Nonequilibrium Flow Computations.
I. An Analysis of Numerical Formulations of
Conservation Laws*

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Modern numerical techniques employing properties of flux Jacobian matrices are extended to general, nonequilibrium flows. Generalizations of the Beam–Warming scheme, Steger–Warming, and van Leer flux-vector splittings, and Roe's approximate Riemann solver are presented for 3-dimensional, time-varying grids. The analysis is based on a thermodynamic model that includes the most general thermal and chemical nonequilibrium flow of an arbitrary gas. Various special cases are also discussed. © 1989 Academic Press, Inc.

INTRODUCTION

The design of the next generation of advanced space transportation systems such as the National Aerospace Plane (NASP) and the Aeroassisted Orbital Transfer Vehicle (AOTV) requires detailed flow computations. The combination of high speed and low density result in the departure of air from a perfect gas due to the excitation of internal modes, dissociation, and ionization. At sufficiently low altitudes (i.e., sufficiently high density), the rate of collisions between particles is high enough so that all these processes are at equilibrium with their respective reverse processes. The only modification in the formulation of the equations is the replacement of the perfect gas law by a general, equilibrium gas law [1]. The corresponding extensions of the numerical algorithms are found in Ref. [2]. There is a significant altitude (i.e., density) range in which the mean free path between collisions is sufficiently small for the continuum approximation to be valid, but the collision rate is not large enough to maintain thermal or chemical equilibrium. This series of papers is devoted to the numerical computation of general, nonequilibrium flows.

Most modern techniques used in CFD utilize the properties of flux Jacobian matrices for the treatment of the inviscid terms in the numerical solution of conservation laws. For central difference methods, the Beam–Warming scheme [3] requires the true flux Jacobian matrices, and their eigenvalues and eigenvectors are needed for the diagonal algorithms [4]. Most upwind methods, such as the

Steger–Warming flux-vector splitting [5], the van Leer flux-vector splitting [6], and the Roe approximate Riemann solver [7], all utilize the properties of the flux Jacobian matrix. Their original derivations relied on the algebraic simplicity of the perfect gas law. The purpose of this paper is to extend these methods to non-equilibrium flows. Only those aspects of the schemes affected by the nonequilibrium assumption are covered. Other investigations [8–10] have been limited to the treatment of flux Jacobian matrices for chemical nonequilibrium.

We first discuss the thermodynamic model as it relates to the formulation of the inviscid flux. It is general enough to include any type of nonequilibrium flow in an arbitrary gas. The exact flux Jacobian matrices, their eigenvalues, and eigenvectors are then presented. This is followed by the generalizations of Steger–Warming and van Leer flux-vector splittings, and the generalization of the Roe average used in Roe's approximate Riemann solver. Finally, we discuss the formulations for several special cases including different treatments of thermal nonequilibrium and chemical nonequilibrium. The analyses are presented for 3-dimensional flow with time-varying grids.

THERMODYNAMIC MODEL

We consider a gas of mixture of chemical species which may include neutral or ionized atoms or molecules, or free electrons. For each species, statistical mechanics provides the molecular basis for deriving the macroscopic equations of state, which relate the internal energy and pressure to the density and possibly several temperatures. To form the fundamental variable, the partition function, one first requires the quantized energy levels and degeneracies derived from quantum mechanics. These are given in principle by the eigenvalues of the Schrödinger equation. In practice, they can only be determined approximately under some assumptions, and with the aid of experimental data.

A given energy level can be characterized by different types of degrees of freedom. Free electrons only have translational degrees of freedom. Atoms also possess electronic and nuclear degrees of freedom. Molecules have additionally vibrational and rotational degrees of freedom. A thermodynamic model is based on the splitting of the energy level into several microscopic modes, each characterized by one or more types of degrees of freedom. The physical conditions determine the extent to which such a splitting is valid. The macroscopic properties also require the distribution of the species over the energy levels. This is given by the Maxwell–Boltzmann distribution characterized by a single temperature if the system is in thermodynamic equilibrium. (Note that we do not attempt to deal with quantum statistics here.) The phenomena we are studying involve thermal and chemical nonequilibrium processes which are not strictly describable by equilibrium statistical mechanics. Nevertheless, these phenomena ordinarily involve systems in what is called *local equilibrium*. This means we assume that at any instant, in the neighborhood of any point in space, the energy level can be expressed as a sum of independent energy modes, where the

distribution of species over each mode can be approximated by a Maxwell–Boltzmann distribution corresponding to some temperature defined for that mode.

For most gasdynamic applications, the nuclear state is rarely altered. Thus, we shall not consider any contribution to the internal energy from the nuclear degrees of freedom in our model. Under most conditions, we can also assume that the gas mixture consists of weakly interacting particles. The splitting of each energy level into a translational mode and an internal structure mode is then completely appropriate. From a macroscopic point of view, this is equivalent to stating that the species internal energy per unit mass ϵ_s is the sum of the *average* translational energy of random thermal motion, ϵ_s^{tran}, and the *average* energy of the internal structure, ϵ_s^{int}. Here the subscript s denotes any particular species in the mixture, whether it is a neutral or ionized atom or molecule, or a free electron. A superscript denotes a macroscopic mode of energy. This splitting leads to the thermally perfect gas law for each species. Specifically, the translational energy is proportional to the translational temperature T_s, and is given by

$$\epsilon_s^{\text{tran}} = \tfrac{3}{2} R_s T_s, \tag{1}$$

where $R_s = \hat{R}/\hat{M}_s$, $\hat{R}$ is the universal gas constant, and $\hat{M}_s$ is the molar mass of species s. Also, the species pressure p_s is given by

$$p_s = \rho_s R_s T_s, \tag{2}$$

where the species density ρ_s is the mass of species s per unit volume.

At this stage, ϵ_s^{int} consists of the internal energy from electronic excitation for atoms, and the *combined* energy of vibration, rotation, and electronic excitation for molecules. To a somewhat poorer approximation, ϵ_s^{int} for molecules can be split into the electronic excitation energy and the combined energy of vibration and rotation. In a further approximation, the latter can be split into separate vibrational and rotational energies. This leads to the rigid-rotator, harmonic-oscillator model and other models with anharmonic corrections. Each macroscopic energy mode may be characterized by a separate temperature or several modes that are approximately in equilibrium with each other could be characterized by a common temperature. One may consult the book by Herzberg [11] or other textbooks on statistical mechanics for the calculation of the internal energy for each mode. It is important to point out that the splitting of ϵ_s^{int} for molecules into separate macroscopic modes cannot be justified at higher temperatures. Rotation produces a centrifugal force that affects the vibration, while vibration changes the moment of inertia that affects the rotation. The centrifugal force and the vibrational frequency also vary, with the electronic state because of different electronic configurations. Thus, the splitting may cause very large errors in calculating the internal energy at very high temperatures [12]. Recently, Jaffe [13] has proposed a more rigorous equilibrium thermodynamic model for diatomic molecules. In his model, for each electronic state, and a given rotational quantum number, one determines an

effective intermolecular potential from which one calculates the allowed energy levels below the potential barrier. The maximum rotational quantum number for each electronic state is that for which the effective intermolecular potential first becomes completely repulsive. ϵ_s^{int} is obtained by summing over these electronic-rotational-vibrational energy levels for all allowed vibrational and rotational quantum numbers and over all known electronic states. We have modified his model for obtaining the energy levels and have written a general computer program for computing the internal energy [1, 12]. Internal energies for many species, based on a simpler thermodynamic model, have been tabulated in the JANAF tables [14] for temperature below 6000 K. While their results are in agreement with ours in this temperature range, the use of the JANAF model would result in significant differences with our calculations at higher temperatures. Although the code operates at a speed of 170 Mflops on a CRAY 2 computer, the computation is rather tedious and cumbersome, and it may involve summing over 20,000 to more than 50,000 energy levels for each diatomic species. Thus, for practical purposes, we also provide vectorizable, linear search, cubic spline interpolations. Typically, for interpolations from a data base of 100 K intervals, the maximum error is less than 0.001% for all the air species except O and N^+, for which the maximum error is less than 0.01% [12]. Jaffe [13] has also proposed a nonequilibrium thermo-dynamic model in which the electronic-rotational-vibrational energy level is split into an electronic mode, a rotational mode, a vibrational mode, and an interaction mode. The electronic and vibrational modes are characterized by a vibrational temperature, the rotational mode is characterized by a rotational temperature, and the interaction mode can be characterized by either the vibrational or rotational temperature. Because of the strong interaction between modes, we believe that this energy level should not be split, but should be characterized by a single internal mode temperature for each species.

In addition to enabling us to determine accurate species internal energies, the thermodynamic model is also needed to determine the rates of energy transfer between different modes, as well as chemical rate constants and transport coefficients. The choice of an appropriate model is therefore a difficult problem. In this paper, we do not attempt to judge which model should be used. Instead we formulate our algorithms as generally as possible so that they could include all possible models, including those that we question.

We restrict our analysis to mixtures of chemical species in which all the heavy particles (i.e., atoms and molecules) are close enough in mass that their trans-lational energies can always be characterized by a single translational temperature T. Since the mass of the electron is so much smaller than those of the heavy particles, the translational energy of free electrons could be characterized by a separate electron temperature T_e. When this occurs, we will use the subscript s' to denote any heavy particle, and the subscript e to denote the free electron. With this notation we can write

$$T_{s'} = T \qquad\qquad (3)$$

for all s'. Under our assumption of a mixture of thermally perfect gases, the pressure p is given as

$$p = \sum_{s'} \rho_{s'} R_{s'} T + \rho_e R_e T_e. \tag{4}$$

We note that the thermally perfect gas assumption may break down at sufficiently high temperatures due to the large orbits associated with high electronic states, or at sufficiently high densities. The assumption is also not strictly true for the charged species, due to the long range nature of the electric field.

Under the assumptions of our model, ϵ_s can in general be expressed as

$$\epsilon_s = \epsilon_s^t(T) + \epsilon_s^e(T_e) + \epsilon_s^i. \tag{5}$$

Here ϵ_s^t is defined to be the sum of ϵ_s^{tran} and the part of ϵ_s^{int} that can be characterized by the translational temperature T. ϵ_s^e is the part of ϵ_s^{int} that can be characterized by the electron temperature T_e. ϵ_s^i is the remaining part of ϵ_s^{int} not in equilibrium with either T or T_e. In practice, ϵ_s^i is characterized by a temperature T_s^i, or possibly several such temperatures. Note the distinction between ϵ_s^t and ϵ_s^{tran}, and also ϵ_s^i and ϵ_s^{int}. In order to obtain simple additive relations for the internal energies of the mixture (see Eqs. (8) and (9)), we have included the energy of formation from a set of elemental species in the definition of ϵ_s^t. Also, the arbitrary constant in the definition of ϵ_s must be determined in terms of the constants chosen for the elemental species. For the free electron, we obtain simply

$$\epsilon_s^t = \epsilon_e^i = 0 \qquad \text{and} \qquad \epsilon_e^e = \tfrac{3}{2} R_e T_e. \tag{6}$$

For the heavy particles, the exact division of the energies in Eq. (5) depends on the choice of models. For example, $\epsilon_{s'}^e$ could be the energy of the bound electrons, and $\epsilon_{s'}^i$ the energy in the vibrational modes, while the energy in the rotational mode would be included in $\epsilon_{s'}^t$. The three temperature model used by Park [15] and Lee [16] is one such example, where they considered the special case in which the vibrational energy of all the diatomic species are characterized by the same vibrational temperature. The model used by Candler and MacCormack [17] is another special case in which $\epsilon_{s'}^e = 0$ for all species, $\epsilon_{s'}^i = 0$ for the monatomic species, and $\epsilon_{s'}^i$ for the diatomic species contains the vibrational energy of the ground state only. At higher temperatures, where the splitting of ϵ_s^{int} into separate modes is not justified, we believe the appropriate model is $\epsilon_{s'}^e = 0$ and $\epsilon_{s'}^i = \epsilon_{s'}^{\text{int}}$. Another possible model would have all the internal energy characterized by T or T_e, so that $\epsilon_s^i = 0$.

FLUX JACOBIAN MATRICES FOR A NONEQUILIBRIUM GAS

To formulate a *complete* set of conservation equations for a multi-temperature, multi-component gas mixture in a thermo-chemical nonequilibrium environment is a nontrivial task. It requires knowledge in advanced kinetic theory and quantum

mechanics. The main difficulty comes from the fact that the gas does not consist of structureless particles. Also, as the temperature gets higher, the upper excited electronic states become populated and some atoms and molecules become ionized. Additional complexity arises since the particles now interact with each other due to long range forces. This can have an important influence on transport, relaxation, radiation, and chemical-reaction processes. Many existing theoretical approaches have neglected this effect or have limited it to a certain degree of complexity. Further research and development is required for more rigorous formulations. Under some condition the ionized gas cannot be treated as electrically neutral. This give rise to induced electric fields and additional source terms in the momentum and energy equations. A rigorous formulation would require the addition of Maxwell's equations to our system. Instead of dealing with all these complications, in this paper we just focus on some numerical aspects of the inviscid flux terms. None of the transport, energy transfer, chemical source, or radiation terms will be discussed here.

The variables defining the state of the gas motion are the mass averaged mixture velocity u, the temperatures T and T_e, and for each chemical species the density ρ_s and $\epsilon_{s'}^i$ (or $T_{s'}^i$). In order to formulate the conservation equations, it is convenient to introduce the internal energy of species s per unit volume

$$\tilde{\epsilon}_s = \rho_s \epsilon_s, \tag{7}$$

with analogous definitions for $\tilde{\epsilon}_{s'}^t$, $\tilde{\epsilon}_s^e$, and $\tilde{\epsilon}_{s'}^i$. Summing over all species, one can express the internal energy of the mixture per unit volume as

$$\tilde{\epsilon} = \tilde{\epsilon}^t + \tilde{\epsilon}^e + \sum_{s'} \tilde{\epsilon}_{s'}^i, \tag{8}$$

where

$$\tilde{\epsilon}^t = \sum_{s'} \tilde{\epsilon}_{s'}^t = \sum_{s'} \rho_{s'} \epsilon_{s'}^t(T) \tag{9a}$$

and

$$\tilde{\epsilon}^e = \sum_{s} \tilde{\epsilon}_s^e = \sum_{s} \rho_s \epsilon_s^e(T_e). \tag{9b}$$

If all the ρ_s are known, T and T_e can be obtained from $\tilde{\epsilon}^t$ and $\tilde{\epsilon}^e$, although this will involve an iterative process if all the $\epsilon_{s'}^t$ or ϵ_s^e are not linear functions of T or T_e, respectively. It is also convenient to introduce the overall density of the mixture ρ, given by

$$\rho = \sum_{s} \rho_s, \tag{10}$$

and the species mass fraction α_s, defined as

$$\alpha_s \equiv \rho_s/\rho. \tag{11}$$

Using Eqs. (10) and (11), one can also define the part of the internal energy in equilibrium with T_e per unit mass of the mixture as

$$\varepsilon^e \equiv \frac{\tilde{\varepsilon}^e}{\rho} = \sum_s \alpha_s \epsilon_s^e(T_e), \tag{12a}$$

and for each species the nonequilibrium part of the species internal energy per unit mass of the mixture as

$$\varepsilon_{s'}^i \equiv \frac{\tilde{\varepsilon}_{s'}^i}{\rho} = \alpha_{s'} \epsilon_{s'}^i. \tag{12b}$$

Note the distinction between $\varepsilon_{s'}^i$ and $\epsilon_{s'}^i$. The enthalpy per unit mass of the mixture is then given by

$$h = \frac{\tilde{\varepsilon} + p}{\rho} \tag{13a}$$

$$= \sum_{s'} \alpha_{s'} [\epsilon_{s'}^t(T) + R_{s'} T] + \alpha_e R_e T_e + \varepsilon^e + \sum_{s'} \varepsilon_{s'}^i. \tag{13b}$$

In order to obtain maximum generality and greater compactness, we employ the vector approach of Ref. [18]. The set of conservative variables per unit volume U can be represented compactly by the algebraic column vector

$$U = \begin{bmatrix} \rho_s \\ \mathbf{m} \\ e \\ \tilde{\varepsilon}_{s'}^i \\ \tilde{\varepsilon}^e \end{bmatrix}, \tag{14}$$

where $\mathbf{m} = \rho \mathbf{u}$ is the momentum of the mixture per unit volume, and $e = \tilde{\varepsilon} + \frac{1}{2}\rho \mathbf{u} \cdot \mathbf{u}$ is the total energy of the mixture per unit volume. Here ρ_s and $\tilde{\varepsilon}_{s'}^i$ contain NS and NI elements respectively, where NS is total number of chemical species, and NI is total numer of energy modes which are not characterized by T and T_e in the mixture. Note that $\mathbf{m}$ is a physical vector, while both e and $\tilde{\varepsilon}^e$ are scalars.

The calculation of the flux of U across a surface element plays a central role in the numerical solution of conservation laws. Let $\mathbf{n}$ be the unit normal vector in a positive direction to a cell surface in a finite-volume grid, or a coordinate surface in a finite-difference grid. If v_n is the normal component of the velocity of a time-varying surface, and $u_n = \mathbf{n} \cdot \mathbf{u}$, we can define the normal relative velocity com-

ponent $u' = u_n - v_n$. The set of inviscid normal flux components per unit area F_n is given by the algebraic column vector

$$F_n = \begin{bmatrix} M_s \\ \mathbf{P} \\ E \\ E_{s'}^i \\ E^e \end{bmatrix} = \begin{bmatrix} \rho_s u' \\ \mathbf{m}u' + p\mathbf{n} \\ eu' + pu_n \\ \tilde{\epsilon}_{s'}^i u' \\ \tilde{\epsilon}^e u' \end{bmatrix}, \tag{15}$$

where M, $\mathbf{P}$, and E denote the normal flux of mass, momentum and energy. Note that the above equations do not include the kinetic energy of the free electrons in the last row of U, or the electron pressure p_e in the corresponding row of F_n. If these terms were included, the equation set would have to be augmented by the momentum equation for the free electrons. In addition to increasing the number of equations, it would require modeling the momentum transfer between the free electrons and the heavy particles. But to avoid the additional complications arising from the introduction of Maxwell's equations, an approximate form of the electron momentum equation is normally used to obtain the induced electric field [19, 15–17]. This results in the presence of the gradient of p_e in the source term for the electron energy, as well as the overall momentum and total energy equations. By excluding the electron kinetic energy and electron pressure from our electron energy equation, we must add an additional term involving p_e to its source term. The effect of the presence of p_e in the source terms on shock-capturing capabilities remains to be investigated.

We can define a flux Jacobian matrix operator A satisfying $dF_n = A \, dU$, using the convention that in forming the product of a matrix element with a column vector element, a dot product is implied if each element is either a physical vector (e.g., $\mathbf{u}$ or $\mathbf{n}$) or a tensor (e.g., $\mathbf{un}$ or $\mathbf{nu}$). The differential of Eq. (4) takes the form

$$dp = \sum_{s'} R_{s'} T \, d\rho_{s'} + R_e T_e \, d\rho_e + \sum_{s'} \rho_{s'} R_{s'} \, dT + \rho_e R_e \, dT_e. \tag{16}$$

The species specific heats are defined by

$$c_{v_{s'}}^i \equiv \frac{d\epsilon_{s'}^i}{dT} \tag{17a}$$

and

$$c_{v_s}^e \equiv \frac{d\epsilon_s^e}{dT_e}. \tag{17b}$$

Using Eq. (17), one can rewrite Eq. (16) in terms of the differentials of internal energy per unit volume as

$$dp = \sum_s \chi_s \, d\rho_s + \kappa \, d\tilde{\epsilon}^i + \kappa^e \, d\tilde{\epsilon}^e, \tag{18}$$

where the pressure derivatives are defined as

$$\kappa \equiv \frac{\sum_{s'} \rho_{s'} R_{s'}}{\sum_{s'} \rho_{s'} c_{v_{s'}}^t} = \frac{\sum_{s'} \alpha_{s'} R_{s'}}{\sum_{s'} \alpha_{s'} c_{v_{s'}}^t}, \tag{19a}$$

$$\kappa^e \equiv \frac{\rho_e R_e}{\sum_s \rho_s c_{v_s}^e} = \frac{\alpha_e R_e}{\sum_s \alpha_s c_{v_s}^e}, \tag{19b}$$

$$\chi_{s'} \equiv R_{s'} T - \kappa \epsilon_{s'}^t - \kappa^e \epsilon_{s'}^e, \tag{20a}$$

and

$$\chi_e \equiv R_e T_e - \kappa^e \epsilon_e^e = R_e T_e (1 - \tfrac{3}{2}\kappa^e). \tag{20b}$$

Equations (4) and (20) can be combined to derive the identity

$$p = \sum_s \rho_s \chi_s + \kappa \tilde{\epsilon}^t + \kappa^e \tilde{\epsilon}^e. \tag{21}$$

Introducing the set of differentials of U, we obtain the final form

$$dp = \sum_s \left(\frac{\kappa}{2} \mathbf{u} \cdot \mathbf{u} + \chi_s \right) d\rho_s - \kappa \mathbf{u} \cdot d\mathbf{m} + \kappa \, de - \kappa \sum_{s'} d\tilde{\epsilon}_{s'}^i + (\kappa^e - \kappa) \, d\tilde{\epsilon}^e. \tag{22}$$

Using Eq. (22), the matrix A can then be written as

$$A = \begin{bmatrix} \delta_{sr} u' - \alpha_s u_n & \alpha_s \mathbf{n} & 0 & 0 & 0 \\ \left(\dfrac{\kappa}{2}\mathbf{u}\cdot\mathbf{u}+\chi_r\right)\mathbf{n}-u_n\mathbf{u} & \mathbf{u}\mathbf{n}-\kappa\mathbf{n}\mathbf{u}+u'\mathbf{I} & \kappa\mathbf{n} & -\kappa\mathbf{n} & (\kappa^e-\kappa)\mathbf{n} \\ \left(\dfrac{\kappa}{2}\mathbf{u}\cdot\mathbf{u}+\chi_r-H\right)u_n & H\mathbf{n}-\kappa u_n\mathbf{u} & \kappa u_n+u' & -\kappa u_n & (\kappa^e-\kappa)\,u_n \\ -\epsilon_{s'}^i u_n & \epsilon_{s'}^i \mathbf{n} & 0 & \delta_{s'r'} u' & 0 \\ -\epsilon^e u_n & \epsilon^e \mathbf{n} & 0 & 0 & u' \end{bmatrix}, \tag{23}$$

where $H = h + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}$ is the total enthalpy per unit mass of the mixture, $\mathbf{I}$ is the identity tensor, and δ_{sr}, $\delta_{s'r'}$ are Kronecker deltas. The subscripts s and r are row and column indices, respectively. One can easily verify the homogeneity property

$$AU = F_n, \tag{24}$$

which is the direct consequence of the assumption of a mixture of thermally perfect gases leading to the form of Eq. (4).

A has the three distinct eigenvalues

$$\lambda_1 = u', \qquad \lambda_2 = u' + c, \qquad \lambda_3 = u' - c, \qquad (25)$$

where c is the frozen speed of sound given by

$$c^2 = \sum_s \alpha_s \chi_s + \kappa h + (\kappa^e - \kappa) \varepsilon^e - \kappa \sum_{s'} \varepsilon_{s'}^i \qquad (26a)$$

$$= (\kappa + 1) \frac{p}{\rho}. \qquad (26b)$$

The second form is obtained using Eq. (21). Note that the number of distinct eigenvalues is unaffected by the number of species and the number of nonequilibrium energy modes in the system. λ_1 is associated with those conservative variables whose flux is purely convective. These are the three types of nonequilibrium variables ρ_s, $\tilde{\varepsilon}_{s'}^i$, and $\tilde{\varepsilon}^e$, and the tangential component of $\mathbf{m}$. Since λ_1 is a repeated eigenvalue, if a diagonal algorithm is applied, the inversion associated with this eigenvalue can be performed simultaneously. This demonstrates one of the advantages of the diagonal algorithms, since one only needs to solve three different scalar equations in each direction whether the gas is perfect, or in thermodynamic equilibrium, or in thermo-chemical nonequilibrium.

In order to construct the four types of linearly independent eigenvectors associated with λ_1, we span the plane normal to $\mathbf{n}$ by an arbitrary set of two basis vectors $\mathbf{b}_i$, and the set of reciprocal basis vector $\mathbf{b}^j$, satisfying $\mathbf{b}_i \cdot \mathbf{b}^j = \delta_i^j$, where δ_i^j is the Kronecker delta. It follows that $\mathbf{b}_i \cdot \mathbf{n} = \mathbf{b}^j \cdot \mathbf{n} = 0$. One can then obtain the similarity transformation $A = R \Lambda R^{-1}$, with the diagonal eigenvalue matrix Λ defined as

$$\Lambda = \begin{bmatrix} \lambda_1 \delta_{sr} & & & & & \\ & \lambda_1 \delta_i^j & & & & \\ & & \lambda_1 \delta_{s'r'} & & & \\ & & & \lambda_1 & & \\ & & & & \lambda_2 & \\ & & & & & \lambda_3 \end{bmatrix}. \qquad (27)$$

The right eigenvector matrix R can then be written as

$$R = \begin{bmatrix} \delta_{sr} & 0 & 0 & 0 & \alpha_s & \alpha_s \\ \mathbf{u} & c\mathbf{b}_i & 0 & 0 & \mathbf{u} + c\mathbf{n} & \mathbf{u} - c\mathbf{n} \\ \frac{1}{2}\mathbf{u} \cdot \mathbf{u} - \frac{\chi_r}{\kappa} & c(\mathbf{u} \cdot \mathbf{b}_i) & 1 & 1 - \frac{\kappa^e}{\kappa} & H + cu_n & H - cu_n \\ 0 & 0 & \delta_{s'r'} & 0 & \varepsilon_{s'}^i & \varepsilon_{s'}^i \\ 0 & 0 & 0 & 1 & \varepsilon^e & \varepsilon^e \end{bmatrix}, \qquad (28)$$

while the left eigenvector matrix R^{-1} can be written as

$$R^{-1} =$$

$$\frac{1}{c^2}
\begin{bmatrix}
c^2\delta_{sr} - \alpha_s\left(\dfrac{\kappa}{2}\mathbf{u}\cdot\mathbf{u}+\chi_r\right) & \alpha_s\kappa\mathbf{u} & -\alpha_s\kappa & \alpha_s\kappa & -\alpha_s(\kappa^e-\kappa) \\[2mm]
-c(\mathbf{b}^j\cdot\mathbf{u}) & c\mathbf{b}^j & 0 & 0 & 0 \\[2mm]
-\varepsilon_{s'}^i\left(\dfrac{\kappa}{2}\mathbf{u}\cdot\mathbf{u}+\chi_r\right) & \varepsilon_{s'}^i\kappa\mathbf{u} & -\varepsilon_{s'}^i\kappa\ c^2\delta_{s'r'}+\varepsilon_{s'}^i\kappa & -\varepsilon_{s'}^i(\kappa^e-\kappa) \\[2mm]
-\varepsilon^e\left(\dfrac{\kappa}{2}\mathbf{u}\cdot\mathbf{u}+\chi_r\right) & \varepsilon^e\kappa\mathbf{u} & -\varepsilon^e\kappa & \varepsilon^e\kappa & c^2-\varepsilon^e(\kappa^e-\kappa) \\[2mm]
\dfrac{1}{2}\left(\dfrac{\kappa}{2}\mathbf{u}\cdot\mathbf{u}+\chi_r-cu_n\right) & \dfrac{1}{2}(c\mathbf{n}-\kappa\mathbf{u}) & \dfrac{1}{2}\kappa & -\dfrac{1}{2}\kappa & \dfrac{1}{2}(\kappa^e-\kappa) \\[2mm]
\dfrac{1}{2}\left(\dfrac{\kappa}{2}\mathbf{u}\cdot\mathbf{u}+\chi_r+cu_n\right) & -\dfrac{1}{2}(c\mathbf{n}+\kappa\mathbf{u}) & \dfrac{1}{2}\kappa & -\dfrac{1}{2}\kappa & \dfrac{1}{2}(\kappa^e-\kappa)
\end{bmatrix}.$$

$$(29)$$

In actual computations, since the eigenvector matrices are used to operate on algebraic vectors or matrices, one probably never needs to form them. By inspecting the structure of R^{-1}, it is more efficient to express it in a different manner. Equation (22) can be expressed compactly as $dp = P^T\, dU$ in terms of the row vector

$$P^T = \left[\frac{\kappa}{2}\mathbf{u}\cdot\mathbf{u}+\chi_s \quad -\kappa\mathbf{u} \quad \kappa \quad -\kappa \quad \kappa^e-\kappa\right]. \tag{30}$$

Then R^{-1} can be partitioned as

$$R^{-1} = \frac{1}{c^2}
\begin{bmatrix}
-\alpha_s \\[1mm]
0 \\[1mm]
-\varepsilon_{s'}^i \\[1mm]
-\varepsilon^e \\[1mm]
\dfrac{1}{2} \\[2mm]
\dfrac{1}{2}
\end{bmatrix}
P^T + \frac{1}{c}
\begin{bmatrix}
c\delta_{sr} & 0 & 0 & 0 & 0 \\[1mm]
-\mathbf{b}^j\cdot\mathbf{u} & \mathbf{b}^j & 0 & 0 & 0 \\[1mm]
0 & 0 & 0 & c\delta_{s'r'} & 0 \\[1mm]
0 & 0 & 0 & 0 & c \\[1mm]
-\dfrac{u_n}{2} & \dfrac{\mathbf{n}}{2} & 0 & 0 & 0 \\[2mm]
\dfrac{u_n}{2} & -\dfrac{\mathbf{n}}{2} & 0 & 0 & 0
\end{bmatrix}. \tag{31}$$

When carrying out the implicit inversions in a diagonal algorithm or forming the limiters in some TVD schemes, one needs to perform the operations $R^{-1}V$ and RW, where V and W are some algebraic column vectors of appropriate structure. Let

$$V = \begin{bmatrix} v_{1s} \\ \mathbf{v}_2 \\ v_3 \\ v_{4s'} \\ v_5 \end{bmatrix} \tag{32}$$

be a five-component algebraic column vector with the structure of U or F_n. In terms of the scalar quantities

$$v_1 = \sum_s v_{1s}, \tag{33a}$$

$$v_4 = \sum_{s'} v_{4s'}, \tag{33b}$$

$$v_6 = \frac{P^T V}{c^2}$$

$$= \frac{1}{c^2}\left[\sum_s \chi_s v_{1s} + \kappa\left(\frac{1}{2}(\mathbf{u}\cdot\mathbf{u})v_1 - \mathbf{u}\cdot\mathbf{v}_2 + v_3 - v_4\right) + (\kappa^e - \kappa)v_5\right], \tag{33c}$$

and

$$v_7 = \frac{1}{c}(\mathbf{n}\cdot\mathbf{v}_2 - u_n v_1), \tag{33d}$$

one can calculate $R^{-1}V$ efficiently as

$$R^{-1}V = \begin{bmatrix} v_{1s} - \alpha_s v_6 \\ \dfrac{1}{c}\left[\mathbf{b}^j\cdot\mathbf{v}_2 - (\mathbf{b}^j\cdot\mathbf{u})v_1\right] \\ v_{4s'} - \varepsilon_{s'}^i v_6 \\ v_5 - \varepsilon^e v_6 \\ \dfrac{1}{2}(v_6 + v_7) \\ \dfrac{1}{2}(v_6 - v_7) \end{bmatrix}. \tag{34}$$

Note that each additional species s involves only an additional add in forming v_1, an additional add and multiply in forming v_6, and an additional add and multiply in forming the first component of $R^{-1}V$. Similarly, each additional species s' that contains $\tilde{\varepsilon}_{s'}^i$ involves only an additional add in forming v_4 and an additional add and multiply in forming the third component of $R^{-1}V$. Thus the addition of new species to the system involves very few additional operations.

Let

$$
W = \begin{bmatrix} w_{1s} \\ w_2^j \\ w_{3s'} \\ w_4 \\ w_5 \\ w_6 \end{bmatrix}
\tag{35}
$$

be any six-component algebraic column vector with structure of $R^{-1}V$. In terms of the scalar quantities

$$
w_1 = \sum_s w_{1s},
\tag{36a}
$$

$$
w_3 = \sum_{s'} w_{3s'},
\tag{36b}
$$

$$
w_7 = w_5 + w_6,
\tag{36c}
$$

and

$$
w_8 = w_5 - w_6,
\tag{36d}
$$

one can calculate RW efficiently as

$$
RW = \begin{bmatrix} w_{1s} + \alpha_s w_7 \\ (w_1 + w_7)\mathbf{u} + c(w_2^j \mathbf{b}_j + w_8 \mathbf{n}) \\ \dfrac{w_1}{2}\mathbf{u}\cdot\mathbf{u} - \dfrac{1}{\kappa}\sum_s \chi_s w_{1s} + c(w_2^j \mathbf{u}\cdot\mathbf{b}_j + w_8 u_n) + H w_7 + w_3 + \left(1 - \dfrac{\kappa^e}{\kappa}\right)w_4 \\ w_{3s'} + \varepsilon_{s'}^i w_7 \\ w_4 + \varepsilon^e w_7 \end{bmatrix}.
\tag{37}
$$

Again, each additional species s involves an additional add in forming w_1, an additional add and multiply in forming the first component of RW, and an additional add and multiply in forming the third component of RW. Similarly, each additional species s' that contains $\tilde{\varepsilon}_{s'}^i$ involves an additional add in forming w_3, and an additional add and multiply in forming the fourth component of RW. Thus, also in this case the addition of new species to the system involves very few additional operations. On some occasions, a matrix of the form $RD(f(\lambda_l))\,R^{-1}$ may be needed, where D is a diagonal matrix whose elements are function of the eigenvalues. One should never form R and R^{-1} individually and then perform the matrix multiplications. The aforementioned techniques should also be applied in this case.

In diagonal algorithms with operator splitting, one needs to form the operator $R_k^{-1}R_l$, where the subscript l refers to a surface with unit normal $\mathbf{n}_l$ and a set of

basis vectors $\mathbf{b}_{il}$, while the subscript k refers to a surface with unit normal $\mathbf{n}_k$ and a set of reciprocal basis vectors $\mathbf{b}_k^j$. From Eqs. (28) and (31) one obtains the matrix

$$
R_k^{-1} R_l = \begin{bmatrix}
\delta_{sr} & 0 & 0 & 0 & 0 & 0 \\
0 & \mathbf{b}_k^j \cdot \mathbf{b}_{il} & 0 & 0 & \mathbf{b}_k^j \cdot \mathbf{n}_l & -\mathbf{b}_k^j \cdot \mathbf{n}_l \\
0 & 0 & \delta_{s'r'} & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & \tfrac{1}{2}\mathbf{n}_k \cdot \mathbf{b}_{il} & 0 & 0 & \tfrac{1}{2}(1+\mathbf{n}_k \cdot \mathbf{n}_l) & \tfrac{1}{2}(1-\mathbf{n}_k \cdot \mathbf{n}_l) \\
0 & -\tfrac{1}{2}\mathbf{n}_k \cdot \mathbf{b}_{il} & 0 & 0 & \tfrac{1}{2}(1-\mathbf{n}_k \cdot \mathbf{n}_l) & \tfrac{1}{2}(1+\mathbf{n}_k \cdot \mathbf{n}_l)
\end{bmatrix}. \tag{38}
$$

Note that entries involve only the grid geometry and are independent of the physical flow variables. Therefore the presence of chemical or thermal nonequilibrium does not require any additional work in operating with the matrix $R_k^{-1} R_l$ on an algebraic vector.

GENERALIZED STEGER–WARMING FLUX-VECTOR SPLITTING

If $|u'| \geqslant c$, it follows from Eq. (25) that the eigenvalues of A are all of one sign, thus allowing upwind differencing to be simply implemented. If $|u'| < c$, the eigenvalues of A are of mixed sign. In flux-vector splitting methods, the flux F_n is written as

$$
F_n = F_n^+ + F_n^-, \tag{39}
$$

so that the split-flux Jacobian operators $A^\pm$ satisfying $dF_n^\pm = A^\pm \, dU$ have the property that $\lambda_i(A^\pm) \gtrless 0$ for all i. (In practice, one can permit some $\lambda_i(A^\pm) \lessgtr 0$ if they are sufficiently small in magnitude.)

Since the homogeneity property Eq. (24) is valid, the two ways of obtaining Steger–Warming flux-vector splitting for a perfect gas can be easily extended here. One way, the so called "eigenvalue splitting" [2, 20, 21], is to expand F_n as

$$
F_n = \sum_{i=1}^{3} F_{ni}, \tag{40}
$$

where each F_{ni} is associated with the distinct eigenvalues λ_i. One can readily obtain the expressions

$$
F_{n1} = \frac{\lambda_1(\gamma-1)}{\gamma}
\begin{bmatrix}
\rho_s \\
\rho \mathbf{u} \\
e - \dfrac{p}{\gamma-1} \\
\bar{\epsilon}_{s'}^i \\
\tilde{\epsilon}^e
\end{bmatrix}, \qquad
F_{n_3^2} = \frac{\lambda_2}{2\gamma}
\begin{bmatrix}
\rho_s \\
\rho(\mathbf{u} \pm c\mathbf{n}) \\
\rho(H \pm cu_n) \\
\bar{\epsilon}_{s'}^i \\
\tilde{\epsilon}^e
\end{bmatrix}, \tag{41}
$$

where

$$\gamma \equiv \frac{\rho c^2}{p} \tag{42a}$$

$$= \kappa + 1. \tag{42b}$$

The generalization of Steger–Warming flux-vector splitting is obtained by letting $F_n^{\pm}$ be the sum of those F_{ni} associated with $\lambda \gtrless 0$. For $-c < u' < 0$ we therefore have

$$F_n^+ = F_{n2} \quad \text{and} \quad F_n^- = F_{n1} + F_{n3}, \tag{43}$$

while for $0 < u' < c$,

$$F_n^+ = F_{n1} + F_{n2} \quad \text{and} \quad F_n^- = F_{n3}. \tag{44}$$

The other way, the so called "plus–minus" splitting, follows the original derivation of Steger and Warming [5] for the perfect gas. One can express the eigenvalue λ_i as

$$\lambda_i = \lambda_i^+ + \lambda_i^-, \tag{45a}$$

where

$$\lambda_i^+ = \frac{\lambda_i + |\lambda_i|}{2}, \qquad \lambda_i^- = \frac{\lambda_i - |\lambda_i|}{2}. \tag{45b}$$

Using the homogeneity property and applying the similarity transformation, one obtains

$$F_n^+ = R\Lambda^+ R^{-1} U \quad \text{and} \quad F_n^- = R\Lambda^- R^{-1} U, \tag{46}$$

where Λ^+ and Λ^- have the diagonal elements λ^+ and λ^-, respectively. Both approaches give identical results. While one cannot prove rigorously for the non-equilibrium case that all the eigenvalues of $A^{\pm}$ have the appropriate sign, this has been shown [20] to be true for equilibrium flow of a diatomic gas with vibrational excitation. It is reasonable to assume that this condition will be approximately satisfied for practical nonequilibrium flows. Furthermore, the numerical stability depends also on other conditions.

Due to the fact that $A^{\pm}$ are discontinuous when λ_i changes sign, "glitches" or oscillations have been observed at sonic points, stagnation points, and shocks in many perfect gas applications. There are many techniques which have been reported in the literature to overcome such phenomena. For example, Steger and Warming [5] suggested adding small blending terms to $\lambda_i^{\pm}$. This yields a smooth sonic transition. Anderson et al. [22] indicated that by using the MUSCL type differencing [23] one can obtain a smooth sonic transition and stable shock

structure. In addition, Buning [21] and Ying [24] utilized a proper "transition operator" so that the sonic glitches and shock oscillations can be avoided. All these techniques can be easily applied to the nonequilibrium flow cases.

GENERALIZED VAN LEER FLUX-VECTOR SPLITTING

Van Leer [6] constructed a different type of flux-vector splitting for a perfect gas in terms of polynomials of u' whose $A^\pm$ are continuous and have one zero eigenvalue. This results in a sharper capture of transonic shocks. The generalization for a nonequilibrium flow is similar to that derived previously for an equilibrium flow [2, 20]. For $|u'| < c$, the continuity conditions necessitate a factor $(u' \pm c)^2$ in the formulas for $F_n^\pm$. Using the fact that the critical values of u' are $\pm c$, one can easily demonstrate that for any $f(u')$ that is either an even or odd function of u',

$$f^+(u') = \pm f^-(-u') \qquad \text{if} \quad f(u') = \pm f(-u'). \tag{47}$$

As a function of u', all components of $F(U)$ can be represented by at most the cubic polynomials

$$f(u') = a_0 + a_1 u' + a_2 u'^2 + a_3 u'^3. \tag{48}$$

The lowest order polynomials for $f^\pm(u')$ satisfying Eqs. (39) and (47), as well as the continuity conditions at $|u'| = c$ can then be expressed as

$$f^\pm(u') = \frac{(u' \pm c)^2}{4c} (a_0^\pm + a_1^\pm u'), \tag{49}$$

where

$$a_0^\pm = \frac{2a_0}{c} \pm (a_1 - c^2 a_3) \tag{50a}$$

and

$$a_1^\pm = 2c a_3 \pm \left(a_2 - \frac{a_0}{c^2} \right). \tag{50b}$$

Using Eqs. (48)–(50), one readily obtains the relations

$$M_s^\pm = \pm \frac{\rho_s}{4c} (u' \pm c)^2, \tag{51}$$

$$E_{s'}^{i\pm} = \pm \frac{\tilde{\varepsilon}_{s'}^i}{4c} (u' \pm c)^2, \tag{52}$$

$$E^{e\pm} = \pm \frac{\tilde{\varepsilon}^e}{4c} (u' \pm c)^2, \tag{53}$$

and

$$\mathbf{P}^{\pm} = \pm \frac{\rho(u' \pm c)^2}{4c} \left[\mathbf{u} - \frac{1}{\gamma} (u' \mp 2c)\mathbf{n} \right]. \tag{54}$$

One can similarly obtain a two term expansion for $E^{\pm}$. But this could not reduce to van Leer's solution for a perfect gas where $A^{\pm}$ has one zero eigenvalue. However, the function $\pm (u' + c)^2 (u' - c)^2$ satisfies the continuity conditions at $u' = \pm c$, and such a term can be added to $E^{\pm}$ without affecting $E(U)$. For a perfect gas, there is only one species, and γ is a constant. The zero eigenvalue condition results if $E^{\pm} = f(M^{\pm}, \mathbf{P}^{\pm}, \mathbf{n}, v_n)$. Guided by the form of Eq. (54), we express the additive function in such a way that $E^{\pm}$ can be written as

$$E^{\pm} = \pm \frac{(u' \pm c)^2}{4c} \left[\rho \frac{\{(\gamma - 1) u' \pm 2c\}^2}{2(\gamma^2 - 1)} + e - \frac{p}{\gamma - 1} - \rho u'^2 \right.$$
$$\left. - \frac{\rho v_n}{\gamma} (u' \mp 2c) + \psi \rho (u' \mp c)^2 \right], \tag{55}$$

where ψ is an arbitrary parameter that is independent of the arbitrary constant in the definition of ϵ_s. For a perfect gas, van Leer's condition results if $\psi = 0$. It is shown in Ref. [20] that $\psi = 0$ is also a reasonable assumption for an equilibrium real gas. For the general nonequilibrium case, it is also simplest to take $\psi = 0$. Again, one cannot prove rigorously that all the eigenvalues of $A^{\pm}$ have the appropriate sign, but it is reasonable that this is approximately true, and one of the eigenvalues will be close to zero.

GENERALIZED ROE'S APPROXIMATE RIEMANN SOLVER

Among the various approximate Riemann solvers, the most common one uses the Roe average because of its simplicity and its ability to satisfy the jump conditions across discontinuities exactly. The derivation in Ref. [7] for a perfect gas employed parameter vectors. To obtain a generalization for a nonequilibrium flow, we use a different, more direct approach, which is similar to that derived previously for equilibrium flow [2, 25].

In approximate Riemann solvers based on local linearization, the flux at a surface separating two states U_L and U_R is based on the eigenvalues and eigenvectors of some average $\bar{A}$. The optimum choice for $\bar{A}$ is one satisfying

$$\Delta F_n = \bar{A} \, \Delta U, \tag{56}$$

where $\Delta(\cdot) = (\cdot)_R - (\cdot)_L$. This choice of $\bar{A}$ captures discontinuities exactly. One way of obtaining $\bar{A}$ is to seek an average state $\bar{U}$, such that

$$\bar{A} = A(\bar{U}). \tag{57}$$

The notation $\bar{U}$ implies only those variables that appear explicitly in Eq. (57). Such a state is known as a Roe-averaged state, and was derived by Roe for a perfect gas. The generalization to a nonequilibrium flow is obtained by substituting Eqs. (14), (15), (23), and (57) into Eq. (56), with $\mathbf{n}$ and v_n fixed at the surface. In general, $\mathbf{u}_L$, $\mathbf{u}_R$, and $\mathbf{n}$ are arbitrary, independent vectors. We can therefore expand $\bar{\mathbf{u}}$ as

$$\bar{\mathbf{u}} = a_L \mathbf{u}_L + a_R \mathbf{u}_R + a_n \mathbf{n}. \tag{58}$$

The independence of $\mathbf{u}_L$ and $\mathbf{u}_R$ and $\mathbf{n}$ also implies the independence of the dot products $\mathbf{u}_L \cdot \mathbf{u}_L$, $\mathbf{u}_L \cdot \mathbf{u}_R$, $\mathbf{u}_R \cdot \mathbf{u}_R$, $\mathbf{u}_L \cdot \mathbf{n}$, and $\mathbf{u}_R \cdot \mathbf{n}$. After substituting Eq. (58) into the momentum component of Eq. (56), and equating coefficients of independent quantities, one readily establishes that

$$a_L = \frac{\sqrt{\rho_L}}{\sqrt{\rho_L} + \sqrt{\rho_R}}, \tag{59a}$$

$$a_R = 1 - a_L = \frac{\sqrt{\rho_R}}{\sqrt{\rho_L} + \sqrt{\rho_R}}, \tag{59b}$$

$$a_n = 0. \tag{59c}$$

Therefore Eq. (58) becomes

$$\bar{\mathbf{u}} = a_L \mathbf{u}_L + a_R \mathbf{u}_R. \tag{60}$$

This is the identical relation derived by Roe for a perfect gas. It satisfies all the terms involving the velocity. The remaining terms in the equation result in the new condition

$$\sum_s \bar{\chi}_s \, \Delta\rho_s + \bar{\kappa} \, \Delta\tilde{\varepsilon}^t + \overline{\kappa^e} \, \Delta\tilde{\varepsilon}^e = \Delta p, \tag{61}$$

where $\Delta\tilde{\varepsilon}^t$ is obtained from the jump of the conservative variables using Eq. (8). This is just the discrete form of Eq. (18), averaged between the two states. This condition is automatically satisfied for a perfect gas. Substituting Eq. (60) into the first, fourth, and fifth components of Eq. (56), one obtains the relations

$$\bar{\alpha}_s = a_L \alpha_{sL} + a_R \alpha_{sR}, \tag{62}$$

$$\overline{\varepsilon_{s'}^i} = a_L \varepsilon_{s'L}^i + a_R \varepsilon_{s'R}^i, \tag{63}$$

$$\overline{\varepsilon^e} = a_L \varepsilon_L^e + a_R \varepsilon_R^e. \tag{64}$$

The third component of Eq. (56) results in the additional relation

$$\bar{H} = a_L H_L + a_R H_R, \tag{65}$$

which is also true for a perfect gas. From the definition of H, Eqs. (60) and (65) can be combined to define a Roe-averaged specific enthalpy as

$$\bar{h} = a_L h_L + a_R h_R + \tfrac{1}{2} a_L a_R \, \Delta\mathbf{u} \cdot \Delta\mathbf{u}. \tag{66}$$

Note that $\bar{h}$ could lie outside the range given by h_L and h_R if the magnitude of $\Delta\mathbf{u}$ is sufficiently large. The Roe-averaged sound speed is given by Eq. (26a) as

$$\bar{c}^2 = \sum_s \bar{\alpha}_s \bar{\chi}_s + \bar{\kappa}\bar{h} + (\overline{\kappa^e} - \bar{\kappa})\,\bar{\varepsilon}^e - \bar{\kappa} \sum_{s'} \overline{\varepsilon_{s'}^I}. \tag{67}$$

For an arbitrary nonequilibrium flow, Eq. (61) provides only one relation for the variables $\bar{\chi}_s$, $\bar{\kappa}$, and $\overline{\kappa^e}$. We thus have the paradoxical situation that not only does a Roe average exist for a nonequilibrium flow, its precise value is not uniquely defined. For the special case in which L and R are precisely those that satisfy the

the exact Riemann solver, even though $\bar{\chi}_s$, $\bar{\kappa}$, and κ^e are not uniquely defined. For a gas dynamic shock wave, which necessitates the conditions $\Delta\alpha_s = \Delta\varepsilon_{s'}^i = \Delta\varepsilon^e = 0$, one obtains [25]

$$\bar{h} = \frac{a_L^2 h_L + a_R^2 h_R}{a_L^2 + a_R^2} \tag{68}$$

and

$$\bar{c}^2 = \frac{\Delta p}{\Delta \rho}. \tag{69}$$

The values of $\bar{h}$ and $\bar{c}^2$ as given by Eqs. (68) and (69) will in general not be consistent with Eqs. (13b) and (26a).

There are two approaches to obtain unique values of $\bar{\chi}_s$, $\bar{\kappa}$, and $\overline{\kappa^e}$. In one approach, average temperatures are defined which are then substituted into Eqs. (19) and (20). The other approach is based on thermodynamic states L and R, and does not attempt to define an average thermodynamic state. In the first approach one can also distinguish between those that employ $\bar{h}$ giving by Eq. (66), and those that do not. Since $\bar{h}$ depends on the velocity $\mathbf{u}_L$ and $\mathbf{u}_R$, the resulting values of $\bar{\chi}_s$, $\bar{\kappa}$, and $\overline{\kappa^e}$ will also depend on these velocities.

In the first approach, one defines $\bar{\varepsilon}^e$ in terms of $\bar{\alpha}_s$ and $\bar{T}_e$ using Eq. (12a) and solves for $\bar{T}_e$ using the Roe conditions Eqs. (62) and (64). $\overline{\kappa^e}$ and $\bar{\chi}_e$ are then obtained from Eqs. (19b) and (20b). If we do not use $\bar{h}$, Eqs. (19a) and (20a) can be considered as parametric definitions of a curve in the $\chi_{s'} - \kappa$ space. A unique solution for $\chi_{s'}$ and κ is obtained if the curve has one intersection with the hyperplane defined by Eq. (61). Unfortunately, there may be cases where there is no intersection, or possibly multiple intersections. On the other hand, one can also obtain $\bar{T}$ from $\bar{h}$ using Eq. (13b). The resulting unique values of $\chi_{s'}$ and κ derived from Eqs. (19a) and (20a) will not, in general, satisfy Eq. (61).

The second approach is an extension of the method described in Ref. [25]. Equations (9a) and (19a) implicitly define the function $\kappa(\rho_{s'}, \tilde{\epsilon}^t)$. One similarly defines $\kappa^e(\rho_s, \tilde{\epsilon}^e)$ from Eqs. (9b) and (19b), and the functions $\chi_s(\rho_s, \tilde{\epsilon}^t, \tilde{\epsilon}^e)$ from Eqs. (9) and (20). The straight line path between states L and R in the $\rho_s - \tilde{\epsilon}^t - \tilde{\epsilon}^e$ space are defined parametrically by

$$\rho_s(\tau) = \rho_{sL} + \tau \, \Delta\rho_s, \tag{70a}$$

$$\tilde{\epsilon}^t(\tau) = \tilde{\epsilon}^t_L + \tau \, \Delta\tilde{\epsilon}^t, \tag{70b}$$

$$\tilde{\epsilon}^e(\tau) = \tilde{\epsilon}^e_L + \tau \, \Delta\tilde{\epsilon}^e, \tag{70c}$$

where the parameter τ is chosen so that $\tau_L = 0$ and $\tau_R = 1$. The integrated averages

$$\bar{\chi}_s = \int_0^1 \chi_s[\rho_s(\tau), \tilde{\epsilon}^t(\tau), \tilde{\epsilon}^e(\tau)] \, d\tau, \tag{71a}$$

$$\bar{\kappa} = \int_0^1 \kappa[\rho_{s'}(\tau), \tilde{\epsilon}^t(\tau)] \, d\tau, \tag{71b}$$

$$\overline{\kappa^e} = \int_0^1 \kappa^e[\rho_s(\tau), \tilde{\epsilon}^e(\tau)] \, d\tau \qquad . \tag{71c}$$

satisfy Eq. (61) exactly.

The use of Eqs. (71) is not practical, so that some approximate quadratures are required. The resulting values of χ_s, κ, and κ^e will also not satisfy Eq. (61) exactly. Let $\hat{\chi}_s$, $\hat{\kappa}$, and $\hat{\kappa}^e$ define either approximations to Eq. (71) or the values derived from $\bar{h}$ in the first approach. One then requires values of $\bar{\chi}_s$, $\bar{\kappa}$, and $\overline{\kappa^e}$ satisfying Eq. (61) which are closest to $\hat{\chi}_s$, $\hat{\kappa}$, and $\hat{\kappa}^e$. This can be formulated geometrically as projecting the point $\hat{\chi}_s$, $\hat{\kappa}$, and $\hat{\kappa}^e$ onto the hyperplane defined by Eq. (61). But in order for the Roe-averaged quantities to be independent of the arbitrary constant in the definition of ϵ_s, one must first recast the problem so that geometric relationships will not be affected by the choice of this constant. This can be accomplished if one first divides Eq. (61) by $\bar{\kappa}$. The orientation of the hyperplane in the space defined by the variables $\bar{\chi}_s/\bar{\kappa}$, $1/\bar{\kappa}$, and $\overline{\kappa^e}/\bar{\kappa}$ is now uniquely defined by states L and R. A further scale factor $\hat{\sigma}$ with the dimension of $\bar{\chi}_s$ must be introduced, since the $\bar{\chi}_s$ are not dimensionless. The final relations can be written as

$$\bar{\chi}_s = \frac{D\hat{\chi}_s + \hat{\sigma}^2 \, \Delta\rho_s \, \delta p}{D - \Delta\rho \, \delta p}, \tag{72a}$$

$$\bar{\kappa} = \frac{D\hat{\kappa}}{D - \Delta p \, \delta p}, \tag{72b}$$

$$\overline{\kappa^e} = \frac{D\hat{\kappa}^e + \Delta\tilde{\epsilon}^e \, \delta p}{D - \Delta p \, \delta p}, \tag{72c}$$

where

$$\delta p = \Delta p - \sum_s \hat{\chi}_s \, \Delta \rho_s - \hat{\kappa} \, \Delta \tilde{\epsilon}^t - \hat{\kappa}^e \, \Delta \tilde{\epsilon}^e, \tag{73}$$

$$D = \sum_s (\hat{\sigma} \, \Delta \rho_s)^2 + (\Delta p)^2 + (\Delta \tilde{\epsilon}^e)^2. \tag{74}$$

A natural choice for the scale factor $\hat{\sigma}$ is

$$\hat{\sigma} = \widehat{\bar{c}^2}. \tag{75}$$

The simplest approximation to Eqs. (71) is the trapezoidal rule

$$\widehat{(\cdot)} = \frac{(\cdot)_L + (\cdot)_R}{2}, \tag{76}$$

although other approximations, such as midpoint rule or Simpson's rule, can be used. Note that the magnitude of the error δp using Eq. (76) is a function of the nonconvexity of the variables χ_s, κ, and κ^e between the two states. On the other hand, the magnitude of δp derived from $\bar{h}$ is also a function of $\Delta \mathbf{u}$.

An important quantity in the approximate Riemann solver is the column vector $R^{-1} \, \Delta U$. Its components are the jumps in the characteristic variables. While the above relations are all that are required to construct a Riemann solver using Roe's linearization, an additional algebraic simplicity can be achieved by expressing differences in conservative variables in terms of differences in primitive variables. If one *formally* defines

$$\bar{\rho} = \sqrt{\rho_L \rho_R}, \tag{77}$$

the expression can be written more simply as

$$\overline{R^{-1}} \, \Delta U = \begin{bmatrix} \Delta \rho_s - \bar{\alpha}_s \, \Delta p / \bar{c}^2 \\ \bar{\rho} \mathbf{b}^j \cdot \Delta \mathbf{u} / \bar{c} \\ \Delta \tilde{\epsilon}_{s'}^i - \overline{\epsilon_{s'}^t} \, \Delta p / \bar{c}^2 \\ \Delta \tilde{\epsilon}^e - \overline{\epsilon^e} \, \Delta p / \bar{c}^2 \\ \frac{1}{2}(\Delta p / \bar{c}^2 + \bar{\rho} \mathbf{n} \cdot \Delta \mathbf{u} / \bar{c}) \\ \frac{1}{2}(\Delta p / \bar{c}^2 - \bar{\rho} \mathbf{n} \cdot \Delta \mathbf{u} / \bar{c}) \end{bmatrix}. \tag{78}$$

SPECIAL CASES

The results presented so far are for the most general case of nonequilibrium flow. There are a number of special cases, which can be derived from the general case by deleting one or several equations, or modifying some of the terms in the equations. These will be detailed below.

We first consider the cases relating to the treatment of thermal nonequilibrium. One such case occurs when $\tilde{\epsilon}^e = 0$, but $\tilde{\epsilon}^i_{s'} \neq 0$. In practice, this would only occur if there were no ionization. Then s and r would equal s' and r' in all the equations, and ρ_e, $\epsilon^e_{s'}$, $\tilde{\epsilon}^e$, and their differentials would be set equal to zero in all the equations in which they appear. In the algebraic vectors and matrices, the fourth row would be absent in Eqs. (27), (29), (31), (34), (35), (38), and (78), while the fifth row would be absent in Eqs. (14), (15), (23), (28), (32), (37), and (41). Similarly, one would eliminate the fourth column in Eqs. (27), (28), and (38), and the fifth column in Eqs. (23), (29), (30), and (31). Note that it is possible to have nonequilibrium resulting from internal structure alone even if there is only one chemical species present.

The other special case of thermal nonequilibrium occurs when $\tilde{\epsilon}^i_{s'} = 0$ and $\tilde{\epsilon} \neq 0$. In practice, this would only occur with non-negligible ionization, so that $\rho_e \neq 0$. Under these assumptions, the nonequilibrium part of $\epsilon^{int}_{s'}$ would all be characterized by T_e. For this case, all $\tilde{\epsilon}^i_{s'}$ and their differentials would be set equal to zero in all the equations in which they occur. In the algebraic vectors and matrices, the third row would be absent in Eqs. (27), (29), (31), (34), (35), (38), and (78), while the fourth row would be absent in Eqs. (14), (15), (23), (28), (32), (37), and (41). Similarly, one would eliminate the third column in Eqs. (27), (28), and (38), and the fourth column in Eqs. (23), (29), (30), and (31).

Both of the above cases can be combined if all the internal energy $\tilde{\epsilon}_s$ is at equilibrium with the translational temperature T, and we only have chemical nonequilibrium. Then, $\tilde{\epsilon}^i_{s'}$, $\tilde{\epsilon}^e$, and their differentials would be absent in all the equations. Since any free electrons would have the temperature T, the distinction between the heavy particles and the free electrons is no longer valid. Thus s' would be replaced by s in all the relations, and terms involving T_e would be absent in Eqs. (4), (13b), and (16). Both sets of rows and columns listed in the previous two paragraphs would be deleted from their respective algebraic vectors and matrices.

We next consider the cases relating to the treatment of chemical nonequilibrium. There are two cases where ρ_e is not present as a conservative variable in the definition of U. One occurs when we assume that charge neutrality exists locally at every point. In terms of the species ionic valence $Z_{s'}$, one can express the free electron density as

$$\rho_e = \frac{1}{R_e} \sum_{s'} \rho_{s'} R_{s'} Z_{s'}. \tag{79}$$

Equation (79) is used in evaluating Eqs. (4), (9b), (10), (12a), (13b), and (19b). Equation (10) can be written as

$$\rho = \sum_{s'} \beta_{s'} \rho_{s'}, \tag{80}$$

where

$$\beta_{s'} \equiv 1 + \frac{R_{s'} Z_{s'}}{R_e}. \tag{81}$$

From Eq. (11) it follows that

$$\sum_{s'} \beta_{s'} \alpha_{s'} = 1. \tag{82}$$

The major change in the equations is to replace s and r by s' and r' in Eqs. (14), (15), (18), and every equation starting with Eq. (21). It is also necessary to replace Eq. (20a) by

$$\chi_{s'} \equiv R_{s'}(T + Z_{s'} T_e) - \kappa \epsilon_{s'}^i - \kappa^e(\epsilon_{s'}^e + \tfrac{3}{2} R_{s'} Z_{s'} T_e). \tag{83}$$

For most engineering purposes, one can take $\beta_{s'} \approx 1$, since $R_{s'} Z_{s'}/R_e \ll 1$. If this small term is not neglected, then the factor $\beta_{s'}$ must appear in a number of terms. This results from expressing dp and du' in terms of the differentials of the conservative variables. The term $\mathbf{u} \cdot \mathbf{u}$ in Eqs. (22) and (30) must be multiplied by $\beta_{s'}$. The following terms must be also multiplied by $\beta_{r'}$: all the terms in the first column of A in Eq. (23) except the u' in the first row and the $\chi_{r'}$ in the second and third rows; the terms involving $\mathbf{u}$ in the first column of R in Eq. (28); all the terms involving $\mathbf{u}$ and u_n in the first column of R^{-1} in Eq. (29) and the second matrix of Eq. (31). In addition, Eqs. (33a) and (36a) must be replaced by

$$v_1 = \sum_{s'} \beta_{s'} v_{1s'}, \tag{84}$$

$$w_1 = \sum_{s'} \beta_{s'} w_{1s'}. \tag{85}$$

The other case in which ρ_e is not a conservative variable is in the absence of ionization, where $\rho_e = 0$. This can be considered as a specialization of the previous case to $Z_{s'} = 0$. It follows from Eq. (81) that $\beta_{s'} = 1$ rigorously, so that individual terms need not be modified. The main difference is that we must also take $\tilde{\epsilon}^e = 0$, with the accompanying changes described earlier.

There are also cases which involve only one conservation equation of mass. The subscripts s, r, s', and r' are then absent. One such case, described earlier, is thermal nonequilibrium due to the internal structure for a gas consisting of a single species. A more important case is that of a mixture in thermodynamic equilibrium, for which $\tilde{\epsilon}^i = \tilde{\epsilon}^e = 0$. Strictly speaking, the flow can not be in *truly* thermodynamic equilibrium unless the flow is uniform. Nevertheless, under the assumption of local equilibrium, all the thermodynamic variables can be determined from the process of maximization of the irreversible entropy. Thus one can replace the species density equations by a single global density equation. All the results for this case have been presented by the authors in an earlier paper [2]. However, one can also deduce the results from the general forms presented here if one formally replaces α by 1. All the relations are still valid, except that the equation of state is given by

$$p = p(\rho, \tilde{\epsilon}), \tag{86}$$

and Eqs. (19) and (20) are replaced by

$$\kappa = \left(\frac{\partial p}{\partial \tilde{\epsilon}}\right)_\rho \tag{87}$$

$$\chi = \left(\frac{\partial p}{\partial \rho}\right)_{\tilde{\epsilon}}. \tag{88}$$

The other change is that Eqs. (24), (26b), and (42b) are no longer valid. The equation of state and the pressure derivatives, Eqs. (86)–(88), can be obtained from Ref. [1]. Similarly, for the perfect gas case, one needs to replace Eqs. (86)–(88) by

$$p = \kappa \tilde{\epsilon}, \tag{89}$$

$$\kappa = \text{const}, \tag{90}$$

$$\chi = 0. \tag{91}$$

As one can see, the main difference in the equations for nonequilibrium, equilibrium, and perfect gas flows is in the expressions for the pressure and its derivatives. The difference for 1-dimensional, 2-dimensional, or 3-dimensional flows is just the number of components in the vectors $\mathbf{u}$, $\mathbf{m}$, $\mathbf{n}$, $\mathbf{b}_i$, and $\mathbf{b}^j$. Thus one can easily build a universal computer code which does nonequilibrium, equilibrium, and perfect gas flow computations in either one, two, or three dimensions.

Conclusions

A thermodynamic model has been established for the most general thermal and chemical nonequilibrium flow of an arbitrary gas. Extensions of modern CFD techniques to general, nonequilibrium flows have been obtained. The results have been presented in a form that reduces readily to various special types of nonequilibrium flows, as well as equilibrium and perfect gas flows. One can therefore construct a universal code that covers all these types of flows in any number of dimensions. Note that the formulation and numerical treatment of the transport, energy transfer, chemical source, or radiation terms has not been covered in this paper. These topics will be detailed in the future as part of this series on nonequilibrium flow computations.

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