Reciprocity Theory of Vibrationally Excited Many-Body Collisions

A A Agbormbai

Department of Aeronautics
Imperial College of Science, Technology and Medicine
Prince Consort Road
London SW7 2BY, UK, England

Abstract. Even though rarefied gas dynamics has been founded on the dilute gas assumption, which supposes that the densities are so low that only binary collisions and single-body gas surface interactions occur, 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. In this paper I apply reciprocity theory to the problem of vibrationally excited many-body collisions. I illustrate the general approach by constructing models for three-body collisions, but the same methods may be applied to any number of interacting bodies. I formulate the reciprocity equation for three-body collisions and then I generalise it to any number of colliding bodies. However, the final transformation model cannot be readily generalised in this manner but must be formulated for each case from the reciprocity equation. I construct models both for rotation-only excitations and for combined rotational and vibrational excitations assuming a classical representation of these modes. The development follows a standard approach illustrated in earlier works (which discuss binary collisions and single-body gas surface interactions). I split the problem into a scattering component, which is formulated as in monatomic collisions, and an energy exchange component which emphasises the internal-translational exchange. Nevertheless, I introduce a correlation between the scattering dynamics and the energy exchange process using an inverse power law. This adds refinement to the energy exchange modelling. Then, focusing on the energy exchange, I formulate three types of models: free exchange, restricted exchange, and simplified restricted exchange. These models are developed for Direct Simulation Monte Carlo (DSMC) computations. The DSMC method is the standard computational technique in rarefied gas dynamics.

I. INTRODUCTION

Collision rate expressions for many body interactions show that the frequency of an \(N\)-body collision increases with the \(N\)th 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 atmosphere the importance of high order collisions increases significantly, so much that in the transition regime between rarefied and continuum flow four-body collisions will become significant (Figure 1, Ref. 1). This means that Direct Simulation Monte Carlo (DSMC) simulations must have the capability to handle three and four body collisions. In this paper I formulate reciprocity models of vibrationally excited many body collisions (with emphasis on three bodies) for use in DSMC computations. I use the partial equilibration approach of Pullin (Ref. 2) and Agbormbai (Ref. 3). This approach models the partial exchange of energy in each collision and the partial establishment of equilibrium by each collision. The models are formulated from a reciprocity equation for many body collisions.

The reciprocity approach has long been recognised as the proper direction for modelling complex interactions in rarefied gas dynamics. Proponents of the approach include Fowler (Ref. 4), Cercignani (Refs. 5 and 6), Pullin (Ref. 2), Agbormbai (Refs. 3 and 7) and Lord (Refs. 8 and 9). These workers have applied reciprocity ideas to modelling gas surface interactions and binary collisions in rarefied gas dynamics. In this paper I consider the collision involving three or more polyatomic gas molecules with internally 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 can suitably model 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.

II. VIBRATIONALLY EXCITED MANY-BODY RECIPROCITY EQUATION

Pullin (Ref. 2) derived a reciprocity equation for rotationally excited binary collisions as:

$$\text{Ga} \left( \xi_{r1} | \gamma_{r1} \right) \text{Ga} \left( \xi_{r2} | \gamma_{r2} \right) G(s') ds' d\xi_{r1} dE_{r1} = \text{Ga} \left( \xi_{r1} | \gamma_{r1} \right) \text{Ga} \left( \xi_{r2} | \gamma_{r2} \right) G(s) ds d\xi_{r2} dE_{r2}$$

where $E_{r1} = (\xi_{r1}, \xi_{r2}), s$ are the correlation variates, $G$ are the correlation densities,

$$\gamma_{m} = \frac{\nu_{m}}{2}, \quad \xi_{r} = \frac{E_{r}}{kT_{m}}, \quad \xi'_{r} = \frac{E'_{r}}{kT'_{m}}, \quad E$$ is the energy, $T_{m}$ is the modal temperature

$$\text{Ga} \left( x | \mu \right) = \frac{1}{\Gamma(\mu)} x^{\mu-1} e^{-x}, \quad (\mu > 0, \quad 0 \leq x \leq \infty)$$ is the Gamma distribution for $x$ with parameter $\mu, \Gamma(\mu)$ is the gamma function. The subscripts are as follows:

$t$ 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, 6 for the solid, 2 or 3 for rotational and 2 or more for vibrational). Single and double primes indicate incident and reflected states.

This equation applies for motion without external forces. In the presence of external forces the centre of mass accelerates through the collision, so that an extra term appears in the reciprocity equation corresponding to the centre of mass motion. We can generalise this equation into vibrational excitations as follows:

$$\text{Ga} \left( \xi_{v1} | \gamma_{v1} \right) \text{Ga} \left( \xi_{v2} | \gamma_{v2} \right) \text{Ga} \left( \xi_{v1} | \gamma_{v1} \right) \text{Ga} \left( \xi_{v2} | \gamma_{v2} \right) G(s) ds d\xi_{v1} dE_{v1}$$

$$= \text{Ga} \left( \xi_{v1} | \gamma_{v1} \right) \text{Ga} \left( \xi_{v2} | \gamma_{v2} \right) \text{Ga} \left( \xi_{v1} | \gamma_{v1} \right) \text{Ga} \left( \xi_{v2} | \gamma_{v2} \right) G(s') ds' d\xi_{v2} dE_{v2}$$

where $E_{v} = (\xi_{v1}, \xi_{v2}, \xi_{v1}, \xi_{v2})$.

This equation also applies for motion without external forces. For $N$ interacting bodies the reciprocity equation becomes:

$$\text{Ga} \left( \xi_{G} | \gamma_{G} \right) \left( \prod_{j=1}^{N-1} \text{Ga} \left( \xi_{vj} | \gamma_{vj} \right) \right) \left( \prod_{k=0}^{N-1} \text{Ga} \left( \xi_{rk} | \gamma_{rk} \right) \text{Ga} \left( \xi_{rk} | \gamma_{rk} \right) \right) G(s) ds' d\xi_{E} dE'_{E}$$

$$= \text{Ga} \left( \xi_{G} | \gamma_{G} \right) \left( \prod_{j=1}^{N} \text{Ga} \left( \xi_{vj} | \gamma_{vj} \right) \right) \left( \prod_{k=0}^{N-1} \text{Ga} \left( \xi_{rk} | \gamma_{rk} \right) \text{Ga} \left( \xi_{rk} | \gamma_{rk} \right) \right) G(s') ds' d\xi_{E} dE'_{E}$$

where $\xi_{G} = (\xi_{r1}, \xi_{r2}, \ldots, \xi_{rN-1}), \xi_{r} = (\xi_{r0}, \xi_{r2}, \ldots, \xi_{rN-1}), \xi_{v} = (\xi_{v0}, \xi_{v2}, \ldots, \xi_{vN-1}), E_{v} = (\xi_{v1}, \xi_{v2})$. The subscripts are as follows:

$G$ for centre of mass, $t$ for translational, $r$ for rotational, $v$ for vibrational.
We have included a centre of mass term in this equation to account for the presence of external forces. Note that this equation assumes a many body interaction to consist of the interaction of a number of reduced particles whose total translational kinetic energy is a sum of squared terms.

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 (distributed) 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. 2) and Agbormbai (Ref. 3) 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:

(transl1 + transl2; \(s_T1\) ) \(\Rightarrow\) 2transl, (2transl + CM; \(s_T2\) ) \(\Rightarrow\) 3transl

(rot1 + rot2; \(s_R1\) ) \(\Rightarrow\) 2rot, (2rot + rot0; \(s_R2\) ) \(\Rightarrow\) 3rot

(3rot + 3transl; \(s_a\) ) \(\Rightarrow\) total

where CM denotes the centre of mass energy

The model is then:

\[
\begin{align*}
\xi_{G1}^* &= (1 - s'_r) \xi_{G1}^* + (1 - s'_r)(1 - s'_a) \xi_{a1}^* , \quad \xi_{G1}^* = (1 - s'_r) \xi_{G1}^* + s'_r s'_a \xi_{a1}^* , \quad \xi_{G2}^* = (1 - s'_r) \xi_{G2}^* + (1 - s'_r) \xi_{a2}^* \\
\xi_{R0}^* &= (1 - s'_r) \xi_{R0}^* + (1 - s'_r) \xi_{a2}^* , \quad \xi_{R0}^* = (1 - s'_r) \xi_{R0}^* + s'_r \xi_{a2}^* \\
\xi_{R2}^* &= (1 - s'_r) \xi_{R2}^* + (1 - s'_r) \xi_{a2}^* \\
\end{align*}
\]

where \(\xi_a = s'_R \xi_{G1}^* + s'_R \xi_{R0}^* + s'_R \xi_{R2}^* + s'_R \xi_{a2}^* \) is the total active energy

with associated correlation densities:

\[
G(s') = \beta(s'_G|\alpha, \gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma) \times \beta(s'_G|\alpha, \gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma) \\
\times \beta(s'_R|\alpha, \gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma) \\
\times \beta(s'_R|\alpha, \gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma, (1-\alpha)\gamma)
\]

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.

For collisions without external forces this model becomes:

\[
\begin{align*}
\xi_{G1}^* &= (1 - s'_r) \xi_{G1}^* + s'_r \xi_{a1}^* \\
\xi_{R0}^* &= (1 - s'_r) \xi_{R0}^* + (1 - s'_r) \xi_{a2}^* \\
\xi_{R2}^* &= (1 - s'_r) \xi_{R2}^* + (1 - s'_r) \xi_{a2}^* \\
\end{align*}
\]

where \(\xi_a = s'_R \xi_{G1}^* + s'_R \xi_{R0}^* + s'_R \xi_{R2}^* + s'_R \xi_{a2}^* \) is the total active energy
with correlation densities:

\[ G(s') = \beta(s'_0|\alpha,\gamma_1,(1-\alpha_1)\gamma_1)\beta(s'_2|\alpha,\gamma_1,(1-\alpha_1)\gamma_1)\beta(s'_0|\alpha,\gamma_0,(1-\alpha_1)\gamma_0)\beta(s'_1|\alpha,\gamma_1,1-(1-\alpha_1)\gamma_1)\beta(s'_2|\alpha,\gamma_2,1-(1-\alpha_1)\gamma_1) \]
\[ \times \beta(s'_1|\alpha,\gamma_1,\gamma_2)\beta(s'_0|\alpha,\gamma_1,\gamma_2,1-\alpha_2)\beta(s'_0,\alpha,\gamma_0,\gamma_1,\gamma_2,1-\alpha_2) \]

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 strategy:

(\text{transl} + \text{transl}; s_{\eta_1}) \Rightarrow 2\text{transl}, \quad (2\text{transl} + \text{CM}; s_{\gamma}) \Rightarrow 3\text{transl}

(\text{rot} + \text{rot}; s_{\eta_1}) \Rightarrow 2\text{rot}, \quad (2\text{rot} + \text{rot}; s_{\eta_1}) \Rightarrow 3\text{rot}

(\text{vib} + \text{vib}; s_{\eta_1}) \Rightarrow 2\text{vib}, \quad (2\text{vib} + \text{vib}; s_{\eta_1}) \Rightarrow 3\text{vib}

(3\text{rot} + 3\text{vib}; s_{\eta_1}) \Rightarrow \text{int}, \quad (\text{int} + 3\text{transl}; s_{\eta_1}) \Rightarrow \text{total}

The model is:

\[ \xi_{\eta_1}^r = (1-s_{\eta_0})\xi_{\eta_1}^r + (1-s'_{\eta_0})(1-s_{\eta_0})\xi_{\eta_2}^r, \quad \xi_{\eta_1}^t = (1-s_{\eta_1})\xi_{\eta_1}^t + s_{\eta_1}(1-s_{\eta_0})\xi_{\eta_2}^t, \quad \xi_{\eta_2}^t = (1-s_{\eta_2})\xi_{\eta_2}^t + (1-s'_{\eta_1})s_{\eta_1}\xi_{\eta_2}^t \]

\[ \xi_{\eta_0} = (1-s_{\eta_0})\xi_{\eta_0} + (1-s'_{\eta_0})(1-s_{\eta_0})\xi_{\eta_2}^r, \quad \xi_{\eta_1} = (1-s_{\eta_1})\xi_{\eta_1} + s_{\eta_1}(1-s_{\eta_0})\xi_{\eta_2}^r, \quad \xi_{\eta_2} = (1-s_{\eta_2})\xi_{\eta_2} + (1-s'_{\eta_1})s_{\eta_1}\xi_{\eta_2}^r \]

where \( \xi_{\eta_i}^r \) and \( \xi_{\eta_i}^t \) are the total active energy with associated correlation densities:

\[ G(s') = \beta(s'_0|\alpha,\gamma_1,(1-\alpha_1)\gamma_1)\beta(s'_2|\alpha,\gamma_1,(1-\alpha_1)\gamma_1)\beta(s'_0|\alpha,\gamma_0,(1-\alpha_1)\gamma_0)\beta(s'_1|\alpha,\gamma_1,1-(1-\alpha_1)\gamma_1) \]
\[ \times \beta(s'_1|\alpha,\gamma_1,\gamma_2)\beta(s'_0|\alpha,\gamma_1,\gamma_2,1-\alpha_2)\beta(s'_0,\alpha,\gamma_0,\gamma_1,\gamma_2,1-\alpha_2) \]

In the absence of external forces this model becomes:

\[ \xi_{\eta_1}^r = (1-s_{\eta_0})\xi_{\eta_1}^r + (1-s'_{\eta_0})(1-s_{\eta_0})\xi_{\eta_2}^r, \quad \xi_{\eta_1}^t = (1-s_{\eta_1})\xi_{\eta_1}^t + s_{\eta_1}(1-s_{\eta_0})\xi_{\eta_2}^t, \quad \xi_{\eta_2}^t = (1-s_{\eta_2})\xi_{\eta_2}^t + (1-s'_{\eta_1})s_{\eta_1}\xi_{\eta_2}^t \]

\[ \xi_{\eta_0} = (1-s_{\eta_0})\xi_{\eta_0} + (1-s'_{\eta_0})(1-s_{\eta_0})\xi_{\eta_2}^r, \quad \xi_{\eta_1} = (1-s_{\eta_1})\xi_{\eta_1} + s_{\eta_1}(1-s_{\eta_0})\xi_{\eta_2}^r, \quad \xi_{\eta_2} = (1-s_{\eta_2})\xi_{\eta_2} + (1-s'_{\eta_1})s_{\eta_1}\xi_{\eta_2}^r \]

where \( \xi_{\eta_i}^r \) and \( \xi_{\eta_i}^t \) are the total active energy with associated correlation densities:

\[ G(s') = \beta(s'_0|\alpha,\gamma_1,(1-\alpha_1)\gamma_1)\beta(s'_2|\alpha,\gamma_1,(1-\alpha_1)\gamma_1)\beta(s'_0|\alpha,\gamma_0,(1-\alpha_1)\gamma_0)\beta(s'_1|\alpha,\gamma_1,1-(1-\alpha_1)\gamma_1) \]
\[ \times \beta(s'_1|\alpha,\gamma_1,\gamma_2)\beta(s'_0|\alpha,\gamma_1,\gamma_2,1-\alpha_2)\beta(s'_0,\alpha,\gamma_0,\gamma_1,\gamma_2,1-\alpha_2) \]
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**

Proceeding as for the free exchange models we get:

\[
\begin{align*}
\xi_0' &= (1 - s')\xi_0', \\
\xi_1' &= s_1'\xi_1', \\
\xi_2' &= (1 - s_1')\xi_2'; \\
\xi_0 &= (1 - s')\xi_0, \\
\xi_1 &= s_1\xi_1, \\
\xi_2 &= (1 - s_1)\xi_2
\end{align*}
\]

with correlation densities:

\[
G(s') = \beta(s' | \alpha, \gamma_T, (1 - \alpha_T) \gamma_T) \beta(s' | \gamma_T, (1 - \alpha_T) \gamma_T) \beta(s' | \gamma_T, \gamma_G) \beta(s' | \gamma_T, \gamma_G) \beta(s' | \gamma_T, \gamma_G)
\]

where:

\[
\begin{align*}
\xi_0' &= (1 - s')\xi_0', \\
\xi_1' &= s_1'\xi_1', \\
\xi_2' &= (1 - s_1')\xi_2'; \\
\xi_0 &= (1 - s')\xi_0, \\
\xi_1 &= s_1\xi_1, \\
\xi_2 &= (1 - s_1)\xi_2
\end{align*}
\]

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

For collisions without external forces the restricted exchange model becomes:

\[
\begin{align*}
\xi_0' &= (1 - s')\xi_0', \\
\xi_1' &= s_1'\xi_1', \\
\xi_2' &= (1 - s_1')\xi_2'; \\
\xi_0 &= (1 - s')\xi_0, \\
\xi_1 &= s_1\xi_1, \\
\xi_2 &= (1 - s_1)\xi_2
\end{align*}
\]

The correlation densities are:

\[
G(s') = \beta(s' | \gamma_T, (1 - \alpha_T) \gamma_T) \beta(s' | \gamma_T, (1 - \alpha_T) \gamma_T) \beta(s' | \gamma_T, \gamma_G) \beta(s' | \gamma_T, \gamma_G) \beta(s' | \gamma_T, \gamma_G)
\]

The simplified restricted exchange model is now:

\[
\begin{align*}
\xi_0' &= (1 - s')\xi_0', \\
\xi_1' &= s_1'\xi_1', \\
\xi_2' &= (1 - s_1')\xi_2'; \\
\xi_0 &= (1 - s')\xi_0, \\
\xi_1 &= s_1\xi_1, \\
\xi_2 &= (1 - s_1)\xi_2
\end{align*}
\]

with correlation densities:

\[
G(s') = \beta(s' | \gamma_T, (1 - \alpha_T) \gamma_T) \beta(s' | \gamma_T, (1 - \alpha_T) \gamma_T) \beta(s' | \gamma_T, \gamma_G) \beta(s' | \gamma_T, \gamma_G) \beta(s' | \gamma_T, \gamma_G)
\]
Using a similar construction procedure to rotational excitations we get the following models:

(a) With external force:

\[
\begin{align*}
\xi_{10}^T &= (1 - \xi_0^T)\xi_{1}^T, & \xi_{11}^T &= s_{11}^T\xi_{1}^T, & \xi_{12}^T &= (1 - \xi_1^T)s_{12}^T, & \xi_{10}^R &= (1 - \xi_1^R)\xi_{1}^R, & \xi_{11}^R &= s_{11}^R\xi_{1}^R, & \xi_{12}^R &= (1 - \xi_1^R)s_{12}^R, \\
\end{align*}
\]

The associated correlation densities are:

\[
G(s) = \beta(s_1^T Y_T, (1 - \alpha_T) Y_T) \beta(s_2^T Y_R, (1 - \alpha_R) Y_R) \beta(s_0 Y_T Y_R, (1 - \alpha_T) Y_T) \beta(s_0^T Y_T Y_R) \beta(s_1^T Y_T Y_R)
\]

(b) Without external force:

\[
\begin{align*}
\xi_{10}^T &= (1 - \xi_0^T)\xi_{1}^T, & \xi_{11}^T &= s_{11}^T\xi_{1}^T, & \xi_{12}^T &= (1 - \xi_1^T)s_{12}^T, & \xi_{10}^R &= (1 - \xi_1^R)\xi_{1}^R, & \xi_{11}^R &= s_{11}^R\xi_{1}^R, & \xi_{12}^R &= (1 - \xi_1^R)s_{12}^R, \\
\end{align*}
\]

The associated correlation densities are:

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 \(s_P\). This gives:

\[
\begin{align*}
\xi_{10}^T &= (1 - \xi_0^T)\xi_{1}^T, & \xi_{11}^T &= s_{11}^T\xi_{1}^T, & \xi_{12}^T &= (1 - \xi_1^T)s_{12}^T, & \xi_{10}^R &= (1 - \xi_1^R)\xi_{1}^R, & \xi_{11}^R &= s_{11}^R\xi_{1}^R, & \xi_{12}^R &= (1 - \xi_1^R)s_{12}^R, \\
\end{align*}
\]

The associated correlation densities are:

\[
G(s) = \beta(s_1^T Y_T, (1 - \alpha_T) Y_T) \beta(s_2^T Y_R, (1 - \alpha_R) Y_R) \beta(s_0 Y_T Y_R, (1 - \alpha_T) Y_T) \beta(s_0^T Y_T Y_R) \beta(s_1^T Y_T Y_R)
\]
The associated correlation densities are:

\[ G(s') = B(s'_0|\gamma, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) \]

\[ \times B(s'_0|\alpha_\gamma, \gamma_v) B(s'_1|\gamma_1, \alpha_\gamma) \]

The associated correlation densities are:

\[ G(s') = B(s'_0|\gamma, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) \]

\[ \times B(s'_0|\alpha_\gamma, \gamma_v) B(s'_1|\gamma_1, \alpha_\gamma) \]

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

\[ \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2, \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2 \]

\[ \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2, \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2 \]

The associated correlation densities are:

\[ G(s') = B(s'_0|\gamma, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) \]

\[ \times B(s'_0|\alpha_\gamma, \gamma_v) B(s'_1|\gamma_1, \alpha_\gamma) \]

The associated correlation densities are:

\[ G(s') = B(s'_0|\gamma, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) \]

\[ \times B(s'_0|\alpha_\gamma, \gamma_v) B(s'_1|\gamma_1, \alpha_\gamma) \]

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

\[ \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2, \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2 \]

\[ \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2, \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2 \]

The associated correlation densities are:

\[ G(s') = B(s'_0|\gamma, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) \]

\[ \times B(s'_0|\alpha_\gamma, \gamma_v) B(s'_1|\gamma_1, \alpha_\gamma) \]

The associated correlation densities are:

\[ G(s') = B(s'_0|\gamma, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) B(s'_1|\gamma_1, \gamma_v) \]

\[ \times B(s'_0|\alpha_\gamma, \gamma_v) B(s'_1|\gamma_1, \alpha_\gamma) \]

(b) Without external force:

\[ \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2, \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2 \]

\[ \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2, \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2 \]

(b) Without external force:

\[ \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2, \xi_0 = s'_0 \xi'_0, \xi_1 = s'_1 \xi'_1, \xi_2 = s'_2 \xi'_2 \]
The associated correlation densities are:

\[ G(s') = \beta(s'_{\gamma_T}|\alpha_{\gamma_T}, (1-\alpha_{\gamma_T})_{\gamma_T}) \beta(s'_{\gamma_{r1}}|\alpha_{\gamma_{r1}}, (1-\alpha_{\gamma_{r1}})_{\gamma_{r1}}) \beta(s'_{\gamma_{r2}}|\alpha_{\gamma_{r2}}, (1-\alpha_{\gamma_{r2}})_{\gamma_{r2}}) \beta(s'_{\gamma_{r1}+\gamma_{r2}}|\gamma_{r1}+\gamma_{r2}) \beta(s'_{\gamma_{r1}+\gamma_{r2}}|\gamma_{r1}+\gamma_{r2}) \]  \hspace{1cm} (16b)

\times \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \]

where \( \gamma_T = 2\gamma_T, \gamma_r = 3\gamma_r + 3\gamma_v \)

The simplified severely-restricted exchange (SSRE) model is:

\[ \xi_{r1} = s_{r1}'s_{r1}^*, \xi_{r2} = (1-s_{r1})s_{r2}'s_{r2}^*, \xi_{r0} = (1-s_{r1})s_{r2}'s_{r2}^* \]
\[ \xi_{r1}' = s_{r1}'s_{r1}^*, \xi_{r2}' = (1-s_{r1})s_{r2}'s_{r2}^* \]
\[ \xi_{r0}' = (1-s_{r1})(1-s_{r1})s_{r2}'s_{r2}^* \]

where \( s_{r1}' = s_{r1} + s_{r1}' + s_{r1}'s_{r1}' + s_{r1}'s_{r1}' + s_{r1}'s_{r1}' \), \( s_{r1}' = (1-s_{r1})s_{r2}'s_{r2}^* \)

The associated correlation densities are:

\[ G(s') = \beta(s'_{\gamma_T}|\alpha_{\gamma_T}, (1-\alpha_{\gamma_T})_{\gamma_T}) \beta(s'_{\gamma_{r1}}|\alpha_{\gamma_{r1}}, (1-\alpha_{\gamma_{r1}})_{\gamma_{r1}}) \beta(s'_{\gamma_{r2}}|\alpha_{\gamma_{r2}}, (1-\alpha_{\gamma_{r2}})_{\gamma_{r2}}) \beta(s'_{\gamma_{r1}+\gamma_{r2}}|\gamma_{r1}+\gamma_{r2}) \beta(s'_{\gamma_{r1}+\gamma_{r2}}|\gamma_{r1}+\gamma_{r2}) \]
\[ \times \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \]
\[ \text{where } \gamma_T = 2\gamma_T, \gamma_r = 3\gamma_r + 3\gamma_v \]

**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 6 per model.

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

\[ \xi_{r1} = s_{r1}'(1-s_{r1})s_{r1}^*, \xi_{r2} = (1-s_{r1})s_{r2}'(1-s_{r2})s_{r2}^*, \xi_{r0} = (1-s_{r1})(1-s_{r2})s_{r2}'s_{r2}^* \]

where \( s_{r1}' = s_{r1} + s_{r1}' + s_{r1}'s_{r1}' + s_{r1}'s_{r1}' + s_{r1}'s_{r1}' \) is the total active energy

with associated correlation densities:

\[ G(s') = \beta(s'_{\gamma_T}|\alpha_{\gamma_T}, (1-\alpha_{\gamma_T})_{\gamma_T}) \beta(s'_{\gamma_{r1}}|\alpha_{\gamma_{r1}}, (1-\alpha_{\gamma_{r1}})_{\gamma_{r1}}) \beta(s'_{\gamma_{r2}}|\alpha_{\gamma_{r2}}, (1-\alpha_{\gamma_{r2}})_{\gamma_{r2}}) \beta(s'_{\gamma_{r1}+\gamma_{r2}}|\gamma_{r1}+\gamma_{r2}) \beta(s'_{\gamma_{r1}+\gamma_{r2}}|\gamma_{r1}+\gamma_{r2}) \]
\[ \times \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \]

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

\[ \xi_{r1} = s_{r1}'(1-s_{r1})s_{r1}^*, \xi_{r2} = (1-s_{r1})(1-s_{r1})s_{r2}'s_{r2}^* \]

where \( s_{r1}' = s_{r1} + s_{r1}' + s_{r1}'s_{r1}' + s_{r1}'s_{r1}' + s_{r1}'s_{r1}' \)

with correlation densities:

\[ G(s') = \beta(s'_{\gamma_T}|\alpha_{\gamma_T}, (1-\alpha_{\gamma_T})_{\gamma_T}) \beta(s'_{\gamma_{r1}}|\alpha_{\gamma_{r1}}, (1-\alpha_{\gamma_{r1}})_{\gamma_{r1}}) \beta(s'_{\gamma_{r2}}|\alpha_{\gamma_{r2}}, (1-\alpha_{\gamma_{r2}})_{\gamma_{r2}}) \beta(s'_{\gamma_{r1}+\gamma_{r2}}|\gamma_{r1}+\gamma_{r2}) \beta(s'_{\gamma_{r1}+\gamma_{r2}}|\gamma_{r1}+\gamma_{r2}) \]
\[ \times \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \beta(s'_{\gamma_{r0}+\gamma_{r0}+\gamma_{r0}}|\gamma_{r0}+\gamma_{r0}+\gamma_{r0}) \]
\[ G(s') = \beta(s'_0|\alpha,\gamma_0,1-\alpha,\gamma_0)\beta(s'_1|\alpha,\gamma_1,1-\alpha,\gamma_1)\beta(s'_2|\alpha,\gamma_2,1-\alpha,\gamma_2) \]
\[ \times \beta(s'_7|\gamma_1,\gamma_1)\beta(s'_8|\gamma_1,\gamma_2,\gamma_1,\gamma_2)\beta(s'_9|\alpha,\gamma_1+\alpha,\gamma_2,\alpha,\gamma_0)\beta(s'_a|\alpha,\gamma_0+\alpha,\gamma_1+\alpha,\gamma_2,2\gamma_1) \]

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

\[ \xi^*_{G} = (1-s'_a)(1-s'_a)\xi_a, \quad \xi^*_{T} = s'_T s'_T s'_T s'_a, \quad \xi^*_{R} = (1-s'_T) s'_T s'_T \xi_a, \quad \xi^*_{S} = (1-s'_R) s'_R s'_R s'_a, \quad \xi^*_{S'} = (1-s'_S) s'_S s'_S s'_a \]

where \( \xi_a = \xi_G + \xi_T + \xi_R + \xi_S + \xi_{S'} + \xi_{R} + s'_T s'_T s'_a \)

is the total active energy

with associated correlation densities:

\[ G(s') = \beta(s'_0|\alpha,\gamma_0,1-\alpha,\gamma_0)\beta(s'_1|\alpha,\gamma_1,1-\alpha,\gamma_1)\beta(s'_2|\alpha,\gamma_2,1-\alpha,\gamma_2) \]
\[ \times \beta(s'_7|\gamma_1,\gamma_1)\beta(s'_8|\gamma_1,\gamma_2,\gamma_1,\gamma_2)\beta(s'_9|\alpha,\gamma_1+\alpha,\gamma_2,\alpha,\gamma_0)\beta(s'_a|\alpha,\gamma_0+\alpha,\gamma_1+\alpha,\gamma_2,2\gamma_1) \]
\[ \times \beta(s'_s|\gamma_0+\gamma_1+\gamma_2+\alpha,\gamma_0+\alpha,\gamma_1+\alpha,\gamma_2|2\gamma_1+\gamma_G) \]

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

\[ \xi^*_{G} = s'_T s'_T s'_T s'_a, \quad \xi^*_{T} = s'_T s'_T s'_T s'_a, \quad \xi^*_{R} = s'_R s'_R s'_R s'_a, \quad \xi^*_{S} = s'_S s'_S s'_S s'_a, \quad \xi^*_{S'} = s'_R s'_R s'_T s'_a \]

where \( \xi_a = \xi_G + \xi_T + \xi_R + \xi_S + \xi_{S'} + \xi_{S'} + s'_T s'_T s'_a \)

is the total active energy

with associated correlation densities:

\[ G(s') = \beta(s'_0|\alpha,\gamma_0,1-\alpha,\gamma_0)\beta(s'_1|\alpha,\gamma_1,1-\alpha,\gamma_1)\beta(s'_2|\alpha,\gamma_2,1-\alpha,\gamma_2) \]
\[ \times \beta(s'_7|\gamma_1,\gamma_1)\beta(s'_8|\gamma_1,\gamma_2,\gamma_1,\gamma_2)\beta(s'_9|\alpha,\gamma_1+\alpha,\gamma_2,\gamma_1,\gamma_2) \]
\[ \times \beta(s'_s|\gamma_0+\gamma_1+\gamma_2+\alpha,\gamma_0+\gamma_1+\gamma_2|2\gamma_1+\gamma_G) \]

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

\[ \xi^*_{T} = (1-s'_a)\xi_a, \quad \xi_a = \xi_T + s'_a \]

The correlation densities are:

\[ G(s') = \beta(s'_0|\alpha,\gamma_1,1-\alpha,\gamma_1)\beta(s'_1|\gamma_1,\gamma_1)\beta(s'_2|2\gamma_1,\gamma_G)\beta(s'_7|\gamma_1,\gamma_2)\beta(s'_9|\gamma_1,\gamma_2,\gamma_1,\gamma_2)\beta(s'_a|\alpha,\gamma_1,\gamma_1,\gamma_T) \]

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

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

\[ G(s') = \beta(s'_0|\gamma_1,\gamma_1)\beta(s'_1|2\gamma_1,\gamma_G)\beta(s'_7|\gamma_r,\gamma_2)\beta(s'_9|\gamma_1,\gamma_2,\gamma_0)\beta(s'_a|\alpha,\gamma_1,\gamma_T) \]

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

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

\[ G(s') = \beta(s'_0|\alpha,\gamma_1,1-\alpha,\gamma_1)\beta(s'_1|\gamma_1,\gamma_1)\beta(s'_2|\gamma_1,\gamma_2,\gamma_1,\gamma_2)\beta(s'_a|\alpha,\gamma_1,\gamma_1,\gamma_T) \]

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

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

\[ G(s') = \beta(s'_0|\gamma_1,\gamma_1)\beta(s'_1|2\gamma_1,\gamma_G)\beta(s'_7|\gamma_1,\gamma_2)\beta(s'_9|\gamma_1,\gamma_2,\gamma_0)\beta(s'_a|\alpha,\gamma_1,\gamma_T) \]
The modifications are the same as for the loosely restricted exchange. The correlation densities are now:

\[ G(s') = \beta(s'_l|Y_1, Y_l)\beta(s'_l|Y_{12})\beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0})\beta(s'_l|\alpha I, Y_l) \]

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

\[ \xi_T = (1 - s'_s) \xi_a \quad \xi_R = (1 - s'_s) s'_s \xi_a \quad \xi_a = \xi_T + \xi_R + s'_s \xi_T' \]

The associated correlation densities are:

\[ G(s') = \beta(s'_l|\alpha_l Y_l)(1 - \alpha_l Y_l)\beta(s'_l|Y_1, Y_l)\beta(s'_l|Y_{12})\beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0}) \]
\[ \times \beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0})\beta(s'_l|\alpha_l Y_l + Y_{1}, Y_{2}, Y_{0}) \]

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

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

\[ G(s') = \beta(s'_l|\alpha_l Y_l)(1 - \alpha_l Y_l)\beta(s'_l|Y_1, Y_l)\beta(s'_l|Y_{12})\beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0}) \]
\[ \times \beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0})\beta(s'_l|\alpha_l Y_l + Y_{1}, Y_{2}, Y_{0}) \]

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

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

\[ G(s') = \beta(s'_l|\alpha_l Y_l)(1 - \alpha_l Y_l)\beta(s'_l|Y_1, Y_l)\beta(s'_l|Y_{12})\beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0}) \]
\[ \times \beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0})\beta(s'_l|\alpha_l Y_l + Y_{1}, Y_{2}, Y_{0}) \]

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

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

\[ G(s') = \beta(s'_l|\alpha_l Y_l)(1 - \alpha_l Y_l)\beta(s'_l|Y_1, Y_l)\beta(s'_l|Y_{12})\beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0}) \]
\[ \times \beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0})\beta(s'_l|\alpha_l Y_l + Y_{1}, Y_{2}, Y_{0}) \]

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

\[ \xi_T = (1 - s'_s) \xi_a \quad \xi_R = (1 - s'_s) s'_s \xi_a \quad \xi_a = \xi_T + \xi_R + s'_s \xi_T' \]

The associated correlation densities are:

\[ G(s') = \beta(s'_l|\alpha_l Y_l)(1 - \alpha_l Y_l)\beta(s'_l|Y_1, Y_l)\beta(s'_l|Y_{12})\beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0}) \]
\[ \times \beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0})\beta(s'_l|\alpha_l Y_l + Y_{1}, Y_{2}, Y_{0}) \]

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

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

\[ G(s') = \beta(s'_l|\alpha_l Y_l)(1 - \alpha_l Y_l)\beta(s'_l|Y_1, Y_l)\beta(s'_l|Y_{12})\beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0}) \]
\[ \times \beta(s'_l|Y_{1}, Y_{12})\beta(s'_l|Y_{1}, Y_{2}, Y_{0})\beta(s'_l|\alpha_l Y_l + Y_{1}, Y_{2}, Y_{0}) \]
Vibrationally excited, severely restricted exchange, without external forces:

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

\[ G(s') = \beta(s'|s_0, y_1, (1 - \alpha) y_2) \beta(s_1'|y_1, y_2, y_3, y_4) \beta(s_2'|y_5, y_6) \beta(s_3'|y_7, y_8) \beta(s_4'|y_9, y_{10}) \beta(s_5'|y_{11}, y_{12}) \]

\[ \times \beta(s_6'|y_{13}, y_{14}, y_{15}) \beta(s_7'|y_{16}, y_{17}, y_{18}) \beta(s_8'|y_{19}, y_{20}, y_{21}) \]

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

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

\[ G(s') = \beta(s_0'|y_1, y_2) \beta(s_1'|y_3, y_4, y_5) \beta(s_2'|y_6, y_7, y_8, y_9) \beta(s_3'|y_{10}, y_{11}, y_{12}) \]

\[ \times \beta(s_4'|y_{13}, y_{14}, y_{15}) \beta(s_5'|y_{16}, y_{17}, y_{18}) \beta(s_6'|y_{19}, y_{20}, y_{21}) \]

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. 10) have described Beta distribution sampling, which is needed in order to evaluate the model equations for each collision.

VI. CONCLUSION

In this paper I have presented a variety of models of rotational and vibrational three 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