

A Molecular Dynamics View of Structure and Reactivity – Francesco Ragone, PhD

Abstract

The field of computer simulations has developed into a very important branch of science providing a guess at the interactions between molecules to obtain predictions of properties as accurate as required, subject to the limitations imposed by the computer power and of the chosen and feasible theory level. Quantum chemical methods are predominantly applied to isolated molecules, which corresponds to the state of an ideal gas. Most chemical processes, however, take place in condensed phase, and the interaction of a molecule with its environment: the dimension and the huge amount of degrees of freedom of the system preclude the possibility of quantum-level calculations.

In this PhD thesis different approaches to treat several aspects of structure and reactivity, through the use of molecular dynamics techniques have been used.

In the first part, behaviour of Ru-complexes relevant as (pre)catalysts for olefin metathesis have been investigated. In particular, it has shed light on a so far underestimated key feature, *i.e.* the flexibility around the N-substituent: this allows NHCs to modulate their encumbrance in the first coordination sphere of the metal to allow the coordination even for incoming bulky substrates.

Furthermore, the reduced electron density on the π MO of the methyldiene group, due to the presence of a π -acid ligand trans have been analyzed, showing that it allows for a favorable interaction with the π -aromatic system of the proximal mesityl group of the NHC ligand, which leads to metallacycle first and subsequently in the formation of a tensioned cyclopropane structure that finally evolves to the experimental product via a Buchner type ring expansion. Since the presence of a transition metal and the bonds breaking/formation the quantum approach is mandatory.

On the other hand, the structure description of a Metal/polymer interface have been treated with classical-coarse grained molecular dynamics approach. The calculated radial density profiles allowed to get atomistic insights in the Metal/polymer interface. In both cases of non-coated and coated gold nanoparticles the polystyrene chains expose the phenyl rings to the nanoparticle surface. In the case of coated nanoparticles there is some penetration of the polystyrene phenyl rings into nanoparticle coating layer. When it is present, the third organic component (8-hydroxyquinoline) is closer to the nanoparticle surface and when in contact with a coated nanoparticle shows a deeper penetration into the thiols layer. The orientation of 8-hydroxyquinoline results short range and parallel with respect to the surface of non-coated gold nanoparticles. Different is the 8-hydroxyquinoline orientation in the case of a coated gold nanoparticle. In this case the orientation results perpendicular to the nanoparticle surface.