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Graphene at fluidic interfaces

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Citation

Belyaeva, L. A. (2019, October 23). *Graphene at fluidic interfaces*. Retrieved from <https://hdl.handle.net/1887/79822>

Version: Publisher's Version

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Issue Date: 2019-10-23

CHAPTER 7

Summary, conclusions and outlook

Graphene is known as a “wonder material” which was believed – 15 years ago – to revolutionize electronic technologies, a physicist’ treasure full of exciting fundamental phenomena, and at the same time, a material that has not yet met the industrial expectations. When it was first isolated in 2004, the research world was astonished by the ultimate simplicity with which it then became possible to produce a material in many aspects excelling the existing ones. Isolating this single material led to a number of fundamental discoveries and motivated several new research fields. In terms of application, the rich functionality of graphene inspired a multitude of new concepts and designs implemented in laboratory settings. However, despite the potential capability to revolutionize a number of current technologies, the much-anticipated transition from laboratory prototypes of graphene-based devices to large scale industrialization faced serious challenges: production, manipulation and design of devices based on large-scale production methods. And while mass-scale production of high-quality graphene now can be done with the CVD growth, methods to transfer and handle large sheets of CVD graphene are still under on-going development, aiming at cleaner and nondisruptive strategies. Finally, during the fabrication and operation of the device, graphene is routinely transferred from surface to surface and is affected by the changing environment – water, supporting substrate, air, electrodes, adsorbates, analytes etc. The overall device performance, therefore, is difficult to predict without assessing the impacts of every step of manipulation (and thus, of different interfaces and environment) on graphene. Graphene-liquid interfaces are of particular interest: they are ubiquitously used in graphene handling and device operation, but, nonetheless, are poorly understood, especially in comparison to graphene-solid interfaces.

This thesis expands the current knowledge on the interactions between graphene and fluidic interfaces, particularly on the effects that liquids have on the structural, electronic and mechanical properties of graphene. Secondly, it offers new liquid-based experimental solutions and methods for improving handling and characterizing graphene. Liquids and liquid interfaces, therefore, transform throughout this thesis from the subjects of studies into the tools for studies and *vice versa*.

7.1. Summary and conclusions

Chapter 2 shows how a biphasic system of two immiscible liquids can be used for graphene transfer. This method avoids polymer contamination typical for most common transfer methods, but also protects the graphene structure from cracking and folding, in contrast to other polymer-free strategies. It was found that liquids underneath and on top of graphene can serve both as a mechanical support and a protecting layer for graphene, similarly to a solid substrate and a polymer film. In fact, liquids can be a more flexible tool to transfer and handle graphene: their properties can be *in situ* modified by mixing with other liquids, freezing, evaporating etc. For example, a cyclohexane phase on top of graphene can be frozen to form a soft plastic crystal polymorph (similarly to a protective polymer film), which after the transfer can be removed by sublimation directly from solid to gaseous phase. Additionally, in Chapter 2 a liquid interface (namely, cyclohexane and water with graphene in between) was harnessed to study electron transport across the graphene sheet. Noteworthy, charge carrier mobilities exceeding the ones measured for the solid substrates were measured.

Chapter 3 concludes that the major reasons behind the measured improved electrical performance of graphene floating at liquid interfaces are lower strain and doping levels, as opposed to supported graphene. Interestingly, strain is well known as a major factor responsible for degraded electrical performance of graphene and graphene-based devices, but is almost impossible to prevent, as solid supports do not match the inherent morphology of graphene and disturb the homogeneity of the graphene surface. In contrast, liquid interfaces, irrespective of their chemical nature, are naturally more homogeneous and adapt to the inherent morphology of graphene.

Chapters 4 and 5 demonstrate how the use of liquids can provide insights where solid supports are impractical. The concept of using liquids, and water specifically, simultaneously as subjects of research and parts of the experimental setup proved particularly fruitful for the wettability studies on graphene. Unlike bulk solids, conventional sessile drop configuration is unstable on free-standing graphene: graphene breaks, due to gravity and surface tension of water. However, graphene is perfectly stable in the inverted configuration where water is used underneath graphene as a support; injection of an air bubble underneath

floating graphene results in an inverted but equivalent (to sessile drop setup) water-graphene-air interface allowing for a stable contact angle measurement (Chapter 4). In Chapter 5 water, this time in the form of ice and hydrogels, was again used as an underlying support for graphene, to probe for the first time the much debated wetting transparency of graphene in water. Altogether, the approaches described in Chapters 4 and 5 resulted in a number of principal insights: 1) graphene is intrinsically hydrophilic (water contact angle of $42^\circ \pm 3^\circ$) 2) graphene is wetting transparent in water, *i.e.* transmits water-water interactions, and 3) the quality of the graphene-substrate interface is a determinative factor for the occurrence of the wetting transparency of graphene.

Chapter 6 is the only part of this thesis that does not use or study interactions between graphene and liquids *per se*. It, however, adds a new important insight to the discourse: wetting properties of graphene at the macroscopic level do not straightforwardly translate into interactions between graphene and individual water molecules. Concepts of hydrophilicity and hydrophobicity are often used to interpret other phenomena, such as adsorption, desorption and chemical affinity to certain types of compounds. And while finding correlations between them provides a wider perspective, generalization can lead to incorrect conclusions. In particular, Chapter 6 demonstrates that the crystallinity of the growth substrate alters the desorption kinetics of water molecules from graphene, but has no effect on its macroscopic wettability.

7.2. Outlook

Graphene and other 2D materials promise unique opportunities for research and technology, but in return demand special approaches and development of alternative tools and characterization methods, different from those conventionally used for 3D materials. The approaches proposed in this thesis have already yielded interesting insights, but more importantly, they provide the ground for further developments. As a most straightforward implication, the knowledge and the methodology developed in this thesis can already be applied to other 2D van der Waals materials, such as hexagonal boron nitride, dichalcogenides and fluorographene.

Furthermore, the characterization and electrical measurements of graphene floating at liquid interfaces, presented in Chapters 2 and 3, provide settings for studying a variety of interfacial phenomena *in situ* – by varying the solvent composition, adding solutes and surfactants, applying gate voltage and magnetic field, and other external stimuli. Chemically functionalized graphene can be used for tuning the interactions with the liquid medium and solutes. Furthermore, the Surface Enhanced Raman Spectroscopy (SERS), instead of conventional Raman spectroscopy used in Chapter 3, can be applied to achieve higher resolution and detect more subtle effects occurring at the interface.

The relaxation of strain and enhanced charge carrier mobilities – arguably, the most significant findings of this thesis – make fluidic interfaces with free-floating graphene particularly appealing for *in situ* sensing in liquids: liquids can allow for increased sensitivity (due to reduced strain and enhanced charge carrier mobilities) and serve as an experimental media at the same time. The technical implementation, however, faces a major challenge: electrical probing of a one-atom-thin graphene layer free-floating on a liquid is extremely difficult (at least, in the way described in Chapter 2) even in laboratory conditions. In order to obtain an electrical response few problems must be first addressed: establishing non-destructive yet reliable graphene-electrodes contacts, preserving structural integrity of graphene and stabilizing graphene on the surface of water. The lack of stability, as the flip side of structural flexibility, is the major drawback of using fluidic interfaces in graphene research in general. As an alternative to direct electrical measurements, remote electrical probing of graphene in liquids can be used to circumvent the stability issues, especially given the rapid advancement that the remote technologies are currently undergoing.

Although liquids cannot fully replace solid substrates in graphene research, this work showed that their advantages as substrates certainly can be used more widely and facilitate several research fields. In a world seeking sustainable energy solutions, liquids with their ubiquitous presence in nature, commercial availability and inexpensiveness (especially compared to the solid substrates used in hi-tech industries) will inevitably have to become an essential part of future technologies. Research presented in this thesis contributed to this emerging trend by developing concepts and tools to harness liquids in application to

graphene, and by proving that simple and sustainable solutions can also yield superior performance.