Modeling of Disequilibrium of Intramolecular Rate Processes: A Review
— For Viability of Reusable Space Transportation Systems —

Kazuhidé Mizobata

Department of Mechanical Systems Engineering, Muroran Institute of Technology, Muroran, Hokkaido

In order to design next-generation reusable space transportation systems, their aerodynamic characteristics influenced severely by so-called real gas effects in their hypersonic regimes must be clarified. The effects are composed of disequilibria in and between intramolecular rate processes and chemical reactions. This paper features methodology for modeling disequilibrium in molecular vibration, i.e. the most dominant one in the rate processes. Methods for describing vibrational transition rates and relaxations, as well as those for coupling between vibration and dissociation-recombination, are outlined. Necessity of microscopic non-empirical modeling and its validation using prospective microscopic experiments is emphasized.

1 Real Gas Effects on Space Transportation Systems

In order to design the configurations and flight trajectories of reusable space transportation systems, their hypersonic aerodynamics must be characterized intensively and precisely. Such characterization has been based on ground testing where aerodynamic forces and moments on subscale models are measured in blow-down hypersonic wind tunnels and shock tunnels. Validity of the ground hypersonic testing was broken down through the first reentry flight of the Space Shuttle Orbiter in 1981, where much larger deflection of its body flaps was needed to keep pitching trim than predicted prior to the flight by ground testing, as shown in Figure 1.

A large controversy rose on this anomaly. Hypersonic flow fields around the Orbiter were analyzed by computational fluid dynamics techniques established in the 1980s. Griffith, Maus, et al. solved flow fields around a simplified Orbiter geometry using the Euler equation and chemical and thermal equilibrium air models, reproducing the body flap deflection favorably. Ten years after the analysis of Griffith et al., nonequilibrium air models were applied to Navier-Stokes calculations around a complete geometry by Weilnöker, Guofo, et al., and the deflection was reproduced precisely. Through these analyses, the anomalously large body flap deflection is believed to have been caused by non-equilibrium finite rate chemistry and disequilibrium in intramolecular rate processes ignored in the preflight analyses based on wind tunnel testing.

The effects of such chemical/thermal phenomena on aerodynamic/flight characteristics of hypersonic vehicles are called real gas effects. They appear in ground wind tunnel testing in a different manner from those in shock layer flows around hypersonic vehicles. Wind tunnel data must, therefore, be intensively
translated for application to design of space transportation systems. Such translation will be available only with a pile of computational fluid dynamics (CFD) solutions based on appropriate chemical/thermal models.

Factors affecting flow structure can be categorized into mechanics and thermo-chemistry. CFD techniques have been focused on analysis of the mechanics whereas the thermo-chemistry has not been sufficiently characterized and modeled. The characterization and modeling can be carried out not only by microscopic and non-empirical methods using theoretical chemistry but also by relatively macroscopic and phenomenological methods where, for instance, model equations are fitted to macroscopic experimental data.

This paper reviews the outlines of such methodology for modeling the nonequilibrium vibrational rate processes. In Section 2, procedures for evaluating the transition rate between two vibrational levels each will be featured. In Section 3, those for vibrational relaxation, that is the history of vibrational energy and distributions contained in air bulk, will be featured. Treatments of coupling between vibration and chemistry will be described in Section 4. Overall comparison of the methods will be shown in Section 5.

2 Modeling of Vibrational Excitation and De-excitation

Molecules of air can be modeled classically by an oscillator composed of a pair of dumbbells and a spring connecting them. The translational and the vibrational motions of the oscillators exchange energies at their collisions. Sometimes a part of translational energy changes into vibrational energy and vice versa at other times. The former is the vibrational excitation, and the latter is the vibrational de-excitation. On the other hand, translating molecules are modeled quantum mechanically by de Broglie waves. Wave functions and correspondent energy eigenvalues change at molecular collisions.

Various theoretical formulations for probabilities of vibrational excitation and de-excitation were proposed from both classical and quantum mechanics, at the dawn of research on molecular vibration. They are based on drastic simplifications called perturbation methods, in which for instance vibrational energy is assumed to be much smaller than translational energy, and thus probability of vibrational excitation/de-excitation is sufficiently small. Analytical results by classical and by quantum mechanics under such simplifications agree well. The most famous one is that by Schwartz, Slawsky, and Herzfeld(SSH).

Its formula for single quantum transitions in collinear collisions is described by:

\[ p_{v 	o v+1}(T) \propto \left( \frac{v + \frac{1}{2} + 1}{2} \right) ^{\frac{3}{2}} \cdot \exp \left\{ -\frac{3}{2} \left( \frac{\epsilon'}{\kappa T} \right)^{1/3} \pm \frac{h\nu}{2\kappa T} \right\} ^{3/2} \]  \hspace{1cm} (1)

\[ \epsilon' = (2\pi \omega l)^2 \mu, \quad \omega = 2\pi \nu \]  \hspace{1cm} (2)

where \( \nu \) is the frequency of the molecular vibration, \( \mu \) is the reduced mass of the colliding molecules, and \( l \) is the distance parameter in the intermolecular exponential-type potential function. This model includes the most popular formula proposed by Landau and Teller for describing single quantum transitions only:

\[ p_{v \to v-1} = v \cdot p_{v \to 0} \]  \hspace{1cm} (3)

\[ p_{v \to v+1} = (v + 1) \cdot p_{v \to 1} \]  \hspace{1cm} (4)

\[ p_{v \to \pm 1 \Delta v} = 0 \quad \text{for} \, \Delta v \neq \pm 1. \]  \hspace{1cm} (5)

Note that the SSH model can describe multi-quantum transitions. In other words, the Landau-Teller model is a noticeable reduction of a low-order approximation model proposed quite early in the research history of molecular vibration. Hence its physical validity is not clear; it cannot describe the phenomena dominant in hypersonic flight regimes such as multi-quantum transitions, anharmonicity, and coupling of vibration and chemistry.

From a classical point of view, the spring connecting the dumbbells will be torn off when molecular vibration grows sufficiently, whereas from a quantal point of view, the dumbbells cannot form a molecule when they excite from the dissociation limit, i.e. the uppermost vibrational energy level. Thus the
Additionally, a modified phenomenological model equation

\[
\frac{d e_{\text{vib}}}{d t} = \frac{e_{\text{vib}}^0 - e_{\text{vib}}}{\tau_v} \left( \frac{e_{\text{vib}}^0 - e_{\text{vib}}}{e_{\text{vib}}^0 - e_{\text{vib}0}} \right)^{s-1}
\]

(10)

\[
s = 3.5 \exp \left( \frac{-5,000}{T_s} \right)
\]

(11)

was proposed by Lee\(^{20,21}\) and Park\(^{22,23}\) to describe a tendency of slow vibrational relaxation in hypersonic shock layers. This was derived from a fitting to a solution for diffusive transitions among upper vibrational levels.

4 Coupling between Molecular Vibration and Chemical Reactions

Since dissociation is governed by the same mechanism as that in vibrational transitions as mentioned in the previous section, dissociation rates are dependent on the states of molecular vibration. In order to describe their coupling phenomena, several models have been proposed as follows:

Coupled Vibration Dissociation model\(^{23}\):

\[
k_{v \rightarrow e} \propto \exp \left( - \frac{D_0 - e_v}{kT} \right)
\]

(12)

Jaffe’s model\(^{25}\) for the dissociative collision cross section:

\[
\sigma_{\text{dis}}(e_{\text{trans}}, e_v) = \sigma_0 \cdot \max \left( 0, 1 - \frac{D_0 - e_v}{e_{\text{trans}}} \right)
\]

(13)

Park’s two temperature model\(^{12,22}\) for the bulk dissociation rate coefficient:

\[
k_{\text{dis}} = k_{\text{dis}}(T_v) \quad T_v = T^\alpha T_s^{1-\alpha}
\]

(14)

(15)

These models have been used with the Bethe-Teller equation. Park’s model is the most popular in CFD analysis mainly because of its simplicity.

Furthermore, in flow fields where dissociation dominates, the vibrational Boltzmann distribution cannot be retained any longer since molecules in the upper levels are consumed more rapidly than those in the lower levels. On the other hand, those in the upper levels are produced more rapidly in the flow fields where recombination dominates. In these flows with non-Boltzmann distributions, deterministic relations between vibrational energy and vibrational temperature fail down, and the models and analyses based on the Bethe-Teller equation will be invalid.

Analyses tolerating non-Boltzmann phenomena are needed, such as those by Adamovich et al. and by Mizobata. A solution by Mizobata is reproduced in Figure 3. A history of vibrational distribution is clearly simulated, where the distribution starts from a Boltzmann at room temperature and approaches a quasi-steady state of excitation-dissociation balancing. Such detailed simulations have become available thanks to the recent evolution of personal computers and work stations, and are expected to be carried out extensively to establish new models for non-Boltzmann vibrational relaxations. Additionally, the impacts of the non-Boltzmann rate processes on hypersonic aerodynamics should be revealed also through microscopic measurements involving spectroscopic techniques.

5 Comparison of Models and Procedures

Models and methods mentioned in this paper are listed and compared in Table 1. Almost all methods depend more or less on macroscopic experimental data such as vibrational relaxation times and bulk dissociation rate coefficients. Such phenomenological features lead naturally to capability of reproducing the
dissociation occurs by the same mechanism that governs vibrational transitions; appropriate models for vibrational transition are believed to be capable of appropriately describing dissociation as well. The curves (a) through (d) in Figure 2 illustrate the values for bulk dissociation rate coefficients of oxygen dilute in argon, evaluated from the Landau-Teller transition model. The differences among them are due to whether or not the anharmonicity and the existence of the dissociation limit are taken into consideration. The order-of-magnitude discrepancy between the curves and the experimental data implies physical invalidity of the Landau-Teller model in which multi-quantum transitions are neglected, although many analyses both classical and quantal, including SSH, have shown the dominance of multi-quantum transitions in high temperature conditions.

In recent years, numerical techniques for evaluating rates of both multi-quantum transitions and dissociation-recombination simultaneously are proposed by Sharma et al. on the basis of SSH theory, by Adamovich et al. on the basis of a semi-classical theory, and by Mizobata using a quasi-classical collision trajectory analysis. In Sharma's and Adamovich's techniques, the collision cross section or the distance parameter in the intermolecular potential is adjusted so as to reproduce experimental vibrational relaxation times; their procedures are somewhat phenomenological. On the other hand, the analysis of Mizobata is quite nonempirical, independent of macroscopic experimental data. The analysis reproduces successfully the bulk dissociation rate coefficients, as shown in Figure 2, though it fails in reproducing vibrational relaxation times.

In addition, an empirical statistical procedure has been proposed to determine transition probability functions with respect to vibrational quantum numbers. This procedure is also dependent on macroscopic experimental data such as vibrational relaxation times.

3 Modeling of Vibrational RateProcesses

The number density of the molecules in the quantum energy level \( v \), \( N_v \), is described theoretically by the following master equation:

\[
\frac{dN_v}{dt} = \sum_{v'v''=0}^{v'v''=0} \left( k_{v'v''v} N_{v'} - k_{v''v'v} N_v \right) \cdot \dot{N}_M.
\]  

(6)

When the Landau-Teller model is applied to the state-to-state transition rate coefficients \( k_{v''v} \), an infinite number of vibrational levels are assumed, and the vibrational distribution is always in equilibrium, the master equation is simplified into the following Beth-Teller equation:

\[
\frac{d\epsilon_{v'b}}{dt} = \frac{\epsilon_{v'b} - \epsilon_{vb}}{\tau_v}
\]

(7)

\[
\epsilon_{vb}(T_{vb}) = \frac{R \theta_{vb}}{\exp \frac{\theta_{vb}}{T_{vb}}} - 1
\]

(8)

\[
\epsilon_{v'b} = \epsilon_{vb}(T_{vb}), \quad \theta_{vb} = \frac{h \nu}{\kappa}
\]

(9)

Here \( \theta_{vb} \) is called the vibrational characteristic temperature, and \( T_{vb} \) is the vibrational temperature that describes the vibrational energy contained in the bulk of air. Note that temporal parameters governing the rate process, the number of which is generally equal to that of vibrational levels, are eliminated to the single one, \( \tau_v \), called the vibrational relaxation time. Its values have been evaluated by observing histories of gas density and spectroscopic absorption after propagating shocks at temperatures lower than 5,000K and at pressures of a few Torr, and by fitting thereby the histories to the flow field solutions based on the Beth-Teller equation. Such experimental data is compiled into an empirical relation between \( \tau_v \) and \( T \).

The physical validity of reduction of the master equation (6) into the Beth-Teller equation (7) is not certain due to the physical invalidity of the Landau-Teller model. But the methodology would be self-consistent, since the theoretically-unknown parameter \( \tau_v \) is evaluated by the same Landau-Teller model.
experimental data, but also to inapplicability to conditions where experimental data do not exist. The cause of the disagreement between the self-consistent non-empirical vibrational relaxation rates by Mizobata and the Bethe-Teller model based experiments should be clarified through more detailed reduction procedures for experimental relaxation times. As for implementation into computational fluid dynamics calculations, methods based on the native master equations are disadvantageous due to their large dimensions, though the evolution of computers would enable it in near future. Research studies must be developed extensively and intensively in theoretical and non-empirical modeling, as well as in experimental identification of microscopic features for validation of theoretical models. For example, quantitative validation of procedures by Sharma, et al, Adamovich et al, Mizobata, and Gonzales-Sakamura will become feasible only when the state-to-state vibrational transition rates are measured experimentally.

6 Summary

In order to design next-generation reusable space transportation systems, their aerodynamic characteristics influenced severely by so-called real gas effects in their hypersonic regimes must be clarified. The effects are composed of disequilibria in and between intramolecular rate processes and chemical reactions. This paper featured methodologies for modeling disequilibrium in molecular vibration, i.e. the most dominant one in the rate processes. Methods for describing vibrational transition rates and relaxations, as well as those for coupling between vibration and dissociation-recombination, were outlined. Necessity of microscopic non-empirical modeling and its validation using prospective microscopic experiments was emphasized.

ACKNOWLEDGMENT

This study was supported partly by the Grant for Scientific Research, Asahi Glass Foundation, Japan.

REFERENCES


Fig. 1: Preflight predictions and flight data of body flap deflection in the first reentry flight of Space Shuttle Orbiter\textsuperscript{1}.

Fig. 2: Quasi-steady-state bulk dissociation rate coefficients of O\textsubscript{2} highly dilute in argon suddenly heated by shocks.\textsuperscript{11} The QCT results are based on molecular collision simulation of 200,000 trajectories at temperatures below 8,000[K], and of 50,000 trajectories at others, using a Morse function for the intramolecular potential of O\textsubscript{2} and a Lennard-Jones(12,6) for O-Ar. Experiments denoted by (i) through (6) are by Wray\textsuperscript{20}, Anderson\textsuperscript{27}, Breuer\textsuperscript{21}, and Byrom\textsuperscript{31}, respectively. The symbols (i) through (6) designate the solutions by the Landau-Teller-type models DHO\textsuperscript{22}, THO, AHO, and AHO-Z\textsuperscript{23}, respectively.

Fig. 3: A history of the vibrational distribution of O\textsubscript{2} highly dilute in argon suddenly heated from a temperature of 300[K] into 12,000[K].\textsuperscript{16} Mass fraction of O\textsubscript{2} is 2%. The vibrational distribution is plotted at 0.6\mu sec intervals from t=0 to t=1.5\mu sec.
Table 1: Comparison of methods for modeling molecular vibration.

<table>
<thead>
<tr>
<th>Method</th>
<th>Transition rate coefficient modeling</th>
<th>Relaxation modeling</th>
<th>Reproductivity of vibrational relaxation time $\tau_{\text{rel}}$</th>
<th>Reproductivity of dissociation rates</th>
<th>Ease in implementation to CFD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>Classical or quantal</td>
<td>Master eqn.</td>
<td>Fitted</td>
<td>Bad.</td>
<td>Not good.</td>
</tr>
<tr>
<td>non-empirical</td>
<td></td>
<td></td>
<td>non-empirical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sakamura(18)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with diffusive correction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>