Reaction of neutral species in homogeneous phase by Molecular Dynamics simulation of Ar/CH_4

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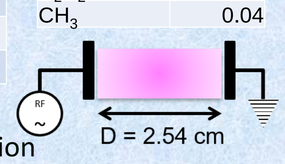
Abstract

Complex Non-equilibrium Hydro-Carbon Plasmas (CNHCP) are weakly ionized gases containing electrons, neutral and charged molecular species, large clusters and, possibly, solid particles. They are nowadays a major tool for the elaboration of advanced carbon materials and nanostructures and several key-applications – drugs sensors, electronic devices, optoelectronics, energy storage, etc. Reactive Molecular Dynamics (MD) is used to study the homogeneous phase by placing all neutral species in a box to determine the distribution in the carbon clusters, the evolution of each species with time, and the bonding order between carbon atoms.

MD input Data

Reference conditions	
Temperature	300K
Pressure	70 Pa
Vrf	100V
Frequency	13.56 MHz
Probability of secondary electrons	0.01
% Argon	96
% Methane	4

Neutral majority	Molar fractions
H_2	0.54
CH_4	0.23
C_2H_4	0.09
C_2H	0.05
C_2H_2	0.05
CH_3	0.04

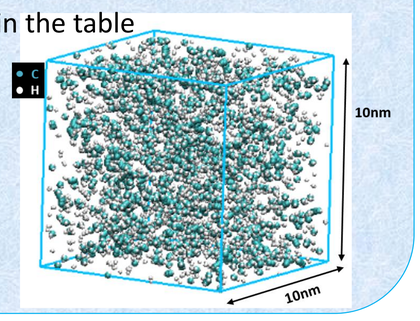


The initial Ar/CH4 plasma composition is determined using a 1D plasma model

Computational details

- LAMMPS is used for molecular dynamics simulation
- The details of the construction of the simulation box can be found in ref.[3]
- the number of each species in the table

Species	Number
H_2	1440
CH_4	630
C_2H_4	243
C_2H	144
C_2H_2	122
CH_3	104

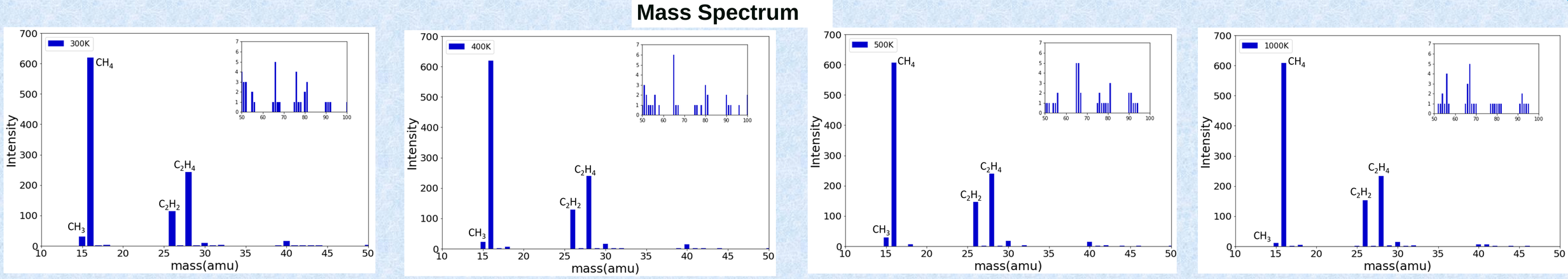


Interaction potential

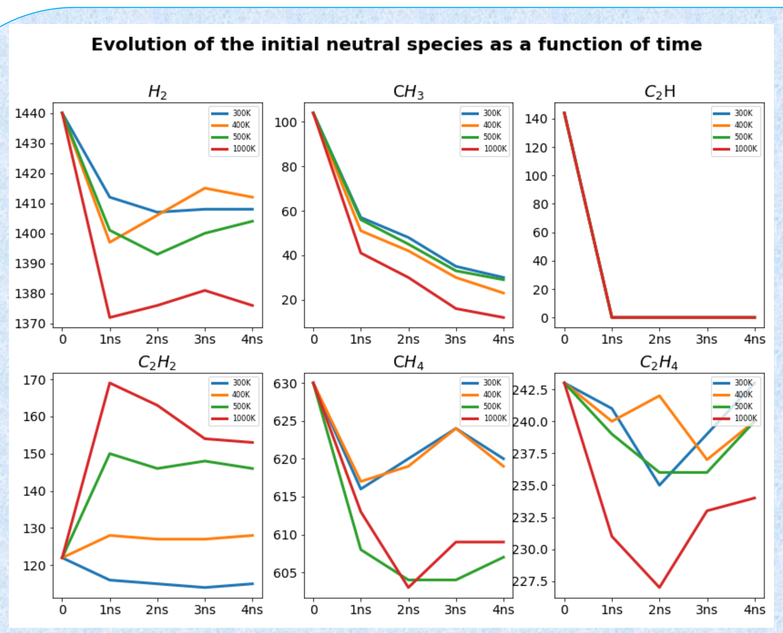
- MD Consists in solving Newton's equations of motion for a set of N atoms, molecules, particles, etc. : $m_i \frac{d^2\vec{r}}{dt^2} = \sum_{i\neq j} \overrightarrow{F_{ij}} = -\sum_{i\neq j} \overrightarrow{\nabla V_{ij}}$
- The interaction potentials V_{ij} must be known with sufficient accuracy: For our problem, it is necessary to consider the reactivity
- the interactions between the atoms of our molecules were modeled by the REBO (Reactive Empirical Bond Order) potential

$$U_{ij} = U(R_{ij}) = U_r(R_{ij}) - b_{ij}U_A(R_{ij})$$

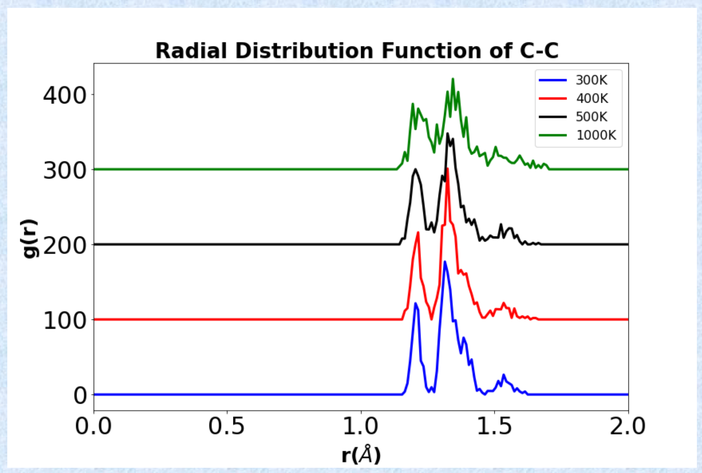
Mass Spectrum



- The species CH_4, C_2H_2, C_2H_4, are the most present. New species are formed such as cyclic hydrocarbons (in very small amounts)

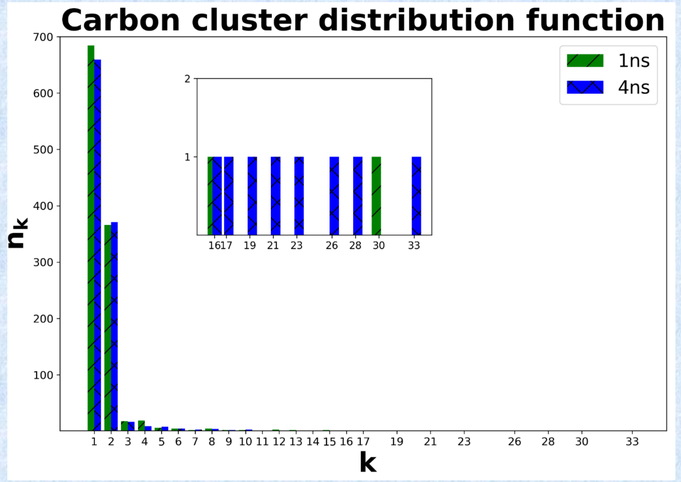


- The H_2 is almost constant, the C_2H has reacted completely.
- The presence of CH_3 decreases with time. The other molecules C_2H_2, CH_4 and C_2H4, There is no noticeable variation except for the drop to 1ns corresponding to the first reactions.



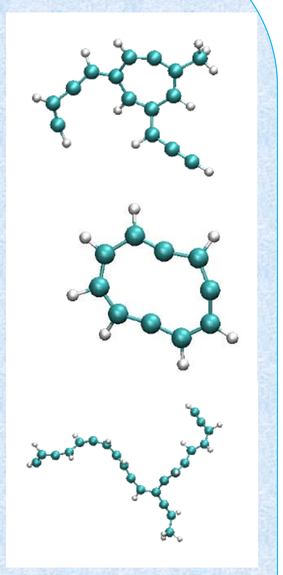
- The determination of the percentage of bond order between pairs of carbon atoms is determined by the Radial Distribution Function (RDF) integral approximation.
- The radial distribution function $g(r)$ describes the probability to find a particle (an atom or molecule) j at a distance r from another particle i.

$$g(r_{ij}) = \frac{V}{N_i.N_j}\left\langle \sum_{i=1}^{N_i}\sum_{j=1}^{N_j} \delta(r - \|r_{ij}\|)\right\rangle$$



- Formation of new carbon clusters at long simulation time

Bond order	300K	400K	500K	1000K
Triple (%)	36	24	20	34
Double (%)	57	72	73	60
Single (%)	7	4	7	6



- Examples of hydrocarbon clusters formed

Conclusions

- Formation of new carbon clusters in the gas phase at long simulation time
- The mass spectrum allowed to identify the molecules in strong presence (CH_4,C_2H_4), When the temperature increases, other species are formed.
- The evolution of the initial species as a function of time highlighted the very weak variation of H_2, the complete reaction of C_2H, the decrease of CH_3 and the there is no well perceptible variation of C_2H_2, CH_4, C_2H_4
- Increasing the temperature, increases the stability of the double bond order between pairs of carbon atoms up to 500K before dropping to 1000K.

Acknowledgements

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[1] P. Brault, « Multiscale Molecular Dynamics Simulation of Plasma Processing: Application to Plasma Sputtering », Front. Phys., **vol. 6**, p. 59, juin 2018, doi: 10.3389/fphy.2018.00059.

[2] L. Schwaederlé, P. Brault, C. Rond, et A. Gicquel, « Molecular Dynamics Calculations of CH_3 Sticking Coefficient onto Diamond Surfaces », Plasma Proc. Polym., **vol. 12**, no 8, p. 764 770, 2015, doi: 10.1002/ppap.201400223.

[3] K. De Bleecker, A. Bogaerts, and W. Goedheer, "Detailed modeling of hydrocarbon nanoparticle nucleation in acetylene discharges," Phys. Rev. E, **vol. 73**, no. 2, p. 026405, Feb. 2006, doi: 10.1103/PhysRevE.73.026405.