

# State-to-state models of physico-chemical processes in Direct Simulation Monte Carlo (DSMC) computations of 2-dimensional flows

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## Abstract

Direct Simulation Monte Carlo (DSMC) is one of the most widely used tools for numerical investigation of strongly non-equilibrium flows. Progress in improving computational efficiency of DSMC methods has allowed for use of detailed state-to-state models of physico-chemical processes in the simulations, instead of the less accurate Larsen-Borgnakke and TCE models. However, in most works, state-to-state models are only applied to the study of relaxation of a spatially homogeneous gas, and few works investigate their effect on flow around 2-dimensional blunt bodies. In the present work, state-to-state models of VT transitions of vibrational energy and dissociation reactions in nitrogen and oxygen flows, based on semiclassical models and quasiclassical trajectory calculations, are applied to DSMC modeling of flows around blunt bodies. The role of multi-quantum transitions is assessed, and comparisons with results obtained with the widely used Larsen-Borgnakke and TCE models are made.

## 1. Introduction

One of the most widely used methods for numerical investigation of super- and hypersonic flows is the Direct Simulation Monte Carlo (DSMC)<sup>10</sup> method. For correct computation of flow parameters and heat fluxes on the surfaces of bodies in the flow (which is of vital importance for thermal protection design), non-equilibrium effects have to be taken into account, such as excitation of internal degrees of freedom and chemical reactions. To include these processes in DSMC, models are required for computation of the probabilities of these processes as functions of the internal states of the colliding particles and their relative velocity.

For modeling vibrational and rotational relaxation, the Larsen-Borgnakke model<sup>13</sup> is widely used, due to its computational efficiency and the fact that it reproduces the energy relaxation rates given by the Jeans and Landau-Teller equations.<sup>28</sup> However, the model has its disadvantages: it is not strictly microscopic, since it requires calculation of temperature-dependent collision numbers in each grid cell, since rotational and vibrational relaxation times are non constant and strongly depend on the gas temperature;<sup>31,35</sup> the widely used Millikan-White<sup>31</sup> formula for vibrational relaxation times significantly underestimates relaxation times at high temperatures;<sup>20,27</sup> finally, the Larsen-Borgnakke model does not allow for accounting for complex state-specific effects.

For modeling of dissociation reactions in DSMC, the Total Collision Energy (TCE) model<sup>10</sup> is commonly used. It is based on the assumptions that the translational and internal energies are described by an equilibrium distribution, and that the macroscopic dissociation rate coefficient is given by the Arrhenius law. Since Arrhenius law parameters are known for a large number of reactions, the TCE model can be used for flows with a wide range of chemical components. However, like the Larsen-Borgnakke model, the TCE model does not describe the preferential dissociation from high vibrational levels. To rectify this, various modifications of the TCE model have been proposed.<sup>18,19</sup> Overviews of the TCE model and other models of dissociation reactions used in DSMC, can be found in<sup>11,21,38</sup>

However, increases in computing power now allow for utilizing state-to-state models of vibrational-translational (VT) energy transitions, vibrational-vibrational (VV) energy exchanges, and chemical reactions in real-life DSMC computations. The same increases in computing power have also led to an increased interest in computation of inelastic process rate coefficients using quasiclassical trajectory calculations (QCT), which, given an accurate interaction potential, provide data that is more accurate than that given by various semiclassical models, which usually contain

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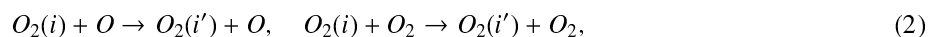
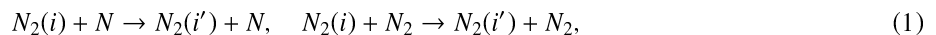
various empirical parameters or have significant limitations. It has even been shown<sup>36,37</sup> that implementing the molecular dynamics simulations within the DSMC method is a feasible, which removes the need for the approximation of QCT results, however, at a cost of a noticeable rise in computational complexity. Inelastic cross-sections obtained using QCT have been studied in<sup>16,23,25</sup> (for collisions of molecular nitrogen with nitrogen atoms), in<sup>5,15,16,26</sup> (for collisions of molecular oxygen with oxygen atoms), in<sup>4</sup> (for oxygen molecule-molecule collisions) and in<sup>3</sup> (for collision of oxygen molecules with nitrogen molecules).

However, despite a growing interest in implementing state-to-state models in DSMC methods, most works on the subject are dedicated to the study of spatially homogeneous vibrational relaxation or one-dimensional modeling of flows behind strong shock waves. Modeling of 2-dimensional flows using state-specific models has been considered in only a few works,<sup>12,14,17,25,29,30,34</sup> with some of the mentioned works not including chemical reactions in the simulation. Therefore, the influence of state-to-state models on 2-dimensional flows is an area which warrants further research. In our previous work,<sup>34</sup> semiclassical and QCT-based models of VT transitions were applied to the problems of spatially homogeneous vibrational relaxation and two-dimensional flow around a cylinder, and it was shown that the Larsen–Borgnakke model overestimates vibrational temperatures in the considered flows. The role of multi-quantum VT transitions was shown to be important in oxygen flows.

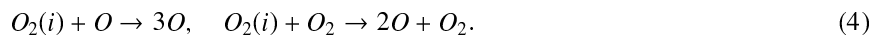
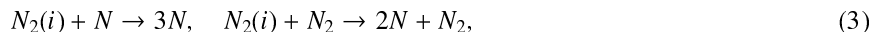
In the present work, we consider the application of semiclassical and QCT-based models of VT transitions and dissociation to hypersonic binary flows of nitrogen and oxygen around a cylinder, and compare results to those obtained using the Larsen–Borgnakke model for vibrational relaxation in conjunction with the TCE model for dissociation reactions.

## 2. Vibrational relaxation and dissociation models

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



and the following dissociation reactions:



For modeling these processes, we use either the Larsen–Borgnakke model for VT transitions and the TCE model for dissociation reactions, or the state-specific models described below. The first set of models will be denoted as “LB+TCE”, while the second one will be denoted as “STS”.

### 2.1 State-specific vibrational relaxation model

We use the following state-specific model, which uses two models for VT transition cross-sections:

1. The semiclassical Forced Harmonic Oscillator (FHO) model<sup>2</sup> for the VT transitions probabilities for molecule-molecule collisions.
2. A model based on the application of the Inverse Laplace Transform to QCT calculations of rate coefficients of VT processes<sup>6,7</sup> for molecule-atom collisions. The rate coefficients were taken from works by Billing et. al<sup>8,9</sup> and the Phys4Entry database.<sup>1</sup> The model gives only mono-quantum VT transition probabilities for collisions of nitrogen molecules with nitrogen atoms.

Based on previous results which show the importance of including multi-quantum transitions in non-equilibrium flow simulations,<sup>17,24,32,34</sup> when using the state-specific model for VT transition probabilities, we account for all multi-quantum VT transitions ( $|i - i'| > 1$ ), however, we restrict the possible transitions to those with  $|i - i'| \leq 5$ , since 1) higher-quantum transitions have an extremely low probability 2) the model for VT cross-sections developed in<sup>6,7</sup> provides unphysical results for transitions with  $|i - i'| > 5$ .

VT transitions for the case  $i' > i$  were computed via the microscopic detailed balance principle:<sup>33</sup>

$$P_{i,i'}(g') = \frac{g^2}{g'^2} P_{i',i}(g) \frac{\sigma_{el}(g)}{\sigma_{el}(g')}, \quad (5)$$

where  $P_{i,i'}$  is the probability of a transition from vibrational level  $i$  to vibrational level  $i'$ ,  $g$  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.

## 2.2 State-specific dissociation model

For modeling dissociation reactions, the state-specific model is following two models:

1. The TCE model<sup>10</sup> for the VT transitions probabilities for molecule-molecule collisions.
2. A model based on the application of the Inverse Laplace Transform to QCT calculations of rate coefficients of dissociation processes<sup>6,7</sup> for molecule-atom collisions. The rate coefficients were taken from the Phys4Entry database.<sup>1</sup>

The use of the TCE model for dissociation for molecule-molecule collisions is due to a lack of QCT data on dissociation rate coefficients for such collisions which can be attributed to the complexity of QCT modeling of such systems (however, recently there have been works on this topic,<sup>3,4</sup> based on the results of which dissociation cross-sections can be computed for molecule-molecule collisions).

## 3. Numerical results and discussion

All simulations were performed in the SMILE++<sup>22</sup> software package. We consider a flow around a sphere with a radius of 0.8m with a non-catalytic wall temperature of 350K. The free-stream conditions were taken as those in the Hermes European Space Vehicle re-entry case: the temperature of the free stream was taken to be 205K, the free-stream velocity was taken to be equal to 7198 m/s, the free-stream pressure was taken to be equal to 2 Pa (which corresponds to a free-stream numeric density equal to  $7.066 \cdot 10^{20}$  1/m<sup>3</sup>). The molar fraction of atoms in the free stream was assumed to be zero.

Figure 1 shows the molar fraction of molecules along the stagnation line for N<sub>2</sub>/N (Fig. 1(a)) and O<sub>2</sub>/O (Fig. 1(b)) flows. In oxygen, where dissociation rates are significantly higher, the flow is nearly fully dissociated in most of the post-shock relaxation zone. Contrary to the case of the nitrogen flow, in oxygen when the LB+TCE model is used, the rate of dissociation is higher, and it can be seen that the fraction of molecules is close to 0; whereas when the STS model is used, the degree of dissociation does not reach 100%. This stronger degree of dissociation can be attributed both to higher dissociation rates predicted by the TCE model and to the faster vibrational relaxation due to the use of the Larsen–Borgnakke model.

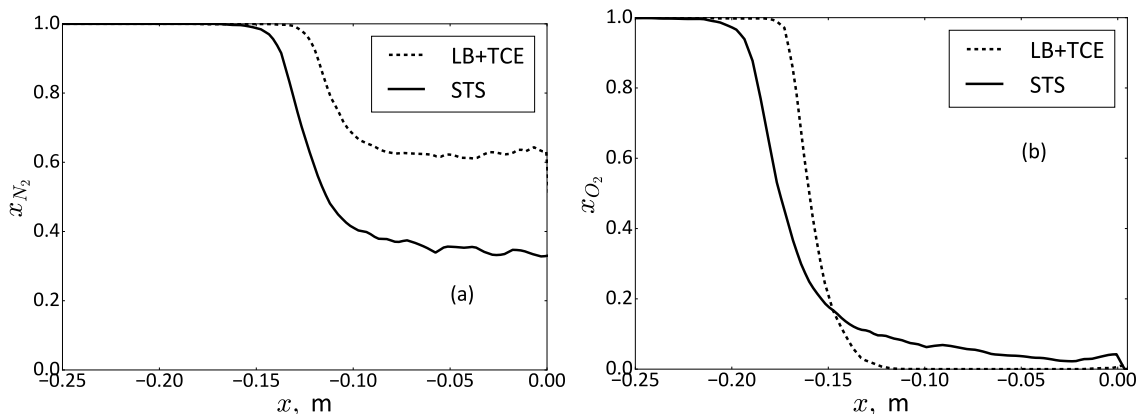


Figure 1: Molar fraction of molecules in binary nitrogen (a) and oxygen (b) flows as a function of distance along the stagnation line.

Figure 2 shows the translational temperature of the flow along the stagnation line for N<sub>2</sub>/N (Fig. 2(a)) and O<sub>2</sub>/O (Fig. 2(b)) flows. We see that in oxygen and nitrogen flows, the STS model predicts a larger shock stand-off distance than the LB+TCE model, and in oxygen, the temperatures predicted by the STS model are noticeable higher than those predicted by the LB+TCE model, especially near the shock front. This behavior can be attributed to both slower vibrational relaxation when the STS model is used,<sup>17,34</sup> and the higher dissociation rates predicted by the LB+TCE model. In nitrogen the peak temperatures predicted by the LB+TCE and STS models are very close, which may be due to the slower VT relaxation predicted by the STS model being compensated by the higher dissociation rate.

Figure 3 shows the vibrational temperature of the flow along the stagnation line for the N<sub>2</sub>/N case. Due to an extremely high degree of dissociation of oxygen molecules in the O<sub>2</sub>/O case, analyzing vibrational temperature is meaningless, therefore, we consider it only for the nitrogen flow, where a large number of molecules do not undergo

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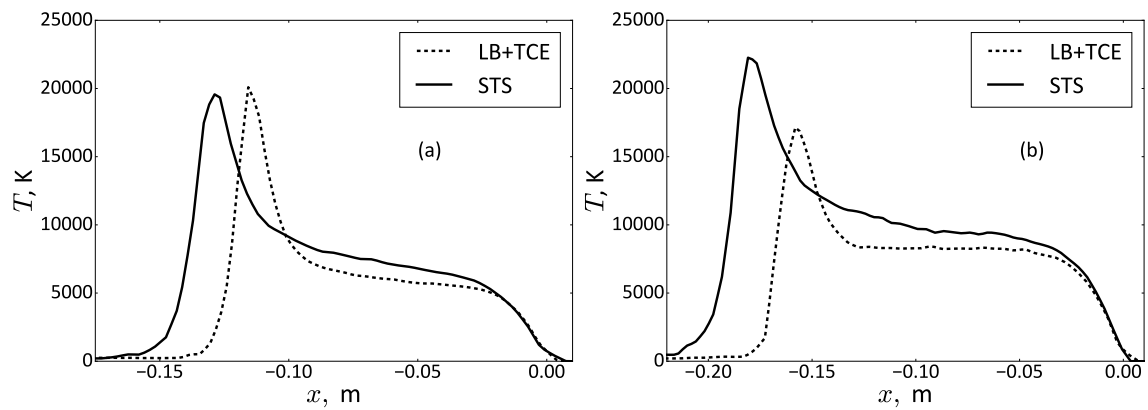


Figure 2: Translational temperature in binary nitrogen (a) and oxygen (b) flows as a function of distance along the stagnation line.

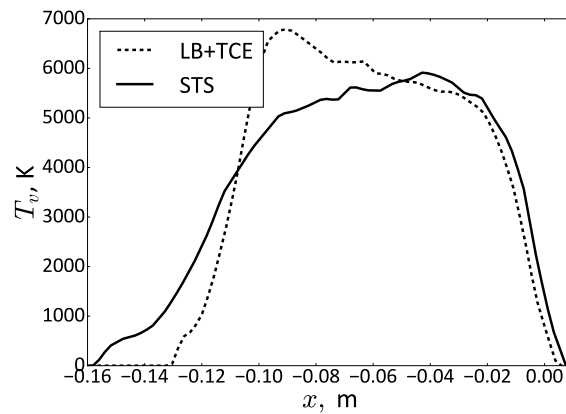


Figure 3: Vibrational temperature in a binary nitrogen flow as a function of distance along the stagnation line.

dissociation. We see that the state-specific model gives somewhat lower values of the vibrational temperature than the LB-TCE model.

Now, we consider the role of the choice of dissociation model — we perform the same computations using the Larsen–Borgnakke model for vibrational relaxation and the state-specific model (ILT) for dissociation, and compare them to the results obtained using the fully state-specific model.

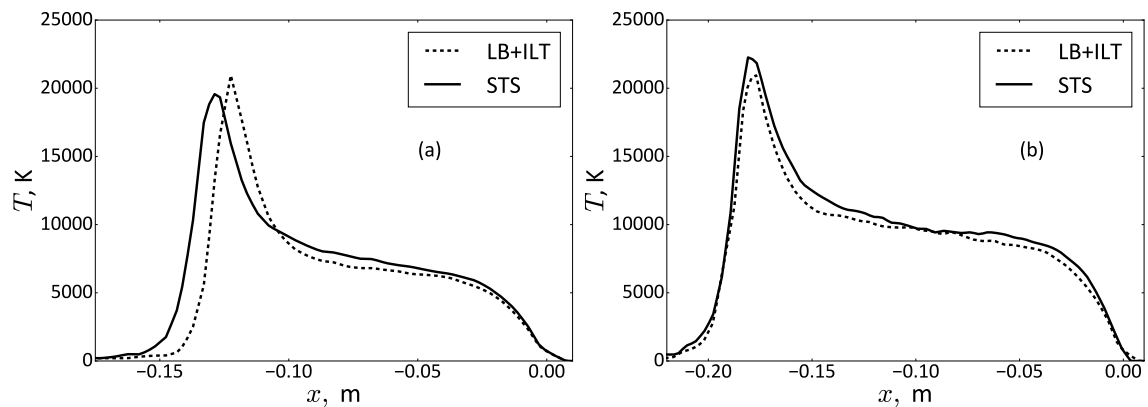


Figure 4: Translational temperature in binary nitrogen (a) and oxygen (b) flows as a function of distance along the stagnation line.

Figure 4 shows the translational temperature of the flow along the stagnation line for  $N_2/N$  (Fig. 2(a)) and  $O_2/O$

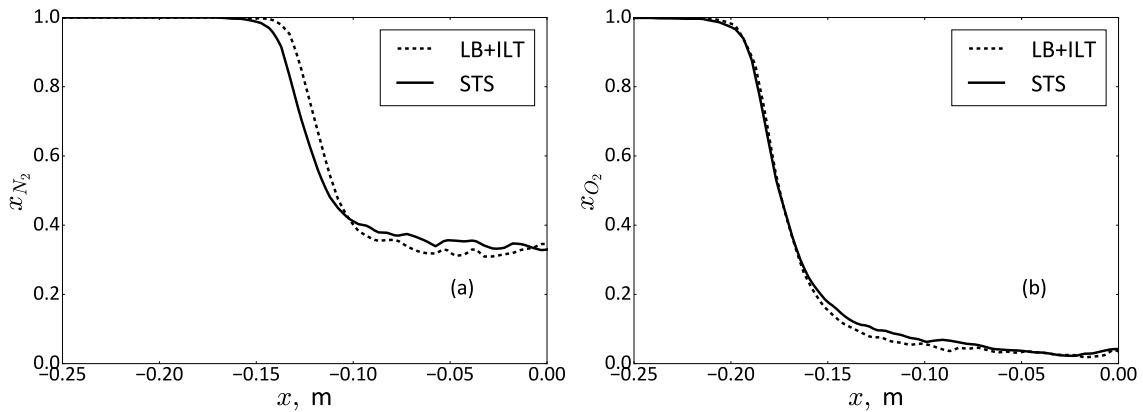


Figure 5: Molar fraction of molecules in binary nitrogen (a) and oxygen (b) flows as a function of distance along the stagnation line.

(Fig. 2(b)) flows. We see that using the state-specific model for dissociation probabilities in combination with the Larsen–Borgnakke model leads to close agreement both with respect to the values of the translational temperatures and the shock stand-off distance, especially in oxygen. The combination of the Larsen–Borgnakke model for vibrational relaxation and state-specific model for dissociation is also in very good agreement with the fully state-specific model on the mixture composition (see Figure 5).

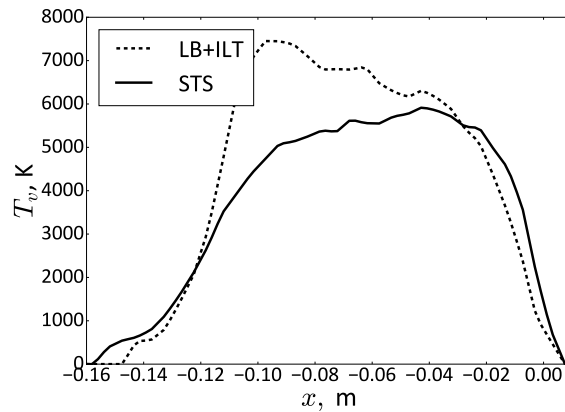


Figure 6: Vibrational temperature in a binary nitrogen flow as a function of distance along the stagnation line.

Finally, Figure 6 shows that the combination of the Larsen–Borgnakke model and the state-specific dissociation model still over-predicts the vibrational temperature along the stagnation line, even more so than the LB+TCE model considered earlier.

#### 4. Conclusion

The application of QCT-based state-specific models of vibrational-translational energy transitions and dissociation reactions to DSMC modeling of rarefied gas flows is studied. The QCT-based models were implemented in the SMILE++ DSMC code and are applied to modeling of two-dimensional flow hypersonic binary flows of nitrogen around a cylinder. The results of numerical modeling are compared to those obtained by using the Larsen–Borgnakke and Total Collision Energy models. It is shown that in nitrogen, a QCT-based state-specific model predicts higher dissociation rates and leads to a significantly lower molar fraction of molecules in the relaxation zone. The temperatures predicted by the state-specific and LB+TCE models are quite close. In oxygen, the STS model gives lower dissociation rates and higher temperatures in the relaxation zone. In both nitrogen and oxygen flows, use of the state-specific models gives a larger shock standoff distance. A combined model, consisting of the Larsen–Borgnakke model for vibrational relaxation and state-specific model for dissociation rates, has also been considered, and it is shown that it gives temperature and mixture composition profiles very close to those obtained using the fully state-resolved model.

## 5. Acknowledgments

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