

Monte Carlo simulation of a homogeneous dissociating diatomic gas

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THE ISOTROPIC relaxation of a homogeneous diatomic gas at constant volume including continuous internal energy modes and dissociation-recombination reactions is treated by the direct simulation technique suitable to rarefied gas flows. The simulation includes five collision types two of which are inelastic and all of which be reactive. The successive selection of collision type is governed by time counters. Collision dynamics is hard-sphere for elastic collisions and hard-sphere statistical for inelastic and reactive collisions. The dissociation reaction occurs in a one step bimolecular collision while recombination occurs in a termolecular collision simulated by two successive bimolecular collisions. Typical CPU-times IBM 370/165 range from 0.75 to 5 seconds for 1000 collisions. Results include the transient approach to equilibrium, the degree of dissociation at equilibrium for various values of density and temperature, and the effect of activation energy on reaction delay for recombination transients.

Problem izotropowej relaksacji dwuatomowego gazu w stałej objętości, przy ciągłych postaciach energii wewnętrznej i przy występowaniu reakcji dysocjacji i rekombinacji został rozwiązany bezpośrednią techniką symulacji stosowaną w teorii przepływów gazów rozrzedzonych. Modelowanych jest pięć różnych typów zderzeń, z których wszystkie są reaktywne prowadzące do reakcji chemicznych a dwa z nich niesprężyste. Wyboru kolejnego typu zderzenia dokonują liczniki czasu. W zderzeniach dynamicznych cząstki modelowane są sztywnymi kulami dla zderzeń sprężystych i statystycznie sztywnymi kulami dla zderzeń niesprężystych i reaktywowanych. Reakcja dysocjacji zachodzi w jednym kroku zderzeń bicząstek, podczas gdy rekombinacja ma miejsce przy zderzeniu termomolekularnym modelowanym przez dwa kolejne zderzenia bicząstek. Typowe jednostkowe czasy zderzeń IBM 370/165 obejmują zakres od 0.75 do 5 sekund na 1000 zderzeń. Wyniki dotyczą chwilowego osiągnięcia stanu równowagi, stopnia dysocjacji w stanie równowagi dla różnych gęstości i temperatury oraz wpływu energii aktywacji na opóźnienie chwilowych reakcji rekombinacji.

Задача изотропной релаксации двухатомного газа в постоянном объеме, при непрерывных видах внутренней энергии и при выступании реакций диссоциации и рекомбинации, решена непосредственной техникой моделирования, применяемой в теории течений разреженных газов. Моделируется пять разных типов столкновений, из которых все реактивные (приводящие к химическим реакциям), а два из них неупругие. Выбор последовательного типа столкновений производят счетчики времени. В динамических столкновениях молекулы моделируются жесткими шарами для упругих столкновений и статистически жесткими шарами для неупругих и реактивных столкновений. Реакция диссоциации происходит в одном шагу столкновений бимолекул, в то время, когда рекомбинация имеет место при термомолекулярном столкновении моделированном через два последовательных столкновения бимолекул. Типичные единичные времена столкновений (IBM 370/165) охватывают интервал от 0,75 до 5 секунд на 1000 столкновений. Результаты касаются мгновенного достижения состояния равновесия, степени диссоциации в состоянии равновесия для разных плотностей и температуры, а также влияния энергии активации на запаздывание мгновенных реакций рекомбинации.

1. Introduction

BECAUSE of the complexity and for the sake of obtaining "exact" solutions, at least for some canonical problems, kinetic gas formulations merit the use of numerical schemes for their solution, such as the direct Monte Carlo simulation technique originally intro-

duced by BIRD (1963) for a monatomic gas. This scheme has more recently been extended to polyatomic gas mixtures by BORGNAKKE and LARSEN (1975) employing a statistical collision model for inelastic energy exchanges. The continued interest in chemically-reacting gas flows at rarefied conditions warrants further exploration of the simulation techniques.

In one of the early Monte Carlo simulations of chemically reacting gases, YOSHIKAWA (1967) considered the irreversible recombination reaction in a homogeneous diatomic gas. The test particle method (HAVILAND 1965) was used and collisions and reactions were treated by the reactive hard-sphere collision model. The recombination reaction was modelled by two successive binary collisions involving an intermediate activated molecule A_2^* whose concentration was always low. Dissociation reactions were not considered, therefore, only the temperature rise associated with the complete recombination of an initial monatomic gas could be studied. CPU-times (HITAC 5020) was given to 100 sec per 1000 collisions.

BIRD (1970) studied the dissociation-recombination relaxation in a homogeneous diatomic gas initially in the molecular state at chemical non-equilibrium. Employing the direct simulation method and hard-sphere particles without internal energy, recombination was modelled by three body collisions. The probability of these was taken to be proportional to the number of particles in a cube with sides equal to the mean free path. Dissociation occurred in binary collisions with a steric probability whenever pair translational energy exceeded the dissociation energy. The case of constant steric probability leads to $\beta = 0$ in the following expression for the equilibrium dissociation

$$(1.1) \quad \alpha^2/(1-\alpha) \sim (T^\beta/\rho) \exp(-e_d/kT),$$

where α denotes the degree of dissociation, ρ the density and e_d the dissociation energy. Equation (1.1) corresponds to the reactive hard-sphere model with a constant cross section. A similar result applies to the ideal dissociating gas of LIGHTHILL (1957). Bird also considered the reactive hard-sphere model with a steric probability proportional to the amount by which the relative translational energy exceeds e_d leading to $\beta = 3/2$ in Eq. (1.1), which agrees with the law of mass action for a translational gas.

KOURA (1974) studied velocity distributions and reaction rates for fast one-step exothermic chemical reaction in a homogeneous gas using the reactive hard-sphere model for particles without internal energy. The Monte Carlo calculations included forward and backward reactions and corresponding rates during the approach to equilibrium which was established in 15–25 mean collision times.

Using a moment method and the sphero-cylinder molecular model PAI and RAMACHANDRA (1974) calculated the shock structure in a dissociating diatomic gas for $M_1 < 30$, where ionization and photo-dissociation is unimportant. A part of the integrations in the evaluation of the collision integral was solved by Monte Carlo techniques.

The purpose of the present study is to show how the internal molecular energy may be accounted for in the simulation of a reacting gas by using a previously developed statistical model for inelastic collisions. The procedure is illustrated for the simulation problem considered by BIRD (1970), the gas now possessing continuous internal energy modes. The initial state is a homogeneous molecular or atomic gas at thermal but not chemical

equilibrium. The constant-volume and adiabatic transient approach to dissociation equilibrium as well as the equilibrium state is simulated by samples of up to 500 molecules (1000 atoms) for different initial states of temperature and density and for different activation energies. Analytical expressions for reaction rates and dissociation equilibrium are derived for the model and compared to the results of the simulation.

The solution procedure applies directly to the collision phase for one cell of constant volume in the direct simulation technique of a rarefied flow in which physical space is divided into many cells. For flow problems the procedure need be supplemented by the phase of particle motion.

2. Flow diagram and initial conditions

Figure 1 shows the overall flow diagram for simulating the reaction

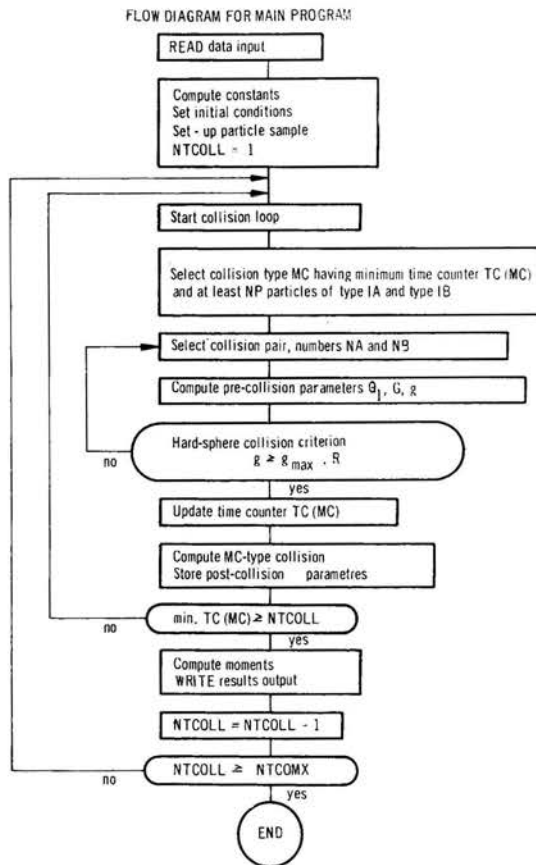


FIG. 1. Flow diagram for main program.

The set-up of the initial particle sample at some temperature T consists in assigning to each particle a speed u according to the isotropic Maxwell-Boltzmann distribution,

$$(2.2) \quad f_a^0(u) du = 4\pi \left(\frac{m_a}{2\pi kT} \right)^{3/2} u^2 \exp\left(-\frac{m_a u^2}{2kT}\right) du,$$

where a denotes the particle type (A or A_2), and assigning to each A_2 -particle an internal energy e_i according to the Boltzmann distribution,

$$(2.3) \quad f_i^0(e_i) de_i = \frac{\chi/2}{\Gamma(\chi/2+1)} \frac{e_i^{\chi/2-1}}{(kT)^{\chi/2}} \exp(-e_i/kT) de_i,$$

where χ denotes the number of internal energy modes, assumed to be continuous. The procedure is well-known (HAVILAND 1965 or DERZKO 1972) for employing random numbers \mathcal{R} from a rectangular distribution, $\mathcal{R} \in [0,1]$, and the implicit rejection technique of von Neumann (HAMMERSLEY and HANDSCOMB 1964, Ch. 3).

The internal energy of atoms is set to zero. The dissociation energy e_d is not included into the internal energy of molecules, but is added or subtracted when calculating recombination or dissociation reactions respectively. For the present isotropic problem only the speed and the internal energy need be stored for each particle. The direction of velocities, required for calculating collisions, are assigned at random whenever needed.

The composition of the two-component mixture of a dissociating diatomic gas is conveniently expressed by the degree of dissociation α defined by

$$(2.4) \quad \alpha = N_A/N_A^0,$$

where $N_A^0 = N_A + 2N_{A_2}$ denotes the total number of atoms in the sample. It follows that $N_{A_2}/N_A^0 = (1-\alpha)/2$.

The initial state is prescribed by the degree of dissociation, temperature and density, where the latter is specified through the probability of a three-particle collision.

The gas is specified by the following quantities: the hard-sphere atomic and molecular diameters σ_A and σ_{A_2} , the particle masses m_A and m_{A_2} , the inelastic collision number Z the number of molecular degrees of internal energy χ , the activation energy e_a and the energy of dissociation e_d .

3. Non-reactive collisions

To account for the exchange of internal energy, non-reactive collisions are treated as being either elastic or fully inelastic. Their relative frequency is specified by the inelastic collision number Z , the ratio of inelastic to total collision time. There are then five types of collisions, $MC = 1 \dots 5$,

$$(3.1) \quad \begin{array}{ll} 1: & A + A \rightarrow A + A \quad (\text{elastic}), \\ 2: & A + A_2 \rightarrow A + A_2 \quad (\text{elastic}), \\ 3: & A + A_2 \rightarrow A + A_2 \quad (\text{inelastic}), \\ 4: & A_2 + A_2 \rightarrow A_2 + A_2 \quad (\text{elastic}), \\ 5: & A_2 + A_2 \rightarrow A_2 + A_2 \quad (\text{inelastic}). \end{array}$$

To ensure that the correct collision frequency is maintained a time counter is kept for each collision type. As shown elsewhere (BORGNAKKE and LARSEN 1975, Eq. A8) the time increment for a hard-sphere collision is

$$(3.2) \quad \delta t_{ab} = [(1 + \delta_{ab})/h_{ab}](vn_a n_b \pi \sigma_{ab}^2 g),$$

where δ_{ab} is the Kronecker delta, h_{ab} equals $(Z_{ab} - 1)/Z_{ab}$ for an elastic and $1/Z_{ab}$ for an inelastic collision, v denotes the volume, n the density, $g = |\mathbf{u}_b - \mathbf{u}_a|$ the relative velocity and $\sigma_{ab} = (\sigma_a + \sigma_b)/2$ the distance between centers. For an approximate estimate we put $\sigma_a \sim m_a^{1/3}$.

Selecting collision type MC with minimum time counter a pair of appropriate particles are picked at random until they satisfy the collision criterion, $g \geq \mathcal{R}g_{\max}$ for hard-spheres, where we take arbitrarily $g_{\max} = 4C_0$, $C_0 = (2kT_0/m_{A2})^{1/2}$, T_0 being a reference temperature. If, after adding the time increment Eq. (3.2) to the time counter, the resulting updated value does not exceed the time at the end of the current time increment, say an integer number of collision times, the collision is included. Otherwise, it is included only on a probabilistic basis in proportion to the remaining time, and in any event the time counter is then advanced to the end of the current time increment.

The calculation of elastic collisions needs no elaboration (see HAVILAND 1965 or DERZKO 1972). Inelastic collisions are treated by the statistical model (BORGNAKKE and LARSEN 1975) which here amounts to the steps stated below. The relative translational energy of the collision pair is $e_t = \frac{1}{2} \mu_{ab} g^2$, where $\mu_{ab} = m_a m_b / (m_a + m_b)$ denotes the reduced mass. Then, the available pair energy for exchange,

$$(3.3) \quad e = e_t + e_{ia} + e_{ib},$$

is first distributed on pair translational and pair internal energies. The probability distribution for this step, normalized to unit maximum value, is

$$(3.4) \quad \mathcal{P}_{e'_t} = \frac{p(e'_t | e'_t = e - e'_i)}{p_{\max}} = \left(\frac{\chi + \eta - 1}{\eta} \right)^\eta \left(\frac{\chi + \eta - 1}{\chi - 1} \right)^{\chi - 1} \left(\frac{e'_t}{e} \right)^\eta \left(1 - \frac{e'_t}{e} \right)^{\chi - 1},$$

where $\eta = 1$ for hard-sphere collision dynamics.

For the case of an $A_2 - A_2$ -collision and $\chi = 2$ for each particle, Eq. (3.4) becomes

$$(3.5) \quad \mathcal{P}_{e'_t} = 4(e'_t/e)(1 - e'_t/e),$$

and the pair translational energy is assigned by the implicit rejection method by satisfying

$$(3.6) \quad \mathcal{P}_{e'_t}(e'_t = \mathcal{R}e) \geq \mathcal{R}.$$

Subsequently $e'_i = e - e'_t$ is divided on the two particles according to the normalized probability density

$$(3.7) \quad P_{e'_{ia}} = 2^{\chi - 2} [(e'_{ia}/e'_i)(1 - e'_{ia}/e'_i)]^{\chi/2 - 1}.$$

For $\chi = 2$, Eq. (3.7) yields $\mathcal{P}_{e'_{ia}} = 1$ which is readily inverted to the explicit form

$$(3.8) \quad e'_{ia} = \mathcal{R}e'_i, \quad e'_{ib} = e'_i - e'_{ia}.$$

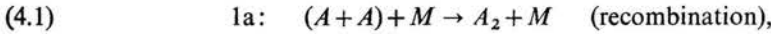
For the case of an $A-A_2$ -collision $e_{ia} = 0$ and pair energy e is distributed on e'_i and e'_{ib} directly by Eq. (3.4) in which e'_i is replaced by e'_{ib} and χ by $\chi/2$. For $\chi = 2$ and $\eta = 1$ this yields $\mathcal{P}_{e'_i} = e'_i/e$ which is readily inverted to the explicit form

$$(3.9) \quad e'_i = \mathcal{R}^{1/2}e, \quad e'_{ib} = e - e'_i.$$

4. Reactive collisions

4.1. Recombination

The recombination reaction, conceived as a hard-sphere three-body collision, is modelled as two successive binary collisions, that is, type 1 of Eq. (3.1) followed by



where the third particle M (of type A or A_2) plays the role as excess energy carrier. Recombination similarly may occur during a type 2 or a type 3 collision provided the third particle M is of type A . Such collisions are treated as the previous one. In each case the dissociation energy e_d is added to the product particles.

The occurrence of reaction 1a of Eq. (4.1) is determined by the probability that a second collision takes place within the estimated collision duration of the first collision, assumed to be given by

$$(4.2) \quad t_{\text{life}} \simeq 2\sigma_{ab}/g.$$

In spite of an obvious oversimplification of the matter it is beyond the scope of the present study to employ more realistic models, such as those discussed by LIGHT et al. (1969). A three-particle collision is then assumed to occur with probability p_{rec} if the probable time t_3 to the next collision is less than t_{life}

$$(4.3) \quad t_3 < t_{\text{life}}.$$

Otherwise the $A-A$ -collision is considered to be elastic.

Treating the colliding $A-A$ -complex as an A_2 -particle, the collision frequency for one such particle with all other particles is

$$(4.4) \quad v_{A_2-M} = \sum_{M=A, A_2} h_{A_2M} n_M \iint f_M g I(\mathbf{g}, \mathbf{k}) d\mathbf{k} d\mathbf{u}_M,$$

where \mathbf{g} is the relative velocity between M and the $A-A$ -complex, which moves with the known center of mass velocity of the original $A-A$ -collision. Ignoring such specifics, we replace the integral by the product of the hard-sphere cross section and the expectation value of g evaluated at the temperature T_M of particle type M . Furthermore, combining elastic and inelastic collisions we recover, to within the constant $3\pi/2\sqrt{2}$, the expression for hard-sphere bimolecular collision frequency per A_2 -particle

$$(4.5) \quad v_3 = (3\pi/2\sqrt{2}) \sum_{M=A, A_2} [2/(1 + \delta_{A_2M})] n_M \sigma_{A_2M}^2 (2\pi k T_M / \mu_M)^{1/2}.$$

Denoting by $p_c(t)$ the probability that collision takes place at $t_3 < t$ then (CHAPMANN and COWLING 1960, § 5.41) $p_c(t) = 1 - \exp(-\nu_3 t)$; the complementary probability of no collision $\exp(-\nu_3 t)$ determines the distribution of times to the next collision. Inverting the latter expression, the time to the next collision is selected at random by

$$(4.6) \quad t_3 = -(\ln \mathcal{R})/\nu_3,$$

and Eq. (4.3) is employed to ascertain whether recombination takes place. Although ν_3 changes as new collisions are calculated, it is satisfactory to re-evaluate ν_3 only when moments are calculated, say once every reference collision time.

In case of recombination a new A_2 -particle is created with a speed equal to the center of mass velocity of the two A-particles, which are then scratched, and with an internal energy equal to the sum of pair translational energy and dissociation energy. The type of the third particle M is then selected at random according to relative densities of A- and A_2 -particles. The subsequent A_2 - M -collision is handled as an inelastic collision which ensures that a part, but not necessarily all, of the dissociation energy is immediately transferred to translational energy.

The flow diagram in Fig. 2 summarizes the foregoing strategy HSPCV, HSPE12 and HSPE22 denoting subroutines for calculating, respectively, hard-sphere post-collision velocities, inelastic energy exchange between the A- A_2 pair, and between the A_2 - A_2 pair.

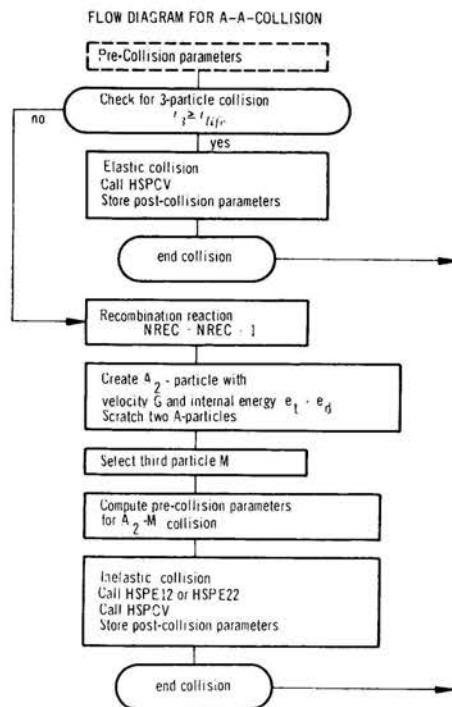
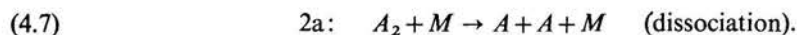


FIG. 2. Flow diagram for A-A-collision.

4.2. Dissociation

The dissociation reaction is assumed to take place in a single-step bimolecular collision,



The reaction occurs with probability p_{diss} in either of the collisions of type 2-5 of Eq. (3.1), provided the energy available in the collision exceeds the sum of an activation energy e_a and the dissociation energy e_d ,

$$(4.8) \quad (e_t + e_{ia} + e_{ib})_{\text{avail}} \geq e_a + e_d,$$

in which case e_d is subtracted from the energy of the product particles. In general the exact form of Eq. (4.8) is not known and various models have been proposed. In the reactive hard-sphere model, for example, only the pair translational energy along the line of centers is considered to be available. Assuming the scattering angle to be uniformly

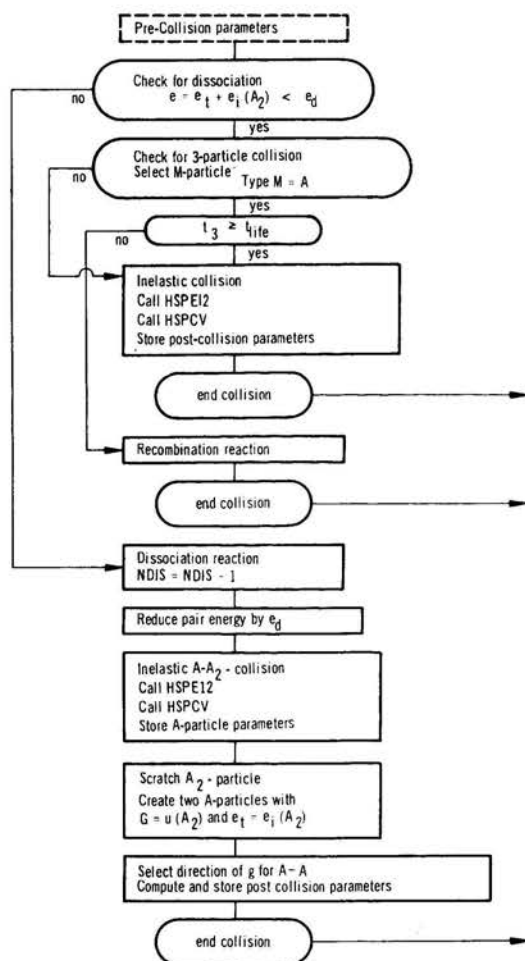


FIG. 3. Flow diagram for $A-A_2$ -collision.

distributed over the interval $0-2\pi$, we have $e_{t, \text{avail}} = \mathcal{R}e_t$. Statistically this represents two degrees of freedom (two square terms). In a rough-sphere model it is conceivable that a portion of e_t greater than $\mathcal{R}e_t$ becomes available. The portion of internal energy modes e_{ia} and e_{ib} available depends on the type of particles involved in the collision and must be determined from experiment. Thus, the total number of degrees of freedom ψ' which are statistically available and associated with both translational and internal energies may be deduced from the temperature dependence of the forward rate constant k_f for the reaction. Written in the standard form

$$(4.9) \quad k_f = C_f T^{\eta_f} \exp(-e_d/kT)$$

we have $\psi' = 3 - 2\eta_f$. Experimental values for ψ' are 4-7 for diatomic gases such as oxygen and nitrogen. Including all translational and rotational modes we have $\psi' = 6$ and 8, respectively, for $A-A_2$ and A_2-A_2 encounters. These values have been used in the present study along with the assumption that $p_{\text{rec}} = p_{\text{diss}} = 1$.

In the case of dissociation the pair energy is reduced by the dissociation energy e_d and an inelastic collision is executed. The resulting post-collision parameters for the participating M -particle are stored. The A_2 -particle, having post-collision velocity u'_b and internal energy e'_{ib} , is then dissociated into two A -particles with the center of mass velocity $G' = u'_b$ and the pair translational energy $e'_t = \frac{1}{2} \mu_{AA} g'^2$. The A_2 -particle is scratched from storage and two A -particles are created. On the assumption of post-dissociation isotropy the direction of the relative velocity g' , say measured relative to the direction of G' , is assigned at random by $\cos\theta = 1 - 2\mathcal{R}$. Then, the speeds u_a and u_b of the two dissociated A -particles are calculated in the usual way. The flow diagram of Fig. 3 summarizes the foregoing strategy.

5. Results

The reactive collision model including internal energy has been employed in the study of two cases of chemical relaxation in a homogeneous gas at constant volume. That is, in the dissociation transient of an initially diatomic gas, and the recombination transient of an initially monatomic gas.

In all simulations the initial temperature T_0 was employed as the reference temperature. Times are made dimensionless with respect to the hard-sphere collision time $t_{0, \text{coll}} = (2\pi)^{1/2} / (4n_0\pi\sigma_{A_2}^2 C_0)$ of A_2 -molecules at density n_0 and most probable speed C_0 . Mass density, which enters in the strategy for recombination, is measured relative to a reference density ρ_{ref} introduced into Eq. (4.2) by rewriting it in dimensionless form as

$$(5.1) \quad \tau_{\text{life}} = 4\sqrt{2\pi} (\sigma^3 n)_{\text{ref}} (\tilde{\sigma}_{ab}/\tilde{g}) (\sigma_{A_2}/\sigma_{\text{ref}})^3 (\rho/\rho_{\text{ref}}),$$

where $\tilde{\sigma}_{ab} = \sigma_{ab}/\sigma_{A_2}$, $\tilde{g} = g/c_0$ and $\rho/\rho_{\text{ref}} = n_0/n_{\text{ref}}$. Employing $p = nkT$ at $p_{\text{ref}} = 1$ atm and $T_{\text{ref}} = 298$ K, and selecting $\sigma_{\text{ref}} = \sigma_{A_2} = 3.55 \cdot 10^{-10}$ m gives $(\sigma^3 n)_{\text{ref}} = 1.1 \cdot 10^{-3}$. Hence, for a given gas of specified e_d each value of $\tilde{e}_d = e_d/kT_0 = \theta_d/T_0$ determines the absolute initial temperature T_0 which, along with a specified density ratio ρ/ρ_{ref} , fixes the initial state.

5.1. Dissociation transient

Each simulation is started with a sample of 500 A_2 -particles at thermal equilibrium at T_0 , and the increment for updating time counters is $t_{0, \text{coll}}$.

Figure 4 shows a typical approach to dissociation equilibrium and the associated decrease in total temperature for the case of $e_d = 2$ and $e_a = 0$. The total temperature of the mixture is calculated from

$$(5.2) \quad T_{\text{mix}} = (T_{t,A} + \alpha_1 T_{\text{tot},A_2}) / (1 + \alpha_1),$$

where $\alpha_1 = (3 + \chi)(1 - \alpha) / 2\alpha$, $T_{t,A}$ is the translational temperature of A -particles, and $T_{\text{tot},A_2} = (3T_{t,A_2} + \chi T_{i,A_2}) / (3 + \chi)$ the total temperature, T_{t,A_2} and T_{i,A_2} respectively the translational and internal temperatures of A_2 -particles evaluated in the usual way from the particle sample.

The initial rate of dissociation of A_2 -particles may be calculated from

$$(5.3) \quad (dn_{A_2}/dt)_0 = -v_{A_2} p \{e \geq e_d + e_a | \text{coll}\} p_{\text{diss}},$$

where the bimolecular collision rate v_{A_2} is $n_{A_2}^2 \sigma_{A_2}^2 (2\pi)^{1/2} C_0$ and the probability that the

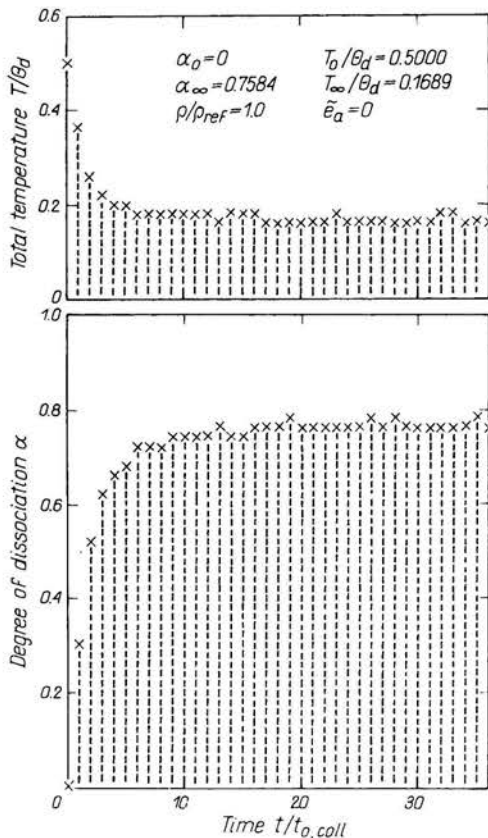


FIG. 4. Dissociation transient for initially diatomic gas; $\bar{e}_a = 0$, $Z = 1.2$, $\chi = 2$, $N_A^0 = 1000$.

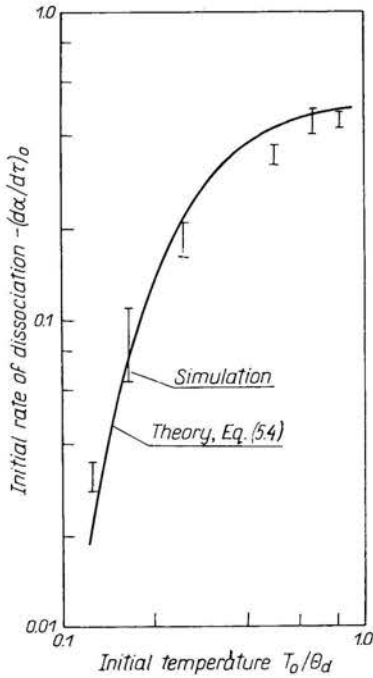


FIG. 5. Initial rate of dissociation of diatomic gas versus initial temperature. Hard-sphere statistical collision model; $\tilde{e}_a = 0$, $Z = 1.2$, $\chi = 2$, $N_A^0 = 1000$.

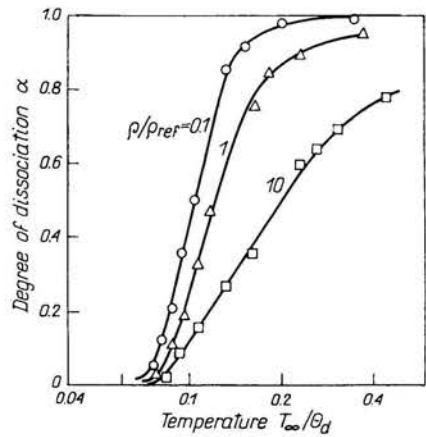


FIG. 6. Equilibrium dissociation versus temperature for selected values of density. Hard-sphere statistical collision model; $\tilde{e}_a = 0$, $Z = 1.2$, $\chi = 2$, $N_A^0 = 1000$.

available energy e in collision exceeds $e_d + e_a$ at equilibrium equals $\int_{e_a + \tilde{e}_d}^{\infty} f_{\psi'}^0(\tilde{e}) d\tilde{e}$. Here

$\tilde{e} = e/kT_0$ and $f_{\psi'}^0(\tilde{e})$ is the equilibrium distribution of ψ' available degrees of freedom, of the form given by Eq. (2.3) replacing χ by ψ' and e_i by e . Taking $e_a = 0$, $p_{diss} = 1$ and $\psi' = 8$ the dimensionless form of Eq. (5.3) becomes

$$(5.4) \quad (d\alpha/d\tau)_0 = -(1/12)(\tilde{e}_d^3 + 3\tilde{e}_d^2 + 6\tilde{e}_d + 6) \exp(-\tilde{e}_d).$$

Figure 5 shows Eq. (5.4) compared to results of simulations. The scatter represents the use of increments from 0.1 to 1.0 times $t_{0, coll}$ for updating time counters in order to approach the limit $\tau \rightarrow 0$.

Figure 6 shows equilibrium dissociation versus temperature for three values of mass density. The theoretical relation is of the form of Eq. (1.1), but more involved. The temperature dependence corresponds approximately to $\beta = -3/2$.

5.2. Recombination transient

The simulations in this case are started with 500 A-particles at thermal equilibrium at temperature T_0 . To accelerate the recombination only the case of high density $\rho/\rho_{ref} = 10$ is studied.

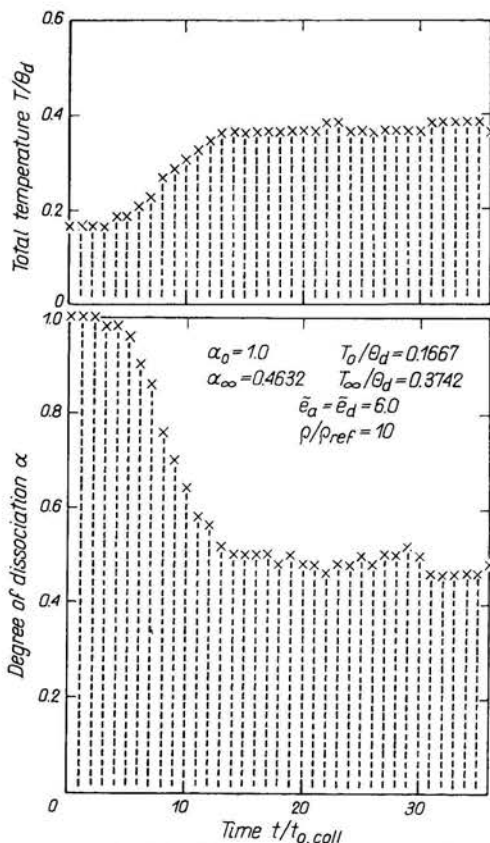


FIG. 7. Recombination transient for initially monatomic gas; $Z = 1.2$, $\chi = 2$, $N_A^0 = 1000$.

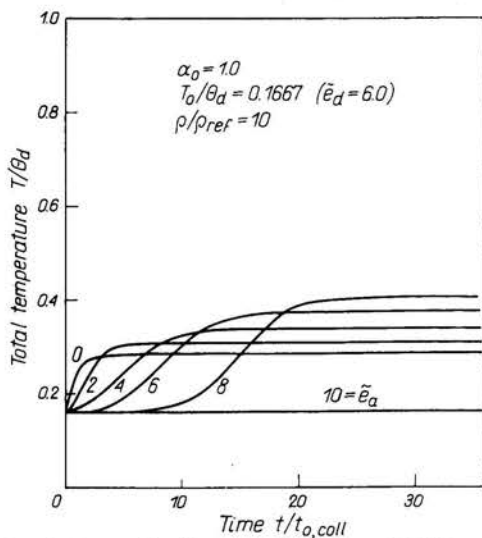


FIG. 8. Recombination transient for initially monatomic gas. Total temperature rise for selected values of activation energy. Hard-sphere statistical collision model; $Z = 1.2$, $\chi = 2$, $N_A^0 = 500$.

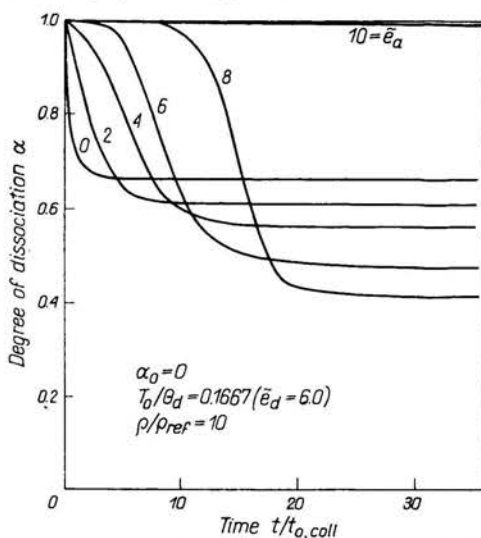


FIG. 9. Recombination transient for initially monatomic gas. Degree of dissociation for selected values of activation energy. Hard-sphere statistical collision model; $Z = 1.2$, $\chi = 2$, $N_A^0 = 500$.

Figure 7 shows the typical approach to dissociation equilibrium with the associated increase in total temperature for the case of $\tilde{e}_d = \tilde{e}_a = 6.0$. Figures 8 and 9 show a parametric study of temperature and degree of dissociation, respectively, for the recombination transient at fixed dissociation energy $\tilde{e}_d = 6.0$ and increasing values of activation energy from 0 to 10. As \tilde{e}_a increases the characteristic reaction delay increases from zero to more than forty $t_{0, \text{coll}}$. Non-zero activation energy has been included to illustrate the simulation of characteristic features of simple exothermic one-step chemical reactions.

5.3. Computer times and storage requirement

Typical CPU-times (IBM 370-165) in seconds per 1000 collisions range from 5 in the first $t_{0, \text{coll}}$ to from 2.5 to 1.2 in the following 36 $t_{0, \text{coll}}$ for the dissociation transient. The corresponding times are 1.8 and 1.3 to 0.75 for the recombination transient. These times include the calculation of moments and other book-keeping. The total time for simulating one curve of Fig. 6 is 150 seconds. The Fortran program comprises about 700 statements and is of size 19 *k*-bytes and is run within a 120 *t*-byte region with the Fastfort compiler.

6. Conclusion

The present study of chemical relaxation in a homogeneous gas illustrates the feasibility of Monte Carlo simulation of rarefied gas flows with a simple chemical reaction, including the contribution of internal energy modes. A variety of reaction models may be constructed by choice of a central force inverse power law other than that of hard-spheres and through adjustment of the parameters χ , Z , p_{diss} and p_{rec} . In addition, the statistical collision model may be used in a modified form in which all collisions are inelastic and the energy exchange is statistically restricted (LARSEN and BORGNACKE 1974). Actually, this model has a minor deficiency, as pointed out by PULLIN (1975), in that the fraction of energy made available for correct statistical exchange during a collision is fixed and not selected statistically, hence micro-reversibility is not satisfied. Nevertheless, the model is able to reproduce satisfactory equilibrium distributions and the use of fixed fractions affords savings in computer time. Still, the model is more time consuming than the one described in the present study.

References

1. G. A. BIRD, *Approach to translational equilibrium in a rigid sphere gas*, Phys. Fluids, **6**, 1518, 1963.
2. G. A. BIRD, *Numerical simulation and the Boltzmann equation*, paper presented at the 7th Int. Symp. on Rarefied Gas Dynamics, Piza 1970.
3. C. BORGNACKE and P. S. LARSEN, *Statistical collision model for Monte Carlo simulation of polyatomic gas mixture*, J. Comp. Phys., **18**, 405-420, 1975.
4. S. CHAPMAN and T. G. COWLING, *The mathematical theory of non-uniform gases*, Cambridge 1960.
5. N. A. DERZKO, UTIAS rev. no. 35, 1972.
6. J. M. HAMMERSLEY and D. C. HANDSCOMB, *Monte Carlo methods*, Methuen and Co Ltd., London 1964.
7. J. K. HAVILAND, *Methods Comp. Phys.*, **4**, 109, 1965.

8. K. KOURA, *Relaxation of a chemically reacting gas*, Rarefied Gas Dynamics (9. Symp.) **1**, B32, 1974, DFVLR-Press, Porz-Wahn.
9. P. S. LARSEN and C. BORGNACKE, *Statistical collision model for simulating polyatomic gas with restricted energy exchange*, Rarefied Gas Dynamics (9. Symp.) **1**, A7, 1974, DFVLR-Press, Porz-Wahn.
10. J. C. LIGHT, J. ROSS and K. E. SHULER, *Rate coefficients, reaction cross section and microscopic reversibility*, Kinetic Processes in Gases and Plasmas, ed. A.R. Hochstim, Academic Press, 1969.
11. M. J. LIGHTHILL, *Dynamics of a dissociating gas. Part I. Equilibrium flow*, J. Fluid Mech., **2**, 1, 1957.
12. T. G. PAI and S. M. RAMACHANDRA, *Shock structure in a dissociating diatomic gas*, Rarefied Gas Dynamics (9. Symp.) **1**, B27, 1974, DFVLR-Press, Porz-Wahn.
13. D. I. PULLIN, Imperial college, London 1975 (private communication).
14. Y. YOSHIKAWA, *A Monte Carlo calculation of a chemical reacting gas*, in Rarefied Gas Dynamics, Vol. I, 641, (5 Symp.) 1967, ed. C. L. Brundin, Academic Press.

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