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## Molecular Dynamics approach to volume and surface molecular reactivity in Ar/CH<sub>4</sub> plasmas

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Reactive Molecular Dynamics (MD) is used to investigate the reactivity in volume and at surfaces of a low-pressure Ar/CH<sub>4</sub> plasma. The initial plasma composition is determined using a 1D plasma model of a radio-frequency discharge. MD simulates the evolution of this composition showing the formation of new molecules in the homogeneous phase, and the molecular interactions with an exposed surface (sticking of plasma species and film growth). Simulations are performed for different temperatures, *i.e.*, 300, 400, 500 and 1000 K.

Reactive plasmas or Complex Non-equilibrium Hydro-Carbon Plasmas (CNHCP) are weakly ionized gases containing solid particles of nanometric or micrometric size in addition to neutral species, electrons and ions. CNHCPs are governed by very different phenomena occurring on length-scales ranging from the molecule to the plasma size. Although the plasma chemistry in hydrocarbon discharges has been extensively studied during the last decades [1], many details remains poorly understood. This is especially the case for the precursors initiating the formation of nanoparticles in the plasma volume on one hand, and of the growth mechanisms of hydrogenated carbon thin films on the other hand. The aim of this work is to use molecular dynamics to study the reactivity of the main neutral species in the homogeneous and heterogeneous phases of an Ar/CH<sub>4</sub> plasma. The mole fractions of the dominant initial species were determined using a fluid model detailed in [2, 3]. For the homogeneous phase, the simulation is performed with 2683 molecules distributed approximately as follows: 54% H<sub>2</sub>, 24% CH<sub>4</sub>, 9% C<sub>2</sub>H<sub>4</sub>, 5% C<sub>2</sub>H, 4% C<sub>2</sub>H<sub>2</sub> and 4% CH<sub>3</sub> in a box of size 10x10x10nm<sup>3</sup>, in agreement with the fluid model [2,3]. Since argon is shown to only plays a thermostat role, it is thus replaced by a Nose-Hoover thermostat in the canonical ensemble. The inter- and intra-molecular interactions of the considered hydrocarbon molecules CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H, CH<sub>3</sub> and H<sub>2</sub> are modeled by the REBO potential [4]. The evolution of the gas composition is simulated during 40 ns with a time step of 0.1 fs. In this first study, we identified new species that result from this evolution. We have also determined their yield of formation (see Fig.1 (a)) as a function of time for four temperature values. This yield rapidly saturates around 3% at all temperatures, indicating that volume reactivity is relatively small. The mass spectra were determined for each temperature and the species with every number of carbon atoms from C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, ..., up to C<sub>14</sub> are present at all temperatures. Other species with larger number of carbon atoms are also observed and the species with the highest carbon number (42) is identified at 500 K. For analysing reactivity, we consider the evolution coefficient (EC) of each initial species, *i.e.*, the ratio between the concentration at time t and the initial concentration. This coefficient is determined for all temperatures considered. Figure 1 (b) shows the evolution coefficient at a temperature of 300 K for all initial species. As one can see, the EC of the C<sub>2</sub>H species is equal to 0 after 1 ns, which means that the species is completely consumed. This observation is valid for all temperatures, and at high temperatures a decrease of this EC is observed in the time interval [0, 1 ns]. These observations would indicate that C<sub>2</sub>H plays a major role in the initial reaction step involved in the generation of larger radicals. The EC of CH<sub>3</sub> species decreases slowly with time, this is observed at all temperatures, with EC being lower at high temperatures. The EC of C<sub>2</sub>H<sub>2</sub> is approximately around 0.9 over time, however, this EC increases with increasing temperature. It can be seen that the EC of

CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> molecules are approximately equal to 1 over time. This is observed at all temperatures for CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> molecules, while for H<sub>2</sub> molecules we observe a decrease of EC at high temperatures. We observed the formation of C<sub>2n</sub>H<sub>3</sub> radicals (n=1, 2, 3) in the time interval [0, 5 ns]. This result is consistent with the fact that these radicals are known to play an important role in film growth [6].

For mimicking deposition on stainless steel surface, MD is performed at a rate of one molecule every 2000 time-steps  $dt$  ( $dt = 0.25$  fs) onto an Fe<sub>67</sub>Cr<sub>17</sub>Ni<sub>14</sub>Mo<sub>2</sub> substrate (40.18x40.18x1.4nm<sup>3</sup>). The Me-C and Me-H interactions are modeled with Lennard-Jones potentials, while metal atom interactions are governed by Embedded Atom Method, and hydrogen and carbon ones again with REBO force field. The sticking probability of each neutral molecule on the metallic substrate is calculated and was observed to decrease when the temperature increases (see Fig.2 (a)). This is consistent with the fact that a larger temperature increases the surface mobility, which makes it more difficult to find a stable anchoring site on the metal surface. The observation of high values of sticking probability for the stable species CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> is due to the fact that the stainless steel is bare. However, the sticking probability of these three species are very low when the surface is covered with hydrocarbon layer. After this first series of simulations, the deposition of the film is simulated by sending all the molecules considered in the previous simulations of the homogeneous phase to the surface. The resulting global sticking probability (see Fig.2 (b)) is decreasing as time and temperature increase. The contribution of each species to the growing film is followed by tagging each carbon atom with its corresponding radical. It allows to observe, as usually considered, that the C<sub>2</sub>H radical is the main contributor to the film growth. Moreover, the grown film is mainly populated by double C=C bonds.

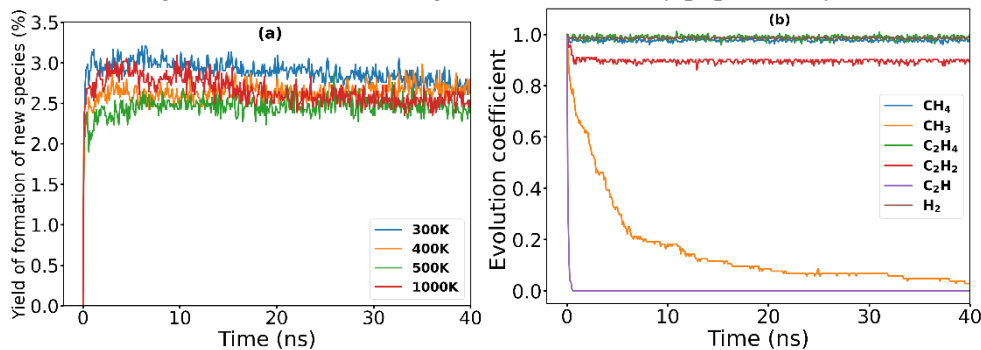


Fig.1 Evolution of the new species % formed in the homogeneous phase (a), Evolution coefficient of each species at 300 K (b).

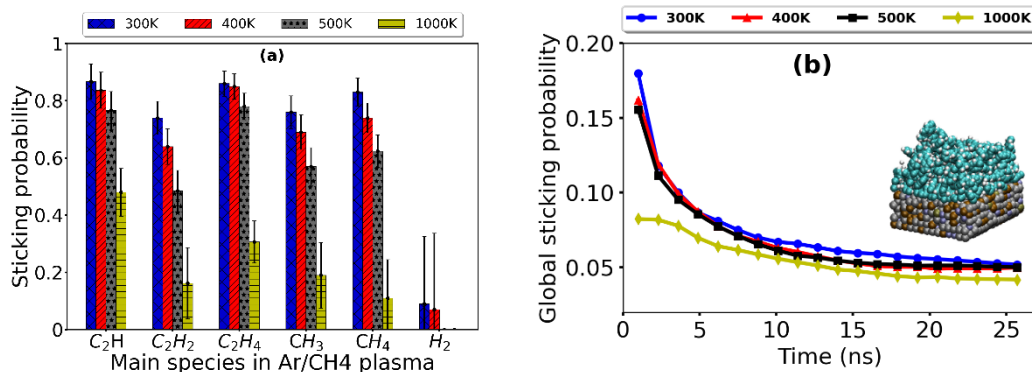


Fig.2 Sticking probability (a) of the main neutral species, and evolution of global sticking probability (b) of the Ar/CH<sub>4</sub> plasma on stainless steel.

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