State-to-State Internal Energy Relaxation Following the Quantum-Kinetic Model in DSMC

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A new model for chemical reactions, the Quantum-Kinetic (Q-K) model of Bird, has recently been introduced that does not depend on macroscopic rate equations or values of local flow field data. Subsequently, the Q-K model has been extended to include reactions involving charged species and electronic energy level transitions. Although this is a phenomenological model, it has been shown to accurately reproduce both equilibrium and non-equilibrium reaction rates. The usefulness of this model becomes clear as local flow conditions either exceed the conditions used to build previous models or when they depart from an equilibrium distribution. Presently, the applicability of the relaxation technique is investigated for the vibrational internal energy mode. The Forced Harmonic Oscillator (FHO) theory for vibrational energy level transitions is combined with the Q-K energy level transition model to accurately reproduce energy level transitions at a reduced computational cost compared to the older FHO models.

Nomenclature

c_r = Relative collision velocity (m/s)
E = Energy of particle (J)
f = Distribution function
g = Energy level degeneracy
$g*$ = Constant in vibrational transition probability (m/s)
k = Boltzmann's constant (1.380 650 x 10^{-23} J/K)
m_r = Reduced mass in collision (kg)
N = Number of particles
P = Total probability of transition
T = Temperature (K)

δ = Dirac delta function
ε = Average number of quanta transferred between vibrational levels
$\Gamma(x)$ = Gamma function of x
$\Pi^{i,j}$ = Probability of transitioning from level i to j
Θ = Characteristic temperature (K)
ω = Viscosity index for VHS potential

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Subscripts

coll = Collision energy
int = Internal energy
i,j,k,m = Internal energy level level indices
max = Maximum internal energy level possible
tr = Translational energy
trans = Transition
vib = Vibrational energy

I.   Introduction

Internal energy relaxation is an important physical process in hypersonic flows. While the rotational energy mode is a concern in all flow regimes, the vibrational and electronic energy modes become more significantly activated in the high-temperature flows generally associated with hypersonic flows. To complicate matters, the relaxation rate of the internal modes is finite, which may lead to a state of thermal non-equilibrium between the translational, rotational, vibrational, and electronic temperatures. Under these conditions, it is also possible for the distribution of the quantized internal energy modes to not follow the equilibrium Boltzmann form.

The method of computation of hypersonic flows depends on where along the trajectory of the vehicle the solution is desired. When the vehicle is in the continuum flow regime, computational fluid dynamics (CFD) is used. For non-continuum flow (i.e. rarefied to transitional), the direct simulation Monte Carlo (DSMC) method is generally used because of the breakdown of the continuum assumptions and thus kinetic methods become more appropriate. In contrast to CFD, DSMC performs a direct physical simulation of the gas at the molecular level. In the simulation, particles are tracked in space and time, accounting for both gas-surface interactions and intermolecular collisions.

Finite rate rotational and vibrational energy mode relaxation is usually modeled in the DSMC method using a probability of energy exchange for each collision that is consistent at the macroscopic level with the derivations of Parker[1] and Landau and Teller[2], respectively. For the fraction of collisions that are selected for rotational or vibrational relaxation, a quantized form[3, 4] of the Larsen-Borgnakke[5] (LB) energy exchange model is employed. These approaches act to equilibrate the translational and rotational/vibrational energy modes of the molecules without regard to transition rates between the individual quantum levels.

Beyond the simple models mentioned above, there has also been work towards state-to-state energy exchange models for both rotational[6-9] and vibrational[10-12] relaxation. These models make use of more detailed evaluations, such as quasi-classical trajectory analysis or forced harmonic oscillator models, to calculate transition rates between quantum levels as a function of the relative velocity/energy of the colliding particles in an attempt to more accurately reproduce the non-equilibrium distribution of the energy levels. These high-fidelity models have allowed much better comparison to measured transition rates and energy level distributions.

Recent advances in DSMC algorithms[13-15], specifically the Quantum-Kinetic (Q-K) chemistry model, have allowed the prediction of equilibrium and non-equilibrium reaction rates using only kinetic theory and fundamental molecular properties (i.e., no macroscopic reaction-rate information is needed). Models such as this are important especially when reaction rate data are limited or the gas is far from equilibrium and an engineering approximation is required.

Following the Q-K model, an electronic energy relaxation model was introduced[16-18] that was shown to reproduce energy level transition rates within the range of transition rates reported in the literature. This model was subsequently added to NASA's DSMC code DAC (DSMC Analysis Code)[19] and compared to CFD predictions of the Fire II flight test[20]. It is the purpose of this study to investigate the applicability of the relaxation model developed for electronic energy to the vibrational energy mode.

II. Extending the Quantum-Kinetic Chemistry Model

One of the attractive properties of the Q-K model of Bird is that it does not rely on any macroscopic information, leveraging instead off of kinetic theory and physical data corresponding to the particles undergoing each individual collision. The new methods that were developed for treating electronic energy level transitions will be generalized to any internal energy mode being described by quantum levels as originally derived.

A. Detailed internal energy level model

In order to implement a model for the distribution of internal energy in the DSMC technique, there are three procedures that must be defined. First, when a particle is introduced into a simulation, it is necessary to obtain a new energy level from a given distribution through statistical sampling. A new energy level is also required when a particle changes its energy after a collision with a surface. Under equilibrium conditions, the distribution has the well-known Boltzmann form. Second, it is necessary to statistically sample a new energy level following a collision, which involves internal energy transfer. Third, a method to reproduce the internal energy transition rate must be defined.

1. Equilibrium sampling

Each energy level j has a distinct energy, E_j, and degeneracy, g_j. The Boltzmann distribution for the internal energy levels at a given temperature T gives the following result for the fraction of particles in level j:

$$f_{int} = \frac{N_j}{N} = \frac{g_j \exp\left(-E_j/kT\right)}{\sum_{i=0}^{i_{max}} g_i \exp\left(-E_i/kT\right)} \qquad (1)$$

This distribution is used when either creating a new particle or after a surface collision in the DSMC simulation at a boundary specified at the temperature T. However, it is not possible to sample an internal energy level j directly from the distribution. Therefore, an acceptance-rejection procedure is used. This is performed by selecting values for j from the following distribution:

$$f'_{int}(j) = \frac{g_j \exp\left(-E_j/kT\right)}{g_J \exp\left(-E_J/kT\right)} \qquad (2)$$

where J is the value of j with Equation (1) maximized. The sampling of a new internal energy level then proceeds, in general, as follows:

1. select at random an energy level, j, evenly distributed between 0 and J_{max}, where J_{max} is the maximum possible energy level;
2. determine the value of J with the Boltzmann distribution in Equation (1) a maximum;

3. accept the value of j if $f'_{\mathrm{int}}(j) > RAND$, a random number
4. if the value of j is not accepted, return to step 1.

2. Post-collision sampling

A phenomenological approach is usually adopted in the DSMC method when a collision occurs that involves energy transfer. The LB method samples a post-collision state from a combined distribution of the translational and internal collision energies of the colliding particles. Based on the approach of Berngemann and Boyd[4] and Boyd[3], the Dirac delta function is used to determine the distribution of energies in Equation (1) in the following form:

$$f_{\mathrm{int}}(E_{\mathrm{int}},j) = \frac{g_j \exp(-E_j/kT)}{\displaystyle\sum_{i=0}^{i_{\max}} g_i \exp(-E_i/kT)} \delta\left(\frac{E_{\mathrm{int}}}{kT} - \frac{E_{\mathrm{int}}^j}{kT}\right) \tag{3}$$

Consideration must now be given to the distribution of translational energy of the colliding particles. This distribution is naturally affected by the intermolecular model used since this determines the collision probability. For the present study, the variable hard sphere (VHS) collision model of Bird[21] is used. However, it is a simple matter to develop the formulation for an alternative collision model such as the variable soft sphere model of Koura[22]. For the VHS model, the distribution of the translational energies is:

$$f_{tr}(E_{tr}) = \frac{1}{\Gamma(\frac{5}{2}-\omega)}\left(\frac{E_{tr}}{kT}\right)^{\frac{3}{2}-\omega} \exp\left(-\frac{E_{tr}}{kT}\right) \tag{4}$$

Using Equations (3) and (4), the combined distribution for sampling a post-collision internal energy level j' from the total collision energy $E_{coll} = E_{tr} + E_{\mathrm{int}} = E'_{tr} + E'_{\mathrm{int}}$ is:

$$f(j';E_{coll}) = \frac{1}{\Gamma(\frac{5}{2}-\omega)} \frac{g_j}{\displaystyle\sum_{i=0}^{i_{\max}} g_i \exp(-E_i/kT)} \left[\frac{E_{coll}-E_{\mathrm{int}}^j}{kT}\right]^{\frac{3}{2}-\omega} \exp\left(-\frac{E_{coll}}{kT}\right) \tag{5}$$

In applying the general LB scheme, it is assumed that local thermodynamic equilibrium prevails. Therefore, the temperature T in Equation (5) is constant. Also, the total collision energy is constant, so it is only necessary to perform sampling of the post-collision state for j' from the following distribution form:

$$g(j';E_{coll}) \propto g_{j'}\left(E_{coll}-E_{\mathrm{int}}^{j'}\right)^{\frac{3}{2}-\omega} \tag{6}$$

Again, an acceptance-rejection procedure is used. The normalized distribution that is required is obtained by finding the value of j' for which Equation (6) is a maximum, J', which can be different for each value of E_{coll}. Therefore, the following distribution is obtained:

$$g'(j';E_{coll}) = \frac{g_{j'}\left(E_{coll}-E_{\mathrm{int}}^{j'}\right)^{\frac{3}{2}-\omega}}{g_{J'}\left(E_{coll}-E_{\mathrm{int}}^{J'}\right)^{\frac{3}{2}-\omega}} \tag{7}$$

In the DSMC code, these procedures are implemented in the following way:

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1. given a pair of particles with total collision energy E_{coll}, which undergoes internal energy exchange, determine J' from Equation (6);
2. determine the maximum allowable internal energy level obtainable from E_{coll}, J_{max};
3. take J^* to be the smaller of J' and J_{max};
4. as described in the previous section on equilibrium sampling, perform an acceptance-rejection procedure to sample j' from

$$g'\left(j';E_{coll}\right) = \frac{g_{j'}\left(E_{coll} - E_{int}^{j'}\right)^{\frac{3}{2}-\omega}}{g_{J^*}\left(E_{coll} - E_{int}^{J^*}\right)^{\frac{3}{2}-\omega}} \tag{8}$$

3. Internal energy level transitions

A transition from internal energy level i to level j for species A can be written in the form of a chemical reation as $A^i + B \rightarrow A^j + B$. Since we are treating the transition as a chemical reaction, there are J_{max} transitions to consider where J_{max} is the maximum energy level possible. The total probability of the transition occurring is then:

$$P_{trans}^{i,j} = \Pi_{int}^{i,j} \frac{g_j\left(E_{coll} - E_{int}^j\right)^{\frac{3}{2}-\omega}}{\sum\limits_{k=0}^{J_{max}} g_k\left(E_{coll} - E_{int}^k\right)^{\frac{3}{2}-\omega}} \tag{9}$$

where $\Pi_{int}^{i,j}$ represents the probability of transitioning from level i to level j (discussed subsequently), and the last term is the probability of choosing level j. In the DSMC code, this process is broken into two parts. First, the energy level transition is chosen by the method outlined in Section 2 above for post-collision sampling. Then, the possibility of transition to that state is tested by comparing the probability $\Pi_{int}^{i,j}$ to a random number. The process for determining if a transition is to occur and what level to transition to is then as follows:
1. determine the value of J_{max} and compute the denominator of Equation (8);
2. perform acceptance-rejection according to Equation (8);
3. calculate the probability $\Pi_{int}^{i,j}$;
4. if the probability is greater than a random number between zero and one, the transition occurs.

B. Application of internal energy model to specific modes

Now that the general procedure for internal energy mode relaxation has been outlined, the procedure is applied to the electronic and vibrational internal energy modes. The new internal energy level transition model as discussed above is investigated by its ability to reproduce transition rates from the literature. The DSMC models are applied in a three-dimensional code where the results are accumulated over all of the cells (1,000 particles per cell in 1,000 cells) to approximate a zero-dimensional simulation. The test gas is molecular nitrogen and temperatures ranged between 2,000 K and 20,000 K at a number density of $1.0e21/m^3$ in an adiabatic cube measuring 1mm on a side. It should be noted that the uncertainty of the currently available measured/calculated rates can be very large. The uncertainty is not always reported and in some cases is unknown. Generally, if more than one source is available for any given rate, the spread is as much as an order of magnitude or, for many cases, more.

1. Electronic energy levels

Very little simplification can be made for the electronic energy level transition model. The electronic energy mode has unequally spaced levels that each have their own degeneracy. This energy mode was the topic of earlier studies[16-18] and the model described herein is nearly as it was in the references. In the electronic energy mode, the probability of transitioning, $\Pi_{ele}^{i,j}$, was originally set by selecting a random possible energy level and then if the randomly selected energy level was equal to the level selected by step (2) above, the transition was allowed to occur. This is equivalent to setting the transition probability equal to the inverse of the number of possible energy levels. The resulting sample transition rate was found to compare well with rates from the literature. An example is presented in Figure 1 for an N_2-N_2 collision for a variety of energy level transitions (0-1, 1-2, 2-3) where the sampled DSMC transition rates are compared to data from Park[23], Flagan[24] and Nagy[25]. Note that the spread in reported transition rates can be quite large. More examples, including other collision partners, are presented in References [16-18].
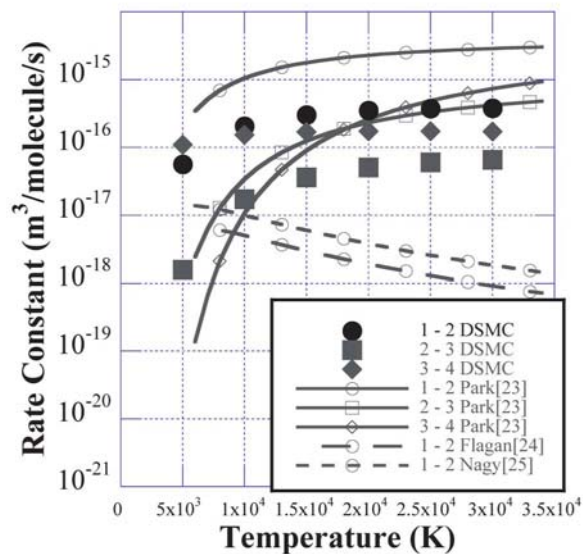

Figure 1. Comparison of sampled and reported electronic energy level transition rates for collisions of molecular nitrogen.

2. Vibrational energy levels

The vibrational energy levels are usually assumed to be described by a simple harmonic oscillator (SHO). While this does not have to be the case, it is overwhelmingly chosen because it is simple to model. However, the SHO model for vibrational energy assumes that the energy levels have a degeneracy of one and are equally spaced by the energy defined by $\Delta E_{vib} = \Theta_{vib} k$, such that the energy in level j is defined as $E_{vib}^{j} = j\Theta_{vib} k$. Therefore, the total probability of transition from Equation (9) becomes:

$$P_{vib}^{i,j} = \Pi_{vib}^{i,j} \frac{\left(E_{coll} - jk\Theta_{vib}\right)^{\frac{3}{2}-\omega}}{\sum_{m=0}^{J_{max}}\left(E_{coll} - mk\Theta_{vib}\right)^{\frac{3}{2}-\omega}} \tag{10}$$

Comparisons of the sampled DSMC vibrational energy level transition rates are made to rates quoted by Hansen[26] for excitation and by Billing[27] for de-excitation. When the probablility $\Pi_{vib}^{i,j}$ is set to the inverse of the number of available states as was done for electronic energy, the resulting transition rates are much too fast as presented in Figures 2 and 3 (Q-K: Original). However, when the Millikan-White[28] formulation of Bird[29] is used, the resulting transition rates are slightly too slow, as has been found by various researchers[10, 12].
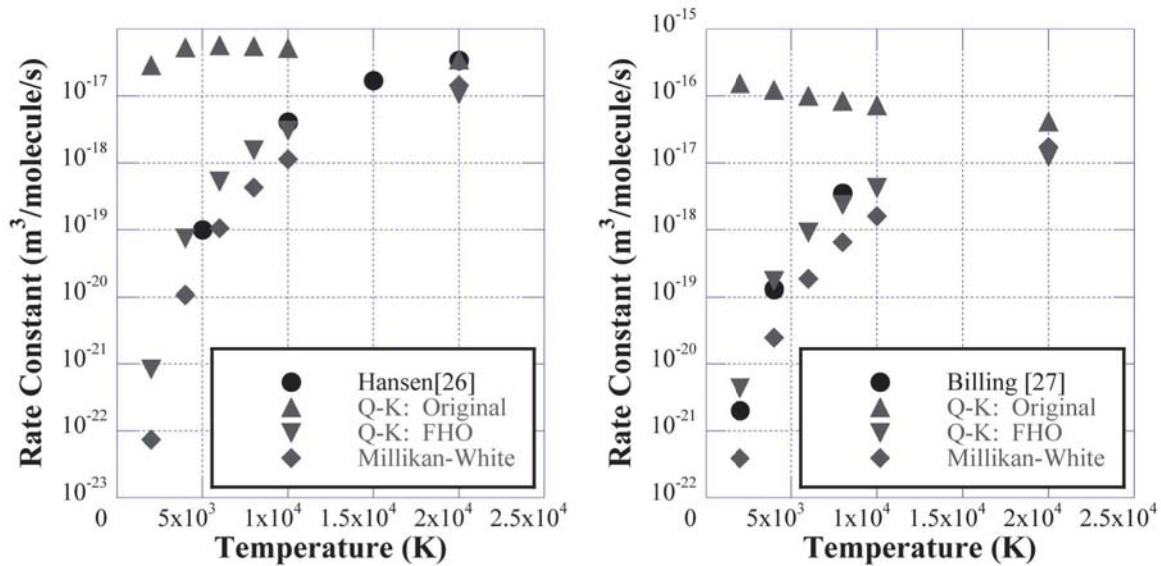
Figure 2: Comparison of sampled and reported vibrational energy level transition rates for collisions of molecular nitrogen between levels 0 and 1 (left) and 1 and 0 (right).
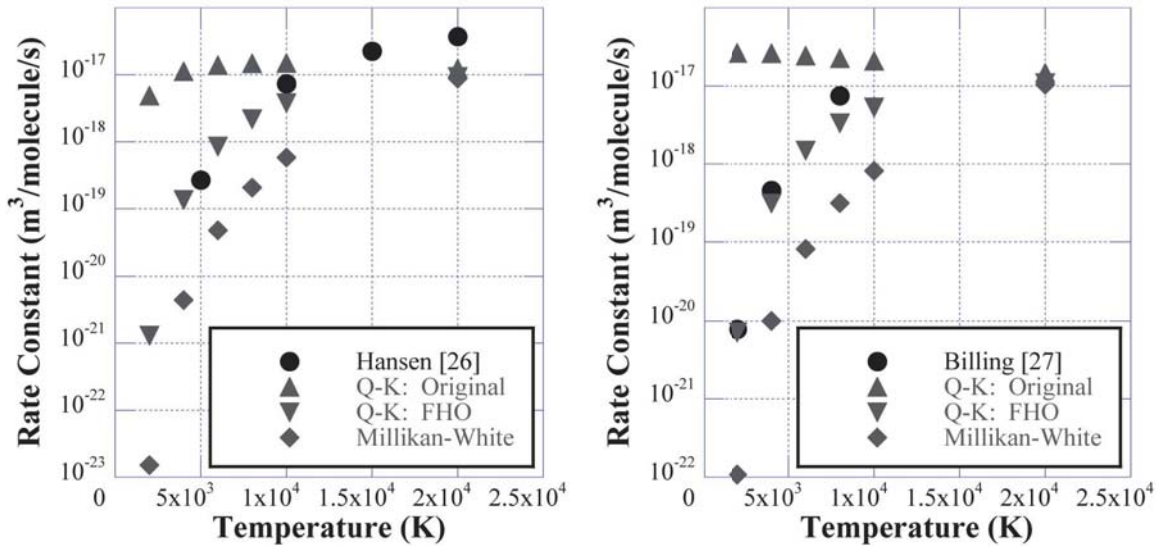

Figure 3: Comparison of sampled and reported vibrational energy level transition rates for collisions of molecular nitrogen between levels 2 and 3 (left) and 3 and 2 (right).

The probability of transitioning from level i to level j for the vibrational mode can be found from sources such as the small perturbation theory of Hansen[26] or the forced harmonic oscillator (FHO) model of Adamovich[30], presented for the DSMC method by Vijayakumar[31]. For example, the probability of transitioning from level i to level j according to the FHO model is:

$$\Pi_{vib}^{i,j} = i!\, j!\, \varepsilon^{i+j} \exp(-\varepsilon) \left| \sum_{r=0}^{n} \frac{(-1)^r}{r!(i-r)!(j-r)!} \frac{1}{\varepsilon^r} \right|^2 \tag{11}$$

and

$$\varepsilon = ae^{-g^*/c_r}$$

$$a = \frac{m_r g^{*2}}{k\Theta_{vib}} \qquad (12)$$

In these two equations, m_r is the reduced mass of the colliding pair, k is Boltzmann's constant, Θ_{vib} is the characteristic vibrational temperature of the relaxing molecule, c_r is the relative velocity of the colliding pair, and g^* is a constant suggested as 62,000 m/s in Ref. [31]. When this probability of transition is used, better comparison is found to the rates from the literature as presented in Figures 2 and 3 (Q-K: FHO).

The advantage of using the Q-K model presented herein over the original model presented by Vijayakumar is computational speed. In the original model, the transition probabilities of each energy level energetically possible must be computed, which could be up to 34 levels for nitrogen. Instead, the current model requires only one of the probabilities to be computed, so the speedup is of the order of 10 times the original. The computational time is comparable to the Millikan-White relaxation model, but comparisons to data from the literature are much better.

III. Conclusion

Extensions to the Quantum-Kinetic chemistry method for direct simulation Monte Carlo simulations have been proposed for internal energy state-to-state transitions. Comparisons have been made for electronic energy level transitions where the proposed transition rates are within the scatter of the reported rates in the literature and for vibrational energy level transitions where the proposed transition rates compare well with reported rates. The primary advantage of the current transition rate prediction model over previous models is, as was the original Q-K model, the simplicity of implementation and the need for only a few basic properties of the particle with the attendant computational speedup.

Several improvements to the proposed model are needed. First, rotational energy should be included in the model. The equilibrium and post-collision energy state assignment routine outlined above is applicable to the quantum model for rotation, but an appropriate energy level transition probability model has not yet been identified. As with the vibrational energy model, an approximation, such as Boyd's collision energy based transition model[3], could be used in place of a state-to-state transition model. The second improvement to the proposed model would be a more rigorous treatment of the electronic energy level transition model by making use of state-to-state transition probabilities such as that of Carlson[32]. However, using a methodology such as this is counter to the simplicity of the Q-K model in that specific reaction rate data would be needed.

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