

Molecular Dynamics simulations for low temperature plasma interacting with materials and liquids

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As plasma processes are atomic and molecular by nature, simulations at the molecular level will be relevant for providing us with insights into core and interface plasma chemistry basic phenomena. Moreover, statistical averaging allows to provide/predict macroscopic data as reaction rates, diffusion coefficients, ... directly comparable with experiment outputs. Among all the available molecular simulation tools, reactive and ab-initio molecular dynamics (MD) simulation techniques are a good compromise between quantum mechanical and kinetic Monte-Carlo methods, especially due to the availability of robust and accurate reactive force fields [1] and fast quantum chemistry methods such as numerous DFT (Density Functional Theory) variants [2]. Moreover, such semi-empirical or quantum calculated reactive forcefields are also determining partial charges at any relevant times using charge equilibration algorithm. In the context of plasma chemistry this will allow to address charge transfer mechanisms. Using these forcefields, MD simulations can calculate the trajectories of a set of particles, by solving the appropriate set of Newton equations of motion leading to the ability of these simulations to address reactivity of relatively large molecular systems (up to 10⁹ atoms). Since plasmas can produce radicals that interact with other species both in gas phase as well with solid and liquid surfaces, including in-diffusion. Since it is not yet possible to directly include the electrons, it limits carrying out simulations with initial conditions including expected plasma composition from experimental measurement, such as mass spectrometry or fluid model [3-5].

Addressing reactive plasma processes remains a quite challenging and useful task. Three examples nicely illustrate the interest of carrying out reactive molecular dynamics simulations: i) nanoparticle growth in the context of plasma sputtering [6] ii) Hydrocarbon plasma deposition, including plasma phase reactivity [4] and ii) plasma-liquid interaction, especially effects of plasma produced reactive oxide and nitride species on organic molecules in water [7]. Both methodological aspects of MD simulation implementation for these plasma processes and determination of statistical data directly comparable with experiments will be reviewed

1) Nanoparticle growth

Two approaches are described here: modelling the NP growth from a sputtered metal vapor (a) in a (reactive) gas or into a liquid and (b) modelling the entire sputtering-transport-deposition-growth processes in a single multiscale simulation. In the former case, the simulation

box is composed of the plasma forming gas (Argon here), a metal vapor (Pd, Pt, Bi, Ni, Cu, or Au) originated from a sputtered target and, if relevant, a reactive gas (O₂ here). The initial conditions of the simulations are deduced from experiments [2, 3]. The composition and morphology of NPs are consistent with experimental findings, especially catalytic properties [4]. In the latter case, it is possible to describe the entire sputtering process and NPs growth and deposition using scaling arguments: it is enough to keep the experimental collision number in the MD simulation box [5]. Moreover, MDs are also implemented to describe the growth of Pt NPs onto glycerol in a sputtering process. Comparison with experiments provides preliminary results on the role of plasma pressure and Pt kinetic energy

2) Hydrocarbon plasmas

Although the plasma chemistry in hydrocarbon discharges has been extensively studied during the last decades, many details remain weakly understood. It is especially the case for the precursors initiating the formation of nanoparticles in the volume and the growth mechanisms of thin films on surfaces.

3) Insights into plasma-liquid interactions: effects of ROS on pollutant molecules in water.

Implementing reactive processes in MD requires knowledge of the interaction potentials, and then the forces between each interacting species. There are two popular reactive force fields families, able to describe chemical reactions: reaxFF and COMB3, which address bond breaking and formation via a distance -dependent bond order. ReaxFF method will be used for addressing pollutant molecules containing only C, H, O and N atoms. Molecules having additional atoms such as sulphur, chlorine, fluorine, or phosphorus will be treated with a DFT scheme coupled to MD method. For all these molecules the MD simulated degradation products will be compared with available experimental results obtained by liquid chromatography, Mass spectrometry, Electrospray ionization tandem mass spectrometry.

References

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