and an approximation for either the substantial derivative of density

$$\eta \frac{\mathrm{D}\rho}{\mathrm{D}t} = -\rho\dot{\sigma} + \frac{1}{a^2}\left[\rho w^2 \mathrm{u}\kappa + \rho w \frac{\partial \mathrm{u}}{\partial t} + \frac{\partial P}{\partial t}\right] \tag{11.204}$$

or pressure

$$\eta \frac{\mathrm{D}P}{\mathrm{D}t} = -\rho w^2\dot{\sigma} + \rho w^2 \mathrm{u}\kappa + \rho w \frac{\partial \mathrm{u}}{\partial t} + \frac{\partial P}{\partial t}\,. \tag{11.205}$$

The effects of transverse divergence can be approximated by an emprical effective curvature function $\kappa(t)$. For a one-dimensional blast wave and a thin reaction zone

$$\frac{j}{R_s - x} \rightarrow \frac{j}{R_s} = \kappa\,. \tag{11.206}$$

The unsteady terms are more challenging to estimate. One approach, motivated by the shock change relations, is to consider these terms as due to effective shock decay rate and equal to the values at the shock front

$$\rho w \frac{\partial \mathrm{u}}{\partial t} + \frac{\partial P}{\partial t} \rightarrow \rho_1 a_1 f \frac{\mathrm{d}U}{\mathrm{d}t}\,. \tag{11.207}$$

A similar approximation can be proposed for the unsteady pressure term in the w equation

$$\frac{1}{\rho w}\frac{\partial P}{\partial t} + \frac{\mathrm{d}U}{\mathrm{d}t} \rightarrow \left[1 + \frac{1}{\rho_1 U}\left(\frac{\partial P}{\partial U}\right)_{\mathcal{H}}\right]\frac{\mathrm{d}U}{\mathrm{d}t}\,, \tag{11.208}$$

using the nondimensional function

$$g = \left[1 + \frac{1}{\rho_1 U}\left(\frac{\partial P}{\partial U}\right)_{\mathcal{H}}\right]\,. \tag{11.209}$$

For perfect gases, this function is independent of shock speed and depends only on the ratio of specific heats

$$g = \frac{\gamma + 5}{\gamma + 1} \qquad 3 \geq g \geq 2.5 \quad \text{for} \quad 1 \leq \gamma \leq 5/3\,. \tag{11.210}$$

Critical evaluation of the approximations (11.206) and (11.207) requires analyzing direct numerical simulations. This is the approach taken by Eckett et al. (2000), Arienti and Shepherd (2005).

Temperature Model The path line energy balance equation can be used to develop an equation for temperature that is more convenient for further simplifications. One version of the balance equation is

$$\frac{\mathrm{D}h}{\mathrm{D}t} = \frac{1}{\rho}\frac{\mathrm{D}P}{\mathrm{D}t}\,. \tag{11.211}$$

Expanding the mixture enthalpy and distributiong the differentiation, we obtain

$$c_p \frac{\mathrm{D}T}{\mathrm{D}t} = -\sum_k h_k \frac{\mathrm{D}Y_k}{\mathrm{D}t} + \frac{1}{\rho}\frac{\mathrm{D}P}{\mathrm{D}t}\,. \tag{11.212}$$

To complete the model, we need an estimate of the substantial derivative of pressure. The exact value is given by (11.192) but as pointed out previously, absent a detailed simulation of the flow field, it is necessary to estimate the unknown terms. A possible approach is to use (11.206) and (11.207) and assume these terms are constant through the reaction zone.

$$\frac{\mathrm{D}P}{\mathrm{D}t} \approx \left.\frac{\mathrm{D}P}{\mathrm{D}t}\right|_{\mathcal{S}} = \frac{1}{\eta}\left[\rho w \left(\frac{\mathrm{d}u}{\mathrm{d}t}\right)_{\mathcal{S}} + \left(\frac{\mathrm{d}P}{\mathrm{d}t}\right)_{\mathcal{S}} + \rho w^2 \mathrm{u}\kappa\right]_{\mathcal{S}} \tag{11.213}$$

where the contribution of thermicity $\dot{\sigma}$ is neglected at the shock front. An equivalent approach is to use the energy equation in the form

$$\frac{\mathrm{D}e}{\mathrm{D}t} = \frac{P}{\rho^2}\frac{\mathrm{D}\rho}{\mathrm{D}t}, \tag{11.214}$$

$$c_v\frac{\mathrm{D}T}{\mathrm{D}t} = -\sum_k e_k\frac{\mathrm{D}Y_k}{\mathrm{D}t} + RT\frac{1}{\rho}\frac{\mathrm{D}\rho}{\mathrm{D}t}, \tag{11.215}$$

and the shock change relations to estimate the substantial derivative of density

$$\frac{1}{\rho}\frac{\mathrm{D}\rho}{\mathrm{D}t} \approx \frac{1}{\rho}\left.\frac{\mathrm{D}\rho}{\mathrm{D}t}\right|_{\mathcal{S}} = \frac{1}{\rho a^2\eta}\left[\rho w\left(\frac{\mathrm{d}u}{\mathrm{d}t}\right)_{\mathcal{S}} + \left(\frac{\mathrm{d}P}{\mathrm{d}t}\right)_{\mathcal{S}} + \rho w^2 \mathrm{u}\kappa\right]_{\mathcal{S}} \tag{11.216}$$

or in terms of shock acceleration

$$\frac{1}{\rho}\frac{\mathrm{D}\rho}{\mathrm{D}t} \approx \frac{1}{\eta}\left[\frac{\rho_1 a_1}{\rho a^2}f\frac{\mathrm{d}U}{\mathrm{d}t} + \frac{w^2}{a^2}\mathrm{u}\kappa\right]_{\mathcal{S}} \tag{11.217}$$

Note that for decaying shock waves with $\kappa > 0$, the contribution of transverse divergence due to wave curvature is positive and that of unsteadiness is negative. The approximate evoluation equation for temperature is

$$\frac{\mathrm{D}T}{\mathrm{D}t} = -\frac{1}{c_v}\sum_k e_k\frac{\mathrm{D}Y_k}{\mathrm{D}t} + \frac{R}{c_v}\frac{T}{\eta}\left[\frac{\rho_1 a_1}{\rho a^2}f\frac{\mathrm{d}U}{\mathrm{d}t} + \frac{w^2}{a^2}\mathrm{u}\kappa\right]_{\mathcal{S}}. \tag{11.218}$$

A more convenient form for comparing the relative size of the terms constributing to temperature change is

$$\frac{1}{T}\frac{\mathrm{D}T}{\mathrm{D}t} = \underbrace{-\frac{1}{c_v T}\sum_k e_k\frac{\mathrm{D}Y_k}{\mathrm{D}t}}_{\text{chemical}} \underbrace{+\frac{1}{\eta}\frac{R}{c_v}\frac{\rho_1 a_1}{\rho a^2}f\frac{\mathrm{d}U}{\mathrm{d}t}}_{\text{unsteady}} \underbrace{+\frac{1}{\eta}\frac{R}{c_v}\frac{w^2}{a^2}\mathrm{u}\kappa}_{\text{curvature}} \tag{11.219}$$

Models that compute temperature along pathlines are incomplete as we need to specify how to compute density and pressure and along the pathlines. One possibility is to simultaneously integrate the density and/or pressure using the shock change equation estimate of the time derivative and assuming the influence of the shock decay is constant through out the reaction zone. If both pressure and density are computed as a function of time, then temperature has to be determined from the equation of state $T(P, \rho, \mathbf{Y})$. Other possibilities are to fix the pressure or else fix the density and use the equation of state in the form $\rho(P, T, \mathbf{Y})$ or $P(\rho, T, \mathbf{Y})$. All of these approaches are ad hoc and inconsistent for an unsteady flow field. In general, an unsteady computation using the equations of reactive fluid motion (Eckett et al., 2000) is required to test the range of validity of these approximations.

11.14   Shock Waves with Vibrational Relaxation

The treatment of shock waves with vibration-translational energy exchange was inaugurated by Bethe and Teller (1945) using the theory of Landau and Teller Landau and Teller (1936) to describe how vibrational energy of a molecule evolves due to collisions with a surrounding gas molecules when the translational and vibrational motions are not in equilibrium. The concept is that a shock wave initially creates a highly non-equilibrium distribution of energy between translational (t), rotational (r), vibrational (v) and possibly electronic (e) quantum states of the molecules and the chemical composition. These non-equilibrium distributions evolve or relax over time to equilibrium distributions with a common temperature in a state of complete thermodynamic equilibrium. Collisions between atoms and molecules are responsible for redistributing the energy and chemical reactions, modeling the coupling between the molecular processes and the flow is the topic of classical high-temperature gas dynamics (Vincenti and Kruger, 1965, Clarke and McChesney, 1964, Zel'dovich and Raizer, 1966).

There is a hierarchy Kondratiev and Nikitin (1981) in the relaxation processes with increasing number of collisions Z or equivalently time τ required to obtain equilibrium for translational motions (τ_{tt}) (initially only the translational energy in the direction to normal to the shock wave is modified), translational-rotational (τ_{tr}), vibrational-vibrational τ_{vv}, translational-vibrational (τ_{tv}), and chemical (τ_{tc}). The energy in the translational motions equilibrates after a few collisions with but it can take 10^6 to 10^8 collisions or more to achieve vibrational-translational equilibrium and orders of magnitude more for chemical equilibrium (Rich and Treanor, 1970) for temperatures $< 10,000$ K. For this reason, it is typical in high-speed gas dynamics to consider the translation-rotational states to implicitly be in equilibrium and to treat explicity the vibrational-electronic and chemical nonequilibrium through models of energy transfer and chemical reaction.

The approach for vibration-translational energy exchange pioneered by Landau and Teller has been widely used in shock wave and hypersonic engineering applications (Park, 1990, Anderson, 1989)and continues to be used in computational fluid dynamic modeling (Candler and Nompelis, 2009). There are significant limitations (Nikitin and Troe, 2008) of the original Landau-Teller approach, there have been numerous efforts to remove these and extend the range of applicability (Oblapenko, 2018). The issues of energy exchange and coupling of vibration and chemical reaction have been extensively explored from a molecular viewpoint using Master equation methods (Adamovich, Igor V. et al., 1995b) with transition probabilities computed from kinetic theory (Adamovich, Igor V. et al., 1995a) and molecular simulations using quasi-classical trajectories on realistic potential energy surfaces (Bender et al., 2015)or direct molecular simulation (Valentini et al., 2015).

We start with the simplest formulation and use the classical Bethe-Teller formulation for the evolution of vibrational energy with empirical formulas for the relaxation time. The steady flow equations of motions for a quasi-one dimensional flow are as given previously:

$$\frac{\mathrm{d}}{\mathrm{d}x}(\rho \mathrm{w} A) = 0 \tag{11.220}$$

$$\rho \mathrm{w}\frac{\mathrm{d}\mathrm{w}}{\mathrm{d}x} = -\frac{\mathrm{d}P}{\mathrm{d}x} \tag{11.221}$$

$$\frac{\mathrm{d}h}{\mathrm{d}x} = -\mathrm{w}\frac{\mathrm{d}\mathrm{w}}{\mathrm{d}x} \tag{11.222}$$

The pressure is given by the ideal gas relation where the temperature T is interpreted as the temperature associated with translational motions only, which are not necessarily in equilibrium with the internal molecular degrees of freedom.

$$P = \rho RT \ . \tag{11.223}$$

The gas is considered to be an ideal gas mixture of K species with average molar mass $\mathcal{W}$ and gas constant $R = \mathcal{R}/\mathcal{W}$

$$\mathcal{W} = \left(\sum_{k=1}^{K} \frac{Y_k}{\mathcal{W}_k}\right)^{-1} \tag{11.224}$$

If the temperature is not too high, the translational and rotational motions are assumed to be in equilibrium and share the common temperature T. However, the vibrational and chemical reaction time scales are significantly longer and these processes are not in equilibrium. The time scales are in the following relationship

$$\tau_{tc} > \tau_{vt} > \tau_{vv} \gg \tau_{tr} , \tau_{tt} \tag{11.225}$$

The energy of each molecular species k is partitioned into the translational-rotational and the vibrational (at high temperatures excited electronic states are often lumped into this contribution) components

$$e_k = e_{tr,k}(T) + e_{v,k} , \tag{11.226}$$

and the translational-rotational energy is associated with a contant specific heat

$$\frac{\mathrm{d}e_{tr,k}}{\mathrm{d}T} = c_{v(tr),k} = \frac{f_{tr}}{2} R_k \tag{11.227}$$

where $R_k = \mathcal{R}/\mathcal{W}_k$ and the combined translation and rotation degrees of freedom are $f_{tr} = 5$ for linear molecules and $f_{tr} = 6$ for nonlinear molecules. The enthalpy of each species is

$$h_k = e_k + R_k T , \tag{11.228}$$

where T is the common temperature associated with translational and rotational motion.

$$h_k = e_{tr,k}(T) + R_k T + e_{v,k} , \tag{11.229}$$

$$h_k = h_{tr,k} + e_{v,k} , \tag{11.230}$$

where

$$h_{tr,k} = e_{tr,k}(T) + R_k T \tag{11.231}$$

The enthalpy of the gas mixture is written as the mass weighted average of the two contributions for each species

$$h = \sum_{k=1}^{K} Y_k h_{tr,k}(T) + \sum_{\{k_v\}} Y_k e_{v,k} , \tag{11.232}$$

where $\{k_v\}$ are the molecular species with significant vibrational excitation. These equations can be manipulated to form a set of ordinary differential equations which are the logical extension of the ZND model to treat vibrational nonequilibrium. The first step is to differentiate (11.223)

$$\frac{1}{P}\frac{\mathrm{d}P}{\mathrm{d}x} = \frac{1}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}x} + \sum_{k=1}^{K} \frac{\mathcal{W}}{\mathcal{W}_k}\frac{\mathrm{d}Y_k}{\mathrm{d}x} + \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}x} \tag{11.233}$$

Eliminating the pressure derivative with (11.221) and using (11.220) to eliminate the density derivative we obtain

$$\left(1 - \frac{\mathrm{w}^2}{RT}\right)\frac{1}{\mathrm{w}}\frac{\mathrm{d}\mathrm{w}}{\mathrm{d}x} = -\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}x} + \sum_{k=1}^{K} \frac{\mathcal{W}}{\mathcal{W}_k}\frac{\mathrm{d}Y_k}{\mathrm{d}x} + \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}x} . \tag{11.234}$$

The temperature derivative can be computed by differentiating (11.232)

$$dh = c_{p(tr)}\mathrm{d}T + \sum_{k=1}^{K} h_k \mathrm{d}Y_k + \sum_{\{k_v\}} Y_k \mathrm{d}e_{v,k} , \tag{11.235}$$

defining the average translational-rotational specific heat at constant pressure

$$c_{p(tr)} = \sum_{k=1}^{K} Y_k c_{p(tr),k} \; , \qquad c_{p(tr),ki} = c_{v(tr),k} + R_k \; , \tag{11.236}$$

and substituting into (11.222) we obtain

$$\frac{1}{T}\frac{dT}{dx} = -\frac{w}{c_{p(tr)}T}\frac{dw}{dx} - \frac{1}{c_{p(tr)}T}\sum_{\{k_v\}} Y_k \frac{de_{v,k}}{dx} - \frac{1}{c_{p(tr)}T}\sum_{k=1}^{K} h_i \frac{dY_k}{dx} \; . \tag{11.237}$$

Using the ideal gas law and the momentum equation, we obtain a parallel expression for density

$$\frac{1}{\rho}\frac{d\rho}{dx} = -\frac{w}{a_{tr}^2}\frac{dw}{dx} - \sum_{k=1}^{K}\left(\frac{\mathcal{W}}{\mathcal{W}_k} - \frac{h_k}{c_{p(tr)}T}\right)\frac{dY_k}{dx} + \frac{1}{c_{p(tr)}T}\sum_{\{k_v\}} Y_k \frac{de_{v,k}}{dx} \; , \tag{11.238}$$

where the vibrationally (and chemically) frozen sound speed is

$$a_{tr} = \sqrt{\gamma_{tr}RT} \qquad \gamma_{tr} = \frac{c_{p(tr)}}{c_{v(tr)}} \qquad c_{v(tr)} = c_{p(tr)} - R \; . \tag{11.239}$$

The vibrationally frozen ratio of specific heats assuming rotational-translational equilibrium is

$$\gamma_{tr} = 1 + 2/f_{tr} \; , \tag{11.240}$$
$$= 1.40 \quad \text{linear molecules} \, , \quad f_{tr} = 5 \; , \tag{11.241}$$
$$= 1.3\bar{3} \quad \text{nonlinear molecules} \, , \quad f_{tr} = 6 \; . \tag{11.242}$$

Substituting (11.237) into (11.234) we obtain the velocity evolution equation which is the extension of (11.47) to vibrational nonequilibrium

$$\frac{dw}{dx} = \frac{w}{1 - w^2/a_{tr}^2}\left[-\frac{1}{A}\frac{dA}{dx} + \sum_{k=1}^{K}\left(\frac{\mathcal{W}}{\mathcal{W}_k} - \frac{h_k}{c_{p(tr)}T}\right)\frac{dY_k}{dx} - \frac{1}{c_{p(tr)}T}\sum_{\{k_v\}} Y_k \frac{de_{v,k}}{dx}\right] \; . \tag{11.243}$$

Evolution equations can be derived for ρ and P from (11.243) and the conservation relation

$$\frac{d\rho}{dx} = -\frac{\rho}{1 - w^2/a_{tr}^2}\left[-\frac{w^2}{a_{tr}^2}\frac{1}{A}\frac{dA}{dx} + \sum_{k=1}^{K}\left(\frac{\mathcal{W}}{\mathcal{W}_k} - \frac{h_k}{c_{p(tr)}T}\right)\frac{dY_k}{dx} - \frac{1}{c_{p(tr)}T}\sum_{\{k_v\}} Y_k \frac{de_{v,k}}{dx}\right] \; , \tag{11.244}$$

$$\frac{dP}{dx} = \frac{-\rho w^2}{1 - w^2/a_{tr}^2}\left[-\frac{1}{A}\frac{dA}{dx} + \sum_{k=1}^{K}\left(\frac{\mathcal{W}}{\mathcal{W}_k} - \frac{h_k}{c_{p(tr)}T}\right)\frac{dY_k}{dx} - \frac{1}{c_{p(tr)}T}\sum_{\{k_v\}} Y_k \frac{de_{v,k}}{dx}\right] \; . \tag{11.245}$$

To complete the model, a set of chemical reaction rates and associated thermochemical models $h_k(T)$ and for each species must be supplied. The evolution of the species mass fractions is computed from

$$w\frac{dY_k}{dx} = \frac{\mathcal{W}_k \dot{\omega}_k}{\rho} \; . \tag{11.246}$$

where $\dot{\omega}_k$ are the net molar reaction rates for species k. The evolution of the vibrational energy for each relaxing species in $\{k_v\}$ is conventionally computed using the Bethe-Teller model

$$w\frac{de_{v,k}}{dx} = \frac{e_{v,k}^*(T) - e_{v,k}}{\tau_k} \quad k \in \{k_v\} \tag{11.247}$$

The quantities denoted by a superscript ( )* are the values assuming complete translation-rotation-vibration (trv) equilibrium, i.e., given by the NASA curve fits to a statistical mechanical computation of the partition function and evaluated at temperature T. The equilibrium energy content $e_{v,k}^*(T)$ is a notional concept representing the amount of vibrational energy that a molecule will have if it is in equilibrium with the surrounding gas at translational-rotational temperature T. The concept behind the Bethe-Teller model is that molecules with $e_v > e_v^*$ will on the average lose vibrational energy in collisions and those with $e_v < e_v^*$ will gain. The form of the rate law can be justified on the basis of molecular considerations (Zel'dovich and Raizer, 1966, Vincenti and Kruger, 1965) but is fundamentally empirical and an approximation that will break down if the vibrational non-equilibrium within and between molecules is too extreme.

The temperature T used to evaluate e_v^* is the temperature T that characterizes the translational and rotational motions of all species. This temperature is also consistent with the ideal gas law and can be computed from the current pressure and density as $T = P/\rho R$, because gas pressure is due to the center of mass energy and momentum of each molecule irrespective of the vibrational or rotational motion.

For a multi-species gas mixture, the relaxation times are estimated using the simple mixture rule

$$\tau_j = \sum_{\{k_v\}} X_k \Big/ \sum_{\{k_v\}} \frac{X_k}{\tau_{jk}} \quad j \in \{k_v\} \tag{11.248}$$

where X_k is the mole fraction of species k and $\{k_v\}$ is the subset of the species that are effective in collisions that result in vibrational relaxation of species j. Evaluating τ_j requires measured or estimated values for the binary relaxation times τ_{jk} for the collision of a dilute species j with a bulk gas consisting of species k. The values of the binary relaxation times are typically selected to fit the Landau-Teller model

$$\tau_{jk} = \frac{1}{P} 10^{-8} \exp(A_{jk}/T^{1/3} - B_{jk}) \,, \tag{11.249}$$

and the units of pressure are atm. The original correlation of Millikan and White (1963) for A and B is a useful guide

$$A_{jk} = 0.00116\mu_{jk}^{1/2}\Theta_v^{4/3} \,, \quad B_{jk} = 0.015\mu_{jk}^{1/3} \,, \quad \mu_{jk} = \frac{\mathcal{W}_j\mathcal{W}_k}{W_j + \mathcal{W}_k} \,, \tag{11.250}$$

but has limitations. Alternative empirical values for A and B for the species relevant to high-temperature air are given in Gehre et al. (2012). The function $e_{v,j}^*(T)$ is the equilibrium vibrational energy evaluated at temperature T and can be computed by standard statistical mechanics methods given the molecular parameters for the vibrational mode or directly from the Cantera thermodynamic data. A common approximation that is used at modest values of T is the rigid-rotator, harmonic oscillator (RRHO) model. For single mode of vibration, i.e., a diatomic molecule, the equilibrium vibrational energy is approximated as

$$e_{v(RRHO),k}(T) = \frac{R_k\Theta_k}{e^{\Theta_k/T} - 1} \,, \tag{11.251}$$

where $\Theta_k = \hbar\omega_k/k_B$ is the characteristic temperature computed from the vibrational frequency ω_k which corresponds to the energy quanta $\hbar\omega_k$ between sucessive vibrational levels in species k. Some nominal values for the diatomic molecules encountered in modeling air are

$$\Theta_{N_2} = 3390 \text{ K} \,, \quad \Theta_{O_2} = 2270 \text{ K}, \quad \Theta_{NO} = 2740 \text{ K} \,. \tag{11.252}$$

The corresponding equilibrium heat capacity is

$$c_{v(RRHO),k}(T) = R_k \left(\frac{\Theta_k}{T}\right)^2 \frac{e^{\Theta_k/T}}{(e^{\Theta_k/T} - 1)^2} \,. \tag{11.253}$$

The enthalpy of each species that is vibrationally relaxing has to be consistent with the standard heat of formation for that species as computed from the equilibrium enthalpy h_k^*

$$\Delta_f h_k^\circ = h_k^*(T^\circ) \text{ where } T^\circ = 298.15 \text{ K} \,. \tag{11.254}$$

If we use the RRHO model for vibration, the equilibrium enthalpy model expression for each relaxing species is approximated as

$$h^*_{RRHO,k}(T) = h^*_k(T^\circ) + c_{p(tr),k}(T - T^\circ) + e_{v(RRHO),k} \; , \tag{11.255}$$

where we have assumed that the contribution of the RRHO vibration model is negligible at T°.

Examples of the equilibrium and RRHO models of the specific heats of N_2, O_2 and NO are shown in Fig. 11.14. The RRHO model is a excellent approximation for N_2 until about 7000 K, at higher temperatures the specific heat increases due to the excitation of the rotational-vibrational modes in first electronic level $A^3\Sigma^+_u$. A similar effect occurs for NO with excitation of the $A^2\Sigma^+$ level above 5000 K. The dependence of O_2 specific heat on temperature departs from the RRHO model above 2000 K due to the excitation of two low-lying electronic states.

In order to account for the departure shown in Fig. 11.14 from the RRHO model, the equilibrium vibrational-electronic energy has to be directly computed from the equilibrium enthalpy h^*_k

$$e^*_{V,k}(T) = h^*_k(T) - \left[h_k(T^\circ) + c_{p(tr),j}(T - T^\circ)\right] \; . \tag{11.256}$$

Here we have adopted the use of a capital V to denote the combined electronic-vibrational energy, following the notation typically used in hypersonic flow as discussed in Gnoffo et al. (1989). This definition of e^*_V will include both nonideal effects in the vibrational-rotational model as well as the excitation of higher electronic states. Including higher electronic states in this fashion is ad hoc as these will in general have different relaxation parameters than the ground state but doing so will ensure that the solution approaches the correct equilibrium end state. The enthalpy for a nonequilibrium value of the vibrational-electronic energy $e_{V,k}$ is then computed as

$$h_k(T) = h^*_k(T) - e^*_{V,k}(T) + e_{V,k} \; . \tag{11.257}$$

The RRHO model is sometimes used to define an effective *vibrational temperature* T_v by setting the nonequilibrium vibrational energy for a species equal to the RRHO value and solving for temperature. From (11.251) we can find an explicit solution for T_v:

$$T_{v,j} = \frac{\Theta_j}{\ln(\Theta_j R_j / e_{v,j} + 1)} \; . \tag{11.258}$$

For molecules with multiple vibrational modes (CO_2), each mode may have different effective temperatures. If a mode has degeneracy g_i, this has to be accounted for in computing an effective temperature. If $e_{v,i}$ is the total vibrational energy in that mode, the appropriate expression for T_v in that case is:

$$T_{v,j} = \frac{\Theta_j}{\ln(g_i \Theta_j R_j / e_{v,j} + 1)} \; . \tag{11.259}$$

Due to the significant non-RRHO behaviour and the importance of electronic excitation, this is not a particularly useful way to define T_v. In the hypersonics research field, an effective vibration-electronic temperature T_V is usually defined (Gnoffo et al., 1989) by setting the nonequilibrium vibrational energy equal to the actual equilibrium energy e^*_V that is in excess of the value predicted from rotation, translation and the heat of formation as computed by (11.256). The value of T_V is found through the numerical solution of the defining relation

$$e^*_{V,j}(T_V) = e_{V,j} \; . \tag{11.260}$$

The simplest way to carry the solution to this implicit definition of T_V is by constructing a tabulation of $e^*_{V,j}(T)$ with sufficient resolution to enable accurate interpolation. The importance of using realistic energy values which include higher electronic states rather than the RRHO approximation for the ground state is shown in Fig. 11.15 in which the contributions to the enthalpy are displayed together with a comparison to the RRHO results for the ground state for N_2.
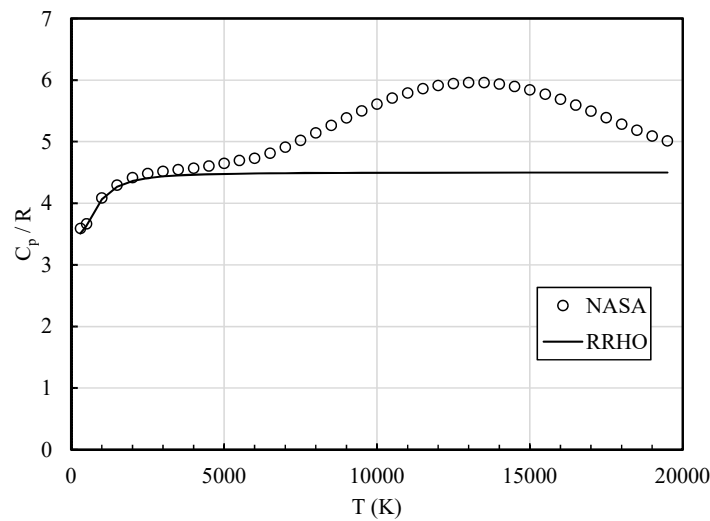
An alternative approach to formulating the evolution equations for the nonequilibrium model is to partition the enthalpy into thermal equilibrium and thermal non-equilibrium departure contributions using the
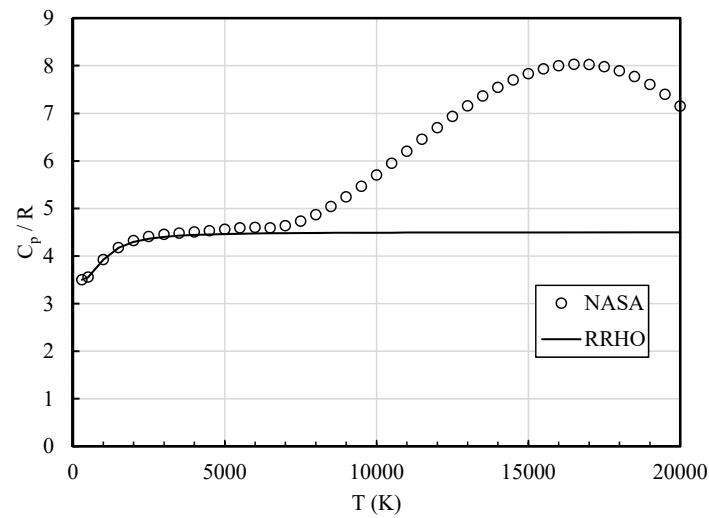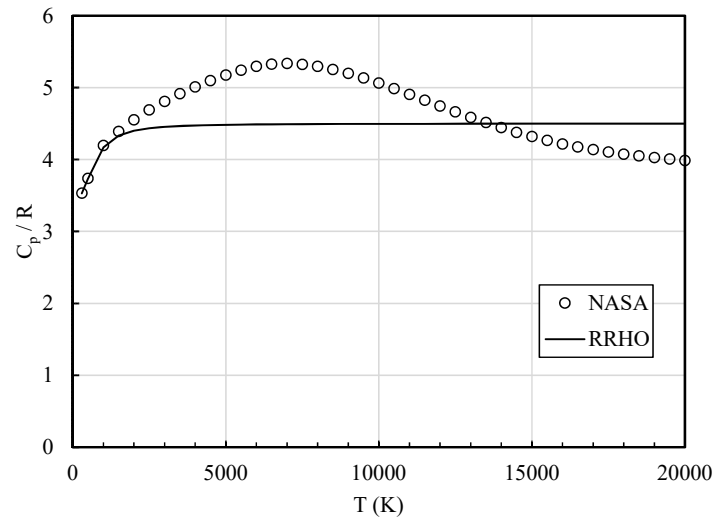
Figure 11.14: Comparison of RRHO model of specific heats with equilibrium values from the NASA compilation for (a) N2, $\Theta_v = 3352.3$ K (b) O2, $\Theta_v = 2238.7$ K, and (c) NO, $\Theta_v = 2697.7$ K.
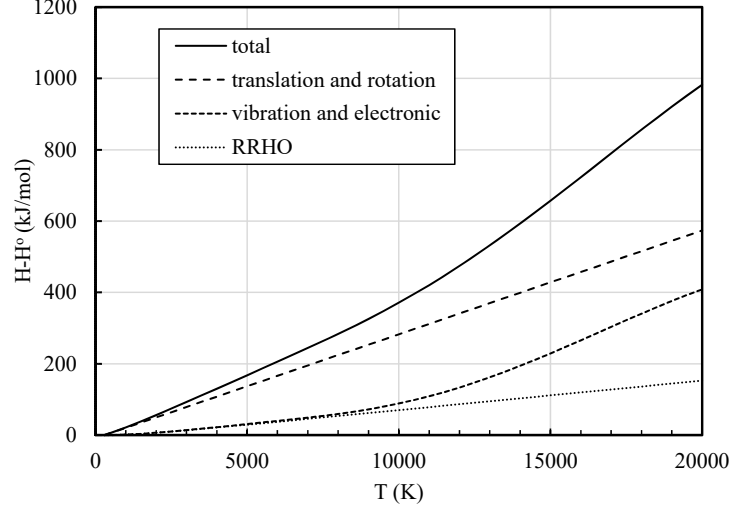
Figure 11.15: Comparison of RRHO model of internal energy for the ground state ($\Theta_v = 3352.3$ K) with equilibrium values from the NASA compilation for N_2.

combined vibrational-electronic energy e_V

$$h = \underbrace{\sum_{i=1}^{K} Y_i h_i^*(T)}_{\text{vt equilibrium}} + \underbrace{\sum_{\{j_i\}} Y_j \left(e_{V,j} - e_{V,j}^*(T) \right)}_{\text{departure from vt equilibrium}} \; , \tag{11.261}$$

$$= \sum_{i=1}^{K} Y_i h_i^*(T) + e_V - e_V^* , \tag{11.262}$$

where

$$e_V = \sum_{\{j_i\}} Y_j e_{V,j} \qquad e_V^* = \sum_{\{j_i\}} Y_j e_{V,j}^*(T) \; . \tag{11.263}$$

Following the derivation steps above, we obtain the following equivalent but alternative expression to (11.238) for the density evolution with distance

$$\frac{\mathrm{d}\rho}{\mathrm{d}x} = -\rho \left[\frac{\mathrm{w}}{a_*^2} \frac{\mathrm{d}\mathrm{w}}{\mathrm{d}x} + \sum_{i=1}^{K} \left(\frac{\mathcal{W}}{\mathcal{W}_i} - \frac{h_i^*}{c_P^* T} \right) \frac{\mathrm{d}Y_i}{\mathrm{d}x} + \frac{1}{c_P^* T} \frac{\mathrm{d}}{\mathrm{d}x} \left(e_V^* - e_V \right) \right] \; , \tag{11.264}$$

where the equilibrium (vt) and chemically frozen specific heat, sound speed and ratio of specific heats are defined as

$$c_P^* = \left(\frac{\mathrm{d}h^*}{\mathrm{d}T} \right)_{\mathbf{Y}} \; , \qquad a_* = \sqrt{\gamma^* R T} \; , \qquad \gamma^* = \frac{c_P^*}{c_v^*} \; . \tag{11.265}$$

The transformation from (11.238) to (11.264) is not obvious but very instructive in that by choosing to partition the enthalpy differently, we can identify more distinctly the contributions of v-t nonequilibrium to the variation in properties along the streamline. However, because v-t nonequilibrium significantly influences the reaction rates and consequently dY_i/dt, this segregation is illusory. Furthermore, as discussed in the next section, there are additional energy transfer (between vibration and translation-rotation modes) contributions associated with vibrational nonequilibrium that have been neglected up to this point.

Eliminating the velocity variation in favor of area change, the analog of (11.244) is

$$\frac{\mathrm{d}\rho}{\mathrm{d}x} = -\frac{\rho}{1 - \mathrm{w}^2/a_*^2}\left[-\frac{\mathrm{w}^2}{a_*^2}\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}x} + \sum_{i=1}^{K}\left(\frac{\mathcal{W}}{\mathcal{W}_i} - \frac{h_i^*}{c_P^*T}\right)\frac{\mathrm{d}Y_i}{\mathrm{d}x} + \frac{1}{c_P^*T}\frac{\mathrm{d}}{\mathrm{d}x}\left(e_V^* - e_V\right)\right] . \tag{11.266}$$

Converting the distance into time derivatives, this is

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{\rho}{1 - \mathrm{w}^2/a_*^2}\left[\underbrace{-\frac{\mathrm{w}^2}{a_*^2}\frac{\mathrm{w}}{A}\frac{\mathrm{d}A}{\mathrm{d}x}}_{\text{flow work}} + \underbrace{\sum_{i=1}^{K}\left(\frac{\mathcal{W}}{\mathcal{W}_i} - \frac{h_i^*}{c_P^*T}\right)\frac{\mathrm{d}Y_i}{\mathrm{d}t}}_{\dot{\sigma}_c \text{ chemical nonequilibrium}} + \underbrace{\frac{1}{c_P^*T}\frac{\mathrm{d}}{\mathrm{d}t}\left(e_V^* - e_V\right)}_{\dot{\sigma}_v \text{ vibrational-electronic nonequilibrium}}\right] . \tag{11.267}$$

In terms of the previous notation for the quasi-one dimensional flow model with chemical nonequilibrium the full set of equations is

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{\rho\mathrm{w}^2}{\eta}\left[\dot{\sigma}_c + \dot{\sigma}_v - \mathrm{w}\alpha\right] , \tag{11.268}$$

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{\rho}{\eta}\left[\dot{\sigma}_c + \dot{\sigma}_v - M^2\mathrm{w}\alpha\right] , \tag{11.269}$$

$$\frac{\mathrm{d}\mathrm{w}}{\mathrm{d}t} = \frac{\mathrm{w}}{\eta}\left[\dot{\sigma}_c + \dot{\sigma}_v - \mathrm{w}\alpha\right] , \tag{11.270}$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \mathrm{w} , \tag{11.271}$$

$$\frac{\mathrm{d}e_{V,j}}{\mathrm{d}t} = \frac{e_{V,j}^* - e_{V,j}}{\tau_j} \quad j \in \{j_i\} , \tag{11.272}$$

$$\frac{\mathrm{d}Y_i}{\mathrm{d}t} = \frac{\mathcal{W}_i\dot{\omega}_i}{\rho} \quad i = 1, 2, \ldots, K , \tag{11.273}$$

$$T = \frac{P}{\rho R} , \tag{11.274}$$

In general

$$\alpha = \frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}x} , \tag{11.275}$$

and for the special case of a shock layer ahead of a stagnation point flow, the Hornung-Stulov model is

$$\mathrm{w}\,\alpha = \frac{\mathrm{w}_2}{\Delta}\frac{\rho_2}{\rho} . \tag{11.276}$$

where Δ is the shock standoff distance. For quasi-steady, one-dimensional flow behind a shock wave propagating with constant speed, $\alpha = 0$ and the equations apply in the shock-fixed frame.

## Contributions to Density Change in Stagnation Point Flows

The estimation Wen and Hornung (1995), Hornung (1972), Stulov (1969) of shock stand-off distance Δ for nonequilibrium hypervelocity flows requires the computation of the average density $\overline{\rho_s}$ in the gas layer between the shock and the body. For example, the flow over a sphere of radius R_N correlation Hornung (1972) of stand-off distance to radius is

$$\frac{\Delta}{R_N} = 0.78\frac{\rho_\infty}{\overline{\rho_s}} \tag{11.277}$$

where ρ_∞ is the density of the freestream flow. The density ρ in the shocked gas layer may vary strongly as a function of distance x between the shock ($x = 0$) and the body ($x = \Delta$). Assuming the variation tangential
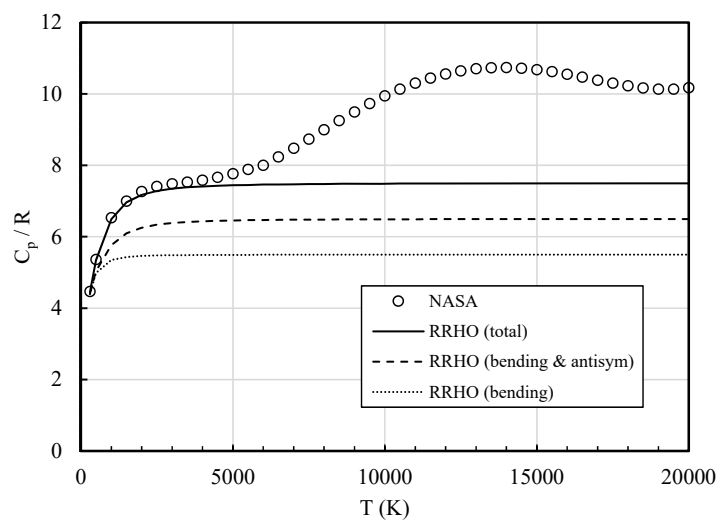
(a)
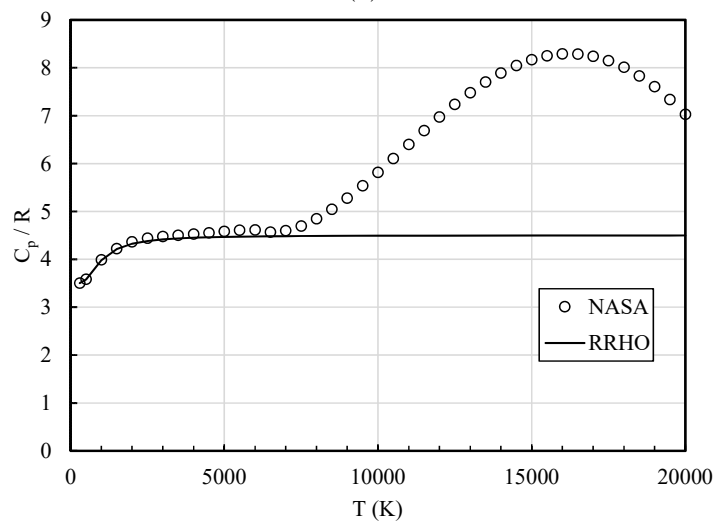
(b)

Figure 11.16: Comparison of RRHO model of specific heats with equilibrium values from the NASA compilation for (a) CO2, $\Theta_v = 959.7$ K (bending, $g = 2$), 1997 K (symmetric, $g = 1$), 3397 K (antisymmetric, $g = 1$). (b) CO, $\Theta_v = 3083.3$ K

is smaller than the variation normal to the shock, we can evaluate the average density along the stagnation streamline

$$\overline{\rho_s} = \frac{1}{\Delta} \int_0^\Delta \rho(x) \, \mathrm{d}x \,, \tag{11.278}$$

using the density computed with the quasi-one dimensional flow model. The individual contributions of flow work, chemical and vibrational nonequilibrium can be identified by integration of (11.264) to obtain the density.

$$\rho(x) = \rho(0) + \int_0^x \frac{\mathrm{d}\rho}{\mathrm{d}x} \, \mathrm{d}x' \,. \tag{11.279}$$

The approach to equilibrium at the stagnation point occurs over a very small distances adjacent to the body where w $\longrightarrow$ 0. Evaluation of the integral as written requires extraordinary spatial resolution near $x = 0$ to obtain accurate results. For this reason, the integration is best carried out by transforming to the particle time coordinate $t(x)$

$$\mathrm{d}x = \mathrm{w} \, \mathrm{d}t \,, \quad \frac{\mathrm{d}\rho}{\mathrm{d}x} = \frac{1}{\mathrm{w}} \frac{\mathrm{d}\rho}{\mathrm{d}t} \,, \quad \rho(x) = \int_0^{t(x)} \frac{\mathrm{d}\rho}{\mathrm{d}t} \, \mathrm{d}t' \,, \tag{11.280}$$

where

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \underbrace{-\rho \frac{\mathrm{w}}{a_*^2} \frac{\mathrm{d}w}{\mathrm{d}t}}_{\rho_t^f} + \underbrace{-\rho \sum_{i=1}^K \left(\frac{\mathcal{W}}{\mathcal{W}_i} - \frac{h_i^*}{c_P^* T} \right) \frac{\mathrm{d}Y_i}{\mathrm{d}t}}_{\rho_t^c} + \underbrace{-\rho \frac{1}{c_P^* T} \frac{\mathrm{d}}{\mathrm{d}t} \left(e_V^* - e_V \right)}_{\rho_t^v} \,. \tag{11.281}$$

The corresponding version based on (11.238) is

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\rho \frac{\mathrm{w}}{a_{tr}^2} \frac{\mathrm{d}w}{\mathrm{d}t} - \rho \sum_{i=1}^K \left(\frac{\mathcal{W}}{\mathcal{W}_i} - \frac{h_i}{c_{p(tr)} T} \right) \frac{\mathrm{d}Y_i}{\mathrm{d}x} + \frac{\rho}{c_{p(tr)} T} \sum_{\{j_i\}} Y_j \frac{\mathrm{d}e_{v,j}}{\mathrm{d}t} \,, \tag{11.282}$$

The density can be written as the sum of the integral of these four components

$$\rho(x) = \underbrace{\rho(0)}_{\rho_0} + \underbrace{\int_0^{t(x)} \rho_t^f(t') \, \mathrm{d}t'}_{\rho^f} + \underbrace{\int_0^{t(x)} \rho_t^c(t') \, \mathrm{d}t'}_{\rho^c} + \underbrace{\int_0^{t(x)} \rho_t^v(t') \, \mathrm{d}t'}_{\rho^v} \,, \tag{11.283}$$

and the average density can be expressed as a sum of four contributions from these components

$$\overline{\rho_s} = \rho_0 + \overline{\rho^f} + \overline{\rho^c} + \overline{\rho^v} \,, \tag{11.284}$$

where

$$\overline{\rho^f} = \frac{1}{\Delta} \int_0^\Delta \rho^f \, \mathrm{d}x \,, \quad \overline{\rho^c} = \frac{1}{\Delta} \int_0^\Delta \rho^c \, \mathrm{d}x \,, \quad \overline{\rho^v} = \frac{1}{\Delta} \int_0^\Delta \rho^v \, \mathrm{d}x \,. \tag{11.285}$$

Computing ρ_t^v

The term ρ_t^v requires special treatment

$$\rho_t^v = -\rho \frac{1}{c_P^* T} \frac{\mathrm{d}}{\mathrm{d}t} \left(e_V^* - e_V \right) \,, \tag{11.286}$$

$$= -\rho \frac{1}{c_P^* T} \sum_{\{k_i\}} \left(e_{V,k}^* \frac{\mathrm{d}Y_k}{\mathrm{d}t} + Y_k \frac{\mathrm{d}e_{V,k}^*}{\mathrm{d}T} \frac{\mathrm{d}T}{\mathrm{d}t} - e_{V,k} \frac{\mathrm{d}Y_k}{\mathrm{d}t} - Y_k \frac{\mathrm{d}e_{V,k}}{\mathrm{d}t} \right) \,. \tag{11.287}$$

The temperature (translational-rotational) time derivative is computed using the gas law and the derivatives for P, ρ, Y_k computed along the stagnation streamline

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{T}{P}\frac{\mathrm{d}P}{\mathrm{d}t} - \frac{T}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}t} - T\sum_{k=1}^{K}\frac{\mathcal{W}}{\mathcal{W}_k}\frac{\mathrm{d}Y_k}{\mathrm{d}t} \tag{11.288}$$

11.15   Modeling Nonequilibrium Processes

Realistic models of nonequilibrium energy exchange and chemical reaction in hypersonic flows require modeling vibrational-vibrational energy exchange as well as the interaction of vibrational nonequilibrium and chemical reaction (particularly dissociation). The starting point is a balance equation for mixture vibrational energy per unit volume. Neglecting molecular transport, the balance can be written in conservation form

$$\frac{\partial E_V}{\partial t} + \nabla \cdot (\mathbf{u}E_V) = \dot{Q}_{int} \, , \tag{11.289}$$

where E_V is the vibrational-electronic energy per unit volume

$$E_V = \rho e_V = \sum_{\{k_i\}} \rho_k e_{V,k} = \rho \sum_{\{k_i\}} Y_k e_{V,k} \, , \tag{11.290}$$

and the right hand side represents the energy exchange with the translational and rotational motions. The energy exchange consists of the sum of vibration-translational (VT) and vibrational-chemical (VC) contributions

$$\dot{Q}_{int} = \dot{Q}_{VT} + \dot{Q}_{VC} \, , \tag{11.291}$$

and the conventional engineering models for these terms are the Landau-Teller model for VT processes

$$\dot{Q}_{VT} = \sum_{\{k_i\}} \frac{E_{V,k}^*(T) - E_{V,k}}{\tau_k} \, , \tag{11.292}$$

and the Treanor-Marrone (Treanor and Marrone, 1962, Marrone and Treanor, 1963) model for QC processes associated with dissociation-recombination or biomolecular exchange reactions

$$\dot{Q}_{VC} = N_A \sum_{\{k_i\}} \sum_{j} \left[\tilde{G}_{kj}\dot{C}_{kj} - \tilde{E}_{kj}\dot{D}_{kj} \right] \tag{11.293}$$

The quantity $\tilde{E}_{kj}$ is the energy loss per molecule reacting due to the forward reaction (e.g., dissociation) and $\tilde{G}_{kj}$ is the energy gain due to the reverse reaction (e.g., recombination) for species k and reaction j. The terms $\dot{C}_{kj}$ and $\dot{D}_{kj}$ represent the forward reaction and reverse reaction rates (kmol m^{-3} s^{-1}) for species k and reaction j defined in Chapter 10. Expanding the vibrational energy into individual components, differentiating and simplifying with the continuity equation we obtain

$$\frac{\partial E_V}{\partial t} + \nabla \cdot (\mathbf{u}E_V) = \rho \sum_{\{k_i\}} Y_k \frac{\mathrm{D}e_{V,k}}{\mathrm{D}t} + \sum_{\{k_i\}} e_{V,k}\mathcal{W}_k\dot{\omega}_k \tag{11.294}$$

$$= \rho \sum_{\{k_i\}} Y_k \frac{\mathrm{D}e_{V,k}}{\mathrm{D}t} + \rho \sum_{\{k_i\}} e_{V,k}\frac{\mathrm{D}Y_k}{\mathrm{D}t} \tag{11.295}$$

To put the terms in the vibrational energy balance equation on an equal footing, we transform the energy gains and losses to a mass basis,

$$\tilde{g}_{kj} = \frac{N_A\tilde{G}_{kj}}{\mathcal{W}_k} \, , \tag{11.296}$$

$$\tilde{e}_{kj} = \frac{N_A\tilde{E}_{kj}}{\mathcal{W}_k} \, , \tag{11.297}$$

and the creation and destruction rates (10.66) can be written in terms of the corresponding mass fraction derivatives

$$\dot{C}_{kj} = \frac{\rho}{\mathcal{W}_k} \left. \frac{\mathrm{D}Y_k}{\mathrm{D}t} \right|_{\dot{C}_j} , \tag{11.298}$$

$$\dot{D}_{kj} = \frac{\rho}{\mathcal{W}_k} \left. \frac{\mathrm{D}Y_k}{\mathrm{D}t} \right|_{\dot{D}_j} . \tag{11.299}$$

With these definitions, we can rewrite the chemistry-vibration exchange term as

$$\dot{Q}_{VC} = \rho \sum_{\{k_i\}} \sum_j \left[\tilde{g}_{kj} \left. \frac{\mathrm{D}Y_k}{\mathrm{D}t} \right|_{\dot{C}_j} - \tilde{e}_{kj} \left. \frac{\mathrm{D}Y_k}{\mathrm{D}t} \right|_{\dot{D}_j} \right] . \tag{11.300}$$

The vibrational-translation exchange term can be written

$$\dot{Q}_{VT} = \rho \sum_{\{k_i\}} \frac{Y_k}{\tau_k} \left(e^*_{V,k}(T) - e_{V,k} \right) . \tag{11.301}$$

With these definitions, the vibrational energy balance can be written

$$\sum_{\{k_i\}} Y_k \frac{\mathrm{D}e_{V,k}}{\mathrm{D}t} = \sum_{\{k_i\}} \frac{Y_k}{\tau_k} \left(e^*_{V,k}(T) - e_{V,k} \right) + \sum_{\{k_i\}} \sum_j \left[(\tilde{g}_{kj} - e_{V,k}) \left. \frac{\mathrm{D}Y_k}{\mathrm{D}t} \right|_{\dot{C}_j} - (\tilde{e}_{kj} - e_{V,k}) \left. \frac{\mathrm{D}Y_k}{\mathrm{D}t} \right|_{\dot{D}_j} \right] \tag{11.302}$$

If we neglect the last term and assume that the V-V exchange is sufficiently rapid, all the molecules will have a common vibrational temperature T_V and the vibrational energy can be evaluated as

$$e_{V,k} = e^*_{V,k}(T_V) \tag{11.303}$$

and the vibrational energy written as

$$\sum_{\{k_i\}} Y_k \frac{\mathrm{d}e^*_{V,k}}{\mathrm{d}T} \frac{\mathrm{D}T_V}{\mathrm{D}t} = \sum_{\{k_i\}} \frac{Y_k}{\tau_k} \left(e^*_{V,k}(T) - e_{V,k} \right) . \tag{11.304}$$

Define the average vibrational specific heat as

$$C^*_{v,V} = \sum_{\{k_i\}} Y_k \frac{\mathrm{d}e^*_{V,k}}{\mathrm{d}T} , \tag{11.305}$$

and the balance equation for vibrational energy is transformed into an evolution equation for vibrational temperature

$$\frac{\mathrm{D}T_V}{\mathrm{D}t} = \frac{1}{C^*_{v,V}} \sum_{\{k_i\}} \frac{Y_k}{\tau_k} \left(e^*_{V,k}(T) - e_{V,k} \right) . \tag{11.306}$$

The computation of the vibrational energy source term in the reaction zone structure equations is simplified. For the formulation using frozen thermodynamic properties we have

$$\dot{\sigma}_V = -\frac{1}{c_{p(tr)}T} \sum_{\{j_i\}} Y_j \frac{\mathrm{d}e_{V,j}}{\mathrm{d}t} , \tag{11.307}$$

$$= -\frac{1}{c_{p(tr)}T} C^*_{v,V} \frac{\mathrm{d}T_V}{\mathrm{d}t} . \tag{11.308}$$

For the formulation using equilibrium thermodynamic properties

$$\dot{\sigma}_V = \frac{1}{c_P^* T} \frac{\mathrm{d}}{\mathrm{d}t} \left(e_V^* - e_V \right) \; , \tag{11.309}$$

which can be simplified using (11.287)

$$\dot{\sigma}_V = \frac{1}{c_P^* T} \left[C_{v,V}^*(T) \frac{\mathrm{d}T}{\mathrm{d}t} - C_{v,V}^*(T_V) \frac{\mathrm{d}T_V}{\mathrm{d}t} + \sum_{\{j_i\}} \frac{\mathrm{d}Y_j}{\mathrm{d}t} \left(e_{V,j}^*(T) - e_{V,j}^*(T_V) \right) \right] \; . \tag{11.310}$$

THIS SECTION UNFINISHED

DRAFT

Part IV

Toolbox Software

The basic functions of the toolbox software, input and output variables are described for each program. The demonstration programs are listed together a brief description.

Chapter 12

Functions

A summary is provided of the major functions of the toolbox. The basic syntax, input, and output are provided for MATLAB and Python. For each function, links are given to both the MATLAB and Python implementations. See the website to download and install the complete software package. There are a number of auxiliary files that are required but are not described here.

Core Functions

The core functions for MATLAB are in subdirectories in the `SDToolbox` subdirectory of the MATLAB toolbox directory, for Python the functions are contained within Python scripts in the `sdtoolbox` subdirectory of the Python `site-packages` directory. Each function contains a header that describes the input and output variables as well as optional parameters.

PostShock CJ speed, frozen and equilibrium state following shock waves

CJSpeed Calculates CJ detonation velocity for a given pressure, temperature, and composition and gas object.

CJSpeed.m

```
FUNCTION SYNTAX:
    If only CJ speed required:
    U_cj = CJspeed(P1,T1,q,mech)
    If full output required:
    [U_cj, curve, goodness, dnew, plot_data] = CJspeed(P1,T1,q,mech)

INPUT:
    P1 = Initial Pressure (Pa)
    T1 = Initial Temperature (K)
    q = string of reactant species mole fractions
    mech = cti file containing mechanism data (i.e. 'gri30.cti')

OUTPUT:
    cj_speed = CJ detonation speed (m/s)
    curve = cfit object of LSQ fit
    goodness = goodness of fit statistics for curve
    dnew = CJ density ratio
    plot_data = structure containing additional parameters to use
```

CJSpeed in postshock.py

```
FUNCTION SYNTAX:
    If only CJ speed required:
    cj_speed = CJspeed(P1,T1,q,mech)
    If full output required:
    [cj_speed,R2,plot_data] = CJspeed(P1,T1,q,mech,fullOutput=True)

INPUT:
    P1 = initial pressure (Pa)
    T1 = initial temperature (K)
    q = reactant species mole fractions in one of Cantera's recognized formats
    mech = cti file containing mechanism data (e.g. 'gri30.cti')

OPTIONAL INPUT:
    fullOutput = set True for R-squared value and pre-formatted plot data
                  (the latter for use with sdtoolbox.utilities.CJspeed_plot)

OUTPUT
    cj_speed = CJ detonation speed (m/s)
    R2 = R-squared value of LSQ curve fit (optional)
    plot_data = tuple (rr,w1,dnew,a,b,c)
                  rr = density ratio
                  w1 = speed
                  dnew = minimum density
                  a,b,c = quadratic fit coefficients
```

PostShock_eq Calculates equilibrium post-shock state for a specified shock velocity, pressure, temperature, and composition and gas object.

PostShock_eq.m

```
FUNCTION SYNTAX:
    [gas] = PostShock_eq(U1,P1,T1,q,mech)

INPUT:
    U1 = shock speed (m/s)
    P1 = initial pressure (Pa)
    T1 = initial temperature (K)
    q = reactant species mole fractions in one of Cantera's recognized formats
    mech = cti file containing mechanism data (e.g. 'gri30.cti')

OUTPUT:
    gas = gas object at equilibrium post-shock state
```

PostShock_eq in postshock.py

```
FUNCTION SYNTAX:
    gas = PostShock_eq(U1,P1,T1,q,mech)

INPUT:
    U1 = shock speed (m/s)
    P1 = initial pressure (Pa)
    T1 = initial temperature (K)
    q = reactant species mole fractions in one of Cantera's recognized formats
    mech = cti file containing mechanism data (e.g. 'gri30.cti')

OUTPUT:
```

```
            gas = gas object at equilibrium post-shock state
```

PostShock_fr Calculates frozen post-shock state for a specified shock velocity, pressure, temperature, and composition and gas object.

PostShock_fr.m

```
FUNCTION SYNTAX:
    [gas] = PostShock_fr(U1,P1,T1,q,mech)

INPUT:
    U1 = shock speed (m/s)
    P1 = initial pressure (Pa)
    T1 = initial temperature (K)
    q = reactant species mole fractions in one of Cantera's recognized formats
    mech = cti file containing mechanism data (e.g. 'gri30.cti')

OUTPUT:
    gas = gas object at frozen post-shock state
```

PostShock_fr in postshock.py

```
FUNCTION SYNTAX:
    [gas] = PostShock_fr(U1,P1,T1,q,mech)

INPUT:
    U1 = shock speed (m/s)
    P1 = initial pressure (Pa)
    T1 = initial temperature (K)
    q = reactant species mole fractions in one of Cantera's recognized formats
    mech = cti file containing mechanism data (e.g. 'gri30.cti')

OUTPUT:
    gas = gas object at frozen post-shock state
```

Reflections Calculated state behind a shock or detonation after reflection from a rigid surface.

reflected_eq Calculates equilibrium post-reflected-shock state.

reflected_eq.m

```
FUNCTION SYNTAX:
    [p3,UR,gas3] = reflected_eq(gas1,gas2,gas3,UI)

INPUT:
    gas1 = gas object at initial state
    gas2 = gas object at post-incident-shock state (already computed)
    gas3 = working gas object
    UI = incident shock speed (m/s)

OUTPUT:
    p3 = post-reflected-shock pressure (Pa)
    UR = reflected shock speed (m/s)
    gas3 = gas object at equilibrium post-reflected-shock state
```

reflected_eq in reflections.py