MULTIPLE REACTIONS AND TRACE SPECIES IN THE DSMC MACROSCOPIC CHEMISTRY METHOD

M.J. GOLDSWORTHY\textsuperscript{1}, M.N. MACROSSAN\textsuperscript{1} & M.M. ABDEL-JAWAD\textsuperscript{2}

\textit{Physics of Fluids, 19: 116102 (2007)}

Abstract

The Macroscopic Chemistry Method is a technique for modelling chemical reactions in the Direct Simulation Monte Carlo (DSMC) method. The approach differs from conventional DSMC chemistry methods in that the change in the number of each species over a time-step is calculated from the overall macroscopic cell parameters, rather than on a collision pair basis. The Macroscopic Chemistry Method (MCM) can be applied in flows where the collision rate is highly non-equilibrium and has previously been applied to model dissociation-recombination reactions of a symmetrical diatomic gas. Here we propose a procedure for applying MCM to a multiple species reaction set which includes exchange reactions, as well as a method by which trace species can be modelled without the need for variable weighting factors.

The procedure is tested in constant volume reservoir relaxation simulations of a high temperature gas and quasi-one-dimensional expansion of a high speed, high temperature gas. Initial compositions are chosen to resemble Earth and Martian atmosphere reacting systems. For the reservoir relaxation simulations, comparisons of the species mole fractions and overall temperature predicted by MCM are made with numerical integration of the reaction rate equations. For the one-dimensional expansion, results using the trace species algorithm are compared with a simulation without the trace species algorithm but with a much larger number of simulator particles. The reaction set consists of 54 chemical reactions (40 dissociation and 14 exchange reactions) amongst 8 species.

The trace species algorithm exactly reproduces the temperature history predicted by numerical integration for the reservoir simulation. Without the trace species algorithm, the errors in the mole fractions are proportional to the inverse of the number of simulator particles used. For both the reservoir and expansion flow simulations, the trace species algorithm gives an improvement in accuracy equivalent to using 100 times the number of simulator particles.

\textsuperscript{1} Centre for Hypersonics, The University of Queensland, Brisbane, 4067, Australia
\textsuperscript{2} ARC Centre for Functional Nanomaterials, The University of Queensland, Brisbane, 4067, Australia
I. INTRODUCTION

The Macroscopic Chemistry Method (MCM) for DSMC simulations of reacting flows was proposed by Lilley and Macrossan\(^1\). MCM differs from conventional particle based DSMC chemistry models in that reacting collisions are not specifically processed. Instead, the local macroscopic parameters in each cell, such as the density, temperature and species concentrations, are combined with reaction rate data to determine the number of ‘chemistry events’ which occur over a time-step. One of the advantages of this approach is that the large quantity of reaction rate data which is commonly used in Computational Fluid Dynamics simulations may be applied directly in DSMC simulations. In addition, multi-temperature reaction rate data such as the two-temperature model of Park\(^2\) can also be used directly\(^3\), as can reaction rates which depend on the fluid density\(^4\). Lilley and Macrossan\(^1\) have applied MCM to investigate dissociation and recombination reactions in a symmetrical diatomic gas. This study demonstrates a procedure for including a multiple species reaction set with exchange reactions. We show that the macroscopic chemistry method is particularly suited to modelling chemical reactions between trace species. By ‘trace’ we mean those species whose concentration corresponds to less than one DSMC simulator particle per sampling region.

The macroscopic method requires knowledge of the forward and reverse reaction rate constants. These are calculated from the time-averaged conditions (usually only the temperatures) in each cell, and modified by a simple non-equilibrium correction factor which takes account of the actual rate at which potential reacting collisions take place in each cell, as found in the DSMC simulation. This correction factor is described by Goldsworthy \textit{et al.}\(^5\). For simplicity of presentation we have ignored this small correction factor in the following work, and have used thermal equilibrium reaction rates in a modified Arrhenius form. The macroscopic method has previously employed a multi-temperature reaction rate\(^6\) to account for dissociation-vibrational coupling, but again for simplicity, we have ignored that possibility here.

Resolution of species which are present at very low concentrations can be important for many applications. As discussed by Bartel\(^6\), it can be difficult to obtain accurate and statistically meaningful samples of reactions involving trace species using conventional particle based chemistry methods which apply a probabilistic steric factor to a potential reaction-collision. A number of authors (see for instance Boyd\(^7\)) have applied species-based weighting factors so that a single simulator particle represents a different number of real particles depending on the identity of the species. One disadvantage of this approach is that it requires modification of the collision and sampling routines. An alternative approach, as employed by Boyd \textit{et al.}\(^8\), is to compute the production and transport of trace species in a decoupled fashion by separately solving the conservation equations for the trace species using information from the underlying DSMC flow-field. Here we demonstrate a coupled trace species transport model which does not require species specific weighting factors.

II. MULTIPLE REACTION SET IMPLEMENTATION

We begin by describing the method as it applies to zero-dimensional calculations. The transportation of trace species between cells is considered later. In previous studies using MCM, a single dissociation-recombination reaction similar to
was modelled. The net change in the number of \( O_2 \) due to forward and reverse reactions with rate constants \( k_f \) \((m^3/s)\) and \( k_r \)(m\(^3\)/s) over a small time period \( \Delta t \) (s) was calculated using a simple Euler method:

\[
\Delta N_{O_2} = \dot{N}_{O_2} \Delta t \tag{1}
\]

where the reaction rate is given by:

\[
\dot{N}_{O_2} = V \left( k_f n_{O_2} n_O - k_r n_{O_2} n_{M} \right) \tag{1a}
\]

Here \( n_i \) is the time averaged number density \((m^{-3})\) of species \( i \) in the cell of volume \( V \)(m\(^3\)). The characteristic chemical reaction time is greater than the collision time, which in turn is greater that the time-step, so that a higher order update scheme is generally not required. The quantity \( \Delta N_{O_2} \) was stored for each cell and carried over to subsequent time steps. When \( \Delta N_{O_2} \) in any cell went outside the range \( \pm 0.5 \) a reaction was modelled; either a single \( O_2 \) molecule (chosen at random from the cell) was split to form two \( O \) atoms (a dissociation ‘event’) or two \( O \) atoms were selected (at random) and combined to form a single molecule (a recombination ‘event’).

Consider now a system consisting of five chemical species, \( CO_2, CO, O_2, C, O \), where the following chemical reactions are modelled:

- \( CO_2 + M \leftrightarrow CO + O + M \) \[a\]
- \( CO + M \leftrightarrow C + O + M \) \[b\]
- \( O_2 + M \leftrightarrow O + O + M \) \[c\]
- \( CO_2 + O \leftrightarrow O_2 + CO \) \[d\]
- \( CO + CO \leftrightarrow CO_2 + C \) \[e\]
- \( CO + O \leftrightarrow O_2 + C \) \[f\]

Reactions \[a]-[c]\] are dissociation-recombination reactions for the molecular species \( CO_2, CO \) and \( O_2 \). The colliding particle, denoted ‘\( M \)’, may be any one of the five species. Reactions \[d]-[f]\] are exchange reactions.

We could store in each cell a ‘reaction coordinate’ for each reaction using an expression similar to Eq. 1. However, in previous implementations of MCM, when a reaction ‘event’ was to be processed, either one molecule was selected for dissociation reactions, or two atoms were selected for recombination reactions. Inspection of reactions \[d]-[f]\] shows that such an implementation would require separate procedures for dissociation-recombination reactions and exchange reactions. Note however, that the exchange reactions may be modelled as a combination of dissociation or recombination ‘events’. For instance, reaction \[d]\) may be expressed as \( CO_2 + O \rightarrow CO + O + O \rightarrow CO + O_2 \) and, as shown below, this allows us to implement only dissociation or recombination events in our chemistry procedures. Rather than storing a reaction coordinate for each reaction, we can store a ‘species coordinate’ for only those species which may themselves dissociate. We label these species \((CO_2, CO, O_2)\), ‘primary’ species.
As an example, suppose that each reaction proceeds in the forward direction by one ‘unit’. The required numbers of reaction events for the primary species are shown in Table 1. Each reaction is expressed as a combination of dissociation or recombination events so that the table does not simply show the net loss or gain of each species.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>Net number of ‘events’</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta CO_2$</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>$\Delta CO$</td>
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<td>-1</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>-3</td>
</tr>
<tr>
<td>$\Delta O_2$</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 1 Net numbers of dissociation/recombination events which must be modelled for reactions [a]-[f] to progress 1 ‘unit’ in the forward direction.

The last column of this table shows that one $CO_2$ net ‘dissociation event’, three $CO$ net ‘dissociation events’ and one $O_2$ net ‘recombination event’ must be simulated in order for reactions [a]-[f] to progress 1 ‘unit’ in the forward direction. Thus, in this case, we remove one $CO_2$ simulator particle from the cell and replace it by one $CO$ particle and one $O$ particle. Similarly, we find three $CO$ molecules in the cell, and replace each by a $C$ and $O$ atom. Finally, we find two $O$ particles in the cell and replace them with a single $O_2$ particle. The specific details of how energy and momentum are conserved as particles are removed and new particles are created in the cell, is discussed later. Here it is important to note that Table 1 does not show the net changes in primary species, rather it shows the numbers of ‘events’ to be performed for each primary species. The correct final numbers of particles of all species are ensured by this process in the most general case when each reaction may progress by varying amounts.

Since, in general, the chemistry time-step should be smaller than the characteristic reaction time of the fastest reaction, the increment will usually be a small fractional number and not an integer as shown in the above table. To account for this, the changes in the number of each primary species over a single chemistry time-step are accumulated and carried over to subsequent time steps. When this cumulative value for a given species becomes larger than 0.5, a single ‘dissociation event’ for that species is modelled and the cumulative value is decreased by 1. Similarly, when the value becomes less than -0.5 a recombination event is modelled and the value increased by 1.

A loop is made over all primary species and any dissociation events are processed initially. In cases where there are insufficient primary species to dissociate, all of the existing primary species are dissociated. The number of ‘dissociation events’ which could not be modelled is recorded, to be processed at the next time-step. Recombination events for all species are then processed. If there are insufficient particles in the cell for the required number of events, the remaining number of events is recorded for later processing. The kinetic energy in the cell is then adjusted by the total change in chemical potential energy from all dissociation and recombination events. We could distribute the change in chemical potential energy over all the thermal energy modes in the cell, but have chosen instead to adjust only the translational thermal energy; the thermal velocity components of each particle are multiplied by a single factor such that the total energy in the cell
is conserved. We rely on subsequent collisions to transfer this energy from the translational mode to the other thermal energy modes.

When performing a dissociation event, a particle of the required species is selected at random from those in the cell. It is replaced by two new particles both having the same position. The centre of mass velocity of the two new particles is the same as the velocity of the original particle. The internal (rotational and vibrational) energy of the original molecule is converted to the relative kinetic energy of the new particles. The direction of the relative velocity vector of the two new particles is selected randomly. When a recombination event is processed, two particles of the required species are selected at random from the cell and replaced by a new particle. The position and velocity of the new particle are set as the centre of mass values of the particle pair which was removed. The relative kinetic energy of the original two particles, as well as any internal energy of those particles, is converted to the internal energy of the new particle. Since we have no detailed information to indicate how to apportion this internal energy, we divided it evenly between the rotational and vibrational modes of the new particle.

In conventional collision-based DSMC chemistry procedures, the product of the time-averaged and instantaneous number densities is employed in the determination of the number of collision (reaction) events to occur over a given time interval. This value, which is not necessarily an integer, must nevertheless be made so, since only an integer number of collision events can be simulated. The fractional collision events or ‘remainders’ are usually accumulated for each pair of collision species. However, during the period of time for which the ‘remainder’ accumulates for a given species collision pair, the collision has not been ‘processed’ and hence it cannot influence the flow-field. By contrast, in the MCM trace species model, the fractional reaction events are included in subsequent reactions. That is, the model keeps track of reactions for species which are not present in the cell as simulator particles, whereas such reactions are simply ignored in collision-based chemistry methods. The rates at which trace species are produced or destroyed depend on the concentrations of all species, including the concentrations of trace species.

Equation 1a shows that the required reaction rates depend, in general, on the local time-averaged densities of all species in the cell. The required time-averages are obtained as part of the normal sampling procedure associated with DSMC simulations with one modification which accounts for “missing species”: for each cell the fraction of unprocessed reaction events is known and thus we know, for all species, the “missing number” $\Delta N_i$. The time-averaged number densities $\bar{n}_i$ are calculated by including the remainder due to the unprocessed reaction events when cell samples are taken, i.e.

$$\bar{n}_i = \frac{1}{S_V} \sum N_i', \quad \text{where} \quad N_i' = N_i + \Delta N_i \quad (2)$$

Here $S$ is the number of samples over which the averaging is made. The value of $\bar{n}_i$ computed using Eq. 2 is then used in Eq. 1a. We do not have to specify in advance which will be the ‘trace’ species.

The method described so far accounts for the chemical source/sink term for all species. Since the free-flight and collisions of species which have a cell number density equivalent to less than one
particle in that cell are not modelled, the convection and diffusion processes for the trace species must now be considered.

Method for including trace species transport

So far we have tacitly assumed that the ‘species remainders’ \( \Delta N_i \) for all primary species are accumulated in each cell. Here we show how the simulator particles in the cell can be used to model the convection and diffusion of the primary species remainders. Since the primary species remainders include (or imply) remainders for all species, we are thereby modelling transport processes for a species which may not have a simulator particle in the given cell. We call this the ‘trace species transport model’.

After the remainder in a cell is updated using Eq. 1 together with Eq. 2, the change in the remainder is distributed evenly amongst all particles in the cell. When the particles are subsequently moved for one time-step, they carry this remainder to different locations (and possibly different cells). After the particles have moved, the remainder for each cell is determined by summing the remainders carried by each particle then in the cell. Thus, the remainders are not associated with the cells, but with the particles; each particle carries with it the remainder of all the primary species. Since no distinction is made regarding the species identity of the ‘carrier’ particle, the transport of trace species is effectively modelled using the mean convection velocity and an overall average mixture diffusivity. That is, we assume that in the flow-field of interest, either species transport via convection is dominant or that the relative diffusion rates between the species are sufficiently similar.

The computational cost in CPU time is small. For any given cell, the method requires two loops over the particles in the cell. In the first loop, the cell remainders are calculated from the values carried by the particles in the cell and in the second, the updated cell remainder is re-distributed to the particles in the cell. The principle cost is in memory; the remainders must be stored for each particle, rather than for each cell. The advantage of the approach is that trace species may be modelled using only as many simulator particles as are required to resolve the flow-field structure.

III. RESERVOIR RELAXATION CALCULATIONS

Reservoir relaxation calculations were made using the DSMC-MCM method and compared with numerical integration of the reaction rate equations. A high temperature gas with an initially molecular composition was allowed to relax under constant volume conditions and the mole-fraction of each species was recorded. The temperature of the isolated system decreased as the dissociation reactions occurred. Thermal equilibrium conditions in the reservoir were enforced at each time-step by computing a sufficiently large number of collision events. As a result, the details of the collision routine, the selection procedure of reacting particles and the mechanics of post-reaction energy disposal are unimportant.

The reaction rate data of Park and of McKenzie as documented by Chen\(^9\) have been used in this study. Eight species \( \{O_2, N_2, O, N, NO, C, CO, CO_2\} \) and 54 chemical reactions comprising 40
dissociation and 14 exchange reactions were modelled. The initial temperature was 10000K. Two cases have been considered with initial mole fractions of 20% O$_2$ and 80% N$_2$ representing an air reaction system and 5% N$_2$ and 95% CO$_2$ representing a Martian atmosphere reaction system. Three-body recombination reactions were not considered (though they are simple to include in MCM) so that binary scaling implies that the results may be evaluated in terms of any 'sufficiently low' density. The time-scale for the relaxation process has thus been normalized using a mean collision time (s): $\tau_m = 5.12 \times 10^{-11} / \rho_n$ (air reaction system) and $\tau_m = 1.08 \times 10^{-10} / \rho_n$ (Martian atmosphere system) calculated from a separate steady-state simulation of the initial condition. Here $\rho_n$ (kg/m$^3$) is the free-stream density.

The species mole fractions and temperature histories are shown in Fig. 1 for the air reaction simulation. The numerical integration results for the reaction rate data of Park (solid lines) and McKenzie (dashed lines) are included as well as the DSMC-MCM results for both reaction sets. N$_2$ and O$_2$ molecules initially dissociate. NO is then formed through recombination of N and O atoms via the exchange reactions. As the NO mole fraction increases, so too does the rate of the reverse exchange reaction and so the NO mole fraction reaches a maximum before decreasing. This characteristic behaviour occurs for both reaction sets. The DSMC-MCM results are in exact agreement with those obtained from the direct integration of the rate equation. The reaction rates of Park are slightly faster, and this is also apparent in the temperature history. It can be seen that there is a change in temperature gradient at approximately the peak in NO concentration. This is due to the exothermicity of the reverse exchange reaction involving the dissociation of NO through collisions with N atoms.

![Figure 1](image_url) Species mole fractions (left) and temperature (right) for air reservoir relaxation simulation. Direct integration of the reaction rate equations of Park (solid lines) and of McKenzie (dashed lines). DSMC-MCM simulation results are given by the symbols. The horizontal axis is normalized by the initial mean collision time.

Results for the Martian atmosphere reservoir simulation using the reaction set of McKenzie are shown in Fig. 2. In the left plot, the symbols correspond to the benchmark DSMC-MCM simulation with $10^6$ simulator particles and without the update algorithm employing $\Delta N$, in Eq.
2. That is, in the benchmark simulation, only the actual simulator particles in the cell were used to determine the reaction rate so that $N'_i = N_i$. There is very close agreement between the integrated (solid lines) and DSMC-MCM results. It may be noted that the mole fraction of $C$ atoms appears to be not well represented. However, without the trace species procedure, it was not possible to resolve a mole fraction below approximately 0.0001. Considering this, the result demonstrates that even using just the actual simulator particles in the cell to evaluate the chemical source term, MCM is capable of maintaining information on the concentration of minor species, whose concentration is below the resolution of the simulation.

The procedure for trace species modelling was implemented using a total of 100 simulator particles. The resultant species mole fraction relaxation history is shown in the right plot of Fig. 2. There is very close agreement between the DSMC-MCM and integrated solutions at mole fractions as small as $10^{-8}$. It is expected that some differences could occur due to statistical variations in the computed temperature owing to the small number of particles used. However, this is not apparent. No ensemble averaging was employed, though four flow-field samples were used to generate each output state. The use of fractional remainders to determine the chemical source term allowed such smooth and accurate species mole fractions to be obtained.

![Figure 2](image_url) Species mole fractions for reaction system of McKenzie. Left: without trace species algorithm and $10^4$ simulator particles. Right: with trace species algorithm and 100 simulator particles. DSMC-MCM results are shown as symbols; results from the direct integration of the reaction rate equations are shown as solid lines. The horizontal axis is normalized by the initial mean collision time.

**IV. QUASI-ID EXPANSION CALCULATIONS**

To obtain benchmark results with which to compare the trace species transport method, we have calculated a 1-D flow using DSMC-MCM with an extremely large number of particles, so that the species concentrations never fall below one simulator particle per cell. The flow is the expansion of a mixture of 5% $N_2$ and 95% CO$_2$ with an inlet temperature of 10000K at a speed of 5km/s. The flow passes through a duct where the volume of each successive cell along its length is given by: $Vol(x) = 1 + 2x^2$ for $0 \leq x \leq 1$ where $x$ is the cell-centre coordinate. Side wall effects are ignored, so the flow is quasi-one-dimensional. The chemical reactions rates are only
significant at the beginning of the expansion, and the effects of convective transport of species out of this region dominate the downstream flow. Four million particles were used for the benchmark simulation. For comparison, simulations with 40,000 particles were made both with and without the trace species transport algorithm.

The reaction rate data of Mckenzie was used for the 59 chemical reactions evaluated with the overall cell temperature. The inlet density was $10^{-4} \text{kg/m}^3$. Three body recombination reactions were included by evaluating the Gibbs function for each species from standard enthalpy and entropy functions. Species specific collision cross-section data of Gupta and Park et al. were used to fit power law viscosity relations for each collision pair. A small degree of thermal non-equilibrium was present due to the rotational and vibrational relaxation rates employed. However, these details do not affect the comparisons between the simulations and thus, they are not discussed further.

The simulation domain extended to one metre in length and 1000 cells were used. The cells were concentrated towards the inlet. Once steady-state conditions had been reached, 6500 flow-field samples were accumulated. Results are normalised by the inlet mean free path $\lambda_0 = 2.4 \times 10^{-3} \text{m}$.

The density of the flow decreased rapidly as the cross-sectional area increased. The temperature also decreased, predominantly because of the endothermic chemical reactions which occurred. Most of the chemical reactions occurred near the inlet where the collision rate and temperature were highest. Plots of the species mole fractions along the nozzle are shown in Fig. 3. In both plots, the solid lines correspond to the simulation without the trace species algorithm, but with 100x the number of simulator particles. All other simulations used the reduced number of simulator particles. In the left plot, the symbols correspond to the simulation without the trace species algorithm. The $\text{CO}_2$, $\text{N}_2$, $\text{CO}$ and $\text{O}$ mole fractions are closely matched. However, there is a significant difference in the $\text{O}_2$ mole fraction, even for values on the order of $10^{-2}$. This demonstrates that relatively fast chemical reactions between trace species can affect the concentration of major species.

Results using the trace species transport model, shown as symbols in the right plot of Fig. 3, agree closely with the benchmark simulation. All primary species remainders were transported with the mean velocity of the simulator particles, which in this case were mainly $\text{CO}_2$ or $\text{N}_2$ particles. Note that the diffusion rate of the species remainders corresponded to that of the two main species since the ‘carrier’ particles underwent collisions in the usual manner. For this flow, species transport via convection is dominant and hence the influence of varying diffusion rates between species is minimal.
V. DISCUSSION AND CONCLUSIONS

We have applied the Macroscopic Chemistry Method to the modelling of a multiple species reaction system including exchange reactions. The method is easily scalable to any number of chemical reactions, provided that a consistent method is used to specify reaction products and reactants. The Martian atmosphere reaction set included 59 chemical reactions, yet only 5 primary species counters were required.

All reactions were modelled as a combination of dissociation or recombination events for a reduced set of ‘primary species’ i.e. the dissociating species. We do not record whether, for instance, a carbon dioxide molecule dissociates in a dissociation reaction ([a]) or in an exchange reaction ([d]). Therefore, we select a carbon dioxide particle for dissociation at random, without regard to the energy stored in any particular mode, and without knowing if it is to dissociate as part of an exchange reaction. It may be that the dissociation reaction should occur preferentially for molecules in high vibrational states and we could select dissociating particles based on their vibrational states. However, we could not then implement a different selection criterion for the exchange reactions. It is important to note that DV coupling, for instance, could be included for the dissociation reactions through a two-temperature reaction rate whereas at the same time modelling exchange reactions with a three-temperature rate. The only limitation of the approach described here is that the preferential selection procedure which determines which particles (as opposed to how many) will ‘react’ must be the same for all reactions. Given that the fraction of collisions which actually result in a reaction is usually very small, it seems unlikely that such details could have an appreciable influence on most flows.

Here we have shown how the effect of unprocessed reactions can immediately be reflected in the reaction rate, and that this procedure has the added benefit that it allows for an accurate representation of reactions involving trace species, species for which the concentration is less than one simulator particle per cell. Each unprocessed reaction represents a fractional number of simulator particles which should be present in the cell. All that is required is to calculate the state
in the cell (the number density of each species) by adding the remainder $\Delta N_i$ to the actual number of simulators in the cell to get the "corrected" number $N_i$ in the cell. When the chemical source terms are evaluated (the reaction rates are evaluated) we base the rate on the corresponding number density.

The transport of the species remainders $\Delta N_i$ was modelled by associating the remainders with all the particles in the cell, so that they are transported through the flow with an average convection and diffusion rate. The trace species methods are expected to be accurate when the rate of convective transport is significantly greater than the rate of diffusive transport, or when the diffusion rates are similar for all the species. The trace species methods were shown to work well for the hypersonic 1-D expansion case. For example, no carbon atom simulator particles were present in the entire 1-D expansion simulation; carbon atoms were represented by remainders only and hence underwent diffusion at the average rate of all simulator particles. Since the simulator particles have a greater mass than the carbon atoms, the average diffusion rate was approximately half the true carbon atom diffusion rate. Nevertheless, since the flow was dominated by convective transport, the distribution of carbon atoms along the expansion was almost exactly the same as for the benchmark results in which all species were represented by simulator particles. Similar results were found for the NO and $N$ species, which were also included in the trace species simulation as remainders only. A simulation which included the chemical source term for trace species (that is the quantity $\Delta N$, in Eq. 2), but did not include the trace species transport model, was found to be less accurate than a simulation which ignored the trace species in both the reaction rate and the movement of the molecules. Hence, if the trace species procedures are implemented for the source terms, they must be implemented for the transport terms as well.

The trace species methods may be applied to the more general multiple species MCM implementation employing the 'reaction coordinate'. In addition, the trace species methods could be used to model particles in vibrationally or electronically excited states as separate 'species'. The one-dimensional simulations of an expanding flow showed that the trace species procedures produced results in close agreement with the benchmark simulation while requiring only 5% of the memory and 1.3% of the CPU time.

REFERENCES


