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Modeling of hydrocarbon species in ECR methane plasmas

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Abstract

ECR methane laboratory plasmas are modeled using both a simple zero-dimensional particle balance model and a fully kinetic model. The kinetic model consists of a two-dimensional in space, three-dimensional in velocity space particle-in-cell model with Monte-Carlo collisions in which electrons, ions and neutrals are treated as particles, moving in self-consistent electric and external magnetic fields. The model results are discussed and compared with experimental data.

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1. Introduction

Low-temperature methane plasmas have been subject of interest already for several decades, mainly because of their wide application in various fields of plasma–surface technologies, such as film deposition, surface etching, and surface modification.

Recently, interest in such plasmas was strongly increased in the fusion community due to the fact that formation of hydrocarbons may enhance the erosion of carbon plasma facing surfaces in fusion devices. Furthermore, particle fluxes from hydrocarbon species formed in peripherial regions might be responsible for hydrogen isotope codeposition discovered in fusion experiments [1]. Thus, understanding of physical and chemical processes in such hydrocarbon plasmas is vitally important for planning future fusion experiments.

In this work, we present modeling of hydrocarbon plasmas with parameters typical of ECR created methane plasmas used for deposition of hydrocarbon films (electron temperature $T_e \sim 2$–4 eV, neutrals temperature $T_n \sim 500$ K, electron density $n_e \sim 10^{10}$–10^{11} cm^{-3}, neutral gas pressure $p \sim 0.1$–20 Pa) [2–4].

At first we will describe a zero-dimensional particle balance model, which we used for determination of the most abundant species in methane plasmas. In this model we account for 14 neutral and 13 ion hydrocarbon species participating in 175 volume chemical reactions.

Further we will present a fully kinetic model of ECR generated methane plasma, which combines kinetic description of both charged particles and neutrals together with chemical inter-species interaction and plasma–surface interaction models. For this purpose, we developed a two-dimensional in space, three-dimensional in velocity space multispicies particle-in-cell code with Monte-Carlo collisions (2d3v PIC MCC), which allows to make full-scale modeling of real experimental devices.

A summary concludes the paper.

2. Chemical kinetics model

In order to get some insight into the complexity of a multispecies hydrocarbon plasma we set up a

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zero-dimensional particle-balance model. We assume that the plasma is uniform, electrons and ions are Maxwellian, electron temperature and density, ion temperature are constant, and that the species densities change only due to volume chemical reactions, external sources and pumping. In this case, all species densities are governed by the system of particle-balance equations:

$$\frac{dn_\alpha}{dt} = \sum_{\beta,\gamma} R^{\alpha}_{\beta\gamma} n_\beta n_\gamma - n_\alpha \sum_{\beta,\gamma} R^{\beta}_{\alpha,\gamma} n_\gamma + S_\alpha - P_\alpha$$

with n_α – densities of species α, $R^{\alpha}_{\beta\gamma}$ – rate coefficient for volume reaction between species β and γ, leading to creation of species α, S_α – volume source and P_α – volume pumping rate of species α. We also include that the total pumping rate is equal to the source gas influx (methane) and that the pumping rate of each species is proportional to its density. As we consider the electron density to be constant, in order to keep quasi-neutrality we multiply ion densities by factor $n_e / \sum_k n_{i_k}$ every time step.

In our model we account for 175 volume reactions involving 14 neutral and 13 charged species: C_2H_6, C_2H_5, C_2H_4, C_2H_3, C_2H_2, C_2H, C_2, CH_4, CH_3, CH_2, CH, C, H_2, H and $C_2H_5^+$, $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, C_2H^+, CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, H_2^+, H^+.

The number of reactions considered was determined by the available data for reactions rate coefficients.

For electron and proton induced methane break-up reactions rate coefficients we used well-known Ehrhardt–Langer analytical fits from [5]. For ion–neutral, neutral–neutral hydrocarbon reactions and electron-impact reactions for hydrocarbons higher then CH_4 we used constant rate coefficient from datasets used in [6,7].

In Figs. 1 and 2 we present the evolutions of neutral species densities calculated for the plasma parameters corresponding those in [2] and [4] together with measured values.

The most important result is that among the most abundant neutral species besides methane and products of its direct dissociation, we can also see the higher hydrocarbon molecules C_2H_2, C_2H_4 and C_2H_6. This reveals the important branch of hydrocarbon reactions in our system: electron impact dissociation of methane yields highly reactive neutral radicals CH_3, CH_2, CH, which then lead to a formation of higher hydrocarbon molecules. This is in quite good agreement with experimental results from [2,4,8,9] and simulations in [6,7].

When comparing the model results with experimental measurements of the neutral densities in ECR methane

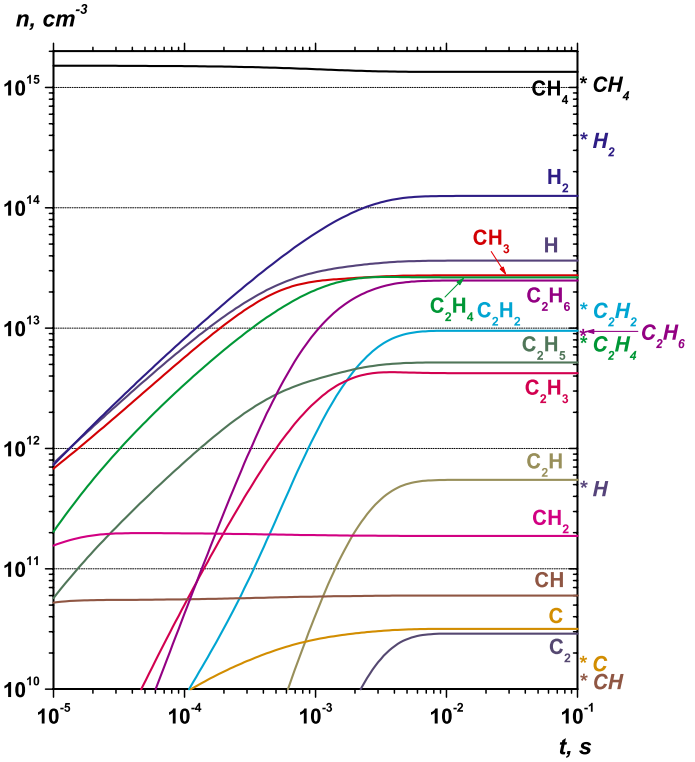

Fig. 1. Evolution of neutral species densities calculated for the case of $T_e = 2.2$ eV, $T_{i,n} = 450$ K, $n_e = 10^{11}$ cm^{-3}, $p = 10$ Pa, constant influx of methane $\Gamma_{CH_4} = 10^{18}$ s^{-1} cm^{-3} (lines) and densities measured in [2] (points).

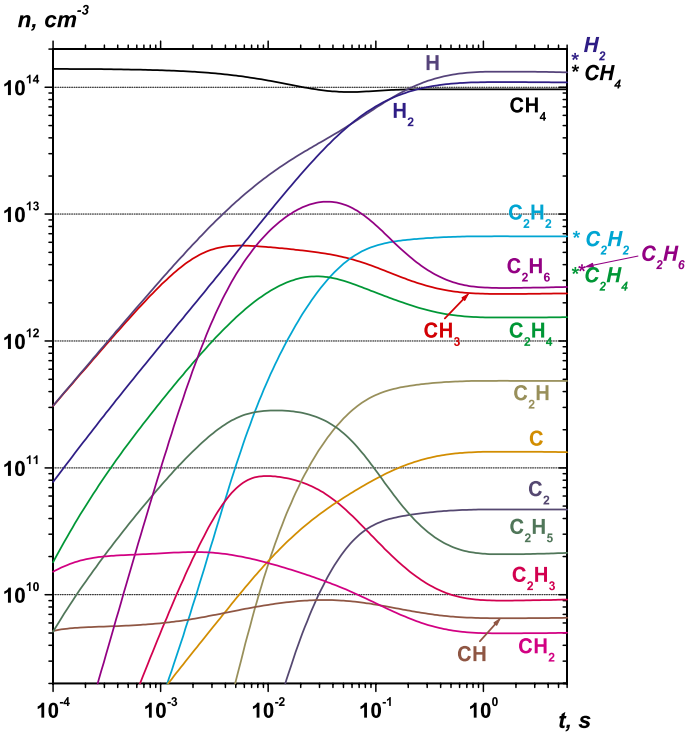

Fig. 2. Evolution of neutral species densities calculated for the case of $T_e = 3.2$ eV, $T_{i,n} = 450$ K, $n_e = 10^{10}$ cm^{-3}, $p = 1.25$ Pa, constant influx of methane $\Gamma_{CH_4} = 2.3 \times 10^{15}$ s^{-1} cm^{-3} (lines) and densities measured in [4] (points).

discharges with similar conditions (Figs. 1 and 2), we can see that overall agreement is quite good. Only for atomic hydrogen our model gives almost two orders of magnitude higher density then the experimental value from [2]. This indicates that the hydrogen balance is somewhat overestimated, a problem which has to be checked in future.

3. Particle in cell model

In order to create a fully kinetic model of our system we started from a two-component electron–ion 2d3v electrostatic PIC MCC code [10], in which electrons and ions are treated as particles, moving in the self-consistent electric and externally applied magnetic fields, two spatial and three velocity components are accounted, and Coulomb collisions are included through a Fokker-Planck collision model [11]. To be able to describe the multispecies hydrocarbon plasma we generalized the code for the case of arbitrary number of ion and neutral species. In order to treat Coulomb collisions in a more accurate way we added a binary Monte-Carlo Coulomb collision model for electron–electron, electron–ion and ion–ion collisions [12], which explicitly conserves energy, momentum and particles. For the implementation of inter-species reactions we utilized a binary inelastic collision model [13] which also explicitly conserves energy, momentum and particles. This enabled us to include in the model all reactions from Ehrhardt–Langer list [5]: electron-impact ionization, dissociation, dissociative ionization and recombinative dissociation as well as charge exchange proton-neutral reactions. Inclusion of other types of elastic and inelastic collisions in the model is now rather straightforward and is only a question of available cross-section data for the collision of interest. Due to the lack of reliable data for reactions cross-section we limited the model to methane break-up reactions from [5] and hydrogen dissociation and ionization reactions from [14]. In total, we take into account 7 neutral and seven charged species: CH_4, CH_3, CH_2, CH, C, H_2, H and CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, H_2^+, H^+, participating in 34 reactions.

We also included in the code a simple surface interaction model in which we suppose that all electrons get absorbed by the target wall, all carbon-containing species are either deposited on the target wall or pumped out. To balance these losses an equal amount of CH_4 is injected into the system from the source side. All hydrogen species (H_2, H, H_2^+, H^+) return from the wall as H_2, except for small amount which gets pumped out. This surface interaction model is a placeholder for more accurate models to be developed in the next iterations between modeling and experiment.

In order to be able to trace the densities of neutral species, which may rise to values several orders of magnitude higher than the electron density, we use a Russian-roulette algorithm, which reduces particle numbers in cells, increasing their weights instead to keep the number of neutral particles below a certain limit. This algorithm explicitly conserves particle mass density and conserves particle energy and momentum in average.

In order to have the possibility to model a closed system, in which all charged particles are generated by ionization inside the volume, we added an ECR heating model, applying an external circularly polarized HF electric field with prescribed spatial distribution. In this case, we get a steady state solution by applying a feedback control loop which adjusts the applied HF field strength to keep the electron density within a desired range.

Below we present results for the case of an ECR methane plasma with parameters ($n_e \sim 10^{10}$ cm^{-3}, $p \sim 0.4$ Pa, ECR power density $P_{HF} \sim 0.01$ W/cm^3) which are similar to those in [3,4]. The magnetic field is directed along the Y-axis. The computation domain length is $Y_{max} = 12$ cm and width – $X_{max} = 0.37$ cm, which corresponds to a thin slab along the plasma core in the real device. We are using periodic boundary conditions in the X direction, symmetry boundary condition in the Y direction at $X = 0$ and target wall boundary conditions with potential $\phi = 0$ at $X = X_{max}$.

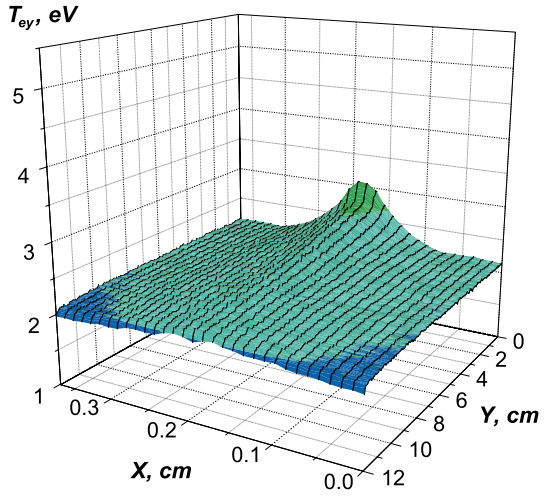

Fig. 3. Calculated profile of parallel electron temperature.

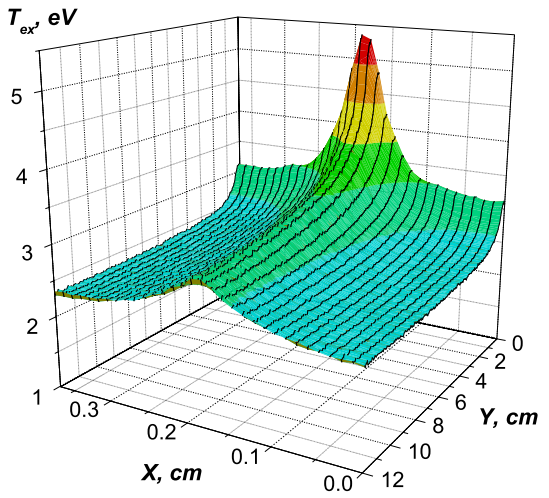

Fig. 4. Calculated profile of perpendicular electron temperature.

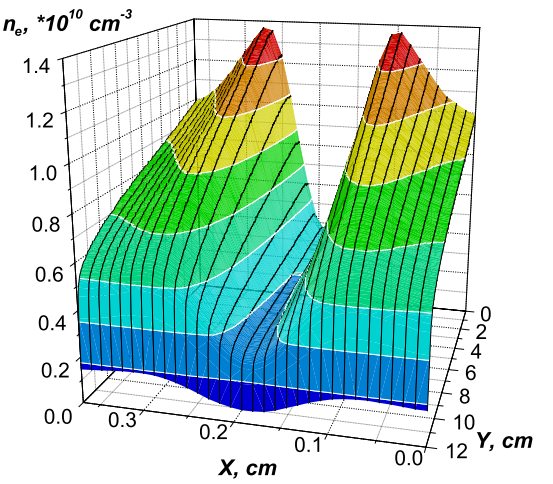

Fig. 5. Calculated profile of electron density.

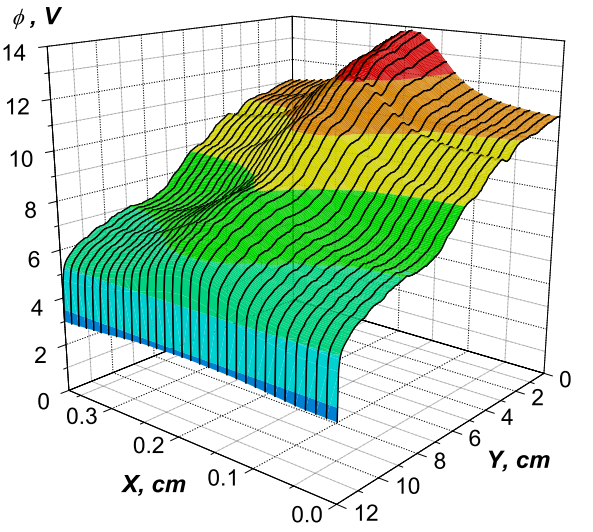

Fig. 6. Calculated profile of plasma potential.

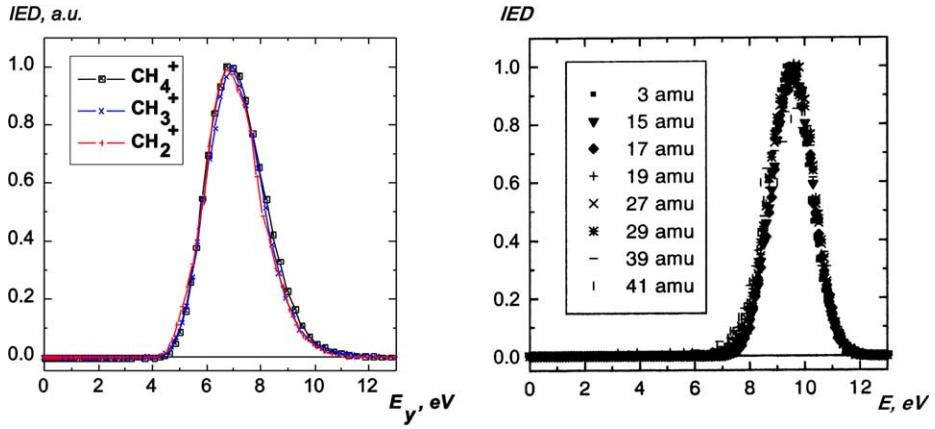

Fig. 7. Ion energy distributions at the target surface. Left: calculations; right: measurements [4,8,9].

The calculations were done on 32 processor Linux cluster in about 10 days, $\sim 5 \times 10^6$ simulation particles were used.

In Figs. 3 and 4 we plot parallel and perpendicular electron temperatures T_{ey} and T_{ex}. On this pictures we can see maxima, which correspond to the profile of absorbed HF power, as well as a pronounced temperature anisotropy, caused by ECR heating. In Fig. 5 we can see the effect of applied strongly non-uniform ECR heating model on electron density profile. In Fig. 6 we present the calculated potential profile. We can easily distinguish the sheath and pre-sheath potential drops. The sheath drop is $U_{sh} \sim 5.2$ V, which agrees quite good with Bohm theory, taking to account $T_y \sim 2.1$ eV. In Fig. 7 we compare the parallel energy distributions for the most abundant ions CH_4^+, CH_3^+ and CH_2^+ calculated at the target surface with the corresponding data from [4,8,9]. We can see that for all ion species the mean energy of random motion $T_{iy} \sim 0.04$ eV is much less than that of the directed motion $E_{iy0} \sim 6.9$ eV, which qualitatively agrees with the experimental results.

4. Summary

We have shown that a reasonable estimation of neutral species composition in low-temperature methane plasmas can be achieved with a rather simple zero-dimensional particle balance model. With this model we have verified the significance of higher hydrocarbons in such plasmas. These stable heavy hydrocarbons, which are formed in reactions between neutral radicals, resulting from the direct methane break-up, may play important role in the formation of flakes in shaded regions in fusion experiments.

For more detailed description of laboratory hydrocarbon plasmas we developed and tested 2d3v PIC MCC code which seems to be a promising tool for modeling of such systems.

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