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Direct Molecular Simulation of a Dissociating Diatomic Gas*

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The direct simulation Monte Carlo method is extended to cover molecular dissociation and recombination reactions. The model also includes internal degrees of freedom with separate relaxation times for rotation and vibration. The model is based on a classical collision theory analysis that provides an expression for the equilibrium state and allows the appropriate simulation parameters to be inferred from thermodynamic data for real gases. The model is first tested by the computation of the constant volume relaxation of a homogeneous gas sample. A finite difference procedure is then used to extend this program to cover the dissociation relaxation zone behind strong normal shock waves. A number of nitrogen cases are computed and the results are in agreement with existing experimental data.

1. INTRODUCTION

The direct simulation Monte Carlo method [1, Chaps. 7–11] is a technique for the computer modeling of a gas flow by some thousands of simulated molecules. The velocity components and position coordinates of these molecules are stored in the computer and are modified with time as the molecules are concurrently followed through representative collisions and boundary interactions in simulated physical space. The existing applications range from homogeneous simple monatomic gas relaxation studies, to multidimensional flows of mixtures of gases with internal degrees of freedom.

A collision theory analysis of the dissociation–recombination reaction that is compatible with the direct simulation Monte Carlo method has recently been developed [1, Chap. 12]. This analytical model incorporates the standard collision theory result for the dissociation reaction rate and leads to an expression for the equilibrium state that is identical in form to the law of mass action. If a particular diatomic gas is to be simulated, a comparison of the theoretical and experimental dissociation rates gives the appropriate value of the reactive cross section, while the corresponding comparison for the equilibrium degree of dissociation provides the effective binary collision lifetime parameter.

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The purpose of the present paper is to present an extension to the theory and to demonstrate its application to a particular reacting gas flow. The extension permits a more realistic relationship between the elastic and reactive cross sections and removes a restriction on the allowable ratio of the forward and backward reaction rate constants. Nitrogen has been chosen as the test gas and the relaxation zone behind a strong normal shock wave serves as the demonstration flow. This flow has been widely studied in shock tube experiments that have provided much of the existing data on dissociation and recombination reaction rates in diatomic gases.

2. Diatomic Gas Model

2.1. *Translational Scattering*

The first choice that must be made relates to the basic scattering model. The inverse power law model is the most convenient because the deflection angle depends on a single parameter. The exponent of the power law may be chosen to match the temperature dependence of the coefficient of viscosity to that of the gas being modeled. The flows under consideration here are, however, quite insensitive to this parameter and advantage has been taken of the computational simplicity of the limiting case of the hard sphere model. This has a fixed total collision cross section σ.

2.2. *Rotational and Vibrational Modes*

The phenomenological models that are described in [1, Sect. 11.3] may be applied to any of the inverse power law models. The Larsen–Borgnakke model [3] must be chosen over the energy sink model for a reacting gas, since it is essential that the high speed tail of the translational distribution function should not be distorted. Previous applications of this method have been restricted to a simple gas with a fixed number of internal degrees of freedom and a single relaxation time. For this study, the model must be extended to cover a mixture of atoms and molecules and to include the partially excited vibrational mode with a separate relaxation time to that for the rotational mode.

The harmonic oscillator approximation may be used to determine the equivalent (noninteger) number of degrees of freedom of vibration. The specific internal energy e_V associated with the vibrational energy is then [2, p. 135]

$$e_V = R\Theta_V/[\exp(\Theta_V/T) - 1], \tag{1}$$

where R is the gas constant, T is the temperature, and Θ_V is the characteristic temperature for vibration. Equipartition requires each fully excited degree of freedom to contain energy $\frac{1}{2}RT$, so that the "equivalent number of degrees of freedom" corresponding to the vibrational energy is

$$\zeta_V = 2(\Theta_V/T)/[\exp(\Theta_V/T) - 1]. \tag{2}$$

The relaxation time in the Larsen–Borgnakke method is adjusted by setting varying proportions of elastic and inelastic collisions. In the present case, the rotational relaxation rate was set by the specification of the fraction g_{r} of collisions with energy interchange to two degrees of freedom and the vibrational relaxation rate by setting the fraction g_{v} of these in which the effective number of degrees of freedom ζ is increased to $2 + \zeta_{\mathrm{v}}$.

The rotational and vibrational energies are stored separately for each molecule and the internal energy E_{i} in a collision is equal to the sum of the individual rotational energies when $\zeta = 2$ and to the sum of the rotational and vibrational energies when $\zeta = 2 + \zeta_{\mathrm{v}}$. The total energy E_{c} in a collision is equal to the sum of E_{i} and the translational energy $E_{\mathrm{t}} = \frac{1}{2} m_{\mathrm{r}} c_{\mathrm{r}}^2$, where m_{r} is the reduced mass and c_{r} is the relative speed. The total energy E_{c} is conserved in the collision, and the postcollision translational energy is sampled from the appropriate distribution function [1, Eq. (11.22)]. The acceptance–rejection method is used for this sampling and the ratio of the probability of a particular value of E_{t}^* to the maximum probability is

$$(\zeta E_{\mathrm{t}}^*/E_{\mathrm{c}})[(1 - E_{\mathrm{t}}^*/E_{\mathrm{c}})/(1 - 1/\zeta)]^{\zeta-1}. \tag{3}$$

The postcollision internal energy E_{i}^* is then given by $E_{\mathrm{c}} - E_{\mathrm{t}}^*$ and the distribution function [1, Eq. (11.24)] for the assignment of internal energy ϵ_{i}, to the first of the two molecules leads to the probability ratio,

$$2^{\zeta-2}[(\epsilon_{\mathrm{i},1}/E_{\mathrm{i}})(1 - \epsilon_{\mathrm{i},1}/E_{\mathrm{i}})]^{\zeta/2-1}. \tag{4}$$

The second molecule is, of course, assigned the internal energy $\epsilon_{\mathrm{i},2} = E_{\mathrm{i}} - \epsilon_{\mathrm{i},1}$. Note that the latter distribution is uniform when $\zeta = 2$.

The Larsen–Borgnakke method is readily extended to the rearrangement of the translational and internal energies of a molecule in collision with an atom. The probability ratio corresponding to Eq. (3) is

$$(\zeta/2)(E_{\mathrm{t}}^*/E_{\mathrm{c}})[1 - E_{\mathrm{t}}^*/E_{\mathrm{c}})/(1 - 2/\zeta)]^{\zeta/2-1}, \tag{5}$$

and there is no longer any need for Eq. (4).

2.3. *Dissociation and Recombination*

The "simulation compatible" collision theory [1, Chap. 12] employs a reactive cross section σ_{R} defined by

$$\begin{aligned} \sigma_{\mathrm{R}} &= 0 && \text{for } \tfrac{1}{2} m_{\mathrm{r}} c_{\mathrm{r}}^2 < E_{\mathrm{a}}, \\ \sigma_{\mathrm{R}} &= \sigma_0 \left(1 - \frac{2E_{\mathrm{a}}}{m_{\mathrm{r}} c_{\mathrm{r}}^2}\right) \left(\frac{m_{\mathrm{r}} c_{\mathrm{r}}^2}{2E_{\mathrm{a}}} - 1\right)^j && \text{for } \tfrac{1}{2} m_{\mathrm{r}} c_{\mathrm{r}}^2 > E_{\mathrm{a}}, \end{aligned} \tag{6}$$

where E_{a} is the activation energy of the reaction and σ_0 is a reference cross section.

For $j = 0$ and hard sphere molecules, this reactive cross section is consistent with a steric factor of σ_0/σ and with the translational energy based on the relative velocity along the line of centers. The minimum usable value of j is -1 and, as $\frac{1}{2}m_r c_r^2 \to E_a$, this case corresponds to a steric factor of σ_0/σ and unrestricted relative energy. Positive values of j yield a "line of centers" cross section that increases with the margin between the relative translational energy and the activation energy.

Separate reference cross sections must be applied to molecule–molecule, molecule–atom, and atom–atom collisions. These are denoted by $\sigma_{0,\mathrm{MM}}$, $\sigma_{0,\mathrm{MA}}$, and $\sigma_{0,\mathrm{AA}}$, respectively. Similarly, the number density n and mass m of the atoms and molecules are distinguished by the single subscripts A and M. The rate of loss of molecules due to dissociation reactions with an energy of dissociation E_d is [1, Eq. (12.13)]

$$-\frac{dn_\mathrm{M}}{dt} = \tfrac{1}{2}n_\mathrm{M}(\sigma_{0,\mathrm{MM}}n_\mathrm{M} + 6^{1/2}\sigma_{0,\mathrm{MA}}n_\mathrm{A})\left(\frac{8kT}{\pi m_\mathrm{A}}\right)^{1/2} \times \Gamma(j+2)\left(\frac{kT}{E_\mathrm{d}}\right)^{j} \exp\left(-\frac{E_\mathrm{d}}{kT}\right), \tag{7}$$

where t is time, k is the Boltzmann constant, and $\Gamma(x)$ is the gamma function. The dissociation rate coefficients $k_{\mathrm{d_M}}$ and $k_{\mathrm{d_A}}$ for the molecule–molecule and molecule–atom collisions can then be written

$$k_{\mathrm{d_M}} = \tfrac{1}{2}\Gamma(j+2)\,\mathcal{N}\sigma_{0,\mathrm{MM}}\left(\frac{8kT}{\pi m_\mathrm{A}}\right)^{1/2}\left(\frac{kT}{E_\mathrm{d}}\right)^{j}\exp\left(-\frac{E_\mathrm{d}}{kT}\right) \tag{8}$$

and

$$k_{\mathrm{d_A}} = (6^{1/2}\sigma_{0,\mathrm{MA}}/\sigma_{0,\mathrm{MM}})k_{\mathrm{d_M}}.$$

Avogadro's number $\mathcal{N}$ has been included to convert from molecule numbers to moles.

Recombination is a ternary reaction that requires the consideration of triple or three-body collisions. This is most conveniently done by assigning a "lifetime" to a binary collision and then regarding the triple collision as a second binary collision between the pair of particles in the binary collision and a third particle. The collision lifetime of an atom–molecule is assumed to have the form

$$a_{t_{\mathrm{AM}}}\sigma_{\mathrm{AM}}^{1/2}/c_r, \tag{9}$$

where $a_{t_{\mathrm{AM}}}$ is a nondimensional collision time parameter and σ_{AM} is the total (elastic) collision cross section for an atom–molecule collision. Recombination is assumed to occur at each triple collision involving at least two atoms, so that the a_t parameters effectively express the recombination probabilities. The elastic cross section for the collision of this pair with another atom is denoted by $\sigma_{\mathrm{A(AM)}}$. The extension of the subscript notation to the other types of collision is obvious. The rate of formtaion of molecules is then [1, Eq. (12.14)]

$$\frac{dn_{\mathrm{M}}}{dt} = n_{\mathrm{A}}{}^2[n_{\mathrm{M}}\{\tfrac{1}{2}a_{t,\mathrm{AA}}\sigma_{\mathrm{M(AA)}}\sigma_{\mathrm{AA}}^{3/2} + (2/3^{1/2})\, a_{t,\mathrm{AM}}\sigma_{\mathrm{A(AM)}}\sigma_{\mathrm{AM}}^{3/2}\} + (\tfrac{3}{8})^{1/2}\, n_{\mathrm{A}}a_{t,\mathrm{AA}}\sigma_{\mathrm{A(AA)}}\sigma_{\mathrm{AA}}]\left(\frac{8kT}{m_{\mathrm{A}}}\right)^{1/2}. \tag{10}$$

In equilibrium, the rate of loss of molecules given by Eq. (9) must be balanced by the corresponding rate of gain given by Eq. (10), and the two equations may be equated. A number of sets of relationships between the collision cross sections and lifetimes exist such that the resulting expression corresponds exactly with the law of mass action. The set given earlier [1, Eq. (12.15)] requires that $k_{\mathrm{d}_{\mathrm{M}}}$ should be twice $k_{\mathrm{d}_{\mathrm{A}}}$. The following set replaces this constant factor of 2 by the arbitrary parameter l;

$$\begin{aligned} \sigma_{0,\mathrm{MM}} &= l6^{1/2}\sigma_{0,\mathrm{MA}} = \sigma_0\,, \\ a_{t,\mathrm{AM}}\sigma_{\mathrm{AM}}^{3/2} &= (3^{1/2}/4)\, a_{t,\mathrm{AA}}\sigma_{\mathrm{AA}}^{3/2}\,, \end{aligned} \tag{11}$$

and

$$a_{\mathrm{A(AM)}} = \sigma_{\mathrm{M(AA)}} = (l/2)(\tfrac{3}{2})^{1/2}\,\sigma_{\mathrm{A(AA)}} = \sigma_{\mathrm{AA}}\,.$$

The equilibrium condition remains [1, Eq. (12.18)]

$$\frac{\alpha^2}{1-\alpha} = \frac{m_{\mathrm{A}}}{\rho}\cdot\frac{\sigma_0\Gamma(j+2)}{4a_{t,\mathrm{AA}}\sigma_{\mathrm{AA}}^{5/2}}\left(\frac{kT}{E_{\mathrm{d}}}\right)^j \exp\left(-\frac{E_{\mathrm{d}}}{kT}\right), \tag{12}$$

where ρ is the density and $\alpha = n_{\mathrm{A}}m_{\mathrm{A}}/\rho$ is the degree of dissociation.

Each time a binary elastic collision involving at least one molecule is computed, the relevant reactive cross section is calculated from Eq. (6), and the ratio of this to the elastic cross section gives the probability of a dissociation. The standard acceptance–rejection method is then used to decide whether the dissociation actually occurs. The dissociation energy is removed from the collision pair, partly from the translational mode through a reduction in the postcollision relative speed and partly from the internal modes. The remaining energy of the molecule that dissociates is then put into the translational relative energy of the two resulting atoms. The overall momentum, as well as energy, is conserved in the reaction.

More extensive extensions of the standard simulation procedures are required to deal with the triple collisions. Just as separate time counting parameters are used for each of the four classes of collision in a binary gas mixture [1, Sect. 10.2], eight time parameters may be specified for the triple collision classes. Four of these classes involve two atoms and may therefore give rise to recombinations. The increment to these time counters at each recombination is generally a very large multiple of the basic time interval Δt_m over which the molecular motion and collisions are uncoupled and care must be taken to prevent distortions in the collision rate. The time counters are initialized by setting them to a random fraction of the first possible recombination and the computation of this collision is not proceeded with further. The time increment is inversely proportional to the product of three number densities corresponding to the molecules involved and to the cross section, which may be proportional to some power of the temperature. Since these may change significantly during the average triple collision time increment, the macroscopic properties at the previous collision are stored and the excess time in the triple collision time counters is modified at each Δt_m to allow for these changes. When a recombination is computed, the precollision center of mass velocity of the three particles is calculated and is retained as the center of mass velocity of the two postcollision particles. The recombination energy is added to the precollision translational energy and the total energy is divided between the two postcollision particles on the assumption that the direction of the postcollision relative velocity may be chosen at random. This effectively assumes hard sphere collision mechanics for the triple collision.

3. Constant Volume Relaxation

The initial test of the real diatomic gas simulation model has been made in a simulation program for the relaxation to equilibrium of a spatially homogeneous gas with all its energy initially in the translational mode. Given a set of molecular parameters, and the final equilibrium temperature T, the specific internal energy of the gas is

$$e = \frac{k}{m_M}\left[\frac{5+\alpha}{2}T + \frac{(1-\alpha)\Theta_V}{\exp(\Theta_V/T)-1} + \alpha\frac{E_d}{k}\right]. \tag{13}$$

The initial temperature of the gas is, therefore, $(2/3)(m_M/k)e$.

Temperatures are normalized by dividing them by the final equilibrium temperature, masses by the mass of an atom, distances by the mean free path in the initial (molecular) gas, and velocities by the most probable speed of an atom at the final temperature. The actual number of simulated molecules is set as data and the density ρ is most conveniently specified by also setting the number of molecules within one cubic mean free path. The other quantities that determine the composition of the gas are the ratio of σ_0 to σ_{AA}, the parameter $a_{t_{AA}}$, the index j, and the dissociation energy E_d. In addition, the fractions g_r and g_V that control the rotational and vibrational relaxation rates must be input as data, together with the time interval Δt_m. The program also makes provision for setting an activation energy E_a less than the dissociation energy. It is envisaged that E_a would be set sufficiently close to E_d that the energy difference would almost always be available in the internal modes of the collision partners.

The program was tested over a wide range of input variables for an initial 500 molecules. It was found always to lead to the final temperature predicted by Eq. (13), with the rotational and vibrational modes in equilibrium with the translational mode, and with the degree of dissociation predicted by Eq. (12).

For gases such as oxygen and nitrogen, it has been shown [3] that Eq. (12) can be written

$$\alpha^2/(1-\alpha) = (\rho_d/\rho)\exp(-E_d/kT), \tag{14}$$

where ρ_d, the characteristic density of dissociation, is very nearly constant over the temperature range 1000 to 7000 K. The suggested values of ρ_d for oxygen and nitrogen are 150 and 130 g cm^{-3}. For our classical model,

$$\rho_d = m_A\sigma_0\Gamma(j+2)(kT/E_d)^j/(4a_{t,AA}\sigma_{AA}^{3/2}) \tag{15}$$

and, for nitrogen, m_A is 2.325×10^{-23} g and σ_{AA} is 2.83×10^{-15} cm^2 when based on a nitrogen molecule diameter of 3.78×10^{-8} cm, with both the atom and molecule being regarded as equal density spheres. Then, for $j = 0$ and σ_0 equal to σ_{AA}, we find that the recombination probability parameter $a_{t_{AA}}$ is very nearly equal to 0.0003. This may be taken as a typical value and shows that recombinations are very rare events in comparison with elastic collisions.

The above order of magnitude study is consistent with the experimental finding that the width of the relaxation zone behind shock wave is of the order of thousands of mean free paths. This means that it is computationally impractical to apply the direct simulation Monte Carlo method to the complete one-dimensional shock wave formation flow in a similar manner to the existing calculations for nonreacting gases [5]. The alternative is to take advantage of the fact that the translational and rotational shock thickness is very small in comparison with the relaxation zone in which these modes are in local thermodynamic equilibrium. The relaxation zone may then be computed by a homogeneous gas calculation similar to that described above. The final equilibrium conditions again supply the reference state with the initial conditions corresponding to a gas in translational and rotational equilibrium, but with zero vibrational excitation and degree of dissociation. The variation of the density and velocity and the modification of the constant volume temperature profile may be determined in a parallel finite difference calculation that is directly coupled to the simulation.

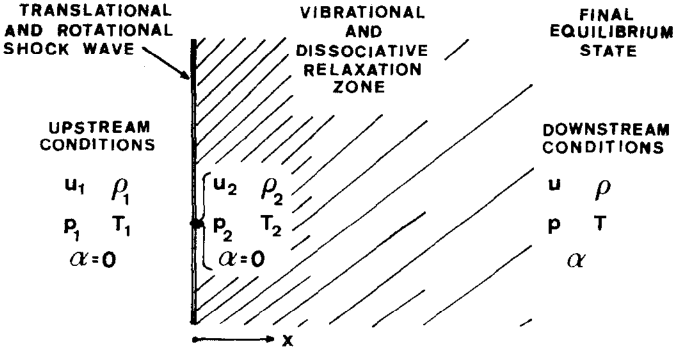

FIG. 1. Assumed physical Model for the shock wave.

4. Theory for the Shock Relaxation Zone

The flow model is shown in Fig. 1. The upstream conditions are denoted by the subscript 1, the conditions behind the translational and rotational shock wave by subscript 2, and the final equilibrium values are unsubscripted. The initial conditions for the Monte Carlo simulation are provided by the subscript 2 gas and the first task is to relate these to the final equilibrium state which serves as the reference state.

The equations of continuity, momentum, energy, and state are, respectively,

$$\rho_1 u_1 = \rho_2 u_2 = \rho u, \tag{16}$$

$$p_1 + \rho_1 u_1^2 = p_2 + \rho_2 u_2^2 = p + \rho u^2, \tag{17}$$

$$e_1 + p_1/\rho_1 + \tfrac{1}{2}u_1^2 = e_2 + p_2/\rho_2 + \tfrac{1}{2}u_2^2 = e + p/\rho + \tfrac{1}{2}u^2 = h_0, \tag{18}$$

and

$$p_1/(\rho_1 T_1) = p_2/(\rho_2 T_2) = p/[(1+\alpha)\,\rho T] = k/m_M, \tag{19}$$

where p is the pressure, u is the flow velocity, and h_0 is the total enthalpy.

The initial internal energy is $e_2 = \frac{5}{2}RT_2$ and the equilibrium energy e is given by Eq. (13). The result for the density is

$$\left.\begin{matrix}\rho_1\\ \rho_2\end{matrix}\right\} = \rho\left[\frac{7}{12}(A+1) \pm \left\{\frac{49}{144}(A+1)^2 - \frac{1}{3}\left(\frac{e}{u^2} + A + \frac{1}{2}\right)\right\}^{1/2}\right]^{-1}, \tag{20}$$

where $A = (1+\alpha)kT/(2m_A u^2)$. The solution with the negative sign for ρ_2 gives the required initial state, while the solution with the positive sign for ρ_1 applies to the complete jump. The initial velocity follows directly from Eq. (16), while the initial temperature is

$$T_2 = \tfrac{2}{7}[(2m_A/k)(e + \tfrac{1}{2}u^2 - \tfrac{1}{2}u_2^2) + (1+\alpha)T]. \tag{21}$$

For the calculation of the relaxation process, the gas may be regarded as a mixture of a diatomic gas with just two fully excited degrees of freedom and a monotamic gas. The excitation of the vibrational mode and the dissociations remove specific heat q from this gas and change its relative composition. The appropriate differential conservation and state equations are

$$\frac{d\rho}{\rho} + \frac{du}{u} = 0, \tag{22}$$

$$\frac{dp}{p} + \frac{2m_A u^2}{(1+\alpha)\,kT}\frac{du}{u} = 0, \tag{23}$$

$$\frac{7+3\alpha}{4}\frac{dT}{T} + \frac{3}{4}d\alpha + \frac{m_A u^2}{kT}\frac{du}{u} = \frac{m_A dq}{kT} \tag{24}$$

and

$$\frac{dp}{p}-\frac{d\rho}{\rho}-\frac{dT}{T}-\frac{d(1+\alpha)}{1+\alpha}=0. \tag{25}$$

These equations lead to the following difference equations for the temperature, velocity, and density;

$$\frac{\Delta T}{T}=\left[\left(\frac{\Delta q}{u^2}-\frac{3A}{2}\frac{\Delta\alpha}{1+\alpha}\right)\left(1-\frac{1}{A}\right)-\frac{\Delta\alpha}{1+\alpha}\right]\Big/\left[1+\frac{7+3\alpha}{2(1+\alpha)}A\left(1-\frac{1}{A}\right)\right] \tag{26}$$

and

$$\frac{\Delta u}{u}=-\frac{\Delta\rho}{\rho}=\frac{\Delta q}{u^2}-\frac{(7+3\alpha)A}{2(1+\alpha)}\frac{\Delta T}{T}-\frac{3A}{2}\frac{\Delta\alpha}{1+\alpha}. \tag{27}$$

5. Computation of the Shock Relaxation Zone

The analysis of Section 4 permits the dissociation relaxation zone behind a normal shock wave to be computed by a straightforward extension of the constant volume relaxation program that was described in Section 3. It is assumed that experimental results and/or equilibrium calculations are available for the definition of the downstream equilibrium gas state. These downstream conditions provide the reference quantities and Eqs. (20), (21), and (16) are used to determine the initial conditions for the computation. A check on the adequacy of the diatomic gas model may be made at this stage, in that experimental degree of dissociation may be compared with the value predicted by Eq. (12).

The following steps are then repeated for each incremental time interval Δt_m.

(i) The collisions, including dissociations and recombinations, appropriate to a constant volume relaxation over this time interval are computed as described in Section 3. The change in the degree of dissociation $\Delta\alpha$ and the heat loss Δq from the translational and rotational modes due to dissociation, recombination, and vibrational excitation are sampled during this process.

(ii) Equation (26) is used to compute the value of ΔT corresponding to the values of $\Delta\alpha$ and Δq from the simulation. The resulting temperature differs from that obtained from the simulation. Appropriate adjustment is made to all the molecular thermal velocities and rotational energies to enforce the temperature change from Eq. (26). The flow velocity and density increments Δu and $\Delta\rho$ are calculated from Eq. (27) and these quantities are adjusted accordingly.

(iii) The direct first-order differencing procedure can be expected to lead to some systematic error and this is monitored by checking the progressive value of the total enthalpy h_0. Should this differ from the initial value, half the difference is "fed back" as an additional change in the molecular velocities and rotational energies.

This has been found to keep the total enthalpy constant to within a small fraction of 1 % over thousands of time increments, with a similar error in the final downstream equilibrium conditions.

(iv) The increment dx in the distance x behind the translational and rotational shock front is equal to $u\,\Delta t_m$.

6. RESULTS FOR NITROGEN

Kewley and Hornung [6] have reported nitrogen dissociation rates based on time-resolved optical inferferometry of the relaxation region behind a shick wave. The rate constant for molecule–molecule collisions over the temperature range 6000–14,000 K was found to be

$$k_{\mathrm{d_M}} = 2.3 \times 10^{29} T^{-3.5} \exp(-113,200/T) \tag{28}$$

cm^3 mole^{-1} sec^{-1}. A comparison of this equation with Eq. (8), keeping in mind that the minimum allowable value of j is -1, shows that this temperature exponent cannot be matched if $\sigma_{0,\mathrm{MM}}$ is regarded as a constant. The alternative is to set $\sigma_{0,\mathrm{MM}}$ in proportion to some power of temperature. This same power law dependence may also be applied to $a_{t,\mathrm{MM}}$ so as not to disturb the functional form of the equilibrium condition, defined by Eq. (12). At 7715 K, this leads to $\sigma_{0,\mathrm{MM}}$ equal to $0.843\sigma_{\mathrm{MM}}$ for $j = -1$, and $12.4\sigma_{\mathrm{MM}}$ for $j = 0$. A ratio $\sigma_{0,\mathrm{MM}}/\sigma_{\mathrm{MM}}$ that is significantly greater than unity is physically unreasonable and $j = -1$ has been preferred. The program does, however, allow $\sigma_{0,\mathrm{MM}}$ to exceed σ_{MM} and the "surplus probability" is taken up by allowing dissociations to occur whenever the sum of the intermolecular translational energy and the internal energies exceeds the dissociation energy. Kewley and Hornung found a $T^{-2.5}$ dependence for the rate constant $k_{\mathrm{d_A}}$ for molecule–atom collisions. A good fit with their results is, however, obtained by retaining the $T^{-3.5}$ dependence and setting the parameter l equal to $\frac{1}{3}$ so that $k_{\mathrm{d_A}} = 3k_{\mathrm{d_M}}$.

Hornung [7] has supplied the density profiles in the relaxation zone for three representative cases listed in Table I. The temperature 7715 K corresponds to Case 3, for which ρ_{d} is approximately 120 g cm^{-1}. Equation (15) then gives 0.00707 for the recombination parameter $a_{t,\mathrm{AA}}$. The predicted degree of dissociation for the model from Eq. (12) is then 0.472 which is in good agreement with the nitrogen value associated with the experiments. The rotational and vibrational relaxation parameters have been set as $g_{\mathrm{r}} = 0.2$ and $g_{\mathrm{v}} = 0.01$. These lead to a rotational relaxation time of about 10 mean collision times and a vibrational relaxation time of the order of 1000 mean collision times. The latter rate corresponds to the measured vibrational rate [8] for nitrogen at this temperature.

The computed profile for Case 3 with an initial 600 simulated molecules is shown in Fig. 2. The assumption of no vibrational excitation or dissociation within the shock has led, as expected, to an initial density that is somewhat lower than the experimental value. The subsequent agreement between the simulated and experi-

TABLE I

Flow Conditions for the Experimental Cases [71]

	Case		
	1	2	3
p_1 (Torr)	31	19	5
ρ_1 (g cm^{-3})	4.67×10^{-5}	2.86×10^{-5}	7.48×10^{-6}
u_1 (km sec^{-1})	4.80	5.60	7.31
T_2 (K)	6590	7100	7715
ρ_2/ρ_1	10	11.4	14.9
α_2	0.094	0.189	0.469

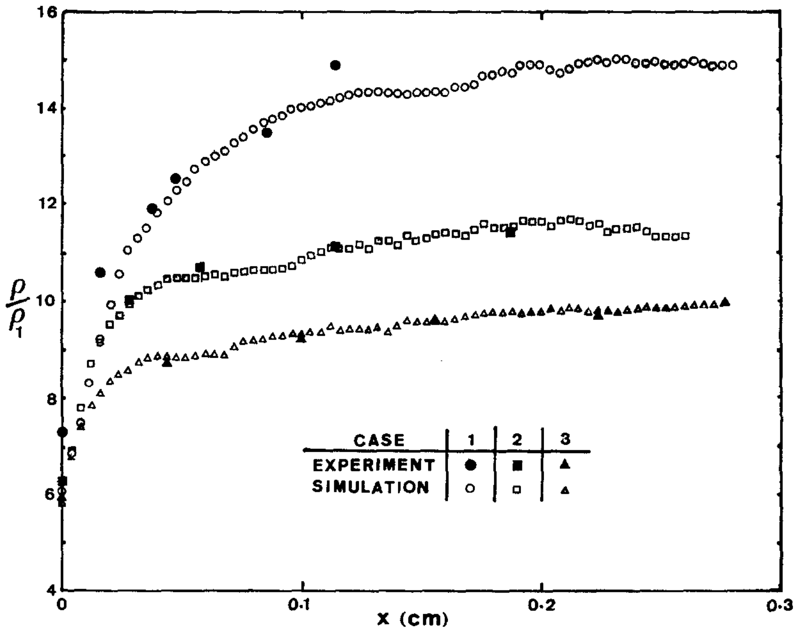

FIG. 2. Comparison of the computed and experimental relaxation zone density profiles in nitrogen.

mental profiles is very satisfactory. The irregularities in the computed profile in the near equilibrium situation are caused by statistical scatter, since only a small number of dissociations and recombinations occur in this region. Between $x = 1.8$ and $x = 2.8$ cm, only 17 dissociations and 14 recombinations occur, while the corresponding number of nonreacting collisions is 4,965,759. This illustrates the difficulties in the simulation of the reaction at a temperature that is approximately one-fifteenth of the characteristic temperature for dissociation. The mean degree of dissociation for x greater than 9.2 cm is 0.476. This is in excellent agreement with the values of 0.472 predicted by Eq. (12) and 0.469 quoted [7] for the Case 3 experiment. A similar computation was made for $j = 0$, but this did not lead to any significant change in the density profile.

Similar simulations for Cases 1 and 2 lead to equilibrium degrees of dissociation equal 0.092 and 0.190, respectively. These also agree well with the values of 0.093 and 0.188 from Eq. (12), and with the experimental values quoted in Table I. Figure 2 also presents a comparison between the computed and experimental density profiles for Cases 1 and 2. The agreement remains generally good, although the computed initial relaxation rate in Case 1 appears faster than the observed rate. For this flow, the initial density gradient is primarily set by the vibrational relaxation rate. It was found that the best curve through the experimental points requires a vibrational rate of approximately one-third of that actually employed. Slightly better overall agreement for the three cases would have been obtained with a slower vibrational rate and a smaller negative power law for the temperature in the dissociation rate equation (28). Similar comparisons with a wider range of experiments would lead to an optimum set of molecular parameters for simulation studies for each gas, and would hopefully provide physical information on the reactions at a more fundamental level than that available from bulk quantities such as the rate constant.

7. CONCLUDING REMARKS

The dissociation rate constants that have been deduced previously from shock relaxation zone measurements have been used to determine the molecular parameters associated with the molecular simulation model. These parameters are physically reasonable and their use in direct simulation flow computations ahs led to results that are in agreement with the original experiments. This has provided a test of the overall consistency of the simulation model, which may now be applied with some confidence to flows with marked translational nonequilibrium. For these flows, the conventional procedure which employs the Navier–Stokes equations with coupled thermodynamic rate equations would not be available.

The application of the direct simulation method to a problem involving marked translational nonequilibrium would generally present a less severe computational problem than the shock relaxation problem that has been treated here. For example, consider a meteor entry problem involving the hypervelocity flow of a diatomic gas past a particle with dimensions comparable with the mean free path. The ratio of the dissociative collision rate to the nonreacting collision rate would be much more favorable, while recombinations would be so unlikely that they could be neglected completely. A small number of ionizing collisions could be dealt with by including an additional reaction cross section similar to thta already employed for dissociation.

The calculations reported were carried out on a Digital Equipment PDP 11/40 system. A total of more than 100 million collisions were computed at a rate exceeding 250,000 per hr. The machine is run for 24 hr a day, 7 days a week without an operator so that the total task was equivalent to 2 week's use of a system with a total initial cost of the order of \$35,000. The same computing task would have required approximately 25 hr of CP time on a CDC 6600. This illustrates the cost effectiveness of a dedicated minicomputer for this type of calculation.

REFERENCES

1. G. A. BIRD, "Molecular Gas Dynamics," Oxford Univ. Press, London, 1976.
2. W. G. VINCENTI AND C. H. KRUGER, "Introduction to Physical Gas Dynamics," Wiley, New York, 1965.
3. P. S. LARSEN AND C. BORGNAKKE, DCAMM Report 52, The Technical University of Denmark, 1973.
4. M. J. LIGHTHILL, *J. Fluid Mech.* **2** (1957), 1.
5. G. A. BIRD, *Phys. Fluids* **13** (1970), 1172.
6. D. J. KEWLEY AND H. G. HORNUNG, *Chem. Phys. Lett.* **25** (1974), 531.
7. H. G. HORNUNG, private communication.
8. J. P. APPLETON, *J. Chem. Phys.* **47** (1967), 3231.