The theoretical basis for the Landau-Teller equation commonly used to model rotational nonequilibrium 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 Landau-Teller model 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.
AIAA–89–1737

A New Rotational Relaxation Model For Use In Hypersonic Computational Fluid Mechanics

Forrest E. Lumpkin III
Dean R. Chapman

Department of Aeronautics and Astronautics
Stanford University, Stanford, CA 94305

Chul Park

NASA Ames Research Center
Moffett Field, CA 94035

AIAA 24th Thermophysics Conference
Buffalo, New York / June 12–14, 1989
A NEW ROTATIONAL RELAXATION MODEL FOR USE IN HYPERSONIC COMPUTATIONAL FLUID DYNAMICS

Forrest E. Lumpkin III
Department of Aeronautics and Astronautics
Stanford University, Stanford, CA 94305

Dean R. Chapman
NASA Ames Research Center
Moffett Field, CA 94035

Chul Park
NASP Ames Research Center
Moffett Field, CA 94035

Abstract

The theoretical basis for the Landau-Teller equation commonly used to model rotational nonequilibrium 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

\[
\begin{align*}
\alpha, \beta, \gamma &= \text{fit constants} \\
AOTV &= \text{Aero-assisted Orbital Transfer Vehicle} \\
c_{\text{rot}} &= \text{rotational specific heat} \\
c_{\text{tr}} &= \text{translational specific heat} \\
D_t &= \text{one-dimensional substantial derivative} \\
e_r &= \text{rotational energy per unit mass} \\
e^{eff}(T_t) &= \text{effective rotational energy of translation} \\
e_r^* &= \text{reference rotational energy} \\
e_t &= \text{translational energy per unit mass} \\
E &= \rho c_s T_t + E_t + 1/2 pu^2. \\
E_r &= \rho e_r, \text{rotational energy per unit volume} \\
\Delta e_r &= \text{an energy difference per unit mass} \\
E_i &= \text{energy of } i^{th} \text{ quantum state} \\
\bar{E}_i &= \text{non-dimensional energy of } i^{th} \text{ state} \\
F(T_t) &= \text{non-dimensional function} \\
\Phi &= \text{flux vector} \\
G(\tilde{T}) &= \text{non-dimensional function} \\
H(\tilde{T}, T_t) &= \text{non-dimensional function} \\
I_{\text{max}} &= \text{maximum allowable quantum number} \\
k &= \text{Boltzmann's constant} \\
K_{i\rightarrow j} &= \text{transition rate from state } i \text{ to } j \\
l &= \text{temporal index} \\
n &= \text{an exponent for the new rotational model} \\
\text{NASP} &= \text{National Aerospace Plane} \\
N_i &= \text{number density of } i^{th} \text{ quantum state} \\
p &= \rho R T_t, \text{thermodynamic pressure} \\
q &= \text{one dimensional monatomic heat flux vector} \\
q_d &= \text{addition to heat flux for diatomic gas} \\
R &= \text{gas constant} \\
\tau &= \text{shock reciprocal thickness} \\
T_n &= \text{normalized temperature} \\
T_r &= \text{rotational temperature} \\
T_{\text{ref}} &= \text{viscosity reference temperature} \\
T_t &= \text{translational temperature} \\
T_0 &= \text{reference temperature used for } K_{i\rightarrow j} \\
T^* &= \text{reference temperature used for } Z_R \\
\tilde{T} &= \text{temperature ratio} \\
\tilde{T} &= \text{function of } \tilde{T} \\
u &= \text{fluid velocity}
\end{align*}
\]
\[ \hat{U} \quad = \text{conservation vector} \\
\dot{W} \quad = \text{source term vector} \\
\omega_r \quad = \text{rotational energy source term} \\
Z_R \quad = \text{rotational collision number for Landau-Teller model} \\
Z_R^\infty \quad = \text{infinite temperature collision number} \\
Z_R \quad = \text{rotational collision number for new rotational model} \\
\alpha, \beta, \delta, m \quad = \text{parameters for } K_{\text{v}\omega f} \\
\Delta_{\rho T} \quad = \text{Shock density temperature separation} \\
\kappa_r \quad = \mu c_w, \text{rotational thermal conductivity} \\
\kappa_t \quad = \frac{\mu}{2} c_{\text{st}}, \text{translational thermal conductivity} \\
\mu \quad = \text{viscosity} \\
\mu_{\text{ref}} \quad = \text{viscosity at } T_{\text{ref}} \\
\omega \quad = \text{viscosity-temperature exponent} \\
\sigma \quad = \text{one dimensional stress tensor} \\
\rho \quad = \text{density} \\
\rho_n \quad = \text{normalized density} \\
\theta_r \quad = \text{characteristic rotational temperature} \\
\tau_c \quad = \pi \mu / 4 \rho, \text{mean collision time} \\

\text{Introduction}

Simulating the flow about planned transatmospheric vehicles, such as AOTV and NASP, and about hypersonic missiles, 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 modifying 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

\[ \frac{d e_r}{d t} = \frac{e_r^*(T_r) - e_r}{Z_R \tau_c}. \]  \( (1) \)

In continuum hypersonic CFD this equation is generally used directly as the computational algorithm. In particular 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 conducted 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)).

\[
Z_R = \frac{Z_R^0}{1 + \frac{\pi n}{2} \left( \frac{T^*}{T_t} \right)^{1/2} + \left( \frac{x^2}{4} + \pi \right) \left( \frac{T^*}{T_t} \right)}
\]  

(Eq. (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 temperature 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 temperatures, 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\(^1\) 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 shock 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.

\[
dN_i \frac{d}{dt} = \sum_{j=0}^{l_{\text{max}}} K_{j \rightarrow i} N_j - \sum_{j=0}^{l_{\text{max}}} K_{i \rightarrow j} N_i \quad ; i = 1, \ldots, l_{\text{max}}
\]  

(Eq. (3))

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

\[
K_{i \rightarrow j} = \alpha_0 F(T_t) \left( \frac{1 + \overline{E}_i/\overline{E}_j}{1 + \overline{E}_i} \right)^2 \exp \left( \frac{-\beta \Delta E_{ij}}{kT_t} \right)
\]  

(Eq. (4a))

where:

\[
\overline{E}_i \equiv 1.5 \frac{E_i}{kT_t} = \frac{1.5 \theta_i (i + 1)}{T_t}
\]

\[
\Delta E_{ij} \equiv E_i - E_j
\]

\[
F(T_t) \equiv \left( 1 - \exp \left( -\frac{m}{1 - \exp \left( -\frac{mT_t}{T_{\text{eq}}} \right)} \right) \right) \sqrt{\frac{T_{\text{eq}}}{T_t}}
\]  

(Eq. (4b))

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

\[
K_{j \rightarrow i} = K_{i \rightarrow j} \left( \frac{2j + 1}{2i + 1} \right) \exp \left( \frac{\Delta E_{ij}}{kT_t} \right)
\]  

(Eq. (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.

\[
e_r = \sum_{i=0}^{l_{\text{max}}} i(i + 1) k \theta_r N_i
\]  

(Eq. (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).

\[
T_t \equiv \frac{e_t}{c_{tt}} = \frac{e_t}{3/2 R}
\]

\[
T_r \equiv \frac{e_r}{c_{tr}}
\]  

(Eq. (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:

\[
\frac{d\Delta e_r}{dt} = \frac{\Delta e_r}{Z_R \tau_c} \frac{e^*_r}{[\Delta e_r]}^n \tag{8a}
\]

where:

\[
e^*_r \equiv \frac{2}{5}(e_1 + e_r) \tag{8b}
\]

\[
\Delta e_r \equiv e^*_r(T_i) - e_r
\]

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 \( T_i \) and when \( T_r \) is greater than \( T_i \). This corresponds to both compressing and expanding flows. It is assumed \textit{a priori} that \( Z_R \) and \( n \) will not be constant but in general functions of both the \( T_i \) and \( T_r \). The conventional Landau-Teller method is recovered if one chooses \( n = 1 \) and \( Z_R(T_i, T_r) = Z_R(T_i) \), a function of translational temperature only.

The parameters \( Z_R \) 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.

\[
\frac{d\Delta e_r}{dt} \big|_l = \sum_{i=0}^{l_{\text{max}}} i(i+1)k\theta_i \frac{dN_i}{dt} \tag{9}
\]

\[
= \sum_{i=0}^{l_{\text{max}}} i(i+1)k\theta_i \left( \sum_{j=0}^{l_{\text{max}}} K_{j \rightarrow i} N_j - \sum_{j=0}^{l_{\text{max}}} K_{i \rightarrow j} N_i \right)
\]

In order to obtain the exponent in Eq. (8a) values of the energy derivative at both \( l \) and \( l - 1 \) are used to eliminate \( Z_R \) 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 \( \Delta e_r > 0 \).

\[
\log_{10} \left( \frac{d\Delta e_r}{d \tau_c} \right)_l = n \log_{10} \left( \frac{\Delta e_r}{e^*_r} \right)_l - \log_{10} \left( Z_R \right)_l \tag{10a}
\]

\[
n_l = \frac{\log_{10} \left( \frac{d\Delta e_r}{d \tau_c} \right)_l - \log_{10} \left( \frac{d\Delta e_r}{d \tau_c} \right)_{l-1}}{\log_{10} \left( \frac{\Delta e_r}{e^*_r} \right)_l - \log_{10} \left( \frac{\Delta e_r}{e^*_r} \right)_{l-1}} \tag{10b}
\]

This assumes that both \( n \) and \( Z_R \) are only weak functions of \( T_i \) and \( T_r \). This assumption will be justified by the results. Now that \( n \) is known, \( Z_R \) is obtained by simple substitution into Eq (8a).

\( Z_R \) and \( n \) were calculated from numerous solutions of the master equation where two parameters, total energy and the ratio \( T_r/T_i \), were varied. Initial rotational quantum state distributions were assumed to be Boltzmann at the temperature \( T_i \). The values of \( Z_R \) 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 \( Z_R \) 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 \( Z_R \). The equations below present curve fits used in the shock simulations presented in this paper.

\[
\overline{Z_R} = 1 + \frac{G(\tilde{T})}{H(\tilde{T}, T_i)} \tag{11a}
\]

\[
n = C_1 + C_2 \tilde{T}^{(C_4 + C_5) \tilde{T}} |\tilde{T}|^{C_6} \tag{11b}
\]

where:
AAA
89-1737
Lions 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\textsuperscript{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 similar 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:

\begin{align}
\sigma &= -p + \frac{4}{3} \mu \frac{\partial u}{\partial x} - \frac{\mu^2}{p} \left[ \frac{\partial u}{\partial x} \right]^2 \\
&\quad - 1.352 \frac{RT_1}{\rho} \frac{\partial^2 \rho}{\partial x^2} + 1.352 \frac{RT_1}{\rho^2} \left[ \frac{\partial \rho}{\partial x} \right]^2 \\
&\quad - .898 \frac{R}{\rho} \frac{\partial \rho}{\partial x} \frac{\partial T_1}{\partial x} + 1.406 \frac{R}{T_1} \left( \frac{\partial T_1}{\partial x} \right)^2 \\
&\quad + .260 \frac{R}{\rho} \left( \frac{\partial^2 T_1}{\partial x^2} \right) \\
\end{align}

\begin{align}
q &= -\kappa T \frac{dT_1}{dx} + \frac{\mu^2}{p} \left[ \frac{10.831}{T_1} \frac{\partial u}{\partial x} \frac{\partial T_1}{\partial x} \right. \\
&\quad - 2.269 \frac{\partial^2 u}{\partial x^2} - \frac{2.060}{\rho} \left( \frac{\partial u}{\partial x} \frac{\partial \rho}{\partial x} \right) \\
\end{align}

Table 3 summarizes the numerical values $A_i, B_i,$ and $C_i$ required to fit Eq. (11) to $n$ and $Z_R$. 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 $Z_R$ 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 $Z_R$ 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., $|T_1 - T_r|/T_r > 1$). 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 $Z_R$ are not strongly dependent on $T_t$ and $T_r$ justifying the assumption necessary to calculate $n$ and $Z_R$ 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\textsuperscript{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 similar 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:
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.

The nonlinear constitutive model presented above differs from the model presented by Chapman, et al., 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).

\[
\rho \frac{De_r}{Dt} - \frac{\partial}{\partial x} \kappa_r \frac{\partial T_r}{\partial x} = \rho w_r, \quad (14\ a)
\]

where:

\[
q = -\kappa_r \frac{\partial T_t}{\partial x} + \frac{95}{8T_t} \frac{\mu^2}{\rho} \frac{\partial u}{\partial x} \frac{\partial T_t}{\partial x}, \quad (13\ b)
\]

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:

\[
\frac{\partial \bar{U}}{\partial t} + \frac{\partial \hat{F}}{\partial x} = \hat{W} \quad (15\ a)
\]

where:

\[
\bar{U} = \begin{pmatrix} \rho \\ \rho u \\ E_r \\ \rho u^2 - \sigma \\ (E - \sigma) u + q + q_d \end{pmatrix}, \quad \hat{F} = \begin{pmatrix} \rho u \\ \rho u^2 - \sigma \\ (E - \sigma) u + q + q_d \end{pmatrix}, \quad (15\ b)
\]

\[
\hat{W} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad q_d = -\kappa_r \frac{\partial T_r}{\partial x}
\]

The method used to solve the above equation set is similar 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 similar 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 temper-
ature 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 down-
stream condition was vibrationally frozen. Table 4 summa-
rizes the normalization values for density and temperature
jumps used in this work. The spatial coordinate was nor-
malized by the upstream mean free path as defined below.

$$\lambda \equiv \frac{\mu}{\rho} \sqrt{\frac{\pi}{2RT_1}} \quad (16)$$

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

$$\mu = \mu_{ref} \left( \frac{T_1}{T_{ref}} \right)^\eta \quad (17)$$

The temperature viscosity exponent was chosen to be 0.72.

Fig. 9 compares the rotational and translational tempera-
ture 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 rela-
tions. 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 qual-
itatively very similar. This suggests that the Landau-Teller
model with a slightly adjusted value of $Z_R$ may reproduce
the results achieved with the new rotational model. Figs. 11
and 12 compare the computed values of shock reciprocal
thickness (as defined in Fig. 8) with experimentally mea-
sured values from Ref. 14. Fiscko and Chapman\cite{10} show
that the Burnett constitutive relations yield shock recipro-
cal thicknesses which are slightly higher than the experi-
mental 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 re-
ciprocal 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.\cite{11,12,13} measured the transition rates up
to 2000K; therefore, the curve fits suggested for the trans-
ition rates may be in error for temperatures higher than
2000K. This would explain the inaccuracy in the new ro-
tational 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 pa-
rameters 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 ex-
perimental 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 ni-
trogen, 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 tempera-
ture 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 num-
ber ($Z_R$) dependent on $T^* / T_1$ as well as $T_1$, and a time rate
of rotational energy change that is proportional to some power
(other than one) of the energy difference, $e^*(T_1) - e^*$. 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 uncer-
tainty 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.*1,12,13 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**

This research is supported by SDIO/IST managed by the Army Research Office under contract DAAH03-86-K-0139, and by ONR/AFOSR/NASA Hypersonic Training and Research Grant NAGW-965. We would also like to acknowledge the Aerothermodynamics Branch of NASA Ames Research Center for providing supercomputer time.

**References**


18 Carnevale, E. H., C. Carey, and G. Larson, "Ultrasonic Determination of Rotational Collision Numbers and Vibrational Relaxation Times of Polyatomic Gases at High


Table 1. Values used in Parker's Model.

<table>
<thead>
<tr>
<th></th>
<th>$T^*$ (K)</th>
<th>$Z_R^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parker</td>
<td>80</td>
<td>15.7</td>
</tr>
<tr>
<td>Lordi/Mates</td>
<td>91.5</td>
<td>23.0</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$ (Pa sec)$^{-1}$</th>
<th>$\beta$</th>
<th>$\delta$</th>
<th>$m$</th>
<th>$T_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6805.1</td>
<td>1.67</td>
<td>1.21</td>
<td>0.1487</td>
<td>295</td>
</tr>
</tbody>
</table>

Table 3. Values used in fits for $Z_R$ and $n$.

<table>
<thead>
<tr>
<th></th>
<th>$A_i$</th>
<th>$B_i$</th>
<th>$C_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.16574</td>
<td>2.026 x $10^{-7}$</td>
<td>1.1282934</td>
</tr>
<tr>
<td>2</td>
<td>3.9166</td>
<td>1.8</td>
<td>5.2602 x $10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>7.919</td>
<td>1250.0</td>
<td>-0.04920</td>
</tr>
<tr>
<td>4</td>
<td>2.1858</td>
<td>500.0</td>
<td>0.762538</td>
</tr>
<tr>
<td>5</td>
<td>5.0616</td>
<td></td>
<td>-0.15419</td>
</tr>
<tr>
<td>6</td>
<td>0.6035</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Values used to normalize shock wave profiles.

<table>
<thead>
<tr>
<th>Mach</th>
<th>$\rho_2$ (kg/m$^3$)</th>
<th>$\rho_2 - \rho_1$ (kg/m$^3$)</th>
<th>$T_3$ (K)</th>
<th>$T_2 - T_1$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>1.526</td>
<td>0.389</td>
<td>338.4</td>
<td>38.44</td>
</tr>
<tr>
<td>1.5</td>
<td>2.119</td>
<td>0.981</td>
<td>396.1</td>
<td>96.07</td>
</tr>
<tr>
<td>2.0</td>
<td>3.035</td>
<td>1.897</td>
<td>506.3</td>
<td>206.3</td>
</tr>
<tr>
<td>3.0</td>
<td>4.390</td>
<td>3.252</td>
<td>803.7</td>
<td>503.7</td>
</tr>
<tr>
<td>5.0</td>
<td>5.691</td>
<td>4.553</td>
<td>1740.0</td>
<td>1440.0</td>
</tr>
<tr>
<td>6.0</td>
<td>5.997</td>
<td>4.858</td>
<td>2382.2</td>
<td>2082.2</td>
</tr>
<tr>
<td>8.0</td>
<td>6.334</td>
<td>5.196</td>
<td>4016.0</td>
<td>3716.0</td>
</tr>
<tr>
<td>11.0</td>
<td>6.558</td>
<td>5.426</td>
<td>7341.3</td>
<td>7041.3</td>
</tr>
</tbody>
</table>
Fig. 1 Rotational collision number vs. temperature.

Fig. 2 Adiabatic box temperature relaxation time histories.

Fig. 3 New rotational model exponent \( n, T_r < T_t \).

Fig. 4 New rotational model collision number \( Z_R, T_r < T_t \).

Fig. 5 New rotational model exponent \( n, T_r > T_t \).

Fig. 6 New rotational model collision number \( Z_R, T_r > T_t \).
Fig. 7 Shock reciprocal thickness in argon. Comparison of experiment and results using nonlinear constitutive 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, $\omega = 0.72$. 