

THE ELECTROSTATIC ORIGIN OF POLAR HYDROPHOBICITY: WETTING AND FRICTION OF FLUORINE-TERMINATED CARBON SURFACES

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KEYWORDS

Fluorinated carbon; wetting; friction; atomic-scale simulations

ABSTRACT

The carbon-fluorine (C-F) bond is a polar, covalent chemical bond that is responsible for the chemical stability, hydrophobicity and low friction of many fluorinated carbon compounds [1,2]. However, the inconsistency between the polarity of F-terminated carbon surfaces and their hydrophobicity is still a controversial phenomenon that goes under the name of “polar hydrophobicity” [3]. Here, we first present the results of quantum-mechanical (QM) simulations that explain the microscopic origin of polar hydrophobicity of F-terminated carbon surfaces. We then show how the QM results can be extended to larger time- and length-scales by means of classical molecular dynamics (MD) simulations that are used to investigate wetting and friction of F-terminated diamond surfaces.

Density functional theory (DFT) simulations of fluorinated and hydrogenated diamond (111) surfaces interacting with single water molecules reveal that, despite the polarity of C-F bonds, “polar hydrophobicity” of the fully F-terminated surfaces is caused by a negligible electrostatic interaction between surface and water [4]. The densely packed C-F surface dipoles generate a short-range electric field that decays within the core repulsion zone of the surface, thus vanishing in regions accessible by adsorbates. As a result, water physisorption on fully F-terminated surfaces is weak and dominated by van der Waals interactions. Conversely, the near-surface electric field generated by loosely packed dipoles on mixed F/H-terminated surfaces has a considerably longer range, resulting in a stronger water physisorption that is dominated by electrostatic interactions. The suppression of electrostatic interactions also holds for perfluorinated molecular carbon compounds, thus explaining the hydrophobicity of many fluorocarbons.

This electrostatic phenomenon is only possible because of the limited electronic spill-out of C-F and C-H bonds. Our QM simulations can indeed be reproduced and rationalized by a simple point-charge model, and a classical force field can be

developed to simulate length- and time-scales that are far beyond those accessible by means of DFT simulations [4]. Examples of classical MD simulations will be presented for friction and wetting of F/H-terminated diamond surfaces (Fig. 1).

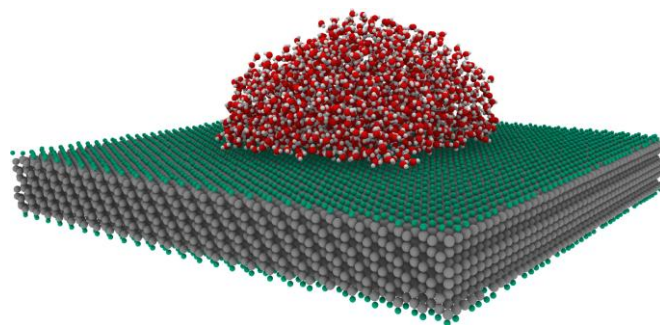


Fig. 1: Classical MD simulation of a 2000-water-molecule droplet on a F-terminated diamond surface

ACKNOWLEDGMENTS

We are grateful to ExxonMobil Research and Engineering for funding and to the John von Neumann Institute for Computing for the computer time provided on the supercomputer JURECA at the Jülich Supercomputing Centre.

REFERENCES

- [1] O'Hagan, D., “Understanding organofluorine chemistry. An introduction to the C-F bond”, Chem. Soc. Rev. 2008, 37, 308–319.
- [2] Bai, S., et al., “Tight-binding quantum chemical molecular dynamics simulations of the low friction mechanism of fluorine-terminated diamond-like carbon films”, RCS Adv. 2014, 4, 33739-33748.
- [3] Biffinger, J. C., Kim, H. W., DiMugno, S. G., “The polar hydrophobicity of fluorinated compounds”, ChemBioChem 2004, 5, 622–627.
- [4] Mayrhofer, L., et al., “Fluorine-terminated diamond surfaces as dense dipole lattices: the electrostatic origin of polar hydrophobicity”, J. Am. Chem. Soc. 2016, 138, 4018-4028.