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**DESIGN AND APPLICATION OF
COMPUTATIONAL TOOLS TO STUDY
SOLID INTERFACES AND MATERIALS TO
REDUCE FRICTION**

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Introduzione

L'attrito è la forza di resistenza al moto che si sviluppa tra due superfici che scorrono o rotolano l'una sull'altra. Si tratta di un fenomeno microscopico comune, la cui origine è da ricercare nelle forze di interazione adesive che si generano tra le superfici a contatto. Le dissipazioni dovute all'attrito causano ingenti costi energetici e ambientali in diversi settori, tra cui quello del trasporto e dell'industria. Si stima infatti che quasi un terzo dell'energia prodotta dai combustibili fossili per alimentare i veicoli venga spesa per vincere l'attrito. Si prevede che migliorare la tribologia delle superfici possa garantire una riduzione degli sprechi energetici pari al 40% entro i prossimi 15 anni. Lo studio dell'attrito richiede una profonda comprensione dei fenomeni microscopici che si sviluppano a livello della superficie. Le simulazioni da principi primi consentono di studiare le proprietà elettroniche e chimiche dei materiali con un alto grado di accuratezza, fornendo un modo per comprendere gli eventi tribologici. Nel corso degli anni, sono stati sviluppati diversi metodi basati sui calcoli a principi primi per studiare le proprietà dei materiali a livello atomico. Tra tutti, l'utilizzo di queste simulazioni in combinazione con un approccio high-throughput si sta diffondendo rapidamente negli ultimi decenni. Lo scopo di questo metodo consiste nel simulare migliaia di materiali in parallelo, in modo da selezionare tra essi un piccolo insieme di candidati con proprietà fisico-chimiche specifiche. L'obiettivo è accelerare la scoperta e la diffusione di nuovi materiali per la scienza e la tecnologia. Questa tesi esplora l'implementazione e l'utilizzo di diverse tecniche computazionali innovative nell'ambito della tribologia. Il lavoro si concentra principalmente sulla descrizione di un software realizzato per automatizzare l'attività di ricerca in nanotribologia ed effettuare studi high-throughput sulle proprietà delle interfacce. Nella sua attuale implementazione, il software consente di combinare qualsiasi coppia di materiali cristallini, che possono differire sia per composizione sia per orientazione, e studiare le loro proprietà tribologiche, come l'adesione e lo shear strength. Il programma è stato utilizzato per studiare le proprietà tribologiche tra due superfici solide a contatto, effettuando uno screening sugli elementi della tavola periodica. Lo studio ha permesso di stimare la relazione tra adesione e resistenza di una interfaccia, permettendo inoltre di identificare un modo per stimare la modalità di failure dei materiali. Un altro importante risultato di questo lavoro è la realizzazione di un modello teorico innovativo che combina la tradizionale tecnica GFMD alla dinamica molecolare a principi primi. Questo metodo ibrido migliora l'accuratezza delle simulazioni atomistiche tenendo conto del ruolo delle proprietà elastiche dei solidi e la propagazione di onde vibrazionali nel determinare l'attrito delle strutture atomiche. Il programma è stato utilizzato per calcolare le proprietà di attrito di una interfaccia diamante-diamante, considerando diversi gradi di passivazione delle superfici. Infine, questo lavoro riporta uno studio condotto sulle proprietà lubrificanti del fosforene, un materiale innovativo bidimensionale a base di fosforo. Dapprima sono stati studiati due strati di fosforene a contatto. Ciò ha permesso di individuare la presenza di una fase super lubrificante per una particolare orientazione degli strati. Tale lavoro costituisce un primo importante passo nella possibile ideazione di lubrificanti a base di fosforene. Successivamente, è stata valutata la capacità del fosforene di lubrificare un substrato di ferro, confrontando i risultati ottenuti con calcoli effettuati per grafene e MoS_2 .

Contents

Introduction

Friction is a force that resists the motion between two surfaces that slide or roll over each other. It is a common microscopic phenomenon that originates from the interaction forces generated between the surfaces in contact. Dissipations due to friction cause huge energy and environmental costs in various sectors, including transport and industry. It is estimated that nearly one-third of the energy produced by fossil fuels to power vehicles is spent to overcome friction [1]. One way to limit this consumption is to improve technologies to reduce friction. Numerous efforts are made in this direction to design increasingly efficient lubricating materials. In fact, improving the tribology of surfaces is expected to guarantee a reduction of the energy waste of 40% within the next 15 years [2].

The study of friction requires a deep understanding of the microscopic phenomena developing at the surface level. These processes are complex and require a microscopic characterization that experimental apparatus often cannot provide. Atomistic simulations give a possible solution to overcome this limitation. First-principle calculations, in particular, solve the fundamental quantum equations of the system without the need for further assumptions. This allows the electronic and chemical properties of materials to be represented with a high degree of accuracy, providing a way to understand the tribological events occurring at the nanoscale. Through the years, different methods and tools based on first-principle simulations were modeled to study the effect of friction and lubrication down to the atomic level [3, 4].

The increasing availability of computational resources has made it possible to use first-principles simulations in combination with a high-throughput approach [5]. The idea of high-throughput is to simulate thousands of materials in parallel to select a small set of candidates with specific properties. The aim is to accelerate the discovery and deployment of new materials for science and technology. The results of such studies, in fact, can assist the experimentalists to focus their research efforts on the most promising compounds. However, implementing high-throughput methods for materials science can be tough. It often requires articulated software and robust IT infrastructure to collect, analyze, and save the data in scientific databases.

This thesis explores the implementation and use of several innovative techniques in the field of computational tribology. The work mainly focuses on the description of the software we designed to automate the research activity in nanotribology. It can be used to carry out high-throughput analysis based on first-principle methods to evaluate various properties of solid interfaces. Chapter 2 provides a detailed description of the full capability of the robust and modular program that we designed. Of particular interest are the high-throughput workflows developed to match and characterize solid-solid interfaces automatically. In its current implementation, it is possible to combine any pair of crystalline materials, which can differ in composition and orientation. The workflows employ first-principle calculations based on density functional theory to obtain the ground-state properties of materials and estimate the adhesion and shear strength of interfaces. The workflows also allow computing the potential energy surface of the interface in a highly efficient manner, exploiting the high-symmetry points of the two mated surfaces. A database is automatically populated with results to ensure that already available data are not unnecessarily recomputed. Computational parameters and slab thicknesses are converged automatically to minimize computational cost while ensuring accurate results. The surfaces are matched according to user-specified maximal cross-section area and mismatches. Example results are presented as a proof of concept to show the capabilities of this approach that will serve as the basis for many more interface studies. Supporting

information for this work is included in Appendix A.

The program was used to perform a comprehensive high-throughput study of the ideal shear and cleavage strengths of elemental crystals, which is reported in Chapter 3. It is based on the detailed analysis of the adhesion energy as a function of lateral, $\gamma(x, y)$, and vertical displacements, $\gamma(z)$, with respect to the considered interface plane. The large amount of computed data is used to derive fundamental insight into the relation of the ideal strength of an interface plane with its adhesion. Moreover, the ratio between the shear and cleavage strengths is found to be a good indicator for the material failure mode - dislocation propagation versus crack nucleation. Supporting information for this study is included in Appendix B.

Another important achievement of this work is the realization of an innovative theoretical model that combines the traditional Green's Function Molecular Dynamics (GFMD) technique [6] to first-principle molecular dynamics. This hybrid method, described in Chapter 4, improves the accuracy of atomistic simulations by considering the role of phonons in determining the friction of atomic structures. In typical first-principle dynamics the number of calculable atoms is limited. This artificially suppresses the energy-dissipative phonons, which are inherently excited during tribological phenomena. The hybrid method removes this limitation and can simulate infinite solid atoms based on the theory of the projection operator. This model was implemented on top of existing scientific codes to describe accurately the temperature, the mechanical stresses, the friction, and the thermal conductivity of non-equilibrium interfaces. The program has been applied to study the sliding interfaces formed by two diamond surfaces (111). Supporting information for this work is included in Appendix C.

Finally, this work describes a computational investigation made to understand the tribological potential of phosphorene. It is a novel layered material composed entirely of phosphorus that has aroused the interest of researchers due to its intriguing physical properties. In Chapter 5, a comprehensive analysis of its static tribological properties based on first-principles calculations is presented. The interlayer binding energy and shear strength are calculated for two relative orientations of the layers. In particular, when the layers are not aligned with the same orientation, the material exhibits a remarkable superlubricity, with a reduction of one order of magnitude in the shear stress. This work uncovers the microscopic origin of such a superlubric phase by analyzing the electronic charge at the layer interface. Supporting information for this work is included in Appendix D.

Chapter 6 extends on previous research by investigating the lubricating effects of phosphorene when used as a solid lubricant for iron. To this aim, the lubrication by phosphorene was analyzed in comparison with well-established solid lubricants, such as graphene and MoS_2 . The firm adhesion of phosphorene with the iron surface is demonstrated, potentially indicating a stable and durable lubricating effect. Furthermore, the simulations prove that a single phosphorene flake can reduce the adhesion energy of two mating iron surfaces more efficiently than any other 2D material. This efficient lubrication is driven by the peculiar structure of phosphorene. Supporting information for this study is included in Appendix E.

Chapter 1

Theoretical framework

This chapter will present the key foundations of computational tribology. After an initial historical overview of the discipline, the basic nanotribological concepts of microscopic surfaces, adhesion, friction, and lubrication will be presented. A particular emphasis will be placed on the computational theories and techniques used in this work to study nanotribological properties.

1.1 Historical perspective

Tribology is a multidisciplinary science that studies the properties of friction, adhesion, lubrication, and wear of interacting surfaces that slide or roll over each other. Its name is derived from the ancient Greek word *tribos* (rubbing) and was coined by Peter Jost in 1966 [7]. Although the current definition is relatively recent, human interest in friction, wear, and related processes date back to the dawn of time, making the search for effective lubricants to reduce friction one of the keys to our success in developing new technologies.

Humans have always studied and sought a way to manipulate friction throughout history. Sleds and rollers have been used to reduce friction and transport large loads since ancient times. Water's lubricating properties, for example, have been known to the Chinese since 3500 BC, while Sumerians and Egyptians used animal and vegetable substances to reduce friction and transport heavy cargo efficiently [8]. In other cases, friction needed to be increased rather than decreased; for instance, lighting a fire requires rubbing two sticks together to generate sparkles due to the heat generated by friction. However, these early approaches were frequently qualitative and trial-and-error in nature, and no systematic treatments were presented until the modern era.

The first to propose a more in-depth analysis about these issues was Leonardo da Vinci (1452-1519). He is regarded as the father of modern tribology and first studied the dry friction properties of various machinery of its time, including the motion of bearings, gears, and screw jacks. However, his work was never published and remained unknown for more than two centuries.

Long after, two scientists, Guillaume Amontons (1663-1705) and Charles Augustin de Coulomb (1736-1806) rediscovered the rules of dry friction and synthesized all of the knowledge of the time into three general laws. They noticed that the frictional force is directly proportional to the applied normal load and independent on the contact area [9] (Amontons' laws) and that kinetic friction is unaffected by sliding speed [10] (Coulomb's law). These empirical rules have a high level of generality and are still used to introduce undergraduates to friction mechanics.

The laws can be summed up in the well-known equation:

$$F_f = \mu \cdot F_N, \quad (1.1)$$

where F_f , μ , and F_N are the friction force, the coefficient of friction, and the normal force, respectively. Keeping this in mind, we come to the typical situation depicted in Fig. 1.1, where we must determine whether the force parallel to the plane will exceed the friction force, causing the block to move.

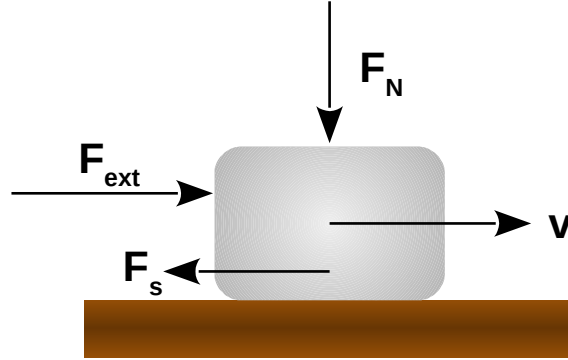


Figure 1.1: A typical frictional force problem with a box moving on a rough surface. To keep things simple, F_N here refers to both the weight force of the box and any possible external load.

Amontons laws are highly qualitative, and despite their simplicity, they represent a macroscopic approximation that is somewhat limited to many situations, as subsequent accurate research by Coulomb demonstrated. He realized that the source of friction had to be investigated at smaller scales, with microscopic asperities and the adhesion between the sliding surfaces playing a significant role in determining friction [10]. This indicates the unlikelihood that a single universal equation can exist to represent friction phenomena. In fact, the coefficient of friction can depend on several parameters [11] and a more sophisticated equation can be defined as:

$$\mu = \mu_0 + a \cdot \ln F_N + b \cdot \ln v + c \cdot \ln L + \dots \quad (1.2)$$

$$= \mu_0 + \ln (F_N^a \cdot v^b \cdot L^c), \quad (1.3)$$

where L is the characteristic size of the system, v is the sliding velocity, and F_N is the normal force.

The idea behind this simple equation proved effective on several physical systems where tribology plays a role, and it served as the basis for further research. It is worth noting the contributions of Dieterich and Ruina, who improved the previous formulation and provided a unified explanation of static and kinetic friction [12, 13, 14]. These findings constitute the foundations of the classical theory of dry friction.

In the nineteenth century, Osborne Reynold (1842-1912) and Richard Stribeck (1861-1950) developed the first phenomenological explanation of lubricated friction, introducing the so-called Stribeck curve. It shows the dependence of the friction force from the sliding speed of the surfaces, the applied load, and the lubricant's viscosity [15, 16, 17].

Until the last century, the study of friction had primarily focused on the macroscopic analysis of the phenomena, but a thorough understanding of the microscopic mechanisms that produce them was still lacking. Frank Philip Bowden (1903-1968) and David Tabor (1913-2005) took an essential first step in understanding the relationship between macroscopic and microscopic friction by introducing the concepts of the real area of contact, adhesive friction, and wear [18]. These intuitions paved the way for understanding the microscopic properties that characterize surface-surface interactions. Still, it was not until the advent of modern microscopy techniques that the study of friction and wear could be extended to micro- and nanostructures.

The introduction of the Scanning Tunnel Microscope (STM) [19, 20], developed by Gerd Binnig (1947-) and Heinrich Rohrer (1933-2013) in 1981, allowed for the first time the imaging of solid surfaces

of conductive materials at the atomic level. Inspired by these concepts, the Atomic Force Microscopy (AFM) [21, 22, 23] was developed to measure the microscopic forces between the probe tip of the instrument and the surface of a material, allowing topographic imaging and atomic manipulation. Along with the evolution of experimental tools, new advanced algorithms and computational techniques have provided a deeper understanding of material properties and possible guidance for interpreting experiments [24]. These methods include molecular dynamics and first-principles atomistic simulations, discussed in more detail in the following sections.

1.2 Nanotribology

The situation in the microscopic world differs dramatically from the predictions of classical physics. Masses and loads are now many orders of magnitude smaller than in the macroscopic case. The quantum confinement of electrons and the high surface-to-volume ratio dominate and alter the physical properties of solids.

The microscopic properties of the surface vary significantly from point to point due to the presence of defects, impurities, and molecular passivating species derived from atmospheric gases or lubricating materials placed on the surface. Surface friction, adhesion, and lubrication properties are governed by atomic-scale interactions at nano-asperity contacts. This makes the atomic-scale research conducted by nanotribology extremely relevant for providing a comprehensive understanding of these tribological phenomena [25, 26, 27, 28, 29].

1.2.1 Solid surfaces

Even the flattest surface is not truly flat, there are always irregularities, both in shape and composition, determining the presence of regions with different physical and chemical properties, which may affect the behavior of the whole material [30, 31]. Surface properties are important not only for tribology but also for optical, electrical, and thermal applications because even the presence of a few atomic layers above a surface can significantly change these properties.

Surfaces are generated by cleaving a crystalline solid along one of its cleavage planes, corresponding to a particular set of Miller indexes (h, k, l) . This “cut” ruptures the cohesive electronic bonds that exist within the bulk and leaves the surface in a high-energy state, resulting in lone-pair electronic orbitals (dangling bonds). The presence of available electronic states on the surface, also caused by impurities and defects, often leaves a chemically reactive surface. Figure 1.2 displays the various layers that typically comprise a material’s surface.

Metals and alloys form oxide layers in air, while other coatings, e.g., sulfides, can develop in different environmental conditions. This oxide region of the surface, defined as the chemically reacted layer, typically grows on top of the clean surface of the material, which may be deformed to some extent. This in-depth deformation results from the industrial processes used to manufacture the material and is specific to metals, alloys, and ceramics. It can extend from one to hundreds of microns deep inside the material and should be carefully considered in mechanical manufacturing and industrial processing.

Thinner surface films may form above the chemically reacted layer as a result of chemisorption and physisorption reactions. The presence of these films can significantly alter the chemistry of surface-surface interactions, influencing friction and wear. For example, during harsh mechanical contacts between surfaces, weakly adsorbed layers may be peeled off or evaporate, causing an increase in friction after an initial phase. On the other hand, greasy and oily films may have greater surface adherence to the interface and provide a more pronounced and stable effect.

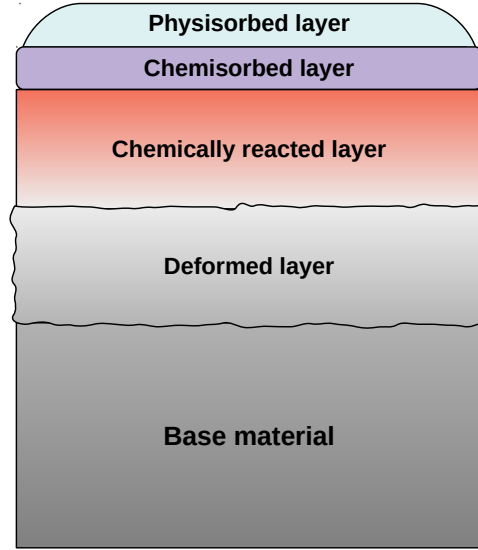


Figure 1.2: Side section showing the typical outer layers of a material surface. The deformed layers grow up to $100\ \mu\text{m}$ and can present different degrees of distortion, which becomes more pronounced near the surface. The overlying layer, which has reacted chemically, can be up to $100\ \text{nm}$ thick. In contrast, the chemisorbed and physisorbed layers are only a few nm.

A chemisorbed layer grows on top of a surface when chemical bonds are formed between the surface and outer molecular species, which attach to the surface and passivate it. The covalent bonds formed due to the chemisorption process are inherently robust and require a significant amount of energy to break (about $10\text{--}100\ \text{kcal/mol}$). Once the surface has been covered with a single molecular layer, chemisorption ceases, and any subsequent layer formation is due only to physisorption or chemical reactions. Note that only the interaction between the adsorbates and the substrate ceases because no more free sites are left to form a bond. However, there may also be covalent interactions above the first chemisorbed monolayer.

The physisorption layer is typically made of a few molecular layers of water vapor, oxygen, or hydrocarbons that interact with the surface via weak London dispersion forces. Due to the weakness of these bonds, a small amount of energy is already sufficient to remove the species from the surface (about $1\ \text{kcal/mol}$).

Regardless of the degree of oxidation of a surface or the presence of layers of passivating species, a tribological system always consists of four elements: two surfaces, the interface, and the environment. Two material surfaces placed in contact form what is called a tribological interface. This region is characterized by high temperatures and intense mechanical stresses. It is here that the sliding or rolling motion between the materials develops, generating friction and wear.

1.2.2 Adhesion and friction

Phenomena at the nanoscale

The contact between two surfaces occurs at discrete contact points, also referred to as interface junctions. As a result, the real area of contact (A_r) is just a tiny fraction of the apparent contact area (A_a), resulting

in $A_r = k \cdot A_a$, with k typically ranging between 10^{-2} to 10^{-6} [31]. Furthermore, this fraction is not constant, but it depends on the surface topography, the material properties, and the interfacial loading conditions [30]. This extraordinary intuition, realized by Bowden and Tabor in the 1950s [18], allowed them to formulate a new classical theory for the coefficient of friction:

$$F_f = A_r \cdot \tau \quad (1.4)$$

where τ represents the shear strength of the material. This equation can be further rearranged in the framework of the Hertzian elastic contact theory [32], predicting the coefficient of friction to vary with the load as $\mu \propto L^{-1/3}$. It is fascinating to see how the simple introduction of the microscopic hypothesis of an effective contact area is sufficient to invalidate Amontons first law.

The adhesion between two surfaces is caused by interatomic interactions that occur when two asperities come close together. If there are no chemical films or adsorbed species on the surfaces, strong adhesion bonds can form between the two solids due to the presence of high-energy dangling bonds. Increasing the external load causes the surfaces to stay closer, resulting in greater asperities in contact and larger adhesion. The insertion of lubricating films at the tribological interface can increase the separation of the asperities, thus preventing the formation of strong covalent bonds across the interface and decreasing adhesive contact.

Furthermore, adhesion is affected by various factors such as temperature and load, complicating the understanding of the phenomenon. Excessive high pressures, in fact, cause the material surfaces to distort at the contact points, causing the tips to deform plastically and, as a result, increasing the area of contact and adhesion due to a reduction in elastic recovery [30].

When two surfaces slide against each other, a lateral force is required to break the adhesive bonds that form between the points of contact. Because new contacts are constantly created, the force must be applied continuously to keep the bodies in relative motion. The adhesive force between two surfaces is one of the most important components of friction. According to Rabinovich's model [33], adhesion is mainly caused by surface interactions and capillary forces between the solids. When the attraction force is modeled with a Lennard Jones potential [34, 35], friction is directly proportional to adhesion. This condition is valid only when the parameters of the model are constant. However, this rarely occurs in realistic systems and it has been found that friction can even increase as adhesion decreases [36]. Additionally, adhesion can cause the friction-load dependence to shift from linear to non-linear as adhesion increases [37].

Other phenomena that develop at the nanoscale include superlubrication [38] and negative coefficients of friction (friction decreases with increasing load) [39, 40]. Superlubricity is typically achieved during the sliding of incommensurate interfaces. The lateral forces acting between the atoms cancel each other out, resulting in an almost frictionless motion [41]. This can lead to coefficients of friction of the order of 0.1 or lower [42, 43, 44, 45]. Superlubricity is a condition common to many 2D materials [46, 47], and it has been observed in both graphene [38, 48, 49] and MoS_2 [50, 51, 52, 53, 54]. This makes the study and engineering of solid lubricants based on 2D materials important for industrial applications.

Friction regimes

In a typical sliding process, two regimes can be distinguished: pre-sliding and gross sliding [55], as shown in Fig. 1.3(a). They are characterized by different microscopic properties. The pre-sliding regime is dominated by adhesive forces and friction is linearly dependent on displacement rather than velocity due to the elastic-plastic deformations occurring at the asperity junctions. As displacement grows, more junctions fail and there is less time to repair them, determining the gross regime. It is distinguished by the continuous formation and removal of asperity junctions, which results in steady-state friction force behavior.

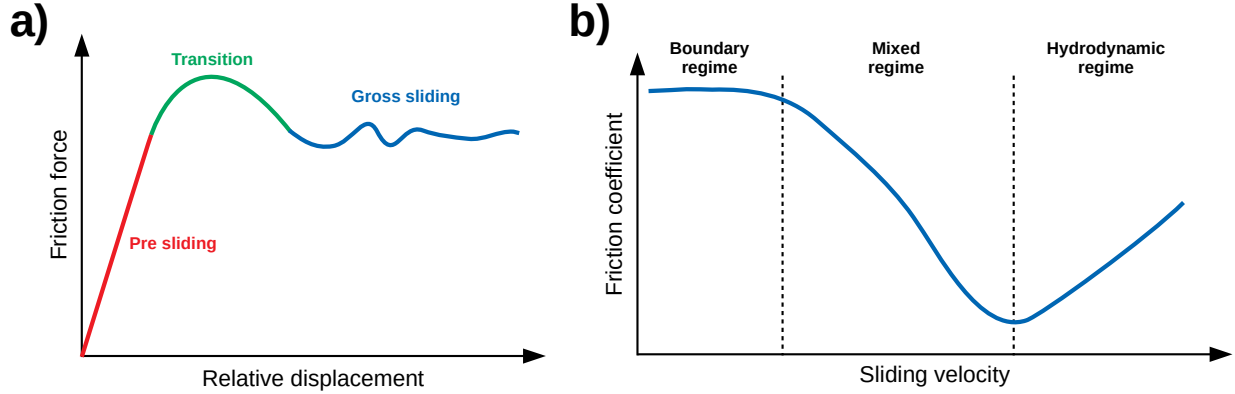


Figure 1.3: (a) Experimental friction force measured for two contact surfaces in relative motion. It displays the occurrence of two sliding regimes: pre-sliding, in which the friction increases with lateral displacement, and gross sliding, in which the coefficient of friction is almost constant. (b) Sketch of the Stribeck curve. The coefficient of friction is affected by the sliding velocity, the applied load, and the lubricant's viscosity. When the sliding velocity increases, a specific trend is observed: the friction initially decreases (velocity weakening) and then increases (velocity strengthening).

In the presence of liquid lubricants, there is a specific dependence of the coefficient of friction on the sliding velocity, the applied load, and the lubricant viscosity. This behavior, known as the Stribeck curve (Fig. 1.3(b)), identifies three different lubricating regimes: the boundary, the mixed, and the hydrodynamic regimes, respectively [16, 17].

In boundary lubrication [56], the interaction between the solid surfaces and the lubricant film is dominating. The lubricant is squeezed out of the interface because the asperities are in contact, resulting in relatively high friction coefficients. This condition is obtained at high loads and low speeds, when friction is governed by the chemistry of the lubricating films [57]. The friction then begins to decrease during the mixed lubricating regime until a minimum is reached (velocity weakening), followed by an increase in the hydrodynamic regime (velocity strengthening).

1.2.3 Lubricants and coatings

Reducing friction is of fundamental importance to reduce economic and environmental costs. Several solutions were identified to tackle this complex challenge in the last decades, and different lubricants were engineered. The primary function of a lubricating media is to keep the microscopic asperities of two interfaced surfaces from coming into direct contact [57]. As a result, the relative pressure and interactions between the two surfaces are reduced, decreasing friction and containing wear and heat. This is especially important in boundary regimes where asperities come into contact.

The materials to reduce friction are classified into two classes based on their function mechanism. Typically, their action is to form liquid films at the tribological interface or coat the substrates with protective solid films.

On the one hand, the most common compounds used to improve tribological performance are liquid lubricants. They operate mainly in boundary and mixed lubrication regimes and are classified as oils (natural or synthetic) and ionic liquids [58]. Their properties are enhanced by adding friction modifier

additives to the liquid lubricant mixtures. Examples of this type of compounds are amphiphilic surfactants and organo-molybdenum friction modifiers [59].

On the other, the intercalation of solid lubricants between two surfaces reduces the resistance to sliding [60, 31]. These lubricants are composed of layers that can easily slide on each other and passivate the surfaces, preventing the formation of chemical bonds across the interface. Graphene and transition metal dichalcogenides (TMDs) are remarkably successful examples of this class of lubricants [31].

Liquid lubricants and friction modifiers

A suitable liquid lubricant should effectively bond with the surface while also having a high packing factor to generate dense protective layers between the contacts. At the same time, a surface should possess high surface energies and a high wetting to be sufficiently reactive towards the lubricant. These conditions are easily met by metal surfaces lubricated by molecules formed by polar head groups and long straight chains with a high packing density [61, 62].

A standard class of oils is petroleum-based oils, often referred to as base oils. They are composed of mixtures of long hydrocarbon chains, which are often added with lubricating nanoparticles to enhance their properties [63, 64, 65, 66]. These additives are used to modify the chemical properties of the oil. Their goal is to generate a protective coating on the surface, improve the properties of the oil or increase its lifespan before degradation [67].

An important example of a lubricant additive is provided by molybdenum dithiocarbamates (MoDTCs), which are a group of chemical compounds commonly used as friction modifiers in the automotive industry [59, 68]. Their success derives from the capability of MoDTCs to be transformed into molybdenum disulfide (MoS_2) in boundary lubrication when the asperities in contact generate high temperatures and stresses.

Solid lubricants

Solid lubricants are materials with low shear strength that are applied to surfaces to form thin coatings to reduce friction and wear. They are used in extreme pressure, temperature, and vacuum conditions where liquid lubricants would solidify or evaporate, as well as in engineering technologies that require high electrical and thermal conductivity. They can be classified based on their hardness and structural properties. Among the others, the most common are carbon-based materials and layered (2D) materials [31].

Carbon-based materials are significant due to the ability of C atoms to form various types of bonds, resulting in a wide range of allotropes and structures [69]. Diamond, diamond-like carbon (DLC), and graphite are a few examples. Diamond is interesting for the tribological behavior of the nanocrystalline films formed by this material, which present low interfacial shears [70]. The friction of diamond against diamond in air environment is found to be very low by experiments, with friction coefficients ranging between 0.01 and 0.1 [71, 72, 73, 74]. This ultralow friction has been measured for different crystalline terminations of the diamond surfaces, such as the (100) [75, 73, 76, 77] and (110) [75] planes, as well as for nanocrystalline diamond films and DLC coatings [74, 78].

The proposed explanation for the low friction of diamond comes from the chemical passivation or the bonds rehybridization occurring on its surface [79]. The presence of adsorbate species screens the strong C-C covalent bond forming across the interface. Although diamond films may be scratched out from asperity tips during sliding, they heal quickly by the continuous flow of passivating molecules from the surrounding atmosphere. On the contrary, friction force rises in a vacuum environment due to the wear-off of the passivating species that are no longer replenished.

Diamond-like carbons (DLCs) are another important class of solid lubricants. They are amorphous carbon structures with a mixed sp^2/sp^3 hybridization of the bonds, displaying an intermediate behavior between diamond and graphene. This material has relatively high hardness and elastic strength and can provide low coefficients of friction and wear [80, 81]. Moreover, different hybridization ratios and degrees of hydrogenation can be used to tune the properties of the compound. Other innovative carbon-based materials showing engaging tribological performances are C_{60} , carbon nanotubes, and onion-like carbons [82].

Layered materials are another class of excellent solid lubricants [83], which often provides performances close to achieving superlubricity [46]. Their diffusion is due to their high chemical stability, lower toxicity, and better overall performance than common friction modifiers [84]. The most well-known 2D lubricant is certainly graphite [85]. It is a solid material composed of carbon nanosheets forming planar sp^2 -hybridized covalent bonds but weak Van der Waals interactions between the planes. Because of this peculiar structure, the layers can be easily peeled off or slide on one another. Furthermore, graphene possesses high stiffness and chemical stability, rendering it extremely interesting for lubricant applications [86, 87]. It works well in harsh tribological and thermal conditions, and the physisorption of water molecules on its surface improves its performance [88, 89].

Transition metal dichalcogenides (TMDs) are also excellent for tribology. Their main representatives are certainly WS_2 and MoS_2 . Molybdenum disulfide crystallizes with a hexagonal lattice and, like graphene, presents strong covalent bonds within the sheet (S-Mo-S bond) but weak van der Waals forces among the layers. MoS_2 is a remarkable solid lubricant under the effect of the mechanical stresses with the capability to reduce the friction of steel by around one order of magnitude [90]. Tribological tests show that in a controlled environment, such as dry inert gas or UHV, it can achieve coefficients of friction of the order of 0.05 [91, 92]. MoS_2 is used primarily in vacuum lubrication since moisture affects its performance by oxidizing the edges of the basal planes when they react with water and oxygen [93].

An important example of a 2D material is phosphorene, defined as a single sheet exfoliated from the bulk structure of black phosphorus. This material acquired interest for electronic technologies due to its direct bandgap of 0.3 eV [94, 95], which can be tuned by varying the number of layers [96] or applying in-plane strains to the layers [97]. However, phosphorene also possesses intriguing mechanical and tribological properties due to its anisotropic Young modulus [98] and the ability to develop ultralow friction (superlubricity) when used as a lubricant additive in aqueous solutions [99]. Various studies evaluated the tribological relevance of phosphorene [100, 101, 102, 99], which is due to the weak inter-planar bonding between the layers and the efficiency of phosphorus atoms in reducing friction and adhesion [103, 104].

The tribological properties of phosphorene are analyzed in this work through computational simulations. The research enabled the identification of a superlubric phase for a specific orientation of the layer. The lubricating capacity of phosphorene towards an iron substrate was also determined, comparing it with those of MoS_2 and graphene. These studies are discussed in Chapters 5 and 6.

1.3 Computational simulations to study surface lubrication

Computational nanotribology has grown in popularity in recent years, and it is now a relevant tool for the study of the properties of materials. Indeed, computational simulations make it possible to describe the chemical features and modifications that occur on surfaces in great detail. It is possible to investigate the interactions between surfaces and understand the effect of lubricants down to the atomic level [3, 4]. Along with mathematical models, computational simulations provide a means of interpreting tribological phenomena in a controlled environment. This avoids the technical constraints that experiments can impose by allowing access to extreme pressure and temperature conditions. This kind of study has lately accelerated

because of advances in algorithms, theory, and hardware used in computer science [105]. The following section will briefly review the state of the art of computational approaches used in this work to study nanotribology.

1.3.1 Density Functional Theory

First-principles simulations are one of the most important tools for modeling and studying systems at the atomic level. They are based on solving the fundamental quantum equations of the system, i.e., the Schrödinger equation, without the need for specific assumptions. As a result, they provide a fundamental technique for investigating material properties based on the fundamental understanding of their electronic behavior. They have gained prominence in a variety of technical disciplines in recent years, including nanotechnology, condensed matter physics, and materials design [106, 107].

Among the various techniques, Density Functional Theory (DFT) has gained a lot of attention and relevance over the years [108, 109]. The central idea of DFT is that the properties of a system can be described as a functional of its electronic charge density $\rho(\vec{r}) = \rho(x, y, z)$. This is critical for overcoming the limitations imposed by the many-body wavefunction of the atomic structure. In quantum mechanics, a system of N electrons requires $3N$ variables to be described, imposing severe computational limitations to the structures that can be studied. On the other hand, DFT simplifies the problem by reducing the number of variables from $3N$ to just 3, since now we only need to know the value of the electric charge density at each position in space.

The origin of DFT can be traced back to two fundamental theorems [110] demonstrated in 1964 by Walter Kohn (1923-2016) and Pierre Hohenberg (1934-2017). The first theorem states that an external potential $v_{ext}(\vec{r})$ acting on a system of N interacting electrons is a unique functional of their ground-state charge density ρ . The second proves that the ground-state energy is a functional of the charge density ($E = E[\rho(\vec{r})]$) who is minimized by the ground-state charge density.

Walter Kohn and Lu Jeu Sham (1938-) simplified the expression of the energy by introducing a non-interacting system of electrons that, when subjected to a local single-particle effective potential, yields the same ground-state density of the corresponding interacting system [111]. The problem reduces to solve the Kohn-Sham equations (KS):

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{KS}(\vec{r}) \right] \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) \quad (1.5)$$

$$v_{KS}(\vec{r}) = v_{ext}(\vec{r}) + v_H(\vec{r}) + v_{XC}(\vec{r}) \quad (1.6)$$

where the KS potential is decomposed into the sum of the external, the Hartree, and the exchange-correlation potentials, respectively. The accuracy of the energy description depends on the search for an accurate approximation for the exchange-correlation functional, which can significantly affect the electronic properties of materials [112].

First-principles calculations based on DFT are essential to describe surface-surface interactions, offering the possibility to characterize the adhesive and shear strengths of materials *in silico*. In typical DFT software, it is possible to apply constant velocities or external forces to the atoms, which helps to simulate mechanical shears and loads, to conduct tribological analysis.

DFT static simulations, which are used to optimize the electronic ground-state and the geometry of the system, can estimate various physical and chemical properties for a wide range of compounds and atomic structures. These studies include electronic properties [113, 114, 115, 116, 117], phonons and vibrational spectra [118, 119, 120], and mechanical and friction properties [121, 122, 123, 124, 125, 126, 127, 128, 129,

130, 131]. Furthermore, ground-state energy alone can be used to identify the most stable structure of a chemical compound, assess binding and defect energies, and estimate phase stability diagrams [5].

1.3.2 Molecular Dynamics

Molecular Dynamics (MD) simulations provide another powerful tool to be used in combination with static calculations [132]. This method is based on the solution of Newtonian equations of motion for an atomic system. The interaction between the particles is described using classical force fields [133], which are typically modeled in the form of pairwise interactions constituted of an attractive term (London dispersion forces) and a repulsive term (core-core repulsion). The most used and known force fields are the Lennard-Jones (LJ) [34] and the Morse potentials [134].

These potentials are parameterized by empirical parameters and do not allow to take into account the quantum nature of the electrons, preventing the analysis of the electronic structure and the formation or breaking of chemical bonds during the simulation. This limits their use and makes them unsuitable for accurately describing the behavior of solid materials. Some progresses have been made by modeling reactive force fields, such as REBO [135, 136, 137, 138], AIREBO [139], and ReaxFF [140]. However, they strongly depend on the chemical composition of the system and their modeling often requires the parameterization of tens of different variables. This greatly complicates their construction and use [141, 142].

Although the higher computational efforts, DFT-based molecular dynamics techniques are more accurate in describing the atomic bonds and the electronic properties of a system of particles. In fact, DFT is not limited to static simulations but also allows to perform molecular dynamics. First-principles MD revealed to be a precious instrument to study tribological phenomena, such as friction [143, 144], and tribochemical reactions [145, 54, 146]. The two possible approaches are Bohr-Oppenheimer (BO) [147] and Car-Parrinello (CP) [148].

The first is based on the BO approximation, which decouples the electronic wavefunctions from those of the ions. In this approach, the KS equations are solved at each simulation step because the electronic eigenvalues represent the external potential felt by the ions, whose motion is propagated using the correspondingly calculated Hellmann-Feynman forces. This scheme is computationally demanding, but it allows for large integration steps of the order of 1 fs and can be applied to any system. In the CP method, on the other hand, the electronic minimization is performed only once at the beginning of the simulation. The electronic degrees of freedom are then propagated as fictitious dynamic variables forming a coupled system of equations of motion with the ions. In this way, the self-consistent calculation performed at each step of the former method is avoided, and the computational time is significantly reduced. However, there is a continuous energy flow between nuclear and electronic degrees of freedom, which must be kept small by adequately tuning the simulation parameters to maintain the electrons close to the initial ground state. For the same reason, it is necessary to keep the time step about an order of magnitude smaller than before, thus requiring more steps to reach the same simulation time.

The use of Green's Function (GF) provides another technique to be used in combination with MD, giving the so-called Green's Function Molecular Dynamics (GFMD) [6]. This method correctly accounts for the effect of long-range elastic deformations in finite dynamical systems constituted of two surfaces placed in contact. In MD simulations, the slabs constituting the interface should have at least a thickness equal to the lateral dimension of the simulation cell to take these elastic effects into account. However, increasing the number of simulated atoms raises the computational costs rapidly, thus limiting the size of the systems that can be simulated efficiently. This problem is solved by GFMD, which integrates out all the internal harmonic modes of the system, providing effective interactions for the particles coupling with external forces. In this way, it is possible to simulate semi-infinite solids with atomic slabs of finite

thickness, improving the description of heat dissipation by phonons generated during friction events [149]. This method has been used for many years and is supplied in several molecular dynamics software, such as LAMMPS [150]. In the present work, we implemented a new GF theoretical model in DFT software, extending this approach to first-principles simulations, as presented in Chapter 4.

1.4 High Throughput approach in Materials Science

The discovery and design of new materials have driven technological advancement in recent years. However, developing new technological solutions is a time-consuming and challenging task that typically takes decades from lab to widespread adoption [5]. One strategy for accelerating this process is integrating experiments with computational tools and simulations to reduce research costs and pre-identify promising candidates for technological solutions.

In the last decades, the high-throughput approach (HT) has spread to computational materials science, allowing for the study and design of new materials using performing algorithms and computational techniques [151, 152]. This method was initially experimental [153, 154, 155], but advances in computer technology and the development of ever-more efficient algorithms enabled its application to computer science.

A computational HT approach typically consists of integrating electronics methods within high-level IT infrastructures related to the construction of databases and the use of artificial intelligence. First-principles computations have become one of the most flourishing approaches in recent years [156], thanks to the development of increasingly sophisticated algorithms and the increased availability of high-performance computing resources [157]. This has created the opportunity to extend the high-throughput approach to computational studies based on DFT, opening the way to materials informatics [158].

A computational high-throughput study can be designed to identify materials with properties relevant to new technologies from a pool ranging from thousands up to millions of candidates [159, 160, 151, 161]. Figure 1.4 depicts an example of a massive screening procedure of this kind. The procedure consists of a series of iterations of the HT algorithm, which progressively skim the candidates by selecting them based on the technological features requested by the user. In other words, at each step, a particular physical or chemical property is simulated for all the candidates in the pool. If the result does not fall within the range of interest, the material is discarded; otherwise, it can proceed to the next step. Typically, only a few dozen suitable candidates are identified at the end of the selection process. They can then be tested in the laboratory to be able to confirm the predicted properties experimentally.

Designing and implementing a program for performing high-throughput calculations is a complex task. It necessitates flexibility and robustness in the implementation of the IT infrastructure. The code must not only allow simulating the properties of the materials but also guarantee the systematic collection and analysis of the extracted features, as well as the storage of the results within accessible databases. Simulations are typically performed through computational workflows. They are computer protocols consisting of a series of elementary operations, which allow the preparation of inputs, the execution of quantum chemistry software, and the collection of results.

The purpose of a high-throughput simulation is to create large databases of calculated physical and chemical properties, both for existing materials and for predicted new ones. In this type of research, it is not always necessary to accurately calculate all the properties of the materials. It is often sufficient to indicate which candidates are the best for a specific application so that experimentalists can test them later in the laboratory. For example, in a multi-property study centered around the evaluation of the electronic bandgap, the procedure can be speed up as follows. First, compounds that fall outside of a loose but

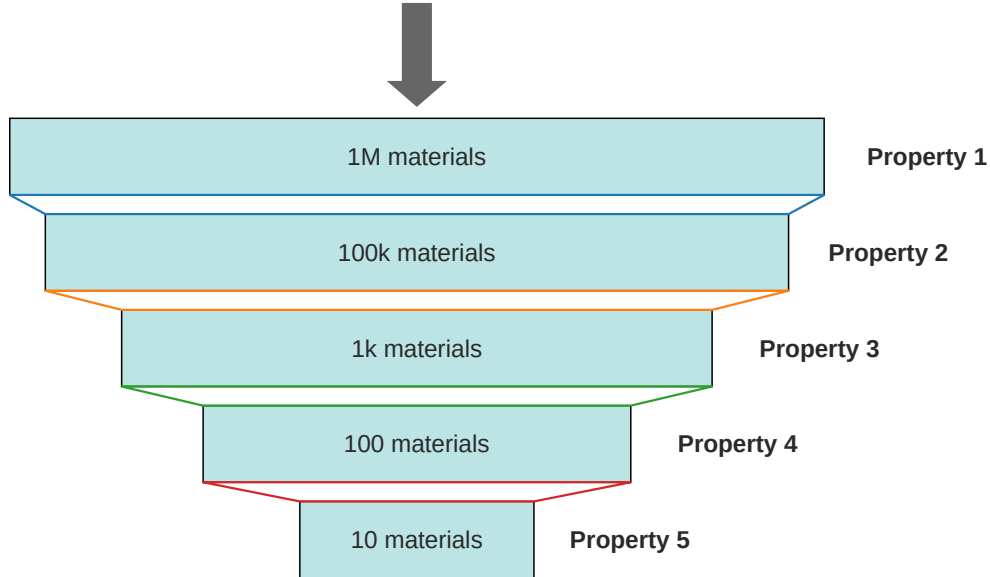


Figure 1.4: The procedure aims to identify the best candidates for a given application from a potential pool of millions of materials. The screening consists of several steps, each of which filters the materials based on a specific physical or chemical property of interest.

meaningful range are rejected. This calculation can be performed with a simple functional, e.g., LDA [111]. After testing other properties, the bandgap can be recalculated with more accurate, albeit computationally expensive, hybrid functionals [162].

The HT approach has been shown to be extremely efficient to predict the properties of novel materials in various scientific fields, such as thermoelectrics [163, 164, 165], catalysis [166, 167, 168], topological insulators [169, 170, 171], Li-ion batteries [172, 173, 174], and hydrogen storage [175]. At the same time, many high-throughput packages and informatics infrastructures have emerged over the years [176, 177, 178, 179, 180, 181], often aided by data-driven strategies [182, 183]. Different online databases are nowadays available, containing both crystal structures and measured physical properties [184, 185, 186, 187, 188]. As these datasets are supplied with new calculated values from HT studies, data analysis using machine learning techniques will become increasingly important, accelerating property predictions and facilitating materials discovery [182, 189, 190, 191].

The high-throughput method has also been used successfully in tribology-related fields. A tribometer has been developed to perform high-throughput analysis on adhesion, wear, and friction calculated on experimental samples [192]. Exciting computational work has been presented in the search for alternative 2D structures that are easy to exfoliate [193] and for innovative superlubricant van der Waals heterostructures [191]. In particular, M. Fronzi et al. [191] employed machine learning algorithms to evaluate the interlayer binding energy and elastic constants of 18 million different interfaces formed by two different paired layered materials.

However, few works are related to the computational study of solid-solid interfaces formed by two semi-infinite surfaces in contact, typically approximated by thick atomic slabs in DFT simulations. To fill the gap, we developed and published a computational protocol [194] to calculate the intrinsic tribological properties

of solid-solid interfaces, such as the adhesion energy γ and the ideal interfacial shear strength τ [195]. We used our software to study the frictional and cleavage strengths of elemental crystals with different orientations [125]. This study focused on homogeneous interfaces formed by matching two equivalent surfaces, e.g., Fe(100) on Fe(100). In its current implementation [196], our software has been extended to heterogeneous interfaces, which are formed by matching two surfaces different in composition and orientation. In this way, it is possible to study thin films and coatings on a substrate, grain boundaries, and solid materials with non-monoatomic bases. Figure 1.5 shows some examples of these types of interfaces.

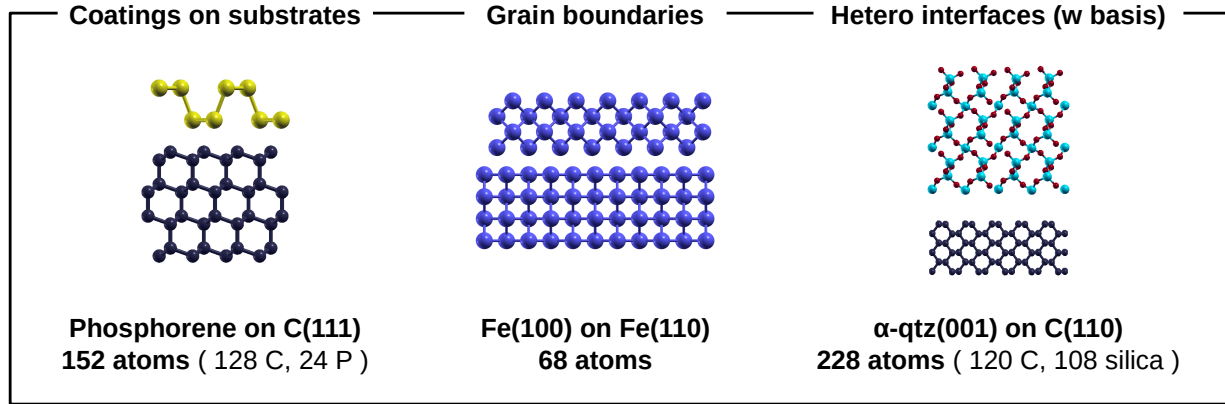


Figure 1.5: Different types of heterogeneous interfaces that can be matched with our software. The crystalline cells are combined by straining, rotating, and replicating the lattice vectors.

The development of a high-throughput method for tribology occupies a prominent position in this work. Chapter 2 contains an in-depth description of our approach and an illustration of the computational workflows we designed. Instead, the results for the homogeneous solid interfaces formed by elemental crystals are reported in Chapter 3.

Chapter 2

TribChem: Materials Science Simulations software

2.1 Introduction

This chapter will provide a comprehensive overview of our high-throughput software, TribChem, focusing on our most recent implementation, which extended the software’s applicability to manipulate any solid heterogeneous interface. Section 2.2 will introduce the concepts related to modeling a solid-solid interface within our code implementation. In Section 2.3 we will give a brief overview of our workflow, its modular structure, and ease of use. In Section 2.4 we present our workflow for PES calculations in detail and also sketch the other minor workflows we developed to make our computations highly efficient. Some example results follow in Section 2.5. Section 2.6 provides a detailed technical description of our software structure and operation, followed by conclusions and outlook in Section 2.7.

2.2 Motivation

Solid-solid interfaces are ubiquitous in many disciplines of material science, physics, and chemistry, and are essential for many applications, ranging from synthetic antiferromagnets and spintronics [197], battery technology [198] to tribology, especially in nanoelectromechanical systems (NEMS) [28]. Experimental studies of interfaces are very challenging, though, since they are not accessible by many experimental probes due to their inherent nature of being “buried” between two solids. Naturally, simulations can overcome these limitations and are uniquely suited to explore solid-solid interfaces. Especially *ab initio* electronic structure methods are valuable for this task, as they do not depend on a priori knowledge of some or many system parameters and in return can provide information on many significant figures of merit of interfaces, like magnetic interactions [199], thermal properties [200], charge density redistribution [201, 202], and tribological properties [195, 125, 203].

The great flexibility and predictive power of electronic structure simulations, most often employing density functional theory (DFT), comes at the price of computational cost and a somewhat complex setup of the computations. However, a major hurdle to overcome is not unique to electronic structure calculations but shared for all atomistic methods using periodic boundary conditions: Constructing a supercell that accommodates both materials forming the interface without imposing unphysical strains. In crystal growth and material deposition, this matching of one crystalline film on another crystalline substrate is known as heteroepitaxy, and algorithms that describe it have existed for more than 35 years, e.g., the one by Zur and McGill [204]. An implementation of this algorithm has been published more recently within the MPIInterfaces package [205], and there are ongoing efforts to integrate it tightly into pymatgen (Python Materials Genomics), a very popular library for material analysis [178]. Most approaches are usually geared towards matching a 2D thin film with a substrate, like the very recent work by Zhang et al. [206]. For matching heterogeneous structures of two 2D materials, the coincidence lattice method is also used [207].

A matching cell is not the only requirement to correctly model a solid-solid interface. A priori, it is not clear which relative lateral position of the two matched slabs leads to the highest binding energy and thus to the equilibrium stacking. For that, the whole potential energy surface (PES; also γ -surface or generalized stacking fault energy surface γ_{GSF}) has to be calculated. It maps all possible lateral shifts to changes in the system's total energy and thus fixes the adhesion energy as its minimum. Many more results may be derived from the PES, e.g. shear strength and static friction [195, 194, 125], dynamic friction with the help of some spring models [208, 209], or information about dislocation structures and energetic [210]. The *ab initio* PES of simple systems, such as adsorbed monolayers on metals and bilayer graphene, was very accurately fitted with three-dimensional, analytical functions [211, 209], and used in conjunction with atomistic simulations to unravel the origin of fundamental frictional phenomena, such as the onset of frictional slip [212], and the size-dependence of static friction [213, 214].

High-throughput studies have become a valuable tool for material advancements, which are of tremendous importance for many industries and closely tied to various societal challenges like clean energy production [5]. As discussed above, especially for solid-solid interfaces, the cost and trouble of experimentally testing the vast number of possible compounds and alloys that could potentially have beneficial properties are often prohibitive. However, the exponential growth of computer power and the development of efficient data mining and curating techniques using machine learning approaches have opened a new avenue of large-scale computational materials research through high-throughput screening (see [151] and references therein). We thus aim to include our effort to efficiently compute PES data for heterogeneous solid-solid interfaces in a more general high-throughput workflow. To this end, we have significantly improved upon our previous work for homogeneous interfaces (analogous to homoepitaxy) [194] to add not only capabilities to treat heterogeneous interfaces but provide far superior error handling, usability, results' extraction, and functionality. Another significant difference is the collection of results in a separate and easily shareable database, which can be easily used to salvage existing results for new analysis and data mining. This is especially useful for other codes that are used to treat interfaces but which depend on pre-defined parameters or classical potentials, which can be trained with the help of *ab initio* data [215, 216, 4].

We have decided to implement our work within FireWorks [176], a Python-based high-throughput framework rooted in the Materials Project [188], and use as many pre-engineered pieces of associated packages (such as *atomate* [177] and *pymatgen* [178]) as possible. Fireworks is a very mature platform, interfaces very well with the VASP package for DFT calculations [217, 218, 219], and provides easy error handling via the *custodian* package [178]. Of course, other high-throughput platforms based on Python are available (e.g., *AiiDA* [220, 221], *pyiron* [222], and *ASR* [223]), and in principle, it should not be hard to port our codes over.

2.3 Computational workflows

TribChem is a software package for analyzing the fundamental tribological, mechanical, and electronic properties of crystalline bulks, surfaces, and solid interfaces. It is entirely written in Python and makes use of VASP [217, 218, 219] to perform Density Functional Theory simulations.

The software structure comprises a series of robust, modular, and *ab initio* high-throughput workflows that match and characterize solid-solid interfaces using DFT calculations with automatic error corrections. All of the results are saved in a NoSQL database, MongoDB [224], which is automatically populated with results to save them for future analysis and ensure that previously available data is not recomputed.

The high-throughput jobs are run with computational workflows, consisting of complex trees of logical operations linked together and run in sequence or parallel to perform a specific task. A sketch of a typical

workflow tree is depicted in Fig. 2.1. TribChem workflows typically consist of tens of smaller units, each managing a specific operation in the workflow processes. Shell scripts, custom Python code, and external software can all be run within these units.

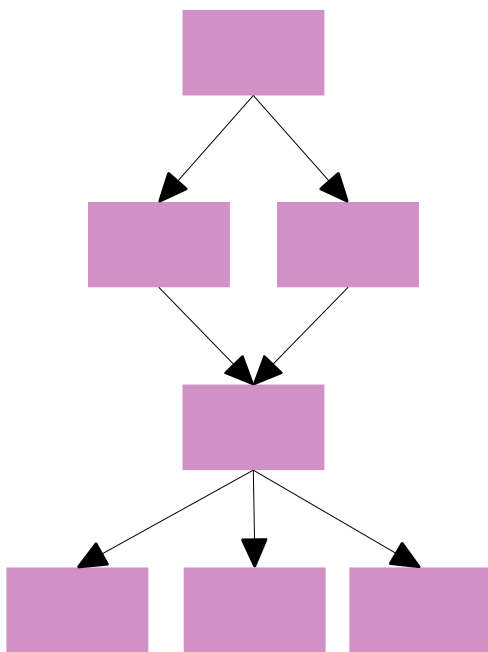


Figure 2.1: The diagram depicts a simplified version of a modular workflow. Each purple box carries out an atomic operation. The logical sequence and combination of tasks can result in complex physical and logical operations that combine first-principles code execution with Python data analysis and database queries.

In the Fireworks framework, each workflow is composed of smaller units, so-called fireworks, which in turn are made up of firetasks. Fireworks can be executed concurrently, whereas firetasks within a single firework are always serial but can easily access data from other firetasks within the same fireworks. On the firetasks level, it is also possible to dynamically create new fireworks and workflows, so the most complexity in our code is on the firetask level, with fireworks frequently containing only a single firetask. In summary, referring to Fig. 2.1, each box represents a firework, which could be made up of a single firetask or multiple firetasks. By combining all of the fireworks, a computational workflow is created that can be used to perform a specific physical study.

We tried to make these firetasks as general as possible, and, of course, we used already implemented computational workflows, fireworks, and tools from the *atomate* [177] and *pymatgen* [178] packages. This enables the skilled user to create new workflows from our fireworks and firetasks in a straightforward manner. However, while some firetasks, such as those that manage data storage in a MongoDB database, are very general and can be used in any workflow, others may be pretty specific to a given topic of material science and can only be used in a few specific workflows.

2.3.1 The workflow to study solid interfaces

Since the first versions of TribChem, released in 2018, we have designed the logic and steps required for a computational workflow to perform a tribological study on solid-solid interfaces. The idea is that implementing this protocol should allow for the simultaneous execution of a single job or, eventually, the start of a high-throughput study on hundreds of materials.

Its primary function is to compute two crucial properties that characterize surface interactions: the adhesion energy, γ , and the ideal interfacial shear strength, τ . These quantities represent the energy required to separate two surfaces from contact and the static friction force per unit area, respectively. The potential energy surface (PES), which is the planar dependence of the interfacial adhesion $\gamma(x, y)$, is also computed quickly by taking advantage of high-symmetry points on the two mated surfaces.

The flowchart in the Figure shows the main components of the workflow for computing potential energy surfaces for solid interfaces. It has a simple structure but is made up of several (sub-)workflows (green rectangles in the figure), which will be discussed in more detail in the following subsections. More complex logic and decisions are handled there, allowing us to focus on the main features that all non-specialist users must know to run calculations.

This workflow can be broken down into three significant steps. The two crystalline bulks of interest are initially chosen, and their computational parameters are converged. The bulks are then cut into slabs of a specific thickness, oriented using the provided Miller indices, and a geometric optimization is performed. Finally, the interface is matched, and the desired electronic and tribological properties are calculated. The reader is directed to Section 2.4 for a detailed description of the three main steps.

This workflow allows for the simulation of homogeneous interfaces, i.e., two symmetrical slabs facing each other (e.g., Al(111)-Al(111)), and heterogeneous interfaces. Interfaces made up of two materials with different orientations or compositions are examples of the latter.

The following steps correspond directly to Fig. 2.2.

- **Reading Input and Initializing:** The input parameters are passed to the workflow. This only has to include very few parameters, mainly the unique identifiers of the basic bulk structures that should be used, the Miller indices for each material to select a slab orientation, if vdW corrections should be used, and the maximal cross-section area of the matched cell. Other parameters, like the functional to be used, might be passed; otherwise, default values are used from a central *json* file.
- **Relax shape:** The workflow check the symmetry of the input structure, and in case a non-cubic structure is found, a cell-shape-relaxation with very high energy cutoff and k-point density is performed at constant volume. This ensures that the cell shape (e.g., c/a ratio) is optimized for the selected functional, while the volume will be optimized in the following steps.
- **Converge Energy Cutoff and K-Point Density:** The energy cutoff is converged with respect to the equilibrium volume and the bulk modulus using subsequent fits to the Birch-Murnaghan equation of state with increasing energy cutoff. The density of the k-point mesh is after that converged with respect to the system's total energy, adopting the energy cutoff found in the previous step. This procedure is done in parallel for both materials.
- **Consolidate Computational Parameters:** The higher values for the energy cutoff and the k-point density are chosen after all convergence loops have finished so that the interfaces calculations will be both efficient and accurate.

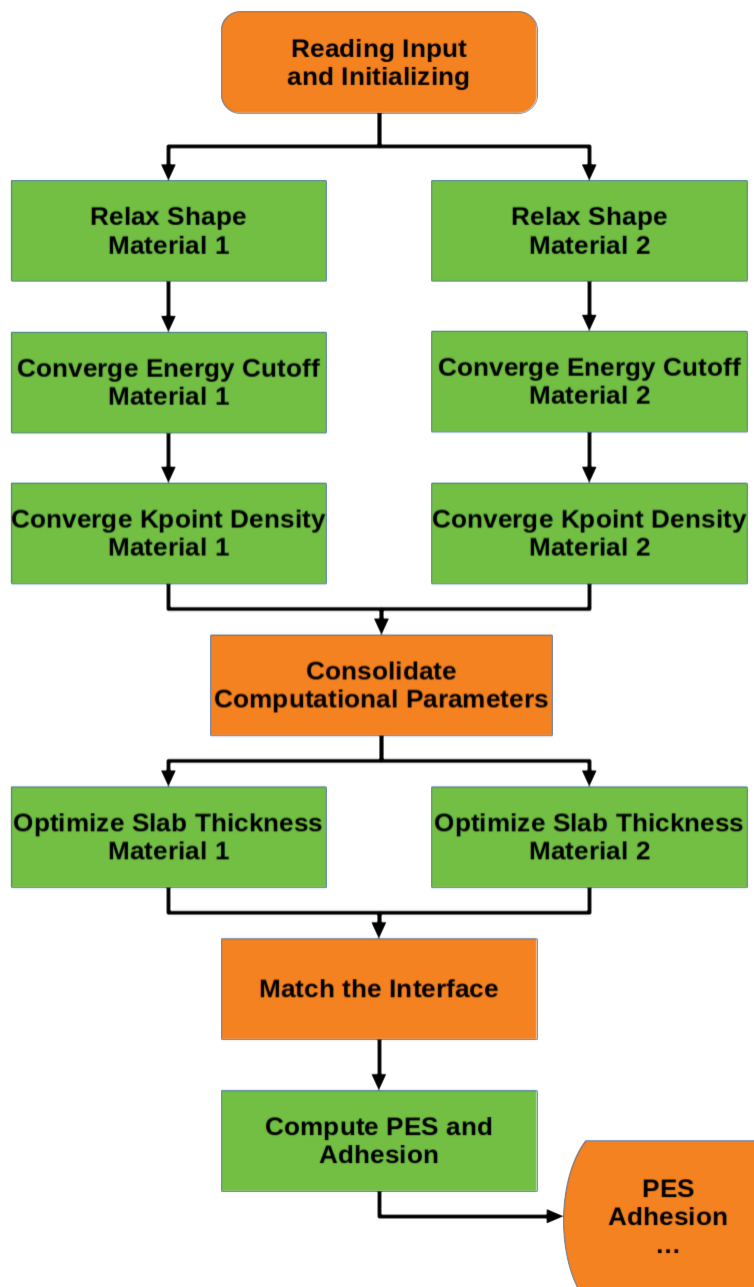


Figure 2.2: Flowchart depicting the entire workflow for calculating potential energy surfaces of solid-solid interfaces. Green rectangles represent combined workflows that can also be used independently. Database entries are read and written at each step, but this procedure is only indicated at the end of the flowchart because it would otherwise clog it.

- **Optimize Slab Thickness:** Slabs are built according to the input Miller indices and desired vacuum. Their thickness is converged with respect to the surface energy.
- **Match Interface:** The interface is matched according to chosen limits in strain, differences in angles, and maximal cross-section area. Lattice strain is divided between the two materials depending on the ratio of the bulk moduli.
- **Compute PES and Adhesion:** The PES is calculated by relaxing the slabs in the direction normal to the interface plane for all the unique combinations of high-symmetry points of both surface slabs, duplicating these results to all equivalent points in the interface plane, and interpolating between them with radial basis functions. At the same time, the matched slabs (which generally differ slightly from the previously relaxed unmatched slabs due to strain in the lattice) are fully relaxed. The adhesion for the interface is calculated by subtracting the total energies of the relaxed matched slabs from the total energy of the interface in the lateral position with the lowest energy.

Other interfacial properties can be calculated from the PES by adding other small workflows to the flowchart in Fig. 2.2, which are not reported here for brevity.

The calculation of microscopic shear strength, which represents the strength of a material before it fails due to shear stress, is of particular interest. It is equivalent to the static friction force per unit area of a defect-free interface. The calculated τ should thus be interpreted as an upper limit for the resistance to sliding along a specific direction. As a result, it is referred to as ideal shear strength. Although it can be calculated along any direction of the PES, an intriguing option is to evaluate it by taking the derivative of the PES along the minimum energy path (MEP), as proposed by Zilibotti et al. [195]. The MEP connects the minima of the PES, requiring only the lowest energy barriers to be overcome. This means that no forces are acting in directions orthogonal to the path, so the MEP has the highest statistical weight of any sliding path. We use the simplified string method to calculate it [225]. After obtaining the PES, the static friction properties of the interface can be calculated by running the minor workflow to calculate the MEP and then the workflow to derive the shear strength.

The perpendicular potential profile $\gamma(z)$, also known as perpendicular-PES (pPES), is another important interfacial property that can be evaluated with a specific workflow. This is usually calculated at the minimum and maximum values of the lateral PES and describes the distance dependence of the surface-surface interaction in both attractive and repulsive regimes. It is calculated by displacing the two slabs normal to the interface plane.

In addition, a workflow for calculating interfacial charge displacement has been developed. This value represents the electronic charge redistribution that occurs due to the matching of two surface materials. This quantity has been discovered to be inextricably linked to the frictional properties of an interface [202].

2.4 Workflows description

All of the workflows described in this section are independent of each other. They can be used in the whole workflow for heterogeneous interfaces shown in Fig. 2.2, as well as in other workflows (e.g. one for homogeneous interfaces, or one that converges computational parameters for a bulk system or slab surface energy).

2.4.1 Convergence the computational parameters

The size of the supercells needed for heterogeneous interfaces can get pretty big very quickly. Therefore, it is important not to waste resources by imposing unnecessarily large plane-wave energy cutoffs or unnecessarily dense k-point grids. We have thus decided to keep the procedures previously introduced in our work on homogeneous interfaces [194] to converge the energy cutoff and the k point density. We opted to include an input option `n_converge` to tell the workflow when it should stop. Setting `n_converge` to n (with $n = 3$ as default) means that convergence is achieved if the last n calculations are within the selected tolerance.

The energy cutoff is converged first by running static calculations of the input bulk structure for five deformations (by default, five different values from -5% to +5% of the input volume) for increasing energy cutoff. The energies are then matched to an equation of state, and the bulk modulus and equilibrium volume are calculated. We can use the bulk modulus workflow already implemented in *atomate* [177] for this task. Now we increase the energy cutoff and repeat the procedure until both the bulk modulus and the equilibrium volume are converged to the chosen accuracy (by default 0.1% for the volume and 1% for the bulk modulus)¹.

For the k-points convergence, we also follow the process described in Ref. [194] and increase the k-point density until convergence of the total energy is achieved to the desired accuracy (by default 1 meV/atom). The energy cutoff for which this convergence is run can be selected and defaults to the value defined by the MPRelax or MPScanRelax vasp input set (520 and 680 eV, respectively). In the full workflow shown in Fig. 2.2 we use the energy cutoff of the previous convergence, and the structure used is set to the equilibrium volume defined in that step as well. We use Γ -centered meshes exclusively for our systems to avoid problems with oscillating total energies between Γ -centered and Monkhorst-Pack meshes [226].

For the full workflow for heterogeneous interfaces described in section 2.3.1, we set the respective higher values for the energy cutoff and the k-point density as new computational parameters for the interfaces system as a whole. We believe this to be a reasonable assumption, especially compared to using the default parameters from the VASP input sets of *pymatgen*, which generally do not depend on the system's constituents at all. Of course, one can run the convergence studies with the whole interface structure as input, but that would require a lot of computer time compared to running them for the comparatively simple bulk systems. It is noteworthy that from a practical point of view, when using high-performance computer clusters with a queuing system, running many small calculations for a convergence study is not necessarily efficient since a significant amount of time might be spent queuing and only a short time executing the jobs. Using FireWorks has the advantage of pulling calculations from a central database by consistently running jobs, avoiding this drawback.

While we have previously published similar work to converge the k-point density and the energy cutoff [194], and methods to converge slab thickness with respect to the surface energy have also been proposed before [227], we are not aware that the efficient sampling of lateral positions of two slabs with respect to each other has been explored.

2.4.2 Slab generation and thickness convergence

After the computational parameters for a given material have been converged, a slab is constructed from the bulk structure using the approach described in [228] and implemented in *pymatgen* [178]. This is conceptually done by reorienting the bulk so that the surface plane of interest (identified by a set of Miller

¹We note that often the lattice parameter is used for convergence studies and not the volume. However, using the volume is better suited for a high-throughput framework as ours since non-cubic materials with more than one independent lattice constant can be treated in precisely the same manner.

indexes) is parallel to the x-y-plane, replicating the bulk along the z-direction to make it thicker, and adding a sufficiently thick vacuum layer on top. This vacuum layer is necessary to prevent mutual interactions between the periodic replica of the system in the z-direction and thus correctly simulating semi-infinite surfaces on either side of the slab. Along with the other two lattice directions, the periodic boundary conditions are preserved.

It is necessary to take an adequate number of atomic layers into account due to the reciprocal influence between the two surfaces, which can lead to unwanted quantum phenomena, edge states, and incorrect interactions that would not be present in the semi-infinite surfaces we intend to represent. Choosing unnecessarily thick slabs can lead to computational bottlenecks, significantly increasing the cost of first principle simulations on these systems. Especially since we couple two slabs to form an interface, where the lattices are multiplied laterally to minimize lattice mismatch, the number of atoms can quickly increase ten- or twenty-fold. In that case, each additional atomic layer considered in excess might add tens of atoms to the interface. Therefore, it is prudent to carefully converge the thickness of the slabs before they are matched so that the needed accuracy is achieved, but unnecessary thickness is avoided.

To solve this problem, we designed a workflow that creates the slab from a bulk structure and at the same time identifies the minimum optimal thickness needed to simulate it accurately. This is reasonably achieved by converging the surface energy of the slab with the number of layers. Indeed, this value is quite sensitive to the slab thickness due to the surface-surface interaction of thin slabs, but after a certain threshold, the bulk-like region in the middle gets thick enough to stabilize the surface energy.

A certain number of oriented slabs with different thicknesses are created starting from the bulk structure, ranging from a minimum number to a maximum number of atomic layers. Those and the increment in layer number can be changed in the initial input dictionary by the user. Default values are set to 4, 12, and 1 for the minimum, maximum, and increment, respectively. Using an increment other than 1 can benefit slowly converging systems or help in the case of uneven layer spacing, e.g. for a diamond 111 slab.

The slabs are then relaxed, and their total energy is calculated from first principles. This is also done for the oriented bulk, i.e., the bulk cell having the same crystalline orientation as the slabs. The oriented bulk is used instead of a simple bulk cell to ensure that the same k-point meshes are used for the bulk and the slab calculations, which is necessary to get accurate surface energies [227]. Subsequently, the surface energy for the different slabs is calculated as:

$$E_{\text{surf}} = \frac{E_{\text{slab}} - E_{\text{bulk}} (N_{\text{slab}}/N_{\text{bulk}})}{2} \quad (2.1)$$

where E refers to the energy and N to the number of atoms, while the subscripts identify the slab and the oriented bulk.

The convergence process is very efficient and can be performed in three different ways, following a serial or parallel approach, as illustrated in Fig. 2.3. In the case of serial and low parallelization, first, the oriented bulk and the minimum/maximum thickness are calculated, then the various intermediate thicknesses are progressively simulated one by one until the surface energy is converged. Differently, in the high parallelization case, all slab relaxations are run simultaneously, and the optimal thickness is chosen afterward. These different modes are designed to allow users to tune the workflow to their computational resources since the highly parallel way is potentially the quickest for machines with many available processors but might carry out “unnecessary” calculations with slabs thicker than needed. At the same time, the serial version might be best suited for small HPC clusters or workstations. The convergence is obtained for the thinnest slab presenting a relative difference of its surface energy with respect to the maximum thickness (the reference) below a selected precision threshold, set by default at 1%.

Here we have to note that our current approach does not discriminate between different surface terminations for equal Miller indices. This means that generally, multi-component crystal structures are not yet handled correctly by this workflow step unless all surface planes are equivalent, e.g., for the (001) and (111) planes of rock-salt-type structures are OK, but the (111) surfaces are not, because they consist of alternating layers for each atom type instead of mixed ones. Additionally, only stoichiometric slabs should be used to ensure Eq. 2.1 is correct. We are working on a more general solution that will automatically identify the lowest energy termination for each surface orientation of all periodic crystals regardless of the number of constituents and modify Eq. 2.1 to be more general, but this is a complex matter which needs further investigation and will be presented in a separate publication.

In the case of an elemental bulk, it is also vital that all the created slabs lead to significant and stable physical systems; otherwise, problems could arise in the convergence loop. This aspect is evident in the oriented bulk case, which is obtained from the slab of minimum thickness by removing the vacuum in the cell. This means that the minimum thickness should correspond to the smallest number of layers, or one of its integer multiples needed to represent the periodicity of a bulk, e.g., three layers in the case of an fcc crystal along the [111] direction.

After the ideal thickness is found, an additional slab is constructed using an implementation of the LLL algorithm [229] to end up with a slab whose surface normal is as parallel to the cell's z-axis as possible, which makes lattice matching significantly easier. This and all other slabs are then saved in the high-level database, along with their surface energies.

A more detailed description of the computational units constituting this workflow, as well as a diagrammatic flowchart, can be found in Appendix A, Section 1.

2.4.3 Matching of the interface

Matching any two kinds of crystalline materials inside a common supercell to perform a DFT simulation might often be a challenging task. The desired result is to accommodate both materials forming the interface without imposing unphysical strains but keeping the simulation cell sufficiently small at the same time. In crystal growth and material deposition, this matching of one crystalline film on another crystalline substrate is known as heteroepitaxy, and algorithms that describe it have existed for more than 35 years, e.g., the one by Zur and McGill [204]. An implementation of this algorithm has been published more recently within the MPInterfaces package [205], and there are ongoing efforts to integrate it tightly into pymatgen (Python Materials Genomics), a prevalent library for material analysis [178].

To match a general solid interface, we have employed the code from MPInterfaces [205] but slightly modifying its approach to be better suited for interfaces of two bulk materials instead of a substrate and a thin film. The main change of our implementation with respect to MPInterfaces' is how the unavoidable lattice strain is handled. In the original implementation, only one of the materials (the thin-film) gets strained, as appropriate for a substrate/thin-film interface. In our work, both slabs are strained to fit an averaged lattice. It is possible to weigh this average, and in our workflow, we chose to use the bulk moduli as weights. Thus, if the bulk modulus of material 1 is twice as large as the bulk modulus of material 2, material 2 will be strained twice as much in a hetero interface of these two materials.² Another modification includes an automatic initial guess of the interface distance by averaging the spacing between all lattice planes of both slabs forming the interface.

²Of course, it is also possible to only strain a 2D structure and not the substrate by setting the weight of the 2D material to zero

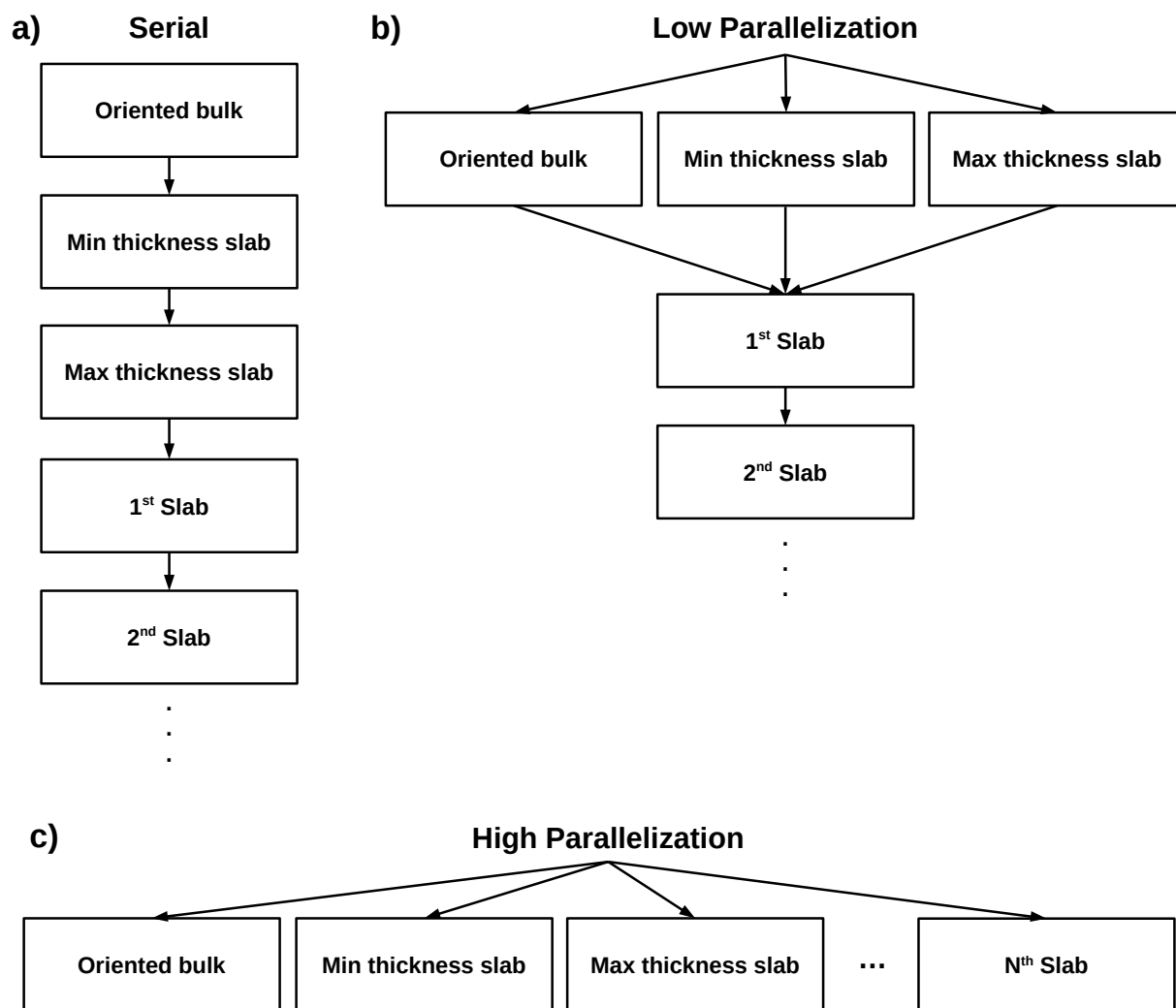


Figure 2.3: Different levels of parallelization implemented in the workflow that generates an optimally thick slab.

2.4.4 Calculation of the Potential Energy Surface

A matching cell is not the only requirement to correctly model a solid-solid interface. A priori, it is not clear which relative lateral position of the two matched slabs leads to the highest binding energy and thus to the equilibrium stacking.

Only homogeneous interfaces were allowed in the first versions of our software, and only a few selected crystal structures and surfaces could be considered. The PES was calculated by sampling pre-defined points for each allowed combination of crystal structure and Miller indices. This approach is not feasible for a more general solid interface, given by heterogeneous interfaces or even homogeneous interfaces with arbitrary surfaces. The method we present here relies instead on symmetry and surface analysis computed on the fly using pymatgen and spglib [178, 230].

The algorithm works as follows:

1. The top surface of the bottom slab and the bottom surface of the top slab get analyzed to find all on-top, bridge, and hollow sites using Delaunay triangulation of the topmost (bottommost) atoms³.
2. Out of these high symmetry points, the unique ones get separated using symmetry operations to detect duplicates. (See Fig. 2.4(b) and (c) for unique (top) and all (bottom) high-symmetry points)
3. The unique high symmetry points of both slabs are combined to find the interface's lateral shifts, e.g. `top_1-hollow_1` and `top_1-bridge_2`. Equivalent shifts that may result from the combination of different high-symmetry points get discarded. (See Fig. 2.4(d)).
4. For the remaining shifts, structures get built and checked for symmetric equivalence (e.g. rotations), and only the truly unique interface structures will be relaxed in DFT simulations. The atoms are only relaxed in the direction normal to the interface plane to ensure that the structure can not relax back into a total minimum.
5. Once all DFT calculations have finished, structures are built from all combinations of the duplicate points set aside in Step 2. These structures are matched to their symmetry-equivalent ones that have been relaxed in the previous step, and the correct energies are assigned. In Fig. 2.4(d), we see that this method is very efficient and only a hand full of points (six in this case) need to be calculated to sample the unit cell densely.
6. Now we have data points all over the unit cell and can start to fit the PES. To this end, we follow the procedure we have developed previously for homogeneous interfaces [194]. The cell is duplicated laterally to avoid edge effects, and radial basis functions are used to interpolate between the points. This makes it possible to represent the PES by a two-dimensional function $\gamma(x, y)$, e.g., to plot the PES on a fine grid or evaluate the shear strength [125].

Fig. 2.4 shows a rather simple example interface (Al(111) on diamond C(111)) and its high symmetry points. Both surfaces have hexagonal symmetry, but the in-plane lattice parameter of Al(111) is about 13% larger than the one for diamond carbon. A reasonable match is found if the Al lattice is rotated by 30° with respect to the carbon lattice, assuming that the *a* and *b* lattice vectors start pointing in the same directions. This is a common configuration of matching hexagonal lattices, known as $\sqrt{3} \times \sqrt{3}$ R30, which works here because $2a_{\text{C111}} \simeq \sqrt{3}a_{\text{Al111}}$. The matched lattice is then an average weighted by the bulk moduli of the

³Note that only three-fold hollows will be classified as hollows, while four-fold hollows will be classified as bridge sites by the triangulation.

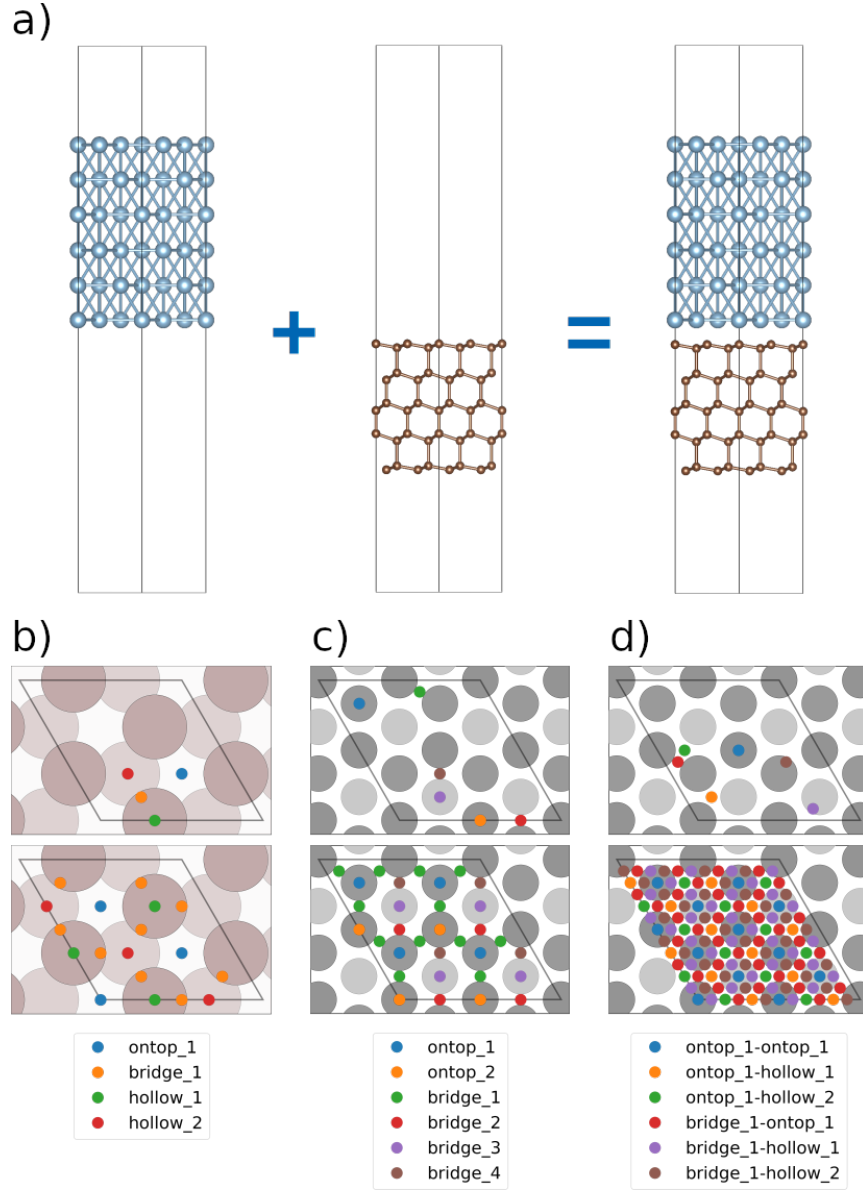


Figure 2.4: A overview of the Al(111)-C(111) interface. (a) Side view of the matched slabs and the resulting interface. (b) High symmetry points of the bottom of the Al slab. (c) High symmetry points on the top of the carbon slab. (d) Unique combinations of high symmetry points for the interface, shown on the C slab.

two materials. Since the bulk modulus of diamond carbon is much higher than those of fcc Al, the strains we end up with are, for both a and b , much larger for Al(111), at 1.7%, than for C(111), at -0.3%.

The interface layers and those adjacent to them can be seen in Fig. 2.4(b) and (c). Also depicted are the high symmetry points found by our algorithm, the unique ones on the top, and the full set on the bottom. A better match with a larger unit cell could, of course, be achieved by tightening the parameter for the matching algorithm, which was set to a maximum of 2% mismatch for this interface and all the others discussed below.

2.5 Heterogeneous interfaces: Example results

We have calculated data for the following heterogeneous interfaces: Al(111)-Cu(111), Al(111)-C(111), Al(111)-Fe(110), Al(111)-Al(110), and Al(111)-Al(100), where C denotes the diamond allotrope of carbon⁴. Since some minor workflows produce interesting data on bulk and slabs as well, we will also show those results. All presented data were calculated spin-polarized with VASP version 6.2.0 and the PBE functional. The potential mapping was taken from the pymatgen MPRelax VASP input sets, and the computational parameters have been increased until the equilibrium volume was converged to 0.1% and the bulk modulus to 1%, which was also the convergence criterion for the surface energy. For the interface matching, a cell smaller than 200 Å² and a maximum mismatch of 2% was set, alongside a maximum angle difference of 1.5 degrees. However, only one of the investigated interfaces showed any angle strain at all, and that was below 0.1°. The tables and figures presented here and in Appendix A were constructed automatically from the high-level database using Python code from our package.

Table 2.1 shows converged bulk moduli, volumes, and lattice parameters and compares them with experimental values. The converged energy cutoffs and k-point densities are also included. For the bulk moduli, we have also shown prediction data taken from the Materials Project and based on statistical learning [161, 231]. Those data are inferred from other *ab initio* data but not directly computed; thus, a somewhat worse fit to experimental values is expected.

The lattice parameters and bulk moduli are plotted against their experimental references in Fig. 2.5, highlighting their excellent agreement.

In Fig. 2.6 we present surface energies and compare the results of this work with our previous calculations [194], which were computed with QuantumEspresso [236] and AiiDA [220] for slabs with a fixed thickness of 6 layers. The current work uses optimized thicknesses between four, Fe(110) and Cu(111), and ten, C(111) and Al(100), layers (see Appendix A for all numbers and details)⁵. Overall this work is in good agreement with the average literature values, showing some improvement with respect to our previous results [194] especially for C(111) and Cu(111). The Al(100) and Al(110) are very close in surface energy, although the average values, our past work, and the data from the Materials Project all point to Al(110) to have slightly higher energy. In this work, this order is reversed, with Al(100) having 30 mJ/m² higher surface energy than Al(110). We believe that the differences in the code and the pseudopotentials used are a significant factor in the slight variations of results here and note that all results for aluminum lie within one sigma of the literature average.

In table 2.2 we show our main results, the data for the heterogeneous interfaces. We present adhesion, corrugation, interfacial separation, cross-section area, and the number of sites in the interface structures. We also give the strains on both lateral lattice vectors and angles of both the top and bottom slabs. In

⁴To be clear about the structures we also state the Materials Project IDs in table 2.1. The structures used are fcc Al and Cu, bcc Fe, and diamond C.

⁵Our past effort counted the C(111) double layers as single ones; thus the slab was thicker than the one we used here.

	Al	Fe	Cu	C
MP-id	mp-134	mp-13	mp-30	mp-66
K^{tw} [GPa]	74.329	177.007	140.879	434.689
$K^{exp.}$ [GPa]	79.38	164.4-173.5	135.3-144.9	444.24
K^{MP} [GPa]	70.804	215.196	161.358	401.042
a^{tw} [Å]	4.045	2.831	3.631	3.573
$a^{exp.}$ [Å]	4.049	2.8633	3.615	3.559
E_{cut}^{opt} [eV]	225	400	475	475
κ^{opt} [1/Å]	4.9	3.6	3.7	2.3
$V^{opt.}$ [Å ³]	16.545	11.349	11.973	11.403

Table 2.1: Bulk properties of Al, Fe, Cu, and C. K is the bulk modulus, a the lattice parameter, E_{cut}^{opt} the optimized cutoff energy, κ^{opt} is the optimized k-point density, and $V^{opt.}$ the volume of the optimized primitive unit cell for each structure. The superscript tw denotes “this work”. Experimental data for lattice constants $a^{exp.}$ was taken from Ref. [194] and references therein, while the reference bulk moduli K^{MP} were queried from the Materials Project database [188]. Experimental bulk modulus data was taken from Ref. [232] for Al, [233] for Fe, [234] for Cu, and [235] for C.

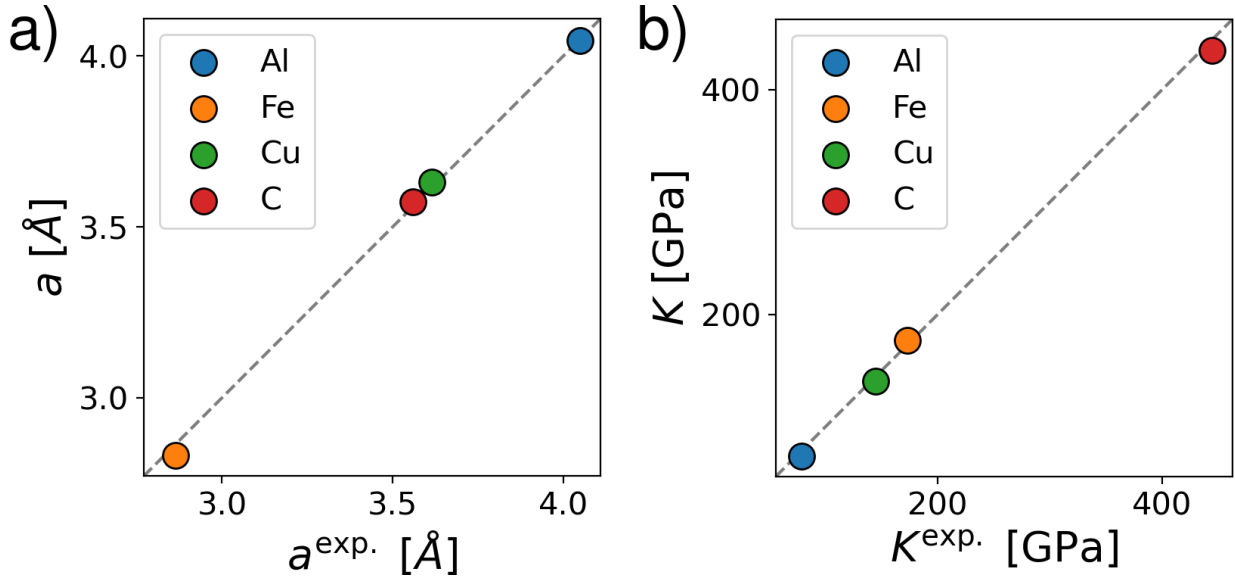


Figure 2.5: Converged lattice parameters (a) and bulk moduli (b) with respect to the experimental values.

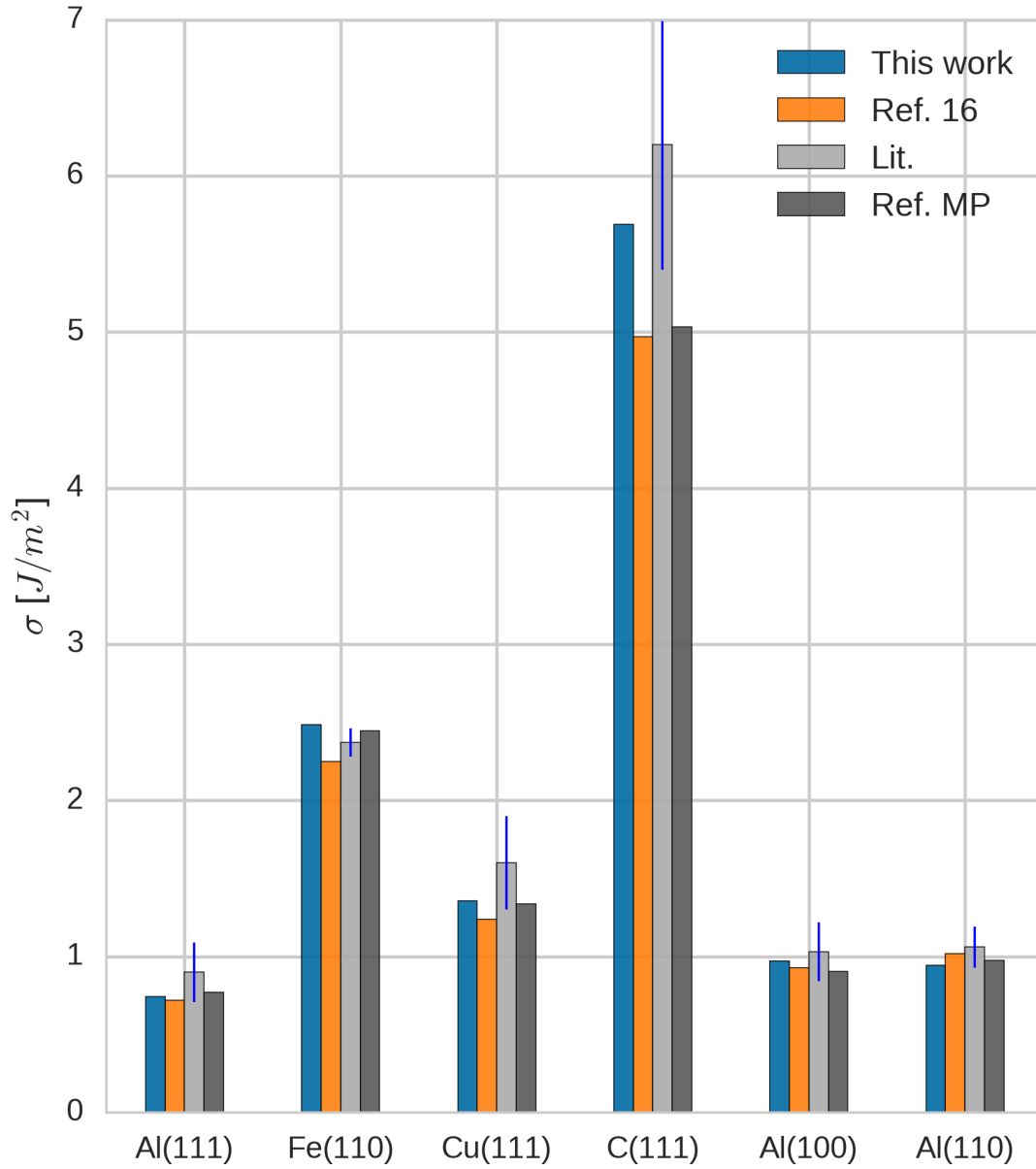


Figure 2.6: Surface energies for the example slabs. Literature values are averages of previous calculations of various codes and groups (see Ref. [194] and references therein), with the error bars denoting one standard deviation. The Ref. MP values are VASP calculations queried from the Materials Project website [188].

Appendix A, we also provide plots of interface stackings for minimum and maximum configurations, high symmetry points, and PESs.

	Al111-Cu111	Al111-Fe110	Al111-C111	Al110-Al111	Al100-Al111
γ_{min} [J/m^2]	2.215	3.108	3.049	1.249	1.479
$\Delta\gamma$ [J/m^2]	0.002	0.135	0.203	0.031	0.038
Δd^{min} [$\text{\AA}$]	2.219	1.818	1.846	2.174	2.194
Δd^{max} [$\text{\AA}$]	2.161	2.105	1.947	2.208	2.464
Num. sites	78	88	58	186	118
HSP ^{min}	hollow1-bridge1	ontop1-ontop1	bridge1-ontop1	ontop1-ontop1	hollow2-bridge2
HSP ^{max}	hollow2-ontop1	ontop1-bridge1	ontop1-hollow2	bridge1-ontop1	bridge1-ontop1
Cross sect. area [$\text{\AA}^2$]	50.751	56.827	21.985	114.521	56.97
strain top	[1.162, 1.162]	[-0.585, 0.855]	[1.705, 1.705]	[0.0, -0.99]	[0.0, -0.513]
strain bot	[-0.602, -0.602]	[0.248, -0.355]	[-0.286, -0.286]	[0.0, 1.01]	[0.0, 0.518]

Table 2.2: Properties of interfaces composed of Al, Cu, Fe, and C slabs with various miller indices where γ_{min} denotes the adhesion energy at the minimum energy configuration, $\Delta\gamma$ the corrugation of the potential energy surface, $\Delta d^{min/max}$ and HSP^{min/max} the interface distances and the matching high symmetry points for the minimum/maximum energy configurations respectively. Values for strain are given in the directions of the two lateral lattice vectors of their respective slabs and are in percentages.

Of course, it is not easy to compare our results with past work or experimental data here since there is, to our best knowledge, no other work that systematically investigates such metal-metal interfaces. However, we can compare the adhesion energies and the PES corrugation with our past results from homogeneous interfaces [125].

For homogeneous aluminum interfaces, we have previously calculated adhesion energies of 1.52 J/m² for the Al(111), 1.84 J/m² for Al(100), and 2.13 J/m² for the Al(110) interfaces. For the Al(110)-Al(111) interface we get 1.25 J/m² and for Al(100)-Al(111) 1.48 J/m². This means that both heterogeneous interfaces have less adhesion energy than the homogeneous Al(111) interface, which is not surprising since the stacking is not ideal across the whole interface area for heterogeneous interfaces in contrast to the homogeneous one. Nevertheless, both Al interfaces show adhesion energies close to the Al(111)-Al(111) interface, which is explainable by the prototypical metallic bonding in aluminum that is not much weakened by the interface as long as both parts of the interface are reasonably close-packed. At the same time the corrugation $\Delta\gamma$ of those heterogeneous interfaces at 0.04 J/m² for Al(100)-Al(111) and 0.03 J/m² for Al(110)-Al(111) is reduced by one order of magnitude compared to the homogeneous one for Al(111) at 0.4 J/m². The incommensurate stacking of the heterointerfaces again explains this. Some parts of the interface stack well, whereas some others do not, at each lateral position, so the total corrugation is comparatively small. However, it should be noted that there are homogeneous interfaces with similarly small $\Delta\gamma$, e.g. the (110) interfaces of the Alkali metals [125].

Some information about the Al(111)-C(111) was already shown in Fig. 2.4, where the interface structure and the high-symmetry points are shown. In Fig. 2.7 we now also show the interpolated PES. It is important to note that the lattice periodicity is not the periodicity of the PES, as many of the stackings are symmetrically equivalent and thus show the same total energy.

The computed adhesion of 3.0 J/m² for Al(111)-C(111) is relatively high compared to the other results presented here, as is the corrugation of 0.2 J/m². Qi and Hector have previously computed results for the same interface [237], although they do use slightly different strains to match the interface cell. They also do not compute a full PES, but just two different stackings, one of which is an ontop-ontop configuration, while the other is an ontop-bridge one. They report only 0.5% energy difference between those stackings

and thus do not compute more. We cannot confirm that result since our calculated PES corrugation is more than 9% of the adhesion energy. The adhesion energy was computed slightly differently, allowing for full atomic relaxations with constant cell shape, rather than relaxing only the z-direction as we did to ensure a well-defined PES. These full atomic relaxations result in adhesion of 3.98 J/m^2 , nearly a third larger than our result. We believe that those relaxations have a larger effect than the lower plane wave cutoff (400 instead of the 475 eV we use), and allowing full relaxations for our minimal PES configurations to compute the adhesion energy is an option we will explore in future work.

For the homogeneous C(111)-C(111) interface, we expect an adhesion energy of $\sim 11.4 \text{ J/m}^2$, according to our calculated surface energy for the C(111) slab. Thus we see again that the adhesion of the heterogeneous interface lies in between the homogeneous ones of the constituents.

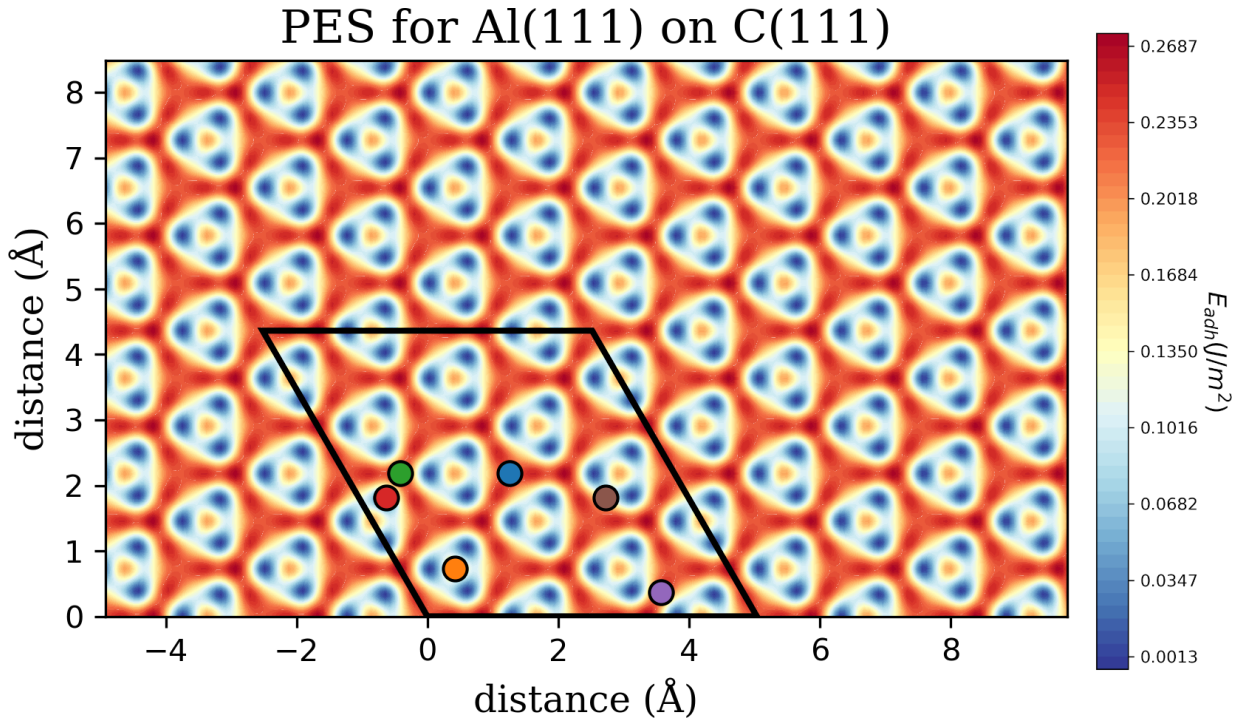


Figure 2.7: Potential energy surface (PES) for the Al(111)-C(111) interface. One unit cell including the unique combined high-symmetry points detailed in Fig. 2.4(d) is also shown.

For Al(111)-Cu(111), we have an adhesion energy of 2.2 J/m^2 which is between the homogeneous limits of Al(111) at 1.5 and Cu(111) at 2.4 J/m^2 . However, the PES corrugation is extremely low at 2 mJ/m^2 , more than two orders of magnitude smaller than the homogeneous cases. The detailed analysis of this ultra-low corrugation will be done once we implement our analysis of the charge density redistribution [202] and ideal shear strength [195].

The Al(111)-Fe(110) interface is a unique case since the iron slab is magnetic. Indeed also some aluminum atoms carry induced magnetic moments in the relaxed minimum structure, but none higher than $0.3 \mu_B$. The adhesion is the highest of all interfaces we discuss here, at 3.1 J/m^2 , which is not surprising due to the significant adhesion of Fe(110) homogeneous interfaces at 4.95 J/m^2 [125]. Compared to the

other heterogeneous interfaces discussed here, the corrugation is also high at 0.1 J/m^2 . The minimum stacking configuration, with one Al and one Fe atom straight on top of each other, is quite surprising since metallic bonding usually prefers higher coordination numbers. However, one must be careful with such simple assessments since this ontop-ontop stacking is just realized in a small part of the unit cell. Again, further analysis using charge density differences, which is beyond the scope of this chapter, is needed for a proper understanding of the situation.

Section 2-3 of Appendix A contains additional details for the examples presented and other results for additional interfaces.

2.6 Structure of the code

Our software is written entirely in Python and makes use of various packages from the Materials Project environment [188] to create new high-throughput workflows for tribology. The two main components of tribchem, whose structure is represented in Fig. 2.8, are the computational kernel and the high-throughput module.

The computational kernel comprises functions and classes that allow basic operations in solid-state physics, math, I/O, and other advanced operations to calculate or analyze electronics, mechanical, and tribological properties. In defining these functions, we used as many pre-engineered pieces of associated packages and physical functions as possible from released open-source scientific Python packages. Nonetheless, it has been necessary to build out our custom modules to handle specific situations in many cases.

When working with software to perform electronic structure calculations, such as DFT, the crystalline cell and atomic positions are typically written in input text files. When using these software “manually”, geometric operations and atomic rearrangement reduce to simple file editing. However, the situation is different in an automated workflow, which executes a series of sequential steps by calling and relying on various modules. In this case, even the most basic operation on the inputs is performed behind the scenes without user intervention. Therefore, the role of the computational physicist in designing the scientific program is critical. Every decision should be weighted to create a code that works and can handle all of the situations and requirements that arise during a DFT simulation. These, of course, include automatic input generation, data collection, effective database management, and error handling.

On the other hand, our high throughput module contains several complex workflows written in the form of advanced Fireworks-based classes to perform high-throughput screening of solid interfaces and analyze their physical and chemical properties. The general configuration of the entire module allows for the easy addition of new parts to calculate other properties of interest outside of the tribological field. When writing fairly complex workflows, it is of uttermost importance to keep the code modular. This allows easy modification and updates to parts of the workflow and makes it possible to generate new workflows with the modular parts. For example, the minor workflows dealing with the convergence of energy cutoff and k-point density can be used routinely by researchers working with VASP. This is, in principle, independent of high-throughput computations. Another example is the efficient generation of slabs with minimal thickness, speeding up all surface science studies.

At the same time, the code also has to be robust and as “smart” as possible. In this context, we define robustness as the ability to handle all, or at least nearly all, possible inputs correctly. That means, for example, including the possibility to add van der Waals (vdW) interactions for weakly bound layered systems and local-on site corrections (DFT+U) for correlated systems. Of course, on-the-fly error correction and recovery during DFT calculations are also of imperative importance for high-throughput. In this respect, we rely on the custodian package, which is tightly integrated with fireworks [176], atomate [177],

and pymatgen [178], and can catch and correct most errors that can happen in VASP calculations.

However, it is better to avoid errors than correct them, so we introduced “smart” methods into our workflows that adapt input parameters based on our expertise in running VASP calculations. We do this by providing specially tuned vasp input sets (based on pymatgen’s MPStatic, MPRelax, MPScanStatic, and MPScanRelax sets), which adapt various flags in the input files of VASP to the specific run, with the user only having to select out of a small list of possible self-explanatory keywords like *bulk_full_relax*, *slab_position_relax*, and *interface_scf*. The flags are then optimized to fit the input structure and the task; e.g., wave function projectors might work in real space or reciprocal space, and the choice depends on system size and the accuracy requirements of the calculation type. The choice of these kinds of parameters, in theory, does not influence the result of a calculation by much, but if cleverly selected, they significantly reduce the chance of errors and also cut down on total computation time.

2.6.1 Computational kernel

TribChem’s computational kernel includes several simple functions for performing basic operations in solid-state physics, math, geometry, file manipulation, plotting, and post-processing. Several sub-modules have been planned to meet these requirements and are schematically described below:

- **base:** It contains a collection of functions for manipulating atomic structures with periodic boundary conditions. It enables, for example, the replication of crystalline cells, the translation or rotation of atomic clusters, and the creation of an orthorhombic-shaped base area for any cell. It also includes some mathematical functions for calculating gradients on three-dimensional surfaces and fitting data to polynomials of any degree. There is also a converter between the various physical units, as well as csv tables of the elemental materials classified based on their properties.
- **dft:** I/O handlers for VASP, Quantum Espresso, and Lammmps are available, allowing the user to load input files into versatile Python dictionaries for further processing or extract information of interest from output files.
- **electronics:** Functions and classes that can be used to combine the electronic charge densities of output files and plot the electronic structure’s bands and density of states.
- **structure:** Mostly advanced classes that allow working on the atomic structures of bulk, slabs, and interfaces. The code heavily relies on existing packages such as pymatgen [178] and MPInterface [205], which contain many utilities and functions helpful in manipulating bulk and slabs, as well as algorithms for geometrically matching two surfaces. The **Shaper** class, for example, is explicitly written to identify the number of atomic layers in a slab, possibly removing or adding new ones to achieve the exact thickness required.
- **dynamics:** A set of tools for analyzing a dynamic simulation and calculating the positions, velocities, and forces acting on a single species or groups of atoms. It also includes many tools for plotting these properties.
- **tribology:** It includes analyzing tools for computing tribological properties, such as functions for matching an interface by combining the high-symmetry points of the surfaces and other classes for calculating interfacial properties such as PES, MEP, and shear strength.

The physics sub-modules work in close synergy and provide functionality used throughout the code.

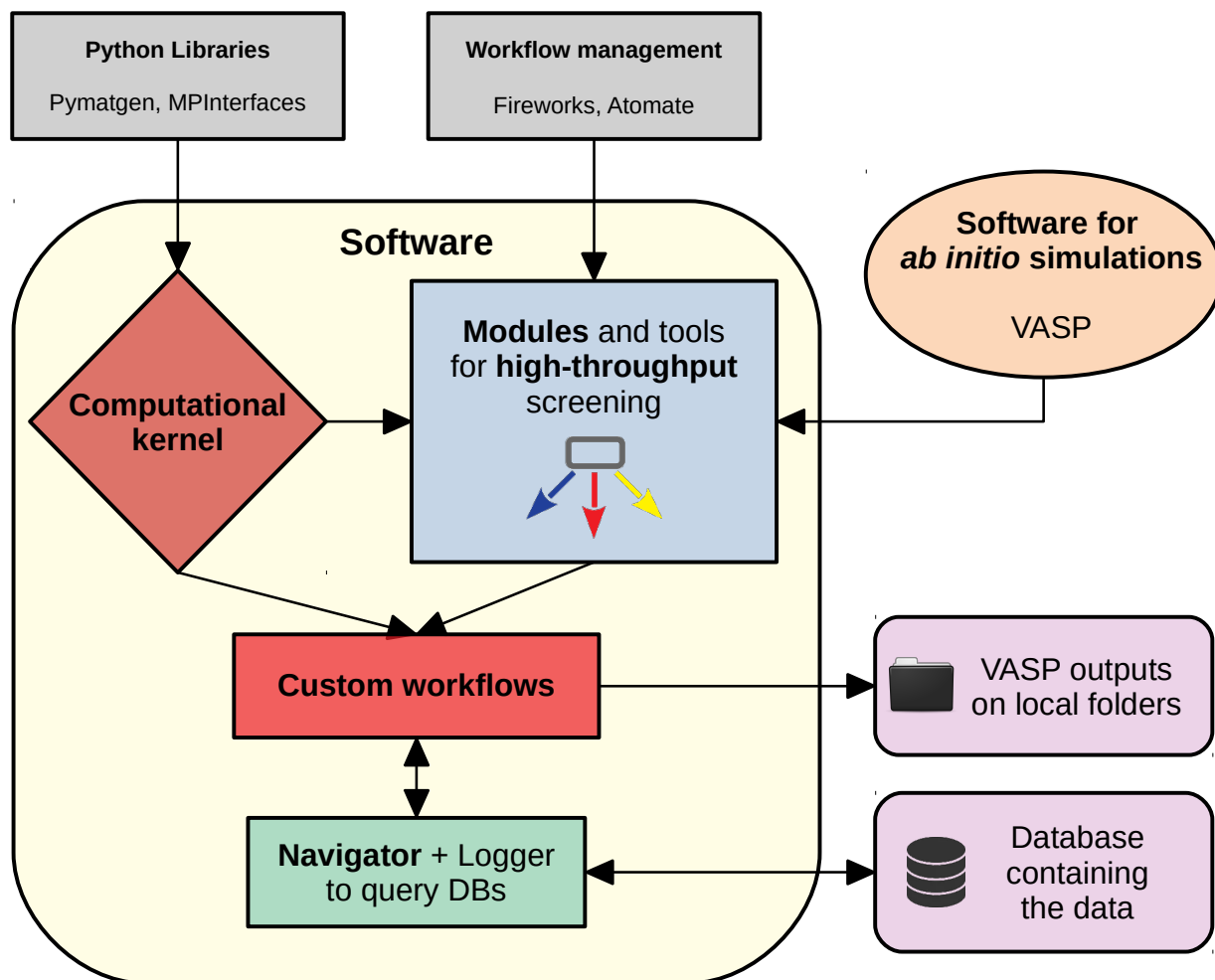


Figure 2.8: Structure of the TribChem package is depicted in the diagram. The computational kernel and the high-throughput module are the two main unit modules that we created. These offer customized workflows for performing automatic DFT simulations and high-throughput screening on various materials. After cleaning procedures, the DFT output is saved in both local folders on the workstation machine and stored in our database. The Navigator class, which we wrote specifically to oversee writing, reading, and data transfer operations, manages the interaction with the database.

2.6.2 High Throughput module

The high-throughput module consolidates all efforts to create an efficient and clean code for HT simulations in materials science. Several functions and classes are present here, written following the informatic recipes of the FireWorks package. The module is made of three sub-modules that contain classes and functions for firetasks, fireworks, and workflows, in that order. Workflows are created by combining one or more fireworks, which are “simply” a grouping of firetasks. This nested structure is essential because the FireWorks package requires a workflow object to run calculation jobs on a workstation. To clarify, the most basic scenario that can occur is as follows:

```
ft = CustomFiretask(...)
fw = Fireworks(ft, name="Firework")
wf = Workflow([fw], name="Workflow")
```

The object `ft` is instantiated from `CustomFiretask`. It is then passed to `Fireworks` to initialize `fw`, which, in turn, is passed to `Workflow` to create `wf`. The object `wf` will be passed as input to the FireWorks package, which is in charge of starting the high-throughput calculation on a workstation. The simplification is that, in this case, `wf` only contains `fw`, which only contains `ft`. However, this is not always the case, and we are frequently interested in performing more complex operations, which may necessitate the use of more `fw` elements. In that case, the connection between the various fireworks should be specified using a Python dictionary. As a result, the fireworks can be combined serially or in parallel, resulting in graphs with various structures. For example, a workflow composed by three serial fireworks can be specified as follows:

```
wf = Workflow([fw1, fw2, fw3], links={fw1: fw2, fw2: fw3}, name="Workflow")
```

In the end, defining fireworks and workflows is merely a formality, and it can be said that the core of the module is defined exclusively by the firetasks. They are the most critical elements of the hierarchy and must be programmed as modularly and broadly as possible. These two aspects are interdependent and inseparable. Any firetask, by its very nature, is structurally modular from an algorithmic standpoint. Everyone can import our firetasks and integrate them into another workflow, but it is necessary to understand whether such code makes sense. The critical point is that the firetasks should be written as general as possible to ensure they can be adapted to any situation. This can be accomplished by programming consciously, for example, by flexibly defining the input variables and customizing the writing and reading interactions with the database. Another key aspect is to carry out long-term planning in software design. The developer should always anticipate possible future additions and leave “room for maneuver” within the code to ensure that existing features can be extended.

We have prepared two firetasks to run VASP (`FT_RunVaspSimulation`) and save the results in the database (`FT_MoveResults`), which serve as an example. They have been implemented in the most general way possible because they perform a few basic operations required by any workflow. The function `FT_RunVaspSimulation` has two different execution modes. The first requires the crystalline structure (as a `pymatgen` object) and the computational parameters to be passed directly as inputs during the initialization of the `ft` object. On the other hand, the second allows us to specify the read entries for the database, leaving to the firetask to retrieve the material information and computational parameters saved there autonomously.

Once the VASP simulation is completed, `FT_MoveResults` retrieve the data saved in the Fireworks database (where all high-throughput records are kept) and save it in a specific location of interest within

the database, i.e., a high-level database containing the final clean data. This firetask makes it possible to specify a series of information about the source and destination databases, including the database file, collection, and entries containing the data to be recovered. Initially, this firetask was created solely to move the VASP output data and save it in a different location in the database, but its potential is far greater. Indeed, by slightly modifying it, we were able to make it versatile and usable in any context, and it can now transfer information from any location in any database to any other location in any other database.

Superior modularity and usability can be achieved at the level of fireworks and workflows as well. Returning to the previous example, we wrote a function called `run_and_save` that calls the two firetasks (`FT_RunVaspSimulation` and `FT_MoveResults`) and combines them to return a firework capable of launching a VASP simulation and saving the results in the database. This function is a stepping stone for the code and is used in almost all of the workflows we have created. Its potential, however, is not limited to this. Sometimes the user does not want to run high-throughput calculations and instead simply wants to open a terminal, retrieve a crystal, and run a simulation automatically. The function has also been optimized for this purpose, i.e., to perform individual DFT simulations on the fly, automate daily scientific research, and allow for high-throughput screening.

The concept of object inheritance provides another compelling way to keep the code modular. Some actions, such as query operations from and to a database, are shared by all the firetasks. It is pointless to rewrite the same piece of code within each firetask because this approach is both harmful and error-prone. For this reason, we developed a firetask core called `FireTaskTribChem`, containing a set of standard methods inherited by all other firetasks.

In short, these methods are:

- `read_runtask`: Read the optional and required parameters of a firetask. These are passed by the user as input arguments when initializing the `ft` object.
- `read_params`: Update the dictionary parameters with default values read from a JSON file.
- `set_filter`: Create a filter to query the database in order to retrieve/store some data.
- `is_done`: Check if there is a specific entry within a MongoDB document that matches the filter. Useful to check if a calculation is already done and decide whether to run or stop a job.
- `query_db`: Retrieve data from a MongoDB database. The database location and tables are specified with keywords: `db_file`, `database`, `collection`, `entry`.
- `update_db`: Update data in the matching field. Data is prepared to be stored in a database creating a dictionary according to the MongoDB guidelines. The database field to be updated is located by: `db_file`, `database`, `collection`, `entry`.
- `insert_db`: Add a new field to a database. The precise position is identified by `db_file`, `database`, and `collection`.
- `query_mp`: Query the Materials Project database, searching for a structure with a selected `mp_id` or searching for the lowest energy structure given a specific chemical formula.
- `save_files`: Create the folders to save the output files on the local machine.

All of these functions are named in accordance with the convention: `action_name`.

All of our custom firetasks have direct access to these methods and often use them when executing workflows. In this way, the development of new firetasks is greatly simplified and typically only necessitates

creating a few methods specific to a particular workflow. Of course, it is always possible to override the parent method in the child classes, creating specific methods for the occurrence.

2.6.3 Available workflows

Here is a concise list of workflows that are currently available within the TribChem package:

- Query online databases to save data to an internal database.
- Kinetic energy cutoff convergence.
- K-points convergence.
- Cohesion energy calculation.
- Calculation of the optimal thickness for a slab.
- Surface energy calculation.
- Matching and generation of a solid interface.
- Calculation of the PES.
- Evaluation of the Adhesion energy.
- Extraction of MEP and shear strength.
- Calculation of the pPES.
- Charge displacement analysis.

2.6.4 Database management

When performing high-throughput calculations, it is critical to dispose of good utilities to read, write, or process the information stored in the project database. Indeed, even the best HT code would be unusable without careful data management and efficient database design. In principle, this is also necessary for the database to be accessible and easily shareable by the various scientific communities. For this reason, we meticulously designed the IT infrastructure to supports our physics and HT modules.

To this end, we created a **database** sub-module, containing a few Python tools for efficiently handling query operations on the database. The main class is **Navigator**, which implements a high-level interface for dealing with database operations by combining various methods from the MongoDB database as implemented in pymongo⁶. It includes all of the methods needed to connect to a database and run queries to find tables, update or insert documents, and delete or drop data. These features are executed at each step of a general workflow to store all the elaborated information.

We created this sub-module to interact with the database having complete control over the executed operations. In principle, this would require implementing every interaction with the database in all the firetasks, slightly convoluting the code structure. That is the reason why we first wrote **Navigator**, to centralize all critical database operations in a single location, allowing for immediate resolution of potential bugs.

⁶<https://pymongo.readthedocs.io/en/stable/>

Furthermore, several scripts were prepared to implement powerful functions to manage query operations on the database automatically. They can also be used by non-technical users who intend to use our package. In fact, rather than dealing with the `Navigator` class and its methods directly, it is more straightforward to call these functions to interact with the database. The functions create an instance of `Navigator` and then call some of its methods. It is precisely these functions that are utilized within the `FiretaskTribChem` to implement the core methods common to all the firetasks of the project.

It could be argued that the firetasks use the pymongo features, which is correct; however, it is worth noting how the code structure is not so simple when you get your hands on it. The logical flow of Python calls begins with the basic pymongo functions and progresses to the robust implementation of the database interactions within our firetasks, as follows:

```
Firetask.method <-- FiretaskTribChem.method <-- functions <-- Navigator <-- pymongo
```

In addition, we have created other secondary tools to read, write, and clean the database correctly. The most important is `convert_dict_to_mongodb`, whose job is to convert Python dictionary to be compatible with pymongo's update methods. This function handles an annoying problem occurring when updating nested Python dictionaries, ubiquitous in our database structure. The update operation on a nested dictionary usually does not update each entry in the innermost dictionary one by one but simply replaces it with the new dictionary that is passed. Let us illustrate this with an example. Define two nested dictionaries and attempt to update entries of the first one with those of the second one.

```
>>> dict1 = {'key': {'data_1': 5 }}
>>> dict2 = {'key': {'data_2': 2 }}
>>> dict2.update(dict1)
>>> print(dict2)
{'key': {'data_1': 5}}
```

The update's goal was to obtain `{'key': 'data_1': 5, 'data_2': 2}`; thus, the operation failed! This was one of the most severe issues we encountered during the initial testing of our code. Everything worked fine, but we could not save the results correctly in the database. If 'key' contains multiple sub-dictionaries, the situation worsens, determining the real risk of overriding everything and losing data from previous calculations. The same thing happens when a MongoDB entry is updated.

To update an existing (nested) dictionary without overriding it, we have written a function named `convert_dict_to_mongodb` to preserve the nested entries of the dictionary and adhere to MongoDB notation. The entries should be written in the form of a series of consecutive keys separated by dots, as follows:

```
>>> convert_dict_to_mongodb(dict1)
{'key.data_1': 5}
```

In this way, the inner dictionary keys are converted into individual entries, and the MongoDB update works.

Another important database-related class is `NavigatorMP`, which provides a high-level interface for connecting to the Materials Project database⁷. This class will be generalized and extended in the future to research material structures and data also from other online scientific archives.

⁷<https://materialsproject.org/>

Design of the database

FireWorks uses MongoDB databases to store workflows, fireworks (smaller workflow units, not to be confused with the package name FireWorks), and calculations. This database must be installed and configured before FireWorks can be used, making it a requirement for our package installation. For running our workflows, we have decided to include a second database layer to store high-level results only, as commonly done in FireWorks high-throughput studies. This makes it much easier to query results and facilitates sharing the (much smaller) database. This database is also used to avoid calculation duplication. For example, if a Fe(100)-Cu(111) workflow has already been run, bulk convergence for the Fe(110)-Au(111) interface is not required for the iron part. The same holds for slab relaxations. The integration of these secondary results databases requires minimal additional setup compared to the standard FireWorks installation.

Our high-level database is called `tribchem` and includes several collections, each dedicated to a different type of materials, with a particular concern for the crystalline structure or the type of functional adopted. In our case, we keep three separate main collections dedicated to bulk, slab, and interfaces, respectively. The naming convention that we use for the collections is `functional.material`. For instance, in the case of elemental bulks, which are crystalline structures with a mono-atomic basis, a collection may be called `PBE.bulk_elements`.

Each document inside a collection contains data about a specific material. Our database design is shown in Fig. 2.9, where aluminum is used as an example to show how information about bulks, surfaces, and interfaces is saved within the database.

In general, we use up to three primary indices to identify the material in the collection. They are the material identifier (`mid`), the chemical formula (`formula`), and a custom name (`name`). The `mid` is the only mandatory field, and it typically corresponds to the ID of the online database from which the material structure is initially retrieved, but it can also be a custom name. The other two fields are optional. In the case of Al, we obtained the initial primitive structure from Materials Project; hence `mid` is `mp-134`, which corresponds directly to the Materials Project ID (MPID). The formula is typically assigned automatically based on the structural composition of the bulks, whereas the name is an additional identifier that may be useful to speed up the search and, in some cases, avoid misinterpretations. For example, if structures related to diamond and graphene end up in the same collection, either the two `mids` are remembered (with the risk of accidentally mixing the structures at some point), or an explicit name is adopted to identify them so that graphene can be queried simply by looking for `name=graphene`.

In the case of a slab, the Miller index is critical for determining the desired crystalline orientation (`millier`). This index should be stored in the database as a Python list of integers of the form `[h, k, l]`. In this case, an Al slab can be correctly identified by specifying the Al `mid` (`mp-134`) and requesting a specific Miller index, such as `[0, 0, 1]` or `[1, 1, 1]`. These identifiers can be modified and extended as needed depending on the case at hand.

The interface identifiers are the most sophisticated. In this case, `mid`, `formula`, `millier`, and `name` are created by combining the identifiers of the two single materials. The notation for each of the indices is then: `"id1_id2"` except for the Miller index, which is now a list of two lists, similar to `[[h1, k1, l1], [h2, k2, l2]]`. Despite the complexity, this is the most secure way to represent an interface unequivocally. As a result, the notation for the homogeneous interface shown in Fig. 2.9 is:

```
mid = "mp-134_mp-134"
formula = "Al_Al"
millier = [[1, 0, 0], [1, 0, 0]]
name = "Al100-Al100"
```

The name is automatically built by combining the formula of the two materials and a string version of the Miller lists, separated by a dash.

In addition to the identifiers, the documents contain the crystalline structures used in the calculations and the physical results collected and processed from the VASP outputs. The dictionary entry **structure** can be found in any document of any collection. The initial (**init**) and optimal (**opt**) structures of the materials are saved there as a pymatgen object exported as a Python dictionary. The init structure is typically the ideal crystalline structure of the material downloaded from online archives or inserted into the database from local input. This structure is used as input for the VASP simulations, which optimize the systems' energy and geometry. The final structure obtained after relaxation is the optimal one and is saved in the database as **opt**.

The results of VASP calculations are also saved in the entry **data** at the highest level of the document. Different data is saved there: total energy, forces and stresses, bandgap, and many others. More information can also be obtained by inspecting the entire VASP output file, which is saved locally in an ordered hierarchical structure of folders (mimicking the structure of the collections) each time a workflow is executed.

The input for VASP is generated using the computational parameters, which must be saved in the database under the key **comp_params**. The latter contains all the information required to run a proper simulation, such as the kinetic cutoff energy, the k-point density, whether the material is a metal, and whether vdW and spin polarization should be used. Unlike the other cases, interfaces also have a **inter_params** dictionary that contains information about the matching of the interface, such as lattice and angle strains.

Finally, all of the other items in Fig. 2.9, particularly for the interface, contain the information obtained after launching the corresponding workflows. To keep the data organized, we save all the results of a specific workflow within a key with a recognizable and unambiguous name. So, for example, all information related to the PES, such as the unique and replicated high symmetry points associated with the corresponding energies, the PES figure converted into bits, and the metadata required to reproduce the PES are saved in a dictionary assigned to the key **pes** within the MongoDB document.

2.6.5 How a workflow run in practice

This section will explain how our high-throughput workflows are run on a workstation. A generic diagram depicting the procedure is shown in Fig. 2.10 and consists of several steps.

First, the crystallographic information for the selected materials should be chosen, cleaned, and entered into the high-level internal database (**tribchem**) for further elaboration. Material structures can be read from external online databases (only the Materials Project API is supported at the moment) or from local sources such as files or JSON dictionaries. Once the crystalline cells are recovered, they are converted to their primitive standard structures, if necessary, and saved in **tribchem**.

The insertion is accomplished by creating a new MongoDB document in the database, which should include the materials identifiers (**mid**, **formula**, etc.), its structure (saved in **structure.init**), and the computational parameters needed to VASP (**comp_params**). These quantities are explained in greater detail in Sec. 2.6.4, which is devoted to the description of our database's design. A typical user may wish to begin with a bulk structure present in the database, converge its computational parameters, build and relax an oriented slab, and generate a solid interface.

The workflows can then be run on a set of materials of interest, or even just one. With FireWorks, it is possible to queue different jobs occupying all the available computational cores, allowing for high-throughput screening. The simplest way to set up a large simulation is to submit many jobs to the Fireworks queue by

Bulk

▼ (1) ObjectId("60b893fcf0991298404d33c7")	{ 7 fields }	Object
_id	ObjectId("60b893fcf0991298404d33c7")	ObjectId
▶ comp_params	{ 9 fields }	Object
formula	Al	String
mid	mp-134	String
▶ structure	{ 2 fields }	Object
▶ data	{ 19 fields }	Object
▶ spacegroup	{ 6 fields }	Object

Surface

▼ (1) ObjectId("60c1f3ccde5bd8ab065a89e4")	{ 8 fields }	Object
_id	ObjectId("60c1f3ccde5bd8ab065a89e4")	ObjectId
mid	mp-134	String
formula	Al	String
▶ miller	[3 elements]	Array
▶ comp_params	{ 6 fields }	Object
▶ structure	{ 2 fields }	Object
▶ thickness	{ 4 fields }	Object
▶ data	{ 17 fields }	Object

Interface

▼ (1) ObjectId("60f190cdc037f48ecb3fb44e")	{ 14 fields }	Object
_id	ObjectId("60f190cdc037f48ecb3fb44e")	ObjectId
mid	mp-134_mp-134	String
formula	Al_Al	String
▶ miller	[2 elements]	Array
▶ comp_params	{ 6 fields }	Object
name	Al100-Al100	String
▶ inter_params	{ 8 fields }	Object
▶ highsym	{ 6 fields }	Object
▶ pes_scf	{ 2 fields }	Object
▶ structure	{ 2 fields }	Object
▶ ppes	{ 2 fields }	Object
▶ charge	{ 3 fields }	Object
▶ data	{ 4 fields }	Object
▶ adhesion	{ 4 fields }	Object

Figure 2.9: Typical design of the MongoDB documents in our database, showing how bulks, surfaces, and interfaces entries are saved. Aluminum is used as a case example.

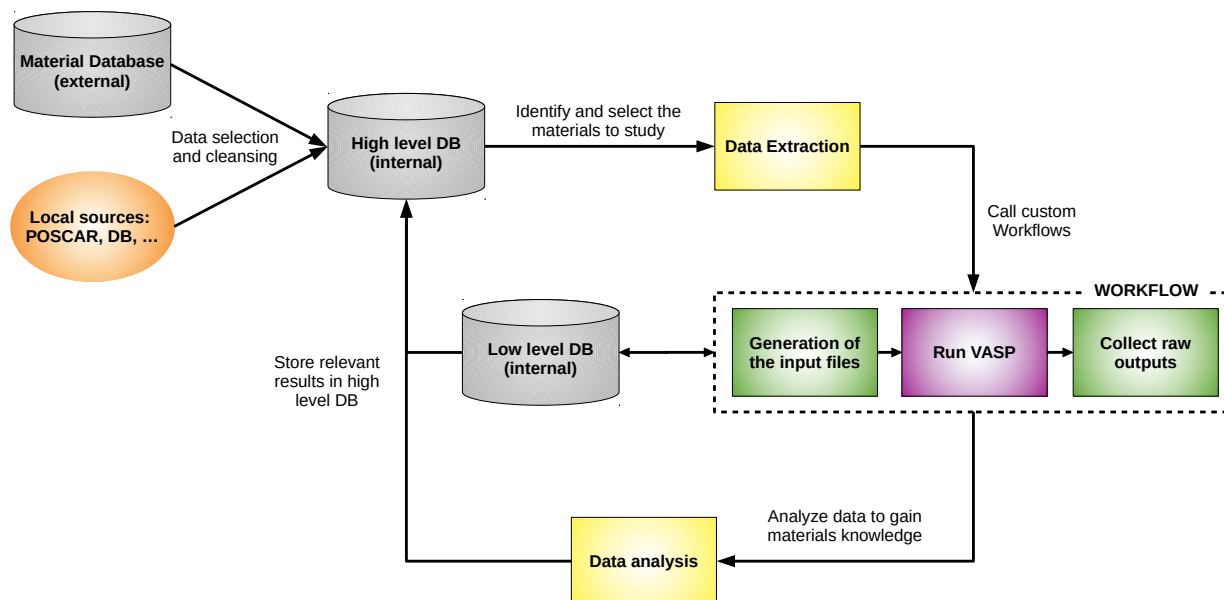


Figure 2.10: Flowchart showing the main logic in the execution of a workflow using the tribchem package. There are four major sequential logical steps to be aware of: 1. Recovery of materials data, 2. Execution of a custom workflow and results collection, 3. Data analysis on the output data.

running the same workflow on different materials multiple times. This is accomplished by iterating over a list of material identifiers, for each of which the workflow is initialized and queued.

Our workflows are designed to identify materials using the IDs saved in the database documents. However, the workflows can be used even in simple scripts outside of a high-throughput procedure. For example, a typical user may be interested in loading a VASP input file containing lattice geometry and ionic positions (POSCAR), utilizing the pymatgen functionalities, and immediately running an automatic workflow once. For this reason, our workflows were designed to take an atomic structure directly as input, allowing them to be used from simple job scripts.

The interaction with the internal database is made possible by the action of intermediate external firetasks, defined as `run_firetasks`, whose aim is to identify the materials in the database, download structure object and computational parameters, and call the effective workflow⁸.

A typical workflow execution consists of several steps that include the generation of inputs, the execution of VASP, and the automatic saving of data by Fireworks into the low-level database. The entire procedure is depicted on the right side of Fig. 2.10. It is especially interesting to see how Fireworks handles simulations with VASP, which requires reading four different input files: `POTCAR`, `POSCAR`, `INCAR`, `KPOINTS`. The first comes automatically from a local folder that must be specified in the Fireworks configuration files, into which all the POTCAR files of the atoms must be placed. The POSCAR file is created using the

⁸As an aside, this implies that the green boxes of Fig. 2.2 are not, as we might expect, the actual workflows. They are, in fact, Workflow objects composed of a single firework containing a single run firetasks, whose purpose is to invoke the actual workflow after querying the database. In any case, the previously discussed theoretical treatment is unaffected, as this is simply an IT expedient to increase the package’s functionality.

material structure provided as pymatgen object ⁹.

The INCAR and KPOINTS file definitions are the most complicated. The first contains the computational parameters that can be calibrated to improve simulation speed, while the second contains the k-point grid of the cell. The files can differ depending on the material and must be customizable for each structure. To generate the INCAR file, we have created `VaspInputSet`. It is a class that employs the pymatgen functions to create the objects to feed Fireworks and automatically generate the input file. The novelty stems from using an external default JSON file that contains valuable default parameters for various situations. Our class can efficiently set up static simulations (energy optimization or geometry relaxation) for bulks, slabs, interfaces, isolated atoms, and molecules. The code also allows customizing the default values by using input kwargs. `VaspInputSet` also processes the KPOINTS file, relying on `MeshFromDensity`, another class we designed specifically to generate a k-point grid corresponding to a linear k-density or a linear k-spacing.

Our workflows make a call to the so-called high-level database (tribchem) at each logical step of the simulation. The intention is to extract, step by step, only the data from the Fireworks database that is relevant to scientific research. This reduces the size of the results database while also keeping it clean. An average heterogeneous interface of about 100 atoms corresponds to a database entry with a maximum size of about 2/3 MB.

The results data can be retrieved from the database, and further data analysis can be performed to gain material knowledge. To this end, we have written numerous Python functions that connect to the database, get the data, and export it as csv tables or Pandas DataFrames [238, 239]. Physical properties and trends can be automatically plotted by comparing different materials, such as surface energy graphs, as the number of atomic layers increases.

2.7 Conclusion

We have created a software package to study the properties of solid interfaces and perform high-throughput screening in the field of tribology. Our robust and modular workflows are structured to form heterogeneous interfaces of two homo-atomic slabs with arbitrary surface orientations and compute their potential energy surfaces. We have taken care to select computational parameters and slab thicknesses to ensure both efficient computations and accurate results, with minimal required user interaction. At the same time, an easily query-able results database is constructed automatically, which also ensures that no calculations are repeated unnecessarily.

The PES itself is a stepping stone to many other interesting interfacial properties, including adhesion, friction- and fracture-characteristics, dislocation properties, and more. We aim to construct additional modules that can be seamlessly integrated into the current workflow to compute these data for a wide array of interfaces that we will publish in the near future.

Further plans include creating tools to allow the use of arbitrary materials, with more than one atomic species and potentially many distinct surface termination possibilities. Even the reliable automatic calculation of surface energies for such arbitrary slabs is challenging, and the number of possible interface combinations can get quite large quickly.

⁹Objects created both with the Structure and the Slab classes are allowed.

Chapter 3

Screening the static friction and cleavage strength of solid interfaces

3.1 Motivation

Tribological problems become relevant whenever materials come into contact while moving laterally to each other. Tribology is the science of adhesion, friction, wear, and lubrication, to date, largely dominated by the experimental community. In the last decades, however, simulations of tribological systems have become more and more common [4]. Due to surface roughness tribological contacts are typically nanoscopic in size [240, 241], even for macroscopic bodies, so it is meaningful to use atomistic models [242, 243, 244, 37, 245, 246], and even employ accurate quantum methods to describe the interatomic interactions [247, 248, 195, 208, 45, 249, 250]. Suppose quantum methods like Density Functional Theory (DFT) are used. In that case, it is possible to extract fundamental properties of the investigated materials without any prior knowledge, which in turn dictate the adhesive properties, the frictional response, the ductility (which ultimately governs the mode of failure of the material), and more.

We have introduced for the first time high throughput computations in tribology [194], which addresses the problem of choosing the suitable materials, coatings, and lubricants for a specific task from a new angle: simulate a large number of different interfaces in a high-throughput manner and choose the most promising to be tested in the laboratory. The present work apply an improved and extended version of the first version of our workflow [194], designed to construct and screen solid-solid interfaces. Here we focus on homogeneous interfaces formed by two equivalent surfaces. Thus we are effectively discussing bulk properties in the language of interfaces, which is better suited to our computational setup based on the γ -surface, also called generalized stacking fault energy or potential energy surface (PES). The PES describes the variation of the adhesion energy between two crystals planes as a function of their relative lateral position. Adhesive friction arises from the barriers that need to be overcome to slide a surface on a substrate. The PES corrugation describes these barriers, $\Delta\gamma$, which is also intimately related to the probability of dislocation nucleation [251, 252, 210, 253]. In the following section, we will present computations of the adhesion energy, ($\gamma_{\min}$), the ideal shear strength, (τ), and the ideal cleavage strength under tensile load (σ) for over 100 interfaces of 45 elemental crystals across the periodic table.

It has to be noted that the calculated material data are “ideal” as they are calculated for defect- and impurity-free, perfect crystals at zero temperature. Therefore the computed values have to be seen as upper bounds of those experimentally measured. Their knowledge helps define *intrinsic* properties that can be used to readily make comparisons among different materials and fix their range of applicability. Moreover, measurements on near-perfect mono-crystalline fibers (whiskers) are found to closely approach the ideal tensile strength values predicted by simulations [254]. In the same spirit, nanoindentation experiments report shear strengths close to the ideal values [255]. In these experiments, the contact between the tip and

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the substrate is so tiny that only a single grain of the material is probed, and the chances are high that there are no preformed dislocations directly below the tip.

Another critical application of ab-initio computed material properties is their use as input parameters for atomistically-informed continuum models. For example, the adhesion energy between two ideally flat planes (as calculated by our workflow) is a crucial parameter for the analysis of rough contacts on the nanoscale [256, 257] and can also be employed in complex models for the description of frictional hysteresis loops [258]. Similarly, the ideal cleavage strength is an important parameter for crack propagation models [259], and the ideal shear strength is, for instance, needed for multiscale approaches to nanoindentation modeling [260].

3.2 Methods

All results in this work are calculated with the first versions of our software package, written within the *Automated Interactive Infrastructure and Database for Computational Science* (AiiDA [220]) framework. At the time, we developed an initial high-throughput AiiDA workflow to calculate interface data automatically with density functional theory (DFT), which we have described in detail in our previous work [194]. The main capabilities are restated here briefly:

- All computational and structural parameters (energy cutoffs, k-point-grids, and lattice parameters) are converged automatically.
- The potential energy surface (PES, also called γ -surface or generalized stacking fault energy) is computed by interpolating between calculated high symmetry points. The minimum energy path (MEP), which is the path through the PES with the least sliding resistance, is computed. The minimum of the PES is equivalent to the adhesion $\gamma_{\min}$ of the interface.
- The ideal shear strength of the interface is determined along with the MEP and some high symmetry directions of the lattice in question.
- We obtain the perpendicular energy profile $\gamma(z)$ by rigidly separating the two slabs forming the interface in discrete steps and computing the interaction energy.

All computations have been performed with the QUANTUM ESPRESSO package [236, 261, 262], using ultrasoft PBE-GGA pseudopotentials [263].

3.3 Results and discussion

We have used our workflow to calculate interfacial properties of 106 different interfaces of 44 elemental crystals. Mostly these are main group metals (and a few lanthanides), but we also include nine different interfaces of two semiconductors, Si and Ge, crystallizing in the diamond structure, as well as three interfaces of α -tin, which shows the diamond structure as well. All raw data, including optimized lattice parameters, surface energies, and γ -surface data, are accessible on the website of the group, while a table with the most critical curated results (lattice parameter, $\gamma_{\min}$, τ_{MEP} , and σ_C) is also presented in Appendix B.

3.3.1 Potential energy surfaces, work of separation, and shear stress

First, we look at the potential energy surface (PES or γ -surface), which allows us to derive several significant characteristics of an interface. The γ -surface represents the adhesive energy as a function of lateral displacement between the two surfaces. We make total energy calculations at carefully selected points $S(x_i, y_j)$ across the unit cell, ensuring that all high symmetry positions are included and the cell is sampled uniformly. During these calculations, the atoms in the slabs are fixed in the coordinates parallel to the interface (x, y) but are free to move perpendicular to it (z). Radial basis functions are used for the interpolation between the computed data to obtain a smooth γ -surface, and the PES is shifted by subtracting the minimum energy (which corresponds to the adhesion energy $\gamma_{\min}$) so that the maximal corrugation $\Delta\gamma$ is easily sighted as the highest peak of the γ -surface. In Fig. 3.1 four examples of different γ -surfaces are presented. The (111) interface of silicon in the cubic diamond structure, the (100) interface of fcc nickel, the (110) interface of bcc iron, and the (0001) interface of hcp cobalt. They all show comparable corrugation $\Delta\gamma$ between 1.8 and 2.2 J/m², with Co exhibiting the lowest and Si the highest $\Delta\gamma$. Also shown in Fig. 3.1 are the associated minimum energy paths (MEPs), which connect the minima of the γ -surfaces by traversing the saddle points. They are computed automatically by applying the improved simplified string method from E, Ren, and Vanden-Eijnden [225, 194]. Once sliding is initiated, the MEP will be the path with the highest statistical weight. The maximal slope encountered by traversing the γ -surface along the MEP is assumed as the ideal shear strength of the interface, τ_{MEP} . The values of the maximal slopes along with two perpendicular high symmetry directions and their ratio are also reported in Appendix B to provide information on the friction anisotropy.

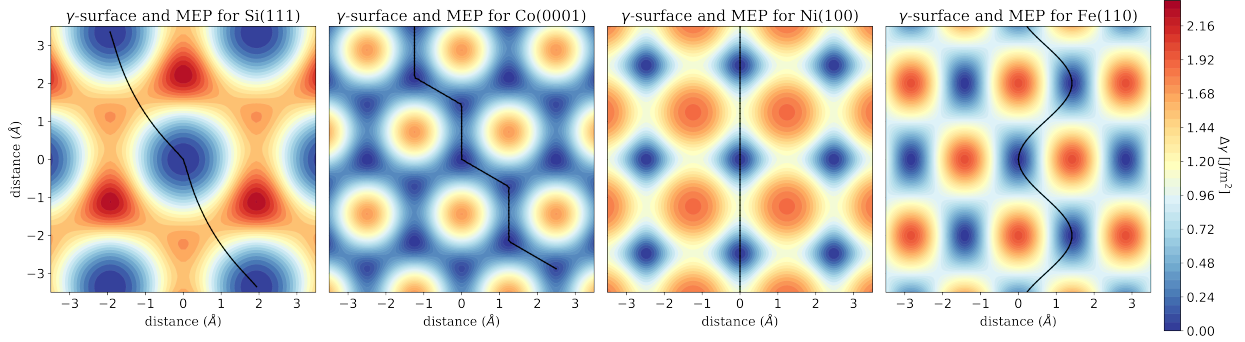


Figure 3.1: PES and MEP for four different lattice structures. All plots use the same scales and the minimum energy paths are shown in black.

While $\Delta\gamma$ of the materials in Fig. 3.1 is comparable, the shear strength along the MEPs differs by more than a factor two from $\tau_{\text{MEP}}(\text{Co}) = 6.95 \text{ GPa}$ to $\tau_{\text{MEP}}(\text{Ni}) = 14.57 \text{ GPa}$. While the potential corrugation of the Ni(100) interface is the second smallest of the four interfaces depicted in Fig. 3.1 at 1.9 J/m², its ideal shear strength is the largest. The barrier height along the MEP plays a more significant role than the total potential corrugation $\Delta\gamma$, but while Si(111) has a 36% higher barrier than Ni(100), the ideal shear strength is nearly 9% lower. Of course, this is routed in the different spacing of the minima and saddle points on the PESs. While the distance between the total minimum and the saddle point is $\sim 2 \text{ Å}$ for Si(111), it is only $\sim 1.2 \text{ Å}$ for Ni(100). This analysis shows the importance of a detailed investigation of the PES shape and its derivative along selected paths.

In Fig. 3.2 we plot two copies of the periodic table colored with respect to the work of separation (the

equivalent of the negative adhesion energy $-\gamma_{\min}$ (a), and the corrugation of the γ -surface $\Delta\gamma$ (b). For all panels, we show the lowest values we have found among the three lattice planes considered for each crystal (excluding hcp, where only the 0001 plane is considered) and indicate the corresponding plane as well as the crystal structure in the table.

The cleavage strength σ_C (a) and the ideal shear strength along the MEP τ_{MEP} (b) are shown in Fig.3.3. This is the first systematic analysis of the ideal strength of elemental solids published so far to the best of our knowledge.

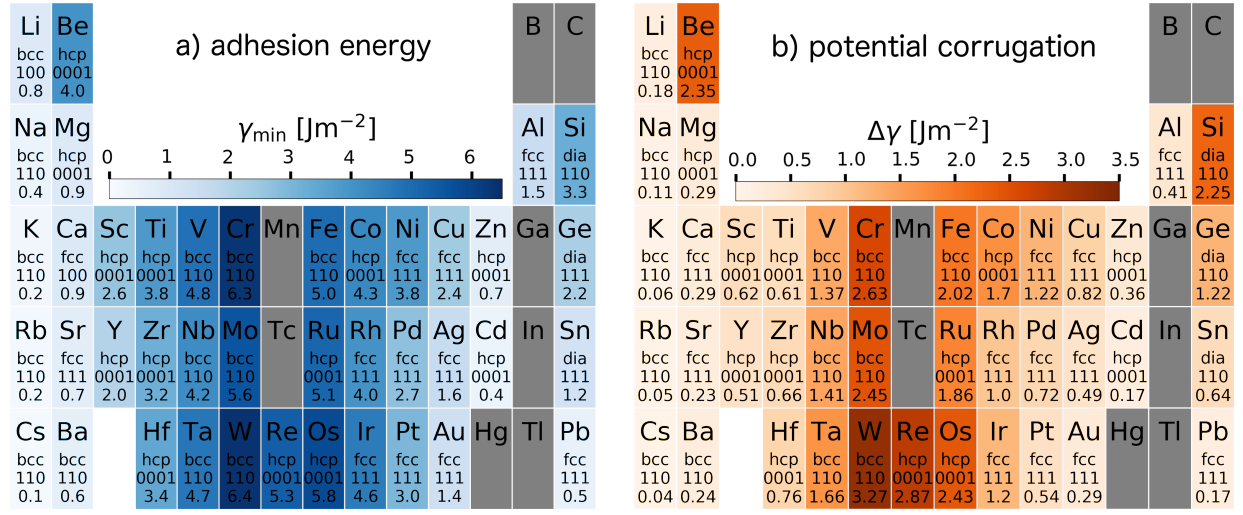


Figure 3.2: Values found for the work of separation $|\gamma_{\min}|$ (a), and the total corrugation of the γ -surface $\Delta\gamma$ (b), for the surface plane where they are minimized.

The corrugation $\Delta\gamma$, and especially the ratio of the $\Delta\gamma$ to the surface energy $-\gamma_{\min}/2$ is an important measure for the ductility of materials since it is related to the relative probabilities of dislocation emission and crack propagation [264]. A periodic table for this ratio is given in Fig. 3.4(a), and it shows that indeed brittle materials (Si, Be, W, ...) have a significantly higher $\Delta\gamma/\gamma$ ratio than ductile materials (Au, Pt, Ti, ...). A similar result can be found in the ratio of the shear to the cleavage strength is considered. This ratio is a good indicator for the material failure mode that is to be expected at an interface. Interfaces with low cleavage strength and high shear strength are likely to fail in brittle cleavage, while high cleavage strength and low shear strength are beneficial for gradual material flow and ductile failure. The results for $\tau_{\text{MEP}}/\sigma_C$ are plotted in Fig. 3.4(b), and we see very similar results compared to Fig. 3.4(a). Brittle materials (like Si, Ge, Be, or W) exhibit a stronger coloring than ductile ones (Au, Pt, Cu, Ti, ...). Since both ratios are dimensionless, it is not surprising that the scales of the subfigures are equivalent. It should be mentioned that the data is computed for all considered interfaces and plotted only for the one with the lowest ratio, corresponding to Figs. 3.2 and 3.3. The data for all considered interfaces are given in Appendix B. If inspected closely, $\tau_{\text{MEP}}/\sigma_C$ in Fig. 3.4(b) correctly shows gold as the material with the best ductility, indicating that this method is superior to estimate the ductility of an interface than $\Delta\gamma/\gamma$.

The scales are different, but the distribution of dark and light colors is very similar for all four subfigures. However, the interface planes where the minimal values for $|\gamma_{\min}|$, τ_{MEP} , and σ_C are found to show some interesting patterns. In the case of the work of separation, bcc crystals show the lowest values for (110)

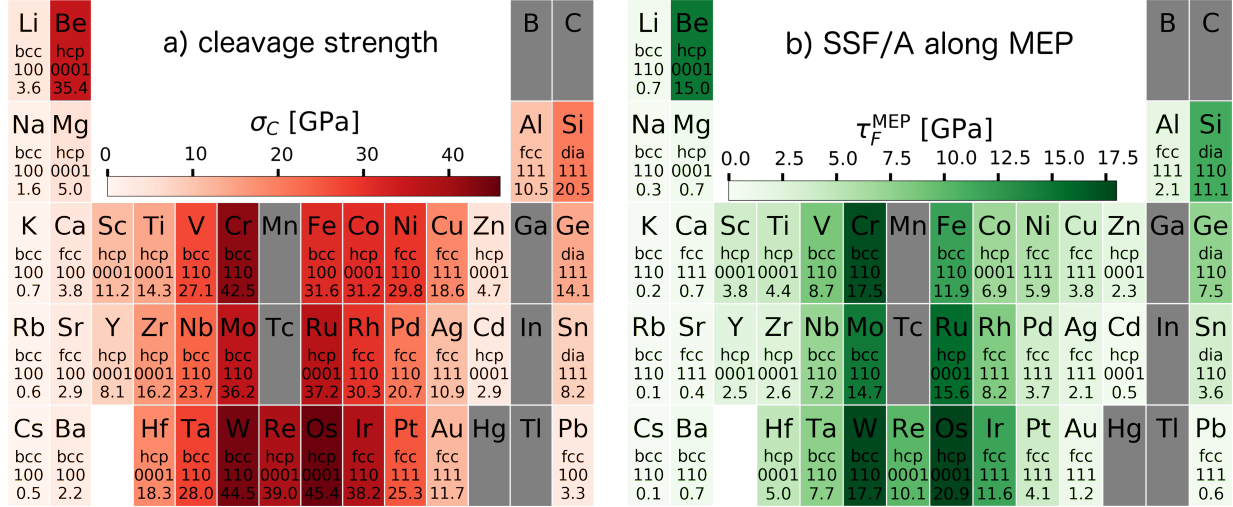


Figure 3.3: Values found for the cleavage strength σ_C (a) the shear strength along the MEP τ_{MEP} (b), for the surface plane where they are minimized.

surfaces, while crystals with fcc and diamond structures have the lowest values for the (111) surfaces. Notable exceptions are Li (bcc, 100, 9.8%), Ca (fcc, 100, 1.6%), and Si (diamond, 110, 2.1%), where the parentheses indicate lattice type, the actual plane with minimal adhesion, and the percentage of adhesion increase with respect to the close-packed plane. For Si, the difference in the work of separation is strongly dictated by the relaxation of the surfaces after separation, as also becomes apparent in Fig. 3.5(c), where they are not considered in the cleavage energy G , and the small difference in γ_{min} between 111 and 110, becomes considerably larger.

For the ideal shear strength, the data are even more homogeneous, with all bcc materials favoring the (110) interface and all fcc crystals in the (111) plane. This is not a surprising result since the bcc(110) and the fcc(111) are the closest packed interfaces of these crystal structures, where we expect them to show the least resistance to sliding. For all three materials in the diamond structure, the (110) plane shows the lowest, and the (100) plane has the largest shear strength values. The trend of high shear strength at the (100) interface continues for both fcc and bcc crystals, but there are exceptions: Li, Rb, Ba, and Ta for bcc, where the (111) plane has the largest shear strength, and Ir, Pt, Al, and Pb for fcc, where it is the (110) interface.

There is a clear split for the bcc crystals for the ideal cleavage strength σ_C , which is discussed in more detail in the next section. The group I and II elements exhibit the least resistance to cleavage normal to the (100) planes, whereas the bcc d -metals favor cleavage along the (110) plane, with Fe being the exception also preferring the (100) plane. In the case of fcc, we observe three different groups: the sp -bonded simple metals Ca, Sr, and Pb cleave easiest at the (100) interface, while the noble metals, Pt, Cu, Ag, Au plus Al prefer the (111) direction. The remaining d -metals Rh, Ir, Ni, and Pd have the (110) interface as the preferred cleavage plane. The contrast to the behavior of the cleavage strength with respect to the adhesion shows that the binding energy alone is not responsible for the cleavage strength, but the shape of the perpendicular potential profiles $\gamma(z)$ is crucial (also see next section).

Since we have only calculated the basal (0001) plane data for hcp systems to date, these systems have

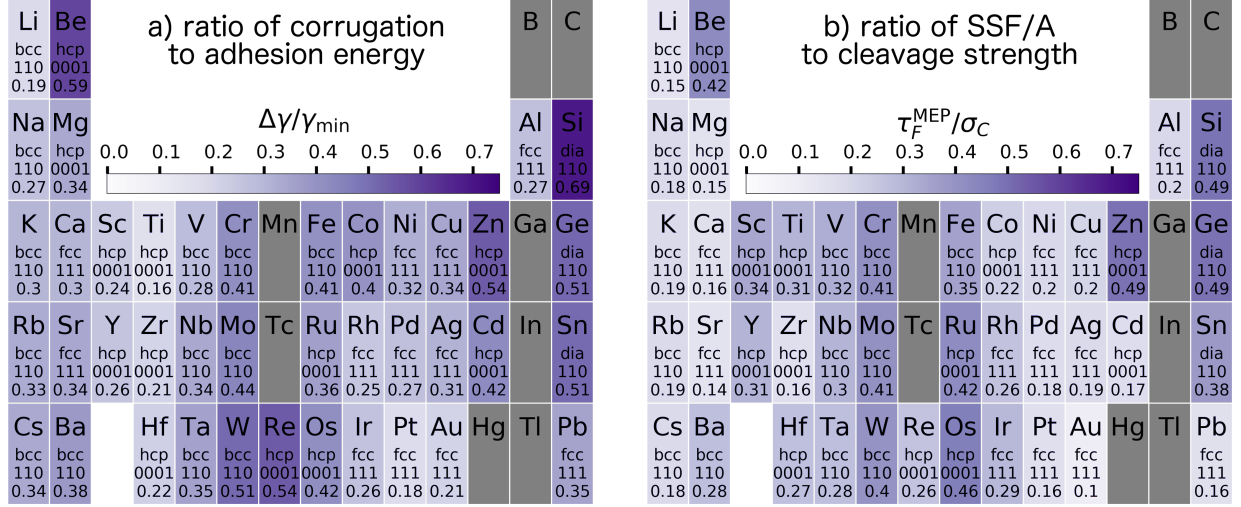


Figure 3.4: Ratios of the figures of merit presented in Fig. 3.2 (a) and Fig.3.3 (b), for the surface plane where they are minimized. These ratios are measures of the ductility of the interface.

not been especially mentioned. However, we will include them in the discussion section when we analyze Figs. 3.2 and 3.3 in more detail.

3.3.2 Perpendicular potential profiles and cleavage strength

We have updated our workflow by fitting the perpendicular potential profiles $\gamma(z)$, to the universal binding energy relation UBER (see e.g. Ref. [265]),

$$\gamma(z) = G \left[1 - \left(1 + \frac{z - z_0}{\ell} \right) \exp \left(-\frac{z - z_0}{\ell} \right) \right] , \quad (3.1)$$

where G is the cleavage energy in the minimum configuration, z is the distance between the slabs, z_0 is their equilibrium distance (commonly set to 0), and ℓ is the critical length, at which $\gamma(z)$ has an inflection point and the cleavage stress σ_c reaches a maximum. Due to the rigid separation model, the cleavage energy G is slightly larger than the work of separation $|\gamma_{\min}|$, where relaxations of the separated slabs are considered.

Under tensile load (forces pulling at the two slabs normal to the interface, also called mode 1 loading) the maximal restoring force is realized at the inflection point and can be easily computed by taking the derivative of equation 3.1 with respect to z , and setting $z_0 = 0$ for simplicity and $z = \ell$ in the following,

$$\frac{d\gamma}{dz}(z) = \frac{G}{\ell^2} z \exp \left(\frac{-z}{\ell} \right) \quad \rightarrow \quad \left. \frac{d\gamma}{dz} \right|_{z=\ell} = \frac{G}{\ell e} . \quad (3.2)$$

In turn, the ideal cleavage strength σ_C follows by dividing this force by the cell cross-section A . Fig. 3.2(b) shows the lowest calculated σ_C along with the corresponding interface plane for each considered element.

While separating the slabs perpendicular to the interface (starting in the global minimum of the γ -surface), we do not allow for any atomic relaxations, which is equivalent to the assumption that the interface fails in a perfectly brittle manner under tensile strain (mode 1 loading). This approach is commonly

known as rigid body separation, and more information about its application can be found in Appendix B. It provides reliable upper limits for the ideal tensile strengths of materials [266] and was shown to be well justified by comparison to a simulation of a crack tip under mode 1 loading [259].

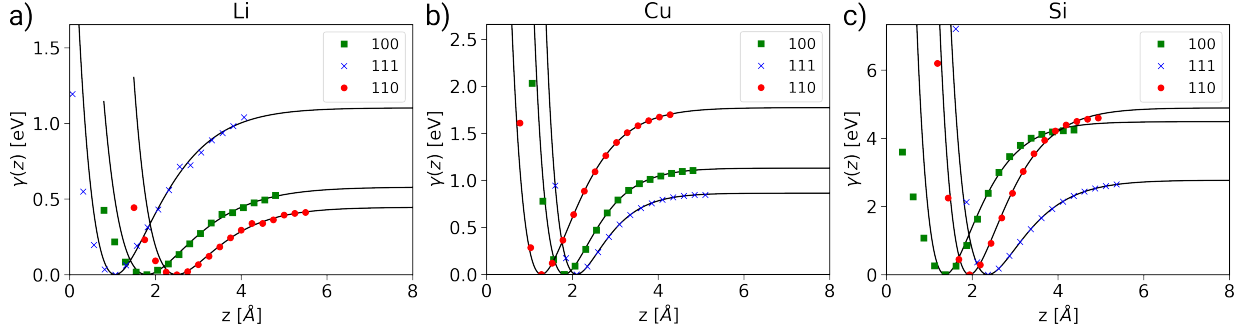


Figure 3.5: Examples for the fit quality of the UBER relations for bcc Li (a), fcc Cu (b), and Si (c) that crystallizes in the diamond structure.

In Fig. 3.5 we plot three UBER fits alongside the computed DFT data to show the quality of the fits. Since we are primarily interested in the ideal strength of the material under tensile loading, the attractive regime, $z > z_0$, is more important, and we have used only those data points for fitting. This results in, sometimes significant, deviations of the fit to the data in the repulsive regime, as it can be seen for Li and Si in Fig. 3.5. However, the fits in the important attractive regime are excellent, and the raw DFT data is available to the reader (see Data availability section) and can be fitted by cubic splines or other smooth functions to represent the whole interaction range [201, 194]. Generally, the quality of the fits is very high, with Li, Fig. 3.5(a) being one of the worst. In Fig. 3.3(b), we see the data for the lowest cleavage strength σ_C of each element, depending on the interface plane.

3.3.3 Discussion

The panels (a) and (b) of Fig. 3.2 and (a) of Fig. 3.3 present similar trends among the elements, which we can trace back to the behavior of the cohesive energy in elemental solids. For the simple *sp*-metals, the cohesive energy is low due to the comparatively weak metallic bonding, leading to low adhesion energy and, in turn, low shear- and cleavage strength. Beryllium, with its large deviations from the free-electron behavior and small atomic radius, is a well-known counter-example [267]. For the *d*-metals, the cohesive energy increases until all five bonding states of the *d*-shell are filled and decrease afterward when the anti-bonding states are populated. This trend can be clearly observed for $-\gamma_{\min}$, τ_{MEP} , and σ_C .

This suggests a close relationship between these three quantities, which is a fascinating result since the computational effort to calculate these three material parameters is not equivalent. The adhesion is easiest to calculate for the systems we consider since the position of the minimum is predetermined by the ideal bulk stacking of the system. For τ_{MEP} , one needs to compute the whole γ -surface and the MEP, which involves not only many more DFT calculations but also interpolation between high-symmetry PES points and some algorithm to find the MEP. Analogous, the computation of σ_C relies on a significant number of DFT calculations and some fitting routines. Thus, finding functional relations $\tau = f(\gamma)$ and $\sigma = g(\gamma)$ would considerably reduce the computational workload to estimate the ideal strength of a material.

These functional relations are plotted in Fig. 3.6. Indeed the data cluster around simple functions: For

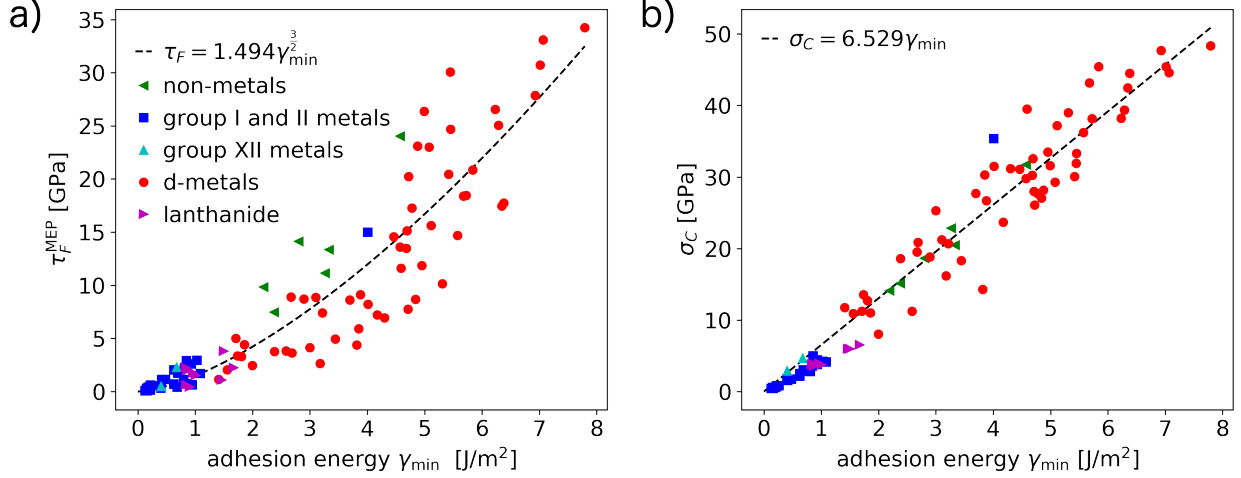


Figure 3.6: Ideal shear strength along the MEP τ_{MEP} (a) and ideal cleavage strength σ_C (b) vs work of separation $-\gamma_{\text{min}}$ for all investigated interfaces. The data are fitted to a power law with exponent $3/2$ in (a) and with a linear function in (b). This least square fits are shown as dashed lines.

the ideal shear strength, we observe a power law with exponent $3/2$, while the ideal cleavage strength is linearly dependent on the work of separation. The results of Fig. 3.6(a) allow us to confirm the correlation between adhesion and friction of clean, flat interfaces, which we established in our previous work [202].

The linear connection between the work of separation $-\gamma_{\text{min}}$ and the ideal cleavage strength σ_C is not too surprising if one recalls equation 3.2 where the restoring force is a linear function of the cleavage energy G . For most materials, G is close to the work of separation $|\gamma_{\text{min}}|$, unless the surfaces relax significantly from the bulk positions. Since the critical length ℓ , which enters in the denominator of equation 3.2, varies only between $0.42 \text{ \AA}$ and $1.28 \text{ \AA}$, its variation perturbs the linear fit only slightly.

The fitted proportionality constants are $\sim 1.5 \text{ skg}^{2/3} \text{ nm}^{-1}$ for the power law and $\sim 6.5 \text{ nm}^{-1}$ for the linear relationship. It should be noted that while these functional relations allow for an estimation of the shear and cleavage strength of materials based on their work of separation, the scattering of the data around the fitted curve has to be considered. The average deviation of the data to the curves is 2.4 GPa for τ_{MEP} , and 2.3 GPa for σ_C , but considering that the absolute values of these data reach over 30 GPa (for τ_{MEP}) and around 50 GPa (for σ_C), the predictive power of the fits are respectable. We clearly have shown that the work of separation is an important descriptor of a given solid material and can be used to estimate material characteristics, which are much harder to compute.

As mentioned in the introduction, we compute the ideal strength of bulk crystals under shear and tensile strain using high throughput methods developed for interfaces. Our approach is based on analysis of the γ -surface and can be easily generalized to more complex interface situations, including adatoms, defects, and heterogeneous slabs. However, the ideal strength of bulk materials is usually calculated in a different way [268, 269]: A bulk cell is put under more and more shear or tensile strain, and the resulting stress on the system is computed. At each strain value, the atomic positions are fully relaxed. The result is a stress-strain curve, and the ideal strength of the material is equivalent to the maximum of this curve.

This common approach is quite different from our methodology, which is specially tailored to interfaces and was developed in the context of adhesive friction [195]. However, for the shear strength calculation,

our usage of the MEP should correspond well to the method of unit cell strain under continuous atomic relaxation since these relaxations ensure the avoidance of highly unfavorable configurations. In the case of tensile strain, the situation is different, as is discussed in Appendix B. As mentioned before, our method implicitly assumes brittle cleavage along the investigated plane, while the stepwise straining of a bulk cell perpendicular to this plane allows ductile failure.

In table 3.1 we compare our data for both τ_{MEP} and σ_C to literature values for some quite common materials of all considered lattice types. In the case of the shear strength, the literature values are computed by quasi-continuous unit cell deformations, while the cleavage strength data are computed analogously to our approach with rigid body separation and fits UBER. Initially, we have to note that traditionally shear strength is computed only for the ‘easy’ planes, e.g., 111 for fcc and 110 for bcc, with other data being hard to find. This highlights the importance of our work for creating a complete database for shear- and cleavage-strengths, since to date, not much data is available for even the typical materials of table 3.1. We could get literature data for the ideal shear strength and generally notice good agreement between our data and the literature, even though the computation method is quite different. The cleavage strength data is in excellent agreement with the literature across the board, with minor deviations rooted in the use of different density functionals.

100				110				111 / 0001			
τ [GPa]		σ [GPa]		τ [GPa]		σ [GPa]		τ [GPa]		σ [GPa]	
Calc.	Lit.	Calc.	Lit.	Calc.	Lit.	Calc.	Lit.	Calc.	Lit.	Calc.	Lit.
Fe	26.4	-	31.6	-	11.9	7.5–8.14	33.5	-	24.7	-	33.3
Mo	26.6	-	38.2	-	14.7	15.1–16.1	36.2	38.8[270]	25.1	-	39.4
W	34.2	-	48.4	47–48[271, 270]	17.7	17.1–18.2	44.5	44[271]	27.9	-	46[271]
Si	24.0	-	31.8	-	11.1	8.0–9.62	22.9	-	13.4	9.6[272]	21[273]
Ge	14.1	-	18.6	-	7.5	-	15.2	-	9.8	-	14.1
Al	4.0	-	12.0	12[273]	5.2	-	11.7	12[273]	2.1	2.8[272]	10.5
Cu	8.9	-	19.5	-	8.7	-	18.8	-	3.8	2.2[272]	18.6
Ni	14.6	-	31.1	33.2[270]	13.6	6.4	29.8	28.5[270]	5.9	5.05[272]	30.3
Mg	-	-	-	-	-	-	-	-	0.7	1.8[272]	5.0
Ti	-	-	-	-	-	-	-	-	4.4	-	14.3
Zn	-	-	-	-	-	-	-	-	2.3	2.2[272]	4.7

Table 3.1: Comparison of some results from this work (Calc.) to previously calculated values from the literature (Lit.), split into 4 groups: bcc, diamond, fcc, and hcp crystals. Literature data ranges are taken from the review by Pokluda and coworkers [269] unless marked otherwise. A table with our results for all considered materials can be found in the Appendix B.

3.4 Conclusion

In summary, we have presented a high-throughput DFT study on the work of separation and the ideal shear and cleavage strength of various lattice planes of solid elemental crystals. We have automatically computed tribological figures of merit for over one hundred different interfaces for elemental crystals in the fcc, bcc, hcp, and diamond structure. Our results are based on the detailed analysis of the γ -surface, which we calculate ab-initio using high symmetry points and interpolation via radial basis functions. By plotting the results in a periodic table, we observe clear trends in the data. Thus we show that the mechanical properties of elemental crystals indeed are closely related to their electronic structure. This confirms the notion that adhesive friction is rooted in the chemical interactions at the interface and ultimately governed by quantum mechanics [202, 274]. We find good agreement of our data with previously published shear strength values and are able to extend the available data significantly for this critical material parameter. We have also found that the work of separation (equivalent to the negative adhesion energy) is a good descriptor for the much harder to compute shear and cleavage strength values for a given interface. The shear strength along the minimum energy path is proportional to the work of separation to the power of $3/2$, while the cleavage strength is directly proportional to the work of separation. The ratio between the shear and the cleavage strengths is provided as an indicator of the material failure mode that is to be expected at an interface. Interfaces with high shear strength/cleavage strength ratio are likely to fail in brittle cleavage, while the low ratio value characterizes ductile failure. We believe that the computed data may become very important as input parameters for large-scale continuum simulations and serve as benchmarks for classical atomistic models. We make all curated and raw data available in an online repository for direct access and further analysis .

Chapter 4

Accurate multiscale simulation of frictional interfaces by quantum mechanics/Green's function molecular dynamics

4.1 Motivation

Understanding frictional phenomena represent a fascinating fundamental science problem with a high potential impact on energy saving and environmental protection. It is estimated that nearly one-third of the energy produced by fossil fuels to power vehicles is spent to overcome friction. Improved tribology technologies could dramatically reduce fuel consumption and CO₂ emissions[2]. However, with respect to other technologies based on materials, tribology is remarkably less advanced. The reason resides in the complexity and variety of the phenomena that occur at the sliding buried interface, which is difficult to monitor in real-time by experiments. Simulations can play a crucial role in this context, yet a methodological step forward is presently needed to fully capture the multiscale nature of the frictional phenomena.

At the atomistic level, frictional forces appear during the relative motion of two surfaces in contact because their interaction energy changes as a function of the relative lateral position, giving rise to a corrugated potential energy surface (PES). The energy for climbing the PES hills, provided by the external force, is partially lost in non-adiabatic hill descents via phonon excitation. It is clear from this simplified description of the frictional slip that the amount of dissipated energy is governed by two main factors: the PES corrugation and the phonon propagation into the bulks in contact. The PES corrugation is determined by the electronic properties of the interface [202], while phonon excitation and propagation depend on the elastic properties of the infinite bulks. The latter also determines how the applied mechanical stresses are transferred to the sliding interface. *In silico* experiments able to provide a quantitative estimate of the kinetic friction coefficient should then rely on a multiscale approach that includes both the electronic degrees of freedom at the interface and the vibrational degrees of freedom in the semi-infinite bulks.

Such a multiscale scheme is highly desirable also to accurately describe the activation mechanisms of tribochemical reactions, chemical processes involving environmental or lubricant molecules confined at the sliding buried interface. The rate of these processes is highly accelerated with respect to reactions thermally activated at the open surface in static conditions because the electronic structure of the confined molecules under tribological conditions is highly destabilized by the mechanical stresses applied [145, 275]. For example, thin films known as "tribofilms" are synthesized *in situ* by mechanical rubbing additive molecules confined within micro-asperities contacts. These films are critical in preventing the cold sealing of nanoasperities and reducing the macroscopic friction and wear resistance of operating machinery parts. Mechanochemistry, which exploits impact forces to efficiently produce functional compounds and medicines without the use of solvents [276, 277] is another important example where the control of the stress-assisted reaction is highly desirable.

Ab initio molecular dynamics based on quantum mechanics (QMMD) calculations can uncover elementary

mechanisms of tribochemical/mechanochemical processes [275, 278]. Indeed they have provided useful insight into several tribological phenomena such as the effects of humidity on the lubricity of carbon-based coatings [279, 79], 2D materials like graphene, and MoS₂ [280, 124]. Moreover, they allowed monitoring in real-time the first stages of tribofilm formation from commercial additives [146, 281, 282] or hydrocarbon molecules [283]. However, these simulations cannot be used to quantify the kinetic friction coefficient because the limited thickness of the slabs typically used in QMMD to model the solid in contacts is too thin to contain the wavelength of the dissipated phonons. Indeed, several studies have reported that the energy dissipation associated with phonons, such as thermal conductivity and friction, are critically dependent on the size of the simulated systems [284, 285, 286, 287].

Green’s function molecular dynamics (GFMD) simulations and the related theory have been used to unleash the limitation of the maximum system size [288, 289, 290, 291, 292, 285, 286, 287, 293, 294]. This approach projects the dynamical response of all the degrees of freedom of the infinite solid into a Green’s function that is used to calculate the dynamics of the surface atoms. The calculation of the Green’s function represents a computational bottleneck for the use of GFMD. A solution for such a problem has been recently proposed for general surfaces [293], based on the elegant analytical solution of the Green’s function using a fast convolution method [295, 296, 297, 298]. Therefore, the GFMD method can now be applied to large-scale simulations of realistic systems previously considered too computationally demanding. However, this framework is based on classical force fields, where the electronic degrees of freedom necessary to accurately describe the surface-surface interaction and the tribochemical processes are not considered.

To overcome this limitation, we propose a new multiscale approach that links QMMD and GFMD, thus combining the strengths of the two methods. The hybrid method (QM/GFMD) is realized by connecting the GFMD atoms to the bottoms of the QMMD slabs, as described more in detail in the following sections. The QM/GFMD method can be used to obtain accurate quantitative estimates of the friction forces taking both interface chemistry and phonon dissipation into account. This can open the way to a novel understanding of tribological phenomena, such as the fundamental relation between kinetic and static friction forces, and allows for the execution of accurate tribochemistry experiments *in silico*.

The first part of the chapter presents a concise description of the QM/GFMD scheme, while its full formulation is reported in the method section. An example of application is provided, focused on the tribological properties of diamond as a function of the surface hydrogenation. We show that the QM/GFMD method is able to provide a quantitative estimation of the kinetic friction force and the calculated friction coefficients are in agreement with the experimental ones. Moreover, the *in silico* experiment revealed that by rubbing clean diamond surfaces, a graphitic layer is produced, the formation of which is inhibited by a small concentration of H atoms. Finally, a discussion on the microscopic origin of the kinetic friction force and its connection with the static friction force is presented.

4.2 QM/GFMD in a nutshell

A pictorial representation of the hybrid QM/GFMD scheme and its application to a prototypical tribochemistry system is offered in Figure 4.1. The chemically active part of the system consists of two surfaces in contact and some molecules eventually confined between them (panel *a*). The inclusion of the electronic degrees of freedom is necessary to capture quantum effects, such as the Pauli repulsion at the short distances imposed by the applied load and the enhanced chemical reactivity of confined species, which deeply affect the tribological behavior. The two semi-infinite bulks are described by a collection of an infinite number of harmonic oscillators of first-principles derived spring constants. Their effect is fully taken into account by the Green’s function atoms, indicated in yellow. The basic idea of Green’s function MD is,

in fact, that all the internal modes of an elastic solid can be integrated out and substituted by effective interactions [299, 291]. In this way, only the trajectory of the quantum atoms is needed, and no other bulk atoms are needed to be included in the simulation.

The three-dimensional displacements of the semi-infinite surface layer are denoted by $\mathbf{u}_1 \in \mathbf{R}^{N \times 3}$, where N is the number of the surface atoms in the unit cell. This quantity is represented by a linear combination of a particular solution $\mathbf{u}_p$ and general solution $\mathbf{u}_g$ [300] of the equation of motion, as

$$\mathbf{u}_1 = \mathbf{u}_p + \mathbf{u}_g. \quad (4.1)$$

The solution $\mathbf{u}_p$ represents trajectories driven by an external force $\mathbf{f}$ applied on the surface layer, at initial conditions $\mathbf{u}_p(t=0) = 0$, $\frac{d}{dt}\mathbf{u}_p(t=0) = 0$. Using a Green's function matrix A , the equation of motion can be written as

$$\begin{aligned} M \frac{d^2}{dt^2} \mathbf{u}_p(t) &= \mathbf{f}_{\text{GF}}(t) \\ \mathbf{f}_{\text{GF}}(t) &= \int_0^t A(t-\tau) \mathbf{f}(\tau) d\tau, \end{aligned}$$

where M is a mass matrix of the constituents atoms.

On the other hand, $\mathbf{u}_g$ is the solution without external force but in the arbitrary initial conditions $\mathbf{u}(t=0)$, $\frac{d}{dt}\mathbf{u}(t=0)$. Notably, $\mathbf{u}_g$ can represent the thermostat and barostat of the system when their statistic features are related to the Green's function, thanks to the projection of infinite degrees of freedom. In other words, when connecting the GFMD system to the QM system, as in Fig. 4.1(a), we can use $\mathbf{u}_g$ as a set of parameters to control the temperature and stresses applied to the system.

The workflow of the QM/GFMD method is shown in Fig. 4.1(b). The model for the bulk crystal is constructed, and static first-principles calculations are used to obtain the force matrix, which is used to calculate the Green's function. The QM and GF systems are finally coupled via an add-remove scheme [301].

Additional details on the numerical techniques and derivation of the GFMD and QM/GFMD procedures are presented in the Methods section.

4.3 Methods

This section describes the theoretical methods that have been computationally implemented and used in this work. We begin by reviewing the fundamental GFMD methodology developed in a previous work by Kajita [293]. Furthermore, we give a simple example of the derivation of Green's functions for a semi-infinite chain and detail the numerical treatments of fast convolution and thermo-barostats. Finally, the hybrid add-remove method is presented, along with a numerical treatment for stabilizing the dynamics in QM/GFMD simulations.

4.3.1 Green's function of one-dimensional chain

We consider a semi-infinite one-dimensional chain composed of harmonic oscillators. Atoms are identical and connected with monotonic bonds modeled with springs of constant K . The equations of motion are:

$$\begin{aligned} m \frac{d^2}{dt^2} u_1(t) &= -K(u_1 - u_2) + f(t) & i = 1 \\ m \frac{d^2}{dt^2} u_i(t) &= -K(2u_i - u_{i+1} - u_{i-1}) & 1 < i < \infty, \end{aligned}$$

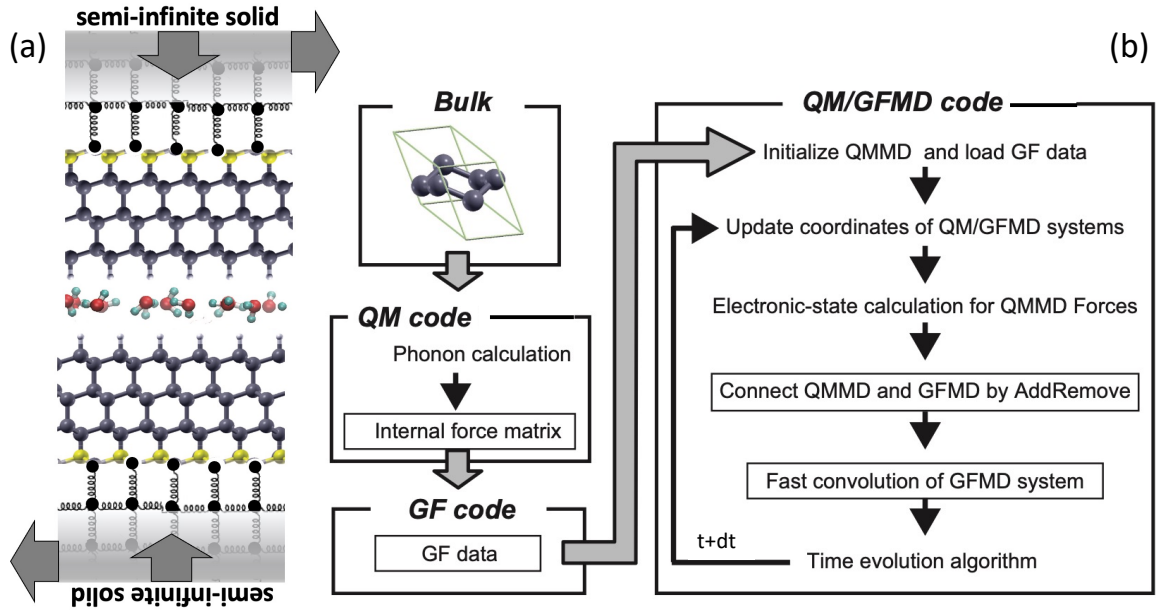


Figure 4.1: Representation of a frictional interface described by the QM/GFMD hybrid scheme (a) and the workflow of the developed QM/GFMD program by linking an open-source *ab initio* code [236, 261, 262] to the in-house developed GFMD code (b).

where m and u_i are the mass and the displacement of the i th atom, respectively. The external force f is applied only on the edge atom $i = 1$. The displacement of the edge atom is mathematically written by the convolution form with the Green's function G [300] as

$$u_1(t) = \int_0^t G(t - \tau) f(\tau) d\tau. \quad (4.2)$$

The Laplace transformation of Eq. 4.2 is

$$u_1(z) = G(z) f(z), \quad (4.3)$$

where z is a coordinate in the complex space. It should be noted that $G(z)$ is more significant than $G(t)$ in GFMD because both of the fast convolution and thermo-barostats methods require $G(z)$.

Then, we add a further atom labeled $i = 0$ on top of the edge atom $i = 1$. The new atom becomes the surface atom under the external forces, and its equation of motion after Laplace transformation is

$$mz^2 u_0(z) = -K(u_0(z) - u_1(z)) + f(z). \quad (4.4)$$

In this system Eq. 4.3 modifies to

$$u_1(z) = K(u_0(z) - u_1(z)) G(z), \quad (4.5)$$

because the external force for the $i = 1$ atom is nothing else than the interaction with u_0 through the spring. By inserting Eq. 4.5 into Eq. 4.4 to eliminate u_1 , we obtain

$$u_0(z) = \left(mz^2 + \frac{K}{1 + KG(z)} \right)^{-1} f(z). \quad (4.6)$$

The critical point is that the addition of the $i = 0$ atom to the semi-infinite system does not essentially alter the system, i.e., the solution of the edge atom is invariant to the shift in the index i . This invariant feature, called semi-infinite periodicity, simplifies the derivation of the Green's function. Namely, because Eq. 4.3 is equivalent to Eq. 4.6, we can derive

$$G(z) = \left(mz^2 + \frac{K}{1 + KG(z)} \right)^{-1}. \quad (4.7)$$

The equation 4.7 is readily solved as

$$G(z) = \frac{1}{2K} \left(-1 + \sqrt{1 + \frac{4K}{mz^2}} \right).$$

Derivation of $G(z)$ without using the semi-infinite periodicity is more complicated as studied in Ref. [286]. Semi-infinite periodicity is a key to generalize the method applicable to any surface system.

4.3.2 Green's function of a general surface

The strategy to derive the Green's function of a general three-dimensional semi-infinite solid is the same as the one-dimensional chain of atoms. Let us consider a general crystalline surface as shown in Fig. 4.2.

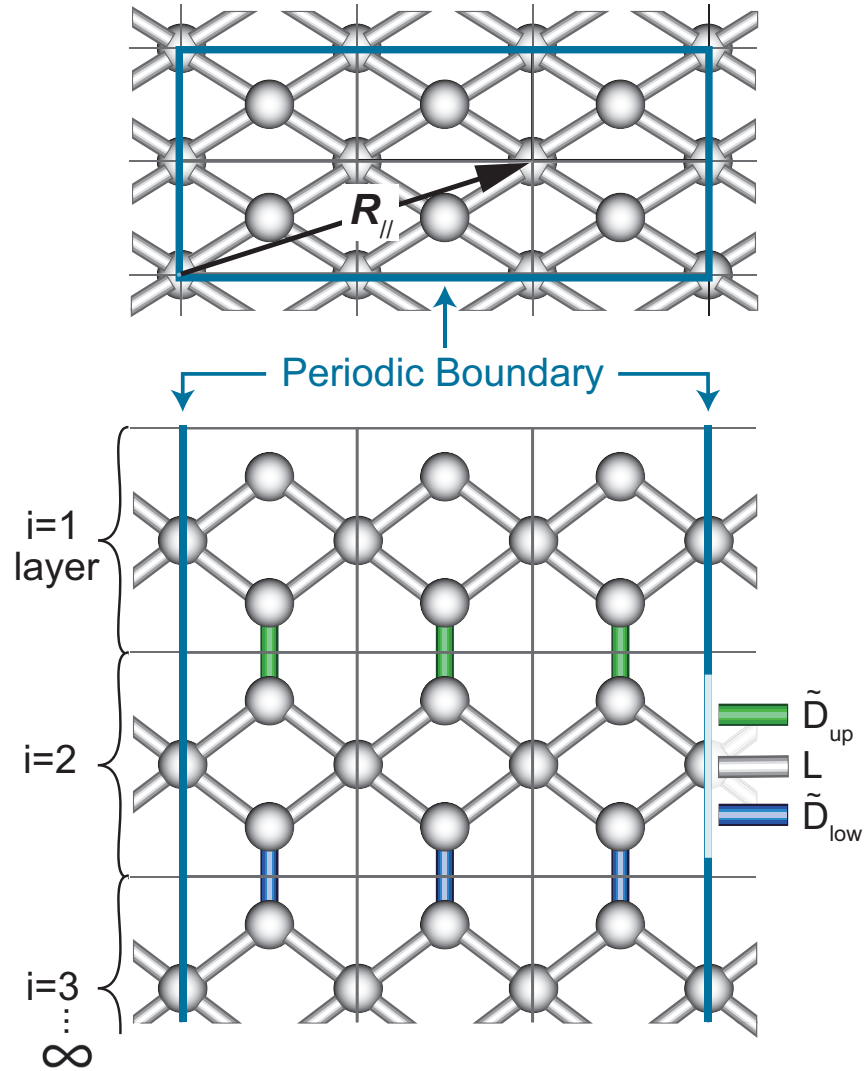


Figure 4.2: Schematic image of the semi-infinite surface system. The supercell consists of unit cells, and it repeats periodically along the surface lateral direction and infinitely along the direction normal to the surface. The layers are labeled by indices i that increase as going to the bulk direction. The colored bonds indicate inter-layer terms $\tilde{D}_{up}$ and $\tilde{D}_{low}$ of the $i = 2$ layer; these quantities are used in Sec 4.3.2.

We define a surface layer as a set of different unit cells replicated and aligned laterally in the periodic boundary conditions. Each layer is labeled with an index starting from the surface $i = 1, 2, \dots \infty$. The infinite concatenation of surface layers along the surface normal direction constitutes the solid. We write the equation of motion for the semi-infinite surface system as

$$\left(M \frac{d^2}{dt^2} + D\right) \mathbf{u}(t) = \mathbf{f}(t), \quad (4.8)$$

where M is the atomic-mass diagonal matrix. The vector $\mathbf{u}$ is the atomic displacements of the entire system, where $\mathbf{u} = (\mathbf{u}_1, \mathbf{u}_2, \dots)^T$ and $\mathbf{u}_i$ is the displacement vector of the atoms in the i th layer. The external force vector $\mathbf{f}$ is applied only to the surface layer $i = 1$. The D matrix is referred to as internal-force matrix and represents the elastic constants of bonding for all the atoms. Vectors, matrices and scalars are indicated in bold, uppercase and lowercase letters, respectively. We normalize Eq. 4.8 by the mass using a $N = M^{-1/2}$ operator, obtaining

$$\left(\frac{d^2}{dt^2} + \tilde{D}\right) \tilde{\mathbf{u}}(t) = \tilde{\mathbf{f}}(t), \quad (4.9)$$

where we define $\tilde{D} = NDN$, $\tilde{\mathbf{u}} = N^{-1}\mathbf{u}$ and $\tilde{\mathbf{f}} = N\mathbf{f}$.

A standard approach to include the periodic boundaries along the surface lateral directions is the discrete Fourier transformation. A set of surface lattice vectors $\mathbf{R}_\parallel$ points to the origins of the lateral positions of the constituent unit cells in the layer (see Fig. 4.2). The discrete Fourier transformation of arbitrary vector $\mathbf{x}$ and matrix X of the layer is

$$\begin{aligned} \mathbf{x}(\mathbf{k}_\parallel) &= \sum_{\mathbf{R}_\parallel} \exp(-i\mathbf{k}_\parallel \cdot \mathbf{R}_\parallel) \mathbf{x}(\mathbf{R}_\parallel) / \sqrt{n}, \\ X(\mathbf{k}_\parallel, \mathbf{k}'_\parallel) &= \sum_{\mathbf{R}_\parallel, \mathbf{R}'_\parallel} \exp(-i\mathbf{k}_\parallel \cdot \mathbf{R}_\parallel) X(\mathbf{R}_\parallel, \mathbf{R}'_\parallel) \\ &\quad \times \exp(i\mathbf{k}'_\parallel \cdot \mathbf{R}'_\parallel) / n, \end{aligned}$$

where $\mathbf{k}_\parallel$ is the surface reciprocal vector of $\mathbf{R}_\parallel$, and n is the number of unit cells in the layer. We use a matrix notation $X(\mathbf{k}_\parallel)$ when the matrix is diagonal with the $\mathbf{k}_\parallel$ basis.

According to Bloch's theorem, the internal-force matrix D is diagonal in the $\mathbf{k}_\parallel$ basis due to the inherent periodicity of the system. In the initial conditions $\mathbf{u}(t=0) = \dot{\mathbf{u}}(t=0) = 0$, Eq. 4.9 after the discrete Fourier and Laplace transformations becomes

$$\begin{aligned} \tilde{\mathbf{u}}(z, \mathbf{k}_\parallel) &= G(z, \mathbf{k}_\parallel) \tilde{\mathbf{f}}(z, \mathbf{k}_\parallel), \\ G(z, \mathbf{k}_\parallel) &= (z^2 + \tilde{D}(\mathbf{k}_\parallel))^{-1}. \end{aligned} \quad (4.10)$$

Recalling the external force vector $\tilde{\mathbf{f}}$ is applied only on the surface layer $i = 1$, $\tilde{\mathbf{u}}_1$ is

$$\tilde{\mathbf{u}}_1(z, \mathbf{k}_\parallel) = G_{11}(z, \mathbf{k}_\parallel) \tilde{\mathbf{f}}(z, \mathbf{k}_\parallel), \quad (4.11)$$

where $G_{ii'}$ is the corresponding element of G in the layer indices i and i' . In the $\mathbf{R}_\parallel$ basis, Eq. 4.11 becomes

$$\tilde{\mathbf{u}}_1(z, \mathbf{R}_\parallel) = \sum_{\mathbf{R}'_\parallel} G_{11}(z, \mathbf{R}_\parallel - \mathbf{R}'_\parallel) \tilde{\mathbf{f}}(z, \mathbf{R}'_\parallel). \quad (4.12)$$

Here the additional layer $i = 0$ is piled up on the surface system by connection with the $i = 1$ layer. Before applying the semi-infinite periodicity, we decompose the internal-force matrix $\tilde{D}$ into an intra-layer term L that represents the bonds within the layer, and inter-layer terms $\tilde{D}_{low} \oplus \tilde{D}'_{low}$ and $\tilde{D}_{up} \oplus \tilde{D}'_{up}$, representing the bonds to the lower and upper layers, respectively (see Fig. 4.2). Namely, the matrix representation of $\tilde{D}$ in the layer index is

$$\begin{aligned} \tilde{D} = & \begin{pmatrix} L & 0 & 0 & 0 & \cdots \\ 0 & L & 0 & 0 & \cdots \\ 0 & 0 & L & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \end{pmatrix} \\ & + \begin{pmatrix} \tilde{D}_{low} & \tilde{D}'_{low} & 0 & 0 & \cdots \\ \tilde{D}'_{up} & \tilde{D}_{up} + \tilde{D}_{low} & \tilde{D}'_{low} & 0 & \cdots \\ 0 & \tilde{D}'_{up} & \tilde{D}_{up} + \tilde{D}_{low} & \tilde{D}'_{low} & \cdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \end{pmatrix}. \end{aligned}$$

As in the previous subsection, we first write the equation of motion of the new layer

$$\begin{aligned} z^2 \tilde{\mathbf{u}}_0(z, \mathbf{R}_{\parallel}) = & - \sum_{\mathbf{R}'_{\parallel}} L(\mathbf{R}_{\parallel} - \mathbf{R}'_{\parallel}) \tilde{\mathbf{u}}_0(z, \mathbf{R}'_{\parallel}) \\ & - \tilde{D}_{low} \tilde{\mathbf{u}}_0(z, \mathbf{R}_{\parallel}) \\ & - \sum_{\mathbf{R}'_{\parallel}} \tilde{D}'_{low}(\mathbf{R}_{\parallel} - \mathbf{R}'_{\parallel}) \tilde{\mathbf{u}}_1(z, \mathbf{R}'_{\parallel}) \\ & + \tilde{\mathbf{f}}(z, \mathbf{R}_{\parallel}), \end{aligned} \quad (4.13)$$

The external force $\tilde{\mathbf{f}}$ is now applied only on the $i = 0$ layer. Then, the $\tilde{\mathbf{u}}_1$ in the form of Eq. 4.12 becomes

$$\begin{aligned} \tilde{\mathbf{u}}_1(z, \mathbf{R}_{\parallel}) = & \sum_{\mathbf{R}'_{\parallel}} G_{11}(z, \mathbf{R}_{\parallel} - \mathbf{R}'_{\parallel}) \\ & \times \left(\tilde{D}_{up} \tilde{\mathbf{u}}_1(z, \mathbf{R}'_{\parallel}) + \sum_{\mathbf{R}''_{\parallel}} \tilde{D}'_{up}(\mathbf{R}'_{\parallel} - \mathbf{R}''_{\parallel}) \tilde{\mathbf{u}}_0(z, \mathbf{R}''_{\parallel}) \right). \end{aligned} \quad (4.14)$$

The Fourier transformation of Eqs. 4.13 and 4.14 yields

$$\begin{aligned} z^2 \tilde{\mathbf{u}}_0(z, \mathbf{k}_{\parallel}) = & - (L(\mathbf{k}_{\parallel}) + \tilde{D}_{low}) \tilde{\mathbf{u}}_0(z, \mathbf{k}_{\parallel}) \\ & - \tilde{D}'_{low}(\mathbf{k}_{\parallel}) \tilde{\mathbf{u}}_1(z, \mathbf{k}_{\parallel}) + \tilde{\mathbf{f}}(z, \mathbf{k}_{\parallel}), \end{aligned} \quad (4.15)$$

$$\begin{aligned} \tilde{\mathbf{u}}_1(z, \mathbf{R}_{\parallel}) = & G_{11}(z, \mathbf{k}_{\parallel}) \\ & \times (\tilde{D}_{up} \tilde{\mathbf{u}}_1(z, \mathbf{k}_{\parallel}) + \tilde{D}'_{up}(\mathbf{k}_{\parallel}) \tilde{\mathbf{u}}_0(z, \mathbf{k}_{\parallel})). \end{aligned} \quad (4.16)$$

Inserting Eq. 4.16 into Eq. 4.15 to erase $\tilde{\mathbf{u}}_1$, we obtain,

$$\tilde{\mathbf{u}}_0(z, \mathbf{k}_{\parallel}) = (z^2 + L(\mathbf{k}_{\parallel}) + \tilde{D}^*(z, \mathbf{k}_{\parallel}))^{-1} \tilde{\mathbf{f}}(z, \mathbf{k}_{\parallel}), \quad (4.17)$$

where $\tilde{D}^*$ is an effective interlayer matrix defined by

$$\begin{aligned} \tilde{D}^* = \tilde{D}_{low} &+ \tilde{D}'_{low}(\mathbf{k}_{\parallel}) (1 - G_{11}(z, \mathbf{k}_{\parallel}) \tilde{D}_{up})^{-1} \\ &\times G_{11}(z, \mathbf{k}_{\parallel}) \tilde{D}'_{up}(\mathbf{k}_{\parallel}). \end{aligned}$$

Finally, the semi-infinite periodicity promises that Eq. 4.11 and 4.17 are equivalent because the new layer should respond to external forces in the entirely same manner as the original surface. Therefore, we derive an equation for the Green's function as

$$G_{11}(z, \mathbf{k}_{\parallel}) = (z^2 + L(\mathbf{k}_{\parallel}) + \tilde{D}^*(G_{11}))^{-1}. \quad (4.18)$$

Numerically, the matrices L and $\tilde{D}$ are estimated by phonon calculations of the bulk system based on *ab initio* calculations and Eq. 4.18 is solved by conventional Newton-Raphson algorithms. Through the inverse Laplace transformation of Eq. 4.12, the trajectory of $\tilde{\mathbf{u}}_1$, then, can be obtained by a convolution of the Green's function as

$$\tilde{\mathbf{u}}_1(t, \mathbf{k}_{\parallel}) = \int_0^t G_{11}(t - t', \mathbf{k}_{\parallel}) \tilde{\mathbf{f}}(t', \mathbf{k}_{\parallel}) dt'. \quad (4.19)$$

4.3.3 Trajectory of GFMD

As stated in Sec. 4.2, a solution of the semi-infinite surface layer $\mathbf{u}_1$ consists in the sum of a particular solution $\mathbf{u}_p$ and the general solution $\mathbf{u}_g$. This section provides numerical recipes on how to generate trajectories of $\mathbf{u}_p$ and meaningful $\mathbf{u}_g$.

Particular solution and convolution

The modification of Eq. 4.19 gives the equation of motion of $\mathbf{u}_p$ as

$$M \frac{d^2}{dt^2} \mathbf{u}_p(t, \mathbf{k}_{\parallel}) = \mathbf{f}_{\text{GF}}(t, \mathbf{k}_{\parallel}) \quad (4.20)$$

$$\mathbf{f}_{\text{GF}}(t, \mathbf{k}_{\parallel}) = \int_0^t A(t - \tau, \mathbf{k}_{\parallel}) \mathbf{f}(\tau, \mathbf{k}_{\parallel}) d\tau, \quad (4.21)$$

where,

$$A(t, \mathbf{k}_{\parallel}) = M N \frac{d^2}{dt^2} G_{11}(t, \mathbf{k}_{\parallel}) N,$$

and the Laplace transformed A is $A(z, \mathbf{k}_{\parallel}) = z^2 G_{11}(z, \mathbf{k}_{\parallel})$. The reduced force $\mathbf{f}_{\text{GF}}$ causes the discrete integral algorithms of the convolution to be computationally demanding, a notorious problem of GFMD. The integral range grows as time t increases, and the entire history of the force trajectory should be saved in memory. Indeed, the simulation time and memory allocation are proportional to $O(t^2)$ and $O(t)$, respectively.

A fast convolution based on modified-Talbot's inverse Laplace transformation (mTILT)[295, 296, 297, 298] reduces the computational costs to $O(t \log(t))$ for the simulation time and $O(\log(t))$ for memory allocation. Conventional inverse Laplace transformation of an arbitrary function $X(z)$ is defined by

$$X(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} X(z) e^{zt} dz,$$

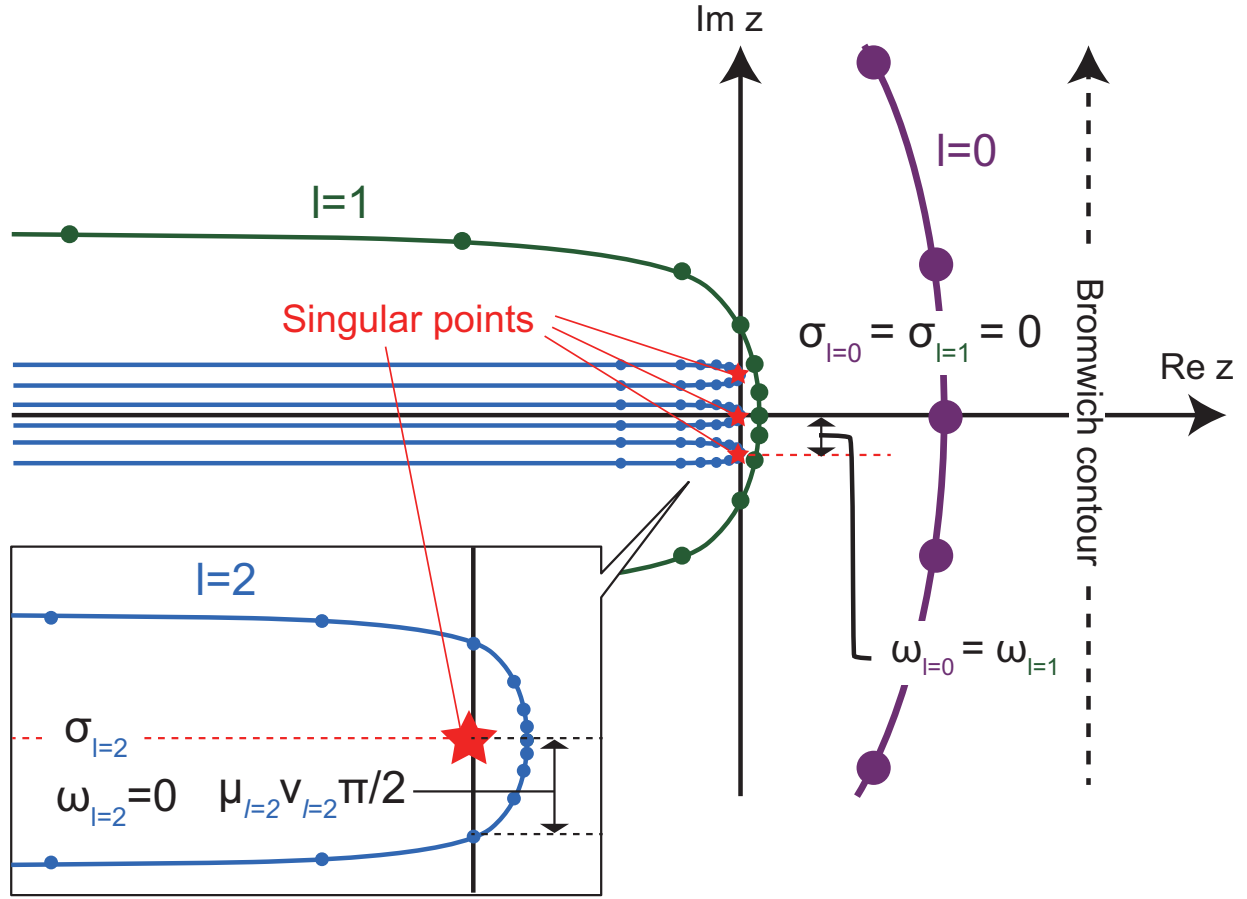


Figure 4.3: Schematic of integral paths of the mTILT. The paths labeled by index l are used in the time range I_l in Eq. 4.22. The parameter σ_l indicates a center of the contour in the imaginary axis, which is set with respect to imaginary parts of the singular points. The ω_l is assigned to the distance of the imaginary parts between the contour center σ_l and the farthest singular point. The width of the l path is the distance of the imaginary parts between σ_l and a cross-section of the contour with the imaginary axis, that is equivalent to $\mu_l \nu_l \pi/2$.

where i is a unit of imaginary number, and the constant c is a real number larger than zero. This integral path is called Bromwich contour. The idea of mTILT is that the Bromwich contour is bent in such a way to encircle singular points of $X(z)$ on the imaginary axis, as shown in Fig. 4.3. Coordinates of the singular points of the Green's function are identified by a line search of $G_{11}(z = i\omega', \mathbf{k}_{\parallel})$, where ω' is a real number variable. Firstly, the mTILT divides the time range $[0, T]$ into a set of time ranges I_l as follows

$$I_0 = [0, h], \quad I_l = [B^{l-1}h, T_l], \quad T_l = (2B^l - 1)h \quad (4.22)$$

where h is a time step and $l = 1, 2, \dots, L$. The integer L satisfies $(2B^L - 1)h \geq T$ and B is an arbitrary integer greater than 1. The integral path used in I_l is defined as

$$z^l(\theta) = i\sigma_l + \mu_l(\theta \cot(\theta) + i\nu_l\theta),$$

where the geometry parameters are $\mu_l = \mu_0/T_l$, $\mu_0 = 8$, $\nu_l = \nu_0(1 + \omega_l/\beta)$, $\nu_0 = 0.6$, and $\beta = \pi\mu_l\nu_0/2$.

For example, Fig. 4.3 illustrates the shapes of the paths z^l . The widths of $l = 0$ and $l = 1$ paths are large enough to enclose all of the three singular points. As l increases, the width of the path $\mu_l\nu_l\pi/2$ decreases because μ_l decreases. The number of $l = 2$ paths, in this example, becomes three, and each path encloses each of the singular points.

In this manner, the mTILT designs the integral paths to secure high numerical accuracy of the inverse Laplace transformation, depending on the time interval I_l . Namely, when $t \in I_l$, the inverse Laplace transformation is

$$\begin{aligned} X(t) &= \frac{1}{2\pi i} \int_{-\pi}^{\pi} X(z^l(\theta)) e^{z^l(\theta)t} \frac{dz^l}{d\theta} d\theta, \\ &\sim \frac{1}{2i(N+1)} \sum_{j=-N}^N X(z^l(\theta_j)) e^{z^l(\theta_j)t} \frac{dz^l(\theta_j)}{d\theta} \\ &\equiv \sum_{j=-N}^N \omega_j^l X(z_j^l) e^{z_j^l t}, \end{aligned} \quad (4.23)$$

where a trapezoidal rule in the integral range $[-\pi, \pi]$ is used with discretization $\theta_j = j\pi/N + 1$, $j = -(N+1), \dots, N+1$. We defined $\omega_j^l = \frac{d}{d\theta} z_j^l / 2i(N+1)$ and $z_j^l = z^l(\theta_j)$. For notation simplicity, Eq. 4.23, which represents the single path embracing all of the singularity, will be used in the following. In the case of the plural paths as $l = 2$ in Fig. 4.3, contributions calculated by Eq. 4.23 are merely summed up.

Then, the mTILT is applied to the convolution task in Eq. 4.21. We divide a range of the simulation time $[0, T]$ according to Eq. 4.22 in the convolution routine. Namely, when $[t - a, t - b] \subseteq I_l$, the convolution is approximated as

$$\begin{aligned} &\int_a^b A(t - \tau, \mathbf{k}_{\parallel}) \mathbf{f}(\tau, \mathbf{k}_{\parallel}) d\tau \\ &\sim \sum_{j=-N}^N \omega_j^l A(z_j^l) e^{z_j^l(t-b)} \mathbf{y}(b, a, z_j^l, \mathbf{k}_{\parallel}), \end{aligned} \quad (4.24)$$

where $\mathbf{y}(b, a, z, \mathbf{k}_{\parallel}) = \int_a^b e^{z(b-\tau)} \mathbf{f}(\tau, \mathbf{k}_{\parallel}) d\tau$. Here we omit $\mathbf{k}_{\parallel}$ variable unless the context needs it explicitly. The quantity $\mathbf{y}(b, a, z)$ is known to be a solution of the following differential equation at $t = b$,

$$\frac{d}{dt} \mathbf{y}(t, a, z) = z \mathbf{y}(t, a, z) + \mathbf{f}(t), \quad \mathbf{y}(a, a, z) = 0. \quad (4.25)$$

We then approximate $\mathbf{y}$ by time-discretized $\mathbf{f}(t_k)$. The time interval $[a, b]$ is split into a sequence of partial intervals $[a + t_k, a + t_{k+1}]$, where $t_k = k \times h$ and $k = 0, \dots, n = (b - a)/h$.

In $t \in [a + t_k, a + t_{k+1}] \subset I_l$, Eq. 4.25 is expressed as

$$\frac{d}{dt}\mathbf{y}(t, a, z) = z\mathbf{y}(t, a, z) + \mathbf{f}(t), \quad \mathbf{y}(a + t_k, a, z) = \mathbf{y}_k.$$

An exact solution of this equation is

$$\mathbf{y}_{k+1} = e^{zh}\mathbf{y}_k + h \int_0^1 e^{(1-\theta)zh}\mathbf{f}(a + t_k + h\theta)d\theta.$$

We apply a linear approximation $\mathbf{f}(a + t_k + h\theta) \sim \theta\mathbf{f}_{k+1} + (1 - \theta)\mathbf{f}_k$, where $\mathbf{f}_k = \mathbf{f}(a + t_k)$. As a result, the approximated solution $\mathbf{y}'_k$ can be obtained via a recursive expression with respect to the index k ,

$$\begin{aligned} \mathbf{y}'_{k+1} &= \mathbf{y}'_k + \frac{e^{zh} - 1}{zh} \left(zh\mathbf{y}'_k + h\mathbf{f}_k + h \frac{\mathbf{f}_{k+1} - \mathbf{f}_k}{zh} \right) \\ &\quad - h \frac{\mathbf{f}_{k+1} - \mathbf{f}_k}{zh}. \end{aligned} \quad (4.26)$$

Since the mathematical components have been prepared, we now describe the fast convolution integral. Denoting $t = t_{n+1}$, we divide the range of convolution into two regions as

$$\left(\int_{t_n}^{t_{n+1}} + \int_0^{t_n} \right) A(t_{n+1} - \tau)\mathbf{f}(\tau)d\tau. \quad (4.27)$$

The modified-Talbot path of I_0 calculates the first term as

$$\begin{aligned} &\int_{t_n}^{t_{n+1}} A(t_{n+1} - \tau)\mathbf{f}(\tau)d\tau \\ &\sim \Phi_1\mathbf{f}(t_n) + \Phi_2 \frac{\mathbf{f}(t_{n+1}) - \mathbf{f}(t_n)}{h}, \end{aligned} \quad (4.28)$$

where

$$\begin{aligned} \Phi_1 &= \int_{t_n}^{t_{n+1}} A(t_{n+1} - \tau)d\tau \\ &= \int_0^h A(h - \tau)d\tau \sim \sum_{j=-N}^N \omega_j^0 \frac{A(z_j^0)}{z_j^0} e^{z_j^0 h} \\ \Phi_2 &= \int_{t_n}^{t_{n+1}} A(t_{n+1} - \tau)(t_{n+1} - \tau)d\tau \\ &= \int_0^h A(h - \tau)\tau d\tau \sim \sum_{j=-N}^N \omega_j^0 \frac{A(z_j^0)}{(z_j^0)^2} e^{z_j^0 h}. \end{aligned}$$

The second term of Eq. 4.27 is decomposed into contributions of the intervals $I_{l=1,2,\dots,L-1}$, where L is the minimum integer that satisfies $t_{n+1} < 2B^L h$. We define $\tau_0 = t_n$, $\tau_L = 0$, and $\tau_l = q_l B^L h$ if $l \neq 0$ nor L . An integer $q_l \geq 1$ is determined so as to satisfy

$$t_{n+1} - \tau_l \in [B^l h, (2B^l - 1)h], \quad l = 1, 2, \dots, L - 1.$$

The time range is divided as $[0, t_n] = \cup_{l=0} [\tau_l, \tau_{l+1}]$. Therefore, by using the approximations in Eqs. 4.24 and 4.26, we derive

$$\begin{aligned} & \int_0^{t_n} A(t_{n+1} - \tau) \mathbf{f}(\tau) d\tau \\ &= \sum_{l=1}^L \int_{\tau_l}^{\tau_{l+1}} A(t_{n+1} - \tau) \mathbf{f}(\tau) d\tau \\ &\sim \sum_{l=1}^L \sum_{j=-N}^N \omega_j^l A(z_j^l) e^{z_j^l(t_{n+1} - \tau_{l+1})} \mathbf{y}'(\tau_{l+1}, \tau_l, z_j^l). \end{aligned} \quad (4.29)$$

In short, the convolution term is calculated by the sum of Eqs. 4.28 and 4.29, along with Eq. 4.26 which is used for efficient calculation of the term $\mathbf{y}'$. Then, because the reduced force is obtained, the motion equation Eq. 4.20 is numerically solved to simulate the trajectory. A simple example of specific steps to show the $\mathbf{y}'$ updating is given in the Appendix C.

Thermostat and barostat

Here we consider the general solution $\mathbf{u}_g$ in Eq. 4.1. The mass-normalized equation of motion for the *whole* system in the $\mathbf{k}_{\parallel}$ space is

$$\begin{aligned} & \left(\frac{d^2}{dt^2} + \tilde{D}(\mathbf{k}_{\parallel}) \right) \tilde{\mathbf{u}}(t, \mathbf{k}_{\parallel}) = 0, \\ & \tilde{\mathbf{u}}(0, \mathbf{k}_{\parallel}) \equiv \tilde{\mathbf{u}}(t=0, \mathbf{k}_{\parallel}), \\ & \tilde{\mathbf{v}}(0, \mathbf{k}_{\parallel}) \equiv \frac{d}{dt} \tilde{\mathbf{u}}(t=0, \mathbf{k}_{\parallel}), \end{aligned} \quad (4.30)$$

where $\tilde{\mathbf{u}} = (\tilde{\mathbf{u}}_g = \tilde{\mathbf{u}}_1, \tilde{\mathbf{u}}_2, \dots)^T$ in the layer index representation. The Laplace transformation of Eq. 4.30 yields

$$(z^2 + \tilde{D}(\mathbf{k}_{\parallel})) \tilde{\mathbf{u}}(z, \mathbf{k}_{\parallel}) = \tilde{\mathbf{v}}(0, \mathbf{k}_{\parallel}) + z \tilde{\mathbf{u}}(0, \mathbf{k}_{\parallel}).$$

Using Eq. 4.10, we can describe the general solution in the Green's function framework, as

$$\tilde{\mathbf{u}}(z, \mathbf{k}_{\parallel}) = G(z, \mathbf{k}_{\parallel}) (\tilde{\mathbf{v}}(0, \mathbf{k}_{\parallel}) + z \tilde{\mathbf{u}}(0, \mathbf{k}_{\parallel})). \quad (4.31)$$

The initial condition includes all the displacements and velocities in the semi-infinite system. Obviously, there is an infinitely large number of possible configurations of the initial conditions. A reasonable policy to select a physically meaningful initial condition is to consider a thermostat. The semi-infinite system is assumed to be located at a temperature T , and the constituent atoms move according to the thermal fluctuation. Let this general solution be denoted by $\tilde{\mathbf{u}}_T$. We modify Eq. 4.31 by using notations $S(z) \equiv zG(z)$ and $\tilde{\mathbf{v}}_T(z, \mathbf{k}_{\parallel}) \equiv z\tilde{\mathbf{u}}_T(z, \mathbf{k}_{\parallel})$, and apply the inverse Laplace transformation.

$$\tilde{\mathbf{v}}_T(t, \mathbf{k}_{\parallel}) = S(t, \mathbf{k}_{\parallel}) (\tilde{\mathbf{v}}_T(0, \mathbf{k}_{\parallel}) + z \tilde{\mathbf{u}}_T(0, \mathbf{k}_{\parallel})). \quad (4.32)$$

Here we use the law of equipartition of energy,

$$\begin{aligned} \langle \tilde{v}_{T;\xi}(t, \mathbf{k}_{\parallel}) \tilde{v}_{T;\xi'}^*(t, \mathbf{k}_{\parallel}) \rangle &= k_B T \delta_{\xi, \xi'} \\ \langle \tilde{v}_{T;\xi}(t, \mathbf{k}_{\parallel}) \tilde{u}_{T;\xi'}^*(t, \mathbf{k}_{\parallel}) \rangle &= 0, \end{aligned}$$

where ξ refers to the components of the atomic coordinates (x, y, z), and $*$ is the complex conjugate. The bracket represents the ensemble averaging operator. By applying the equipartition law, Eq. 4.32 becomes

$$\langle \tilde{v}_{T;\xi}(t, \mathbf{k}_{\parallel}) \tilde{v}_{T;\xi'}^*(0, \mathbf{k}_{\parallel}) \rangle = k_B T S_{\xi, \xi'}(t, \mathbf{k}_{\parallel}), \quad (4.33)$$

that is called the fluctuation-dissipation theorem. This relation tells that an auto-correlation of the general solution of the velocity should be equivalent to the Green's function.

Another useful general solution represents normal and shear stresses. Let us consider that a semi-infinite system is located at 0 K temperature under a uniform stress applied to the surface $\mathbf{f}(t, \mathbf{k}_{\parallel}) = -\delta_{\mathbf{k}_{\parallel}, \mathbf{0}} \mathbf{f}_s$. The velocity solution of this system is

$$\tilde{\mathbf{v}}(t, \mathbf{k}_{\parallel}) = -\delta_{\mathbf{k}_{\parallel}, \mathbf{0}} \mathbf{f}_s \int_0^t S_{11}(\tau, \mathbf{k}_{\parallel}) d\tau,$$

where δ is the Kronecker delta.

As time t goes, the semi-infinite system deforms by the applied stress. In the limit of $t \rightarrow \infty$, the deformation eventually stops at a configuration that balances the applied stress and elastic force; namely $\tilde{\mathbf{v}}(t \rightarrow \infty, \mathbf{k}_{\parallel}) = 0$. At this stage, the elastic energy stored by the deformation produces a general solution $\tilde{v}_S(\mathbf{k}_{\parallel})$ that satisfies,

$$\begin{aligned} \tilde{\mathbf{v}}(t \rightarrow \infty, \mathbf{k}_{\parallel}) &= -\delta_{\mathbf{k}_{\parallel}, \mathbf{0}} \mathbf{f}_s S_{11}(z=0, \mathbf{k}_{\parallel}) + \tilde{v}_S(\mathbf{k}_{\parallel}) \\ &= 0. \end{aligned}$$

We obtain

$$\tilde{\mathbf{v}}_S(\mathbf{k}_{\parallel}) = \delta_{\mathbf{k}_{\parallel}, \mathbf{0}} \mathbf{f}_s S_{11}(z=0, \mathbf{k}_{\parallel}).$$

This equation indicates that the velocity term is proportional to the applied stress multiplied by the Green's function. In conclusion, by adding $d\tilde{\mathbf{u}}_g/dt = \tilde{\mathbf{v}}_T + \tilde{\mathbf{v}}_S$ to the trajectory of the surface layer, we can control the temperature and the shear stresses acting on the semi-infinite system.

Numerical treatment of thermostat

We present a numerical scheme for generating the random velocity terms in Eq. 4.33 that satisfy the fluctuation-dissipation theorem, on the basis of an algorithm proposed by Berkowitz [302]. By assuming that $\tilde{v}_{T;\xi}(t, \mathbf{k}_{\parallel})$ is periodic in an enough long period P , the Fourier series expansion yields

$$\tilde{v}_{T;\xi}(t, \mathbf{k}_{\parallel}) = \sum_{n=1}^{\infty} (a_{\xi,n} \cos(\omega_n t) + b_{\xi,n} \sin(\omega_n t)), \quad (4.34)$$

where $\omega = 2\pi n/P$. The random variables $a_{\xi,n}$ and $b_{\xi,n}$ are assumed to be independent. By inserting Eq. 4.34 into the left side of Eq. 4.33, it becomes

$$\begin{aligned} \langle \tilde{v}_{T;\xi}(t, \mathbf{k}_{\parallel}) \tilde{v}_{T;\xi'}^*(0, \mathbf{k}_{\parallel}) \rangle &= \sum_{n=1}^{\infty} \langle a_{\xi,n} a_{\xi',n}^* \rangle \cos(\omega_n t) \\ &+ \langle b_{\xi,n} a_{\xi',n}^* \rangle \sin(\omega_n t). \end{aligned} \quad (4.35)$$

We extend the domain $t \geq 0$ of $S_{\xi,\xi'}(t, \mathbf{k}_{\parallel})$ to $\infty \geq t \geq -\infty$ by using $S_{\xi,\xi'}(|t|, \mathbf{k}_{\parallel})$. The right side of of Eq. 4.33 is modified as

$$\begin{aligned} S_{\xi,\xi'}(|t|, \mathbf{k}_{\parallel}) &= \frac{2k_B T}{P} \sum_{n=1}^{\infty} \cos(\omega_n t) \int_{-P/2}^{P/2} S_{\xi,\xi'}(|t'|, \mathbf{k}_{\parallel}) \cos(\omega_n t') dt' \\ &= \frac{4k_B T}{P} \sum_{n=1}^{\infty} \cos(\omega_n t) \int_0^{P/2} S_{\xi,\xi'}(t', \mathbf{k}_{\parallel}) \cos(\omega_n t') dt'. \end{aligned}$$

Because of the assumption that P is enough large, we can use the cosine transformation $\mathcal{C}[X](\omega) = 1/2 \int_0^{\infty} (\exp[-i\omega t] + \exp[i\omega t]) X(t) dt$. Therefore,

$$S_{\xi,\xi'}(|t|, \mathbf{k}_{\parallel}) = \frac{4k_B T}{P} \sum_{n=1}^{\infty} \mathcal{C}[S_{\xi,\xi'}](\omega_n, \mathbf{k}_{\parallel}) \cos(\omega_n t). \quad (4.36)$$

Inserting Eqs. 4.35 and 4.36 into Eq. 4.33, we obtain relations of the random variables required by the fluctuation-dissipation theorem, as

$$\begin{aligned} \langle a_{\xi,n} a_{\xi',n}^* \rangle &= \frac{4k_B T}{P} \mathcal{C}[S_{\xi,\xi'}](\omega_n, \mathbf{k}_{\parallel}) \\ \langle b_{\xi,n} a_{\xi',n}^* \rangle &= 0. \end{aligned}$$

Because randomness of the $\tilde{v}_{T;\xi}(t, \mathbf{k}_{\parallel})$, the ensemble average of the magnitudes of $a_{\xi,n}$ and $b_{\xi,n}$ are equivalent: $\langle a_{\xi,n} a_{\xi',n}^* \rangle = \langle b_{\xi,n} b_{\xi',n}^* \rangle$.

Then, we construct a covariance matrix Σ to generate the random variables a and b .

$$\begin{aligned} \Sigma &= \left\langle \begin{pmatrix} a_{1,n} \\ b_{1,n} \\ \vdots \\ a_{\xi,n} \\ b_{\xi,n} \\ \vdots \end{pmatrix} (a_{1,n}^*, b_{1,n}^*, \dots, a_{\xi,n}^*, b_{\xi,n}^*, \dots) \right\rangle \\ &= \frac{4k_B T}{P} \begin{pmatrix} \mathcal{C}[S_{1,1}] & 0 & \dots & \mathcal{C}[S_{1,\xi}] & 0 & \dots \\ 0 & \mathcal{C}[S_{1,1}] & \dots & 0 & \mathcal{C}[S_{1,\xi}] & \dots \\ \vdots & \dots & \dots & \dots & \dots & \dots \\ \mathcal{C}[S_{\xi,1}] & 0 & \dots & \mathcal{C}[S_{\xi,\xi}] & 0 & \dots \\ 0 & \mathcal{C}[S_{\xi,1}] & \dots & 0 & \mathcal{C}[S_{\xi,\xi}] & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix} \end{aligned} \quad (4.37)$$

This matrix is the Hermite matrix, given the fact that $\mathcal{C}[S_{\xi,\xi'}] = \mathcal{C}[S_{\xi',\xi}]^*$. A stochastic vector $\mathbf{x} = (A_{1,n}, B_{1,n}, \dots, A_{\xi,n}, B_{\xi,n}, \dots)$ that satisfies Eq. 4.37 can be generated by considering a multi-variable

Gauss distribution N with the covariance matrix Σ .

$$N = \frac{1}{(2\pi)^D |\Sigma|^{1/2}} \exp\left(-\frac{1}{2} \mathbf{x}^\dagger \Sigma^{-1} \mathbf{x}\right), \quad (4.38)$$

where the number of elements of $\mathbf{x}$ is $2D$. We define a matrix U that diagonalizes Σ and its eigenvalue matrix λ . The variable $\mathbf{x}^\dagger \Sigma^{-1} \mathbf{x}$ is transformed as,

$$\mathbf{x}^\dagger \Sigma^{-1} \mathbf{x} = \mathbf{x}^\dagger U^{-1} \lambda^{-1} U \mathbf{x} = \mathbf{y}^\dagger \lambda^{-1} \mathbf{y} = \sum_i^{2D} \frac{|y_i|^2}{\lambda_i}, \quad (4.39)$$

where $\mathbf{y} = U \mathbf{x}$. Inserting Eq. 4.39 into Eq. 4.38, the Gauss distribution becomes,

$$N = \frac{1}{(2\pi)^D |\Sigma|^{1/2}} \prod_i^{2D} \exp\left(-\frac{|y_i|^2}{2\lambda_i}\right). \quad (4.40)$$

Equation 4.40 indicates that we express the independent Gaussian product with no correlation between the variables. Therefore, we can use Box-Muller method which generates stochastic variables regulated by the Gauss distribution. The variable y_i is calculated by

$$y_i = \sqrt{-2\lambda_i \log \theta_1} \exp(2\pi i \theta_2),$$

where θ_1 and θ_2 are uniform random variables ranging from 0.0 to 1.0. Then, converting $\mathbf{x} = U^{-1} \mathbf{y}$, we obtain the thermal velocity terms $\tilde{v}_{T;\xi}(t, \mathbf{k}_\parallel)$ via Eq. 4.34. In this study, we use $P = 2^{19} h$.

4.3.4 Coupling QM and GFMD systems

Add-remove method

To couple two systems of different scales, their junction should be bridged smoothly [303, 304, 305, 301]. This study uses an add-remove method, which is one of the hybrid schemes for solids [301]. Hydrogens are often used to cap the boundaries of a QM system to stabilize lone-pair electrons of the edge atoms, while mechanical contributions such as forces from the artificial cap atoms are eliminated because they should not be present in the junction [305, 301]. Figure 4.4 shows an outline of the method in the diamond slab, where H_{cap} and C_{link} denote the cap hydrogens and linked carbons, respectively. A surface carbon generated by GFMD is indicated by C_{GF} .

The add-remove method works as follow:

1. $H_{\text{cap}}-C_{\text{link}}$ bonds are removed by subtracting the corresponding bond generated with classical force fields.
2. The QMMD and GFMD systems are connected with a classical bond between C_{link} and C_{GF} .
3. The positions of H_{cap} are located along the projection of the straight line connecting C_{link} and C_{GF} . The bond length of $H_{\text{cap}}-C_{\text{link}}$ is fixed at its equilibrium distance.
4. The forces are corrected due to the constrain of the H_{cap} position.

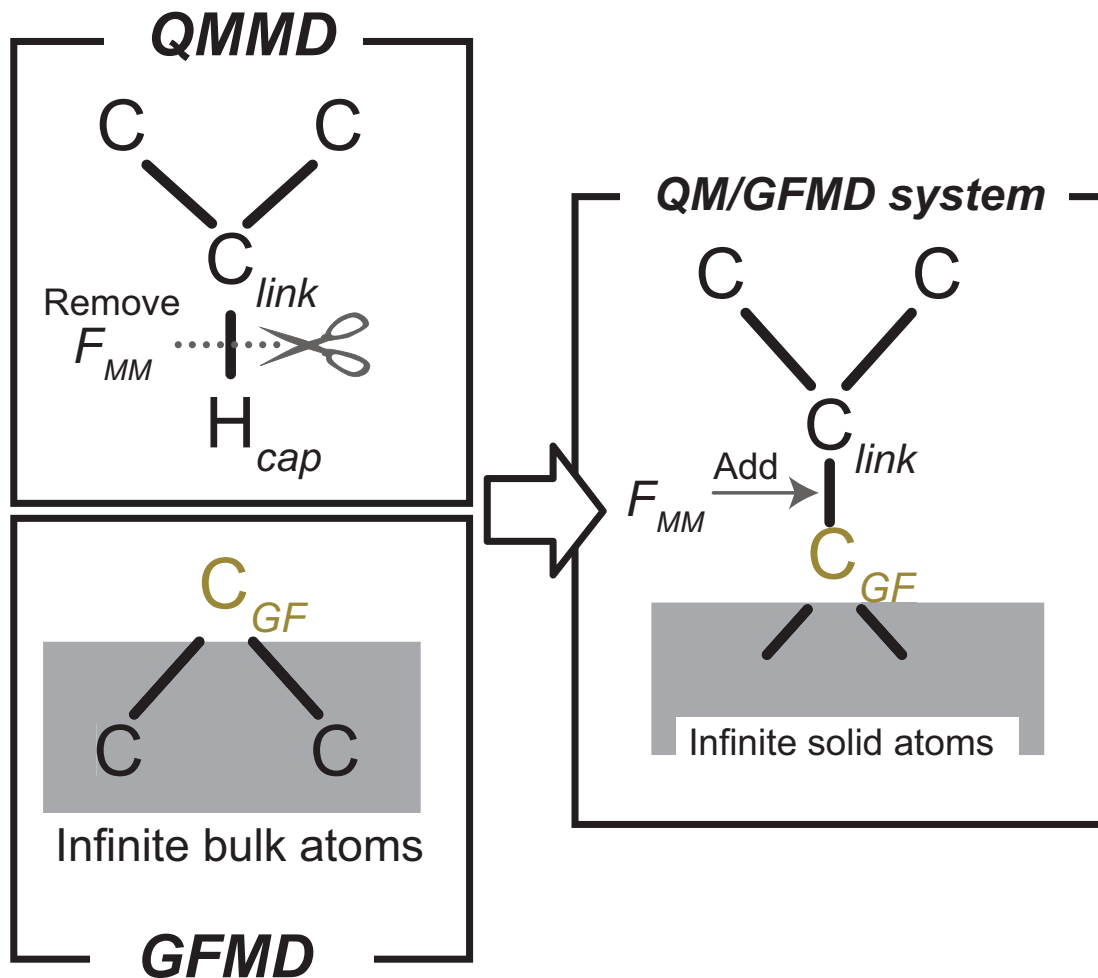


Figure 4.4: Schematic of the add-remove method in a diamond surface of the QM/GFMD system. The force F_{MM} indicates a classical force field of the corresponding bond.

We present numerical descriptions of points 3 and 4. The constrained position of the cap hydrogen $\mathbf{r}_{\text{cap}}$ are

$$\begin{aligned}\mathbf{r}_{\text{cap}} &= \mathbf{r}_{\text{link}} + r_{eq} \mathbf{u}_{\text{link-GF}} \\ \mathbf{u}_{\text{link-GF}} &= \frac{\mathbf{r}_{\text{GF}} - \mathbf{r}_{\text{link}}}{|\mathbf{r}_{\text{GF}} - \mathbf{r}_{\text{link}}|}\end{aligned}\tag{4.41}$$

where $\mathbf{r}_{\text{link}}$ and $\mathbf{r}_{\text{GF}}$ are the positions of C_{link} and C_{GF} , respectively. The symbol r_{eq} indicates the bond length between H_{cap} and C_{link} that is obtained from its stable state.

Due to the $\mathbf{r}_{\text{cap}}$ constrain, the forces should be corrected. We consider a Hamiltonian of the whole system $\mathcal{H}$ including contributions of the add-remove method.

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_{\text{QM}} + \mathcal{H}_{\text{GF}} \\ &\quad + \mathcal{H}_{\text{add}}(\mathbf{r}_{\text{link}}, \mathbf{r}_{\text{GF}}) - \mathcal{H}_{\text{remove}}(\mathbf{r}_{\text{link}}, \mathbf{r}_{\text{cap}}),\end{aligned}$$

where $\mathcal{H}_{\text{QM}}$ and $\mathcal{H}_{\text{GF}}$ indicate the original Hamiltonians of the QM and GFMD systems, respectively. The addition and removal operations in Fig. 4.4 are represented by $\mathcal{H}_{\text{add}}$ and $\mathcal{H}_{\text{remove}}$, which come from the classical interactions of $\text{C}_{\text{link}}\text{-C}_{\text{GF}}$ and $\text{H}_{\text{cap}}\text{-C}_{\text{link}}$, respectively. Given the constrained $\mathbf{r}_{\text{cap}}(\mathbf{r}_{\text{link}}, \mathbf{r}_{\text{GF}})$ in Eq. 4.41, the forces acting on C_{GF} and C_{link} atoms are

$$\begin{aligned}\mathbf{f}_{\text{GF}} &= -\frac{\partial(\mathcal{H}_{\text{GF}} + \mathcal{H}_{\text{add}})}{\partial \mathbf{r}_{\text{GF}}} \\ &\quad - \frac{\partial(\mathcal{H}_{\text{QM}} - \mathcal{H}_{\text{remove}})}{\partial \mathbf{r}_{\text{cap}}} \frac{\partial \mathbf{r}_{\text{cap}}}{\partial \mathbf{r}_{\text{GF}}}\end{aligned}\tag{4.42}$$

$$\begin{aligned}\mathbf{f}_{\text{link}} &= -\frac{\partial(\mathcal{H}_{\text{QM}} + \mathcal{H}_{\text{add}} - \mathcal{H}_{\text{remove}})}{\partial \mathbf{r}_{\text{link}}} \\ &\quad - \frac{\partial(\mathcal{H}_{\text{QM}} - \mathcal{H}_{\text{remove}})}{\partial \mathbf{r}_{\text{cap}}} \frac{\partial \mathbf{r}_{\text{cap}}}{\partial \mathbf{r}_{\text{link}}}\end{aligned}\tag{4.43}$$

$$\begin{aligned}\frac{\partial \mathbf{r}_{\text{cap}}}{\partial \mathbf{r}_{\text{GF}}} &= \frac{R_{eq}}{|\mathbf{r}_{\text{GF}} - \mathbf{r}_{\text{link}}|} (I - \mathbf{u}_{\text{link-GF}}(\mathbf{u}_{\text{link-GF}})^T) \\ \frac{\partial \mathbf{r}_{\text{cap}}}{\partial \mathbf{r}_{\text{link}}} &= I - \frac{\partial \mathbf{r}_{\text{cap}}}{\partial \mathbf{r}_{\text{GF}}}\end{aligned}$$

where I is the unit matrix. Note that $\mathbf{u}(\mathbf{u})^T$ indicates the dyadic product. The first terms on the right sides of Eqs. 4.42 and 4.43 consist of interaction forces obtained by GFMD in Eq. 4.21 and QMMD simulations along with the add-remove classical force terms, respectively. The second terms in Eqs. 4.42 and 4.43 come from the constraint of Eq. 4.41. These force terms become zero if the classical force of $\text{H}_{\text{cap}}\text{-C}_{\text{link}}$ completely agree with the QM bond. However, because the classical model cannot reproduce the quantum method perfectly, these constraint-force corrections should be included.

Refresh treatment

Simulations of sliding friction typically require several hundred thousand steps (~ 10 ps) because tribological reactions are relatively rare events in this simulation time scale. As shown in Eq. 4.21, the convolution of the GFMD increases its integral time range as time evolves. This fact induces an accumulation of the

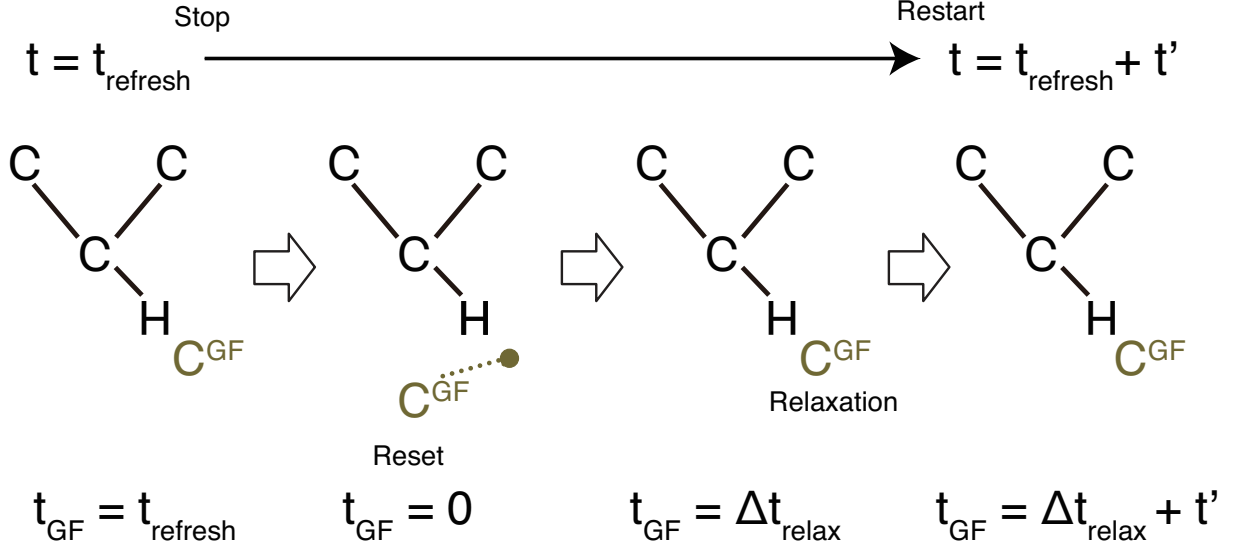


Figure 4.5: Schematic of process of the refresh treatment. The dotted line indicates a spring that is used for the relaxation step presented in the main text.

integral errors in such a long simulation, leading to inaccurate dynamics and overall instability of the GFMD simulation. This subsection provides a remedy for this issue.

Given that the error comes from the extension of the integral region, an idea would be to reset the convolution before the error cannot be ignored anymore. Figure 4.5 presents an outline of this treatment, which we call "refresh". Two clocks t and t_{GF} are prepared for QM and GFMD systems, respectively. The two clocks advance exactly in the same manner at the start of the QM/GFMD simulation. Once they arrive at a user-defined t_{refresh} , at which the GFMD numerical error is considered critical, the positions $\mathbf{r}_{\text{GF}}(t_{\text{refresh}})$ are saved as anchors in the memory. At this point, the t clock stops, but only the t_{GF} clock is reset to zero to make the integral range of the convolution zero. The positions $\mathbf{r}_{\text{GF}}$ are connected to the anchored positions with specific springs to be arranged to their initial positions with respect to $\mathbf{r}_{\text{link}}$. When we start the t_{GF} clock, but still keep the t clock stopped, the springs pull the C_{GF} in such a way that $\mathbf{r}_{\text{GF}}$ returns to the anchored positions as a result of the relaxation. After a certain relaxation time Δt_{relax} , the springs are removed and the t clock starts to run together with t_{GF} .

By iterating this refresh every time $t_{\text{GF}} = t_{\text{refresh}}$, we can perform long and stable GFMD simulations. This treatment, however, provides artificial effects to C_{link} when the t clock restarts because the velocities of C_{GF} are lost as a consequence of the relaxation. Nonetheless, because C_{link} are the junction atoms of the hybrid system in the QM bulk region (see Fig. 4.1), this error is expected not to affect surface phenomena considerably if the QM slab model consists of several atomic layers.

4.3.5 Computational conditions

The internal force matrix is calculated by static *ab initio* calculations of the diamond bulk, based on density functional theory (DFT) and a DFT linear-response approach to phonons calculation [306], performed

with the pw.x and ph.x solvers from the Quantum Espresso package [236, 261, 262]. The Perdew, Burke, and Ernzerhof generalized gradient approximation is used for the exchange-correlation functional [263]. Electronic wave functions are expanded on a plane-wave basis set with a cutoff energy of 25 Ry, and ionic species are described by ultra-soft pseudopotentials [307]. The matrix is approximated so that it only contains elements related to the nearest-neighbor interactions. The off-diagonal elements of the directional indices are also eliminated for the sake of numerical simplicity.

For the add-remove method, the classical force field of the $C_{\text{link}}-C_{\text{GF}}$ bond is set at the value of the corresponding element of the internal force matrix. The $C_{\text{link}}-H_{\text{cap}}$ spring constant is estimated from *ab initio* static calculations performed on a fully H-terminated 2×1 (111) diamond slab of 12 atomic layers. The estimated spring constant of the surface normal direction is 0.2575 Ht/bohr, while for the surface lateral direction is 0.0365 Ht/bohr. The stable bond length of $C_{\text{link}}-H_{\text{cap}}$ is $r_{eq} = 2.1043$ bohr.

We implemented the QM/GFMD hybrid method into the Car-Parrinello solver cp.x. Time development of cp.x is solved by the Verlet method, which does not use velocities of atoms explicitly. On the other hand, the GFMD uses the general solutions to impose the temperature and stress by adding the velocity corrections $\mathbf{v}_T$ and $\mathbf{v}_S$. In order to merge the velocity correction into the QMMD algorithm, we used the leap-frog method that explicitly leverages the velocity term but is compatible to the Verlet method, as follows.

$$\begin{aligned} \mathbf{p}_{\text{GF}}(t + \frac{h}{2}) &\leftarrow \mathbf{p}_{\text{GF}}(t - \frac{h}{2}) + h\mathbf{f}_{\text{GF}}(t) \\ \mathbf{v}_{\text{GF}}(t + \frac{h}{2}) &\leftarrow M^{-1}\mathbf{p}_{\text{GF}}(t + \frac{h}{2}) + \mathbf{v}_T(t) + \mathbf{v}_S \\ \mathbf{r}_{\text{GF}}(t + h) &\leftarrow \mathbf{r}_{\text{GF}}(t) + h\mathbf{v}_{\text{GF}}(t + \frac{h}{2}), \end{aligned}$$

where $\mathbf{p}_{\text{GF}}$, $\mathbf{v}_{\text{GF}}$, and $\mathbf{r}_{\text{GF}}$ are momentum, velocity, and position vectors of the GFMD atoms respectively. The time step is set to $h = 0.1$ fs, and the reduced force $\mathbf{f}_{\text{GF}}$ is calculated by Eq. 4.21. The parameters of mTILT are $B = 11$ and $N = 60$, which is equivalent to the 121 integral points in the contour. The singular points of the Green's function are searched by evaluating its first and second derivatives on the imaginary axis. In the refresh treatment, we use $t_{\text{refresh}} = 50,000h$, the anchor spring constant is 0.05 Ht/bohr for all the x, y, and z directions, and the relax time is $2,000h$. Temperature is set to 300 K by the thermostat of the GFMD method.

The QM ions are thermalized by applying a Nosé-Hoover thermostat with a frequency of 80 THz and imposing an average electronic kinetic energy of 0.25 atomic units on the electron degrees of freedom. The electronic mass and the time step of the molecular dynamics are selected to be 100 and 4 atomic units, respectively. At the beginning of our dynamic simulations, the CP solver is employed to obtain the ground state energy of the electronic wave functions with the steepest descent algorithm. Subsequently, the hybrid QM/GFMD code is used to carry out the dynamic simulation. The computational parameters adopted for the CP scheme have been carefully selected to achieve good accordance between the temperatures of the QM and GF atoms during the dynamics for the system under study.

4.4 Results and Discussion

Kinetic friction

We employed our QM/GFMD solver to study the sliding interface between two diamond crystals and quantitatively estimate the friction coefficient considering different concentrations of H atoms at the sliding

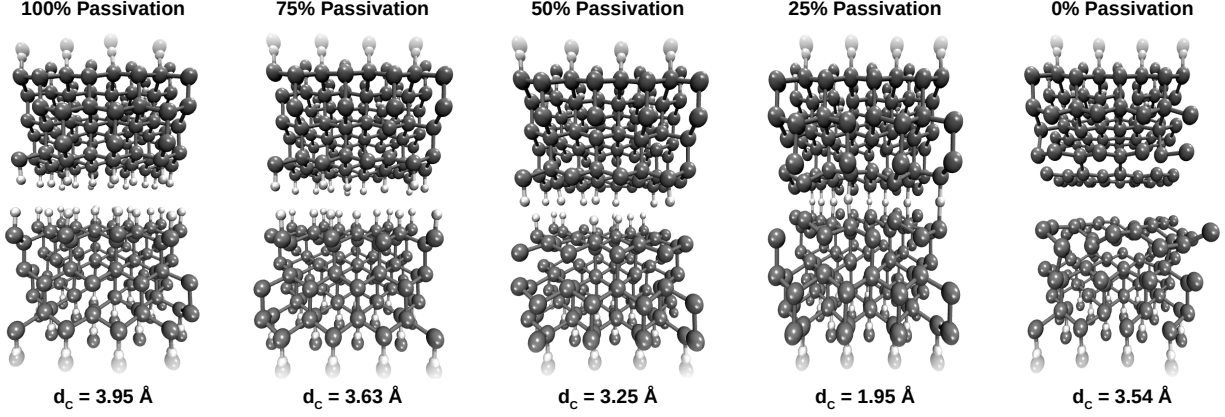


Figure 4.6: Lateral view of the diamond on diamond systems at the end of the dynamic simulations. The averaged vertical separation between the carbon surfaces, denoted by d_c , is shown below the pictures. The surface energy increases with the number of unsaturated carbon atoms, producing higher adhesion and smaller separation. When hydrogen is completely removed, a partial graphitization of the interface can be recognized, and the interfacial separation becomes similar to the interlayer distance of graphene (3.3 Å).

interface. We focused our attention on the C(111) surface, the most accessible cleavage plane of diamond, and modeled the diamond-diamond interface by adopting a supercell with (4×2) in-plane size, containing two-faced slabs; each constituted of three bilayers of carbon atoms. The slabs are externally passivated by hydrogen atoms, which are used as caps to passivate the dangling bonds, and the GF atoms are linked to these capping atoms, as described in the previous section. The interfacial region, where the two surfaces are faced, contains hydrogen atoms in different concentrations and randomly distributed. A lateral view of all the considered systems at the end of the sliding simulation is reported in Fig. 4.6.

We performed molecular dynamics simulations in the presence of load and shear stresses of 5 GPa. To generate the sliding motion, we applied forces with the same magnitude but opposite signs on the outermost atoms of each slab. The simulations lasted 15 ps, corresponding to about 150,000 simulation steps. Three values of the H-coverage, θ , turned out to be high enough to enable the sliding motion under the effects of the applied lateral force. Instead, the other coverages were too low to prevent chemical bonds from forming across the interface and impede the lateral displacement. In table 4.1 we report the average values of the interfacial separation, sliding velocity, kinetic friction force per unit area, and friction coefficient. The symbol $\langle \rangle$ represents the average on the simulation time. The kinetic friction force is calculated as the difference between the total forces in the upper and lower slabs: $F_x^k = |\sum_{up} f_x - \sum_{low} f_x|$, where the sums run on the atoms of each slab, and f_x is the single-atom force along the sliding direction. The coefficient of friction is calculated as the ratio between the kinetic friction force per unit area A , $\langle F_x^k/A \rangle$, and the applied load.

A decrease in the hydrogen coverage results in a friction increase: μ^k almost doubles every time the H coverage is reduced by one quarter. A corresponding reduction in the sliding velocity and the average slab separation, shown in Fig 4.7(a), is also observed. This behavior can be explained in terms of the chemical reactivity of the facing diamond surfaces. When H atoms are removed from the diamond surface, the terminal C atoms expose dangling bonds, which are very reactive. The dangling bonds of two surfaces in contact interact and cause a significant increase in the adhesive friction of the system. The calculated

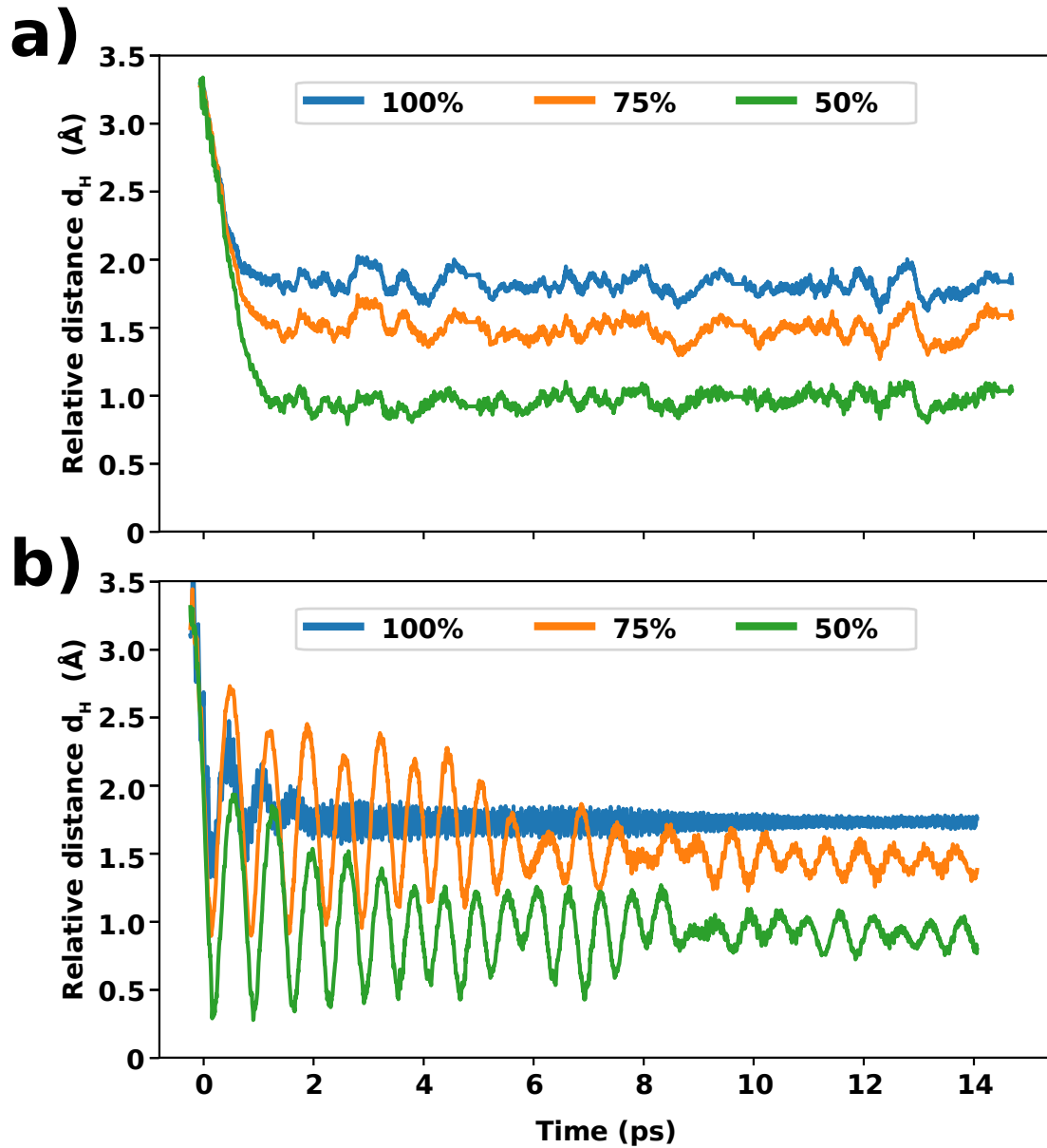


Figure 4.7: Vertical separation of the slabs for the three most passivated systems during the dynamic simulation for GFMD (a) and QMMD (b) simulations. The interslab separation shown is calculated by considering the hydrogen coordinates at the interface.

θ	$\langle d_C \rangle$	$\langle v_x \rangle$	$\langle F_x^k/A \rangle$	μ_k
100%	3.95	279	0.2	0.03
75%	3.63	277	0.3	0.06
50%	3.25	270	0.5	0.10

Table 4.1: The interfacial H coverage, θ , surface separation, d_H (Å), average sliding velocity, v_x (m/s), kinetic friction force along the sliding direction per unit area, F_x^k/A (GPa), and kinetic friction coefficient, μ^k , obtained during the QM/GFMD simulation are reported.

friction coefficients are in agreement with diamond on diamond experiments in an air environment, where the coefficient of friction always ranges between 0.01 and 0.1 [72, 73, 74]. This extreme low friction has been detected for different surfaces of diamonds, for instance, the (100) [75, 73, 76, 77] and (110) [75], and also for nanocrystalline diamond films and diamond-like carbon (DLC) employed as coatings in technological applications [74, 78]. In particular, for the (111) diamond face, experimental results predict a friction coefficient of the order of 0.05 [77], which is almost constant along any possible sliding directions and independent from the load.

The critical role of surface passivation by hydrogen or by environmental molecules, such as water molecules, for achieving low friction coefficients has been highlighted by different experimental works, both for diamond and DLC films [70, 308, 309]. Static first-principles calculations have quantified this effect on the ideal interfacial shear strength [310, 195, 311, 79] and *ab initio* MD simulations allowed to model the tribochemical processes occurring at the sliding diamond interface interacting with water molecules [275]. As a further step, we quantify the effects of the surface passivation on kinetic friction. The accuracy of the performed simulations relies upon the capability of our QM/GFMD method to provide proper control of temperature, mechanical stresses, and energy dissipation in non-equilibrium conditions.

We further reduce the H coverage by considering passivation of 25% and an H-free interface. In the former case, the sliding motion occurs only in the first stages of the simulations but then the slabs interlock due to the strong bonding between the two surfaces, which the applied lateral force can not encompass. On the contrary, in the clean interface, the motion occurs with no interlocking. In Fig. 4.6e, a snapshot of the system acquired during the simulation reveals that a graphitization of the surfaces is taking place due to a partial re-hybridization of the carbon surface bonds from sp^3 to sp^2 . This determines the formation of interfacial graphene layers, which become almost detached from the diamond slabs.

The mechanism of graphitization of carbon films induced by sliding has been observed experimentally [312, 313, 314] and in MD simulations [315, 79]. It has been considered as the origin of the ultralow friction coefficient of the diamond. The realistic simulations here performed reveal that surface passivation can also provide ultralow friction coefficients for diamond interfaces. When the H coverage decreases below a threshold value, the friction coefficient dramatically increases. In our simulations, the friction coefficient corresponding to a coverage of 25% H is so high to prevent the sliding motion under the applied lateral force of 5 GPa. In the absence of passivating species (or at extremely low coverages), the graphitization phenomenon occurs, and the sliding motion is recovered. It is interesting to observe that there exists a second threshold for the concentration of passivating species, below of which surface graphitization takes place. Above this threshold, the sp^3 to sp^2 transition seems inhibited, according to our simulations.

In order to evaluate the effects of the elastic properties of the semi-infinite bulks on the sliding dynamics and friction coefficients, we compare the results of QM/GFMD with those of QMMD, obtained by decoupling the atomistic slabs from the bath of harmonic oscillators. Figure 4.7(b) shows the vertical separations of

the diamond surfaces during this second simulation, where the same initial relative position of the two surfaces, external load, and shear of the GFMD simulation are considered. It is possible to observe that a marked bumping of the surfaces is predicted in QMMD simulations, which is instead absent in the GFMD simulations. The bumping oscillations fade away quickly in the case of complete superficial passivation while it persists for the 75% and 50% cases, recalling the behavior of a damped harmonic motion. While the average values of the surface separations are similar to the GFMD ones, the lack of contact between the surfaces after each bouncing event produces large system accelerations and makes any quantitative estimate of frictional parameters absolutely not meaningful.

θ	ΔE_{max}	ΔE_{mep}	$\langle \Delta E \rangle$	τ_x	τ_y	τ_{mep}	μ_s
100%	0.077	0.012	0.037	0.74	0.9	0.3	0.06
75%	0.274	0.035	0.08	2.1	2.5	1.1	0.22
50%	0.262	0.034	0.100	2.5	2.8	1.4	0.28

Table 4.2: Corrugation of the global PES, ΔE_{max} , and corrugation along specific paths corresponding to the MEP (in yellow), ΔE_{MEP} , and the path sampled during the QM/GFMD simulation, $\langle \Delta E \rangle$, in black. Shear strength along x, y, and MEP and static coefficient of friction. The energy are expressed in (J/m^2) and the stresses in GPa.

4.4.1 Discussion

The accuracy of the QM/GFMD allows for a reliable quantitative estimation of kinetic friction. This novel achievement opens the way to fundamental investigations on the nature of frictional phenomena. For example, one may ask how the static friction properties compare with the kinetic ones. To answer this question, we calculated the potential energy surface (PES) that describes the adhesion energy, γ , between the two surfaces in contact as a function of their relative lateral position. The PES corrugation can be interpreted as the maximum amount of energy that can be dissipated through phonons excitation during each frictional slip. While the derivative of the PES profile along a given direction corresponds to the force experienced by the slider when moving along the substrate in that direction. The minimum energy path (MEP) is usually considered as the path most likely followed during sliding, and thus the ideal shear strength is calculated along that path as [195]:

$$\tau_{MEP} = \max |\nabla_{MEP} \gamma(x, y)|$$

Figure 4 displays the PES obtained for the 100%, 75%, and 50% passivated interfaces under 5 GPa load, as considered in the dynamic simulations. Further details on the calculated PESes are reported as SI. As can be seen in the picture and in Tab. 4.2, the corrugation of the three calculated PESes, ΔE_{max} increases with the number of unsaturated bonds at the surface.

We tracked the path followed by the system during the sliding motion in non-equilibrium conditions on the PES during the GFMD simulations. As shown in Fig. 4.8, this path (in black) does not resemble the MEP. It passes through higher energy regions than the MEP (in yellow). Indeed, the calculated potential corrugation experienced along the dynamic path, $\langle \Delta E \rangle$ is higher than that along the MEP, actually $\langle \Delta E \rangle \simeq \frac{1}{2} \Delta E_{max}$ (see Tab. 4.2). This finding highlights that the driving force applied to the surfaces in contact plays a relevant role in determining their relative motion. In particular, we may expect that the system will tend to recover the most energetically favorable path by decreasing the magnitude of the

external lateral force. That is, the capability of the system to follow the MEP depends on the magnitude of the applied shear stresses, i.e., whereas equilibrium thermodynamic prevails over non-equilibrium kinetic.

Another fundamental observation concerns the collective nature of the frictional phenomena that clearly appears if one compares the magnitude of the kinetic friction force per unit area F_x^k/A (Tab. 4.1) with shear strength τ (Tab. 4.2). Independently from the path along which τ is calculated, its value always results higher than the kinetic friction force per unit area. This results from collective mechanisms: while some particles are descending the PES hills, other particles are climbing them, and a partial cancellation of the lateral atomic forces F_x occurs. Indeed, we have previously shown that the onset of frictional slip is a nucleation process, where the particles are not coherently displaced along the PES [212]. This analysis clearly explains the reason why the kinetic friction coefficient is always higher than the static friction coefficient. In the present study, $\mu_s > \mu_k$ for all the three considered coverages, where μ_s is calculated as the ratio between the shear strength along the MEP and the applied load. Moreover, the shear strength τ shows a less pronounced dependence on the surface passivation than the kinetic friction force per unit area.

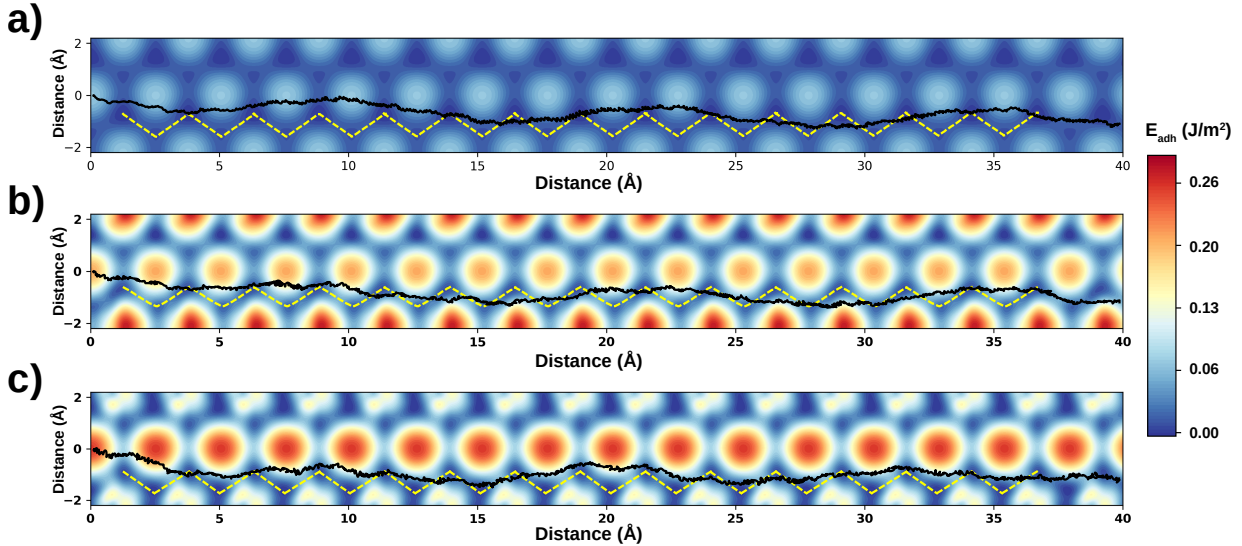


Figure 4.8: Dynamic trajectories (black) represented on the PESes calculated for the 100% (a), 75% (b), and 50% (c) passivated systems. The MEPs are also reported in yellow. A common energy scale is used.

4.5 Conclusion

In conclusion, we developed and applied a multiscale method that links *ab initio* molecular dynamics to Green's Function. This method is above the state-of-the-art techniques used in computational tribology as it allows for a realistic description of the chemical interactions, thermal reservoir, mechanical stresses applied, and energy dissipation due to phonons in non-equilibrium conditions. We calculated the kinetic friction coefficient of two diamond semi-infinite bulks in contact by employing this multiscale approach, obtaining results in close agreement with experiments. We found that the friction coefficient and the interface morphology strongly depend on the degree of passivation of the diamond surfaces. We observe a

superlubric regime at high H coverages. The friction coefficient is very sensitive to the degree of surface passivation and increases with the number of unsaturated carbon bonds dangling at the surface. Below a threshold coverage, covalent bonds are established across the interface that causes the surface interlocking - in our simulations at 25% coverage, a shear stress of 5 GPa was not high enough to promote the sliding motion. This regime persists until the concentration of adsorbates becomes low enough to allow for a change of hybridization of the carbon atoms at the surface from sp^3 to sp^2 . Thanks to surface graphitization, the sliding motion is recovered. Our results indicate that this phenomenon can occur only when passivating species are almost absent from the interface; indeed, we observed graphitization for a clean diamond interface.

A second exciting result highlighted by our realistic simulations concerns the difference between the static and the kinetic tribological properties. First, we observed that the path followed by the system during sliding in non-equilibrium conditions deviates considerably from the MEP, which is the path most likely followed in equilibrium conditions. This suggests that the ability of the system to follow the MEP and thus experience lower frictional forces depends on the magnitude of the shear stress applied, i.e., on the sliding velocity. For sufficiently small velocities, the system motion may be approximated by a succession of quasi-static equilibrium configurations, where the MEP has the highest statistical weight. This fundamental aspect is the subject of ongoing investigations. Second, we show that the kinetic friction force (coefficient) is much smaller than the static friction force (coefficient) due to the collective effects that take place in the many-particle system.

The case studied concerning the kinetic friction of diamond on diamond showed the great potentiality of the QM-GF method, which is above the state-of-the-art methods used in computational tribology and can provide highly accurate insights into non-equilibrium and tribochemistry processes.

Chapter 5

Superlubricity in phosphorene identified by means of ab initio calculations

5.1 Motivation

Black phosphorous and its single-layer constituent, phosphorene, are emerging as promising materials for technological applications in opto- and electronics devices. Thanks to its direct bandgap of around 0.3 eV [94, 95] phosphorene band gap lays between the almost zero band gap of graphene and the relatively large (1.5 – 2.5 eV) gap of transition metal dichalcogenides (TMDs). More importantly, the bandgap of phosphorene films can be tuned by changing the number of layers [96] and by applying an in-plane strain to the film [97]. This intriguing property allows modifying the nature of phosphorene conductivity from a direct to an indirect bandgap semiconductor, semimetal, or metal.

The mechanical properties of phosphorene are also extremely interesting. Thanks to its peculiar puckered structure, phosphorene shows highly anisotropic Young's moduli, the zigzag direction being about twice times stiffer than the armchair one [98], a property relatively uncommon in 2D and, more in general, 3D materials. This intrinsic anisotropy can favor the development of new phosphorene-based devices useful not only for electronic but also for photonic and thermoelectric applications [316].

Likewise other 2D layered materials, such as graphene and TMDs, black phosphorous layers are weakly bonded through van der Waals (vdW) interactions. Therefore, phosphorene layers have the intrinsic property to easy shear between each other, leading to an extraordinary potential for tribological applications. Moreover, P-based lubricant additives are commonly employed in engine oils to reduce friction and adhesion in high-pressure applications [103, 104].

Despite these premises, only a few works investigating the tribological relevance of phosphorene are present in the literature [100, 101, 102, 99]. In particular, a superlubricity regime and a meager shear resistance have been experimentally detected when black phosphorus nanosheets, modified by OH groups, are employed as lubricant additives in aqueous solutions [99]. Superlubricity is usually obtained during the sliding of incommensurate interfaces, where the lateral forces acting between atoms cancel one with each other [41], leading to an almost frictionless motion during sliding [42, 43, 44, 45]. A structural superlubricity is observed in different layered materials [46, 47], such as graphene [38, 48, 49, 317] and MoS₂ [50, 51, 52, 53, 54].

Here we investigate the tribological properties of phosphorene by first principles calculations. This approach allows for an accurate description of the adhesive contribution to friction and has been successfully applied to describe the static friction properties of solid interfaces [318, 208, 249] and the interlayer slipperiness of layered materials, such as graphene [280, 201] and TMDs [319, 126, 250]. In particular, it predicted the superior performances of graphene than MoS₂ [124] as recently verified by nanotribological experiments [83].

Material from: 'Gabriele Losi, Paolo Restuccia & Maria Clelia Righi, High-throughput screening of the static friction and ideal cleavage strength of solid interfaces, 2D Mater. 7 (2020) 025033, IOP Publishing, CC BY 4.0'

An *ab initio* study of the interlayer slipperiness of black phosphorous properties lacks to the best of our knowledge. We first analyze phosphorene films' structural and energetic properties of different thicknesses, adopting five different exchange-correlation functionals. We start from the most common schemes, and then we introduce vdW corrections, which are implemented in both semi-empirical and self-consistent ways. Then, we proceed by calculating the adhesion energy, potential energy surface, and shear strength for two different bilayer orientations. Extremely low corrugation and shear strength are detected when the upper layer is rotated by 90° around the z axis with respect to the lower layer. This orientation is stable and gives rise to a structural superlubricity, whose origin is explained by analyzing the electronic charge distribution within the interlayer region.

5.2 Methods and systems

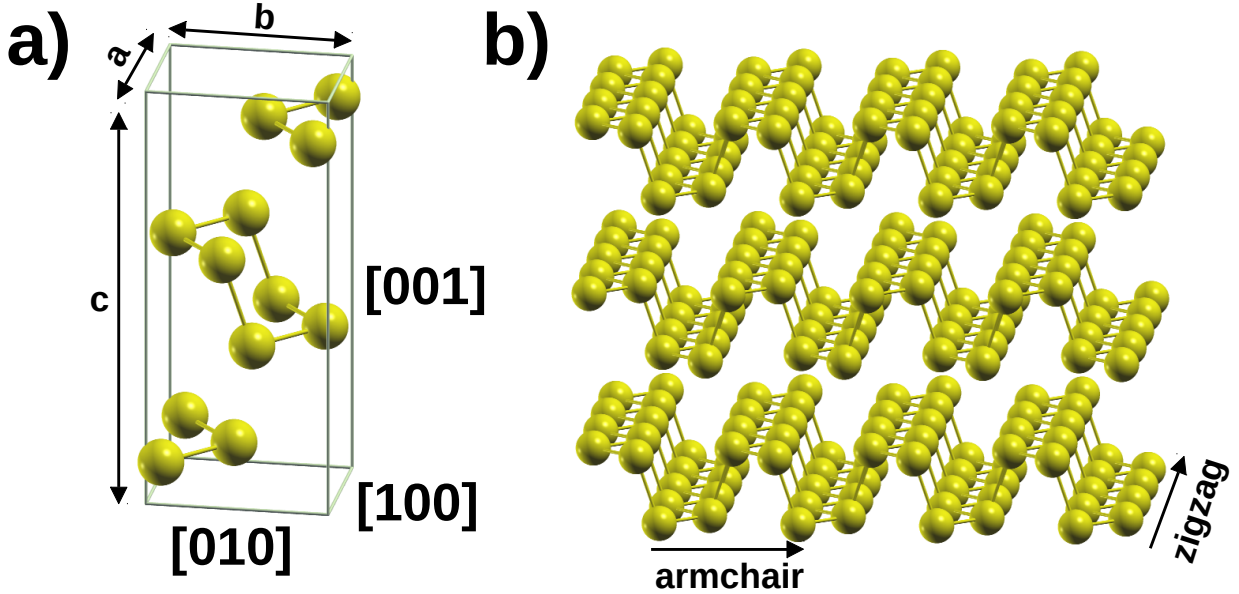


Figure 5.1: Side view of the orthorhombic unit cell for black phosphorus bulk (a) and for a three-layer phosphorene film (b).

We perform density functional theory (DFT) calculations using the Quantum Espresso package [320, 321], in which the electronic wave functions are expanded in plane waves, and the ionic species are described by ultrasoft pseudopotentials [322]. Two different approximations are considered for the exchange-correlation (XC) functional: the local density approximation (LDA) [323] and the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) parameterization [263]. Dispersion interactions are included according to different vdW schemes implemented on top of PBE, namely PBE+D2 [324], vdW-DF2 [325], and rVV10 [326]. According to the PBE+D2 scheme, a semi-empirical correction term is added to the total energy by evaluating atomic pair interactions, while, in the vdW-DF2 and rVV10 schemes, the nonlocal contribution is calculated *ab initio*. A scaling factor s_6 equal to 0.75 is chosen in PBE+D2 as it optimizes the interlayer distance of bulk phosphorene.

After test calculations on the bulk structure, a kinetic energy cutoff of 30 Ry is adopted to truncate the plane wave expansion in all the calculations apart from the vdW-DF2, where a value of 35 Ry is used. The energy cutoff for the charge density is chosen to be either 8 times (LDA, PBE, PBE+D2) or 10 times (vdW-DF2, rVV10) the one for the kinetic energy of the wave functions. The Brillouin zone of the bulk cell is sampled by means of a $12 \times 9 \times 4$ Monkhorst-Pack grid [226].

We first model phosphorene films of different thicknesses and analyze the variation of the structural and electronic properties as a function of the number of layers, N , which is increased from one to five. After a full relaxation of all the structures, including the lateral cell dimensions, the interlayer distance, d_{int} , is obtained as the average distance between the innermost planes of each couple of layers contained in the supercell. The interlayer binding energy is calculated as $\gamma = \frac{E_N - N \cdot E_1}{(N-1)A}$, where E_N is the energy of the film composed by N layers, E_1 is the energy of a single relaxed layer (calculated within the same supercell), and A is the in-plane area of the supercell. In the case of a bilayer, the interlayer binding energy is also referred to as adhesion energy, γ .

As the second step in our analysis, we study the interlayer slipperiness of phosphorene layers by applying a Workflow, which was initially developed by our group to perform high-throughput calculations of interfacial properties, including tribological figures of merits [194, 125]. In particular, the potential energy surface (PES) of the sliding interface is constructed automatically by calculating the adhesion energy γ , which is the opposite of the work of separation [327], as a function of the relative lateral positions of the two surfaces in contact, in the present case represented by two layers. For each layer stacking, the (x, y) coordinates of all the atoms are kept fixed, while their z coordinate is allowed to relax. The whole bidimensional PES is obtained from a finite number of data by interpolating with radial basis functions. The values reported on the PES correspond to the corrugation, $\Delta\gamma$, obtained by subtracting to the interlayer energy its minimum value, γ . The maximum value of the PES corrugation, $\Delta\gamma_{max}$, is obtained for the most unfavorable stacking configuration.

The ideal shear strength, which corresponds to the maximum resistance to sliding for an interface, is calculated as the derivative of the PES profile along the high symmetry directions and along the minimum energy path (MEP) [195]. The MEP is automatically identified employing the improved, simplified string method, which is implemented in our Workflow [225]. When an interface is formed by mating two isolated surfaces, the charge spilling out from each surface is typically removed from the near-surface region and accumulated at the middle of the interface. These charge displacement $\Delta\rho$ is calculated by subtracting from the total charge of the bilayer, the charge of the single layers as $\Delta\rho(\mathbf{r}) = \rho_{bilayer}(\mathbf{r}) - \rho_{up}(\mathbf{r}) - \rho_{down}(\mathbf{r})$. The total amount of charge that is redistributed $\rho_{redist} = \frac{1}{2z_o} \int_{-z_o}^{+z_o} |\Delta\rho| dz$, where z_o is half of the interlayer distance, has been shown to be directly related to the interfacial adhesion [202] and is analyzed according to the procedure described in Ref. [194].

5.3 Results and discussion

5.3.1 Structural and electronic properties

Black phosphorus is characterized by non-planar layers, where each P atom is covalently bonded with the other three P atoms (Fig. 5.1a). Having five valence electrons, each P atom presents a 3s lone pair that may also determine a minor covalent character in the interlayer bonds.

The nature of the layer-layer interaction is analyzed in Fig. 5.2a, where the charge displacement is calculated for the phosphorene bilayer. We observe that the charge spilling out from each surface is removed from the near-surface region and accumulates at the middle of the interface for all the employed

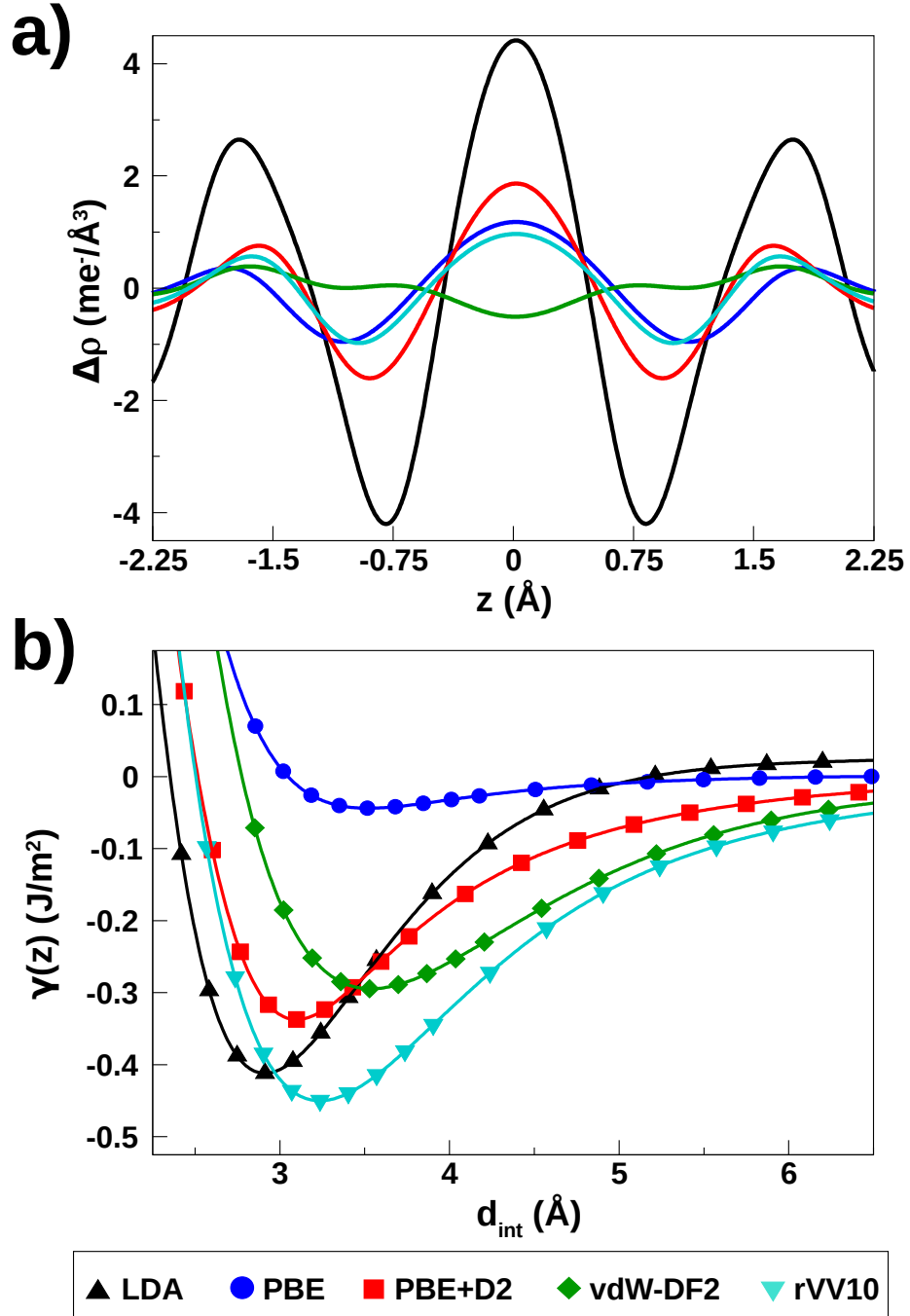


Figure 5.2: Planar average of the bilayer charge displacement (a) and binding energy as a function of the interlayer distance (b) for different XC functionals.

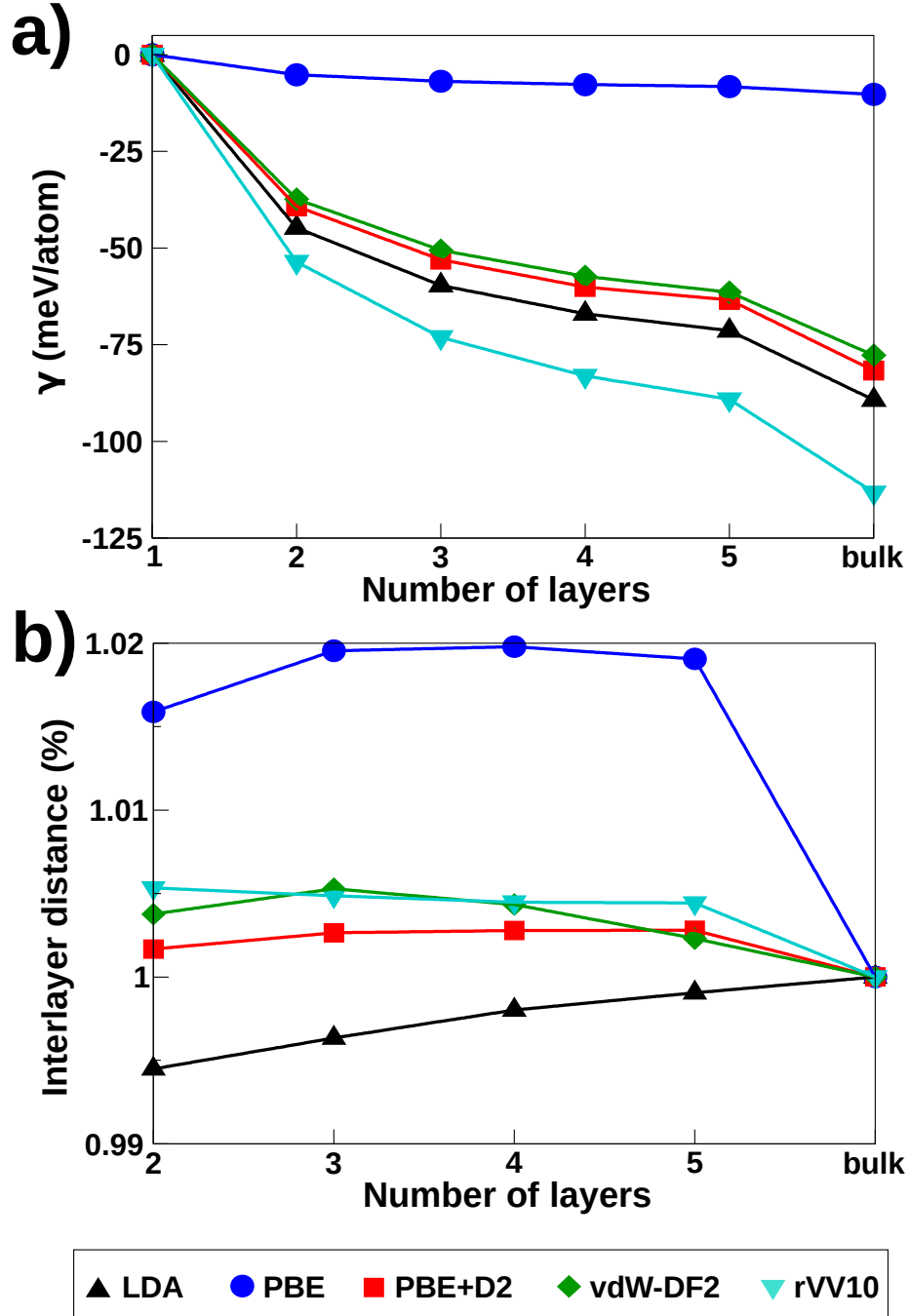


Figure 5.3: Interlayer binding energies (a) and interlayer distances (b) of multilayer phosphorene for different XC functionals. The interlayer distances (b) are normalized to the bulk values.

Bulk	a (Å)	b (Å)	c (Å)	d_{int}^{eq} (Å)
LDA	3.31 (3.27)	4.13 (4.33)	10.17	2.93
PBE	3.31 (3.30)	4.55 (4.61)	11.24	3.50
PBE+D2	3.32 (3.31)	4.42 (4.56)	10.46	3.09
vdW-DF2	3.39 (3.38)	4.74 (4.79)	11.35	3.52
rVV10	3.35 (3.33)	4.53 (4.62)	10.76	3.22
Theory ^{a,b,c,d,e,f,g,h}	3.24÷3.37 (3.298÷3.35)	4.07÷4.54 (4.52÷4.627)	9.88÷11.22	2.79÷3.36
Exp ^{i,j}	3.31	4.37÷4.38	10.47÷10.48	3.07÷3.11

^aRef. [328], ^bRef. [329], ^cRef. [330], ^dRef. [331], ^eRef. [332], ^fRef. [333], ^gRef. [334], ^hRef. [335], ⁱRef. [336], ^jRef. [337]

Table 5.1: Cell parameters and interlayer distances calculated for black phosphorus, compared with theoretical and experimental data from the literature. The cell parameters of single-layer phosphorene are reported inside the parentheses.

XC functionals. The only exception to this behavior is with vdW-DF2 functional, for which a weakly pronounced negative peak is observed. Even though this behavior is in agreement with previous Diffusion Monte Carlo calculations [338], this feature may be dictated by the different description of the nonlocal kernel term compared to rVV10 one, which is the other nonlocal functional considered in this study and leads to bulk lattice parameters significantly different from the experimental ones.

The charge accumulation here observed is in agreement with previous calculations performed both on black and blue phosphorous and employing the same XC functionals [338, 339], and suggests that the interlayer bonds possess a certain degree of covalency. Although Diffusion Monte Carlo simulations predicted a massive charge depletion, an interlayer covalent character can not be excluded *a priori* in layered materials. Indeed, recent Synchrotron X-ray diffraction experiments showed that in TiS₂, interlayer bonds have a more prominent covalent character than theoretical predictions [340]. TMDs materials present non-planar structures, as phosphorene, which may play a role in determining the nature of interlayer bonds.

The bilayer binding energy, calculated within different schemes, is represented as a function of the interlayer distance in Fig. 5.2b. As expected, both LDA and PBE are not able to describe the long-range energy contribution: the former shows a pronounced increase of energy with distance until unphysical positive values are reached above 5 Å, whereas the latter predicts atomically weak interlayer binding. By adding the Grimme-D2 correction to PBE, the description of long-range interactions improves, and the potential well becomes eight times deeper. The considered nonlocal functionals, i.e., rVV10 and vdW-DF2, predict stronger binding, especially at long range. The energy minimum of rVV10 is the lowest, whereas vdW-DF2 has a similar binding energy to PBE+D2 but shifted to higher distances. The relative positions between peaks and the depth of minima are in agreement with those reported by Shulenburger et al. [338].

The interlayer binding changes with the number of layers, as can be observed in Fig. 5.3a. In particular, for every functional adopted in this study, the layers have higher binding energy in absolute value when their number increases, progressively approaching the correspondent bulk energy. At the same time, as shown in Fig. 5.3b, the vdW schemes show a decrease in the interlayer distance when the thickness of the slab is increased, whereas the opposite behavior is observed for LDA. In the former approaches, the

values of the interlayer distances are the closest to their bulk counterpart with a coherent energy-distance trend, which leads to closer layers when the adhesion is higher. In multilayer structures, the two outermost pairs of layers are found to be closer to the neighboring layer than the bulky pairs due to the presence of a boundary. This effect is enhanced by the use of LDA, which tends to overbind structures, as confirmed by the higher charge accumulation that is predicted for bilayer phosphorene (Fig. 5.2a).

It is clear from this analysis that vdW corrections are crucial to adequately describing phosphorene films' structure and energy. The geometrical parameters calculated for black phosphorus and phosphorene are reported in Table 5.1 for all the analyzed methods. Despite its simplicity, PBE+D2 is found to provide the best agreement with experiments, and we thus adopt it for our subsequent analysis. Our group has made the same computational choice to investigate the tribological properties of graphene and TMDs [319, 201, 280]. This allows for a close comparison between these materials.

5.3.2 Tribological properties

To evaluate the potentiality of phosphorene as a solid lubricant, we calculate its interlayer slipperiness and compare it with multilayer graphene and MoS₂, which are commonly used to reduce the friction of solid interfaces. We consider two different layer orientations for the analysis of phosphorene tribological properties: a “parallel” orientation (Fig. 5.4a), where the zigzag and armchair directions of the two layers are aligned, and a “perpendicular” orientation (Fig. 5.4b) where the upper layer is rotated by 90° with respect to the lower one. This latter structure is modeled with a supercell having 4×3 in-plane size, where an initial geometrical mismatch of 0.5% is present between the two planar lattice vectors of the supercell. The mismatch has been reduced to 0.04% after we performed a variable-cell relaxation, where both the atomic positions and in-plane lattice cell vectors are optimized.

The calculated PES for both the parallel and perpendicular layer orientations are reported in Fig. 5.4. The relative position of the interfacial P planes is also represented from a top view for the stacking configurations corresponding to the minima and maxima of the PES.

The most energetically favorable stacking for the parallel orientation, AB, corresponds to a configuration where the atoms of the two interfacial P planes are in a hollow position and occupy the typical stacking of black phosphorus layers. This bilayer stacking is characterized by a binding energy of -0.35 J/m^2 and an interlayer distance of $3.1 \text{ \AA}$. The less favorable staking, AB', corresponds to an on-top disposition of the interfacial atoms, where the Pauli repulsion caused by the overlap of the electronic clouds is maximum, leading to an increase of binding energy and distance to -0.17 J/m^2 and $3.7 \text{ \AA}$, respectively. The transition from AB to AB' stacking can occur during interlayer sliding along the armchair direction, while it never occurs along the zigzag direction. This gives rise to a friction anisotropy, as can be seen from the energy profiles reported at the bottom of the PES in Fig. 5.4a. The derivative of the energy profiles makes it possible to obtain the ideal shear strength, which is the system's resistance to failure to shear. The calculated values of 1.5 GPa and 1.2 GPa along the armchair and zigzag directions confirm friction anisotropy.

This anisotropy has also been measured experimentally when sliding an Atomic Force Microscopy tip on phosphorene films $\simeq 30 \text{ nm}$ thick. The friction measured along the armchair direction always resulting higher than that measured along the zigzag direction [100]. This behavior has been attributed to the different values of Young's modulus along the armchair (27.2 GPa) and zigzag (58.6 GPa) directions [98], determining lower lateral deformation and friction along zigzag direction than the armchair direction. Here we add a new piece of information concerning the anisotropy of the interlayer sliding. This effect may play a relevant role, especially in the situation where the tip drags a phosphorene flake, and the sliding interface is shifted from the tip-phosphorene tribopair to the phosphorene-phosphorene one.

The sliding path with the highest statistical weight is the MEP that connects the PES minima passing

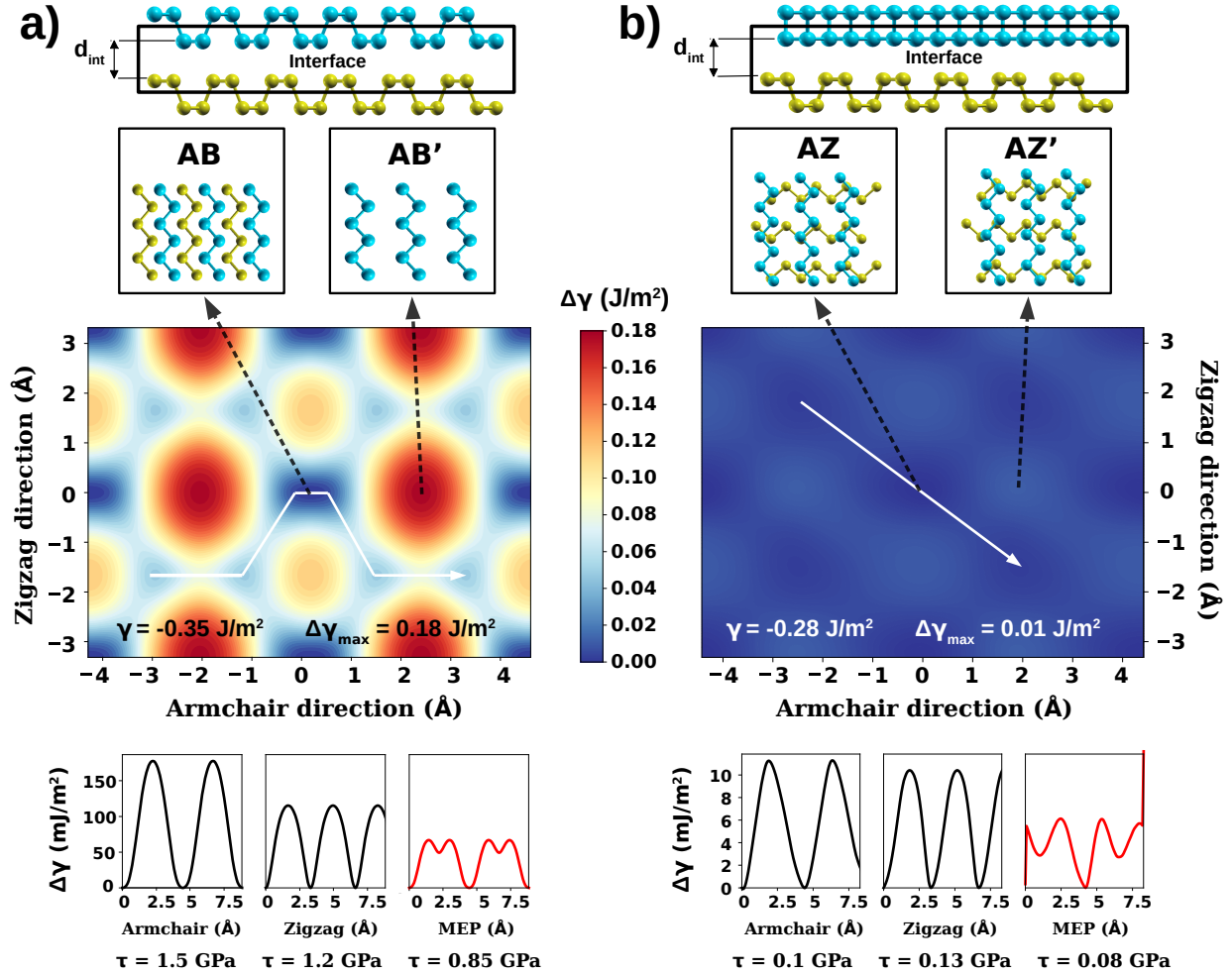


Figure 5.4: PES of bilayer phosphorene for the parallel orientation (a) and the perpendicular orientation (b). The disposition of the atoms mating at the interface is represented for relevant PESes stackings in the upper part of the picture. The MEPs are represented on top of the PESes with solid white lines, and the potential energy profiles along the MEPs are displayed in the bottom part of the picture. The values of adhesion energy γ , corrugation $\Delta\gamma_{\text{max}}$, and shear strength τ along the armchair, zigzag, and MEPs are also reported.

through the saddle points. The MEP is marked in white on the 2D plots of the PESes in Fig. 5.4, and the corresponding energy profile is described by a solid red line below, with an associated shear strength of 0.85 GPa.

	$d_{\text{int}}^{\text{eq}}$ (Å)	γ (J/m ²)	$\Delta\gamma_{\text{max}}$ (J/m ²)	τ_{MEP} (GPa)
Graphene ^{a, b}	3.31÷3.35	-0.26÷-0.19	0.06	0.14÷0.21
MoS ₂ ^{a, c}	3.08÷3.10	-0.30÷-0.27	0.10	0.16÷0.50
Phosphorene AB	3.09	-0.35	0.18	0.85
Phosphorene AZ	3.31	-0.28	0.01	0.08

^aRef. [124] ^bRef. [341] ^cRef. [342]

Table 5.2: The tribological properties calculated for phosphorene are compared with those of graphene and MoS₂. The interlayer distance $d_{\text{int}}^{\text{eq}}$, the adhesion energy γ , the corrugation energy $\Delta\gamma_{\text{max}}$ and the shear strength along the MEP τ_{MEP} are reported.

The PES obtained for the perpendicular orientation appears flat when compared to the PES for the parallel one on the same energy scale, indicating that all the relative lateral configurations in the former case are almost energetically indistinguishable (Fig. 5.4b). In particular, the minimum and maximum energy stackings referred to as AZ and AZ' in Fig. 5.4b, differ only by 0.01 J/m² being ten times smaller compared to the parallel orientation. The friction anisotropy almost disappears, and the shear strength along the MEP is reduced by one order of magnitude, becoming equals to 0.08 GPa. This strongly points at the existence of a structural superlubricity that may result in ultralow friction coefficients, as evidenced in a classical simulation of a sliding tip on phosphorene [343]. As can be observed in Fig. 5.5, the AZ (AB') configuration is less stable than the AB configuration by 20% (51%). This smaller decrease in the adhesion energy for the AZ stacking is nevertheless accompanied by a reduction of one order of magnitude in the corrugation and shear strength.

In Table 5.2 the interlayer tribological properties of black phosphorus are compared with those of graphite and MoS₂ [341, 342, 124]. The adhesion energy and shear strength of the parallel orientation are of the same order of magnitude compared to other 2D materials, being only slightly larger than those of MoS₂. Instead, the perpendicular orientation presents resistance to sliding of about one-half compared to graphene. These results confirm that phosphorene may be successfully employed as a solid lubricant, suggesting possible applications for this material in nanotribological devices operating in vacuum or dry conditions, as well as in aerospace environments, due to its instability when exposed to air [344]. Phosphorene has been successfully employed as a lubricant additive in water-based solutions, giving rise to a superlubrication regime [99]. Since the parallel and perpendicular orientations present similar stability, we expect the presence of both orientations between dispersed phosphorene flakes, and this may play a significant role in achieving a superlubricant regime.

A similar electronic charge distribution between the PES maxima and minima results in a slammer PES corrugation, as explained in Ref. [202]. It is evident from the planar average of the total electronic charge reported in Fig. 5.6 that the charge rearrangement occurring when moving from the minima to the maxima is more consistent for the parallel layers than for the perpendicular ones as the amount of charge at the middle of the interface is much higher in AB than AB', while it is almost the same in AZ and AZ'. We also observe a superimposable charge displacement for this configuration, reported in Appendix D.

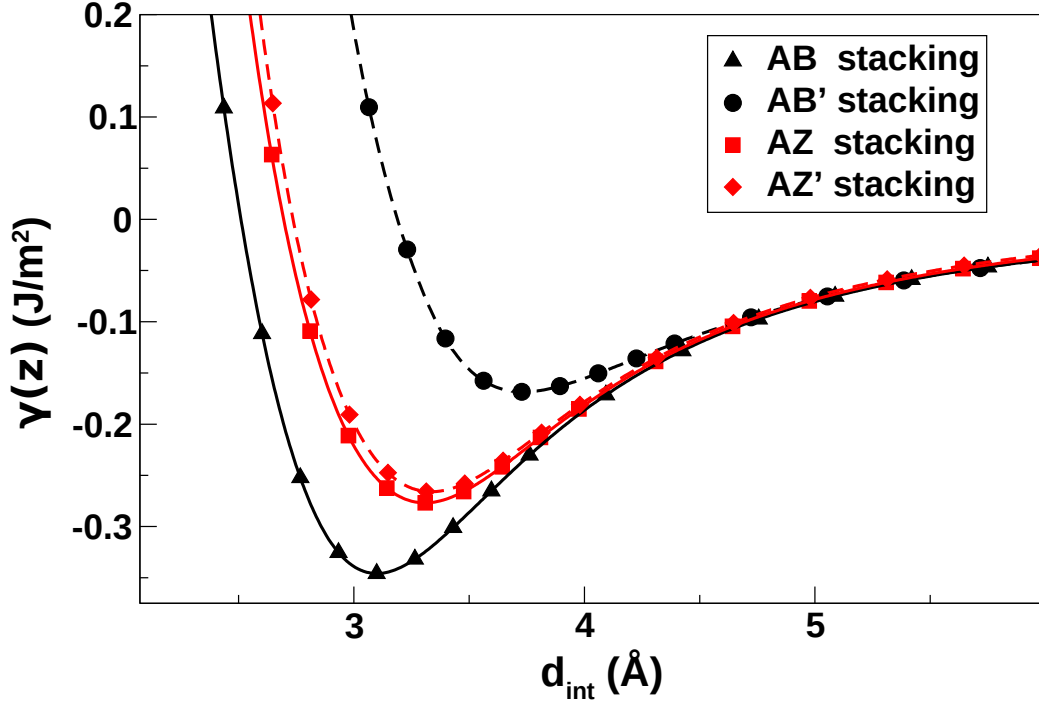


Figure 5.5: Interlayer binding energy for the parallel orientation (AB, AB' stackings) and the perpendicular orientation (AZ, AZ' stackings).

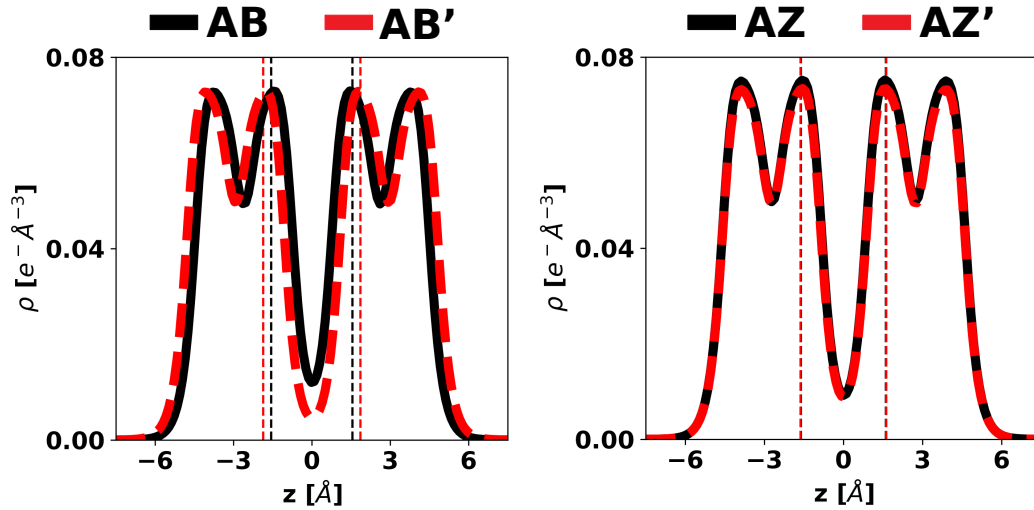


Figure 5.6: Electronic charge density integrated along the xy plane for the minimum and maximum stacking configurations of the parallel (left) and perpendicular orientations (right).

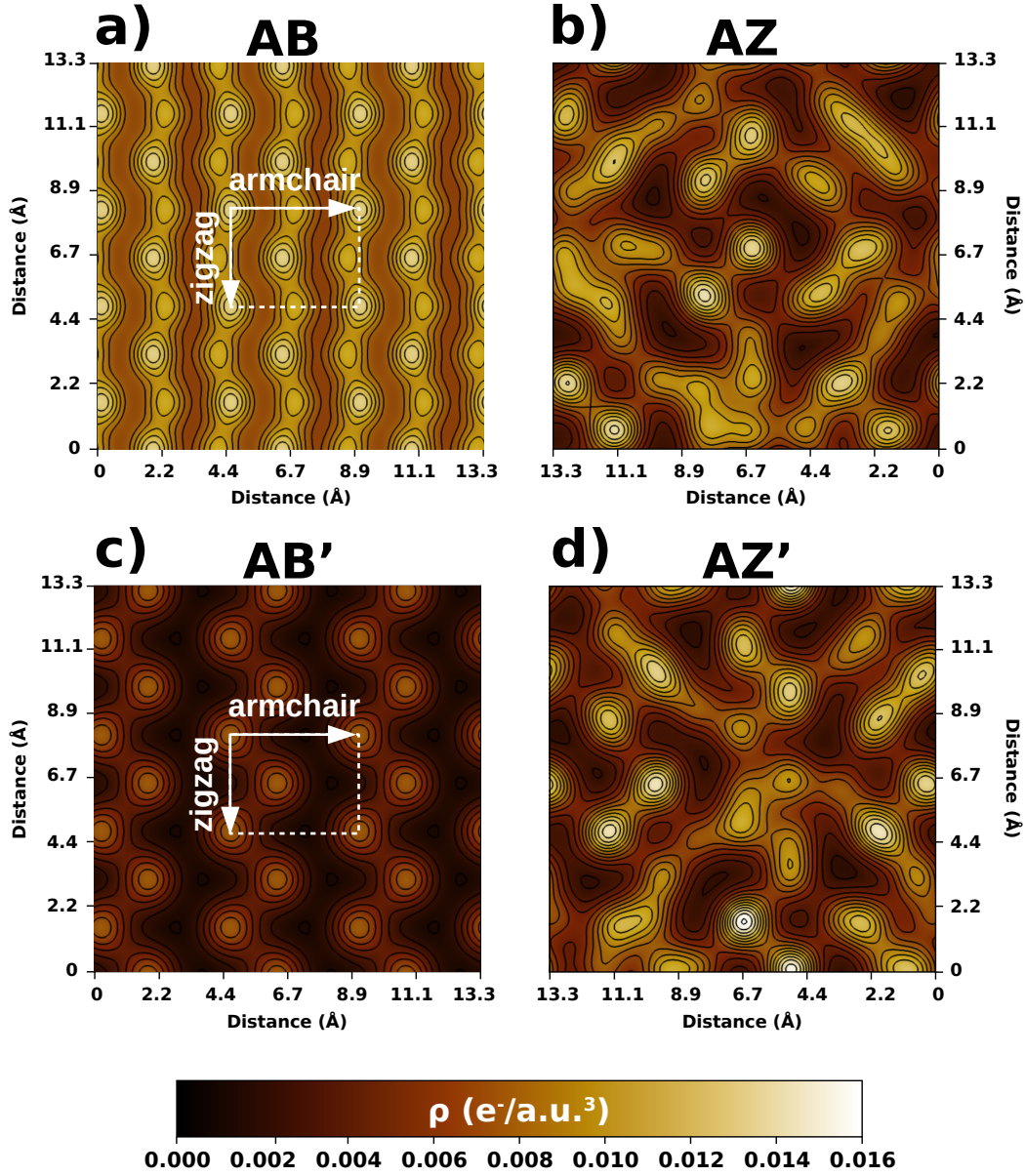


Figure 5.7: The electronic charge density on the xy plane at the middle of the interlayer region for the AB (a), AZ (b), AB' (c), and AZ' (d) stackings. The charge for the AB and AB' configurations is represented on a replicated 4×3 cell in order to compare it with the supercell adopted for the AZ and AZ' ones. Phosphorene unit cell is also reported on the plots. Charge density is expressed in $e^-/\text{a.u.}^3$ units.

A possible explanation of the superlubricant behavior of the AZ stacking can be found looking at the distribution of the electronic charge at the interface, as can be seen in Fig. 5.7a–d, where the total charge present on a plane located at the middle of the interface is represented. The AB stacking shows a nonuniform electronic charge distribution, characterized by horizontal strips connecting the mated atoms. On the contrary, in AZ stacking, the charge is present only nearby the atoms of the two layers in contact and is almost zero in the interstitial regions. This strong localization determines the formation of sparse charge bridges between the two layers. Due to the incommensurate disposition of the phosphorene atoms within the layers, this grid-like pattern is maintained for all the possible relative lateral shifts between the two layers, making all the lateral configurations energetically equivalent.

5.4 Conclusion

In this study, we investigated for the first time to our knowledge the static tribological properties of phosphorene by means of *ab initio* calculations. We compared different exchange-correlation schemes in describing the structural and electronic properties of films with different layers and found that PBE+D2 describes black phosphorus in closest agreement with experiments.

The analysis of the interlayer shear strength showed that black phosphorus has similar tribological properties to other layered materials commonly used as solid lubricants. Moreover, a considerable reduction in the PES corrugation and shear strength has been detected for a perpendicular orientation of the layers, where the armchair direction is aligned to the zigzag one. The stability of this superlubric configuration of the layers is similar to that of the parallel orientation; thus, flakes containing both phases are expected in phosphorene-based lubricant solutions. The microscopic origin of the observed structural superlubricity has been explained by analyzing the electronic charge at the interface. The perpendicular layers are bounded by several localized bonds where the charge is localized. In this situation, all the relative lateral positions become equivalent from the energetic point of view, and sliding can occur quickly on the flat PES. Our study represents a relevant step towards the complete understanding of the atomistic origin of phosphorene lubricant properties, which can be of paramount importance for the tribological community and applications in several micro and nanodevices.

Chapter 6

Lubricating effects of phosphorene and MoS₂ on iron compared to graphene

6.1 Motivation

According to the International Energy Agency, the most impacting technologies to reduce CO₂ in the near future should be related to end-use energy efficiency [345]. It has been estimated that 23% of the world's total energy consumption is due to friction, and this huge energy waste can be reduced up to 40% in the next 15 years by improving the tribology technologies. Nowadays, these technologies are based on materials; thus, the design and development of lubricant and coatings to reduce friction and wear in machine components is of paramount importance for energy efficiency and CO₂ emission reduction on a global scale [2].

Two-dimensional (2D) materials, thanks to the weak interlayer interaction and surface chemical stability, present remarkably low friction properties. In recent years, significant advances have been made in the scientific research and industrial applications of anti-friction, anti-wear, and lubrication of 2D materials, both at the nano- and macro-scale.

Among the most recently considered 2D materials, phosphorene -a single layer of black phosphorus [346, 347, 100, 348, 99] - has shown very promising properties for reducing friction. Superlubricity has been observed using treated black phosphorus nanosheets in an aqueous solution for a wide range of sliding velocities, additive concentrations, and applied pressures [99]. Even if phosphorene flakes undergo ambient degradation, they seem to maintain their lubricating properties [347] thanks to the strong interactions between P-OH groups and water molecules [346]. Superlubricity of phosphorene has also been identified at the nanoscale, where a perpendicular orientation of the layers has been shown to reduce the interlayer binding energy and the shear strength by one order of magnitude with respect to the standard layer orientation [349]. Phosphorus is also a key element for extreme-pressure additives included in the engine oils. As shown by *in situ* spectroscopy analysis, the capability of organophosphorus additives to reduce the friction coefficient of steel-on-steel is related to the tribologically-induced formation of iron phosphite [104, 350]. The P-rich tribofilm is formed thanks to the release of elemental phosphorus by the dissociative chemisorption of the molecules [350], promoted by the tribological conditions, as shown by *ab initio* molecular dynamics simulations [351, 352]. The lubricating effect of adsorbed phosphorus resides in its ability to form P-P bonds that reduce the reactivity of the iron substrate, especially at high coverage [353].

The above findings suggest that phosphorene may be a good lubricant for steel. Here we use first-principles calculations to explore the capability of phosphorene to chemisorb on iron and reduce its adhesion and friction. A similar analysis is performed for MoS₂, a well-known solid lubricant, which can also be formed on steel as a product of tribochemical reactions involving lubricant additives, such as molybdenum dithiocarbamates [354, 355, 356]. The results are compared with graphene, which we have previously shown to be able to reduce iron adhesion and shear strength efficiently [357, 280], in agreement with the experimental evidence [358, 359, 360].

Using density functional theory (DFT) calculations, we show that phosphorene chemisorbs on iron more strongly than MoS₂ and graphene [280]. Moreover, phosphorene can outperform these two well-established solid lubricants at low coverage conditions. The reason resides in the ability of the single phosphorene layer to split into two separate atomic planes once intercalated at the iron interface. Such peculiar behavior, governed by the interplay between the Fe-P and P-P interactions, is particularly advantageous for obtaining the simultaneous passivation of the substrate and the countersurface, with a consequent drop of adhesive friction.

6.2 Methods

We performed DFT simulations employing the Quantum Espresso software [320, 321]. The electronic wave functions are expanded on a plane-wave basis set, and ultrasoft pseudopotentials are used for describing the ionic species, including the core electrons [322]. We employed the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) parameterizations as exchange-correlation functional [263]. London dispersion forces are kept into account by adopting the D2 scheme [324], using the value for the s_6 scaling factor suggested in the original paper ($s_6 = 0.75$). This type of dispersion scheme gave excellent results for computing not only organic [361, 362, 363, 364, 365] but also inorganic materials properties [366, 367]. Furthermore, PBE-D2 provides a good description of black phosphorus and phosphorene interlayer energy [338]. Previous studies performed in our group regarding the tribological properties of graphene and transition metal dichalcogenides demonstrated that PBE-D2 can accurately describe interlayer sliding properties [319, 124, 93, 280, 349]. The kinetic energy cutoff to expand the wave function and the charge densities are 30 Ry and 240 Ry, respectively, for the phosphorene on iron. Instead, for MoS₂ on iron, the *ecutwfc* and *ecutrho* values are set to 40 Ry and 320 Ry, respectively. All the different systems were constructed with at least 15 Å of vacuum between vertical replicas.

We considered the (110) Fe surface, which is the most stable surface of iron [280, 125]. The adopted unit cell is orthorhombic with cell vectors equal to a and $\sqrt{2}a$, where a is the iron bulk lattice parameter (body-centered cubic unit cell) relaxed at the PBE-D2 level ($a=2.85$ Å). To reduce the mismatch between 2D materials and iron, supercells were taken into consideration. The layer material is slightly deformed to fit into the considered supercell, while the Fe lattice is kept at equilibrium. For matching phosphorene and iron, a $(3 \times 4\sqrt{2})$ iron supercell and a (2×5) phosphorene supercell were adopted, where the mismatch between iron and phosphorene is 2.6% and 2.3% for the a and b cell vectors. A $(2 \times 4\sqrt{2})$ iron supercell is instead adopted for iron for matching a $(\sqrt{3} \times 5)$ MoS₂ supercell with a corresponding mismatch of 2.9% and 1.8% along the sides of the supercell. The iron surface is simulated using two layer-thick slabs (one A-B Fe layer) to reduce the computational costs as much as possible. This model simplification, already adopted in previous calculations [368], is dictated by the computational cost of the presented calculations. It is justified by the small energy difference observed when considering two instead of three layers which corresponds to a small fraction ($\sim 2\%$) of the phosphorene chemisorption energy (see supporting information).

The iron interfaces were constructed using the same supercells adopted for the surface calculations. In this case, two iron slabs were included in the supercell. One or two layers of the 2D material were intercalated within the iron slab, depositing each layer at an initial distance of 1.5 Å from the metal surface. The interface geometry was then allowed to relax to the equilibrium configuration. MoS₂ presents two possible different equilibrium stacking [319]. In the current work, the 2L-R0 stacking was adopted. We also evaluate the potential energy surfaces (PES) of the different sliding interfaces. It describes the adhesion energy between two surfaces in contact as a function of their relative lateral position, $\gamma(x, y)$. The PES is calculated by shifting the upper surface to different lateral positions with respect to the lower

surface, defining a grid of points with ~ 0.7 Å spacing along the x and y directions. The equilibrium separation between the layers is obtained for every lateral position by optimizing the z degree of freedom while keeping the x and y coordinates fixed. The PES is calculated by interpolating the adhesion energies at each grid point with radial basis functions [194, 125]. On top of the PES, it is possible to estimate the minimum energy path (MEP), which connects the PES minima passing through saddle points and constitutes the most favorable sliding path. The ideal shear strength is then calculated along the MEP [195]. The latter estimates the maximum shear resistance and is strictly connected to the static friction of the sliding interface. The MEP has been obtained with the simplified string method [225], as implemented in a workflow for throughput interfaces developed by our group [194, 125]. To understand the connection between adhesive friction and interfacial electronic properties, we evaluate the charge redistribution occurring in the interfacial region, as described in Ref. [356] and later in the text. To compare different systems, the charge redistribution is normalized by the average number of electrons per atom.

6.3 Results and discussion

6.3.1 Chemisorption of phosphorene and MoS₂ on iron

As a first step in our analysis, we have evaluated the capability of the 2D material to adhere to the metallic substrate. To this aim, we have deposited one layer on the Fe(110) surface at an initial distance of 1.5 Å. After the structural optimization, the adhesion of the layer to the metallic substrate is evaluated as:

$$E_{adh} = (E_{tot} - E_{layer} - E_{iron})/A \quad (6.1)$$

where E_{tot} is the energy of adsorbate system, while E_{layer} and E_{iron} are the energies of the isolated layer and the substrate, respectively, A is the in-plane area of the supercell. The relaxed structures are reported in Fig. 6.1.

The calculated binding energies and distances reported in the picture indicate that phosphorene strongly chemisorbs on iron, presenting an adhesion energy about three times larger than that of graphene, which is -0.89 J/m². The stronger chemisorption of phosphorene with respect to graphene on transition metals surfaces has also been observed in Ref. [369]. We noticed that upon adsorption, the distance between the two atomic planes forming the phosphorene increases by 4.7% with respect to its value in the isolated layer. This indicates that the strong interaction between the layer and the substrate weakens the intralayer interaction. The adhesion energy of MoS₂ is in-between those of graphene and phosphorene, i.e., -1.60 J/m². In this case, the structure of the 2D material is preserved with a vertical expansion of just 0.6% with respect to the isolated layer.

6.3.2 Phosphorene and MoS₂ at the iron interface

The adhesion energies of phosphorene and MoS₂ on iron indicate that both the materials can adhere to the native iron surface and resist against the peeling-off by a rubbing countersurface better than graphene. As a next step, we evaluated the friction-reduction capability of the thin coatings. Therefore, we constructed an interface composed of two iron slabs, which mimics a nano-asperity contact, and calculated the interfacial adhesion both in the absence and in the presence of intercalated layers. In the second case, we first covered the substrate and then both the substrate and the countersurface. The optimized structures of the considered interfaces are reported in Figure 6.2, where the results previously obtained for graphene [280], are also shown for comparison. A summary of the calculated data is also reported in Tab. 6.2 and Figure 6.3.

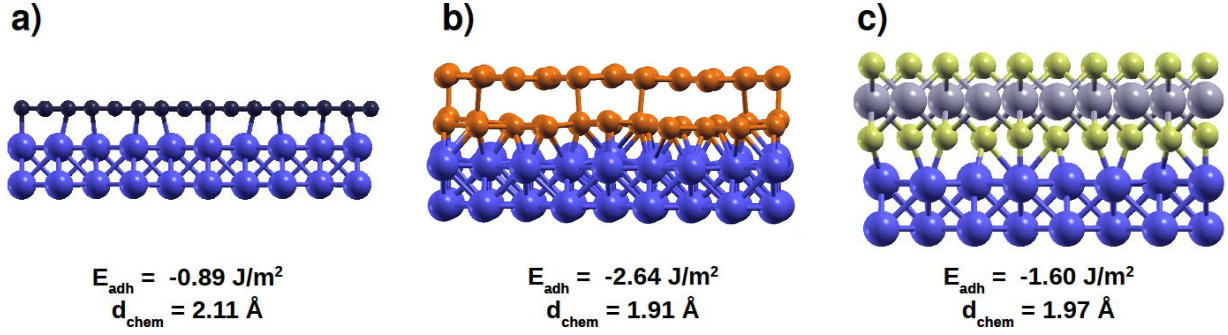


Figure 6.1: Binding geometries of graphene (a), phosphorene (b), and MoS₂ (c) on native Fe(110) surface. The equilibrium chemisorption distance, d_{chem} , is defined as the distance from the bottom atomic plane of each 2D layer to the underlying iron substrate.

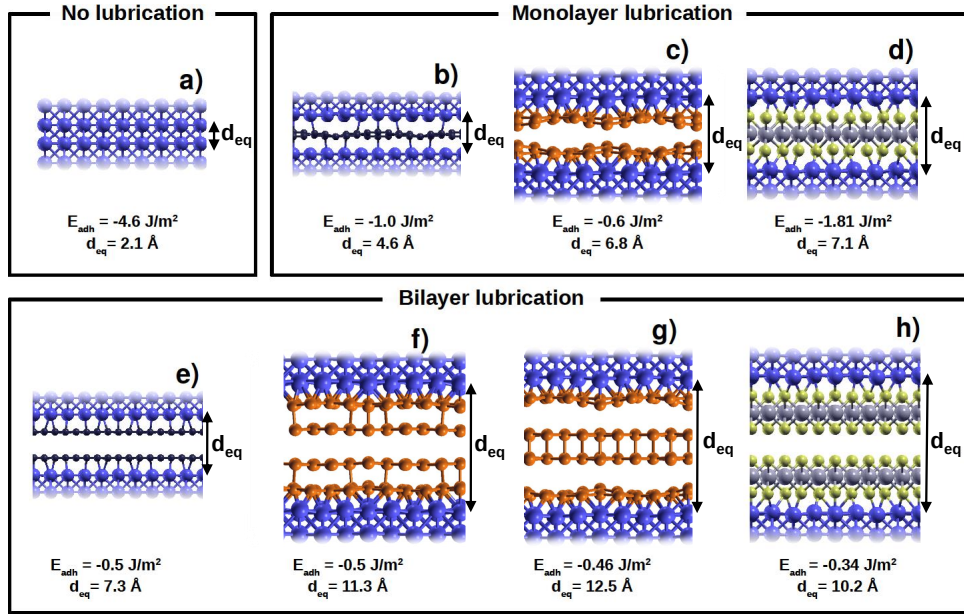


Figure 6.2: The optimized structure of the interface obtained by mating two native iron surfaces (a) is compared with those obtained by mating a native surface with a coated substrate (b-d) and two coated surfaces (e-h). The interfacial adhesion, E_{adh} , and metal-metal separation, d_{eq} , are also reported.

	one layer	two layers
Graphene [280]	-1.0 (78%)	-0.5 (89%)
Phosphorene	-0.6 (87%)	-0.5 (89%)
MoS_2	-1.8 (61%)	-0.3 (93%)

Table 6.1: Adhesion energies (in J/m^2) of the iron-iron interface intercalated with one layer and two layers of 2D materials. The percentage reductions of the adhesion energy with respect to the clean iron-iron interface (-4.6 J/m^2) are reported in brackets.

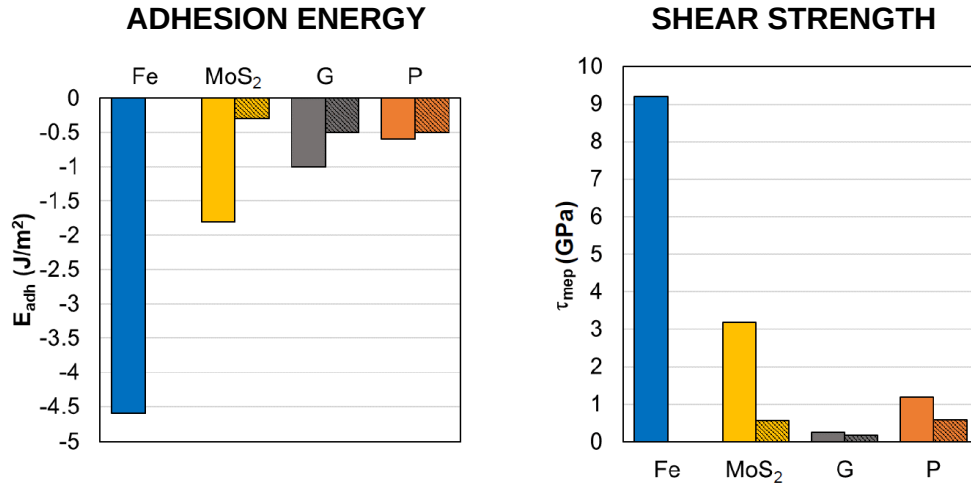


Figure 6.3: Adhesion energies and shear strengths for the bare and lubricated iron interfaces. Lighter colors indicate single intercalation and darker colors double intercalation.

The adhesion energy calculated for the most stable configuration of the clean iron interface, corresponding to the bulk stacking sequence, is -4.6 J/m^2 , i.e., twice the energy of the Fe(110) surface. The intercalation of a layer of a 2D material produces a reduction of the adhesion energy, see Tab. 6.2 and Fig. 6.3. Interestingly, when a phosphorene single layer is intercalated at the iron interface, it spontaneously dissociates into two thin atomic planes that simultaneously passivate the two iron surfaces in contact, see Figure 6.2 c). Therefore, the adhesion energy between the two P-saturated iron surfaces becomes as low as -0.6 J/m^2 , corresponding to one-eighth of the adhesion energy between two pristine iron slabs. This result indicates that phosphorene has great potential as a solid lubricant for iron/steel in dry conditions.

The adhesion reduction of phosphorene is more pronounced than that of MoS₂ and single graphene layers, as can be seen from Fig. 6.3. Both MoS₂ and graphene have a passivating effect different from phosphorene. They do not break apart with an overall limited structure deformation. In this case, the coating interacts with the countersurface as it interacts with the substrate, making the mechanism of adhesion reduction less efficient.

To get insights into the interaction between the coating and pristine countersurface, we computed the adhesion as a function of the separation of the surfaces (Fig. 6.4). The energy values in the minimum correspond to the adhesion values reported in Tab. 6.2. The adhesion-vs-separation curve obtained for the interface with an intercalated phosphorene layer presents a shallow minimum at a large distance ($z > 3 \text{ \AA}$), indicating that the surfaces interact by weak vdW forces. MoS₂ and graphene produce a deeper minimum located at a smaller distance ($z \sim 2 \text{ \AA}$), indicating the presence of chemical bonds between the 2D material and the countersurface. At this level of coverage, only phosphorene is capable of shielding chemical interaction across the interface.

The energy of adhesion between surfaces has roots in electrons interactions. Upon interface formation, the electronic density is perturbed due to bond formation and/or electrostatic interactions. These effects induce a redistribution of the electronic charge, the amount of which was found to be proportional to the adhesion in Ref. [202]. To investigate this phenomenon, we reported the charge redistribution, i.e., the difference between the total charge of the interface and the sum of the charges of the separated surfaces, as a function of the surfaces separation, z , in Fig. 6.5. It is evident that the larger redistribution occurs at the interfacial region, being the most perturbed when the two surfaces are mated. In this region, we calculated the integral of the charge redistribution, i.e., ρ_{redist} , which is reported in Tab. 6.2. This quantity well correlates with E_{adh} , uncovering the link between the charge redistribution and adhesion [202].

We estimated the capability of the considered 2D materials in reducing the resistance to sliding by calculating the ideal interfacial shear stress, i.e., the static friction force per unit area. The interface failure against sliding most likely occurs along the minimum energy path (MEP), which connects the minima passing through saddle points of the potential energy surface (PES). The calculated PESes are reported in Fig. 6.6, while the maximum resistance force along the MEP, τ_{mep} , is reported in Tab. 6.2. Our results indicate that a single layer of 2D material can effectively reduce the resistance to sliding of iron by screening the metal-metal interaction. The presence of the coating keeps the mated iron surfaces at non-bonding distances.

We then considered two layers of material intercalated at the iron interface to mimic a lubricated contact where both the substrate and the countersurface are covered by the solid lubricant. In these conditions, the adhesion energies are further reduced, see Fig. 6.3, and the adhesion-vs-separation curves resemble those of isolated bilayers of 2D materials, see Fig. 6.4b. This is a consequence of the full passivation of both iron surfaces, which are now distanced by at least $7 \text{ \AA}$ and present a weak interaction. The charge redistribution occurring at the interface is strongly reduced, as well as the adhesion energy, see Fig. 6.5.

The adhesion reduction obtained by including a second phosphorene layer between two iron surfaces is smaller compared with MoS₂ and graphene, see Fig. 6.3 and Fig. 6.4a. Indeed, as mentioned before, thanks

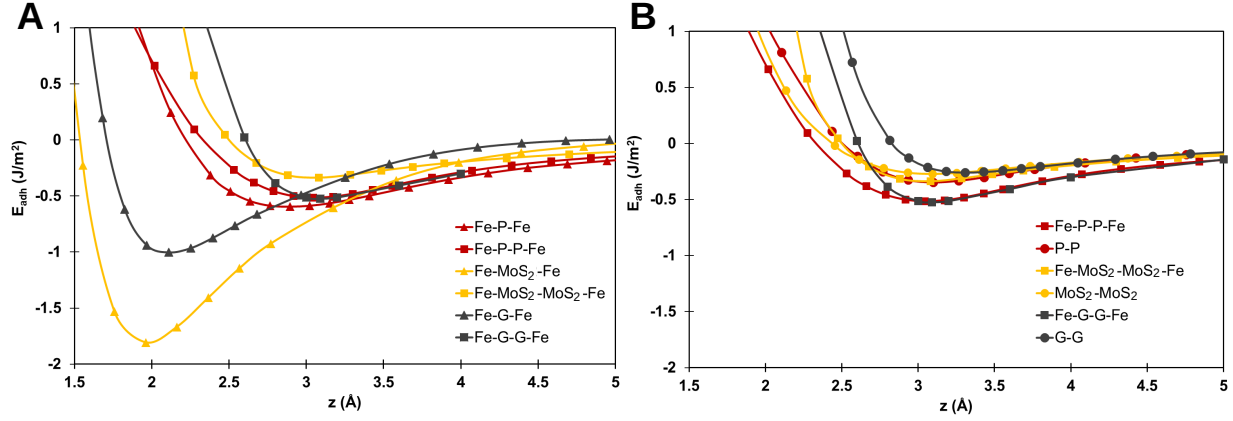


Figure 6.4: Adhesion energy profile along the perpendicular direction to the interface for A) single and double 2D-material intercalated iron-iron interfaces, B) double 2D-material intercalated iron-iron interfaces and bare 2D-material/2D-material interfaces.

to its structure, a single phosphorene layer can provide two separated atomic-thin coatings to passivate almost completely both the surfaces at the interface, making the additional coating of the countersurface not necessary. The ideal shear strength τ_{mep} follows the trend of the adhesion energy. The most efficient in lubrication is graphene, with τ_{mep} equal to 0.17 GPa [280].

	d_{eq} (Å)	E_{adh} (J/m ²)	ΔE_{adh} (J/m ²)	τ_{mep} (GPa)	ρ_{redist} ($10^{-3} e^-/\text{\AA}^3$)
Fe-Fe	2.1	-4.60	1.60	9.20	21
Fe-P-Fe	6.8	-0.60	0.24	1.18	0.26
Fe-P-P-Fe	12.5	-0.46	0.10	0.59	0.22
Fe-MoS ₂ -Fe	7.1	-1.81	0.27	3.18	0.90
Fe-MoS ₂ -MoS ₂ -Fe	10.2	-0.34	0.11	0.57	0.04
Fe-G-Fe	4.6	-1.00	0.10	0.24	0.97
Fe-G-G-Fe	7.3	-0.50	0.08	0.17	0.20

Table 6.2: Comparison of the tribological figures of merit of the selected lubricant coatings. Fe-X-Fe and Fe-X-X-Fe stands for single and double intercalation, with X= P, MoS₂ and G. P stands for Phosphorene, and G for graphene.

6.4 Conclusion

Our results uncover promising properties of phosphorene as a solid lubricant for iron/steel. Phosphorene strongly chemisorbs on native iron surfaces, showing higher binding energy than MoS₂ and graphene [280]. The higher is the adhesion between the lubricant and the substrate, the more stable is the surface passivation, which can resist the peeling-off produced by rubbing. Furthermore, our simulations indicate that a single layer of phosphorene can passivate both the substrate and countersurface, thanks to its peculiar structure that splits into two atomic-thin coatings upon intercalation. In this way, phosphorene is expected to reduce

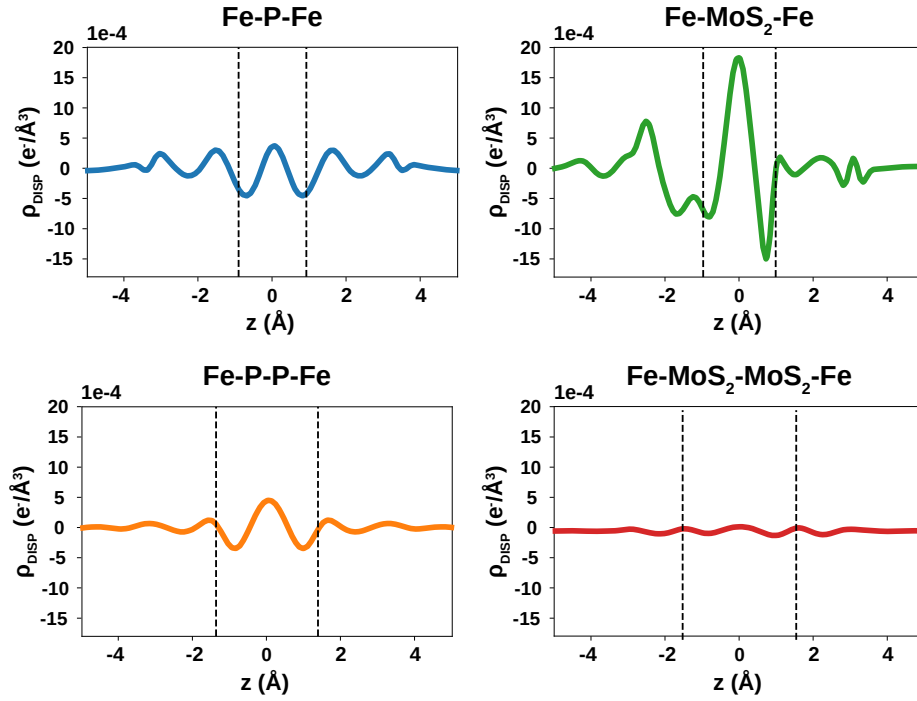


Figure 6.5: Charge displacement at the interfaces under study. Dotted lines indicate the boundaries of the interfacial region. The charge redistribution is calculated by integrating the $\rho_{DISP}(z)$ curve in this interval.

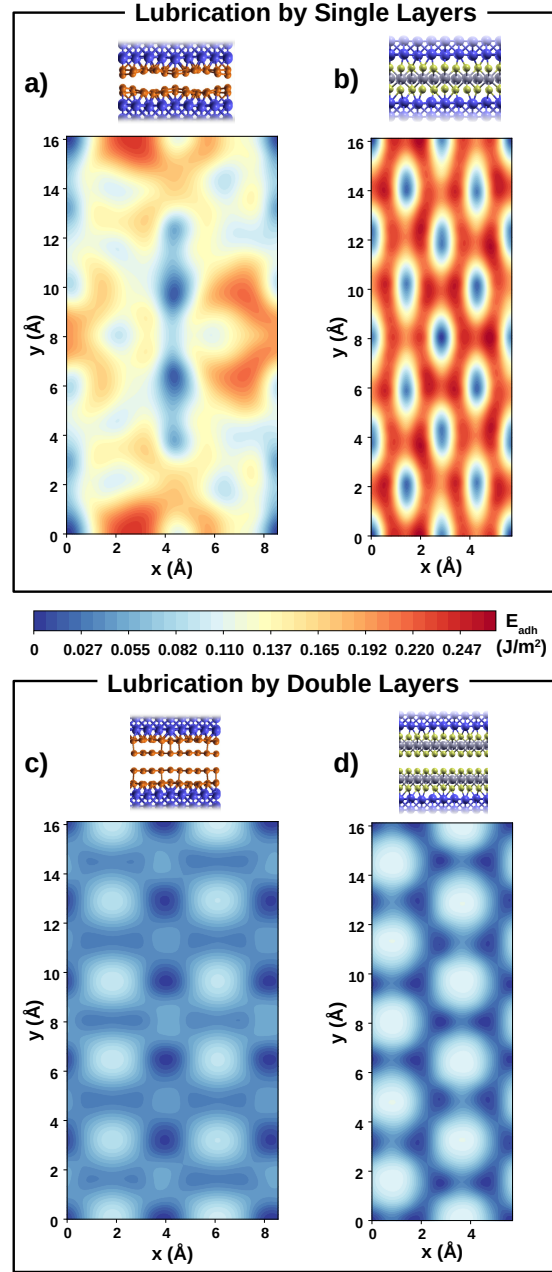


Figure 6.6: Potential Energy Surface of a Fe(110)-Fe(110) interface, passivated by a monolayer of phosphorene (a) and MoS₂ (b), and by a bilayer of phosphorene (c) and MoS₂ (d), intercalated at the interface. For the sake of comparison, all the PES are represented on the same energy scale.

adhesion more efficiently than other well-established solid lubricants at low concentrations.

Chapter 7

Conclusions

The aim of this thesis is to develop and supply advanced techniques and tools to study tribology with computer simulations. The benefit of using these methods, even in a field closely related to experiments like tribology, is to accelerate the discovery of fundamental properties of materials for technological applications. Laboratory measurements are frequently complex and challenging to automate. They often necessitate multiple techniques that make measurement and interpretation of the experiments difficult. On the contrary, computational methods allow a higher control over the system under investigation. They provide valuable insights into friction and lubrication at solid interfaces by uncovering the atomistic mechanisms underlying these phenomena.

In this work, a software package was created to study tribology. It assembles in a unique scientific code all of the computational steps required to perform a full analysis of the properties of an interface. The creation of the software is the result of a long work process necessary to implement all its features and refine them. The goal was to create a flexible and modular software structure, which allows the easy insertion of new possible modules in the future. The program can calculate the adhesion and shear strength of solid interfaces from first principles. All the data obtained during a high-throughput study, often concerning hundreds of materials, are collected in small databases to be easily shared with the scientific community. A typical procedure for performing a tribology study is structured in three steps, as follows:

- Retrieve a bulk from an online material database and converge its computational parameters.
- Generate a slab along a specific direction and converge its thickness by calculating how surface energy changes with the number of layers.
- Combine two slabs to form an interface and evaluate its tribological properties. The current implementation allows the combination of any pair of crystalline materials.

One of the most relevant tribological indicators that can be computed in a high-throughput procedure is certainly the potential energy surface (PES). It is a 3D function that maps how the adhesion energy between two surfaces in contact changes as a function of their lateral position. The calculation of the PES opens the way to study many other interesting interfacial properties, such as adhesion, friction characteristics, and dislocation properties.

The software was used to perform a high-throughput study on the solid interfaces formed by the elements of the periodic table. About one hundred interfaces consisting of two equivalent crystalline surfaces were studied for the elements crystallizing in the bcc, fcc, and hcp structures. The study revealed the existence of a close connection between the adhesive friction and the chemical interactions between the surfaces. Another major finding of this study is that the shear strength τ and cleavage strength σ scale with the adhesion energy γ . In particular, $\tau \propto \gamma^{3/2}$ and $\sigma \propto \gamma$. From these relations, it emerges that the adhesion energy is a good descriptor for assessing the resistance property of an interface. This is critical to speed up the computational research since shear and cleavage strengths are harder to compute, whereas adhesion requires a few simulations. Furthermore, the ratio between the shear and the cleavage strength is provided as a

good predictor of the material failure mode that is likely to occur at the interface. Materials with a high ratio are more likely to fail in brittle cleavage, whereas a low ratio characterizes ductile failure.

Another significant achievement of this thesis concerns the development and application of a multiscale technique connecting first-principle molecular dynamics to Green's Function. This method allows for the realistic description of the thermal reservoir, the mechanical stresses, and the energy dissipation due to phonons in molecular dynamics simulations. It has been applied to calculate the kinetic friction coefficient of two diamond semi-infinite bulks in contact. The friction showed to be dependent on the degree of passivation of the diamond surfaces. Ultralow coefficient of friction of the order of 0.01 was observed for an interface fully saturated with hydrogen atoms. On the contrary, covalent bonds form across the interface below a threshold coverage, thus causing surface interlocking. This research also demonstrated that the sliding path deviates from the minimum energy path, which is the most likely trajectory in equilibrium conditions. This implies that the ability of the system to follow the MEP and thus experience lower frictional forces is proportional to the magnitude of the shear stress applied. Therefore, only for sufficiently low velocities, the motion can be approximated by a sequence of quasi-static equilibrium configurations, with the MEP having the highest statistical weight.

Another important contribution of this thesis is related to studying the lubricating properties of phosphorene as a solid lubricant. Phosphorene is an innovative 2D material that possesses great potential for tribological applications due to its layered structure and for the capability of phosphorus to reduce friction and adhesion in steel-steel contacts. This work aims to unravel the physical origin of phosphorene properties by using density functional theory simulations. The analysis of the static friction between two phosphorene sheets in contact revealed that layers stacked with the same orientation (armchair-armchair and zigzag-zigzag) are slippery as common solid lubricants, as MoS₂ and graphite. On the contrary, the armchair-zigzag orientation shows a remarkable superlubricity, with a reduction of one order of magnitude for the shear stress. The microscopic origin of such a superlubric phase is attributed to the peculiar localization of electronic charge at the layer interface.

An interesting open question was how the properties of phosphorene could vary as a function of the physical properties of a substrate. To fill this gap, the capability of phosphorene to lubricate an iron surface is performed using density functional theory. The study is carried out in comparison with graphene and MoS₂. Phosphorene chemisorbs more strongly than the other 2D materials on a native iron surface, indicating it as a promising coating for iron interfaces. The higher adhesion suggests that stable passivation occurs at the metal substrate, which can be related to low wear rate and stable lubricant performances. Furthermore, the simulations show that phosphorene has a high lubricant capability even at low concentrations. Indeed, a single phosphorene sheet can already passivate both the mated iron surfaces, lowering adhesion energy more effectively than MoS₂ and graphene.

The following articles summarize the research activities related to the topics covered in this thesis:

- 1) Restuccia, G. Levita, M. Wolloch, **G. Losi**, G. Fatti, M. Ferrario, M.C. Righi, *Ideal adhesive and shear strengths of solid interfaces: A high throughput ab initio approach*. Computational Materials Science, Volume 154, 517-529, ISSN 0927-0256, (2018), [DOI](#).
- 2) M. Wolloch, **G. Losi**, M. Ferrario, M. C. Righi, *High-throughput screening of the static friction and ideal cleavage strength of solid interfaces*. Sci Rep 9, 17062 (2019), [DOI](#).
- 3) M. Wolloch, **G. Losi**, O. Chehaimi, F. Yalcin, M. Ferrario, M. C. Righi. *High-throughput generation of potential energy surfaces for solid interfaces*, submitted to Computational Materials Science.
- 4) S. Kajita, **G. Losi**, N. Kikkawa, M. C. Righi, *Accurate multiscale simulation of frictional interfaces by Quantum Mechanics / Green's Function molecular dynamics*, in preparation.

- 5) **G. Losi**, P. Restuccia, M. C. Righi, *Superlubricity in phosphorene identified by means of ab initio calculations*. 2D Mater. 7, 025033 (2020), [DOI](#).
- 6) **G. Losi**, M. Cutini, P. Restuccia, M. C. Righi, *Phosphorene and MoS₂ Interacting with Iron: Lubricating Effects Compared to Graphene*, submitted to Journal of Nanostructure in Chemistry (JNSC).

In addition, further contributions to other research activities (not reported in this thesis) have been synthesized in the following article:

- 7) **G. Losi**, S. Peeters, F. Delayens, H. Vezin, S. Loehlé, B. Thiebaut and M. C. Righi, *Experimental and Ab-Initio Characterization of Mononuclear Molybdenum Dithiocarbamates in Lubricant Mixtures*. Langmuir 2021, 37, 16, 4836–4846, [DOI](#).
- 8) S. Peeters, P. Restuccia, **G. Losi**, S. Loehlé, B. Thiebaut, M. C. Righi. *Crystallization of MoS₂ from central units of MoDTC by ab-initio simulations*, in preparation.

Appendix A

Supporting information for: TribChem: Materials Science Simulations software

A.1 The intimate structure of a workflow

As an example of how a workflow can be constructed, it is reported here a complete description of the workflow that can generate slabs with a given orientation and converge their thickness by evaluating how the surface energy varies with the number of atomic layers. For the sake of clarity, the corresponding flowchart is reported in Fig. A.1, where each Firetask, Firework, and Workflows is identified with solid black rectangles, black dashed boxes, and colored dashed boxes, respectively.

The code consists of two nested smaller workflows: the outermost control the convergence process of the slab thickness, while the innermost is responsible for generating the slabs and calculating the surface energy. In subsequent paragraphs, the steps carried out by the various steps of the flowchart of Fig. A.1 are presented.

A.1.1 Initializing Firework

The workflow to calculate the optimal thickness is started within the main workflow with an initializing Firework. **Start Thickness Convergence** starts the sub-workflow. Check if a specific slab (identified by a material ID and Miller indexes) is already present in the database. In that case, the software checks whether an optimal thickness has already been calculated. In case of a negative answer, the structure of the corresponding bulk material is queried by the database, and the outer sub-workflow to evaluate the optimal slab thickness is called.

A.1.2 Workflow: Converge slab thickness

It consists of two Fireworks and manages the convergence process of the entire sub-workflow. In particular, the *Start Surface Energy Convergence* element has the task of calling the innermost unit (see next section), which calculates the surface energy for the selected slabs, while *End Surface Energy Convergence* checks whether the convergence has been reached. If not, the sub-workflow calls itself recursively on a different set of slabs. If the convergence is not reached after all allowable slabs have been simulated, the maximum thickness selected by the user is assumed to be the optimum.

- **Start Surface Energy Convergence:** Start the Surface Energy sub-workflow, which creates one or more slabs out of an input bulk structure and find their energies through first-principle simulations made with VASP. The surface energies are calculated by comparing the energies of the oriented bulk structure with those of each slab.

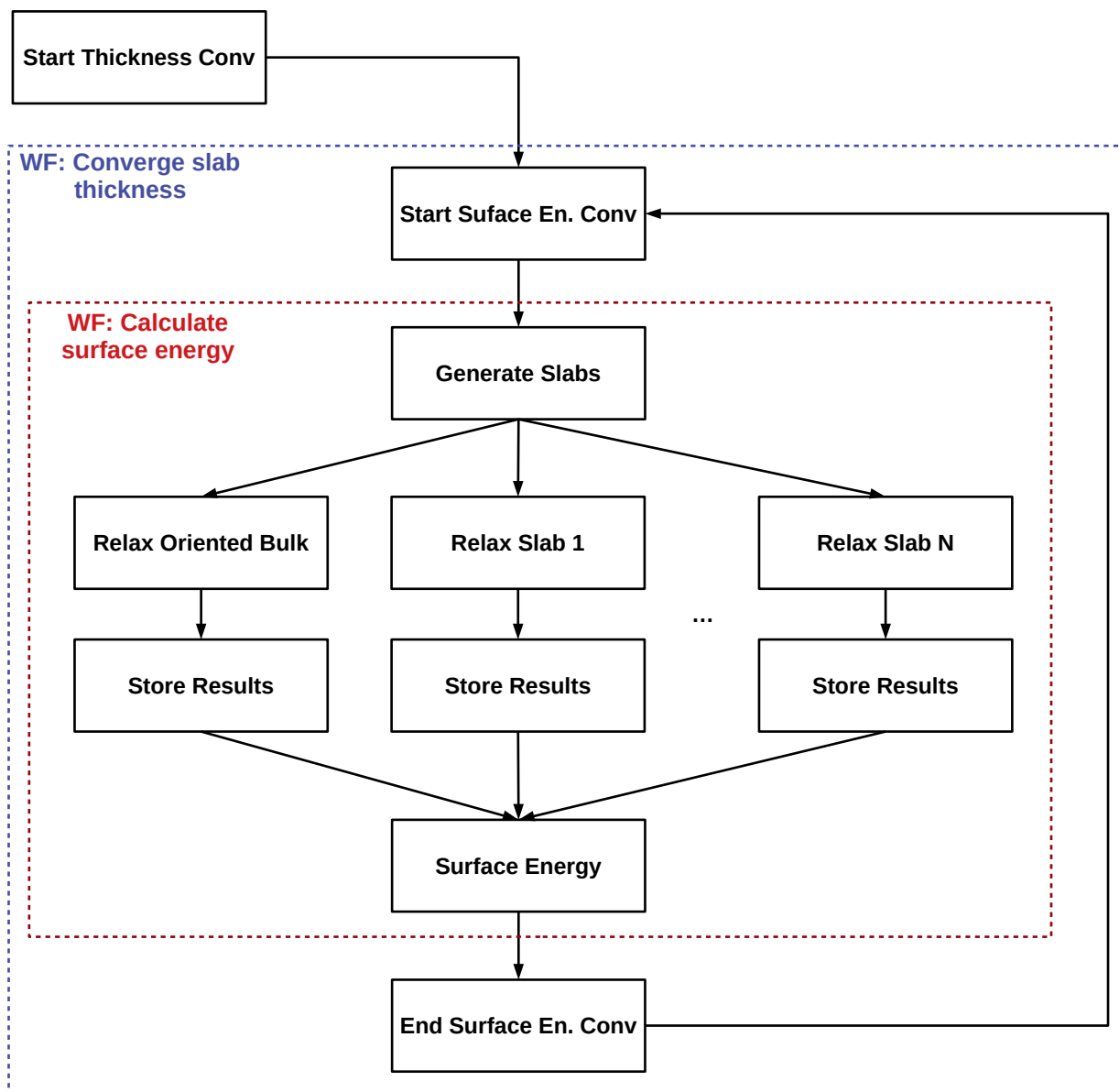


Figure A.1: Flowchart of the two nested sub-workflows used to generate crystalline slabs and converge their atomic thickness by evaluating the surface energy.

- **End Surface Energy Convergence:** Compares the surface energies calculated so far with the reference surface energy, defined as the surface energy of the maximum allowed thickness. When the relative difference in surface energy of one slab with the reference is lower than a certain threshold, the convergence process is concluded, and the data relative to that slab is stored in the database as the optimal one. If the convergence is not reached after one more iteration, the previous Firetask to run the inner sub-workflow is called recursively on a new set of slabs with increased thickness. The recursion is repeated until the maximum allowed thickness, set by the user, is reached. If the convergence is not achieved, the maximum thickness is assumed to be the optimal one.

A.1.3 Workflow: Calculate the surface energy

This is the innermost unit of this workflow, and it is composed of four different Firetasks. It takes a bulk structure as input, a list of atomic thickness, and a set of Miller indexes. After the slabs are generated, their optimal structure and energy are calculated through first-principles simulations. The surface energy is then calculated and saved.

- **Generate Slabs:** Generate a slab or a list of slabs out of a given bulk structure. The necessary parameters are Miller indexes, desired slab thicknesses, and cell vacuum. It is also possible to generate an oriented bulk instead of a slab by providing a zero vacuum as input.
- **Relax Structure:** Perform a Kohn-Sham energy minimization on the atomic structure, which is passed as input by calling Atomate optimization Fireworks. The latter automatically creates an input from the data and executes VASP to perform the relaxation of the cell. The structure can be a bulk, a slab, or an interface. The calculation is performed only if the database does not already have output data matching the input provided, i.e., if the calculation has not already been performed before.
- **Store Results:** Retrieve the data obtained from the first principle simulations and store them in the collection and database of interest provided by the user. This Firetask is combined with the previous one within the same Firework.
- **Surface Energy:** Calculate the surface energy of a given number of slabs with respect to the correspondingly oriented bulk. The energy is taken by querying the database. It ends the calculation of the surface energy sub-workflow.

A.2 Additional details for the example results

In table A.1 we report the data visualized in Chapter 2 in table form alongside the number of layers and slab thickness used. For C(111), one should note that the layer distances are not equally spaced, and the close “double layers” are counted as two layers each by our workflow. For this reason, the increment of layers to add was set to 2 for C(111), in contrast to all other slabs where it was set to 1. In contrast, our previous work [194] used a slab that was 6 double layers thick, which corresponds to 12 layers in our current scheme.

A.3 Details and results for additional interfaces

In Figs. A.2-A.6, we report the top views of the interfaces at the minimum and maximum energy configurations with only a single layer of the top and bottom slabs closest to the interface region shown.

	Al(111)	Fe(110)	Cu(111)	C(111)	Al(100)	Al(110)
MP-id	mp-134	mp-13	mp-30	mp-66	mp-134	mp-134
$\sigma^{\text{tw}} [J/m^2]$	0.74	2.49	1.35	5.69	0.97	0.94
$\sigma^{\text{ref}} [J/m^2]$	0.72	2.25	1.24	4.97	0.93	1.02
$\sigma^{\text{lit}} [J/m^2]$	0.9	2.37	1.6	6.2	1.03	1.06
$\sigma^{\text{MP}} [J/m^2]$	0.77	2.45	1.34	5.03	0.91	0.98
$d^{\text{opt}} [\text{\AA}]$	11.89	6.00	6.19	8.55	18.26	11.41
$d^{\text{opt}} (N_L)$	6	4	4	10	10	9

Table A.1: Slab properties of Al, Fe, Cu, and C for various miller indices where σ are the surface energies and d^{opt} are optimized slack thicknesses in angstroms and number of layers. Reference calculated values for surface energies σ^{ref} and reference literature values σ^{lit} were taken from Ref. [194] whereas σ^{MP} values was queried from the Materials Project[188].

Then, in Figs. A.7-A.11 we have the unique high symmetry points of the matched slabs and the interfaces, along with the potential energy surfaces (PES). For some of the interfaces, such as Al(100)-Al(111), one of the matched lattice vectors is longer than the other, so we have a narrow cell, which in turn affects the PES.

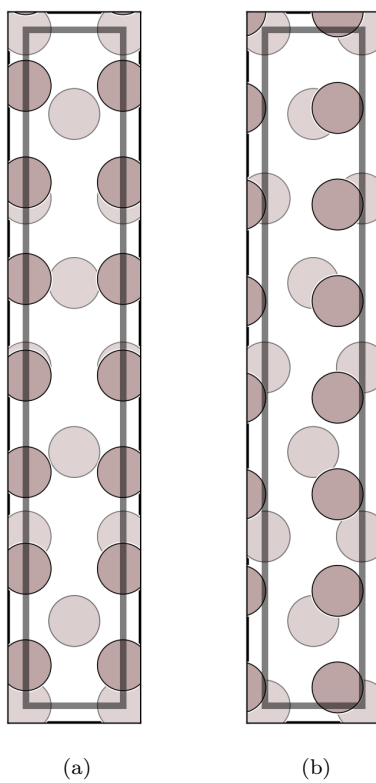


Figure A.2: Top view of the interface region at the minimum (a) and maximum (b) energy configurations of Al(100)-Al(111) interface with the matched unit cell.

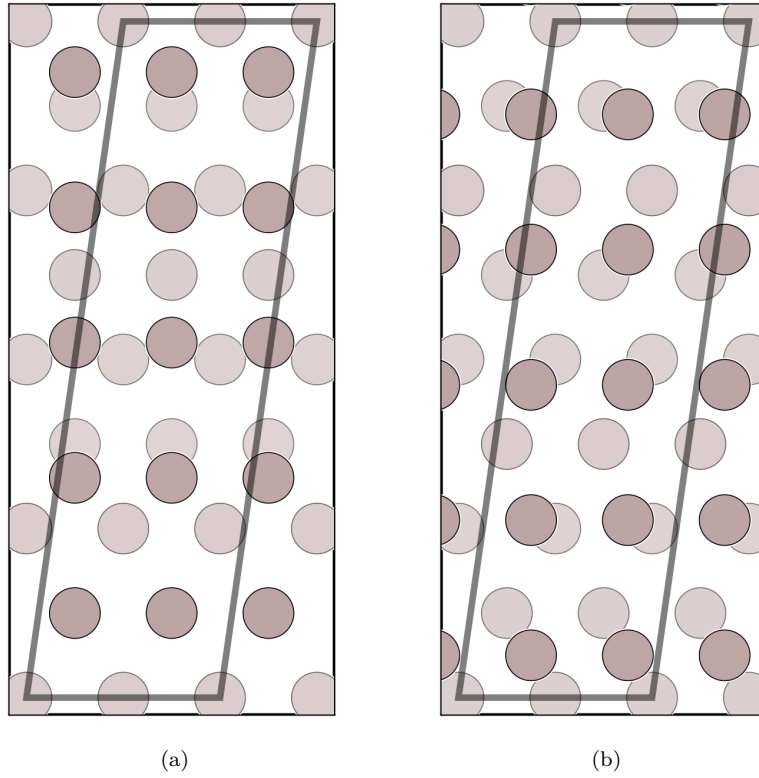


Figure A.3: Top view of the interface region at the minimum (a) and maximum (b) energy configurations of Al(110)-Al(111) interface with the matched unit cell.

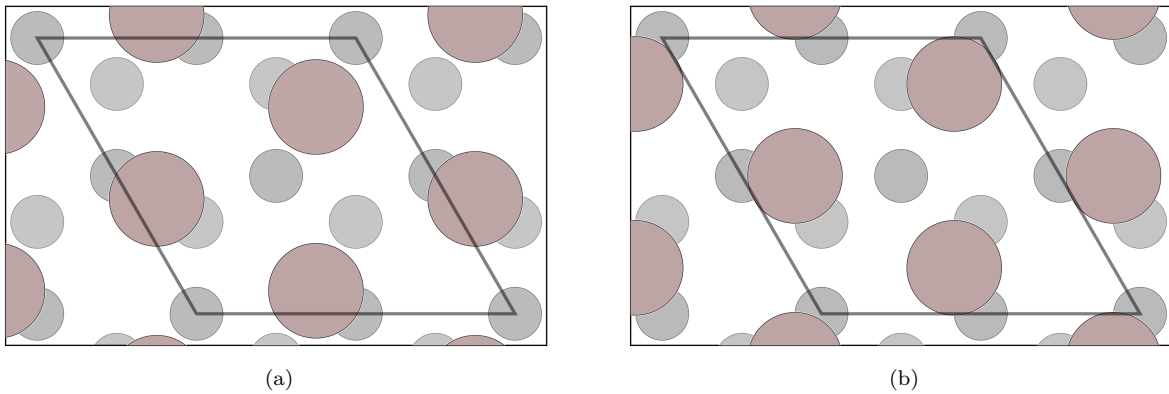


Figure A.4: Top view of the interface region at the minimum (a) and maximum (b) energy configurations of Al(111)-C(111) interface with the matched unit cell.

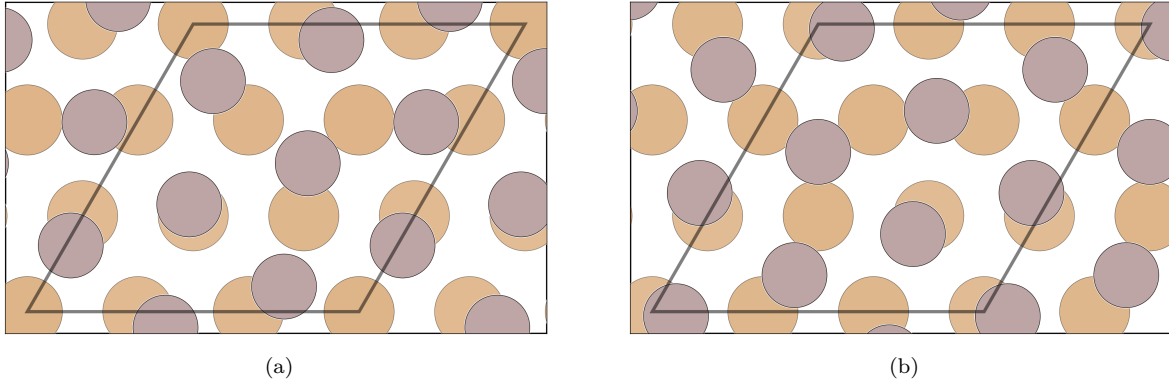


Figure A.5: Top view of the interface region at the minimum (a) and maximum (b) energy configurations of Al(111)-Cu(111) interface with the matched unit cell.

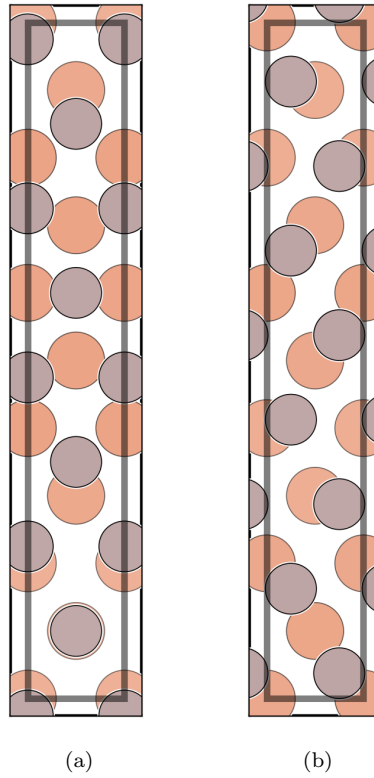


Figure A.6: Top view of the interface region at the minimum (a) and maximum (b) energy configurations of Al(111)-Fe(110) interface with the matched unit cell.

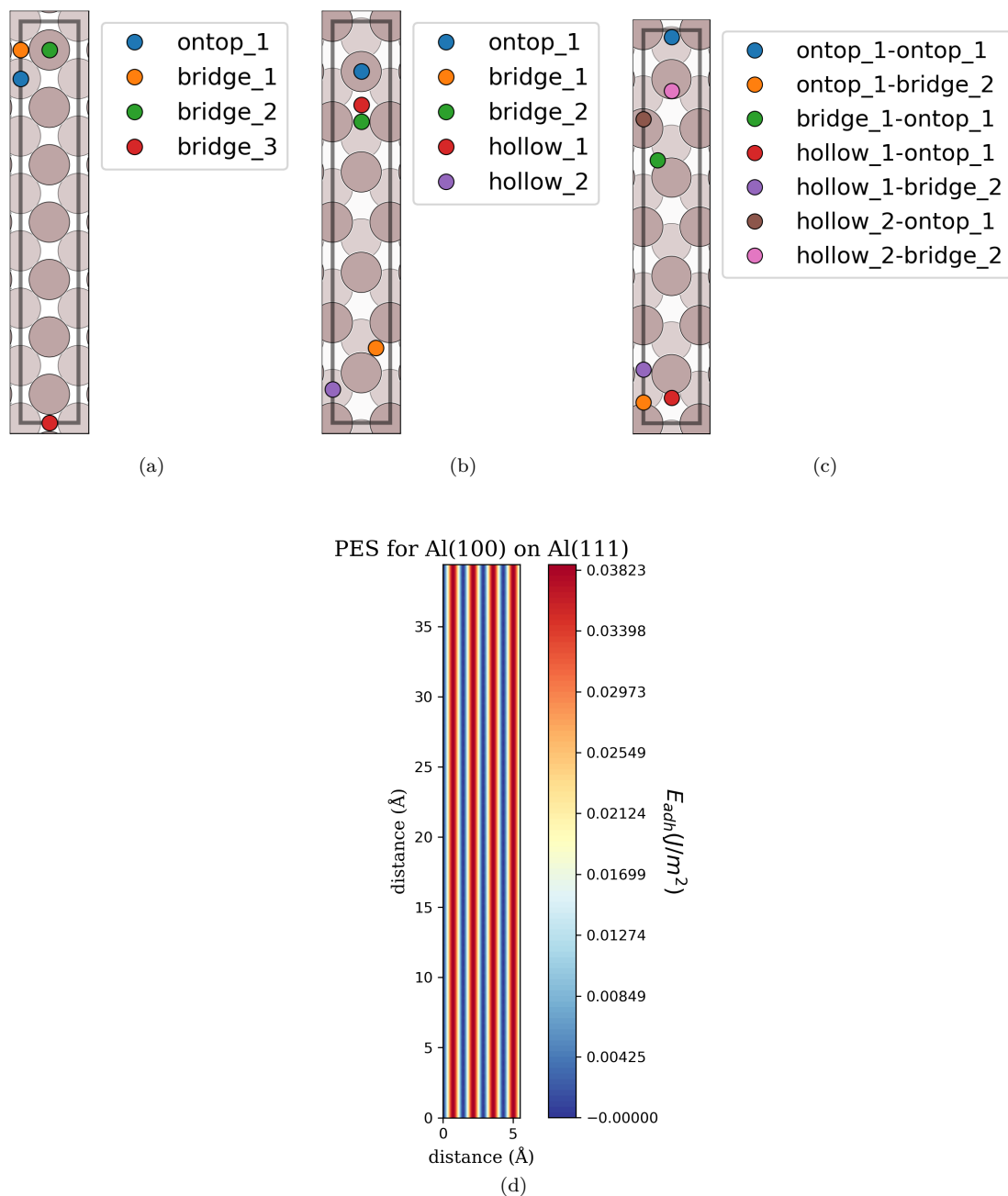


Figure A.7: An overview of the Al(100)-Al(111) interface. (a) High symmetry points of the top (Al(100)) slab. (b) High symmetry points of the bottom (Al(111)) slab. (c) High symmetry points of the matched interface. (d) Potential energy surface (PES) of the interface.

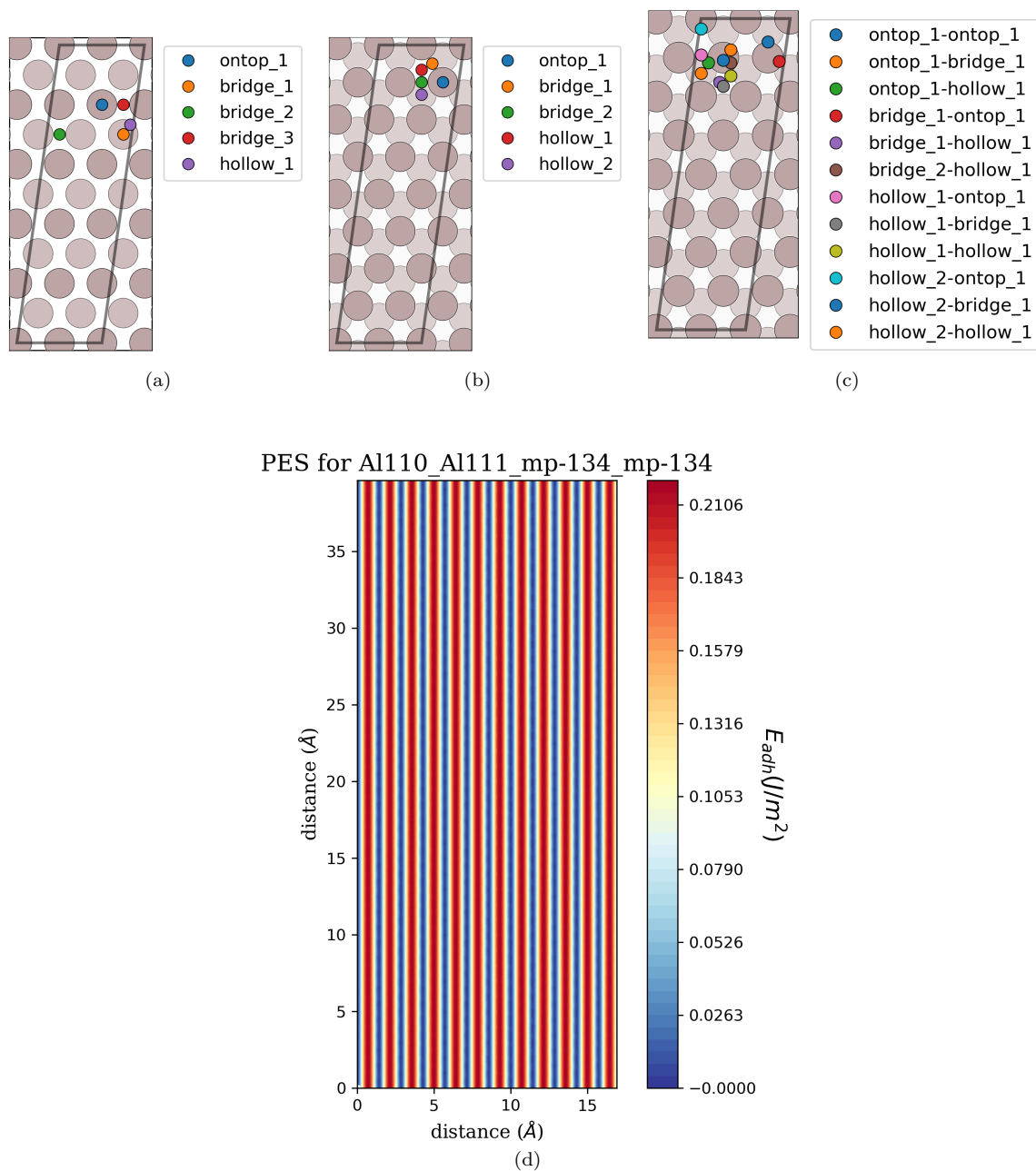


Figure A.8: An overview of the Al(110)-Al(111) interface. (a) High symmetry points of the top (Al(110)) slab. (b) High symmetry points of the bottom (Al(111)) slab. (c) High symmetry points of the matched interface. (d) Potential energy surface (PES) of the interface.

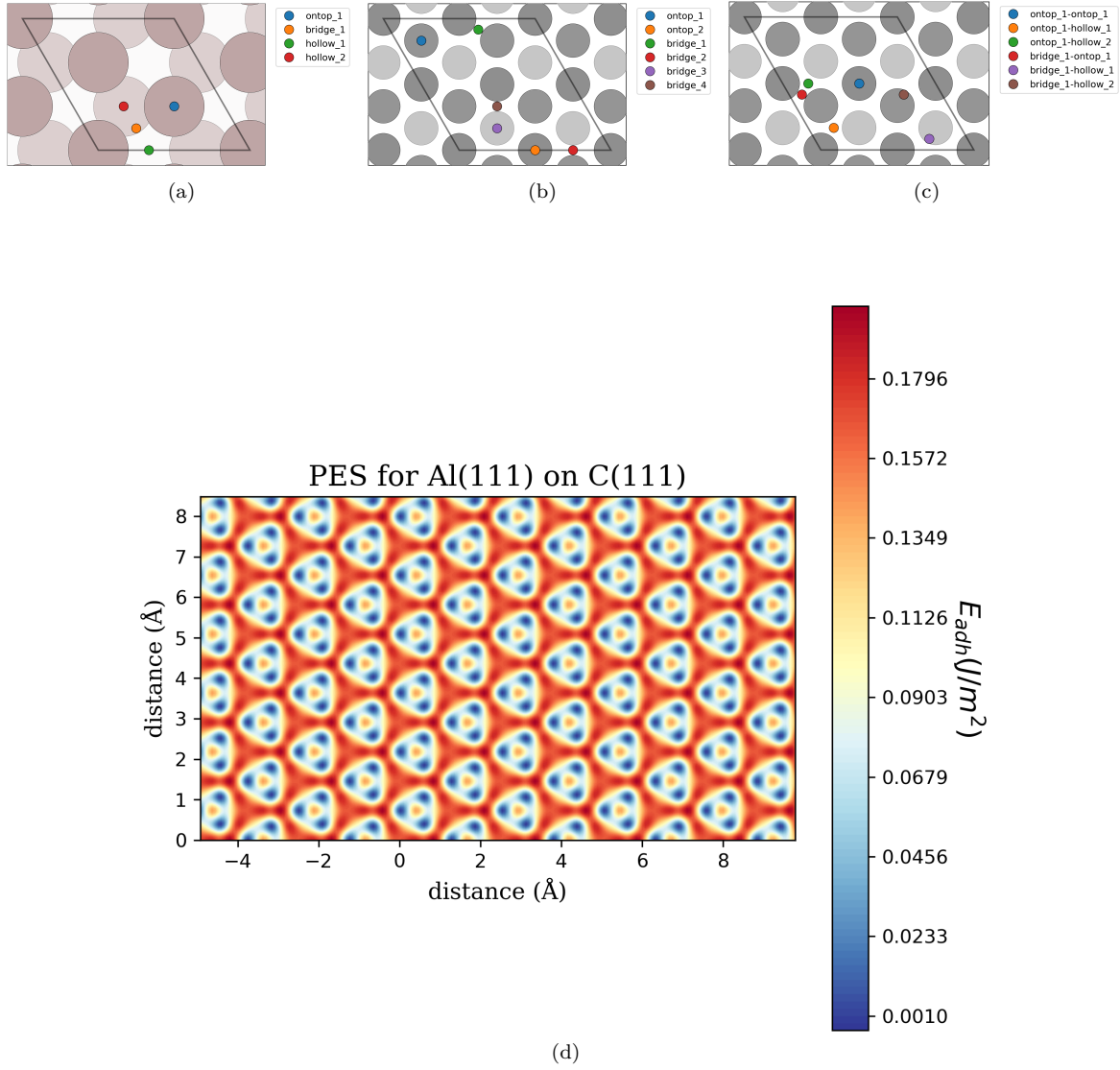


Figure A.9: An overview of the Al(111)-C(111) interface. (a) High symmetry points of the top (Al(111)) slab. (b) High symmetry points of the bottom (C(111)) slab. (c) High symmetry points of the matched interface. (d) Potential energy surface (PES) of the interface.

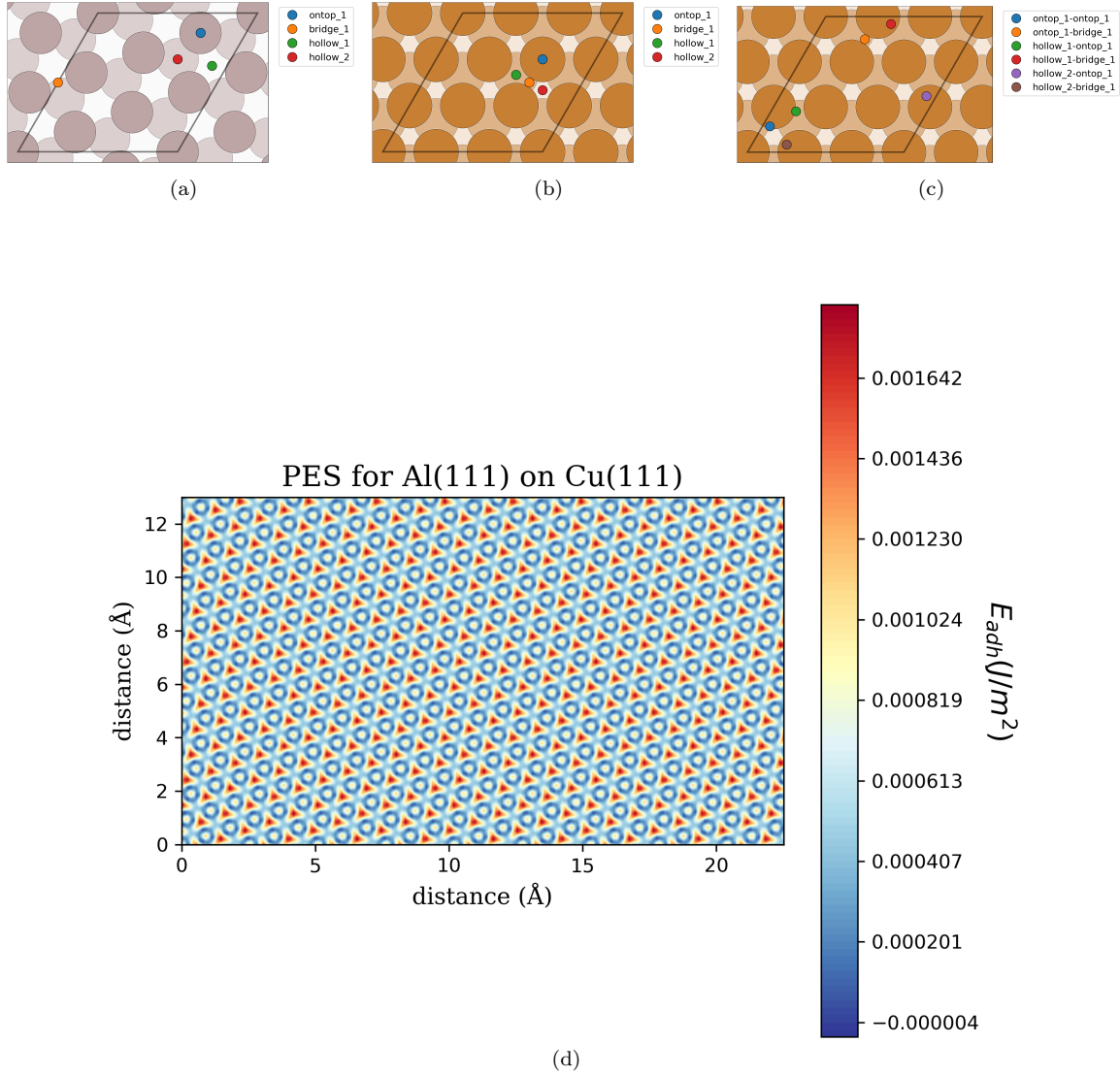


Figure A.10: An overview of the Al(111)-Cu(111) interface. (a) High symmetry points of the top (Al(111)) slab. (b) High symmetry points of the bottom (Cu(111)) slab. (c) High symmetry points of the matched interface. (d) Potential energy surface (PES) of the interface.

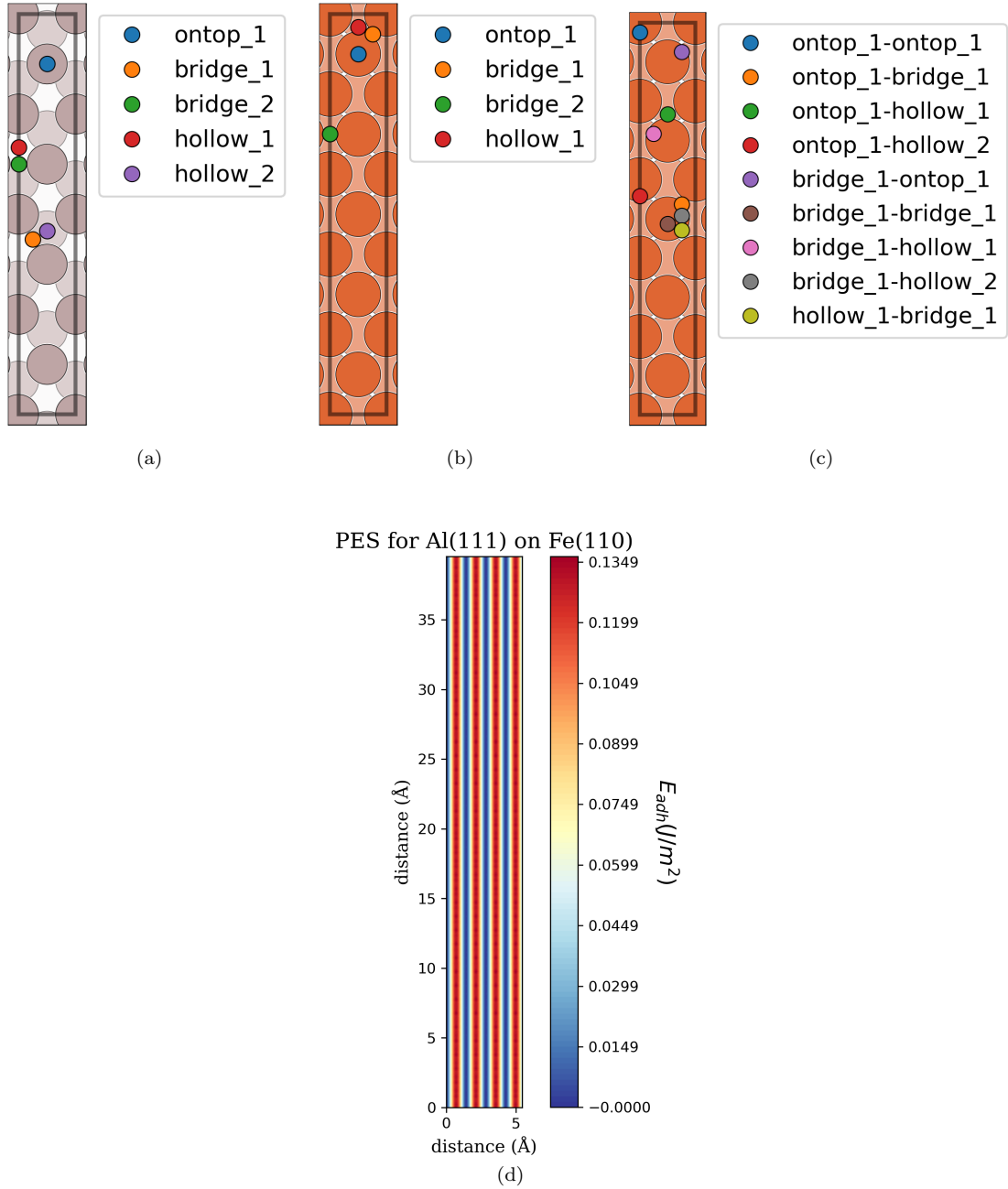


Figure A.11: An overview of the Al(111)-Fe(110) interface. (a) High symmetry points of the top (Al(111)) slab. (b) High symmetry points of the bottom (Fe(110)) slab. (c) High symmetry points of the matched interface. (d) Potential energy surface (PES) of the interface.

Appendix B

Supporting information for: Screening the static friction and cleavage strength of solid interfaces

B.1 Computed high-level data for all considered interfaces

Table B.1 shows the most important results we computed for all considered interfaces. In table B.2 the different values for the ideal shear strength τ are listed in detail. Together with τ along the MEP, we present the values along two high symmetry directions which are orthogonal to each other. For some interfaces the differences are considerable, and the ratio between the two numbers may be viewed as a measure for the frictional anisotropy of the sliding system.

In table B.3 we compare our data for the cleavage strength σ_C for some example materials (the same as used in the table in Chapter 3) to previously calculated data for the ultimate tensile strength σ_{ut} of these materials. We note that the cleavage strength is fitting well for the more brittle materials at surfaces that are cleavage planes (e.g. W(110) and Si(111)) as expected. For more ductile materials or other lattice planes, the materials will rather fail through slip along a lattice plane that is at an angle to the investigated interface or through the creation and slip of dislocations. In these cases, the computed cleavage strength is considerably higher than the ultimate tensile strength.

B.2 Details about the rigid separation model and the UBER fits

The rigid separation model might seem like a crude approximation to a material failing under tensile strain. However, it is specifically designed to model brittle fracture, for which it performs well [271].

Including relaxations of atomic layers perpendicular to the interface plane is possible. However, one must take several finite-size effects into account to achieve a physically consistent solution [273, 266]: When elastic effects are considered, the surfaces should separate when the strain energy exceeds the cleavage energy. However, the strain energy per unit area decreases with the system size, as does the critical stress, which is linearly dependent on it for small enough strains. Thus, if the crystal is large enough, both strain energy and critical stress go to zero, and the crystal is not stable with respect to uniaxial strain. To overcome this unphysical result, one has to consider further that the energy barrier for the separation, which can be calculated by transition state theory, increases with the square root of the number of layers in the system [266]. To summarize, the correct treatment of relaxations while separating interfaces under tensile strain is complex, and one needs to investigate system size-dependent energies rather than stresses. On the other hand, the simple rigid body separation model we employ is not size-dependent, provides reliable upper limits for the ideal tensile strengths of materials [266] and was shown to be well justified by comparison to a simulation of a crack tip under mode I loading [259].

In Fig. B.1 we plot the UBER fits for each lattice type (for bcc and fcc lattices, only the curves with the lowest cleavage strength σ_C are plotted to avoid cluttering of the plots). The color coding corresponds

Appendix B. Supporting information for: Screening the static friction and cleavage strength of solid interfaces

Table B.1: We report the lattice parameter a (Å), the adhesion energy γ (J/m²), the ideal shear strength τ along the MEP (GPa), and the cleavage strength σ_C (GPa) for all the analysed materials and interfaces.

Z	Element	a	100			110			111/0001		
			γ	τ	σ_C	γ	τ	σ_C	γ	τ	σ_C
3	Li	3.47	0.85	2.93	3.6	0.93	0.66	4.46	1.03	2.95	4.25
4	Be	2.28							4.01	15.01	35.4
11	Na	4.26	0.41	1.15	1.57	0.4	0.33	1.79	0.48	1.14	1.78
12	Mg	3.32							0.86	0.75	4.99
13	Al	4.04	1.84	4.0	11.96	2.13	5.22	11.72	1.52	2.06	10.51
14	Si	5.47	4.57	24.03	31.76	3.26	11.13	22.88	3.33	13.35	20.48
19	K	5.28	0.21	0.63	0.7	0.21	0.16	0.85	0.26	0.55	0.86
20	Ca	5.47	0.93	2.61	3.82	1.08	1.72	4.14	0.95	0.65	4.14
21	Sc	3.32							2.58	3.82	11.22
22	Ti	2.94							3.81	4.38	14.29
23	V	2.99	4.88	23.09	28.16	4.84	8.7	27.06	5.42	20.46	30.06
24	Cr	2.86	7.07	33.1	44.61	6.35	17.46	42.47	7.01	30.73	45.44
26	Fe	2.83	4.99	26.36	31.58	4.95	11.86	33.48	5.45	24.68	33.31
27	Co	2.49							4.3	6.95	31.16
28	Ni	3.5	4.46	14.57	31.09	4.57	13.59	29.78	3.85	5.92	30.32
29	Cu	3.63	2.67	8.9	19.53	2.9	8.71	18.82	2.38	3.76	18.58
30	Zn	2.65							0.67	2.29	4.68
32	Ge	5.76	2.8	14.12	18.64	2.38	7.46	15.15	2.19	9.82	14.09
37	Rb	5.68	0.17	0.4	0.58	0.15	0.12	0.61	0.19	0.43	0.62
38	Sr	6.04	0.69	1.73	2.87	0.8	1.14	3.05	0.68	0.44	3.07
39	Y	3.65							2.0	2.47	8.06
40	Zr	3.24							3.18	2.64	16.18
41	Nb	3.28	4.72	20.24	26.1	4.17	7.22	23.71	4.78	17.27	27.65
42	Mo	3.15	6.23	26.56	38.24	5.57	14.71	36.25	6.28	25.07	39.4
44	Ru	2.72							5.11	15.62	37.21
45	Rh	3.83	4.69	15.12	32.59	4.68	13.47	30.26	4.01	8.23	31.51
46	Pd	3.95	3.1	8.86	21.24	3.22	7.4	20.68	2.68	3.66	20.85
47	Ag	4.15	1.7	5.0	11.25	1.86	4.43	11.01	1.56	2.07	10.93
48	Cd	3.04							0.4	0.5	2.91
50	Sn	6.66	1.75	5.85	10.68	1.26	3.61	9.53	1.22	3.81	8.19
55	Cs	6.16	0.14	0.31	0.46	0.12	0.09	0.48	0.16	0.09	0.48
56	Ba	5.0	0.62	2.06	2.16	0.62	0.71	2.54	0.81	2.23	2.82
58	Ce	5.27	1.49	3.8	5.96	1.67	2.25	6.51	1.46	1.1	5.99
63	Eu	5.54	0.87	2.02	3.61	1.0	1.53	3.75	0.9	0.43	3.7
70	Yb	5.5	0.83	2.24	3.73	0.96	1.75	3.94	0.84	0.63	3.91
72	Hf	3.2							3.44	4.96	18.33
73	Ta	3.32	5.08	22.99	29.29	4.71	7.74	28.0	5.45	30.08	31.92
74	W	3.19	7.79	34.23	48.37	6.38	17.74	44.5	6.93	27.86	47.69
75	Re	2.77							5.31	10.15	39.0
76	Os	2.75							5.84	20.85	45.44
77	Ir	3.88	5.68	18.4	43.17	5.72	18.46	38.16	4.59	11.63	39.5
78	Pt	3.98	3.7	8.61	27.71	3.88	9.13	26.7	2.99	4.13	25.29
79	Au	4.15	1.74	3.38	13.55	1.8	3.29	12.73	1.41	1.16	11.75
82	Pb	5.04	0.53	1.12	3.28	0.78	1.67	4.78	0.5	0.64	4.0

Appendix B. Supporting information for: Screening the static friction and cleavage strength of solid interfaces

Table B.2: We report the ideal shear strength along the MEP τ and two high symmetry directions τ_{hkl} (GPa), as well as their ratios, for all the analyzed materials and interfaces.

Z	Element	100				110				111/0001			
		τ_{100}	τ_{010}	τ	τ_{100}/τ_{010}	τ_{001}	$\tau_{\bar{1}10}$	τ	$\tau_{001}/\tau_{\bar{1}10}$	τ_{101}	τ_{121}	τ	τ_{101}/τ_F^{121}
3	Li	2.93	2.93	2.93	1.0	1.6	1.15	0.66	1.38	2.84	2.95	2.95	0.95
4	Be									20.45	28.53	15.01	0.72
11	Na	1.15	1.15	1.15	1.0	0.79	0.58	0.33	1.36	1.19	1.14	1.14	0.98
12	Mg									1.45	2.52	0.75	0.58
13	Al	4.01	4.01	4.0	1.0	5.22	8.18	5.22	0.64	3.08	2.06	2.06	0.82
14	Si	26.83	24.03	24.03	1.12	11.13	24.28	11.13	0.46	14.14	13.35	13.35	1.07
19	K	0.63	0.63	0.63	1.0	0.38	0.27	0.16	1.4	0.59	0.55	0.55	0.96
20	Ca	2.61	2.61	2.61	1.0	1.72	4.36	1.72	0.39	1.26	0.65	0.65	0.61
21	Sc									4.7	5.92	3.82	0.79
22	Ti									4.99	5.81	4.38	0.86
23	V	23.1	23.1	23.09	1.0	13.6	9.64	8.7	1.41	22.36	20.46	20.46	0.83
24	Cr	33.1	33.1	33.1	1.0	27.63	17.72	17.46	1.56	34.48	30.73	30.73	0.82
26	Fe	26.36	26.36	26.36	1.0	21.95	13.44	11.86	1.63	26.82	24.68	24.68	1.09
27	Co									11.17	18.32	6.95	0.61
28	Ni	14.57	14.57	14.57	1.0	13.6	23.2	13.59	0.59	9.6	5.92	5.92	0.71
29	Cu	8.92	8.92	8.9	1.0	8.71	14.58	8.71	0.6	6.09	3.76	3.76	0.69
30	Zn									3.6	4.26	2.29	0.85
32	Ge	14.15	16.35	14.12	0.87	7.46	11.90	7.46	0.04	10.43	9.82	9.82	1.08
37	Rb	0.4	0.4	0.4	1.0	0.27	0.2	0.12	1.35	0.43	0.43	0.43	0.97
38	Sr	1.73	1.73	1.73	1.0	1.14	2.94	1.14	0.39	0.87	0.44	0.44	0.58
39	Y									3.25	4.36	2.47	0.75
40	Zr									4.19	5.93	2.64	0.71
41	Nb	20.28	20.28	20.24	1.0	12.76	8.33	7.22	1.53	20.98	17.27	17.27	0.77
42	Mo	26.56	26.56	26.56	1.0	23.13	15.38	14.71	1.5	38.69	25.07	25.07	1.03
44	Ru									18.57	22.69	15.62	0.82
45	Rh	15.13	15.13	15.12	1.0	13.48	20.62	13.47	0.65	11.12	8.23	8.23	0.88
46	Pd	8.88	8.88	8.86	1.0	7.41	14.73	7.4	0.5	5.61	3.66	3.66	0.82
47	Ag	5.01	5.01	5.0	1.0	4.44	7.98	4.43	0.56	3.31	2.07	2.07	0.65
48	Cd									1.0	1.56	0.5	0.64
50	Sn	5.87	10.2	5.85	0.58	3.61	5.86	3.61	0.62	4.15	3.81	3.81	1.1
55	Cs	0.31	0.31	0.31	1.0	0.21	0.15	0.09	1.35	0.44	0.09	0.09	1.11
56	Ba	2.06	2.06	2.06	1.0	1.51	0.96	0.71	1.57	2.18	2.23	2.23	0.92
58	Ce	3.81	3.81	3.8	1.0	2.25	5.66	2.25	0.4	1.48	1.1	1.1	0.76
63	Eu	2.02	2.02	2.02	1.0	1.53	4.14	1.53	0.37	0.94	0.43	0.43	0.53
70	Yb	2.25	2.25	2.24	1.0	1.75	3.81	1.75	0.46	1.27	0.63	0.63	0.59
72	Hf									5.89	7.12	4.96	0.83
73	Ta	23.01	23.01	22.99	1.0	15.75	9.47	7.74	1.66	30.97	30.08	30.08	1.03
74	W	34.25	34.25	34.23	1.0	30.47	21.38	17.74	1.42	31.88	27.86	27.86	1.14
75	Re									15.31	27.74	10.15	0.55
76	Os									24.2	28.96	20.85	0.84
77	Ir	18.42	18.42	18.4	1.0	18.47	22.87	18.46	0.81	15.06	11.63	11.63	1.03
78	Pt	8.66	8.66	8.61	1.0	9.14	15.61	9.13	0.59	5.86	4.13	4.13	1.38
79	Au	3.38	3.38	3.38	1.0	3.3	5.97	3.29	0.55	2.11	1.16	1.16	0.65
82	Pb	1.13	1.13	1.12	1.0	1.67	2.67	1.67	0.63	1.01	0.64	0.64	0.93

Appendix B. Supporting information for: Screening the static friction and cleavage strength of solid interfaces

Table B.3: Comparison of some results from this work for the ideal cleavage strength (σ_C) to previously calculated values of uniaxial tensile strength (σ_{ut}) from previous works. Data are split into 3 groups: bcc, diamond, and fcc crystals.

	100			110			111	
	σ_C [GPa]	σ_{ut} [GPa]		σ_C [GPa]	σ_{ut} [GPa]		σ_C [GPa]	σ_{ut} [GPa]
Fe	31.6	10.6–14.2[269]		33.5	16.7–33[269]		33.3	19.3–27.7[269]
Mo	38.2	26.7–28.8[269]		36.2	32.6–40.7[269]		39.4	28.4–29.9[269]
W	48.4	27.7–29.5[269]		44.5	35.9–54.3[269]		47.7	39–40.1[269]
Si	31.8	26.3–27.5[269]		22.9	17–17.9[269]		20.5	21–24.8[269]
Ge	18.6	16.4–16.8[269]		15.2	11.8[269]		14.1	14–14.6[269]
Al	12.0	9–13.1[269]		11.7	4.5–4.92[269]		10.5	8.8–11.52[269, 370]
Cu	19.5	9.3–36[269, 371]		18.8	4.6–31[269]		18.6	7.5–29[269]
Ni	31.1	18.3–36.1[269]		29.8	9.1–10.5[269]		30.3	15.4–34.1[269]

to the cleavage energy E_C , with dark blue lines showing the lowest values and dark red the highest.

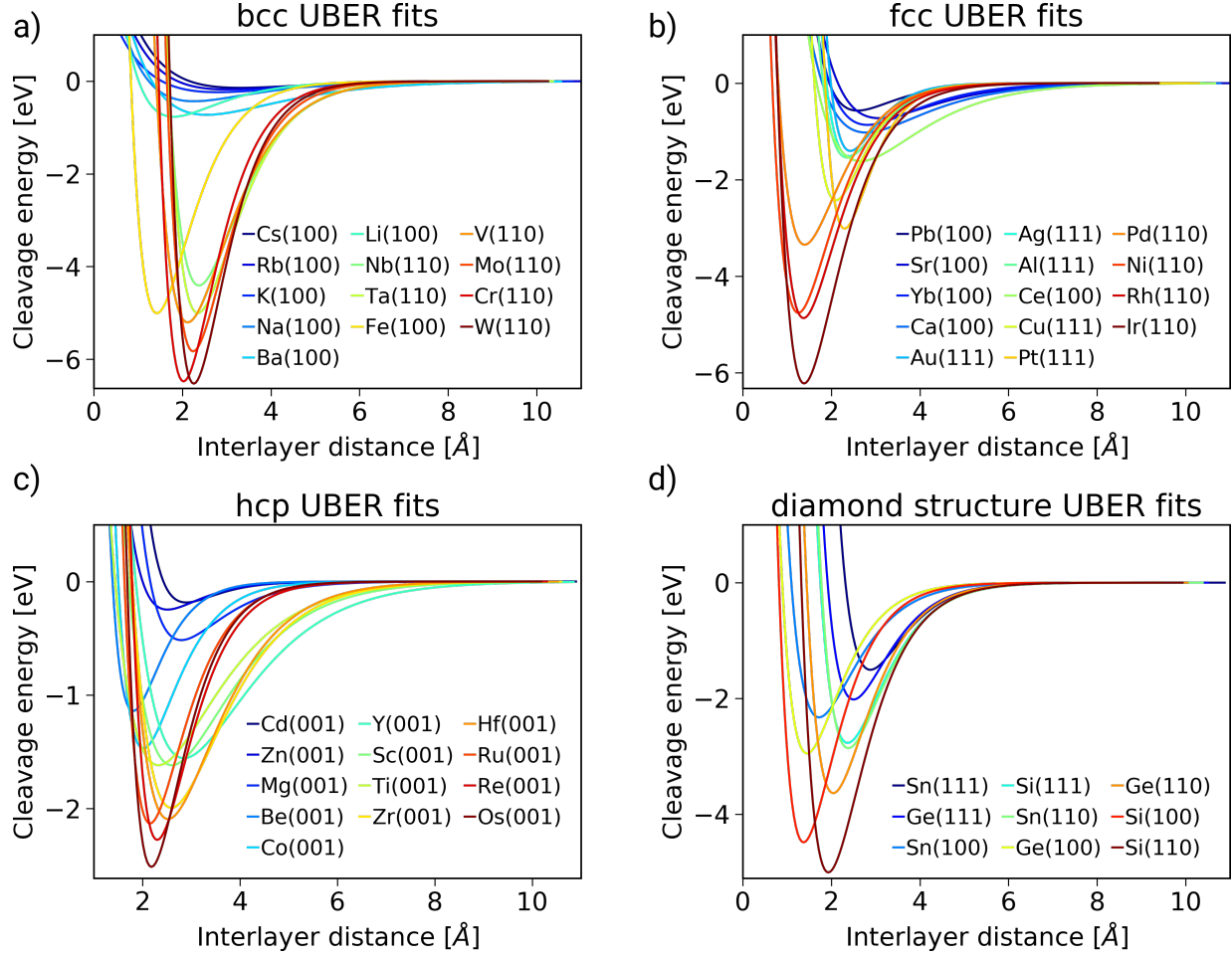


Figure B.1: Universal binding energy relation fits to the attractive regime of the computed $\gamma(z)$ data. For the lattice types a) bcc and b) fcc, only the interface planes with the smallest cleavage strengths are shown since the graphs would be too cluttered otherwise. For c) hcp and d) diamond lattices, we show all available data. Note the different scales on the subplots.

Appendix C

Supporting information for: Accurate multiscale simulation of frictional interfaces by Quantum Mechanics / Green's Function molecular dynamics

C.1 Example of fast convolution steps

The fast convolution is an elegant technique but complicated to understand to some extent. We illustrate this procedure with an example with $B = 2$ (this appendix is provided by referring to an excellent description of this method in Ref. [298]). In this case, the time intervals are $I_0 = [0, h]$, $I_1 = [h, 3h]$, $I_2 = [2h, 7h]$, $I_3 = [4h, 15h]$, $\dots$, and the integral range $[0, t_{n+1}]$ is divided as shown in Fig. C.1. The formula in the main text can be rewritten here as

$$\mathbf{y}'_{k+1} = \mathbf{y}'_k + \frac{e^{zh} - 1}{zh} \left(zh\mathbf{y}'_k + h\mathbf{f}_k + h \frac{\mathbf{f}_{k+1} - \mathbf{f}_k}{zh} \right) - h \frac{\mathbf{f}_{k+1} - \mathbf{f}_k}{zh}, \quad (\text{C.1})$$

$$\int_{t_n}^{t_{n+1}} A(t_{n+1} - \tau) \mathbf{f}(\tau) d\tau \sim \Phi_1 \mathbf{f}(t_n) + \Phi_2 \frac{\mathbf{f}(t_{n+1}) - \mathbf{f}(t_n)}{h}, \quad (\text{C.2})$$

$$\Phi_1 = \sum_{j=-N}^N \omega_j^0 \frac{A(z_j^0)}{z_j^0} e^{z_j^0 h}, \quad \Phi_2 = \sum_{j=-N}^N \omega_j^0 \frac{A(z_j^0)}{(z_j^0)^2} e^{z_j^0 h},$$

$$\int_0^{t_n} A(t_{n+1} - \tau) \mathbf{f}(\tau) d\tau \sim \sum_{l=1}^L \sum_{j=-N}^N \omega_j^l A(z_j^l) e^{z_j^l (t_{n+1} - \tau_{l-1})} \mathbf{y}'(\tau_{l-1}, \tau_l, z_j^l), \quad (\text{C.3})$$

z , A , and $\mathbf{f}_k$ are the coordinate in the complex space, the Green's function, and the time-discretized force, respectively. The parameters L , N , and ω_j^l indicate the numbers of the integral paths, the discretization of the paths, and the coefficient of the integral, respectively (see the main text for detailed definitions).

Numerical steps of the time evolution are:

1. The first time step is $n = 0, t_{n+1} = h, L = 0$ and $\tau_0 = 0$. Thus, the convolution consists only of Eq. C.2.
2. The second step is $n = 1, t_{n+1} = 2h, L = 1, \tau_0 = h$ and $\tau_1 = 0$. The convolution term $\int_h^{2h} A(2h - \tau) \mathbf{f}(\tau) d\tau$ is calculated by Eq. C.2, and the rest is obtained by Eq. C.3, as

$$\int_h^{2h} A(2h - \tau) \mathbf{f}(\tau) d\tau \sim \sum_{j=-N}^N \omega_j^1 A(z_j^1) e^{z_j^1 h} \mathbf{y}'(h, 0, z_j^1).$$

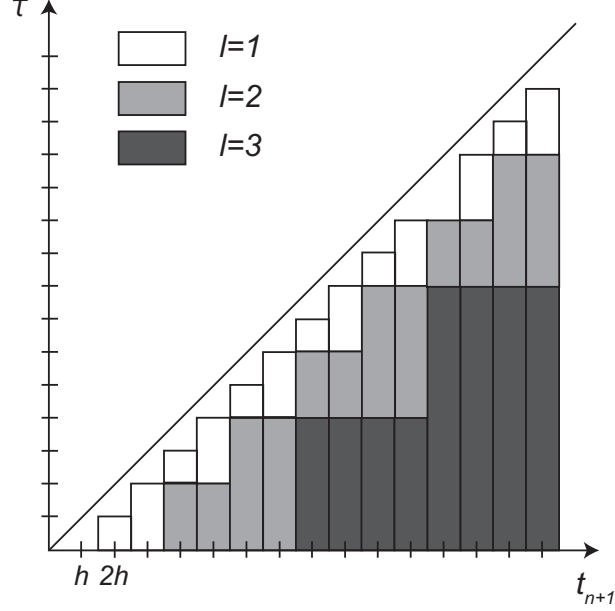


Figure C.1: Schematic image of the divided intervals of the fast convolution in the case of $B = 2$. Gray scales in the rectangles indicate the mTILT performed by the corresponding l contour.

According to Eq. C.1, $\mathbf{y}'(h, 0, z_j^1)$ is derived from values of $\mathbf{f}(h)$ and $\mathbf{f}(0)$.

$$\mathbf{f}(h), \mathbf{f}(0) \rightarrow \mathbf{y}'(h, 0, z_j^l) \quad l \geq 1$$

The critical point is that here we save $\mathbf{y}'(h, 0, z_j^l)$ values for all of the l contours in the memory. The force $\mathbf{f}(0)$ is not necessary to be saved.

3. The third step is $n = 2, t_{n+1} = 3h, L = 1, \tau_0 = 2h$ and $\tau_1 = 0$. As for the second step, $\int_{2h}^{3h} A(3h - \tau) \mathbf{f}(\tau) d\tau$ is calculated by Eq. C.2, and the rest is obtained by Eq C.3, as

$$\int_0^{2h} A(3h - \tau) \mathbf{f}(\tau) d\tau \sim \sum_{-N}^N \omega_j^1 A(z_j^1) e^{z_j^1 h} \mathbf{y}'(2h, 0, z_j^1).$$

$\mathbf{y}'(2h, 0, z_j^l)$ values are also calculated from the force terms and $\mathbf{y}'(h, 0, z_j^l)$ via Eq. C.1 and stored.

$$\mathbf{y}'(h, 0, z_j^l), \mathbf{f}(2h), \mathbf{f}(h) \rightarrow \mathbf{y}'(h, 0, z_j^l) \quad l \geq 1$$

The force $\mathbf{f}(h)$ is not necessary to be saved any more.

4. The next step is $n = 3, t_{n+1} = 4h, L = 2, \tau_0 = 3h, \tau_1 = h$ and $\tau_2 = 0$. The first term $\int_{2h}^{3h} A(3h - \tau) \mathbf{f}(\tau) d\tau$ is calculated by Eq. C.2. Because now L becomes 2, the rest convolution consists of the

contributions of $l = 1$ and $l = 2$,

$$\begin{aligned} \int_{2h}^{3h} A(4h - \tau) \mathbf{f}(\tau) d\tau &\sim \sum_{-N}^N \omega_j^1 A(z_j^1) e^{z_j^1 h} \mathbf{y}'(3h, 2h, z_j^1). \\ \int_0^{2h} A(4h - \tau) \mathbf{f}(\tau) d\tau &\sim \sum_{-N}^N \omega_j^2 A(z_j^2) e^{2z_j^2 h} \mathbf{y}'(2h, 0, z_j^2), \end{aligned}$$

Here we can import the $\mathbf{y}'(2h, 0, z_j^2)$ value that was saved at the previous step. Note that the superscript indicates the l index, not the square of the corresponding variable. The $\mathbf{y}'(3h, 2h, z_j^1)$ term is calculated by Eq. C.1,

$$\mathbf{f}(3h), \mathbf{f}(2h) \rightarrow \mathbf{y}'(3h, 2h, z_j^1).$$

We also proceed the time step forward to the saved $\mathbf{y}'$ values as

$$\mathbf{y}'(2h, 0, z_j^l), \mathbf{f}(3h), \mathbf{f}(2h) \rightarrow \mathbf{y}'(3h, 0, z_j^l). \quad l \geq 2$$

The force $\mathbf{f}(2h)$ is not necessary to be saved.

5. In the same manner, we calculate the convolution. Especially, the $\mathbf{y}'$ value we need is

$$\mathbf{y}'(3h, 2h, z_j^1), \mathbf{f}(4h), \mathbf{f}(3h) \rightarrow \mathbf{y}'(4h, 2h, z_j^1).$$

Then, the saved $\mathbf{y}'$ values are proceeded by one time step in order to prepare the subsequent time evolution.

$$\mathbf{y}'(3h, 0, z_j^l), \mathbf{f}(4h), \mathbf{f}(3h) \rightarrow \mathbf{y}'(4h, 0, z_j^l). \quad l \geq 2$$

As shown above, we do not need to save all the history of the force during the dynamic simulation. Instead, the stored $\mathbf{y}'$ values are updated at each time step, and the updated values are used to perform the convolution employing mTILT. This procedure allows us to decrease the memory allocation and simulation time dramatically.

C.2 GFMD Simulations

Figure C.2 reports all the relevant information about the trajectories obtained with GFMD for the different diamond-diamond interfaces under study. Moving from left to right, we find the temperature and internal stresses calculated along the motion direction (x) and perpendicularly to it (z) for all three systems. Since the curves often possess marked oscillations, in the figure we report the original data left in transparency on the background, together with the corresponding curves smoothed with the algorithm provided by Metzner et al. [372].

The temperature is reported for both the atoms simulated with the Car-Parrinello technique and the C atoms connected to the Green's function. It is possible to notice the presence of periodical drops to zero of the temperatures. The same occurs for the lateral and loading stresses. This behavior is caused by the refresh treatment, which temporarily arrests the simulation for repositioning the GF atoms in their initial

position and reduce the integral error that accumulates during the dynamics. In these simulations, we have applied this technique every 5 ps. A description of this method is detailed in the Methods section of Chapter 4.

The shear and load stresses, reported as well in Fig. C.2, are the internal forces of the atoms of the system. They are calculated by subtracting the forces of the upper slab from those of the lower one, as follows:

$$\tau_x^{GFMD} = \frac{1}{A} \left[\left(\sum_i F_x^i \right)_{up} - \left(\sum_i F_x^i \right)_{down} \right] \quad (C.4)$$

$$\tau_z^{GFMD} = \frac{1}{A} \left[\left(\sum_i F_z^i \right)_{up} - \left(\sum_i F_z^i \right)_{down} \right] \quad (C.5)$$

where the sum over i is performed on all the atoms of the upper slab and the lower one. The values are normalized by the area of the crystalline cell of the system. By taking the ratio between the average value of the curves, it is possible to estimate a coefficient of friction as in the Amontons law [9].

The applied lateral force produces, at the steady-state, a relative linear motion along the x-direction between the two surfaces in contact, as shown in Fig. C.3. The velocities are very similar, slightly decreasing with the reduction of the hydrogen passivation, and have been calculated with linear regression.

C.2.1 Computational parameters and temperature control

Concerning the temperature, the ideal situation would be not to apply any thermostat on the CP atoms and let the system thermalize due to the only temperature fluctuations of the GF atoms. However, without applying any thermostat on the quantum atoms, the diamond slabs heat up very slowly, and there is a not negligible discrepancy between the temperature of the classical and quantum parts of the systems. For this reason, we decided to tune the computational parameters of the CP atoms to achieve the most favorable result in terms of temperature. We thermalized the CP atoms by applying a Nosé-Hoover thermostat with a frequency of 80 THz only on the electrons degrees of freedom and imposing an average electronic kinetic energy of 0.25 atomic units (a.u.). At the same time, we adopted a fictitious electron mass of 100 a.u. and a time step of 4 a.u. for the molecular dynamics. However, if a Nosé-Hoover thermostat is also used on the ions, the frequency value should be carefully chosen to be as close to the material's vibrational frequencies as possible to heat the system efficiently. In particular, for the (111) H-passivated diamond surfaces, the frequency is about 85 (65) Hz for hydrogenated (deuterated) surfaces [373, 374].

C.3 Comparison with static simulations

We calculated the potential energy surfaces (PES) for the three diamond interfaces of this work by performing relaxation simulations using the pw.x software from the Quantum Espresso suite [236, 261, 262]. Firstly, we started by applying a load of 5 GPa to the external atoms of the slabs in order to obtain the equilibrium configuration of the interface under load. We allowed the atoms to move only along z but kept them fixed in the xy plane to preserve the relative positioning between the surfaces. The lateral configurations were chosen by employing a 6x10 point grid, obtained by dividing the edges of the cell into approximately equally spaced sections. The grid coordinates with respect to the cell origin provided the lateral displacements to be applied to the upper slab in order to span the entire energy landscape of the interface

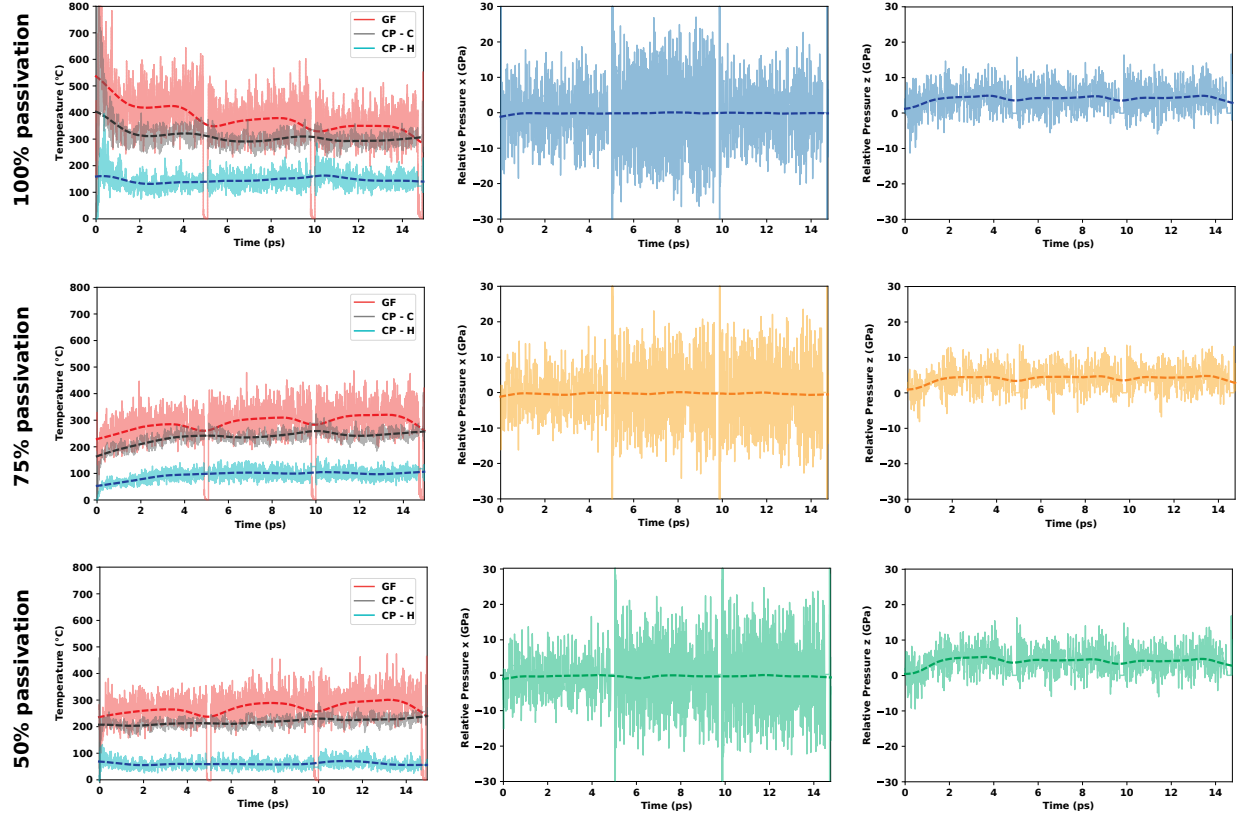


Figure C.2: Profiles of temperature and internal forces per unit area along the direction of motion (x) and perpendicularly to it (z) for the diamond interfaces. The picture can be read horizontally. Moving along the panels, the system temperature and the shear stress and load trends through the simulation are reported for all the coverages.

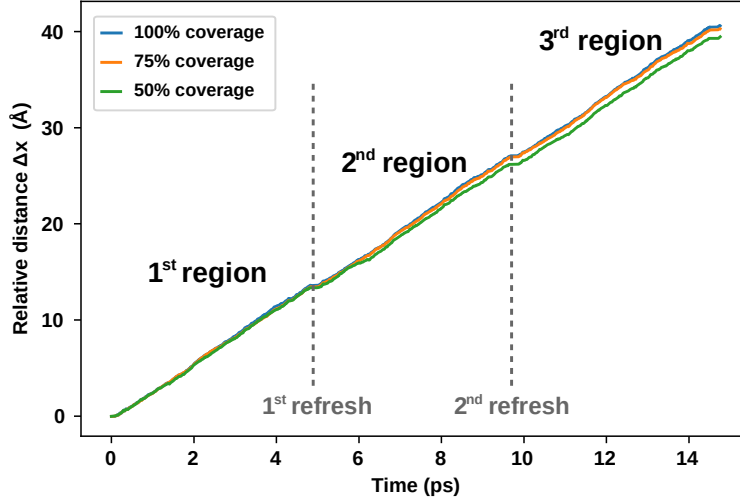


Figure C.3: Relative motion of the diamond interfaces along the sliding direction (x).

The PESes are reported in Fig. C.4 on their own scale, the hydrogen coverage decreases moving to the right. It can be seen how the energy corrugation, i.e., the maximum of the PES, slightly increases with the decrease of the surface coverage. Also, it is possible to observe a slight change in the PES shape, specifically in the 75% and 50% passivation cases, where the two equivalent maxima assume now different energy heights.

The minimum energy path (MEP) for the different landscapes is shown on the PES plots. They display the most favorable sliding path that will occur adiabatically if the surfaces in motion are placed under non-severe conditions of shear and load. However, in the presence of harsh external forces, the surfaces possess higher energy and their motion may deviate from the MEP.

To understand the sliding of the diamond slabs, we compared the dynamic trajectory obtained with the GFMD with the PES of the system, considering the motion occurring over the energy landscape (Fig. 4.8 of Chapter 4). The potential energy barrier encountered by the surfaces is shown for the various coverages in Fig. C.5, together with the corresponding force per unit area along the trajectory. This force is obtained as the derivative of the energy profile. It represents the magnitude of the lateral force during the motion in the xy plane.

As the surface coverage decreases, the slabs progressively face situations with higher potential energy during their motion. Two factors determine this situation. With the decrease of the coverage, the energy corrugation of the PES increases and the peaks change their shape and height slightly. At the same time, the fluctuation occurring during the sliding may cause the slabs to pass closer near the PES maxima in certain situations. The average potential barrier along the trajectory is 0.037 J/m^2 (0.1 J/m^2) in the case of surface passivation of 100% (75%-50%).

The maximum lateral force in absolute value can be defined as the ideal shear strength τ_{traj} along the trajectory, which indicates the maximum sliding resistance. The shear strength increases noticeably with the decrease in the H-coverage, revealing how the adhesive interactions between the surfaces play a significant role in defining the friction of the interface. Although τ_{traj} provides a precise indication of the maximum resistance to sliding, it can be considerably influenced by the local fluctuations encountered by

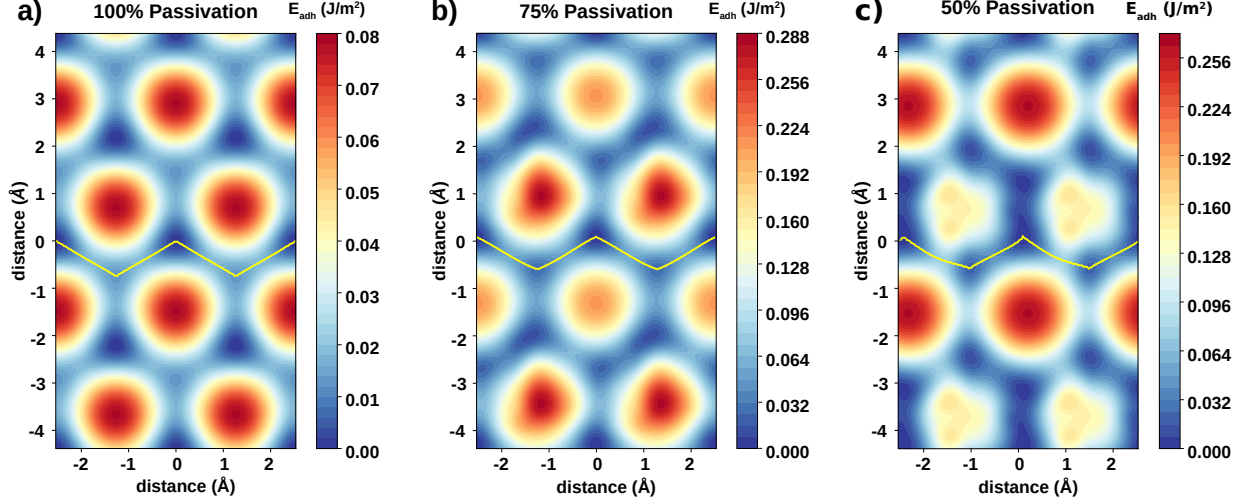


Figure C.4: PESes of the three systems under study in presence of a load of 10 GPa. The calculated MEPs are reported on top of the energy landscape as yellow lines.

the system. Therefore, in this case, the average force (in absolute value) encountered along the trajectory could provide a more relevant parameter for determining a dynamic shear strength. Table C.1 reports these values, showing that the mean value of the shear strength is the same for the 75% and 50% passivation case, despite the maximum ideal shear strength being higher for the 75% case.

These data can be compared with the motion along the MEP. The energy and force profiles are reported similarly as the trajectory case in Fig. C.6, and the values of the calculated shear strength are listed in Table C.1. Although the relative height and the PES maxima modify, as it can be observed in Fig. C.4, the global pattern still displays a hexagonal shape. Therefore, the MEP for the different cases is very similar, and this is reflected in the potential energy profiles of Fig. C.6. The only difference arises from the irregularities of the PES shape coming from the lack of hydrogen atoms and the variation of the PES corrugation. As a result the average potential barrier along the MEP for a surface passivation of 100% (75%-50%) results 0.012 J/m² (0.035 J/m²).

By analyzing the ratio between the mean shear along the trajectory and the MEP, one can notice that decreasing the coverage progressively increases the likelihood between the two τ . While for the 100% case $\langle \tau_{traj} \rangle$ is more than twice the MEP one, in the 50% passivation case this value reduces to 1.42. This factor is probably due to the increase in the corrugation of the PES and the consequent presence of greater forces, which impose the motion to following the MEP more. Otherwise, with a complete passivation of the interface, the potential energy barrier becomes a third, and the interaction between the surfaces is significantly reduced.

Passivation	$\langle \tau_{traj} \rangle$ (τ_{traj})	$\langle \tau_{MEP} \rangle$ (τ_{MEP})	$\langle \tau_{traj} \rangle / \langle \tau_{MEP} \rangle$
100%	0.36 (0.90)	0.16 (0.32)	2.25
75%	0.97 (3.31)	0.57 (1.10)	1.70
50%	0.95 (2.81)	0.67 (1.41)	1.42

Table C.1: Calculated shear strengths along the GFMD trajectory and the MEP over the PES. The column reports the τ (expressed in GPa) calculated as the average function value of the force curve, as $1/(b-a) \cdot \int_a^b |f| dl$. The maximum value of the shear strengths are also reported enclosed within brackets.

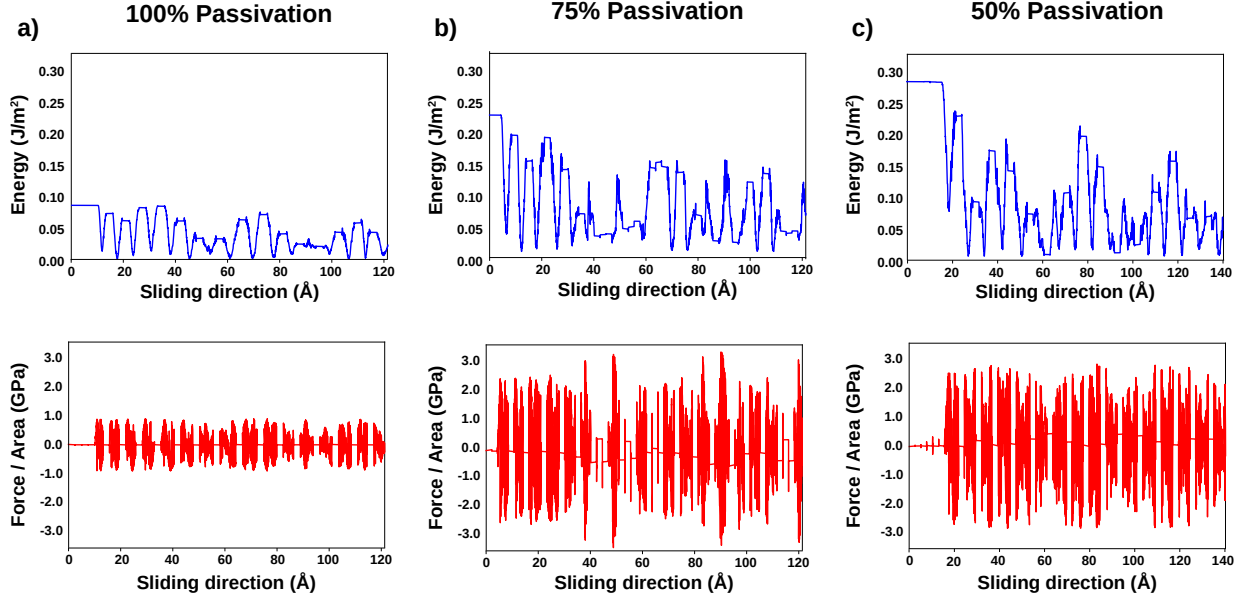


Figure C.5: Values of the potential energy (blue) and force (red) along the trajectories of the GFMD simulations occurring over the static PES. The dynamic simulations of the 100% (a), 75% (b), and 50% (c) passivated systems are displayed.

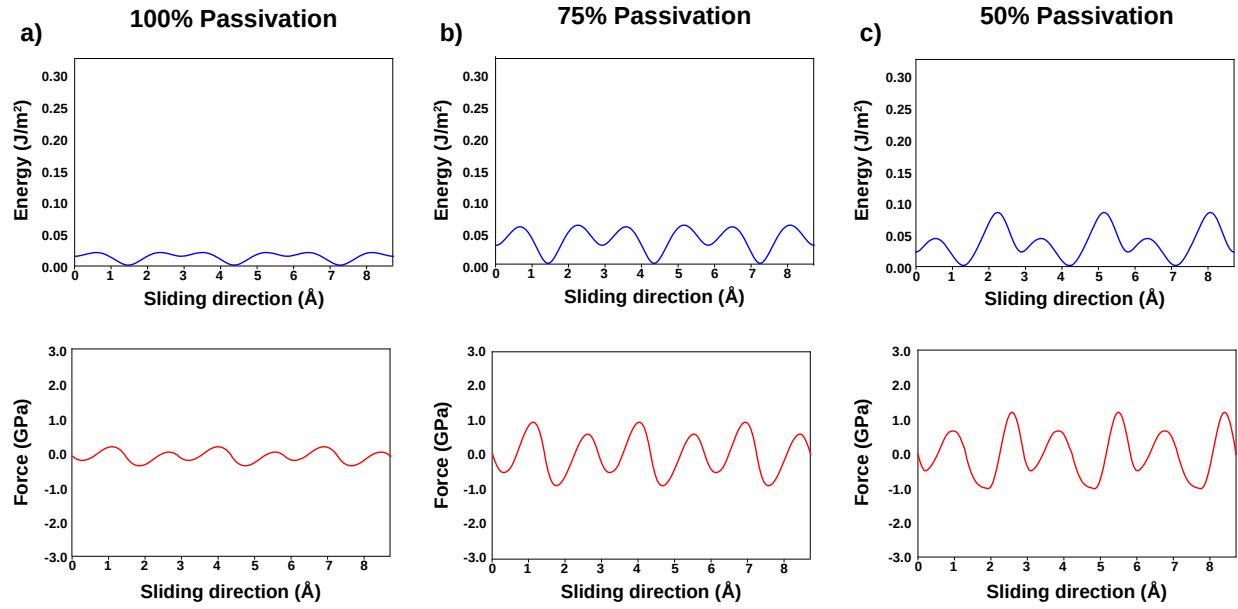


Figure C.6: Profiles of potential energy (blue) and force (red) evaluated along the Minimum Energy Path of the PES for the 100% (a), 75% (b), and 50% (c) passivated systems, respectively.

Appendix D

Supporting information for: Superlubricity in phosphorene identified by means of ab initio calculations

D.1 Charge displacement and redistribution

The charge displacement for a bilayer represents the electronic charge rearrangement occurring at the mated interface, calculated as $\rho_{diff} = \rho_{12} - \rho_1 - \rho_2$. The charge redistribution [202], $\rho_{redist} = \frac{1}{2z_o} \int_{-z_o}^{z_o} |\rho_{diff}| dz$, is instead a measure of the global redistribution of the electronic charge within the interlayer region.

The charge displacement ρ_{diff} and its profile along z are presented in Fig. D.1. The interfacial adhesion can be related to the amount of charge ρ_{redist} that is redistributed when an interface is formed, as shown by Wolloch et al. [202]. The values assumed by this figure of merit correspond to the shaded areas in the profile $\rho_{diff}(z)$ and are reported in each panel along with the adhesion energy, E_{adh} . Increasing the charge redistribution, a correspondent increasing in the adhesion energy is observed, and the trend fits the predicted linear scaling [202] between E_{adh} and ρ_{redist} . Looking at the profile of the electronic charge perpendicular to the surfaces (panel e), we notice that the charge at the interface is higher in AB than in AB' stacking, whereas two coincident curves are found for AZ and AZ' stackings, for which we also observe a superimposable charge redistribution (Fig. D.1b–d). In addition, the AB electronic charge is also slightly higher than the AZ one, which is consistent with the slightly higher adhesion energy of the AB stacking.

D.2 PES for perpendicular orientation

Here, the Potential Energy Surface for the antiparallel orientation is reported in Fig.D.2 adopting its proper scale. The energy landscape is clearly flat, and the MEP direction forms an angle of about 37° with the horizontal.

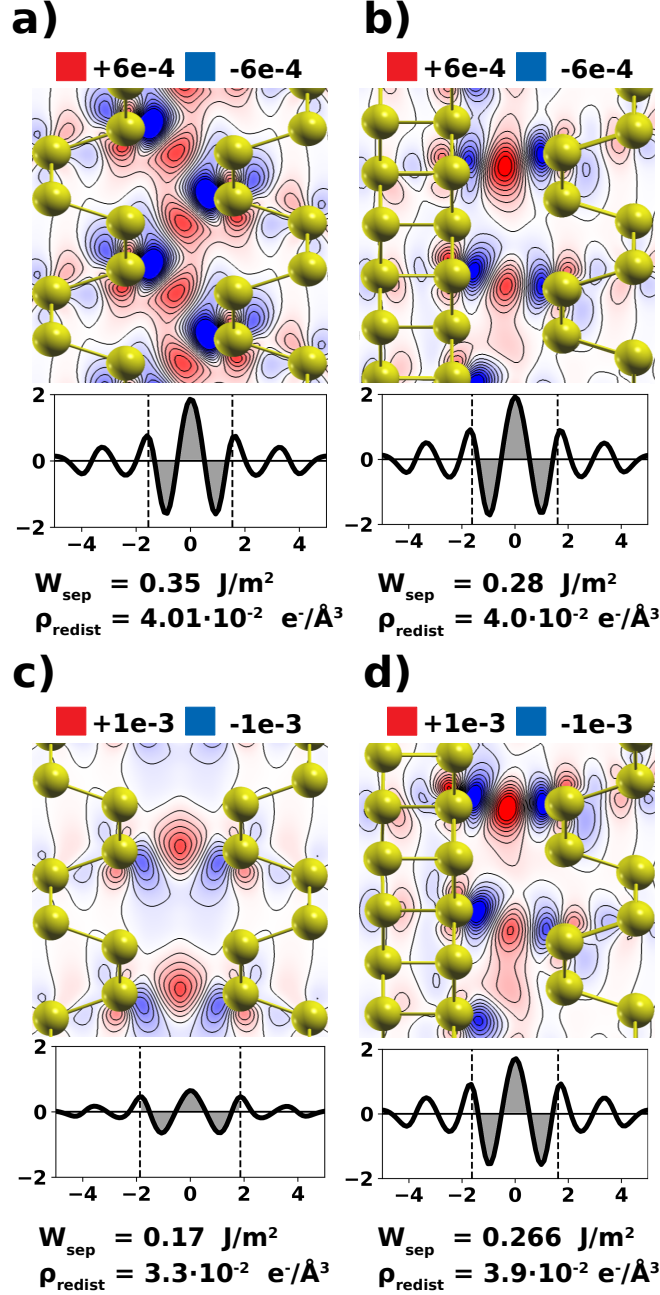


Figure D.1: The charge displacement ρ_{diff} is represented for the AB (a), AZ (b), AB' (c), and AZ' (d) stackings of phosphorene. The electronic charge in the plots is expressed in $e^-/\text{\AA}^3$. In lower panels the profile of the charge displacement integrated along the xy plane is reported, alongside with the work of separation W_{sep} and the charge redistribution ρ_{redist} calculated for each stacking configuration.

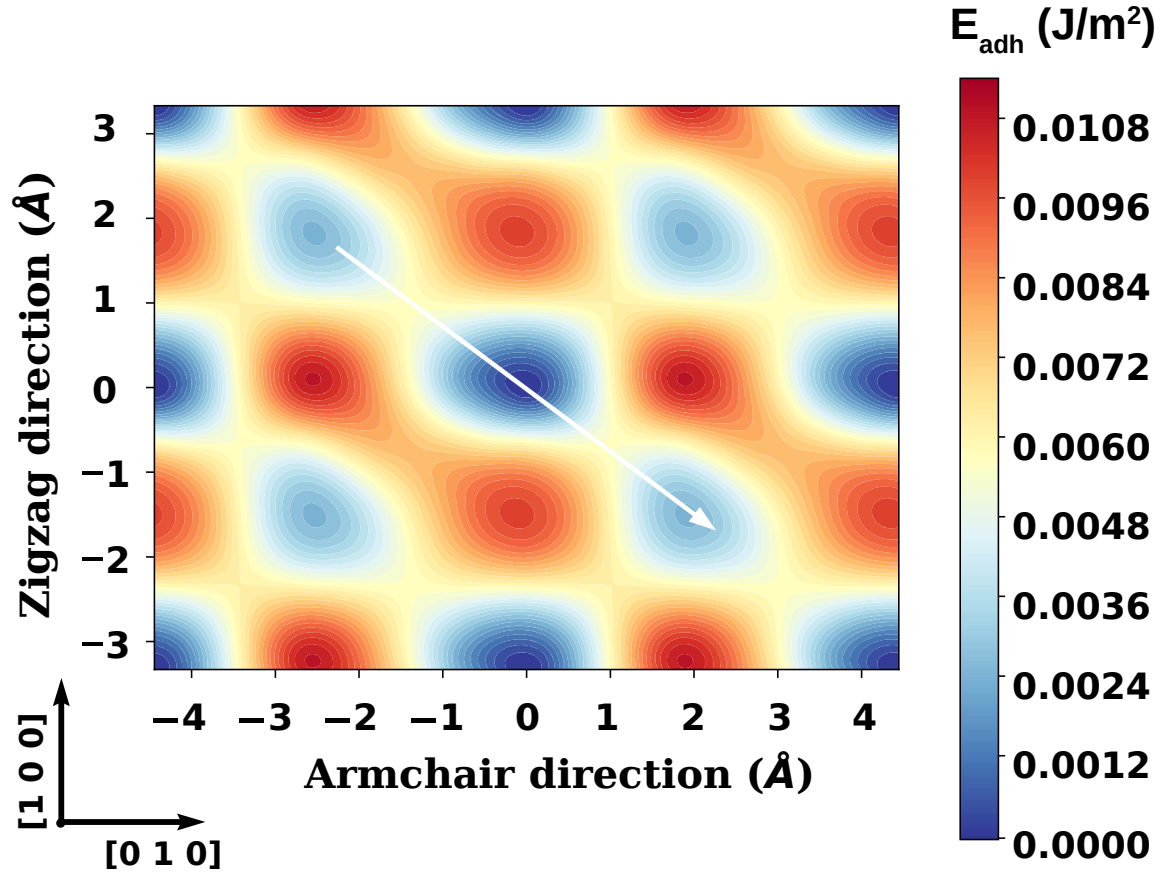


Figure D.2: Potential Energy Surface and minimum energy path for the perpendicular orientation. The Cartesian axis are referred to the upper layer.

Appendix E

Lubricating effects of phosphorene and MoS₂ on iron compared to graphene

E.1 Choice of atomic structures and XC functional

To estimate the minimum thickness needed to correctly simulate the iron slab in this study, we analyzed how the adhesion energy changes for a phosphorene layer placed on an iron surface (110). We performed this check, by considering two and three atomic iron layers respectively, in the presence of three different exchange-correlation functionals (XC), namely LDA, PBE, and PBE+D2. The results are in Tab. E.1 and show that the change in energy is quite contained to the iron content. In the case of LDA, the greatest variation in the energy is observed, equal to almost 4%, while with PBE and PBE+D2 the error is below 2.5%. Since these adhesions are calculated by energy differences, e.g., $E_{adh} = E_{Fe+P} - E_P - E_{Fe}$, the overall numerical error tends to balance out. For this reason, we have decided to use two atomic layers for representing the iron slab, as well as to reduce the electronic dimensions of the system and make the DFT simulation computationally feasible.

To understand the effect of the XC functionals on adhesion we analyzed the adhesion energy of a layer of MoS₂ and phosphorene on iron, comparing it with the results obtained for graphene. The data is reported in Tab. E.1 and shows a common trend between the materials. LDA is known for overbinding atomic structures and it can be observed that its adhesion values are among the highest. PBE alone is unable to represent long-range interactions, resulting in rather small adhesion values. The exception case here is phosphorene, which has a rather high adhesion even with PBE, although numerically it remains the lowest. This is probably due to the strong covalent interaction that is created between the phosphorus atoms and the iron [353]. For the choice of the functional, we adopted PBE+D2, which provides long-range empirical corrections necessary to correctly represent the VdW dispersion interactions in layered materials and give rise to stable structures and rather high adhesions. Despite the simplicity of this method, it can correctly detect the interlayer distance between layered materials and has been used in the past to study various structures for tribological purposes[349, 280, 319, 124, 93, 126].

E.2 Potential Energy Surfaces

The Potential Energy Surfaces are reported for all the different lubrication cases analyzed for the iron-iron interface. Each plot is represented on its scale, depicted as a legend next to the figure, to show the morphology of the three-dimensional landscape in more detail. The plots also display the minimum energy paths, which have been calculated through the improved simplified string method [225], as implemented in our software [194, 125]. To get a more extended representation of the path that two surfaces in relative motion could follow along with the PES, we started placing a string centered on the origin of the cell, and whose extreme points extend from -1.5 to 1.5 times the long lattice parameter x and y . The string is then

	# Fe layer	E (J/m ²)	E (eV/atom)	Diff. %
LDA	2	-3.07	-0.621	3.77 %
	3	-3.19	-0.645	
PBE	2	-1.80	-0.388	1.01 %
	3	-1.82	-0.391	
PBE+D2	2	-2.64	-0.567	2.34 %
	3	-2.70	-0.581	

Table E.1: How the adhesion energy of a phosphorene monolayer on a Fe(110) substrate varies with the XC functional and with the number of atomic layers of iron considered. The energy is reported in J/m² and eV per phosphorene atom.

	Fe-C[280] (J/m ²)	Fe-P (J/m ²)	Fe-MoS ₂ (J/m ²)
LDA	-0.75	-3.07	-1.71
PBE	+0.01	-1.80	-0.73
PBE+D2	-0.89	-2.64	-1.60

Table E.2: Adhesion energy of a monolayer of phosphorene, MoS₂, and graphene chemisorbed on a Fe(110) substrate, calculated with different XC functionals.

made to converge in the final position as shown in the figure, moving between the minima of the PES and passing through the saddle points. Along the given path, the maximum ideal shear strength is calculated as $\tau_{MEP} = \max |\nabla \gamma(x, y)|$.

E.3 Charge Displacement

To understand the chemical processes that develop at the interface, we have calculated the electronic charge density and the electronic charge redistribution for the various interfaces, as reported in Fig. E.2. There, we represent for all the studied interfaces, the planar average electronic charge density along the Z direction of the cell. The highest peaks are typically attributable to the presence of atoms.

We reported the curve of the charge of the whole system and also the charge of the two isolated surfaces that constitute the interface. By making the difference between these curves it is possible to obtain the red curve represented in the various quadrants: The charge displacement. This provides us with an indication of how the electronic charge density is redistributed to the interface when passing from two separate slabs or surfaces that are then joined to form a solid interface.

E.4 Graphene monolayer lubrication

To complete the study of iron lubrication, we report here the PES and the charge displacement calculate for a single layer of graphene intercalated at the iron-iron interface. Both plots are shown in Fig. E.3, note that the PES is reported both on its scale (a) and the scale of the interface lubricated by a MoS₂ monolayer. In the case of a single graphene sheet, we find a corrugation of 0.098 J/m², leading to shear strength of 0.25 GPa and a charge redistribution of 0.012 $e^-/\text{\AA}^3$.

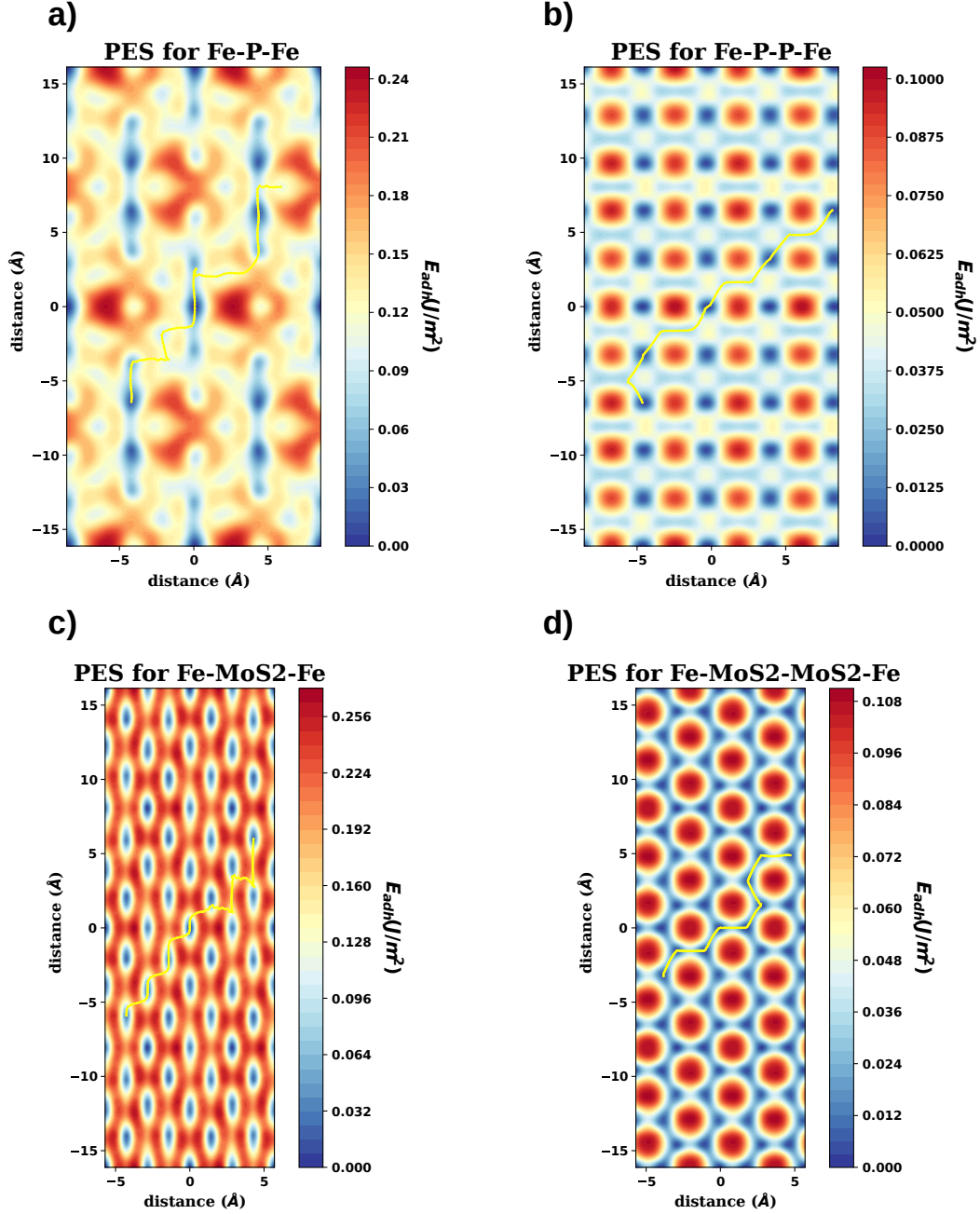


Figure E.1: Potential Energy Surfaces for a solid iron-iron interface lubricated with phosphorene monolayer (a) and bilayer(b), and molybdenum disulfide monolayer (c) and bilayer (d), intercalated at the interface.

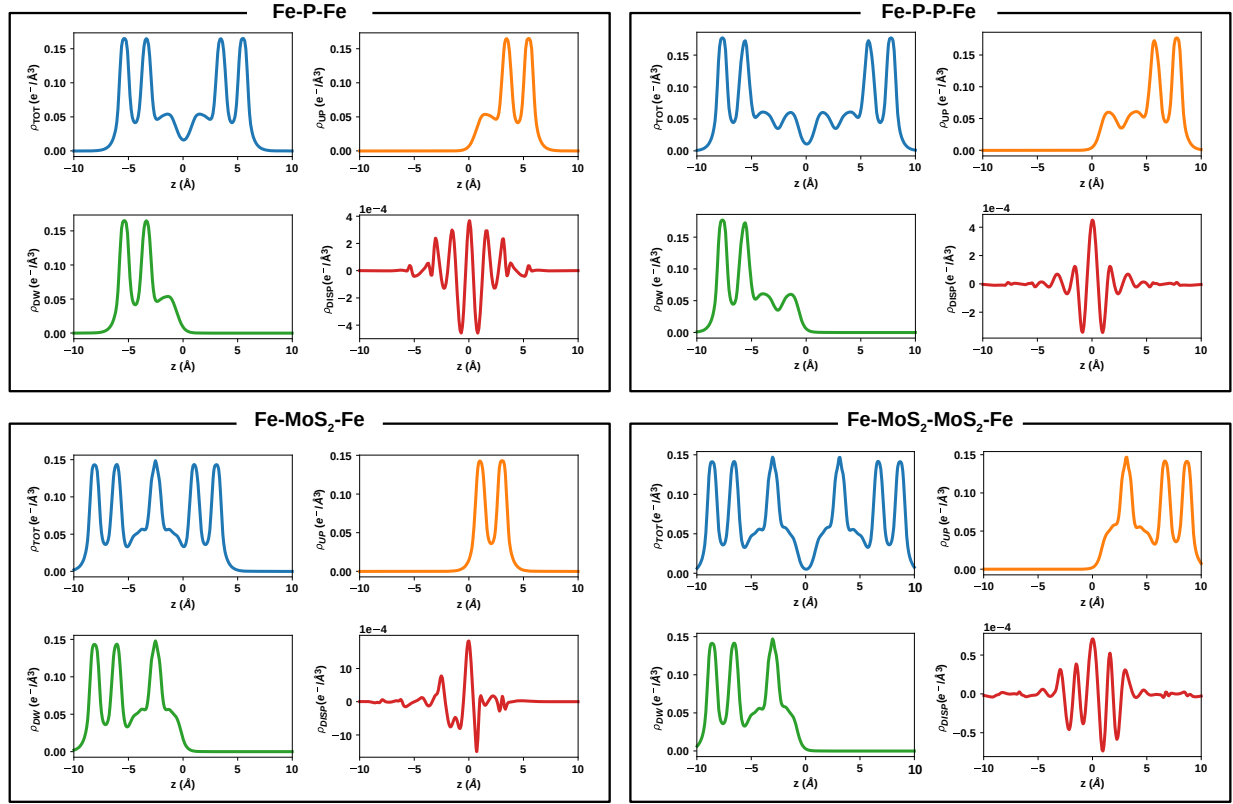


Figure E.2: Electronic charge density and charge density redistribution for all the interfaces. Inside each box, indicating a different type of lubrication of the iron-iron interface, and moving clockwise from the figure positioned at the top left, we have: the electronic charge of the whole interface, the electronic charge of the upper surface, the charge displacement, and the electronic charge of the lower surface.

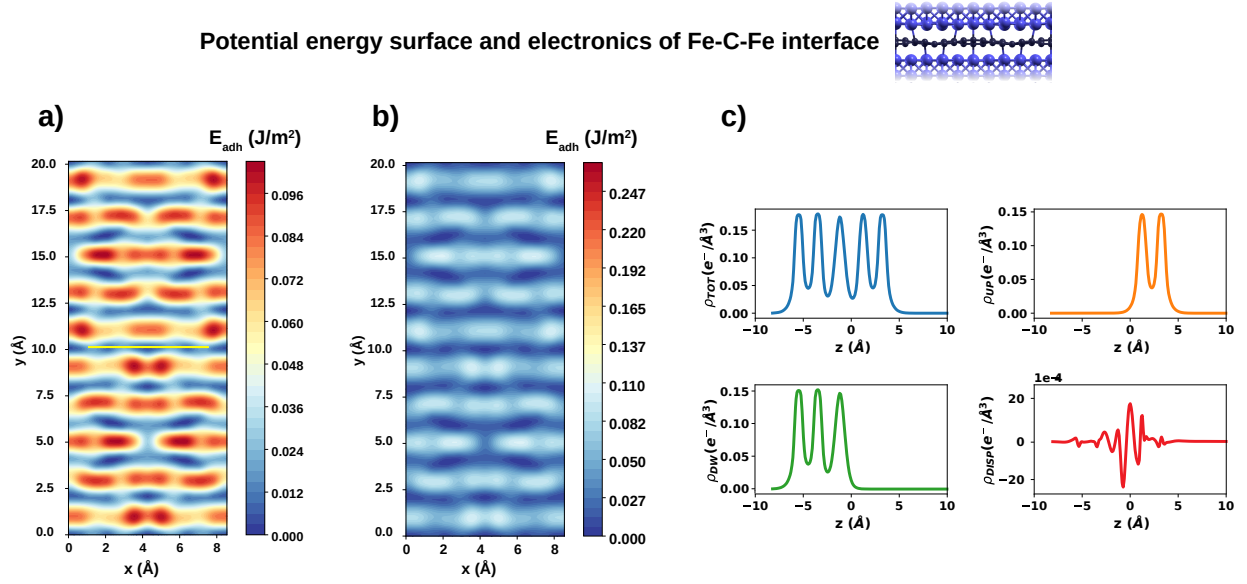


Figure E.3: PES for the iron interface lubricated with monolayer graphene (a-b). The electronic charge and charge displacement are reported in panel (c), going clockwise from the top left we have: charge of the interface, the charge of the upper slab, charge displacement, the charge of the lower slab.

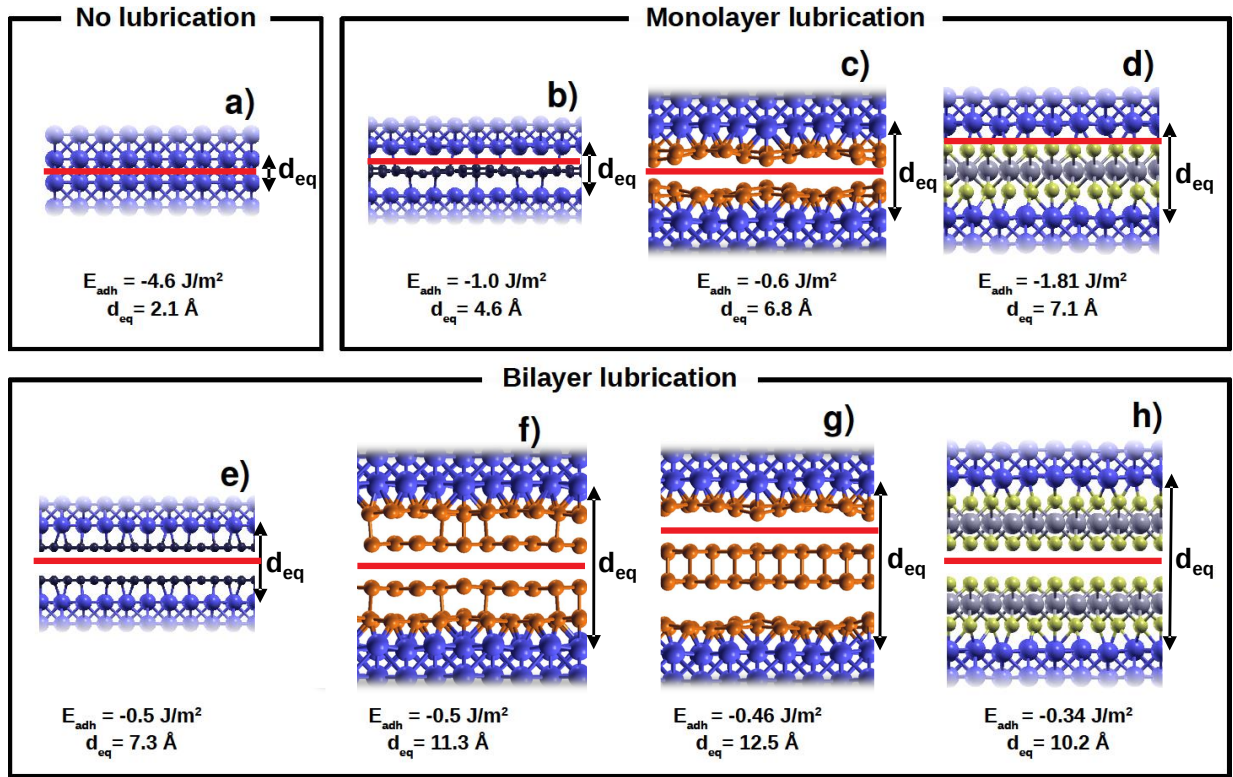


Figure E.4: Adhesion energies (in J/m^2) of the iron-iron interface intercalated with one layer and two layers of 2D materials. The red horizontal line separates the two separate slabs considered in the adhesion calculation.

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