Code-Verification Techniques for Hypersonic Reacting Flows in Thermochemical Nonequilibrium

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The study of hypersonic flows and their underlying aerothermochemical reactions is particularly important in the design and analysis of vehicles exiting and reentering Earth’s atmosphere. Computational physics codes can be employed to simulate these phenomena; however, code verification of these codes is necessary to certify their credibility. To date, few approaches have been presented for verifying codes that simulate hypersonic flows, especially flows reacting in thermochemical nonequilibrium. In this paper, we present our code-verification techniques for hypersonic reacting flow in thermochemical nonequilibrium, as well as their deployment in the Sandia Parallel Aerodynamics and Reentry Code (SPARC).

I. Introduction

Hypersonic flows are distinguished by flow velocities and stagnation enthalpies that are high enough to induce chemical reactions and excitation of thermal energy modes. In particular, the time scales of the reactions and thermal excitation are comparable to the characteristic flow time, requiring a fully coupled modeling approach. The study of hypersonic flows and their underlying aerothermochemical phenomena is particularly important in the design and analysis of vehicles exiting and reentering Earth’s atmosphere.\textsuperscript{1,2} For much of this flight regime, the gas can be modeled as a continuum. The relevant chemical species are each tracked, such that the interactions within the flow field are accounted for in the evolution of the chemical state. Similarly, considering each internal energy mode allows the different modes to relax towards equilibrium while accounting for the flow and chemical states. As the flow velocity or stagnation enthalpy increases, more complex chemical kinetics and internal energy models must be included, and ionization, radiation, and other phenomena may become important.

To model such flows, the Sandia Parallel Aerodynamics and Reentry Code (SPARC)\textsuperscript{2–5} is presently being developed at Sandia National Laboratories. SPARC is a compressible computational fluid dynamics code designed to model transonic and hypersonic reacting turbulent flows. SPARC can also solve the transient heat equation and the equations associated with decomposing and non-decomposing ablators. One- and two-way multiphysics couplings exist between the fluid-dynamics and ablation solvers.

As with other computational physics codes, verification and validation of the choice of governing equations and their implementation in SPARC are necessary to develop confidence in the credibility of the simulations. Validation assesses how well the models instantiated in the code represent the relevant physical phenomena. It is typically performed by comparing simulation results with experimental results to assess the suitability of the models, the model error, and the practical bounds of validity of the models. On the other hand, verification assesses the accuracy of the approximate numerical solutions the code produces, as well as the code’s performance, relative to the assumptions and expectations associated with its numerical methods. Following Roache,\textsuperscript{6} Salari and Knupp,\textsuperscript{7} and Oberkampf and Roy,\textsuperscript{8} verification can be divided into code verification and solution verification. Solution verification focuses on numerical-error estimation for a particular simulation, whereas code verification focuses on the correctness of the numerical-method implementation in the code. A review of code and solution verification is presented by Roy.\textsuperscript{9}

This paper focuses on code verification. When solving the aforementioned equations numerically, the equations must be discretized using, for example, finite differences, finite volumes, or finite elements. Due to
the finite nature of the discretization, the equations and, consequently, their solutions incur a discretization error. As the discretization is refined, the discretization error should decrease. More rigorously, a code should achieve an expected order of accuracy: as the mesh is refined by a factor, the error should decrease at a rate that is an expected power of that factor. In practice, since the exact solution is generally unavailable, manufactured solutions are frequently employed.\textsuperscript{10}

Code verification has been performed on computational physics codes associated with several physics disciplines, including fluid dynamics,\textsuperscript{11–14} solid mechanics,\textsuperscript{15} fluid–structure interaction,\textsuperscript{16} heat transfer in fluid–solid interaction,\textsuperscript{17} multiphase flow,\textsuperscript{18} radiation hydrodynamics,\textsuperscript{19} electrodynamics,\textsuperscript{20} and electromagnetism.\textsuperscript{21} Though not as common, code-verification techniques for hypersonic flow have been presented by Roy et al.,\textsuperscript{22} for a single-species perfect gas and by Gollan and Jacobs\textsuperscript{23} for a multi-species gas in thermal equilibrium.

In this paper, we discuss the code-verification techniques we have employed for SPARC. The most noteworthy contribution of this work is our approach to verifying hypersonic reacting flow in thermochemical nonequilibrium. Additionally, for flows without discontinuities, our techniques employ the more rigorous $L^\infty$-norm, of which we demonstrate the greater effectiveness when assessing spatial discretization. Our techniques employ manufactured and exact solutions; nonuniform meshes; and a method for verifying the thermochemical source term. As the scope of this paper is limited to code verification, subsequent instances of ‘verification’ are used to abbreviate ‘code verification’.

This paper is organized as follows. Section II describes the governing conservation, energy-exchange, and chemical-kinetics equations. Section III details our approach for verifying the spatial discretization of SPARC. Section IV presents our approach for verifying the thermochemical source term. Section V demonstrates the effectiveness of the verification techniques for the spatial discretization. Section VI demonstrates the effectiveness of the verification techniques for the thermochemical source term. Section VII provides conclusions and an outlook for future work.

## II. Governing Equations

In this paper, we consider hypersonic reacting flows in thermochemical nonequilibrium. We make the following approximations: (1) electronic energy is negligible, (2) vibrationally excited molecules can be characterized by a single vibrational temperature $T_v$, and (3) the translational and rotational temperatures are in thermal equilibrium: $T_t = T_r = T$.

With these approximations, we model the conservation of mass, momentum, and energy for a gas in thermochemical nonequilibrium:\textsuperscript{1,24}

$$\frac{\partial \mathbf{U}}{\partial t} + \nabla \cdot \mathbf{F}_c(\mathbf{U}) = -\nabla \cdot \mathbf{F}_p(\mathbf{U}) + \nabla \cdot \mathbf{F}_d(\mathbf{U}) + \mathbf{S}(\mathbf{U}),$$

where the conservative-variable state vector $\mathbf{U}$, convective flux $\mathbf{F}_c$, pressure flux $\mathbf{F}_p$, diffusive flux $\mathbf{F}_d$, and thermochemical source term $\mathbf{S}$ are

$$\mathbf{U} = \begin{bmatrix} \rho \\ \rho v \\ \rho E \\ \rho e_v \end{bmatrix}, \quad \mathbf{F}_c(\mathbf{U}) = \begin{bmatrix} \rho v^T \\ \rho v v^T \\ \rho E v^T \\ \rho e_v v^T \end{bmatrix}, \quad \mathbf{F}_p(\mathbf{U}) = \begin{bmatrix} 0 \\ \rho I \\ \rho v^T \\ 0 \end{bmatrix}, \quad \mathbf{F}_d(\mathbf{U}) = \begin{bmatrix} -\mathbf{J} \\ \tau \left(\mathbf{v} - \mathbf{q} - \dot{\mathbf{J}} \mathbf{h} \right)^T \\ -\mathbf{q} - \dot{\mathbf{J}} \mathbf{e}_v \end{bmatrix},$$

$$\mathbf{S}(\mathbf{U}) = \begin{bmatrix} \dot{\mathbf{w}} \\ 0 \\ 0 \\ Q_{t-v} + \mathbf{e}_v \mathbf{w} \end{bmatrix}.$$
The mixture vibrational energy per mass is

\[ e_v = \sum_{s=1}^{n_s} \frac{\rho_s}{\rho} e_{v_s}, \]

where \( e_v = \{e_{v_1}, \ldots, e_{v_{n_s}}\}^T \) is the vector of vibrational energies per mass of the species, such that

\[ e_{v_s} = \begin{cases} \sum_{m=1}^{n_{v_s}} e_{v_s,m}(T_v) & \text{for molecules,} \\ 0 & \text{for atoms,} \end{cases} \]

and

\[ e_{v_s,m}(T') = \frac{R}{M_s} \theta_{v_s,m} \exp \left( \frac{\theta_{v_s,m}}{T'} \right) - 1. \]

\( n_{v_s} \) is the number of vibrational modes of species \( s \) \( (n_{v_s} = 0 \) for atoms), and \( \theta_{v_s,m} \) is the characteristic vibrational temperature of mode \( m \) for species \( s \). \( Q_{t-v} \) is the translational–vibrational energy exchange.

The total energy per mixture mass is

\[ E = \frac{|v|^2}{2} + \sum_{s=1}^{n_s} \frac{\rho_s}{\rho} \left( c_{v_s} T + e_{v_s} + h^o_s \right). \]

c\( v_s \) is the specific heat at constant volume of species \( s \), which is the sum of the translational and rotational contributions. For molecules, \( c_{v_s} = \frac{5}{2} \frac{R}{M_s} \) and, for atoms, \( c_{v_s} = \frac{3}{2} \frac{R}{M_s} \). \( h^o_s \) is the formation enthalpy of species \( s \).

II.A. Diffusive-Term Modeling

We use Fick’s first law to model the diffusion flux of the species: \( J = -\rho D \nabla \rho \), where \( D = \text{diag} \{D_1, \ldots, D_{n_s}\} \) contains the effective diffusion coefficients of the species.

Assuming the flow is Newtonian and satisfies Stokes’ hypothesis, we model the viscous stress tensor as

\[ \tau = \mu \left( \nabla v + (\nabla v)^T \right) - \frac{2}{3} \mu \left( \nabla \cdot v \right) I, \]

where \( \mu \) is the dynamic viscosity.

To model the heat fluxes, we employ Fourier’s law: \( q = -\kappa \nabla T \) and \( q_v = -\kappa_v \nabla T_v \), where \( \kappa \) and \( \kappa_v \) are, respectively, the translational–rotational and vibrational heat conductivities of the mixture.

\( \mu \) and \( \kappa \) for the mixture are computed using Wilke’s mixing rule.

II.B. Translational–Vibrational Energy Exchange Modeling

The translational–vibrational energy exchange is computed using the Landau–Teller model:\(^{25}\)

\[ Q_{t-v} = \sum_{s=1}^{n_s} \rho_s \sum_{m=1}^{n_{v_s}} \frac{e_{v_s,m}(T) - e_{v_s,m}(T_v)}{\langle \tau_{s,m} \rangle}, \]

where \( \langle \tau_{s,m} \rangle \) is the translational–vibrational energy relaxation time for mode \( m \) of species \( s \).

To compute the relaxation time, we use the semi-empirical approach of Millikan and White,\(^ {26}\) which is extended to account for higher temperatures:\(^ {27,28}\)

\[ \langle \tau_{s,m} \rangle = \left( \sum_{s'=1}^{n_s} y_s \tau_{s,m,s'} \right)^{-1} + \left( N_A \sum_{s'=1}^{n_s} \rho_{s'/M_{s'}} \sigma_{v'} \sqrt{ \frac{8 R T}{\pi M_{s'}} } \right)^{-1}, \]

where

\[ y_s = \frac{\rho_s/M_s}{\sum_{s'=1}^{n_s} \rho_{s'/M_{s'}}}. \]
where

\[ \tau_{s,m,s'} = \frac{\exp \left[ a_{s,m,s'} \left(T^{-1/3} - b_{s,m,s'}\right) - 18.42 \right]}{p'} \]  \hspace{1cm} (3)

\( p' \) is the pressure in atmospheres. For many gases, \( a_{s,m,s'} \) and \( b_{s,m,s'} \) can be modeled by

\[ a_{s,m,s'} = 1.16 \times 10^{-3} \mu_{s,s'}^{1/2} \rho_{v,s,m}' \]
\[ b_{s,m,s'} = 0.015 \mu_{s,s'}^{1/4} \]  \hspace{1cm} (4)

where \( \mu_{s,s'} = \frac{M_s M_{s'}}{M_s + M_{s'}} \) is the reduced mass of species \( s \) and \( s' \). Additionally,

\[ \sigma_{v,s} = \sigma_{v,s} \left( \frac{50,000 \text{ K}}{T} \right)^2, \]

where \( N_A = 6.022140857 \times 10^{26} \text{ kmol}^{-1} \) is the Avogadro constant, \( \sigma_{v,s} \) is the collision-limiting vibrational cross section, and \( \sigma'_{v,s} \) is the collision-limiting vibrational cross section at 50,000 K.

II.C. Chemical-Kinetics Modeling

The density production rate for species \( s \) is modeled by

\[ \dot{w}_s = M_s \sum_{r=1}^{n_r} \left( \beta_{s,r} - \alpha_{s,r} \right) (R_{f_r} - R_{b_r}), \]  \hspace{1cm} (5)

where \( \alpha_{s,r} \) and \( \beta_{s,r} \) are, respectively, the stoichiometric coefficients for reactant and product species \( s \) in reaction \( r \). \( R_{f_r} \) and \( R_{b_r} \) are the forward and backward reaction rates for reaction \( r \).

The reaction rates are defined by

\[ R_{f_r} = \gamma k_{f_r} \prod_{s=1}^{n_s} \left( \frac{1}{\gamma M_s} \right)^{\alpha_{s,r}} \]  \hspace{1cm} (6)
\[ R_{b_r} = \gamma k_{b_r} \prod_{s=1}^{n_s} \left( \frac{1}{\gamma M_s} \right)^{\beta_{s,r}} \]  \hspace{1cm} (7)

such that, in (6) and (7), \( k_{f_r}, k_{b_r}, \) and \( \rho_s/M_s \) are expressed using the centimeter–gram–second system of units (CGS), \( R_{f_r} \) and \( R_{b_r} \) are expressed using the meter–kilogram–second system of units, and \( \gamma \equiv 1000 \text{ cm}^3 \text{ kmol}^{-1} \text{ mol} \) is the conversion factor. The forward and backward reaction rate coefficients \( k_{f_r} \) and \( k_{b_r} \) are modeled using the approach of Park;\(^{29}\)

\[ k_{f_r}(T_c) = C_f, T_c^{\eta_r} \exp \left( -\theta_r/T_c \right), \]
\[ k_{b_r}(T) = \frac{k_{f_r}(T)}{K_{e_r}(T)}, \]

where \( C_f \) and \( \eta_r \) are empirical parameters, and \( \theta_r \) is the activation energy of reaction \( r \), divided by the Boltzmann constant. \( T_c \) is the rate-controlling temperature, it is set to \( T_c = \sqrt{T \gamma} \) for dissociative reactions and \( T_c = T \) for exchange reactions. \( K_{e_r} \) is the equilibrium constant for reaction \( r \), modeled by

\[ K_{e_r}(T) = \exp \left[ A_{1r} \left( \frac{T}{10000} \right) + A_{2r} + A_{3r} \ln \left( \frac{10000}{T} \right) + A_{4r} \frac{10000}{T} + A_{5r} \left( \frac{10000}{T} \right)^2 \right], \]  \hspace{1cm} (8)

where \( A_{ir} \) are empirical curve-fit coefficients.

In SPARC, \( K_{e_r}(T) \) is limited to \([\exp(-81), \exp(81)]\), and, when computing the density production rates, \( T \) and \( T_c \) are increased to 500 K if they are less than 500 K.
This paper considers the five-species air model, which consists of $N_2$, $O_2$, NO, N, and O. These species can undergo the dissociation and exchange reactions listed in Table 1. Additional properties of the species and their reactions are listed in the Appendix.

### II.D. Gas Modeling

This paper considers the five-species air model, which consists of $N_2$, $O_2$, NO, N, and O. These species can undergo the dissociation and exchange reactions listed in Table 1. Additional properties of the species and their reactions are listed in the Appendix.

### III. Verification Techniques for Spatial Discretization

We begin our approach to code verification by measuring the spatial accuracy. To measure the spatial accuracy, we compare the solution to the discretized equations with the solution to the continuous equations. For each of the flow variables, we compute error norms and compare the rates at which the error norms decrease with respect to the rates at which the mesh size increases.

#### III.A. Spatial Accuracy

In a steady state, the governing system of partial differential equations (1) can be written generally as

$$r(U; \mu) = 0,$$

where $r$ is the residual vector, $U = U(x)$ is the state vector, and $\mu$ is the vector of parameters used to characterize the problem.

To solve (9) numerically, it must be discretized:

$$\tilde{r}(\tilde{U}; \mu) = 0,$$

where the $\tilde{r}$ is the residual of the discretized system of equations, and $\tilde{U}$ is the solution to the discretized equations.

For a locally $p^{th}$-order-accurate discretization, the discretization error is

$$e(x) = \tilde{U}(x) - U(x) = C(x)h^p(x) + O(h^{p+1}),$$

where $h$ provides a relative characterization, between meshes, of the cell sizes with respect to a single dimension. In this paper, $h$ is defined as a constant across the domain, such that the individual cell sizes may be non-uniform functions of $h$. Once the meshes are fine enough that the approximation is within the asymptotic region, $h^p(x) \ll h^{p(x)}$, then $e(x) \approx C(x)h^p(x)$. $C(x)$ is a function of derivative(s) of the state vector $U$ at $x$, and, in the asymptotic region, is approximately constant between meshes.

The observed accuracy can be computed using two meshes. For example, let the coarser mesh be characterized by $h$. The second mesh, if $q$-times as fine in each dimension as the first, is characterized by $h/q$. For each scalar field $\alpha(x)$ in $U(x)$ (e.g., $\alpha = \{ \rho_1, \ldots, \rho_n, u, v, w, T, T_e \}$), each mesh has a discretization error: $e^q_1(x) = C_\alpha(x)h^{p(x)}$ and $e^q_2(x) = C_\alpha(x)h^{p(x)}/q^{p(x)}$. $p(x)$ is computed by

$$\hat{p}(x) = \frac{\log|e^q_2(x)/e^q_1(x)|}{\log q} = \log_q |e^q_1(x)/e^q_2(x)|.$$

#### III.B. Solutions

Computing the spatial accuracy $\hat{p}$ in (11) requires computing errors $e$, which, in turn, require solutions $U$. Therefore, we employ exact and manufactured solutions.

<table>
<thead>
<tr>
<th>$r$</th>
<th>Reaction</th>
<th>Type of Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–5</td>
<td>$N_2 + M \rightarrow N + N + M$, $M = {N_2, O_2, NO, N, O}$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>6–10</td>
<td>$O_2 + M \rightarrow O + O + M$, $M = {N_2, O_2, NO, N, O}$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>11–15</td>
<td>$NO + M \rightarrow N + O + M$, $M = {N_2, O_2, NO, N, O}$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>16</td>
<td>$N_2 + O \rightarrow N + NO$</td>
<td>Exchange</td>
</tr>
<tr>
<td>17</td>
<td>$NO + O \rightarrow N + O_2$</td>
<td>Exchange</td>
</tr>
</tbody>
</table>

Table 1: Five-species air model: Reactions.
III.B.1. Exact Solutions

For limited cases, there exist exact solutions \( U_{\text{Exact}} \) to (9), which can be directly compared with the computed solutions \( \tilde{U} \) from (10) with negligible implementation effort. For codes such as SPARC, however, available exact solutions only span a small subset of the application space, so we require additional approaches to thoroughly test the capabilities of the code.

III.B.2. Manufactured Solutions

Manufactured solutions \( U_{\text{MS}} \) enable us to develop solutions that exercise the features we intend to test. Unless the manufactured solutions are exact solutions, they will not satisfy (9): \( r(U_{\text{MS}}; \mu) \neq 0 \). Therefore, a forcing term is added to (10) to account for the presence of the manufactured solutions:

\[
\tilde{r}(\tilde{U}; \mu) = r(U_{\text{MS}}; \mu). \tag{12}
\]

\( r(U_{\text{MS}}; \mu) \) in (12) is computed analytically since \( r \) and \( U_{\text{MS}} \) are known. Specifically, in SPARC, \( r(U_{\text{MS}}; \mu) \) is computed symbolically through the automatic differentiation tool Sacado.

Because the equations are differential and the discretization error is a function of derivatives of the state vector, the manufactured solutions should be smooth, continuously differentiable functions with generally nonzero derivatives. Additionally, for the approximation to be in the asymptotic region without requiring especially fine meshes, variations over the domain should not be large.

III.C. Norms

The global spatial accuracy \( p \) can be computed from a functional of the local spatial accuracy across the domain: \( p = f(\bar{p}(\mathbf{x})) \) (e.g., \( f(\bar{p}(\mathbf{x})) = \min_{\mathbf{x} \in \Omega} \bar{p}(\mathbf{x}) \)); however, this approach has two shortcomings: (1) for cell-centered schemes, none of the cell centroids of a coarser mesh coincide with those arising after mesh refinement, and (2) in regions where the errors vanish, the computed spatial accuracy is meaningless. Therefore, we use error norms to quantify the spatial accuracy:

\[
p = \log_q \left( \frac{\varepsilon_{\alpha_1}}{\varepsilon_{\alpha_2}} \right). \tag{13}
\]

We consider two norms in particular:

1. \( L^1 \)-norm:

\[
\varepsilon_{\alpha}^1 = \| \alpha(\mathbf{x}) - \tilde{\alpha}(\mathbf{x}) \|_1 = \int_\Omega |\alpha(\mathbf{x}) - \tilde{\alpha}(\mathbf{x})| d\Omega. \tag{14}
\]

The \( L^1 \)-norm enables us to compute the spatial accuracy based on the average error throughout the domain without significant contamination from localized deviations. Such localized deviations can arise from discontinuities, such as shocks, as well as from boundary conditions discretized with lower-order spatial accuracy than what is used for the domain interior.

2. \( L^\infty \)-norm:

\[
\varepsilon_{\alpha}^\infty = \| \alpha(\mathbf{x}) - \tilde{\alpha}(\mathbf{x}) \|_\infty = \max_{\mathbf{x} \in \Omega} |\alpha(\mathbf{x}) - \tilde{\alpha}(\mathbf{x})|. \tag{15}
\]

Unlike the \( L^1 \)-norm, the \( L^\infty \)-norm catches the aforementioned localized deviations by computing the maximum error throughout the domain. This is particularly useful when such deviations are unexpected.

For flows without discontinuities, the observed orders of accuracy computed by the \( L^1 \)-norm and \( L^\infty \)-norm should be the same. Some references use only the \( L^2 \)-norm, which may not detect localized deviations.
IV. Verification Techniques for Thermochemical Source Term

While measuring the spatial accuracy is an effective technique for assessing the discretization, it does not directly reveal errors in the coding of the source term \( S(\mathbf{U}) \) in (1). With manufactured solutions, for example, terms containing derivatives in (1) are evaluated numerically when computing \( \mathbf{r}(\mathbf{U}; \mu) \) in (12) and analytically when computing \( \mathbf{r}(\mathbf{U}_{MS}; \mu) \). The difference between \( \mathbf{r}(\mathbf{U}; \mu) \) and \( \mathbf{r}(\mathbf{U}_{MS}; \mu) \) due to the discretization error is manifested in \( \mathbf{U} - \mathbf{U}_{MS} \). The thermochemical source terms are similarly evaluated on both sides of (12); however, because the algebraic source-term evaluation does not depend on the spatial discretization, these evaluations use the same source code. Therefore, there are no differences in the evaluation on each side, and, as a result, errors in the source-term implementation are not detected.

To address this limitation, we independently developed a code to compute the source terms, specifically \( Q_{\text{I-v}}(\rho, T, T_v) \), \( e_v(\rho, T, T_v) \), and \( \mathbf{w}(\rho, T, T_v) \) in (1). We compute these terms for many values of \( \{\rho, T, T_v\} \) and compare with those obtained from \textsc{SPARC} for a single-cell mesh when initialized to those values with no velocity.

While it may be instinctive to dismiss this approach as a typically low-rigor code-to-code comparison, we clarify the distinctive and rigorous features.

1. This code is independently developed, using the same models and material properties expected to be employed by \textsc{SPARC} but taken directly from the original references. Alternatively, external software could be used, but, given the variety of published models and material properties, quantifying the agreement and, consequently, assessing the implementation becomes non-trivial.

2. Because the models and material properties are the same, when computing the difference in the source terms, the burden for success is reduced from what may typically be a few percent to near machine precision.

3. Whereas code-to-code comparison is typically employed for only a single or few operating conditions, this comparison is queried for thousands of conditions that span extreme ranges.

The effectiveness of these features in demonstrated in Section VI.

V. Spatial-Discretization Verification Results

\textsc{SPARC} employs a cell-centered finite-volume discretization. The simulations presented herein use the Steger–Warming flux-vector splitting scheme. The expectation is that \textsc{SPARC} is second-order accurate \((p = 2)\) for flows without discontinuities. Therefore, because the midpoint rule has a discretization error of \( O(h^2) \), we integrate \( \mathbf{r}(\mathbf{U}_{MS}; \mu) \) in (12) using the midpoint rule, without decreasing the order of accuracy. We additionally use approximations to compute the \( L^1 \)-norm in (14) and the \( L^\infty \)-norm in (15):

\[
\varepsilon^1_\alpha \approx \sum_{i=1}^n |\Omega_i| \left| \alpha(x_i) - \tilde{\alpha}(x_i) \right|,
\]

\[
\varepsilon^\infty_\alpha \approx \max_{1 \leq i \leq n} |\alpha(x_i) - \tilde{\alpha}(x_i)|,
\]

where \( x_i \) and \( \Omega_i \) are, respectively, the centroid and volume of cell \( i \).

Our verification of \textsc{SPARC} begins with the simplest tests, and, as these tests are satisfied, we add complexity to the subsequent tests. We begin by verifying single-species supersonic inviscid flow, ultimately increasing the complexity to multi-species hypersonic inviscid flow in thermochemical nonequilibrium.

For many of our two-dimensional manufactured solutions, we use the following solution structures, or subsets thereof:
\[ \rho_{N_2} (x, y) = \bar{\rho}_{N_2} \left[ 1 - \varepsilon \sin \left( \frac{5}{4} \pi x \right) \left( \sin \left( \pi y \right) + \cos \left( \pi y \right) \right) \right], \]
\[ \rho_{O_2} (x, y) = \bar{\rho}_{O_2} \left[ 1 + \varepsilon \sin \left( \frac{3}{4} \pi x \right) \left( \sin \left( \pi y \right) + \cos \left( \pi y \right) \right) \right], \]
\[ \rho_{NO}(x, y) = \bar{\rho}_{NO} \left[ 1 + \varepsilon \sin \left( \frac{1}{2} \pi x \right) \left( \sin \left( \pi y \right) \right) \right], \]
\[ \rho_{N} (x, y) = \bar{\rho}_{N} \left[ 1 + \varepsilon \sin \left( \frac{1}{4} \pi x \right) \left( \cos \left( \frac{1}{4} \pi y \right) \right) \right], \]
\[ \rho_{O} \ (x, y) = \bar{\rho}_{O} \left[ 1 + \varepsilon \sin \left( \pi x \right) \left( \sin \left( \pi y \right) + \cos \left( \frac{3}{4} \pi y \right) \right) \right], \]
\[ u \ (x, y) = \bar{u} \left[ 1 + \varepsilon \sin \left( \frac{1}{4} \pi x \right) \left( \sin \left( \pi y \right) + \cos \left( \pi y \right) \right) \right], \]
\[ v \ (x, y) = \bar{u} \left[ - \varepsilon \sin \left( \frac{3}{4} \pi x \right) \left( \sin \left( \pi y \right) \right) \right], \]
\[ T \ (x, y) = \bar{T} \left[ 1 + \varepsilon \sin \left( \frac{3}{4} \pi x \right) \left( \sin \left( \pi y \right) + \cos \left( \frac{3}{4} \pi y \right) \right) \right], \]
\[ T_v \ (x, y) = \bar{T_v} \left[ 1 + \varepsilon \sin \left( \frac{1}{4} \pi x \right) \left( \sin \left( \frac{1}{4} \pi y \right) + \cos \left( \frac{3}{4} \pi y \right) \right) \right]. \] (16)

These solutions are shown in Figure 1 for \((x, y) \in [0, 1] \times [0, 1]\). The inflow and outflow boundaries are located at \(x = 0\) and \(x = 1\). The velocity field ensures the flow is tangential to the slip-wall (tangent-flow) boundaries located at \(y = 0\) and \(y = 1\). 

![Figure 1: 2D manufactured solutions.](image-url)
V.A. Single-Species Inviscid Flow in Thermochemical Equilibrium

The first set of tests consists of a single species \( n_s = 1, \rho = \rho \) inviscid \( (F_d = 0) \) flow in thermochemical equilibrium \( (S = 0, \ T = T_v) \). For this type of flow, the reference velocity \( \bar{u} \) is determined from a reference Mach number \( \bar{M} \):

\[
\bar{u} = \bar{M} \sqrt{\gamma R \bar{T}},
\]

where \( R \) is the specific gas constant of air.

V.A.1. 1D Supersonic Flow using a Manufactured Solution

For this test, we simulate a simple, one-dimensional flow using manufactured solutions:

\[
\rho(x) = \bar{\rho} [1 - \epsilon \sin(\pi x)],
\]

\[
u(x) = \bar{\nu} [1 - \epsilon \sin(\pi x)],
\]

\[
T(x) = \bar{T} [1 + \epsilon \sin(\pi x)],
\]

with \( x \in [0, 1] \) m, \( \bar{\rho} = 1 \) kg/m\(^3\), \( \bar{M} = 2.5 \), \( \bar{T} = 300 \) K, and \( \epsilon = 0.05 \).

Upon solving (12), the observed order of accuracy \( p \) is computed from (13) for \( \alpha = \{\rho, u, T\} \). Five 1D meshes are used, consisting of 50, 100, 200, 400, and 800 elements.

Table 2 shows the observed accuracy from the original state of the code using the \( L^\infty \)-norm and \( L^1 \)-norm. The \( L^1 \)-norm indicates second-order accuracy \( (p = 2) \), whereas the \( L^\infty \)-norm indicates first-order accuracy \( (p = 1) \). This example demonstrates the usefulness of the \( L^\infty \)-norm. The \( L^1 \)-norm suggests the code, on average, is second-order accurate; however, the \( L^\infty \)-norm captures localized deviations in the accuracy. These deviations are due to the supersonic-inflow and supersonic-outflow boundary-condition implementations being only first-order accurate. For this case, the accuracy reduction is limited to the vicinity of the boundaries.

<table>
<thead>
<tr>
<th>Mesh</th>
<th>( L^\infty )-norm</th>
<th>( L^1 )-norm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \rho )</td>
<td>( u )</td>
</tr>
<tr>
<td>1–2</td>
<td>1.0008</td>
<td>1.0008</td>
</tr>
<tr>
<td>2–3</td>
<td>1.0002</td>
<td>1.0002</td>
</tr>
<tr>
<td>3–4</td>
<td>1.0001</td>
<td>1.0001</td>
</tr>
<tr>
<td>4–5</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

Table 2: 1D MMS, \( n_s = 1, T_v = T, \bar{w} = 0 \): Observed accuracy \( p \) from original BCs.

We corrected the two boundary-condition implementations to be second-order accurate, which is confirmed in Table 3. Additionally, Figures 2 and 3 show the two error norms for each of the flow variables, before and after correcting the boundary conditions. As shown in Figure 2, the maximum errors are reduced by orders of magnitude upon correcting the boundary conditions. Furthermore, Figure 3 shows that the correct boundary conditions reduce the average error by a factor of approximately three.

<table>
<thead>
<tr>
<th>Mesh</th>
<th>( L^\infty )-norm</th>
<th>( L^1 )-norm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \rho )</td>
<td>( u )</td>
</tr>
<tr>
<td>1–2</td>
<td>2.0313</td>
<td>2.0362</td>
</tr>
<tr>
<td>2–3</td>
<td>2.0157</td>
<td>2.0184</td>
</tr>
<tr>
<td>3–4</td>
<td>2.0079</td>
<td>2.0093</td>
</tr>
<tr>
<td>4–5</td>
<td>2.0040</td>
<td>2.0047</td>
</tr>
</tbody>
</table>

Table 3: 1D MMS, \( n_s = 1, T_v = T, \bar{w} = 0 \): Observed accuracy \( p \) from corrected BCs.
\[ \log_{10}(\varepsilon_{\infty}^{\alpha}/\bar{\alpha}), \alpha = \{\rho, u, T\} \]

\[ O(h) \quad O(h^2) \quad \rho, \text{original BCs} \quad u, \text{original BCs} \quad T, \text{original BCs} \quad \rho, \text{corrected BCs} \quad u, \text{corrected BCs} \quad T, \text{corrected BCs} \]

Figure 2: 1D MMS, \( n_s = 1, T_v = T, \dot{w} = 0 \): \( L^\infty \)-norms of the error.

\[ \log_{10}(\varepsilon_{1}^{\alpha}/\bar{\alpha}), \alpha = \{\rho, u, T\} \]

\[ O(h) \quad O(h^2) \quad \rho, \text{original BCs} \quad u, \text{original BCs} \quad T, \text{original BCs} \quad \rho, \text{corrected BCs} \quad u, \text{corrected BCs} \quad T, \text{corrected BCs} \]

Figure 3: 1D MMS, \( n_s = 1, T_v = T, \dot{w} = 0 \): \( L^1 \)-norms of the error.
V.A.2. 2D Supersonic Flow using a Manufactured Solution

This test increases the complexity of the first test by including variations along a second dimension. In addition to the supersonic-inflow and supersonic-outflow boundary conditions of the first test, the slip-wall boundary condition is exercised.

The manufactured solutions for this case for \( \alpha = \{ \rho, u, v, T \} \) are listed in (16) and shown in Figure 1. For \( \rho, \rho = \rho_N \), and \( \bar{\rho} = \bar{\rho}_N \) in (16) and in Figure 1. The domain is a square with \((x, y) \in [0, 1] \times [0, 1] \), and \( \bar{\rho} = 1 \) kg/m\(^3\), \( \bar{M} = 2.5 \), \( \bar{T} = 300 \) K, and \( \epsilon = 0.05 \).

Upon solving (12), the observed order of accuracy \( p \) is computed from (13). Five 2D meshes are used, consisting of \( 25 \times 25 \), \( 50 \times 50 \), \( 100 \times 100 \), \( 200 \times 200 \), and \( 400 \times 400 \) elements. These meshes are chosen to test the spatial accuracy of the discretization for nonuniform meshes. The \( 50 \times 50 \) mesh is shown in Figure 4.

![Figure 4: 2D MMS, \( n_s = 1 \), \( T_v = T \), \( \bar{w} = 0 \): Mesh with 50 × 50 elements.](image)

Table 4 shows the observed accuracy using the \( L^\infty \)-norm and \( L^1 \)-norm. Both norms indicate first-order accuracy \( (p = 1) \), despite the second-order-accuracy expectation. This inconsistency is due to the supersonic-inflow, supersonic-outflow, and slip-wall boundary-condition implementations being only first-order accurate. Unlike the first case, the implications of the first-order-accurate boundary conditions are global for this case.

<table>
<thead>
<tr>
<th>Mesh</th>
<th>( L^\infty )-norm</th>
<th>( L^1 )-norm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \rho )</td>
<td>( u )</td>
</tr>
<tr>
<td>1–2</td>
<td>0.9420 0.9409 0.9721 0.9628</td>
<td>1.0083 0.9838 0.9255 0.9861</td>
</tr>
<tr>
<td>2–3</td>
<td>0.9850 0.9902 0.9910 0.9874</td>
<td>1.0082 0.9980 0.9686 0.9957</td>
</tr>
<tr>
<td>3–4</td>
<td>0.9960 1.0002 0.9924 0.9952</td>
<td>1.0043 1.0008 0.9871 0.9985</td>
</tr>
<tr>
<td>4–5</td>
<td>0.9989 1.0009 0.9959 0.9984</td>
<td>1.0022 1.0008 0.9943 0.9995</td>
</tr>
</tbody>
</table>

Table 4: 2D MMS, \( n_s = 1 \), \( T_v = T \), \( \bar{w} = 0 \): Observed accuracy \( p \) from original BCs.

The corrected boundary-condition implementations are confirmed to be second-order accurate \( (p = 2) \) in Table 5. Figures 5 and 6 show the two error norms for each of the flow variables, before and after correcting the boundary conditions. For \( \alpha = v, \bar{\nu} = \bar{u} \). The correct boundary conditions reduce both the maximum and average error by orders of magnitude. For the subsequent results, we omit the \( L^1 \)-norm and consider only the corrected boundary conditions.
<table>
<thead>
<tr>
<th>Mesh</th>
<th>$\rho$</th>
<th>$u$</th>
<th>$v$</th>
<th>$T$</th>
<th>$\rho$</th>
<th>$u$</th>
<th>$v$</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–2</td>
<td>2.0623</td>
<td>1.9188</td>
<td>1.8174</td>
<td>1.8598</td>
<td>2.2440</td>
<td>2.1789</td>
<td>2.1000</td>
<td>2.1802</td>
</tr>
<tr>
<td>2–3</td>
<td>2.1304</td>
<td>1.9450</td>
<td>1.9221</td>
<td>1.9280</td>
<td>2.1701</td>
<td>2.1248</td>
<td>2.0745</td>
<td>2.1038</td>
</tr>
<tr>
<td>3–4</td>
<td>2.0902</td>
<td>1.9603</td>
<td>1.9671</td>
<td>1.9586</td>
<td>2.0788</td>
<td>2.0577</td>
<td>2.0436</td>
<td>2.0461</td>
</tr>
<tr>
<td>4–5</td>
<td>2.0128</td>
<td>1.9823</td>
<td>1.9860</td>
<td>1.9809</td>
<td>2.0303</td>
<td>2.0246</td>
<td>2.0230</td>
<td>2.0220</td>
</tr>
</tbody>
</table>

Table 5: 2D MMS, $n_s = 1$, $T_v = T$, $\dot{w} = 0$: Observed accuracy $p$ from corrected BCs.

Figure 5: 2D MMS, $n_s = 1$, $T_v = T$, $\dot{w} = 0$: $L^\infty$-norms of the error.

Figure 6: 2D MMS, $n_s = 1$, $T_v = T$, $\dot{w} = 0$: $L^1$-norms of the error.
V.A.3. 2D Supersonic Flow using an Exact Solution

This test exercises the same boundary conditions exercised in Section V.A.2, but for an exact solution. The exact solution is a steady, isentropic vortex, which we simulate in a quarter-annulus domain.\textsuperscript{31–33}

The exact solutions for this case are

\[
\rho(r) = \rho_i \left[ 1 + \frac{\gamma - 1}{2} M_i^2 \left( 1 - \left( \frac{r_i}{r} \right)^2 \right) \right]^{rac{1}{\gamma - 1}},
\]

\[u_r(r) = 0,\]

\[u_\theta(r) = a_i M_i \frac{r_i}{r},\]

\[T(r) = T_i \left[ 1 + \frac{\gamma - 1}{2} M_i^2 \left( 1 - \left( \frac{r_i}{r} \right)^2 \right) \right],\]

with \(\rho_i = 1, a_i = 1, M_i = 2.25,\) and \(T_i = 1/(\gamma R)\). The solutions are shown in Figure 7. \(r\) is the distance from the center of the full annulus, and the annulus is bounded between \(r_i = 1\) and \(r_o = 1.384\).

Upon solving (10), the observed order of accuracy \(p\) is computed from (13) for \(\alpha = \{\rho, u, v, T\}\). Six 2D meshes are used, consisting of \(32 \times 8, 64 \times 16, 128 \times 32, 256 \times 64, 512 \times 128,\) and \(1024 \times 256\) elements. The 64 \(\times\) 16 mesh is shown in Figure 8.
Figure 8: 2D Exact, \( n_s = 1, T_v = T, \dot{w} = 0 \): Mesh with 64 \( \times \) 16 elements.

Table 6 shows the observed accuracy, using the \( L^\infty \)-norm, which indicates second-order accuracy (\( p = 2 \)). Figure 9 shows the \( L^\infty \)-norm for each of the flow variables. For \( \alpha = u \) and \( \alpha = v \), \( u_i = a_i M_i \) and \( v_i = a_i M_i \).

<table>
<thead>
<tr>
<th>Mesh</th>
<th>( \rho )</th>
<th>( u )</th>
<th>( v )</th>
<th>( T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–2</td>
<td>1.9896</td>
<td>1.9119</td>
<td>1.9943</td>
<td>1.9699</td>
</tr>
<tr>
<td>2–3</td>
<td>1.9735</td>
<td>1.9589</td>
<td>2.0070</td>
<td>1.9979</td>
</tr>
<tr>
<td>3–4</td>
<td>1.9954</td>
<td>1.9760</td>
<td>2.0099</td>
<td>2.0076</td>
</tr>
<tr>
<td>4–5</td>
<td>1.9972</td>
<td>1.9879</td>
<td>2.0054</td>
<td>2.0044</td>
</tr>
<tr>
<td>5–6</td>
<td>1.9986</td>
<td>1.9940</td>
<td>2.0029</td>
<td>2.0025</td>
</tr>
</tbody>
</table>

Table 6: 2D Exact, \( n_s = 1, T_v = T, \dot{w} = 0 \): Observed accuracy \( p \) using \( L^\infty \)-norms of the error.

Figure 9: 2D Exact, \( n_s = 1, T_v = T, \dot{w} = 0 \): \( L^\infty \)-norms of the error.
V.A.4. 3D Supersonic Flow using a Manufactured Solution

For this test, we consider a three-dimensional flow. The manufactured solutions for this case are

\[
\begin{align*}
\rho(x, y, z) &= \bar{\rho}[1 - \epsilon \sin\left(\frac{5}{4}\pi x\right) \sin(\pi y) + \cos(\pi y)\sin(\pi z) + \cos(\pi z)], \\
u(x, y, z) &= \bar{\mu}[1 + \epsilon \sin\left(\frac{1}{4}\pi x\right) \sin(\pi y) + \cos(\pi y)\sin(\pi z) + \cos(\pi z)], \\
v(x, y, z) &= \bar{v}[ - \epsilon \sin\left(\frac{5}{4}\pi x\right) \sin(\pi y)\sin(\pi z) + \cos(\pi z)], \\
w(x, y, z) &= \bar{w}[ - \epsilon \sin\left(\frac{1}{4}\pi x\right) \sin(\pi y)\sin(\pi z) + \cos(\pi z)], \\
T(x, y, z) &= \bar{T}[1 + \epsilon \sin\left(\frac{5}{4}\pi x\right) \sin(\pi y)\sin(\pi z) + \cos(\pi z)],
\end{align*}
\]

with \((x, y, z) \in [0, 1] \times [0, 1] \times [0, 1]\), and \(\bar{\rho} = 1 \text{ kg/m}^3\), \(\bar{M} = 2.5\), \(\bar{T} = 300 \text{ K}\), and \(\epsilon = 0.05\).

Upon solving (12), the observed order of accuracy \(p\) is computed from (13) for \(\alpha = \{\rho, u, v, w, T\}\). Five 3D meshes are used, consisting of \(25 \times 25 \times 25\), \(50 \times 50 \times 50\), \(100 \times 100 \times 100\), \(200 \times 200 \times 200\), and \(400 \times 400 \times 400\) elements. These meshes are chosen to test the spatial accuracy of the discretization for nonuniform meshes. The \(50 \times 50 \times 50\) mesh is shown in Figure 10.

![Figure 10: 3D MMS, \(n_s = 1\), \(T_v = T\), \(w_0 = 0\): Mesh with \(50 \times 50 \times 50\) elements.](image)

Table 7 shows the observed accuracy, using the \(L^\infty\)-norm, which indicates second-order accuracy \((p = 2)\). Figure 11 shows the \(L^\infty\)-norm for each of the flow variables. For \(\alpha = v\) and \(\alpha = w\), \(v_0 = u_0\) and \(w_0 = u_0\).
Table 7: 3D MMS, $n_s = 1$, $T_v = T$, $\mathbf{w} = \mathbf{0}$: Observed accuracy $p$ using $L^\infty$-norms of the error.

<table>
<thead>
<tr>
<th>Mesh</th>
<th>$\rho$</th>
<th>$u$</th>
<th>$v$</th>
<th>$w$</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–2</td>
<td>2.0849</td>
<td>1.8731</td>
<td>1.9841</td>
<td>1.7039</td>
<td>1.9404</td>
</tr>
<tr>
<td>2–3</td>
<td>2.1406</td>
<td>1.9923</td>
<td>1.9295</td>
<td>1.8621</td>
<td>1.9774</td>
</tr>
<tr>
<td>3–4</td>
<td>2.0990</td>
<td>2.0115</td>
<td>1.9623</td>
<td>1.9349</td>
<td>1.9922</td>
</tr>
<tr>
<td>4–5</td>
<td>2.0585</td>
<td>2.0100</td>
<td>1.9820</td>
<td>1.9571</td>
<td>1.9964</td>
</tr>
</tbody>
</table>

Figure 11: 3D MMS, $n_s = 1$, $T_v = T$, $\mathbf{w} = \mathbf{0}$: $L^\infty$-norms of the error.

V.B. Five-Species Inviscid Flow in Chemical Nonequilibrium

This set of tests uses the five-species air model ($n_s = 5$, $\rho = \{\rho_{N_2}, \rho_{O_2}, \rho_{NO}, \rho_N, \rho_O\}$) mentioned in Section II.D. The flow is inviscid ($\mathbf{F}_d = \mathbf{0}$) and in chemical nonequilibrium ($\mathbf{w} \neq \mathbf{0}$). For this type of flow, the reference velocity $\bar{u}$ is determined from a reference Mach number $\bar{M}$:

$$\bar{u} = \bar{M} \sqrt{\gamma \left( \sum_{s=1}^{n_s} \frac{\rho_s \bar{R}}{\rho s} \right) \bar{T}}.$$

While these tests do not directly test the thermochemical-source-term implementation (as described in Section IV), they do test the coupling of the source term with the differential terms, as well as the spatial discretizations of multiple species and temperatures.

V.B.1. 2D Supersonic Flow in Thermal Equilibrium using a Manufactured Solution

For this test, the flow is in thermal equilibrium ($T = T_v$). The manufactured solutions for this case for $\alpha = \{\rho_{N_2}, \rho_{O_2}, \rho_{NO}, \rho_N, \rho_O, u, v, T\}$ are listed in (16) and shown in Figure 1.

The domain is a square with $(x, y) \in [0, 1] \times [0, 1]$, and $\bar{\rho}_{N_2} = 0.77$ kg/m$^3$, $\bar{\rho}_{O_2} = 0.20$ kg/m$^3$, $\bar{\rho}_{NO} = 0.01$ kg/m$^3$, $\bar{\rho}_N = 0.01$ kg/m$^3$, $\bar{\rho}_O = 0.01$ kg/m$^3$, $\bar{M} = 2.5$, $\bar{T} = 3500$ K and $\epsilon = 0.05$.

Upon solving (12), the observed order of accuracy $p$ is computed from (13) for $\alpha = \{\rho_{N_2}, \rho_{O_2}, \rho_{NO}, \rho_N, \rho_O, u, v, T\}$. Seven 2D meshes are used, consisting of $25 \times 25$, $50 \times 50$, $100 \times 100$, $200 \times 200$, $400 \times 400$, $800 \times 800$, and $1600 \times 1600$ elements. These meshes are the same nonuniform meshes as those used in Section V.A.2.

Table 8 shows the observed accuracy, using the $L^\infty$-norm, which indicates second-order accuracy ($p = 2$). Figure 12 shows the $L^\infty$-norm for each of the flow variables. For $\alpha = v$, $\bar{v} = \bar{u}$. 
Table 8: 2D MMS, \( n_s = 5 \), \( T_v = T \), \( \dot{w} \neq 0 \): Observed accuracy \( p \) using \( L^\infty \)-norms of the error.

<table>
<thead>
<tr>
<th>Mesh</th>
<th>( \rho_{N_2} )</th>
<th>( \rho_{O_2} )</th>
<th>( \rho_{NO} )</th>
<th>( \rho_N )</th>
<th>( \rho_O )</th>
<th>( u )</th>
<th>( v )</th>
<th>( T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–2</td>
<td>2.0608</td>
<td>2.1382</td>
<td>2.0698</td>
<td>2.0644</td>
<td>2.1885</td>
<td>1.8425</td>
<td>1.8289</td>
<td>1.7351</td>
</tr>
<tr>
<td>2–3</td>
<td>2.1161</td>
<td>2.1219</td>
<td>2.1127</td>
<td>2.1072</td>
<td>2.1697</td>
<td>1.8875</td>
<td>1.9220</td>
<td>1.7923</td>
</tr>
<tr>
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<td>2.0798</td>
<td>2.0813</td>
<td>1.8555</td>
<td>2.0754</td>
<td>2.0971</td>
<td>1.9200</td>
<td>1.9686</td>
<td>1.8525</td>
</tr>
<tr>
<td>4–5</td>
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<td>2.0806</td>
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<td>1.9871</td>
<td>1.9079</td>
</tr>
<tr>
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<td>2.0243</td>
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<td>1.9485</td>
</tr>
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<td>2.0318</td>
<td>1.9865</td>
<td>1.9969</td>
<td>1.9737</td>
</tr>
</tbody>
</table>

Figure 12: 2D MMS, \( n_s = 5 \), \( T_v = T \), \( \dot{w} \neq 0 \): \( L^\infty \)-norms of the error.
V.B.2. 2D Hypersonic Flow in Thermal Nonequilibrium using a Manufactured Solution

For this test, the flow is in thermal nonequilibrium \((T \neq T_v)\). The manufactured solutions for this case for \(\alpha = \{\rho_{N_2}, \rho_{O_2}, \rho_{NO}, \rho_N, \rho_O, u, v, T, T_v\}\) are listed in (16) and shown in Figure 1.

The domain is a square with \((x, y) \in [0, 1] \times [0, 1]\), and \(\bar{\rho}_{N_2} = 0.0077\) kg/m\(^3\), \(\bar{\rho}_{O_2} = 0.0020\) kg/m\(^3\), \(\bar{\rho}_{NO} = 0.0001\) kg/m\(^3\), \(\bar{\rho}_N = 0.0001\) kg/m\(^3\), \(\bar{\rho}_O = 0.0001\) kg/m\(^3\), \(M = 8\), \(\bar{T} = 5000\) K, \(T_v = 1000\) K, and \(\epsilon = 0.05\).

Upon solving (12), the observed order of accuracy \(p\) is computed from (13) for \(\alpha = \{\rho_{N_2}, \rho_{O_2}, \rho_{NO}, \rho_N, \rho_O, u, v, T, T_v\}\). Seven 2D meshes are used, consisting of \(25 \times 25, 50 \times 50, 100 \times 100, 200 \times 200, 400 \times 400, 800 \times 800,\) and \(1600 \times 1600\) elements. These meshes are the same nonuniform meshes as those used in Section V.A.2.

Table 9 shows the observed accuracy, using the \(L^\infty\)-norm, which indicates second-order accuracy \((p = 2)\). Figure 13 shows the \(L^\infty\)-norm for each of the flow variables. For \(\alpha = v, \bar{v} = \bar{u}\).

<table>
<thead>
<tr>
<th>Mesh</th>
<th>(\rho_{N_2})</th>
<th>(\rho_{O_2})</th>
<th>(\rho_{NO})</th>
<th>(\rho_N)</th>
<th>(\rho_O)</th>
<th>(u)</th>
<th>(v)</th>
<th>(T)</th>
<th>(T_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–2</td>
<td>1.5659</td>
<td>1.6370</td>
<td>1.6555</td>
<td>1.5846</td>
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<td>1.7337</td>
<td>1.7814</td>
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<td></td>
</tr>
<tr>
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<td>1.8819</td>
<td>1.8916</td>
<td>1.8701</td>
<td>1.8768</td>
<td>1.9150</td>
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</tr>
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Table 9: 2D MMS, \(n_s = 5\), \(T_v \neq T\), \(\vec{w} \neq 0\): Observed accuracy \(p\) using \(L^\infty\)-norms of the error.

![Figure 13: 2D MMS, \(n_s = 5\), \(T_v \neq T\), \(\vec{w} \neq 0\): \(L^\infty\)-norms of the error.](image)

VI. Thermochemical-Source-Term Verification Results

To assess the correctness of the thermochemical-source-term implementation, we query SPARC and the independent code described in Section IV to compute \(Q_t\), \(e_v\), \(\bar{e}_v\), and \(\bar{w}\) in (1). We generate 100,000 Latin hypercube samples using the ranges and spacings listed in Table 10.

For each of the queries, we compute a symmetric relative difference, defined by

\[
\delta_\beta = 2 \left| \frac{\beta_{\text{SPARC}} - \beta'}{\beta_{\text{SPARC}} + \beta'} \right|, \tag{17}
\]

where \(\beta = \{Q_{t-v}, e_{N_2}, e_{O_2}, e_{NO}, w_{N_2}, w_{O_2}, w_{NO}, w_N, w_O\}\), and the prime denotes computation by the independent code.
Table 10: $S(U), n_s = 5, T_v \neq T, \dot{w} \neq 0$: Ranges and spacings for Latin hypercube samples of $\rho, T, T_v$.

Figures 14–16 show the distributions of the absolute values of the translational–vibrational energy exchange $Q_{t-v}$, the vibrational energies per mass $e_v$, and the absolute values of the density production rates $\dot{w}$, as computed from the independent code for the 100,000 simulations. Furthermore, since $Q_{t-v}$ and $\dot{w}$ can be non-positive, their ranges are listed in Table 11. All of these values vary drastically in magnitude, and, with the exception of $e_v$, in sign.

Figure 14: $S(U), n_s = 5, T_v \neq T, \dot{w} \neq 0$: Absolute value of the translational–vibrational energy exchange $Q_{t-v}$.

Table 11: $S(U), n_s = 5, T_v \neq T, \dot{w} \neq 0$: Ranges for $Q_{t-v}$ and $\dot{w}$ from simulations.

Figures 17a, 18a, 18c, and 18e show the nonzero relative differences (17) in $Q_{t-v}$ and $e_v$. As mentioned in Section IV, the relative differences are expected to be near machine precision; however, this is clearly not the case. As shown in Figure 17a, for approximately 8.8% of the simulations, $\delta_{Q_{t-v}}$ is greater than 10%, and, for 29% of the simulations, $\delta_{Q_{t-v}}$ is greater than 1%. Additionally, as shown in Figures 18a, 18c, and 18e, although $\delta_{e_v}$ is near machine precision for most of the simulations, $\delta_{e_v}$ is greater than 100% for a few
Figure 15: $S(U), n_s = 5, T_v \neq T, \mathbf{w} \neq 0$: Vibrational energies per mass $e_v$. 
Figure 16: \( S(U), n_s = 5, T_v \neq T, \dot{w} \neq 0 \): Absolute values of the density production rates \( \dot{w} \).
of the simulations.

These high relative differences were due to two causes.

1. The lookup table used by SPARC contained incorrect values for the vibrational constants used in (3) for $N_2$ and $O_2$ when the colliding species is NO. These incorrect values introduced an error in $Q_{t-v}$ for all simulations.

2. The convergence criteria specified in the implementation of Newton’s method used to compute $T_v$ from $\rho e_v$ was loose. Though sufficient for most values of $T_v$, these criteria prove unsuitable for low values. These criteria introduced errors in $Q_{t-v}$ and $e_v$ for a few simulations. For a converged, steady problem, however, the original convergence criteria is not expected to affect the final solution.

Upon correcting the lookup-table values and tightening the convergence criteria, we reran the SPARC simulations and recomputed $\delta Q_{t-v}$ and $\delta e_v$, the nonzero values of which are shown in Figures 17b, 18b, 18d, and 18f. These results are consistent with our expectations, as all $\delta Q_{t-v}$ values are less than $10^{-10}$, and all $\delta e_v$ values are less than $10^{-14}$. The twenty-eight $\delta Q_{t-v}$ values greater than $10^{-12}$ occur when $T$ and $T_v$ have a relative difference of less than 0.2%. As a result, in the numerator of (2), $e_{v,s,m}(T)$ and $e_{v,s,m}(T_v)$ share many of the leading digits; therefore, precision is lost when computing their difference.

To determine the impact of these modifications, we reran a high enthalpy (20 MJ/kg), hypersonic, laminar double-cone flow case, where we observed up to a 1.4% and 2.7% change in the pressure and heat flux, respectively, on the surface of the body.

Finally, Figure 19 plots the nonzero relative differences in $\dot{w}$. These results are consistent with our expectations, as all $\delta \dot{w}$ values are less than $10^{-9}$. Of the 100,000 simulations, 0.085% have $\delta \dot{w}$ values greater than $10^{-12}$. These slightly elevated differences are a result of the precision loss that can occur from subtraction in 5.
Figure 18: $S(U)$, $n_s = 5$, $T_v \neq T$, $\dot{w} \neq 0$: Relative differences in the vibrational energies per mass $e_v$, using the original convergence criteria (a, c, e), and the tighter convergence criteria (b, d, f).
Figure 19: $S(U)$, $n_s = 5$, $T_v \neq T$, $\dot{w} \neq 0$: Relative differences in the density production rates $\dot{w}$. 
VII. Conclusions

The study of hypersonic flows and their underlying aerothermochemical reactions is particularly important in the design and analysis of vehicles exiting and reentering Earth’s atmosphere. In this paper, we presented our code-verification techniques for hypersonic reacting flow in thermochemical nonequilibrium, as well as their deployment in the Sandia Parallel Aerodynamics and Reentry Code (SPARC). These techniques enabled us to detect and correct multiple implementation shortcomings.

While the scope of this paper has been limited to flows in vibrational nonequilibrium with five species that undergo dissociation and exchange reactions, these techniques could be analogously extended to address more complex flows in rotational and electronic nonequilibrium that contain additional species capable of undergoing ionization reactions.

Appendix: Five-Species Air Model Properties

The molecular weights $M_s$ and formation enthalpies $h^0_{o,s}$ for the five species are tabulated in Table 12.

<table>
<thead>
<tr>
<th>$s$</th>
<th>Species</th>
<th>$M_s$ [g/mol]</th>
<th>$h^0_{o,s}$, 0 K [J/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N$_2$</td>
<td>28.016</td>
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<tr>
<td>2</td>
<td>O$_2$</td>
<td>32.000</td>
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<tr>
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<tr>
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<td>N</td>
<td>14.008</td>
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<td>O</td>
<td>16.000</td>
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Table 12: Five-species air model: Molecular weights $M_s$ and formation enthalpies $h^0_{o,s}$.

The characteristic vibrational temperatures $\theta_{v,s,m}^{34}$ and collision-limiting cross sections at 50,000 K $\sigma'_{v,s}^{27,28}$ are tabulated in Table 13.

<table>
<thead>
<tr>
<th>$s$</th>
<th>Species</th>
<th>$n_{v,s}$</th>
<th>$\theta_{v,s,m}$ [K]</th>
<th>$\sigma'_{v,s}$ [m$^2$]</th>
</tr>
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<tbody>
<tr>
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<td>O$_2$</td>
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<td>2239</td>
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<td>2817</td>
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</table>

Table 13: Five-species air model: Characteristic vibrational temperatures $\theta_{v,s,m}^{34}$ and collision-limiting cross sections at 50,000 K $\sigma'_{v,s}^{27,28}$.

The vibrational constants $a_{s,m,s'}$ and $b_{s,m,s'}$ for Equation (3), associated with the reactions listed in Table 1, are listed in Table 14.

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<th>O$_2$</th>
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<td>Equation (4)</td>
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<td>Equation (4)</td>
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<td>72.4</td>
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Table 14: Five-species air model: Vibrational constants $a_{s,m,s'}$ and $b_{s,m,s'}$.27
The stoichiometric coefficients $\alpha_{s,r}$ and $\beta_{s,r}$ associated with the reactions listed in Table 1 are listed in Table 15.

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Table 15: Five-species air model: Stoichiometric coefficients $\alpha_{s,r}$ and $\beta_{s,r}$.

The reaction-rate-coefficient dependencies $C_{f_r}$, $\eta_r$, and $\theta_r$ associated with the reactions listed in Table 1 are listed in Table 16.

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<th>$\eta_r$</th>
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Table 16: Five-species air model: Reaction-rate-coefficient dependencies $C_{f_r}$, $\eta_r$, and $\theta_r$.²⁹
The equilibrium-constant coefficients, for Equation (8), associated with the reactions listed in Table 1 are listed in Table 17.

<table>
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<th>$r$</th>
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<th>$A_4$</th>
<th>$A_5$</th>
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<td>6–10</td>
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Table 17: Five-species air model: Equilibrium-constant coefficients $A_1$, $A_2$, $A_3$, $A_4$, and $A_5$.$^{29}$

Acknowledgments

The authors thank Derek Dinzl, Travis Fisher, Micah Howard, and Ross Wagnild, for their valuable assistance with SPARC and the underlying models and properties. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA-0003525.

References


