Automatic Assembling of Kinetic Reaction Schemes for Plasma Modelling Applications

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Abstract: Numerical modelling of plasma chemistry systems while resolving spatial dimensions becomes increasingly complex and computationally costly with increasing number of plasma species considered in the model and number of collisional processes between the species. It is therefore of great importance to define ways to assemble self-consistent reaction schemes containing a minimum number of species and processes while preserving all the reaction pathways relevant to the application and plasma parameters.

Keywords: Plasma modelling, global models, reaction schemes

1. Introduction

Plasma technologies can change surface properties with less damage than purely chemical processes and hence plasmas get wide-ranging industrial applications from semiconductor industry to environmental applications for gas abatement. Plasma processes are defined by quantum effects, their behaviour is strongly nonlinear and hard to control. However, efficient control of plasma processes results in improved manufacturability, better yield and a shorter time to market. Many companies and research groups are working on computational plasma models to reduce R&D risks during product design and perform material selection.

Modelling plasma systems in complex gas environment usually means dealing with reaction schemes containing tens of species and up to a thousand of reactions [1, 2]. Incorporating such complex chemical schemes is usually impossible task for spatially resolved (2D and 3D) plasma models due to the high computational cost. Another problem with very complex chemistry sets is robustness and the credibility of the rate coefficients or cross sections associated with each reaction [3]. The aim of this work is to develop a robust algorithmic method for reduction of reaction schemes as an add-on tool for the Quantemol Database (QDB) [4]. The Quantemol Plasma Chemistry Generator (QPCG) will help to build up reaction kinetics schemes for plasma modelling applications, which have been reduced to account for only selected species of interest. The reduction method will start with the full collisional cascade obtained from the Quantemol Database based on the composition of the specified feed gases. This complex reaction chemistry set at first includes all the relevant species and reactions found in the QDB database and is subsequently reduced to a minimal size while keeping all the reaction pathways relevant to the user selected species and acceptable estimated error.

2. Quantemol Database and Chemistry Generator

QDB is a web-based supported database of electron and heavy species collisional data. Apart from data and cross-

sections for collisional and reactive gas-phase and surface processes, QDB also provides pre-assembled and validated self-consistent chemistry sets for selected plasma related applications. The idea behind the Chemistry Generator is to develop an algorithm which could take in user inputs as parameters and assemble a robust self-consistent reaction scheme of a minimal possible size. The user inputs relevant to the reaction scheme development would be:

- 1. Feed gases
- 2. Plasma pressure
- 3. Absorbed power
- 4. Plasma reactor dimensions
- 5. Neutral species temperature
- 6. Species of interest

The Chemistry Generator algorithm will compile the full reaction scheme of all the species and processes in the QDB relevant to the given set of feed gases and perform a reaction scheme reduction based on all the other input parameters. The reaction scheme reduction will be based on 0D (global) modelling of plasma species densities and electron temperature.

3. Reaction Scheme Reduction

Reduction of comprehensive sets of reactions is a common problem in plasma modelling and there are several methods available to do this.

The most widely used in the literature is the simplest one, based on a single evaluation of a global model and where species and reactions are simply discounted if they do not reach pre-defined thresholds of minimal particle density and minimal contribution to a production rate of any of the species respectively. The minimal particle density threshold of species considered for removal from the system might be based on a value relative to either the total electron density or the total species density. Such a method has been used, see [2, 5, 6]. In this method, the global model needs to be run only once which is a big advantage for an algorithm which needs to be run on a web-based database server. However, the disadvantages are that the threshold values are completely arbitrary and often (especially in the case of reducing the number of species in the system) there are exceptions needed to be made, e.g. when species with densities lower than the threshold value heavily influence densities of other more abundant species [6]. Setting the correct threshold values and dealing with exceptions requires the expertise of a skilful researcher.

Another possible reduction method employs a systematic Monte-Carlo based screening similar to the Morris method [7]. Although the Morris method is usually associated with a sensitivity or uncertainty analysis of reaction schemes [6], its modification can be used to identify species and reactions irrelevant to evolution of densities of other species of interest. This Monte-Carlo based systematic screening procedure relies on randomly disabling reactions and species from the reaction scheme one at a time and evaluating the global model with each perturbed input. From a large enough sample of such perturbed inputs and modelled species densities and electron temperatures, one can evaluate an effect of i^{th} reaction to a modelled density of j^{th} species or to a modelled electron temperature. This information can be used to remove reactions from the scheme with a negligible effect on the modelled densities of species of interest and to remove species involved only in the reactions with a negligible effect on the same species of interest. Disadvantage of this method is that it might require hundreds to thousands global model evaluations. which might be too costly for the intended purpose.

Other reaction scheme size reduction methods exist such as analysing the dominant reaction pathways [8, 9] and lumping excited states into a few groups with similar energies [10].

4. Results

We considered a pure NF3 plasma reaction scheme presented in [11, 12] (the sources present a reaction scheme for O₂/Ar/NF₃ mixture, but for our case, only reactions involving fragments of NF₃ were considered). The full (comprehensive) reaction scheme as provided consists of 20 species and 188 reactions. We employed a reduction method based on the Monte-Carlo perturbations procedure outlined in the section 3, generating the reduced reaction scheme consisting of 14 species and 46 reactions. For this case study, the reduction process was performed only with the objective of preserving the modelled density of atomic F with tolerance up to 10%, but the objective might be arbitrarily complex in practice, such as preserving densities of multiple species with different tolerance levels as well as electron density n_e and electron temperature T_e . The 0D model used in the reduction algorithm and for validation of the results was Global Kin [13, 14] and the model calculated the reaction rate coefficients from its internal library of cross sections and assuming Maxwellian electron energy distribution function. But in practice, different Global_Kin model settings or even completely different backend models might be used.

The Table 1 shows all the species included in the comprehensive and reduced reaction schemes, with the

ones neglected in the reduced scheme highlighted in bold font.

Model	Tracked Species
Comprehensive	NF ₃ , NF ₃ ⁺ , NF ₂ , NF ₂ ⁺ , NF, NF ⁺ , N ₂ ,
	$N_2(v), N_2^*, N_2^+, N, N^*, N^+, F_2, F_2^*,$
	$F_{2}^{+}, F, F^{*}, F^{+}, F^{-}$
Reduced	NF_3 , NF_2 , NF , N_2 , $N_2(v)$, N_2^* , N_2^+ , N ,
	$F_2, F_2^*, F, F^*, F^+, F^-$

Table 1: Species included in the model for the
comprehensive and reduced reaction schemes. The bold
font highlighted species were neglected in the reduced
reaction scheme.

Generally, one might expect that reduced reaction scheme (irrespectively of the employed reduction method) will only be valid for plasma conditions close to the conditions considered when performing the reduction algorithm. The Figures 1-3 show how the atomic F density changes as a function of absorbed power P, pressure p and gas temperature T_g (in our case study, gas temperature was not solved for self-consistently but rather was treated as an input to the 0D model). The reaction scheme reduction was performed for the base conditions of P = 5000 W, p =100 Pa and $T_g = 500$ K and one can clearly see in the presented graphs that the agreement between the F particle density modelled with the comprehensive and reduced reaction schemes is satisfactory close enough to the base conditions (which the reduced reaction scheme was tailored for) and can diverge further away from the base conditions.



Fig. 1. Variation of F atom particle density as a function of absorbed power for both comprehensive and reduced reaction schemes. Values shown are results of a 0D model with p = 100 Pa, $T_g = 500$ K.



Fig. 2. Variation of F atom particle density as a function of plasma pressure for both comprehensive and reduced reaction schemes. Values shown are results of a 0D model with P = 1000 W, $T_g = 500$ K.



Fig. 3. Variation of F atom particle density as a function of gas temperature for both comprehensive and reduced reaction schemes. Values shown are results of a 0D model with P = 1000 W, p = 100 Pa.

5. Conclusions

We present an automatic reaction scheme reduction procedure can deliver great reduction in number of species (from 20 to 14) and reactions (from 188 to 46) without sacrificing a predictive power of a 0D model with respect to certain chosen model parameters. The reduction procedure used is too computationally costly to be deployed on a web-based database server for a real-time reaction set reduction and therefore further work is needed to develop a faster method.

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