JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 6, No. 4, Oct.–Dec. 1992

Monte Carlo Simulation of Nonequilibrium Shock Fronts

David P. Olynick*
North Carolina State University, Raleigh, North Carolina 27695
James N. Moss†
NASA Langley Research Center, Hampton, Virginia 23665
and
H. A. Hassan‡
North Carolina State University, Raleigh, North Carolina 27695

A direct simulation of a shock tube experiment carried out by AVCO, (pressure of 1 Torr and velocity of 6.4 km/s) repeated by Sharma and Gillespie, and used by Park to develop his two-temperature model, is presented. Results show that the electronic ground state of N_2 is not in rotational or vibrational equilibrium with that of N_2^+. Moreover, a two-temperature model is inadequate to describe nonequilibrium flows behind shocks. The role of impurities is examined. It is shown that the effects of a small fraction of H_2O are insignificant. Good agreement with the measurements of Sharma and Gillespie is indicated.

Introduction

THE two-temperature model of Park[1] is widely used in calculations involving chemical and thermal nonequilibrium. This model was developed by comparing computed properties with measurements carried out at AVCO in shock tubes using nitrogen.[2] Some of the parameters in the calculations were adjusted in order to improve the agreement between theory and experiment. With the exception of the vibrational temperature, the procedure developed by Park[1] seemed to be in good agreement with experiment.

The calculated vibrational temperature was that of the ground electronic state of nitrogen. On the other hand, the measured vibrational and rotational temperatures were those of the first negative system of N_2^+, $N_2^+(1-)$. Because of this, one should not expect that the two vibrational temperatures be equal. Nevertheless, Park[1] attributed part of the discrepancy to the use of the nitrogen dissociation rate of Appleton et al.[3] He thought that such rates should be reinterpreted using a two-temperature model.

The need to clarify the above situation prompted Sharma and Gillespie[4] to repeat the AVCO experiment. This was accomplished using a clean arc-driven shock tube. Armed with more precise spectral measurements and more precise data reduction techniques, they proceeded to measure the rotational and vibrational temperatures of $N_2(2+)$. They concluded that their measured rotational temperature was consistent with that of AVCO, but the measured vibrational temperature was not. Although their measurements of the vibrational temperature were consistent with the calculations of Park,[1] the measured rotational temperature in the nonequilibrium region was not in equilibrium with the translational temperatures. This contradicts the two-temperature assumption of Park.[1]

Unfortunately, the measurements of Ref. 4 were limited to one nonequilibrium and one equilibrium measurement. This makes it difficult to explain the trends exhibited by the AVCO experiment. In particular, the vibrational temperatures measured in the AVCO experiment were below the equilibrium value. This contradicts the measurements of Ref. 4, which showed that, in the nonequilibrium region, the measured value of the temperature is above the equilibrium value.

The issues raised by the measurements and computations are extremely important in the development of a thermochemical model suited for use at high velocities and temperatures. Thus, the first objective of this study is a direct simulation of the shock tube experiments of Refs. 2 and 4. The simulation considers pure nitrogen at a pressure of 1 Torr, room temperature and a velocity of 6.4 km/s. Because the degree of ionization for this set of conditions is very small, the simulation does not take ionization into consideration. However, even in the absence of ionization, the problem is a challenging calculation for direct simulation Monte Carlo methods because the pressure chosen is that representative of a 45 km altitude. Thus, the calculation is essentially a continuum calculation.

In a Direct Simulation Monte Carlo (DSMC) calculation, the internal energy of a gas and, hence, the vibrational temperature is controlled by the distribution of energy between the translational and internal modes after an inelastic collision. The probability of an inelastic collision determines the rate at which energy is transferred between the translational and internal modes after an inelastic collision. For a given collision, the probabilities of rotational or vibrational relaxation are designated by relaxation numbers. The relaxation number is the number of collisions it takes, on average, for a molecule to relax. Hence, the inverse of the relaxation number is the probability of relaxation occurring for one collision. In the DSMC, the relaxation numbers are traditionally given as constants on the order of $Z_R = 5$ for rotation and $Z_v = 50$ for vibration. In this study, variable relaxation numbers for the rotation are used that are function of the translational temperature of the gas. The vibrational numbers are temperature- and species-dependent[5] and are based on the Millikan and White[6] measurements. Using these models, a one-dimensional calculation, similar to that of Bird,[7] is carried out. Far downstream, the flow is assumed to approach equilibrium.

In Park's work, it was found that the calculated vibrational temperature of the ground electronic state of nitrogen was much higher than the vibrational temperature of the $N_2^+(1-)$

Received April 9, 1991; presented as Paper 91-1341 at the AIAA 26th Thermophysics Conference, Honolulu, HI, June 24–26, 1991; revision received Oct. 4, 1991; accepted for publication Oct. 4, 1991.

*Research Assistant, Mechanical and Aerospace Engineering. Student Member AIAA.

†Research Engineer, Aerothermodynamics Branch, Space Systems Division. Fellow AIAA.

‡Professor, Mechanical and Aerospace Engineering. Associate Fellow AIAA.

measured in the AVCO experiment. Initial calculations in this work yielded similar results. Examination of the AVCO data suggests that the lower vibrational temperatures in the nonequilibrium region is a direct result of a process that deactivates the vibrational modes. Because of this, it was thought that a small amount of impurity may have been present in the AVCO experiment. It is known[8,9] that H_2O has a rather high cross section for deactivation of the vibrational levels of N_2. As a result, a small fraction of H_2O in the experiment could have had a large influence on the vibrational temperature. Therefore, the effect of an H_2O impurity is included in this study.

The physical processes modeled in the simulation are rotational and vibrational excitations, and dissociation and recombination. The pressure employed in the experiments of Refs. 2 and 4 are representative of an altitude of 45 km. Because the mean freepath is very small, the simulation is well within the continuum flow regime. Therefore, another objective of this study is to compare the results of the Monte Carlo simulation with the results and assumptions of the continuum approach.

Formulation of the Problem

The DSMC method of Bird provides a general physical framework for the study of complex flowfields.[10] However, because it is a direct simulation method, any results from a flow calculation are dependent on the physical model employed for that calculation. In this section, the physical models used in this study will be discussed.

Traditionally, the DSMC employs a rotational relaxation number on the order of $Z_R = 5$. This means that, on average, a molecule rotationally relaxes once every five collisions. This is generally a good engineering approximation. However, a more realistic expression that is a function of the translational temperature has been developed by Parker.[11] This expression is given by

$$Z_R = \frac{Z_{R,\infty}}{1 + (\pi^{3/2}/2)(T^*/T)^{1/2} + (\pi^2/4 + 4)(T^*/T)} \tag{1}$$

with $Z_{R,\infty}$ and T^* being species-dependent. For nitrogen, values of $Z_{R,\infty}$ and T^* are chosen as 16 and 91.5 K, respectively, following the suggestion of Boyd.[12] A value for Z_R is calculated in each cell.

The vibrational relaxation numbers used in this study are based on Millikan and White's[6] correlation of available experimental data. The correlation made use of the Landau-Teller theory of vibrational relaxation, which has a limited range of applicability. As a result, Millikan and White's[6] correlations are not valid at high temperatures. To remedy the situation, Park[1] suggested an empirical correlation. As a result of this correction, the vibrational relaxation time τ is given by

$$\tau = \tau_L + \tau_{cs} \tag{2}$$

where[6]

$$\tau_L = (1/p)\exp[A(T^{-1/3} - 0.015\mu^{1/4}) - 18.42]$$

$$A = 1.16 \times 10^{-3}\mu^{1/2}\Theta_v^{4/3} \tag{3}$$

and[1]

$$\tau_{cs} = (1/c_s\sigma_v n_s)$$

with

$$\sigma_v = 10^{-21}(50{,}000/T)^2,\ m^2$$

$$c = \sqrt{(8kT/\pi m_s)} \tag{4}$$

In the above equation, p is the pressure in atmospheres, T is the translational temperature in degrees Kelvin, Θ_v is the characteristic vibrational temperature, μ is the reduced mass, k is the Boltzman constant, and m_s and n_s give the particle mass and number density of species s.

To obtain the vibrational relaxation collision number, the quantity τ must be multiplied by the collision frequency v. The average collision frequency v_s for species s is given by

$$v_s = \sum (n_q\overline{\sigma_{T_{sq}}c_{r_{sq}}}) \tag{5}$$

where $\sigma_{T_{sq}}$ is the total collision cross section for collisions involving particles s and q. This cross section is calculated using the variable hard sphere model.[7] The quantity $c_{r_{sq}}$ is the relative velocity of particles s and q

The quantity

$$(1/Z_v) \equiv (1/\tau v) \tag{6}$$

determines the probability of a vibrational relaxation for a given collision. This quantity is calculated in each cell. Thus, with the inclusion of vibrational relaxation model that is a function of temperature and species, the presence of multispecies in the simulation does not pose any problems.

Rates for the relaxation of H_2O are available in Refs. 8 and 9. In this study, a relaxation time for N_2-H_2O system is obtained from the more recent data of Ref. 9. A formula for the relaxation time is given by

$$\ln (p_T)_{N_2 - H_2O} = -1.7325 + 11.3267\ T^{-1/3},\ (\mathrm{atm} - \mu\mathrm{s}) \tag{7}$$

where T is the translational temperature of the gas.

H_2O is a nonlinear molecule and, as such, has three rotational and three vibrational modes.[13] The vibrational modes consist of a bending mode with the energy of the first mode (010) being 1595.0 cm^{-1}, a symmetric stretching mode with an energy of the first mode (100) of 3651.7 cm^{-1}, and a nonsymmetric stretching mode with an energy of the first mode (001) of 3755.8 cm^{-1}.

It was found that using the vibrational temperature of the first bending mode of H_2O, $\Theta_v = 2294.9$, in the Millikan-White[6] correlation, Eq. (3), resulted in a good approximation to Eq. (7). The resulting formula tended to underpredict the relaxation time by a factor of two or less for temperatures up to 20,000 K. Because of this, the Millikan-White[6] correlation was used for this study. The Millikan-White[6] formulation was also used for the relaxation of H_2O by N using $\Theta_v = 2294.9$.

The dissociation and recombination reactions considered in this investigation are

$$N_2 + M \Leftrightarrow N + N + M, \qquad M = N, N_2 \tag{8}$$

The steric factors needed for the simulation were determined by a procedure suggested by Bird.[14] These factors, which are function of energy yield rates of the type

$$CT^n \exp(-T_R/T) \tag{9}$$

when the distribution function used in calculating the rates is Maxwellian at temperature T. For the reactions indicated in Eq. (8), two sets of rates were used. The first is the one used by Park[1] and the second is the one suggested by Byron,[15] for which the constants appearing in Eq. (9), n, C, T_R for N and N_2 are

-1.5	4.085×10^{22} cm^3 mole^{-1} s^{-1},	1.13×10^5 K
-0.5	4.7×10^{17} cm^3 mole^{-1} s^{-1},	1.13×10^5 K

H_2O was not considered as a collision partner for purposes of dissociation and recombination, but was considered a collision partner for purposes of rotational and vibrational excitation and deexcitation.

The rotational and vibrational temperatures are calculated from the rotational and vibrational energies using their equilibrium expressions. The vibrational energies for N_2 and H_2O were calculated assuming the various modes behave like harmonic oscillators. Thus, for H_2O, the vibrational energy e_v is given by

$$e_v = \sum_{i=1}^{3} \frac{k\theta_{vi}}{\exp(\theta_{vi/T} - 1)} \tag{10}$$

where θ_{vi} = 2294.9, 5254.0, and 5283.3 K.

Results and Discussion

The problem under consideration is well within the continuum regime. This imposes severe grid and time-step requirements. Initial calculations employed 4000 cells. Later calculations employed 8000 cells. Figure 1 compares the cell width relative to the local mean free path λ. As seen from the figure, the coarse grid does not meet the requirements of the DSMC, but the fine grid does. Therefore, all subsequent calculations were carried out using the fine grid. The simulation employed about 10^5 computational molecules.

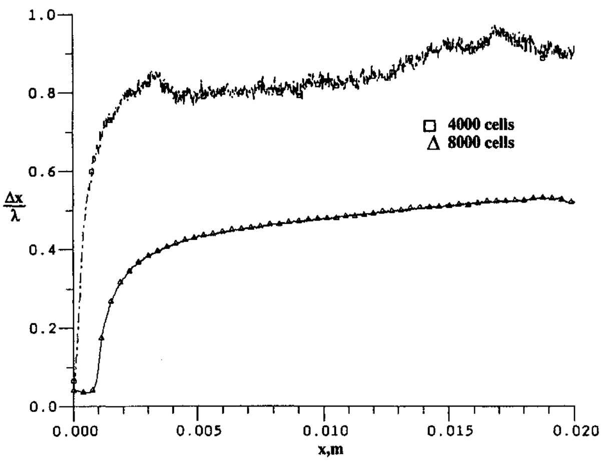

Fig. 1 Ratio of cell width to local mean freepath.

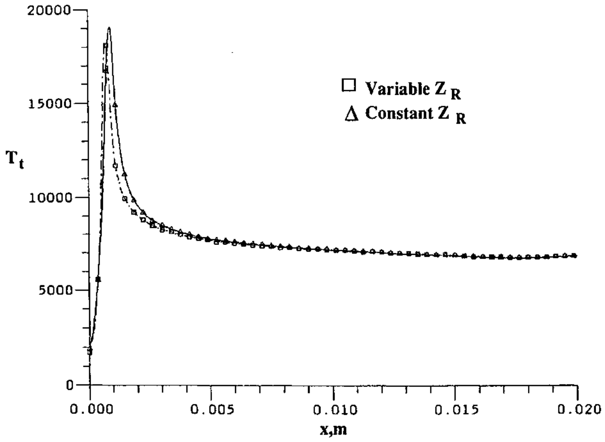

Fig. 2 Effect of rotational number on translational temperature.

Figures 2–4 show the effects of a variable rotational relaxation number on the translational temperature T_t the rotational temperature T_r and the vibrational temperature T_v. As indicated earlier, these temperatures were calculated from corresponding energies assuming equilibrium expressions. In the case of vibrational energy, the equilibrium expression was computed on the assumption that each mode behaves like a harmonic oscillator. As seen from the figures, the effect of a variable rotational relaxation number is small. For the range of temperatures indicated in the figure T^*/T in Eq. (1) is small. As a result, Z_R lies in the range 8–12 for the temperature range of interest. Thus, it takes more time to reach rotational equilibrium. The small reduction in the transla-

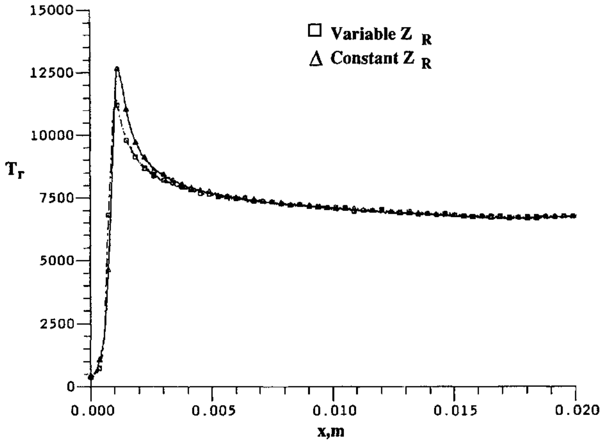

Fig. 3 Influence of rotational number on rotational temperature.

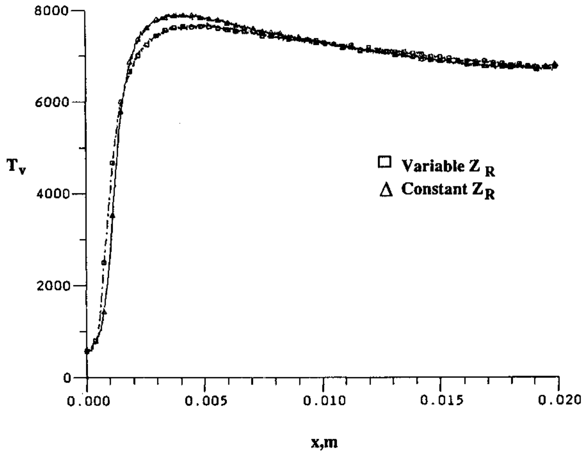

Fig. 4 Effect of rotational number on vibrational temperature.

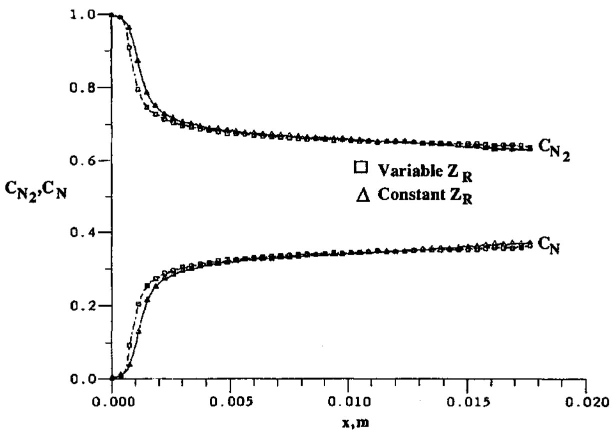

Fig. 5 Influence of rotational number on concentration.

tional temperature is a result of the fact that, with reduced energy transfer from translational modes to the internal modes, more energy is available for dissociation with the result that the translational energy is reduced slightly. This is confirmed by the results shown in Fig. 5, which shows the mass fractions of N_2 and N.

Figure 6 compares the effects of reaction rates on the results. The Appleton rates used by Park[1] result in smaller amounts of dissociation and a corresponding small shift in peak temperatures. As is seen from the figure, the effects of the rate expression is somewhat small. Because of this, subsequent results employed Byron's rates.

The role of H_2O is seen in Fig. 7. Two H_2O mole fractions, 0.1% and 1%, were considered in the simulation. The results indicated in Fig. 7 are those appropriate for the 1% case. The vibrational temperature of H_2O in the nonequilibrium region is higher than that of N_2, because of the higher energy exchange cross section. The small shift in the peak rotational and vibrational temperatures of N_2 indicated in Figs. 8 and 9 can be attributed to the presence of H_2O and its higher deactivation rate of N_2.

Figures 10 and 11 compare the present computations with the experimental results of Refs. 2 and 4 and the two-temperature model of Park.[1] Because the effects of a variable rotation number and the presence of H_2O impurity were essentially small, comparisons are made for the case of constant rotational number. The present results for the rotational temperature underpredict the rotational temperature of N_2^+ measured in Ref. 2 and is in excellent agreement with the point measured by Sharma and Gillispie,[4] which was reported as 8800 ± 230 K. As may be seen from Fig. 10, the suggestion made in Ref. 4 that the rotational temperatures of N_2 and N_2^+ are in equilibrium is not supported by the present calculation.

Figure 11 shows that the electronic ground state of N_2 and N_2^+ are not in vibrational equilibrium. The measured temperature[4] is 6100 ± 560. Again, the present calculation is in excellent agreement with experiment. The discrepancy between our calculations and those of Park[1] suggests that Park's vibrational model does not have the correct dependance on vibrational temperature.

Finally, Fig. 12 shows a typical plot of translational, rotational, and vibrational temperatures. As may be seen from

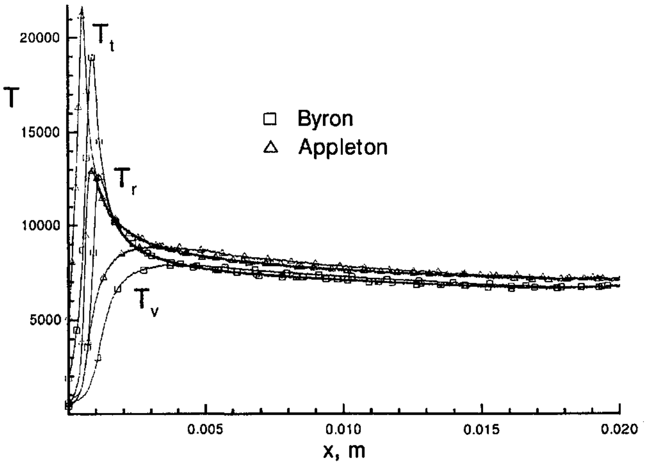

Fig. 6 Comparison of temperatures for different rate sets.

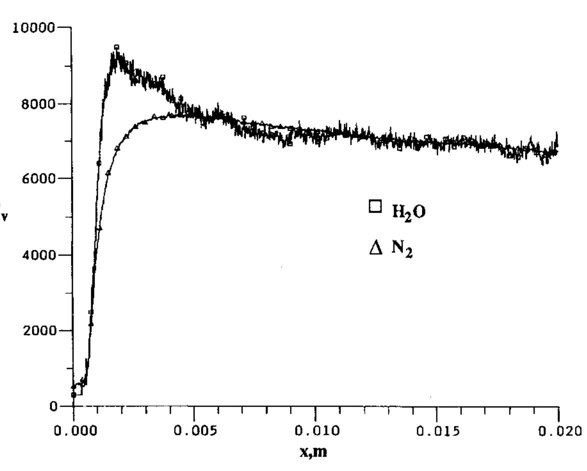

Fig. 7 Effect of H_2O impurity on vibrational temperature.

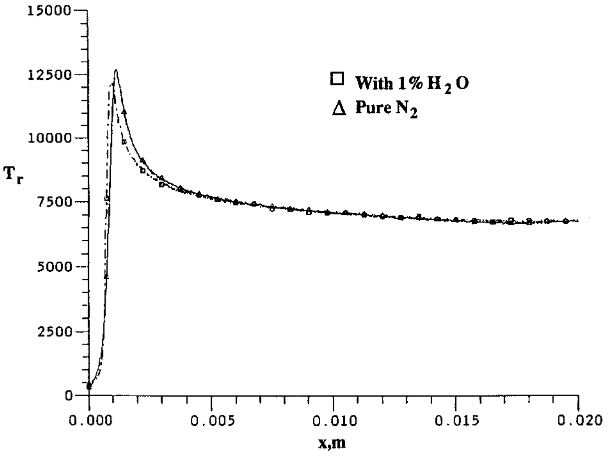

Fig. 8 Effect of H_2O on N_2 rotational temperature.

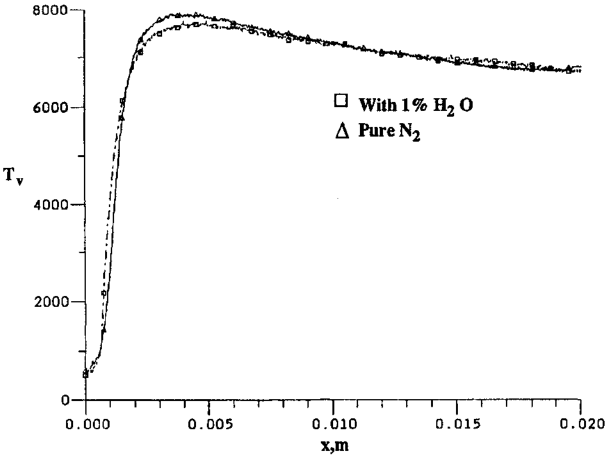

Fig. 9 Effect of H_2O on N_2 vibrational temperature.

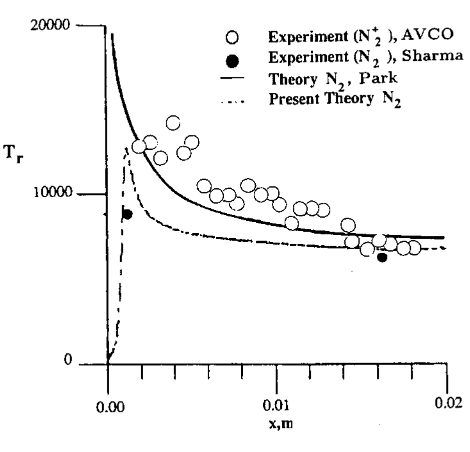

Fig. 10 Comparison of theory and experiment, rotational temperature.

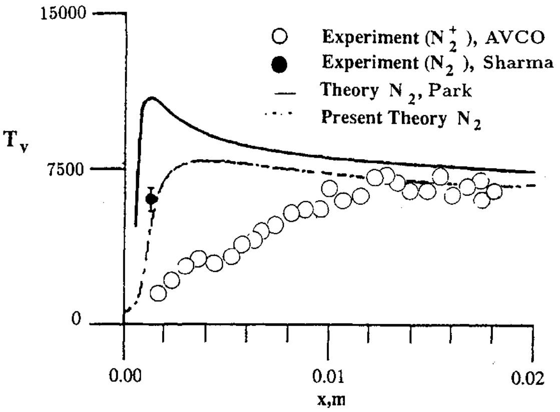

Fig. 11 Comparison of theory and experiment, vibrational temperature.

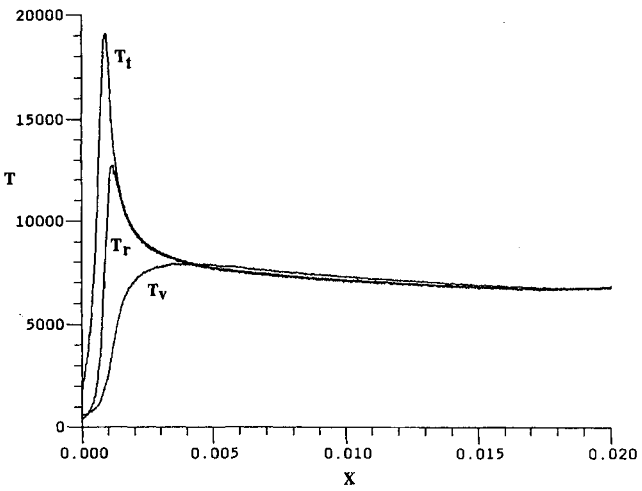

Fig. 12 Temperature distribution behind shock wave.

the figure, the present calculations support the conclusion of Ref. 4, that a two-temperature model is not adequate to describe nonequilibrium regions behind shock waves.

The question arises as to why DSMC calculations are more accurate than continuum calculations. Two important reasons can be advanced. First, DSMC requires the use of cross sections that are energy-dependent. On the other hand, continuum calculations require the use of rates. In order to calculate rates from cross sections, one needs to specify a distribution function and the temperatures that appear in the distribution function. Such information is not known a priori. This introduces major uncertainties into continuum calculations.

The second reason is grid resolution. In continuum methods, grid size cannot be less than a local mean freepath. On the other hand, DSMC requires a grid resolution that is typically of the order of a third of a local mean freepath. Thus, continuum methods cannot possibly compete with the accuracy of DSMC methods in regions where large gradients exist.

Concluding Remarks

Park's two-temperature theory was developed assuming that N_2 and N_2^+ were in rotational equilibrium and that rotational and translational temperatures were in equilibrium. Both of the above assumptions were not substantiated by the present calculations. Because rate expressions should depend on all relevant temperatures in nonequilibrium flows, it is suggested that Park's two-temperature model should be re-examined and modified to reflect the results of the current simulation and the experiment of Sharma and Gillespie.[4]

Acknowledgments

This work is supported in part by NASA's Cooperative Agreement NCCI-112; the Hypersonic Aerodynamic Program Grant NAGW-1022 funded jointly by NASA, the Air Force Office of Scientific Research, the Office of Naval Research, and the Mars Mission Center funded by NASA Grant NAGW-1331. The authors thank G. A. Bird for his guidance and advice.

References

[1] Park, C., "Assessment of a Two-Temperature Kinetic Model for Dissociating and Weakly Ionizing Nitrogen," *Journal of Thermophysics and Heat Transfer*, Vol. 2, Jan. 1988, pp. 8–16.

[2] Allen, R. A., "Nonequilibrium Shock Front Rotational, Vibrational and Electronic Temperature Measurements," AVCO Everett Research Lab., Research Rept. 186, Aug. 1964.

[3] Appleton, J. P., Steinberg, M., and Liquornik, D. J., "Shock-Tube Study of Nitrogen Dissociation using Vacuum-Ultraviolet Light Absorption," *Journal of Chemical Physics*, Vol. 48, Jan. 1968, pp. 599–608.

[4] Sharma, S. P., and Gillespie, W., "Nonequilibrium and Equilibrium Shock Front Radiation Measurement," *Journal of Thermophysics and Heat Transfer*, Vol. 5, July–Sept. 1991, pp. 257–265.

[5] Olynick, D. P., Moss, J. N., and Hassan, H. A., "Monte Carlo Simulation of Re-Entry Flows using a Bimodal Vibrational Model," *Journal of Thermophysics and Heat Transfer*, Vol. 4, July 1990, pp. 273–277.

[6] Millikan, R. C., and White, D. R., "Systematics of Vibrational Relaxation," *Journal of Chemical Physics*, Vol. 39, Dec. 1963, pp. 3209–3213.

[7] Bird, G. A., "Direct Simulation of AOTV Entry Flows," AIAA Paper 86-1310, June 1986.

[8] Blauer, J. A., and Nickerson, G. R., "A Survey of Vibrational Relaxation Rate Data for Processes Important to CO_2-N_2-H_2O Infrared Plume Radiation," AIAA Paper 74-536, June 1974.

[9] Kurian, J., and Sreekanth, A. K., "Density Gradient Measurements of Vibrational Relaxation in (N_2 + H_2O) and (AR + H_2O) Mixtures," *16th International Shock Tube Symposium*, Aachen, Germany, 1987, pp. 411–419.

[10] Bird, G. A., "Nonequilibrium Radiation During Reentry at 10 km/sec," AIAA Paper 87-1543, June 1987.

[11] Parker, J. G. "Rotational and Vibrational Relaxation in Diatomic Gases," *Physics of Fluids*, Vol. 2, July–Aug. 1959, pp. 449–462.

[12] Boyd, I. D., "Rotational-Translational Energy Transfer in Rarefied Nonequilibrium Flow," *Physics of Fluids*, Vol. 2, March 1990, pp. 447–452.

[13] Herzberg, G., *Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, Reinhold, NY, 1945, pp. 280–281.

[14] Bird, G. A., "Monte-Carlo Simulation in an Engineering Context," *Progress in Astronautics and Aeronautics Series: Rarified Gas Dynamics*, Vol. 74, Part 1, edited by S. S. Fisher, 1981, pp. 239–255.

[15] Vincenti, W. G., and Kruger, C. H., Jr., *Introduction to Physical Gas Dynamics*, Robert E. Krieger, Malabar, FL, 1986, p. 231.