Gasdynamic equations with the number of gasdynamic variables exceeding the number of summational invariants

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Abstract. An asymptotic new method of solving the generalized Boltzmann equation previously developed by the authors is presented, and its difference from the traditional Chapman-Enskog method is discussed. The application of this new method is considered by an example of an O2/O dissociating mixture flow with separation around a double cone. A comparison with available literature and experimental data is presented. The computed and measured surface heat fluxes are found to be in reasonable agreement. The computed surface heat flux is analyzed through comparisons to numerical results of other researchers and codes.

1 Introduction
In modeling complex flows with physical and chemical transformations, the gasdynamic equations are most often used for an extended list of variables, not only for those corresponding to summational invariants (SI) of the original Boltzmann equation (BE), but also for a number of other variables. For the case of chemically reacting gases, these are, first of all, chemical components’ densities and, in a more detailed description, temperatures of the internal degrees of freedom, translational temperatures of various components (for mixtures with significantly different components’ masses), etc. Extension of the list of gasdynamic variables is relevant due to the high computational cost of solving the kinetic equations, even in their simplified form. If the gasdynamic variable does not correspond to the SI, source terms appear in the corresponding gasdynamic equation (reaction rates, momentum and energy exchange rates, etc.), which are either determined from phenomenological considerations or calculated from the BE using equilibrium distribution functions. The traditional method of deriving gasdynamic equations from kinetic equations does not yield correct results from the asymptotic point of view [1]. It may even lead to divergency of higher-order expansion terms with respect to the asymptotic expansion parameter in the corresponding source terms. It was shown [1,2] that the use of equilibrium distributions, which are traditionally employed for the source terms’ calculation, can lead to significant inaccuracies. This makes the development of a new approach for derivation of gasdynamic equations relevant.

A new asymptotic method for solving the Boltzmann equation was proposed in [2]. Initially it was developed for reaction rates’ calculation [3-5]. It was also applied for deriving a homogeneous nucleation rate [6] and rates of momentum and energy exchange in a mixture of heavy and light gases [7]. In all cases, the resultant reaction and relaxation rates demonstrate a complex dependence of the source terms on the components’ densities (partial pressures). This leads to the need to abandon the concept of rate constants for chemically reacting mixtures, for instance. Here, it should be mentioned that, in studying the nucleation process and deriving the expression for the nucleation rate within the quasi-chemical nucleation model, the resulting corrections to its classical (Frenkel-Zeldovich) expression were small. Now it is clear that this is a consequence not of the method [2] itself, but of the method of solving the corresponding equations for corrections to the equilibrium distribution function, connected with the clusters’ internal vibrations. Those corrections were calculated by expansion into series over the complete set of polynomials. As shown in [8] by an example of an exactly solvable model, the series expansion method significantly underestimates the impact of vibrational non-equilibrium; therefore, we expect significant corrections to the nucleation rate obtained by building a new model for clusters’ vibrations and applying our method to the quasi-chemical nucleation model, as it is done for the reaction rates in [5].

Here we present one more flow example, with non-equilibrium diatomic molecule dissociation behind a shock wave. A two-temperature model with quasi-stationary reaction rates is employed.

The paper is organized as follows. In the next section we briefly present the method leading to new expressions for reaction and relaxation rates, describe the problem statement, and discuss the computation results; the conclusions are drawn in the last section.

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2 Problem statement

2.1 Asymptotic method for solving the Boltzmann equation

The starting point for building the asymptotic procedure is the generalized Boltzmann equation

$$\left( \frac{\partial}{\partial t} + v \cdot \nabla \right) F = \frac{1}{\varepsilon} I,$$  \hspace{1cm} (1)

where $t$ is the time, $r$ is the spatial coordinate, $v$ is the particle velocity, $F$ is the distribution function, $I$ is the collisional operator describing the chemical reactions, $\varepsilon = t_c / t_g$, and $t_c$ and $t_g$ are the characteristic time scales of the inelastic processes and the gas dynamics, respectively. The convective characteristic time is assumed to be of the order of the gasdynamic time, and therefore, it is sufficient to introduce only one dimensionless parameter $\varepsilon$ [2].

In our method, the collisional integral part responsible for the chemical reactions is not considered as a small correction (perturbation) of the order of $\varepsilon$. Additionally to the traditional exact summation invariants (ESI), for which $\langle \psi_i, I_\alpha \rangle = 0$ ($i$ numerates corresponding invariants, and $\alpha$ numerates the mixture species), approximate summation invariants (ASI), $\psi_i$, are introduced, which are invariants of the collisional operator $I$ within the small parameter $\varepsilon$: $\langle \psi_i, I_\alpha \rangle \leq \varepsilon$, where $\langle \phi, \psi \rangle = \sum_k q \phi_k q \psi_k d\nu_a$ is the scalar product. Gasdynamic variables are introduced by corresponding ASI averaging: $\Gamma_i = \langle \psi_i, I_\alpha \rangle$. The distribution function is represented as a sum of two terms, $F_a = F^{eq}_a + \Phi_a$. The first term is a function of time and spatial coordinates only via the gasdynamic variables $F^{eq}_a = F^{eq}_a(\Gamma_i^a)$, for which the function obtained from the maximum entropy principle is used. The generalized Boltzmann equation is written as a singularly perturbed system of equations for the gasdynamic, $\Gamma_i$, and fast, $\Phi_a$, variables. The formulated asymptotic method sets an algorithm to determine sequentially the corrections of different orders in $\varepsilon$ to the quasi-equilibrium distribution $F^{eq}_a$.

As $F^{eq}_a$ is not a solution of the equation $I(F) = 0$, the correction to $F^{eq}_a$ occurs at the zeroth order. At the same time, $I(F^{eq}_a)$ is assumed to be of the order of $\varepsilon$. As a result, the reaction and relaxation rates in the transport equations (called generalized relaxation rates (GRR)) contain a description of non-equilibrium effects in the zeroth-order (Euler) approximation. The resulting expressions for the reaction and relaxation rates can be referred to as quasi-stationary.

2.2 Diatomic gas dissociation model

The gasdynamic equations for a dissociating diatomic gas were derived in [5]. The main model positions are as follows. A mixture of molecules $A_2$ and atoms $A$ is considered. The corresponding reactions include:

$$\begin{align*}
A_2 + A_2 & \leftrightarrow A_2 + 2A, \\
A_2 + A & \leftrightarrow 3A.
\end{align*}$$  \hspace{1cm} (2, 3)

A set of ASIs that leads to the traditional set of gasdynamic variables is chosen: the Kronecker symbol as an ASI corresponds to the species number density $\Gamma_\alpha n_\alpha = n_\alpha$, $\alpha = A_2, A$.

The momentum $p$ corresponds to $\Gamma_\alpha = \rho u$, where $\rho$ and $u$ are the mixture mass density and velocity, respectively.

The total energy constitutes to the total energy density of the mixture: $\Gamma_\varepsilon \equiv E = \hat{E} + q u^2 / 2 + E'$. $\hat{E} = 3nk_B T / 2 + E + E' = \sum_\alpha n_\alpha \hat{E}_\alpha$ is the internal energy density of the mixture, $k_B$ is the Boltzmann constant, $\hat{E}_\alpha$ is the internal energy of the species $E$, $E'$, and $E' = \sum_\alpha n_\alpha E'_\alpha$ are the rotational, vibrational, and formation energy densities of the mixture, and $E'_\alpha$ is the formation energy of the species $\alpha$.

The vibrational energy density $\Gamma_{v'v} \equiv E' = \sum_\alpha n_\alpha E'_{\alpha}$ finalizes the list of gasdynamic variables.

For our specific case, where only one diatomic species is considered, the subscript in the expressions concerning the internal energy characteristics can be omitted. Denoting the molecule number density as $n_m$, where $m \equiv A_2$, its vibrational energy density can be written as $E' = n_m E'_m$. Further on, the subscripts indicating a diatomic molecule are omitted where this does not lead to confusion.

The cutoff harmonic oscillator model is employed for the diatomic molecules’ vibrational energy $e'_v = h\omega_v (q + 1/2)$, where $\omega_v$ is the oscillator frequency and $q$ is the vibrational quantum number. Though it leads to some inaccuracies, it is widely used to describe molecular internal vibrations when complex chemical reactions are studied [9, 10]. On the other hand, this model yields analytical expressions for final quantities (reaction and relaxation rates), which makes the parametric analysis clear. In this case, instead of the energy density, $E' = h\omega_v (\bar{q} + 1/2)n_m$, the mean quantum value density, $\Gamma_{v'} = n_m \bar{q}$, can be used as a gasdynamic variable, where $\bar{q}$ is the traditional mean quantum value.

For that set of gasdynamic variables, the quasi-equilibrium distribution reads

$$F^{eq}_a = n_{\alpha_s} \frac{\rho_{\alpha_s}(T_{\alpha_s})}{Q_{\alpha_s}(T_{\alpha_s})} \exp \left( - \frac{1}{k_B T} \left( \frac{m_{\alpha_s} c_{\alpha_s}^2}{2} + e'_r + e'_v \right) \delta_{\alpha,m} \right) \left( \frac{\rho_{\alpha_s}}{k_B} \left( \frac{1}{T_{\alpha_s}} - \frac{1}{T} \right) q \delta_{\alpha,m} \right).$$  \hspace{1cm} (4)

Here $s_{\alpha}(j_{\alpha})$ is the statistical weight of the rotational quantum levels, $Q_{\alpha}(T)$ is the partition function, $c_{\alpha} = v_{\alpha} - u$ is the peculiar species velocity, and $e'_r$ is the rotational energy of the species $\alpha$.

The equations for these variables, $n_\alpha$, $\rho u$, $E$, and $\Gamma_{v'}$, were derived in [5]:

$$\begin{align*}
\frac{\partial n_\alpha}{\partial t} + \nabla \cdot (n_\alpha u) &= R^{\alpha}_{v'}(\nabla, u, E, \Gamma_{v'}), \quad \alpha, \beta = A, A_2, \\
\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u u) + \nabla p &= 0, \quad p = n k_B T, \\
\frac{\partial E}{\partial t} + \nabla \cdot (E u) &= 0, \\
\frac{\partial \Gamma_{v'}}{\partial t} + \nabla \cdot (\Gamma_{v'} u) &= R^{\alpha}_{v'}.
\end{align*}$$  \hspace{1cm} (5–8)

Here $R^{\alpha}_{v'}((n_{\beta}), u, E, \Gamma_{v'})$ and $R^{\alpha}_{v'}((n_{\beta}), u, E, \Gamma_{v'})$ are the quasi-stationary GRRs: $R^{\alpha}_{v'} = (\delta_{\alpha \beta}, I_{\beta}(F^{eq})) +$
The quasi-stationary GRRs are determined not only by the equilibrium distribution, but by the first-order rates of the reaction and relaxation contributions to this sum. The presence of additional terms within the traditional Chapman-Enskog method contains correcion to the quasi-equilibrium distribution function of the reaction and relaxation rates. Equations derived (further the superscript (1) will be omitted because only correction to the quasi-equilibrium distribution function corresponding source terms vanish) for ESIs, only ASIs in Kolesnichenko’s collisional operator, determines the quasi-stationary GRRs in their non-equilibrium parts. The exact solution of Eq. (10) was derived:

\[
\frac{R_{m}^{q}}{R_{m}^{n}} = -\left(\frac{P_{dq}X_{m}^{n} - P_{eq}n_{s}^{1}}{P_{eq}n_{s}^{1}}\right), \tag{13}
\]

\[
R_{v}^{q} = \frac{R_{m}^{q}}{R_{m}^{n}}(1 - e^{-\nu}) + q_{m}R_{v}^{n}, \quad Y_{v} = \frac{h_{0}^{2}k_{s}^{2}}{n_{s}^{1}T_{v}} \frac{1}{\tau_{v}}. \tag{14}
\]

Here \(P_{dq}\) is the dissociation rate constant of the considered molecule from the level \(q\), \(P_{eq}\) is the corresponding recombination rate constant with the formation of the molecule at the vibrational state \(q\), \(q_{m}\) is the highest vibrational level, \(n_{s}\) is the number density of the atoms \(A\), and \(P_{10}\) is the probability of the VT-transition from level 1 to level 0.

There are no spatially inhomogeneous non-equilibrium corrections (proportional to hydrodynamic velocity divergence) within the harmonic oscillator model [5]. The spatially homogeneous corrections are

\[
P_{v}^{n} = \frac{P_{dqq}X_{m}^{n}(1 - e^{-\nu})}{(1 + \beta_{v}^{-1})}\psi_{v}(\theta_{v},a_{1}), \tag{15}
\]

where \([a_{1}] = \frac{a_{1} - 1}{a_{1} + 1}a_{1}^{-1}, a_{1} = (e^{\nu} + \beta_{v}^{-1})/(1 + \beta_{v}^{-1}), \beta_{v}^{-1} = Q_{10}^{e}P_{v}^{n}\theta_{v}/P_{10}, \theta_{v} = h_{0}^{2}k_{s}^{2}k_{B}T_{v}, \]

\[
R_{v}^{n} = q_{m}n_{s}^{1}\left(1 + P_{10}\right)/P_{dqq}. \tag{16}
\]

The renormalizing coefficients are

\[
A_{mm} = \frac{P_{dqm}X_{m}^{n}(1 - e^{-\nu})}{(1 + \beta_{v}^{-1})^{2}}\sum_{a_{1}}(\theta_{v},a_{1}), \tag{17}
\]

\[
A_{m} = \frac{P_{dqm}X_{m}^{n}(1 + \beta_{v}^{-1})}{n_{m}^{1}(1 + \beta_{v}^{-1})^{2}}, \tag{18}
\]

\[
A_{v} = q_{m}P_{dqq}P_{10}^{n}e^{-\nu}\sum_{a_{1}}(\theta_{v},a_{1}), \tag{19}
\]

\[
\Sigma_{q}(\theta_{v},a_{1}) = \sum_{a_{1}(1 + \beta_{v}^{-1})e^{q\nu}}(1 + \beta_{v}^{-1})^{-1}/q. \tag{20}
\]

The coefficients \(A_{mm}\) and \(A_{m}\) are proportional to the ratio of the vibrational and chemical time scales, which increase with temperature and may reach rather large values. That ratio is independent of the Knudsen number; therefore, the renormalizing coefficients cannot be neglected even if the Knudsen number approaches zero. On the other hand, it means that expressions (11) and (12) cannot be derived by summing over the corresponding terms of a different order of the traditional Chapman-Enskog expansion.

Expressions (11) and (12) transform into each other by means of permutation of the subscripts \(m\) and \(v\). This symmetry emphasizes the mathematical similarity of these quantities. From the physical point of view, it means the mutual impact of the reaction and relaxation processes. While the reactions’ impact on the relaxation rates is well known [11], the opposite effect was obtained in [5] for the cut-off oscillator model. Within that model, only one-quantum vibrational transitions are obtained in [5]. Nevertheless, it should be noted that this opposite effect is negligibly small for the considered regimes due to the small values of the \(A_{mv}\) coefficients.
3 Simulations

3.1 Problem formulation

The governing equations (5) – (8) are solved numerically with Ansys Fluent: system (5) – (8) is adopted to a form consistent with the Ansys Fluent’s form. Equation (8) is added as a user defined scalar. GRRs (11) and (12) are computed as source terms in user defined functions. A density-based solver is used for computations with the second-order upwind scheme and AUSM for the inviscid flux. Other details can be found in [5].

3.2 Computational domain and boundary conditions

An O₂/O binary mixture flow around a double cone is simulated numerically under conditions of Run 87 considered in [12]. The computational domain is highlighted in Fig. 1 with the grey color. The following boundary conditions are used. Segment AB is the axis. Segment BC is a supersonic flow with boundary conditions are used. Segment AB is the axis. Segment CD is the outlet where all variables are extrapolated from the interior. Segment DA is an isothermal wall at Ti = 300 K with no-slip and zero diffusion flux conditions (non-catalytic wall). The free-stream parameters correspond to the Mach number M∞ = 8.06, and the total enthalpy is h₀ = 9.85 MJ/kg.

![Figure 1](image)

**Fig. 1.** Computational domain, boundary conditions, and translational-rotational temperature isolines.

Figure 1 also shows the temperature isolines computed using the quasi-stationary expressions (11) – (12) for the GRRs. It predicts a typical flow structure, which includes an oblique shock wave, bow shock, and separation bubble.

Numerical simulation is performed on a hexa-mesh with 500×300 cells (along and normal to the double cone surface, respectively). The mesh is refined towards the double cone surface in order to resolve the boundary layer. The height of the first cell from wall is 14 μm. Further mesh refinement by two times in both directions showed no influence on the surface heat flux distribution. Therefore, the 500×300 mesh was chosen for further analysis.

4 Results

4.1 Effect of quasi-stationary and quasi-equilibrium rates

Expressions (11) – (12) for the quasi-stationary GRRs capture non-equilibrium of the vibrational distribution function, which is not taken into account in the classical equilibrium rates (13) – (14). Expressions (11) – (12) contain information on the ratio of chemical and vibrational time scales in the renormalizing coefficients given by expressions (17)–(20). In order to assess the influence of non-equilibrium effects on the surface heat flux distribution, we performed two computations with different reaction and relaxation rates. The first computation used the quasi-stationary expressions (11) – (12) for the GRRs and is denoted as “qs.” The second computation used the quasi-equilibrium expressions (13) – (14) and is denoted as “qe.” The corresponding surface heat flux distributions are shown in Fig. 2. Additionally, we provide the double cone geometry and experimental data [12] as a reference.

As shown in [5], the A_mmn value determines the dissociation regime. At |A_mmn| ≪ 1, the vibrational relaxation time is significantly smaller than the corresponding chemical (dissociation) time. It means that the vibrational distribution is close to the quasi-equilibrium state (4), and dissociation is determined mainly by the R_m (|A_mmn|, |A_mmn| < |A_mmn|), i.e. is proportional to P_qe bull. At |A_mmn| ≫ 1, the vibrational time significantly prevails over the chemical one, the highest vibrational level is essentially depleted, and dissociation occurs only when the vibrational quanta are delivered to the highest vibrational level, so that vibrational relaxation is the bottleneck of the dissociation process. In this regime, the dissociation rate does not depend on P_qe bull, and is determined by the vibrational rates P and Q. Such a regime cannot be described within the traditional method, based on the equilibrium reaction rates. In all our simulations, we have |A_mmn| ≫ 1 in the entire computational domain, so that the second (relaxational) regime is realized.

The surface heat flux in Fig. 2 shows that the qs-computation predicts a separation point at x ≈ 6.8 cm, while the qe-computation predicts it at x ≈ 7.4 cm. The separation point location differs from the experimental data in both qs- and qe-computations. The qe-computation predicts the heat flux peak in the reattachment region shifted upstream as compared to the qs-computation. The heat flux rise agrees better with the experimental data in the qs-computation; nevertheless, the peak does not perfectly match the experimental points.
4.2 Comparison to other numerical results

In order to assess the fidelity of the presented new model of the quasi-stationary expressions (11) – (12) for the GRRs, we performed a comparison between the surface heat fluxes computed by different models and codes. The first numerical result is taken from [10] and is denoted as “Ninni, 2022.” Additionally, we repeated the simulation with the HyCFS code being developed at ITAM. The HyCFS uses the model described in [13] (see model: Park, Cdis = 0.3Ed).

Figure 3 shows all three curves of the surface heat flux. The widely used models (HyCFS and Ninni, 2022) predict the separation point location further downstream compared to the present model. The widely used models also give an earlier rise of the surface heat flux. Strictly speaking, none of the models provides perfect agreement with the experimental data.

4.3 Free-stream uncertainty

The experimental facility usually includes a nozzle, which provides a free stream for the considered body. Numerically computed parameters of the free stream (being a jet from the nozzle) also depend on the reaction and relaxation rates. Therefore, the free-stream parameters [12] could be inconsistent with the quasi-stationary expressions (11) – (12) for the GRRs. Accurate simulation of the nozzle flow under experimental conditions seems to be impossible due to the lack of the nozzle geometry. However, it is still possible to assess approximately how the surface heat flux distribution changes with the free-stream parameters. Here, we use alternatively the free-stream parameters computed in [10]. These free-stream parameters are still inconsistent with the presented model; however, a comparison between the original and alternative free-stream parameters allow quantifying the uncertainty in this regard. The alternatively computed free-stream parameters [10] are $u_\infty = 3845$ m/s, $p_\infty = 148$ Pa, $T_\infty = 540$ K, $T_v,\infty = 1075$ K, and $Y_{O_2} = 0.878$. The alternatively computed free-stream parameters correspond to $M_\infty = 8.09$ and $h_0 = 9.85$ MJ/kg.

Figure 4 shows the surface heat flux distributions for the original [12] and alternative [10] free-stream parameters. One can see that the locations of the separation point and heat flux peak differ noticeably. Also, the rise of the heat flux in the reattachment region slightly changed the location.

5 Conclusion

One more example of the new method for deriving gasdynamic equations is considered. The simulations performed using the quasi-stationary expressions (11) – (12) show that they provide an adequate flow structure around a double cone with a separation bubble. The surface heat flux computed using Eqs. (11) – (12) agrees fairly well with the experimental data. The presented model predicts an earlier location of the separation point and a later surface heat flux rise as compared to the numerical data computed by other researchers and codes.

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