Monte Carlo Evaluation of The Temperature Dependence of Molecular Transport Integrals*

R. G. Rehm and J. W. Rich

Aerodynamic Research Department, Cornell Aeronautical Laboratory, Inc., Buffalo, New York 14221

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A Monte Carlo method is proposed for evaluating integrals arising in molecular transport property calculations. The method, which couples the variance-reducing technique of importance sampling with specific features of the integral, allows computation of the complete temperature dependence of the integral in a straightforward and efficient fashion. The value of the method is verified by detailed numerical calculation of a one-dimensional and a multidimensional example.

1. Description of The Technique

Thermal equilibrium in a monatomic or polyatomic gas is described by the well-known Boltzmann distribution function. For a monatomic gas this distribution function is simply the Maxwellian function of the velocity components along the three Cartesian coordinate axes. For a polyatomic gas this distribution function is a product of the Maxwellian function for a monatomic gas and another distribution function depending upon internal coordinates of the molecule.

There exists an important class of multidimensional integrals, encountered in kinetic theory (transport property calculations) and chemical kinetics, which reduce to the average with respect to the Boltzmann distribution f of a property Q for the gas. These integrals are carried out over the phase space τ of velocity components and the internal coordinates and momenta of the molecule. The integrals have the form [1]

$$\bar{Q} = \int_{\tau} Qf \, d\tau, \tag{1}$$

where $\bar{Q}$ is the average of property Q.

In general, the multidimensional integrals are impossible to evaluate analytically.

339

Standard numerical quadrature techniques for one-dimensional integrals, when applied to multidimensional integrals of large dimension, are found to be very inefficient. Therefore, to an increasing extent these integrals are being evaluated by Monte Carlo techniques.

The idea of the Monte Carlo technique is to select "at random" many trials or sets of values of the integration variables in the phase space τ. For each set of values the property Q is evaluated, and a sum of the evaluations is used to approximate $\bar{Q}$.

The central problem in any Monte Carlo calculation is the determination of an algorithm which will require a minimal time to calculate a reliable result. Such a scheme is termed efficient. The usual method for increasing the efficiency of a calculation is through the utilization of variance-reducing techniques [2, 3]. The variance is a measure of the accuracy of a particular scheme after a given number of trials.

Importance sampling is one of the well-known techniques for reducing the variance during a Monte Carlo calculation [2, 3]. The random values of the integration variables are selected preferentially in the regions of the phase space where the integrand is largest in magnitude; that is, the sampling of the random values is done preferentially in important regions as determined by the integrand. This technique, as all of the variance-reducing techniques, utilizes knowledge of the behavior of the integrand to make the Monte Carlo calculation more efficient.

Frequently the property Q can only be evaluated numerically, e.g., through integration of the equations of motion describing a binary collision between molecules. When such a calculation is the most time-consuming aspect of the numerical integration procedure, it is highly desirable to minimize the number of numerical evaluations of the property required.

The Boltzmann distribution f, and therefore the complete integral $\bar{Q}$ appearing in Eq. (1), depends upon the temperature T. Usually the value of the integral $\bar{Q}$ is desired for more than one temperature, and often the complete functional dependence upon temperature is desired. In this paper a technique is described which allows one, in principle, to compute by the Monte Carlo method the temperature dependence of integrals of the form given in Eq. (1) in a straightforward and efficient fashion. The method couples the variance-reducing technique of importance sampling with the features of integral (1) that (i) The temperature dependence of the integral arises only through the Boltzmann distribution f, and (ii) evaluation of property Q is a quite time-consuming calculation.

A probability density function is selected which is independent of temperature and which copies the gross behavior of the integrand. From this density function one set of trials is selected, and a corresponding set of values for the property Q is computed. For each temperature, then, a differently weighted sum of these values of Q is calculated to give an estimate for the average $\bar{Q}$. In this fashion

the time required to compute the complete temperature dependence of $\bar{Q}$ can be made quite comparable in principle to the time required for computation of $\bar{Q}$ for only one temperature.

A one-dimensional integral is examined in detail in the next section, and, for this example, the usefulness of the technique is verified by numerical calculation. In Section 3 the technique is applied to a multidimensional integral and some computed results are presented. The computational time required to calculate the temperature dependence of the integral by this scheme is indeed found to be comparable to the time required for the computation of the integral for only one temperature. A brief summary of the conclusions is given at the end of the paper.

2. One-Dimensional Integral Example

As an example of this technique a one-dimensional integral of interest in chemical kinetics will be considered. This integral describes the thermal average of the probability for a diatomic molecule, originally in the lowest (ground) quantum vibrational state, to make a transition to another quantum vibrational state upon collision with an atom. The model chosen for this interaction has been highly idealized. The diatomic molecule has been taken to be a quantum mechanical harmonic oscillator. Only collisions for which the atom strikes the molecule along the line determined by the axis of the diatomic molecule are considered.

For such a colinear collision of an atom A with a molecule B–C, initially in its ground vibrational state, Ref. [4] gives as the probability for excitation to the n-th vibrational state

$$p_{0n}(V) = \frac{1}{n!} A^n V^{2n} \operatorname{sech}^{2n} \left(\frac{2\omega L}{V} \right) e^{-AV^2 \operatorname{sech}^2(2\omega L/V)}, \qquad (2)$$

where

V = relative translational velocity of the atom and molecule,

$A = \dfrac{1}{\hbar\omega} \dfrac{\tilde{m}}{\mu} \left(\dfrac{m_C}{m_B + m_C} \right)^2$,

ω = oscillator radial frequency,

μ = oscillator reduced mass = $\dfrac{m_B m_C}{m_B + m_C}$,

$\tilde{m}$ = system reduced mass = $\dfrac{m_A(m_B + m_C)}{m_A + m_B + m_C}$,

L = exponential range of atom–molecule potential.

The probability averaged over a one-dimensional Maxwellian distribution of relative translational velocities at temperature T can be expressed as

$$P_{0n}(T) = \frac{\tilde{m}}{kT} \int_0^\infty V e^{-\tilde{m}V^2/2kT} p_{0n}(V)\, dV. \tag{3}$$

In order to calculate this integral by Monte Carlo methods a probability density function g, from which values of V are chosen to evaluate the integrand, must be selected. It is essential to the technique of this paper to choose a density which is independent of the temperature T. The functional form of g with respect to V in this case is selected on the basis of physically motivated considerations. The probability density function is chosen to be a Maxwellian distribution in V at a "ficticious temperature" ϑ, this parameter being introduced to increase the flexibility of the scheme,

$$g(V; \vartheta) = \frac{\tilde{m}}{k\vartheta}\, V \exp\left[-\frac{\tilde{m}V^2}{2k\vartheta}\right]. \tag{4}$$

Note that other functional forms for the probability density function could have been chosen as well, and perhaps some of these density functions would be more efficient for computation of integral (2). However, density function (4) has the advantage of being physically understandable, a Maxwellian function at temperature ϑ, and of easy generalization to multi-dimensional integrals.

According to the variance-reducing technique of importance sampling, divide and multiply the integrand in (3) by $g(V; \vartheta)$. Then introduce the dimensionless velocity

$$v = \sqrt{\frac{\tilde{m}}{k\vartheta}}\, V. \tag{5}$$

Eq. (3) becomes

$$P_{0n}(T) = \int_0^\infty F(v, T; \vartheta)\, G(v)\, dv, \tag{6}$$

where

$$F(v, T; \vartheta) = \frac{\vartheta}{T}\, p_{0n}\left(\sqrt{\frac{k\vartheta}{\tilde{m}}}\, v\right) \exp\left\{-\frac{\vartheta}{2}\, v^2\left(\frac{1}{T} - \frac{1}{\vartheta}\right)\right\},$$

$$G(v) = v \exp(-v^2/2).$$

The nondimensionalized velocities v_i, distributed according to the density

function $G(v)$, can be obtained from random numbers Y_i distributed uniformly between 0 and 1,

$$\int_0^{v_i} G(v) \, dv = Y_i$$

or

$$v_i = [-2 \ln(1 - Y_i)]^{1/2}. \tag{7}$$

After N trials (i.e., after the selection of N random numbers v_i and the corresponding calculation of $F(v_i, T; \vartheta)$), an estimate $P_{0n}^{(N)}(T)$ of the integral can be made,

$$P_{0n}^{(N)}(T) = \frac{1}{N} \sum_{i=1}^{N} F(v_i, T; \vartheta). \tag{8}$$

Similarly an estimate $\sigma_{(N)}^2$ of the variance σ^2 for the distribution of $F(v_i, T; \vartheta)$ can be made after N trials,

$$\sigma_{(N)}^2 = \frac{1}{N-1} \sum_{i=1}^{N} [F(v_i, T; \vartheta)]^2 - \frac{N}{N-1} [P_{0n}^{(N)}(T)]^2. \tag{9}$$

The estimate $\Sigma_{(N)}^2$ of the variance for the distribution of $P_{0n}^{(N)}(T)$ can then be made (Ref. [2]),

$$\Sigma_{(N)}^2 = \sigma_{(N)}^2 / N. \tag{10}$$

In terms of the calculation of the integral (3) therefore, one can say that the estimate $P_{0n}^{(N)}(T)$ for the integral $P_{0n}(T)$ is within the range $P_{0n}(T) - 3\Sigma_{(N)} \leqslant P_{0n}^{(N)}(T) \leqslant P_{0n}(T) + 3\Sigma_{(N)}$ with probability 0.997.

Estimates of the integral in Eq. (3) were performed according to Eq. (8) for $n = 1$. In addition, estimates of the variance in Eq. (9) were calculated simultaneously with $P_{0n}^{(N)}(T)$. The temperature T, the parameter ϑ, and the number of trials N are all variables in these calculations. Each of these parameters was varied independently to determine its effect upon both the efficiency and the sensitivity of the results.

Calculations were performed using molecular constants appropriate for collisions between oxygen molecules (O_2) and argon atoms (Ar). For this system, the model from which Eq. (2) is derived is of interest over a temperature range of approximately $300 \leqslant T \leqslant 10{,}000°K$. Calculations (cf. Table I) were carried out over this range.

Several conclusions about the scheme can be drawn from these calculations.

TABLE I

Comparison of the values of the integral $P_{01}(T)$ in Eq. (3) calculated by the Monte Carlo technique and by Gauss-Laguerre quadrature.

$T(°K)$	$P_{01}^{(N)}(T)$ Monte Carlo $N = 1000$, $\vartheta = 10{,}000$	$P_{01}(T)$ Gauss–Laguerre	$\Sigma_{(N)}(T)$	$\Sigma_{(N)}(T)/P_{01}^{(N)}(T)$
300	2.45×10^{-9}	2.54×10^{-9}	0.153×10^{-9}	6.25×10^{-2}
500	1.25×10^{-7}	1.23×10^{-7}	0.0650×10^{-7}	5.20×10^{-2}
700	1.15×10^{-6}	1.17×10^{-6}	0.0525×10^{-6}	4.56×10^{-2}
1000	9.51×10^{-6}	9.94×10^{-6}	0.383×10^{-6}	4.04×10^{-2}
3000	1.88×10^{-3}	1.87×10^{-3}	0.0692×10^{-3}	3.68×10^{-2}
5000	1.10×10^{-2}	1.06×10^{-2}	0.0485×10^{-2}	4.41×10^{-2}
10000	5.07×10^{-2}	5.04×10^{-2}	0.301×10^{-2}	5.94×10^{-2}

The major conclusion is that for fixed N and ϑ, $P_{01}(T)$ can be estimated fairly accurately over the entire range of values of temperature for one set of trials. This conclusion is illustrated in Table I. Here are listed the Monte Carlo approximation $P_{01}^{(N)}(T)$ after $N = 1000$ trials and the exact value for $P_{01}(T)$ for seven values of temperature spanning the range $300 \leqslant T \leqslant 10{,}000°K$. The parameter ϑ has been chosen to be $10{,}000°K$. The property $p_{01}(V)$ has been evaluated only 1000 times (corresponding to the 1000 random velocities selected). Each of the estimates $P_{01}^{(N)}(T)$ was made by summing differently weighted averages, depending upon the temperature T, of these evaluations according to Eq. (8).

The exact value of $P_{01}(T)$ at each temperature was determined by 6- and 7-point Gauss–Laguerre quadrature, and was adjudged to be accurate to within one per cent. To get accuracy within a few per cent by this Monte Carlo scheme, as shown in Table I, 1000 trials were necessary. Therefore, the Monte Carlo technique is much less efficient for one-dimensional integrals than standard quadrature techniques, particularly those of the Gauss-quadrature type. For multi-dimensional integrals the relative efficiency of the Monte Carlo technique improves significantly.

The variance $\Sigma_{(N)}(T)$ calculated for each temperature is also shown in Table I. It provides an estimate of the accuracy of the Monte Carlo estimate of the integral at each temperature. For each calculation shown in Table I, where the correct value of the integral is known, the estimate is within $\pm 2\Sigma_{(N)}(T)$ of the exact value $P_{01}(T)$. (The probability that the estimated value of the integral will be within $\pm 2\Sigma_{(N)}(T)$ of the exact value is 95.4 %.)

In a Monte Carlo calculation for which the exact value of the integral is not known, the variance would be used to estimate the accuracy of the computed approximation to the integral. For the purpose of comparing the accuracy at

different temperatures, the relative error $\Sigma_{(N)}(T)/P_{01}^{(N)}(T)$, listed in the last column of Table I, is a better indicator. This relative error is seen to be less than seven per cent over the entire temperature range. It is found to yield a minimum at the intermediate temperature of 3000°K for the calculations shown.

A second conclusion which arises from these calculations is that the convergence, for fixed ϑ and for an individual value of T, as a function of N is not found to be rapid. The reason for this relatively slow convergence can be understood as follows. Generally, the variance-reducing technique of importance sampling improves the convergence of the Monte Carlo estimate as the probability density function more closely mimics the behavior of the integrand. A density function selected to imitate the integrand moderately well over a large range of temperatures will not be expected to produce an estimate which converges rapidly for any single temperature. In effect, the very important and valuable conclusion that the Monte Carlo estimates converge over the entire range of temperature is obtained at the expense of rapid convergence at any single temperature.

Figures 1 and 2 illustrate this conclusion. Figure 1 shows two estimates (case 1 and case 2) of the integral (3) as functions of N for $\vartheta = 10,000°K$ and $T = 1000°K$.
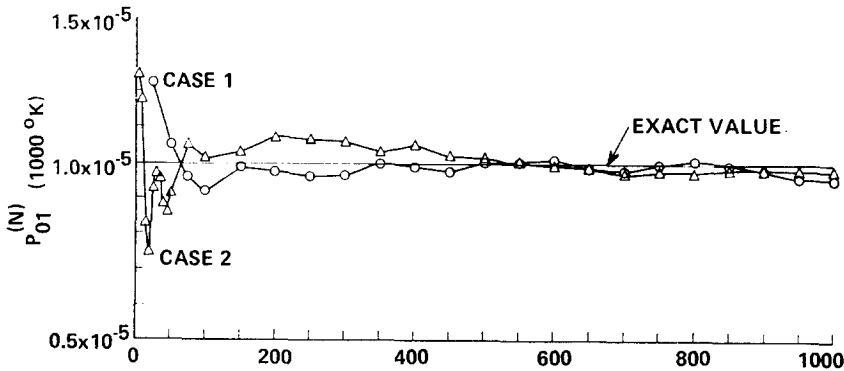

FIG. 1. Monte Carlo estimates $P_{01}^{(N)}$ of integral (3) as a function of the number N of trials for a temperature T of 1000°K and for parameter $\vartheta = 10,000°K$. Case 1 and Case 2 are estimates calculated from separate sets of random values selected for the integration variable.

Each estimate is made in exactly the same fashion from separate sets of random numbers. The more accurate value of the integral, as calculated by Gauss–Laguerre quadrature, is also shown for comparison. Figure 2 is a similar set of estimates using the same sets of random numbers and the same value of ϑ, but for $T = 10,000°K$. The estimates calculated for Fig. 2 are almost four orders of magnitude larger than those for Fig. 1 and were performed concurrently with those estimates. Both figures show that all estimates have settled down to within 5% of the exact value by $N = 600$ trials.

The final conclusion which can be drawn from these computations is that the estimates made for the integral are not very sensitive to the value of ϑ chosen. Computations have been performed with ϑ assuming values of 5000°K, 10,000°K, and 15,000°K to determine the variation in the Monte Carlo estimates for fixed N and T. For these three values of ϑ Fig. 3 shows plots of the relative error
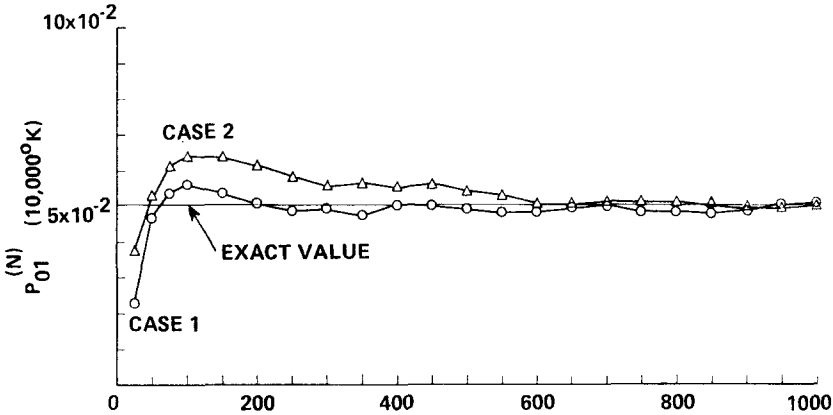

FIG. 2. Monte Carlo estimates $P_{01}^{(N)}$ of integral (3) as a function of the number N of trials for a temperature T of 10,000°K and for parameter $\vartheta = 10,000$°K. Case 1 and Case 2 are estimates calculated from separate sets of random values selected for the integration variable.
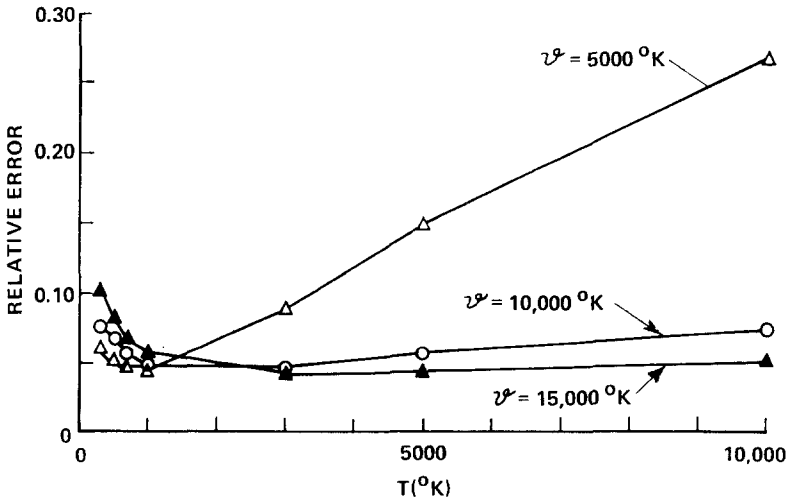

FIG. 3. Relative error $\Sigma_{(N)}(T)/P_{01}^{(N)}(T)$ calculated as a function of temperature T for three values of the parameter ϑ. The relative error in each case was computed after $N = 600$ Monte Carlo trials.

$\Sigma_{(N)}(T)/P_{01}^{(N)}(T)$ after $N = 600$ trials over the complete temperature range. At the lowest temperatures (less than about 1000°K) the relative error for each ϑ is smaller than 11 %, and variation in the values of the relative error is not large. In contrast, at the high temperatures the relative error for $\vartheta = 5000°K$ approaches 30 %, while the other relative error values remain less than 10 %. The reason for the breakdown in the accuracy at high temperatures and small ϑ can be explained as follows. The integrand in Eq. (3) is a product of $p_{01}(V)$ and the one-dimensional Maxwellian function of velocity at temperature T. For the temperatures of interest the maximum in $p_{01}(V)$, and therefore the maximum in the integrand, occurs at a higher value of V than the maximum in the Maxwellian function. Therefore, a density function with a maximum closer to the maximum of the integrand, i.e., one for which $\vartheta > T$, can be expected to give a better Monte Carlo estimate.

For each value of ϑ the plot of the relative error as a function of temperature assumes a minimum. At the temperature corresponding to this minimum the distribution function, for the specified value of ϑ, imitates best the integrand. As expected the smallest value of ϑ yields the best relative error at the lowest temperatures while the largest value of ϑ produces the best relative error at the highest temperatures.

For this one-dimensional example, then, convergence of the Monte Carlo estimate over the entire range of values of temperature ($300 \leqslant T \leqslant 10{,}000°K$) is found for a single value of ϑ. Only one set of calculations of the quantity $p_{01}(V)$, for random values of V, is required. Differently weighted sums of this set of values give the estimates of the integral at each of the temperatures of interest. Convergence of each estimate as a function of the number of trials is not found to be rapid because of the wide range of temperature over which convergence occurs. The technique is not sensitively dependent upon the value of the parameter ϑ chosen for the computations, provided only that ϑ is large enough.

3. Multidimensional Example

The technique described and illustrated in the previous sections has been applied to calculate multidimensional integrals of interest in molecular collision theory. These integrals describe the thermally averaged probability for the vibrational excitation of a diatomic or linear triatomic molecule upon collision with an atom, and represent a generalization of the one-dimensional example of the preceding section.

It is assumed that the vibrational motion of the molecule can be described by the usual normal mode representation of uncoupled, harmonic oscillators [5]. If, in the collision, an amount of energy ΔE_{v_i} is transferred to the i-th vibrational mode, it has been shown [4] that the probability P_{mn}^i for a quantum mechanical

transition from the m-th vibrational level to the n-th vibrational level is approximately

$$p_{mn}^i(\epsilon_i) = m!\, n!\, e^{-\epsilon_i} \epsilon_i^{m+n} S_{mn}^2 , \qquad (11)$$

where

$$\epsilon_i = \Delta E_{vi}/\hbar\omega_i ,$$

$$S_{mn} = \sum_{j=0}^{\mu} \frac{(-1)^j \, \epsilon_i^{-j}}{(n-j)!\, j!\, (m-j)!} \quad \text{and} \quad \mu = \min(m, n).$$

Here $\hbar$ is Planck's constant divided by 2π and the ω_i are the natural frequencies for the normal modes of vibration.

The nondimensional energy ϵ_i transferred to the i-th mode is a function of the initial orientation and relative velocities of the molecule–atom system. For each collision this energy is calculated numerically by integration of the classical equations of motion for the molecule–atom system. Thus

$$\epsilon_i = \epsilon_i(V_0 , b, \alpha_0 , \beta_0 , \gamma_0 , j_0).$$

Here, with reference to Fig. 4, V_0 is the initial relative velocity of the atom–molecule pair, b is the impact parameter, α_0 and β_0 are polar angles defining the initial orientation of the axis of the linear molecule, and j_0 and γ_0 are the magnitude and direction of the initial angular momentum vector for the molecule. (Note that only one angle, γ_0 , is required to completely define the direction of the angular momentum vector, since, for a linear molecule, the angular momentum vector is perpendicular to the molecular axis.)

The probability is averaged over a Maxwellian distribution at temperature T of relative translational velocities V_0 and of angular momenta j_0 . It is also averaged over impact parameter b and the angles α_0 , β_0 , and γ_0 describing the initial conditions. The resulting thermally averaged probability $P_{mn}^i(T)$ of a transition from state m to state n in the i-th mode can be written

$$P_{mn}^i = \frac{1}{2} \left(\frac{M}{kT} \right)^2 \frac{1}{(2\pi)^2\, IkT} \int_0^\infty \exp\left[-\frac{MV_0^2}{2kT} \right] V_0^3\, dV_0 \int_0^{b_*} 2\, \frac{b}{b_*} \frac{db}{b_*}$$

$$\cdot \int_0^\pi \sin\beta_0\, d\beta_0 \int_0^\pi d\alpha_0 \int_0^{2\pi} d\gamma_0 \int_0^\infty j_0\, dj_0 \exp\left[-\frac{j_0^2}{2IkT} \right] p_{mn}^i(\epsilon_i). \quad (12)$$

Here M is the reduced mass for the molecule–atom system, I is the moment of inertia of the molecule about its center of mass, and b_* is a cutoff impact parameter.

The probability $P_{mn}^i(T)$ in Eq. (12) is derived for collisions of a fully three-dimensional character. Calculation of a trajectory and of the energy transfer for each three-dimensional collision is a rather time-consuming task. A simpler and

shorter computation arises when a collision is restricted so that the atom and the molecule always lie in the plane determined initially by the atom and by the molecular axis. Such a coplanar calculation reduces the computational time to evaluate $P_{mn}^i(T)$ in two ways. First, the time required to calculate the coplanar trajectory is much smaller than that required to calculate the trajectory for a
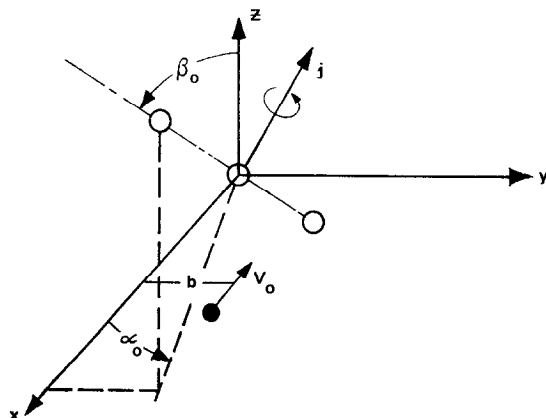

FIG. 4. Orientation of the molecule and the approaching structureless particle before a collision. See Section 3 for definition of symbols.

fully three-dimensional collision. Second, for a coplanar collision the angles β and γ are such that $\beta = \pi/2$ and $\gamma = \pm\pi/2$ throughout the collision. As a result the expression for the thermally-averaged probability $P_{mn}^i(T)$ in Eq. (12) reduces to a four-dimensional integral. The computational time reduction occurs principally for the first reason. Consequently, most of the calculations described in this section will be those obtained from evaluation of Eq. (12) for the coplanar (four-dimensional integral) case.

If the integrand is denoted by $f(\alpha_0, \beta_0, \gamma_0, b, V_0, j_0)$, the integral for P_{mn}^i can be written as

$$P_{mn}^i(T) = \int_0^\pi d\alpha_0 \int_0^\pi d\beta_0 \int_0^{2\pi} d\gamma_0 \int_0^{b_*} db \int_0^\infty dV_0 \int_0^\infty dj_0 f(\alpha_0, \beta_0, \gamma_0, b, V_0, j_0). \quad (13)$$

We multiply and divide f by the probability density function g,

$$g(\alpha_0, \beta_0, \gamma_0, b, V_0, j_0, \vartheta) = \frac{1}{2}\left(\frac{M}{k\vartheta}\right)^2 \exp\left[-\frac{MV_0^2}{2k\vartheta}\right] V_0^3 \left(2\frac{b}{b_*^2}\right)$$

$$\cdot \left(\frac{1}{2}\sin\beta_0\right) \frac{1}{2\pi^2} \frac{j_0}{Ik\vartheta} \exp\left[-\frac{j_0^2}{2Ik\vartheta}\right], \quad (14)$$

so that

$$P^i_{mn}(T) = \int_0^\pi d\alpha_0 \int_0^\pi d\beta_0 \int_0^{2\pi} d\gamma_0 \int_0^{b_*} db \int_0^\infty dV_0 \int_0^\infty dj_0 \left[\frac{f}{g}\right] g. \qquad (15)$$

The probability density function g is again, as in the one-dimensional example, a Maxwellian distribution at a "fictitious temperature" ϑ; the present function is, of course, generalized to a multi-dimensional distribution. Since the probability $p^i_{mn}(\epsilon_i)$ for energy transfer in any particular collision is small except for the most energetic collisions, the collisions with large initial values of V_0 and j_0. will contribute most to the energy transfer process. Therefore, the fictitious temperature ϑ is chosen to be near the high end of the temperature range of interest in the integral.

We introduce the convenient scale factors $V_\infty = (k\vartheta/M)^{1/2}$ and $j_\infty = (Ik\vartheta)^{1/2}$ together with the new integration variables $v = V_0/V_\infty$, $q = j_0/j_\infty$, and $\tilde{b} = b/b_*$. The expression for P^i_{mn} becomes

$$P^i_{mn}(T) = \int_0^\pi \frac{d\alpha_0}{\pi} \int_0^\pi \frac{d\beta_0}{\pi} \sin\beta_0 \int_0^{2\pi} \frac{d\gamma_0}{2\pi} \int_0^1 2\tilde{b}\, d\tilde{b} \int_0^\infty \frac{1}{2} v^3\, dv \exp\left(-\frac{v^2}{2}\right)$$
$$\cdot \int_0^\infty q\, dq \exp\left(-\frac{q^2}{2}\right) \left\{\left(\frac{\vartheta}{T}\right)^3 \exp\left[-\frac{\vartheta}{2}(v^2 + q^2)\left(\frac{1}{T} - \frac{1}{\vartheta}\right)\right] p^i_{mn}(\epsilon_i)\right\} \qquad (16)$$

For the Monte Carlo estimate of this integral the probability density function is given by $g(\alpha_0, \beta_0, \gamma_0, \tilde{b}, v, q; \vartheta)$. A large number N of sets of values for α_0, β_0, γ_0, $\tilde{b}$, v, and q are selected at random from this density function. Note that each set of values represents initial conditions for a trajectory and that each set is independent of the particular value chosen for T in the integral. Let the k-th set of values be denoted by $\alpha_0^{(k)}$, $\beta_0^{(k)}$, $\gamma_0^{(k)}$, $\tilde{b}^{(k)}$, $v^{(k)}$, and $q^{(k)}$, and

$$F^{(k)}(\vartheta, T; i, m, n) = \left(\frac{\vartheta}{T}\right)^3 \exp\left[-\frac{\vartheta}{2}((v^{(k)})^2 + (q^{(k)})^2)\left(\frac{1}{T} - \frac{1}{\vartheta}\right)\right] p^i_{mn}(\epsilon_i^{(k)}), \qquad (17)$$

where $P^i_{mn}(\epsilon_i^{(k)})$ has been evaluated for the k-th set of values. The Monte Carlo approximation to $P^i_{mn}(T)$ is given by

$$P^i_{mn}(T) \cong \frac{1}{N} \sum_{k=1}^N F^{(k)}(\vartheta, T; i, m, n), \qquad (18)$$

while the variance for the distribution of $F^{(k)}$ is given by

$$\sigma^2_{(N)} \cong \frac{1}{N} \sum_{k=1}^N [F^{(k)}(\vartheta, T; i, m, n)]^2 - [P^i_{mn}(T)]^2. \qquad (19)$$

Estimates of the integral in Eq. (12) over the temperature range $300°K \leqslant T \leqslant$

$8000°K$ were performed according to Eq. (18) for $m = 0$ and $n = 1, 2, 3$. The molecular parameters and potential constants were selected to simulate excitation of the bending mode of the carbon dioxide molecule upon collision with another carbon dioxide molecule. In this case one of the molecules is regarded as structure-less for the model to be applicable. Simultaneously, estimates of the variance of the distribution of P_{mn}^i given by Eqs. (19) and (10) were calculated. The temperature T, the parameter ϑ, and the number of trials are all variables in these calculations, and for the coplanar calculations (four-dimensional integrals), each was varied independently to determine its effect upon the results. Limited computations were performed for the general case involving three-dimensional collisions (six-dimensional integrals), and one plot of these results is shown.

The calculations performed for the coplanar collisions (four-dimensional integrals) indicate that all of the conclusions drawn from the one-dimensional integral example are valid also in this multi-dimensional case. For a single value of ϑ and for a fixed number of trials, the convergence of the Monte Carlo estimate of the four-dimensional integral is found to be comparable to the convergence obtained for the one-dimensional integral over a similar temperature range. The difference in the molecular parameters and the potential constants between the

TABLE II

Comparison after $N = 180$ trials of the values of the integral $P_{01}^{1(N)}(T)$ in Eq. (12) for two values of the parameter θ (for CO_2-CO_2 collision model).

	$\vartheta = 2000°K$		$\vartheta = 5000°K$	
$T(°K)$	$P_{01}^{1(N)}$	Rel. error	$P_{01}^{1(N)}$	Rel. error
300°	4.59×10^{-5}	0.330	7.85×10^{-6}	0.467
500°	4.96×10^{-4}	0.166	3.02×10^{-4}	0.354
700°	1.78×10^{-3}	0.137	1.70×10^{-3}	0.299
1000°	5.90×10^{-3}	0.106	6.55×10^{-3}	0.214
3000°	6.27×10^{-2}	0.183	8.09×10^{-2}	0.082
4000°	6.64×10^{-2}	0.208	1.15×10^{-1}	0.068
5000°	6.02×10^{-2}	0.225	1.39×10^{-1}	0.068
6000°	5.14×10^{-2}	0.236	1.53×10^{-1}	0.076
7000°	4.28×10^{-2}	0.245	1.58×10^{-1}	0.088
8000°	3.55×10^{-2}	0.251	1.57×10^{-1}	0.100

one-dimensional and the four-dimensional integrals examined here does not allow direct comparison of the estimates of these integrals. However, the relative error calculated for each estimate does provide a basis for comparison. For the one-dimensional example of Section 2 with $\vartheta = 5000°K$ and after $N = 180$ trials, the relative error has a minimum value of 0.088 near $T = 1000°C$. In addition, the

relative error remains less than 0.16 for the temperature range $300°C \leqslant T \leqslant 3000°$. In the present example the relative error for $\vartheta = 5000°$ after $N = 180$ trials is listed together with other results in Table II. Here the relative error achieves a minimum of 0.068 between $T = 4000°C$ and $T = 5000°C$. In the temperature range $3000°C \leqslant T \leqslant 8000°C$, the relative error remains less than 0.10.

Examination of the relative errors determined for both values of ϑ given in Table II shows that, as in the one-dimensional case, the relative error for each ϑ has a minimum as a function of T: for small values of T and for large values, the relative error increases rapidly. The rate at which the relative error increases for large and small T appears to be more rapid than in the one-dimensional case. Consequently, it is concluded that, for given ϑ, the range of temperatures over which the scheme calculates the integral accurately in a multidimensional case may be somewhat reduced from that in the one-dimensional case.

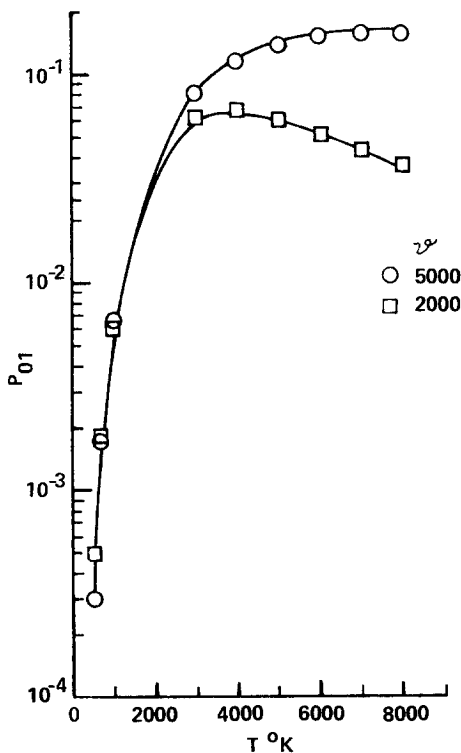As in the one-dimensional example the convergence of the Monte Carlo estimates

FIG. 5. Monte Carlo coplanar estimates $P_{01}^{1(N)}$ of integral (12) after $N = 180$ trials as functions of temperature T for two values of the parameter ϑ.

are not found to be sensitively dependent upon the value of ϑ used. This result is illustrated in Table II where the values of $P_{01}^{1(N)}$ and the relative error has been tabulated for two values of ϑ, 2000°K and 5000°K, after $N = 180$ trials. The agreement between the values of $P_{01}^{1(N)}$ calculated for $\vartheta = 2000$°K and those calculated for $\vartheta = 5000$°K is quite good for temperatures in the range 500°K $\leqslant T \leqslant 3000$°K. For temperatures greater than 3000°K the agreement becomes poorer. Agreement can be expected to be best in the region where the relative error for both values of ϑ is small.

The values of $P_{01}^{1(N)}$ vs T for $\vartheta = 2000$°K and for $\vartheta = 5000$°K listed in Table II have been plotted in Fig. 5 to more graphically illustrate the sensitivity of results to choice of ϑ. Where the relative error is small, the values of $P_{01}^{1(N)}$ for each ϑ are quite comparable. The choice of ϑ is important for determining the range of temperature over which the computation is accurate, but its choice does not sensitively affect the estimate of $P_{01}^{1(N)}$ determined for a specific temperature within this range.

Figure 5 also illustrates an important check which the technique allows. If the multidimensional integral is desired for a larger range of temperatures than a single value of ϑ affords, two or more values of ϑ are required. Generally, there will then exist a subrange of temperatures common to two of the values of ϑ over
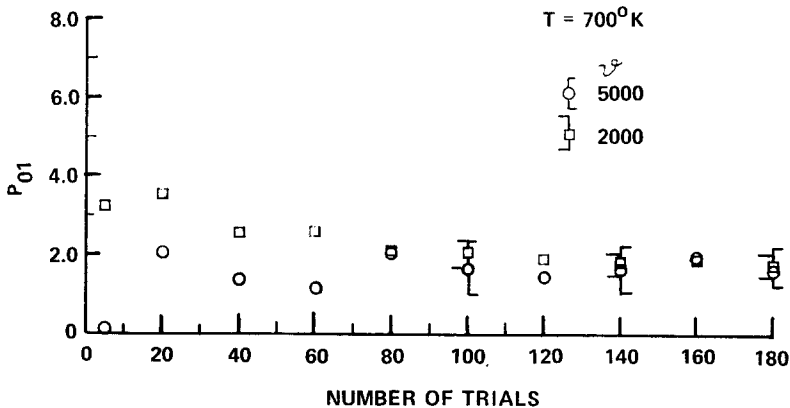

FIG. 6. Monte Carlo coplanar estimates $P_{01}^{1(N)}$ of integral (12) as functions of the number of trials N for $T = 700$° and for two values of the parameter ϑ. Error bars indicate a standard deviation for each estimate.

which the estimates calculated for the integral should coincide. If these estimates coincide to within the accuracy expected from the computed relative errors, the estimates can be adjudged reliable. If, however, the results do not coincide to the expected accuracy, then an error has been made in the computation.

Figure 6 shows plots of $P_{01}^{1(N)}$ vs N for $T = 700°K$ and for two values of ϑ, $2000°K$ and $5000°K$. Error bars at various values of N indicate one standard deviation above and below the calculated estimate. Once again, as in the one-dimensional example, the convergence for an individual value of T and a value of ϑ is not rapid. However, for a fixed ϑ, $P_{01}^{1(N)}$ converges for a substantial range of temperatures. The number of trials for $\vartheta = 5000°K$ was carried out to $N = 490$ trials to examine the convergence for a large number of trials in the multidimensional case. The value of $P_{01}^{1(N)}$ after 490 trials was found to be
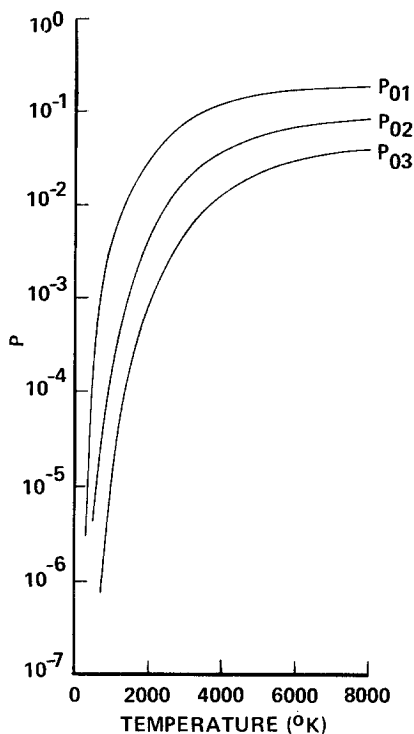

FIG. 7.   Monte Carlo estimates $P_{0n}^{1(N)}$ of integral (12) as functions of temperature T for three-dimensional collisions (six-dimensional integrals).

1.84×10^{-3} and the relative error was calculated to be 0.160. All subsequent coplanar calculations were performed with only 180 trials, however, since the slow rate of convergence does not justify a large number of trials.

Figure 7 illustrates the results determined from calculating an approximation to Eq. (12) for three-dimensional collisions. As mentioned above, these calculations

require more computer time primarily because of the longer time necessary to calculate each trajectory. Only $N = 100$ trajectories were calculated for this case. Comparison of these calculations with those performed for the coplanar case showed that the numerical results were not substantially different.

The technique described in the Introduction and illustrated by computation of a one-dimensional integral in Section 2 has been applied to multidimensional integrals. The integrals are four- and six-dimensional integrals arising in the description of vibrational excitation processes in linear molecules. The results indicate that the conclusions drawn from the one-dimensional example are valid in the multi-dimensional case. First, for one set of calculations of the integrand $(p^i_{mn}(\epsilon_i))$, the thermally averaged integral $(P^i_{mn}(T))$ can be determined over a large temperature range. (The range of temperatures over which the estimate of the integral converges satisfactorily may be reduced over that found in the one-dimensional example, however.) Second, the estimate of the integral at any particular temperature is not sensitively dependent upon the value of ϑ chosen. Finally, as in the one-dimensional example, the convergence of the estimate of the integral for given values of ϑ and T as a function of the number of trials N is not rapid because of the wide range of temperatures over which this convergence is obtained.

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