The use of the loaded-sphere molecular model for computer simulation of diatomic gases

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An approximate binary collision procedure is devised for the loaded-sphere molecular model and is used with Bird's direct simulation technique for computer experiments on diatomic gases. The collision procedure is tested by simulating the approach to equilibrium of a constant-speed gas of loaded spheres and good agreement with Jeans's (1904) theoretical prediction is obtained. The procedure is then used to study the structure of normal shock waves in the diatomic gas, giving mean velocity, density and temperature profiles. It is found that the present procedure consumes considerably more computer time than comparable simulations of monatomic gases.

1. Introduction

The direct simulation Monte Carlo method developed by Bird (1969) has previously been used to study a number of rarefied gas flows in which the molecules could be suitably represented by the inverse-power law models, the hard sphere being a particular member of this family. Bird's technique has provided almost perfect agreement with experimental results for shock-wave profiles (Schmidt 1969) where the inverse-power intermolecular potential was selected to fit transport data. While the shock structure is of the simplest gaseous phenomena (due to the lack of molecule–surface interactions and the prior knowledge of the upstream and downstream equilibrium conditions obtained from the conservation equations) Bird's method has also given good agreement with experimental results for the more complex flows around bodies (Vogenitz *et al.* 1968). The inverse-power law models are, however, only capable of exhibiting relaxation processes between the translational degrees of freedom and so are not suitable for studying phenomena in polyatomic gases involving relaxation between the translational and internal degrees of freedom. The success of Bird's technique leaves little doubt as to its validity and justifies its extension to more complex molecular models which are capable of representing the internal degrees of freedom of the gas.

This paper reports a first attempt to simulate a diatomic gas having rotation as its only form of internal energy. The process of most importance then is the coupling between the translational and rotational degrees of freedom. The model

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chosen to simulate the molecule is the loaded-sphere model, which is probably the simplest classical model capable of representing the five degrees of freedom of the gas. A binary collision procedure compatible with Bird's general technique is devised for the model and tested by simulating the approach to equilibrium of a sample of gas having initially constant translational and rotational molecular speeds. This procedure is then used to generate the shock wave.

2. Molecular model

The rigid loaded-sphere model was introduced by Jeans (1904) and has been used in a number of studies. In particular, Dahler & Sather (1963) have investigated transport properties of the loaded-sphere gas; Haight & Lundgren (1967) have used the model for a theory of strong shocks in diatomic gases. Only those details of the model pertinent to the present study will be given here. Further details are to be found in the above references.

The model may be described as a rigid sphere of mass m and diameter σ with its centre of mass offset a distance ϵ from the geometric centre. The mass distribution is symmetric about the axis joining the geometric and mass centres, and the moment of inertia about any axis normal to this symmetry axis is given as I, say. The dynamic state of the particle is defined by the position vector $\mathbf{L}$ of its centre of mass relative to some 'fixed' origin, the unit orientation vector $\hat{\mathbf{l}}$ indicating the direction from the centre of mass to the geometric centre, a translational velocity $\mathbf{v}$ and angular velocity $\boldsymbol{\omega}$. An arbitrary point on the surface of the sphere is given by the vector $\mathbf{s}$ relative to the centre of mass, where $\mathbf{s} = \epsilon\hat{\mathbf{l}} + \frac{1}{2}\sigma\hat{\mathbf{k}}$ and $\hat{\mathbf{k}}$ is the unit vector along the outward normal to the surface.

The particles are rigid, so that at collision an impulsive force is directed along the surface normal at the point of impact, giving rise (owing to the eccentricity of the mass distribution) to a moment about the centre of mass of the body and thus energy transfer between the translational and rotational modes. The body has only two rotational degrees of freedom, the third being dormant as a result of the component $\boldsymbol{\omega} . \hat{\mathbf{l}}$ being unchanged at collision. The collision dynamics have been formulated by a number of authors. Following Haight & Lundgren (1967) we consider a collision between two molecules 1 and 2 (figure 1). $\hat{\mathbf{k}}$ is the surface normal at the impact point and $i\hat{\mathbf{k}}$ is the vector impulse experienced by the molecule 2. Then, indicating the post-collisional variables with primes, we have that

$$\left. \begin{aligned} \mathbf{v}_1' &= \mathbf{v}_1 - (i/m)\,\hat{\mathbf{k}}, \quad \mathbf{v}_2' = \mathbf{v}_2 + (i/m)\,\hat{\mathbf{k}}, \\ \boldsymbol{\omega}_1' &= \boldsymbol{\omega}_1 - (i/I)\,(\mathbf{s}_1 \times \hat{\mathbf{k}}), \quad \boldsymbol{\omega}_2' = \boldsymbol{\omega}_2 + (i/I)\,(\mathbf{s}_2 \times \hat{\mathbf{k}}), \end{aligned} \right\} \tag{1}$$

where $\qquad i = -\acute{\mathbf{g}} . \hat{\mathbf{k}} / \{1/m + (1/2I)\,(\mathbf{s}_1 \times \hat{\mathbf{k}})^2 + (1/2I)\,(\mathbf{s}_2 \times \hat{\mathbf{k}})^2\}$

and $\qquad\qquad \acute{\mathbf{g}} = \mathbf{v}_2 + \boldsymbol{\omega}_2 \times \mathbf{s}_2 - \mathbf{v}_1 - \boldsymbol{\omega}_1 \times \mathbf{s}_1$

is the relative velocity of the impact points immediately prior to collision.

The method of generating the shock wave makes it necessary to formulate the collision of the loaded sphere with a specularly reflecting boundary moving at constant speed. This is readily done as such a collision may be represented by the

collision between a loaded sphere, and an unloaded sphere having the same translational velocity as the boundary but an infinite mass. The modifications to (1) to describe such a collision are obvious.
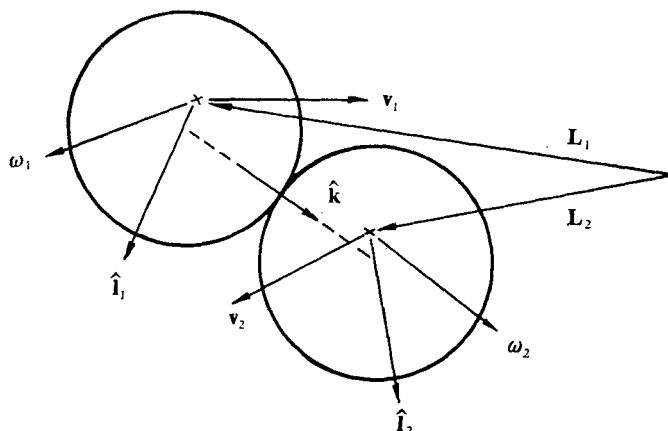

FIGURE 1. Loaded-sphere collision geometry.

Gas	Z_R
H_2	200–600
N_2	3–20
O_2	3–40

TABLE 1. Approximate ranges of rotational collision number Z_R obtained from experiment (see Herzfeld & Litovitz 1959)

Jeans (1904) showed that for a uniform loaded-sphere gas (having $\epsilon \ll \sigma$) of number density n, the relaxation between the translational and rotational energies is described by the relation

$$d\{\ln |e_r - \tfrac{2}{3}e_t|\}/dt = -\tfrac{5}{3}n\beta e_t^{\frac{1}{2}},\qquad(2)$$

where e_r = average rotational energy per molecule, e_t = average translational energy per molecule and β is a function of the model parameters,

$$\beta = (16\epsilon^2\sigma^2/3I)\,(\tfrac{2}{3}\pi m)^{\frac{1}{2}}.$$

For small departures from equilibrium $|e_r - \tfrac{2}{3}e_t|$ is approximately exponential in time, reducing to $1/e$ of its initial value in the relaxation time τ, where

$$\tau = \frac{3}{5\beta\pi e_t^{\frac{1}{2}}} = \frac{9}{20}\left(\frac{I}{m\epsilon^2}\right)\tau_c = Z_R\tau_c,\qquad(3)$$

τ_c being the mean time between collisions and Z_R the rotational collision number. Rotational energy is readily transferred for small values of Z_R, the rate of equilibration of energy becoming slower as Z_R increases. Typical values of Z_R are given in table 1 (see Hertzfeld & Litovitz 1959).

It is to be noted that the loaded sphere is probably the simplest (classical)

model for the diatomic molecule and, as such, suffers from a number of deficiencies. It can experience multiple encounters (or 'chattering collisions') and by doing so invalidates the assumption of molecular chaos: that precollisional states of collision pairs are uncorrelated. It is also to be noted that the model is more a convenient representation than a realistic one, the translation–rotational coupling arising probably as a result of molecular field, rather than mass, asymmetry (Hirschfelder, Curtiss & Bird 1954).

3. The method
3.1. *Collision simulation*

The crux of Bird's method lies in the probabilistic simulation of the binary collisions and the loading of the time advance of the whole system by the value of the relative translational velocity of each collision pair. It is in the development of an approximate binary collision procedure for the loaded-sphere gas that this work departs from earlier uses of Bird's technique. The general method followed is that reported by Bird (1969) in his review paper and only the necessary additional details are given here.

The simulated spatial region is divided into a number of cells and only those molecules residing in the same cell are considered as possible members of a collision pair in any elemental time interval. The determination of the molecules residing within any cell is carried out through the use of arrays which store the absolute and relative positions of the molecules, along with the number of molecules in cells up to the nth, where n may take values from 2–C, C being the total number of cells in the one-dimensional simulated region. For purposes of choosing the collision pair the relative positions of the molecules within the same cell are considered unimportant and the selection of the collision pair is then only dependent on the dynamic state of the molecules in that cell. For example, in a gas of hard spheres (Bird 1967) a molecular pair is selected at random and retained or rejected such that the probability of retention is proportional to the relative speed. If a pair is retained, an impact parameter (corresponding to the line of centres at impact) is chosen at random and the collision is computed, the new translational velocities being stored in place of the old, and a time counter advanced. Collisions of hard spheres (and general inverse-power law bodies) are easily and efficiently computed as a result of the symmetry of the model and the need to consider only the translational velocity components when selecting a collision pair. However, the addition of rotational motion and asymmetry in the case of the loaded sphere greatly adds to the complexity and programming detail involved in the collision procedure.

It may be seen from figure 1 and equations (1) that in order to calculate a collision it is necessary to specify $\mathbf{v}_1$, $\mathbf{v}_2$, $\boldsymbol{\omega}_1$, $\boldsymbol{\omega}_2$, $\hat{\mathbf{l}}_1$, $\hat{\mathbf{l}}_2$ and $\hat{\mathbf{k}}$. Of these variables the translational and rotational velocities, $\mathbf{v}$ and $\boldsymbol{\omega}$ respectively, are stored for each molecule and the orientation vector is restricted by the condition that $\boldsymbol{\omega} \cdot \hat{\mathbf{l}}$ is zero. This latter restriction is imposed in order to facilitate the selection of the orientation vector $\hat{\mathbf{l}}$ at collision and does not in any way detract from the model since $\boldsymbol{\omega} \cdot \hat{\mathbf{l}}$ is invariant for binary collisions and collisions with the specularly

reflecting boundaries. In describing the binary collision of loaded spheres Haight & Lundgren (1967) defined an interaction surface S (for fixed orientations $\hat{l}_1$ and $\hat{l}_2$) as the surface traced by the centre of mass of particle 2 as it moves in contact with particle 1. It was then shown that only 2-particles with mass centres in the volume $-\mathbf{g}.\hat{k}\,dt\,dS$ would collide with 1-particle on the element of surface dS during the period dt. For the loaded sphere $dS = \sigma^2\,d\hat{k}$, so the volume becomes $-\mathbf{g}.\hat{k}\sigma^2\,dt\,d\hat{k}$. Hence the probability of a pair of molecules with a particular set of orientations colliding is proportional to $-\mathbf{g}.\hat{k}$. One could construct a collision procedure to faithfully satisfy this result. A pair of molecules could be selected at random to give $\mathbf{v}_1$, $\mathbf{v}_2$, $\boldsymbol{\omega}_1$, $\boldsymbol{\omega}_2$, a set of orientation vectors $\hat{l}_1$, $\hat{l}_2$, $\hat{k}$ could then be suitably selected and $-\mathbf{g}.\hat{k}$ calculated. The collision pair, along with the orientations, would then be retained or rejected such that the probability of retention is proportional to the value of $-\mathbf{g}.\hat{k}$. However, such a method would be excessively time consuming as a result of the selection and rejection of a relatively large amount of information. The usefulness of this Monte Carlo technique is critically dependent on the efficiency of selection of the precollisional variables. An approximate collision procedure is devised.

It is assumed that $\epsilon/\sigma \ll 1$ so that to a reasonable approximation the molecular pair may be selected as for the unloaded hard sphere. That is, a pair is selected at random and retained or rejected such that the probability of retention is proportional to the relative velocity of the centres of mass. It is also assumed that $\hat{k}$ may be selected as for the unloaded spheres. The vectors $\mathbf{v}_1$, $\mathbf{v}_2$, $\boldsymbol{\omega}_1$, $\boldsymbol{\omega}_2$ and $\hat{k}$ obtained by this procedure are then retained while $\hat{l}_1$ and $\hat{l}_2$ are selected. The value of $-\mathbf{g}.\hat{k}$ is calculated. If $-\mathbf{g}.\hat{k}$ is negative $\hat{l}_1$ and $\hat{l}_2$ are rejected since it is a condition of the precollisional state that $-\mathbf{g}.\hat{k}$ is positive. If $-\mathbf{g}.\hat{k}$ is positive l_1 and l_2 are retained or rejected such that their probability of retention is proportional to $-\mathbf{g}.\hat{k}$. If they are rejected then a new set of orientations is selected, keeping the current values of $\mathbf{v}_1$, $\mathbf{v}_2$, $\boldsymbol{\omega}_1$, $\boldsymbol{\omega}_2$ and $\hat{k}$, and if retained, the collision is computed and the new values for $\mathbf{v}_1$, $\mathbf{v}_2$, $\boldsymbol{\omega}_1$, $\boldsymbol{\omega}_2$ stored in place of the old. The time advance associated with each collision was assumed to be that for the unloaded hard sphere of the same diameter and relative translational velocity (Bird 1967).

As mentioned in §2, it is also necessary to compute molecule–surface collisions when using the present method of shock generation. This is relatively simple for the specularly reflecting boundary since the surface normal (corresponding to $\hat{k}$ for the binary collision) for such collisions is fixed for each boundary. This leaves only the molecular orientation $\hat{l}$ to be selected at each collision. This orientation is selected at random from the range of possible directions and retained or rejected such that its probability of retention is proportional to the component of the relative velocity of the impact points (prior to collision) in the direction normal to the surface.

The collision procedure described above is essentially heuristic and it was considered necessary to test its validity before using it to simulate the shock. The test situation chosen was that of a sample of molecules, initially of constant translational and rotational speeds, relaxing towards equilibrium. A description of the relaxation simulation and the results obtained follows.

3.2. *Relaxation simulation*

A sample of molecules was set up such that each molecule had the same translational speed, the directions of the velocity vectors being isotropically distributed in three-dimensional space. Similarly, the angular speed was the same for each molecule and again the vector directions were isotropically distributed. No account was taken of the relative positions of the molecules, and the sample may thus be considered analagous to a single cell in the general procedure. At zero time the molecules were allowed to begin colliding and the evolution of the sample was monitored.

In such a system it is to be expected that, while the total average energy per molecule remains constant in time, the gas would relax towards equilibrium with the translational and rotational energies e_t and e_r respectively, finally exhibiting equipartition. That is, if $e(t)/e(0)$, $e_t(t)/e(0)$ and $e_r(t)/e(0)$ denote the ratios of the instantaneous average total, translational and rotational energies, respectively, to the initial average total energy, then

$$e(t)/e(0) = 1 \quad (t \geqslant 0)$$

and
$$\left.\begin{aligned} e_t(t)/e(0) &\to 0\cdot6, \\ e_r(t)/e(0) &\to 0\cdot4, \end{aligned}\right\} \quad (t \to \infty)$$

or
$$\left|e_r(t) - \tfrac{2}{3}e_t(t)\right|/e(0) \to 0 \quad (t \to \infty).$$

Further, as $t \to \infty$ the distribution of translational and rotational speeds should tend toward the Maxwellian and Rayleigh distributions respectively.
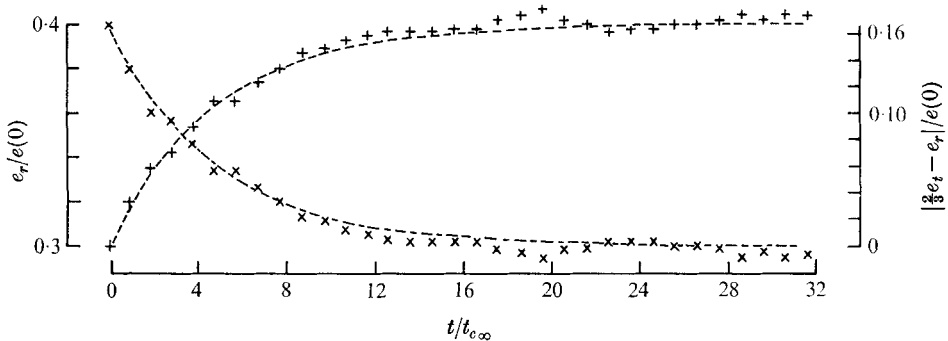

FIGURE 2. Relaxation of uniform gas of loaded spheres from constant-speed initial state. $Z_R = 5$, $e(0) = 0\cdot5$, $e_t(0) = 0\cdot35$, $e_r(0) = 0\cdot15$; – – – – –, Jeans's theory.

The results of such a simulation are shown in figures 2–4. Values of m, I and ϵ were assigned to the molecules to give $Z_R = \frac{9}{20}(I/m\epsilon^2) = 5$. The sample size is 4500 molecules, obtained by ensemble averaging the results of 3 separate runs of 1500 molecules, each run having a different random number sequence. Figure 2 shows the ratios $e_r(t)/e(0)$ and $\left|e_r(t) - \tfrac{2}{3}e_t(t)\right|/e(0)$, where $t_{c\infty}$ is the theoretical mean collision time at equilibrium. Also plotted are the curves predicted by Jeans's theory for $Z_R = 5$ and this set of initial conditions. It may be seen that the agreement between Jeans's theory and the present results is very good up to $t/t_{c\infty} \simeq 10$, after which the Monte Carlo results tend to give larger average
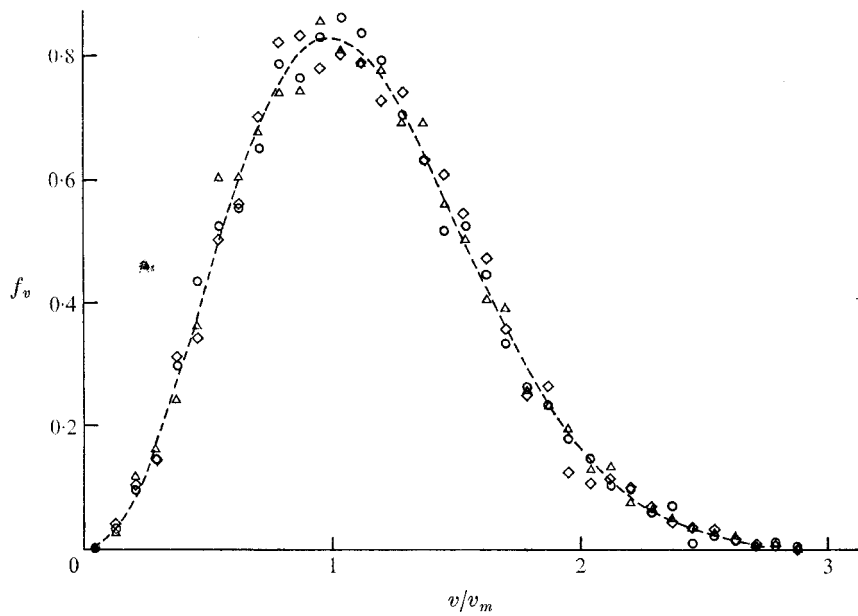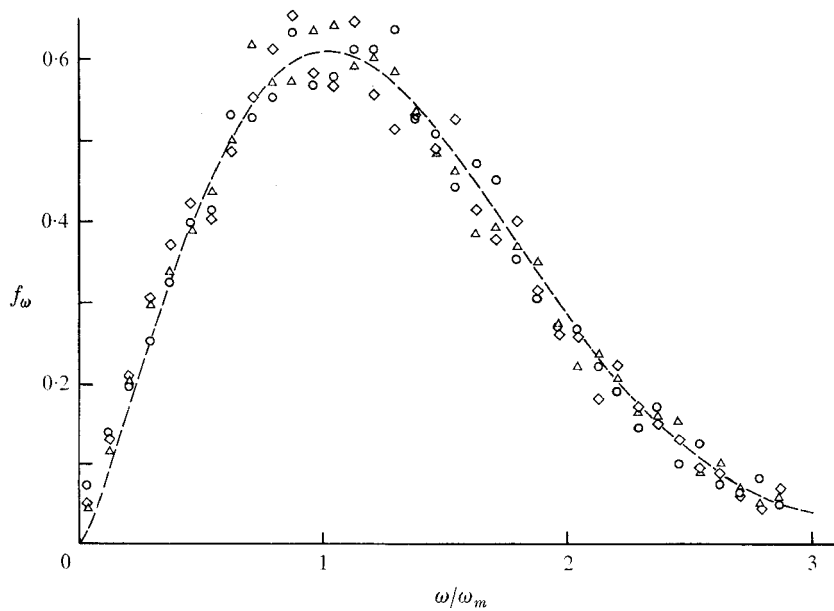
FIGURE 3. Translational speed distribution function at $Z_R = 5$ plotted as function of v/v_m, where v_m is the most probable translational speed. $\bigcirc$, $t/t_{c_\infty} = 10\cdot6$; $\triangle$, $t/t_{c_\infty} = 24\cdot6$; $\diamondsuit$, $t/t_{c_\infty} = 29\cdot6$; — — —, Maxwellian distribution.

FIGURE 4. Rotational speed distribution function at $Z_R = 5$ plotted as function of ω/ω_m, where ω_m is the most probable rotational speed. $\bigcirc$, $t/t_{c_\infty} = 19\cdot6$; $\triangle$, $t/t_{c_\infty} = 24\cdot6$; $\diamondsuit$, $t/t_{c_\infty} = 29\cdot6$; — — —, Rayleigh distribution.

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rotational energies. The Monte Carlo results reach equilibrium values at approximately $t/t_{c\infty} = 20$, after which a slight excess of rotational energy is apparent through the scatter of the results. The translational and rotational speed distributions were sampled throughout the relaxation process. Distributions sampled at $t/t_{c\infty} = 19\cdot6$, $24\cdot6$ and $29\cdot6$ are given here. The translational speed distributions obtained for these times are shown in figure 3, along with the Maxwellian distribution. Figure 4 displays the corrresponding rotational distributions with the Rayleigh distribution. It was considered that these results did represent the simple relaxation process to an acceptable accuracy and justified the use of the collision procedure to simulate the shock in a diatomic gas. A description of the shock simulation follows.

3.3. *Shock-wave simulation*

The method of generating the shock is an analogue of the simple piston-driven shock tube. A sample of gas, initially at rest and contained between two plane parallel boundaries, is set in motion as one of the walls begins to move with constant velocity towards the opposite wall. The disturbance caused by the collision of the molecules with the moving boundary propagates into the sample, via binary collisions, giving rise to the shock front. The wall (or piston) velocity is determined from the usual equation relating the velocity change across the plane shock to the shock Mach number, M_s. The value of the specific heat ratio in this equation is set at $\frac{7}{5}$ to account for the five degrees of freedom of the gas.

The sample is initially set up with the molecules uniformly distributed between the boundaries. Translational and rotational speeds are assigned to the molecules to give the Maxwellian and Rayleigh distributions respectively and the vector directions corresponding to these speeds are distributed isotropically in both cases. The region between the boundaries is divided into a number of cells. This number remains constant in time and the cell boundaries are moved accordingly to account for the decreasing extent of the simulated region. These cells are used, as indicated in §3.1, to define possible collision pairs. The cells are also used to define regions over which macroscopic flow variables (density, temperature, etc.) may be obtained from averaging of molecular variables.

At zero time the specularly reflecting boundary is set in motion, the binary and molecule–wall collisions computed and the molecules moved accordingly. (See Bird (1969, figure 1) for the general flow diagram of the technique.) For much of the time a large, but decreasing, proportion of the molecules ahead of the advancing shock is unaffected by the shock and remains in equilibrium. A significant saving in computer time is afforded by considering this region as a collisionless gas. Collisions are computed in the region between the moving wall and a 'line' ahead of, but fixed relative to, the advancing shock. After a time the shock formation processes are completed and a stationary shock exists relative to the shock path. The stationary shock profiles are obtained by averaging the molecular variables in a family of cells with boundaries fixed relative to the shock path. A number of samples may be taken at different times and averaged to reduce the statistical scatter.

The preceding description corresponds to one typical run of the program.

Owing to the limited size of the computer used, one such run was not sufficient to obtain statistically reliable results. To reduce the scatter the program was run a number of times, with different random number sequences, and the results from all the runs were then ensemble averaged to give the final shock profiles obtained. The computations were carried out on an IBM 7040 machine having $32K$ storage. A typical run lasted 2 h.

4. Results

The shock profiles presented here are for $M_s = 4\cdot6$ and $Z_R = 10$, allowing comparison with the kinetic theory results of Venkataraman & Morse (1969) and the continuum theory results of Talbot & Scala (1961). While comparison with the experimental profiles of density and rotational temperature for nitrogen ($Z_R \simeq 5$, $M_s = 1\cdot61$, $1\cdot71$, $7\cdot0$, $12\cdot9$) obtained by Robben & Talbot (1966) would have been more desirable, it was considered that the approximations involved in the collision procedure would be more appropriate to the higher collision numbers.
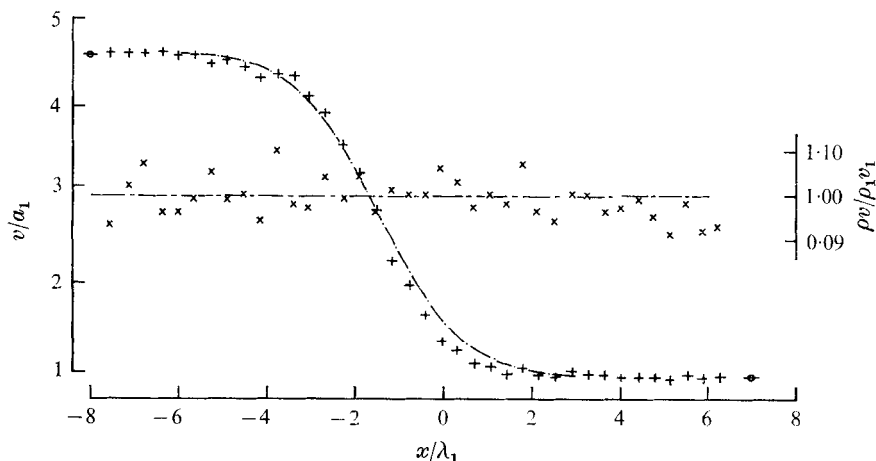

FIGURE 5. Mean velocity profile through the shock: $+$, present results; —·—·—, continuum results of Talbot & Scala (1961). Mass flux ratio through the shock: $\times$, present results; — — — — —, conservation condition. $M_s = 4\cdot6$, $Z_R = 10$.

The initial piston–wall spacing was 50 mean free paths ($50\lambda_1$) of the upstream equilibrium gas. The demarcation between the collisionless gas and the region in which collisions were computed was set at $10\lambda_1$ downstream of the shock path. In each complete run of the program the gas was simulated by 2400 molecules. Each run produced 6 steady shock samples, the proximity of the fixed boundary preventing further sampling. The program was run a total of five times to give the results presented here. In all the profiles presented the origin of the stream-wise position co-ordinate x/λ_1 is the position of the shock path given by the discontinuous shock equations. At no time was there any indication, within the scatter of the results, of translation of the profiles relative to this datum.

Profiles of the shock are shown in figures 5–8. Figure 5 shows the velocity profile plotted as v/a_1, where a_1 is the upstream speed of sound; the continuum profile of Talbot & Scala (1961) is given for comparison. The Monte Carlo results give a slightly larger maximum gradient in the central region of the shock. The mass flux ratio $\rho v/\rho_1 v_1$ is also given. The mass conservation condition requires
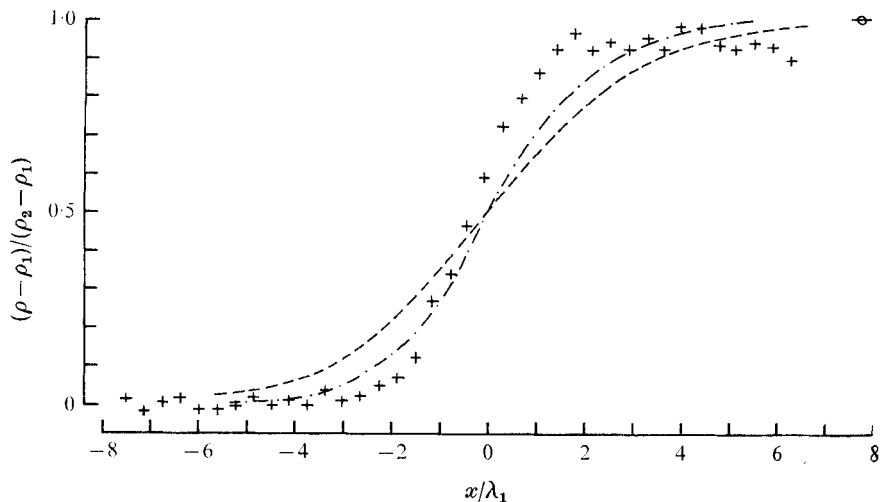

FIGURE 6. Density profile through the shock for $M_s = 4\cdot6$, $Z_R = 10$. +, present results; —·—·—, continuum results of Talbot & Scala (1961); — — —, kinetic theory results of Venkataraman & Morse (1969).
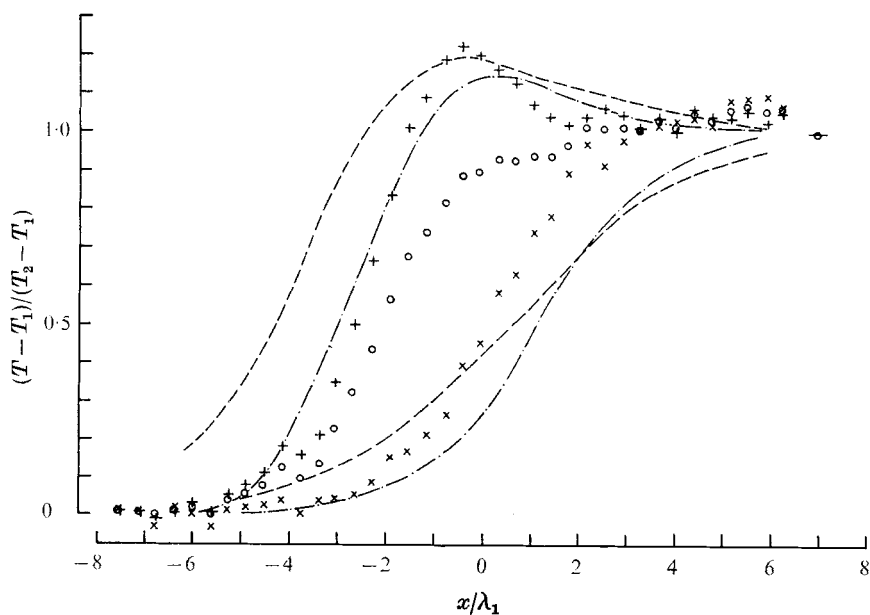

FIGURE 7. Temperature profiles through the shock for $M_s = 4\cdot6$, $Z_R = 10$. Present results: ○, overall temperature ratio; +, translational temperature ratio; ×, rotational temperature ratio. —·—·—, continuum results of Talbot & Scala (1961). — — — kinetic theory results of Venkataraman & Morse (1969).

that this ratio be unity but while this condition appears to be satisfied, within the scatter of the results in the upstream region, a mass flux deficit becomes apparent on moving downstream. From figure 6, where the normalized density ratio is given, it may be seen that this error in the mass flux is primarily due to the failure of the gas to maintain the downstream equilibrium density. Comparison of the present results with the continuum and the kinetic theory profiles shows that they give a smaller maximum density-gradient thickness than both the other results. The translational temperature T_t, rotational temperature T_r and overall temperature T, where $T = \frac{1}{5}(3T_t + 2T_r)$, are plotted as their normalized ratios in figure 7. They show qualitative agreement with the theoretical predictions but again the smaller thickness given by the present results is apparent. Good agreement with Venkataraman & Morse is obtained in determining the streamwise position and magnitude of the maximum translational temperature attained in the shock. As for the density profiles, the temperature profiles fail to maintain the downstream equilibrium temperature. The translational temperature may be further divided into a component associated with the longitudinal thermal components of velocity and another associated with the lateral components. These temperature profiles are shown in figure 8. It is interesting to note the presence of a slight maximum in the lateral temperature within the shock region as compared with monatomic shock profiles where the corresponding temperature is monotonically increasing.
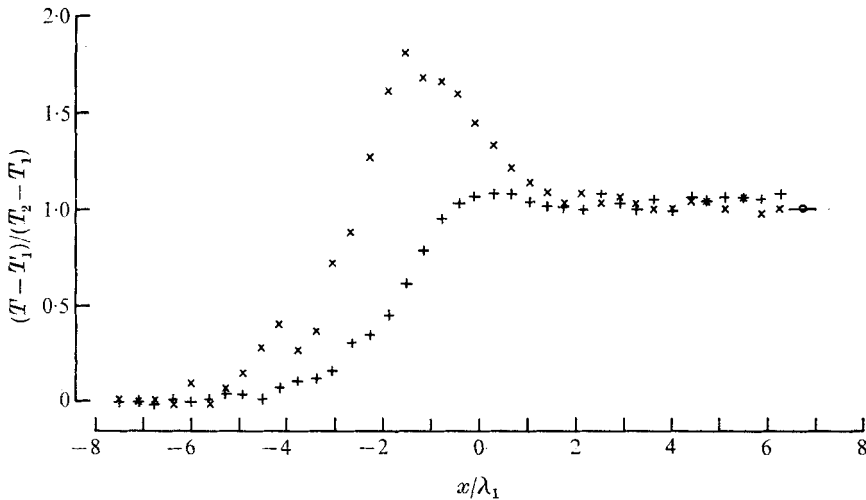

FIGURE 8. Translational temperature non-equilibrium through the shock for $M_s = 4 \cdot 6$, $Z_R = 10$. $\times$, longitudinal temperature ratio; $+$, lateral temperature ratio.

5. Discussion

The results of these numerical experiments with the loaded-sphere model indicate that the present method is capable of giving qualitative agreement (and in some aspects quantitative agreement) with the results of theoretical studies. The most outstanding feature of the shock profiles presented here is the failure of the gas to maintain the downstream equilibrium condition. The reasons for

this behaviour are not at all clear and it would be particularly difficult to determine them with any degree of certainty. However it is thought that the error may arise from (i) the approximations involved in the collision procedure which in the simple relaxation experiment gave rise to a slight excess of rotational energy on approaching equilibrium and/or (ii) the assumption of a specularly reflecting piston which may cause erroneous energy-transfer processes in the downstream region.

The present results have been obtained at the expense of relatively long computer runs and since the plane shock simulation is one of the simplest one-dimensional problems it is to be expected that the time involved in using the present collision procedure may prove prohibitive for more complex flows. As Bird's direct simulation technique has advantages over the analytical methods when studying multi-dimensional flows having complex boundary conditions, this problem of computer run time is quite critical. As for all Monte Carlo methods Bird's technique involves 'playing for' variables which are defined in a probabilistic manner. In the present study one 'plays for' the collision pair and then for the molecular orientations at collisions. This process may be divided into three stages: (*a*) selecting variables within the bounds of the physical constraints (involving molecular positions and geometry), (*b*) processing the variables to obtain numerical values for parameters upon which acceptance/rejection decision is based and (*c*) accepting/rejecting the values selected in (*a*). If one rejects the current values selected then one returns to (*a*) and selects a new set. The computer run time increases as the number of cycles through the loop (*a*) $\rightarrow$ (*b*) $\rightarrow$ (*c*) $\rightarrow$ (*a*), before acceptance of the variables selected in (*a*), increases. Run time also increases as the amount of detailed programming involved in (*a*), (*b*) and (*c*) increases. For the symmetric-power law bodies (and rough-sphere model, Bird (1970)) these operations can be quickly and efficiently carried out. With the loaded-sphere model the asymmetry gives rise to more constraints on the values that the variables may take and so (*a*) is more time consuming. The larger number of variables that have to be selected increases the detailed programming in both (*a*) and (*b*).

The study of relaxation processes involving the internal degrees of freedom of the gas is of importance in a number of problem areas of current interest. The use of Bird's technique, with models which faithfully represent the molecular interactions and are efficiently simulated, may prove to be a powerful tool in the examination of these problems. However, the present study using the loaded-sphere model, which is one of the simplest *classical* models capable of representing the internal modes, would tend to indicate that the detailed programming involved in simulating the classical models may prove prohibitive. Bird (private communication) has recently obtained diatomic shock profiles which show good agreement with the experimental results of Robben & Talbot (1966), using a molecular model (the 'energy sink' model) which was specifically designed for computer simulation. This model demands much less computer time than the loaded-sphere model. One may conclude that the development of models specifically designed for use with the direct simulation technique may prove more fruitful than attempts to adapt the classical models.

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