

École polytechnique de Louvain

Commensurate-incommensurate transition in van der Waals heterostructures : a study based on the one-dimensional Frenkel-Kontorova model

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Enjoy your reading!

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Abstract

This thesis aims at developing and applying a new framework for the prediction of commensurate or incommensurate phases for the ground state of Van der Waals heterostructures. It builds upon the recent work by B. Van Troeye *et al* : "First-principles investigation of 2D lattice coherency in van der Waals heterostructures" [1]. In their article the commensurability of different van der Waals heterostructures (vdWHS) was predicted using the mathematical model developed by J. Frenkel and T. Kontorova [2] and then revisited by F. Frank and J. Van der Merwe [3]. In the present work, the analytical solution of Franck and Van der Merwe is first checked for more general situations than in the original proposal of Frenkel and Kontorova, using a numerical implementation. Then, the same mathematical framework is used to develop more criteria unveiling the possibility to probe more possible ground phases than B. Van Troeye *et al*, also more accurately. The application of our model to eleven actual vdWHS shows more detailed understanding than the model of B. Van Troeye *et al*. It is also expected to agree better with experimental results, but the latter are too scarce at the time of writing.

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Introduction

"Make it thinner". In the world of material science, this injunction seems now unlikely to give any additional result. Indeed, with the advent of graphene, the first truly two-dimensional (2D) material, thinner is not an option anymore [25]. However, if for some, it seems the end of a long journey, it represents a world of new possibilities for others [26]. Creating atomically-thin structures was a long-time dream for engineers. It is now in their grasp, ready to unveil a multitude of interesting phenomena [27] [28] [29]. The exfoliation of graphene snowballed as various other 2D materials were synthesized and some researchers started to stack them [30]. Interestingly, those materials do not make any covalent bonds between each other, relying on van der Waals interactions to create a coherent structure. This feature allows to alleviate one of the main constraint limiting the fabrication of thin film: lattice matching [31]. Here, any 2D material can be stacked on another one, without having to care for the property of each layer, just as Lego blocks. With several 2D materials at hand and the ability to stack them at will, the possibilities of design are infinite.

Getting back on track with this thesis, those stacks of layers create structures called van der Waals heterostructures (vdWHS). With them goes a lot of possibility to design new devices but also a lot of physical phenomena. Here, we are interested in understanding the various arrangement of stacking of the vdWHS. Indeed, if we do not have to care for lattice matching anymore, it does not mean the structural arrangement of those structure can not be analyzed. In fact, when two layers are stacked on one another, electronic interactions give rise to an interlayer potential that might push the atoms to adopt preferentially certain configurations. If we consider two layers with different lattice parameters stacked on one another, without atomic reconstruction, an interference pattern appears. This particular pattern is called a Moiré pattern. Without any modification of each structure, such stacking is called incommensurate as no particular order appears and various local environments are found at different places. However, if the interlayer potential is too important, the atoms might prefer to rearrange themselves by stretching the monolayer to adopt more favorable configuration. In that case, a commensurate structure is found. Understanding the transition between those two stacking orders is important for design as it leads to different electronic properties. This thesis aims at understanding when this transition occurs.

To do so, a simple mathematical model is used on top of first-principles calculations. This model was developed by J. Frenkel and T. Kontorova in the first half of the 20th century [2]. The beauty of this model resides in its ease of use. It is especially appropriate to our problem as it involves the same parameters: a potential energy and an elastic energy. This model was already extensively studied by others, but not in the context of first-principles calculations.

It attracted special interest among mathematicians but, overall, among physicists due to its ability to describe non-linear phenomena [32]. Two scientists, F. Frank and J. Van der Merwe, extended this model in such a way that they defined a criterion for the transition between the commensurate and incommensurate phases [3]. This extension is implemented numerically in this thesis, to get acquainted with the model, and to measure its ability to describe the transition.

This thesis might be considered a sequel to the work of B. Van Troeye *et al* in their submitted article "First-principles prediction of lattice coherency in van der Waals heterostructures" [1]. B. van Troeye and coworkers analyzed the transition between the commensurate phase and incommensurate phase by using the Frenkel-Kontorova (FK) model with parameters from first-principles calculations. Here, we try to refine their results by decomposing the sole criterion used in their work in several sub-criteria. As this thesis directly follows their work, most of the theory involved comes out of their article.

The structure of this thesis is the following: the first chapter takes the shape of an introduction to the 2D world and its possible outcomes. The different materials involved in this thesis are described. A comment on fabrication techniques and possible applications is also found in this chapter. The second chapter is focused on the various effects arising upon stacking. A large comment on band gap engineering is provided with a first introduction to the transition between the commensurate and incommensurate phase. The third chapter is dedicated to the presentation of the FK model and its numerical implementation. The different steps involved to obtain our final implementation are described and illustrated. The fourth and final chapter presents the evolution of the work initiated by B. Van Troeye *et al* with the development of the different criteria used. The application of our model to different vdWHS and the associated results are also presented in this chapter.

Chapter 1

2D materials and van der Waals heterostructures

1.1 Discovery and perspectives

This whole thesis is one of the many sequels of the groundbreaking work performed by A. Geim and K. Novoselov. In 2004, when they exfoliated a monolayer of graphite, more commonly known as graphene, the first 2D material ever synthesized, manipulated and characterized, they opened a whole new world in material sciences [25]. The story of their work is well known among the scientists working in the condensed matter field. Indeed, their experiments led to the Nobel Prize of physics of 2010. Until 2004, all the works performed on 2D materials were either for theoretical purposes such as in [33] where the study of graphene served as an intermediate step to analyze graphite or to study monolayers deposited on substrate as illustrated in [34]. Nobody thought at that time that it would be possible to exfoliate monolayers of materials and isolate it to make measurements. To overcome this difficulty, A. Geim and K. Novoselov used a rather simple technique. They mechanically exfoliated, with what is called "magic tape", graphene from graphite by repeated peeling until one to three layers remained on the tape.

As already stated, this experiment opened a branch of the condensed matter science still unexplored. Lots of research has already been done in this quite recent field of the 2D materials, but a lot of areas remain unexplored at this time. One of the extraordinary topics arising from this discovery is the advent of the van der Waals heterostructures (vdWHS). Those are stacks of several atomically thin layers of various materials unable to make covalent bonds in the out of plane direction. The layers make a coherent structure which holds together thanks to van der Waals interactions (hence the name). With the discovery of different 2D materials and the possibility to associate them at will, the field is not ready to run dry of new findings. This chapter aims at giving a first description of the main 2D materials synthesized to this day and introduces the possible applications allowed by the creation of vdWHS. A brief overview of some of the fabrication techniques enabling their synthesis will also be made.

1.2 Materials and properties

1.2.1 General considerations

Before considering some of the most studied layered materials, it is important to give a first description and to know what to look for in order to tell if a material can give a 2D equivalent.

Every 2D material consists of covalently bond, dangling-bond-free lattice [12]. Those layers can therefore only interact with its neighbor layers by van der Waals interactions.

To evaluate if a material can be stable in its 2D form, one can already consider three things: the melting temperature of the 3D form, the chemical activity of its surface and its electronic nature [26]. For the first criterion, a melting temperature well above room temperature is a good rule of thumbs to know if the 2D phase will remain solid once exfoliated. Indeed, the fusion point is known to arrive earlier passing from bulk to monolayer. Then, the materials must be as chemically inert as possible in order to avoid decomposition during the exfoliation. Finally, insulator and semiconductor are more likely to allow the synthesis of a 2D counterpart than metals as they are less reactive.

Homogeneity and absence of pinholes are two other important criteria that can be evaluated by electrical measurements (either in plane or out of plane following the electrical nature of the 2D layer). This allows to discard materials inappropriate for 2D synthesis.

It is worth noting that 2D materials are the extreme case of surface science pairing with considerations about natural passivation and adsorption, not always compatible with fabrication techniques [26].

From all these points it can be concluded that many possible materials will not be stable at room temperature if exfoliated and therefore the 2D materials library is a lot smaller than its 3D counterpart. Yet, a fair number of 2D materials has already been produced and analyzed unveiling extraordinary physics and new perspectives for applications in electronics and optoelectronics [35]. This is in part due to high crystal quality which can be obtained when the materials are mechanically exfoliated (a comment on the fabrication techniques is available in the Section 1.3) [36]. In the following sections, the main 2D materials are presented, namely graphene, transition metal dichalcogenides (TMDs), hexagonal boron nitride and phosphorene. It has to be noted that most of the properties evolves with the number of layer and therefore the following informations are only valid for monolayers, except when stated otherwise.

1.2.2 Graphene

Lattice and mechanical properties

Graphene is a sheet of carbon atoms arranged in hexagonal lattice composed of two interleaving triangular sublattices as presented in Figure 1.1. Each carbon atom is hybridized sp^2 and makes σ bonds with its neighbors while having its p_z orbital perpendicularly to the sheet plane. That orbital can create π bonds with the neighboring atoms which can hybridize leading to the formation of π and π^* band. Those bands are half-filled and responsible for most of the electronic properties of graphene [4].

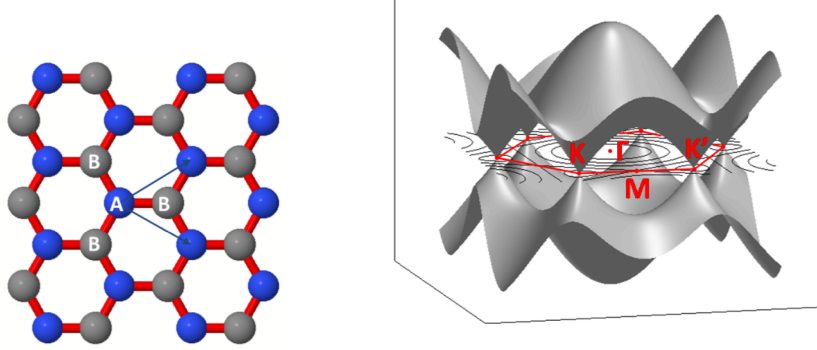


Figure 1.1 – Left: Graphene lattice with its two inequivalent triangular sublattices highlighted by a blue color for sublattice A and a grey color for sublattice B. Each A atom has three B atoms as neighbors. The arrows indicate the vectors of the unit cell. Right: Graphene valence and conduction band in the first Brillouin zone with the K and K' points highlighted. Both adapted from [4].

The σ bonds are quite strong leading to incredible mechanical properties [5]. The breaking strength of graphene is of about 40 N/m [37] (close to the breaking strength of a defect free atomic sheet) while its Young modulus has been evaluated to 1 TPa [38]. Graphene is also foldable as well as brittle [39] and can be strained elastically up to $\sim 20\%$ [38].

From a thermal point of view, graphene presents the highest thermal conductivity with value of ~ 5000 W/(K·m) reported (at room temperature) [40]. Uncommonly, graphene shrinks with increasing temperature because of the dominance of membrane phonons. Theoretical work estimated its melting temperature above 4000K [41].

Electronic properties

All those mechanical properties make it a good candidate for integration in devices such as transistor or solar cells but its electronic properties are even more interesting; if not more. Graphene is a semi-metal with zero overlap between the conduction band and the valence band or a semiconductor with zero band gap. Its valence band and conduction band are presented in Figure 1.1. In the figure, it can be seen that the conduction band and the valence band meet at 6 points called the Dirac points. The 6 points are divided in two subsets of three points each labeled K and K' . The two subsets are inequivalent and lead to a valley degeneracy $g_v = 2$. Due to its band construction, the wave function in the vicinity of the K -points can be constructed from two-component spinors [5]. This allows the introduction of what is called a pseudospin : a number equivalent to quantum number. It permits to distinguish if the particle is localized more around the sublattice A or sublattice B. It is also associated with a notion of chirality (the projection of the pseudospin on the momentum), which yields electron and holes having opposite momentum originating from the same sublattice [6]. The conservation of those quantity can help explain the transport properties of graphene.

By looking closely to the Dirac points, one can observe that, in the low energy range, the

band structure looks like two cones put on the tip of one another. The dispersion relation in that area is linear which is the signature of Dirac fermions (i.e. (quasi-)relativistic particles) [4]:

$$E_{\pm}(k) \approx \pm \hbar v_F |k - K| \quad (1.1)$$

with E the energy of the particle, k the momentum of the particle, $\hbar$ the Planck constant and K the momentum associated to the Dirac point K , $v_F \approx 10^6 \text{m/s}$ the Fermi velocity and the '+' ('-') sign describing the upper (lower) band. Therefore, electrons and holes can be seen as relativistic particles in the vicinity of the Fermi level. This leads to phenomenon such as the Klein tunneling which has been observed already in 2009 [42]. This phenomenon describes the tunneling of a particle through a big barrier of potential. In the non-relativistic frame, a particle would have nearly zero probability to cross the barrier as its wave function would vanish. For relativistic particle, the uncertainty principle of Heisenberg allows the electron that hits the barrier to transform in a positron (for which the barrier is in fact a well), and to exit the barrier as an electron [43]. This leads to a probability of transmission, at a normal incidence, of one. In graphene, the chirality leads to variation of transmission probability following the angle of incidence [4].

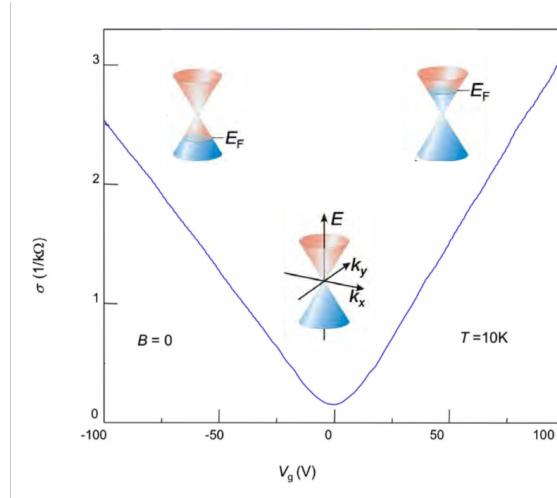


Figure 1.2 – Illustration of the ambipolar effect in graphene. The gate voltage modifies the position of the Fermi level as indicated in the insets, introducing 'artificial' doping to the layer. Adapted from [5] with insets from [6].

Three final comments can be made. First, the zero band gap structure makes possible doping by applying a gate voltage on the graphene sheet (one can even apply different gate voltage on different zone and to probe electron optics phenomenon [44]). Even doped, the graphene conserves its extraordinary mobility. This phenomenon is illustrated in Figure 1.2. Secondly, its extraordinary mechanical properties (notably the fact that nearly defect-free layers can be exfoliated) and electronic properties allows to observe quantum effect similar to the quantum Hall effect (QHE, quantization of the conductivity by condensation of the density of state in Landau levels under the application of a magnetic field) at room temperature. An interesting property of this effect is the fact that the plateaus of conductance are shifted by 1/2 with

respect to the classical QHE. This leads to the presence of a quantized level at zero bias voltage which is shared by electrons and holes. This can be explained by the presence of a Berry phase (phase acquired during cyclic, slow, adiabatic evolution of the system [45]) of π in the wave functions at the Dirac points, adding an additional phase shift in the QHE [6]. Finally, graphene presents a non-zero conductivity at zero bias voltage (i.e. at the Dirac points where the density of state is zero). It is usually larger than expected by the theory. This is either due to crumpling of the layer or by substrate effect which makes tiny variation of potential. This provoke small doping effect near the Dirac points and gives rise to puddles of electrons and holes free to move [4]. This non-zero conductivity is a problem when producing field effect transistor as it lowers the on-off ratio of conductance.

Other properties

The properties of the graphene layers can also be tuned by adding different adsorbents [37]. One could also tune properties of other materials by creating composite, for example, of polymer and intercalated graphene [36]. It has to be noted that all the exceptional electronic properties of graphene vanish when the number of layers increases.

1.2.3 Transition metal dichalcogenides

Transition metal dichalcogenides (TMDs) are, as their name implies, crystals composed of one transition metal and two chalcogen atoms which makes them fit the formula MX_2 with M a transition metal atom and X a chalcogen atom. This family of 2D material has a hexagonal structure with three layers of atom (the transition metal atoms are sandwiched between two layers of chalcogen atoms) [30]. Their structure is illustrated in Figure 1.3. As for graphene, the atoms are covalently bonded in the plane direction and the layer interact through van der Waals interaction with other layers.

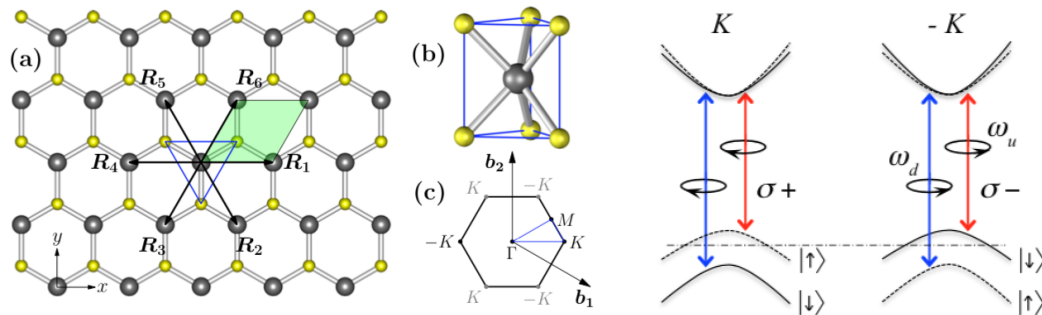


Figure 1.3 – Left: (a) TMDs lattice from the top view with metal atoms in gray and chalcogen atoms in yellow ; (b) side view of the lattice; (c) Scheme of the First Brillouin zone highlighting the different K and K' points. Adapted from [7]. Right: Schematized conduction and valence band of TMDs at the K and K' points with circular polarized light also represented to illustrate how optical pumping is achievable. Adapted from [8].

The progressive filling of the d band leads to various electronic nature of the TMDs, ranging from insulating to metallic [30]. The most studied materials are those falling in the

semi-conducting categories, with among others MoS₂, MoSe₂, WS₂ and WSe₂, because of their great potential for electronic applications. The two compounds containing sulfur also present a broken inversion symmetry which implies piezoelectric properties. On the other hand, the metallic compounds are mostly under study for theoretical purpose as they present a charge density wave phase (accompanied by a metal-insulator transition) as well as a superconducting phase. The competition between the two phases (which requires the opening of a band gap and hence a zero density of state at the Fermi level for the former and a finite density of state for the second) was still not well understood in 2016 [30].

The semiconducting materials are direct band gap (of about 1-2 eV, i.e. in the visible range) semiconductor but transition to indirect band gap semiconductors when several layers are stacked together [12] [26]. The direct band gap property is especially interesting for optoelectronic application. Two types of transition are mainly researched in this field (mainly in MoS₂): A and B. Those can be better understood by looking at the band structure which is presented in a simplified manner in Figure 1.3. Similarly to graphene, two subsets of K and K' points can be distinguished. Due to strong spin-orbital coupling, two distinct bands (one for each spin) are presents at the K points. One can therefore play with the valley degeneracy or with the spin. This can be performed by utilizing circularly polarized light which will allow transition at one K-point or the other, while the photon energy will select the transition band as presented in Figure 1.3 [46]. The transition between the band for each spin are labelled A and B [47].

The TMDs are therefore really interesting to create new devices using spintronic, valleytronic and/or optoelectronic. Their on/off ratio can be as high as 10^8 with a mobility of $100 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at room temperature in the case of MoS₂ [48].

It has to be noted that MoS₂ is the most studied TMD material because it is the most available in the nature [26].

Phosphorene, hexagonal boron nitride and other 2D materials

Phosphorene

Phosphorene is a monolayer of black phosphorus. It is composed of phosphorus atoms arranged in a honeycomb lattice (its structure is visible on the left-hand side of Figure 1.4). The phosphorene is a semiconducting material with direct or nearly-direct band gap (following the number of layers) of varying size (the size of the gap increases when the number of layers decreases with a maximal size of about 1.5 eV) [49]. The mobility in phosphorene is higher than in TMDs with values of $1000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ measured at room temperature [50]. The lattice presents the particularity to be vertically staggered along the armchair direction which leads to high anisotropic optical and transports characteristics [30]. It also presents an on/off ratio between 10^3 and 10^5 [50]. Its intermediate properties bridge the gap between TMDs and graphene, which makes it also a good candidate for various electronic and optoelectronic applications.

Hexagonal boron nitride

Hexagonal boron nitride (hBN) is relatively similar to graphene with a honeycomb lattice and lattice parameters only 2% off those of graphene (its structure is visible on the right hand

side of Figure 1.4). Its main properties remain its high band gap (5.97 eV), its weak interaction with other layer and its great crystal quality [51] [52]. Those make it a nearly perfect substrate for graphene and other 2D materials. It is encapsulated in hBN layers that the highest mobility of graphene charge carriers at room temperature ($>100000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) were recorded [53]. hBN can also be used as a tunnel barrier, as it withstands electric field up to $0.8 \text{ V} \cdot \text{nm}^{-1}$ [26].

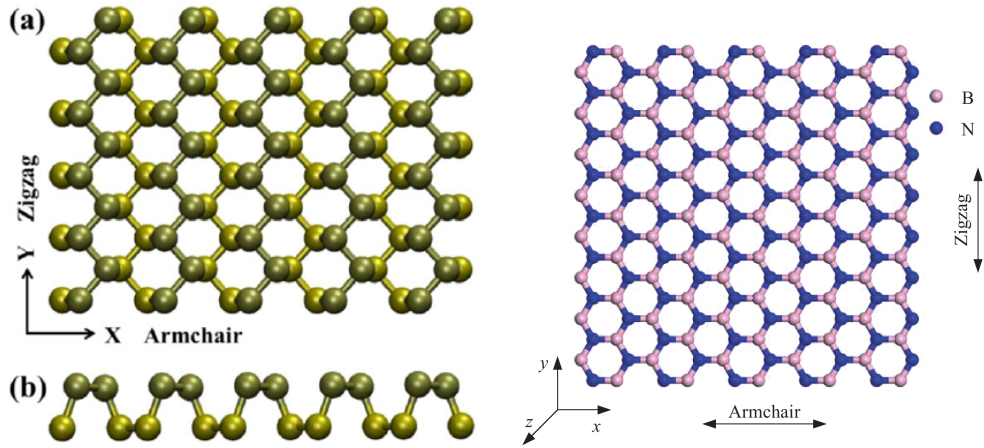


Figure 1.4 – Left: Phosphorene atomic structure from the top view (a) and side view along the armchair direction (b). Adapted from [9]. Right: hBN atomic structure. The boron atoms are in pink and the nitrogen atoms are in blue. Adapted from [10].

Other 2D materials

Among the whole library of materials, metal-oxides, perovskites, topological insulators, TMDs alloys, metal chalcogenides, polymeric organic solids, functionalized layers present characteristics that seems promising but are yet to be fully explored. A brief description of each is given here under.

Metal-oxides present the advantage to be relatively inert when exposed to air. The layers in those materials are connected through weak covalent bonds making exfoliation possible [26]. One of the drawbacks of those materials is their polycrystallinity which makes exfoliation possible only on high quality crystals. They present a lot of potential in diverse area such as anodes for batteries, superconductors or passivating layers [30] [54] [55].

Perovskites are known for their high optical absorption making good candidate for solar cells technology [56].

Topological insulators present the particularity to be insulating in their bulk, while conducting at their surface. In 2D, the conduction occurs at the edges of the surface which gives a new degree of freedom to build heterostructures [57].

TMDs alloys (layer composed of different TMD) allow one to tune the band gap by controlling the concentration of each TMD. This permits to tune electronic and optical properties of the layer [58].

Metal chalcogenides combine the orthorhombic structure of graphene with the broken

inversion symmetry of TMDs. They also present a strong piezoelectric effect. Some of them are indirect-band gap semiconductors but possess the same feature as TMD making them also good candidates for valleytronic application (by using linearly polarized light this time) while they are less appealing for optoelectronic applications [59].

Finally, it is worth mentioning that polymer solids can be exfoliated under the form of layers which have saturated surface bonds and therefore interact through van der Waals forces [60]. Also, some layers can be functionalized for example one can add hydrogen on graphene (the resulting layer of graphene with hydrogen atoms adsorbed is called graphane) [61] and some layers can be attached laterally to one another to create multi-domain 2D layers [62].

All those possibilities make the construction of vdWHS a rich field which is not likely to run dry soon, as it will be presented in Section 1.4.

1.3 Fabrication techniques

Several techniques are used nowadays to obtain 2D materials [12]. The most common ones are the mechanical exfoliations, the mechanical sonication - chemical intercalation process and chemical vapor deposition (CVD). One can then either characterizes this monolayer and/or integrates it in a device and/or stack it on top of another monolayer, building up a vdWHS. The aim of this section is to describe briefly the aforementioned techniques of fabrication of monolayer and some techniques to create vdWHS. It is not intended here to be exhaustive neither to go deeply into technical considerations but rather to give a brief overview of the methods.

1.3.1 Isolation of atomically thin material layer

Mechanical exfoliation

Mechanical exfoliation was the first technique used to successfully isolate a monolayer of graphene. This technique is quite simple and efficient. It uses scotch tape to exfoliate layer by layer a bulk material. This technique has been applied to graphite, molybdenite and black phosphorus [12] [37] [63]. The following presentation of the mechanical exfoliation uses graphene as an example and comes from the work of A. Geim [43]. The steps are similar for the different 2D materials (able to withstand them).

To perform a mechanical exfoliation, the first step is to make sure to work in a clean environment (and to have a clean substrate). Then one can begin the exfoliation. To do so, one needs to attach a graphite flake to a scotch tape and fold the latter by an angle of about 45° around the graphite flake (with the sticky side oriented towards the flake). Then, by slowly peeling the scotch, two graphite flakes are obtained. By repeating the two latter steps several times (conserving each time the obtained graphite flakes), graphene is eventually isolated on the tape. The final step consists on depositing the cleaved graphite (with possibly graphene flakes) on the substrate. This is possible by pressing the flake for a few minutes on the substrate, removing the air bubbles if needed, before slowly peeling off the tape. Then, the search for graphene flakes can begin with optical microscope. This search is easier if a contrast of color exists between graphene and graphite. This is achieved, for example, with SiO_2 substrate.

This technique usually yields high quality samples, but at a small throughput. This is, therefore, ideally suited for research but not for industrialization processes.

Mechanical sonication and chemical intercalation process

This method is a succession of two steps: mechanical sonication and chemical intercalation [64] [65]. These two steps both take place in solution. In the mechanical sonication step, vibrations are induced to disperse the bulk material in several few layers flakes. Then a solvent with surface energy matching the one of the monolayers is introduced to exfoliate the few layers sample in monolayers. The result of this technique is a solution with monolayer flakes in suspension. This process is relatively simple but the intense steps taking place might damage the monolayer or introduce impurities. This scalable method is still of great interest in the eventuality of industrialization process.

Chemical vapor deposition (CVD)

CVD is the most common technique used to produce 2D layers [12]. The basic principle of this technique is presented in the Figure 1.5. The different steps go as follows : 1) a gas mixture composed of the elements to be deposited and the possible species required for the reactions to take place enter, at a control flux, the CVD furnace (its parameters, pressure and temperature, are controlled for the specific reaction) in which the substrate has been deposited beforehand; 2) adsorption/chemisorption at the surface of the substrate followed by surface reactions; 3) desorption of the products 4) transport of the leftover gas mixture out of the chamber [66]. This technique is able to achieve higher throughput than the mechanical exfoliation technique. It also produces samples of good quality, making it one of the most used and promising technique in the aim of industrial production.

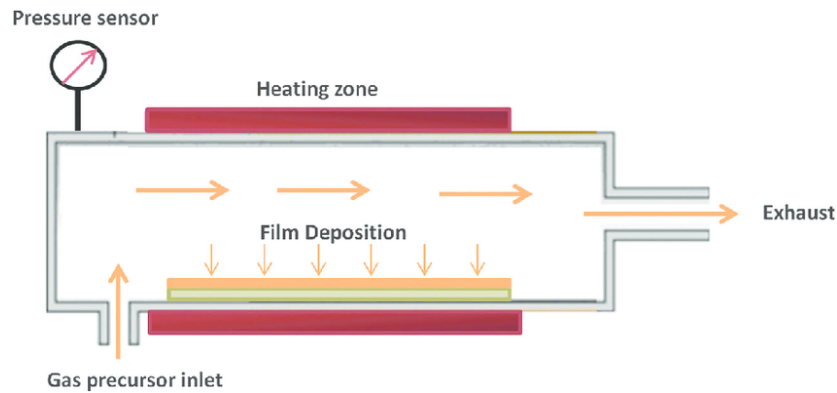


Figure 1.5 – Scheme of the basic principle of the CVD method. Adapted from [11].

1.3.2 Conception of heterostructures

The conception of heterostructures [12] [13] can be summed up quite simply as the different methods are all relying on the same basic principles. A summary of the different steps involved

is presented in Figure 1.6. The first step is to produce the two isolated layers, using one of the techniques described above, one layer being already deposited on the final substrate. Then, to bring the second layer on top of the first, one can proceed in various ways but all of them require putting the layer on a stamp which will be attached to a transfer microscope equipped with micro-manipulators. The latter will finally position the layer on top of the other, adjusting the angle between the two (this is important as it will be shown latter) and stack it on the other layer. The stamp can then be removed either by dissolution or by peeling-off. The two layers can also stay attached (intentionally) to the stamp, to be deposited on top of a third layer.

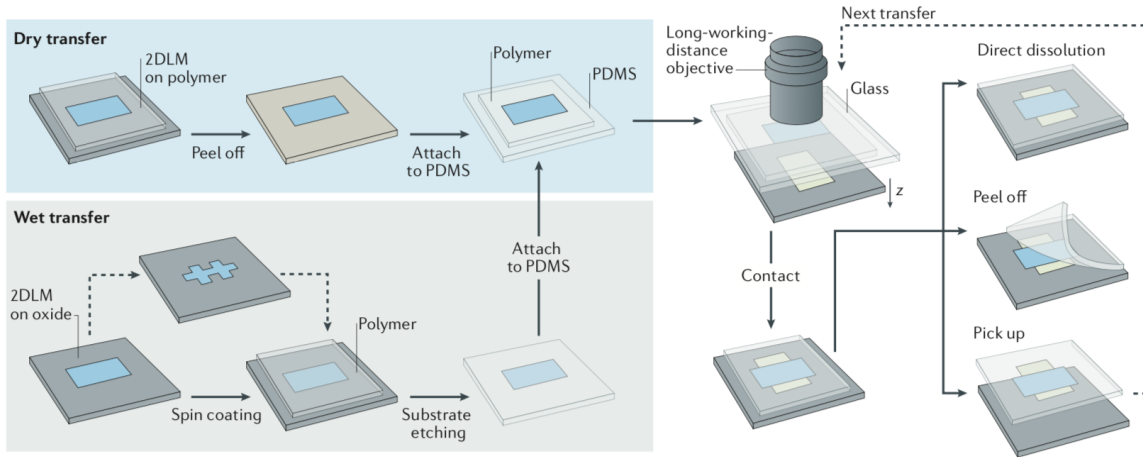


Figure 1.6 – Scheme illustrating the different steps to produce an heterostructure. Adapted from [12].

As stated just above, various methods exist to place the second layer on the stamp. Here, two of them are described: one wet transfer technique and one dry transfer technique, namely the poly(methyl methacrylate) (PMMA) carrying layer transfer method and the van der Waals pick-up transfer method. Other methods can be found in [13].

The PMMA carrying layer transfer method is schematized in the top of Figure 1.7. The number between parenthesis refers to the steps illustrated in the figure. In this method, the layer to be transferred is deposited on a silicon substrate coated by a soluble layer and PMMA (1). The soluble layer is then dissolved by immersing it into water (2). The PMMA layer with the flake on top is then left floating and easy to grab (3). They are then placed on a glass slide positioning them on top of the other layers (4). The layer is then deposited and the PMMA peeled-off slowly (5-6).

The different steps of the van der Waals pick-up transfer method are illustrated in the bottom of the Figure 1.7. The number between parenthesis refers to the steps illustrated in the figure. This technique takes the advantage of the adhesion arising from the van der Waals forces between two clean and completely flat sample. The stamp in this case is a flake of hBN which is positioned on a layer of polypropylene carbonate (PC) covering a layer of PDMS (1). The stamp (attached to a glass slide) is then brought close to the layer to be transferred (2).

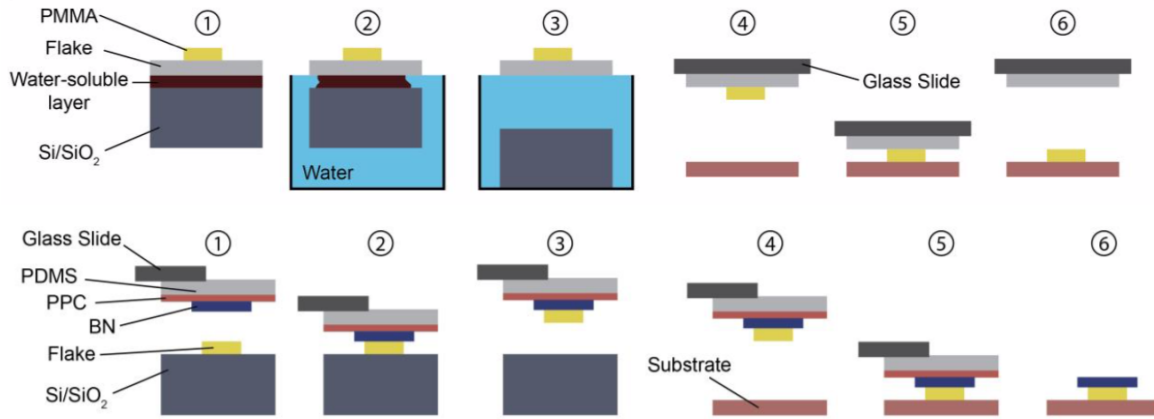


Figure 1.7 – Top: Scheme illustrating the different steps to perform the PMMA carrying layer transfer method. Bottom: Scheme illustrating the different steps to perform the van der Waals pick-up transfer method. Both adapted from [13].

The layer, deposited on a silicon substrate, will then stick to the hBN and, by carefully pulling away the stamp, be removed from the substrate (3). The stamp can then be brought on top of the other layer (4-5) where the layer is deposited, capped by hBN.

Another way to produce vdWHS is by CVD growth of different layers but this technique requires specific growth condition for each layer making it difficult to stack various layers. Also, even though vdWHS interact via van der Waals forces, the relative angle of rotation between the layer can lead to different properties. With the CVD technique, this angle, referred later as the twisting angle, cannot be tuned. Therefore, the pick-and-place is most often used [12]. In the perspective of scaling up the process, the stacking step has to be optimized [26].

1.4 Van der Waals heterostructures and devices

The possibility to stack at will different materials at the atomic scale is a dream for material science engineers. The advent of vdWHS allows them to finely tune the properties of materials having sizes in the nanometer range. This is especially interesting in the frame of electronic device ranging from transistors to photovoltaic cells. This section will present some of those applications, detailing in which way 2D materials are interesting with respect to conventional ones. The limitation of integration of those 2D materials in devices will also be highlighted. This section does not intend to be comprehensive (as the field is in expansion every day) but will rather give an overview of the state-of-the-art devices found in the literature. Lots of designs have already been proposed, including vertical and lateral heterostructures. The latter, consisting of the juxtaposition of two different layers, will not be considered extensively. Here, devices quite similar to what is found in the "classical" silicon technology are presented. This includes various design of transistor as well as optoelectronic devices. The modification of the electronic properties (for example, band gap engineering) will be the subject of the next chapter.

Planar transistors

The first devices considered is equivalent to a MOSFET (metal oxide semiconductor field effect transistor) where the channel has been replaced by a 2D material. The usual design involves a TMD as the channel and graphene to bridge the latter with the drain and source. The purpose of graphene is to decrease the size of the Schottky barrier found at the interface between semi-conductor and metal contacts by modulating its work function [12]. This also allows preventing to damage the 2D layer by breaking covalent bonds. An example of a design for planar transistor is presented in the left of Figure 3.12.

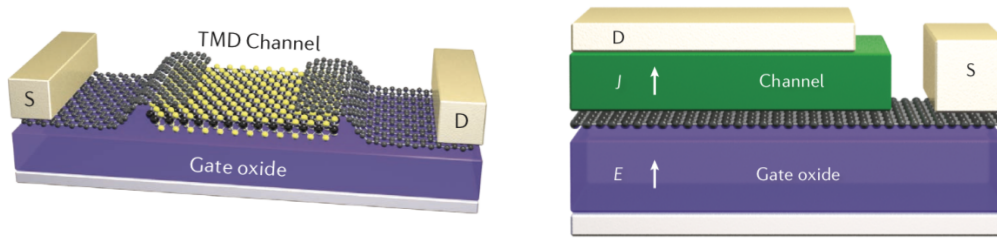


Figure 1.8 – Left: Scheme of a planar transistor using a TMD channel (yellow and black atoms are for the chalcogenide atoms and transition metal atoms respectively) with graphene layers (grey atoms) bridging the channel to the drain and source. Right: Scheme of a vertical transistor with a graphene layer (grey atoms) allowing the transistor to operate vertically rather than horizontally. Both adapted from [12].

Graphene-based vertical transistor

The possibility to integrate graphene in semi-conducting device can lead to new ways of designing transistors. Taking advantage of the extraordinary properties of graphene, it is possible to design transistors which operates at high speed, low-power and which are flexible [12]. One possible design integrates a graphene layer on top of the gate oxide, bridging the source to a channel or tunneling layer oriented vertically. This implies that the current flows in a much shorter direction through a wider area than in the case of planar transistor, improving the speed of the device. Since the current and the capacitance are now proportional to the same area, the cut-off frequency does not depend on the size of the device. This also removes the need for precise lithographic technique and reduce the cost. Finally, those devices can operate in bended environment, since it will not damage the channel or tunneling layer. An example of a design for vertical transistor with a channel is presented in the right of Figure 3.12.

Such transistor are declined in two ways: thermionic vertical transistors and tunneling transistor [12]. The first uses a thin film semiconductor to create a channel. By tuning the gate potential, one can change the size of the Schottky barrier between the semiconductor and the graphene yielding high on/off ratio. In the tunneling transistor [67], two graphene layers are used. One operates as the drain electrode and the other as the source, and they are spaced by an insulating layer. The gate voltage controls the density of state of the bottom

layer of graphene, tuning the tunnel current through the junction. On/off ratio of 50 were obtained by using BN as an insulator. Semiconductor can also be used as tunnel barrier allowing one to switch between the two designs and enhancing the on/off ratio (up to $\sim 10^6$ [68]).

Non-graphene based vertical diodes and transistors

It is also possible to create p-n junction with 2D semiconducting materials. The fact that the depletion region is wider than the device leads to completely new physics. One of the main interests of these devices is that the $I-V$ relation can be tuned by electrostatic gating [69] [70]. Unfortunately, the current density is not as important as in silicon-based device.

Light-harvesting and detection devices

2D materials offer the advantage to have tunable band gap either by stacking different materials or by twisting or straining them (see next chapter) [71] [72] [17]. This is an interesting feature when it comes to light-harvesting devices. One of the possible designs sandwiches a layer of TMD between two graphene layers [12]. While graphene is relatively transparent to light, with an absorbance of $\sim 2.3\%$ in the visible range; (still high for a thickness of only $3.3\text{\AA}$) [73], the TMD are direct band gap material with band gap in the visible range. This makes them good light harvesting material [35]. On the other hand, the graphene actively collects the carriers. Again, the work-function of graphene can be tuned to select potential offset. This has a great impact on the short-circuit current as well as on the open-circuit voltage. The short distance and the tunable offset allow fast and efficient carrier collection, and therefore good efficiency of the device even though it is quite thin. Similar device can be used for light-detection. In that case, a $p-n$ junction is sandwiched between the graphene layer. This is illustrated in Figure 1.9. The majority carrier density can also be tuned via gate voltage. The addition of graphene layers avoids dealing with long lateral channel where the mobility is low and permits a higher carrier collection [35]. The use of TMD-TMD materials is especially interesting, for they present a type II band alignment (i.e. with the bottom of the conduction band and the top of the valence band in the two different layers, more information on this in the next chapter), facilitating the charge carrier separation [35] [74].

Light-emitting devices

Light-emitting devices are relatively similar to light-harvesting ones [12]. The only difference is that one has to find a way to effectively introduce current in the active area. Lateral heterojunctions are not very efficient in that aim. Simply stacking two semiconductors also introduces large lateral resistance. To overcome this problem, the stack of semiconductors can be sandwiched between a layer of graphene and a 3D doped bulk material (the graphene is doped via gate voltage to inject to complementary carrier type in the active region). This allows a good recombination and therefore a good electron-to-photon conversion [75] [76] by reducing charge leakage, and effectively injecting vertically the charges. Those devices show performances nearly as good as organic LEDs or quantum-dots LEDs [12].

Importance of interfaces

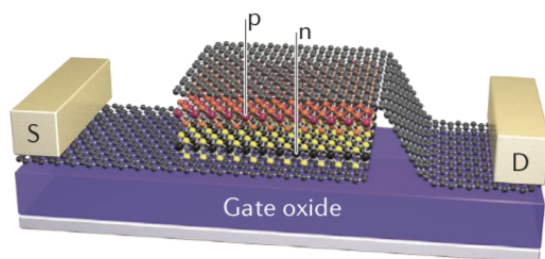


Figure 1.9 – Example of a design of an optoelectronic device. A $p-n$ junction is sandwiched between two layers of graphene (grey atoms). The TMDs are indicated by light red, dark red, yellow and black atoms, with the light red and yellow for chalcogen atoms and dark red and black for transition metal atoms. Adapted from [12].

As already mentioned, the possibility to stack at will 2D materials allows one to create finely tailored devices. This has been achievable since a few years now and new design concepts have already emerged such as vertical transistors. This expansion calls for better understanding of the possibility to tune the band gaps, and this passes through two steps: first by understanding how van der Waals interaction between the layers impact the band structure and secondly by having a better understanding of the mesoscopic structure. If simulation tool already exists for the first point (tight-binding model and density functional theory are both applicable to 2D materials), the material science world is still looking for a model easily probing the stacking order in vdWHS. An overview of both points will be made in the next chapter.

Chapter 2

Overview of the interface playground

In the previous chapter, the basics building blocks used to create van der Waals heterostructures (vdWHS) have been presented. Those materials already present some interesting properties that can be used in various devices. Yet, most often, those layers will not be found standing free and will either be deposited on a substrate or stacked (vertically) as shown in the section on applications in the previous chapter (Section 1.4). In this chapter, we will explore the common effects observed when the layers are stacked together in vdWHS. Substrate effects will not be mentioned, even though the extension is quite similar to what will be presented here, with an interlayer coupling which is comparable, but arising from the surface of a bulk material rather than a stack of monolayers [77].

vdWHS are stacks of 2D layers which present no out-of-plane dangling bond to bind the layers covalently. Therefore, the cohesion of the structure arises from van der Waals interactions between the different components. Even though this interaction is relatively weak, it will modify the potential landscape felt by each layer. This modification can then be the starting point of various effects. Indeed, this variation of potential energy can push the atoms to adopt different configurations.

This chapter is structured as follows: first, definitions of commensurate and incommensurate structures will be provided. This will be followed by a comment on the first observed impact of stacking. Then, several examples of band engineering in vdWHS will be provided. Finally, an analysis of transition between the commensurate and incommensurate phases will be made following the work of Lebedev *et al* [21,23,78-80].

2.1 Distinction between commensurate and incommensurate structures

The words "commensurate" and "incommensurate" are used in different context in the literature. It is therefore important to define those terms before going any further. Indeed, in the literature, some use the word "commensurate" to describe superstructures, which we will avoid here. This is due to the fact that, to compute band structure, one has to find a certain periodicity in the problem. In the case where there is a lattice mismatch or when two layers are twisted with respect to each other, Moiré patterns appear. Those are interference patterns possessing a periodicity which is given by the lattice mismatch and/or twist angle. This periodicity is always larger than the one of the unit cells of the monolayers. In the

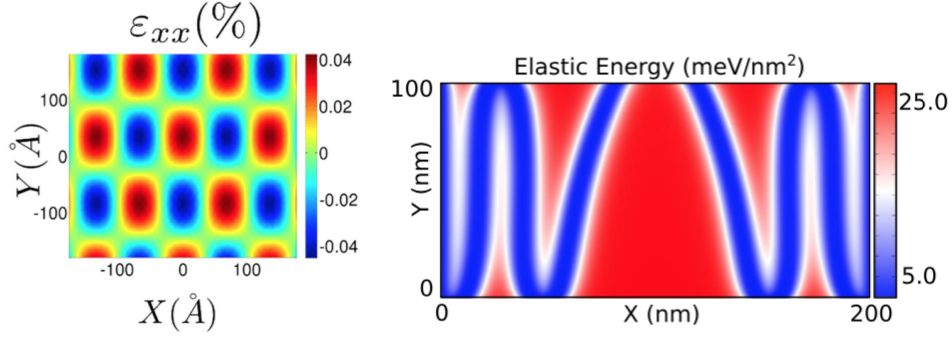


Figure 2.1 – Left: Strain field ϵ_{xx} in Moiré pattern observed in graphene in aligned graphene-hBN heterostructures. The color bar indicates the amount of strain. The Figure is seen from the top. Adapted from [14]. Right: Amount of elastic energy in commensurate-incommensurate structure. The sample shown is bilayer graphene with the bottom layer stretched uniaxially. The red area corresponds to commensurate domains with high amount of elastic energy and the blue domain are incommensurate as they present less strain (but more potential energy, not shown here). Adapted from [15].

case of two layers of the same material, one can obtain a "commensurate" superstructure for certain angle of twisting [81] [19]. Those correspond to the angle at which the Moiré pattern corresponds to a certain number of repetitions of the unit cell in the two directions. This is often used to perform band structure computations. Those angles follow the rule [81]:

$$\theta = \cos^{-1} \left(\frac{n^2 + 4nm + m^2}{2(n^2 + nm + m^2)} \right) \quad (2.1)$$

with (n, m) the number of repetition of the unit cell in each direction. This definition of commensurate structure is different from the one used in this text. Here, commensurate structure will only refer to stacks of layers where the atomic arrangement is identical in both layers. This means that the strain field is not periodic: either the whole layer is stretched in order to match the periodicity of the other, or the layers have identical unit cells and are aligned, in which case no strain is necessary to match the atomic structure of each layer.

On the other hand, all Moiré patterns (superstructure with periodicity larger than those of the unit cell of the layers) will enter the category of incommensurate structure. In that case, the strain field will either be null or quasi-null. In real structures, the monolayer will try to favor the areas of small interlayer potential by inducing small amount of strain locally [14] [18]. In that case, the strain field will match the periodicity of the Moiré pattern. This is illustrated in the left-hand side of Figure 2.1.

Finally, heterostructures composed of both phases also exist and are called commensurate-incommensurate structure. In those structures, commensurate areas are separated by incommensurate ones where the amount of strain is quasi-null. This is illustrated in the right-hand side of Figure 2.1.

Two main methods allow one to switch between the different phases. It can be done by either applying strain, or by twisting the layer. Observation of such phenomenon is common, and some will be exemplified throughout this chapter.

To summarize this point, if the unit cells of each layer are stretched in such a way that

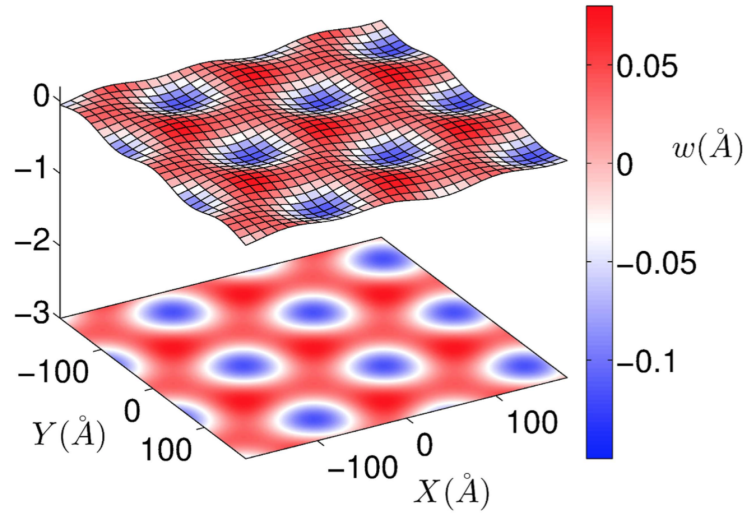


Figure 2.2 – Out-of-plane displacement of a monolayer of graphene induced by the superposition over hBN in the aligned case. Adapted from [15].

their lattice parameters match one another, the structure is commensurate. In any other cases, the structure is incommensurate. In some structure, both phases are found with a certain periodicity, those structures are called commensurate-incommensurate.

2.2 First observation in stacking

As mentioned above, following the lattice mismatch, two main configurations can be obtained when two layers are stacked: commensurate and incommensurate. Yet, for small twisting angle [82] or small lattice mismatch [79] commensurate structure can be observed. In those case, the layers are strained lightly such as to have the two unit cells match each other. If those little adaptations do not occur, an incommensurate phase would be found. Stretching is obviously associated with an energetic cost, but this is compensated by a gain in interlayer energy (the potential energy induced by bringing the layers close to one another). This energy is dependent on the relative shift between the layers (also called stacking configuration). Indeed, following how the atoms of each layer are positioned with respect to each other, various electronic forces are felt. This implies that some configurations are favored with respect to each other. As the layers interact via van der Waals forces, this gain in energy is small but could be sufficient to induce strain in the lattice. This is the main object of this thesis.

Another important thing is that the aforementioned different configurations leads to variation in the interlayer distance. This is illustrated in Figure 2.2. It can be seen that this displacement is of about 0.05 Å for graphene on hBN heterostructure. For twisted TMDs, it can go up to 0.6 Å [18]. Due to its small magnitude in most of the case, this displacement is often neglected. In the following, it will be assumed that the layers are completely flat except when mentioned otherwise.

2.3 Band gap engineering

Understanding the transition between commensurate and incommensurate phases or the formation of multiphase structure presents great interest in electronic and optoelectronic. It is expected that the stacking order influence the electronic properties of the materials [74]. Therefore, controlling the stacking in vdWHS by applying strain or by twisting different layers offers a large playground for scientists in order to create devices with finely tuned properties. In this section, different examples will be provided to illustrate how the band gap of the structures can be tuned. This review will overview the impact of the number of layers in TMDs, how the band gap evolves when different TMDs are stacked, how the band gap is modified following the configuration of stacking as well as the impact of strain and twist. This section will mostly focus on TMDs as their band gap is the most interesting to modulate, but it can already be noted that exotic properties appear in bilayer graphene. The most extraordinary of which is the existence of a superconducting state at a twisting angle of $\sim 1.1^\circ$ [83] [29] [30]. This state is the result of coupling between the layer which induces the formation of flat band (dispersion is null) at the neutrality point [84] [29]. It was also shown that the Fermi velocity decreases in bilayer graphene for small twisting angle [71] [85].

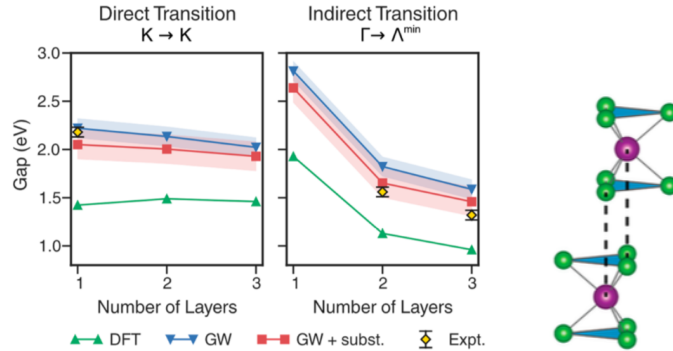


Figure 2.3 – Left: Evolution of the computed band gap in function of the number of layer in MoSe₂ stack. The figure shows the results for density functional theory computation (green), GW computations (blue and red with the screening effect of the substrate) and results from experiments (diamonds). Right: The used alignment to make the computations. The Mo atoms are in purple and the Se atoms are in green. Both adapted from [16].

Band gap evolution in function of the number of layers in TMDs

For TMD bilayers, the stacking leads to a transition in the nature of the band gap from direct at the K point in the monolayer to indirect $\Gamma-A_{\min}$ ($A_{\min}$ is the point halfway between Γ and K). This transition has been highlighted by Bradley *et al* [16] and He *et al* [86] among others. The explanation given by Bradley *et al* is that the valence band maximum (VBM) and the conduction band minimum (CBM) at the K -point in monolayer are essentially the result of the d orbital of the transition metal. In bilayer, those orbitals do not interact with each other and the gap remains nearly the same at the K -point. On the other hand, the VBM at the Γ -point is the result of the p orbital of the chalcogen atom which is a lot closer to the other

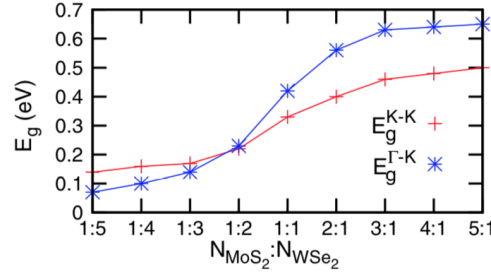


Figure 2.4 – Evolution of the band gap with respect to the thickness ratio (n:m means n bilayers of MoS_2 and m bilayers of WSe_2). The direct band gap follows the blue curve while the indirect band gap follows the red curve. Adapted from [17].

layer and more likely be subject to hybridization. Then, the CBM at $\Lambda_{\min}$ is highly delocalized and influenced by the spatial confinement. The two latter states are therefore modified by the stacking of another TMD layer. They form a smaller band gap, but which is also indirect. The evolution of the direct and indirect band gap is shown in Figure 2.3 for the MoSe_2 but similar results can be found for different TMDs in [86]. The results are shown for the preferred alignment of TMD which has been found by He *et al* and corresponds to an alignment of the chalcogen atoms of one layer with the transition metal atoms of the second [86]. This is shown in the right of Figure 2.3. This configuration will be denoted AB in this report.

Band gap in TMD heterostructures

When different TMDs are stacked, it does not necessarily lead to a direct-indirect band gap transition [17] [74]. It is observed that certain combination of bilayers maintains a direct band gap and that in those cases the band gap can be tuned with respect to the thickness ratio of the different layers. This effect is illustrated for the case of MoS_2 - WSe_2 in Figure 2.4. In the case of Mo_2 - WSe_2 , the band structure appears as a combination of the band structure of the two isolated layers (which present direct band gap at the K -point). The configuration used in this case is the same as the one described in the previous point: AB. The first interesting observation of the band structure is that the VBM and CBM are spatially separated, the first originating from the valence band (VB) of WSe_2 and the second from the conduction band (CB) of the MoS_2 . This is especially interesting in the case of charge separation, as pair of holes and electrons will be localized in different layers at their formation. The main contribution to the conservation of the direct band gap arises from the spin-orbit coupling in the VB of WSe_2 leading to a smaller band gap as the band of MoS_2 are retained. The band gap at the K -point is reduced due to this effect.

Band gap in function of the configuration in TMD bilayers

Some observed that the band gap also varies in function of the configuration [74]. Indeed, the previous computations assumes a constant configuration of stacking. If the mismatch is taken into account in MoS_2 - WSe_2 , Moiré pattern appears. Those Moiré pattern involves different stacking configuration which can be probed. Zhao *et al* found that the band gap is

modulated by about 0.15 eV in the same Moiré pattern. To obtain this, they analyzed four different stacking configurations in their sample. They found that the direct band gap is retained (as shown previously) but that its value ranges from 1.14 eV to 1.3 eV. This large band gap modulation can be interesting for application using those superlattices. Apart from the band gap, the electronic properties at the Γ -point are also strongly modulated as the spacing between chalcogen atoms (mostly responsible for the VB at this point) varies with the different configuration encountered. As those observations are experimental, the impact of the variation of the interlayer distance is included.

Band gap in function of twist

The effect of twisting has been probed by M. Naik *et al* [18] for two different twisting angles, 3.5° and 56.5° , in TMD bilayers. They identified six different high symmetry configurations (three for each twisting angle) in the Moiré pattern. To study the effect of the twisting angle, they considered two cases: one with a fixed interlayer spacing and one with a relaxed interlayer spacing. The effect of twisting itself is relatively similar to what has been presented in case of the evolution of the band gap for different TMD stacked. Indeed, the previous case implied a lattice mismatch which leads to a Moiré pattern just as the twisting angle here. The different configurations have therefore indirect band gap which varies following the coupling between the chalcogen atoms. One of the interesting things highlighted by M. Naik *et al* is the impact of interlayer spacing. This has a big impact in TMD/TMD heterostructure as the spacing can change by 0.6 Å. Considering the interlayer spacing variations is important in order to predict which configuration leads to the smallest band gap. This is illustrated in the Figure 2.5.

Carr *et al* tried to probe in a more continuous manner the change in the band gap for TMD bilayers [19]. Their results are shown in the Figure 2.6. They obtained a modulation of the band gap (by retaining the VBM and CBM for different twisting angle) of 76 meV by twisting continuously the layer to an angle of 28.6° . The twisting also implies strong modulation of the density of states deep into the valence band. They also performed those computation for bilayer graphene and found strong modulation of the Van Hove singularities. A Van Hove singularity is the result of the displacement of the Dirac cones of the two layers in the momentum space. For some angle, those cones overlap. The hybridizations at the overlaps give the Van Hove singularities. Similar results are found by Koshino *et al* [87].

Band gap in function of strain

Finally, strain attracted also a lot of attention [17, 72, 81, 14, 85, 88]. All the results point in the same direction: strain impacts the band gap and allows continuous tuning of it. Fang *et al* used tight-binding computations to show that the band gap can be tuned by about -100 meV/% in TMDs monolayer [72]. Z. Khatibi *et al* showed, also by using tight-binding computations, that for certain twisted bilayer graphene superlattice, a band gap was opened and continuously tunable by applying strain [81]. Moreover, they showed that for mixed biaxial strain state, a direct-indirect band gap transition is induced (their study covers twisting angle of $\sim 32^\circ$ and $\sim 38^\circ$). Kumar *et al* showed that in-plane stress up to 1.27% was induced in MoS₂-WS₂ heterostructure when stacked with a twisting angle of 10° . The band gap can be reduced by 190 meV in such cases [14]. In the same manner, they identified a reduction of 130 meV in MoSe₂-WSe₂ heterostructure (the corresponding strain in that case was 1.32%).

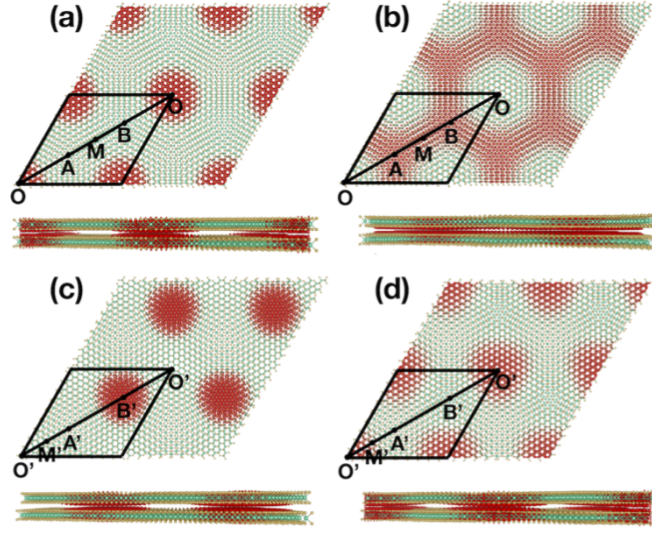


Figure 2.5 – Evolution of the charge density of the VBM in MoS₂ bilayer twisted by an angle of 3.5°((a) and (b)) and 56.5°((c) and (d)) with (a) and (c) corresponding to a rigid stacking and (b) and (d) to a relaxed stacking. The similar configuration in each Moiré pattern are indicated by the letter O, A, M and B to allowing to identify the impact of considering the relaxing of the interlayer spacing. Adapted from [18].

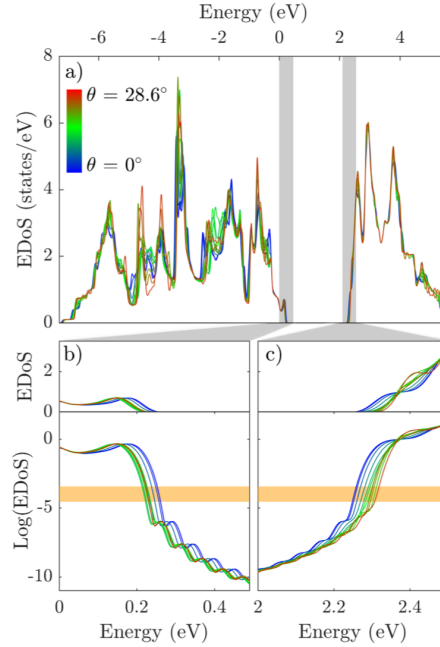


Figure 2.6 – Electronic density of state of MoS₂ bilayer for twisting angle ranging from 0°(blue) to 28.6°(red) (a) with focus on the valence band (b) and conduction band (c). Adapted from [19].

They completed their study by considering the out-of-plane displacement and the associated strain to conclude that this displacement can lead to an additional variation of 200 meV in the case MoS₂ bilayer. A last example of the impact of strain is provided by Zhao *et al.* They observed the impact of strain in TMD heterostructures and conclude that the direct band gap is maintained in the range -0.6% to 2% in-plane strain and up to -4.3% out-of-plane strain [17].

Comment on band gap engineering

All the various methods of engineering the band gap presented above rely on the configuration of stacking. Indeed, if the interlayer coupling is small (observable by the band structures which are nearly superposition of the band structure of the two layers), it is not negligible. This motivates the search for means able to easily predict the stacking order of heterostructures. Then, the case of hBN-graphene was not debated here even though opening of a band gap is predicted [87] which could be an interesting feature to develop.

2.4 Commensurate-Incommensurate transition in the literature

The next chapters will provide some tools to predict the commensurability of vdWHS. The instruments will be able to probe the transition between the phases, but give little insight on how this transition takes place. To illustrate this transition, the case of bilayer graphene (BLG) will be used. In its ground state, BLG is supposed to be completely commensurate. However, it is often found to present a commensurate-incommensurate phase, even when thoroughly aligned [20] [82]. This is essentially due to fabrication imperfections, such as crumpling of the layers. In those cases, the layers might present some incommensurate areas. To get a completely commensurate stacking, a macroscopic movement would be required, which is obviously not likely due to a high potential barrier [27]. Similarly, but in a more theoretical framework, one can obtain this commensurate-incommensurate phase by stretching pristine BLG. This approach is easier to apprehend as it is more gradual and gives better insights of the physics at play. Both cases will be illustrated here. This section will first provide the basic information needed to understand how the transition occurs by illustrating the situation. To this end, experimental results will be presented. Then, a theoretical development will help to get deeper in the understanding. Finally, some comments will be made on how extension to other structures can be performed, and what role this transition can play with respect to electronic transport properties.

Bilayer graphene

To describe bilayer stacking, the first step is to identify the remarkable (i.e. clearly defined) configurations of stacking. As already mentioned above, graphene layers are honeycomb lattice with unit cells containing two inequivalent carbon atoms. From this fact, two main configurations in the aligned case exist: AA and AB. The first one corresponds to a perfect match of the two lattices: each carbon atom of the top layer is above one of the bottom layer. The second stacking configuration arises from stacking two inequivalent atoms one on top of the other. The Figure 2.7 shows how the interlayer potential varies with relative displacement u_x , u_y (not indicated in the figure) along armchair and zigzag direction respectively. A

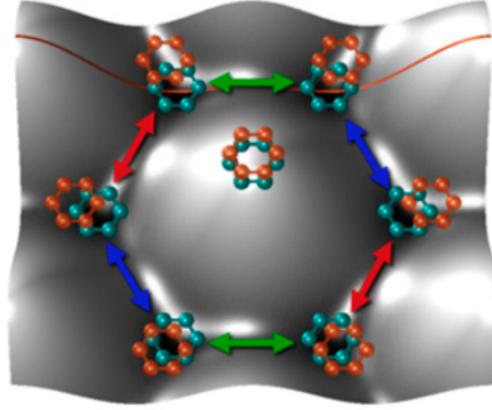


Figure 2.7 – Interlayer energy landscape for the relative displacement along armchair and zigzag direction respectively. The stacking configurations at the minimum are indicated by the orange (top layer) and green (bottom layer) atoms. The arrows indicate the possible paths to go from an AB to a BA stacking configuration with arrows of the same color leading to the same Burger vectors, $\mathbf{b}$. The AA stacking is illustrated in the center of the figure. Adapted from [20].

specific configuration corresponding to the translation u_x , u_y will be described by the order parameter $\mathbf{u}$. In this figure, one can observe that the AA stacking corresponds to the less energetically favorable configuration, while the AB configuration (or BA, which is the case where the two other inequivalent atoms are stacked together) is the most favorable one. When the two graphene layers are aligned, the commensurate domains are, logically, of the AB or BA types.

Actually, when observing bilayer graphene, one can see commensurate domains separated by incommensurate boundaries. Those boundaries are dislocations which take the shape of soliton. A soliton is mathematical object describing the evolution of the phase of the position between two ground states in this case. The phase is evaluated with respect to the phase of one of the two ground states. It is done such that, from one end to the other of the soliton, the phase increases by 2π . The shape of the soliton is obtained by solving the sine-Gordon equation. The terms "dislocation" and "soliton" are used to describe the domain boundaries.

The Figure 2.8 shows how those domain walls appear in bilayer graphene [20]. To characterize the domain walls, the parameter $\Delta\mathbf{u}$, describing the translation path to pass from the commensurate configuration in one domain to the adjacent one, is introduced. As this path should encounter the minimum resistance possible, $\Delta\mathbf{u}$ is in fact one of the six vectors linking configuration AB to BA. They are indicated by double arrows in the Figure 2.7. In the right part of the Figure 2.8, it can be seen that the order parameter $\mathbf{u}$ rotates by 2π ¹ around the dislocation node which is a typical feature of topological defect [20]. When heated up, the dislocation might move to create bigger commensurate domains. This might involve annihilation of dislocation with opposite $\Delta\mathbf{u}$. Those dislocations are indeed associated to a formation

1. Pay attention to the fact that this phase does not correspond to the phase of the soliton mentioned above: one describes the phase of atom positions in one dislocation while the other describes the rotation of the order parameter.

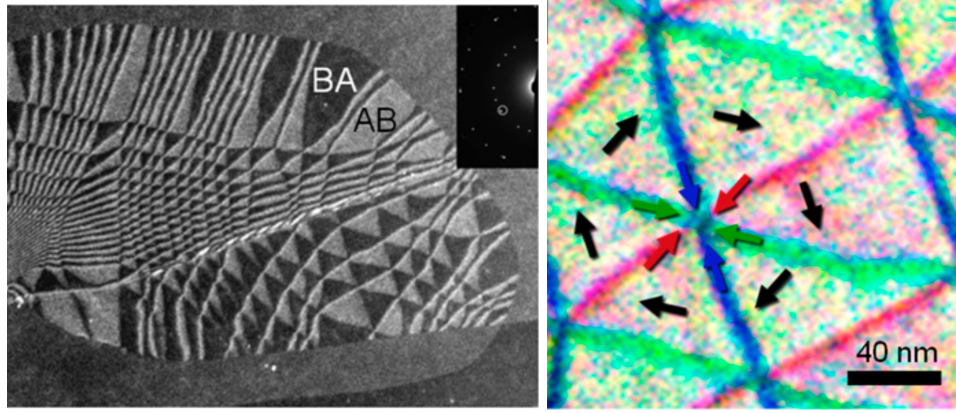


Figure 2.8 – Left: Dark-field scanning transmission microscopy (DF-STM) image of distinguishing the AB from BA domains (for more details on imaging techniques, refer to [20]). Right: Meeting of 6 commensurate domains probed by DF-STM imaging. The black arrows indicate the order parameter, while the blue, red and green arrows represent the interlayer translation $\Delta\mathbf{u}$. Both adapted from [20].

energy that can be suppressed, since the outer commensurate domains are equivalent and can therefore be linked. Those phenomena have been probed by Alden *et al* [20].

The next step is to bring some clarification on the formation of those domain. One can already spot two different networks of dislocation in the left hand part of Figure 2.8: a triangular network in the center, and a stripped network on the outside of the BLG sample. One can investigate the formation of such phases in a slightly different approach. This was done by Lebedev *et al* and Lebedeva *et al* who analyzed the formation of commensurate-incommensurate domain in BLG [21, 23, 78–80]. Their development is theoretical. It starts with a BLG where they stretch one of the two layers and analyze when the other will stop accumulate strain to introduce dislocation. They found that small amount of strain is required to introduce a dislocation. This explains the apparition of commensurate-incommensurate domains in experiment as those amounts of strains are easily reached due to imperfections. The following of this section describes their theoretical model. It describes, step by step, the progressive introduction of dislocations as well as the formation of different networks of domain boundaries.

The first domain wall

I. V. Lebedeva *et al* derived the formation energy of a dislocation under uniaxial strain [21] by using a two-dimensional Frenkel-Kontorova (FK) model. They modeled a layer of graphene as an array of particle linked by springs undergoing the influence of a potential (here the interlayer potential). The case under study is presented in Figure 2.9. The dislocations under study are called partial, as their Burgers vector $\mathbf{b}$ does not correspond to a lattice vector, a_0 . Instead, it has the length of the bond length, l and one of the directions mentioned in the Figure 2.7 (i.e. $\mathbf{b}$ is one of the $\Delta\mathbf{u}$ forming a path between AB and BA). In the following, the two layers are considered equidistant at every point. Here, the bottom layer is stretched while

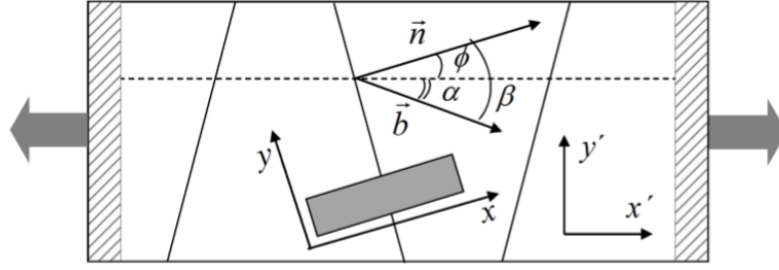


Figure 2.9 – Scheme of bilayer graphene under uniaxial strain in the bottom layer (shaded area). $\mathbf{n}$ is the normal to the boundary between two commensurate domains, $\mathbf{b}$ is the Burgers vector, ϕ is the angle between $\mathbf{n}$ and the direction of elongation, α is the angle between $\mathbf{b}$ and the direction of elongation and $\beta = \alpha + \phi$ is the angle between $\mathbf{n}$ and $\mathbf{b}$. x - y is the coordinate system associated to the dislocation while x' - y' is the one associated with the elongation [21].

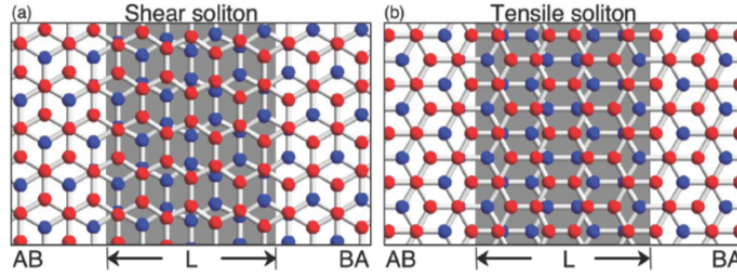


Figure 2.10 – Crystal representation of the two specific kinds of dislocation found in bilayer graphene. (a) is a shear dislocation and (b) is a tensile dislocation. Blue and red atoms distinguish the atoms of each layer [22].

the top one is free to relax. As we are interested in the formation of the first domain wall, it is assumed that the commensurate domains are bigger than the width of the dislocations and that there is no boundary crossing. Edge effects are also neglected. Also, the relative displacement of atom in the dislocation is only a function of the x coordinate, the boundary being along the direction y as indicated in Figure 2.9.

In their relatively general approach, several angles have to be distinguished (see Figure 2.9), ϕ is the angle between the normal, $\mathbf{n}$, and the direction of stretching, α is the angle between the burger vector, $\mathbf{b}$, and the direction of stretching. β is the angle between $\mathbf{n}$ and $\mathbf{b}$. The following development will try to provide the preferred angle β_c ($\phi_c = \alpha - \beta_c$) and the critical elongation, ϵ_c for a given value of α . In other words, a direction of elongation is chosen, α takes all the value from 0° to 90° . For each of those configurations, the orientation of the domain wall is optimized. Then, the critical elongation for this configuration is found. To better illustrate how the dislocation takes place, two distinct types of dislocations are shown in Figure 2.10: the tensile dislocation where $\alpha = 0^\circ$ and the shear dislocation where $\alpha = 120^\circ$.

The variation of energy per unit length associated with the introduction of a dislocation, ΔW [J/m] is given by [21]:

$$\Delta W = \Delta W_0 + \Delta W_e \quad (2.2)$$

with ΔW_0 the energy in the absence of external strain and ΔW_e the energy change provided by the external load :

$$\Delta W_0 = \int_{-\infty}^{+\infty} \left(\frac{1}{4} K(\mathbf{u}') l^2 |\mathbf{u}'|^2 + V(\mathbf{u}) \right) dx + \int_{-\infty}^{+\infty} K(\mathbf{a}') l^2 |\mathbf{a}'|^2 dx \quad (2.3)$$

$$\Delta W_e = El(\epsilon_{xx} + \nu \epsilon_{yy}) \Delta u_x + Gl \epsilon_{xy} \Delta u_y \quad (2.4)$$

where the order parameters $\mathbf{u} = \frac{\mathbf{v}_1 - \mathbf{v}_2}{l}$ and $\mathbf{a} = \frac{\mathbf{v}_1 + \mathbf{v}_2}{2l}$, with $\mathbf{v}_i$ the relative displacement of atoms of layer i with respect to the commensurate configuration are introduced. We also have $\mathbf{u}' = \frac{d\mathbf{u}}{dx}$ and $\Delta \mathbf{u} = \mathbf{u}(+\infty) - \mathbf{u}(-\infty) = -\frac{\mathbf{b}}{l}$. $K(\mathbf{u}') = E \cos^2 \theta(\mathbf{u}') + G \sin^2 \theta(\mathbf{u}')$ describes the dependance of the elastic constant in function of the configuration of the elongation with $\theta(\mathbf{u}') = \sin^{-1} \frac{u'_y}{|\mathbf{u}'|}$, $E = \frac{k}{(1-\nu^2)}$, $G = \frac{k}{2(1+\nu)}$ with k the elastic constant and ν the Poisson's ratio, ϵ_{xx} (ϵ_{yy}) is the elongation in the x (y) direction and ϵ_{xy} is the shear strain. $V(\mathbf{u})$ is the interlayer potential for a displacement, $\mathbf{u}$ between the layer.

The mathematical development leading to the rest of this section is summarized in Appendix A. Only the main results will be presented here under.

The first interesting results provided by Lebedeva *et al* is that width of such dislocation, l_D is dependent on the angle β and is given by:

$$l_D = \frac{l}{2} \sqrt{\frac{K(\beta)}{V_{\max}}} \quad (2.5)$$

where $V_{\max}$ is the maximum of the potential in the path from AB to BA stacking. The dislocation width ranges from 11 nm to 6-7 nm for tensile and shear dislocations respectively. Lebedeva *et al* also found that the optimal angle of dislocation, β_c and the associated critical strain, ϵ_c can be derived by minimizing the energy formation given by Equations (2.2)-(2.4) which yields that:

$$\tan(\alpha - \beta_c) = -\frac{k \sin 2\beta_c}{4(1-\nu)K(\beta_c)} \quad (2.6)$$

and

$$\epsilon_c(\alpha) = \frac{\Delta W_0(\beta_c)}{kb \cos \alpha \cos(\alpha - \beta_c)} \quad (2.7)$$

It has to be noted that the direction of formation of the boundaries in real sample will depend on the length of the dislocation, so only part of the scheme is presented here. Yet, ϵ_c and β_c are always given by the above equations (Equations 2.6-2.7).

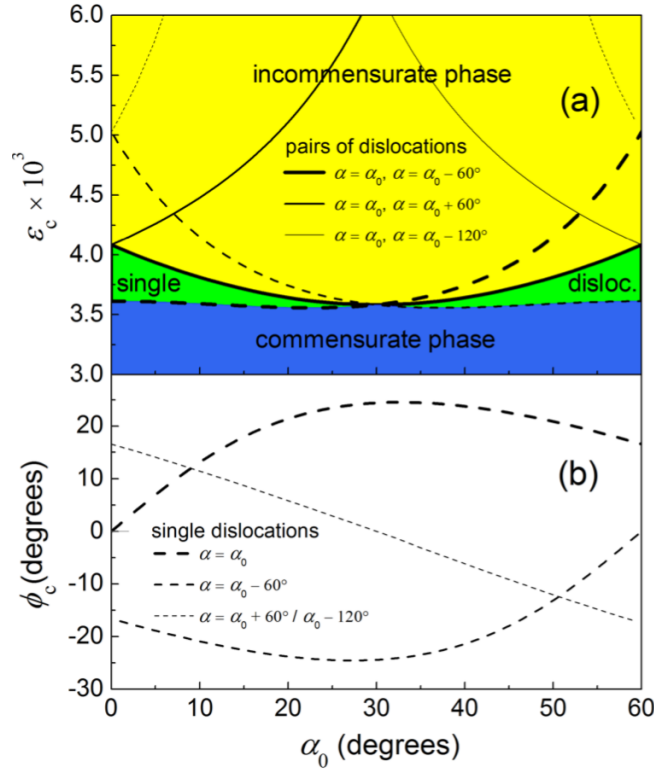


Figure 2.11 – (a) Phase diagram presenting the critical elongation, ϵ_{c1} for each of the three possible partial dislocations in graphene in function of the angle between the direction of the uniaxial elongation and one of the armchair directions of the bilayer, α_0 . Three single dislocations are possible; in that case, they are followed by the formation of three different pairs of dislocation. (b) ϕ_c in function of α_0 . Adapted from [21].

The formation of a partial dislocation in bilayer graphene can be summarized by a phase diagrams predicting the critical elongation for various transitions. This phase diagram is provided in Figure 2.11 with the optimal angle, ϕ_c . It shows the dependency on the direction of the direction of stretching on the critical elongation. Three main regions are distinguished : commensurate (blue), a single dislocation is formed (green) and the incommensurate phase (yellow) where the density of dislocation becomes the order parameter. As already mentioned, the Burger vector can only take 6 different values, which can be grouped in three pairs of parallel vectors, with different orientations. The transition to a single dislocation is relatively independent of the direction of elongation and about 0.3% of relative elongation. It quickly arrives to the state where a second dislocation is formed. The successive dislocation are not parallel as it would not be energetically favorable. The obtained pattern is a succession of tilted domain walls. Those results are in concordance with the work of Kumar *et al* who computed a critical strain of 0.5% for the formation of the first pair of dislocation [15].

The phase diagram has to be read as follows: one select an α_0 angle, and increases the elongation. The first line encountered will give the type of dislocation generated. This information can be reported to the graph below to obtain the angle of tilting of this dislocation with respect to the direction of elongation. Stretching further, a second line is crossed associated

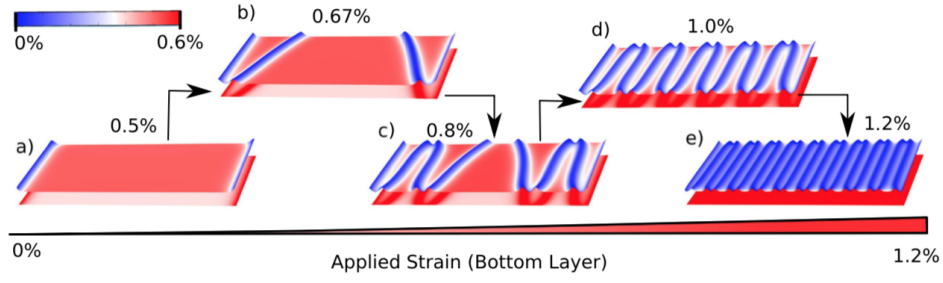


Figure 2.12 – Introduction of incommensurate boundaries between commensurate phases in function of applied uniaxial strain. Adapted from [15].

with the introduction of a second dislocation in the structure. Its relative angle with respect to the first dislocation is indicated in the figure.

To better visualize the introduction of dislocation in bilayer graphene, the Figure 2.12 presents how the dislocations are introduced into the layers. One can observe that above 1.2% the density of dislocation makes the structure rather incommensurate than commensurate-incommensurate as the size of the commensurate domains shrink greatly.

Formation of a triangular network of domain walls

We can now probe the transition between commensurate graphene and commensurate-incommensurate graphene with a triangular network of domain walls such as the one presented in Figure 2.8. To study the formation of such network, the bottom layer is exposed to biaxial strain, ϵ , while the top layer is free to relax [80]. The dislocations considered here are tensile dislocations. Therefore, $\beta_c = 0$. In that case, the formation energy of the network ΔW_T [J/m²] is:

$$\Delta W_T = -\Delta W_{el} + \Delta W_{dw} + \Delta W_{dn} \quad (2.8)$$

where ΔW_{el} is the elastic energy linked to the biaxial elongation ϵ_0 , ΔW_{dw} is the formation energy of the domain walls and ΔW_{dn} is the energy formation associated to the nodes. The surface of a domain is given denoted $S_T = \frac{\sqrt{3}L_T}{4}$, with L_T the length of a dislocation. The formation of a triangular network is associated with the elongation $\epsilon_0 = \frac{\sqrt{3}l}{2L_T}$ in each of the layer since the center of each domain is separated by a distance of $\frac{L_T}{\sqrt{3}}$. The formation energy therefore, compares the system with relative elongation ϵ to the commensurate system with relative biaxial elongation $\epsilon - \epsilon_0$.

In that case, they found that the critical elongation for the formation of a triangular domain wall is given by:

$$\epsilon_{c1} = \sqrt{\frac{V_{\max}(1-\nu)}{k(1+\nu)}} \left(\frac{3\sqrt{3}}{\pi} - 1 \right) = (1-\nu) \frac{\Delta W}{kl} \quad (2.9)$$

Further stretching

The stripped network observed in the left-hand part of Figure 2.8 can also be analyzed [23]. It is interesting to have an idea of the energy associated to this network in order to predict which network will be the ground state of our bilayer. In the stripped network, it is assumed that the Burgers vectors alternate from one boundary to the other by an angle of $\pi/3$ (i.e. β takes the value $\pm\pi/6$ for two consecutive walls). Reproducing the above reasoning one can find a second critical elongation, ϵ_{c2} [23]:

$$\epsilon_{c2} = \epsilon_{c1} \frac{\sqrt{\frac{(7+4\nu)(7-\nu)}{6}} - 2}{\sqrt{7+4\nu} - 2} \quad (2.10)$$

The transition between the two networks is of the first order, so the two networks can coexist on the same sample. The transition from the triangular network to the stripped one will occur by gradually aligning two boundaries in different zigzag directions, associated to the same armchair one while the third wall of the domain will disappear. Finally, it is argued that for big strain a Moiré pattern will appear. Such pattern possesses the same symmetry as the triangular network. Hence by conducting the same reasoning as before but by considering average of the potential rather than its actual shape and adapting the size of the domains, one obtain a reentrant phase transition for a critical elongation; ϵ_{c3} , given by :

$$\epsilon_{c3} = \frac{3}{2} \sqrt{\frac{\sqrt{3}(7-\nu)V_{\max}}{2\pi k}} \quad (2.11)$$

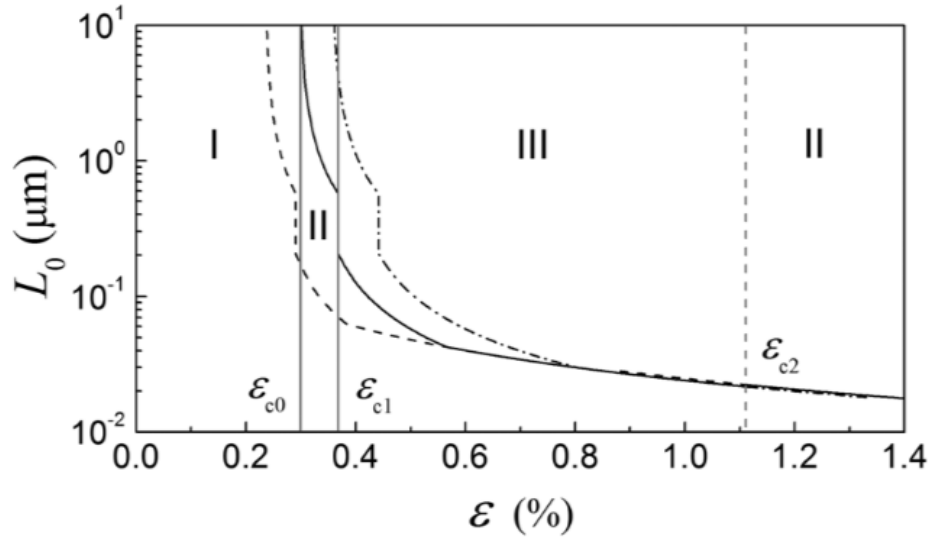


Figure 2.13 – Phase diagram presenting the size of superstructure in function of the relative biaxial elongation (solid line), ϵ . The different phases are labeled I, II and III for the commensurate phase, the triangular network of domain walls and the stripped network respectively. The dashed (dash-dotted) line represents the results obtained by considering a $V_{\max}$ smaller (greater) of 40%. Adapted from [23].

The resulting phase diagram is presented in Figure 2.13. The diagram also presents the variation of the superstructure size which has not been presented here. This model gives

a relatively complete insight on the different energetic components at play. It shows the great importance of the Poisson coefficient (and obviously the elasticity constant) and of $V_{\max}$ in the formation of the networks. However, this description of the different phases in BLG is based on observation. This tool seems a bit complex to be used for prediction computations.

Heterostructures

Those considerations are valid in the case of partial tensile dislocations in bilayer materials (it is applicable to hBN bilayer for example [21]). To adapt the above development to other heterostructures one has to adapt the type of dislocation to the heterostructure under study and also modify the term $K(\mathbf{u}')$ found in Equation 2.3 [79]. In the case of graphene-hBN, this is done by writing $E = E_C E_{\text{BN}} / (E_C + E_{\text{BN}})$ and $G = G_C G_{\text{BN}} / (G_C + G_{\text{BN}})$ where $E_X = k_X / (1 - \nu_X^2)$ and $G_X = k_X / 2(1 + \nu_X)$ where X is either C (properties of graphene) or BN (properties of hBN).

Those small modifications allow one to recover the rest of the development shown above to evaluate the different transition. Since the starting point is different in the case of graphene-hBN (which is incommensurate since there is a lattice mismatch), one has to take into account the preliminary introduction of a small amount of strain to have a quasi-commensurate structure as a starting point.

In the case of TMD heterostructures, computations have been performed by Kumar *et al* for uniaxial elongations [15]. They show similar results to those presented above: dislocations are progressively introduced above a certain amount of strain (about 1.5-2.5% following the TMD heterostructure). The difference is that instead of passing from AB stacking configuration to BA in neighboring domain, only AB stacking domains are present (AB refers to the preferred stacking order of the TMD in the commensurate configuration). The dislocations introduced are therefore parallel to each other rather than tilted.

Twisting

Introduction of dislocations in twisted heterostructures has not been addressed, theoretically speaking, to the best of my knowledge. However, the phase transition between commensurate-incommensurate state and incommensurate state has been observed by Woods *et al* in hBN-graphene heterostructure [27]. They found that the transition occurs at a twist angle comparable to the lattice mismatch. In this case, the lattice mismatch is of about 1.8% with the hBN bigger than graphene [27]. Therefore, the critical twist angle is of about 1° . No complete commensurate phase was observed because of the fabrication imperfection (i.e. commensurate phases are only possible locally). The competition of energy is similar upon twisting than it is upon straining as the main energetic components remain the same (elastic energy due to local strain to adjust the lattice and interlayer potential). In their search, they also showed that the commensurate phase disappears if a second layer of hBN is deposited on top of the graphene layer (i.e. creating an hBN-graphene-hBN heterostructure). They observed that the graphene would not stay commensurate to the bottom layer of hBN (even if they were thoroughly aligned) if the top layer is misaligned. This topic was not studied (to the best of my knowledge) for strained layers (were more than two layers are stacked and some are strained). Woods *et al* suggested that interference between the two interlayer potentials

decreases the gain possible in potential energy by creating commensurate domains.

Yoo *et al* made experiments on twisted bilayer graphene. They found a transition between the commensurate-incommensurate state to the incommensurate state for an angle of about 1° . Before that, formation of a triangular network of domain walls was observed for angles $< \sim 0.8^\circ$ while striped network was observed for angles between 0.8° and 1.2° .

Transport properties through boundaries

The impact of the formation of domain walls is not to be neglected. Indeed, the transport is different in commensurate and incommensurate phases, as illustrated earlier. Creating domain walls in the structure can therefore lead to the formation a network of incommensurate 1D channels which are more or less conducting than the commensurate phase. The case of graphene-hBN is an example of this behavior, where commensurate domains are rather insulating, and the incommensurate domains are conducting states [27]. In the case of bilayer graphene, several researches have also been performed [89] [22] [82]. First, Koshino *et al* demonstrated via theoretical computations that boundaries may act as barrier for electron transport [89]. The nature of the dislocation (shear or tensile, for example) gives different behavior. Some give different transmission probability for electrons having momentum corresponding to K -point with respect to electrons of the K' -points. Other barriers are quite opaque to transport and could lead to gate tuned resistance. Then, San-Jose *et al* explained how bilayer graphene could behave as a small band gap semiconductor, while pristine bilayer graphene is a semi-metal [22]. They demonstrated that the introduction of boundaries could hinder the transport. Finally, Yoo *et al* showed that the transport characteristics of twisted bilayer graphene was strongly dependent on the angle [82]. They showed that atomic reconstruction (adjustment of the atom of the layers to create a commensurate state) has a great impact on the transport properties leading to a smaller transport than in the incommensurate state.

Chapter 3

The Frenkel-Kontorova model and its implementation

As of now, we have described some of the materials composing the 2D world and what happened when we stack them. It was shown that the configuration of stacking is an important feature to consider for design. In our quest for a model able to predict which phases is favored, several tools were used. This chapter is dedicated to their presentation. It will present the 1D Frenkel-Kontorova (FK) model, as revisited by F. Frank and J. Van der Merwe [3] and reformulated by B. Van Troeye *et al* [1]. As a reminder, the 2D extension of this model was used in the previous chapter to probe the transition between the different phases (commensurable and commensurable-incommensurable in their case) [21, 78, 80, 90]. It was also used to understand the transition between commensurate and incommensurate phases in graphene-hBN heterostructures [27]. To get acquainted with the model, a numerical implementation of the FK model is performed and compared to the results obtained by F. Frank and J. Van der Merwe. A good agreement of the two models is found for a certain range of parameters which is the most critical region, but to depart from it clearly in the other (less interesting) zones. This appears not to have been done in the literature previously. For pedagogical purpose, some of the main difficulties encountered during this part will be mentioned.

This chapter is structured as follow : first, the FK model will be presented as approached by F. Frank and J. Van der Merwe, and more recently reformulated by B. Van Troeye *et al*. Then, as we advance towards the numerical implementation of the model, our methodology will be presented and illustrated. Three sections are then dedicated to various numerical algorithm used in the evolution of our implementation. Finally, the results of our implementation are shown.

3.1 The 1D Frenkel-Kontorova model

This part follows the development and the notation presented by B. Van Troeye *et al* in the supplementary material of the submitted article "First-principles prediction of lattice coherency in van der Waals heterostructures" [1].

The FK model described the behavior of a chain of $2N + 1$ atoms linked by springs (with elastic constant, k and equilibrium distance, a_0) placed in a periodic background potential, $V(x)$. The analysis of this system is performed for N tending to infinity. The basic interplay of

energy is the same as the one leading us from the beginning of this thesis: the elastic energy, E_{elast} and the potential energy of the atoms. In this system, the atoms adjust themselves to find the best configuration possible (i.e. the configuration with the least amount of accumulated energy). This simple model attracted a lot of interest due to its simplicity (arising, notably, from the assumption of harmonic interatomic forces) and its ability to describe non-linear phenomena [32].

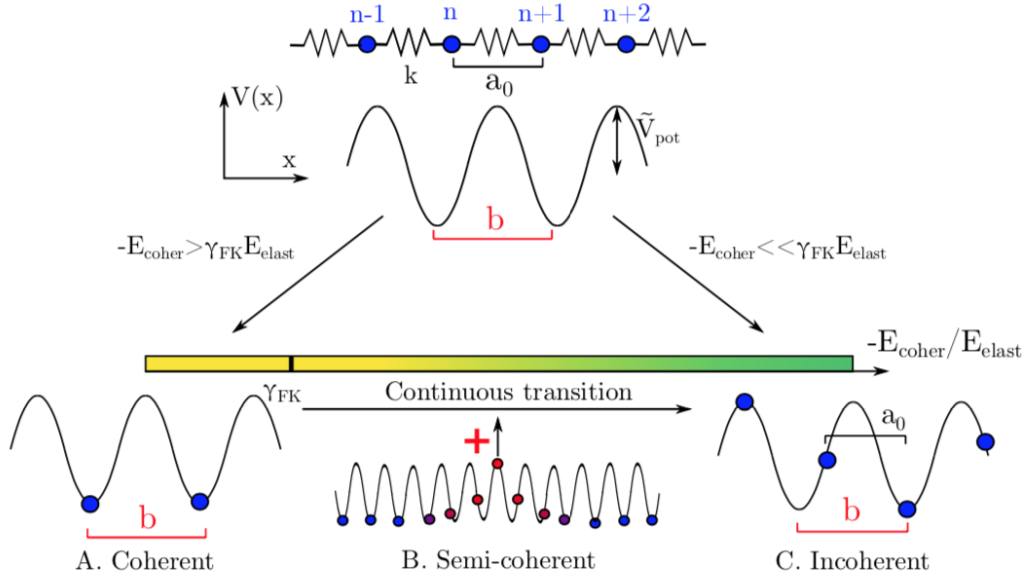


Figure 3.1 – Illustration of the FK model. The basic interplay of energy is illustrated for three cases: A. the coherent phase is privileged when the coherency energy is a lot bigger than the elastic energy; B. the inverse situation gives an incoherent state; C. a ratio of the two quantities close to $\gamma_{\text{FK}} = \frac{\pi^2}{8}$ gives a semi-coherent phase where dislocations are introduced progressively. [1]

The Figure 3.1 illustrates how the FK model can help predicting if a certain configuration of chain and background potential yields a coherent or incoherent phase. A coherent phase is observed when the coherency energy (i.e. the gain in energy provided by pinpointing the atoms at the bottom of the potential) is much bigger than the elastic energy required to achieve this state. On the other hand, if the cost in elastic energy is much bigger than the possible gain in potential energy, an incoherent phase is found, where the atoms tend to be positioned close to their equilibrium distance. Between the two states, a progressive introduction of dislocation occurs, similarly to what has been presented in the previous chapter. The ground state of a given system of chain and potential is obtained by minimizing the total energy given by:

$$E_{\text{tot}}(x_n) = \sum_{n=-N+1}^N \frac{k}{2} (x_n - x_{n-1} - a_0)^2 + \sum_{n=-N}^N V(x_n) \quad (3.1)$$

where x_n is the position of the n -th atom of the chain. The ground state is therefore given by the condition:

$$-k(2x_n - x_{n+1} - x_{n-1}) - \frac{\partial V(x_n)}{\partial x_n} = 0 \quad (3.2)$$

This model provides an analytical way to probe the transition. It can already be noted that the coherent configuration will be preferred if:

$$E_{\text{elast}} < V_{\text{min}} \quad (3.3)$$

where V_{min} corresponds to the minimum of energy of the background potential, V . In a more general way, it has been shown that the coherent configuration is favored if:

$$\gamma E_{\text{elast}} < |E_{\text{coher}}| \quad (3.4)$$

where γ is an intrinsic property of the background potential which will be defined latter and

$$E_{\text{coher}} = V_{\text{min}} - \langle V \rangle \quad (3.5)$$

with $\langle V \rangle = 1/b \int_0^b V(x)dx$ and b is the period of the potential. This quantity takes a relatively important place in this thesis. Mathematically speaking, this expression compares the minimum value of the stacking energy with the average value of the potential. Physically speaking, it is the average gain of interlayer energy made by adopting a configuration corresponding to the minimum of stacking energy with respect to any other configuration. The coherency energy is therefore the term associated to the background potential that will be compared the elastic energy. The latter is scaled by a factor γ , whose origin will now be reviewed.

To do so, a sinusoidal potential will be used as a first example. In the continuum limit (n becomes a continuous variable), one can rewrite the position of the atoms x_n in function of a phase factor:

$$x_n = nb + \frac{b}{2\pi} \varphi_n \quad (3.6)$$

By noting that $2\varphi_n - \varphi_{n+1} - \varphi_{n-1} \approx -\frac{d^2 \varphi_n}{dn^2}$, Equation [3.2](#) becomes the 1D sine-Gordon equation:

$$-\frac{d^2 \varphi_n}{dn^2} = \frac{4\pi^2 V_{\text{max}}}{b^2 k} \sin(\varphi_n) = \beta^2 \sin(\varphi_n) \quad (3.7)$$

where V_{max} correspond to the height of the maximum of the sinusoidal potential. The solution of the sine-Gordon equation is well known and takes the shape of a soliton described by:

$$\varphi_n = \pm 4 \tan^{-1} \left(\exp \left[-\frac{2\pi}{b} \sqrt{\frac{V_{\text{max}}}{k}} n \right] \right) \quad (3.8)$$

This illustrates how n can be expressed in function of φ_n . Taking now the case of a potential in the form of a Fourier series:

$$V(x) = \sum_m \tilde{V}_m \exp\left(i \frac{2\pi}{b} mx\right) \quad (3.9)$$

where $\tilde{V}_m$ is the height of the different Fourier component. The corresponding expression for n in function of the phase factor is:

$$\pm \int_{\varphi_{\max}}^{\varphi_n} \frac{b\sqrt{k}}{2\pi\sqrt{2}} \frac{d\varphi}{\sqrt{K + W(b\varphi/2\pi)}} = n \quad (3.10)$$

where the $W(x) = V(x) - \langle V \rangle$ is used instead of $V(x)$ for convenience. This potential is supposed to have only one maximum and one minimum. $\varphi_{\max}$ is the phase corresponding to the maximum of the external potential. K is the integration constant. It has to be bigger than $-W_{\min}$, the minimum of the modified potential. This constant tends to $-W_{\min}$ to have only one dislocation. This allows to write the condition for the introduction or removal of one dislocation in the system:

$$\frac{2\pi}{\sqrt{2}} \sqrt{k} |b - a_0| = \int_0^{2\pi} \sqrt{K + W(b\varphi/2\pi)} d\varphi \quad (3.11)$$

The transition between the semi-coherent and coherent phase is given by:

$$\sqrt{\frac{k}{2}} |b - a_0| = \int_0^{2\pi} \sqrt{W(b\varphi/2\pi) - W_{\min}} d\varphi = \gamma^{-1/2} \sqrt{-W_{\min}} \quad (3.12)$$

where we defined:

$$\gamma^{-1/2} = \frac{1}{2\pi} \int_0^{2\pi} \sqrt{1 - \frac{W(b\varphi/2\pi)}{W_{\min}}} d\varphi \quad (3.13)$$

Using the primary form of the potential again and squaring both side of Equation [3.12](#), one recovers the aforementioned transition criterion:

$$-E_{\text{coher}} \geq \gamma \frac{k}{2} (b - a_0)^2 = \gamma E_{\text{elast}} \quad (3.14)$$

The γ value can also be rewritten as a function of the primary potential as:

$$\gamma^{-1/2} = \frac{\langle (V_{\text{ext}} - V_{\min})^{1/2} \rangle}{(\langle V_{\text{ext}} \rangle - V_{\min})^{1/2}} \quad (3.15)$$

The rest of this work is based on the development here above. In the following, demonstration of the variation of the γ value will be provided for different periodic potentials. The value provided for actual 1D potentials will also be given to compare with the usual value of $\frac{\pi^2}{8}$ obtained for sinusoidal potential. Defining different potentials and applying Equation [3.15](#), values of γ were found in the range of 1 to approximately 1.5 using different gaussian function interpolated by Fourier series^{[1](#)}. The next part of this chapter will try to implement this criterion and compare it to numerical optimization of various test cases.

1. Any gaussian $f(x) = a \exp(-(x - b)^2/(2c^2))$ works, the interpolation with a Fourier series makes the potential periodic, the number of component allows to follow more or less the trend of the gaussian. By tuning the parameter c , different values of γ are found.

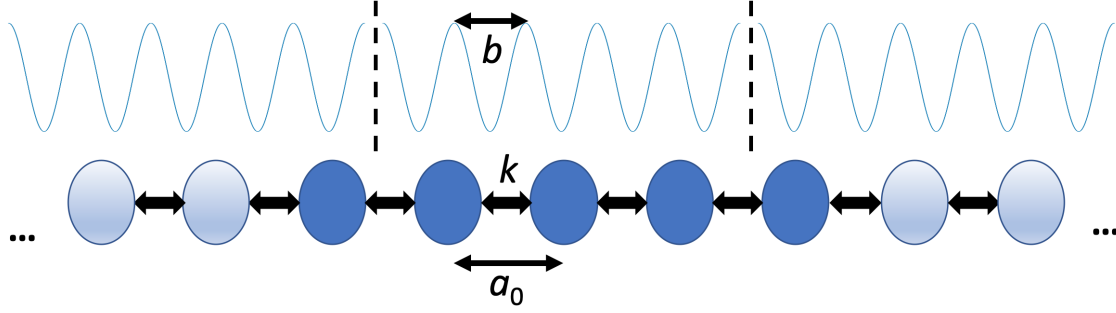


Figure 3.2 – Illustration of the two main components of the system used to recover the criterion given by Equation 3.14. The background potential of given shape is designed (here a sinusoidal shape is used for illustration purposes) and period, b , is the first component. The atomic chain with atoms linked by spring with equilibrium distance, a_0 , and elastic constant, k , forms the second component. Here, $n_{\min} = n_{\text{at}} = 5$.

3.2 Testing the theory

Here, we want to apply the FK model to recover the criterion given by Equation 3.14 with the γ value of Equation 3.15. In that aim, the first step is to define a system. This system has two main components: an atomic chain linked by springs with equilibrium distance, a_0 , and elastic constant, k , and a background potential of given shape and given periodicity, b . Those components are represented in Figure 3.2. Then, as we cannot consider an infinite number of atoms or background potential periods, a certain number of atoms, n_{at} is selected as well as a number of period of the background potential, $n_{\min}$ and boundary conditions are set. Note that it is not imposed that $n_{\text{at}}a_0 = n_{\min}b$. In fact, the chain is stretched or compressed to make the number of atoms fit the size, L , of the system. This size is set to 1 such that $b = L/n_{\min} = 1/n_{\min}$.

Every parameter mentioned up to now can be adapted, leading to a different starting system. To simplify the comparison between various systems, we fix the potential such that $n_{\min}$, b and L as well as the shape of the potential are constants of the problem. This leaves n_{at} , k and a_0 as parameters of the model.

To recover the criterion of Equation 3.14, we have to find when the incommensurate state is favored with respect to the commensurate state. The simplest commensurate case we can think of in this situation is a system with an equivalent number of atoms and period of the background potential (i.e. $n_{\text{at}} = n_{\min}$). On the other hand, the closest incommensurate states correspond to $n_{\text{at}} = n_{\min} \pm 1$ (those cases correspond to the introduction of a dislocation with respect to the commensurate state). For the chains to be comparable, their k and a_0 values have to be the same. Hence, we have three starting configurations which are obtained from the same chain. The Figure 3.3 illustrates how the two starting components (illustrated in Figure 3.2) create three starting configurations by stretching by different amounts the same chain.

The next step is therefore to compare the energy of those different configurations, as the state with the smaller amount of energy will be favored. The energy of a configuration is given by Equation 3.1 with $2N + 1 = n_{\text{at}}$. Before comparing the energy, the system has to be optimized so the energy is comparable. This is the hard part of the implementation and it

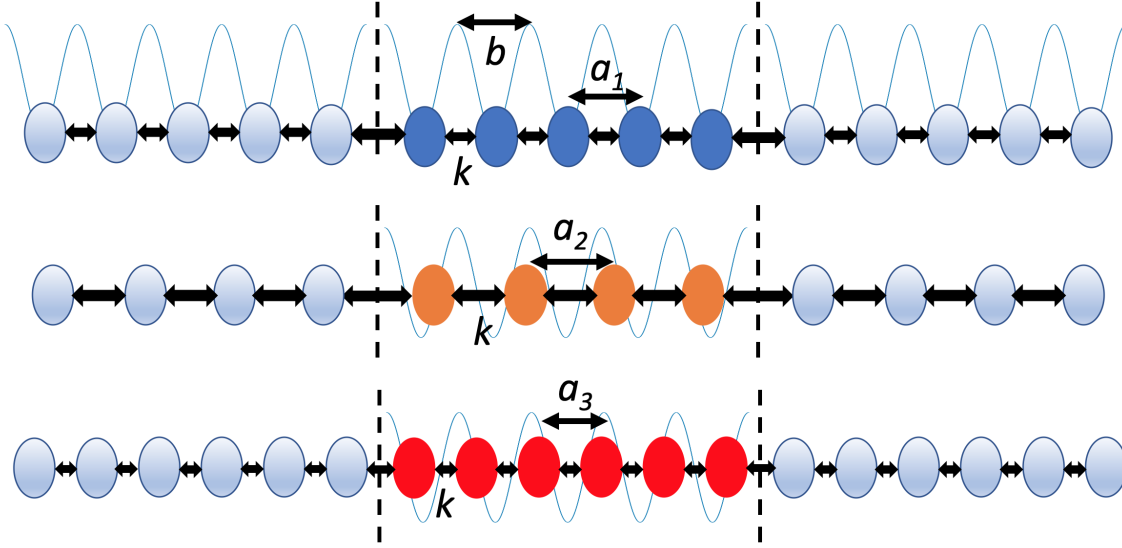


Figure 3.3 – Illustration of the distinction between commensurate state (blue chain) and incommensurate states (orange and red chains). The blue chain is obtained by compressing the chain of Figure 3.2 until the atoms are spaced by a_1 . The same principle applies to the two other chain with final spacings between the atoms of a_2 and a_3 .

will be described extensively here under.

We now have everything needed to compare a commensurate case with an incommensurate case. The next step consists in finding when the transition between the two cases occurs. The basis of our problem consists now in a periodic potential with $n_{\min}$ periods, a chain with parameters $n_{\text{at}} = n_{\min}$, k and a_0 compressed to fit a length $L = 1$ and two chains with parameters $n_{\text{at}} = n_{\min} \pm 1$, k and a_0 compressed to fit a length $L = 1$. As the number of atoms is now defined, two parameters are left to be tuned: k and a_0 . The transition can be found by setting k to an arbitrary value and obtaining the evolution of the total energy of the three starting systems as a function of a_0 . The total energy in function of a_0 is expected to follow a quadratic law as a_0 appears in the elastic energy given by, for the commensurate state:

$$E_{\text{elast}} = k(b - a_0)^2 \quad (3.16)$$

Therefore, to obtain the curves of the total energy, only three points are required for each starting system. They can then be interpolated, and the resulting curves can be compared to one another as illustrated in Figure 3.4. The curves are compared in energy units per atom.

The final step is to compare the transition found with the criterion of Equation 3.14. This is done by computing the coherency energy of the designed potential and elastic energy given by:

$$E_{\text{elast}} = k(b - a_{\text{tr}})^2 \quad (3.17)$$

with a_{tr} the equilibrium distance of the chain at the transition between the two states.

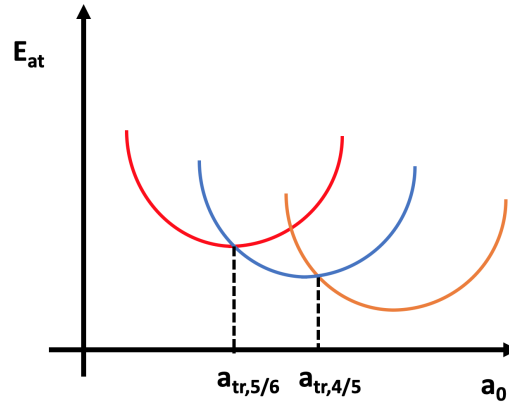


Figure 3.4 – Illustration of the comparison of the energy curves. The red curve corresponds to the total energy of the red chain with $n_{\text{at}} = 6$; the blue curve corresponds to the total energy of the commensurate case (blue chain); and the orange curve corresponds to the total energy of the orange chain with $n_{\text{at}} = 4$. The energy of the curves is given per atom. The value of the equilibrium distance corresponding to the transitions between the commensurate and incommensurate states (i.e. the intersections of the curves) are indicated by dashed lines.

To get closer to the analytical solution, the value of n_{at} needs to tend to ∞ . The value of n_{at} is therefore set as high as possible with respect to computational time. Yet, this value is strongly limited due to an important increase of computational time.

To obtain a comprehensive view, different values of k are tested such that phase diagrams showing the different phases in the $\{a_0, k\}$ space can be drawn.

As explained above, the knowledge of the ground state configuration of the system and the associated energy is of paramount importance to compare the different systems. In that aim, different algorithms were implemented with varying level of success. The three next sections present, in chronological order, those algorithms, with the reason of using them. The implementation of the algorithms can be found in Appendix [B](#).

3.3 Implementation using molecular dynamics

Description of the algorithm

Molecular dynamic (MD) algorithms are often used in physics to optimize the configurations of group of molecules [\[91–94\]](#). Its principle is quite simple. A system of particles is designed. The position and velocity of the particle are defined. Then one can introduces several forces that will rule how the particles react one with another. Usually, forces are computed and then Newton equations of motion are used. The evolution of the system is decomposed in time steps of length Δt . At each step, the forces are computed, the acceleration is derived, and the velocities of the particle is modified accordingly. In a close system, the algorithm runs indefinitely as the energy is conserved. To obtain the minimal energy configuration, a damping

is introduced. This corresponds to the Verlet algorithm [95,96]. The forces are computed by using Equation 3.2 and the accelerations are obtained with:

$$F_i(t) = ma_i(t) + \eta mv_i(t) \quad (3.18)$$

where F is the force, m is the mass of the particle, a is the acceleration, v is the velocity and η is the damping factor and i indicates that characteristics are for the i -th atom. The positions at each steps are generated by:

$$x_i(t + \Delta t) = x_i(t) + \left(\frac{2}{1 + \eta} - 1\right)v_i(t)\Delta t + \left(\frac{1}{1 + \eta}\right)\frac{F_i(t)}{m}\Delta t^2 \quad (3.19)$$

Here, $\eta = 1$ was chosen which corresponds to the steepest descent method. The starting velocity of the particle is 0. The starting positions are equidistant with a number n_{at} of particle in an interval of length $L = 1$.

Implementation of the algorithm

The algorithm has to take the following parameter as argument: the starting positions, the number of particle treated, n_{at} , per length of interval, L , m , η , k , Δt , a_0 and the background potential [2]. A convergence criterion was set in the algorithm to stop the algorithm when the gap in energy between two steps was less than 10^{-20} (this might be a too cautious). In the following, the parameter m will be set equal to $m = 1$ for the sake of simplicity (just as it was done for η and L). The derivative of the potential was computed by using:

$$\frac{\partial V(x)}{\partial x} \approx \frac{V(x - 2h) - 8V(x - h) + 8V(x + h) - V(x + 2h)}{12h} \quad (3.20)$$

Here, $h = 0.000005$ and the error made is $O(h^4)$.

The MD is relatively simple to implement (implementation in Appendix B.1) and the results in simple cases are in accordance with more efficient algorithms, but the speed of convergence is quite slow, as illustrated in Figure 3.3. This is partly due to the high convergence criterion, but precision is important for the following step (even though a smaller convergence criterion, such as 10^{-16} should work). Yet, good results were often found, as illustrated in Figure 3.3 where the apparition of a soliton can be observed. However, it was also noticed that, in some case, the algorithm could not overcome some saddle point in the energy function. This is shown in Figure 3.3. One can see that the MD algorithm leaves an atom on a position of high potential, while it should have fallen in one of the minima to obtain a minimum of the total energy (the energy of the configuration presented here is $E_{\text{tot}} = -16.316$, while a configuration with $E_{\text{tot}} = -18.196$ can be found). This configuration corresponds to a saddle point in the energy function [97]. As the slope of the potential is null for the atom at its starting position and the problem is symmetric around it, the force is always zero at this point and the atom is pinpointed.

2. An additional option allowed one to consider the case with periodic boundary conditions or aperiodic. As only the first case was investigated thoroughly, the aperiodic case will not be reviewed here

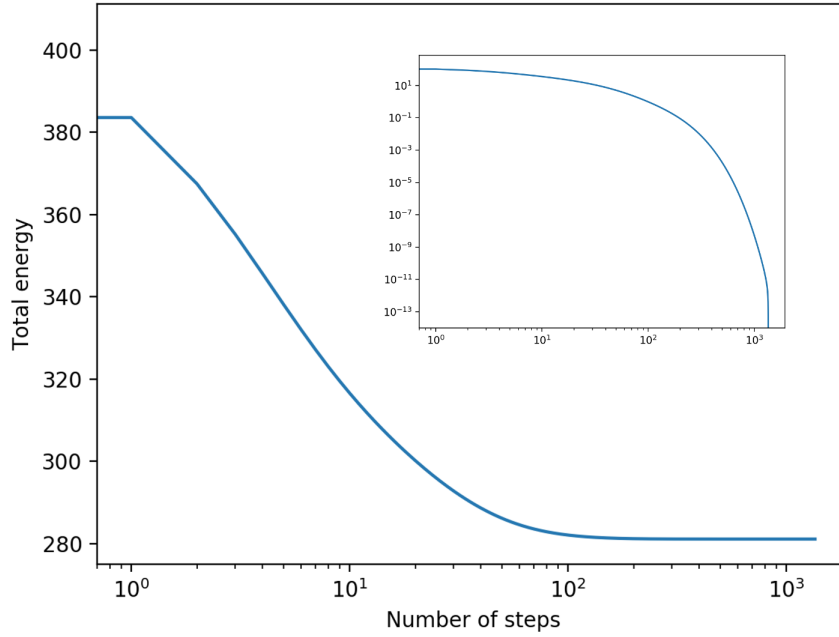


Figure 3.5 – Convergence speed of the MD algorithm for a starting configuration with the position of 19 atoms per period in a potential with 20 equivalent minima. The equilibrium distance was set to $a_0 = 0.07$, the elastic constant was $k = 10000$, and the time step was $dt = 0.001$. The inset shows, in logarithmic scale, the difference of energy of the step with the minimum energy.

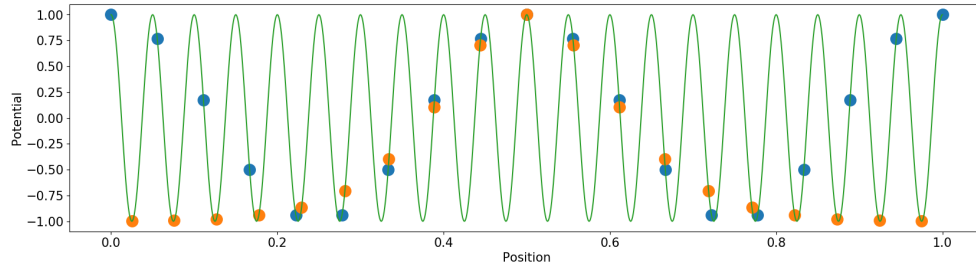


Figure 3.6 – Optimization with the MD algorithm of the position of 19 atoms per period in a potential with 20 equivalent minima. The equilibrium distance was set to $a_0 = 0.07$, the elastic constant was $k = 100000$, and the time step was $dt = 0.001$. The optimized position with the MD algorithm for the starting position shown (blue balls) are indicated by orange balls.

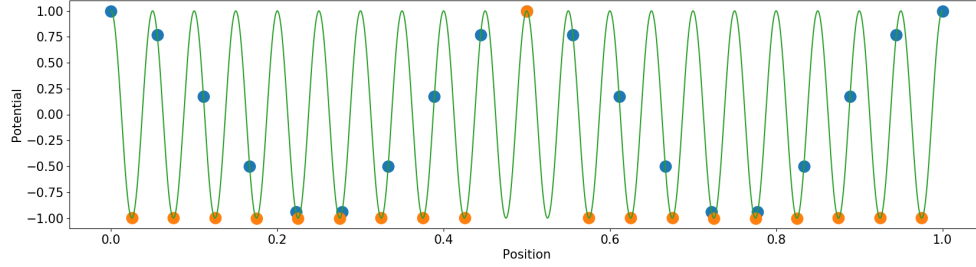


Figure 3.7 – Optimization with the MD algorithm of the position of 19 atoms per period in a potential with 20 equivalent minima. The equilibrium distance was set to $a_0 = 0.07$, the elastic constant was $k = 200$, and the time step was $dt = 0.001$. The optimized position with the MD algorithm for the starting position shown (blue balls) are indicated by orange balls. The atom in the center stays at a point of high potential where it should fall in one of the two minima next to it.

To enhance the convergence speed and short-cut the problems linked to the saddle points, a Newton-Raphson algorithm was then implemented and is presented hereunder.

3.4 The Newton-Raphson algorithm

The use of the Newton-Raphson (NR) algorithm (implementation in Appendix [B.2](#)) requires the knowledge of the second derivative of the function to optimize; here the total energy of the system given by Equation [3.1](#) [98](#). The elements of the hessian associated with this quantity are given by:

$$\frac{\partial^2 E(\mathbf{x})}{\partial x_i \partial x_j} = k(2\delta_{ij} - \delta_{i-1,j} - \delta_{i+1,j}) + \frac{\partial^2 V(x_i)}{\partial x_i \partial x_j} \quad (3.21)$$

The second derivative of the potential is null outside of the diagonal terms. On the other hand, these latter are approximated by:

$$\frac{\partial^2 V(x_i)}{\partial x_i^2} \approx \frac{-V(x_i + 2h) + 16V(x_i + h) - 30V(x_i) + 16V(x_i - h) - V(x_i - 2h)}{12h^2} \quad (3.22)$$

With the knowledge of the hessian, the total energy can be written as a Taylor expansion:

$$E(\mathbf{x}) \approx E(\mathbf{x}_0) + \mathbf{g}_0(\mathbf{x} - \mathbf{x}_0) + \frac{1}{2}(\mathbf{x} - \mathbf{x}_0)^T \mathbf{H}_0(\mathbf{x} - \mathbf{x}_0) \quad (3.23)$$

with $\mathbf{g}_0$ the matrix containing the n_{at} first derivative evaluated for the vector of position $\mathbf{x}_0$ and $\mathbf{H}_0$ is the hessian evaluated for the same vector. The next position vector is therefore given by:

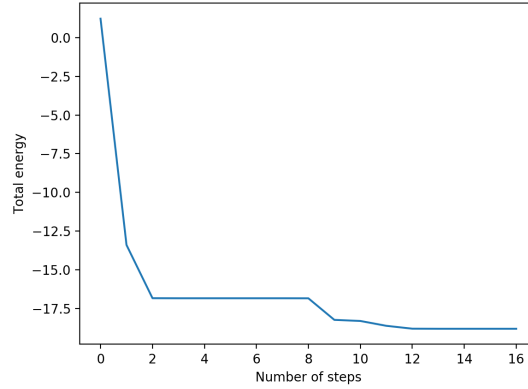


Figure 3.8 – Convergence speed of the NR algorithm for a starting configuration with the position of 19 atoms per period in a potential with 20 equivalent minima. The equilibrium distance was set to $a_0 = 0.07$, the elastic constant was $k = 200$, and the time step was $dt = 0.001$.

$$\mathbf{x} = \mathbf{x}_0 \mathbf{H}_0^{-1} \mathbf{g}_0 \quad (3.24)$$

For the algorithm to converge towards a minimum, it is required that the hessian is defined positive. The hessian is therefore computed at each step. If it is defined positive, the computations goes on, else a few steps (<20) of molecular dynamics are performed.

The Figure 3.4 shows how the number of steps was decreased significantly using this algorithm (the illustration is given for a different case as the one in Figure 3.3 but similar trends were observed for every case considered). It also allowed to avoid (most of the times) the saddle points sometimes found with the MD algorithm as shown in top part of Figure 3.4. The bottom part of the same figure represents a similar chain in a similar potential but with a phase modified by half a cycle. In that case, a different final position is found with $E_{\text{tot}} = -17.708$. This corresponds to a local minimum of the problem. It illustrates the sensitivity of the algorithm to the starting position. Since we are interested only in one of the global minima of the problem, these local minima should be avoided. It does not mean they are not interesting to analyze. For example, this type of solution is similar to the commensurate-incommensurate phases found in bilayer graphene thoroughly aligned: the local starting position will adapt itself but it will not agree with the phase of the ensemble and an additional dislocation is introduced. A completely commensurate structure would be a global minimum, but this configuration is not found as the starting position could not lead to this global minimum of energy.

However, in our case, local minima are not wanted. The first idea to overcome this difficulty was either to sample different starting configurations or to use the same potential with different phases and compare the final energies to find the ground state. This trick works for simple potentials. One could even try to predict the starting position which could lead to the global minimum with some experience to avoid the sampling part. However, as the potential

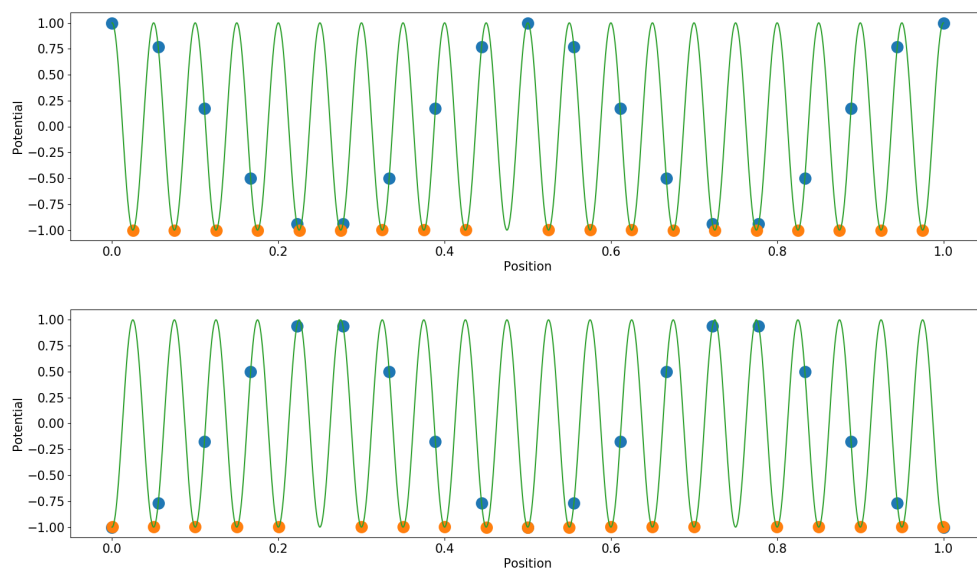


Figure 3.9 – Optimization of the position with the NR algorithm of 19 atoms per period in a potential with 20 equivalent minima. The equilibrium distance was set to $a_0 = 0.07$, the elastic constant was $k = 200$, and the time step was $dt = 0.001$. Top: Illustration of the convergence speed of the NR algorithm for the same starting position as in Figure 3.3. Bottom: Same configuration but with the potential phase modified by a factor π . A local minimum is found by putting the two atoms in the same minimum of potential.

becomes more and more complex, the algorithm reaches its limit.

In order to find a global minimum, a different algorithm had to be used. From the literature, two algorithms were tested: the simulated annealing (SA) algorithm [99] and the differential evolution (DE) algorithm [100–104]. The first algorithm mimics the process of annealing in metallurgy where heating a sample remove some defects to obtain a better crystallinity. Here, this phenomenon is transposed by introducing in the algorithm a certain probability to reverse the search for a minimum. This allows the algorithm to climb some potential barrier around a local minimum to find a global minimum. The probability to climb a barrier is reduced as the process goes on to finally become zero. This algorithm requires to optimize a lot of parameters to be efficient. Its implementation was also judged more complex than the one of the differential evolution. The latter was therefore implemented. Its principle is explained hereunder.

3.5 Implementation using differential evolution algorithm

Contrary to the NR algorithm, the differential evolution is not deterministic at all. Its principle is in fact quite simple and can be explained in a few steps. Here the method is presented as done by Storn *et al* [104] and Brest *et al* [100]. The starting point of the algorithm generates a certain population, P_0 , of position vectors in the multi-dimensional space that contains all possible solutions, where every single position is random. Each of this position vector corresponds to a certain energy. Then, the algorithm compares the energy of each line with the energy of a set of positions generated by:

$$\begin{cases} x_{new,n} = x_{prev,n} + F(x_{i,n} - x_{j,n}) & \text{for } n \text{ in } \mathbf{L} \\ x_{new,n} = x_{prev,n} & \text{else} \end{cases} \quad (3.25)$$

where the subscripts x_{new} denotes the component of the new set, x_{prev} , is the set of positions of comparison, x_i and x_j are two other sets of positions taken in the starting population, F is a number randomly chosen in the range $[0,1]$ (it can stay fixed but it was suggested that choosing it randomly could enhance the algorithm efficiency [100]) and the subscript n refers to the n -th component of the position vector. $\mathbf{L}$ is a set of random number taken in the set of possible values of n . This subset is modified for each line. The energies of the two position vectors are compared and if the new vector gives a better result than the previous one, it takes its place in the initial population to give the population of the next step, P_1 .

Those steps are repeated for all the population vectors a certain number of time (predefined and noted y_{lim}). The use of a convergence criterion is somewhat risky as some local minima are scanned along the process and could lead to small variation of the energies. It is also possible that no x_{new} enhanced the total energy for a round, leading to a difference of energy null while the next round could find a better position. To avoid this, test cases are performed to analyze the speed of convergence and establish a success rate. In the literature, those success rates are good (usually well above 99%) for complex functions. Those rates compare well with the SA algorithm. The Table 3.1 compares the different success rates of the implemented algorithm for different configurations and potentials. It is found that for simple potentials a number of cycles y_{lim} of 500 was sufficient, while for more complex potentials, a value between 3000 and

5000 was enough following the value of k . In our final algorithm, a value of 3000 was set to optimize all the configurations scanned a first time.

y_{lim}	k	$p=[0, 1, 0]$	$p=[0, 1, 1, 2, 1]$	$p=[0, 1, 1, 2, 1, 4, 2]$
500	200	50/50		
500	1000	50/50	49/50	0/50
1000	1000			45/50
1000	2000			48/50
3000	1000			48/50
3000	1000000			32/50
5000	1000000			50/50

Table 3.1 – Success rate of the DE algorithm for different potential and starting configuration. Here, $a_0 = 0.07$, $n_{\text{at}} = 19$, $n_{\text{min}} = 20$. The value of k and the number of cycle y_{lim} are modified for each case. The potential are given in the form of a Fourier series: the vector p contains the height of each Fourier component where the first term is the offset and the rest goes by pair with the first element being the factor associated with a cosinusoidal function and the second to a sinusoidal function of the same periodicity. The success rate are measured by the number of time the algorithm falls within 10^{-6} of the minimum energy over 50 trials. The ground state were confirmed visually. The number of atoms can also play a role but it is not shown here.

Here, every position vector is sorted at each step to avoid changing the nature of the problem and probing solutions that are out of boundary and certainly energetically not favorable. One of the element of the initial population set was also defined as the equidistant vector position used in the NR and MD algorithm. This is done to enhance the speed of the search as this positions are close to the final position. Halfway through the process, the worst half (with the highest energy) of the vector population is also removed to allow the search to focus around the most promising elements. Various other ways of enhancing the algorithm can be found in [101] while the implementation of the algorithm can be found in Appendix B.3.

The main drawback of the DE algorithm is that the computational time is important (since no convergence criterion can be used). Yet, the Figure 3.10 illustrates how the DE algorithm performed better when cases with more than one minimum per atom are considered (the background potential takes the shape of one of the potential found in P-MoS₂ systems and that will be considered in the next chapter).

3.6 Confirmation of the model

This long search for an algorithm giving the ground state for various configuration done, we can finally scan all the configurations mentioned earlier to find the transition point and compare it with the criterion found by F. Frank and J. Van der Merwe and Benoit Van Troeye *et al* (Equation 3.14).

The Figure 3.11 shows a first example of transition between a configuration of 16 atoms for

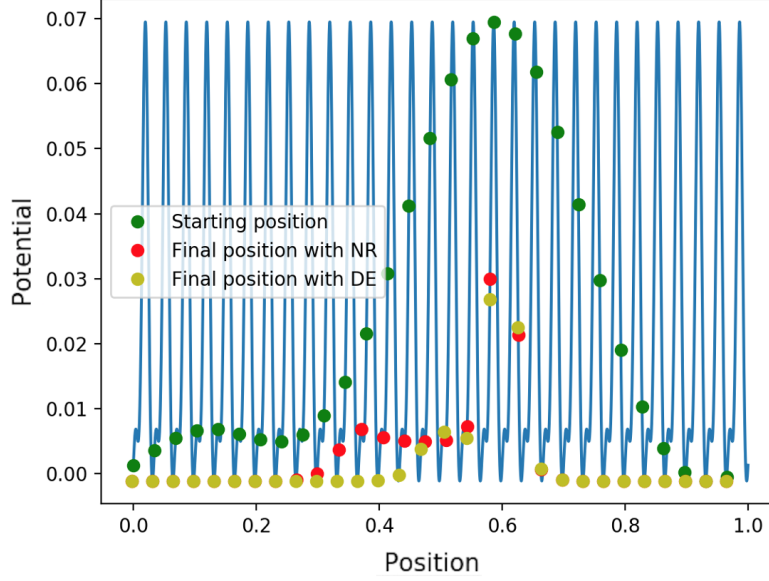


Figure 3.10 – Comparison between the ground state found with the NR algorithm (and sampling) and the one found with the DE algorithm. $a_0 = 0.05$, $k = 3000$. The background potential has two minima per period.

16 minima (the background potential was sinusoidal) and 15 or 17 atoms for the same number of minima. This graph allows to distinguish several things. First, the transition between 15 and 16 atoms is symmetric with the transition between 16 and 17 atoms. This confirms the fact that introducing a dislocation with one more or one less atoms follows the same criterion of transition. Then, the arrows on the figure indicate different points which are thought to contain numerical errors. They are left here for illustration purpose. Those points could be recalculated several times to be compared and corrected. Finally, three regions are identified along the curves: two flat regions for small and big values of k and a transition region between the two.

The transition in the region of big values of k is essentially determined by the ratio of elastic energy per atom. The energy curves of each configuration can therefore be approximated by three second order polynomials with minima in $(n_{\text{at}}/n_{\text{at}} + 1)b$, b and $(n_{\text{at}}/n_{\text{at}} - 1)b$ for the curves with $n_{\text{at}} + 1$, n_{at} and $n_{\text{at}} - 1$ atoms with $n_{\text{at}} = n_{\text{min}} = 1/b$. Neglecting the potential energy, the transition is therefore situated at mid-distance between the two minima. The transition between the case with $n_{\text{at}} = n_{\text{min}}$ and $n_{\text{at}} + 1$ is therefore given by:

$$a_{\text{tr},k \rightarrow \infty} = 1 \left(\frac{n_{\text{min}}}{n_{\text{min}} + 1} b + b \right) = \frac{1}{n_{\text{min}}} \left(1 - \frac{1}{2} \left(\frac{1}{n_{\text{min}} + 1} \right) \right) \quad (3.26)$$

In the same way, the transition between $n_{\text{at}} = n_{\text{min}}$ and $n_{\text{at}} - 1$ is given by:

$$a_{\text{tr},k \rightarrow \infty} = 1 \left(\frac{n_{\text{min}}}{n_{\text{min}} - 1} b + b \right) = \frac{1}{n_{\text{min}}} \left(1 + \frac{1}{2} \left(\frac{1}{n_{\text{min}} - 1} \right) \right) \quad (3.27)$$

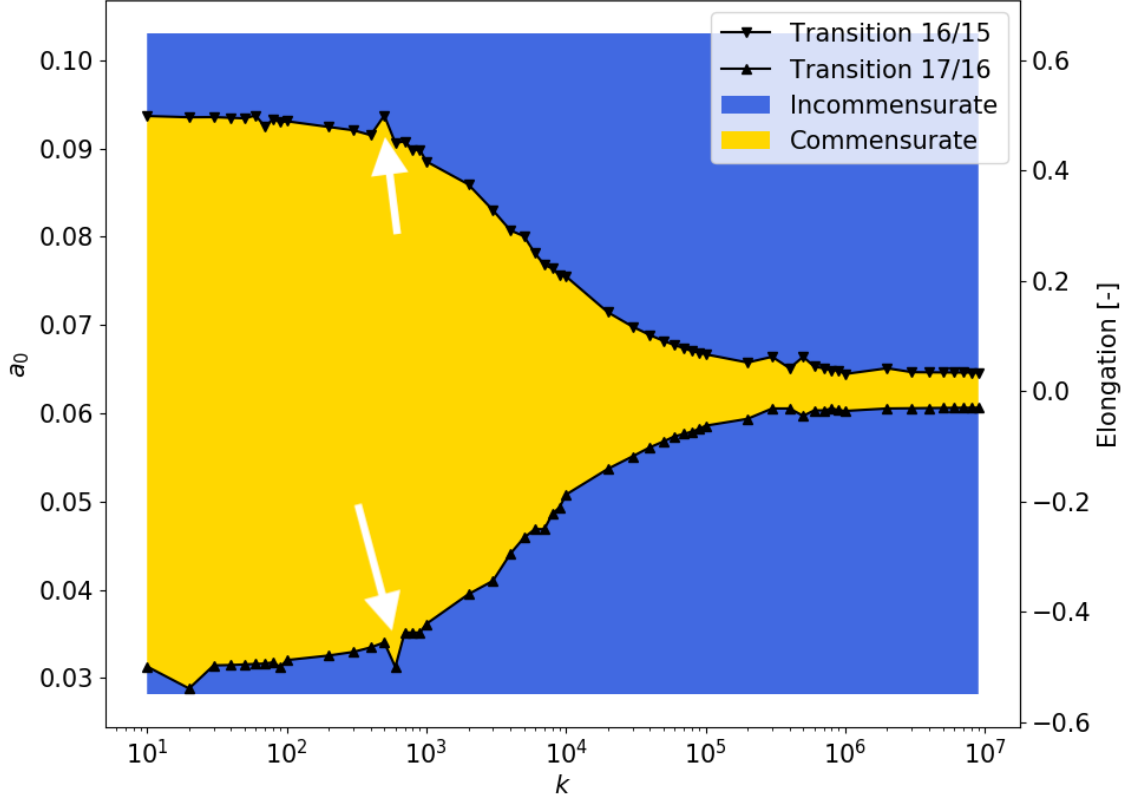


Figure 3.11 – Phase diagram of a chain of 16 atoms in a sinusoidal potential with 16 minima and periodic boundary conditions. The introduction of a dislocation with a supplementary atom is favored under the orange line and the introduction of a dislocation with one less atom is favored above the blue line. The black arrows indicate the main points where numerical imprecisions are suspected.

However, for small values of k , all the atoms are pinpointed to the minima of the background potential. If $n_{\text{at}} = n_{\text{min}} \pm 1$, one minima is found with two atoms nearly on top of one another or empty, respectively. All the atoms have therefore the same potential energy and again, only the elastic energy has to be compared. The transition between $n_{\text{at}} = n_{\text{min}}$ and $n_{\text{at}} + 1$ is given by:

$$(b - a_0)^2 \geq (b - a_0)^2 \frac{n_{\text{min}}}{n_{\text{min}} + 1} + a_0^2 \frac{1}{n_{\text{min}} + 1} \implies a_{\text{tr},k \rightarrow 0} = \frac{1}{2n_{\text{min}}} \quad (3.28)$$

And the transition between $n_{\text{at}} = n_{\text{min}}$ and $n_{\text{at}} - 1$ is given by:

$$(b - a_0)^2 \geq (b - a_0)^2 \frac{n_{\text{min}} - 2}{n_{\text{min}} - 1} + (2b - a_0)^2 \frac{1}{n_{\text{min}} - 1} \implies a_{\text{tr},k \rightarrow 0} = \frac{3}{2n_{\text{min}}} \quad (3.29)$$

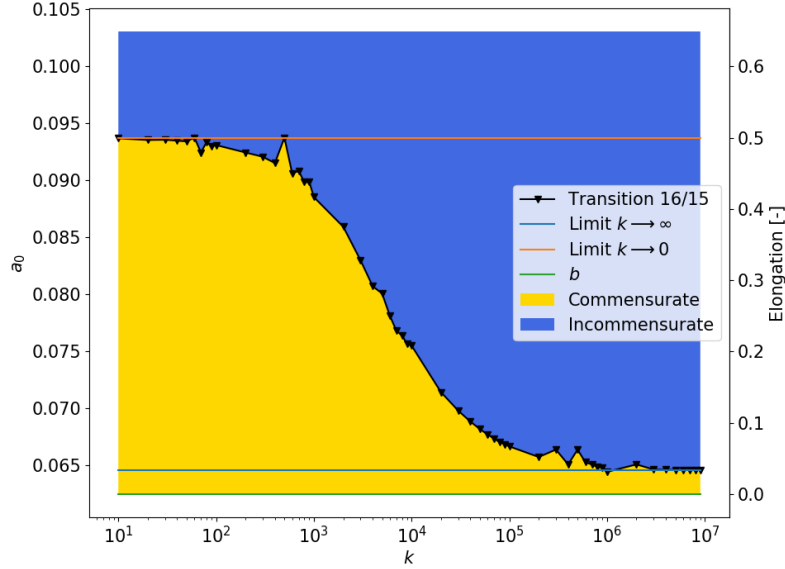


Figure 3.12 – Zoom on the limit between the phase with 15 atoms and 16 atoms for $n_{\min} = 16$ presented in Figure 3.11 with the limit for small k ($a_{\text{tr}} = \frac{3}{2n_{\min}}$) indicated by a green line and the limit for big values of k ($a_{\text{tr}} = \frac{1}{n_{\min}} \left(1 + \frac{1}{2} \left(\frac{1}{n_{\min}-1}\right)\right)$) indicated by an orange line. A red line indicates the value of b .

Those limits were found in good agreement with our computations as illustrated in Figure 3.12.

The two flat regions do not exist in the continuous case described in the theory. In fact only the transition region correspond to the criterion of Equation 3.14. This is illustrated in Figures 3.13. One can observe that the value of γ_{FK} is recovered for a sinusoidal background potential. It can also be noted that the width of the plateau where this criterion is valid increases toward the higher value of k as the discreteness of the problem decreases as illustrated in Figure 3.14. It is believed that the criterion is not found for small values of k even with $n_{\text{at}} \rightarrow \infty$ as the theoretical model does not allow for two atoms to fall in the same minimum or that one minimum is left empty. Yet, comparing the variation of $(b - a_0)/b$ to the elongation of the chain, it is found that our plateau describes well what happens for small strain (up to ~ 0.15) which is the domain of interest.

Finally, the criterion should be validated for potentials with γ value different from γ_{FK} . To this end, a potential with $\gamma \approx 1.31$ was chosen. A period of this potential is found in Figure 3.15. As real cases are closer to the continuous approximation than the graph presented here, it can be concluded that the model presented above gives a good description of the transition. Our graphs confirm that the γ value found with Equation 3.15 is in good agreement with our simulations using a different approach. Those graphs are given here apparently for the first time. The behavior and impact of discreteness was developed and debated in [32] (they discuss in particular the Peierls-Nabarro potential, barrier of potential arising from the discrete

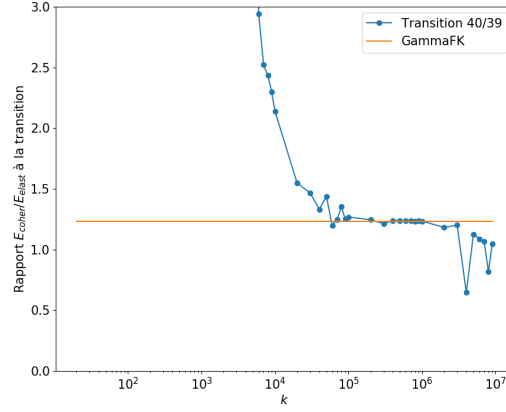


Figure 3.13 – Comparison of the criterion of Equation 3.14 with the ratio $E_{\text{coher}}/E_{\text{elast}}$ at the transition found with the DE algorithm for sinusoidal background potential. The value γ_{FK} is indicated in the figure by an orange line. The figure corresponds to the transition between $n_{\text{min}} = n_{\text{at}} = 40$ and $n_{\text{at}}=39$. Some numerical noise is present, with some points being clearly wrong, but the appearance of a plateau at the right ratio is also clear.

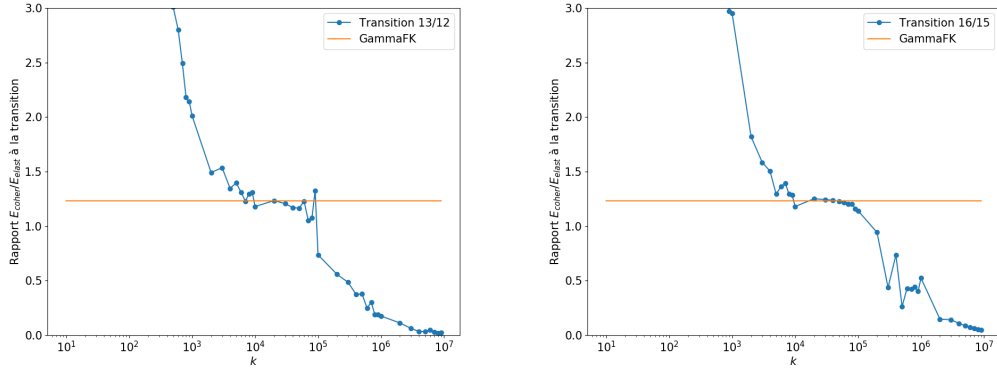


Figure 3.14 – Comparison of the criterion of Equation 3.14 with the ratio $E_{\text{coher}}/E_{\text{elast}}$ at the transition found with the DE algorithm for sinusoidal background potential. The value γ_{FK} is indicated in the figure by an orange line. The figure corresponds to the transition between $n_{\text{min}} = n_{\text{at}} = 12$ and 16 and $n_{\text{at}}=13$ and 15, respectively. Some numerical noise is present, with some points being clearly wrong, but the appearance of a varying width plateau at the right ratio is also clear.

character of the chain, and its impact on dislocation's motion) but no implementation were ever performed to describe the transition from a discrete case to a continuous case. Our simulation tool could therefore be used to investigate deeper the 1D FK model, with the possibility to treat aperiodic cases left unexplored. Interaction with second and third nearest neighbors

could also be integrated in the code. The possibility to use the NR algorithm to find local minima also allows to approach the FK model with several minima per period in a different manner. The algorithm also provides a way to evaluate the energetic cost of dislocations and their positions (and therefore their length). Those possible explorations are left for future investigations.

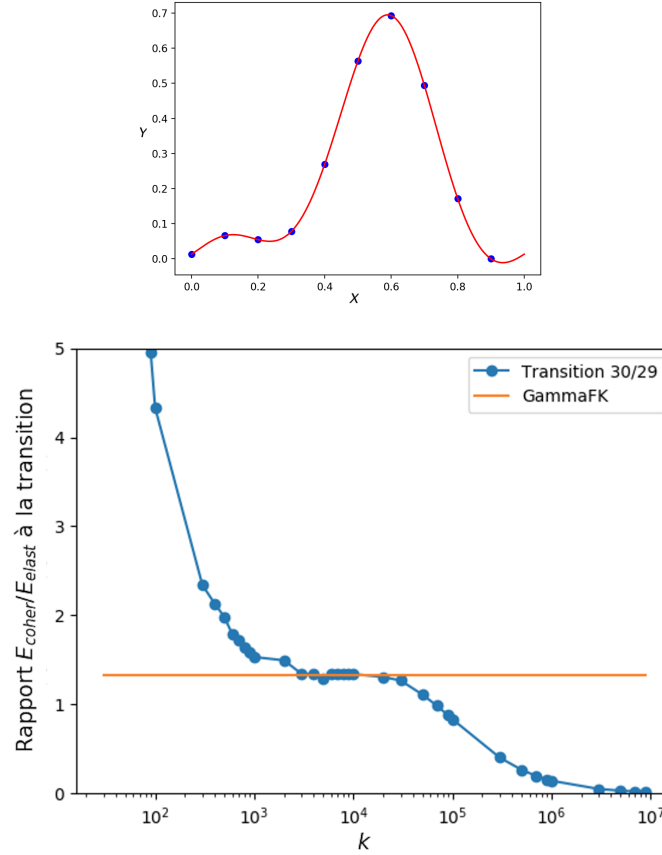


Figure 3.15 – Top: Potential used to test if the transition criterion remains correct for different potentials. The blue points are the points used to create the potential by an interpolation using three Fourier components. Bottom: Comparison of the ratio $E_{\text{coher}}/E_{\text{elast}}$ for the case of $n_{\text{min}} = 30$.

Chapter 4

Probing the commensurability of heterostructures

This chapter presents the continuation of the work initiated by B. Van Troeye *et al* in their article "First-principles investigation of 2D lattice coherency in van der Waals heterostructures" [1]. In their article, the commensurability or not of various vdWHS was predicted using the FK model presented earlier. Their predictions relied on a single criterion, kept constant: $\gamma_{\text{FK}} \approx 1.2334$. This criterion was compared to the coherency energy of a 2D potential and elastic energy obtained by DFT computations (the detail of the computations can be found in their supplementary material). With this sole criterion, two phases can be distinguished: completely commensurate and completely incommensurate. If the ratio $|E_{\text{coher}}|/E_{\text{elast}}$ was close to γ_{FK} a semi-coherent regime could be suspected.

Here, we try to go one step further by (1) introducing two possible new phases and (2) adapting the γ value to correspond to the background potential. The two new phases are called *CI* and *IC*. The first phase corresponds to a structure commensurate along the first direction and incommensurate along the second direction and the second phase corresponds to the opposite situation (keeping the same two characteristic directions in both cases). To be able to distinguish those phases, the 2D potential used is analyzed more finely in order to evaluate which potential is actually felt in the structure when a dislocation is introduced.

This chapter is structured as follow. The first section will present the problem in a more extensive way. The second section will be dedicated to the derivation of the four criteria. The third section will show two ways of using the four criteria in order to predict the ground phase of structure. Finally, the results of our methods applied to 11 vdWHS (P-MoSe₂, P-G, P-hBN, MoS₂-MoSe₂, MoS₂-WS₂, MoS₂-WSe₂, MoSe₂-MoTe₂, MoSe₂-WS₂, MoSe₂-WSe₂, MoTe₂-WSe₂ and WS₂-WSe₂) are shown and discussed.

4.1 Problem and methodology

Stacking energy

The energy of interest in our problem, along with the elastic energy, is the stacking energy,

E_{stack} which is the amount of energy originating from stacking. Indeed, this is potential energy that will enable us to compute the coherency energy that appears in the FK model. The stacking energy associated to the stacking of two subsystems (1) and (2) is defined as (by unit area) [105]:

$$E_{\text{stack}}[\tau] = E_s^{(1+2)}[\tau] - E_s^{(1)} - E_s^{(2)} \quad (4.1)$$

with $E_s^{(1+2)}[\tau]$ the total energy per unit area of the structure, $E_s^{(1)}$ is the energy associated to the first system, $E_s^{(2)}$ is the energy associated with the second system and τ the in-plane shift between the two layers.

This stacking energy is important since the rest of this thesis relies on it. This energy is therefore, the energy associated with a certain configuration of stacking. One can obtain it by DFT computations. This was done by B. Van Troeye *et al.* To compute this stacking energy, the isolated subsystems were relaxed and then rigidly stacked together. This means that we kept the relaxed lattice parameters of each layer in the final structure. The variation of the interlayer distance is also not probed by such stacking.

An example of stacking energy translational landscape is given in Figure 4.1. One can observe that it has the same periodicity as the unit cell. Indeed, if a translation of an integer number of unit cell is performed, one recovers the same stacking configuration found at its starting point. Therefore, to have the complete potential landscape, one has to sample the unit cell of the structure. This means that (1) one stacks the two layers in an aligned manner, (2) compute the stacking energy, (3) then select a translation vector inside the unit cell and (4) apply the translation to the upper layer while keeping the bottom layer fixed. (5) The energy associated to this new configuration is computed and (6) the operation is done again until a complete map is obtained. Here, 25 to 100 points were computed for each heterostructures.

Now, one could be wondering if all those computations are really efficient. In fact, all of the heterostructures analyzed here present a lattice mismatch. This means that when one wants to perform DFT computations, it has to consider superstructure with thousands of atoms [106]. The approach presented above allows to consider only local arrangement with a limited number of atoms. Even repeating the computations a 100 times is still a lot faster and a lot easier than having to compute the relaxed configuration of the superstructure to determine the ground phase. The DFT computations, coupled with our method are therefore a relatively efficient tool to predict the phase (commensurate or incommensurate) of a structure.

Decoupling a 2D problem in two 1D problems

With the translation energy landscape of our structure, a coherency energy and a γ can be computed. Similarly, one can compute the elastic energy required to obtain a commensurate state via DFT computations. Those energies can then be compared, and the determination of the ground phase is possible thanks to the criterion of Equation 3.14. This way of proceeding is relatively simple and fast. It corresponds to the method used by B. Van Troeye *et al* in their article [1]. Here, we try to elaborate on this model to get more details of the physics at play. To do so, we observe the problem under the two characteristic directions of the unit cell. This allows in the end to distinguish more ground phases and with more accuracy than previously done by B. Van Troeye *et al.*

To illustrate our approach, we consider the following case: we start with the MoSe₂-MoTe₂

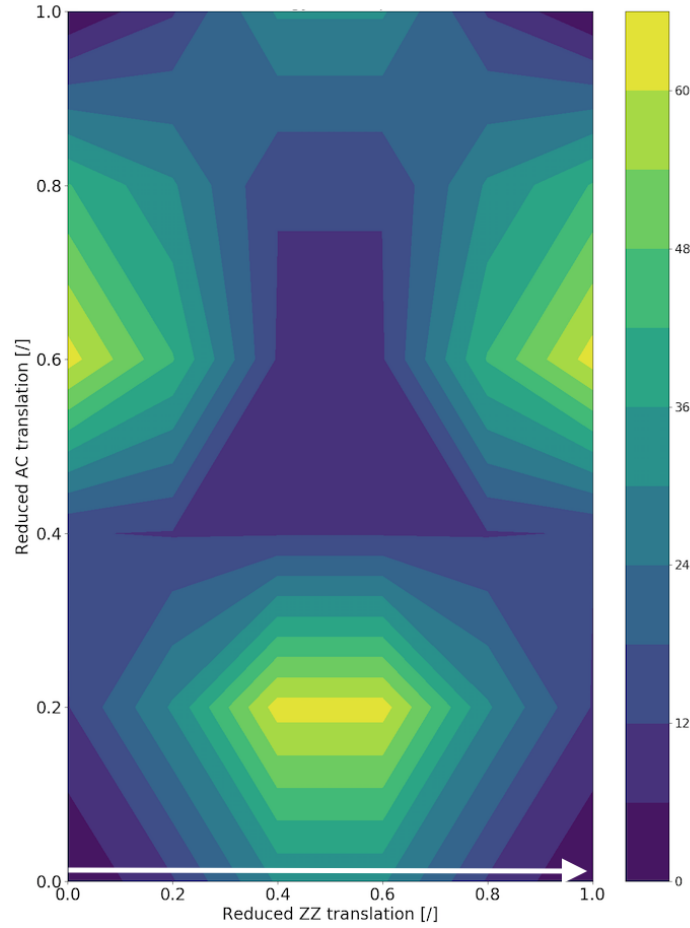


Figure 4.1 – Translational energy landscape of MoSe₂-MoTe₂. "AC" stands for armchair and "ZZ" stands for zigzag. The white arrow illustrates the translational path encountered in a dislocation.

vdWHS associated with the potential landscape presented in Figure 4.1. In our fictional example we assume the structure to be coherent along the armchair direction such that the lattice parameters of both layers in this direction matches one another. This is equivalent to state, that along this direction, only one configuration of stacking is found. For a dislocation to be introduced along the zigzag direction, the elastic energy should be bigger than the coherency energy associated to the path from the point of minimum energy along the armchair direction to the next corresponding equivalent configuration (i.e. the translational path is identical to the zigzag unit cell vector as indicated by the arrow in Figure 4.1). The choice of this path is justified as a commensurate structure should adopt a configuration with minimum stacking energy. Therefore, the first dislocation should link to commensurate states and encounters the configurations (as the positions of the atoms in both layers are out of phase in the dislocation) crossed by the arrow in Figure 4.1.

This one-dimensional energy path takes a certain shape following the relief of the potential landscape and is therefore associated to a γ value and a coherency energy. By computing the

elastic energy required to pass from the incommensurate state along the zigzag direction to the commensurate state along the same direction, one can evaluate, using the criterion derived in the previous chapter, if a dislocation is introduced or not. This leads to two situations following if the criterion for coherency is met: the structure is commensurate along both directions or commensurate along the armchair direction and incommensurate along the zigzag direction.

In a second scenario, the same vdWHS is found incommensurate in the armchair direction. Hence, we do not have a clear energy path to evaluate if the introduction of a dislocation is favored or not. Indeed, following where we are in the structure, different translation paths along the zigzag direction are found. In our approach we decide to treat this feature in the following way. Since all the translation paths are possible, we average them to obtain a one-dimensional energy landscape corresponding to the value of the interlayer energy found, on average, at a certain translation along the zigzag direction.

This one-dimensional potential is also associated to a certain γ value and a certain coherency energy which can be compared to the elastic energy needed to obtain a commensurate phase along the zigzag direction. By comparing the elastic energy required to obtain a commensurate phase along the zigzag direction, keeping the armchair direction incommensurate, to the coherency energy of the derived potential, one can probe if the zigzag direction is commensurate or not. Two outcomes are therefore possible in this scenario: incommensurate along both directions or incommensurate along the armchair direction and commensurate along the zigzag direction.

This simple reasoning is at the basis of the development of the criteria made in the next section. It already deals with the four phases our model will try to predict: *CC*, *CI*, *IC* and *II*, where *CC* denotes a commensurate state along both directions while *II* denotes an incommensurate state along both directions.

The next section brings some mathematical formalism to the above reasoning with the development of four criteria which will be used to distinguish the different phases.

4.2 Development of the different criteria

This section mainly follows the work of B. Van Troeye *et al.* Their notation is also used for clarity.

In the previous chapter, a criterion for the transition was presented and is recalled here: a commensurate state is favored if:

$$\gamma E_{\text{elast}} < |E_{\text{coher}}| \quad (4.2)$$

This criterion was demonstrated to be true in one dimension in the previous chapter and its extension in two dimensions was used in different researches including the one of B. Van Troeye *et al.* [1][90]. Here, since we work in aligned structures, we can decouple the problem along the characteristic directions of the unit cell. It means that rather than averaging the potential in the two dimensions to obtain the E_{coher} , each direction will be considered separately as explained earlier.

Using the definition of the stacking energy of Equation [4.1], the coherence energy is given explicitly as:

$$E_{\text{coher}} = \min_{\boldsymbol{\tau}} \{E_{\text{stack}}[\boldsymbol{\tau}]\} - \langle E_{\text{stack}}[\boldsymbol{\tau}] \rangle_{\boldsymbol{\tau}} \quad (4.3)$$

In order to obtain a criterion for the coherency along each direction, one has to decompose this system. We denote τ_1 and τ_2 the two components of the shift vector $\boldsymbol{\tau}$ along direction 1 and direction 2. We start from an incommensurate system and try to find if the coherency is favored along the direction 1 while leaving the direction 2 incommensurate. In that case, the potential felt by the atoms, for each value of τ_1 , is approximated by the average value of the potential for all the value of τ_2 (for each value of τ_1 , one takes the mean value of the potential over all the values of τ_2). The potential of interest can be written as:

$$E_{\text{stack}}^{\langle \tau_2 \rangle}[\tau_1] = \langle E_s^{(1+2)}[\tau_1, \tau_2] \rangle_{\tau_2} \quad (4.4)$$

and the coherency energy is:

$$E_{\text{coher}}^{\langle \tau_2 \rangle} = \min_{\tau_1} \{E_{\text{stack}}^{\langle \tau_2 \rangle}[\tau_1]\} - \langle E_{\text{stack}}[\boldsymbol{\tau}] \rangle_{\boldsymbol{\tau}} \quad (4.5)$$

We also need a criterion to evaluate whether this state of coherency along the direction 1 is favored with respect to the complete commensurate state. In that case the cost in elastic energy should be compared to the coherency energy given by the potential linking two minima of the potential landscape. The potential of interest is therefore a cut along a given direction for a given value of τ_1 (corresponding to the position of a minimum) in the 2D potential landscape:

$$E_{\text{coher-1D}}(\tau_1) = \min_{\tau_2} \{E_{\text{stack}}[\tau_1, \tau_2]\} - \langle E_{\text{stack}}[\tau_1, \tau_2] \rangle_{\tau_2} \quad (4.6)$$

Those coherency energies have to be compared to a certain cost in elastic energy. In the linear elastic regime, this energy is given by:

$$E_{\text{elast}} = \frac{1}{N_{\text{at}}} \left(\frac{a_{0,1}^{(1)} a_{0,2}^{(1)} n_1^{(1)} n_2^{(1)}}{2} \sum_{\alpha, \beta} \tilde{c}_{\alpha\beta}^{(1)} \epsilon_{\alpha}^{(1)} \epsilon_{\beta}^{(1)} + \frac{a_{0,1}^{(2)} a_{0,2}^{(2)} n_1^{(2)} n_2^{(2)}}{2} \sum_{\alpha, \beta} \tilde{c}_{\alpha\beta}^{(2)} \epsilon_{\alpha}^{(2)} \epsilon_{\beta}^{(2)} \right) \quad (4.7)$$

with N_{at} the number of atoms in the unit cell considered, a_0 is the lattice vector of the relaxed isolated system, the subscripts 1 and 2 distinguish directions 1 and 2, ϵ denotes an strain, the parameters α and β takes the values (1,2), $\tilde{c}$ is a component of the elastic tensor of the subsystem, n is the number of repetition of the unit cell of one of the two subsystems in a specific direction. In this equation, all the values are known from literature and/or DFT computations except for the elongations. To find those, four cases have to be considered: completely incommensurate in each direction, completely commensurate or commensurate in direction 1 and incommensurate in direction 2 and the opposite. In the incommensurate state, the elongation are given by the trivial system:

$$\begin{cases} \epsilon_{11} = 0 \\ \epsilon_{12} = 0 \\ \epsilon_{21} = 0 \\ \epsilon_{22} = 0 \end{cases} \quad (4.8)$$

This system is an approximation as it was shown that small amount of strain were present in incommensurate system [14]. The second system, for the commensuration along both directions, requires a matching of the parameter of the unit cell of each subsystem and a tension null in both directions. Those constraints give the following system:

$$\begin{cases} n_1^{(1)} a_{0,1}^{(1)} (1 + \epsilon_1^{(1)}) - n_1^{(2)} a_{0,1}^{(2)} (1 + \epsilon_1^{(2)}) = 0 \\ n_2^{(1)} a_{0,2}^{(1)} (1 + \epsilon_2^{(1)}) - n_2^{(2)} a_{0,2}^{(2)} (1 + \epsilon_2^{(2)}) = 0 \\ \frac{a_{0,1}^{(1)} a_{0,2}^{(1)} n_1^{(1)} n_2^{(1)}}{a_{0,1}^{(1)} n_1^{(1)}} (\tilde{c}_{11}^{(1)} \epsilon_1^{(1)} + \tilde{c}_{12}^{(1)} \epsilon_2^{(1)}) + \frac{a_{0,1}^{(2)} a_{0,2}^{(2)} n_1^{(2)} n_2^{(2)}}{a_{0,1}^{(2)} n_1^{(2)}} (\tilde{c}_{11}^{(2)} \epsilon_1^{(2)} + \tilde{c}_{12}^{(2)} \epsilon_2^{(2)}) = 0 \\ \frac{a_{0,1}^{(1)} a_{0,2}^{(1)} n_1^{(1)} n_2^{(1)}}{a_{0,2}^{(1)} n_2^{(1)}} (\tilde{c}_{21}^{(1)} \epsilon_1^{(1)} + \tilde{c}_{22}^{(1)} \epsilon_2^{(1)}) + \frac{a_{0,1}^{(2)} a_{0,2}^{(2)} n_1^{(2)} n_2^{(2)}}{a_{0,2}^{(2)} n_2^{(2)}} (\tilde{c}_{21}^{(2)} \epsilon_1^{(2)} + \tilde{c}_{22}^{(2)} \epsilon_2^{(2)}) = 0 \end{cases} \quad (4.9)$$

In the commensurate-incommensurate case (commensurate along one direction and incommensurate along the other), the constraint of matching in the two directions is alleviated as it only concerns one direction. In the case of commensurability in direction 1, the system to solve is:

$$\begin{cases} n_1^{(1)} a_{0,1}^{(1)} (1 + \epsilon_1^{(1)}) - n_1^{(2)} a_{0,1}^{(2)} (1 + \epsilon_1^{(2)}) = 0 \\ \frac{a_{0,1}^{(1)} a_{0,2}^{(1)} n_1^{(1)} n_2^{(1)}}{a_{0,1}^{(1)} n_1^{(1)}} (\tilde{c}_{11}^{(1)} \epsilon_1^{(1)} + \tilde{c}_{12}^{(1)} \epsilon_2^{(1)}) + \frac{a_{0,1}^{(2)} a_{0,2}^{(2)} n_1^{(2)} n_2^{(2)}}{a_{0,1}^{(2)} n_1^{(2)}} (\tilde{c}_{11}^{(2)} \epsilon_1^{(2)} + \tilde{c}_{12}^{(2)} \epsilon_2^{(2)}) = 0 \\ (\tilde{c}_{21}^{(1)} \epsilon_1^{(1)} + \tilde{c}_{22}^{(1)} \epsilon_2^{(1)}) = 0 \\ (\tilde{c}_{21}^{(2)} \epsilon_1^{(2)} + \tilde{c}_{22}^{(2)} \epsilon_2^{(2)}) = 0 \end{cases} \quad (4.10)$$

We can therefore rewrite the criterion for the transition. We introduce the notation *II*, *CI*, *IC* and *CC* to denote the phases incommensurate along both directions, commensurate along the first direction and incommensurate along the second direction, incommensurate along the first direction and commensurate along the second direction and commensurate in both directions respectively. The transition from *II* to *CI* is favored if :

$$E'_{\text{elast},1} < \frac{|E_{\text{coher}}^{<\tau_2>}|}{\gamma} \quad (4.11)$$

where $E'_{\text{elast},1}$ is the elastic energy associated with the *CI* phase. The transition from the *CI* phase to the *CC* phase is favored if:

$$E'_{\text{elast},2} < \frac{|E_{\text{coher-1D}}(\tau_2)|}{\gamma} \quad (4.12)$$

where $E'_{\text{elast},2}$ is the difference of energy between the commensurate case and the *CI* phase. With:

$$\gamma = \frac{(\langle V \rangle - V_{\min})}{(\langle (V - V_{\min})^{1/2} \rangle)^2} \quad (4.13)$$

and the generic expression of the cohesion energy:

$$E_{\text{coher}} = V_{\min} - \langle V \rangle \quad (4.14)$$

the four criteria are given in their complete form as:

— *CI* phase preferred to *II* phase if (Criterion 1, C1):

$$|E_{\text{elast}}^{ci}| < \left(\frac{1}{a_1} \int_0^{a_1} \left(E_{\text{stack}}^{<\tau_2>}[\tau_1] - \min_{\tau_1} \left\{ E_{\text{stack}}^{<\tau_2>}[\tau_1] \right\} \right)^{1/2} d\tau_1 \right)^2 < E_{C1} \quad (4.15)$$

— *CC* phase preferred to *CI* phase if (Criterion 2, C2):

$$|E_{\text{elast}}^{cc} - E_{\text{elast}}^{ci}| < \left(\frac{1}{a_2} \int_0^{a_2} \left(E_{\text{stack}}[\tau_{1,opt}, \tau_2] - \min_{\tau_1, \tau_2} \left\{ E_{\text{stack}}[\tau_1, \tau_2] \right\} \right)^{1/2} d\tau_2 \right)^2 < E_{C2} \quad (4.16)$$

— *IC* phase preferred to *II* phase if (Criterion 3, C3):

$$|E_{\text{elast}}^{ic}| < \left(\frac{1}{a_2} \int_0^{a_2} \left(E_{\text{stack}}^{<\tau_1>}[\tau_2] - \min_{\tau_2} \left\{ E_{\text{stack}}^{<\tau_1>}[\tau_2] \right\} \right)^{1/2} d\tau_2 \right)^2 < E_{C3} \quad (4.17)$$

— *CC* phase preferred to *IC* phase if (Criterion 4, C4):

$$|E_{\text{elast}}^{cc} - E_{\text{elast}}^{ic}| < \left(\frac{1}{a_1} \int_0^{a_1} \left(E_{\text{stack}}[\tau_1, \tau_{2,opt}] - \min_{\tau_1, \tau_2} \left\{ E_{\text{stack}}[\tau_1, \tau_2] \right\} \right)^{1/2} d\tau_1 \right)^2 < E_{C4} \quad (4.18)$$

4.3 Integration of the criteria to determine the phase

This section presents two models to predict the final phases. The first of the two models described is an intermediate step in our reflexion to a more accurate model. At the time of developing this first model, we had defined all the four aforementioned potentials. To understand the possible outcomes linked to the development of the criteria linked to those potential, the idea to compare them to the elastic energy associated to the elongation ϵ_{11} and ϵ_{22} was emitted. By approaching the problem with that angle, we discard the impact of the Poisson's ratio (done here by setting $\tilde{c}_{12} = \tilde{c}_{21} = 0$). Nonetheless, it permits to unveil some subtleties of the problem and makes a first step towards a better comprehension of the physic at play. This model is called "Neglect of off-diagonal elements" (NODEC). The second model is more accurate and gives a better representation of the interactions. It also uses the four criteria presented above but in their complete form. This second method is called the "16 cases" method.

4.3.1 Neglect of off-diagonal elements (NODEC)

We draw the attention of the reader to the fact that this section is less accurate than the method that follows: the "16 cases" method.

We now have four criteria to find one ground state in any material. The idea here is to analyze each direction separately discarding the term $\tilde{c}_{12}$ in the elastic energy. By doing this, the elastic energy of the commensurate state should be equal to the sum of elastic energies of the *CI* and *IC* phase. We can therefore compare criterion C1 and C2 to the elastic energy associated to the elongation ϵ_{11} and C3 and C4 to the elastic energy associated to the elongation ϵ_{22} .

To visualize how those criteria interact with each other, phase diagrams were drawn where the four criteria were separated along the direction each will affect. This gives, as already mentioned, two subsets of two criteria: Criterion 1 and 2 and Criterion 3 and 4. In each subset, the order of the criterion can be bigger or smaller than the other one. Following this fact, four phase diagrams can be extracted for each possibility. By noting that the possibility of $C1 > C2$ with $C3 < C4$ and $C1 < C2$ with $C3 > C4$ is equivalent to switch direction 1 and 2, only three generic phase diagrams are to be drawn. They are given in Figures 4.2-4.4. Those diagrams are labelled "Type 1", "Type 2" and "Type 3".

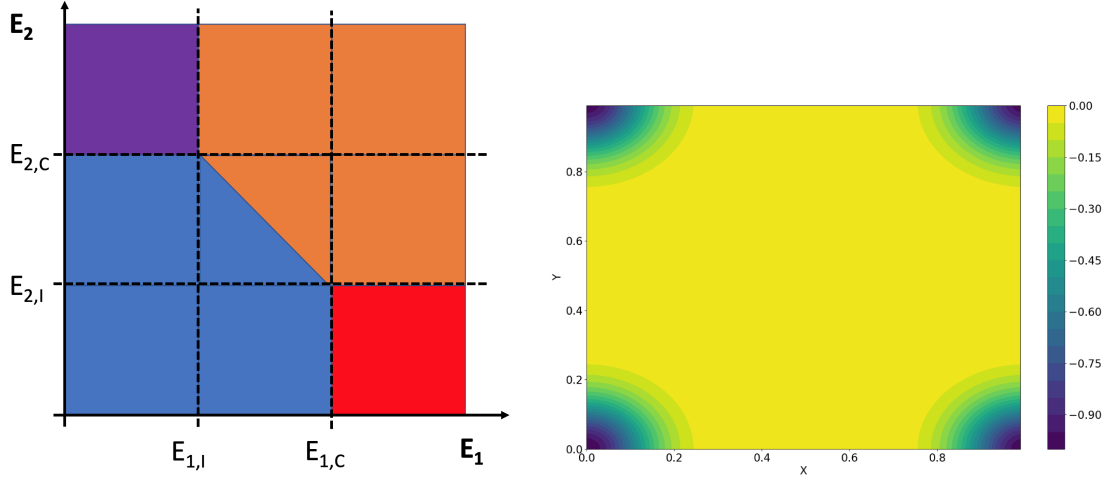


Figure 4.2 – Left: The "Type 1" phase diagram with phases: (blue)=*CC*, (purple)=*CI*, (red)=*IC* and (orange)=*II*. If two colors are in the same square, both phases are possible. The top left is called "Type 1", the top right "Type 2" and the bottom one "Type 3". The four criteria are labelled $E_{1,I}$, $E_{1,C}$, $E_{2,I}$ and $E_{2,C}$ by correspondence with Criterion 1, Criterion 2, Criterion 3 and Criterion 4, respectively. Right: Example of 2D potential leading to a "Type 1" phase diagram.

In each of these diagrams, the phases are indicated by color. To better understand what would be the generic shape of the potential associated to those diagrams, different potential landscapes were designed, and are illustrated along their corresponding phase diagrams. It is found that a potential with a big and sharp well at the preferred stacking configuration but relatively flat elsewhere (i.e. with a plateau of energy well above the one of the best stacking configuration) leads to a diagram "Type 1". On the contrary, having wide, flat well around a big sharp barrier of potential at the worst favorable configuration of stacking leads to a "Type 2" phase diagram. Finally, having a potential with a strong unidirectional behavior (relatively flat in one direction while having more relief on the other, like a wave at sea) leads to a "Type

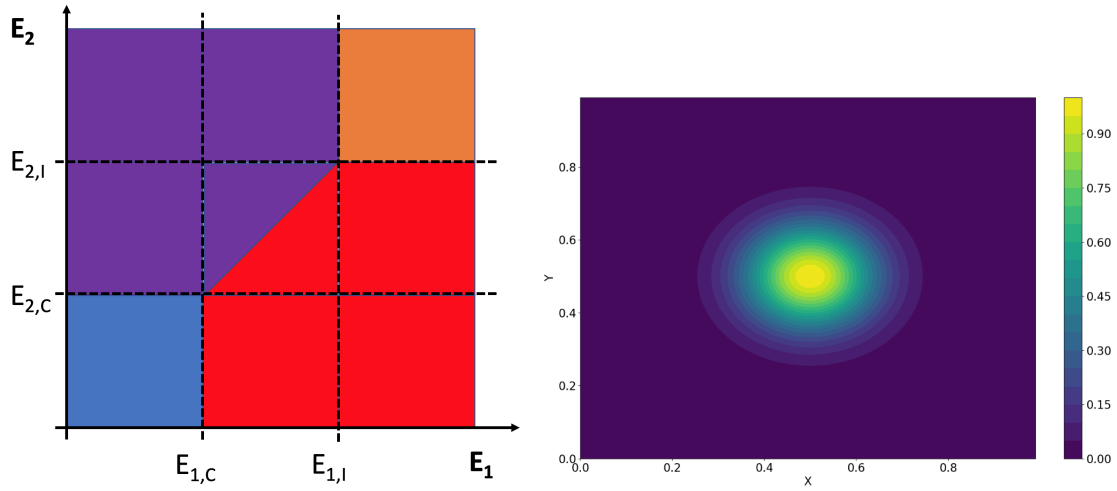


Figure 4.3 – Left: The "Type 2" phase diagram with phases: (blue)= CC , (purple)= CI , (red)= IC and (orange)= II . If two colors are in the same square, both phases are possible. The top left is called "Type 1", the top right "Type 2" and the bottom one "Type 3". The four criteria are labelled $E_{1,I}$, $E_{1,C}$, $E_{2,I}$ and $E_{2,C}$ by correspondence with Criterion 1, Criterion 2, Criterion 3 and Criterion 4, respectively. Right: Example of 2D potential leading to a "Type 2" phase diagram.

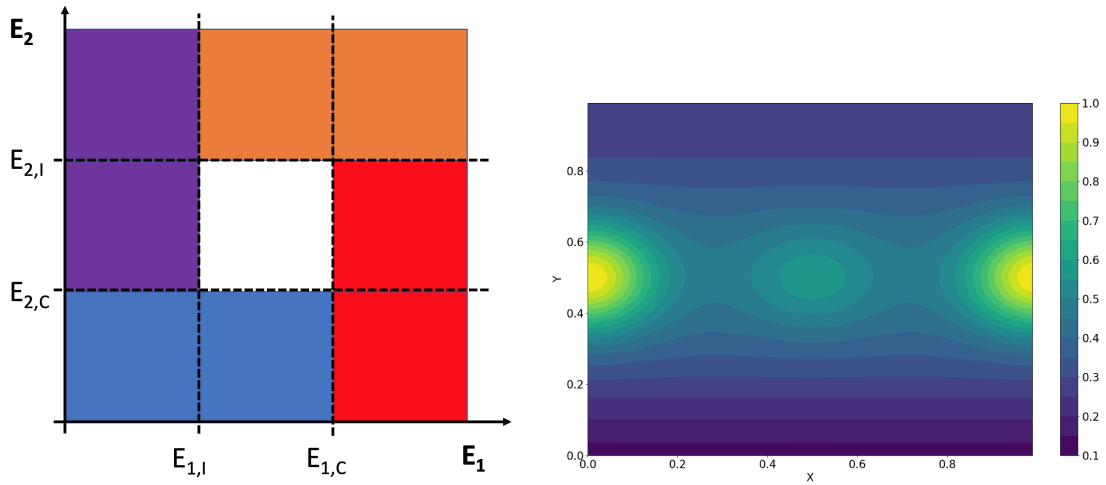


Figure 4.4 – Left: The "Type 3" phase diagram with phases: (blue)= CC , (purple)= CI , (red)= IC , (orange)= II and (white)=undetermined. If two colors are in the same square, both phases are possible. The top left is called "Type 1", the top right "Type 2" and the bottom one "Type 3". The four criteria are labelled $E_{1,I}$, $E_{1,C}$, $E_{2,I}$ and $E_{2,C}$ by correspondence with Criterion 1, Criterion 2, Criterion 3 and Criterion 4, respectively. Right: Example of 2D potential leading to a "Type 3" phase diagram.

3" diagram. The axis of the diagrams indicate the elastic energies introduced in the system associated to the elongation of the first and second direction. Those energies were computed

as:

$$E_1 = \frac{1}{N_{\text{at}}} \left(\frac{a_{0,1}^{(1)} a_{0,2}^{(1)} n_1^{(1)} n_2^{(1)}}{2} \tilde{c}_{11}^{(1)} (\epsilon_1^{(1)})^2 + \frac{a_{0,1}^{(2)} a_{0,2}^{(2)} n_1^{(2)} n_2^{(2)}}{2} \tilde{c}_{11}^{(2)} (\epsilon_1^{(2)})^2 \right) \quad (4.19)$$

and

$$E_2 = \frac{1}{N_{\text{at}}} \left(\frac{a_{0,1}^{(1)} a_{0,2}^{(1)} n_1^{(1)} n_2^{(1)}}{2} \tilde{c}_{22}^{(1)} (\epsilon_2^{(1)})^2 + \frac{a_{0,1}^{(2)} a_{0,2}^{(2)} n_1^{(2)} n_2^{(2)}}{2} \tilde{c}_{22}^{(2)} (\epsilon_2^{(2)})^2 \right) \quad (4.20)$$

Discarding the term Poisson's ratio leads to gross approximation in the total elastic energy but those graphs can still be used as a first approach to solve the problem.

To attribute each region to a phase, a simple reasoning is performed. Here is an illustration for the middle bottom square of the "Type 1" diagram (top left diagram, cf. caption of Figure 4.2):

We have $E_2 < E_{2,I} < E_{2,C}$ and therefore the heterostructure is always commensurate along direction 2. This means we have to use $E_{1,C}$ as a criterion to know if it is commensurate along direction 1. As the criterion is fulfilled, the final phase is *CC*.

This search for the different ground phases encountered three unexpected cases: two bistable cases (*II/CC* and *CI/IC*) and a dark zone where our criterion fails to find one phase but rather leave the possibility open to the four phases to take place. A more powerful than the one at hand is required to find the preferred ground phase.

The bistable phases arise from the double inequalities. Since we have two criteria for one elastic energy, two inequalities can be written for each direction. Following which one is considered first, one of the two phases is found. For undetermined phases, a loop in the criteria makes it impossible to find a self-consistent way to realize the criteria.

In the end, the NODEC method unveils seven possible scenarios with the four different phases already mentioned at the beginning of the chapter: *CC*, *CI*, *IC* and *II*. Then two bistable cases and a case where our method fails to determine a phase are also found by our method which lacks precision in those situation. Nonetheless, the NODEC method gives a simple and visual tool to appreciate in which direction commensuration seems favorable. It is therefore a good intermediate step between the simple model with one criterion and the more accurate model described hereunder. Going one step further, one could also imagine navigating throughout those phase diagrams by straining the layer in both directions.

4.3.2 The "16 cases" method

This section presents a more accurate method to solve the problem of finding the ground state of vdWHS using the Frenkel-Kontorova model by considering the elastic energies more precisely.

Here we approach the criteria differently. Rather than trying to visualize them, one can try to list all the possibilities to fulfill them. As there are four criteria with the possibility to

be realized or not, $2^4 = 16$ cases are to be considered. The 16 cases with the corresponding phases are given in Table 4.1. Then, in the same manner as for the previous method, one can try to observe which potential is felt in each direction when a certain criterion is met until it is self-consistent. For example, one can consider the sixth line of the table: (C1:●, C2:●, C3:○, C4:●). The first criteria indicated that the *CI* is favored to the *II* phase. C2 indicates that the structure is not against jumping to the *CC* phase. Along the other direction, one as therefore to check if the system is stable along the other direction by looking at C4. We see that a self-consistent state is found. The other phases are found using the same reasoning. For the other rows, one can use the Figure 4.5 to determine the phases. The explanation on how to use it is found in the caption.

This table is the only tool needed to compare the energies computed and determined the phase of a vdWHS. This method might give less insights on the potential encountered but is more correct physically speaking.

Criterion 1	Criterion 2	Criterion 3	Criterion 4	Phase
○ ○ ○	○ ○ ●	○ ○ ○	○ ● ○	II
● ○ ●	● ● ●	● ● ○	● ● ●	CC
● ● ●	○ ○ ○	○ ○ ●	○ ● ●	CI
○ ○ ●	○ ● ●	● ● ●	○ ○ ○	IC
○ ●	○ ●	● ○	● ○	undetermined
●	○	●	○	CI - IC
○	●	○	●	CC - II

Table 4.1 – Table with the 16 possibilities to fulfill the 4 criteria independently with the resulting equilibrium phases predicted. A '○' means the criterion is not fulfilled while a '●' means it is fulfilled.

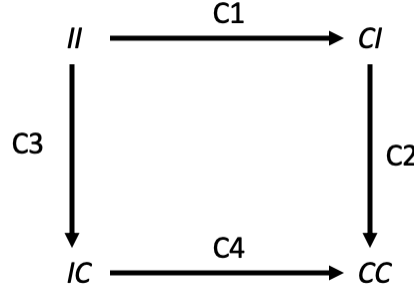


Figure 4.5 – Tool to determine the phases. One starts from the II phases and try to pass each arrow. If the criterion is met, it goes to the next phase. If one arrives at the CC at has to check whether the criterion on the other side is met. If not, it moves against the direction indicated by the arrow. Once blocked in a corner, the corresponding phase is added to the ground phases (more than one ground phase is possible).

4.4 Material data and methodology

The lattice constants and 2D elastic tensor components of the different materials investigated here are given in Table 4.2. In this thesis, unit cell with directions along the zigzag (ZZ) direction (direction 1) and along the armchair (AC) direction (direction 2) are considered. Some computations were performed with unit cells with two zigzag directions (for TMD heterostructures). In those cases, c_{12} was not given for these two directions and was assumed unchanged with respect to the ZZ-AC data given in Table 4.2. This approximation makes the results not completely reliable. They are nonetheless given as the value of coherency energies can be compared. It has also to be noted that the bulk values of black phosphorus and graphene were used for the computations (computation with the values of the monolayer are given for comparison). The use of the bulk values is a way to take into account the mean field energy. This energy is the amount of interlayer energy gain or lost by passing from an incommensurate configuration to a commensurate configuration. In other words, by straining the two layers to obtain a commensurate configuration, the stacking energy is different. This impacts especially heterostructures with phosphorene [1].

Material	a	b	$\tilde{c}_{11}$	$\tilde{c}_{22}$	$\tilde{c}_{12}$
Graphene (G)	2.466 (2.46)	4.272 (4.261)	291	291	63.8
hBN	2.508	4.344	354	354	64.4
Phosphorene (P)	3.297 (3.31)	4.594 (4.42)	103	23	17.3
MoS ₂	3.165	5.482	129	129	28.9
MoSe ₂	3.289	5.697	109	109	22.3
MoTe ₂	3.551	6.151	77.1	77.1	15.6
WS ₂	3.172	5.495	147	147	29.9
WSe ₂	3.283	5.686	123	123	20.3

Table 4.2 – Data used to compute the elastic energies. a [Å] is the unit cell length along the zigzag direction, b [Å] is the unit cell length along the armchair direction. $\tilde{c}_{11}$, $\tilde{c}_{22}$ and $\tilde{c}_{12}$ are the component of the elastic tensor for the directions zigzag (subscript 1) and armchair (subscript 2) [J/m²]. The value in parenthesis are those corresponding to the bulk values of black phosphorus and graphite which were used for computations. The data used are taken from [1] (DFT computation) except for MoTe₂ [24].

As for the methodology, the 2D potentials were graciously provided by Benoit Van Troeye. For each of them, an "identity file" was obtained with the four different potentials and the phases diagrams presented in the previous method. For the TMD, two 2D potential maps were derived: one along the ZZ-AC directions and one along both ZZ directions. In those cases, the potentials given by B. Van Troeye were for translations along both ZZ directions. The potential was therefore reproduced along those directions and the points were translated to enter an orthorhombic unit cell. The operation gives two sets of points one of which can be extracted to compute the 1D potentials. An example of an identity file is given in Figure 4.6. All the identity files can be found in Appendix C. The potentials are found by interpolating the points computed by B. Van Troeye with Fourier series. This approximated form of the potential is used to derive γ and E_{coher} in order to obtain the four criteria. Those criteria are then compared to the elastic values (found using the systems of Equation 4.9 and 4.10) as indicated in the Equations 4.15-4.18. The integration steps are performed using a composite integration:

$$\int_{-h}^h V(x)dx = \frac{2h}{180}(7V(x-h/2)+32V(x-h/4)+12V(x)+32V(x+h/4)+7V(x+h/2))+O(h^7) \quad (4.21)$$

where $2h$ is the length of one interval and $O(h^7)$ is order of the error for one interval. The way the different criteria are met is reported in Table 4.1 and the phase is found.

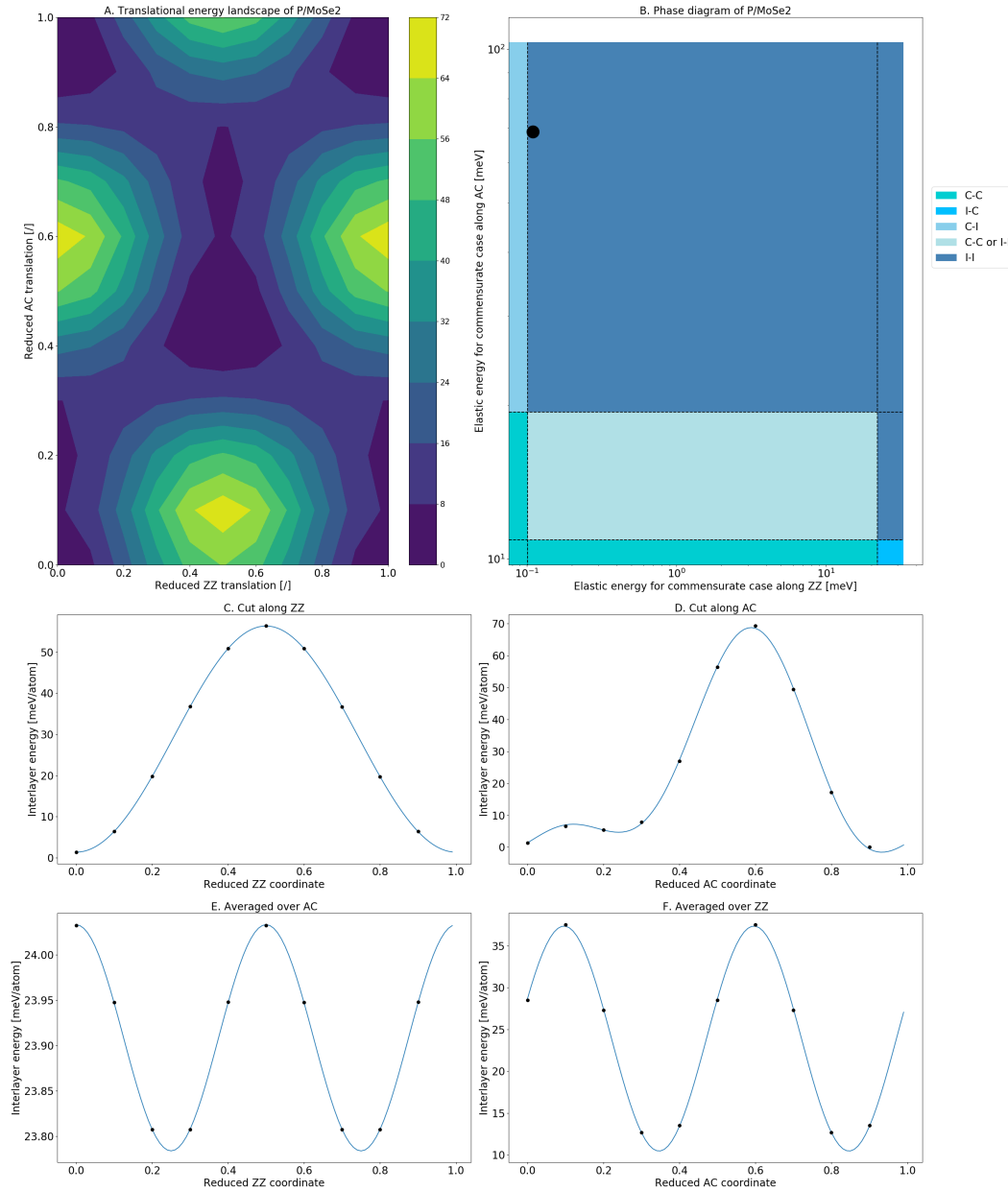


Figure 4.6 – Identity file of P-MoSe₂. A. 2D translation potential as obtained by B. Van Troeye via DFT computations. B. Phase diagram: a "Type 1" Phase diagram was found. The '●' symbol indicates the position {E₁, E₂}. C. and D. Cut of the potential along the zigzag direction and armchair direction starting from the origin (set as the minimum of the potential). The points indicate the data used to interpolate the curves. E. and F. Average of the potential along the armchair and zigzag direction seen along the zigzag direction and armchair direction respectively.

4.5 Presentation of the results

This section presents the results of the three methods: first, the results of B. Van Troeye *et al* are recalled then the results of the method with the phase diagrams and the "16 cases" method are shown. Each of these results will be shortly commented individually then compared. Finally, a global discussion will take place with comparison with the results from the literature and possibility of amelioration of the model will be emitted.

4.5.1 Results of each method

Results of B. Van Troeye *et al*

The Table 4.3 summarizes the results obtained by B. Van Troeye *et al*. It can be seen that most of the studied materials are predicted to be coherent with a few of them disagreeing with our findings. Most of the materials disagreeing with our findings have ratio $|E_{\text{coher}}|/E_{\text{elast}}$ relatively close to the value of γ_{FK} (note that this ratio is computed with respect to the 2D potential landscape and with DFT computations for the elastic energy). The case of hBN-P, relatively anisotropic, is also found to disagree with our results.

Heterostructure	$ E_{\text{coher}} /E_{\text{elast}}$	Phase
P-MoSe ₂	0.343	II
MoTe ₂ -WSe ₂	1.38	CC
MoSe ₂ -MoTe ₂	1.61	
G-P	2.81	
WS ₂ -WSe ₂	4.78	
MoS ₂ -WSe ₂	5.17	
MoS ₂ -MoSe ₂	5.25	
MoSe ₂ -WS ₂	5.58	
hBN-P	9.11	
MoS ₂ -WS ₂	216	
MoSe ₂ -WSe ₂	512	

Table 4.3 – Table with the results of Benoit Van Troeye using the "basic" F-K criterion. The heterostructures written in red are those which are not coherent with the results found by the two methods developed here. Those in blue are those which differ from the "16 cases" method only. In both case the comparison is performed with respect to the value for the ZZ-AC unit cells and with bulk values for the heterostructure containing phosphorene.

Results of the NODEC method

The Table 4.4 presents the results obtained by the method using phase diagrams. It can already be noted that several materials with ratio $|E_{\text{coher}}|/E_{\text{elast}}$ close to the γ_{FK} value yields different ground phase, even though the elastic energy is underestimated.

Heterostructure	Phase diagram type	Phase
P-MoSe ₂	1	II
MoTe ₂ -WSe ₂ MoSe ₂ -MoTe ₂	1	II
G-P	3	IC
WS ₂ -WSe ₂	1	CC
MoS ₂ -WSe ₂ MoS ₂ -MoSe ₂ MoSe ₂ -WS ₂	1	CC
hBN-P	1	IC
MoS ₂ -WS ₂ MoSe ₂ -WSe ₂	1	CC

Table 4.4 – Table with the results of the NODEC method. Direction 1 and direction 2 are ZZ and AC respectively. The heterostructures in blue are those for which the predicted phase differs from the "16 cases method".

One of the advantages of this method is its ability to directly categorize the potentials encountered. Here the three phase diagrams are found (the illustration of the potential landscapes can be found in the Appendix C; only the potential of MoSe₂-MoTe₂ is given for the unit cells along both zigzag directions). "Type 1" diagram is found in P-MoSe₂, hBN-P and all the TMD heterostructures when the potential is observed along the armchair and zigzag directions. Except for the hBN-P, the potential presents similar characteristics with high potential barriers on the sides and a relatively flat well in the center being close to the generic potential defined earlier if one makes a translation of 0.5 in one of the two directions. For hBN-P, the potential is more unidirectional with two potential waves parallel to the zigzag direction of translation. If those waves had varying size along the zigzag direction, it would have fall in the "Type 3" category as it is the case for G-P which presents the same symmetry with bigger contrast along the zigzag direction. This potential is therefore close to be a "Type 3" diagram. "Type 2" phase diagrams are found for three TMD heterostructures (MoS₂-WSe₂, MoS₂-MoSe₂ and MoSe₂-WS₂) when their potential is considered along the two zigzag directions. In those case, the height of the potential barrier encountered along the two characteristic directions is smaller than the highest point found in the middle of the potential.

It corresponds relatively well to the generic potential given for "Type 2" diagrams.

The *II* phases found in the case of $\text{MoSe}_2\text{-MoTe}_2$ and $\text{MoTe}_2\text{-WSe}_2$ are essentially the reflect of high elastic energy required to obtain any of the commensurate or semi-commensurate phases. Indeed, their coherency energy is relatively similar to those of the other TMD heterostructure except those of $\text{MoS}_2\text{-WS}_2$ and $\text{MoSe}_2\text{-WSe}_2$ (which also shows the lowest amount of elastic energy in this type of heterostructures). The discrepancy between our results and the results of B. Van Troeye *et al* are essentially the reflect of smaller coherent energy for the heterostructures $\text{MoTe}_2\text{-WSe}_2$, $\text{MoSe}_2\text{-MoTe}_2$ and G-P. The G-P heterostructures also appear to require different elongation to obtain commensuration in both directions which is not probed by B. Van Troeye *et al*. A similar comment can be made for hBN-P.

Results of the "16 cases" method

The Table 4.5 gives the results for the "16 cases" method. It can be observed that the results obtained with the phase diagrams are refined. Indeed, nearly every heterostructure showing discrepancy with the results of B. Van Troeye *et al* also present different phases here. The case of P-MoSe₂ is also different, with a new state found: *CI*. This seems plausible as the elastic energy required to obtain this state is really small and it was not considered in that form before. hBN-P and G-P also present a new outcome: undetermined. This is linked to the relatively unidirectional behavior of their potential and small amount of elastic energy needed to meet any of the four simple phases. This phases clearly highlight the anisotropy of the potential and the fact that different elastic energies are involved in the two directions. This method takes better account of those different energies, and the phases predicted here should better represent the interactions between the two directions as the Poisson' ratio is considered.

Heterostructure	Criterion 1	Criterion 2	Criterion 3	Criterion 4	Phase
P-MoSe ₂	●	○	○	●	CI
MoTe ₂ -WSe ₂ MoSe ₂ -MoTe ₂	○	○	○	○	II
G-P	○	○	●	●	undetermined
WS ₂ -WSe ₂ MoS ₂ -WSe ₂ MoS ₂ -MoSe ₂ MoSe ₂ -WS ₂	○	●	●	●	CC
hBN-P	○	○	●	●	undetermined
MoS ₂ -WS ₂ MoSe ₂ -WSe ₂	●	●	●	●	CC

Table 4.5 – Table with the results of the "16 cases" method. A '○' means the criterion is not fulfilled while a '●' means it is fulfilled. .

4.5.2 Review of the different phases obtained for the different methods

The Table 4.6 presents a comparison between the different values. It can be observed that the bottom of the table is in good agreement for the three methods whereas the top part of the table shows more spread. In this top part, the two methods presented here arrive somewhat to the same conclusions: the ground phases of those heterostructures is more complex than a simple *II* phase. This table highlights the evolution of the phases found with the intermediate step bridging the discrepancy between the results of B. Van Troeye *et al* and the results of the "16 cases" method.

Heterostructure	"16 cases" Method	NODEC method	B. Van Troeye <i>et al</i>
P-MoSe ₂	CI	II	II
MoSe ₂ -MoTe ₂	II	II	CC
MoTe ₂ -WSe ₂			
G-P	undetermined	IC	CC
WS ₂ -WSe ₂	CC	CC	CC
MoS ₂ -WSe ₂			
MoS ₂ -MoSe ₂			
MoSe ₂ -WS ₂			
hBN-P	undetermined	IC	CC
MoS ₂ -WS ₂	CC	CC	CC
MoSe ₂ -WSe ₂			

Table 4.6 – Comparaison of the phases obtained with the three methods described.

4.6 Discussion

Close phases

In several cases, the difference between the criterion and the elastic energy is quite small (the detail of the values can be found in Appendix D). The numerical errors of the problem and the rounding of the starting values could therefore, in those cases, lead to a different ground state. Before discussing the results it is therefore important to clarify those points. The following discussion is only valid for the "16 cases" method.

For hBN-P, C1 is really small and the elastic energy falls in a range of ± 1 meV of E_{C1} in the case of bulk values and in the case of monolayer values. If the criterion changes to true, the corresponding phase would be *CI*.

For bulk values only, the elastic energy also falls in the range ± 1 meV of E_{C2} . If this

criterion becomes true, the corresponding phase would be *CC* (same as if the two first criteria become true).

For monolayer values only, the elastic energy falls in the range ± 1 meV of E_{C3} . If the criterion becomes false, the corresponding phase would be *II*. If the first and third criteria change, the corresponding phase would be *CI*.

For MoS₂-WS₂, the elastic energy falls in a range of ± 1 meV of E_{C1} (in the case of the ZZ-AC unit cell). The change of this criterion does not affect the ground state.

For P-G, the elastic energy falls in a range of ± 1 meV of E_{C1} in the cases of bulk and monolayer values. If this criterion becomes true, the phase is *CI* in both cases.

In the case of monolayer value only, the elastic energy falls in a range of ± 1 meV of E_{C3} . If this criterion becomes true, the phase is undetermined. If the first and third criteria change, the phase is *CI*.

For P-MoSe₂, the elastic energy falls in a range of ± 1 meV of E_{C1} for the cases of bulk and monolayer values. It also falls in the range of $\pm 10\%$ of the criterion in the case of bulk value. If this criterion become falls, the phase is *II*.

Finally, for MoTe₂-WSe₂, the elastic energy falls in the range ± 1 meV of E_{C2} and fourth criterion in the case of the conventional unit cell. For both criteria, the elastic energy falls in the range $\pm 10\%$ of the criterion. If the second criterion becomes false, the phase is *CI*. If the E_{C4} becomes false, the phase is *IC*. If both criteria become false, the phase is *CI-IC*.

Discussion of the results

As it was shown before that the NODEC method is less accurate and essentially consists in an intermediate step between the work of B. Van Troeye *et al* and the "16 cases" method, only the results of the latter will be debated here.

To start the discussion, the approximations and limits of this study will be recalled before comparing when possible the predicted phases with what is found in the literature.

The results presented in the Table 4.6 correspond to various translational landscapes which have not yet been presented. Those potentials were computed for different orderings and unit cells. In the case of TMD heterostructures, it was shown in the previous chapter that they stack preferentially with a twist angle of 60° . The potential in those cases is therefore computed for this starting configuration. Then, for hBN-P and P-G, the unit cells were repeated 3 and 4 times along the armchair direction for P and G/hBN respectively. Indeed, creating a superlattice in the armchair direction reduces the amount of strain required to obtain a commensurate interface (note here that this commensurate interface is of higher order than what has been debated until here). Now for P-MoSe₂, the armchair and zigzag direction of the two heterostructures were aligned to perform the computations. Hence, this thesis does not take into account twisting angle or pre-strained layers.

Then, the linear elastic model makes a good first approximation of the elastic energy required to obtain the various phases. However, big strains were encountered in the case of

P-MoSe₂ for example where this limit becomes questionable. With a maximal strain of $\approx 20\%$ along the armchair direction (the phosphorene is softer than MoSe₂ along the armchair direction and takes most of the strain), this approximation could be too strong and the addition of higher order component of the elastic energy could enhance the results. The Table D.2 shows how the computation of the elastic energy performed here, compared with DFT computations. In most of the cases, the values found falls within a few meV of more accurate results. It is therefore safe to say that even if our computations lack of accuracy, it should not impact too greatly the results of our method.

Finally, numerical inaccuracy can arise from the interpolation of the potential and be amplified by the following numerical integration. The small number of points used to create the translational potential landscape can also hide some of the details of the later but it is expected that this should not have a big impact on the results. Indeed, the main feature of interest arising from this potential are the value of γ and E_{coher} . The first is slightly dependent on small variations of the potential while the second gives essentially a measure of the height of the potential and its macroscopic shape (large well, thin barrier, ...) which is well reproduced with our interpolation.

We now look more closely to the Table 4.6. The six last TMD heterostructure with CC phases predicted seem easy to analyze. In those cases, the amount of elastic energy is relatively small with respect to the gain in coherency energies. The two last rows were already correctly predicted by B. Van Troeye *et al* ([107,108] cited by [1]). For the other, TMD heterostructures, the literature suggests a rather incoherent phase, at least for bilayer heterostructure. This is found by extensive DFT computation over more than 800 unit cells for MoS₂-MoSe₂ heterostructures [106]. Moiré pattern were also observed for MoS₂-WSe₂ [74]. One year after the writing of the article of B. Van Troeye *et al*, no other experimental studies of TMD heterostructures characterizing their commensuration were found.

Here, the "16 cases" methods gives three TMD heterostructures with CC phase and two with II phase. The main differences between the two subgroups arises from the elastic energies. Indeed, the coherency energy stay in the same range for the five of them (see Annex D). We know from the literature and from the potential shape that every TMD heterostructure between the second and eight row is likely to be incommensurate, which disagrees with our findings. B. Van Troeye *et al* explained this by the presence of flat wells in translation potential. Here, by using our 1D model, different cut can be performed to obtain the dislocation path with the least resistance to the formation of a dislocation. Finding this path has been proven to be important for probing the transition between commensurate and incommensurate phases [90] [15]. Here by changing the cut line to find a potential landscape with less relief, as indicated in Figure 4.7, the coherence energy drops from about 17 meV to less than a meV facilitating the introduction of dislocation. Similar results are obtained for all the other TMDs heterostructure. It changes the ground phase to undetermined (II in the case of the conventional unit cell) for all of them except for MoS₂-WS₂ and MoSe₂-WSe₂ as their elastic energy is still small enough to favor a coherent interface. This way of proceeding is in better agreement with the literature. Yet, the starting point of this dislocation is not situated in the minimum of the potential which should be a requirement. The possibility of a dislocation path that is a bit more complex than a straight line (two straight lines could be used, for ex-

ample, as illustrated in Figure 4.7). Still, it has to be noted that the values found here are for heterostructures repeated periodically in the out-of-plane direction while the literature gives the results for bilayer heterostructures. This impacts the interlayer energy potential, reducing the stacking energy and by extension the amount of coherency energy.

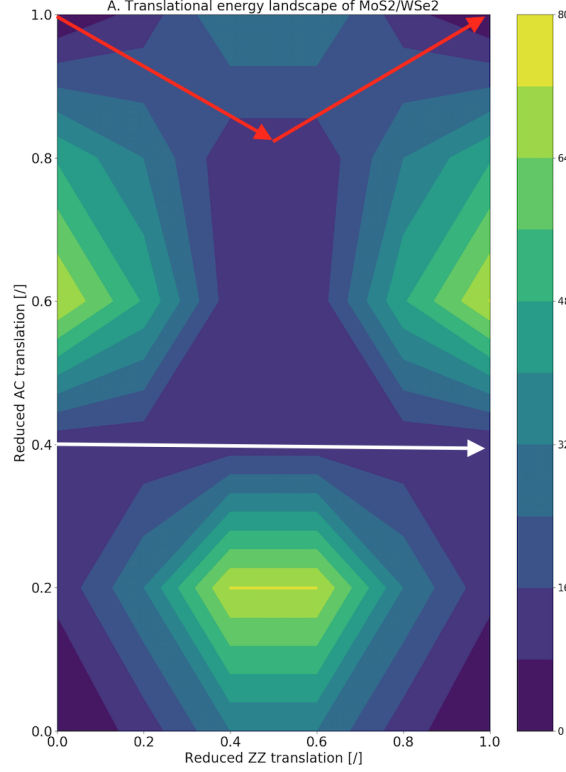


Figure 4.7 – Illustration of the dislocation path used to compare the coherent energy (white arrows) and a more plausible dislocation path in actual structures.

Three structures containing phosphorene were also analyzed with findings similar to those of B. Van Troeye *et al.* In this case, changing the cut line does not modify the results as it is clear that those lines already correspond to the least resistance path. It is found that hBN-P, and G-P heterostructures are undetermined. This goes along with a lot of close phases described here above. For G-P heterostructures, B. Van Troeye *et al.* obtained a close to semi-coherent configuration which does not disagree with us neither with the literature ([109] cited by [1]). The literature does not give any characterization of the ground phase of two other heterostructures. Yet, a new phase of coherency is found for P-MoSe₂: CI. Such phases were not described before. The Figure 4.8 illustrates how commensuration in one direction could take place. One can observe that a common direction is shared while an interference pattern is still observable in the other direction. It is expected that small adjustments of the lattice parameter in the incommensurate direction occur. Indeed, the criterion C1 is true but it is based on an average potential. This is equivalent to state that in most of the translation path, the coherency energy is sufficient to favor a commensurate structure. Yet, some of the

configurations found along the incommensurate direction correspond to high stacking energy which has to be avoided. Since one of the direction is locked, some additional strain could be found in the incommensurate direction to find a local configuration more favorable energetically speaking.

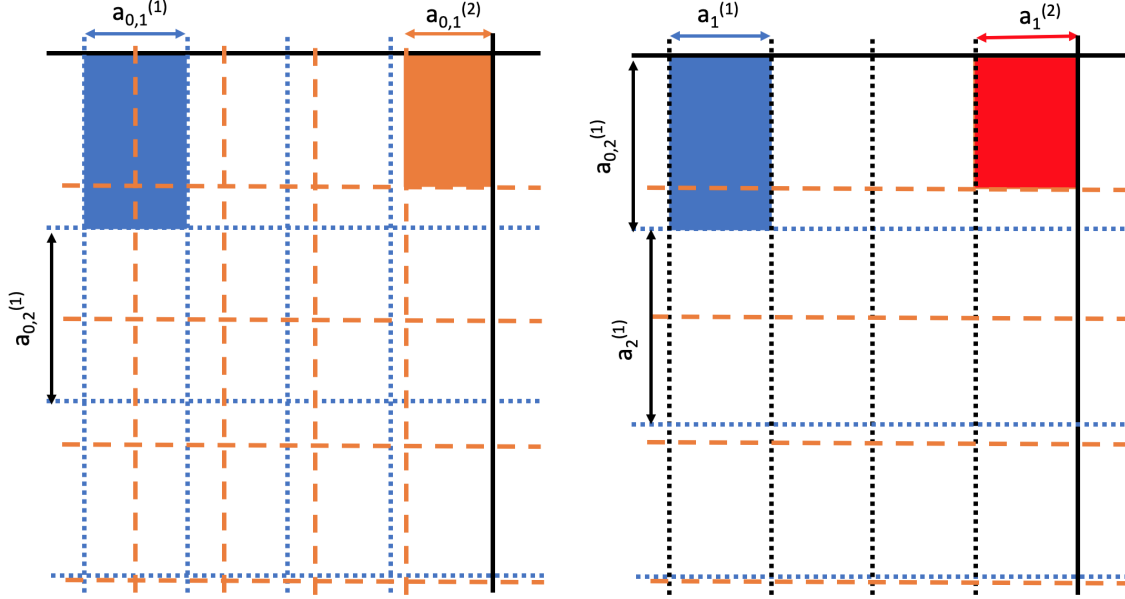


Figure 4.8 – Left: initial stacking configuration with the the two lattices of the two subsystem in blue and orange. Right: Case where a CI configuration is favored. The black line indicates common direction of the two subsystems. Some shifts are expected in the length of the unit cell in the incommensurate direction as indicated by the change of length of the blue lattice.

One of the main outcomes of this thesis with respect to the previous model used by B. Van Troeye *et al* is that using the coherency energy associated with the 2D potential landscapes tends to overestimate the coherency energy (see Table D.1). Using a one-dimensional model is a lot more accurate in that aim. This is well illustrated for the two TMDs, MoTe₂-WSe₂ and MoSe₂-MoTe₂ that are more likely to be described accurately with our model. The discussion about the dislocation path can also rejoin this point.

A column of the Table 4.8 is dedicated to the results found with the phase diagrams. They follow a similar trend as the results found in the "16 cases" method. In cases relatively symmetric (TMD heterostructures), this method yields the same results as the "16 cases" method. It could therefore be used in those cases. Slightly asymmetric cases are also in good agreement. Yet, the case of P-MoSe₂ illustrates the limit of using only the commensurate elastic energy. Indeed, the sole effect of the Poisson's ratio gives elongations much bigger along the zigzag direction than it would be observed in the CI phase. This method should therefore be used carefully or to evaluate the impact of strain from a defined starting configuration (this could be especially useful for bilayer materials).

One of the questions asked at the beginning of this thesis was to know if the adaptation of the γ value was pertinent. In the cases study, the γ spans from ~ 1.209 to ~ 1.392 . The γ_{FK} value is therefore a good first approximation. Yet, a finer description of the physic is obtained with an adapted γ value. In our numerical approach, its integration is quite natural as the criteria are evaluated using Equations [4.15](#)[4.18](#) where its form is hidden in the final function.

Finally, the "16 cases" model presented here is expected to show better performances than the model presented by B. Van Troeye *et al.* Several ameliorations could still improve its performances. First, the elastic energy could be computed more accurately by taking into account higher order terms (even though entering the range were those terms have a significant impact often implies an high elastic energy which is a sign that the coherence along the corresponding direction is not likely). Then, more point could be used to interpolate the potentials, allowing a higher precision of the γ value. Considering more complex dislocation paths could help get a better understanding of the physics involved. All those elements could help create a really simple and accurate model. Finally, our model also unveils the possibility of new phases which are not distinguished in the previous model such as the *CI* phases found for the P-MoSe₂ heterostructure. Improving the aforementioned points could help unveil more of those phases as explained in the part on close phases.

Conclusion

All along this thesis, some of the marvelous features of the 2D world were unveiled. Yet, we only scratched the surface of all the possibility brought by the advent of van der Waals heterostructure (vdWHS). This field is expected to grow even more in the following years.

By describing part of the 2D materials library, it was demonstrated that no electrical family are missing. The explanations on how those materials were synthesized were provided. It showed that this field requires some improvements to be able to bring the 2D world to the industrial scale. Then a first introduction to vdWHS was done by the mean of design of devices for electronic applications.

We took a closer look to the impact of stacking. Creating vdWHS or bilayer materials could lead to variation of the band gap. This feature, if well understood and applied, could lead to different ways to design conventional electronic devices by finely and easily tuning the band gap. The variation of the later was shown to take different values following the configuration of stacking. In twisted bilayer or in bilayer with lattice mismatch, it pairs with the possibility to have a band gap varying spatially. Then, since the heterostructure is build piece by piece, strain could be induced in each layer at will, to also modify this band gap. All those degrees of freedom are not found in thin films or conventional 3D materials or at least not with the same flexibility. Stacking 2D materials can also lead to the formation of commensurate and incommensurate domains. The transition between the two was analyzed and the impact of domain boundaries was illustrated.

In the Frenkel-Kontorova (FK) model, a good agreement between numerical computations and analytical model was found. Our implementation used different algorithm. If the Newton-Raphson method was the fastest, the differential evolution was the more accurate, avoiding most of the local minima. In the end, the algorithm can still be improved but still gives correct results in a reasonable amount of time. The ability to play with the FK model remains to be further investigated. Here, the criterion developed by F. Frank and J. Van der Merwe is found for a specific range of k values. This range is expected to grow towards higher values of k by considering bigger n_{at} , recovering the criterion of the continuous case for most of the k values. The fact that the range grows towards higher values of k and not towards lower values is explained by the inability of the analytical model to consider anything different than one atom per period. In our case, this is not a problem, as in the continuous limit, the range of value of k corresponds to small elongation, which is the domain of interest.

Applying the FK model to actual heterostructures, a new method, called the "16 cases"

method was developed to probe the ground phases of various vdWHS. Our model allows to distinguish between four ground phases: *CC*, *CI*, *IC* and *II*, *CI-IC*, *CC-II*. but also, three cases in which the ground state phase is not univocally determined using the present tools, based on four simple criteria. These three cases are: (1) the bistable *CI-IC* case, in which the *CI* phase and the *IC* phase are favored over the *CC* and *II* phases, but the criteria do not allow to distinguish between the latter; (2) the bistable *II-CC* case, in which the *CC* or the *II* are favored with respect to the *IC* and *IC* phases, but the latter cannot be discriminated; (3) the completely undetermined case. The three undetermined cases would need more powerful tools than the present ones to be handled. To do so, it uses four simple criteria that can be extracted from linear elasticity model and 2D potential landscape computed by DFT computations. This model also integrates an accurate way to compute the γ value from the FK model to allow a fine tuning of the transition region.

The prediction of coherent phases for $\text{MoS}_2\text{-WS}_2$, $\text{MoS}_2\text{-WSe}_2$, $\text{MoSe}_2\text{-WS}_2$, $\text{MoSe}_2\text{-WSe}_2$, $\text{WS}_2\text{-WSe}_2$ and $\text{MoS}_2\text{-MoSe}_2$ was made and found in agreement with B. van Troeye's results. Such prediction was compared with available experimental data. A good agreement between the literature and our results was found for $\text{MoS}_2\text{-WS}_2$ and $\text{MoSe}_2\text{-WS}_2$. On the other hand, the literature found incommensurate phases for $\text{MoS}_2\text{-WSe}_2$ and $\text{MoS}_2\text{-MoSe}_2$. A possible explanation could be found in the way to design our dislocation paths, which encounter relatively high barriers of potential. It is expected that a finer description of this feature, a more realistic one, could improve our results for $\text{MoS}_2\text{-WSe}_2$ and $\text{MoS}_2\text{-MoSe}_2$ as well as for $\text{MoSe}_2\text{-WS}_2$ and $\text{WS}_2\text{-WSe}_2$.

The two last TMD heterostructures analyzed ($\text{MoTe}_2\text{-WSe}_2$ and $\text{MoSe}_2\text{-MoTe}_2$) are predicted to adopt an incommensurate phase. This is essentially due to a higher elastic energy needed to obtain a commensurate phase (along one of the direction or the two directions).

Three components with phosphorene were also considered. For G-P and hBN-P, undetermined cases are found. It is believed that local arrangement has a bigger impact than in the other structures. Their translational landscape is relatively unidirectional in those cases leaving one of the directions relatively free to introduce dislocation or not while the other direction should react to this adaptation. The last compound analyzed is P-MoSe₂ which should, following our computations, presents a *CI* phase. Indeed, the barrier of potential is quite high along the zigzag direction compared to the elastic energy required to be commensurate along that direction and it should not be a surprise to find this ground phase in actual sample.

Compared to the previous model derived by B. Van Troeye *et al*, ours is expected to differentiate more phases and more finely.

Our model can therefore still add some features to be more accurate but already makes a step towards a simple tool using the 1D FK model for predicting ground phases.

Appendix A

Computations of Lebedeva *et al*

I. V. Lebedeva *et al* derived the formation energy of a dislocation under uniaxial strain [21] by using a two-dimensional Frenkel-Kontorova (FK) model. They modeled a layer of graphene as an array of particle linked by springs and undergoing the influence of a potential (here the interlayer potential). The case under study is presented in Figure A.1. The dislocations under study are called partial as their Burgers vector $\mathbf{b}$ does not correspond to a lattice vector, a_0 . Instead, it has the length of the bond length, l and one of the direction mentioned in the Figure 2.7 (i.e. $\mathbf{b}$ is one of the $\Delta\mathbf{u}$ forming a path between AB and BA). In the following, the two layers are considered equidistant at every point. Here, the bottom layer is stretched while the top one is free to relax. As we are interested in the formation of the first domain wall, it is assumed that the commensurate domains are bigger than the width of the dislocations and that there is no boundary crossing. Edges effect are also neglected. Also, the relative displacement of atom in the dislocation is only a function of the x coordinate, the boundary being along the direction y as indicated in Figure A.1.

In this problem, several angles have to be distinguished (see Figure A.1), ϕ is the angle between the normal, $\mathbf{n}$, and the direction of stretching, α is the angle between the burger vector, $\mathbf{b}$, and the direction of stretching. β is the angle between $\mathbf{n}$ and $\mathbf{b}$. The following development will try to provide the preferred angle β_c ($\phi_c = \alpha - \beta_c$) and the critical elongation, ϵ_c for a given value of α . In other words, a direction of elongation is chosen, α takes all the value from 0° to 90° . For each of these configuration, the orientation of the domain wall is optimized. Then, the critical elongation for this configuration is found. To better illustrate how the dislocation takes place, two distinct types of dislocations are shown in Figure A.2 : the tensile dislocation where $\alpha = 0^\circ$ and the shear dislocation where $\alpha = 120^\circ$.

The variation of energy per unit length associated with the introduction of a dislocation, ΔW [J/m] is given by [21]:

$$\Delta W = \Delta W_0 + \Delta W_e \quad (\text{A.1})$$

with ΔW_0 the energy in the absence of external strain and ΔW_e the energy change provided by the external load :

$$\Delta W_0 = \int_{-\infty}^{+\infty} \left(\frac{1}{4} K(\mathbf{u}') l^2 |\mathbf{u}'|^2 + V(\mathbf{u}) \right) dx + \int_{-\infty}^{+\infty} K(\mathbf{a}') l^2 |\mathbf{a}'|^2 dx \quad (\text{A.2})$$

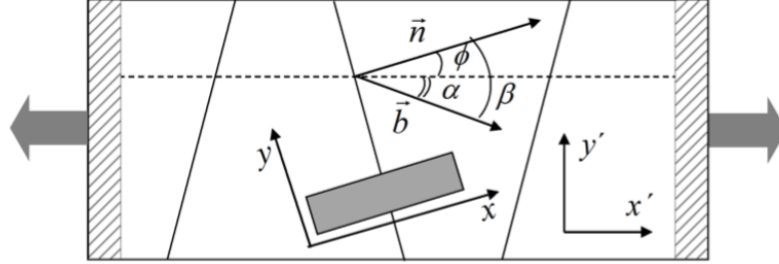


Figure A.1 – Scheme of bilayer graphene under uniaxial strain in the bottom layer (shaded area). $\mathbf{n}$ is the normal to the boundary between two commensurate domains, $\mathbf{b}$ is the Burgers vector, ϕ is the angle between $\mathbf{n}$ and the direction of elongation, α is the angle between $\mathbf{b}$ and the direction of elongation and $\beta = \alpha + \phi$ is the angle between $\mathbf{n}$ and $\mathbf{b}$. x - y is the coordinate system associated to the dislocation while x' - y' is the one associated with the elongation [21].

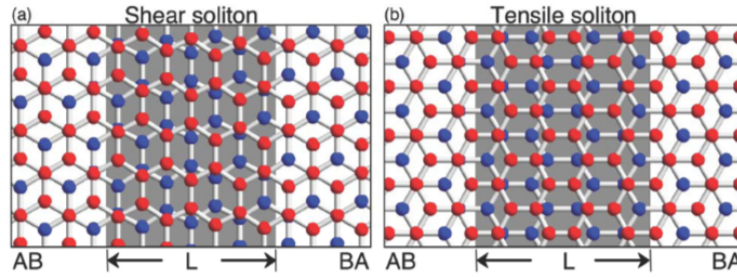


Figure A.2 – Crystal representation of the two specific kinds of dislocation found in bilayer graphene. (a) is a shear dislocation and (b) is a tensile dislocation. Blue and red atoms distinguish the atoms of each layer [22].

$$\Delta W_e = El(\epsilon_{xx} + \nu\epsilon_{yy})\Delta u_x + Gl\epsilon_{xy}\Delta u_y \quad (\text{A.3})$$

where the order parameters $\mathbf{u} = \frac{\mathbf{v}_1 - \mathbf{v}_2}{l}$ and $\mathbf{a} = \frac{\mathbf{v}_1 + \mathbf{v}_2}{2l}$, with $\mathbf{v}_i$ the relative displacement of atoms of layer i with respect to the commensurate configuration are introduced. We also have $\mathbf{u}' = \frac{d\mathbf{u}}{dx}$ and $\Delta \mathbf{u} = \mathbf{u}(+\infty) - \mathbf{u}(-\infty) = -\frac{\mathbf{b}}{l}$. $K(\mathbf{u}') = E \cos^2 \theta(\mathbf{u}') + G \sin^2 \theta(\mathbf{u}')$ describes the dependance of the elastic constant in function of the configuration of the elongation with $\theta(\mathbf{u}') = \sin^{-1} \frac{u'_y}{|\mathbf{u}'|}$, $E = \frac{k}{(1-\nu^2)}$, $G = \frac{k}{2(1+\nu)}$ with k the elastic constant and ν the Poisson's ratio, ϵ_{xx} (ϵ_{yy}) is the elongation in the x (y) direction and ϵ_{xy} is the shear strain. $V(\mathbf{u})$ is the interlayer potential for a displacement, $\mathbf{u}$ between the layer.

In the case of small dislocation density, the formation energy can be rewritten as the geometrical mean of the elastic energy and interaction energy :

$$\Delta W_0 = \int_{-\infty}^{+\infty} \sqrt{K(\mathbf{u}')l^2|\mathbf{u}'|^2V(\mathbf{u})}dx \quad (\text{A.4})$$

The formation energy can be expressed in function of β as (in the limit of zero external strain) :

$$\Delta W_0(\beta) = W_0 \sqrt{\frac{K(\beta)}{k}} \quad (\text{A.5})$$

with $W_0 = \sqrt{kl^2} \int_0^1 \sqrt{V(u)}du$. This formation energy varies between two extreme cases represented in Figure 2.10 : shear and tensile dislocation with energy of formation varying from $\Delta W_0(90^\circ) = \frac{W_0}{\sqrt{2(1+\nu)}}$ (shear dislocation) and $\Delta W_0(0^\circ) = \frac{W_0}{\sqrt{1-\nu^2}}$ (tensile dislocation).

The width of such dislocation, l_D is given by :

$$l_D = \frac{l}{2} \sqrt{\frac{K(\beta)}{V_{\max}}} \quad (\text{A.6})$$

where $V_{\max}$ is the maximum of the potential in the path from AB to BA stacking. The dislocation width ranges from 11 nm to 6-7 nm for tensile and shear dislocations respectively. Finally, the optimal angle of dislocation, β_c and the associated critical strain, ϵ_c can be derived by minimizing the energy formation given by Equations (A.1)-(A.3) which yields that :

$$\tan(\alpha - \beta_c) = -\frac{k \sin 2\beta_c}{4(1-\nu)K(\beta_c)} \quad (\text{A.7})$$

and

$$\epsilon_c(\alpha) = \frac{\Delta W_0(\beta_c)}{kb \cos \alpha \cos(\alpha - \beta_c)} \quad (\text{A.8})$$

It has to be noted that the direction of formation of the boundaries in real sample will depend on the length of the dislocation so only part of the scheme is presented here. Yet, ϵ_c and β_c are always given by the above equations (Equations A.7-A.8).

Formation of a triangular network of domain walls

We can now probe the transition between commensurate graphene and commensurate-incommensurate graphene with a triangular network of domain walls such as the one presented in Figure 2.8. To study the formation of such network, the bottom layer is exposed to biaxial strain, ϵ , while the top layer is free to relax [80]. The dislocations considered here are tensile dislocations. Therefore, $\beta_c = 0$. In that case, the formation energy of the network ΔW_T [J/m²] is :

$$\Delta W_T = -\Delta W_{el} + \Delta W_{dw} + \Delta W_{dn} \quad (\text{A.9})$$

where ΔW_{el} is the elastic energy linked to the biaxial elongation ϵ_0 , ΔW_{dw} is the formation energy of the domain walls and ΔW_{dn} is the energy formation associated to the nodes. The surface of a domain is given denoted $S_T = \frac{\sqrt{3}L_T}{4}$ with L_T the length of a dislocation. The formation of a triangular network is associated with the elongation $\epsilon_0 = \frac{\sqrt{3}l}{2L_T}$ in each of the layer since the center of each domain is separated by a distance of $\frac{L_T}{\sqrt{3}}$. The formation energy therefore compare the relative elongation ϵ to the commensurate system with relative biaxial elongation $\epsilon - \epsilon_0$.

The different terms of formation energy are given by :

$$\Delta W_{el} = \frac{2k}{(1-\nu)} (\epsilon^2 - (\epsilon - \epsilon_0)^2) = \frac{2\sqrt{3}k\epsilon}{(1-\nu)} \frac{l}{L_T} - \frac{3k}{2(1-\nu)} \left(\frac{l}{L_T} \right)^2 \quad (\text{A.10})$$

$$\Delta W_{dw} = \frac{3}{2} \frac{L_T}{S_T} \Delta W = \frac{2l}{L_T} \sqrt{\frac{3kV_{\max}}{(1-\nu^2)}} \left(\frac{3\sqrt{3}}{\pi} - 1 \right) \quad (\text{A.11})$$

$$\Delta W_{dn} = 3 \left(\frac{l_D}{L_T} \right)^2 \left(V_{in} + \frac{k}{2(1-\nu)} \left(\frac{l}{l_D} \right)^2 \right) = \left(\frac{l}{L_T} \right)^2 \frac{3(5+2\nu)k}{4(1-\nu^2)} \quad (\text{A.12})$$

with $V_{in} = 3V_{\max}$ the average potential in the node (the center of the node correspond to a AA stacking [20]). This allows to write the energy of the bilayer with the network compared to the one of the commensurate state as :

$$\Delta W_T = A \frac{l}{L_T} + B \frac{l^2}{L_T^2} \quad (\text{A.13})$$

where

$$A = -2\sqrt{3} \left(\frac{k\epsilon}{(1-\nu)} - \sqrt{\frac{kV_{\max}}{(1-\nu^2)}} \left(\frac{3\sqrt{3}}{\pi} - 1 \right) \right) \quad (\text{A.14})$$

and

$$B = \frac{3(7+4\nu)k}{4(1-\nu^2)} \quad (\text{A.15})$$

Then the triangular network becomes the ground state when A becomes negative. The equilibrium length of the domain walls is given by :

$$L_0 = -\frac{2B}{A} l \quad (\text{A.16})$$

which correspond to the formation energy $\Delta W_0 = \frac{-A^2}{4B}$. The critical elongation associated ϵ_{c1} is given by :

$$\epsilon_{c1} = \sqrt{\frac{V_{\max}(1-\nu)}{k(1+\nu)}} \left(\frac{3\sqrt{3}}{\pi} - 1 \right) = (1-\nu) \frac{\Delta W}{kl} \quad (\text{A.17})$$

Further stretching

The stripped network observed in the left hand part of Figure 2.8 can also be analyzed [23]. It is interesting to have an idea of the energy associated to this network in order to predict which network will be the ground state of our bilayer. In the stripped network, it is assumed that the Burgers vector alternate from one boundary to the other by an angle of $\pi/3$ (i.e. β takes the value $\pm\pi/6$ for two consecutive walls). Reproducing the above reasoning one can find a second critical elongation, ϵ_{c2} [23]:

$$\epsilon_{c2} = \epsilon_{c1} \frac{\sqrt{\frac{(7+4\nu)(7-\nu)}{6}} - 2}{\sqrt{7+4\nu} - 2} \quad (\text{A.18})$$

The transition between the two network is of the first order and the two networks can coexist on the same sample. The transition from the triangular network to the stripped one will occur by gradually aligning two boundaries in different zigzag direction associated to the same armchair one while the third wall of the domain will disappear. Finally, it is argued that for big strain a Moiré pattern will appear. Such pattern possess the same symmetry as the triangular network. Hence by conducting the same reasoning as before but by considering average of the potential rather than its actual shape and adapting the size of the domains, one obtain a reentrant phase transition for a third critical elongation; ϵ_{c3} :

$$\epsilon_{c3} = \frac{3}{2} \sqrt{\frac{\sqrt{3}(7-\nu)V_{\max}}{2\pi k}} \quad (\text{A.19})$$

The resulting phase diagram is presented in Figure 2.13. The diagram also presents the variation of the superstructure size which has not been presented here. This model gives a relatively complete insight on the different energetic components at play. It show the great importance of the Poisson coefficient (and obviously the elasticity constant) and of $V_{\max}$ in the formation of the networks. However, this description of the different phases in BLG is based on observation. This tool seems a bit complex to be used for prediction computations.

Appendix B

Implementation of the different algorithms

B.1 The Molecular Dynamic implementation

```
import math
from scipy import misc
import matplotlib
import matplotlib.pyplot as plt
import numpy as np

def MolDyn(pos, parameters, V, opt):

    #####Parameters#####

    m=parameters[0] # mass
    g=parameters[1] # viscous damping constant
    k=parameters[2] # Stiffness Cst
    L=parameters[3] # Period length
    dt=parameters[4] # Time step
    a0=parameters[5] # Equilibrium distance
    cvcr=10**(-20) # Convergence criterion
    #####List for calculations & plot#####
    l=len(pos) # Number of particles

    prevpos=pos # Previous position
    F=[0]*l # Force on each particle
    vel=[0]*l # Velocity of each particle
    Vprim=[0]*l # Derivative of the potential
    acc=[0]*l # Acceleration of each particle
```

```

#Energy total
E0=0 #Conserved energy
E=0 #Computed energy
E1=[] #Energy with respect to time

#Energy cin
Ecin=0 #Ecin of each particle

#Energy pot
Epot=0 #Epot of each particle

#Strating energy
##Associacted to the first ball (being pulled by the last one
## of the previous period)
Epot=k/2*(pos[0]+(L-pos[l-1])-a0)**2+V(pos[0])
E0+=Epot

##Associated to the following ones
for o in range(1,l):
    Ecin=1/2*m*((pos[o]-prevpos[o])/(2*dt))**2
    Epot=k/2*(pos[o]-pos[o-1]-a0)**2+V(pos[o])
    E0+=Ecin+Epot

Delta=cvcr*2    #To enter the 'while'

y=0
while Delta>cvcr:
    #Counter
    y+=1

    #Derivative of the potential 0(h**4)
    for h in range(1):
        Vprim[h]=(+V(pos[h]-0.00001)\
        -8*V(pos[h]-0.000005)-V(pos[h]+0.00001)\
        +8*V(pos[h]+0.000005))/(12*0.000005)

    #Force on the particle=Attraction/repulsion
    # by the two neighbors and slope of the potential
    ## Boundary conditions for the periodic case
    if opt=='P':
        F[0]=-k*(2*pos[0]-pos[1]+(L-pos[l-1]))-Vprim[0]
        F[l-1]=-k*(2*pos[l-1]-(L+pos[0])-pos[l-2])-Vprim[l-1]

```

```

else :
    F[0]=0
    F[l-1]=-k*(pos[l-1]-pos[l-2])-Vprim[l-1]

for i in range(1,l-1):
    F[i]=-k*(2*pos[i]-pos[i+1]-pos[i-1])-Vprim[i]

#Visous Damping Algorithm

for j in range(1):
    acc[j]=F[j]/m-g*vel[j] #Acceleration of each particle
    vel[j]=vel[j]+acc[j]*dt #Velocity of each particle
    prevpos[j]=pos[j] #Previous position=current one
    #Update of the position
    pos[j]=pos[j]+(2/(1+g)-1)*vel[j]*dt+(1/(1+g))*F[j]/m*dt*dt

#Energy computation

E=0
Ecin=0
Epot=0

Ecin=1/2*m*((pos[0]-prevpos[0])/(2*dt))**2
Epot=k/2*(pos[0]+(L-pos[l-1])-a0)**2+V(pos[0])
E+=Ecin+Epot

for o in range(1,l):
    Ecin=1/2*m*((pos[o]-prevpos[o])/(2*dt))**2
    Epot=k/2*(pos[o]-pos[o-1]-a0)**2+V(pos[o])
    E+=Ecin+Epot
Delta=abs(E0-E)

El.append(E)
E0=E

return [pos,E]

```


B.2 The Newton-Raphson implementation

```

def NewRaph(k,a0,pos,nmin,p=[0,1,0],zlim=5000,L=1,m=1,\
g=1,dt=0.005,opt='P'):
    #Nombre de boule=dimension du problème
    nat=len(pos)
    nat1=nat-1
    cvcr=10**(-28)#Convergence criterion
    Delta=1#Value to enter the while

    #Starting energy
    E=0
    Epot=0
    ##First ball being pulled by the last one of the previous period
    Epot=k/2*(pos[0]+(L-pos[nat1])-a0)**2+PotFDE(pos[0],p,nmin)
    E+=Epot

    ##All the others being pulled by the previous one
    for o in range(1,nat):
        Epot=k/2*(pos[o]-pos[o-1]-a0)**2+PotFDE(pos[o],p,nmin)
        E+=Epot

    E2=[E]
    E1=0
    y=0

    Vprim=[0]*nat
    Vsec=[0]*nat
    Eprim=[0]*nat

    F=[0]*nat #Force on each particle
    vel=[0]*nat #Velocity of each particle
    acc=[0]*nat #Acceleration of each particle

    Hess=np.ones([nat,nat])
    C=0

    #Boucle de convergence
    while Delta>cvcr:

        y+=1
        #and Delta<10**(-14)
        #Avoid infinity loop
        if y>zlim:
            print('y exceeded ',zlim)
            return [pos,E]

```

```

#Vecteur de la dérivée du potentiel (1 x N)

#Pas de dérivation
h=0.0000005

#Calcul des dérivées (O(h**4))
Vprim[0]=(PotFDE(pos[0]-2*h,p,nmin)-8*PotFDE(pos[0]-h,p,nmin)\
-PotFDE(pos[0]+2*h,p,nmin)+8*PotFDE(pos[0]+h,p,nmin))/(12*h)

Vsec[0]=1/(12*h**2)*(-PotFDE(pos[0]+2*h,p,nmin)\
+16*PotFDE(pos[0]+h,p,nmin)-30*PotFDE(pos[0],p,nmin)\
+16*PotFDE(pos[0]-h,p,nmin)-PotFDE(pos[0]-2*h,p,nmin))

Eprim[0]=k*(2*pos[0]-(pos[nat-1]-L)-pos[1])+Vprim[0]

for i in range(1,nat-1):
    Vprim[i]=(PotFDE(pos[i]-2*h,p,nmin)\
-8*PotFDE(pos[i]-h,p,nmin)\
-PotFDE(pos[i]+2*h,p,nmin)\
+8*PotFDE(pos[i]+h,p,nmin))/(12*h)

    Vsec[i]=1/(12*h**2)*(-PotFDE(pos[i]+2*h,p,nmin)\
+16*PotFDE(pos[i]+h,p,nmin)-30*PotFDE(pos[i],p,nmin)\
+16*PotFDE(pos[i]-h,p,nmin)-PotFDE(pos[i]-2*h,p,nmin))

    Eprim[i]=k*(2*pos[i]-pos[i-1]-pos[i+1])+Vprim[i]

Vprim[nat1]=(PotFDE(pos[nat1]-2*h,p,nmin)\
-8*PotFDE(pos[nat1]-h,p,nmin)\
-PotFDE(pos[nat1]+2*h,p,nmin)\
+8*PotFDE(pos[nat1]+h,p,nmin))/(12*h)

Vsec[nat1]=1/(12*h**2)*(-PotFDE(pos[nat1]+2*h,p,nmin)\
+16*PotFDE(pos[nat1]+h,p,nmin)-30*PotFDE(pos[nat1],p,nmin)\
+16*PotFDE(pos[nat1]-h,p,nmin)-PotFDE(pos[nat1]-2*h,p,nmin))

Eprim[nat1]=k*(2*pos[nat1]-pos[nat-2]-(L+pos[0]))+Vprim[nat1]

#Computation of the hessian

for i in range(nat):
    for j in range(nat):
        Hess[i,j]=k*(2*Dirac(i,j)-Dirac(i-1,j)\

```

```

        -Dirac(i+1,j))+Dirac(i,j)*Vsec[i]

#Evaluation of the eigenvalues to have a minimum
# (all the eigenvalues must be positive
# (Hessian is definite positive) to have a minimum)

B=DefPos(Hess)
if B==False: #Hessian is not definite positive
    E1=Decimal(E)
    if C>100:
        print('This should be a saddle point\
              (energy probably not converged)')

        return [pos,E]
    else:
        C+=1

#####List for calculations & plot#####

prevpos=pos #Previous position

##20 cycles to approach the solution
z=0
while z<20:
    #Derivative of the potential
    z+=1
    for h in range(nat):
        Vprim[h]=(+PotFDE(pos[h]-0.00001,p,nmin)\
                  -8*PotFDE(pos[h]-0.000005,p,nmin)\
                  -PotFDE(pos[h]+0.00001,p,nmin)\
                  +8*PotFDE(pos[h]+0.000005,p,nmin))/(12*0.000005)

    #Force on the particle
    # (neighboring balls pulling
    # and gradient of the potential)
    #Boundary cdts for the periodic case
    if opt=='P':
        F[0]=-k*(2*pos[0]-pos[1]+(L-pos[nat-1]))\
              -Vprim[0]

        F[nat1]=-k*(2*pos[nat1]-(L+pos[0])-pos[nat-2])\
              -Vprim[nat1]

    #Non periodic case
    else:

```

```

F[0]=0
F[nat1]=-k*(pos[nat1]-pos[nat-2])-Vprim[nat1]

for i in range(1,nat1):
    F[i]=-k*(2*pos[i]-pos[i+1]-pos[i-1])-Vprim[i]
#Visous Damping Algorithm
for j in range(nat):
    acc[j]=F[j]/m-g*vel[j]# Acceleration
    vel[j]=vel[j]+acc[j]*dt#Velocity
    prevpos[j]=pos[j]

    pos[j]=pos[j]+(2/(1+g)-1)*vel[j]*dt\
    +(1/(1+g))*F[j]/m*dt*dt#Update of the positions

#Energy computation

E=0
Ecin=0
Epot=0

Ecin=1/2*m*((pos[0]-prevpos[0])/(2*dt))**2
Epot=k/2*(pos[0]+(L-pos[nat1])-a0)**2\
+PotFDE(pos[0],p,nmin)

E+=Ecin+Epot

for o in range(1,nat):
    Ecin=1/2*m*((pos[o]-prevpos[o])/(2*dt))**2
    Epot=k/2*(pos[o]-pos[o-1]-a0)**2\
    +PotFDE(pos[o],p,nmin)
    E+=Ecin+Epot
E2.append(E)

E=Decimal(E)
Delta=abs(E-E1)
else:
    HessInv=np.linalg.inv(Hess) #Inversion of the matrix
    dpos=np.matmul(HessInv,Eprim)
    pos=pos-dpos #Update of the positions

    E1=Decimal(E)
    #Evaluation of the energy associated to the new positions
    E=Decimal(k/2*(pos[0]+(L-pos[nat-1])-a0)**2\
    +PotFDE(pos[0],p,nmin))

```

```

    ##Toutes les suivantes sont tirées par la précédente
    for i in range(1,nat):
        E+=Decimal(k/2*(pos[i]-pos[i-1]-a0)**2\
+PotFDE(pos[i],p,nmin))

        E2.append(E)
        E=Decimal(E)
        Delta=abs(E-E1)
    return [pos,E]

def DefPos(H):
    eigval0=np.linalg.eig(H)
    eigval=eigval0[0]
    l=len(eigval)
    #print('eigval=',eigval)
    for i in range(l):
        if eigval[i]<0:
            return False
        elif eigval[i]==0:
            print('Watch out : might be a saddle point')

    return True

def Dirac(a,b):
    if a==b:
        return 1
    else:
        return 0

```

B.3 The Differential evolution implementation

```

import math
from scipy import misc
import numpy as np
from EnergyDislocation import Pot,PotFDE,PotFit
from NewRaph import NewRaph
import sys
import random
from decimal import Decimal

def VecPosGen(nat,pos):
    #Fonction générant une matrice
    #de 5*nat vecteurs de positions aléatoires
    # (à l'exception de
    # la première ligne prédéterminée

```

```

# soit de manière générique soit en reprenant
#la précédente position
# optimisant le problème ==>
# Risque de répéter une erreur si min local
#ou de provoquer chute dans un min
# locale)
#nat= nombre d'atomes

NP=5*nat
vec=np.ones((NP,nat))
vec[0,:]=pos
for i in range(1,NP):
    for j in range(nat):
        vec[i,j]=random.random()
    vec[i,:]=sorted(vec[i,:])
return vec

def Diff_Ev(nat,kspr,a0,Len,pos,lim,nmin,p=[0,1,0]):
#Implémentation de l'algorithme d'évolution différentielle
#Generation 0 de vecteur
    vec=VecPosGen(nat,pos)
#Population
    l=len(vec[:,0])
#Initialisation du vecteur reprenant toutes les énergie
# associées à chaque échantillon
    Evec=[0]*l
#Variable pour calculer l'énergie
    E=0
#Variable pour stocker l'énergie minimum
    Emin=10000
#Variable pour garder la position du vecteur associé à l'énergie min
    Imin=-1
#Vecteur pour générer les vecteurs tests
    vbar=[0]*nat
#Etat de la première génération
    for i in range(l):
        E=Energie(vec[i,:],kspr,a0,nmin,p,Len)
        Evec[i]=E
        if E<Emin:
            Emin=E
            Imin=i
#Variable qui permet de gérer la charge de calcul (limitée par lim)
    y=0
#Première boucle
    while y<lim/2:
        y+=1

```

```

#Génération de nouveau vecteurs dans vbar et où l'on conservent
#certaines composantes de vec[i,:] et
#modifie certaine selon une loi pseudo
# probabiliste en cherchant la meilleure direction
for i in range(1):
    F=random.random()
    prevec=vec[i,:]
    n=random.randint(0,nat-1)
    L=random.randint(1,nat)
    randomRows=ChooseLines(i,l)
    modulo=[0]*(L)
    for j in range(n,n+L):
        modulo[j-n]=j%nat
    for j in range(nat):
        if j in modulo:
            vbar[j]=vec[randomRows[0],(j)]\
            +F*(vec[randomRows[1],(j)]\
            -vec[randomRows[2],(j)])
        else:
            vbar[j]=prevec[j]
    #Prévention pour éviter les vecteurs
    # désordonnés qui ne donneraient
    #de ttes façons pas l'Emin
    vbar=sorted(vbar)

    #Comparaison des énergies et remplacement si nouveau
    # vecteur meilleur que le précédent
    E0=Evec[i]
    E1=Energie(vbar,kspr,a0,nmin,p,Len)

    if E1<E0:
        vec[i,:]=vbar
        Evec[i]=E1
        #Test pour voir si un nouveau minimum est trouvé
        if E1<Emin:
            Emin=E1
            Imin=i

#Deuxième phase où la moitié des moins
# bons vecteurs sont supprimés
# (ils sont comparés deux à deux et
# celui avec la plus basse énergie est retenu
l1=math.ceil(1/2)
vec1=np.ones((l1,nat))
Evec1=[0]*l1
#On garde la position de Imin en anticipant qu'il sera conservé

```

```

if Imin>l1-1:
    Imin=l-Imin
for i in range(l1):
    if Evec[i]<=Evec[l-1-i]:
        vec1[i,:]=vec[i]
        Evec1[i]=Evec[i]
    else:
        vec1[i,:]=vec[l-1-i,:]
        Evec1[i]=Evec[l-1-i]
Emin=min(Evec1)
#Deuxième boucle
while y<lim:
    y+=1
    for i in range(l1):
        F=random.random()
        prevec=vec1[i,:]
        n=random.randint(0,nat-1)
        L=random.randint(1,nat)
        randomRows=ChooseLines(i,l1)
        modulo=[0]*(L)
        for j in range(n,n+L):
            modulo[j-n]=j%nat

        for j in range(nat):
            if j in modulo:
                vbar[j]=vec1[randomRows[0],(j)]+\
                F*(vec1[randomRows[1],(j)]\
                -vec1[randomRows[2],(j)])
            else:
                vbar[j]=prevec[j]

        vbar=sorted(vbar)

        E0=Evec1[i]
        E1=Energie(vbar,kspr,a0,nmin,p,Len)
        if E1<E0:
            vec1[i,:]=vbar
            Evec1[i]=E1
            if E1<Emin:
                Emin=E1
                Imin=i

pos=vec[Imin,:]

```



```

print( 'Emin= ', Emin)

return pos, Emin

def Energie( pos, kspr, a0, nmin, p=0, Len=1):
#Calcule l'énergie d'un système donné
    nat=len( pos)
    E=Decimal( kspr/2*( pos[0]+( Len-pos[ nat-1])-a0)**2\
+PotFDE( pos[0], p, nmin))

    for o in range(1, nat):
        E+=Decimal( kspr/2*( pos[o]-pos[o-1]-a0)**2\
+PotFDE( pos[o], p, nmin))
    return E

def ChooseLines(i, l):
#Sélectionne 3 lignes qui ne sont pas la ligne traitée
    randomRows=np.random.randint( l, size=3)
    for s in range(3):
        if i==randomRows[s]:
            ChooseLines(i, l)
    return randomRows

```

Appendix C

Identity files of the heterostructures

C.1 Link between the potentials and the criterion

- Criterion 1 = criterion for transition associated with $\text{Pot}_{1,\text{av}}$ which has to be compared with $E_{\text{elast,CI}}$.
- Criterion 2 = criterion for transition associated with Pot_1 which has to be compared with $|E_{\text{elast,CC}} - E_{\text{elast,CI}}|$.
- Criterion 3 = criterion for transition associated with $\text{Pot}_{2,\text{av}}$ which has to be compared with $E_{\text{elast,IC}}$.
- Criterion 4 = criterion for transition associated with Pot_2 which has to be compared with $|E_{\text{elast,CC}} - E_{\text{elast,IC}}|$.

C.2 Heterostructures

C.2.1 P-MoSe₂

Visual Summary

The Figure [C.1](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.233	0.125	0.101 (0.015)	0.101	● ● ●	
Pot ₁	1.239	27.174	66.315 (48.325)	21.929	○ ○ ○	
Pot _{2,av}	1.234	13.441	62.024 (44.706)	10.896	○ ○ ○	
Pot ₂	1.319	25.630	4.391 (3.634)	19.424	○ ○ ●	

Table C.1 – Data related to the four 1D potentials extracted from the 2D potential landscape of P-MoSe₂ with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a ● or a ○ following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled. The elastic value in parenthesis are those corresponding to the case where the monolayer unit cell of P is considered.

Data	Bulk	Monolayer
$E_{\text{elast,CC}}$	66.415	48.431
Phase "16 cases"	CI	CI
Phase NODEC	II	II
Diagram type	1	1

Table C.2 – Summary of the phases and elastic energy computed for P-MoSe₂ with the data of the bulk and monolayer.

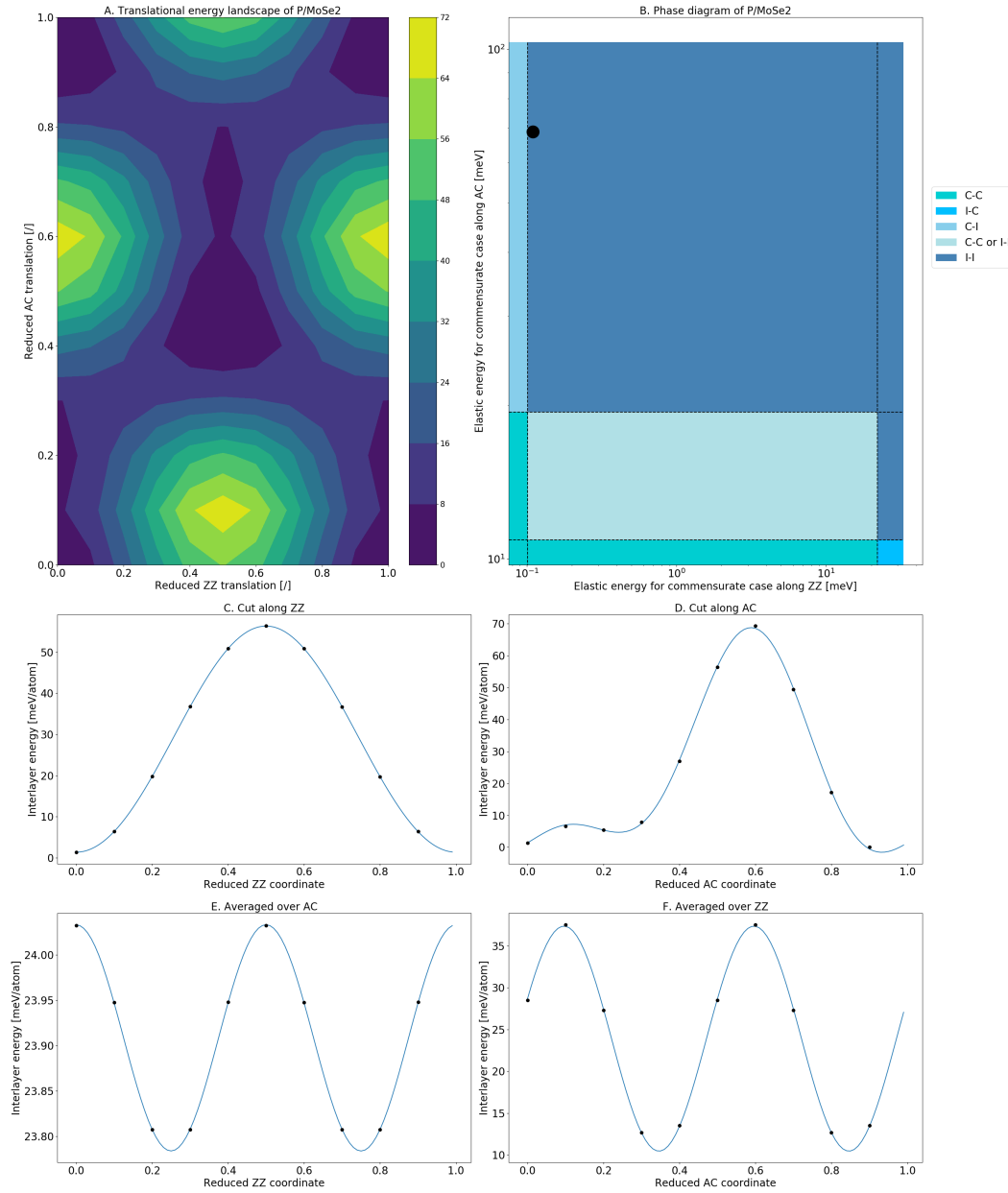


Figure C.1 – A : 2D potential landscape of P-MoSe₂. B : Phase diagram obtained from the NODEC method (the position E₁-E₂ is indicated by the '•' symbol). C and D : 1D cut of the 2D potential landscape along the ZZ direction and along the AC direction respectively. E and F : Averaged potential over AC and ZZ seen along ZZ and AC direction respectively.

C.2.2 MoSe₂-MoTe₂

Visual Summary

The Figure [C.12](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.235	0.248	13.411	0.201	○ ○	○
Pot ₁	1.242	16.833	20.400	13.554	○ ○	○
Pot _{2,av}	1.230	14.792	13.421	12.029	○ ○	○
Pot ₂	1.283	25.794	20.390	20.899	● ●	○

Table C.3 – Data related to the four 1D potentials extracted from the 2D potential landscape of MoSe₂-MoTe₂ for the directions ZZ-AC with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a ● or a ○ following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled.

Data	ZZ-AC	ZZ-ZZ
$E_{\text{elast,CC}}$	33.81	39.024
Phase "16 cases"	II	CC
Phase NODEC	II	CC
Diagram type	1	1

Table C.4 – Summary of the phases and elastic energy computed for MoSe₂-MoTe₂ with the data for the direction ZZ-AC and ZZ-ZZ.

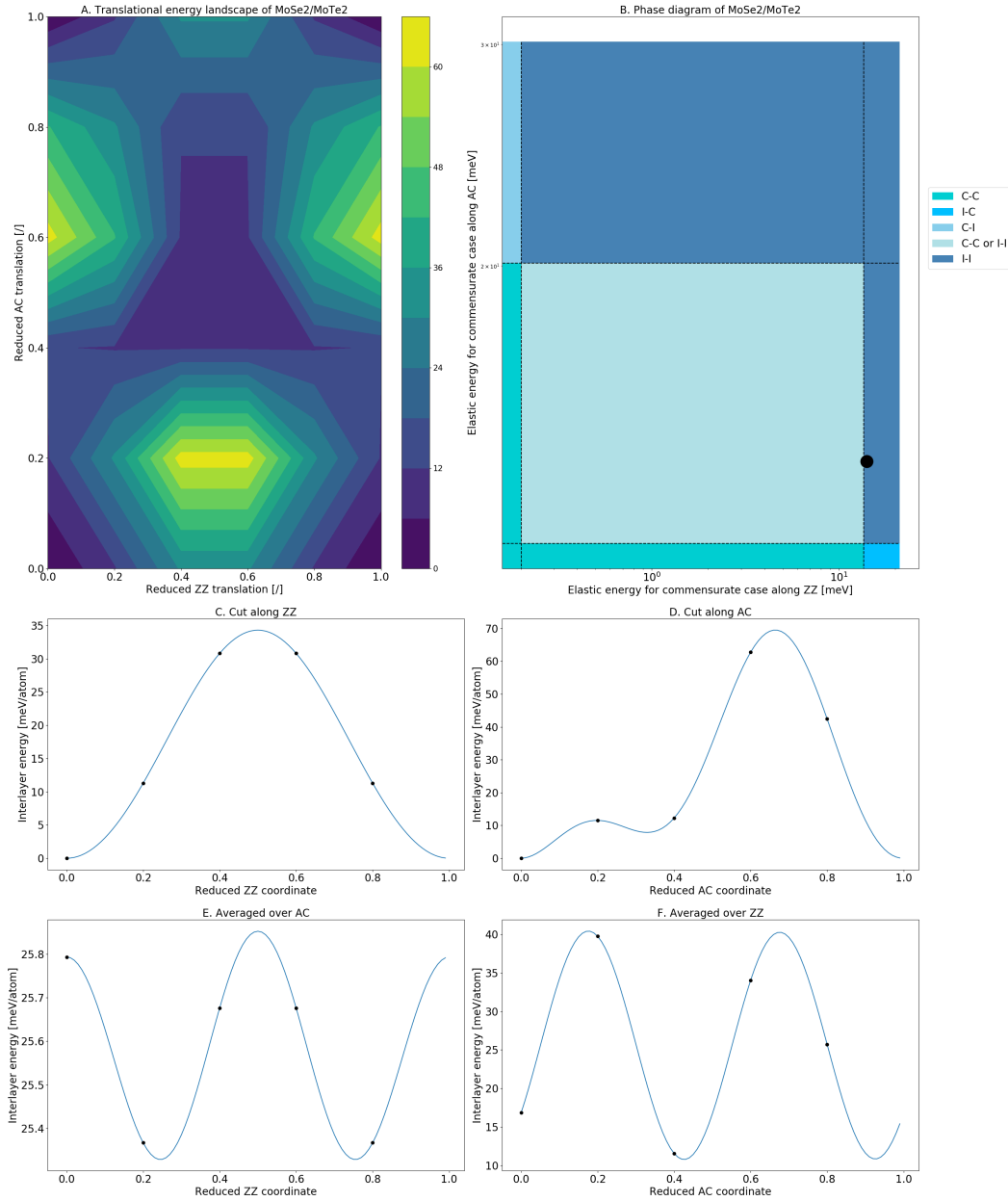


Figure C.2 – A : 2D potential landscape of MoSe₂-MoTe₂. B : Phase diagram obtained from the NODEC method (the position E₁-E₂ is indicated by the '•' symbol. C and D : 1D cut of the 2D potential landscape along the ZZ1 direction and along the ZZ2 direction respectively. E and F : Averaged potential over ZZ2 and ZZ1 seen along ZZ1 and ZZ2 direction respectively.

C.2.3 MoTe₂WSe₂

Visual Summary

The Figure [C.3](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.234	0.234	14.811	0.189	○ ○	○
Pot ₁	1.242	15.768	21.759	12.689	○ ○	○
Pot _{2,av}	1.228	13.548	14.862	11.030	○ ○	○
Pot ₂	1.270	24.173	21.708	19.033	○ ○	○

Table C.5 – Data related to the four 1D potentials extracted from the 2D potential landscape of MoTe₂WSe₂ for the directions ZZ-AC with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a ● or a ○ following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled.

Data	ZZ-AC	ZZ-ZZ
$E_{\text{elast,CC}}$	36.57	42.154
Phase "16 cases"	CC	CC
Phase NODEC	CC	II
Diagram type	1	1

Table C.6 – Summary of the phases and elastic energy computed for MoTe₂WSe₂ with the data for the direction ZZ-AC and ZZ-ZZ.

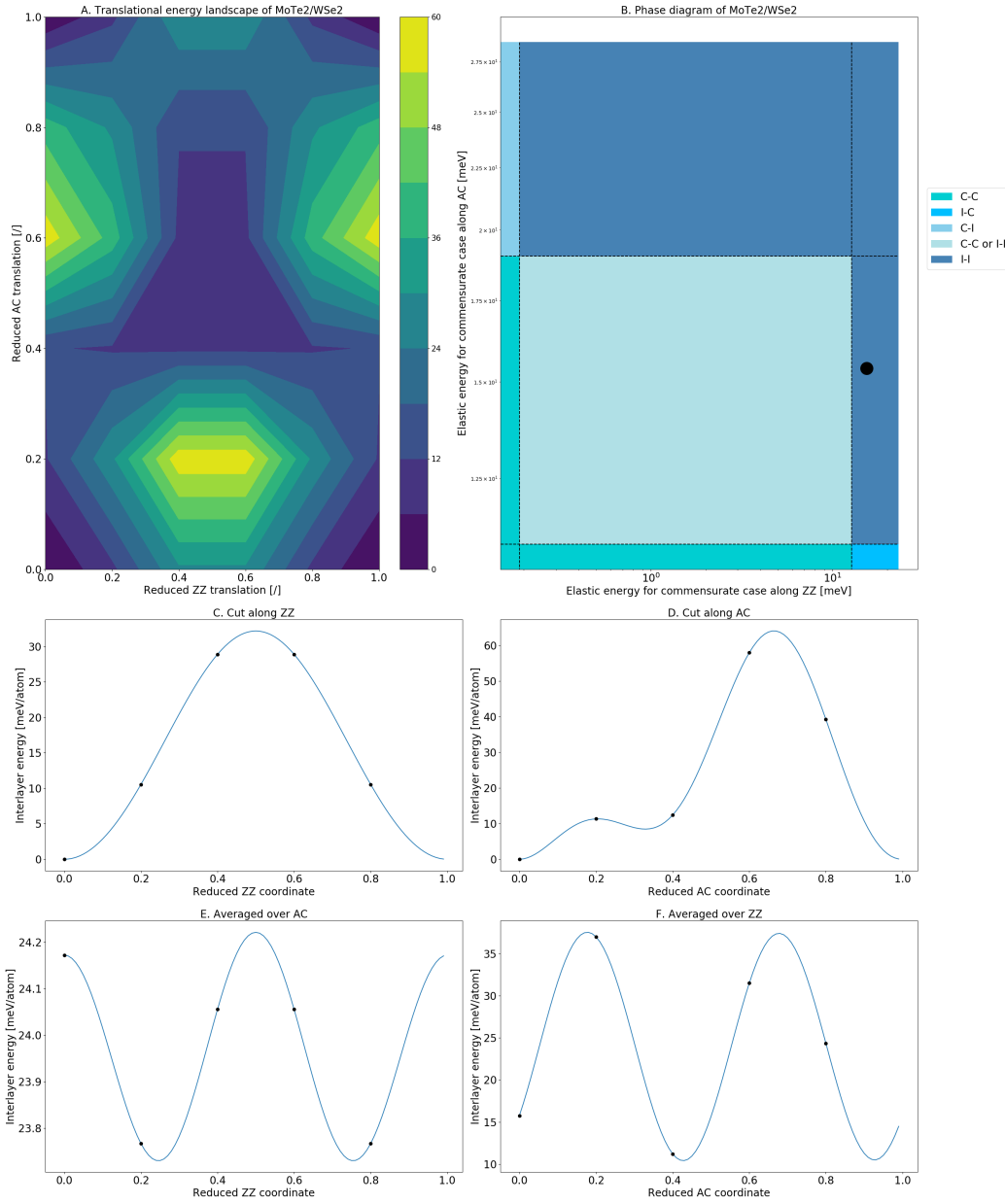


Figure C.3 – A : 2D potential landscape of MoTe₂WSe₂. B : Phase diagram obtained from the NODEC method (the position E₁-E₂ is indicated by the '•' symbol. C and D : 1D cut of the 2D potential landscape along the ZZ1 direction and along the ZZ2 direction respectively. E and F : Averaged potential over ZZ2 and ZZ1 seen along ZZ1 and ZZ2 direction respectively.

C.2.4 hBN-P

Visual Summary

The Figure [C.4](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.226	0.0215	0.366 (0.723)	0.00175	●(●) ○ ○	○
Pot ₁	1.239	0.0791	0.120 (2.244)	0.0638	● ○ ○	○
Pot _{2,av}	1.216	3.938	0.275 (2.858)	3.238	○(●) ○ ●	●
Pot ₂	1.200	4.021	0.211 (0.109)	3.349	○ ○ ●	●

Table C.7 – Data related to the four 1D potentials extracted from the 2D potential landscape of hBN-P with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a ● or a ○ following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled. The elastic value in parenthesis are those corresponding to the case where the monolayer unit cell of P is considered.

Data	Bulk	Monolayer
$E_{\text{elast,CC}}$	0.486	2.967
Phase "16 cases"	undertermined	undetermined
Phase NODEC	IC	IC
Diagram type	1	1

Table C.8 – Summary of the phases and elastic energy computed for hBN-P with the data of the bulk and monolayer.

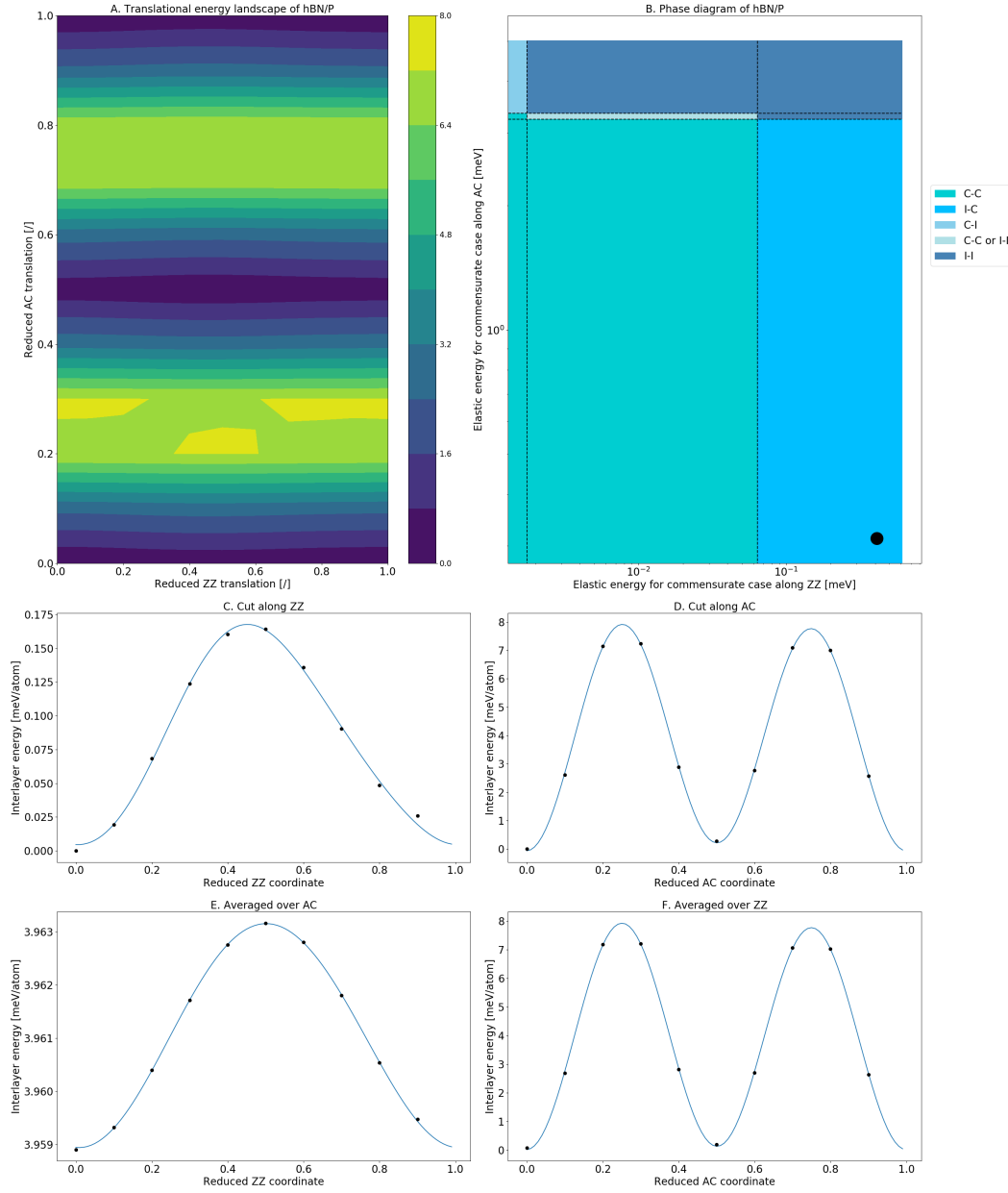


Figure C.4 – A : 2D potential landscape of hBN-P. B : Phase diagram obtained from the NODEC method (the position E_1-E_2 is indicated by the '•' symbol). C and D : 1D cut of the 2D potential landscape along the ZZ direction and along the AC direction respectively. E and F : Averaged potential over AC and ZZ seen along ZZ and AC direction respectively.

C.2.5 G-P

Visual Summary

The Figure [C.5](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.231	0.0196	0.275 (0.0255)	0.0160	●(●) ○ ○	
Pot ₁	1.250	0.114	1.771 (5.486)	0.0916	● ○ ○	
Pot _{2,av}	1.209	4.982	1.194 (4.706)	4.120	○(●) ○ ●(○)	
Pot ₂	1.230	4.871	0.852 (0.806)	3.961	○ ○ ●	

Table C.9 – Data related to the four 1D potentials extracted from the 2D potential landscape of G-P with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a ● or a ○ following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled. The elastic value in parenthesis are those corresponding to the case where the monolayer unit cell of P is considered.

Data	Bulk	Monolayer
$E_{\text{elast,CC}}$	2.046	5.512
Phase "16 cases"	undertermined	II
Phase NODEC	IC	II
Diagram type	3	3

Table C.10 – Summary of the phases and elastic energy computed for G-P with the data of the bulk and monolayer.

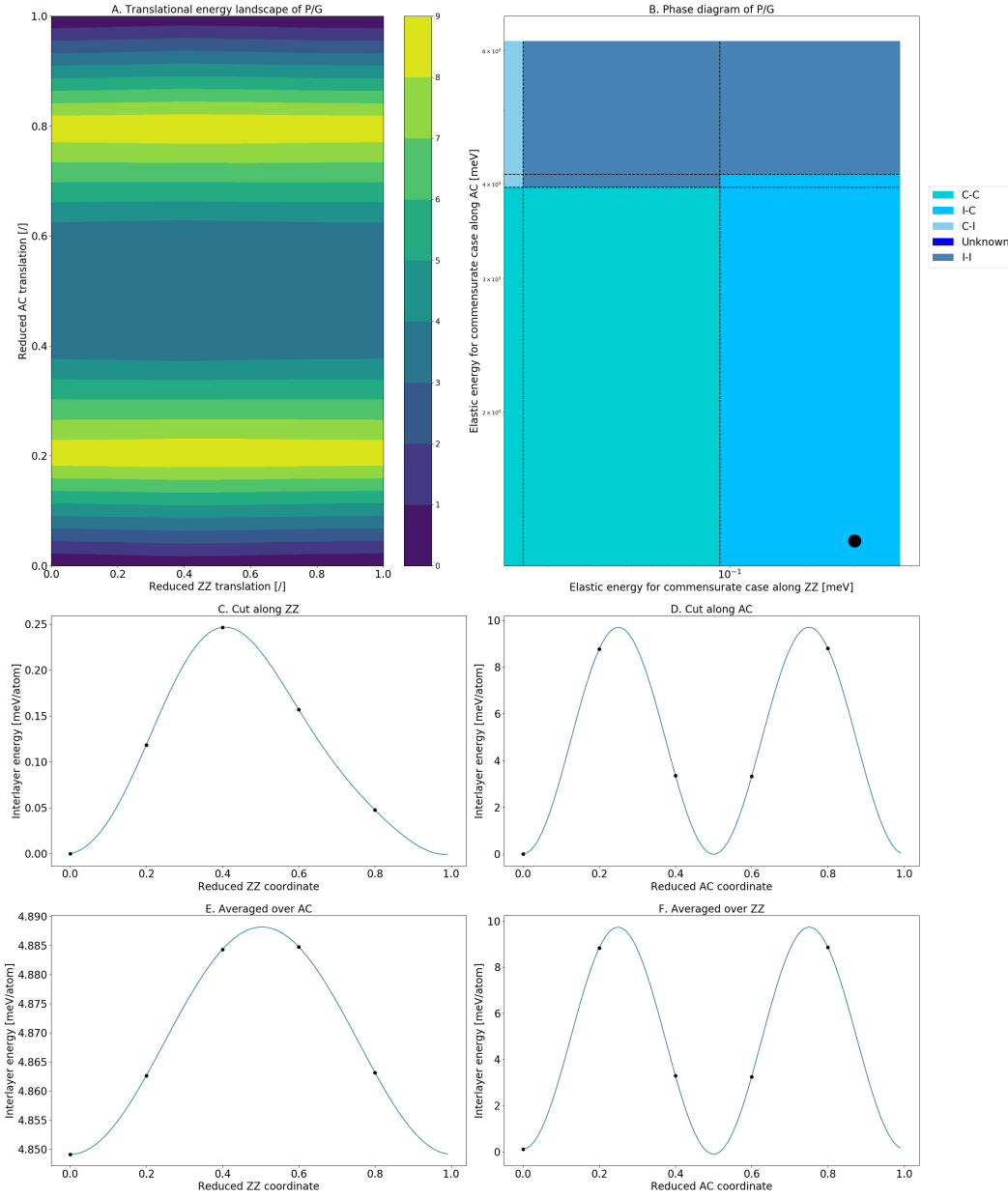


Figure C.5 – A : 2D potential landscape of G-P. B : Phase diagram obtained from the NODEC method (the position E_1 - E_2 is indicated by the '•' symbol. C and D : 1D cut of the 2D potential landscape along the ZZ direction and along the AC direction respectively. E and F : Averaged potential over AC and ZZ seen along ZZ and AC direction respectively.

C.2.6 WS₂-WSe₂

Visual Summary

The Figure [C.6](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.234	0.778	3.958	0.630	o o	o
Pot ₁	1.249	17.204	5.141	13.771	o o	•
Pot _{2,av}	1.220	17.352	3.551	14.224	o o	•
Pot ₂	1.338	27.734	5.189	20.725	o o	•

Table C.11 – Data related to the four 1D potentials extracted from the 2D potential landscape of WS₂WSe₂ for the directions ZZ-AC with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a • or a o following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled.

Data	ZZ-AC	ZZ-ZZ
$E_{\text{elast,CC}}$	8.739	10.157
Phase "16 cases"	CC	CC
Phase NODEC	CC	CC
Diagram type	1	1

Table C.12 – Summary of the phases and elastic energy computed for WS₂WSe₂ with the data for the direction ZZ-AC and ZZ-ZZ.

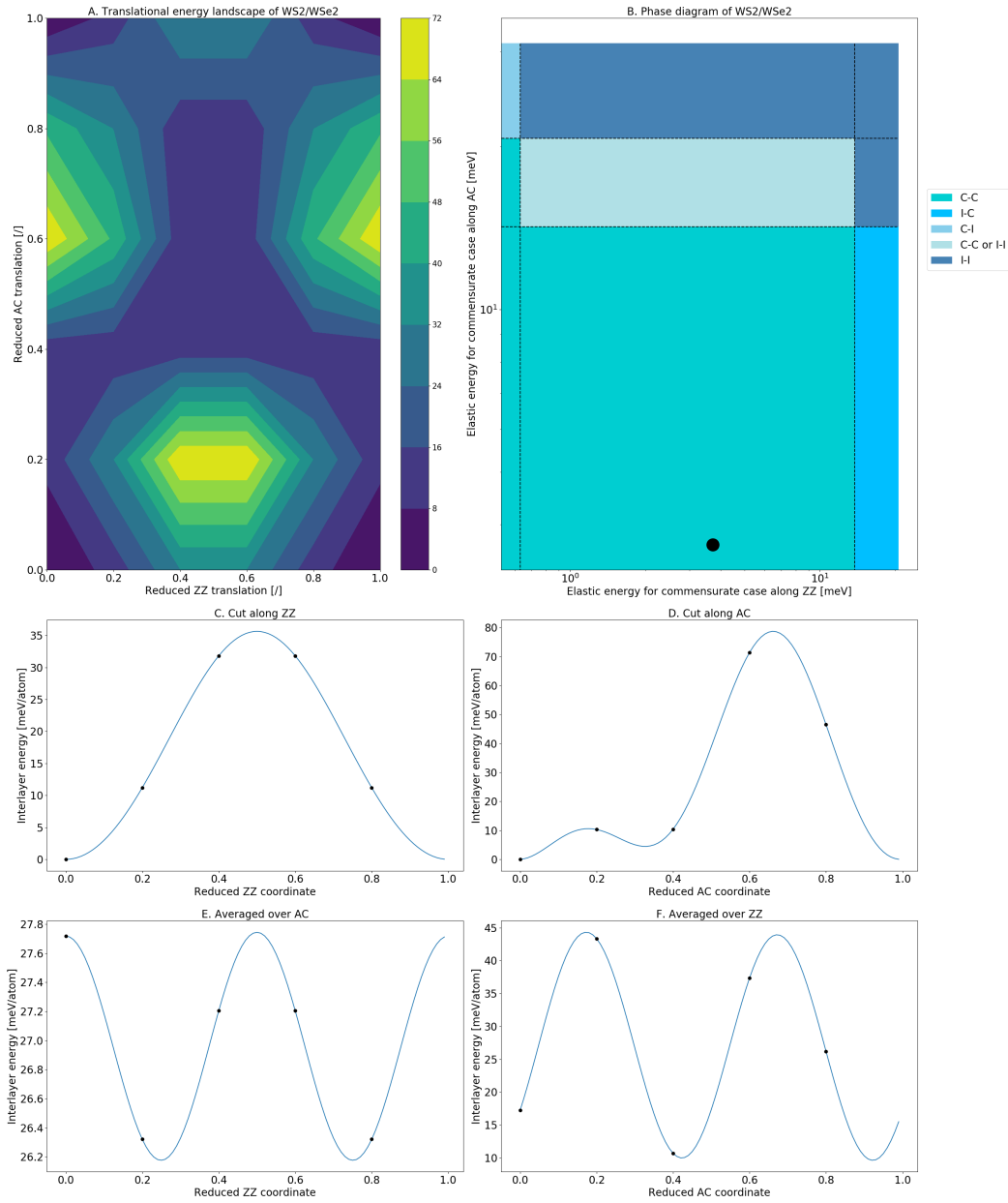


Figure C.6 – A : 2D potential landscape of WS₂-WSe₂. B : Phase diagram obtained from the NODEC method (the position E₁-E₂ is indicated by the '•' symbol). C and D : 1D cut of the 2D potential landscape along the ZZ1 direction and along the ZZ2 direction respectively. E and F : Averaged potential over ZZ2 and ZZ1 seen along ZZ1 and ZZ2 direction respectively.

C.2.7 MoS₂-WSe₂

Visual Summary

The Figure [C.7](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.234	0.824	3.807	0.668	○ ○	○
Pot ₁	1.250	17.207	5.609	13.765	○ ○	●
Pot _{2,av}	1.219	17.683	3.793	14.504	○ ○	●
Pot ₂	1.351	27.856	5.623	20.617	○ ○	●

Table C.13 – Data related to the four 1D potentials extracted from the 2D potential landscape of MoS₂WSe₂ for the directions ZZ-AC with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a ● or a ○ following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled.

Data	ZZ-AC	ZZ-ZZ
$E_{\text{elast,CC}}$	9.416	10.893
Phase "16 cases"	CC	CC
Phase NODEC	CC	CC
Diagram type	1	2

Table C.14 – Summary of the phases and elastic energy computed for MoS₂WSe₂ with the data for the direction ZZ-AC and ZZ-ZZ.

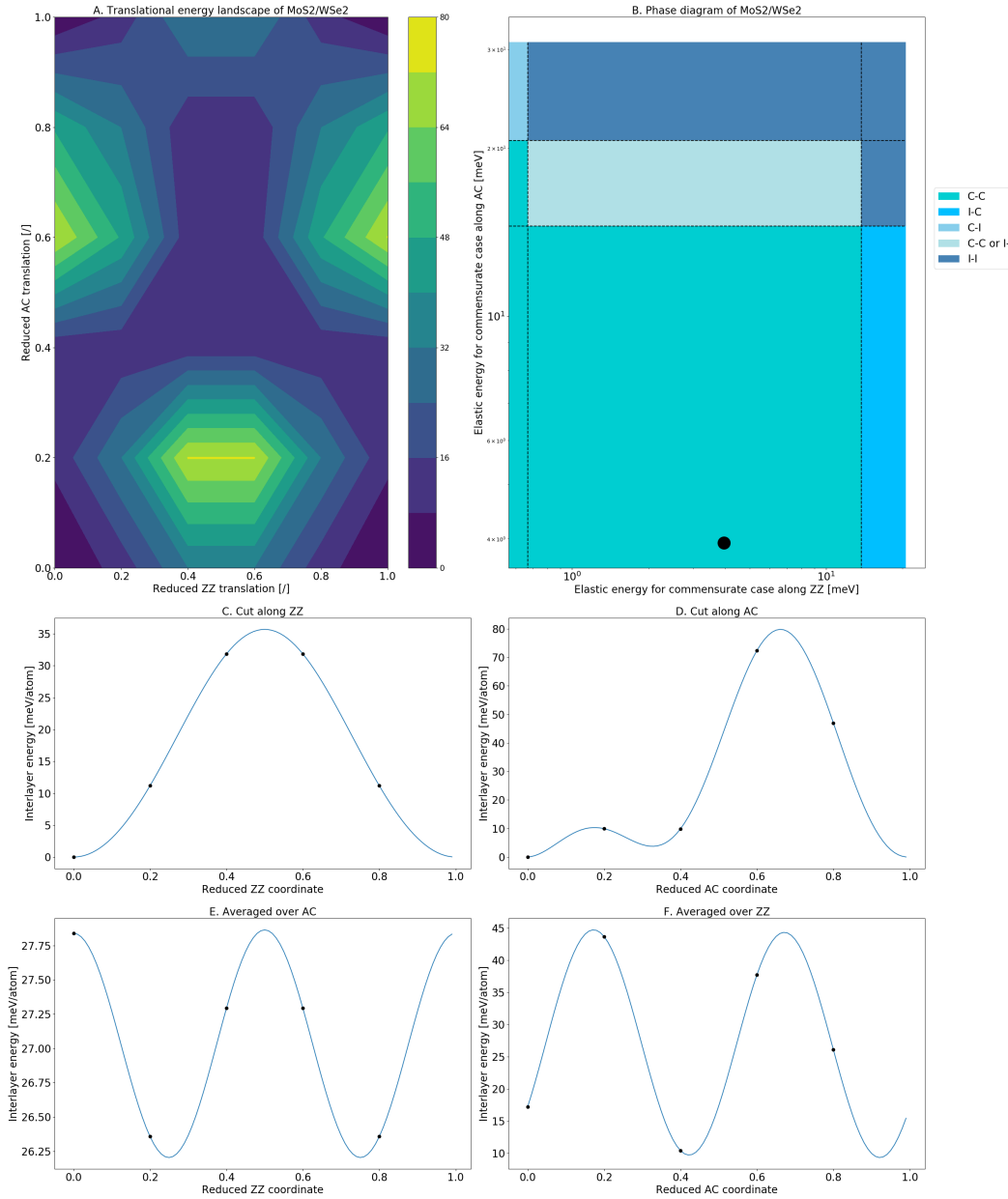


Figure C.7 – A : 2D potential landscape of MoS₂-WSe₂. B : Phase diagram obtained from the NODEC method (the position E₁-E₂ is indicated by the '●' symbol. C and D : 1D cut of the 2D potential landscape along the ZZ1 direction and along the ZZ2 direction respectively. E and F : Averaged potential over ZZ2 and ZZ1 seen along ZZ1 and ZZ2 direction respectively.

C.2.8 MoS₂-MoSe₂

Visual Summary

The Figure [C.8](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.236	0.970	3.915	0.786	○ ○	○
Pot ₁	1.252	17.790	6.038	14.213	○ ○	●
Pot _{2,av}	1.218	19.162	3.923	15.737	○ ○	●
Pot ₂	1.392	29.102	6.030	20.914	○ ○	●

Table C.15 – Data related to the four 1D potentials extracted from the 2D potential landscape of MoS₂MoSe₂ for the directions ZZ-AC with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a ● or a ○ following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled.

Data	ZZ-AC	ZZ-ZZ
$E_{\text{elast,CC}}$	9.953	11.481
Phase "16 cases"	CC	CC
Phase NODEC	CC	CC
Diagram type	1	2

Table C.16 – Summary of the phases and elastic energy computed for MoS₂MoSe₂ with the data for the direction ZZ-AC and ZZ-ZZ.

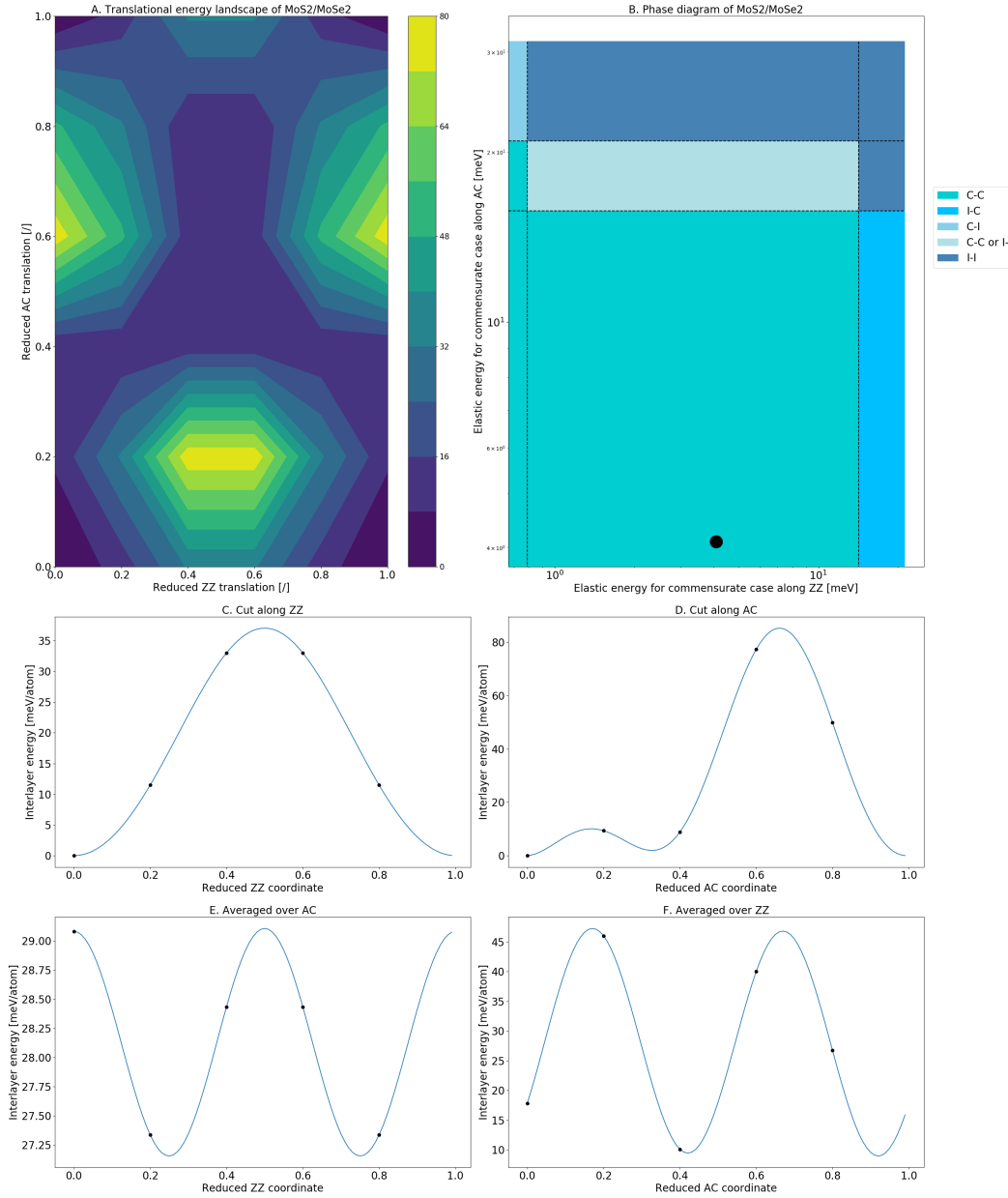


Figure C.8 – A : 2D potential landscape of MoS₂-MoSe₂. B : Phase diagram obtained from the NODEC method (the position E₁-E₂ is indicated by the '•' symbol). C and D : 1D cut of the 2D potential landscape along the ZZ1 direction and along the ZZ2 direction respectively. E and F : Averaged potential over ZZ2 and ZZ1 seen along ZZ1 and ZZ2 direction respectively.

C.2.9 MoSe₂-WS₂

Visual Summary

The Figure [C.9](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.234	0.906	3.706	0.735	○ ○	○
Pot ₁	1.251	17.742	5.565	14.184	○ ○	●
Pot _{2,av}	1.218	18.715	3.681	15.361	○ ○	●
Pot ₂	1.373	28.866	5.589	21.025	○ ○	●

Table C.17 – Data related to the four 1D potentials extracted from the 2D potential landscape of MoSe₂WS₂ for the directions ZZ-AC with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a ● or a ○ following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled.

Data	ZZ-AC	ZZ-ZZ
$E_{\text{elast,CC}}$	9.271	10.739
Phase "16 cases"	CC	CC
Phase NODEC	CC	CC
Diagram type	1	2

Table C.18 – Summary of the phases and elastic energy computed for MoSe₂WS₂ with the data for the direction ZZ-AC and ZZ-ZZ.

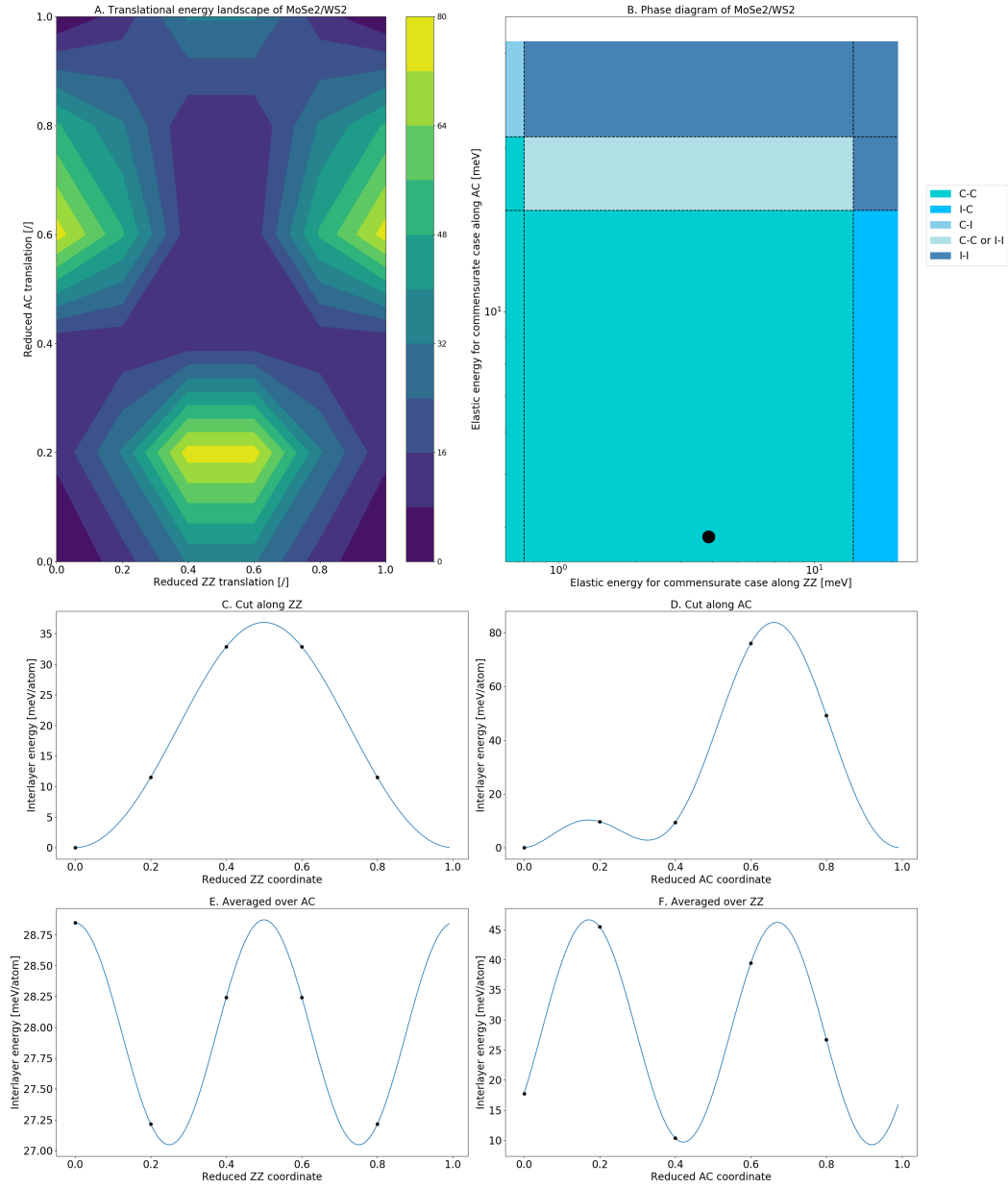


Figure C.9 – A : 2D potential landscape of MoSe₂-WS₂. B : Phase diagram obtained from the NODEC method (the position E₁-E₂ is indicated by the '●' symbol). C and D : 1D cut of the 2D potential landscape along the ZZ1 direction and along the ZZ2 direction respectively. E and F : Averaged potential over ZZ2 and ZZ1 seen along ZZ1 and ZZ2 direction respectively.

C.2.10 MoS₂-WS₂

Visual Summary

The Figure [C.10](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.234	0.156	0.0145	0.127	● ○	●
Pot ₁	1.241	6.537	0.0256	5.267	○ ○	●
Pot _{2,av}	1.221	5.980	0.0167	4.898	○ ○	●
Pot ₂	1.291	10.209	0.0229	7.906	○ ○	●

Table C.19 – Data related to the four 1D potentials extracted from the 2D potential landscape of MoS₂WS₂ for the directions ZZ-AC with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a ● or a ○ following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled.

Data	ZZ-AC	ZZ-ZZ
$E_{\text{elast,CC}}$	0.0396	0.0425
Phase "16 cases"	CC	CC
Phase NODEC	CC	CC
Diagram type	1	1

Table C.20 – Summary of the phases and elastic energy computed for MoS₂WS₂ with the data for the direction ZZ-AC and ZZ-ZZ.

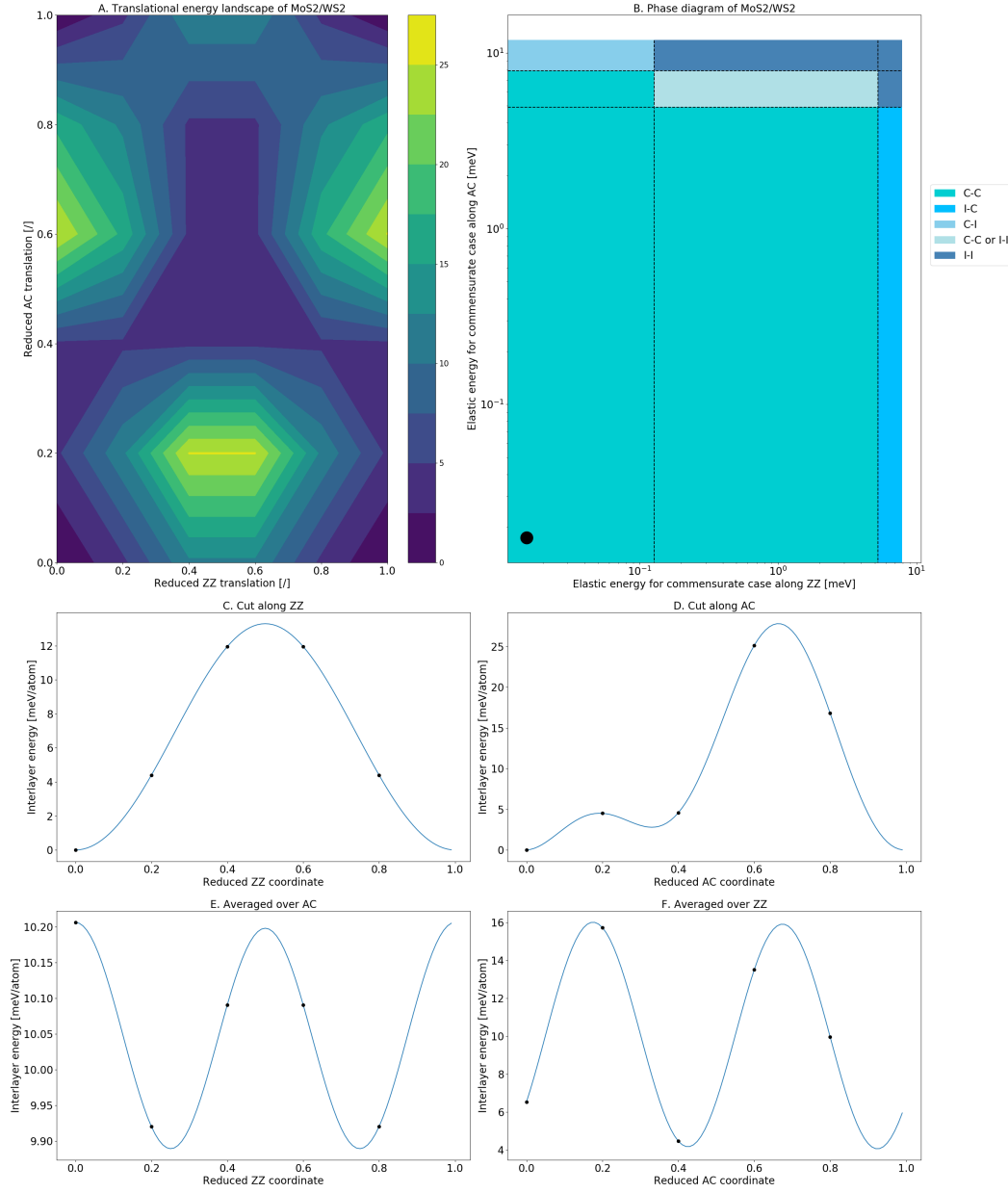


Figure C.10 – A : 2D potential landscape of MoS₂-WS₂. B : Phase diagram obtained from the NODEC method (the position E₁-E₂ is indicated by the '•' symbol). C and D : 1D cut of the 2D potential landscape along the ZZ1 direction and along the ZZ2 direction respectively. E and F : Averaged potential over ZZ2 and ZZ1 seen along ZZ1 and ZZ2 direction respectively.

C.2.11 MoSe₂-WSe₂

Visual Summary

The Figure [C.11](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.234	0.270	0.00905	0.219	● ○ ●	
Pot ₁	1.246	8.159	0.0145	6.548	○ ○ ●	
Pot _{2,av}	1.223	7.355	0.0102	6.013	○ ○ ●	
Pot ₂	1.275	12.916	0.0134	10.128	○ ○ ●	

Table C.21 – Data related to the four 1D potentials extracted from the 2D potential landscape of MoSe₂-WSe₂ for the directions ZZ-AC with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a ● or a ○ following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled.

Data	ZZ-AC	ZZ-ZZ
$E_{\text{elast,CC}}$	0.0257	0.0235
Phase "16 cases"	CC	CC
Phase NODEC	CC	CC
Diagram type	1	1

Table C.22 – Summary of the phases and elastic energy computed for MoSe₂-WSe₂ with the data for the direction ZZ-AC and ZZ-ZZ.

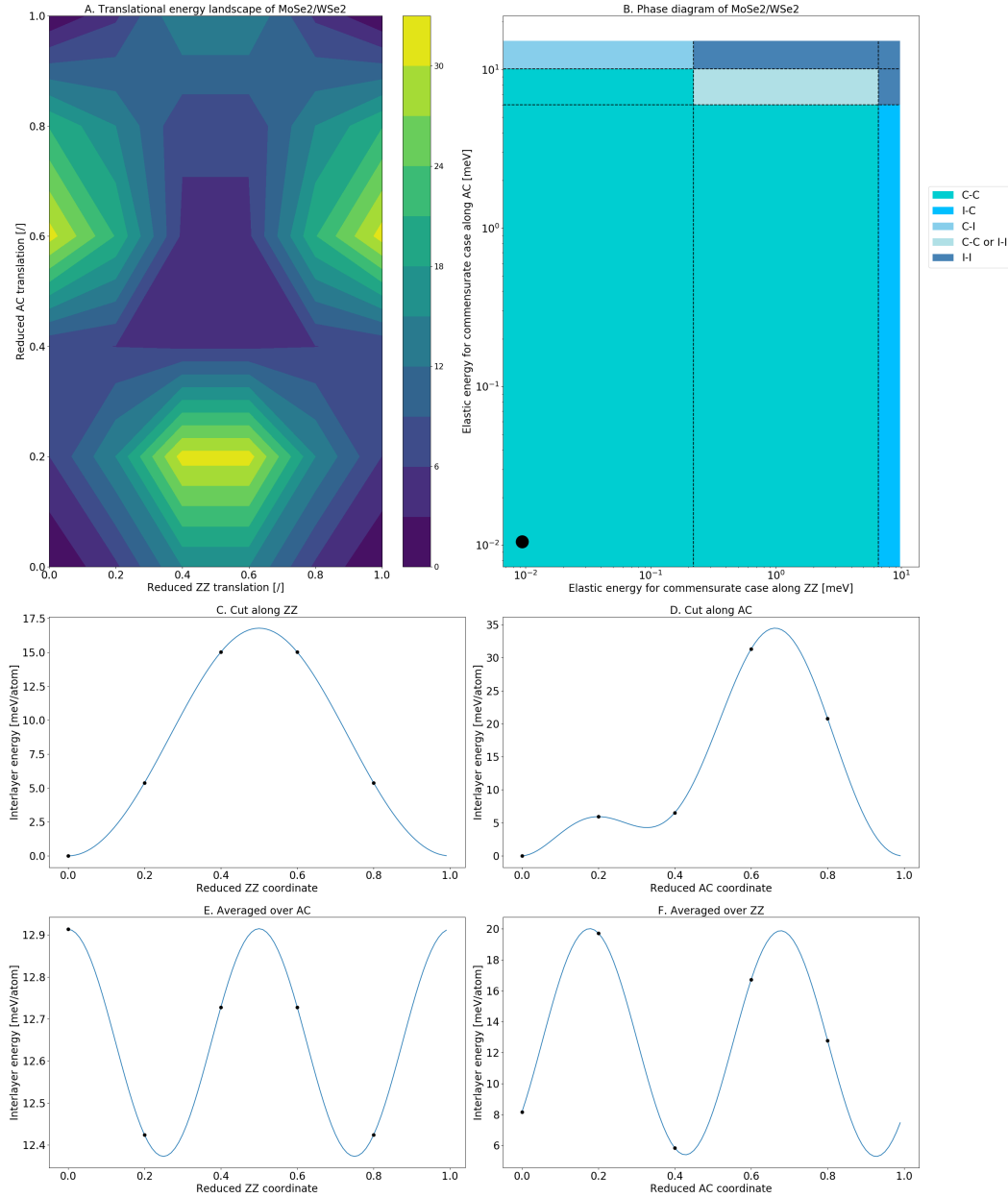


Figure C.11 – A : 2D potential landscape of MoSe₂-WSe₂. B : Phase diagram obtained from the NODEC method (the position E₁-E₂ is indicated by the '•' symbol. C and D : 1D cut of the 2D potential landscape along the ZZ1 direction and along the ZZ2 direction respectively. E and F : Averaged potential over ZZ2 and ZZ1 seen along ZZ1 and ZZ2 direction respectively.

C.3 Potential landscape along ZZ-ZZ of MoSe₂-MoTe₂

C.3.1 Visual summary

The Figure [C.12](#) presents the potential landscape, the phase diagram obtained by the NODEC method and the different potentials used along the method which will be denoted by the subscripts "1", "2", "1,av" and "2,av" throughout this section.

C.3.2 Characteristics of the potential and phase predicted

Potential	γ	E_{coher}	E_{el}	Transition criterion	Δ	Realization
Pot _{1,av}	1.235	29.453	15.484	23.855	o o	•
Pot ₁	1.242	33.666	23.539	27.108	o o	•

Table C.23 – Data related to the four 1D potentials extracted from the 2D potential landscape of MoSe₂-MoTe₂ for the directions ZZ-ZZ (Pot₂ and Pot_{2,av} are equivalent to Pot₁ and Pot_{1,av} respectively) with corresponding criterion. the elastic energy to be compared with the criteria are give. The Delta column gives two symbols : the first is either a • or a o following if the elastic energy falls in a range of ± 1 meV of the criterion or not, the second symbol take the same form following if the elastic energy falls in a range of $\pm 10\%$ of the criterion. The final row tells if the criterion is fulfilled.

Data	ZZ-AC	ZZ-ZZ
$E_{\text{elast,CC}}$	33.81	39.024
Phase "16 cases"	II	CC
Phase NODEC	II	CC
Diagram type	1	1

Table C.24 – Summary of the phases and elastic energy computed for MoSe₂-MoTe₂ with the data for the direction ZZ-AC and ZZ-ZZ.

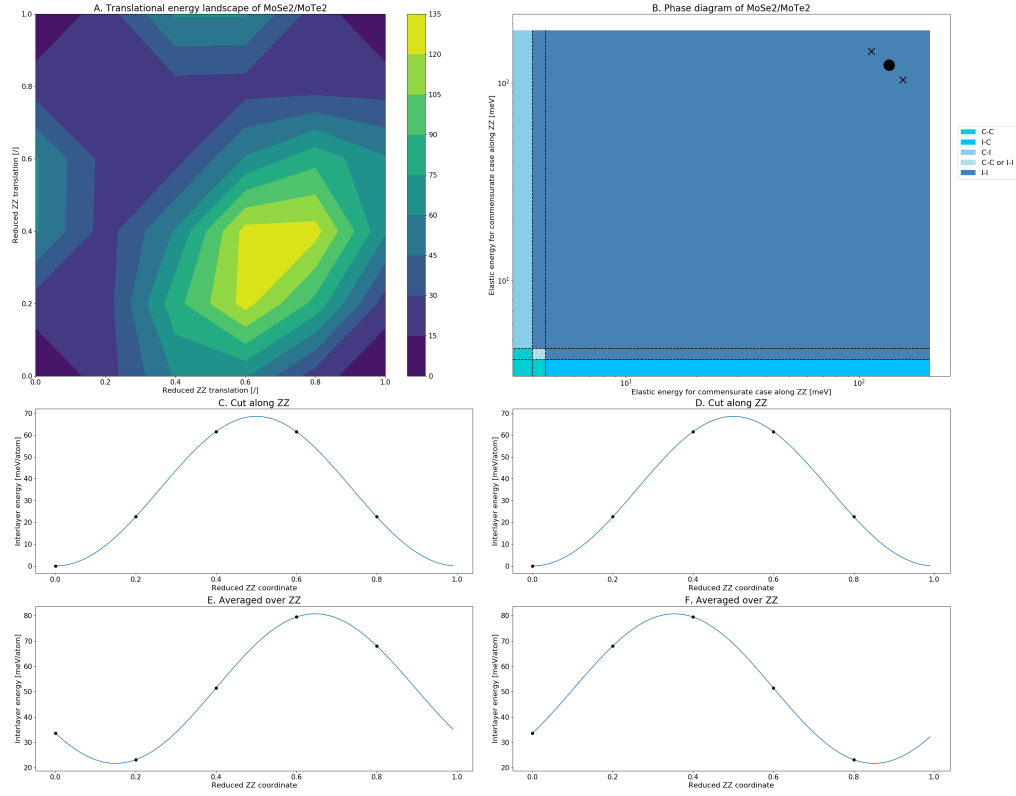


Figure C.12 – A : 2D potential landscape of MoSe₂-MoTe₂. B : Phase diagram obtained from the NODEC method (the position E₁-E₂ is indicated by the '•' symbol. C and D : 1D cut of the 2D potential landscape along the ZZ1 direction and along the ZZ2 direction respectively. E and F : Averaged potential over ZZ2 and ZZ1 seen along ZZ1 and ZZ2 direction respectively.

Appendix D

Table of results

D.1 Summary of the results of the "16 cases" method

D.2 Comparison of the criterion and elastic energy of the the different methods

Heterostructure	Criterion 1	Criterion 2	Criterion 3	Criterion 4	Criterion Benoit
P-MoSe ₂	0.101	21.929	10.896	19.424	27.15
MoSe ₂ -MoTe ₂	0.201	13.554	12.029	20.899	37.77
MoTe ₂ -WSe ₂	0.189	12.689	11.030	19.033	35.75
hBN-P	0.00175	0.0638	3.238	3.349	3.20
G-P	0.0160	0.0916	4.120	3.961	3.95
WS ₂ -WSe ₂	0.630	13.771	14.224	20.725	41.74
MoS ₂ -WSe ₂	0.668	13.765	14.504	20.617	41.26
MoS ₂ -MoSe ₂	0.786	14.213	15.737	20.914	45.55
MoSe ₂ -WS ₂	0.735	14.184	15.361	21.025	42.71
MoS ₂ -WS ₂	0.127	5.267	4.898	7.906	15.97
MoSe ₂ -WSe ₂	0.270	6.548	6.013	10.128	19.12

Table D.1 – Comparison of the different criteria used in the different methods. All the values are given in [meV/atom]. The data of this table are given for ZZ-AC unit cells.

Heterostructure	$E_{\text{elast,CC}}$	$E_{\text{elast,CI}}$	$E_{\text{elast,IC}}$	E_{elast} Benoit
P-MoSe ₂	66.415 (48.431)	0.101 (0.015)	62.024 (44.706)	75.3
MoSe ₂ -MoTe ₂	33.81	13.411	13.421	28.9
MoTe ₂ -WSe ₂	36.57	14.811	14.862	31.9
hBN-P	0.486 (2.967)	0.366 (0.723)	0.275 (2.858)	0.43
G-P	2.046 (5.512)	0.275 (0.0255)	1.194 (4.706)	1.73
WS ₂ -WSe ₂	8.739	3.598	3.551	10.8
MoS ₂ -WSe ₂	9.416	3.807	3.793	9.84
MoS ₂ -MoSe ₂	9.953	3.915	3.923	10.7
MoSe ₂ -WS ₂	9.271	3.706	3.681	9.45
MoS ₂ -WS ₂	0.0396	0.0145	0.0167	0.09
MoSe ₂ -WSe ₂	0.0235	0.00905	0.0102	0.05

Table D.2 – List of all the E_{elast} used in the "16 cases" method and in the work of Benoit Van Troye. All the values are given in [meV/atom]. The data of this table are given for ZZ-AC unit cells. The data in parenthesis corresponds to the case where monolayer parameters was used.

D.3 Results for unit cells along ZZ-ZZ

Heterostructure	Criterion 1	Criterion 2	Criterion Benoit
MoSe ₂ -MoTe ₂	23.855	27.108	37.77
MoTe ₂ -WSe ₂	21.486	25.387	35.75
WS ₂ -WSe ₂	27.265	27.541	41.74
MoS ₂ -WSe ₂	27.744	27.531	41.26
MoS ₂ -MoSe ₂	29.955	28.426	45.55
MoSe ₂ -WS ₂	29.309	28.368	42.71
MoS ₂ -WS ₂	9.439	10.534	15.97
MoSe ₂ -WSe ₂	11.653	13.095	19.12

Table D.3 – Comparaison of the different criteria used in the different methods. All the values are given in [meV/atom]. The data of this table are given for the conventional unit cell of TMD heterostructures.

Heterostructure	$E_{\text{elast,CC}}$	$E_{\text{elast,CI}}$	$E_{\text{elast,IC}}$	E_{elast} Benoit
MoSe ₂ -MoTe ₂	39.024	15.484	15.484	28.9
MoTe ₂ -WSe ₂	42.154	17.102	17.102	31.9
WS ₂ -WSe ₂	10.158	4.154	4.154	10.8
MoS ₂ -WSe ₂	10.893	4.396	4.396	9.84
MoS ₂ -MoSe ₂	11.481	4.521	4.521	10.7
MoSe ₂ -WS ₂	10.739	4.279	4.279	9.45
MoS ₂ -WS ₂	0.0425	0.0167	0.0167	0.09
MoSe ₂ -WSe ₂	0.0257	0.0104	0.0104	0.05

Table D.4 – List of all the E_{elast} used in the "16 cases" method and in the work of Benoit Van Troye. All the values are given in [meV/atom]. The data of this table are given for the conventional unit cell of TMD heterostructures.

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