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Computational study of synthesis, structure, property and application of low-dimensional materials

by

Yuanyue Liu

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APPROVED, THESIS COMMITTEE

Boris I. Yakobson, Chair
Professor, Department of Materials Science and NanoEngineering

Jun Lou
Professor, Department of Materials Science and NanoEngineering

James M. Tour
Professor, Department of Chemistry

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ABSTRACT

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Low-dimensional materials have attracted intense interest due to their unconventional properties and promising potential for applications. In this thesis, state-of-art computational methods are employed to study the syntheses, structures, properties, and applications of low-dimensional materials, including carbon nanotube, graphene, boron nitride and transition metal dichalcogenides. Special focus is given to the atomistic mechanism of chemical vapor deposition growth, defect structure and properties, Li-ion battery, and catalytic hydrogen production. Design of novel materials based on Materials Genome approach will also be presented.
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Chapter 1

Computational methods

This chapter describes the computational methods used in the thesis, including both classic and quantum-mechanic theories.

1.1. Density functional theory

Density functional theory (DFT) is one of the most popular quantum mechanical theory. It has been widely used in computational physics, and chemistry.

The main objective of DFT is to replace the many-body electronic wave function with the electronic density as the basic variable. Whereas the many-body wave function is dependent on $3N$ spatial variables, the electron density is a function of only three spatial variables and is a simpler quantity to deal with both conceptually and practically.

$$\hat{H}\psi = \sum_{i}^{N} -\frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i}^{N} V(r_i) + \sum_{i,j,i\neq j}^{N} U(r_i, r_j) \psi$$
The many-body system can be described by the above equation, where $V$ represents the ion-electron interaction, and $U$ is the electron-electron interaction. The most common implementation of DFT is through the Kohn-Sham method, where the many-body problem of interacting electrons in a static external potential is reduced to a problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the exchange-correlation interactions.

However, application of DFT is limited in a number of cases, e.g. it fails to give reasonably accurate band gap of semiconductors. Hybrid functionals are a class of approximations to the exchange–correlation energy functional in DFT that incorporate a portion of exact exchange from Hartree–Fock theory with exchange and correlation from other sources (ab initio or empirical). The exact exchange energy functional is expressed in terms of the Kohn–Sham orbitals rather than the density, so is termed an implicit density functional. One of the most commonly used versions is the HSE (Heyd-Scuseria-Ernzerhof) exchange-correlation functional. It uses an error function screened Coulomb potential to calculate the exchange portion of the energy in order to improve computational efficiency.

### 1.2. Molecular dynamics simulation

In molecular dynamics, successive configurations of the system are generated by integrating Newton’s law of motion. It results in a trajectory that specifies how the positions and velocities of the particles in the system vary with time. The interactions between particles can be implemented with empirical force field, semi-empirical force field, or even DFT.

One of the most commonly used force field for carbon system is the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential. It consists of three terms:
\[ E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[ E_{ij}^{\text{REBO}} + E_{ij}^{\text{LJ}} + \sum_k \sum_{l \neq i,j,k} E_{ijkl}^{\text{TORSION}} \right] \]

Where the \( E^{\text{REBO}} \) term has the same functional form as the hydrocarbon REBO potential developed by Brenner. For most cases it will produce the same energies, forces and statistical averages as the original REBO potential from which it was derived. However, it also has the reactive capabilities and only describes short-ranged C-C, C-H and H-H interactions (< 2 Å). These interactions have strong coordination-dependence through a bond order parameter, which adjusts the attraction between the \( i, j \) atoms based on the position of other nearby atoms and thus has 3- and 4-body dependence. The \( E^{\text{LJ}} \) term adds longer-ranged interactions using a form similar to the standard Lennard Jones potential. The \( E^{\text{TORSION}} \) term is an explicit 4-body potential that describes various dihedral angle preferences in hydrocarbon configurations.
This chapter starts from a theory on the edge of sp² carbon, and apply it to study the growth of carbon nanotube and graphene. This chapter also explores the synthetic routes to facilitate the experimental realization of currently non-existing material, e.g. two-dimensional boron.

2.1. Chirality-controlled CNT growth: insight from its edge energy

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While the lattice of graphene is very strong, significant variability at its edges defines the electronic properties as well as the growth dynamics,⁶ similar to the growth of its close sibling, the nanotube. Motivated by the challenge of possible selectivity, here we derive the graphene edge energy, from armchair (A) to zigzag (Z) and all intermediate orientation chiral angles. Supported by the first-principles computations, the essential dependence is always a sinusoid, \( \gamma(\chi) \sim \cos(\chi + C) \), but its “chemical phase shift” C varies with the conditions. This determines the variation in the equilibrium shape of graphene isles or ribbons. Moreover, it has profound implications in the
context of nanotube growth, offering rational ways to control their chiral symmetry, a tantalizing yet so far elusive goal.

Edge or surface energies both quantify the disruption of interatomic bonds. If all dangling bonds were equal in graphene, the edge energy proportional to their density would be higher for the more tightly packed armchair than for the less dense zigzag, by exactly a factor of $2/\sqrt{3} = 1.15$ [Figs. 2.1a and 1b]. However, this very difference in spacing allows the armchair atoms A to form triple bonds and thus lower their energy relative to the zigzag Z. This delicate competition of the energy per atom and their density makes the overall energy balance nontrivial and sensitive to the chemical conditions at the edge.

To derive an analytical expression for the edge energy, we begin with a simple observation that any lattice cut exposes two distinctly different types of atoms: either having another edge-atom neighbor, as in a purely armchair edge, or bonded to the 3-coordinated bulk-lattice neighbors, as in a purely zigzag edge. In Figs. 2.1a–c, the computed charge density maps, for pure A, pure Z, and a generic chiral edge, show this distinction clearly and support the energy-decomposition ansatz: An arbitrary edge energy can be evaluated as $C_A \varepsilon_A + C_Z \varepsilon_Z$ by counting the edge carbon atoms.
Figure 2.1. Different atomic spacing along the armchair (A) and zigzag (B) edges results in distinctly different electron density distribution, with armchair edge atoms forming shorter and stronger triple bonds. This distinction between the two types of atoms is preserved in a mixed chiral edge (c), as the computed electron density illustrate (from blue for zero up to red for the highest value). Schematics of the edge (d) along the \((n,m)\) direction assists the atom counting: \(2m\) A atoms (count along the red line at 30°) and \(n-m\) Z atoms (count along the horizontal black line segment). Dividing these numbers by the length \((n^2+m^2+nm)^{1/2}\) of the edge (the diagonal on the left) yields the necessary densities \(C_A\) and \(C_Z\); in this example of the \((8, 3)\) edge, there are 6 of the A atoms and 5 of the Z atoms.

With a basis in a honeycomb lattice, an arbitrary edge direction can be specified by two components \((n, m)\) or by the angle between the edge line and the zigzag atomic motif, \(\chi\). Inspection of Fig. 2.1d then reveals \(2m\) of A atoms and \((n-m)\) of Z atoms, over the edge span of \(\sqrt{n^2 + m^2}\)
\( +n^*m \), henceforth using the lattice parameter \( l = 2.46 \text{ Å} \) as a unit. Eventually one obtains the edge energy as

\[
\gamma'(\chi) = |\gamma'| \cos(\chi + C')
\]

The last identity makes it clear that the energy must universally depend on the edge direction as sinusoid, with the phase-shift constant determined by the basic edges only: \( C' = \arctan(\sqrt{3} - 2 \frac{\gamma_A'}{\gamma_Z'}) = 1.2^\circ \).

Upon arriving at such a simple relationship, one is compelled to compare it with direct computations. Before turning to this, we note that the junctions between the A and Z domains along an arbitrary cut may add an AZ-mix energy correction. Energy can be computed at different levels of theory, all to be compared with Eq. (2.1), whose derivation is not based on any particular model Hamiltonian. Figure 2.2 shows the energies for A, Z, and a few chiral edges (analogs of the low-index and the vicinal planes in crystals) computed directly with classical forces or with density functional approximations. The data of all four methods follow the theoretical curves very closely, with small and always-negative AZ-mix corrections in the range of 10 meV/Å.
Figure 2.2. Edge energy $\gamma(\chi)$ as a function of chiral angle. The values are computed directly (dots) and obtained from Eq. (2.2) (lines). A pristine edge (black) is computed with four different levels of atomistic theory, as labeled: GGA (most realistic among the four, thick line) and LDA, as well as classical force fields REBO and AIREBO. Dark blue: The H-terminated edge data, with H taken either from an isolated atom state or from a $\text{H}_2$ molecule, to sample different chemical potential values. Light blue: Edge terminated by the Ni atom row, either from an isolated atom or from the bulk. Also in light blue is shown termination by a two-dimensional Ni atomic layer.

The logic above remains unchanged if the edge is terminated by another element, but the energy definition must be augmented by subtracting the cost $\mu N$ of the terminating atoms borrowed from a reservoir of chemical potential $\mu$. If the edge is attached to a cluster of fixed size $N$, this constant term is of no particular interest. Often, however, the terminating groups are docked to the edge atoms in one-to-one correspondence. In this case, the edge energy becomes:

$$
\gamma(\chi) = |\gamma| \cos(\chi + C)
$$

(2.2)
The prime sign in the notation is now omitted, for the edge terminated by other elements. In the latter, the amplitude $|\gamma|$ and phase shift $C$ are fully defined by the values for basic A and Z edges and the chemical potential of the terminating reactant. This analytical result can again be validated by comparison with direct ab initio computations. Figure 2.2 shows good agreement. More importantly, it reveals that the different chemistry of termination (the element H or Ni and its chosen chemical potential $\mu$) does change the phase shift $C$, as Eq. (2.2) predicts.

An analytical result (2.2) is compact yet general. It allows one to quickly evaluate the energy for arbitrary orientation (especially if matches no rational $m/n$, yielding aperiodic, computationally unaffordable structures). Deriving the equilibrium shape through Wulff construction from $\gamma(\chi)$ becomes a trivial exercise. The essential physics of the edge energy is all wrapped into a single parameter $C$. This “chemical phase” tells whether A, Z, or some intermediate edge has lowest or highest energy.
Figure 2.3. (a) The thick sinusoid is the normalized energy $\gamma(\chi)/|\gamma|$ versus the extended argument $\chi + C$. The thin segments each represent a 30° range of chiral angle for each specific case of edge termination, with accordingly computed chemical phase shifts C. The segments are labeled in the order of vertical positions, spaced to avoid overlap, for clarity. Change of the chemical potential $\mu$ can move the blue (red) segments within the blue (red) section of the sinusoid; Cu with a middle $\mu$ value is shown as an example. A chiral-angle window (light blue, here placed at the pristine graphene area) slides left or right according to the chemical conditions at the edge. (b)–(d) For nanotubes, the probabilities of nucleation outcome are calculated versus their edge chirality, as determined by the energy of fluctuations. The preferred chirality depends on the chemical phase C: At the left domain, a chiral tube could emerge (b); in the middle, the zigzag has lowest energy (c); and on the right, the armchair is most probable (d).

To this end, Fig. 2.3a shows the normalized edge energy $\gamma(\chi)/|\gamma|$ as a function of its extended argument $\chi + C$, where $\chi$ is a geometrical angle while $C$ is the chemical phase (determined by the chemical type of terminating element and its chemical potential). For each given case, only
the A and Z for basic edges need to be directly computed; then with the proper choice of $\mu$, the chemical phase shift is $C = \arctan[(\sqrt{3} - 2 \gamma_A / \gamma_Z + \mu / \sqrt{3} \gamma_Z) (1 - \mu / \sqrt{3} \gamma_Z)]$. In this summary plot we omit for clarity the comparison details of Fig. 2.3 but extend the number of examples: pristine edges (four methods), terminated by an atom row (H; F; Co; Cu; Fe; Ni) or a 2D monolayer of Ni. We first note the variability between the terminating elements, when the A edge is preferred for some, while the Z edge has lower energy with the others. We also note how, even for a given element, the change of its source (feedstock) chemical potential alters the phase $C$ in a broad range. Interestingly, all termination types divide formally into two families, marked by different colors: If $\sqrt{3} \gamma_A < 2 \gamma_Z$, then the phase $C$ varies from $-30^\circ$ up to $150^\circ$ (blue), while if $\sqrt{3} \gamma_A > 2 \gamma_Z$, then the phase $C$ varies from $-30^\circ$ down to $-210^\circ$ (red), upon the increase of chemical potential. Accordingly, the 30-wide chirality window (light blue) slides along the sinusoid, defining the edge energy behavior.

The above analysis gives the energies of graphene edges, from A to Z, through all intermediate chiral directions. It shows how the preferred orientation depends on termination and how it can—at least in principle—be broadly controlled by the chemical potential of the terminating species. Equation (2.2) makes predicting the equilibrium shapes of graphene islets straightforward. Dependence on termination conditions suggests a variety of ways to control the shape of graphene during its growth. This does not change the graphene “body” yet is important for the edge properties.

It cannot escape one’s notice that the very same analysis has profound implications for nanotubes, where the origin of chirality and possibility of its control remain elusive in spite of its tremendous importance. The tube chirality is set at the nucleation stage, when a complete cap (hemifullerene made up of hexagons and a required sextet of isolated pentagons) emerges from carbon atoms fluctuating on a catalyst. The probability of fluctuations is controlled by the energy, which includes the catalyst, $sp^2$-carbon cap, and their contact along the circular edge [Figs. 2.3b–d),
insets]. Among these contributions, only the latter depends on the edge type, determined by the angle — also the chiral angle of the commencing tube. Therefore, the probability of different chiral types is defined by the edge energy. Since the diameter $d$ is constrained by the size fit with the catalyst particle, the cap curvature energy varies little, leaving the chiral angle as the essential variable defining the probability $\sim e^{-\pi d \gamma(\chi) / k_b T}$. We see that the preferred tube chirality is defined by the function in Eq. (2.2). A number of observations follow. First, a strong energy bias in the case of a bare edge could be good for strict chirality choice, but the high energies in this case destabilize an open tube and disable its growth without a catalyst being attached, as is well known. Attachment of foreign species mitigates the energy differences among chiralities, reducing $|\epsilon_A - \epsilon_Z|$ to a seemingly negligible several meV. The factor $\pi d \sim 30$, however, brings the total edge energy variation back to values $> k_b T$ and therefore sufficient to discriminate among the chiral types. As Fig. 2.3 shows, chirality selection is fully determined by the phase $C$, depending in turn on the chemistry of species docked to the tube edge. Fig. 2.3 not only suggests the ways of broad variability of chiral bias, it also reveals potential difficulties due to the sheer mathematical form of cosine. It is easy to imagine a swap from A to Z preference by shifting the chirality window from the downhill to the uphill side of the sinusoid [from Fig. 2.3d to c)]. It appears challenging, though, to tune the energy minimum to the middle of the $30^\circ$ window, to a chiral type [Fig. 2.3b]: Needed for this, a convex $\gamma(\chi)$ is available only if $-210^\circ < C < -180^\circ$, in the domain of negative interface energies, where the growth is unlikely. We refrain from saying it is impossible, but it may require special quasi-equilibrium conditions, to favor a chiral tube edge yet not to cause its dissolution. It should also be noted that control by chemical potential is irrelevant if the catalyst is a fixed-size monoelemental, as $N$ remains constant independent of $\mu$. On the other hand, this tuning knob can be fully utilized if the number of terminating atoms directly correlates with the number of edge atoms, which can be the case for binary compositions with different affinity of the components to carbon.
A number of details can be added to the above theory, especially how the graphene is docked to a bulk substrate or how a cylindrical tube matches the catalyst particle, which imposes its own crystallinity and possibly facets. This complicates the analyses but can also reveal more ways for chirality control through the carbon-catalyst interface energetics. We realize the limitations of the present work but believe it does capture and quantify the principal factors. With more evidence and supporting arguments, this approach can offer a road map for graphene edge design and especially rational chirality control.

2.2. Atomistic mechanisms of graphene growth

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The morphology of graphene is crucial for its applications, yet an adequate theory of its growth is lacking: It is either simplified to a phenomenological-continuum level or is overly detailed in atomistic simulations, which are often intractable. Here we put forward a comprehensive picture dubbed nanoreactor, which draws from ideas of step-flow crystal growth augmented by detailed first-principles calculations. As the carbon atoms migrate from the feedstock to catalyst to final graphene lattice, they go through a sequence of states whose energy levels can be computed and arranged into a step-by-step map. Analysis begins with the structure and energies of arbitrary edges to yield equilibrium island shapes. Then, it elucidates how the atoms dock at the edges and how they avoid forming defects. The sequence of atomic row assembly determines the kinetic anisotropy of growth, and consequently, graphene island morphology, explaining a number of experimental facts and suggesting how the growth product can further be improved. Finally, this analysis adds a useful perspective on the synthesis of carbon nanotubes and its essential distinction from graphene.
Recent years have seen development of ever simpler and cheaper methods to produce graphene on metal substrates. Yet the quality of as-produced material suffers from defects and polycrystallinity, with electronic transport orders of magnitude inferior to mechanically exfoliated graphene. Understanding the atomistic mechanisms governing the sp² carbon growth remains a scientific challenge, critical for production of quality graphene, as well as controllable growth of nanotubes. Experimentally, graphene grows at very different conditions, on many different substrates, and from various precursors. Detailed atom-by-atom sequence of carbon accretion to the sp² lattice remains essentially unknown. How are these states ordered in space and in energy scale? Accordingly, which are populated or empty, and what serves as the bottleneck controlling the growth rates of different crystallographic faces? The answers to these questions determine how the equilibrium shape is replaced by its kinetic alternative, and how the excess nonequilibrium, $\Delta \mu \equiv \mu - \mu_0 > 0$, might impose defects into the generally highly periodic lattice.

These questions compel one to step to a more detailed and quantitative view, by assigning specific energies to different locations of C-atoms, migrating toward the edge of graphene lattice, across the metal-carbon interface zone, a nanoreactor. To this end, here we combine crystal growth theory and first-principles atomistic computations. First, the edge energy $\gamma(\chi)$, definitive for the equilibrium shapes, is calculated for all edge orientations (angle $\chi$, measured from the zigzag lattice direction) on different catalyst substrates. Then we turn to non-equilibrium to investigate how the energy changes upon addition of C-atoms, and focus on the nucleation of consecutive atomic rows. Computed energy levels at different sites (on the catalyst or at the edge, including possible imperfections) dictate their occupancies, resembling a form of Fermi-statistics, with each site occupied by no more than one atom. Further, the step flow growth ideas combined with computed nucleation barriers allow one to evaluate the growth rates $v(\chi)$, for different directions. Notably, the similar growth kinetics manifests itself in strikingly different ways for carbon nanotubes (CNT) and graphene. For graphene, as a simple corollary of kinetic Wulff construction, the perimeter type
is selected and the island shape is defined. This kinetic shape selection contrasts with nanotubes whose edge chirality is locked by their cylindrical topology and thus each individual tube just keeps growing with its own chirality-controlled speed. For the substrate, we used trigonal surfaces of four metals: Ni, Fe, Co, and Cu, catalysts often used for CVD growth of both graphene (Ni, Cu, Co) and CNT (Ni, Fe, Co); the main focus is on Ni, used frequently for the synthesis of both CNT and graphene.

In equilibrium, an obvious initial concern is the structure and the lowest ground-state energy of the edge. Given the edge free energy per unit length $\gamma(\chi)$, the Wulff construction readily yields the thermodynamically optimal shape. We make use of the analytical expression, $\gamma(\chi) = 2\gamma_A \sin(\chi) + 2\gamma_Z \cos(30^\circ - \chi)$, which reduces the direct computations to just the energies of two principal directions, A and Z.
Figure 2.4. Equilibrium shapes of graphene. (A) Graphene edge structures and notations. (B) DFT edge energies on different metals and in vacuum, for comparison. (C) Wulff constructions for graphene on metals; blue lines denote Z edge, red represent A edge (on Cu) or A5'-edge (on Ni, Fe, Co), green curve is a polar plot of the edge energy.

Using DFT, we computed edge energies for graphene on metals, including not only generic A and Z edges, but also their self-passivating reconstructions that reduce dangling bond density at the expense of lattice strain, A5 and Z57 (Fig. 2.4A). Unexpectedly, the A5 structure turned out to be
unstable on all the metals: Geometry optimization led to another structure, which we refer to as A5’ for open pentagon armchair. Moreover, for Fe, Co, and Ni this structure has lower energy than the unreconstructed A edge, making it the ground state for A-orientation. Because the surface atoms that bridge twofold- and single-coordinated carbon atoms are pulled slightly (approximately 0.3 Å) out of the metal surface plane, the open pentagons can alternatively be viewed as buckled hetero-hexagons with one carbon substituted by metal, Fig. 2.4A, Bottom. Fig. 2.4B summarizes the edge energies on all four metals and in vacuum, revealing interesting trends. First, the Z57 is energetically unfavorable (in contrast to vacuum, where it happens to be the lowest energy edge known). Second, the unreconstructed A edge has higher energy than unreconstructed Z—again, in a marked contrast to vacuum environment. Finally, the A5’ edge energy is lower than that of Z edges on Fe and Co, and the two are almost equal on Ni. All these trends are explicable: Whereas in vacuum it pays off energetically to saturate dangling bonds at the expense of lattice strain by forming nonhexagonal polygons, on a substrate metal atoms provide some saturation without straining the lattice, making reconstruction unnecessary (moreover, the high edge energy on Cu correlates with the low solubility).

With full γ(χ) at hand, the Wulff construction plots can be readily obtained (Fig. 2.4C). We only show one quadrant for each metal, but full shapes can be recovered by reflection symmetry. Red and blue lines denote A and Z edge directions, and the green is the polar plot of γ(χ). The variety of shapes covers the full spectrum of possibilities. On Ni, the small difference of Z and A5’ edge energies leads to a smooth rounded equilibrium shape. On Fe and Co, the energy of A5’ edge is so low that it dominates the hexagonal shape completely. Finally, on Cu, the equilibrium shape of a graphene isle is a hexagon having only Z edges. Thus, the thermodynamically optimal shapes of graphene islands are diverse and vary from metal to metal.
Near the equilibrium, slow growth cannot invalidate Wulff construction abruptly. At very low rate of carbon accretion, an island of size \(L\) still tends to preserve its thermodynamic shape, maintained by the diffusion \((D)\) around its perimeter, if the redistribution time \(t_{\text{diffusion}} \propto L^2/D\) is much shorter than the size-change time \(t_{\text{growth}} \propto L/v\). This condition \(vL \ll D\) holds for small islands and slow growth. One concludes that in this quasi-equilibrium regime the island simply scales up with the apparent propagation speed of each facet proportional to its energy, \(v(\chi) \propto \gamma(\chi)\).

Further away from equilibrium, more relevant for the actual growth conditions, the growth rate of each facet does not depend on others and is determined by the process of atoms attachment. To unravel its details, here we invoke the ideas of step-flow growth of crystals in the canonical Burton–Cabrera–Frank representation. The growing edge of graphene assumes the role of the surface step. It moves forward by incorporating to its active sites the carbon atoms arriving through the substrate. We first consider the docking of atoms to the two fundamental graphene edge directions (A and Z) on the Ni catalyst. We then discuss arbitrary edge orientations on Ni and other metal catalysts.

**Figure 2.5.** The nanoreactor diagram for A5’ and Z edges growth on Ni substrate. Carbon atoms migrate from the source (metal substrate, leftmost levels) to the product (graphene, rightmost) by...
sequentially populating energy levels in the middle that represent energies of nth carbon atom at the extending row already containing $n - 1$ atoms. (The occupancies at $kT = 0.1$ eV are marked by thicker segments.) Lowest-energy atomic configurations are shown in the bottom. The green line sets the chemical potential $\mu$ of carbon atoms (established by the feedstock gas).

Starting from perfect A5’ or Z edges we sequentially add atoms, and for each such addition screen multiple metastable configurations. Covering both lowest-energy structures and possible defects such as pentagons, heptagons, or dangling linear chains, we compute the energies using DFT to assess their formation probability. The results are summarized in Fig. 2.5. C atoms from feedstock (chemical potential $\mu$ set by horizontal dashed line) are first adsorbed on the metal substrate. Fig. 2.5 left, shows the computed energies of available sites marked as lines, with thicker segments representing their probability-occupancy by incoming atom, evaluated at $kT = 0.1$ eV by the Fermi function $p(\epsilon) = 1/[1+e^{(\epsilon-\mu)/k_BT}]$, accounting for the exclusion principle of no more than one atom per site. In spite of its limited applicability to a non-equilibrium high gradient process, it serves best to assess the likelihood of different configurations. The rightmost line represents the binding energy $\mu_0$ of graphene, on Ni. The multiple lines/levels in between represent binding energies $\epsilon_n$ for each successive carbon atom addition, $n = 1; 2; 3…$, and are filled sequentially. Red and blue correspond to the A and Z edges.

This quantitative diagram could be detailed further by including other possibilities on/in the metal (Left), considering additional specific configurations at the graphene edges (Center), or considering other substrates. Yet already in present form it captures main behaviors and reveals a number of important aspects. Overall, it shows the substrate’s key roles in the $sp^2$ lattice assembly: Not only (i) does it serve as a planar template, but (ii) it also prevents formation of defects at the very front of growth, thus making their posterior annealing unnecessary. Indeed, the lowest-energy states sequence in the bottom of Fig. 2.5, defining the lattice-building path, never includes defects. Notably, the states containing pentagons or heptagons, a 5/7, or dangling carbon chains are all
higher in energy and consequently are suppressed. This suppression would not happen in vacuum, with no substrate: Pentagon and heptagon formations are relatively low in energy and therefore probable, causing reconstruction of sp\(^2\) edges with 5s and/or 7s, which are responsible for closure of nanotubes or fullerene cages. Further, (iii) the nanoreactor scheme of Fig. 2.5 also explains the highly defective outcome of essentially all molecular dynamics or Monte Carlo simulations of growth [regardless the choice of interatomic force field]. The exceedingly high rate of carbon deposition in MD studies corresponds to the excessive chemical potential which populates the defect states—higher levels in Fig. 2.5—so they do form frequently and corrupt the lattice. Besides explaining the prevention of topological defects, (iv) the diagram also shows that protruding fingers are higher in energy and unlikely to happen, which prevents branching into dendrites—unless again \(\mu\) is raised high enough to allow their formation. This observation can explain the dendrite flakes often forming on Cu, which indeed has higher energies for C sites in the left of Fig. 2.5. In spite of the diagram’s complexity, there are notable regularities. (v) After just a few initial atoms, a periodic up-down alternating level sequence is established. The energy variation amplitudes differ for A and Z edges, but the average value for either edge is the same, and equals the binding energy of graphene (the rightmost level). Interestingly, (vi) this diagram shows clearly how beneficial it might be to have carbon provided in the form of C\(_2\) (dimers). If the substrate favors them rather than monomers, the dimers’ subsequence skips the heights, permitting faster and perhaps better quality growth (yet less chance for defects). (vii) The initial atomic levels are crucial and show a fundamental distinction between A and Z edges: For Z, the first atom addition is strongly endoergic, and it is likely to fall back onto the substrate, whereas the subsequent Z levels all lie below the high-energy states for the A edge sequence.
Figure 2.6. Free energy evolution during growth, Δμ = 0 (Top) and Δμ = 0.3 eV (Bottom, with characteristic nucleation barrier). Green lines represent kinkflow growth of skewed (6, 1) edge. Dashed lines show periodic repetitions due to finite size of supercells used in calculations, which corresponds to the growth of a next atomic row upon the completion of the previous.

This row-nucleation stage is convenient to analyze using the total free energy evolution in Fig. 2.6, obtained as the partial sums over lowest-energy states in Fig. 2.5, \( \Delta G(N) = \sum_{n=1}^{N} (\varepsilon_n - \mu) \).

More telling is the lower plot of Fig. 2.6, showing free energy variation at a moderate value of Δμ = 0.3 eV. For Z edge, a substantial barrier has to be overcome to nucleate a new row, after which growth proceeds with a monotonous decrease of energy. For A edge, the nucleation barrier is much smaller, but remains present at every other atom addition (a somewhat larger Δμ \( \geq 0.7 \) eV is needed for A edge to grow unobstructed downhill). It is evident that growth of Z edge comprises two stages. The first is nucleation of a new atomic row, and then the sequential addition of atoms to the kink sites at its ends (Fig. 2.5), or kink flow. The first stage is slow, and the second is very fast. At intermediate orientations, edges contain both Z terraces and kink sites, and concentration of kinks becomes the dominant factor for the overall growth rate. The green line in Fig. 2.6 shows calculations for the (6,1) edge, with the same oscillation amplitude as in the kink propagation stage.
in Z plot, but with no nucleation/termination of kinks, so that the overall growth of the skewed edge ends up being faster than both A and Z edges.

**Figure 2.7.** Anisotropy of growth velocity. (A) Concentrations of different active sites (per lattice parameter) with respect to edge orientation $\chi$. Red, blue, and green lines represent A, Z, and kink sites. (B) Kinetic Wulff construction for graphene on Ni. Green line is a polar plot of $v(\chi)$, red and blue lines show envelope velocities of pure A and Z edges. The left half uses artificially raised $kT=0.3$ eV, and the right uses a realistic $kT = 0.1$ eV but a log$_{10}$ scale. (C) DFT-computed free energy nucleation barriers for edge propagation on different metals, for $\Delta \mu = 0$.

We are now ready to formulate an expression for direction-dependent growth velocity, $v(\chi)$. We obtain closed-form expressions for the concentrations $s_K$, $s_A$, and $s_Z$ of the active sites at kinks, armchair, and zigzag edge-segments, and they are plotted in Fig. 2.7A. Then, the carbon precipitation rate, i.e., growth velocity, is proportional to the sum of site concentrations times the respective probability factors:

$$v(\chi) = 2s_K e^{-\frac{E_K}{k_bT}} + 2s_A e^{-\frac{E_A}{k_bT}} + N^* s_Z e^{-\frac{E_Z}{k_bT}}$$

(2.3)
Here, $E$ represents the free energy barriers and $N^*$ is the critical Z nucleus size, and so plugging our computed above DFT values we obtain the speed of propagation as a function of arbitrary edge direction $v(\chi)$, plotted in Fig. 2.7B. For graphene, a simple immediate corollary obtained with kinetic Wulff construction, is that a growing island is a hexagon with entirely Z perimeter. Same holds for the other metals, and Fig. 2.7C compares the growth barriers for A and Z propagation, the shape-defining minima of $v(\chi)$. The barrier difference $E_Z - E_A$ is invariably large, from 0.8 eV (the smallest, on Co) and up to as much as 2.4 eV, on Cu. Therefore, A sides advance much faster, and the overall shape must always be limited by the lagging Z edges, a conclusion being universal independent of the substrate metal, in contrast with the thermodynamic equilibrium shapes on Fe, Co, and Ni (while on Cu, graphene grows in the equilibrium shape).

These results suggest a simple morphological evolution scenario for a graphene flake of arbitrary initial shape. At nearly equilibrium conditions, the lateral transport ensures that it grows with the thermodynamic shape being maintained. [Note that in this regime, $v(\chi) \propto \gamma(\chi)$, and thus both equilibrium and kinetic Wulff’s recipes concur.] Away from equilibrium, when the transport around the entire perimeter is relatively slow, the individual edges/facets establish their own propagation speeds $v(\chi)$, with sharp minima for the basic A and Z facets ($\chi = 0$ or $30^\circ$). Consequently, all skewed edges advance quickly via kink flow, are weeded out into Z and A segments, and finally to the slowest all-Z perimeter hexagon—the asymptotic steady state result of kinetic Wulff construction. Such selection changes any initial flakes into Z-edged hexagons, growing further via nucleation of new atomic rows and kink flow. This convergent evolution is in striking contrast with growth of tubes, whose cylindrical topology forbids edge chiral angle from changing, leading to different kinetic behavior. For a nanotube, the atomic dynamics in the nanoreactor zone near the edge is essentially the same as for graphene. However, its chirality prescribes the edge orientation, and cylindrical topology makes kink propagation perpetual barring formation of 5/7 defects that change chirality, as observed in simulations. Consequently, there is no simple kinetic
selection of the edge type (like for flat graphene), but instead each tube maintains its own stationary chiral edge structure and its own growth speed.

Beside the several behaviors derivable directly from the nanoreactor diagram (defectless growth, nucleation of edge-additions, speed vs. direction, edge energies and shapes, either equilibrium or kinetic), additional interesting aspects can be related and further explored separately. Our results can offer an interpretation of nonlinear, high power concentration dependence of graphene growth rate. As described above, the late-stage growth rate is limited by formation of kinks upon nucleation of new atomic rows on Z edges, with some critical nucleus size causing the power dependence (see Fig. 3). A power-law dependence on concentration of C feedstock can be a natural consequence of the nucleation–kink-flow scenario. Moreover, factors such as carrier gas, presence of water vapor, or molecular hydrogen are seen to play important but poorly understood roles in the growth of carbon nanomaterials. They may deplete specific sites in the nanoreactor, thus improving the transport and avoiding defects or even growth termination. Experiments with graphene show a broad variety of flake shapes, from hexagons with almost exclusively Z edges to continuous shapes with smooth or rough sides to dendrites. The latter are undesirable for applications and typically result from diffusion-limited aggregation, when carbon sticks to most positions—which in Fig. 2.5 happens if chemical potential excess $\Delta \mu$ is greater than the edge energy (per atom), and protruding hexagons can form uninhibited. The diagram suggests a window $0 < \Delta \mu < 1$ eV (gray band in Fig. 2.5) to avoid dendrites while maintaining growth (as opposed to etching/dissolution). Notably, calculated levels on Cu are rather high, and this placement correlates with often observed dendritic shapes.

In summary, we recast a complicated non-equilibrium dynamics near the border of a growing graphene lattice into the detailed yet tractable diagram (Fig. 2.5) of energy levels available to C atoms as they move from substrate to the carbon phase. As a key to growth mechanisms of
graphe (and, with some modification, nanotubes), this nanoreactor scheme represents an advance from a qualitative VLS paradigm, canonical in nanotubes and wires growth research. It invokes the seminal concepts of crystal growth theory, enriched with a bulk of important quantitative details of carbon-metal interactions computed with first principles methods. In the equilibrium case, we determine the edge structures and energies, and accordingly, plot the Wulff construction shapes, varying among the substrates (Co, Cu, Fe, or Ni). Through the nanoreactor diagram, we find that metal substrates prevent formation of nonhexagonal edge reconstructions and any defective configurations during growth (and also explain the excessive disorder in the bulk of MD simulations). Further, it shows exact steps of carbon accretion: Kink propagation has a small energy barrier (which might even fully vanish if the feedstock and catalyst provide carbon in the dimer form, C2), but for creation of kinks, considerable nucleation barriers must be overcome—especially on the zigzag edge. Together, these data allow one to calculate the general growth speed dependence on the facet direction $v(\chi)$, and to easily establish—by virtue of kinetic Wulff construct—the non-equilibrium shape. Because the zigzag edge is decidedly the slowest, an effect that is especially pronounced if Cu is used as the substrate, the growing graphene isles are universally hexagonal with zigzag perimeter, as observed in a large body of experimental evidence. This behavior notably contrasts with nanotubes, where similar interface dynamics is at play, but because of their cylindrical topology, it leads to entirely different conclusions. First, tube chirality is invariant, precluding changes of edge type. Then, common kinetic effects favor nanotubes with near-armchair edges, whereas in graphene growth, zigzag edge seems to dominate universally.

2.3. Synthetic routes for two-dimensional boron

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The synthesis of novel two-dimensional (2D) materials has attracted considerable interest due to their various unique properties. While the experimental realization of 2D boron (2D-B) sheets remains a challenge, it is important to theoretically investigate the possible fabrication methods. Here we explore the formation of B sheets on metal (Cu, Ag, Au) and metal boride (MgB\textsubscript{2}, TiB\textsubscript{2}) substrates via first-principles calculations. Our results suggest that B sheets can be grown on the Ag(111) or Au(111) surfaces by deposition. B atoms decomposed from precursor, and driven by the gradient of the chemical potential, will assemble into 2D clusters and further grow to a larger sheet, while formation of three-dimensional B (3D-B) structures could be impeded due to a high nucleation barrier. In addition, saturation of B-terminated MgB\textsubscript{2} surface in B rich environment can also lead to the formation of B sheets. These sheets are weakly bound to the substrates, suggesting feasible post-synthesis separation into the free-standing forms. Our work proposes feasible approaches to synthesize 2D-B, and could possibly pave the way towards its application in nano-electronics.

The B sheets\textsuperscript{9-25} are among those 2D materials which promise to have interesting properties and applications, yet remain impeded by the difficulties of experimental synthesis.\textsuperscript{26-29} In particular, the metallic character of 2D-B makes it a potential complement to graphene, h-BN, and metal-disulfides that may constitute ultimate building components in device designs. Unlike graphene, however, the accumulated theoretical knowledge on 2D-B has not yet materialized experimentally. In contrast to previous theoretical studies,\textsuperscript{9-25} focused on the structures and stability of hypothetical 2D-B sheets, here we attempt to assess the feasibility of, and suggest some guidelines for practical routes towards their synthesis. Such theoretical investigation of the synthesis before its experimental realization is challenging, and cannot be comprehensive, but can quantify certain aspects and possibilities.

We propose and analyse synthesis methods, based on those established for graphene. One would be the exfoliation\textsuperscript{30,31} from layered materials with weak inter-layer binding; however, no
such precursor boron material exists in nature, which rules out the exfoliation approach. (i) 
Deposition, especially chemical vapor deposition$^{32,33}$ of B on catalytic substrate, either a pure metal or metal-terminated metal boride. The observed reconstruction of B-terminated boride surfaces$^{34}$ suggests another approach; (ii) Saturation by B deposition on the B-terminated surface of borides under B-rich environment, to form a B sheet; (iii) Evaporation of metal atoms$^{35}$ from metal borides at high temperature. In order to probe the feasibility of these methods, we perform first-principles calculations focusing on the following fundamental questions: (1) What are the atomic structures of $^{2D}$B on substrates and how they compare to the theoretically studied free-standing B sheets? (2) Is it energetically favorable to form $^{2D}$B on substrates, compared to other configurations such as B adatoms, clusters, or $^{3D}$B phases? (3) If formed, would it be possible to separate the B sheets from substrates after synthesis?

The choice of substrate is critical for the synthesis process. The epitaxial growth of graphene on Cu(111) surface$^{36,37}$ suggests that a good substrate should have low B solubility$^{38}$ while serving as a flat template for $^{2D}$B. Many metals are known to form borides, including those widely used for carbon nanotube growth (Fe, Co, Ni).$^{39,40}$ Group-11 elements, Cu, Ag, and Au, do not form borides, thus are selected here as substrates to model the deposition of B. In particular, the Ag(111) surface has been utilized in recent experiments on synthesizing 2D silicon$^{29}$ and ZnO.$^{26}$ The $^{2D}$B can also be expected to form from the borides which are composed of alternating metal and graphene-like B layers, e.g., MgB$_2$ and TiB$_2$, used here to represent the family of non-transition metal borides and the transition metal borides, respectively.

A broad variety of $^{2D}$B sheets can be described as B$_{1-x}$V$_x$ pseudoalloys,$^{20}$ where V represents vacancy in a parent triangular lattice (for example, $x = 1/3$ corresponds to a hexagonal sheet). In vacuum, the energetically optimal fraction of vacancies falls in the range $0.1 < x < 0.15$, where numerous sheet structures with various vacancy patterns are found to be nearly degenerate in
energy, suggesting a polymorphic state.\textsuperscript{20} One of the most stable sheets, the α-sheet \((x = 1/9)\),\textsuperscript{20} and its structural relatives have been intensively studied.\textsuperscript{10, 11, 13, 16-18, 22, 24, 25} Here, ten types of B sheets with different vacancy concentration \(x = v/27\) \((v = 0–9)\), are constructed to explore general trends in properties as a function of \(x\). Details of the construction procedure can be found in the Supporting Information (SI). These sheets are among the most stable ones in vacuum for given \(x\).\textsuperscript{20} With the above provisions, we can formulate more specifically the scenarios for synthesizing 2D B: (i) Deposition of B on the (111) surfaces of fcc Cu, Ag, Au, and the metal-terminated (0001) surfaces of MgB\(_2\) and TiB\(_2\); (ii) Saturation of B-terminated MgB\(_2\) or TiB\(_2\) surface in B rich environment; (iii) Evaporation of MgB\(_2\) or TiB\(_2\) at high temperatures. For each of these possibilities, we address the set of questions (1–3) posed above.
Figure 2.8. Atomic structure of 2DB sheets \((x = 0, 1/9, \text{ and } 1/3)\) in vacuum and on substrates: Ag(111) and Mg-terminated MgB2(0001) surfaces. 2DB is represented as a line network and the larger bright spheres are metal atoms (for clarity, only the topmost metal layer is rendered). The plot shows the chemical potential \(\mu\) (Eq. 2.4) of B sheets as a function of vacancy concentration \(x\) in vacuum and on different substrates: Cu(111), Ag(111), Au(111), Mg-terminated MgB2, and Ti-terminated TiB2 surfaces. The vertical axis is broken at the \(\mu\) of bulk \(\alpha\)-B.

To compare the stability of different B sheets (the first question), we calculate the energy of B atoms in the corresponding configurations (essentially, the chemical potential \(\mu\) at zero temperature, as shown in the SI) as:
\[ \mu = \frac{(E_{\text{B-sheet/substrate}} - E_{\text{substrate}} - N_B E_{\text{B-atom}})}{N_B} \]  

where \( E_{\text{B-sheet/substrate}} \) is the total energy of the B sheet with the substrate, \( E_{\text{substrate}} \) is the energy of the substrate without B, \( E_{\text{B-atom}} \) is the energy of B atom in vacuum, and \( N_B \) is the total number of B atoms in the system. The \( \mu \) values of B sheets are shown in Fig. 2.8.

In vacuum, we find that the free-standing hexagonal B sheet (\( x = 1/3 \)) cannot preserve its hexagonal lattice under small perturbations (in accord with the detected existence of unstable phonon modes). It would collapse into a disordered sheet with close-packed triangular domains and large voids, as shown in Fig. 2.8. The nearly-amorphous sheet has energy much lower than the periodic hexagonal sheet by almost 0.7 eV/atom. In this case, although “vacancy concentration” is not a well-defined term, we can still use it for consistency with literature. In fact, at high vacancy concentration (\( x > 5/27 \)), all the low-energy B sheets appear amorphous (structures are shown in the SI). The clustering of vacancies into large holes in B sheets has also been noted recently in other reports\(^{11,41}\). The amorphous structures are also known to exist in the B fullerenes\(^ {42}\). Nevertheless, at low \( x < 6/27 \), the hexagonal framework is sustained and the \( \alpha \)-sheet is the most stable one in this set.

When placed on Cu, Ag, Au, the B sheets with \( x > 6/27 \) are also amorphous. Fig. 2.8 shows the atomic structures of B sheets on Ag. At low B coverage (high \( x \)), the sheet is composed of stripes and voids, while it gradually restores the hexagonal framework at high B coverage (low \( x \)). In contrast, on MgB\(_2\) and TiB\(_2\), the B sheets with high \( x \) retain the hexagonal lattice, as a natural continuation of the bulk structure. One common feature shared by the B sheets is that they become more buckled with the decrease of \( x \) (increase of B coverage). In vacuum, the amorphous sheet is flat, while the \( \alpha \)-sheet buckles by 0.4 Å\(^{13}\) and the triangular sheet has height variation of 0.9 Å. On Ag, the buckling increases from 0.4 Å for \( x = 1/3 \), to 0.8 Å for \( x = 1/9 \), then to 1.8 Å for \( x = 0 \). Similarly, on MgB\(_2\), it varies from flat, to 0.4 Å, and then to 1.6 Å. Fig. 2.8 also shows that on
substrates the α-sheet is no longer the most stable one. Interestingly, the optimal vacancy concentration of 2D B sheets shifts to a higher x value, that is lower density, compared to that in vacuum.

Which type of B sheet could be synthesized depends on the formation route: (i) In deposition, B adatoms from the decomposed precursor should possibly assemble into a sheet with the lowest μ in Fig. 2.8. For illustration, Fig. 2.9 shows the atomic structures on MgB₂ and Ag. On the Mg-terminated surface of MgB₂, the B sheet has a hexagonal framework located on top of 3-fold hollow sites at ~1.8 Å distance from the surface, which is slightly larger than the distance between the B layer and Mg layer in bulk MgB₂ ~1.7 Å. A third of the hexagon centers (x = 2/9) are filled with B atoms, which sit on top of metal atoms with ~0.4 Å separation from the hexagonal plane. On Ag, the B sheet (β-type[1e]) is flatter (x = 4/27) but more distant from the substrate, ~2.5 Å, implying weaker interaction.

**Figure 2.9.** Atomic structure of B sheets, representing different synthesis methods: (a) deposition on metals and (b) metal-terminated surface of borides, (c) saturation of B-terminated surface of borides, and (d) evaporation of borides. Ag and MgB₂ are shown as representatives for metals and metal borides, respectively. Both top and side views are shown.
Unlike the deposition method, where the lowest-$\mu$ sheet is expected to grow,\textsuperscript{43} methods (ii) and (iii) lead to different forms of $^{2D}$B. (ii) For surface saturation, B atoms from the environment fill in the centers of B hexagons on the B-terminated surface.\textsuperscript{34} The vacancy concentration is fully determined by $\mu$ of B in the environment. By tuning $\mu$, one can in principle obtain various B sheets, from hexagonal to triangular,\textsuperscript{44} in contrast to the mono-type sheet produced by method (i). Fig. 2.9c shows the sheet with the weakest adhesion to MgB$_2$ substrate ($x = 1/9$, i.e., the $\alpha$-sheet, at $\sim 2.2$ Å distance from the surface). (iii) At the surface of metal borides, two hexagonal B layers are intercalated with one metal layer. According to the phase diagram of MgB$_2$,\textsuperscript{45,46} at $\sim 1100$ K and 1 atm pressure, the Mg atoms sublimate, leaving behind two hexagonal B layers inter-connected and forming a hexagonal bilayer on the surface, Fig. 2.9d. Our calculations show that the interlayer distance of the bilayer is only 1.5 Å. A similar mechanism operates in the formation of graphene via SiC evaporation,\textsuperscript{47} where, in contrast, the two carbon hexagonal layers bind with each other very weakly,\textsuperscript{48} resulting in an easy separation of the top graphene sheet from the underlying material.

In methods (ii)-saturation and (iii)-evaporation, hexagonal B layers pre-exist on the substrate. However, in method (i)-deposition, it is not obvious whether the B adatoms on the substrate would aggregate, or would tend to form disconnected populations. We find that on all the substrates, $\mu_{\text{adatoms}} > \mu_{\text{2D-cluster}} > \mu_{\text{sheet}}$, providing a driving force for growth. Figure S3 in the SI shows the decrease of $\mu$ as B assembles on Ag as an example, which asymptotically approaches $\mu$ of B sheet. However, as shown in Fig. 2.8, aside from TiB$_2$, the other substrates cannot decrease $\mu$ of $^{2D}$B below the value for bulk $^{3D}$B.\textsuperscript{49} At first glance, the bulk $^{3D}$B instead of the 2D sheet could be the growth product on these substrates. However, as shown in the SI, the high nucleation energy of $^{3D}$B could impede its formation, and thus the small B nuclei always have planar structures.\textsuperscript{50-55} In addition, the low solubility of B into substrates and fast diffusion on surfaces could help the B adatoms transport in a 2D channel,\textsuperscript{38} and grow the nucleus into a monolayer structure. The detailed analysis can be found in the SI.
The question (3) posed in the beginning can be addressed by calculating the adhesion energy, the work required to separate $^{2D}$B from the substrate. Fig. 2.10 shows the adhesion energies for different growth methods. As discussed above, growth by surface saturation of borides can result in various 2D-forms depending on $\mu$ of B in the environment, but only weakly bound ones can be separated from substrate. Therefore the sheet with lowest adhesion energy is chosen for comparison. The adhesion energies of graphite$^{56}$ and graphene on Cu(111) surface$^{57}$ are taken from the literature. The TiB$_2$ surface has strong adhesion with the B sheet, $> 0.2 \text{ eV/Å}^2$, in agreement with the high cohesive energy of bulk TiB$_2$. Only the $^{2D}$B grown by deposition on Ag, Au, or saturation of B-terminated MgB$_2$ surface has adhesion energy of the same order of magnitude as graphene on Cu, $< 0.10 \text{ eV/Å}^2$, thereby narrowing the synthesis options to deposition on Ag, Au, and saturation of B-terminated MgB$_2$ surface. The weak adhesion of the B sheet to Ag and Au surfaces has already been hinted at above by the large distance from the substrates $\sim 2.5 \text{ Å}$. The charge density difference plots shown in the inset of Fig. 2.10 illustrate how the electrons are redistributed upon the sheet-substrate contact formation. The electrons are transferred from Ag to B, while the Mg atoms under B sheet retain their original ionic states. Both substrates cause the depletion of in-plane $\sigma$ states and accumulation of out-of-plane $\pi$ electrons. However, it should be noted that the computational method employed here (density-functional theory, PBE exchange-correlation functional) generally underestimates the adhesion energy between substrates and adsorbates,$^{57}$ and an efficient computational scheme to obtain very accurate values is still lacking. Nevertheless, the current method is helpful, at least, to screen out the strongly-adhesive substrates.
Figure 2.10. Adhesion energies of B sheets to substrates, representing different synthesis methods: deposition on Cu, Ag, Au, MgB2 and TiB2; evaporation of borides, saturation of B-terminated surfaces of borides-MgB2 and TiB2. The adhesion energies of graphite\textsuperscript{56} and graphene on Cu\textsuperscript{57} are indicated. The cohesive energy values are those of bulk MgB2 and TiB2. The inset shows the charge density difference isosurfaces for B sheet on Ag and MgB2. The electrons accumulation is shown in blue and depletion is in red. The B layers are represented as light red ball-and-sticks and the topmost metal layers are shown as gray circles.

In conclusion, our analysis of growth scenarios based on first-principles calculations suggests the possibility of synthesizing $^{2D}$B on metals or metal boride surfaces. (i) Deposition of B on Au or Ag(111) surface can result in growth of $^{2D}$B, whereas a high nucleation barrier could impede the formation of 3D-structures; (ii) Saturation of B-terminated MgB2 surface under B-rich conditions can also lead to the formation of $^{2D}$B. In both cases, the B sheets bind weakly to the
substrates, suggesting a relatively easy post-growth separation. The present analysis may be potentially beneficial not only for B but could also provide a roadmap for theoretical investigation of growth of 2D-materials in general, and possibly help with their experimental realizations.
Chapter 3

Defects in low-dimensional materials

This chapter studies and compares the defect structure and electronic properties in various two-dimensional materials: graphene, boron nitride, phosphorus.

3.1. Cones, Pringles, and Grain Boundary Landscapes in Graphene

Topology

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Graphite is a polycrystalline bulk material whose three dimensions permit a variety of grain orientations, grain boundaries (GB), several types of dislocations, and point defects, all which have been studied for decades. In contrast, when reduced to the two dimensions, sheets of graphene cannot have the same rich variety of imperfections and their types are more restricted. High-resolution microscopy has made it possible to gain evidence of defects, even their temporal dynamics, in the context of carbon nanotubes and
recently graphene. The evidence of GB, the borders between the tilted perfect crystal domains of a single layer graphene, remains rather scarce. Yet they must form when graphene islands nucleate at different sites of a substrate and the neighbor islands are misoriented by some angle $\alpha$. As such islands grow large and run onto each other, the GB form (Fig. 3.1a). What atomic organizations emerge when all covalent bonds are sealed at the GB at its lowest energy? What are the elementary constituent defects in the GB, what extra energies do they carry, and how does the total GB energy depend on the tilt angle? These are generic questions in any GB study, yet in the context of graphene not systematically addressed. The goal of this work is to quantify the regularities in the GB structures, generally disordered and complex at the atomics scale, their energy behaviors, and their manifestations in the nonplanar distortions warping.

**Figure 3.1.** (a) Two-dimensional domains misoriented by the tilt angle $\alpha$ are separated by the GB, made up of 5-pentagons and 7-heptagons. (b) Defect energies computed for an isolated 5, a 7, and a 5|7-dislocation, as a function of size $R$ of the lattice cluster. (c) Fully
relaxed lattice containing a 5 becomes a nonplanar cone. (d) Graphene lattice containing a single 7 warps into a shape of a nanopingle with $\delta' = 63^\circ$.

Direct simulations by molecular dynamics (MD) are possible by placing the misoriented graphene domains in contact within the plane and observing what morphologies emerge upon interface annealing. This remains of limited value, as the annealing is computationally costly while generated disordered structures offer limited insight with the emerging 5-pentagonal and 7-heptagonal patterns that are rather random (an excessive disorder problem that plagues the MD simulations of growth). Here we choose a different approach and analyze the structures and energies of different configurations, starting from the most elementary “particles”, the two types of Volterra disclinations in graphene, which are positive (5-pentagon) and negative (7-heptagon). From the analysis of their energies, significantly reduced by permitted off-plane relaxation, we note that their elastic energies diverge with the sample size much slower than in the case of bulk three-dimensional (3D) continuum. This suggests that a pair-dipole 5|7 should have converging energy, which can be evaluated, and serves as a building block for the low-angle GB at $\alpha \ll 1$. Going beyond the low-angle case, we proceed to computing the energies of a whole range of GB from the armchair interface ($\alpha_{AC} \approx 0$) toward the zigzag interface ($\alpha_{ZZ} \approx \pi/3$). We find the GB energy function $G(\alpha)$ to follow an arch-curve, accompanied by interesting transition from one type of elementary dislocations 5|7 to another 5|6|7 through regrouping of the 5′s and 7′s within the GB. Energy-reducing off-plane relaxation also manifests itself in possible formation of ridges and landscapes of substantial heights, observable with AFM when the atomic resolution is not achievable to detect the GB.
To reveal the structures and evaluate the energies of the constituent defects and the GB, we use large scale energy minimization (preceded by finite temperature annealing, to ensure that we reach global minimum). By necessity, the system size (~$10^4$ atoms) makes the first-principle calculations impractical. Similarly, tight-binding approximation level is also insufficiently fast. Well-developed classical interatomic potentials appear to be adequate for the task of finding general behaviors and regularities. Choice for hydrocarbons is Tersoff-Brenner type potential, more specifically AIRIBO, as implemented in LAMMPS. To extract the defect energy more accurately, we compute the total energies (either of large clusters, or with periodic boundary conditions, PBC) and subtract the total energies of perfect graphene systems of identical number of carbon atoms and identical perimeter of H-passivated edges.

It has been suggested in very early work that the GB in graphene contain the pear-shaped polygons, later recognized as adjacent pentagons “5” and heptagons “7”. These elementary defects can appear individually, or as 5|7-pairs, or as series of such pairs, to fit the intergrain misorientation. It is important to appreciate that these seemingly “local” defects are qualitatively different from the true point defects (interstitials, vacancies, Stone-Wales transforms 5|7/7|5, etc.). All of the latter can be easily annealed by adding or removing an atom or two, or by rotating a bond back into its native position. In contrast, neither an isolated 5, or a 7, or their pair 5|7, cannot be corrected, annealed by any local reorganization of the lattice, either mass-conserving or not. Indeed, creating an isolated 5 in graphene requires a cutout of a whole “wedge” within an angle $\Delta = \pi/3 = 60^\circ$ (positive disclination). To form a 7, one needs to seamlessly insert a similar wedge (negative disclination). In a 3D bulk material, such disclinations cause extreme deformations and
normally are energetically prohibitive. In a 2D lattice, like graphene, they can relax through off-plane distortion, reducing the deformation energy to “affordable” levels discussed below (Fig. 3.1b).

In the case of a 5-pentagon, simple geometrical analysis shows that a free lattice will form a cone (Fig. 3.1c) with axial angle \( \delta = \sin^{-1}(1 - \Delta/2\pi) \). It is useful to derive the energy of resulting elastic deformation (and compare it with the energy of computed atomistic structures) to highlight the difference from the regular point defects, having well-defined formation energies. In case of a cone, the curvature at a distance \( r \) from the apex is \( \kappa \sim 1/[r \tan(\delta)] \), and the elastic energy \( \sim \kappa: \sim 1/r^2 \) should be integrated over the entire cone, which yields \( E = \pi D (\cos^2 \delta / \sin \delta) \int (dr/r) \). While the natural lower-limit is the interatomic distance (bond length, \( a \)), at the upper limit the slowly decreasing integrand \( (\sim 1/r) \) causes a divergence; the energy grows with the sample size as \( \ln(R) \) and cannot be defined as an intrinsic defect property. Instead, the defect energy depends explicitly on the cone radius, \( E(R) = \pi D (\cos^2 \delta / \sin \delta) (\ln R - \ln a) \). Fig. 3.1b shows that the data points from atomistic computations follow the \( \ln(R) \) dependence closely. Further, knowing the angle \( \delta = 56.4^\circ \), the slope of this line can be used to extract the flexural rigidity constant of graphene, \( D = 1.1 \text{ eV} \), which is close to reported.

An isolated 7-heptagon, a similar disclination but of opposite sign, turns the geometry complicated; in contrast to the cone, here the axial symmetry is broken as the membrane bifurcates (yielding to the internal compression caused by extra material) into a shape of popular Pringles. From the 7-center of negative Gaussian curvature, the warped graphene canopy extends in all directions. Although exact equation for this extremal
surface is not readily available, its self-similarity suggests that the curvature decreases as $1/r$, and the total energy must grow with size as $\ln(R)$, similar to a cone. The data points in Fig. 3.1b again follow the $\ln(R)$ dependence very closely. On the basis of this agreement, one can conveniently write down the energies of these defects as $E = E_{\text{core}} + E_{\text{elast}} \ln(R/a)$.

Being assigned formally, $E_{\text{core}}$ can in principle be either positive or negative (if $1/r$ overestimates the strain near the 7). Important observation here is that individual 5 or 7 causes globally nonplanar geometries, so-called nondevelopable surfaces. This can be a likely a reason for a variety of stable, nonfluctuative landscapes and wrinkles observed on graphene with an atomic force microscope (AFM). Remarkably, the cones of graphene have been synthesized in all five varieties corresponding to the 1, 2, 3, 4, or 5 pentagons at the apex (and the angles $\delta = 56.4, 42, 30, 19.5, \text{or } 9.6^\circ$, respectively; 6 pentagons correspond to $\delta = 0$, that is, parallel walls of a nanotube). In contrast, we are not aware of any observations of graphene pringles, although they have comparable or lower formation energies, Fig. 3.1b.

Since the energies of the 5's and of 7's are quite large, caused by the delocalized lattice strain, their pairing up into dipoles is energetically favorable. By analogy to electrostatics, such dipole of positive $+\Delta$ and negative $-\Delta$ disclinations is expected to produce a strain field $\propto 1/r^2$ at the distance $r$ [a derivative of the field from the monopole, $\partial / \partial r(1/r)$], so that the elastic energy density of the surrounding lattice falls as $1/r^4$, and thus its integral value should converge. Thus, one should be able to define the energy of a 5|7, in contrast to the 3D crystals where dislocation energy diverges logarithmically.

Having a 5 and a 7 nearby in a lattice creates a dislocation of arbitrary Burgers vector. The simplest are the well-known 5|7 of Burgers vector $\mathbf{b} = (1,0)$ in notations of nanotubes (or
2,−1,−1,0) in crystallographic notations for graphite), or a 5|6|7 of Burgers vector \( \mathbf{b} = (1,1) \). A full relaxation of a series of graphene islands with single 5|7 yields the values \( E(R) \) varying insignificantly, much slower than for the bare disclinations (Fig. 3.1b). Computational limitations prevent one from reaching a clear asymptotic value. It can be evaluated from consideration of dislocation walls, which we are turning to next.

A GB separates the domains tilted to some angle \( \alpha \). Typically it bisects the tilt at \( \alpha/2 \) angle relative to the crystal planes of the grains. Generally, it may deviate by some angle \( \beta \) from the bisector, dividing the tilt angle into \( \alpha/2 \pm \beta \). The GB must contain imperfections to accommodate for the tilt. Macroscopically, considering a closure failure around the contour shows that the Burgers vector density per unit length is \( \frac{d\mathbf{B}}{ds} = 2 \sin(\alpha/2)(\mathbf{n} \times \mathbf{\alpha}) \), where \( \mathbf{n} \) is a unit vector along the boundary and \( \mathbf{\alpha} \) is a tilt vector. Beyond this macroscopic Frank equation, to explore the details of the GB structure and energy, we perform the systematic atomistic calculations. Before considering the role of the tilt angle \( \alpha \), we perturb the boundary by gliding (via the Stone-Wales rotations) the constituent 5|7-cores, Fig. 3.2a-c. The plot in Fig. 3.2d shows increase in energy. This agrees with the well-known preferred vertical alignment of two identical edge dislocations, \( \perp \) (in contrast to a pair of opposite dislocations, \( \perp \) and its inversion twin, which form a stable dipole aligning at 45°). The GB nearly bisecting the tilt angle must be therefore the main choice of detailed energy analysis. Nevertheless, low mobility of constituent dislocations suggests that the no-bisector GB, if formed in the course of growth, can be kinetically stabilized and encountered in observations as well.
Figure 3.2. Simple GB structure in its generic bisector position (a), slanted by $\beta = \pm 12^\circ$ (b), and $\beta = \pm 24^\circ$ (c), and their relative energies (d). In (e), an interface joining a ZZ edge and an
AC edge between the domains tilted to $\alpha = 30^\circ$; note the “fly-head” pattern where the atomic rows removed to reduce the interface mismatch strain.

One example of interest is a possible $30^\circ$ tilt interface formed by a zigzag (ZZ) domain edge on one side and an armchair-oriented (AC) domain on the other, as shown in Fig. 3.2e. Formally, they can be matched by a series of close packed and slanted 5|7’s, as shown. (Structure closely resembles the reconstructed ZZ edge, reczag.) This appears as topologically satisfactory solution, but the period of the zigzag $(2(3)^{\sqrt{2}}a)$ exceeds the period of armchair side domain $(3a)$ by 15.5%. Such mismatch would cause a high energy distortion. To form a well-matched GB, a certain number of atomic rows (about every eighth and occasionally seventh) should be removed on the ZZ side, which is equivalent to insertion of sparsely spaced 5|7 cores. Upon full relaxation, one obtains a GB without remote stress. In the sites of the extra 5|7 insertions, it displays a peculiar “fly-head” 7/5\7 structure, where the standard pentagon-heptagon dislocation cores appear flip-altering their orientation from 5/7 to 7\5. Since the AC|ZZ mismatch is an irrational number, the locations of the fly head pattern cannot be periodic. This one example illustrates the rich realm of possibilities in the prime units (5-pentagon and 7-heptagon) organization of low energy GB. As expected, the computed energy of this interface is higher than the bisector types for the $\sim 30^\circ$ tilt.

Now we consider the subset of GB, which are the bisectors, as a most realistic choice and turn to the question of how they change with the tilt angle. Since the direct computations of numerous possibilities are extensive, a preliminary analysis gives some guidance. For low-angle GB, the generic structures are well discussed; it is a series of edge
dislocations, of Burgers vector \( \mathbf{b} \) (in case of 5|7, it is one lattice parameter, \( b = (3)^{1/2}a \)), and spaced by a distance \( b/[2 \sin(\alpha/2)] \sim b/\alpha \). If the energy \( E \) of individual dislocation is defined, then the GB energy is roughly proportional to the density of these defects, \( G \sim \alpha(dG/d\alpha)_0 \sim \alpha \cdot E/b \). Increasing the tilt \( \alpha \) makes the dependence nonlinear, but the opposite limit becomes simple again. For graphene, at \( \alpha = \pi/3 \) the perfect lattice is fully restored, while in its vicinity the dislocations sparsely placed along the GB give rise to its energy, \( G \sim -(\pi/3 - \theta)(dG/d\alpha)_{\pi/3} \). It is easy to see that in this “near ZZ” limit the elementary dislocation is different, a 5|6|7 of larger Burgers vector \( \mathbf{b}' = 3a \), larger energy, and consequently different slope. Further, the overall functional behavior \( G(\alpha) \) should be periodic, sought as a sum of a few Fourier overtones, with a leading term \( -\sin(3\alpha) \).

Fig. 3.3 summarizes the results of energy computations for a number of constructed GB from nearly AC contact (small \( \alpha \)) to the nearly ZZ interface (\( \alpha \approx \pi/3 \)). Fig. 3.3b–f shows the GB structures, placed near their respective tilt angles. The overall energy \( G(\alpha) \) behavior is rather close to sine-function, although nonequivalence of the left- and right-limit structures (AC and ZZ interfaces) causes some asymmetry; the maximum is not necessarily in the middle (\( \alpha = \pi/6 \)) yet it appears rather close. The overall range of energies is up to 4.5 eV/nm, much lower than that for the bare graphene edges (~10–13 eV/nm, depending on the type).
Figure 3.3. a) Grain boundary energy $G(\alpha)$ as a function of tilt angle, based on 26 computed data points (solid squares) and fitted by the three-terms of Fourier series (thick line). (b) Nearly AC interface low-angle GB ($\alpha = 3.5^\circ$) with gray-level-coded strain energy per atom, shown in meV. (c) Maximum 5|7 density GB, $\alpha = 21.8^\circ$. (d) Maximum 5|6|7 density GB, $\alpha = 32.2^\circ$. (e) Nearly-ZZ interface low-angle GB ($\alpha - 60^\circ = 13.2^\circ$) comprised of 5|6|7 and (f) its alternative split into slanted 5|7’s, higher in energy in this case (solid circle).

The energy-arch is interesting to follow from left to right, to understand the logic of GB structure changes as the tilt angle changes. At small values it is simply a series of separate 5|7; see Fig. 3.3b. As the angle increases, they get closer to each other and become crowded. Eventually, we reach the highest density in a sequence $(5|7)6(5|7)6(5|7)6(5|7)6...$; here the 5|7’s are separated by single hexagons only; see Fig. 3.3c. Further tilt increase causes peculiar regrouping when pentagons and heptagons abandon the original partners (by insertion of one 6-hexagon) and pair up with the ones on
the opposite side, as $5|6|7|6|5|6|7|6|5|6|7$ and so on. After that, the energy descent corresponds simply to increasing spacing between the new elementary dislocation cores 5|6|7, which eventually leads to the ZZ interface. Fig. 3.3–f shows the important intermediate GB structures, as well as the simple cases of the low-tilt boundaries near AC ($\alpha = 0$) and ZZ ($\alpha = \pi/3$) edges, where the two grains merge perfectly, $G(0) = G(\pi/3) = 0$.

While the full fit in the Figure 3 was done with three harmonics, a behavior is roughly captured by approximation $G(\alpha) = 5 \sin(3\alpha)$, eV/nm (the next two coefficients are 0.1 and 0.3). Besides the overall energy behavior, one can evaluate the energy of a single $5/7$ from the low-angle limit in which case the leftmost point in the plot gives $E_{5/7} \approx 5$ eV. This value is marked in the Fig. 3.1b (gray horizontal line) and is the asymptotic value for the single-$5/7$ data, apparently reaching this limit from below.

In our computations, we rely on PBC along the GB direction but consider limited width in perpendicular $x$-direction (after checking the results insensitivity to further increase of this width). Rapid decrease with the distance $x$ from the boundary is illustrated by the gray-level local strain energy representation (per atom) in Fig. 3.3b. This near-field ($x < b/\alpha$) analysis complements the known analytical result for the strain energy, $\sim x^2 \alpha^4 e^{-4\pi x/b}$ at $x > b/\alpha$.

Noting that in 3D crystals the elastic energy is usually lowered by splitting the dislocations $(1,1) \rightarrow (1,0) + (0,1)$ to smaller Burgers vectors, we consider a GB in Fig. 3.3f as alternative to Fig. 3.3e. In contrast to 3D continuum, in a freestanding 2D-lattice such a split is unfavorable and the energy is $\sim 1$ eV/nm lower for the 5|6|7 cores.
This example of the larger Burgers vector being energetically preferred (Fig. 3.3e-f) as well as convergence of the 5|7 energy in a free graphene is due to additional freedom to warp off-plane. As a result, the initially 2D flat sheet forms rather pronounced 3D landscapes. Extreme manifestations of this are of course the cone and pringle, which cannot be developed onto a plane at all. Their pairs can, yet both small 5|7 and especially large Burgers vector 5|66666|7 dislocations cause great distortions, as computed structure in Fig. 3.4a shows. The roughness of emerging stable landscape can be characterized by the heights, \( h_{5-7} \). Although obviously random, the typical height can be estimated from our knowledge of the topology-induced conical shape (with \( \cos \delta \sim 0.5 \)) and the peak-valley distances \( \sim b_{5-7} \) (that is 5–7 distance, proportional to the Burgers vector associated with a 5–7 dipole): \( h_{5-7} \sim b_{5-7} \). Remarkably, we see that the randomly scattered disclinations at concentration \( n \) of pentagons and heptagons cause the roughness inversely proportional to the defect concentration, \( h_{5-7} \sim n^{-1/2} \). In this context, an interesting extreme case of highest defect concentration (\( n_{5-7} \to \infty \)) is the 5′s and 7′s closely packed into so-called pentaheptite crystal of planar geometry (\( h_{5-7} \to 0 \)).
Figure 3.4. (a) A computed (full energy relaxation) landscape due to the presence of scattered 5 and 7 defects in a perfect graphene lattice, shows elevation roughly equal to the distances between the 5’s and 7’s. (b) A regular GB from 5|7 dislocations forms a ridge shape. (c) Flattening effect of the van der Waals attraction to the substrate, as computed for the two values $4V$ and $V$, when the elevation $(h - h_{\text{flat}})$ approximately doubles.

If organized in linear motifs of grain boundaries, they form linear ridges, as one in Fig. 3.4b. When grown or placed on a substrate, topologically induced graphene landscape is partially flattened by the “gravity” of van der Waals attraction (energy $V$ per area). To estimate the resulting elevation, we note that there is only one other essential parameter, the flexural rigidity $D$. Dimensionality consideration yields the elevation $(h - h_{\text{flat}}) \sim (D/V)^{1/2}$. Two ridge-profiles in Fig. 3.4c, computed at two different strengths of attraction (contact surface energy, $V$) show good agreement with this dependence.

One can easily imagine that the lattice distortions near the GB do change the electronic structure in its vicinity, and therefore will cause scattering of electrons, affecting the transport phenomena both across and along the GB direction. Magnetism of the GB can
also be of further interest. These aspects, although both interesting and potentially important, require further study beyond the scope of present report.

### 3.2. Dislocations and grain boundaries in two-dimensional boron nitride

Dislocations and grain boundaries (GBs) play an important role in the properties of materials. Dislocations in carbon hexagonal lattice have been well documented and recently significant progress has been made to reveal the structures of GBs and their influence on properties of graphene. However, little is known about dislocations and GBs for ‘white graphene’: two-dimensional (2D) hexagonal boron nitride (BN), in spite of its promising application in nano-electronics and optoelectronics. Although both materials are one atom thick, mechanically strong against stretching and flexible under bending, the hetero-elemental nature of h-BN brings more complexity compared to homo-elemental graphene. In graphene, the energy of dislocation is dominated by its elastic strain, therefore the core of dislocations is constituted by pentagon-heptagon pairs (5|7s) because of their lower strain energy than other polygon pairs, for example, square-octagon pairs (4|8s). In BN, the energy of dislocation consists not only of topological strain but also possible homo-elemental bonding, which is weaker than hetero-elemental bonding in perfect lattice. 5|7s have lower strain energy, but they inevitably introduce home-elemental bonding (either B-B or N-N); 4|8s are free of any homo-elemental bonding while suffering from higher strain energy. Which one constitutes the core of dislocation? The
delicate balance between the strain and chemical bonding contributions calls for quantitative analysis, as presented in this work. Knowing the structure of dislocation, we are able to further study structures and properties of GBs, which are composed of aligned dislocations. In the synthesis of BN by chemical vapor deposition (CVD), GBs are formed where two grains meet each other by propagating growth fronts. The growth fronts can have elemental polarity, for example, B (or N) terminated edges, which may lead to B-rich (or N-rich) GB. The growth fronts can also retain B:N=1:1 as interior of materials, which may lead to non-polar GB. Although overall polycrystalline BN keeps its stoichiometry as 1:1, it can locally deviate from this balance along GB. Would those polar GBs ‘react’ with each other by pairing of their extra atoms through diffusion and eventually become non-polar? Or would non-polar GBs spontaneously develop polarity allowing enough diffusion time? How do these behaviors correlate with the structure of GBs? Under thermodynamic equilibrium, these questions can be answered by the energies of GBs. Finally, the properties of GB are discussed, featuring charge accumulation and bandgap decreasing.

We start our discussion by searching for structure of dislocation core. Dislocation with burgers vector \( b = (1,0)a \), where \( a \) is the lattice vector of 2D BN, corresponds to removal of one armchair (AC) atomic chain from perfect lattice. Its core is constituted by a single 5|7 while 4|8 is topologically forbidden. However, dislocation with larger burgers vector \( b = (1,1)a \), corresponds to removal of two zigzag (ZZ) chains from perfect lattice. Its core can be constituted by a single 4|8, as shown in Fig. 3.5a, or alternatively, by 5|7s with homo-elemental bonds, obeying \((1,1) = (1,0) + (0,1)\). These 5|7s can be thought as being formed by insertion or subtraction of BN dimers sequentially to dislocation core(s). Our calculations indicate that 4|8 is more energetically favorable than 5|7s, by 1.05, 1.51, and
2.29 eV, from left to right in Fig. 3.5a. Fig. 3.5 shows only one set of 5|7s which have N-N bond spatially close to the compressed region of the sheet and B-B close to the expanded part (denoted as N-N|B-B). The other set of 5|7s (B-B|N-N) is also energetically unfavorable than 4|8 by 1.84, 0.94, and 2.12 eV, respectively. These results suggest 4|8 as dislocation core of BN. In contrast, the same type of dislocation in graphene is constituted by 5|7s which are adjacent to each other according to our calculations. This indicates that BN is able to avoid the unfavorable homo-elemental bonding at the cost of increasing lattice strain. In fact, the lattice strain in 2D system is eased by relaxation in the third dimension. All of these defects induce buckling of free standing sheet in the out-of-plane direction (Fig. 3.5b), which effectively screens strain from dislocation core. Constraining the sheet to be planar hinders strain screening and reverses the energy order of 4|8 and 5|7s: 5|7s are lower in energy than 4|8 by 2.43, 5.61, 6.96 eV for N-N|B-B, and 0.09, 5.42, 6.97 eV for B-B|N-N. Clearly, the preference of 4|8 is facilitated by buckling, which is one distinct feature of 2D system. However, it should be noted that the dislocation dipole, formed under mechanical tension, is composed of two 5|7s, instead of 4|8s. This is because, if written in terms of dislocations, 5|7s are generated by \((0,0) = (1,0) + (-1,0)\), while 4|8s are obtained by \((0,0) = (1,1) + (-1,-1)\). The larger dislocations in 4|8 dipoles make it unfavorable compared to 5|7s.
Figure 3.5. (a) Top view of dislocation core with burgers vector $|b|=\sqrt{3}a$, where $a$ is the lattice parameter of 2D BN. From left to right: two ZZ lines are cut from hexagonal lattice, dangling bonds are reconnected forming 4|8, 5|6|7, adjacent 5|7s or sparse 5|7s. (b) Side view of the dislocation constituted by 4|8 (left) or 5|6|7 (right). Red balls represent B and blues ones for N. Red (blue) lines highlight B-B (N-N) bonds. Dislocation cores are marked by shadows.

Having known the structures of dislocations, we can construct the GBs by aligning dislocations with their density prescribed by the tilt angle between two titled grains, $\alpha$. Here we focus on GBs which bisect $\alpha$ ($\alpha = 0^\circ$ means two grains connected along AC direction. The illustration of $\alpha$ is shown in Supporting Information.) since they have lower energies compared to inclined GBs. Different from GBs in graphene, where $\alpha$ has only $120^\circ$ periodicity, two grains of BN have to rotate by $240^\circ$ in order to recover their initial
positions, as shown in Fig. 3.6. However, $\alpha$ is not enough to describe all the GBs. There are two distinct families of GBs which have to involve another variable to distinguish them: (i) grains in the first family (right side of Fig. 3.6) has mirror symmetry with respect to GB, thus it is called symmetric GB (sym-GB) later. (ii) In the asymmetric GB (asym-GB) family (left side of Fig. 3.6), one grain can be thought as mirror operation of the other one plus additional flip perpendicular to GB. These two families can be transformed into each other by rotations of grains. However, due to the imposition of constraint that GBs bisect $\alpha$, this notation becomes necessary.

**Figure 3.6.** Structures of GBs constituted by 5|7s as a function of tilt angle. The middle panel shows a perfect BN lattice which can be thought as two grains are connected perfectly either along green or purple dashed lines. Rotation of two grains with respect to
green dashed line leads to symmetric GBs (right panel), and purple dashed lines result in asymmetric GBs (left panel). See details in the text.

Asymmetric GBs can be possibly constituted by 5|7s, similar to graphene. Fig. 3.6 shows their atomic structures. Following the purple arrows, GBs transform from AC junctions, to straight 5|7s, to 5|6|7s (or inclined 5|7s depending on energy preference), then to ZZ junctions, and full way back to start the next 120° circle. 60° and 180° GBs correspond to perfect BN, while 0°, 120°, and 240° ones have alternating B-B and N-N bonds along GB. For all the GBs, there are always equal amount of B-B and N-N bonds, which can be fully eliminated by reconstruction to 4|8s (left side of Fig. 3.9). Their energies are shown in Fig. 3.7 by purple scatters (squares for 4|8s and circles for un-reconstructed 5|7s) as examples. It can be clearly seen that 4|8s are always lower in energy, even at 0° (60° and 180°) where GBs are made by hexagons. Although sparse dislocations induce the buckling in the direction perpendicular to the sheet, increase of defects concentration reduces buckling due to the cancellation of strain field between two neighboring dislocations. For asym-0° (120° and 240°), the planarity is retained. The buckling of GB can be measured by its inflection angle, as shown in Supporting Information. In short, the asym-GBs are constituted by 4|8s.
**Figure 3.7.** Energy of GB as a function of tilt angle $\alpha$. Scatters are computed data, which are connected by lines. Hollow circles are GBs made by 5|7s, and solid squares are for 4|8s. Purple for asym-GBs, red for B-rich sym-GBs, blue for N-rich sym-GBs, and green for the average energy of B-rich GBs and their corresponding N-rich analogs. Note that energies of polar GBs depend on chemical potential, thus red and blue lines are shown just for illustration.

Sym-GBs can also be possibly constituted by 5|7s, but with elemental polarity (either B- or N-rich) along GB except several special $\alpha$ where perfect BN is recovered. Following the green arrows in Fig. 3.6, GBs transform from AC junctions, to B-rich straight 5|7s, to B-rich inclined 5|7s, then to B-rich ZZ junctions, and full way back to start the next 120° rotation which is N-rich region. The extra B (or N) atoms are located at B-B (or N-N)
bonds, which cannot be eliminated by local reconstruction of 5|7s to 4|8s because there are no compensation N-N (or B-B) bonds along the same GB. On the other hand, in a global view, extra B (N) from B-rich (N-rich) GB could probably pair up with each other and result in the elimination of polarity. Two examples of GBs ‘reactions’ are demonstrated in Fig. 3.8, where polarity disappears through 5|7s->4|8s reconstruction. We find that these reactions are endothermic, illustrated by the energies of ‘products’ (green squares) and ‘reactants’ (green circles) in Fig. 3.7. The dashed lines connect the ‘average’ energies of two GBs with reverse elemental polarity, i.e. one is B-rich (with angle $\alpha$) and the other must be N-rich (with angle $120^\circ+\alpha$). Increasing chemical potential of B decreases the energy of B-rich GB, but increases that of N-rich one. Nevertheless, the average value keeps unaffected by chemical potential. The averaged value can also be used to quantify the energies of GBs in multiple BN layers, which follow A-A’ stacking (B on top of N or vice versa) thus might guide the B-rich and N-rich GBs stacked together.

**Figure 3.8.** Reaction of polar GBs. Extra B and N atoms from GBs pair up and 4|8s are generated during these reactions.
Figure 3.9. Ground state structures of GBs as a function of tilt angle. They are similar to those shown in Fig. 3.6 except that asymmetric GBs are un-polar and made by 4|8s.

Fig. 3.9 summarizes the ground state structures of GBs. The asym-GBs are un-polar and constituted by 4|8s. The sym-GBs are polar and composed by 5|7s. All of them can co-exist in polycrystalline BN, suggesting a wide variation of structures and related properties under different circumstances. The balance between substrate flattening and defects induced corrugation leads to three-dimensional landscape in BN membrane, with its roughness scaling inversely with the defects concentration, as reported in graphene.\textsuperscript{64} Similar to graphene, GBs in BN should serve as fracture nucleation center under high tension load,\textsuperscript{75,76} while their mechanic properties are more complicated due to the existence of homo-elemental bonds and the variation between 5|7s and 4|8s. For example, the better accommodation of 5|7 to the elastic strain suggests possible transformation from 4|8 to 5|7 under mechanical loading. This topic deserves further investigation. More
interestingly, since B-N bond has ionic feature with electrons transferred from B to N, the polar GBs carry net charges brought by extra atoms. Figure 6b plots the electrostatic potential from sym-60° (B-rich) to sym-180° (N-rich) GB (the potential is averaged along GB direction in the plane 3 Å above 2D BN). The monotonic decrease of potential indicates B-rich GB is positively charged and N-rich GB carries negative charges, agreeing with the charge transfer in perfect BN. This intrinsic electric field, which does not exist in graphene, could be utilized to find GBs using Kelvin probe force microscope or electrostatic force microscope. Furthermore, the electronic properties of GBs are also remarkable. The electronic signals should be most prominent at GB with highest concentration of defects, for example, boundaries full of B-B bonds (sym-60°), N-N bonds (sym-180°), or 4|8 (asym-0°). Their density of states (DOS) are shown in Figure 6a. Sym-180° have occupied states contributed by extra N atoms appearing above the valence band maximum (VBM) of perfect BN, while for sym-60°, extra B atoms bring in unoccupied states below the conduction band minimum (CBM). Analysis of energy-decomposed charge density plot indicates that these extra electronic states are located at GBs only, and decrease the bandgap by 38% (1.5eV/4eV, though DFT cannot give the precise value of bandgap), in contrast to GBs in graphene which generally open the bandgap.71,73 However, 4|8s do not shift VBM and CBM significantly. The decreased bandgap could probably create optical peaks closer to the visible light region and might be utilized to identify GBs. To facilitate experimental observations, simulated scanning tunneling microscope (STM) images are also shown. They are conducted at the constant height model, with 2 Å above BN and positive bias 0.5 Volt with respect to VBM. Distinct electronic fingerprints can be clearly seen through these images. B-rich sym-60° GB has higher charge density at B-B bonds,
while its N-rich analogy sym-180° GB, has intense charge at N atoms which form N-N bonds. 4|8s induce charge accumulation around N atoms as well, in spite of isoelectronic structure as perfect BN.
Figure 3.10. (a) Left: density of electronic states (left) for perfect BN (bottom), BN containing asym-0° GB (middle), and BN containing sym-180° and sym-60° GB (top). Vertical dashed lines indicate Fermi level. Right: simulated STM image for sym-180° (top),
sym-60° (middle) and asym-0° (bottom) GBs. Atomic structures are put in front of STM images. Red balls represent B and blue for N. (b) Electrostatic potential distribution in the plane 3 Å above the polycrystalline 2D BN which contains sym-60° and sym-180° GBs. The potential is averaged along GB directions.

To summarize, we present the topology and energies of dislocations and GBs in 2D BN. Different from graphene, dislocation with burgers vector (1,1) is comprised from 4|8, instead of 5|7s. In fact, the similarity has been observed in BN cages and tube caps, where even-number rings exist instead of odd-number rings, as a distinguishing feature different from carbon materials. Depending on the tilt angle of grains, GBs can be either polar (B-rich or N-rich), constituted by 5|7s, or un-polar, composed of 4|8s. Polar GBs have net charges and smaller bandgap compared to perfect BN. Given the hetero-elemental nature of many other 2D systems, like transition-metal disulfides, the results could probably be generalized into these materials, though detailed energy calculations are desired. The extra variable in atom type, would open many possibilities for structures of defects, as well as expected novel properties and applications.

3.3. Two-Dimensional Mono-Elemental Semiconductor with Electronically Inactive Defects

This work has been submitted.

Defect-created deep states within the electronic band gap of semiconductors typically degrade device performance for electronics and optoelectronics. They act as undesirable sinks for charge carriers and electron-hole recombination centers through
the Shockley–Read–Hall process.\textsuperscript{87, 88} This has been one of the drawbacks for the applications of two-dimensional (2D) metal dichalcogenides (MX\textsubscript{2}),\textsuperscript{89-91} though they have attracted great interest for nano-devices.\textsuperscript{92, 93} In addition, the relatively low mobility of charge carriers, and the lack of efficient means to tune their type and concentration, together impede MX\textsubscript{2} applications.\textsuperscript{92, 93}

Most of the defect states in MX\textsubscript{2}, especially those of grain boundaries (GBs), originate from the chemical disorder brought about by the homo-elemental bonds (M–M or X–X), which are not present in the perfect lattice.\textsuperscript{89} Similarly, GBs in boron nitride (BN) with homo-elemental bonds (B–B or N–N) also create deep gap states.\textsuperscript{94} These “wrong” bonds can possibly be avoided in a mono-elemental system, even in presence of structural disorder. Therefore, a 2D semiconductor made of only one type of element is desirable (recently investigated mono-elemental 2D boron shows all its polymorphs being metallic\textsuperscript{20}). This brings into our focus 2D phosphorus (P), a semiconductor which has recently been exfoliated from black P—the most stable form of P at ambient conditions.\textsuperscript{95-97} It has attracted intense interest due to its proper band gap and high mobility.\textsuperscript{95, 96, 98-102} Here, based on density-functional-theory (DFT) calculations, we show that the structural defects in 2D P are electronically inactive, thanks to its mono-elemental makeup. In addition, we demonstrate the feasibility of tuning the charge carrier type and concentration by doping with foreign atoms. These properties together distinguish 2D P as promising candidate material for nano-electronics and optoelectronics.

Although topologically (in its bonds-atoms connectivity) equivalent to hexagonal graphene, the 2D P is composed of buckled hexagons, and has a rectangular symmetry (Fig.
3.11a). The P atoms are subdivided into two planes, forming an armchair-like pattern. Each P atom forms three bonds with its neighbors by sharing its three \( p \) electrons, leaving one lone-pair \( s \) electron. Two bonds are formed with the P atoms in the same layer, and the third one is with the other layer atom. The lattice direction in 2D P can be described by a vector \( na + mb \), where \( a \), \( b \) are the primitive vectors, with \( |a| = 4.62 \text{ Å}, |b| = 3.30 \text{ Å} \), and \((n, m) = \) integers. The low symmetry of 2D P leads to higher structural complexity compared to other 2D materials, such as graphene, BN, and MoS\(_2\), which have a hexagonal symmetry. There are two types of in-plane armchair directions: \( A \) at \( 0^\circ \) indexed \((1,0)\) and \( A' \) at \( 65^\circ \) indexed \((1,3)\), as well as two types of zigzag directions, \( Z \) at \( 90^\circ \) indexed \((0,1)\) and \( Z' \) at \( 35.5^\circ \) indexed \((1,1)\), as shown in Fig. 3.11a. In contrast, the hexagonal 2D materials have only one type of armchair direction. This complexity gives rise to more variation in defect structures, as shown later.
Figure 3.11. (a) Structure of 2D P. Atoms in different layers are shown in black and white. Arrows indicate the primitive cell vectors, and lines show other basic lattice directions. (b) Band structure and density of states; inset shows the band gap calculated by different methods. (c) Charge density distribution of the states corresponding to the VBM and the CBM.

Fig. 3.11b shows the electronic band structure of 2D P, a direct band gap semiconductor with an electrical band gap > 1.5 eV; computational details are given in the
Supporting Information (SI). The state corresponding to the valence band maximum (VBM) is mainly located between the P atoms in different planes, while the state of the conduction band minimum (CBM) is formed by the atoms in the same plane, Fig. 3.11c. These features will help distinguish the interior and the edge states, as shown later.

The intrinsic defects in 2D materials can be categorized into two types: (i) line defects, i.e., edges, dislocations, and GBs; (ii) point defects, including bond-distortion complexes, vacancies, and interstitials. Fig. 3.12a shows the core structure of the primary dislocation with a Burgers vector (0,1). The dislocation core consists of a buckled pentagon and heptagon pair (5|7). This is similar to the other 2D materials with hexagonal lattice, such as graphene,\textsuperscript{64,103} BN\textsuperscript{94} and MoS\textsubscript{2}.\textsuperscript{89} Note that the bonding configuration at the dislocation core is the same as that in the prefect lattice, i.e., each atom forms three P–P bonds, two of which are with the atoms in the same layer, and one bond with that in the other layer. This is in contrast to the dislocation cores of MoS\textsubscript{2} and BN, most of which have homo-elemental bonds never present in the perfect lattice.\textsuperscript{89,94}

The GBs are composed of linear dislocation arrays. Fig. 3.12b shows the structures corresponding to different misorientation angles (\(\alpha\)). These GBs are the lowest-energy ones at given \(\alpha\), and their energies are shown in Fig. 3.12c. Most GBs are still made of 5|7s, which buckle in different ways depending on \(\alpha\). One interesting exception is the boundary between two \(Z'\) terminated grains (71.1\(^{\circ}\)), which does not have topological defects and thus represents a local minimum in the energy profile. In contrast, the boundary between two \(A'\) terminated grains (130\(^{\circ}\)) is made of quadrilaterals and octagons (4|8). These polygons have been observed in BN and MoS\textsubscript{2}.\textsuperscript{89,94} Note that the GB energies are lower than those of
graphene, BN, and MoS$_2$. This suggests that the chemical stability of GBs in 2D P is closer to the perfect lattice, compared with that in other 2D materials. To study the effect of GB on the electronic structure of 2D P, we embed the corresponding GBs in a polycrystalline sheet (see SI). Due to the computational limitations, the distance between GBs is $\approx 1.8$ nm. The interaction between GBs could have additional effects on the electronic structure. Nevertheless, across all of the diverse structures considered, the GBs generally do not exhibit deep gap states, as shown in Fig. 3.12d. These properties are in stark contrast to MoS$_2$, where GBs create deep gap states and in some cases even become metallic. This difference originates from the absence of the chemical disorder ("wrong" bonds) within the GBs of 2D P.

**Figure 3.12.** (a) The core structure of the primary dislocation with a Burgers vector (0, 1), viewed from various directions. (b) Structure of grain boundaries at various misorientation angles. (c) Energy of grain boundaries, as a function of the misorientation angle. The line is to guide the eye. (d) Electronic density of states of the polycrystalline 2D P sheet, with corresponding grain boundaries embedded. $\alpha = 0^\circ$ is equivalent to a perfect 2D P sheet.
The edge is another important form of line defect. MoS$_2$ edges are known to suffer from the deep gap states, regardless of passivation.$^{104,105}$ Similarly, the edge states of BN also cannot be eliminated by passivation.$^{106}$ In contrast, we find that the edge states of 2D P can be removed from the band gap by hydrogen passivation. To study the effect of edge on the electronic structure of 2D P, we use a nanoribbon terminated with corresponding edges. Fig. 3.13a shows the band structure of a P nanoribbon terminated along the AC direction. For a pristine edge, there are isolated bands in the gap. The charge density of the isolated bands is located at the edge (Figure S2) owing to the presence of dangling bonds. The edge can reconstruct, but the bonds cannot be fully saturated (see SI), and therefore the edge states still remain (Figure S3). However, after H passivation, that band disappears, and visualization of the nanoribbon VBM and CBM shows that they are contributed by the interior P (Fig. 3.13b). The pattern of VBM and CBM is the same as that in the perfect 2D P, confirming that the edge states are fully eliminated from the band gap. The effect of H passivation applies to other edge directions, as verified by the charge density distribution of the VBM and CBM in the corresponding nanoribbons (Fig. 3.13b).
Figure 3.13. (a) Band structure of P ribbons with bare (left) and and H-passivated A edge (right). (b) Charge density distribution of the states at VBM and CBM, for P ribbons with various types of H-passivated edges.

Point defects in the 2D P have structural similarities to graphene, since 2D P can be viewed as a mono-elemental sheet made of bucked hexagons. The lowest-energy point defect is a di-vacancy ($V_{P2}$), which is composed of two buckled pentagons and one octagon (Fig. 3.14). The bond rotation creates a Stone–Wales (SW) defect with two 5|7 pairs and slightly higher energy. A mono-vacancy ($V_P$) reconstructs by forming a pentagon. The interstitial P atom ($P_i$) forms two bonds with P atoms in different layers, and leaves one dangling bond. Similar to GBs, the formation energies of the point defects are much lower than those in graphene. The primary defects — $V_{P2}$ and SW — do not induce gap states.
because their bonds are fully saturated. The $V_p$ and $P_i$ create spin-polarized p-type states right above the VBM ($< 0.1$ eV), due to the presence of dangling bonds. Those states, on one hand, are a possible origin of p-type conductivity observed experimentally in 2D P$_{96, 107}$ On the other hand, for a p-type 2D P, these defects will not act as sinks for the major charge carriers (holes), as there are no compensating electrons.

**Figure 3.14.** Intrinsic point defects in 2D P, including di-vacancy (VP2), Stone–Wales (SW), mono-vacancy (VP), and interstitial (Pi). Structures are shown in the top panels with the formation energies indicated, and the corresponding electronic densities of states are shown in the bottom panels. For spin-polarized systems, the two spin states are shown in different colors.

Next we discuss the possibility of tuning charge carrier type and concentration. Many electronic devices, such as p-n junctions, require the ability of the semiconductor to be both p-doped and n-doped. A good p-type dopant should have empty states close to the
VBM. Group-IV elements have one less electron than P, and therefore can create empty states in the band gap. Among them, C has the strongest electron affinity, suggesting the lowest energy of the states. Indeed, Fig. 3.15 shows that C is a good p-type dopant. We further find Zn, which has two less electrons than P, is also a good p-type dopant. Similarly, a good n-type dopant should have filled states close to the CBM. The chalcogen group has one more electron than P, and therefore can create filled states in the band gap. Among them, Te has the lowest electron ionization energy, suggesting the highest energy of the states. However, we find that these states are still far from the CBM (Fig. 3.15), indicating that the chalcogen group is not a proper n-type dopant. Alternatively, the alkali group has lower ionization energy, and thus could have the donor states closer to the CBM. As an example, Fig. 3.15 shows that potassium adsorption, which has been used to achieve high n-doping in MoS$_2$ and WSe$_2$,\textsuperscript{108} can also induce n-type conductivity in 2D P.

![Figure 3.15](image)

**Figure 3.15.** The electronic density of states of 2D P doped by foreign atoms. For spin-polarized systems, the two spin states are shown in different colors.

In summary, we find that the defects in 2D P are electronically inactive, in contrast to other 2D hetero-elemental semiconductors like MX$_2$. Both the type and the concentration of charge carriers can by tuned by doping foreign atoms. These properties, together with its
high charge carrier mobility, suggest 2D P as a promising candidate for electronic and optoelectronic applications.

3.4. BN White Graphene with “Colorful” Edges: The Energies and Morphology

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Current attention to the atomic monolayers of carbon—graphene, and especially the need to introduce an electronic gap in this gapless sheet, has brought to the spotlight its sibling two-dimensional (2D) material of hexagonal boron nitride, h-BN. Its bulk phase (often called white graphite) with weak interlayer bonding permits separation into individual sheets of white graphene. Furthermore, analogous to carbon nanotubes, tubular BN structures have been theoretically predicted, consequently synthesized, and display a number of properties of fundamental and practical importance.

Morphologically alike to the honeycomb graphene and even with quite similar bond length (instead of 2.46 Å in C, lattice parameter in BN is \( l = 2.51 \text{ Å} \), henceforth used as a unit of length), the chemical alternation of B and N atoms causes the ionic nature of this distinctly different, insulating crystal. This makes BN interesting not only on its own, but especially as a counterpart to carbon graphene. Recent work has advanced the connection between the white and black graphene beyond the sheer analogy toward producing actual layers of hybridized BN and graphene domains. These experiments suggest the intriguing possibility of interfacing the white graphene (BN) with the “black” (C) within the same monolayer plane.
Energy analysis suggests that BNC mixtures should separate into immiscible BN and C. If indeed the distinct phases of BN and C coexist as the phase-separate epitaxial domains, their shape must be guided by the thermodynamic interface preferences. The corresponding quantity is the interface energy $\Gamma(\chi)$ for different orientation angles, $\chi$. This is of course closely related with a more basic property, the energy of pristine BN edges, $\gamma(\chi)$. Here we investigate how these interface energies can be calculated despite low symmetry of the lattice and reveal their variability with chemical potential of constituents. We further define the equilibrium shape of either free BN-clusters or of the inclusions of C in BN and vice versa and discuss rather briefly what effects they have on their electronic and magnetic properties.

The BN/C interfaces and the free BN edges can be of different kinds, depending on the edge-cut direction. In analogy to graphene, the basic edges are either along the zigzag (Z) atomic motif or along the armchair (A) pattern; in between, a variety of chiral edges can be cut at some angle $\chi$. At this however the similarity ends, as the distinctly different physics of BN edges is caused by the lack of inversion symmetry in the lattice and its binary composition. We will see that the former complicates the definition of the edge energies, while the latter may offer an advantage: having two chemical constituents instead of one adds extra degree of freedom in the Gibbs phase rule, that is a freedom to balance the chemical potential between B and N, which permits control of the shapes, properties, and can be of practical interest.

Despite these fundamental differences, we can initially use the energy decomposition ansatz to represent the edge energy as a sum over the atoms of A and Z.
types. For BN though, an immediate generalization must be made to account for the fact that its zigzag edges are “chemically unbalanced” and expose either all B or all N atoms, henceforth ZB or ZN. Consequently, the nontrivial chiral angles range doubles to 60° instead of 30° for graphene or carbon tubes. Choosing the armchair BN-bond direction as reference for $\chi = 0$, we obtain

$$\gamma(\chi) = |\gamma| \cos(\chi + C)$$

(3.1)

where $|\gamma| = 2(\gamma_A^2 + \gamma_{Zx}^2 - \sqrt{3} \gamma_A \gamma_{Zx})^{1/2}$ and $C = \text{sgn}(\chi) \cdot \arctan(\sqrt{3} - 2 \gamma_{Zx}/\gamma_A)$ with the subscript $x = N$ at $-30^\circ < \chi < 0$ or $x = B$ at $0 < \chi < 30^\circ$. This equation determines the energy of arbitrary edge, as long as the basic energies $\gamma_A, \gamma_{ZB},$ and $\gamma_{ZN}$ are known (that is for $\chi = 0$ and $\pm 30^\circ$). We therefore proceed finding these important quantities.

A common way to find a surface or edge energy is to compute the total slab energy, subtract the energy of equivalent material in its bulk form, and assign the rest to the edges. For BN ribbons with the basic edges of length $L$ (in units of $l$) one has (Fig. 3.16a, b)

$$\gamma_A = \frac{(E_s - M_{BN}\mu_{BN})}{2L}$$

$$\gamma_A = \frac{(\gamma_{ZB} + \gamma_{ZN} - M_{BN}\mu_{BN})}{2} = \frac{(E_s - M_{BN}\mu_{BN})}{2L}$$

(3.2)

Here $E_s$ is the total energy of a ribbon (subscript “$s$”) oriented along either A or Z direction, $M_{BN}$ is a number of constituent BN-pairs, and $\mu_{BN} = \mu_B + \mu_N$ is their energy in the BN sheet. It can be chosen as zero level, while the chemical potentials for individual species can vary as $\mu_{B,N} = 1/2 \mu_{BN} \pm \mu$. This approach, straightforward in case of graphene, gets
however only “half job” done for BN. Although computations do yield $\gamma_A = 1.91$ eV and $\gamma_Z = 3$ eV, the latter is just a nominal average of the B- and N-rich edges (Fig. 3.16b), while the true physical values remain elusive: only found is the sum of the opposite sides, but they seem to remain inseparable. This general issue with materials of lower symmetries, especially noninvariant upon inversion like BN, has been underscored by Cahn. Having such problem encountered earlier for 3D semiconductors, we have overcome it by considering the polyhedra with identical faces. For a simpler 2D case of BN, one can consider the triangles surrounded by either all-ZB or all-ZN (Fig. 3.16c, d). Subtracting the material “cost” from the total energy of such triangle and omitting the insignificant contribution from the corners (which does not scale with size $L$), one recovers their true edge energies. The triangle inversion alters the excess of B to the excess of N around the perimeter

\[
\frac{(E_\uparrow - M_{BN}\mu_{BN} - L\mu_B)}{3L} = \gamma_{ZB} (\mu) = \gamma_{0ZB} - \mu/3
\]

(3.3a)

\[
\frac{(E_\downarrow - M_{BN}\mu_{BN} - L\mu_N)}{3L} = \gamma_{ZN} (\mu) = \gamma_{0ZN} + \mu/3
\]

(3.3b)

For a $\uparrow$-triangle of size $L$, direct counting yields $M_{BN} = 1/2L(L + 3)$, one extra N omitted as a corner correction, and $L$ extra B atoms. The latter is important as it means that the edge energy depends linearly on the chemical potential, as the right-hand side specifies. For the inverted $\downarrow$-triangle, B and N are interchanged; see eq. 3.3b. Direct energy calculations for a series of B-rich and N-rich triangular clusters of increasing size yield the data in Fig. 3.16e. Clearly linear plots show that the size is sufficient, and their slopes determine the edge
energies. By choosing the elemental chemical potentials as equal, $\mu_B = \mu_N = 1/2\mu_{BN}$, that is $\mu = 0$, we determine the values $\gamma_{ZB}^\circ = 3.26$ eV and $\gamma_{ZN}^\circ = 2.72$ eV. The average $[\gamma_{ZB}(\mu) + \gamma_{ZN}(\mu)]/2 = 2.99$ eV is independent of $\mu$ and agrees with $\gamma_Z$ of eq. 3.2 to 0.1%, showing excellent consistency. What one gained is now well-defined energies for the basic edges of BN, at arbitrary chemical conditions

$$\gamma_A = 1.9, \gamma_{ZB} = 3.3 - \mu/3, \gamma_{ZB} = 2.7 + \mu/3$$

(3.4)

all in eV. Together with eq. 3.1, eq. 3.4 describes the BN edge of arbitrary direction, including the basic A, ZB, ZN, and the chiral types, at any chosen chemical potential $\mu$. This in turn enables the use of Wulff construction to easily determine the equilibrium shapes of pristine BN clusters at different conditions. We note that unlike in case of monoelemental graphene, the shapes can vary broadly with the chemical potential $\mu$. If BN edges reconstruct, similar to graphene, their energies can also be obtained, in principle, through either ribbon or triangle models as described above.
Figure 3.16. Relaxed geometries of selected BN structures with boron atoms red and nitrogen blue: (a) an armchair ribbon, note the edge N-atoms buckle out; (b) zigzag ribbon, highlighted B and N at the opposite edges; (c) B-rich triangle and (d) N-rich triangle of size $L = 10$. (e) Total energy in a series of triangles shown as a function of their size $L$, red for B-rich and blue for N-rich.

More important than the isolated clusters are possible epitaxial BN inclusions into C-graphene, or vice versa, the inclusions of black-graphene C into white-graphene BN matrix, in their hybrid monolayers. For these systems of emerging interest, we go on now to determine the energies $\Gamma(\chi)$ of BN/C interfaces (Fig. 3.17a), which control the equilibrium morphology of such hybrids. The above approach can be undertaken again, in principle. In practice however, computations for the inclusion of BN in C (or C in BN) become exceedingly expensive. It is more efficient then to use already determined pristine edge values of eq. 3.4 and adjust them by the appropriate binding energies $E_{BN-C}$ at interface

$$\Gamma_{BN/C} = \gamma_{BN} + \gamma_{C} \cdot E_{BN-C}$$

(3.5)
Figure 3.17. (a) ZB/C interface with graphene bonds in black. (b) ZN-H edge passivated by hydrogen, white atoms. (c) The interface energy as a function of chemical potential of B: thick lines for bare edges, red is ZB, blue is ZN, purple is A edge; thin lines are for interfaces, red for ZB/C, blue for ZN/C, purple for A/C; dotted lines are red for ZB-H, blue for ZN-H, and purple for A-H.
For clarity the material-subscripts are included here, while elsewhere the blank \( \Gamma \) or \( \gamma \) refer to the BN/C interface or BN pristine edge. It is opportune that the binding energy, as just a difference between the joint and detached counter-sides (similar to the work of adhesion or cleavage energy) does not depend on \( \mu \), and its calculation is unobstructed by the low symmetries. Then, since \( \gamma_{\text{BN}} \) depends on chemical potential, so does the \( \Gamma_{\text{BN/C}} \). We also include as example the hydrogen-passivated edges BN-H, Fig. 3.17b. The data in Fig. 3.17c show that the termination of the dangling bonds significantly reduces the energy in both cases, compared to pristine edge, as expected. Still, the chemical balance between B and N (\( \mu \) value) controls the interface energy in the same way as for pristine edge.

As a conductor-in-insulator hybrid, graphene embedded in BN matrix appears more interesting than the opposite. Any practical realization would greatly benefit from some degree of control of domain patterns. This poses an important question of what equilibrium shapes to expect, as determined by Wulff construction, based in turn on the interface energy \( \Gamma(\chi) \)? Fig. 3.18 shows the basic interface energies along with the computed Wulff constructions for a range of chemical conditions quantified by the value of \( \mu \). Modulation of the latter should allow one to broadly vary the shapes of inclusions, in striking contrast to pure graphene where the equilibrium islands are nearly hexagonal or more rounded polygons. Notably, nonintuitive shapes such as sharp triangles become preferred at N-rich (left) or B-rich (right) conditions, Fig. 3.18. In the middle, the Wulff construct is hexagon with truncated-rounded polygons at the transient \( \mu \) values.
Figure 3.18. (a) The energies for the boron-rich zigzag (ZB/C, red), armchair (A/C, purple) and nitrogen-rich zigzag (ZN/C, blue) interfaces, as a function of chemical potential of B.

Dotted line shows the magnetism, per unit of perimeter, in Bohr magnetons \( \mu_B \), as it changes along with the equilibrium shape of graphene inclusions shown in (b–f), from triangle at N-rich condition, to a nonagon (c) and nonmagnetic hexagon (d), and further to inverted nonagon (e) and B-rich triangle again (f). The outline colors mark the interface composition, red for ZB/C, purple for A/C, and blue for ZN/C, and the shapes are computed for \( \mu = -0.86, 0.42, 0.85, 1.55, \) and \( 2.69 \) eV. Thin arrows length is proportional to the magnitude of magnetism.
Along with the shape, other properties such as electronic gap and especially magnetism also change. The magnetism originates from π-electrons of carbon and is localized at the Z-edge. Computations show that triangle graphene domains are ferromagnetic with the total spin equal to the half of excess number of B or N atoms around the perimeter, obeying the Lieb’s theorem. The thin arrows in Fig. 3.18b-f show the cumulative spin around the borders of different domains: triangles have the largest magnetic moment, reduced as the shapes get truncated, and then vanishing for nonmagnetic armchair-edge hexagon. The calculated change of magnetic moment per perimeter unit |μ| is summarized in Fig. 3.18a by a dotted line. While the details of magnetism and electronics of the emerging islands deserve a separate study, beyond the scope of this report, we mention a few basic features. As example, we computed the spin density for the ferromagnetic triangles, either B-rich (Fig. 3.19a) or N-rich (Fig 3.19b) at the borders with the densities of opposite spin shown in opposite shades of gray. If these mutually inverted triangles were to coexist in the same lattice, their magnetic moments would be antiparallel.
Figure 3.19. Spin density (a,b) and band structure (c,d) of graphene triangle embedded in BN matrix. Data in (a,c) correspond to boron-rich borders B/C, while (b,d) correspond to nitrogen-rich border N/C. In (a,b), black isosurface is for the density of spin up and gray for the spin down with isolevel set at 1/10 of maximum. The energy bands in (c,d) are plotted along high symmetry directions of rectangular Brillouin zone for graphene inclusion QD of size $L = 3$, smaller than in (a,b), embedded in a rectangular BN unit cell. $\Gamma$, $X$, $M$, $Y$ indicate
(0, 0), (1, 0), (1, 1) and (0, 1) points. Black and gray dotted curves show the bands for the opposite spins. Dashed lines show the Fermi level, and the vertical arrows show the band gaps.

Because of quantum confinement, the intrinsically semimetallic graphene isles gain the characteristics of a quantum dots (QD, similar to vacancy clusters in graphane); Fig. 3.19c, d shows the computed flat, dispersionless bands with significant HOMO–LUMO distances. The band gap $E_g$ scales with the size $M$ of the isle-QD as $E_g \sim 1/\sqrt{M}$, following the trend for confined Dirac fermions.) Further, in contrast to nonmagnetic hexagonal QD, a magnetic triangular isle displays distinctly different energy gaps for the spin majority and minority bands. Calculations show that the B-terminated QD have larger band gaps for spin majority than minority, while in the N-terminated QD the band gaps are in the reverse order, smaller for majority-spin bands and greater for minority.

A systematic way discussed above allows one to determine the energies $\gamma(\chi)$ of arbitrary h-BN edges, for the basic directions given in eq. 3.4. The dependence on chemical potential difference $\mu$ between B and N species suggests that the equilibrium nanoparticles should be triangular (a counterintuitive shape of larger perimeter) with zigzag edges, except the narrow middle range of chemical conditions where more compact hexagons with armchair edge dominate. In fact, experimental observations and particularly the shape evolution between hexagonal and triangular nanoplates strongly support the notion of morphology control discussed above. Making further connection to BN nanotubes, their chiral distribution is not detailed, but believed in recent reports to be mostly zigzag; this contrasts to carbon tubes, and can be explained by the preference of zigzag edge (Fig.
3.17c) in either boron-rich or nitrogen-rich conditions. For graphene isles in BN, the BN/C interface energies are also unambiguously computed, as \( \Gamma_A = 0.56 \) and \( \Gamma_{ZA} = (0.95 - \mu/3) \), \( \Gamma_{ZN} = (0.38 + \mu/3) \), Fig. 3.18a. Their variability suggests a way to selectively synthesize the inclusions of desirable shapes, with triangular quantum-dots islands displaying largest magnetic moment. Further work can clear the ways to use the balance between the B, N and C, and possibly the electronic chemical potential as additional controlling parameter, for design and growth of their hybridized domains with desirable physical properties. A concluding disclaimer can hardly be more precise than a quote from Conyers Herring’s classics: “Although the interpretation of experiments in such fields as the shapes of small particles and the thermal etching of surfaces usually involves problems of kinetics rather than mere equilibrium considerations, it is suggested that a knowledge of the relative free energies of different shapes or [edge] configurations may provide a useful perspective.”
Chapter 4

Graphene-based anode for lithium-ion battery

This chapter studies the fundamental limit of graphene as Li-ion battery anode. Strategies of improvement are also discussed.

4.1. Feasibility of Lithium Storage on Graphene and Its Derivatives

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The search for high energy density electrodes is one of the central topics in lithium (Li) ion battery studies. The energy density is proportional to the product of full-cell voltage times Li capacity. Nano-materials have been expected to have high storage capacities due to their high surface-to-mass ratio, as compared to three-dimensional (3D) bulk materials. For example, two-dimensional (2D) carbon -- graphene, with its record surface-to-mass ratio of 2630 m²/kg, has proven to be a promising matrix for hydrogen
However, the experimental studies of Li storage on graphene remain controversial, and it is still not clear whether graphene could have a higher capacity than graphite, which is used commercially as an anode with a capacity of 372 mAh/g (340 mAh/g, including Li own weight). Some experiments do show high Li capacity for graphene nano-sheets, within a few charge/discharge cycles. Yet detailed examination of graphene quality attributes the Li storage to binding with defects, which are created during the fabrication of nano-sheets. Furthermore, in situ Raman spectroscopy indicates that the amount of Li absorbed on monolayer graphene is greatly reduced compared to graphite, while the intercalation of Li into few layer graphene seems to resemble that of graphite. In order to further clarify this issue, we perform first-principles computations to assess the Li storage in the carbon (C) based nano-materials. We start from the general description of obtaining battery characteristics from calculations, and then apply it to Li-graphene system, which shows a distinguishing Li storage behavior compared with graphite. The feasibility of modifying graphene for the Li storage is further explored, which leads to the finding that the layered C₃B compound could be a promising storage medium.

The materials used as electrodes for Li storage should have binding strength with Li within certain range. On the one hand, binding to anode material matrix (M) should be weaker than on the cathode side, to ensure the chemical potential driving force for subsequent Li migration from anode to cathode during discharge; this binding energy difference divided by electron charge e gives the average discharge voltage. On the other hand, this binding energy $\varepsilon_{\text{Li-M}}$ should be greater than cohesive energy $\varepsilon_{\text{Li}}$ of bulk Li, in order to prevent phase separation and formation of hazardous Li dendrites. The theoretical capacity of the matrix (M) is determined by the highest Li:M ratio (commonly
expressed in the units of mAh/g) that can be achieved in the stable compounds without phase separation, i.e. Li precipitation on the anode. Generally, it can be found by considering the energy $\varepsilon(x')$ per *average atom* in the composition $\text{Li}_x\text{M}_{1-x}$, $\varepsilon(x')$ curve.\(^{129}\) In context of electrode, since the matrix $\text{M}$ essentially retains its fixed amount, here we find it more convenient to determine the capacity from the lithiation energy $E$ per *matrix unit* versus composition variable $x$ in $\text{Li}_x\text{M}$, a lithiation curve $E(x)$ defined as:

\[
E(x) \equiv E(\text{Li}_x\text{M}) + x\varepsilon_{\text{Li}} - E(\text{M}),
\]

(4.1)

where $E(\text{Li}_x\text{M})$ is the energy of $\text{Li}_x\text{M}$ and $E(\text{M})$ is the energy of matrix $\text{M}$, both w.r.t atomic states of constituent elements. The number of $\text{M}$ atoms in the matrix unit, can be normalized to 6 atoms, so that graphite’s known charged phase would have $x = 1$, which allows for a convenient comparison of capacities for different matrix materials. A number of physical quantities can be extracted from the lithiation curve. First, according to Eq. 4.1, the lithium–matrix binding energy $\varepsilon_{\text{Li-M}}$, relative to the cohesive energy $\varepsilon_{\text{Li}}$ of bulk Li, can be determined from the curves as $\varepsilon_{\text{Li-M}} - \varepsilon_{\text{Li}} = -E(x)/x$ (and is linearly related to the average discharge voltage, as mentioned above). Second, following the basic thermodynamics definitions, the value of Li chemical potential (again, relative to the bulk Li, and neglecting temperature and entropy effects) is simply a derivative of the lithiation curve, $\partial E(x)/\partial x$. Thus, a negative slope of the lithiation curve suggests that more Li can be stored, while a positive slope means that Li would rather precipitate from that composition, leading to the phase separation and the formation of dendrites. Therefore, the achievable capacity limit is determined by the position $x$ of the minimum of the $E(x)$ curve (possibly with some excess
permitted by the nucleation barrier to the Li precipitation). We obtain the E(x) plots by first-principles computations, assisted by the cluster expansion method.\textsuperscript{130,131} The detailed description of calculations can be found in Supporting Information (SI). Representative points from the full lithiation curves (shown in SI) are plotted in Fig. 4.1 and 3. These points correspond to the ground-state configurations at each respective composition. The solid circles mark the Li-saturated (fully charged) phases, while the continued dashed curves show the concentration ranges prone to metallic Li precipitation.

In Fig. 4.1, the graphite lithiation curve is negative with a minimum at x = 1, corresponding to a stable compound, LiC\textsubscript{6}, with a capacity of 372 mAh/g, in agreement with the literature.\textsuperscript{109} The atomic structure of LiC\textsubscript{6} is shown in Fig. 4.1 as well, where the numbers (in eV) are the energy cost for adding (or removing) a single Li atom to (or from) bulk LiC\textsubscript{6} of large size. All the numbers are positive, indicating that the compound is indeed stable.

For graphene, in contrast, the lithiation energy in Fig. 4.1 is always positive, monotonically increasing with Li loading, indicating that the capacity is, in fact, zero! The contrasting lithiation behaviors result from the different ε\textsubscript{Li-M}. Although in both cases Li loses its 2s electron to C, producing ionic Li–C bonding, the bonding energies are different: ε\textsubscript{Li-graphite} > ε\textsubscript{Li} > ε\textsubscript{Li-graphene}. For example, at x = 1, ε\textsubscript{Li-graphite} - ε\textsubscript{Li} = 0.07 eV, while ε\textsubscript{Li-graphene} - ε\textsubscript{Li} = -0.61 eV. Therefore, when loaded with Li, the energy of Li–graphite system drops due to the increase in the favorable Li–graphite bonding, until reaching the LiC\textsubscript{6} composition, where further Li loading results in a strong repulsion between Li ions at neighboring hexagons.\textsuperscript{132} In contrast, the energy of Li–graphene system rises during lithiation due to the
increasing amount of relatively unfavorable Li–graphene interactions, accompanied by the Li–Li ions repulsion. Moreover, the positive lithiation energy of graphene means that the Li adatoms on it should aggregate into clusters and eventually macroscopic dendrites, instead of forming any stable Li–graphene mixture phase.

Why does the $\varepsilon_{\text{Li-M}}$ differ so much between graphite and graphene? In graphite, the Li ions are intercalated between two C layers, while on graphene, the Li ions are only adsorbed on surface. The intercalation configuration raises the $\varepsilon_{\text{Li-M}}$ due to the increased Li coordination (greater “contact area” with the matrix). The role of intercalation is further evident in the lithiation of bilayer, as shown in Fig. 4.1. Our calculations show that it is energetically favorable for the Li ions to enter between the C layers, rather than to be adsorbed on the exterior surface. Due to the available intercalation sites, bilayer graphene can store Li in the form of LiC$_{16}$. Another nearly-degenerate in energy form LiC$_{12}$ is also found, with the Li ordering between two layers similar to that in graphite, Fig. 4.1 (energy difference being only $\sim$2 meV, which is within calculation accuracy; proper treatment of van der Waals interactions might help distinguish their energies). The $\varepsilon_{\text{Li-bilayer}}$ is close to the $\varepsilon_{\text{Li-graphite}}$ at the corresponding Li-saturated configurations, with the former binding slightly stronger by 0.06 eV/Li, indicating again that the enhanced binding is mainly due to the intercalation configuration. In summary, although graphene (monolayer or multilayer) provides more accessible surface area, the exposed surfaces turn relatively inactive, with Li binding weak, which is unable to prevent Li phase separation, and consequently leads to a reduced capacity.
However, the accessibility of the open graphene forms and almost certainly faster surface diffusion are very attractive for better kinetic performance of the electrodes. To remedy the insufficient binding, graphene surfaces might be “activated” by several means briefly assessed below.

*Elastic deformation.* One can reasonably hypothesize that curvature of graphene lattice should change purely sp\(^2\)-hybridization to partially sp\(^3\) (often quantified by the pyramidalization angle),\(^{134,135}\) making C lattice more chemically active. To evaluate this possibility, we have computed the binding energies, to show in Fig. 4.2 how the purely elastic curvature of carbon nanotube (CNT) wall enhances binding with a single Li atom. As the diameter increases, the $\varepsilon_{\text{Li-CNT}}$ decreases and asymptotically approaches the $\varepsilon_{\text{Li-graphene}}$. Interestingly, the single Li atom prefers adsorption on the outer rather than the inner surface of CNT wall (though the difference is small, $< 0.03$ eV), while at high Li concentrations, the inner surfaces become more favorable than the outer. However, for small-diameter CNT such as (5, 5), the energy preferences are reversed. While any systematic investigation of elastic curvature effects on binding strength is beyond the scope of this study, several computed samples are already informative. In all cases, the $\varepsilon_{\text{Li-CNT}}$ is still less than the cohesive energy $\varepsilon_{\text{Li}}$ of bulk Li, which indicates that the single-wall CNT cannot form stable compound with Li and thus has low capacity.

*Native structural disorder,* such as pentagons, heptagons, dislocations, Stone-Wales defects, mono- or di-vacancies, ad-dimers, and edges. Fig. 4.2 shows the configurations of Li complexes with such defects, and the relative binding energies, $\varepsilon_{\text{Li}} - \varepsilon_{\text{Li-defect}}$. While pristine graphene cannot effectively adsorb a single Li atom from its bulk state (0.31 eV
endothermic) most of defects can bind Li exothermically, and therefore stably w.r.t. clustering. The strongest binding site is at the zigzag edge, due to the presence of dangling bonds. Our results suggest that Li can be stored in disordered graphene, which could possibly give rise to the capacity observed in some experiments. In order to achieve a high Li capacity for practical applications, one would need to fabricate highly defective graphene. This is in the contrary to the mainstream efforts to synthesize defect-free graphene, but may be possible with amorphous graphene produced by irradiation.

**Anchoring of other Li-adsorbing materials** (silicon, metal oxides, etc.) to graphene surface should be mentioned, although we do not perform here any actual computations of specific systems. Not only the high surface-mass ratio but also the high conductivity of graphene could be utilized in this approach. However, the clustering of Li-adsorbing materials could be a potential problem, similar to the reduction of hydrogen uptake induced by the clustering of hydrogen-adsorbing metals.

**Chemical doping.** Since Li donates its 2s electron to the matrix, an electron-deficient matrix, such as B-substituted C, could better accommodate for extra electrons. Fig. 4.2 shows that, indeed, binding is stronger at B substitution site than on pristine graphene, while it is weaker at the electron-abundant N-substitution site. Besides, such dopants are inherent part of the matrix lattice, which eliminates the problem of dopant clustering. Therefore, highly B-doped graphene, or in other words, 2D C-B compound, should be a good candidate for Li storage. In fact, recent studies have confirmed that the Li storage can be enhanced by B doping. Graphene can also be doped with other elements such as Si,
P, and S. For comparison, the Li binding energies \( \varepsilon_{Li} - \varepsilon_{Li-M} \) where \( M = B, N, Si, P, S \) are calculated, which are \(-0.88, 0.82, -0.40, -0.38, 0.21\) eV/atom, respectively. Clearly the B-doped graphene has the strongest binding with Li, suggesting a possibly highest capacity. In addition, only B and N dopants can keep the originally planar structure of graphene, while the other dopants are buckled by \( \sim 1.6 \) Å. The significant distortions imply the possible instability of these dopants. Moreover, solid experimental evidence of stable 2D C-Si, -P, and -S compounds are still lacking. We therefore focus on the C-B system. The experimentally available 2D compound with the highest B:C ratio is \( 2D C_3B \), which has a 2D structure with C-hexagons connected by B atoms\(^{150-155} \) shown in Fig. 4.3. The \( C_3B \) layers can be stacked up to form graphite-like 3D structure \( 3D C_3B \), with weak van der Waals interactions between layers\(^{156,157} \). In the following, we discuss the Li storage in the \( C_3B \) in some detail since it appears potentially interesting for anode applications.

The lithiation curves and atomic structures of the Li-saturated \( C_3B \) are shown in Fig. 4.3. The corresponding atomic structures are shown in Figure S2. During lithiation, the \( 3D C_3B \) preserves its layered structure but changes the stacking from AB order\(^ {158} \) to AA (every next layer is directly on top of the previous one). This behavior is similar to that of graphite, suggesting a small volume variation in discharge/charge cycles. The Li-saturated \( 3D C_3B \) has all the hexagons occupied by Li except those composed entirely of C, resulting in the Li\(_{1.5}\)C\(_3B\) composition with a capacity of 857 mAh/g, which is 2.3 times greater than that of graphite. Though \( 2D C_3B \) has both its sides exposed for adsorbing Li, fewer hexagons are occupied in the fully-lithiated state, which has the Li\(_{1.25}\)C\(_3B\) composition with a capacity of 714 mAh/g. Once again, we see that the 2D material does not necessarily have higher capacity than its corresponding 3D form, in spite of higher surface-to-mass ratio. The
reason of the Li capacity reduction in the 2D C3B is similar to that of graphene: binding for surface adsorption is weaker than that for intercalation. For example, at Li:C3B = 0.5 (x = 0.75) this difference is $\varepsilon_{\text{Li-2D C3B}} - \varepsilon_{\text{Li-3D C3B}} = -1.20 \text{ eV}$. On the other hand, the weaker binding to 2D C3B could turn beneficial for battery voltage: if used as the anode, the 2D C3B should yield higher average voltage than 3D C3B by 0.52 V. Taking the cathode half-cell voltage of 3.7 V (corresponding to the commercially used cathode material LiCoO2),111 the estimated energy densities for 2D C3B and 3D C3B are very close, 2121 and 2100 Wh/kg, respectively, both far surpassing that of graphite (1347 Wh/kg). It is further interesting to note that if only one side of C3B is allowed to adsorb Li, it could reach the same high capacity as 3D C3B (Li1.5C3B, 857 mAh/g), while also maintaining a voltage even higher than for both-sides lithiation (surpassing the 2D C3B by 0.25 V, with an energy density of 2760 Wh/kg), as shown in the SI. It suggests a superior anode could be made of C3B capped single-wall nanotubes or foams,159 where the Li ions cannot penetrate through the tubes into the inner region160 and thus are mainly adsorbed onto the exterior of tubes.

As discussed above, the enhanced Li storage in C3B results from the greater binding, $\varepsilon_{\text{Li-C3B}}$. This strong binding is explained by the charge density difference between Li-saturated and pure C3B, as shown in Fig. 4.4. There are no valence electrons surrounding Li, indicating that Li is fully ionized. The electrons transferred from Li to C3B are mainly concentrated on B, filling the originally empty $p_z$ states of B. Due to the better accommodation of the transferred electrons C3B has a higher binding energy with Li than that of graphite.
In spite of significantly different binding energies $\varepsilon_{\text{Li,M}}$, the diffusion activation barriers for the Li ions in both matrices are similar. One of the diffusion mechanisms at high Li concentration is vacancy hopping, shown in Fig. 4.4, which has a barrier of 0.40 eV, comparable with that in graphite 0.34 eV (using consistent calculations settings, shown in the SI). In reality, the diffusion is more complicated since the large size anode inevitably contains defects which impact the diffusivity in different ways. For example, the Li transport perpendicular to the basal plane of graphite is facilitated by the defects, whereas the diffusion parallel to the plane is limited by the defects.\textsuperscript{161} The influence of the defects on Li diffusivity deserves further study. Although the pristine C3B sheet is a semiconductor with a band gap of \(~0.5\) eV,\textsuperscript{162} it becomes metallic during lithiation, as demonstrated by the electronic density of states plot in the Fig. 4.4. The similar ionic and electronic conductivity between C\textsubscript{3}B and graphite should give comparable discharge/charge rates for the battery. Overall, C\textsubscript{3}B has a larger capacity and similar power density compared to graphite, but somewhat lower voltage as a consequence of larger $\varepsilon_{\text{Li,M}}$.

In summary, although nanomaterials provide more free surfaces for adsorption compared with bulk materials, they might suffer from the weakened adsorbate-adsorbent binding, which could lead to the adsorbates clustering and a decreased adsorbate capacity. This conclusion is exemplified by Li storage in graphene, where Li phase separation results in significant capacity limitations (down to zero for pristine monolayer graphene). The feasibility of modifying graphene to store Li more efficiently is discussed, including its doping, and leading one to stoichiometric 2D compound C\textsubscript{3}B as a promising electrode material. Its capacity is about twice larger than graphite, with comparable power density and small volume variation during discharge/charge cycles. Our results help to clarify the
fundamentals of Li storage in low-dimensional materials, and shed light on the rational design of nano-architectures for energy storage.
Figure 4.1. Left: lithiation energy (defined in Equation 1) as a function of Li amount $x$ in different C matrices: graphite, graphene, and bilayer graphene. The positive and negative binding energy domains are shown in different scales. Right: atomic structures of Li-saturated graphite and bilayer graphene (top and perspective views). The Li is represented by balls and the C matrix by sticks. The arrows indicate the primitive cell vectors. The numbers are the energies of adding (removing, in italics) a Li atom to (from) the empty (Li-filled) hexagons, all in eV. For the bilayer, the energies of Li intercalation/deintercalation
between the layers are shown in the top view, and those for Li adsorption/desorption at the exterior are marked in the perspective view.

Figure 4.2. Energies and structures of Li adsorbed on carbon nanotubes (CNT) and defects. The balls show Li, and the sticks represent C lattice. The numbers are calculated as εLi – εLi-M, in eV. The energy of a single Li atom adsorption on pristine graphene (hexagon) is also shown for comparison. The plots show εLi – εLi-CNT as a function of diameter for
(5, 5), (10, 10), and (15, 15) CNTs, for adsorption on inner or outer surfaces, at high (LiC6, solid lines) or low ((LiC∞, dashed lines) concentrations.

Figure 4.3. Lithiation energy (defined in Equation 1) as a function of Li amount in C3B matrix, and atomic structures of Li-saturated bulk and monolayer C3B. The matrix is shown by sticks with B-substitutions marked by black balls, and the Li ions are represented by the
pink circles (solid for top/front and unfilled for bottom/back sides of monolayer C3B). The arrows indicate the primitive cell vectors. The numbers are the energy change upon adding (or removing) a Li ion to (from) the empty (Li-filled) hexagons. For monolayer C3B, the energies are shown for Li adsorption/desorption on the top surface.

**Figure 4.4.** Top left: charge density difference between Li-saturated and Li-free 3DC3B; the electron accumulation region is shown by blue isosurfaces, for both top and side views. The matrix is shown by sticks with B-substitutions marked by black balls, and the Li ions are...
represented by the pink balls. Top right: electronic density of states of Li-saturated 3DC3B, with Fermi level at 0 eV. Bottom: energies and pathways of vacancy-hopping diffusion in Li-saturated 3DC3B. The insets from left to right show the initial, transition state, and final structures, respectively.

4.2. Assessing carbon-based anodes for lithium-ion batteries: A universal description of charge-transfer binding

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The growing demand for energy storage emphasizes the urgent need for higher-performance Li-ion batteries (LIBs). Several key characteristics of LIB performance—namely, reversible capacity, voltage, and energy density—are ultimately determined by the binding between Li and the electrode material. Graphite has long been used commercially as a LIB anode, and recently, defective graphene and other $sp^2$ C derivatives have shown promise as high-capacity and high-power anodes. However, these seemingly similar substrates exhibit a wide range of Li-C binding energies. For example, pentagon-heptagon pairs are the dominant structural features in both Stone-Wales defects and in certain graphene divacancy complexes, yet theoretical Li binding on the two differs by 0.8 eV. Similar variations are observed for carbon nanotubes (CNTs) with comparable diameters but different chiralities. This in turn contributes to significant variability in the measured voltages and capacities of C-based anodes, ranging from hundreds to thousands of mAh/g. Defect incorporation has also demonstrated increases in voltage and capacity, yet the specific defect
identities and their role in battery performance merit further exploration. These facts suggest a key factor is missing in the current physical understanding of the underlying Li binding mechanism on C-derived structures, limiting predictive capability.

In this letter, we use plane-wave Density Functional Theory (DFT) calculations to demonstrate how the binding energy of Li on $sp^2$ C-based LIB anode candidates derives from specific features in the intrinsic electronic structure of the substrate, and in most cases can be straightforwardly predicted using a relatively simple descriptor. We further suggest that this same binding descriptor could be generalized to other systems with charge transfer-dominated adsorption behavior. A wide variety of C substrates are considered, including pristine, defective, and strained graphene; graphene-derived molecular clusters; CNTs; C edges modeled by graphene nanoribbons (GNRs); and multilayer graphene. Several point defects are examined: the Stone-Wales (SW) defect, the 5-8-5 (DV$_{585}$) and 555-777 (DV$_{557}$) divacancies, a monovacancy (MV), and single-site substitution by nitrogen (N$_C$) or boron (B$_C$).

The binding energy of a single Li atom is:

$$\varepsilon_{Li-X} = \frac{[E(X) + E(Li\text{-atom}) - E(Li-X)]}{N_{Li}}$$

(4.2)

where $E(X)$, $E(Li\text{-atom})$, and $E(Li-X)$ are the energies of the Li-free substrate X, an isolated Li atom, and the Li-adsorbed substrate X, respectively. $N_{Li}$ is the number of adsorbed Li atoms in the supercell. We report the values with respect to the cohesive energy of bulk Li ($\varepsilon_{Li-Li}$) according to $\Delta \varepsilon_{Li-X} \equiv \varepsilon_{Li-Li} - \varepsilon_{Li-X}$; lower values represent stronger binding.
**Figure 4.5.** (a) Band structure of graphene (6x6 cell) without (left) and with (right) Li. The Fermi level (blue line) is set to zero. (b) Charge density difference between Li-free and Li-adsorbed graphene for states above (left) and below (middle) the Dirac point, and for all states (right). Electron accumulation (depletion) upon Li adsorption (purple) is indicated by the yellow (blue) isosurface of 10⁻³/Bohr³. (c) Band structure of a DVt5t7 defect (6x6 cell) without (left) and with (right) Li.
Upon dilute Li adsorption (concentrations below LiC$_{10}$, where LiC$_n$ represents a Li : C ratio of 1 : n), the Dirac cone near the Fermi level ($\varepsilon_f$) of pristine graphene retains its shape, while $\varepsilon_f$ is shifted to a higher energy, as shown in Fig. 4.5a. The number of occupied states above the Dirac point (DP) equals the number of Li atoms, indicating complete ionization of Li via charge transfer to the substrate. The states occupied upon Li-to-C electron transfer have completely delocalized π character (left-hand panel, Fig. 4.5b). We refer to this behavior as “states-filling”, as it describes a rigid occupation shift against a backdrop of otherwise unchanged π states in the vicinity of $\varepsilon_f$. In this respect, Li on graphene appears to behave similarly to an electronic dopant in the energy window near $\varepsilon_f$. This response differs from that of many transition metal adatoms, which tend to create new states within the Dirac cone.$^{171,172}$ Nevertheless, we emphasize that the effect of Li is not that of pure electronic doping, since the potential from the adsorbed ion also alters the character of the deeper valence states; this can be seen in the center panel of Fig. 4.5b, in which valence charge density has accumulated near the ionized Li$^+$ adsorbate.

The states-filling behavior of pristine graphene is largely retained for almost all of the other substrates we tested, provided binding occurs on the basal plane (edge binding is discussed later). In each case, Li acts as a dopant near $\varepsilon_b$, donating its electron to previously unoccupied π C states without introducing additional bands. As an example, Fig. 4.5c shows the band structure of a DV$_{1557}$ point defect undergoing a mostly rigid shift upon Li binding. Other tested point defects exhibit analogous behavior, despite their strongly dissimilar electronic structures.
If we consider only the electronic doping character (i.e., rigid band shift) near $\epsilon_f$, then states-filling behavior suggests that $\epsilon_{\text{Li-X}}$ should correlate with the work required to fill empty C states with the Li-donated excess electron. With all energies referenced to the vacuum level, this work is defined as (per Li):

$$W_{\text{filling}} = \int_{\epsilon_{\text{LUS}}}^{\epsilon'} \frac{\epsilon D(\epsilon)}{N_{\text{Li}}} d\epsilon$$

(4.3)

where $\epsilon$ is the Kohn-Sham (KS) energy, $D(\epsilon)$ is the density of states (DOS) of the Li-free C supercell, and $\epsilon'$ satisfies the charge-conservation criterion:

$$\int_{\epsilon_{\text{LUS}}}^{\epsilon'} D(\epsilon) / N_{\text{Li}} d\epsilon = 1$$

(4.4)

Here, LUS is the lowest unoccupied state: the Fermi level ($\epsilon_f$) for a metal, the conduction-band minimum ($\epsilon_{\text{CBM}}$) for a non-metal, or the LUMO level for a finite system. We refer to Eq. 4.3 and 4.4 as the states-filling model (SFM). There are two cases of Equation 2 that deserve special consideration: (1) on a finite cluster, $\epsilon$ is discrete, and $W_{\text{filling}}$ becomes the LUS (LUMO); (2) in the infinitely dilute adsorption limit, $D(\epsilon)/N_{\text{Li}}$ diverges, and $W_{\text{filling}}$ again converges to the LUS ($\epsilon_f$ or $\epsilon_{\text{CBM}}$). Note that $W_{\text{filling}}$ implicitly depends on two factors: the C electronic structure and the Li concentration.
Figure 4.6. Linear dependence of $\Delta \varepsilon_{\text{Li-X}}$ on $W_{\text{filling}}$ for: (a) pristine graphene with different Li concentrations; (b) graphene under varying isotropic tensile strain, based on the percent increase in the lattice parameter; (c) defective graphene, where black circles represent adsorption directly at a defect site (Def), and blue triangles at an off-defect region (Off-def); (d) different-sized hexagonal graphene clusters with NC C atoms and Li
adsorption at the center; (e) CNTs of similar diameter (9.0-9.8 Å) but different chiralities (~ LiC600), with top-right (bottom-left) points representing semiconducting (metallic) CNTs; (f) all tested substrates. Red lines are linear fits.

Examination of the dependence of $\Delta \varepsilon_{\text{Li-X}}$ on $W_{\text{filling}}$ for dilute Li adsorption on a wide variety of $sp^2$ C forms shows that not only are the quantities indeed positively correlated, but that the relation is linear for each class of substrate modification (Fig. 4.6). The simplicity of the result is surprising, since the SFM deliberately ignores all perturbations to the deeper valence states. Fig. 4.6a shows the linearity with varying Li concentrations on pristine graphene up to LiC$_{72}$ (dense adsorption is addressed later). Increasing the concentration requires more high-energy states to be filled, which raises both $W_{\text{filling}}$ and $\Delta \varepsilon_{\text{Li-graphene}}$. Note that there is a concentration dependence of $W_{\text{filling}}$ even at very dilute adsorptions, a consequence of the delocalized nature of the newly filled π states (Fig. 4.5b). Fig. 4.6b shows the effect of isotropic tensile strain at fixed Li concentration (LiC$_{72}$) on graphene. $W_{\text{filling}}$ decreases with increased strain, and Li binding is stabilized. In Fig. 4.6c, Li is adsorbed on graphene with various point defects (~ LiC$_{72}$), which have very different electronic structures and hence a wide range of $W_{\text{filling}}$ values. Here we test two scenarios, one with Li placed in a region away from the defect and another with Li placed directly on the defect site. Either way, the linearity is manifest, deviating only slightly for direct adsorption on DV$_{1517}$ and B$_C$. The slope at the defect sites is steeper, reflecting additional changes to the low-energy states (confirmed by visualization of the electron accumulation). Fig. 4.6d shows the dependence of $\Delta \varepsilon_{\text{Li-cluster}}$ on the size of a finite graphene-like cluster. Smaller clusters have larger band gaps, which result in higher $W_{\text{filling}}$, and consequently, higher $\Delta \varepsilon_{\text{Li-cluster}}$. In Fig. 4.6e, Li is adsorbed on several chiralities of CNTs (~ LiC$_{600}$) with
similar diameters (9.0-9.8 Å). Metallic tubes have the lowest $W_{\text{filling}}$ and the strongest binding.

With all data viewed globally, the positive correlation between $\Delta \varepsilon_{\text{Li-X}}$ and $W_{\text{filling}}$ is clear (Fig. 4.6f). However, each type of modification has a unique slope and intercept within its individual linear relation. If rigid band shifts were solely responsible for the differences in Li-C binding, then one should always expect a slope of unity, yet this is not generally the case. In KS DFT, the total energy is:

$$E = \int \varepsilon D(\varepsilon) d\varepsilon - \frac{e^2}{2} \int dr \int dr' \frac{\rho(r)\rho(r')}{|r - r'|} + E_{\text{ion-ion}}$$

(4.5)

where successive terms represent the total energy of the occupied KS eigenstates, the Hartree energy, and the ion-ion Coulomb energy. In the SFM, $W_{\text{filling}}$ directly accounts only for energy changes in the states above $\varepsilon_{\text{LUS}}$ under the rigid-band approximation, which contribute to the first term in Eq. 4.5. Other possible contributions to $\varepsilon_{\text{Li-X}}$ that are not included in the SFM include: (1) deviations from the rigid-band approximation or changes in eigenstates below $\varepsilon_{\text{LUS}}$, (2) changes in the Hartree energy, and (3) changes in $E_{\text{ion-ion}}$.

Notably, the observed universal linearity between $\varepsilon_{\text{Li-X}}$ and $W_{\text{filling}}$ leads to the nontrivial conclusion that all collective remaining contributions to $\varepsilon_{\text{Li-X}}$ must also depend linearly on $W_{\text{filling}}$. We suspect that this dependence derives in part from two factors contained in $W_{\text{filling}}$ that also determine the screening of the adsorbate-induced electric field within the substrate: $^{173-175}$ the adsorbate concentration and the DOS at $\varepsilon_f$. As the concentration increases and the DOS decreases (i.e., fewer available states and generally larger $W_{\text{filling}}$),
screening becomes poorer and the electronic density becomes more inhomogeneous, impacting the effective Hartree potential. Within this interpretation, our observed linear relation is consistent with recent calculations by Santos and Kaxiras,\textsuperscript{176} who demonstrated a similar linear dependence between the in-plane electric susceptibility of graphene ribbons and the number of available atoms (i.e., states) across which charge may be redistributed.

The success of the SFM straightforwardly explains the observed diversity in $\varepsilon_{Li-X}$ values across substrates. For instance, the SW and DV\textsubscript{15t7} defects, both comprised of pentagon-heptagon pairs, have very different electronic structures: the DV\textsubscript{15t7} defect has a lower $\varepsilon_f$ (below the DP) due to its missing C atoms/electrons, and a higher DOS near $\varepsilon_f$ (compare Figs. 1c and S1). As a result, DV\textsubscript{15t7} shows lower $W_{\text{filling}}$ and stronger Li binding.\textsuperscript{163} Similarly, the lower $W_{\text{filling}}$ of metallic CNTs with respect to semiconducting CNTs explains the stronger Li binding to the former.\textsuperscript{169} In addition, substitutional B\textsubscript{C} and N\textsubscript{C} have similar DOS at $\varepsilon_f$\textsuperscript{177} yet the former has stronger $\varepsilon_{Li-X}$ due to its lower $\varepsilon_f$\textsuperscript{163} this is borne out in experiments demonstrating higher capacity for B treatment than N treatment.\textsuperscript{149}

The DOS dependence of $W_{\text{filling}}$ in Eq. 4.3 suggests that a key limitation of Li capacity in graphene derivatives lies in how easily excess electrons can be absorbed. This is closely related to the quantum capacitance $C_q(V) = e^2D(\varepsilon)$, the integral of which gives the potential-dependent ($V$) charge storage capacity.\textsuperscript{177,178} A high $C_q(V)$ near $\varepsilon_f$ therefore correlates with stronger binding. Accordingly, the intrinsically poor quantum capacitance of graphene becomes a vital consideration in the design of higher-capacity LIB anodes, much as it does in the design of C-based supercapacitors\textsuperscript{177,179} and field-effect transistors.\textsuperscript{180,181}
According to Eq. 4.3, $W_{\text{filling}}$ also depends on the vacuum-referenced $\epsilon_{\text{LUS}}$. In this regard, the SFM is a charge-transfer-binding analogue to the “$d$-band center” theory in transition-metal catalysis, which connects a higher metal $d$-band center to easier filling of antibonding states, and hence to stronger binding.\(^{182}\) It also justifies the observed dependence of surface molecular dissociation barriers (related to binding strength) on the catalyst work function, which converges to the vacuum-referenced $\epsilon_f(\epsilon_{\text{LUS}})$ for high-DOS metals.\(^{183}\)

Significantly, the SFM suggests simple guidelines for designing effective $sp^2$ C-based anodes, since a low $\epsilon_{\text{LUS}}$ and high $C_q(V)$ will lead to stronger Li binding and typically higher Li capacity. Accordingly, electron-withdrawing groups and $p$-type dopants are good candidates, which explains why materials such as BC$_3$ have high theoretical capacities.\(^{163}\) Point defects\(^{163}\) and curvature may also improve capacity, since they tend to elevate $C_q(V)$ near $\epsilon_f$.\(^{177}\) This probably contributes to experimentally observed voltage and capacity increases upon defect incorporation,\(^{124,126,148,149}\) which contrasts with the low Li adsorption limits found for pristine graphene.\(^{127}\)
Figure 4.7. (a) Band structure of graphene with dense Li concentration (LiC₆). (b) Concentration dependence of ΔεLi-graphene, showing the breakdown of linear dependence at high Li loading. (c) Band structure of a GNR with Li adsorbed at an armchair (AC) edge (black/red are spin up/down). Insets for (a) and (c) show charge density contributions from the states marked by arrows. (d) ΔεLi-graphene as a function of separation between periodically stacked LiC₆ layers, with the corresponding evolution of the Li-induced electron accumulation shown. (e) Electrostatic potential (-U; minimum set to zero) normal to stacked LiC₆ layers at the separations in (d), decreasing from top to bottom.
Although we have specifically developed the SFM to explain the physical principles underlying Li binding on the π manifold of $sp^2$ C, we emphasize that it should be generalizable to other systems and applications where charge transfer dominates the adsorption behavior. Nevertheless, there are some important conditions for its application. First, it contains no information about the site dependence of the binding energy, since it is based on the total DOS. Accordingly, it is best applied to systems where such sensitivity is low, such as when newly occupied states are delocalized.

Second, the SFM assumes charge transfer to the substrate is complete. As such, it fails at very high Li concentrations on low-DOS substrates, where the energetic cost for excess charge storage is large enough that charge transfers back to the Li as free-electron states (Fig. 4.7a). On pristine graphene, this occurs at concentrations beyond $\sim$ LiC$_8$ ($W_{\text{filling}} \sim -3.0$ eV), lowering $\Delta \epsilon_{\text{Li-graphene}}$ and leading to deviations from ideal states-filling behavior (Fig. 4.7b). This places an absolute limit on the $W_{\text{filling}}$ for which the SFM is expected to hold; once free-electron Li-derived states are introduced, adsorption can no longer be treated as dilute. Nevertheless, experimentally realizable reversible capacities of less-disordered C-based materials often fall well below this dilute threshold. 126

Third, the SFM relies on band rigidity near $\epsilon_{\text{LUS}}$ and therefore does not apply when bands/states are created in this region upon adsorption. One example is σ-binding of Li to graphene edges, where the Li electron localizes at the edge atoms and creates a new flat band (Fig. 4.7c).

Fourth, the SFM assumes that the within a modification class, the presence of the adsorbate perturbs deeper electronic states similarly for every value of $W_{\text{filling}}$. This
prevents direct comparisons between surface-adsorbed graphene and intercalated graphite, since the latter exhibits a qualitatively different π-electron density distribution due to overlap of the electrostatic potential wells of the individual stacked Li-adsorbed graphene sheets (Fig. 4.7d). As a result, graphite binds Li stronger than graphene by 0.7 eV (at LiC$_6$) yet has a very similar $W_{\text{filling}}$.

An added advantage of the SFM is that binding properties can be quickly predicted based only on the substrate electronic structure, which is useful for rapid primary screening. For instance, we can easily estimate the Li capacity of a candidate C-based anode, which is the critical concentration $c$ satisfying:

$$\varepsilon_{\text{Li-X}}(c) + c \frac{d\varepsilon_{\text{Li-X}}(c)}{dc} = 0$$

Solving Eq. 4.6 requires the continuous $\varepsilon_{\text{Li-X}}(c)$ function, which necessitates a large supercell calculation for each discretized value of $c$. If we apply the SFM, only two concentrations are needed to obtain the linear $\varepsilon_{\text{Li-X}}(W_{\text{filling}})$ equation for the chosen class of surface modification. By extracting $W_{\text{filling}}(c)$ from the continuous DOS of the unlithiated primitive cell, $\varepsilon_{\text{Li-X}}(c)$ and the corresponding Li capacity can then be straightforwardly determined. Capacity values obtained in this way show good agreement with explicit calculations of $\varepsilon_{\text{Li-X}}(c)$. A second example is how the dependence of $\varepsilon_{\text{Li-X}}$ on tensile strain can be easily computed at any given Li concentration.

In summary, we propose a simple descriptor that captures the essential physics of charge transfer-dominated binding on planar carbon, based on the work required to fill up the rigid electronic states of the substrate. Applied to C-based LIB anodes, our model
explains the physical origin of the wide range of Li-C binding energies reported in the literature, and suggests a link to the significant variability in the reported performance of graphene-derived anodes. It also provides guidelines for engineering more effective anodes; these predictions are consistent with experimentally demonstrated improvements via substrate modification. By drawing upon similar considerations to those used in catalyst and supercapacitor electrode design, the descriptor straightforwardly connects anode performance to intrinsic electronic structure and establishes the broader role of the latter in interfacial electrochemical systems.
This chapter discovers a new class of efficient hydrogen production electrocatalysts using a combined theoretical and experimental approach. This is achieved by using theory to extract a simple descriptor for surface electrocatalytic activity, then applying this descriptor to rapidly screen the periodic table for metal dichalcogenides with possible surface activity. We conclude that group 5 metal disulfides (TaS$_2$, VS$_2$, NbS$_2$) are excellent candidates. This prediction is directly verified by synthesizing and testing TaS$_2$, which show exceptional performance—better than any reported metal dichalcogenide. In addition, the performance actually improves with cycling due to self-catalyzed nanostructural changes.

This work has been submitted.
Hydrogen is not only an ideal energy carrier, but also an important agent for many chemical products. One popular method for generating hydrogen sustainably is via the hydrogen evolution reaction (HER), in which aqueous protons are electrochemically reduced with the aid of an appropriate catalyst—traditionally, an expensive precious metal. Recently, layered molybdenum (Mo) and tungsten (W) transition-metal dichalcogenides (MX$_2$) have attracted substantial interest as earth-abundant, inexpensive replacements for precious-metal HER catalysts. Unfortunately, their performance is limited by the low density of catalytically active sites, which are mainly located at the edges. An intrinsically surface-active MX$_2$ candidate is therefore highly desirable. In this report, we use first-principles calculations to unravel the underlying electronic factors that correlate with surface catalytic activity on MX$_2$, leading to the prediction and experimental demonstration of high activity for group 5 metal sulfides.

The HER proceeds via two steps, as illustrated in Fig. 5.1A: (i) H first adsorbs on the catalyst by H$^+$ + e$^-$ + $*$ → H$^*$ (Volmer reaction), where * denotes a catalytic site; (ii) then an H$_2$ molecule is formed and desorbed by either 2H$^*$ → H$_2$ + 2$*$ (Tafel reaction) or H$^*$ + e$^-$ + H$^*$ → H$_2$ + $*$ (Heyrovsky reaction). An ideal catalyst should provide an optimal balance between adsorption and desorption—a phenomenon known as the Sabatier principle, typified by the “volcano plot”. If the substrate interaction is too weak, then the Volmer reaction is inhibited; if it is too strong, then the Tafel/Heyrovksy reaction cannot proceed. The relative adsorption free energy of the H$^*$ intermediate therefore acts as an indicator of the catalytic activity.
Computing the adsorption free energy on all possible MX$_2$ combinations is tedious; in principle, it depends on the loading density and must be done even for dilute concentrations, which require large unit cells. Instead, we look for a descriptor based on the intrinsic substrate electronic structure that can readily predict adsorption without the need for explicit calculation, permitting rapid primary screening of MX$_2$ catalysts. To test possible descriptors, we initially target successful prediction of the dilute H adsorption energy, which we assume captures the dominant contributions to the adsorption free energy (full justification is given later). We define this adsorption energy as:

$$E_a = \frac{\left[ E(H+MX_2) - E(MX_2) - N_H E(H_2)/2 \right]}{N_H}$$  \hspace{1cm} (5.1)

where $E(H+MX_2)$, $E(MX_2)$ and $E(H_2)$ are the energy of H-adsorbed MX$_2$, pure MX$_2$, and an H$_2$ molecule, respectively. $N_H$ is the number of adsorbed H atoms. All quantities are calculated using Density Functional Theory (DFT).

An appropriate descriptor for the dilute H adsorption energy is suggested by examining changes in the underlying electronic structure of representative metallic (TiS$_2$) and semiconducting (MoS$_2$) MX$_2$ candidates upon adsorption. We use a single adsorbate in a 4×4 unit cell to approximate dilute adsorption. For metallic TiS$_2$ (Fig. 5.1C), H adsorption does not change the overall profile of the electronic density of states (DOS), but rather shifts the Fermi level ($\varepsilon_F$) to a slightly higher energy (i.e., occupies previously empty states). This shift in $\varepsilon_F$ corresponds to 1e per H adsorbate, indicating complete charge transfer to TiS$_2$. The charge density distribution shows that the transferred electrons are delocalized throughout the M layer. For semiconducting MoS$_2$ (Fig. 5.1D), the DOS profile also remains largely intact, with the exception of a new narrow band immediately below the conduction
band minimum ($\epsilon_{\text{CBM}}$) that is occupied by the transferred electrons. In other words, H behaves like a shallow $n$-type dopant. The charge density distribution shows that this state is quasi-localized in space. We can extrapolate the behavior of both materials to the infinitely dilute adsorption limit, where the number of transferred electrons becomes negligible with respect to the total DOS. In this case, the Fermi level of the metallic system (TiS$_2$) would remain unchanged by adsorption, whereas the Fermi level of the semiconducting system (MoS$_2$) would shift to the newly created localized state, which is pinned close to $\epsilon_{\text{CBM}}$. In addition, the DOS profile of each would be retained. Notably, this behavior is consistent with a model based on the ‘states-filling work’, which was recently proposed as an appropriate descriptor for predicting charge-transfer binding on sp$^2$-carbon substrates.$^{200}$ It is based on a rigid-band approximation, which assumes the underlying substrate DOS profile is unaffected by the adsorbate. Moreover, when operating at the dilute adsorption limit, the states-filling work converges to the energy of the lowest unoccupied state (LUS) $\epsilon_{\text{LUS}}$, defined as $\epsilon_F$ for metals or $\epsilon_{\text{CBM}}$ for semiconductors;$^{200}$ this agrees well with the two representative cases in the infinitely dilute limit, and is the definition we use here.
Figure 5.1. Applicability of the states-filling approach as a descriptor. (A) Schematic of MX2-catalyzed HER. (B) Correlation between $\varepsilon_{\text{LUS}}$ and the surface adsorption energy $E_a$ (Eq. 5.1) of H on a subset of MX2 candidates. TaS$_2$ (filled circles) are experimentally synthesized and tested later. (C) DOS of pristine and H-adsorbed TiS$_2$ (coverage of H:Ti = 1:16), with the Fermi level respect to vacuum. Right: charge density isosurface for states within the energy range of Fermi level to -0.025 eV below. (D) Same as (C) but for MoS$_2$. M: blue; X: yellow; H: black; charge density isosurface: red.

The suitability of $\varepsilon_{\text{LUS}}$ as a descriptor is confirmed in Fig. 5.1B. We calculate this quantity for a subset of known MX$_2$ species (based on the substrate alone without an adsorbate) and compare the result to the dilute H adsorption energy, evaluated explicitly
using Eq. 5.1. The two values correlate linearly with a slope of near unity (Fig. 5.1B). This implies that differences in $E_a$ amongst the various substrates originate almost exclusively from differences in $\epsilon_{\text{LUS}}$, and that the key to adjusting the H adsorption energy lies in the vacuum-referenced placement of the substrate LUS level. For comparison, we also tested two other possible adsorption descriptors. One uses the charge on X at the adsorption site, which assumes the interaction is largely electrostatic. The other uses the d-band center of the metal species, common for adsorbates on metal surfaces;\textsuperscript{182,201,202} this assumes the interaction involves hybridization with the metal orbitals, either directly or else mediated by the X atom. Neither descriptor reproduces the adsorption trends, confirming that the underlying adsorption mechanism is based on charge transfer rather than electrostatic attraction or hybridization.

Having established $\epsilon_{\text{LUS}}$ as a viable descriptor for $E_a$ on MX$_2$ surfaces, we proceed to select a target value that will give a reasonable range of surface adsorption strengths for primary catalyst screening. A target estimate for $\epsilon_{\text{LUS}}$ is obtained by examining results for the H phases of MoX$_2$ and WX$_2$. According to Fig. 5.1B, these surfaces have a comparatively high $\epsilon_{\text{LUS}}$ (> -4.5 eV), which leads to weak surface adsorption ($E_a > 2.0$ eV/H). This prevents the Volmer reaction from taking place and inhibits surface activity.\textsuperscript{186,187} In contrast, the active edges of these materials have much stronger $E_a$ (calculated as $\sim$ -0.4 eV/H for MoS$_2$ edge), which is apparently more appropriate for effective catalysis. Substituting $E_a = -0.4$ eV/H into the linear trend in Fig. 5.1B, we conclude that materials with $\epsilon_{\text{LUS}} \sim -6.3$ eV would have adsorption strengths competitive with MoX$_2$ and WX$_2$ edges. We broaden this criterion for viable candidates to -$0.5$ eV/H $< E_a < +0.5$ eV/H, corresponding to -$6.4$ eV $< \epsilon_{\text{LUS}} < -$5.5 eV. As additional validation, we point out the $T'$ phases of MoS$_2$ and WS$_2$ have
values of \( \varepsilon_{\text{LUS}} \) within this range (-5.7 and -5.6 eV, respectively), and each has recently demonstrated correspondingly enhanced HER activity with respect to the ordinary \( H \) phases.\textsuperscript{189,190,197}

Applying our \( \varepsilon_{\text{LUS}} \) criterion to all \( \text{MX}_2 \) substrates in their most stable phases (\( H \) for group 5 and 6, \( T \) for group 4 and 10, \( T' \) for group 7), we narrow the list of viable surface-active HER catalysts to a small handful of candidates (Fig. 5.2A). Two general features are observed: (1) for a given \( M \), \( \varepsilon_{\text{LUS}} \) increases in the order \( S < Se < Te \), and hence \( E_a \) increases in the order \( S < Se < Te \); and (2) metallic \( \text{MX}_2 \) candidates (from groups 4 and 5) have lower \( \varepsilon_{\text{LUS}} \) and hence stronger \( E_a \) than semiconducting \( \text{MX}_2 \) candidates (from groups 6, 7, and 10). The group 5 metal disulfides (\( \text{VS}_2 \), \( \text{NbS}_2 \), and \( \text{TaS}_2 \)) show particular promise, having a relatively low \( \varepsilon_{\text{LUS}} \) (< -5.8 eV) and a correspondingly strong \( E_a \).
Figure 5.2. Prediction of group 5 MX2 as surface-active HER catalysts. (A) Computed $\varepsilon_{\text{LUS}}$ for all MX2 candidates, with the target screening range indicated by dotted lines. Row 4/5/6 elements are shown in green/red/blue, with the different chalcogens separated into
columns within each group. (B) Coverage dependence of $G_{\text{tot}}$ (from Eq. 5.2) for H adsorption on the group 5 MX2. (C) $G_{\text{diff}}$ (from Eq. 5.3) for low adsorbate coverage on the group 5 MX2 (H: M = 1: 16), with values for Pt and Ni surfaces (from 186) and for active MoS2 edges shown for comparison.

Next, we perform a more accurate assessment of the group 5 metal disulfides by computing the concentration-dependent free energy of surface H adsorption, including entropic contributions and explicit calculation of $E_a$. For the HER at pH = 0 and at zero potential relative to the standard hydrogen electrode, the free energy of $H^+ + e^-$ is by definition the same as that of $1/2 H_2$ at standard conditions. Sabatier's principle implies that on an optimal catalyst, the free energy of the reaction intermediate—in this case, adsorbed H—should be close to this value, which we define to be zero. 186, 193, 198, 199 In examining concentration dependence, it is necessary to distinguish between the total ($G_{\text{tot}}$) and differential ($G_{\text{diff}}$) free energies:

$$G_{\text{tot}} = (E_a + \Delta E_{\text{ZPT}} - T\Delta S) N_H$$  \hspace{1cm} (5.2)

$$G_{\text{diff}} = \partial G_{\text{tot}} / \partial N_H$$  \hspace{1cm} (5.3)

Here, $\Delta E_{\text{ZPT}}$ is the zero-point energy difference between adsorbed H and $1/2 H_2$, and $T\Delta S$ is the entropy correction (-0.29 eV at room temperature 186). The minimum of $G_{\text{tot}}$ determines the thermodynamic equilibrium H coverage on the catalyst. On the other hand, $G_{\text{diff}}$ at the equilibrium H coverage represents the free energy cost to adsorb/desorb H on/from the catalyst, which in turn reflects the kinetics of catalysis near equilibrium. 186, 193, 198, 199
According to Fig. 5.2B, $G_{\text{tot}}$ increases monotonically with the H coverage on the surface of group 5 disulfides. The behavior indicates that at zero potential, dilute H adsorption will be thermodynamically favored over dense adsorption. This further justifies our choice to focus on the low-coverage limit when considering $\varepsilon_{\text{LUS}}$ as a descriptor. Figure 2C shows that at low surface coverage, each of the group 5 disulfides has a low $G_{\text{diff}}$ ($< 0.4$ eV/H at the coverage H : M = 1 : 16), supporting our initial supposition that these materials are promising candidates for surface-active HER catalysis. Moreover, the shallow slopes of the curves in Fig. 5.2B below ~ 25% surface coverage indicate that low $G_{\text{diff}}$ will be retained even at somewhat higher coverages. In addition, each of the group 5 disulfides is metallic, unlike the semiconductors MoX$_2$ and WX$_2$; their higher intrinsic electronic conductivity should further benefit their operation as electrocatalysts. 192
Figure 5.3. Electrocatalysis of HER on TaS2 and MoS2. (A) Polarization curves for H-TaS2, H-MoS2, T-MoS2 and T-TaS2, measured in 0.5 M H2SO4 with a scan rate of 5 mV s⁻¹. The H-TaS2 and H-MoS2 were first cycled for 5000 cycles between 0.2 and -0.6 V vs. RHE at 100 mV s⁻¹ before the polarization curve measurement. (B) Corresponding Tafel plots for catalysts in (A); numbers indicate the Tafel slopes. (C) The exchange current density obtained by fitting the Tafel plots. (D) Change of current density (recorded at -0.5 V) during cycling.
We directly verify the predicted HER activity of one of the group 5 disulfides by synthesizing \( H \) phases of TaS\(_2\) platelets. Polarization curve of \( H \)-TaS\(_2\) for HER electrocatalysis is measured versus the reversible hydrogen electrode (RHE), and compared to those of commercial \( H \)-MoS\(_2\) platelets with similar dimensions (Fig. 5.3A). The as-synthesized \( H \)-TaS\(_2\) platelets have lateral size up to 20 \( \mu \)m and thicknesses \(~ 100 - 600\) nm (Fig. 5.4B), and show high crystallinity according to X-ray diffraction, Raman spectroscopy (Fig. 5.4E), and high-resolution transmission electron microscope (HRTEM) (Fig. 5.4D). \( H \)-TaS\(_2\) exhibits a nearly zero onset overpotential after 5000 potential cycles, similar to Pt and far superior to \( H \)-MoS\(_2\) under identical cycling conditions. The current density is also much higher, reaching 15 mA/cm\(^2\) at 150 mV, compared with 0.1 mA/cm\(^2\) for \( H \)-MoS\(_2\). In Fig. 5.3A, we also benchmark the performance of \( H \)-TaS\(_2\) against the \( T \) phases of both MoS\(_2\) and TaS\(_2\) (\( T \) are higher in energy compared with \( H \) for both materials). These tests were motivated by recent reports indicating that the \( T \) phase has higher HER activity than the \( H \) phase in the case of MoS\(_2\) (confirmed here).\(^{190, 197}\) In contrast, the performance of \( H \)-TaS\(_2\) far exceeds that of the \( T \) samples. This can be expected from their \( \varepsilon_{\text{LUS}} \) values: \( T \)-TaS\(_2\) has a larger \( \varepsilon_{\text{LUS}} \) and therefore weaker \( E_a \) than those of \( H \)-TaS\(_2\) (Fig. 5.1B).

Tafel plots extracted from the polarization curves (Fig. 5.3B) allow for quantification of the exchange current density for each of the systems. We find that \( H \)-TaS\(_2\) has an exchange current density \((9.2 \times 10^{-4} \text{ A cm}^{-2}, \text{Fig. 5.3C})\) which is \( > 200 \) times that of \( H \)-MoS\(_2\) and \( T \)-MoS\(_2\), and \( > 10,000 \) times that of \( T \)-TaS\(_2\). In addition, the Tafel slope of \( H \)-TaS\(_2\) is lower than that of \( H \)-MoS\(_2\), implying a different rate-determining HER step; this would be expected for a shift in the catalytically active site from a stronger-adsorption edge site (\( H \)-MoS\(_2\)) to a weaker-adsorption surface site (\( H \)-TaS\(_2\)). Notably, the \( H \)-TaS\(_2\) has the best HER...
activity over all the reported MX$_2$ materials (Table S1), in terms of onset overpotential, exchange current density, and current density observed at 150 mV. Collectively, the electrochemical tests for $H$-TaS$_2$ are fully consistent with an efficient surface-active HER electrocatalyst, as predicted by our theoretical investigation.

**Figure 5.4.** Origin of the self-improving performance for H-TaS$_2$. (A) Schematic illustrations of HER at the surface sites of stacked layers; spheres represent produced H$_2$ bubbles. (B-E) AFM, low-magnification TEM, HRTEM image and Raman spectra for H-TaS$_2$ before cycling, respectively. Inset in (C) shows the statistical distribution of thickness for total 50 platelets. (F-H) Analogous data but for the H-TaS$_2$ after cycling.

One interesting consequence of surface activity would be that: for multilayer MX$_2$, the H$_2$ produced at surface sites between layers could lead to peeling off the layers (Fig. 4A). In fact, similar effects have been observed in chemical exfoliation of van der Waals (vdW) solids by the lithium intercalation and reaction with water.$^{190,203}$ The peeling off of
layered MX$_2$ could improve the H accessibility of surface sites, and increases the electron transfer as well. These would lead to enhancement of HER activity as the reaction proceeds, i.e. self-improving performance.

The H-TaS$_2$ multilayer platelets show self-improving performance with cycling (~3500-fold increase in cathodic current density after 5000 cycles, Fig. 5.3D), as predicted before. Raman spectra and HRTEM confirm the retaining of H phase of TaS$_2$ after cycling (Fig. 4E and 4H). Atomic force microscope (AFM) (Fig. 4B and F) and TEM (Fig. 4C and G) show the platelets indeed become thinner, and the electron transfer charge resistance drops by ~ 600 times, as a result of exfoliation induced by surface activity. In contrast, the performance of surface-inactive H-MoS$_2$ retains similar performance after cycling. We point out that the self-improving behavior requires H intercalation into the weakly coupled interlayers, a unique property for vdW solids.

In summary, the abundance of active sites, combined with properly tuned adsorption thermodynamics and high intrinsic electrical conductivity, establish H phases of the group 5 metal disulfides as promising surface-active HER electrocatalysts. This prediction was verified by synthesizing and testing one such candidate, H-TaS$_2$, which demonstrated electrocatalytic HER activity superior to all reported edge-active MX$_2$ materials. The discovery owes its origin to a fundamental understanding of the underlying electronic motivation, from which a simple descriptor was derived for primary computational screening. In addition to opening the door to the use of group 5 metal disulfides as surface-active and self-improving HER electrocatalysts, our work lays out a
scheme for assessing activity towards other reactions where charge-transfer binding dominates.
References


48. Kim, S.; Ihm, J.; Choi, H. J.; Son, Y.-W., Origin of Anomalous Electronic
176802.
Kurakevych, O. O.; Solozhenko, V. L., Ionic high-pressure form of elemental boron.
50. Piazza, Z. A.; Li, W.-L.; Romanescu, C.; Sergeeva, A. P.; Wang, L.-S.; Boldyrev, A.
I., A photoelectron spectroscopy and ab initio study of B_{21}^-: Negatively charged
51. Sergeeva, A. P.; Piazza, Z. A.; Romanescu, C.; Li, W.-L.; Boldyrev, A. I.; Wang, L.-
S., B_{22}^- and B_{23}^-: All-Boron Analogues of Anthracene and Phenanthrene. J. Am. Chem.
Soc. 2012, 134, 18065-18073.
52. Alexandrova, A. N.; Boldyrev, A. I.; Zhai, H.-J.; Wang, L.-S., All-boron aromatic
clusters as potential new inorganic ligands and building blocks in chemistry. Coord.
tubular Structural Transition in Boron Clusters: B_{20} as the Embryo of Single-walled
54. Boustani, I.; Zhu, Z.; Tománek, D., Search for The Largest Two-dimensional
55. Oger, E.; Crawford, N. R. M.; Kelting, R.; Weis, P.; Kappes, M. M.; Ahlrichs, R.,
Boron Cluster Cations: Transition from Planar to Cylindrical Structures. Angew.
56. Liu, Z.; Liu, J. Z.; Cheng, Y.; Li, Z.; Zheng, Q., Interlayer Binding Energy of
205418.
57. Olsen, T.; Yan, J.; Mortensen, J. J.; Thygesen, K. S., Dispersive and Covalent
Interactions between Graphene and Metal Surfaces from the Random Phase
58. Hirth, J. P.; Lothe, J., Theory of dislocations. A Wiley-Interscience Publication:
59. Yakobson, B. I., Mechanical relaxation and “intramolecular plasticity” in
Imaging active topological defects in carbon nanotubes. Nat. Nanotechnol. 2007, 2,
358-360.
62. Dumitrica, T.; Hua, M.; Yakobson, B. I., Symmetry-, time-, and temperature-
dependent strength of carbon nanotubes. Proc. Natl. Acad. Sci. USA 2006, 103, 6105-
6109.
63. Banhart, F.; Kotakoski, J.; Krasheninnikov, A. V., Structural Defects in


121. Wang, G.; Shen, X.; Yao, J.; Park, J., Graphene nanosheets for enhanced lithium storage in lithium ion batteries. Carbon 2009, 47, 2049-2053.
122. Lian, P.; Zhu, X.; Liang, S.; Li, Z.; Yang, W.; Wang, H., Large reversible capacity of high quality graphene sheets as an anode material for lithium-ion batteries. Electrochimica Acta 2010, 55, 3909-3914.


