NASA TECHNICAL NOTE

NASA TN D-8100

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MONTE CARLO CALCULATIONS OF DIATOMIC MOLECULE GAS FLOWS INCLUDING ROTATIONAL MODE EXCITATION

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JANUARY 1976

1. Report No.
NASA TN-8100

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
MONTE CARLO CALCULATIONS OF DIATOMIC MOLECULE GAS FLOWS
INCLUDING ROTATIONAL MODE EXCITATION

5. Report Date
January 1976

6. Performing Organization Code

7. Author(s)
Kenneth K. Yoshikawa and Yukikazu Itikawa

8. Performing Organization Report No.
A-6196

9. Performing Organization Name and Address
Ames Research Center, NASA
Moffett Field, Calif. 94035

10. Work Unit No.
506-26-21

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D. C. 20546

13. Type of Report and Period Covered
Technical Note

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

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A sample of 1000 model molecules was observed as the gas relaxed to a steady state starting from three specified initial states. The initial states considered are: (1) complete equilibrium, (2) nonequilibrium equipartition (i.e., all rotational energy states are assigned the mean energy level that obtains at equilibrium with a Boltzmann distribution at the translational temperature), and (3) nonequipartition (i.e., the mean rotational energy is different from the equilibrium mean value with respect to the translational energy states). Since only uniform flow is considered, the effect of elastic collisions is ignored in the Monte Carlo simulation.

In all cases investigated the present model satisfactorily simulated the principal features of the relaxation effects in nonequilibrium flow of diatomic molecules.

17. Key Words (Suggested by Author(s))
Fluid mechanics
Numerical analysis
Statistics and probability
Thermodynamics

18. Distribution Statement
Unlimited

STAR Category - 34

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages
49

22. Price*
$3.75

*For sale by the National Technical Information Service, Springfield, Virginia 22161

NOMENCLATURE

A	constants appearing in equations (23) and (25)
$A^{(\ell)}$	integral appearing in cross section (see eq. (6))
B	constant associated with intermolecular potential (eq. (23))
b	impact parameter
C	constant associated with intermolecular potential (eq. (23))
C_α	coefficient of wave function (eq. (13))
C_6	coefficient associated with R^6 term (eq. (23))
c	molecular speed
c_o	rms molecule speed, $\sqrt{\frac{3kT}{M}}$
D_α	transition amplitude
d	strength associated with intermolecular potential
E	kinetic energy or energy
f	distribution function
g	relative speed
$\hbar$	Planck's constant divided by 2π
I	quantity given in equation (25)
$\tilde{K}$	matrix whose element is defined by equation (20)
k	Boltzmann constant
m	magnetic quantum number; also molecular weight
N	number of simulated molecules within the cell
n	number density
P	transition probability
$\tilde{P}$	modified transition probability
Q	collision cross section

R	intermolecular distance
T	temperature
t	time
V	interaction potential
W	eigenenergy of the rotational Hamiltonian
$\|\alpha>$	eigenfunction of the rotational Hamiltonian
$\Delta\tau$	increment of collision time
δ	index of power associated with point centers of repulsion model (eq. (5)) or delta function (eq. (16))
λ	quantity defined in equation (25)
μ	reduced mass
ν	collision frequency
σ	effective collision diameter
τ	characteristic collision time based on initial translational temperature, $1/(n\pi\sigma^2 c_0)$
χ	deflection angle defined in equation (1) or molecular orientation angle (eq. (22))
Ψ	wave function
ω	difference eigenenergy

Subscripts:

C	distance of closest approach of pair of molecules
i,j	rotational states
max	maximum value
0	initial
r	rotational
t	total
tr	translational
α	rotational state

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SUMMARY

The direct simulation Monte Carlo method is used to solve the Boltzmann equation for flows of an internally exicted nonequilibrium gas, namely, of rotationally excited homonuclear diatomic nitrogen. In this study, the semiclassical transition probability model of Itikawa is investigated for its ability to simulate flow fields far from equilibrium. The behavior of diatomic nitrogen is examined for several different nonequilibrium initial states that are subjected to uniform mean flow without boundary interactions.

A sample of 1000 model molecules was observed as the gas relaxed to a steady state starting from three specified initial states. The initial states considered are: (1) complete equilibrium, (2) nonequilibrium equipartition (i.e., all rotational energy states are assigned the mean energy level that obtains at equilibrium with a Boltzmann distribution at the translational temperature), and (3) nonequipartition (i.e., the mean rotational energy is different from the equilibrium mean value with respect to the translational energy states). Since only uniform flow is considered, the effect of elastic collisions is ignored in the Monte Carlo simulation.

In all cases investigated the present model satisfactorily simulated the principal features of the relaxation effects in nonequilibrium flow of diatomic molecules.

INTRODUCTION

Understanding the energy balance, as well as the energy transfer mechanisms, within the internal excited states of a nonequilibrium rarefied flowing gas, is important, in indeed, to a number of problem areas within the broad categories of planetary reentry, combustion, and pollution. In this paper, results are presented on translation-rotation relaxation. Furthermore, these results are obtained by solving Boltzmann's equation by the Monte Carlo direct simulation technique, a method that has received considerable recent attention (refs. 1-11). A feature of this method is that it gives insight into the effects of relaxation on the microscopic level during molecular

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collisions; in particular, the instantaneous distributions of internal states can be continuously followed.

The method is described in detail elsewhere (refs. 1 and 6-9). Briefly, the flow is computed by following in detail several thousand model molecules that are allowed to interact with each other. The coordinates of each molecule in phase space (including rotational state) are at all times known. These coordinates change only during a collision and the modeling of these intermolecular encounters is the essence of an accurate simulation. To account for these encounters, a molecule and a near neighbor are each selected at random as are also their impact parameter and deflection angles - all in a manner representative of typical molecules undergoing encounters. They are accepted for an interaction or rejected depending on a selected rule that depends on cross section and, therefore, on intermolecular potential and the relative velocity of the collision pair. Since the initial coordinates (relative velocity, impact parameter, and pair of rotational states) are known, there remains only to find the final rotational state. This is found by computing the distribution (transition probability) of all final states accessible from the known initial states. The final state is then determined by a random selection from this distribution.

The procedure for handling the "translational" interactions parallels other investigations (refs. 1 and 6-9) treating monatomic gases. The procedure described in this paper differs, however, from other investigations of the treatment of internal state interactions. These other investigations fall into four categories: (1) semi-empirical, (2) classical, (3) semi-classical, and (4) quantum mechanical. The semi-empirical models, energy sink (ref. 11), and rough spheres and loaded spheres (ref. 12), while adequate for steady flows at or near equilibrium, lack sufficient physical detail to inspire confidence in their use for highly nonequilibrium flows.

The classical models (refs. 13 and 14), although consistent with the classical direct simulation Monte Carlo procedure used here, necessarily include approximations to make the models sufficiently tractable to a study of the type that is the subject of this report. Those approximations, although yielding appropriate macroscopic behavior for a nonequilibrium gas, do not adequately describe its microscopic behavior. For example, molecular encounters can occur that violate energy and momentum conservation. One, therefore, is at a loss as to how to treat the negative energies and momentum that arise during a simulation.

Semiclassical models (refs. 10, 15, and 16) appear to be based on physically realistic criteria; however, the Pearson and Hansen model was too simplified. Although this model would not seriously violate equilibrium concepts, it was subject to slow drifts from equipartition (ref. 10) (i.e., the rotational temperature would drift from equality with the translational temperature). Although, by heuristic arguments this model could be altered to qualitatively satisfy proper interaction behavior, we have based our investigation described here on the semiclassical model of Itikawa (ref. 16). This model is founded on more rigorous concepts and, in addition, allows for treatment of molecular collisions. The model also satisfies conservation of probability.

In this paper we treat translation-rotation interactions for a uniformly flowing gas far removed from solid boundaries. In fact, we assume that the rotational relaxation does not affect the flow; we are concerned only with understanding the rotational relaxation behavior. Results are given based on calculations starting from three different sets of initial conditions: (1) complete equilibrium, (2) nonequilibrium equipartition (distribution of energy is constant for all molecules - the energy value is based on the total energy within the rotational states at complete equilibrium that is to be uniformly distributed to each molecule; that is, total energy in rotation is physically correct but distributed incorrectly), and (3) nonequipartition (same as (2) except partition of energy within rotational states is not based on complete equilibrium). Throughout this paper the key mathematical relations essential to the Monte Carlo simulation are defined. Readers desiring a more comprehensive treatment of the method are referred elsewhere (refs. 1 and 6-9).

PROCEDURE

The essential aspects of the procedure are described in the introduction. The analytical relations peculiar to this investigation are described in the text that follows.

Selection Rule Defining the Occurrence of an Encounter

The key to an accurate simulation is the procedure for selecting the molecular pair to reach in a collision, determining whether a reaction occurs, advancing the time parameter in a systematic manner until the next collision occurs, and so on. Both the probability and time intervals are strongly dependent on collision frequency which, in turn, is dependent on the uncertain relation for intermolecular potential.

To aid this discussion, it is worthwhile to refer briefly to classical relations and how those relations depend on, for example, an intermolecular potential base and on a two-parameter repulsion between the point-center model.

In this case, where the intermolecular potential V(R) is spherically symmetric, the deflection angle of an encounter, $\chi(b,g)$, which depend on impact parameter b and relative velocity of approach, g, and the ℓth moment "transport" cross section, $Q^{(\ell)}$, are given by

$$\chi(b,g) = \pi - 2\int_{R_C}^{\infty} (bdR/R^2)/\sqrt{1 - (b/R)^2 - V(R)/(1/2)\mu g^2} \qquad (1)$$

$$Q^{(\ell)}(g) = 2\pi\int_0^{\infty}(1 - \cos^{\ell} \chi)bdb \qquad (2)$$

where R_C and μ are the distance of closest approach and reduced mass, respectively. (For example, see chap. 8, ref. 12.) The collision frequency ν is then given by

$$\nu = nQ^{(\ell)}g \tag{3}$$

From this relation, we can compute the collision time Δt of an encounter and the elapsing time t. There results

$$\begin{aligned} \Delta t &= \frac{2}{N}\frac{1}{\nu} \\ t &= \sum \Delta t \end{aligned} \tag{4}$$

where N is the number of particles in a simulated cell. The collision frequency is not, however, accurately known in general.

In the case when the potential can be described by

$$V(R) = \frac{d}{R^{\delta}} \tag{5}$$

the frequency is given by

$$\nu = \pi n \left(\frac{\delta d}{\frac{1}{2}\mu}\right)^{2/\delta} A^{(\ell)}(\delta) g^{(\delta-4)/\delta} \tag{6}$$

If ν_{max} and g_{max} are the maximum values possible in a cell then the dimensionless ratios in the equation

$$\left(\frac{\nu}{\nu_{max}}\right) = \left(\frac{g}{g_{max}}\right)^{(\delta-4)/\delta} \tag{7a}$$

define a curve for specified values of δ. If one accepts the above relation as representative of molecular encounters, then any point in the region below the curve represents a valid encounter, and points above the curve are invalid. We can then use the relation as a "selection rule," defining whether an encounter occurs or not.

Rather than accept the above relations as completely valid, we also investigated results using the linear relation

$$\frac{\nu}{\nu_{max}} = B + (1 - B)\frac{g}{g_{max}} \tag{7b}$$

where B is an adjustable parameter that gives the best results in the case $B \simeq 0.3$. The reasons underlying this choice are described later.

Discussion of transition probabilities is given in the next section. Given the fact that a rotational transition has occurred, however, trajectories are required by the method so that the particle coordinates in phase-space can be recomputed.

Collision Dynamics

The relative velocity after the collision is obtained by knowing the rotational energy and momentum before and after a collision. These relations are classical relations given by

$$(g')^2 = g^2 - \frac{2}{\mu}\left(E'_{r1} - E_{r1} + E'_{r2} - E_{r2}\right) \tag{8}$$

and

$$b' = \frac{\left[gb - \left(M'_{r1} - M_{r1} + M'_{r2} - M_{r2}\right)/\mu\right]}{g'} \tag{9}$$

where E_{r2} and M_{r2} are rotational energy and momentum before a collision and a prime denotes value after a collision, the transition probabilities as well as calculation of a trajectory are based on $|g' - g|/g << 1$ and $|b' - b|/b << 1$; that is, the relative velocities and impact parameters are only slightly perturbed as a result of the rotational transitions.

The deflection angle (eq. (1)), although also dependent on intermolecular potential, can be adequately approximated to obtain trajectory results by the infinite-rise, rigid-spherical molecule of diameter σ. Such a relation yields

$$\chi(b) = 2 \cos^{-1}\left(\frac{b}{\sigma}\right) \tag{10}$$

To properly account for the effect of inelastic collisions, we use the following mean value:

$$\bar{\chi}(b) = \frac{[\chi(b) + \chi(b')]}{2} \tag{11}$$

The derivation of the relation for rotational transition probabilities is briefly reviewed in the next section.

ROTATIONAL TRANSITION PROBABILITY

The details of the method and its applicability are discussed in reference 16. Only major derivations and results will be presented here for the purpose of direct application to the Monte Carlo simulation.

The interaction considered in the calculation of rotational transition probability is described by the reaction:

$$N_2(j_1) + N_2(j_2) \rightarrow N_2(j_1') + N_2(j_2') \tag{12}$$

The calculation is based on a semi-classical theory. To make numerical calculations tractable, several approximations are made. Whether these approximations are valid is difficult to assess, except that they lead to the correct qualitative behavior in the several applications considered. The total wave function of the system is expanded in terms of a set of wave functions based on a "rotational" Hamiltonian and given by:

$$\psi = \sum_{\alpha} C_\alpha(t)|\alpha> \exp\left(- \frac{i}{\hbar} W_\alpha t\right) \tag{13}$$

Here α specifies the rotational state of the molecules and W_α and $|\alpha>$ are, respectively, the eigenenergy and eigenfunction of that state. The time-dependent coefficient $C_\alpha(t)$ is then determined by:

$$i\hbar \frac{dC_{\alpha'}}{dt} = \sum_{\alpha} \langle\alpha'|V|\alpha\rangle \exp(i\omega_{\alpha'\alpha}t)C_\alpha \tag{14}$$

where V is the interaction potential and $\omega_{\alpha'\alpha} = (W_{\alpha'} - W_\alpha)/\hbar$. We separate the Hamiltonian into isotropic (spherically symmetric) and nonisotropic parts. Since our interest is in inelastic collisions, the elastic process due to the isotropic part of the potential, $V^{(0)}$, is eliminated by introducing the distorted-wave type coefficient defined by:

$$D_\alpha(t) = C_\alpha(t)\exp\left\{\frac{i}{\hbar}\int_{-\infty}^{t} V^{(0)}[R(t')]dt'\right\} \tag{15}$$

where $R(t)$ is the distance separating gravity centers of the molecules at time t. The coefficient D_α satisfies the equation

$$\begin{aligned} i\hbar \frac{dD_{\alpha'}}{dt} &= \sum_{\alpha} \left[\langle\alpha'|V|\alpha\rangle - V^{(0)}\delta_{\alpha'\alpha}\right]\exp(i\omega_{\alpha'\alpha}t)D_\alpha \\ &= \sum_{\alpha} \langle\alpha'|\tilde{V}|\alpha\rangle \exp(i\omega_{\alpha'\alpha}t)D_\alpha \end{aligned} \tag{16}$$

and the initial condition

$$D_\alpha(t = -\infty) = \begin{cases} 1 & \text{for } \alpha = \alpha_o \\ 0 & \text{for } \alpha \neq \alpha_o \end{cases} \tag{17}$$

The second line in equation (16) defines the reduced matrix element $\langle\alpha'|\tilde{V}|\alpha\rangle$.

The transition probability for the process $\alpha_o \rightarrow \alpha$ is given by

$$P(\alpha_o \rightarrow \alpha) = |D_\alpha(t = \infty)|^2 \tag{18}$$

In a rigorous treatment, the state α depends on the rotational angular momenta, j, and the projections, m, of both molecules. For the present problem, we are only interested in the probability averaged over the m states. We use Rabitz method (ref. 17) to eliminate the m-dependence of the interaction matrix (effective potential method). We solve equation (16) with:

$$\alpha \equiv (j_1 j_2),\ D_\alpha \equiv D_{j_1 j_2} \quad \text{and} \quad \langle \alpha' | \tilde{V} | \alpha \rangle \equiv \left\langle j_1' j_2' | \tilde{V}^{eff} | j_1 j_2 \right\rangle$$

This treatment is discussed in more detail in appendix A.

We can further approximate the solution of equation (16) by introducing the exponential approximation (refs. 18-20).

$$\begin{aligned} D_{\alpha'}(\infty) &= \langle \alpha' | \exp \tilde{K} | \alpha_o \rangle \\ &= \sum_{n=o}^{\infty} \frac{1}{n!} \langle \alpha' | \tilde{K}^n | \alpha_o \rangle \end{aligned} \tag{19}$$

where $\tilde{K}$ is a matrix whose element is defined by

$$\langle \alpha_i | \tilde{K} | \alpha_j \rangle = - \frac{i}{h} \int_{-\infty}^{\infty} dt \langle \alpha_i | \tilde{V}^{eff} | \alpha_j \rangle \exp(i\omega_{\alpha_i \alpha_j} t) \tag{20}$$

The element of $\tilde{K}^n$ is evaluated by

$$\langle \alpha' | \tilde{K}^n | \alpha_o \rangle = \sum_{\alpha_1 \alpha_2, \ldots, \alpha_{n-1}} \langle \alpha' | \tilde{K} | \alpha_{n-1} \rangle \langle \alpha_{n-1} | \tilde{K} | \alpha_{n-2} \rangle \ldots \langle \alpha_1 | K | \alpha_o \rangle \tag{21}$$

For $N_2 + N_2$ we select the following interaction potential as the relavant interaction (refs. 21-22),

$$\begin{aligned} V = {} & V^{(0)}(R) + V^{(1)}(R)[P_2(\cos \chi_1) + P_2(\cos \chi_2)] \\ & + V^{(2)}(R) P_2(\cos \chi_1) P_2(\cos \chi_2) \end{aligned} \tag{22}$$

Here P_2 is the Legendre function of order two, R is the separation distance between the two molecules as before, and χ_i is the angle between the directions of the inter-molecular vector and the axis of ith molecule; the two molecules are not necessarily in a single plane. $V^{(2)}$ induces a simultaneous rotational transition in both molecules in first order. Each term of the potential is assumed to have the form

$$\left.\begin{aligned} V^{(0)}(R) &= C\exp(-\alpha R) - C_6/R^6 \\ V^{(1)}(R) &= AC\exp(-\alpha R) \\ V^{(2)}(R) &= BC\exp(-\alpha R) \end{aligned}\right\} \tag{23}$$

(See appendix A for further discussion.)

In the present calculation the trajectory $R(t)$ is determined by solving the classical equation of motion approximated by

$$\frac{1}{2}\mu\left(\frac{dR}{dt}\right)^2 = E - C\,e^{-\alpha R} + \frac{C_6}{R_C{}^6} - \frac{Eb^2}{R_C{}^2} \tag{24}$$

where μ is the reduced mass of the system, b is the impact parameter, R_C is the distance of closest approach, and E is the kinetic energy of the relative motion. This provides a semiclassical version of the modified wave number approximation (ref. 23) with the assumption that the gradients of the attractive part of the potential and the centrifugal force are much smaller than those of the repulsive potential, in the region where most of the rotational transition takes place. The solution of equation (24) can be obtained analytically and the time integration in equation (20) can be performed readily. We have, then

$$\langle\alpha_i|\tilde{K}|\alpha_j\rangle = -i(\alpha_i|\alpha_j)I \tag{25}$$

with

$$I = \frac{\pi}{\alpha\lambda A}\operatorname{cosech}\left(\frac{\pi}{2A}\right)$$

$$\lambda = \hbar(2\mu\tilde{E})^{-1/2}$$

$$A = \frac{\alpha}{2|\omega_{\alpha_i\alpha_j}|}\left(\frac{2\tilde{E}}{\mu}\right)^{1/2}$$

and

$$\tilde{E} = E\left(1 - \frac{b^2}{R_C{}^2}\right) + \frac{C_6}{R_C{}^6}$$

Two important properties of the transition probability should be mentioned: the conservation of probabilities and detailed balancing. The exponential approximation self-ensures the conservation of probabilities:

$$\sum_{j_1'j_2'} P(j_1j_2 \rightarrow j_1'j_2') = 1 \tag{26}$$

To satisfy the detailed balancing relation, we choose, as the kinetic energy E in the calculation of $\langle\alpha_i|\tilde{V}eff|\alpha_j\rangle$, the mean value of the initial and final channel energies (i.e., $E = (1/2)(E_i + E_j)$). The channel energy E_i for the ith channel is defined by

$$E_i = E_t - W_{\alpha_i} = (E_0 + W_{\alpha_0}) - W_{\alpha_i} \tag{27}$$

where E_0 is the initial relative kinetic energy and E_t is the total energy (which is conserved during the collision). This procedure results in a symmetry relation

$$P(j_1j_2 \rightarrow j_1'j_2';E_0) = P(j_1'j_2' \rightarrow j_1j_2;E_0') \tag{28}$$

where

$$E_0 + W_{j_1j_2} = E_0' + W_{j_1'j_2'}$$

In order to have a properly detailed balance, we modify our result by

$$\left.\begin{aligned} &\tilde{P}(j_1j_2 \rightarrow j_1'j_2') = \frac{(2j_1^< + 1)(2j_2^< + 1)}{(2j_1 + 1)(2j_2 + 1)} P(j_1j_2 \rightarrow j_1'j_2') \\ &\text{for } (j_1j_2) \neq (j_1'j_2'), \text{ and} \\ &\tilde{P}(j_1j_2 \rightarrow j_1j_2) = 1 - \sum_{j_1'j_2'(\neq j_1j_2)} \tilde{P}(j_1j_2 \rightarrow j_1'j_2') \end{aligned}\right\} \tag{29}$$

Here $j_i^<$ designates the smaller of j_i and j_i'. These modified transition probabilities, $\tilde{P}$, satisfy both the detailed balancing relation and the conservation of probabilities.

The program listings for calculating rotational transition probability are presented in appendix B.

RESULTS AND DISCUSSION

Calculations were performed using three different sets of initial conditions. These initial conditions, described in the introduction, are: (1) complete equilibrium, (2) nonequilibrium equipartition, and (3) non-equipartition. The first case, equilibrium, was run to test whether the method remains in equilibrium for long computational times; that is, to verify that the model would not drift to improper internal distribution (ref. 10). The second case tests whether, indeed, the model has an internal mechanism to drive itself to equilibrium within a reasonable physical time scale. The third case provides insight into relative internal time scales to reach (1) a quasi-Boltzmann distribution characterized by a rotation temperature $T_{rot} \neq T$ and then (2) the time scale for this quasi-distribution to decay to equilibrium $T_{rot} = T$. The simulations, therefore, permit us to observe energy partitioning and the relaxation mechanisms, as well as relaxation rates. Because we are here interested only in rotational transitions that lead to a final equilibrium state, all elastic collisions have been ignored in order to expedite the calculations.

Equilibrium Case and Collision Frequency

Many of the physical properties for one-dimensional calculations have been based on the hyperbolic function trajectory sech(at) (ref. 15); some others are based on the effective potential, and the classical equations of motion are solved for this interaction potential including the step by step energy conservation.

Collision frequency, however, cannot be evaluated analytically for these potentials (see eqs. 1-3). It is also not feasible to use the Monte Carlo method to compute and thereby describe intermolecular potentials numerically. Nevertheless, we can semi-empirically determine a macroscopically (statistically) correct collision frequency by using the results of equation (7) for the equilibrium case; that is, we determine the most probable index of power δ in equation (7) by varying $\delta = 4$ (Maxwellian molecules) to $\delta = \infty$ (hard-sphere molecules). The simulation should maintain equilibrium when the proper value of δ is chosen. The effect of the parameter δ on rotational energy is sensitive to the higher velocity collisions. We find that rotational temperature increases as the parameter δ increases. Figure 1 shows the computed rotational temperature history from an initial equilibrium state as the value of δ is varied. The proper value for which the model (point centers of repulsion) fits close to the present model, is found to be approximately $C \simeq 0.45$, or $\delta \simeq 7.3$, where $C = (\delta - 4)/\delta$. Also presented in the same figure are the results of the temperature variation obtained by using the linear selection formula of equation (7b) where the parameter B was varied from 0 to 0.5. The best value of B that satisfies this selection rule seems to be $B \simeq 0.3$. Temperature histories computed using this value ($C = 0.45$) are shown next.

In figures 2 through 7, translational and rotational temperatures for different initial conditions are plotted as functions of nondimensional collision time. These temperatures should asymptotically approach the equilibrium values shown by the dotted line at the end of the time scale. Also shown in figure 2 for several time intervals, $t/\tau = 0, 5, 10$, and 20, are the translational and rotational distribution functions. The translational distribution function f_{tr} is plotted as a function of molecular speed ratio c/c_o, where c_o is the rms speed defined by $\sqrt{3kT/M}$. The rotational distribution function f_r is presented in terms of the rotational energy level j for the same collision times corresponding to the translational distribution functions. Mean collision time τ is calculated based on the initial translational temperature, kept always at room temperature $T_{tr} \simeq 320°$ K. Note that initial equilibrium distribution functions for rotational and translational energies are selected at random from the Rayleigh and Maxwellian distributions, respectively, (their distributions, therefore, do not represent analytical functions), and all subsequent distributions evolve from the present simulation using the Itikawa model.

Throughout the testing, all distributions and temperatures represented equally valid equilibrium states. Figures 3a and 3b show the comparison of the Monte Carlo solutions with theoretical (equilibrium) functions for the nondimensional time at $t/\tau = 15$ and 20. Since the Monte Carlo solution - the so called Klimontovich function (ref. 24) - does not, in general, present a smooth function, a mean distribution function (Boltzmann solution), time averaged over the last five collision times (from $t/\tau = 15$ to 20), is shown in figure 3c. This mean value can be compared with the theoretical value when the gas approaches equilibrium. The agreement with theory seems to be very good.

Nonequilibrium Case

The result of the equipartition, nonequilibrium test is shown in figure 4. The gas initially starts in the equipartition state with the rotational energy of all molecules assigned the mean equilibrium energy corresponding to the level of $j = 10$, and where the translational energy is specified as in the previous case. Several energy distribution functions are shown at nondimensional times of 0, 1, 2, 3, 5, 20, and 35. The simulation again seems very good. The distribution functions for $t/\tau = 30$ and 35, and the mean distribution functions averaged over these time intervals, are compared with theoretical calculations in figure 5; once again the agreement is good. Notice that only even-numbered rotational energy levels are occupied. This follows since we have considered a homonuclear model to be initially in an even-numbered level, and we have not allowed changes in nuclear spin.

The last test investigated is for the nonequipartition and nonequilibrium case. All gases initially start with the rotational energy level of $j = 12$ (corresponding to a rotational temperature of $T_r = 455°$ K) and where the translational energy is selected at random from the Maxwellian distribution corresponding to a translational temperature of 320° K. In figure 6, both the rotational and translational temperatures approach an equilibrium state, corresponding to a temperature of 374° K. This occurs in an exponential manner. Transition distribution functions are shown at $t/\tau = 0, 1, 2, 3, 5$, and 20 in the same figure. The present model also appears to perform very well in this case. This is the case (initial rotational temperature higher than translational temperature) for which the modified Pearson-Hansen model failed to show satisfactory performance when extended to higher temperatures (ref. 10).

The distribution functions for $t/\tau = 15$ and 20, and the mean distribution functions of rotational and translational energy, averaged over $t/\tau = 15$ to 20, are shown in figure 7. Comparison with theoretical distributions is very satisfactory.

Notice that in both figures 4 and 6 the gas relaxes asymptotically to equilibrium. The approach is rapid initially and quite slow finally.

Of all the models tested to date, the semiclassical model of Itikawa appears most satisfactory. However, this model with 1000 molecules consumes about 100 sec of the CDC 7600 machine computing time to travel one characteristic collision time. The model, therefore, may still need further simplification to permit its practical use in the more complex molecular simulations, such as, for example, shock wave structure and gas-surface interactions.

CONCLUSION

The Itikawa model when used with the appropriate representations for collision frequency provides an adequate physical description of a homonuclear diatomic gas in rotational relaxation. This model appears to hold the most immediate promise for further application to more complex problems. However, because of the computational time required to do rigorous calculations at each Monte Carlo collision event, subsequent investigations will require simplification of the algorithm. Nevertheless, the present model will permit one to examine the principal features of rotational effects in nonequilibrium flow of diatomic molecules, such as shock wave structure.

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Moffett Field, Calif., 94035, July 1975

APPENDIX A

INTERMOLECULAR POTENTIAL AND INTERACTION MATRIX ELEMENT

Interaction Potential

Each term of the interaction potential (eq. (23)) is assumed to be defined by the representations given in the text. The first term, $V^{(0)}$, can be determined fairly reliably from either the result of molecular beam experiments (ref. 21) or the analysis of transport coefficients (ref. 22). These parameters are $C = 3.44\times10^3$ eV, $C_6 = 73.4$ eV Å^{-6} and $\alpha = 3.16$ Å^{-1}. Unfortunately, we have little information about the anisotropy of the interaction potential for $N_2 + N_2$. Therefore, we adopt the form given by $V^{(1)}$ and $V^{(2)}$ in equation (23), similarly as in reference 15, and regard A and B as adjustable parameters. The values employed in this report are A = B = 0.2.

Interaction Matrix

Applying the effective potential method (ref. 17) to the interaction potential given by equations (22) and (23), we can calculate the matrix element as follows:

$$\begin{aligned}\langle j_1'j_2'|\tilde{V}^{\mathrm{eff}}|j_1j_2\rangle &= \langle j_1'j_2'|V^{\mathrm{eff}}|j_1j_2\rangle - V^{(0)}(R)\delta_{j_1'j_1}\delta_{j_2'j_2}\\ &= (j_1'j_2'|j_1j_2)C\exp[-\alpha R(t)] \qquad \text{(A1)}\end{aligned}$$

$$\begin{aligned}(j_1'j_2'|j_1j_2) = {} & [(2j_1+1)(2j_2+1)(2j_1'+1)(2j_2'+1)]^{1/4}(-1)^L\\ & \times\Bigg\{\frac{A}{\sqrt{5}}\Bigg[(-1)^{j_2}(2j_2+1)^{-1/2}\begin{pmatrix} j_1' & j_1 & 2\\ 0 & 0 & 0\end{pmatrix}\delta_{j_2'j_2}\\ & +(-1)^{j_1}(2j_1+1)^{-1/2}\begin{pmatrix} j_2' & j_2 & 2\\ 0 & 0 & 0\end{pmatrix}\delta_{j_1'j_1}\Bigg]\\ & +\frac{B}{5}\begin{pmatrix} j_1' & j_1 & 2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} j_2' & j_2 & 2\\ 0 & 0 & 0\end{pmatrix}\sum_{m=0,2,4}(2m+1)^{1/2}\begin{pmatrix} 2 & 2 & m\\ 0 & 0 & 0\end{pmatrix}\Bigg\}\end{aligned}$$

(A2)

where $\begin{pmatrix} j_i' & j_i & j\\ 0 & 0 & 0\end{pmatrix}$ is the 3 - j symbol and $L = \max\,(j_1 + j_2,\ j_1' + j_2')$.

APPENDIX B

PROGRAM LISTING FOR ROTATIONAL TRANSITION PROBABILITY CALCULATION

```
*DECK MAIN
      PROGRAM MAIN(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
CROSS SECTION CALCULATION
      COMMON /LLMIT/ LL1MIN,LL1MAX,LL2MIN,LL2MAX
      DIMENSION PWAVE(20,20),SIGMA(20,20),LABCSA(16)
      DIMENSION SIG(20)
      COMMON /CM1/ PWAVE,EKIN,L10,L20,BIMP,NMAX,NPRINT,L1PAR,L2PAR
      COMMON /CM2/ JEL1,JEL2,LABCSA,LLMAX
      COMMON /CM3/ VA,VB,IPRT1,IPRT2,IPRT3,IPRT4
      COMMON /CMVR1/ VC,VALPHA,VC6,BBIMP,EEEE
      COMMON /CV1/ ABCC(40,40,9)
      JMAX= 20
      PAI2= 6.283185
C** INITIAL CLEAR OF ABCC, SHOULD BE MADE FOR EACH VA,VB
      DO 5009 I=1,40
      DO 5009 J=1,40
      DO 5009 K=1,9
      ABCC(I,J,K)= 0.0
 5009 CONTINUE
 5010 CONTINUE
      DO 5016 I=1,JMAX
      DO 5016 J=1,JMAX
      SIGMA(I,J)=0.0
      PWAVE(I,J)= 0.0
 5016 CONTINUE
C** INPUT **  IMPACT PARAMETER (IN ANGSTROM)
C**           CALCULATION FROM 'BIMPI' TO 'BIMPF'   WITH STEP 'DBIMP'
      READ(5,4) BIMPI,DBIMP,BIMPF
    4 FORMAT(3F10.0)
      IF(BIMPI.LT.0.0) GO TO 5999
C** INPUT **  CROSS SECTION CALCULATION (ICROS=1) OR NOT (0)
      READ(5,3) ICROS
C** INPUT **  RELATIVE KINETIC ENERGY (IN EV)
      READ(5,1) EKIN
    1 FORMAT(F10.0)
C** INPUT **  INITIAL ROTATIONAL STATES
      READ(5,2) L10,L20
    2 FORMAT(2I5)
```

```
C** INPUT **  MAX NO. OF TERMS IN EXP
      READ(5,3) NMAX
    3 FORMAT(I5)
C** INPUT ** INDEX FOR PRINT OUT
      READ(5,6) IPRT1,IPRT2,IPRT3,IPRT4
    6 FORMAT(4I5)
C** INPUT **  POTENTIAL PARAMETERS FOR SPHERICAL PART
C**           V(R)= VC*EXP(-VALPHA*R)-VC6/R**6
C**           V IN EV, R IN ANGSTROM
      READ(5,7) VC,VALPHA,VC6
    7 FORMAT(3F10.0)
C** INPUT **  POTENTIAL PARAMETERS FOR NON-SPHERICAL PART
      READ(5,5) VA,VB
    5 FORMAT(2F5.0)
C** INPUT **  WHEN IPRTSG=0,PRINT PARTIAL SUM OVER BIMP
      READ(5,3) IPRTSG
C** INPUT **  LIMITATION OF RANGE OF L1,L2
C**           L1= L1MIN-L1MAX, L2=L2MIN-L2MAX
      READ(5,8) L1MIN,L1MAX,L2MIN,L2MAX
    8 FORMAT(4I5)
      LL1MIN= L1MIN+1
      LL1MAX= L1MAX+1
      LL2MIN= L2MIN+1
      LL2MAX= L2MAX+1
      J1MIN= (LL1MIN+1)/2
      J1MAX= (LL1MAX+1)/2
      J2MIN= (LL2MIN+1)/2
      J2MAX= (LL2MAX+1)/2
      WRITE(6,5900)
     1              BIMPI,DBIMP,BIMPF,
     2              ICROS ,
     3              EKIN,
     4              L10,L20 ,
     5              NMAX,
     6              IPRT1,IPRT2,IPRT3,IPRT4,
     7              VC,VALPHA,VC6,
     8              VA,VB,
     9              IPRTSG
 5900 FORMAT(1H1/5X,10HINPUT DATA/
     1        5X,18HBIMPI,DBIMP,BIMPF/,3F10.2/
     2        5X, 6HICROS/,I5/
     3        5X, 5HEKIN/,F10.6/
     4        5X, 8HL10,L20/,2I5/
     5        5X, 5HNMAX/,I5/
     6        5X,24HIPRT1,IPRT2,IPRT3,IPRT4/,4I5/
```

```
     7          5X,14HVC,VALPHA,VC6/,3F10.4/
     8          5X, 6HVA,VB/,2F5.2/
     9          5X, 7HIPRTSG/,I5//)
      WRITE(6,5902)  L1MIN, L1MAX, L2MIN, L2MAX
 5902 FORMAT(1H0/5X,4H L1=I4,3H - ,I4,3X,4H L2=I4,3H - ,I4/)
C********  NPRINT
      NPRINT= NMAX-3
      BIMP= BIMPI
      IF(ICROS.EQ.0) IPRT4=0
      IF(ICROS.EQ.0) GO TO 5500
      H3= DBIMP/3.0*PAI2
      NSUM= 0
      MPRINT=0
      H3B= H3*BIMP
      CALL PROB
 5100 CONTINUE
      DO 5111  I=J1MIN,J1MAX
      DO 5111  J=J2MIN,J2MAX
      SIGMA(I,J)= SIGMA(I,J)+H3B*PWAVE(I,J)
 5111 CONTINUE
      BIMP=BIMP+DBIMP
      CALL PROB
      H4B=4.0*H3*BIMP
      DO 5112  I=J1MIN,J1MAX
      DO 5112  J=J2MIN,J2MAX
      SIGMA(I,J)=SIGMA(I,J)+H4B*PWAVE(I,J)
 5112 CONTINUE
      BIMP= BIMP+DBIMP
      CALL PROB
      H3B=H3*BIMP
      DO 5113  I=J1MIN,J1MAX
      DO 5113  J=J2MIN,J2MAX
      SIGMA(I,J)= SIGMA(I,J)+H3B*PWAVE(I,J)
 5113 CONTINUE
      IF(IPRTSG.EQ.1) GO TO 5120
      GO TO 5300
 5120 CONTINUE
      IF(BIMP.GT.BIMPF-0.5*DBIMP) GO TO 5200
      NSUM= NSUM+2
      GO TO 5100
 5200 CONTINUE
      MPRINT =1
      IF(IPRTSG .EQ.0) GO TO 5400
 5300 CONTINUE
C***************SEARCH FOR MAX OF SIGMA
```

```
      SMAX=0.0
      DO 5305 I=J1MIN,J1MAX
      DO 5305 J=J2MIN,J2MAX
      IF(SIGMA(I,J).GT.SMAX) SMAX= SIGMA(I,J)
 5305 CONTINUE
C************ PRINT
      L1PARO= MOD(L10,2)+1
      L2PARO= MOD(L20,2)+1
      WRITE(6,5901) BIMPI,BIMP,NSUM,L10,L20,EKIN
 5901 FORMAT(1H1/5X,23HCROSS SECTION FOR BIMP=F6.2,3H - ,F6.2,7H (NSUM=
     1I2,1H),3X,5H(L10=I2,1X,4HL20=I2,1H),3X,5HEKIN=F13.5//3X,2HL2)
      DO 5311 JINV=J2MIN,J2MAX
      J= J2MIN+J2MAX-JINV
      L2= 2*J-3+L2PARO
C**********  NORMALIZATION TO SMAX
      DO 5310 I=J1MIN,J1MAX
      SIG(I)= SIGMA(I,J)/SMAX
 5310 CONTINUE
      JF= J1MIN+15
      IF(JF.GT.J1MAX) JF= J1MAX
      WRITE(6,5911) L2,(SIG(I),I=J1MIN,JF)
 5911 FORMAT(1H0,3X,I2,16(1PF6.3,1X))
 5311 CONTINUE
      WRITE(6,5912) (LABCSA(I),I=1,16)
 5912 FORMAT(1H0,4X,16(3X,I2,2X),3H L1)
      SMAX= 0.1*SMAX
      WRITE(6,5919) SMAX
 5919 FORMAT(1H0/3X,15HNORMALIZ FACTOR,2X,E13.5,2X,11HANGSTROM**2)
      SEL= -SIGMA(JEL1,JEL2)
C********* ELASTIC
      WRITE(6,5918) SEL
 5918 FORMAT(1H0,4X,29HTOTAL INELASTIC CROSS SECTION,2X,E13.5)
      IF(MPRINT.EQ.1) GO TO 5400
      GO TO 5120
 5400 CONTINUE
C*********  ROTATIONAL CONSTANT IN EV
      BROT= 0.2512E-3
      S= 0.0
      SWW= 0.0
      W0= BROT* FLOAT(L10*(L10+1)+L20*(L20+1))
      DO 5415 I=J1MIN,J1MAX
      LI= 2*I-3+L1PARO
      DO 5414 J=J2MIN,J2MAX
      IF(I.EQ.JEL1.AND.J.EQ.JEL2) GO TO 5414
      L2= 2*J-3+L2PARO
```

```
      W1= BROT* FLOAT(L1*(L1+1)+L2*(L2+1))
      WW= (W0-W1)**2
      SWW= SWW+SIGMA(I,J)*WW
      S=S+SIGMA(I,J)
 5414 CONTINUE
 5415 CONTINUE
      WRITE(6,5916) S
 5916 FORMAT(1H0,4X,29HTOTAL INELASTIC CROSS SECTION,2X,E13.5)
      WRITE(6,5917) SWW
 5917 FORMAT(1H0/4X,27H*****  SUM OF PCORCT  *****,3X,4HSWW=E13.5/)
      GO TO 5010
 5500 CONTINUE
      IF(BIMP.LT.0.0) GO TO 5010
      CALL PROB
      IF(BIMP.GE.BIMPF-0.5*DBIMP)GO TO 5010
 5501 CONTINUE
      BIMP=BIMP+DBIMP
      GO TO 5500
 5999 CONTINUE
      STOP
      END


*DECK PROB
      SUBROUTINE PROB
C*********  MAIN PROGRAM FOR THE CALC. OF TRANS. PROB.
      COMMON /LLMIT/ LL1MIN,LL1MAX,LL2MIN,LL2MAX
      DIMENSION PODD(20,20),PEVN(20,20),PWAVE(20,20)
      DIMENSION AKSUM0(20,20),AKSUM1(20,20)
      DIMENSION LABCSA(16)
      COMMON /MV1/ AMATRX(20,20,9)
      COMMON /MV2/ VBB,VAA,BROT,ETOT,BRC,VVALP
      COMMON /CMVR1/ VC,VALPHA,VC6,BIMP,EEEE
      COMMON /MV3/ NCOUNT
      COMMON /CM1/ PWAVE,EKIN,L10,L20,BBBB,NMAX,NPRINT,L1PAR,L2PAR
      COMMON /CM2/ JEL1,JEL2,LABCSA,LLMAX
      COMMON /CM3/ VA,VB,IPRT1,IPRT2,IPRT3,IPRT4
      ICLOCK=0
      BIMP=BBBB
      JMAX=20
      LMAX= 2*JMAX-2
C*********  REDUCED MASS IN AMU
      RMASS= 14.02
C*********  ROTATIONAL CONSTANT IN EV
      BROT= 0.2512E-3
```

```
      VVALP= 0.045723*VALPHA/ SQRT(RMASS)
      VAA= 0.4472136*VA
      VBB= 0.2*VB*0.6298283
      ETOT= EKIN+ FLOAT(L10*(L10+1)+L20*(L20+1) )*BROT
      EB= ETOT/BROT
      EB1= SQRT(EB)
      LLMAX= INT(EB1)+1
      IF(IPRT1.EQ.1) GO TO 11
      WRITE(6,901) BIMP,L10,L20,EKIN,ETOT,LLMAX,EB,VC,VALPHA,VC6,VA,VB
  901 FORMAT(1H1,5X,5HBIMP=F6.2,5HANGST,5X,6H( L10=I2,5H L20=I2,2H ),
     1         5X,5HEKIN=E13.5,3HEV ,3X,5HETOT=E13.5,3X,6HLLMAX=I2,
     2 3X,3HEB=F8.2/6X,3HVC=F10.2,2X,7HVALPHA=F8.3,2X,4HVC6=F7.2,2X,
     3 3HVA=F7.2,2X,3HVB=F7.2/)
   11 CONTINUE
      IF(LLMAX.GT.LMAX) LLMAX=LMAX
      IF(LL1MAX.GT.LLMAX) LL1MAX= LLMAX
      IF(LL2MAX.GT.LLMAX) LL2MAX= LLMAX
      DO 18 I=1,JMAX
      DO 18 J=1,JMAX
      PEVN(I,J)= 0.0
      PODD(I,J)= 0.0
      PWAVE(I,J)= 0.0
      AKSUM0(I,J)=0.0
      AKSUM1(I,J)= 0.0
      DO 16 M=1,9
      AMATRX(I,J,M)= 0.0
   16 CONTINUE
   18 CONTINUE
      LL10= L10+1
      LL20= L20+1
      JEL1= (LL10+1)/2
      JEL2=(LL20+1)/2
      L1PAR= MOD(L10,2)+1
      L2PAR= MOD(L20,2)+1
      IF(L1PAR.LT.LL1MIN) L1PAR= LL1MIN
      IF(L2PAR.LT.LL2MIN) L2PAR= LL2MIN
      CL0= FLOAT((2*L10+1)*(2*L20+1))
      PE0= 0.0
C*********  N= 1
      N=1
      LL1I= LL10
      LL2I= LL20
      NCOUNT= 0
      DO 59 K=1,9
      CALL VMATRX(LL1I,LL2I,K)
```

```
 59 CONTINUE
    LL1FMN= MAX0(LL10-2,L1PAR)
    LL1FMX= MIN0(LL10+2,LL1MAX)
    LL2FMN= MAX0(LL20-2,L2PAR)
    LL2FMX= MIN0(LL20+2,LL2MAX)
    K= 1
    JJI1= (LL1I+1)/2
    JJI2= (LL2I+1)/2
    DO 64 I=1,3
    LL2F= LL20-4+2*I
    DO 63 J=1,3
    LL1F= LL10-4+2*J
    IF(LL2F.LT.1.OR.LL1F.LT.1) GO TO 62
    JJF1= (LL1F+1)/2
    JJF2= (LL2F+1)/2
    AKSUMO(JJF1,JJF2)= AMATRX(JJI1,JJI2,K)
 62 K=K+1
 63 CONTINUE
 64 CONTINUE
    TOTPW= 0.0
    TOTPC= 0.0
    DO 74 LL1F=LL1FMN,LL1FMX,2
    DO 73 LL2F=LL2FMN,LL2FMX,2
    JJF1= (LL1F+1)/2
    JJF2= (LL2F+1)/2
    PODD(JJF1,JJF2)= AKSUMO(JJF1,JJF2)
    PEVN(JJF1,JJF2)= 0.0
    IF(LL1F.EQ.LL1I.AND.LL2F.EQ.LL2I) PEVN(JJF1,JJF2)=1.0
    PWAVE(JJF1,JJF2)= PODD(JJF1,JJF2)**2*4.0+PEVN(JJF1,JJF2)**2
    P=PWAVE(JJF1,JJF2)
    LO1=LL1F-1
    LO2=LL2F-1
    IF(IPRT2.EQ.1 ) GO TO 72
    PCORCT= P
    WRITE(6,902) N,LO1,LO2,P,PCORCT,PODD(JJF1,JJF2),AKSUMO(JJF1,JJF2)
902 FORMAT(1H0,2X,2HN=I2,3X,5H L1F=I2,2X,5H L2F=I2,5X,6HPWAVE=E13.5,
   1       3X,7HPCORCT=E13.5,3X,5HPODD=E13.5,5X,6HAKSUM=E13.5)
 72 CONTINUE
    TOTPW=TOTPW+P
 73 CONTINUE
 74 CONTINUE
    IF(IPRT1.EQ.1) GO TO 75
    WRITE(6,904) N, TOTPW,ICLOCK,NCOUNT,TOTPC
 75 CONTINUE
    IF(NMAX.EQ.1) GO TO 300
```

```
      N= 2
C*********100
  100 CONTINUE
      NCOUNT= 0
      N2= 2*N-2
      LL2IMN=MAX0(LL20-N2,L2PAR)
      LL2IMX= LL20+N2
      IF(LL2IMX.GE.LLMAX) LL2IMX= LLMAX
      DO 149 LL2I=LL2IMN,LL2IMX,2
      JJI2= (LL2I+1)/2
      EB2= SQRT(EB- FLOAT(LL2I-1)**2)
      LLMAX1= INT(EB2)+1
      LL1I=LL10+N2
      JJI1=(LL1I+1)/2
      IF(LLMAX1.GE.LL1MAX) LLMAX1= LL1MAX
      IF(LL1I.GT.LLMAX1) GO TO 130
      DO 114 K=5,8,3
      CALL VMATRX(LL1I,LL2I,K)
  114 CONTINUE
      DO 119 K=3,9,3
      CALL VMATRX(LL1I,LL2I,K)
  119 CONTINUE
      IF(LL1I-2.LT.1) GO TO 125
      AMATRX(JJI1,JJI2,4) = AMATRX(JJI1-1,JJI2,6)
      K=4
      IF(LL2I.EQ.LL20-N2.OR.LL2I.EQ.LL20+N2)  CALL  VMATRX(LL1I,LL2I,K)
      AMATRX(JJI1,JJI2,7)= AMATRX(JJI1-1,JJI2+1,3)
      K= 7
      IF(LL2I.EQ.LL20+N2-2.OR.LL2I.EQ.LL20+N2) CALL  VMATRX(LL1I,LL2I,K)
      IF(LL2I-2.LT.1) GO TO 130
      AMATRX(JJI1,JJI2,1)= AMATRX(JJI1-1,JJI2-1,9)
      K= 1
      IF(LL2I.EQ.LL20-N2+2.OR.LL2I.EQ.LL20-N2) CALL  VMATRX(LL1I,LL2I,K)
  125 CONTINUE
      IF(LL2I-2.LT.1) GO TO 130
      AMATRX(JJI1,JJI2,2) = AMATRX(JJI1,JJI2-1,8)
      K= 2
      IF(LL2I.EQ.LL20-N2)  CALL  VMATRX(LL1I,LL2I,K)
  130 CONTINUE
      LL1I=LL10-N2
      JJI1= (LL1I+1)/2
      IF(LL1I.LT.L1PAR) GO TO 149
      DO 134 K=5,8,3
      CALL VMATRX(LL1I,LL2I,K)
  134 CONTINUE
```

```
      DO 139 K=1,7,3
      CALL VMATRX(LL1I,LL2I,K)
  139 CONTINUE
      AMATRX(JJI1,JJI2,6)= AMATRX(JJI1+1,JJI2,4)
      K= 6
      IF(LL2I.EQ.LL20-N2.OR.LL2I.EQ.LL20+N2)  CALL VMATRX(LL1I,LL2I,K)
      AMATRX(JJI1,JJI2,9)= AMATRX(JJI1+1,JJI2+1,1)
      K=9
      IF(LL2I.EQ.LL20+N2-2.OR.LL2I.EQ.LL20+N2) CALL VMATRX(LL1I,LL2I,K)
      IF(LL2I-2.LT.1) GO TO 149
      AMATRX(JJI1,JJI2,2)= AMATRX(JJI1,JJI2-1,8)
      K= 2
      IF(LL2I.EQ.LL20-N2) CALL VMATRX(LL1I,LL2I,K)
      AMATRX(JJI1,JJI2,3)= AMATRX(JJI1+1,JJI2-1,7)
      K= 3
      IF(LL2I.EQ.LL20-N2+2.OR.LL2I.EQ.LL20-N2) CALL VMATRX(LL1I,LL2I,K)
  149 CONTINUE
C*********  150
      LL1IMN= MAX0(LL10-N2+2,L1PAR)
      LL1IMX= LL10+N2-2
      IF(LL1IMX.GE.LL1MAX) LL1IMX= LL1MAX
      DO 199 LL1I=LL1IMN,LL1IMX,2
      JJI1= (LL1I+1)/2
      EB2= SQRT(EB- FLOAT(LL1I-1)**2)
      LLMAX1=INT(EB2)+1
      LL2I= LL20+N2
      JJI2= (LL2I+1)/2
      IF(LLMAX1.GE.LL2MAX) LLMAX1= LL2MAX
      IF(LL2I.GT.LLMAX1) GO TO 180
      DO 164 K=5,9
      IF(LL1I.EQ.LL10+N2-2.AND.K.EQ.6) GO TO 163
      CALL VMATRX(LL1I,LL2I,K)
      GO TO 164
  163 CONTINUE
      AMATRX(JJI1,JJI2,6)= AMATRX(JJI1+1,JJI2,4)
  164 CONTINUE
      IF(LL2I-2.LT.1) GO TO 175
      AMATRX(JJI1,JJI2,2)= AMATRX(JJI1,JJI2-1,8)
      AMATRX(JJI1,JJI2,3)= AMATRX(JJI1+1,JJI2-1,7)
      IF(LL1I-2.LT.1) GO TO 180
      AMATRX(JJI1,JJI2,1)= AMATRX(JJI1-1,JJI2-1.9)
  175 CONTINUE
      IF(LL1I-2.LT.1) GO TO 180
      AMATRX(JJI1,JJI2,4)= AMATRX(JJI1-1,JJI2,6)
  180 CONTINUE
```

```
      LL2I=LL20-N2
      JJI2= (LL2I+1)/2
      IF(LL2I.LT.L2PAR) GO TO 199
      DO 184 K=5,6
      IF(LL1I.EQ.LL10+N2-2.AND.K.EQ.6) GO TO 183
      CALL VMATRX(LL1I,LL2I,K)
      GO TO 184
  183 CONTINUE
      AMATRX(JJI1,JJI2,6)= AMATRX(JJI1+1,JJI2,4)
  184 CONTINUE
      DO 189 K=1,3
      CALL VMATRX(LL1I,LL2I,K)
  189 CONTINUE
      AMATRX(JJI1,JJI2,8)= AMATRX(JJI1,JJI2+1,2)
      AMATRX(JJI1,JJI2,9)= AMATRX(JJI1+1,JJI2+1,1)
      IF(LL1I-2.LT.1) GO TO 199
      AMATRX(JJI1,JJI2,4)= AMATRX(JJI1-1,JJI2,6)
      AMATRX(JJI1,JJI2,7)= AMATRX(JJI1-1,JJI2+1,3)
C*********  199
  199 CONTINUE
      LL1FMX=LL10+2*N
      LL2FMX= LL20+2*N
      LL1FMN= LL10-2*N
      IF(LL1FMN.LT.L1PAR) GO TO 201
      LL11=LL1FMN+2
  200 CONTINUE
      LL2FMN=LL20-2*N
      IF(LL2FMN.LT.L2PAR) GO TO 202
      LL22= LL2FMN+2
      GO TO 205
  201 CONTINUE
      LL1FMN= L1PAR
      LL11= L1PAR
      GO TO 200
  202 CONTINUE
      LL2FMN=L2PAR
      LL22= L2PAR
  205 CONTINUE
      LL22F= LL2FMX-2
      IF(LL2FMX.LE.LL2MAX) GO TO 206
      LL2FMX= LL2MAX
      LL22F= LL2MAX
  206 CONTINUE
      DO 249 L2=LL22,LL22F,2
      LL11F= LL1FMX-2
```

```
      EB2= SQRT(EB- FLOAT(L2-1)**2)
      LLMAX1= INT(EB2)+1
      IF(LLMAX1.GE.LL1MAX) LLMAX1= LL1MAX
      IF(LL1FMX.GE.LLMAX1) LL11F= LLMAX1
      DO 248 L1= LL11,LL11F,2
      K1= 1
      K2= 0
      L22=L2-2
      L11= L1-2
      IF(L2.LE.L2PAR) L22= L2PAR
      IF(L1.LE.L1PAR) L11= L1PAR
      IF(L2.LE.L2PAR) K1=4
      IF(L1.LE.L1PAR) K2= 1
      K= K1
      J1= (L1+1)/2
      J2= (L2+1)/2
      AK= AKSUMO(J1.J2)
      L2P2=L2+2
      DO 219 LL2= L22.L2P2,2
      K= K+K2
      L1P2=L1+2
      DO 218 LL1=L11.L1P2.2
      JJ1= (LL1+1)/2
      JJ2= (LL2+1)/2
      AKSUM1(JJ1,JJ2)= AK*AMATRX(J1,J2,K)+AKSUM1(JJ1,JJ2)
      K= K+1
  218 CONTINUE
  219 CONTINUE
C*********  PRINT OF AMATRX
      IF(N.LT.IPRT3) GO TO 248
      LO1=L1-1
      LO2= L2-1
      IF(L2.GE.LL22F-1.AND.LL20+2*N.LE.LLMAX+2)  GO TO 220
      IF(L1.GE.LL11F-1.AND.LL10+2*N.LE.LLMAX+2)  GO TO 220
      IF(L2.EQ.LL22.AND.LL20-2*N.GE.L2PAR-2)  GO TO 220
      IF(L1.EQ.LL11.AND.LL10-2*N.GE.L1PAR-2)  GO TO 220
      GO TO 248
  220 CONTINUE
      WRITE(6,906) LO1,LO2
  906 FORMAT(1H0,5X,15HCHECK OF AMATRX,5X,3HL1=I2,2X,3HL2=I2)
      WRITE(6,907) (AMATRX(J1,J2,J),J=1,9)
  907 FORMAT(1H ,2X,9E13.5)
  248 CONTINUE
  249 CONTINUE
C*********  250
```

```
      LL1FMX= LL10+2*N
      TOTPW= 0.0
      DO 299 LL2F=LL2FMN,LL2FMX,2
      LL11F= LL1FMX
      EB2= SQRT(EB- FLOAT(LL2F-1)**2)
      LLMAX1= INT(EB2)+1
      IF(LLMAX1.GE.LL1MAX) LLMAX1= LL1MAX
      IF(LL1FMX.GE.LLMAX1) LL11F= LLMAX1
      DO 298 LL1F=LL1FMN,LL11F,2
      JJF1= (LL1F+1)/2
      JJF2= (LL2F+1)/2
      AKSUM1(JJF1,JJF2)= AKSUM1(JJF1,JJF2)/ FLOAT(N)
      IF(MOD(N,2).NE.0) GO TO 294
      AKSUM1(JJF1,JJF2)= -4.0*AKSUM1(JJF1,JJF2)
      PEVN(JJF1,JJF2)= PEVN(JJF1,JJF2)+ AKSUM1(JJF1,JJF2)
      PWAVE(JJF1,JJF2)= PODD(JJF1,JJF2)**2*4.0+PEVN(JJF1,JJF2)**2
      GO TO 295
  294 CONTINUE
      PODD(JJF1,JJF2)= PODD(JJF1,JJF2)+ AKSUM1(JJF1,JJF2)
      PWAVE(JJF1,JJF2)= PODD(JJF1,JJF2)**2*4.0+PEVN(JJF1,JJF2)**2
  295 CONTINUE
      P= PWAVE(JJF1,JJF2)
      L01= LL1F-1
      L02= LL2F-1
C********* PRINT OF PWAVE
      IF(N.LE.NPRINT) GO TO 297
      IF(P.GE.0.1E-4) GO TO 296
      IF(LL1F.EQ.LL1FMN) GO TO 296
      IF(LL1F.GT.LL11F-2) GO TO 296
      GO TO 297
  296 CONTINUE
      PCORCT= P
      WRITE(6,902) N,L01,L02,P,PCORCT,PODD(JJF1 ,JJF2) ,AKSUM1(JJF1,JJF2)
  297 CONTINUE
      TOTPW= TOTPW+P
      AKSUM0(JJF1,JJF2)= AKSUM1(JJF1,JJF2)
      AKSUM1(JJF1,JJF2)= 0.0
  298 CONTINUE
  299 CONTINUE
      PE1=PWAVE(JEL1,JEL2)
      PE10= ABS((PE1-PE0)/PE1)
      IF(IPRT1.EQ.1) GO TO 3904
      WRITE(6,904) N,TOTPW,ICLOCK,NCOUNT,TOTPC
  904 FORMAT(1H0//2X,8H***** N=I2,5X,13HSUM OF PWAVE=E13.5,
     15X,7HICLOCK=I10,3HSEC,5X,7HNCOUNT=I10,5X,6HTOTPC=E13.5)
```

```
 3904 CONTINUE
      IF(ABS(TOTPW-1.0).LT.0.1E-3.AND.PE10.LT.0.1E-3) GO TO 300
      IF(N.EQ.NMAX) GO TO 300
      N=N+1
      PE0= PE1
      GC TO 100
  300 CONTINUE
C*********  ELASTIC
      DELST1= PEVN(JEL1,JFL2)
      DELST2= -2.0*PODD(JFL1,JEL2)
C*********  FINAL PRINT
      MPRINT=0
      L1PAR0= MOD(L10,2)+1
  301 CONTINUE
      WRITE(6,901) BIMP,L1C,L20,EKIN,ETOT,LLMAX,EB,VC,VALPHA,VC6,VA,VB
      WRITE(6,910) N,TOTPW,ICLOCK,TOTPC
  910 FORMAT(1H ,5X,5HNMAX=I2,2X,6HTOTPW=E13.5,2X,6HCLOCK=I5,3HSEC,
     1   2X,6HTOTPC=E13.5//3X,2HL2)
      IMN= LL2FMN
      IMX=LL2FMX
      IF(MOD(LL2FMX-L2PAR,2).NE.0) IMX= LL2FMX-1
      DO 319 I=IMN,IMX,2
      LL2F= IMX+IMN-I
      J2= (LL2F+1)/2
      LL11F= LL1FMX
      EB2= SQRT(EB- FLOAT(LL2F-1)**2)
      LLMAX1= INT(EB2)+1
      IF(LLMAX1.GE.LL1MAX) LLMAX1= LL1MAX
      IF(LL1FMX.GE.LLMAX1) LL11F=LLMAX1
      J1MX= (LL11F+1)/2
      J1MX1= J1MX
      J1MN= (L1PAR+1)/2
      IF(J1MX-J1MN.GT.15) J1MX= J1MN+15
      L02=LL2F-1
      WRITE(6,911) L02,(PWAVE(J1,J2),J1=J1MN,J1MX)
  911 FORMAT(1H0/3X,I2,16(1PF6.3,1X))
      IF(MPPINT.EQ.1) GO TO 319
      LMIN2= MIN0(L20,L02)
      CL10= FLOAT(2*LMIN2+1)
      DO 318 J1= J1MN,J1MX1
      L01= 2*J1-3+L1PAR0
      LMIN1= MIN0(L10,L01)
      CL1= CL10* FLOAT(2*LMIN1+1)
      P= PWAVE(J1,J2)
      PCCRCT= CL1/CL0*P
```

```
      TOTPC= TOTPC+PCORCT
      PWAVE(J1,J2)= PCORCT
  318 CONTINUE
  319 CONTINUE
      LABCSA(1)= L1PAR-1
      DO 320 I=2,16
      LABCSA(I)=LABCSA(1)+(I-1)*2
  320 CONTINUE
      WRITE(6,912)  (LABCSA(J),J=1,16)
  912 FORMAT(1H0,4X,16(3X,I2,2X),3H L1)
      IF(MPRINT.EQ.1) GO TO 9906
C*********  PRINT OF PCORCT WITH PELASTIC MODIFIED
      PWAVE(JEL1,JEL2)= 1.0-TOTPC+PWAVE(JEL1,JEL2)
      IF(IPRT4.EQ.1) GO TO 1000
      MPRINT=1
      GO TO 301
 9906 CONTINUE
      WRITE(6,9909) TOTPC
 9909 FORMAT(1H0/2X,35H*******PCORCT WITH ELASTIC MODIFIED,5X,
     1      7H(TOTPC=E13.5,2H )/)
 1000 CONTINUE
      PWAVE(JEL1,JEL2)= PWAVE(JEL1,JEL2)-1.0
      WRITE(6,9911) DELST1,DELST2
 9911 FORMAT(1H0,1X,28H***** FOR ELASTIC SCATTERING,3X,3HD1=E13.5,
     1       2X,3HD2=E13.5)
      RETURN
      END


*DECK VMAT
      SUBROUTINE VMATRX(LL1,LL2,K)
      COMMON /MV1/ AMATRX(20,20,9)
      COMMON /MV2/ VBB,VAA,BROT,ETOT,BRC,VVALP
      COMMON /CMVR1/ VC,VALPHA,VC6,BIMP,EIJ
      COMMON /MV3/ NCOUNT
      COMMON /CV1/ ABCC(40,40,9)
      JJ1= (LL1+1)/2
      JJ2= (LL2+1)/2
      L1J= LL1-1
      L2J= LL2-1
      IF(K.GT.3) GO TO 1011
      L2I= L2J-2
      IF(L2I.LT.0) GO TO 1510
      GO TO 1100
 1011 IF(K.GT.6) GO TO 1012
```

```
      L2I= L2J
      GO TO 1100
 1012 L2I= L2J+2
 1100 CONTINUE
      IF(MOD(K,3).NE.1) GO TO 1111
      L1I= L1J-2
      IF(L1I.LT.0) GO TO 1510
      GO TO 1200
 1111 IF(MOD(K,3).NE.2) GO TO 1112
      L1I= L1J
      GO TO 1200
 1112 L1I= L1J+2
 1200 CONTINUE
      ABC= ABCC(LL1,LL2,K)
      IF(ABC.NE.0.0) GO TO 1299
CALCULATION OF VEFF(L1I,L2I / L1J,L2J )
      CC1= CG20(L1I,L1J)
      CC2= CG20(L2I,L2J)
 1211 CONTINUE
      IF(K.LE.5) CSIGN= (-1.0)**(L1J+L2J)
      IF(K.GE.6) CSIGN= (-1.0)**(L1I+L2I)
      C= FLOAT((2*L1I+1)*(2*L2I+1)*(2*L1J+1)*(2*L2J+1))**0.25 *CSIGN
 1212 CONTINUE
      B= VBB*CC1*CC2
 1213 CONTINUE
      A= 0.0
      IF(L2I.NE.L2J) GO TO 1215
      A= VAA*CC1/ SQRT(FLOAT(2*L2I+1))
      IF(MOD(L2I,2).NE.0) A= -A
 1215 IF(L1I.NE.L1J) GO TO 1219
      AA= VAA*CC2/ SQRT(FLOAT(2*L1I+1))
      IF(MOD(L1I,2).NE.0) AA= -AA
      A= A+AA
 1219 CONTINUE
      ABC= C*(B+A)
      ABCC(LL1,LL2,K)= ABC
 1299 CONTINUE
      WI= BROT*FLOAT(L1I*(L1I+1)+L2I*(L2I+1))
      WJ= BROT*FLOAT(L1J*(L1J+1)+L2J*(L2J+1))
      WIJ= ABS(WI-WJ)
      EI= ETOT-WI
      EJ= ETOT-WJ
      IF(EI.LE.0.0.OR.EJ.LE.0.0) GO TO 1510
      EIJ= 0.5*(EI+EJ)
      CALL ROOT(RC)
```

```
      BRC= 1.0-(BIMP/RC)**2+VC6/EIJ/RC**6
      EIJ1= EIJ*BRC
      IF(K.EQ.5) GO TO 1500
      IF(L1I.EQ.L2J.AND.K.EQ.3) GO TO 1500
      IF(L1I.EQ.L2J.AND.K.EQ.7) GO TO 1500
      AIJ= VVALP* SQRT(EIJ1)/WIJ
      EW= EIJ1/WIJ
      DBALPH= EW/AIJ
      APAI= 1.570796327/AIJ
      F=  EXP(-APAI)
      FAIJ= 2.0*APAI*F/(1.0-F*F)
      AAA= ABC*DBALPH*FAIJ
C*** 999  CHECK PRINT
  999 CONTINUE
 1498 CONTINUE
      NCOUNT= NCOUNT+1
 1499 CONTINUE
      AMATRX(JJ1,JJ2,K)= AAA
      RETURN
 1500 CONTINUE
      AAA= ABC/VVALP* SQRT(EIJ1)
      GO TO 1498
 1510 CONTINUE
      AAA= 0.0
      GO TO 1499
      END


      SUBROUTINE ROOT(RC)
C*****  REVISED  8/26/74
      COMMON /CMVR1/ VC,VALPHA,VC6,BIMP,EKIN
      RMIN= 1.12
      RRO= ALOG(VC/EKIN)/VALPHA
      IF(RRO.GE.4.1) RRO= 4.1
      N=1
 3099 CONTINUE
      RR=RRO
 3100 CONTINUE
      RL= EKIN*BIMP**2/RR**2
      V= VC* EXP(-VALPHA*RR)
      V1= -VALPHA*V
      IF(VC6.EQ.0.0) GO TO 3101
      VR= VC6/RR**6
      V= V-VR
      V1= V1+6.0*VR/RR
```

```
 3101 CONTINUE
      F= (V+RL-EKIN)/(2.0*RL/RR-V1)
      IF(ABS(F/RR).LT.0.1E-5) GO TO 3199
      IF(N.GE.100) GO TO 3299
      RR= RR+F
      IF(RR.LT.RMIN) GO TO 3900
      N=N+1
      GO TO 3100
 3199 CONTINUE
      RC= RR
      RETURN
 3299 CONTINUE
      WRITE(6,998) RR,F,RRO
  998 FORMAT(1H0//5X,14HERROR N GT 100,3X,3HRR=F13.5,3X,2E13.5//)
      RR=RRO
      GO TO 3199
 3900 CONTINUE
      RRO= 0.5*(RRO+RMIN)
      GO TO 3099
      END


*DECK CG20
      FUNCTION CG20(J1,J2)
      IF(J2.EQ.J1+2.OR.J2.EQ.J1-2) GO TO 8001
      IF(J2.EQ.J1) GO TO 8002
      C= 0.0
      GO TO 8100
 8001 CONTINUE
      IF(J2.EQ.J1+2) J=J1
      IF(J2.EQ.J1-2) J= J2
      X1= FLOAT(J+2)/FLOAT(2*J+5)
      X2= FLOAT(J+1)/FLOAT(2*J+3)
      X3= 1.0/FLOAT(2*J+1)
      C=  SQRT(1.5*X1*X2*X3)
      GO TO 8099
 8002 CONTINUE
      J= J1
      X1= FLOAT(J+1)/FLOAT(2*J+3)
      X2= FLOAT(J)/FLOAT(2*J+1)
      X3= 1.0/FLOAT(2*J-1)
      C= - SQRT(X1*X2*X3)
 8099 IF(MOD(J,2).NE.0) C= -C
 8100 CG20= C
      RETURN
      END
```

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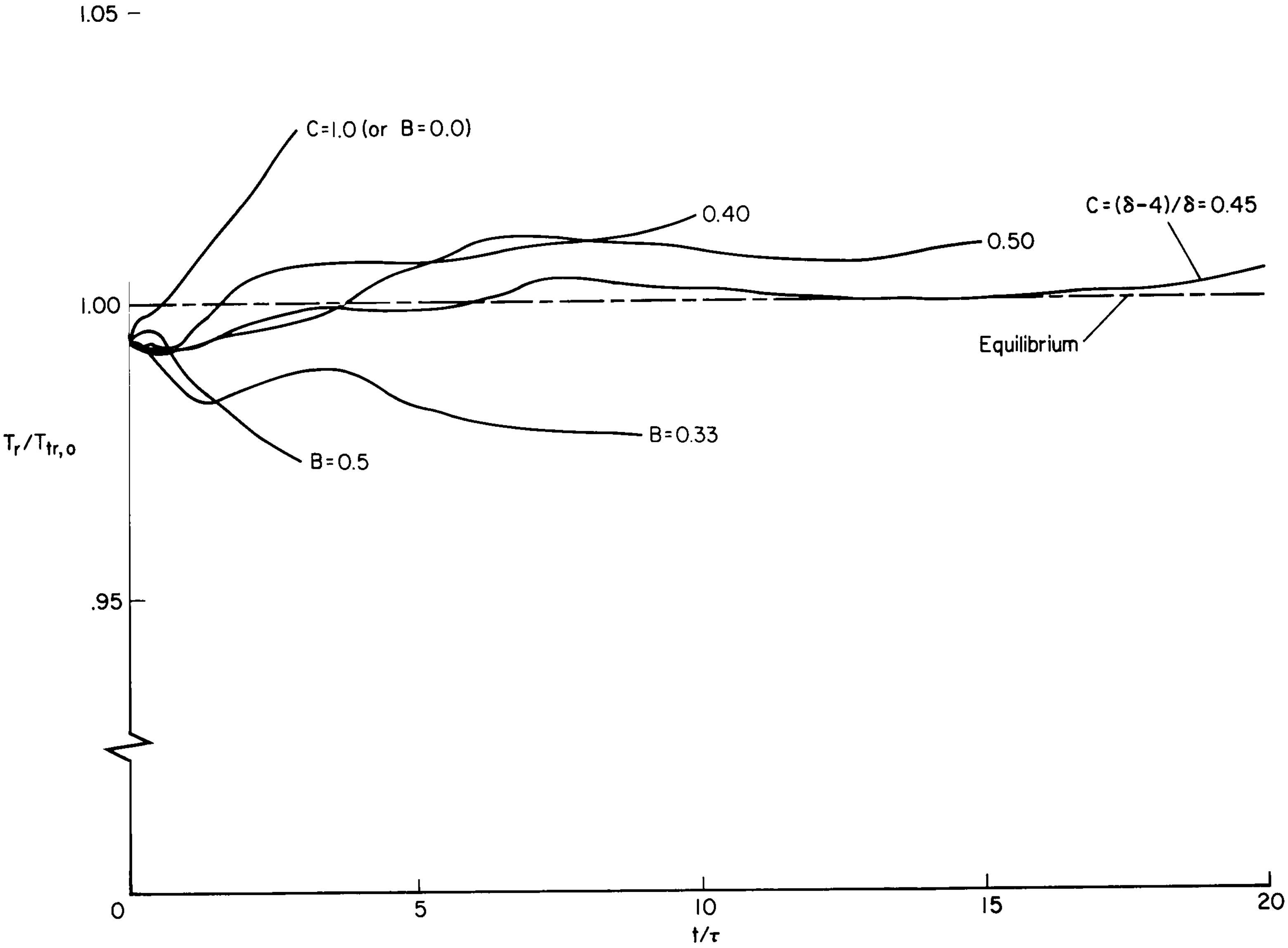


Figure 1.- Variation of rotational temperature depending on specified values for the potential parameters.

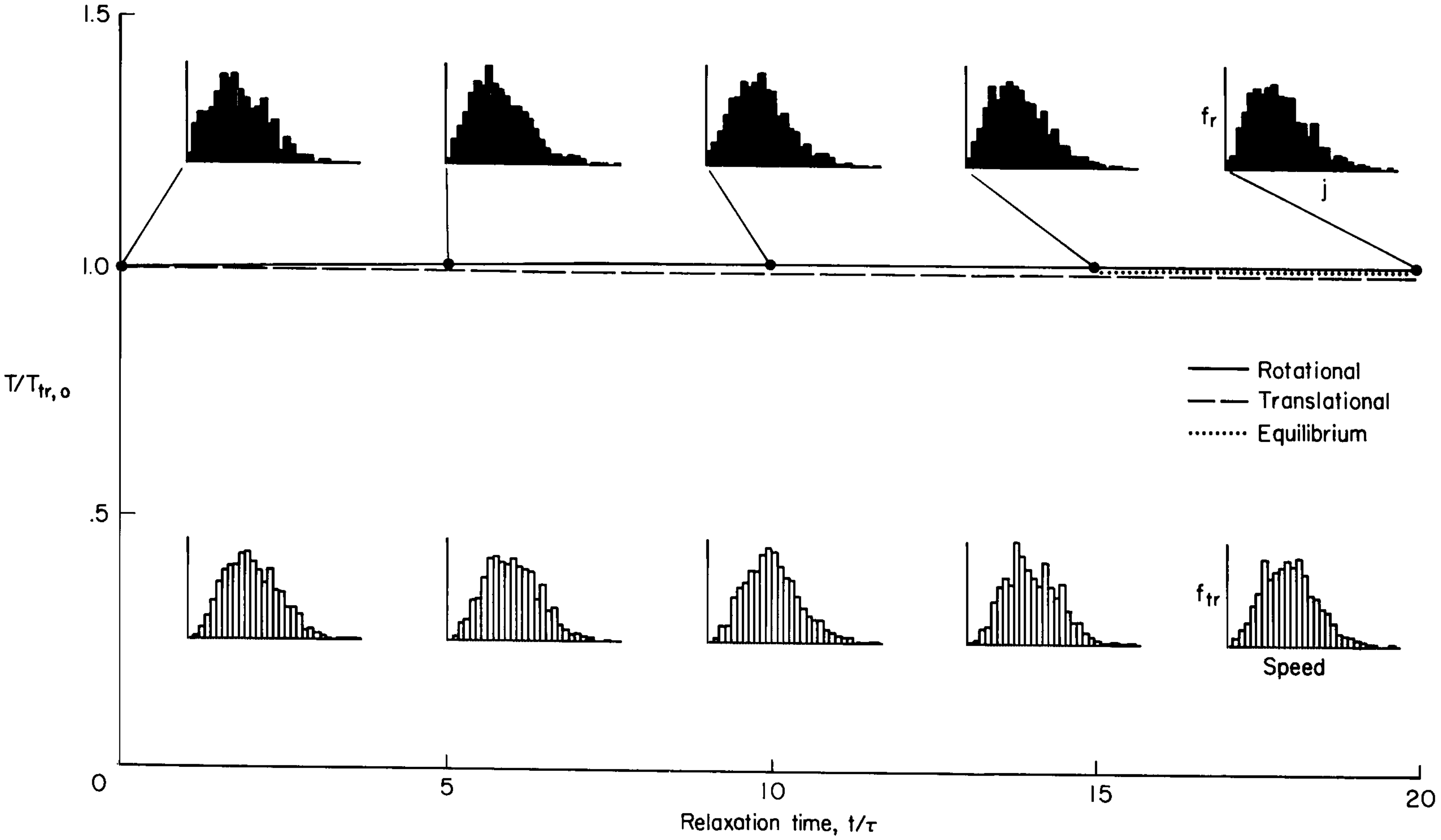
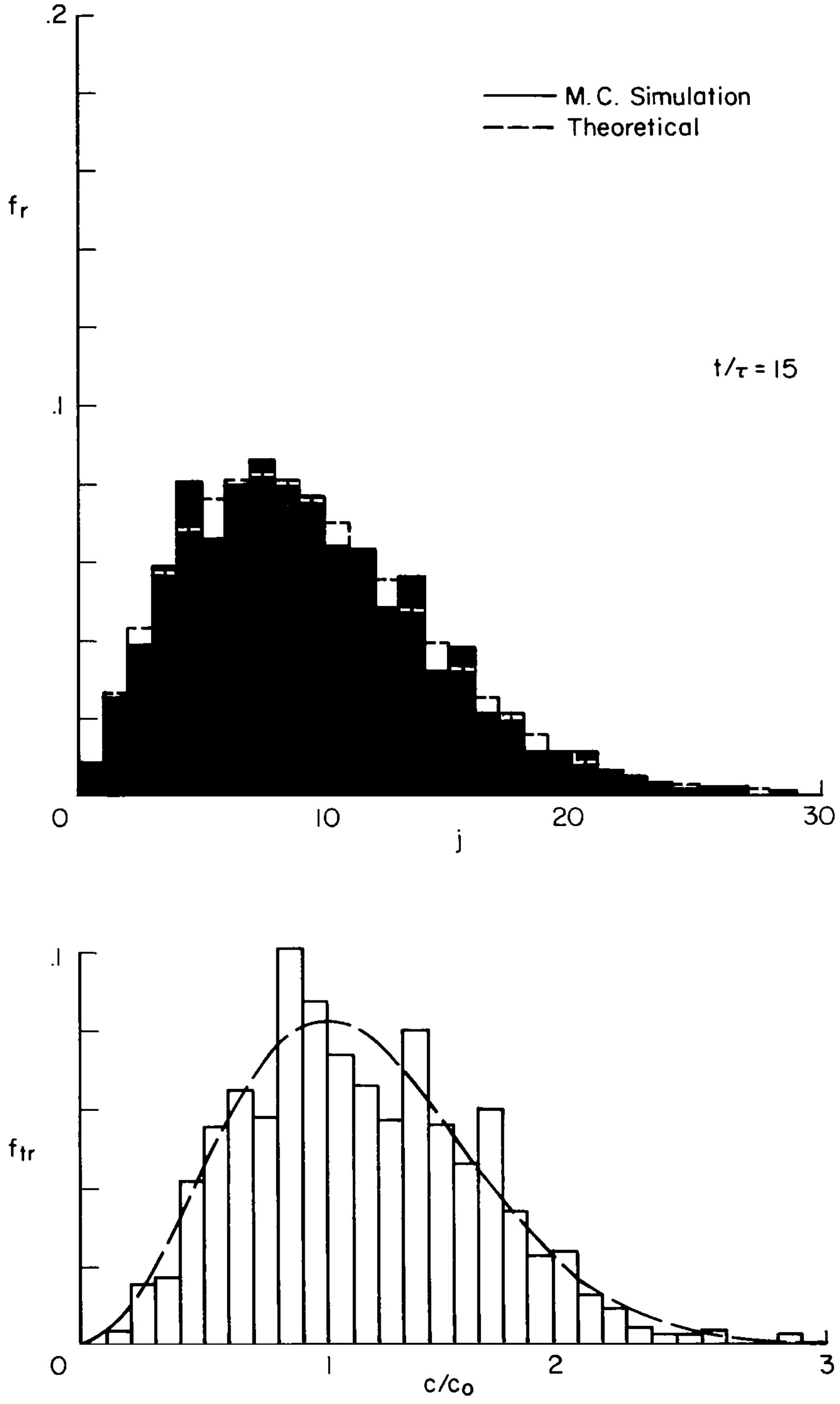
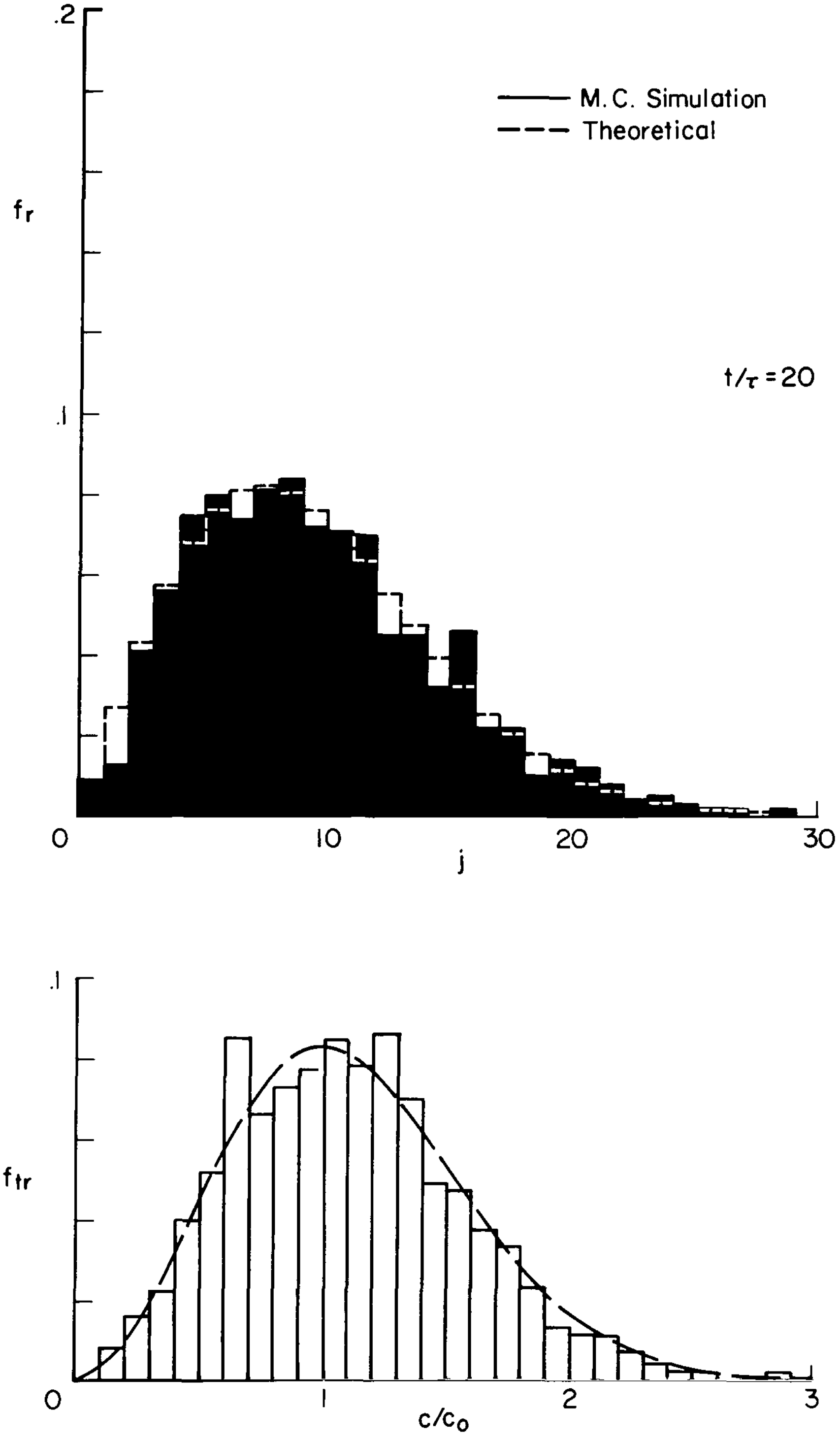


Figure 2.- Temperature and distribution functions: Complete equilibrium initial conditions.



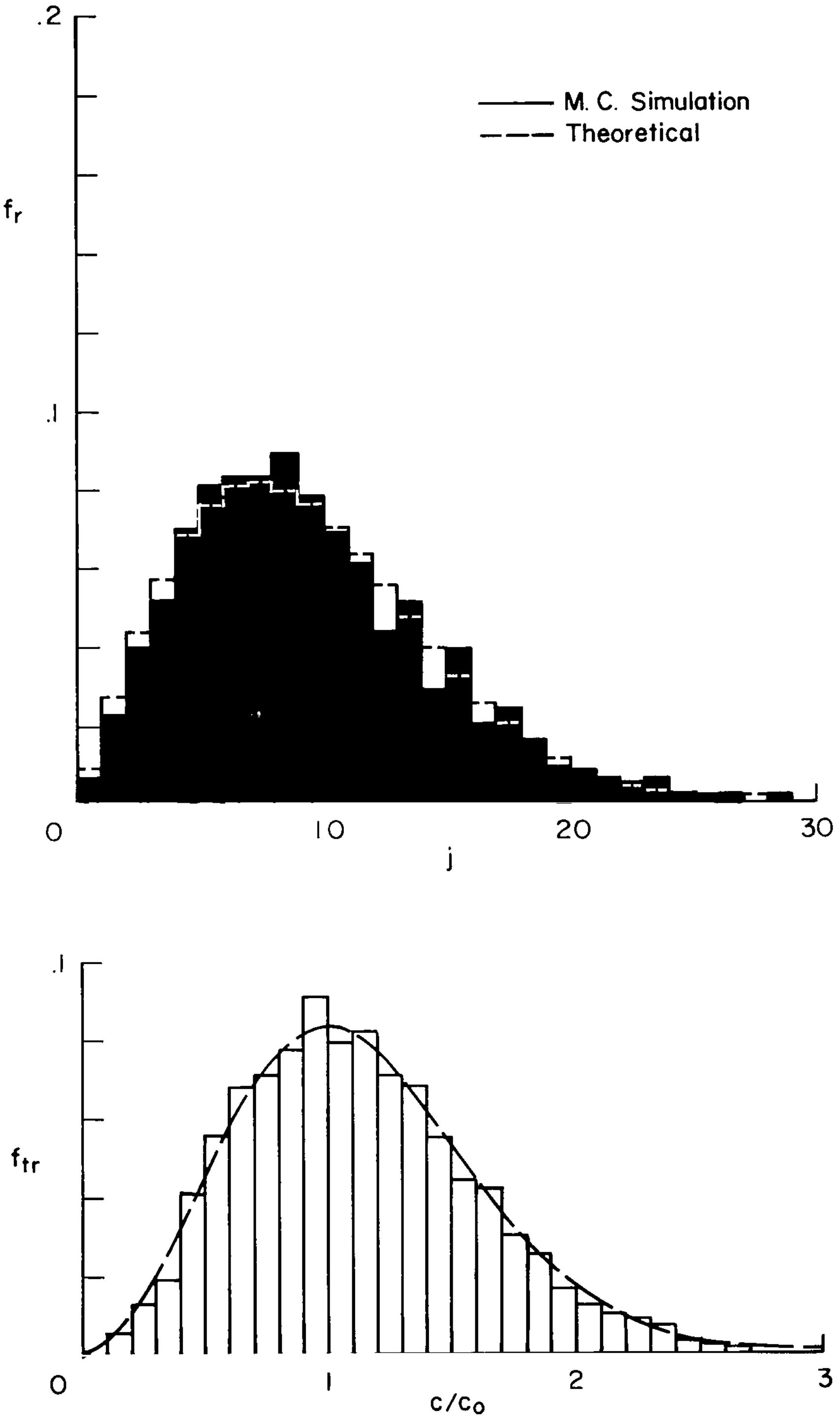
(a) t/τ = 15

Figure 3.- Translational and rotational distribution functions: Complete equilibrium initial conditions.



(b) t/τ = 20

Figure 3.- Continued.



(c) Mean value.

Figure 3.- Concluded.

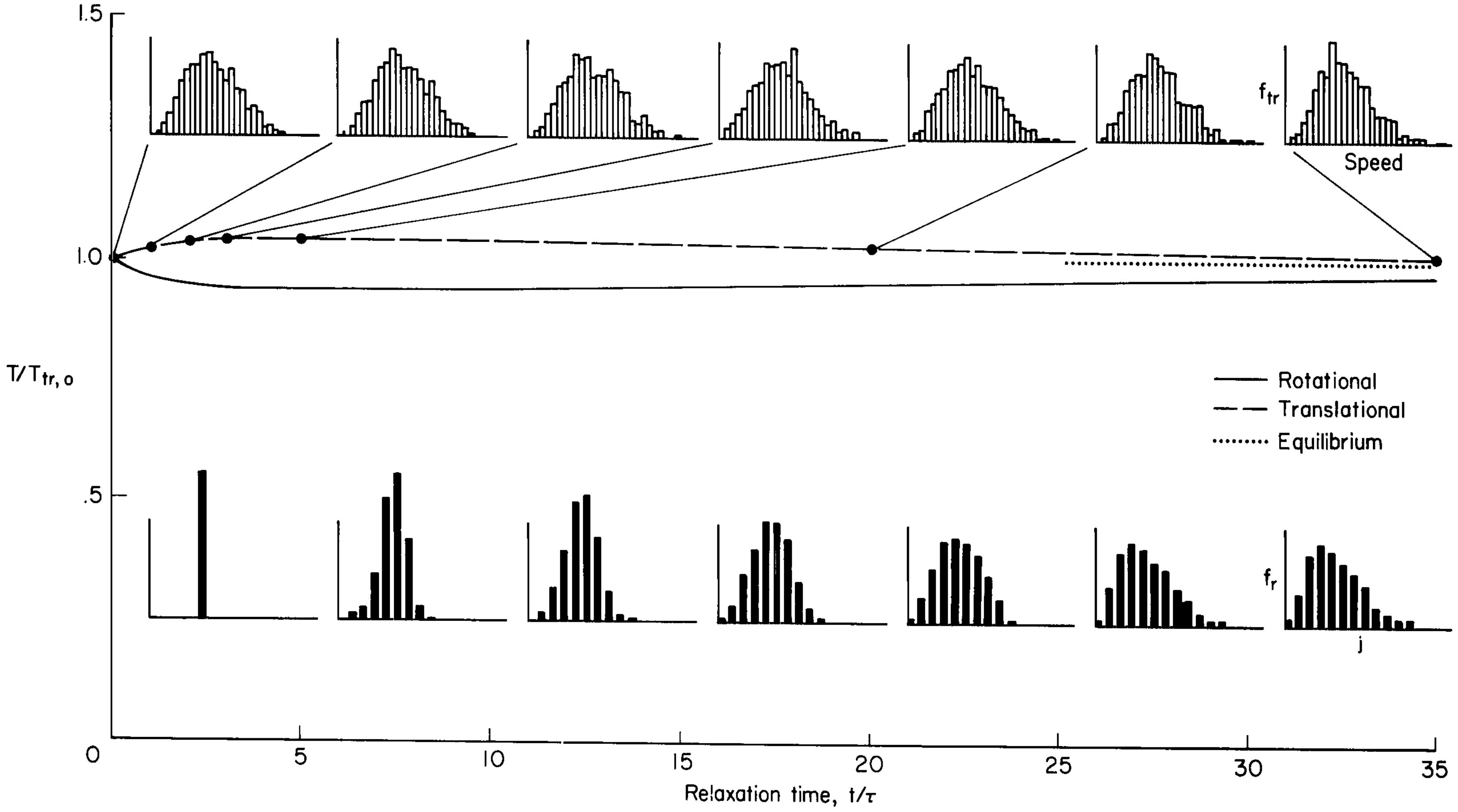
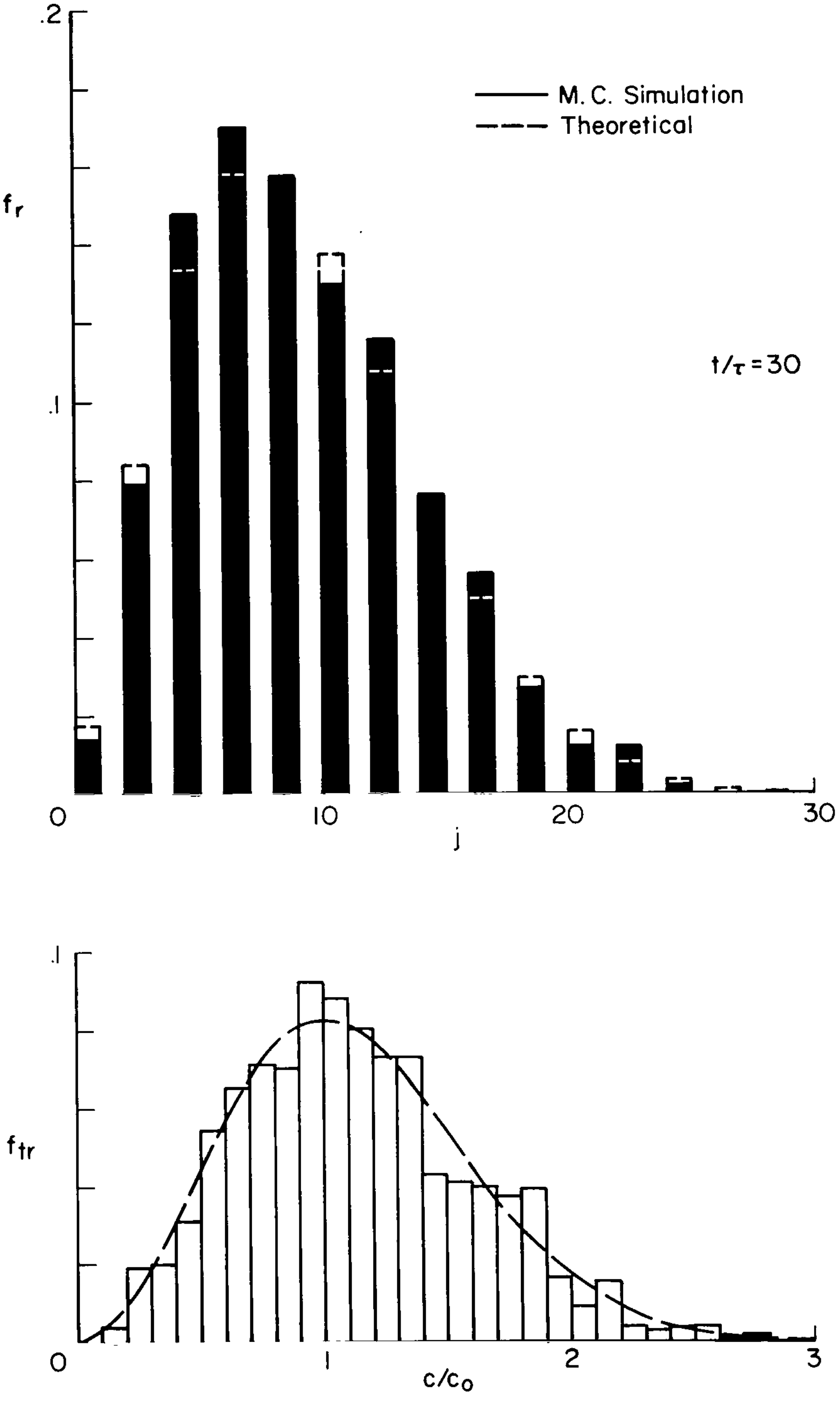
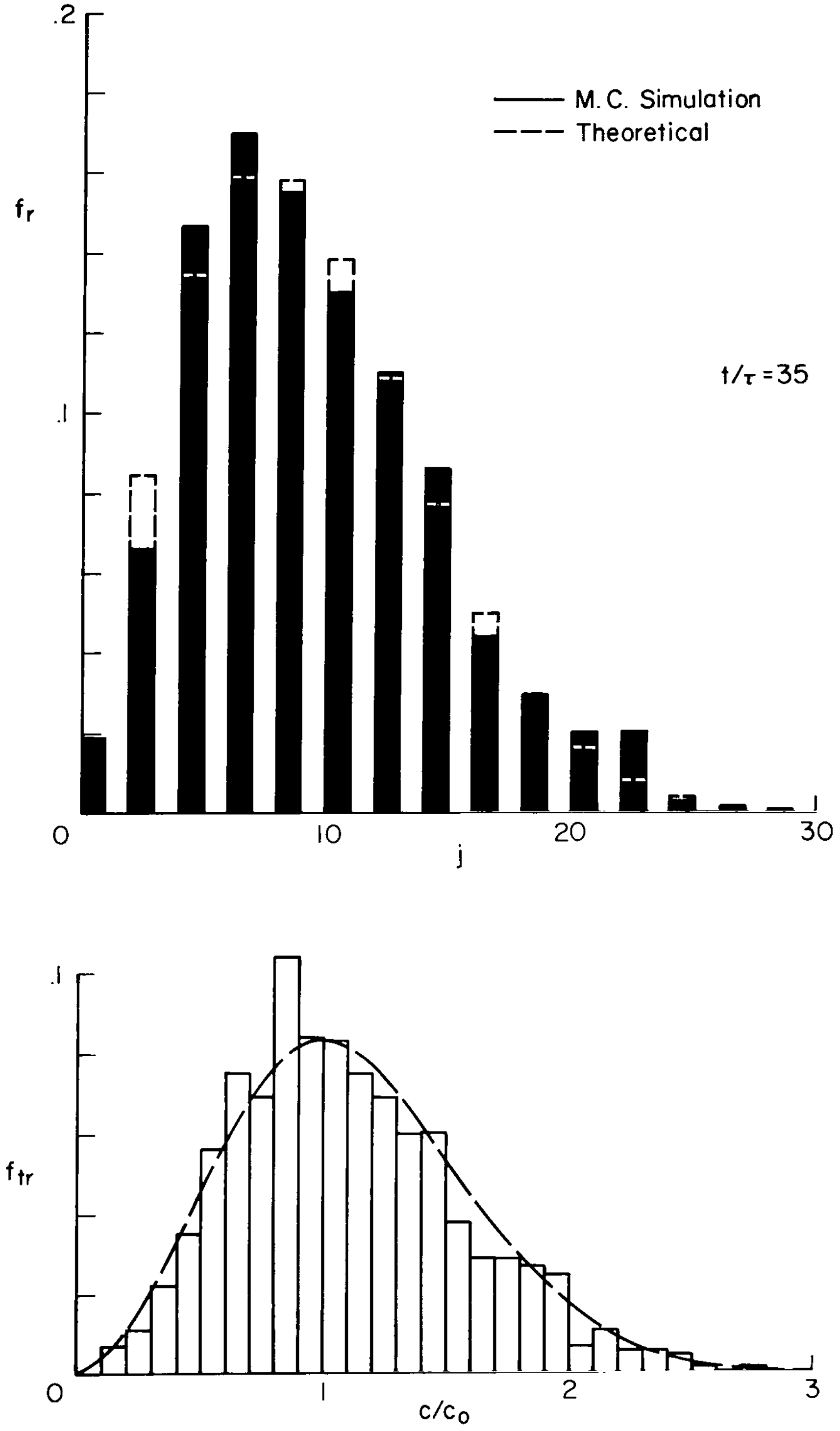


Figure 4.- Temperature and distribution functions: Equipartition initial conditions.



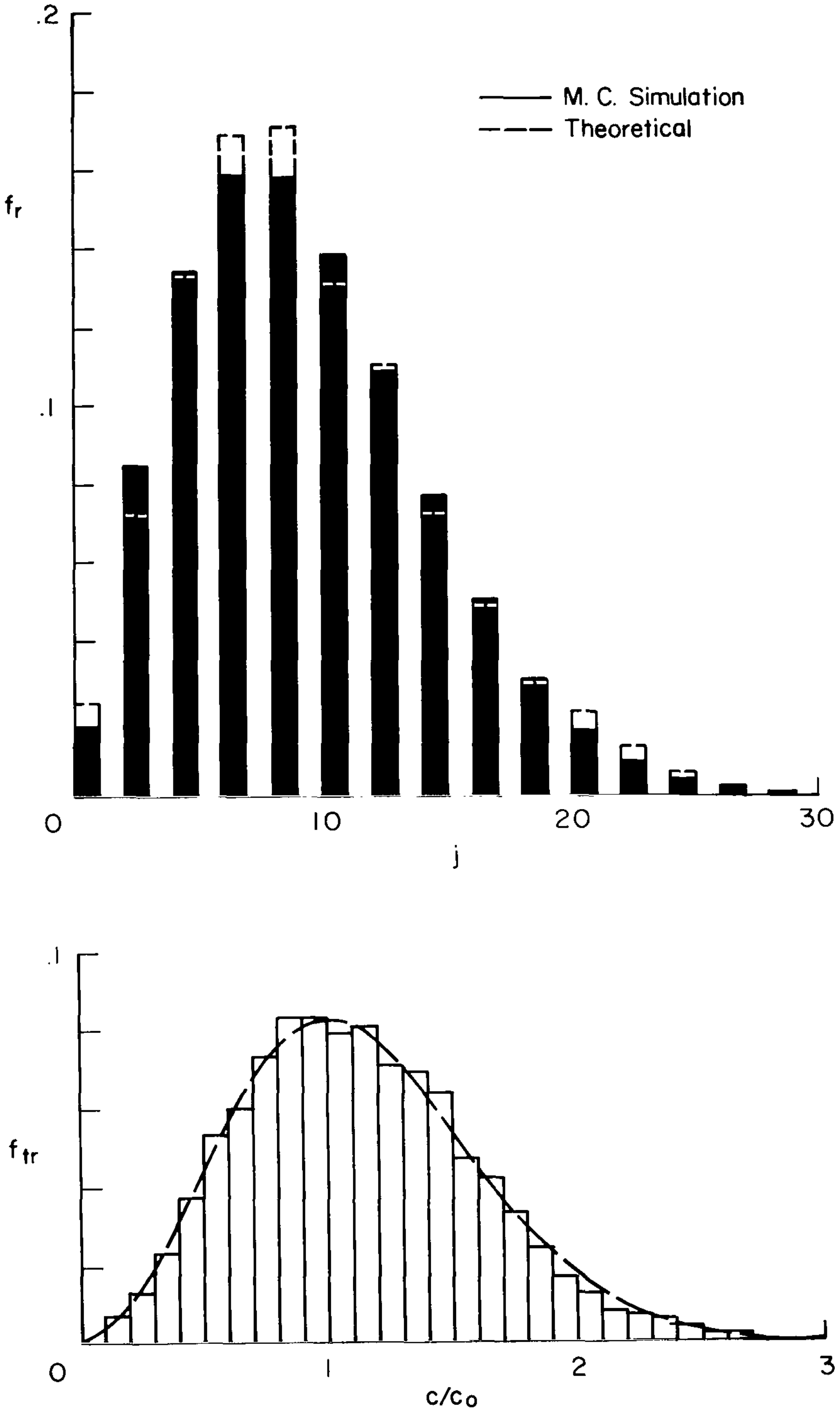
(a) $t/\tau = 30$

Figure 5.- Translational and distribution functions: Equipartition initial conditions.



(b) t/τ = 35

Figure 5.- Continued.



(c) Mean value.

Figure 5.- Concluded.

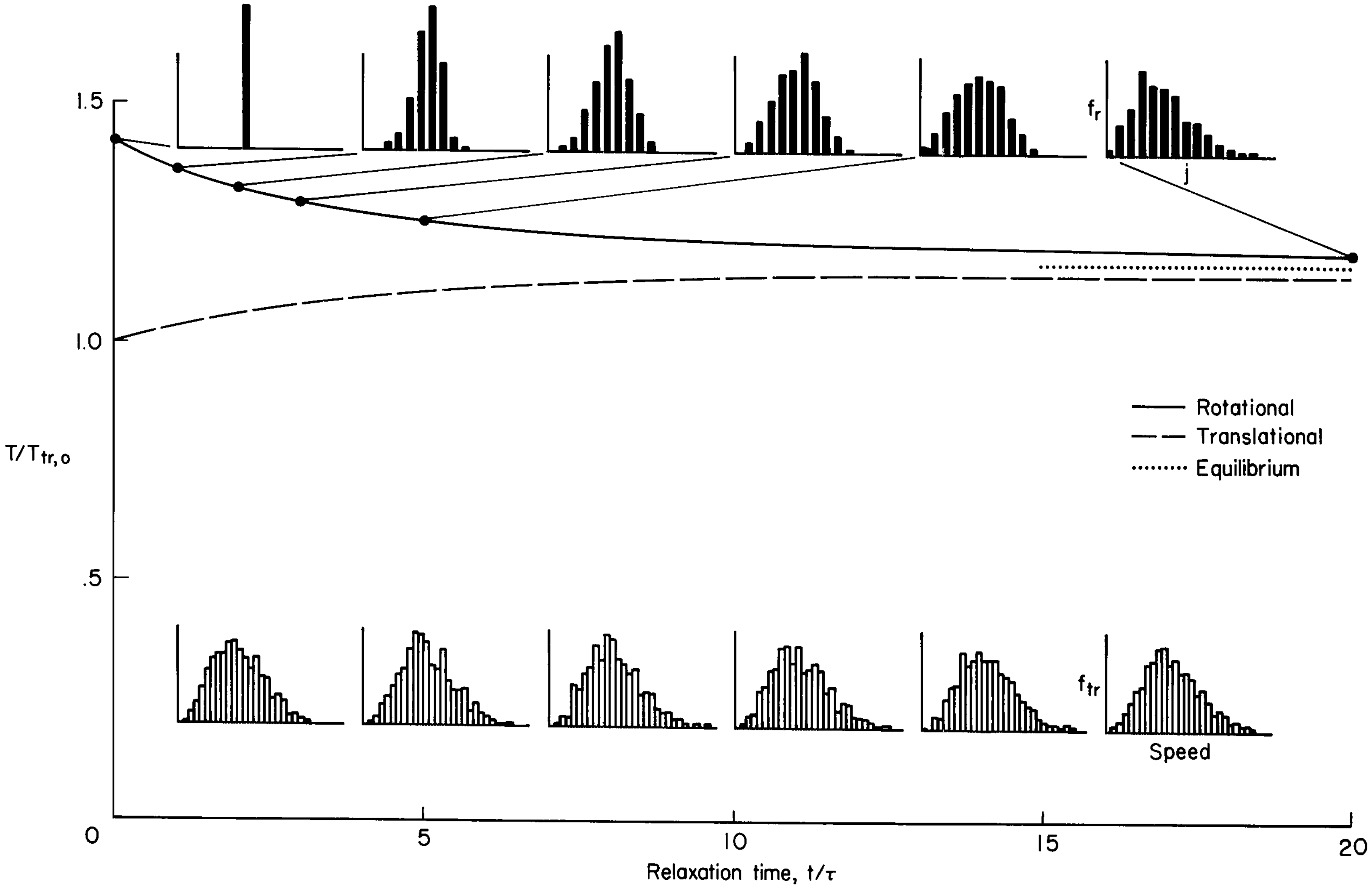
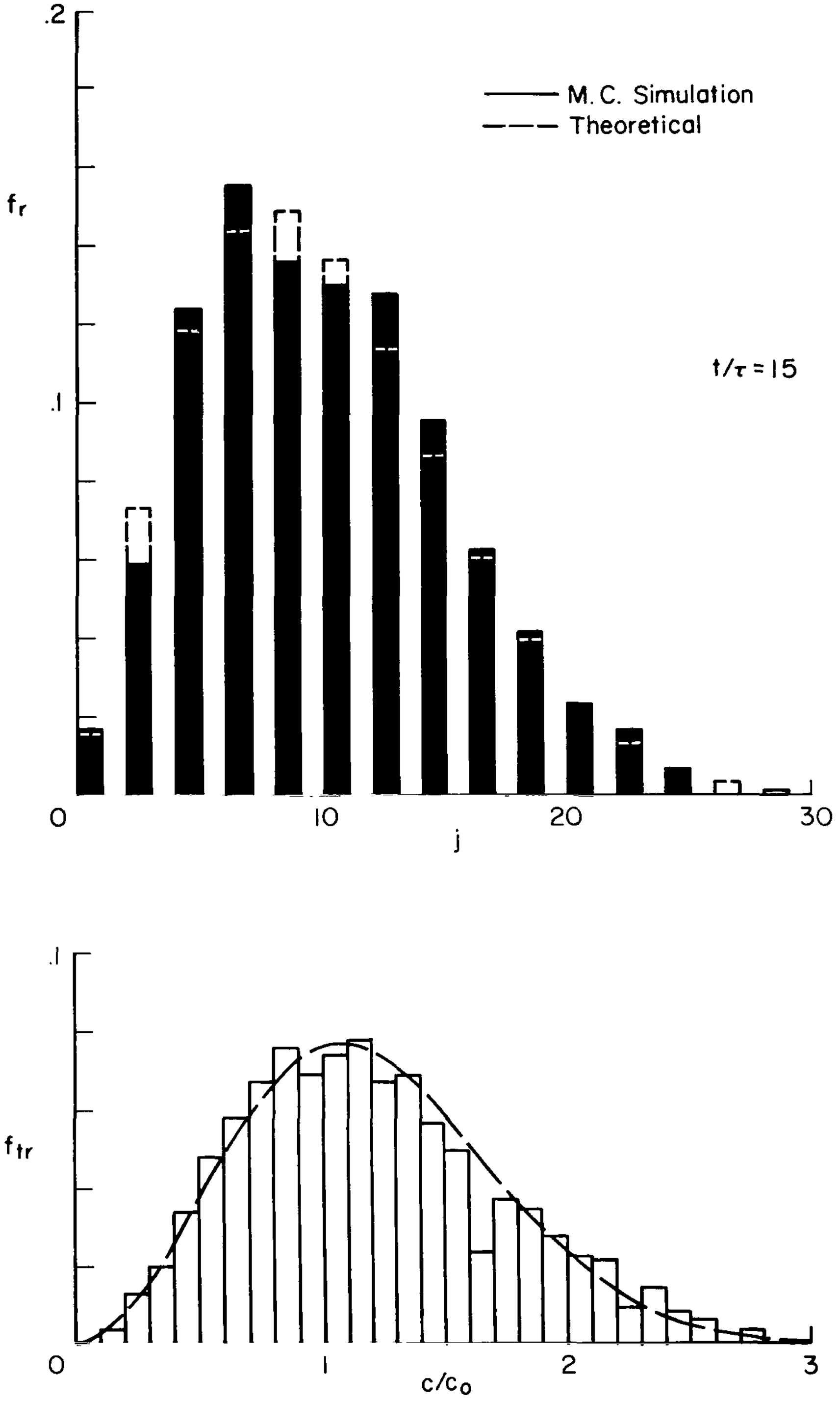
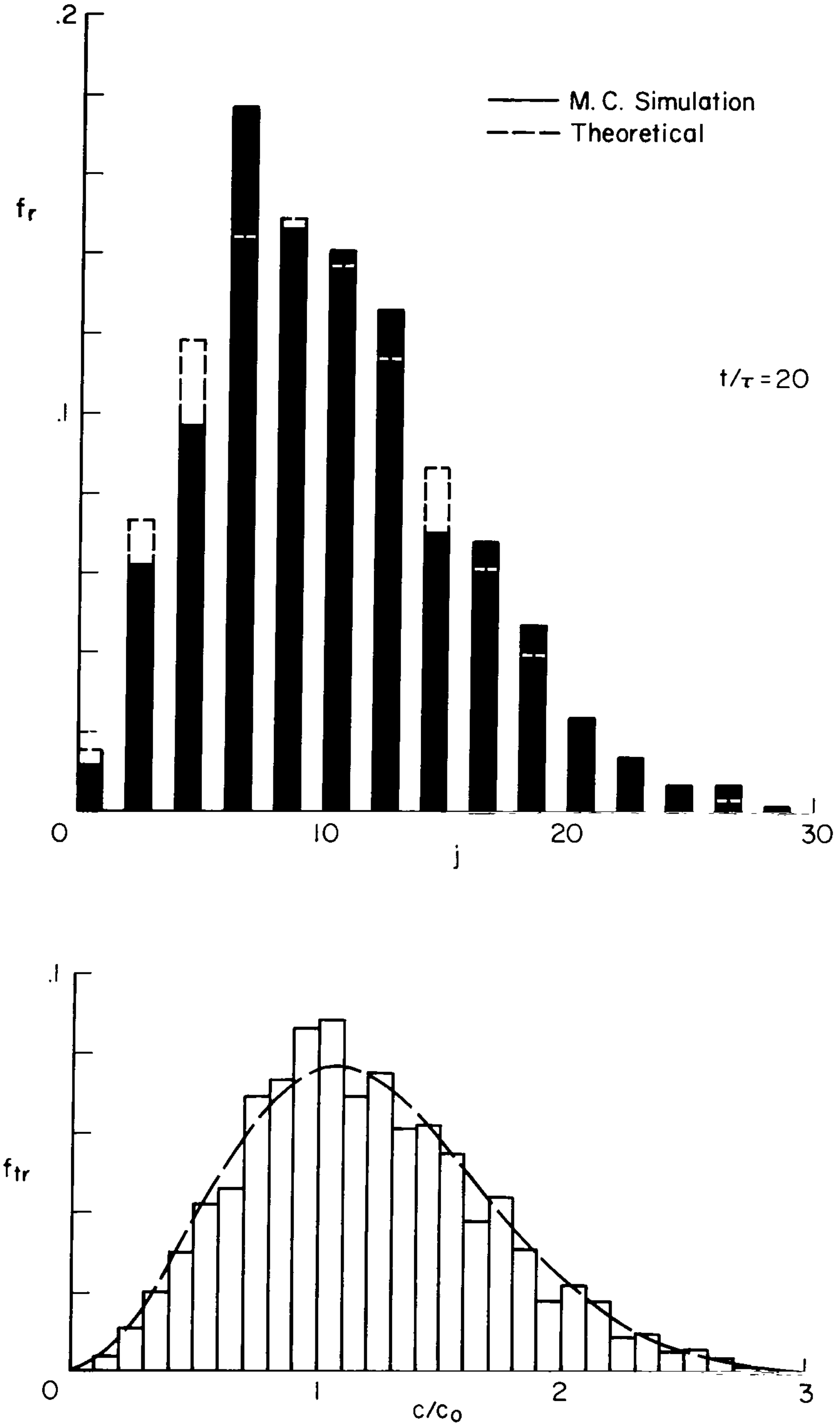


Figure 6.- Temperature and distribution functions: Nonequipartition initial conditions.



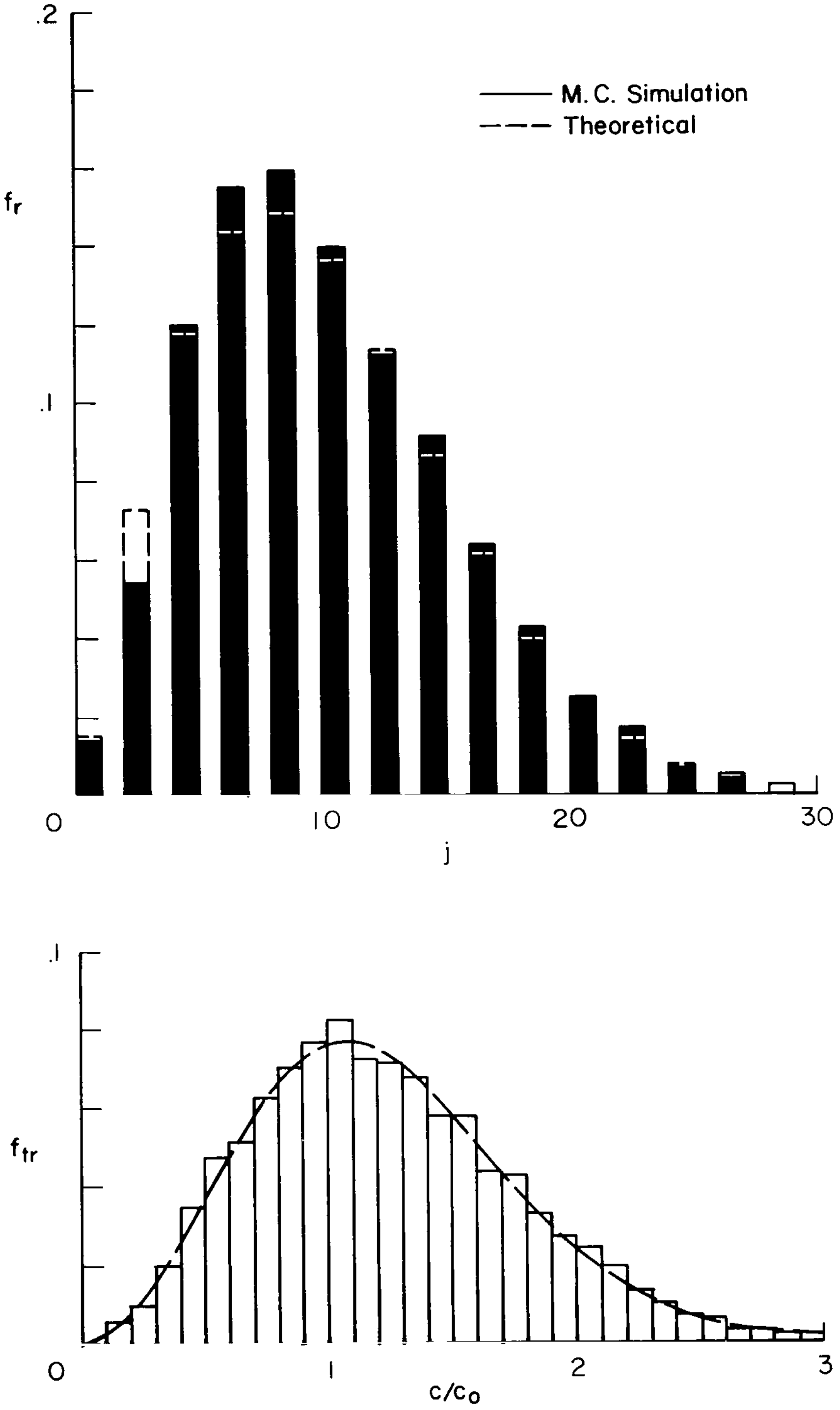
(a) $t/\tau = 15$

Figure 7.- Translational and rotational distribution functions: Nonequipartition initial conditions.



(b) $t/\tau = 20$

Figure 7.- Continued.



(c) Mean value end.

Figure 7.- Concluded.

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