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# Vibrational Relaxation in Hypersonic Flow Fields

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## Summary

Mathematical formulations of vibrational relaxation are derived from first principles for application to fluid dynamic computations of hypersonic flow fields. The highlights include the following: (1) a demonstration that fast near-resonant vibrational-vibrational (V-V) energy-transfer collisions support the assumption of a vibrational temperature, at least for a single-species gas; (2) the identification of vibrational-translational (V-T) collisions as having sole responsibility for the equilibration of vibration and translation after a strong initial jolt places a gas in a highly nonequilibrium state; (3) the derivation of an improved vibrational relaxation time for use in the vibrational temperature equation; (4) a demonstration that vibrational relaxation times appropriate for temperature equations are very different from those appropriate for energy equations when the difference between translational and vibrational temperatures is large; and (5) a demonstration that linearized models are generally valid only in the energy representation of vibrational relaxation.

## Introduction

Computational fluid dynamics (CFD) of highly nonequilibrium real gases is an area of primarily theoretical research that is critically important to the design and performance of hypersonic vehicles. Examples include aerobraking of entry vehicles, aeroassisted orbital transfer vehicles, and the National Aero-space Plane. Although work in this area began at least as early as the 1960's, with many significant advances in subsequent years, comprehensive validated models still do not exist.

Serious modeling difficulties, which appear at almost every turn, range from uncertainties in the mathematical formulations of fundamental relaxation processes to uncertainties in such CFD input data as transport coefficients, rate coefficients for chemical reactions, and relaxation times. Questions also arise with regard to the use of different temperatures for the different energy modes of the constituent species of a gas in order to reduce the number of quantum states to a practical size that otherwise would have to be treated individually. Potential problems with this practice, which is more or less in the general spirit of the methods of nonequilibrium thermodynamics (ref. 1), are especially acute in the usual restriction to just two temperatures (refs. 2 and 3), one for the translational and rotational modes of all molecules and the other for free electrons and all vibrational and electronic excitation modes. Rapid and efficient coupling mechanisms clearly must operate for such assumptions to be valid. A history, survey, and partial resolution of some of the issues pertaining to this extremely complex problem area are given by Park (ref. 2).

The purpose of the present, very limited study is to provide a more physically credible mathematical representation of the equilibration of translational and vibrational motions of diatomic molecules after a strong hypersonic compression deposits sufficient energy to raise the translational or random temperature of the ambient, low-pressure (high-altitude) atmosphere to tens of thousands of degrees Kelvin. Because conventional fluid mechanics, as described by the Navier-Stokes and constitutive equations, is supported by Enskog's perturbation solution to the Boltzmann equation only for small departures from equilibrium (ref. 4), an immediate concern is how to describe the highly nonequilibrium initial situation encountered here.

As previously mentioned, a standard approach is to introduce a vibrational temperature ($T_v$) and allow it to approach the translational temperature ($T$) as the gas proceeds downstream into the shock layer (refs. 2 and 3). This additional thermodynamic parameter $T_v$ imposes two requirements on theoretical models of the flow field: (1) demonstration in derivations or applications of the models that mechanisms exist and operate to achieve instantaneous Boltzmann distributions of the populations of the vibrational levels (otherwise, the $T_v$ concept

is not justified); and (2) introduction of a differential equation for $T_v$ to allow its temporal and spatial evolution to be dictated by the laws of physics.

These two modeling requirements, neither of which is satisfied in a totally compelling manner in the current literature (as will be shown), are the primary foci of the present paper. Their importance to hypersonic aerothermodynamics cannot be overemphasized because what happens within and immediately behind a shock wave sets the tone everywhere in the shock layer. For example, the rates at which translation and vibration equilibrate and whether dissociation occurs early in the flow may determine, to a significant extent, the nonequilibrium overshoot of the radiation field produced downstream and the subsequent radiative heat load of the hypersonic vehicle. Failures of current CFD codes to meet either or both of these modeling standards could explain some of the major discrepancies found between predicted radiative heating and flight data (ref. 5). We must emphasize, however, the danger of jumping to conclusions based on the results of an analysis of just one aspect of such a complex problem.

Other features not considered here, like the rapid diffusion caused by the immense gradients in hypersonic shock waves, may well mask the effects of moderate to fairly large changes in relaxation times. Orders-of-magnitude reductions in the times generally used for the equilibration of the vibrational and translational temperature may be required (and, in fact, we show that they may occur) to make that process operative on the short time scale established by diffusion for the existence of gas parcels within the peak-temperature region of a shock layer.

The approach used in this study includes the following steps: (1) detailed derivations from first principles (meaning rate equations for populations of individual vibrational levels) of vibrational relaxation times and combination rules; (2) identification of mechanisms for achieving vibrational temperatures; (3) identification of the proper roles of vibrational-translational (V-T) and resonant vibrational-vibrational (V-V) energy exchange collisions; and (4) comparisons with existing formulations, especially the two-temperature CFD code of Gnoffo, Gupta, and Shinn (ref. 3) and Park's diffusion model (ref. 2).

## Symbols

| | |
|---|---|
| $a$ | $= \exp(-\phi/T)$ |
| $a'$ | $= \exp(-\phi/T_v)$ |
| $a_s$ | $= \exp(-\phi_s/T)$ for molecular species $s$ |
| $a'_s$ | $= \exp(-\phi_s/T_v)$ for molecular species $s$ |
| $a_v$ | $= \exp[-(E_{v+1} - E_v)/kT]$ |
| $a_{v'}$ | $= \exp[-(E_{v'+1} - E_{v'})/kT]$ |
| $C_{v,v}(T_v)$ | vibrational heat capacity per molecule at constant volume averaged over all molecular species, J/K |
| $C^s_{v,v}(T_v)$ | vibrational heat capacity per molecule at constant volume for molecular species $s$, J/K |
| $\langle C^s_{v,v} \rangle$ | vibrational heat capacity per molecule of species $s$ at constant volume averaged over temperature range from $T_v$ to $T$, J/K |
| $E_v$ | energy of vibrational level $v$, J |
| $E_{v'}$ | energy of vibrational level $v'$, J |
| $e_{vs}(T \text{ or } T_v)$ | average vibrational energy per unit mass of molecular species $s$ evaluated at $T$ or $T_v$, J/kg |

| | |
|---|---|
| $G$ | supply term for vibrational energy (including effects of diffusion, thermal conduction, and recombination or dissociation events), J/m$^3$-sec |
| $h$ | Planck's constant, $6.626 \times 10^{-34}$ J-sec |
| $K$ | rate coefficient $K(10, 00)$, m$^3$/sec |
| $K(v, v')$ | effective rate coefficient for $v \rightarrow v'$ vibrational transition, m$^3$/sec |
| $K(vv'', v'v''')$ | detailed rate coefficient for $v \rightarrow v'$ vibrational transition of molecule in question upon colliding with like molecule that undergoes $v'' \rightarrow v'''$ vibrational transition, m$^3$/sec |
| $K_{sa}$ | rate coefficient for $1 \rightarrow 0$ vibrational transition of molecule of species $s$ upon colliding with atom of species $a$, m$^3$/sec |
| $K_{sj}$ | rate coefficient for $1 \rightarrow 0$ vibrational transition of molecule of species $s$ upon colliding with particle of species $j$; equals $K_{sa}$ if $j = a$ and equals $K_{sj}(10, 00)$ if $j$ is a molecule of species $j$, m$^3$/sec |
| $k$ | Boltzmann constant, $1.380622 \times 10^{-23}$ J/K |
| $m_s$ | mass of molecule of species $s$, kg |
| $n$ | total number density of molecules in single-species gas, m$^{-3}$ |
| $n_j$ | number density of particles of species $j$, m$^{-3}$ |
| $n_m$ | total number density of all molecules in gas mixture, m$^{-3}$ |
| $n_s$ | total number density of molecules of species $s$, m$^{-3}$ |
| $n_{sv}$ | number density of $s$-species molecules in vibrational level $v$, m$^{-3}$ |
| $n_v$ | number density of molecules (single-species gas) in vibrational level $v$, m$^{-3}$ |
| $n_v^*$ | equilibrium number density of molecules (single-species gas) in vibrational level $v$ and evaluated at $T$, m$^{-3}$ |
| $Q_v(T)$ | vibrational partition function for single species |
| $Q_v^s(T_v)$ | vibrational partition function per $s$-species molecule |
| $T$ | translational and rotational temperature, K |
| $T_v$ | vibrational temperature, K |
| $t$ | time, sec |
| $\mathbf{u}$ | flow velocity vector, m/sec |
| $v, v', v'', v'''$ | vibrational quantum number |
| $X_s$ | defined in equation (B1) |
| $\alpha$ | ratio $K(20, 11)/K$ of rate coefficients for resonant vibrational-vibrational and nonresonant vibrational-translational energy-transfer collisions |
| $\gamma$ | nondimensional time ($\gamma = Knt$) |
| $\nu$ | oscillator frequency of low-lying vibrational levels of diatomic molecules in single-species gas, sec$^{-1}$ |
| $\nu_s$ | oscillator frequency of low-lying vibrational levels of $s$-species diatomic molecules, sec$^{-1}$ |

| | |
|---|---|
| $\xi$ | dummy variable |
| $\rho_m$ | total molecular mass density, kg/m$^3$ |
| $\rho_s$ | mass density of $s$-species molecules, kg/m$^3$ |
| $\rho_v$ | $= n_v/n_v^*$ |
| $\rho_{v'}$ | $= n_{v'}/n_{v'}^*$ |
| $\tau$ | average vibrational relaxation time (also called $\tau_t$), sec |
| $\tau'$ | Landau-Teller vibrational relaxation time for single-species gas of diatomic molecules, sec |
| $\tau_e$ | energy version of average vibrational relaxation time (measures translational-vibrational energy equilibration rate), sec |
| $\tau_s$ | combination vibrational relaxation time for $s$-species molecules resulting from collisions with all particles (also called $\tau'$ if gas is single species), sec |
| $\tau_{sj}$ | vibrational relaxation time for $s$-species molecules resulting from collisions with particles of species $j$, sec |
| $\tau_{sv}$ | vibrational relaxation time defined by equation (35), sec |
| $\tau_t$ | temperature version of average vibrational relaxation time (measures translational-vibrational temperature equilibration rate), sec |
| $\overline{\tau_v}$ | vibrational relaxation time defined by equation (61) in reference 3 |
| $\phi$ | characteristic temperature ($h\nu/k$) of diatomic molecules in single-species gas, K |
| $\phi_s$ | characteristic temperature ($h\nu_s/k$) of diatomic molecules of species $s$, K |
| $\nabla$ | operator |

Subscript:

| | |
|---|---|
| $r$ | only relaxation effects included |

Abbreviations:

| | |
|---|---|
| CFD | computational fluid dynamics |
| V-T | vibrational-translational |
| V-V | vibrational-vibrational |

## Vibrational Energy Equation

Conventional two-temperature models (ref. 3) of hypersonic flow fields assume that a single vibrational temperature ($T_v$) describes the vibrational population distributions for all molecular species in the gas. In particular, mechanisms are assumed to operate that instantaneously establish not only Boltzmann distributions for each species but somehow also couple the species to each other in this sense. The current study addresses the first of these requirements in a subsequent section, but not the second which may occur only after the production by ionization processes of sufficient electrons to act as effective coupling agents. Park (ref. 2) qualitatively discusses this and other roles of free electrons.

The differential equation for the temporal and spatial evolution of $T_v$ can be written (ref. 4, p. 505; also ref. 3) as

$$n_m \, C_{v,v}\,(T_v) \, \frac{DT_v}{Dt} = \frac{n_m \, C_{v,v}\,(T_v)}{\tau}\,(T - T_v) + G \tag{1}$$

where $D/Dt$ is the substantial derivative $(\partial/\partial t) + \mathbf{u} \cdot \nabla$, $\mathbf{u}$ is the flow velocity, $n_m$ is the number density of all molecules, $T$ is the translational temperature describing random motion, $\tau$ is an average vibrational relaxation time to be determined, $G$ is a supply term for vibrational energy (including the effects of diffusion, thermal conduction, and recombination or dissociation events), and $C_{v,v}(T_v)$ is an average vibrational heat capacity per molecule at constant volume satisfying

$$n_m \, C_{v,v}(T_v) = \sum_{s=\text{mol.}} n_s \, C^s_{v,v}(T_v) \tag{2}$$

in terms of quantities pertaining to molecular species $s$.

An important feature of equation (1) is the assumption that the rate of change of $T_v$ caused by vibrational-translational (V-T) energy-transfer collisions satisfies the Landau-Teller relaxation form (ref. 6)

$$\left(\frac{\partial T_v}{\partial t}\right)_r = \frac{T - T_v}{\tau} \tag{3}$$

The subscript $r$ stands exclusively for this relaxation process.

As straightforward and simple as equations (1)–(3) may appear, they nevertheless are loaded with uncertainties about mathematical form and what to substitute for the various parameters. Not the least of the difficulties is the proper choice of $\tau$, which is ordinarily regarded as a function of $T$ (and specifically not $T_v$) on the basis that collision frequency and relative collision velocity are the controlling factors for energy exchange between modes. However, this argument is predicated on equation (3) being correct in the sense that it displays $\tau$ in just the right relation to everything else; otherwise, $\tau$ will not have the physical interpretation necessary for the argument to hold. One need only recall the circumstances of Landau and Teller's derivation of equation (3) to appreciate the dangers involved here. They treated the propagation and absorption of small-signal sound waves, not the properties of hypersonic shock layers. Because there is no reason to expect a linear dependence on temperature difference in highly nonequilibrium situations, the $\tau$ in equation (3) may have to be a function of both $T$ and $T_v$ to compensate for a physically poor mathematical formulation of vibrational relaxation.

## Vibrational Rate Equations

Further insight into the character of $\tau$ can be gained by considering rate equations for the populations of individual vibrational levels. To the extent that diatomic molecules can be regarded as linear harmonic oscillators, the first term on the right-hand side of equation (1) becomes

$$\frac{n_m \, C_{v,v}\,(T_v)}{\tau}\,(T - T_v) = \sum_{s=\text{mol.}} \sum_{v} \phi_s k v \left(\frac{\partial n_{sv}}{\partial t}\right)_r \tag{4}$$

where $k$ is Boltzmann's constant, $n_{sv}$ is the number density of $s$-species molecules in vibrational level $v$, $\phi_s$ is the characteristic temperature $h\nu_s/k$ of $s$ molecules ($\phi_s = 3352$ K for $N_2$), and the partial derivatives satisfy conventional rate equations. We have ignored the vibrational zero-point energy $h\nu/2$ because only energy differences and derivatives of energy are physically meaningful.

For initial purposes, to be generalized later, the gas is considered to be a single species. The first step in writing rate equations for $n_v$ is the introduction of the effective rate coefficients

$$n\,K(v,v') = \sum_{v'',v'''}{}' \, n_{v''}\,K(vv'',v'v''') \tag{5}$$

for molecules making vibrational transitions from $v$ to $v'$ as a result of collisions with other molecules. Each $K(v,\,v')$ is a weighted sum over the more detailed rate coefficients $K(vv'',\,v'v''')$ showing the specific $v''$-to-$v'''$ transitions of the collision partner. The prime on the summation sign indicates that terms like $K(v,\,v+j;\;v+j,\,v)$ are to be ignored because they leave the vibrational states of the colliding molecules unchanged overall and thus cannot contribute to equations specifying the rates of change of the populations of individual levels.

Several relations can be imposed to reduce the number of detailed rate coefficients, and they are listed as follows: (1) $K(vv'',\,v'v'') = K(v0,\,v'0)$ on the assumption that the vibrational state of the collision partner is irrelevant if it does not change; (2) no quantum jump exceeding one level per molecule per collision (exact dipole selection rule for linear harmonic oscillators and perhaps not too bad for anharmonic oscillators, except for very large $v$); (3) no change in combined vibrational quantum number exceeding unity per collision because transition probabilities decrease rapidly with increasing inelasticity of collisions; and (4) $K(v0;\,v+1,\,0) = a_v\,K(v+1,\,0;\,v0)$ from detailed balancing, where

$$a_v = \exp\left[\frac{-\left(E_{v+1}-E_v\right)}{kT}\right] \tag{6}$$

and $E_v$ is the energy of level $v$. A detailed discussion of the rationale for applying detailed balancing to nonequilibrium gases is given in appendix A.

For illustrative purposes and to set the stage for a later special application, we apply equation (5) and the relations between detailed rate coefficients to a gas of four-level molecules. The results are given as

$$K(0,1) = a_0\,K(10,00) + \frac{n_2}{n}\,K(02,11) + \frac{n_3}{n}\,K(03,12) \tag{7}$$

$$K(1,0) = K(10,00) + \frac{n_1}{n}\,K(11,02) + \frac{n_2}{n}\,K(12,03) \tag{8}$$

$$K(1,2) = a_1\,K(20,10) + \frac{n_1}{n}\,K(11,20) + \frac{n_3}{n}\,K(13,22) \tag{9}$$

$$K(2,1) = K(20,10) + \frac{n_0}{n}\,K(20,11) + \frac{n_2}{n}\,K(22,13) \tag{10}$$

$$K(2,3) = a_2\,K(30,20) + \frac{n_1}{n}\,K(21,30) + \frac{n_2}{n}\,K(22,31) \tag{11}$$

$$K(3,2) = K(30,20) + \frac{n_0}{n}\,K(30,21) + \frac{n_1}{n}\,K(31,22) \tag{12}$$

all of which can be generalized (no restriction on the number of levels) to

$$K(v,v+1) = a_v\,K(v+1,0;v0) + \frac{1}{n}\sum_{v'}{}' \, n_{v'}\,K\left(vv';v+1,v'-1\right) \tag{13}$$

$$K(v+1,v) = K(v+1,0;v0) + \frac{1}{n}\sum_{v'}{}' \, n_{v'-1}\,K\left(v+1,v'-1;vv'\right) \tag{14}$$

Primes on the summation signs have the same meaning as before. Note the two kinds of energy-exchange processes in equations (13) and (14). Even though the first term in each expression represents a V-T collision, those summed over are near-resonant V-V with minimal change in the translational energy of a colliding pair.

Rate equations are formulated from the $K(v,\, v')$ coefficient according to

$$\begin{aligned}
\frac{1}{n}\left(\frac{\partial n_v}{\partial t}\right)_r &= \sum_{v'}\Big[K(v',v)\ n_{v'} - K(v,v')\ n_v\Big] \\
&= K(v-1,v)\ n_{v-1} - K(v,v-1)\ n_v + K(v+1,v)\ n_{v+1} - K(v,v+1)\ n_v \\
&= n_{v-1}\left(a_{v-1} - \frac{n_v}{n_{v-1}}\right) K(v0; v-1, 0) - n_v\left(a_v - \frac{n_{v+1}}{n_v}\right) K(v+1, 0; v0) \\
&\quad + \frac{1}{n}\sum_{v'}{}' \ n_{v'}\left[n_{v-1}\left(\frac{a_{v-1}n_{v'+1}}{a_{v'}n_{v'}} - \frac{n_v}{n_{v-1}}\right) K\big(vv'; v-1, v'+1\big)\right. \\
&\quad \left. -n_v\left(\frac{a_v n_{v'+1}}{a_{v'}n_{v'}} - \frac{n_{v+1}}{n_v}\right) K\big(v+1, v'; v, v'+1\big)\right]
\end{aligned} \tag{15}$$

Detailed balancing (see appendix A) is used on the near-resonant V-V rate coefficients in equation (13) to obtain this form.

An interesting first application is given to the aforementioned four-level molecules regarded as linear harmonic oscillators so that the relations (ref. 7)

$$K\big(vv'; v-1, v''\big) = v\ K\big(1v', 0v''\big) \tag{16}$$

and

$$K\big(v-1, v'; vv''\big) = v\ K\big(0v', 1v''\big) \tag{17}$$

are satisfied. These expressions yield

$$K(20,11) = 2K(10,01)$$

$$K(12,03) = 3K(10,01)$$

and

$$K(31,22) = 2K(30,21) = 6K(10,01)$$

for V-V collisions, whereupon

$$K(12,03) = 1.5K(20,11)$$

and

$$K(31,22) = 3K(20,11)$$

Equation (15) then becomes

$$\frac{1}{Kn}\left(\frac{\partial n_1}{\partial t}\right)_r = an_0 - (1+2a)\,n_1 + 2n_2 + \frac{\alpha}{2n}\left[4\left(n_0n_2 - n_1^2\right) + 3\left(n_0n_3 - n_1n_2\right) - 6\left(n_1n_3 - n_2^2\right)\right] \tag{18}$$

$$\frac{1}{Kn}\left(\frac{\partial n_2}{\partial t}\right)_r = 2an_1 - (2+3a)\,n_2 + 3n_3 - \frac{\alpha}{2n}\left[2\left(n_0n_2 - n_1^2\right) - 3\left(n_0n_3 - n_1n_2\right) - 12\left(n_1n_3 - n_2^2\right)\right] \tag{19}$$

and

$$\frac{1}{Kn}\left(\frac{\partial n_3}{\partial t}\right)_r = 3\left(an_2 - n_3\right) - \frac{3\alpha}{2n}\left[\left(n_0 n_3 - n_1 n_2\right) + 2\left(n_1 n_3 - n_2^2\right)\right] \tag{20}$$

if $K = K(10,00)$, $\alpha = K(20,11)/K$, and $a_v = a = \exp(-\phi/T)$ for all values of $v$.

Equations (18)–(20) were solved numerically for the problem of a static low-temperature $N_2$ gas ($n_1 = n_2 = n_3 = 0$ initially; $n = n_0 + n_1 + n_2 + n_3 =$ Constant) that is suddenly jolted to a fixed translational temperature $T$ of 33 520 K. The resulting density ratios $n_2/n_1$ and $n_3/n_2$ are plotted against $n_1/n_0$ in figures 1 and 2 for a four-level diatomic gas and as a function of the ratio $\alpha$ of rate coefficients for resonant V-V and nonresonant V-T energy-transfer collisions. Here, dimensionless time ($\gamma = Knt$) increases diagonally upward and to the right from the origin and eventually reaches the point at which translation and vibration are fully equilibrated according to the second law of thermodynamics. A straight line of slope unity in each case represents instantaneous realization at every point of a Boltzmann distribution of populations of vibrational levels, which is seen to occur only for sufficiently large values of $\alpha$. Otherwise, the upper levels are relatively overpopulated by the jolt that generates the highly nonequilibrium initial conditions. Because $\alpha$ is expected to be large on the basis that resonant V-V collisional energy transfers (no change in the total translational energy of a colliding pair) are generally much easier than nonresonant ones (see, for example, ref. 2, p. 61), this analysis seems to justify the concept of a vibrational temperature ($T_v$) being established on a very short time scale compared with that of intermodal equilibration.

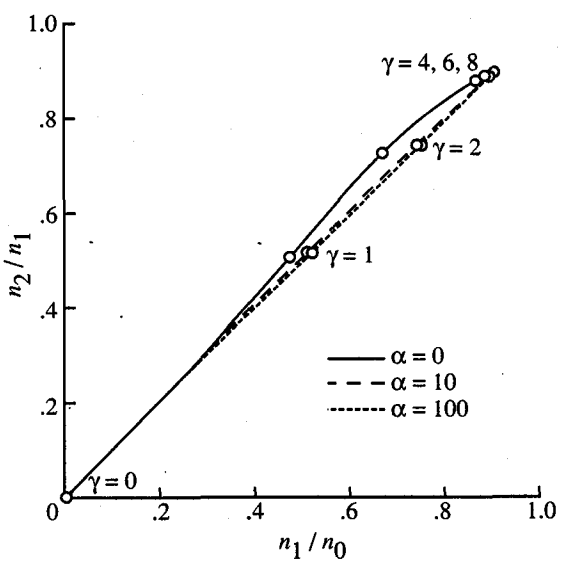


Figure 1. Ratio of populations of second vibrational level to first excited vibrational level plotted against ratio of populations of first excited vibrational level to ground-state vibrational level.

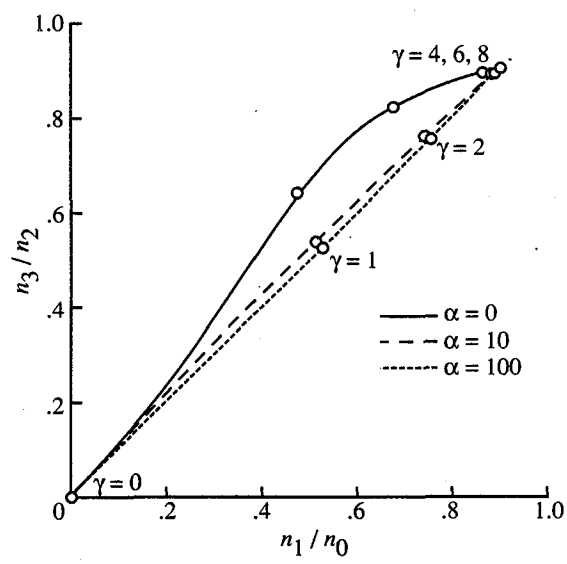


Figure 2. Ratio of populations of third vibrational level to second excited vibrational level plotted against ratio of populations of first excited vibrational level to ground-state vibrational level.

## Relative Roles of V-V and V-T Energy-Transfer Processes

Having identified near-resonant V-V collisions as the agents for establishing and maintaining vibrational temperatures, we now return to equations (1), (4), and (15) to see what other roles they may play and to continue the development of a mathematical formulation of vibrational relaxation. As can be deduced most easily by adding the products of equations (18), (19), and (20) with equations (1), (2), and (3), respectively, the V-V terms precisely cancel in

the summation over $v$ in equation (4) to yield the following version of equation (15) for a single-species gas of linear harmonic oscillators:

$$\sum_v \frac{v}{n}\left(\frac{\partial n_v}{\partial t}\right)_r = K(a-a')\sum_v (v+1)\,n_v \tag{21}$$

where

$$K(v+1,0;v0) = (v+1)\,K(10,00) = (v+1)\,K$$

and $a' = \exp(-\phi/T_v)$ is introduced to go with $a = \exp(-\phi/T)$. The cancellation of the V-V terms is independent of the relations between the V-V rate coefficients mentioned immediately prior to equations (18)–(20). This result should not be strongly affected by whether the oscillators are linear harmonic or anharmonic.

In addition to providing an enormous simplification to the modeling of vibrational relaxation, equation (21) states that V-T collisions alone are responsible for vibrational-translational equilibration. They are the rate-determining processes of current interest. The role of V-V collisions was described completely in the preceding section as underlying the concept of vibrational temperature. Although such a distinction of roles makes ultimate physical sense, the following brief digression shows that some existing CFD codes are not so simply interpreted.

## Diffusion Model

The diffusion model, as presented by Park (ref. 2), is so named because it describes the adjustment of a jolted gas as an upward population diffusion through a continuum of vibrational levels. Its derivation begins with the following approximation to equation (15):

$$\frac{1}{nn_v^*}\left(\frac{\partial n_v}{\partial t}\right)_r = \sum_{v'}\left[\frac{n_{v'}^*}{n_v^*}\,K(v',v)\,\rho_{v'} - K(v,v')\,\rho_v\right] \approx \sum_{v'} K\,(v,v')\,(\rho_{v'}-\rho_v) \tag{22}$$

where $n_v^*$ and $n_{v'}^*$ are equilibrium number densities evaluated at $T$, $\rho_v = n_v/n_{v'}^*$ and $\rho_{v'} = n_{v'}/n_{v'}^*$. However, the critical step in equation (22) is the assumption

$$K(v',\,v) = K(v,\,v')\exp\left[-\frac{(E_v - E_{v'})}{kT}\right]$$

which is an incorrect application of detailed balancing to the effective rate coefficients $K(v,\,v')$ instead of the detailed $K(vv'',\,v'v''')$. A potentially significant error is thus introduced, as can be assessed by considering relations like

$$K(v,v+1) - a_v\,K(v+1,v) = \frac{a_v}{n}\sum_{v'}{}'\,n_{v'}\left(\frac{a'_{v'}}{a_{v'}} - 1\right)K(v+1,v';v,v'+1) \tag{23}$$

obtained by subtracting equation (14) from equation (13) after applying detailed balancing to the V-V rate coefficients in the second expression and assuming the existence of $T_v$. (See appendix A for details.)

Equation (23) supports equation (22) only if the energy difference between adjacent vibrational levels is so small compared with $kT$ and $kT_v$ that the exponentials represented by $a$ and $a'$ can be set to unity. Although this condition is certainly approached at the higher quantum numbers, it is not actually achieved short of dissociation, and thus this condition is a very dangerous assumption. For example, it significantly changes the true relation between $T$ and $T_v$ that is so

apparent in equation (21) and that will be so important in the subsequent development. It also negates the critical cancellation of near-resonant V-V collisions that should occur in descriptions of vibrational-translational equilibration, which means that the roles of V-V and V-T energy-transfer processes become confused or lost in Park's application of the diffusion model. Finally, we should note that the $K(v+1,\, v';\, v,\, v'+1)$ terms on the right-hand side of equation (23) are the largest detailed rate coefficients appearing in the problem.

Our conclusion is that neither the diffusion model nor Park's use of it to derive a bridging formula (ref. 2) for including anharmonic effects in the Landau-Teller theory is physically acceptable. On the other hand, the apparent success (ref. 8) of the bridging formula in matching radiation data from shock tube and flight experiments cannot be ignored. This success may be explained by the introduction of additional parameters that were empirically adjusted to fit certain data, but which also served to conceal improper physics. We prefer the foundation and interpretation of equation (21) and will proceed from there.

## Relaxation Times

Equation (21) is easily generalized to a mixture of species and then combined with equation (4) to give

$$\frac{n_m\, C_{v,v}\left(T_v\right)}{\tau}\left(T-T_v\right)=\sum_{s=\text{mol.}}\sum_{j}\sum_{v}\left(v+1\right)\phi_s k K_{sj} n_{sv} n_j\left(a_s-a_s'\right) \tag{24}$$

where the $j$ summation is over all heavy-particle species, $K_{sj}$ is given as $K_{sj}(10,\,00)$ for molecule-molecule collisions and as $K_{sa}(1,\,0)$ for molecule-atom collisions, and $a_s$ and $a_s'$ satisfy

$$a_s=\exp\left(\frac{-\phi_s}{T}\right) \qquad a_s'=\exp\left(\frac{-\phi_s}{T_v}\right) \tag{25}$$

Two potential problems may occur in applications of equation (24). One problem is the previously mentioned assumption of a common vibrational temperature for all molecular species with no apparent mechanism to couple them, especially within and immediately behind hypersonic shock waves where free-electron coupling agents are not produced. Another problem is the restriction to linear harmonic oscillators, which is alleviated somewhat by the use of empirical expressions and other considerations to be discussed. An anharmonic generalization of equation (24) can be derived in a similar manner and written as

$$\begin{aligned}\frac{n_m\, C_{v,v}\left(T_v\right)}{\tau}\left(T-T_v\right)=&\sum_{s=\text{mol.}}\sum_{j}\sum_{v} n_j n_{sv}\left(E_{s,v+1}-E_{sv}\right)\\ &\times\left\{\exp\left[-\frac{\left(E_{s,v+1}-E_{sv}\right)}{kT}\right]-\exp\left[-\frac{\left(E_{s,v+1}-E_{sv}\right)}{kT_v}\right]\right\}K_{sj}\left(v+1,0;v0\right)\end{aligned} \tag{26}$$

where $E_s$ denotes the vibrational energy of molecular species $s$. However, the disadvantage to practical CFD applications of long strings of unknown rate coefficients is obvious.

As shown in full detail in appendix B, equation (24) can be transformed by straightforward mathematical manipulations into the expression

$$\frac{n_m\, C_{v,v}\left(T_v\right)}{\tau}\left(T-T_v\right)-\sum_{s=\text{mol.}}\sum_{j}\frac{\phi_s k K_{sj} n_s n_j}{Q_v^s\left(T_v\right)}\left(a_s-a_s'\right)\left(1-a_s'\right)^{-2} \tag{27}$$

where $Q_v^s(T_v)$ is the vibrational partition function per $s$ molecule satisfying

$$Q_v^s(T_v) = \sum_i (a_s')^i = (1 - a_s')^{-1} \tag{28}$$

Appropriate derivatives of $Q_v^s(T_v)$ give the average vibrational energy per unit mass of molecular species $s$ as

$$e_{vs}(T_v) = \frac{kT_v^2}{m_s}\frac{d}{dT_v}\ln Q_v^s(T_v) = \frac{\phi_s k}{m_s}\left[\exp\left(\frac{\phi_s}{T_v}\right) - 1\right]^{-1} \tag{29}$$

and the vibrational heat capacity per $s$ molecule at constant volume as

$$C_{v,v}^s(T_v) = m_s\frac{d}{dT_v}\, e_{vs}(T_v) = k\left(\frac{\phi_s}{T_v}\right)^2\left[\exp\left(\frac{\phi_s}{T_v}\right) - 1\right]^{-2}\exp\left(\frac{\phi_s}{T_v}\right) \tag{30}$$

Two convenient definitions of characteristic times are suggested by equation (27). They are

$$\frac{1}{\tau_{sj}} = \frac{K_{sj}n_j}{Q_v^s(T)} \tag{31}$$

for vibrational-translational equilibration caused by collisions between $s$ molecules and particles of species $j$ and the combination relaxation time

$$\frac{1}{\tau_s} = \sum_j \frac{1}{\tau_{sj}} \tag{32}$$

for collisions between $s$ molecules and all heavy particles, including other $s$ molecules. Three features are worth noting: (1) $\tau_{sj}$ and $\tau_s$ are determined by collision frequencies and relative collision velocities (and thus are independent of $T_v$), as should be required of relaxation times; (2) reciprocals of relaxation times are added in equation (32), which is typical of lifetimes appearing in rate equations; and (3) equation (32) contrasts sharply with equation (55) of reference 3, where Gnoffo, Gupta, and Shinn add relaxation times instead of their reciprocals.

Existing CFD codes for hypersonic flow fields all use empirical expressions for relaxation times, examples of which are the mathematical formulations and sets of adjustable parameters deduced by Millikan and White (ref. 9) from shock tube data. Their relaxation times are directly identified as the $\tau_{sj}$ term of equation (31).

Perhaps the most important change proposed in this paper to the CFD code of reference 3, and certainly the most dramatic one, is the use in equation (1) of

$$\frac{1}{\tau} = \left[\sum_{s=\text{mol.}} n_s\, C_{v,v}^s(T_v)\right]^{-1} \sum_{s=\text{mol.}} \frac{T_v^2 n_s\, C_{v,v}^s(T_v)}{(T - T_v)\,\phi_s\tau_s}\left[\frac{1 - \exp(-\phi_s/T_v)}{1 - \exp(-\phi_s/T)}\right] \times \left\{\exp\left[\phi_s\left(\frac{1}{T_v} - \frac{1}{T}\right)\right] - 1\right\} \tag{33}$$

which is obtained from equation (27) by substituting equations (2), (28), (30), (31), and (32). The more general result for anharmonic oscillators is similarly obtained from equation (26) to be

$$\frac{1}{\tau} = \left[\sum_{s=\text{mol.}} n_s\, C^s_{v,v}\left(T_v\right)\right]^{-1} \sum_{s=\text{mol.}} \sum_{v} \frac{n_{sv}\, Q^s_v\left(T\right)}{\left(T - T_v\right)\tau_{sv}} \left(E_{s,v+1} - E_{sv}\right)$$

$$\times \left\{\exp\left[-\frac{\left(E_{s,v+1} - E_{sv}\right)}{kT}\right] - \exp\left[-\frac{\left(E_{s,v+1} - E_{sv}\right)}{kT_v}\right]\right\} \tag{34}$$

where $Q^s_v(T)$ and $C^s_{v,v}(T_v)$ must be corrected for anharmonicity and $\tau_{sv}(T)$ is defined by

$$\frac{1}{\tau_{sv}} = \sum_j \frac{n_j}{Q^s_v\left(T\right)} K_{sj}\left(v+1, 0; v0\right) \tag{35}$$

in analogy with equation (31).

Several general features of equation (33) should be noted before making qualitative comparisons with existing codes. The restriction of equation (31) to linear harmonic oscillators is alleviated to some extent by $\tau_s$ being a combination of empirical Millikan-White functions presently spanning (ref. 10) a temperature range from 300 K to 9000 K. The cancellation of $Q^s_v(T)$ factors between equations (31) and (33) also helps because it is the translational temperature ($T$) that achieves the very high values in hypersonic shock waves. However, nothing can really compensate for using the expression within the braces in equation (33) instead of the more physical expression within the braces in equation (34). This is an error that must be accepted if the simpler algorithm is retained.

Another interesting feature of equations (33) and (34) is their approach to

$$\frac{1}{\tau} = \left[\sum_{s=\text{mol.}} n_s\, C^s_{v,v}\left(T\right)\right]^{-1} \sum_{s=\text{mol.}} \frac{n_s\, C^s_{v,v}\left(T\right)}{\tau_s} \tag{36}$$

and

$$\frac{1}{\tau} = \left[\sum_{s=\text{mol.}} n_s\, C^s_{v,v}\left(T\right)\right]^{-1} \sum_{s=\text{mol.}} \frac{Q^s_v\left(T\right)}{kT^2} \left\{\sum_v \frac{n_{sv}}{\tau_{sv}} \left(E_{s,v+1} - E_{sv}\right)^2 \exp\left[-\frac{\left(E_{s,v+1} - E_{sv}\right)}{kT}\right]\right\} \tag{37}$$

respectively, when the two temperatures $T$ and $T_v$ are not very different. Although equation (36) is merely an extension of the simple Landau-Teller result to a multiple-species gas of linear harmonic oscillators, equation (37) provides the proper correction for anharmonic oscillators. For example, the $\tau$ given by equation (37) can be used to generalize the Landau-Teller theory for the absorption of small-signal sound waves to arbitrarily high gas temperatures if all the $K_{sj}(v+1,\ 0;\ v0)$ coefficients in equation (35) are known from quantum mechanics.

A final, but extremely important, feature of equations (33) and (34) is that they both give $\tau = \tau(T,\ T_v)$ for highly nonequilibrium gases, which means that $\tau$ is different from a relaxation time in the conventional sense. The time $\tau$ has to correct for the fact that the linear forms assumed in equations (3) and (4) do not explicitly reveal the true dependence on temperature difference. This possibility was anticipated in a previous section.

## Qualitative Comparisons With CFD Codes

Because of the linearization assumption, that is,

$$e_{vs}\left(T\right) - e_{vs}\left(T_v\right) \approx C^s_{v,v}\left(T_v\right)\left(T - T_v\right)$$

in equation (59) of reference 3 and in subsequent definitions, comparisons of relaxation times are most easily made for a single-species gas of diatomic molecules. The $\tau$ of equation (33) is then supposed to represent the same quantity and be used in the same context as the $\overline{\tau_v}$ defined by equation (61) of reference 3. Equation (33) reduces to

$$\frac{1}{\tau} = \frac{T_v^2}{(T - T_v)\,\phi\tau'} \left[\frac{1 - \exp(-\phi/T_v)}{1 - \exp(-\phi/T)}\right] \left\{\exp\left[\phi\left(\frac{1}{T_v} - \frac{1}{T}\right)\right] - 1\right\} \tag{38}$$

where we have primed the Landau-Teller relaxation time to distinguish it from the $\tau$ in question. According to equations (31) and (32), it satisfies

$$\frac{1}{\tau'} = \frac{Kn}{Q_v(T)} \tag{39}$$

and thus is independent of $T_v$.

Because $\tau'$ is also the $\overline{\tau_v}$ of reference 3 under the same circumstances, equation (38) relates the present relaxation time to that of reference 3 in this special case. Figure 3 shows how the ratio $\tau'(T)/\tau(T, Tv)$ varies with $T_v$, as computed from equation (39) for $N_2$ with $T$ held fixed at 40 000 K. The huge values at small $T_v$ are caused by the factor $\exp(\phi/T_v) = \exp(3352/T_v)$. In a hypersonic shock layer, of course, the large $T$ generated by the deposition of energy into random motion during compression does not remain constant, but rather it decreases as translational energy is transformed into vibration, dissociation, and other modes. Nevertheless, the much smaller $\tau$ of equation (33), perhaps by as much as seven orders of magnitude near the temperature peak of the shock wave, may make translational-vibrational equilibration highly competitive with the fast diffusion caused by large gradients. If so, this equilibration could give a very different description of how processes begin and thereby set a different tone for what happens in the shock layer.

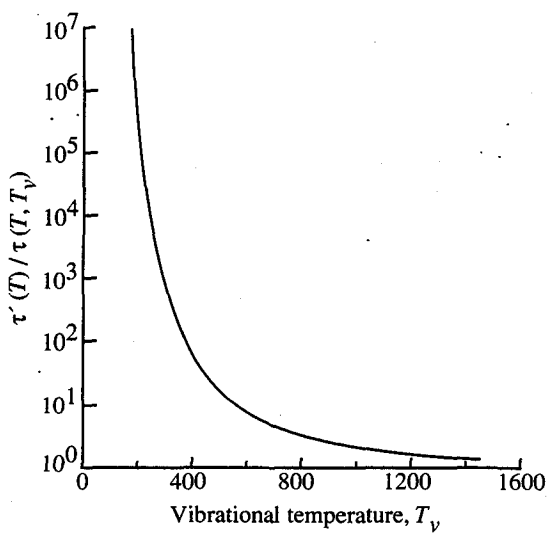


Figure 3. Ratio of Landau-Teller vibrational relaxation time ($\tau'$) to vibrational relaxation time of this paper ($\tau$) as a function of vibrational temperature ($T_v$) of an $N_2$ gas at translational temperature of 40 000 K.

A possible scenario based on the use of equation (33) instead of $\overline{\tau_v}$ in CFD codes would be a sharper decline of the translational temperature inward toward the hypersonic vehicle from its peak value (also possibly lower), a more rapid rise of the vibrational temperature in the same region, a correspondingly faster equilibration of the two temperatures at a lower value of $T$, a lower nonequilibrium contribution (radiation overshoot) to the radiation field produced farther

inward, and thus lower radiative heating of the vehicle. This trend, which could well lead to substantially different numerical results, is clearly in the right direction to correct the generally large overpredictions, compared with flight data, of the radiative heat load of reentry vehicles (ref. 5). In any event, equation (33) has been derived more or less from first principles and should replace $\overline{\tau_v}$ on physical grounds alone.

## Energy Relaxation Times Versus Temperature Relaxation Times

The $\tau(T, T_v)$ term given by equations (33) or (34) was derived specifically to fit equations (3) and (4). Accordingly, it can be called the temperature version of the relaxation time because it measures how fast the translational and vibrational temperatures equilibrate. We label it $\tau_t$. A similar $\tau$ can be derived to measure how fast the translational and vibrational energies equilibrate. We call this $\tau$ the energy version and label it $\tau_e$. Although the current literature rarely distinguishes between the two, as is evidenced by $\tau_t$ and $\tau_e$ being used interchangeably throughout Park's book (ref. 2), we show in this section that they are generally different.

A convenient derivation of $\tau_e$ starts with the following definition of the average vibrational heat capacity per $s$ molecule at constant volume:

$$\begin{aligned}\left\langle C_{v,v}^s\right\rangle &= \frac{1}{T-T_v}\int_{T_v}^{T} C_{v,v}^s\left(T\right)\,dT = \frac{k\phi_s}{T-T_v}\int_{\phi_s/T}^{\phi_s/T_v} e^{\xi}\left(e^{\xi}-1\right)^{-2}\,d\xi \\ &= \frac{T_v^2\,C_{v,v}^s\left(T_v\right)}{\left(T-T_v\right)\phi_s}\left[\frac{1-\exp\left(-\phi_s/T_v\right)}{1-\exp\left(-\phi_s/T\right)}\right]\left\{\exp\left[\phi_s\left(\frac{1}{T_v}-\frac{1}{T}\right)\right]-1\right\} \qquad (40)\end{aligned}$$

Equation (30) for linear harmonic oscillators was used in this evaluation. As expected, $\left\langle C_{v,v}^s\right\rangle \approx C_{v,v}^s(T_v)$ for $T_v$ when not very different from $T$; also, equation (40) bears a striking resemblance to a large portion of the right-hand side of equation (33) for the reciprocal $\tau$ (now $\tau_t$). Because the average vibrational energy per unit mass of molecular species $s$, as defined by equation (29), satisfies

$$\begin{aligned}m_s\left[e_{vs}\left(T\right)-e_{vs}\left(T_v\right)\right] &= \int_0^T C_{v,v}^s\left(T\right)\,dT - \int_0^{T_v} C_{v,v}^s\left(T\right)\,dT \\ &= \int_{T_v}^{T} C_{v,v}^s\left(T\right)\,dT \\ &= \left(T-T_v\right)\left\langle C_{v,v}^s\right\rangle \qquad (41)\end{aligned}$$

substitution of this expression and equation (40) into equations (1), (2), (3), and (33) yields

$$\begin{aligned}\rho_m\left(\frac{\partial e_v}{\partial t}\right)_r &= n_m\,C_{v,v}\left(T_v\right)\left(\frac{\partial T_v}{\partial t}\right)_r \\ &= \frac{n_m\,C_{v,v}\left(T_v\right)}{\tau_t}\left(T-T_v\right) \\ &= \sum_{s=\text{mol.}}\frac{n_s}{\tau_s}\left(T-T_v\right)\left\langle C_{v,v}^s\right\rangle \\ &= \sum_{s=\text{mol.}}\frac{\rho_s}{\tau_s}\left[e_{vs}\left(T\right)-e_{vs}\left(T_v\right)\right] \\ &= \frac{\rho_m}{\tau_e}\left[e_v\left(T\right)-e_v\left(T_v\right)\right] \qquad (42)\end{aligned}$$

where $\rho_s = n_s m_s$ and

$$\rho_m = \sum_{s=\text{mol.}} \rho_s \tag{43}$$

are mass densities.

Equation (42) gives the proper relation between the two relaxation times for linear harmonic oscillators, which becomes

$$\tau_e = \tau' = \tau_t \frac{\langle C_{v,v} \rangle}{C_{v,v}(T_v)} = \frac{\tau_t T_v^2}{(T - T_v)\,\phi} \left[ \frac{1 - \exp(-\phi/T_v)}{1 - \exp(-\phi/T)} \right] \left\{ \exp\left[ \phi \left( \frac{1}{T_v} - \frac{1}{T} \right) \right] - 1 \right\} = \overline{\tau_v} \tag{44}$$

for a single-species gas. This result, which reintroduces the $\tau'$ defined by equation (39) to distinguish the Landau-Teller parameter or the Millikan-White parameter, summarizes some of the principal conclusions of the current study at the simplest level. Highlights include the following points: (1) $\tau_e = \tau_e(T) = \tau' = \tau'(T)$, whereas $\tau_t = \tau_t(T, T_v)$ for temperature differences corresponding to departures from equilibrium larger than first order; (2) identification of the relaxation time $\overline{\tau_v}$ of reference 3 with both $\tau'$ and the correct energy version of $\tau$; and (3) recognition that $\overline{\tau_v}$ is an acceptable temperature version only if the vibrational heat capacity at $T_v$ can be replaced with its average value over the range from $T_v$ to $T$, which is obviously not justified within hypersonic shock waves.

The bottom line is that a price must be paid for replacing the vibrational energy equation with a vibrational temperature equation, as was done in reference 3 in order to reduce the number of species-dependent parameters that must be evaluated and carried along in the computations. Linearized models involving simple differences between translational and vibrational parameters are generally not valid in the latter description because both $T$ and $T_v$ are introduced into the theory in exponential terms, the first by detailed balancing and the second by instantaneous Boltzmann population distributions generated and maintained by near-resonant V-V collisional energy transfers. In fact, the linear energy expression in equation (42) is itself remarkable for highly nonequilibrium gases, as was noted by Vincenti and Kruger (ref. 11) in their discussion of a similar result obtained for the much simpler problem of a relatively few diatomic molecules imbedded in a heat bath of many inert gas atoms.

## Practical Difficulties

Although the proposed changes in the mathematical formulation of vibrational relaxation are more solidly based on fundamental physical principles than those occurring in existing CFD codes, accurate assessments of their impact will be difficult because of other uncertainties. The problems have to do mostly with the multitude of scarcely known parameters that plague applications and will continue to do so until a more reliable input data base is available. For example, Hartung, Mitcheltree, and Gnoffo (ref. 5) have demonstrated a high sensitivity of radiative heating to three such parameters, all of which appear within the rather narrow confines of the vibrational energy or temperature equations. They are the cross sections introduced by Park (ref. 2) to correct the Millikan-White (ref. 9) relaxation times at high temperatures, the rate-controlling temperature in the Arrhenius rate coefficient for molecular dissociation, and the vibrational energy removed or added in each dissociation or recombination event.

The point being made is that inadequate physical models are easily masked, and good physical models are not made worth the additional effort by merely adjusting these parameters to fit available data. On the other hand, Hartung, et al. do show that radiative heating is not predicted satisfactorily when the parameters are constrained within what is considered to be reasonable physical limits, which means that some degree of assessment of the proposed changes is possible and definitely should be attempted. In any event, because of the overall complexity

of hypersonic flow fields, numerous possible explanations will exist for whatever gap between theory and experiment may remain after implementation of the changes.

## Concluding Remarks

Mathematical formulations of vibrational relaxation are derived from first principles for application to fluid dynamic computations of hypersonic flow fields. The highlights include the following: (1) a demonstration that fast near-resonant vibrational-vibrational (V-V) energy-transfer collisions support the assumption of a vibrational temperature, at least for a single-species gas; (2) the identification of vibrational-translational (V-T) collisions as having sole responsibility for the equilibration of vibration and translation after a strong initial jolt places a gas in a highly nonequilibrium state; (3) the derivation of an improved vibrational relaxation time for use in the vibrational temperature equation; (4) a demonstration that vibrational relaxation times appropriate for temperature equations are very different from those appropriate for energy equations when the difference between translational and vibrational temperatures is large; and (5) a demonstration that linearized models are generally valid only in the energy representation of vibrational relaxation.

Modifications are suggested to improve the physical content of an existing computational fluid dynamics (CFD) code and perhaps its agreement with flight data on the radiative heat load of hypersonic vehicles. In particular, the proposed temperature version of the vibrational relaxation time may be orders of magnitude smaller within a shock wave than the one currently used; consequently, translational-vibrational equilibration can be highly competitive with the rapid diffusion there and result in a substantially reduced and more realistic nonequilibrium radiation field within the shock layer. The modifications are presented in two forms: one form for linear harmonic oscillators (partially corrected for anharmonicity) that is easily implemented with no additional parameters to evaluate, and the other form for anharmonic oscillators that is more formal and requires additional rate coefficients. Both are applicable to multicomponent gas mixtures typical of Earth and planetary atmospheres.

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## Appendix A

## Detailed Balancing in Highly Nonequilibrium Gases

The principle of detailed balancing states that the forward and backward rates of any chemical reaction are precisely equal if the gas in question is in total equilibrium. This principle is a powerful tool for relating rate coefficients to each other and thus significantly reducing the number of independent parameters required for CFD codes. It is used in just this manner in several places in the present paper, despite the fact that it is strictly an equilibrium concept and that hypersonic flow fields represent highly nonequilibrium conditions. The rationale for such applications needs to be thoroughly understood.

We first recognize that the detailed rate coefficients $K(vv'', v'v''')$ introduced in equation (5) depend on the translational temperature ($T$), but never on the vibrational temperature ($T_v$). This statement is rigorously true for anharmonic as well as linear harmonic oscillators because these $K$ coefficients deal at the microscopic level with the specific vibrational transitions that are possible when molecules in given states collide, and not with the number of molecules in these given states. Only the latter concept can introduce $T_v$. Accordingly, only parameters affecting quantum mechanical transition probabilities are relevant—for example, translational temperature insofar as it determines relative collision velocities.

Such being the character of the detailed rate coefficients, we can certainly say that whatever relation exists between $K(vv'', v'v''')$ and $K(v'v''', vv'')$ for one gas condition must be true for all gas conditions (total equilibrium or not) having the same translational temperature ($T$). We choose total equilibrium and write the detailed-balancing relation as

$$K(v'v''', vv'') = \frac{n_v^* n_{v''}^*}{n_{v'}^* n_{v'''}^*} K(vv'', v'v''') = \frac{\exp(-E_v/kT)\ \exp(-E_{v''}/kT)}{\exp(-E_{v'}/kT)\ \exp(-E_{v'''}/kT)} K(vv'', v'v''') \quad \text{(A1)}$$

with supreme confidence that it holds for vibrational-translational nonequilibrium at the same value of $T$. The temperature $T$ is introduced into the rate equations through the starred number densities, which denote total equilibrium and thus Boltzmann distributions.

Although risking redundancy, we cannot state too strongly that detailed balancing is applicable only at the level of the detailed $K$ coefficients in equation (A1). It does not apply to the average $K(v, v')$ defined by equation (5), which is the source of our contention with Park's formulation of the diffusion model (ref. 2) to incorporate the effects of anharmonic oscillators. The key expression in that discussion is equation (23), which we derive here to illustrate a typical application of equation (A1) and other points.

The appropriate form of equation (A1) for this particular application is

$$\begin{aligned} K(v, v'+1; v+1, v') &= \frac{\exp\left[-\left(E_{v+1} - E_v\right)/kT\right]}{\exp\left[-\left(E_{v'+1} - E_{v'}\right)/kT\right]} K(v+1, v'; v, v'+1) \\ &= \frac{a_v}{a_{v'}} K(v+1, v'; v, v'+1) \end{aligned} \quad \text{(A2)}$$

where $a_v$ and $a_{v'}$ are shorthand notations for the exponentials. Equation (13) of the text becomes

$$K(v,v+1) = a_v\ K(v+1,0;v0) + \frac{1}{n}\sum_{v'}{}' n_{v'}\ K\big(vv';v+1,v'-1\big)$$

$$= a_v\ K(v+1,0;v0) + \frac{1}{n}\sum_{v'}{}' n_{v'+1}\ K\big(v,v'+1;v+1,v'\big)$$

$$= a_v\ K(v+1,0;v0) + \frac{a_v}{n}\sum_{v'}{}' \frac{n_{v'+1}}{a_{v'}}\ K\big(v+1,v';v,v'+1\big)$$

$$= a_v\ K(v+1,0;v0) + \frac{a_v}{n}\sum_{v'}{}' \frac{a'_{v'}n_{v'}}{a_{v'}}\ K\big(v+1,v';v,v'+1\big) \tag{A3}$$

upon changing the summation index after the second equality, using equation (A2) after the third equality, and assuming that $T_v$ exists after the fourth equality so that

$$\frac{n_{v'+1}}{n_{v'}} = \exp\left[\frac{-\left(E_{v'+1}-E_{v'}\right)}{kT_v}\right] = a'_{v'} \tag{A4}$$

Equation (14) can be rewritten in similar fashion as

$$a_v\ K(v+1,v) = a_v\ K(v+1,0;v0) + \frac{a_v}{n}\sum_{v'}{}' n_{v'}\ K\big(v+1,v';v,v'+1\big) \tag{A5}$$

Subtraction of equation (A5) from equation (A3) then yields equation (23) in the form

$$K(v,v+1) - a_v\ K(v+1,v) = \frac{a_v}{n}\sum_{v'}{}' n_{v'}\left\{\frac{\exp\left[-\left(E_{v'+1}-E_{v'}\right)/kT_v\right]}{\exp\left[-\left(E_{v'+1}-E_{v'}\right)/kT\right]} - 1\right\} K\big(v+1,v';v,v'+1\big) \tag{A6}$$

the right-hand side of which does not vanish. This result clearly shows the error in applying detailed balancing at the average $K(v,\ v')$ level for a gas of diatomic molecules in vibrational-translational nonequilibrium (i.e., $T_v$ different from $T$). As noted in the text, the $K(v+1,\ v';\ v,\ v'+1)$ terms on the right-hand side of equation (A6) refer to near-resonant V-V collisions and thus are the largest detailed rate coefficients appearing in the problem.

One exception to our conclusion is the special problem of a relatively few diatomic molecules mixed in a heat bath of many inert-gas atoms regarded as having no excitable internal energy modes. Because collisions of molecules with atoms will totally dominate collisions with other molecules, the contributions of the molecule-molecule $K(v+1,\ v';\ v,\ v'+1)$ can be ignored in this case, and then equation (A6) reduces to the detailed-balancing form

$$K(v,v+1) = a_v\ K(v+1,v) \tag{A7}$$

assumed by Park for the diffusion model. Unfortunately, what is true for a heat bath is not true for hypersonic aerothermodynamics, even though much of the simpler methodology discussed by Vincenti and Kruger (ref. 11) for the first problem seems to have been applied to the second problem all too often in the literature.

## Appendix B

### Derivation of Temperature Form of Vibrational Energy Equation

Because equation (27) of the text is a key expression for subsequently determining the vibrational relaxation times appropriate for the temperature version of the vibrational energy equation, in this appendix we give the details of its derivation from equation (24). We begin by looking specifically at the $v$ summation

$$X_s = \sum_v (v+1)\, n_{sv} \tag{B1}$$

in the form of equation (24):

$$\frac{n_m\, C_{v,v}\,(T_v)}{\tau}\,(T - T_v) = \sum_{s=\text{mol.}} \sum_j \phi_s k K_{sj} n_j \left(a_s - a_s'\right) X_s \tag{B2}$$

Expansion of equation (B1) with the use of $n_s = n_{s0} + n_{s1} + n_{s2} + \ldots$ yields

$$\begin{aligned}
\frac{1}{n_s} X_s &= \frac{1}{n_s}\left(n_{s0} + 2n_{s1} + 3n_{s2} + \ldots\right) \\
&= \left(1 + \frac{n_{s1}}{n_{s0}} + \frac{n_{s2}}{n_{s0}} + \frac{n_{s3}}{n_{s0}} + \ldots\right)^{-1} + 2\left(\frac{n_{s0}}{n_{s1}} + 1 + \frac{n_{s2}}{n_{s1}} + \frac{n_{s3}}{n_{s1}} + \ldots\right)^{-1} \\
&\quad + 3\left(\frac{n_{s0}}{n_{s2}} + \frac{n_{s1}}{n_{s2}} + 1 + \frac{n_{s3}}{n_{s2}} + \ldots\right)^{-1} + \ldots
\end{aligned} \tag{B3}$$

Because the density ratios satisfy

$$\frac{n_{sv'}}{n_{sv}} = \exp\left[\frac{-\left(v' - v\right)\phi_s}{kT_v}\right] = \left(a_s'\right)^{v'-v} \tag{B4}$$

for Boltzmann distributions of populations of the vibrational levels of linear harmonic oscillators at the vibrational temperature $T_v$, we have

$$\begin{aligned}
\frac{1}{n_s} X_s &= \left[1 + a_s' + \left(a_s'\right)^2 + \left(a_s'\right)^3 + \ldots\right]^{-1} + 2\left[\left(a_s'\right)^{-1} + 1 + a_s' + \left(a_s'\right)^2 + \ldots\right]^{-1} \\
&\quad + 3\left[\left(a_s'\right)^{-2} + \left(a_s'\right)^{-1} + 1 + a_s' + \ldots\right]^{-1} + \ldots \\
&= \left[1 + a_s' + \left(a_s'\right)^2 + \left(a_s'\right)^3 + \ldots\right]^{-1}\left[1 + 2a_s' + 3\left(a_s'\right)^2 + \ldots\right] \\
&= \frac{\left(1 - a_s'\right)^{-2}}{Q_v^s\,(T_v)}
\end{aligned} \tag{B5}$$

upon using equation (28) for the vibrational partition function per $s$ molecule.

Substitution of equation (B5) into equation (B2) finally gives

$$\frac{n_m\, C_{v,v}\left(T_v\right)}{\tau}\left(T - T_v\right) = \sum_{s=\text{mol.}} \sum_{j} \frac{\phi_s k K_{sj} n_s n_j}{Q_v^s\left(T_v\right)}\left(a_s - a_s'\right)\left(1 - a_s'\right)^{-2} \tag{B6}$$

which is equation (27).

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Mathematical formulations of vibrational relaxation are derived from first principles for application to fluid dynamic computations of hypersonic flow fields. Relaxation within and immediately behind shock waves is shown to be substantially faster than that described in current numerical codes. The result should be a significant reduction in nonequilibrium radiation overshoot in shock layers and in radiative heating of hypersonic vehicles; these results are precisely the trends needed to bring theoretical predictions more in line with flight data. Errors in existing formulations are identified and qualitative comparisons are made.

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