

Modeling Dissociation-Vibration Coupling with the Macroscopic Chemistry Method

Charles R. Lilley, and Michael N. Macrossan

Citation: *AIP Conference Proceedings* **762**, 1019 (2005); doi: 10.1063/1.1941668

View online: <https://doi.org/10.1063/1.1941668>

View Table of Contents: <http://aip.scitation.org/toc/apc/762/1>

Published by the *American Institute of Physics*

Modeling Dissociation-Vibration Coupling with the Macroscopic Chemistry Method

Charles R. Lilley* and Michael N. Macrossan*

*Centre for Hypersonics, School of Engineering, The University of Queensland, Brisbane, 4072, Australia

Abstract. We test the recently developed macroscopic approach to modeling chemistry in DSMC, by simulating the flow of rarefied dissociating nitrogen over a blunt cylinder. In this macroscopic method, chemical reactions are decoupled from the collision routine. Molecules are chosen to undergo dissociation at each time step, after the collisions are calculated. The required number of reaction events is calculated from macroscopic reaction rate expressions with macroscopic information taken from the time-averaged cell properties. One advantage of this method is that “state-of-the-art” macroscopic information about reaction rates can be used directly in DSMC in the same way as in continuum codes. Hybrid Navier-Stokes/DSMC codes can therefore easily use the same chemical models in both rarefied and continuum flow regions. Here we show that the macroscopic method can capture dissociation-vibration (DV) coupling, which is an important effect in vibrationally cold blunt body flows because it results in increased surface heat fluxes. We use the macroscopic method with Park’s two-temperature rate model, often used in continuum studies, to capture DV coupling in DSMC. This produces a flowfield in reasonable agreement with that calculated using the conventional collision-based threshold line dissociation model.

INTRODUCTION

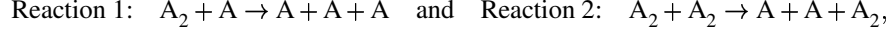
In the hypersonic flow of rarefied gas over a blunt body, gas molecules generally have insufficient collisions to achieve local equilibrium conditions before being swept downstream. The shock layer is characterized by different kinetic temperatures of translation T_{tr} , rotation T_{rot} and vibration T_{vib} . T_{tr} rises rapidly through the shock layer, and is closely followed by T_{rot} , because translation-rotation energy exchange requires relatively few collisions. Many collisions are needed to transfer energy to the vibrational mode, so T_{vib} is typically much lower than both T_{tr} and T_{rot} . Collision-induced dissociation of diatomic gas molecules occurs preferentially from higher vibrational energy levels, a phenomenon we call dissociation-vibration (DV) coupling. In vibrationally cold flows, DV coupling reduces the dissociation rate relative to that expected for a gas at thermal equilibrium. For blunt bodies in rarefied hypersonic flow, the delay in dissociation increases the heat transfer rate \dot{Q} relative to that for a flow without DV coupling.

Rarefied gas flows are usually simulated with the direct simulation Monte Carlo (DSMC) method [1]. Many models have been proposed to simulate chemical reactions with the DSMC method. In most, a reaction probability P_R is calculated at the time of collision. A reaction is performed if $P_R > R_f$, where R_f is a uniformly distributed random fraction between 0 and 1. Here such collision-based chemistry procedures are called conventional chemistry models. Several conventional models have been developed specifically to capture DV coupling, as summarized by Wadsworth and Wysong [2] and Wysong *et al.* [3].

Recently, Lilley and Macrossan [4] proposed the macroscopic chemistry method for DSMC calculations, in which collisions and chemical reactions are decoupled. Unlike conventional collision-based chemistry models, reactions are performed after the collision routine. As an example of the versatility of the macroscopic method, we show that it can capture the expected effects of DV coupling, by using Park’s two-temperature rate model [5]. We have used the hypersonic flow of rarefied dissociating nitrogen over an axisymmetric blunt cylinder as a test case. To demonstrate more fully that the macroscopic method can accurately capture DV coupling, we compare it to the conventional collision-based threshold line dissociation (TLD) model which has been adapted for the DSMC method by Boyd [6]. We calculated the equilibrium dissociation rates realized by the TLD model with a Monte Carlo sampling procedure, and then used these rates in the macroscopic method with Park’s two-temperature model to capture DV coupling. We show that the resulting flowfield is similar to that calculated with the TLD model.

THE MACROSCOPIC CHEMISTRY METHOD

The fundamental premise of the macroscopic method [4] is that chemical reactions are infrequent events, and provided that the macroscopic reaction rate is maintained, the details of reaction events have a minimal influence on the flowfield properties of engineering interest. The number of reaction events performed in each cell is based on the number required to maintain the macroscopic reaction rate. Lilley and Macrossan [4] developed the macroscopic method for a symmetrical diatomic gas, in which dissociation proceeds via the two reactions



which have the respective rates k_1^+ and k_2^+ . The number of reaction events required in a cell during a time step Δt is

$$\Delta N_{A_2} \approx - \left(\bar{N}_A/2 + \bar{N}_{A_2} \right) \dot{\alpha} \Delta t,$$

where \bar{N}_i is the time-averaged number of species i particles in the cell. Here, $\dot{\alpha}$ is calculated using

$$\dot{\alpha} = \bar{\rho} (1 - \bar{\alpha}) [k_1^+ \bar{\alpha} + k_2^+ (1 - \bar{\alpha})/2] / \mathcal{M}_N,$$

where \mathcal{M}_N is the molar mass of atomic nitrogen in kg/kmol. This expression considers dissociation events only and ignores recombination. $\bar{\alpha}$ is calculated using $\bar{\alpha} = \bar{N}_A / (\bar{N}_A + 2\bar{N}_{A_2})$. Here k_1^+ and k_2^+ are calculated from local kinetic temperatures, but it is important to note that they can be any function of the local macroscopic conditions.

For each dissociation event, a single diatom is selected from the cell, and is dissociated into two atoms. The internal energy of the dissociating diatom is manifested as the relative translational energy of the atoms. Each dissociation event requires an amount of energy $\varepsilon_d = k\Theta_d$ where Θ_d is the characteristic dissociation temperature. To account for this dissociation energy, the thermal velocities of all particles in the cell are adjusted. This involves calculating a factor

$$\Psi = (1 - \Delta E / E_{tr})^{1/2}$$

where $\Delta E = -\Delta N_{A_2} \varepsilon_d$ and E_{tr} is the total translational thermal energy in the cell. The j velocity components v_j of each particle are then adjusted according to $v'_j = \Psi v_j + \bar{v}_j (1 - \Psi)$.

A selection rule must be applied to select dissociating diatoms. Here we consider two possible options. Lilley and Macrossan [4] selected dissociating diatoms with the probability $P_s = \varepsilon_{int} / (\varepsilon_{int})_{max}$, where the internal energy $\varepsilon_{int} = \varepsilon_{rot} + \varepsilon_{vib}$ is the sum of rotational and vibrational energies for a diatom, and $(\varepsilon_{int})_{max}$ is the maximum instantaneous internal energy in the cell. This selection method was used to approximate the selection of dissociating diatoms in the conventional total collision energy (TCE) chemistry model [7]. Here we call this method A. This selection method is applied to randomly selected diatoms, which are then dissociated if $P_s > R_f$. This is an acceptance-rejection procedure that continues until the required number of diatoms have been dissociated for the cell.

For diatoms with DV coupling, the dissociation probability should depend primarily on the vibrational energy. Diatoms in higher vibrational energy levels should be more likely to dissociate. To account for this, a second selection method, called method B, could be $P_s = (0.5 + q_{vib}) / q_d$. Here, q_{vib} is the vibrational energy level for harmonic oscillators and q_d is the level immediately below the dissociation limit. The 0.5 added to q_{vib} accounts for the ground state energy and removes difficulties that occur when $q_{vib} = 0$. For nitrogen $q_d = 33$.

BLUNT CYLINDER CALCULATIONS

Fig. 1 shows the blunt cylinder simulation geometry and freestream conditions. We used the VHS nitrogen model from Lilley and Macrossan [4]. Borgnakke-Larsen procedures [8] were used for internal energy exchange. Multiple relaxation events were prohibited, and constant exchange probabilities of 0.3 and 0.01 were used for rotation and vibration respectively. The logic of Gimelshein *et al.* [9] was used to select inelastic collisions. The time step Δt was 3.743×10^{-7} s, and the sampling interval was $7\Delta t$. Cell-based weighting factors were used, and at steady state, the mean number of particles per cell was ~ 20 . A hot wall at 1000 K with diffuse reflection was used. Atom recombination was ignored. Using the VHS mean free path [1] and cylinder diameter $2r_c$, the Knudsen number Kn was about 0.026. A continuum breakdown parameter $B \equiv Kn M_\infty$ was about 0.9. Both Kn and B show that rarefied effects are important

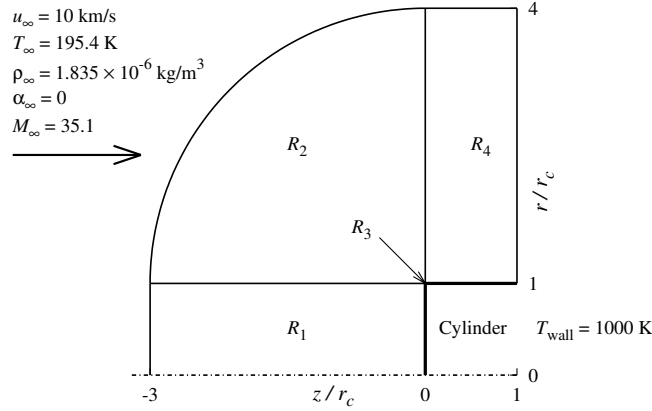


FIGURE 1. Blunt cylinder simulation geometry and freestream conditions. Cylinder radius $r_c = 0.5$ m. The domain contained rectangular regions R_1 and R_4 and radial regions R_2 and R_3 . The small radial region R_3 contained only one cell, and extended to a distance $r_c/100$ from the cylinder edge. R_1 contained (180×200) cells in the $(z \times r)$ directions with a geometric progression in cell sizes in the z direction, increasing away from the cylinder. The ratio of z dimensions for adjacent cells, denoted f_z , was 1.0152. R_2 contained 80 cells in the radial direction and 40 in the angular direction. The ratio of radial dimensions for adjacent cells was 1.01. R_4 contained (80×80) cells in the $(z \times r)$ directions, with $f_z = f_r = 1.01$.

TABLE 1. Surface flux results for blunt cylinder calculations. MCM = macroscopic chemistry method.

Chemistry model	C_D	C_H	Chemistry model	C_D	C_H
Kewley and Hornung rates:			TLD rates:		
Conventional TCE model	1.771	0.232	Conventional TLD model	1.787	0.162
MCM, k_{Arr}^+ (T_{kin}), method A	1.771	0.234	MCM, k_{Arr}^+ (T_{kin}), method A	1.793	0.143
MCM, k_{2T}^+ ($T_{\text{tr+rot}}, T_{\text{vib}}, 0.7$), method A	1.770	0.258	MCM, k_{2T}^+ ($T_{\text{tr+rot}}, T_{\text{vib}}, 0.9$), method A	1.787	0.155
MCM, k_{2T}^+ ($T_{\text{tr+rot}}, T_{\text{vib}}, 0.7$), method B	1.771	0.261	MCM, k_{2T}^+ ($T_{\text{tr+rot}}, T_{\text{vib}}, 0.9$), method B	1.787	0.159
MCM, k_{2T}^+ ($T_{\text{tr+rot}}, T_{\text{vib}}, 0.5$), method A	1.771	0.277	No chemistry	1.771	0.289
MCM, k_{2T}^+ ($T_{\text{tr+rot}}, T_{\text{vib}}, 0.5$), method B	1.772	0.277			

for this flow, and that thermal non-equilibrium conditions are expected in the flowfield.

The blunt cylinder flowfield was first calculated without chemistry, and then with chemistry in the absence of DV coupling. To calculate reacting flow without DV coupling, both the macroscopic method and the conventional collision-based TCE chemistry model [7] were used, with the dissociation rates of Kewley and Hornung [10]. These dissociation rates are in the Arrhenius form $k_{\text{Arr}}^+(T) = C(T/\Theta_d)^\eta \exp(-\Theta_d/T)$. For nitrogen $\Theta_d = 113200$ K. For reactions 1 and 2 in nitrogen, Kewley and Hornung [10] give

$$k_1^+ = 1.97 \times 10^{10} \left(\frac{T}{\Theta_d}\right)^{-2.5} \exp\left(-\frac{\Theta_d}{T}\right) \frac{\text{m}^3}{\text{kmol} \cdot \text{s}} \quad \text{and} \quad k_2^+ = 4.71 \times 10^8 \left(\frac{T}{\Theta_d}\right)^{-3.5} \exp\left(-\frac{\Theta_d}{T}\right) \frac{\text{m}^3}{\text{kmol} \cdot \text{s}}.$$

The macroscopic method simply used these rates with the overall kinetic temperature T_{kin} [4], calculated in each cell from time-averaged samples, instead of T . In the TCE calculations, the procedure of Haas [11] was used to distribute energy amongst the various modes after reaction events. The drag coefficients C_D and heat transfer coefficients $C_H = 2\dot{Q}/(\rho u_\infty^3)$ for these calculations are shown in Table 1. There is good agreement between the surface fluxes for the macroscopic and TCE methods. There was also good agreement between the entire flowfields. Lilley and Macrossan [4] reported similar results, and it seems that the macroscopic method can accurately capture the flowfield of dissociating nitrogen, relative to that predicted by the TCE model.

In continuum calculations, Park's empirical two-temperature rate model [5] is often used to capture DV coupling. In this model, an effective temperature $T_e \equiv (T_{\text{vib}}/T_{\text{tr+rot}})^{1-s} T_{\text{tr+rot}}$ replaces T in the Arrhenius equation, to give the two-temperature dissociation rate $k_{2T}^+(T_{\text{tr+rot}}, T_{\text{vib}}, s)$. Under non-equilibrium conditions, the vibrational kinetic temperature T_{vib} and the combined kinetic temperature of translation and rotation $T_{\text{tr+rot}}$ [4] are used. Lilley and Macrossan [4] used

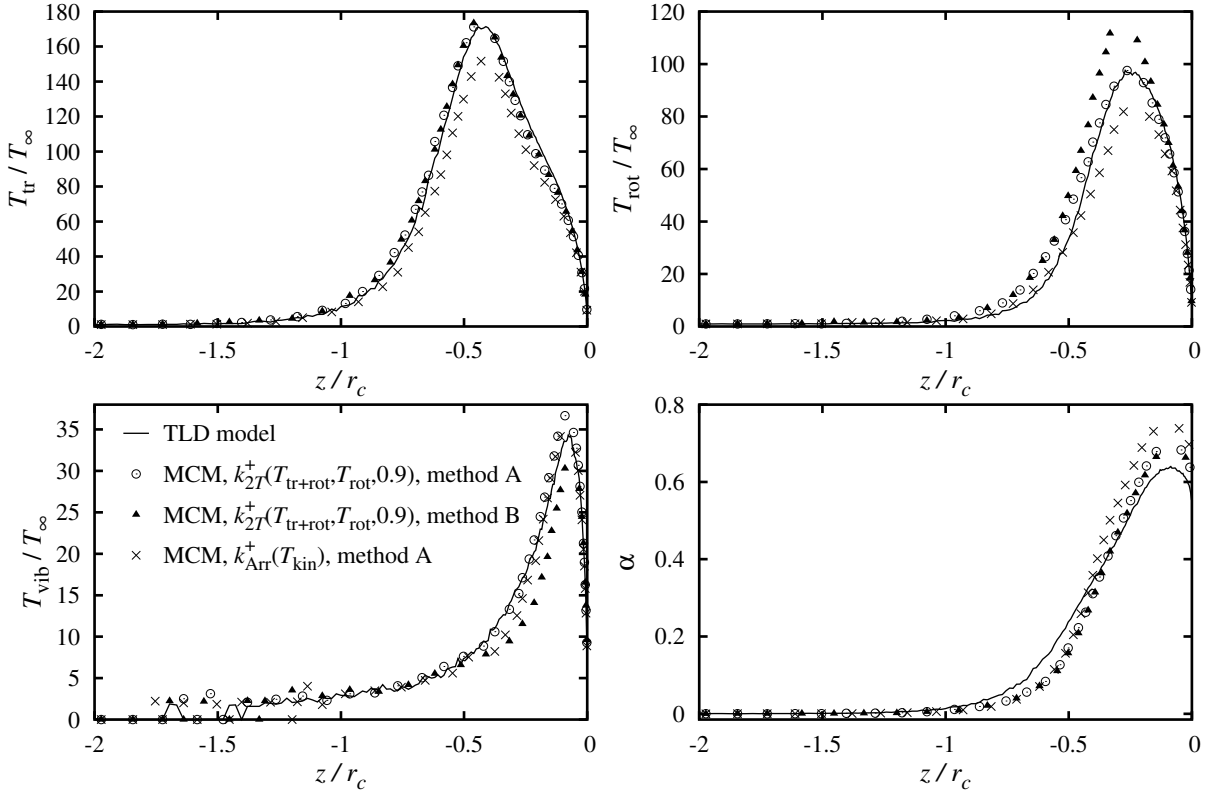


FIGURE 2. Stagnation streamline profiles for blunt cylinder calculations with TLD rates. The density profiles were almost identical, so are not shown here. MCM = macroscopic chemistry method.

this two-temperature model in the macroscopic method to simulate dissociating nitrogen flow downstream of a strong shock. It was shown that the macroscopic method with the two-temperature model and $s = 0.5$ can capture the expected delay in dissociation more accurately than the single-temperature Arrhenius rate $k_{Arr}(T_{kin})$.

We used Park's two-temperature model with the rates of Kewley and Hornung [10] to capture DV coupling for the blunt cylinder flow. We tested both particle selection methods, with $s = 0.5$ and $s = 0.7$. The C_D and C_H values are shown in Table 1. It seems that the macroscopic method with Park's two-temperature model can capture the expected DV coupling behavior, in that dissociation rates decrease and C_H increases relative to the cases without DV coupling. Also, C_H decreases with increasing s . In these cases, the different particle selection methods had little effect on the flowfield or surface fluxes.

To confirm that the macroscopic method can capture DV coupling with acceptable accuracy, comparison with a flowfield computed with a conventional collision-based DSMC chemistry model, formulated specifically to include DV coupling, is required. Here we have chosen the TLD model for the comparison, which was proposed by Macheret and Rich [12, 13] for diatomic gases in which $T_{vib} < T_{tr+rot}$. The TLD model is based on the premise that dissociation can occur only when the relative translational energy of colliding molecules ϵ_g exceeds some threshold energy ϵ_F which depends on the vibrational energy. Boyd [6] adapted the TLD model for conventional DSMC chemistry calculations. Distinctly different forms of ϵ_F and dissociation probability P_R^+ apply for low and high vibrational levels. Boyd [6] and Wadsworth and Wysong [2] give details of the DSMC implementation of the TLD model. We used Boyd's formulation here. The TLD model was used to calculate the blunt cylinder flowfield, and the resulting coefficients C_D and C_H are included in Table 1. Stagnation streamline profiles of T_{tr}/T_∞ , T_{rot}/T_∞ , T_{vib}/T_∞ and α are shown in Fig. 2.

The macroscopic dissociation rates realized by the TLD model are required to test the macroscopic method. We obtained these with a Monte Carlo technique that involved sampling collision energies from theoretical equilibrium distributions, and then using these sampled energies to calculate P_R^+ . The equilibrium distribution of reduced energy

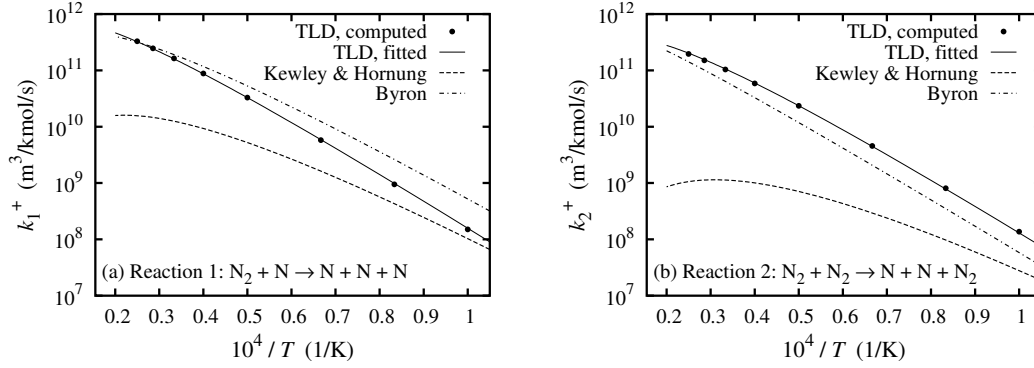


FIGURE 3. Calculated macroscopic TLD rates compared to fitted rates and the published rates of Byron [15] and Kewley and Hornung [10]. (a) Reaction 1: $k_1^+ \approx 2.0 \times 10^{12} (T/122000)^{-1.1} \exp(-122000/T)$ m³/kmol/s. (b) Reaction 2: $k_2^+ \approx 1.0 \times 10^{12} (T/122000)^{-1.3} \exp(-122000/T)$ m³/kmol/s.

in collisions between VHS molecules, denoted $\tilde{\epsilon}_g \equiv \epsilon_g/(kT)$, is given by the gamma distribution

$$f(\tilde{\epsilon}_g) = \tilde{\epsilon}_g^{1-\nu} \exp(-\tilde{\epsilon}_g) / \Gamma(2 - \nu).$$

The Cheng-Feast algorithm [14] was used to sample $\tilde{\epsilon}_g$ efficiently. We used the VHS parameters ν , μ_r and T_r from Ref. [4]. Rotational energy was sampled using $\epsilon_{\text{rot}} = -\ln(R_f)kT$ and the harmonic oscillator energy level using $q_{\text{vib}} = \lfloor -\ln(R_f)T/\Theta_{\text{vib}} \rfloor$. Following Wadsworth and Wysong [2], the vibrational energy was then given by $\epsilon_{\text{vib}} = (0.5 + q_{\text{vib}})k\Theta_{\text{vib}}$ to include the ground state vibrational energy. For nitrogen $\Theta_{\text{vib}} = 3390$ K. These sampled energies were then used to calculate the TLD dissociation probability P_R^+ . In $\text{N}_2 + \text{N}$ collisions the diatom was tested for dissociation, and in $\text{N}_2 + \text{N}_2$ collisions the first diatom only was tested for dissociation. A reaction event was counted when $P_R^+ > R_f$. At a given temperature, the dissociation rate $k^+(T)$ is then obtained from

$$k^+(T) = \langle P_R^+ \rangle \frac{\mathcal{N}\Xi}{f_s} \left(\frac{T}{T_r} \right)^{1/2-\nu} = \frac{N_R}{N_{\text{colls}}} \frac{\mathcal{N}\Xi}{f_s} \left(\frac{T}{T_r} \right)^{1/2-\nu}$$

where $\langle P_R^+ \rangle$ is the mean dissociation probability, N_{colls} is the number of collision energies sampled, N_R is the number of collisions resulting in a reaction event. The symmetry factor f_s is two for like particles and unity otherwise and $\mathcal{N} = 6.02 \times 10^{26}$ /kmol is Avogadro's number. The constant

$$\Xi \equiv \frac{15}{2} \frac{kT_r/\mu_r}{(2-\nu)(3-\nu)}$$

includes the VHS parameters of the collision pair. Monte Carlo sampling continued until 10^5 reaction events occurred for each temperature considered. The resulting rates are shown in Fig. 3. These rates differ from those computed by Boyd [6], which may be due to the use of different VHS parameters.

The TLD expressions for P_R^+ have singularities at certain energies [6, 2, 3], giving $P_R^+ > 1$. In such cases, a single dissociation event only is performed in most DSMC codes. In the Monte Carlo sampling performed here to determine the TLD rates, the fraction of events with $P_R^+ > 1$ often exceeded 50%. The existence of singularities is an important limitation of the TLD model [3].

The macroscopic method was used to simulate the blunt cylinder flowfield with the fitted TLD rates from Fig. 3. The effects of DV coupling were captured with Park's two-temperature model [5]. Here $s = 0.9$ was used, which was found by running test simulations with various s values. The C_D and C_H results are shown in Table 1, and stagnation streamline profiles are shown in Fig. 2. The agreement between the results obtained using the TLD and macroscopic methods is generally reasonable. The profiles shown in Fig. 2 indicate that particle selection method A is slightly better than method B, which contrasts with the behavior expected for DV coupling. Further investigations are required to determine the best selection method. The similar results obtained for the two different selection methods confirm the original premise of the macroscopic method, in that the details of reaction processes are relatively unimportant.

DISCUSSION AND CONCLUSIONS

For the hypersonic flow of dissociating nitrogen over a blunt cylinder, the results presented here show that the macroscopic method can capture the expected effects DV coupling, in that dissociation rates are reduced and heat transfer rates are increased, relative to flowfields calculated without DV coupling. Furthermore, it has been shown that the macroscopic method can give a flowfield similar to that calculated using the conventional collision-based TLD model, which was formulated specifically to capture DV coupling.

The most important advantage of the macroscopic method is that it can use any macroscopic rate expressions, which can be any function of the local macroscopic conditions. This allows DSMC chemistry calculations to be performed using rates for which no conventional collision-based DSMC chemistry model may be available. The large amount of literature on reaction rates used in continuum studies can therefore be applied directly in DSMC chemistry calculations. This permits hybrid codes, which use continuum solvers in near-equilibrium regions and the DSMC method in non-equilibrium regions, to use the same chemistry models throughout the entire simulation domain.

The form of α used here accounted for dissociation events only. Lilley and Macrossan [4] used a form that also accounted for recombination events. This meant that the macroscopic method considered net reactions only, so that no reactions were performed where chemical equilibrium existed. This avoids the detailed balancing problems that can be an issue when using conventional DSMC chemistry models. In this sense, the macroscopic method is similar to continuum solvers, which also consider net reactions and for which detailed balancing is not an issue.

As noted above for the TLD model, conventional DSMC chemistry models often suffer from singularities where $P_R^+ > 1$. In such cases, only a single reaction event is usually performed, so these singularities certainly result in reduced reaction rates relative to the expected rates. However, there may be more subtle effects introduced by the singularities which are not immediately obvious. The macroscopic method does not suffer from numerical instabilities.

REFERENCES

1. Bird, G. A., *Molecular gas dynamics and the direct simulation of gas flows*, Clarendon Press, Oxford, 1994.
2. Wadsworth, D. C., and Wysong, I. J., *Phys. Fluids*, **9**, 3873–3884 (1997).
3. Wysong, I. J., Dressler, R. A., Chiu, Y. H., and Boyd, I. D., *J. Thermophys. Heat Transfer*, **16**, 83–93 (2002).
4. Lilley, C. R., and Macrossan, M. N., *Phys. Fluids*, **16**, 2054–2066 (2004).
5. Park, C., *Nonequilibrium hypersonic aerothermodynamics*, John Wiley & Sons, New York, 1990.
6. Boyd, I. D., *Phys. Fluids*, **8**, 1293–1300 (1996).
7. Bird, G. A., “Simulation of multi-dimensional and chemically reacting flows,” in *Rarefied gas dynamics: Proceedings of the 11th International Symposium*, edited by R. Campargue, CEA, Paris, 1979, vol. 1, pp. 365–388.
8. Borgnakke, C., and Larsen, P. S., *J. Comp. Phys.*, **18**, 405–420 (1975).
9. Gimelshein, N. E., Gimelshein, S. F., and Levin, D. A., *Phys. Fluids*, **14**, 4452–4455 (2002).
10. Kewley, D. J., and Hornung, H. G., *Chem. Phys. Lett.*, **25**, 531–536 (1974).
11. Haas, B. L., *J. Thermophys. Heat Transfer*, **6**, 200–207 (1992).
12. Macheret, S. O., and Rich, J. W., *Chem. Phys.*, **174**, 25–43 (1993).
13. Macheret, S. O., Fridman, A. A., Adamovich, I. V., Rich, J. W., and Treanor, C. E., “Mechanisms of nonequilibrium dissociation of diatomic molecules,” in *AIAA Paper 94-1984*, AIAA, Washington, 1994.
14. Cheng, R. C. H., and Feast, G. M., *Applied Statistics*, **28**, 290–295 (1979).
15. Byron, S., *J. Chem. Phys.*, **44**, 1378–1388 (1966).