Improved Null-Collision Technique in the Direct Simulation Monte Carlo Method: Application to Vibrational Relaxation of Nitrogen

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Abstract—The improved null-collision (INC) technique in the direct simulation Monte Carlo (DSMC) method is developed for the simulation of diatom-diatom collision processes and detailed for elastic and rotationally and vibrationally inelastic collision processes in a spatially homogeneous cell using the realistic cross-sections. The accuracy of the INC-DSMC method is assessed by comparing with the solution of the master relaxation equation for the vibrational relaxation of nitrogen in an isolated spatially homogeneous cell. The feasibility of the INC-DSMC method for practical use is verified by simulating a hypersonic rarefied nitrogen flow over a circular cylinder.

Keywords—Improved null-collision technique, Direct simulation Monte Carlo method, Vibrational relaxation, Hypersonic rarefied flow.

1. INTRODUCTION

The null-collision technique [1,2] in the direct simulation Monte Carlo (DSMC) method [3] is useful for the simulation of elastic collision processes and extended [4] to the simulation of rarefied real gases undergoing various molecular collision processes such as elastic, inelastic, and reactive collisions. However, it is rather difficult to estimate precisely the maximum value of the total cross-section (multiplied by the relative collision velocity) given by the sum of all the cross sections for various collision processes. This difficulty may be overcome by introducing null collisions into each of molecular collision processes so that the maximum value of each cross section (multiplied by the relative collision velocity) is estimated accurately instead of that of the total cross-section. This idea was tentatively employed in the improved null-collision (INC) technique [5] for the Monte Carlo test-particle simulation of atom-diatom collision processes.

In this paper, the INC technique is developed for the Monte Carlo direct simulation of diatom-diatom collision processes and detailed for the elastic and rotationally and vibrationally inelastic collision processes in a spatially homogeneous cell. Assessment of the accuracy of the INC-DSMC method is made by comparing with the solution of the master relaxation equation for the vibrational relaxation of nitrogen in an isolated spatially homogeneous cell. The feasibility of the INC-DSMC method for practical use is examined by simulating a hypersonic rarefied nitrogen flow over a circular cylinder. To produce macroscopically accurate data in the simulation of rarefied...
real gases with the DSMC method, a realistic and efficient molecular model is required. In this work, the elastic and rotationally inelastic cross-sections are, respectively, taken as the variable soft sphere (VSS) model [6-8] and the statistical inelastic cross-section (SICS) model [9] for continuous rotational energy. The vibrationally inelastic cross-section for translational-vibrational (TV) energy transfer is modeled [10] by combining the line-of-centers cross-section (LCCS) with the ITFITS (improvement to forced oscillator, impulsive transfer semiclassical) vibrational transition probability [11] extended to diatom-diatom collisions [12]. The extended ITFITS (EITFITS) probability is given in an analytical form and in good agreement with quantum mechanical results for TV energy transfer but not for resonant vibrational-vibrational (VV) energy transfer [12]. Therefore, the vibrationally inelastic cross-section for resonant VV energy transfer is modeled by combining the LCCS with the two-state semiclassical (TSS) probability [13] for VV energy transfer, because the TSS probability is given in a simple analytical form and in reasonable agreement with experimental results [14].

2. IMPROVED NULL-COLLISION TECHNIQUE

The INC technique for the Monte Carlo direct simulation of diatom-diatom collision processes is described in detail for the elastic and rotationally and vibrationally inelastic collision processes during a time step $\Delta t$ in a spatially homogeneous cell with a volume $\Delta V$.

(a) For given elastic [$\sigma_e(\epsilon)$], total rotational [$\sigma_r(\epsilon, \xi_1, \xi_2)$], and total vibrational [$\sigma_v(\epsilon, i, j)$] cross-sections, the maximum values of $\sigma_e(\epsilon)$, $\sigma_r(\epsilon, \xi_1, \xi_2)$, and $\sigma_v(\epsilon, i, j)$ for all the collision pairs are evaluated to be

\[
S_e = \max[\sigma_e(\epsilon)], \quad g \leq g_{\text{max}},
\]

\[
S_r = \max[\sigma_r(\epsilon, \xi_1, \xi_2)], \quad g \leq g_{\text{max}},
\]

\[
S_v = \max[\sigma_v(\epsilon, i, j)], \quad g \leq g_{\text{max}},
\]

where $g$ is the relative velocity, $\epsilon = \mu g^2/2$ is the relative translational energy, $\mu = m/2$ and $m$ being the reduced and molecular masses, respectively, $\xi_1$ and $\xi_2$ are the continuous rotational energies, and $i$ and $j$ are the vibrational quantum levels of two colliding molecules. $g_{\text{max}}$ is the maximum value of $g$ of all the collision pairs and evaluated to be $2v_{\text{max}}$ from the maximum velocity $v_{\text{max}}$ of all the molecules in the cell. The null-collision cross-sections for elastic and rotationally and vibrationally inelastic collisions are, respectively, defined by

\[
\sigma_e(\text{null}) = S_e - \sigma_e(\epsilon),
\]

\[
\sigma_r(\text{null}) = S_r - \sigma_r(\epsilon, \xi_1, \xi_2),
\]

\[
\sigma_v(\text{null}) = S_v - \sigma_v(\epsilon, i, j).
\]

(b) Assuming that all the collision pairs have the total maximum value of $S_t$ given by

\[
S_t = S_e + S_r + S_v,
\]

the total collision frequency (including null collisions) $\nu_t$ is evaluated to be

\[
\nu_t = \left( \frac{N}{2} \right) n S_t,
\]

where $N$ and $n = N/\Delta V$ are the molecular number and density, respectively.

(c) A time interval $\Delta t_c$ between successive collisions is assigned by the probability density function

\[
p(\Delta t_c) = \nu_t \exp(-\nu_t \Delta t_c),
\]
or \( \Delta t_e = - \ln R/\nu_t \), where \( R \) is a uniform random number in the range 0–1. When the summation of \( \Delta t_e \) exceeds \( \Delta t \), the molecular collision simulation during \( \Delta t \) in the cell ends.

(d) A collision pair is randomly chosen from all the molecules in the cell, because all the collision pairs have the same value of \( S_t \). If the same molecule is selected, then the collision is taken to be null and the procedure (c) is repeated. The collision is assigned to be elastic or rotationally or vibrationally inelastic by the elastic \( (p_e) \) and rotationally \( (p_r) \) and vibrationally \( (p_v) \) inelastic probabilities \( (p_e + p_r + p_v = 1) \) given by

\[
\begin{align*}
p_e &= \frac{S_e}{S_t}, \\
p_r &= \frac{S_r}{S_t}, \\
p_v &= \frac{S_v}{S_t}.
\end{align*}
\]  

(10)

(e) For elastic collision, the collision is determined to be real or null by the real \( (p_{real}) \) and null \( (p_{null}) \) probabilities given by

\[
\begin{align*}
p_{real} &= \frac{g \sigma_e(e)}{S_e}, \\
p_{null} &= \frac{g \sigma_e(null)}{S_e} = 1 - p_{real},
\end{align*}
\]  

(11)

where \( e \) is the precollision relative translational energy. If the collision is null, then the molecular state is not changed and the procedure (c) is repeated. If the collision is real, then the velocities \( v' \) and \( w' \) after collision are calculated from the precollision velocities \( v \) and \( w \) to be

\[
\begin{align*}
v' &= V + \frac{g'}{2}, \\
w' &= V - \frac{g'}{2}, \\
V &= v + w, \\
g' &= \left(1 - \frac{\Delta E}{e}\right)^{1/2} (g \cos \chi + G \sin \chi),
\end{align*}
\]  

(12)

and the procedure (a) is repeated, where \( \chi \) is the deflection angle assigned by a given probability density function \( p(\chi) \), \( \Delta E \) is the gap between post- and pre-collision internal energies and taken to be zero for elastic collision, \( g\left[= (g_{x}, g_{y}, g_{z}) \right] = v - w \) is the precollision relative velocity, and \( G\left[= (G_{x}, G_{y}, G_{z}) \right] \) is given in Cartesian coordinates \((x, y, z)\) by

\[
\begin{align*}
G_x &= -g_{yz} \sin \phi, \\
G_y &= \frac{g_{xz} g_{y} \sin \phi - g_{yz} \cos \phi}{g_{yz}}, \\
G_z &= \frac{g_{xz} g_{y} \sin \phi + g_{yz} \cos \phi}{g_{yz}},
\end{align*}
\]  

(13)

in which \( g_{yz} = (g_{z}^{2} + g_{z}^{2})^{1/2}, g = (g_{x}^{2} + g_{y}^{2} + g_{z}^{2})^{1/2} \), and \( \phi \) is the azimuthal angle chosen to be \( \phi = 2\pi R \).

(f) For rotationally inelastic collision, the collision is determined to be real or null by the real \( (p_{real}) \) and null \( (p_{null}) \) probabilities given by

\[
\begin{align*}
p_{real} &= \frac{g \sigma_r(\epsilon, \xi_1, \xi_2)}{S_r}, \\
p_{null} &= \frac{g \sigma_r(null)}{S_r} = 1 - p_{real},
\end{align*}
\]  

(14)
where $\xi_1$ and $\xi_2$ are the precollision rotational energies. If the collision is null, then the molecular state is not changed and the procedure (c) is repeated. If the collision is real, then the rotational energies $\xi'_1$ and $\xi'_2$ after collision are assigned by the probability density function

$$p(\xi'_1, \xi'_2) = \frac{\Delta \sigma_r(\epsilon, \xi_1 \rightarrow \xi'_1, \xi_2 \rightarrow \xi'_2)}{\sigma_r(\epsilon, \xi_1, \xi_2)},$$

where $\Delta \sigma_r(\epsilon, \xi_1 \rightarrow \xi'_1, \xi_2 \rightarrow \xi'_2)$ is the rotationally inelastic cross-section for rotational energy changes $\xi_1 \rightarrow \xi'_1 + \Delta \xi'_1$ and $\xi_2 \rightarrow \xi'_2 + \Delta \xi'_2$ in the ranges $\Delta \xi'_1$ and $\Delta \xi'_2$ and the total rotational cross-section is given by

$$\sigma_r(\epsilon, \xi_1, \xi_2) = \int \frac{\Delta \sigma_r(\epsilon, \xi_1 \rightarrow \xi'_1, \xi_2 \rightarrow \xi'_2)}{\Delta \xi'_1 \Delta \xi'_2} d\xi'_1 d\xi'_2.$$

The velocities $v'$ and $w'$ after collision are calculated from equation (12) with the rotational energy gap $\Delta E = \xi'_1 + \xi'_2 - \xi_1 - \xi_2$ and the procedure (a) is repeated.

For vibrationally inelastic collision, the collision is determined to be real or null by the real ($p_{\text{real}}$) and null ($p_{\text{null}}$) probabilities given by

$$p_{\text{real}} = \frac{g \sigma_v(\epsilon, ij)}{S_v},$$
$$p_{\text{null}} = \frac{g \sigma_v(\text{null})}{S_v} = 1 - p_{\text{real}},$$

where $i$ and $j$ are the precollision vibrational levels. If the collision is null, then the molecular state is not changed and the procedure (c) is repeated. If the collision is real, then the vibrational levels $i'$ and $j'$ after collision ($i'j' \neq ij$) are assigned by the probability

$$p_{i'j'} = \frac{\sigma_{u',jj'}(\epsilon)}{\sigma_v(\epsilon, ij)},$$

where $\sigma_{u',jj'}(\epsilon)$ is the vibrationally inelastic cross-section for vibrational level transitions $i \rightarrow i'$ and $j \rightarrow j'$ and the total vibrational cross-section is given by

$$\sigma_v(\epsilon, ij) = \sum_{i'j' \neq ij} \sigma_{u',jj'}(\epsilon),$$

in which the summation over $i'$ and $j'$ excludes the elastic collision with $i' = i$ and $j' = j$ ($i'j' \neq ij$). The velocities $v'$ and $w'$ after collision are calculated from (12) with the vibrational energy gap $\Delta E = E'_v + E'_j - E_i - E_j$ and the procedure (a) is repeated.

3. MODEL CROSS-SECTIONS AND IMPROVED NULL-COLLISION TECHNIQUE

3.1. Elastic Cross-Section

The elastic cross-section $\sigma_e(\epsilon)$ is taken as the VSS model [6-8]

$$\sigma_{\text{VSS}}(\epsilon) = c e^{-\omega}$$

with the constant parameters $c$ and $\omega$. The probability density function $p(\chi)$ for the VSS model is given by

$$p_{\text{VSS}}(\chi) = \alpha \cos^{2\alpha-1} \left(\frac{\chi}{2}\right) \sin \left(\frac{\chi}{2}\right),$$
from which the deflection \( \cos \chi \) is obtained to be
\[
\cos \chi = 2\frac{R^1}{\alpha} - 1,
\]
where the parameter \( \alpha \) may depend on \( \epsilon \). The parameters \( \alpha, \omega, \text{ and } \alpha \) are determined from the viscosity and diffusion coefficients of real gases. For \( \sigma_{\text{VSS}}(\epsilon) = C(\epsilon/k)^{-\omega} \) in \( \text{Å}^2 \) and \( \alpha = C_\alpha(\epsilon/k)^{\omega_\alpha} \), \( k \) being the Boltzmann constant, the values of the constant parameters \( C, \omega, C_\alpha, \) and \( \omega_\alpha \) are presented in [7,8] for various molecules; for nitrogen, \( C = 188.2, \omega = 0.215, C_\alpha = 1.139, \) and \( \omega_\alpha = 0.0231 \) in the temperature range \( T = 300 - 15,000 \text{K} \).

The value of \( S_\epsilon \) defined by (1) is estimated for \( \omega \leq 0.5 \) to be
\[
S_\epsilon = g_{\text{max}}\sigma_{\text{VSS}}(\epsilon_{\text{max}}),
\]
where \( \epsilon_{\text{max}} = \mu g^2_{\text{max}}/2 \).

### 3.2. Rotationally Inelastic Cross-Section

The rotationally inelastic cross-section is taken as the SICS model [9] for continuous rotational energy and given by
\[
\Delta \sigma_r(\epsilon, \xi_1 \rightarrow \xi_1', \xi_2 \rightarrow \xi_2') = \sigma_{\text{VSS}}(\epsilon)\zeta(E_r, \xi_1', \xi_2') \Delta \xi_1' \Delta \xi_2',
\]
where
\[
\zeta(E_r, \xi_1', \xi_2') = C(E_r)(E_r - \xi_1' - \xi_2') \sigma_{\text{VSS}}(E_r - \xi_1' - \xi_2'), \quad E_r \geq E_{\text{th}},
\]
\[
\zeta(E_r, \xi_1', \xi_2') = 0, \quad E_r < E_{\text{th}},
\]
where \( E_r = \epsilon + \xi_1 + \xi_2 = \epsilon' + \xi_1' + \xi_2' \) is the total energy for rotationally inelastic collision, \( \epsilon' \) being the postcollision relative translational energy, \( E_{\text{th}} \) is the threshold energy taken to be \( 6k\theta_r \) for homonuclear diatomic molecule with the characteristic rotational temperature \( \theta_r(=2.863 \text{K} \text{ for nitrogen}[15]) \), and the function \( C(E_r) \) is determined to be
\[
C(E_r) = \frac{2\Delta E_r(E_r)}{G(E_r)},
\]
\[
G(E_r) = \frac{2cE_r^4}{(2 - \omega)(3 - \omega)(4 - \omega)},
\]
using Parker's rotational energy gain function [16,17]
\[
\Delta E_r(E_r) = \frac{E_r/2 + (2\pi/3)(E_rE_*)^{1/2} + (2 + \pi^2/4)E_*)}{Z_r^{\infty}},
\]
in which \( E_* \) and \( Z_r^{\infty} \) are the constant parameters taken to be [18] \( E_*/k = 79.8 \text{K} \) and \( Z_r^{\infty} = 21 \) for nitrogen [17]. The total rotational cross-section defined by (16) is obtained to be
\[
\sigma_r(\epsilon, \xi_1, \xi_2) = Z(E_r)\sigma_{\text{VSS}}(\epsilon),
\]
\[
Z(E_r) = \frac{(4 - \omega)\Delta E_r(E_r)}{E_r}, \quad E_r \geq E_{\text{th}},
\]
\[
Z(E_r) = 0, \quad E_r < E_{\text{th}}.
\]

The value of \( S_r \) defined by (2) is estimated for \( \omega \leq 0.5 \) to be
\[
S_r = \max[g_{\text{th}}\sigma_{\text{VSS}}(E_{\text{th}})Z(E_{\text{th}}), g_{\text{max}}\sigma_{\text{VSS}}(\epsilon_{\text{max}})Z(\epsilon_{\text{max}})],
\]
where \( g_{\text{th}} = (2E_{\text{th}}/\mu)^{1/2} \). In the selection of postcollision rotational energies \( \xi_1' \) and \( \xi_2' \) by the probability density function \( p(\xi_1', \xi_2') \) given by (15), the acceptance-rejection method is employed with the normalized probability density function
\[
\bar{P}(\xi_1', \xi_2') = \frac{p(\xi_1', \xi_2')}{\max[p(\xi_1', \xi_2')]} = \left[1 - \frac{\xi_1' + \xi_2' - \epsilon_r}{E_r}\right]^{1-\omega}.
\]
If \( \xi_1' = R_1E_r \) and \( \xi_2' = R_2E_r \) satisfy the conditions \( \xi_1' + \xi_2' < E_r \) and \( \bar{P}(\xi_1', \xi_2') > R_3 \), then \( \xi_1' \) and \( \xi_2' \) are accepted, where \( R_1, R_2, \) and \( R_3 \) are uniform random numbers in the range \( 0 - 1 \).
3.3. Vibrationally Inelastic Cross-Section

The EITFITS probability \( P_{\nu, j', j'}(\epsilon) \) for vibrational level transitions \( i \rightarrow i' \) and \( j \rightarrow j' \) is given by [12]

\[
P_{\nu, j', j'}(\epsilon) = P_{\nu}(\epsilon) P_{j', j'}(\epsilon),
\]

\[
P_{\nu}(\epsilon) = \left( \frac{H}{J} \right) q^{j'-j} e^{-q} \left[ L_j^{(J-1)}(q) \right]^2,
\]

where \( L_j^{(a)}(x) \) is the associated Laguerre polynomial, \( I = \min(i, i') \), \( J = \max(i, i') \), and \( q \) is the state-dependent energy transfer given by

\[
q = 2 \left\{ \left( \frac{\pi}{\alpha_\nu} \right) r_v \text{csch} \left[ \left( \frac{\pi}{\alpha_\nu} \right) \left( \frac{m_v}{2} \right)^{1/2} \left( \frac{k \theta_\nu}{\langle \epsilon \rangle} \right)^{1/2} \right] \right\}^2
\]

with \( \alpha_\nu = h(2\pi L_v)^{-1} (m_k \theta_\nu)^{-1/2} \), \( r_v = (1/2)(1 + m_v^{-1})^{-1} \), and \( m_v = 1/2 \) for homonuclear diatomic molecule, in which \( h \) is the Planck constant, \( L_v \) is the steepness parameter of the intermolecular potential, and \( \theta_\nu \) is the characteristic vibrational temperature taken to be 3,393 K for nitrogen [15]. In (35), the velocity symmetrization correction

\[
\langle \epsilon \rangle^{1/2} = \frac{\epsilon^{1/2} + \epsilon'^{1/2}}{2}
\]

is employed so that the microscopic reversibility relation

\[
P_{\nu, j', j'}(\epsilon) = P_{\nu, i, j, j'}(\epsilon')
\]

is satisfied, where \( \epsilon' = \epsilon - \Delta E_{\nu, j', j'} \) is the postcollision relative translational energy obtained from the energy conservation for vibrationally inelastic collision and \( \Delta E_{\nu, j', j'} = E_{\nu} + E_{j'} - E_i - E_j \) is the change in the vibrational energy \( E_i = k \theta_\nu i \) of harmonic oscillator in the vibrational level \( i \).

The vibrationally inelastic cross-section \( \sigma_{\nu, j', j'}(\epsilon) \) for TV excitation transitions \( i \rightarrow i' \) and \( j \rightarrow j' \) with \( \Delta E_{\nu, j', j'} > 0 \) is derived by combining the EITFITS probability with the LCCS \( \sigma_{\nu, j', j'}(\epsilon) = \eta_\nu \sigma_{\nu, j', j'}(\epsilon) \) as [10]

\[
\sigma_{\nu, j', j'}(\epsilon) = \eta_\nu \sigma_{\nu, j', j'}(\epsilon) \left( 1 - \frac{\Delta E_{\nu, j', j'}}{\epsilon} \right) P_{\nu, j', j'}(\epsilon), \quad \epsilon \geq \Delta E_{\nu, j', j'},
\]

\[
\sigma_{\nu, j', j'}(\epsilon) = 0, \quad \epsilon < \Delta E_{\nu, j', j'},
\]

where \( \eta_\nu \) is the vibrational steric factor and the velocity symmetrization is used in the VSS cross-section so that \( \sigma_{\nu, j', j'}(\epsilon) \) for TV de-excitation transitions \( i \rightarrow i' \) and \( j \rightarrow j' \) with \( \Delta E_{\nu, j', j'} \leq 0 \) is obtained from the microscopic reversibility relation

\[
\epsilon \sigma_{\nu, j', j'}(\epsilon) = \epsilon' \sigma_{\nu, i', j'}(\epsilon')
\]

in the simple form

\[
\sigma_{\nu, j', j'}(\epsilon) = \eta_\nu \sigma_{\nu, j', j'}(\epsilon) P_{\nu, j', j'}(\epsilon).
\]

The constant parameters \( L_v \) and \( \eta_\nu \) may be determined from the Millikan-White (MW) correlation formula [19] and experimental data of the vibrational relaxation time.

The vibrationally inelastic cross-section \( \sigma_{\nu, j', j'}(\epsilon) \) for resonant VV transitions \( i \rightarrow i' \) and \( j \rightarrow j' \) with \( \Delta E_{\nu, j', j'} = 0 \) is given by (40) with \( \langle \epsilon \rangle = \epsilon \), i.e.,

\[
\sigma_{\nu, j', j'}(\epsilon) = \eta_\nu \sigma_{\nu}(\epsilon) P_{\nu, j', j'}(\epsilon).
\]
The probability $P_{i',j';j'}(e)$ for one-quantum VV transitions $i \rightarrow i \pm 1$ and $j \rightarrow j \mp 1$ is taken as the TSS model [13] given by

$$P_{i',j';j'}(e) = \sin^2 \left[ (IJ)^{1/2} (2\omega_v L_v)^{-1} g \right], \quad i' = i \pm 1 \text{ and } j' = j \mp 1,$$

(42)

where $I = \max(i, i')$, $J = \max(j, j')$, $\omega_v = \frac{2\pi k \Theta_v}{h}$ is the oscillator angular frequency, and $g = \frac{(2\epsilon/\mu)^{1/2}}{h}$ is the relative velocity. The probability $P_{i',j';j'}(e)$ for multiple-quantum transitions $i \rightarrow i'$ and $j \rightarrow j'$ with $\Delta E_{i',j'} = 0$ is taken as the EITFITS probability given by (33).

The value of $S_v$ defined by (3) is estimated for $\omega \leq 0.5$ to be

$$S_v = (2 + 4\epsilon) \eta_b g_{\text{max}} \sigma_{\text{SS}} (\epsilon_{\text{max}}).$$

(43)
In the selection of postcollision vibrational levels \( i' \) and \( j' \) by the probability \( p_{ij} \) given by (18), the acceptance-rejection method is employed with the normalized probability density function

\[
\overline{P}_{i'j'} = \frac{P_{i'j'}}{\max(P_{i'j'})},
\]

(44)

If \( i' \) and \( j' \) chosen randomly from integers in the range \( 0 \geq i' \geq i \), \( E_{i'} + E_{j'} < \epsilon + E_i + E_j \), and \( \overline{P}_{i'j'} > R \), then \( i' \) and \( j' \) are accepted, where \( i_{\text{max}} \) is the topmost vibrational level given by the integer part of \( \theta_d/\theta_v \), \( \theta_d \) being the characteristic dissociation temperature. For nitrogen [15], \( \theta_d = 113,250 \text{K} \) and \( i_{\text{max}} = 33 \). It is noted that numerical tables of \( \sigma_{ij} \) and \( \max[\sigma_{i'j'}(\epsilon)] \) for precollision discrete states \( (\epsilon_k,ij) \) make the evaluation of \( \sigma_{ij} \) in (17) and \( \max[\sigma_{i'j'}(\epsilon)] \) in (44) very efficient and that a proper truncation of the number of level step, \( \Delta v = |i - i'| \) and \( |j - j'| \), for transitions \( i \to i' \) and \( j \to j' \) in (44) reduces effectively the computation time.

4. VIBRATIONAL RELAXATION OF NITROGEN

4.1. Master Relaxation Equation

The vibrational relaxation of nitrogen in a spatially homogeneous cell, where the velocity distribution maintains the Maxwell distribution at the translational temperature \( T \), is described by the master relaxation equation (MRE)

\[
\frac{dy_i}{dt} = n \sum_{i',j'} \sum_j [K_{i'i',j'}(T)y_{i'j'} - K_{ij'}(T)y_{ij'}],
\]

(45)

where \( t \) is the time, \( y_i = n_i/n \) is the vibrational distribution, \( n_i \) is the number density of molecules in the vibrational level \( i \), \( n = \sum_i n_i \) is the constant molecular number density, and \( K_{i'i',j'}(T) \) is the rate constant at the translational temperature \( T \) for vibrational transitions \( i \to i' \) and \( j \to j' \) given by

\[
K_{i'i',j'}(T) = \left( \frac{8kT}{\pi \mu} \right)^{1/2} \left( kT \right)^{-2} \int_0^\infty \epsilon \sigma_{i'i',j'}(\epsilon) \exp \left( -\frac{\epsilon}{kT} \right) d\epsilon
\]

(46)
and satisfies the detailed balance

$$K_{ii', jj'}(T) = K_{jj', ii'}(T) \exp \left( -\frac{\Delta E_{ii', jj'}}{kT} \right),$$

(47)

because of the microscopic reversibility relation given by (39).

At low translational energies (temperatures) where the state-dependent energy transfer \( q \) given by (35) is much smaller than unity, the vibrational transition probability \( P_{ii'}(\epsilon) \) given by (34) is reduced to the Landau-Teller probability \( P_{i+1,i}(\epsilon) = (i+1)P_{10}(\epsilon) \) with \( P_{10}(\epsilon) = q \) and \( P_{i,i\pm1}(\epsilon) \sim q \gg P_{i,i\pm2}(\epsilon) \sim q^2 \gg P_{i,i\pm3}(\epsilon) \sim q^3 \gg \ldots \). In the first-order (\( \sim q \)) perturbation approximation (FOPA), the MRE leads to the vibrational energy relaxation equation

$$\frac{dE_v}{dt} = \frac{E_v(T) - E_v}{\tau_v},$$

(48)

where \( E_v = \sum_i y_i E_i \) is the mean vibrational energy, \( E_v(T) = \sum_i y_i(T)E_i \) is that for the Boltzmann distribution \( y_i(T) \) at the translational temperature \( T \), and \( \tau_v \) is the vibrational relaxation time given by

$$\tau_v = \frac{kT[1 - \exp(-\theta_v/T)]^{-1}}{K_{10}(T)},$$

(49)
in which \( p = nkT \) is the pressure and \( K_{10}(T) \) is equal to \( K_{10,\epsilon}(T) \) obtained from \( \sigma_{10,\epsilon}(\epsilon) \) with \( P_{10,\epsilon}(\epsilon) = P_{10}(\epsilon) \). The vibrational parameters \( L_\nu \) and \( \eta_\nu \) are contained in \( K_{10}(T) \) and may be determined at low temperatures by fitting (49) to the MW formula \([19]\)

\[
\ln[p_T(\text{atm} \cdot \text{s})] = A \left\{ \left[ T(K) \right]^{-1/3} - 0.015 \left[ \frac{\mu}{\text{mol}} \right]^{1/4} \right\} - 18.42
\]

(50)

with the constant parameter \( A \) taken to be 220 for nitrogen. Using the fact that \( L_\nu \) and \( \eta_\nu \) dominate the slope and magnitude of the Landau-Teller plot of \( \ln(p_T) \) versus \( T^{-1/3} \), respectively, the fitting values of \( L_\nu = 0.25\text{Å} \) and \( \eta_\nu = 1.2 \) are obtained for nitrogen in the low temperature range \( T = 500 - 3,000 \text{K} \), as is shown in Figure 1.

At high translational energies (temperatures) where \( q \) is not small, the vibrational relaxation time \( \tau_\nu \) defined by (48) is obtained by solving the MRE (45) with the Runge-Kutta-Gill method for the constant translational temperature \( T \) and evaluating \( E_\nu = \sum_i y_i E_i \) and \( \frac{dE_\nu}{dt} = \sum_i \left( \frac{dE_i}{dt} \right) E_i \), where the initial vibrational distribution is taken to be \( y_0(0) = 1 \) \( [y_i(0) = 0, i \geq 1] \). Because the value of \( \tau_\nu \) is almost constant except at an initial transient stage, the Landau-Teller plot of the constant relaxation time \( p_T \) is presented in Figure 1. The MRE relaxation time is in good
agreement with the MW formula in the low temperature range $T = 500-3,000$ K and in reasonable agreement with the FOPA solution over the exhibited temperature range. It is noted that the MRE relaxation time rises at $T > 10^5$ K with increasing $T$ much slower than Park's correction [20] for the MW formula by adding the empirical elastic collision time $\tau_c = \left[n(8kT/\pi\mu)^{1/2}\sigma_v\right]^{-1}$ with $\sigma_v = \sigma'_v(50,000/T)^2$ and $\sigma'_v = 0.3\text{Å}^2$ for nitrogen.

4.2. Relaxation in Isolated Cell

The Monte Carlo direct simulation of vibrational relaxation of nitrogen in an isolated spatially homogeneous cell is implemented using the INC technique. The initial vibrational distribution is taken to be $y_0(0) = 1$ [$y_i(0) = 0, i \geq 1$], corresponding to zero vibrational temperature. The initial translational and rotational distributions are, respectively, taken as the Maxwell and Boltzmann distributions at the same initial temperature $T(0) = 10,000$ K. The number of simulation molecules is taken to be $N = 10,000$. 

Figure 6. Translational temperature contour (increment 5) obtained by the INC-DSMC method for the molecular number $\Delta N = 100$ (---) and 10 (---) in each adaptive collision cell.
The relaxation of the translational temperature $T_t/T_\infty$, the rotational temperature $T_r/T_\infty = \langle \xi \rangle / kT_\infty$, $\langle \xi \rangle$ being the mean rotational energy, and the mean vibrational energy $E_v/E_v(T_\infty)$ normalized by their equilibrium values is presented in Figure 2, as compared with the MRE solution for the constant total energy $E_t = (5/2)kT + E_v$, where the time $t$ is normalized by the VSS collision time $t_c = \{n[2kT(0)/m]^{1/2}\sigma_{\text{VSS}}[kT(0)]\}^{-1}$. The equilibrium temperature $T_\infty$ is obtained from the energy conservation relation, $(5/2)kT_\infty + E_v(T_\infty) = (5/2)T(0)$. The translational and rotational temperatures are in agreement within some statistical scatter and monotonically decrease to the equilibrium value of $T_\infty$, while the mean vibrational energy increases monotonically to the equilibrium value of $E_v(T_\infty)$. The INC-DSMC result is in good agreement with the MRE solution, because the velocity (rotational) distribution maintains the Maxwell (Boltzmann) distribution within some statistical scatter.

The relaxation of normalized vibrational distribution $y_l/y_0$ is presented in Figure 3, as compared with the MRE solution. The INC-DSMC distribution is shown for $y_l/y_0 > 10^{-4}$ (= $1/N$) in good agreement with the MRE solution. It is noted that the mean vibrational energy is accurately evaluated for $y_l/y_0 > 10^{-4}$, as is indicated in Figure 2.
4.3. Hypersonic Rarefied Flow over Circular Cylinder

The INC-DSMC method is applied to the simulation of a hypersonic rarefied nitrogen flow over a circular cylinder. The computation domain is taken as a rectangular form with the freestream boundary conditions except at the downstream boundary, where the streamwise gradient is assumed to be negligible. The computation domain is divided into small rectangular data cells for calculating macroscopic data, where a cell occupied in part by the circular cylinder is taken as it is. For the simulation of molecular collisions from time $t$ to $t + \Delta t$, each data cell is adaptively divided at the time $t$ into small rectangular collision cells according to the instantaneous molecular number in the data cell at the time $t$, so that the molecular number $\Delta N$ in each collision cell remains nearly a given value. Figure 4 exhibits typical adaptive collision cells.

The computation is made for the freestream Knudsen number $Kn_\infty = 0.1$, Mach number $M_\infty = 20$, and temperature $T_\infty = 300 K$, where $d$ is the diameter of cylinder and $\lambda_\infty = (16/5) \left[ n_\infty (2\pi \mu T_\infty)^{1/2} \right]^{-1}$ $\mu_\infty$ is the freestream mean free path of the hard-sphere viscosity expression, $n_\infty$ and $\mu_\infty$ being the freestream number density and viscosity coefficient, respectively. For $\mu_\infty = A T_\infty^s$ in $\mu Pa \cdot s$ and $T_\infty$ in $K$, the values of the constant parameters $A$ and $s$ are taken...
to be $A = 0.300$ and $s = 0.715$ for nitrogen [8] in the temperature range $T_\infty = 300-15,000$ K. The cylinder surface is taken as a diffuse reflection wall with the constant wall temperature $T_w = T_\infty$. The data-cell size is taken as $\frac{d}{2} \times \frac{d}{2}$ and the molecular number in each adaptive collision cell is taken to be $\Delta N = 100$ and 10 to examine the effect of small molecular number.

The contours of number density $n/n_\infty$ and translational $(T_{tr}/T_\infty)$, rotational $(T_r/T_\infty)$, and vibrational $(T_v/T_\infty)$ temperatures normalized by their freestream values are presented in Figures 5–8, respectively, where the vibrational temperature $T_v$ is defined by the mean vibrational energy relation

$$E_v = \sum_i y_i(T_v) E_i$$

for the Boltzmann distribution $y_i(T_v)$ at the vibrational temperature $T_v$ and evaluated from the mean vibrational energy $E_v$. It is noted that the contours are little different between $\Delta N = 100$ and 10. The peak number density and translational, rotational, and vibrational temperatures on the stagnation line are $n/n_\infty = 35.5$, $T_{tr}/T_\infty = 94.2$, $T_r/T_\infty = 28.3$, and $T_v/T_\infty = 4.0$. The peak positions of the rotational and vibrational temperatures in front of the cylinder are closer...
to the cylinder than that of the translational temperature, because the rotational and vibrational temperatures relax slower than the translational temperature.

The effect of the truncation of the number of vibrational level step $\Delta v$ on the contour of vibrational temperature $T_v/T_\infty$ for $\Delta N = 100$ is indicated in Figures 9 and 10 for $\Delta v = 5$ and 1, respectively. The contour is little different between $\Delta v = 5$ and no truncation but significantly different between the one-quantum transition $\Delta v = 1$ and no truncation. The computation time for no truncation and $\Delta v = 5$ is, respectively, about 3 and 1.5 times larger than that for the simulation without vibrationally inelastic collisions.

5. CONCLUDING REMARKS

The improved null-collision (INC) technique is developed for the Monte Carlo direct simulation of diatom-diatom collision processes by introducing null collisions into each of molecular collision processes. The accuracy and feasibility of the INC technique for use in the direct simulation Monte Carlo (DSMC) method are verified by simulating the vibrational relaxation of nitrogen in an isolated spatially homogeneous cell and in a hypersonic rarefied flow over a circular cylinder, respectively, using the realistic cross-sections. The computation time for the simulation a hyper-
sonic cylinder flow is confirmed to be within practical use. Therefore, it may be concluded that the INC-DSMC method is favorable for the Monte Carlo direct simulation of rarefied real gases.

REFERENCES