Ab initio adsorption of organic additives on an iron surface

P. Bedolla Velazquez[1], S. Eder[2], N. Dörr[2] , A. Vernes[1,2*]

[1)] Institute of Applied Physics, Vienna University of Technology, Wiedner Hauptstraße 8 - 10 /134, 1040 Vienna, Austria.
[2)] Austrian Center of Competence for Tribology, Viktor-Kaplan-Straße 2, 2700 Wiener Neustadt, Austria.

[*]Corresponding author for vernes@ac2t.at

1. Introduction

The main goal of the present contribution is to understand by simulating on a quantum mechanical basis the physi- and chemisorption of organic additives on metallic surfaces, the formation of additive films in nanotribological systems. In particular, here the adsorption of isooctane and ethanol on a bcc Fe(001) surface will be in detail investigated..

2. Computational details

All quantum mechanical calculations were performed in the framework of the density-functional theory (DFT) [1] using the generalized gradient approximation (GGA) [2] as implemented within the Vienna Ab initio Simulation Package (VASP) [3]. Projector augmented wave (PAW) pseudopotentials [4] are considered to describe the potential between the ions [5] and a cut-off energy of 400 eV was applied for the plane-wave-basis set. The k-space integrations were performed using a 2×2×1 Monkhorst-Pack mesh [6], where the tetrahedron method with Blöchl corrections was employed for the static calculations and a Gaussian smearing with a width of 0.2 eV for the relaxations.

3. Set-up of nanotribological systems

In order to simulate the adsorption of isooctane and ethanol on a bcc Fe (001) surface, it was employed a supercell containing a 10-layer Fe slab with a 5×5 surface (250 atoms in total). The Fe slabs were separated by a vacuum of 29.73 Å (4.5 times the calculated DFT bulk lattice constant) and repeated periodically throughout space. The previously relaxed organic molecules, i.e., isooctane and ethanol, were placed above this slab at a distance Z_C. As depicted in Fig.1, the isooctane was oriented in such a way that the plane formed by the carbons of the main chain was parallel to the Fe surface as suggested by previous studies [7]. This setup was tested and showed to be sufficient to avoid interaction between neighboring slabs and molecules.

4. Preliminary results and outlook

The set-up introduced above was constructed for different values of Z_C. Each of these systems was relaxed allowing the ions of the top four layers of the slab and the molecule to move in all directions with the only constrain that the distance between the ions marked in Fig. 1 remains constant. The energy of the nanotribological system as a function of Z_C, in case of isooctane shows a binding energy of approximately 46 meV and a equilibrium distance between the slab and the molecule of 5.25 Å, see Fig. 2. In addition, extensive static and dynamic calculations will be performed to simulate the formation of additive films.

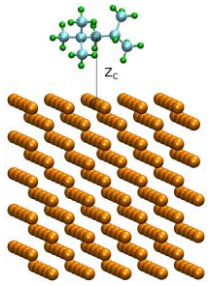

Fig. 1: An isooctane molecule at a given distance Z_C above the bcc Fe(001) slab.

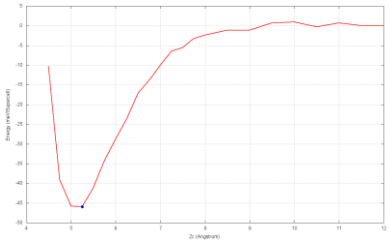

Fig. 2: Energy as a function of Z_C. The mark point corresponds to the energy of the system in Fig. 1.

5. References

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