

Searching for an electronic fingerprint on 2D materials

2d-materials-based sensing in liquid solvents

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In Short

- (Bio)sensors based on liquid gated field effect transistors (FETs)
- VdW interactions of analytes/solvents with graphene, graphene-oxide and molybdenum disulfide (MoS_2)
- Combining ab-initio DFT and classical MD simulations
- Development of novel interaction potentials

Two dimensional materials such as graphene and transition metal dichalcogenides (TMDCs) show great potential being employed in newly developed sensing devices. When integrated in *liquid-gated* field-effect transistors (FETs) they are able to detect small inorganic molecules such as NH_3 but also larger biomolecules like proteins or DNA [1]. Graphene based FETs (GFETs) are hereby functionalized with short, target-specific oligonucleotides (DNA aptamers) allowing for a high selectivity and sensitivity regarding molecular (bio)sensing. A sensing response is recorded via a shift of the so called *Dirac voltage*. This minimum of the drain current at different gate voltages marks the transition point between the hole-mobility-dominated and the electron-mobility-dominated regimes inside the conducting material.

Measurements using GFETs and other 2d-materials-based bio-sensors have to take place in a physiological, liquid environment. The formation of a diffuse ionic layer as well as the structure of the solvent molecules at the slab materials interface are believed to play a vital role for the sensing response and have to be considered to fully understand the mechanism and the electronic reaction of the underlying materials. Here atomistic simulations can give further insights and help to understand the experimentally observed electronic response.

As part of a DFG funded research training group, the project tries to further investigate the solvents' and analyte molecules' influence on the electronic response of the 2d materials. The change of the interfacial electronic structure induced by molecular adsorption will be analysed for solvents and analytes with different polarity at an electronic resolution.

Figure 1 shows the charge density difference of a guanine molecule on a graphene surface calculated with a vdW-dispersion corrected functional demonstrating the polarizable nature of the graphene sheet.

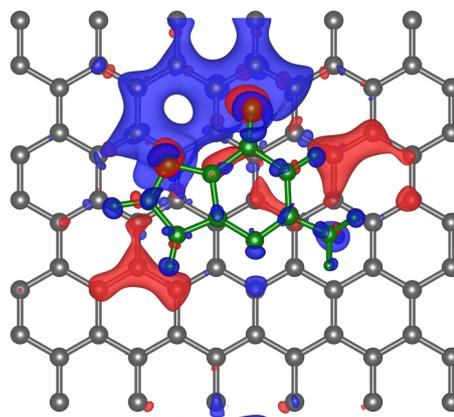


Figure 1: Charge density difference of guanine (in green) adsorbed on a graphene C(0001) surface in vacuum. Cutoffs are $+0.003$ and $-0.003 \text{ e}/\text{\AA}^3$ for the blue and red isosurfaces, respectively.

Solvent molecules hereby encompass, with decreasing polarity: water, ethanol, benzene and toluene. The studied analytes will, among others, include the DNA nucleobase guanine as well as several polar, charged and apolar amino acids and carbohydrates. As 2d slab materials, we will assemble systems of graphene, graphene-oxide and molybdenum disulfide (MoS_2). In the initial phase of the project we will focus on polarisation patterns and shifts of phonon frequencies caused by local perturbations conducting ab-initio DFT simulations. Furthermore classical interaction potentials between 2d materials and solvents/analytes will be developed and optimized to enable larger scaled simulations involving proteins and DNA. Calculations of adsorption forces and free energies will then be comparable to single molecule force spectroscopy measurements.

The simulations have to account for the non-covalent dispersion interactions between the analytes/solvents and the slab material. The investigated analytes are physisorbed (and not covalently bonded as one might expect) to the surface, thus, making the use of van-der-Waals corrected first-principle calculations inevitable. For this purpose different correction schemes can be employed and have been tested such as the vdW-D3 pair-potential [3] and the vdW-DF2 corrected exchange-correlation functional [4]. The force field employed for the classical calculations is based on the CHARMM36 force field.

In the case of graphene it is extended via the recently developed GRAPPA [2] force field which incorporates parameters for the polarisability of graphene using a *rigid rod* model. We will establish a *fingerprint* caused by perturbations of the electron density of analytes adsorbed to the surface in vacuum and in solution as can be seen in Figure 2.

- [4] K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist, D. C. Langreth, *Phys. Rev. B* **82**, 081101 (2010). doi:110.1103/PhysRevB.82.081101

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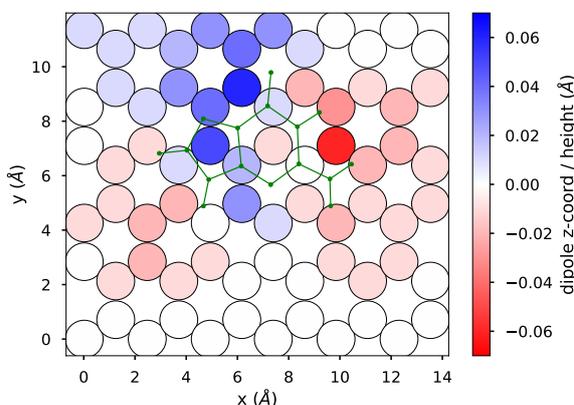


Figure 2: Dipole fingerprint of guanine adsorbed on a graphene C(0001) surface using the GRAPPA[2] polarisable force field.

Combining results gained from ab-initio DFT and classical MD simulations we will enhance currently available force fields as well as develop new interaction force field parameters for several combinations of 2d materials, solvents and analytes. As it is not feasible to fully describe a system containing larger analytes (e.g. DNA or protein molecules) as well as hundreds of solvent molecules solely using ab-initio DFT methods, in its final stage the project aims to develop a mixed QM/MM approach. This approach should accurately describe the overall surface interactions using the developed classical force field potentials while at the same time employing higher resolution DFT methods to describe the locally perturbed areas of the slab surface.

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More Information

- [1] N. Green, M. L. Norton, *Anal. Chim. Acta* **853**, 127-142 (2015). doi:10.1016/j.aca.2014.10.023
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