



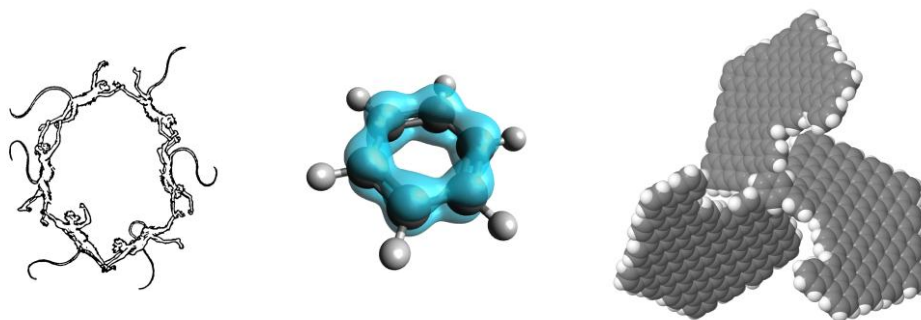
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Ph.D. thesis presentation

On the 19th of March 2018, Orestis George Ziogos will present his Ph.D. Thesis, entitled

"Multiscale Simulations of Discotic Materials"

in front of his seven-member examination committee. The presentation will take place in the "Nikos Koumoutsos" hall of the Chemical Engineering building at 12:00.



Abstract

Soluble disc-shaped organic molecules with the ability to self-organize into intricate supramolecular assemblies constitute a very promising materials family for a plethora of applications. In the case of polyaromatic hydrocarbon (PAH) mesogens, delocalized π interactions enable such materials to be used as active media for organic electronic applications.

This doctoral dissertation is primarily focused on multiscale simulations of discotic materials by means of *ab-initio* Density Functional Theory (DFT) calculations and empirical Molecular Mechanics and Molecular Dynamics (MD) simulations for the determination of structure-property relationships, ranging from electronic and charge transfer properties at the quantum level of description to structural, mechanical, and dynamical characterization of periodic bulk systems at the nanoscale regime.

As regards systems under study, molecules belonging to the so-called nanographene family are examined, with particular focus placed on the hexa-*peri*-hexabenzocoronene (HBC) molecule and its derivatives, utilizing a variety of peripheral functional groups. Quantum mechanical (QM) calculations are employed for the conduction of comparative studies involving molecules from the very smallest discotic unit, i.e. the benzene molecule, up to large polyaromatic assemblies, covalently-linked into forming articulate discotic "super-molecules". Electronic and charge transfer properties are examined at the single molecule and molecular dimer levels of description via ground-state DFT calculations.

Alkyl-substituted HBC derivatives, either in non-polar or polar variants by means of iodine atom peripheral functionalization, are examined through empirical MD simulations, aiming at the determination of structural, mechanical, and dynamical properties for given temperature and pressure conditions. PAH stacking patterns are thoroughly examined, a structural feature of paramount importance, since QM studies both in this work and in the literature confirm the direct link between charge transfer capabilities and core packing motifs.

Amphiphilic, “Janus-type” HBC derivatives are also examined by means of MD simulations. Mesogens under study carry both hydrophilic and hydrophobic side chains, thus enabling the formation of lamellar molecular crystals. The effect of temperature rise on structural and dynamical properties is examined, while gaining an atomistic insight of the melting process for such materials.

Atomistic MD simulations are also put to use for the examination of molecular crystals of functionalized extended discotics, namely the superphenalene C96 and the tetragonal C132 molecules, characterized by a 3-fold and 4-fold expansion, respectively, compared to HBC. Apart from single core discotics, covalently-linked assemblies in the form of the HBC dumbbell and star-shaped, tri-arm “super-molecules” with HBC, C96, and C132 terminal cores are modeled by means of MD simulations, elucidating their tendency to form structurally robust chiral molecular nanowires, densely packed into hexagonal molecular crystals. A multiscale methodology is adopted, using information from *ab-initio* DFT calculations, in order to provide insight for possible charge transfer mechanisms pertinent to such assemblies.

As regards initial configurations to be used as input for atomistic simulations, in cases where crystallographic constructions are not applicable or desirable, a hybrid MC bond-by-bond growth methodology is proposed and utilized, capable of growing soft nanophases out of rigid nanostructured areas in a given simulation domain.