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Quantum Mechanics/Molecular Mechanics (QM/MM) applied to tribology: real-time monitoring of tribochemical reactions of water at graphene edges

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Abstract

Tribological phenomena, such as wear and boundary lubrication, are deeply influenced by tribochemical reactions, i.e., chemical reactions occurring in the presence of mechanical stresses. Atomistic descriptions of these processes are still in their infancies because of the high computational costs required to properly describe the buried sliding interface by theoretical methods. In this paper we outline the application of the Quantum Mechanics/Molecular Mechanics approach to simulate tribochemical reactions during sliding and show that it can accurately describe the tribochemistry of graphene interacting with water molecules, a system which is of relevance for technological applications. Comparison with *ab initio* (Car-Parrinello) and classical (using the ReaxFF force field) molecular dynamics calculations highlights the advantages of this hybrid approach both in terms of computational costs and accuracy of the results.

Keywords: Tribology, Tribochemistry, QM/MM, DFT, graphene, water, friction

1. Introduction

The search for novel lubricant materials and coatings has gained increasing importance in recent years to reduce the massive economic and environmental costs of friction and wear. The functionality of many lubricant materials depends on chemical reaction occurring at the buried interface during sliding, therefore it is highly desirable to understand how they take place. However,

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tribochemical reactions are different from thermally activated ones at the surface because tribological conditions involve also molecular confinement plus applied mechanical stresses (load and shear), and they are difficult to monitor in real time by experiments. In this context, very powerful tools are provided by atomistic simulations, especially those based on an *ab initio* approach that allows to accurately describe chemical processes occurring in conditions of enhanced reactivity.

The use of first principles calculations to investigate tribochemical processes has increased significantly in the last decades. Within this approach, the tribochemistry of different lubricant materials such as diamond [1–4], layered materials [5–10] and lubricant additives [11–18] have been successfully studied. The main focus of these previous studies has been on the effects of tribochemical modifications on the adhesion and shear strength, while few studies [2–4, 7, 10] analyze the occurrence of these reactions in real time. The high computational costs of *ab initio* Molecular Dynamics (MD) has limited its application to small systems, constituted by few hundreds atoms with simulation times in the range from 10 to 200 ps [2, 4].

One can try to go beyond these limitations by using classical MD together with a reactive force field, such as, for example, ReaxFF [19], which permits chemical reactions within a classical framework. This approach, used in recent years to study different tribochemical mechanisms [20–26], allows to increase significantly the time and length scales compared to *ab initio* methods [27–30]. However, current parametrizations do not necessarily reproduce accurately the interactions under tribological conditions, where the confinement and the mechanical stresses can destabilize the electronic structure of the compounds, with consequent changes in their reactivity.

A possible solution, combining the computational advantages of molecular mechanics (MM) with the accuracy of quantum mechanics (QM), is given by the QM/MM approach, first developed by Warshel and Levitt [31] in 1976. In this method only the expected chemical active region is treated at a full quantum level, while the interactions in the remaining part of the simulation box are described by classical force fields. The QM/MM is nowadays widely employed for the simulation of biomolecular systems [32], where the reactive site can be clearly identified and circumscribed, less frequently to study mechanical properties in material science [33]. We apply the QM/MM method to simulate a model system composed of graphene layers and graphene ribbons interacting in the presence of water, by means of the LAMMPS [34] computational suite

coupled to the Quantum ESPRESSO [35] computational suite. Understanding the tribochemistry of graphene/graphite interacting with water is highly relevant for their tribological application, because humidity deeply effects the performances of these solid lubricants for reasons that are not yet completely understood [36–54].

In this paper we show that the QM/MM method is able to provide an accurate description of the processes occurring when graphitic materials interact with water molecules under tribological conditions. The results of the QM/MM simulation are compared with both *ab initio* Car-Parrinello MD and ReaxFF MD simulations, and the accuracy and computational costs of these three approaches are discussed.

2. Computational Methods

First, we perform an *ab initio* MD simulation by using a modified version of the Car-Parrinello (CP) [55] code provided in the Quantum ESPRESSO suite for dynamical processes in tribological systems [2], and a classical MD calculation with two different types of ReaxFF parametrization implemented in the LAMMPS package [34]: the first one was developed by Chenoweth et al. [56] (from now on ReaxCHO) and has been already used to describe the interaction between water and graphene [57]; the second was proposed by Liu et al. [58] (from now on ReaxLG) to better describe van der Waals interactions within the parametrization developed by Strachan et al. for hexahydro-1,3,5-trinitro-1,3,5-s-triazine (RDX) decomposition [59], by adding a low gradient London dispersion term.

The simulation cells used to model the reference systems within the CP and MD approaches are illustrated in Fig. 1. The CP simulation cell is laterally a rectangle of dimensions $12.8 \text{ \AA} \times 14.8 \text{ \AA}$, with periodic boundary conditions, and contains a graphene ribbon and 6 water molecules intercalated between two external graphene layers, for a total of 204 atoms. The classical MD simulation box has an in-plane size four times larger and two additional graphene layers have also been included to increase the stiffness of the boundary layers, for a total number of atoms equal to 1392. All the geometrical details of the simulated systems are reported in Table 1 together with the corresponding timestep values.

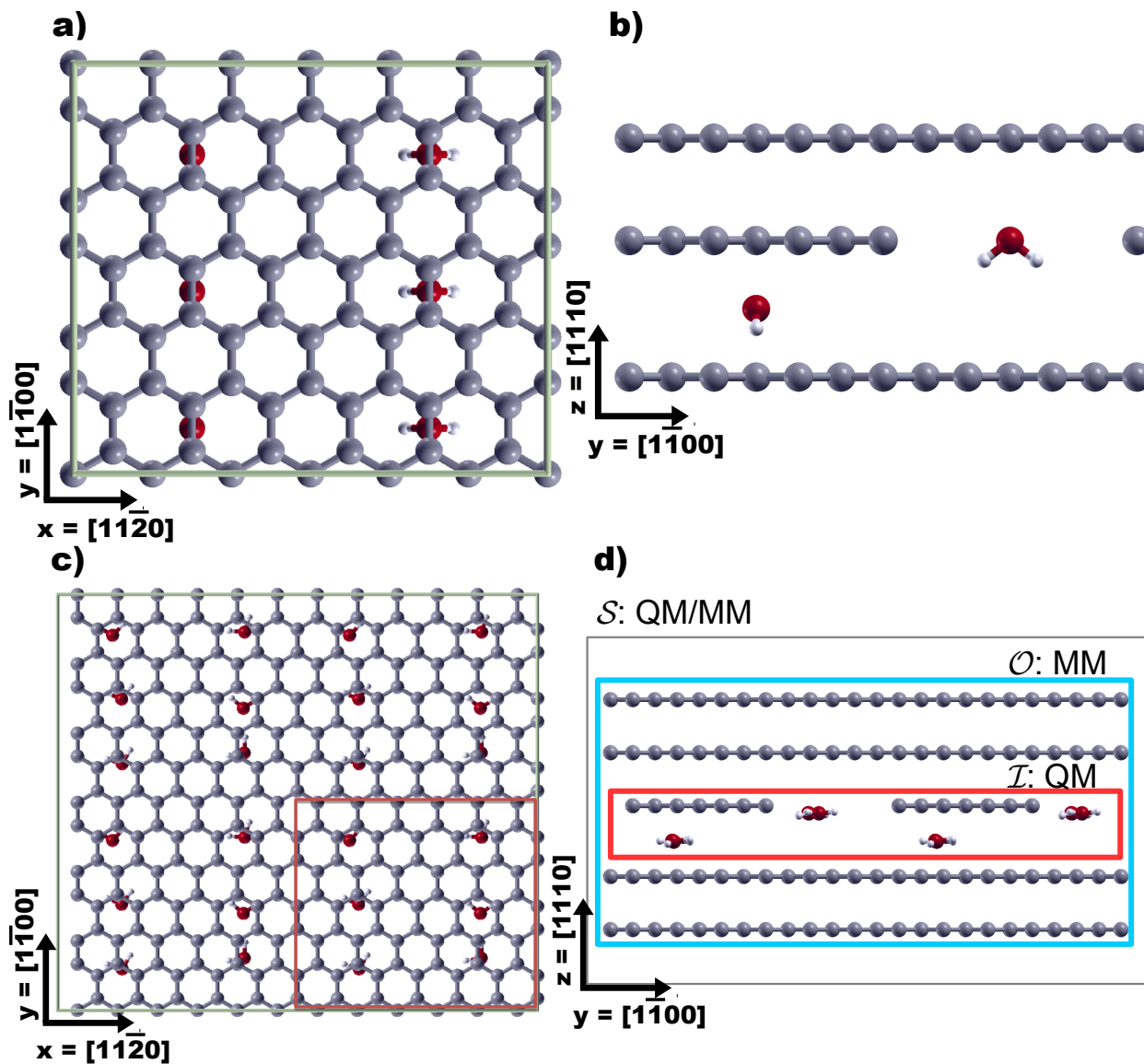


Figure 1: Ball and stick representations of the lateral and top views for the simulation systems used in the QM (a-b) and in the MM-QM/MM (c-d) calculations. The simulation boxes are indicated by solid green lines. In panel (c), the QM simulation box is marked with an orange line for comparison. In panel (d), a pictorial representation of the partitioning of system S within the QM/MM approach is shown: the classical region (O) is represented with blue line, while the quantum region (I) is detailed by the red line.

Table 1: Parameters of the simulation cells adopted in each of the computational approaches. The cell box size is in \AA^3 , while the timestep is in fs.

Method	Cell box size	Atoms	H ₂ O molecules	Ribbons	Boundary layers	Timestep
QM (CP)	$12.8 \times 14.8 \times 24.7$	204	6	1	2	0.12
MM (ReaxFF)	$26.0 \times 30.0 \times 30.0$	1392	24	2	4	0.10
QM/MM	$25.7 \times 29.6 \times 30.0$	1392	24	2	4	1

Before starting the simulations, we optimize the geometry of the systems under an applied load of 11 GPa. Although such a value for the stress may appear to be quite large compared to the experimental values, one has to keep in mind that the simulated systems are small, periodically space filling, idealized surfaces which are thought to represent what happens in small contact area of mesoscopic systems. Similar numerical values have been commonly used in tribological ab-initio calculations [2, 10], where such high values are in particular instrumental in obtaining a significant number of activated chemical events in the relatively short times over which it is possible to integrate the dynamics using ab-initio calculated forces.

The systems are then thermalized at constant temperature $T = 300$ K by means of a Nosé-Hoover-chain (NHC) thermostat with a damping parameter of 33.3 fs. In the CP simulation, a NHC thermostat with a damping parameter of 5 fs is also added to the electronic degrees of freedom of the system. After thermalization, a shear stress of 1 GPa is applied along the $[1\bar{1}00]$ direction of the outermost graphene layers. The lateral shear stress is then removed and the systems are let free to evolve without any lateral force applied.

The description of electronic structure in CP calculations is based on the following computational choices: the Perdew-Burke-Ernzerhof parametrization [60, 61] for the exchange correlation functional, corrected with the semi-empirical Grimme scheme (PBE-D) [62] to take into account the effect of van der Waals interactions. The Brillouin zone is sampled at the Gamma point. The cut-off for the plane-wave (density) expansion is set to 40 (320) Ry, an electron fictitious mass of 450 a.u. $[= 4.1 \cdot 10^{-28} \text{ kg}]$ is used and the hydrogen nuclei of the water molecules are replaced

with deuterium to reduce possible unphysical couplings between electronic and ionic degrees of freedom during the dynamics.

For the QM/MM simulation, we divide the whole simulation box (\mathcal{S}) shown in Fig. 1(d) into two separate regions: the inner quantum region (\mathcal{I}), in which the atoms are treated by the first principles approach (DFT in this case) and the outer classical region (\mathcal{O}) in which the atomic interactions are described by means of a classical force field. The total energy E_{tot} is separated into three terms:

$$E_{\text{tot}} = E_{\text{QM}} + E_{\text{MM}} + E_{\text{QM/MM}} \quad (1)$$

where E_{QM} is the energy of the QM sub-region, E_{MM} is the energy of MM sub-region and $E_{\text{QM/MM}}$ is the energy arising from the interaction between the QM and MM sub-regions. The $E_{\text{QM/MM}}$ contribution can be calculated in different ways, depending on the implementation of the QM/MM approach. In particular, within the Quantum ESPRESSO/LAMMPS (QE/L) combined code, $E_{\text{QM/MM}}$ is obtained through a subtractive scheme [32]:

$$E_{\text{QM/MM}} = E_{\text{MM}}^{\mathcal{S}} - E_{\text{MM}}^{\mathcal{I}} + E_{\text{QM}}^{\mathcal{I}} \quad (2)$$

where $E_{\text{MM}}^{\mathcal{S}}$ is the energy of the complete simulation cell calculated with the classical force field, $E_{\text{QM}}^{\mathcal{I}}$ is the energy of sub-region \mathcal{I} evaluated by means of DFT calculations, and $E_{\text{MM}}^{\mathcal{I}}$ is the energy of the same sub-region evaluated with classical forces. The same scheme is used for the calculation of the forces, which is essential to perform a correct dynamical simulation. The interactions and the forces within the sub-region \mathcal{I} are treated at a full quantum level. The advantage of this approach is the simplicity of the implementation, which does not require to make further assumptions to couple the QM and MM regions. Indeed, in the QE/L program the exchange of coordinates and forces for the atoms in the the \mathcal{I} region is performed simply by MPI communications. Then, the hybrid code performs the dynamical integration within the QM/MM hybridization. Further details on the QM/MM implementation are provided as Supplemental Materials (SM). The same simulation cell is used for both the QM/MM and the classical MD calculations.

With the scheme described above we assign the infinite graphene layers to the classical \mathcal{O}

region, while the graphene ribbons plus the water molecules are assigned to the I region. We, in fact, expect that the chemical reactions will involve the graphene edges and the water molecules. We use the following set of classical force fields to describe the atomistic forces occurring in the O region. The carbon-carbon interactions within graphene layers are described by second generation REBO potential [63, 64]. The Lennard-Jones parameters reported in Table 2 are used for the description of the graphene interlayer, the C-O and C-H interactions. There is no need to include an explicit classical description for the water-water interaction since this is fully treated *ab initio*.

Table 2: ϵ and σ parameters for the Lennard-Jones potentials used for the description of the graphene interlayer, the C-O and C-H interactions. The values for the graphene interlayer interaction are taken from Ref. 65, while Ref. 66 reports the values used for the C-O and C-H interactions.

	ϵ (kcal/mol)	σ (Å)
C-C	0.055	3.41
C-O	0.060	3.19
C-H	0.031	2.81

The QM/MM dynamical simulation is carried out for 11 ps following the same procedure adopted for the CP and MD simulations. The sampling of the initial velocities is obtained by a Maxwell-Boltzmann distribution at 300 K. We use three separate NHC thermostats (one for the uppermost graphene layers, one for the intercalated graphene ribbons and the water molecules and another one for the lowermost graphene layers) to thermalize the system for 1 ps, adopting the same temperature and damping parameter as for the CP and MD calculations. After that, we remove the thermostat for the intercalated region and let it to evolve freely without any temperature control. We set the energy (density) cut-off for the plane-wave expansion to 25 (200) Ry in the QM/MM calculation to speed up the convergence of the self-consistent calculation.

3. Results and discussion

3.1. Accuracy in describing tribochemical reactions

In this section we compare the atomic trajectories obtained within the QM, MM, and QM/MM computational schemes described above. They are made available as movies in the SM.

For all the dynamical simulations, the water molecules initially intercalated between the basal plane of the graphene ribbons and the underlying graphene layer move outside this region and occupy the interstitial gap between ribbons (Fig. 2). This behavior is independent from the adopted computational scheme and is in agreement with experimental [42] and theoretical observations [67] that the interlayer spacing in graphite is independent from the environment. This sheds light on the mechanisms of friction reduction in graphitic materials. It make it possible to rule out one of the proposed hypothesis to explain graphite lubricity in humid environment, based on the increase of layer separation due to water molecules intercalation [68], and point out the pivotal role of tribochemical reactions occurring at graphene reactive sites, as also suggested by recent experiments [42, 47, 49, 50, 54].

The QM simulation, reported in movie 1 of SM, shows a large number of chemical reactions taking place at graphene edges, which become completely passivated in the first two ps of the dynamics. The reaction products are consistent with those expected on the basis of first principles calculations of water chemisorption [67]. This confirms the reliability of the modified CP program in the study of chemical reactions occurring under tribological conditions [2, 3, 10]. However, the limited system size imposed by the computational cost of the QM simulation effectively reduces the variety of processes that can be observed. For example, one would be interested in considering the presence of a larger number of water molecules and more than one graphene ribbon per cell in order to investigate possible competitions between water-edge and edge-edge interactions.

We try to address this issue firstly by performing a MM simulation using ReaxFF. Before starting the dynamic simulation we tested how well both the ReaxCHO and the ReaxLG parametrizations reproduce the chemisorption energies obtained by DFT calculations [67, 69]. The results of this preliminary study, which is detailed in the SM, indicate that both parametrizations of the ReaxFF force field correctly describe the reaction energy for water dissociation along graphene

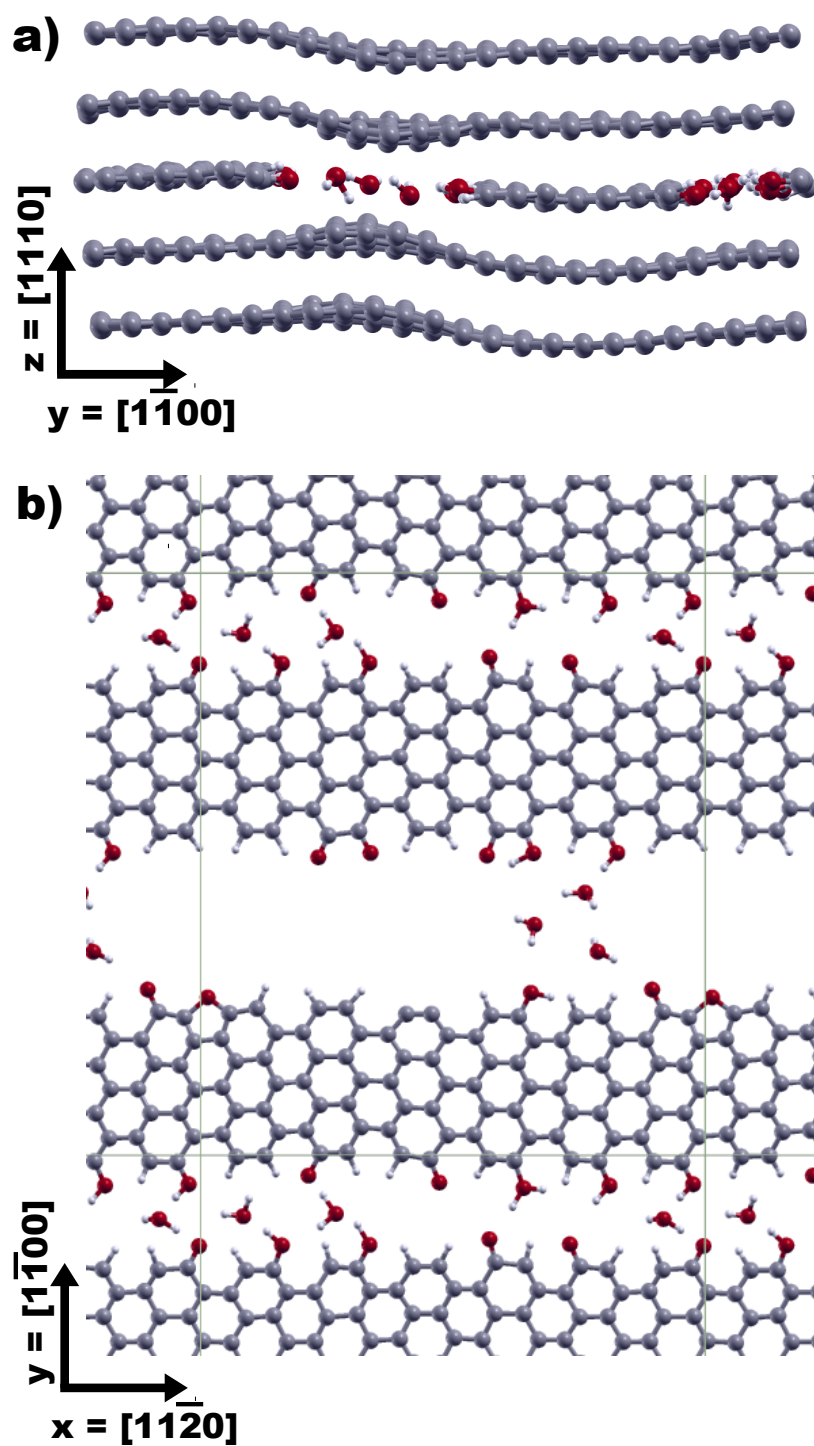


Figure 2: Lateral (a) and on top (b) snapshots acquired at the end of the QM/MM simulation.

edges. Therefore, it came as unexpected (see movie 2) the absence of any reactivity during the MM simulations, on a time interval which is much longer than the one for the corresponding QM simulation. We were able to observe the occurrence of chemical reactions only after removing, in the MM simulations, the temperature control on the ribbon and water degrees of freedom, i.e. by letting the temperature rise in the inner region, something which strongly suggests that those two ReaxFF parametrizations do overestimate in a significant way the most relevant activation barriers. However, the observed reaction paths and products were found not to be consistent with the DFT calculations (e.g., H_2 molecules are formed instead of adsorbed H and OH fragments) and very quickly, in about 20 ps, the graphene structure is completely decomposed, burnt down by violent reactions with the water molecules (movie 3). These results indicate that these two parametrizations of ReaxFF for water-graphene interaction, the ones which are currently available within LAMMPS, cannot properly reproduce the reaction pathways under tribological conditions for the system under consideration. Indeed the transferability of a specific force-field parametrization, especially to the harsh conditions imposed by the applied mechanical stresses, remains the problematic issue in the MM approach. While we are not currently interested in optimizing an ad-hoc parametrization for C-H-O interactions within some particular force field approach, such a step will necessarily be based on accurate ab-initio calculations of the relevant reactions paths occurring in tribological conditions. Here we show that it is at the same time simple and very effective to introduce an hybrid QM/MM scheme for this system that permits to give a satisfactory solution to the reported limitations of the pure QM or MM approaches.

As it can be seen in movie 4 of the SM, the products for water dissociation are perfectly consistent with those expected on the basis of the DFT calculations [67, 69], and the observed tribochemical reactions lead to the passivation of graphene edges as observed in the dynamic QM simulation. These facts merely validate the adopted hybrid scheme. Much more interestingly, the QM/MM simulation additionally uncovers cooperative processes that we could not observe in the QM simulation because of the too limited number of water molecules interacting with a single graphene ribbon. One remarkable example is the formation of a hydronium group (H_3O^+) during the simulation: at 1.7 ps [Fig. 3(a)], four water molecules form a cluster close to the graphene edge. One of these molecules interacts with the ribbon and dissociates forming a hydroxyl group, while

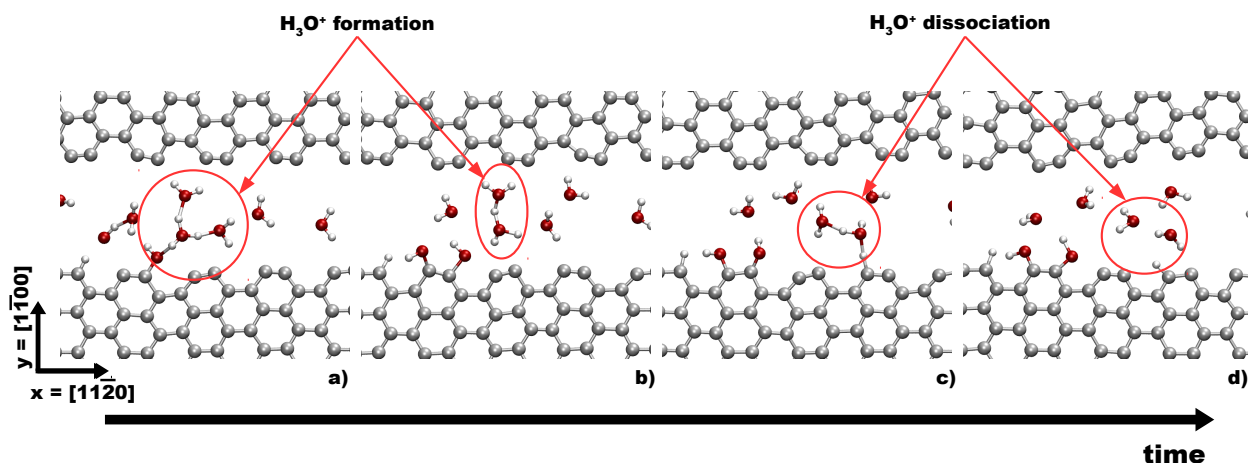


Figure 3: Snapshots, with time increasing from left to right, that show the formation and dissociation process of the H_3O^+ cation during the QM/MM simulation.

the leftover hydrogen atom is shared by two water molecules, leading to the formation of the H_3O^+ fragment [Fig. 3(b)]. Due to the high instability of this cation, in around 0.2 ps, as soon as the H_5O_2^+ group diffuses close to the ribbon [Fig. 3(c)], the additional proton is lost [Fig. 3(d)] completing the dissociation process. Another remarkable reaction path uncovered with the QM/MM simulation is the one shown in Fig. 4, leading to the formation of an epoxy group C-O-C along the graphene edge. This adsorption configuration is predicted as the most energetically favorable by DFT [67], but we could never observe it in our CP simulations. As shown in Fig. 4, the epoxy group is formed thanks to a cooperative process that involves three different water fragments: the free-standing water molecule in Fig. 4(a) pivots the move of a hydrogen atom from the hydroxyl group to the free oxygen attached on the ribbon [Fig. 4(b)-(c)]. Once the free oxygen is close enough to the carbon dimer of the edge, it can form an epoxy group which partially saturates graphene dangling bonds [Fig. 4(d)]. The formation of epoxy group in graphene has been confirmed experimentally and theoretically in several works [70, 71].

3.2. Computational costs

Having established the accuracy and the advantages of using the QM/MM method to describe tribochemical reactions, we now compare its computational performances with the QM simulation based on the CP approach.

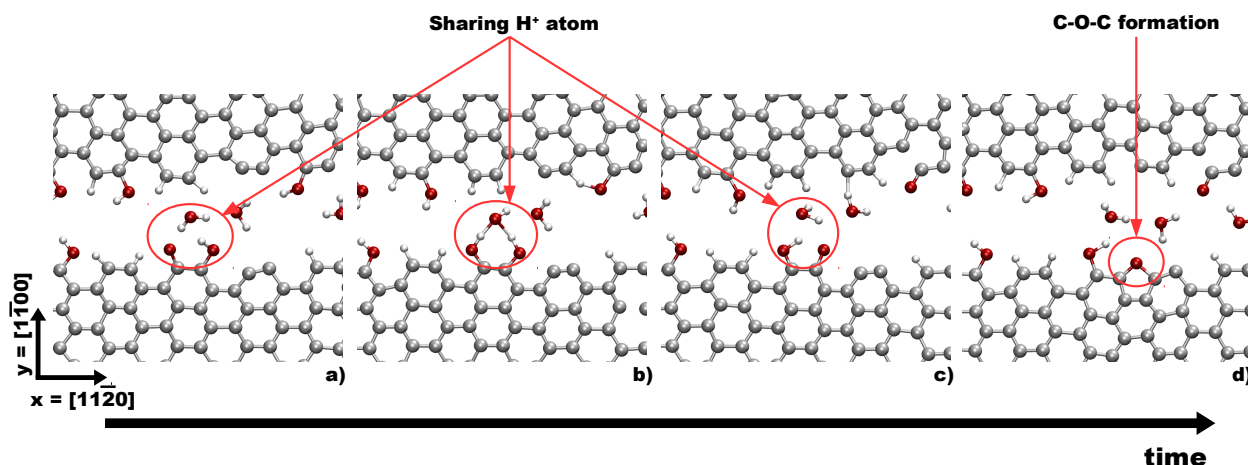


Figure 4: Snapshots, with time increasing from left to right, showing the formation of the C-O-C bridge during the QM/MM simulation.

As it can be seen in Table 3, the CPU time needed to simulate 1 ps of dynamics is, for the large system, reduced by a factor of at least 25 times when the hybrid QM/MM simulation is performed in place of the full QM one. The gain is much reduced when the smaller system is considered, but this is partly expected because of the relatively higher fraction of QM described atoms. The results are impressive and open up new perspectives for tribological simulations, with the possibility to consider the application of QM/MM to systems of larger size, which currently cannot be tackled with fully *ab initio* simulations due to the prohibitive computational costs. For completeness the corresponding CPU time required by the classical MD simulation is included. As expected, this is orders of magnitude smaller, but as long as currently available force fields do not provide a reliable description of the phenomena the advantages of the MM approach cannot be exploited. In this respect the rich variety of results obtained with the QM/MM approach constitute a relevant benchmark dataset to be compared with, for the development of more accurate force field parametrizations, of paramount importance to perform large-scale simulations in tribological conditions.

4. Conclusions

We describe, in an exemplary case, how to apply the QM/MM approach to tribology. This approach consists in finding a suitable subdivision of the system into a (smaller) part where in-

Table 3: Computational costs of the different methods performed on a Lenovo Adam Pass HPC facility, with Intel Xeon Phi 7250 processors.

Method	Atoms	Electrons	CPU-hours/ps
CP	204	792	5200
QM/MM	204	216	1570
CP	1392	5472	595000
QM/MM	1392	864	22050
MM	1392	-	2

teractions need to be treated by quantum mechanics, and another (larger) part where interactions can be accurately described by classical force fields. In a tribological system the most suitable subdivision is easily identified as chemical reactions usually take place at the interface, where the lubricant/environmental molecules are confined, while the semi-infinite bulks do not participate directly to the reactions. Our reference system is graphene, which is presently considered as a strategic system for tribological applications ranging from the nano- to the macro- scale and for which the effects of air humidity are very important but yet not clearly understood.

An important outcome of the present work concerns the microscopic understanding of the effects of moisture on graphene/graphite. Our simulations rule out water intercalation as the origin of graphite lubricity in the presence of humidity and point out the primary role of passivation of reactive graphene edges. The implications of our findings on the conclusive understanding of the effects of humidity on the lubricity of graphitic materials is discussed in a dedicated paper [72]. We find that water dissociation along the edges occurs at a very high rate under tribological conditions, and prevents the direct interaction of the sticky graphene edges with other graphene ribbons/flakes and with the sliding media. We believe this mechanism, monitored for the first time in real time by our simulations, to be key for graphite lubricity in humid environments.

The close comparison of the QM/MM scheme with state-of-the-art computational methods used in tribochemistry, namely *ab initio* MD based on the CP approach and classical MD based

on ReaxFF, highlights the great potential of the hybrid method. We, in fact, prove, for our system, QM/MM to be as accurate as the fully QM in describing tribochemical reactions, while the ReaxFF parametrizations considered in this study fails. Moreover, we show that the QM/MM scheme adopted in the present study offers the possibility to consider a system with almost 7 times more atoms without the exploding computational costs of QM dynamics and that this large size is essential for capturing collective atomistic processes, which can play a crucial role in tribochemistry processes. We show for example that the cooperative behavior of water molecules favor H diffusion and lead to the passivation of graphene edges in the energetically most efficient way, a cooperative behavior that did not occur in the smaller-size QM simulation due to the limited number of atoms we could consider.

Acknowledgments

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