Two-dimensional PIC–MCC simulations of a capacitively coupled radio frequency discharge in methane

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Abstract
A two-dimensional capacitively coupled radio frequency discharge in methane is simulated by the PIC–MCC method. The results were obtained in the pressure range 50–300 mTorr and the voltage range 40–180 V for a discharge frequency of 13.56 MHz. The electron energy and electron–methane reaction rate spatial distributions show the existence of two regimes of discharge glow: (a) with active sheaths, when electrons are hot in electrode sheaths and cold in the middle of discharge so that the electron–neutral reactions strongly dominate in the sheath regions; (b) with volume domination, when the electron energy is more uniform and the reactions take place over the total discharge volume. The second regime is usually observed for low discharge voltages, and turns to the first one with increasing voltage. In addition, simulation of chemical reactions in the methane plasma was performed to find the gas mixture composition in the discharge volume. The results are in agreement with the known experimental data.

1. Introduction
The radio frequency (rf) methane plasma, used for producing carbon films in plasma-enhanced chemical vapour deposition (PECVD) reactors, is a subject of interest for investigation. Numerical modelling of capacitively coupled radio frequency (ccrf) plasma reactors has a great importance for understanding the processes in methane plasma and their influence on carbon film deposition, which helps in reactor design and improvement of plasma technologies.

Basic experimental information about the CH₄ ccrf discharge plasma composition was obtained by the group of Sugai [1, 2]. The numerical models of methane plasma have been intensively developed during the present decade. The most widely used approach is the fluid plasma model developed in [3–10] (a comprehensive overview of their results can be found in [4, 6]) and also in [11, 12]. In most of these works, the electron energy distribution function (EEDF) is found using various approaches and then the rate constants of electron–neutral reactions are evaluated by integration of the EEDF with the known energy-dependent section of each reaction. Another technique, more accurate but demanding much more computational effort, is direct particle simulation [13], called the particle-in-cell Monte Carlo collision method (PIC–MCC). This approach allows one to obtain EEDF and the rates of electron–neutral reaction by direct Monte Carlo simulations of particle trajectories. For a methane discharge, such simulations in the one-dimensional case were performed in [14, 15]. In [14], each type of chemical species present in the plasma was treated by the particle simulation method, but to make the calculations efficient, a limited number of species (electrons, ions and five neutrals) was chosen, and the scheme of chemical reactions was simplified. Also, the electron-impact vibrational excitation reactions, which affect the electron energy distribution, were not considered. Another approach was presented in [15], where the PIC–MCC simulations were done only for electrons taking account of 18 electron–neutral reactions, thus providing the reaction rates, while the kinetics of ions and neutral species (with a total number of 20) was treated using diffusion-drift approximation and mass balance.

Since the pioneering work of Levitskii [16], different modes of ccrf discharge operation have been studied...
heating-mode transition was observed in a low pressure argon and helium. Another type of gas phase chemistry in the discharge plasma was simulated in one-dimensional simulations using the combined PIC–MCC algorithm. The phase diagram of mode location was chosen as 10

In the ccrf discharge in silane, the transition between different modes was studied experimentally [19, 20] and numerically [23]. In [24], the transition between different modes of the ccrf discharge in methane was studied in two-dimensional simulations using the PIC–MCC approach. The phase diagram of mode location was constructed for a wide range of gas pressures and discharge currents. Hysteresis was found in the ccrf discharge behaviour with current variation.

In this work, we present a two-dimensional PIC–MCC simulation of ccrf methane discharge in an axisymmetrical reactor, using the PIC–MCC approach for both electron and ion kinetics. One of the points of interest was the existence of different regimes in two-dimensional simulations. In addition, the gas phase chemistry in the discharge plasma was simulated and compared with experiment.

2. Discharge simulation algorithm

The PIC–MCC approach developed here is two-dimensional in space and three-dimensional for particle motion (2D3V). In Monte Carlo collision simulations of electron kinetics, besides the elastic scattering, six electron–methane reactions were considered (listed in table 1), with the same cross sections as in [11, 15]. Electron–electron Coulomb scattering, secondary electron emission and wall reflection were neglected, so all particles reaching the chamber walls were eliminated.

In a methane plasma, four main types of positive ions are present [1]: CH3+, CH2+, CH+ and C2H5+. Two of them are produced by fast gas phase reactions:

\[ \text{CH}_4 + \text{CH}_2^+ = \text{CH}_3^+ + \text{CH}_3, \]
\[ \text{CH}_4 + \text{CH}_3^+ = \text{C}_2\text{H}_5^+ + \text{H}_2 \]

with reaction rate constants \(1.5 \times 10^{-15} \text{ m}^3 \text{s}^{-1}\) and \(1.2 \times 10^{-15} \text{ m}^3 \text{s}^{-1}\), respectively. Estimation shows that for the considered pressure range, CH2+ and CH3+ ions exist for a few free paths only before conversion to CH2+ and C2H6+, which are stable. The ion CH2+ is dominant (as observed in [1]), since ionization to CH2+ has a lower barrier. Also, other ions have a similar form of density profile (shown, for example, by simulations in [11]). So, in PIC–MCC ion kinetics, all the positive ions, for simplicity, were represented by this ion type only. The methane discharge plasma can be treated as electropositive [9], so negative ions were not taken into account. For positive ions, the transport cross sections were taken to match the experimental results of ion mobility in methane [25, 26]. Ion–ion and ion–electron collisions were not considered.

The time of free flight in MCC simulations is treated by the null collisions method. The equations of motion were solved explicitly, using the energy conserving scheme with second-order accuracy (described in [27], chapter 10.3). The time step was chosen as \(10^{-11} \text{s}\) for electrons and 40 times larger for ions. The number of simulated particles was usually 100 000 for both electrons and ions. The space charge density, used for solving the Poisson equation, is approximated using the PIC technique.

The self-bias voltage was adjusted to keep the time-averaged current equal to zero and its value was imposed on the grounded electrode. The potential on the powered electrode was set equal to the applied rf voltage. The Poisson equation was solved on a two-dimensional cylindrical grid with 150–200 nodes in the discharge axis direction and 50–80 nodes in the radial direction, condensing near the outer electrode edge. A more fine axial grid is required for accurate treatment of the large potential gradient in the electrode sheath regions.

The main assumption of the discharge model is that the kinetics of charged particles was simulated in pure methane. As the characteristic time of relaxation of the gas mixture composition is \(10^3–10^5\) rf cycles, for the complete PIC–MCC discharge simulation including plasma chemistry dynamics, a special algorithm devoted to this problem should be developed, which is the subject of further work. The calculations of plasma chemical composition using electron–methane reaction rates obtained in discharge simulations are presented in section 4. It was shown, for methane pumping through the reactor chamber at such rates, that the time of gas residence in the discharge volume \(\tau\) is 0.1 s by order of magnitude; the most abundant chemical species usually have densities \(10^3\) times less than methane (see below), so we expect that the kinetics should not change critically. Also the abundance of the excited state of methane is neglected, which is a common assumption [14, 15].

The axisymmetrical physical domain for plasma simulation is shown in figure 1. The chosen dimensions of reactor refer to the experimental set-up [1]. The gas phase chemistry simulation domain is also shown.

To accelerate the convergence of PIC–MCC simulation, the algorithm described in [28] was applied. The steady state solution is found by splitting the fast relaxation of electron distribution and slow relaxation of ions. After each treated rf cycle, the equations of motions are also solved for \(K\) additional rf cycles for ions only, without solving the Poisson equation but using a modified electric field (see details in [28]). As these additional periods are treated with a large time step for ions, they do not increase the CPU time significantly, but the solution takes much fewer simulated rf periods to

| Reaction | Energy threshold (eV) |
|----------|----------------------|
| 1 \(\text{CH}_4 + e = \text{CH}_2^+ + e\) | 0.162 |
| 2 \(\text{CH}_4 + e = \text{CH}_3^+ + e\) | 0.361 |
| 3 \(\text{CH}_4 + e = \text{CH}_3 + \text{H} + e\) | 8.0 |
| 4 \(\text{CH}_4 + e = \text{CH}_2 + 2\text{H} + e\) | 8.0 |
| 5 \(\text{CH}_4 + e = \text{CH}_2^+ + 2e\) | 12.6 |
| 6 \(\text{CH}_4 + e = \text{CH}_3^+ + \text{H} + 2e\) | 14.3 |

Table 1. Electron–methane reactions involved in Monte-Carlo collision simulation.
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Figure 1. Geometry of the reactor, showing the physical domains for plasma and gas phase chemistry simulation.

Figure 2. Relaxation of total ion number in the plasma during PIC–MCC simulation for two values of acceleration factor $K_A$.

3. Results of discharge simulations

Simulations were performed for a discharge frequency of 13.56 MHz in a cylindrical reactor with 14 cm diameter and 6 cm interelectrode spacing (figure 1) in the pressure range $P$ from 50 to 300 mTorr and rf voltage $U_{rf}$ ranging from 40 to 180 V.

As the number of simulated particles is not large (10^5 particles for 10^4 grid cells), this may cause electric field numerical fluctuations and artificial particle heating. To check its influence, some simulations were performed twice, with 50'000 and 100'000 particles. If the electron energy varied within a few per cent, we accepted the results. We find that the artificial heating was significant for pressures less than 30 mTorr, and at 50 mTorr and higher the effect was small.

The main information obtained was two-dimensional distribution of plasma density and potential, mean electron energy and electron–methane reaction rates. Previous one-dimensional simulations of rf methane plasma [15, 24] show that for some discharge parameters in the centre of the discharge gap, where electrons are trapped by the rf electric field, accumulation of relatively cold electrons occurs. Hence the average electron energy in this region is much smaller than in electrode sheaths. In noble gases also, this effect was observed [29, 30]. In one-dimensional simulations, electron energy in the sheaths may be several electronvolts, and in the centre of discharge it may be one order of magnitude less. Hence, the electron–methane reactions strongly dominate in the sheath region. We call this the ‘active-sheath’ (AS) discharge regime, in contrast to the another observed ‘volume-dominated’ (VD) regime, when electron energy has a more uniform profile and electron–neutral reactions proceed in all reactor volume [24].

We observed the existence of these regimes in two-dimensional simulations as well and studied the transition between them for different discharge parameters. To illustrate the main features of the regimes, two examples are presented below. The results of simulation for $P = 123$ mTorr and $U_{rf} = 120$ V are shown in figure 3. The electron density, averaged over a period (figures 3(a) and (d)), is asymmetrical with maximum shifted to the powered electrode due to the self-bias voltage (this was also observed in experiment [1] and predicted by one-dimensional PIC–MCC simulation with artificial bias imposing in [14]). It is seen that electrons in the centre of the discharge gap are relatively cold (average energy is 0.75 eV while in sheaths it exceeds 2 eV), see figure 3(b) and also the solid line in figure 3(e). This explains the behaviour of electron reaction rates, which have steep maxima in regions with hot electrons. In figure 3(c), the two-dimensional distribution of dissociation reaction rate $\text{CH}_4 + e \rightarrow \text{CH}_3 + \text{H} + e$ is shown. It is chosen for illustration as the main methane dissociation channel; the profiles of other dissociation and ionization rates have a similar form. It is seen that the reaction proceeds in sheath regions and also at the outer reactor edge, and is suppressed (the rate falls by two orders of magnitude) in most of the discharge volume (see figure 3(c)). On the axial profile (solid curve in figure 3(f)), the absolute maximum of the rate is located where the maximum of electron energy coincides with large electron density; a second small maximum of the rate corresponds to the second maximum of energy but with lower plasma density. For the two-dimensional case, the difference of electron energy in the centre and in the sheaths is not as large as in one-dimensional simulations [15, 24], where it reaches one order of magnitude. This may be explained by the influence of reactor edge region, where cold electrons converge. The advantage of this method is illustrated in figure 2, where the total number of ions in the discharge volume during simulation is plotted versus the number of simulated rf periods for two different values of acceleration factor $K_A$. The simulations were done for the geometry shown in figure 1, at pressure 50 mTorr and $U_{rf} = 80$ V. It can be seen that the convergence of simulation results is nearly $K_A$ times faster, thus saving the computational amount by the same factor. In practice, the $K_A$ factor is limited (usually to 5–7) because it strongly increases the statistical noise and oscillations of solution. Convergence usually required 500–3000 rf cycles, the larger value associated with higher voltages and pressures. Simulation of 1000 rf cycles took about 40–60 h on a Pentium III 800 MHz processor.
are not trapped by the electric field as strongly as in the one-dimensional discharge geometry, and hence they may diffuse in the radial direction, which leads to a flatter spatial profile of electron energy.

The case described above is an example of the AS regime. Another discharge regime is shown in figure 4, obtained by simulation at $P = 50$ mTorr and $U_{rf} = 60$ V. Here we see a smooth profile of electron energy (figures 4(b) and (e)) and the reaction rate follows the electron density (see figures 4(c) and (f)). This corresponds to the VD discharge regime.

In general, for two-dimensional simulations the discharge properties are radially uniform in the inner reactor area only (up to half of the reactor radius). In the AS regime, near the reactor edge the vertical electron energy profile tends to be more uniform (dashed curve in figure 3(e)) and the reaction rate is not as strongly suppressed in the gap centre (dashed curve in figure 3(f)). Note that the average electron energy near the edge is higher than in the inner region, and although the plasma density gradually decreases towards the edge, the reaction rate even increases.

To investigate the transition between the two regimes, we performed calculations with different rf voltages $U_{rf}$ for pressures 50, 123 and 300 mTorr. The results are presented in one-dimensional graphics, showing the period-averaged plasma parameters plotted along the reactor axis (for $r = 0$).

For the first case, $P = 50$ Torr, the obtained plasma potential, electron density, mean electron energy and CH$_4$ → CH$_3$+H dissociation rate profiles are shown in figures 5(a)–(d) for several applied $U_{rf}$. It is seen in figure 5(a) that the potential drop in electrode sheaths increases with $U_{rf}$, and near the powered electrode (with zero time-averaged potential) it is a few times larger than near the other one (its potential is equal to bias). The transition from the VD to the AS regime is noticeable in the electron energy profiles. With increasing voltage, the energy decreases and for $U_{rf}$ over 100 V an area with relatively cold electrons appears, making a valley in the electron energy profile (figure 5(c)). A relatively large energy maximum appears in the sheath of the powered electrode and a small one in the grounded sheath. It is interesting that increasing $U_{rf}$ from 120 to 180 V changes the energy profile very weakly, while the electron density still increases (figure 5(b)). The form of all density profiles is almost identical, varying only in scale. The maximum is slightly shifted to the powered electrode due to the self-bias voltage.

Figure 3. Contour lines for a period-averaged two-dimensional distribution of mean electron energy, eV (a), electron density, cm$^{-3}$ (b) and CH$_4$ → CH$_3$+H dissociation rate, cm$^{-3}$s$^{-1}$ (c) for $P = 123$ mTorr and $U_{et} = 120$ V. The one-dimensional profiles (d)–(f) are plotted along the reactor axial direction at $r = 0$ (——) and $r = 6$ cm (---).
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The electron reaction rate profile is wide for low voltages, and narrows with increasing voltage (figure 5(d)), indicating that the electron reactions tend to localize in the sheath region. The statistical noise is clearly seen on the rate profiles, although they are averaged over 100 recent rf cycles. To make the picture readable, in figure 5(d) not all rate profiles are shown and the curves are plotted normalized to the maximum value of each.

The results for $P = 123\, \text{mTorr}$ are shown in figure 6. The transition from the VD to the AS regime is clearly seen here. For $U_{\text{rf}} = 40\, \text{V}$ the central minimum of electron energy is hardly seen (curve 1 in figure 6(c)), but the regime is already transitional to AS, as can be seen from the reaction rate (40 V curve in figure 6(d))—in the sheath near the powered electrode it is 2–3 times larger than in the volume. With increasing $U_{\text{rf}}$, the energy minimum becomes wider and deeper, making narrow maxima in both sheaths. Again the larger maximum is observed in the powered electrode sheath. The second maximum near the grounded electrode is better seen than for $50\, \text{mTorr}$, possibly due to the larger potential drop in this sheath at higher pressure (compare figures 5(a) and 6(a)). The form of electron energy profile also tends to saturate for $U_{\text{rf}}$ larger than 150 V, while the form of the larger maximum becomes established near $U_{\text{rf}} = 100\, \text{V}$. Electron density increases with $U_{\text{rf}}$, as shown in figure 6(b). For 150 and 180 V it is not shown, but has the identical form as for 120 V, scaled to maximum $3.7 \times 10^9\, \text{cm}^{-3}$ and $5.7 \times 10^9\, \text{cm}^{-3}$, correspondingly. The position of the density maximum shifts to the powered electrode (as observed in [1], shown by points in figure 6(b)) and for $U_{\text{rf}}$ larger than 80 V it does not move. The dissociation rate (figure 6(d)) exhibits two maxima near both sheath regions, with strong rate suppression in the central region with increasing $U_{\text{rf}}$, thus indicating transition to the AS regime. The larger maximum corresponds to both energy and density maxima near the powered electrode, with increasing $U_{\text{rf}}$ it strongly enlarges without broadening; the second maximum, near the grounded electrode, is smaller and diminishes with increasing $U_{\text{rf}}$ due to cooler electrons in this sheath. The points in figures 6(b) and (c) are taken from measurements made for $P = 123\, \text{mTorr}$ in [1]. The best fit with our simulations is obtained for $U_{\text{rf}} = 80\, \text{V}$. Unfortunately, the voltage in [1] is not indicated, but the estimated volume dissipation of energy in simulations (it varied from nearly 1 to 3 W for voltages 60–180 V) is in agreement with experiment conditions, where the rf source power was 10 W.

Figure 4. The same graphics as in figure 3 for $P = 50\, \text{mTorr}$, $U_{\text{rf}} = 60\, \text{V}$. 

Figure 5. The electron reaction rate profile is wide for low voltages, and narrows with increasing voltage (figure 5(d)), indicating that the electron reactions tend to localize in the sheath region. The statistical noise is clearly seen on the rate profiles, although they are averaged over 100 recent rf cycles. To make the picture readable, in figure 5(d) not all rate profiles are shown and the curves are plotted normalized to the maximum value of each.

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Figure 5. Axial profiles ($r = 0$) of period-averaged plasma potential ($a$), electron density ($b$), mean electron energy ($c$) and CH$_4$ → CH$_3$+H dissociation rate ($d$) for $P = 50$ mTorr, and different $U_{rf}$: 40 (curve 1), 60 (2), 80 (3), 120 (4) and 180 V (5). Dissociation rate ($d$) is plotted normalized to its maximal value, which is (cm$^{-3}$ s$^{-1}$): $8 \times 10^{13}$ for 40 V, $1.8 \times 10^{15}$ for 80 V, 4.8 $\times 10^{14}$ for 180 V.

Figure 6. The same graphics as in figure 5, but for $P = 123$ mTorr and $U_{rf} = 40$ (curve 1), 60 (2), 80 (3), 100 (4), 120 (5), 150 (6) and 180 V (7). Dissociation rate ($d$) is plotted normalized to its maximal value, which is (cm$^{-3}$ s$^{-1}$): $8 \times 10^{13}$ (40 V), $1.8 \times 10^{14}$ (60 V), $3.8 \times 10^{14}$ (120 V), $6 \times 10^{14}$ (150 V), $8 \times 10^{14}$ (180 V).

Figure 7. The same graphics as in figure 5, but for $P = 300$ mTorr and $U_{rf} = 60$ (curve 1), 80 (2), 100 (3), 120 (4), 150 (5) and 180 V (6). Electron densities ($b$) and dissociation rates ($d$) are plotted normalized to maximal value. Maximum values for densities are (cm$^{-3}$): $4.5 \times 10^7$, $4.2 \times 10^8$, $7.6 \times 10^8$, $1.2 \times 10^9$, $3.8 \times 10^9$, $8.5 \times 10^9$. Maximum values of dissociation rates (cm$^{-3}$ s$^{-1}$): $1.5 \times 10^{13}$ (60 V), $3.5 \times 10^{14}$ (80 V), $8 \times 10^{14}$ (120 V), $1.7 \times 10^{15}$ (180 V).

Comparison with simulations of the same discharge parameters using a fluid model [5] shows good agreement in the plasma potential profile (within a few volts) and electron density (within 20%) but different electron energies, which were, in [5], 3–4 eV in the plasma bulk and near the grounded electrode but increased to 11–13 eV in the powered electrode sheath. Such a difference between PIC–MCC and fluid simulations is caused by underestimation of cold electron abundance in the fluid model. This is explained in detail in [15], where both methods are compared for similar methane discharge conditions but in one-dimensional simulations.

The last set of simulations was performed for $P = 300$ mTorr (figure 7). For $U_{rf} = 60$ V the regime is VD, with a symmetrical plasma density profile and a hardly noticeable minimum in the energy profile (curve 1 in figures 7(b) and (c)) but enhanced reaction rates in the sheaths (60 V curve in figure 7(d)). For $U_{rf} = 80$ V, the regime is closer to AS (seen from the reaction rate profile, 80 V curve in figure 7(d)), the plasma density is one order of magnitude larger than for 60 V and asymmetrical (curve 2 in figure 7(b)), although the electron energy profile (curve 2 in figure 7(c)) does not exhibit a deep minimum.

With further increase of $U_{rf}$, narrow energy maxima appear again in both sheaths, but unlike for the previous pressures, the maximum in the grounded electrode sheath is larger than the other one. Such a difference in the energy profile evolution may possibly be explained by comparing the plasma potential behaviour (compare figures 6(a) and 7(a)). At 300 mTorr, the potential drop in the powered electrode...
sheath is 16–18 V smaller than at 123 mTorr, while near the grounded one it is larger: for $U_{tr}$ from 80 to 180 V the drop varies from 30 to 40 V instead of 23 to 28 V for 123 mTorr. Sheath thickness is nearly the same for both pressures (near 0.9 cm in the AS regime). As for previous pressures, the energy profiles tend to saturate with voltage over 150 V.

The behaviour of electron density is shown in figure 7(b). As it varies by more than two orders of magnitude, the profiles are also plotted normalized to maximal value of each. However, it can be seen from this graphic that VD–AS transition leads to accumulation of cold electrons in central region of discharge electric field, where the plasma potential has a plateau.

4. Gas phase chemistry simulation

For simulation of gas phase chemistry, the balance equations for neutral species density $n_{i}(r,z)$ were solved, where $r$ is the distance from the reactor axis (radial direction) and $z$ is the distance from the powered electrode (axial direction). The physical domain for chemistry simulation is reduced to interelectrode space, as shown in figure 1. The convection is also taken into account:

$$\frac{dn_{i}}{dt} = R_{i} + \text{div} \vec{J}_{i},$$

$$\vec{J}_{i} = D_{i} \vec{V} n_{i} + n_{i} \vec{V},$$

where $R_{i}$ is the sum of generation and loss for $i$th species due to chemical reactions, $\vec{J}_{i}$ is the flux, $D_{i}$ is the diffusivity and $\vec{V}$ is the gas velocity in the plasma reactor, given as a two-dimensional vector field.

The chemical model includes radicals H, CH, CH2, CH3, C2H4, and stable species H2, CH2, C2H6, C2H5, C3H8. For balance equations of radicals, which have non-zero coefficient $s$ of sticking to the surface, the additional loss terms were included at the electrode boundaries:

$$J_{ib} = \frac{n_{ib} v_{i}}{4} \frac{s_{i}}{1 - s_{i}/2},$$

where $n_{ib}$ is radical density at the boundary, $v_{i}$ is thermal velocity and the value of $s_{i}$ was assumed to be 0.01 for all types of radicals except for CH2, for which $s_{i} = 0.025$ was assumed [11]. The diffusivities were taken as in [7] for radicals, and as in [11] for stable species.

The set of gas phase chemical reactions was taken as in [6] with reactions responsible for C2H5 radical balance added from [11] (see table 2). The volume rates of electron–methylene reactions are obtained in the discharge simulation as two-dimensional profiles and used as production terms for corresponding species. Taking account of ion–methane reactions 5 and 6 requires information about ion mixture composition, which is not considered in PIC–MCC simulations. However, preliminary calculations show that a simplification can be made to exclude the ion reactions from the chemical model. As was mentioned in section 2, CH3 and CH4 ions exist for a few free paths only before conversion to CH2 and C2H5, which do not take part in the gas phase chemistry. As each type of ion has only one way of chemical conversion, the volume rate of reaction 5 can be assumed equal to that of 3. The same applies to reactions 6 and 4. So the reactions 3, 5 and 4, 6 may be combined and replaced by:

$$3, 5 : \quad 2\text{CH}_{4} + e = \text{CH}_{2}^{+} + \text{CH}_{3} + 2e,$$

$$4, 6 : \quad 2\text{CH}_{4} + e = \text{C}_{2}\text{H}_{5}^{+} + \text{H}_{2} + H + 2e$$

with the rates equal for those of reactions 3 and 4, respectively. Thus the effect of ion–methylene reactions is accounted for through their production rates and only neutral species remain in the chemical reaction system.

The rate constant of reaction 10, found in the literature, ranged from $k_{10} = 10^{-20}$ [1] to $10^{-18}$ [6, 9] and $1.7 \times 10^{-17}$ m³ s⁻¹ [3]. This rate constant strongly affects the solution for the CH2 radical, because CH4 has the largest density and reaction 10 is the main loss term for CH2. For the other species its influence is weak. We used it as a fitting parameter, and found that the best agreement with experiment [2] is achieved for $k_{10} = 1.5 \times 10^{-18}$ m³ s⁻¹, which is close to that used in [6] and [9].

To take into account the effect of convection, we considered a reactor with a gas inlet through the centre of the reactor and outpumping at the outer boundary. For these model calculations the field of gas velocity $V(r,z)$ was simplified:

$$V_{v}(r, z) = 0,$$

$$V_{v}(r, z) = \frac{V_{0}r_{0}}{r}, \quad r > r_{0}; \quad \frac{V_{0}r}{r_{0}}, \quad r < r_{0},$$

where $r_{0}$ is the gas inlet radius (taken as 0.5 cm). The density of CH4 was held constant at $r < r_{0}$ in order to make the incoming feed gas flux. The value of $V_{0}$ was defined to give a chosen time $r$ of gas residence in the reactor, which was varied in calculations from $r = 15$ ms to $r = 300$ ms. Although assuming $V_{v}$ to be zero may be a rough approximation, it will be shown below that for slow enough gas motion (this was the case

| N | Reaction | Rate constant $k_{N}$ (m⁻³ s⁻¹) | Reference |
|---|----------|---------------------------------|-----------|
| 1 | $\text{CH}_{4} + e = \text{CH}_{3} + \text{H} + e$ | Obtained by MCC |
| 2 | $\text{CH}_{4} + e = \text{CH}_{2} + 2\text{H} + e$ | Obtained by MCC |
| 3 | $\text{CH}_{4} + e = \text{CH}_{2}^{+} + 2\text{e}$ | Obtained by MCC |
| 4 | $\text{CH}_{4} + e = \text{CH}_{2}^{+} + \text{H} + 2\text{e}$ | Obtained by MCC |
| 5 | $\text{CH}_{4} + \text{CH}_{2}^{+} = \text{CH}_{5}^{+} + \text{CH}_{3}$ | $1.5 \times 10^{-15}$ | [3] |
| 6 | $\text{CH}_{4} + \text{CH}_{2}^{+} = \text{C}_{2}\text{H}_{5}^{+} + \text{H}_{2}$ | $1.2 \times 10^{-15}$ | [3] |
| 7 | $\text{CH}_{3} + \text{H} = \text{CH}_{4}$ | $8 \times 10^{-17}$ | [6] |
| 8 | $\text{CH}_{3} + \text{H} = \text{CH}_{4}$ | $1.2 \times 10^{-16}$ | [6] |
| 9 | $\text{CH}_{2} + \text{H} = \text{CH}_{3}$ | $2.7 \times 10^{-16}$ | [6] |
| 10 | $\text{CH}_{2} + \text{H} = \text{CH}_{3}$ | $1.5 \times 10^{-18}$ | fitted, see text |
| 11 | $\text{CH}_{3} + \text{CH}_{3} = \text{CH}_{4} + \text{H}_{2}$ | $5.3 \times 10^{-17}$ | [6] |
| 12 | $\text{CH}_{3} + \text{CH}_{3} = \text{CH}_{4} + \text{H}$ | $10^{-16}$ | [11] |
| 13 | $\text{CH} + \text{CH}_{3} = \text{CH}_{2} + \text{H}$ | $10^{-16}$ | [11] |
| 14 | $\text{CH} + \text{CH}_{3} = \text{CH}_{2} + \text{H}$ | $10^{-16}$ | [11] |
| 15 | $\text{C}_{2}\text{H}_{5} + \text{H} = \text{CH}_{1} + \text{CH}_{3}$ | $6 \times 10^{-17}$ | [11] |
| 16 | $\text{C}_{2}\text{H}_{5} + \text{H} = \text{CH}_{2} + \text{H}_{2}$ | $3 \times 10^{-18}$ | [11] |
| 17 | $\text{C}_{2}\text{H}_{5} + \text{CH}_{2} = \text{C}_{2}\text{H}_{6}$ | $4.2 \times 10^{-18}$ | [11] |
in experiment [1, 2]) the radical density profiles are not very sensitive to the \( V \) field, but depend mostly on the radicals’ local diffusion and chemical decay, especially in the outer reactor region, where the experimental profiles were measured.

The balance equations are approximated using a finite-difference scheme in the cylindrical physical domain (see figure 1) and integrated over time by the Runge–Kutta method until the solution converged to steady state. The densities of radicals converge quickly, while the solution for stables requires a physical time of about 2\( \tau \).

A typical result of a two-dimensional gas phase chemistry simulation is presented in figures 8 and 9. The electron–methane reaction rates were taken for a discharge at \( P = 123 \) mTorr, \( U_d = 80 \) V; \( \tau \) was chosen as 150 ms.

Figure 8 shows two-dimensional density profiles of the main radicals \( \text{CH}_3 \) and \( \text{CH}_2 \). As the discharge regime is close to AS, the density has maxima near the electrode sheaths, where electron–methane reactions are localized (see figure 6(d)). The profile of \( \text{CH}_3 \) is flatter due to its larger time of chemical decay.

Figure 9 shows one-dimensional density profiles of the radicals \( \cdots \) and stable species \( \cdots \), in the radial direction at \( z = 1.2 \) cm (a), and in the axial direction at \( r = 7 \) cm (b), for the same discharge conditions as in figure 8. The density of \( \text{CH}_3 \) radical is multiplied by 1000.

The profile of \( \text{CH}_3 \) is flatter due to its larger time of chemical decay.

Calculations with various \( \tau \) show that the density profiles of stable species, whose main loss term is convection, are approximately proportional to \( \tau \). For radicals, the profiles are also determined by diffusion and chemical decay, so for low gas velocities the influence of convection is weak. The effect of \( \tau \) variation on \( \text{CH}_3 \) density profile is shown in figure 10. The upper curve was obtained with zero convection term, when the distribution of radicals is determined by diffusion only. Of course, this situation is non-physical, because the stable species abundance will never reach a steady state. Besides, our discharge simulation remains valid only for small enough \( \tau \) (of 100 ms order of magnitude), while we can still neglect the change of gas composition, so this curve only shows that convection influence on radical profiles is very weak for these values of \( \tau \).

It is seen that the density saturates with increasing \( \tau \), at first in the outer region, where the gas velocity is smaller. For \( \tau > 100 \) ms it becomes saturated for most of the reactor, so we usually made calculations with \( \tau = 150 \) ms (for our reactor geometry and \( P = 123 \) mTorr this corresponds to gas feed rate of 55 sccm, which is close to that used in experiments [1, 2]).

The behaviour of \( \text{H} \) and \( \text{C}_2\text{H}_5 \) profiles is similar. For \( \text{CH}_2 \) and \( \text{CH} \), the profiles are much less sensitive to \( \tau \) because the main loss term for them is the chemical decay.

Figure 9(b) shows profiles \( n_i(z) \) of the same species in the axial direction at the outer edge of electrodes \( (r = 7 \) cm), where all densities are maximal. The profiles of \( \text{CH} \), which has in our calculations density less than \( 10^7 \) cm\(^{-3} \), are enlarged by factor of 1000. For \( \tau = 150 \) ms, the most abundant stable \( \text{CH}_3 \) has maximal density \( 10^3 \) times less than that of methane \((4.3 \times 10^{15} \) cm\(^{-3} \)), so there is a possibility of neglecting the influence of chemistry on the discharge physics.

5. Comparison with experiment

Calculations with various pressure were made to compare the profiles of the \( \text{CH}_3 \) and \( \text{CH}_2 \) radicals with those observed in [2]. The simulated pressures were 300, 140 and 57 mTorr; the other conditions were the same as for figure 8. The results are presented in figures 11(a) and (b) for \( \text{CH}_3 \) and figures 11(c) and (d) for \( \text{CH}_2 \). Figure 11(a) shows \( \text{CH}_3 \) profiles, plotted at
parameter was the rate constant $k$. The calculated density is somewhat larger, especially near the profile exhibits two maxima, similar to experiment, but the developed kinetic model is not very accurate. In figures 11(50 to 150 mTorr for both radicals, especially for CH$_3$. Also for CH$_2$, the calculated density is very small in the centre of the discharge gap. This may be caused by underestimation of the electron–molecule reaction rates in the discharge centre at high pressures. This shows that for pressures of 300 mTorr and higher the developed kinetic model is not very accurate. In figures 11(b) and (d) both radical profiles are shown for 57 mTorr. Although the calculated profiles are steeper than in experiment, especially for 300 mTorr, the agreement for 140 mTorr is again good, but profiles are steeper than the observed ones, the agreement can be considered satisfactory.

We can say the calculated profiles exhibit similar behaviour to that observed in experiment. The shape described in [2] as density humps and transition to flat profiles with decreasing pressure are well simulated. We suppose that the appearance of density humps indicates the transition from the VD to the AS regime, which is consistent with our simulations. The quantitative agreement is good in the pressure range from 50 to 150 mTorr, especially for CH$_3$. Also for CH$_2$ it is within 30% in range 50–300 mTorr. As for CH$_3$, the calculated densities in the plasma bulk are underestimated for pressures higher than 150 mTorr.

6. Summary

The accelerated PIC–MCC method was applied to two-dimensional simulation of a ccrf discharge in methane. The obtained spatial distributions of mean electron energy and electron–molecule reaction rates show the existence of two regimes of discharge glow. The first, with active sheaths, is characterized by hot electrons localized in the electrode sheaths and relatively cold electrons in other discharge volume, hence the reactions proceed in the electrode sheath regions and are suppressed in the plasma bulk. In the second case, with volume domination, the electron energy is more uniform and the reactions take place in the entire discharge volume.

The transition between discharge regimes for one-dimensional geometry was previously studied in [24] using the combined PIC–MCC model. Unlike the one-dimensional results, where the transition occurs abruptly at some critical current density, in the two-dimensional case, the transition is gradual, with continuous evolution of mean electron energy and reaction rate profiles. For the considered reactor geometry it was found that the VD regime is observed at low rf voltages (40–60 V), and turns to AS with increasing voltage. The transition proceeds in $U_{\text{rf}}$ range from 60 to 120 V and is noticed first at the spatial profile of electron–molecule reaction rates. For $U_{\text{rf}}$ over 120 V the regime is definitely AS. It was also noted that the mean electron energy profile tends to saturate for $U_{\text{rf}}$ over 150 V, and changes very little with further increase in voltage. For another reactor geometry the quantitative results may differ.

To find the gas mixture composition in the discharge volume, simulations of chemical reactions in methane plasma were also performed, with the diffusion and convection flux of species included. The results show good agreement with the known experimental data, especially for the pressure range from 50 to 150 mTorr. At a higher pressure, in the region of 300 mTorr, a qualitative agreement, in the form of the shapes of radical density profiles, is obtained.

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