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Computational Study of Carbon-Based Low-Dimensional Materials on Structures, Properties and Applications

BY

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ABSTRACT

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Low-dimensional materials including both 1D and 2D scenarios exhibit unique properties distinguished from their bulk states. In this thesis, computational modeling of low-dimensional materials on their structures, properties and applications has been investigated. First-principles simulations are employed to investigate the following topics. First of all in the 1D scenario, a comprehensive study on carbiyne-one dimensional carbon chain-from its structure to properties has been conducted, and the extreme mechanical performance and intriguing metal-insulator transition under tension has been demonstrated. The properties of proposed 1D boron nanostructures have also been investigated and a constant-tension structural transition between two boron phases has been revealed. Secondly, two examples for the energy application of low-dimensional materials have been presented. The first example contains the energy storage with graphene and its derivatives applied in Li-ion batteries as well as the examination on the lithium nucleation process on graphene. The second example is the exploration of the energy conversion with N-doped carbon materials as effective catalysts in electrochemical reduction of CO₂. Lastly, the simplified model- jellium model- has
been applied as metal catalyst in carbon nanotube growth to investigate the termination effect and chiral selectivity.
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## Nomenclature

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<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DFTB</td>
<td>Density Functional Tight Binding</td>
</tr>
<tr>
<td>BLA</td>
<td>Bond Length Alternation</td>
</tr>
<tr>
<td>PES</td>
<td>Potential Energy Surface</td>
</tr>
<tr>
<td>ZPV</td>
<td>Zero Point Vibration</td>
</tr>
<tr>
<td>CHE</td>
<td>Computational Hydrogen Electrode</td>
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Chapter 1

Introduction

1.1. Density functional theory

Density functional theory (DFT) is a quantum mechanical modeling method used in computational physics and chemistry. It is based on the Hohenberg-Kohn theorem which demonstrates that the ground state properties of a many-electron system are uniquely determined by the electron density. The goal of DFT methods is to design functionals connecting the electronic density with the energy. Within the framework of Kohn-Sham DFT (KS DFT), the intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential.

\[
\hat{H}\psi = \left[ \sum_{i}^{N} -\frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i}^{N} V(\mathbf{r}_i) + \sum_{i,j,i\neq j}^{N} U(\mathbf{r}_i,\mathbf{r}_j) \right] \psi
\]
The kinetic energy functional of such a system is known exactly. The effective potential includes the external potential and the effect of the Coulomb interactions between the electrons, e.g., the exchange and correlation interactions. There are different approximations to model these two interactions. (2) Local-density approximation (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated:

\[ E_{XC}^{LDA} [n] = \int \varepsilon_{XC}(n) n(r) \, d^3r \]

Generalized gradient approximations (GGA) are still local but also take into account the gradient of the density at the same coordinate:

\[ E_{XC}^{GGA} [n] = \int \varepsilon_{XC}(n, \nabla n) n(r) \, d^3r \]

Heyd-Scuseria-Ernzerhof (HSE) exchange functional uses an error function screened Coulomb potential to calculate the exchange portion of the energy in order to improve computationally efficiency,

\[ E_{XC}^{wPBEh} = \alpha E_{x}^{HF,SR} (w) + (1 - \alpha) E_{x}^{PBE,SR} (w) + E_{x}^{PBE,LR} (w) + E_{C}^{PBE}, \]

Where \( \alpha \) is the mixing parameter and \( w \) is an adjustable parameter controlling the short-rangerness of the interaction. Standard value of \( \alpha=1/4 \) and \( w=0.2 \) has been called HSE06.(3)
1.2. Overview of thesis

Low-dimensional materials including both 1D and 2D scenarios exhibit unique properties distinguished from their bulk states. In this thesis, based on density functional theory, computational studies on low-dimensional materials on their structures, properties and applications have been discussed. First of all, the one-dimensional carbon chain- carbyne has been investigated comprehensively from its structures, mechanical properties and electronic properties. Combined with continuum mechanical model, we provided the full set of elastic moduli for carbyne, showing its extreme mechanical performance. The strain-induced metal-insulator transition in carbyne has also been discussed. Followed by 1D carbon, we explored the possibility of another elemental monoatomic chain-1D boron chains. The properties of proposed 1D boron nanostructures and a constant-tension structural transition between two boron phases have been revealed.

Secondly, two examples for the energy application of low-dimensional materials have been presented. The first example contains the energy storage with graphene and its derivatives applied in Li-ion batteries as well as the examination on the lithium nucleation process on graphene. The second example is the exploration of the energy conversion with N-doped carbon materials as effective catalysts in electrochemical reduction of CO₂. Lastly, the simplified model- jellium model- has been applied as metal catalyst in carbon nanotube growth to study the termination effect and chiral selectivity.
Chapter 2

One-Dimensional Carbon and Boron Chains

2.1. Carbyne from first-principles

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2.1.1. Introduction:

Carbon exists in the form of many allotropes: zero-dimensional $sp^2$ fullerenes,(4) the two-dimensional $sp^2$ honeycomb lattice of graphene(5) (parent to graphite and carbon nanotubes), or three-dimensional $sp^3$ crystals—diamond and lonsdaleite. Each allotrope has notably different electronic and mechanical properties. For instance, graphene has the characteristic semimetal electronic structure with a linear band dispersion(6) and an extraordinarily high electron
mobility.\(^7\) In contrast, diamond is a wide-band-gap insulator and one of the hardest natural materials known.

Carbon can also exist in the form of carbyne, an infinite chain of \(sp\)-hybridized carbon atoms. It has been theoretically predicted that carbyne may be stable at high temperatures (~3000 K).\(^8\) Indications of naturally-formed carbyne were observed in such environments as shock-compressed graphite, interstellar dust, and meteorites.\(^9-11\) The carbyne-ring structure is the ground state for small (up to about 20 atoms) carbon clusters.\(^12\) Experimentally, many different methods of fabrication of finite-length carbon chains have been demonstrated, including gas-phase deposition, epitaxial growth, electrochemical synthesis, or ‘pulling’ the atomic chains from graphene or carbon nanotubes.\(^13-20\) Recently, chains with length of up to 44 atoms have been chemically synthesized in solution.\(^21\) Many interesting physical applications of carbynes have been proposed theoretically, including nanoelectronic/spintronic devices,\(^22-26\) and hydrogen storage.\(^27\) Moreover, very recently, such complex molecular mechanisms as rotaxanes based on carbyne chains have been synthesized.\(^28, 29\) All of these advances make the understanding of mechanical behavior of carbyne more and more important.

Albeit there exists a considerable body of literature on the structure\(^30, 31\) and mechanics\(^32-35\) of carbyne, it is very scattered and has thus failed so far to provide a well-rounded perspective. Here we address this shortage and put forward
a coherent picture of carbyne mechanics and its interplay with chemical and electronic phenomena.

2.1.2. The mechanical properties of carbyne: ultra-strong and stiff

We begin by discussing the structure of carbyne. One textbook structure of one-dimensional chain of C atoms is the cumulene (=C=C=), known to undergo a Peierls transition(36) into the polyyne (–C≡C–) form. Our calculations confirm this instability, showing an energy difference of 2 meV per atom in favor of the polyyne structure. The calculated cohesive energy of polyyne is $E_c = 6.99$ eV per atom. It must be noted that pure DFT methods underestimate the band gap, and this results in a much weakened Peierls instability. Higher-level quantum chemistry techniques or exact-exchange hybrid functionals can correct this deficiency,(26, 37) however it is not of prime importance for the mechanical properties of carbyne, and thus we do not need to resort to these more costly computational methods.
Figure 2.1 – Carbyne under tension. (a) DFT calculations of energy as a function of strain $\varepsilon$. The electronic density of carbyne (polyyne) (b) in equilibrium and (c) under tension shows a more pronounced bond alternation in strained carbyne. (d) Bond length alternation and (e) band gap increase as a function of strain.

**Carbyne under tension: the strongest nanowire.** The most basic mechanical property of the carbyne chain is its tensile stiffness, defined as

$$C = \frac{1}{a} \frac{\partial^2 E}{\partial \varepsilon^2},$$

**Equation 2.1 – Tensile stiffness of carbyne.**
where $a$ is the unit cell length (2.565 Å), $E$ is the strain energy per two C atoms, and $\varepsilon$ is the strain. Fitting Equation 2.1 to our DFT data with a fourth-order polynomial (Figure 2.1 – Carbyne under tension. (a) DFT calculations of energy as a function of strain $\varepsilon$. The electronic density of carbyne (polyyne) (b) in equilibrium and (c) under tension shows a more pronounced bond alternation in strained carbyne. (d) Bond length alternation and (e) band gap increase as a function of strain. yields a tensile stiffness of $C = 95.56$ eV/Å in agreement with earlier work.(38) (Note that negative strain values are mainly of academic interest; however, it may be possible to realize some degree of compression in finite-length chains below the onset of Euler buckling—see next section on bending stiffness,—or with chains confined inside channels, e.g., carbon nanotubes.(39)) A more informative measure from the engineering standpoint is the specific stiffness of the material, which for carbyne works out to be $\sim 10^9$ N·m/kg. This is a more than twofold improvement over the two stiffest known materials—carbon nanotubes and graphene ($4.5 \times 10^8$ N·m/kg(40-42))—and almost threefold, over diamond ($3.5 \times 10^8$ N·m/kg(43)).

Another important metric of engineering materials is their specific strength. The tensile strength is generally difficult to predict theoretically, therefore we approach the problem from two complimentary perspectives. One method to evaluate the ideal strength of carbyne is to compute the phonon instability point—the strain at which imaginary frequencies appear in the phonon spectrum.(41) We found that in carbyne, this event occurs at a critical strain of 18–19%, at a pulling force of 11.66 nN. Notably, this coincides with the change from direct to indirect
Another approach is to treat fracture as an activated bond rupture process and compute its activation barrier $E_a(\varepsilon)$ as a function of strain. The computed $E_a(\varepsilon)$ dependence shows the expected decrease with tension, and at a strain of $\sim 9\%$ (9.3 nN) it reaches a characteristic magnitude of 1 eV for which transition state theory predicts an expected lifetime on the order of $\sim 1$ day. Thus the estimated breaking force of a carbyne chain is 9.3–11.7 nN (this is $>10 \times$ the previous literature report of 0.9 nN, demonstrating the inadequateness of the ReaxFF forcefield used therein for carbyne mechanics). This force translates into a specific strength of $6.0-7.5 \times 10^7$ N·m/kg, again significantly outperforming every known material including graphene ($4.7-5.5 \times 10^7$ N·m/kg), carbon nanotubes ($4.3-5.0 \times 10^7$ N·m/kg), and diamond ($2.5-6.5 \times 10^7$ N·m/kg). The details of calculations are described as follows:

We used two methods to estimate the strength. Figure 2.2 – Determination of the tensile strength of carbyne. (a–c) Phonon dispersion plots at 0, 15%, and 19% strain showing phonon instability (imaginary frequencies in (c)). (d) Bond breaking reaction profiles and (e) activation energy as a function of strain. The inset in (e) shows the force vs. strain curve. (a–c) illustrates the evolution of phonon dispersions of carbyne (calculated with the finite-displacement method using the PHON software with a 12-atom supercell). At a 19% strain (c), imaginary frequencies appear (shown as negative), which marks the onset of the phonon instability corresponding to the upper limit of ideal strength of a material. (At the same time, the force vs. strain plot starts going down—not shown.)
The other approach is to treat bond breaking as an activated process. In the standard Arrhenius form, the bond-breaking rate is $R = A \exp\left[-E_a(\varepsilon) / kT\right]$ where $E_a$ is the activation energy and $A$ is the “attempt frequency” prefactor. $A$ can be estimated based on the bond stretching phonon frequency, e.g., in Figure 2.2 – Determination of the tensile strength of carbyne. (a–c) Phonon dispersion plots at 0, 15%, and 19% strain showing phonon instability (imaginary frequencies in (c)). (d) Bond breaking reaction profiles and (e) activation energy as a function of strain. The inset in (e) shows the force vs. strain curve, as $4 \times 10^{13} \text{s}^{-1}$. $E_a$ is computed using a supercell setup (24 atoms) where one of the bonds is incrementally stretched by $\Delta d$ relaxing the positions of all other atoms to get a potential energy profile, as shown in Figure 2.2(d). The resulting exponential decrease of $E_a$ with strain is illustrated in Figure 2.2 (e). As a useful point of reference, $E_a = 1 \text{ eV}$ corresponds to a lifetime of about $R^{-1} \approx 1 \text{ day}$ at room temperature. This occurs at a strain of 9%, corresponding to a force of 9.2–9.3 nN (inset). It should be noted that for a chain with $N$ bonds, the prefactor is multiplied by $N$; another way to view this is to replace $E_a$ with the free energy barrier $\Delta G^* = E_a - kT \log N$. We see that this addition results in only a logarithmic correction in $E_a$, and since $E_a$ is exponential in strain, the breaking strain and force change negligibly slowly with $N$ (as $\sim \log[\log N]$).
Figure 2.2 – Determination of the tensile strength of carbyne. (a–c) Phonon dispersion plots at 0, 15%, and 19% strain showing phonon instability (imaginary frequencies in (c)). (d) Bond breaking reaction profiles and (e) activation energy as a function of strain. The inset in (e) shows the force vs. strain curve.

It is interesting to see what happens to the bond length alternation (BLA) of carbyne under tension.\(^\text{(44)}\) Since the strength of Peierls distortion is extremely sensitive to the choice of methods,\(^\text{(49)}\) we performed additional computations using the local density approximation and the hybrid HSE06 functional incorporating exact exchange.\(^\text{(50)}\) The most trustworthy method—HSE06—yields an increase of BLA from 0.088 Å in free carbyne to 0.248 Å when \(\varepsilon = 10\%\) (Figure 2.1(b)). Figure 2.1(c, d) shows the electronic densities of carbyne in free-standing state and at a 10% strain. While in the first case (c), the BLA is barely noticeable in the plot, the second (d) shows very clear distinction between the ‘single’ and ‘triple’ bonds.
Naturally, this change in the BLA has big ramifications for the electronic properties of carbyne. Figure 2.1(e) shows the variation of the band gap with strain computed using many-body perturbation theory ($G_0W_0$) in two settings: the standard LDA+$GW$ scheme and using the more realistic HSE06 geometry (HSE06/LDA+$GW$). The difference between the two plots in Figure 2.1(e) is easily understood from the plot of $GW$ correction magnitudes as a function of BLA shown in Figure 2.1(f), where the data points from both sets fall closely on the same line. Clearly, an accurate reproduction of BLA is essential for the computation of band gap. The HSE06/LDA+$GW$ band gap varies almost linearly with strain from 2.58 eV at 0% to 4.71 eV at 10% strain, an 83% change. This extreme sensitivity of band gap to mechanical tension shows carbyne’s great prospects for opto-/electromechanical applications. The nature of this effect and its unusual consequences are explored more deeply elsewhere.\(^{(26)}\)

**Bending stiffness: nanorod or nanorope?** Given the extreme tensile stiffness of carbyne, it is interesting to investigate how this material performs under bending deformations. The bending stiffness is defined as

$$ K = \frac{1}{a} \frac{\partial^2 E}{\partial q^2}, $$

**Equation 2.2 – Bending stiffness of carbyne.**

where $a$ is again the unit cell and $q$ is the curvature. To calculate the bending energy of carbyne, we use the model of carbon rings because of their advantage of
having a constant uniform curvature defined by their radius, \( q = 1/R \) (Figure 2.3(a)). The BLA pattern is retained in the rings having an even number of atoms, as seen from the electronic density distribution in Figure 2.3(a). Additional care must be taken with carbyne rings since the Jahn–Teller distortion (the counterpart of Peierls instability in non-linear molecules) is different in the \( C_{4N} \) and \( C_{4N+2} \) families of rings.\(^{52-54}\) The \( C_{4N+2} \) rings undergo a second-order distortion which produces little/no BLA at small \( N \). Because of this, the bending stiffness in the two families differs for small rings, but as \( N \) increases \((q \to 0)\), the difference gradually disappears, and the stiffness of both families approaches the common limit of infinite straight carbyne, which the extrapolation of our results places at \( K = 3.56 \) eV·Å. A similar extrapolation of the ring energies disagrees with an explicit periodic infinite-chain calculation by only about 0.3 meV/atom, showing the robustness of our procedure.
Figure 2.3 – Bending stiffness of carbyne. (a) The carbon ring model with its electron density distribution, showing the usual bond alternation pattern. (b) The energy as a function of ring curvature calculations used to extract the bending modulus value.

Persistence length. In order to determine whether this value of $K$ is large or small, we can further characterize the bending stiffness of carbyne using the concept of persistence length familiar from polymer physics. It is defined as $l_p = K/k_B T$, where $k_B$ is the Boltzmann constant and $T$ is the temperature. Using our value of $K$, 

the persistence length of carbyne at 300 K is roughly \( l_p = 14 \) nm, or about 110 C atoms. This can be compared to the persistence length of various important polymers, as presented in Table 2.1. As we see, carbyne is relatively stiff for a polymer and comparable to narrowest graphene nanoribbons, and it is about 13 times as stiff as a dsDNA rod (mind the 2-nm diameter of the latter).

**Carbyne under torsion: chemically modulated spring.** The torsional stiffness of a rod of length \( L \) is expressed as

\[
H = L \frac{\partial^2 E}{\partial \theta^2},
\]

*Equation 2.3 – Torsional stiffness of carbyne.*

where \( \theta \) is the torsion angle. Looking at the electron density distribution along the atomic chain (Figure 2.4, a), one immediately recognizes a problem with this definition. Because of the cylindrical symmetry of the density—and, consequently, all relevant physical observables—it is impossible to define \( \theta \), and thus \( H \) has to be zero. However, we can solve this problem by attaching functional group ‘handles’ at the chain ends to break the cylindrical symmetry (Figure 2.4, b and c). Further, depending on the character of the passivation—\( sp^3 \) or \( sp^2 \)—one should expect different effects on the torsional stiffness. (32)
Figure 2.4 – End-group-induced torsional stiffness of carbyne. (a) Cross-section of the electronic density of carbyne. (b) Front and (c) side view of a carbyne chain with attached =CH₂ handles, showing the helical HOMO isosurface. (d) Band gap and (e) energy as a function of the torsional angle. (f) Band gap and (g) torsional stiffness dependence on the chain length. The blue line in (f) is fitted by $E = A/L$ and black line is fitted by $E = A/(L + L_0)$.

We considered different functional groups, including methyl (CH₃), phenyl (C₆H₅), and hydroxyl (OH) as $sp^3$ radicals, and amine (NH₂, planar) and methylene
(CH₂) groups from the sp² family. With methyl and hydroxyl, we find that the single C–R bond at the end interfaces so smoothly with the single-triple bond system of carbyne as to result in a completely free unhindered rotation. Moreover, phenyl handles also rotated freely, suggesting a single bond between the carbyne and the aromatic ring. Only the =CH₂ (and, weakly, NH₂) termination shows a detectable torsional stiffness. As the “handles” are twisted out-of-plane, the frontier π orbitals assume a characteristic helical structure with the total twist angle following the dihedral angle between the handle group planes—see Figure 2.4(b,c).

**Figure 2.5** – The evolution of highest occupied molecular orbital (HOMO) in an 18-atom carbyne chain with =CH₂ end-group handles under torsion. Green and red represent the opposite signs of the π orbital.

Before we present the numerical results, an interesting question to consider is how this stiffness could emerge at the electronic-structure level. Consider the
behavior of band gap as a function of the torsional angle. As the torsional angle increases, the band gap shrinks and completely closes at 90°, as shown in Figure 2.4(d). From the molecular orbitals perspective, at 0°, the planar geometry can sustain two fully orthogonal $p$-bands formed by $p_y$ and $p_z$ orbitals, respectively,—the HOMO and LUMO of the molecule ($D_{2h}$ symmetry). However, when the handles are at 90° ($D_{2d}$), the two orbitals become completely equivalent by symmetry and, hence, degenerate. As a result, the energy of the system is increased—Figure 2.4(e).

We can estimate this energy change as $2 \times [E_g/2] = E_g$, the band gap of the planar molecule, and the resulting potential energy (PE) curve can be approximated by its first Fourier term as $E(\theta) = \frac{1}{2} (1 - \cos 2 \theta)E_g$. Then, according to Equation 2.3 the torsional stiffness is $H(E_g, L) = 2E_g \times L$.

Next we examine the behavior of $E_g$ as a function of $L$. Treating carbyne as a 1D potential well of width $L \equiv Na$, the HOMO and LUMO energies are $E_N \propto k_N^2 \propto N^2/L^2$ and $E_{N+1} \propto k_{N+1}^2 \propto (N + 1)^2/L^2$, and therefore, $E_g \propto (1 + 2N)/L^2 \propto 1/L$ for long chains, $N \gg 1$. The inverse dependence of the band gap on the length, $E_g = C/L$, leads to $H = 2C = \text{const}$, i.e., the torsional stiffness of carbyne has a finite constant value.

Both predictions—$E_g \propto 1/L$ and a constant torsional stiffness $H$—are confirmed by our DFT calculations, as shown in Figure 2.4 (f) and (g), respectively. Although this stiffness is not, strictly speaking, inherent to carbyne in the sense that it relies on the endgroups to break the rotational symmetry, from the mechanical perspective the carbon chain between the handles behaves just like a classical
torsion rod. With the =CH₂ termination, the maximum stiffness value we observe is 
\( H \approx 10.3 \text{ eV} \cdot \text{Å}/\text{rad}^2 \). This figure is about half the torsional stiffness of dsDNA,\(^{(55)}\) which is truly remarkable given carbyne’s one-atom thickness.

Two more interesting aspects of carbyne’s behavior as a torsional spring deserve to be highlighted. First, upon passing 90° twist, the energy evolution is reversed, and the differential stiffness becomes formally negative. This behavior is quite intriguing, since for a normal beam, the energy would increase monotonously during twisting, whereas for this 1-D carbon chain, the torsional energy exhibits a periodic behavior. Second, as is typical for such situations, the frontier orbital degeneracy at 90° can be lifted \textit{via} spin unpairing. Indeed, our calculations show that at near-90° angles, the spin-triplet state is energetically more favorable\(^{(32)}\) and, in fact, becomes the local energy minimum (Figure 2.4 (e)). A separate torsional stiffness can be defined for this minimum, \( H_T = 8.6 \) and 3.7 eV·Å/rad\(^2\) for \( N = 18 \) and 66 carbyne chains, respectively.

\textbf{Equivalent continuum-mechanics model.} To gain further insight and appreciation of the mechanical properties of carbyne, we need to establish the link between the computed atomistic properties and the concepts of continuum elasticity such as the Young’s modulus \( Y \), the bending stiffness \( K \), the shear modulus \( G \). The fully assembled system of equations looks, where all the atomistic quantities (Equation 2.1, Equation 2.2, Equation 2.3) are assembled on the left and their counterparts from continuum mechanics, on the right.
\[ C = \frac{1}{L^2} \frac{\partial^2 E}{\partial \epsilon^2} = \frac{\pi r^2 Y}{L}. \]

**Equation 2.4** – Tensile stiffness in continuum model for elastic cylindrical beam.

\[ K = \frac{1}{L} \frac{\partial^2 E}{\partial (1/R)^2} = \frac{1}{4} \pi r^4 Y, \]

**Equation 2.5** – Bending stiffness in continuum model for elastic cylindrical beam.

\[ H = L \frac{\partial^2 E}{\partial \theta^2} = \frac{1}{2} G \pi r^4. \]

**Equation 2.6** – Torsional stiffness in continuum model for elastic cylindrical beam.

From Equation 2.4 and Equation 2.5, we can estimate the effective mechanical radius and the Young’s modulus of carbyne: \( r = 0.386 \) Å and \( Y = 32.71 \) TPa. Knowing the radius, we are now able to compute the shear modulus from (6): \( G = 47.2 \) TPa, and thus the effective Poisson’s ratio \( n = Y/(2G) - 1, n = -0.65. \)

Comparing with the hardest natural materials diamond and graphene (\( Y_{\text{diamond}} = 1.22 \) TPa, \( Y_{\text{graphene}} = 1 \) TPa, \( G_{\text{diamond}} = 0.5 \) TPa), we see that carbyne, outperforms them by a factor of about 30 (owing in part to its extremely small mechanical radius). For convenience, the elastic parameters of carbyne are summarized in Table 2.2.
**Chemical stability of carbyne.** An important concern for any nanoscale material is its stability with respect to dimerization.\(^{(56)}\) For carbyne, formation of cross-links between chains is a mechanism of degradation known from experiments,\(^{(14)}\) and hence must be studied. Figure 2.6(a) shows a relaxed potential energy surface scan using the distance between C atoms in the middle of two carbyne chains as the constraint onto which the reaction coordinate is projected. To avoid introducing bias due to the cumulene/polyyne transformation during the cross-link formation, we used two chains with \(2N\) and \(2N + 1\) atoms to simulate the reaction, so that both before and after the reaction there is exactly one chain with an (unfavorable) odd number of atoms in the system. We estimated an activation energy barrier of about \(E_a = 0.6\) eV that is independent of the length of reacting chains (from 8 to 24 atoms) as well as of the dihedral angle formed by the chains. (The overall exothermicity of the reaction showed a weak decrease with the chain length; \(i.e.,\) shorter chains have a stronger tendency to link.) This barrier suggests the viability of carbyne in condensed phase at room temperature on the order of days.\(^{(56)}\)
What will happen if two parallel long carbyne chains are brought into contact? Every cross-link formed will create local curvature, raising the energy of the system. We can estimate the maximum frequency of such cross-links using a simple geometrical model. Assuming all bond angles about a cross-link being 120° and the carbyne curvature between the links remains constant, the length of the arc between two cross-links is $L = (\pi/3)R$. The corresponding elastic energy is
\[ E_{\text{bend}} = \frac{KL}{2R^2} = \frac{K\pi^2}{18L} = 1.95/L \text{ eV}. \] This energy cost is offset by the gain from forming the extra bonds between the chains, which is about \( E_f = 0.25 \text{ eV/atom} \) from Figure 2.6 (a). Using this value, we arrive at an estimate for \( L \approx 7.8 \text{ Å} \), or about \( N = 5 \) atoms between the cross-links. Compared to the results of DFT calculations presented in Figure 2.6 (b), which predict an 8-atom threshold spacing, this is an underestimate that can be straightforwardly attributed to our model’s ignoring the \( \pi \)-electron conjugation which is perturbed by the cross-links. Since the energy of conjugation interruption should also scale approximately as \( 1/L \), the general form of \( E_{\text{bend}+\pi} = K^*/L \) should still hold. In this case, it is easy to show that the equilibrium separation between kinks in an infinite system (one that minimizes the total energy per atom) is exactly twice the threshold separation (at which \( E_{\text{bend}+\pi} = E_f \)), and can be estimated from our DFT data as one cross-link per 17 atoms, or 21.8 Å.

Note the oscillating behavior of the DFT data points as the number of atoms between sequential cross-links switches between odd and even. It indicates that the atoms that make the cross-link form a double bond and thus are connected to the chain segments by single bonds, which is only possible to seamlessly integrate into the single–triple alternation pattern of polyyne when the number of atoms in between is even. In fact, odd-number systems are instable in the sense that if the unit cell is doubled, an \( N = 2M+1 \) system tends to reconstruct into a superstructure. An alternative that is favorable for shorter-period systems is to form a pair of adjacent cross-links, resulting in a square \( C_4 \) unit.
Our finding of a large (~2 nm) equilibrium cross-link spacing explains the experimental observations where single-zigzag–wide graphene nanoribbons show instability and split into pairs of atomic chains. In summary, carbyne chains can be robust against cross-linking at not-too-high temperatures, and mechanical constraints can further prevent them from forming multiple bonds with each other.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$l_p$ (nm)</th>
</tr>
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<tbody>
<tr>
<td>polyacrylonitrile$^{67}$</td>
<td>0.4–0.6</td>
</tr>
<tr>
<td>polyacetylene$^{68}$</td>
<td>1.3</td>
</tr>
<tr>
<td>single-stranded DNA$^{69,70}$</td>
<td>1–4</td>
</tr>
<tr>
<td>polyaniline$^{71}$</td>
<td>9</td>
</tr>
<tr>
<td>double-stranded DNA (dsDNA)$^{56}$</td>
<td>45–50</td>
</tr>
<tr>
<td>graphene nanoribbons$^{72}$</td>
<td>10–100</td>
</tr>
<tr>
<td>carbyne (present work)</td>
<td>14</td>
</tr>
</tbody>
</table>

**Table 2.1 – Persistence length of carbyne as compared to several important polymers.**

<table>
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<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>thickness 2r</td>
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</tr>
<tr>
<td>Young’s modulus Y</td>
<td>32.71 TPa</td>
</tr>
<tr>
<td>shear modulus G</td>
<td>47.2 TPa</td>
</tr>
<tr>
<td>Poisson’s ratio n</td>
<td>-0.65</td>
</tr>
<tr>
<td>persistence length at 300 K</td>
<td>14 nm</td>
</tr>
</tbody>
</table>
2.1.3. The electronic properties of carbyne: metal-insulator transition

Carbyne—the linear allotrope of carbon—is perhaps one of the most unusual materials due to its ultimate one-atom thinness. Although carbyne is elusively hard to prepare and has been perceived as an exotic or even completely fictitious material, the development of methods to synthesize carbon chains proceeds at a steady rate, with input from both experiments and theory. (16-20, 57, 58) Among the most notable recent achievements, chains with length of up to 44 atoms (21) and such complex molecular machines as carbyne-based rotaxanes (28, 29) have been synthesized. This progress is driven by carbyne’s attractive physical properties such as unusual electrical transport (22, 23) and intriguing mechanics, (59) or its large specific area. (27) A better theoretical understanding of this material is becoming more and more relevant.

The π-system of carbyne has two valence electrons per atom occupying two degenerate π bands, yielding a metal with two half-occupied bands. As a result, carbyne is susceptible to the Peierls transition (60-63) that converts it from the cumulene (=C=C=)\textsubscript{n} to the polyyne (–C≡C–)\textsubscript{n} form. (64) Further, zero-point vibrations (ZPV) may have an amplitude comparable to the Peierls distortion, making quantum lattice dynamics effect important. (65) Subsequent studies with Hubbard-type model Hamiltonians have suggested that quantized atomic vibrations
may sometimes destroy the Peierls ground state. As the symmetric and broken-symmetry forms have very distinct electronic properties (metallic and insulating, respectively), this issue is crucial from both the fundamental physicochemical perspective and for applications in 1D conducting systems.

A whole new dimension is added to the situation by the unusual effects of stretching on carbyne recently found through first-principles calculations. Specifically, stretching increases the bond length alternation (BLA, defined as the difference between the long and short bonds) and the band gap. Although the effect of strain on the band gap is well-known in semiconductors, the present case is very abnormal, both in the sign of the dependence and the greater amplitude ($\partial E_g/\partial \epsilon = 12–30$ eV, see Figure 2.7a), indicating a different nature of the effect.

Thus, we start with an exploration of the effect of strain on the static Peierls transition. We use a simple analytical model to explain why tension amplifies the Peierls effect. Then we investigate through first-principles Born–Oppenheimer potential energy surface calculations how the atomic vibrations manifest themselves in an unloaded chain or under tension. We confirm that the ZPV level lies well above the Peierls transition energy, and the instability is eliminated. As this energy is increased by tension, we arrive at the prediction of a strain threshold whereupon carbyne switches from the ZPV– to Peierls–dominated regime, accompanied by a sharp change in the electrical conductivity. Our first-principles numerical analysis validates this prediction, placing this transition around 3% strain, well below the breaking threshold. Besides carbyne, our findings
naturally suggest that this novel physical effect must also be observable in other one-dimensional systems exhibiting Peierls behavior, such as conducting polymers, charge/spin density–wave compounds, or carbon nanotubes. (68)

![Figure 2.7 – Electronic properties of carbyne under strain. (a) Bond length alternation (BLA), band gap ($E_g$), and Peierls barrier ($E_P$, inset) as a function of strain in the static case. Points, DFT calculation results. Lines, fitting based on the analytical model. The fitting is performed in the $[-5\%, 5\%]$ strain range assuming that the lattice stiffness decreases linearly with strain, and is done independently for BLA and $E_g$. The $E_P$ line in the inset is computed based on the BLA fit. (b) Carrier effective masses (dashed) and mobilities (solid) of polyynes as a function of strain: filled, electrons; hollow, holes.]

Our first-principles data on the amplification of the Peierls instability under tension are presented in Figure 2.7a. The Peierls distortion is extremely sensitive to the electronic exchange interaction and, in particular, is poorly described by regular density functional theory,(49) calling for the use of hybrid functionals. In such schemes, larger amounts of exact exchange lead to wider band gaps and stronger electron–phonon coupling, and a correct amount is important for quantitative accuracy. Here we used the HSE06 functional,(50, 69) closely related to the PBE0
functional which offers the most accurate description of band gaps in Peierls systems.\(^{(70)}\) All calculations were also repeated with the PBE generalized-gradient functional,\(^{(71)}\) showing complete qualitative agreement. Circles and squares represent the BLA (left axis) and the band gap \(E_g\) (right axis). The Peierls transition energy \(E_p\)—energy difference between polyyne and cumulene structures—is shown in the inset. The striking increase of all quantities observed so pronouncedly in Figure 2.7a calls for an explanation.

One can understand the behavior of the static Peierls transition under strain using a simple and general model as follows. The change in electronic energy due to the Peierls effect is \(E_e \propto a|V_k|^2 \log |V_k| / k\), where \(k\) is the Brillouin zone edge \((k = \pi/a)\) and \(V_k\) is the corresponding Fourier component of the lattice potential. To determine \(E_e(a)\), some definite form of the \(V_k(a)\) dependence is needed. We use a simple Kronig–Penney type model with two delta-function atoms per period \(2a\) with coordinates \(x_1 = 0\) and \(x_2 = (a - b)/2\), where \(b\) is the BLA (we assume \(b > 0\)). The potential in the unit cell is \(V(x) = -\delta(x - x_1) - \delta(x - x_2)\), and then \(|V_k| = 2|\sinh(\pi b/2a)| = \pi|b|/a + O(|b|^3/a^3)\). The electronic contribution is counteracted by the lattice deformation energy, \(E_l = Cb^2/2 + O(b^4)\). The value of \(b\) must minimize the total energy, \(\frac{\partial (E_e + E_l)}{\partial b} = \pi b \mp 2\pi b \log(\pi b/a) + Cb = 0\), and we have the answer as \(b = (a/\pi) \exp(-1/2 - C/2\pi)\). The derivative \(db/da\) is positive when \(2\pi - a \cdot dC/da > 0\), which shows that the Peierls dimerization is increased by tension unless the restoring force constant increases with strain (at least as fast as \(C = C_0 + 2\pi \log a\)—and usually the trend is opposite).
To demonstrate the excellent agreement of our very simple model with the DFT calculations, we have fitted it to our DFT data (Figure 2.7). The fitting was done assuming simple linearly decreasing stiffness, $C \approx C_0 + D(a_0 - a)$, and used only the data points in the $[-5\%, 5\%]$ strain interval. The fitting was performed independently for the BLA and $E_g$, and the former fit was used to compute the line for $E_P$.

To further appreciate the effect of strain on the physical properties of polyyne, Figure 2.7b shows the effective masses $m^*$ of charge carriers in polyyne extracted from the HSE06 band structures (dashed lines, right axis). Notably, both electron (filled disks) and hole (hollow circles) effective masses are rather low, less than 4% electron mass, and increase with stretching. Carrier mobilities (solid lines, left axis) were estimated in the deformation-potential approximation(72) for 1D systems(73) assuming the dominant scattering mechanism to be via coupling with longitudinal acoustic phonons. The mobilities show a fast decrease with tension, but due to the small effective masses, they still remain high, e.g., the hole mobility in free polyyne is $\mu_h = 10^4 \text{cm}^2/\text{V} \cdot \text{s}$. The calculated electron mobility considerably exceeds that of holes: $\mu_e \approx 2 \times 10^5 \text{cm}^2/\text{V} \cdot \text{s}$ at zero strain, which is about the highest mobility measured in graphene.(7) The apparent “ballistic” singularity under compression comes from the deformation potential crossing zero. In this range the theory needs to be modified to include nonlinear effects as follows. Due to thermal phonons, the chain is never at a single value of strain, but rather is locally compressed or extended in most points, resulting in nonzero “average” electron–phonon scattering. We can estimate the amplitude of this local
compression/stretching from the tensile stiffness of carbyne (59) by treating each unit cell as an oscillator at a temperature $T$. This results in an averaging window for the deformation potential (about 1.5% wide at 300 K) that provides a finite upper limit on mobility. Clearly, other sources of scattering such as contacts or chemisorbed molecules can also limit the mobility.

Since our analytical model is fully general, similar effects as those shown in Figure 3.1 should be observed in other Peierls-active systems. While carbyne with its wide band gap is atypical in this respect, most common compounds experience the Peierls transition only at very low temperatures (due to smaller gap). According to our findings, then, tension could be used to increase the critical temperature of Peierls transition. On the other hand, below the Peierls temperature, compression could enhance mobility via decreasing the deformation potential and suppressing the acoustic phonon scattering.

Up until now, we have confined ourselves to the static picture of classical carbon atoms. Within this picture, only the polyyne form of carbyne is stable, and stretching it produces merely quantitative changes in the band gap—a phenomenon known in solid state physics, even though its origin here is unusual. However, as we demonstrate below, the quantized nuclear motion changes the picture dramatically. If ZPV can overpower the Peierls instability in freely-suspended unloaded chain and restore the symmetric metallic structure, then one is led to expect that above some critical strain, the stronger Peierls instability may reverse this phenomenon—causing a qualitative change in properties. Our calculations indeed confirm this.
For the vibrational analysis we computed the Born–Oppenheimer potential energy surface (PES) profiles along the BLA coordinate, $E_a(b)$, as the lattice constant $a$ was increased from its equilibrium value. Because of the extreme anharmonicity of the $\omega$-shaped PES profiles, we had to turn to numerical calculations of the vibrational levels at each strain value. Following earlier work,(38, 66, 74) we assume that the longitudinal vibrations can be decoupled from transverse phonons, which is justified by the considerable bending stiffness of carbyne.(59) We focus on just the Peierls-active phonon mode (in the vicinity of $k = \pi/a$ wavevector for cumulene or $\Gamma$-point for polyyne) which serves as a proxy for the average ZPV energy in the entire phonon branch, which allows for a clear and intuitive exposition of the phenomenon. Literature suggests that such a flat-band model leads to qualitatively same conclusions as a more complete treatment including phonon dispersion.(75) Our calculations confirm that inclusion of dispersion does not change the present conclusions and yields a very close magnitude for the average ZP energy in the whole phonon branch.

The results are presented in Figure 2.8, which is the central figure of this paper. The black curves show the $\omega$-shaped PES as computed using the HSE06 functional, blue horizontal lines denote the computed vibrational levels with filling below the zero level, and the red-to-blue curves plot the ZPV wavefunction. All quantities are normalized per 2-atom cell (the cumulative ZP energy scales with the chain length $N$, and is estimated as $\frac{1}{2} \sum_{i=1}^{N} \hbar \omega_0(k_i) \approx \frac{1}{2} N \hbar \omega_0(\pi/a)$ in the flat-band model). The right panels show reconstructed real-space densities of nuclei at the respective strain values. The profile along the horizontal axis is the squared
vibrational wavefunctions with an arbitrary transverse broadening. Colors represent which values of BLA (positive or negative in the left-hand side plots) correspond to the position.

Clearly, the unloaded (0% strain) system has a single wavefunction maximum with a width exceeding the BLA \( (65) \) corresponding to the cumulene structure of carbyne with lattice parameter \( a/2 \). Thus, ZPV stabilize the cumulene form even though it is a maximum on the PES. In accordance with the above discussion, the central PES maximum \( (E_P) \) rises with tension, and at 3\%, the wavefunction develops a slight dip in the center, resulting in a picture of ‘elongated’ atoms. At 7\% strain, the ground-state wavefunction is clearly separated in two blobs, and the first excited level approaches the ground state, indicative of the transition to the double-well potential-like regime. Under further stretching (10\%), the first excited level is well below room-temperature \( k_B T \) from the ground state, as in two independent potential wells. The second level dives below the Peierls barrier, and the third begins to approach it (at 15\% strain these two also become degenerate; data not shown).
Figure 2.8 – Zero-point vibrations under strain. (left) Evolution of the vibrational structure of carbyne with strain. The ω-shaped lines show the potential energy as a function of BLA. Horizontal lines show the vibrational levels, the shaded region is below the ZPV level. All quantities are normalized per 2-atom cell. (right) Real-space atomic density distributions based on ZPV wavefunctions (three one-atom unit cells shown, color indicates which part of the BLA wavefunction the density comes from).

The above-described sequence of events has a profound consequence. As the strain is increased, carbyne transitions from the conducting electronic behavior of
cumulene to the nonconductive polyyne structure with its sizable band gap (see Figure 2.7a). In essence, tension serves to increase the electron–phonon interaction, which results in the crossing of the Peierls phase boundary.\(^{(65)}\) One can go a step further and compute a strain–temperature “phase diagram” for carbyne. First, the temperature-dependent nuclear densities \(n_T(b)\) are computed from squared wavefunctions using Bose statistics. A rising temperature and strain-induced depression of vibrational levels start to populate the first excited states which have small amplitude near \(b = 0\), and \(n_T(b)\) becomes wider until its central maximum splits in two. To determine the polyynic or cumulenic character, for the role of order parameter we used a measure of the distribution shape: the ratio \(R = n_T(0)/\max_b(n_T(b))\), which is 1 always when there is a single central minimum (pure cumulene) and less than 1 when the symmetry is broken. Figure 2.9 shows a contour map of \(R\). The region to the left of the \(R = 1\) contour corresponds to pure cumulene. At low temperatures, the threshold strain is 3% and it decreases with temperature starting from about 200 K, until at 900 K, the cumulene form becomes unstable (unless compressed, which is hard to picture with carbyne but may be feasible for other systems such as carbon nanotubes). Note that in the canonical Peierls effect, high temperatures tend to restore symmetry.\(^{(68)}\) That is an electronic excitation effect, and it should be negligible given polyyne’s wide band gap. (Further, this effect could only result in a shift of the transition to larger strains.) Thus, once again we see that the inclusion of nuclear degrees of freedom in the picture has led to unexpected qualitative changes of behavior.
Figure 2.9 – Strain–temperature “phase diagram” of the polyyne–cumulene transition. The order parameter $R$ (see the text) measures the shape of the nuclear density distribution, with one maximum (cumulene) at $R=1$ and two (polyyne) at $R<1$.

Besides the strain and temperature, the composition of carbyne offers another degree of freedom. With $^{13}\text{C}$ instead of $^{12}\text{C}$, all levels would experience a slight red-shift, moving the cumulene stability boundary closer to the origin. Formally, lighter C isotopes (had such existed) or lighter elements (assuming constant bond stiffness) would have moved the boundary up and to the right. One may naturally wonder if other group IV elements such as Si and Ge could display similar phenomena. However, the electronic structure of these elemental chains shows a third band crossing the Fermi energy, which breaks the exact half-occupancy of bands needed for the Peierls transition.\(^{(76)}\) Moreover, literature data\(^{(76)}\) and our own phonon dispersion calculations suggest that monoatomic chains of Si and Ge are unstable (at least, without external tension).
Since our computations focus on the Raman–active Peierls mode in the Γ point, they can be used directly to predict the evolution of Raman shifts under strain, offering an additional experimental test. Because of the anharmonicity, the structure of vibrational transitions becomes complex. Without strain, the first transition (between ZP and 1st level) is at 1119 cm\(^{-1}\), and there is a group of higher-level transitions upward of 1650 cm\(^{-1}\). Under stretching, the transitions experience a rapid redshift, so that at 10% strain, the first transition is at 110 cm\(^{-1}\) (the 0\(^{th}\) and 1\(^{st}\) vibrational levels become almost degenerate as the system converts from single-well to double-well character) and the higher transitions begin at 931 cm\(^{-1}\). This contrasts profoundly with the harmonic picture which predicts a (non-scaled) vibrational frequency of 1742 cm\(^{-1}\), comparatively insensitive to strain, demonstrating the failure of harmonic approximation.

So far our calculations treated carbyne as an infinite chain. The PES of infinite carbyne contains pairs of minima and is invariant under translation by one-half the unit cell of polyyne, which corresponds to the exchange of triple and single bonds. However, the ends of the carbyne chain, inevitable in any real experiment, will impose some boundary conditions that can break this degeneracy. (Note that our predictions should still apply directly to carbyne rings.) As a simple example, the two finite structures described by structural formulae

\[
\text{H–C}(\equiv C - C \equiv)_n C - \text{H}
\]

and

\[
\text{H} \equiv C(-C \equiv C -)_n C \equiv \text{H}
\]
are very nondegenerate, because H cannot even form stable triple bonds with C. On the other hand, the use of groups that interface with the chain through a double bond, such as methylene =CH₂, could favor the cumulene structure and stabilize the symmetry. The effect of end-groups will clearly have a different strength for different moieties, and a comprehensive investigation is an extensive task (further aggravated by the complexity of collective atomic motions in such many-atom systems) that is beyond the scope of the present study. However, simply looking at how the BLA depends on the end-group type in finite carbyne fragments already provides a useful glance into the issue.

![Figure 2.10 – Effect of endgroups on carbyne BLA. Termination of the chain with sp³ groups (methyl –CH₃ and phenyl –C₆H₅) increases the BLA, whereas the sp² methylene group (=CH₂) decreases it, as compared to an unterminated infinite chain (black dashed line). The data for 12- and 100-atom chains show a weak decrease of BLA with chain length away from the ends with methylene termination.](image)

The results of our finite-chain calculations with different terminating groups are presented in Figure 2.10. The strip from 1.27 to 1.30 Å denotes the bond lengths.
in the ideal infinite polyyne chain (ignoring the ZPV). The bond lengths in the $sp^3$-terminated systems ($-\text{CH}_3$, $-\text{C}_6\text{H}_5$) fall outside this strip, showing the enhanced polyyne-like character of the systems. On the other hand, $sp^2$-type $=\text{CH}_2$ termination reduces the BLA effectively to zero ($< 0.01 \text{ Å}$ for a 12-atom chain and $< 0.005 \text{ Å}$ in the middle of a 100-atom chain), suggesting that this type of passivation may even be used to shift the transition boundary towards higher strains/temperatures. (Indeed, $sp^2$-type groups are preferable from the electronics applications standpoint, providing metallic ‘leads’ at the ends of the chain.) We see that in experimental realizations, the switching effect may be destroyed by improper chemical termination of carbyne chains, and thus, precise control over both the tension and chemistry is essential. The endgroup effect can also explain why the harmonic approximation can accurately reproduce the vibrational structure of small polyynes with $sp^3$-type termination yet fails so profoundly for infinite carbyne.

In conclusion, one can try formulating the insight gained in the simplest terms. In a chain of (carbon) atoms, the quantum uncertainty of the nuclei positions is sufficient to maintain their spatial periodicity against the possible bond length alternation and, accordingly, the gapless metallic state is sustained. Under applied tension however, larger atomic spacing permits greater amplitude of Peierls distortion, exceeding the spatial uncertainty, which brings about the bond alternation and opens the electronic gap. First principles calculations place this metal–insulator transition at about 3% tensile strain. This effect naturally applies to other one-dimensional Peierls systems, as illustrated by our analytical model. Our findings are both important as an interesting new fundamental physical effect and
highly practically relevant for the science of conducting polymers, charge/spin density–wave materials, and electromechanical applications. Although carbyne remains an exotic, its unique properties will continue to fuel the effort to achieve its synthesis in practically useful quantities.

The DFT computations were performed using the VASP code(78) with projector-augmented wave basis sets,(79, 80) using the Data Analysis and Visualization Cyberinfrastructure funded by NSF under Grant OCI-0959097. To numerically solve the vibrational problem we utilized the Fourier grid Hamiltonian method,(81) which had been previously used to study the ZPV effect on Peierls transition in unstrained polyacetylene,(74) e with a uniform grid of 250 points in \(-0.4 \, \text{Å} \leq b \leq 0.4 \, \text{Å}\) from an interpolation of DFT-computed values of energy, and 6.005 a.m.u.—the reduced mass of two C atoms—for the oscillator mass.

2.2. One dimensional boron chain

2.2.1. Introduction

Carbon nanostructures have spearheaded a revolution in materials(82), beginning with fullerenes and nanotubes(83). More recently graphene has created a boom of research(84). Another exotic form of carbon—one dimensional chains, also known as carbyne—has been a subject of scientific controversy since 1960’s but with the advent of more powerful synthetic and measurement techniques is becoming more and more accessible(85, 86). Meanwhile, boron nanostructures are being actively investigated. Boron fullerenes were theoretically proposed(87) and
more recently synthesized experimentally (88). Atomically thin 2D films have long 
since been predicted theoretically (89-92) and finally experimentally 
synthesized (93-95). Evidence for elongated ribbonlike B₄₄H₂ clusters has also been 
reported (96). In context of this remarkable progress one naturally wonders what 
the structure and properties of 1D boron nanostructures could eventually look 
like—especially because for carbon, the 1D form is expected to have most extreme 
properties both mechanically and electronically (57, 59, 97, 98). As we demonstrate 
in the present first-principles theoretical study, 1D boron indeed has a fascinating 
combination of properties, including a reversible structural phase transition 
between metallic and wide-gap semiconducting forms under tension.

2.2.2. The structure and properties of boron chains:

Calculations by others (99) have showed that for boron, a carbyne-like linear 
chain (henceforth denoted as C) structure has higher energy than a ribbonlike (R) 
structure with two staggered atomic rows. Therefore the C structure is not stable in 
mechanical equilibrium. However, the two structures have a twofold difference in 
linear density (Figure 2.11 a,d). From this we can hypothesize that external tension 
can be used to stabilize C over R, using mechanical work to overcome the energy 
difference. In this study we show that this mechanical driven phase transition is 
indeed possible, in the sense that (1) it is energetically preferred to simple breaking 
of R; (2) it is reversible; and (3) it happens on practically useful time scales. Before 
discussing these findings in detail, we explore the remarkably different electronic 
and mechanical properties of the two phases separately. While we cannot
confidently rule out other 1D structures, our efforts to detect thicker wirelike phases with triangular or square cross-section have failed to find any simple candidate structures with energy lower than that of R.

The R structure is convenient to think of as an infinite extension of previously observed ribbonlike clusters. The chemistry of latter is analogous to linear carbon with every rhombic B₄ unit playing the role of a C₂ unit because boron has half as many π electrons per atom(100, 101). One might conclude that perfectly symmetric R structure must be a metal with half-band filling in each of the two π bands, which appears to fulfil the conditions of Peierls theorem(61-63) and thus should spontaneously tetramerize, as carbyne’s cumulene structure is predicted to dimerize(64), in the fixed-nuclei approximation. However, unlike in carbyne, the planar symmetry of R breaks the degeneracy of πₓ and πᵧ bands (shown in Figure 2.11c). As a result, the bands are split and the system has two Fermi wavevectors (Figure 2.11b), neither lying at Brillouin zone middle, resulting in no charge-density waves (CDW) commensurate with reasonably small-size supercell and hence absence of any detectable structural rearrangement.

The C structure (Figure 2.11d) has one fewer π electron per atom than carbyne and thus can be interpreted as carbyne with ¼ band filling (Figure 2.11e). As a result one would expect again a Peierls tetramerization with a π/4a CDW period. Instead, however, our calculations show formation of a spin-density wave (SDW) with almost no atomic rearrangement (Figure 2.11f). We identified two stable solutions: a bond-SDW (↑↑↓↓) and site-SDW (↑∙↓∙) as shown in Figure 2.11g,h,
respectively, with the latter 5 meV/atom higher in energy (HSE functional) and
strictly zero bond length alternation due to symmetry, and the bond-SDW state
showing a negligibly weak dimerization. The band gap of the bond-SDW is 1.52 eV
(HSE). As expected for all similar 1D systems(26), stretching increases the band gap
to 1.76 eV at 10% strain which is appreciable though not as dramatic as carbyne
CDW(26, 59). The gap increase here is not due to electron–phonon coupling(26) but
rather an increased SDW amplitude, which grows from 0.25 $\mu_B$ per atom to 0.3 $\mu_B$ at
10% strain.

Figure 2.11 – Electronic structure of 1D boron ribbons and chains. Ribbons (a)
have two nondegenerate Fermi wavevectors (see band structure in b)
stemming from broken $\pi$-band symmetry (spatial distributions of
corresponding electron densities shown in c) which prevents Peierls
transition from opening a band gap. Chains (d) undergo an antiferromagnetic
transition with a 4-cell spin density wave (SDW) period (band structure e → f)
with two almost-degenerate solutions: a bond-SDW ground state (g) and a site-SDW 5 meV/atom higher (h).

The most basic property of any solid material is its resistance to deformation. In this section we calculate the elastic moduli to demonstrate that R and C phases are true stable materials with distinct mechanics.

The calculation of tensile stiffness is shown in Figure 2.12a. As the unit cell size is scaled we observe two distinct minima separated by $\Delta E_c = 1$ eV, the cohesive energy difference between the two phases. The curvature of each minimum defines the tensile stiffness of the respective phase. We obtain 72 and 46 eV/Å, which is about ¾ and ½ that of carbyne, respectively for R and C phases. However, the lattice constant of C-boron is about 20% larger than carbyne and the atomic weight is a further 10% smaller, which brings the specific stiffness of C-boron to $6.4 \times 10^8$ Nm/kg, almost 2/3 of carbyne’s value. At the same time the twice-higher linear density of the R phase makes it the softer of the two on per-mass basis ($5.2 \times 10^8$ Nm/kg, about half of carbyne).

The hill between the two energy minima is the primary direct evidence of the phase transition. If we start with the R structure and stretch it to some point on the black curve in Figure 2.12a between the minima, for a large sample it will always be favorable to separate into R and C regions, instead of stretching uniformly, with the total energy being lowered to the green line. The latter is defined as the common tangent of the two potential wells, and its slope yields the equilibrium tension $F_{eq} = 2.13$ nN which is the value at which both phases have identical enthalpy, $H = E + FL$. 
Above it, R has higher enthalpy and thus gets converted into C, and vice versa. Under fixed-length boundary conditions between the two tangent points the system will relax toward a R–C mixture in such proportions that the tension equals $F_{eq}$, which can be used to make a fixed-tension nanospring with a stretching range of about 100%.

By taking the slope of Figure 2.12a plot at the inflection points of energy–strain curves we can estimate the ideal breaking strength of both phases, yielding 7.38 nN and 9.73 nN for C and R, respectively. These values correspond to $64 \cdot 10^6$ and $44 \cdot 10^6$ Nm/kg specific strength, respectively (85% and 60% of carbyne). Importantly, $F_{eq}$ is well below both breaking points.
Figure 2.12 - Mechanics of one-dimensional boron. (a) Energy-strain curve showing two distinct minima for ribbons (R) and chains (C). The equilibrium tension $F_{eq}$ is defined as the common tangent for the two minima. The curvature of the plot in the minima yields tensile stiffness of the phases, and the maximum slope provides an estimate of breaking strength. (b) Bending stiffness of R phase as calculated using a ring model. Black squares and orange disks represent energy and band gap, respectively, showing nonlinearities around curvature values where bending causes degeneracies between different-symmetry $\pi$ orbitals. (c) Ring model calculations for bending stiffness of C phase, with alternating antiferromagnetic (AFM) and nonmagnetic (NM) ground-state solutions. (d) Twisting of R phase for torsional stiffness fitting.

To calculate the bending stiffness, as before(59), we use rings of increasing radius (decreasing curvature) to extract the $E(1/r^2)$ asymptote slope, where $E$ is the energy of ring of radius $r$. When plotted in respective coordinates, the energy $E_R$ of R “nanobelts” (Figure 2.12b) shows a strikingly nonlinear behavior. The upwards deviation from straight line in Figure 2.12b turns out to be again rooted in symmetries. The upwards deviation of bending energies correspond to closing HOMO-LUMO gaps. However, the gap closing is not because of the curvature but due to the periodicity of the ribbon ring cluster. To get an estimate of the bending stiffness of the infinite R phase we computed the stiffness for each value of $r$ based on ring energy $E_R(r)$ and the cohesive energy of the infinite ribbon $E_R(\infty)$, and took the lowest value, 2.6 eV·Å, which yields a persistence length of 10 nm at room temperature—roughly on par with carbyne.

The C phase of boron also at first seems to behave extremely nonlinearly when curved into rings as seen in Figure 2.12c. However, the oscillatory behavior is
easily understood by dividing the rings in two families—B$_{8N}$ and B$_{8N+4}$—with $E_C(r)$ for each perfectly following the predicted asymptotic of $\sim 1/r^2$. This situation is analogous to the first-/second-order Jahn–Teller effect in carbyne rings(52, 59).

Interestingly, the ground state of B$_{8N+4}$ rings is nonmagnetic. The intersection of the two lines in Figure 2.12c (around B$_{40}$) thus can be interpreted as a “curvature-induced magnetic transition”. The stiffness is 0.81 eV·Å for nonmagnetic rings (low-curvature asymptotic) and 1.25 eV·Å for antiferromagnetic, the latter corresponding to a room-temperature persistence length of 4.9 nm.

Finally, the planar symmetry of R structure makes it possible to define a torsion stiffness without a need for symmetry-breaking “handles”(59). The model system, illustrated in Figure 2.12d, consists of a supercell in which the ribbon makes a 360° twist. By varying the supercell size we can calculate the energy as a function of twist per unit cell and determine the stiffness by extrapolation, yielding a value of $\sim$5 eV·Å, about $\frac{1}{2}$ the value for carbyne.

$$C = \frac{1}{aR} \frac{\partial^2 E}{\partial \varepsilon^2} = \frac{btY}{aR},$$

Equation 2.7 – Tensile stiffness in continuum model for elastic cuboid beam.

$$K = \frac{1}{aR} \frac{\partial^2 E}{\partial \left(\frac{1}{R}\right)^2} = \frac{1}{12} bt^3 Y,$$

Equation 2.8 – Bending stiffness in continuum model for elastic cuboid beam.
\[ H = a_R \frac{\partial^2 E}{\partial \theta^2} = J \cdot G. \]

**Equation 2.9 – Torsional stiffness in continuum model for elastic cuboid beam.**

Similarly to previous work (59) we can use the calculated properties to define equivalent continuum models for both phases. With the cylindrical rod representation for C-boron we find a nominal Young’s modulus of \( Y_C = 21.6 \) TPa at a nominal thickness of \( 2r_C = 0.66 \) Å. For simplicity we approximate the R phase as a rectangular “plank” of thickness \( t \) and width \( b = 1.5 \) Å, and the system of equations governing the elastic behavior is then

Here \( J \) is the torsional constant approximately given by

\[ J = bt^3 \left[ \frac{1}{3} - 0.21 \frac{t}{b} \left( 1 - \frac{t^4}{12b^4} \right) \right] \approx 0.1. \]

**Equation 2.10 – Torsional constant.**

Solving the system yields an effective thickness of \( t = 0.658 \) Å, Young’s modulus of \( Y = 11.7 \) TPa, and a shear modulus of \( G = 8 \) TPa. The corresponding Poisson’s ratio is \(-0.27\). In sum, while the nominal elastic moduli for 1D boron are smaller than for carbyne (59), they are still very formidable, once again emphasizing the unusual mechanical properties of one-dimensional nanomaterials.

Having characterized the R and C phases of 1D boron as stand-alone phases with their own remarkable and very distinct properties, we now proceed to study
the phase transition that connects them. To check whether it is at all possible, we first performed a molecular dynamics simulation of stretching a 64-atom R supercell with the density-functional tight binding (DFTB) method. Under stretching the system gradually underwent smooth transition into the C phase via a series of nucleation events followed by interface propagation. We observed multiple interface nucleations resulting from the high temperature, as explained below. Upon collisions of C|R and R|C interfaces as an R domain shrank we observed formation of diamond-like “knots” which would persist almost to the end of stretching run. We also performed a reverse simulation starting from the structure at 65% elongation (chosen so as to have a fragment of R phase still intact to serve as a “seed”) and compressed to original length. The trajectory shows growth of R structure at the expense of C back to the original all-R structure. During both molecular dynamics runs we monitored the average tension for each elongation value (Figure 2.13a). The stretching run shows an initial “overstretching” behavior indicative of a nucleation event, and then remains effectively constant up to full stretching. Compression is also accompanied by constant (and somewhat lower) tension value. The equilibrium tension computed as in Figure 2.13a using DFTB is 2.43 nN, close to the DFT value and in excellent agreement with the tension value during molecular dynamics compression.

Our molecular dynamics simulations validate the prediction of a R–C phase transition in 1D boron under tension—even at the rather high strain rates and temperatures required imposed by computational resource limitations. Therefore it is compelling to study the phase transition kinetics under more relevant conditions.
of lower strain rates and temperatures. With that aim we calculated step-by-step energies and activation barriers for the transformation of R into C using a 24-atom supercell. The calculations are performed under constant tension corresponding to phase equilibrium, where the relevant thermodynamic quantity is the enthalpy $H = E + FL$. While it is easy to perform variable-cell geometry relaxations to ensure exactly the right tension, the problem of locating transition states becomes much more difficult under constant-tension boundary conditions. We thus adopted a grid-search approach. We performed fixed-cell transition state searches (using manual scan with a suitable choice of reaction coordinate or with the climbing-image nudged elastic band method, further refined by the dimer method) with different cell lengths chosen so as to ensure that the transition states thus located bracket the equilibrium tension. Then the energy (enthalpy) barrier under equilibrium tension was determined using interpolation. This approach enables us to not only compute the kinetics of phase transition under equilibrium tension, but further to directly evaluate how the kinetic barriers are affected by loads above or below equilibrium.

We find that the nucleation of C structure (N1-N2-N3-N4 in Figure 2.13b) is limited by the first bond-breaking event with a 2.7 eV barrier. After that the enthalpy quickly sets into a repetitive pattern with a period of 4 and a maximum barrier height of 0.4 eV within a period, which corresponds to interface propagation. The periodic behavior can be considered an artifact of a finite model system due to electron-counting rules for bond conjugation (100, 101), and in an idealized system with two semi-infinite phases there would be no such oscillation.
Figure 2.13 – Chain-ribbon phase transition. (a) Evolution of tension in molecular dynamics simulations of stretching (including reversal), see Supplementary Videos. (b) Enthalpy variation over sequential steps of R–C phase transition under equilibrium tension. The corresponding structures are shown with red X marking sequential bond breakings. (c) Domain length (inverse concentration of R|C and C|R interfaces) in 1D boron under thermal and mechanical equilibrium. (d) Ductility diagram showing contours of phase transition timescales—from (s)econds to (y)ears—as a function of temperature and tension, assuming nucleation at ribbon ends, i.e., the
activation barrier used is half the 2.7 eV (b) value. The inset (e) shows a full-barrier estimate corresponding to “homogeneous” mid-ribbon nucleation of C phase.

By averaging the energies of states in the propagation part and dividing by two (number of interfaces in the model system) we can estimate the free energy (enthalpy) of a single R|C interface as $H^* = 1.0 \pm 0.07$ eV. Based on this we can evaluate the concentration of domain interfaces in mechanical and thermal equilibrium as a function of temperature, $c^{-1} \sim a_R \exp(-H^*/k_B T)$. As Figure 2.13c shows, the interface energy is large enough that at room temperature one should expect to observe millimeter-scale coherent phase domains. As the temperature increases we gradually enter the domain where the system is expected to become a homogeneous mixture of small nanometer-scale domains at temperatures above $\sim 500$ K. This is consistent with multiple nucleation seen in MD simulation.

Finally, from kinetic barriers we can estimate the speed of the phase transition. Knowing not only the values of barriers but also how they react to changes in tension we can construct the contour diagram in Figure 2.13d. The horizontal axis shows the tension (the left boundary is the equilibrium value of 2.13 nN), the vertical axis shows temperature $T$, and contours denote the levels where the frequency of crossing the nucleation barrier per unit cell length is one per time unit: (y)ear, (d)ay, (h)our, (m)inute, (s)econd. The frequency is estimated as $f = 10^{13}$ \exp[-\delta H^*(F)/k_B T]$ where $\delta H^*(F)$ is the interpolated activation barrier height at tension $F$, and the prefactor is on the order of $k_B T/h(45)$. The mobility of the interface can be similarly estimated (assuming unilateral motion) by substituting
$\delta H'(F)$ with the periodic oscillation barrier $\sim 0.4$ eV and multiplying the resulting frequency by $a_R$. This yields values on the millimeter-per-second order at 300 K.

### 2.2.3. Conclusion

The arguments against possibility of phases in 1D are well known. In spite of that our present calculations show that on practically relevant time- and length-scales boron forms two well-defined phases—chains and ribbons. The two phases are linked by a reversible phase transition. The dynamics of the transition can be tuned over many orders of magnitude by external tension and temperature. Each phase by itself has formidable mechanical properties with different interesting nonlinearities. Further, one (ribbon) is a true 1D metal robust to Peierls distortion, and the other (chain) is a strain-tunable wide-gap antiferromagnetic semiconductor. Thus, electronically the two-phase system represents a stretchable Schottky junction, and from the mechanics standpoint it is a constant-tension spring with a fundamentally fixed tension value of 2.13 nN. This diversity of behaviors of 1D boron is certainly very interesting from the fundamental standpoint, and may lead to interesting novel electromechanical applications. Finally, other chemical compositions such as silicon were found to also have R-like structures in 1D(76), and our analysis straightforwardly generalized to all these materials, too.
Two-Dimensional Materials Applied in Energy Storage and Conversion

3.1. Graphene based anode materials in LIB

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3.1.1. Introduction

Graphite has been used as an anode material for Li-ion battery since the 1990s. The capacity of the Li-ion battery with the graphite anode is known to be 372 mAh/g, corresponding to a LiC₆ configuration, where intercalated Li ions are distributed on every other hexagon of the graphene lattice. (102) Dendrite growth and Li atom plating are the main problems which limit the operation and can cause
the failure of Li-ion batteries.\textsuperscript{(103),(104)} Both problems are related to the Li cluster nucleation on graphite. Recently, other carbon materials such as graphene\textsuperscript{(105),(106),(107)} and carbon nanotubes (CNTs)\textsuperscript{(108),(109)} have been proposed as replacement anode materials. Both materials have an added advantage of accessible large surface area, which could potentially increase the capacity of the battery. Although the thermal capacity of graphene anode has since been demonstrated to be lower than that of graphite in both experiments and theoretical studies,\textsuperscript{(110),(111)} the nucleation of Li on graphene has barely been studied.\textsuperscript{(112),(113)} The dendrite formation has been explored and simulated from the macroscopic point of view,\textsuperscript{(103)} where it was assumed that a nucleation center has been formed already.\textsuperscript{(114)} Investigating the conditions under which a nucleation center forms requires atomistic simulation and modeling. It is known that metal atom clustering happens in carbon materials, such as on SWNT.\textsuperscript{(115)} In this work, we applied first principles calculations to study Li clusters on graphene. Our results show that although the binding energy of Li on graphene is weaker than Li in the bulk, the nucleation barrier may prevent the phase separation of Li clusters and graphene. The nucleation barrier depends on the chemical potential of Li which in turn depends on the concentration of Li on graphene. We applied first-principles calculations and macroscopic modeling to roughly estimate the nucleation size and energy barrier under various Li concentrations. We also analyzed the charge transfer during nucleation, gaining insights into the interactions between the Li ions and graphene as well as the nucleation process.
We applied density functional theory (DFT) with generalized gradient approximation (GGA) as implemented in VASP to relax the atomic structures and obtain the total energies. The Projector augmented waves (PAW) and PW91 functional have been used.\textsuperscript{(116), (117)} The plane wave energy cutoff was 400 eV. The sequence of Li concentrations on graphene was calculated by increasing the size of the graphene supercell from $5 \times 5$, to $6 \times 6$, to $7 \times 7$, to $8 \times 8$, to $9 \times 9$. For each supercell, the convergence of K-point mesh was tested. In cluster calculations, a $9 \times 9$ graphene supercell was used with a vacuum space of 15 Å along the z direction. The Brillouin zone was sampled using a $\Gamma$-centered $3 \times 3 \times 1$ K-point grid in all cases. For electronic structure calculations, a $6 \times 6$ graphene supercell was used. Since the bonding between Li and graphene is mostly ionic,\textsuperscript{(118)} the role of van der Waals interactions is minor, and van der Waals corrections are not essential here. We also note that in systems with a well-pronounced charge transfer states such as ours, semilocal functionals may not yield accurate results due to their well-known delocalization error. To verify the accuracy of PW91 functional, we performed an additional calculation using a hybrid HSE functional for the adsorption energy of LiC\textsubscript{6}. We obtained values of -0.95 and -0.92 eV/atom for the Li adsorption energy with PW91 and HSE functionals, respectively. As expected, the interaction energy given by HSE is smaller, consistent with the fact that (semi)local functionals overestimate binding of charge transfer states. However, the difference between the two values is not very large, validating applicability of PW91 to this system.
3.1.2. Lithium nucleation on graphene and its implications in LIB

The structure of Li clusters on graphene. We considered clusters with the numbers of atoms \( n \) up to 13; Figure 3.1 shows the obtained low-energy configurations for clusters with \( n \) up to 11. Unlike graphite, the adsorption energy of a single Li atom on graphene is higher than the bulk Li; therefore, in the thermodynamical limit, Li atoms would tend to aggregate into large clusters rather than adsorb on graphene separately.\(^{(110),(111)}\) However, there will be a nucleation barrier due to the high surface energy of small clusters. We searched for the lowest energy structures by considering several possible configurations for each cluster. For smaller clusters \((n=3, 4, 5)\), all possible configurations were searched, and cluster with the lowest energy were selected as the ground state. For larger clusters \((n>5)\), global optimization was impractical, and two alternative approaches were used to identify low energy structures. One is to simply add an atom to a previously found low energy \((n-1)\)-atom cluster. Another is to start with the ground state geometry in vacuum,\(^{(119),(120)}\) bring the cluster in contact with graphene, and perform relaxation. In some cases \((n=6, 8, 9)\), both approaches led to same geometries. For the remaining clusters \((n=7, 10, 11, 12, 13)\), the first method yielded geometries with the energy that is lower than that obtained by starting from the equilibrium geometry in vacuum. It is possible that the found geometries do not represent the true ground states for these clusters; however it is likely that their energies are quite close to them, considering the inherent polymorphism of few-atom metal clusters.
Figure 3.1 – The most stable structures of Li clusters on graphene from n=3 to 11. Balls represent Li atoms and are colored in the order of increasing distance from graphene: purple (closest to graphene), red, yellow, and light purple (farthest from graphene).

The most stable configurations of Li clusters (Li\(_n\)) on graphene are not necessary the same as in vacuum. For \(n=2\), the Li atoms form a dimer with the optimized distance of 2.65-2.78 Å in vacuum;\(^{(121)}\) however, for two Li atoms attached to graphene, the effective pair interaction is repulsive, and the formation energy of the dimer is larger than the sum of bonding energies of individual Li atoms. Hence, the dimer structure for Li\(_2\) is not favorable on graphene. For \(n=3\), Li atoms form an isosceles triangle in vacuum.\(^{(119)}\) The Li\(_3\) on graphene forms isosceles triangle as well but the third atom prefers to stay above the other two rather than attaching on graphene to form the equilateral triangle. It points to the
start of the nucleation, where the cluster prefers forming a three-dimensional shape rather than being attached on graphene surface. For \( n=4 \), the Li atoms form a rhombus in vacuum, but the most stable structure for \( \text{Li}_4 \) on graphene is a tetrahedron.\(^{(119)}\) All other cluster configurations for \( n=2\text{--}5 \) and their energy differences are listed in the Supporting Information. The observed non-intuitive behavior for the small Li clusters \((n<7)\) to prefer planar configurations in vacuum,\(^{(119)}\) but form three-dimensional shapes on graphene is discussed below from the electronic structure point of view.

*The cluster formation energy and macroscopic model.* Based on the determined most stable structures, we estimate the formation energy of clusters. The formation free energy \( \Delta G(n) \) of each cluster at concentration \( x \) is defined as

\[
\Delta G(n) \equiv E(\text{Li}_n@\text{graphene}) - E(\text{graphene}) - n \cdot \mu(\text{Li}@\text{Li}_x\text{C})
\]

*Equation 3.1 – Formation free energy of clusters.*

where \( \mu(\text{Li}@\text{Li}_x\text{C}) \) is the chemical potential of Li under various conditions. In Li-ion batteries, the Li\(^+\) ions arrive at the surface and are adsorbed on graphene first.\(^{(122)}\) We use this adsorbed phase as a reference, and define the chemical potential of Li as

\[
\mu(\text{Li}@\text{Li}_x\text{C}) = \frac{[E(\text{Li}_x\text{C}) - E(\text{C})]}{x} - TS(x)
\]

*Equation 3.2 – Chemical potential of lithium.*
The nucleation process depends strongly on the chemical potential of Li atoms. For instance, if the chemical potential is chosen to be that of atomic Li, the cluster energy would be negative, and the formation of Li clusters is strongly favored, whereas if the chemical potential is chosen to be that of Li in the bulk phase, the formation energy is positive, meaning that cluster formation is unlikely. When the adsorbed phase used as a reference, the chemical potential of Li will be concentration-dependent. We compute the $\mu_{\text{Li@Li}_x\text{C}}$ for Li:C ratios ranging from 1:162 to 1:6. We also include the configurational entropy correction at a dilute limit into the chemical potential of the reference phase. The configurational entropy of the clusters is much smaller than that of the reference phase and can be neglected. The entropy of the reference phase is estimated by counting the number of adsorption configuration at a given concentration. The entropy $S$ (per adsorbed Li atom) of the adsorbed phase is given by:

$$-S(x) = k_B \left[ \ln 2x + (1 - 2x) \ln \left( \frac{1 - 2x}{2x} \right) \right]$$

*Equation 3.3 – Configurational entropy of Lithium.*

Here, $x = \text{Li: C}$, and $k_B$ is the Boltzmann constant. The temperature was taken to be 300 K.

We also estimate the formation energy of Li clusters on graphene using a macroscopic model. The model is useful when considering cluster sizes that are not accessible with the atomistic calculations. The spherical model of Li clusters can be
used to do a quick estimation but a more accurate equilibrium shape of a Li cluster in vacuum should be determined utilizing Wulff construction.\textsuperscript{(124)} The equilibrium shape of Li clusters in vacuum is obtained by minimizing the surface energy of cluster $E_s$ at a given size. If the cluster shape is a polyhedron, the formation energy with respect to the bulk phase is given by:

$$E_s = \sum \gamma_i A_i$$

\textbf{Equation 3.4 – Surface energy of clusters.}

where $\gamma_i$ is the surface energy of the $i$th facet of the polyhedron and $A_i$ is the area of the facet. According to the Wulff theorem, the distances of the crystal facets from the center are proportional to the facet surface energies when the crystal is at equilibrium. Based on cluster size $n$, one can estimate the volume of Li clusters from the atomic volume, and by simple geometry analysis according to Figure 3.2b, the change of the surface area $A_i$ with $n$ can be derived. We construct the equilibrium shape using the values of 29 meV/Å$^2$, 31 meV/Å$^2$, and 35 meV/Å$^2$ for the formation energies of the (100), (110), and (111) facets of Li, respectively, as obtained with the DFT calculation using GGA.\textsuperscript{(125)} The equilibrium particle shape is shown in Figure 3.2b. After accounting for various contributions, the particle formation free energy $\Delta G(n)$ is given by:

$$\Delta G(n) = E_s + E_{\text{bulk}} - A_{(100)} \gamma_{\text{interface}} - \mu n$$
Equation 3.5 – Formation free energy of clusters from macroscopic model.

Here, $n$ is the number of atoms in the cluster, $E_{\text{bulk}}$ is the atomization energy of bulk Li, $A_{(100)}$ is the area of the particle (100) facet, and $\mu$ is the chemical potential of the reference phase (in this case, a submonolayer amount of Li on graphene at a given concentration). We chose the (100) facet because it has the largest surface area. For the interface energy $\gamma_{\text{interface}}$ of Li(100) on graphene, we obtained a value of 14 meV/Å², by calculating the graphene-Li interaction energy for a Li slab on graphene with six Li layers. The cluster formation curves based on the macroscopic cluster model are shown in dashed lines in Figure 3.2a. The few-atom Li clusters considered in our work do not have facets corresponding to well-defined crystal surfaces that normally exist in large metal particles. Hence, the model of a bulk crystal truncated by several low-energy crystalline planes is not directly applicable in this case. Not surprisingly, the model, when used in an unmodified form, predicts formation energies that are different (too high) from the actual cluster formation energies. We also considered an altered model assuming the same scaling of the formation energy, $E \sim n^{2/3}$, but with a prefactor that is different in case of very small clusters. The prefactor was obtained by fitting the calculated formation energies, and can be conveniently incorporated into the interface energy. We got the value of $\sim 150$ meV/Å² for the effective interface energy, with the fitting curves shown as solid lines in Figure 3.2a. It should be noticed that when the clusters become larger and approach the macroscopic limit, the nucleation behavior should be represented by the dashed lines. Any changes in
the cluster shape upon the adsorption were neglected, and the formation energy on graphene was calculated using the equilibrium shape in vacuum.

![Figure 3.2](image.png)

**Figure 3.2** - (a) Cluster formation energies at different chemical potentials: symbols represent atomistic results, as given by Equation 3.1; the dashed lines are obtained from the macroscopic Wulff construction model (Equation 3.5), and solid lines show the fitting of Equation 3.5 by modifying the interface energy $\gamma_{\text{interface}}$. The equilibrium crystal shape from the Wulff construction is shown in (b).

The comparison of the cluster formation energy as predicted by Equation 3.5 and calculated formation energies of actual clusters by Equation 3.1 are shown in Figure 3.2a, with good agreement. Using the analytical expression, we get the critical cluster size and the nucleation barrier. The critical cluster sizes and nucleation barriers at various reference Li concentrations are listed in Table I. As we can see, the cluster sizes for nucleation are small, but the nucleation barriers are not negligible. For example, the smallest nucleation barrier at high concentration limit is around 0.27 eV; for the dilute case (Li:C=1:162), the barrier is as high as ~14.7 eV.
We conjecture that overcoming this nucleation barrier and forming a metal particle may be important for the initial nucleation of a dendrite. However, answering the question of how the dendrite that was nucleated by a Li nucleus proceeds to grow into mesoscopic and macroscopic sizes is beyond the scope of this work.

<table>
<thead>
<tr>
<th>Li:C</th>
<th>N</th>
<th>ΔGbarrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:6</td>
<td>1</td>
<td>0.27</td>
</tr>
<tr>
<td>1:24</td>
<td>3</td>
<td>0.53</td>
</tr>
<tr>
<td>1:72</td>
<td>40</td>
<td>3.23</td>
</tr>
</tbody>
</table>

Table 3.1 – Cluster sizes at the nucleation barrier obtained from the analytical cluster model at various reference Li concentrations on graphene.

The electronic structure and electron transfer during clustering. Based on the previous discussions, the interaction between Li clusters and graphene is stronger than neutral metallic bulk Li on graphene, which indicates the stronger ionic bonding and charge transfer from Li to graphene. A single Li adatom binds to graphene by donating its electron to the delocalized π states of graphene, and becomes fully ionized.(126) When the cluster is formed, the Li electrons should be localized inside the cluster, similar to bulk Li where each Li has zero net charge. At intermediate cluster sizes, the transition from the adatom to bulk behavior occurs. For Li₂ in vacuum, the Li electrons pair up and form the Li-Li bond. However, when adsorbed on graphene, our calculations indicate that the Li electrons are mainly
transferred to graphene by filling up the upper Dirac cone, as shown in Figure 3.3a. It suggests that the Li$_2$ is ionized and each Li carries +1 charge. For Li$_3$, a flat band appears below the Fermi level. Its charge density distribution at Γ point indicates that two electrons are shared between the Li$_3$ cluster (Figure 3.3b). The remaining electron is transferred to graphene. Therefore, on average, each Li carries +1/3 charge. For Li$_4$ (Figure 3.3c), two electrons are localized inside the cluster, and thus each Li has +1/2 charge averagely. As the cluster grows larger, the net charge of Li asymptotically approaches the zero charge of bulk Li. The low energy of the electron localized inside the Li clusters (from Li$_3$ to Li$_4$) might be an additional driving force for the nucleation. To test the extent of applicability of DFT band structures to describe quasiparticle energies in real systems, we have additionally carried out a GW calculation for the band structure of LiC$_6$. As can be seen from the figure, the main impact of including many-body effects into the quasiparticle energies is the lowering of quasiparticle bands with respect to the Fermi level. Another observation is that the electron occupation of the Li band is higher in GW, suggesting decreased charge transfer from Li to graphene relative to PW91 results. From the above comparison, we expect that our qualitative analysis of the charge transfer process from adsorbed Li to graphene should remain valid.
Figure 3.3 – Electronic structure of Li cluster on graphene for (a) Li$_2$ (b) Li$_3$ (c) Li$_4$. Red and black dots in (a) show the spin-polarized states of the magnetic Li$_2$. The Li$_3$ and Li$_4$ are non-magnetic and thus the states are doubly-occupied. The Fermi level is set to zero. The charge density distribution of the flat band at Γ point is shown in the bottom panel. For (a), the isosurface is displayed in yellow to indicate the state is unoccupied.

3.1.3. Conclusion

In summary, we investigated the Li cluster formation process using first principle calculations and found that the Li nucleation barrier depends strongly on the concentration of Li ions on graphene. This nucleation barrier would prevent the phase separation from occurring under certain concentrations. The electronic structure of those clusters on graphene indicates that the low energy electrons localized inside the Li clusters might be the driving force for the nucleation.
3.2. N-doped carbon materials as catalysts in electrochemical CO₂ reduction reaction

This work has been published on ACS. Nano 9(5), 5364-5371 (2015); Angew. Chem. 127 (46), 13905-13909 (2015) and Nano Lett. 16(1), 466-470 (2015).

3.2.1. Introduction

Mastery of the electrochemical conversion of carbon dioxide and water to fuels using renewable electricity has the potential to shed light on understanding the nature of artificial photosynthesis and offer an approach to mitigate the negative impact of anthropogenic carbon dioxide emissions on the planet. The field, however, has not substantially advanced in the last 30 years primarily because of the challenge of discovery of chemically active and structurally stable electrocatalysts and membrane architectures. An ideal catalyst for the electroreduction of CO₂, e.g. \( \text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O} \), is capable of mediating proton-coupled electron transfer, possessing a low overpotential for CO₂ activation while being sluggish towards hydrogen evolution, exhibiting a preferable selectivity towards a target product, and retaining structural integrity over a long operation. Significant progress has been made since 2011, addressing the chemical activity originated from oxide scale or tuned ionic-liquid/catalyst interfaces. Silver and gold can selectively convert CO₂ to CO, a feedstock for the synthesis of methanol in the Fischer-Tropsch process, while the ionic liquid can function as a co-catalyst to lower the overpotential and subsequently
improve the reaction kinetics. Copper and tin are known non-precious metallic catalysts. Copper is found to be active towards the formation of hydrogen carbon and alcohols.\(^{128, 133-135}\) Tin exhibits a superior selectivity towards the formation of formate with a Faradaic efficiency up to 98\%.\(^{129}\) A rapid performance degradation was observed in both Sn- and Cu-based electrode after approximately 30 minutes from the start of CO\(_2\) electrolysis.\(^{128, 136-138}\) As a result, it is compelling to search for efficient, durable and inexpensive alternatives to metal electrocatalysts for CO\(_2\) conversion.

Nitrogen-doped carbon nanotubes (NCNTs) are known to be an effective electrocatalyst for oxygen reduction reaction (ORR). The activity of NCNT catalyst is originated from its both local defects that mediate the electronic structure,\(^{139, 140}\) and its surface morphology that regulates atomic arrangement and coordination.\(^{140}\) So far there are very limited reports on the use of CNTs or NCNTs as the catalyst for the electroreduction of CO\(_2\). CNTs have been applied as the support for the catalytically active species rather than a catalyst itself.\(^{141, 142}\) NCNTs with a modification of polyethyleneimine was ever found to function as a catalyst to reduce CO\(_2\) to formate but at a high overpotential.\(^{143}\) The activity of NCNTs towards the reduction of CO\(_2\) remains largely unknown. Therefore, in this study we investigated the NCNT, further extended into N-doped graphene as an efficient electrocatalysts for CO\(_2\) reductions reactions based on computational hydrogen electrode (CHE) model \(^{144}\) and density functional theory (DFT) simulations implemented in Vienna Ab-initio Simulation Package (VASP) \(^{145}\). Moreover, the experimental results demonstrated this performances.
3.2.2. N-doped CNT for electrocatalysis of CRR

We consider the reaction mechanism of electroreduction of CO$_2$ to CO on pristine CNTs and NCNTs surface through the adsorbed intermediates COOH* and CO*. Similar intermediates have been proposed for the electroreduction of CO$_2$ on late transition metals like Au, Pt and Cu.\textsuperscript{(144, 146)} The elemental reaction steps for the CO$_2$ electrocatalytic reduction to CO are shown in steps (1-3).\textsuperscript{(146)}

\[
\text{CO}_2(g) + \ast + \text{H}^+(aq) + e^- \leftrightarrow \text{COOH} \ast \quad (1)
\]
\[
\text{COOH} \ast + \text{H}^+(aq) + e^- \leftrightarrow \text{CO} \ast + \text{H}_2\text{O(l)} \quad (2)
\]
\[
\text{CO} \leftrightarrow \text{CO}_2(g) + \ast \quad (3)
\]

where \(\ast\) denotes a free step site. This reaction mechanism involves two coupled electron-proton transfer reaction steps (1) and (2); and one non-electrochemical step, CO desorption (3). The corresponding free energy diagram for the lowest-energy pathways for CO$_2$ reduction to CO through this scheme is shown in Figure 3.4, which is calculated based on the CHE model.\textsuperscript{(144, 147)} The overpotential strongly depends on free energies of the first two electrochemical steps. For NCNTs, the activation of CO$_2$ to form adsorbed COOH* is associated with an uphill process of the first electron-proton pair transfer at 0 V vs. RHE. After the adsorption of COOH, the free-energy pathway becomes thermodynamically downhill to transfer the second electron-proton pair to form adsorbed CO. This CO is weakly bound to NCNTs surface, leading to the production of CO gas. The potential-limiting step is the formation of adsorbed COOH*, requiring an onset potential of -0.30 V vs. RHE at
which the step becomes exergonic (downhill in free energy) at the pyridinic N site. It implies an existence of limiting (least-negative) overpotential of -0.20 V. The calculated limiting overpotential for pyridinic N is lower than theoretical values for Cu (-0.31 V), Au (-0.63 V) and Ag (-0.79 V). The most efficient N configuration is pyridinic N followed by pyrrolic and graphitic N. In the case of CNTs, the potential-limiting step is also the formation of adsorbed COOH*, but requiring an overpotential of -1.9 V, much higher than that for NCNTs.

Figure 3.4 – Calculated free energy diagram for CO₂ electroreduction to CO on pristine CNTs and NCNTs. The free energy diagram shows the lowest energy pathway at 0 V vs. RHE as well as at an applied least-negative potential of -0.3 V vs. RHE at which the pathway becomes exergonic.
Moreover, in order to elucidate the high selectivity of NCNTs towards CO production, we correlated the kinetic activity towards CO production with the adsorption energies of COOH ($E_{B[COOH]}$) and CO ($E_{B[CO]}$).\cite{146,148} Essentially, a highly selective catalyst for CO$_2$ reduction to CO is required to possess the capability of immobilizing COOH but loosening CO at the same time. In other words, it requires strong COOH binding but a weak CO adsorption. The $E_{B[COOH]}$ and $E_{B[CO]}$ for pristine and different N functionalities doped CNTs were calculated, and the results are shown in Figure 3.5. The data of metal catalysts from ref. \cite{148} are also included in Figure 3.5. For the elemental metal catalysts, the $E_{B[COOH]}$ and $E_{B[CO]}$ are linearly correlated with a small positive slope less than one (around 0.73), which suggests that increasing the bonding strength of COOH to the metal surface is accompanied by a sharp increase of CO adsorption energy. Therefore, all elemental metals are off the maximum of kinetic activity to electroreduce CO$_2$ to CO. For the CNTs materials, the $\Delta E_{COOH}$ versus $\Delta E_{CO}$ is also positively linear. However, the slope for the linear relationship has a much larger magnitude of around 37, and thus a significant increase of $E_{B[COOH]}$ only causes a slight increase of $E_{B[CO]}$ in NCNTs, which fulfills the essential requirement for a highly selective catalyst for CO evolution. The binding energy profile indicates the highest selective site towards CO production is pyridinic N followed by pyrrolic and graphitic N. The pyridinic N has very negative value of $E_{B[COOH]}$ as reactive metals like Pt and Ni so that COOH can bind tightly. On the other hand, it owns a weak $E_{B[CO]}$ similar with Au and Ag which renders the feasible desorption of adsorbed CO*. Both pyrrolic and graphitic N are also calculated to have stronger $E_{B[COOH]}$ and weaker $E_{B[CO]}$ than the most CO selective elemental metal
catalysts like Au and Ag. As a result, gas product of CO is favorably produced on NCNTs instead of hydrocarbons and alcohols, as CO is released easily from active N sites on NCNTs before it can be further reduced by the successive electrons. The binding energy profile of COOH and CO for the three N configurations provides insight into the high FE of CO up to 80% for NCNTs in our measurements. For the CNTs, although the binding energy for both COOH and CO are reasonable for selective CO production, the free energy barrier for the first electron-proton pair transfer is too high resulting in a very high onset overpotential at which the HER is also promoted and predominates over CO₂ reduction. Therefore, CNTs exhibit a low yield of CO.

Figure 3.5 – Kinetic activity of NCNTs and metal catalysts. (a) The correlation of calculated adsorption energies of the key bound intermediates of COOH* and CO*. The binding energy data for lattice surface (211) of metals are adopted from Ref. (149).
3.2.3. N-doped graphene for electrocatalysis of CRR

The role of different N moieties in N-doped graphene towards CRR was examined using density functional theory (DFT) calculations based on computational hydrogen electrode (CHE) model. (144, 146, 148) We applied a 5×6 graphene with 60 carbon atoms in the first principles simulations doped by graphitic, single-pyridinic, triple-pyridinic and pyrrolic N respectively. We considered the reaction mechanism of electro-reduction of CO₂ to CO through the adsorbed intermediates, COOH* and CO* on pristine as well as N-doped graphene (Figure 3.8). Similar intermediates have been proposed for the electroreduction of CO₂ on late transition metals like Au, Pt, and Cu. (144, 146, 148) The corresponding free energy diagram for the lowest energy pathways of CO₂ reduced to CO through this scheme is shown in Figure 3.8a. The overpotential originates from the uphill barrier of the first proton-coupled electron transfer step forming COOH* for pristine graphene, graphitic, triple-pyridinic and single-pyridinic N doped graphene. After adsorption of COOH*, the free-energy pathway becomes thermodynamically downhill for the transfer of the second proton-coupled electron to form adsorbed CO*. The pristine graphene has the highest free energy barrier for the first step of COOH* adsorption which hinders CRR. The CRR activity is, however, enhanced by introducing the electronegative N atoms in the graphitic lattice. The COOH* bonds to N defects at pyridinic and pyrrolic N sites while the positively charged carbon atom adjacent to nitrogen is the active site for graphitic N. The free energy barrier for COOH* adsorption drops dramatically with N defects because of dangling N bonds that binding intermediate COOH* fragment much stronger. Triple-pyridinic N
lowers the barrier of COOH* adsorption step to the most followed by single-pyridinic and graphitic N. Interestingly, COOH* adsorption at a pyrrolic N-defect site is exergonic. However, the release of chemisorbed CO from pyrrolic-N through a non-electrochemical desorption step possesses an energy barrier of ~ 0.6 eV, which is independent of applied voltage.

Figure 3.6 – DFT modeling of electrocatalysis of CO$_2$ on NG. (a) Free energy diagram of electrochemical reduction of CO$_2$ to CO on NG and (b) schematic of N configuration and CO$_2$ reduction pathway.
3.2.4. Experimental synthesized N-doped CNT and graphene for CRR

The activity of NCNTs towards the electrocatalytic reduction of CO$_2$ was evaluated in a full electrochemical cell employing a circulating electrolyte of 0.1 M KHCO$_3$. The cyclic voltammetry (CV) curves of NCNTs acquired in Ar saturated 0.1 M KHCO$_3$ show the onset potential of -0.82 V for hydrogen evolution reaction (HER) which indicates high overpotential (-0.41 V) with reference to the apparent standard cell potential (-0.41 V under pH = 7 for 0.1 M KOH) for HER. The suppression of HER on NCNTs is beneficial for CO$_2$ reduction. The CO starts to be formed with a Faradaic efficiency (FE) of 37% at an applied cell potential as low as -0.70 V which corresponds to an overpotential of -0.18 V with respect to the apparent standard cell potential of -0.52 V for CO$_2$ reduction to CO in the electrolyte of 0.1 M KHCO$_3$. NCNTs display lower onset overpotential and higher correspondent FE of CO than that for Ag nanoparticles (-0.27 V with FE of CO 17%) and Au powder (-0.27 V with FE of CO 12%) under the identical testing condition. This onset overpotential is also lower than that recently reported using carbon nanofibers (-0.23 V) mediated by ionic liquid of EMIM-BF$_4$. The maximum FE of CO reaches around 80% at -0.78 V which also corresponds to a low overpotential of -0.26 V. The achievable maximum FE of CO for NCNTs is comparable to that for Ag nanoparticles and Au powder; however, the overpotential to reach this highest FE of CO is far lower for NCNTs compared to noble metal Ag and Au catalysts, which means more energy efficient for NCNTs than Ag and Au. To reach 80% FE of CO, NCNTs show much lower overpotential than most of the Ag and Au electrodes except oxide-derived Au nanoparticles and ionic liquid mediated Ag powder.
These two cases are distinct from conventional polycrystalline metal catalysts with aqueous electrolyte. Oxide derived Au electrode comprised of 20-40 nm Au nanoparticles exhibits enhanced CO₂ reduction activity compared to polycrystalline Au electrode possibly due to the presence of highly active sites on its grain boundary surfaces as similar as oxide derived Cu electrodes.(152) The enhancement of activity for Ag powder is attributed to the presence of ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) that complexes with the (CO₂)⁻ intermediate to lower the initial reduction barrier.(131)

As a benchmark, we also performed CO₂ reduction on pristine CNT arrays. These CNTs show poor activity towards CO₂ reduction. The formation of CO starts at a cell potential of -1.38 V that is more negative than that for NCNTs. Moreover, the FE of CO is around 3.5% at this potential, much lower than that for NCNT. In addition to CO, formate is detected for CO₂ reduction on CNTs but has a low yield as similar as CO with a FE around 2.0-3.5% in the applied potential range of -1.38 ~ -2.10 V. The effect of trace metal (i.e. Fe in our case) on the catalytic activity towards ORR is an issue under debate. Actually, Fe has been proven to have no activity towards CO₂ reduction, resulting in H₂ evolution of ~100% in Faradaic efficiency.(153) In our case, we have intentionally chosen the CNTs sample containing relatively higher Fe residuals than NCNTs, as evidenced by the higher current density of Fe residual redox peaks in the CV performed in a glassy carbon electrode. The much lower activity of CNTs than NCNTs suggests the active sites are mainly attributed to N-doping rather than the Fe residuals.
Partial current density for CO production ($j_{CO}$) as a function of potential was extracted from data for the constant potential electrolyses (Figure 3.7c). The $j_{CO}$ for NCNTs is one order of magnitude higher than that for CNTs. The huge difference in activity between CNTs and NCNTs indicates the significant role of N dopant playing in the electrocatalysis process. The CO$_2$ reduction kinetics is facilitated as the cell potential sweeps cathodically leading to the increase of $j_{CO}$ for NCNTs. The $j_{CO}$ for NCNTs undergoes a plateau as the cell potential shifts more negatively beyond overpotential -0.41 V, reflecting mass transport limitation of CO$_2$ to the electrodes (Figure 3.7c). The FE of CO decreases after the achievement of mass transport limitation because more electrons are consumed by HER than CO$_2$ reduction reaction.
Figure 3.7 – Performance of NCNTs for selectively electrochemical reduction of CO$_2$ to CO. (a) CVs for NCNTs in Ar and CO$_2$ saturated 0.1 M KHCO$_3$ electrolyte, 50 mV s$^{-1}$. (b) Dependence of FE of CO on applied cell potential during electrocatalysis of CO$_2$ reduction for both NCNTs and CNTs catalysts. (c) Partial current density of CO versus applied cell potential for NCNTs and CNTs catalysts. (d) Stability of performance of NCNTs for CO$_2$ reduction operated at potentiostatic mode of -0.8 V for 10 h. Both current density and FE of CO maintain steady over the duration of test.

We also experimentally tested the performance of N-doped graphene (NG) for CRR. Different NG samples were synthesized under different temperatures with various nitrogen doping. The comparison of catalytic activity towards CO$_2$ reduction among various NG catalysts is shown in Figure 3.8. A high selectivity towards CO production is also observed with other NG catalysts. NG-800 exhibits the highest activity towards CO$_2$ reduction, catalyzing CO formation at the lowest overpotential (-0.19 V) followed by NG-700 (-0.39 V), NG-900 (-0.47) and NG-1000 (-0.67 V). In addition, NG-800 displays a maximum FE for CO ~85% at a low overpotential -0.47 (Figure 3.8a). The same trend is observed for the onset overpotential for HCOO$^-$ production. NG-800 shows the highest FE for HCOO$^-$ among all other NG catalysts (Figure 3.8b). As a benchmark, we also performed CO$_2$ reduction on pristine 3D graphene foam under same conditions. Neither CO nor HCOO$^-$ is detected on a pristine graphene electrode, while exclusive H$_2$ evolution is observed in the same potential range.

In order to understand the correlation between catalytic activity and the type of the N-defects, the trend in maximum FE for CO along with its corresponding potential versus concentrations of different N species in various NG catalysts is
investigated (Figure 3.8c). The maximum FE for CO increases and the corresponding potential shifts anodically as the pyridinic-N content increases, whereas no such a trend is observed for pyrrolic- and graphitic-N. These results suggest pyridinic-N is the most active site for CO$_2$ reduction though the contribution from other N-defects can’t be completely ruled out. The determination of the most active site of pyridinic-N in NG is a further step forward compared to NCNTs where the highly active defect is not easily distinguishable between pyridinic- and graphitic-N due to the coupled effect of curvature or tube diameter.\textsuperscript{(154)}

Figure 3.8 – Comparison of the electrocatalytic activities of nitrogen-doped graphene with doping temperature ranging from 700 to 1000 °C. (a) Faradaic efficiency of CO vs. potential. (b) Faradaic efficiency of HCOO$^-$ vs. potential. (c) Maximum Faradaic efficiency of CO and its corresponding potential versus N functionality content.
3.2.5. Conclusion

In summary, we have demonstrated nitrogen doped carbon nanotubes and graphene as highly active, selective and stable catalysts for electrocatalytic reduction of CO\textsubscript{2} to CO. Compared to noble metals Au and Ag, NCNTs exhibit lower overpotentials to achieve the similar selectivity towards the production of CO. The maximum FE of CO reaches around 80% at a low overpotential of -0.26 V. As a contrast, pristine CNTs and graphene show poor activity and selectivity towards electroreduction of CO\textsubscript{2}. A combination of experimental and theoretical investigations reveals distinct catalytic activity of different N functionalities. The pyridinic-N defects exhibit the highest catalytic activity by lowering the free energy barrier to form adsorbed COOH*, eventually leading to CO formation. Moreover, the suitable binding energy of the key intermediates enables strong COOH adsorption and feasible CO desorption that contributes to the high selectivity towards CO formation. This work demonstrates the directions for future efforts to deliberately incorporate high pyridinic-N content in carbon nanostructures as metal-free electrocatalysts for CO\textsubscript{2} reduction.

3.3. Transition metal disulfides as catalyst in electrochemical oxygen evolution reaction

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3.3.1. Introduction

Electrochemical water splitting to form H\textsubscript{2} and O\textsubscript{2} enabling large scale storage of intermediate energy from renewable sources has triggered intense studies recently.\(^{(155, 156)}\) However, the energy efficiency of water splitting is significantly restricted to the slow kinetics of oxygen evolution reaction (OER) in comparison to hydrogen evolution reaction (HER).\(^{(157, 158)}\) Therefore enormous interest grows towards the development of active and stable catalyst system accelerating the OER by reducing the large overpotential. Noble metal oxides such as IrO\textsubscript{2} and RuO\textsubscript{2} exhibit the best OER activity, but the elemental scarcity and high cost have imposed great constrain on their widespread applications. Enormous research efforts have been devoted to exploit low-cost OER electrocatalysts on the basis of first-row transition metals and their oxides such as cobalt phosphate composites\(^{(159)}\), nickel borate composites\(^{(160)}\), cobalt oxide nanoparticles and thin films as well as mesoporous structure of manganese oxide\(^{(161-163)}\). Other strategies, like making hybridization of different metal catalysts by taking advantage of synergistic metal-metal interactions\(^{(164-170)}\), have been adopted to facilitate the OER activity to a level that is comparable to the benchmark IrO\textsubscript{2} and RuO\textsubscript{2} catalysts in base medium. Perovskites, like Ba\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3-δ}, and SrNb\textsubscript{0.1}Co\textsubscript{0.7}Fe\textsubscript{0.2}O\textsubscript{3-δ} were also reported as an efficient OER catalyst in alkaline electrolyte.\(^{(171, 172)}\) Recently bulk layered double hydroxides (LDH) along with the novel effort of monolayer or ultrathin nanosheets of LDHs greatly boost up the OER activity in alkaline medium.\(^{(173-176)}\) However, from the practical application point of view, the hydrogen production of water splitting in base medium is limited by its
relatively low production rate and the lack of solid electrolyte membrane.(177) Compared to the alkaline electrolysis, acid water splitting implemented in proton exchange membrane electrolysers has distinct advantages such as high efficiency at high current density, the ability to manage fluctuating power inputs, a solid electrolyte, and a fast start up.(178) Harsh acidic and oxidizing conditions at the anode render most of the electrocatalysts inactive or unstable, except for oxides of Ir or Ru.(179, 180) Therefore, exploring earth abundant element based catalysts without compromising the high catalytic performances of OER in acid media is still a great challenge. Manganese oxide was reported as a functionally stable oxygen evolution catalyst but also shows limited activity in acidic solution.(181)

Herein, for the first time, we report the highly electrocatalytic activity toward OER in acid media of two dimensional (2D) transition metal dichalcogenides (TMDs), taking 2H-MoS₂ from group VI semiconducting metal disulphides and 2H/1T-TaS₂ from group V conducting metal disulphides. Liquid phase and lithium intercalation chemistry mediated exfoliation was employed to prepare 2D TMDs nanosheets to enhance the performance. Furthermore, we unravelled the polymorphic dependence of electrocatalytic activity, such as trigonal prismatic 2H versus octahedral 1T phase in TMDs of MoS₂ and TaS₂. Coupled with the well-known excellent electrocatalytic activity toward HER for 2D TMDs(182-184), the performance of OER, as reported here, suggests the potential of these materials as bifunctional catalysts for both anode and cathode reactions in the water splitting process.
3.3.2. MoS$_2$ and TaS$_2$ for electrocatalysis of OER

The electrocatalytic activity toward OER in acid medium (e.g. 0.5 M H$_2$SO$_4$) of the TMD nanosheets loaded on carbon paper was investigated by linear sweep voltammetry (LSV). LSV results show that 1T-MoS$_2$ exhibits the most efficient catalytic performance with the overpotential of 0.42 V to reach the benchmark of current density of 10 mA cm$^{-2}$ (Figure 3.9). In comparison, 1T-TaS$_2$, 2H-MoS$_2$ and 2H-TaS$_2$ need overpotential of 0.45 V, 0.48 V and 0.54 V, respectively, to reach the same current density. The current density obtained from the bare carbon paper substrate shows negligible OER activity suggesting the high catalytic activity originates from the TMD sample itself. The efficiency is still a little worse than the noble metal based oxides IrO$_x$ and one such report in colloidal form with overpotential of ~ 0.39 V at 10 mA cm$^{-2}$ in acid medium(185). But the performance of 1T-MoS$_2$ exceeds some of the benchmark electrocatalysts like Mn oxide (0.54 V) (186), Mn$_3$O$_4$/CoSe$_2$ (0.45 V) (187) or even in close competition with 20 wt% Ir/C (0.38 V) and 20 wt% Ru/C (0.39 V) and Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ perovskite (0.40 V) in alkaline solution (171, 186).

It's worth pointing out that an activation process of catalytic performance was observed for these 2D TMDs during potential cycling between 1.2 and 2.0 V. Figure 3.9b shows the polarization curves of 1T MoS$_2$ sample after different cycles. It is evidently revealing that the catalytic current density at a specific potential increases with the increasing of cycles until saturation comes after 2000 cycles.
Figure 3.9 – Electrochemical performance of 1T and 2H forms of MoS2 and TaS2 nanosheets for OER. (a) iR-corrected polarization curves of MoS2 and TaS2 catalysts and carbon paper in 0.5 M H2SO4 at a scan rate of 5 mV s\(^{-1}\). The benchmark catalyst IrO2 is also included. (b) iR-corrected polarization curves of 1T MoS2 catalyst taken after different number of cycles measured between 1.2 and 2.0 V vs. RHE at 100 mV s\(^{-1}\). (c) The corresponding Tafel plots of polarization curves in (a). (d) Chronopotentiometric curves operated under constant current densities of 10 mA cm\(^{-2}\). The chronopotentiometric curves were recorded after cycling 2000 times between 1.2 and 2.0 V vs. RHE at 100 mV s\(^{-1}\). For each sample the catalyst loading is ~1 mg cm\(^{-2}\).

Two possible 2H MoS\(_2\) and TaS\(_2\) edges—the (10\(\overline{1}\)0) Mo/Ta-edge and (\(\overline{1}010\)) S-edge with 0%, 50%, and 100% sulfur coverage and 1T edges have been considered for the theoretical study as illustrated in Figure 3.10a. Generally OER involves four elemental steps with three adsorbed intermediates \(*\text{OH}, \text{O}^*, \text{*OOH}\)
interacting in the similar way at the surface of catalysts like metals, sulphides, oxides and nitrides (Figure 3.10b).\cite{188, 189} Based on this reaction mechanism, the density functional theory (DFT) calculations reveal that the OER activity of TaS$_2$ and MoS$_2$ comes from edge sites rather than basal plane sites (Table S1 in Supporting Information). We further compared the activity of edge sites, two different types of M-edge (M = Mo or Ta) and S-edge in 2H phase with a variety of sulfur coverages and the edge of 1T phase (only one type of edge in 1T structure). The free energy diagram in Figure 3.10b illustrates the least activation barrier for the 1T phase edges and the most active edge sites containing 50% sulfur coverage in 2H phase. The overpotential originates from overcoming the limiting step barrier of O=O bond formation, which is splitting a second water molecule via a one proton–electron transfer process ($O^* + H_2O \rightarrow ^*OOH + H^+ + e^-$) for most cases, except for S-edge sites of 2H-TaS$_2$, for which the associative step to form oxygen molecule via OOH* (OOH* $\rightarrow ^* + O_2 + H^+ + e^-$) has the largest free energy difference. Using the minimum overpotential at which all elemental reactions become exothermic as a criterion of the electrocatalytic activity, the 1T phase shows higher activity than its correspondent 2H polymorph. The predicted trend of activity follows as: 1T-MoS$_2 >$ 1T-TaS$_2 >$ 2H-MoS$_2 >$ 2H-TaS$_2$, in a good agreement with the experimental observation. Figure 3.10c resents volcano plot, that is, the overpotential versus binding energy difference of $\Delta G_{O^*}^\circ - \Delta G_{OOH^*}^\circ$, which shows the activity of edges of 1T-MoS$_2$ and TaS$_2$ is close to that of manganese oxides and IrO$_2$. 
Figure 3.10 – Mechanistic study of OER on TMDs catalysts. (a) Edge structures of 2H and 1T-MS₂ (b) The reaction pathway of OER on the most active edge sites in acidic media. (c) Volcano plot of overpotential versus the difference in the adsorption energy of O* and OH*. The metal oxides data are adapted from reference (189)

3.3.3. Conclusion

In summary, we have, for the first time, successfully introduced TMD materials like group 6 member MoS₂ and group 5 member TaS₂ as the OER catalysts. These layered materials, exfoliated as nanosheets, exhibit excellent OER
performance in acidic solution. In the series, the best performer 1T MoS$_2$ shows the
catalytic efficiency comparable to the best known IrO$_2$ electrocatalyst. The OER
active sites lie in the edge instead of basal surface sites as DFT calculated. Both
experimental and theoretical results reveal the same trend of activity that 1T
polymorph possesses higher activity than the 2H counterpart. The TMD catalysts
demonstrate moderate stability in harsh acid medium. The study will likely lead to
extensive exploration of TMD layered nanostructures with highly active sites
advancing water splitting process in PEM electrolyser.
Chapter 4

Jellium model - a simplified metal catalyst - fundamentals and applications in CNT growth

4.1. Introduction

4.1.1. Theoretical background

The Jellium model was firstly designed by Kohn and Lang in 1970 as a simplified model for metal clusters.\(^{(190)}\) It is firstly applied to metal clusters by Knight to explain why certain sizes of cluster are more stable and observed as the marked peaks in the mass spectra of Na clusters which demonstrated the electronic shell structure in free alkali clusters.\(^{(191)}\) For clusters of alkali and noble metals, the ionic core does not affect the properties rather than the electronic structure which is governed by the number of valence electrons. In jellium model, the detailed
ionic structure is neglected and the cluster is equalized to a single large atom with uniformly distributed positive charges as background. In this sense, the electronic structure can be calculated using various approximations for the interacting electron gas. The electronic density can be described in terms of single-particle wavefunction.

Starting from quantum many-body problem, the exact Hamiltonian for a neutral cluster consisting of N nuclei with Z electrons each is:

\[
\hat{H} = \sum_{\alpha=1}^{N} \left\{ \frac{p_{\alpha}^2}{2M} + \sum_{i=1}^{Z} \frac{P_{\alpha i}^2}{2m} + \sum_{\beta=1}^{N} \left[ \frac{1}{2} \frac{(Ze)^2}{|R_\alpha - R_\beta|} + \sum_{i=1}^{Z} \frac{Ze^2}{|r_{\beta i} - r_{\alpha}|} + \frac{1}{2} \sum_{j=1}^{Z} \frac{e^2}{|r_{\alpha i} - r_{\beta j}|} \right] \right\}
\]

**Equation 4.1 – Hamiltonian for a neutral cluster consisting of N nuclei with Z electrons each.**

The first approximation is Born-Oppenheimer hypothesis where the dynamics of the nuclei is neglected. The total Hamiltonian is reduced to N interacting ions, and \( \omega \) valence electrons of each atom interacting in the external field \( V_t \) provided by the ions: \( H = H_{\text{ions}} + H_{\text{electrons}} + H_{\text{electron-background}} \). Where,

\[
H_{\text{ions}} = \frac{1}{2} \sum_{\alpha=1}^{N} \sum_{\beta(\neq \alpha)=1}^{N} \frac{(\omega e)^2}{|R_\alpha - R_\beta|}
\]

**Equation 4.2 – Hamiltonian of ions.**
\[ H_{\text{electron}} + H_{\text{electron-background}} = \sum_{i=1}^{\omega N} \left( \frac{p_i^2}{2m} + V_I(r_i) + \frac{1}{2} \sum_{j(\neq i)=1}^{\omega N} \frac{e^2}{|r_i - r_j|} \right) \]

**Equation 4.3 – Hamiltonian of electrons and electrons interacting with external fields.**

The ionic potential \( V_I(r_i) \) is called “pseudopotential” or “effective core potential” and it is a smoothed function which includes the influence of the core electrons. In self-consistent jellium model, the ionized core is treated as a constant positive background with a density in a finite volume. The finite volume of the jellium background can be spherical, ellipsoidal, a plane slab, or arbitrarily deformed.

In spherical jellium for example, the ionic uniform background charge with density \( \rho(r) (=\text{constant}) \) distributes in a sphere with radius \( R_p \). This background charge gives the ionic potential (illustration in Figure 4.1)

\[
V_I(r) = \begin{cases} 
\frac{-\omega N e^2}{2R_p} (3 - \left( \frac{r}{R_p} \right)^2), & r \leq R_p \\
\frac{-\omega N e^2}{r}, & r > R_p 
\end{cases}
\]
Figure 4.1 – The illustration of ionic potential of spherical jellium with radius $R_p$ and density $\rho_i$. The pink curve is $-\frac{\omega N e^2}{r}$, and the purple curve is $-\frac{\omega N e^2}{2R_p} (3 - \left(\frac{r}{R_p}\right)^2)$. So the green curve represents the ionic potential of jellium sphere.

The jellium model calculations so far have been performed within density-functional theory. In density functional theory, the total energy of the cluster is the function of the local electron density $\rho(r)$:

$$E[\rho] = T[\rho] + E_{XC}[\rho] + \int \left\{ V_I(r) \rho(r) + \frac{1}{2} \rho(r) \left[ e^2 \int \frac{\rho(r')}{|r - r'|} d^3 r' \right] \right\} d^3 r + E_I$$

Equation 4.4 – total energy of the cluster in DFT.

$T[\rho]$ is the non-interacting kinetic-energy density and $E_{XC}[\rho]$ is the exchange-correlation energy density. $V_I(r)$ is related to the jellium charge density $\rho_i(r)$ by
\[ V_I(r) = e^2 \int \frac{\rho_I(r')}{|r-r'|} d^3 r'. \] The \( E_I \) is the electrostatic energy associated with the jellium background. It does not depend on the electron density but is included so that \( E[\rho] \) represents the total binding energy of the cluster. The density \( \rho(r) \) must be normalized to the total number \( \omega N \) of the valence electrons. As we mentioned before, in jellium model, the electron density is written in terms of single-particle wavefunction \( \varphi_i(r) \) as \( \rho(r) = \sum_{i=1}^{\omega N} |\varphi_i(r)|^2 \)

\[
T_s[\rho] = \frac{\hbar^2}{2m} \int \left\{ \sum_{i=1}^{\omega N} |\nabla \varphi_i(r)|^2 \right\} d^3 r
\]

**Equation 4.5 – Non-interacting kinetic-energy density in jellium model.**

\[
E_I = \frac{3}{5} \frac{(\omega Ne)^2}{R_p}
\]

**Equation 4.6 – Ionic energy in spherical jellium model.**

The variation of \( E[\rho] \) with respect to \( \varphi_i(r) \) gives the Kohn-Sham equation and can be solved in many DFT codes.

\[
\{ \hat{T} + V_{KS}(r) \} \varphi_i(r) = \varepsilon_i \varphi_i(r);
\]

**Equation 4.7 – The Kohn-Sham equation.**

\[
V_{KS}(r) = V_{XC}[\rho(r)] + V_H[\rho(r)] + V_I(r)
\]
Equation 4.8 – The Kohn-Sham effective potential.

Where $\hat{T}$ is a kinetic-energy, $V_H[\rho(r)]$ is the Hartree potential, $V_I(r)$ is jellium potential, $V_{XC}[\rho(r)] = \frac{\delta}{\delta \rho(r)} E_{XC}[\rho]$. Most applications of the jellium model(192) have been restricted to the local-density approximation (LDA).

As an example, Figure 4.2 shows the calculated self-consistent effective single-particle potential ($V_{KS}$) for lithium, sodium and potassium clusters using jellium LDA scheme and electron occupation of the energy level.(193) In this work, they calculated binding energy showing the discontinuities at certain cluster sizes which originate from the electronic shell filling sequence.

Figure 4.2 – (a) Self-consistent effective potential of jellium sphere with 40 atoms for Li, Na, and K. (b) the electron occupation of energy levels in Na$_{40}$. From reference(193).
This electronic shell structure actually does not require the self-consistent density functional approach. In spherical jellium mode, since the electron density is spherically symmetric, the free electrons confined in such potential well gives the shell structure where the valence electrons fill the degenerate levels. In a spherically symmetric field, the solution for Schrödinger equation for a single-electron wavefunction is written as a product of radial, angular and spin wavefunctions (analogous to that for hydrogen):

$$\varphi_{nlm\sigma} = \frac{1}{r} P_{nl}(r) Y_{lm}(\theta, \phi) X_\sigma$$

**Equation 4.9 – The wavefunction of single-electron in a symmetric potential.**

Where n, l, m and $\sigma$ are the radial, angular momentum, magnetic and spin quantum numbers. For each shell, the radial quantum number $n$ and the angular momentum $l$ are two characteristic values. Figure 4.3 shows the energy level structure for three spherically symmetric wells; and it can be seen that changing the well shape not only changes the relative level spacing, but may even change their ordering. (194)
Figure 4.3 – Energy-level occupations for spherical three-dimensional, harmonic oscillator (left), a square-well (right) and a potential intermediate between the two (middle). The energy-level labels and the total number of states are given. From book of Mayer and Jensen, 1955(194)

In jellium system, the ionic density (jellium density) $\frac{1}{\rho_I} = \frac{4\pi}{3} (r_s a_0)^3 = \frac{\Omega}{N}$, the $r_s$ is the Wigner-Seitz radius measured in the unit of Bohr radius $a_0$, and in spherical jellium model the jellium particle radius is $R_I = r_s N^{1/3}$.

The spherical jellium model is the simplest and reasonable approximation for electronically closed-shell clusters; thus there are limitations in this model. Because of the ignorance of the detailed ionic structure, the limitations of jellium model are
1) the valance electron must be delocalized; 2) the valance electron has an s-wave character which means the binding should be no directional. Therefore, jellium model has been applicable for alkali metals clusters, such as sodium, potassium and heavier metals, and to some extent, the group 11 metals such as copper and silver. More details of the success and failures of the spherical jellium model have been discussed in Brack and de Heer’s reviews.

In past few years, jellium model was generally applied as a theoretical framework for metal clusters to offer their electronic structure, work function, photoionization, ground-state binding energy, the ionization potential, and the dipole polarization. It is a useful tool to connect the properties of large clusters with the bulk and macroscopic surface properties; even though the question of “how many atoms are needed to make a piece of bulk material” is still not clear. The spherical jellium model only works well for those systems with low-density alkali metals. For high-density metals, such as aluminum, it gives negative surface energies. The plain jellium model describes best for sodium and potassium. For smaller clusters (N~20), the local-spin-density approximation gives better quantitative description. The spherical jellium model approximation is only justified for electronically closed-shell clusters. There is Jahn-Teller effect in open-shell clusters where the spherical shape is unstable towards distortion. Therefore, for open-shell clusters, the ellipsoidal Clemenger-Nilsson shell model was developed and should be applied. Recently, more high-level than LDA correlated approaches are developed for jellium model, such as meta-GGA, quantum Monte Carlo to give more accurate surface energies.
4.1.2. Motivation of applied Jellium model in CNT growth

Carbon nanotubes have very promising applications because of their properties.\(^{(205)}\) The properties of CNT depend strongly on its structures characterized by the chiral index \((n, m)\). For example, if \(n = m\), the tube is metallic; if \((n-m)\) is a multiple of three, then the tube is semiconducting with a very small band gap, otherwise the tube is semiconducting. Therefore, controlling the structure during synthesis is a significant step towards the applications. In carbon nanotube growth, catalytic chemical vapor deposition (CCVD) synthesis process is a well-established method to produce large yield of CNT.\(^{(206)}\) The catalytic particles are generally iron-group metals (Fe, Co, Ni)\(^{(207-210)}\), heavy late-transition (Pd, Pt)\(^{(211)}\) and inert coinage metals\(^{(212, 213)}\) (Cu, Ag, Au) and their alloys. The composition, size of the catalyst metal cluster plays an important role in determining tube’s growth, chirality etc. The ultimate goal is to understand the growth mechanism and control the chirality precisely. The vapor-liquid-solid model is a widely accepted mechanism for CNT growth.\(^{(214, 215)}\) The atomistic modeling is essential for understanding the mechanism controlling the growth rate, chirality, length and quality.\(^{(216-218)}\) However, due to the huge timescale discrepancy between atomistic simulation and experimental conditions, the goal for the simulations to converge experiments remains challenging for decades. For instance, in molecular dynamics (MD)\(^{(219, 220)}\) or Monte Carlo simulations\(^{(221)}\), they failed to produce a defect-free and well-defined tube. In DFT simulation, it can informatively provide some insights in catalytic growth from energy point of view\(^{(222, 223)}\) but the atomistic structure of the catalysts is not clear, and not
always known experimentally. In atomistic modeling, the particular surfaces of metal slab(224), step edges(225, 226) or certain size of clusters(227) to fit specific tubes are required. Moreover, the great computational expense in first-principles calculations is the catalyst, while most of the atoms are not actually participated in the catalysis. Therefore, to apply jellium model as a substitute of metal catalysts in studying the growth mechanism is highly desirable because it, on one hand, saves on catalyst computation by reducing number of electrons (by a factor of ~10) but still compatible with quantum-mechanical treatment; on the other hand, the atomistic structure is neglected here so it reduces the degrees of freedom for geometry optimization (by a factor of ~1000). Although the detailed structures of catalyst particle are missing, it still good for revealing robust universal features of the termination effects on sizes, chiral selectivity.

So far, few trials have been made applying jellium model in the study of carbon nanotubes. For example, the contact of tube with metal electrode has been modeled by jellium-nanotube interface to investigate the quantum conductance.(228) Jellium model is not restricted to simulate metals, the jellium approximation has been used for graphite and isolated single-walled nanotubes for charge transfer induced by dimensional changes.(229) The cylindrical jellium-like surface barrier has been utilized for effective interaction near the surface of nanotube to study the image-potential state for single- and multi-walled carbon nanotubes.(230) The jellium model has been applied to study the initial stage of growth for single-walled carbon nanotubes (Figure 4.4). The role and action of the metal catalyst in growth process can be captured successfully by jellium through the
charge transfer between the jellium and the carbon atoms.\textsuperscript{(231)} In CNT growth, there are three stages: nucleation of a carbon “cap-precursor”; “cap-to-tube” transformation and continued growth. In our study, we applied the spherical jellium model to simulate the third stage — the continued growth on metal clusters, to capture the termination effect in determining the defect formation, chiral selectivity and other features in CNT growth.

Figure 4.4 – Example of jellium model applied in initial stage of CNT growth. The random configuration of the C\textsubscript{154} cluster (top) is annealed at 1300 K and slowly cooled down to 0 K in a vacuum (bottom left) and in the jellium medium (bottom right). The open end of the tubular-like structure is marked in red. From reference \textsuperscript{(231)}

Overall, with assistance of jellium model, the goal is to obtain a qualitative description for the microscopic mechanism for the role of metal catalyst in CNT growth with minimum of calculation effort, to demonstrate that jellium model is a useful way for providing reasonable description for catalysts in CNT growth.
4.2. Jellium model applied in CNT growth

4.2.1. The validation for spherical jellium

To validate the spherical jellium model, we first chose the sodium clusters (Na$_1$, Na$_4$, Na$_9$) and the spherical jellium clusters with the same charge density as in sodium bulk and same number of electrons as in sodium clusters (valence electrons only) to calculate the electronic spectra. Figure 4.5 shows the molecular orbital (MO) level for sodium cluster and jellium representation, respectively. For the single atom, jellium can give the same MO levels; for four atoms cluster, the ground state is the spin-triplet state while the spin-singlet is the excited state which is also captured by jellium. From the comparison, although in jellium model the geometry of the cluster is missing, which makes the atomistic representation more precise, the average trends of the properties can be captured by jellium model very well.
Figure 4.5 – The electron spectra of sodium clusters in atomistic and spherical jellium representation. In jellium sphere, the charge density and number of valence electrons are the same as in Na. The red and blue short lines are spin up and spin down energies. Calculations are from V. I. Artyukhov.

4.2.2. The interaction between jellium and CNT precursor- C and C₂

In spherical jellium model, there are two characteristic parameters: one is the number of electrons in the cluster $n_e$ (in neutral clusters, the total ionic charge in jellium $n_i = n_e$) and the radius of the volume per electron $r_s$ called Wigner-Seitz radius measured by Bohr radius $a_0$. The cluster radius $r_p = n_e^{1/3} * r_s$. Various “flavors” of the jellium clusters can be determined by changing these two parameters. The pseudopotential of the metal particle with certain size can be generated based on $n_e$ and $r_s$. (Note: for example the pseudopotential can be generated as a format for Quantum Espresso). Before investigating the interaction between jellium particle and carbon species, we notice that $n_e$ and $r_s$ can be varied independently; therefore, firstly it has to be determined which parameter is more representative in jellium-C interactions. In order to test that, we take two jellium particles with radius 4.5 Å and 4.1 Å; by tuning $n_e$ and $r_s$ they represent same size jellium particles but different jellium “flavors”. The binding energy of single atomic carbon or one carbon dimer with jellium particle can be calculated as

$$E_b = E(\text{Je} + C/C_2) - E(\text{Je}) - E(C/C_2).$$

The number of electrons $n_e$ and density $r_s$ can be used as variables and the result is shown in Figure 4.6. Since $n_e$ as a variable give the similar trend of $E_b$ while $r_s$ can sometimes give reverse trend, it indicates that number of electron is the main parameter than the radius.
Figure 4.6 – The binding energy of carbon monomer and dimer on jellium particles as a function of Wigner-Seitz radius (a) and the number of electrons (b). The solid and empty points represent the jellium particle size $r_p=4.1$ Å and 4.5 Å. The red is for the binding of $C_2$ and black is that of carbon monomer.

After determined the representative parameter in jellium model, we can explore the interactions between jellium particle and carbon species. Is jellium model able to produce the reasonable interaction with carbon species? In terms of interaction strength, what kind of metals can jellium describe? Since tuning the number of electrons may change the “flavor” of jellium, we screen $n_e$ from 20 to 58 and calculate the binding energy of C and $C_2$ on jellium particle with $r_p = 4.5$ Å, shown in Figure 4.7b. The oscillation of the binding energy can be partially explained by plotting the magnetic moment (Figure 4.7a) of pure jellium particles. The magnetic moment shows the shell model behavior with the magic numbers $n_e=20, 34, 40,$ and 58 which have zero magnetism. Those magic numbers correspond to the closed shell structures which have weak interactions with carbon monomer and dimer. Compared with the binding energy of C and $C_2$ on metal
slabs (232) showed in dashed lines; for carbon monomer, $E_b$ on Ag (3.2~3.7 eV) and in bulk Au (3.5 eV) fall into the range of C on jellium, while results on other metals are beyond the scope and thus not shown. For carbon dimer, all metals can be represented by jellium, except for Ni with $E_b = 6.8$ eV (too strong) and Ag, Au with $E_b = 5.8$ eV (too weak), which cannot be well produced by jellium. To summarize, jellium interacts significantly weak with carbon monomer compared to metals; and the interaction with dimer is comparable to most metals.

Figure 4.7 – Changing the number of electrons from 20 to 58 in $r_p = 0.45$ nm jellium particle, (a) the magnetic moment of jellium particle; (b) the binding energy of carbon monomer and dimer on jellium. The dashed lines are the binding energies of C and $C_2$ on metals from reference (232)
In following discussion, we chose the jellium particle with radius of 4.5 Å and 34 electrons as a representative catalyst to investigate other properties which matter in CNT growth. First we examined the binding energy of single carbon atom as a function of Je-C distance which is measured from the center of jellium particle to the center of carbon atoms (Figure 4.8a). The energy minimum is at d~5.1 Å (it means the carbon atom is out of the jellium surface with a height of 0.6 Å) with the binding energy ~ 2 eV/atom. We also tested how the average binding energy changes when more carbon atoms are adsorbed on jellium particle. The configurations of min-energy of electrons on a sphere have been used and the average binding energy per atom is in Figure 4.8b.

**Figure 4.8 – (a) The binding energy of single carbon atom on jellium particle \( r_p = 4.5 \) Å as a function of the distance of C to the center of jellium particle. (b) the average binding energy of separated carbon atoms adsorbed on the surface of jellium particle.**
4.2.3. The interaction between Jellium and carbon nanotubes

After verifying the rationality of jellium models in the interaction with carbon monomer and dimer, next we investigate the binding strength between jellium and short tubes. Considered the achiral tube first, to make a comprehensive comparison with accurate DFT models, Figure 4.9a,b present the binding energies and interface energies of zigzag and armchair tubes on metal clusters and surfaces/steps, respectively, as compiled from references.(227, 232-234) Generally, coinage metals have lower binding energies compared to late-transition metals. Among them, Ag has the lowest binding energies, which originates from its lowest energy position for $d$ bands.(235) Since interface energy is an opposite of binding energy, Ag has the highest interface energy for CNTs, as shown in Figure 4.9b. To efficiently study the CNT growth on jellium particle, we select certain particle of $r_p=4.5$ Å with five jellium “flavors” $n_e = 34, 42, 47, 48, 49$ to study the interaction with carbon fragments. Those numbers have been chosen because the magnetic moments of jellium particle are ranging from zero to maximum, which represent the weak and strong interaction with carbon species. Four representative nanotubes — (5,5), (6,6), (10,0), and (11,0) are selected. The binding energies are summed up in Figure 4.9c. The binding energies for zigzag tubes are notably higher than those for armchair tubes (about 1 eV/atom). The general trend is consistent with DFT calculations for SWNT on metal clusters.(227, 233), Moreover, by comparing the binding and interface energies from jellium models (Figure 4.9c,d) with those from DTF (Figure 4.9a,b), jellium shows similar behaviors as Ag particles. Combined with results for carbon monomer and dimer, jellium can be adopted as a good
simplification for Ag particles. It is consistent with spherical jellium model as mentioned before that since the electrons are distributed evenly in a sphere and the valence electron has an s-wave character with respect to the ionic cores. Therefore the jellium model has the main applicability in the alkali metal and to some extent the group 11 metals such as copper and silver.\(^{(192)}\)

Figure 4.9 – The comparison of the binding energy \(E_b\) and interface energy \(\gamma\) of achiral tube on metals (a) (b) and on jellium with five “flavors” (c) (d). The binding and interface energy for CNT on metal surface and steps are from references \((232, 234)\); the binding energy for CNT on metal clusters are from references \((227, 233)\).
4.2.4. Chiral tubes on Jellium

The structural control and the selectivity of chirality are two goals in CNT growth which have not been achieved completely. In recent years, together with the chirality characterization methods (236), the experimental synthesis in catalytic growth shows a highly chiral-selective growth of carbon nanotubes from monometallic Co catalyst (210), Co nanoparticles (237) or solid W-Co alloy (238). The physical theory can reveal the mechanism with the assistance of atomistic simulation and macroscopic modeling. (216, 222, 239) The combination of tube/catalyst interface thermodynamics with the kinetic growth theory showed that the energetic preference towards achiral versus faster growth kinetics lead to the near-armchair tubes. (240) To understand the termination effects in CNT growth, we extensively investigate chiral tubes on jellium and examine if the growth theory is applicable to jellium model. A series of carbon nanotubes with similar diameters have been considered. In this section, based on the interfacial energies between chiral tube and jellium particle, we will discuss following issues in the application of jellium model: 1) the interface energies of chiral tubes and the CNT-type distribution predicted from jellium model. 2) The tube relaxation on jellium: are the tubes rigid or there are any edge reconstructions of the tube on jellium? 3) The lowest energy configurations for edges: how the kinks distributed at the edge on jellium? 4) If the Klein edge is more energetically favorable than regular edges on jellium, or not.
4.2.4.1. Interface energies of chiral tubes on jellium and CNT-type distribution

A series \((n,m)\) tubes - \((9,0)\), \((9,1)\), \((8,2)\), \((8,3)\), \((7,4)\), \((6,5)\), and \((5,5)\) are selected, their diameters vary from 6.78 Å to 7.71 Å. We thus selected the jellium particles larger than tubes with diameter 9 Å, 10.8 Å and 11.4 Å. We chose magic numbers \(n_e = 34, 58\) and \(68\) with the same density as three representative jellium particles. The tubes are consisted of two hexagonal tall wall with hydrogen passivation at one end. The interface energy per length is calculated as \(\gamma = \frac{\gamma_i}{L} = \frac{[E(Je + tube) - E(Je) - \frac{1}{2} E(double tube)]}{L}\) (\(L\) is the perimeter of the edge); and the result is shown in Figure 4.10. The curve is the fitting of \(\gamma(\chi) = \gamma' \cos(\chi + C) + \delta * 4\sin\chi \frac{\sin(30°-\chi)}{\cos(30°+\chi)}\) from reference \((241)\) for solid-like case; and the dashed line is calculated as \(\gamma(\chi) = 2\gamma_{AC}\sin\chi + 2\gamma_{ZZ}\sin(30° - \chi)\) for liquid-like case\((240, 241)\). The interface energy for zigzag tubes is lower than armchair tubes on clusters in contrast with on metal slabs, which is consistent with previous studies. \((240, 242)\)
Figure 4.10 – The interface energies for chiral tubes on jellium particles with \( d_p = 9 \, \text{Å}, 10.8 \, \text{Å} \) and \( 11.4 \, \text{Å} \). The solid lines are fitted with analytical expression and the dashed line is calculated as \( \gamma(\chi) = 2\gamma_{AC} \sin \chi + 2\gamma_{ZZ} \sin(30^\circ - \chi) \) from reference (241).

The interface energy relates to the probability \( N_{n,m} \) of certain chiral tube (240): \( N(\chi, d) \propto e^{-\pi d \gamma / k_B T} \) and achiral tubes in that sense are favorably to form than chiral tubes. The relative abundance \( A_{n,m} = N_{n,m} R_{n,m} \) depends also on the growth rate \( R(\chi, d) \) which relates to the growth barrier of adding carbon dimers to form a new ring of hexagons. Thus next we considered the energy profile of adding dimers to the edge of tubes. There are no barriers for chiral tubes. For armchair tubes, one dimer has been added each time to form a loop. For zigzag tubes, since the Klein edge is not stable in jellium model which is relaxed into pentagon; we first added three atoms to form a hexagon as a nuclei and added dimers afterwards. The results are shown in Figure 4.11a. Combined with nucleation probability and growth rate, we can estimate the abundance of tubes predicted by jellium model based on
The distribution is in Figure 4.11b and near zigzag tube is highly promoted in spherical jellium model compared with the flat catalyst where the near armchair ones are dominated. The observation of near-zigzag tubes synthesized is also reported experimentally.\(^{(243)}\)

\[\text{Figure 4.11 – (a) The free energy profile during the tube growth of adding new rings of hexagons at the tube’s edges as a function of carbon atoms. (b) The predicted tube distributions based on growth theory.}\]

\[\text{4.2.4.2. Tube relaxation on jellium particle}\]

Since the jellium particle is envisioned as a spherical surface, when the interface with tube formed, what tube’s edge structure looks like? Does the tube act as a whole rigid piece on jellium or the edges would adjust to fit the particle’s size? We fix the tube and only relax jellium particle to fit with the tube. By comparing the interface energies in this case and the one with tube plus jellium full relaxed, the fixed tube has higher interface energies (Figure 4.12a), which indicates that the tube
acts not like a rigid piece but would adjust its edges to fit the jellium particle. The tube opens the end to fit the particle’s size (geometries are in Figure 4.12b).

![Graph and Figure 4.12](image)

**Figure 4.12** – (a) The interface energy for chiral tubes with fully relaxation and fixed tube. (b) the geometries of unfixed and fixed tube on jellium.

### 4.2.4.3. Kinks in tube on jellium

The chiral tubes have various possible edge configurations, which depend to a large extent on the atomic species and shape of its host material. For each chiral angle, when cutting the tube perpendicular to its axis, it forms the shortest edge with kinks separated and evenly spaced. This is the structure we used in calculations of Figure 4.10. Since the kinks can have different positions to form other edge configurations without changing the chirality, simple question is what the lowest energy edge configuration is? In other words, do the kinks prefer to attract or repel each other? We considered two more edge configurations for above tubes, one is all kinks locating next with each other; another is all edges become
zigzag. Figure 4.13 illustrates three edges with (6,4) as an example: (a) is the shortest edge with two kinks separated by four armchair atoms; (b) is the two kinks locating next to each other; (c) is all edges are zigzag.

![Diagram of three edge configurations](image)

**Figure 4.13 – Three typical edge configurations for (6,4) (a) the shortest edge with two kinks separated by four armchair atoms; (b) two kinks locating next to each other with armchair and zigzag edges segregated; (c) all the edges are zigzag which forms the longest edge. Generated from reference (244).**

We calculated the interfacial energies for those three, and type (b) gives up to 3.8 meV/A lower interfacial energies than (a); type (c) gives up to 0.15 eV/A higher than (a). The effective attraction of kinks causes the armchair and zigzag edge segregation to reduce the total energies. This result might explain the off-axis placement of carbon nanotubes on catalyst particles.
4.2.4.4. The Klein edges on jellium

We also tested the Klein edge on jellium since in atomistic DFT simulations, the Klein edge can sometimes be energetically more favorable than regular edges. But on jellium particle, all the Klein edges are reconstructed to form pentagons (Figure 4.14), so the conclusion is Klein edge is not stable on jellium. The reason for that is the interaction between jellium and carbon atoms are much weaker than carbon with metal atoms. Therefore the dangling bonds in Klein edge cannot be stabilized by jellium and the pentagon is energetically preferred.

![Image of Klein edge on jellium](image.png)

**Figure 4.14** – The Klein edge in (10,0) tubes on jellium, after relaxation, the Klein edge reconstructed into pentagon indicating the Klein edge are not stable on jellium.

4.2.1. Defects formation during CNT growth on Jellium

The defect formation is one structural factor limiting the tube growth. The general defects in CNT include a pentagon, a heptagon, the pentagon-heptagon pair (5|7), or the Stone-Wales defect (5|7/7|5). Among the defects, the formation of
pentagon shrinks the tube and if it cannot be healed, it further induces the tube into a cone. The formation of heptagon increases the diameter of the tube and further causes the tube to flare into a horn. A $5|7$ is an edge dislocation core in CNT wall that changes the tube’s chirality.\(^{(223, 245)}\) An illustration for the defect-induced CNT structural change from reference (223) is showed in Figure 4.15. Although the defects can be healed by efficient catalysts such as Fe according to atomistic simulations\(^{(223, 246)}\), quantifying possible mechanisms for defect formation is still crucial. More specifically, does the particle’s size or shape play a role? Does the defect formation correlate to the tube’s chirality or the tube’s diameter?

![Figure 4.15 - Structural transformation by defects. (a) an isolated pentagon turns a (10,0) CNT into a cone shape. (b) a heptagon turns it into a horn. (c) $5|7$ with one orientation changes (10,0) into (9,0) and another orientation (d) changes it into (9,1). From reference (223).](image)

To understand the above issues, we took both near zigzag ((9, 1), (8, 1), (7, 1)), near armchair ((6, 5), (5, 4), (4, 3)) and (8, 4) tubes as examples, creating single
pentagon or heptagon at the edge of tube on jellium, while other side of tubes are passivated by hydrogen. Both defects energetically prefer to form at the kink and pentagon is more favorable than heptagon. Figure 4.16a,b show the energy difference between the inclusion of heptagons and pentagons on two jellium particles with radius of 0.45 and 0.9 nm as a function of chiral angle and the diameter ratio of tube and particle. The correlation between the E(7)-E(5) and the chiral angle is not clear (Figure 4.16a) while this energy difference shows clear trend as a function of the ratio between tube and jellium particle diameters, shown in Figure 4.16b, despite different slopes for different particles. It should be noticed that for larger particle size (d_{tube}/d_{particle} ~ 0.1), the heptagon would be favored. More importantly, it reflects a negative feedback in tube growth. If the pentagon is energetically favored than heptagon, the diameter of the tube decreases, while the energy difference between heptagon and pentagon decreases with increasing possibility of generating a heptagon. When the heptagon generates, the diameter of the tube increases, avoiding the tube closure; and the tube can continue growing.
Figure 4.16 – The energy difference between a heptagon and a pentagon formed at the edge of chiral tubes as function of (a) chiral angle and (b) diameter ratio of tube and the particles. The solid points are with the jellium particle $d_{\text{particle}}=0.9$ nm and hollow symbols are with $d_{\text{particle}}=1.8$ nm. The inset image illustrates the structures we used in the calculation. The right one is for heptagon formed in (5, 4) at $d_{\text{particle}}=0.9$ nm; and the left is for pentagon formed in (5,4) at $d_{\text{particle}}=1.8$ nm.

Another topological defect is 5|7 pairs. The 5|7 prefers to form at the kink and changes the chirality of the tube. There are six orientations of 5|7 pairs; each of them either changes the chirality or the diameter of the tube or both. Figure 4.17 shows the example of six 5|7 orientations in (5,4) tube. For each 5|7 from 1-6, the $(n, m)$ tube changes to $(n, m-1)$ via 5|7-1; $(n+1, m-1)$ via 5|7-2; $(n+1, m)$ via 5|7-3; $(n, m+1)$ via 5|7-4; $(n-1, m+1)$ via 5|7-5; and $(n-1, m)$ via 5|7-6.
Figure 4.17 – (5,4) tube as an example, there are six 5|7 pair orientations. For each orientation, the (5, 4) tube changes to (5, 3) via 1; (6,3) via 2; (6, 4) via 3; (5, 5) via 4; (4, 5) via 5; (4, 4) via 6.

The energy change upon the formation of 5|7 \((E - E_0)\) could be adopted to measure the feasibility of the chiral control. Similarly, which orientation is energetically favorable? Does it correlate to tube’s diameter or chirality? We explored \((E - E_0)\) as a function of either change of chiral angle \((\chi - \chi_0)\) or diameter \((d/d_0)\), shown in Figure 4.18. \(\chi_0\) and \(d_0\) is the original chiral angle and diameter. \(\chi\) and \(d\) is the new chiral angle and diameter after the 5|7 formation. The lowest energy configuration among the six 5|7 orientations is set as \(E_0\). While \((E - E_0)\) oscillates as function of \((\chi - \chi_0)\), it shows monotonic increase as the diameter deviates from the original ones. Therefore, we conclude that the diameter rather than chiral angle change is the governing factor for defects energies.

![Diagram a](image1.png)

![Diagram b](image2.png)

Figure 4.18 – The relative energy of six orientations for 5|7 defects in (5,4); (6,5) and (9,1) as a function of chiral angle and diameter changes. The chiral index shows the value of the new chiral index caused by each 5|7 in the \((n, m)\) tube.
4.3. Computational methods

The density functional calculations were performed with implemented in Quantum Espresso 5.0.3. The kinetic energy cutoff for wavefunction is 30 Ry and the kinetic energy cutoff for charge density is 240 Ry. The Gaussian smearing with 5.D-4 Ry spreading has been applied. The self-consistent convergence is 1.D-7 Ry. For each calculation, the vacuum space has been set around 10 Å to eliminate the interaction of periodic images of the system.

4.4. Conclusion

In this chapter, we reviewed the jellium model from its theoretical development for metal clusters and the attempts to apply it into CNT growth. We utilized the spherical jellium model as a virtual catalyst particle to simulate CNT growth. This efficient “substitute” for fully-atomistic model replaces the particle with a uniformly charged sphere and electron gas. It saves computation resources without losing the feature of catalyst particle. We validated the jellium model and found that it behaves like Ag particle in the interactions with carbon species. We further verified the classical growth theory and studied the termination effect for defects and chiral selectivity in CNT growth.
References