Investigation of shock wave structure in CO\textsubscript{2} based on the continuum and DSMC approaches

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Abstract. A comparison is made between the continuum and kinetic approaches in studying the shock wave structure in argon, nitrogen, and carbon dioxide. Using the kinetic-theory methods, one-temperature and two-temperature fluid-dynamic equations are derived and closed. Calorically non-perfect gas model is applied, with vibrational energy explicitly calculated. The algorithm for the calculation of transport coefficients including bulk viscosity is implemented. For argon and nitrogen, a good agreement of the solutions obtained using both the continuum approach and direct statistical simulations (DSMC) with experimental results is shown. For carbon dioxide, the one-temperature Navier–Stokes equations do not reproduce non-monotonic temperature behaviour. The two-temperature model yields the results qualitatively similar to those given by DSMC; quantitative discrepancies are however significant. The DSMC relaxation rate strongly depends on the vibrational collision numbers in various CO\textsubscript{2} modes.

1. Introduction

Shock wave structure is a reference problem for the qualitative assessment of various approaches in rarefied gas dynamics. Studying this problem allows one to estimate the advantages and shortcomings of various models, as well as to establish the limits of their applicability. To resolve the shock wave structure, a continuum or kinetic approach can be applied. In the first case, the Navier-Stokes-Fourier (NSF) equations \[1, 2\] or moment methods \[3\] leading to generalized fluid-dynamic equations are solved. In the case of the kinetic approach, either model equations \[4\] or direct simulations Monte Carlo (DSMC) \[5\] are used; some comparisons of various approaches can be found in \[3, 6, 7\].

Most studies deal with shock waves in monoatomic and simple diatomic species; there are experimental data \[8\] on the density profiles used to validate the models. On the other hand, growing interest to polyatomic gases shows the need in accurate simulations of species with complex relaxation mechanisms. Several studies of shock wave structure in CO\textsubscript{2} were carried out recently using the both model equation \[4\] and NSF approach \[9, 10, 6\]. The influence of large bulk viscosity of polyatomic gases \[11\] on the CO\textsubscript{2} shock structure was studied in \[4\] and showed interesting effects; however later, the large bulk viscosity was not confirmed neither theoretically \[6\] nor experimentally \[12\]. In \[9, 10\] we applied the one-temperature NSF approach to evaluate the shock wave structure in CO\textsubscript{2} using more realistic bulk viscosity values; in \[6\], it was argued that multi-temperature models are more adequate in predicting the flow parameters.

In this study, two approaches are used for simulations of the shock wave structure in carbon dioxide: DSMC and two-temperature NSF approach based on the kinetic-theory methods for the closure of non-equilibrium fluid-dynamic equations and accurate calculations of the transport.
coefficients: thermal conductivity, shear and bulk viscosity; no standard assumptions of a
calorically perfect gas with constant specific heats and Prandtl number are applied. First,
we develop the theoretical model. Then we simulate the shock wave structure in argon and
nitrogen and assess various approaches by comparison with experimental data. Finally, we
apply the developed models to modeling the shock wave structure in carbon dioxide by different
approaches.

2. Theoretical models

2.1. Two-temperature Navier-Stokes equations

We consider a one-dimensional problem. The set of governing equations is derived based on the
kinetic-theory approach [13] for the case of rapid translational, rotational relaxation and VV
intra-mode exchanges of vibrational quanta and slow vibrational-translational VT relaxation. In
the present NSF model, we do not distinguish various channels of vibrational relaxation such as
inter-mode vibrational energy transitions; this is beyond the scope of this study and represents
a challenge for our future work. Thus, we obtain the fluid-dynamic equations coupled to the
vibrational energy relaxation equations:

$$\frac{\partial \mathbf{U}}{\partial t} + \frac{\partial \mathbf{F}}{\partial x} = \mathbf{R},$$ \hspace{1cm} (1)

the vectors of conservative variables $\mathbf{U}$, the flux vector $\mathbf{F}$, and the relaxation term vector $\mathbf{R}$ have
the following form

$$\mathbf{U} = \begin{pmatrix} \rho \\ \rho v \\ \rho E \\ \rho E_{\text{vibr}} \end{pmatrix}, \quad \mathbf{F} = \begin{pmatrix} \rho v \\ \rho v^2 + p - P \\ \rho v H + q_{\text{tr,rot}} + q_{\text{vibr}} - P v \\ \rho v E_{\text{vibr}} + q_{\text{vibr}} \end{pmatrix}, \quad \mathbf{R} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ r \end{pmatrix}. \hspace{1cm} (2)$$

Here, $\rho$ is the density, $v$ is the gas velocity, $E$ is the total energy per unit mass including the
kinetic and internal ($E_{\text{int}}$) energy, $H$ is the total enthalpy per unit mass:

$$H = \frac{p}{\rho} + E, \quad E = \frac{v^2}{2} + E_{\text{int}}. \hspace{1cm} (3)$$

The specific internal energy includes contributions of the translational, rotational and vibrational
energies:

$$E_{\text{int}} = E_{\text{tr}}(T) + E_{\text{rot}}(T) + E_{\text{vibr}}(T_v), \hspace{1cm} (4)$$

where:

$$E_{\text{tr}} = \frac{3kT}{2m}, \quad E_{\text{rot}} = \frac{kT}{m}, \quad E_{\text{vibr}} = \frac{1}{m Z_{\text{vibr}}(T_v)} \sum_{i_1,i_2,i_3} s_{i_1,i_2,i_3} \varepsilon_{i_1,i_2,i_3} \exp \left( -\frac{\varepsilon_{i_1,i_2,i_3}}{kT_v} \right), \hspace{1cm} (5)$$

$k$ is the Boltzmann constant, $m$ is the molecular mass, $T$ is the gas temperature specified
by the local equilibrium (translational and rotational) degrees of freedom, $T_v$ is the vibrational
temperature, $\varepsilon_{i_1,i_2,i_3}$ is the vibrational energy of the molecule at the level $i = (i_1, i_2, i_3)$, quantum
numbers $i_1$, $i_2$, $i_3$ correspond to the symmetric, bending, and asymmetric modes, $s_{i_1,i_2,i_3} = i_2 + 1$
is the statistical weight characterizing the degeneracy of the vibrational state of the molecule
with the energy $\varepsilon_{i_1,i_2,i_3}$ and $Z_{\text{vibr}}(T_v)$ is the non-equilibrium vibrational partition function
which, similarly to the vibrational energy, depends on the vibrational temperature [13]. Thus,
we calculate the vibrational energy explicitly and do not apply the common assumption of a
calorically perfect gas and constant specific heat.
The expressions for the viscous stress tensor component and heat fluxes are derived by the kinetic-theory methods [13]:

\[
P = -P_{xx} + p = \left( \frac{4}{3} \eta + \zeta \right) \frac{\partial v}{\partial x}, \quad q_{\text{tr,rot}} = -\lambda_{\text{tr,rot}}(T) \frac{\partial T}{\partial x}, \quad q_{\text{vibr}} = -\lambda_{\text{vibr}}(T, T_v) \frac{\partial T_v}{\partial x},
\]

where the shear and bulk viscosity \( \eta, \zeta \), as well as translational-rotational and vibrational thermal conductivity \( \lambda_{\text{tr,rot}}, \lambda_{\text{vibr}} \) coefficients are calculated according to the algorithms developed in [13, 14].

The relaxation term \( r \) is calculated using the conventional Landau–Teller formula

\[
r = \frac{E_{\text{vib}}(T) - E_{\text{vib}}(T_v)}{\tau_{\text{vibr}}},
\]

with the vibrational relaxation time \( \tau_{\text{vibr}} \) measured experimentally in [15]. Note that recently, generalized Landau–Teller equations accounting for various CO\(_2\) vibrational relaxation mechanisms were derived in [16]. Implementation of those new models is, however, beyond the scope of this study.

In the case of the one temperature NSF approximation, the set of governing equations is reduced to the mass, momentum and energy conservation equations; the vibrational energy becomes the function of temperature; the heat flux depends on the temperature derivative with a single thermal conductivity coefficient \( \lambda \); more details can be found in [13, 2]. It should be only noted that taking into account the bulk viscosity makes it possible to take into account the relaxation of the internal degrees of freedom for the case of weak deviations from equilibrium.

There are several studies on the role of bulk viscosity in CO\(_2\) [6, 11, 17, 9, 10]. In the present work, we use the method proposed in [6] since it provides good agreement with recent experiments reported in [12].

To solve the Navier-Stokes equations, the numerical method described in [2] is used. The equations are discretized on a structured grid by the finite volume method [18, 19]. An explicit Euler scheme is used for time integration. The first-order scheme is used to interpolate primitive variables from the cell centroid to the face centroid. In order to find fluxes through the cell face, a Riemann problem is solved by the Godunov’s exact iteration method. The computational domain is divided into 50 cells for Ar and N\(_2\), and 100 cells for the CO\(_2\) test case. The right hand side \( r \) is calculated after the fluxes have been calculated. Fluid-dynamic parameters \((T, T_v, p)\) are taken from the vector of conservative variables \( \mathbf{U} \) from the previous time step for the corresponding cell.

2.2. DSMC approach

Direct simulation Monte Carlo is used as a kinetic approach. In the DSMC simulations [5], a gas is represented by a set \( \mathbf{X}(t) \) of \( N \) simulated particles. The main algorithm of DSMC can be described as 3 basic operations. The variation of \( \mathbf{X}(t) \) is divided into small time steps, each time interval is \( \Delta t \). At every time step, \( \mathbf{X}(t) \) changes into \( \mathbf{X}(t + \Delta t) \), this process is modeled by a sequence of three operations: 1) collisionless motion of particles; 2) performing the collisions of particles (consider inelastic and elastic collisions in order); 3) implementing boundary conditions.

The most widely used phenomenological model for inelastic collisions is the Larsen-Borgnakke (LB) model [20]. If a collision is regarded as inelastic, the total pre-collision energy is redistributed between the translational and internal modes by applying the acceptance-rejection procedure to select the post-collision energy of each mode based on the equilibrium distributions of these modes that are appropriated to this total energy. The relaxation rate is controlled by regarding the fraction of the collisions as inelastic. Also this model considers the vibrational energy redistribution before rotational.
More reliable approaches for simulating internal energy transitions and chemical reactions in DSMC are based on direct implementation of the cross sections of inelastic collisions using the discrete energy states [21]. For CO$_2$, however, there is a lack of data on the vibrational energy transitions, especially between different modes. An attempt is done in [22] to derive a DSMC model for collisions with inter-mode VV transitions; and we plan to implement this model in the future studies. The results of present simulations based on the LB model can be considered only as preliminary.

The DSMC simulations were performed using the open source code DSMC1S of Graeme Bird [5], which is a modified one-dimensional program for the study of normal shock waves. At each simulation, the Variable Soft Sphere (VSS) molecular collision model was employed. The processes of translational-internal energy transfer were simulated by using the LB model. Both temperature-dependent and constant vibrational collision numbers were used [23]. The particle-selection technique permitting double relaxation was implemented. In our simulations, each DSMC computation takes into account only the rotation-translation and vibration-translation energy transfer.

We consider molecules as rough-spheres for the rotational energy, and as harmonic oscillators for simulating their vibrational modes. The harmonic oscillators are employed for each of the three vibrational mode of CO$_2$, and for symmetric, bending, and asymmetric vibrational modes, the characteristic vibrational temperatures $\Theta_v$ are of 1918.6, 959, and 3382.6 K, respectively.

The original program DSMC1S includes only the routines that are required for the simulation of molecules with rotational degrees of freedom. A modified routines were employed in the program DSMC1S to account for the vibrational degrees of freedom. The quantum version of the LB model was used for simulating translation-vibration energy transfer. Considering a molecule at the $i$-th level of a particular vibrational mode, the harmonic oscillator gives the vibrational energy of that mode as

$$\varepsilon_i = i k \Theta_v$$

where $i = (i_1, i_2, i_3)$ and $\Theta_v = (\Theta_1, \Theta_2, \Theta_3)$, the subscripts correspond to the symmetric, bending, and asymmetric vibrational temperatures. At a collision, the total collision energy $E_c$, which is the sum of the pre-collision vibrational energy of the molecule and the relative translational energy, is redistributed to the molecule. The ratio of the probability of a particular level to that of the ground state is

$$\frac{P}{P_{\text{max}}} = \left(1 - \frac{i^* k \Theta_v}{E_c}\right)^{3/2-\omega};$$

the acceptance-rejection procedure is applied to this probability ratio in order to find the post-collision vibrational level $i^*$ of that molecule. The post-collision vibrational level was selected from the integers between 0 and the maximum level $i_{\text{max}}^*$ by using random numbers,

$$i_{\text{max}}^* = \left[\frac{E_c}{k \Theta_v}\right].$$

In this paper, the quantum version of LB model was applied separately to all three vibrational modes of CO$_2$. Both constant and temperature-dependent vibrational collision numbers of each vibrational mode were used. First, $Z_v = 20$ for all three vibrational modes of CO$_2$ was used similarly to the value proposed in the open source code SPARTA [24]. Then the constant vibrational collision numbers were calculated at the equilibrium translational temperature behind the shock wave by using the Millikan-White model [23] for the symmetric, bending, asymmetric modes respectively:

$$Z_{v,1} = 35407, \quad Z_{v,2} = 2330, \quad Z_{v,3} = 10^9.$$
Finally, the temperature-dependent vibrational collision numbers were calculated by using the Millikan-White model [23] at each step. The temperature-dependent rotational collision number $Z_r$ was calculated by using the Parker equation [25]

$$Z_r = \frac{Z_{\infty}^{\text{rot}}}{1 + (\pi^{0.5}/2)(T^*/T_{tr})^{0.5} + (\pi + \pi^{2}/4)(T^*/T_{tr})}$$

(12)

where $T_{tr}$ is the translational temperature, $Z_{\infty}^{\text{rot}} = 20.39$ and $T^* = 91.5$ K for carbon dioxide.

Simulations were carried out for argon, nitrogen and carbon dioxide. At each computation over $1 \times 10^6$ simulated particles were used. The cell width was chosen to be of the order of the equilibrium mean free path, and the time step has been chosen to be 1% the mean collision time for a particle. The VSS parameters of argon, nitrogen and carbon dioxide are listed in Table 1.

| species          | $T_{ref}$ (K) | $d_{ref}$, $(\times 10^{-10}$ m) | $\omega$ | $\alpha$ | $m$, $(\times 10^{-26}$kg) |
|------------------|---------------|---------------------------------|----------|----------|--------------------------|
| argon            | 273           | 4.11                            | 0.81     | 1.4      | 6.63                     |
| nitrogen         | 273           | 4.11                            | 0.72     | 1.36     | 4.65                     |
| carbon dioxide   | 273           | 5.54                            | 0.8      | 1.61     | 7.31                     |

Table 1. The VSS parameters for argon, nitrogen and carbon dioxide

![Normalized density profile](image)

Figure 1. Normalized density profiles for argon (left) and nitrogen (right). Comparison with experimental data of [8].

3. Results and discussion
Let us compare the solutions obtained using the continuum and kinetic approaches. To validate the methods, shock waves in argon and nitrogen were first studied; the results are compared with experiment [8]. Free stream conditions for both cases are: $p_L = 6.66$ Pa, $T_L = 300$ K, $M_L = 6.1$. Dimensionless variables are calculated using the formulas:

$$\hat{\rho} = \frac{\rho - \rho_L}{\rho_R - \rho_L}, \quad \hat{T} = \frac{T - T_L}{T_R - T_L}.$$  

(13)
Here, the index $R$ corresponds to the final equilibrium value of the parameters behind the shock, $L$ to the initial values.

Figure 1 shows the normalized density profiles for argon and nitrogen calculated using both approaches and measured experimentally. One can notice a good agreement of the calculated density profiles with experimental data. It can be seen that in a certain range, the DSMC method gives a more accurate solution compared to the continuum approach, which is not surprising. Nevertheless, we conclude that our NSF model also yields rather good accuracy. In particular, for nitrogen the improvement is due to correct account for the bulk viscosity, see also [1].

Figure 2. Normalized temperature profiles in CO$_2$; one-temperature (left) and two-temperature NSF solution (right). Comparison with the DSMC solution obtained with $Z_v = 20$.

Figure 3. Normalized temperature profiles in CO$_2$ for DSMC solution with different $Z_v$. Temperature (left); translational and vibrational temperatures (right).

Figure 2 shows a comparison of the temperature profiles for different approximations: NSF (one- and two-temperature, 1T and 2T) and DSMC; in this case $Z_v = 20$, as proposed in [24]. The overall temperature profiles found using the kinetic and 1T continuum approaches for carbon dioxide are generally similar; however, the 1T model cannot describe non-monotonic temperature behaviour. For the 2T case, the profiles are qualitatively similar. Nevertheless,
differences are seen both in the maximum temperature and in the relaxation rate. In the DSMC solution with the collision number $Z_v = 20$, relaxation starts noticeably faster.

To check the relaxation rates in the DSMC solution, we used other vibrational collision numbers. The results are presented in Figure 3. Varying the collision numbers significantly alters the solution. For $Z_v = 20$ suggested in SPARTA, the relaxation is faster than in the NSF solution; the relaxation zone is rather narrow. For the temperature-dependent $Z_v$, the relaxation rate is intermediate with respect to the NSF solution and that obtained with Eq. (11); however the maxima of $T$ and translational-rotational temperatures attain greater values. At the same time, the 2T solution found in the present study is close to that obtained in [6] by solving two-temperature Euler equations. Thus, the reason for the discrepancy between the NSF and DSMC approaches needs additional studies. One has to keep in mind that in the present formulation, the DSMC solution does not take into account interaction between different CO$_2$ modes caused by inter-mode VV transitions. In our future studies we plan to include these processes.

4. Conclusion

The shock wave structure is analyzed in the framework of continuum and kinetic approaches. The one-temperature and two-temperature continuum models are developed on the basis of the Chapman–Enskog method in the first-order approximation. The resulting Navier–Stokes equations do not use any assumptions about transport coefficients (shear and bulk viscosity, translational-rotational and vibrational thermal conductivity coefficients) which are computed on demand using the kinetic-theory algorithms. Moreover, no assumption about calorically perfect gas and constant specific heat ratio is introduced; the vibrational energy is calculated explicitly.

Simulations are performed using the derived Navier-Stokes equations and DSMC. For argon and nitrogen, solutions are rather close, and a good agreement with experiment is shown. For CO$_2$, the DSMC solution strongly depends on the values of vibrational collision numbers in various modes. The accurate choice of collision numbers requires further assessment.

The NSF approach is more efficient numerically and can be further generalized by taking into account different vibrational temperatures of all CO$_2$ modes. In the DSMC approach, we plan to implement more advanced models of vibrational relaxation including intra-mode vibrational energy exchange.

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References

[1] Elizarova T, Khokhlov A and Montero S 2007 Phys. Fluids 19 068102
[2] Alekseev I and Kustova E 2020 Vestnik St. Petersburg University: Mathematics 53 344–350
[3] Timokhin M, Struchtrup H, Kokhanchik A and Bondar Y 2017 Phys. Fluids 29 037105
[4] Kosuge S and Aoki K 2018 Phys. Rev. Fluids 3 023401
[5] Bird G 1994 Molecular Gas Dynamics and the Direct Simulation of Gas Flows (Oxford, England, UK: Clarendon)
[6] Kustova E, Mekhonoshina M and Kosareva A 2019 Phys. Fluids 31 046104
[7] Shoev G, Timokhin M and Bondar Y 2020 Phys. Fluids 32 041703
[8] Almeyer H 1976 J. Fluid. Mech. 74 497–513
[9] Alekseev I, Kosareva A, Kustova E and Naguibeda E 2018 AIP Conference Proceedings 1959 060001
[10] Alekseev I, Kosareva A, Kustova E and Naguibeda E 2019 AIP Conference Proceedings 2132 060005
[11] Cramer M 2012 Phys. Fluids 24 066102
[12] Wang Y, Ubachs W and van de Water W 2019 J. Chem. Phys. 150 154502
[13] Nagnibeda E and Kustova E 2009 Nonequilibrium Reacting Gas Flows. Kinetic Theory of Transport and Relaxation Processes (Berlin, Heidelberg: Springer Verlag)
[14] Kustova E and Nagnibeda E 2006 Chem. Phys. 321 293–310
[15] Losev S, Makarov V, Pogosbekyan M, Shatalov O and Nikolsky V 1994 AIAA Paper 94-1990
[16] Kustova E and Mekhonoshina M 2020 Phys. Fluids 32 096101
[17] Chikitkin A, Rogov B, Tirsky G and Utyuzhnikov S 2015 Applied Numerical Mathematics 93 47–60
[18] Volkov K, Emelyanov V, Karpenko A, Smirnov P and Teterina I 2013 Computational Methods and Programming 14 82–90
[19] Godunov S, Zabrodin A, Ivanov M, Kraiko A and Prokopov G 1976 Numerical solution of multidimensional problems of gas dynamics (Moscow: Nauka)
[20] Borgnakke C and Larsen P 1975 J. Comp. Physics 18 405–420
[21] Gimelshein S and Wysong I 2019 Physical Review Fluids 4 033405
[22] Molchanova A, Kustova E, Kashkovsky A and Bondar Y 2016 AIP Conference Proceedings 1786 050019
[23] Boyd I and Schwartzentruber T 2017 Nonequilibrium Gas Dynamics and Molecular Simulation (Cambridge, UK: Cambridge University Press)
[24] open source code SPARTA (Stochastic Parallel Rarefied-gas Time-accurate Analyzer) https://sparta.sandia.gov/ date: 2020-11-22
[25] Parker J 1959 Phys. Fluids 2 449