

A MULTIVIBRATIONAL MODE RELAXATION SCHEME FOR TWO-TEMPERATURE THERMOCHEMICAL STATE MODELS

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ABSTRACT

An approach to estimate the effective vibrational relaxation time for polyatomic molecules under the context of two-temperature thermochemical state model is proposed. Landau-Teller vibrational relaxation equation is used as a basis, and vibrational energies are estimated with partition energy functions assuming harmonic oscillator model. A special weighting procedure is presented, and effective vibrational relaxation time is derived. A series of numerical experiments with CO₂ and NH₃ mixtures is performed, and the aeroheating results are presented. The results of CO₂ environment simulations are compared with the vibrational relaxation model of Park et al. [JTHT, 8(1994), pp. 9–23]. The simulations are also conducted with a modified Landau-Teller expression.

Index Terms— Vibrational relaxation time, Park model, Two-temperature, Thermochemical nonequilibrium, Landau-Teller, Hypersonics

1. INTRODUCTION

In high speed entry, the molecules are excited enough to push the gas to a thermal nonequilibrium state. An important parameter in simulating such thermochemical nonequilibrium states is the vibrational electronic energy exchange that depends on a so-called vibrational relaxation time. Typically, the vibrational relaxation time is estimated from semi-empirical correlations such as the one proposed by Milikan and White [1] that provides an estimation to the vibrational relaxation time due to species inelastic collisions at low temperatures (< 8,000 K). For higher temperatures, Park [2] suggested a correction that accounts for their elastic collisions.

Diatomic molecules have single vibrational characteristic temperature and thus, typical semi-empirical correlations are sufficient to estimate the vibrational relaxation time. For polyatomic molecules, such as NH₃ (Ammonia) and CO₂, however, there are more than one vibrational frequencies and

multiple vibrational characteristic temperatures, and therefore, semi-empirical relations that account for only single vibrational temperature cannot be used. Park et al. [3] developed a model for CO₂-N₂ mixtures that directly provides coefficients for the Milikan-White relaxation equation. This model is specific to CO₂. In the present work, an approach to estimate the effective vibrational relaxation time for general polyatomic molecules under the context of two-temperature thermochemical state model is proposed. The method uses Landau-Teller vibrational relaxation equation that approximates vibrational energies using partition energy functions as a basis. A lump sum, effective, vibrational relaxation time is then derived through a special weighting procedure. The results show that the proposed model yields the vibrational relaxation model of Park et al. [3] for CO₂ environment. The multivibrational relaxation model is then applied to NH₃, for which no vibrational relaxation model was available, and the results are discussed in detail.

2. PRELIMINARY

For thermally reacting nonequilibrium flows, the energy exchange between the translational and vibrational energy modes may be significant. In computational fluid dynamic (CFD) simulations, this energy exchange is often considered as a source term in the rate of change of vibrational energy equation in form of the Landau-Teller expression [4]:

$$Src^{T \leftrightarrow V} \equiv \frac{dE_v}{dt} = \sum_{s=\text{molecule}} \rho_s \frac{ev_s^0(T) - ev_s(T)}{\tilde{\tau}_s}, \quad (1)$$

where ρ_s are the species density, ev_s are the species vibrational energies per unit mass, ev_s^0 are the species equilibrium vibrational energies per unit mass, and $\tilde{\tau}_s$ are the *averaged* species vibrational relaxation times. Vibrational relaxation time generally depends on collision partners, but such dependency is imbedded implicitly in $\tilde{\tau}_s$ through a proper averaging procedure.

The Landau-Teller relation describes the rate at which vibrational energy approaches equilibrium vibrational energy.

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The above formula is routinely approximated in the multitemperature nonequilibrium flow simulations by assuming that the vibrational energy is a function of vibrational temperature, $ev_s(T_{ve})$, rather than the temperature, $ev_s(T)$. Therefore, the following formula is employed to describe translational-vibrational energy exchange modes:

$$Src^{T \leftrightarrow V} \equiv \frac{dE_v}{dt} = \sum_{s=\text{molecule}} \rho_s \frac{ev_s^0(T) - ev_s(T_v)}{\tilde{\tau}_s}. \quad (2)$$

In the two-temperature mode of Gnoffo et al. [5], the vibrational and electronic energies are lumped together, and as a result the ev_s are defined as species vibrational-electronic energies per unit mass. Gnoffo's two-temperature model is also used in the present study.

The averaged species vibrational relaxation time, $\tilde{\tau}_s$, depends on collision partners, and can be expressed as a function of vibrational relaxation time of a molecule s in a medium r ; i.e.,

$$\tilde{\tau}_s = f(\tau_{sr}). \quad (3)$$

This is typically done through an appropriate averaging applied on τ_{sr} . Gnoffo et al. [5] suggested a weighted arithmetic mean approach to be applied on MW vibrational relaxation time; i.e.,

$$\tilde{\tau}_s^{\text{MW}} = \frac{\sum_{r \neq e^-} n_r \tau_{sr}^{\text{MW}}}{n = \sum_{r \neq e^-} n_r} = \frac{\sum_{r \neq e^-} \frac{\rho_r}{\text{Mw}_r} \tau_{sr}^{\text{MW}}}{\sum_{r \neq e^-} \frac{\rho_r}{\text{Mw}_r}}. \quad (4)$$

A better and more consistent approach, which also supports the Boltzmann kinetic theory, is to employ a weighted harmonic mean; i.e.,

$$\tilde{\tau}_s^{\text{MW}} := \frac{\sum_{r \neq e^-} n_r}{\sum_{r \neq e^-} n_r / \tau_{sr}^{\text{MW}}} = \frac{\sum_{r \neq e^-} \frac{\rho_r}{\text{Mw}_r}}{\sum_{r \neq e^-} \frac{\rho_r}{\text{Mw}_r \tau_{sr}^{\text{MW}}}}. \quad (5)$$

Note that $\tilde{\tau}_s^{\text{MW}}$ obtained through the weighted harmonic mean is always less than the relaxation time evaluated with the weighted arithmetic mean because $\sum_i A_i B_i \leq \sum_i A_i \sum_i B_i$.

Millikan and White [6] provided a ground breaking empirical relation for τ_{sr} correlating then available measurements (mostly diatomic species) into a simple straight line, in logarithmic scale, as

$$p\tau_{sr}^{\text{MW}} = \exp \left[a_{sr}(T^{-1/3} - b_{sr}) - 18.42 \right], \quad (6)$$

where the Millikan-White (MW) vibrational relaxation τ_{sr}^{MW} can be described as the vibrational relaxation time of a molecule s in a medium r species gas at a total pressure p . In this relation, a_{sr} and b_{sr} are, the MW relaxation constants and are given as

$$\begin{aligned} a_{sr} &= 0.00116 \mu_{sr}^{1/2} \theta_{v,s}^{4/3} \\ &= 0.00116 \mu_{ss}^{1/2} \theta_{v,s}^{4/3} \left(\frac{\mu_{sr}}{\mu_{ss}} \right)^{1/2}, \end{aligned} \quad (7)$$

$$b_{sr} = 0.015 \mu_{sr}^{1/4}, \quad (8)$$

where $\mu_{sr} = \text{Mw}_s \text{Mw}_r / (\text{Mw}_s + \text{Mw}_r)$ is the reduced mass, Mw_s are species molecular weights, and $\theta_{v,s}$ are the species vibrational characteristic temperatures.

The accuracy of Eq. (6) has been characterized by Millikan and White [6] to be within 50% of experimental values for most species, but also noted that this relation could give values that are off by as much as 5 folds, particularly at low temperatures. Equation (6) does not account for the effects of elastic collisions. Including the effects of elastic collision cross section proposed by Park [2, 3] leads to the following total vibrational relaxation time

$$\tilde{\tau}_s = \tilde{\tau}_s^{\text{MW}} + \tilde{\tau}_s^{\text{Park}}, \quad (9)$$

where Park's elastic correction can be expressed, after some algebra, in a more practical form as

$$\begin{aligned} \tilde{\tau}_s^{\text{Park}} &= \frac{1}{\left(\sum_{r \neq e^-} n_r \right) \sqrt{8kT/\pi m_s} \sigma' (50,000/T)^2}, \\ &= \frac{1}{N_A \underbrace{\sqrt{8kN_A/\pi}}_{\sqrt{8R/\pi}} \left(\sum_{r \neq e^-} \rho_r / \text{Mw}_r \right) \sqrt{T/\text{Mw}_s} \sigma' (50,000/T)^2}, \\ &= \frac{1.1412 \times 10^{-29}}{\left(\sum_{r \neq e^-} \rho_r / \text{Mw}_r \right) \sqrt{T/\text{Mw}_s} \sigma' (50,000/T)^2}, \\ &= 5.5648 \times 10^{-39} \frac{T \sqrt{T \text{Mw}_s}}{\sigma' \sum_{r \neq e^-} \rho_r / \text{Mw}_r}, \end{aligned} \quad (10)$$

where m_s are the species mass, N_A is the Avogadro constant, k is the Boltzmann constant, R is the universal gas constant, and σ' is regarded as a tuning parameter for fitting existing experimental data but often chosen arbitrarily, typically 10^{-20} m^2 [7, 2, 3] or 10^{-21} m^2 [7], due to a lack of experimental data.

Equation (9) along with Eqs. (6) and (10) requires temperature, T , and species vibrational characteristic temperature, $\theta_{v,s}$, to be closed. Diatomic molecules have single characteristic temperature, and so Eq. (9) and the vibrational-translational energy exchange source term can be computed with no difficulty. For polyatomic molecules such as NH_3 (Ammonia) and CO_2 (Carbon dioxide), however, there are more than one vibrational frequencies, ν , and thus, multiple vibrational characteristic temperatures are present:

$$\theta_v = \frac{h\nu}{k}, \quad (11)$$

where h and k are, respectively, the Plank and Boltzmann constants. Often, the vibrational frequencies are given in unit $[\text{cm}^{-1}]$ and therefore Eq. (11) may be reduced to the following simplified relation:

$$\theta_v [\text{K}] = 1.43877687750393380 \nu [\text{cm}^{-1}]. \quad (12)$$

using the latest published physical constants available in the National Institute of Standard and Technology (NIST) [8].

Carbon dioxide (CO₂) has three characteristic vibrational frequencies corresponding to two degenerate bending modes, the symmetric stretching, and the antisymmetric stretching. These are given in Table 1, where the vibrational charac-

Table 1. CO₂ Vibrational frequencies [9].

ν [cm ⁻¹]	θ_v [K]	mode type	degeneracy [#]
667	959.66	bending	2
1333	1917.89	symmetric stretching	1
2349	3379.69	antisymmetric stretching	1

teristic temperatures are evaluated from their corresponding frequencies using Eq. (12). Similarly, Ammonia (NH₃) has four characteristic vibrational frequencies [9], corresponding to the symmetric deformation, two degenerate deformation, the symmetric stretching, and two degenerate stretching. The NH₃ vibrational frequencies along with calculated characteristic vibrational temperatures are tabulated in Table 2.

Table 2. NH₃ Vibrational frequencies [9].

ν [cm ⁻¹]	θ_v [K]	mode type	degeneracy [#]
950	1366.84	symmetric deformation	1
1627	2340.89	degenerate deformation	2
3337	4801.19	symmetric stretching	1
3444	4955.15	degenerate stretching	2

For CO₂ environment, Park et al. [3] suggested a series of new MW relaxation time coefficients a_{sr} and b_{sr} that are constant and independent of CO₂ vibrational characteristic temperatures. These constant coefficients are tailored for two-temperature simulations in the Martian atmosphere consists of CO₂, CO, N₂, C, O, N, Ar species. Due to its simplicity, the Park vibrational relaxation model [3] is widely used [10, 11, 12, 13]. One of the objectives of the present study is to extend this model to other polyatomic molecules and compare the Park model with the multivibrational mode relaxation scheme proposed here.

For NH₃ environment, which is a typical species in reaction control system (RCS) nozzles of many spacecrafts [11, 14, 15], there exists no Park-like model that can be used as MW relaxation time coefficients. Thus, the RCS exhaust is typically treated as a single species with mixture molecular weights and transport properties [15]. In the present study, we present a multivibrational relaxation scheme that accounts for all vibrational frequencies of species.

3. MULTIVIBRATIONAL MODE

RELAXATION SCHEME

The objective is to develop a simple procedure to incorporate multiple characteristic vibrational frequencies into the vibrational relaxation time. This is explained by first revisiting a lump-sum approach, where either vibrational relaxation times are estimated with constants that are independent of vibrational characteristic temperatures, or simply a collision independent vibrational characteristic temperature is used and inserted in the classical MW relaxation coefficients. The goal is to find a formulation that resembles a lump-sum approach and can be adopted to accept polyatomic molecules with multiple characteristic vibrational frequencies. The benefit of this strategy is that the existing codes such as LAURA [16, 17] can take advantage of the proposed methodology and adopt the new scheme with less effort.

3.1. A lump-sum approach – revisited

Consider the Landau-Teller formulation, Eq. (2), for diatomic molecules, and reexpress it in terms of a difference in temperature and vibrational-electronic temperature as

$$Src^{T \leftrightarrow V} \equiv \frac{dE_v}{dt} \simeq \sum_{s=\text{molecule}} \rho_s \frac{c_{vv,s} (T - T_{ve})}{\tilde{\tau}_s}, \quad (13)$$

where $c_{vv,s}$ are the vibrational-electronic component of species specific heats. This expression is more consistent with direct derivation from the Boltzmann kinetic theory and the zeroth order Chapman-Enskog expansion [18], and may also be obtained directly from Eq. (2) by assuming that the difference between the equilibrium vibrational energy and the vibrational energy can be approximated as

$$dev_s := ev_s^0 - ev_s \simeq c_{vv,s} (T - T_{ve}). \quad (14)$$

Equation (13) can also be further simplified and rewritten in terms of the mixture vibrational-electronic specific heat capacity, c_{vv} , and an *effective* relaxation time, $\bar{\tau}$, as

$$Src^{T \leftrightarrow V} \equiv \frac{dE_v}{dt} \simeq \frac{\rho c_{vv} (T - T_{ve})}{\bar{\tau}}, \quad (15)$$

where ρ is the mixture density, and the *effective* vibrational relaxation time is evaluated, after some algebra, as

$$\bar{\tau} = \frac{\sum_{s=\text{molecule}} \rho_s c_{vv,s}}{\sum_{s=\text{molecule}} \rho_s c_{vv,s} / \tilde{\tau}_s} \simeq \frac{\sum_{s=\text{molecule}} \rho_s / \text{Mw}_s}{\sum_{s=\text{molecule}} \rho_s / (\text{Mw}_s \tilde{\tau}_s)}, \quad (16)$$

where the species vibrational specific heat capacity is assumed to be proportional to the species gas constant, R_s .

The vibrational relaxation source term, Eq. (15), is now very concise and efficient with virtually no explicit species dependent terms. Note that the $\tilde{\tau}_s$ is implicitly dependent on species vibrational relaxation time, and has to be evaluated by accounting for all of the species collision partners. That is, the

first term of Eq. (9) must be evaluated through an appropriate averaging procedure as given in Eq. (5).

In summary, the lump-sum procedure is as follows:

- evaluate Park's relaxation correction term, $\tilde{\tau}_s^{\text{Park}}$, using Eq. (10)
- estimate the Millkan-White averaged vibrational relaxation time, $\tilde{\tau}_s^{\text{MW}}$, using Eq. 5 along with Eq. (6)
- Sum the previous two relaxation times: i.e., Eq. (9)
- evaluate the *effective* vibrational relaxation time, $\bar{\tau}$, using Eq. (16)
- estimate the translational-vibrational energy exchange source term, $\text{Src}^{T \leftrightarrow V}$, from Eq. (15)

The lump-sum procedure outlined above is only applicable for species with single-mode vibrational characteristic temperature or for Park-model CO₂ species.

3.2. Multivibrational mode approach

In Sec. 3.1, a lump-sum procedure is presented and the Landau-Teller equation was expressed in a compact form, Eq. (15), with an *effective* vibrational relaxation time, Eqs. (16). Here, we present a process that takes the same compact form of the Landau-Teller equation and extend the *effective* vibrational relaxation time to also be a function of multimode characteristic vibrational frequencies.

The Landau-Teller equation presented in Eq. (2) is vibrational mode independent. To account for the vibrational energy mode, we replace the vibrational energy difference in the Landau-Teller equation with the sum of vibrational energy difference for each mode to arrive at the following vibrational-translational energy exchange source term:

$$\begin{aligned} \text{Src}^{T \leftrightarrow V} &= \sum_{s=\text{molecule}} \rho_s \left(\sum_{m=\text{mode}} \frac{ev_{s,m}^0 - ev_{s,m}}{\tau_s(T, \theta_{v,m})} \right), \\ &= \sum_{s=\text{molecule}} \rho_s \frac{ev_s^0 - ev_s}{\tilde{\tau}_s}, \\ &\simeq \sum_{s=\text{molecule}} \rho_s \frac{C_{vv,s}(T - T_{ve})}{\tilde{\tau}_s} = \frac{\rho C_{vv}(T - T_{ve})}{\bar{\tau}}, \end{aligned} \quad (17)$$

where $\theta_{v,m}$ is the vibrational characteristic temperature associated with the m th vibrational mode, $ev_{s,m} := ev_{s,m}(T_{ve}, \theta_{v,m})$ are the m th mode of the vibrational energy of species s , and $ev_{s,m}^0 := ev_{s,m}(T, \theta_{v,m})$ are the m th mode of the equilibrium vibrational energy of species s . Note that the vibrational energy depends on vibrational-electronic temperature T_{ve} , while the equilibrium vibrational energy is a function of

translational temperature T . The averaged multivibrational mode relaxation time, $\tilde{\tau}_s$, is defined as

$$\tilde{\tau}_s = \frac{\sum_{m=\text{mode}} |ev_{s,m}^0(T, \theta_{v,m}) - ev_{s,m}(T_{ve}, \theta_{v,m})|}{\sum_{m=\text{mode}} \frac{|ev_{s,m}^0(T, \theta_{v,m}) - ev_{s,m}(T_{ve}, \theta_{v,m})|}{\tau_s(T, \theta_{v,m})}}, \quad (18)$$

where the absolute value is used to ensure positivity in the estimated relaxation time. Note that for monatomic and diatomic molecules $\tilde{\tau}_s = \tau_s$, as it should, and therefore, the new formulation recovers the original Landau-Teller expression for molecules that have a single vibrational relaxation temperature.

The vibrational energy mode of species are evaluated with an assumption that they obey the harmonic oscillator model and therefore, can be defined as

$$ev_{s,m}^0(T, \theta_{v,m}) = g_m \frac{R_s \theta_{v,m}}{e^{\frac{\theta_{v,m}}{T}} - 1}, \quad (19)$$

$$ev_{s,m}(T_{ve}, \theta_{v,m}) = g_m \frac{R_s \theta_{v,m}}{e^{\frac{\theta_{v,m}}{T_{ve}}} - 1}, \quad (20)$$

where the vibrational energies are weighted with their degeneracy modes, g_m .

The effective multivibrational mode relaxation time can now be easily evaluated using Eqs. (16) along with the averaged multivibrational mode relaxation time defined in Eq. (18), evaluated similarly as Eq. (10). The only exception is that the MW vibrational relaxation time should now be computed with corresponding vibrational characteristic temperature for each mode; i.e.,

$$\tilde{\tau}_s(T, \theta_{v,m}) = \tilde{\tau}_s^{\text{MW}}(T, \theta_{v,m}) + \tilde{\tau}_s^{\text{Park}}(T). \quad (21)$$

The proposed multivibrational mode relaxation approach follows the following steps:

- evaluate Park's relaxation correction term, $\tilde{\tau}_s^{\text{Park}} := \tilde{\tau}_s^{\text{Park}}(T)$, from Eq. (10)
- For each characteristic vibrational mode, m , estimate the Millkan-White vibrational relaxation time, $\tau_{sr}^{\text{MW}} := \tau_{sr}^{\text{MW}}(T, \theta_{v,s,m})$, as given in Eq. (6), for every species collision partner r
- Evaluate the Millkan-White averaged vibrational relaxation time, $\tilde{\tau}_s^{\text{MW}} := \tilde{\tau}_s^{\text{MW}}(T, \theta_{v,s,m})$ using the weighted harmonic mean approximation as given in Eq. 5
- Sum the previous two relaxation times; i.e., Eq. (21)
- evaluate the vibrational energy modes, $ev_{s,m} := ev_{s,m}(T, \theta_{v,m})$, and equilibrium vibrational energy mode, $ev_{s,m}^0 := ev_{s,m}^0(T_{ve}, \theta_{v,m})$, from Eqs. (19) and (20), respectively
- evaluate the averaged multivibrational mode relaxation time, $\tilde{\tau}_s$, from Eq. (18)

- evaluate the *effective* vibrational relaxation time, $\bar{\tau}$, from Eq. (16)
- estimate the translational-vibrational energy exchange source term, $Src^{T \leftrightarrow V}$, from Eq. (15)

3.3. Modified effective multivibrational mode relaxation time

The underlying assumption regarding the Landau-Tetter expression given in Eq. (2) is that the translation temperature T and vibrational-electronic temperature T_{ve} are not too far from each other. Otherwise, the relaxation time will either be underestimated ($T \ll T_{ve}$) or overestimated ($T_{ve} \ll T$). Kustova and Oblapenko [19, 18] proposed a modification to the Landau-Tetter expression, which is then applied to hypersonic separated flows by Shoev et al. [20]. Adopting such modification into the present generalized expression, Eq. (15), leads to the following simple formula:

$$\bar{\tau}_s^{\text{modified}} = \bar{\tau}_s \frac{T_{ve}}{T}. \quad (22)$$

4. RESULTS

Simulations are carried out using LAURA code [17] with two-temperature thermochemical nonequilibrium state model in mixture of gases that contain polyatomic species such as NH_3 or CO_2 . In all simulations, Park's elastic collision cross section correction with $\sigma' = 10^{-21}$ is applied. The presented solutions are considered converged when the L_2 norms are at machine zero level. For separated flows, the solution is assumed to be converged when the predicted surface heating in the separated region changes less than 1% after 5,000 iterations. For separated flows, presented results are not time-averaged; they are the snapshot after the convergence criterion is reached.

4.1. Mars entry environment

The Marsian atmosphere is used as a comparison with the Park two-temperature model. In this case, a 10 species CO_2 mixture (CO_2 , CO , O_2 , N_2 , NO , C_2 , CN , C , N , O) is used to simulate arothermodynamic environment of an entry capsule. Thermodynamic properties of the mixture are presented in Fig. 1. A 4km/sec entry condition is simulated using the proposed multivibrational mode relaxation scheme and the results are compared against the Park's relaxation model. Figure 2 shows that the proposed multivibrational mode scheme essentially recovers the Park model for CO_2 mixture. The benefit of the multivibrational relaxation scheme presented here is that it can be applied to a wide range of species.

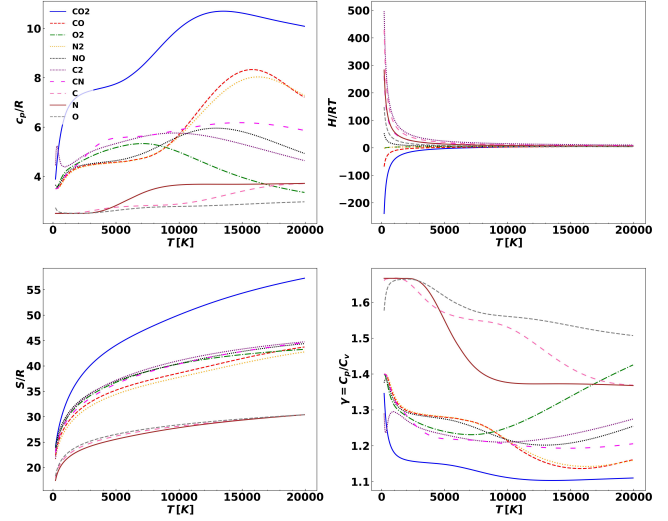


Fig. 1. Thermodynamic properties of 10-species CO_2 environment based on the thermodynamic coefficients of McBride et al. [21].

4.2. Reaction control surface nozzle

A simple 3-species Ammonia gas mixture (NH_3 , N_2 , H_2) is considered for a reaction control system. The plenum pressure and temperature are set to 147 psi and 1365K, respectively. Thermodynamic properties of NH_3 is plotted in Fig. 3. For the range of temperature expected in this case, the two thermodynamic curves are nearly identical. Here, the data from Burcat and Ruscic [22] are used.

The NH_3 molecule has multiple vibrational frequencies, and there is no Park-like relaxation model for Ammonia. However, the present multivibrational mode relaxation model can be easily applied to this case. Figure 4 shows the predicted translational and vibrational temperatures for the Ammonia mixture obtained with the multivibrational mode relaxation scheme. The results are also compared with the modified Landau-Teller expression, Eq. (22). The temperature profiles along the nozzle centerline show that vibrational temperature is largely underpredicted in the divergent section with original Landau-Teller expression. This is also followed by a small overprediction of translational temperature. The reason for this behavior is that the original Landau-Teller expression underpredicts the estimated relaxation time by as much as 150%. This is shown in Fig. 5.

5. CONCLUSIONS

A general vibrational relaxation scheme was proposed that can be applied to polyatomic molecules with multiple vibrational characteristics temperature. A step by step procedure was outlined that can easily be applied to existing codes that use a lump-sum approach or single vibrational characteristic

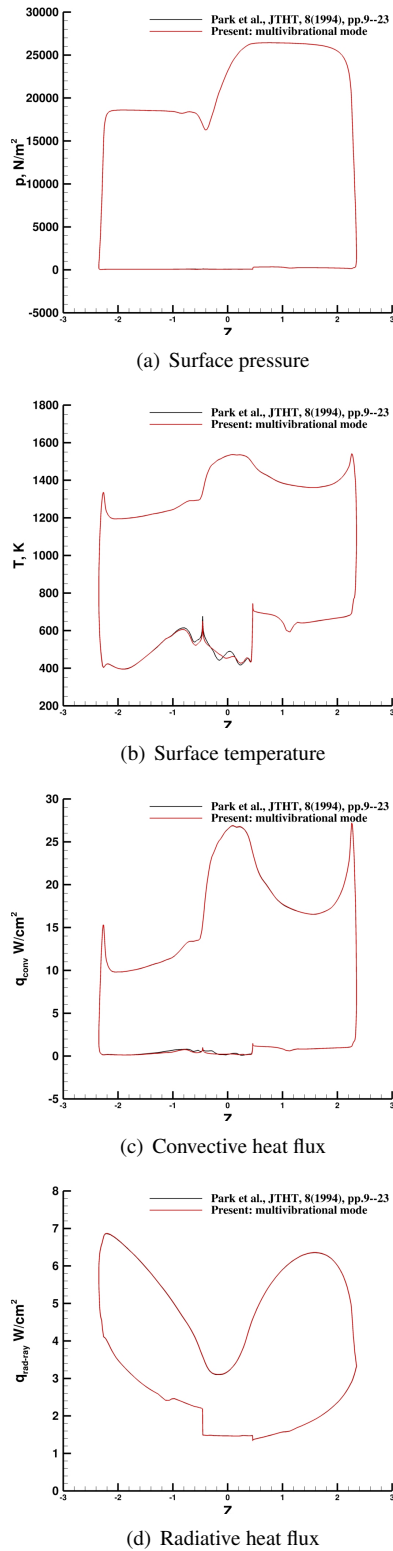


Fig. 2. Predicted surface properties comparison along the vehicle symmetry line between the Park model and the present multivibrational mode model for Mars environment.

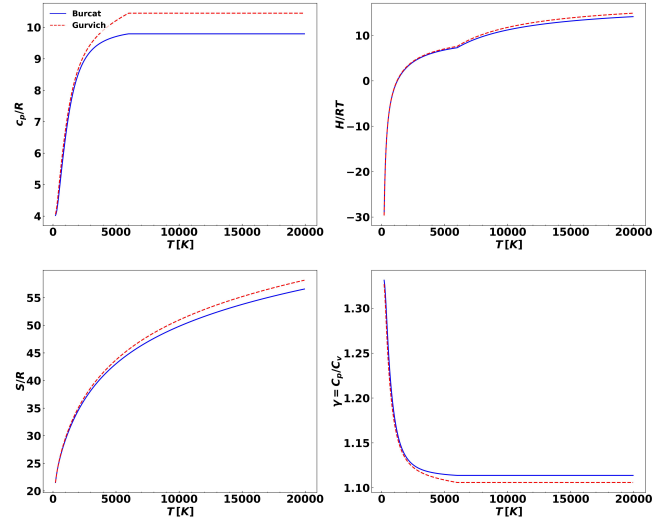


Fig. 3. NH₃ thermodynamic properties from the data of Gurvich et al. [23] and Burcat and Ruscic [22].

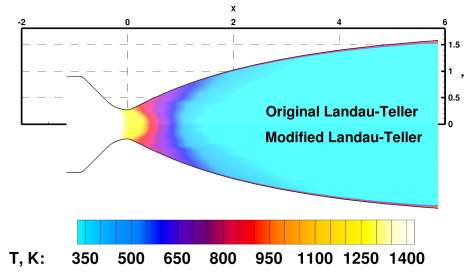
temperature. The scheme is applied to a 10-species CO₂, and it was shown that the presented scheme recovers the widely used model proposed by Park et al. We also applied the scheme to an Ammonia mixture for which there exists no Park-like model. The results were also compared with modified Landau-Teller expressions. It was shown that the original Landau-Teller expression underpredicts vibrational relaxation time by as much as 150%.

6. ACKNOWLEDGMENTS

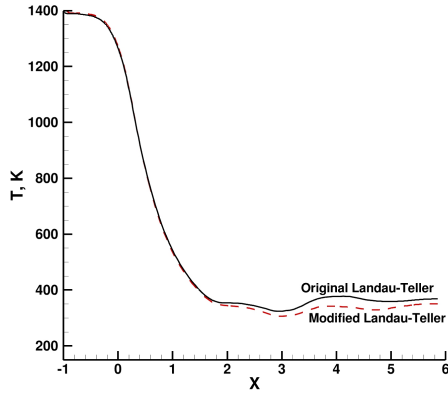
The author would like to thank Brett Cruden, AMA Inc. at NASA Ames Research Center, for many useful discussions.

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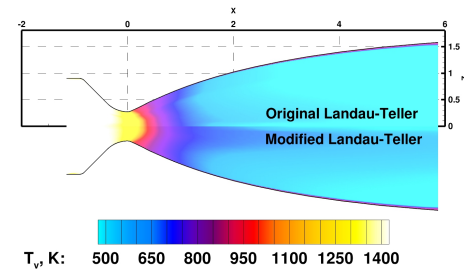
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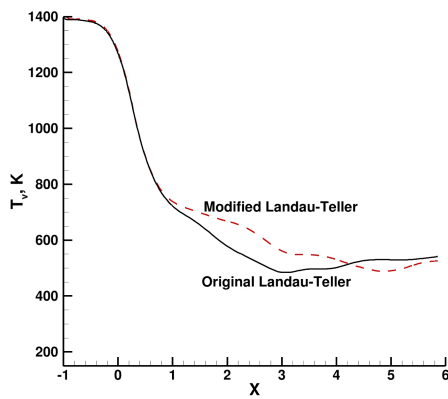
(a) Temperature, T



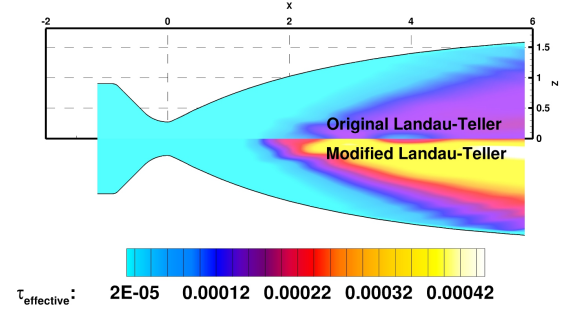
(b) Centerline temperature, T



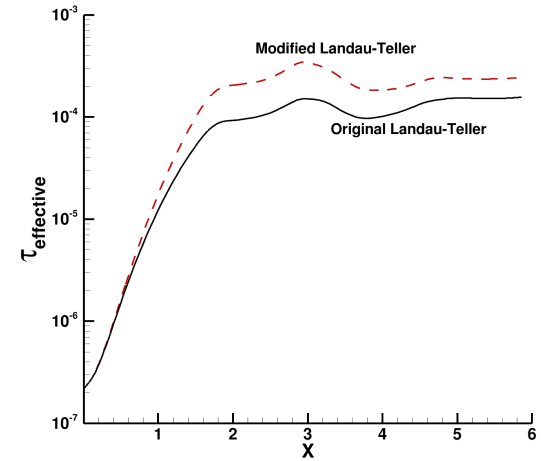
(c) Vibrational temperature, T_v



(d) Centerline vibrational temperature, T_v



(a) Relaxation time, $\tau_{\text{effective}}$



(b) Relaxation time along the centerline

Fig. 5. Effective vibrational relaxation time with and without correction to the Landau-Teller. Both simulations are done using the present multivibrational mode relaxation scheme.

Fig. 4. Translational and vibrational temperatures with and without correction to the Landau-Teller. Both simulations are done using the present multivibrational mode relaxation scheme.

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