Graphene biosensors: Modeling the hydrophobic graphene/electrolyte interface

Stefan Birner[1], Andreas Lippert[1], Markus Dankerl[1], José A. Garrido, Nadine Schwierz[2], Roland R. Netz[2], and Peter Vogl[1]

Graphene, with its unique combination of physical and electronic properties, is a very promising material not only for electronics, but also for biosensor and bioelectronic applications. In this respect, a quantitative understanding of the sensitivity of graphene solution-gated field effect transistors (SGFET) capable of operation in aqueous environments is important. Here, we present results of numerical calculations on the variation of the charge carrier concentrations under electrolyte gate control. The effect of the solution-gate potential on the electronic properties of graphene is explained using a model which considers the microscopic structure of water at the graphene/electrolyte interface.

We calculate self-consistently the spatial charge and electrostatic potential distribution in the graphene/electrolyte system by solving the nonlinear Poisson equation. The model has been implemented into the next**nano** software [1]. It includes a spatially varying static dielectric constant in the electrolyte which is proportional to the water density variation according to Ref. [2], and varies from $\varepsilon_r = 1$ at the interface to $\varepsilon_r = 78$ further away from the interface. The distributions of the different ions (Na^+, Cl^-) in the electrolyte are calculated using an *extended* Poisson-Boltzmann approach that takes into account recently published [2] ionic potentials of mean force (PMFs). The fitting functions of the PMFs correspond to hydrophobic (i.e. nonpolar) solid/liquid interfaces based on data obtained from atomistic molecular dynamics simulations [2]. The PMFs have the effect of repelling the ions from the interface and are zero at distances larger than 1.4 nm from the interface.
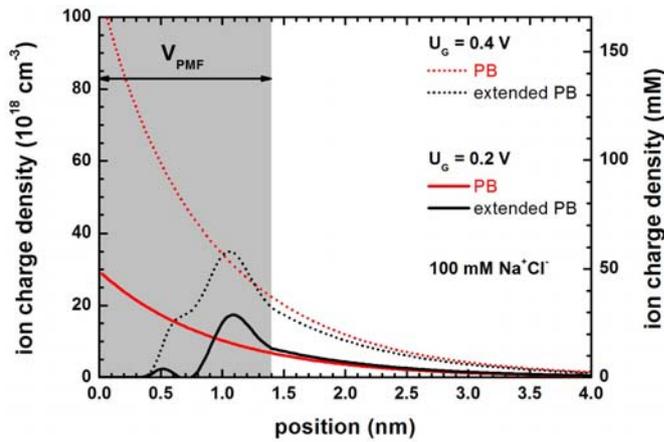
Fig. 1: Total ion charge density profile for $U_G = 0.2$ V (solid lines) and $U_G = 0.4$ V (dotted lines) for i) the standard Poisson-Boltzmann model (red lines) and the ii) extended Poisson-Boltzmann model (black lines), which considers a hydrophobic solid/liquid interface. The grey rectangle indicates the region where the potentials of mean force are nonzero and thus repel the ions from the graphene surface which is at 0 nm.

We compare this approach with the traditional Poisson-Boltzmann equation where no PMFs are employed while assuming a constant value of $\varepsilon_r = 78$ for the static dielectric constant of the electrolyte. We find significant differences for the spatial distribution of the resulting ion density (Fig. 1), as well as for the potential distribution, sheet carrier density and capacitance (Fig. 2). The variation of the electrostatic potential across the graphene/electrolyte interface is shown in Fig. 2a) for two different values of the applied gate potential U_G revealing a significant potential drop in the electrolyte for the extended Poisson-Boltzmann model, whereas in the

[1]WSI. Corresponding author: SB, phone: +49-89-289-12752, email: stefan.birner@nextnano.de
[2]Physics Department (T37), Technische Universität München, 85748 Garching
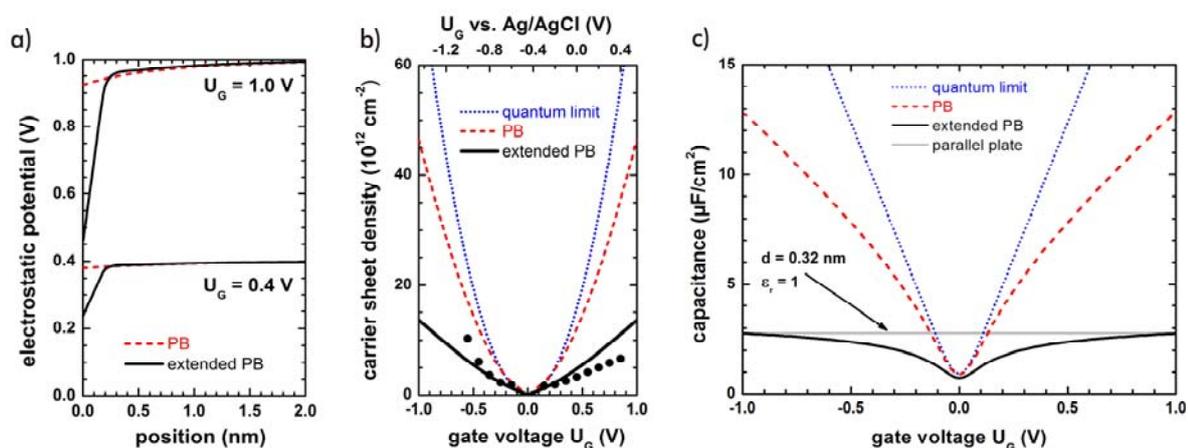
Fig. 2: a) Potential distribution in the electrolyte for the hydrophobic solid/liquid interface (extended Poisson-Boltzmann model) and the standard Poisson-Boltzmann approach (PB) at two different voltages. b) Carrier density in the graphene layer as a function of applied gate electrode potential comparing three different models with experimental data. c) Interfacial capacitance of the graphene/electrolyte system as a function of applied gate voltage for the extended PB and the standard PB model. The blue line shows the quantum limit.

case of the simple Poisson-Boltzmann (PB) model, the potential drop in the electrolyte is almost negligible and most of the potential drops in the graphene layer, i.e. the electrostatic potential in graphene approximately equals U_G. This situation resembles the "quantum limit" condition where a shift in U_G corresponds directly to a shift of the Fermi level with respect to the Dirac point, i.e. $E_{F,graphene} = eU_G$. In the case of the extended PB model, an important potential drop occurs in the electrolyte, which strongly reduces the electrostatic potential in the graphene film. The carrier density versus applied gate voltage obtained for the two different models, together with the quantum limit, is shown in Fig. 2b). Here, the hydrophobic model (extended PB) leads to results very close to the measured electron and hole densities in graphene [3]. The results of the total capacitance calculations ($C = \partial Q / \partial U_G$) using the standard PB model and the extended PB model are compared in Fig. 2c) to the case of the quantum limit. Here, the grey line corresponds to a simple plate capacitor model (width $d = 0.32$ nm, $\varepsilon_r = 1$). Consequently, at large voltages the plate capacitor model describes nicely the hydrophobic double layer capacitance whereas for small voltages the quantum capacitance of graphene dominates. The interfacial capacitance is a series capacitance of the quantum capacitance of graphene and the double layer capacitance of the electrolyte. Thus, the double layer capacitance at the graphene/electrolyte interface is about 3 μF/cm². In conclusion, a proper description of the graphene/electrolyte interface, which considers the effect of the solid surface on the dielectric properties of the water, can explain the experimentally measured low value of the double layer capacitance.

[1]   http://www.nextnano.de
[2]   N. Schwierz, D. Horinek, R. R. Netz, Langmuir **26**, 7370 (2010)
[3]   M. Dankerl et al., Advanced Functional Materials, *in print* (2010)