

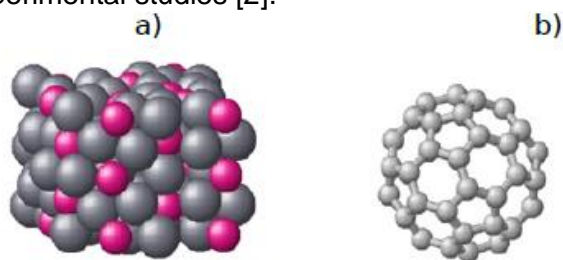
# Rational Design of Molecular Nano-Architectures on Complex Metallic Surfaces

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Self-assembly of 2D molecular films on metal surface templates presents major applications in the fields of molecular sensors/electronic, self-lubrication and photovoltaics. In this context, **the expansion of self-assembly on intermetallic complex surfaces with regards to usual simple metallic surfaces should help to achieve a better understanding of this process, and lead to the rational design of new systems with potentially innovative physical properties.** We therefore propose, in this thesis, to investigate these questions based on a multiscale theoretical approach, using 2D molecular films self-assembled on quasicrystalline-related substrates. Indeed, only a few attempts to formally refine the predictions of self-assembly have been made in materials science [1]. One major obstacle is that the corresponding thermodynamic equilibrium structure is the result of a subtle interplay between the energy gained upon molecular adsorption and association and the entropy lost during the surface confinement. To tackle this problematics, we will consider **model systems** constituted by **binary quasicrystalline approximant as substrates**, like  $\text{Al}_9\text{Co}_2(001)$  and  $\text{Al}_{13}\text{Co}_4(100)$  (Figure 1.a). The set of molecules will be  **$\text{C}_{60}$  molecules** (Figure 1.b) as a primary objective since they are an archetypal model system for the proposed approach of self-assembly and they have been the subject of previous experimental studies [2].



**Figure 1** : Basic systems of the projected study.  
a) Lattice of a complex intermetallic  $\text{Al}_{13}\text{Co}_4$ .  
b) Fullerene  $\text{C}_{60}$ .

The methodology that will be implemented during the thesis is based on **multi-scale modelling**: Density Functional Theory (DFT) method for electronic structure calculations, off-lattice Monte Carlo (MC) method for simulating large 2D molecular patterns and Molecular Dynamic (MD) to have access to trajectories of adsorbed molecules. DFT calculations will be performed to set appropriate force fields (FF) or energy models both for the molecule-substrate and molecule-molecule interactions. We will develop interatomic potentials at different degrees of simplification. Interactions for Carbon-Carbon, Carbon-Metal and Metal-Metal interactions will be generated within the Tight-Binding (TB) method [3,4] which will enable to obtain a set of modular energy models while keeping a significant influence of the electronic structure. Such models can be directly implemented in off-lattice MC simulations. Then, simplified versions of the potentials will be also developed for MD simulations, since in this case forces are required [5]. The work will be performed in close collaboration with prof. E. Gaudry (IJL, Nancy).

## References

- [1] *Predicting molecular self-assembly at surfaces: a statistical thermodynamics and modelling approach*, S. Conti and M. Cecchini, Phys. Chem. Chem. Phys., 18 (2016) 31480; *Self-assembled monolayers in organic electronics*, S. Casalini et al., Chem. Soc. Rev., 46 (2017) 40-71.
- [2] *Self-Organized Molecular Films with Long-Range Quasiperiodic Order*, V. Fournée, É. Gaudry, J. Ledieu, M.-C. de Weerd, D. Wu, T. Lograsso, ACS Nano 84 (2014) 3646-3653.
- [3] Ordering trends in transition metal alloys from tight-binding electronic structure calculations, J. H. Los, C. Mottet, G. Tréglia, C. Goyhenex, Phys. Rev. B 84 (2011) 180202 (R).
- [4] *A tight-binding potential for atomistic simulations of carbon interacting with transition metals: Application to the Ni-C system*, H. Amara et al., Phys. Rev. B 79 (2009) 014109.
- [5] *Chemical Physics at Interfaces within a Refrigerant-Lubricated Contact: From Electronic Structure to Large-Scale Molecular Dynamics Simulations*, S. Tromp, L. Joly, M. Cobian, N. Fillot, J. Phys. Chem. C 122 (2018) 5420-5429.