

Stoichiometric projection methods for plasma simulations

C.E.M. Schoutrop¹, J.H.M. ten Thije Boonkamp², W.A.A.D. Graef³, J. van Dijk¹

¹*Department of Applied Physics, Eindhoven University of Technology*

²*Department of Mathematics and Computer Science, Eindhoven University of Technology*

³*Plasma Matters B.V, Eindhoven*

Abstract: A method for exploiting stoichiometry in chemically reacting flows, as previously applied to porous media [6,7] is put in the framework of plasma physics. By taking linear combinations of the governing conservation laws, the original system is transformed to a new, equivalent system. Where several differential equations become homogeneous. This explicitly captures conserved quantities, and may allow for application of simpler discretization schemes to part of the system without loss of accuracy.

Keywords: Numerical simulation, orthogonal projection, stoichiometric transformation

1. Introduction

Renewable forms of electricity generation have the property that they are not always available. Moreover, not all energy is consumed as electricity. Traditional generation methods, like the combustion of fossil fuels, can assist to close the gap between supply and demand. However, these methods are polluting, which is detrimental to the environment.

An alternative is to spend excess electricity produced from renewable sources to decompose CO₂ into CO. The produced CO can be used as a base ingredient for the production of carbon-based fuels via the Fischer-Tropsch process [1]. Such fuels present a fully carbon-neutral storage medium for energy, compatible with existing infrastructure.

A promising method for the decomposition of CO₂ is a microwave plasma reactor. Additionally processes such as vibrational laddering could play a role in the dissociation [1,2]. The dissociation fraction of CO₂ with microwave plasmas at time of writing varies; 9% [3], 37% [4]. Energy efficiencies of 23% have been achieved [4]. One of the tools for optimizing dissociation fraction and efficiency, and gaining further insight in the decomposition of CO₂ by microwave plasmas is numerical simulation.

However, a fully resolved numerical simulation of such a system is challenging. The complex reaction mechanisms, stiff equations and high dimensionality present a challenge even on modern, high-end hardware.

Here a transformation of the underlying system of equations is presented. By combining the governing conservation laws, a new set of equations is obtained with explicit species conservation built in. This transformation eliminates several source terms, as a result part of the new system can be exploited with simpler discretization schemes. The resulting system could then be solved by a method similar to Gummel iteration [5].

Furthermore if the transport operator is linear, the transformation leads to a partial decoupling of the underlying system of differential equations. Additionally there exist special cases in which transformed densities are constant altogether. These effects may result in more favorable numerical properties.

Here the method is illustrated for an argon case, however it can be generalized in a straightforward manner.

2. Conservation laws

Consider a system consisting of the Ar atom, Ar⁺ ion and the electron e⁻. Here only one forward-backward reaction set is needed (1):



The generic form of a set of the conservation laws reads:

$$\frac{\partial \mathbf{n}}{\partial t} + \nabla \cdot \vec{\Gamma}(\mathbf{n}) = \mathbf{S}\mathbf{R}(\mathbf{n}). \quad (2)$$

Here \mathbf{n} is a vector of species number densities, and $\vec{\Gamma}$ is a matrix containing the components of the fluxes. For the argon system these are, (3):

$$\mathbf{n} = \begin{bmatrix} n_{\text{Ar}^+} \\ n_{\text{Ar}} \\ n_{e^-} \end{bmatrix}, \quad \vec{\Gamma} = \begin{bmatrix} \vec{\Gamma}_{\text{Ar}^+} \\ \vec{\Gamma}_{\text{Ar}} \\ \vec{\Gamma}_{e^-} \end{bmatrix}. \quad (3)$$

The quantity \mathbf{S} in equation (2) represents the stoichiometric matrix and \mathbf{R} the rate vector. For the argon case these are given by (4);

$$\mathbf{S} = \begin{bmatrix} 1 \\ -1 \\ 1 \end{bmatrix}, \quad \mathbf{R} = [R(\mathbf{n})]. \quad (4)$$

The matrix \mathbf{S} can be interpreted as: "for every Ar^+ produced, one Ar is consumed and one e^- is released". Since there is only one reaction, the vector \mathbf{R} is a vector of size 1.

For clarity of presentation the 1D conservation equation is examined here (5):

$$\frac{\partial \mathbf{n}}{\partial t} + \frac{\partial \Gamma(\mathbf{n})}{\partial x} = \mathbf{S}\mathbf{R}(\mathbf{n}). \quad (5)$$

3. Stoichiometric transformation

The idea is to take linear combinations of the equations (5), in order to capture conserved quantities in the resulting set of equations. To do this stoichiometry is utilized. In the argon system with three species present (Ar^+ , Ar and e^-), and one reaction. Two "building blocks" can be identified from which the remaining species can be formed. Such building blocks would have the property that they cannot be created, nor destroyed in chemical reactions. One way to exploit this concept for the argon system would be to take linear combinations in the following way:

$$\frac{\partial (n_{\text{Ar}^+} + n_{\text{Ar}})}{\partial t} + \frac{\partial (\Gamma_{\text{Ar}^+} + \Gamma_{\text{Ar}})}{\partial x} = 0, \quad (6a)$$

$$\frac{\partial (n_{\text{Ar}^+} - n_{e^-})}{\partial t} + \frac{\partial (\Gamma_{\text{Ar}^+} - \Gamma_{e^-})}{\partial x} = 0, \quad (6b)$$

$$\frac{\partial n_{\text{Ar}}}{\partial t} + \frac{\partial \Gamma_{\text{Ar}}}{\partial x} = -R(\mathbf{n}). \quad (6c)$$

Note that two source terms are 0, indicating no production or destruction. The first equation (6a) indicates conservation of the amount of argon ($n_{\text{Ar}^+} + n_{\text{Ar}}$), the second (6b) indicates that charge $e(n_{\text{Ar}^+} - n_{e^-})$ cannot be produced or destroyed. Here e is the elementary charge. In a way the transformed variables, the *total* amount of argon, and the *total* amount of charge can be seen as fundamental building blocks to construct the remaining species; argon.

To construct such a linear combination in general, a method previously utilized in the context of porous media [6,7] is applied to plasmas. Here a closer look is taken at the stoichiometry given by the matrix \mathbf{S} in equation (4). From this, two other matrices are constructed, \mathbf{S}^* and \mathbf{S}^\perp . The matrix \mathbf{S}^* contains all linearly independent columns of \mathbf{S} and \mathbf{S}^\perp is an orthogonal complement to \mathbf{S}^* . I.e., the columns of \mathbf{S}^\perp are orthogonal to the columns of \mathbf{S}^* . Additionally \mathbf{S}^\perp must be constructed such that its columns are also linearly independent. However, note that for a general reaction network \mathbf{S}^* and \mathbf{S}^\perp are not unique. For the argon example, a possible set is given by (7):

$$\mathbf{S}^* = \begin{bmatrix} 1 \\ -1 \\ 1 \end{bmatrix}, \quad \mathbf{S}^\perp = \begin{bmatrix} 1 & -1 \\ 1 & 0 \\ 0 & 1 \end{bmatrix}. \quad (7)$$

Furthermore, also a matrix \mathbf{A} is defined, such that $\mathbf{S} = \mathbf{S}^*\mathbf{A}$. Matrix \mathbf{A} constructs \mathbf{S} from the linearly independent columns \mathbf{S}^* . The idea is to project the original densities \mathbf{n} and fluxes Γ on a subspace, and a subspace orthogonal to that subspace. To do this the equations (5) are multiplied from the left by the matrices

$$(\mathbf{S}^{*T}\mathbf{S}^*)^{-1}\mathbf{S}^{*T} = \frac{1}{3} \begin{bmatrix} 1 & 2 & 1 \\ -1 & 1 & 2 \end{bmatrix}, \quad (8)$$

and by

$$(\mathbf{S}^{\perp T}\mathbf{S}^\perp)^{-1}\mathbf{S}^{\perp T} = \frac{1}{3} \begin{bmatrix} 1 & -1 & 1 \end{bmatrix}, \quad (9)$$

respectively. Here $\mathbf{S}^{*T}\mathbf{S}^*$ and $\mathbf{S}^{\perp T}\mathbf{S}^\perp$ are invertible, since the columns of both \mathbf{S}^* and \mathbf{S}^\perp are linearly independent. The matrices (8) and (9) can be viewed as a special case of the Moore-Penrose inverse for matrices \mathbf{S}^* and \mathbf{S}^\perp . Namely the case where \mathbf{S}^* and \mathbf{S}^\perp have full column rank.

Note that the term $\mathbf{S}\mathbf{R}$ can be written as $\mathbf{S}^*\mathbf{A}\mathbf{R}$, and by definition of the orthogonal complement;

$$\mathbf{S}^{\perp T}\mathbf{S}^* = 0, \quad \mathbf{S}^{*T}\mathbf{S}^\perp = 0. \quad (10)$$

It then follows that the right hand side of equation (5) reduces to:

$$(\mathbf{S}^{\perp T}\mathbf{S}^\perp)^{-1}\mathbf{S}^{\perp T}\mathbf{S}^*\mathbf{A}\mathbf{R} = \mathbf{0}, \quad (11)$$

for the first set, and

$$(\mathbf{S}^{*T}\mathbf{S}^*)^{-1}\mathbf{S}^{*T}\mathbf{S}^*\mathbf{A}\mathbf{R} = \mathbf{A}\mathbf{R}, \quad (12)$$

for the second set. Additionally the new, transformed densities are introduced, the first set and second set become:

$$\boldsymbol{\xi} = (\mathbf{S}^{*T}\mathbf{S}^*)^{-1}\mathbf{S}^{*T}\mathbf{n}, \quad (13a)$$

$$\boldsymbol{\eta} = (\mathbf{S}^{\perp T}\mathbf{S}^\perp)^{-1}\mathbf{S}^{\perp T}\mathbf{n}. \quad (13b)$$

A set analogous to equations (13a) and (13b) is defined for the fluxes.

Then the left-multiplication of equation (5) with (8) and (9) respectively yields:

$$\frac{\partial \boldsymbol{\eta}}{\partial t} + \frac{\partial \Gamma_{\boldsymbol{\eta}}}{\partial x} = \mathbf{0}, \quad (14a)$$

$$\frac{\partial \boldsymbol{\xi}}{\partial t} + \frac{\partial \Gamma_{\boldsymbol{\xi}}}{\partial x} = [\mathbf{A}\mathbf{R}(\mathbf{n})]_{\boldsymbol{\xi}}. \quad (14b)$$

Here $[\mathbf{A}\mathbf{R}(\mathbf{n})]_{\boldsymbol{\xi}}$ indicates the $\boldsymbol{\xi}$ -component of $[\mathbf{A}\mathbf{R}(\mathbf{n})]$. The transformed densities and fluxes are given by;

$$\boldsymbol{\eta} = \frac{1}{3} \left(\begin{bmatrix} 1 \\ -1 \end{bmatrix} n_{Ar^+} + \begin{bmatrix} 2 \\ 1 \end{bmatrix} n_{Ar} + \begin{bmatrix} 1 \\ 2 \end{bmatrix} n_{e^-} \right), \quad (15a)$$

$$\boldsymbol{\Gamma}_\eta = \frac{1}{3} \left(\begin{bmatrix} 1 \\ -1 \end{bmatrix} \Gamma_{Ar^+} + \begin{bmatrix} 2 \\ 1 \end{bmatrix} \Gamma_{Ar} + \begin{bmatrix} 1 \\ 2 \end{bmatrix} \Gamma_{e^-} \right), \quad (15b)$$

and the corresponding $\boldsymbol{\xi}$ set:

$$\boldsymbol{\xi} = \frac{1}{3} (n_{Ar^+} - n_{Ar} + n_{e^-}), \quad (16a)$$

$$\boldsymbol{\Gamma}_\xi = \frac{1}{3} (\Gamma_{Ar^+} - \Gamma_{Ar} + \Gamma_{e^-}). \quad (16b)$$

The resulting system, equations (14), is unfortunately not as clear in terms of the physical insight as (6). However, it does have the benefit that the reverse transformation from $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$ is guaranteed to exist, and is of the simple form [6]:

$$\mathbf{n} = \mathbf{S}^* \boldsymbol{\xi} + \mathbf{S}^\perp \boldsymbol{\eta}, \quad (17)$$

for the densities. For the fluxes a similar transformation holds:

$$\boldsymbol{\Gamma} = \mathbf{S}^* \boldsymbol{\Gamma}_\xi + \mathbf{S}^\perp \boldsymbol{\Gamma}_\eta. \quad (18)$$

Alternatively a linear combination could be obtained in terms of a matrix \mathbf{M} previously studied in the specific context of LTE-plasmas [8]:

$$\mathbf{M} = \begin{bmatrix} \mathbf{S}^{*T} \\ \mathbf{S}^{\perp T} \end{bmatrix} = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 1 & 0 \\ -1 & 0 & 1 \end{bmatrix}, \quad (19)$$

with the transformation

$$\begin{bmatrix} \boldsymbol{\xi} \\ \boldsymbol{\eta} \end{bmatrix} = \mathbf{M} \mathbf{n}, \quad \mathbf{n} = \mathbf{M}^{-1} \begin{bmatrix} \boldsymbol{\xi} \\ \boldsymbol{\eta} \end{bmatrix}, \quad (20)$$

which may be utilized to gain more favorable properties. Furthermore, since the orthogonal complement \mathbf{S}^\perp is not unique, there may be a specific construction that allows for more physical, or other properties to be incorporated. As opposed to applying a more generic transformation in terms of equations (8) and (9).

4. Applications of transformed system

The benefit of the transformed system (12) is that conservation of ‘‘building blocks’’ is explicitly incorporated into the structure of the differential equations.

Furthermore, the absence of a source term allows for the use of simpler discretization schemes for several equations. Such as the homogeneous flux scheme, instead of the more general complete flux scheme [9,10]. This may lead to less overhead when solving the system numerically, while still taking the ‘‘source term’’ into account exactly in the $\boldsymbol{\eta}$ -set of equations, equation (14a).

The entire set of $\boldsymbol{\eta}$ and $\boldsymbol{\xi}$ equations could be solved by a method similar to Gummel iteration [5]. By first solving the $\boldsymbol{\eta}$ -set, and substituting the corresponding number densities in the set of $\boldsymbol{\xi}$ -equations. Then the result of the $\boldsymbol{\xi}$ -part is then substituted back into the $\boldsymbol{\eta}$ -equations, and so on until convergence is achieved.

By first solving the homogeneous part, substituting the result in the inhomogeneous part and solving the second set. Then the inhomogeneous result is substituted back into the homogeneous set and so on until convergence is achieved.

Additionally if the fluxes $\boldsymbol{\Gamma}$ are linear functions of the species number densities \mathbf{n} , then the homogeneous equations in (14a) are also decoupled.

Finally, by taking specific linear combinations one may exploit quantities that not only have no source, but are constant as well. For example, if specific boundary conditions are imposed on equations (6) such that a closed system is obtained, it follows that:

$$n_{Ar^+} - n_{e^-} = const, \quad (21)$$

indicating conservation of charge. Furthermore, in such a case:

$$n_{Ar} + n_{Ar^+} = const, \quad (22)$$

as there would be no gain/loss of argon atoms.

5. Outlook

A further step could be to apply a time-scale analysis using a Schur-decomposition analysis, similar to [11]. Here the timescales of the reactions present in the system are investigated. However, such analysis should be applied to the transformed system. The idea of the resulting time scale analysis is to replace the fast reactions by an equilibrium condition. Hence some differential equations may be replaceable by an algebraic equilibrium condition.

6. Conclusions

A method previously applied to porous media has been examined for computational plasma physics [6,7]. Linear combinations of the governing conservation equations are taken, such that several components of the original system have their source term eliminated. This yields explicit expressions for conserved quantities. Furthermore, this also allows for (simpler) numerical schemes to be applied without loss of accuracy.

In the case of a linear flux, partial decoupling of the equations can also be obtained. In special cases the linear combinations may even lead to (transformed) species that are constant in space and time. An additional method for taking linear combinations, and a method to analyze the resulting system based on a timescales is outlined.

7. Acknowledgements

This research is supported by the Netherlands Organisation for Scientific Research (NWO), which is partly funded by the Ministry of Economic Affairs. And The Netherlands eScience Center in the framework of the JCER program. The Netherlands eScience Center is funded by NWO and SURF.

8. References

- [1] van den Bekerom, D. C. M. (2018). Vibrational excitation for efficient chemistry in CO₂ microwave plasmas
- [2] Aerts, R., Martens, T., & Bogaerts, A. (2012). Influence of Vibrational States on CO₂ Splitting by Dielectric Barrier Discharges. *The Journal of Physical Chemistry C*, 116(44), 23257-23273. doi:10.1021/jp307525t
- [3] Vesel, A., Mozetic, M., Drenik, A., & Balat-Pichelin, M. (2011). Dissociation of CO₂ molecules in microwave plasma. *Chemical Physics*, 382(1-3), 127-131. doi:10.1016/j.chemphys.2011.03.015
- [4] Belov, I., Vermeiren, V., Paulussen, S., & Bogaerts, A. (2018). Carbon dioxide dissociation in a microwave plasma reactor operating in a wide pressure range and different gas inlet configurations. *Journal of CO₂ Utilization*, 24, 386-397. doi:10.1016/j.jcou.2017.12.009
- [5] Gummel, H. (1964). A self-consistent iterative scheme for one-dimensional steady state transistor calculations. *IEEE Transactions on Electron Devices*, 11(10), 455-465. doi:10.1109/t-ed.1964.15364
- [6] Krättele, S., & Knabner, P. (2005). A new numerical reduction scheme for fully coupled multicomponent transport-reaction problems in porous media. *Water Resources Research*, 41(9). doi:10.1029/2004wr003624
- [7] Krättele, S., & Knabner, P. (2007). A reduction scheme for coupled multicomponent transport-reaction problems in porous media: Generalization to problems with heterogeneous equilibrium reactions. *Water Resources Research*, 43(3). doi:10.1029/2005wr004465
- [8] Rini, P., Vanden Abeele, D., & Degrez, G. (2005). Closed form for the equations of chemically reacting flows under local thermodynamic equilibrium. *Physical Review E*, 72(1). doi:10.1103/physreve.72.011204
- [9] Ten Thije Boonkkamp, J. H., & Anthonissen, M. J. (2010). The Finite Volume-Complete Flux Scheme for Advection-Diffusion-Reaction Equations. *Journal of Scientific Computing*, 46(1), 47-70. doi:10.1007/s10915-010-9388-8
- [10] Ten Thije Boonkkamp, J. H., Van Dijk, J., Liu, L., & Peerenboom, K. S. (2012). Extension of the Complete Flux Scheme to Systems of Conservation Laws. *Journal of Scientific Computing* doi:10.1007/s10915-012-9588-5
- [11] Rehman, T. (2018). Studies on plasma-chemical reduction.