

Models of Thermal Relaxation Mechanics for Particle Simulation Methods

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An improved phenomenological microscopic model is introduced in the present study and compared to existing models for simulating molecular vibrational relaxation in rarefied flows. These models are employed in statistical particle simulation methods such as the direct simulation Monte Carlo (DSMC) technique. In the traditional Borgnakke-Larsen model, collision energies are partitioned among contributing energy modes as dictated by fractions sampled from equilibrium distributions. Application of this method to fully excited continuous energy modes alone, such as in translation-rotation (T-R) exchange, promotes the equilibrium state. However, application to translation-vibration (T-V) exchange is afforded by unrealistically approximating the quantized distribution as continuous and partially excited, and employing individual collision "temperatures" in an attempt to capture the temperature-dependence of the necessary distributions. As proven in theoretical and numerical analyses, such an implementation of the Borgnakke-Larsen method may fail to promote the equilibrium relaxed state exactly and poses computational difficulties. The improved technique of the present work iterates between translation-rotation and rotation-vibration exchanges which does promote equilibrium exactly if the model for the latter process is compatible with quantized oscillators. This may be achieved by quantizing the total internal energy of a molecule and dividing the quanta randomly among the rotational and vibrational energy modes. This iteration-equipartition model retains computational simplicity and promotes thermal equilibrium even when applied to multi-species gas mixtures of non-degenerate anharmonic quantized oscillators. © 1993 Academic Press, Inc.

INTRODUCTION

Statistical particle simulation methods, such as the direct simulation Monte Carlo (DSMC) method pioneered by

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Bird [1] and adaptations of this method [2], provide an appropriate means of simulating rarefied high-temperature flows. Such flows may be characterized by thermal and/or chemical nonequilibrium resulting from the relative scarcity of molecular collisions. A flow in thermal nonequilibrium, where the temperatures associated with the translational, rotational, and vibrational thermal energy modes are unequal, will relax toward the equilibrium state via successive molecular collisions which promote exchanges of energy between these modes. The present work addresses modeling the mechanics of thermally relaxing collisions in the context of a direct particle simulation.

Particle methods employ phenomenological models to simulate the motion and interaction of discrete particles in accordance with the principles of kinetic theory and statistical mechanics. The dynamics experienced by each of the many simulated particles which compose the multi-dimensional flowfield are computed, including any changes in velocity, internal energies, and molecular composition due to possible reaction for those particles which experience collisions during a given time step of the simulation. Thermo-chemical relaxation is simulated by decoupling the selection and mechanics of inelastic collisions. Although not discussed in detail here, selection of particles for thermal [3-7] and reactive [8-10] collisions controls the relaxation rate and is accomplished by assigning probabilities for each type of interaction to pairs of neighboring particles in the flowfield, followed by testing each of these probabilities for acceptance or rejection. Selected pairs of colliding particles then experience the appropriate energy-exchange mechanics such as those associated with thermal relaxation addressed in the present work.

The objective when modeling such mechanics is to determine an appropriate post-collision state of the energy modes associated with a given pair of interacting particles. For thermal relaxation, pre-collision energies ε must be

partitioned into post-collision energies ε' in a manner which promotes equilibrium and satisfies conservation of energy as follows:

$$\varepsilon_T = \varepsilon_g + \varepsilon_{r1} + \varepsilon_{v1} + \varepsilon_{r2} + \varepsilon_{v2}, \quad (1)$$

$$= \varepsilon'_g + \varepsilon'_{r1} + \varepsilon'_{v1} + \varepsilon'_{r2} + \varepsilon'_{v2}. \quad (2)$$

Here, ε_T is the total thermal energy in the collision, ε_g represents the relative translational energy between the colliding particles, and ε_r and ε_v are the rotational and vibrational energies of each particle in the pair distinguished by subscripts 1 and 2. Conservation of linear momentum dictates that the center-of-mass velocity of a colliding pair of particles must remain unchanged during collision and therefore does not contribute to the thermal energy of Eq. (1). In the context of vibrational relaxation, the models below specifically address mechanisms involving exchanges of energy among all thermal modes, known as translation-rotation-vibration (T-R-V) exchange processes, rather than vibration-vibration (V-V) exchange processes which dominate at lower temperatures [11].

Since the characteristic temperatures of translation and rotation are small relative to flowfield temperatures typical of atmospheric entry, these energy modes are modeled in the particle simulation as continuously distributed and fully excited. However, the characteristic temperature of vibration is significant in comparison to these flow temperatures such that the quantum nature of the vibrational energy mode must be considered. Accurate modeling of the vibrational mode is important, given its significant impact upon thermal, reactive, and radiative behavior in high-temperature gases [12].

Borgnakke and Larsen proposed a model for the exchange of internal and translational energies during particle collisions [13]. When applied to collisions involving the exchange of continuous energies only, this model promotes relaxation toward thermal equilibrium. As proven in the present work, however, application of this model to molecules with a quantized vibrational energy mode is troublesome and may lead to errors in the energy distributions pertaining to the relaxed ensemble of particles.

McDonald proposed an alternative means of partitioning total thermal energy among the contributing energy modes which is based upon a numerically efficient iteration scheme [2]. First, energy is exchanged strictly between the rotational and vibrational modes (R-V exchange) in a manner which is compatible with the quantized nature of the vibrational energy mode. The Borgnakke-Larsen method above is then employed, exchanging energy strictly between the continuous translational and rotational modes (T-R exchange). Repeating these exchanges during individual collisions promotes relaxation of the ensemble of particles toward equilibrium among all three thermal energy modes.

The mechanism employed by McDonald for R-V exchange is applicable only to the simple harmonic oscillator and fails to promote detailed balance when applied to general anharmonic oscillators.

For simulating reactive flows via particle simulation methods, Haas proposed an alternative mechanism for R-V exchange based upon equipartition mechanics [14]. As proven in the present work this exchange mechanism, in concert with Borgnakke-Larsen mechanics for T-R exchange of McDonald's iteration scheme, promotes detailed balance and thermal equilibrium for simple harmonic and non-degenerate anharmonic quantized oscillators.

It is essential to recognize that all of these models are statistical and phenomenological in nature, designed to simulate the appropriate macroscopic relaxation behavior via microscopic models. These simple models are not appropriate for simulating the microscopic kinetics of relaxation requiring detailed computation of quantum-level transitions.

PROPERTIES OF MOLECULAR ENERGY MODES

Molecules contain energy in the principle velocity components of translational motion, as well as in the internal energy modes corresponding to molecular rotation and vibration and the state of orbiting electrons. The contribution of the electron configuration is neglected in the present work. Hinshelwood [15] noted that the energy ε associated with one or more continuous energy modes is distributed in Boltzmann form at equilibrium temperature T as

$$f^*(\varepsilon) d\varepsilon = \frac{1}{\Gamma(\zeta/2)} \left(\frac{\varepsilon}{kT}\right)^{\zeta/2-1} \exp\left(-\frac{\varepsilon}{kT}\right) \frac{d\varepsilon}{kT}. \quad (3)$$

Here, superscript "*" denotes equilibrium, k is Boltzmann's constant, and ζ is the non-integral number of degrees of freedom associated with the energy modes. The mean energy $\langle \varepsilon \rangle$ associated with the Boltzmann distribution is related to ζ as

$$\langle \varepsilon \rangle = \frac{\zeta}{2} kT. \quad (4)$$

Accordingly, there are three degrees of freedom for the translational energy mode ($\zeta_t = 3$) and two for the rotational mode ($\zeta_r = 2$) of species which dominate planetary atmospheres including diatomic species (O_2 , N_2 , NO , CO) and linear triatomic species (CO_2). If ε_T represents a sum of mode energies, each distributed as in Eq. (3), the corresponding distribution of ε_T will be of Boltzmann form

as well with ζ_T degrees of freedom given by the sum of the individual mode degrees of freedom ζ .

Associated with each pair of colliding particles in the flowfield is a relative translational speed, g , given by the magnitude of the difference in particle velocities. The corresponding relative translational energy ε_g is then given by

$$\varepsilon_g = \frac{1}{2}\mu g^2, \quad (5)$$

where $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass of the pair. The number of degrees of freedom ζ_g associated with ε_g accounts for biasing [9] of colliding particles,

$$\zeta_g = 4 - 4/\alpha, \quad (6)$$

where α is the exponent of the inverse-power repulsive intermolecular potential employed in the collision selection rule [4] and assumes values in the range between the Maxwell molecule limit ($\alpha = 4$) and the hard-sphere limit ($\alpha = \infty$).

Models of the Quantized Vibrational Mode

In the present work, vibrational energies ε_v can only assume discrete energy values distinguished by quantum levels q , with their relationship defined by some function, $\varepsilon_v = V(q)$. Likewise, the relationship between quantum level q and vibrational energy $V(q)$ may be inverted to yield $q(V)$ when assuming there are no degenerate energy levels. In the particular case of a simple harmonic oscillator (SHO) with characteristic vibrational temperature θ_v , vibrational energies are spaced uniformly and are proportional to the quantum level when measured relative to the ground state $k\theta_v/2$,

$$\varepsilon_v|_{\text{SHO}} = V(q) = qk\theta_v. \quad (7)$$

For non-degenerate anharmonic oscillators (AHO), the function $V(q)$ is non-linear. Regardless, there are two degrees of freedom associated with the potential and kinetic vibrational energies, meaning that ε_v has the following quantized distribution, distinguished by capital "F," which exhibits simple exponential behavior at equilibrium [16] as

$$F^*(\varepsilon_v) = \exp(-\varepsilon_v) \left/ \sum_{q=0}^{q_D} \exp[-V(q)] \right. \quad (8)$$

The denominator simply normalizes the distribution. The maximum quantum level, q_D , defines the dissociation limit for the anharmonic oscillator associated with dissociation threshold energy $D = k\theta_D$. In the SHO model the number of quantum levels is unbounded ($q_D = \infty$).

Effective Number of Vibrational Degrees of Freedom

Employing the continuum relationship of Eq. (4), an effective number of vibrational degrees of freedom may be defined in terms of the mean quantized vibrational energy as

$$\begin{aligned} \zeta_v &= 2 \frac{\langle \varepsilon_v \rangle}{kT} \\ &= 2 \left[\frac{\sum_{q=0}^{q_D} \left(\frac{V(q)}{kT} \right) \exp\left(-\frac{V(q)}{kT}\right)}{\sum_{q=0}^{q_D} \exp\left(-\frac{V(q)}{kT}\right)} \right]. \end{aligned} \quad (9)$$

When applied to the SHO vibrational model, Eq. (9) leads to a closed form expression for ζ_v as a function of temperature [16],

$$\zeta_v|_{\text{SHO}} = 2 \frac{\theta_v/T}{\exp(\theta_v/T) - 1}. \quad (10)$$

The discrete distribution $F(\varepsilon_v)$ in two degrees of freedom is often approximated by a partially excited continuous distribution $f(\varepsilon_v) d\varepsilon_v$ with ζ_v effective degrees of freedom. Such an approximation is employed when the Borgnakke-Larsen model is applied to the vibrational energy mode.

BORGNAKKE-LARSEN MODEL OF THERMAL RELAXATION

Borgnakke and Larsen [13] proposed a means of exchanging energy among continuous thermal modes during inelastic molecular collisions in a manner which promotes thermal equilibrium. Here, the total thermal energy of a given collision, ε_T , is partitioned among the various energy modes according to the appropriate equilibrium distributions. Specifically, the post-collision relative translational energy ε'_g is computed as a fraction \mathcal{F} of the total thermal collision energy,

$$\varepsilon'_g = \varepsilon_T \mathcal{F}. \quad (11)$$

The remaining energy, $\varepsilon_T(1 - \mathcal{F})$, is divided among the various internal energy modes in a similar manner. For each inelastic collision in the flowfield, fraction \mathcal{F} is sampled randomly from its equilibrium distribution, $f^*(\mathcal{F})$, given by

$$\begin{aligned} f^*(\mathcal{F}) d\mathcal{F} &= \frac{\Gamma(\zeta_T/2)}{\Gamma(\zeta_g/2) \Gamma((\zeta_T - \zeta_g)/2)} \\ &\times \mathcal{F}^{\zeta_g/2 - 1} (1 - \mathcal{F})^{(\zeta_T - \zeta_g)/2 - 1} d\mathcal{F}. \end{aligned} \quad (12)$$

The corresponding degrees of freedom are defined as

$$\zeta_T \equiv \zeta_g + \zeta_{r1} + \zeta_{v1} + \zeta_{r2} + \zeta_{v2}, \quad (13)$$

$$\zeta_r = \begin{cases} 0, & \text{if monatomic;} \\ 2, & \text{if diatomic;} \end{cases} \quad (14)$$

where ζ_g and ζ_v are given in Eqs. (6) and (9), respectively, having approximated the distribution of vibrational energies with a continuous Boltzmann distribution in ζ_v effective degrees of freedom. Derivation of Eq. (12) is given in Appendix A. The mean fraction $\langle \mathcal{F} \rangle$ sampled from distribution $f^*(\mathcal{F})$ is given by the first moment,

$$\langle \mathcal{F} \rangle = \int_0^1 \mathcal{F} f^*(\mathcal{F}) d\mathcal{F} = \frac{\zeta_g}{\zeta_T}. \quad (15)$$

Equation (15) indicates that the average fraction of total collision energy that is composed of relative translational energy at equilibrium is given simply by the ratio of the corresponding number of degrees of freedom, and thus by the ratio of mean energies, $\langle \varepsilon_g \rangle / \langle \varepsilon_T \rangle$.

Note that the dependence of $f^*(\mathcal{F})$ upon temperature results only from that associated with the effective vibrational degrees of freedom ζ_v contributing to ζ_T . However, to model rotational relaxation involving exchanges of energy only between the translational and rotational modes, ζ_v would not contribute to ζ_T and therefore $f^*(\mathcal{F})$ would be independent of temperature. Consequently, one may employ the Borgnakke–Larsen model for rotational relaxation (T-R exchanges only) throughout the flowfield regardless of local temperatures and the extent of thermal nonequilibrium. In practice, an adequate sample from the distribution of Eq. (12) may be tabulated. Sampling from the distribution then simply requires random selection from the table.

Application to the Vibrational Mode

To apply the Borgnakke–Larsen method to vibrational relaxation, the quantized distribution $F(\varepsilon_v)$ must be approximated by an effective continuous distribution $f(\varepsilon_v)$ which is dependent upon local temperatures in the flowfield. Macroscopic temperatures are ill-defined under general nonequilibrium conditions and are computationally expensive to assess. Nonetheless, a microscopic “collision temperature,” \tilde{T} , may be employed [1] as defined for a given collision by the relative translational energy,

$$\varepsilon_g = \frac{1}{2} \mu g^2 = \frac{\zeta_g}{2} k \tilde{T} \Rightarrow \tilde{T} \equiv \frac{\mu g^2}{\zeta_g k}. \quad (16)$$

In this manner, \tilde{T} may be used to compute an effective number of vibrational degrees of freedom [17], denoted by $\tilde{\zeta}_v$ via Eq. (10), leading to an effective total number of degrees of freedom $\tilde{\zeta}_T$ for use in Eq. (12). Consequently, the distribution which is sampled for the partitioning fraction \mathcal{F} in this manner is *not* a function of temperature T , but rather is a function of relative translational energy via \tilde{T} , and will be denoted $f(\mathcal{F} | \tilde{T})$.

Unfortunately, application of the Borgnakke–Larsen

model to vibrational relaxation via collision temperature \tilde{T} does promote equilibrium exactly and is not compatible with the quantized nature of the energy mode. This is verified by computing the ensemble-averaged distribution $\tilde{f}(\mathcal{F} | T)$ and its mean $\langle \tilde{\mathcal{F}} \rangle$ at equilibrium temperature T and by comparing them to their equilibrium counterparts $f^*(\mathcal{F})$ and $\langle \mathcal{F} \rangle$ from Eqs. (12) and (15). Distribution $\tilde{f}(\mathcal{F} | T)$ and mean $\langle \tilde{\mathcal{F}} \rangle$ are found by integrating over the distribution of relative energies as

$$\tilde{f}(\mathcal{F} | T) = \int_0^\infty f(\mathcal{F} | \tilde{T}) f^*(\tilde{T} | T) d\tilde{T}, \quad (17)$$

$$\langle \tilde{\mathcal{F}} \rangle = \int_0^1 \mathcal{F} \tilde{f}(\mathcal{F} | T) d\mathcal{F}, \quad (18)$$

where $f^*(\tilde{T} | T)$, when employing the definition from Eq. (16), is of Boltzmann form from Eq. (3) at equilibrium temperature T with ζ_g degrees of freedom.

Results are presented in Fig. 1 of numerical evaluation of integral (17) for thermal relaxation involving pairs of simple harmonic oscillators at various temperatures. The intermolecular potential used for collision selection pertains to the Maxwell molecule ($\alpha = 4$). Accurate numerical integration of Eqs. (17) and (18) employed simple trapezoidal summation over 10,000 points in each domain pertaining to \tilde{T} and \mathcal{F} , respectively.

It is evident that $\tilde{f}(\mathcal{F} | T)$ is a fair approximation of $f^*(\mathcal{F})$ at very low and very high temperatures. However, the distributions differ more noticeably at intermediate temperatures near $T/\theta_v = 1.0$. The effect of these differences is apparent in the net temperature-dependence of the resulting mean fractions $\langle \mathcal{F} \rangle$ and $\langle \tilde{\mathcal{F}} \rangle$ in Fig. 2. Results are given for Maxwell molecules ($\alpha = 4$) and hard-sphere molecules ($\alpha = \infty$). Note that $\langle \tilde{\mathcal{F}} \rangle$ is higher than $\langle \mathcal{F} \rangle$ at all tem-

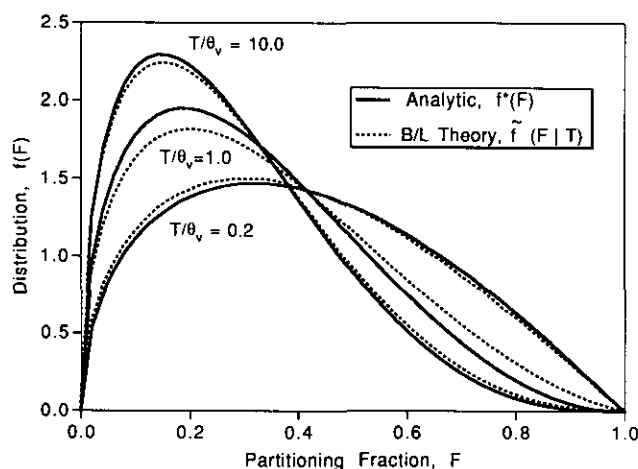


FIG. 1. Comparison of equilibrium distributions of partitioning fractions $f^*(\mathcal{F})$ to the distributions resulting from the Borgnakke–Larsen model $\tilde{f}(\mathcal{F} | T)$ pertaining to T-R-V exchanges of energy.

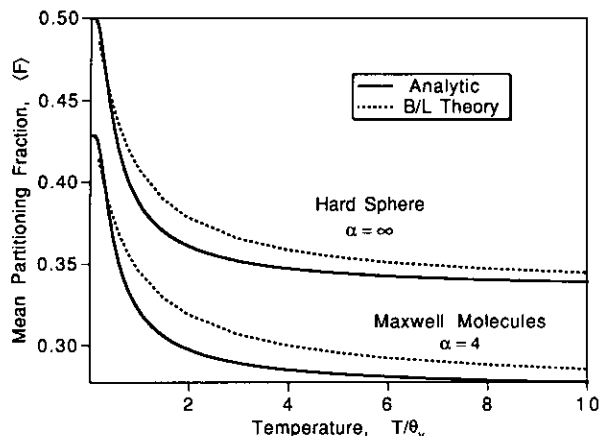


FIG. 2. Comparison of mean partitioning fractions at equilibrium $\langle \mathcal{F} \rangle$ to those resulting from the Borgnakke-Larsen model $\langle \mathcal{F} \rangle$ pertaining to T-R-V exchanges of energy.

peratures. This indicates that the Borgnakke-Larsen model, employing a collision temperature for vibrational relaxation, will place more energy into the relative translational model upon collision than is needed to maintain equilibrium. This is because application of this model to the vibrational mode at equilibrium does not reproduce the equilibrium distribution; that is, $\tilde{f}(\mathcal{F}|T) \neq f^*(\mathcal{F})$. Similarly, for dividing the remaining internal energy into rotational and vibrational components, use of \tilde{T} would lead to errors in the corresponding mean sampled fraction.

Note that in Fig. 2, curves corresponding to $\langle \mathcal{F} \rangle$ and $\langle \mathcal{F} \rangle$ should converge to the same point at $T/\theta_v = 0$, although numerical integration at this limit is unstable. It is also noteworthy that, when employing the correct analytic distribution $f^*(\mathcal{F})$, numerical integration leads to the expected analytic result of Eq. (15).

One may compensate for the inaccuracies of the Borgnakke-Larsen implementation above by employing two separate collision temperatures, \tilde{T}_1 and \tilde{T}_2 , pertaining to each molecule in the collision [18]. Here, \tilde{T}_1 is defined from the collection of relative translational energy of the pair and internal energy of the molecule as

$$\varepsilon_g + \varepsilon_{r1} + \varepsilon_{v1} = \frac{\zeta_g + \zeta_{r1} + \zeta_{v1}}{2} k \tilde{T}_1. \quad (19)$$

A similar expression defines \tilde{T}_2 . Since it employs a collection of energies, Eq. (19) more closely approximates the exact expression of Eq. (4) than did Eq. (16). More importantly, however, by employing distinct temperatures and sampling from separate distributions, the resulting distribution $\tilde{f}(\mathcal{F}|T)$ preserves the high and low energy tails of the desired equilibrium distribution for vibrational energy pertaining to the gas as a whole.

Although this latter implementation of the Borgnakke-Larsen technique promotes equilibrium, it involves considerable computational complexity since it requires iteration to compute \tilde{T}_1 and \tilde{T}_2 for each collision. Such calculation may be particularly costly when applied to anharmonic oscillators for which exact expressions of ζ_v as functions of ε_v and \tilde{T} are of the complex form in Eq. (9). Furthermore, sampling from distributions $f^*(\mathcal{F})$ for both implementations above requires repeated calculations of the distribution involving intrinsic functions which is very inefficient computationally. In non-equilibrium flows at very high temperatures, where the rate of vibrational excitation is comparable to the collision frequency, such calculations would be costly. These limitations may be circumvented by employing a fixed number of vibrational degrees of freedom ζ_v , leading to an invariant distribution $f^*(\mathcal{F})$ which may be tabulated for sampling. However, this prescribed condition fails to account for variable contributions of the vibrational energy mode throughout the flowfield which is characteristic of its quantum nature. Furthermore, this approach is not suited to multi-species gas mixtures which may involve several different characteristic vibrational temperatures θ_v and intermolecular potentials α . Regardless, all of these implementations above employ the physically unrealistic assumption of a continuous (rather than quantized) vibrational mode.

ITERATION ALGORITHM FOR QUANTIZED THERMAL RELAXATION

McDonald [2] proposed a computationally efficient iteration scheme for T-R-V thermal relaxation which decouples T-R exchanges from R-V exchanges. Iterating between these independent exchanges promotes thorough mixing of energy among all three thermal modes. The T-R exchange represents simple rotational relaxation and can be achieved via the Borgnakke-Larsen model described above. Note that under these circumstances, the total number of degrees of freedom, $\zeta_T = \zeta_g + \zeta_{r1} + \zeta_{r2}$, is independent of temperature, and the difficulties associated with using \tilde{T} are avoided.

Truncation Model for R-V Exchange

The R-V exchange can be modeled without employing the continuum assumption by sampling quantized vibrational energy ε'_v directly from its discrete equilibrium distribution, $F(\varepsilon_v)$. However, since both rotational and vibrational energies are distributed with two degrees of freedom at equilibrium, McDonald observed for the simple harmonic oscillator that ε'_v may effectively be sampled directly from the continuous distribution $f(\varepsilon_v)$ in a quantized manner by simply truncating the pre-collision

rotational energy ε_r down to the nearest vibrational quantum level q' . The remaining internal energy is then placed into rotation as

$$q' = \left\lfloor \frac{\varepsilon_r}{k\theta_v} \right\rfloor, \quad (20)$$

$$\varepsilon'_v = q'k\theta_v, \quad (21)$$

$$\varepsilon'_r = \varepsilon_r + \varepsilon_v - \varepsilon'_v, \quad (22)$$

where brackets " $\lfloor \]$ " denote truncation. Note that the quantum nature of ε'_v is preserved.

Proving that this R-V truncation scheme satisfies the equilibrium constraint, given by $\tilde{f}(\mathcal{F} | T) = f^*(\mathcal{F})$, simply requires verification that the distribution of post-collision vibrational energies $F(\varepsilon'_v)$ obtained via the truncation algorithm matches the equilibrium distribution $F^*(\varepsilon'_v)$. Employing the Boltzmann distribution $f^*(\varepsilon_r)$ for rotational energy with $\zeta_r = 2$ degrees of freedom, the distribution $F(\varepsilon'_v)$ resulting from truncation of ε_r is determined as follows:

$$F(\varepsilon'_v) = \int_{V(q')}^{V(q'+1)} f^*(\varepsilon_r) d\varepsilon_r \quad (23)$$

$$\sim \int_{q'k\theta_v}^{(q'+1)k\theta_v} \exp\left(-\frac{\varepsilon_r}{kT}\right) d\varepsilon_r \quad (24)$$

$$\sim \exp\left(-\frac{q'k\theta_v}{kT}\right) \quad (25)$$

$$= F^*(\varepsilon'_v). \quad (26)$$

Since $F(\varepsilon'_v)$ matches the equilibrium distribution $F^*(\varepsilon'_v)$, it follows that the resulting distribution $\tilde{f}(\mathcal{F} | T)$ would match the equilibrium distribution $f^*(\mathcal{F})$ as a direct result of the derivation in Appendix A.

Limitations of the R-V Truncation Algorithm

The truncation algorithm of Eqs. (20)–(22) for R-V exchange promotes vibrational relaxation in a computationally simple manner which avoids the difficulties associated with the Borgnakke–Larsen method. However, this model does not provide for general partitioning of total internal energy ε_{int} without access to nearly equilibrated pre-collision rotational energies ε_r in Eq. (20). This problem is encountered when simulating reactive flows in which the total post-reaction internal energy ε_{int} must be divided into ε'_r and ε'_v .

The truncation algorithm is also restricted to application only to simple harmonic oscillators since it leads to nonequilibrium distributions when applied to general anharmonic oscillators (AHO). To verify this difficulty, assume that the vibrational mode is modeled by the Morse oscillator for which the relationship between quantum levels

q and vibrational energies ε_v are characterized by the non-linear relationship,

$$\varepsilon_v |_{\text{AHO}} = V(q) = qk\theta_v \left(1 - \frac{1}{4} \frac{\theta_v}{\theta_D} q\right). \quad (27)$$

From Eq. (23), the distribution of vibrational energies resulting from application of the truncation algorithm would be of the form

$$F(\varepsilon'_v) \sim \left(1 - \exp\left[-\frac{\theta_v}{T} \left(1 - \frac{1}{4} \frac{\theta_v}{\theta_D} - \frac{1}{2} \frac{\theta_v}{\theta_D} q'\right)\right]\right) \times \exp\left(-\frac{\varepsilon'_v}{kT}\right). \quad (28)$$

Note that the appearance of q' in the leading term above means that this distribution does *not* exhibit the simple exponential behavior expected at equilibrium. The extent of this difficulty will be explored below via simulation of thermally relaxing gas reservoirs.

EQUIPARTION MODEL FOR QUANTIZED VIBRATIONAL RELAXATION

In simulating reactive flows, the difficulties associated with the R-V truncation algorithm are circumvented by employing an equipartion model [14] adapted from Baganoff [19]. Based upon the fundamental theory of statistical mechanics, this model stipulates that all possible divisions of total energy into quantized components are equally probable [16]. As proven below, this model for R-V exchange may then be used in concert with the iteration scheme above, employing Borgnakke–Larsen mechanics for rotational relaxation (T-R exchange), to promote vibrational relaxation of simple harmonic and non-degenerate anharmonic quantized oscillators in multi-species gas mixtures.

Employing the inverse function $q(V)$ to identify the maximum quantum level with energy less than or equal to V , define the quantum level Q associated with the total internal energy ε_{int} of a given diatomic molecule as

$$\varepsilon_{\text{int}} = \varepsilon_r + \varepsilon_v, \quad (29)$$

$$Q = \begin{cases} q(\varepsilon_{\text{int}}), & \varepsilon_{\text{int}} < D; \\ q_D, & \varepsilon_{\text{int}} \geq D. \end{cases} \quad (30)$$

Note that Q cannot exceed the maximum level q_D , even if the internal energy exceeds the dissociation threshold, $\varepsilon \geq D$.

Consistent with the equipartition principle, the post-collision quantum level q' of the vibrational energy of a diatomic molecule may assume any integer value in the range $[0, Q]$ with equal probability. Employing a uniformly generated random number \mathfrak{R} in the range $[0, 1)$, quantum level q' is selected as

$$q' = \lfloor \mathfrak{R} \cdot (Q + 1) \rfloor. \quad (31)$$

The vibrational energy associated with quantum level q' is then subtracted from ε_{int} and placed into rotation,

$$\varepsilon'_v = V(q'), \quad (32)$$

$$\varepsilon'_r = \varepsilon_{\text{int}} - \varepsilon'_v. \quad (33)$$

This algorithm for R-V exchange is computationally simple and is applicable to both thermal and reactive collisions requiring partitioning of internal energy into rotational and quantized vibrational components. This method is readily applicable to gas mixtures in which each species has a unique vibrational character defined by $V(q)$. In addition to diatomic species, the method is also applicable for each of the vibrational modes of linear polyatomic molecules such as CO_2 which have two rotational degrees of freedom. Analytic validation of the method is presented in Appendix B.

APPLICATION OF RELAXATION MODELS

Thermal relaxation of nonequilibrium gas reservoirs may be simulated to demonstrate the capabilities of the models described above.

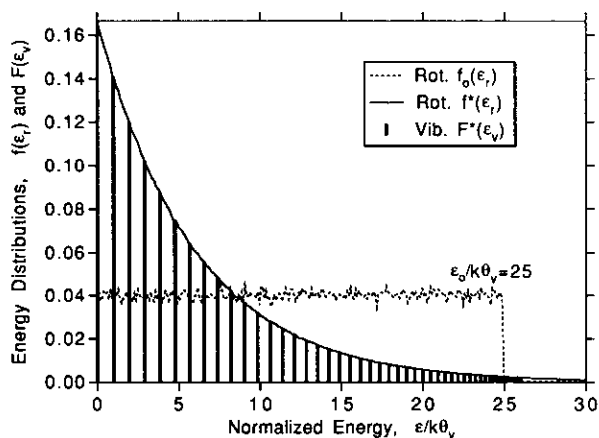


FIG. 3. Initial and relaxed distributions of rotational and vibrational energies resulting from the equipartition R-V exchange model applied to the Morse anharmonic oscillator.

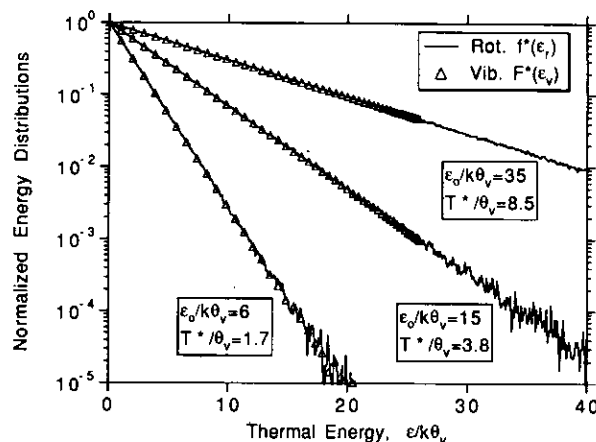


FIG. 4. Equilibrium steady-state distributions of rotational and vibrational energies resulting from the equipartition R-V exchange model applied to the Morse anharmonic oscillator. Each distribution is normalized by its value at $\varepsilon_0 = 0$.

Simulation of R-V Exchange

A constant-volume adiabatic reservoir of diatomic gas, initialized with no vibrational energy and with molecular rotational energies uniformly distributed up to some limit ε_0 , exists in a state of considerable thermal nonequilibrium. Such reservoirs were simulated with the particle technique employing the quantum equipartition R-V exchange model of Eqs. (31)–(33) during thermal relaxation to steady state. The vibrational mode was represented by the Morse anharmonic oscillator of Eq. (27). Contributions of the translational mode were not accounted for in these cases in order to focus upon the R-V exchange process alone.

The initial and final energy distributions are plotted in Fig. 3 for the initial condition $\varepsilon_0/k\theta_v = 25$. The steady-state distributions for rotational and vibrational energies clearly

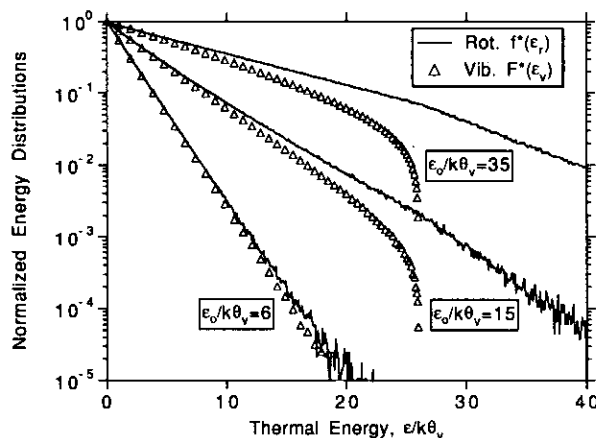


FIG. 5. Nonequilibrium steady-state distributions of rotational and vibrational energies resulting from the truncation R-V exchange model applied to Morse anharmonic oscillators. Each distribution is normalized by its value at $\varepsilon_0 = 0$.

exhibit the exponential Boltzmann forms expected at equilibrium, $f^*(\epsilon_r)$ and $F^*(\epsilon_v)$. Repeating such tests for initial conditions $\epsilon_0/k\theta_v = [6, 15, 35]$ leads to steady-state distributions plotted in Fig. 4. Equal slopes for each distribution verify that rotation and vibration are at the same temperature, indicating relaxation to the expected equilibrium states. Note the unequal spacing of the vibrational quantum levels in each figure, characteristic of anharmonic oscillators.

Repeating these reservoir simulations, but employing the truncation R-V exchange algorithm, leads to dissimilar energy distributions in rotation and vibration as presented in Fig. 5. Note the non-linearity of $F(\epsilon_v)$ and the inequality of the slopes of each distribution, consistent with the results of Eq. (28). However, when applied to the simple harmonic oscillator for which it was developed, the truncation algorithm indeed promotes equilibrium as demonstrated in Fig. 6. Identical behavior is obtained for the equipartition method when applied to the SHO model [14].

Simulation of T-R-V Relaxation

To test both the Borgnakke-Larsen and iteration/equipartition methods for T-R-V exchanges, several relaxing reservoirs of O₂ were simulated with high initial translational energy but with no initial internal energy. At steady state following thermal relaxation for simple harmonic oscillators, the resulting ratio of mean translational energy to internal energy, $\langle \epsilon_t \rangle / \langle \epsilon_r + \epsilon_v \rangle$, is plotted over a considerable temperature range in Fig. 7a and compared to the analytic curve represented by the ratio of degrees of freedom, $3/(2 + \zeta_v)$. Results for the Morse anharmonic oscillator are presented in Fig. 7b. Close agreement verifies that the iteration/equipartition scheme indeed promotes thermal equilibrium. In these simulations, only one

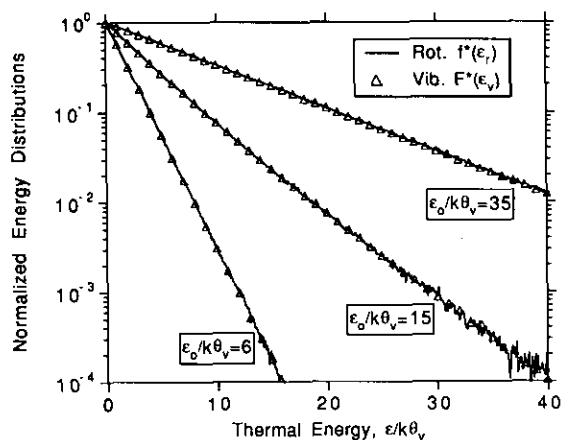


FIG. 6. Equilibrium steady-state distributions of rotational and vibrational energies resulting from the truncation R-V exchange model applied to the simple harmonic oscillator. Each distribution is normalized by its value at $\epsilon_0 = 0$.

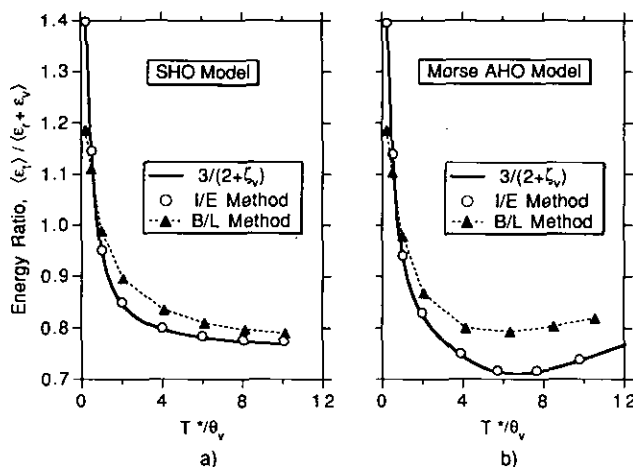


FIG. 7. Ratio of mean energies in simulated O₂ reservoirs relaxed by the Borgnakke-Larsen (T^* from Eq. (16)) and iteration/equipartition methods compared to the equilibrium result given by the ratio of the number of degrees of freedom pertaining to (a) the simple harmonic oscillator and (b) the Morse anharmonic oscillator.

iteration (R-V/T-R) was employed per collision. Minor discrepancies result from statistical sensitivity inherent to the particle simulation. The Borgnakke-Larsen method, employing collision temperatures T^* defined from Eq. (16), clearly does *not* promote the correct energy ratios, leading to errors as high as 5.7% and 11.3% for the SHO and AHO models, respectively. This is consistent with the analytic predictions from Figs. 1 and 2. Maxwell molecules ($\alpha = 4$) were employed for all cases.

TABLE I

Comparison of Computational Operation Counts per Method^a

Simple operation	Borgnakke Larsen 1 ^b	Borgnakke Larsen 2 ^c	Iteration equipartition
+, -	22	32	20
×	26	30	20
÷	4	14	0
Totals	52	74	40
Complex operation			
Generate \mathfrak{R}	10	10	6
Exp	10	14	0
Ln	8	8	0
Totals	28	32	6

^a Assumes two iterations (for sampling or exchange) in each technique when applied bimolecular collisions of diatomic simple harmonic oscillators.

^b Computes T^* from Eq. (16).

^c Computes T_1^* and T_2^* in three iterations from Eq. (19).

Comparison of Computational Efficiency

In computing the relaxation cases above, significant computational efficiency was achieved with the iteration/equipartition method in comparison to the Borgnakke-Larsen method. While computational effort associated with any given method is greatly dependent upon the specific algorithm, program structure, and computer architecture employed, meaningful comparison can be made by simply counting the number and type of computer operations required of each method as demonstrated in Table I. Note that simple operations including addition, subtraction, multiplication, and division of floating-point numbers require far fewer computer clock cycles to complete than complex operations including the exponential and natural logarithm functions. Consequently, operation counts for each type are independently summarized in the table. For the iterative sequences inherent to each method it was assumed that, on average, two iterations were required. Table I clearly demonstrates that the iteration/equipartition method represents a significant reduction in required computational effort in comparison to either of the Borgnakke-Larsen methods in modeling vibrational relaxation.

CONCLUDING REMARKS

Phenomenological models are applied at the microscopic scale in statistical particle methods to simulate the macroscopic thermal relaxation associated with translation-rotation-vibration (T-R-V) exchanges of energy. The Borgnakke-Larsen method for exchanging energies among continuous thermal energy modes is effective in modeling rotational relaxation. Application to vibrational relaxation requires that the discrete distribution associated with quantized vibrational oscillators be approximated unrealistically by an effective continuous distribution. The method then requires an estimate of temperature which is ill-defined at the microscopic scale and poses computational difficulties to implement. When an effective "collision temperature" \bar{T} is defined from the relative translational energy of colliding particles, the resulting distributions fail to promote equilibrium partitioning of post-collision energies. Computing \bar{T} for each molecule independently from its relative and internal energies would improve significantly upon the accuracy of the method but would involve additional calculation, particularly for anharmonic oscillators. Furthermore, sampling from these distributions poses considerable additional computational burden. Employing an invariant tabulated distribution avoids these difficulties but is not well suited to multi-species gas mixtures and fails to capture the dynamic energy contributions which characterize the quantized vibrational mode.

A simple iteration method developed by McDonald decouples T-R and R-V exchanges of thermal energy. The T-R exchange associated with rotational relaxation is effectively modeled with the Borgnakke-Larsen method since the distributions involved are continuous and independent of flowfield temperature. As an alternative to the limited truncation model for R-V exchange, the fundamentals of equipartition may be employed to model the R-V exchange of continuous rotational and quantized vibrational energies in a manner which promotes the correct equilibrium partitioning of post-collision energies. Here, the total internal energy is quantized and randomly divided into post-collision quanta for each mode. These techniques circumvent the difficulties associated with sampling from temperature-dependent distributions and account realistically for the quantum nature of the vibrational energy mode. Relaxation rates are controlled with selection probability functions [5-7, 9]. As verified both analytically and numerically, the iteration/equipartition method maintains and promotes exact equilibrium for vibrational relaxation involving simple harmonic or non-degenerate anharmonic quantized oscillators in a computationally efficient manner.

APPENDIX A: DERIVATION OF THE BORGNAKKE-LARSEN DISTRIBUTION

Since it is cast in an unusual form, the distribution $f^*(\mathcal{F})$ as employed in the Borgnakke-Larsen method of partitioning post-collision thermal energy from Eqs. (11)-(12) is derived here. Defining normalized energies $E_g \equiv \varepsilon_g/kT$ and $E_T \equiv \varepsilon_T/kT$, each distributed in Boltzmann form with ζ_g and ζ_T degrees of freedom, respectively, the distribution $f^*(\mathcal{F})$ may be found from the joint distribution,

$$\begin{aligned} f^*(E_g, E_T) dE_g dE_T &= f^*(E_g) f^*(E_T - E_g) dE_g dE_T, \quad (34) \\ &= \frac{E_g^{\zeta_g/2-1} (E_T - E_g)^{\zeta_T - \zeta_g/2 - 1}}{\Gamma(\zeta_g/2) \Gamma((\zeta_T - \zeta_g)/2)} \\ &\quad \times e^{-E_T} dE_g dE_T. \quad (35) \end{aligned}$$

Employing a change of variables from the definition of \mathcal{F} ,

$$E_g = E_T \mathcal{F} \Rightarrow dE_g = E_T d\mathcal{F}, \quad (36)$$

leads to

$$\begin{aligned} f^*(\mathcal{F}, E_T) d\mathcal{F} dE_T &= \frac{\mathcal{F}^{\zeta_g/2-1} (1 - \mathcal{F})^{\zeta_T - \zeta_g/2 - 1}}{\Gamma(\zeta_g/2) \Gamma((\zeta_T - \zeta_g)/2)} \\ &\quad \times E_T^{\zeta_T/2-1} e^{-E_T} d\mathcal{F} dE_T. \quad (37) \end{aligned}$$

The distribution $f^*(F)$, from which energy partition frac-

tions \mathcal{F} are sampled in the Borgnakke–Larsen method, is then found by integrating over E_T ,

$$\begin{aligned} f^*(\mathcal{F}) d\mathcal{F} &= \int_{E_T=0}^{\infty} f^*(\mathcal{F}, E_T) dE_T d\mathcal{F}, \quad (38) \\ &= \frac{\Gamma(\zeta_T/2)}{\Gamma(\zeta_g/2) \Gamma((\zeta_T - \zeta_g)/2)} \\ &\quad \times \mathcal{F}^{\zeta_g/2-1} (1 - \mathcal{F})^{(\zeta_T - \zeta_g)/2-1} d\mathcal{F}. \quad (39) \end{aligned}$$

APPENDIX B: VERIFICATION OF EQUIPARTITION MODEL AT EQUILIBRIUM

As proven for the simple harmonic oscillator [14], the equipartition algorithm maintains equilibrium distributions, $F^*(\varepsilon_r)$ and $f^*(\varepsilon_r)$. A similar proof for general oscillators, presented here, employs normalized energies for rotation ($r \equiv \varepsilon_r/kT$), vibration ($v \equiv \varepsilon_v/kT$), and dissociation ($\mathcal{D} \equiv D/kT = v(q_D)$), where $v(q) \equiv V(q)/kT$ is the normalized energy associated with quantum level q . Similarly, $q(v)$ represents the maximum quantum level associated with some normalized energy value v . The joint distribution of statistically independent energies r and v is given by the product

$$f^*(r, v) dr = F^*(v) f^*(r) dr. \quad (40)$$

Defining normalized internal energy, $E = r + v$ and employing the corresponding change of variables, $dr = dE$, leads to the joint distribution of statistically dependent energies v and ε :

$$\begin{aligned} f(E, v) dE &= F^*(v) f^*(E - v) dE, \\ &\sim e^{-v} e^{-(E-v)} dE, \\ &\sim e^{-E} dE. \quad (41) \end{aligned}$$

The distribution $f(E)$ is found by summing over all vibrational quantum energy levels q in the range $[0, Q]$,

$$\begin{aligned} f^*(E) dE &= \sum_{q=0}^Q f(E, v) dE, \\ &= (Q + 1) e^{-E} dE, \quad (42) \end{aligned}$$

where Q is given in Eq. (30). Consistent with the equipartition algorithm, the distribution of quanta Q associated with energy E can be found by integrating the distribution of continuous internal energy $f^*(E)$ over the quantum interval $[Q, Q + 1]$,

$$\begin{aligned} F^*(Q) &= \int f^*(E) dE, \\ &= \begin{cases} \int_{v(Q)}^{v(Q+1)} (Q + 1) e^{-E} dE, & \text{for } E < \mathcal{D}, Q < q_D, \\ \int_{\mathcal{D}}^{\infty} (q_D + 1) e^{-E} dE, & \text{for } E \geq \mathcal{D}, Q = q_D, \end{cases} \quad (43) \\ &= \begin{cases} (Q + 1) [e^{-v(Q)} - e^{-v(Q+1)}], & Q < q_D; \\ (q_D + 1) e^{-\mathcal{D}}, & Q = q_D. \end{cases} \quad (44) \end{aligned}$$

Consistent with equipartition, the outcome quantum level q' is equally probable among the $Q + 1$ possibilities $[0, 1, 2, \dots, Q]$, leading to a *conditional* distribution of q' which is uniform,

$$F(q' | Q) = \frac{1}{Q + 1}. \quad (45)$$

The joint distribution $F(q', Q)$ is then given by the product

$$\begin{aligned} F(q', Q) &= F(q' | Q) F^*(Q), \quad (46) \\ &= \begin{cases} e^{-v(Q)} - e^{-v(Q+1)}, & Q < q_D; \\ e^{-\mathcal{D}}, & Q = q_D. \end{cases} \quad (47) \end{aligned}$$

Noting the definition $\mathcal{D} = v(q_D)$, the final distribution of post-collision vibrational quanta q' is found by summing over all possible total internal energy quantum levels Q in the range $[q', q_D]$,

$$F(q') = \sum_{Q=q'}^{q_D} F(q', Q), \quad (48)$$

$$= F(q' | q_D) F^*(q_D) + \sum_{Q=q'}^{q_D-1} F(q' | Q) F^*(Q), \quad (49)$$

$$= e^{-\mathcal{D}} + \sum_{Q=q'}^{q_D-1} [e^{-v(Q)} - e^{-v(Q+1)}], \quad (50)$$

$$= e^{-v(q_D)} + [e^{-v(q')} - e^{-v(q'+1)}] \\ + [e^{-v(q'+1)} - e^{-v(q'+2)}] + \dots \quad (51)$$

$$+ [e^{-v(q_D-1)} - e^{-v(q_D)}], \\ = e^{-v(q')}. \quad (52)$$

The final expression for $F(q')$ retains the exponential Boltzmann form associated with the vibrational energy distribution at equilibrium, $F^*(q')$, indicating that the equipartition model preserves the equilibrium state when applied to general oscillators. Note that the desired result, $F(q') = F^*(q')$, was only achieved because the $Q + 1$ term in Eq. (44) was cancelled by the particular expression for

$F(q'|Q)$ in Eq. (45). This expression applies *only* to the equipartition principle; an algorithm based upon a different principle would fail to yield the form in Eq. (45) and, therefore, fail to promote equilibrium.

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