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Abstract

The theoretical basis for the Landau-Teller equation commonly used to model rotational nonequilbrium is reviewed. Several assumptions underlying this model are indicated to be unrealistic for rarefied hypersonic flow. A new rotational nonequilibrium model based on recent measurements up to 2000K of quantum state transition rates is presented. The new model is applied to the continuum study of normal shock wave structure using both the Burnett equations and a simplified nonlinear constitutive relation. Comparisons are made between shock wave temperature profiles generated from the new model and those generated using the Landau-Teller model. Comparisons of shock reciprocal thicknesses between experimental data for nitrogen and continuum solutions using both rotational models are made. The new rotational model agrees well with experiment up to Mach 6, and under predicts shock thickness at higher Mach numbers. The Landau-Teller model agrees well with experimental shock thickness up to Mach 3, and over predicts the thickness at higher Mach numbers. A modification to the rotational collision number in the Landau-Teller model is found to give results which agree with experimental shock thicknesses at all Mach numbers up to 11.

Nomenclature

A_i, B_i, C_i	=curve fit constants
AOTV	= Aero-assisted Orbital Transfer Vehicle
c_{vr}	= rotational specific heat
c_{vt}	= translational specific heat
$\frac{D}{Dt}$	= one-dimensional substantial derivative
e_r	= rotational energy per unit mass
$e_r^{eq}(T_t)$	= effective rotational energy of translation
e_r^*	= reference rotational energy
e_t	= translational energy per unit mass
E	= $\rho c_{vt} T_t + E_r + 1/2\,\rho u^2$, total fluid energy per unit volume
E_r	= ρe_r, rotational energy per unit volume
Δe_r	= an energy difference per unit mass
E_i	= energy of i^{th} quantum state
$\widetilde{E_i}$	= non-dimensional energy of i^{th} state
$F(T_t)$	= non-dimensional function
$\hat{F}$	= flux vector
$G(\bar{T})$	= non-dimensional function
$H(\bar{T}, T_t)$	= non-dimensional function
I_{max}	= maximum allowable quantum number
k	= Boltzmann's constant
$K_{i\Rightarrow j}$	= transition rate from state i to j
l	= temporal index
n	= an exponent for the new rotational model
NASP	= National Aerospace Plane
N_i	= number density of i^{th} quantum state
p	= $\rho R T_t$, thermodynamic pressure
q	= one dimensional monatomic heat flux vector
q_d	= addition to heat flux for diatomic gas
R	= gas constant
t_ρ	= shock reciprocal thickness
T_n	= normalized temperature
T_r	= rotational temperature
T_{ref}	= viscosity reference temperature
T_t	= translational temperature
T_o	= reference temperature used for $K_{i\Rightarrow j}$
T^*	= reference temperature used for Z_R
$\bar{T}$	= temperature ratio
$\hat{T}$	= function of $\bar{T}$
u	= fluid velocity

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$\hat{U}$ = conservation vector
$\hat{W}$ = source term vector
w_r = rotational energy source term
Z_R = rotational collision number for Landau-Teller model
Z_R^∞ = infinite temperature collision number
$\widetilde{Z}_R$ = rotational collision number for new rotational model
α, β, δ, m = parameters for $K_{i \Rightarrow j}$
$\Delta_{\rho T}$ = Shock density temperature separation
κ_r = μc_{vr}, rotational thermal conductivity
κ_t = $\frac{5}{2}\mu c_{vt}$, translational thermal conductivity
μ = viscosity
μ_{ref} = viscosity at T_{ref}
ω = viscosity-temperature exponent
σ = one dimensional stress tensor
ρ = density
ρ_n = normalized density
θ_r = characteristic rotational temperature
τ_c = $\pi\mu/4p$, mean collision time

Introduction

Simulating the flow about planned transatmospheric vehicles, such as AOTV and NASP, and about hypersonic missles, requires the inclusion of rotational thermal nonequilibrium in rarefied flow codes. This is due to the shock wave thickness becoming a sizable portion of the flowfield at sufficiently high altitudes. Chapman, *et al*.,[1] have shown that the Navier-Stokes equations require the inclusion of rotational thermal nonequilibrium as well as modified constitutive relations to achieve experimentally measured shock thicknesses in diatomic gases such as N_2. Furthermore, they show that the inclusion of rotational thermal nonequilibrium is equally as important as the modifing the constitutive relations; whereas, Fiscko and Chapman[2] have shown that modifying the constitutive relations alone is sufficient to obtain good agreement with measured shock thicknesses in monatomic gases.

Computational models for internal energy relaxation are usually based on the the well-known Landau-Teller equation. The model has been widely applied to both vibrational and rotational nonequilibrium. The Landau-Teller formulation in terms of rotational relaxation is

$$\frac{de_r}{dt} = \frac{e_r^{eq}(T_t) - e_r}{Z_R \tau_c} \qquad (1)$$

In continuum hypersonic CFD this equation is generally used directly as the computational algorithm. In particulate CFD (e.g., the Direct Simulation Monte Carlo (DSMC) technique), it is used indirectly by handling the transfer of internal and translational energy during a molecular collision with the technique outlined by Larsen and Borgnakke.[3] This treatment of internal energy relaxation is constucted to give results which conform closely to the Landau-Teller model. Unfortunately, as discussed below, the Landau-Teller equation is derived under relatively restrictive assumptions which are not fully realistic for hypersonic flow conditions. This is the case for both vibrational and rotational energy relaxation.

The principal shortcomings of the Landau-Teller model when applied to *vibrational* relaxation are embodied in the underlying assumptions (1) that a vibrating diatom can be modeled as a harmonic oscillator hence allowing quantum jumps of only one state in a collision, and (2) that dissociation does not affect vibrational relaxation. These assumptions are overly restrictive when considering the high temperature conditions in hypersonic flows. In attempts to overcome these shortcomings, models have been developed which account for more "diffusion-like" (i.e., allowing for quantum jumps greater than one) relaxation (e.g., Keck[4]) and for removal of highly excited vibrational states through dissociation of the diatomic molecules (e.g., Marrone and Treanor[5]). For vibrational relaxation, therefore, departures from Landau-Teller relaxation have long been recognized, and alternative models have been used in some recent hypersonic flow computations (e.g., Candler and MacCormack[6]).

However, for the case of *rotational* thermal nonequilibrium, we are not aware of any computational algorithm being used in continuum CFD other than Landau-Teller. Wang Chang and Uhlenbeck[7] have shown that the Landau-Teller equation can be derived for an internal energy mode out of equilibrium with translational energy if the following conditions apply:

(1) Internal and translational temperatures are nearly equal.
(2) Internal to translational energy exchange is very slow.
(3) Internal energy is in a Boltzmann distribution.

For rotational energy, assumption (1) is unrealistic for rarefied hypersonic flow, and assumption (2) is unrealistic for diatomic gases such as N_2, O_2, and NO, for which rotational/translational energy exchange is not exceedingly slow. Thus, while assumptions underlying the derivation of the Landau-Teller model for rotational nonequilibrium are of questionable accuracy for rarefied hypersonic flow in diatomic molecules, a validation of the Landau-Teller model for such conditions has not been presented, nor has a more realistic alternative been advanced for use in hypersonic CFD.

It should be noted that existing determinations of Z_R, the number of collisions for rotational relaxation, generally *assume* the Landau-Teller equation to apply. Such is the case for the theoretical determination of Z_R by Parker[9] (Eq. (2)).

$$Z_R = \frac{Z_R^{\infty}}{1 + \frac{\pi^{3/2}}{2}\left(T^*/T_t\right)^{1/2} + \left(\frac{\pi^2}{4} + \pi\right)\left(T^*/T_t\right)} \qquad (2)$$

Lordi and Mates[9] also make the same assumption in their computation of Z_R. Table 1 summarizes the parameters supplied for Eq. 2 by Parker and the values required to fit the Parker model to the Lordi and Mates computations. In the case of experimental determinations, some fluid dynamic measurement such as sound absorption/dispersion, shock-wave profiles, or free-jet expansion profiles are used to deduce Z_R from the Landau-Teller equation. Furthermore, most of the experimental data are limited to relatively low temperatures compared to those encountered in hypersonic flight. Fig. 1 summarizes the analytic, computational, and experimental values for Z_R. The data are widely scattered at room tempertature and do not extend beyond about 1200 Kelvin.

In view of the questionable theoretical basis of the Landau-Teller model and the relative uncertainty of Z_R at even low temeratures, it appears that the appropriate macroscopic model for treating rotational thermal nonequilibrium in high temperature rarefied flows is uncertain. Therefore, this paper proposes a new approach for the computation of rotational energy relaxation. It is founded on some relatively recent measurements by the inverse Raman spectroscopy method of rotational quantum state transition probabilities for nitrogen. Objectives of the present research are:

(1) To develop from the spectroscopic data a new macroscopic model for rotational relaxation.

(2) To employ the new model and the Landau-Teller model in a continuum simulation of shock wave structure in nitrogen, a flow with a large amount of rotational nonequilibrium. Two different constitutive relations will be used: (1) the Burnett equations shown by Fiscko and Chapman[10] to yield accurate shock profiles for monatomic gases, and (2) a simplified nonlinear constitutive relation based on earlier work of Chapman, *et al*.,[1]

(3) To evaluate the accuracy of the both rotational models by comparing computed shock reciprocal thicknesses with experimentally measured reciprocal thicknesses for nitrogen.

Development of New Rotational Relaxation Model

The method used to develop the new algorithm involves solving the master equation for stationary adiabatic rotational relaxation. The master equation (Eq. (3)) is a set of rate equations which describe the evolution of rotational quantum state populations.

$$\frac{dN_i}{dt} = \sum_{j=0}^{I_{max}} K_{j\Rightarrow i} N_j - \sum_{j=0}^{I_{max}} K_{i\Rightarrow j} N_i \quad ; i = 1, \ldots, I_{max} \qquad (3)$$

Eq. (4) represents an empirically fit relation presented by Rahn, *et al*.,[11,12,13] for the upward ($i < j$) transition rates.

$$K_{i\Rightarrow j} = \alpha p F(T_t) \left(\frac{1 + \widetilde{E_i}/\delta}{1 + \widetilde{E_i}}\right)^2 \exp\left(\frac{-\beta \Delta E_{ij}}{kT_t}\right) \qquad (4a)$$

where:

$$\widetilde{E_i} \equiv \frac{1.5 E_i}{kT_t} = \frac{1.5\theta_r i(i+1)}{T_t}$$
$$\Delta E_{ij} \equiv E_i - E_j \qquad (4b)$$
$$F(T_t) \equiv \left(\frac{1 - \exp(-m)}{1 - \exp\left(-mT_t/T_o\right)}\right)\sqrt{\frac{T_o}{T_t}}$$

The downward transition rates ($i > j$) are obtained from the upward rates by microscopic reversibility (Eq. (5)).

$$K_{j\Rightarrow i} = K_{i\Rightarrow j} \frac{2j+1}{2i+1} exp\left(\frac{\Delta E_{ij}}{kT_t}\right) \qquad (5)$$

Table 2 gives the values suggested by Rahn, *et al*.,[11,12,13] for use with N_2 in Eq. (4). Solution of the master equation yields the population densities as a function of time, and by summing over quantum states, as shown in Eq. (6), rotational energy as a function of time for the adiabatic relaxation process is achieved.

$$e_r = \sum_{i=0}^{I_{max}} i(i+1)k\theta_r N_i \qquad (6)$$

Since the process is adiabatic, total energy is constant, and translational energy is easily obtained by subtracting rotational energy from the prescribed total energy. Temperatures are defined in terms of energies as shown by Eq. (7).

$$T_t \equiv \frac{e_t}{c_{vt}} = \frac{e_t}{3/2\ R}$$
$$T_r \equiv \frac{e_r}{c_{vr}} \qquad (7)$$

Fig. 2 compares temperature-time relaxation from master equation and solution from the Landau-Teller equation using Parker's model for Z_R. Here the parameters in Parker's model are adjusted to fit the Lordi and Mates computations (see Table 1).

It is from these adiabatic relaxation simulations that a new *single rate equation* model for rotational relaxation can be inferred. A new macroscopic model for rotational thermal nonequilibrium is proposed having the following form:

$$\frac{de_r}{dt} = \frac{\Delta e_r}{\widetilde{Z}_R\ \tau_c}\ \frac{e_r^*}{|\Delta e_r|}\left(\frac{|\Delta e_r|}{e_r^*}\right)^n \qquad (8a)$$

where:

$$e_r^* \equiv \frac{2}{5}(e_t + e_r)$$
$$\Delta e_r \equiv e_r^{eq}(T_t) - e_r \qquad (8b)$$

Note that the reference energy, e_r^*, represents the value of rotational energy that would be present if the total thermal energy present were equipartitioned. This choice makes the reference energy constant for the adiabatic relaxation process, but it will not be constant in an actual application such as the shock wave problem. The form of Eq. (8) is such that it is applicable to both situations when T_r is less than T_t and when T_r is greater than T_t. This corresponds to both compressing and expanding flows. It is assumed *a priori* that $\widetilde{Z}_R$ and n will not be constant but in general functions of both the T_t and T_r. The conventional Landau-Teller method is recovered if one chooses $n = 1$ and $\widetilde{Z}_R(T_t, T_r) = Z_R(T_t)$, a function of translational temperature only.

The parameters $\widetilde{Z}_R$ and n were determined as follows. As mentioned above, the master equation solution yields the time rate of change of rotational energy. Since the solution procedure used was a numerical technique for solving stiff systems of ordinary differential equations, one obtains the energies at a discrete number of points in time rather than continuously over time. The temporal derivative of the rotational energy was then obtained by summing the master equation (Eq. (3)) over quantum space at each discrete point, l, in time.

$$\frac{de_r}{dt}\Big|_l = \sum_{i=0}^{I_{max}} i(i+1)k\theta_r \frac{dN_i}{dt}$$
$$= \sum_{i=0}^{I_{max}} i(i+1)k\theta_r \left(\sum_{j=0}^{I_{max}} K_{j\Rightarrow i}N_j - \sum_{j=0}^{I_{max}} K_{i\Rightarrow j}N_i\right) \qquad (9)$$

In order to obtain the exponent in Eq. (8a) values of the energy derivative at both l and $l-1$ are used to eliminate $\widetilde{Z}_R$ by subtracting the common logarithms of Eq. (8a) evaluated at the above mentioned points. The resulting equation is then solved for n as shown by Eq. (10) for the case $\Delta e_r > 0$.

$$\log_{10}\left(\frac{de_r}{dt}\frac{\tau_c}{e_r^*}\right)_l = n\log_{10}\left(\frac{\Delta e_r}{e_r^*}\right)_l - \log_{10}\left(\widetilde{Z}_R\right) \qquad (10a)$$

$$n_l = \frac{\log_{10}\left(\frac{de_r}{dt}\frac{\tau_c}{e_r^*}\right)_l - \log_{10}\left(\frac{de_r}{dt}\frac{\tau_c}{e_r^*}\right)_{l-1}}{\log_{10}(\Delta e_r/e_r^*)_l - \log_{10}(\Delta e_r/e_r^*)_{l-1}} \qquad (10b)$$

This assumes that both n and $\widetilde{Z}_R$ are only weak functions of T_t and T_r. This assumption will be justified by the results. Now that n is known, $\widetilde{Z}_R$ is obtained by simple substitution into Eq (8a).

$\widetilde{Z}_R$ and n were calculated from numerous solutions of the master equation where two parameters, total energy and the ratio T_r/T_t, were varied. Initial rotational quantum state distributions were assumed to be Boltzmann at the temperature T_r. The values of $\widetilde{Z}_R$ and n were calculated only at points near the initial condition since it was found that as the rotational energy departed from Boltzmann distributions the values of $\widetilde{Z}_R$ and n were no longer properties of macroscopic quantities, but began to depend on the distribution itself. This assumption unfortunately limits the new model; however, as mentioned above, the derivation of Wang Chang and Uhlenbeck also makes this assumption. Furthermore, ultrasonic determinations of Z_R and the spectroscopic determinations of $K_{i\Rightarrow j}$ are made using data that is taken when a Boltzmann distribution over rotational states exists.

In order to apply the above results to hypersonic CFD, it is desirable to obtain suitable curve fits for n and $\widetilde{Z}_R$. The equations below present curve fits used in the shock simulations presented in this paper.

$$\widetilde{Z}_r = 1 + \frac{G(\tilde{T})}{H(\tilde{T}, T_t)}$$
$$n = C_1 + C_2 T_t^{(C_3\hat{T}+C_4)}\hat{T}\,|\hat{T}|^{C_5} \qquad (11a)$$

where:

$$\tilde{T} \equiv \frac{T_r}{T_t}$$

$$\hat{T} \equiv 1 - \tilde{T}$$

$$G(\tilde{T}) \equiv A_1 + A_2\left(\left|\tilde{T}\right|^{A_3} - 1\right) - A_4\left[\tilde{T}^{A_5} - 1\right]^2 + A_6\hat{T}$$

$$H(\tilde{T}, T_t) \equiv B_1\left\{\frac{B_2}{T_t}\left[B_3 + \frac{B_4}{\pi}\arctan\left(-\hat{T}\right)\right]^{B_2+1} + T_t^{B_2}\right\} + 1 \qquad (11b)$$

Table 3 summarizes the numerical values A_i, B_i, and C_i required to fit Eq. (11) to n and $\widetilde{Z_R}$. These curve fits were arrived at by simple trial and error and are probably more complicated than required, they however do accurately fit the calculated values for n and $\widetilde{Z_R}$ for temperatures below 5000 Kelvin and for a wide range of T_r/T_t, including both $T_r < T_t$ and $T_r > T_t$.

Figs. 3, 4, 5, and 6 show both calculated and curve fit values of n and $\widetilde{Z_R}$ as function of T_t for selected values of T_r/T_t. The exponent n departs from Landau-Teller value (n=1) for high temperatures and a high degree of thermal nonequilibrium (i.e., $|T_t - T_r|/T_t >> 1$). The exponent n also behaves in a fundamentally different manner for temperature ratios corresponding to expanding flows compared with temperature ratios corresponding to compressing flows. The exponent seems to asymptote to constant value (with respect to T_t) of 1.128 as the temperature ratio T_r/T_t approaches the limiting values of one from both compressing and expanding values. The fact that this value is only 13% different than the Landau-Teller value suggests that perhaps the Landau-Teller equation may be sufficient as a rough model for rotational nonequilibrium even though the theoretical basis of the model is questionable. Also note that n and $\widetilde{Z_R}$ are not strongly dependent on T_t and T_r justifying the assumption necessary to calculate n and $\widetilde{Z_R}$ above.

Constitutive Relations for Use in Shock Wave Structure

It has long been known that the Navier-Stokes equations are inaccurate for flows that contain strong departures from translational equilibrium. Such flows are characterized by large changes in flow quantities over the space of a few mean free paths. Normal shock structure, where flow quantities such as translational temperature can jump by as much as two orders of magnitude in the space of ten or so mean free paths, is one such flow where the Navier-Stokes equations yield erroneous results.

In the case of shock wave structure, the shortcomings of the Navier-Stokes equations are the constitutive relations, not the continuum description of the fluid. This has been shown by Fiscko and Chapman[10] for monatomic gases by utilizing the Burnett equations to solve for shock wave structure and comparing the results with shock structures from a non-continuum DSMC calculation. Fiscko and Chapman found that the Burnett equations yield significantly improved continuum solutions of shock structure over the Navier-Stokes equations.

The Burnett equations are derived by retaining second order terms in the Chapman-Enskog expansion of the Boltzmann equation. The Navier-Stokes equations can be derived in a similiar fashion by retaining only first order terms in the Chapman-Enskog expansion. The Burnett equations differ from the Navier-Stokes equations only in the expressions for the stress tensor and the heat flux vector. The Burnett stress tensor and heat flux vector are the Navier-Stokes stress tensor and heat flux vector plus several additional terms. The Burnett stress tensor and heat flux vector in one spatial dimension for a hard sphere gas are:

$$\sigma = -p + \frac{4}{3}\mu\frac{\partial u}{\partial x} - \frac{\mu^2}{p}\left[1.749\left(\frac{\partial u}{\partial x}\right)^2 - 1.352\frac{RT_t}{\rho}\frac{\partial^2\rho}{\partial x^2} + 1.352\frac{RT_t}{\rho^2}\left(\frac{\partial\rho}{\partial x}\right)^2 - .898\frac{R}{\rho}\frac{\partial\rho}{\partial x}\frac{\partial T_t}{\partial x} + 1.406\frac{R}{T_t}\left(\frac{\partial T_t}{\partial x}\right)^2 + .260\,R\frac{\partial^2 T_t}{\partial x^2}\right] \qquad (12a)$$

$$q = -\kappa_t\frac{dT_t}{dx} + \frac{\mu^2}{\rho}\left[\frac{10.831}{T_t}\frac{\partial u}{\partial x}\frac{\partial T_t}{\partial x} - 2.269\frac{\partial^2 u}{\partial x^2} - \frac{2.060}{\rho}\frac{\partial u}{\partial x}\frac{\partial\rho}{\partial x}\right]. \qquad (12b)$$

Due to the complexity of the Burnett equations a simplified constitutive model has been developed based on an earlier model developed by Chapman, *et al*.[1] This model, hereafter refered to as the nonlinear constitutive model, attempts to capture the significant features of the Burnett constitutive relations with only two additional terms to the Navier-Stokes constitutive relations as shown below.

$$\sigma = -p + \frac{4}{3}\mu\frac{\partial u}{\partial x} - 9.5\frac{\mu^2}{p}\left(\frac{\partial u}{\partial x}\right)^2 \qquad (13a)$$

$$q = -\kappa_t \frac{\partial T_t}{\partial x} + \frac{95}{8T_t}\frac{\mu^2}{\rho}\frac{\partial u}{\partial x}\frac{\partial T_t}{\partial x} \qquad (13b)$$

The additional terms in the stress and heat flux have been chosen such that the model, when applied to shock wave structure in argon, gives experimentally measured shock wave reciprocal thickness and approximately the same separation between the temperature and density profiles calculated by Fiscko and Chapman for argon using the DSMC technique. Fig. 7 shows the reciprocal thicknesses calculated using the nonlinear constitutive model and those experimentally measured by Alsmeyer[14].

The nonlinear constitutive model presented above differs from the the model presented by Chapman, *et al*.,[1] only in the coefficient of the velocity gradient squared term in the stress, which has been changed from 7 to 9.5. This change is because the earlier model was developed to give the correct shock thicknesses in nitrogen when using the Landau-Teller model and the Parker expression for Z_R adjusted to fit the Lordi-Mates computations. Since the purpose of this paper is to evaluate rotational models, it was necessary to develop constitutive relations that are not dependent on the rotational model employed. Thus, comparison to argon reciprocal thickness was chosen to *calibrate* the nonlinear constitutive model. It is then assumed that the nonlinear constitutive model will be as effective in modeling the true stress and heat flux in a diatomic gas as in a monatomic gas.

Application of Rotational Nonequilibrium to Shock Wave Structure

As mentioned above the study of shock wave structure in diatomic gases requires the inclusion of rotational thermal nonequilibrium. A method which "fully couples" these nonequilibrium effects into the equations describing the fluid mechanics was chosen in this study. This is done by including a rotational energy equation into the continuum equations of motion. In order to do this the relaxation model must be transformed from the stationary forms presented above into a form which accounts for bulk fluid motion. In addition conduction of rotational energy must be included in the form of the Fourier Law of Heat Conduction in both the rotational and total energy equations. Eq. (1) and Eq. (8) thus become Eq. (14).

$$\rho\frac{De_r}{Dt} - \frac{\partial}{\partial x}\kappa_r\frac{\partial T_r}{\partial x} = \rho w_r \qquad (14a)$$

where:

$$w_r \equiv \begin{cases} \dfrac{\Delta e_r}{Z_R \tau_c}, & \text{Landau-Teller} \\ \dfrac{\Delta e_r}{Z_R \tau_c}\dfrac{e_r^*}{|\Delta e_r|}\left(\dfrac{|\Delta e_r|}{e_r^*}\right)^n, & \text{New Model} \end{cases} \qquad (14b)$$

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + u\frac{\partial}{\partial x}$$

Note that the ordinary derivative has been replaced by a substantial derivative to account for convection of rotational energy due to fluid motion. Also note that Eq. (14a) is no longer homogeneous, but now has a thermal source term. Thus, the governing equations for one dimensional shock structure in "conservation law" form for a diatomic gas are:

$$\frac{\partial \hat{U}}{\partial t} + \frac{\partial \hat{F}}{\partial x} = \hat{W} \qquad (15a)$$

where:

$$\hat{U} = \begin{pmatrix} \rho \\ \rho u \\ E \\ E_r \end{pmatrix}, \hat{F} = \begin{pmatrix} \rho u \\ \rho u^2 - \sigma \\ (E-\sigma)u + q + q_d \\ E_r u + q_d \end{pmatrix}, \quad \hat{W} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \rho w_r \end{pmatrix}, q_d = -\kappa_r\frac{\partial T_r}{\partial x} \qquad (15b)$$

The method used to solve the above equation set is similiar to the one used for monatomic gases in Ref. (10) which treats the Euler terms explicitly and the viscous terms implicitly. The main difference here is the non-homogeneous source term in the rotational energy equation. The equation set for the monatomic case is homogenous. This requires a slight modification to the numerical technique outlined in Ref. (10). The source term here is treated in an implicit manner similiar to the treatment of the viscous terms. Details of handling source terms implicitly are outlined in Refs. (15,16).

Shock Structure Results

The continuum technique described above was used to calculate shock wave structure for four combinations of constitutive model and rotational model at eight Mach numbers. The four cases considered were Burnett constitutive relations (Eq. 12) with both the new rotational model and the Landau-Teller model (using the Lordi-Mates values for Z_R) and the nonlinear model constitutive relations (Eq. 13) with the same two rotational models considered above. Shock structures were calculated at Mach 1.2, 1.5, 2, 3, 5, 6, 8, and 11. In all cases upstream temperatures were chosen

to be in equilibrium and at 300K, and upstream pressure was chosen to be one atm. Shock structure density and temperature profiles were normalized as shown schematically in Fig. 8. The normalization values $\rho_2 - \rho_1$ and $T_2 - T_1$ were calculated analytically with the assumption that the downstream condition was vibrationally frozen. Table 4 summarizes the normalization values for density and temperature jumps used in this work. The spatial coordinate was normalized by the upstream mean free path as defined below.

$$\lambda \equiv \frac{\mu}{\rho}\sqrt{\frac{\pi}{2RT_t}} \qquad (16)$$

Nitrogen was modeled as having a spherically repulsive potential. This gave the following relation between viscosity and temperature.

$$\mu = \mu_{ref}\left(\frac{T_t}{T_{ref}}\right)^{\omega} \qquad (17)$$

The temperature viscosity exponent was chosen to be 0.72.

Fig. 9 compares the rotational and translational temperature profiles of the new rotational model and the Landau-Teller model when Burnett constitutive relations are used to calculate a Mach 6 shock structure. Fig. 10 makes the same comparison for the nonlinear constitutive relations. In both comparisons the new rotational model gives a lower peak translational temperature than the Landau-Teller model. However the profiles in both comparisons are qualitatively very similar. This suggests that the Landau-Teller model with a slightly adjusted value of Z_R may reproduce the results acheived with the new rotational model. Figs. 11 and 12 compare the computed values of shock reciprocal thickness (as defined in Fig. 8) with experimentally measured values from Ref. 14. Fiscko and Chapman[10] show that the Burnett constitutive relations yield shock reciprocal thicknesses which are slightly higher than the experimental data for argon; therefore, any differences between the computed and experimental shock thicknesses in Fig. 11 do not allow a rigorous evaluation of the rotational model employed. The nonlinear model was adjusted to give the correct shock thickness in argon over the range of Mach numbers from 1 to 11 (Fig. 7); therefore, the comparison of computed and measured reciprocal thicknesses in Fig. 11 should provide insight as to the validity of the rotational models employed.

The new rotational model accurately predicts shock reciprocal thickness at Mach numbers below six; however, above Mach 6 the new rotational model over predicts shock reciprocal thickness. The Landau-Teller model using the Lordi-Mates values for Z_R agrees with experiment to only Mach 3 and under predicts reciprocal thickness thereafter. The deficiency in the new model is thought to be in the measured transition rates that were used to develop the model. Rahn, *et al.*,[11,12,13] measured the transition rates up to 2000K; therefore, the curve fits suggested for the transition rates may be in error for temperatures higher than 2000K. This would explain the inaccuraccy in the new rotational model at Mach numbers higher than six where the downstream temperature is in excess of 2000K.

Finally in view of the inaccuracies of both rotational models at high Mach numbers, the expression for Z_R in the Landau-Teller equation was modified in an attempt to give correct shock reciprocal thicknesses. The value of Z_R^{∞} was adjusted to 18.0 while T^* was maintained at 91.5K. The results of this simple modification are also presented in Fig. 12 and agree well with the experimental data at all Mach numbers up to 11.

Conclusion

In conclusion, the Landau-Teller equation is presently being used to model rotational relaxation in hypersonic CFD, even though the assumptions used to derive the Landau-Teller equation are probably violated in hypersonic flow fields. However, it has been found that by adjusting parameters in Parker's analytical expression for the rotational collision number Z_R, the Landau-Teller model along with a nonlinear constitutive model will accurately reproduce experimental shock reciprocal thicknesses for nitrogen. Thus, while neither Landau-Teller relaxation, nor $Z_R^{\infty} = 18.0$ in Parker's expression may be individually accurate for nitrogen, the combination of the two yields accurate shock thicknesses up to Mach 11, the limit of the experimental data. Due to a lack of experimental shock wave temperature profiles in nitrogen, it is unclear how well this method reproduces the detailed structure of the nitrogen shock.

In an effort to more realistically capture the true physics of rotational thermal nonequilibrium, an alternative to the Landau-Teller equation which is based on the more rigorous master equation has been developed. This alternative, in contrast to Landau-Teller, yields a rotational collision number ($\widetilde{Z_R}$) dependent on T_r/T_t as well as T_t, and a time rate of rotational energy change that is proportional to some power (other than one) of the energy difference, $e_r^{eq}(T_t) - e_r$. This new model has accurately reproduced experimental shock reciprocal thicknesses in nitrogen up to Mach 6 and slightly over predicts shock reciprocal thickness above Mach 6. It is believed that the deficiency in the new model is the uncertainity at the high temperatures found in these high Mach number shocks of the transition rates–extrapolated above 2000K–upon which the model is based.

Finally, it should be noted that while the rotational transition rates of Rahn, *et al.*,[11,12,13] have an applicable temperature range of under 2000K, the applicability of this approach is not so limited. As these rates become better known through the efforts of experimentalists and computational chemists, the improved values can be similarly used to arrive at even more refined models for rotational thermal nonequilibrium.

Acknowledgements

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Table 1. Values used in Parker's Model.

	T^* (K)	Z_R^∞
Parker	80	15.7
Lordi/Mates	91.5	23.0

Table 2. Values used in empirical fit of $K_{i\Rightarrow j}$.

α (Pa sec)$^{-1}$	β	δ	m	T_o (K)
6805.1	1.67	1.21	0.1487	295

Table 3. Values used in fits for $\widetilde{Z}_R$ and n.

i	1	2	3	4	5	6
A_i	6.16574	3.9166	7.919	2.1858	5.0616	0.6035
B_i	2.026×10^{-7}	1.8	1250.0	500.0		
C_i	1.1282934	5.2602×10^{-4}	−0.04920	0.762538	−0.15419	

Table 4. Values used to normalize shock wave profiles.

Mach	ρ_2 (kg/m^3)	$\rho_2 - \rho_1$ (kg/m^3)	T_2 (K)	$T_2 - T_1$ (K)
1.2	1.526	0.389	338.4	38.44
1.5	2.119	0.981	396.1	96.07
2.0	3.035	1.897	506.3	206.3
3.0	4.390	3.252	803.7	503.7
5.0	5.691	4.553	1740.0	1440.0
6.0	5.997	4.858	2382.2	2082.2
8.0	6.334	5.196	4016.0	3716.0
11.0	6.558	5.420	7341.3	7041.3

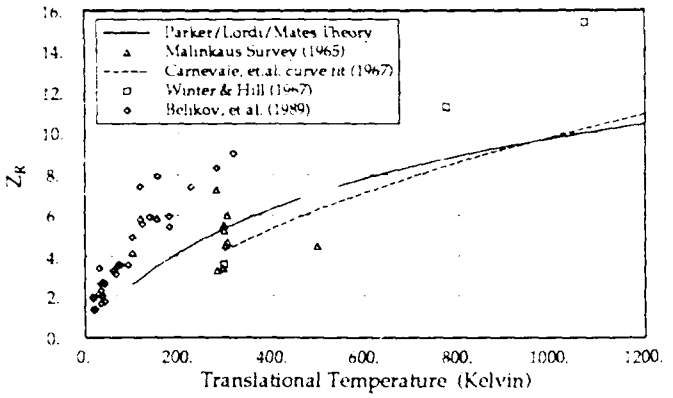

Fig. 1 Rotational collision number vs. temperature.

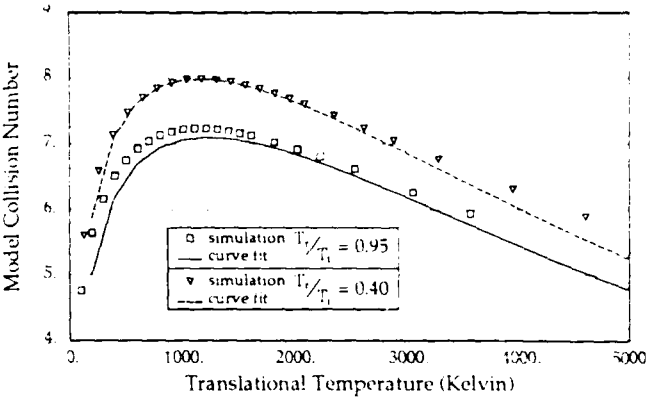

Fig. 4 New rotational model collision number $\widetilde{Z}_R, T_r < T_t$.

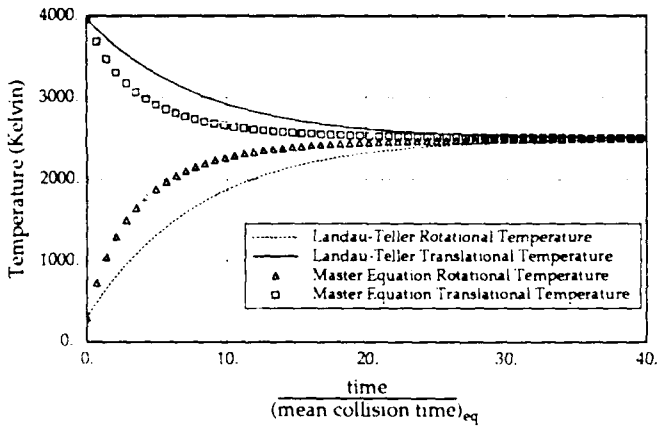

Fig. 2 Adiabatic box temperature relaxation time histories.

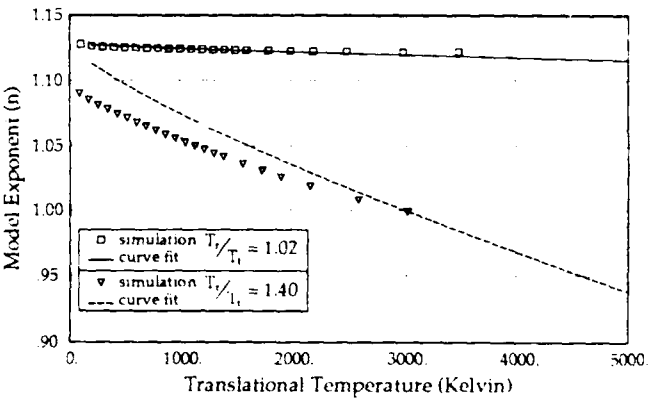

Fig. 5 New rotational model exponent $n, T_r > T_t$.

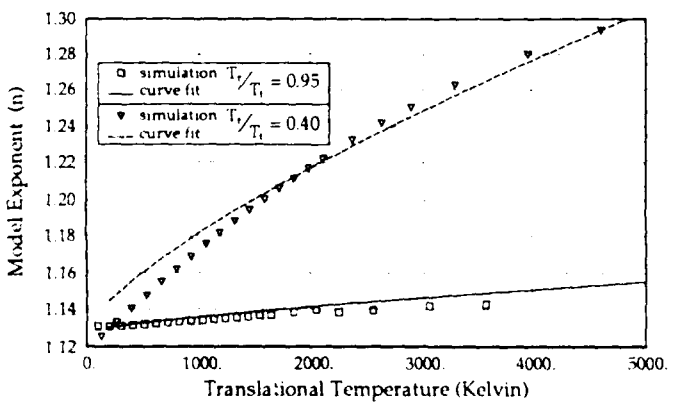

Fig. 3 New rotational model exponent $n, T_r < T_t$.

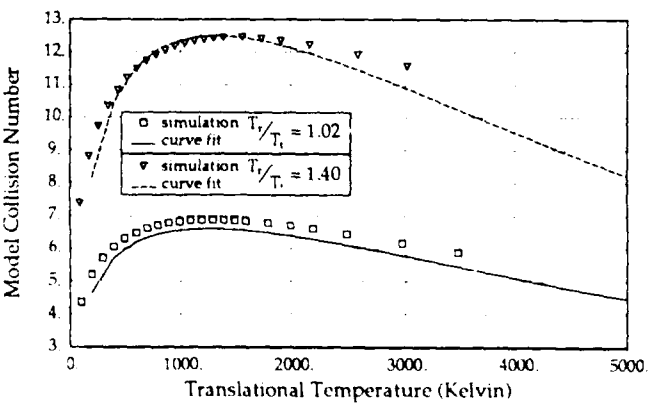

Fig. 6 New rotational model collision number $\widetilde{Z}_R, T_r > T_t$.

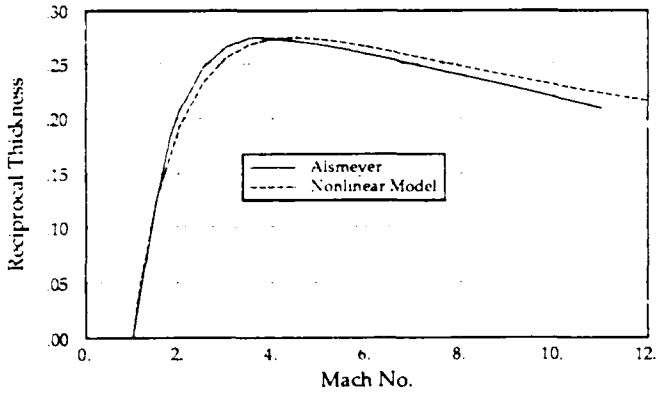

Fig. 7 Shock reciprocal thickness in argon. Comparison of experiment and results using nonlinear constiutive model.

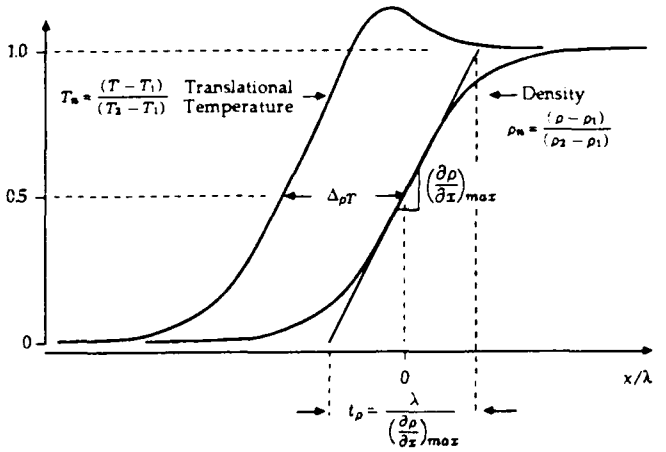

Fig. 8 Schematic of shock structure parameters and normalizations.

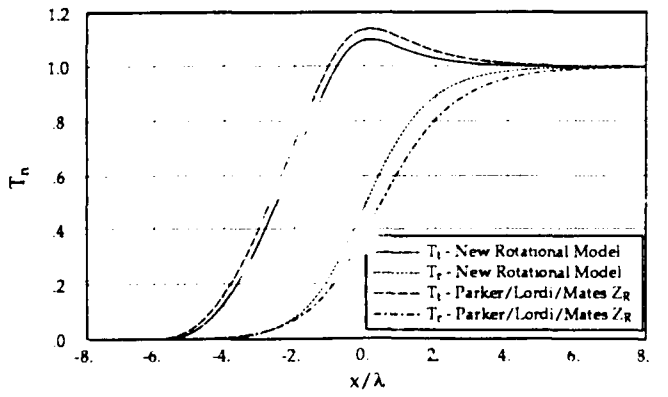

Fig. 9 Mach 6 temperature profiles using Burnett constitutive relations. Nitrogen, $\omega = 0.72$.

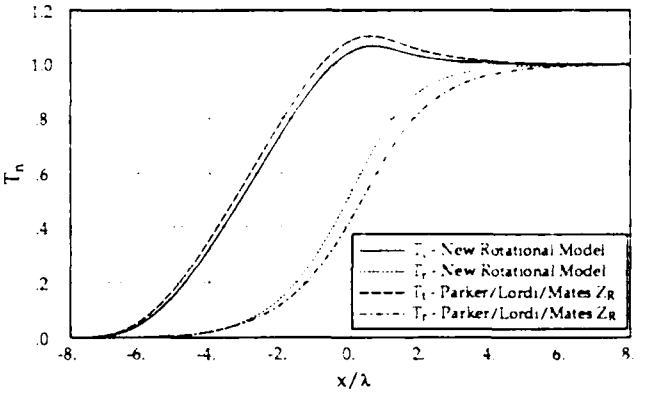

Fig. 10 Mach 6 temperature profiles using nonlinear model constitutive relations. Nitrogen, $\omega = 0.72$.

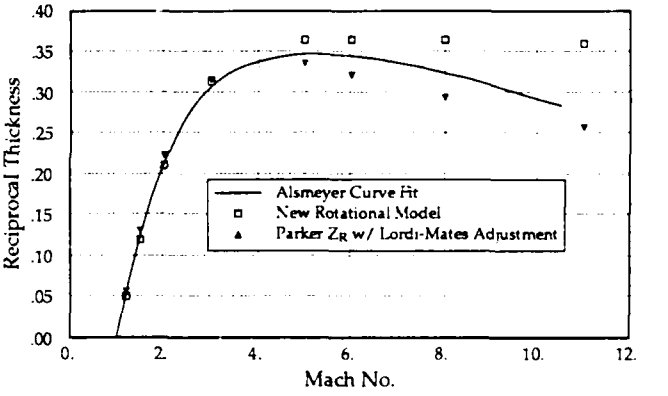

Fig. 11 Shock reciprocal thickness - comparison of Burnett results and experiment. Nitrogen, $\omega = 0.72$.

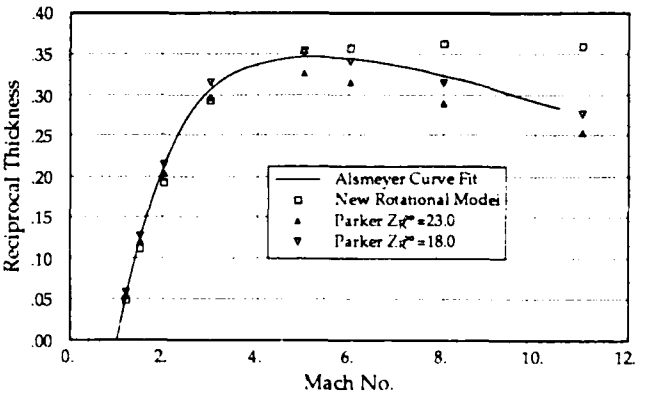

Fig. 12 Shock reciprocal thickness - comparison of nonlinear model results and experiment. Nitrogen, $\omega = 0.72$.