## Boltzmann-based second-order constitutive models of diatomic and polyatomic gases including the vibrational mode

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**Abstract:** Describing diatomic and polyatomic gases at high temperatures requires a deep understanding of the molecules' excitation to a higher vibrational level. We developed new second-order constitutive models for diatomic and polyatomic gases with vibrational degrees of freedom, starting from the modified Boltzmann-Curtiss kinetic equation. The closing-last balanced closure and cumulant expansion of the calortropy production associated with the Boltzmann collision term are key to the derivation of the second-order models, compatible with the second law of thermodynamics. The topology of the constitutive models showed the presence of highly nonlinear and coupled protruding or sunken regions in the compression branch. It was also shown that the vibrational mode reduces the level of nonlinearity in the topology. In addition, analysis of a strong shock structure highlighted the interplay between the second-order effects in the constitutive relations and the vibrational-translational relaxation. Finally, the analysis showed that the results of the second-order models were in better agreement with the direct simulation Monte Carlo data, when compared with the results of the first-order models, especially in the profiles and slopes of density, velocity, and vibrational temperatures.

**Keywords:** Vibrationally excited gases; Non-equilibrium flow; Boltzmann-Curtiss equation; Constitutive relations; Shock structure.

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### I. INTRODUCTION

High temperature gas dynamics has been a subject of continuing interest because of the complexities of the flow physics involved at a fundamental level.<sup>1-3</sup> Understanding diatomic and polyatomic gases at high temperatures<sup>3,4</sup> requires a deep knowledge of several physical processes, such as the excitation of molecules to higher vibrational and electronic quantum levels, and changes in the structure or the identity of the molecules resulting from chemical reactions<sup>5-7</sup> and ionization. High speed flow around re-entry vehicles flying through layers of Earth's atmosphere provides a challenging and interesting example of high temperature gas flows.<sup>8</sup> During its descent at hypersonic speed, the vehicle has to endure harsh conditions and extremely high temperatures, particularly in the shock and the post-shock regions. In addition, the rapidly increasing rarefaction at high altitudes results in a high degree of non-equilibrium in the flow, which further complicates the situation.

Numerical simulations are often employed to gain a deeper understanding of these hightemperature re-entry flows. The two prominent strategies for simulating re-entry flows are computational fluid dynamics (CFD) methods, based on the Navier-Stokes-Fourier (NSF) equations,<sup>9,10</sup> and the direct simulation Monte Carlo (DSMC) method.<sup>11-14</sup> The NSF equations are based on the conservation laws of mass, momentum and energy and first-order constitutive relations. Combined with additional equations for vibrational energy and species, they have been widely used to study hypersonic high temperature air flows at lower altitudes (< 55 km). Nonequilibrium in the trans-rotational and vibrational modes of energy, and the effect of chemical reactions in the flow are handled through source terms in the equations of the vibrational energy balance and species balance, respectively. In sharp contrast to the CFD methods based on the NSF equations in the partial differential equations, the DSMC is not based on any partial differential equations, but a statistical method that directly simulates the motion of gases through probabilistic collision models.<sup>11,15</sup> The non-equilibrium in the flow and the chemical reactions are handled with phenomenological inelastic<sup>16,17</sup> and reactive collision models, respectively.<sup>11,18,19</sup>

The basic form of the NSF equations was derived in 1822, and they are considered the *de facto* mathematical models for every possible flow problem. However, a vital assumption was introduced in the derivation of the NSF constitutive relations, near the local-thermal-equilibrium (LTE), and as a result, their validity may be seriously questioned for flows whose status is not near the LTE condition. For instance, the NSF constitutive relations may be inappropriate at altitudes higher than 55 km, because of the limitations of the first-order constitutive relations originally derived for non-rarefied gases. Also, the DSMC simulations become too computationally expensive for simulating flows at altitudes below 70 km. These shortcomings provide an opportunity to develop an alternative method that is not only more accurate than the first-order NSF-based methods but also less resource-intensive than the DSMC method. The so-called second-order nonlinear coupled constitutive relations (NCCR) based on Eu's generalized hydrodynamics<sup>20,21</sup> were first proposed by Myong<sup>22-24</sup> in 1999 and have been studied since by other researchers<sup>25-29</sup> as a novel alternative to the traditional approaches.

In the NCCR approach, the second-order constitutive models are derived by first differentiating the statistical definition of the non-conserved variables (the viscous stress tensor, the heat flux vector, and the excess normal stress in the case of diatomic and polyatomic gases) with time and then combining them with the Boltzmann<sup>2,20,30</sup> or Boltzmann-Curtiss kinetic equations.<sup>22,31-34</sup> The constitutive equations for the non-conserved variables are in partial differential form and have non-vanishing dissipative terms due to the collision operator of the Boltzmann or Boltzmann-Curtiss kinetic equations. Upon simplification using the adiabatic assumption and the second-order

balanced closure,<sup>24</sup> these partial differential equations are reduced to a set of algebraic equations. Further, the second-order approximation of the dissipative term in the constitutive equations takes the form of a highly non-linear hyperbolic sine function.<sup>20-23,35</sup>

According to the balanced closure theory, <sup>24</sup> the approximation on either side of the constitutive equations—kinematic (movement) and dissipation (interaction) terms—should be consistent and of the same order. Otherwise, the mismatch in the orders of approximation, such as Grad's original formulation, <sup>36,37</sup> leads to a blow-up singularity in the high Mach number shock structure problem.<sup>24</sup> A detailed description of the second-order effects on the shock structure with respect to the shock thickness at high Mach number flows was previously reported.<sup>38,39</sup>

In addition to treating the high Mach number flows encountered in re-entry situations, the NCCR and NSF models have been employed to understand flows in the transition regime of microscale gases<sup>34,40-42</sup> and, recently, in dusty and granular gases<sup>43,44</sup> as well. In passing, it is worth mentioning that diatomic and polyatomic gases require an additional constitutive equation of the excess normal stress in a non-Stokesian framework. This results in the introduction of a non-zero bulk viscosity<sup>45-47</sup> which plays a critical role in the molecular theory of diatomic and polyatomic gases.

The second-order NCCR theory has been well established for studying monoatomic, diatomic, and (linear) polyatomic gases at temperatures lower than the vibrational excitation temperature; for example, 1000 K. However, the NCCR theory needs to be extended to account for the high-temperature effects, such as vibrational excitations and chemical reactions, to accurately model re-entry flows at various flight conditions.

To tackle this challenge, we aim to develop new NCCR models for diatomic and polyatomic gases with vibrational degrees of freedom. The translational and rotational modes of energy are

assumed to be in equilibrium with each other, similar to the two-temperature model proposed by Park.<sup>1,48</sup> The two-temperature model is a reasonable assumption, since the number of collisions required to attain translational and rotational equilibrium is less than those required to establish equilibrium between the translation and vibrational modes. In addition to the equations for the collisional-invariant moments of the Boltzmann kinetic equation, mass, momentum, and energy, an equation for the conservation of vibrational energy ( $\rho e_v$ )<sup>49</sup> is required, as reported by Olejniczak and Candler.<sup>50</sup> They formulated a source term by employing coupling models in the Landau-Teller equation<sup>51</sup> to handle the non-equilibrium between the trans-rotational and vibrational modes of energy. The conservation of the vibrational energy equation in non-reactive gas flows takes the following form:

$$\frac{\partial(\rho e_{v})}{\partial t} + \nabla \cdot (\rho e_{v} \mathbf{u}) + \nabla \cdot \mathbf{Q}_{v} = \frac{\rho e_{v}(T) - \rho e_{v}(T_{v})}{\tau_{v}}, \qquad (1)$$

where  $\tau_v$  is the vibrational relaxation time and is commonly modeled by an expression given by Millikan and White.<sup>52</sup> The additional non-conserved term  $\mathbf{Q}_v$  in the equation accounts for the heat flux in the vibrational degrees of freedom (or simply, the vibrational heat flux). The first-order approximation of vibrational heat flux is a product of the gradient of the vibrational temperature and thermal conductivity for the vibrational degrees of freedom:

$$\mathbf{Q}_{\mathbf{v}} = -k_{\mathbf{v}} \nabla T_{\mathbf{v}}.$$
 (2)

The formulation of vibrational heat flux (2) is similar to Fourier's law for heat flux. Further, the vibrational energy can be expressed by either assuming a simple harmonic oscillator (SHO) or a more realistic anharmonic oscillator (AO) model. The vibrational relaxation time needs to be modeled appropriately depending on the choice of the oscillator model. Based on this equation,

Olejniczak and Candler<sup>50</sup> reported accurate results for the shock stand-off distance and the interference patterns for the conditions considered.

There exists a large body of literature on the theory of diatomic and polyatomic gases in a state away from thermal equilibrium. Based on extended nonequilibrium distributions and Boltzmann collision terms and the so-called extended thermodynamic theory, Ruggeri and Sugiyama and their collaborators<sup>53-58</sup> investigated the dispersion relation of ultrasonic wave and the shock structure of CO<sub>2</sub> at low Mach number and low temperature range below the vibrational excitation temperature. Pavic-Colic *et al.*<sup>59</sup> also studied the shock structure of diatomic and polyatomic gases at low Mach number and low temperature range using the 6-fields theory. Struchtrup and his collaborators<sup>60-62</sup> developed a high-order macroscopic model without the vibrational mode for rarefied polyatomic gases, based on rational extended thermodynamic theory. Aoki and his collaborators<sup>63,64</sup> also investigated the shock structure of CO<sub>2</sub> at low Mach number and low temperature range, based on the ellipsoidal statistical (ES) model of Boltzmann kinetic equation, and compared with the results of the direct solution of ES model and Taniguchi et al.53 Kustova et al.65 studied the Boltzmann equation in the form of Wang Chang-Uhlenbeck with vibrational mode and investigated the shock structure of CO<sub>2</sub> at high Mach number and high temperature range. Based on the Chapman-Enskog method and a first-order closure, they also reported that the bulk viscosity value of  $CO_2$  is in the range of  $0.5 \sim 2.6$ , when the vibrational mode is included.

In this study, we first propose a modified Boltzmann-Curtiss kinetic equation which includes the vibrational mode of energy. We then derive the second-order NCCR models for the nonconserved variables (viscous stress tensor, excess normal stress, heat flux, and heat flux for vibrational energy) from the modified Boltzmann-Curtiss kinetic equation. The effect of the nonequilibrium of the non-conserved variables—not only the heat flux for the vibrational degrees of freedom, but also the viscous stress tensor—is a significant contribution which is absent in the first-order NSF theory. This non-equilibrium effect is amplified due to the coupled nature of the second-order NCCR theory. *To the authors' best knowledge, no study has been reported in the past on the Boltzmann-Curtiss-based second-order constitutive model that includes the vibrational mode and, at the same time, is applicable to very high Mach number gas flows.* 

Section II explains the modification of the Boltzmann-Curtiss kinetic equation in detail, introduces the statistical formula for conserved and non-conserved variables, and derives the exact conservation laws and second-order NCCR models. The contrast between the first-order and second-order approximations is discussed at length. Section III explores the topological ramifications of the second-order NCCR models and explains the effect of non-equilibrium on the topology of the second-order NCCR models. Finally, conclusions and a brief discussion of future topics in line with the present study are given.

### II. THERMODYNAMICALLY CONSISTENT SECOND-ORDER CONSTITUTIVE MODEL FOR VIBRATING MOLECULES

### A. Modified Boltzmann-Curtiss kinetic equation

The Boltzmann kinetic equation derived by Boltzmann in 1872 is the basic kinetic equation describing the statistical behavior of monoatomic molecules. For diatomic and (linear) polyatomic molecules with rotational degrees of freedom, Curtiss<sup>32</sup> in 1981 proposed an extension to the Boltzmann kinetic equation, where the probability distribution function has an additional dependent variable for the rotational quantum level and angular momentum. The kinetic equation governing the statistics of diatomic and polyatomic gases with both rotational and vibrational

degrees of freedom—which is essential to derive the second-order NCCR models—can be obtained by extending the Boltzmann-Curtiss kinetic equation.

The premise of the governing kinetic equation is that molecules in various vibrational levels can be treated as molecules belonging to different species. The interaction between two diatomic or polyatomic molecules with vibrational energy exchange can be described in the following reaction format:

$$a(i) + a(j) \to a(k) + a(l). \tag{3}$$

where *a* is a molecule and *i*, *j*, *k* and *l* are vibrational levels. For the cases i = k and j = l, then, the interaction is said to have undergone an elastic collision; otherwise, the interaction is termed an inelastic collision. The Boltzmann-Curtiss equation is suitable for describing diatomic and polyatomic gases with only elastic collisions, represented by Eq. (3). This is true for gas flows at temperatures lower than the characteristic temperature for vibrational excitation. The gas flows often encountered in micro-channel applications at conditions close to standard temperature are such an example. However, this is not the case for diatomic and polyatomic gas flows at high temperatures, where a modification to the original Boltzmann-Curtiss equation is necessary.

We propose a modified Boltzmann-Curtiss equation for the interaction (3) in the following form:

$$\frac{\partial f_i}{\partial t} + \mathbf{v} \cdot \nabla f_i + \mathbf{L} \cdot \nabla_r f_i = \sum_j \sum_k \sum_l \int dv_j \int d\Omega W(i, j, |k^*, l^*; \Omega) (f_k^* f_l^* - f_i f_j)$$

$$= \sum_j C[f_i, f_j].$$
(4)

Here  $f_i$  is the distribution function of the population of molecules in the *i*<sup>th</sup> vibrational level. The variables  $r_i$ ,  $\mathbf{v}_i$ ,  $\mathbf{L}_i$ , and *t* represent the position, velocity, angular velocity, and time, respectively. For simplicity, the subscripts are dropped, since the molecules essentially belong to the same

species. The terms with an asterisk in the superscripts represent the post-collision states. The term  $W(i, j, |k^*, l^*; \Omega)$  is the probability of the interaction among molecules in the *i*<sup>th</sup> and *j*<sup>th</sup> vibrational levels undergoing inelastic collision to the *k*<sup>th</sup> and *l*<sup>th</sup> vibrational quantum level, and  $\Omega$  is the solid angle. The summation over the *j*<sup>th</sup>, *k*<sup>th</sup>, and *l*<sup>th</sup> vibrational levels ensures that interactions over all possible post-collision combinations of vibrational levels are handled.

#### B. Statistical formula of conserved and non-conserved variables

As with elastic collisions, during an inelastic collision, the mass, momentum, and total energy, which includes translational, rotational, and vibrational degrees of freedom, are conserved. However, the energies in the individual degree of freedom are not conserved during such a collision due to inelastic energy exchange. The density of diatomic and polyatomic molecules in the *i*<sup>th</sup> vibrational level is defined as:

$$\rho_i = \langle mf_i \rangle \,, \tag{5}$$

where *m* is the mass of the molecule of the same type and  $f_i$  is the distribution function of the molecules at the *i*<sup>th</sup> vibrational level. The symbol  $\langle \rangle$  denotes the integral in velocity space and the azimuthal angle. The total density, which is the total of densities in all vibrational levels, is a conserved quantity, while the density in the individual vibrational quantum level is not a conserved quantity. The total density (simply called density) is defined as:

$$\rho = \sum_{i} \rho_{i} = \langle m \sum_{i} f_{i} \rangle .$$
(6)

The velocity distribution of molecules in the individual vibrational levels is assumed to be equal to the velocity distribution for the ensemble of molecules residing in all vibrational levels. The remaining collisional invariant, namely the momentum and total energy for individual vibrational levels and their summation, are defined as follows:

$$\rho_i \mathbf{u} = \langle m \mathbf{v} f_i \rangle, \qquad \qquad \rho \mathbf{u} = \sum_i \rho_i \mathbf{u} = \langle m \mathbf{v} \sum_i f_i \rangle, \qquad (7)$$

$$\rho_i e_i = \langle (m \frac{\mathbf{c} \cdot \mathbf{c}}{2} + H_{r,i} + H_{v,i}) f_i \rangle, \qquad \rho e = \sum_i \rho_i e_i = \langle \sum_i (m \frac{\mathbf{c} \cdot \mathbf{c}}{2} + H_{r,i} + H_{v,i}) f_i \rangle, \qquad (8)$$

where **v** is the molecular velocity, **u** is the average velocity and **c** is the peculiar velocity,  $H_{r,i}$ and  $H_{v,i}$  are the molecular energies in the rotational and vibrational degrees of freedom. The total vibrational energy and vibrational energy at the *i*<sup>th</sup> level are similarly defined as:

$$\rho_i e_{\nu,i} = \langle H_{\nu,i} f_i \rangle, \qquad \qquad \rho e_{\nu} = \sum_i \rho_i e_{\nu,i} = \langle \sum_i H_{\nu,i} f_i \rangle. \qquad (9)$$

The non-conserved variables for the modified Boltzmann-Curtiss equation: stress tensor ( $\Pi$ ), excess normal stress ( $\Delta$ ), heat flux for trans-rotational energy ( $\mathbf{Q}$ ), and vibrational heat flux ( $\mathbf{Q}_v$ ), are similarly defined at the *i*<sup>th</sup> level and the total overall vibrational levels as follows:

$$\mathbf{\Pi}_{i} = \langle m[\mathbf{cc}]^{(2)} f_{i} \rangle, \qquad \qquad \mathbf{\Pi} = \sum_{i} \mathbf{\Pi}_{i} = \langle m[\mathbf{cc}]^{(2)} \sum_{i} f_{i} \rangle, \qquad (10)$$

$$\Delta_{i} = \langle (m \operatorname{Tr}(\mathbf{cc})/3 - p/n)f_{i} \rangle, \qquad \Delta = \sum_{i} \Delta_{i} = \langle (m \operatorname{Tr}(\mathbf{cc})/3 - p/n)\sum_{i} f_{i} \rangle, \quad (11)$$

$$\mathbf{Q}_{i} = \langle (m\frac{\mathbf{c} \cdot \mathbf{c}}{2} + H_{r,i})\mathbf{c}f_{i} \rangle, \qquad \mathbf{Q} = \sum_{i} \mathbf{Q}_{i} = \langle \sum_{i} (m\frac{\mathbf{c} \cdot \mathbf{c}}{2} + H_{r,i})\mathbf{c}f_{i} \rangle, \qquad (12)$$

$$\mathbf{Q}_{\mathbf{v},i} = \langle H_{\mathbf{v},i} \mathbf{c} f_i \rangle, \qquad \mathbf{Q}_{\mathbf{v}} = \sum_i \mathbf{Q}_{\mathbf{v},i} = \langle \sum_i H_{\mathbf{v},i} \mathbf{c} f_i \rangle, \qquad (13)$$

where subscript *i* denotes the vibrational level of the molecular entity, and the term *p* in the definition of excess normal stress is the hydrostatic pressure calculated over the local equilibrium distribution ( $f^0$ ) given by

$$p = \langle \frac{1}{3}m \sum_{i} \operatorname{Tr}(\mathbf{cc}) f_{i}^{0} \rangle.$$
<sup>(14)</sup>

The governing equations for conserved variables for the density, momentum, total energy, vibrational energy, and the constitutive equations for non-conserved variables are derived for the aggregate or total quantities and not for the individual vibrational levels. Since diatomic nitrogen and oxygen molecules are known to have 55 and 37 vibrational levels,<sup>66</sup> respectively, this simplified procedure makes the systems of equations manageable and practical. The definitions of conserved and non-conserved variables can be summarized by the statistical formula

$$\phi^{(k)} = \left\langle \sum_{i} h_{i}^{(k)} f_{i} \right\rangle, \tag{15}$$

where  $h^{(k)}$  indicates the molecular expressions for variables. The leading elements of the set of the conserved and non-conserved variables are defined as,<sup>67</sup>

$$\phi^{(1)} = \rho, \ \phi^{(2)} = \rho \mathbf{u}, \ \phi^{(3)} = \rho e, \ \phi^{(4)} = \rho e_{\nu},$$
  
$$\phi^{(5)} = \mathbf{\Pi} = \left[\mathbf{P}\right]^{(2)}, \ \phi^{(6)} = \Delta = \frac{1}{3} \operatorname{Tr}(\mathbf{P}) - p, \ \phi^{(7)} = \mathbf{Q}, \ \phi^{(8)} = \mathbf{Q}_{\nu},$$
(16)

with the molecular expressions corresponding to this set:

$$h^{(1)} = m, \ h^{(2)} = m\mathbf{v}, \ h^{(3)} = (m\frac{\mathbf{c}\cdot\mathbf{c}}{2} + H_{r,i} + H_{v,i}), \ h^{(4)} = H_{v,i},$$

$$h^{(7)} = m[\mathbf{c}\mathbf{c}]^{(2)}, \ h^{(6)} = \frac{1}{3}m\mathrm{Tr}(\mathbf{c}\mathbf{c}) - p / n, \ h^{(7)} = (\frac{m\mathbf{c}\cdot\mathbf{c}}{2} + H_{r,i} + H_{v,i})\mathbf{c}, \ h^{(8)} = H_{v,i}\mathbf{c}.$$
(17)

### C. Exact conservation laws

Upon differentiating the statistical definitions of total density (6), total momentum (7) and total energy (8) with time, substituting the Boltzmann-Curtiss equation and invoking the collision invariance of mass, momentum, and energy, the following conservation laws for mass, momentum, and energy are obtained:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \qquad (18)$$

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u}\mathbf{u} + p\mathbf{I}) + \nabla \cdot (\mathbf{\Pi} + \Delta \mathbf{I}) = 0, \qquad (19)$$

$$\frac{\partial(\rho e)}{\partial t} + \nabla \cdot ((\rho e + p)\mathbf{u}) + \nabla \cdot ((\mathbf{\Pi} + \Delta \mathbf{I}) \cdot \mathbf{u}) + \nabla \cdot \mathbf{Q} + \nabla \cdot \mathbf{Q}_{v} = 0.$$
<sup>(20)</sup>

In contrast to these equations, the conservation of vibrational energy equation has a nonvanishing collisional term, since the vibrational energy is not a collisional invariant. The collision term in the present work is modeled based on similar arguments made by Olejniczak and Candler.<sup>50</sup> The conservation of vibrational equation takes the following form:

$$\frac{\partial(\rho e_{v})}{\partial t} + \nabla \cdot (\rho e_{v} \mathbf{u}) + \nabla \cdot \mathbf{Q}_{v} = \frac{\rho e_{v}(T) - \rho e_{v}(T_{v})}{\tau_{v}}.$$
(21)

# D. Second-order constitutive models: Closing-last balanced closure and cumulant expansion

The constitutive equations for the non-conserved quantities, namely, stress tensor, excess normal stress, heat flux, and vibrational heat flux, are derived using the same procedure. They are in a partial differential form, comprised of several kinematic terms on the left-hand side and a single collision term on the right-hand side, as follows,

$$\rho \frac{d(\mathbf{\Pi}/\rho)}{dt} + \nabla \cdot \boldsymbol{\psi}^{(\mathbf{\Pi})} + 2[\mathbf{\Pi} \cdot \nabla \mathbf{u}]^{(2)} + 2(p+\Delta)[\nabla \mathbf{u}]^{(2)} = \Lambda(\mathbf{\Pi}), \qquad (22)$$

$$\rho \frac{d(\Delta/\rho)}{dt} + \nabla \cdot \psi^{(\Delta)} + 2\gamma' (\mathbf{\Pi} + \Delta \mathbf{I}) : \nabla \mathbf{u} + \frac{2}{3}\gamma' p \nabla \cdot \mathbf{u} = \Lambda(\Delta),$$
<sup>(23)</sup>

$$\rho \frac{d(\mathbf{Q}/\rho)}{dt} + \nabla \cdot \psi^{(\mathbf{Q})} + \psi^{(\mathbf{P})} : \nabla \mathbf{u} + \mathbf{Q} \cdot \nabla \mathbf{u} + \frac{d\mathbf{u}}{dt} \cdot \mathbf{\Pi} + \mathbf{\Pi} \cdot \nabla (C_p T) + (p + \Delta) \nabla (C_p T) = \Lambda(\mathbf{Q}), \quad (24)$$

$$\rho \frac{d(\mathbf{Q}_{v} / \rho)}{dt} + \nabla \cdot \psi^{(\mathbf{Q}_{v})} + \mathbf{Q}_{v} \cdot \nabla \mathbf{u} + \mathbf{\Pi} \cdot \nabla (C_{p,v} T_{v}) + (p + \Delta) \nabla (C_{p,v} T_{v}) = \Lambda(\mathbf{Q}_{v}),$$
<sup>(25)</sup>

where  $\gamma'$ , *T*,  $T_{\nu}$ ,  $C_p$  and  $C_{p,\nu}$  are the ratio of the rotational specific heat capacity energy to specific heat capacity at constant volume, defined as  $\gamma' = (5-3\gamma)/2$ , trans-rotational temperature,

the temperature associated with the vibrational energy of gas molecules,<sup>1,48</sup> specific heat capacity at constant pressure, and vibrational specific heat capacity at constant pressure, respectively.

The collision terms  $\Lambda(\mathbf{\Pi})$ ,  $\Lambda(\Delta)$ ,  $\Lambda(\mathbf{Q})$ , and  $\Lambda(\mathbf{Q}_v)$  on the right-hand side of the equations are defined as,

$$\Lambda^{(k)} = \left\langle \sum_{i} h_i^{(k)} C[f_i, f_j] \right\rangle,$$

and represent the dissipation in the non-conserved quantities which is attributed to the collisional operator in the transport equation. The kinematic higher-order terms on the left-hand side are defined as

$$\psi^{(\mathbf{II})} = \left\langle m[\mathbf{cc}]^{(2)}\mathbf{c}\sum_{i} f_{i} \right\rangle, \ \psi^{(\Delta)} = \left\langle (m\mathrm{Tr}(\mathbf{cc})/3 - p/n)\mathbf{c}\sum_{i} f_{i} \right\rangle, \ \psi^{(\mathbf{P})} = \left\langle m\mathrm{ccc}\sum_{i} f_{i} \right\rangle$$
$$\psi^{(\mathbf{Q})} = \left\langle \sum_{i} (m\frac{\mathbf{c} \cdot \mathbf{c}}{2} + H_{r,i})\mathbf{cc}f_{i} \right\rangle - C_{p}T\left(\mathbf{\Pi} + (p + \Delta)\mathbf{I}\right), \ \psi^{(\mathbf{Q}_{v})} = \left\langle \sum_{i} H_{v,i}\mathbf{cc}f_{i} \right\rangle.$$

At this point, it should be mentioned that the constitutive equations for the non-conserved variables (22)-(25) are an exact consequence of the modified Boltzmann-Curtiss equation (4) and are thus capable of capturing the whole flow physics, if they are provided with the accurate closure on the open higher-order terms  $\psi^{(k)}$  and  $\Lambda^{(k)}$ . However, the kinematic higher-order terms  $\psi^{(k)}$  and the dissipative terms  $\Lambda^{(k)}$  contain the unknown distribution function (*f*), which needs to be resolved to obtain a closed system of equations.

When treating the kinematic higher-order terms  $\psi^{(k)}$ , simply repeating the same procedure used in subsection II-C will only add more open terms to the present already-complicated set of equations. Instead, we will develop a closure theory to close the constitutive equations in the second-order accuracy. On the other hand, the dissipative higher-order terms  $\Lambda^{(k)}$  can be handled in a thermodynamically consistent manner such that the system conforms correctly to the second law of thermodynamics in all orders. The key idea is to approximate the non-equilibrium distribution function as an infinite series of higher-order moments. This requires defining the so-called calortropy first introduced by Eu,<sup>20</sup> a term representing a non-equilibrium extension of the Clausius (equilibrium) entropy, and the derivation of the balance equation for the calortropy. The calortropy production is then used to calculate the dissipative terms directly related to the irreversible processes. This process and the introduction of the conjugate function are described in detail in the Appendix.

The form of the conjugate functions is similar in nature to those calculated for gases with translational and rotational degrees of freedom. However, the difference is apparent in the formulation of the conjugate function for vibrational heat flux, which contains the vibrational temperature and vibrational specific heat capacity at constant pressure. The final constitutive equations for the non-conserved quantities with the vibrational degrees of freedom are:

$$\rho \frac{d(\mathbf{\Pi}/\rho)}{dt} + \nabla \cdot \psi^{(\mathbf{\Pi})} + 2[\mathbf{\Pi} \cdot \nabla \mathbf{u}]^{(2)} + 2(p+\Delta)[\nabla \mathbf{u}]^{(2)} = \frac{1}{T} \sum_{l=1}^{\infty} R^{(\mathbf{\Pi}l)} X^{(l)} q(\kappa_1^{(\pm)}, ...),$$
(26)

$$\rho \frac{d(\Delta/\rho)}{dt} + \nabla \cdot \psi^{(\Delta)} + 2\gamma' (\mathbf{\Pi} + \Delta \mathbf{I}) : \nabla \mathbf{u} + \frac{2}{3} \gamma' p \nabla \cdot \mathbf{u} = \frac{1}{T} \sum_{l=1}^{\infty} R^{(\Delta l)} X^{(l)} q(\kappa_{l}^{(\pm)}, ...),$$
<sup>(27)</sup>

$$\rho \frac{d(\mathbf{Q}/\rho)}{dt} + \nabla \cdot \psi^{(\mathbf{Q})} + \psi^{(\mathbf{P})} : \nabla \mathbf{u} + \mathbf{Q} \cdot \nabla \mathbf{u} + \frac{d\mathbf{u}}{dt} \cdot \mathbf{\Pi} + \mathbf{\Pi} \cdot \nabla(C_p T) + (p + \Delta) \nabla(C_p T)$$

$$= \frac{1}{T} \sum_{l=1}^{\infty} R^{(\mathbf{Q}l)} X^{(l)} q(\kappa_1^{(\pm)}, ...),$$

$$\rho \frac{d(\mathbf{Q}_v/\rho)}{dt} + \nabla \cdot \psi^{(\mathbf{Q}_v)} + \mathbf{Q}_v \cdot \nabla \mathbf{u} + \mathbf{\Pi} \cdot \nabla(C_{p,v} T_v) + (p + \Delta) \nabla(C_{p,v} T_v)$$

$$= \frac{1}{T_v} \sum_{l=1}^{\infty} R_v^{(\mathbf{Q},l)} X^{(l)} q(\kappa_1^{(\pm)}, ...).$$
(28)
$$(29)$$

Again, these equations are an exact representation of the modified Boltzmann-Curtiss equations. How to approximate these equations will determine the order of the constitutive equations and associated hydrodynamics.

The system of partial differential equations of non-conserved variables, which is a function of time and space, can be simplified into a compact form by introducing a series of approximations. The dissipation terms of non-conserved variables always involve open higher-order terms. However, arbitrarily choosing the order of approximation of the dissipation term without proper treatment of the terms on the left-hand side of the equation can lead to disastrous consequences. Myong<sup>24</sup> in 2014 demonstrated that the unbalanced nature of the approximations of the terms on either side of the equation of the viscous stress tensor leads to the well-known Grad's high Mach number problem (HMNP)<sup>37</sup> where a singularity in the shock wave structure is observed for Mach numbers greater than 1.65.

According to the new closure theory developed by Myong,<sup>24</sup> known as the '*closing-last balanced closure*,' when closing open terms in the moment equations derived from the kinetic equation, the number of places to be closed is two (movement and interaction), rather than one (movement only), having been misled by the Maxwellian molecule assumption in the previous theory.<sup>37</sup> For example, there are two terms requiring closure in the constitutive equation of viscous stress (26):  $\nabla \cdot \Psi^{(II)}$  and  $\langle h^{(5)}R[f] \rangle$ . Therefore, the order of approximations in handling the two terms—kinematic (movement) and dissipation (interaction) terms—must be the same to satisfy balancing, for instance, the second-order for both terms, thus achieving a balance between the kinematic and collision term approximation, namely, the second-order closure for the kinematic terms,

$$\nabla \cdot \Psi^{(\mathbf{\pi})} = \nabla \cdot \Psi^{(\Delta)} = \nabla \cdot \Psi^{(\mathbf{Q})} + \Psi^{(\mathbf{P})} : \nabla \mathbf{u} = \nabla \cdot \Psi^{(\mathbf{Q}_v)} = 0, \qquad (30)$$

while maintaining the same second-order closure for  $\langle h^{(5,6,7,8)}R[f] \rangle$ . The key physical argument in this closure is simply to impose the same level of approximations on both places so that the resulting constitutive equation may remain balanced even in high nonequilibrium. In this closinglast balanced closure theory, third-order closure for  $\langle h^{(5,6,7,8)}R[f] \rangle$  may not be essential; in fact, unbalanced higher-order closure in the modified moment method may not provide improved solutions as promised, especially in the case of the high Mach number shock structure problem.<sup>22,24</sup> The balanced closure theory can be also applied in the same manner to the constitutive equations for the non-conserved quantities for the vibrational degrees of freedom.

Furthermore, the temporal dependence in the equations can be neglected owing to the very short relaxation times of the non-conserved variables, being on the order of 10<sup>-10</sup> second,<sup>22</sup> compared to those for conserved variables and the characteristic times of the flow process. This so-called adiabatic approximation reduces the unsteady partial differential equation to a set of steady-state equations. This greatly reduces the numerical complexities involved in solving the constitutive equations.

Once these two tenets—the aforementioned closing-last balanced closure and Eu's cumulant expansion based on the canonical distribution function in the exponential form to the explicit calculation of the dissipation term—are applied to the moment equations (26)-(29) and after introducing the adiabatic approximation, the following second-order constitutive model for diatomic and polyatomic gases with the vibrational degrees of freedom can be derived:

$$2[\mathbf{\Pi} \cdot \nabla \mathbf{u}]^{(2)} + 2(p + \Delta)[\nabla \mathbf{u}]^{(2)} = -\frac{p}{\mu} \mathbf{\Pi} q_{2\mathrm{nd}}(\kappa), \qquad (31)$$

$$2\gamma'(\mathbf{\Pi} + \Delta \mathbf{I}): \nabla \mathbf{u} + \frac{2}{3}\gamma' p \nabla \cdot \mathbf{u} = -\frac{2}{3}\gamma' \frac{p}{\mu_b} \Delta q_{2nd}(\kappa), \qquad (32)$$

$$\mathbf{\Pi} \cdot \nabla(C_p T) + (p + \Delta) \nabla(C_p T) = -\frac{pC_p}{k} \mathbf{Q} q_{2\mathrm{nd}}(\kappa), \qquad (33)$$

$$\mathbf{\Pi} \cdot \nabla (C_{p,v} T_{v}) + (p + \Delta) \nabla (C_{p,v} T_{v}) = -\frac{p C_{p,v}}{k_{v}} \mathbf{Q}_{v} q_{2\mathrm{nd}}(\kappa) , \qquad (34)$$

where  $q_{2nd}(\kappa) = \sinh(\kappa) / \kappa$ . During the derivation, it is also assumed that the effect of the terms  $\mathbf{Q} \cdot \nabla \mathbf{u}$  and  $\mathbf{Q}_v \cdot \nabla \mathbf{u}$  in the equations for the heat flux and the vibrational heat flux is negligible.

The final algebraic form of the second-order constitutive equations for diatomic and polyatomic gases with the vibrational degrees of freedom is highly non-linear due to the second-order term of kinematic nature  $(2[\mathbf{\Pi} \cdot \nabla \mathbf{u}]^{(2)})$  and the hyperbolic sine term of dissipative nature  $(q_{2nd}(\kappa))$ . Besides, these algebraic equations are tightly-coupled through the second-order kinematic term  $2[\mathbf{\Pi} \cdot \nabla \mathbf{u}]^{(2)}$  and the cumulant  $\kappa$  in  $q_{2nd}(\kappa)$ , which represents the contribution from all non-conserved variables in the dissipation. Hence, these equations are named the *nonlinear coupled constitutive relations* (NCCR).

The exact form of the first-order cumulant expansion  $\kappa$  appearing in the collision integrals of (26)-(29) or (31)-(34) can be calculated using the Chapman-Enskog theory.<sup>30</sup> The first-order reduced collision integral is expressed as a modified Rayleigh-Onsager dissipation function:

$$\kappa = \frac{(mk_B)^{1/4}}{\sqrt{2}d} \frac{T^{1/4}}{p} \left[ \frac{\mathbf{\Pi} : \mathbf{\Pi}}{2\mu} + \gamma' \frac{\Delta^2}{\mu_b} + \frac{\mathbf{Q} \cdot \mathbf{Q}/T}{k} + \frac{\mathbf{Q}_v \cdot \mathbf{Q}_v / T_v}{k_v} \right]^{1/2}, \tag{35}$$

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where d and m are the molecular diameter and molecule mass, respectively.

The second-order NCCR (31)-(34) are reduced to the following conventional first-order NSF constitutive relations, when the first-order approximations and the zero bulk viscosity assumption,  $\mu_b = 0$ , are employed,

$$2p[\nabla \mathbf{u}]^{(2)} = -\frac{p}{\mu} \mathbf{\Pi} \implies \mathbf{\Pi} = -2\mu[\nabla \mathbf{u}]^{(2)}, \qquad (36)$$

$$p\nabla(C_p T) = -\frac{pC_p}{k} \mathbf{Q} \implies \mathbf{Q} = -k\nabla T, \qquad (37)$$

$$p\nabla(C_{p,\nu}T_{\nu}) = -\frac{pC_{p,\nu}}{k_{\nu}}\mathbf{Q}_{\nu} \implies \mathbf{Q}_{\nu} = -k_{\nu}\nabla T_{\nu}, \qquad (38)$$

meaning that the NSF is simply a subset of the NCCR. Here  $\mu$ , k and  $k_{\nu}$  are the coefficients of viscosity, thermal conductivity, and vibrational thermal conductivity, respectively.

It should be noted that these first-order laws were obtained after very crude approximations; all of the kinematic terms except for the thermodynamic force term were neglected, and the dissipation terms were linearized. Those first-order approximations are valid, when a composite number Kn·*M*—not the Knudsen number alone—is small. The composite number is defined as the ratio of the viscous force ( $\Pi$ ) to the thermodynamic pressure (*p*) and represents the degree of thermal nonequilibrium in thermodynamic space, since the viscous force is a direct consequence of the thermal nonequilibrium effect.<sup>22,24</sup> On the other hand, when a composite number Kn·*M* is not small (the high Knudsen, the high Mach, or both), the second-order NCCR (31)-(34) should be used. Finally, the conservation laws (18)-(20) and the vibrational energy equation (21) with these first-order constitutive relations form the set of equations reported by Olejniczak and Candler,<sup>50</sup> as summarized in Table I. It is apparent that the NCCR describes the second-order effects through the nonlinear terms and the tightly-coupled cumulant  $\kappa$ , and introduces the effect of the diatomic and polyatomic gases through the excess normal stress  $\Delta$ .

 Table I. Summary of the conservation laws and constitutive equations of the first-order NSF and second-order NCCR theories.

	Previous first-order NSF <sup>50</sup>	New second-order NCCR
ρ	$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$	$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$
ρ <b>u</b>	$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u}\mathbf{u} + p\mathbf{I}) + \nabla \cdot \mathbf{\Pi} = 0$	$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u}\mathbf{u} + p\mathbf{I}) + \nabla \cdot (\mathbf{\Pi} + \Delta \mathbf{I}) = 0$
ρe	$\frac{\partial(\rho e)}{\partial t} + \nabla \cdot ((\rho e + p)\mathbf{u}) + \nabla \cdot (\mathbf{\Pi} \cdot \mathbf{u}) + \nabla \cdot \mathbf{Q} + \nabla \cdot \mathbf{Q}_{v} = 0$	$\frac{\partial(\rho e)}{\partial t} + \nabla \cdot ((\rho e + p)\mathbf{u}) + \nabla \cdot ((\mathbf{\Pi} + \Delta \mathbf{I}) \cdot \mathbf{u}) + \nabla \cdot \mathbf{Q} + \nabla \cdot \mathbf{Q}_{v} = 0$
$ ho e_v$	$\frac{\partial(\rho e_{v})}{\partial t} + \nabla \cdot (\rho e_{v} \mathbf{u}) + \nabla \cdot \mathbf{Q}_{v} = \frac{\rho e_{v}(T_{v}) - \rho e_{v}(T)}{\tau_{v}}$	$\frac{\frac{\partial(\rho e_{v})}{\partial t} + \nabla \cdot (\rho e_{v} \mathbf{u}) + \nabla \cdot \mathbf{Q}_{v}}{\frac{\rho e_{v}(T_{v}) - \rho e_{v}(T)}{\tau_{v}}}$
П	$\mathbf{\Pi} = -2\mu [\nabla \mathbf{u}]^{(2)}$	$2[\mathbf{\Pi} \cdot \nabla \mathbf{u}]^{(2)} + 2(p + \Delta)[\nabla \mathbf{u}]^{(2)} = -\frac{p}{\mu}\mathbf{\Pi}q_{2nd}(\kappa)$
Δ	$\Delta = 0$	$2\gamma'(\mathbf{\Pi} + \Delta \mathbf{I}): \nabla \mathbf{u} + \frac{2}{3}\gamma' p \nabla \cdot \mathbf{u} = -\frac{2}{3}\gamma' \frac{p}{\mu_b} \Delta q_{2nd}(\kappa)$
Q	$\mathbf{Q} = -k\nabla T$	$\mathbf{\Pi} \cdot \nabla(C_p T) + (p + \Delta) \nabla(C_p T) = -\frac{pC_p}{k} \mathbf{Q} q_{2nd}(\kappa)$
Q <sub>v</sub>	$\mathbf{Q}_{v} = -k_{v}\nabla T_{v}$	$\mathbf{\Pi} \cdot \nabla (C_{p,v} T_v) + (p + \Delta) \nabla (C_{p,v} T_v) = -\frac{p C_{p,v}}{k_v} \mathbf{Q}_v q_{2nd}(\kappa)$
<i>q</i> (к)	$q_{1st}(\kappa) = 1$	$q_{2nd}(\kappa) = \frac{\sinh \kappa}{\kappa}$

## III. TOPOLOGICAL ASPECTS OF NONLINEAR COUPLED CONSTITUTIVE RELATIONS WITH VIBRATIONAL NON-EQUILIBRIUM

#### A. A dimensionless compact form of the second-order constitutive model

Studies of topology are concerned with the properties of systems that are preserved under continuous changes. Since the constitutive relation is such a case, the topological representation of the constitutive relations can provide new information and fascinating insights into the physics of fluids,<sup>68,69</sup> which otherwise may not be attainable. Recently, Singh *et al.*<sup>70</sup> reported the topology of the second-order constitutive relations for diatomic and polyatomic gases at temperatures lower than the vibrational excitation temperature. It was found in the case of velocity shear that the topology of the second-order constitutive model was governed by a simple algebraic form; from an ellipse to a circle, to a parabola, and then finally to a hyperbola, with increasing bulk viscosity. The exact same topology was found in the orbits of planets and comets in the Solar System; for example, the case of diatomic gas with the ratio of the bulk viscosity to the shear viscosity 0.2722 is equivalent to the case of the Earth's orbit with the eccentricity 0.0167.

They also investigated the trajectories of the shock structure solution on the topology of the second-order constitutive model. The effect of bulk viscosity on the Rayleigh-Onsager dissipation function and the non-linear behavior of the second-order kinematic coupling term were also described at length. Since the topology of the constitutive relations is separate from the conservation laws, it can provide essential information about the connections between various non-conserved variables, especially in the case of second-order constitutive relations.

In the present work, a similar study was conducted to highlight the non-linear coupling effects on the topology of the second-order constitutive relations. For this purpose, the dimensional form of the second-order constitutive relation needs to be transformed into a non-dimensional form, in order to reduce the number of dimensions in phase space. The following dimensionless variables and the definitions of non-dimensional parameters (such as the Mach number (M), Reynolds number (Re), Eckart number (Ec), Prandtl number (Pr), Knudsen number (Kn) and nondimensional rarefaction parameter  $N_{\delta}$ ) are employed:

$$\begin{split} \mu^{*} &= \mu / \mu_{r}, & k^{*} = k / k_{r}, & u^{*} = u / u_{r}, & T^{*} = T / T_{r}, \\ p^{*} &= p / p_{r}, & \rho^{*} = \rho / \rho_{r}, & C_{p}^{*} = C_{p} / C_{p_{r}}, & d^{*} = d / d_{r}, \\ \Pi^{*} &= \Pi / (\mu_{r} u_{r} / L), & \Delta^{*} = \Delta / (\mu_{r} u_{r} / L), & Q^{*} = Q / (k_{r} T_{r} / L), & f_{b} = \mu_{b_{r}} / \mu_{r}, \\ M &= u_{r} / \sqrt{\gamma R T_{r}}, & \text{Re} = \rho_{r} u_{r} L / \mu_{r}, & \text{Ec} = u_{r}^{2} / (C_{p_{r}} T_{r}), & \text{Pr} = C_{p_{r}} \mu_{r} / k_{r} \\ N_{\delta} &= \gamma M^{2} / \text{Re}, & \text{Kn} = \sqrt{\pi / 2\gamma} N_{\delta} / M, & \varepsilon = 1 / (\text{Ec} \text{Pr}). \end{split}$$

The starred quantities represent the non-dimensional quantities; terms with subscript *r* are reference quantities chosen appropriate to the flow problem. In the case of a shock structure problem, generally, the driver side is a suitable choice for the reference quantities. The factor  $f_b = \mu_{b_r} / \mu_r$  is the ratio of the bulk viscosity to the shear viscosity. Its value may be experimentally determined using a sound wave absorption measurement. In addition to the above mentioned non-dimensional entities, a new set of non-dimensional quantities and new parameters are defined for the vibrational degrees of freedom:

$$k_{v}^{*} = k_{v} / k_{v,r}, \qquad T_{v}^{*} = T_{v} / T_{v,r}, \qquad C_{p,v}^{*} = C_{p,v} / C_{p,v_{r}}, \qquad \mathbf{Q}_{v}^{*} = \mathbf{Q}_{v} / (k_{v,r} T_{v,r} / L),$$
  

$$\mathrm{Ec}_{v} = u_{r}^{2} / (C_{p,v_{r}} T_{v,r}), \qquad \mathrm{Pr}_{v} = C_{p,v_{r}} \mu_{r} / k_{v,r}, \qquad \varepsilon_{v} = 1 / (\mathrm{Ec}_{v} \mathrm{Pr}_{v}).$$

After those non-dimensional quantities and parameters are substituted into the modified Rayleigh-Onsager dissipation function ( $\kappa$ ), we obtain

$$\kappa = c \frac{N_{\delta}}{p^*} \left[ \mathbf{\Pi}^* : \mathbf{\Pi}^* + \frac{2\gamma'}{f_b} \Delta^2 + \frac{\mu^*}{k^*} \frac{\mathbf{Q}^* \cdot \mathbf{Q}^*}{T^*/(2\varepsilon)} + \frac{\mu^*}{k_v^*} \frac{\mathbf{Q}_v^* \cdot \mathbf{Q}_v^*}{T_v^*/(2\varepsilon_v)} \right]^{1/2}.$$
<sup>(39)</sup>

In this expression, the coefficient c was first derived by Myong<sup>22</sup> with a simple gas assumption (due to Chapman and Cowling<sup>30</sup>):

$$c = \left(\frac{(mk_B T_r)^{1/4}}{2d_r \sqrt{\mu_r}}\right) = \left[\frac{2\sqrt{\pi}}{5} A_2(\nu) \Gamma[4 - 2/(\nu - 1)]\right]^{1/2},$$
(40)

where v is the exponent of the inverse power laws; it turns out that the following relation holds

$$\left(\frac{T^{*1/4}}{d^*\sqrt{\mu^*}}\right) = 1.$$
 (41)

Upon substituting the non-dimensional form of  $\kappa$  into the NCCR (31)-(34), and dropping the asterisk superscript for simplicity, the final second-order constitutive relations are:

$$\hat{\mathbf{\Pi}}q_{\text{2nd}}(c\hat{R}) = (1 + f_b\hat{\Delta})\hat{\mathbf{\Pi}}_0 + [\hat{\mathbf{\Pi}}\cdot\nabla\hat{\mathbf{u}}]^{(2)}, \qquad (42)$$

$$\hat{\Delta}q_{2\mathrm{nd}}(c\hat{R}) = \hat{\Delta}_0 + \frac{3}{2}f_b(\hat{\mathbf{\Pi}} + f_b\hat{\Delta}\mathbf{I}):\nabla\hat{\mathbf{u}}, \qquad (43)$$

$$\hat{\mathbf{Q}}q_{2\mathrm{nd}}(c\hat{R}) = (1 + f_b\hat{\Delta})\hat{\mathbf{Q}}_0 + \hat{\mathbf{\Pi}}\cdot\hat{\mathbf{Q}}_0, \qquad (44)$$

$$\hat{\mathbf{Q}}_{v}q_{2\mathrm{nd}}(c\hat{R}) = (1+f_{b}\hat{\Delta})\hat{\mathbf{Q}}_{v,0} + \hat{\mathbf{\Pi}}\cdot\hat{\mathbf{Q}}_{v,0}, \qquad (45)$$

where

$$\hat{\mathbf{\Pi}} \equiv \frac{N_{\delta}}{p} \mathbf{\Pi}, \qquad \hat{\Delta} \equiv \frac{N_{\delta}}{p} \Delta, \qquad \hat{\mathbf{Q}} \equiv \frac{N_{\delta}}{p} \frac{\mathbf{Q}}{\sqrt{T/(2\varepsilon)}}, \qquad \hat{\mathbf{Q}}_{\mathbf{v}} \equiv \frac{N_{\delta}}{p} \frac{\mathbf{Q}_{\mathbf{v}}}{\sqrt{T_{\mathbf{v}}/(2\varepsilon_{\mathbf{v}})}},$$

$$\hat{\mathbf{\Pi}}_{0} \equiv \frac{-N_{\delta}(2\mu[\nabla\mathbf{u}]^{(2)})}{p}, \quad \hat{\Delta}_{0} \equiv \frac{-N_{\delta}\mu_{b}\nabla\cdot\mathbf{u}}{p}, \quad \hat{\mathbf{Q}}_{0} \equiv \frac{N_{\delta}}{p}\frac{-k\nabla T}{\sqrt{T/(2\varepsilon)}}, \quad \hat{\mathbf{Q}}_{v,0} \equiv \frac{N_{\delta}}{p}\frac{-k_{v}\nabla T_{v}}{\sqrt{T_{v}/(2\varepsilon_{v})}},$$
  
and  $\hat{R} = \left[\hat{\mathbf{\Pi}}:\hat{\mathbf{\Pi}} + \frac{2\gamma'}{f_{b}}\hat{\Delta}^{2} + \hat{\mathbf{Q}}\cdot\hat{\mathbf{Q}} + \hat{\mathbf{Q}}_{v}\cdot\hat{\mathbf{Q}}_{v}\right]^{1/2}.$ 

The structure of the NCCR for diatomic and polyatomic gases with the vibrational degrees of freedoms is exactly the same as that for diatomic and polyatomic gases without the vibrational degrees of freedoms, except for the additional relation (45) and extra term  $\hat{\mathbf{Q}}_v \cdot \hat{\mathbf{Q}}_v$  in the modified Rayleigh-Onsager dissipative function.

# B. Decomposition of the second-order constitutive model in elementary flows and its topology in velocity shear

In order to investigate the topology of the second-order constitutive model, we consider monatomic, diatomic, and polyatomic gases. In general, the second-order constitutive relations (42)-(45) consist of twelve unknowns: five components of the traceless viscous stress tensor  $(\Pi_{xx}, \Pi_{yy}, \Pi_{zz} (= -\Pi_{xx} - \Pi_{yy}), \Pi_{xy}, \Pi_{xz}, \Pi_{yz})$ , the scalar excess normal stress ( $\Delta$ ), three components of the heat flux vector ( $Q_x, Q_y, Q_z$ ), and three components of the vibrational heat flux vector ( $Q_{v,x}, Q_{v,y}, Q_{v,z}$ ). Because of the twelve-dimensional topology in phase space and its highly nonlinear and coupled nature, investigating the topology in any meaningful way seems very difficult. Nevertheless, the topology can be rather efficiently investigated based on the concept of decomposition, which was first introduced by Myong.<sup>23</sup>

In general, the viscous stress and heat flux components on a line (or interface) in the physical plane induced by the thermodynamic forces of velocity and temperature gradients can be decomposed (or split) into two elementary subsets; one for the velocity shear flow, and another for

the gaseous compression and expansion flow. In the *velocity shear flow* subset, the stresses  $(\Pi_{xx}, \Pi_{xy}, \Delta)$  induced by the thermodynamic force  $v_x \equiv \partial v / \partial x$  can be determined from (42)-(43) as follows,

$$\hat{\Pi}_{xx}q_{2nd}\left(c\hat{R}\right) = -\frac{2}{3}\hat{\Pi}_{xy}\hat{\Pi}_{xy_{0}},$$

$$\hat{\Pi}_{xy}q_{2nd}\left(c\hat{R}\right) = \left(1 + f_{b}\hat{\Delta} + \hat{\Pi}_{xx}\right)\hat{\Pi}_{xy_{0}},$$

$$\hat{\Delta}q_{2nd}\left(c\hat{R}\right) = 3f_{b}\hat{\Pi}_{xy}\hat{\Pi}_{xy_{0}},$$
(46)

where

$$\hat{R}^{2} = 3\hat{\Pi}_{xx} \left[ \left( 1 + \frac{9}{2} f_{b} (f_{b} + 3\gamma') \right) \hat{\Pi}_{xx} - 1 \right].$$

When the first two components of equations in (46) are divided by each other, the nonlinear coupling factor  $q_{2nd}(c\hat{R})$  and the driving force  $\hat{\Pi}_{xy_0}$  are canceled out, leaving only a kinematic stress constraint,

$$\frac{2}{3}\hat{\Pi}_{xy}^{2} + \left(1 - \frac{9}{2}f_{b}^{2}\right)\hat{\Pi}_{xx}^{2} + \hat{\Pi}_{xx} = 0.$$
(47)

The vibrational heat flux does not play any role in the velocity shear flow, so that the topology remains the same as those of the non-vibrating diatomic and polyatomic gases,<sup>70</sup> as reproduced in Fig. 1. Note that the topology shows rich and complex patterns; for example, with increasing  $f_b$ , the conic section varies from an ellipse for  $0 \le f_b < \sqrt{2}/3$  (including a circle for  $f_b = \sqrt{6}/9$ ) to a parabola for  $f_b = \sqrt{2}/3$ , and then to a hyperbola for  $f_b > \sqrt{2}/3$ .



Figure 1. Topology of the second-order Boltzmann-Curtiss-based constitutive models in the velocity shear flow problem in a phase space ( $\Pi_{xx}$ ,  $\Pi_{xy}$ , p) for  $f_b$  =0 and  $f_b$  =1.0. Reproduced with permission from S. Singh, A. Karchani, K. Sharma, and R. S. Myong, "Topology of the second-order constitutive model based on the Boltzmann-Curtiss kinetic equation for diatomic and polyatomic gases," Physics of Fluids 32, 026104 (2020). Copyright 2020 AIP.

### C. Topology of the second-order constitutive model in compression and expansion: sinhdominated topology

Similar to the previous velocity shear flow, another elementary flow, gaseous compression and expansion, can be obtained based on the concept of decomposition. From (42)-(45), the viscous stresses and the heat fluxes, including the vibrational mode driven by thermodynamic forces  $u_x = \partial u/\partial x$  and  $T_x = \partial T/\partial x$ , can be determined as follows:

$$\begin{pmatrix} \hat{\Pi}_{xx} \\ \hat{\Delta} \\ \hat{Q}_{x} \\ \hat{Q}_{v,x} \end{pmatrix} = \operatorname{fn} \begin{pmatrix} \hat{\Pi}_{xx_{0}} \\ \hat{\Delta}_{0} \\ \hat{Q}_{x_{0}} \\ \hat{Q}_{v,x_{0}} \end{pmatrix}, c, f_{b} \end{pmatrix} \Rightarrow \begin{pmatrix} \hat{\Pi}_{xx} \\ \hat{\Delta} \\ \hat{Q}_{x} \\ \hat{Q}_{v,x} \end{pmatrix} q_{2nd} (c\hat{R}) = \begin{pmatrix} (1+f_{b}\hat{\Delta}+\hat{\Pi}_{xx})\hat{\Pi}_{xx_{0}} \\ (1+3(f_{b}\hat{\Delta}+\hat{\Pi}_{xx}))\hat{\Delta}_{0} \\ (1+f_{b}\hat{\Delta}+\hat{\Pi}_{xx})\hat{Q}_{x_{0}} \\ (1+f_{b}\hat{\Delta}+\hat{\Pi}_{xx})\hat{Q}_{v,x_{0}} \end{pmatrix},$$
(48)

where

$$\hat{R}^{2} = \frac{3}{2}\hat{\Pi}_{xx}^{2} + \frac{2\gamma'}{f_{h}}\hat{\Delta}^{2} + \hat{Q}_{x}^{2} + \hat{Q}_{v,x}^{2}$$

This highly nonlinear mapping function in four-dimensional phase space is strongly dependent on the ratio of the bulk viscosity to the shear viscosity,  $f_b$ , whereas its dependence on the coefficient of potential in the gaseous power laws c (=1.1038 in the present study) is negligible. When the first two components of the equations in (48) are divided by each other, the nonlinear coupling factor  $q_{2nd}(c\hat{R})$  and the driving force  $\hat{\Pi}_{xx_0}$  are canceled out, leaving only a kinematic stress constraint between the viscous shear and excess normal stresses,

$$9f_b\hat{\Pi}_{xx}^2 + (9f_b^2 - 4)\hat{\Pi}_{xx}\hat{\Delta} - 4f_b\hat{\Delta}^2 + 3f_b\hat{\Pi}_{xx} - \hat{\Delta} = 0.$$
(49)

It is noteworthy that the topological features of the present mapping function are very similar to that of the diatomic and polyatomic gases without vibrational degrees of freedom. This is primarily because the vibrational heat flux term is connected to the viscous stresses only through the common nonlinear coupling factor of dissipative nature,  $q_{2nd}(c\hat{R})$ , which cancels out in the present framework. In contrast to the velocity shear case, the second-degree polynomial equation (49) in the compression and expansion cases always results in the topology of a hyperbola with the following eccentricity for all values of  $f_b$ ,

$$e = \frac{\sqrt{2}\sqrt[4]{81f_b^4 + 97f_b^2 + 16}}{\sqrt{5f_b + \sqrt{81f_b^4 + 97f_b^2 + 16}}}.$$
(50)

At zero bulk viscosity  $f_b = 0$ , the eccentricity is equal to  $\sqrt{2}$ . The variation in eccentricity with respect to the bulk viscosity has a well-shaped profile which reaches the minimum value of  $\sqrt{13}/2$  at  $f_b = \sqrt{2}/3$  and asymptotically recovers the initial value of  $\sqrt{2}$  as the bulk viscosity ratio approaches infinity.

In order to further investigate the topology of the second-order constitutive model for the relationship between the unknown stresses and heat fluxes  $(\hat{\Pi}_{xx}, \hat{\Delta}, \hat{Q}_x, \hat{Q}_{v,x})$  and the known driving (stress and thermal) forces of  $(\hat{\Pi}_{xx_0}, \hat{Q}_{x_0}, \hat{Q}_{v,x_0})$ , the constitutive model should be calculated for the given driving forces, either analytically or numerically. For the first-order Navier-Fourier constitutive relations, the excess normal stress is linearly related to the viscous stress in a non-Stokesian framework through the relation  $\Delta_0 = 0.75 f_b \Pi_{xx_0}$  in one-dimensional cases.

On the other hand, in an implicit form the second-order constitutive model (48) can be solved numerically in terms of the driving forces  $\hat{\Pi}_{xx_0}$ ,  $\hat{Q}_{x_0}$ ,  $\hat{Q}_{v,x_0}$  in conjunction with (39), using the method of iteration. The first case with zero bulk viscosity is reduced to a monoatomic gas, in which case the vibrational degrees of freedom are absent. In the present study, this case represents a gas with vibrational degrees of freedom, with the bulk viscosity asymptotically approaching to zero.

The second case is defined by considering a diatomic nitrogen gas whose bulk viscosity ratio is equal to 0.8. At this stage, it should be mentioned that the available experimental data for the bulk viscosity of diatomic and polyatomic gases obtained in 1960-80s from the measurement of sound wave attenuation are a matter of controversy.<sup>71,72</sup> Recent new experimental data reported by Wang *et al.*<sup>73</sup> using Rayleigh-Brillouin light scattering spectroscopy indicated that the values of  $f_b$  in gases (such as CO<sub>2</sub>) previously known to possess very large values are questionable; for example, the value of CO<sub>2</sub> was claimed smaller than 1.0. In addition, a recent theoretical study<sup>65</sup> based on the Boltzmann equation in the form of Wang Chang-Uhlenbeck with vibrational mode and the Chapman-Enskog method showed that the value of CO<sub>2</sub> is in the range of  $0.5 < f_b < 2.6$ *when the vibrational model is included*, not an order of 100 or 1000. In this study, even though there is no limitation for the value of  $f_b$  in the present formulation, we focus on  $f_b = 0.8$  case, since our primary interest is in the air flows around reentry and hypersonic vehicles on the Earth, dominated by nitrogen and oxygen ( $f_b$  being smaller than 1). We hope to work more on the larger bulk viscosity cases in the future.

For each set of simulations at a specified bulk viscosity ratio, the non-conserved variables,  $\hat{\Pi}_{xx}, \hat{\Delta}, \hat{Q}_x, \hat{Q}_{v,x}$ , are calculated for the given thermodynamic driving forces,  $\hat{\Pi}_{xx_0}, \hat{Q}_{x_0}, \hat{Q}_{v,x_0}$  (or  $\hat{\Pi}_0, \hat{Q}_0, \hat{Q}_{v,0}$  in simpler notation). This will yield a topology in a four-dimensional space such as ( $\hat{\Pi}_0, \hat{Q}_0, \hat{Q}_{v,0}, \hat{\Pi}_{xx}$ ). For visualization in a three-dimensional space, surface plots of a nonconserved variable as a function of the driving forces (stress,  $\hat{\Pi}_0$ , and thermal,  $\hat{Q}_0$ ) are constructed at a specified vibrational thermal force,  $\hat{Q}_{v,0}$ , and the given bulk viscosity ratio.

Figure 2 (a) shows the three-dimensional topology of viscous normal stress in  $(\hat{\Pi}_0, \hat{Q}_0, \hat{\Pi}_{xx})$  at zero vibrational thermal force and at the vanishing bulk viscosity ratio. The topology well matches one constructed for a monoatomic gas reported previously.<sup>70</sup> The corresponding topology of the first-order Navier-Stokes-Fourier constitutive model is a simple linear surface, since they are

nothing but  $\hat{\Pi} \leftarrow \hat{\Pi}_0$ ,  $\hat{Q} \leftarrow \hat{Q}_0$ . Figure 2 (b)-(c) shows the topology at a non-zero vibrational thermal force, when the bulk viscosity is neglected. It can be noted that the vibrational mode reduces the level of nonlinearity in the topology, including the case with a vanishing thermal force.

Figure 3 (a) shows the three-dimensional topology of viscous normal stress at the bulk viscosity ratio,  $f_b = 0.8$ , when the vibrational degrees of freedom are absent. Figure 3 (b)-(c) shows the effect of the vibrational heat flux on the viscous normal stress in the second-order constitutive model. As in Figure 2 (b)-(c), the vibrational mode reduces the level of nonlinearity, especially in the compression branch (positive stress force  $\hat{\Pi}_0 > 0$ ).

Figure 4 (a) shows a cross section of the topology of viscous normal stress at the plane defined by  $\hat{Q}_0 = 0$ , or zero thermal force. Compared with the linear NF relation, the expansion (negative stress force  $\hat{\Pi}_0 < 0$ ) branch is significantly flattened, while the compression branch shows a high degree of non-linearity and approaches to the logarithmic (sinh<sup>-1</sup>) asymptotes. However, the most noticeable feature of the topology is a distinct '*protruding region*' in the positive compression branch, where the viscous normal stress of the second-order constitutive model remains bigger than that of the first-order Navier-Fourier constitutive model. The ultimate reason behind this behavior is the presence of the second-order kinematic stress-strain coupling term,  $\hat{\Pi}_{xx}\hat{\Pi}_{xx_0}$ , in the second-order constitutive model (48),  $\hat{\Pi}_{xx}q_{2nd}(c\hat{R}) = (1 + f_b\hat{\Delta} + \hat{\Pi}_{xx})\hat{\Pi}_{xx_0}$ . When the stress force  $\hat{\Pi}_{xx_0}$  is small, the coupling term  $\hat{\Pi}_{xx}\hat{\Pi}_{xx_0}$  of quadratic nature on the right-hand side will prevail over the dissipation term  $\hat{\Pi}_{xx}q_{2nd}(c\hat{R})$  of hyperbolic sine nature on the left-hand side, resulting in  $\hat{\Pi}_{xx} > \hat{\Pi}_{xx_0}$ . On the other hand, when the stress force  $\hat{\Pi}_{xx_0}$  increases, the dissipation term  $\hat{\Pi}_{xx}q_{2nd}(c\hat{R})$  of the hyperbolic sine *exponential* nature will dominate over the coupling term  $\hat{\Pi}_{xx}\hat{\Pi}_{xx_0}$  of quadratic nature, leading to the logarithmic (sinh<sup>-1</sup>) asymptote.

Similar to Figure 3 (b)-(c), with increasing vibrational thermal force, the level of nonlinearity in the second-order constitutive model decreases, as shown in Fig. 4 (b). This trend remains the same for the non-zero bulk viscosity ratio. It is also interesting to note that the profiles of excess normal stress become symmetrical with increasing vibrational thermal force.



Figure 2. Three-dimensional topology of viscous normal stress  $\hat{\Pi}_{xx}$  for varying stress and thermal forces at a specified vibrational thermal force  $\hat{Q}_{v,0}$  and  $f_b = 0$ .



Figure 3. Three-dimensional topology of viscous normal stress  $\hat{\Pi}_{xx}$  for varying stress and thermal forces at a specified vibrational thermal force  $\hat{Q}_{v,0}$  and  $f_b = 0.8$ .



Figure 4. A cross-section of the topology of viscous normal stress  $\hat{\Pi}_{xx}$  at the plane defined by  $\hat{Q}_0 = 0$  or a zero thermal force at three different vibrational thermal forces and two different ratios: a)  $f_b = 0$  and b)  $f_b = 0.8$  (left).

Figures 5 (a) and 6 (a) show the three-dimensional topology of heat flux in  $(\hat{\Pi}_0, \hat{Q}_0, \hat{Q}_x)$  at zero vibrational thermal force and at the bulk viscosity ratios,  $f_b = 0$  and  $f_b = 0.8$ , respectively. As expected, the heat flux is more strongly affected by the thermal force than the stress force. Interestingly, there are two regions with higher values of heat flux in the compression branch near  $\hat{\Pi}_{xx_0} = 4$ ; one '*protruding region*' for positive  $\hat{Q}_0$ , another '*sunken region*' for positive  $\hat{Q}_0$ . They are the same in nature, since the heat flux satisfies the asymmetric property of the heat flux,  $\hat{Q}(-\hat{Q}_0) = -\hat{Q}(\hat{Q}_0)$  in (49). Again, the reason behind such distinct regions is closely related to the presence of the second-order kinematic coupling term,  $\hat{\Pi}_{xx}\hat{Q}_{x_0}$ , in the second-order constitutive model (48),  $\hat{Q}_x q_{2nd}(c\hat{R}) = (1 + f_b \hat{\Delta} + \hat{\Pi}_{xx})\hat{Q}_{x_0}$ .



Figure 5. Three-dimensional topology of heat flux  $\hat{Q}_x$  for varying stress and thermal forces at a specified vibrational thermal force  $\hat{Q}_{v,0}$  and  $f_b = 0$ .



Figure 6. Three-dimensional topology of heat flux  $\hat{Q}_x$  for varying stress and thermal forces at a specified vibrational thermal force  $\hat{Q}_{v,0}$  and  $f_b=0.8$ .



Figure 7. A cross-section of the topology of  $\hat{Q}_x$  at the plane defined by  $\hat{\Pi}_0 = 0$  or a zero stress force at three different vibrational thermal forces and two different ratios: a)  $f_b = 0$  and b)  $f_b = 0.8$ .

Like the viscous normal stress in Fig. 2, Figs. 5 (b)-(c) and 6 (b)-(c) show that the vibrational mode reduces the level of nonlinearity in the topology. This is because the contribution of each mode in  $(\hat{\Pi}_{xx}, \hat{\Delta}, \hat{Q}_x, \hat{Q}_{v,x})$  is calculated by the *quadratic* form of the modified Rayleigh-Onsager dissipation,  $\hat{R}^2 = 3\hat{\Pi}_{xx}^2/2 + 2\gamma\hat{\Delta}^2/f_b + \hat{Q}_x^2 + \hat{Q}_{v,x}^2$ , leading to a reduction in  $\hat{\Pi}_{xx}, \hat{\Delta}, \hat{Q}_x$  by the addition of the vibrational heat flux mode  $\hat{Q}_{v,x}$ .

Figure 7 (a) shows the cross-section of the topology of heat flux at the plane defined by  $\hat{\Pi}_{xx_0} = 0$ , or for varying thermal force. The topology of heat flux in the first-order constitutive model denoted by solid lines is linear and uncoupled, meaning that the heat flux is a function of the thermal force only, but is independent of the stress force. On the other hand, the second-order constitutive model not only presents the tight coupling of stress and thermal components, shown in Figs. 5 and 6, but also the nonlinear behavior in the thermal force. At zero vibrational thermal force, the topology takes an asymmetric functional form of  $\sinh(c\hat{Q}_x) = c\hat{Q}_{x_0}$  or  $\hat{Q}_x = \frac{1}{c}\sinh^{-1}(c\hat{Q}_{x_0})$ .
With increasing vibrational thermal force, the topology of the heat flux experiences a substantial reduction in nonlinearity for both  $f_b = 0$  and  $f_b = 0.8$ .

Figure 8 shows the three-dimensional topology of excess normal stress in  $(\hat{\Pi}_0, \hat{Q}_0, \hat{\Delta})$  at the bulk viscosity ratio,  $f_b = 0.8$ , and for three cases of the vibrational thermal force,  $\hat{Q}_{v,0} = 0,10,20$ . As in Figs. 3 and 6, the level of nonlinearity decreases with increasing vibrational thermal force, and particularly, in the compression branch (positive stress force  $\hat{\Pi}_0 > 0$ ).

Figure 9 shows the three-dimensional topology of vibrational heat flux in  $(\hat{\Pi}_0, \hat{Q}_0, \hat{Q}_v)$  at the bulk viscosity ratio,  $f_b = 0.8$ , and for three cases of the vibrational thermal force,  $\hat{Q}_{v,0} = 0,10,20$ . Obviously, as seen in Fig. 9 (a), the vibrational heat flux vanishes for zero vibrational thermal force, consistent with the physical requirement that the non-equilibrium stress and heat flux should vanish when there are no thermodynamic driving forces. However, as the vibrational thermal force increases, an interesting topology emerges: a 'protruding region' with higher values of vibrational heat flux in the compression branch near  $\hat{\Pi}_{xx_0} = 4$ . The reason behind this region is again related to the dominant role of the second-order kinematic coupling term,  $\hat{\Pi}_{_{XX}}\hat{Q}_{_{V,X_0}}$ , in the second-order constitutive model of vibrational heat flux in (48),  $\hat{Q}_{v,x}q_{2nd}(c\hat{R}) = (1 + f_b\hat{\Delta} + \hat{\Pi}_{xx})\hat{Q}_{v,x_n}$ . The combination with the same type of second-order constitutive model of heat flux,  $\hat{Q}_x q_{2nd}(c\hat{R}) = (1 + f_b \hat{\Delta} + \hat{\Pi}_{xx}) \hat{Q}_{x_0}$ , results in a maximum near  $\hat{\Pi}_{xx_0} = 4$ ,  $\hat{Q}_{x_0} = 0$ , which is a unique feature in the present second-order constitutive model with the vibrational heat flux. This in turn demonstrates the strong coupling between the various non-conserved variables that are neglected in the first-order Navier-Fourier constitutive model.



Figure 8. Three-dimensional topology of excess normal stress  $\hat{\Delta}$  for varying stress and thermal forces at a specified vibrational thermal force  $\hat{Q}_{v,0}$  and  $f_b=0.8$ .



Figure 9. Three-dimensional topology of vibrational heat flux  $\hat{Q}_v$  for varying stress and thermal forces at a specified vibrational thermal force  $\hat{Q}_{v,0}$  and  $f_b=0.8$ .



Figure 10. Three-dimensional topology of non-vibrational and vibrational heat fluxes in a)  $(\hat{Q}_0, \hat{Q}_{v,0}, \hat{Q})$  and b)  $(\hat{Q}_0, \hat{Q}_{v,0}, \hat{Q}_v)$  at a zero driving stress force and  $f_b = 0.8$ .

Figure 10 shows the three-dimensional topology of non-vibrational and vibrational heat fluxes in  $(\hat{Q}_0, \hat{Q}_{v,0}, \hat{Q}), (\hat{Q}_0, \hat{Q}_{v,0}, \hat{Q}_v)$ , respectively, at zero driving stress force, and at the bulk viscosity ratio,  $f_b = 0.8$ . In this case, the topology is dominated by the dissipation term  $(\hat{Q}_x, \hat{Q}_{v,x})q_{2nd}(c\hat{R})$ of hyperbolic sine (or sinh<sup>-1</sup>) nature. In addition, due to a relation,  $\hat{Q}_v / \hat{Q} = \hat{Q}_{v,0} / \hat{Q}_0$ , in the secondorder constitutive model in (48), the two topologies are basically identical in form. However, it should be pointed out that, although the topologies of the non-vibrational and vibrational heat fluxes are the same in the non-dimensional hat form, dimensional heat fluxes may deviate from each other, when a difference exists between the value of thermal conductivity and vibrational thermal conductivity, and in the absolute value of the trans-rotational and vibrational temperatures.

# IV. EFFECTS OF VIBRATIONAL MODE ON THE SHOCK STRUCTURE OF DIATOMIC AND POLYATOMIC GASES

#### A. Shock structure with vibrational degrees of freedom

The maximum temperature limit for the present Boltzmann-Curtiss-based second-order model is around 2,800 K, which does not exceed substantially the initiation temperature of dissociation of oxygen (approximately 2,500 K).<sup>3</sup> The Mach number range has no upper limit, but the realistic maximum Mach number is around M=26 when the downstream temperature of normal shock wave for the low upstream temperature (20 K) reaches the maximum temperature limit, 2,800 K. The Knudsen number range is up to the transition regime including the shock wave structure, for example, up to Kn=1.0~2.0.

A shock structure with strong gradients is considered one of the fundamental problems in the kinetic theory of gases, including the high temperature regime. The one-dimensional shock structure in a single component of diatomic and polyatomic gases can be described by the following one-dimensional system of equations, which are derived from the conservation laws of mass, momentum, energy, and vibrational energy (18)-(21):

$$\frac{\partial}{\partial t} \begin{pmatrix} \rho \\ \rho u \\ \rho e \\ \rho e_{v} \end{pmatrix} + \frac{\partial}{\partial x} \begin{pmatrix} \rho u \\ \rho u^{2} + p + \Pi_{xx} + \Delta \\ u(\rho e + p) + u(\Pi_{xx} + \Delta) + Q_{x} + Q_{v,x} \\ \rho u e_{v} + Q_{v,x} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \dot{\omega}_{v} \end{pmatrix},$$
(51)

where  $\rho$ ,  $\rho u$ ,  $\rho e$ , and  $\rho e_v$  represent the conserved quantities; the density, momentum in the *x*direction, energy, and vibrational energy, respectively. With the constitutive models ((31)-(35) in the NCCR theory or (36)-(38) in the Navier-Fourier theory) for undetermined non-conserved variables,  $\Pi_{xx}$ ,  $\Delta$ ,  $Q_x$ ,  $Q_{y,x}$ , and the equation of state,  $p = \rho RT$ , the system (51) can be closed. The non-zero source term  $\dot{\omega}_{\nu} (\equiv (\rho e_{\nu}(T) - \rho e_{\nu}(T_{\nu})) / \tau_{\nu})$  in the equation of vibrational energy is modelled using the Landau-Teller equation. The following relaxation time  $\tau_{\nu}$  in the source term in (51) can be obtained:

$$\tau_{v} = Z_{V-T} \tau_{c} \,, \tag{52}$$

where  $Z_{V-T}$  is a constant relaxation factor (assumed to be 50 in the present study) and  $\tau_c$  is the cell mean collision time. The modified Millikan-White relation<sup>52</sup> with Park's correction factor<sup>1</sup> may also be considered; however, it was not adopted in the present shock structure analysis for the sake of simplicity.

$$M_1, \rho_1, T_1, p_1, u_1, a_1, \gamma_1$$
  $M_2, \rho_2, T_2, p_2, u_2, a_2, \gamma_2$ 

Figure 11. A shock tube problem with the driver side on the left and the driven side on the right side (nitrogen gas with  $f_b$ =0.8).

Figure 11 shows a shock tube partitioned into two sections and separated by a diaphragm. The driver side or the pre-shock state (left side) is filled with nitrogen gas at standard temperature ( $T_1$ ; with the subscript 1 denoting the upstream state) to ensure that all of the nitrogen molecules occupy the vibrational ground state. There are five total degrees of freedom for the nitrogen molecule in the driver side (three for the translational mode ( $\zeta_1$ ) and two for the rotational modes ( $\zeta_r$ )). At sufficiently large Mach numbers, the driven side or the post-shock state (right side) is at temperature ( $T_2$ ; with the subscript 2 denoting the downstream state) greater than the characteristic

temperature for vibrational excitation,  $\theta_{\nu}$  (=3,371 K), and the nitrogen molecules are excited to higher vibrational levels. In addition to the five degrees of freedom, the gas in the driven side has additional degrees of freedom for the vibrational mode ( $\zeta_{\nu}$ ) given by,

$$\zeta_{\nu} = \frac{2e_{\nu}(T_2)}{RT_2} \text{ where } e_{\nu} = \frac{R\theta_{\nu}}{\exp(\theta_{\nu}/T_2) - 1}.$$
(53)

This excitation of vibrational degrees of freedom leads to a shock structure problem that has a varying ratio of specific heat at constant pressure to specific heat at constant volume ( $\gamma$ ) on the two sides of the diaphragm. The post-shock conditions for a given set of pre-shock conditions can be analytically determined using the following generalized Rankine-Hugoniot<sup>74,75</sup> shock relations, which include the effect of the varying ratio  $\gamma$ :

$$\frac{(1+\gamma_1 M_1^2)^2}{(\frac{\gamma_1}{\gamma_1 - 1} + \frac{\gamma_1}{2} M_1^2) \gamma_1 M_1^2} = \frac{(1+\gamma_2 M_2^2)^2}{(\frac{\gamma_2}{\gamma_2 - 1} + \frac{\gamma_2}{2} M_2^2) \gamma_2 M_2^2},$$
(54)
$$\frac{T_2}{T_1} = \frac{\frac{\gamma_1}{\gamma_1 - 1} + \frac{\gamma_1}{2} M_1^2}{\frac{\gamma_2}{\gamma_2 - 1} + \frac{\gamma_2}{2} M_2^2},$$
(55)
$$\frac{u_2}{u_1} = \sqrt{\frac{\gamma_2}{\gamma_1}} \frac{M_2}{M_1} \sqrt{\frac{\frac{\gamma_1}{\gamma_1 - 1} + \frac{\gamma_1}{2} M_1^2}{\frac{\gamma_2}{\gamma_2 - 1} + \frac{\gamma_2}{2} M_2^2}}.$$
(56)

It is noteworthy that the post-shock Mach number is related to the post-shock specific heat ratio, which is in turn dependent on the post-shock temperature, resulting in an implicit system. An iterative numerical procedure is needed to obtain the post-shock conditions using the generalized Rankine-Hugoniot relations. In a hypothetical case with zeroth-order assumptions for the non-conserved variables and assuming an infinitely fast vibrational-translational relaxation, the shock structure is a simple Heaviside step function on the pre- and post-shock conditions, centered on the diaphragm. However, the realistic modeling employed in a two-temperature framework in the present study is intended to describe an explicit interplay between the gradients of the non-conserved variables and the vibrational-translational relaxation.

#### B. Effects of vibrational mode on the shock structure

The order of constitutive relations (the second-order NCCR or the first-order NSF), when determining the non-conserved variables in the conservation laws, has a big impact on the shock structure. The thin structure of the shock wave is ultimately the region with a high degree of thermal non-equilibrium, across which the gas properties change drastically and the kinetic energy of the gas transforms into thermal energy, which is always an irreversible process. In the present study, a flow of diatomic nitrogen gas with a high Mach number with M=15 (driver side:  $p_1 = 101,325$  Pa ,  $u_1 = 5,054.4$  m/s and  $T_1 = 273$  K , driven side:  $p_2 = 27,773,949$  Pa ,  $u_2 = 672.16$  m/s and  $T_2 = 9,957.03$  K ) is considered to validate the second-order vibrational relaxation models for non-equilibrium flows of diatomic and polyatomic gases.

The first theory (denoted NSF) is based on the single-temperature first-order Navier-Stokes-Fourier constitutive relations with a zero bulk viscosity assumption. In this case, the temperatures for the different modes of energy are assumed to be at equilibrium at all conditions across the shock structure. The excess normal stress, vibrational energy, and vibrational heat flux in (51) are assumed to be zero.

The second theory (denoted NCCR) is based on the single-temperature second-order nonlinear coupled constitutive relations with a finite bulk viscosity ratio equal to 0.8. The vibrational energy and vibrational heat flux are set to be zero.

The third theory (denoted NSF + vib) is based on the two-temperature first-order Navier-Stokes-Fourier constitutive relations with a zero bulk viscosity assumption and in conjunction with an additional equation of conservation of vibrational energy, as reported by Olejniczak and Candler.<sup>50</sup> It is assumed that the pre-shock and post-shock vibrational temperatures are equal to the respective trans-rotational temperatures.

The last theory (denoted NCCR + vib) is based on the two-temperature second-order nonlinear coupled constitutive relations with a finite bulk viscosity ratio equal to 0.8, which include the vibrational degrees of freedom derived in the present study.

The transport coefficients (viscosity, thermal conductivity, and vibrational thermal conductivity) are modeled using the following temperature-dependent power laws:

$$\mu(T) = \mu_r \left(\frac{T}{T_r}\right)^{\omega},\tag{57}$$

$$k(T) = \frac{\mu(T)C_p}{\Pr},$$
(58)

$$k_{\nu}(T,T_{\nu}) = \mu(T)R \frac{(\theta_{\nu}/T_{\nu})^{2} \exp(\theta_{\nu}/T_{\nu})}{(\exp(\theta_{\nu}/T_{\nu}) - 1)^{2}} / \Pr,$$
(59)

where  $\omega(=1.0)$  is the coefficient of the gaseous power law, Pr(=0.75) is the assumed Prandtl number,  $\mu_r$  (=1.66×10<sup>-5</sup> Pa s) is the reference viscosity at the given reference temperature ( $T_r$ =273 K).

Although the shock structure problem does not involve any solid boundary, the accurate calculation of the shock structure presents severe theoretical and computational challenges,<sup>76,77</sup> because of its inherent nonlinearity in the formation of the shock wave through self-steepening. For instance, the high order hydrodynamic approach based on the Grad's moment method and the

associated assumption of Maxwellian molecules failed to yield shock structure solutions beyond a relatively small Mach number value  $(M \doteq 1.65)$ .<sup>37</sup>

In the present study, we developed a one-dimensional finite volume method (FVM) code based on the second-order monotonic upwind scheme for conservation laws (MUSCL)<sup>78</sup> with a min-mod limiter, Harten-Lax-van Leer-Contact (HLLC) flux solver<sup>79</sup> for the convective scheme and the central difference scheme for the viscous term, and a third-order strong-stability preserving Runge-Kutta time integrator. The shock structure calculation requires numerical solutions for the compression branch of the second-order NCCR in the FVM code, the essences of which were described in previous works.<sup>23,34,38</sup> To verify the one-dimensional codes, numerical solutions of the NSF model were compared with analytic solutions of the NSF equations with the temperaturedependence of transport cofficients.<sup>80</sup> For all other theories where no analytical solutions were available, grid convergence studies were conducted to ensure the accuracy of the numerical solutions.

Figure 12 shows the profiles of normalized density, velocity, trans-rotational temperature, and pressure as a function of the distance normalized using mean free path. The reference mean free path is defined as  $\lambda = \sqrt{\pi/2} \mu_r / (\rho_r \sqrt{RT_r})$  based on the pre-shock conditions. The origin,  $x/\lambda=0$ , represents the center of the shock structure, where the normalized density is equal to 0.5. The second-order NCCR theory results in thicker shock structure profiles compared with the first-order NSF theory.

Theories based on a two-temperature model, both the first-order NSF and second-order NCCR models, show broader shock structure profiles, and in particular, for temperatures and density near downstream, compared to the single-temperature model. In addition, the two-temperature theories

show an earlier initiation of shock transition near upstream. These highlight the effects of thermal non-equilibrium and vibrational heat flux on the shock structure of diatomic gases.



Figure 12. Mach 15 shock profiles of a) normalized density, b) velocity, c) trans-rotational temperature, and d) pressure with respect to the distance normalized using mean free path.

The single-temperature NSF theory predicts shock thickness on the order of a few mean free paths. The single-temperature NCCR theory predicts a shock thickness that is greater than that of the corresponding NSF theory. On the other hand, in two-temperature theories (both NSF and NCCR), the shock thickness is predicted to be approximately the size of the constant vibrational relaxation factor, equal to 50 times the mean free path. In addition, the profiles of pressure and velocity are shown to relax to the downstream conditions much quicker than those of temperature and density.



Figure 13. Mach 15 shock profiles of a) normalized viscous stress and b) trans-rotational heat flux with respect to the distance normalized using mean free path.



Figure 14. Trajectories of Mach 15 shock structure in the phase space of viscous stress and heat flux.

There is a qualitative change to the shock structure when the theory employs a two-temperature framework, by including the vibrational heat flux. Figure 12 (bottom left) shows an overshoot in the trans-rotational temperature in the downstream part of the shock structure. In contrast, in the single-temperature theories, no such overshoot was found, and all of the profiles remain completely monotonic. The origin of this overshoot is basically related to the finite nature of the translational-vibrational relaxation process, which distributes the energy in the two degrees of freedom at different rates.

Figures 13 and 14 show profiles of the normalized non-conserved variables (viscous stress and heat flux) and their trajectories in the phase space, respectively. The variables are normalized using the minimum and maximum values. As expected, both the viscous stress and heat flux quickly reach a peak in the middle of the shock structure and then relatively slowly return to the equilibrium state downstream. Consistent with Fig. 12, the two-temperature theories show an earlier initiation of the shock transition near upstream than the single-temperature theories do. In addition, Fig. 14 clearly shows that the shock structure is not symmetrical in the phase space of the non-conserved variables. The trajectories of the upstream parts of the shock structure (indicated by the lower curves) show higher magnitudes of heat flux than those in the downstream part (indicated by the upper curves), for a given value of viscous stress. (If the shock structure is symmetric, there should only be one overlapped curve.)

The overshoot in the trans-rotational temperature observed in the downstream part of shock structure in Fig. 12 is also noticeable in Figs. 13 (right) and 14. The change in the sign of the normalized trans-rotational heat flux values represents the region of overshoot. This observation indicates that the origin of overshoot is closely related to the treatment of heat flux in the two-temperature theories. That is, in the conservation laws of energy (51), initially one heat flux mode

 $Q_x$  in the upstream part of the shock structure will be split into two modes  $(Q_x, Q_{v,x})$  as the gas molecules move to the downstream of the shock structure with high temperature. Since the contribution of vibrational heat flux  $Q_{v,x}$  on the sum of heat fluxes  $(Q_x + Q_{v,x})$  increases with the shock transition in the upstream part of the shock structure, there must be a peak in the downstream part of the shock structure, where its contribution reaches maximum, before returning to a vanishing contribution in the downstream of the shock structure. And, in turn, this peak in the vibrational heat flux significantly reduces the trans-rotational heat flux, such that the monotonicity of the trans-rotational heat flux and associated temperature profiles is no longer maintained, ultimately resulting in an overshoot.



Figure 15. Mach 15 shock profiles for a) normalized trans-rotational and vibrational temperatures and b) heat fluxes with respect to the distance normalized using mean free path.

In fact, this explanation is clearly supported by the profiles of the trans-rotational and vibrational temperatures and heat fluxes shown in Fig. 15. Note that the overshoot in the trans-rotational heat flux is caused by a combination of the finite values of the vibrational heat flux after its peak, and the rapid decrease in the trans-rotational heat flux values near downstream of the

shock structure. In passing, it is worth mentioning that the vibrational temperature never exceeds the trans-rotational temperature. Also, the vibrational temperature has a well-developed asymmetric profile, since the relaxation process is proportional to the difference between vibrational energies calculated at the trans-rotational and vibrational temperatures.

Overall, the shock structure can be roughly divided into two zones in the two-temperature framework; pre-peak and post-peak zones, separated by the peak in the trans-rotational temperature. It is apparent that the shock structure profiles of the second-order NCCR theory, especially the trans-rotational temperature and heat flux profiles in the pre-peak zone, are substantially different from those in the first-order NSF theory, while both theories are in close agreement with each other in the post-peak zone. This points to the fact that the constitutive relations of the non-conserved variables have a profound effect on the flow physics in the pre-peak regime, whereas the relaxation processes dominate in the post-peak regime, resulting in similar profiles.

In fact, it is this competition of the two rival processes, the second-order effects of the constitutive relations and V-T relaxation, that determine the accuracy of the profiles of shock structure for diatomic and polyatomic gases with an activated vibrational mode. A detailed analysis of the effects of Mach number, bulk viscosity, and relaxation models will provide interesting insights in the fundamental study of shock structure for diatomic and polyatomic gases and will be taken up in more detail in the future.

#### C. Connection between sinh-dominated topology and shock structure solution

The existence of a topology—the properties of systems that are preserved under continuous changes—in the constitutive model implies that, when the diatomic and polyatomic gases undergo compression in the shock structure, the non-conserved variables appearing in the conservation

laws must be determined on the surface of the compression (positive stress force  $\hat{\Pi}_0 > 0$ ) of sinhdominated topology in the phase space, as shown in Figs. 2-10. Therefore, it will be instructive to investigate the connection between the topology and a flow solution by computing the trajectories of the shock structure solution on the second-order sinh-dominated topology. Singh *et al.*<sup>70</sup> showed such trajectories in the shock structure solution for monatomic and non-vibrating diatomic gases.



Figure 16. Trajectories of the shock structure solutions on the topology of normal viscous stress (top) and trans-rotational heat flux (bottom) in nitrogen gas with vibrational non-equilibrium.

Figure 16 depicts the connection between the shock structure solution and the topology of viscous normal stress in diatomic gases with vibrational non-equilibrium. The present problem would require a topology in a four-dimensional space such as  $(\hat{\Pi}_0, \hat{Q}_0, \hat{Q}_{v,0}, \hat{\Pi}_{xx})$ . However, since it is not possible to visualize a four-dimensional topology, a three-dimensional snapshot of the

topology of viscous normal stress is instead obtained by assuming a zero vibrational thermal force,  $\hat{Q}_{v,0} = 0$ . Therefore, the present comparison of the topology and the trajectories in the shock structure solution in the three-dimensional space should be considered approximate, rather than exact. As already noted, the trajectories in the shock structure solution are located in the fourth quadrant, defined by positive viscous normal stress and negative trans-rotational heat flux. Similar to the observations in the previous work on monatomic and non-vibrating diatomic gases,<sup>70</sup> the shape of the trajectories in the shock structure solution in vibrating diatomic gases is notoverlapped, and the upstream branch is closer to the zero thermal force than the downstream branch.

#### D. Comparison with direct simulation Monte Carlo solutions

Validation of the high Mach shock structure solutions for nitrogen gas obtained in the present work is not feasible, mainly because of the lack of available experimental data. However, direct simulation Monte Carlo (DSMC) simulations can be used as an alternative tool. Several DSMC simulations<sup>81,82</sup> of shock structure, and comparisons with experimental data,<sup>83</sup> have been reported for monoatomic and diatomic molecules with vibrational non-equilibrium. Recently, Wysong *et al.*<sup>84</sup> also reported comparative studies of chemistry and vibrational DSMC models and a high energy oxygen shock tube experiment.<sup>85</sup>

In this study, we first consider a very challenging high Mach number case with M=15 and the upstream temperature 273 K. In addition, to avoid the strong chemical effect that may present in such high Mach flow, especially the dissociation of oxygen, we consider another case, Mach 9 flow with the relatively low upstream temperature 150 K, where the downstream temperature of shock wave reaches approximately 2,260 K, which is far beyond the vibrational excitation temperature (800-1,000 K)<sup>3</sup> but lower than the initiation of non-negligible chemical reaction (2,800 K).

One-dimensional shock structure simulations were performed using the DSMC method employing the variable hard sphere (VHS) model to handle collisions, and the Larsen-Borgnakke (LB) model with constant rotational and vibrational relaxation factors for the inelastic energy exchange. The parameters of the VHS collision model,  $\omega = 1.0$ ,  $v = \omega - 0.5 = 0.5$ ,  $d_{ref} = 4.74381 \times 10^{-10} m$ , were chosen in such a manner that the gas molecules behave like a Maxwellian gas. Since both the first-order and second-order theories assume that the translational and rotational energy modes are in equilibrium with each other, the relaxation factor for the rotational energy exchange in the DSMC simulation was set to one.

The initial conditions for the driven and the driver side of the shock tube were the same as those used in the CFD simulations. The time step chosen for the DSMC simulation was a fraction of the mean collision time, corresponding to the driver side. To avoid the random walk effect which leads to dispersion of the shock structure, a large number of representative particles (3,000,000 particles per cell in the driver section) were used. Although this increases the computational cost considerably, the shock structure will not be affected by any undesirable effects of artificial stabilization techniques.

Figure 17 compares the results of the first-order NSF, second-order NCCR, and DSMC for conserved variables, including trans-rotational and vibrational temperatures. The *x*-axis for the DSMC results was normalized using the same mean free path  $\lambda$  employed in the NSF and NCCR simulations. Again, the origin,  $x/\lambda=0$ , represents the center of the shock structure, where the normalized density is equal to 0.5. For the temperature profiles in DSMC results, all three temperatures (translational, rotational, and vibrational) are plotted. In the case of temperature profiles in the NSF and NCCR results, two temperatures (trans-rotational and vibrational) are plotted.



Figure 17. Mach 15 shock profiles for a) normalized density, b) velocity, c) temperatures and d) pressure with respect to the distance normalized using mean free path. ( $T_1$ =273 K, nitrogen)

The DSMC shock profiles show a smoother transition at the initiation of the shock structure near upstream compared to the first-order NSF and second-order NCCR shock profiles. Previous studies<sup>86-88</sup> have also shown a similar slower rise near upstream of the shock structure. On the other hand, it is apparent from these plots that the second-order NCCR results are in better agreement with the DSMC data when compared with the first-order NSF results, and in particular, in the profiles and slopes of density, velocity, and vibrational temperatures.

The peak translational temperature in the DSMC simulation is higher than the peak transrotational temperature in the NSF and NCCR simulations. The trans-rotational temperature profile of the second-order NCCR simulation is surprisingly close to the rotational temperature profile in the DSMC simulation. This is because, although the translational-rotational relaxation factor for the DSMC simulation is unity, it does not ensure that the rotational relaxation is precisely synchronized with the translational relaxation across the shock structure. This is apparent from the temperature profiles shown in Fig. 17. The rotational energy modes equilibrate with the translational mode only through a collision event. This results in slightly different profiles for translational and rotational temperatures in the DSMC simulations, unlike the first-order NSF and second-order NCCR continuum-based simulations. These arguments do not affect the non-thermal quantities, such as the density and momentum. For a more accurate comparison of the present high Mach number shock structure solutions with experimental data,<sup>85</sup> in future the present secondorder NCCR theory needs to be extended to include the effects of chemical reactions.

Finally, we consider another high Mach number flow with M=9 but the relatively low upstream temperature 150 K. This flow can serve as an ideal case to test the present Boltzmann-Curtiss-based second-order constitutive models including the vibrational mode, since the downstream temperature of shock wave reaches approximately 2,260 K, which is far beyond the vibrational excitation temperature but lower than the initiation temperature of non-negligible chemical reaction. Figure 18 compares the results of the first-order NSF, second-order NCCR, and DSMC for conserved variables, including trans-rotational and vibrational temperatures, for nitrogen gas flow with M=9 and 150 K upstream temperature. As expected, it can be observed that the second-order NCCR results are closer to the DSMC data in the M=9 case when compared with the first-order NSF results.



Figure 18. Mach 9 shock profiles for a) normalized density, b) velocity, c) temperatures and d) pressure with respect to the distance normalized using mean free path. ( $T_1$ =150 K, nitrogen)



Figure 19. Mach 15 (top;  $T_1$ =273 K) and Mach 9 (bottom;  $T_1$ =150 K) shock profiles for a) viscous stress and b) heat flux with respect to the distance normalized using mean free path. (Nitrogen)

Figure 19 compares profiles of the normalized non-conserved variables (viscous stress and heat flux) for M=15, M=9 cases. Both the viscous stress and heat flux quickly reach a peak in the middle of the shock structure and then relatively slowly return to the equilibrium state downstream. As with Figs. 17, 18, the second-order NCCR results are closer to the DSMC data in the lower Mach number (M=9) case.

Table II. Comparison of two key measures to characterize the shock structure profiles of nitrogen gas for the first-order NSF, second-order NCCR, and DSMC results.

M=15, T=273 K	Inverse shock thickness	Temperature-density separation
NSF	0.1446	5.0741
NCCR	0.1112	8.0789
DSMC	0.1083	8.9072
M=9, T=150 K	Inverse shock thickness	Temperature-density separation
NSF	0.1661	4.7404
NCCR	0.2370	2.8746
DSMC	0.2680	3.2662

The judgement on the comparison of precise shock profiles is very subtle and requires careful attentions. The stiff shock structure is well known as one of the toughest problems to solve numerically and numerical results of the shock structure are found to be very sensitive to various factors such as the extent of the computational domain, the imposed downstream boundary conditions, the level of intrinsic viscosity and thermal conductivity, physical and artificial, and so on, making accurate comparisons of various results very challenging. Furthermore, there exist some theoretical gaps between the NCCR and DSMC: 1) DSMC employs a three-temperature model, instead of the two-temperature model of NCCR and NSF; 2) the angular momentum of particle is not monitored in the kinematic module of DSMC code and, instead, its effect is considered during the inelastic collision, while the angular motion is included in both places (kinematic and collisional terms) in the case of Boltzmann-Curtiss kinetic equation.

With these limitations, we compare again the first-order NSF, second-order NCCR, and DSMC results, but based on two key measures which can best characterize the essence of shock structure profiles—the inverse shock density thickness and shock temperature–density separation.<sup>80</sup> Table II summarizes two key characteristics of shock profiles for M=15, M=9 cases. It can be observed

that the second-order NCCR results improve key measures substantially; for example, reduction of deviation in the inverse shock thickness, from 34% to 3% and from 38% to 12%, in case of M=15, M=9, respectively.

Numerical computations of the flow problems studied so far indicated that the computing time of the one-dimensional NCCR code is comparable to that of the NSF code. The only excess load, which is caused by the addition of few iterations (less than 10 in most cases) when the stress and heat fluxes are calculated from the implicit algebraic constitutive equations for given thermodynamic forces, occupies a small fraction of computing time in the code (less than 30 percent).<sup>38,39</sup> The NSF, NCCR and DSMC simulations were conducted on Intel Zeon workstation using 24 processors. Total run time in this one-dimensional problem for the three methods (NSF, NCCR and DSMC) were found to be 147, 175 and 621 CPU hours, respectively, resulting in 19% increase compared with the run time of NSF code.

## V. CONCLUSIONS

New second-order constitutive models of conserved variables for diatomic and (linear) polyatomic gases, including the heat flux associated with vibrational nonequilibrium, were derived based on a modified Boltzmann-Curtiss kinetic equation. These models are a natural extension of the previous nonlinear coupled constitutive relations developed for monoatomic, diatomic, and (linear) polyatomic gases at temperatures lower than the vibrational excitation temperature. The closing-last balanced closure and the cumulant expansion of the calortropy production associated with the Boltzmann collision term play key roles in the derivation of the second-order constitutive models, compatible with the second law of thermodynamics.

The second-order constitutive models were first studied by considering their topology. The properties of the models were preserved under continuous changes. Since the topology of the constitutive relations is separate from the conservation laws, it can provide essential information about the connection between various non-conserved variables and the thermal driving forces. The topology was found to be highly nonlinear and tightly coupled, as illustrated by the presence of protruding or sunken regions and logarithmic (sinh<sup>-1</sup>) asymptotes, in the compression branch in the topology. It was also found that the vibrational mode reduces the level of nonlinearity in the topology.

The second-order constitutive models for diatomic and polyatomic gases with the vibrational degrees of freedom were then applied to the classical shock structure problem. A comparative study of the shock structures, on the basis of the first-order, second-order constitutive models and the direct simulation Monte Carlo method, was carried out. The second-order NCCR theory resulted in thicker shock structure profiles, compared with the first-order NSF theory. The two-temperature theories showed an earlier initiation of shock transition near upstream than the single-temperature theories.

The two-temperature theories also produced a qualitative change in the shock structure, an overshoot in the trans-rotational temperature in the downstream part of the shock structure. The existence of the overshoot was attributed to a combination of finite values in the vibrational heat flux after its peak, and the rapid decrease in the trans-rotational heat flux values near downstream of the shock structure. The analysis showed that competition between the two rival processes—second-order effects of constitutive relations and V-T relaxation—determines the accuracy of the shock structure profiles for diatomic and polyatomic gases with activated vibrational mode. Finally, the analysis concluded that the second-order NCCR results were in better agreement with the

DSMC data, compared with the first-order NSF results, and particularly, in the profiles and slopes of density, velocity, and vibrational temperatures.

This study focused on the effect of vibrational non-equilibrium combined with the secondorder constitutive models of trans-rotational non-equilibrium within the hydrodynamic framework. To fully cover all re-entry flow regimes, from ground to altitudes higher than 55 km and to the boundary of earth's atmosphere, it will be essential to include chemical non-equilibrium. We hope to report the results of our study of this problem in due course.

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# Appendix: Thermodynamic solution of the modified Boltzmann-Curtiss kinetic equation and the cumulant expansion of the collision term

Like the statistical definition of moments of Boltzmann equation, the calortropy<sup>20</sup> can also be defined for molecules in the  $i^{\text{th}}$  vibrational level as follows:

$$\rho \hat{\Psi} = \sum_{i} \rho_{i} \hat{\Psi}_{i} = \sum_{i} \left\{ -k_{B} \langle [\ln f_{i}^{c} - 1] f_{i} \rangle \right\} = -k_{B} \langle \sum_{i} [\ln f_{i}^{c} - 1] f_{i} \rangle.$$
(A1)

The non-equilibrium canonical distribution  $f_i^c$  represents the thermodynamic branch of the modified Boltzmann-Curtiss kinetic equation  $f_i$ . By differentiating the calortropy  $\hat{\Psi}$  with time and combining it with the modified Boltzmann-Curtiss kinetic equation (4), the following balance equation for the calortropy can be obtained:

$$\rho \frac{d\hat{\Psi}}{dt} + \nabla \cdot (-k_B \sum_i \left\langle \mathbf{c}(\ln f_i^c - 1) f_i \right\rangle) + k_B \left\langle \sum_i f_i (\frac{d}{dt} + \mathbf{c} \cdot \nabla) \ln f_i^c \right\rangle = \sigma_c$$

$$\equiv -k_B \sum_i \left\langle \ln f_i^c C[f_i, f_j] \right\rangle$$

$$= \frac{1}{4} k_B \sum_i \sum_j \sum_k \sum_l \int d\mathbf{v}_i \int d\mathbf{v}_j \int d\Omega W(i, j \mid k^*, l^*; \Omega) \ln(f_k^* f_l^* / f_i f_j) (f_k^* f_l^* - f_i f_j) \ge 0.$$
(A2)

In calculating the dissipation term, it was assumed that the difference between the distribution function  $f_i$  and the corresponding thermodynamic branch  $f_i^c$  is negligible, which is equivalent to neglecting fluctuations in the distribution function. The last expression in equation (A2) clearly indicates that the present formulation satisfies the positivity of the calortropy production  $\sigma_c$ . This will guarantee that any subsequent calculation of the dissipation term based on the equation (A2) will be compatible with the second law of thermodynamics.

Unlike Grad's Hermite polynomial expansion,<sup>36,37</sup> the expansion of the distribution function in the exponential form assures the non-negativity of the distribution function regardless of the level of approximations. What is more, in the physical sense the exponential form is the only form that satisfies the additive property of the calortropy and calortropy production, all of which are in the logarithmic form. When the terms of vibrational non-equilibrium, (*i.e.* trans-rotational and vibrational temperatures) are added to the exponential form in the distribution function, the distribution function at the *i*<sup>th</sup> vibrational level,  $f_i^c$ , can be expressed as

$$f_{i}^{c} = \exp\left[-\beta(\frac{1}{2}m\mathbf{c}\cdot\mathbf{c} + H_{r,i} + \sum_{n=1}^{\infty}X^{(n)}h_{i}^{(n)} - N) - \beta_{v}(H_{v,i} + \sum_{n=1}^{\infty}X_{v}^{(n)}h_{v,i}^{(n)} - N_{v})\right],$$
(A3)  
$$\exp(-\beta N) = \frac{1}{n_{d}}\left\langle\exp[-\beta(\frac{1}{2}m\mathbf{c}\cdot\mathbf{c} + \sum_{i}H_{r,i} + \sum_{i}\sum_{n=1}^{\infty}X^{(n)}h_{i}^{(n)})]\right\rangle, \beta \equiv \frac{1}{k_{B}T},$$
$$\exp(-\beta_{v}N_{v}) = \frac{1}{n_{d}}\left\langle\exp[-\beta_{v}(\sum_{i}H_{v,i} + \sum_{i}\sum_{n=1}^{\infty}X_{v}^{(n)}h_{v,i}^{(n)})]\right\rangle, \beta_{v} \equiv \frac{1}{k_{B}T_{v}}.$$

The terms  $h_i^{(n)}$ ,  $X^{(n)}$  and N represent the molecular expression for  $n^{th}$  moments (stress tensor, excess normal stress, and trans-rotational heat flux etc.), the conjugate variables to  $h_i^{(n)}$ , and the normalization factor, respectively. On the other hand, the terms  $h_{v,i}^{(n)}$ ,  $X_v^{(n)}$  and  $N_v$  represent the molecular expression for higher-order moments related to vibrational energy (vibrational heat flux etc.), the respective conjugate variables, and the respective normalization factor. The terms  $\beta$  and  $\beta_v$  turn out to be the factors  $(k_BT)^{-1}$  and  $(k_BT_v)^{-1}$ , respectively. With a short notation for the exponent, the distribution function at the  $i^{th}$  vibrational level can be rewritten

$$f_i = f_i^{(0)} \exp(-x_i), \text{ where } x_i \equiv \beta(\sum_{n=1}^{\infty} X^{(n)} h_i^{(n)} - N) + \beta_{\nu} (\sum_{n=1}^{\infty} X_{\nu}^{(n)} h_{\nu,i}^{(n)} - N_{\nu}),$$
(A4)

where the term  $f^{(0)}$  represents the Maxwell-Boltzmann equilibrium distribution function at the temperatures of the trans-rotational and vibrational modes of energy, T and  $T_v$ . After substituting the definitions of the distribution functions (pre-collision:  $f_i = f_i^{(0)} \exp(-x_i)$ ,  $f_j = f_j^{(0)} \exp(-x_j)$ , post-collision:  $f_k^* = f_k^{(0)} \exp(-y_k)$ ,  $f_l^* = f_l^{(0)} \exp(-y_l)$  into (A2), the calortropy production can be expressed as

$$\sigma_{c} = \frac{1}{4} k_{B} \sum_{i,j,k,l} \int d\mathbf{v}_{i} \int d\mathbf{v}_{j} \int d\Omega W(i,j \mid k^{*},l^{*};\Omega) f_{i}^{(0)} f_{j}^{(0)} (x_{ij} - y_{kl}) [\exp(-y_{kl}) - \exp(-x_{ij})].$$
(A5)

where  $x_{ij} = x_i + x_j$  and  $y_{kl} = y_k + y_l$ .

This form of mathematical equation is suitable for the so-called cumulant expansion. The mathematical theory of cumulant expansion and its application to the expansion of Boltzmann collision integral terms have been reported in Eu's works<sup>20,21,88</sup> and another previous study.<sup>24</sup> In essence, in the cumulant expansion, the moment-generated function as the expectation value of the

exponential function,  $e^{\lambda x}$ , is expanded in series of the 1st-mean  $\kappa_1$ , 2nd-variance  $\kappa_2$ , 3rd-skewness  $\kappa_3$ , 4th-excess (or kurtosis)  $\kappa_4$ , etc.,

$$\left\langle e^{\lambda x} \right\rangle \left( \equiv \int e^{\lambda x} f(x) dx \right) = \exp\left[\sum_{l=0}^{\infty} \frac{\lambda^l}{l!} \kappa_l^{(+)}\right].$$
 (A6)

Note that the cumulant expansion assures the non-negativity of the distribution function regardless of the level of approximations, which is not guaranteed for the polynomial expansion,

$$\left\langle e^{\lambda x} \right\rangle = \sum_{l=0}^{\infty} \frac{\lambda^l}{l!} \left\langle x^l \right\rangle.$$

The derivation for diatomic and polyatomic gases with the vibrational degrees of freedom is a simple extension, summed over the vibrational levels, and is hence skipped in the present study for conciseness.

In addition, when the distribution function (A4) is inserted into the definition of the calortropy terms  $\sigma_c$ , the dissipative terms can be shown to be directly related to the calortropy terms,

$$\sigma_{c} = -k_{B} \left\langle -\beta \sum_{i} \sum_{n=1}^{\infty} X^{(n)} h_{i}^{(n)} C[f_{i}, f_{j}] \right\rangle - k_{B} \left\langle -\beta_{v} \sum_{i} \sum_{n=1}^{\infty} X_{v}^{(n)} h_{v,i}^{(n)} C[f_{i}, f_{j}] \right\rangle$$

$$= \frac{1}{T} \sum_{n=1}^{\infty} X^{(n)} \Lambda^{(n)} + \frac{1}{T_{v}} \sum_{n=1}^{\infty} X_{v}^{(n)} \Lambda_{v}^{(n)}.$$
(A7)

Similar to the classification of the higher-order moments, the dissipative terms are also grouped into two bins: those associated with trans-rotational energy ( $\Lambda^{(n)}$ ) and those associated with vibrational energy ( $\Lambda^{(n)}_{\nu}$ ). Finally, the explicit form of the dissipation term can be derived by calculating the first reduced collision integrals ( $\kappa_1$ ) in terms of the scalar coefficients of the collision bracket integrals ( $R^{(nl)}$  and  $R^{(nl)}_{\nu}$ ) and the conjugate functions ( $X^{(l)}$  and  $X^{(l)}_{\nu}$ ) of the higher-order moments:

$$\Lambda^{(n)} = \frac{1}{T} \sum_{l=1}^{\infty} R^{(nl)} X^{(l)} q(\kappa_1^{(\pm)}, \cdots),$$
(A8)

$$\Lambda_{v}^{(n)} = \frac{1}{T_{v}} \sum_{l=1}^{\infty} R_{v}^{(nl)} X_{v}^{(l)} q(\kappa_{1}^{(\pm)}, \cdots), \qquad (A9)$$

where  $q(\kappa_1^{(\pm)}, \cdots)$  represents the cumulant expansion series and the leading term is

$$q(\kappa_1) = \frac{\sinh \kappa_1}{\kappa_1} \,. \tag{A10}$$

The conjugate variables, which were first introduced in (A3) of the distribution function, can be determined in terms of macroscopic variables using the generalized Gibbs ensemble theory.<sup>89,90</sup> The leading order approximate solutions for the four primary non-conserved higher moments of the modified Boltzmann-Curtiss equation (viscous stress, excess normal stress, heat flux, vibrational heat flux) can be expressed as

$$X(\mathbf{\Pi}) = -\frac{\mathbf{\Pi}}{2p}, \ X(\Delta) = -\frac{3\Delta}{2p}, \ X(\mathbf{Q}) = -\frac{\mathbf{Q}}{pC_pT}, \ X(\mathbf{Q}_v) = -\frac{\mathbf{Q}_v}{pC_{pv}T_v}.$$
(A11)

# DATA AVAILABILITY

The data that supports the findings of this study are available within the article [and its supplementary material].

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