PumpKin: A tool to find principal pathways in plasma chemical models

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Introduction

We have developed a software tool called 
PumpKin (pathway reduction method for plasma kinetics) to find all principal pathways, i.e. the dominant reaction sequences, in chemical reaction systems [1]. The goal is to explain, understand and eventually reduce complex plasma chemistry models. PumpKin is a universal tool, which only requires from the user the temporal profile of the densities of species and the reaction rates, as well the stoichiometric matrix of the system. Also, the user should specify the timescale of interest. Our approach is based on algorithm described in [9]. PumpKin is freely available at www.pumpkin-tool.org.

Physical model

The time evolution of the species densities in a plasma can be written as a set of coupled rate equations:

\[ \frac{d[n_i]}{dt} = \sum_{j=1}^{p} R_{ij}(t) \]

where \(n_i\) is the densities of species \(i = 1, \ldots, n_s\) and the source terms \(R_{ij}\) correspond to the contributions from different processes. Electron transport and rate coefficients can be obtained, for instance, from the BOLSIG+ solver.

Recently many non-commercial [2,3,4] and commercial [5] packages have been developed to follow the time evolution of the species densities and gas temperature in non-thermal plasmas with complex chemistry.

The typical output of [2] is the temporal evolution of reduced field, gas and electron temperatures, density of species, reaction source rates and reaction-specific production rates of species for sensitivity analysis. Depending on the complexity of the chemical model, output can be around 100 Mb of raw data.

Tools like QPlasKin [6] are developed to analyze the results from a plasma kinetic code such as ZPlasKin, Global_Kin in a GUI (graphical user interface).

Example

As an example, we take dry air (N₂O = 80:20) at STP [1]. We use ZPlasKin plasma kinetic solver to simulate post-discharge kinetics. Maximum electric field is 460 Td and pulse duration is 250 ns. Simulation total duration is 1 s. We use kinetics from [2], containing 53 species and 650 reactions. The time dependent electric field is obtained. Initial electron density is taken as 6.4 e¹⁹ cm⁻³. We choose NO as the species of interest.

Reduce

If the user has no species as the species of interest, then he/she can specify the maximum number of the most important pathways (or reactions). For a given (simulation) time interval, PumpKin will return the most important pathways sorted by the rate of pathway. For example, in the time interval of [3.0e-7, 1.0e-5] the first 9 pathways of output are:

- \( \ce{O2 + N2 <--> O3 + O + N2} \)
- \( \ce{O2 + O2 + M <--> O3 + M} \)
- \( \ce{O2 + O2 + M <--> O3 + 2O} \)
- \( \ce{O + O2 + N <--> N + O3 + O} \)
- \( \ce{O3 + O2 + N <--> NO + NO2 + O} \)
- \( \ce{O2 + 2O2 + O <--> 3O2} \)
- \( \ce{O2 + O2 + M <--> 2O3} \)
- \( \ce{e + 2O2 + M <--> O3 + O2} \)
- \( \ce{O2 + O2 + M <--> O3 + e} \)

Explain

If the user is interested in a species like NO in post-discharge phase after 1.0e-5 s, then air kinetics can be reduced down to the following 7 reactions, out of initial 650:

- Production: \( \ce{NO2 + O <--> NO + O2} \)
- Net: \( \ce{N2 + 2O2 <--> 2NO + 3O + e} \)
- Destruction: \( \ce{O2 + NO <--> NO2 + O} \)
- Net: \( \ce{3NO2 + N2 <--> NO + NO2 + NO + N} \)

PumpKin tool

The growing interest in plasma chemistry significantly increases the complexity of chemical models. Recent kinetic models of atmospheric chemistry [7] or of industrial applications [8] contain thousands of chemical reactions and species. Here one should take into consideration that different species have different lifetimes, reaction reaction rates depend on externally applied electric field as well as on temperature. As a result, researchers and engineers are facing with the problem of evaluating very complex models. In some cases, it is crucial to be able to reduce the chemical reaction system to more compact chemical pathways, which will have much less reactions and will consider less species. For example, such techniques have been successfully applied in atmospheric chemistry to investigate ozone destruction [9].

In the present work we have developed the software PumpKin to find all principal pathways, i.e. the important reaction sequences. The user should solve first the full chemical reaction system, but only once. The output is later used as an input for PumpKin. Pseudocode of PumpKin algorithm is the following:

\[ \text{begin} \]
| read input files |
| initialize pathways := individual pathways |
| repeat |
| choose fast species \$S\$ merge pathways producing \$S\$ with pathways consuming \$S\$ |
| delete insignificant pathways |
| determine and split sub-pathways |
| until there are no fast species \$S\$ remaining |
\[ \text{end} \]

References