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State-to-state models of vibrational relaxation in Direct Simulation Monte Carlo (DSMC)

G P Oblapenko[1], A V Kashkovsky[2] and Ye A Bondar[1,2]

[1] Saint-Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034 Russia
[2] Institute of Theoretical and Applied Mechanics, 4/1 Institutskaya ul., 630090 Russia

E-mail: kunstmord@kunstmord.com

Abstract. In the present work, the application of state-to-state models of vibrational energy exchanges to the Direct Simulation Monte Carlo (DSMC) is considered. A state-to-state model for VT transitions of vibrational energy in nitrogen and oxygen, based on the application of the inverse Laplace transform to results of quasiclassical trajectory calculations (QCT) of vibrational energy transitions, along with the Forced Harmonic Oscillator (FHO) state-to-state model is implemented in DSMC code and applied to flows around blunt bodies. Comparisons are made with the widely used Larsen–Borgnakke model and the influence of multi-quantum VT transitions is assessed.

1. Introduction

Direct Simulation Monte Carlo (DSMC) [1] methods are widely used for modeling of non-equilibrium high-temperature flows. Modeling of high-temperature flows requires accounting for excitation and relaxation of internal energy modes and chemical reactions, which is essential for correct computation of flow parameters, such as temperature profiles and heat fluxes.

The Larsen–Borgnakke model [2] is commonly used for modeling of rotational and vibrational non-equilibrium in Direct Simulation Monte Carlo methods. It has several advantages, those being 1) it satisfies the detailed balance principle 2) it recovers energy relaxation rates as given by the Jeans and Landau–Teller equations [3]. However, the model is not strictly microscopic, since it requires computation of temperature-dependent collision numbers because rotational and vibrational relaxation times are non constant and strongly depend on the gas temperature [4, 5]; also, the Millikan–White formula [5] (even with Park's correction [6]), commonly used to compute the vibrational collision number, has been shown to poorly approximate VT relaxation times at high temperatures [7, 8, 9]. Therefore, given that the use of state-to-state vibrational transition models is feasible from a computational point of view, it is of interest to assess their influence on various flows.

Various semiclassical models exist for computation of VV and VT transition probabilities, such as the Schwartz-Slavsky-Herzfeld (SSH) model [10], "vibrationally inelastic cross section" (VICS) model [11], and the Forced Harmonic Oscillator model [12]. More accurate models of inelastic processes are based on quasiclassical trajectory calculations (QCT). Performing molecular dynamics simulations using an accurate interaction potential, cross sections of inelastic processes can be recovered, which can then be implemented in the DSMC method. Inelastic cross-sections for collisions of molecular nitrogen with nitrogen atoms were studied in [13, 14, 15],

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while inelastic cross-sections for collisions of molecular oxygen with oxygen atoms were discussed in [16, 13, 17, 18]. In works [19, 20], the molecular dynamics simulations are implemented within the DSMC method itself, which removes the need for the approximation of QCT results, but leads to an increase in computational cost.

However, while there exist works concerned with the application of accurate state-to-state models of vibrational transitions (either semiclassical or based on QCT calculations), most of are concerned only with spatially homogeneous vibrational relaxation, and do not study the effects of the choice of vibrational relaxation models on non-equilibrium flows around real bodies. Only a few works have investigated 2-dimensional flows with state-to-state vibrational relaxation models [21, 22, 15]. In all of these works, a significant influence of the vibrational transition model on the temperature profiles was found. It should be noted that only in [21] VV exchanges were accounted for. While VV exchanges do not influence the translational and vibrational temperatures, they can significantly affect vibrational level populations [21, 23].

Therefore, the influence of state-to-state models on 2-dimensional bodies warrants further research. The aim of this work is to 1) apply both semiclassical vibrational transition models and QCT-based models to DSMC modeling of various high-temperature 2-dimensional flows 2) compare results obtained using these models to results computed using the Larsen–Borgnakke model 3) study the role of multi-quantum VT transitions and how they affect macroscopic flow parameters.

2. State-to-state vibrational relaxation models

We consider binary flows of nitrogen (N_2/N) oxygen (O_2/O) with the following VT transitions:

$$N_2(i) + N \rightarrow N_2(i') + N, \quad N_2(i) + N_2 \rightarrow N_2(i') + N_2, \tag{1}$$

$$O_2(i) + O \rightarrow O_2(i') + O, \quad O_2(i) + O_2 \rightarrow O_2(i') + O_2, \tag{2}$$

where i denotes the initial vibrational levels, and i', denotes the post-collisional vibrational levels.

The following models for VV and VT processes were considered:

1. The Forced Harmonic Oscillator (FHO) model [12]. It is a semiclassical model for VV and VT processes, which allows for multi-quantum VV and VT transitions and accounts for vibrational anharmonicity. It provides good agreement with experimental and QCT data.
2. A model based on the application of the Inverse Laplace Transform to QCT calculations of rate coefficients of VV and VT processes [24, 25] (further referred to as the QCT-ILT model). The QCT calculations of rate coefficients used where taken from works by Billing et. al [26, 27] and the Phys4Entry database [28]. The model gives expressions for cross-sections of VV exchanges and VT transitions (for collisions of molecules with atoms).

It should be noted that the model developed in [24, 25] provides expressions only for monoquantum VT transitions in nitrogen flows, while allowing for multi-quantum VT transitions in oxygen flows. In strongly non-equilibrium flows, especially those of oxygen, the effect of multi-quantum transitions on the flow parameters can be significant [29, 21, 30]. The application of the FHO model and other semiclassical models to modeling nitrogen flows in DSMC has been discussed in [21, 31, 22].

While the QCT-ILT model gives expressions for multi-quantum VT transitions for collisions of oxygen molecules with oxygen atoms, for $|i - i'| > 5$ the model fails to provide physically meaningful results, and thus, the maximum change in the vibrational level considered when performing calculations in oxygen using the model was taken to be 5. The QCT-ILT model also does not provide VT transition probabilities for collisions of molecules with molecules, and,

therefore, the FHO model was used to compute them, this combined model is referred to as the combined FHO and QCT ILT-model.

To compute the probabilities of reverse processes, the microscopic detailed balance principle [32] was utilized:

$$P_{rev}(g') = \frac{g^2}{g'^2} P_f(g) \frac{\sigma_{el}(g)}{\sigma_{el}(g')}, \tag{3}$$

where P_{rev} is the probability of a reverse process, P_f is the probability of a forward process, g is the magnitude of the relative velocity of the colliding particles, g' is the post-collisional magnitude of the relative velocity of the colliding particles, $\sigma_{el}(g)$ is the elastic cross-section.

3. Numerical results

All simulations where performed in the SMILE++ [33] software package. Probabilities of dissociation reactions were modeled using the Vibrationally Favoured Dissociation (VFD) model described in [34]. The vibrational temperature T_v in a cell was calculated using the assumption that the vibrational energies of the molecules obey a Boltzmann distribution, and, therefore, the vibrational temperature can be found from the equation

$$\frac{1}{Z_{vibr}\left(T_v\right)} \sum_i \varepsilon_i \exp\left(-\frac{\varepsilon_i}{kT_v}\right) = E_{vibr}, \tag{4}$$

where E_{vibr} is the computed vibrational energy in a computational cell, Z_{vibr} is the vibrational partition function, and ε_i is the vibrational energy of vibrational level i of the molecules being considered.

3.1. Model validation: vibrational relaxation of a spatially homogeneous gas

The FHO and QCT-ILT models were used to study vibrational relaxation of a spatially homogeneous gas. The initial conditions were taken to be as follows: the translational temperature T was in equilibrium with the rotational temperature T_r and was taken to be equal to 15000K, while the vibrational temperature T_v was taken to be equal to 300K. The molar fraction of the atoms was taken to be 0.5, while the numeric density was equal to 10^20 $1/\mathrm{m}^3$. Computations done with the FHO model did not account for transitions with $|i - i'| > 5$ due to their low probability and the possibility of obtaining a total inelastic process probability larger than 1, which can lead to unphysical results.

Figure 1 shows the temporal evolution of the translational and vibrational temperatures in a spatially homogeneous gas computed using different vibrational transition models. It can be seen for both cases that all state-to-state models lead to lower vibrational relaxation rates than the Larsen–Borgnakke model. In nitrogen, the combined FHO and QCT-ILT model gives slower vibrational relaxation than the FHO model, however, this is partially due to the absence of expressions for multi-quantum transitions in nitrogen in the QCT-ILT model. In oxygen, the combined FHO and QCT-ILT model gives slightly faster relaxation rates than the FHO model.

Let us consider the effect of multi-quantum transitions on vibrational relaxation rates. Figure 2 shows the temporal evolution of the translational and vibrational temperatures in a spatially homogeneous gas computed using different vibrational transition models with different restrictions on the maximum change in the vibrational level. In nitrogen (figure 2(a)) it can be seen that the effect of multi-quantum transitions when performing computations using the FHO model is small. Computation results using the combined FHO and QCT-ILT model for different number of allowed vibrational energy transitions for molecule-molecule collisions (1- and 5-quantum transitions) are extremely close. Therefore, it can be concluded that multi-quantum VT transitions in nitrogen have a noticeable effect on the vibrational relaxation rate

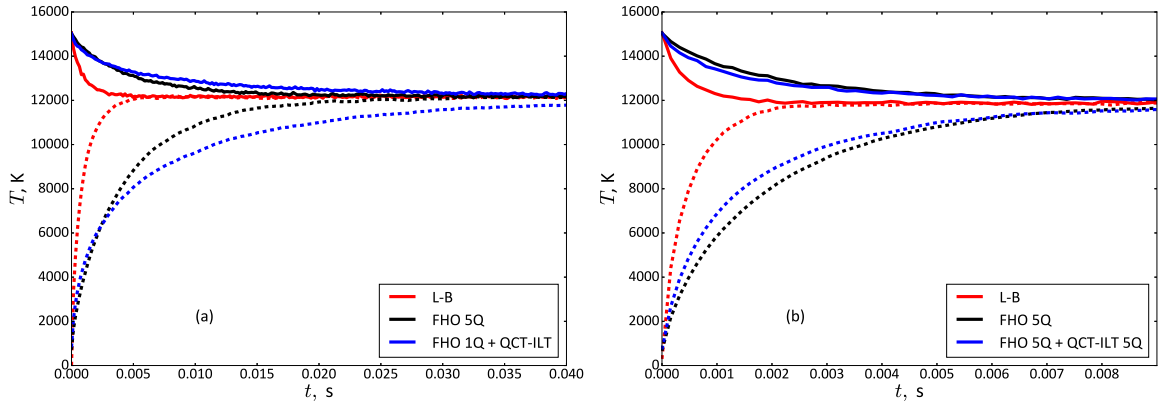


Figure 1. Values of translational (solid lines) and vibrational temperatures (dotted lines) as functions of time in N_2/N (a) and O_2/O (b) mixtures computed various models: Larsen–Borgnakke model (L-B), FHO model with up to 5-quantum transitions (FHO 5Q) and the combined FHO and QCT-ILT model with only one-quantum transitions in N_2/N (FHO 1Q + QCT-ILT) and up to 5-quantum transitions in O_2/O (FHO 5Q + QCT-ILT 5Q).

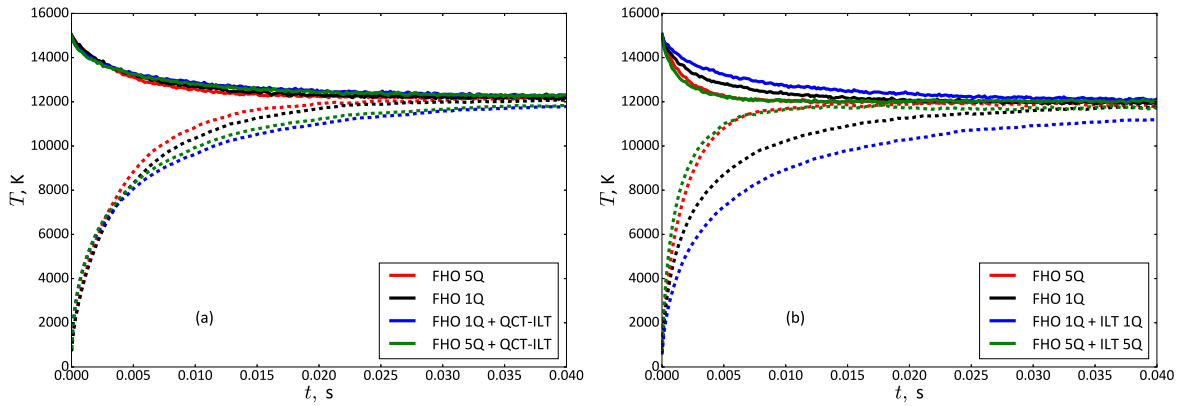


Figure 2. Values of translational (solid lines) and vibrational temperatures (dotted lines) as functions of time in N_2/N (a) and O_2/O (b) mixtures computed various models: FHO model with up to 5-quantum transitions (FHO 5Q), FHO model with monoquantum transitions (FHO 1Q), the combined FHO and QCT-ILT model with only one-quantum transitions in N_2/N (FHO 1Q + QCT-ILT) and O_2/O (FHO 1Q + QCT-ILT 1Q) and up to 5-quantum transitions in O_2/O (FHO 5Q + QCT-ILT 5Q), and the combined FHO and QCT-ILT model with up to 5-quantum transitions for molecule-molecule collisions (computed using the FHO model) and only one-quantum transitions for molecule-atom collisions (computed using the QCT-ILT model) in N_2/N (FHO 5Q + QCT-ILT).

only in molecule-atom collisions. From these results, it follows that in nitrogen flows, accounting for only monoquantum transitions does not significantly affect the relaxation rate.

It can be seen that in oxygen (figure 2(b)), multi-quantum transitions play a significantly more important role. Not including them in the simulations leads to a noticeable decrease in the vibrational relaxation rates. When only monoquantum transitions are accounted for, the combined FHO and QCT-ILT model gives slower vibrational relaxation rates than the FHO model, while when multi-quantum transitions are taken into consideration, the situation is reversed, as can be seen from figure 1(a).

3.2. Flow around a cylinder

Let us now consider the influence of the vibrational relaxation models on a 2-dimensional flow around a cylinder. The parameters of the flow are: the free stream velocity was taken to be equal to 7.5 km/s, and the free stream temperature was assumed to be 188K. The density of the free stream flow was taken to be 3.43e-6 kg/m^3. The molar fraction of the atoms in the free stream was equal to 0.5. The radius of the cylinder was taken to be equal to 0.8 m. A wall temperature of 500K was used.

We consider the following vibrational relaxation models:

1. In nitrogen flows, we consider the Larsen–Borgnakke model, the FHO model with monoquantum and 5-quantum transitions, and the QCT-ILT model with monoquantum transitions for molecule-atom collisions and 5-quantum transitions for molecule-molecule collisions.
2. In oxygen flows, we consider the Larsen–Borgnakke model, the FHO model with 5-quantum transitions, and the QCT-ILT model with monoquantum and 5-quantum transitions.

Therefore, we study the effect of multi-quantum transitions in the QCT-ILT model for oxygen flows and provide comparisons with the Larsen–Borgnakke and FHO models. In nitrogen flows, since the QCT-ILT model does not allow for multi-quantum transitions, we consider the influence of the multi-quantum transitions on relaxation rates when performing flow simulations using the FHO model.

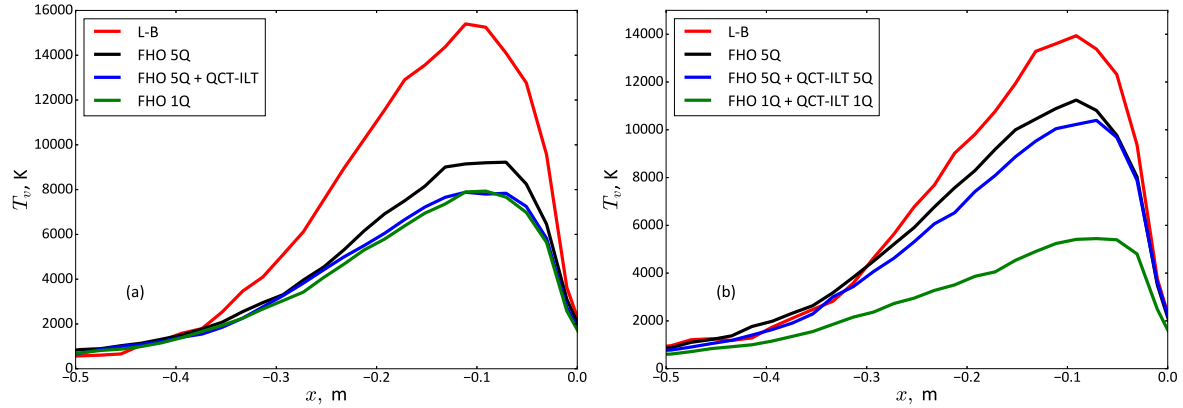


Figure 3. Values of vibrational temperature along the stagnation line as a function of distance from the cylinder in N_2/N (a) and O_2/O (b) mixtures computed various models: Larsen–Borgnakke model (L-B), FHO model with up to 5-quantum transitions (FHO 5Q), FHO model with monoquantum transitions (FHO 1Q), the combined FHO and QCT-ILT model with only one-quantum transitions in O_2/O (FHO 1Q + QCT-ILT 1Q) and up to 5-quantum transitions in O_2/O (FHO 5Q + QCT-ILT 5Q), and the combined FHO and QCT-ILT model with up to 5-quantum transitions for molecule-molecule collisions (computed using the FHO model) and only one-quantum transitions for molecule-atom collisions (computed using the QCT-ILT model) in N_2/N (FHO 5Q + QCT-ILT).

Figure 3 shows the values of vibrational temperature along the stagnation line as a function of distance from the cylinder computed using various models. We see that both for nitrogen and oxygen flows, the Larsen–Borgnakke model gives higher values of the vibrational temperature than the various state-to-state models. In nitrogen (figure 3(a)), all state-to-state models give similar results with significantly lower values of vibrational temperature than the Larsen–Borgnakke model, the difference reaching up to 8000K. Accounting for multi-quantum transitions

when using the FHO model leads to a slight increase in the peak value of vibrational temperature. However, accounting for multi-quantum transitions only for molecule-molecule collisions does not have any noticeable effect on the vibrational temperature profile — both the FHO model with only monoquantum transitions (FHO 1Q) and the combined FHO QCT-ILT model with up to 5-quantum transitions for molecule-molecule collisions and only one-quantum transitions for molecule-atom collisions provide virtually identical results. The lack of difference between the FHO and QCT-ILT model computations is not surprising, since the QCT-ILT cross-sections were based on trajectory calculations given in [26, 27], with which the FHO model is in good agreement [12].

In oxygen (figure 3(b)), the difference between the Larsen–Borgnakke model and the state-to-state models is not as pronounced as in nitrogen: the difference between the peak vibrational temperatures for models which account for multi-quantum transitions (FHO 5Q, FHO 5Q + QCT-ILT 5Q) is less than 4000K. We see that multi-quantum transitions have a significant influence on the vibrational temperatures. Accounting for them leads to nearly a 100% (as compared to the model with only one-quantum VT transitions) increase in vibrational temperature. The FHO and combined FHO QCT-ILT models, when multi-quantum transitions are included in the simulation, give noticeably similar results. The FHO model gives a slightly larger value of the peak vibrational temperature.

4. Conclusion

The application of state-to-state VT transitions models to DSMC modeling of rarefied gas flows is studied. A model based on semiclassical collision theory (FHO model) and a model based on the application of the inverse Laplace transform to quasiclassical trajectory calculations (QCT-ILT model) are both implemented in DSMC. Validation of the models is done by considering the problem of vibrational relaxation of a spatially homogeneous gas. It is shown that all state-to-state models give lower vibrational relaxation rates than the commonly used Larsen–Borgnakke model. In nitrogen, the effect of multi-quantum transitions is shown to be negligible, and the difference between the QCT-ILT and FHO models is small. In oxygen, accounting for multi-quantum transitions leads to a noticeably faster relaxation rate compared to state-to-state models with only monoquantum transitions.

The models are applied to a two-dimensional flow around a cylinder, and the vibrational temperature along the stagnation line is studied. In nitrogen flows, vibrational temperature computed using the state-to-state models is twice as low as the vibrational temperature computed the Larsen–Borgnakke model. Again, multi-quantum VT transitions do not affect the vibrational temperature significantly. In oxygen flows, the state-to-state models give values of the vibrational temperature that are slightly lower than those predicted by the Larsen–Borgnakke model. The QCT-ILT model gives smaller values of the vibrational temperature than the FHO model. Accounting only for monoquantum transitions leads to a significant underestimation of the vibrational temperature.

Acknowledgments

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