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Prediction of Vibrational Relaxation in Hypersonic Expanding Flows Part 1: Model Development

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A number of experiments in nozzles have indicated that the Landau–Teller vibrational relaxation model fails to accurately predict the relaxation process in expanding flows. In the present study vibrational transition rate equations are solved and the detailed calculations are used to develop a simplified relaxation model. The present simplified relaxation model allows both non-Boltzmann population distributions in vibrationally heating and cooling flows. This simplified model also includes the effect of anharmonicity on vibrational transition rates and energy transfer.

Nomenclature

E_v = energy in level v per molecule, erg
$(e_{\text{vib}})_m$ = vibrational energy of species m per unit mass (relative to ground state), erg/g
F_v = normalized adiabaticity function for simplified anharmonic model
f'_v = adiabaticity function for simplified anharmonic model
h = Planck's constant, 6.6256×10^{-27} erg-s
$K_{v,v'}$ = transition rate coefficient from v to v', cm^3/s
k = Boltzmann's constant, 1.38054×10^{-16}, erg/K
$m_{m,s}$ = reduced mass of collision pair of molecule m with species s, g
N = number density of gas mixture, cm^{-3}
$P_{v,v'}^{v_2,v_2'}$ = thermally averaged probability of transition from v to v' and from v_2 to v_2'
p = static pressure, dyne/cm^2
T = translational temperature, K
T_{vib} = vibrational temperature based on energy in vibrational mode, K
T_{vib_v} = vibrational temperature based on population at levels v and $v + 1$, K
t = time coordinate, s
u = streamwise flow velocity, cm/s
v = vibrational quantum level
$vmax$ = highest bound vibrational quantum level
x = streamwise spatial coordinate, cm
α = interaction range parameter in exponentially repulsive potential, cm^{-1}
ΔE = energy transferred from translation to vibration per collision, erg
η_s = mole fraction of species s
$(\theta_v)_m$ = characteristic vibrational temperature of species m, K
ρ = density of gas mixture, g/cm^3
τ = vibrational relaxation time, s
ϕ = local acceleration factor, $\dot{e}_{\text{vib}}/\dot{e}_{\text{vib}}^{\text{LT}}$
$\bar{\phi}$ = constant overall acceleration factor

Subscripts
E = thermal equilibrium condition
LT = Landau–Teller model
m = diatomic chemical species m
s = chemical species s
t = stagnation condition
v = vibrational quantum level v

Superscripts
LT = Landau–Teller model
VT = vibration-translation collisions
VV = vibration-vibration exchange collisions

Introduction

IN high-temperature flows related to vehicles at hypersonic speeds significant excitation of the vibrational energy modes of the gas can occur. The vibrational energy is out of equilibrium with translation in much of the external fluid region and in engine inlets and nozzles. This thermal nonequilibrium can affect both the radiative and convective heat transfer to hypersonic vehicles.

The Landau–Teller relaxation equation is widely used to describe vibrational energy transfer in high-temperature molecular gases. The Landau–Teller model[1] is given by

$$\frac{\mathrm{D}(e_{\text{vib}})_m}{\mathrm{D}t} = \sum_s \frac{(e_{\text{vib}_E})_m - (e_{\text{vib}})_m}{(\tau_{\text{LT}})_{m,s}} \tag{1}$$

where $(e_{\text{vib}})_m$ is the local value of energy in vibration for molecule m, and $(e_{\text{vib}_E})_m$ is the equilibrium value. $(\tau_{\text{LT}})_{m,s}$ is the vibrational relaxation time for a collision of molecule m with species s. In the present study the correlation by Millikan and White[2] is used to determine $(\tau_{\text{LT}})_{m,s}$. With vibrational relaxation times inferred from postshock flows, this equation has been shown to give good predictions for relaxation in vibrationally heating environments.

A number of experiments in nozzles have indicated that vibrational relaxation is faster in expanding flows than the Landau–Teller model predicts. The amount of acceleration observed in expanding flows is often described in terms of a $\bar{\phi}$, by which the Landau–Teller rate must be multiplied in order to agree with experimental data. A review of these experiments and a discussion of the experimental uncertainties is given by Ruffin.[3]

The vibrational master equations describe the details of the vibrational relaxation process. These rate equations are governed by the rates at which molecules transition from one quantum state to another during collisions. The two fundamental types of collisions that can occur are vibration-translation (V-T) and vibration-vibration (V-V) collisions. In a V-T collision one particle does not change its vibrational quantum state. In a V-V collision both colliding partners change

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their quantum states. The highest probability type of V-V collision is a V-V exchange collision in which one molecule increases its vibrational quantum state by one and the other decreases by one quantum state. In these collisions the net change in vibrational energy is transferred to the translational/rotational mode.

Theoretical models proposed by Bray,[4] Bray,[5] and Treanor et al.[6] indicate that anharmonic collisional effects can accelerate vibrational relaxation in three ways:

1) Anharmonic V-T rates are faster than those assumed by the Landau–Teller model and will tend to accelerate relaxation when there is a large degree of vibrational excitation.

2) Rapid V-V exchange rates cause mid and upper quantum levels to be overpopulated, thus weighting the faster anharmonic V-T rates.

3) V-V exchange collisions transfer small amounts of energy to translation directly due to anharmonicity. The Bray model, which was based on transition rates by Schwartz, Slawsky, and Herzfeld[7] (SSH), has been shown to give qualitative, but not quantitative, agreement with an experiment performed by Blom et al.[8] Studies by Center and Caledonia[9] indicate that anharmonicity can cause mild relaxation accelerations for some cases in which experimental data has been taken. Center and Caledonia[9] have introduced an analytical expression for the ground state vibrational temperature, assuming that there is no acceleration in the vibrational energy transfer rate. It is unclear, however, whether or not there are conditions for which significant acceleration in the vibrational energy transfer rate can occur.

Calculation of the multidimensional flowfield around hypersonic vehicles of interest requires theoretical models that are both accurate and efficient. Because solution of the vibrational master equations is so computationally intensive a more efficient model is desired for use in conventional real-gas codes. In this study a simplified relaxation model is developed that allows both non-Boltzmann population distributions and includes anharmonic transition rates and energy transfer. The temperatures and pressures considered are such that the rotational mode is fully excited and in the present analysis detailed vibrational-rotational coupling is neglected for simplicity. The model is designed to be much more computationally efficient than a detailed master equation solver while maintaining reasonable accuracy over a wide range of conditions.

Anharmonic Model Overview

Extensive master equation calculations[3] demonstrate that in flows in which the vibrational temperature is greater than the translational temperature (i.e., $T_{\mathrm{vib}}/T > 1$), vibrational energy transfer occurs more rapidly than the Landau–Teller equation predicts. T_{vib} is the vibrational temperature based on energy in vibration and is defined as

$$T_{\mathrm{vib}} \equiv \frac{\theta_v}{\ln[(\hat{R}/\hat{M})(\theta_v/e_{\mathrm{vib}}) + 1]} \tag{2}$$

where $\hat{R}$ is the universal gas constant, and $\hat{M}$ is the molecular weight of the molecule. The observation of faster relaxation when $T_{\mathrm{vib}}/T > 1$ supports the mechanisms proposed in Refs. 4–6. In order to accurately predict vibrational relaxation for these conditions, two basic factors, which are not considered by the Landau–Teller model, must be addressed.

First, the mid- and upper-level anharmonic V-T transition rates can be much faster than those assumed by the Landau–Teller model. In the model developed in this section the deviation of the anharmonic rates from the harmonic oscillator approximation is considered. An adiabaticity function is developed that is a measure of the deviation of the realistic rates from the harmonic oscillator rates. Also in this section an energy transfer rate equation is derived that is quite general and matches the results of the master equation solutions.

The second major consideration that must be addressed is the fact that population distributions are not always the Boltzmann distributions implied by the Landau–Teller model. In expanding flows the mid and upper levels are often overpopulated relative to a Boltzmann distribution. This tends to weight the fast upper-level V-T rates and further accelerate relaxation. In this section, a very general population distribution function is developed. This distribution function is general in that it can describe typical distributions in both heating and cooling relaxations.

Population Distribution Model

The vibrational relaxation equation derived in the next subsection relies on the use of a realistic population distribution function. The Boltzmann distribution implied by the Landau–Teller model is inappropriate for cooling relaxations sufficiently far from thermal equilibrium. We begin by studying two types of typical population distribution found in expansions. A general model is then introduced that approximates the most important observed features.

A typical population distribution for a diatomic species undergoing vibrational cooling is shown in Fig. 1. This type of distribution is typical at temperatures for which the V-V exchange rates in the lowest levels are much greater than the V-T rates in the lowest levels. The corresponding equilibrium vibrational transition rates at the same translational temperature are shown in Fig. 2. As described by Caledonia and Center[10] and by Bender,[11] the distribution consists of the three regions illustrated in Figs. 1 and 2. These regions are described in the following paragraphs.

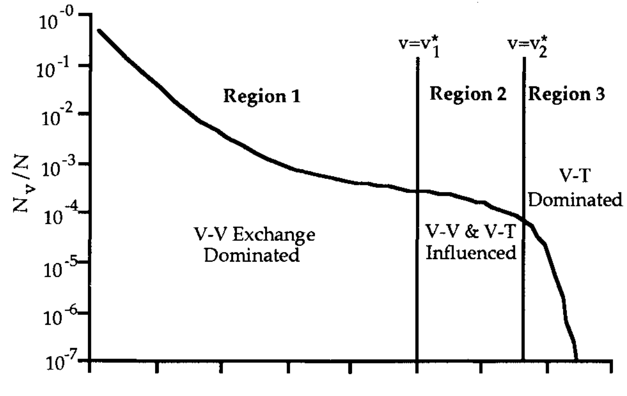

Fig. 1 Typical population distribution for vibrational cooling of a molecule dominated by V-V exchange rates in the lower quantum levels.

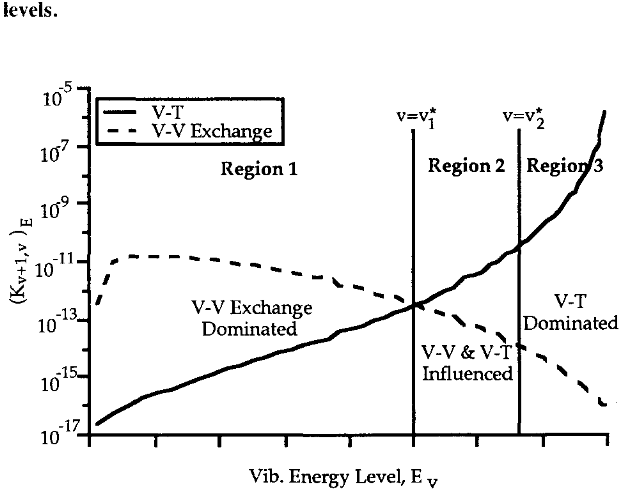

Fig. 2 Typical equilibrium transition rates for a molecule dominated by V-V exchange rates in the lower quantum levels.

Region 1 corresponds to the low vibrational levels in which the V-V exchange rates are much greater than the V-T rates. For the example given, the equilibrium V-V exchange rates are up to four orders of magnitude greater than the V-T rates (the y axis is on a log scale). After a very short time period, the V-V exchange quasiequilibrium described by Treanor et al.[6] is established. The near resonant V-V exchanges pump vibrational quanta upward toward regions 2 and 3. The distribution in region 1 is described quite well by a Treanor distribution[6] given by

$$(N_v)_m = \frac{(N)_m}{Q_{\text{vib}}} \exp\left[-v\left(\frac{\theta_v}{T_{\text{vib}_0}} - \frac{\theta_v}{T}\right) - \frac{E_v}{kT} \right] \tag{3}$$

T_{vib_0} is the ground state vibrational temperature and is related to the slope of the population distribution at the lowest level. Q_{vib} is the vibrational partition function and is the summation of the exponential term in Eq. (3). It should be pointed out that the Treanor distribution is equally applicable in both vibrational heating as well as cooling relaxations as long as the V-V exchanges are larger than the V-T rates in the lower levels. In the present simplified model we will approximate the vibrational energy level values by the first two terms of the Dunham expression. The energy relative to the ground state is

$$E_v \approx vk\theta_v[1 - x_e(v + 1)] \tag{4}$$

The anharmonicity factor x_e is a measure of the departure from a harmonic oscillator and the values used in the present study are given by Chase et al.[12] Beyond a certain quantum level this two-term approximation results in values of E_v, which decrease with increasing quantum number. The approximation is nonphysical beyond this level so that the maximum quantum number that can be considered with a two-term Dunham expression is

$$vmax' = \min\{vmax, [(1 - x_e)/2x_e]\} \tag{5}$$

where $vmax$ is the actual maximum bound vibrational quantum level.

In region 2 the V-T transition rates also become important because the equilibrium rates are of the same magnitude or greater than the V-V exchange rates. In this region the V-V exchange rates still influence the distribution by tending to pump vibrational quanta upward, however, the V-T rates then act to transfer energy to translation. The V-T rates, which increase with quantum number, limit the overpopulation caused by the V-V exchange rates. This region is characterized by a nearly constant slope of the number densities. Region 2 is often responsible for much of the acceleration in relaxation rates in expansions because the anharmonic V-T rates can be much greater than those assumed by Landau–Teller.

As vibrational quantum number increases further, the V-V exchange rates decrease and the V-T rates increase. In region 3, which corresponds to the uppermost levels, the V-T rates are much greater than the V-V exchange rates and are also much greater than the V-T rates in the lower levels. The V-V exchange rates are no longer effective in significantly pumping quanta upward, and region 3 reaches equilibrium with translation much faster than the remainder of the vibrational levels. The distribution is Boltzmann at the local translational temperature, i.e.,

$$(N_v)_m = [(N)_m/Q_{\text{vib}}]\exp[-(E_v/kT)] \tag{6}$$

The second type of case considered is for a relaxation in which the V-V exchange rates are smaller than the V-T rates for all levels. This type of situation exists at sufficiently high translational temperatures because V-T rates increase more rapidly with temperature than V-V exchange rates. The entire distribution is governed by the effects of V-T transition rates and the lower vibrational levels are essentially in nearly a Boltzmann distribution at some representative vibrational temperature. In the higher quantum levels the anharmonic V-T rates become increasingly greater than those assumed by Landau–Teller. Because the rates in the upper levels are so rapid, these levels relax more quickly and achieve equilibrium before the lower levels. The upper region behavior for this V-T dominated case is similar to that in region 3 of the V-V exchange dominated case.

We now develop a population distribution model that captures the dominant features in a wide variety of flows. The assumed distribution consists of up to three regions and the regions correspond to the three regions identified in Figs. 1 and 2. The quantum number that is the boundary between regions 1 and 2 is taken to be v_1^*, and the boundary between regions 2 and 3 is v_2^*. These parameters are obtained from the equilibrium transition rates and are thus only functions of translational temperature.

For $v \leq v_1^*$, the V-V exchange rates dominate. v_1^* is defined as the quantum number at which the equilibrium V-T rates become greater than the equilibrium V-V exchange rates, i.e.,

v_1^* = minimum v for which

$$(K^{\text{VT}}_{v+1,v})_{m,s_E} > (K^{\text{VV}}_{v+1,v})_{m,s_E} \tag{7}$$

Note that if the V-T rates are greater than the V-V exchange rates for all quantum levels, as is typical at sufficiently high temperatures, then $v_1^* = 0$.

For $v > v_2^*$, the most rapid anharmonic V-T rates dominate as in region 3 of Fig. 1. v_2^* is thus defined as the quantum number at which the equilibrium V-T rates are much greater than the equilibrium V-V exchange rates, and the equilibrium V-T rates are much greater than those assumed by the Landau–Teller model. Both of these criteria must be satisfied for the onset of region 3. In the present solver the following criteria are used to define v_2^*:

v_2^* = minimum v for which both

$$\begin{aligned} (K^{\text{VT}}_{v+1,v})_{m,s_E} &> 1 \times 10^3 (K^{\text{VV}}_{v+1,v})_{m,s_E} \leftarrow \text{criterion 1} \\ (K^{\text{VT}}_{v+1,v})_{m,s_E} &> 10(v + 1)(K^{\text{VT}}_{1,0})_{m,s_E} \leftarrow \text{criterion 2} \end{aligned} \tag{8}$$

The assumed population distribution for the present model is shown in Fig. 3 for a V-V exchange dominated flow. The true distribution is found from a solution of the master equa-

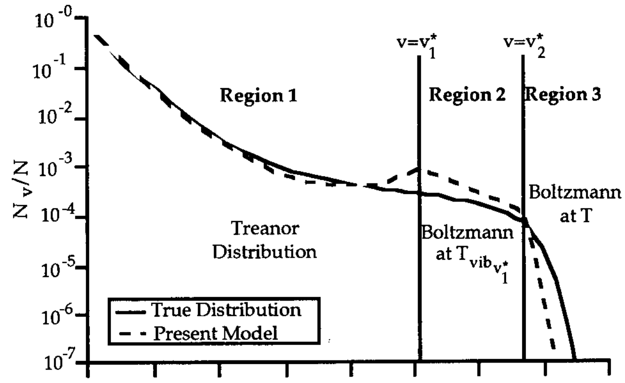

Fig. 3 Comparison of the present population distribution model to a typical distribution in vibrational cooling of a molecule dominated by V-V exchange rates in the lower quantum levels.

tions. The population distribution for the present simplified model can be expressed by

$$(N_v)_m = [(N)_m/Q_{\mathrm{vib}}]\exp\left[-v\left(\frac{\theta_v}{T'_{\mathrm{vib}_v}}\right)\right] \tag{9a}$$

where

$$Q_{\mathrm{vib}} = \sum_{v=0}^{v\max'} \exp\left(-v\frac{\theta_v}{T'_{\mathrm{vib}_v}}\right) \tag{9b}$$

and T'_{vib_v} is a type of vibrational temperature at level v. The population distribution for the present anharmonic model uses the following expressions for T'_{vib_v}:

$$T'_{\mathrm{vib}_v} \equiv \begin{cases} \dfrac{T_{\mathrm{vib}_0}}{1 - x_e \dfrac{T_{\mathrm{vib}_0}}{T}(v + 1)} & \text{for } v \leq v_1^* \\[2ex] \dfrac{T_{\mathrm{vib}_0}}{1 - x_e \dfrac{T_{\mathrm{vib}_0}}{T}(v_1^* + 1)}\left[\dfrac{1 - x_e(v_1^* + 1)}{1 - x_e(v + 1)}\right] & \text{for } v_1^* < v \leq v_2^* \\[2ex] T'_{\mathrm{vib}_{v-1}}\left[\dfrac{v}{(v - 1) + \dfrac{T'_{\mathrm{vib}_{v-1}}}{T}(1 - 2x_e v)}\right] & \text{for } v > v_2^* \end{cases} \tag{10}$$

For $v \leq v_1^*$, the V-V exchange rates dominate and the distribution is approximated by the Treanor distribution given in Eq. (3). For $v_1^* < v \leq v_2^*$, the V-T rates are significant and the distribution is approximated by a Boltzmann distribution at $T'_{\mathrm{vib}_{v_1^*}}$. For flows in which the V-V exchanges dominate in the lowest levels we saw that the slope of the distribution varies quite slowly in region 2. For flows in which the V-T rates dominate at all levels the slope in this region is also nearly constant. The present model uses a constant slope in the population distribution for $v_1^* < v \leq v_2^*$, and is thus an appropriate approximation for both types of flows. For $v > v_2^*$, the distribution is in thermal equilibrium due to very rapid anharmonic V-T rates. The slope of the distribution is constant in this region and that portion of the distribution is in equilibrium with translation.

The advantages of the population distribution model given in Eqs. (9) and (10) are its generality and accuracy. It is equally applicable to both heating and cooling flows over a very wide temperature range, and to both V-V exchange and V-T dominated gases through specification of v_1^* and v_2^*. These parameters are only functions of translational temperature and require knowledge of V-T and V-V exchange transition rates for the molecule under study. The transition rates computed in Ref. 3 are used to determine v_1^* and v_2^* for collisions involving N_2 and CO. These parameters are plotted in Figs. 4 and 5 for $N_2 - N_2$ collisions. The results of the transition rate calculations are well-correlated by the following curve-fitted expressions:

$$N_2 - N_2\text{:}\ \begin{cases} v_1^* = 24.62 + 6.424 \times 10^{-2}\exp(8.648 \times 10^{-4}T) \\ v_2^* = 30.11 + 5.294 \times 10^{-3}T \end{cases} \tag{11a}$$

$$N_2 - N\text{:}\ \begin{cases} v_1^* = 0 \\ v_2^* = 2.242 + 6.285\exp(3.893 \times 10^{-4}T) \end{cases} \tag{11b}$$

$$\mathrm{CO} - \mathrm{CO}\text{:}\ \begin{cases} v_1^* = 15.29 + 4.765\exp[-2.680 \\ \qquad \times 10^{-4}(T - 3000)] + 1.331\exp[1.045 \\ \qquad \times 10^{-3}(T - 3000)] \\ v_2^* = 32.82 + 9.796 \times 10^{-3}T \end{cases} \tag{11c}$$

$$\mathrm{CO} - \mathrm{Ar}\text{:}\ \begin{cases} v_1^* = 0 \\ v_2^* = 4.404 + 4.444\exp(4.654 \times 10^{-4}T) \end{cases} \tag{11d}$$

For Eq. (11) T is measured in Kelvin. Also, because v_1^* and v_2^* represent quantum numbers, the values obtained from Eq. (11) should be rounded to the nearest integer values.

It should be noted that v_1^* and v_2^* are functions of the specific collision pair (m and s) being considered. However, the population model given in Eqs. (9) and (10) represents the resulting distribution of molecule m in a gas through collisions with all possible collision partners. Thus, some aggregate values of v_1^* and v_2^* must be determined for use in Eq. (10) when a mixture of various species is being considered. We can introduce mixture components of these parameters and designate them by $\bar{v}_1^*$ and $\bar{v}_2^*$. The most accurate method of determining $\bar{v}_1^*$ and $\bar{v}_2^*$ is quite involved and requires additional comparisons of upper level V-V exchange and V-T transition rates for all collision pairs and with variable species concentrations. The complexity of the present model would increase significantly if we included all the details of these upper level transition probabilities. Instead, we seek a simple, but general approximation for $\bar{v}_1^*$ and $\bar{v}_2^*$. In the present study the mixture components are taken to be weighted averages of the collision-specific values defined in Eqs. (7) and (8). Consider the collision of the diatomic molecule m with species s. The influence of species s on the vibrational distribution of m is proportional to the amount of species s present, i.e., η_s, and the vibrational transition rates for the collision pair $m - s$, i.e., $(K_{v,v'})_{m,s}$. In this study the parameters v_1^* and v_2^* for collision $m - s$ are weighted by the mole fraction of species s and the ground state V-T transition rate $(K_{1,0})_{m,s}^{\mathrm{VT}}$. The ground state V-T transition rate is related to the Landau–Teller relaxation time by

$$(K_{1,0})_{m,s}^{\mathrm{VT}} \propto [1/(\tau_{\mathrm{LT}})_{m,s}]$$

and so, the weighting factor used for collision $m - s$ is

$$W_{m,s} = \eta_s/(\tau_{\mathrm{LT}})_{m,s}$$

Thus, the approximations used for the mixture components are given by

$$(\bar{v}_1^*)_m = \sum_s (v_1^*)_{m,s}W_{m,s} \bigg/ \sum_s W_{m,s} \tag{12a}$$

$$(\bar{v}_2^*)_m = \sum_s (v_2^*)_{m,s}W_{m,s} \bigg/ \sum_s W_{m,s} \tag{12b}$$

For gas mixtures these expressions are used in Eq. (10) instead of the collision pair-specific values of v_1^* and v_2^*.

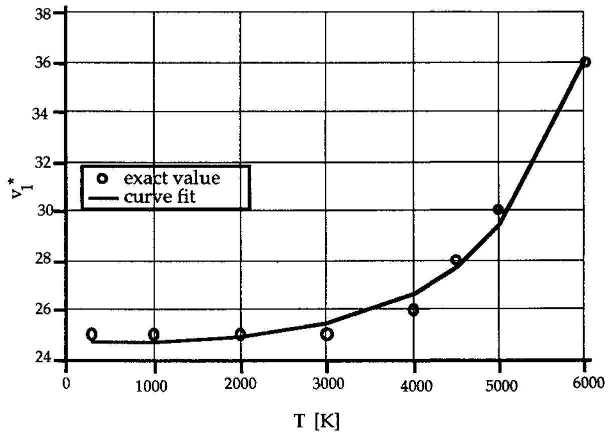

Fig. 4 v_1^* **vs translational temperature for** $N_2 - N_2$ **collisions.**

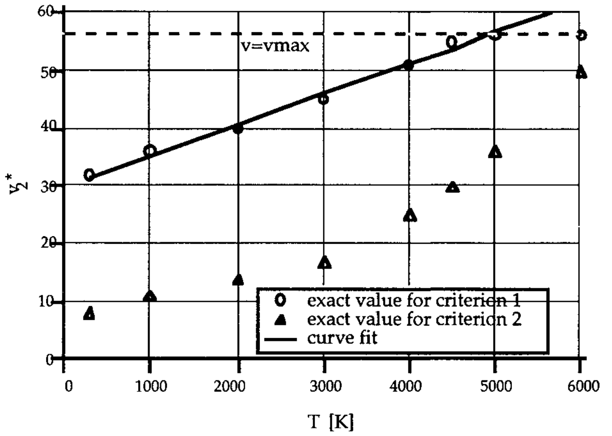

Fig. 5 v_2^* **vs translational temperature for** $N_2 - N_2$ **collisions. See Eq. (8) for definitions of criterion 1 and criterion 2.**

Vibrational Energy Transfer Rate

In this section we derive an equation that predicts the vibrational energy transfer rate of an anharmonic oscillator undergoing either vibrational heating or cooling. In Ref. 3 it is shown that vibrational energy transfer is accomplished almost exclusively through V-T transitions for a very wide range of conditions. The efficiency of these transitions is affected by the overpopulated distributions caused by V-V exchange collisions. However, the energy transfer caused directly by V-V exchange collisions is only found to be significant for extreme conditions of thermal nonequilibrium (e.g., $T_{\mathrm{vib}}/T > 4.5$ for N_2 with $T = 5000$ K). If we refer to the three causes of vibrational acceleration discussed in the Introduction, it is reasons 1 and 2 that by far have the most dominant effect. Accordingly, the simplified relaxation model presented in this section neglects energy transfer accomplished directly through V-V exchange collisions. Neglecting V-V exchange energy transfer greatly simplifies the resulting relaxation equation without introducing significant error for a very wide variety of cases.

The Landau–Teller model approximates the molecules as harmonic oscillators and implicitly assumes that the population distribution is Boltzmann. Because the Landau–Teller relaxation equation considers only harmonic oscillators, the assumed V-T probabilities for that model are of the form

$$P^{v_2,v_2}_{v+1,v} = (v + 1)P^{0,0}_{1,0} \tag{13}$$

However, the anharmonic V-T rates increase more rapidly with quantum number than this expression indicates. As the quantum number increases the spacing between the energy levels, i.e.,

$$\Delta E_v \equiv E_{v+1} - E_v \approx k\theta_v[1 - 2x_e(v + 1)] \tag{14}$$

decreases. The transition matrix elements and other terms in the probability are functions of ΔE_v and can cause the anharmonic probability to be significantly different from the Landau–Teller, harmonic oscillator, value given in Eq. (13). We can write the anharmonic V-T transition rate for collision of species s with molecule m as

$$P^{v_2,v_2}_{v+1,v} = (v + 1)\underbrace{(f'_v/f'_0)_{m,s}}_{\equiv(F_v)_{m,s}}P^{0,0}_{1,0} \tag{15}$$

where $(f'_v)_{m,s}$ is an adiabaticity factor that is a function of v (and ΔE_v), and describes the departure of the most accurate transition rate values from those assumed by Landau–Teller. The adiabaticity factor is normalized so that $(F_{v=0})_{m,s} = 1$ and the ground state value of the probability matches the Landau–Teller rate.

Computing the most accurate vibrational transition rates can be a very computationally intensive process. For the present simplified model we seek an accurate but relatively simple expression for the adiabaticity. An accurate expression for the V-T probabilities is given and validated in Ref. 3. By studying the order of magnitude of each of the terms it can be shown that the variation in the probability can be approximated quite well if the following adiabaticity factor used for collision pair $m - s$:

$$(F_v)_{m,s} = \max\left[\left(\frac{f'_v}{f'_0}\right)_{m,s}, 1\right] \tag{16a}$$

where

$$(f'_v)_{m,s} = \frac{1}{\Delta E_v}\exp\left[C_f(\Delta E_v)^{2/3} + \frac{C_2^{\mathrm{VT}}}{k}\left(\frac{T}{\theta_v}\right)(\Delta E_v)\right] \tag{16b}$$

$$C_f \equiv -3\left[\frac{2\pi^4 m_{m,s}}{(\alpha h)^2 kT}\right]^{1/3} \tag{16c}$$

ΔE_v and the first term in the exponential are based solely on known molecular parameters and are easily computed for various diatomic species. The second term in the exponential is a correction factor to the SSH rates that improves the accuracy of the transition rates at high temperatures. The constant C_2^{VT} is a function of the collision pair considered, and $C_2^{\mathrm{VT}} = 1.72 \times 10^{-3}$ is used for $N_2 - N_2$ collisions, whereas $C_2^{\mathrm{VT}} = 1.92 \times 10^{-3}$ is used for CO – CO collisions. These values are obtained by correcting the SSH rates so that they agree closely with the more realistic Billing semiclassical model.[13] The values given result in realistic rates for $N_2 - N_2$ up to at least 6000 K, and for CO – CO up to approximately 3000 K. Using $C_2^{\mathrm{VT}} = 0$ results in rates that agree well with the original SSH[7] and the Keck and Carrier[14] formulations.

Now that we have an expression for the anharmonic V-T transition rates we can develop the energy relaxation equation. We begin with the vibrational master equation. If we consider only nearest neighbor transitions and use probabilities in the form given by Eq. (15), then we can show that the anharmonic vibrational energy transfer rate reduces to

$$\frac{\mathrm{D}(e_{\mathrm{vib}})_m}{\mathrm{D}t} = \sum_s \frac{(e_{\mathrm{vib}_E})_m - (e_{\mathrm{vib}})_m}{(\tau_{\mathrm{LT}})_{m,s}}\,\phi_{m,s} \tag{17a}$$

where

$$\phi_{m,s} = \frac{1}{\rho(e_{\mathrm{vib}})_m} \sum_{v=0}^{vmax'-1} (v + 1)\Delta E_v (F_v)_{m,s}(N_{v+1})_m \tag{17b}$$

This expression is quite general, and the local acceleration factor $\phi_{m,s}$ is the ratio of the anharmonic energy transfer rate to that predicted by the Landau–Teller model. Equation (17b) is evaluated for the present model by using the expressions for $vmax'$, ΔE_v, $(F_v)_{m,s}$, and $(N_v)_m$ given in Eqs. (5), (14), (16), and (9), respectively.

In order to compute the population distribution at a given location in the flowfield [i.e., $(N_v)_m$], we need to know the value of T_{vib_0} at that location. We need to be able to determine T_{vib_0} as a function of vibrational energy at that location. Unfortunately, for a realistic anharmonic population distribution there is no closed-form analytical expression for T_{vib_0} as a function of $(e_{\mathrm{vib}})_m$. However, we can determine T_{vib_0} for a given value of $(e_{\mathrm{vib}})_m$ by using an efficient Newton–Raphson iterative scheme. In a Newton–Raphson scheme we determine the value of T_{vib_0} for which the function $g(T_{\mathrm{vib}_0}) = 0$. We assume an initial value for T_{vib_0}, and the $(n + 1)$th approximation for T_{vib_0} is given by

$$T^{n+1}_{\mathrm{vib}_0} = T^{n}_{\mathrm{vib}_0} - \frac{g^n}{g'^n} \tag{18a}$$

where

$$g^n = \frac{(N)_m}{\rho}\left(\frac{G_2}{G_1}\right) - (e_{\mathrm{vib}})_m \tag{18b}$$

$$g'^n = \frac{(N)_m}{\rho}\frac{\theta_v}{(T^n_{\mathrm{vib}_0})^2}\left(\frac{G_1G_4 - G_2G_3}{G_1^2}\right) \tag{18c}$$

$$G_1 \equiv \sum_{v=0}^{vmax'} \exp\left(-v\frac{\theta_v}{T'^n_{\mathrm{vib}_v}}\right) \tag{19a}$$

$$G_2 \equiv \sum_{v=0}^{vmax'} E_v \exp\left(-v\frac{\theta_v}{T'^n_{\mathrm{vib}_v}}\right) \tag{19b}$$

$$G_3 \equiv \sum_{v=0}^{vmax'} v \exp\left(-v\frac{\theta_v}{T'^n_{\mathrm{vib}_v}}\right) \tag{19c}$$

$$G_4 \equiv \sum_{v=0}^{vmax'} vE_v \exp\left(-v\frac{\theta_v}{T'^n_{\mathrm{vib}_v}}\right) \tag{19d}$$

$T'^n_{\mathrm{vib}_v}$ is the value of T'_{vib_v} given in Eq. (10) based on $T^n_{\mathrm{vib}_0}$. The initial value of $T^n_{\mathrm{vib}_0}$used in the present study is

$$T^{n=0}_{\mathrm{vib}_0} = \frac{T_{\mathrm{vib}}}{1 + x_e[(T_{\mathrm{vib}}/T) - 1][(v_1^*/2) + 1]} \tag{20}$$

Using this initial value normally allows the following convergence criterion to be met in three iterations:

$$\mathrm{error}^n \equiv |g^n/(e_{\mathrm{vib}})_m| \leq 1.0 \times 10^{-3}$$

By using this procedure, we can determine T_{vib_0}, $(N_v)_m$, $\phi_{m,s}$, and the vibrational energy transfer rate for an anharmonic oscillator.

Conclusions

In this article an anharmonic relaxation model is developed that is much more realistic than the widely used Landau–Teller model and much less computationally demanding than a master equation calculation. The model is based on anharmonic transition probabilities and allows non-Boltzmann population distribution that may occur in expansions as well as compressions.

Having now presented the anharmonic vibrational relaxation model we must address three key questions:

1) How accurate is the model compared to master equation solutions and experimental data.

2) What is its range of applicability.

3) Is the computational requirement prohibitive for use in multidimensional flow codes. These issues are addressed in Part 2 of this study.[15] In that article, the performance of the simplified model is compared with experimental data, detailed master equation results, and with the Landau–Teller model.

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