Physical-chemical gas-dynamics: challenges and solutions

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Abstract: One of the main problems of the non-equilibrium physical-chemical gas-dynamics is considered: derivation of gas-dynamics equations for reactive gas mixtures. By non-equilibrium effects we mean all kinds of effects caused by deviation of the distribution function from its quasi-equilibrium value. The method which is used to obtain the normal solution for the generalized Boltzmann equation is discussed. As opposed to the traditional approach, it permits a description of experimentally observed pressure dependence of the reaction rates (low- and high-pressure limits) and to generalize the theory of thermal dissociation for the arbitrary reaction case and for spatially inhomogeneous systems. Conclusions concerning the necessity of revising the traditional approach to the chemical reaction description and of developing the non-equilibrium chemistry are argued. In the framework of the non-equilibrium chemistry, chemical reactions are no longer independent of each other (Guldberg and Waage law is not applicable under the non-equilibrium conditions) and corresponding reaction rates are functions of the reacting mixture composition. Exact expressions for reaction and relaxation rates for the cut-off harmonic oscillator model are obtained. Only the case of hard potentials in Grad's meaning is considered, while soft potentials remain an issue.

1 Introduction

Gas-dynamics is one of the most formalized areas of physics, which has given rise to a now global industry that is the computational fluid dynamics (CFD). However there are still many

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unsolved issues in this field, which mostly concern attempts to take into account complex physical-chemical processes. These processes are usually connected with the non-equilibrium effects, by which we mean all kinds of effects caused by the deviation of the distribution function from its quasi-equilibrium value. In many cases non-equilibrium effects themselves are the reason for the deviation and therefore need a self-consistent description. For reacting gases non-equilibrium effects lead to a dependence of the reaction rates, not only on temperature, but also on velocity and concentrations of mixture species, i.e. on the composition of the mixture [1, 2]. The nucleation problem meets the same problem, what is clear from recent investigations [3] and from the quasi-chemical model analysis [4].

It is worth noting that such processes determine the behavior of gases under high Mach number conditions, of plasma (rf- and other discharges are widely used in PECVD reactors), etc, which means searching for their appropriate description is of great importance.

One of the challenging problems faced is: derivation of gas-dynamic equations for reacting gas mixtures. After pioneering works on thermal dissociation of Stupochenko et al [5], the quasi-stationary state (QSS) method for quasi-stationary distribution function calculation, and thus for non-equilibrium reaction rates calculation was proposed and used in publications [6]. In paper [7] the expression was derived for the reaction rate within the model that allows the exact solution. This is a one-temperature model for the small admixture of the reacting gas, for which is assumed the perturbation of the Maxwell-Boltzmann distribution for translational and vibrational degrees of freedom for all components is negligible. In paper [8] the comparison was between our expressions for reaction rates with corresponding results of the QSS method and appreciable differences were observed. The QSS method is used in solving the set of state-to-state equations, derived from the Boltzmann equation under the assumption the translational (and in some case rotational) degrees of freedom obey the Maxwell-Boltzmann distribution. It does not permit building the rigorous asymptotic approach for the gas dynamic equations derivation, within the QSS methodology. No consequential asymptotic procedure within the QSS method is considered; only the path to calculate the quasi-stationary state (zero-order approximation) and first-order corrections is discussed. Thus, any approach that involves an asymptotic method based on the Boltzmann equation is more general than the QSS method. Besides that, considering only state-to-state equations, none of the QSS methodology authors deal with the spatially inhomogeneous effects. Taking the above into account as well as the reasons discussed in [1, 2], the new method of deriving the solution for the generalized Boltzmann equation for chemically reacting gases, proposed in [1] is the most general to date method.

As discussed in paper [1] the difficulties one meets when trying to obtain macroscopic equations, which can describe experimentally observed switching of the dependence of unimolecular reactions under pressure from the square-law dependence at low pressures (bimolecular mechanism), to the linear dependence at higher pressures (unimolecular mechanism). Analysis of the thermal dissociation problem [5] have shown that for reactive gas mixtures corresponding reaction rates are the functions of the small parameter of the theory (Knudsen number). This means that to describe the experimentally observed system behavior the re-normalized theory allowing the summation of the contribution of the terms of different orders of magnitude is needed to be build. For this the new method of obtaining a normal solution for the generalized Boltzmann equation for reacting gas mixtures was proposed. It is based on the following items: (i) slow variables are introduced via approximate summational invariants (ASI), defined within the method, (ii) a renormalized asymptotic procedure is formulated, which is made up of the distribution function separated into 'slow' and 'fast' parts. The kinetic equation is presented in the form of a singularly perturbed system for gas-dynamic (slow) variables and for the 'fast' part of the distribution function, (iii) a collisional integral is not expanded into the series over the Knudsen number (no assumption is made that the part of a collisional integral, responsible for the chemical reactions, can be treated as the perturbation of its 'elastic' part, as was suggested in publication [9] and since has been the basis for the

general approach [10, 11]). While deriving the gas-dynamic equations it was shown that the role of non-equilibrium effects is far more essential in our approach, than is generally accepted. Physically non-equilibrium effects originate from the high sensitivity of the high-threshold-physical-chemical processes, to the distribution function perturbations.

From several examples it was ascertained that non-equilibrium corrections and the traditional equilibrium rate constants could be of the same order of magnitude. Our previous studies [2, 12] show that via kinetics of high threshold physical-chemical processes, all generalized relaxation processes described by Euler equations, became interdependent. By generalized relaxation processes here we mean all processes that are described by gas-dynamic variables related to the approximate summational invariants introduced in [1]. Evolution equations for these variables contain source terms that determine coupling of their behavior with the evolution of other variables. Derived gas-dynamic equations have more symmetrical form in comparison with traditional equations from the point of view of describing the impact of the gas-dynamic variables on each other. Due to symmetry mentioned above these source terms will be called "generalized relaxation rates" (GRR). All GRR, being the rates of corresponding reaction/relaxation processes, are the complex functions of species concentrations and coincide with the corresponding equilibrium values [10, 11] only if the ratio of vibration and chemical characteristic time is set to zero. In this sense these terms are called re-normalized. First attempt to obtain general expressions for these re-normalized GRR was done in paper [12].

Detailed in this paper are the generalized relaxation rates considering the two-temperature approximation and cut-off harmonic oscillator model. It is shown that the GRR are expressed as a linear combination of the quasi-equilibrium GRR (i.e. calculated via quasi-equilibrium distribution function) with coefficients being the functions of the set of gas-dynamic (slow) variables.

The paper is organized as follows. First the basic items of our method of solving the generalized Boltzmann equation for reacting gases are described. The expressions for GRR for the cut-off harmonic oscillator model are derived in the second section. As discussed the analysis pays attention to the non-solved problems and traces further research.

2   State-of-the-art

2.1   Method description

Here the set of generalized Boltzmann kinetic equations for reacting gases, written in the dimensionless form is under review

$$\frac{\partial F_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \nabla F_\alpha = \frac{1}{\varepsilon} I_\alpha(F), \tag{1}$$

where F_α, I_α and $\mathbf{v}_\alpha$ is the distribution function normalized to the number density, the collisional integral and the velocity of the molecule of sort α respectively; ε is the ratio of characteristic times of inelastic process to characteristic gas-dynamic time. The collisional integral can be represented as [7, 13]

$$I_\alpha = \sum_{\nu,\nu'}^{|\nu'|\leq 2 \vee |\nu|\leq 1} {\sum_{k_\nu,k_{\nu'}}}' \int' d\mathbf{v}_\nu d\mathbf{v}_{\nu'} W_{\alpha,\nu}^{\nu'}(\mathbf{v}_\alpha,k_\alpha,\mathbf{v}_\nu,k_\nu|\mathbf{v}_{\nu'},k_{\nu'}) \left[\prod_{\beta \in \nu'} \frac{F_\beta}{s_\beta(k_\beta)} - \frac{F_\alpha}{s_\alpha(k_\alpha)} \prod_{\beta \in \nu} \frac{F_\beta}{s_\beta(k_\beta)} \right]. \tag{2}$$

Here W is the transition probability that satisfies the microscopic reversibility law $W_\nu^{\nu'}(\mathbf{v}_\nu,k_\nu|\mathbf{v}_{\nu'},k_{\nu'}) = W_{\nu'}^\nu(\mathbf{v}_{\nu'},k_{\nu'}|\mathbf{v}_\nu,k_\nu)$; ν characterizes the reaction channel: $\nu = \{\nu_1,...,\nu_\alpha,...\}$, where ν_α is a number of particles of sort α in channel ν; $|\nu| = \nu_1 + ... + \nu_\alpha + ...$ is a total number of particles in channel ν; $k_\nu = \{k_\alpha : \alpha \in \nu\}$ and k_α are quantum numbers of species α, the subindex at $\mathbf{v}_\nu$ has the same meaning; the summation in (2) is carried out over all pairs of channels for which the number of

particles in the initial or final channel does not exceed two (with an arbitrary number of particles in the opposite channel); $s_\beta(k_\beta)$ is a statistical weight of state k_β. Primes over sums and integrals mean that the corresponding summation and integration is performed in a way which avoided multiple accounts of the same states.

The method of introduction of slow (gas-dynamic) variables is unobvious for the systems for which a number of slow variables exceeds the number of exact summational invariants. Therefore the description of gases with internal degrees of freedom appears to be a challenge to the theory. This problem can be solved by generalizing the definition of slow variables. They should be determined not only by summational invariants, but also by approximate summational invariants (ASI) ψ_i [1], that are defined by the following relationship

$$\langle \psi_i, I(F) \rangle \leq O(\varepsilon), \qquad \langle \psi, \varphi \rangle = \sum_\alpha \sum_{k_\alpha} \int d\mathbf{v}_\alpha \psi_\alpha (\mathbf{v}_\alpha, k_\alpha) \varphi_\alpha (\mathbf{v}_\alpha, k_\alpha). \tag{3}$$

Here the angle brackets denote the scalar product. The corresponding set of slow variables is determined as

$$\Gamma_i = \langle \psi_i, F \rangle. \tag{4}$$

According to this definition variables Γ_i evolve over a long time scale. Equations for slow variables are derived by multiplying the Eq. (1) by ASI and integration over velocities and summation over quantum numbers.

Following our previous publication [1], where $F_\alpha = F_\alpha^{qe} + \Phi_\alpha$, the first item does not depend on either time or coordinates explicitly, i.e. it depends only on slow variables $F_\alpha^{qe} = F_\alpha^{qe}(\{\Gamma_i\})$. For quasi-equilibrium distribution functions F_α^{qe} we chose the function that maximizes the entropy density for a fixed set of slow variables: $F_\alpha^{qe} = \exp\left(\ln s_\alpha(k_\alpha) - \sum_{i=1}^M \gamma_i \psi_{i\alpha}(\mathbf{v}_\alpha, k_\alpha)\right)$. Here γ_i are determined by the relationship (4), when F^{qe} is substituted instead of F. Φ_α satisfies the equation

$$\langle \psi_i, \Phi \rangle = 0. \tag{5}$$

The advantage of an introduced quasi-equilibrium distribution function is that it normalizes the procedure of introducing generalized thermodynamics (multi-temperature for instance).

Using the new variable Φ the Eq. (1) together with the corresponding equation for slow variables can be transformed into the singularly perturbed set of equations:

$$\varepsilon \frac{\partial \Phi_\alpha}{\partial t} = J_{F^{qe}\alpha}(F^{qe} + \Phi) - \varepsilon \mathbf{v} \cdot \nabla \Phi_\alpha + \varepsilon \sum_{i=1}^M \frac{\partial F_\alpha^{qe}}{\partial \Gamma_i} \left(\nabla \cdot \langle \mathbf{v}\psi_i, F^{qe} + \Phi \rangle - \mathbf{v} \cdot \nabla \Gamma_i \right) \tag{6}$$

$$J_\Omega(F) = I(F) - \sum_{i=1}^M \frac{\partial \Omega}{\partial \Gamma_i} \langle \psi_i, I(F) \rangle,$$

$$\frac{\partial \Gamma_i}{\partial t} = \frac{1}{\varepsilon} \langle \psi_i, I(F^{qe} + \Phi) \rangle - \nabla \cdot \langle \mathbf{v}\psi_i, (F^{qe} + \Phi) \rangle. \tag{7}$$

Equation (6) coinciding with that commonly used only where all ψ_i are exact summational invariants (ESI). Additional terms in the modified collisional operator J are due to the slow evolution of the system: relaxation of slow variables adiabatically impacts the collision process.

2.2 Gas-dynamic Equations

Considering a so-called 'weak' non-equilibrium situation, where Φ_α function is assumed to be of the order of ε, for the one-velocity model the following zero-order (Euler) gas-dynamic equations

have been derived [1]. Following the Chapman-Enskog asymptotic procedure modified in [1] the expressions for Φ and $\partial\Gamma/\partial t$ are represented as

$$\Phi = \sum_{s=0}^{\infty} \varepsilon^s \Phi^{(s)} \left(\Gamma, \nabla\Gamma, ..., \nabla^{s+1}\Gamma\right), \qquad \frac{\partial\Gamma_i}{\partial t} = \sum_{s=0}^{\infty} \varepsilon^s B^{(s)} \left(\Gamma, \nabla\Gamma, ..., \nabla^s\Gamma\right). \qquad (8)$$

Then for the zero order approximation we obtain

$$J'_{F^{qe}}(F^{qe})\Phi^{(0)} = -\frac{1}{\varepsilon}J_{F^{qe}}(F^{qe}) + \sum_{i=1}^{M} \frac{\partial F^{qe}}{\partial\Gamma_i} \left[\mathbf{v}\cdot\nabla\Gamma_i - \nabla\cdot\langle\mathbf{v}\psi_i, F^{qe}\rangle\right], \qquad (9)$$

$$\frac{\partial\Gamma_i}{\partial t} = \frac{1}{\varepsilon}\langle\psi_i, I(F^{qe})\rangle + \left\langle\psi_i, I'(F^{qe})\Phi^{(0)}\right\rangle - \nabla\cdot\langle\mathbf{v}\psi_i, F^{qe}\rangle. \qquad (10)$$

Here J' is the linearized modified collisional operator, that is determined via the linearized collisional operator I' as

$$J'_{F^{qe}}(F^{qe})\Phi^{(0)} = I'(F^{qe})\Phi^{(0)} - \sum_{i=1}^{M} \frac{\partial F^{qe}}{\partial\Gamma_i} \left\langle\psi_i, I'(F^{qe})\Phi^{(0)}\right\rangle. \qquad (11)$$

As in traditional approaches, function $\Phi^{(0)}$ can be represented as a linear combinations of terms, proportional to gradients of gas-dynamic variables. Taking into account that only scalar part of $\Phi^{(0)}$ and the part which is proportional to mean velocity divergency, contributes the zero-order gas-dynamic equations (10), these equations have the following form:

$$\frac{\partial n_\alpha}{\partial t} + \nabla\cdot(\mathbf{u}n_\alpha) = R_\alpha(\{\Gamma\}), \qquad \alpha = 1,...N,$$

$$(12)$$

$$R_\alpha = \langle\psi_{n_\alpha}, I(F^{qe})\rangle + \left\langle\psi_{n_\alpha}, I'(F^{qe})\left(\Phi_1^{(0)} + \Phi_2^{(0)}\nabla\cdot\mathbf{u}\right)\right\rangle \equiv R_\alpha^{qe} + R_\alpha^{ne} + R_{2\,\alpha}^{(0)}\nabla\cdot\mathbf{u},$$

$$\frac{\partial\rho\mathbf{u}}{\partial t} + \nabla\cdot(\rho\mathbf{uu}) + \nabla p = 0, \qquad p = \frac{1}{3}\left\langle m\mathbf{c}^2, F^{qe}\right\rangle = n/\gamma_E, \qquad (13)$$

$$\frac{\partial\Gamma_E}{\partial t} + \nabla\cdot((\Gamma_E + p)\mathbf{u}) = 0, \qquad (14)$$

$$\frac{\partial\Gamma_i}{\partial t} + \nabla\cdot(\mathbf{u}\Gamma_i) = R_i(\{\Gamma\}), \qquad i = N+5,...,M,$$

$$(15)$$

$$R_i = \langle\psi_{\Gamma_i}, I(F^{qe})\rangle + \left\langle\psi_{\Gamma_i}, I'(F^{qe})\left(\Phi_1^{(0)} + \Phi_2^{(0)}\nabla\cdot\mathbf{u}\right)\right\rangle \equiv R_i^{qe} + R_i^{ne} + R_{2\,i}^{(0)}\nabla\cdot\mathbf{u}.$$

Here $\{\Gamma\} = \{\Gamma_{n_\alpha}, \Gamma_{\mathbf{p}}, \tilde{\Gamma}_E, \Gamma_{ai}\}$. R_α are the reaction rates. The sum of the first two terms in the RHS of Eq. (12), $R_\alpha^{sh} = R_\alpha^{qe} + R_\alpha^{ne}$, describe the kinetics of chemical reactions in spatially homogeneous systems, the last term, $R_\alpha^{(sih)} = R_{2\,\alpha}^{(0)}\nabla\cdot\mathbf{u}$, describes the impact of spatial inhomogeneity. R_i are the relaxation rates for Γ_i variables. Similarly, the sum of the first two terms in the RHS of Eq. (15), $R_i^{sh} = R_i^{qe} + R_i^{ne}$, describe the relaxation in spatially homogeneous systems, while the last term $R_i^{(sih)} = R_{2\,i}^{(0)}\nabla\cdot\mathbf{u}$ arises in spatially inhomogeneous systems. Due to the similar structure of all R-terms we will call them "generalized relaxation rates" (GRR).

Euler equations derived within the presented approach differ from the traditional [10, 11] by source terms: they consider additional summands $R_\alpha^{ne} + R_{2\,\alpha}^{(0)}\nabla\cdot\mathbf{u}$ and $R_i^{ne} + R_{2\,i}^{(0)}\nabla\cdot\mathbf{u}$ in Eqs. (12) and (15) respectively, so that the non-equilibrium effects are taken into account within the zero-order approximation. This is the consequence of not assuming the chemical reactions as being the

perturbation in the collisional integral in Eq. (1). It was discussed in the previous papers [1, 2] in detail.

It should be emphasized that in contrast to the traditional method our approach does not include any assumptions other than this: the ratio $\varepsilon = \tau_{fp}/\tau_{gd}$ is small, where τ_{fp} is the fast process characteristic time and τ_{gd} is the gas-dynamic characteristic time. For example we don't use the expansion of the collisional integral over the Knudsen number; [9] being the starting point. This means that the gas-dynamic equations derived in paper [1] are of the most general form. Considered here 'weak' non-equilibrium situation is the simplification of the result, obtained in [1], but is still beyond the assumptions of the general approach [10, 11] and catches the majority of non-equilibrium effects mentioned above.

In situations where corrections to the reaction rates are not small non-equilibrium effects dramatically impact the chemical kinetics of the reacting gas mixture [8]. This leads to the necessity of the revision of the concept of ascertaining information on the reaction rates from the experiments.

3 Two-temperature approximation within cut-off harmonic oscillator model

3.1 Gas-dynamic equations

Two-temperature approximation means that the vibrational quantum number of the selected vibrational mode, q_1, is assumed to be the approximate summational invariant (only one vibration mode is assumed for simplicity), thus $\psi_V = q_\alpha \delta_{\alpha 1}$; it is additional to traditional Kronecker's delta, $\psi_{n_1}(\alpha) = \delta_{\alpha,1}$, (which corresponds to species number densities), mixture momentum, $\psi_{\mathbf{p}} = m_\alpha \mathbf{v}_\alpha$, and mixture total energy, $\psi_E = e_\alpha^{(T)}(\mathbf{v}_\alpha) + e_\alpha^{(i)}(k_\alpha)$, where $e_\alpha^{(T)} = m_\alpha \mathbf{v}_\alpha^2/2$ and $e_\alpha^{(int)}$ are translational and internal energies of the molecules of sort α respectively, and k_α are the quantum numbers determining the internal energy of the molecule. Corresponding gas-dynamic variables defined according to (4), are number densities of species, n_α, the mean mixture momentum, $\Gamma_{\mathbf{p}} = \mathbf{p}$, the mean total energy $\Gamma_E = \Gamma_{E^{(kin)}} + \Gamma_{E^{(tr)}} + \Gamma_{E^{(i)}}$, (where $\Gamma_{E^{(kin)}} = \mathbf{p}^2/2\rho$, $\Gamma_{E^{(tr)}} = 3n/2\gamma_E$) and quantum number density Γ_V. It is connected with the usual mean quantum number $\bar{q}_1$ [14] by the relationship $\Gamma_V = n_1 \bar{q}_1$. Thus the quasi-equilibrium distribution function can be written as

$$F_\alpha^{qe} = n_\alpha \frac{s_\alpha(k_\alpha)}{Q_\alpha(\gamma_E,\gamma_V)} \exp\left[-\gamma_E\left(\frac{m_\alpha}{2}(\mathbf{v}_\alpha - \mathbf{u})^2 + e_\alpha^{(i)}(k_\alpha)\right) - \gamma_V q_\alpha \delta_{\alpha,1}\right], \qquad (16)$$

where s_α is a statistical weight, Q_α a statistical sum and γ_E is connected with the gas temperature: $\gamma_E = 1/k_B T$. Parameters $\gamma_V(\{\Gamma_{n_\alpha}\}, \tilde{\Gamma}_E, \Gamma_V)$ and $\gamma_E(\{\Gamma_{n_\alpha}\}, \tilde{\Gamma}_E, \Gamma_V)$ should be determined from the relationships below

$$\tilde{\Gamma}_E = \frac{3}{2}\frac{n}{\gamma_E} + \sum_\alpha \sum_{k_\alpha} e_\alpha^{(i)}(k_\alpha) X_{\alpha,k_\alpha}^{qe}, \quad \Gamma_V = \sum_{q_1=0}^{q_m} q_1 X_{1,q_1}^{qe},$$

$$X_{1,q_1}^{qe} = \frac{n_1 s_1(q_1)}{Q_1^{(v)}} \exp\left[-\gamma_E e_1^{(v)}(q_1) - \gamma_V q_1\right], \tag{17}$$

where $\sum_{k_\alpha \neq q_1} \int d\mathbf{v}_\alpha F_\alpha = X_{\alpha,q_1}$ is a vibrational population density and summation is aggregated over all quantum numbers except q_1; $\tilde{\Gamma}_E = \Gamma_{E^{(tr)}} + \Gamma_{E^{(i)}}$; $e_1^{(v)}(q_1)$ is the energy of the corresponding vibrational mode uncoupled with other degrees of freedom: $e_1^{(i)}(k_1) = e_1^{(v)}(q_1) + e_1'$; e_1' is the energy of the remaining internal degrees of freedom; $Q^{(i)} = Q_1^{(v)} Q^{(i)'}$ and $Q_1^{(v)} = \sum_{q_1} \exp\left[-\gamma_E e_1^{(v)}(q_1) - \gamma_V q_1\right]$ is a vibrational statistical sum.

For the harmonic oscillator $e_1^{(v)}(q_1) = \hbar\omega_{e1}(q_1 + 1/2)$ and $Q_{1\,har}^{(v)} \approx e^{-\gamma_E \hbar \omega_{e1}/2} / \left(1 - e^{-\theta_V}\right)$, where $\theta_V = \gamma_E \hbar \omega_e + \gamma_V$. Therefore (17) is reduced to the Boltzmann distribution with a vibrational temperature that can be introduced by the relationship $k_B T_V = \hbar \omega_{e1}/\theta_V$.

For the above mentioned set of slow variables the zero-order gas-dynamic equations are as follows: for Γ_{n_α}, $\Gamma_{\mathbf{p}}$, Γ_E they are (12), (13) and (14) respectively, while for Γ_V the set of equations (15) reduces to one equation:

$$\frac{\partial \Gamma_V}{\partial t} + \nabla \cdot (\mathbf{u}\Gamma_V) = R_V(\Gamma_{n_\alpha}, \Gamma_{\mathbf{p}}, \tilde{\Gamma}_E, \Gamma_V),$$

(18)

$$R_V = \left\langle \psi_V, I\left(F^{qe}\right)\right\rangle + \left\langle \psi_V, I'\left(F^{qe}\right)\left(\Phi_1^{(0)} + \Phi_2^{(0)}\nabla \cdot \mathbf{u}\right)\right\rangle \equiv R_V^{qe} + R_{V\,1}^{(0)} + R_{V\,2}^{(0)}\nabla \cdot \mathbf{u}.$$

3.2 Generalized Relaxation Rates

To calculate the spatially homogeneous part of GRR the scalar part of distribution functions, $\Phi_{1\alpha}^{(0)}$, should be calculated. For simplicity we consider the model within which the Maxwell-Boltzmann distribution for translational and rotational degrees of freedom for all components is assumed. Therefore the equation for $\Phi_1^{(0)}$, obtained from Eq. (9) by gathering scalar terms, can be reduced to the equation for the 'fast' part, $X_{1,q}^{(0)}$, of the vibrational population density $X_{1,q}$ of species 1, as is done in [7], by representing the distribution function in factorized form $F_\alpha = F_\alpha^{qe\,TR}X_{\alpha,q}$, $\sum_{j_\alpha}\int d\mathbf{v}_\alpha F_\alpha = X_\alpha(q_\alpha)$, where $F_\alpha^{qe\,TR}$ is a translational-rotational part of a distribution function. This means that the vibrational and rotational modes are assumed to be independent.

The vibrational collisional operator $I_1^{(V)}$, that is the operator I_1 from equation (1), integrated over velocities $\mathbf{v}_1$ and summed over rotational quantum numbers j_1, is represented as

$$I_{1,q}^{(V)} = I_{1,q}^{(ch)} + I_{1,q}^{(VT)} + I_{1,q}^{(VV)},$$

(19)

where superscripts ch, VT and VV correspond to chemical reactions (both unimolecular and collisional) and to Vibration-Translation and Vibration-Vibration transitions respectively. For one-quantum transitions probabilities of VT and VV transitions can be represented as $P_{p,q} = (\delta_{p,q+1} + \delta_{p,q-1})P_{p,q}$, $Q_{p,q}^{s,l} = (\delta_{p,q+1}\delta_{l,s+1} + \delta_{p,q-1}\delta_{l,s-1})Q_{p,q}^{s,l}$, respectively; thus the relaxation parts of the collisional operator becomes

$$I_{1,q}^{(VT)} = (1 - \delta_{q,0})\left(P_{q-1,q}X_{1,q-1} - P_{q,q-1}X_{1,q}\right) - (1 - \delta_{q,q_m})\left(P_{q,q+1}X_{1,q} - P_{q+1,q}X_{1,q+1}\right),$$

$$I_{1,q}^{(VV)} = (1 - \delta_{q,0})\sum_{l=0}^{q_m-1}\left(Q_{q-1,q}^{l+1,l}X_{1,q-1}X_{1,l+1} - Q_{q,q-1}^{l,l+1}X_{1,q}X_{1,l}\right)$$

$$+ (1 - \delta_{q,q_m})\sum_{l=0}^{q_m-1}\left(Q_{q+1,q}^{l,l+1}X_{1,q+1}X_{1,l} - Q_{q,q+1}^{l+1,l}X_{1,q}X_{1,l+1}\right)$$

$$\equiv (1 - \delta_{q,0})Q_{q-1,q}(X)X_{1,q-1} - Q_{q,q-1}(X)X_{1,q} - (1 - \delta_{q,q_m})\left(Q_{q,q+1}(X)X_{1,q} - Q_{q+1,q}(X)X_{1,q+1}\right).$$

(20)

where q_m is the highest vibrational level. Introducing the effective transition probabilities $\tilde{P}_{i,j}(X_1) = P_{i,j} + Q_{i,j}(X_1)$, the following expression for the vibrational collisional operator is derived:

$$I_{1,q}^{(V)}(X_1) = -(1 - \delta_{q,0})\tilde{j}_{q-1}(X_1)X_1 + (1 - \delta_{q,q_m})\tilde{j}_q(X_1)X_1 - \delta_{q,q_m}\left(P_{d,q}X_{1,q} - P_{r,q}n_3 n_4\right),$$

(21)

$$\tilde{j}_q(X)Y = \tilde{P}_{q+1,q}(X)Y_{q+1} - \tilde{P}_{q,q+1}(X)Y_q.$$

Here $P_{d,q}$ is the dissociation probability of the molecule in state q; $P_{r,q}$ is the recombination probability of the dissociation products to initial molecule in state q respectively, and subindexes 3 and 4 denote the dissociation products. $P_{d,q}$ and $P_{r,q}$ with $q < q_m$ assumed to be negligible. The linearized collision operator $I_{1,q}^{(V)}(X_1)$ can be expressed as:

$$I_{1,q}^{(V)\prime}(X_1^{qe})X_{1,q} = -(1-\delta_{q,0})\tilde{j}_{q-1}(X_1^{qe})X_{1,q} + (1-\delta_{q,q_m})\tilde{j}_q(X_1^{qe})X_{1,q}$$

$$-(1-\delta_{q,0})\tilde{j}_{q-1}'(X_1)X_{1,q}^{qe} + (1-\delta_{q,q_m})\tilde{j}_q'(X_1)X_{1,q}^{qe} - \delta_{q,q_m}P_{d,q}X_{1,q}, \tag{22}$$

$$\tilde{j}_q'(X)Y = Q_{q+1,q}(X)Y_{q+1} - Q_{q,q+1}(X)Y_q.$$

For the model under consideration, after integration over velocities and summation over quantum numbers, scalar part of the Eq. (9) can be written for the new variable, $X_1 = X_1^{qe} + \varepsilon X_1^{(0)}$. For this the following notations have been introduced: $R_1 = R_1^{qe} + \varepsilon R_1^{(0)}$, $R_{VV} = R_{VV}^{qe} + R_{VV}^{(0)}$, $R_{VC} = R_{VC}^{qe} + R_{VC}^{(0)}$, $R_V = R_V^{qe} + \varepsilon R_V^{(0)}$, where equations $\tilde{j}_q(X_1^{qe})X_1 = \tilde{j}_q(X_1^{qe})X_1^{qe} + \tilde{j}_q(X_1^{qe})X_1^{(0)}$ and $\tilde{j}_q'(X_1^{(0)})X_1^{qe} = \tilde{j}_q'(X_1)X_1^{qe}$ are taken into account. The last equation follows from the relationships $\tilde{j}_q'(X+Y)Z = \tilde{j}_q'(X)Z + \tilde{j}_q'(Y)Z$ and $\tilde{j}_q'(X_1^{qe})X_1^{qe} = 0$. Here

$$R_1^{qe} = \langle \psi_{n_1}, I(F_1^{qe}) \rangle = \langle \psi_{n_1}, I^{(V)}(X_1^{qe}) \rangle' = -\sum_{q=0}^{q_m} \left(P_{d,q}X_{1,q}^{qe} - P_{r,q}n_3n_4 \right),$$

$$R_1^{(0)} = \left\langle \psi_{n_1}, I'(F_1^{qe})X_1^{(0)} \right\rangle = \left\langle \psi_{n_1}, I^{(V)\prime}(X_1^{qe})X_1^{(0)} \right\rangle' = -\sum_{q=0}^{q_m} P_{d,q}X_{1,q}^{(0)}, \tag{23}$$

$$R_V^{qe} = \langle \psi_V, I(F_1^{qe}) \rangle = \langle \psi_V, I^{(V)}(X_1^{qe}) \rangle' = R_{VV}^{qe} + R_{VC}^{qe},$$

$$R_{VV}^{qe} = -\sum_{q=0}^{q_m-1} \tilde{j}_q(X_1^{qe})X_1^{qe}, \qquad R_{VC}^{qe} = -\sum_{q=0}^{q_m} q\left(P_{d,q}X_1^{qe} - P_{r,q}n_3n_4 \right),$$

$$R_V^{(0)} = \left\langle \psi_V, I'(F_1^{qe})F_1^{(0)} \right\rangle = \left\langle \psi_V, I^{(V)\prime}(X_1^{qe})X_1^{(0)} \right\rangle' = R_{VV}^{(0)} + R_{VC}^{(0)}, \tag{24}$$

$$R_{VV}^{(0)} = -\sum_{q=0}^{q_m-1} \left(\tilde{j}_q(X_1^{qe})X_1^{(0)} + \tilde{j}_q'(X_1^{(0)})X_1^{qe} \right), \qquad R_{VC}^{(0)} = -\sum_{q=0}^{q_m} qP_{d,q}X_{1,q}^{(0)},$$

where $R_{VV}^{qe,(0)}$ contains only vibrational transition probabilities, while $R_{VC}^{qe,(0)}$ contains reaction probabilities; ψ_{n_1} and ψ_V are introduced at the beginning of the previous section. Prime sign over the angular brackets in the last formulas mean that, unlike the previous definition, the corresponding scalar products don't contain the integration over velocities and summation over rotational quantum numbers. Sums in expressions (23) and (24) reduce to their last terms, since we neglect all dissociation and recombination processes except at the highest excitation level.

As a result, from Eq. (9) we obtain (dimensional variables are used here)

$$(1-\delta_{q,0})\tilde{j}_{q-1}(X_1^{qe})X_1 - (1-\delta_{q,q_m})\tilde{j}_q(X_1^{qe})X_1 + (1-\delta_{q,0})\tilde{j}_{q-1}'(X_1)X_1^{qe}$$

$$-(1-\delta_{q,q_m})\tilde{j}_q'(X_1)X_1^{qe} + \delta_{q,q_m}\left(P_{d,q}X_{1,q} - P_{r,q}n_3n_4 \right) + S(X_{1,q}^{qe})R_1 + \frac{\partial X_{1,q}^{qe}}{\partial \Gamma_V}R_V = 0. \tag{25}$$

From expressions for R_1 and R_V it is seen that the reaction rates are determined not by the equilibrium or quasi-equilibrium distribution, but by the quasi-stationary, X_1^{qs}, which is the solution of Eq. (25).

For solving Eq. (25) the procedure proposed is similar to what was applied in the one-temperature case in paper [7]. The only difference is that additional variable, Γ_V, needs the additional relationship $\Gamma_V = \sum_{q=0}^{q_m} q X_{1,q}$ to be satisfied. Then we obtain the following expression for the quasi-stationary distribution

$$X_{1,q}^{qs} = (\alpha_q/\tilde{a} + A_q + R_1 B_q + R_V B_{V\,q})\, X_{1,q}^{qe}, \tag{26}$$

$$A_q = \tilde{\tilde{c}}_q(X_1^{qs}) - \alpha_q \tilde{\tilde{C}}(X_1^{qs})/\tilde{a}, \qquad B_q = \tilde{c}_q - \alpha_q \tilde{C}/\tilde{a}, \qquad B_{V\,q} = \tilde{c}_{Vq} - \alpha_q \tilde{C}_V/\tilde{a},$$

$$\alpha_q = \prod_{m=0}^{q-1}\left(1 - \frac{\tilde{j}_m(X_1^{qe})X_1^{qe}}{\tilde{P}_{m+1,m}(X_1^{qe})X_{1,m+1}^{qe}}\right), \qquad \tilde{c}_q = \sum_{m=0}^{q-1}\frac{S(\Theta^{(m)})}{\tilde{P}_{m+1,m}(X_1^{qe})X_{1,m+1}^{qe}},$$

$$\tilde{c}_{V\,q} = \sum_{m=0}^{q-1}\frac{\partial\Theta^{(m)}/\partial\Gamma_V}{\tilde{P}_{m+1,m}(X_1^{qe})X_{1,m+1}^{qe}}, \qquad \tilde{\tilde{c}}_q(X_1) = -\sum_{m=0}^{q-1}\frac{\tilde{j}_m'(X_1)X_1^{qe}}{\tilde{P}_{m+1,m}(X_1^{qe})X_{1,m+1}^{qe}},$$

$$\tilde{a} = \sum_{n=0}^{q_m}\alpha_q X_{1,q}^{qe}/n_1, \quad \tilde{\tilde{C}} = \sum_{q=1}^{q_m}\tilde{\tilde{c}}_q X_{1,q}^{qe}/n_1, \quad \tilde{C} = \sum_{q=1}^{q_m}\tilde{c}_q X_{1,q}^{qe}/n_1, \quad \tilde{C}_V = \sum_{q=1}^{q_m}\tilde{c}_{Vq}X_{1,q}^{qe}/n_1.$$

Further the following consequences of the detailed balance relationship are used: $P_{p,q}X_{1,p}^B = P_{q,p}X_{1,q}^B$ and $Q_{p,q}^{s,l}X_{1,p}^B X_{1,s}^B = Q_{q,p}^{l,s}X_{1,q}^B X_{1,l}^B$, while for isoquantum transitions we also have $Q_{p,q}^{s,l}X_{1,p}^{Tr}X_{1,s}^{Tr} = Q_{q,p}^{l,s}X_{1,q}^{Tr}X_{1,l}^{Tr}$, where Treanor distribution function $X^{Tr} = X^{qe}$ is defined by (16) and $X^B = X^{Tr}(\gamma_q = 0)$ is the Boltzmann distribution function. Thus we have $\tilde{j}_q(X^{qe})X^{qe} = P_{q+1,q}X_{1,q+1}^{qe}(1 - e^{\gamma_V}) = P_{q,q+1}X_{1,q}^{qe}(e^{-\gamma_V} - 1)$.

Substituting expression (26) for $X_{1,q}$ into the expression for relaxation rate (24): $R_V = R_{VV} + q_m R_1$, $R_{VV}(X_1) = -\sum_{q=0}^{q_m-1}\left(\tilde{j}_q(X_1^{qe})X_1 + \tilde{j}_q'(X_1)X_1^{qe}\right)$, and into expression for reaction rate (23), we obtain the following equations for generalized relaxation rates

$$R_V\left(1 - R_{VV}(B_V X_1^{qe})\right) = R_{VV}(\alpha X_1^{qe})/\tilde{a} + R_{VV}(A X_1^{qe}) + \left(R_{VV}(B X_1^{qe}) + q_m\right)R_1,$$

$$R_1\left(1 + P_{d,q_m}B_{q_m}X_{1,q_m}^{qe}\right) = -P_{d,q_m}\left(\alpha_{q_m}X_{1,q_m}^{qe}/\tilde{a} + A_{q_m}X_{1,q_m}^{qe} + R_V B_{V q_m}X_{1,q_m}^{qe}\right) + P_{r,q_m}n_3 n_4. \tag{27}$$

Functions A_q, B_q and $B_{V\,q}$ are defined in Eq. (26). Such a simple relationship is a consequence of the assumption that the dissociation takes place only from the highest vibrational level.

Using the first relationship from (27), expression (26) can be written as

$$X_{1,q}^{qs} = \left(\Delta' + A_q' + R_1 B_q'\right)X_{1,q}^{qe}, \qquad \Delta_q' = \Delta_q + \frac{B_{Vq}R_{VV}(\alpha X_1^{qe}/\tilde{a})}{1 - R_{VV}(B_V)}, \qquad \Delta_q = \frac{\alpha_q}{\tilde{a}},$$

$$A_q' = A_q + B_{Vq}\frac{R_{VV}(A X_1^{qe})}{1 - R_{VV}(B_V X_1^{qe})}, \qquad B_q' = B_q + B_{Vq}\frac{R_{VV}(B X_1^{qe}) + q_m}{1 - R_{VV}(B_V X_1^{qe})}. \tag{28}$$

Finally, using the second relationship from (27), the scalar parts of the generalized relaxation rates are represented as

$$R_1 = -\frac{P_{d,q_m}\left(\Delta_{q_m}' + A_{q_m}'\right)X_{1,q_m}^{qe} - P_{r,q_m}n_3 n_4}{1 + P_{d,q_m}B_{q_m}'X_{1,q_m}^{qe}}, \tag{29}$$

$$R_V = \frac{R_{VV}(\alpha X_1^{qe}/\tilde{a}) + R_{VV}(A X_1^{qe}) + (R_V{}_V(B X_1^{qe}) + q_m) R_1}{1 - R_V{}_V(B_V X_1^{qe})}.$$ (30)

The expression for relaxation rate R_V can be represented as a sum of two terms [14]: $R_V = R_V^{(r)} + R_V^{(ch)}$, one of which, $R_V^{(r)}$, is responsible for the quantum number density Γ_V relaxation due to energy exchange between vibrational and translational degrees of freedom, and $R_V^{(ch)}$ is responsible for Γ_V relaxation due to chemical reactions. The last term being proportional to R_1.

3.3   Cut-off Harmonic Oscillator Model

For the cut-off harmonic oscillator model, expressions (29) and (30) can be simplified. Using that

$$P_{m+1,m} = (m+1)P_{10}, \qquad Q_{m+1,m}^{l,l+1} = (l+1)(m+1)Q_{10}^{01},$$ (31)

and that

$$\Gamma_V = \sum_{q=0}^{q_m} q X_{1,q}^{qe} = X_{1,0}^{qe} \left(\frac{e^{-\theta_V}\left(1 - e^{-\theta_V(q_m+1)}\right)}{(1 - e^{-\theta_V})^2} - \frac{(q_m+1)e^{-\theta_V(q_m+1)}}{1 - e^{-\theta_V}} \right)$$

$$= \frac{e^{-\theta_V}}{1 - e^{-\theta_V}} \left(n_1 - (q_m+1)X_{q_m}^{qe} \right), \qquad \theta_V = \gamma_E \hbar \omega_e + \gamma_V,$$ (32)

we can calculate

$$j_m'(X_1)X_1^{qe} = Q_{10}^{01}(m+1)X_{1,m}^{qe} \left(\sum_{l=0}^{q_m-1} (l+1)e^{-\theta_V}X_{1,l} - \Gamma_V \right)$$

$$= Q_{10}^{01}(m+1)X_{1,m}^{qe} \left(e^{-\theta_V}\left(\Gamma_V - q_m X_{q_m} + n_1 - X_{q_m}\right) - \Gamma_V \right)$$

$$= Q_{10}^{01}(m+1)X_{1,m}^{qe}(q_m+1)e^{-\theta_V} \left(X_{1,q_m}^{qe} - X_{1,q_m} \right).$$

Applying operators $\frac{\partial}{\partial \Gamma_V}$ and S to both parts of Eq. (32), and using that $\frac{\partial n_\alpha}{\partial \Gamma_V} = \frac{\partial \Gamma_V}{\partial n_\alpha} = 0$, we obtain

$$S(\theta_V) = \kappa_0 \left(e^{\theta_V} - 1\right)\Gamma_V/n_1^2, \qquad \frac{\partial \theta_V}{\partial \Gamma_V} = -\kappa_0 \left(e^{\theta_V} - 1\right)/n_1,$$

$$\kappa_0 = \left[1 + \Gamma_V/n_1 + (q_m + 1 - \Gamma_V/n_1)\left(\left(e^{\theta_V} - 1\right)\Gamma_V/n_1 - 1\right)\right]^{-1}.$$ (33)

Taking into account that

$$\tilde{P}_{m+1,m} = (m+1)\left(P_{10} + Q_{10}^{01}e^{\theta_V}\sum_{l=0}^{q_m-1}(l+1)X_{1,l+1}^{qe}\right) = (m+1)\left(P_{10} + Q_{10}^{01}e^{\theta_V}\Gamma_V\right),$$

$\tilde{\tilde{c}}_q$ can be represented as

$$\tilde{\tilde{c}}_q(X_1) = -\frac{(q_m+1)\left(X_{1,q_m}^{qe} - X_{1,q_m}\right)}{e^{\theta_V}\Gamma_V(\beta_V + 1)}q, \qquad \beta_V = \frac{P_{10}}{Q_{10}^{01}e^{\theta_V}\Gamma_V}.$$

After some algebra one derives

$$A_q(X_1^{qs}) = -\frac{(q_m+1)}{(1+\beta_V)e^{\theta_V}} \left(X_{1,q_m}^{qe} - X_{1,q_m}^{qs}\right) \left(\frac{q}{\Gamma_V} - \frac{\alpha_1^q}{\tilde{A}}\right),$$

$$R_{VV}(A_q(X_1^{qs})X_1^{qe}) = -\left(\Delta'_{q_m} - 1 + A'_{q_m}(X_1^{qs}) + B'_{q_m}\right) A_R \frac{(1-(e^{\theta_V}-1)\Gamma_V/n_1)P_{10}n_1}{(1+\beta_V)e^{\theta_V}}, \quad (34)$$

$$A_R = e^{\gamma_V} - (e^{\gamma_V}-1) \times \left(\frac{\Gamma'_V}{\Gamma_V} - \frac{\tilde{\Gamma}_V}{\tilde{a}\,(1+\beta_V e^{\gamma_V})\,n_1}\right).$$

where

$$\tilde{\Gamma}_V = \sum_{m=1}^{q_m} m\alpha_1^m X_{1,m}^{qe} \approx \alpha_1\Gamma_V \frac{(e^{\theta_V}-1)^2}{(e^{\theta_V}-\alpha_1)^2}, \qquad \Gamma'_V = \sum_{q=1}^{q_m} q^2 X_{1,q}^{qe} \approx \frac{\Gamma_V}{1-e^{-\theta_V}},$$

$$\alpha_q = \left(\frac{\beta_V e^{\gamma_V}+1}{\beta_V+1}\right)^q = \alpha_1^q = 1 + O(\beta_V), \qquad \tilde{a} = \frac{\left(1-e^{-\theta_V}\right)\left(1-\left(\alpha_1 e^{-\theta_V}\right)^{q_m+1}\right)}{\left(1-e^{-\theta_V(q_m+1)}\right)\left(1-\alpha_1 e^{-\theta_V}\right)}$$

$$\approx \frac{1-e^{-\theta_V}}{1-\alpha_1 e^{-\theta_V}} = \frac{(1-e^{-\theta_V})(1+\beta_V)}{1-e^{-\theta_V}+\beta_V(1-e^{\gamma_V-\theta_V})} = 1 + O(\beta_V).$$

Here and further on the sign "$\approx$" is practiced to designate that approximations based on the following relationships: $e^{-\theta_V(q_m+1)} \ll 1$ and $1/q_s \ll 1$ are used. These expressions make it possible to calculate $A'_q(X_1^{qs})$ according expression from (28):

$$A'_q(X_1^{qs}) = \left(\Delta'_{q_m} - 1 + A'_{q_m}(X_1^{qs}) + R_1 B'_{q_m}\right) Q_q X_{1,q_m}^{qe},$$

$$Q_q = \frac{(q_m+1)}{(1+\beta_V)e^{\theta_V}} \left(\frac{q}{\Gamma_V} - \frac{\alpha_1^q}{\tilde{a}n_1} - \frac{A_R P_{10}}{1-R_{VV}(B_V X_1^{qe})} B_{Vq}\right) \quad (35)$$

$$\approx \frac{(q_m+1)\Gamma_V}{(1+\beta_V)(n_1+\Gamma_V)} \frac{1+\beta_V(1+2\tilde{A}_R)}{1+\beta_V(1+\tilde{A}_R)} \left(\frac{q}{\Gamma_V} - \frac{\alpha_1^q}{\tilde{a}n_1}\right),$$

$$A_R \approx \tilde{A}_R = 1 + (1-e^{\gamma_V})\beta_V\tilde{a}_R, \qquad \tilde{a}_R = \frac{(1+(1-e^{\gamma_V})\Gamma_V/n_1)}{1+\beta_V(1+(1-e^{\gamma_V})\Gamma_V/n_1)} \frac{\Gamma_V}{n_1}.$$

Solved for $q = q_m$, this equation leads to the explicit expression for $A'_{q_m}(X_1^{qs})$

$$A'_{q_m}(X_1^{qs}) = \left(\Delta'_{q_m} - 1 + R_1 B'_{q_m}\right) \frac{Q_{q_m} X_{1,q_m}^{qe}}{1-Q_{q_m} X_{1,q_m}^{qe}}. \quad (36)$$

Being substituted into equation (29), it leads to the renormalized expression for the reaction rate, which is exact for the cut-off harmonic oscillator model, and to corresponding changes in the expression for relaxation rate (30):

$$R_1 = -\frac{P_{q_m,d}(\Delta'_{q_m} - Q_{q_m}X_{1,q_m}^{qe})X_{1,q_m}^{qe} - P_{q_m,r}n_3n_4(1-Q_{q_m}X_{1,q_m}^{qe})}{1+(P_{q_m,d}B'_{q_m} - Q_{q_m})X_{1,q_m}^{qe}}. \quad (37)$$

This equation can be written as

$$R_1 = R_1^{qe}F - \left(P_{d,q_m}\Delta''_{q_m} + Q_{q_m}P_{r,q_m}n_3n_4\right)X_{1,q_m}^{qe}F, \qquad R_1^{qe} = -\left(P_{d,q_m}X_{1,q_m}^{qe} - P_{r,q_m}n_3n_4\right),$$

$$F = \left(1 + (P_{d,q_m}B'_{q_m} - Q_{q_m})X_{1,q_m}^{qe}\right)^{-1}, \qquad \Delta''_{q_m} = \Delta'_{q_m} - 1 - Q_{q_m}X_{1,q_m}^{qe}, \tag{38}$$

For R_V we obtain

$$R_V = \frac{R_{VV}(\alpha X_1^{qe}/\tilde{a}) + R_{VV}(A(X_1^{qs})X_1^{qe}) + (R_{VV}(BX_1^{qe}) + q_m)R_1}{1 - R_{VV}(B_V X_1^{qe})}$$

$$= \frac{R_V^{qe} + (1 - e^{\gamma_V})\left(1 - \dfrac{\tilde{\Gamma}_V}{\tilde{a}(1 + \beta_V e^{\gamma_V})\Gamma_V}\right)P_{10}\Gamma_V - q_m R_1^{qe}}{1 - R_{VV}(B_V X_1^{qe})}$$

$$- \frac{(q_m+1)(\Delta'_{q_m}-1)e^{-\theta_V}A_R P_{10}X_{1,q_m}^{qe}}{(1+\beta_V)(1-Q_{q_m}X^{qe})(1-R_{VV}(B_V X_1^{qe}))} \tag{39}$$

$$+ \frac{\left(R_{VV}(BX_1^{qe}) + q_m - \dfrac{(q_m+1)B'_{q_m}e^{-\theta_V}A_R P_{10}X_{1,q_m}^{qe}}{(1+\beta_V)(1-Q_{q_m}X^{qe})}\right)R_1}{1 - R_{VV}(B_V X_1^{qe})},$$

where

$$R_V^{qe} = R_{VV}^{qe} + q_m R_1^{qe}, \qquad R_{VV}^{qe} = R_{VV}(X_1^{qe}) = -(1 - e^{\gamma_V})P_{10}\Gamma_V,$$

so that R_1 and R_V are represented as linear combinations of corresponding quasi-equilibrium rates, and

$$B_{q_m} \approx \frac{\Sigma_{q_m}}{(1+\beta_V)Q_{10}^{01}n_1^2}, \qquad \Sigma_q(\theta_V) = \sum_{m=1}^{q}\frac{e^{\theta_V m}-1}{m}, \qquad \Sigma_{q_m} \sim \frac{e^{\theta_V(q_m+1)}}{e^{\theta_V}-1}\ln q_m,$$

$$\overline{\Sigma} = \sum_{q=1}^{q_m}\Sigma_q(\theta_V)\frac{X_{1,q}^{qe}}{n_1} \sim q_m \ln q_m,$$

$$R_{VV}(BX_1^{qe}) \approx -\frac{\beta_V}{1+\beta_V}\left[e^{\gamma_V}q_m - (e^{\gamma_V}-1)\left(\frac{\Gamma_V}{n_1}\left(\frac{\Gamma'_V}{\Gamma_V} - \frac{\tilde{\Gamma}_V}{\tilde{a}(1+\beta_V e^{\gamma_V})n_1}\right)\right.\right.$$

$$\left.\left. + \left(1 + \frac{\Gamma_V}{n_1}\right)\left(\frac{\Gamma''_V}{n_1} - \frac{\overline{\Sigma}\tilde{\Gamma}_V}{\tilde{a}(1+\beta_V e^{\gamma_V})n_1}\right)\right)\right], \qquad B_{V q_m} \approx -\frac{q_m/\Gamma_V - \alpha_1^{q_m}/\tilde{a}n_1}{(1+\beta_V)Q_{10}^{01}(n_1+\Gamma_V)},$$

$$\Gamma''_V = \sum_{q=1}^{q_m}q X_{1,q}^{qe}\Sigma_q, \qquad R_{VV}\left(\frac{\alpha_1^q X_{1,q}^{qe}}{\tilde{a}}\right) = \frac{P_{10}(e^{\gamma_V}-1)\tilde{\Gamma}_V}{\tilde{a}(1+\beta_V e^{\gamma_V})}, \qquad R_{VV}(B_V X_1^{qe}) \approx -\frac{\beta_V}{1+\beta_V}\tilde{A}_R.$$

Expressions (38) and (39) can be significantly simplified if smallness of the parameter β_V is used. Taking into account that $R_{VV}(BX_1^{qe}) \sim R_{VV}(B_V X_1^{qe}) \sim \beta_V$, we finally obtain ($\gamma_V =$

$\hbar\omega_e \left(1/T_V - 1/T\right)/k_B$

$$R_1 = R_1^{qe} \left(1 - Q_{q_m} X_{1,q_m}^{qe}\right) F_0, \qquad R_V = P_{10} \left(e^{\gamma_V} - 1\right) \Gamma_V + q_m R_1^{qe} F_0,$$

$$F_0 = \left(1 + q_m \left(\frac{P_{d,q_m}}{Q_{10}^{01}\Gamma_V}\Sigma_{q_m} - \frac{(q_m+1)n_1}{n_1+\Gamma_V}\right)\frac{X_{1,q_m}^{qe}}{n_1}\right)^{-1}. \tag{40}$$

Obtained expressions have a traditional form. Though it should be mentioned that under assumption $\beta_V \ll 1$, the ratio of two-temperature non-equilibrium reaction rate constants of forward and reverse reactions does not depend on the kinetic parameters (transition probabilities) and can be expressed via the equilibrium constant (thermodynamic function). This is not the case for a non-simplified expression (38), obtained for the arbitral value β_V. The expression for R_V has a common structure: the sum of the relaxation term and the term responsible for the 'thermal' effect caused by dissociation-recombination reactions. The relaxation term is presented as containing factor $e^{\gamma_V} - 1$. The Landau-Teller equation, strictly speaking, is correct only for the harmonic oscillator model, while the obtained expression is correct for arbitral models with one-quantum transitions.

4   Discussion

Considering the two-temperature approximation and the widely used cut-off harmonic oscillator model, we have shown that generalized relaxation rates (reaction and relaxation rates) are the linear combinations of the quasi-equilibrium ones (calculated with the quasi-equilibrium distribution function). Coefficients in these expressions are the functions of the whole set of gas-dynamic variables. This result is important for modeling the reacting gas flows, using existing data on rate constants, since, as was shown in papers [2, 12], only equilibrium reaction rates can be calculated using rate constant conception. The obtained result is also of high importance for developing the methodology of getting data on chemical reaction rates from experiments.

Attention should be drawn to the fact that for high energies F^{qe} is of the order of ε and therefore $F^{qe} \approx \varepsilon\Phi$ here. This high-energy range is responsible for reaction-rate values and thus high-energy particles play an important role in the macroscopic description of the reacting gases, in spite of their limited number. One of the advantages of our method is that it permits the correct description of the contribution of high-energy particles into the gas-dynamic equations.

Here it should be mentioned that the method under development is valid only for the hard potentials in Grad's meaning [16]. As was found by Grad, the spectrum of the Boltzmann collision operator for the case of soft potentials (power potentials $V = V_0(r_0/r)^s$ with $s < 4$) dramatically differing from the case of hard potentials ($s \geq 4$). For hard potentials the collision operator has five zero eigenvalues and continuous spectrum, which is separated from zero by the value $\nu_0 = \nu(\xi = 0) = 2\pi\beta_0 2^\alpha \Gamma(\alpha)$, $\alpha = (2s-4)/(s-1)$, β_0 is a multiplier in the total cross-section that is independent of the relative velocity of colliding particles $\xi = |\mathbf{v} - \mathbf{v}'|$ [16]. For $\xi \to \infty$ we have $\nu(\xi) \to \infty$, so that continuous spectra fills the zone $\omega \leq -\nu_0$ of the complex plane. Opposite to this, for soft potentials continuous spectra fills the strip $-\nu_0 \leq \omega < 0$. It should be pointed out that for high velocities the spectrum is infinitesimally close to zero ($\nu(\xi) \to 0$, while $\xi \to \infty$). Though the existence of the Boltzmann equation solution is proofed for the general case [16], the asymptotic theory of obtaining the solution thereto has been built for the hard potentials only. So, the approach to the quasi-equilibrium of the perturbed distribution can have non-exponential time dependence. This can have far-reaching consequences for the corresponding gas-dynamic equations. Corresponding integral equations of the Chapman-Enskog method are incorrect in the sense that the reverse to the linearized collisional operator is unbounded. This leads to the results being very sensitive to the chosen basis, when a traditional expansion of the kinetic equation over the full set of orthogonal functions is used within the Chapman-Enskog method. Mentioning that plasma

and nuclear matter are described by soft potentials (Coulomb and Yukawa), deriving gas-dynamic equations for these cases is of great importance. Some aspects of this problem were considered in [17]. There it was shown that the perturbation relaxation in spatially homogenous gas for soft potentials obeys the $t^{-\alpha}e^{-\delta t^{\beta}}$ law, not the $e^{-\nu t}$ law as for hard potentials, where δ and β are the functions of the potential parameter s. So the perturbation decay rate is slower for the soft potentials. Conclusions have yet to be formed on how this fact impacts the gas-dynamic equation structure and thus is one of the challenges of contemporary physical-chemical gas-dynamics.

In this connection one more result of the recent research should be mentioned. As it is discussed in [18], there is an even more profound problem with applying classical statistical mechanics to systems with so called long-range (LR) forces. These forces are described by the potentials which decay with exponents smaller than the dimensionality of the embedding space: $V = V_0(r_0/r)^s$, where $s < d$ and d is the dimensionality of the space. For such systems traditional thermodynamics fails and the velocity distribution in the stationary state will not have the characteristic MaxwellBoltzmann form. As it is mentioned in [18], examples of such systems include galaxies and globular clusters, colloids at interfaces as well as magnetically confined plasmas. We hope that listed challenges will attract the attention of the experts in the physical-chemical gas dynamics and related fields.

Further work on developing of our approach will consist in: (1) Choosing the suitable set of polynomials, (2) Integral brackets calculation, (3) Tabulating of the generating functions for generalized thermodynamics.

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