PLASIMO global model of a CO₂ plasma

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Abstract: A zero-dimensional global model of a CO₂ plasma is realised using the plasma modeling platform PLASIMO. The aim of the model is to study the chemistry for application of advanced chemical reduction techniques and application in spatially resolved models.

Keywords: Global model, CO₂.

1. Introduction

In recent decades, concerns about climate change have sparked interest into reducing CO₂ emissions. Combined with diminishing fossil fuel reserves, demand for alternative forms of energy is on the rise in society and general industry. However, many forms of alternative energy depend on nature and therefore fail to deliver consistently and reliably.

Both problems can be tackled simultaneously by converting CO₂ into fuels that can directly replace fossil fuels. One mechanism for achieving this is plasma assisted CO₂ conversion. The aim is to use a plasma source to convert CO₂ into CO, which can then be converted in for example methanol in subsequent processes.

For this particular application several plasma sources are under investigation, and an important part of this research is modelling. However, the presence of multiple molecules with many different excited states (most notably vibrational) in this kind of plasma, makes the chemistry quite complex and therefore hard to model.

The goal of this research is to investigate the CO₂ chemistry, and to determine main reaction paths and species. The aim is to also investigate the applicability of advanced reduction techniques such as Intrinsic Low Dimensional Manifold (ILDM) [1] and Principal Component Analysis (PCA) [2]. The knowledge gained can be used to implement a reduced but accurate chemistry in spatially resolved models.

The first step is to implement an extensive CO₂ chemistry in a global model.

2. Global Model

A spatially resolved plasma model containing a large amount of species and reactions is a challenge with respect to its computational demand. Therefore, the employment of a global model is favourable, since it allows for time resolved calculations while still being manageable when it comes to the required computational effort. The model is realised using the plasma modelling platform PLASIMO [3]. PLASIMO is a framework for modelling low-temperature plasma sources, which has been developed at the Eindhoven University of technology. Its global model module is used for the current study.

The global model does not calculate physical quantities spatially resolved but averaged over a certain volume. This means no transport throughout the plasma is included, allowing for a complex chemistry containing many species and reactions. Although the PLASIMO global model module allows for transport processes into and out of the plasma volume, such as diffusion and flow, they are not included in the model, so only the bulk chemistry is modelled.

The module calculates the species densities and electron energy density as function of time. The calculation is an initial value problem defined by differential equations. For each included species this equation reads

$$\frac{d}{dt} n_s = S_s,$$

where \(n_s\) and \(S_s\) are the density and source of species \(s\), respectively. The source is calculated from the reactions defined in the model by

$$S_s = \sum_{r} \left( (v^r_{s_i} - v^r_{s_f}) k_r \prod_{i} (n_i)^{v^r_{i}} \right),$$

where \(v^r_{s_i}\) and \(v^r_{s_f}\) are the right-hand and left-hand side stoichiometric coefficients of reaction \(r\) for species \(s\), and \(k_r\) is the accompanying rate coefficient. The sum runs over all reactions in which species \(s\) is involved, and the product includes all species \(i\) included in the reaction.

For the electron energy density the differential equation is

$$\frac{d}{dt} \left( \frac{3}{2} n_e k_B T_e \right) = P_{input}(t) - Q_{inelas} - Q_{elas},$$

where \(n_e\) and \(T_e\) are the electron density and temperature, \(k_B\) is the Boltzmann constant, \(P_{input}\) is the input power, and \(Q_{inelas}\) and \(Q_{elas}\) are inelastic and elastic energy losses.

The set of equations is then solved using an ode solver, given a set of initial densities.

The inputs required by the module are a description of the chemistry, i.e., the species and reactions involving the species with accompanying rate coefficients, and the input power. The input power is a function of time and can have any desired shape. The rate coefficients can be functions
of the electron energy, but can also be defined by cross sections. For instance, in the case of an electron excitation the rate coefficient is calculated given the current electron energy distribution as defined by the current electron temperature. This means that at all times a Maxwellian distribution of the electron energy is assumed.

3. Chemistry
The chemistry is based on the work of Kozák et al. [4], which in turn is based on Aerts et al. [5]. The models mainly differ in the amount of vibrationally excited species that are included. The chemistry included by Kozák is listed in table 1. In Aerts only a single asymmetric vibrationally excited CO\textsubscript{2} species and one vibrationally excited CO level are included.

<table>
<thead>
<tr>
<th>Neutrals, radicals</th>
<th>CO\textsubscript{2}</th>
<th>CO</th>
<th>C\textsubscript{2}O</th>
<th>C</th>
<th>C\textsubscript{2}</th>
<th>O</th>
<th>O\textsubscript{2}</th>
<th>O\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive ions</td>
<td>CO\textsuperscript{4+}</td>
<td>CO\textsuperscript{+}</td>
<td>O\textsuperscript{2+}</td>
<td>C\textsubscript{2}O\textsuperscript{2+}</td>
<td>C\textsubscript{2}O\textsubscript{3+}</td>
<td>C\textsubscript{2}O\textsubscript{4+}</td>
<td>C\textsuperscript{+}</td>
<td>C\textsubscript{2}\textsuperscript{+}</td>
</tr>
<tr>
<td>Negative ions</td>
<td>CO\textsuperscript{-}</td>
<td>CO\textsuperscript{2-}</td>
<td>O\textsuperscript{-}</td>
<td>O\textsuperscript{2-}</td>
<td>O\textsuperscript{3-}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Excited states</td>
<td>CO\textsubscript{2}v\textsubscript{1}</td>
<td>CO\textsubscript{2}v\textsubscript{2}</td>
<td>CO\textsubscript{2}v\textsubscript{3}</td>
<td>CO\textsubscript{2}v\textsubscript{4}</td>
<td>CO\textsubscript{2}v\textsubscript{5}</td>
<td>CO\textsubscript{2}v\textsubscript{6}</td>
<td>CO\textsubscript{2}v\textsubscript{7}</td>
<td>CO\textsubscript{2}v\textsubscript{8}</td>
</tr>
</tbody>
</table>

The goal is to include the complete chemistry as used by Kozák, but in the first iteration of our model we will restrict ourselves to the chemistry as used by Aerts. Both works report the complete set of reactions in which for the excited species shifted cross sections and scaling laws for rate coefficients are used.

4. Conclusion
Evidently, the chemistry is quite complex, and any spatially resolved modelling is hardly feasible. Reducing this chemistry to an accurate lean representation is far from straightforward. To that end the applicability of the ILDM method is investigated. By categorizing the chemistry according to reaction speed, this method can identify the trajectory towards which the system will move on short timescales, and along which the system will subsequently evolve. This trajectory is a so-called manifold representing a lower dimensional space that fully describes the chemistry on sufficiently long time scales. After the complete chemistry has been realised in the global model, the aim is to apply the ILDM technique to obtain a leaner chemistry, so a comparison between the two chemistries can be made.

5. References