Reciprocity Modelling of Vibrationally Excited Four-Body Collisions

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Abstract. Rarefied gas dynamics has traditionally rested on the dilute gas assumption, which presupposes that the densities are so low that only binary collisions and single-body gas surface interactions occur. However, expressions for many-body collision rates and for many-body gas surface interaction (GSI) rates seem to suggest that at lower heights the dilute gas assumption is not valid. In particular, in the pure rarefied regime, two-body GSIs and some three-body interactions occur whereas, in the transition regime into continuum flow, four body collisions and four-body GSIs occur. To improve the accuracy of DSMC computations at lower heights it is necessary to be able to model three- and four-body encounters. This paper explains how to model four-body collisions using reciprocity theory. The paper follows a similar train of thought to a previous paper, which models three-body collisions. A reciprocity equation is written down for four-body collisions and then statistical models are formulated from the reciprocity equation. Three classes of models are formulated: free exchange, restricted exchange, and simplified restricted exchange. The free exchange models provide the greatest opportunity for achieving highly accurate computations. However, they fail on efficiency when applied to many-body collisions. The restricted exchange models provide the best compromise between accuracy and efficiency for many-body collisions. The simplified restricted exchange models are the most efficient of the three, but do not satisfy reciprocity and equipartition. Therefore they are best used with systems that remain in non-equilibrium throughout. The models are formulated for rotationally excited and vibrationally excited gases in the context of the Direct Simulation Monte Carlo (DSMC) method. The DSMC method is the standard method for computing rarefied gas dynamics.

I. INTRODUCTION

The reciprocity formalism has long been recognised as the correct approach for modelling complex interactions in rarefied gas dynamics. Proponents of the approach include Fowler (Ref. 1), Cercignani (Refs. 2 and 3), Pullin (Ref. 4), Agbormbai (Refs. 5 and 6) and Lord (Refs. 7 and 8). These workers have applied reciprocity ideas to modelling gas surface interactions and binary collisions in rarefied gas dynamics.

In this paper I consider the inelastic collision involving four polyatomic gas molecules with vibrationally excited states. The molecules may be part of a gas mixture, and may thus belong to different chemical species. This means that the number of degrees of freedom in each molecule will be different. I treat the internal excitations classically, with the justification that rotational quantum levels are close enough together to behave like a continuum. Vibrational quantum levels are spaced much further apart, and it is possible for a collision to cause simply a transition between one vibrational level and another. However, the general interest lies in overall relaxation phenomena which are governed by the exchange of energy among different energy modes rather than by transitions within given energy modes. For this overall treatment a classical approach suffices as long as we incorporate the quantum mechanical feature of incomplete excitation of higher internal modes in the collisions. We do so by introducing model parameters that control the degree of excitation allowed, and hence control the collisional efficiency in interchanging energy and therefore the overall relaxation rate.

Collision rate expressions for many body interactions (Ref. 9) show that the frequency of an N-body collision increases with the Nth power of the density and with the (N − 1)/2 power of the temperature. Both the density and the temperature of the atmosphere increase as the height falls. It appears that as a spacecraft flies lower into the atmosp-
phere the importance of high order collisions increases significantly, so much that in the transition regime between rarefied and continuum flow (Figure 1, Ref. 1) four-body collisions become significant. This means that Direct Simulation Monte Carlo (DSMC) computations must have the capability to handle four body collisions. In this paper I formulate reciprocity models of vibrationally excited four body collisions for use in DSMC computations. The analysis extends the work of Ref. 10 and follows a similar train of thought.

II. THE RECIPROCITY EQUATION

The reciprocity equation for $N$ interacting bodies is given in Ref. 10 as:

$$
G(a^c_{ij|j}|T) \left( \prod_{j=1}^{N-1} G(a^c_{ij|j}|T) \right) \left( \prod_{k=0}^{N-1} G(a^c_{ij|j}|T) \right) \left( \prod_{k=0}^{N-1} G(a^c_{ij|j}|T) \right) G(s^c)ds'd\xi'dE_i
$$

(1)

where: $\xi_j = (\xi_{j1}, \xi_{j2}, ..., \xi_{jN-1})$, $\xi_j = (\xi_{j1}, \xi_{j2}, ..., \xi_{jN-1})$, $\xi_j = (\xi_{j1}, \xi_{j2}, ..., \xi_{jN-1})$, $E_j = (\xi_j, \xi_j)$, $s$ are the correlation variates, $G$ are the correlation densities

$$
\gamma_m = \frac{\nu_m}{2}, \quad \xi_j = \frac{\epsilon_j}{kT_m}, \quad \xi_j = \frac{\epsilon_j}{kT_m}
$$

$\epsilon$ is the energy, $T_m$ is the modal temperature.

$$
G(x|\mu) = \frac{1}{\Gamma(\mu)} x^{\mu-1} e^{-x}, \quad (\mu > 0, \quad 0 \leq x \leq \infty)
$$

is the Gamma distribution for $x$

with parameter $\mu$, $\Gamma(\mu)$ is the gamma function. The subscripts are as follows:

$G$ for centre of mass, $t$ for translational, $r$ for rotational, $v$ for vibrational

In these expressions $\nu_m$ is the number of degrees of freedom of a mode ($4$ for translational, $6N_s$ for the solid, $2$ for rotational and $2$ for vibrational). Single and double primes indicate incident and reflected states.

Note that this equation assumes that a many body interaction consists of the interaction of a number of reduced particles whose total translational kinetic energy is a sum of squared terms.

We can derive the four-body equation from this, as:

$$
G(a^c_{ij|j}|T) G(a^c_{ij|j}|T) G(a^c_{ij|j}|T) G(a^c_{ij|j}|T) G(s^c)ds'd\xi'dE_i
$$

(2)

$$
G(a^c_{ij|j}|T) G(a^c_{ij|j}|T) G(a^c_{ij|j}|T) G(a^c_{ij|j}|T) G(s^c)ds'd\xi'dE_i
$$

The problem of solving our four body collision is simply one of formulating the correlation densities $G$. We do so by formulating a set of transformation equations, which constitute our desired model, to convert the pre-collision state to the post-collision state and vice versa. The overall transformation model is formulated gradually, by judiciously putting together a number of elementary transformations derived from distribution calculus. As we construct the overall transformation the correlation densities are generated automatically as part of the mathematics. Both transformation model and correlation densities are symmetrical with respect to the forward and inverse processes; i.e. the same transformation equations and correlation densities can perform the forward or inverse process. This means that the forward and inverse transformations have identical forms; also the forward and inverse correlation densities are identical.
III. CONSTRUCTING THE STATISTICAL MODELS

To construct the statistical transformations we split each energy mode into active and inactive components. Both the total active and total inactive energies are conserved in the interaction. Thus, we split the pre-collision energies into active and inactive components and then recombine the active components into the total active energy. This total active energy is then split (redistributed) into post-collision active components, which are finally recombined with the pre-collision inactive components to get the final post-collision energies. The whole point is that only the active components are interchanged in the interaction. Inactive components are not. This means that the post-collision inactive components remain equal to their pre-collision inactive counterparts.

In the free exchange model each energy component appearing in the reciprocity equation participates directly in the exchange and so is split and recombined as described above. The restricted exchange models lump sets of energy components together before modelling the exchange. The loosely restricted exchange models do not carry out this lumping far enough. They combine rotational and vibrational components into separate rotational and vibrational totals before calculating the exchange. The severely restricted exchange models lump all internal modes into a single total internal energy before exchanging with the translational mode. Pullin (Ref. 4) and Agbormbai (Ref. 5) have illustrated the general construction approach for these models so I provide only an abbreviated procedure here.

The Free Exchange Models

Rotationally excited

Choose the following active energy assembly / redistribution strategy:

\[
\begin{align*}
\text{trans}2 + \text{trans}3; \ sR2 \Rightarrow 2\text{transl}, & \quad \text{(trans}2 + \text{trans}1; \ sT1) \Rightarrow 3\text{transl}, \\
\text{rot}2 + \text{rot}3; \ sR3 \Rightarrow 2\text{rot}, & \quad \text{(rot}2 + \text{rot}1; \ sT1) \Rightarrow 3\text{rot}, \\
4\text{rot} + 4\text{transl}; \ sa \Rightarrow \text{total} & \quad \text{where CM denotes the centre of mass energy}
\end{align*}
\]

The model is then:

\[
\xi^* = (1 - s'_G)\xi'_G + (1 - s'_T)(1 - s'_a)\xi' _a, \quad \xi^*_{a1} = (1 - s'_T)s'_T r(1 - s'_a)\xi' _a, \quad \xi^*_{a2} = (1 - s'_T)s'_T r(1 - s'_a)\xi' _a,
\]

\[
\xi^*_{a3} = (1 - s'_T)s'_T r(1 - s'_a)\xi' _a, \quad \xi^*_{a0} = (1 - s'_T)s'_T r(1 - s'_a)\xi' _a, \quad \xi^*_{s1} = (1 - s'_T)s'_T r(1 - s'_a)\xi' _a,
\]

\[
\xi^*_{s2} = (1 - s'_T)s'_T r(1 - s'_a)\xi' _a, \quad \xi^*_{s3} = (1 - s'_T)s'_T r(1 - s'_a)\xi' _a,
\]

where \(\xi_a = s'_G\xi'_G + s'_T\xi' _T + s'_a\xi' _a\) is the total active energy

with associated correlation densities:

\[
G(s) = \beta(s'_G|\alpha_G, (1 - \alpha)_G)\beta(s'_T|\alpha_T, (1 - \alpha)_T)\beta(s'_a|\alpha_a, (1 - \alpha)_a)\beta(s'_{a1}|\alpha_{a1}, (1 - \alpha)_a) \times \beta(s'_{a2}|\alpha_{a2}, (1 - \alpha)_a) \times \beta(s'_{a3}|\alpha_{a3}, (1 - \alpha)_a) \times \beta(s'_{s1}|\alpha_{s1}, (1 - \alpha)_s) \times \beta(s'_{s2}|\alpha_{s2}, (1 - \alpha)_s) \times \beta(s'_{s3}|\alpha_{s3}, (1 - \alpha)_s)
\]

Note that we have not included the transformation equations for the post-collision correlation variates because we do not use them in simulations. Although we have included the equation for the post-collision centre-of-mass energy we would normally work out the motion of the centre of mass from dynamical considerations.
with correlation densities:

\[ G(s') = \beta(s'_1|\alpha, \gamma_1,(1-\alpha), \gamma_1)\beta(s'_2|\alpha, \gamma_1,(1-\alpha), \gamma_1)\beta(s'_3|\alpha, \gamma_1,(1-\alpha), \gamma_1)\beta(s'_4|\alpha, \gamma_1,(1-\alpha), \gamma_1) \times \beta(s'_1|\alpha, \gamma_1,(1-\alpha), \gamma_1)\beta(s'_2|\alpha, \gamma_1,(1-\alpha), \gamma_1)\beta(s'_3|\alpha, \gamma_1,(1-\alpha), \gamma_1) \times \beta(s'_1|\alpha, \gamma_1,(1-\alpha), \gamma_1)\beta(s'_2|\alpha, \gamma_1,(1-\alpha), \gamma_1) \]

Note that when no external force acts the centre of mass does not participate in the energy exchange.

**Vibrationally excited**

Choose the following active energy assembly / redistribution scheme:

(trans2 + transl3; s1) \rightarrow 2transl, (trans2 + transl1; s2) \rightarrow 3transl, (trans2 + CM; sR) \rightarrow 4transl

(rot2 + rot3; s2) \rightarrow 2rot, (rot2 + rot1; sR1) \rightarrow 3rot, (rot3 + rot0; sR2) \rightarrow 4rot

(vib2 + vib3; s1) \rightarrow 2vib, (vib2 + vib1; s1) \rightarrow 3vib, (vib2 + vib0; sR) \rightarrow 4vib

(4rot + 4vib; sR) \rightarrow int, (int + 4transl; s1) \rightarrow total

The model is:

\[ \xi_G = (1-s'_1)\xi'_{G0} + (1-s'_1)(1-s'_4)\xi'_{G0} \quad \xi'_{G0} = (1-s'_1)\xi'_{G1} + (1-s'_1)(1-s'_1)\xi'_{G2} \quad \xi'_{G1} = (1-s'_1)\xi'_{G2} + \xi'_{G1}' \]

\[ \xi'_{G2} = (1-s'_2)\xi'_{G3} + \xi'_{G2}' \quad \xi'_{G3} = (1-s'_2)\xi'_{G4} + \xi'_{G3}' \]

\[ \xi'_{G4} = (1-s'_2)\xi'_{G5} + \xi'_{G4}' \quad \xi'_{G5} = (1-s'_2)\xi'_{G6} + \xi'_{G5}' \]

\[ \xi_{a} = \xi_{G0} + \xi_{G1} + \xi_{G2} + \xi_{G3} + \xi_{G4} + \xi_{G5} \]

with associated correlation densities:

\[ G(s') = \beta(s'_1|\alpha, \gamma_0,(1-\alpha), \gamma_0)\beta(s'_2|\alpha, \gamma_0,(1-\alpha), \gamma_0)\beta(s'_3|\alpha, \gamma_0,(1-\alpha), \gamma_0) \times \beta(s'_1|\alpha, \gamma_0,(1-\alpha), \gamma_0)\beta(s'_2|\alpha, \gamma_0,(1-\alpha), \gamma_0)\beta(s'_3|\alpha, \gamma_0,(1-\alpha), \gamma_0) \times \beta(s'_1|\alpha, \gamma_0,(1-\alpha), \gamma_0)\beta(s'_2|\alpha, \gamma_0,(1-\alpha), \gamma_0) \]

In the absence of external forces this model becomes:

\[ \xi'_{G0} = (1-s'_1)\xi'_{G0} + (1-s'_4)\xi'_{G0} \quad \xi'_{G1} = (1-s'_1)\xi'_{G1} + (1-s'_1)(1-s'_1)\xi'_{G2} \quad \xi'_{G2} = (1-s'_1)\xi'_{G2} + \xi'_{G1}' \]

\[ \xi'_{G3} = (1-s'_2)\xi'_{G3} + \xi'_{G2}' \quad \xi'_{G4} = (1-s'_2)\xi'_{G4} + \xi'_{G3}' \]

\[ \xi'_{G5} = (1-s'_2)\xi'_{G5} + \xi'_{G4}' \quad \xi'_{G6} = (1-s'_2)\xi'_{G6} + \xi'_{G5}' \]

\[ \xi_{a} = \xi_{G0} + \xi_{G1} + \xi_{G2} + \xi_{G3} + \xi_{G4} + \xi_{G5} \]

where \[ \xi_{a} = \xi_{G0} + \xi_{G1} + \xi_{G2} + \xi_{G3} + \xi_{G4} + \xi_{G5} \]
with associated correlation densities:

\[ G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

These free exchange models are highly sophisticated and detailed, but they require sampling from a great number of Beta distributions for each collision. Therefore inefficiency will be a problem even with the rapid advances in computer technology. They are only recommended for cases where accuracy is crucial, and where the available computer technology can handle the huge demands on computer time. It appears that for many body collisions (especially as the number of bodies increases) restricted exchange models will be the choice, as they require fewer Beta sampling for each collision.

The Loosely Restricted Exchange Models

Rotational Excitations

For interactions under a force the transformation model is:

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

The correlation densities are:

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

Note that we have not included the transformation equations for the post-collision correlation variates because we do not use them in simulations. Although we have included the equation for the post-collision centre-of-mass energy we would normally work out the motion of the centre of mass from dynamical considerations. See Ref. 10.

For collisions without external forces this model becomes:

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

The correlation densities are:

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

The correlation densities are:

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

The correlation densities are:

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

The correlation densities are:

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]

The correlation densities are:

\[
G(s') = \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \beta(s'_0 | x_i, y_i, (1 - x_i) y_i) \beta(s'_1 | x_i, y_i, (1 - x_i) y_i) \]
Note that when no external force acts the centre of mass does not participate in the exchange.

We can obtain a simplified form of this model, called the simplified loosely-restricted exchange (SLRE) model, by averaging over the starting variates of the exchange process - i.e. the variates $s_T$ and $s_r$. This gives:

\[
\begin{align*}
\xi_G^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_G^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_G^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_G^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\end{align*}
\]  
(5a)

where:

\[
\begin{align*}
\xi_G^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_G^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_G^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_G^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\end{align*}
\]

The correlation densities are:

\[
G(s') = \beta(s'_1|\alpha_T\gamma_T, \alpha_r\gamma_T)\beta(s'_2|\gamma_T, \gamma_T)\beta(s'_3|\gamma_T, \gamma_T, \gamma_T)\beta(s'_4|\gamma_T, \gamma_T, \gamma_T, \gamma_T)
\]  
(5b)

This model satisfies energy conservation but does not satisfy reciprocity. However, it has two less Beta distributions to sample from and is thus faster.

For collisions without external forces this model becomes:

\[
\begin{align*}
\xi_{G1}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G2}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G3}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G4}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\end{align*}
\]  
(6a)

where:

\[
\xi_{G1}^* = (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G2}^* = (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G3}^* = (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G4}^* = (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\end{align*}
\]

The correlation densities are:

\[
G(s') = \beta(s'_1|\alpha_T\gamma_T, \alpha_r\gamma_T)\beta(s'_2|\gamma_T, \gamma_T)\beta(s'_3|\gamma_T, \gamma_T, \gamma_T)\beta(s'_4|\gamma_T, \gamma_T, \gamma_T, \gamma_T)
\]  
(6b)

Vibrational Excitations

For interactions under a force the transformation model is:

\[
\begin{align*}
\xi_{G1}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G2}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G3}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G4}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\end{align*}
\]  
(7a)

where:

\[
\begin{align*}
\xi_{G1}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G2}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G3}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G4}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\end{align*}
\]

The associated correlation densities are:

\[
G(s') = \beta(s'_1|\alpha_T\gamma_T, (1-\alpha_T)\gamma_T)\beta(s'_2|\gamma_T, \gamma_T)\beta(s'_3|\gamma_T, \gamma_T, \gamma_T)\beta(s'_4|\gamma_T, \gamma_T, \gamma_T, \gamma_T)
\times \beta(s'_1|\gamma_T, \gamma_T, \gamma_T)\beta(s'_2|\gamma_T, \gamma_T, \gamma_T, \gamma_T)\beta(s'_3|\gamma_T, \gamma_T, \gamma_T, \gamma_T)\beta(s'_4|\gamma_T, \gamma_T, \gamma_T, \gamma_T) 
\]  
(7b)

\[
G(s') = \beta(s'_1|\alpha_T\gamma_T, (1-\alpha_T)\gamma_T)\beta(s'_2|\gamma_T, \gamma_T)\beta(s'_3|\gamma_T, \gamma_T, \gamma_T)\beta(s'_4|\gamma_T, \gamma_T, \gamma_T, \gamma_T)
\times \beta(s'_1|\gamma_T, \gamma_T, \gamma_T)\beta(s'_2|\gamma_T, \gamma_T, \gamma_T, \gamma_T)\beta(s'_3|\gamma_T, \gamma_T, \gamma_T, \gamma_T)\beta(s'_4|\gamma_T, \gamma_T, \gamma_T, \gamma_T) 
\]  
(7c)

In the absence of external forces the model becomes:

\[
\begin{align*}
\xi_{G1}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G2}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G3}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G4}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\end{align*}
\]  
(8a)

where:

\[
\begin{align*}
\xi_{G1}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G2}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G3}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\xi_{G4}^* &= (1-s_T^*)\xi_{G1}^* + (1-s_r^*)\xi_{G2}^*, \\
\end{align*}
\]
The associated correlation densities are:

$$G(s') = \beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)$$

$$\times \beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)$$

$$\times \beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)$$

(8b)

The simplified loosely-restricted exchange (SLRE) model is obtained by averaging over the starting variates of the exchange process - i.e. $s_t, s_R$ and $s_y$. This gives:

$$G(s') = \beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)$$

(9a)

$$\times \beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)$$

The associated correlation densities are:

$$G(s') = \beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)\beta(s'|\alpha_y, y, (1-\alpha_y)T_y)$$

(9b)

In the absence of external forces the model becomes:

$$\xi_{11} = (1-s_1')\xi_7, \xi_10 = (1-s_1')\xi_7, \xi_13 = (1-s_1')\xi_7$$

(10a)

$$\xi_{12} = (1-s_1')\xi_7, \xi_12 = (1-s_1')\xi_7, \xi_13 = (1-s_1')\xi_7$$

The associated correlation densities are:

$$\xi_{11} = (1-s_1')\xi_7, \xi_10 = (1-s_1')\xi_7, \xi_13 = (1-s_1')\xi_7$$

(10b)

The Severely Restricted Exchange Models

**Rotational Excitations**

In this case the severely restricted exchange schemes are identical to the loosely restricted exchange schemes.

**Vibrational Excitations**

For interactions under a force the transformation model is:

$$\xi_{11} = (1-s_1')\xi_7, \xi_10 = (1-s_1')\xi_7, \xi_13 = (1-s_1')\xi_7$$

(11a)
The associated correlation densities are:

\[
G(s') = \beta(s'_1|\alpha_T, Y_T, \gamma_T, (1-\alpha_T))\gamma_T)\beta(s'_1|\alpha_T, Y_T, (1-\alpha_T)Y_T)\beta(s'_2|Y_T, \gamma_T)\beta(s'_3|2Y_T, \gamma_T)\beta(s'_4|3Y_T, \gamma_T)\beta(s'_5|Y_T, \gamma_T, \gamma_T)
\]

(11b)

\[
\times \beta(s'_6|Y_T, \gamma_T, \gamma_T)\beta(s'_5|Y_T, \gamma_T, \gamma_T)\beta(s'_4|Y_T, \gamma_T, \gamma_T)\beta(s'_3|Y_T, \gamma_T, \gamma_T)\beta(s'_2|Y_T, \gamma_T, \gamma_T)\beta(s'_1|Y_T, \gamma_T, \gamma_T)
\]

where \( \gamma_T = \gamma_G + \gamma_T \), \( \gamma_R = \gamma_R + \gamma_T \), \( \gamma_T = \gamma_T + \gamma_T \), \( \gamma = \gamma_T + \gamma_T + \gamma_T \), \( \gamma_T = \gamma_T + \gamma_T \).

In the absence of external forces the model becomes:

\[
\xi_{T'}^* = (1 - s'_1)^2 s_{T'}^*, \quad \xi_{T0}^* = (1 - s'_0)^2 s_{T0}^*, \quad \xi_{T1}^* = (1 - s'_0)^2 s_{T1}^*, \quad \xi_{T2}^* = (1 - s'_1)^2 s_{T2}^*, \quad \xi_{T3}^* = (1 - s'_1)^2 s_{T3}^*,
\]

(12a)

\[
\xi_{T0}^* = (1 - s'_0)^2 s_{T0}^*, \quad \xi_{T1}^* = (1 - s'_0)^2 s_{T1}^*, \quad \xi_{T2}^* = (1 - s'_0)^2 s_{T2}^*, \quad \xi_{T3}^* = (1 - s'_0)^2 s_{T3}^*,
\]

\[
\xi_{T0}^* = (1 - s'_0)^2 s_{T0}^*, \quad \xi_{T1}^* = (1 - s'_0)^2 s_{T1}^*, \quad \xi_{T2}^* = (1 - s'_0)^2 s_{T2}^*, \quad \xi_{T3}^* = (1 - s'_0)^2 s_{T3}^*,
\]

where : \( \xi_{T}^* = (1 - s'_0)^2 s_{T}^* \), \( \xi_{0}^* = (1 - s'_0)^2 s_{0}^* \), \( \xi_{1}^* = (1 - s'_0)^2 s_{1}^* \), \( \xi_{2}^* = (1 - s'_0)^2 s_{2}^* \), \( \xi_{3}^* = (1 - s'_0)^2 s_{3}^* \).

The associated correlation densities are:

\[
G(s') = \beta(s'_1|\alpha_T, Y_T, (1-\alpha_T))\gamma_T)\beta(s'_1|\alpha_T, Y_T, (1-\alpha_T)Y_T)\beta(s'_2|Y_T, \gamma_T)\beta(s'_3|2Y_T, \gamma_T)\beta(s'_4|3Y_T, \gamma_T)\beta(s'_5|Y_T, \gamma_T, \gamma_T)
\]

(12b)

\[
\times \beta(s'_6|Y_T, \gamma_T, \gamma_T)\beta(s'_5|Y_T, \gamma_T, \gamma_T)\beta(s'_4|Y_T, \gamma_T, \gamma_T)\beta(s'_3|Y_T, \gamma_T, \gamma_T)\beta(s'_2|Y_T, \gamma_T, \gamma_T)\beta(s'_1|Y_T, \gamma_T, \gamma_T)
\]

The simplified severely-restricted exchange (SSRE) model is obtained by averaging over the starting variates of the exchange process – i.e. \( s_T \) and \( s_T \). This gives:

\[
\xi_{T}^* = (1 - s'_0)^2 s_{T}^*, \quad \xi_{0}^* = (1 - s'_0)^2 s_{0}^*, \quad \xi_{1}^* = (1 - s'_0)^2 s_{1}^*, \quad \xi_{2}^* = (1 - s'_0)^2 s_{2}^*, \quad \xi_{3}^* = (1 - s'_0)^2 s_{3}^*,
\]

(13a)

\[
\xi_{T0}^* = (1 - s'_0)^2 s_{T0}^*, \quad \xi_{T1}^* = (1 - s'_0)^2 s_{T1}^*, \quad \xi_{T2}^* = (1 - s'_0)^2 s_{T2}^*, \quad \xi_{T3}^* = (1 - s'_0)^2 s_{T3}^*,
\]

\[
\xi_{T0}^* = (1 - s'_0)^2 s_{T0}^*, \quad \xi_{T1}^* = (1 - s'_0)^2 s_{T1}^*, \quad \xi_{T2}^* = (1 - s'_0)^2 s_{T2}^*, \quad \xi_{T3}^* = (1 - s'_0)^2 s_{T3}^*,
\]

where : \( \xi_{T}^* = (1 - s'_0)^2 s_{T}^* \), \( \xi_{0}^* = (1 - s'_0)^2 s_{0}^* \), \( \xi_{1}^* = (1 - s'_0)^2 s_{1}^* \), \( \xi_{2}^* = (1 - s'_0)^2 s_{2}^* \), \( \xi_{3}^* = (1 - s'_0)^2 s_{3}^* \).

The associated correlation densities are:

\[
G(s') = \beta(s'_1|\alpha_T, Y_T, (1-\alpha_T))\gamma_T)\beta(s'_1|\alpha_T, Y_T, (1-\alpha_T)Y_T)\beta(s'_2|Y_T, \gamma_T)\beta(s'_3|2Y_T, \gamma_T)\beta(s'_4|3Y_T, \gamma_T)\beta(s'_5|Y_T, \gamma_T, \gamma_T)
\]

(13b)

\[
\times \beta(s'_6|Y_T, \gamma_T, \gamma_T)\beta(s'_5|Y_T, \gamma_T, \gamma_T)\beta(s'_4|Y_T, \gamma_T, \gamma_T)\beta(s'_3|Y_T, \gamma_T, \gamma_T)\beta(s'_2|Y_T, \gamma_T, \gamma_T)\beta(s'_1|Y_T, \gamma_T, \gamma_T)
\]

In the absence of external forces the model becomes:

\[
\xi_{T}^* = (1 - s'_0)^2 s_{T}^*, \quad \xi_{0}^* = (1 - s'_0)^2 s_{0}^*, \quad \xi_{1}^* = (1 - s'_0)^2 s_{1}^*, \quad \xi_{2}^* = (1 - s'_0)^2 s_{2}^*, \quad \xi_{3}^* = (1 - s'_0)^2 s_{3}^*,
\]

(14a)

\[
\xi_{T0}^* = (1 - s'_0)^2 s_{T0}^*, \quad \xi_{T1}^* = (1 - s'_0)^2 s_{T1}^*, \quad \xi_{T2}^* = (1 - s'_0)^2 s_{T2}^*, \quad \xi_{T3}^* = (1 - s'_0)^2 s_{T3}^*,
\]

\[
\xi_{T0}^* = (1 - s'_0)^2 s_{T0}^*, \quad \xi_{T1}^* = (1 - s'_0)^2 s_{T1}^*, \quad \xi_{T2}^* = (1 - s'_0)^2 s_{T2}^*, \quad \xi_{T3}^* = (1 - s'_0)^2 s_{T3}^*,
\]

where : \( \xi_{T}^* = (1 - s'_0)^2 s_{T}^* \), \( \xi_{0}^* = (1 - s'_0)^2 s_{0}^* \), \( \xi_{1}^* = (1 - s'_0)^2 s_{1}^* \), \( \xi_{2}^* = (1 - s'_0)^2 s_{2}^* \), \( \xi_{3}^* = (1 - s'_0)^2 s_{3}^* \).

The associated correlation densities are:

\[
G(s') = \beta(s'_1|\alpha_T, Y_T, (1-\alpha_T))\gamma_T)\beta(s'_1|\alpha_T, Y_T, (1-\alpha_T)Y_T)\beta(s'_2|Y_T, \gamma_T)\beta(s'_3|2Y_T, \gamma_T)\beta(s'_4|3Y_T, \gamma_T)\beta(s'_5|Y_T, \gamma_T, \gamma_T)
\]

(14b)

\[
\times \beta(s'_6|Y_T, \gamma_T, \gamma_T)\beta(s'_5|Y_T, \gamma_T, \gamma_T)\beta(s'_4|Y_T, \gamma_T, \gamma_T)\beta(s'_3|Y_T, \gamma_T, \gamma_T)\beta(s'_2|Y_T, \gamma_T, \gamma_T)\beta(s'_1|Y_T, \gamma_T, \gamma_T)
\]
IV. MODEL PARAMETER DETERMINATION

For rotationally excited collisions the rotational parameter is determined by matching rotational relaxation data, whereas the translational parameter is simply set to unity (full excitation of the translational mode). For vibrationally excited collisions the vibrational parameter is determined by matching vibrational relaxation data, whereas the translational and rotational parameters are set to unity (full excitation of both the rotational and the translational modes). These relaxation rates can be measured experimentally for different temperatures and used to determine a functional form for the model parameters. This is an area for further work. When the lower level parameters are set to unity the model transformations simplify somewhat. Below I have written down these simplified forms by including only the transformation equations that are affected. The equations that are left intact remain as before and are not shown. The simplified forms of the Beta distribution set are shown complete. The number of Beta distributions is reduced by as many as 8 per model.

**Rotationally excited, free exchange, with external forces:**

\[ \xi_0^* = (1 - s_1^r) (1 - s_0^a) \xi_{0a}, \quad \xi_1^* = (1 - s_1^t) s_1^r (1 - s_0^a) \xi_{0a}, \quad \xi_2^* = s_1^t s_1^r (1 - s_0^a) \xi_{0a}, \quad \xi_3^* = (1 - s_1^t) s_1^t s_1^r (1 - s_0^a) \xi_{0a} \]

where \( \xi_{0a} = \xi_{0a} + \xi_{1a} + \xi_{2a} + \xi_{3a} + s_0^a \xi_{0a} + s_1^a \xi_{1a} + s_2^a \xi_{2a} + s_3^a \xi_{3a} \)

with associated correlation densities:

\[ G(s) = \beta(s_0^a | \alpha, \gamma, \sigma_0, \alpha_0 Y_0) \beta(s_1^r | \alpha, \gamma, \sigma_1 Y_1, (1 - \alpha_0) Y_0) \beta(s_2^r | \alpha, \gamma, \sigma_2 Y_2, (1 - \alpha_0) Y_0) \beta(s_3^r | \alpha, \gamma, \sigma_3 Y_3, (1 - \alpha_0) Y_0) \]

\[ \times \beta(s_1^t | 2 \gamma, \gamma_1) \beta(s_2^t | \gamma, \gamma_1, \gamma_2) \beta(s_3^t | \alpha, \gamma, \gamma_2, \alpha_3 Y_3) \beta(s_4^t | \alpha, \gamma, \gamma_2, \alpha_3 Y_3, \gamma_1 + \alpha_3 Y_3) \]

\[ \times \beta(s_0^* | \alpha, \gamma, \gamma_0 + \alpha, \gamma, \gamma_2 + \alpha, \gamma, \gamma_3, \alpha Y_3) \beta(s_1^* | \alpha, \gamma, \gamma_0 + \alpha, \gamma, \gamma_2 + \alpha, \gamma, \gamma_3, \alpha_0 Y_0) \]

**Rotationally excited, free exchange, without external forces:**

\[ \xi_0^* = (1 - s_1^r) (1 - s_0^a) \xi_{0a}, \quad \xi_1^* = (1 - s_1^t) s_1^r (1 - s_0^a) \xi_{0a}, \quad \xi_2^* = s_1^t s_1^r (1 - s_0^a) \xi_{0a}, \quad \xi_3^* = (1 - s_1^t) s_1^t s_1^r (1 - s_0^a) \xi_{0a} \]

where \( \xi_{0a} = \xi_{0a} + \xi_{1a} + \xi_{2a} + \xi_{3a} + s_0^a \xi_{0a} + s_1^a \xi_{1a} + s_2^a \xi_{2a} + s_3^a \xi_{3a} \)

with associated correlation densities:

\[ G(s) = \beta(s_0^a | \alpha, \gamma, \sigma_0, \alpha_0 Y_0) \beta(s_1^r | \alpha, \gamma, \sigma_1 Y_1, (1 - \alpha_0) Y_0) \beta(s_2^r | \alpha, \gamma, \sigma_2 Y_2, (1 - \alpha_0) Y_0) \beta(s_3^r | \alpha, \gamma, \sigma_3 Y_3, (1 - \alpha_0) Y_0) \]

\[ \times \beta(s_1^t | 2 \gamma, \gamma_1) \beta(s_2^t | \gamma, \gamma_1, \gamma_2) \beta(s_3^t | \alpha, \gamma, \gamma_2, \alpha_3 Y_3) \beta(s_4^t | \alpha, \gamma, \gamma_2, \alpha_3 Y_3, \gamma_1 + \alpha_3 Y_3) \]

\[ \times \beta(s_0^* | \alpha, \gamma, \gamma_0 + \alpha, \gamma, \gamma_2 + \alpha, \gamma, \gamma_3, \alpha Y_3) \beta(s_1^* | \alpha, \gamma, \gamma_0 + \alpha, \gamma, \gamma_2 + \alpha, \gamma, \gamma_3, \alpha_0 Y_0) \]

**Vibrationally excited, free exchange, with external forces:**

\[ \xi_0^* = (1 - s_1^r) (1 - s_0^a) \xi_{0a}, \quad \xi_1^* = (1 - s_1^t) s_1^r (1 - s_0^a) \xi_{0a}, \quad \xi_2^* = s_1^t s_1^r (1 - s_0^a) \xi_{0a}, \quad \xi_3^* = (1 - s_1^t) s_1^t s_1^r (1 - s_0^a) \xi_{0a} \]

\[ \xi_0^* = (1 - s_0^a) s_0^a s_0^a \xi_{0a}, \quad \xi_1^* = (1 - s_0^a) s_0^a s_0^a \xi_{0a}, \quad \xi_2^* = s_0^a s_0^a s_0^a \xi_{0a}, \quad \xi_3^* = (1 - s_0^a) s_0^a s_0^a \xi_{0a} \]

where \( \xi_{0a} = \xi_{0a} + \xi_{1a} + \xi_{2a} + \xi_{3a} + s_0^a \xi_{0a} + s_1^a \xi_{1a} + s_2^a \xi_{2a} + s_3^a \xi_{3a} \)

with associated correlation densities:

\[ G(s) = \beta(s_0^a | \alpha, \gamma, \sigma_0, \alpha_0 Y_0) \beta(s_1^r | \alpha, \gamma, \sigma_1 Y_1, (1 - \alpha_0) Y_0) \beta(s_2^r | \alpha, \gamma, \sigma_2 Y_2, (1 - \alpha_0) Y_0) \beta(s_3^r | \alpha, \gamma, \sigma_3 Y_3, (1 - \alpha_0) Y_0) \]

\[ \times \beta(s_1^t | 2 \gamma, \gamma_1) \beta(s_2^t | \gamma, \gamma_1, \gamma_2) \beta(s_3^t | \alpha, \gamma, \gamma_2, \alpha_3 Y_3) \beta(s_4^t | \alpha, \gamma, \gamma_2, \alpha_3 Y_3, \gamma_1 + \alpha_3 Y_3) \]

\[ \times \beta(s_0^* | \alpha, \gamma, \gamma_0 + \alpha, \gamma, \gamma_2 + \alpha, \gamma, \gamma_3, \alpha Y_3) \beta(s_1^* | \alpha, \gamma, \gamma_0 + \alpha, \gamma, \gamma_2 + \alpha, \gamma, \gamma_3, \alpha_0 Y_0) \]

\[ \times \beta(s_0^* | \alpha, \gamma, \gamma_0 + \alpha, \gamma, \gamma_2 + \alpha, \gamma, \gamma_3, \alpha Y_3) \beta(s_1^* | \alpha, \gamma, \gamma_0 + \alpha, \gamma, \gamma_2 + \alpha, \gamma, \gamma_3, \alpha_0 Y_0) \]
Vibrationally excited, free exchange, without external forces:

\[ \xi^*_{\text{f}} = (1 - s'_{\text{f}}) s'_{\text{f}} \xi_a, \quad \xi^*_{\text{r}} = s'_{\text{r}} s'_{\text{f}} (1 - s_a) \xi_a, \quad \xi^*_{\text{r}} = (1 - s'_{\text{f}}) s'_{\text{r}} \xi_a, \quad \xi^*_{\text{R}} = (1 - s'_{\text{R}}) s'_{\text{f}} \xi_a \]

\[ \xi^*_{\text{f}} = (1 - s'_{\text{f}}) s'_{\text{f}} \xi_a, \quad \xi^*_{\text{r}} = s'_{\text{r}} s'_{\text{f}} (1 - s_a) \xi_a, \quad \xi^*_{\text{r}} = (1 - s'_{\text{f}}) s'_{\text{r}} \xi_a, \quad \xi^*_{\text{R}} = (1 - s'_{\text{R}}) s'_{\text{f}} \xi_a \]

where \( \xi_a = \xi^*_{\text{f}} + \xi^*_{\text{r}} + \xi^*_{\text{r}} + \xi^*_{\text{R}} + \xi^*_{\text{s}'} + \xi^*_{\text{s}'} + \xi^*_{\text{s}'} \)

with associated correlation densities:

\[
G(s) = \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \\
\times \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}}) \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}})
\]

Rotationally excited, loosely restricted exchange, with external forces:

\[ \xi^*_{\text{f}} = (1 - s'_{\text{f}}) s'_{\text{f}} \xi_a, \quad \xi^*_{\text{r}} = \xi^*_{\text{r}} + s'_{\text{r}} \xi^*_{\text{r}} \]

The correlation densities are:

\[
G(s) = \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \\
\times \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}}) \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}})
\]

Rotationally excited, loosely restricted exchange, without external forces:

The modifications are the same as for loosely restricted exchange. The correlation densities are now:

\[
G(s) = \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \\
\times \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}}) \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}})
\]

Rotationally excited, simplified loosely restricted exchange, with external forces:

The modifications are the same as for loosely restricted exchange. The correlation densities are now:

\[
G(s) = \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \\
\times \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}}) \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}})
\]

Rotationally excited, simplified loosely restricted exchange, without external forces:

The modifications are the same as for loosely restricted exchange. The correlation densities are now:

\[
G(s) = \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \\
\times \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}}) \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}})
\]

Vibrationally excited, loosely restricted exchange, with external forces:

\[ \xi^*_{\text{f}} = (1 - s'_{\text{f}}) s'_{\text{f}} \xi_a, \quad \xi^*_{\text{r}} = (1 - s'_{\text{f}}) s'_{\text{f}} \xi_a \]

The associated correlation densities are:

\[
G(s) = \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \beta(s'_{\text{f}} | \alpha_{\text{f}}, \gamma_{\text{f}}, (1 - \alpha_{\text{f}}) \gamma_{\text{f}}) \beta(s'_{\text{r}} | \alpha_{\text{r}}, \gamma_{\text{r}}, (1 - \alpha_{\text{r}}) \gamma_{\text{r}}) \\
\times \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}}) \beta(s'_{\text{f}} | \gamma_{\text{f}}, \gamma_{\text{f}}) \beta(s'_{\text{r}} | \gamma_{\text{r}}, \gamma_{\text{r}})
\]
**Vibrationally excited, loosely restricted exchange, without external forces:**

The modifications are the same as for loosely restricted exchange. The correlation densities are now:

\[
G(s') = \beta(s'|\alpha_y, \gamma_Y) (1-\alpha_Y) \gamma_Y \beta(s'_1|Y_1, \gamma_1) \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_1 + \gamma_2 + \gamma_3, \gamma_{r,0}) \times \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_3|\alpha_Y, \gamma_Y + \gamma_R, \gamma_T)
\]

**Vibrationally excited, simplified loosely restricted exchange, with external forces:**

The modifications are the same as for loosely restricted exchange. The correlation densities are now:

\[
G(s') = \beta(s'_1|Y_1, \gamma_1) \beta(s'_2|Y_2, \gamma_2) \beta(s'_3|Y_3, \gamma_3) \beta(s'_1|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_2|Y_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|\alpha_Y, \gamma_Y + \gamma_R, \gamma_T)
\]

**Vibrationally excited, simplified loosely restricted exchange, without external forces:**

The modifications are the same as for loosely restricted exchange. The correlation densities are now:

\[
G(s') = \beta(s'_1|\alpha_y, \gamma_Y) (1-\alpha_Y) \gamma_Y \beta(s'_1|Y_1, \gamma_1) \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_1 + \gamma_2 + \gamma_3, \gamma_{r,0}) \times \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_3|\alpha_Y, \gamma_Y + \gamma_R, \gamma_T)
\]

**Vibrationally excited, severely restricted exchange, with external forces:**

The modifications are the same as for severely restricted exchange. The correlation densities are:

\[
G(s') = \beta(s'_1|\alpha_y, \gamma_Y) (1-\alpha_Y) \gamma_Y \beta(s'_1|Y_1, \gamma_1) \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_1 + \gamma_2 + \gamma_3, \gamma_{r,0}) \times \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_3|\alpha_Y, \gamma_Y + \gamma_R, \gamma_T)
\]

**Vibrationally excited, severely restricted exchange, without external forces:**

The modifications are the same as for severely restricted exchange. The correlation densities are:

\[
G(s') = \beta(s'_1|\alpha_y, \gamma_Y) (1-\alpha_Y) \gamma_Y \beta(s'_1|Y_1, \gamma_1) \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_1 + \gamma_2 + \gamma_3, \gamma_{r,0}) \times \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_3|\alpha_Y, \gamma_Y + \gamma_R, \gamma_T)
\]

**Vibrationally excited, simplified severely restricted exchange, with external forces:**

The modifications are the same as for severely restricted exchange. The correlation densities are now:

\[
G(s') = \beta(s'_1|\alpha_y, \gamma_Y) (1-\alpha_Y) \gamma_Y \beta(s'_1|Y_1, \gamma_1) \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_1 + \gamma_2 + \gamma_3, \gamma_{r,0}) \times \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_3|\alpha_Y, \gamma_Y + \gamma_R, \gamma_T)
\]

**Vibrationally excited, simplified severely restricted exchange, without external forces:**

The modifications are the same as for severely restricted exchange. The correlation densities are now:

\[
G(s') = \beta(s'_1|\alpha_y, \gamma_Y) (1-\alpha_Y) \gamma_Y \beta(s'_1|Y_1, \gamma_1) \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_1 + \gamma_2 + \gamma_3, \gamma_{r,0}) \times \beta(s'_2|Y_2, \gamma_2 + \gamma_3, \gamma_{r,0}) \beta(s'_3|Y_3, \gamma_3, \gamma_{r,0}) \beta(s'_3|\alpha_Y, \gamma_Y + \gamma_R, \gamma_T)
\]
The modifications are the same as for severely restricted exchange. The correlation densities are now:

\[ G(s') = \beta(s'_0|\gamma'_1, \gamma'_1) \beta(s'_2|\gamma'_2, \gamma'_3) \beta(s'_{12}|\gamma'_2 + \gamma'_3, \gamma'_1) \beta(s'_{13}|\gamma'_1 + \gamma'_2 + \gamma'_3, \gamma'_1) \]

\[ \times \beta(s'_{10}|\gamma'_2, \gamma'_3) \beta(s'_{23}|\gamma'_2 + \gamma'_3, \gamma'_1) \beta(s'_{31}|\gamma'_1 + \gamma'_2 + \gamma'_3, \gamma'_0) \beta(s'_{23}|\gamma'_2, \gamma'_3) \beta(s'_{31}|\gamma'_1, \gamma'_3) \]

V. NUMERICAL SIMULATIONS

To perform a calculation for a given pre-collision molecule we sample the required correlation variates from the correlation densities. Then we substitute these into the model equations along with the pre-collision state. Evaluating the RHS of the equations gives the post-collision energy. Phillips and Beightler (Ref. 11) have described beta distribution sampling which is required to evaluate the model equations for each collision.

VI. CONCLUSION

In this paper I have presented a variety of models of rotational and vibrational four body collisions to meet a variety of gas dynamic needs. These models provide varying degrees of sophistication, accuracy, and efficiency, ranging from the free exchange model to the severely restricted exchange model. The choice of model depends of course on the requirements of the application as well as on practical constraints such as the available computer technology.

VII. REFERENCES