possible to distinguish contributions of various degrees of freedom to the heat conductivity and bulk viscosity, it provides a slower convergence than the expansion in the total internal energy. In the case of strong deviations from the equilibrium, in particular, in the state-to-state and multi-temperature approaches, the expansion in the total energy is not convenient. In Refs. [139, 140, 60] it is suggested to choose the trial functions for the polynomials in accordance with the right-hand sides of the linear integral equations for the coefficients at the gradients of the macroscopic

parameters in the representation for $f_{cij}^{(1)}$. Hence, the trial functions are specified by the collision invariants of rapid processes. Such an approach significantly simplifies the calculations and makes it possible to obtain the main dependences for the transport coefficients already in the first non-vanishing expansion terms.

Analyzing the structure of the right-hand sides of the integral equations (2.31), (2.34), and (2.35) in the state-to-state approach, one can notice that the functions $\mathbf{A}_{cij}$, $F_{cij}$, and $G_{cij}$ should be expanded into a double polynomial system: the Sonine polynomials in the reduced peculiar velocity and those of Waldmann-Trübenbacher in the reduced rotational energy. The structure of the right-hand sides of the equations (2.32), (2.33) provides simpler expansions for the functions $\boldsymbol{B}_{cij}$, $\mathbf{D}_{cij}^{dk}$ in terms of only the Sonine polynomials. The expansions for all functions have the form

$$\mathbf{A}_{cij} = -\frac{m_c \mathbf{c}_c}{2kT} \sum_{rp} a_{ci,rp} S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j^{ci}}{kT} \right), \tag{5.2}$$

$$\mathbf{D}_{cij}^{dk} = \frac{m_c \mathbf{c}_c}{2kT} \sum_r d_{ci,r}^{dk} S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right), \tag{5.3}$$

$$\boldsymbol{B}_{cij} = \frac{m_c}{2kT} \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \boldsymbol{I} \right) \sum_r b_{ci,r} S_{5/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right), \tag{5.4}$$

$$F_{cij} = \sum_{rp} f_{ci,rp} S_{1/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j^{ci}}{kT} \right), \tag{5.5}$$

$$G_{cij} = \sum_{rp} g_{ci,rp} S_{1/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j^{ci}}{kT} \right). \tag{5.6}$$

Let us express the transport coefficients in terms of the coefficients in the expansions (5.2)–(5.6). For this purpose, the expansions are substituted into the relations (2.44), (2.49), and (2.51). After some transformations, taking into account the conditions of normalization and orthogonality for the Sonine and Waldmann-Trübenbacher polynomials, as well as the constraints (2.36), (2.38), and (2.39) we obtain

$$\lambda' = \sum_{ci} \frac{5}{4} k \frac{n_{ci}}{n} a_{ci,10} + \sum_{ci} \frac{m_c}{2} \frac{n_{ci}}{n} c_{\text{rot},ci} a_{ci,01}, \tag{5.7}$$

$$D_{cidk} = \frac{1}{2n} d_{ci,0}^{dk}, \tag{5.8}$$

$$D_{Tci} = -\frac{1}{2n} a_{ci,00}, \tag{5.9}$$

$$\eta = \frac{kT}{2} \sum_{ci} \frac{n_{ci}}{n} b_{ci,0}, \tag{5.10}$$

$$\zeta = -kT \sum_{ci} \frac{n_{ci}}{n} f_{ci,10}, \qquad (5.11)$$

$$p_{\mathrm{rel}} = kT \sum_{ci} \frac{n_{ci}}{n} g_{ci,10}. \qquad (5.12)$$

Thus all transport coefficients are expressed in terms of the first non-vanishing elements of the expansions for the functions $\mathbf{A}_{cij}$, $\mathbf{B}_{cij}$, $\mathbf{D}_{cij}^{dk}$, $F_{cij}$, and $G_{cij}$ in the chosen polynomial systems.

## 5.1.2 Systems of Equations for the Expansion Coefficients

Let us obtain the systems of equations for the expansion coefficients $a_{ci,rp}$, $d_{ci,r}^{dk}$, $b_{ci,r}$, $f_{ci,rp}$, and $g_{ci,rp}$.

First, the system of equations for the coefficients $a_{ci,rp}$, specifying the coefficients of thermal conductivity and thermal diffusion, is considered. Substituting the expansion (5.2) into the integral equation (2.31), multiplying both sides of this equation by the value

$$Q_{cij}^{rp} = \sqrt{\frac{m_c}{2kT}} \mathbf{c}_c S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j^{ci}}{kT} \right), \qquad (5.13)$$

integrating over the velocity and summing over the rotational levels, we obtain a system of linear algebraic equations for the coefficients $a_{ci,rp}$:

$$\sum_{dk} \sum_{r'p'} \Lambda_{rr'pp'}^{cidk} a_{dk,r'p'} = \frac{15kT}{2} \frac{n_{ci}}{n} \delta_{r1}\delta_{p0} + 3m_c T \frac{n_{ci}}{n} c_{\mathrm{rot},ci} \delta_{r0}\delta_{p1}, \qquad (5.14)$$

$$c = 1,...,L, \ i = 0,1,...,L_c, \ r,p = 0,1,...$$

The procedure for the expansion of the unknown functions into the infinite series was proposed by S. Chapman and T. Cowling [57]. It makes it possible to obtain infinite systems of algebraic equations for the expansion coefficients. Then the determinants of these systems are also expanded into the infinite series which are further on truncated at the term $K$. Later, J. Ferziger and H. Kaper [82] demonstrated that such a method is equivalent to the truncation of the series (5.2)–(5.6) or the expansions for the unknown functions into the finite series. Hereafter, we use the finite expansions truncating the series (5.2)–(5.6) at the $K^{th}$ term.

The coefficients of the equations (5.14) are expressed in terms of the vibrational level populations and bracket integrals introduced by the formula (2.47):

$$\Lambda_{rr'pp'}^{cidk} = \sqrt{m_c m_d} \left( \delta_{cd}\delta_{ik} \sum_{bn} \frac{n_{ci}n_{bn}}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]_{cibn}' + \frac{n_{ci}n_{dk}}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]_{cidk}'' \right),$$

where $Q_{cij}^{rp}$ is given by the expression (5.13). The partial bracket integrals depend on the cross sections of elastic collisions and those with RT transitions and are defined by the formulae (2.45), (2.46).

For $r = p = 0$, the system (5.14) is not linearly independent. It follows from the momentum conservation and symmetry of the bracket integrals $\Lambda_{rr'pp'}^{cidk} = \Lambda_{r'rp'p}^{dkci}$ [82]. In order to provide the unique solution for the system (5.14), one should complement it by the additional constraint following from the condition of normalization (2.36) for the function $\mathbf{A}_{cij}$:

$$\sum_{ci} \frac{\rho_{ci}}{\rho} a_{ci,00} = 0. \tag{5.15}$$

If we replace one of the equations in the system (5.14) with the constraint (5.15), we obtain the linearly independent system.

Keeping only the first non-vanishing terms in the expansion (5.2), we can simplify the system (5.14):

$$\sum_{dk} \left( \Lambda_{0000}^{cidk} a_{dk,00} + \Lambda_{0100}^{cidk} a_{dk,10} + \Lambda_{0001}^{cidk} a_{dk,01} \right) = 0,$$

$$\sum_{dk} \left( \Lambda_{1000}^{cidk} a_{dk,00} + \Lambda_{1100}^{cidk} a_{dk,10} + \Lambda_{1001}^{cidk} a_{dk,01} \right) = \frac{15kT}{2} \frac{n_{ci}}{n}, \tag{5.16}$$

$$\sum_{dk} \left( \Lambda_{0010}^{cidk} a_{dk,00} + \Lambda_{0110}^{cidk} a_{dk,10} + \Lambda_{0011}^{cidk} a_{dk,01} \right) = 3m_c T \frac{n_{ci}}{n} c_{\mathrm{rot},ci},$$

$$c = 1,...,L, \;\; i = 0,1,...,L_c.$$

The expressions for the bracket integrals in the system (5.16) are given below in this Chapter.

Note that keeping only the lowest terms of the series (5.2) at $p = r = 0$, $p = 0, r = 1$, and $p = 1, r = 0$ in the system (5.16) requires additional justification. As is shown in Refs. [57, 82, 262], for a monoatomic gases, such an assumption practically does not affect the accuracy of the calculation for the transport coefficients; thus the higher-order corrections to the viscosity coefficient do not exceed 2%. The situation can change dramatically for a mixture with essentially different masses of the components. For example, one can consider the Lorentz gas, which represents a binary mixture with a negligibly small ratio of component masses, and the concentration of the light component tending to zero.

The convergence of the Sonine polynomials for such a hypothetic case was studied in Refs. [57, 177, 178], and it was shown that the series converge considerably slower compared to the case of a single-component gas, especially for the diffusion coefficients. A particular example of a mixture with significantly different component masses is an ionized gas, in which electrons appear. In this case, the lowest approximation does not provide a satisfactory accuracy. For the calculation of the transport coefficients it is necessary to retain the second and the third term in the expansions [69, 186, 46, 261, 53]. The explicit expressions for the single-component gas transport coefficients taking into account the higher-order terms in the expansions, are obtained in Ref. [172]. In the present study, we assume that the mixture is composed of gases with approximately equal masses.

Solving the system (5.16) complemented with the constraint (5.15) for the coefficients $a_{ci,00}$, $a_{ci,10}$, and $a_{ci,01}$, we can find the coefficients of thermal conductivity and thermal diffusion using the relations (5.9), (5.7). It is obvious, that the system contains a great number of equations and, therefore, its solution requires efficient numerical algorithms. The most evident way for the solution of transport systems consists in the calculation of their determinants and the subsequent application of the Cramer's rule. This method is used in the classical monographs on the kinetic theory [57, 112, 82] for the computation of transport coefficients in a multi-component mixture weakly deviating from the equilibrium. Nevertheless, the calculations based on the Cramer's rule are extremely computationally expensive, especially in the state-to-state approach.

Another explicit method for the solution of linear algebraic systems based on the Gauss algorithm, is considered in Refs. [70, 119, 259]. This method is more efficient than the Cramer's rule, but still remains expensive from the computational point of view, like all explicit schemes. New algorithms for the solution of transport systems based on the iterative schemes are elaborated in [76]. In this study, the mathematical properties of linear systems for the calculation of the transport coefficients are considered, the iterative schemes are constructed for both singular and regular matrices, and the rigorous proof of the convergence for the proposed algorithm is given. These methods make it possible to calculate transport coefficients in multi-component mixtures efficiently and accurately.

Although the algorithms for the solution of transport systems described in Ref. [76] are rather efficient in the one-temperature and multi-temperature approaches, the calculation of the state-to-state transport coefficients remains a very complicated technical problem since a great number of equations should be solved. Thus the system (5.15) consists of $3N_{\mathrm{vibr}} + 2L_a$ equations ($N_{\mathrm{vibr}}$ is the total number of vibrational states in a mixture, $L_a$ is the number of atomic species). Simplified systems of algebraic equations specifying the transport coefficients in the state-to-state approach and containing fewer equations are considered in Section 5.5.

Now we consider the diffusion coefficients. The equations for the coefficients $d_{ci,r}^{dk}$ of the expansion (5.3) can be obtained from the linear integral equations (2.32) multiplying the latter by the function

$$Q_c^r = \sqrt{\frac{m_c}{2kT}} \mathbf{c}_c S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right),$$

integrating over the velocity and summing over the rotational energy levels:

$$\sum_{dk} \sum_{r'} \gamma_{rr'}^{cidk} d_{dk,r'}^{bn} = 3kT \left( \delta_{cb}\delta_{in} - \frac{\rho_{ci}}{\rho} \right) \delta_{r0}, \tag{5.17}$$

$$b,c = 1,...,L, \quad i = 0,1,...,L_c, \quad n = 0,1,...,L_b, \quad r = 0,1,...,K,$$

where

$$\gamma_{rr'}^{cidk} = \sqrt{m_c m_d} \left( \delta_{cd}\delta_{ik} \sum_{bn} \frac{n_{ci}n_{bn}}{n^2} \left[ Q^r, Q^{r'} \right]_{cibn}' + \frac{n_{ci}n_{dk}}{n^2} \left[ Q^r, Q^{r'} \right]_{cidk}'' \right).$$

It is obvious that the bracket integrals $\gamma_{rr'}^{cidk}$ represent a particular case of the integrals $\Lambda_{rr'pp'}^{cidk}$ at $p = p' = 0$ due to the normalization of the Waldmann-Trübenbacher polynomials:

$$\gamma_{rr'}^{cidk} = \Lambda_{rr'00}^{cidk}.$$

The system (5.17) is also linearly dependent and should be solved together with the additional constraint (2.37), which, after the substitution of the expansion (5.3) takes the form

$$\sum_{ci} \frac{\rho_{ci}}{\rho} d_{ci,0}^{dk} = 0, \ d = 1,...,L, \ k = 0,1,...,L_d. \tag{5.18}$$

Retaining only the first non-vanishing term of the expansion (5.3), we obtain the simplified system of equations:

$$\sum_{dk} \gamma_{00}^{cidk} d_{dk,0}^{bn} = 3kT \left( \delta_{cb}\delta_{in} - \frac{\rho_{ci}}{\rho} \right), \tag{5.19}$$

$$b,c = 1,...,L, \ i = 0,1,...,L_c, \ n = 0,1,...,L_b.$$

The multi-component state-to-state diffusion coefficients $D_{cidk}$ can be now found using the relation (5.8), while solving the system (5.19), (5.18) for the expansion coefficients $d_{ci,0}^{dk}$.

In order to calculate the shear viscosity coefficient, it is necessary to find the first term $b_{ci,0}$ of the series (5.4). The equations for $b_{ci,0}$ are derived similarly and have the form

$$\sum_{dk}\sum_{r'} H_{rr'}^{cidk} b_{dk,r'} = \frac{2}{kT} \frac{n_{ci}}{n} \delta_{r0},$$

$$c = 1,...,L, \ i = 0,1,...,L_c, \ r = 0,1,...,K,$$

where the bracket integrals

$$H_{rr'}^{cidk} = \frac{2}{5kT} \left( \delta_{cd}\delta_{ik} \sum_{bn} \frac{n_{ci}n_{bn}}{n^2} \left[ Q^r, Q^{r'} \right]_{cibn}' + \frac{n_{ci}n_{dk}}{n^2} \left[ Q^r, Q^{r'} \right]_{cidk}'' \right)$$

are calculated with respect to the polynomials

$$Q_c^r = \frac{m_c}{2kT} S_{5/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I} \right).$$

The equations for the coefficients $b_{ci,r}$ are linearly independent and can be simplified keeping only the first non-vanishing term of the expansion (5.4):

$$\sum_{dk} H_{00}^{cidk} b_{dk,0} = \frac{2}{kT} \frac{n_{ci}}{n}, \tag{5.20}$$

$$c = 1,...,L, \ i = 0,1,...,L_c.$$

Substituting the solution of this system to Eq. (5.10), we obtain the shear viscosity coefficient.

In order to calculate the bulk viscosity coefficient, it is necessary to consider the system of equations for $f_{ci,rp}$, following from the integral equation (2.34) after the substitution of the series (5.5):

$$\sum_{dk} \sum_{r'p'} \beta_{rr'pp'}^{cidk} f_{dk,r'p'} = \frac{1}{c_{\text{tr}} + c_{\text{rot}}} \left( -\frac{n_{ci}}{n} c_{\text{rot}} \delta_{r1} \delta_{p0} + \frac{\rho_{ci}}{\rho} c_{\text{rot},ci} \delta_{r0} \delta_{p1} \right), \quad (5.21)$$

$$c = 1,...,L, \quad i = 0,1,...,L_c, \quad r,p = 0,1,...,K.$$

The difference between the rotational specific heats $c_{\text{rot}}$ and $c_{\text{rot},ci}$ is discussed in Section 1.1: while $c_{\text{rot}}$ is the overall specific heat of all rotational degrees of freedom in a mixture, $c_{\text{rot},ci}$ is the rotational specific heat of molecular species $c$ on the vibrational level $i$. These values are connected by the relation (1.22).

The coefficients of the system (5.21) are the bracket integrals

$$\beta_{rr'pp'}^{cidk} = \delta_{cd} \delta_{ik} \sum_{bn} \frac{n_{ci} n_{bn}}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]'_{cibn} + \frac{n_{ci} n_{dk}}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]''_{cidk},$$

where

$$Q_{cij}^{rp} = S_{1/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j^{ci}}{kT} \right). \quad (5.22)$$

For $r = p = 0$, the system (5.21) is not linearly independent, and consequently, it should be complemented by the constraints on the coefficients $f_{ci,rp}$, following from the normalization conditions (2.38), (2.40). The additional constraints have the form

$$f_{ci,00} = 0, \quad c = 1,...,L, \quad i = 0,1,...,L_c,$$

$$\sum_{ci} \frac{n_{ci}}{n} \left( c_{\text{tr}} f_{ci,10} + c_{\text{rot},ci} f_{ci,01} \right) = 0. \quad (5.23)$$

The first constraint is already taken into account for the derivation of Eq. (5.11). The system (5.21), (5.23) for the coefficients $f_{ci,rp}$ of the expansion (5.5) has the unique solution. Retaining only the lowest-order expansion terms at $p = r = 0$, $p = 0, r = 1$, and $p = 1, r = 0$, we obtain the simplified system

$$\sum_{dk} \left( \beta_{1100}^{cidk} f_{dk,10} + \beta_{1001}^{cidk} f_{dk,01} \right) = -\frac{n_{ci}}{n} \frac{c_{\text{rot}}}{c_{\text{tr}} + c_{\text{rot}}},$$

$$\sum_{dk} \left( \beta_{0110}^{cidk} f_{dk,10} + \beta_{0011}^{cidk} f_{dk,01} \right) = \frac{\rho_{ci}}{\rho} \frac{c_{\text{rot},ci}}{c_{\text{tr}} + c_{\text{rot}}}, \quad (5.24)$$

$$c = 1,...,L, \quad i = 0,1,...,L_c.$$

Solving these equations together with Eq. (5.23) with respect to the coefficients $f_{ci,10}$ and then substituting the solution into the formula (5.11), we find the bulk viscosity coefficient $\zeta$.

The system for the coefficients $g_{ci,rp}$ of the expansion (5.6) can be obtained similarly:

$$\sum_{dk}\sum_{r'p'}\beta^{cidk}_{rr'pp'}g_{dk,r'p'} = \frac{n_{ci}}{n}\frac{\Sigma_{ci}R^{(0)}_{ci}\left(\frac{3}{2}kT + \left\langle\varepsilon^{ci}_j\right\rangle_{\mathrm{rot}} + \varepsilon^c_i + \varepsilon_c\right)}{\rho T(c_{\mathrm{tr}} + c_{\mathrm{rot}})}\times$$

$$\times\left(\frac{3}{2}\delta_{r1}\delta_{p0} + \frac{m_c c_{\mathrm{rot},ci}}{k}\delta_{r0}\delta_{p1}\right) + \frac{R^{(0)}_{ci}}{n}\delta_{r0}\delta_{p0} - \frac{1}{n}\sum_j\int S^{(r)}_{1/2}P^{(p)}_j J^{\mathrm{sl}(0)}_{cij}d\mathbf{u}_c, \quad (5.25)$$

$$c = 1,...,L,\ i = 0,...,L_c,\ r,p = 0,1,...,K.$$

The coefficients $\beta^{cidk}_{rr'pp'}$ of the latest system coincide with those of the system (5.21). The additional constraints providing the uniqueness of the solution for the system (5.25) follow from Eqs. (2.39), (2.41):

$$g_{ci,00} = 0,\ \ c = 1,...,L,\ \ i = 0,1,...,L_c, \tag{5.26}$$

$$\sum_{ci}\frac{n_{ci}}{n}\left(c_{\mathrm{tr}}g_{ci,10} + c_{\mathrm{rot},ci}g_{ci,01}\right) = 0. \tag{5.27}$$

The condition (5.26) is already taken into account in the formula (5.12).

Keeping only the expansion terms at $p = r = 0$, $p = 0, r = 1$, and $p = 1, r = 0$, we can reduce the system (5.25) to the simplified form:

$$\sum_{dk}\left(\beta^{cidk}_{1100}g_{dk,10} + \beta^{cidk}_{1001}g_{dk,01}\right) =$$

$$= \frac{3}{2}\frac{n_{ci}}{n}\Phi - \frac{1}{n}\sum_j\int\left(\frac{3}{2} - \frac{m_c c^2_c}{2kT}\right)J^{\mathrm{sl}(0)}_{cij}d\mathbf{u}_c,$$

$$\sum_{dk}\left(\beta^{cidk}_{0110}g_{dk,10} + \beta^{cidk}_{0011}g_{dk,01}\right) =$$

$$= \frac{m_c c_{\mathrm{rot},ci}}{k}\frac{n_{ci}}{n}\Phi + \frac{1}{n}\sum_j\int\left[\frac{\varepsilon^{ci}_j}{kT}\right]'_{\mathrm{rot}}J^{\mathrm{sl}(0)}_{cij}d\mathbf{u}_c, \tag{5.28}$$

$$c = 1,...,L,\ \ i = 0,1,...,L_c.$$

Here, the following notation is used:

$$\Phi = \frac{\Sigma_{ci}R^{(0)}_{ci}\left(\frac{3}{2}kT + \left\langle\varepsilon^{ci}_j\right\rangle_{\mathrm{rot}} + \varepsilon^c_i + \varepsilon_c\right)}{\rho T(c_{\mathrm{tr}} + c_{\mathrm{rot}})}.$$

The system (5.28), (5.27) uniquely specifies the coefficient $g_{ci,10}$, and consequently, it is possible to find the relaxation pressure $p_{rel}$ on the basis of the formula (5.12).

Let us emphasize an important feature of the transport system (5.25), (5.28) for the coefficients $g_{ci,rp}$. In contrast to the coefficients of all the remaining expansions (5.2)–(5.5), which are specified only by the bracket integrals depending on the cross sections of the most frequent collisions, the equations (5.25), (5.28) contain the integral operator for slow processes in the zero-order approximation $J_{cij}^{sl(0)}$. Therefore, the coefficients of thermal conductivity, diffusion, thermal diffusion, and shear and bulk viscosity are calculated on the basis of the cross sections of only rapid processes. On the other hand, the relaxation pressure, as well as the rate coefficients of the non-equilibrium energy exchanges and chemical reactions, depend on the cross sections of both the most probable processes and slow relaxation processes. In the absence in a system of inelastic processes proceeding on the macroscopic time scale $\theta$, the relaxation pressure is equal to zero.

Thus, the formulae (5.7)–(5.12) establish the connection of the transport coefficients with the coefficients of the expansions (5.2)–(5.6). For the expansion coefficients, the systems of linear algebraic equations are derived. To obtain the numerical solution of the systems (5.15)–(5.16), (5.18)–(5.19), (5.20), (5.23)–(5.24), and (5.27)–(5.28) it is necessary to simplify the bracket integrals. The algorithms for the bracket integrals calculation in various approaches are considered in Section 5.3.

## 5.2  Quasi-stationary Approaches

The procedure for the derivation of transport linear systems for the calculation of transport coefficients in the quasi-stationary approaches is similar to that described in Section 5.1. Let us consider first the multi-temperature kinetic model.

### 5.2.1  Multi-Temperature Approach

In this subsection, the transport terms in the equations (3.33)–(3.36) in the first order approximation of the modified Chapman-Enskog method are studied. The stress tensor, diffusion velocity, heat flux, and vibrational quanta flux in the generalized multi-temperature approach are given by the expressions (2.43), (3.78), (3.81), and (3.82). The transport coefficients (2.44), (3.79), (3.80), and (3.83), entering into the transport terms, are expressed as functions of the bracket integrals (3.74), including the cross sections of the most probable collisions, i.e., in the present case, elastic collisions and those resulting in RT- and $VV_1$ transitions. The functions $\mathbf{A}_{cij}$, $\mathbf{A}_{cij}^{d(1)}$, $\boldsymbol{B}_{cij}$, $\mathbf{D}_{cij}^{dk}$, $F_{cij}$, and $G_{cij}$, specifying the transport coefficients, are the solutions of the linear integral equations (3.58)–(3.63) with the additional constraints (3.64)–(3.73) providing the uniqueness of the solutions.

Following the standard technique, while searching the solutions of the linear integral equations, we expand the unknown functions into the series of the Sonine

and Waldmann-Trübenbacher polynomials. The trial functions are chosen in accordance with the right-hand sides of the integral equations, which are specified by the zero-order distribution function $f_{cij}^{(0)}$. In the generalized multi-temperature approach considered here, $f_{cij}^{(0)}$ takes the form (3.7) and describes the equilibrium distribution over the velocity and rotational energy and non-equilibrium distribution over the vibrational energy. This determines some particular features of the polynomials choice in the present case. Thus, in order to express the dependence of the unknown functions on the internal energy, the Waldmann-Trübenbacher polynomials are introduced for the rotational energy as well as for the part of vibrational energy.

First, the functions $\mathbf{A}_{cij}$, $\mathbf{A}_{cij}^{d(1)}$, $\boldsymbol{B}_{cij}$, and $\mathbf{D}_{cij}^{dk}$, specifying the coefficients of thermal conductivity, shear viscosity, and diffusion are considered. For them, the following expansions are proposed:

$$\mathbf{A}_{cij} = -\frac{m_c \mathbf{c}_c}{2kT} \sum_{rpq} a_{c,rpq} S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j^c}{kT} \right) P_i^{(q)} \left( \frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} \right), \qquad (5.29)$$

$$\mathbf{A}_{cij}^{d(1)} = \frac{m_c \mathbf{c}_c}{2kT} \sum_r a_{c,r}^{d(1)} P_i^{(r)} \left( \frac{i\varepsilon_1^c}{kT_1^c} \right), \qquad (5.30)$$

$$\mathbf{D}_{cij}^d = \frac{m_c \mathbf{c}_c}{2kT} \sum_r d_{c,r}^d S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right), \qquad (5.31)$$

$$\boldsymbol{B}_{cij} = \frac{m_c}{2kT} \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \boldsymbol{I} \right) \sum_r b_{c,r} S_{5/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right). \qquad (5.32)$$

The polynomials $S_v^{(r)}$ and $P_j^{(p)} \left( \varepsilon_j^c/(kT) \right)$ are introduced in the previous Section, for the state-to-state model. In the multi-temperature approach, the additional polynomials $P_i^{(p)}(y_i)$, depending on the vibrational energy levels are also defined. For their definition, another averaging operation is chosen, namely, the averaging over the vibrational spectrum is carried out using the formula (3.47) on the basis of the non-equilibrium quasi-stationary Treanor distribution (3.14). Such a choice of polynomials proposed in Ref. [60], provides the simplest algebraic equation systems, and, furthermore, makes it possible to simplify the expressions for the diffusion velocity and heat flux. Note that for the harmonic oscillator model, the value $\varepsilon_i^c - i\varepsilon_1^c$ is equal to zero, and VV exchange appears to be resonant. In the latter case, the function $\mathbf{A}_{cij}$ is expanded into a double polynomial system: Sonine polynomials in the velocity and those of Waldmann-Trübenbacher in the rotational energy. The function $\mathbf{A}_{cij}^{d(1)}$ is expanded into the series of the Waldmann-Trübenbacher polynomials in the vibrational energy $\varepsilon_i^c = i\varepsilon_1^c$.

Let us now express the coefficients of shear viscosity, diffusion, and thermal diffusion in terms of the coefficients of the expansions (5.29), (5.31), and (5.32). For this purpose, the indicated expansions should be substituted into the formulae (2.44), (3.79), and (3.80). After some transformations taking into account the normalization and orthogonality of the polynomials, we obtain

$$\eta = \frac{kT}{2} \sum_c \frac{n_c}{n} b_{c,0}, \tag{5.33}$$

$$D_{cd} = \frac{1}{2n} d^d_{c,0}, \tag{5.34}$$

$$D_{Tc} = -\frac{1}{2n} a_{c,000}, \tag{5.35}$$

$$D^{d(1)}_{Tc} = 0.$$

The latest relation makes it possible to simplify the expression for the diffusion velocity (3.78), excluding the last term from the consideration, and hence to pass to the formula (3.84).

Substituting the expansions (5.29), (5.30) into the relations (3.83) for the thermal conductivity coefficients and taking into account the orthogonality of the polynomials, we obtain the following connection of the thermal conductivity coefficients with the expansion coefficients:

$$\lambda' = \sum_c \frac{5}{4} k \frac{n_c}{n} a_{c,100} + \sum_c \frac{m_c}{2} \frac{n_c}{n} c_{\text{rot},c} a_{c,010} + \sum_c \frac{m_c}{2} \frac{n_c}{n} c^T_{\text{anh},c} a_{c,001},$$

$$\lambda_{\text{vt},c} = \frac{m_c}{2} \frac{n_c}{n} c^T_{\text{w},c} a_{c,001},$$

$$\lambda_{\text{tv},c} = \frac{m_c}{2} \frac{n_c}{n} c^{T_1}_{\text{anh},c} a^{c(1)}_{c,1},$$

$$\lambda_{\text{vv},cd} = \delta_{cd} \lambda_{\text{vv},c},$$

$$\lambda_{\text{vv},c} = \frac{m_c}{2} \frac{n_c}{n} c^{T_1}_{\text{w},c} a^{c(1)}_{c,1},$$

where the coefficients $c^T_{\text{anh},c}$, $c^{T_1}_{\text{anh},c}$ have a meaning of partial specific heats associated with the anharmonicity of vibrations:

$$c^T_{\text{anh},c}(T, T^c_1) = \frac{\partial (E_{\text{vibr},c} - \varepsilon^c_1 W_c)}{\partial T}, \qquad c^{T_1}_{\text{anh},c} = \frac{\partial (E_{\text{vibr},c} - \varepsilon^c_1 W_c)}{\partial T^c_1}.$$

It can be easily shown that

$$c^T_{\text{v},c} = c^T_{\text{w},c} + c^T_{\text{anh},c}, \qquad c^{T_1}_{\text{v},c} = c^{T_1}_{\text{w},c} + c^{T_1}_{\text{anh},c}.$$

Consequently, the thermal conductivity coefficients can be rewritten in the simplified form:

$$\lambda'_{\text{trv}} = \lambda' + \sum_c \lambda_{\text{vt},c} =$$

$$= \sum_c \frac{5}{4} k \frac{n_c}{n} a_{c,100} + \sum_c \frac{m_c}{2} \frac{n_c}{n} c_{\text{rot},c} a_{c,010} + \sum_c \frac{m_c}{2} \frac{n_c}{n} c_{\text{v},c}^T a_{c,001}, \tag{5.36}$$

$$\lambda_{\text{v},c} = \lambda_{\text{tv},c} + \lambda_{\text{vv},c} = \frac{m_c}{2} \frac{n_c}{n} c_{\text{v},c}^{T_1} a_{c,1}^{c(1)}. \tag{5.37}$$

Taking into account these relations, as well as the zero additional thermal diffusion coefficients, we can rewrite the heat flux (3.81) in the reduced form (3.85).

The equations for the expansion coefficients are found using the algorithm similar to that described in the previous section:

$$\sum_d \sum_{r'p'q'} \Lambda_{rr'pp'qq'}^{cd} a_{d,r'p'q'} = \frac{15kT}{2} \frac{n_c}{n} \delta_{r1} \delta_{p0} \delta_{q0} + 3 m_c T \frac{n_c}{n} c_{\text{rot},c} \delta_{r0} \delta_{p1} \delta_{q0} +$$

$$+ 3 m_c T \frac{n_c}{n} c_{\text{anh},c}^T \delta_{r0} \delta_{p0} \delta_{q1}, \quad c = 1, ..., L, \quad r, p, q = 0, 1, ..., K. \tag{5.38}$$

Here, the bracket integrals with respect to the polynomial products

$$Q_{cij}^{rpq} = \sqrt{\frac{m_c}{2kT}} \mathbf{c}_c S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j^c}{kT} \right) P_i^{(q)} \left( \frac{\varepsilon_i^c - i\varepsilon_i^c}{kT} \right)$$

are introduced on the basis of the definitions (3.75), (3.76) for the partial bracket integrals:

$$\Lambda_{rr'pp'qq'}^{cd} = \sqrt{m_c m_d} \left( \delta_{cd} \sum_b \frac{n_c n_b}{n^2} \left[ Q^{rpq}, Q^{r'p'q'} \right]_{cb}' + \right.$$

$$\left. + \frac{n_c n_d}{n^2} \left[ Q^{rpq}, Q^{r'p'q'} \right]_{cd}'' \right).$$

Let us emphasize once again that the bracket integrals depend on the cross sections of rapid processes: elastic collisions, RT- and VV$_1$ transitions. In the state-to-state approach, the bracket integrals were specified by the cross sections of only elastic collisions and RT-exchanges.

For the unique solution of the system (5.38), which is not linearly independent in the case $r = p = q = 0$, we have the additional constraint on the coefficients $a_{c,rpq}$, following from the normalization condition (3.64):

$$\sum_c \frac{\rho_c}{\rho} a_{c,000} = 0. \tag{5.39}$$

The system (5.38), (5.39) has the unique solution.
The equations for the coefficients $a_{c,r}^{d(1)}$ can be written as follows

$$\sum_d \sum_{r'} \alpha_{rr'}^{cd} a_{d,r'}^{b(1)} = 3 m_c T \frac{n_c}{n} c_{\text{w},c}^{T_1} \delta_{r1}, \quad b, c = 1, ..., L, \quad r = 0, 1, ..., K, \tag{5.40}$$

where

$$\alpha_{rr'}^{cd} = \sqrt{m_c m_d} \left( \delta_{cd} \sum_b \frac{n_c n_b}{n^2} \left[ Q^r, Q^{r'} \right]_{cb}' + \frac{n_c n_d}{n^2} \left[ Q^r, Q^{r'} \right]_{cd}'' \right);$$

$$Q_{ci}^r = \sqrt{\frac{m_c}{2kT}} \mathbf{c}_c P_i^{(r)} \left( \frac{i\varepsilon_1^c}{kT_1^c} \right).$$

Complementing the system (5.40) with the additional constraint following from the condition (3.65)

$$\sum_c \frac{\rho_c}{\rho} a_{c,0}^{d(1)} = 0, \quad d = 1, ..., L, \tag{5.41}$$

we obtain the system of linearly independent algebraic equations for the coefficients $a_{c,r}^{d(1)}$.

The system for the coefficients $d_{c,r}^d$ of the expansion (5.31) is obtained in a similar way:

$$\sum_d \sum_{r'} \gamma_{rr'}^{cd} d_{d,r'}^b = 3kT \left( \delta_{cb} - \frac{\rho_c}{\rho} \right) \delta_{r0}, \quad b,c = 1, ..., L, \quad r = 0, 1, ..., K. \tag{5.42}$$

Here,

$$\gamma_{rr'}^{cd} = \sqrt{m_c m_d} \left( \delta_{cd} \sum_b \frac{n_c n_b}{n^2} \left[ Q^r, Q^{r'} \right]_{cb}' + \frac{n_c n_d}{n^2} \left[ Q^r, Q^{r'} \right]_{cd}'' \right);$$

$$Q_c^r = \sqrt{\frac{m_c}{2kT}} \mathbf{c}_c S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right).$$

The system becomes linearly independent if we invoke the constraint (3.66), which, in the present case, takes the form

$$\sum_c \frac{\rho_c}{\rho} d_{c,0}^d = 0, \quad d = 1, ..., L. \tag{5.43}$$

Thus solving the systems (5.38)–(5.39), (5.40)–(5.41), and (5.42)–(5.43) and substituting the solutions into the formulae (5.34)–(5.37), we can find the coefficients of thermal conductivity, thermal diffusion, and diffusion. Note that retaining only the first non-vanishing terms in the expansions, we can obtain the systems for the computation of the transport coefficients, similar to Eqs. (5.16), (5.19).

At the next step, the transport coefficients in the stress tensor should be considered. Let us remind that the stress tensor, coefficients of shear and bulk viscosity, and relaxation pressure are given by the expressions (2.43), (2.44), whereas the bracket integrals in the multi-temperature approach are specified by the relations (3.74)–(3.76).

For the calculation of the shear viscosity coefficient, it is necessary to solve the equations for the coefficients $b_{c,r}$:

$$\sum_d \sum_{r'} H_{rr'}^{cd} b_{d,r'} = \frac{2}{kT} \frac{n_c}{n} \delta_{r0}, \tag{5.44}$$

$$c = 1, ..., L, \ \ r = 0, 1, ..., K,$$

where the bracket integrals

$$H_{rr'}^{cd} = \frac{2}{5kT} \left( \delta_{cd} \sum_b \frac{n_c n_b}{n^2} \left[ Q^r, Q^{r'} \right]'_{cb} + \frac{n_c n_d}{n^2} \left[ Q^r, Q^{r'} \right]''_{cd} \right)$$

with respect to the polynomials

$$Q_c^r = \frac{m_c}{2kT} S_{5/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I} \right).$$

appear. This system has a unique solution. Substituting the obtained coefficient $b_{c,0}$ into Eq. (5.33), we find the shear viscosity coefficient.

The calculation of the bulk viscosity coefficient and relaxation pressure in the generalized multi-temperature approach represents a more complicated task. Indeed, the choice of the orthogonal polynomials for the expansion of the functions $F_{cij}$ and $G_{cij}$, specifying these transport coefficients, is a non-trivial problem. Taking into account the right-hand side of the integral equation (3.62), we can present the function $F_{cij}$ in the form

$$F_{cij} = \sum_{rpq} f_{c,rpq} S_{1/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j^c}{kT} \right) P_i^{(q)} \left( Y_i^{(1)} \right), \tag{5.45}$$

where the trial function for the second Waldmann-Trübenbacher polynomial $Y_i^{(1)}$ is given by the formula

$$Y_i^{(1)} = \frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} - \frac{c_{\mathrm{w},c}^T}{c_{\mathrm{w},c}^{T_1}} \frac{T}{T_1^c} \frac{i\varepsilon_1^c}{kT_1^c}.$$

Such a choice for the trial functions makes it possible to obtain the connection of the bulk viscosity coefficient with the expansion coefficients:

$$\zeta = -kT \sum_c \frac{n_c}{n} f_{c,100}$$

and, furthermore, to derive a reasonably simple system for the coefficients $f_{c,rpq}$:

$$\sum_d \sum_{r'p'q'} \beta_{rr'pp'qq'}^{cd} f_{d,r'p'q'} = \frac{p}{\Phi_0 T} \left[ \frac{n_c}{n} \left( \frac{3}{2} - \frac{\Phi_0 T}{p} \right) \delta_{r1} \delta_{p0} \delta_{q0} + \right.$$

$$+ \frac{\rho_c}{\rho} \frac{m_c}{k} c_{\mathrm{rot},c} \delta_{r0} \delta_{p1} \delta_{q0} + \frac{\rho_c}{\rho} \frac{m_c}{k} \left( c_{\mathrm{anh},c}^T - \left( \frac{T_1^c}{T} \right)^2 \frac{c_{\mathrm{anh},c}^{T_1}}{c_{\mathrm{w},c}^{T_1}} \right) \delta_{r0} \delta_{p0} \delta_{q1} \left. \right],$$

$$c = 1, ..., L, \ \ r, p, q = 0, 1, ..., K.$$

The value $\Phi_0$ is defined by Eq. (3.52), whereas the coefficients of the system are introduced as follows:

$$\beta^{cd}_{rr'pp'qq'} = \delta_{cd} \sum_b \frac{n_c n_b}{n^2} \left[ Q^{rpq}, Q^{r'p'q'} \right]'_{cb} + \frac{n_c n_d}{n^2} \left[ Q^{rpq}, Q^{r'p'q'} \right]''_{cd}, \quad (5.46)$$

$$Q^{rpq}_{cij} = S^{(r)}_{1/2} \left( \frac{m_c c_c^2}{2kT} \right) P^{(p)}_j \left( \frac{\varepsilon^{ci}_j}{kT} \right) P^{(q)}_i \left( Y^{(1)}_i \right).$$

The additional constraint providing the uniqueness of the solution for this system is obtained from the condition of normalization (3.69):

$$\sum_c \frac{n_c}{n} \left( c_{\text{tr}} f_{c,100} + c_{\text{rot},c} f_{c,010} + \left( c^T_{\text{anh},c} - \left( \frac{T^c_1}{T} \right)^2 \frac{c^{T_1}_{\text{anh},c}}{c^{T_1}_{\text{w},c}} \right) f_{c,001} \right) = 0.$$

More sophisticated is the choice of the trial functions for the polynomials in the vibrational energy in the expansion of the function $G_{cij}$:

$$G_{cij} = \sum_{rpq} g_{c,rpq} S^{(r)}_{1/2} \left( \frac{m_c c_c^2}{2kT} \right) P^{(p)}_j \left( \frac{\varepsilon^c_j}{kT} \right) P^{(q)}_i \left( Y^{(2)}_i \right). \quad (5.47)$$

Starting from the right-hand side of the integral equation (3.63), we can suggest selecting the trial function $Y^{(2)}_i$ in the form

$$Y^{(2)}_i = \frac{\varepsilon^c_i - i\varepsilon^c_1}{kT} - \frac{\Phi_2}{\rho_c c^T_{\text{w},c} \Phi_1} \frac{T}{T^c_1} \frac{i\varepsilon^c_1}{kT^c_1}, \quad (5.48)$$

where the functions $\Phi_1$ and $\Phi_2$ are given by the expressions (3.53), (3.54).

The choice of the trial function in the form (5.48) makes it possible to derive the linear systems of algebraic equations for the expansion coefficients (5.47). The bracket integrals in the left-hand sides of the obtained system are introduced by Eq. (5.46). The right-hand sides of the system include the integral operator of slow processes and are specified, in the present case, by the cross sections of $VV_2$, VT transitions, and chemical reactions. The additional constraints providing the unique solution, are found from the conditions (3.68), (3.70), and (3.72).

The properties of the relaxation pressure in gases with strong vibrational excitation and slow chemical reactions are still practically unknown. Only in several studies, the relaxation pressure is considered in a single-component gas [37, 139]. In the case of a single-component gas of anharmonic oscillators, the expression (5.48) can be simplified [139]:

$$Y^{(2)}_i = \frac{\varepsilon_i - i\varepsilon_1}{kT} - \frac{c_u}{c^{T_1}_v} \frac{T}{T_1} \frac{i\varepsilon_1}{kT_1}. \quad (5.49)$$

Moreover, the right-hand sides of the system for the expansion coefficients are determined by the cross sections of VT transitions. One should keep in mind that for

harmonic oscillators, the relaxation pressure is specified by rapid inelastic RT exchange, and slow inelastic processes. Therefore, the coefficient $p_{\text{rel}}^{\text{vibr}}$ in Eq. (3.77), arising as a result of rapid non-resonant $VV_1$ transitions, is equal to zero. Calculations of $p_{\text{rel}}$ in a single-component gas of harmonic oscillators [37] show that the relaxation pressure is small compared to the hydrostatic gas pressure. For the general case of a multi-component mixture, no estimations of the relaxation pressure in the multi-temperature approach were carried out in the literature. Consequently, this problem requires further study.

### 5.2.2 One-Temperature Approach

In the one-temperature approach for a reacting mixture flow, the transport terms in the governing equations (4.9)–(4.11) are given by the formulae (2.43), (3.84), and (4.38), whereas the transport coefficients in these relations are expressed via the bracket integrals (3.74). The latter have the same form as those in the multi-temperature approach, but contain the cross sections not only of elastic collisions, RT and VV exchanges, but also of all inelastic collisions excepting those of chemical reactions. In order to calculate the transport coefficients, it is necessary to solve the linear integral equations (4.27)–(4.31) for the functions $\mathbf{A}_{cij}$, $\boldsymbol{B}_{cij}$, $\mathbf{D}_{cij}^d$, $F_{cij}$, and $G_{cij}$, complemented by the constraints (4.32)–(4.37), and (3.73).

　　The one-temperature approach was widely studied in the literature: thus in monographs [82, 183], mixtures without chemical reactions are considered in detail, and in [76], reacting mixture flows are discussed. Therefore, in the present monograph, we only briefly consider the main steps for the transport coefficients calculation. First, the shear viscosity and diffusion coefficients are computed similarly to the case of the multi-temperature model. These coefficients are found from the formulae (5.33), (5.34), the coefficients $b_{c,0}$, $d_{c,0}^d$ of the expansions (5.32), (5.31) are the solutions for the linear algebraic equation systems (5.44) and (5.42), (5.43), respectively. The difference consists in the definition of the bracket integrals, which in the one-temperature approach, as is already mentioned, depend on the cross sections of all internal energy transitions.

　　The functions $\mathbf{A}_{cij}$, $F_{cij}$, and $G_{cij}$ are expanded into the double polynomial systems; the polynomials are chosen in accordance with the zero-order distribution function (4.4), which represents the thermal equilibrium Maxwell-Boltzmann distribution over the velocity and internal energy levels:

$$\mathbf{A}_{cij} = -\frac{m_c \mathbf{c}_c}{2kT} \sum_{rp} a_{c,rp} S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_{ij}^{(p)} \left( \frac{\varepsilon_{ij}^c}{kT} \right), \tag{5.50}$$

$$F_{cij} = \sum_{rp} f_{c,rp} S_{1/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_{ij}^{(p)} \left( \frac{\varepsilon_{ij}^c}{kT} \right), \tag{5.51}$$

$$G_{cij} = \sum_{rp} g_{c,rp} S_{1/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_{ij}^{(p)} \left( \frac{\varepsilon_{ij}^c}{kT} \right). \tag{5.52}$$

The trial function for the Waldmann-Trübenbacher polynomials is the overall dimensionless internal energy $\varepsilon_{ij}^c/(kT)$, the averaging is performed with the equilibrium Boltzmann distribution over the internal energy levels (see the formula (5.1)).

Taking into account the expansions (5.50)–(5.52), we obtain the thermal conductivity, thermal diffusion, bulk viscosity coefficients, and relaxation pressure in the form

$$\lambda' = \sum_c \frac{5}{4} k \frac{n_c}{n} a_{c,10} + \sum_c \frac{m_c}{2} \frac{n_c}{n} c_{\mathrm{int},c} a_{c,01},$$

$$D_{Tc} = -\frac{1}{2n} a_{c,00},$$

$$\zeta = -kT \sum_c \frac{n_c}{n} f_{c,10},$$

$$p_{\mathrm{rel}} = kT \sum_c \frac{n_c}{n} g_{c,10}.$$

The systems for the calculation of the expansion coefficients are derived using the common technique. Thus, for the coefficients $a_{c,r'p'}$ the following system is found

$$\sum_d \sum_{r'p'} \Lambda_{rr'pp'}^{cd} a_{d,r'p'} = \frac{15kT}{2} \frac{n_c}{n} \delta_{r1} \delta_{p0} + 3m_c T \frac{n_c}{n} c_{\mathrm{int},c} \delta_{r0} \delta_{p1}, \qquad (5.53)$$

$$c = 1,\dots,L, \qquad r,p = 0,1,\dots,K,$$

where

$$\Lambda_{rr'pp'}^{cd} = \sqrt{m_c m_d} \left( \delta_{cd} \sum_b \frac{n_c n_b}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]_{cb}' + \frac{n_c n_d}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]_{cd}'' \right),$$

$$Q_{cij}^{rp} = \sqrt{\frac{m_c}{2kT}} \mathbf{c}_c S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_{ij}^{(p)} \left( \frac{\varepsilon_{ij}^c}{kT} \right).$$

The system (5.53) should be complemented by the constraint

$$\sum_c \frac{\rho_c}{\rho} a_{c,00} = 0,$$

providing the uniqueness of the solution.

The system of equations for the unique definition of the coefficients $f_{c,r'p'}$ has the form

$$\sum_d \sum_{r'p'} \beta_{rr'pp'}^{cd} f_{d,r'p'} = \frac{1}{c_V} \left( -\frac{n_c}{n} c_{V,\mathrm{int}} \delta_{r1} \delta_{p0} + \frac{\rho_c}{\rho} c_{\mathrm{int},c} \delta_{r0} \delta_{p1} \right),$$

$$c = 1,\dots,L, \; r,p = 0,1,\dots,K,$$

$$\sum_c \frac{n_c}{n} \left( c_{\mathrm{tr}} f_{c,10} + c_{\mathrm{int},c} f_{c,01} \right) = 0.$$

The coefficients of this system are the bracket integrals of the type

$$\beta^{cd}_{rr'pp'} = \delta_{cd} \sum_b \frac{n_c n_b}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]'_{cb} + \frac{n_c n_d}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]''_{cd},$$

$$Q^{rp}_{cij} = S^{(r)}_{1/2} \left( \frac{m_c c_c^2}{2kT} \right) P^{(p)}_{ij} \left( \frac{\varepsilon^c_{ij}}{kT} \right).$$

The system for the determination of the relaxation pressure in the present approach looks similarly:

$$\sum_{dk} \sum_{r'p'} \beta^{cd}_{rr'pp'} g_{d,r'p'} = \frac{n_c}{n} \frac{\sum_c R^{\text{react}(0)}_c \left( \frac{3}{2} kT + \left\langle \varepsilon^c_{ij} \right\rangle + \varepsilon_c \right)}{\rho T c_V} \times$$

$$\times \left( \frac{3}{2} \delta_{r1} \delta_{p0} + \frac{m_c c_{\text{int},c}}{k} \delta_{r0} \delta_{p1} \right) + \frac{R^{\text{react}(0)}_c}{n} \delta_{r0} \delta_{p0} -$$

$$-\frac{1}{n} \sum_{ij} \int S^{(r)}_{1/2} P^{(p)}_{ij} J^{\text{sl}(0)}_{cij} d\mathbf{u}_c, \quad c = 1,...,L, \quad r,p = 0,1,...,K. \tag{5.54}$$

The additional constraint required for the existence of the unique solution for the system (5.54), follows from the normalization condition (3.70) and has the form

$$\sum_c \frac{n_c}{n} \left( c_{\text{tr}} g_{c,10} + c_{\text{int},c} g_{c,01} \right) = 0.$$

As a result, similarly to the approaches considered above, we express the coefficients of thermal conductivity, diffusion, thermal diffusion, shear and bulk viscosity, as well as the relaxation pressure in terms of the expansion coefficients for the functions $A_{cij}$, $B_{cij}$, $D^d_{cij}$, $F_{cij}$, and $G_{cij}$ in the Sonine and Waldmann-Trübenbacher polynomials. The systems of linear algebraic equations for the calculation of the expansion coefficients are obtained. The next step for the calculation of the transport coefficients is the simplification of the bracket integrals.

## 5.3 Bracket Integrals

Algorithms for the bracket integrals calculation are discussed in detail in monographs [57, 112, 82, 262] for the case of non-reacting gas mixtures under weakly non-equilibrium conditions. In the present Section, we consider the bracket integrals in reacting gas mixtures in the state-to-state and multi-temperature approaches taking into account strong vibrational and chemical non-equilibrium, as well as in the one-temperature approach accounting for non-equilibrium chemical reactions.

### 5.3.1 State-to-State Approach

Let us introduce the averaging operator in accordance with the linearized operator of the most frequent collisions (2.24):

$$\langle F \rangle_{cidk} = \left( \frac{kT}{2\pi m_{cd}} \right)^{1/2} \sum_{jlj'l'} \frac{s_j^{ci} s_l^{dk}}{Z_{ci}^{rot} Z_{dk}^{rot}} \int F\gamma^3 \exp\left( -\gamma^2 - \mathcal{E}_j^{ci} - \mathcal{E}_l^{dk} \right) \times$$

$$\times \sigma_{cd,ijkl}^{j'l'} d^2\Omega d\gamma. \tag{5.55}$$

Here, $m_{cd} = m_c m_d / (m_c + m_d)$ is the reduced mass for particles of chemical species $c$ and $d$, $F$ is some function depending on the velocity, chemical species $c$, and internal energy levels $i$, $j$; $\gamma = (m_{cd}/(2kT))^{1/2} g$ and $\mathcal{E}_j^{ci} = \varepsilon_j^{ci}/(kT)$ are the dimensionless relative velocity and rotational energy, respectively. This operator takes into account the zero-order distribution function (2.4) and includes the cross sections $\sigma_{cd,ijkl}^{j'l'}$ of the most probable elastic collisions and those resulting in the rotational energy variation.

On the basis of the operator (5.55) it is convenient to define the integrals $\Omega_{cidk}^{(l,r)}$ required for the calculation of the bracket integrals:

$$\Omega_{cidk}^{(1,1)} = \langle \gamma^2 - \gamma\gamma' \cos\chi \rangle_{cidk}, \tag{5.56}$$

$$\Omega_{cidk}^{(2,2)} = \left\langle \gamma^4 - \gamma^2\gamma'^2 \cos^2\chi - \frac{1}{6}(\Delta\mathcal{E}_{cidk}^{rot})^2 \right\rangle_{cidk}, \tag{5.57}$$

$$\Omega_{cidk}^{(1,2)} = \langle \gamma^4 - \gamma^3\gamma' \cos\chi \rangle_{cidk}, \tag{5.58}$$

$$\Omega_{cidk}^{(1,3)} = \langle \gamma^6 - \gamma^3\gamma'^3 \cos\chi \rangle_{cidk}, \tag{5.59}$$

where $\chi = \chi_{cidk}(b,g)$ is the deflection angle in a collision, depending on the relative velocity and impact parameter $b$; the prime denotes the particle relative velocity after the collision. The value $\Delta\mathcal{E}_{cidk}^{rot}$ is associated with the rotational energy resonance defect in a collision and is defined as follows:

$$\Delta\mathcal{E}_{cidk}^{rot} = \Delta\mathcal{E}_{ci}^{rot} + \tilde{\Delta}\mathcal{E}_{dk}^{rot},$$

$$\Delta\mathcal{E}_{ci}^{rot} = \mathcal{E}_{j'}^{ci} - \mathcal{E}_j^{ci},$$

$$\tilde{\Delta}\mathcal{E}_{dk}^{rot} = \mathcal{E}_{l'}^{dk} - \mathcal{E}_l^{dk}.$$

The tilde is introduced in order to distinguish one of the partners in a collision of particles of the same chemical species $d = c$ on the same vibrational levels $k = i$.

For the convenience of notations, let us introduce some additional coefficients:

$$\tilde{A}_{cidk} = \frac{1}{2} \frac{\Omega_{cidk}^{(2,2)}}{\Omega_{cidk}^{(1,1)}}, \quad \tilde{B}_{cidk} = \frac{1}{3} \frac{5\Omega_{cidk}^{(1,2)} - \Omega_{cidk}^{(1,3)}}{\Omega_{cidk}^{(1,1)}}, \quad \tilde{C}_{cidk} = \frac{1}{3} \frac{\Omega_{cidk}^{(1,2)}}{\Omega_{cidk}^{(1,1)}}. \tag{5.60}$$

It is convenient to use these dimensionless functions since they are slowly varying functions of temperature and their values are close to unity.

In addition to that, the binary diffusion coefficients can be defined:

$$\mathscr{D}_{cidk} = \frac{3kT}{16nm_{cd}} \frac{1}{\Omega^{(1,1)}_{cidk}}, \qquad \mathscr{D}_{ci} = \mathscr{D}_{cici} = \frac{3kT}{8nm_c} \frac{1}{\Omega^{(1,1)}_{cici}}, \qquad (5.61)$$

as well as the effective diffusion coefficients for the rotational energy (by analogy to those introduced in Ref. [188] for the diffusion of internal energy):

$$\mathscr{D}_{ci\,\mathrm{rot},dk} = \frac{3kT}{16nm_{cd}} \frac{1}{\Omega^{(1,1)}_{ci\,\mathrm{rot},dk}}.$$

The integrals $\Omega^{(1,1)}_{ci\,\mathrm{rot},dk}$ have the form

$$\frac{m_c c_{\mathrm{rot},ci}}{k} \Omega^{(1,1)}_{ci\,\mathrm{rot},ci} = \left\langle \mathscr{E}'_{cij} \left[ \left( \mathscr{E}'_{cij} - \mathscr{E}'_{cil} \right) \gamma^2 - \left( \mathscr{E}'_{cij'} - \mathscr{E}'_{cil'} \right) \gamma \gamma' \cos\chi \right] \right\rangle_{cici},$$

$$\frac{m_c c_{\mathrm{rot},ci}}{k} \Omega^{(1,1)}_{ci\,\mathrm{rot},dk} = \left\langle \mathscr{E}'_{cij} \left( \mathscr{E}'_{cij} \gamma^2 - \mathscr{E}'_{cij'} \gamma \gamma' \cos\chi \right) \right\rangle_{cidk},$$

$$i \neq k \quad \text{or} \quad c \neq d,$$

and the following notation is introduced

$$\mathscr{E}'_{cij} = \mathscr{E}^{ci}_j - \left\langle \mathscr{E}^{ci}_j \right\rangle_{\mathrm{rot}}.$$

The integrals $\Omega^{(1,1)}_{ci\,\mathrm{rot},dk}$ differ from $\Omega^{(1,1)}_{c\,\mathrm{int},d}$ defined in Refs. [188, 76] since they depend on the vibrational quantum number of colliding particles and are obtained on the basis of the operator (5.55) specified by the cross sections of rapid processes rather than those of all collisions.

In addition to the effective diffusion coefficients, it is also convenient to define the effective coefficients of viscosity $\eta_{cidk}$ and thermal conductivity $\lambda_{cidk}$:

$$\eta_{cidk} = \frac{5}{8} \frac{kT}{\Omega^{(2,2)}_{cidk}}, \quad \eta_{ci} = \eta_{cici} = \frac{5}{8} \frac{kT}{\Omega^{(2,2)}_{cici}}, \qquad (5.62)$$

$$\lambda_{cidk} = \frac{75k^2T}{64m_{cd}\Omega^{(2,2)}_{cidk}}, \quad \lambda_{ci} = \lambda_{cici} = \frac{75k^2T}{32m_c\Omega^{(2,2)}_{cici}}.$$

The above relations specify all values necessary for the calculation of bracket integrals without any additional assumptions. Using the technique described in the studies [57, 112, 179, 180, 188, 82], we can write the bracket integrals as linear combinations of the different order $\Omega^{(l,r)}_{cidk}$ integrals, integrals $\Omega^{(1,1)}_{ci\,\mathrm{rot},dk}$, and those depending on the rotational energy resonance defect $\Delta\mathscr{E}^{\mathrm{rot}}_{cidk}$. Further simplification of the bracket integrals requires some additional assumptions.

In the present monograph, we follow the assumptions formulated in the studies of E. Mason and L. Monchick [179, 180, 188] and widely used in the kinetic theory [82, 262, 76]. First, we suppose that the probability for collisions resulting in the simultaneous variation of the rotational and vibrational energy as well as for the multi-quantum jumps, is low. This makes it possible to define the time $\tau_{cidk}$ for the rotational relaxation of molecular species $c$ on the vibrational level $i$ as a result of their collisions with particles of $d$ species in the vibrational state $k$:

$$\frac{1}{\tau_{cici}^{\mathrm{rot}}} = \frac{2kn}{m_c c_{\mathrm{rot},ci}} \left\langle (\Delta \mathcal{E}_{cici}^{\mathrm{rot}})^2 \right\rangle_{cici}, \quad \frac{1}{\tau_{cidk}^{\mathrm{rot}}} = \frac{4kn}{m_c c_{\mathrm{rot},ci}} \left\langle \Delta \mathcal{E}_{ci}^{\mathrm{rot}} \Delta \mathcal{E}_{cidk}^{\mathrm{rot}} \right\rangle_{cidk}.$$

These definitions are similar to those proposed in Refs. [188, 76] for the internal energy relaxation time.

It is also convenient to introduce the collision number $\zeta_{cidk}^{\mathrm{rot}}$ required for the equilibration of the rotational degrees of freedom in particles of $c$, $i$ species as a result of collisions with particles of $d$, $k$ species:

$$\zeta_{cidk}^{\mathrm{rot}} = \frac{4}{\pi} \frac{p\,\tau_{cidk}^{\mathrm{rot}}}{\eta_{cidk}}.$$

It is interesting to notice that the values $\tau_{cidk}^{\mathrm{rot}}$ and $\zeta_{cidk}^{\mathrm{rot}}$ are not invariant with respect to the subscripts interchange. The calculation or experimental measurement of the rotational relaxation time depending on the partner in a collision is a complicated task and has not been carried out up to now. It is commonly assumed that [188, 76] the relaxation times and collision numbers satisfy the following relations

$$\tau_{cidk}^{\mathrm{rot}} = \tau_{ci}^{\mathrm{rot}}, \qquad \zeta_{cidk}^{\mathrm{rot}} = \zeta_{ci}^{\mathrm{rot}} \qquad \forall\, d\,, k.$$

Such an assumption simplifies the calculations significantly.

Furthermore, let us assume the translational and internal motion of molecules to be independent, which leads to the following relations

$$\left\langle \mathcal{E}_{cij}' \boldsymbol{\gamma} \left( \gamma^s - \gamma'^s \cos\chi \right) \right\rangle_{cidk} = 0 \qquad \forall\, c, d, i, k,$$

$$\left\langle \mathcal{E}_{cij}' \boldsymbol{\gamma} \left( \mathcal{E}_{dkl}' \gamma^s - \mathcal{E}_{dkl'}' \gamma'^s \cos\chi \right) \right\rangle_{cidk} = 0, \qquad d, k \in S_{ci}.$$

Here, $S_{ci}$ denotes the set of subscripts $d$, $k$ such as $\delta_{ik}\delta_{cd} = 0$. These relations are also useful for the calculation of the bracket integrals.

Taking into account the assumptions formulated by E. Mason and L. Monchick, we can express all bracket integrals in terms of the integrals $\Omega_{cidk}^{(l,r)}$ and rotational relaxation times.

Another assumption is that the collision diameter, as well as the deflection angle $\chi_{cidk}$, are supposed to be independent of the vibrational levels of colliding particles. One should be careful using the latter assumption. In Refs. [83, 118, 168, 98] it is shown that the collision diameter increases for vibrationally excited molecules. In

particular, a nitrogen molecule at $i > 38$ appears to be approximately twice as large as that in the ground vibrational state [168]. However, in many cases, the populations of upper vibrational levels are low, and the molecular excitation cannot affect the transport coefficients considerably. For instance, in Ref. [38], it is demonstrated that taking into account the dependence of the elastic cross section on the vibrational level, yields only a negligible correction to the transport coefficients even in the strongly non-equilibrium conditions.

The last assumption makes it possible to write

$$\Omega_{cidk}^{(l,r)} = \Omega_{cd}^{(l,r)}, \qquad \Omega_{ci\,rot,dk}^{(1,1)} = \Omega_{c\,rot,d}^{(1,1)}, \tag{5.63}$$

$$\tilde{A}_{cidk} = \tilde{A}_{cd}, \quad \tilde{B}_{cidk} = \tilde{B}_{cd}, \quad \tilde{C}_{cidk} = \tilde{C}_{cd},$$

$$\mathscr{D}_{cidk} = \mathscr{D}_{cd}, \quad \mathscr{D}_{ci\,rot,dk} = \mathscr{D}_{c\,rot,d}, \quad \eta_{cidk} = \eta_{cd}, \quad \lambda_{cidk} = \lambda_{cd}.$$

Taking into account the above assumptions, we can write the bracket integrals in the systems (5.16), (5.19), (5.20), (5.24), and (5.28) for the transport coefficients calculation in the state-to-state approach.

Thus the bracket integrals required for the calculation of the thermal conductivity and thermal diffusion coefficients take the form

$$\Lambda_{0000}^{cidk} = \gamma_{00}^{cidk} = -\frac{3kT}{2n}\frac{x_{ci}x_{dk}}{\mathscr{D}_{cd}}, \qquad d,k \in S_{ci}, \tag{5.64}$$

$$\Lambda_{0000}^{cici} = \gamma_{00}^{cici} = \frac{3kT}{2n}\sum_{b,n\in S_{ci}}\frac{x_{ci}x_{bn}}{\mathscr{D}_{cb}}, \tag{5.65}$$

$$\Lambda_{1000}^{cidk} = \frac{3kT}{4n}\frac{x_{ci}x_{dk}}{\mathscr{D}_{cd}}\frac{m_d}{m_c+m_d}(6\tilde{C}_{cd}-5), \quad d,k \in S_{ci}, \tag{5.66}$$

$$\Lambda_{1000}^{cici} = -\frac{3kT}{4n}\sum_{b,n\in S_{ci}}\frac{x_{ci}x_{bn}}{\mathscr{D}_{cb}}\frac{m_b}{m_c+m_b}(6\tilde{C}_{cb}-5), \tag{5.67}$$

$$\Lambda_{0001}^{cidk} = 0 \qquad \forall\, d,k, \tag{5.68}$$

$$\Lambda_{1100}^{cidk} = -\frac{3kT}{2n}\frac{x_{ci}x_{dk}}{\mathscr{D}_{cd}}\frac{m_c m_d}{(m_c+m_d)^2}\left[\frac{55}{4} - 3\tilde{B}_{cd} - 4\tilde{A}_{cd}-\right.$$

$$\left. -\frac{20}{3}\frac{\tilde{A}_{cd}}{k\pi}\left(\frac{m_c c_{rot,ci}}{\zeta_{ci}^{rot}} + \frac{m_d c_{rot,dk}}{\zeta_{dk}^{rot}}\right)\right], \qquad d,k \in S_{ci}, \tag{5.69}$$

$$\Lambda_{1100}^{cici} = \frac{3kT}{2n} \sum_{b,n \in S_{ci}} \frac{x_{ci}x_{bn}}{\mathscr{D}_{cb}} \frac{m_c m_b}{(m_c + m_b)^2} \left[ \frac{15}{2} \frac{m_c}{m_b} + \frac{25}{4} \frac{m_b}{m_c} - \right.$$

$$\left. -3\frac{m_b}{m_c}\tilde{B}_{cb} + 4\tilde{A}_{cb} + \frac{20}{3}\frac{\tilde{A}_{cb}}{k\pi} \left( \frac{m_c c_{\mathrm{rot},ci}}{\zeta_{ci}^{\mathrm{rot}}} + \frac{m_b c_{\mathrm{rot},bn}}{\zeta_{bn}^{\mathrm{rot}}} \right) \right] +$$

$$+ \frac{3kT}{2n}\frac{x_{ci}^2}{\mathscr{D}_{cc}} \left[ 2\tilde{A}_{cc} + \frac{20}{3}\frac{\tilde{A}_{cc}}{k\pi}\frac{m_c c_{\mathrm{rot},ci}}{\zeta_{ci}^{\mathrm{rot}}} \right], \tag{5.70}$$

$$\Lambda_{1001}^{cidk} = -\frac{6T}{n\pi}\tilde{A}_{cd}\frac{x_{ci}x_{dk}}{\mathscr{D}_{cd}}\frac{m_d}{m_c + m_d}\frac{m_d c_{\mathrm{rot},dk}}{\zeta_{dk}^{\mathrm{rot}}}, \qquad d,k \in S_{ci}, \tag{5.71}$$

$$\Lambda_{1001}^{cici} = -\frac{6T}{n\pi} \sum_{b,n \in S_{ci}} \tilde{A}_{cb}\frac{x_{ci}x_{bn}}{\mathscr{D}_{cb}}\frac{m_c}{m_c + m_b}\frac{m_c c_{\mathrm{rot},ci}}{\zeta_{ci}^{\mathrm{rot}}} -$$

$$-\frac{6T}{n\pi}\tilde{A}_{cc}\frac{x_{ci}^2}{\mathscr{D}_{cc}}\frac{m_c c_{\mathrm{rot},ci}}{\zeta_{ci}^{\mathrm{rot}}}, \tag{5.72}$$

$$\Lambda_{0011}^{cidk} = 0, \qquad d,k \in S_{ci}, \tag{5.73}$$

$$\Lambda_{0011}^{cici} = \frac{3T}{2n} \sum_{b,n \in S_{ci}} x_{ci}x_{bn}\frac{m_c c_{\mathrm{rot},ci}}{\mathscr{D}_{c\,\mathrm{rot},b}} + \frac{3T}{2n}x_{ci}^2\frac{m_c c_{\mathrm{rot},ci}}{\mathscr{D}_{c\,\mathrm{rot},c}} +$$

$$+ \frac{18T}{5n\pi} \sum_{b,n \in S_{ci}} \tilde{A}_{cb}\frac{x_{ci}x_{bn}}{\mathscr{D}_{cb}}\frac{m_c}{m_b}\frac{m_c c_{\mathrm{rot},ci}}{\zeta_{ci}^{\mathrm{rot}}} + \frac{18T}{5n\pi}\tilde{A}_{cc}\frac{x_{ci}^2}{\mathscr{D}_{cc}}\frac{m_c c_{\mathrm{rot},ci}}{\zeta_{ci}^{\mathrm{rot}}}. \tag{5.74}$$

For the calculation of the shear viscosity coefficients, we obtain the following bracket integrals

$$H_{00}^{cidk} = 2\frac{x_{ci}x_{dk}}{\eta_{cd}}\frac{m_c m_d}{(m_c + m_d)^2} \left( -\frac{5}{3\tilde{A}_{cd}} + 1 \right), \qquad d,k \in S_{ci}, \tag{5.75}$$

$$H_{00}^{cici} = 2 \sum_{b,n \in S_{ci}} \frac{x_{ci}x_{bn}}{\eta_{cb}} \left[ \frac{5}{3\tilde{A}_{cb}}\frac{m_c m_b}{(m_c + m_b)^2} + \frac{m_b^2}{(m_c + m_b)^2} \right] + \frac{x_{ci}^2}{\eta_c}. \tag{5.76}$$

The bracket integrals necessary for the calculation of the bulk viscosity coefficient, relaxation pressure, and rate coefficients for the vibrational energy exchange and chemical reactions, take the form

$$\beta_{1100}^{cidk} = -5kT \frac{x_{ci}x_{dk}}{\tilde{A}_{cd}\eta_{cd}} \frac{m_c m_d}{(m_c+m_d)^2} +$$

$$+ \frac{4T}{\pi} \frac{x_{ci}x_{dk}}{\eta_{cd}} \frac{m_c m_d}{(m_c+m_d)^2} \left( \frac{m_c c_{\text{rot},ci}}{\zeta_{ci}^{\text{rot}}} + \frac{m_d c_{\text{rot},dk}}{\zeta_{dk}^{\text{rot}}} \right), \quad d,k \in S_{ci}, \qquad (5.77)$$

$$\beta_{1100}^{cici} = \sum_{b,n \in S_{ci}} \left[ 5kT \frac{x_{ci}x_{bn}}{\tilde{A}_{cb}\eta_{cb}} \frac{m_c m_b}{(m_c+m_b)^2} + \right.$$

$$\left. + \frac{4T}{\pi} \frac{x_{ci}x_{bn}}{\eta_{cb}} \frac{m_b^2}{(m_c+m_b)^2} \left( \frac{m_c c_{\text{rot},ci}}{\zeta_{ci}^{\text{rot}}} + \frac{m_b c_{\text{rot},bn}}{\zeta_{bn}^{\text{rot}}} \right) \right] +$$

$$+ \frac{4T}{\pi} \frac{x_{ci}^2}{\eta_c} \frac{m_c c_{\text{rot},ci}}{\zeta_{ci}^{\text{rot}}}, \qquad (5.78)$$

$$\beta_{0110}^{cidk} = -\frac{4T}{\pi} \frac{x_{ci}x_{dk}}{\eta_{cd}} \frac{m_c}{m_c+m_d} \frac{m_c c_{\text{rot},ci}}{\zeta_{ci}^{\text{rot}}}, \qquad d,k \in S_{ci}, \qquad (5.79)$$

$$\beta_{0110}^{cici} = -\frac{4T}{\pi} \sum_{b,n \in S_{ci}} \frac{x_{ci}x_{bn}}{\eta_{cb}} \frac{m_b}{m_c+m_b} \frac{m_c c_{\text{rot},ci}}{\zeta_{ci}^{\text{rot}}} - \frac{4T}{\pi} \frac{x_{ci}^2}{\eta_c} \frac{m_c c_{\text{rot},ci}}{\zeta_{ci}^{\text{rot}}}, \qquad (5.80)$$

$$\beta_{0011}^{cidk} = 0, \qquad d,k \in S_{ci}, \qquad (5.81)$$

$$\beta_{0011}^{cici} = \frac{4T}{\pi} \sum_{b,n \in S_{ci}} \frac{x_{ci}x_{bn}}{\eta_{cb}} \frac{m_c c_{\text{rot},ci}}{\zeta_{ci}^{\text{rot}}} + \frac{4T}{\pi} \frac{x_{ci}^2}{\eta_c} \frac{m_c c_{\text{rot},ci}}{\zeta_{ci}^{\text{rot}}}. \qquad (5.82)$$

The remaining bracket integrals are calculated on the basis of the symmetry properties:
$$\Lambda_{rr'pp'}^{cidk} = \Lambda_{r'rp'p}^{dkci}, \qquad \beta_{rr'pp'}^{cidk} = \beta_{r'rp'p}^{dkci}.$$

In the formulae for the bracket integrals, $x_{ci} = n_{ci}/n$ is the molar fraction of molecular species $c$ on the vibrational level $i$. Let us remind that $d,k \in S_{ci}$ means that all vibrational levels $k$ of molecular species $d \neq c$, as well as the vibrational levels $k \neq i$ of molecular species $c$ are considered, i.e., the following relation is fulfilled: $\delta_{cd}\delta_{ik} = 0$.

Thus we derived the expressions for all bracket integrals required for the calculation of the transport coefficients in the state-to-state approach. They depend on the vibrational level populations $n_{ci}$, gas temperature $T$, as well as the collision integrals over the cross sections of elastic collisions and those resulting in inelastic RT energy exchange, and integrals specified by the rotational energy resonance defect

$\Delta \mathscr{E}^{\text{rot}}_{cidk}$ in inelastic RT transitions. The latter integrals can be expressed in terms of the rotational relaxation time.

Let us consider some possibilities for a further simplification of the bracket integrals. First, it can be noted that the contribution of integrals depending on $\Delta \mathscr{E}^{\text{rot}}_{cidk}$ to the thermal conductivity, thermal diffusion, and diffusion coefficients of homonuclear molecules appears to be negligibly small. This is explained by the fact that, for the temperature higher than the room temperature, the rotational energy transferred in a molecular collision is considerably lower than the total kinetic energy of colliding particles, except for light gases and some polar molecules. In the studies [132, 139, 140], it is shown that the contribution of the integrals specified by the resonance defect to the thermal conductivity coefficient of molecules $N_2$, $O_2$, does not exceed 1–2%. Therefore, in many cases, in the bracket integrals $\Lambda^{cidk}_{rr'pp'}$ the terms containing $\zeta^{\text{rot}}_{ci}$ can be neglected. It is obvious that for the calculation of the relaxation pressure and bulk viscosity coefficient, the integrals containing $\Delta \mathscr{E}^{\text{rot}}_{cidk}$ should be necessarily taken into account since it is the resonance defect in inelastic collisions in rapid processes that provides the reason for the appearance of $p_{\text{rel}}$ and $\zeta$. If we assume that the values $\tau^{\text{rot}}_{ci}$ are the same for all $i$, then the rotational relaxation time can be calculated using the Parker theory [212]. The formulae for the rotational relaxation time are given in section 5.4.

One more assumption simplifying the calculation of bracket integrals is that the diffusion coefficient of the rotational energy $\mathscr{D}_{c\text{rot},d}$ can be approximated by the ordinary binary diffusion coefficient: $\mathscr{D}_{c\text{rot},d} = \mathscr{D}_{cd}$. Such a relation for the internal energy diffusion coefficient $\mathscr{D}_{c\text{int},d}$ was justified in Ref. [188, 90] for non-polar gases. For polar gases, it is valid for $c \neq d$, whereas for the coefficient $\mathscr{D}_{c\text{rot},c}$, the relation $\mathscr{D}_{c\text{rot},c} = \mathscr{D}_{cc}(1 + \delta_c)$, where $\delta_c$ is a function of temperature, is suggested.

Now, to calculate the bracket integrals, we need only the temperature dependence of the integrals $\Omega^{(l,r)}_{cd}$. The calculation of these standard integrals is based on the particular models for the inter-molecular interaction potential, and is discussed in Section 5.4.

### 5.3.2  Multi-Temperature Approach

The algorithm for the calculation of bracket integrals in the multi-temperature approach is similar to that described above for the state-to-state model. The difference is that the averaging operator is introduced on the basis of the zero-order distribution function (3.7):

$$\langle F \rangle_{cd} = \left( \frac{kT}{2\pi m_{cd}} \right)^{1/2} \sum_{iki'k'} \sum_{jlj'l'} \frac{s^c_{ij} s^d_{kl}}{Z^{\text{rot}}_c Z^{\text{vibr}}_c Z^{\text{rot}}_d Z^{\text{vibr}}_d} \int F\gamma^3 \times$$

$$\times \exp\left( -\gamma^2 - \mathscr{E}^{ci}_j - \mathscr{E}^{dk}_l - \mathscr{E}^{c(1)}_i - \mathscr{E}^{d(1)}_k - \mathscr{E}^{c(2)}_i - \mathscr{E}^{d(2)}_k \right) \sigma^{i'j'k'l'}_{cd,ijkl} d^2 \Omega d\gamma. \quad (5.83)$$

In this expression, $Z_c^{\text{vibr}} = Z_c^{\text{vibr}}(T, T_1^c)$ is calculated using the formula (3.13),

$$\mathscr{E}_i^{c(1)} = \frac{\varepsilon_i^c - i\varepsilon_1^c}{kT}, \qquad \mathscr{E}_i^{c(2)} = \frac{i\varepsilon_1^c}{kT_1^c} \tag{5.84}$$

are the dimensionless energy constituents associated with the anharmonicity of vibrations and the harmonic part of the vibrational energy, respectively. The operator (5.83) includes the cross sections of elastic collisions, those with RT transitions and, in addition to that, the cross sections of collisions resulting in the $VV_1$ exchange.

The integrals $\Omega_{cd}^{(l,r)}$ in the multi-temperature approach can be defined on the basis of the averaging operator (5.83) using the formulae similar to (5.56)–(5.59). It should be noted that in the latter definitions, not only the resonance defect $\Delta\mathscr{E}_{cidk}^{\text{rot}}$ in rotational energy transitions, but also the energy variation in the $VV_1$ exchange appears, $\Delta\mathscr{E}_{cd}^{\text{vibr}}$:

$$\Delta\mathscr{E}_{cd}^{\text{vibr}} = \Delta\mathscr{E}_c^{\text{vibr}} + \tilde{\Delta}\mathscr{E}_d^{\text{vibr}},$$

$$\Delta\mathscr{E}_c^{\text{vibr}} = \mathscr{E}_{i'}^c - \mathscr{E}_i^c,$$

$$\tilde{\Delta}\mathscr{E}_d^{\text{vibr}} = \mathscr{E}_{k'}^d - \mathscr{E}_k^d,$$

$\mathscr{E}_i^c = \varepsilon_i^c/(kT)$ is the dimensionless vibrational energy. In the present case, it seems to be appropriate to introduce the resonance defects for the values $\Delta\mathscr{E}_{cd}^{(1)}$ and $\Delta\mathscr{E}_{cd}^{(2)}$ from Eq. (5.84) rather than the energy variation $\Delta\mathscr{E}_{cd}^{\text{vibr}}$. However, since the vibrational quantum number $i$ is the invariant of the most frequent collisions, in rapid processes the values $i\varepsilon_1^c/(kT)$ and $i\varepsilon_1^c/(kT_1^c)$ are conserved, and, therefore, in the bracket integrals only the resonance defect of the total vibrational energy $\Delta\mathscr{E}_{cd}^{\text{vibr}}$ appears.

Furthermore, the additional effective diffusion coefficients can be introduced:

$$\mathscr{D}_{c\,\text{anh},d} = \frac{3kT}{16nm_{cd}} \frac{1}{\Omega_{c\,\text{anh},d}^{(1,1)}}, \qquad \mathscr{D}_{c\,\text{vibr},d} = \frac{3kT}{16nm_{cd}} \frac{1}{\Omega_{c\,\text{vibr},d}^{(1,1)}},$$

where the integrals $\Omega_{c\,\text{anh},d}^{(1,1)}$, $\Omega_{c\,\text{vibr},d}^{(1,1)}$ are equal to

$$\frac{m_c c_{\text{anh},c}^T}{k}\,\Omega_{c\,\text{anh},c}^{(1,1)} = \left\langle \mathscr{E}_{ci}^{(1)'} \left[ \left( \mathscr{E}_{ci}^{(1)'} - \mathscr{E}_{ck}^{(1)'} \right) \gamma^2 - \left( \mathscr{E}_{ci'}^{(1)'} - \mathscr{E}_{ck'}^{(1)'} \right) \gamma\gamma'\cos\chi \right] \right\rangle_{cc},$$

$$\frac{m_c c_{\text{anh},c}^T}{k}\,\Omega_{c\,\text{anh},d}^{(1,1)} = \left\langle \mathscr{E}_{ci}^{(1)'} \left( \mathscr{E}_{ci}^{(1)'} \gamma^2 - \mathscr{E}_{ci'}^{(1)'} \gamma\gamma'\cos\chi \right) \right\rangle_{cd}, \quad c \neq d,$$

$$\frac{m_c c_{\text{w},c}^{T_1}}{k}\,\Omega_{c\,\text{vibr},c}^{(1,1)} = \left\langle \mathscr{E}_{ci}^{(2)'} \left[ \left( \mathscr{E}_{ci}^{(2)'} - \mathscr{E}_{ck}^{(2)'} \right) \gamma^2 - \left( \mathscr{E}_{ci'}^{(2)'} - \mathscr{E}_{ck'}^{(2)'} \right) \gamma\gamma'\cos\chi \right] \right\rangle_{cc},$$

$$\frac{m_c c_{\text{w},c}^{T_1}}{k} \, \Omega_{c\,\text{vibr},d}^{(1,1)} = \left\langle \mathscr{E}_{ci}^{(2)'} \left( \mathscr{E}_{ci}^{(2)'} \gamma^2 - \mathscr{E}_{ci'}^{(2)'} \gamma\gamma' \cos\chi \right) \right\rangle_{cd}, \quad c \neq d.$$

Here,

$$\mathscr{E}_{ci}^{(1)'} = \frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} - \left\langle \frac{\varepsilon_i^c - i\varepsilon_1^c}{kT} \right\rangle_{\text{vibr}}, \qquad \mathscr{E}_{ci}^{(2)'} = \frac{i\varepsilon_1^c}{kT_1^c} - \left\langle \frac{i\varepsilon_1^c}{kT_1^c} \right\rangle_{\text{vibr}}.$$

In order to calculate the bracket integrals in the multi-temperature approach, we again use the assumptions of E. Mason and L. Monchick formulated above. Moreover, in the calculation of the integrals $\Lambda_{rr'pp'qq'}^{cd}$, the contribution of the integrals depending on $\Delta\mathscr{E}_{cidk}^{\text{rot}}$ and $\Delta\mathscr{E}_{cd}^{\text{vibr}}$ is neglected. The smallness of the rotational energy variation in RT transitions for most homo-nuclear molecules is already discussed in the previous Section. Concerning the vibrational energy exchange, it is known that for most vibrational levels, single-quantum transitions prevail (with the exception of high levels, with the small value of the vibrational quantum). In single-quantum transitions, $\Delta\mathscr{E}_{cd}^{\text{vibr}}$ is proportional to the anharmonic parameter $\alpha_c$ (which is much smaller than the vibrational energy quantum) and to the value $(k - i - 1)$ [140]. It is obvious that the resonance defect in the transitions between the adjacent states is negligibly small. When $k - i$ grows, it increases, but at the same time the probability of $VV_1$ exchange, with its maximum near $k = i$, decreases. For harmonic oscillators, the vibrational energy exchange is always resonant. Therefore, in the calculation of $\Lambda_{rr'pp'qq'}^{cd}$ neglecting the integrals containing $\Delta\mathscr{E}_{cd}^{\text{vibr}}$ affects the accuracy of the thermal conductivity coefficients only slightly (within 1–2%).

Finally, taking into account all these assumptions, we obtain the expressions for the bracket integrals $\Lambda_{rr'pp'qq'}^{cd}$ and $\alpha_{11}^{cd}$ specifying the thermal conductivity, thermal diffusion, and diffusion coefficients, in the form

$$\Lambda_{000000}^{cd} = \gamma_{00}^{cd} = -\frac{3kT}{2n} \frac{x_c x_d}{\mathscr{D}_{cd}}, \qquad d \neq c, \tag{5.85}$$

$$\Lambda_{000000}^{cc} = \gamma_{00}^{cc} = \frac{3kT}{2n} \sum_{b \neq c} \frac{x_c x_b}{\mathscr{D}_{cb}}, \tag{5.86}$$

$$\Lambda_{100000}^{cd} = \frac{3kT}{4n} \frac{x_c x_d}{\mathscr{D}_{cd}} \frac{m_d}{m_c + m_d} (6\tilde{C}_{cd} - 5), \qquad d \neq c, \tag{5.87}$$

$$\Lambda_{100000}^{cc} = -\frac{3kT}{4n} \sum_{b \neq c} \frac{x_c x_b}{\mathscr{D}_{cb}} \frac{m_b}{m_c + m_b} (6\tilde{C}_{cb} - 5), \tag{5.88}$$

$$\Lambda_{110000}^{cd} = -\frac{3kT}{2n} \frac{x_c x_d}{\mathscr{D}_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} \left( \frac{55}{4} - 3\tilde{B}_{cd} - 4\tilde{A}_{cd} \right), \quad d \neq c, \tag{5.89}$$

$$\Lambda_{110000}^{cc} = \frac{3kT}{2n} \sum_{b \neq c} \frac{x_c x_b}{\mathscr{D}_{cb}} \frac{m_c m_b}{(m_c + m_b)^2} \left( \frac{15}{2} \frac{m_c}{m_b} + \right.$$

$$\left. + \frac{25}{4} \frac{m_b}{m_c} - 3 \frac{m_b}{m_c} \tilde{B}_{cb} + 4\tilde{A}_{cb} \right) + \frac{3kT}{n} \frac{x_c^2 \tilde{A}_{cc}}{\mathscr{D}_{cc}}, \qquad (5.90)$$

$$\Lambda_{001100}^{cd} = \Lambda_{000011}^{cd} = \alpha_{11}^{cd} = 0, \qquad d \neq c,$$

$$\Lambda_{001100}^{cc} = \frac{3T}{2n} \sum_{b \neq c} x_c x_b \frac{m_c c_{\text{rot},c}}{\mathscr{D}_{c\,\text{rot},b}} + \frac{3T}{2n} x_c^2 \frac{m_c c_{\text{rot},c}}{\mathscr{D}_{c\,\text{rot},c}},$$

$$\Lambda_{000011}^{cc} = \frac{3T}{2n} \sum_{b \neq c} x_c x_b \frac{m_c c_{\text{anh},c}^T}{\mathscr{D}_{c\,\text{anh},b}} + \frac{3T}{2n} x_c^2 \frac{m_c c_{\text{anh},c}^T}{\mathscr{D}_{c\,\text{anh},c}},$$

$$\alpha_{11}^{cc} = \frac{3T}{2n} \sum_{b \neq c} x_c x_b \frac{m_c c_{\text{w},c}^{T_1}}{\mathscr{D}_{c\,\text{vibr},b}} + \frac{3T}{2n} x_c^2 \frac{m_c c_{\text{w},c}^{T_1}}{\mathscr{D}_{c\,\text{vibr},c}}.$$

The remaining bracket integrals $\Lambda_{rr'pp'qq'}^{cd}$ are zero due to the assumption about negligible values of integrals depending on the energy variation in RT and VV$_1$ exchanges, and normalization of the Waldmann-Trübenbacher polynomials.

The bracket integrals $H_{00}^{cd}$ in the formula for the shear viscosity are reduced to the expressions

$$H_{00}^{cd} = 2 \frac{x_c x_d}{\eta_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} \left( -\frac{5}{3\tilde{A}_{cd}} + 1 \right), \qquad d \neq c, \qquad (5.91)$$

$$H_{00}^{cc} = 2 \sum_{b \neq c} \frac{x_c x_b}{\eta_{cb}} \left[ \frac{5}{3\tilde{A}_{cb}} \frac{m_c m_b}{(m_c + m_b)^2} + \frac{m_b^2}{(m_c + m_b)^2} \right] + \frac{x_c^2}{\eta_c}. \qquad (5.92)$$

In this case, the coefficients $\tilde{A}_{cd}$, $\tilde{B}_{cd}$, $\tilde{C}_{cd}$, $\eta_{cd}$, and $\mathscr{D}_{cd}$ are calculated on the basis of the formulae (5.60)–(5.62) taking into account the relations (5.63). Note that the integrals $\Omega_{cd}^{(l,r)}$ in the multi-temperature approach are introduced using the operator (5.83) and, by definition, do not depend on the vibrational energy levels.

As is already mentioned, it is impossible to neglect the energy resonance defect while deriving the expressions for bracket integrals $\beta_{rr'pp'qq'}^{cd}$. In order to simplify the integrals associated with $\Delta\mathscr{E}_{cidk}^{\text{rot}}$, we can again use the definition for the rotational relaxation time which, in the multi-temperature approach, takes the form

$$\frac{1}{\tau_{cc}^{\text{rot}}} = \frac{2kn}{m_c c_{\text{rot},c}} \left\langle (\Delta\mathscr{E}_{cc}^{\text{rot}})^2 \right\rangle_{cc}, \qquad \frac{1}{\tau_{cd}^{\text{rot}}} = \frac{4kn}{m_c c_{\text{rot},c}} \left\langle \Delta\mathscr{E}_c^{\text{rot}} \Delta\mathscr{E}_{cd}^{\text{rot}} \right\rangle_{cd}.$$

In this expression, we assume that the rotational energy does not depend on the vibrational level of a molecule (like, for instance, in the case of rigid rotators), and, consequently, $\Delta\mathcal{E}^{\text{rot}}_{cidk} = \Delta\mathcal{E}^{\text{rot}}_{cd}$. This makes it possible to find the rotational relaxation time depending only on the chemical species. The collision number $\zeta^{\text{rot}}_{cd}$ required for the equilibration of the rotational mode in molecules of species $c$ in their collisions with particles of $d$ species, is introduced as follows

$$\zeta^{\text{rot}}_{cd} = \frac{4}{\pi}\frac{p\,\tau^{\text{rot}}_{cd}}{\eta_{cd}}.$$

Hereafter we suppose that $\tau^{\text{rot}}_{cd}$ and $\zeta^{\text{rot}}_{cd}$ do not depend on the chemical species of the partner in a collision: $\tau^{\text{rot}}_{cd} = \tau^{\text{rot}}_c$ and $\zeta^{\text{rot}}_{cd} = \zeta^{\text{rot}}_c$.

Formally, using similar formulae, one can also introduce the time for the vibrational relaxation associated to the resonance defect $\Delta\mathcal{E}^{\text{vibr}}_{cd}$. However, it has not any practical sense. Indeed, the relaxation times are introduced to connect the integrals depending on the energy variation with experimentally measurable values. In fact, the vibrational relaxation time specified by the averaging operator (5.83) corresponds to the characteristic time for VV relaxation in each molecular species. On the other hand, in experiments the mean time for VT relaxation is commonly measured. Therefore, it is consistent to calculate the integrals associated with the resonance defect of vibrational energy in the explicit form using the existing models for the rate coefficients of VV$_1$ vibrational energy transitions (see Chapter 6).

Taking into account the definition of the collision number necessary for the rotational energy relaxation, we obtain the following expressions for the bracket integrals $\beta^{cd}_{rr'pp'qq'}$ appearing in the systems of algebraic equations for the computation of bulk viscosity coefficient and relaxation pressure:

$$\beta^{cd}_{110000} = -5kT\frac{x_c x_d}{\tilde{A}_{cd}\eta_{cd}}\frac{m_c m_d}{(m_c + m_d)^2} + 4x_c x_d \frac{m_c m_d}{(m_c + m_d)^2} \times$$

$$\times \left[\frac{T}{\pi\eta_{cd}}\left(\frac{m_c c_{\text{rot},c}}{\zeta^{\text{rot}}_c} + \frac{m_d c_{\text{rot},d}}{\zeta^{\text{rot}}_d}\right) + \left\langle(\Delta\mathcal{E}^{\text{vibr}}_{cd})^2\right\rangle_{cd}\right], \quad d \neq c,$$

$$\beta^{cc}_{110000} = \sum_{b \neq c}\left[5kT\frac{x_c x_b}{\tilde{A}_{cb}\eta_{cb}}\frac{m_c m_b}{(m_c + m_b)^2} + 4x_c x_b \frac{m_b^2}{(m_c + m_b)^2} \times\right.$$

$$\left.\times \left[\frac{T}{\pi\eta_{cb}}\left(\frac{m_c c_{\text{rot},c}}{\zeta^{\text{rot}}_c} + \frac{m_b c_{\text{rot},b}}{\zeta^{\text{rot}}_b}\right) + \left\langle(\Delta\mathcal{E}^{\text{vibr}}_{cb})^2\right\rangle_{cb}\right]\right] +$$

$$+\frac{4T}{\pi}\frac{x_c^2}{\eta_c}\frac{m_c c_{\text{rot},c}}{\zeta^{\text{rot}}_c} + 2x_c^2 \left\langle(\Delta\mathcal{E}^{\text{vibr}}_{cc})^2\right\rangle_{cc},$$

$$\beta_{011000}^{cd} = -\frac{4T}{\pi}\frac{x_c x_d}{\eta_{cd}}\frac{m_c}{m_c+m_d}\frac{m_c c_{\mathrm{rot},c}}{\zeta_c^{\mathrm{rot}}}, \qquad d \neq c,$$

$$\beta_{011000}^{cc} = -\frac{4T}{\pi}\sum_{b\neq c}\frac{x_c x_b}{\eta_{cb}}\frac{m_b}{m_c+m_b}\frac{m_c c_{\mathrm{rot},c}}{\zeta_c^{\mathrm{rot}}} - \frac{4T}{\pi}\frac{x_c^2}{\eta_c}\frac{m_c c_{\mathrm{rot},c}}{\zeta_c^{\mathrm{rot}}},$$

$$\beta_{010010}^{cd} = -4x_c x_d\frac{m_c}{m_c+m_d}\left\langle \Delta\tilde{\mathscr{E}}_c^{\mathrm{vibr}}\Delta\mathscr{E}_{cd}^{\mathrm{vibr}}\right\rangle_{cd}, \quad d\neq c,$$

$$\beta_{010010}^{cc} = -4\sum_{b\neq c}x_c x_b\frac{m_b}{m_c+m_b}\left\langle \Delta\mathscr{E}_c^{\mathrm{vibr}}\Delta\mathscr{E}_{cb}^{\mathrm{vibr}}\right\rangle_{cb} -$$

$$-2x_c^2\left\langle (\Delta\mathscr{E}_{cc}^{\mathrm{vibr}})^2\right\rangle_{cc},$$

$$\beta_{001100}^{cd} = \beta_{000011}^{cd} = 0, \qquad d\neq c,$$

$$\beta_{001100}^{cc} = \frac{4T}{\pi}\sum_{b\neq c}\frac{x_c x_b}{\eta_{cb}}\frac{m_c c_{\mathrm{rot},c}}{\zeta_c^{\mathrm{rot}}} + \frac{4T}{\pi}\frac{x_c^2}{\eta_c}\frac{m_c c_{\mathrm{rot},c}}{\zeta_c^{\mathrm{rot}}},$$

$$\beta_{000011}^{cc} = 4\sum_{b\neq c}x_c x_b\left\langle (\Delta\mathscr{E}_c^{\mathrm{vibr}})^2\right\rangle_{cb} + 2x_c^2\left\langle (\Delta\mathscr{E}_{cc}^{\mathrm{vibr}})^2\right\rangle_{cc}.$$

Thus in the multi-temperature approach, the bracket integrals are reduced to the expressions including the molar fractions of chemical species $x_c = n_c/n$, gas temperature, standard integrals $\Omega_{cd}^{(l,r)}$ specified by the cross sections of elastic collisions and those resulting in RT and VV$_1$ transitions, rotational relaxation times $\tau_c^{\mathrm{rot}}$ for molecules of $c$ species, and integrals depending on the vibrational energy resonance defect $\Delta\mathscr{E}_{cd}^{\mathrm{vibr}}$.

### 5.3.3 One-Temperature Approach

In the thermal equilibrium approach, the averaging operator is introduced on the basis of the zero-order distribution function (4.4) [188, 76]:

$$\langle F\rangle_{cd} = \left(\frac{kT}{2\pi m_{cd}}\right)^{1/2}\sum_{iki'k'}\sum_{jlj'l'}\frac{s_{ij}^c s_{kl}^d}{Z_c^{\mathrm{int}}Z_d^{\mathrm{int}}}\int F\gamma^3\times$$

$$\times\exp\left(-\gamma^2 - \mathscr{E}_{ij}^c - \mathscr{E}_{kl}^d\right)\sigma_{cd,ijkl}^{i'j'k'l'}d^2\Omega d\gamma. \tag{5.93}$$

Here, $Z_c^{\text{int}} = Z_c^{\text{rot}}(T)Z_c^{\text{vibr}}(T)$, and $\mathscr{E}_{ij}^c = \varepsilon_{ij}^c/(kT)$ is the dimensionless internal energy. The operator (5.93) depends on the cross sections of elastic and all inelastic collisions resulting in RT, VV, and VT transitions.

In the considered approach, the integrals $\Omega_{cd}^{(l,r)}$ are defined using the operator (5.93) [188, 76] and include the resonance defect $\Delta\mathscr{E}_{cd}^{\text{int}}$ of the internal energy in all inelastic collisions:

$$\Delta\mathscr{E}_{cd}^{\text{int}} = \Delta\mathscr{E}_c^{\text{int}} + \tilde{\Delta}\mathscr{E}_d^{\text{int}},$$

$$\Delta\mathscr{E}_c^{\text{int}} = \mathscr{E}_{i'j'}^c - \mathscr{E}_{ij}^c,$$

$$\tilde{\Delta}\mathscr{E}_d^{\text{int}} = \mathscr{E}_{k'l'}^d - \mathscr{E}_{kl}^d.$$

The effective diffusion coefficients of the internal energy are introduced similarly to Ref. [188]:

$$\mathscr{D}_{c\,\text{int},d} = \frac{3kT}{16nm_{cd}}\frac{1}{\Omega_{c\,\text{int},d}^{(1,1)}},$$

$$\frac{m_c c_{\text{int},c}}{k}\Omega_{c\,\text{int},c}^{(1,1)} = \left\langle \mathscr{E}_{cij}'\left[\left(\mathscr{E}_{cij}' - \mathscr{E}_{ckl}'\right)\gamma^2 - \left(\mathscr{E}_{ci'j'}' - \mathscr{E}_{ck'l'}'\right)\gamma\gamma'\cos\chi\right]\right\rangle_{cc},$$

$$\frac{m_c c_{\text{int},c}}{k}\Omega_{c\,\text{int},d}^{(1,1)} = \left\langle \mathscr{E}_{cij}'\left(\mathscr{E}_{cij}'\gamma^2 - \mathscr{E}_{ci'j'}'\gamma\gamma'\cos\chi\right)\right\rangle_{cd}, \quad c \neq d,$$

The integrals $\Omega_{c\,\text{int},d}^{(1,1)}$ coincide with those defined in Refs. [188, 76].

Assuming the rotational and vibrational energy to be independent, we can introduce the relaxation time for the internal energy:

$$\frac{1}{\tau_{cc}^{\text{int}}} = \frac{2kn}{m_c c_{\text{int},c}}\left\langle (\Delta\mathscr{E}_{cc}^{\text{int}})^2\right\rangle_{cc}, \quad \frac{1}{\tau_{cd}^{\text{int}}} = \frac{4kn}{m_c c_{\text{int},c}}\left\langle \Delta\mathscr{E}_c^{\text{int}}\Delta\mathscr{E}_{cd}^{\text{int}}\right\rangle_{cd} \tag{5.94}$$

and the collision number $\zeta_{cd}^{\text{int}}$ required for the equilibration of the internal degrees of freedom in particles of $c$ species as a result of their collisions with those of $d$ species:

$$\zeta_{cd}^{\text{int}} = \frac{4}{\pi}\frac{p\tau_{cd}^{\text{int}}}{\eta_{cd}}.$$

Using the assumptions made by E. Mason and L. Monchick, we can easily derive the expressions for the bracket integrals in the one-temperature approach, which coincide with those given in Refs. [188, 76]. Thus the expressions for $H_{00}^{cd}$ are given by the formulae (5.91), (5.92). If, in order to calculate $\Lambda_{rr'pp'}^{cd}$, we neglect the integrals specified by the resonance defect of the internal energy $\Delta\mathscr{E}_{cd}^{\text{int}}$, then we find that the expressions for bracket integrals $\Lambda_{0000}^{cd}$, $\Lambda_{1000}^{cd}$, and $\Lambda_{1100}^{cd}$ coincide with the formulae (5.85)–(5.90), whereas the integrals $\Lambda_{0011}^{cd}$ take the form

$$\Lambda_{0011}^{cd} = 0, \qquad d \neq c,$$

$$\Lambda_{0011}^{cc} = \frac{3T}{2n}\sum_{b\neq c}x_c x_b\frac{m_c c_{\text{int},c}}{\mathscr{D}_{c\,\text{int},b}} + \frac{3T}{2n}x_c^2\frac{m_c c_{\text{int},c}}{\mathscr{D}_{c\,\text{int},c}}.$$

Taking into account the definition (5.94) for the internal energy relaxation time, we can reduce the expressions for bracket integrals $\beta^{cd}_{rr'pp'}$ to the formulae:

$$\beta^{cd}_{1100} = -5kT \frac{x_c x_d}{\tilde{A}_{cd}\eta_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} +$$

$$+ \frac{4T}{\pi} \frac{x_c x_d}{\eta_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} \left( \frac{m_c c_{\text{int},c}}{\zeta^{\text{int}}_c} + \frac{m_d c_{\text{int},d}}{\zeta^{\text{int}}_d} \right), \quad d \neq c,$$

$$\beta^{cc}_{1100} = \sum_{b \neq c} \left[ 5kT \frac{x_c x_b}{\tilde{A}_{cb}\eta_{cb}} \frac{m_c m_b}{(m_c + m_b)^2} + \frac{4T}{\pi} \frac{x_c x_b}{\eta_{cb}} \frac{m_b^2}{(m_c + m_b)^2} \times \right.$$

$$\left. \times \left( \frac{m_c c_{\text{int},c}}{\zeta^{\text{int}}_c} + \frac{m_b c_{\text{int},b}}{\zeta^{\text{int}}_b} \right) \right] + \frac{4T}{\pi} \frac{x_c^2}{\eta_c} \frac{m_c c_{\text{int},c}}{\zeta^{\text{int}}_c},$$

$$\beta^{cd}_{0110} = -\frac{4T}{\pi} \frac{x_c x_d}{\eta_{cd}} \frac{m_c}{m_c + m_d} \frac{m_c c_{\text{int},c}}{\zeta^{\text{int}}_c}, \quad d \neq c,$$

$$\beta^{cc}_{0110} = -\frac{4T}{\pi} \sum_{b \neq c} \frac{x_c x_b}{\eta_{cb}} \frac{m_b}{m_c + m_b} \frac{m_c c_{\text{int},c}}{\zeta^{\text{int}}_c} - \frac{4T}{\pi} \frac{x_c^2}{\eta_c} \frac{m_c c_{\text{int},c}}{\zeta^{\text{int}}_c},$$

$$\beta^{cd}_{0011} = 0, \quad d \neq c,$$

$$\beta^{cc}_{0011} = \frac{4T}{\pi} \sum_{b \neq c} \frac{x_c x_b}{\eta_{cb}} \frac{m_c c_{\text{int},c}}{\zeta^{\text{int}}_c} + \frac{4T}{\pi} \frac{x_c^2}{\eta_c} \frac{m_c c_{\text{int},c}}{\zeta^{\text{int}}_c}.$$

Finally, in the one-temperature approach all bracket integrals are expressed in terms of the molar fractions of the chemical species $x_c = n_c/n$, temperature, collision integrals $\Omega^{(l,r)}_{cd}$ (depending on the cross sections of all elastic and inelastic collisions), and internal energy relaxation times $\tau^{\text{int}}_c$ of molecular species $c$.

## 5.4  $\Omega$-Integrals and Relaxation Times

As is shown in the previous Section, the calculation for the transport coefficients is basically reduced to that for the integrals $\Omega^{(l,r)}_{cd}$ and relaxation times. Let us discuss some methods for the determination of these values.

### 5.4.1 $\Omega$-Integrals

Strictly speaking, the calculation of the integrals $\Omega_{cd}^{(l,r)}$ in each particular approach, should be based on the corresponding averaging operator (5.55), (5.83), and (5.93). However, for practical calculations, it is often assumed that the scattering cross sections do not depend on the internal energy of molecules. Such an assumption is justified, for instance, in Refs. [82, 90]. In this case, the integrals $\Omega_{cd}^{(l,r)}$ are reduced to those specified by the cross sections of elastic collisions, which are determined as follows [82]:

$$\Omega_{cd}^{(l,r)} = \left(\frac{kT}{2\pi m_{cd}}\right)^{1/2} \int_0^\infty \exp(-\gamma^2)\gamma^{2r+3} \mathcal{Q}_{cd}^{(l)} d\gamma, \tag{5.95}$$

where

$$\mathcal{Q}_{cd}^{(l)} = 2\pi \int \left(1 - \cos^l \chi_{cd}(b,\gamma)\right) b\, db.$$

$\mathcal{Q}_{cd}^{(l)}$ are called average scattering cross sections or, sometimes, transport cross sections.

From the definition (5.95), it is easy to obtain a recurrent relation connecting the integrals for a given $l$ [82]:

$$\Omega_{cd}^{(l,r+1)} = T\frac{\partial \Omega_{cd}^{(l,r)}}{\partial T} + \left(r + \frac{3}{2}\right)\Omega_{cd}^{(l,r)}. \tag{5.96}$$

In the general case, the integrals $\Omega_{cd}^{(l,r)}$ cannot be calculated analytically, since the dependence of the scattering angle $\chi$ on the relative velocity $\mathbf{g}$ and impact parameter $b$ is usually very complex. Analytical expressions for the integrals $\Omega_{cd}^{(l,r)}$ can be obtained only for the rigid sphere model, the interaction potential of which is given by the formula

$$\varphi(r) = \begin{cases} \infty, & \sigma < r, \\ 0, & \sigma > r, \end{cases}$$

where $r$ is the distance between the centers of mass of molecules, $\sigma = \sigma_{cd} = (\sigma_c + \sigma_d)/2$ is the distance between the centers of two molecules with diameters $\sigma_c$ and $\sigma_d$ in the instant of a collision. For the rigid sphere model,

$$\left(\Omega_{cd}^{(l,r)}\right)_{r.s.} = \left(\frac{kT}{2\pi m_{cd}}\right)^{1/2}\frac{(r+1)!}{2}\left[1 - \frac{1+(-1)^l}{2(l+1)}\right]\pi\sigma_{cd}^2.$$

The rigid sphere model is rather far from physically adequate interaction potentials and is convenient only for rapid and rough estimates. On the basis of this model, the reduced integrals $\Omega$ can be defined:

$$\Omega_{cd}^{(l,r)*} = \frac{\Omega_{cd}^{(l,r)}}{\left(\Omega_{cd}^{(l,r)}\right)_{r.s.}}.$$

The temperature dependence of the reduced integrals is rather weak compared to the case of non-normalized integrals. Moreover, the reduced integrals are close to unity, which makes them convenient for practical calculations.

The functions $\tilde{A}_{cd}$, $\tilde{B}_{cd}$, and $\tilde{C}_{cd}$, given by the relations (5.60), can also be expressed in terms of the reduced integrals:

$$\tilde{A}_{cd} = \frac{\Omega_{cd}^{(2,2)*}}{\Omega_{cd}^{(1,1)*}}, \quad \tilde{B}_{cd} = \frac{5\Omega_{cd}^{(1,2)*} - 4\Omega_{cd}^{(1,3)*}}{\Omega_{cd}^{(1,1)*}}, \quad \tilde{C}_{cd} = \frac{\Omega_{cd}^{(1,2)*}}{\Omega_{cd}^{(1,1)*}}.$$

More realistic models of inter-molecular interaction are represented by the Sutherland, Lennard–Jones, Stockmayer, Buckingham, Morse and some other potentials (see [82]). Numerical calculations of the integrals $\Omega_{cd}^{(l,r)}$ for various interaction potentials were carried out by a number of authors, a large number of tables as well as approximate formulae obtained by the interpolation of the tabulated data, can be found in Refs. [112, 260, 82, 106, 41, 52]. For practical calculations, it is important to select the proper interaction model and, therefore, the data on the elastic collision integrals in accordance with the specific flow conditions. A review of the inter-molecular interaction potentials, as well as the discussion of their influence on the dissipative properties of gases are given in the study [234].

One of the most popular interaction model is that of Lennard–Jones, in which the interaction potential is:

$$\varphi(r) = 4\frac{\varepsilon}{k}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right].$$

Here, $\sigma$ is the value of $r$, for which the sign of the potential function is altered, whereas $\varepsilon$ is the minimum value of the potential (at $r = 2^{1/6}\sigma$). In the moderate temperature range, this model provides consistency of the transport coefficients with a great amount of experimental data using only two parameters.

The potential parameters are commonly selected by a comparison between the transport coefficients calculated with a given potential and those measured experimentally. In particular, a great variety of data for the parameters of the Lennard–Jones potential are available (see [112, 10, 95, 120, 121]). The importance of the

**Table 5.1** The thermal conductivity coefficient of $N_2$ ($\lambda \cdot 10^3$, W/m· K) calculated with different parameters of the Lennard–Jones potential

| $T$, K | $\lambda_{exp}$ | [121] | [112] |
|--------|-----------------|-------|-------|
| 200    | 18.3            | 19.5  | 19.0  |
| 300    | 25.7            | 27.0  | 26.2  |
| 400    | 32.4            | 33.5  | 32.5  |
| 600    | 44.6            | 45.3  | 43.4  |
| 800    | 55.4            | 56.2  | 52.9  |
| 1000   | 65.0            | 66.4  | 61.4  |

**Table 5.2** The shear viscosity coefficient of $N_2$ ($\eta \cdot 10^6$, Pa·s), calculated with different parameters of the Lennard–Jones potential

| $T$, K | $\eta_{\mathrm{exp}}$ | [121] | [112] |
|---|---|---|---|
| 250 | 15.5 | 15.6 | 15.1 |
| 300 | 17.9 | 17.9 | 17.5 |
| 400 | 22.1 | 22.3 | 21.6 |
| 500 | 25.9 | 26.1 | 25.4 |
| 600 | 29.3 | 29.7 | 28.8 |
| 800 | 35.2 | 36.1 | 35.1 |

appropriate selection of the parameters for the calculation of the transport coefficients and heat flux is discussed in Refs. [53, 224, 142, 145, 52, 144, 155].

The coefficients of thermal conductivity and shear viscosity in molecular nitrogen, measured experimentally [250] and calculated, for the case of a thermal equilibrium gas, on the basis of the Lennard–Jones potential with the parameters from [112] and [121] are presented in Tables 5.1, 5.2. A comparison shows that when the temperature rises, the use of the parameters $\sigma$ and $\varepsilon$ from [112] leads to substantial underestimation of transport coefficients. Recommended values for the Lennard–Jones potential parameters for air components are given in Table 5.3.

The experimental data for the transport coefficients are mostly available for pure gases; therefore, the potential parameters are commonly calculated for single-component gases. In order to find the parameters of the interaction potential in a mixture, the following relations can be used [82]:

$$\varepsilon_{cd}\sigma_{cd}^6 = \sqrt{\varepsilon_c\sigma_c^6\varepsilon_d\sigma_d^6}, \tag{5.97}$$

$$\sigma_{cd} = \frac{1}{2}(\sigma_c + \sigma_d).$$

While the first expression is rigorously justified and makes it possible to reach consistency with the experimental data, the second relation is analogous to that for rigid spheres and displays insufficient theoretical justification [82]. To describe the interaction of particles with comparable masses, a simplified version of the relation (5.97) is often used:

$$\varepsilon_{cd} = \sqrt{\varepsilon_c\varepsilon_d}.$$

With a rise in the gas temperature, repulsive forces become more important in the molecular interaction. Under the condition $kT/\varepsilon > 10$, the Lennard–Jones potential does not describe the interaction law correctly, and in order to calculate the transport coefficients, it is preferable to use the repulsive Born–Mayer potential in the form suggested in Ref. [66]

$$\varphi(r) = \varphi_0\exp(-\beta r), \tag{5.98}$$

**Table 5.3** The recommended parameters of the Lennard–Jones potential

| Interaction | $\sigma$, Å | $\varepsilon/k$, K | Reference |
|---|---|---|---|
| $N_2 - N_2$ | 3.621 | 97.5 | [121] |
| $O_2 - O_2$ | 3.458 | 107.4 | [121] |
| NO – NO | 3.47 | 119 | [95] |
| N – N | 3.298 | 71.4 | [121] |
| O – O | 2.75 | 80 | [121] |

**Table 5.4** The recommended parameters of the Born–Mayer potential

| Interaction | $\varphi_0$, eV | $\beta$, Å$^{-1}$ | Reference |
|---|---|---|---|
| $N_2 - N_2$ | 415.7 | 2.573 | [224] |
| $N_2 - O_2$ | 2316 | 3.267 | [224] |
| $N_2 - NO$ | 52.38 | 1.761 | [224] |
| $N_2 - N$ | 184.9 | 2.614 | [224] |
| $N_2 - O$ | 860.4 | 3.331 | [224] |
| $O_2 - O_2$ | $1.485 \cdot 10^4$ | 3.964 | [224] |
| $O_2 - NO$ | 6373 | 3.644 | [224] |
| $O_2 - N$ | 905.7 | 3.32 | [224] |
| $O_2 - O$ | 4530 | 4.039 | [224] |
| NO – NO | 2678 | 3.303 | [224] |
| NO – N | 428.6 | 2.983 | [224] |
| NO – O | 2142 | 3.717 | [224] |
| N – N | 86.0 | 2.68 | [66] |
| N – O | 348.2 | 3.41 | [66] |
| O – O | 1410 | 4.14 | [66] |

where $\varphi_0$ and $\beta$ are the potential parameters. The values of the parameters recommended in Ref. [224] for the repulsive potential (5.98) for the air components are given in Table 5.4.

In Refs. [142, 145, 144, 155], the transport coefficients of air components were studied taking into account various interaction potentials and different parameters for these potentials. The Lennard–Jones potential with the parameters from [112, 121, 95] was used, as well as the repulsive potential (5.98) with the parameters from [224], and also approximate formulas for the calculation of integrals $\Omega_{cd}^{(l,r)}$ suggested in Ref. [52]. The results were compared with the experimental data from [241, 113, 250] and those obtained on the basis of the Blottner approximate expressions for the shear viscosity coefficient [25].

Figs. 5.1, 5.2 present the shear viscosity coefficients calculated for NO molecules and partially dissociated air ($\eta \cdot 10^6$, Pa·s. We can see that for moderate temperatures $200 < T < 1000$ K, the coefficients calculated using the Lennard–Jones potential
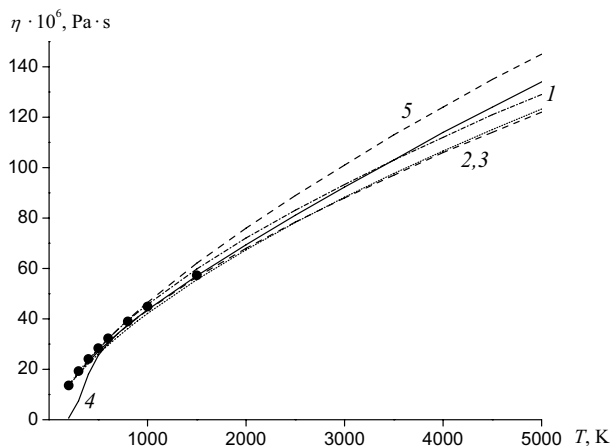
**Fig. 5.1** The shear viscosity coefficient in NO. Dots correspond to the experimental data from [241]. Curves *1, 2* are obtained using the Lennard–Jones potential with the parameters from [95] and [121], respectively, *3* is based on the Blottner approximation, *4* is calculated with the repulsive potential (5.98), and *5* with the data from [52]

show the best agreement with the experimental data, providing the accuracy within 2% for the parameters from Ref. [95] and that within 5% for the parameters proposed in [121]. At low temperatures ($T < 500$ K), the use of repulsive potential (5.98) for the calculation of transport coefficients leads to a substantial underestimation for $\eta$, whereas at higher temperatures, it provides satisfactory agreement with the experimental results. The Blottner approximation yields underestimated values for the viscosity coefficients at high temperatures (with the accuracy of about 5–7%), and the formulae for the calculation of integrals $\Omega_{cd}^{(l,r)}$ suggested in Ref. [52] provide some overestimation for the shear viscosity coefficient (the accuracy within 3–4%).

Analyzing the shear viscosity coefficient calculated for a partially dissociated air, we can notice that in the high temperature range, the use of the Lennard–Jones potential yields substantially underestimated values of the coefficient $\eta$, whereas the use of the Born–Mayer potential for the calculation of integrals $\Omega_{cd}^{(l,r)}$ (applying the approximated expressions given in Refs. [41] and [52]) provides the best fit to the experimental data. The integrals calculated by K. Yun and E. Mason in Ref. [260] also provide a satisfactory accuracy; however for $3000 < T < 6000$ K it is lower than that provided by the collision integrals obtained on the basis of models suggested in Refs. [41] and [52]. The use of the data from [106] results in considerable underestimation for the viscosity coefficient at high temperatures.

Thus for the calculation of transport coefficients we can recommend either the Lennard–Jones potential for $kT/\varepsilon < 10$ and repulsive potential (5.98) for $kT/\varepsilon > 10$, or the approximate formulae from Ref. [52] for the entire temperature range.
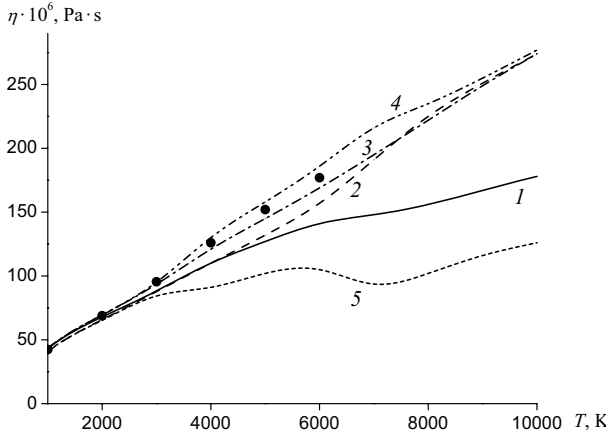
**Fig. 5.2** The shear viscosity coefficient in a partially dissociated air. Dots correspond to the experimental data from [250]. Curve *1* is obtained using the Lennard–Jones potential, *2* using the tables [260], *3* is found for the repulsive potential (5.98), *4* is calculated using the data from [52], and *5* is based on the data provided in [106]

The approximate expressions for the calculation of reduced integrals $\Omega_{cd}^{(1,1)*}$ and $\Omega_{cd}^{(2,2)*}$ on the basis of the Lennard–Jones potential are obtained in the form:

$$\Omega_{cd}^{(l,r)*} = \left( f_1^{(l,r)} + \frac{f_2^{(l,r)}}{x_{l,r}^2} + \frac{f_3^{(l,r)}}{x_{l,r}} + f_4^{(l,r)} x_{l,r} + f_5^{(l,r)} x_{l,r}^2 + f_6^{(l,r)} x_{l,r}^3 \right)^{-1}. \tag{5.99}$$

Here, $x_{l,r} = \ln(kT/\varepsilon_{cd}) + a_{l,r}$, and the coefficients $a_{l,r}$, $f_n^{(l,r)}$ are presented in Table 5.5.

**Table 5.5** Coefficients $f_n^{(l,r)}$ in the formula (5.99)

| $l,r$ | $a_{l,r}$ | $f_1^{(l,r)}$ | $f_2^{(l,r)}$ | $f_3^{(l,r)}$ | $f_4^{(l,r)}$ | $f_5^{(l,r)}$ | $f_6^{(l,r)}$ |
|-------|-----------|---------------|---------------|---------------|---------------|---------------|---------------|
| 1, 1  | 1.4       | − 0.16845     | − 0.02258     | 0.19779       | 0.64373       | − 0.09267     | 0.00711       |
| 2, 2  | 1.5       | − 0.40811     | − 0.05086     | 0.34010       | 0.70375       | − 0.10699     | 0.00763       |

In order to calculate reduced integrals $\Omega_{cd}^{(1,1)*}$ and $\Omega_{cd}^{(2,2)*}$ on the basis of the repulsive potential (5.98), we recommend to use the approximate formulae suggested in Ref. [41]:

$$\Omega_{cd}^{(1,1)*} = \left( r_* \ln \frac{v_*}{T_*} \right)^2 \left( 0.89 + \frac{A_1}{T_*^2} + \frac{A_2}{T_*^4} + \frac{A_3}{T_*^6} \right),$$

$$\Omega^{(2,2)*}_{cd} = \left( r_* \ln \frac{v_*}{T_*} \right)^2 \left( 1.04 + \frac{A_4}{(\ln T_*)^2} + \frac{A_5}{(\ln T_*)^3} + \frac{A_6}{(\ln T_*)^4} \right).$$

Here, the following notations are introduced:

$$T_* = \frac{kT}{\varepsilon}, \quad v_* = \frac{\varphi_0}{\varepsilon}, \quad r_* = \frac{1/\beta}{\sigma}$$

(while calculating $v_*$, values $\varphi_0$ and $\varepsilon$ should be of the same dimension). The coefficients $A_k$ are computed using the expressions

$$A_k = a_{k1} + \frac{1}{(r_* \ln(v_*/10))^2} \left( a_{k2} + \frac{a_{k3}}{\ln(v_*/10)} + \frac{a_{k4}}{(\ln(v_*/10))^2} \right). \qquad (5.100)$$

The coefficients $a_{ki}$ are presented in Table 5.6.

**Table 5.6**  Coefficients $a_{ki}$ in the formula (5.100) [41]

| $k$ | $a_{k1}$ | $a_{k2}$ | $a_{k3}$ | $a_{k4}$ |
|---|---|---|---|---|
| 1 | $-267.0$ | $201.570$ | $174.672$ | $54.305$ |
| 2 | $26700$ | $-19226.5$ | $-27693.8$ | $-10860.9$ |
| 3 | $-8.90 \cdot 10^5$ | $6.3201 \cdot 10^5$ | $1.0227 \cdot 10^6$ | $5.4304 \cdot 10^5$ |
| 4 | $-33.0838$ | $20.0862$ | $72.1059$ | $68.5001$ |
| 5 | $101.571$ | $-56.4472$ | $-286.393$ | $-315.4531$ |
| 6 | $-87.7036$ | $46.3130$ | $277.146$ | $363.1807$ |

The remaining integrals appearing in the expressions for the transport coefficients can be calculated using the recurrent formula (5.96).

### 5.4.2  Relaxation Times

A great number of experimental and theoretical studies have been devoted to the determination of the rotational and vibrational relaxation time. The analysis of these results is beyond the scope of our monograph. Here, we only present several references and commonly used theoretical relations.

Experimental data concerning the rotational relaxation time in various gases can be found, for instance, in Refs. [104, 54, 218, 183] (see also the bibliography in [236, 100, 262]). In the theoretical calculations for $\tau^{rot}_c$, the Parker's formula [212] with the corrections introduced in Ref. [30] is often used. Thus the number of collisions required for the equilibration of the rotational degrees of freedom is equal to

$$\zeta^{rot}_c(T) = \frac{\zeta^\infty_c}{F_c(T)},$$

where the function $F_c(T)$ is given by the expression

$$F_c(T) = 1 + \frac{\pi^{3/2}}{2}\left(\frac{kT}{\varepsilon_c}\right)^{-1/2} + \left(\frac{\pi^2}{4} + 2\right)\left(\frac{kT}{\varepsilon_c}\right)^{-1} + \pi^{3/2}\left(\frac{kT}{\varepsilon_c}\right)^{-3/2}.$$

The values $\zeta_c^\infty$ are found by fitting the theoretical results to experimental data. For instance, in Ref. [262], it is recommended to take $\zeta_c^\infty = 4.3$ for $N_2$ and $\zeta_c^\infty = 4.6$ for $O_2$.

Experimental measurements of the vibrational relaxation time in air are available up to $T < 8000$ K (see the references in monographs [236, 100]). For such temperatures, a satisfactory approximation for $\tau_{cd}^{vibr}$ is given by the semi-empirical formula derived by R. Millikan and D. White [185]:

$$\lg(p\tau_{cd}^{vibr}) = 5 \cdot 10^{-4}\mu_{cd}^{1/2}\vartheta_c^{4/3}\left(T^{-1/3} - 0.015\mu_{cd}^{1/4}\right) - 8.0.$$

Here, $\tau_{cd}^{vibr}$ is the time of vibrational relaxation for molecular species $c$ in collisions with particles $d$, $\mu_{cd}$ is the reduced molar mass (g/mole), $1/\mu_{cd} = 1/\mu_c + 1/\mu_d$, and $\vartheta_c = h\nu_c/k$ is the characteristic vibrational temperature. The time $\tau_{cd}^{vibr}$ is measured in seconds, and the pressure $p$ in atm.

For higher temperatures, $T > 8000$ K, the Millikan–White formula gives unrealistically low relaxation time, in contrast to more rigorous calculations. C. Park in [209, 211] suggested an empirical correction to the relaxation time for high temperatures:

$$(\tau_c^{vibr})^{-1} = n\bar{\sigma}\langle v_c\rangle,$$

where $\langle v_c\rangle$ is the mean thermal velocity of molecules, $\bar{\sigma}$ is an effective parameter which has the sense of the mean scattering cross section and is the same for all molecules. The Park formula can be useful for qualitative estimations of the vibrational relaxation time.

A rigorous method of the kinetic theory for the calculation of the rotational and vibrational relaxation time consists in the calculation of the integrals (5.55), (5.83) or (5.93), depending on the cross sections of collisions resulting in the rotational and vibrational energy transitions, for the values $\Delta\mathcal{E}_{cd}^{rot}$, $\Delta\mathcal{E}_{cd}^{vibr}$ (see, for instance, the definition of the vibrational relaxation time for anharmonic oscillators (3.128)).

## 5.5 Simplified Formulas for Transport Coefficients in the State-to-State Approach

The objective of this Section is to consider in detail the linear systems for the calculation of state-to-state transport coefficients, in order to simplify the procedure for their computation. When transport coefficients accounting for the detailed state-to-state kinetics are calculated, some difficulties arise. First, in order to solve the linear transport systems (5.15), (5.16); (5.18), (5.19); (5.20); (5.23), (5.24); and (5.27), (5.28) the bracket integrals should be calculated. The latter are specified by the cross

sections of elastic collisions and of those with RT transitions depending on the vibrational states and chemical species of collision partners. The second problem is the necessity to solve linear systems with a great number of algebraic equations.

Let $N_{tot}$ be a total number of chemical and vibrational species in a mixture: $N_{tot} = \sum_{c=1}^{L_m} L_c + L_a$, where $L_m$, $L_a$ are the numbers of molecular and atomic species, respectively, $L_c$ is that of excited vibrational levels in molecules of $c$ species. Then, $N_{vibr} = \sum_{c=1}^{L_m} L_c$ denotes the total number of different vibrational states in the mixture. In order to calculate the thermal conductivity coefficient $\lambda'$, we should solve the system (5.15), (5.16) containing $3N_{vibr} + 2L_a$ linear algebraic equations, whereas the system (5.20) specifying the shear viscosity coefficient $\eta$ consists of $N_{tot}$ equations.

The most tedious problem is the calculation of the diffusion coefficients: in total, in a mixture, $N_{tot}^2$ coefficients $D_{cidk}$ should be determined, each of them being the solution of a system of $N_{tot}$ algebraic equations. The number of independent coefficients is, however, smaller and equal to $N_{tot}(N_{tot} + 1)/2$, since the diffusion coefficients are invariant with respect to the subscript interchange: $D_{cidk} = D_{dkci}$.

Let us consider an example of a mixture of atomic and molecular nitrogen $N_2/N$ taking into account 46 vibrational states of $N_2$. The number of independent diffusion coefficients in such a mixture is 1128, each of them is found as the solution of a system of 47 algebraic equations. In the same mixture, the calculation for the thermal conductivity and viscosity coefficients requires solving 140 and 47 equations, respectively.

Obviously, such a scheme cannot be applied for a numerical simulation of a nonequilibrium viscous conducting gas flow, since the transport coefficients should be calculated in each spatial cell and time step of the integration. A simplified technique for the calculation of the transport coefficients, which maintains the main advantages of the state-to-state approach, is suggested in Ref. [134].

Let us analyze the assumptions suggested for the realization of the simplified algorithm, as well as the corresponding simplifications. First, the assumptions introduced by E. Mason and L. Monchick make it possible to express the bracket integrals in terms of integrals $\Omega_{cidk}^{(l,r)}$ and rotational relaxation times. Furthermore, we suppose that the integrals depending on the resonance defect of rotational energy $\Delta \mathscr{E}_{cd}^{rot}$ are negligible in the calculation of the diffusion, shear viscosity, and thermal conductivity coefficients. Next, we assume that the cross sections for elastic collisions do not depend on the vibrational states of colliding particles. The latter assumption makes it possible to write the bracket integrals in the form (5.64)–(5.82). In addition to that, if the rotational motion is simulated by the rigid rotator model, the rotational specific heat $c_{rot,ci}$ given by the formula (1.21) is independent of the vibrational level $i$: $c_{rot,ci} = c_{rot,c} \; \forall i$. After these simplifications, the bracket integrals $\Lambda_{rr'pp'}^{cidk}$ and $H_{rr'}^{cidk}$ become functions of the vibrational level populations and of the standard collision integrals with respect to the cross sections of elastic collisions. In this representation, the only parameter depending on the vibrational state, is the population $n_{ci}$. Such a form for the bracket integrals makes it possible to simplify the original linear algebraic systems.

First, we will consider the simplest system (5.20). Since the dependence of the bracket integrals $H_{00}^{cidk}$ on $i$, $k$ is reduced to the linear dependence on $n_{ci}$, $n_{dk}$, after some transformations we conclude that the coefficients $b_{ci,0}$ do not depend on the vibrational quantum number, and the expression (5.10) for the shear viscosity coefficient takes the form

$$\eta = \frac{kT}{2} \sum_c \frac{n_c}{n} b_{c,0},$$

whereas the coefficients $b_{c,0}$ are found from the simplified system of equations:

$$\sum_d H_{00}^{cd} b_{d,0} = \frac{2}{kT} \frac{n_c}{n}, \quad c = 1,...,L.$$

This system, in contrast to (5.20), includes only $L$ equations instead of $N_{tot}$. The expression for $\eta$ formally coincides with that obtained in Section 5.2 for the shear viscosity coefficient in the one-temperature approach. However, in the state-to-state approach, the integrals $\Omega_{cd}^{(l,r)}$ are specified by the cross sections of only elastic collisions and those with RT transitions, whereas in the one-temperature approach, they are determined by the cross sections of elastic and all inelastic collisions resulting in the internal energy variation.

Thus, under the assumptions formulated above, the shear viscosity does not depend on the molecular distributions over the vibrational levels. This conclusion is in accordance with the fact that the shear viscosity describes the momentum transfer and, hence, depends essentially on the particle velocity rather than the energy of the internal degrees of freedom.

Let us consider now the coefficients of thermal conductivity and thermal diffusion. The system (5.16) can be simplified since, for rigid rotators, the rotational specific heats are independent of the molecular vibrational state. Therefore, the expression (5.7) is reduced to a simpler formula:

$$\lambda' = \sum_c \frac{5}{4} k \frac{n_c}{n} a_{c,10} + \sum_c \frac{m_c}{2} \frac{n_c}{n} c_{rot,c} a_{c,01}, \qquad (5.101)$$

where the coefficients $a_{c,10}$ and $a_{c,01}$ are obtained solving the simplified system:

$$\sum_d \left( \Lambda_{0000}^{cd} a_{d,00} + \Lambda_{0100}^{cd} a_{d,10} + \Lambda_{0001}^{cd} a_{d,01} \right) = 0,$$

$$\sum_d \left( \Lambda_{1000}^{cd} a_{d,00} + \Lambda_{1100}^{cd} a_{d,10} + \Lambda_{1001}^{cd} a_{d,01} \right) = \frac{15kT}{2} \frac{n_c}{n}, \qquad (5.102)$$

$$\sum_d \left( \Lambda_{0010}^{cd} a_{d,00} + \Lambda_{0110}^{cd} a_{d,10} + \Lambda_{0011}^{cd} a_{d,01} \right) = 3 m_c T \frac{n_c}{n} c_{rot,c},$$

$$c = 1,...,L.$$

The system (5.102) is complemented with the constraint (5.15), which after summation over $i$ takes the form

$$\sum_c \frac{\rho_c}{\rho} a_{c,00} = 0.$$

(5.103)

As a result, the number of equations is significantly reduced: we obtain only $3L_m + 2L_a$ equations (5.102) with the additional constraint (5.103), instead of $3N_{vibr} + 2L_a$ equations of the system (5.14), (5.15). Furthermore, from the relation $a_{ci,00} = a_{c,00}$ for any $i$, it follows that the thermal diffusion coefficients are also independent of the vibrational energy level: $D_{Tci} = D_{Tc} \, \forall i$.

The expressions for the thermal conductivity and thermal diffusion coefficients are formally similar to those obtained in the one-temperature approach, if we replace the rotational specific heat $c_{rot,c}$ with the heat capacity $c_{int,c}$ of all internal degrees of freedom. However, as is mentioned above, the integrals $\Omega_{cd}^{(l,r)}$ in various approaches are specified by the cross sections of different processes. Under the accepted assumptions, in the state-to-state approach the thermal conductivity is also independent of the vibrational distributions, as well as the shear viscosity. In this case, the vibrational energy is transported due to diffusion of vibrationally excited molecules.

While calculating the multi-component diffusion coefficients, we find that the main part of the coefficients $d_{dk,0}^{bn}$, except for $d_{bn,0}^{bn}$, does not depend on $k$ and $n$: $d_{dk,0}^{bn} = d_{d,0}^{b} \, \forall d \neq b, \, \forall k,n$ and $d_{bk,0}^{bn} = d_{b,0}^{b} \, \forall n, \, \forall k \neq n$. Then the system (5.19) is simplified:

for $c = b$, $i = n$

$$\gamma_{00}^{bnbn} d_{bn,0}^{bn} + \sum_{k \neq n} \gamma_{00}^{bnbk} d_{b,0}^{b} + \sum_{d \neq b} d_{d,0}^{b} \sum_k \gamma_{00}^{bndk} = 3kT \left( 1 - \frac{\rho_{bn}}{\rho} \right),$$

(5.104)

for $c = b$, $i = 0, ..., n-1, n+1, ..., L_b$

$$\sum_{i \neq n} \left( \gamma_{00}^{bibn} d_{bn,0}^{bn} + \sum_{k \neq n} \gamma_{00}^{bibk} d_{b,0}^{b} + \sum_{d \neq b} d_{d,0}^{b} \sum_k \gamma_{00}^{bidk} \right) = -3kT \frac{\rho_b - \rho_{bn}}{\rho},$$

(5.105)

for $c = 1, ..., b-1, b+1, ..., L$, $i = 0, ..., L_c$

$$\sum_i \left( \gamma_{00}^{cibn} d_{bn,0}^{bn} + \sum_{k \neq n} \gamma_{00}^{cibk} d_{b,0}^{b} + \sum_{d \neq b} d_{d,0}^{b} \sum_k \gamma_{00}^{cidk} \right) = -3kT \frac{\rho_c}{\rho},$$

(5.106)

$$b = 1, ..., L, \, n = 0, ..., L_b.$$

In this case, the additional constraint (5.18) is replaced by the relation

$$\frac{\rho_{bn}}{\rho} d_{bn,0}^{bn} + \frac{\rho_b - \rho_{bn}}{\rho} d_{b,0}^{b} + \sum_{d \neq b} \frac{\rho_d}{\rho} d_{d,0}^{b} = 0, \, b = 1, ..., L, \, n = 0, 1, ..., L_b.$$

(5.107)

The system (5.104)–(5.107) contains only $L+1$ equations compared to $N_{tot}$ in the case of the system (5.19), (5.18). The number of diffusion coefficients is also significantly reduced: we have $N_{vibr}$ different coefficients $D_{cici}$ for each vibrational level $i$ of molecular species $c$, $L_m$ coefficients $D_{cc} = D_{cick}$ $\forall i$, $\forall k \neq i$, and $L^2$ coefficients $D_{cd} = D_{cidk}$ $\forall d \neq c \forall i,k$. The total number of independent diffusion coefficients is $N_{vibr} + L_m + L(L+1)/2$.

Returning to the mixture $N_2/N$, after the simplification we obtain 49 independent diffusion coefficients, each of which is found from the system of three algebraic equations. In order to calculate the thermal conductivity and shear viscosity coefficients, we solve systems of five and three equations, respectively.

Using the reduced multi-component diffusion and thermal diffusion coefficients, we can also simplify the expressions for the diffusion velocity and heat flux, (2.48) and (2.50), respectively, in the state-to-state approach:

$$\mathbf{V}_{ci} = -D_{cici}\mathbf{d}_{ci} - D_{cc}\sum_{k \neq i}\mathbf{d}_{ck} - \sum_{d \neq c}D_{cd}\mathbf{d}_d - D_{Tc}\nabla\ln T,$$

$$\mathbf{q} = -\lambda'\nabla T - p\sum_{c}D_{Tc}\mathbf{d}_c + \sum_{ci}\left(\frac{5}{2}kT + \left\langle\varepsilon_j^{ci}\right\rangle_{rot} + \varepsilon_i^c + \varepsilon_c\right)n_{ci}\mathbf{V}_{ci}.$$

It is important to emphasize that in these formulae, after the simplifications, only the self-diffusion coefficients $D_{cici}$ depend explicitly on the vibrational quantum number.

The bulk viscosity coefficient depending on the internal (in the considered case, rotational) energy excitation is specified by the resonance defect $\Delta\mathscr{E}_{cidk}^{rot}$; therefore the integrals depending on $\Delta\mathscr{E}_{cidk}^{rot}$ cannot be neglected in the calculation for $\zeta$. The bracket integrals $\beta_{rr'pp'}^{cidk}$ are connected with the numbers of vibrational quanta not only via $n_{ci}$ and $n_{dk}$, but also via the rotational relaxation times $\tau_{ci}^{rot}$. However, assuming that the rotational relaxation time depends only on the chemical species and not on the vibrational state, i.e. $\tau_{ci}^{rot} = \tau_c^{rot}$ $\forall i$, the system (5.23), (5.24) can also be simplified. Finally, the bulk viscosity coefficient is calculated using the relation

$$\zeta = -kT\sum_{c}\frac{n_c}{n}f_{c,10},$$

whereas the equations for the coefficients $f_{c,10}, f_{c,01}$ take the form

$$\sum_{d}\left(\beta_{1100}^{cd}f_{d,10} + \beta_{1001}^{cd}f_{d,01}\right) = -\frac{n_c}{n}\frac{c_{rot}}{c_{tr} + c_{rot}},$$

$$\sum_{d}\left(\beta_{0110}^{cd}f_{d,10} + \beta_{0011}^{cd}f_{d,01}\right) = \frac{\rho_c}{\rho}\frac{c_{rot,c}}{c_{tr} + c_{rot}},$$

$$c = 1,...,L.$$

The additional constraint on $f_{c,rp}$ is given by the equation

$$\sum_{c}\frac{n_c}{n}\left(c_{tr}f_{c,10} + c_{rot,c}f_{c,01}\right) = 0.$$

Finally, the simplified systems for the calculation of the diffusion, viscosity and thermal conductivity coefficients have been obtained. They can be solved using the efficient numerical algorithms elaborated in Ref. [76] for the solution of linear algebraic systems, or more traditional techniques mentioned in Section 5.1. The presented results give a practical possibility to take into account the state-to-state transport coefficients in numerical simulations of viscous conducting gas flows under the conditions of strong vibrational and chemical non-equilibrium.

Let us consider in more detail the diffusion coefficients in the state-to-state approach. They were introduced for the first time in Ref. [145] and then were studied for various non-equilibrium flows in Refs. [147, 17, 49]. For a binary mixture of diatomic molecules $A_2$ and atoms A, analytical expressions for the state-specific diffusion coefficients can be obtained from Eqs. (5.104)–(5.107). After some transformations, they can be expressed in terms of the mass fractions of molecules in different vibrational states ($Y_{A_2i} = \rho_{A_2i}/\rho$), mass fractions of atoms ($Y_A = \rho_A/\rho$) and molecules ($Y_{A_2} = \rho_{A_2}/\rho$), and binary and self-diffusion coefficients defined by the formulae (5.61). Thus, introducing the coefficients $\mathscr{D}_{AA_2}$, $\mathscr{D}_{A_2}$ for the mixture $A_2/A$

$$\mathscr{D}_{AA_2} = \frac{3kT}{16nm_{AA_2}} \frac{1}{\Omega^{(1,1)}_{AA_2}}, \qquad \mathscr{D}_{A_2} = \frac{3kT}{8nm_{A_2}} \frac{1}{\Omega^{(1,1)}_{A_2}},$$

($m_{AA_2}$ is the reduced mass of atoms and molecules) we find the following relations for the diffusion coefficients:

$$D_{A_2iA_2i} = \mathscr{D}_{AA_2} \left(\frac{m_A}{\rho/n}\right)^2 \frac{\dfrac{Y_A}{\mathscr{D}_{A_2}} + \dfrac{2}{\mathscr{D}_{AA_2}}\left(\dfrac{1}{Y_{A_2i}} - Y_A - 1\right)}{\dfrac{Y_{A_2}}{2\mathscr{D}_{A_2}} + \dfrac{Y_A}{\mathscr{D}_{AA_2}}}, \quad i = 0, ..., L_{A_2}, \quad (5.108)$$

$$D_{A_2A_2} = D_{A_2iA_2k} = \mathscr{D}_{AA_2} \left(\frac{m_A}{\rho/n}\right)^2 \frac{\dfrac{Y_A}{\mathscr{D}_{A_2}} - \dfrac{2}{\mathscr{D}_{AA_2}}(Y_A + 1)}{\dfrac{Y_{A_2}}{2\mathscr{D}_{A_2}} + \dfrac{Y_A}{\mathscr{D}_{AA_2}}} \quad \forall k \neq i, \quad (5.109)$$

$$D_{AA_2} = -\mathscr{D}_{AA_2} \frac{m_A m_{A_2}}{(\rho/n)^2},$$

$$D_{AA} = \mathscr{D}_{AA_2} \frac{m_A m_{A_2}}{(\rho/n)^2}\left(\frac{1}{Y_A} - 1\right).$$

Note, that the expressions for $D_{AA_2}$ and $D_{AA}$ are similar to the well known formulae for the binary diffusion coefficients (see [82]). The coefficients $D_{A_2iA_2i}$ depending on the vibrational quantum number are specified by the mass fractions of species and vibrational level populations. These are the only coefficients depending explicitly on the state-to-state vibrational distributions. In the limit of a single-component diatomic gas ($Y_A = 0$), the coefficients $D_{A_2iA_2i}$ and $D_{A_2A_2}$ take the form [137]

$$D_{A_2 i A_2 i} = \mathscr{D}_{A_2} \left( \frac{1}{Y_{A_2 i}} - 1 \right), \qquad D_{A_2 A_2} = -\mathscr{D}_{A_2}.$$

The simplifications described in the present Section help to prove some additional properties of the diffusion coefficients and to establish the link between heat fluxes calculated in the state-to-state and quasi-stationary approaches.

## 5.6    Transition Between the Transport Terms in the State-to-State and Quasi-stationary Approaches

In this Section, we aim at demonstrating a possibility of a limit transition from the equation (2.50) for the state-to-state heat flux to the relations (3.85) or (4.38) in the situation when the vibrational level populations are described by the quasi-stationary distributions. Strictly speaking, the limit transition from the governing equations (2.16)–(2.18) valid in the state-to-state approach to the equations of multi-temperature (3.33)–(3.36) or one-temperature (4.9)–(4.11) kinetics is justified only in the zero-order approximation of the generalized Chapman–Enskog method (i.e. in the case of an inviscid non-conductive gas flow). In the first-order approximation (in a viscous conductive flow), the transition between various levels of the flow description performed by a direct substitution of the quasi-stationary distributions to the governing equations is impossible, since the transport coefficients in each approach are specified by cross sections of different rapid processes. If, however, we assume that the coefficients of diffusion, viscosity and thermal conductivity are specified only by the cross sections of elastic collisions, we can find a connection between the transport terms in various approaches. The justification for this assumption is given in Section 5.3, where it is shown that the contribution of the inelastic collision cross sections to the coefficients of diffusion, thermal conductivity, and shear viscosity is negligible. From this point of view, the formal transition between the state-to-state and quasi-stationary approaches is impossible only for the normal mean stress containing the relaxation pressure and shear viscosity coefficient depending explicitly on the cross sections of inelastic processes. As to the energy flux, the simplifications suggested in the previous Section make it possible to reduce the equation (2.50) to the relations (3.85) or (4.38) substituting the corresponding distribution into Eq. (2.50).

For the sake of simplicity, we will consider a binary mixture $A_2/A$. In this case, the expression (2.48) for the diffusion velocities of atoms $\mathbf{V}_a$ and molecules $\mathbf{V}_{m,i} = \mathbf{V}_i$ on the vibrational level $i$ can be rewritten in the form

$$\mathbf{V}_a = -D_{ma}\mathbf{d}_m - D_{aa}\mathbf{d}_a - D_{Ta}\nabla \ln T, \qquad (5.110)$$

$$\mathbf{V}_i = -(D_{ii} - \tilde{D}_{mm})\mathbf{d}_i - \tilde{D}_{mm}\mathbf{d}_m - D_{ma}\mathbf{d}_a - D_{Tm}\nabla \ln T. \qquad (5.111)$$

In these relations, $D_{ma}$ is the binary diffusion coefficient of atoms and molecules, the coefficient $\tilde{D}_{mm}$ is given by the formula (5.109), the tilde is necessary to

distinguish this coefficient from the ordinary self-diffusion coefficient of molecules $D_{mm}$, which is introduced in the quasi-stationary distributions (see, for instance, the formula (3.79) for $c = d$).

Let us discuss some properties of the diffusion coefficients. It follows from the relations (5.108), (5.109) that the difference $D_{ii} - \tilde{D}_{mm}$ is inversely proportional to the molar fraction $x_i = n_i/n$:

$$D_{ii} - \tilde{D}_{mm} = \frac{\tilde{D}}{x_i}, \quad \text{where} \quad \tilde{D} = \left( \frac{x_m}{\mathscr{D}_m} + \frac{x_a}{\mathscr{D}_{ma}} \right)^{-1}.$$

A similar relation can also be easily obtained for the self-diffusion coefficient of molecular species $D_{mm}$:

$$D_{mm} - \tilde{D}_{mm} = \frac{\tilde{D}}{x_m}. \tag{5.112}$$

Taking into account these expressions and the definition for the thermodynamic diffusive forces $\mathbf{d}_i$ and $\mathbf{d}_m$ (2.27), we can rewrite the molecular diffusion velocity on the vibrational level $i$ in the form

$$\mathbf{V}_i = -\tilde{D}\frac{n}{n_i}\left[ \nabla\left(\frac{n_i}{n}\right) + \left(\frac{n_i}{n} - \frac{\rho_i}{\rho}\right)\nabla \ln p \right] -$$

$$-\tilde{D}_{mm}\left[ \nabla\left(\frac{n_m}{n}\right) + \left(\frac{n_m}{n} - \frac{\rho_m}{\rho}\right)\nabla \ln p \right] - D_{ma}\mathbf{d}_a - D_{Tm}\nabla \ln T.$$

Since

$$\nabla \ln\left(\frac{n_i}{n}\right) = \nabla \ln\left(\frac{n_i}{n_m}\right) + \nabla \ln\left(\frac{n_m}{n}\right),$$

we obtain

$$\mathbf{V}_i = -\tilde{D}\nabla \ln\frac{n_i}{n_m} - \tilde{D}\frac{n}{n_m}\left[ \nabla\left(\frac{n_m}{n}\right) + \left(\frac{n_m}{n} - \frac{\rho_m}{\rho}\right)\nabla \ln p \right] -$$

$$-\tilde{D}_{mm}\left[ \nabla\left(\frac{n_m}{n}\right) + \left(\frac{n_m}{n} - \frac{\rho_m}{\rho}\right)\nabla \ln p \right] - D_{ma}\mathbf{d}_a - D_{Tm}\nabla \ln T,$$

or, taking into account Eq. (5.112),

$$\mathbf{V}_i = -\tilde{D}\nabla \ln\frac{n_i}{n_m} - D_{mm}\mathbf{d}_m - D_{ma}\mathbf{d}_a - D_{Tm}\nabla \ln T.$$

Thus, in the state-to-state approach, the diffusion velocity of molecules on the vibrational level $i$ can be expressed as a sum of three terms:

$$\mathbf{V}_i = \mathbf{V}_i^{TD} + \mathbf{V}_i^{MD} + \mathbf{V}_i^{DVE},$$

whereas for atoms, two terms appear in the diffusion velocity:

$$\mathbf{V}_a = \mathbf{V}_a^{TD} + \mathbf{V}_a^{MD}.$$

Here, $\mathbf{V}_i^{\mathrm{TD}}$, $\mathbf{V}_{\mathrm{a}}^{\mathrm{TD}}$, $\mathbf{V}_i^{\mathrm{MD}}$, $\mathbf{V}_{\mathrm{a}}^{\mathrm{MD}}$, and $\mathbf{V}_i^{\mathrm{DVE}}$ are, respectively, the contributions of the thermal diffusion, mass diffusion, and diffusion of vibrational energy:

$$\mathbf{V}_i^{\mathrm{DVE}} = -\tilde{D}\nabla\ln\frac{n_i}{n_{\mathrm{m}}},$$

$$\mathbf{V}_i^{\mathrm{TD}} = -D_{T\mathrm{m}}\nabla\ln T, \qquad \mathbf{V}_{\mathrm{a}}^{\mathrm{TD}} = -D_{T\mathrm{a}}\nabla\ln T,$$

$$\mathbf{V}_i^{\mathrm{MD}} = -D_{\mathrm{mm}}\mathbf{d}_{\mathrm{m}} - D_{\mathrm{ma}}\mathbf{d}_{\mathrm{a}}, \qquad \mathbf{V}_{\mathrm{a}}^{\mathrm{MD}} = -D_{\mathrm{ma}}\mathbf{d}_{\mathrm{m}} - D_{\mathrm{aa}}\mathbf{d}_{\mathrm{a}}.$$

It is obvious that $\mathbf{V}_i^{\mathrm{TD}}$, $\mathbf{V}_i^{\mathrm{MD}}$ do not depend on the vibrational state $i$ of a molecule and are specified only by its chemical species. These terms formally coincide with the corresponding terms in the relation (3.84) for the diffusion velocity in the multi-temperature and one-temperature approaches. The difference is determined by the fact that the transport coefficients in these expressions depend on the cross sections of various processes. Assuming that the diffusion and thermal diffusion coefficients are specified by the cross sections of only elastic collisions, we find

$$\mathbf{V}_i = \mathbf{V}_{\mathrm{m}}^{\mathrm{QS}} + \mathbf{V}_i^{\mathrm{DVE}},$$

where $\mathbf{V}_{\mathrm{m}}^{\mathrm{QS}}$ is the diffusion velocity in the quasi-stationary approach. The second term, which depends on the vibrational state and describes the transport of vibrational energy, appears only in the state-to-state model.

Now we proceed to the discussion of the heat flux. For a binary mixture $A_2/A$, the total energy flux takes the form

$$\mathbf{q} = -\lambda'\nabla T - p\left(D_{T\mathrm{m}}\mathbf{d}_{\mathrm{m}} + D_{T\mathrm{a}}\mathbf{d}_{\mathrm{a}}\right) +$$

$$+ \sum_i\left(\frac{5}{2}kT + \langle\varepsilon_j^i\rangle_{\mathrm{rot}} + \varepsilon_i + \varepsilon_{\mathrm{m}}\right)n_i\mathbf{V}_i + \left(\frac{5}{2}kT + \varepsilon_{\mathrm{a}}\right)n_{\mathrm{a}}\mathbf{V}_{\mathrm{a}}, \qquad (5.113)$$

$\varepsilon_{\mathrm{m}}$, $\varepsilon_{\mathrm{a}}$ are the energies of formation for molecules and atoms.

The contribution of several dissipative processes to the heat flux can be distinguished:

$$\mathbf{q} = \mathbf{q}^{\mathrm{HC}} + \mathbf{q}^{\mathrm{MD}} + \mathbf{q}^{\mathrm{TD}} + \mathbf{q}^{\mathrm{DVE}}, \qquad (5.114)$$

where $\mathbf{q}^{\mathrm{HC}}$, $\mathbf{q}^{\mathrm{MD}}$, $\mathbf{q}^{\mathrm{TD}}$, and $\mathbf{q}^{\mathrm{DVE}}$ are, respectively, energy fluxes associated with the thermal conductivity of translational and rotational degrees of freedom, mass diffusion, thermal diffusion, and the transfer of vibrational energy:

$$\mathbf{q}^{\mathrm{HC}} = -\lambda'\nabla T,$$

$$\mathbf{q}^{\mathrm{MD}} = \rho_{\mathrm{m}}h_{\mathrm{m}}\mathbf{V}_{\mathrm{m}}^{\mathrm{MD}} + \rho_{\mathrm{a}}h_{\mathrm{a}}\mathbf{V}_{\mathrm{a}}^{\mathrm{MD}},$$

$$\mathbf{q}^{\mathrm{TD}} = -p\left(D_{T\mathrm{m}}\mathbf{d}_{\mathrm{m}} + D_{T\mathrm{a}}\mathbf{d}_{\mathrm{a}}\right) + \rho_{\mathrm{m}}h_{\mathrm{m}}\mathbf{V}_{\mathrm{m}}^{\mathrm{TD}} + \rho_{\mathrm{a}}h_{\mathrm{a}}\mathbf{V}_{\mathrm{a}}^{\mathrm{TD}},$$

$$\mathbf{q}^{\text{DVE}} = \sum_i \left( \frac{5}{2}kT + \langle \varepsilon_j^i \rangle_{\text{rot}} + \varepsilon_i \right) n_i \mathbf{V}_i^{\text{DVE}}.$$

Analyzing the expressions for various constituents of the heat flux, we can see that only $\mathbf{q}^{\text{DVE}}$ depends explicitly on the non-equilibrium state-to-state vibrational distributions, while the remaining components in Eq. (5.114) are similar to the corresponding terms in Eqs. (3.85) and (4.38) for the heat flux in the quasi-stationary approach.

The last term in Eq. (5.114) can be written in the alternative form. Taking into account that $\sum_i \nabla(n_i/n_{\text{m}}) = 0$ and $\sum_i \varepsilon_i \nabla(n_i/n_{\text{m}}) = m_{\text{m}} \nabla E_{\text{vibr,m}}$, we can obtain the following relation for the heat flux connected to the vibrational energy transport:

$$\mathbf{q}^{\text{DVE}} = -\tilde{D} \rho_{\text{m}} \nabla E_{\text{vibr,m}}.$$

Under the conditions when the quasi-stationary vibrational distributions is established in a gas flow, the specific vibrational energy of molecules $E_{\text{vibr,m}}$ is specified by the gas temperature (in the one-temperature approach) or the vibrational temperature (in the multi-temperature approach) rather than by the vibrational level populations, as in the state-to-state approach. Thus, for the anharmonic oscillator model, $E_{\text{vibr,m}} = E_{\text{vibr,m}}(T, T_1)$, and the expression for $\mathbf{q}^{\text{DVE}}$ takes the form

$$\mathbf{q}^{\text{DVE}} = -\tilde{D} \rho_{\text{m}} \left( c_{\text{v}}^T \nabla T + c_{\text{v}}^{T_1} \nabla T_1 \right).$$

Solving the system (5.38) and (5.40) for the determination of the thermal conductivity coefficient in a binary mixture, we obtain

$$\lambda_{\text{vt}}' = \lambda_{\text{anh}} + \lambda_{\text{vt}} = c_{\text{v}}^T \tilde{D} \rho_{\text{m}}, \qquad \lambda_{\text{v}} = \lambda_{\text{tv}} + \lambda_{\text{vv}} = c_{\text{v}}^{T_1} \tilde{D} \rho_{\text{m}}.$$

Therefore,

$$\mathbf{q}^{\text{DVE}} = -\lambda_{\text{vt}}' \nabla T - \lambda_{\text{v}} \nabla T_1, \tag{5.115}$$

and the expression for the total heat flux in a binary mixture in the state-to-state approach is reduced to the relation (3.85) (under the assumption that the thermal conductivity coefficients depend only on the cross sections of elastic collisions). It is obvious that the expression (5.115) coincides with that for the heat flux $\mathbf{q}_{\text{vibr}}$ in a single-component gas (see Eq. (3.141)).

For the harmonic oscillator model, the vibrational energy of gas molecules per unit mass is specified only by the vibrational temperature, $E_{\text{vibr,m}} = E_{\text{vibr,m}}(T_{\text{v}})$, and

$$\mathbf{q}^{\text{DVE}} = -\tilde{D} \rho_{\text{m}} c_{\text{v}}^{T_{\text{v}}} \nabla T_{\text{v}} = -\lambda_{\text{vv}} \nabla T_{\text{v}}.$$

If the thermal equilibrium one-temperature distribution over the vibrational energy levels is established in a mixture, then $E_{\text{vibr,m}} = E_{\text{vibr,m}}(T)$, and

$$\mathbf{q}^{\text{DVE}} = -\tilde{D} \rho_{\text{m}} c_{\text{vibr}} \nabla T = -\lambda_{\text{vibr}} \nabla T.$$

Thus, if in a binary mixture of molecules and atoms the quasi-stationary two-temperature or one-temperature vibrational distribution is established in the zero-order approximation, then, assuming the independence of transport coefficients of the cross sections for inelastic collisions, we can obtain the expression for the heat flux directly substituting the quasi-stationary distribution into the formula for **q** in the state-to-state approach. A similar limit transition can also be performed for a multi-component gas mixture.

In the case of local thermodynamic equilibrium (both thermal and chemical), the concentrations of the mixture components in the zero-order approximation are specified only by the gas temperature and pressure. For weak deviations from the local equilibrium, the gradients of the molar fractions of chemical species can be approximately expressed in terms of the temperature and pressure gradients, and after some transformations the energy flux can be reduced to

$$\mathbf{q} = -\lambda \nabla T,$$

where $\lambda = \lambda_{\mathrm{tr}} + \lambda_{\mathrm{rot}} + \lambda_{\mathrm{vibr}} + \lambda_{\mathrm{react}}$, whereas the coefficient $\lambda_{\mathrm{react}}$ represents a combination of diffusion coefficients and thermal diffusion ratios and characterizes the thermal conductivity associated to chemical reactions. Such a representation for the heat flux was obtained for the first time in the studies of R. Brokaw and J. Butler [39, 32, 33].

## 5.7 A Single-Component Gas: The Generalized Eucken Formula

Let us consider the particular case developed in Section 3.7 for a single-component diatomic gas under the strongly non-equilibrium conditions. In this situation, the zero-order distribution function is described by the combined distribution (3.113) or (3.116), which differs from the Treanor distribution at intermediate and high vibrational levels, whereas the first-order distribution function takes the form (3.134). In the case of a pure single-component gas, it appears to be possible to derive analytical expressions for all transport coefficients. The functions $\mathbf{A}_{ij}$, $\mathbf{A}_{ij}^{(1)}$, $\boldsymbol{B}_{ij}$, $F_{ij}$, and $G_{ij}$ are expanded into the series of orthogonal Sonine and Waldmann-Trübenbacher polynomials, the trial functions are selected in accordance with the right-hand sides of the integral equations (3.135)–(3.139) [139]:

$$\mathbf{A}_{ij} = -\frac{m\mathbf{c}}{2kT} \sum_{rpq} a_{rpq} S_{3/2}^{(r)}\left(\frac{mc^2}{2kT}\right) P_j^{(p)}\left(\frac{\varepsilon_j}{kT}\right) P_i^{(q)}\left(\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT}\right),$$

$$\mathbf{A}_{ij}^{(1)} = \frac{m\mathbf{c}}{2kT} \sum_r a_r^{(1)} P_i^{(r)}\left(\frac{\beta\varepsilon_1}{kT_1}\right),$$

$$\boldsymbol{B}_{ij} = \frac{m}{2kT}\left(\mathbf{cc} - \frac{1}{3}c^2\boldsymbol{I}\right)\sum_r b_r S_{5/2}^{(r)}\left(\frac{mc^2}{2kT}\right),$$

$$F_{ij} = \sum_{rpq} f_{rpq} S_{1/2}^{(r)} \left( \frac{mc^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j}{kT} \right) P_i^{(q)} \left( \frac{\varepsilon_\alpha + \varepsilon_\beta - \beta \varepsilon_1}{kT} - \frac{c_w^T}{c_w^{T_1}} \frac{T}{T_1} \frac{\beta \varepsilon_1}{kT_1} \right),$$

$$G_{ij} = \sum_{rpq} g_{rpq} S_{1/2}^{(r)} \left( \frac{mc^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j}{kT} \right) P_i^{(q)} \left( \frac{\varepsilon_\alpha + \varepsilon_\beta - \beta \varepsilon_1}{kT} - \frac{c_u}{c_v^{T_1}} \frac{T}{T_1} \frac{\beta \varepsilon_1}{kT_1} \right).$$

Then the transport coefficients are expressed in terms of the expansion coefficients, and the integral equations (3.135)–(3.139) are reduced to the algebraic ones using the transformation described in Section 5.2. As a result, the thermal conductivity coefficients in the expression for the heat flux (3.141), are found in the form [139, 140, 143]

$$\lambda_{tr} = \frac{5k}{4} a_{100}, \qquad \lambda_{rot} = \frac{mc_{rot}}{2} a_{010},$$

$$\lambda'_{vt} = \frac{mc_v^T}{2} a_{001}, \qquad \lambda_v = \frac{mc_v^{T_1}}{2} a_1^{(1)},$$

the coefficient $a_1^{(1)}$ is the solution of the equation

$$\alpha_{11} a_1^{(1)} = 3mT c_w^{T_1},$$

whereas $a_{rpq}$ are found from the system of three algebraic equations:

$$\Lambda_{110000} a_{100} + \Lambda_{100100} a_{010} + \Lambda_{100001} a_{001} = \frac{15}{2} kT,$$

$$\Lambda_{011000} a_{100} + \Lambda_{001100} a_{010} + \Lambda_{001001} a_{001} = 3mT c_{rot},$$

$$\Lambda_{010010} a_{100} + \Lambda_{000110} a_{010} + \Lambda_{000011} a_{001} = 3mT c_{anh}^T.$$

The bracket integrals $\Lambda_{rr'pp'qq'}$ and $\alpha_{11}$ in these equations, after the simplifications accounting for the assumptions of E. Mason and L. Monchick (see Section 5.3) are reduced to the expressions

$$\alpha_{11} = m \left( 4\Omega^{(1,1)} \frac{mc_w^{T_1}}{k} + \frac{3}{4} \beta_{vibr} \right),$$

$$\Lambda_{110000} = m \left( 4\Omega^{(2,2)} + \frac{25}{12} \beta_{rot} + \frac{25}{12} \beta_{vibr} \right),$$

$$\Lambda_{001001} = \Lambda_{000110} = 0,$$

$$\Lambda_{001100} = m \left( 4\Omega^{(1,1)} \frac{mc_{rot}}{k} + \frac{3}{4} \beta_{rot} \right),$$

$$\Lambda_{100100} = \Lambda_{011000} = -\frac{5}{4} m\beta_{rot},$$

$$\Lambda_{000011} = m \left( 4\Omega^{(1,1)} \frac{mc_{anh}^T}{k} + \frac{3}{4} \beta_{vibr} \right),$$

$$\Lambda_{100001} = \Lambda_{010010} = -\frac{5}{4} m\beta_{vibr}.$$

Here, $\Omega^{(l,r)}$ are the integrals (5.95) for the case of a pure single-component gas ($c = d$). In the general case, the integrals $\Omega^{(1,1)}$, $\Omega^{(2,2)}$ depend on the cross sections of all rapid processes; however, in practical calculations, the inelastic collision cross sections are usually neglected. The integrals $\beta_{\text{rot}}$ and $\beta_{\text{vibr}}$ are specified by the resonance defects of the rotational and vibrational energy in rapid processes:

$$\beta_{\text{rot}} = \left\langle (\Delta \mathscr{E}^{\text{rot}})^2 \right\rangle, \qquad \beta_{\text{vibr}} = \left\langle (\Delta \mathscr{E}^{\text{vibr}})^2 \right\rangle,$$

the averaging operator is introduced on the basis of the Boltzmann distribution over the rotational energy and two-temperature combined distribution (3.115) over vibrational levels:

$$\langle F \rangle = \frac{2}{(Z^{\text{rot}} Z^{\text{vibr}})^2} \left( \frac{kT}{\pi m} \right)^{1/2} \sum_{iki'k'} \sum_{jlj'l'} s_{ij} s_{kl} \exp\left( -\mathscr{E}_j - \mathscr{E}_l - \mathscr{E}_i^{(I)} - \mathscr{E}_k^{(I)} \right) \times$$

$$\times \int F \gamma^3 \exp\left( -\gamma^2 \right) \sigma_{ijkl}^{i'j'k'l'} d^2 \Omega d\gamma.$$

The non-equilibrium partition function $Z^{\text{vibr}}$ is given by the formula (3.117), $\mathscr{E}_j = \varepsilon_j / (kT)$ is the dimensionless rotational energy, and $\mathscr{E}_i^{(I)}$ is expressed by the relation

$$\mathscr{E}_i^{(I)} = -\frac{\varepsilon_{\alpha(i)} + \varepsilon_{\beta(i)} - \beta(i)\varepsilon_1}{kT} - \frac{\beta(i)\varepsilon_1}{kT_1} + \ln \frac{i_* + 1}{\gamma(i) + 1}.$$

The resonance defect of the internal energy in the case of a single-component gas is introduced by the simple expression

$$\Delta \mathscr{E} = \frac{1}{kT} \left( \varepsilon_{i'} + \varepsilon_{j'} + \varepsilon_{k'} + \varepsilon_{l'} - \varepsilon_i - \varepsilon_j - \varepsilon_k - \varepsilon_l \right) = \Delta \mathscr{E}^{\text{rot}} + \Delta \mathscr{E}^{\text{vibr}}.$$

The integral $\beta_{\text{rot}}$, as is mentioned above, can be associated with the rotational relaxation time $\tau^{\text{rot}}$:

$$\beta_{\text{rot}} = \frac{3}{2n} \frac{c_{\text{rot}}}{c_{\text{u}}} \frac{1}{\tau^{\text{rot}}}$$

(let us remind that $c_{\text{u}} = c_{\text{tr}} + c_{\text{rot}} + c_{\text{v}}^T$).

The integral $\beta_{\text{vibr}}$ is calculated analytically, if the rate coefficients for the VV and VT transitions are known (see Chapter 6).

Solving the linear transport systems for the expansion coefficients $a_{rpq}$, $a_r^{(1)}$, we obtain the analytical formulae for the thermal conductivity coefficients.

The viscosity coefficients are found using a similar technique. The shear viscosity coefficient $\eta$ has the form

$$\eta = \frac{5kT}{8\Omega^{(2,2)}}.$$

The bulk viscosity coefficient $\zeta$ consists of two terms specified by the rapid inelastic transitions of the rotational and vibrational energy:

$$\zeta = \zeta_{\mathrm{rot}} + \zeta_{\mathrm{vibr}},$$

$$\zeta_{\mathrm{rot}} = \frac{kT}{\beta_{\mathrm{rot}}} \left( \frac{c_{\mathrm{rot}} c_{\mathrm{w}}^{T_1}}{c_{\mathrm{u}} c_{\mathrm{w}}^{T_1} - c_{\mathrm{w}}^{T} c_{\mathrm{v}}^{T_1}} \right)^2, \quad \zeta_{\mathrm{vibr}} = \frac{kT}{\beta_{\mathrm{vibr}}} \left( \frac{c_{\mathrm{anh}}^{T} c_{\mathrm{w}}^{T_1} - c_{\mathrm{w}}^{T} c_{\mathrm{anh}}^{T_1}}{c_{\mathrm{u}} c_{\mathrm{w}}^{T_1} - c_{\mathrm{w}}^{T} c_{\mathrm{v}}^{T_1}} \right)^2.$$

The temperature dependence of thermal conductivity and shear and bulk viscosity coefficients calculated in the molecular nitrogen at $T_1 = 5000$ K is given in Figs. 5.3, 5.4. The coefficients $\eta$, $\lambda_{\mathrm{tr}}$, $\lambda_{\mathrm{rot}}$, and $\zeta_{\mathrm{rot}}$ do not depend on the vibrational temperature $T_1$ and increase almost linearly with the gas temperature $T$. In addition, the coefficient $\lambda_{\mathrm{rot}}$ reaches about 40% of $\lambda_{\mathrm{tr}}$, whereas the coefficient $\zeta_{\mathrm{rot}}$ is close to the shear viscosity coefficient $\eta$. The dependence of coefficients $\lambda_{\mathrm{v}}$, $\lambda_{\mathrm{vt}}'$, and $\zeta_{\mathrm{vibr}}$ on $T_1$ is well pronounced. Whereas for moderate excitation of the vibrational energy ($T_1/T < 3$), $\lambda_{\mathrm{vt}}'$ and $\zeta_{\mathrm{vibr}}$ are negligible, with rising the vibrational energy storage these coefficients can exceed $\lambda_{\mathrm{tr}}$ and $\eta$, respectively. Furthermore, in Ref. [133, 139] it is shown that in the molecular nitrogen, under the strong vibrational non-equilibrium ($T_1/T > 4$), neglecting intermediate vibrational states can result in underestimation of the coefficients $\lambda_{\mathrm{v}}$, $\lambda_{\mathrm{vt}}'$, and $\zeta_{\mathrm{vibr}}$ by the factor of two to five. In these studies, the contribution of the relaxation pressure to the normal mean stress is found to be small.

Note that for $T_1/T < 1$, the anharmonicity of vibrations and the non-Boltzmann form of vibrational distributions weakly affect the thermal conductivity and bulk viscosity: the coefficients $\zeta_{\mathrm{vibr}}$ and $\lambda_{\mathrm{vt}}'$ are negligible, whereas the coefficient $\lambda_{\mathrm{v}}$ is close to that calculated for the harmonic oscillator model [140]. In this case, the contribution of vibrational degrees of freedom to the thermal conductivity is smaller than that of translational and rotational modes (see also [6, 239]). For the great vibrational energy storage ($T_1/T \gg 1$), anharmonic effects and non-Boltzmann distributions significantly influence the coefficients $\zeta_{\mathrm{vibr}}$, $\lambda_{\mathrm{vt}}'$, and $\lambda_{\mathrm{v}}$. The non-monotonic temperature dependence of these coefficients is explained by the similar behavior of
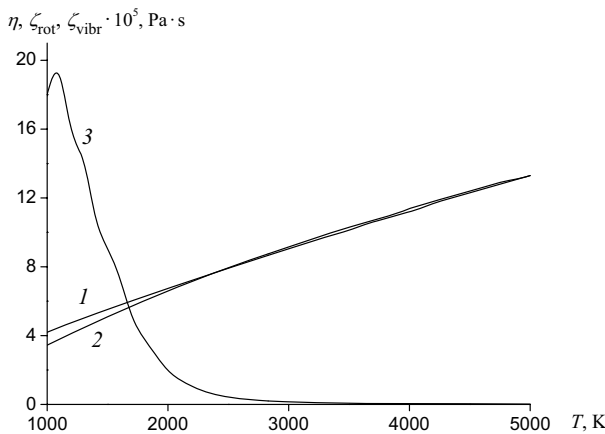


**Fig. 5.3** The coefficients of shear $\eta$ and bulk $\zeta_{\mathrm{rot}}$, $\zeta_{\mathrm{vibr}}$ viscosity in $N_2$ at $T_1 = 5000$ K. Curves *1*, *2*, and *3* correspond to the coefficients $\eta$, $\zeta_{\mathrm{rot}}$, and $\zeta_{\mathrm{vibr}}$
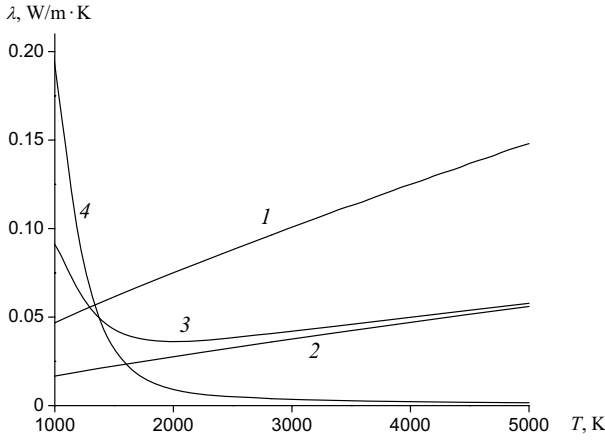
**Fig. 5.4** Temperature dependence of the thermal conductivity coefficients in $N_2$ at $T_1 = 5000$ K. Curves *1*, *2*, *3*, and *4* are, respectively, for the coefficients $\lambda_{tr}$, $\lambda_{rot}$, $\lambda_v$, and $-\lambda'_{vt}$

specific heats in the expressions for the transport coefficients and is connected with the deviation of the zero-order distribution function from the Boltzmann distribution. The areas of non-monotonicity for the specific heats coincide with those of the sharp variation in the vibrational energy as a result of anharmonicity at $3 < T_1/T < 10$. Moreover, the anharmonic effects are enhanced with the temperature increase. At high temperatures, in a system of anharmonic oscillators, the equilibrium specific heat and, hence, the coefficient $\lambda$ are greater than those for harmonic oscillators even for $T_1 = T$.

Let us consider in detail the thermal conductivity coefficients. In the limit case $\Delta \mathscr{E}^{rot} = \Delta \mathscr{E}^{vibr} = 0$, the expressions for them do not include the inelastic collision integrals $\beta_{rot}$, $\beta_{vibr}$ and take the form

$$\lambda_{tr} = \frac{75k^2 T}{32m\Omega^{(2,2)}}, \qquad \lambda_{rot} = \frac{3kT}{8\Omega^{(1,1)}} c_{rot},$$

$$\lambda'_{vt} = \frac{3kT}{8\Omega^{(1,1)}} c_v^T, \qquad \lambda_v = \frac{3kT}{8\Omega^{(1,1)}} c_v^{T_1}. \tag{5.116}$$

The comparison of the thermal conductivity coefficients calculated with the accurate formulae and simplified expressions (5.116) is presented in Refs. [132, 140, 142] for $N_2$, $O_2$, and CO. The maximum discrepancy (1.5%) is found for the coefficients $\lambda_{rot}$ associated with the rotational energy transitions. Nevertheless, the inaccuracy of the total thermal conductivity coefficient $\lambda$ at the temperature gradient does not exceed 1%. Therefore, for a great variety of gases, the assumption $\Delta \mathscr{E}^{rot} = \Delta \mathscr{E}^{vibr} = 0$ does not reduce the accuracy of calculations for thermal conductivity coefficients. This means that the cross sections of inelastic collisions make only a minor contribution to the thermal conductivity, whereas the main influence of strong non-equilibrium,

vibrational distributions and anharmonicity on the thermal conductivity is related to non-equilibrium constituents of the specific heat capacities.

In this connection, a question arises: is it possible to use the simple expressions derived by E. Eucken and J. Hirschfelder [81], [111] improved by taking into account the non-equilibrium effects only for the calculation of the specific heats? The Eucken formula was derived in 1913 [81] on the basis of the elementary mean free path theory and appears to have been the first attempt to account for the influence of the internal degrees of freedom on the thermal conductivity of a molecular gas. E. Eucken proposed to split the coefficient $\lambda$ into $\lambda_{tr}$ and $\lambda_{int}$ associated with the transport of the translational and internal energy, respectively, and to write them in the form

$$\lambda = \lambda_{tr} + \lambda_{int} = (c_{tr}f_{tr} + c_{int}f_{int})\eta, \tag{5.117}$$

where $f_{tr} = 5/2$; $f_{int} = 1$. This formula, as well as the more accurate Hirschfelder formula [111], are widely used in the transport theory and provide a satisfactory agreement with the experimental results under the conditions of weak deviations from the equilibrium.

When deviations from the equilibrium over the vibrational degrees of freedom are strong, in the limit case $\Delta \mathscr{E} = 0$, we obtained the expressions (5.116). They can be rewritten in the form

$$\lambda = \lambda_{tr} + \lambda_{rot} + \lambda_{vt}' = \frac{5}{2}\left(\frac{c_{tr}}{c_u} + \frac{2}{5}\frac{\rho D}{\eta}\frac{c_{rot} + c_v^T(T,T_1)}{c_u}\right)\eta c_u,$$

$$\lambda_v = \rho D c_v^{T_1}(T,T_1), \tag{5.118}$$

where $D$ is the self-diffusion coefficient

$$D = \frac{3}{8}\frac{kT}{\rho \Omega^{(1,1)}}.$$

The expression derived for the coefficient $\lambda$ formally coincides with the Hirschfelder formula [111]; the difference is due to the fact that Eq. (5.118) includes the non-equilibrium specific heats. If, similarly to Ref. [82], we assume in Eq. (5.118) the factor $\rho D/\eta$ to be equal to unity, we obtain the relations

$$\lambda = \frac{5}{2}\left(1 - \frac{3}{5}\frac{c_{rot} + c_v^T(T,T_1)}{c_u}\right)\eta c_u,$$

$$\lambda_v = \eta c_v^{T_1}(T,T_1). \tag{5.119}$$

The former expression coincides with the Eucken formula [81]; however, it contains the non-equilibrium specific heats.

The relations (5.119) are reasonably consistent with the more accurate formulae (5.118) for a moderate vibrational energy storage ($T_1/T < 4$). With the increase in the ratio $T_1/T$, it is necessary to take into account the deviation of the factor $\rho D/\eta$

from unity. In Ref. [111], it is shown that this factor can be replaced with its mean value 1.328. In this case, the expressions (5.118) take the form

$$\lambda = \frac{5}{2}\left(\frac{c_{\mathrm{tr}}}{c_{\mathrm{u}}} + 0.5312\frac{c_{\mathrm{rot}} + c_{\mathrm{v}}^{T}(T,T_1)}{c_{\mathrm{u}}}\right)\eta c_{\mathrm{u}},$$

$$\lambda_{\mathrm{v}} = 1.328\eta c_{\mathrm{v}}^{T_1}(T,T_1). \tag{5.120}$$

Figure 5.5 presents the thermal conductivity coefficient $\lambda$ calculated as a function of $T_1$ with the use of accurate expressions of the kinetic theory, as well as the Eucken formula with equilibrium specific heats and those of Eucken and Hirschfelder with non-equilibrium specific heats. Taking the non-equilibrium effects into account considerably improves the accuracy of the Eucken formula at $T_1/T > 3$. For $T_1/T < 3$, the discrepancy between the thermal conductivity coefficients calculated on the basis of the precise formulae of the kinetic theory and those derived using the above simplifications, does not exceed 6–7%. A significant difference appears with the increase in the vibrational energy storage (temperature $T_1$). For $2500 < T_1 < 4000$ K, it is important to take into account that the factor $\rho D/\eta$ is not equal to unity. The discrepancy between $\lambda$ calculated using the accurate expressions (5.118) and the generalized Hirschfelder formula (5.120), is less than 1.5%. On the one hand, the formulae (5.120) provide a good accuracy, and, on the other hand, they are rather simple since they express the coefficients $\lambda$ and $\lambda_{\mathrm{v}}$ only in terms of the experimentally measurable shear viscosity coefficient and the non-equilibrium specific heats. Therefore, these expressions can be recommended for practical calculations for the thermal conductivity coefficients in a non-equilibrium gas. The non-equilibrium
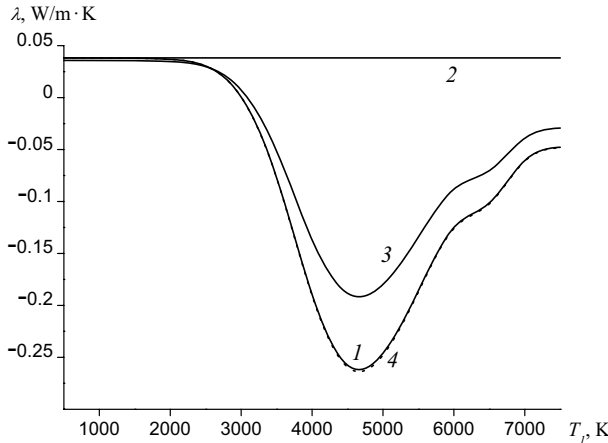


**Fig. 5.5** The thermal conductivity coefficient in $N_2$ as a function of $T_1$ at $T = 500$ K. The curve *1* is based on Eq. (5.118), the curves *2, 3* are obtained using the Eucken formula with the equilibrium (5.117) and non-equilibrium (5.119) specific heats, respectively, and the curve *4* corresponds to the Hirschfelder formula (5.120) with the non-equilibrium specific heats

effects and anharmonicity are taken into account in the suggested expressions (5.120) via the non-equilibrium specific heats.

It may seem peculiar that the coefficient $\lambda$ at the temperature gradient becomes negative in a certain area. However, if we calculate the local entropy production caused by collisional processes, then, in addition to the common terms $(\lambda_{\mathrm{tr}} + \lambda_{\mathrm{rot}})|\nabla \ln T|^2$ and $\lambda_{\mathrm{v}}|\nabla \ln T_1|^2$, imposing the property of non-negativeness on the coefficients $\lambda_{\mathrm{tr}}$, $\lambda_{\mathrm{rot}}$, and $\lambda_{\mathrm{v}}$, we find a supplementary term $\lambda'_{\mathrm{vt}}\nabla \ln T \nabla \ln T_1$, which is equal to zero for harmonic oscillators. When the gradients of translational and vibrational temperatures have different signs (this condition is fulfilled in flows behind shock waves, in boundary layers, etc.), the coefficient $\lambda'_{\mathrm{vt}}$ should be negative. For $4 < T_1/T < 10$, the coefficient $\lambda'_{\mathrm{vt}}$ substantially exceeds $\lambda_{\mathrm{tr}}$ and $\lambda_{\mathrm{rot}}$ [140]. Therefore, the negativeness of the total coefficient $\lambda$ does not contradict to the second law of thermodynamics. The similar behavior of thermal conductivity coefficients in the case of a high vibrational energy storage was found in Ref. [71].

The obtained computational formulae for the transport coefficients can be applied to numerical simulations of a viscous conductive gas flow under the conditions of strong vibrational excitation. The suggested approach provides a completely closed and self-consistent description of a flow, and the simplified expressions for the transport coefficients facilitate the solution of the problem considerably.

# Chapter 6
# Reaction Rate Coefficients

An important feature of modeling of real gas flows under the conditions of strong deviations from the equilibrium is that the set of governing equations for macroscopic parameters includes not only the conservation equations for the momentum and total energy, but also the relaxation equations. The latter equations contain the rates of slow physical-chemical processes proceeding on the gas-dynamic time scale. It is necessary to know the rate coefficients for these processes in order to solve the equations of non-equilibrium aerodynamics and calculate the flow parameters taking into account vibrational and chemical kinetics.

In this Chapter, the rate coefficients for chemical reactions and various types of vibrational energy exchange are considered in the state-to-state and quasi-stationary multi-temperature and one-temperature approaches.

In a gas with rapid and slow processes, the rate coefficients of slow processes are specified by cross sections of corresponding collisions after their averaging over the distributions established as a result of rapid processes. In the detailed state-to-state description of non-equilibrium vibrational and chemical kinetics, the collision cross sections are averaged taking into account the Maxwell–Boltzmann distribution over the velocity and rotational energy levels or weak deviations from these distributions. In the case of quasi-stationary models, the rates of chemical reactions are obtained by averaging cross sections of chemically reactive collisions with the Maxwell–Boltzmann distributions over the velocity and rotational energy and quasi-stationary distributions over vibrational levels.

The mutual influence of chemical reactions and molecular distributions over the velocity and internal energy levels has been considered in a number of studies based on methods of kinetic theory. One of the first works in this area is that by I. Prigogine [220], followed by studies of R. Present [219], and G. Ludwig and M. Heil [171].

The effect of non-equilibrium distributions on the chemical reaction rate coefficients was considered by B. Shizgal [231, 232]. Later on, this effect was studied by many authors using various distributions of reacting gas molecules over the internal energy (see, for instance, Refs. [127, 122, 85, 229, 19]). Most models are based on weakly non-equilibrium one-temperature distributions or non-equilibrium Boltzmann distributions over the vibrational energy of the reagents.

Studies for the detailed state-to-state kinetics of non-equilibrium processes in reacting gas mixtures and significant advances achieved in this direction during the recent years, inspired development of more rigorous models for non-equilibrium reaction rates. For instance, in Refs. [128, 48, 64, 148], the dissociation rate coefficients were calculated on the basis of vibrational level populations found as the solutions of the equations of state-to-state kinetics in different gas flows. The obtained dissociation rate coefficients essentially differ from both the equilibrium ones described by the Arrhenius law and the multi-temperature rate coefficients.

In the studies [195, 1, 173, 19, 154], the influence of the non-Maxwell distributions on the chemical reaction rates is considered, with the use of the first-order approximation for various modifications of the Chapman–Enskog method. In particular, in the latest of the studies, non-Maxwell corrections to the state-to-state rate coefficients for chemical reactions are analyzed. It is important to take into account deviations of molecular distributions from the Maxwell's in the calculations for reaction rate coefficients in the course of the solution for numerous problems of kinetics and physical gas dynamics, especially in order to integrate the complete set of governing equations in a viscous conductive gas flow in the Navier–Stokes approximation.

In the present Chapter, using the results obtained in Refs. [154, 59, 148], we derive the expressions for the rate coefficients of non-equilibrium chemical reactions and energy exchanges in the zero- and first-order approximations of the Chapman–Enskog method. The state-to-state and quasi-stationary approaches are considered. Some estimates for the rates of non-equilibrium processes in particular reacting gas flows are made in Chapters 7–9.

## 6.1  State-to-State Approach: Zero-Order Chapman–Enskog Approximation

In this Section, we consider the equations (2.21) for the vibrational level populations $n_{ci}$, corresponding to the zero-order approximation of the Chapman–Enskog method generalized in Chapter 2 for the condition (1.43). These equations involve the rate coefficients for energy exchanges (2.60), bimolecular chemical reactions (2.65), and dissociation-recombination reactions (2.68), (2.71) in the zero-order approximation. These coefficients depend on the vibrational states of reacting molecules and the gas temperature. They can be obtained by averaging the cross sections of corresponding inelastic collisions and chemical reactions with the Maxwell–Boltzmann distribution over the velocity and rotational energy levels.

For the sake of convenience, let us consider a binary mixture that consists of $A_2$ molecules and $A$ atoms, in which the vibrational energy transitions, dissociation, and recombination occur. Then the equations (2.21) for the molecular vibrational level populations $n_i$ and atomic number densities $n_a$ can be written in the form:

$$\frac{dn_i}{dt} + n_i \nabla \cdot \mathbf{v} = R_i, \qquad i = 0, ..., L,$$

$$\frac{dn_\mathrm{a}}{dt} + n_\mathrm{a} \nabla \cdot \mathbf{v} = R_\mathrm{a},$$

From this point on, $L$ denotes the number of excited vibrational levels in an $A_2$ molecule. The right-hand sides of these equations describe the variation of $n_i$ as a result of VV and VT vibrational energy exchanges, dissociation, and recombination:

$$R_i = R_i^{\mathrm{vibr}} + R_i^{\mathrm{diss-rec}} = R_i^{\mathrm{VV}} + R_i^{\mathrm{VT}} + R_i^{\mathrm{diss-rec}} \tag{6.1}$$

and the variation of number density of atoms caused by chemical reactions:

$$R_\mathrm{a} = -2 \sum_i R_i^{\mathrm{diss-rec}}.$$

For an $A_2$/A binary mixture, the operator for exchange reactions $R_i^{2 \rightleftharpoons 2}$ is equal to zero, and hence, $R_i^{\mathrm{react}} = R_i^{2 \rightleftharpoons 3}$. This operator is hereinafter denoted as $R_i^{\mathrm{diss-rec}}$. Moreover, in this Section, the superscript "0" indicating that the production terms and reaction rate coefficients are considered in the zero-order approximation, is omitted.

### 6.1.1 Rate Coefficients for Vibrational Energy Transitions

The expressions for the rate of the variation of the vibrational level population as a result of VV and VT energy transitions are as follows:

$$R_i^{\mathrm{VV}} = \sum_k \sum_{k' \neq k} \sum_{i' \neq i} \left( k_{i'i}^{k'k} n_{i'} n_{k'} - k_{ii'}^{kk'} n_i n_k \right), \tag{6.2}$$

$$R_i^{\mathrm{VT}} = \sum_{d=\mathrm{a,m}} n_d \sum_{i' \neq i} \left( k_{i'i}^d n_{i'} - k_{ii'}^d n_i \right). \tag{6.3}$$

In order to calculate $R_i^{\mathrm{VV}}$ and $R_i^{\mathrm{VT}}$, it is necessary to determine the rate coefficients for VV exchanges and VT transitions of the vibrational energy $k_{ii'}^{kk'}$, $k_{ii'}^d$. In the literature, a number of theoretical and experimental estimates for the rate coefficients for vibrational energy transitions in different temperature intervals are available. Up to the recent time, the most commonly used were the formulae of the R. Schwartz, Z. Slawsky and K. Herzfeld theory (known as the SSH-theory), developed for the harmonic oscillator model in Ref. [228] and later generalized for anharmonic oscillators in Refs. [100, 101], as well as the Landau-Teller theory (for the VT exchange) with various semi-empirical expressions for the vibrational relaxation time [185, 235]. In addition to that, semi-empirical formulae for the rate coefficients of vibrational energy transitions written in the form similar to the expressions of the SSH-theory are often used; they provide a satisfactory consistency with the experimental results due to introduction of some additional empirical parameters. For the

harmonic oscillator model, the SSH-theory establishes the following dependence of the rate coefficients for VV and VT transitions on the vibrational energy level (in this case, only single-quantum transitions are allowed, while the probability of multi-quantum transitions can be neglected):

$$k_{i+1,i}^{k,k+1} = k_{10}^{01}(T)(i+1)(k+1), \qquad (6.4)$$

$$k_{i+1,i}^{d} = k_{10}^{d}(T)(i+1), \qquad (6.5)$$

whereas the expressions for the coefficients $k_{10}^{01}(T)$, $k_{10}^{d}(T)$ can be found in monographs [236, 58]. For VT exchanges, the Landau-Teller theory yields an inversely proportional dependence on the vibrational relaxation time for the coefficient $k_{10}^{d}$:

$$p\tau_{cd}^{\text{vibr}} = \frac{kT}{k_{10}^{d}\left[1 - \exp\left(-\dfrac{h\nu_c}{kT}\right)\right]}.$$

The vibrational relaxation time $\tau_{cd}^{\text{vibr}}$ is commonly retrieved from experimental measurements [185, 236, 100].

From the analysis of experimental data, the following dependence of the coefficient $k_{10}^{d}$ on the temperature was derived:

$$k_{10}^{d}(T) = A^{d}\exp(B^{d}T^{-1/3}),$$

where $A^{d}$, $B^{d}$ are empirical constants. The values for these parameters for different systems are presented, for instance, in Refs. [236, 100, 58].

The generalization of the expressions (6.4), (6.5) for the anharmonic oscillators model, results in the following connection rules:

$$k_{i+1,i}^{k,k+1} = k_{10}^{01}(T)(i+1)(k+1)e^{-\delta_{\text{VV}}|i-k|}\left(\frac{3}{2} - \frac{1}{2}e^{-\delta_{\text{VV}}|i-k|}\right), \qquad (6.6)$$

$$k_{i+1,i}^{d} = k_{10}^{d}(T)(i+1)\,e^{\delta_{\text{VT}}i}, \qquad (6.7)$$

where $\delta_{\text{VV}}$, $\delta_{\text{VT}}$ are the anharmonic corrections (see [100, 101, 58]).

More accurate results are based on the quantum-mechanical and semi-classical techniques applied to the calculation of the cross sections for inelastic collision and probabilities for vibrational and rotational energy transitions in various gases [21, 22], as well as on the trajectory calculations [165, 166, 79]. In particular, in Ref. [13] it is shown that at low temperatures, the SSH-theory does not provide a satisfactory accuracy for the evaluation of the atoms efficiency in VT energy transitions. Furthermore, at high temperatures, the SSH-theory overestimates the probabilities for VT transitions from high vibrational states (compared to those obtained in [21, 22]). Unfortunately, practical implementation of the quantum-mechanical

methods and trajectory calculations is restricted by the computational costs of the calculation of the cross section for each specific transition.

Among the up-to-date analytical models for the calculation of the vibrational transition probabilities, we can recommend the semi-classical model of forced harmonic oscillator [2, 3, 4], which makes it possible to obtain correct values for the rate coefficients of VV and VT transitions (including multi-quantum jumps) at high temperatures. A model proposed in Ref. [97] based on the information theory can also be appreciated.

The analytical approximations for the probabilities of different vibrational energy transitions in air components were obtained in Refs. [14, 48] by interpolation the accurate numerical results presented by G. Billing in Refs. [21, 22]. These approximate formulae are useful for practical calculations. The rate coefficient $k_{i+1,i}^{k,k+1}$ for a single-quantum VV exchange in the molecular nitrogen

$$N_2(i+1) + N_2(k) \longrightarrow N_2(i) + N_2(k+1)$$

is found in the form:

$$k_{i+1,i}^{k,k+1} = 2.5 \cdot 10^{-14}(i+1)(k+1) \left( \frac{T}{300} \right)^{3/2} e^{-\delta_{VV}|i-k|} \times$$

$$\times \left( \frac{3}{2} - \frac{1}{2} e^{-\delta_{VV}|i-k|} \right), \qquad \delta_{VV} = \frac{6.8}{\sqrt{T}}. \qquad (6.8)$$

For the rate coefficients $k_{i,i-1}^{N_2}$, $k_{i,i'}^{N}$ of VT transitions

$$N_2(i) + N_2 \longrightarrow N_2(i-1) + N_2,$$

$$N_2(i) + N \longrightarrow N_2(i') + N,$$
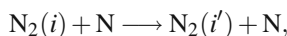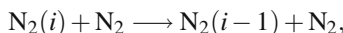
the following expressions are suggested:

$$k_{i,i-1}^{N_2} = i k_{10}^{N_2} e^{\delta_{VT}(i-1)}, \qquad (6.9)$$

$$k_{10}^{N_2} = \exp\left( -3.24093 - 140.69597/T^{0.2} \right),$$

$$\delta_{VT} = 0.26679 - 6.99237 \cdot 10^{-5} T + 4.70073 \cdot 10^{-9} T^2.$$

If in a VT transition, the collision partner is an atom then following Ref. [21], it is necessary to take into account multi-quantum jumps with the following rate coefficients:

$$k_{i,i'}^{N} = \exp\left[ b_0 + b_1(i-i') + b_2(i-i')^2 + \right.$$

$$\left. + i\left( c_0 + c_1(i-i') + c_2(i-i')^2 \right) \right], \quad i > i', \qquad (6.10)$$

where the coefficients $b_i$, $c_i$ are given by:

$$b_0 = -25.708 - 5633.1543/T,$$
$$b_1 = -0.1554 + 111.3426/T,$$
$$b_2 = 0.0054 - 2.189/T,$$
$$c_0 = 0.0536 + 122.4835/T,$$
$$c_1 = 0.0013 - 4.2365/T,$$
$$c_2 = -1.197 \cdot 10^{-4} + 0.0807/T.$$

We can see that, while the dependence of the coefficients $k_{i+1,i}^{k,k+1}$ and $k_{i,i-1}^{N_2}$ on the vibrational quantum number is similar to that given by the formulae (6.6), (6.7) of the generalized SSH theory, the coefficient $k_{i,i'}^{N}$ essentially differs from (6.7). Figure 6.1 presents the dependence of the vibrational transition rate coefficients for nitrogen on the vibrational level $i$ at $T = 6000$ K. We can notice that for high vibrational states, the SSH-theory overestimates all coefficients. The rate coefficients for VV transitions calculated from the expressions (6.6) and (6.8) differ approximately by an order of magnitude for all $i$, whereas the shape of the curves appears to be similar. For low levels, the SSH-theory significantly underestimates the probabilities for VT transitions. This can affect substantially the results of calculations for the vibrational distributions and macroscopic flow parameters in dissociating gases.

The formulae similar to Eqs. (6.8)–(6.10) derived for $N_2$, were also obtained in Ref. [48] for the molecular oxygen. The rate coefficients for VV transitions are calculated from the relations
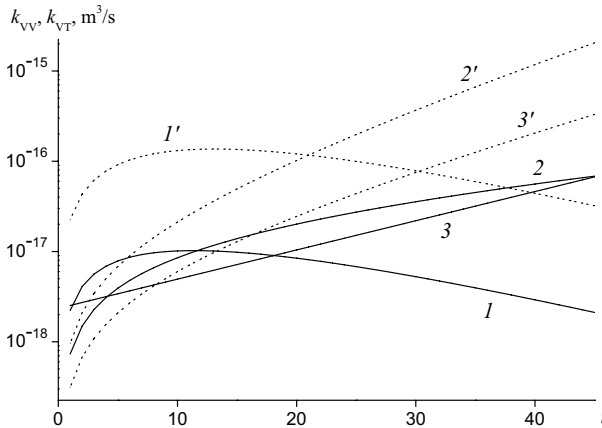


**Fig. 6.1** The rate coefficients for vibrational energy transitions in nitrogen as functions of $i$ at $T = 6000$ K. The curves *1, 1′* — $k_{i+1,i}^{0,1}$; *2, 2′* — $k_{i,i-1}^{N_2}$; *3, 3′* — $k_{i,i-1}^{N}$. The solid curves correspond to the formulae (6.8)–(6.10); the dashed curves are obtained using the expressions (6.6), (6.7) of the SSH-theory

$$k_{i+1,i}^{k,k+1} = 2.8 \cdot 10^{-18}(i+1)(k+1)T^{3/2}e^{\delta_{VV}(i-k)}, \quad i \le k,$$

$$\delta_{VV} = \frac{2.4}{\sqrt{T}}.$$

The rate coefficient $k_{i,i-1}^{O_2}$ for a VT transition in a collision with a molecule $O_2$ is:

$$k_{i,i-1}^{O_2} = i k_{10}^{O_2} e^{\delta_{VT}(i-1)},$$

$$k_{10}^{O_2} = \frac{T}{1.8 \cdot 10^{12} \exp\left(122/T^{1/3}\right)\left(1 - \exp\left(-2273.7/T\right)\right)},$$

$$\delta_{VT} = \frac{2.99}{\sqrt{T}}.$$

For the coefficient $k_{i,i-1}^{O}$, the following relation is obtained

$$k_{i,i-1}^{O} = (3i-2)\frac{\varepsilon_1^{O_2} - \varepsilon_0^{O_2}}{0.124}\frac{7 \cdot 10^{-14}}{\exp\left(30/T^{1/3}\right)},$$

where the energy of the zero and first vibrational levels in an oxygen molecule is given in $cm^{-1}$. In this Section, the dimension of all rate coefficients is $cm^3 \cdot s^{-1}$.

### 6.1.2 Dissociation Rate Coefficients

The rate of the variation of the vibrational level populations as a result of dissociation and recombination is given by the relation:

$$R_i^{\text{diss–rec}} = \sum_{d=a,m} n_d \left(k_{\text{rec},i}^d n_a^2 - k_{i,\text{diss}}^d n_i\right). \tag{6.11}$$

The rate coefficients for dissociation from different vibrational levels have been studied much less widely than for vibrational energy transitions. Two models are commonly used in the literature: the ladder-climbing model assuming dissociation only from the last vibrational level (see, for instance, [205, 15, 14, 48]), and that of Treanor and Marrone [176] allowing for dissociation from any vibrational state.

Firstly, we will consider the ladder-climbing model allowing for dissociation only from the last vibrational level:

$$k_{i,\text{diss}}^d = \begin{cases} 0, & i < L, \\ k_{L,\text{diss}}^d, & i = L. \end{cases}$$

Therefore,

$$R_i^{\text{diss–rec}} = 0, \qquad\qquad\qquad\qquad\qquad i < L,$$

$$R_i^{\text{diss–rec}} = R_L^{\text{diss–rec}} = \sum_{d=a,m} n_d \left(k_{\text{rec},L}^d n_a^2 - k_{L,\text{diss}}^d n_L\right), \quad i = L.$$

In this case, the rate of dissociation is specified by the number of molecules occurring on the last vibrational level. As a rule, the pseudo-level $L' = L + 1$ is introduced, located immediately above the last level $L$, and it is assumed that dissociation and recombination occur through this level [15]. Taking into account only single-quantum VT and VV transitions to the level $L + 1$, we obtain

$$R_L^{\text{diss–rec}} = \sum_{d=\text{a, m}} n_d \left( k_{\text{rec}, L}^d n_{\text{a}}^2 - k_{L,L+1}^d n_L \right) - n_L \sum_{i=0}^{L} k_{L,L+1}^{i,i-1} n_i.$$

Consequently, the dissociation rate is totally specified by the probabilities for the vibrational energy transitions $k_{L,L+1}^d$ and $k_{L,L+1}^{i,i-1}$, and the dissociation rate coefficients in collisions with molecules and atoms are given respectively by the expressions:

$$k_{L,\text{diss}}^{\text{m}} = k_{L,L+1}^{\text{m}} + \frac{1}{n_{\text{m}}} \sum_{i=0}^{L} k_{L,L+1}^{i,i-1} n_i, \tag{6.12}$$

$$k_{L,\text{diss}}^{\text{a}} = k_{L,L+1}^{\text{a}}, \tag{6.13}$$

$n_{\text{m}}$ is the number density of molecules.

The recombination rate coefficients $k_{\text{rec}, i}^d$ are connected to the coefficients $k_{i,\text{diss}}^d$ via the relations (2.76), which in the considered case can be written as

$$k_{\text{rec}, i}^d = k_{i,\text{diss}}^d K_i(T), \tag{6.14}$$

$$K_i(T) = \left( \frac{m_{\text{m}}}{m_{\text{a}}^2} \right)^{3/2} h^3 \left( 2\pi k T \right)^{-3/2} Z^{\text{rot}} \exp \left( -\frac{\varepsilon_i - D}{kT} \right). \tag{6.15}$$

For the ladder-climbing model, in these relations we should assume $i = L$.

Now let us discuss the case when dissociation can occur from any vibrational level. The rate coefficient for dissociation of a molecule on the vibrational level $i$ can be presented in the form:

$$k_{i,\text{diss}}^d = Z_i^d(T) k_{\text{diss,eq}}^d(T). \tag{6.16}$$

Here, $k_{\text{diss,eq}}^d(T)$ is the thermal equilibrium dissociation rate coefficient obtained by averaging the state-dependent rate coefficient with the one-temperature Boltzmann distribution (4.17); $Z_i^d$ is the factor taking into account the non-equilibrium (the non-equilibrium factor). It can be determined using the Treanor–Marrone model [176]. In this study, the following relation is introduced:

$$p_i^d = \frac{k_{i,\text{diss}}^d n_i}{k_{\text{diss}}^d n_{\text{m}}}, \tag{6.17}$$

which has the sense of the fraction of molecules dissociated from the level $i$ (with respect to the total number of dissociated molecules). The total dissociation rate coefficient in the formula (6.17) is equal to

$$k_{\text{diss}}^d = \frac{1}{n_{\text{m}}} \sum_i n_i k_{i,\text{diss}}^d. \tag{6.18}$$

In Ref. [176], the following expression for $p_i^d$ is suggested:

$$p_i^d = Cn_i \exp\left(-\frac{D - \varepsilon_i}{kU^d}\right) \exp\left(-\frac{D - \varepsilon_i}{kT}\right),$$

where $C$ is found from the condition of normalization $\sum_i p_i = 1$, and $U^d$ is the model parameter which has the dimension of temperature and characterizes the decrease in the dissociation rate with decreasing in the vibrational level. It is commonly assumed that $U^d$ is independent of the partner in the collision, and hence, $U^d = U$ and $p_i^d = p_i$.

Taking into account that $k_{i,\text{diss}}^d$ does not depend on $n_i$, we can write

$$k_{i,\text{diss}}^d = k_{\text{diss}}^d \frac{p_i}{n_i/n_{\text{m}}} = k_{\text{diss,eq}}^d \frac{p_i^{\text{eq}}}{(n_i/n_{\text{m}})^{\text{eq}}}.$$

Then the expression for $Z_i^d(T)$ can be obtained:

$$Z_i^d(T) = Z_i(T,U) = \frac{Z^{\text{vibr}}(T)}{Z^{\text{vibr}}(-U)} \exp\left[\frac{\varepsilon_i}{k}\left(\frac{1}{T} + \frac{1}{U}\right)\right], \tag{6.19}$$

$Z^{\text{vibr}}$ is the equilibrium vibrational partition function (3.19).

Thus, using the Treanor–Marrone model, the state-dependent dissociation rate coefficient $k_{i,\text{diss}}^d$ can be expressed in terms of the averaged thermal equilibrium coefficient $k_{\text{diss,eq}}^d(T)$ and non-equilibrium factor (6.19). To calculate $k_{\text{diss,eq}}^d(T)$, the empirical Arrhenius law can be applied:

$$k_{\text{diss,eq}}^d = AT^n \exp\left(-\frac{D}{kT}\right), \tag{6.20}$$

the coefficients $A$ and $n$ are generally obtained as a best fit to experimental data. The tables of the coefficients in the Arrhenius formula for various chemical reactions can be found in Refs. [236, 5, 126, 89, 211, 58].

For a practical implementation of the Treanor–Marrone model, it is important to select the parameter $U$ so that a good consistency is reached for the dissociation rate coefficient with experimental data or the results of calculations based on more accurate models. The following approximations for $U$ are commonly used: $U = \infty$, $U = D/(6k)$, and $U = 3T$. For $U = \infty$, dissociation is assumed to be equiprobable for each vibrational level, whereas the other values of the parameter describe preferential dissociation from high vibrational states.

Figure 6.2 presents the dependence of the non-equilibrium factor $Z_i$ in $N_2$ on the vibrational quantum number for $T = 5000$ K and different values of the parameter $U$. The comparison shows that at low levels ($i < 30$), $U = \infty$ overestimates the
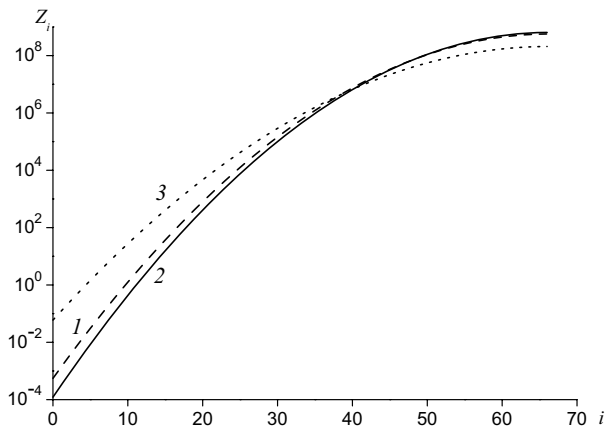
**Fig. 6.2** The non-equilibrium factor $Z_i$ as a function of $i$ for $T = 5000$ K. The curve *1* corresponds to $U = D/(6k)$; *2* to $U = 3T$; *3* to $U = \infty$

non-equilibrium factor, at intermediate levels ($30 < i < 50$) all parameter values yield roughly the same results, whereas for $i > 50$, the choice $U = \infty$ results in lower $Z_i$ compared to that obtained for $U = D/(6k)$ and $U = 3T$.

In Ref. [80], the dissociation rate coefficients $k^d_{i,\,\text{diss}}$ calculated within the framework of the Treanor–Marrone model are compared with those obtained from trajectory calculations [79], some recommendations for the optimum choice for the parameter $U$ for the specific reactions are given. Figure 6.3 presents the temperature dependence of the state-dependent dissociation rate coefficients $k^{N_2}_{i,\,\text{diss}}$ in an ($N_2$, N) mixture. The coefficients are calculated for different values of the parameter $U$ for two vibrational quantum numbers: $i = 0$ and $i = 20$. The results of trajectory calculation for $k_{i,\,\text{diss}}$ taken from Ref. [79] are also plotted. We can see that for low vibrational levels, the choice for $U = \infty$ results in significant overestimation for $k_{i,\,\text{diss}}$, which confirms the common assumption of the preferential dissociation from high vibrational states.

With the increase in the vibrational quantum number, for $U = \infty$ we obtain more realistic values for $k_{i,\,\text{diss}}$, and for $i > 40$, we have the best agreement with the results of accurate trajectory calculations. $U = D/(6k)$ and $U = 3T$ provide good consistency for $k_{i,\,\text{diss}}$ at intermediate levels ($20 < i < 40$). Furthermore, $U = D/(6k)$ results in better consistency for low temperatures, whereas $U = 3T$ is good in the high temperature range ($T > 6000$ K).

It should be emphasized that using the same value for the parameter $U$ for any $i$ and $T$ can result in considerable errors in the calculation for the state-to-state dissociation rate coefficients. The choice for the parameter should be specified by the conditions of a particular problem (the temperature range, basic channels of dissociation, etc.).

In some studies [45, 14, 48], a possibility for dissociation from any vibrational state is suggested within the framework of the ladder-climbing model. To this end, it is supposed that a transition to the continuum occurs as a result of multi-quantum
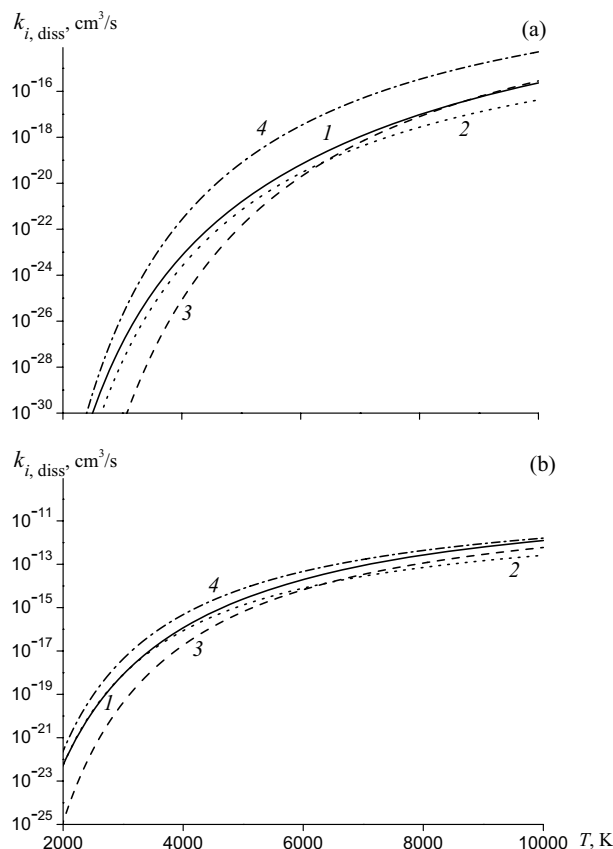
**Fig. 6.3** The temperature dependence of the dissociation rate coefficient $k_{i,\text{diss}}^{N_2}$ for $i = 0$ (*a*) and $i = 20$ (*b*). The curve *1* represents the results obtained in Ref. [79], curves *2–4* correspond to $U = D/(6k)$, $U = 3T$, and $U = \infty$

vibrational energy transfers. From this point of view, the authors of Ref. [45] conclude that dissociation from low vibrational levels is preferential for a high gas temperature. A similar effect is also mentioned in Ref. [251]. However, this conclusion has not been justified either by accurate trajectory calculations or in experiments.

The rate coefficients for bimolecular exchange reactions depending on the vibrational states of reagents and products have been less thoroughly studied than those for dissociation processes. Theoretical and experimental studies for the influence of the vibrational excitation of reagents on reaction rates were started by J. Polanyi [217]; some experimental results were also obtained in [23]. The accurate theoretical approach to this problem primarily requires a calculation for the state-dependent differential cross sections for collisions resulting in chemical reactions, and their subsequent averaging over the velocity distributions. In the recent years, the dynamics of atmospheric reactions has been studied, and quasi-classical

trajectory calculations for the cross sections and state-dependent rate coefficients for the reactions $N_2(i) + O \rightarrow NO + N$ and $O_2(i) + N \rightarrow NO + O$ have been carried out by several authors. For example, the reactions of NO formation are considered in [216, 93]; the effect of translational, rotational, and vibrational energy of reagents on the reaction $NO + N \rightarrow N_2 + O$ is discussed in Refs. [91, 92].

For the application of the existing results to the problems of non-equilibrium fluid dynamics, the analytical expressions for the dependence of the reaction rate coefficients on the vibrational states of molecules participating in the reactions are needed. Two kinds of such expressions are available in the literature. The first kind includes analytical approximations for numerical results obtained for particular reactions (see Refs. [29, 58, 48, 51]). These expressions are sufficiently accurate and convenient for practical use; however, their application is restricted by the considered temperature range. Another approach is based on the generalizations of the Treanor–Marrone model to exchange reactions suggested in Refs. [122, 123, 230, 9]. These models can be used for more general cases, but the theoretical expressions for the rate coefficients contain additional parameters, which should be validated using experimental data. A lack of the data for these parameters restricts the implementation of the above semi-empirical models.

Therefore, the development of justified theoretical models for cross sections of reactive collisions and state-dependent rate coefficients for exchange reactions remains a very important problem of the non-equilibrium kinetics.

## 6.2 Quasi-stationary Approaches

In the generalized multi-temperature approach, the equations of state-to-state kinetics (2.21) in an inviscid non-conductive gas flow are reduced to the equations (3.39) for the number densities of chemical species and Eqs. (3.42) for the specific numbers of vibrational quanta in molecular species depending on the gas temperature $T$ and effective temperatures of the first vibrational level $T_1^c$. In this Section, the multi-temperature chemical reaction rate coefficients (3.92)–(3.94) in the equations of chemical kinetics (3.39) are discussed. These coefficients depend on the gas temperature and vibrational temperatures of the first levels of reagents. We can see from Eqs. (3.92)–(3.94) that in the zero-order approximation the multi-temperature reaction rate coefficients are obtained by averaging the corresponding state-dependent coefficients over the vibrational energy of reagents taking into account the generalized Treanor distribution.

Neglecting the anharmonic effects, we can find the multi-temperature reaction rate coefficients (3.102)–(3.104) averaged over the non-equilibrium Boltzmann distribution with the vibrational temperatures of reagents.

In a thermal equilibrium gas mixture, the reaction rate coefficients depend only on the gas temperature and are specified by the expressions (4.15)–(4.17).

Let us consider, as above, a binary mixture ($A_2$, A) with dissociation and recombination reactions. In this case, the equations of non-equilibrium multi-temperature kinetics in an inviscid non-conductive gas flow (3.39), (3.42) take the form:

$$\frac{dn_{\mathrm{m}}}{dt} + n_{\mathrm{m}} \nabla \cdot \mathbf{v} = R^{\mathrm{diss-rec}}, \tag{6.21}$$

$$\frac{dn_{\mathrm{a}}}{dt} + n_{\mathrm{a}} \nabla \cdot \mathbf{v} = -2R^{\mathrm{diss-rec}}, \tag{6.22}$$

$$\rho_{\mathrm{m}} \frac{dW}{dt} = R^{\mathrm{w}} - m_{\mathrm{m}} W R^{\mathrm{diss-rec}}. \tag{6.23}$$

The right-hand sides of Eqs. (6.21), (6.22) are obtained from Eq. (6.1) by summation over the vibrational energy levels (taking into account that $\sum_i R_i^{\mathrm{vibr}} = 0$):

$$R^{\mathrm{diss-rec}} = \sum_i R_i^{\mathrm{diss-rec}} = \sum_{d=\mathrm{a,\,m}} n_d \left( k_{\mathrm{rec}}^d n_{\mathrm{a}}^2 - k_{\mathrm{diss}}^d n_{\mathrm{m}} \right).$$

The averaged rate coefficients for dissociation and recombination are:

$$k_{\mathrm{diss}}^d(T, T_1) = \frac{1}{n_{\mathrm{m}}} \sum_i k_{i,\,\mathrm{diss}}^d(T) n_i, \tag{6.24}$$

$$k_{\mathrm{rec}}^d(T) = \sum_i k_{i\,\mathrm{rec}}^d(T). \tag{6.25}$$

The right-hand sides in Eqs. (6.23) take the form:

$$R^{\mathrm{w}} = R^{\mathrm{w,\,VT}} + R^{\mathrm{w,\,diss-rec}}.$$

In the considered binary mixture, no $VV_2$ vibrational energy transitions occur. Since simultaneous TRV transitions of the translational, rotational, and vibrational energy appear to be less probable than VT exchanges, and, moreover, the number of vibrational quanta is conserved during $VV_1$ transitions, the variation of the specific number of vibrational quanta caused by vibrational energy exchange is described only by VT transitions.

The production term $R^{\mathrm{w,\,VT}}$ can be calculated with the use of two methods. Firstly, we can apply the expression (6.3) for $R_i^{\mathrm{VT}}$:

$$R^{\mathrm{w,\,VT}} = \sum_i i R_i^{\mathrm{VT}}.$$

In this case, it is necessary to determine the state-to-state rate coefficients for VT transitions. Another technique for the calculation of $R^{\mathrm{w,\,VT}}$ is to express the production term as a function of the experimentally measurable time for VT relaxation with the formula similar to (3.128):

$$\frac{1}{\tau_{\mathrm{VT}}} = \frac{R^{\mathrm{w,\,VT}}}{\rho_{\mathrm{m}} \left( W^{\mathrm{eq}} - W \right)}.$$

Experimental data on the vibrational relaxation time in different gases are presented in numerous studies, for instance, in Refs. [185, 236, 100, 211, 58].

The variation of the specific number of vibrational quanta caused by chemical reactions is described by the formula:

$$R^{\text{w, diss–rec}} = \sum_i i R_i^{\text{diss–rec}},$$

where the expression for $R_i^{\text{diss–rec}}$ is given by the relation (6.11).

Let us derive the expressions for the averaged dissociation and recombination rate coefficients within the ladder-climbing and TreanorMarrone models. For the simplest ladder-climbing model, assuming that dissociation occurs only from the last vibrational level $L$, the right-hand side of the equation (6.21) is as follows:

$$R^{\text{diss–rec}} = R_L^{\text{diss–rec}} = \sum_{d=a,m} n_d \left( k_{\text{rec},L}^d n_a^2 - k_{L,\text{diss}}^d n_L \right),$$

and the coefficients $k_{L,\text{diss}}^d$, $k_{\text{rec},L}^d$ are calculated using the expressions (6.12)–(6.14).

For the ladder-climbing model, the term $R^{\text{w, diss–rec}}$ which determines the variation of the specific number of vibrational quanta formed as a result of dissociation and recombination takes the form:

$$R^{\text{w, diss–rec}} = L R_L^{\text{diss–rec}}.$$

Allowing dissociation from each vibrational level and substituting the expression (6.16) for the state-to-state coefficients $k_{i,\text{diss}}^d$ into the formula (6.24), we obtain

$$k_{\text{diss}}^d = \frac{k_{\text{diss,eq}}^d}{n_m} \sum_i n_i Z_i(T,U). \tag{6.26}$$

Taking into account the relation (6.14) between the state-to-state rate coefficients for dissociation and recombination, as well as the relations (6.16) and (6.25), we can derive the following expression for $k_{\text{rec}}^d$:

$$k_{\text{rec}}^d = k_{\text{diss,eq}}^d \sum_i K_i(T) Z_i(T,U),$$

where the coefficients $K_i(T)$ are given by the formula (6.15). Substituting the expression (6.19) for the non-equilibrium factor found within the Treanor–Marrone model into the last formulae, and the Treanor distribution (3.14) into the formula (6.26), we can find the averaged dissociation and recombination rate coefficients in the two-temperature approach:

$$k_{\text{diss}}^d(T,T_1) = \frac{k_{\text{diss,eq}}^d Z^{\text{vibr}}(T)}{Z^{\text{vibr}}(-U) Z^{\text{vibr}}(T,T_1)} \sum_i s_i \exp\left[ \frac{i\varepsilon_1}{k}\left( \frac{1}{T} - \frac{1}{T_1} \right) + \frac{\varepsilon_i}{kU} \right],$$

$$k_{\text{rec}}^d(T) = k_{\text{diss,eq}}^d h^3 (2\pi kT)^{-3/2} Z^{\text{rot}}(T) Z^{\text{vibr}}(T) \left( \frac{m_m}{m_a^2} \right)^{3/2} \exp\left( \frac{D}{kT} \right).$$

While the equilibrium vibrational partition functions $Z^{\mathrm{vibr}}(T)$ and $Z^{\mathrm{vibr}}(-U)$ are calculated with the formula (3.19), the non-equilibrium partition functions $Z^{\mathrm{vibr}}(T,T_1)$ are given by Eq. (3.13).

In the most studies (see [176, 229, 58]), the multi-temperature dissociation rate coefficient $k_{\mathrm{diss}}^d$ is associated with the equilibrium averaged coefficient $k_{\mathrm{diss,eq}}^d$ by introducing the two-temperature non-equilibrium factor $Z(T,T_1,U)$ rather than the state-to-state factor $Z_i(T,U)$:

$$k_{\mathrm{diss}}^d = Z(T,T_1,U)k_{\mathrm{diss,eq}}^d(T). \qquad (6.27)$$

Taking into account the definition for the averaged dissociation rate coefficient (6.18) and the formula (6.16), we can see that

$$Z(T,T_1,U) = \frac{1}{n_{\mathrm{m}}}\sum_i n_i Z_i(T,U).$$

In the considered case, the factor $Z$ is given by the relation

$$Z(T,T_1,U) = \frac{Z^{\mathrm{vibr}}(T)}{Z^{\mathrm{vibr}}(-U)Z^{\mathrm{vibr}}(T,T_1)}\sum_i s_i \exp\left[\frac{i\varepsilon_1}{k}\left(\frac{1}{T}-\frac{1}{T_1}\right)+\frac{\varepsilon_i}{kU}\right]. \qquad (6.28)$$

For the harmonic oscillator model, the non-equilibrium factor is specified by the vibrational temperature $T_{\mathrm{v}}$ and can be calculated using the expression following from Eq. (6.28):

$$Z(T,T_{\mathrm{v}},U) = \frac{Z^{\mathrm{vibr}}(T)Z^{\mathrm{vibr}}(T_{\mathrm{f}})}{Z^{\mathrm{vibr}}(-U)Z^{\mathrm{vibr}}(T_{\mathrm{v}})}, \qquad (6.29)$$

where the effective temperature $T_{\mathrm{f}}$ is defined as

$$T_{\mathrm{f}} = \left(\frac{1}{T_{\mathrm{v}}}-\frac{1}{T}-\frac{1}{U}\right)^{-1},$$

and the partition functions are calculated using the formula (3.19). For the first time, the non-equilibrium factor was obtained in such a form in Ref. [176]. In Ref. [61], the expression for $Z(T,T_1,U)$ was obtained for the case of a strongly non-equilibrium vibrational distribution (3.115), which coincides with the Treanor distribution only at low vibrational levels.

Figure 6.4 presents the temperature dependence of the non-equilibrium factor $Z(T,T_1,U)$ in nitrogen for fixed vibrational temperature values. The non-equilibrium factor is calculated for both anharmonic (6.28) and harmonic (6.29) oscillator models. We can see that for minor deviations from the equilibrium ($T_1/T \sim 1$), both models yield similar results, whereas for the ratio $T_1/T$ essentially different from unity, the values of $Z$ for harmonic and anharmonic oscillators differ considerably. In particular, for the selected dissociation model, the non-equilibrium factor and hence the dissociation rate coefficient of harmonic oscillators at $T_1/T > 1$ significantly exceed $Z$ and $k_{\mathrm{diss}}^d$, respectively, when calculated for anharmonic oscillators.
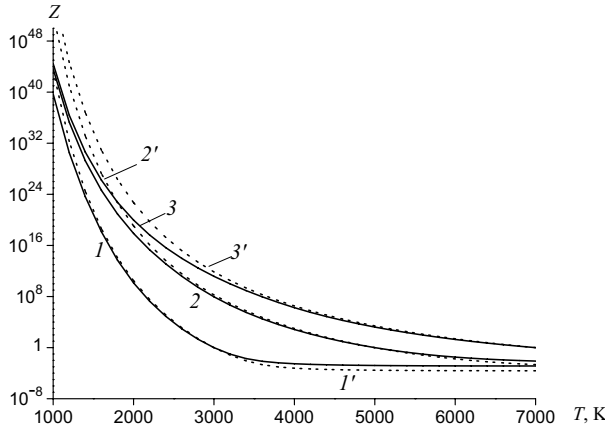
**Fig. 6.4** The non-equilibrium factor $Z$ in $N_2$ as a function of temperature $T$ for fixed temperatures $T_1$ and $U = D/(6k)$. The solid lines represent anharmonic oscillators, dashed — harmonic oscillators. The curves $1, 1'$ — $T_1 = 3000$; $2, 2'$ — $T_1 = 5000$; $3, 3'$ — $T_1 = 7000$ K

For $T_1/T < 1$, the use of the harmonic oscillator model yields lower $Z$ and $k_{\text{diss}}^d$ than those obtained taking into account anharmonic effects.

Using the definition (6.27) for the non-equilibrium factor $Z(T,T_1,U)$, we can derive the final expression for the right-hand sides of the equations of chemical kinetics (6.21), (6.22), convenient for practical implementation:

$$R^{\text{diss–rec}} = Z(T,T_1,U) \sum_{d=\text{a,m}} k_{\text{diss, eq}}^d n_d \left( n_a^2 F_{\text{rec}} - n_{\text{m}} \right). \qquad (6.30)$$

The function $F_{\text{rec}}$ has the form:

$$F_{\text{rec}}(T,T_1,U) = Z^{\text{vibr}}(T,T_1) \frac{\sum_i K_i(T) \exp\left[ \dfrac{\varepsilon_i}{k} \left( \dfrac{1}{T} + \dfrac{1}{U} \right) \right]}{\sum_i s_i \exp\left[ \dfrac{i\varepsilon_1}{k} \left( \dfrac{1}{T} - \dfrac{1}{T_1} \right) + \dfrac{\varepsilon_i}{kU} \right]}. \qquad (6.31)$$

Let us consider the right-hand sides in the equation for the specific number of vibrational quanta (6.23). The variation of the number of quanta in a system as a result of dissociation and recombination $R^{\text{w, diss–rec}}$ can be transformed taking into account the Treanor distribution (3.14), the expressions (6.16) and (6.19) for the state-to-state dissociation rate coefficient $k_{i,\text{diss}}^d$ and non-equilibrium factor $Z_i$, respectively, and the formula (6.27) for the multi-temperature dissociation rate coefficient. Then $R^{\text{w, diss–rec}}$ can be written in the form similar to (6.30):

$$R^{\text{w,diss–rec}} = Z(T,T_1,U) \sum_{d=\text{a,m}} k_{\text{diss, eq}}^d n_d \left( n_a^2 G_{\text{rec}} - n_{\text{m}} G_{\text{diss}} \right) =$$

$$= R^{\text{w,rec}} + R^{\text{w,diss}}. \qquad (6.32)$$

The functions $G_{\mathrm{diss}}$ and $G_{\mathrm{rec}}$ are introduced by the relations:

$$G_{\mathrm{diss}}(T,T_1,U) = \frac{\sum_i i s_i \exp\left[\frac{i\varepsilon_1}{k}\left(\frac{1}{T}-\frac{1}{T_1}\right)+\frac{\varepsilon_i}{kU}\right]}{\sum_i s_i \exp\left[\frac{i\varepsilon_1}{k}\left(\frac{1}{T}-\frac{1}{T_1}\right)+\frac{\varepsilon_i}{kU}\right]}, \tag{6.33}$$

$$G_{\mathrm{rec}}(T,T_1,U) = Z^{\mathrm{vibr}}(T,T_1)\frac{\sum_i i K_i(T)\exp\left[\frac{\varepsilon_i}{k}\left(\frac{1}{T}+\frac{1}{U}\right)\right]}{\sum_i s_i \exp\left[\frac{i\varepsilon_1}{k}\left(\frac{1}{T}-\frac{1}{T_1}\right)+\frac{\varepsilon_i}{kU}\right]}. \tag{6.34}$$

The expression for $R^{\mathrm{w,rec}}$ can be simplified if we substitute Eqs. (6.28) and (6.34) for $Z$ and $G_{\mathrm{rec}}$ into the formula (6.32):

$$R^{\mathrm{w,rec}}(T,U) = \frac{Z^{\mathrm{vibr}}(T)}{Z^{\mathrm{vibr}}(-U)}\sum_i i K_i(T)\exp\left[\frac{\varepsilon_i}{k}\left(\frac{1}{T}+\frac{1}{U}\right)\right]. \tag{6.35}$$

The latter expression indicates that the rate of the variation of a specific number of vibrational quanta due to recombination $R^{\mathrm{w,rec}}$ does not depend on the vibrational temperature $T_1$.

Thereby, all production terms in the two-temperature approach are expressed through the thermal equilibrium dissociation rate coefficients $k^d_{\mathrm{diss,\,eq}}(T)$, two-temperature non-equilibrium factor $Z(T,T_1,U)$, and functions $F_{\mathrm{rec}}(T,T_1,U)$, $G_{\mathrm{diss}}(T,T_1,U)$, and $G_{\mathrm{rec}}(T,T_1,U)$, specified by the expressions (6.28), (6.31), (6.33), and (6.34) (or using the formula (6.35) for $R^{\mathrm{w,rec}}$).

For harmonic oscillators, the function $G_{\mathrm{diss}}$ is:

$$G_{\mathrm{diss}}(T,T_{\mathrm{v}},U) = \frac{1}{Z^{\mathrm{vibr}}(T_{\mathrm{f}})}\sum_i i s_i \exp\left(-\frac{\varepsilon_i}{kT_{\mathrm{f}}}\right)$$

and depends on $T$ and $T_{\mathrm{v}}$.

Note in addition that the ratio of the dissociation and recombination rate coefficients $K_{\mathrm{rec-diss}}$ under the non-equilibrium conditions can also be expressed in terms of the averaged non-equilibrium factor. Let us introduce the averaged non-equilibrium factor $Z$ taking into account the definitions for the state-to-state factor $Z_i(T)$ (6.16) and for the averaged dissociation rate coefficient $k^d_{\mathrm{diss}}$ (6.18):

$$Z = \frac{k^d_{\mathrm{diss}}}{k^d_{\mathrm{diss,eq}}(T)} = \sum_i \frac{n_i}{n_{\mathrm{m}}}Z_i(T).$$

Using this relation, it is easy to find

$$K_{\mathrm{rec-diss}} = \frac{k^d_{\mathrm{rec}}}{k^d_{\mathrm{diss}}} = \frac{1}{Z}K^{\mathrm{eq}}_{\mathrm{rec-diss}}(T),$$

where $K^{\text{eq}}_{\text{rec–diss}}(T)$ is the ratio of the dissociation and recombination rate coefficients in a thermal equilibrium gas. Calculating $Z$ from the state-to-state or quasi-stationary vibrational distributions $n_i/n$ for various dissociation models, we can find $K_{\text{rec–diss}}$ under thermal non-equilibrium conditions and estimate its deviation from the equilibrium constant.

The relations between rate coefficients for dissociation and recombination in a non-equilibrium gas are discussed by many authors. For example, in Refs. [207, 208], the law of mass action was generalized in the framework of non-equilibrium linear thermodynamics. In particular, it was emphasized that under the steady-state conditions near the equilibrium, the recombination rate coefficient can depend on both the gas temperature and vibrational temperature (most likely, in the case of comparable times for the establishing of vibrational temperature and for dissociation–recombination).

## 6.3 First-Order Approximation of the Chapman–Enskog Method

In this Section, we consider the rate coefficients for slow processes in the state-to-state approach on the basis of the first-order distribution functions. We use the expressions from Section 2.5, as well as the solutions for the linear integral equations discussed in Chapter 5.

Within the state-to-state approach, we obtained the formulae (2.59), (2.61), and (2.62) for the rate coefficients for vibrational energy transitions, and expressions (2.64), (2.66), (2.67), (2.69), (2.70), (2.72), and (2.73) for the reaction rate coefficients in the first-order approximation. These relations include the coefficients $k^{(1)}_\gamma(n_{ci}, T)$, $k^{(2)}_\gamma(n_{ci}, T, \nabla \cdot \mathbf{v})$, specified by the functions $F_{cij}$, $G_{cij}$; the latter satisfy the linear integral equations (2.34), (2.35). Note that, as is shown above, the function $F_{cij}$ also specifies the bulk viscosity coefficient, whereas the functions $F_{cij}$ and $G_{cij}$ specify the relaxation pressure (see Eqs. (2.44)). The method for the solution for the integral equations (2.34), (2.35) and the technique that makes it possible to reduce them to linear algebraic equations are discussed in Chapter 5. The functions $F_{cij}$ and $G_{cij}$ are expressed in the form of the series (5.5) and (5.6) of the Sonine and Waldmann-Trübenbacher polynomials with respect to the velocity and rotational energy. For the coefficients $f_{ci,rp}$ of the expansion (5.5), the algebraic equations (5.21), (5.23) are derived, whereas the coefficients $g_{ci,rp}$ of the expansion (5.6) are found from the equations (5.25), (5.27). As is shown in Section 5.1, 5.3, the systems for $f_{ci,rp}$ and $g_{ci,rp}$ display the same coefficients $\beta^{cidk}_{rr'pp'}$ and differ only in their right-hand sides. The simplified expressions for the bracket integrals $\beta^{cidk}_{rr'pp'}$ are given by the formulae (5.77)–(5.82).

Substituting the expansions (5.5) and (5.6) into the formulae (2.61), (2.62), (2.66), (2.67), (2.69), (2.70), (2.72), and (2.73), we can express the coefficients $k^{(1)}_\gamma$, $k^{(2)}_\gamma$ for different $\gamma$ in terms of $f_{ci,rp}$, $g_{ci,rp}$, and integrals obtained after averaging the cross sections of inelastic collisions over the Maxwell-Boltzmann distribution.

The expressions for the rate coefficients $k_{c,\,ii'}^{d,\,kk'(1)}$ for vibrational energy transitions take the form:

$$k_{c,\,ii'}^{d,\,kk'(1)} = -\frac{1}{n}\sum_{rp} g_{ci,rp} \sum_{jlj'l'} \int \frac{f_{cij}^{(0)}}{n_{ci}} \frac{f_{dkl}^{(0)}}{n_{kl}} Q_{cij}^{rp} g\sigma_{cd,ijkl}^{i'j'k'l'} d^2\Omega\, d\mathbf{u}_c\, d\mathbf{u}_d - $$

$$-\frac{1}{n}\sum_{rp} g_{dk,rp} \sum_{jlj'l'} \int \frac{f_{cij}^{(0)}}{n_{ci}} \frac{f_{dkl}^{(0)}}{n_{kl}} Q_{dkl}^{rp} g\sigma_{cd,ijkl}^{i'j'k'l'} d^2\Omega\, d\mathbf{u}_c\, d\mathbf{u}_d, \qquad (6.36)$$

where the functions $Q_{cij}^{rp}$ are introduced by the relations (5.22). These formulae can be simplified if we retain only the zero and the first terms in the expansion (5.6): $p = r = 0$, $p = 0, r = 1$, and $p = 1, r = 0$. The coefficients $g_{ci,rp}$ are found from the simplified systems (5.28). In order to obtain the coefficients $k_{c,\,ii'}^{d,\,kk'(2)}$, we should replace the values $g_{ci,rp}$ in the equation (6.36) with $f_{ci,rp}$ multiplied by the velocity divergence. The expressions for the remaining coefficients $k_\gamma^{(1)}$ and $k_\gamma^{(2)}$ are similar.

The integrals appearing in Eq. (6.36) can be expressed in terms of collision integrals $\Omega_{cidk}^{(l,r)}$ over the cross sections of inelastic collisions resulting in vibrational energy transitions and chemical reactions.

Let us introduce the generalized averaging operator similar to (5.55), but in contrast to (5.55) containing the cross sections of slow inelastic processes:

$$\langle F\rangle_{cidk}^\alpha = \left(\frac{kT}{2\pi m_{cd}}\right)^{1/2} \sum_{jlj'l'} \frac{s_j^{ci} s_l^{dk}}{Z_{ci}^{rot} Z_{dk}^{rot}} \int F\gamma^3 \exp\left(-\gamma^2 - \mathscr{E}_j^{ci} - \mathscr{E}_l^{dk}\right) \times$$

$$\times \sigma^\alpha d^2\Omega d\gamma. \qquad (6.37)$$

The cross sections $\sigma^\alpha$ in the formula (6.37) depend on the process under consideration. In Eq. (5.55) for the most probable collisions ($\alpha = \mathrm{rap}$), $\sigma^{(\alpha)} = \sigma_{cd,ijkl}^{j'l'}$. Now, for the vibrational energy transitions ($\alpha = \mathrm{vibr}$), $\sigma^{(\alpha)} = \sigma_{cd,ijkl}^{i'j'k'l'}$, and so on for reactive collisions. As a result, the integrals in Eq. (6.36) can be reduced to

$$\tilde{\Omega}_{cidk}^{\mathrm{vibr}(r,p)} = \langle\gamma^{2r}\left(\mathscr{E}_j^{ci}\right)^p\rangle_{cidk}^{\mathrm{vibr}}.$$

Note that $\tilde{\Omega}_{cidk}^{\mathrm{vibr}(0,0)} = k_{c,\,ii'}^{d,\,kk'(0)}$.

Taking into account the simplifications discussed in Section 5.3, we obtain the final expression for the coefficient $k_{c,\,ii'}^{d,\,kk'(1)}$:

$$k_{c,\,ii'}^{d,\,kk'(1)} = \frac{m_d g_{ci,10} + m_c g_{dk,10}}{m_c + m_d}\left(\frac{3}{2} k_{c,\,ii'}^{d,\,kk'(0)} - \langle\gamma^2\rangle_{cidk}^{\mathrm{vibr}}\right) -$$

$$-\frac{g_{dk,01} m_c E_{\mathrm{rot},ci} + g_{ci,01} m_d E_{\mathrm{rot},dk}}{kT} k_{c,\,ii'}^{d,\,kk'(0)} +$$

$$+ g_{ci,01}\langle\mathscr{E}_j^{ci}\rangle_{cidk}^{\mathrm{vibr}} + g_{dk,01}\langle\mathscr{E}_l^{dk}\rangle_{dkci}^{\mathrm{vibr}}.$$

The state-to-state rate coefficients for the remaining processes are similar and contain the cross sections of corresponding transitions.

In order to obtain the expressions for the multi-temperature and one-temperature reaction rate coefficients in the first order approximation, the similar technique can be applied. Starting from Eqs. (3.89), then substituting the expansions for the functions $F_{cij}$ and $G_{cij}$ over triple systems of orthogonal polynomials used in the multi-temperature approach into the formulae (3.96), (3.97), we can express the coefficients $k_{cd}^{c'd'\,(1)}$, $k_{cd}^{c'd'\,(2)}$, $k_{c,\,\mathrm{diss}}^{d\,(1)}$, and $k_{c,\,\mathrm{diss}}^{d\,(2)}$ in terms of $g_{c,rpq}$, $f_{c,rpq}$, and collision integrals over the cross sections of chemical reactions. The expressions for these integrals can be found introducing the averaging operator based on the non-equilibrium vibrational distribution (similarly to the operator (5.83)) and containing the cross sections of chemically reactive collisions.

In the one-temperature approach, the expressions for the coefficients $k_{cd}^{c'd'\,(1)}$, $k_{cd}^{c'd'\,(2)}$, $k_{c,\,\mathrm{diss}}^{d\,(1)}$, and $k_{c,\,\mathrm{diss}}^{d\,(2)}$ can be obtained using the expansions (5.51) and (5.52) over double polynomial systems. In this case, the averaging operator is introduced taking into account the thermal equilibrium Boltzmann distribution over the vibrational energy (in the same way as in Eq. (5.93)); the integral operator is defined for the cross sections of chemically reactive collisions. Formulae for the first-order corrections to the rate coefficients of dissociation, recombination, and exchange reactions in the one-temperature approach, as well as the expressions connecting them to the bulk viscosity and relaxation pressure are derived in the recent study [157] using the kinetic theory methods.

As is already noted, the equations of non-equilibrium kinetics in a reacting gas flow obtained in the first-order approximation of the generalized Chapman–Enskog method (in the state-to-state, multi-temperature, or one-temperature approaches), include the first-order corrections to the rate coefficients of slow processes. However, in most practical simulations for the equations of dynamics of viscous conducting gases coupled to the equations of non-equilibrium kinetics, the reaction rate coefficients in the latter equations are calculated using the zero-order distribution function. Up to now, no reliable calculations for the first-order reaction rate coefficients are available; they could make it possible to estimate the role of first-order corrections and to justify their neglecting in the complete set of viscous flow governing equations. For instance, some asymptotic estimates show that the contribution of the first-order corrections to the reaction rates in the boundary layer equations is small. Nonetheless, in the general case this conclusion is not justified, therefore, the calculation for the first-order reaction rate coefficients under different non-equilibrium conditions still presents an important unsolved problem in chemical kinetics.

# Chapter 7
# Non-equilibrium Kinetics and its Influence on the Transport Processes Behind Strong Shock Waves

In Chapters 7–9, we consider the applications of the above-developed kinetic theory of transport and relaxation processes to some particular problems of non-equilibrium gas dynamics. In this Chapter, the peculiarities of the relaxation zone behind strong shock waves occurring in a hypersonic gas flow are considered. The rapid gas compression within a thin shock front with the characteristic length of about several mean free paths, results in a temperature jump which, due to the significant difference in relaxation times, occurs essentially without a variation in the mixture composition and molecular distributions over the vibrational energy. After that, in the relaxation zone behind the shock front, the excitation of vibrational degrees of freedom and chemical reactions take place, and as a result of relaxation processes, the total thermal and chemical equilibrium is established. The length of the relaxation zone reaches many tens and even hundreds mean free paths. The gas state in the unperturbed flow before the shock front is usually supposed to be equilibrium, and therefore, as a consequence of the gas propagation through the shock wave and relaxation zone, one equilibrium state is transformed to another. In the vibrational relaxation and chemical reactions behind the shock wave, equilibrium or weakly non-equilibrium distributions over the translational and rotational degrees of freedom established in the shock front are maintained. The assumed invariance of the Maxwell distribution corresponds to the Euler approximation for an inviscid non-conducting gas flow. Taking into account deviations from the Maxwell distribution makes it possible to study dissipative processes in a non-equilibrium viscous gas.

In this Chapter, we consider non-equilibrium vibrational distributions, macroscopic flow parameters, and dissipative properties of gas mixtures behind strong shock waves, in an $A_2/A$ binary mixture and in air, within the framework of the state-to-state, multi-temperature, and one-temperature kinetic models.

## 7.1 State-to-State Kinetics in Binary Mixtures with Dissociation and Recombination

We consider the detailed vibrational and chemical kinetics behind a plane shock wave on the basis of the equations (2.21)–(2.23) obtained in the zero-order

approximation of the Chapman–Enskog method, which corresponds to the Maxwell–Boltzmann distribution over the translational and rotational degrees of freedom and strong vibrational and chemical non-equilibrium. The flow is assumed to be one-dimensional and steady-state. In this case, the system (2.21)–(2.23) is substantially simplified, the conservation equations can be integrated in quadratures, whereas the equations of non-equilibrium kinetics are reduced to ordinary differential equations. Similarly to Section 6.1, a flow of a binary mixture of $A_2$ molecules and A atoms with dissociation and recombination reactions and TV and VV vibrational energy transitions is studied. Under these assumptions, the set of equations for the vibrational level populations $n_i$, atomic number densities $n_a$, macroscopic gas velocity $\mathbf{v}$, and temperature $T$ takes the form:

$$\frac{d(vn_i)}{dx} = R_i^{\text{vibr}} + R_i^{\text{diss–rec}}, \quad i = 0, ..., L, \tag{7.1}$$

$$\frac{d(vn_a)}{dx} = -2 \sum_i R_i^{\text{diss–rec}}, \tag{7.2}$$

$$\rho_0 v_0 = \rho v, \tag{7.3}$$

$$\rho_0 v_0^2 + p_0 = \rho v^2 + p, \tag{7.4}$$

$$h_0 + \frac{v_0^2}{2} = h + \frac{v^2}{2}, \tag{7.5}$$

where $x$ is the distance from the shock front. The subscript "0" denotes the parameters in the free stream, the specific enthalpy $h$ is equal to

$$h = h_m Y_m + h_a Y_a, \tag{7.6}$$

$Y_m = \rho_m / \rho$, $Y_a = \rho_a / \rho$ are the mass fractions of molecules and atoms,

$$h_a = \frac{5}{2} \hat{R}_a T + \frac{\varepsilon_a}{m_a}, \qquad h_m = \frac{7}{2} \hat{R}_m T + E^{\text{vibr}} + \frac{\varepsilon_m}{m_m},$$

$$E^{\text{vibr}} = \frac{1}{\rho_m} \sum \varepsilon_i n_i.$$

The right-hand sides of Eqs. (7.1), (7.2) are given by the relations (6.2), (6.3), and (6.11) and include the state-to-state coefficients for various vibrational energy transitions, dissociation, and recombination.

The distribution in the free stream is assumed to be the Boltzmann's with a given temperature $T_0$. The influence of the non-equilibrium distributions over the vibrational energy before the shock front on the kinetics in the relaxation zone is discussed in Refs. [128, 141, 206]. Here, we present the results obtained by the numerical solution of the system (7.1)–(7.5) for the $N_2$/N mixture under the following conditions in the free stream: $T_0 = 293$ K, $p_0 = 100$ Pa, $M_0 = 15$. The vibrational energy is simulated by the Morse anharmonic oscillator, the rate coefficients for vibrational energy transitions are calculated on the basis of the SSH-theory generalized

for anharmonic oscillators [100, 101], dissociation is described using the Treanor–Marrone model with different values for the parameter $U$ and parameters $A$, $n$ in the Arrhenius law (6.20). The vibrational level populations and macroscopic flow parameters are computed in the state-to-state, two-temperature, and one-temperature approaches. In the two-temperature approach instead of Eqs. (7.1), we solve the equations for the number density and for the temperature of the first vibrational level $T_1$ of molecules $N_2$, whereas in the one-temperature approach, the set of governing equations for a thermal equilibrium gas flow is simulated. The quasi-stationary vibrational distributions for different distances from the shock front are calculated using the obtained values for the macroscopic parameters.
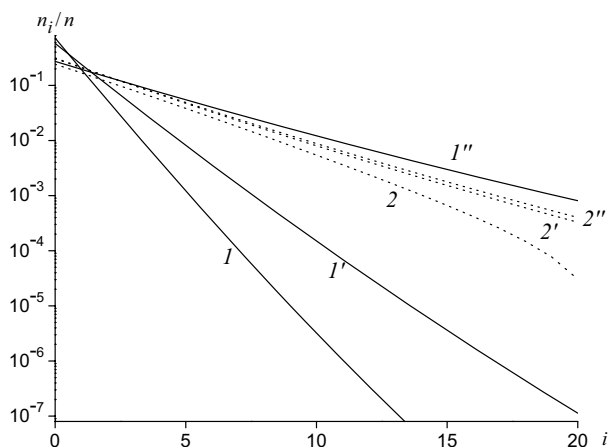


**Fig. 7.1** The vibrational level populations. The curves *1, 2* represent the state-to-state model; *1′, 2′* the two-temperature approach; *1″, 2″* the one-temperature model. The solid curves correspond to $x = 0.03$, the dashed to $x = 0.8$ cm

In Figure 7.1, the dimensionless vibrational level populations $n_i/n$ calculated within the above three models are given as functions of $i$ for various distances from the shock front. We can see a substantial discrepancy between the vibrational distributions obtained within different models close to the shock front, where the quasi-stationary distributions have not been established yet. The two-temperature and one-temperature approaches overestimate the vibrational level populations in a thin layer immediately behind the shock front. This discrepancy decreases with the distance from the shock front.

Figure 7.2 presents the variation of the gas temperature, calculated for the three approaches, as a function of the distance from the shock front. Within the one-temperature and two-temperature models, the temperature is underestimated, since these approaches assume the existence of quasi-stationary distributions immediately behind the shock front and do not take into account the process of vibrational excitation in the very beginning of the relaxation zone.
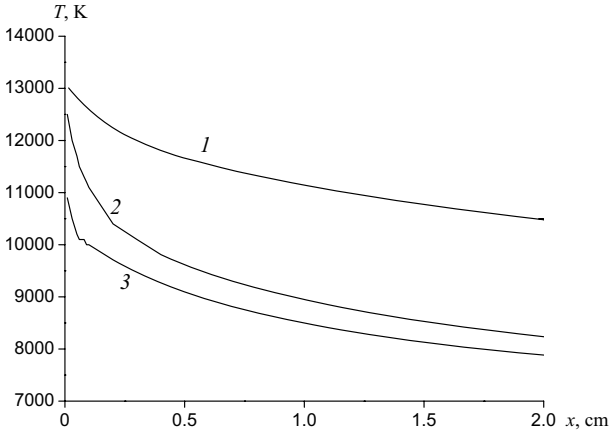
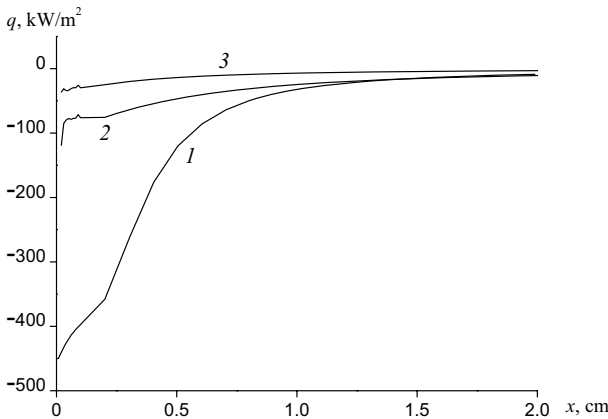**Fig. 7.2** The gas temperature $T$ behind the shock as a function of $x$. The curves *1, 2, 3* represent the state-to-state, two-temperature, and one-temperature approaches, respectively
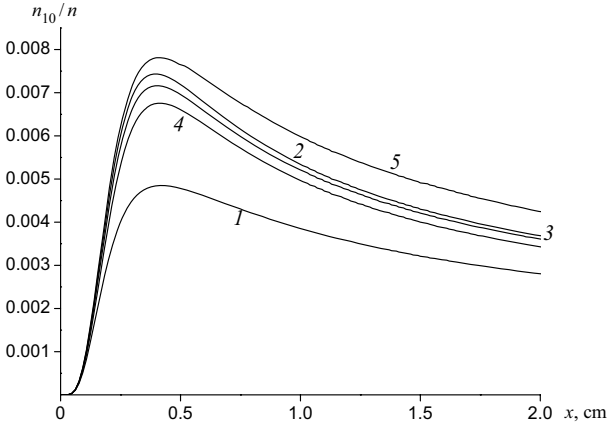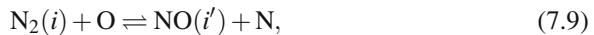


**Fig. 7.3** The 10th level population as a function of $x$. *1*: $U = D/(6k)$ (the parameters $A$, $n$ are taken from Ref. [127]); *2*: $U = D/(6k)$; *3*: $U = 3T$; *4*: $U = \infty$ (for *2–4* the parameters $A$, $n$ are taken from Ref. [89]); *5*: ladder-climbing model

The influence of the dissociation model on the vibrational level populations is shown in Figure 7.3, where the population of the tenth level is presented for different values for the parameters $U$, $A$, and $n$, as well as for the ladder-climbing model. Three values for $U$ are considered: $U = D/(6k)$, $U = 3T$, and $U = \infty$, the parameters in the Arrhenius formula are taken from [127, 229] and [89]. We can see that the vibrational distributions and macroscopic parameters calculated within the ladder-climbing dissociation model are significantly different from those obtained using the Treanor–Marrone model.

In Fig. 7.4, the number densities of nitrogen atoms calculated in the three approaches are compared. We can notice that the one-temperature model does not
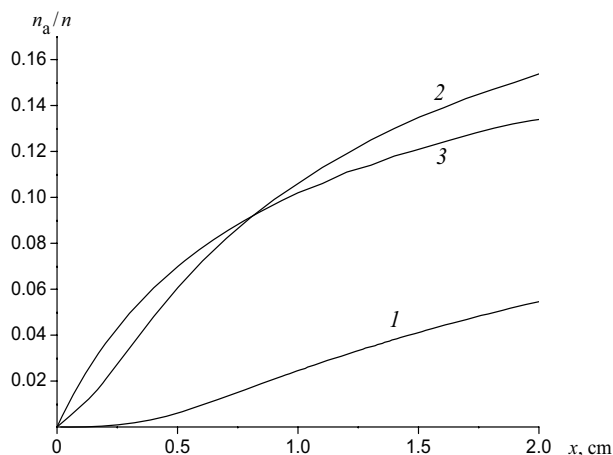
**Fig. 7.4** The atomic molar fraction $n_a/n$ behind the shock front as a function of $x$. The curves *1, 2, 3* represent the state-to-state, two-temperature, and one-temperature approaches, respectively
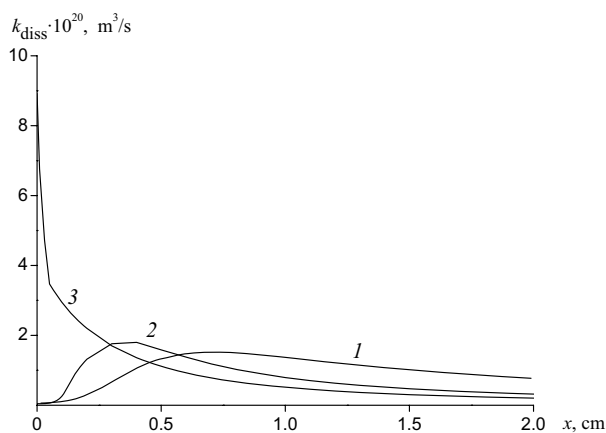


**Fig. 7.5** The averaged dissociation rate coefficient $k_{diss}^{N_2}$ as a function of $x$. The curves *1, 2, 3* represent the state-to-state, two-temperature, and one-temperature approaches, respectively

describe the dissociation delay immediately behind the shock front. Both quasi-stationary models overestimate the dissociation degree in the vicinity of the front.

From the vibrational distributions found behind the shock wave for the state-to-state, two-temperature, and one-temperature approaches, the averaged dissociation rate coefficient $k_{diss}^{N_2}$ can be calculated. For this purpose, the vibrational level populations, molecular number density $n_m$, and temperature $T$ obtained in the state-to-state and two-temperature approaches for various points behind the shock are substituted

into the formula (6.18). In the one-temperature approach, the dissociation rate co-
efficient is calculated using the Arrhenius formula (6.20). The results are presented
in Fig. 7.5. It is seen that the one-temperature model describes the behavior of the
dissociation rate coefficient inadequately, particularly close to the shock front. The
two-temperature approach provides more realistic values for the dissociation rate
coefficient, overestimating however $k_{\mathrm{diss}}^{\mathrm{N_2}}$ in comparison to the state-to-state approx-
imation at $x < 0.5$ cm.

## 7.2  Diffusion and Heat Transfer

In order to evaluate transport properties in the state-to-state approach, it is neces-
sary to solve numerically the system (2.16)–(2.18) for the macroscopic parameters
$n_i$, $n_a$, $\mathbf{v}$, and $T$ in the first-order approximation of the Chapman–Enskog method.
In the frame of the rigorous formalism, the state-dependent transport coefficients in
the equations (2.16)–(2.18) should be calculated at each step of the numerical so-
lution. Such a technique, even taking into account the simplifications described in
Section 5.5, appears to be extremely time-consuming.

In Refs. [141, 147], an approximate approach for evaluation of gas dissipative
properties was suggested. First, the vibrational level populations, molar fractions
of atoms, and temperature are found from the governing equations in the zero-order
approximation (7.1)–(7.5). Then the obtained non-equilibrium distributions are used
to calculate the transport coefficients, diffusion velocities, and heat flux with the
accurate formulae of the kinetic theory.

Here, we present the results obtained with this approximate approach. The dis-
sipative properties of a binary $A_2/A$ mixture behind a shock wave are studied in
the state-to-state, multi-temperature, and one-temperature approaches. In the state-
to-state approach, the simplified expressions for the diffusion velocity of atoms $\mathbf{V}_a$
and molecules in different vibrational states $\mathbf{V}_i$ have the form (5.110), (5.111); the
total energy flux is given by the formula (5.113). The expressions for the thermal
conductivity and diffusion coefficients are obtained in Section 5.5. The comparison
of the results found in three approaches shows that the behavior of the diffusion co-
efficients is specified mainly by the distribution of macroscopic parameters behind
the shock front. Figure 7.6 presents the dependence of the coefficient $D_{\mathrm{N_2-N}}$ on
the distance $x$. The discrepancy between the coefficients $D_{\mathrm{N_2-N}}$ calculated within
three models for the flow description, is explained by different values of the molar
fractions of atoms and molecules in the corresponding approaches.

The diffusion coefficients for the vibrational states $D_{ii}$ appreciably depend on
the vibrational level populations and increase substantially with $i$. Furthermore, the
analysis of the results confirms the common assumption adopted in the kinetic the-
ory about small absolute values for the thermal diffusion coefficient compared to
those for the mass diffusion of atoms and molecules. As to the thermal conduc-
tivity, coefficient $\lambda'$ is specified not only by the temperature and species concentra-
tions, but also by the approach itself. For example, in the one-temperature approach,
$\lambda'$ noticeably exceeds the thermal conductivity coefficient obtained within the
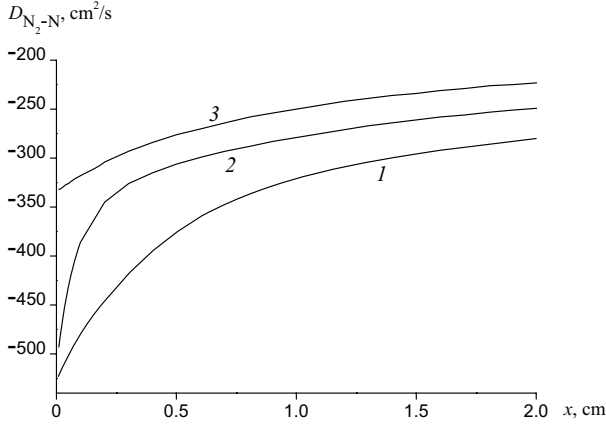
**Fig. 7.6** The diffusion coefficient $D_{N_2-N}$ as a function of $x$. The curves *1, 2, 3* represent the state-to-state, two-temperature, and one-temperature approaches, respectively

two-temperature and state-to-state models since, in the former case, it includes the coefficient $\lambda_{vibr}$ associated with the vibrational energy transfer (see also [147]).

In Fig. 7.7, the variation of the total energy flux in the relaxation zone behind the shock front is given. The one-temperature and two-temperature approaches substantially underestimate the absolute values for the heat flux in the very beginning of the relaxation zone, where the process of vibrational excitation is essential, and the more rigorous state-to-state approach should be applied.

In order to understand the role of various processes in the relaxation zone behind the shock front, the total heat flux is compared to those calculated successively taking into account one of the possible dissipative processes: 1) when $q$ is specified only by the thermal conductivity and all diffusion processes are neglected (the



**Fig. 7.7** The heat flux $q$ as a function of $x$. The curves *1, 2, 3* represent the state-to-state, two-temperature, and one-temperature approaches, respectively
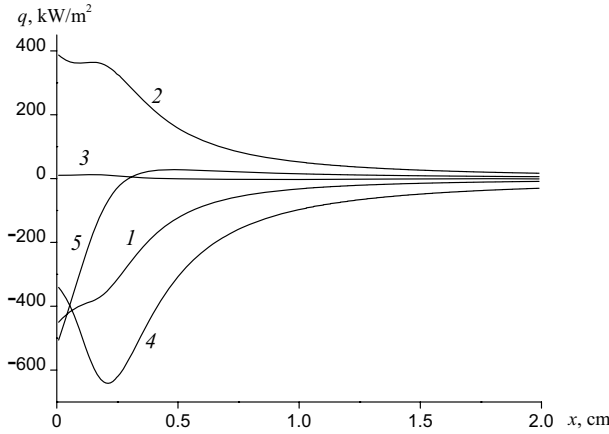
**Fig. 7.8** The heat flux $q$ as a function of $x$. The curve *1* displays the total heat flux; *2* the Fourier energy flux; *3* the heat flux due to the thermal diffusion; *4* the flux associated with the mass diffusion; *5* the flux caused by the diffusion of vibrational energy

Fourier flux $q^{HC}$), 2) taking into account only the thermal diffusion ($q^{TD}$), 3) including only the mass diffusion ($q^{MD}$), and 4) considering solely the diffusion of vibrational energy ($q^{DVE}$). Figure 7.8 presents the results of the calculations.

Close to the shock front ($x < 0.3$ cm, or about twenty mean free path lengths in the unperturbed flow), in the domain of simultaneous vibrational relaxation and chemical reactions, the mass diffusion and diffusion of the vibrationally excited molecules affect the heat flux significantly; their contributions to the total energy flux are approximately of the same order of magnitude. Then, when the quasi-stationary distributions over the vibrational energy are established, the level populations vary only slightly, and the mass diffusion dominates. The influence of thermal diffusion on the heat flux behind the shock front is essentially negligible, and its contribution does not exceed several percents.

## 7.3 Vibrational and Chemical Kinetics and Transport Processes in Air Mixtures

In the simulation of vibrational and chemical relaxation in air, a five-component mixture ($N_2$, $O_2$, NO, N, O) is usually considered, and the following reactions are taken into account:

$$N_2(i) + M \rightleftharpoons N + N + M, \tag{7.7}$$

$$O_2(i) + M \rightleftharpoons O + O + M, \tag{7.8}$$

$$N_2(i) + O \rightleftharpoons NO(i') + N, \tag{7.9}$$

$$O_2(i) + N \rightleftharpoons NO(i') + O, \qquad (7.10)$$

$$NO(i) + M \rightleftharpoons N + O + M. \qquad (7.11)$$
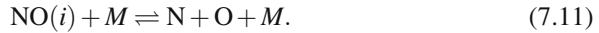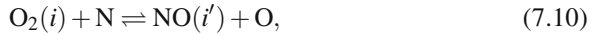
In order to study the state-to-state vibrational and chemical kinetics in such a mixture, 114 equations for the populations of the vibrational levels of $N_2$, $O_2$, and NO, as well as the equations for the atomic number densities are to be solved. To reduce the number of the equations, it is often supposed [48] that NO molecules forming as a result of the reactions (7.9)–(7.11) are in the ground vibrational state. This makes it possible to consider only a single vibrational level of NO instead of 36. In the quasi-stationary multi-temperature approach, the number of kinetic equations is substantially reduced: instead of equations for the populations of vibrational levels $n_{N_2 i}$, $n_{O_2 i}$, and $n_{NO i}$, we should solve the equations for the molecular number densities $n_{N_2}$, $n_{O_2}$, and $n_{NO}$, and effective temperatures of the first vibrational levels $T_1^{N_2}$, $T_1^{O_2}$, and $T_1^{NO}$. In addition to that, the distribution of NO molecules over the vibrational states is usually supposed to be thermal-equilibrium with $T_1^{NO} = T$, since the vibrational relaxation time for NO molecules is appreciably smaller than that for $N_2$ and $O_2$ [236]. In our study, this assumption is also applied, although it should be noted that in the recent years, some information about a deviation of the NO vibrational temperature from the gas temperature was revealed (see, for instance, Ref. [237]). In the harmonic oscillator approach, the equations for the temperatures of the first vibrational levels $T_1^{N_2}$, $T_1^{O_2}$ are reduced to those for vibrational temperatures $T_v^{N_2}$, $T_v^{O_2}$ (see Section 3.3).

Below, we present the results from Ref. [59], where the kinetics, dynamics, and transport processes behind strong shock waves propagating in air are studied on the basis of the reaction scheme (7.7)–(7.11) in three quasi-stationary approaches: 1) the multi-temperature (generalized Treanor) approach based on the distribution (3.14); 2) the multi-temperature Boltzmann approach for harmonic oscillators based on the distribution (3.16), and 3) the one-temperature thermal equilibrium approach (for the distribution (3.18)). A numerical solution for the equations for the chemical species number densities $n_{N_2}$, $n_{O_2}$, $n_{NO}$, $n_N$, and $n_O$, velocity $\mathbf{v}$, and temperatures ($T$, $T_1^{N_2}$, and $T_1^{O_2}$ in the first case; $T$, $T_v^{N_2}$, and $T_v^{O_2}$ in the second case, and $T$ in the third case), yielded the macroscopic flow parameters behind the shock front. The conditions in the free stream are as follows: $M_0 = 15$, $T_0 = 271$ K, $p_0 = 100$ Pa, $n_{N_2}/n = 0.79$, $n_{O_2}/n = 0.21$.

Figure 7.9 presents the variation of the gas temperature as well as of the temperatures $T_1^{N_2}$, $T_1^{O_2}$, $T_v^{N_2}$, and $T_v^{O_2}$ behind the shock wave. We can see that the one-temperature model substantially underestimates the gas temperature in the relaxation zone. The comparison of the results obtained within the second and third models makes it possible to estimate the influence of anharmonicity of molecular vibrations: while it essentially does not affect the gas temperature $T$, the temperatures $T_1^{N_2}$, $T_1^{O_2}$ calculated for anharmonic oscillators differ from $T_v^{N_2}$, $T_v^{O_2}$ obtained for harmonic oscillators. The maximum discrepancy is found for $T_1^{O_2}$ and $T_v^{O_2}$.
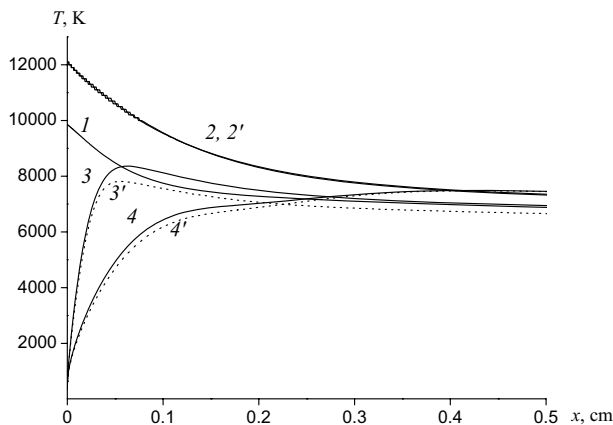
**Fig. 7.9** The temperatures $T$, $T_1^{N_2}$, and $T_1^{O_2}$ as functions of $x$. The curve *1* displays $T$ calculated in the one-temperature approach; *2, 2′*: $T$ in the multi-temperature approaches for anharmonic and harmonic oscillators, respectively; *3*: $T_1^{O_2}$; *3′*: $T_v^{O_2}$; *4*: $T_1^{N_2}$; *4′*: $T_v^{N_2}$

The dependence of the molecular molar fractions on the distance $x$ is presented in Fig. 7.10. Since the one-temperature approach does not account for the dissociation delay caused by the finite time of the excitation of the vibrational degrees of freedom, this approach overestimates the dissociation and exchange reaction rates. As a result, the rate of the decomposition of molecules $N_2$ and $O_2$, as well as of the formation of NO appears to be substantially higher than that in the multi-temperature approaches. The influence of the anharmonicity on the concentrations of chemical species behind the shock wave is rather weak.
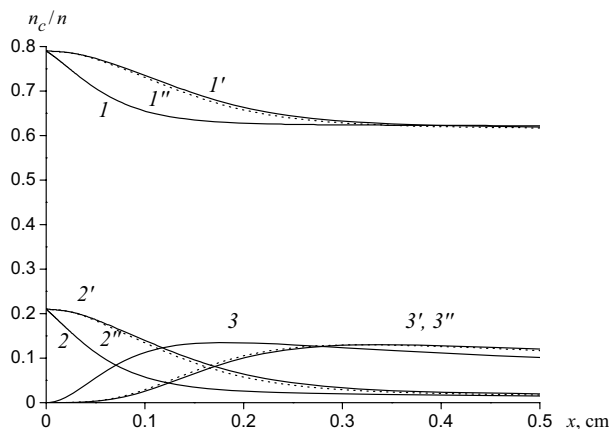


**Fig. 7.10** The molecular molar fractions $n_{N_2}/n$ (*1, 1′, 1″*), $n_{O_2}/n$ (*2, 2′, 2″*), and $n_{NO}/n$ (*3, 3′, 3″*) as functions of $x$. The curves *1–3* arepresent the one-temperature approach; *1′–3′*: the multi-temperature approach (anharmonic oscillator); *1″–3″*: the multi-temperature approach (harmonic oscillator)
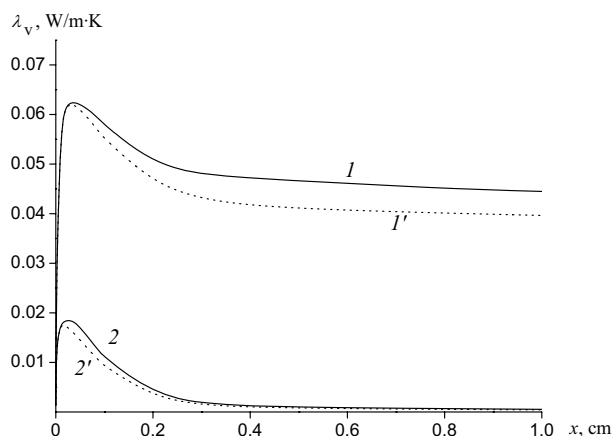
**Fig. 7.11** The thermal conductivity coefficients $\lambda_{v,N_2}$ (*1, 1'*) and $\lambda_{v,O_2}$ (*2, 2'*) in the multi-temperature approach as functions of $x$. The curves *1, 2* represent the case of anharmonic oscillators; *1', 2'* of harmonic oscillators

The thermal conductivity and diffusion coefficients, as well as the diffusion velocity and heat flux, are calculated with the formulae of the kinetic transport theory for a multi-component reacting mixture derived in Chapter 3 and Section 5.2. Figure 7.11 presents the variation in the relaxation zone of the thermal conductivity coefficients $\lambda_{v,N_2}$ and $\lambda_{v,O_2}$ associated with the transport of vibrational energy, whereas Fig. 7.12 displays the behavior of the diffusion coefficients $D_{N_2-NO}$ and $D_{N_2-O_2}$. The effect of anharmonicity of vibrations on the thermal conductivity
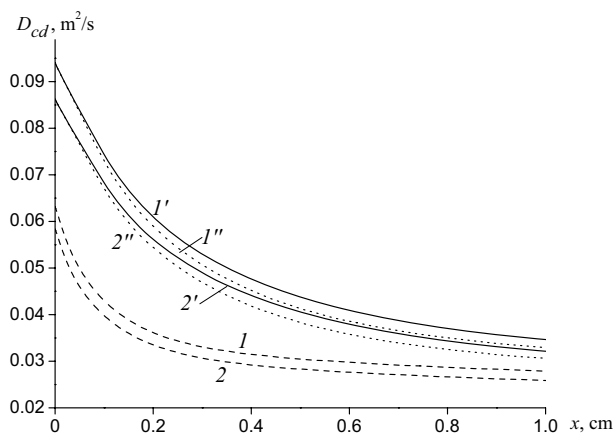


**Fig. 7.12** The diffusion coefficients $D_{N_2-NO}$ (*1, 1', 1''*) and $D_{N_2-O_2}$ (*2, 2', 2''*) as functions of $x$. The curves *1, 2* correspond to the one-temperature approach; *1', 2'* to the multi-temperature approach (anharmonic oscillator); *1'', 2''* to the multi-temperature approach (harmonic oscillator)
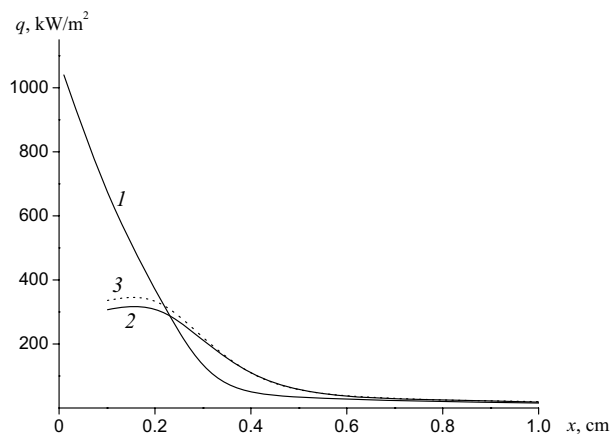
**Fig. 7.13** The heat flux $q$ as a function of $x$. The curves *1–3* represent the one-temperature, multi-temperature (anharmonic oscillator), and multi-temperature (harmonic oscillator) approaches, respectively

coefficients is appreciably stronger than that for the diffusion coefficients. It is consistent with the fact that the diffusion coefficients are mainly specified by the species concentrations and gas temperature rather than by the internal state of particles. This also explains the substantial difference between the diffusion coefficients obtained in the one-temperature and multi-temperature approaches.

The energy flux calculated within three approaches using the results obtained for the distribution of macroscopic parameters and transport coefficients behind the shock front, is plotted in Fig. 7.13. It is important to emphasize that the one-temperature approach yields the inadequately high heat flux for $x < 0.2$ cm, which can be explained by the overestimated role of the diffusion processes in the beginning of the relaxation zone. As is mentioned above, the one-temperature approach does not describe the dissociation delay, and, consequently, results in the overrated gradients of species concentrations in the vicinity of the shock front. The influence of anharmonicity on the heat flux under the conditions considered in this Section, appears to be of minor importance.

# Chapter 8
# Heat Transfer and Diffusion in a Non-equilibrium Boundary Layer

Close to the surface of a hypersonic space vehicle reentering the Earth atmosphere, strongly non-equilibrium conditions are established. While crossing the bow shock, the gas is substantially compressed and heated. Due to the high temperature in the flow, the dissociation rate increases and strong vibrational excitation occurs. In the vicinity of the cold surface, the temperature of translational and rotational degrees of freedom drops sharply, and the vibrational temperature appears to be higher than that of the gas. Under such conditions, the distribution of molecules over the vibrational levels significantly differs from equilibrium, dissociation near the high-temperature external edge of the boundary layer as well as recombination near the cold surface are substantially non-equilibrium, which, in turn, results in the formation of the non-Boltzmann vibrational distributions. These strongly non-equilibrium distributions may noticeably affect the transport processes.

The non-equilibrium heat transfer in the vicinity of a body surface is considered in a number of studies (see, for instance, Refs. [5, 20, 240] and references therein). This is due to the necessity to develop efficient thermal protection systems for hypersonic vehicles. In early studies in this domain, non-equilibrium chemical reactions were considered for the case of weak deviations from the equilibrium for the internal degrees of freedom [171]. The influence of vibrational excitation on the kinetics, dynamics, and heat transfer near the surface was studied in Refs. [264, 164, 139] within the framework of various multi-temperature models. However, the development of the state-to-state approach and its application to the modeling of non-equilibrium kinetics in a boundary layer [14, 48, 16] indicated that the vibrational distributions near the surface are far from being quasi-stationary. In the studies [174, 40], a more rigorous approach was used to describe diffusion and heat transfer, taking into account the deviation of the vibrational distributions from the multi-temperature distributions. The evaluation of the heat fluxes on the basis of the state-to-state vibrational distributions obtained in Refs. [14, 48, 16], was performed in the studies [17, 12, 153]. In particular, it was shown that the diffusion of vibrationally excited molecules contributes appreciably to the heat transfer near the surface.

The chemical activity of the surface presents another important aspect of the non-equilibrium kinetics in a boundary layer; it may substantially affect the

mixture composition and the heat flux near the wall. The catalytic properties of the surface are commonly modeled using different phenomenological relations (see, for instance, Refs. [116, 24]), based on the experimental values for the rate coefficients of heterogeneous reactions. Results for experimental measurements of the rate coefficients for recombination of atoms in their interaction with different materials are presented in Ref. [20]. Phenomenological models usually neglect the role of catalycity in the vibrational kinetics of the gas phase. However, some recent studies [12, 16] show that recombination of atoms on the surface may substantially perturb the vibrational distributions and influence the heat flux towards the wall [72].

## 8.1   Equations for a Non-equilibrium Boundary Layer in the State-to-State Approach

Let us write the boundary layer equations for a flat stationary flow in the state-to-state approach. Under the condition $\mathrm{Re} \gg 1$ ($\mathrm{Re} = u_* L_* / v$ is the Reynolds number, $u_*$, $L_*$ are the characteristic velocity and length, and $v = \eta / \rho$ is the kinematic viscosity coefficient), the boundary-layer thickness $\delta$ is substantially smaller than the characteristic length $L_*$ ($\delta / L_* \ll 1$), and all parameters vary across the boundary layer appreciably more rapidly than along the body surface. Due to such anisotropy of a boundary layer, the dimensionless Boltzmann equation (1.38) under the condition (1.43) takes the form:

$$\varepsilon \left( \frac{\partial f_{cij}}{\partial t} + u_x \frac{\partial f_{cij}}{\partial x} \right) + \sqrt{\varepsilon} u_y \frac{\partial f_{cij}}{\partial y} = J_{cij}^{\mathrm{el}} + J_{cij}^{\mathrm{rot}} + \varepsilon J_{cij}^{\mathrm{vibr}} + \varepsilon J_{cij}^{\mathrm{react}}.$$

The small parameter in the kinetic equations is introduced as before: $\varepsilon = \tau_{\mathrm{rap}} / \tau_{\mathrm{sl}} \sim \tau_{\mathrm{el}} / \theta$, however, the successive approximations of the Chapman–Enskog method are obtained with the small parameter $\sqrt{\varepsilon}$ rather than $\varepsilon$ [196]. The distribution function is expanded into the series similar to (1.48) in the powers of $\sqrt{\varepsilon}$:

$$f_{cij}(\mathbf{r}, \mathbf{u}, t) = \sum_r \left( \sqrt{\varepsilon} \right)^r f_{cij}^{(r)} (\mathbf{u}, \rho_\lambda, \nabla \rho_\lambda, \nabla^2 \rho_\lambda, ...).$$

In the conditions of normalization (2.8)–(2.13), only the equation for the normal velocity is found in the different form [196]:

$$\sum_{cij} m_c \int u_{cy} f_{cij}^{(0)} d\mathbf{u}_c = 0, \quad \sum_{cij} m_c \int u_{cy} f_{cij}^{(1)} d\mathbf{u}_c = \rho v_y,$$

$$\sum_{cij} m_c \int u_{cy} f_{cij}^{(r)} d\mathbf{u}_c = 0, \quad r \geq 2,$$

the remaining conditions are written similarly.

Using the formalism of the generalized Chapman–Enskog method and taking into account the above modifications, in the first-order approximation we obtain the following set of equations:

$$\frac{\partial}{\partial x}(n_{ci}v_x) + \frac{\partial}{\partial y}(n_{ci}v_y) + \frac{\partial}{\partial y}(n_{ci}V_{ciy}) = R_{ci}, \tag{8.1}$$

$$c = 1,..,L, \quad i = 0,...,L_c,$$

$$\rho\left(v_x\frac{\partial v_x}{\partial x} + v_y\frac{\partial v_x}{\partial y}\right) + \frac{dp}{dx} - \frac{\partial}{\partial y}\left(\eta\frac{\partial v_x}{\partial y}\right) = 0, \tag{8.2}$$

$$\rho\left(v_x\frac{\partial h}{\partial x} + v_y\frac{\partial h}{\partial y}\right) - v_x\frac{dp}{dx} + \frac{\partial q_y}{\partial y} - \eta\left(\frac{\partial v_x}{\partial y}\right)^2 = 0 \tag{8.3}$$

instead of the equations (2.16)–(2.18).

Strictly speaking, the production terms $R_{ci}$ in the equations (8.1) are specified by the first-order distribution function. Nevertheless, it can be shown that the contribution of the first-order corrections to the reaction rate coefficients in a boundary layer is negligible, and hence, in this case $R_{ci}$ can be calculated using the expressions (2.52), (2.53), and (2.54) for the zero-order rate coefficients of the vibrational energy exchange and chemical reactions.

Introducing the mass fractions $Y_{ci}$ of the molecular species $c$ at the vibrational level $i$, we can rewrite the equations (8.1) in the alternative form:

$$\rho\left(v_x\frac{\partial Y_{ci}}{\partial x} + v_y\frac{\partial Y_{ci}}{\partial y}\right) + \frac{\partial}{\partial y}(\rho Y_{ci}V_{ciy}) = m_c R_{ci}.$$

Let us consider the transport terms in the equations (8.1)–(8.3). Since the pressure remains constant across the boundary layer, the expression (2.27) for the diffusive driving force $\mathbf{d}_{ci}$ is simplified:

$$\mathbf{d}_{ci} = \nabla\left(\frac{n_{ci}}{n}\right),$$

whereas the component $V_{ciy}$ of the diffusion velocity is calculated using the relation

$$V_{ciy} = -\sum_{dk}D_{cidk}\frac{\partial}{\partial y}\left(\frac{n_{dk}}{n}\right) - \frac{D_{Tc}}{T}\frac{\partial T}{\partial y}.$$

Taking into account the simplified expression for the diffusive driving force in the boundary layer, we can find the projection of the heat flux vector onto the axis of ordinates $y$:

$$q_y = -\lambda'\frac{\partial T}{\partial y} - p\sum_c D_{Tc}\frac{\partial}{\partial y}\left(\frac{n_c}{n}\right) + \sum_{ci}\left(\frac{5}{2}kT + \langle\varepsilon^{ci}\rangle_{\mathrm{rot}} + \varepsilon_i^c + \varepsilon_c\right)n_{ci}V_{ciy}.$$

The boundary conditions for the equations (8.1)–(8.3) should be imposed at both the external edge of the boundary layer (at $y \to \infty$ or $y = \delta$) and the surface (at $y = 0$). According to the general boundary layer theory, the macroscopic flow parameters at the external edge are supposed to be known:

$$n_{ci} = n_{cie}, \qquad c = 1, ..., L, \quad i = 0, ..., L_c,$$

$$v_x = v_e,$$

$$h = h_e \quad \text{or} \quad T = T_e.$$

The chemical species distribution in the external flow is usually assumed to be equilibrium at a given temperature $T_e$ and pressure $p_e$, whereas the vibrational distributions are the Boltzmanns' with the temperature $T_e$.

The conditions for the level populations, velocity, and gas temperature at the surface are derived from the microscopic boundary conditions [124, 18]. One of the methods used to derive the boundary conditions is based on the assumption that the distribution function in the first-order approximation of the Chapman–Enskog method is valid up to the surface. A more rigorous approach requires the consideration of a thin (of the order of the mean free path length) Knudsen layer, where the boundary layer equations are violated, and we should solve the Boltzmann equation (see, for instance, the study [159], where the Knudsen layer is considered in the case of the two-temperature relaxation).

If we assume that the Chapman–Enskog distribution function is valid up to the surface, then, in the absence of molecular adsorption on the wall, we can write the microscopic boundary conditions in the form:

$$f_{cij}^{(1)} u_{cn} \Big|_{u_{cn}>0} = \sum_{dkl} \int_{u_{dn}<0} f_{dkl}^{(1)} |u_{dn}| T_{dkl}^{cij}(\mathbf{u}_c, \mathbf{u}_d) \, d\mathbf{u}_d, \tag{8.4}$$

where $\mathbf{u}_c$, $\mathbf{u}_d$ are, respectively, the velocities of incident and reflected particles, $u_{cn}$ is the component of the velocity normal to the surface, $T_{dkl}^{cij}(\mathbf{u}_c, \mathbf{u}_d)$ is the scattering function (the boundary transform). In the absence of the adsorption on the surface, the scattering function is normalized in the half-space of the velocity $u_{cn} > 0$:

$$\sum_{cij} \int_{u_{cn}>0} T_{dkl}^{cij}(\mathbf{u}_c, \mathbf{u}_d) \, d\mathbf{u}_d = 1.$$

Multiplying the boundary conditions (8.4) by the collision invariants of rapid processes, integrating over the half-space of the velocity $u_{cn} > 0$, and summing over the internal states and chemical species of incident particles, we obtain the boundary conditions for the corresponding macroscopic parameters (while deriving the conditions for $n_{ci}$, we perform the summation only over the rotational levels).

The form of the scattering function depends on the surface properties. Various types of the gas–surface interaction are discussed in the monograph [105]. One of the most popular approximations for the scattering function was proposed by Maxwell for the specular-diffusive reflection. It is constructed under the assumption that some part of molecules $(1 - \sigma)$ is reflected specularly, whereas the remaining part $\sigma$ undergoes diffusive reflection. On the basis of the Maxwell scattering function, the accommodation coefficients for the momentum, translational, and internal

energy, associated with the fractions of the momentum and energy transferred to the surface by incident particles, are often introduced.

The equations (8.1)–(8.3) represent the general system of governing equations for a flat stationary flow in the boundary layer in the state-to-state approach. A numerical simulation of this system encounters substantial difficulties, since it requires the solution of a large number of equations and calculation of the state-dependent transport coefficient in each cell of the numerical mesh. In the studies [15, 14, 13, 48, 16], an approximate method is proposed for the investigation of the state-to-state kinetics in the boundary layer. A flow in the vicinity of the stagnation point is considered on the basis of the simplified equations for fluid dynamics, and the transport coefficients are expressed in terms of the viscosity coefficient and constant Prandtl and Schmidt numbers:

$$\mathrm{Pr} = \frac{\eta\, c_p}{\lambda'} = \mathrm{const}, \qquad \mathrm{Sc}_{cidk} = \frac{\eta}{\rho D_{cidk}} = \mathrm{Sc} = \mathrm{const}.$$

In Refs. [17, 12, 153], the vibrational distributions and the gas-dynamic parameters obtained within this simplified approach are used to evaluate the state-specific transport coefficients and the heat flux calculated using the rigorous formulae of the kinetic theory.

Using the Lees-Dorodnitsyn coordinate transformation for the flat flow

$$\xi = \int_0^x \rho_e \eta_e v_e dx, \qquad \eta = \frac{v_e}{\sqrt{2\xi}} \int_0^y \rho dy$$

makes it possible to reduce the boundary layer equations in the vicinity of the stagnation point to one-dimensional equations. In an $A_2/A$ binary mixture, the set of simplified equations for the mass fractions $Y_i$ of molecules at different vibrational levels ($i = 0, ..., L$) and atoms ($i = L+1$), and dimensionless temperature $\vartheta = T/T_e$ takes the form:

$$Y_i'' + f\,\mathrm{Sc}\,Y_i' = S_i, \quad i = 0, ..., L+1, \tag{8.5}$$

$$\vartheta'' + f\,\mathrm{Pr}\,\vartheta' = S_T. \tag{8.6}$$

The derivatives are calculated with respect to the co-ordinate $\eta$ normal to the surface; $f$ is the stream function, which, in the vicinity of the stagnation point, can be approximated by a polynomial in $\eta$ [14]. The right-hand sides $S_i$, $S_T$ in the equations (8.5), (8.6) are given in Refs. [15, 14, 13, 48, 16] for various mixtures. At the external edge of the boundary layer, the gas-dynamic parameters $T = T_e$, $p = p_e$, and $\rho = \rho_e$ are fixed, as well as the velocity gradient along the surface $\beta = dv_e/dx$; the vibrational distributions are assumed to be equilibrium with the temperature $T_e$. At the surface, the no-slip velocity condition is imposed, the temperature is fixed at $T = T_s$. In this study, the slip velocity and the temperature jump are neglected. On the basis of this approach, non-equilibrium flows in the boundary layer near both non-catalytic and catalytic surface are evaluated, and various catalytic mechanisms are considered. The results are discussed in the following Sections.

## 8.2   A Flow of $N_2/N$ Mixture Near the Non-catalytic Surface

In this Section, we study a flow of an $N_2/N$ binary mixture in the vicinity of the stagnation point. The VV, VT vibrational energy transitions, dissociation, and recombination are taken into account:

$$N_2(i+1) + N_2(k) \rightleftharpoons N_2(i) + N_2(k+1), \tag{8.7}$$

$$N_2(i) + N_2 \rightleftharpoons N_2(i-1) + N_2, \tag{8.8}$$

$$N_2(i) + N \rightleftharpoons N_2(i') + N, \tag{8.9}$$

$$N_2(i) + M \rightleftharpoons N + N + M. \tag{8.10}$$
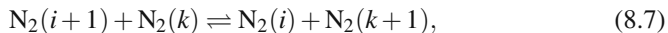
The rate coefficients for the processes (8.7)–(8.9) are given in Section 6.1, multi-quantum VT transitions in collisions with atoms are taken into account, dissociation and recombination are described using the ladder-climbing model. The boundary conditions for the equations (8.5) in the case of a non-catalytic wall take the form:

$$\left.\frac{\partial Y_i}{\partial \eta}\right|_{\eta=0} = 0, \quad i = 0, ..., 46. \tag{8.11}$$

The non-equilibrium vibrational and chemical kinetics in such a flow is studied in Refs. [15, 14] with the use of the simplified fluid dynamic equations (8.5), (8.6) and constant Prandtl and Schmidt numbers ($Sc = 0.49$, $Pr = 0.71$).

Figure 8.1 presents the populations of $N_2$ vibrational levels for various distances from the wall: at the surface $\eta = 0$, whereas at the external boundary layer edge $\eta = 4$. We can point out the essentially non-equilibrium shape of the vibrational distributions, especially close to the wall, where recombination perturbs the vibrational level populations appreciably. It can be seen from the comparison of the results obtained using the complete reaction scheme (8.7)–(8.10) (VV, VT transitions, recombination, and dissociation), and a simplified scheme neglecting VV exchanges and recombination. The important role of recombination can also be seen in Fig. 8.2, which presents the molar fraction of atoms calculated taking into account all kinetic processes (8.7)–(8.10) and neglecting VV transitions and recombination. We can see a substantial decrease in the number density of atoms $n_a$ in the vicinity of the cold wall as a result of recombination. The effect of these processes on the temperature distribution across the boundary layer is insignificant.

The values for the vibrational level populations, number densities of chemical species, and temperature found for different $\eta$, are used in the study [17] for the calculation of the state-dependent transport coefficients and heat flux along the stagnation line. To this end, the obtained values for the macroscopic flow parameters are substituted into the accurate expressions for the diffusion and thermal conductivity coefficients given in Chapter 5. In order to calculate the diffusion velocity
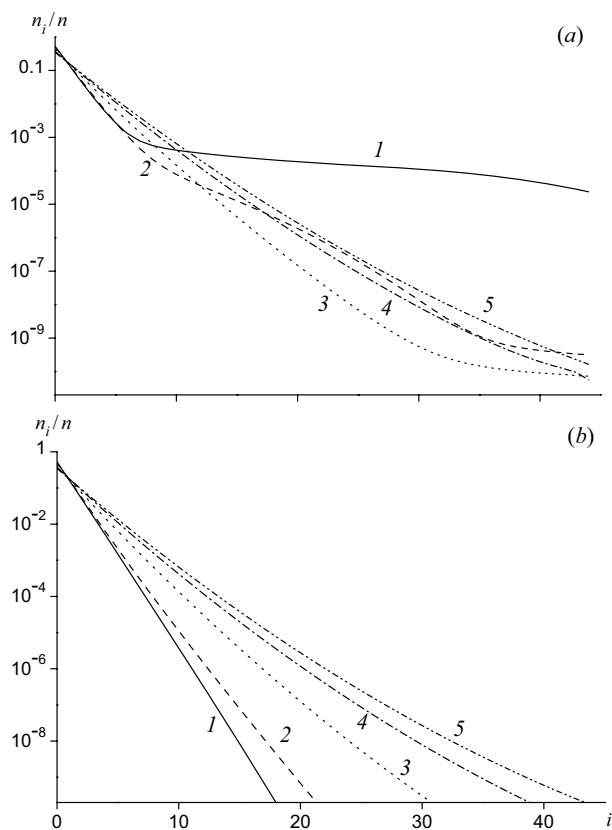
**Fig. 8.1** The vibrational level populations in a boundary layer for different $\eta$. *(a)* all reactions; *(b)* recombination and VV exchange are neglected. N$_2$, $T_e = 5000$, $T_s = 300$ K, $p_e = 1000$ Pa, $\beta = 5000$ s$^{-1}$. The curves *1*: $\eta = 0$; *2*: $\eta = 1$; *3*: $\eta = 2$; *4*: $\eta = 3$; *5*: $\eta = 4$

and heat flux, the simplified expressions obtained in the previous section for the boundary layer approximation are applied. The estimates for the transport coefficients show that the thermal conductivity coefficient increases with the temperature from the body surface towards the external edge of the boundary layer. The effect of VV transitions and recombination on $\lambda'$ is small. The coefficients of thermal diffusion are essentially smaller than those of mass diffusion, whereas the self-diffusion coefficient for atoms substantially exceeds the coefficients $D_{ma}$ and $D_{mm}$. The non-equilibrium vibrational distributions make the most important contribution to the coefficients $D_{ii}$, which increase with the quantum number $i$. The coefficients $D_{mm}$, $D_{ma}$, and $D_{aa}$ practically do not depend on $n_i$ and are specified by the gas temperature and number densities of molecular and atomic species. A similar behavior of these coefficients is found in the case of weak deviations from the equilibrium.
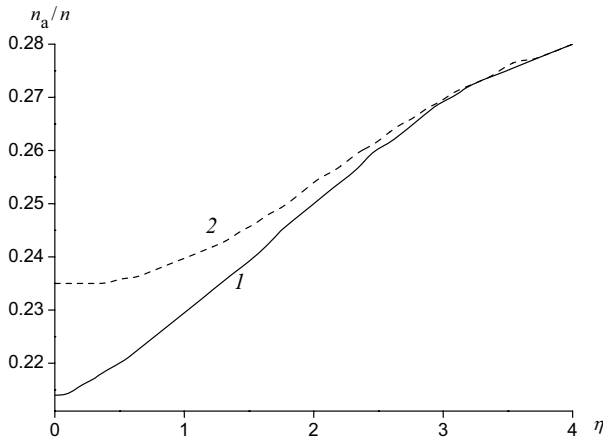
**Fig. 8.2** The molar fraction of atoms as a function of $\eta$. The curve *1*: all reactions; *2*: recombination and VV exchange are neglected
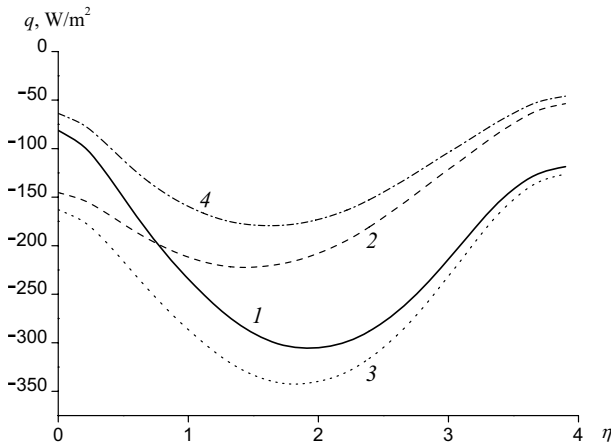


**Fig. 8.3** The heat flux $q$ as a function of $\eta$. The curve *1*: the total heat flux; *2*: the Fourier flux; *3*: the heat flux neglecting thermal diffusion; *4*: the heat flux neglecting mass diffusion

The heat flux $q$ is plotted in Fig. 8.3 as a function of the co-ordinate $\eta$ [1]. The total energy flux $q$ is compared to the Fourier flux $q^{HC}$ caused by heat conduction. In order to estimate the role of diffusion processes in the heat transfer, we also calculated the energy flux neglecting diffusion and thermal diffusion. It is interesting to emphasize noticeable competition of the thermal and mass diffusion processes. It is commonly assumed that the effect of thermal diffusion in the boundary layer can be

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[1] It should be noted that in Ref. [17] the heat flux is calculated using the derivatives with respect to the co-ordinate $\eta$ rather than $y$. In order to obtain the actual values for the heat flux, one should multiply the plotted values by the factor $\sqrt{\rho_e v_e / \mu_e}$. Thereby, the actual heat flux is about 1000 times higher than that presented in Figs. 8.3–8.5, 8.11–8.14
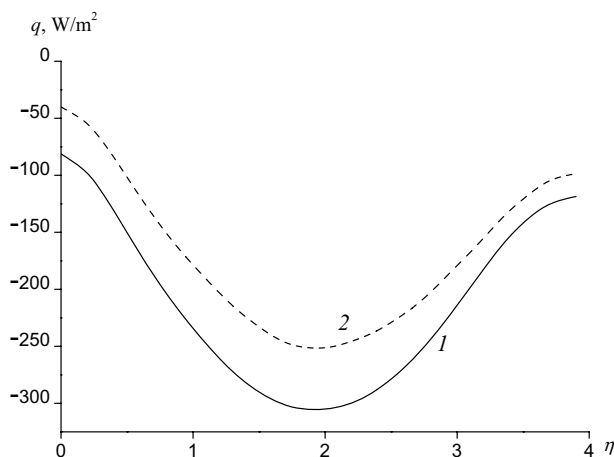
**Fig. 8.4** The heat flux $q$ as a function of $\eta$. The curve *1* displays $q$ for all reactions; *2*: recombination and VV exchange are neglected

neglected since the thermal diffusion coefficients are small. However, the estimates show that close to the wall the thermal diffusion plays an important role in the heat transfer, reducing the heat flux by the factor of two- to three; this effect decreases to 3–5% near the external edge. The significant contribution of thermal diffusion (despite the small values for the thermal diffusion coefficients) is explained by the high temperature gradient near the surface. The mass diffusion tends to increase the heat flux, its contribution rises from 1% close to the wall up to 60–65% at the external edge of the boundary layer.

The important effect of recombination and VV transitions on the total energy flux can be seen in Fig. 8.4. It should be noted that the heat flux $q^{HC}$ caused by the heat conduction is approximately the same regardless to taking into account or neglecting recombination and VV exchange; consequently, recombination influences mainly the diffusive part of the heat flux.

Figure 8.5 presents the comparison of the heat flux calculated using the non-equilibrium state-to-state distributions with that obtained on the basis of the one-temperature Boltzmann distribution. The maximum discrepancy is about 18–20% in the region of strong vibrational non-equilibrium close to the surface. Near the external edge, the distributions approach to equilibrium, and the difference between $q$ and $q^{eq}$ decreases.

It should be pointed out that the results discussed above are obtained using the simplified set of governing equations (8.5), (8.6), and constant Prandtl and Schmidt numbers. Although such an approach is not completely self-consistent, since the flow parameters and transport terms remain uncoupled, it can still be considered as the first attempt to estimate the influence of the state-to-state kinetics on the flow parameters and wall heat transfer. Recently, a similar N$_2$/N flow was studied in Ref. [204] within a more rigorous model incorporating the transport algorithms developed in Chapter 5 into the boundary layer equations. In this paper, the accurate
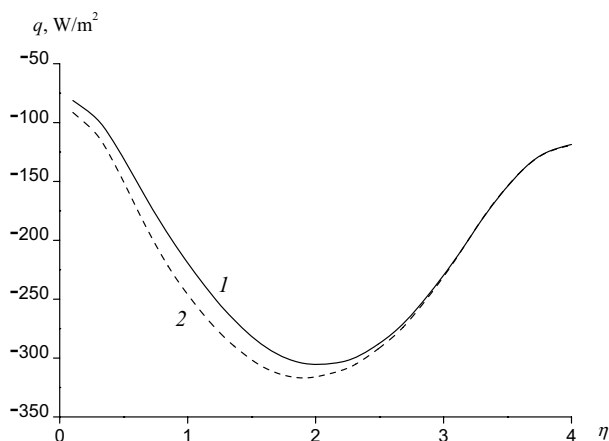
**Fig. 8.5** The heat flux $q$ as a function of $\eta$. The curve *1* represents the state-to-state approach; *2*: the one-temperature approach

set of the fluid dynamic equations was solved, and the results are compared to those obtained within the simplified formulation of the problem (8.5), (8.6). Thereby, for the first time, the state-to-state kinetics and transport properties were coupled self-consistently, and the role of the detailed vibrational kinetics in the heat transfer was estimated.

## 8.3  A Flow of O₂/O Mixture Near the Catalytic Surfaces

A heterogeneous chemical reaction appears to be a substantially more complex physical-chemical process than a gas-phase reaction. It includes several elementary stages: the adsorption-desorption of particles by the surface, the diffusion of adatoms (atoms adsorbed by the surface), the interaction of adatoms with gas-phase particles, the relaxation of the energy released during recombination, etc. A simple phenomenological theory of heterogeneous recombination, as well as a review of experimental techniques used to measure the recombination probability $\gamma_{rec}$ for different surfaces, and a set of experimental data for $\gamma_{rec}$ can be found, for instance, in the monograph [20]. In most studies, two main mechanisms of heterogeneous recombination are distinguished. According to the Eley-Rideal mechanism, a molecule is formed as a result of the interaction of a gas-phase particle impinging the surface, with an adatom; the Langmuir-Hinshelwood mechanism assumes that two adatoms recombine at the surface. Only a few studies (see [117, 199, 102, 43, 42]) present theoretical modeling for the rate coefficients for heterogeneous recombination. We can mention [43, 42], where the recombination rate coefficients for several particular systems are obtained using trajectory calculations based on semi-classical methods. In total, the heterogeneous recombination rate coefficients have been studied rather poorly.

In this Section, we consider a flow of a binary $O_2$/O mixture near a catalytic silica surface on the basis of the results obtained in Refs. [16, 153]. The problem is similar to that considered in the previous Section: the set of governing equations (8.5), (8.6) is solved in the vicinity of the stagnation point. In addition to the gas-phase processes (VV, VT transitions, dissociation, and recombination)

$$O_2(i) + O_2(k) \rightleftharpoons O_2(i-1) + O_2(k+1),$$

$$O_2(i) + O_2 \rightleftharpoons O_2(i-1) + O_2,$$

$$O_2(i) + O \rightleftharpoons O_2(i-1) + O,$$

$$O_2(i) + M \rightleftharpoons O + O + M$$
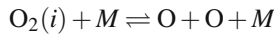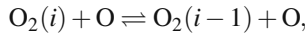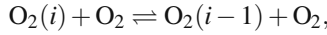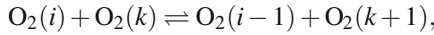
heterogeneous processes are taken into account. First of all, surface reactions occurring in accordance with the Eley-Rideal recombination mechanism [42, 16]

$$O + O^* \rightleftharpoons O_2(i) + \text{surface}, \tag{8.12}$$
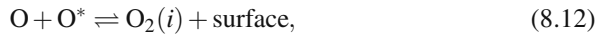
and with the Langmuir-Hinshelwood mechanism [42, 16]

$$O^* + O^* \rightleftharpoons O_2(i) + \text{surface} \tag{8.13}$$
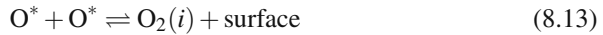
are included in the reaction scheme ($O^*$ is an oxygen adatom at the surface). Furthermore, the dissociation of molecular oxygen at the surface:

$$O_2(i) + \text{surface} \longrightarrow O + O \tag{8.14}$$

and deactivation of vibrationally excited molecules by the surface

$$O_2(i) + \text{surface} \rightarrow O_2(i-1) + \text{surface} \tag{8.15}$$
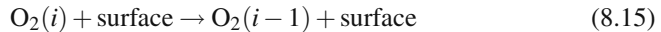
are taken into account.

Now we consider the boundary conditions for the equations (8.5), (8.6). At the external edge, the pressure, temperature, and the velocity gradient are fixed, the species concentrations and vibrational distributions are assumed to be equilibrium at the gas temperature. At the surface, we impose the non-slip condition for the velocity and specify the gas temperature. In such a model, similarly to Ref. [16], the slip velocity and temperature jump at the surface are neglected. The boundary conditions for the mass fractions $Y_i$ are written within the framework of three models.

The model (1) assumes the surface to be catalytic, and takes into account heterogeneous dissociation, recombination, and deactivation of vibrationally excited molecules. In this case, the boundary conditions for $Y_i$ and $Y_O$ were obtained in Ref. [16]:

$$\left.\frac{\partial Y_i}{\partial \eta}\right|_{\eta=0} = \frac{\gamma_i}{D}\sqrt{\frac{kT}{2\pi m}} Y_O - \gamma_{\text{diss}} Y_i - \gamma_{\text{deact}} Y_i + \gamma_{\text{deact}} Y_{i+1}, \quad i = 0, 1, ..., 32, \tag{8.16}$$

$$\left.\frac{\partial Y_O}{\partial \eta}\right|_{\eta=0} = -\frac{\sum_i \gamma_i}{D}\sqrt{\frac{kT}{2\pi m}}Y_O + \sum_i \gamma_{\text{diss}}Y_i, \qquad (8.17)$$

where the recombination coefficient $\gamma_i$ represents the ratio of the number of atoms recombining at the surface to the total number of atoms impinging the wall. The diffusion coefficient $D$ is assumed to be independent of the vibrational state. In the relations (8.16) and (8.17), the first term describes recombination at the surface, the second is associated with heterogeneous dissociation, whereas the third and the fourth terms are connected to the deactivation of molecules by the surface.

The model (2) also supposes that the surface is catalytic, however, it includes only heterogeneous recombination (forward processes in the reactions (8.12)–(8.14)). In this case,

$$\left.\frac{\partial Y_i}{\partial \eta}\right|_{\eta=0} = \frac{\gamma_i}{D}\sqrt{\frac{kT}{2\pi m}}Y_O, \qquad i = 0, 1, ..., 32, \qquad (8.18)$$

$$\left.\frac{\partial Y_O}{\partial \eta}\right|_{\eta=0} = -\frac{\sum_i \gamma_i}{D}\sqrt{\frac{kT}{2\pi m}}Y_O. \qquad (8.19)$$

Finally, in the model (3), the surface is non-catalytic, and the boundary conditions are given by Eqs. (8.11).

The non-equilibrium kinetics for such a problem was studied in Ref. [16] for the following boundary conditions: $T_e = 7000$ K, $p_e = 1000$ Pa, $T_s = 1000$ K. Later on, the influence of the state-to-state kinetics and recombination model on the heat transfer was estimated in Ref. [153]. In these studies, the rate coefficients for the vibrational energy transitions in the gas phase are calculated using the approximate expressions given in Ref. [48], the dissociation rate coefficients are given by the ladder-climbing model, whereas the recombination rate coefficients are obtained using the detailed balance principle. For silica surfaces, the probability for heterogeneous oxygen recombination to any vibrational state, as well as the probability for dissociation $\gamma_{\text{diss}}$ and deactivation $\gamma_{\text{deact}}$ are calculated in the studies [43, 42, 16] using the semi-classical method. In the previous studies [72, 43], it was assumed that molecules can occur only at several vibrational levels as a result of near-resonant exchange between the excited electronic states, which are formed at the beginning of the recombination process, and selected vibrational levels of the ground electronic state. For such a model, the dissipative properties of a flow were studied in Ref. [12] where the reaction (8.15) and heterogeneous dissociation were neglected.

Let us discuss some results obtained in Refs. [16, 153]. Figures 8.6–8.8 present the non-equilibrium state-to-state vibrational distributions obtained within the models (1)–(3) for different $\eta$. The plots illustrate the evolution of the vibrational distributions across the boundary layer, from the strongly non-equilibrium distributions at the surface ($\eta = 0$) to the equilibrium Boltzmann distribution in the external flow ($\eta = 8$). It is seen that close to the wall, the shapes of the distributions obtained for different models appear to be substantially different. For the non-catalytic surface, the level populations are appreciably smaller than those for the catalytic wall; the plateau in the distribution is formed due to the recombination in the gas phase. For
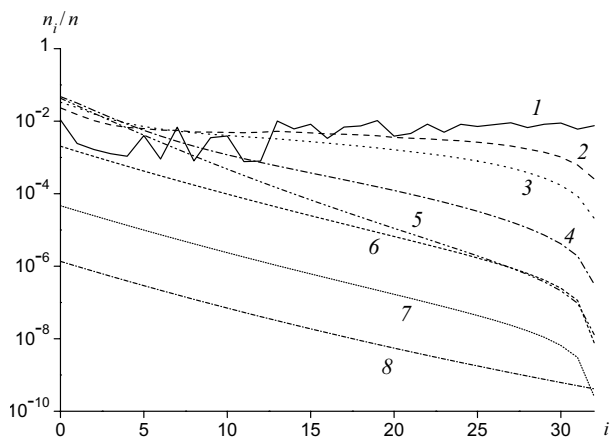
**Fig. 8.6** The vibrational level populations in a boundary layer for different $\eta$. $O_2$, $T_e = 7000$ K, $T_s = 1000$ K, $p_e = 1000$ Pa. The model (1) (all heterogeneous processes are taken into account, see the conditions (8.16), (8.17)). The curve *1*: $\eta = 0$; *2*: $\eta = 0.1$; *3*: $\eta = 0.2$; *4*: $\eta = 0.5$; *5*: $\eta = 1$; *6*: $\eta = 4$; *7*: $\eta = 6$; *8*: $\eta = 8$
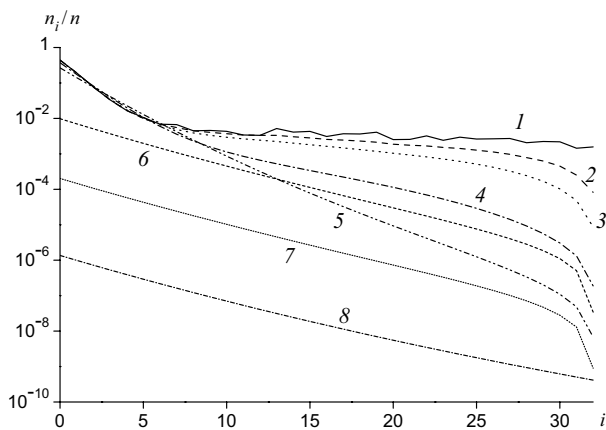


**Fig. 8.7** The vibrational level populations in a boundary layer at different $\eta$. The model (2) (Eqs. (8.18), (8.19)). The curve *1*: $\eta = 0$; *2*: $\eta = 0.1$; *3*: $\eta = 0.2$; *4*: $\eta = 0.5$; *5*: $\eta = 1$; *6*: $\eta = 4$; *7*: $\eta = 6$; *8*: $\eta = 8$

the catalytic surface, heterogeneous dissociation plays an important role; neglecting this reaction results in the level populations overestimated by more than an order of magnitude, and in the different shape of the distributions.

As is noted in [16], deactivation of the vibrational states (8.15) weakly affects the shape of the distribution. The non-monotonic behavior of the distribution at $\eta = 0$ is explained by the non-monotonic dependence of the probability for surface recombination on the vibrational quantum number.
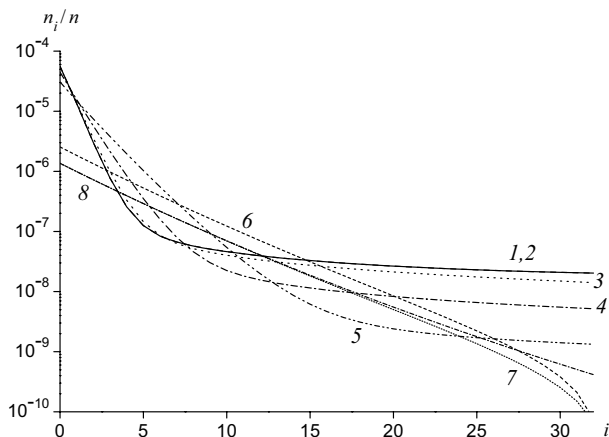
**Fig. 8.8** The vibrational level populations in a boundary layer at different $\eta$. The model (3) (non-catalytic surface). The curve $1$: $\eta = 0$; $2$: $\eta = 0.1$; $3$: $\eta = 0.2$; $4$: $\eta = 0.5$; $5$: $\eta = 1$; $6$: $\eta = 4$; $7$: $\eta = 6$; $8$: $\eta = 8$

Figures 8.9, 8.10 present the gas temperature and mass fraction of oxygen molecules across the boundary layer found within the above three models. In the case of the complete kinetic scheme (8.12)–(8.15), the temperature near the surface exceeds those in two other cases, since recombination and deactivation are usually accompanied by energy release. In the case of a non-catalytic surface, the concentration of molecules is very small compared to $Y_{O_2}$ calculated within two other models. The comparison between the curves $1$ and $2$ illustrates the competition of the dissociation and recombination near the surface: neglecting the heterogeneous dissociation results in overestimated $O_2$ concentration.
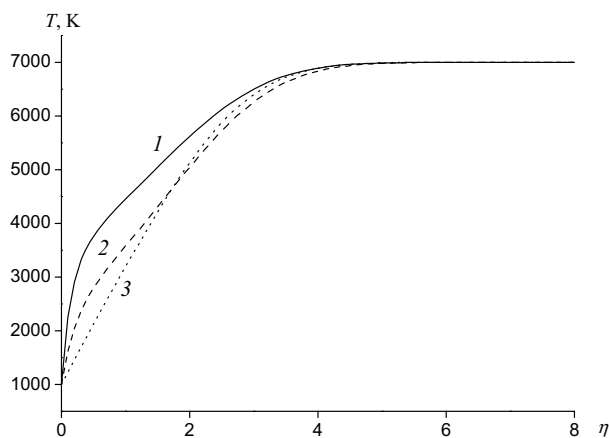


**Fig. 8.9** The gas temperature $T$ as a function of $\eta$. The curves $1$–$3$ correspond to the models (1), (2), (3), respectively
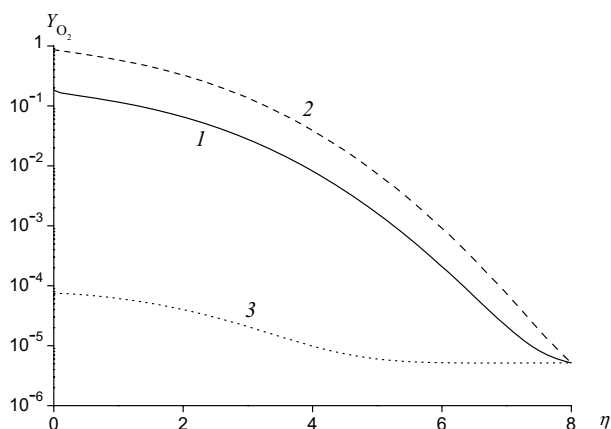
**Fig. 8.10** The mass fraction of $O_2$ as a function of $\eta$. The curves *1–3* correspond to the models (1), (2), (3), respectively

The vibrational level populations, atomic number densities, and gas temperature calculated in Ref. [16] along the stagnation line were used in the study [153] to estimate the thermal conductivity and diffusion coefficients, heat flux, and averaged dissociation rate coefficient. Below, we discuss the revealed influence of the strongly non-equilibrium distributions in the boundary layer on the heat transfer and dissociation rate.

Figures 8.11, 8.12 present the total heat flux and the Fourier flux due to heat conduction, calculated within three models for the surface catalycity[2]. We can see that close to the wall, the complete kinetic scheme (1) yields qualitatively different behavior of the heat flux. Moreover, the absolute value for $q$ in this model at $\eta \sim 0$ exceeds substantially the corresponding values within the other models. Note that at $\eta > 1$, the solutions obtained within the models (1) and (3) become close to each other, whereas the solution found within the model (2) considerably deviates from them even with rising $\eta$.

Such a discrepancy is explained by the diffusion processes, since the Fourier fluxes associated to the thermal conductivity practically coincide for both models at $\eta > 1$. For the non-catalytic wall, the total heat flux is approximately equal to the Fourier flux (within the accuracy of 1%), which indicates a minor contribution of the diffusion processes to the heat transfer in the considered case (in contrast to that analyzed in Section 8.2, for which the role of diffusion was noticeable even for the non-catalytic surface).

We would like to emphasize the importance of simultaneous consideration of recombination and dissociation at the surface. Indeed, heterogeneous recombination substantially increases the concentration of molecules in a mixture, and, in the absence of the reverse process, results in a sharp variation of the concentrations at $\eta \sim 0$ (see Fig. 8.10). Neglecting dissociation at the surface we overestimate the

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[2] See the footnote in page 209.
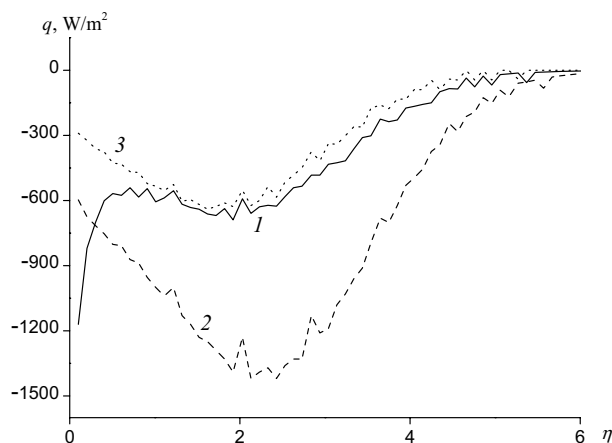
**Fig. 8.11** The heat flux $q$ as a function of $\eta$. The curves *1–3* correspond to the models (1), (2), (3), respectively
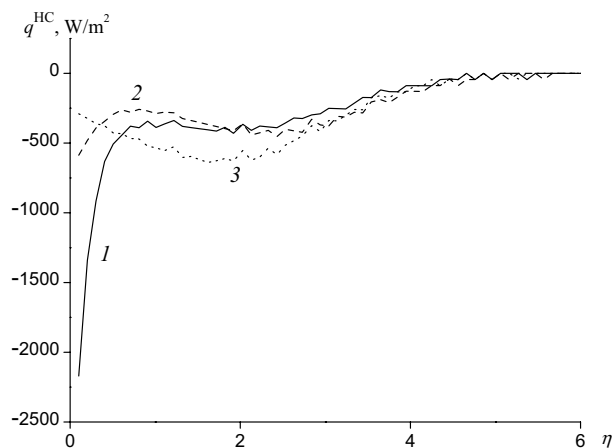


**Fig. 8.12** The Fourier flux $q^{HC}$ as function of $\eta$. The curves *1–3* correspond to the models (1), (2), (3), respectively

role of diffusion in the heat transfer. It is seen from Figs. 8.13, 8.14, where the contribution of various dissipative processes to the total heat flux is analyzed for the models (1) and (2). In contrast to the results obtained for the $N_2/N$ mixture, in the considered case the effect of thermal diffusion is rather insignificant (its contribution does not exceed 5–7%). For the complete kinetic model (1), the contribution of mass diffusion of atoms to the heat transfer also appears to be insignificant, and the main role belongs to the processes of heat conduction and diffusion of vibrational energy. Near the wall, these processes strongly compete. For the model (2), the contribution of all the processes is approximately the same, which confirms that neglecting heterogeneous dissociation results in overestimation of mass diffusion.
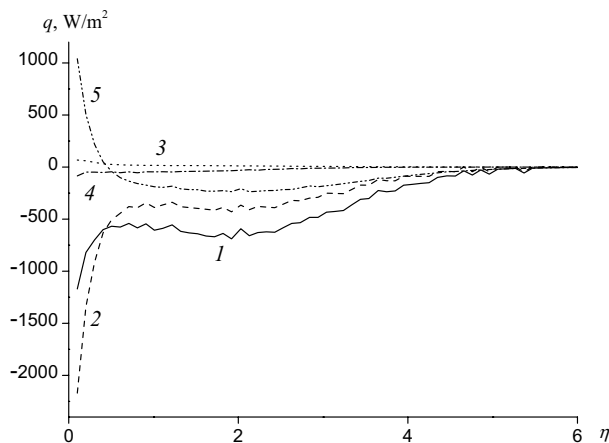
**Fig. 8.13** The contribution of various processes to the heat flux for the model (1). The curve *1* displays the total heat flux; *2* the Fourier flux; *3* the heat flux due to thermal diffusion; *4* the heat flux due to mass diffusion of atoms; *5* the flux due to diffusion of the vibrational energy
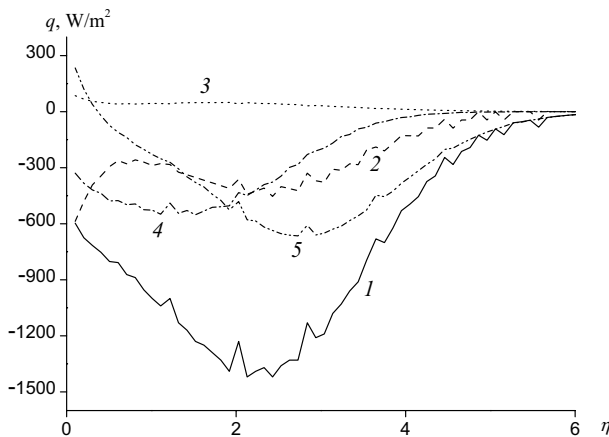


**Fig. 8.14** The contribution of various processes to the heat flux for the model (2). The curve *1* displays the total flux $q$; *2*: $q^{\mathrm{HC}}$; *3*: $q^{\mathrm{TD}}$; *4*: $q^{\mathrm{MD}}$; *5*: $q^{\mathrm{DVE}}$

To calculate the averaged dissociation rate coefficient $k_{\mathrm{diss}}(T)$ for different $\eta$, we use the expression (6.18). The state-to-state coefficients $k^d_{i,\mathrm{diss}}$ are calculated within the ladder-climbing model [205, 15]. Figure 8.15 presents the averaged dissociation rate coefficients in the gas phase $k^d_{\mathrm{diss}}$ calculated for the non-equilibrium vibrational distributions using the formula (6.18) compared with the corresponding thermal equilibrium coefficients found with the use of the Arrhenius law (6.20). Figure 8.15 presents the results for the catalytic surface (Model (1)); for the remaining two models, qualitatively similar results are obtained. As in other non-equilibrium flows (see, for instance, Refs. [48, 64, 148] and Fig. 7.5), the behavior
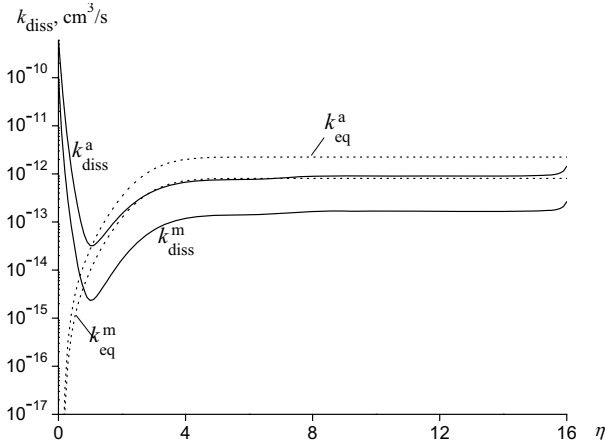
**Fig. 8.15** The averaged dissociation rate coefficients $k_{diss}^d$ and the corresponding equilibrium coefficients $k_{diss,eq}^d$ as functions of $\eta$ for the model (1)

of the dissociation rate coefficients in strongly non-equilibrium areas, where the distributions are far from Boltzmann's, is substantially non-Arrhenius. In the present case, such a dependence is observed in the vicinity of the body surface. While approaching the equilibrium external flow, the averaged dissociation rate coefficients become close to those given by the Arrhenius law.

The surface catalyticity is found to be even more important in the case of metal surfaces. The state-to-state kinetics and heat transfer in the five-component air mixture for different surface materials are studied in Ref. [11].

Thereby, similarly to the case of flows behind strong shock waves, we can conclude that in the boundary layer, the non-equilibrium vibrational distributions significantly influence the energy transfer and dissociation rate. Furthermore, while evaluating the heat flux for catalytic surfaces, it is necessary to account for heterogeneous reactions. The modeling of the state-to-state rate coefficients for chemical reactions and energy transfers occurring as a result of the interaction of gas particles with the surface presents an important and still unsolved problem.

# Chapter 9
# Non-equilibrium Kinetics and Its Influence on the Parameters of Nozzle Flows

Establishing of strongly non-equilibrium conditions in molecular gas flows in nozzles and jets is connected with rapid gas cooling and essential differences between the relaxation times for translational and internal degrees of freedom. Under the conditions of sharp expansion of a preliminarily heated gas, the flow is accelerated, whereas its pressure and temperature drop dramatically. Due to the significant discrepancy between the relaxation rates of the translational and internal modes, the vibrational energy in each elementary volume of a moving gas varies considerably slower than the translational energy, and cannot achieve the value corresponding to the equilibrium state at a local gas temperature. As a result, the vibrational energy appears to exceed translational substantially, and the relaxation processes display the regime of strong vibrational excitation. In expanding flows, the non-equilibrium distributions of molecules over the vibrational levels occur also as a result of chemical reactions, particularly recombination, which becomes more important with a decrease in the temperature.

The necessity to take into account the strongly non-equilibrium kinetics in expanding flows of reacting gases becomes apparent in practical simulations for the flow parameters in high-enthalpy facilities, in the development of gas-dynamic lasers, and in calculations for jet-propulsion engines. In order to select an optimum kinetic model, it is important to study how the non-equilibrium distributions influence the variation of the gas-dynamic parameters and heat transfer. In the present Chapter, we apply the kinetic models considered in Chapters 2–4 to non-equilibrium reacting flows in nozzles. Our consideration is mainly focused on the most rigorous state-to-state approach. In this approximation, we study the non-equilibrium vibrational distributions and gas-dynamic parameters in a gas flow, and estimate its dissipative properties. The obtained solutions are compared with the results based on quasi-stationary distributions, and the influence of the choice of the kinetic model on the gas dynamics and heat transfer is discussed.

## 9.1 Flow Equations, Non-equilibrium Distributions and Macroscopic Parameters

In nozzle flows, several non-equilibrium regimes follow one another. In the pre-chamber, the gas is commonly assumed to be equilibrium. Calculations show that

in the convergent part of a nozzle up to the throat, the gas state is also close to the equilibrium. In an expanding flow behind the throat, the gas undergoes cooling, and the regime of strong non-equilibrium is established, for which the vibrational energy in each elementary gas volume substantially exceeds the translational. Due to the temperature decrease, the rates of physical-chemical processes (energy transitions, dissociation, exchange reactions) become lower, and the frozen regime may occur, when the energy transfer between the various degrees of freedom is terminated.

One of the approximate methods for the simulation of gas flows with physical-chemical processes in nozzles, is that of instantaneous freezing [31, 5], which assumes that the transition from the equilibrium regime to the frozen flow occurs instantaneously. This method was widely used in the 50–60-ies of the last century. Later on, more accurate theoretical models describing the non-equilibrium kinetics in nozzles were developed. Most models are based on the quasi-stationary distributions (see the references in [170, 5], and also the studies [123, 36, 193, 61]). It should be noted, however, that the populations of the vibrational levels in nozzle flows may substantially deviate from the quasi-stationary distributions due to the perturbations caused by chemical reactions. Under such conditions, non-equilibrium distributions vary on the same time scale as the macroscopic flow parameters do, and, as is already mentioned above, the equations for the vibrational level populations in a gas flow should be coupled to the gas-dynamic equations. This approach to the investigation of the kinetics and dynamics in nozzle flows was applied in studies [225, 62, 233, 64, 65, 151], whereas in Refs. [49, 151], the transport processes accounting for the state-to-state kinetics were considered.

Let us write the set of equations characterizing a flow of a non-equilibrium reacting gas mixture in a nozzle using the state-to-state model. Similarly to Chapters 7, 8, for the sake of simplicity, we consider a binary mixture of molecules $A_2$ and atoms A, in which dissociation, recombination, as well as VV and VT vibrational energy transitions may occur. The flow is assumed to be steady-state and quasi-one-dimensional [244], the gas is supposed to be inviscid and non-conductive. We do not consider gas-dynamic aspects connected to the above simplifications, concentrating on the models for the non-equilibrium kinetics and its effect on the flow parameters in a nozzle.

We consider the set of equations (2.21)–(2.23), describing a flow of a multi-component reacting mixture of perfect gases in the state-to-state approach. Taking into account the above assumptions, this system can be rewritten for a nozzle flow in the form [151]:

$$\frac{d}{dx}(n_i vS) = S\left(R_i^{\text{vibr}} + R_i^{\text{diss–rec}}\right), \quad i = 0, 1, ..., L, \tag{9.1}$$

$$\frac{d}{dx}(n_a vS) = -2S\sum_i R_i^{\text{diss–rec}}, \tag{9.2}$$

$$\rho v\frac{dv}{dx} + \frac{dp}{dx} = 0, \tag{9.3}$$

$$\frac{dh}{dx} + v\frac{dv}{dx} = 0, \tag{9.4}$$

where $x$ is the distance from the throat along the nozzle axis, $S(x)$ is the area of the nozzle cross section, the specific enthalpy $h$ is calculated using the expression (7.6), whereas the relaxation terms $R_i^{\text{vibr}}$, $R_i^{\text{diss–rec}}$ are given by the formulae (6.2), (6.3), and (6.11).

The numerical simulation for the equations (9.1)–(9.4) was carried out by a number of authors. In Refs. [64, 49] and [233], flows of $N_2/N$ and $O_2/O$ mixtures in profiled nozzles of a particular shape were studied; in Ref. [65], the state-to-state kinetics of a five-component mixture $N_2$, $O_2$, NO, N, O in a nozzle was considered. In Ref. [151], flows of $N_2/N$ and $O_2/O$ mixtures in a conical nozzle with the half-angle of $15°$ were studied in the state-to-state and quasi-stationary approaches.

Here, in our consideration for the non-equilibrium kinetics, gas dynamics and heat transfer in a conical nozzle we follow the results obtained in Ref. [151]. The flows of $O_2/O$ and $N_2/N$ binary mixtures are considered for the following initial conditions in the reservoir: $T_* = 4000$ K, $p_* = 100$ atm (for $O_2/O$), and $T_* = 7000$ K, $p_* = 100$ atm (for $N_2/N$). In the pre-chamber, the distributions of mixture particles over the chemical species and vibrational levels are supposed to be equilibrium corresponding to the temperature $T_*$ and pressure $p_*$. We use the expressions given in Refs. [14, 48] for the rate coefficients of vibrational energy transitions, the Treanor-Marrone model for those of dissociation, and the detailed balance principle for the recombination rate coefficients. Figures 9.1, $a$ – 9.8, $a$ present the results for the $O_2/O$ mixture, whereas Figures 9.1, $b$ – 9.8, $b$ correspond to the results obtained for the mixture $N_2/N$.

In Fig. 9.1, the dimensionless vibrational level populations $n_i/n$ are given for various nozzle cross sections (for various values of $x/R$, $R$ is the throat radius) as functions of $i$. The Figure shows the evolutions of the initial equilibrium distributions and formation of non-equilibrium non-Boltzmann distributions with a plateau section at intermediate levels. Note that the plateau for the distributions in nitrogen appears to be shorter than that in oxygen.

An important role of recombination in the process of formation of the non-equilibrium distributions in a nozzle is demonstrated in Fig. 9.2. In this Figure, the vibrational distributions of oxygen and nitrogen molecules found in the cross section $x/R = 50$ taking into account dissociation and recombination, only dissociation, or only recombination, as well as neglecting all chemical reactions, are compared. It is seen that dissociation weakly affects the vibrational level populations, whereas taking into account recombination changes the shape of the distributions substantially.

It is interesting to compare the vibrational level populations obtained in the state-to-state approach with the vibrational distributions found in the quasi-stationary approximations. While studying nozzle flows, it is not sufficient to consider the quasi-stationary Treanor distribution (3.14) for the total manifold of vibrational levels since, due to the high supply of the vibrational energy, not only the lowest but also intermediate vibrational levels are significantly populated. Therefore in the present case, the quasi-stationary distribution (3.115) for a single-component gas, as well as its generalization for a mixture with dissociation and recombination proposed in Ref. [61], appear to be more accurate. This distribution coincides with the Treanor distribution only at low levels. At intermediate levels, it displays the plateau
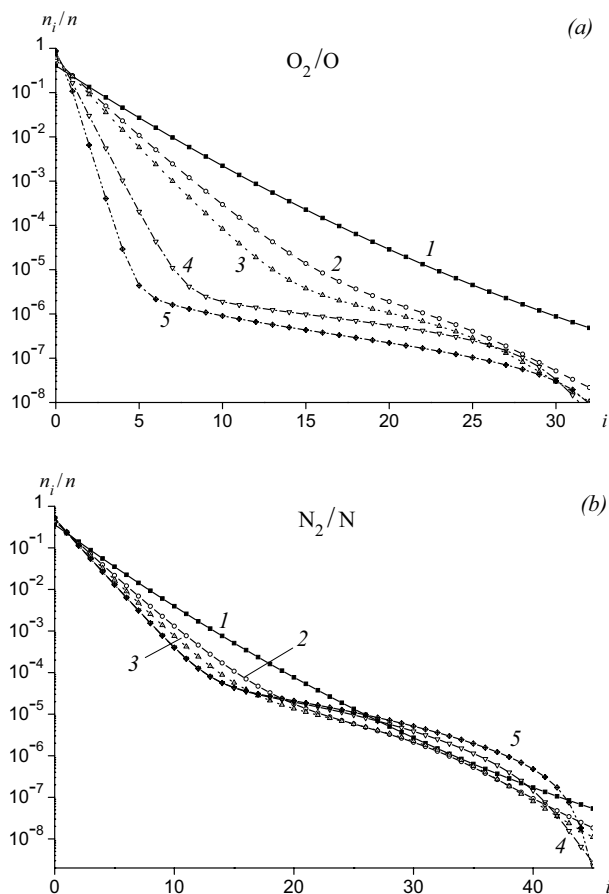
**Fig. 9.1** The vibrational level populations $n_i/n$ as functions of $i$ in various cross sections $x/R$. *a*: $O_2/O$ mixture for $T_* = 4000$ K, $p_* = 100$ atm; *b*: $N_2/N$ mixture at $T_* = 7000$ K, $p_* = 100$ atm. The curves *1*: $x/R = 0$; *2*: $x/R = 1$; *3*: $x/R = 2$; *4*: $x/R = 10$; *5*: $x/R = 50$

shape, and at upper levels, it takes the form of one-temperature Boltzmann distribution. The vibrational level populations in this approach are specified by the number density of molecules $n_m$, gas temperature $T$, and the temperature of the first vibrational level $T_1$. For harmonic oscillators, $T_1 = T_v$, and the distribution (3.115) is reduced to the Boltzmann's with the temperature $T_v$. For the thermal equilibrium case, it takes the form of the Boltzmann distribution with the temperature $T_1 = T_v = T$.

A flow of a dissociating gas mixture in a nozzle was studied using the following four approaches: 1) the state-to-state model, 2) the model based on the two-temperature quasi-stationary combined distribution for anharmonic oscillators (see Section 3.7), 3) the model based on the non-equilibrium Boltzmann distribution for harmonic oscillators, and 4) the thermal equilibrium one-temperature approach. The set of governing equations was written in these four approaches and solved
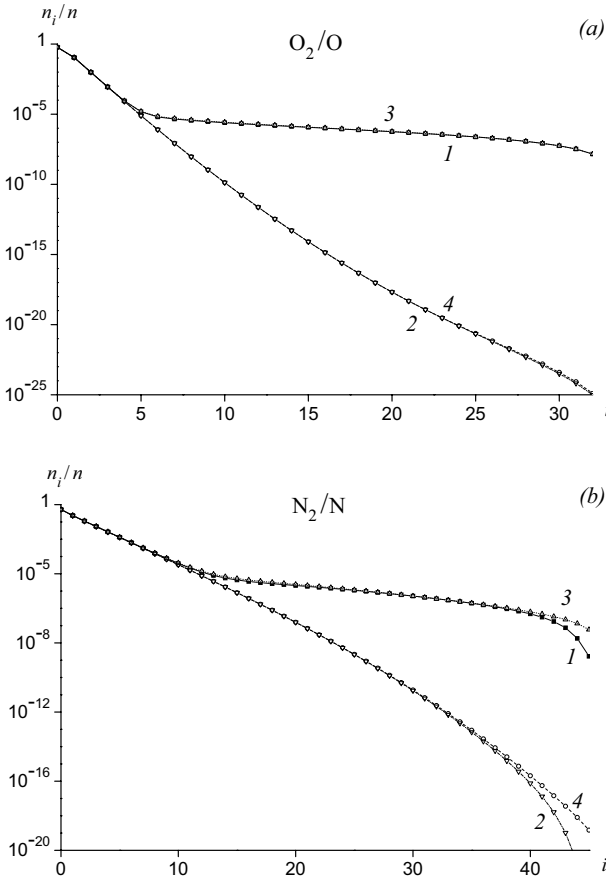
**Fig. 9.2** The vibrational level populations $n_i/n$ as functions of $i$ at $x/R = 50$. In the curve *1*, dissociation and recombination are taken into account; in the curve *2*, only dissociation; in the curve *3*, only recombination; in the curve *4*, both dissociation and recombination are neglected

numerically for the same conditions in the nozzle reservoir. Let us analyze the vibrational distributions and macroscopic flow parameters obtained within the four models.

Figure 9.3 presents the comparison between the state-to-state, quasi-stationary non-Boltzmann's (3.115), non-equilibrium Boltzmann's, and thermal equilibrium vibrational distributions in the cross section $x/R = 50$.

We can see a noticeable discrepancy between the distributions obtained for different approaches. The thermal equilibrium approach underestimates the vibrational level populations for both $O_2$ and $N_2$. The quasi-stationary distributions are close to those obtained in the state-to-state approach for several low states, however, with the increase in $i$, the difference increases rapidly.
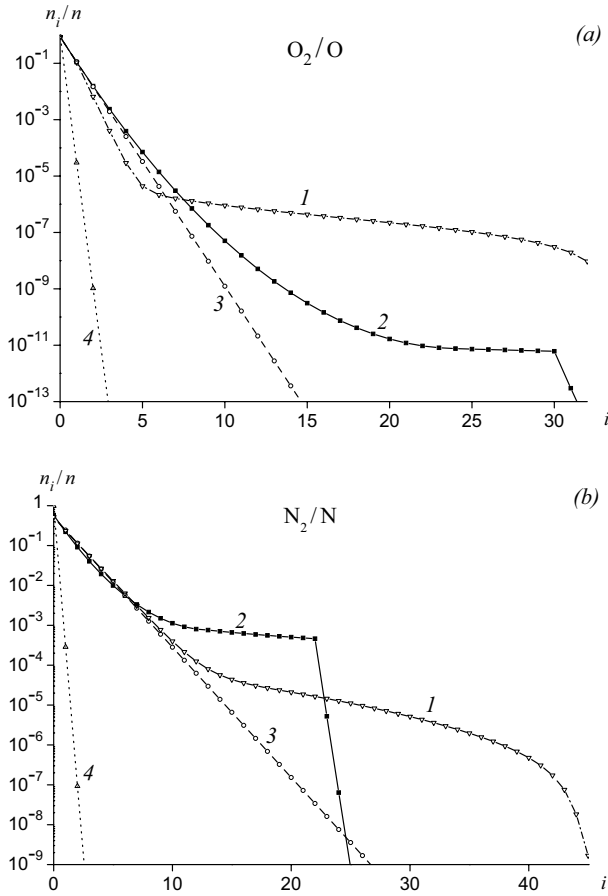
**Fig. 9.3** The vibrational level populations $n_i/n$ as functions of $i$ at $x/R = 50$ in different approaches. The curves *1–4* correspond to the state-to-state, two-temperature (anharmonic oscillators), two-temperature (harmonic oscillator), and one-temperature model, respectively

The values of the temperatures $T$ and $T_1$ calculated in different approaches appear to be appreciably closer to each other than the distributions (in the state-to-state approach, the temperature $T_1$ is calculated with the formula $T_1 = \varepsilon_1/[k\ln(n_0/n_1)]$) (see Ref. [242]).

As we can see from Fig. 9.4, the gas temperature calculated within the state-to-state model slightly deviates from that found in the quasi-stationary approaches: the maximum discrepancy does not exceed 2% for anharmonic oscillators and 4% for harmonic oscillators. The one-temperature approach yields a larger deviation, with the maximum difference from the state-to-state results reaching 40–50% for the mixture $O_2/O$. The temperatures of the vibrational degrees of freedom $T_v$ and $T_1$ in the mixture $O_2/O$ calculated in the quasi-stationary approaches practically
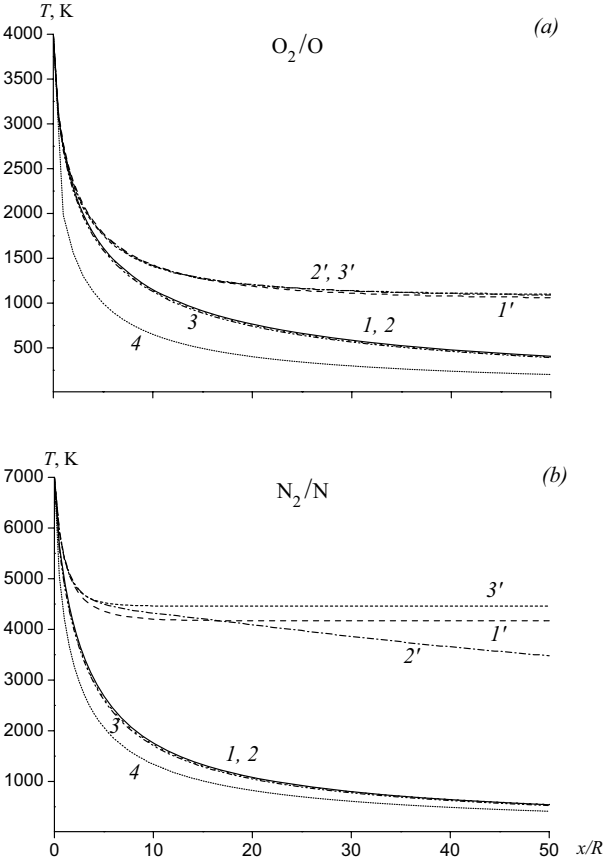
**Fig. 9.4** The gas temperature $T$ and vibrational temperatures $T_1$ ($T_v$) as functions of $x/R$ in different approaches. The curves $1$, $1'$ display $T$ and $T_1$ in the state-to-state approach; $2$, $2'$: $T$ and $T_1$ in the two-temperature approach (anharmonic oscillator); $3$, $3'$: $T$ and $T_v$ in the two-temperature approach (harmonic oscillator); $4$: $T$ in the one-temperature approach

coincide with $T_1$ found using the state-to-state flow description, whereas for the mixture $N_2/N$, the discrepancy reaches 10–15%.

The above results indicate that in order to calculate the temperature with a satisfactory accuracy, the quasi-stationary distribution for anharmonic oscillators in the form (3.115), and even the simple non-equilibrium Boltzmann distribution valid for harmonic oscillators, may be used. Such a conclusion is important for practical simulations, since the implementation of quasi-stationary distributions requires substantially lower computational costs than the state-to-state model.

Note that studying a flow behind a shock wave we saw a more substantial effect of the non-equilibrium kinetics on the gas-dynamic flow parameters, in particular, on the gas temperature, than in nozzle flows. This is explained by the fact that the main contribution to the gas-dynamic parameters is made by low vibrational states.

The estimates show that in expanding flows the populations of low vibrational levels found in various approaches differ significantly less than those obtained behind shock waves (see Fig. 7.1 and Fig. 9.3 for comparison).

## 9.2    The Influence of Non-equilibrium Kinetics on Gas Dynamics and Transport Processes

Now we will consider the phenomena of diffusion and heat transfer in nozzle flows, and the influence of non-equilibrium distributions on these processes. For this purpose, we use the kinetic theory for transport processes developed in Chapters 2–5. As is already noted, the transport coefficients in a non-equilibrium gas depend not only on the temperature but also on the populations of all vibrational levels in the state-to-state approach, or on the temperature $T_1$ in the two-temperature approach, as well as on the non-equilibrium concentrations of the chemical species in a mixture. Using a rigorous approach to the solution of the system of governing equations for a viscous conducting gas flow, we should calculate all the transport coefficients at each step of the numerical integration. It is obvious that such a technique requires very high computational costs. Therefore, similarly to Chapters 7–8, we use an approximate method for the evaluation of the dissipative properties: first, the macroscopic flow parameters and their gradients are found from simplified equations, and then, the transport coefficients are calculated using the accurate formulas of the kinetic theory and the obtained values of the macroscopic variables.

For the first time, the dissipative properties of reacting gases in nozzles were studied in the state-to-state approach in Ref. [49]. The comparison of the results found in various approaches is presented in Ref. [151]. Here, we discuss some results of these studies.

Figure 9.5 presents the thermal conductivity coefficient $\lambda'$ at the gradient of the gas temperature $T$ in the expression for the total heat flux, as well as the coefficient $\lambda_v$ appearing at the gradient of the vibrational temperature $T_1$ or $T_v$ in the multi-temperature approaches. The coefficients are calculated within four models: the state-to-state approach, the two-temperature model for anharmonic and harmonic oscillators, and the one-temperature approach. The expressions for the heat flux in various approaches are given by the formulae (2.50), (3.85), and (4.38). The discrepancy between the coefficients obtained in various approaches appears to be more pronounced in the mixture $N_2/N$, since in this case the non-equilibrium factor $T_1/T$ is sufficiently high (the ratio reaches 8 under the considered conditions). Therefore, in the mixture $N_2/N$, the influence of anharmonicity on the coefficients $\lambda'$ and $\lambda_v$ is more important. The one-temperature approach results in underestimation for the coefficient $\lambda'$, although it includes the coefficient $\lambda_v$. This is a consequence of inadequately low temperature found in this approach.

In Fig. 9.6, the heat flux $q$ calculated in the four approaches is presented. The heat flux decreases with $x$, since the gradients of the macroscopic parameters also decrease with the distance from the throat. While the one-temperature model yields underestimated heat flux, the two-temperature quasi-stationary models provide a
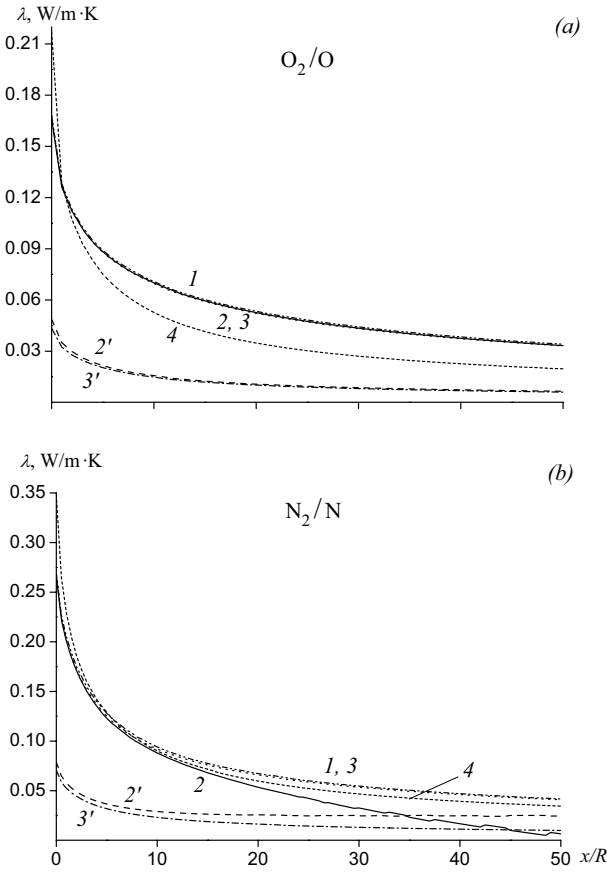
**Fig. 9.5** The thermal conductivity coefficients $\lambda'$, $\lambda_v$ as functions of $x/R$ in different approaches. The curve *1*: the coefficient $\lambda'$ in the state-to-state approach; *2, 2'*: the coefficients $\lambda'$ and $\lambda_v$ in the two-temperature approach (anharmonic oscillator); *3, 3'*: the coefficients $\lambda'$ and $\lambda_v$ in the two-temperature approach (harmonic oscillator); *4*: the coefficient $\lambda'$ in the one-temperature approach

satisfactory accuracy for $q$. For the $N_2/N$ mixture , the deviation of the heat flux found in the non-equilibrium quasi-stationary approaches from that obtained within the most rigorous state-to-state model is 4 and 10% for anharmonic and harmonic oscillators, respectively, and, correspondingly, 7 and 10% for the $O_2/O$ mixture.

The fact that non-equilibrium vibrational distributions essentially do not affect the heat flux seems to be unexpected, especially if we take into account the strong discrepancy between the distributions. If we recall the behavior of the heat flux behind a shock wave (Chapter 7), we will see a strong influence of the vibrational distributions on the heat flux, although the difference in the shape of the state-to-state and quasi-stationary distributions is substantially smaller than that in the case of a nozzle flow.
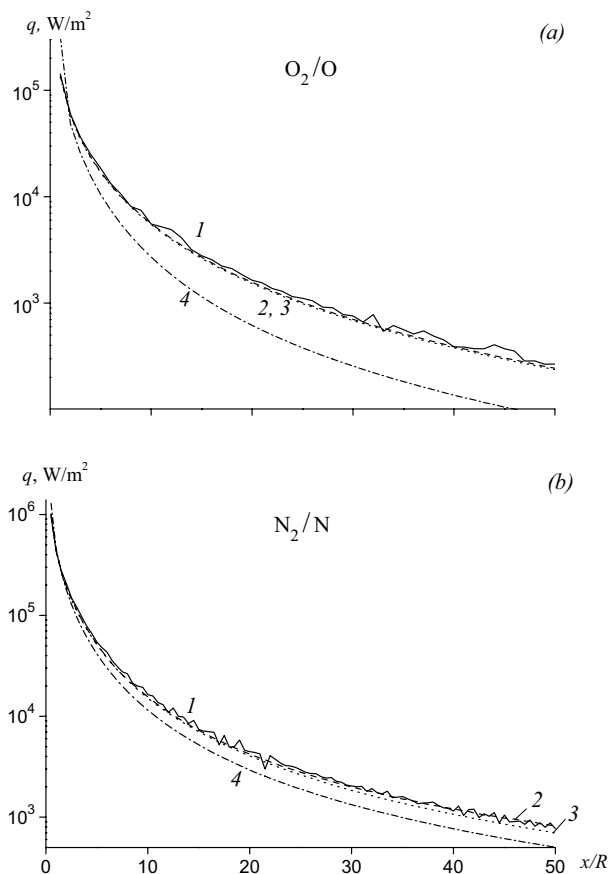
**Fig. 9.6** The heat flux $q$ as a function of $x/R$ in different approaches. The curve *1* represents the state-to-state model; *2* the two-temperature approach for anharmonic oscillators; *3* the two-temperature approach for harmonic oscillators; *4* the one temperature model

In order to understand the reason for such a small influence of the model for the non-equilibrium distributions on the transport properties in a nozzle, we will consider the contribution of different dissipative processes to the total energy flux in the state-to-state approach. In Fig. 9.7, the ratios of the fluxes associated with different processes, to the total heat flux, are compared. The values $q^{HC}/q$, $q^{TD}/q$, $q^{MD}/q$, and $q^{DVE}/q$ are plotted, where $q^{HC}$ is the flux related to heat conduction, $q^{TD}$ is the part of the heat flux associated with thermal diffusion, $q^{MD}$ is the flux caused by mass diffusion of atoms, and, finally, $q^{DVE}$ is the vibrational energy flux connected to diffusion of vibrationally excited molecules. Let us remind that the transport of the vibrational energy due to diffusion occurs only in the state-to-state approach, whereas in the quasi-stationary models, this process is associated with the gradient of the vibrational temperature. We can see that the role of thermal diffusion in
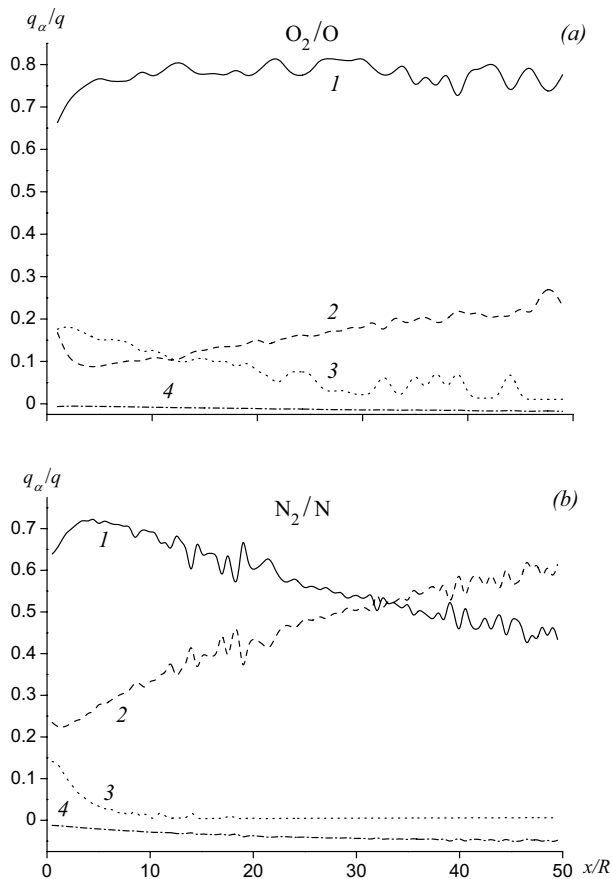
**Fig. 9.7** The contribution of different processes to the heat flux in the state-to-state approach. The curve $1$: $q^{HC}/q$; $2$: $q^{MD}/q$; $3$: $q^{DVE}/q$; $4$: $q^{TD}/q$

the heat transfer is negligible, which confirms again the common kinetic theory assumption of the small contribution of thermal diffusion to transport processes. In the $O_2/O$ mixture under the considered conditions, the heat flux caused by heat conduction is about 70–80% of the total heat flux, whereas the contributions of mass diffusion and that of vibrationally excited molecules are approximately equal in the vicinity of the throat (about 15–20%), and further on, the value of $q^{DVE}$ decreases with $x$. In the $N_2/N$ mixture, there is a competition between the processes of heat conduction and mass diffusion of atoms, whereas the contribution of diffusion of the vibrational energy reaches its maximum of about 15% near the throat, and then decreases rapidly, substantially faster than in the $O_2/O$ mixture. This is a consequence of the fact that under the considered conditions, the vibrational level populations in the $N_2/N$ mixture become frozen appreciably more rapidly than in the $O_2/O$ mixture.

In this connection, it is still unclear why the non-Boltzmann distributions affect the heat flux in a nozzle so weakly. In order to clarify the reasons for such a
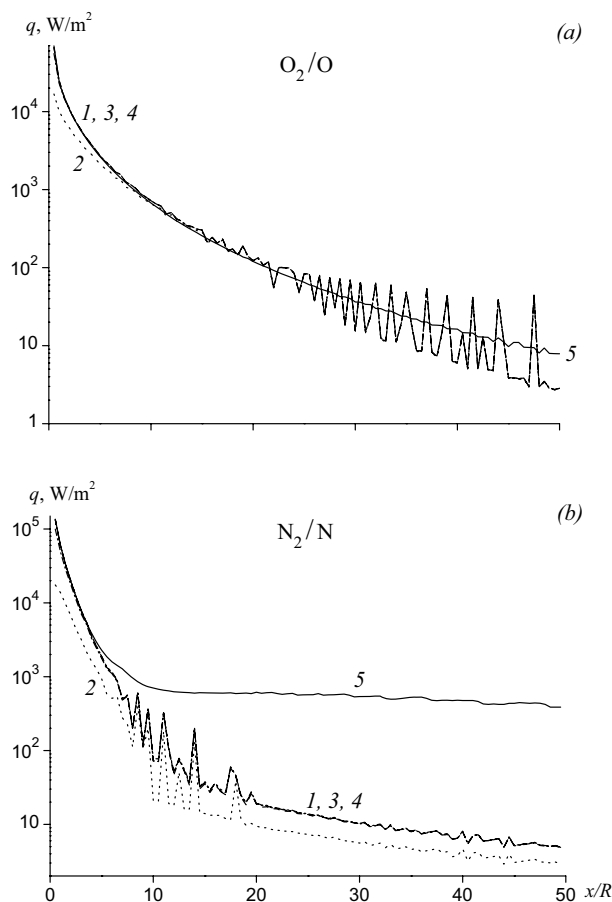
**Fig. 9.8** The flux associated with diffusion of the vibrational energy $q^{DVE}$ and the vibrational energy flux in the two-temperature approach $q_{vibr}$. The curve *1*: $q^{DVE}$, $L = 33\,(46)$; *2*: $L = 5$; *3*: $L = 10$; *4*: $L = 20$; *5*: $q_{vibr}$

peculiarity (and an apparent contradiction), let us estimate the contribution of different vibrational levels to the constituent $q^{DVE}$ of the total heat flux.

Figure 9.8 presents the heat flux associated with diffusion of the vibrational energy calculated taking into account different numbers of vibrational levels. The curves *1* are obtained accounting for all vibrational states (33 for oxygen and 46 for nitrogen), the curves *2–4* correspond to $q^{DVE}$ calculated for 5, 10, and 20 levels, respectively. We can see that only the curves *2* deviate slightly from the precise values. For oxygen, it is sufficient to consider 10 lowest states, whereas for nitrogen, 15–20 levels are required. Thus, the main contribution to the flux $q^{DVE}$ is made by several low vibrational states. Returning to Fig. 9.3, we can notice that for these levels, the state-to-state distributions are close to the quasi-stationary. This makes it possible to conclude that, in the considered case, the flux of the vibrational

energy due to diffusion of excited molecules practically coincides with the vibrational energy flux $q_{\mathrm{vibr}}$ calculated using the expression (3.141), and hence, the relation (5.115) is satisfied approximately. The curves *5* in Fig. 9.8 correspond to the vibrational energy flux $q_{\mathrm{vibr}}$. It is obvious that for the $O_2/O$ mixture, $q_{\mathrm{vibr}}$ is the mean value of $q^{\mathrm{DVE}}$, and our assumption about close values of $q^{\mathrm{DVE}}$ and $q_{\mathrm{vibr}}$ is justified. This explains the fact that the state-to-state and quasi-stationary approaches yield such close results while calculating the heat flux.

The situation is somewhat different for the $N_2/N$ mixture. In this case, $q_{\mathrm{vibr}}$ coincides with $q^{\mathrm{DVE}}$ only in the vicinity of the throat, and then there is a considerable difference between two fluxes. This is due to the discrepancy between the state-to-state and quasi-stationary distributions at intermediate levels ($i = 10 - 20$), which make a significant contribution to the flux $q^{\mathrm{DVE}}$ in nitrogen. However, under the considered conditions, the role of diffusion of the vibrational energy at $x/R > 5$ becomes negligible (see Fig. 9.7, *b*), and in the region of the considerable discrepancy between $q_{\mathrm{vibr}}$ and $q^{\mathrm{DVE}}$, the non-equilibrium state-to-state distributions affect the heat flux only slightly.

It is interesting to note that, in a high-temperature gas flow behind a shock wave, a significant difference between the heat fluxes calculated using the state-to-state and quasi-stationary approaches, is found. It is explained by the fact that the vibrational distributions behind the shock front calculated within the state-to-state and quasi-stationary models, deviate substantially at low levels (see Fig. 7.1). Therefore, the role of diffusion of vibrationally excited molecules becomes substantially more important than that in an expanding supersonic flow.

Thereby, to calculate the macroscopic parameters and to estimate the transport properties in nozzle flows, the two-temperature approach providing a satisfactory accuracy can be used. Nevertheless, to simulate the non-equilibrium distributions, the more detailed and rigorous state-to-state model should be applied. Calculations for the global dissociation rate in nozzle flows performed in Ref. [152] using different approaches show the importance of the state-to-state modeling and a substantial discrepancy between the rates obtained in the state-to-state and quasi-stationary approaches.

# Conclusion

To conclude, the authors will make some remarks. In our book, we developed closed models for strongly non-equilibrium gas flows based on the kinetic theory. We took into account different rates of physical and chemical processes and in accordance with collisional invariants of rapid processes introduced extended sets of determining macroscopic parameters. As a result, for numerous practically important regimes of the non-equilibrium state, the self-consistent systems of equations for macroscopic parameters were derived as well as the relations expressing the stress tensor, diffusion velocities, heat flux, and the rates for non-equilibrium processes in terms of these parameters.

The use of kinetic theory techniques and their generalization for gases with rapid and slow processes resulted in construction of new strict procedures for calculation of transport coefficients in the approximation of state-to-state kinetics and on the basis of quasi-stationary distributions, including the non-Boltzmann ones. In addition to that, we suggested some considerable simplifications for practical application of the constructed procedures and estimated the accuracy for these simplifications. The developed calculation technique for transport coefficients may be used directly in numerical integration of Navier–Stokes equations for strongly non-equilibrium mixtures of reacting gases. Application of the models to flows behind shock waves, in non-equilibrium boundary layers, in a shock layer near a blunt body, in nozzles made it possible to study the effect of non-equilibrium kinetics on gas dynamics and heat transfer.

The principles for construction of theoretical models of transport and relaxation processes in strongly non-equilibrium flows of reacting mixtures of molecular gases stated in our work may be (and partly have already been) applied to a further extension of the range of physical-chemical processes considered in the modeling of real flows.

Thus here we did not discuss mixtures containing molecules that consist of three and more atoms. Modeling of non-equilibrium kinetics and transport in such gases is noticeably complicated by the presence of several vibrational modes in polyatomic molecules and, consequently, by the vast variety of relaxation channels and different rates for intra- and inter-mode exchange of vibrational energy. The basis for the kinetic theory of transport in such mixtures, particularly in those containing carbon dioxide molecules, in the conditions of a strong vibrational non-equilibrium state, was laid in the studies [146, 149]. In [146], non-equilibrium quasi-stationary

distributions in $CO_2$ and their impact on dissipative processes were considered, while in [149, 156] the $CO_2$ kinetics and transport properties in the state-to-state approximation were analyzed.

The further development for the kinetic theory of strongly non-equilibrium gases consisting of complex molecules is very important and promising for the solution of a number of practical problems, such as modeling for the reentry of space vehicles into the atmosphere of Mars and Venus, the improvement of laser and chemical technologies, the study of combustion and detonation processes, the control of the atmospheric pollution etc. Recently the advanced model proposed in Ref. [150] for mixtures containing $CO_2$ was applied for the simulation of a shock layer near a space craft reentering into the Mars atmosphere, and the developed transport algorithms were implemented directly into the computational fluid dynamics schemes [158].

Beyond the range of processes considered in this book are electron excitation, radiation, and ionization. For high temperatures, taking these processes into account becomes a necessity; the construction of justified kinetic models taking them into consideration is challenging for the kinetic theory. In the study [136, 135] on the basis of the approach formulated here, the kinetics, dynamics, and transport processes in gases with non-equilibrium radiation and excited electronic degrees of freedom are analyzed in the frame of the state-to-state approximation.

The modeling of kinetics and dissipative processes in a partially ionized gas is a promising but complicated problem, since the behavior of plasma is specified by relations of a substantially larger number of characteristic scales than required to describe a neutral gas. In addition, the modeling of interaction of charged particles still presents a serious problem.

The development of the transport theory in gases and plasma in the presence of a magnetic field also presents vital practical interest. In these conditions, the transport coefficients are of the tensor nature, which noticeably complicates the calculation for the diffusion velocity, the flux of energy, and the density of electric current.

An important problem of kinetics, which is crucial for the further development and refinement of the transport theory in non-equilibrium gases, is the determination of the cross-sections of inelastic collisions with physical-chemical transformations and of the state-to-state rates for different types of inelastic energy exchange and chemical reactions.

By now, mechanisms of inelastic interaction in collisions of molecules in a gas flow have not been sufficiently studied. No justified data on cross sections for chemically reactive collisions are available; elementary processes of the flow interaction with the surfaces of the streamlined bodies have not been essentially considered. Such models are particularly necessary to calculate heat fluxes and to solve the problem of heat protection for the surfaces of space vehicles.

We have outlined only a few of important issues that should be developed to solve up-to-date problems of physical gas dynamics. The use of fundamental principles of the kinetic theory in the studies of strongly non-equilibrium gas flows in combination with justified models of elementary processes occurring in collisions of molecules specifies a promising approach to the solution of new problems of aerothermodynamics and to the development of new technologies.

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