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Modelling of Transport in Non-Equilibrium Atmospheric Plasmas

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In traditional low-pressure plasma modelling, the transport of the species of interest is described relative to a stationary and uniform background gas, like helium or argon. The transport flux densities are commonly modelled with a Fick-like diffusion term, augmented with a drift contribution for the charged species.

Some modern applications share the non-thermal nature with those discharges, but operate at much higher pressures and are created in flowing compound gases, like air. Examples are the discharges that are presently being considered for biomedical plasma applications. As a result, gas heating can play a role and the concept of a static, abundant background gas may no longer apply.

Consequently, existing low-pressure gas discharge models cannot be used unaltered for the simulation of such atmospheric discharges. In this contribution, we will provide an overview of the challenges involved in the successful numerical simulation of such plasmas. The discussion will zoom in on the modelling of the species' transport fluxes. The conceptual problems of the drift-diffusion model in flowing plasmas will be explained, followed by a presentation of an alternative approach, which is based on the Stefan-Maxwell equations. Special attention will be paid to the numerical aspects of the transport algorithms and the novel discretisation method that we have developed.

Transport in Multi-Component Fluids

Let us consider a plasma that consists of several species, labelled s, with masses m_s, particle densities n_s and species-averaged velocities $\vec{u}_s$. The evolution of the species densities is governed by the particle balances

$$\frac{\partial n_s}{\partial t} + \nabla \cdot n_s \vec{u}_s = S_s, \tag{1}$$

where S_s is the net volumetric production rate of species s. If we multiply with m_s and define the species mass densities $\rho_s = m_s n_s$ and mass flux densities $\vec{J}_s = \rho_s \vec{u}_s$ we get

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot \vec{J}_s = m_s S_s. \tag{2}$$

Since no mass is produced or lost in reactions, summation yields the (mass) continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \vec{u} = 0, \tag{3}$$

where we have introduced the mass density and barycentric velocity field through the relations

$$\rho = \sum_s \rho_s, \tag{4}$$

$$\rho \vec{u} = \sum_s \vec{J}_s, \tag{5}$$

in that order. For a given mass density field ρ, the pressure and barycentric velocity fields can be calculated from the Navier-Stokes equations and the continuity equation (3).

So far, no significant assumptions have been made, other than that mass densities are additive, and that mass is conserved in chemical reactions. Most modelling effort goes into the specification of the species velocities $\vec{u}_s$, which will be discussed below. That said, the treatment above, and equation (5) in particular, teaches us an important constraint: whatever recipe we choose for calculating $\vec{u}_s$, the results ought to be such that the species mass fluxes add up to the product of the mass density and barycentric velocity field.

The species *diffusion velocities* $\vec{v}_s$ are defined as the velocities, measured relative to the barycentric velocity field,

$$\vec{v}_s = \vec{u}_s - \vec{u}. \tag{6}$$

This definition allows us to rewrite the species mass balances as

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot (\rho_s \vec{u} + \vec{J}_s^d) = m_s S_s, \tag{7}$$

where the diffusive mass fluxes have been introduced as

$$\vec{J}_s^d \equiv \rho_s \vec{v}_s. \tag{8}$$

From the previous relations it is readily found that the sum of the diffusive mass fluxes must vanish,

$$\sum_s \vec{J}_s^d = \vec{0}. \tag{9}$$

Now, do they?

Let us consider the simplified drift-diffusive model for the particle fluxes in a non-flowing plasma, where the mass flux densities are given by

$$m_s \left(\mu_s \vec{E} n_s - D_s \nabla n_s \right), \tag{10}$$

where μ_s is the mobility of species s, $\vec{E}$ the electric field, and D_s the species' diffusion coefficient. This expression does not respect any of the constraints above: firstly, the 'diffusion' fluxes $-m_s D_s \nabla n_s$ do not sum up to $\vec{0}$. Secondly, it is not clear how the effect of flow can be incorporated into the equation. Various studies simply add a 'flow velocity' —whatever that may be— to the drift velocity, to arrive at

$$m_s \left((\vec{u} + \mu_s \vec{E}) n_s - D_s \nabla n_s \right), \tag{11}$$

but again this is not consistent with the mass continuity equation (3).

The Stefan-Maxwell Equations

A more systematic approach is to use the Stefan-Maxwell equations, which establish relations between pairs of diffusive velocities,

$$\sum_p f_{sp} (\vec{v}_s - \vec{v}_p) = \vec{d}_s, \tag{12}$$

where $\vec{d}_s$ are the *driving forces* and the *friction coefficients* are given by $f_{sp} = n_s k T_s n_p k T_p / p^2 D_{sp}$, where the D_{sp} are the binary diffusion coefficients and k is Boltzmann's constant. If we consider one particular spatial component of all vectors, and bundle the component values for all species in 'vectors' like $\mathbf{v}$, we get the relation

$$\mathbf{F} \mathbf{v} = \mathbf{d}, \tag{13}$$

where the *friction matrix* $\mathbf{F}$ is a symmetric matrix with elements

$$F_{sp} = \begin{cases} \sum_{p \neq s} f_{sp} & \text{if } s = p, \\ -f_{sp} & \text{if } s \neq p. \end{cases} \tag{14}$$

Since the row (and column) sums of $\mathbf{F}$ vanish, the matrix cannot be inverted. The system of equations must be augmented with the constraint that the diffusive mass fluxes add up to 0. This can be done —and *has* been done by various authors— by simply replacing one of the Stefan

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Maxwell equations with equation (9). The result is a non-symmetric and possibly ill-conditioned system; in particular when the species that has been singled out has a low mass fraction. Therefore we recommend against this practice.

Instead, Giovangigli [1] has shown that a well-behaved system is obtained by incorporating the constraint (9) by adding a multiple of $y_s \sum_p y_p v_p = 0$ to each equation, where $y_s = \rho_s/\rho$ is the *mass fraction* of species s. The regularised friction matrix can be written as

$$\tilde{F}_{sp} = F_{sp} + \alpha y_s y_p, \quad \text{or} \quad \tilde{\mathbf{F}} = \mathbf{F} + \alpha \mathbf{y} \otimes \mathbf{y}, \tag{15}$$

where α is an arbitrary positive value, best chosen to be equal to a typical value of F_{ii}. The modified system is invertible and the diffusion velocities are obtained as

$$\mathbf{v} = \tilde{\mathbf{F}}^{-1}\mathbf{d}. \tag{16}$$

In the presence of ordinary, pressure, thermal and forced diffusion, the driving forces $\mathbf{d}$ can be expressed as a linear combination of the mass fractions and their gradients [1]. If we denote the components of the gradient of $\mathbf{y}$ as $\mathbf{y}'$, we may write

$$\mathbf{d} = \mathbf{A}\mathbf{y} + \mathbf{B}\mathbf{y}' \tag{17}$$

and arrive at

$$\mathbf{v} = \tilde{\mathbf{F}}^{-1}\left(\mathbf{A}\mathbf{y} + \mathbf{B}\mathbf{y}'\right). \tag{18}$$

By left-multiplying with the diagonal matrix $\mathrm{diag}(\rho_s)$ that contains the species' mass densities we obtain the diffusive mass fluxes $\mathbf{J}$. By adding the component of the convective mass fluxes of the species, $\rho_s u = \rho u y_s$, we find that the (total) mass fluxes can be written as

$$\mathbf{J} = \mathbf{C}\mathbf{y} + \mathbf{D}\mathbf{y}', \ \text{with} \ \mathbf{C} = \mathrm{diag}(\rho u) + \mathrm{diag}(\rho_s)\tilde{\mathbf{F}}^{-1}\mathbf{A} \ \text{and} \ \mathbf{D} = \mathrm{diag}(\rho_s)\tilde{\mathbf{F}}^{-1}\mathbf{B}. \tag{19}$$

Optionally, an ambipolar constraint can be incorporated in the system of equations, and also magnetised plasmas can be dealt with without essentially altering the structure of this equation. We will not elaborate on these possibilities in this text.

Discretisation and Solution of the System of Equations

From equation (19) we see that the mass flux density of an individual species s is given by

$$J_s = \sum_p \left(C_{sp} y_p + D_{sp} y'_p\right) \equiv \sum_p J_{sp}. \tag{20}$$

When solving the mass balance equation (2) in a control volume setting, we need to express the flux on a control volume boundary e (east), say, in terms of the values of $\mathbf{y}$ in the adjacent *nodal points*, here denoted as C and E. It is well-established that an ill-chosen *discretisation scheme*, like the central-difference scheme, leads to non-physical solutions when the flux is advection-dominated (high Péclet numbers). The Scharfetter-Gummel scheme does not have this drawback, and is therefore commonly used in the simulation of convection-diffusion phenomena.

Applying the classical Scharfetter-Gummel scheme to each term J_{sp} separately seems to be a reasonable approach at first sight and would lead to the flux approximation [2]

$$J_{sp}(x_e) \doteq \Delta x^{-1} D[B(-P_{sp}) y_p(x_C) - B(P_{sp}) y_p(x_E)], \tag{21}$$

where $B(P) = P(e^P - 1)^{-1}$ is the *Bernoulli function*, and $P_{sp} = \Delta x D_{sp}^{-1} C_{sp}$ is the grid Péclet number that characterises the importance of convection over diffusion, with $\Delta x = x_E - x_C$. The left graph in Fig. 1 shows the results of applying this scheme to a mixture of argon and hydrogen gas without source terms, in the presence of a flow field. The boundary fractions of argon and hydrogen are fixed. The results are dramatic: for small numbers of grid points (high Péclet numbers), non-physical oscillating results are obtained.

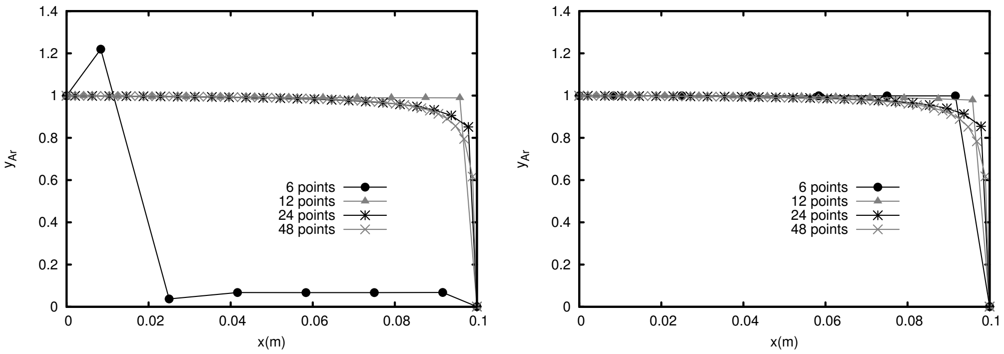

Fig. 1: The argon mass fraction in a mixture of argon and hydrogen with Dirichlet boundary conditions without sources. The scalar exponential scheme (left) yields unphysical non-monotonic results for large Péclet numbers, whereas the coupled scheme (right) is well-behaved unconditionally.

Obviously, our techniques for solving individual convection-diffusion equations fall short when applied to coupled equations. Therefore, a novel discretisation scheme has been developed. In this (coupled) *homogeneous flux scheme* [3, 2], the expression for the boundary flux at the interface point e between C and E is obtained as the analytical solution of the equation $\mathbf{J}'(\mathbf{y}) = \mathbf{0}$, subjected to the Dirichlet boundary conditions $\mathbf{y}(x_C) = \mathbf{y}_C$ and $\mathbf{y}(x_E) = \mathbf{y}_E$. In the derivation of the scheme it is assumed that the convection and diffusion matrices $\mathbf{C}$ and $\mathbf{D}$ are constant in the interval $[x_C, x_E]$. These assumptions, and the derivation of the scheme are analogous to those leading to the usual Scharfetter-Gummel scheme, but instead of a scalar Péclet number, a Péclet *matrix* $\mathbf{P}$ occurs in the final results,

$$\mathbf{P} = \Delta x \mathbf{D}^{-1}\mathbf{C}, \tag{22}$$

and the flux is given by

$$\mathbf{J}_e \doteq \Delta x^{-1}\mathbf{D}\left[\mathbf{B}(-\mathbf{P})\mathbf{y}_C - \mathbf{B}(\mathbf{P})\mathbf{y}_E\right], \tag{23}$$

where $\mathbf{B}(\mathbf{P}) = \mathbf{P}\left(\exp(\mathbf{P}) - \mathbf{I}\right)^{-1}$ is the *matrix* Bernoulli function. Note that the scheme has exactly the same mathematical structure as the original Scharfetter-Gummel scheme, the difference being that scalar algebra has made way for expressions involving matrices. The second graph in Fig. 1 shows that the novel scheme gives realistic results even for limited numbers of grid points (high Péclet numbers). The mathematical proof that this is always the case is beyond the scope of the present text; for details we refer to Refs. [2] and [3], which also present a rigorous derivation.

Summary

Atmospheric plasmas of present interest require that the drift-diffusion concept originating from low-pressure plasma physics is revised to take into account the effects of gas heating, flow and, possibly, the absence of a dominant, static background gas. This requires, among other things, that the species transport is modelled using a self-consistent approach, for example based on the Stefan-Maxwell equations. In the present work we have discussed the advantages of this approach, and elaborated on the numerical do's and dont's when this strategy is used.

References

[1] V. Giovangigli 1990 Impact Comput. Sci. Engrg. 2 73–97

[2] K.S.C. Peerenboom et al. 2010 *A coupled discretization method for the continuity equations in multi-component mixtures* submitted to the Journal of Computational Physics

[3] J.H.M. ten Thije Boonkkamp et al. 2010 The finite-volume-complete flux scheme for one-dimensional advection-diffusion-reaction systems. In preparation.