Internal Energy Excitation and Chemical Reaction Models for Rarefied Gases

Domenico Bruno

Istituto di Metodologie Inorganiche e dei Plasmi
Consiglio Nazionale delle Ricerche
Via G. Amendola, 122/D
70125 Bari, Italy

domenico.bruno@cnr.it

ABSTRACT

Models for internal energy exchange and for chemical reactions developed for DSMC simulations are reviewed.

1.0 INTRODUCTION

DSMC [1, 2] is a standard tool for the simulation of rarefied gas flows. It has, therefore found widespread application in the aerospace community for the simulation of high altitude vehicle aerodynamics. New developments and new goals in the field pose new challenges for the simulation. Planetary exploration missions entail high speed entries into atmospheres different from air; the same missions ask for simulation of very high speed re-entries into Earth atmosphere where ionization phenomena become relevant and accurate estimation of the emitted radiation is crucial to thermal protection design. Assessment of advanced concepts like the use of Magneto Hydro Dynamic interaction to reduce heat transfer to the vehicle require the modelling of plasma effects. As a result, new physical models need be included in DSMC simulation for the correct treatment of the energy relaxation, chemical kinetics and plasma dynamics of high temperature, partially ionized, chemically reacting gas mixtures. This includes extending available models to different gases (in particular to polyatomic gases and to ionized species). In addition, technological development calls for more stringent requirements on the predictive capabilities of the simulations so that new solutions must be sought, beyond the standard models, to accommodate more details of physical realism in a practically tractable model.

This work discusses the available models for internal energy relaxation and chemical reactions to use in DSMC simulation. The focus is on physical content rather than on computational efficiency. Also, the flexibility of the model with respect to application to different gases or to different flow regimes is analysed. Issues of currently available models and challenges for the development of new ones are outlined.

Section 2 discusses the modelling of the collision frequency and its connection to the transport properties of the simulated gas; section 3 explains the rationale behind the commonly adopted algorithms for choosing among different available exit channels in a collision event; sections 4 and 5 summarise the models for internal energy exchange and for chemical reactions, respectively; section 6 discusses the issues connected with modelling the interaction of the gas with solid surfaces.

2.0 KINETIC CROSS SECTION

The first step in modelling collisions concerns the evaluation of the collision frequency. To this end the total collision cross section is needed as a function of the colliders'energies. Since every collision, either

elastic or inelastic exchanges linear momentum, the choice of any particular model affects the transport properties of the species involved in the collision. Therefore, as a rule, the modelling focuses on reproducing the known viscosity properties. In particular, the Variable Soft Sphere model [3] is simple and efficient and it allows reproducing the available data on the temperature dependence of viscosity, thermal conductivity and diffusion. In this model the total cross section is inversely proportional to the collision kinetic energy:

$$\sigma_T \propto E_k^{1/2-\omega} \tag{1}$$

ω being a parameter of the model.

With this model, the viscosity has a power law dependence on temperature:

$$\eta \propto T^\omega \tag{2}$$

The scattering angle distribution is modelled as:

$$\chi = 2\cos^{-1}\left\{ \left(\frac{b}{d}\right)^{1/\alpha} \right\} \tag{3}$$

where χ is the scattering angle, b is the impact parameter, $d = \sqrt{\sigma_T/\pi}$ the cross section diameter and α a second model parameter.

This parameter allows the separate tuning of the momentum transfer cross section that defines the diffusion properties.

Overall, the VSS model reproduces the behaviour of particles interacting via an Inverse Power Law (IPL) potential and it finds widespread application in DSMC simulations.

For particular applications, different models are available [1]. This is the case when a more refined modelling of the viscosity coefficient is needed, or when charge exchange collisions make a meaningful contribution [4], or else when distinct features of the differential scattering cross sections are studied (as in the simulation of molecular beam experiments).

Before proceeding it is worth recalling that viscosity data give information essentially on the elastic cross section only. Modelling the total collision cross section based on viscosity data therefore neglects the role of inelastic processes in modifying the transport properties. This is not significant up to relatively high temperatures because inelastic processes probabilities remain small [5, 6]. Extrapolating the known behaviour to higher temperatures, however, may lead to inconsistencies (see Section 5, below and [7]).

3.0   SELECTION METHOD

Once a particular pair of particles is selected for collision, a selection method is required in order to test which exit channel will be chosen among all the possible outcomes. The method should, in principle:

- be efficient: there is no need to compute all transition probabilities in advance;

- be precise: when different inelastic channels are available they do not interfere;

- be general: can be extended to any number of channels.

Different methods have been proposed [8] but the most appealing is also the most conceptually simple [9] and is summarised below.

First the probability of a chemical reaction occurring is evaluated. Assuming that different, independent chemical reaction processes are available with probabilities P_r^i, then the probability that the collision results in a chemical reaction is $P_r = \sum_i P_r^i$. If the reaction occurs, the specific reaction path i is selected with probability P_r^i / P_r; otherwise a check for internal energy transfer will be performed.

Internal energy transfer can be modelled in one of two ways. One is to use cross section data for internal energy exchange and select a particular energy exchange process based on the knowledge of its probability; the other is to apply the phenomenological Larsen-Borgnakke method [10] thus modelling each relaxation channel via a relaxation-type equation. In order to prevent interference among different channels the best strategy is to test each collision partner and each channel independently and to prohibit that more than one relaxation event happen in a single collision.

Within this modelling strategy, the cross section for each particular collision outcome is:

$$\sigma_i = \sigma_T P_i \tag{4}$$

It is therefore essential that all the probabilities for chemical reactions and inelastic processes sum up to a value smaller than unity so that these processes do not interfere and the required macroscopic relaxation, or reaction) rates are reproduced.

4.0 INTERNAL ENERGY EXCHANGE

The internal degrees of freedom of the molecule can be modelled as continuous or discrete spectra. This choice depends on the energy separation of the internal energy levels of each mode as compared to the mode total energy content and therefore varies with each particular application. In aerospace applications it is a common rule to model rotation with a continuous spectrum and to treat vibrational and electronic modes as discrete energy levels. There are, of course, differences in the implementation of all reaction models to continuous or discrete energy levels, respectively. Models for continuous spectra reproduce macroscopic relaxation rates exactly but the resultant energy distribution functions may differ substantially from those obtained from the discrete spectrum model [9]. This can have great impact on the resulting chemical reaction rates and on the emitted radiation.

Models for internal energy exchange are either based on the knowledge of the cross sections for internal energy exchange events or are devised to reproduce the internal energy relaxation kinetics as obtained from experiments. Experimental data are essentially shock tube data of vibrational and rotational temperature relaxation. These data are reduced in the framework of a simple relaxation equation, the so-called Jeans or Landau-Teller equation:

$$\frac{dE_i}{dt} = \frac{E_i^* - E_i}{\tau} \tag{5}$$

where E_i^* is the equilibrium internal energy content and τ is the relaxation time.

A very general method to implement this kind of relaxation kinetics is the Larsen-Borgnakke method [10].

4.1   Larsen-Borgnakke method

The method is described in detail in [10]. The general principle is that there is a probability for the collision to produce relaxation. This probability relates to the relaxation time in eq. (5) via:

$$P_i \propto \frac{1}{Z_i} = \frac{\tau_c}{\tau} \tag{6}$$

where τ_c^{-1} is the collision frequency and Z_i is the collision relaxation number.

The relaxation number therefore depends on the kinetic cross section since the experiments usually measure the relaxation time τ. This must be kept in mind when reducing data from different sources [11].

Care must also be exercised when translating collision relaxation numbers from continuum to particle models as explained in [12].

Temperature dependent collision relaxation numbers can also be modelled, the most used being Parker model [13, 11] for rotational relaxation and Millikan-White [14] fitting formula for vibrational relaxation.

If the collision is accepted for relaxation, available energy is distributed to the internal degrees of freedom according to the equilibrium distribution. The model therefore reproduces correctly the thermodynamic equilibrium. In addition it can handle any combination of degrees of freedom, either continuous or discrete.

Due to its flexibility, the method has widespread use in the DSMC community. It suffers, however, from important drawbacks.

Being a phenomenological method, it is strictly applicable only to situations for which experimental data exist. Since most of these data refer to shock tube experiments, the method works best for conditions where the gas temperature is higher than internal temperatures. For the opposite condition where internal energy content is higher than its equilibrium value (like in expansion flows) the LB method produces too fast a relaxation as compared to more detailed kinetic models.

After a relaxing collision the available energy is distributed according to equilibrium distributions disregarding the state of the collision partners prior to the collision itself. As such, there is no correlation among the internal states of the colliding particles before and after the collision. It is therefore very difficult to include in the model specific features of state-to-state kinetic models like the role of energy resonant relaxation processes. Also, in the framework of a selection method prohibiting multiple relaxation, it is not possible to accommodate intrinsicly nonlinear processes like VV collisions.

In order to overcome these limitations, modelling of the energy relaxation must be based on the evaluation of the cross sections for all energy exchange processes. In the following, available models are described for the relaxation of molecular internal energies.

4.2   Rotational relaxation

Cross section based models have been developed to model rotational relaxation in gases. In general terms, these can be classified as being dynamical or phenomenological in nature.

Dynamical models retrieve the cross section data from Molecular Dynamics calculations whereas phenomenological models assume some functional form for the cross sections. While the former include

more physics of the system under study, phenomenological models are more flexible.

While detailed, state resolved, energy exchange Molecular Dynamics studies are certainly possible for a limited number of systems [15], their output must, in any case, be processed before implementation into a DSMC simulation. This case will be discussed further in the next section.

It is thus useful to derive reduced models, based on simplifying assumptions, applicable to selected conditions. An example of this strategy is the use of model Lennard-Jones curves to model the interaction among particles and to derive for these the required relaxation cross sections [16]. The model can satisfactorily reproduce experimental results of rotational relaxation in shock waves [17] but, of course, it cannot be extended to model vibrational relaxation or dissociation kinetics.

Prototypical examples of phenomenological models are the SICS models by Koura for continuous [18] and for discrete [19] energy spectra. They include all essential physical constraints (conservation laws, microscopic reversibility, selection rules) that can be derived without detailed knowledge of any particular system. The parameters of the model can then be adjusted to reproduce macroscopic relaxation rates obtained either by experiments or by theoretical means. Additional details can also be included naturally in the model. As compared to LB modelling, this approach has the advantage that it can equally be applied to strongly nonequilibrium conditions.

However, at the temperatures relevant for high speed flow modelling, LB modelling of continuum rotation with Parker collision relaxation number [13] gives satisfactory results and is used routinely.

This is not to say that the contribution of rotational energy content to other relaxation processes can be safely neglected. It is, instead, the subject of considerable debate.

4.3   Vibrational relaxation

Vibrational relaxation cannot be modelled by continuous spectra methods. Also, VV processes in expansion flows cannot be captured by LB type models. Several attempts have been made to model accurately vibrational energy exchanges on a state-to-state (STS) basis [20-23]. In these studies, energy exchange and chemical reaction cross sections are obtained from Quasi Classical Trajectory (QCT) calculations run on adiabatic potential energy surfaces (PES) obtained from quantum chemistry calculations. Differences arise essentially from differences in the underlying PES. These can be more or less refined, they always carry a definition of the energy range of applicability and can include some estimation of nonadiabatic effects. Besides differences in the PES, QCT studies may also differ with respect to the kind of reaction channels included (dissociation, exchange reactions). In addition, these works usually address vibrational energy relaxation so that the role of rotational energy content is either neglected or included in a simplified manner. There is universal consensus that rotation has nontrivial impact on vibrational energy exchanges; complete state-to-state cross section data are now available for some systems [24, 15]. The work of Panesi [23] has demonstrated, however, that simulation of real gas mixtures with inclusion of the complete STS cross section data is unfeasible even for the simplest systems. Modelling is thus unavoidable.

QCT studies have attracted considerable interest in that they provide a good compromise between physical consistency and computational cost. Therefore, complete sets of cross sections can be produced in a reasonable time. Of course these results, being classical in nature, do not account for intrinsicly quantal phenomena like tunnelling or energy resonant transitions. Other methods have therefore been developed to study vibrational energy exchanges. These methods range from the simple SSH theory [25], to the FHO theory [26, 27] to the refined semiclassical calculations of Billing [28, 29] and Kunc [30], up to full quantum calculations [15]. Increasing the physics content of the calculation, however, increases the computational cost so that the most refined calculations cannot span the whole set of available reactive

channels. In many cases, statistical scatter on the obtained cross sections is large enough that the results can only be in the form of temperature averaged rate coefficients.

For this reason and also for historical reasons, rate coefficients are available in the literature more often than cross sections. Therefore, another approach is to use rate coefficients data as an input to Laplace inversion in order to obtain energy dependent cross sections. This approach has been pursued in some works [31, 32]. However, being Laplace inversion an ill-posed problem, this procedure must be exercised with great care as it may potentially lead to unphysical results.

4.4   Electronic excitation and radiation modelling

When radiation is important either because the radiative heat flux becomes a measurable contribution, or because emission spectra are to be obtained, the electronic excited state kinetics is needed. A recent example is [33].

Electronic excited state kinetics has been studied in the low temperature plasma literature, that also highlighted its coupling to the vibrational kinetics [34]. In low temperature plasma applications, however, the gas is usually subsonic and essentially all energy input comes from free electrons. Therefore, electronic excitation in collisions between heavy particles is somewhat less studied. There is essentially no information concerning internal kinetics (vibration, rotation) of electronic excited states of molecular species.

The request to extend the range of application of DSMC simulations comes from the need to study very high speed flows as they occur in re-entry stages of planetary exploration missions, from the increasing interest in supersonic combustion or from innovative proposals to use the Magneto Hydro Dynamic (MHD) interaction with the plasma surrounding the vehicle to mitigate heat flux to the surface.

The inclusion of free electron kinetics or of radiation transfer into DSMC, while possible in principle, makes the problem untractable in practice. DSMC models the kinetics on a microscopic basis: the inclusion of free electron kinetics or of radiative transfer therefore entails the inclusion in the physical model of greatly differing timescales. These multiscale problems can only be approached by hybrid methods (see eg. [35, 36]).

5.0   CHEMICAL REACTIONS

Chemical reaction modelling is essential because endothermic reactions absorb a large fraction of the flow enthalpy but also because some molecules are strong emitters and their concentration is needed to accurately determine the emission spectra (NO, CO, …)

The widely used TCE model [37] is an extension to chemical reactions of the LB method. It is a phenomenological method whose parameters are determined in order to reproduce known rate constants in Arrhenius form. It is defined by:

$$P_r(E_c) = C_1 \frac{(E_c - E_a)^{C_2 + \xi_c/2 + 1}}{E_c^{\xi_c/2 - 1}} \tag{7}$$

where E_c is the total energy in collision, ξ_c is the average number of degrees of freedom and C_1, C_2, E_a are model parameters.

Minor modifications are needed to apply the method, originally developed for continuous internal

energies, to discrete energy levels. Note that, in order to estimate ζ_c a knowledge is required of cell-averaged gas and internal temperatures.

In this model, all energy modes contribute equally to the reaction probability. This is particularly unsatisfying for dissociation reactions for which a varying degree of vibrational favoring is established. Several models have been proposed to overcome this limitation and they have been reviewed in [38] and again in [7] where they are compared against measured cross sections. There, it is also pointed out that, at high enough collision energies, dissociation cross sections can become larger than the total cross section, the latter being derived from extrapolation of low temperature viscosity data.

In order to overcome the limitations of the TCE model, the Q-K model has been introduced [39]. It is based on the simple assumption that dissociation reactions occur whenever there is enough energy available in collision. Endothermic exchange and chain reactions, instead, occur when a trial LB redistribution of the sum of the relative kinetic energy and the vibrational energy of one collision partner results in a vibrational energy exceeding the activation energy for the reaction. Steric factors for the reverse reaction are then obtained from the equilibrium constant based on the appropriate collision temperature. In this model no reference is made to macroscopic gas properties and all reaction probabilities explicitly depend on the vibrational state of the colliding molecules.

The model has been tested [40] against measured Arrhenius rates for near-equilibrium conditions and with both measured rates and other theoretical models for far-from-equilibrium conditions showing good agreement.

Therefore, both TCE and Q-K models agree with available data in near-equilibrium conditions. The TCE model, however, assumed a thermal distribution of reactant energies in order to obtain reaction probabilities from rate coefficients so that the new model is expected to be more accurate in nonequilibrium regions of the flow. Recent studies [41] show measurable differences in the predictions of the two models for the Orion entry simulations, in particular at higher altitude where nonequilibrium effects are more important.

Summarising, "TCE and Q-K models can provide equally good results when reliable data is available for the chemical rate coefficients over the full range of temperatures that are encountered in the application. On the other hand, if the rate data is not available or if the application necessitates the extrapolation of the data to temperatures well outside the temperature range of the underlying measurements, the advantages of the Q-K model are overwhelming." [39].

Still, there is no physical foundation for a model that is essentially phenomenological. Also, the issue to include the rotational energy content in the estimation of the reaction probability has not been solved.

Again, the required information can only come from dynamical studies. This information must then be processed in order to be directly input into DSMC modelling.

The relevance of STS modelling with respect to TCE modelling has been demonstrated in few cases as in the following examples.

The first testcase is the 2D computation of the flow of Nitrogen over a wedge for Mach number M=7.7 and Knudsen number Kn=6.5×10^{-4}. Computations were carried out with the RGDAS software system.

The TCE model is compared to a model where cross sections are obtained from Laplace inversion of the nonequilibrium rate coefficients from the Kuznetsov model.
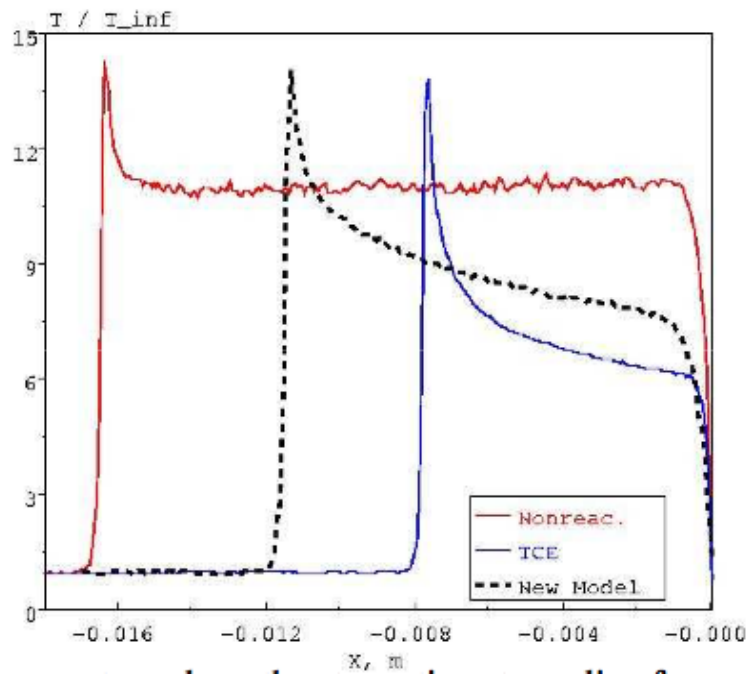
Figure 1. Translational temperature along the stagnation streamline for reacting flow with different chemical models and for nonreacting flow (wedge angle 62.5 deg).

A second example considered a simplified axy-symmetric EXPERT profile, considering two re-entry trajectory points (70 and 80 km, for the trajectory with 5 km/s at the interface, angle of -5.5°, mass of 436 kg). For these calculations, the TCE model is compared to a detailed STS model obtained from QCT calculations [24].
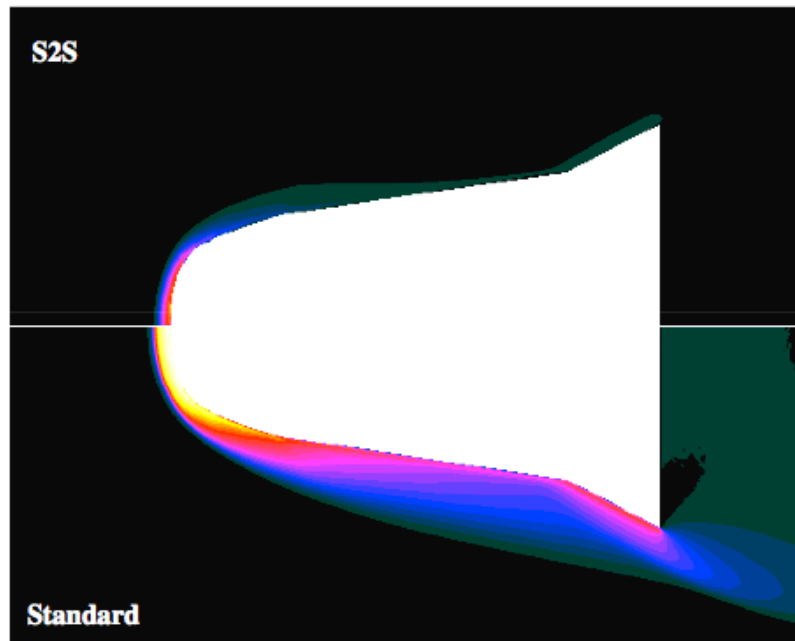
Figure 2. Oxygen atom number density maps for the 80 km trajectory point.
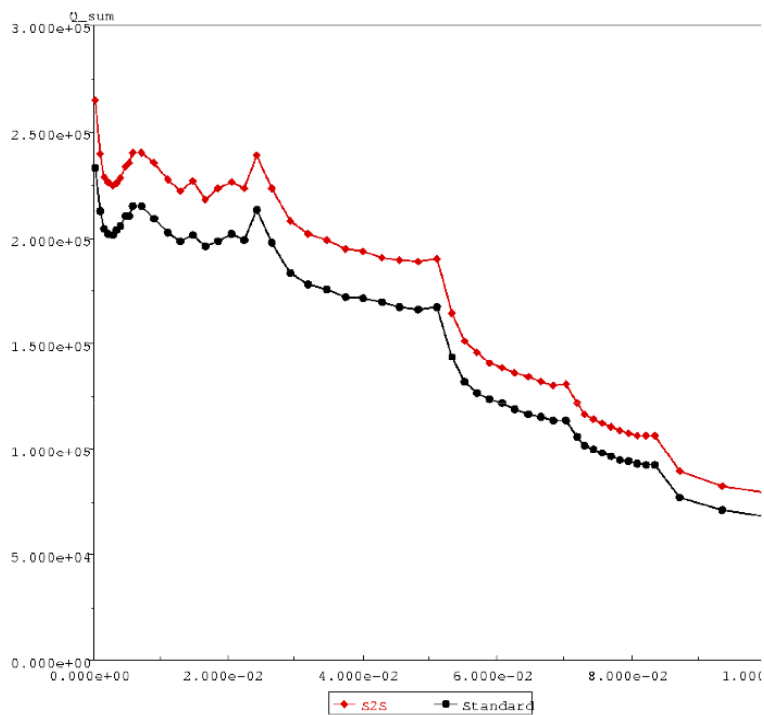

Figure 3. Fourier heat flux on the vehicle surface for the 80 km trajectory point.

The effects on a realistic re-entry configuration are therefore significant.

5.1   Recombination

The role of recombination in high speed rarefied flows is usually negligible. When needed, however, it can be modelled by applying detailed balance to the dissociation cross sections. Note that obtaining reverse reaction rates from equilibrium constants in a nonequilibrium framework may be subject to criticism [42]. The derivation of recombination cross sections from Dynamical studies entails however a discussion of quasi-bound states and of recombination mechanisms [43].

6.0   SURFACE REACTIONS

In rarefied flows, collisions with the solid boundary are essential to the shaping of the flowfield. Therefore the issue must be addressed properly. The kinetic theory of gas-surface interaction in the framework of the Boltzmann equation has been studied by Cercignani [44]. In the cited works the scattering kernel formalism is developed as a consistent boundary condition to the Boltzmann equation. It also has a straightforward interpretation in terms of particle modelling as the scattering kernel is the probability transition matrix between incoming and reflected particles states.

Several models in the literature are able to reproduce measured properties of gas-surface interaction (Maxwell, Cercignani-Lampis-Lord, Nocilla, see [45] for a review). These are usually expressed in terms of accommodation coefficients. These models, however, cannot capture some features of the underlying physics like the interplay of different components of the particle velocity on rough surfaces and the role of internal energy [45]. When these effects become relevant, more detailed models based on Molecular Dynamics data must be devised.

More relevant for aerospace applications the role of surface catalytic properties on the vibrational and chemical kinetics [46]. These studies point to the need for accurate data on STS relaxation and reaction probabilities.

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