Vibrational relaxation rates in multi-temperature flows of molecular air species

E.V. Kustova* and G.P. Oblapenko**[†] Saint-Petersburg State University 198504 Universitetskiy pr., 28, Saint Petersburg, Russia * elena_kustova@mail.ru ** kunstmord@kunstmord.com [†]Corresponding author

Abstract

Vibrational relaxation rates are studied within the framework of the Chapman-Enskog method for strongly non-equilibrium multi-temperature flows in the zero-order (non-viscous) and first-order (viscous) approximations for binary mixtures of air species. A modified version of the commonly used Landau-Teller formula is proposed, and comparisons are made with strict kinetic theory calculations. The influence of cross-coupling between dissociation and different slow VT transitions, along with the influence of velocity divergence on the vibrational relaxation rates are considered for N2 and O2 molecules with harmonic vibrational spectra for various ratios of the vibrational and translational temperatures. The limits of applicability of simplified expressions such as the original and modified Landau-Teller formulas are discussed.

1. Introduction

Vibrational relaxation rates are required for the solution of the fluid-dynamic transport equations of thermally and chemically non-equilibrium gas flows. Although a number of models for rates of slow processes in non-equilibrium flows have been developed, they are usually unsuitable for strongly non-equilibrium flows. For reacting viscous flows it is known¹⁻⁴ that cross-coupling between various slow processes (such as chemical reactions and vibrational energy exchanges) arises, however, most existing models of cross-coupling (such as CVDV⁵ and CVCV⁶) are semi-empircal and applicable only to inviscid flows. Therefore, it is of interest to study relaxation rates in viscous flows and estimate the conditions under which simpler models which do not account for flow compressibility and cross-coupling can be used without sacrificing accuracy, and where more strict approaches are needed.

Based on a strict kinetic-theory approach to computation of rates of slow processes in viscous flows,⁷ a simplified method for calculating relaxation rates in multi-temperature flows of harmonic oscillators is developed in the present paper, and the validity of the commonly used Landau–Teller formula describing rates of VT relaxation is investigated for flows with coupling between dissociation and vibrational energy transitions.

1.1 Governing equations

We consider a mixture of molecular and atomic species, accounting for the rotational and vibrational energies of the molecules. The vibrational spectra of the molecules are taken to be harmonic, that, is, the vibrational energy ε_i^c of vibrational state *i* of a molecule of species *c*, when counted from the first level, is given by

$$\varepsilon_i^c = h v_c = i \varepsilon_1^c, \tag{1}$$

where h is the Planck constant and v_c is the species-dependent frequency.

We consider flows with the following relation between characteristic times of microscopic collisional processes:

$$\tau_{tr} < \tau_{rot} < \tau_{VV} \ll \tau_{VV'} < \tau_{VT} < \tau_{react} \sim \vartheta, \tag{2}$$

where τ_{tr} , τ_{rot} , τ_{VV} , τ_{VT} , τ_{react} are the characteristic times of elastic collisions, rotational energy exchanges, VV exchanges of vibrational energy between molecules of the same species, VV' exchanges of vibrational energy between

Copyright © 2015 by E.V. Kustova, G.P. Oblapenko. Published by the EUCASS association with permission.

molecules of different species, VT transitions of vibrational energy into translational, chemical reactions, and ϑ is the gas-dynamic time.

The Boltzmann equation for flows with internal degrees of freedom with both rapid and slow processes takes on the following form

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = \frac{1}{\varepsilon} J_{cij}^{rap} + J_{cij}^{sl},\tag{3}$$

where f_{cij} is the distribution function of particles of species c at the *i*-th vibrational and *j*-th rotational levels, \mathbf{u}_c is the velocity of particles of species c, J_{cij}^{rap} and J_{cij}^{sl} are the integral operators of rapid and slow processes, respectively, $\varepsilon = \tau_{VV}/\vartheta$ is the small parameter in which the distribution function is expanded in the generalized Chapman–Enskog method.

Under condition (2), a multi-temperature approach can be used.^{8,9} The set of macroscopic parameters for such flows, assuming the harmonic oscillator model, is defined via the distribution functions, and is as follows:

$$n_c = \sum_{ij} \int f_{cij} d\mathbf{u}_c, \quad c = 1, \dots, L,$$
(4)

$$\rho \mathbf{v} = \sum_{cij} \int m_c \mathbf{u}_c f_{cij} d\mathbf{u}_c, \tag{5}$$

$$\rho_c E_{vibr,c} = \sum_{ij} \varepsilon_i^c \int f_{cij} d\mathbf{u}_c, \quad c = 1 \dots, L_m,$$
(6)

$$\rho U = \frac{3}{2}nkT + \sum_{c=1}^{L_m} \rho_c E_{rot,c} + \sum_{c=1}^{L_m} \rho_c E_{vibr,c} + \sum_{c=1}^{L} \rho_c E_{f,c} = \sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_j^c + \varepsilon_i^c + \varepsilon_c\right) f_{cij} d\mathbf{u}_c,\tag{7}$$

Here n_c is the number density of particles of species c, \mathbf{v} is the flow velocity, ρ is the mixture density, U is the total energy per unit of mass, ρ_c is the density of particles of species c, L is the number of chemical species in the mixture, and L_m is the number of molecular species, $\mathbf{c}_c = \mathbf{u}_c - \mathbf{v}$ is the peculiar velocity of a particle of species c, ε_c is the formation energy, $E_{rot,c}$, $E_{vibr,c}$, $E_{f,c}$ are the specific rotational, vibrational and formation energies of molecular species c.

Given the above conditions, the transport equations take on the following form:⁹

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c^{react}, \ c = 1, \dots, L,$$
(8)

$$\rho \frac{d\mathbf{v}}{dt} = \nabla \cdot \mathbf{P},\tag{9}$$

$$\rho \frac{dU}{dt} = -\nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v},\tag{10}$$

$$\rho_c \frac{dE_{vibr,c}}{dt} + \nabla \cdot \mathbf{q}_{vibr,c} = R_c^{vibr} - E_{vibr,c} m_c R_c^{react} + E_{vibr,c} \nabla \cdot (\rho_c \mathbf{V}_c), \ c = 1, \dots, L_m,$$
(11)

where \mathbf{V}_c is the diffusion velocity of particles of species c, \mathbf{P} is the stress tensor, \mathbf{q} is the energy flux, $\mathbf{q}_{vibr,c}$ is the vibrational energy flux of species c. The set of governing equations (8)–(11) includes conservation equations for the momentum and total energy (9), (10) coupled to the equations of multi-temperature chemical kinetics (8) and relaxation equations for specific vibrational energies $E_{vibr,c}$.

The transport terms in equations (8)-(11) \mathbf{V}_c , \mathbf{P} , \mathbf{q} , $\mathbf{q}_{w,c}$ are defined by the following expressions:

$$n_c \mathbf{V}_c = \sum_{ij} \int \mathbf{c}_c f_{cij} d\mathbf{u}_c, \qquad (12)$$

$$\mathbf{P} = -\sum_{cij} \int m_c \mathbf{c}_c \mathbf{c}_c f_{cij} d\mathbf{u}_c, \tag{13}$$

$$\mathbf{q} = \sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_j^c + \varepsilon_i^c + \varepsilon_c \right) \mathbf{c}_c f_{cij} d\mathbf{u}_c, \tag{14}$$

$$\mathbf{q}_{vibr,c} = \sum_{ij} \varepsilon_i^c \int \mathbf{c}_c f_{cij} d\mathbf{u}_c.$$
(15)

The relaxation terms are defined as follows:9

$$R_c^{vibr} = \sum_{ij} \varepsilon_i^c \int J_{cij}^{sl} d\mathbf{u}_c = \varepsilon_1^c R_c^w, \qquad R_c^{react} = \sum_{ij} \int J_{cij}^{react} d\mathbf{u}_c, \tag{16}$$

where $J_{cij}^{react} = J_{cij}^{2 \rightleftharpoons 2} + J_{cij}^{2 \rightleftharpoons 3}$ is the collision operator for chemical reactions. The integral operator J_{cij}^{sl} can be split into separate operators corresponding to specific slow processes (for each specific process *r*, the pre- and post-collisional vibrational levels and chemical species of the colliding particles are considered fixed)

$$J_{cij}^{sl} = \sum_{r=1}^{N_{VV'}} v_{r,ci} J_{cij}^{VV',r} + \sum_{r=1}^{N_{VT}} v_{r,ci} J_{cij}^{VT,r} + \sum_{r=1}^{N_{2\neq2}} v_{r,ci} J_{cij}^{2\neq2,r} + \sum_{r=1}^{N_{2\neq2}} v_{r,ci} J_{cij}^{2\neq3,r}.$$
(17)

Here, $N_{VV'}$, N_{VT} , $N_{2\neq2}$, $N_{2\neq3}$ denote respectively the amount of VV'–exchanges, VT transitions, chemical exchange reactions and dissociation-recombination reactions occurring in the mixture; $J_{cij}^{VV',r}$, $J_{cij}^{VT,r}$, $J_{cij}^{2\neq2,r}$ and $J_{cij}^{2\neq3,r}$ are the operators for the *r*-th VV'-exchange, VT transition, chemical exchange and dissociation reactions, correspondingly;⁹ $v_{r,ci}$ are the global stoichiometric coefficients for the r-th transition. Based on this representation, the rate of a specific reaction r is introduced $:^{7,10}$

$$\dot{\xi}_r = \frac{1}{N_a} \sum_j \int J_{cij}^r d\mathbf{u}_c \tag{18}$$

and the corresponding reaction rate coefficient:

$$k_r = N_a \sum_{jlj'l'} \int \frac{f_{cij} f_{dkl}}{n_{ci} n_{dk}} g \widetilde{\sigma}_{f,r} d\mathbf{u}_d d\mathbf{u}_c, \tag{19}$$

where **g** is the colliding particles relative velocity, $\tilde{\sigma}_{f,r} = \tilde{\sigma}_{f,r}(g)$ is the integral cross-section for the *r*-th process (i.e. the differential cross-section integrated over velocities of particles after collisions⁹) and N_a is the Avogadro number.

To simplify notation, we denote the different sets of types of slow processes as follows:

$$\mathcal{V} = \{VV', VT\}, \quad \mathcal{R} = \{2 \rightleftharpoons 2, 2 \rightleftharpoons 3\}, \quad \mathcal{VR} = \{VV', VT, 2 \rightleftharpoons 2, 2 \rightleftharpoons 3\}.$$
(20)

Then the relaxation terms R_c^{vibr} , R_c^{react} can be expressed in terms of reaction rates:

$$R_c^{react} = N_a \sum_i \sum_{\gamma \in \mathcal{R}} \sum_{r=1}^{N_{\gamma}} \nu_{r,ci} \dot{\xi}_{\gamma,r}, \qquad (21)$$

$$R_{c}^{vibr} = N_{a} \sum_{i} \varepsilon_{i}^{c} \sum_{\gamma \in \mathcal{VR}} \sum_{r=1}^{N_{\gamma}} \nu_{r,ci} \dot{\xi}_{\gamma,r} = N_{a} \sum_{\gamma \in \mathcal{VR}} \sum_{r=1}^{N_{\gamma}} \Delta \varepsilon_{i}^{c} \dot{\xi}_{\gamma,r},$$
(22)

where $\Delta \varepsilon_i^c = \varepsilon_{i'}^c - \varepsilon_i^c$, and *i'* denotes the vibrational level after the inelastic collision.

2. Zero-order approximation

In the zero-order approximation of the Chapman-Enskog method, the distribution function for a molecule with a harmonic vibrational spectrum is a combination of Maxwell-Boltzmann distributions over velocity and rotational energy and a non-equilibrium Boltzmann distribution over vibrational energy:

$$f_{cij}^{(0)} = \left(\frac{m_c}{2\pi kT}\right)^{3/2} \frac{n_c}{Z_c^{int}} s_{ij}^c \exp\left(-\frac{m_c c_c^2}{2kT} - \frac{\varepsilon_j^c}{kT} - \frac{\varepsilon_i^c}{kT_v}\right),\tag{23}$$

Here, k is the Bolztmann constant, T_v^c is the vibrational temperature of chemical species c and Z_c^{int} is the internal partition function, given by

$$Z_c^{int} = Z_c^{rot} Z_c^{vibr}, \quad Z_c^{rot} = \sum_j s_j^c \exp\left(-\frac{\varepsilon_j^c}{kT}\right), \quad Z_c^{vibr} = \sum_i \exp\left(-\frac{\varepsilon_i^c}{kT_v^c}\right).$$
(24)

By substituting the zero-order distribution function into the integral reaction operators and applying microscopic laws of energy conservation during collisions, it is possible to obtain that

$$J_{cij}^{r(0)} = \Gamma^r \sum_{lj'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} g \widetilde{\sigma}_{f,r} d\mathbf{u}_d.$$
⁽²⁵⁾

In the case of VT–exchanges one should omit summation over l' and in the case of dissociation reactions one should omit summation over j'l'. Here

$$\Gamma^r = 1 - \exp\left(\frac{A_r}{kT}\right),\tag{26}$$

 A_r are quantities introduced by analogy with affinities of chemical reactions.⁴ For the harmonic oscillator model, these generalized affinities take on the following form:

$$A_{VV',r} = \Delta \varepsilon_i^c \left(1 - \frac{T}{T_v^c} \right) + \Delta \varepsilon_k^d \left(1 - \frac{T}{T_v^d} \right), \tag{27}$$

$$A_{VT,r} = \Delta \varepsilon_i^c \left(1 - \frac{T}{T_v} \right), \tag{28}$$

$$A_{2\vec{c}^{2}2,r} = \frac{3}{2}kT \ln \frac{m_{c}m_{d}}{m_{c'}m_{d'}} + kT \ln \frac{Z_{c'}^{int}Z_{d'}^{int}}{Z_{c'}^{int}Z_{d'}^{int}} - kT \ln \frac{n_{c}n_{d}}{n_{c'}n_{d'}} + \varepsilon_{c'} + \varepsilon_{d'} - \varepsilon_{c} - \varepsilon_{d} + \varepsilon_{0}^{c'} + \varepsilon_{0}^{d'} - \varepsilon_{0}^{c} - \varepsilon_{0}^{d} + \varepsilon_{i}^{c} \left(\frac{T}{T_{v}^{c}} - 1\right) + \varepsilon_{k}^{d} \left(\frac{T}{T_{v}^{d}} - 1\right) - \varepsilon_{i'}^{c'} \left(\frac{T}{T_{v}^{c'}} - 1\right) - \varepsilon_{k'}^{d'} \left(\frac{T}{T_{v}^{d'}} - 1\right), \quad (29)$$

$$A_{2 \neq 3,r} = \frac{3}{2} kT \ln \frac{m_c}{m_{c',a} m_{f',a}} - \frac{3}{2} \ln(2\pi kT) + 3kT \ln h + kT \ln Z_c^{int} - kT \ln \frac{n_c}{n_{c',a} n_{f',a}} + \varepsilon_{c',a} + \varepsilon_{f',a} - \varepsilon_c - \varepsilon_0^c + \varepsilon_i^c \left(\frac{T}{T_v^c} - 1\right), \quad (30)$$

where indices c', a and f', a denote the atomic products of the dissociation reaction and $\varepsilon_0^c = \frac{1}{2}h\nu_c$ is the energy of the lowest vibrational level.

The zero order reaction rates are linear functions of quantities Γ^r

$$\dot{\xi}_{r}^{(0)} = \Gamma^{r} k_{f,r}^{(0)} \prod_{c=1}^{L} \prod_{i=1}^{L_{c}} \left(\frac{n_{ci}}{N_{a}} \right)^{\nu_{r,ci}^{(r)}}$$
(31)

and involve zero-order reaction rate coefficients $k_{f,r}^{(0)}$ obtained by substituting the distribution function (23) into the definition (19). Here L_c denotes the number of vibrational levels in chemical species c, $v_{r,ci}^{(r)}$ is the reactant stoichiometric coefficient.

The expression for the specific vibrational energy of chemical species c in the zero-order approximation is given by

$$E_{vibr,c}(T_v^c) = \frac{1}{\rho_c} \sum_i \varepsilon_i^c n_{ci} = \frac{1}{m_c Z_c^{vibr}(T_v^c)} \sum_i \varepsilon_i^c \exp\left(-\frac{\varepsilon_i^c}{k T_v^c}\right).$$
(32)

Relaxation equations of specific vibrational energies (11) in the zero-order approximation reduce to

$$\rho_c \frac{dE_{vibr,c}}{dt} = R_c^{vibr} - E_{vibr,c} m_c R_c^{react}, \ c = 1, \dots, L_m.$$
(33)

In computational fluid dynamics, the rate of vibrational energy production due to VT transitions is commonly calculated using the Landau–Teller expression:¹¹

$$R_c^{vibr,VT} = \rho_c \frac{E_{vibr,c}^{eq}(T) - E_{vibr,c}(T_v^c)}{\tau_c^{VT}},$$
(34)

where $E_{vibr,c}^{eq}(T)$ is the equilibrium vibrational energy per unit of mass, τ_c^{VT} is the VT relaxation time for species *c* It has been shown⁷ that an expression similar to (34) can be obtained from the strict definition of relaxation terms in the zero-order approximation (21) under the following assumptions: (1) harmonic oscillator model; (2) weak deviation from

equilibrium ($T \approx T_{\nu}$); (3) constant specific heats; and (4) assumption of independence of VT relaxation time on the chemical species of the collision partner. A more general expression for the rate of vibrational energy production due to VT transitions was derived,⁷ which assumed only weak deviations from equilibrium and harmonicity of vibrational spectra:

$$R_{c}^{vibr,VT(0)} = \frac{T}{T_{v}^{c}} \left(T - T_{v}^{c}\right) \rho_{c} c_{vibr,c} \sum_{d} \frac{n_{d}}{n \tau_{cd}^{VT}},$$
(35)

where τ_{cd}^{VT} is the VT relaxation time τ_{cd}^{VT} for collisions between particles of species *c* and *d*. It was shown that under conditions of strong non-equilibrium, formula (35) provides results which are in much better agreement with strict kinetic-theory calculations than those given by the Landau–Teller expression.

3. First-order approximation

The first-order correction to the distribution function can be written as $f_{cij}^{(1)} = f_{cij}^{(0)}\phi_{cij}$, where function ϕ_{cij} satisfies the integral equation

$$-\sum_{d} n_c n_d I_{cijd}(\phi) = D f_{cij}^{(0)} - J_{cij}^{sl(0)},$$
(36)

 I_{cijd} is the linearized integral operator of rapid processes,⁹ and the streaming operator $Df_{cij}^{(0)}$ is given by the following expression:

$$Df_{cij}^{(0)} = f_{cij}^{(0)} \left(\frac{d \ln f_{cij}^{(0)}}{dt} + \mathbf{c}_c \cdot \nabla f_{cij}^{(0)} - \frac{d \mathbf{v}}{dt} \nabla_{\mathbf{c}_c} \ln f_{cij}^{(0)} - \left(\nabla_{\mathbf{c}_c} \ln f_{cij}^{(0)} \right) \mathbf{c}_c : \nabla \mathbf{v} \right).$$
(37)

Calculating the streaming operator on the basis of the zero-order distribution function (23) and zero-order transport equations, one can rewrite the first-order distribution function in terms of the gradients of macroscopic variables:

$$f_{cij}^{(1)} = \frac{f_{cij}^{(0)}}{n} \bigg(-\mathbf{A}_{cij} \cdot \nabla \ln T - \sum_{d=1}^{L_m} \mathbf{A}_{cij}^{d(1)} \cdot \nabla \ln T_1^d - \sum_{d=1}^{L} \mathbf{D}_{cij}^d \cdot \mathbf{d}_d - \mathbf{B}_{cij} : \nabla \mathbf{v} - F_{cij} \nabla \cdot \mathbf{v} - \sum_{\gamma \in \mathcal{VR}} \sum_r G_{cij}^{\gamma, r} \Gamma^{\gamma, r} \bigg),$$
(38)

where \mathbf{d}_c are diffusive driving forces:

$$\mathbf{d}_{c} = \nabla \left(\frac{n_{c}}{n}\right) + \left(\frac{n_{c}}{n} - \frac{\rho_{c}}{\rho}\right) \nabla \ln p.$$
(39)

 $\mathbf{A}_{cij}, \mathbf{A}_{cij}^{d(1)}, \mathbf{B}_{cij}, \mathbf{D}_{cij}^{d}, F_{cij}, G_{cij}^{\gamma,r}, \gamma \in \mathcal{VR}$ are unknown functions of the peculiar velocity and macroscopic variables, which are defined as solutions of integral equations obtained by substituting representation (38) into (36) and equating corresponding terms in the right- and left-hand sides of the resulting equation. For $G^{\gamma,r}$ the terms appearing in the right-hand side of the corresponding equations (36) are multipliers in front of the generalized thermodynamic forces $\Gamma^{\gamma,r}$.

The integral equations defining $G^{\gamma,r}$ take on the following form

$$\sum_{d} \frac{n_c n_d}{n^2} I_{cijd} \left(G^{\gamma, r} \right) = \frac{1}{n} f_{cij}^{(0)} \Phi_{cij}^{\gamma, r}, \ r = 1, \dots, N_{\gamma}, \ \gamma \in \mathcal{VR}$$

$$\tag{40}$$

where $\Phi_{cii}^{\gamma,r}$ is defined as follows:

$$\Phi_{cij}^{\gamma,r} = -N_a \frac{H_{cj}}{c_u} \sum_{d=1}^{L_m} \sum_k \frac{k_d}{\rho_d} \frac{\partial U}{\partial T_v^d} \left(\frac{\partial W_d}{\partial T_v^d}\right)^{-1} K_{dk,r}^{VT} + N_a \left[\frac{\varepsilon_i^c}{kT_v^c}\right]' \frac{1}{T_v^c} \left(\frac{\partial W_c}{\partial T_v^c}\right)^{-1} \sum_k \frac{k_c}{\rho_c} K_{ck,r}^{\gamma} - \widetilde{J}_{\gamma,rc}, \quad \gamma \in \mathcal{V}$$

$$(41)$$

$$\Phi_{cij}^{\gamma,r} = -N_a \frac{H_{cj}}{c_u} \sum_{d=1}^{L_m} \sum_k \frac{k_d - W_d m_d}{\rho_d} \frac{\partial U}{\partial T_v^d} \left(\frac{\partial W_d}{\partial T_v^d} \right)^{-1} K_{dk,r}^{\gamma} - N_a \frac{H_{cj}}{\Phi_0} \sum_{d=1}^{L} \sum_k \frac{\partial U}{\partial n_d} K_{dk,r}^{\gamma} + N_a \left[\frac{\varepsilon_i^c}{k T_v^c} \right]' \frac{1}{T_v^c} \left(\frac{\partial W_c}{\partial T_v^c} \right)^{-1} \sum_k \frac{k_c - W_c m_c}{\rho_c} K_{ck,r}^{\gamma} + \frac{N_a}{n_c} \sum_k K_{ck,r}^{\gamma} - \widetilde{J}_{\gamma,rc}, \quad \gamma \in \mathcal{R}.$$
(42)

The quantities c_u , K_{cir}^{γ} , H_{cj} are given by the expressions

$$c_u = \frac{\partial U}{\partial T},\tag{43}$$

$$K_{ci,r}^{\gamma} = \nu_{r,ci} k_{f,\gamma r}^{(0)} \prod_{d=1}^{L} \prod_{k=1}^{L_d} \left(\frac{n_{dk}}{N_a} \right)^{\nu_{r,dk}^{(r)}}, \ \gamma \in \mathcal{VR},$$
(44)

$$H_{cj} = \frac{1}{T} \left(-\frac{3}{2} + \frac{m_c c_c^2}{2kT} + \left[\frac{\varepsilon_j^c}{kT} \right]' \right). \tag{45}$$

Additional constraints for the functions $G_{cij}^{\gamma,r}$ follow from the normalization conditions imposed on the distribution function:

$$\sum_{ij} \int f_{cij}^{(0)} G_{cij}^{\gamma,r} d\mathbf{u}_c = 0, \quad c = 1, ..., L, \quad r = 1, ..., N_{\gamma}, \quad \gamma \in \mathcal{VR},$$
(46)

$$\sum_{cij} \int f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2} + \varepsilon_{ij}^c \right) G_{cij}^{\gamma, r} d\mathbf{u}_c = 0, \quad r = 1, ..., N_{\gamma}, \quad \gamma \in \mathcal{VR}.$$
(47)

$$\sum_{ij} \varepsilon_i^c \int f_{cij}^{(0)} G_{cij}^{\gamma, r} d\mathbf{u}_c = 0, \quad c = 1, ..., L_m, \quad r = 1, ..., N_{\gamma}, \quad \gamma \in \mathcal{VR}.$$
(48)

The first order corrections to the reaction rates can be written out as follows:⁷

$$\dot{\xi}_{r,\gamma} - \dot{\xi}_{r,\gamma}^{(0)} = \frac{1}{N_a} \left\{ \left[G^{\gamma,r}, F \right] \nabla \cdot \mathbf{v} + \sum_{\beta,s} \left[G^{\gamma,r}, G^{\beta,s} \right] \Gamma^{\beta,s} \right\}.$$
(49)

It can be seen that in viscous flows, reaction rates are not independent quantities, and flow compressibility also influence the rates of slow processes.

For numerical modeling, the functions $G_{cij}^{\gamma,r}$ are expanded in terms of Sonine polynomials $S_{1/2}^{(q)}$ and Waldmann– Trübenbacher polynomials $P_{ij}^{(p)}$:

$$G_{cij}^{\gamma,r} = \sum_{qp} g_{c,qp} S_{1/2}^{(q)} \left(\frac{m_c c_c^2}{2kT} \right) P_{ij}^{(p)} \left(\frac{\varepsilon_j^c}{kT} + \frac{\varepsilon_i^c}{kT_v^c} \right), \quad \gamma \in \mathcal{VR}.$$
(50)

System of linear equations for determination of the expansion coefficients $g_{c,qp}^{\gamma,r}$ are obtained by multiplying equations (40) by

$$Q_{cij}^{qp,\gamma,r} = S_{1/2}^{(q)} \left(\frac{m_c c_c^2}{2kT} \right) P_{ij}^{\gamma,r(p)}$$
(51)

integrating over \mathbf{u}_c and summation over *i*, *j*. The systems have to be supplemented by conditions imposed on the expansion coefficients which follow from the normalization conditions (46)–(48).

4. Results of numerical modeling

Numerical modeling of vibrational relaxation rates under various conditions was done for binary mixtures of nitrogen and oxygen: N_2 , N and O_2 , O. In such mixtures, slow processes include VT transitions and dissociation-recombination reactions. The cross-sections of these processes where assumed to be in the form

$$\sigma_{sl,r} = P_{sl,r}\sigma_{tot,el},\tag{52}$$

where $P_{sl,r}$ is the probability of the slow process being considered and $\sigma_{tot,el}$ is an elastic total cross-section. The Variable Soft Sphere (VSS) model^{12,13} was used to calculate all elastic cross-sections. Probabilities of VT transitions where calculated using Forced Harmonic Oscillator (FHO) model,¹⁴ while the probability $p_{diss,i}^c$ of dissociation of a molecule of species *c* with vibrational energy ε_i^c was calculated using the following formula:

$$p_{diss,i}^{c} = \begin{cases} 0, & E < D_{c}, \\ 1 - \frac{D_{c}}{E}, & E \ge D_{c}, \end{cases}$$
(53)

where D_c is the dissociation energy of molecular species c and $E = m_{cd}g^2/2 + \varepsilon_i^c$, where m_{cd} is the collision-reduced mass and g is the magnitude of the relative velocity of the colliding particles.

In a binary mixture of the form A_2 , A, where A_2 denotes the homonuclear molecular component and A — the atomic component, expression (22) for the vibrational energy production rate can be reduced to

$$R_{A2}^{vibr} = N_a \sum_{r=1}^{N_{VT}} \Delta \varepsilon_i^c \dot{\xi}_{VT,r} + N_a \sum_{r=1}^{N_{2\neq3}} \Delta \varepsilon_i^c \dot{\xi}_{2\neq3,r} = R_{A2}^{vibr,VT} + R_{A2}^{vibr,2\neq3},$$
(54)

where $R_{A_2}^{vibr,VT}$ corresponds to the vibrational energy production rate due to VT transitions and $R_{A_2}^{vibr,2\neq3}$ corresponds to the vibrational energy production rate due to dissociation-recombination reactions.

It is of interest to study two different phenomena: firstly, the contribution of $R_{A2}^{vibr,2z^23}$ to the vibrational energy production rate in the zero- and first-order approximations, and secondly, the influence of cross-coupling between VT transitions and dissociation-recombination reactions on the vibrational energy production rate due to VT transitions $R_{A2}^{vibr,VT}$, since it is usually modelled using the Landau–Teller formula which does not take these effects into account.



Figure 1: Contribution of VT transitions to the vibrational energy productions terms for a N_2 , N flow with $x_N = n_N/n = 0.5$ and $T_v = 2000K$ (a), $T_v = 6000K$ (b)

Fig. 1 shows the contribution of VT transitions to the vibrational energy productions terms $R_{N2}^{vibr,VT}/R_{N2}^{vibr}$ in the zero- and first-order approximations. It can be seen that far from the point of vibrational equilibrium ($T = T_v$), dissociation-recombination reactions have an insignificant influence on vibrational energy relaxation, while near the point of vibrational equilibrium, dissociation due to thermo-chemical non-equilibrium is the primary contributor to the vibrational energy production rate. The qualitative and quantitative behaviour of the relative contributions of different processes remains virtually the same both for viscous and inviscid flows. Moreover, from Fig. 1 it can also be seen that for the case of $T < T_v$, the contributions of dissociation and VT transitions to the vibrational energy production have opposite effects.

Fig. 2 gives the ratio of relaxation terms $R_{N2}^{vibr,VT}$ due to VT transitions to the Landau–Teller vibrational energy production term (34) for various models. It can be seen that the viscous contributions to vibrational relaxation rates are significant at high temperatures under conditions of strong vibrational non-equilibrium, while the influence of dissociation on rates of VT transitions via cross-coupling is significant only near vibrational equilibrium. It can also be seen from Fig. 2 (b) that the influence of dissociation on VT transition rates near vibrational equilibrium is less than in the case of $T_v = 2000K$, which is due to the point $T = T_v = 6000$ being closer to the temperature at which chemical equilibrium occurs than the point $T = T_v = 2000k$.

In agreement with previous results,⁷ the original Landau–Teller model significantly underestimates vibrational relaxation rates for the case of $T > T_{\nu}$ and overestimates them for the case of $T < T_{\nu}$, while the modified Landau–Teller formula (35) gives values of vibrational energy production rates more consistent with those obtained by strict kinetic-theory calculations.



Figure 2: Ratio of relaxation terms $R_{N2}^{vibr,VT}$ to the Landau–Teller vibrational energy production term for a N_2 , N flow with $x_N = n_N/n = 0.5$ and $T_v = 2000K$ (a), $T_v = 6000K$ (b)



Figure 3: Contribution of VT transitions to the vibrational energy productions terms for a O_2 , O flow with O_2 , O flow with $x_0 = n_0/n = 0.5$ and $T_v = 2000K$ (a), $T_v = 6000K$ (b))



Figure 4: Ratio of relaxation terms $R_{O2}^{vibr,VT}$ to the Landau–Teller vibrational energy production term for a O_2 , O flow with $x_O = n_O/n = 0.5$ and $T_v = 2000K$ (a), $T_v = 6000K$ (b)

For oxygen, the situation is slighly different, which can be attributed to a lower dissociation energy, and therefore, larger dissociation cross-sections. This leads to a significant influence of dissociation at high temperatures on the first-order corrections to relaxation rates, as shown on Fig. 4. Overall, for oxygen, the influence of dissociation-recombination reactions on vibrational energy production terms is significantly larger than for nitrogen, especially at high flow temperatures.

5. Conclusion

Vibrational relaxation rates in multi-temperature flows are studied in the inviscid and viscous approximations Chapman– Enskog method. For molecules with harmonic vibrational spectra, a simplified method for calculating first-order corrections to reaction rates is presented, along with a modification of the widely-used Landau–Teller formula.

Vibrational energy production rates are calculated for binary flows of nitrogen and oxygen (N_2 , N and O_2 , O) using various models; the influence of dissociation-recombination reactions on vibrational relaxation rates in viscous flows is assessed. It is shown that both for nitrogen and oxygen, first-order corrections are significant at high temperatures and conditions of strong vibrational non-equilibrium; in nitrogen flows, dissociation plays a noticeable role only near vibrational equilibrium. For oxygen, due to the lower dissociation energy of O_2 molecules, the effect of dissociation on vibrational energy production is more significant, especially at high temperatures. The modified Landau–Teller expression provides significantly better agreement with results obtained using rigorous kinetic-theory methods than the original Landau–Teller formula.

6. Acknowledgements

The research leading to these results has received funding from the Russian Foundation for Basic Research, projects 15-08-03371 and 15-01-02373, and the Saint Petersburg State University, project 6.37.163.2014.

References

- [1] Belouaggadia N., Brun R. Chemical Reaction Rates in Nonequilibrium Flows. *Journal of Thermophysics and Heat Transfer*, Vol. 12, N 4, 1998, p. 482.
- [2] Kustova E.V. Thermal Relaxation Rate in Viscous Multi-Temperature Gas Flows. In *Rarefied Gas Dynamics:* 27th International Symposium, edited by D. Levin et al., 2011, Vol. 1333 of AIP Conference Proceedings, pp. 1221–1226.
- [3] Kustova E.V., Nagnibeda E.A., Chauvin A. State-to-state nonequilibrium reaction rates. *Chemical Physics*, Vol. 248, N 2–3, 1999, pp. 221-232.
- [4] Kustova E.V. Scalar Forces/Fluxes and Reciprocity Relations in Flows with Strong Thermal and Chemical Non-Equilibrium. In *Rarefied Gas Dynamics: 28th International Symposium*, edited by M. Mareschal, A. Santos, 2012, Vol. 1501 of *AIP Conference Proceedings*, pp. 1078–1085.
- [5] Marrone P.V., Treanor C.E. Chemical Relaxation with Preferential Dissociation from Excited Vibrational Levels. *Physics of Fluids*, Vol. 6, N 9, 1963, pp. 1215–1221.
- [6] Knab O., Frühauf H.H., Messerschmid E.W. Theory and Validation of the Physically consistent Coupled Vibration-Chemistry-Vibration Model. *Journal of Thermophysics and Heat Transfer*, Vol. 9, N 2, 1995, pp. 219– 226.
- [7] Kustova E.V., Oblapenko G.P. Reaction and internal energy relaxation rates in viscous thermochemically nonequilibrium gas flows. *Physics of Fluids*, Vol. 27, N 1, 2015.
- [8] Chikhaoui A., Dudon J.P., Kustova E.V., Nagnibeda E.A. Transport Properties in Reacting Mixture of Polyatomic Gases. *Physica A*, Vol. 247, N 1–4, 1997, pp. 526–552.
- [9] Nagnibeda E.A., Kustova E.V. Nonequilibrium Reacting Gas Flows. *Kinetic Theory of Transport and Relaxation Processes*. Springer, Berlin, 2009.
- [10] Kustova E.V., Giordano D. Cross-coupling effects in chemically non-equilibrium viscous compressible flows. *Chemical Physics*, Vol. 379, N 1–3, 2011, pp. 83–91.
- [11] Landau L., Teller E. Theory of sound dispersion. Phys. Z. Sowjetunion. Vol. 10, 1936, p. 34.
- [12] Koura K., Matsumoto H. Variable soft sphere molecular model for inverse powerlaw or LennardJones potential. *Physics of Fluids A: Fluid Dynamics*. Vol. 3, N 10, 1991, pp. 2459–2465.
- [13] Koura K., Matsumoto H. Variable soft sphere molecular model for air species. *Physics of Fluids A: Fluid Dynam*ics. Vol. 4, N 5, 1992, pp. 1083–1085.
- [14] Adamovich I.V., Macheret S.O., Rich J.W., Treanor C.E., Vibrational energy transfer rates using a forced harmonic oscillator model *Journal of Thermophysics and Heat Transfer*, Vol. 12, N 1, 1998, pp. 57–65.