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The Coupling of PIC/MCC Models of Discharge Plasmas with Vibrational and Electronic Kinetics

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Abstract: A 1D in position and 2D in velocity Particle in Cell with Monte Carlo Collision model of a low-pressure nitrogen discharge plasma has been coupled to a 1D reaction-diffusion kinetics for the whole vibrational ladder of the N₂(X) state, for the vibrationally lumped N₂(A), N₂(B), N₂(C), N₂(a') states as well as for N atoms. The model includes several electron-molecule as well as molecule-molecule processes. The effect of the self-consistent coupling of the two models on the results in the case of a parallel-plate RF discharge is discussed for two different values of the RF frequency.

1. INTRODUCTION

Most non-equilibrium plasmas of interest are characterized by a large number of electrons in the Debye sphere: in these conditions the interaction between charged particles can be approximated by a particle-space charge field interaction. This point of view is assumed in the so-called Particle-in-Cell, or PIC approach [1-5]. The advantage of particle methods such as the PIC over macroscopic 'fluid' approaches is the possibility of calculating the electron energy distribution function, or eedf, f(ε). This function is defined in such a way that the fraction of electrons with kinetic energy between ε and ε+δε is given by ε₁/₂ f(ε) dε. It gives an information on the electron kinetics that cannot be summarised by any single macroscopic parameter in the non-equilibrium case, differently from the near-equilibrium one, where the translational energy is distributed according to the Maxwell-Boltzmann law, which is completely characterized by the translational temperature T. Despite the impressive power and success of PIC/MCC approach, in order to apply it to the free electrons in low temperature plasmas it is necessary to include the interaction between the gas chemistry and the electron dynamics in the non-equilibrium case; that is, including state-to-state chemical kinetics with all the relevant electron-molecule collisions. The most important effect of the interaction between vibro-electronics kinetics and free electron kinetics is due to the effect of the super-elastic, or second kind collisions of electrons with excited molecules in the discharge plasma, leading to a change in shape of the eedf and thereby influencing the values of the rate coefficients for the state-specific kinetics [6]. In the following the present status of a comprehensive coupled particle (1Dr2Dv) / continuum (1D) model for discharge plasmas in pure Nitrogen realized in the last two years will be described.

2. DESCRIPTION OF THE MODEL

In the PIC approach the Newton equations for a large ensemble (10⁴ - 10⁵ particles) of electrons and positive ions are solved taking into account the local electric field as it results from local interpolation within a cell of a mathematical mesh (from what follows the name 'Particle in Cell'). After any calculation step of the motion equations, the electric charge in any cell of the mesh is determined from the number of electrons and positive ions found in the cell itself. Known the electric charge density, the electric potential and field are determined by solving the Poisson Equation on the same mesh. Symbolically

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\[
\Delta \varphi(r) = -\rho(r) / \varepsilon_0 \\
E(r) = -\nabla \varphi(r) \\
\frac{d^2 r_i(t)}{dt^2} = (q / m_i)E(r) \\
(\mathbf{r}_i, q_i)_{\text{all particles}} \rightarrow \rho(r)
\] (1)

Any simulated particle is really a 'superparticle', characterized by a 'weight' \( w \) which must be taken into account when sampling particles to deduce the charge density \( \rho \) but does not affect the \( \frac{q}{m} \) ratio. Therefore 'superparticles' follow the same equation of motions of the physical electrons or ions but they contribute \( wq \) to the space charge.

In the following we will consider a 1D model in space, with two limiting surfaces at \( x=0 \) and \( x=L \). The mesh used for space charge and the Poisson equation consist on \( n+1 \) equispaced points at the positions \( jh \), with \( j=0,1,\ldots,n \), and \( h = \frac{L}{n} \) is the grid spacing.

To sample the particles in space we use the so-called CIC (Cloud-in-Cell) sampling which assigns the (super)particle charge \( wq \) to the two neighbouring grid points (one on the right and one on the left of the particle) in two fractions depending on the particle position, for any particle \( i \):

\[
jh \leq x_i \leq (j+1)h \\
Q(j+1) \leftarrow Q(j+1) + wq_i \frac{x_i - jh}{h} \\
Q(j) \leftarrow Q(j) + wq_i \frac{(j+1)h - x_i}{h}
\] (2)

where the index \( j \) labels the mesh cells while \( i \) runs over particles. The mesh-interpolated space charge is calculated from the quantities \( Q(j) \) as

\[
\rho(j) = (hS)^{-1}Q(j)
\] (3)

where \( S \) is the plasma cross section, which can be put equal to 1 (actually in a 1D system superparticles are infinitely thin 'sheaths' of charge, and the relevant charge density is a line density, measured in coulomb \( m^{-1} \). The factor \( S \) disappears when calculating \( E \) from \( \rho \). The same formulas must be used to weight (interpolate) the electric field acting on any particle, otherwise non-physical self-forces appear.

The Newton equations are solved using a simple scheme with interlaced grids for velocity and position, the so-called Leapfrog method:

\[
v'_i = v_i + \frac{q_i}{m_i}E(r, t)\Delta t \\
r'_i = r_i + v'_i \Delta t
\] (4)

Note that the difference with respect to the explicit Euler method is just the substitution of \( v \) with \( v' \) in the second equation. This simple method is excellent for PIC provided it operates within its stability domain \( \pi v_{pl} \Delta t < 1 \), where \( v_{pl} \) is the electron plasma frequency. The Poisson equation, is solved numerically. The grid spacing \( h \) selected must be not too much higher then the electron Debye length and possibly smaller, and at the same time sufficiently large to avoid average-speed electrons travelling more than \( h \) in a single timestep. In order to apply the PIC method to collisional discharge plasmas, the electron (ion) / neutral collisions must be included. The inclusion is realized by the test-particle, null-collision
Monte Carlo method. The overall simulation technique is called PIC/MCC, where MCC stands for Monte Carlo Collisions. PIC/MCC simulation of plasmas produced by high-frequency electric discharge has given results in remarkable agreement with experiments for what regards the electron dynamic quantities, in particular the eedf [7].

The cross section for the electron-null species collision is chosen to obtain a constant total collisions frequency $v_{\text{tot}}$, given by

$$v_{\text{tot}} = \max_A \left( \frac{2 \varepsilon}{m_e} \sum_p n_p(x) \sigma_p(\varepsilon) \right)$$

(5)

where the sum runs over collision process, $\sigma_p(\varepsilon)$ is the cross section and $n_p(x)$ the number density of the collision partner. The $A$ range is defined as $0 < x < L$ and $\varepsilon < \varepsilon_{\text{lim}}$, where $\varepsilon_{\text{lim}}$ is the limit of the scale of kinetic energy used to interpolate the cross sections. It is essential to maximize the frequency in space as well as in energy to calculate $v_{\text{tot}}$, since the gas composition is a function of position in the model. In this case the collision times are in fact distributed according to the law of free (flight) times

$$f(t) = v_{\text{tot}} \exp(-v_{\text{tot}} t)$$

(6)

and the time to the next collision can be calculated by

$$t_c = -v_{\text{tot}}^{-1} \ln \eta$$

(7)

where $\eta$ is an element of a set of random numbers uniformly distributed between the values 0 and 1. The kind of collision process (including the null one) which occurs after the free flight is also randomly selected according to the related collision frequencies. After any collision, the new electron energy and the scattering angle is easily determined depending on the nature of the collision itself. The new charged particle speed is calculated according to the energy loss (or gain, for an exothermic 'super-elastic' or 'second-kind' collision). Elastic collisions also contribute to the energy loss (gain) because a superthermal particle transfers an energy fraction about $2m_b/\hbar$ to the neutral, while subthermal particles are heated by elastic collisions with neutrals at the gas temperature $T$: this is important for ions in the bulk region of the RF discharge. 'Superelastic' collision cross sections are calculated from the corresponding inelastic one in order to guarantee a Maxwell eedf in the equilibrium case, by

$$g \varepsilon \sigma_{\text{sup}}(\varepsilon) = g^* (\varepsilon + \Delta \varepsilon) \sigma_{\text{in}} (\varepsilon + \Delta \varepsilon)$$

(8)

where $g$ and $g^*$ are the intrinsic statistical weight of the target molecule for the two processes.

Treatment of scattering is very simple if isotropic scattering is assumed:

$$\cos \vartheta = 1 - 2 \eta$$

$$\sin \vartheta = \sqrt{1 - \cos^2 \vartheta}$$

(9)

where $\eta$ is again a real random numbers in the (0,1) range, but in this case the elastic collision frequency must be calculated using the momentum transfer cross section in order to match the drift and diffusion coefficients in the energy space. In order to fit the Monte Carlo random collision times and the PIC timestep, the particle timestep flow-chart must be modified in order to allow collisions to take place at any intermediate time within the timestep, even more than once within a single PIC timestep [1]. The alternative method to treat collision events exactly at the end of the PIC timestep [3] is faster but can be used only for very low gas pressure (on the order of the mtorr). The code described in this paper as well
as in ref. [4,5] is based on the modified timestep cycle: any particle is represented by the set of numbers {i, r(i), v(i), t_c(i), f(i)}. Here i identifies the i-th simulated particle, r and v are the position and velocity vectors assigned to the particle, t_c is the time left to the next Monte Carlo collision event, and f is a flag representing the nature of the particle (electron or ion, f=0 is used for particles to be deleted from the simulation at subsequent steps).

Let us now describe the coupling of the code described above with the reaction-diffusion kinetics of neutrals (fig.1)

\[ v_{r1}A_1 + v_{r2}A_2 + \ldots \rightarrow v'_{r1}A_1 + v'_{r2}A_2 + \ldots \] (10)

must be updated by solving the equations for their reaction and diffusion kinetics, taking into account that the parameters entering these equations will not be constant, but on the contrary they will result by applying some linear functional to the local electron energy distribution function \( f(\varepsilon, x, t) \), this last is sampled on the kinetic grid from the PIC-MCC simulation. The grid used for the chemical kinetics is not the same as the one used for the Poisson equations. It consist of N grid points located at \( x_j = (j-1/2)H \), with \( j=1,\ldots,N \), where \( H=L/N \) is the grid spacing. Particles are assigned to the grid by the NGP (Nearest Grid Point) sampling:

for any particle i:

\[ (j-1)H \leq x_i \leq jH \]

\[ (k-1)\Delta \varepsilon \leq \varepsilon_i \leq k\Delta \varepsilon \]

\[ F_{j,k} \leftarrow F_{j,k} + w \]

where \( \Delta \varepsilon \) is the energy grid spacing, and \( \varepsilon_i \) the kinetic energy of the electron. The local eedf, particle density and mean energy are calculated from the function \( F_{j,k} \).
The treatment of ions is exactly the same.

In reacting plasmas usually the relaxation times of the chemical kinetics are by far higher that the corresponding ones for the electron kinetics, therefore an adiabatic approach to the solution for the steady state can be applied. Our method consists in solving the vibration and diffusion kinetics up to the steady state at different times \{t_n\} during the PIC-MCC simulation (which is by far more computationally expensive). At each \(t_n\) the space-dependent values of rate coefficients and electron density are obtained from the PIC-MCC, time-averaged over the period \(t_{n-1} - t_{n-1}\). The solution of the chemical and diffusion kinetics gives a new state-to-state composition and related electron-molecule collision frequencies for the PIC-MCC. The state-to-state gas composition is obtained differently for charged and neutral particles. Charged particle densities are in fact obtained by the PIC-MCC simulations. As for neutral densities, they are obtained by finding a stationary solution for the following set of non-linear, one-dimensional reaction and diffusion equations

\[
\frac{\partial n_s}{\partial t} = D_s \frac{\partial^2 n_s}{\partial x^2} + \sum_r (v'_{rs} - v_{rs})k_r \prod_{s'} n_{s'}^{v_{rs'}}
\]

which holds if the reactions (14) are elementary; otherwise the proper kinetic laws must be included. Here \(n_s\) is the particle density and \(D_s\) is the diffusion coefficient of the given species, while \(k_r\) is the rate coefficient of the \(r\)-th reaction and the product is extended to reactants only. The chemistry of gas molecules interacting with the reactor walls is connected with boundary conditions of the system. Let us consider only first order or pseudo first order reactions

\[
A_s \rightarrow v_{r1}A_1 + v_{r2}A_2 + \ldots
\]

taking place on surface, with probability \(p_{rs}\). The catalytic boundary conditions are:

\[
-D_s \left. \frac{\partial n_s}{\partial x} \right|_{x=0} = D_s \left. \frac{\partial n_s}{\partial x} \right|_{x=L} = -\sum_{rs} p_{rs} \phi_s + \sum_{r's'} p_{r's'} v_{r's'} \phi_{s'}
\]

where \(\phi_s\) is the thermal diffusion flux of \(A_s\) particles to the wall surface, given by

\[
\phi_s = (KT / 2\pi m_s)^{1/2} n_s (x = 0)
\]

for \(x=0\), and analogously for \(x=L\). Let us now consider some examples of chemical reactions included in the model. A typical example is the so-called mono-quantum VV or VT relaxation process

\[
\begin{align*}
\text{VV: } & N_2(v) + N_2(w) \rightarrow N_2(v-1) + N_2(w+1) \\
\text{VT: } & N_2(v) + N_2 \rightarrow N_2(v-1) + N_2
\end{align*}
\]
These processes have rate coefficients which depend on the vibrational status of the colliding molecules as well as on the translational temperature.

\[
\begin{align*}
    k_{VV} &= f(T, v, w) \\
    k_{VT} &= f(T, v)
\end{align*}
\] (20)

The explicit expression of \( k \) is calculated fitting by the SSH theory the results of molecular dynamics calculations, as in [8]. Another important class of chemical processes in plasmas is the eV one, i.e. the transition between two different states of a molecular species due to electron impact, for example:

\[
e + N_2(X, v) \rightarrow e + N_2(X, v')
\] (21)

The rate coefficient of the process in this case has a more complex expression because of the strongly non-Maxwellian shape of the electron energy distribution in typical cold plasmas. It depends on the whole \( \varepsilon (\varepsilon) \) and cannot be written as a function of macroscopic parameters, say the electron 'temperature'

\[
k = \sqrt{\frac{2}{m_e}} \int_0^\infty \varepsilon f(\varepsilon) \sigma(\varepsilon) d\varepsilon
\] (22)

where \( f \) is the electron energy distribution, \( m_e \) the electron mass and \( \sigma(\varepsilon) \) the cross section of the elementary process.

In the model described, the 1D reaction-diffusion equations after introducing the mesh is solved for the steady state by a partially-linearized Gauss-Seidel relaxation method [5].

3. CASE STUDY: RF DISCHARGE IN NITROGEN

The model was applied to a discharge in pure Nitrogen, produced into a parallel-plate high frequency reactor within the two plane electrodes. One of the plates (the so called 'grounded electrode') is constantly kept at zero voltage, while the other one (the 'powered electrode') is driven by an external generator, not explicitly simulated, to an oscillating voltage. This approximate treatment neglects the circuit as well the surface charge effects.

Table I: simulation parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF voltage</td>
<td>500</td>
</tr>
<tr>
<td>RF frequency (MHz)</td>
<td>13.5 (case a)</td>
</tr>
<tr>
<td>&quot;</td>
<td>27 (case b)</td>
</tr>
<tr>
<td>discharge gap (cm)</td>
<td>4</td>
</tr>
<tr>
<td>pressure (torr)</td>
<td>0.1</td>
</tr>
<tr>
<td>simulated particles</td>
<td>15000 (case a)</td>
</tr>
<tr>
<td>&quot;</td>
<td>36000 (case b)</td>
</tr>
<tr>
<td>timestep (s.)</td>
<td>(10^{-10})</td>
</tr>
<tr>
<td>simulation time (s.)</td>
<td>(3 \times 10^{-4})</td>
</tr>
<tr>
<td>PIC grid spacing (cm.)</td>
<td>0.01</td>
</tr>
<tr>
<td>kinetic grid spacing (cm.)</td>
<td>0.1</td>
</tr>
<tr>
<td>secondary emiss. coeff.</td>
<td>0</td>
</tr>
<tr>
<td>particle reflection coefficient</td>
<td>0</td>
</tr>
<tr>
<td>accomod. coeff. (vibrational)</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>accomod. coeff. (electronic)</td>
<td>1</td>
</tr>
</tbody>
</table>
The boundary conditions are accordingly

\[ \varphi(0,t) = 0 \]
\[ \varphi(L,t) = V_{\text{rf}} \cos 2\pi ft \]  \hspace{1cm} (23)

where \( f \) is the RF frequency. Only electrons and \( \text{N}_2^+ \) ions are moved as particles. The choice of the prevalent ion is discussed in [4]. Numerous electron-molecule collision processes are included, while for the ion/neutral we have included the elastic and charge transfer \( \text{N}_2^+/\text{N}_2 \) processes. Details are in [4,5]. As regards the simulation conditions, they are reported on Table I. Concerning the vibrational kinetics, the model includes 46 vibrational levels of \( \text{N}_2 \) and a 47th pseudo-level to take into account dissociation by the 'ladder-climbing' mechanism [6]. The e-V excitation processes of \( \text{N}_2 \) molecules have been included by using the formula (22) with scaled e-V cross section from the literature in order to cover the whole vibrational ladder. Details in ref. [4,5].

A simplified electronic kinetics of nitrogen molecules has also been included in the reaction/transport code. We considered the following electronic states: \( X^1\Sigma_g \) (ground state), \( A^3\Sigma \) (6.17 eV), \( B^3\Pi \) (7.35 eV), \( a^1\Sigma (8.40 \text{ eV}), C^3\Pi (11.03 \text{ eV}) \). The excited states are primarily produced in discharge conditions through electron-impact excitation processes. At the same time, bimolecular processes involving heavy particles collisions have been considered using the kinetic scheme of Garscadden and Nagpal [9], but taking into account the threshold of internal energy for the \( X \) partner in the \( A+X \rightarrow B+X \) reaction channel, i.e. we wrote

\[ \text{N}_2(X,v \geq 5) + \text{N}_2(A) \rightarrow \text{N}_2(B) + \text{N}_2(X) \]  \hspace{1cm} (24)

as shown experimentally by Piper [10]. This last point is very important because vibrational kinetics affects the electronic kinetics also through the strong dependence of the rate coefficient of reaction above on the vibrational temperature. Let us examine the results. Figure 2 shows the time-averaged electron and ion density at the steady state, while Figure 3 shows the result for the particle mean energy. The known phenomenological characteristics of the RF parallel plate discharge are displayed by the model results. High energy electrons are produced in the sheath region when they enter a 'contracted' sheath region and are consequently subjected to strong electric fields during the sheath expansion stage ('\( \alpha \) regime RF' discharge).

Figure 2: electron (full line) and ion (dashed line) density calculated at (a) 13.5 MHz and (b) 27 MHz
The fast electrons diffuse in the bulk, and as a result the mean electron energy in the bulk plasma is by far higher than the one which could be calculated by solving the quasi-isotropic, uniform Boltzmann Equation according to the bulk effective electric field ('non local' electron kinetics). At the same time, positive ions in the bulk plasma are at room temperature because of the effective energy exchange with neutrals, while they are accelerated up to quite high values of the mean energy close to the electrode surfaces. Furthermore, it can be observed the effect on the results of increasing the RF frequency. In a pure $\alpha$ regime as the one shown here the RF frequency $f$ is expected to have a strong effect on the discharge characteristics, since the sheath expansion frequency is equal to $f$ and the peak sheath expansion speed is an increasing function of $f$. It can be seen that, due to the larger energy depositions, the

Figure 3: electron (full line) and ion (dashed line) mean energy calculated at (a) 13.5 MHz and (b) 27 MHz. $\alpha$: full model, $\beta$: neglecting the change of gas composition on the PIC/MCC

Figure 4: electron energy distribution functions calculated at (a) 13.5 MHz and (b) 27 MHz. $\alpha$: bulk plasma, $\beta$: close to the left electrode ($x=0.8$ cm), $\gamma$: bulk plasma, but neglecting the change of gas composition on the PIC/MCC
bulk ionisation degree is larger. The ionisation degree is higher also in the sheath region, and consequently the peak sheath region extension is reduced: this kind of 'buffering' effect reduces the energy transfer to the bulk discharge, but the overall effect of increasing the RF frequency is by far higher pumping. In fig.4 it is shown time/averaged, steady state eedf calculated in two different positions in the discharge gap. As can be seen, the eedf near the electrode surface has a very long tail, which can be retraced in the high energy tail of the bulk plasma eedf, again confirming the strongly nonlocal conditions. In the same figure it is also shown the effect of the coupling of the PIC/MCC with the vibro-electronic kinetics, by comparison with a bulk plasma eedf calculated for a 'cold' gas in the same conditions.

Figure 6: density of selected electronic states of N₂ molecules calculated at (a) 13.5 MHz and (b) 27 MHz
Figure 7: relative difference between the time averaged electric field near the left electrode calculated with the full model and neglecting the change of gas composition on the PIC/MCC.

It can be observed that the eedf in the bulk plasma is strongly influenced by the coupling with the chemical kinetics in the energy range of vibrational excitation processes in both cases, while at the higher frequency the eedf is also influenced in the energy range for electronic excitation processes, due to electronic super-elastic collisions, specially $e/N_2(a')$. In fig. 5 one can observe that the change in shape of the eedf is able to influence strongly the shape of the vdf, by increasing the energy input through e-V inelastic processes to be redistributed by VV processes (and quenched by VT one on the very tail of the vdf, as can be seen from the figure). Finally fig 6 shows the calculated space dependent densities of the selected electronic states of Nitrogen molecules. For these calculations an accommodation on the wall equal to 1 was selected, and the result is a strong gradient of concentration at the boundary: the value of the accommodation coefficient is however not an essential parameter here, since electronic states are mainly destroyed by volume processes (collisional and radiative).

The effect of the vibro-electronic kinetics on the PIC/MCC particle dynamics is reflected in turn on the electric field itself, as it is shown in fig. 7, showing the relative difference between the time averaged value of the local electric field with and without self-consistent coupling.

<table>
<thead>
<tr>
<th></th>
<th>13.56 MHz</th>
<th>13.56 MHz</th>
<th>27 MHz</th>
<th>27 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(full model)</td>
<td>(decoupled)</td>
<td>(full model)</td>
<td>(decoupled)</td>
</tr>
<tr>
<td>electr. density (cm$^{-3}$)</td>
<td>$6.2 \times 10^9$</td>
<td>$6.4 \times 10^9$</td>
<td>$2.1 \times 10^9$</td>
<td>$2.5 \times 10^9$</td>
</tr>
<tr>
<td>electr. m. energy (eV)</td>
<td>0.94</td>
<td>0.80</td>
<td>1.22</td>
<td>0.71</td>
</tr>
<tr>
<td>T$_{01}$ (K)</td>
<td>2800</td>
<td>2200</td>
<td>4600</td>
<td>2700</td>
</tr>
</tbody>
</table>

The combined effect of chemical kinetics and discharge frequency is better observed by inspecting table II, which also reports the $T_{01}$ 'bulk vibrational temperature' defined according to the 'Boltzmann' relation for the ratio $vdf(1)/vdf(0)$. As can be shown, the effect of the super-elastic collisions on the PIC/MCC kinetics is an increasing of the electron mean energy and a slight reduction of the...
plasma density. This last point may sound strange compared to the phenomenology of OD plasmas, but it can be understood for an RF discharge: the most of the low-energy electron are in fact trapped by the rather shallow ambipolar potential well. Super-elastic collisions raise the mean energy of the bulk electrons allowing them to reach the oscillating sheath regions, thereby increasing the energy deposition in the vibrational excitation channel but with no significant effect on the tail of the eedf. At the same time, charged particle loss takes place by ambipolar diffusion as the ions enter the pre-sheath region at Bohm velocity $v_B = (K T_d / m_i)$, and this dynamics is automatically reproduced by the PIC/MCC: therefore the increasing of the electron mean energy due to super-elastic collisions also increase the ambipolar diffusions losses.

4. CONCLUSIONS

A 1Dr2Dv PIC/MCC model for bounded Nitrogen plasmas has been coupled self-consistently to a 1D vibrational, electronic and diffusion kinetics for molecules. The coupling produces effects on macroscopic plasma parameters and on the vibrational kinetics through a complex interplay of plasma dynamics and heavy particle kinetics which has no analogues in the uniform plasma models. Results confirm the necessity of full self-consistent modelling of chemical plasmas for 1D (and presumably 2D) RF discharge studies, specially at the higher frequencies.

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