

Global plasma simulations using dynamically generated chemical models

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(Received 1 October 2007; accepted 4 February 2008; published 1 July 2008)

Extensive molecular data are a key requirement in understanding modern technical plasmas. A method for coupling molecular data with chemical models in a global plasma simulation to enable rapid testing and evaluation of new plasmas is presented. A global plasma model (GLOBALKIN) is extended using an expert system (Quantemol-P) to enable *ad hoc* simulations using new plasma recipes. A set of atomic and molecular species to be considered in the plasma simulation is specified by the user. The expert system generates a complete set of reaction pathways for both the gas and surface reactions in a plasma. This set is pruned by discarding unphysical reactions and reaction data not appropriate to technical plasmas (such as autodetachment). The species, gas phase reactions, surface reactions, and plasma properties can be adjusted to control the simulation. The reaction list is populated through a database of molecular parameters and cross sections; missing data can be calculated through molecular cross sections using a further expert system (Quantemol-N) which applies the *R*-matrix method to electron-molecule collisions. For cases where the *R*-matrix method is not appropriate, other methods are used to maximize the range of cross-section data available. The Quantemol-P expert system allows rapid creation of new plasma recipes and investigation of their effects allowing a greater level of flexibility than previously achievable. © 2008 American Vacuum Society. [DOI: 10.1116/1.2889433]

I. INTRODUCTION

Plasmas are vital for many technological processes, yet for the vast majority of these, the only method available to optimize or change the process involves an expensive procedure of trial and error. There is no doubt that robust modeling could play a key role in improving the design of, for instance, etching reactors. Even models that accurately predict trends can have an important role in both eliminating unpromising recipes and signposting directions for improvements. However, to tailor plasmas, one should really be able to build and run a range of calculations rapidly with only the minimum input.

As is well documented,^{1,2} models of technological plasmas demand large quantities of atomic and molecular data which is often not available. This places severe limitations on the scope and usefulness of such models.

We have collaborated on the development of an expert system Quantemol-N (Ref. 3) which runs the UK molecular *R*-matrix codes.⁴ Quantemol-N requires limited input allowing calculations to be started both rapidly and reliably. The present article reports progress on constructing another expert system, Quantemol-P, for building and running plasma simulations.

II. BACKGROUND: PLASMA INPUT AND MODEL REQUIREMENTS

The plasma model in Quantemol-P is based on the zero-dimensional global-kinetics simulation code GLOBALKIN developed over a number of years by Kushner

and co-workers.⁵⁻⁷ Constructing a valid model requires consideration of a variety of issues. Thus, even for a zero dimensional plasma model, it is, for instance, necessary to specify the plasma geometry for use in the ideal gas equation.

A global model such as GLOBALKIN can apply to a variety of plasma situations, including flowing plasmas⁷ such as plug flow systems and well-mixed plasma reactors.^{8,9} In the flowing plasmas case, mole fractions for the various gases included are calculated with respect to position. In the etching reactors, mole fractions for the various gases are calculated with respect to time.

The physical properties of the plasma as, for example, power input as a function of time, initial pressure, temperature, etc., must be specified. These are then added to the initial chemical composition of the plasma both in terms of species and mole fractions of the gas, and the gas flow rates. We will refer to this whole specification as the plasma recipe.

A given plasma recipe implies a key set of chemical reactions. However, even for simple chemical mixtures, the number of possible contributing reactions is large. Below, we describe a scheme for the automatic generation of the plasma chemistry which considers all possible gas phase reactions and the likely surface reactions. These reactions, which are sorted by importance, generate database requirements in terms of both cross sections or rates for gas phase reactions, and surface reaction probabilities. For even the simplest recipes, there are data items not available, so a strategy is necessary for populating the database, at least for processes considered essential for the model.

The outputs of a successful model, as performed by Quantemol-P, are of course fairly standard. They comprise the gas temperature, electron temperature, gas pressure, and

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mole fractions of the various species involved in the plasma recipe. All these properties are obtained as a function of space (for a flowing plasma, such as a plug flow) or time (for a well-mixed plasma reactor).

It is important to note that although this model and models like it produce accurate and testable predictions they are constructed empirically according to what is required. For instance, the use of cross-section data is beneficial but an incomplete set does not necessarily produce a physically accurate kinetic model of the system.¹⁰ Also, rates and cross sections need to be carefully defined and should be used appropriately, see Robson *et al.*¹¹ for an attempt at creating a model with a rigorous treatment of the fundamental processes.

III. METHOD

A. Automatic chemistry generation

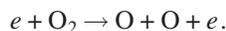
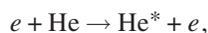
In order to understand the way in which the list of chemical reactions is automatically constructed, we need the following definitions, which are close to the standard usage of the terms.

Element. An atomic element except that no charge is associated with it. Charges are only treated when considering species and reactions. Examples: C (carbon) and H (hydrogen).

Species (unstateful). A combination of elements (including just a single element) in any state of excitation, which has an associated electronic charge. Examples: O₂ and H₂⁺.

Species (stateful). A species as described above but with an associated state label. Here, we use the convention that where no state label is specified, the species is assumed to be in its ground state. Example: O₂(¹Δ).

Reaction. An exchange of elements and charge between species, which includes the creation of new species, and/or the change of a state associated with one or more of the species. The standard chemical rules apply for balancing the chemical reaction. Examples:



From the total list of N species provided, i.e., all species to be treated according to the plasma recipe, a list of reactants is generated. This species list includes the electron and an arbitrary third body (M). The list of reactants forms the left hand side (LHS) of the reaction equation and includes all the combinations of reactions between any two species along with all combinations of two-body reactions with the arbitrary third body (M). This gives some N^2 combinations for the LHS of the reaction equations.

Given the list of reactants, the complete reaction equations are generated. For each combinations of reactants, this involves first generating a list of elements that exist on the LHS of the equation and then using that list to construct all combinations of species that can be generated from the reactants. The number of combinations here depends upon a

number factors but this list of potential products can be large. Algorithmically, forming a set of elements into partitions (unstateful species here) is known as “all the partitions of an N set.” For this step, we use Nijenhuis and Wilf’s NEXEQU algorithm (Ref. 12) to efficiently count through these possibilities.

Once the right hand side of the equation has been generated, all the possible charge transfer processes are added, up to and including two electron processes. The reactions are also copied to count over possible starting and final states of the various species.

The reactions are then ordered according to a number of heuristics, such that unlikely reactions—like autoattachment at low pressure—are given a low priority while likely reactions—such as electron impact reactions—are given a high priority. Developing these ordering rules is a process of constant enhancement.

Finally, a look-up operation includes all the reactions for which data exist. At this point, there is an opportunity for the calculation of missing data that is considered important using—for instance—Quantemol-N.

B. Database issues

GLOBALKIN contains an extensive but far from complete database. To this Quantemol-P has added the ability to generate electron collision data using the Quantemol-N expert system.³ Quantemol-N is designed to treat low energy electron impacts, specifically those processes which lie below the ionization threshold of the species concerned. This is the key energy regime for molecular plasmas.

Quantemol-N is an expert system designed to run the fully *ab initio* UK molecular R -matrix codes.⁴ These codes have been shown to give reliable results for collisions of electron with a range of small molecules. Under certain circumstances, these R -matrix calculations can produce results competitive or even more accurate than laboratory measurements.^{13,14} A major advantage of these codes is that they can treat electron collisions with radicals, a process which is very difficult to study experimentally. For example, they have been used for a series of studies on electron collisions with CF_x radicals.^{15–18} Quantemol-N allows these calculations to be constructed rapidly and efficiently, and thus provides a natural way of supplying missing electron collision data for the database.

At present, Quantemol-N provides both electron collision cross sections and rates for elastic and inelastic processes. Quantemol-N does not provide data on electron impact ionization; however, this is easily generated using the semi-empirical binary encounter Bethe model of Kim and co-workers.^{19–21}

C. Reaction selection

As shown below, even for simple plasma recipes, the number of possible reactions become very large. It is therefore essential to have some means of selecting key reactions.

TABLE I. Species included in the He/O₂ plasma mix.

Type	Species
Special	e (electron) M (third body)
Atomic	He He* He ⁺ O O(¹ D) O(¹ S) O ⁻ O ⁺
Diatomic	O ₂ O ₂ (v) O ₂ (¹ Δ) O ₂ (¹ Σ) O ₂ ⁺ O ₂ ⁻
Triatomic	O ₃ O ₃ ⁻

Traditionally, this selection has always been made with a strong bias toward those reactions for which data are available.

Clear grounds for excluding reactions are given by kinetic and energetic considerations. Some products are too high in energy to be readily accessible at the temperatures available, and therefore reactions leading to them can be excluded.

Kinetically, some reactions are known to be slow. For example, radiative association, $X+Y$ giving XY plus a photon, is a very inefficient process and makes no significant contribution to technological plasmas. Conversely the process $X+Y$ giving XY in the presence of a third body (M) does not require photon emission and may be important in high pressure plasmas. Similarly, reactions between two trace or very short-lived species is unlikely to be important.

The process of defining an optimal chemistry is a compromise between completeness, availability of data, and complexity of the plasma for which one wishes to run a model.

IV. SAMPLE AUTOMATED CHEMISTRY

Here, we present an example of automatic chemistry generation for a mixture of He and O₂. This type of plasma is important in the production of O₂(¹Δ) for the operation of chemical oxygen-iodine lasers and has been the subject of much experimental and theoretical study, see Refs. 7 and 22–26 for just some of the studies and Ref. 27 for a review. More generally, O₂ plasmas are important because of the wide array of applications.^{28–33} It is chosen here because of its relative chemical simplicity. Even then, the number of possible reactions is large.

Table I gives all the species fundamental to the He/O₂ chemistry. In Table II, we give all the left-hand sides of the reaction equations, here including only the unstateful species as state is not treated until after the initial list of chemical reactions has been generated. Table III gives a very small subset of the reaction list finally generated. In this example, 13 490 possible reactions are generated and 153 reactions are included in our calculation, just 1.1% of the total. Table III also shows whether the rate or cross section is included in the automated model and the source of input data. The subset of reactions featured in Table III are included in the calculation as cross sections not just rates.

V. SAMPLE RESULTS

In order to validate our approach, we have performed sample calculations following the example of Stafford and

TABLE II. Reactant list as generated between all combinations of (unstateful) species. The (+ M) signifies that each combinations of reactants is repeated but including that arbitrary third body (M) for when pressure sensitive reactions are required.

Reactants		
$e+\text{He}(+M)$	He ⁺ +O ⁺ (+ M)	O ⁻ +O ⁻ (+ M)
$e+\text{He}^+(+M)$	He ⁺ +O ⁻ (+ M)	O ⁻ +O ₂ (+ M)
$e+\text{O}(+M)$	He ⁺ +O ₂ (+ M)	O ⁻ +O ₂ ⁺ (+ M)
$e+\text{O}^+(+M)$	He ⁺ +O ₂ ⁺ (+ M)	O ⁻ +O ₂ ⁻ (+ M)
$e\text{O}^-(+M)$	He ⁺ +O ₂ ⁻ (+ M)	O ⁻ +O ₃ (+ M)
$e+\text{O}_2(+M)$	He ⁺ +O ₃ (+ M)	O ⁻ +O ₃ ⁻ (+ M)
$e+\text{O}_2^+(+M)$	He ⁺ +O ₃ ⁻ (+ M)	O ₂ +O ₂ (+ M)
$e+\text{O}_2^-(+M)$	O+O(+ M)	O ₂ +O ₂ ⁺ (+ M)
$e+\text{O}_3(+M)$	O+O ⁺ (+ M)	O ₂ +O ₂ ⁻ (+ M)
$e+\text{O}_3^-(+M)$	O+O ⁻ (+ M)	O ₂ +O ₃ (+ M)
He+He(+ M)	O+O ₂ (+ M)	O ₂ +O ₃ ⁻ (+ M)
He+He ⁺ (+ M)	O+O ₂ ⁺ (+ M)	O ₂ ⁺ +O ₂ ⁺ (+ M)
He+O(+ M)	O+O ₂ ⁻ (+ M)	O ₂ ⁺ +O ₂ ⁻ (+ M)
He+O ⁺ (+ M)	O+O ₃ (+ M)	O ₂ ⁺ +O ₃ (+ M)
He+O ⁻ (+ M)	O+O ₃ ⁻ (+ M)	O ₂ ⁺ +O ₃ ⁻ (+ M)
He+O ₂ (+ M)	O ⁺ +O ⁺ (+ M)	O ₂ ⁻ +O ₂ (+ M)
He+O ₂ ⁺ (+ M)	O ⁺ +O ⁻ (+ M)	O ₂ ⁻ +O ₃ (+ M)
He+O ₂ ⁻ (+ M)	O ⁺ +O ₂ (+ M)	O ₂ ⁻ +O ₃ ⁻ (+ M)
He+O ₃ (+ M)	O ⁺ +O ₂ ⁺ (+ M)	O ₃ +O ₃ (+ M)
He+O ₃ ⁻ (+ M)	O ⁺ +O ₂ ⁻ (+ M)	O ₃ +O ₃ ⁻ (+ M)
He ⁺ +He ⁺ (+ M)	O ⁺ +O ₃ (+ M)	O ₃ +O ₃ ⁻ (+ M)
He ⁺ +O(+ M)	O ⁺ +O ₃ ⁻ (+ M)	

Kushner⁷ (SK) who also used GLOBALKIN to perform the one-dimensional simulation of a plug flow reactor. Many of the aspects of our sample calculation use precisely the same approach as GLOBALKIN, e.g., diffusion, heat conduction, etc. Our calculations do, however, differ from SK with respect to

TABLE III. Sample stateful reaction list, generated by considering reactions between electrons and O₂ only.

Reactants⇒Products	Included?	Data sources
$e+\text{O}_2\Rightarrow e+\text{O}_2$	Y	Quantemol-N or Ref. 34
$e+\text{O}_2\Rightarrow e+\text{O}_2(v)$	Y	Quantemol-N or Ref. 34
$e+\text{O}_2\Rightarrow e+\text{O}_2(^1\Delta)$	Y	Quantemol-N or Ref. 34
$e+\text{O}_2\Rightarrow e+\text{O}_2(^1\Sigma)$	Y	Quantemol-N or Ref. 34
$e+\text{O}_2\Rightarrow \text{O}+\text{O}^-$	Y	Reference 34
$e+\text{O}_2\Rightarrow \text{O}(^1D)+\text{O}^-$	N	
$e+\text{O}_2\Rightarrow \text{O}(^1S)+\text{O}^-$	N	
$e+\text{O}_2\Rightarrow \text{O}_2^-$	N	
$e+\text{O}_2\Rightarrow e+\text{O}+\text{O}$	Y	Quantemol-N or Ref. 34
$e+\text{O}_2\Rightarrow e+\text{O}+\text{O}(^1D)$	Y	Quantemol-N or Ref. 34
$e+\text{O}_2\Rightarrow e+\text{O}+\text{O}(^1S)$	N	Quantemol-N
$e+\text{O}_2\Rightarrow e+\text{O}(^1D)+\text{O}(^1D)$	N	Quantemol-N
$e+\text{O}_2\Rightarrow e+\text{O}(^1D)+\text{O}(^1S)$	N	Quantemol-N
$e+\text{O}_2\Rightarrow e+\text{O}(^1S)+\text{O}(^1S)$	N	Quantemol-N
$e+\text{O}_2\Rightarrow e+\text{O}^++\text{O}^-$	N	
$e+\text{O}_2\Rightarrow e+e+\text{O}_2^+$	Y	BEB or Ref. 34
$e+\text{O}_2\Rightarrow e+e+\text{O}+\text{O}^+$	Y	Reference 35
$e+\text{O}_2\Rightarrow e+e+\text{O}(^1D)+\text{O}^+$	N	
$e+\text{O}_2\Rightarrow e+e+\text{O}(^1S)+\text{O}^+$	N	

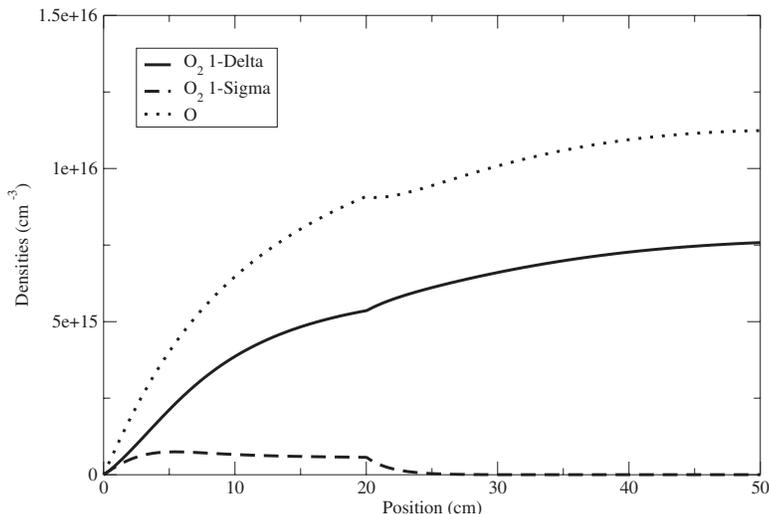


FIG. 1. Densities of O, $O_2(^1\Delta)$, and $O_2(^1\Sigma)$ for a pure O_2 plug flow. Initial flow velocity is 1000 cm/s at a pressure of 3 Torr, the discharge power is 0.5 W/cm^3 , and the discharge region extends from 0 to 20 cm.

the chemical model because of our automated approach to chemistry generation. Notably, we include a greater set of cross sections, scattering reaction cross sections for all the species are included. Also, our generic treatment of three body reactions (using the notional M species) means that we can only include a single rate to describe all third-body mediated reactions. Whereas, SK included a number of specific rates for three body reactions with the major species as the third body.

Figures 1 and 2 show sample results given a plug flow reactor of length 50 cm and an internal diameter of 4.83 cm. The discharge region is from 0 to 20 cm and the last 30 cm are treated as an afterglow region. The pressure is set at 3 Torr, the power at 0.5 W/cm^3 , and the initial flow velocity is 1000 cm/s.

Figure 1 shows the densities of O, $O_2(^1\Delta)$, and $O_2(^1\Sigma)$ plotted against position for a pure O_2 mixture while Fig. 2 show the densities of O, $O_2(^1\Delta)$, and $O_2(^1\Sigma)$ plotted against position for a mixture of 70% He and 30% O_2 by mole fraction. These results match very closely the results of SK.

Finally, we have also performed a calculation designed to be comparable to measurements of temperature by Carroll *et al.*²³ Here, the plug flow consists of pure O_2 at 2 Torr at a flow rate of 5 mmol/s with a total of 265 W of power dissipated in the discharge region. We find that the temperature of the plasma rises to a maximum of 509.5 K as compared to an experimental temperature of about 545 K. As noted by SK, this difference is primarily due to GLOBALKIN assuming constant temperature at the discharge tube wall.

VI. CONCLUSIONS

For a long time, process engineers and plasma scientists have been limited in their ability to perform accurate simulations of working systems because of weak chemical models predicated on little molecular data. The problem of molecular data is beginning to be solved by systems such as Quantemol-N.³ Quantemol-P is a first attempt at making a useful tool to generate reasonable models of the chemistry through a combination of automation and this molecular

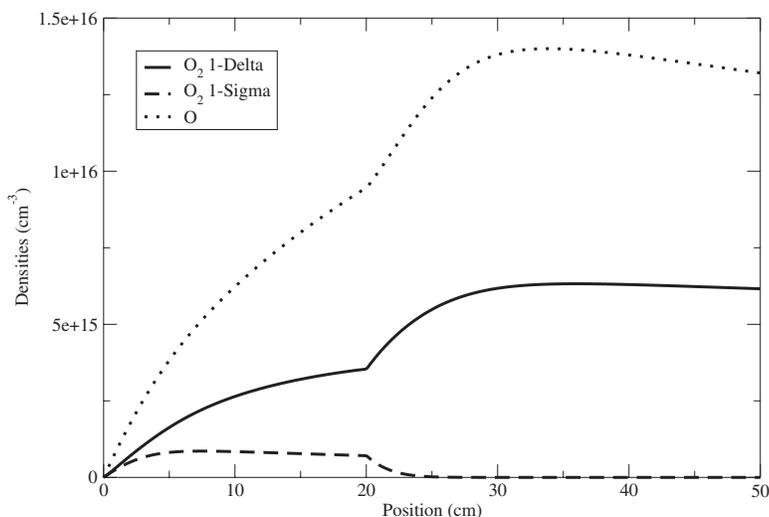


FIG. 2. Densities of O, $O_2(^1\Delta)$, and $O_2(^1\Sigma)$ for a 70% He and 30% O_2 plug flow. Initial flow velocity is 1000 cm/s at a pressure of 3 Torr, the discharge power is 0.5 W/cm^3 , and the discharge region extends from 0 to 20 cm.

data. While not yet predictive—our calculation essentially matches the previous results of SK—this system will allow an expert user to perform the same kind of analysis (as SK) at a faster rate than previously possible.

ACKNOWLEDGMENTS

The authors thank Mark Kushner for providing the GLOBALKIN code. This work was supported by the U.K. Engineering and Physical Sciences Research Council.

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