On the Mechanics of 2-Dimensional Carbon Allotropes

by

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Abstract

This thesis reviews the progress leading to the modern picture of 2-dimensional carbon materials, while providing new contributions into the mechanics and failure of the graphyne family of materials. A first original contribution involves a discussion of material failure across the graphyne family and discussion of a proposed spring abstraction for these materials under mechanical loading. A second contribution is the contrast of these behaviors with graphene and the implications for proposed applications. We apply the mathematical framework of category theory to articulate the precise relation between structure and mechanics of a microscopic system in a macroscopic model domain, by maintaining the chosen molecular properties across a multitude of length scales, from the nanoscale to the continuum scale. The process demonstrates how it becomes possible to 'protoype a model', as category theory enables us to maintain certain information across disparate fields of study, distinct scales, or physical realizations of an abstract system. This method can be thought of as a prototyped model in which a behavior is brought to a different realization as a case study, we use large-scale multi-material printing to examine the scaling of the Young’s modulus of a particular family 2-D carbon allotropes at the macroscale and validate the printed model using experimental testing. The resulting hand-held materials can be examined more readily and yield insights beyond those available in purely digital representations which is shown through a twisting analysis.

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List of Journal Publications

I am the author of all work presented in this thesis. Research was conducted as a graduate student of the Department of Mechanical Engineering Department. Parts of the work has been, or are in the process of being, contributions to the following publications (chronological):

Chapter 1: Introduction and Motivation

A research project synthesizing 3-D printing, computational nanomaterial science, and category theory may not have been possible decades ago. Computers have empowered researchers in immeasurable ways, and it is clear that they will remain a centerpiece of research and development for the foreseeable future. Therefore it is not surprising that in the fourth fiscal quarter of 2013 Apple, Microsoft and Google made up 3 out of the top 4 companies as ranked by market capital. These companies have grown through increased demand for computational technologies. Researchers have reaped the benefit of this growth powered both by faster and a larger quantity of resources combined with the Internet’s capacity for massive online sharing of findings. Formalized efforts in this regard have been made in the development of open source code such as the GNU General Public License, which allows users “the four essential freedoms”: to run the program, to change the program in source code form, to redistribute exact copies, and, finally, to distribute modified versions. One can imagine the utility of this for tasks that are done by large groups of users such as text processing, security, and basic mathematical operations. For scientists GNU licenses present an opportunity to share and use the progress of peers more efficiently than is possible by just reading methods sections of academic papers.

This rapid sharing has diminished many barriers that previously existed between fields. With regular collaboration across fields it becomes clear that new tools may be required to facilitate communication. This study will discuss how category theory can be used to take the results of molecular simulation and implement them in the field of additive manufacturing. This master’s thesis makes contributions in bringing together three modern, exciting fields of research: molecular simulation, category theory, and 3-D printing. This is written on the premise that for the material science community to grow optimally, it must make optimal use of available tools, regardless of the disciplines in which they classically fall.
1.1 Introduction

1.1.1 A Computational Society

Computers have reshaped how our world interprets, processes, and shares information. Technological advancement thrives on the dynamics of information. The scientific community is now able to explore questions at increasingly rapid rates. Although this affects various aspects of everyday life, as scientists these effects may be the most transparent. With predictive modeling growing ever more prevalent, we become able to complement experiments and test hypotheses at unprecedented rates.

During World War II, top mathematicians and physicists from the allies congregated in Los Alamos New Mexico to create the first weaponized critical assembly of radiological materials. The development of nuclear weapons through the Manhattan Project brought computers to the forefront as Nicolas Metropolis showed the power of multiple simple calculations on a computer to complement existing theory, and in turn invented the metropolis algorithm that is the basis for the Monte Carlo method. The Manhattan Project is an early example of how computation can accelerate the results of experiments to solve a previously unresolved issue on a seemingly impossible deadline. The work was still groundbreaking when it was declassified almost five years later. This accomplishment indicated that computers would have an increasing role in experimental science. This study elucidates and utilizes aspects of this interplay and explains how a computational model can be translated to a physical realization.

1.1.2 Increasingly Smarter Tools

Equal in significance to data-sharing is the rate at which computers have accelerated in recent years. Computers originally consisted of vacuum tubes, which left much to be desired in terms of utility. A lack of miniaturization made it somewhat impossible to imagine computers distributed throughout academic institutions, let alone having personal computers. Nonetheless, these preliminary computers were useful to many and sped up calculations midway through the 20th century.
In more recent years there has been an emergence of GPU’s and massively parallel architectures which speed up the calculations we perform, allowing progress to be made at increasingly higher rates. GPU’s have received great attention due to increased interest in video games and entertainment. Driving a monitor is not a task that requires particular elegance rather it takes many very simple calculations. Thus when a GPU states that it has x-thousand cores, these cores are quite different from those found in CPUs. They are made for a specific purpose and use floating point operation. Luckily for computational scientists, many calculations are based on simple operations and thus these massively parallel architectures are finding their way into the work of many.

1.1.3 The Role of the Scientist

It becomes clear that the role of the human in research is forever changing. Just 100 years ago, we were still using slide rules, and rudimentary adding machines. In the current era, many computational operations are standardized and can be run without any input by the user. In the extreme case of the purely Bayesian framework, one requires no prior understanding of a problem but merely allows the machine to crunch numbers. Additionally, the Internet has allowed for individuals to be able to share their code and thus the work of others can be at the scientist’s fingertips with a mere download. LAMMPS, the Large-scale Atomistic/Molecular Massively Parallel Simulator used in this thesis, is a great example of the fruits of code sharing. It seems that the place for the user is to be the conductor of the symphony of tools and to steer them towards a problem in need of solving. Furthermore, there is a required mastery and knowledge of the capabilities of the tools available and how they connect with what is required for a given problem. Finally, a scientist must be able to see what is missing and assess how his or her methods can best be used to bridge any such gap. This is particularly true in the field of computational material science.

1.1.4 Computational Material Science
There are many fields of science and engineering that rely on a few fundamental equations, where the work lies in the means of solving them. Paul Dirac described similar phenomena in a paper entitled “Quantum Mechanics of Many-Electron Systems.”

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of a complex atomic systems without too much computation”

To computational scientists this quote serves as both a warning and an opportunity. The warning lies in tacking the word “well” onto the end. Computational material scientists typically use numerical methods to solve analytical representations and answer fundamental questions about a complex system. For material scientists these approaches can be thought of in two fundamentally different ways, for diagnostics or for design. Diagnostics are more concerned with realizing what exists and design inspires the creation of new materials. The laws that are used and developed arise from the same fundamental physics and thus the tools are the same. As this falls into engineering as much as it does science, it is important to recognize that results trump elegance. It becomes an issue of finding the right tool for the right job. For computational material scientists, the limiting factor is often computational time, and a means to get around that limitation is to embrace the “multi-scale material design paradigm.”

1.1.4 The multi-scale material design paradigm

If told that the Schrödinger Equation can describe everything in the universe, one might consider entering it into a machine and beginning to design materials. But it would be instantly apparent that with all the computational resources in the world, one could not design even a human cell with adequate resolution, let alone a macroscopic organism. Only the simplest systems can be modeled using direct solvation of the Schroedinger equation and in all situations, simplifications and approximations must be made. One
must ask oneself, "What does the structure we want to design require?" And secondly, "What tools must we have to properly represent this structure?" There exists an appropriate tool at each length scale both for experiments and simulations. Figure 1 is a pictorial representation of this paradigm for modeling.

**Figure 1: Multi-Scale Modeling Diagram:** At the smallest scale, that of Angstroms, we see reliance on quantum mechanical methods such as density functional theory and quantum Monte Carlo. As we increase we can access in the nanometers both reactive and non-reactive molecular dynamics. Between the 100's of nanometers and continuum are meso-scale models, which consist of coarse-grained molecular simulations. Figure reprinted from [1], copyright © 2009, with permission from the Nature Publishing Group.

In Figure 1 we see that at the ends of the spectrum are quantum mechanical methods such as quantum Monte Carlo, a direct Monte Carlo sampling of the Schrödinger equation. It should be noted that there are now also finite-element approaches to directly solving the Schrödinger Equation. Additionally there is density functional theory, which consists of a mean-field approximation to making the equations more tractable. If we skip ahead to the micron/meter length scale there exists continuum methods. These
methods, which see no limit in their scaling up, as it is simply a Taylor expansion of the laws of continuum mechanics. There exist both challenges and opportunities at the scales between the extremes. There exists a similar picture for experiments as depicted in Figure 2.

**Figure 2: Multi-Scale Diagram for Experiments:** This diagram displaces the corresponding diagram for the length scales accessible by various experimental techniques. Additional color coating to label whether the technique is to measure thermal, structural, chemical, or mechanical information.

Similar to computational models, experiments contain similar models that are required to obtain useful information from measurements.

### 1.2 Motivation

As stated above, the world is able to make, create, and share knowledge at increasing rates. This is particularly pronounced in the material science community. New materials are often discovered by experiment and by simulation. It is necessary to communicate these findings in such a way that the entire community can know of their existence and begin to refine the material in question.
1.2.1 Design New Materials

For the computational material scientist there exists a unique magnitude of freedom and in turn a unique magnitude of responsibility. Anyone can make a model and suggest that they have created a material but it is the role of the material scientist to both identify a context for their new material and make an educated assessment of the potential success it will have in context. To do this, one grounds oneself in experimental data to form a representative model. Initial diagnostic modeling is used to identify mechanisms. Once mechanisms are identified, one can perform a sort of optimization in which these mechanisms are magnified by manipulating the properties of the material from which they derive. Following this, it is then the job of an experimentalist to refine the findings of the modeler and test claims through experimentation. During experimentation new discoveries and information emerge, which are further tools to the modeler. And the cycle continues. The cycle is depicted in Figure 3.

**Figure 3:** Multi-Scale Design Paradigm: The methodology of a multi-scale material designer. There exists a feedback loop in which experiments inspire models, which can be converted into modified models. These modified models are used to inspire new experiments to evaluate improved properties.
1.2.2 Maximize Impact of Findings

Web of Science, Scopus, and other organizations are interested in linking scientists such that they can optimally build off one another’s work. Certainly, the concept of a journal is not a new thing, but the idea that one can so simply search so many materials allows scientists to build off of the work of others as efficiently as possible.

1.2.3 Scope of Document

Though the original contributions of this master’s thesis fit into a more specific scope of 2-dimensional carbon mechanics and the failure of 2-dimensional carbon, there also exists a contribution towards a unifying narrative of graphene science both in the evolution of understanding the material itself as well as in the tools that describe graphene. Additionally, this work touches on the unique nature of graphene that makes for an inherently different scientific approach.
Chapter 2 Background

2.1 Introduction to Graphene

Historically, there are examples of single materials that enable technologies that truly advance civilization. Europe saw its bronze age around 2000 BC and in which bronze, an alloy of copper and tin, enabled technologies from armor in battle to sustainable city plumbing. A similar shift was seen when iron was invented in which those who had it held significant advantage over civilizations that did not. The invention of Roman Concrete enabled the construction of the great Roman Empire and artifacts that can still be seen today. Many have said that in recent history we have and continue to witness the Silicon Age as computers have become intertwined with nearly all facets of daily life. It is the new materials that lay at the centerpiece of these grand societal shifts. Aware of this phenomenon, there is great effort in material science to create and understand such materials. Furthermore there is great desire to advance the rate at which applications are realized after discovery. A perfect example of this is graphene, which has been arguably the most speculated material in recent history. Since its initial extraction in 2004, this material has lead to a multitude of applications in only ten years. Now we will discuss briefly how this came to pass.

2.1.1 The “Rise” of Graphene

Graphene has been a material of great interest for the past ten years and has seen sudden and increasing interest behind it. Since its first prediction as early as the 1940’s to modern day, the development of the modern picture of graphene has been complex and contains many facets in all realms of material science. Figure 4 is a timeline of major events in the opinion of this author.
The interest in such a material is unprecedented and has been deemed, the “rise of graphene.” To understand the origin of this excitement, one must go back decades. In 1947 Wallace stated that there existed in a single graphite sheet a zero-band gap for the x-y plane using simple argument through symmetry. At the time this was interesting from an academic standpoint but without an example of an isolated low dimension carbon, the findings here could not be implemented, that is until discovery of a peculiar spherical molecule known as the buckyball.

Before graphene engineering, there was already great interest in the creation of new low-dimensional carbon materials. In 1985 Kroto et al. published a paper entitled “C-60 – Buckminsterfullerene”, more commonly known as a buckyball. This molecule was the first of its kind in that with 60 atoms, it is a massive molecule; it was still confined to a spherical shell. A large pristine material occupying the surface of a sphere was the first material of its kind. The buckyball is depicted in Figure 5.
These buckyballs feature 60 carbon atoms and were the first molecule discovered in which the carbon occupied a single surface which in a sense was a foreshadowing of graphene.

The fascination of the zero-band gap in two-dimensional graphite arose from its symmetry and low-dimensionality. The creation of this material exposed that low dimensional carbon was not only stable but relatively easy to synthesize. In my opinion, this can be argued as the birth of modern carbon. Let us now briefly recap how we reached the current day. Kroto’s paper has been cited nearly 12000 times making it truly one of the legendary papers in modern history. One highlight after this included the formation of the bucktubes which, as verified by Transmission Electron Microscopy (TEM) bared a similar structure to buckyballs but extended beyond a radial symmetric and approached the shape of a tube, similar to what would be seen in years to come.

After the age of buckyballs, carbon emerged in other states of matter building of this initial geometry. Dresselhaus et al. postulated that from a fractional fullerene, one could nucleate a tube with hexagonal basis, which would be capped on the other end by a partial fullerene. This bares interest in that it allows a stable 3-dimensional carbon structure that is not a buckball. Buckyballs or C60 carbon were first synthesized in Potentially more interesting is the fact that the pseudo 2-D nature of this leads to very interesting effects involving the band-gap. More work was done involving the chirality.
This structure naturally emerges from hexagonal symmetry and creates a material without residual stresses and is stable. It became apparent that carbonic materials were a playground for relatively simple formulas to reach engineering and became a playground for state of the art solid-state physics.

2.1.3 The Age of Graphene

The past two decades have seen an increased interest in low-dimensional carbon materials. In the 1990’s carbon nanotubes were greatly studied for their remarkable electronic properties which displayed how dramatically the electronic structure varies with atomic arrangement. More recently, the field has been dominated by applications for graphene. Initially motivated its electronic structure, graphene has been studied also for its unmatched optical, thermal, and mechanical performance. Although initially successfully isolated less than a decade ago, the synthesis of graphene has since become somewhat routine and large-scale fabrication has enabled industrial applications.

2.1.4 Graph-yne, Carbyne, and Heterogeneous Bond-Order Carbonic Solids

Similarly, additional two-dimensional carbon allotropes have emerged and invoke remarkable properties of their own. Following the story of graphene these novel materials may too reach large-scale fabrication in a field in which theory and fabrication can be separated by less than a decade. Recent reports of manufacturing of such new materials along with the technological implications of various new carbon allotropes greatly motivates an expedition of this process.
Receiving particular interest is the material of graphdiyne due to its recent fabrication\textsuperscript{17}. Graphdiyne is a member of the graphyne family and is the primary subject of this thesis. This family of allotropes has been categorized by Hayley et al.\textsuperscript{18}. Graphynes often contain of aromatics, the building blocks of graphene, but these differ by the presence of carbyne-like chains. (\textbf{Figure 6}). Of particular interest has been graphdiyne, one of the few graphynes that was successfully synthesized\textsuperscript{17,19}. Ivanovskii provides a review of current progress on these materials\textsuperscript{20}. These carbyne like chains are sp\textsuperscript{1}-hybridization acetylene, which by definition contains an alternating single-triple bond structure (\textbf{Figure 6}). \textbf{Figure 6} shows the geometry of a larger crystal of graphdiyne. The development and study of graphynes have been motivated by various electronic properties, which include direction-dependent Dirac cones\textsuperscript{21}. Graphdiyne has been shown to exhibit size dependent band gaps\textsuperscript{22}. Beyond electronics, graphynes featuring a natural porosity which permits filtering applications without having to sacrifice chemical stability to enable pores\textsuperscript{23}. Graphdiyne has also been shown as a potential candidate for lithium storage\textsuperscript{24}, presenting many other opportunities. These materials allow for engineering with pristine variations rather than the doping of graphene that usually consists of adding defects, which has been shown to be controllable experimentally\textsuperscript{25}. 

\textbf{Figure 6}: Extended Graphyne Geometries: This depicts the geometries explored in this thesis. The symmetries of these materials is apparent as is the relative decrease in void fraction.
2.2 Introduction to category theory

Category theory was developed as an effort to formalize the language of mathematics and make connections between seemingly disparate fields of mathematics. The approach was developed in part by members of the field of algebraic topology as an effort to harness the power of algebra to solve geometric problems. Since this time, various fields, both within mathematics (algebraic geometry, representation theory) and out (computer science, linguistics, physics) have benefitted from the power of these tools.

Mathematics is the language of formal reasoning. The extent to which a topic has been formalized mathematically is the extent to which it has been scrubbed of the specifics in which it was observed, leaving only the form, which is to be analyzed. For example population growth may be modeled by a differential equation, but handing the ODE off to a computer, which takes no account of the population model, requires the mathematical abstraction of form from content. That is, by abstracting away from the specifics, a more general theory can be applied. Moreover, the similarities between different models, e.g. the logistic curve found in constrained population growth and that found in the adoption of new technologies, serve as metaphors for human reasoning, giving rise to a kind of cross-pollination between disciplines.

Mathematics has provided such formal systems for reasoning about the physical world. The problem are looking to avoid is relates closer to information: in the modern era of big data and information overload, how do we capture the conceptual core of a model in such a way that others can receive the communication and faithfully recreate it in another lab, another experimental context, or even another discipline?

This issue has been felt acutely in mathematics for many years. The process of distilling essential features is not only useful in going from reality to abstraction, but between different abstractions. For example, as mentioned above, the mathematical fields of algebra (the study of multivariable equations) and topology (the study of multi-dimensional shapes) are very different domains of abstraction, but it was found that
algebraic invariants are incredibly powerful tools for discerning differences and similarities in topological spaces. Similarly, algebra can be made geometric, allowing the human visual system to play a role in finding solutions to seemingly intractable syntactic problems. Only if the translation captures the essential features of the algebra in the geometry can the geometry be of any use. This is the value proposition of category theory.

These procedures for transferring problems and solutions between fields turned out to be quite valuable, giving insights to people like Henri Poincare, who used such a rigorous mapping between topology and algebra to formulate a problem which took a century to solve. However, the rate at which such mappings could be made was drastically increased when, in the 1940s, a new mathematical field called category theory was invented. Its purpose was to formalize the very notion of mathematical domain and the very notion of rigorous mapping. Indeed, the domains of topology and algebra were each formalized as a category, and Poincare's fundamental group operation was formalized as a functor between them.

2.3 Additive Manufacturing for Material Scientists

2.3.1 Introduction

Although it seemed futuristic and long from now as little as ten years ago, it is hard to find a journal that does not feature some story on a new capability of 3-D printers. In May 2014 Wen et al. showed that through 3-D printing one can create a material that is in some ways indistinguishable from shark-skin. It is because of the inherent and ever improving flexibility that has leads both industry and consumers are fascinated and eager to know more of these technologies. It seems that much like computers, 3-D printers will maintain as an important and integral part of everyday consumer life.
Engineers have had a different experience in additive manufacturing. On the one hand, 3-D printers make it easier to prototype designs and make it capable to build pieces that even the best machining will have troubles with. Engineers are also aware of the inherent limitations both in capability and material choice. There also exists another limit, which is coupled between material choice and printing capability. Printing capability refers to spatial limitations and minimum feature size. The most common materials to print are plastics and therefore often those materials quoted as printed with the best specifications. When moving away form plastics, there are capabilities for printing with other materials such as ceramics and metals but they are not nearly as common for lower-end expense printers. In this section I will briefly discuss the history, path to and current status, as well as those technologies appearing on the horizon. Following this I will discuss why materials scientists both need and are needed in the development of 3-D printers.

2.3.2 The Change that 3-D Printers Bring

There are many products in the past that could have been 3-D printed with modern technology. Consider Barbie, kitchen utensils, or lawn tools, all of these could have been produced using 3-D printers but were certainly not. This points out something that must be put succinctly and bluntly which is that 3-D printing does not necessarily make new things but rather offers versatility in production. The industrial revolution brought forth several machines capable of cutting, forging, casting, molding, and other processes that only to a skilled eye would appear different than 3-D printing. Below is a table of modern manufacturing tools:

<table>
<thead>
<tr>
<th>Tool</th>
<th>Description</th>
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What separates 3-D printing is that to change a component is as simple as changing the input while the tool can stay the same. Often 3-D printers are designed to figure out how to carry out the differences and complexities such as tool paths need not be modified. But before 3-D printing what were the technologies capable of such versatility.
Chapter 3 Methods

3.1 Introduction

3.2.1 Molecular Simulation

Molecular simulation involves simulating interactions between collections of atoms using interactions that are derived and inspired from quantum mechanics. Although there are many different methods that are discussed in the next section, in this section we will discuss molecular dynamics, as it is the primary tool.

3.2.2 Molecular Dynamics Fundamentals: Movement

The formulation of molecular dynamics begins with classical mechanics. Newton’s second law of motion relates a force to a mass and acceleration:

\[
\frac{d^2 r_i(t)}{dt^2} = a_i = \frac{F_i}{m}
\]

In the context of molecular dynamics the above equation is still true but the objects that we are considering are often atoms or small groups of atoms. The force is derived from quantum mechanics, which includes contributions of effects that are not seen at continuum. Empirical force fields are the method to calculate a force between the objects of our system. With the force and the mass is given, the acceleration can then be calculated. The next step is using this information to advance the simulation in time. To use this we use a Taylor expansion of the classical equations of motion. They are formulated in the following:
\[ r_i(t_0 + \Delta t) = r_i(t_0) - r_i(t - \Delta t) + \Delta t^2 \frac{d^2 r_i(t)}{dt^2} \]

Now the only missing variable is that of velocity. To understand where this arises we must do a quick review of statistical physics. Temperature is the manifestation of the motions of particles. These velocities follow a Maxwell-Boltzmann distribution for various temperatures, which is depicted in Figure 7.

**Figure 7: Maxwell Boltzmann distributions for various temperatures:** Note that as the temperature is increased, the distribution and average of the distribution are shifted and the shape is broadened. One can imagine that this trend increases as temperature is decreased velocity profile approaches that of a delta function.

As the temperature is increased, there is a broadening of velocities and at low temperatures the distribution approaches the shape similar to a delta function. In any case, there is something called a thermostat which is a program that enforces the statistics.
of the above distribution within the simulation. The basic algorithm is to rescale using the velocities after a given number of time steps. If a system is in equilibrium and the system is modeled well, the temperature should be maintained naturally. A good modeler must also be careful as these thermostats can cause fictitious transitions in non-equilibrium phenomena. Imagine a crack propagating; certainly there is an increased velocity at the crack tip relative to the temperature. Any rescaling of this velocity will effectively reduce the fracture energy of the propagation and this must be taken into account when constructing a model.

3.2.3 Molecular Dynamics Fundamentals: Force Calculation

Although there exists complexity in deciding an integration scheme, it arguable pales in comparison to that associated with force-field selection. Force-fields look at geometric ensembles of particles and use this to calculate the forces between them. Some force-fields are simple and handle only simple pairwise interactions meaning there is a contribution of forces between each set of two atoms but none more complex. We will now discuss these potentials in order of increased complexity. The Lennard-Jones interaction is the simplest and potentially most common potential used:

\[ V_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]

The above captures the essential features of the energy landscape needed to constitute a molecular interaction. In the brackets, the left term describes the repulsion felt when the nuclei are close where the second term dictates the attraction felt at long range. Therefore the potential has the following shape:
Figure 8: Energy Landscape of Lennard-Jones potential: Up to equilibrium spacing, the force is negative representing the repulsion between two nuclei. In contrast beyond equilibrium spacing atoms experience long range attraction. At some far distance attraction is negligible and usually not included. Beyond a certain distance the interaction of particles is negligible and a cutoff is applied to conserve calculation time. There are many different force fields that are developed for specific types of materials. Potentially the most abundant arsenal of potentials is that for proteins. For proteins there exists CHARMM\textsuperscript{27}, AMBER\textsuperscript{28} and many other force fields. Although these are capable of modeling the carbon-carbon bonds found in graphene, they are not necessarily capable of capturing all effects associated with the ever-changing bond-order and even bond rupture found in these systems. There exist potentials designed specifically for this purpose. To be able to model these effects, the dominant two potentials are those of AIREBO\textsuperscript{29} and ReaxFF\textsuperscript{30}. ReaxFF calculates the bond-order of the system, which is found from the following equation:

\[ BO'_{ij} = \exp [p_{bo,1} \cdot \left( \frac{r_{ij}}{r_0} \right)^{p_{bo,2}}] + \exp [p_{bo,3} \cdot \left( \frac{r_{ij}}{r_0} \right)^{p_{bo,4}}] + \exp [p_{bo,5} \cdot \left( \frac{r_{ij}}{r_0} \right)^{p_{bo,6}}] \]

The force field then uses that information to calculate the energy associated with each bond:
\[ E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \]

This potential incorporates visibly more information and performs a more precise description of the energy landscape in the systems it describes. If we go term by term through the equation above we can begin to understand how this constructs a complete picture of the energy landscape of carbon structures. \( E_{\text{bond}} \) represents the energy stored in a given bond and is a function of the bond order. \( E_{\text{over}} \) and \( E_{\text{under}} \) are used to address respective over and under coordination. \( E_{\text{val}}, E_{\text{pen}}, E_{\text{tors}} \) include the energies associated with the valence and torsion energy in the bond where there also exists a penalty function as well. Finally the last three terms describe conjugated, van der Waals and cumblic interactions. The complex numerical landscape that this many variables creates brings a need to tread lightly when working with this. The functional above is trained to energies from density functional theory simulations to gain values for the parameters. It is important to know what the training sets were for a particular flavor of ReaxFF to guarantee good results.

We should briefly discuss the treatment of charges within ReaxFF. Charge equilibration is performed by a program known as QEq\textsuperscript{31}. Especially in the case of broken bonds, it is important to have an accurate picture of where the electrons are in a given system. QEq is a program fit to known charge distributions for various systems. When a configuration is generated, QEq is called to calculate the charge on each of the atoms. This value is then used in the calculation of forces described above. With a force-field and integration scheme, we can now simulate ensembles of atoms at various temperatures and pressures.

3.2.4 Mechanics in Molecular Dynamics

Although we previously discussed that temperature is a statistical phenomenon we will give now a brief background into statistical thermodynamics and how it empowers the molecular modeler to derive valuable mechanical information. We follow from Buehler
We can define the Helmholtz free energy as $F$:

$$F = U - TS$$

If we now define the free energy per volume as $\psi$ and strain (a deformation) as $\varepsilon$ we can define stress as:

$$\sigma = \frac{\partial \psi}{\partial \varepsilon}$$

The final tool needed is implementation of the Cauchy-Born rule to describe that the above relation can be extended to a continuum strain.\textsuperscript{32}

### 3.2.5 Modeling Graphene and other 2-Dimensional Carbon by Molecular Dynamics

As stated above, ReaxFF has shown effective and accurate in the modeling of graphene. It should be briefly discussed the other methods by which one can study graphene which includes; other empirical interatomic potentials, full-density functional theory modeling, and coarse-grained methods. Figure 9 is a table of the different interatomic potentials and their advantages and disadvantages in modeling carbon.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
</table>
| ReaxFF    | • Capable of accurately modeling systems involving (C,H,O,N,S, and Si)  
• Able to model the breaking of bonds | • Computationally expensive which limits system sizes to 1000’s of atoms and simulation times $< 1$ nS  
• Complexity of potential often causes false convergence during minimizations  
• Systems deviating from training set can give false results |
| AIREBO    | • Capable of accurately modeling systems involving C and H  
• Accurately models change of bond order and therefore can be used in systems in which bonds are breaking | • Only able to model systems involving C and H  
• Relatively computationally expensive when compared to simpler potentials |
Relative simplicity of potential allows for rapid simulation and more accuracy in minimization

| Tersoff | • Limited to systems involving carbon  
• Simplicity of potential is considerably faster than ReaxFF or AIREBO and approaches that of Lennard-Jones | • Cannot model systems in which bonds are broken  
• Cannot model systems involving multiple species  
• As bonds are deformed, accuracy of potential diminishes |

**Figure 9: Table comparing various carbon interatomic potentials for modelling graphene:** We make a brief list of advantages and limitations of the ReaxFF, AIREBO, and Tersoff interatomic potentials. Such tabulations are helpful in determining the force-field necessary for a given simulation.

It should be mentioned that the covalent nature of graphene has made it a perfect candidate for modeling using tight-binding. Tight-binding uses a superposition of wave-functions to describe the different electronic interactions. Covalence limits the number of interacting electrons and therefore simplifies the calculation. Simplicity equals speed and thus graphene can be modeled relatively quickly using tight-binding. This is still not fast enough to perform large systems for mechanical testing which is why we choose to use empirical potentials. Nonetheless P.R. Wallace utilized tight-binding in 1947 in a work entitled “The Band Theory of Graphite” which contains nearly 3000 citations. This paper showed with relatively simply operations that the band structure of a 2-dimensional sheet of graphite had the interesting behaviors at the band-edge that are seen in modern graphene. With the extraction graphene as a 2-dimensional material many years on the horizon, this work was sampling discussing the band gap of graphite in its classical, bulk, 3-D context.

### 3.2.5 Sample Geometry Generation

As a means of creating the system geometries a contribution of this thesis was a script that can generate geometries of graphene, the graphynes, and even add cracks to the various systems. The user inputs a number of tessellations of the unit cell in the x-direction and the number of rows of unit cells in the y-direction. A pristine geometry
obeys the user inputs can be created. Following this, the user specifies the dimensions of the crack as a percentage of the width and height of the pristine sample. After this occurs, the resulting material is a cracked un-passivated carbon structure. The script contains information from prior simulations as to which structures need to be passivated in order to have a stable and therefore meaningful mechanical simulation. This involves appending hydrogen to any structures that are known to contain dangling bonds. **Figure 10** shows the visualization of a pristine graphene sample with passivation as output by the geometry script. Whereas **Figure 11** shows graphdiyne with a passivated crack inserted in the middle of it.

![Pristine Graphene With Passivation](image)

**Figure 10: Pristine Graphene With Passivation as generated by script:** The user specifies the dimensions and the passivation is applied post carbon. The vertical passivation does not effect the testing drastically, due to the boundary conditions, but is necessary in the horizontal direction to mitigated unwanted instabilities.
Figure 11: Graphdiyne with crack and passivation as generated by script: there are hydrogens on the edges to passivate carbon and mitigate reactivity. A crack is added to localize stress for mechanical testing. This crack also features automated passivation to mitigate unwanted instabilities that would take away from the continuum nature of this numerical experiment. A user dictates the size of the crack relative to the size of the sample, this crack is 10% of the x-dimension and 40% of the y-dimension.

With a means of geometry generation, a testing procedure, and the other tools discussed in this section we can continue to different aspects of the analysis which extend beyond molecular simulation towards category theory and additive manufacturing.

3.3 Category Theory as a Method

3.3.1 The basics of category theory

In this section, we briefly describe the main tools of category theory, which are of relevance to this work.
Sets
A set is a collection of things of any sort. Denoted with curly brackets, {}, we might think of a set as a bunch of numbers such as A = {1,3,5}. Its elements need not be limited to numbers, as will be seen later, it can also be the set {1,banana, green,...}. A set in our cases of interest will often be defined by a context but this does not need to be the case.

Functions
A function maps one set to another. Imagine the two sets B = {1,2,3} and C = {2,3,4}. These are both subsets of N, the set of natural numbers. Let g be the function that adds one to each natural number. Restricting g to {1,2,3}, we can see that it maps B to C.

Sets
Sets and functions form a category. But more generally we have mere objects and morphisms.

Objects
Objects are the elements of a category. They are similar to sets but abstracted to the generality of categories.

Morphisms
Morphisms are maps between objects. A morphism starts at an object (called the domain) and maps to another (called the codomain).

Category
A category is a collection of objects and morphism, together with information about how morphisms compose.

Functor
A functors is a map between categories A->B in which each object in A maps to an object in B and each morphism in A maps to a morphism in B.
3.3.2 Model Abstraction through Category Theory and Ologs

Ologs are human-readable categories, designed to build a bridge between science and mathematics, between reality and abstraction, and are described in detail in our earlier work\(^{35-38}\). Like a mathematically rigorous version of a concept web, an olog assembles a person’s (or group’s) insights in regards to a subject. The olog is structured according to simple mathematical rules, such as those that define a set, a function, and a composition of function chains, more concisely, those that define a category\(^ {39}\). The result is a mathematical-linguistic articulation of the subject-matter, which serves a dual role as database schema. In other words, once one has structured ideas as an olog, they have a ready-made repository for recording experimental data about that subject in a database.

An olog consists of boxes and arrows, each labeled with English text. This text must conform to certain rules (linguistic reflections of the mathematics) so that the entire olog can serve its dual role. That is, the boxes and arrows must read as English sentences that communicate ideas, and at the same time they must refer to intentional sets and functions that will be fulfilled by incoming data. An olog additionally includes so-called *path equivalence declarations* that specify when two paths through the web are intended to be conceptually equivalent. Some ologs contain even more category-theoretic structure\(^ {35}\).

Ologs have been successfully used to create formal analogies between hierarchical protein materials and social networks\(^ {36}\), and between musical harmony and spider silk fibrils held together by weak interactions\(^ {37}\). Furthermore, they have been shown to provide a basis for building block replacement strategies with potential application to bottom-up materials design\(^ {37}\).

3.4 3-D Printing/Testing

3.4.1 3-D Printing: Basic Principles

In this work we use the technology of 3-D printing to physically realize in bulk a molecular effect seen in the extended graphynes. A 3-D printer functions by taking a
source material and extracting it (usually in liquid form) and having spatial control of
where it is placed. It may be useful now to take an example of a simple 3-D printer and
discuss its functionality before showing the more complicated printer used in our
discussion. Figure 12 is the schematic of a representative 3-D printer featuring the
critical components needed for printing.

Figure 12: Schematic of representative 3-D printer: At the top-left corner is a resevoir
for the printed material. At the top-right corner there is a motor to drive motion in the X-
Y plane, by moving the linear-rails directly below the resevoir. Similarly for control of z
motion, in the center left there is a Z-Motion lead-screw which is drive by a Z-motion
motor on the bottom left. On the right side there is a heated nozzle from which material is
extracted. In the bottom right corner rests the printed object that sits on a substrate. The
substrate is often heated to ensure smoothness of printing.

It is potentially useful to think of a 3-D printer as a two dimensional printer that prints a
controlled thickness in z. Thus at a given height the linear rails for x-y motion can access
the entire x-y plane with the resolution dictated by the specifications of the printer. The
printer head moves by driving the linear rails with the x-y motion motor. Taking an input
from the computer, the printer head goes to locations containing materials and extrudes
the finite thickness of material. In the simplest case, the material sets due to the decrease
in temperature. The substrate is heated to a temperature below but near the melting point
such that the material is not shocked and makes a smooth product. Once all points in a
given x-y plane are given material, the z-motion motor spins the lead screw which raises the printer head. The same process is repeated at for the next x-y plane, which is how most 3-D printers work. It may be intuitive to consider this a pseudo 3-D printer that is prints 2-D planes of finite thicknesses at different heights z.

3.4.2 Multi-Material Printing

The particular 3-D printer used was the Straysys Objet Connex500 multi-material printer in the Precision Compliant Systems Laboratory at the Massachusetts Institute of Technology. This printer is often nicknamed by its users as the “Rolls-Royce” of 3-D printers as it has the highest precision of multi-material printers and represents the practical limit of consumer printers. A multi-material printer such as this uses jetting materials to print two materials simultaneously. The Connex500 has a total of eight printing heads. These heads are connected to liquid cartridges of TangoBlackPlus (the softest available material) and VeroWhitePlus (the hardest available material) which are the base materials used for the experiments in this thesis and are discussed in more detail later. This printer functions in principle in a similar manner to that described above. The differences are few but must be stated. For example rather than relying on the temperature gradient alone, the printer head is equipped with a UV-light. All materials are UV-curable, meaning they harden upon exposure to UV light. The presence of UV light causes a relative increase in cure time, which increases the spatial resolution of the printer. Additionally, through a very intricate mechanism of 96 50 micron nozzles working in tandem for both base materials used. As this account for four of the printer heads mentioned above, the remaining four are designated to deliver support material. Support material acts to give mechanical stability to the printed piece, thereby further increasing the spatial resolution of the printer. Thus rather than printing just where the desired piece is, support is added under the piece at all locations. The user can define the amount of support coverage. After printing, this material is water soluble and removed via high pressure water which leaves a pristine piece.

3.4.3 3-D Printing: Model Development
The user dictates the manner in which an object is printed. The process to print starts with a Computer-Aided Design (CAD) drawing of the desired material to be printed. This can be done in most CAD programs. The geometry is then exported in STL (stereolithography) files corresponding with which part of the original is printed with which material. Following this, the printer has software used to interpret the STL files and defines that path that the printer head will take. In this program the user defines which materials will be used for each file and also the amount of support used. Figure 13 shows the output of the printer in the form of samples covered in support material.

Figure 13: Printed samples and view of inside of 3-D printer: On the left one can see 3-D printer head described. The silver-colored nozzles on the head are where the material comes out. Additionally there is massive amounts of electronics on the head to control and power motion. On the back one can see linear rail for motion in x and y. Samples are covered in solution and sit on top of heated surface.
3.4.4 3-D Printing: Testing

Following the output depicted in Figure 14, the samples are then mounted such that they can be tested through an instron. The mounted samples are depicted in Figure 15. Holes are drilled in the sample so such that clevis pins can be used to secure the sample to the instron.

![Mounted 3-D printed geometries](image)

**Figure 14: Mounted 3-D printed geometries:** In this we show geometries mounted before testing. We note holes for mounting to mitigate out of plane torsions.

With clevis pins in place, out of plane motions are mitigated as are unaccounted for stresses. A load-cell designed for softer materials is used to ensure accuracy in measured force values.
Chapter 4: Introduction to the Mechanics of the Graphynes

4.1 Introduction to the Mechanics of 2-D Carbon

For an application to be realized, additional considerations must be taken into account when compared with controlled experiments: If a given application relies on a structure that is mechanically compromising, it is not economical or practical. By understanding how these materials perform mechanically and how they fail, the origins of strength can be understood. This understanding can then become part of the design process. As previously stated, the past two years have seen an increased amount of attention paid to the mechanical properties of graphynes\textsuperscript{40}. In earlier work our group has reported a preliminary investigation of graphyne mechanics, which was followed by an investigation on the mechanical properties of the whole family of extended graphynes\textsuperscript{40,41} in which the length of acetylene repeats present in the structure were found to decrease the strength of a given graphyne. The dependence of strength was explained using a simple spring model in which the acetylenes are the aromatics are springs of different constant. Figure 15 explains in greater detail the model introduced by Cranford et al.
Figure 15: Simple spring-network model representation of extended graphynes (A) Spring representation of acetylene links and aromatic carbons derived from mechanical simulation performed by Steven Cranford. The stiffness of a single segment is the sum of $k_0$ (the stiffness of the benzene ring) and $k_1$ (the stiffness of a single acetylenic link which constitutes the connection in the mesh).

The stress-strain behavior responsible for justifying this model can be found in the work of Cranford et al. These results are necessary for the basis of the linear spring model abstraction of this model. In Chapter 6 this will be necessary in formulating a categorical abstraction for these behaviors.

Such simplicity arises from the covalent and localized nature of these bonds. Additionally, when the bulk material is loaded in the x and y directions, it is clear using simple geometric arguments that the above elements are only loaded in tension. These earlier studies were accompanied by a series of papers by Peng et al. and Kang et al. A similar study has been conducted on graphdiyne by Pei. Several other analyses have been conducted to express the general behavior of these materials.

4.2 Preliminary Fracture Study:

In order to assure out elastic characterization is not adversely affected by the finite model samples and imposed boundary conditions, we further undertook a set of simulations in which the graphyne sheets were subject to fracture (e.g., mode I crack propagation). In effect, in order to control the location of the failure (e.g., fracture nucleation), each sample was modified by a discrete crack/wedge (a ubiquitous protocol in fracture mechanics studies). Due to the relatively small model sizes (and relatively high crack
length ratio), combined with the discreteness of the atomistic geometry (e.g., a lattice spacing for graphtetrayne approximately one-half the crack length), the fracture results are not intended to characterize the complete fracture properties of such materials (e.g., $K_{IC}$, $J_{IC}$, etc.), but rather provide a benchmark for future, more systematic fracture analysis, support the elastic characterization, and shed insight on the potential failure mechanisms of graphynes.

**Figure 16: Fracture mechanics of graphynes.** Each graphyne sheet was subject to mode 1 fracture via the introduction of a crack/wedge. (A) Stress–strain results of each model. We note a near-linear stress...
versus strain behavior for each model, supporting the purely elastic results. In terms of critical stress (onset of fracture) we see failure events consistent with those predicted about by the linear spring model (with ultimate stresses decreasing from approximately 30 GPa for graphyne to less than 10 GPa for graphitriyne/graphitetrayne). (B) Visualizations of the failure indicate that, as anticipated, fracture initiates at the crack and propagates along a plane defined by the single-carbon bonds of the acetylene links (indicated by arrows). A pronounced shifting (e.g., geometric alignment) of the finite samples is observed in the higher allotropes (n = 3, 4), facilitating the observed “two-tier” effect. Figure reproduce from 40 with permission of Authors and Royal Society of Chemistry.

Each cracked model was subject to tensile strain until ultimate failure (defined by zero sustained stress), and the stress-strain response is plotted in Figure 16A. From the plot, we note an initial linear stress versus strain behavior for each model, supporting the purely elastic results (moduli calculated from this plot are slightly lower due to the relative size of the introduced crack). In this plot we see for graphene what we would expect which is that of linearly increased stress with strain (ultimate stress of approximately 60 GPa at a failure strain of approximately 8%) and then a large drop at the moment of failure (e.g., brittle-like). Looking at the visualizations in Figure 16B, these events can be clearly seen. While similar, the response is more complicated for the graphynes. Starting with an initial linear trend in stress versus strain (decreasing as a function of n), we see failure events consistent with those predicted about by the linear spring model (with ultimate stresses decreasing from approximately 30 GPa for graphyne to less than 10 GPa for graphitriyne/graphitetrayne). As anticipated, fracture initiates at the crack and propagates along a plane defined by the single-carbon bonds of the acetylene links. This is similar to the preferred “weakest” planes in graphene, namely along the armchair or zigzag directions.47,48

That being said, after the initial fracture (failure of aligned acetylene links) we observe a secondary event in which there is secondary regime of linear stress v. strain, due to a geometric effect as depicted in Figure 16. While the first fracture even corresponds to the aligned linear acetylene links, failure results in (a) stress relief and (b) realignment of remaining acetylene chains to the direction of load. As the number of links is regular, we see a secondary fracture event which corresponds to these failing at approximately
equivalent stress levels. This “two-tier” fracture effect becomes more pronounced for the higher allotropes, when initial breakage results in both a higher relative stress drop and more pronounced realignment. Whether these features are a unique result of small sample size, discrete geometry, and boundary conditions warrants future study of this interesting family of materials.

We note that the emergent failure mechanism (e.g. local buckling, two-tier fracture) may be a direct result of our simulations conditions and not universally applied to graphynes in general. Indeed, the current study is limited to isolated, pristine, 100 A x 100 A sheets ideally loaded in either the reclined chair or zigzag directions. It has been shown in graphene, for example, that variation in aspect ratio (length to width) results in a transition from membrane or sheet-like behavior to ribbon-like behavior. More critical, the lattice spacing would certainly become a factor for smaller length scales. A 5nm thickness for example, would allow only four repeat units for $n = 4$. Moreover, it can be anticipated that edge effects (e.g., chirality and termination) would greatly influence the mechanical properties similar to graphene. The properties presented here can be considered representative of bulk behavior – full characterization of critical size effects warrants future study and analysis. This analysis will be performed in the following chapter through a study of graphdiyne and comparison with graphene.
Chapter 5: Failure of Carbon: Graphynes and Graphene

5.1 Introduction

The main subject of this chapter is graphdiyne, one of the few graphynes that has been fabricated in large quantities. This work complements that of the previous chapter in which the full family of extended graphynes was studied. In this chapter we wish to investigate further the two-step failure mechanism and compare it to graphene, a system that does not contain carbyne like chains. Graphdiyne has shown to exhibit a delocalized fracture mechanism that is different from the localized unzipping seen in graphene. This mechanism has implications for the toughness and robustness of this material, which is topical for many device applications recently proposed in the literature. In this study we perform fracture analysis on graphdiyne and find a delocalized failure of mechanism in which a crack propagates along a diagonal with respect its original direction. This behavior is supported by the covalence of the material, which allows for this simple but intriguing phenomenon to be investigated. Graphene is also tested to failure to compare this behavior. Connections of such delocalized failure are made to that of hidden length in some biological systems such as proteins, bone and nacre. Finally, we make comparisons and discuss the implications of delocalized failure on the material’s strength.

5.2 Methodology and System Geometry

We investigate the failure of the material in the pristine case with a continuum crack as depicted in Figure 17.
Figure 17: Structure of graphdiyne, geometry of model and application of boundary conditions. (A, B), The structure of graphdiyne contains aromatics of the sp² motif linked by sp¹ acetylene that consist of alternating triple and single bonds, where there are two triple and three single bonds. This is a distinct departure from the structure of graphene. (C), Geometry of the test specimen with relevant dimensions to complement description in methods section. The sample is loaded in the x-direction in mode I. This figure is reproduced from [49].

The mechanical properties of graphene have been measured using atomic force microscopy and calculated from first principles [50,51], which has confirmed preliminary findings and motivated further investigations. Great attention has also been paid to the failure of graphene, both in the role of grain boundaries and the ripping directions [47,52]. Graphdiyne is chemically pure with a structure that does not deviate from tessellations of its primitive cell. Preliminary analyses of the fracture mechanics of graphdiyne were reported in earlier work [40], which we extend here to provide a detailed analysis of stress fields and fracture mechanisms, and a direct comparison with graphene.
5.1.2 Simulation Details

All simulations are performed using the LAMMPS molecular dynamics solver. The first principles based ReaxFF potential is used to calculate forces, a potential that has proven effective for systems involving hydrocarbons and has been used extensively for graphene and other two-dimensional carbon systems. Geometries are generated using a tessellation script and are initially two-dimensional, with all \( z \) coordinates equal to zero. Bond lengths are in accordance with those found for equilibrium with ReaxFF in our previous work. A pristine and rectangular sample is produced and the edges are passivated with hydrogen. A perfectly symmetric crack (shown in Figure 17C) is taken out of the pristine specimen. Then the bonds that are broken are also subject to hydrogen passivation. This is done to minimize interactions that are artifacts of the setup and not part of the bulk fracture process. We also create a graphene geometry bearing a crack for comparison. It should be noted that this graphene samples measures only \(~10 \text{ nm} \times ~10 \text{ nm} \). The purpose of this is analysis is to demonstrate the implications of structural difference between graphene and graphdiyne on the failure of these two materials.
5.1.3 Simulation Geometry

5.1.4 Testing Procedure

The simulation procedure is as follows: In LAMMPS, the geometry is allowed to equilibrate in an $NVT$ ensemble at 20 K, with the atoms free to move in all directions without the boundary condition described above imposed. The duration of this was determined by preliminary situations to consist of the time in which the residual stresses from the geometry generation became negligible. The regions shown in

Figure 17 are defined before the dynamic run in order to maintain symmetry. This means that the atoms in the various regions are marked but allowed to move. The boundary condition is applied to these same atoms even if they have moved slightly out of the area, in an effort to maintain symmetry. The loading procedure consists of a series of instantaneous displacement steps separated by minimizations. The material is deformed from its current size by 0.06991% per displacement step, which is relative to the width of the entire material in the previous step. This specific number was chosen from preliminary tests in an attempt to not have multiple failures within one deformation step.
It should be noted that this causes a slight increase in displacement size throughout the simulation.

The samples are loaded in the reclined chair or the \( x \)-direction as shown in

5.2.1 Comparison of Stress-Strain Response for Graphene and Graphdiyne

We present the results of the fracture tests in Figure 18 in which the stress-strain curve is plotted for the cracked graphdiyne sample and the cracked graphene sample as a reference.
Figure 18: Stress-strain plot and connection with geometry: (A), Stress-strain curves for loading in the x-direction comparing graphene and graphdiyne. A “saw-tooth” behavior can be seen for graphdiyne. Our data shows the implications of the bond breaking mechanisms on the overall stress of this material. (B and D) and (C and E) show principal stress distributions for graphene and graphdiyne, respectively. These materials are at a point near the first bond-breaking event. This figure is reproduced from [9].

We observe several local stress minima at higher strain for graphdiyne, suggesting a means by which the material is responding to relieve the stress (saw-tooth regime). On the contrary, the failure of graphene is less elucidated by its stress strain curve. The
failure of graphene is consistent with the results reported in previous work, in which the failure of graphene is directional and localized \(^{40}\)

### 5.2.3 Increased Resolution

To analyze the results in greater detail perform a more intensive analysis on the graphdiyne failure samples. See Figure 18B-E for a comparison between graphene and graphdiyne. We note that the stress distributions for the respective graphdiyne and graphene systems in Figure 18B-E are both relatively symmetric. This maintains for graphene in that the fracture propagates in the y-direction. This is not true for graphdiyne, which in later deformation yields a directional failure along a diagonal. An important difference between the two systems is that the stress field in graphdiyne is more heterogeneous, as can be confirmed in the detailed view depicted in Figure 19 which shows the mechanism of propagations of the crack in graphdiyne.

![Figure 19: Mechanism of failure in graphdiyne, visualized using principal stress distributions.](image)

The field plots are presented at different deformation states to show the propagation of the crack and to expose the delocalized failure mechanism. The respective strains are A=3.9\%, B=4.2\%, C=4.4\%, D=4.5\%, E=5.5\%, and F=6.5\%. We notice that the crack begins to propagate along the y-axis but almost immediately progresses along a diagonal. This causes a reorganization of stress concentration that deviates from the
failure behavior of graphene that is directed along the axis of the initial crack (see also Figure 21). This figure is reproduced from [49].

We see by comparing to Figure 18B and Figure 18D that as the crack propagates it causes a breaking of symmetry for the stress distribution at a local scale. This explains the origin of the directional failure of graphdiyne along the diagonal. The crack appears to turn and realign itself along this diagonal. The initial failure occurs of graphdiyne occurs at the horizontal bond located at the crack tip. This failure involves the single bond centered between the two triple bonds, where Figure 20 provides a close look at the onset of fracture and propagation of the crack, clearly revealing the region of partial fracture.

Figure 20: Detailed view of the molecular mechanism of failure of graphdiyne, clearly revealing the two-tiered fracture process. The horizontal propagation occurs at a faster rate than that of the diagonal bonds such that the region of partial fracture grows as the system is loaded. We present here a closer view of the samples above at strains of A=3.9%, B=4.2%, C=4.4%, D=4.5%, E=5.5%, and F=6.5%, respectively. This figure presents the crack from the formation of a small group of delocalized voids to (E) and (F) in which several bonds are broken in isolation from the continuous crack. This figure is reproduced from [49].
We find that after the initial horizontal bond breaks, the diagonal bond breaks. Figure 20A shows that the second bond to break is that of the initially horizontal bond above and to the right of the original bond that broke. Figure 20B and Figure 20C show that after the initial bond breaks, a combination of initially horizontal and initially diagonal bonds fail. It is of note that the single bond located between the two triple bonds is always the one to fail. This failure can be anticipated as the bonds of the acetylynes that link that aromatics are hybrid single and aromatic. Thus the only pure single bond, and therefore the weakest bond, is that in the center of the acetylyne and the only bond which breaks. By performing these tests using an energy minimization approach this method is both quasi-static and without temperature. The authors believe that this makes the material more brittle. As temperature is increased, we must also consider that any instability induced by the broken structure will be magnified which will be detrimental to the delocalization. Zhao et al. studied the temperature dependence of the fracture strength of graphene which can motivate future studies from this work 56.

A notable observation that can be seen in Figure 19 and in more detail in Figure 20 is that a delocalized region forms, in which the horizontal bonds have broken but where the diagonal bonds are still intact.

Here, Figure 20D shows that the delocalized failure region is only one broken horizontal band. Figure 20E and Figure 20F show that as the crack propagates, the region of this delocalized failure increases to three and then five bonds, respectively. A localization of stress is relieved with these individual bonds breaking, suggesting that this mechanism explains the saw-tooth regime seen in the stress-strain plot. Figure 20 clearly shows that a continuous crack is not created until several horizontal bonds along the same diagonal break, exposing the delocalized failure. Figure 20 further shows that as the crack propagates, the lateral location of the concentration in stress is shifted, and further spread out. This is partly due to the directionality of the crack. This directionality is a direct result of this material’s pristine geometry coupled with a heterogeneous bond arrangement. This heterogeneity in bond order corresponds with one in strength.

5.2.4 Comparison of Large Strain Morphology for Graphene and Graphdiyne
With an understanding of the origins and process to initiation of failure, detailed comparisons can now be made between to the same phenomena in graphene. Before we proceed, we must point out that an anisotropic response is expected in this material. The failure that is seen for graphdiyne in this loading is an extreme case in that we loaded parallel to the direction of the bonds that broke. We anticipate that anisotropic loadings may cause similar failure but other geometric effects may outweigh the relative bond strengths. What we wish to show here is the extreme case for this effect and the implications that it has on crack propagation. Figure 21A and Figure 21B show that the horizontal acetylenes continue to break more frequently than the diagonal acetylenes.

**Figure 21: Comparison of crack propagation for graphene and graphdiyne.**

Graphene (panels A and C) is shown at a strain of 17.2% while graphdiyne (panels B and D) is shown at a strain of 6.5%. The difference in direction in crack propagating is that graphene follows a path that is straight in the y-direction and graphdiyne’s propagates along a path that is diagonal to the vertical. Graphene experiences symmetric stress distributions about the crack and graphdiyne’s crack turns and re-centers itself along the diagonal. This figure is reproduced from [49].

This induces a crack arrest in which the continuous crack does not propagate, but rather a delocalized fracture of the initially horizontal acetylenes continues. The most vulnerable
bonds are the single bonds located between the triple bonds in the acetylenes. When the crack is oriented in its initial direction, the next horizontal bond on the diagonal is expected to break. As the material fails and deforms we recognize that previously diagonal bonds are deformed such that they will fail. The combination of these two effects is responsible for the delocalized failure and crack arrest seen in these systems. We can also compare the results for graphdiyne with those of graphene. We see that the propagation of the crack in graphene in on axis as consistent with previous studying of ripping graphene. It is also of note that there is a resemblance of crack bridging. Although to the best of our knowledge this has not been observed experimentally a similar mechanism has been found in the work of Ni et al. Additionally, in the work of Chuvilin et al. single carbon chains were observed experimentally between regions of pristine graphene and looks qualitatively similar to the fracture morphology of graphene in Figure 2.

We would like to briefly discuss the intermediate structures, which involve free carbyne chains. It has been shown that these structures are unstable and susceptible to chemical reactions such as oxidation. Future studies to address this would include repeating the tests within a real environment. The purpose of this work is a preliminary survey of the energy landscape and fracture at an introductory level.

5.3 Conclusions and Connections to Biological Materials

Multi-step failure mechanisms are ubiquitous in nature. Sacrificial bonds are found in nature and known to provide hidden length that increases the fracture strength of these materials. Specifically, crack arrest and delocalized failure are predominantly seen in certain biological materials such as nacre or bone. The effect resembles a delayed failure of the material allowing it to overcome higher deformation. Biological materials contain simple building blocks that are arranged in a complex manner that often leads to heterogeneous structure. It is known that the heterogeneous structure seen in these materials can, in some cases, cause crack arrest and/or delocalized failure. Although graphdiyne is atomically homogenous and consists of regular tessellations of a single unit
cell, the bond structure of this material is heterogeneous, as the bonds vary in strength. As such, the part that differentiates graphdiyne from biological materials is that the delayed failure occurs in a pristine material. We note that this not an increase in fracture toughness, as is seen in biological materials, but rather an increase in toughness. Therefore this effect should also be differentiated from hidden length but we hope the analogy is clear. Additionally, it should be noted that this heterogeneity combined with a loading direction (in our case, the x-direction), could cause the weaker single bonds to act like sacrificial bonds and greatly increase the failure strain of this material. It should be noted that in biological materials, sacrificial bonds are often those bonds that can easily be reformed such as hydrogen bonds\textsuperscript{66}. The results presented here show no indication that the carbyne chains would reform in this system. Figure 21B shows a mechanism similar to that of bone or nacre in which the crack has arrested locally but progressed further beyond a non-cracked region thereby leaving bridges\textsuperscript{64}. In this case, the bridges are periodic in the material. It should be pointed out that there exists a few orders of magnitude between the scales of these biological materials and those of 2D carbon, but the analogy still holds. It should be taken away that the breaking of these bonds delays the total failure of graphdiyne and increases its ultimate strain by the mechanism described here.
Chapter 6: Application of Category theory to 2-D Carbon

6.1 Introduction to framework

The purpose of this chapter is to introduce and apply a framework for incorporating mechanisms found through scientific models to engineered systems in a way that is robust, transparent, and expedient. Specifically, we seek to demonstrate a process by which a mechanism derived through models can be realized as a physical system in a distinct domain: ‘prototyping a model’. In this study, we map an atomistic scale mechanism to a modeled abstraction, which is realized through 3-D printing. 3-D printing is a crowd favorite, which represents a larger field of additive manufacturing. To complement previous work in bioinspired design\textsuperscript{67-70}, this method can be extended to formalize the design process to make certain results universally unambiguous and reproducible. This process is similar to the concepts shown in earlier work, but using a more formal mathematical approach to facilitate the transitions between domains\textsuperscript{71} and an emphasis on accommodating the specific needs of the prototyping community. The earlier study\textsuperscript{71} explored a construction scheme found in bone and nacre that incorporates hard and soft building blocks to create a composite with higher fracture toughness.

6.1.2 Previous Abstractions without Category Theory

Abstraction is a ubiquitous component of bioinspired design, marking this as a an important starting point to address fundamental challenges in translation between natural systems and engineering. Subjects of bioinspired design include the investigation of
remarkable adhesion of the gecko foot\textsuperscript{72-75}, silica-like systems with increased fracture toughness\textsuperscript{65}, lotus leaf like geometries for superhydrophobicity\textsuperscript{76}, and the production of biomimetic microvascular networks using fractals for efficient transport of fluids\textsuperscript{77}.

Calculus, differential equations, and tensor analysis have provided systematic means for reasoning about the physical world in various fields of science, including bioinspired design. Human understanding is built up of models, which distill essential features about observed phenomena. These models are useful both to transfer from reality to abstraction as well as between different abstractions. Here we show that the rate at which such mappings could be made can be drastically increased with the introduction of category theory, a field designed to formalize the notion of a mathematical domain and rigorous mapping. Hearing about an engineering solution to a biomimicry problem is exciting, but does not readily allow others to reproduce the results. The creative process involved in manufacturing gecko gloves may remain a mystery, but its output should be made as transparent as possible: at the end of the day, what was discarded and what was preserved?

As we discussed above, the process involves 1. observing phenomena, 2. distilling the essential characteristics that seem to make it work, and 3. then reproducing these in a human-usable domain. Clever individuals can focus their attention and make this work, but to be efficient we look to distribute the work over many individuals and not constantly reinvent the wheel. A key step for avoiding reduplication of efforts can be inserted in the process at the second stage, namely by rigorously formalizing the model.

Science often looks to nature for inspiration because nature performs complex processes in a way that is energetically efficient. The process of taking an observation, describing it with a model, and using it to fabricate something is hence ubiquitous in the process of bio-inspired and biomimetic materials. Consider the case of the gecko foot and the remarkable adhesion associated with it\textsuperscript{75}. This has attracted great attention both from a standpoint of investigating the phenomenon as well that to harness this property for application as an adhesive \textsuperscript{72,73}. The latter of Siti et al. is of greater relevance to this work.
The ability of the gecko to adhere comes from a field of features bearing a characteristic length scale. These features are known as the gecko foot hair. This has allowed for artificial vehicles to climb walls. In the case of Santos et al., the goal was to incorporate the origins of adhesion in gecko feet for the specific application of climbing up vertical. The problem is well defined and motivated. Geckos have the ability to climb up flat vertical walls. Success is also clearly defined, if such a material can be fabricated that enables a robot to scale a wall, it is certainly a success, and this group achieved just that. The framework that we present in this paper looks to apply mathematical formalism to ensure that no information is lost from the understanding of the origins of a phenomenon to the application. Such ability allows harnessing the full power of the model.

Beyond the gecko adhesion there are many other examples of bioinspired materials in which a scientific understanding was abstracted with a model and then harnessed to design new engineering materials. Such examples include scale armor inspired by scales, airplane wing inspired by bird, and many modern examples [Bar-Cohen].

### 6.2 Introduction to Context of this Work

The specific scientific context of this paper is two-dimensional carbon, which will serve as our point of inspiration for design. In the 1950’s, the Dirac cone structure was predicted in the hexagonal symmetry of graphite. In the 1990’s Satio et al. displayed tunable band-gap of carbon nanotubes. Novosolev et al. successfully extracted graphene, and since then the study of graphene has exposed a range of exceptional thermal, electronic, and mechanical properties. Most recently there has been an emergence of new allotropes that are similar to graphene but depart from the aromatic structure, presenting a generalization of the concept of graphene to a large family of materials with potentially vastly distinct chemical and physical properties for various applications. Such applications include hydrogen filtration by graphynes, lithium ion storage by graphdiyne, and filtration of ions and contaminants.
by graphyne nanowebs. The continuing growth and interest in the field of carbon nanomaterials suggest a potential benefit from the mathematical tools of organization utilized in this study. We begin our work with the presentation of a category theoretic analysis as applied to the extended graphyne allotropes.

### 6.2.2 Review of Model

Graph-\(n\) for integers \(n\) are a set of model materials based on 2-D carbon allotropes. In these materials aromatics are arranged in a triangular lattice connected by alkyne chains that consist of alternating single and triple bonds. These chains consist of \(n\) repetitions of single and triple carbon bonds. Only Graph-0 (graphene) and Graph-2 (graphdiyne) have been fabricated, but many more have been simulated, e.g. Graph-2 (graphdiyne), Graph-3 (graphtriyne), and Graph-4 (graphtetriyne) using the AIREBO and ReaxFF interatomic potentials. In earlier work we have explained the scaling of the Young’s modulus with \(n\) using a network of springs that serves as the model to be printed. Therein each aromatic is modeled as an isotropic spring array with spring constant \(k_1\) and each alkyne chain is modeled as a spring with spring-constant \(k_2\). Through geometric arrangement in a triangular lattice the overall spring constant can be determined in “reclined chair” and “zigzag” loading directions. This yields a scaling behavior with increasing \(n\) for the Young’s modulus that matches predictions from atomistic simulation in both loading directions. Here we take this spring-model of graph-\(n\) and articulate it category-theoretically as a material olog. The resulting model can be 3-D-printed with minimal disturbance from unaccounted assumptions allowing this work to reach its full impact and reusability, and further analysis in a macroscopic domain. The olog is designed to reproduce the scaling behavior identified for the Young’s modulus in zigzag and armchair loading directions across the extended graphynes.

### 6.3.1 Realization through Manufacturing Techniques

3-D printers have become essential tools to prototype for scientists and engineers. With a relatively low technical entry, combined with sufficient and increasingly profound proficiency in spatial control material selection, multi-material 3-D printers are expected
to become a viable tool to realize complex geometries and unique material combinations. These features make this technology into a perfect candidate in the framework of realizing a model.

6.3.2 Material selection

When we map our olog into the space of additive manufacturing, i.e. to a specific 3-D printer, we must choose the combination that best suits the model from the printer’s materials. We performed all 3-D printing on an Objet Connex500 printer. The materials are proprietary formulas of Stratasys and are chosen based on the mechanical property data to the user. This decision is made in conjunction with the material combinations known to create a reliable interface when printed simultaneously, which is another practical consideration. The final constraint arises from the model published in our previous work\(^40\), where the hard material is considered effectively infinitely more rigid than the soft material, and thus we must choose the most extreme differential in stiffness. We select TangoBlack+ and VeroWhite as the soft and hard materials, respectively, as they were the hardest and softest respectively that meet the aforementioned constraints. The material selection appears limiting in the context of the model in that the spring ratios are infinite. In reality, the finite difference between material stiffnesses is acceptable in our work to illustrate the translation of the scaling law, as we will show.

6.3.3 3-D-printing and sample preparation

A major goal of ologs is to compartmentalize and package a contribution of human understanding such that hidden assumptions or matters of experimental convenience cannot disturb it, such that the model is laid bare. In accordance with this, the computer-aided design (CAD) files for printing are created using a script that follows the dictates of our olog, requiring only a “real number” as an input and moderate post-processing to resulting geometry such that it can be loaded into a tensile test machine. It should be noted that moderate modifications are required to the resulting file but the system is otherwise push-button. This CAD file is loaded into the software of the printer and the printing can begin. As the purpose of this study is to understand mechanical properties, exceptional care is taken in the removal and cleaning of the samples to ensure that no
members are preloaded in a way that would disrupt the testing. **Figure 24** shows the resulting samples of the 3-D printer with added mounting for stability in testing. The soft material is the darker, TangoBlack+, while the hard material is the lighter, VeroWhite. The samples are provided four metal-strips, two in each direction, to distribute the load evenly when the materials are tested.

### 6.3.4 Sample testing and Simulation

The resulting material bulk material behaves more like a fabric or chain-like material rather than a traditional rigid substrate. As a result, “slack” must be mitigated through moderate initial loading to approach a regime in which the entire material experiences tension. This is acceptable, as we are only looking for the scaling of Young’s modulus and not the specific values of stress at a given strain. The Young’s modulus was inferred from the slope in a consistent linear regime for each sample on the stress-strain curve. In the configuration of **Figure 24**, two metal strips are adhered to each sample covering consistent number of geometric repeats. A hole is drilled into the middle of each metal strip to mitigate out-of-plane loadings and enforce uniaxial tension.

The LAMMPS molecular dynamics solver was used for the simulated twisting. The ReaxFF potential designed for hydrocarbons was used to determine the forces between atoms. Geometries are generated using a MATLAB script that uses tessellations to create custom-sized geometries. The sample is pristine and all carbons are hydrogen passivated to ensure bond order is satisfied. The system is equilibrated in an NVT ensemble at 100K for 40,000 time steps with a step size of 0.2 fs. Following this, the sample was reduced to 20K and twisted with the top and bottom fixed as is shown in **Figure 26**. The period of rotation was 100000 fs. Visualizations are used for qualitative comparison with experiments.

### 6.4 Results
6.4.1 Tabulation of Abstractions

Figure 22 provides a tabulation of each object at the atomistic scale alongside its counterpart in the 3-D printed specimen:

<table>
<thead>
<tr>
<th>Box-Name</th>
<th>Atomistic Interpretation</th>
<th>Visualization</th>
<th>Printing Interpretation</th>
<th>Visualization</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>an aromatic</td>
<td>![Image]</td>
<td>an extruded vertex</td>
<td>![Image]</td>
</tr>
<tr>
<td>AL</td>
<td>an aromatic and an in-plane loading arrow through its center of mass</td>
<td>![Image]</td>
<td>an extruded vertex and an in-plane loading arrow through its center of mass</td>
<td>![Image]</td>
</tr>
<tr>
<td>C</td>
<td>an alkyne chain</td>
<td>![Image]</td>
<td>an extruded edge</td>
<td>![Image]</td>
</tr>
<tr>
<td>MS</td>
<td>a 2D material sample</td>
<td>![Image]</td>
<td>an extruded 2D material sample</td>
<td>![Image]</td>
</tr>
<tr>
<td>MSL</td>
<td>a 2D material sample together with a choice of in-plane loading arrow through the center of mass</td>
<td>![Image]</td>
<td>an extruded 2D material sample together with a choice of in-plane loading arrow through the center of mass</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

Figure 22: Functorial translation between the atomistic structure and function of Graph-X and the macroscale printed material. Each aromatic is to be realized by a 3-D-printer as a vertex, and each acetylene is realized as an extruded edge.
At both length scales the object is visualized. This can be thought of as a key when beginning to navigate the olog. Figure 23 displays the olog, which maps a molecular mechanism, the scaling of Young’s modulus within the extended graphyne 2-D carbon allotropes, to realization by 3-D printer. If we start near the bottom left corner, we see AL, which is defined as “an aromatic and an in-plane loading arrow through its center of mass.” We recognize that this is MSL, “a 2-D material sample together with choice of in-plane loading arrow through center of mass.” One cannot physically realize a continuum 2-D material and thus it “becomes, using experimental interspatial distance” VolL, “a 3-D volume with a line through it.” This has as length R, which is “a real number.” R is the push-button input for this model, which maps the scaling of Young’s moduli for the extended graphynes. By following the arrows as has been done here, the processes through realization can be tracked completely.

The commutative diagrams in Figure 23 illustrate several specific features of our model.
C: an alkyne chain

AL: an aromatic and an in-plane loading arrow through its center of mass

MSL: a 2D material sample together with a choice of in-plane loading arrow through the center of mass

Vol: a (3D) volume

MS: a 2D material sample

Vol: a (3D) volume

K: a spring constant

Commutative Diagrams

(i) \( a; g = c; l; h \)
(ii) \( b; a = a \)
(iii) \( b; b = id_c \)
(iv) \( b; c = c \)
(v) \( b; d = d \)
(vi) \( b; e = f \)
(vii) \( b; f = e \)
(viii) \( c; k = d; k \)
(ix) \( l; i = k; q \)
(x) \( n; o = m; k \)
(xi) \( n; p = m; j \)
Figure 23: Olog formalizing graph-X model from\textsuperscript{40}, used for 3-D printing. Graph-X is modeled as a symmetric graph, consisting of aromatics (A) and alkyne chains (C). Each chain has a length of 3 Å. An aromatic is considered a 2-D material sample (MS), each alkyne chain is realized as a 2-D material sample with either axial or orthogonal loading direction (MSL). All loaded 2-D material samples are characterized by a spring constant (K), and the aromatics are isotropic. 2-D material samples are given a 3-D representation using 1 Å cutoff around their surface (Vol, VolL). The commutative diagrams are shown in the upper right box. Note that a standard tensile test for 2-D materials does not yet exist, but any standard like the ASTM will suffice.

The length of an alkyne chain is equal to the distance between the “force-inlet points” under axial chain load. An alkyne chain is represented as an undirected edge in a symmetric graph. In other words, every edge has a symmetric dual, i.e. an arrow in the opposite direction that has equal properties. This results in the following six statements:

The length of an alkyne chain is equal to the length of its symmetric dual. The symmetric dual of the symmetric dual of an alkyne chain is the original alkyne chain. The axial/orthogonal loading of the symmetric dual of an alkyne chain yields the same 2-D loaded material sample as the axial/orthogonal loading of the original alkyne chain. The source/target of the symmetric dual of an alkyne chain is the same aromatic as the target/source of the original alkyne chain. Independent of its loading direction, an alkyne chain is realized as the same 2-D material sample. Independent of its loading direction, a 2-D material sample becomes a well-defined 3-D volume using our cutoff for the out-of-plane direction. An aromatic, as a 2-D material sample, is assigned an in-plane loading arrow through its center of mass. An aromatic has the same spring constant regardless of the in-plane loading direction through its center of mass, \textit{i.e.}, it is isotropic.
Figure 24: Geometries of Samples: 3-D Printed and Atomistic

(a) Printed samples with mounting. Samples are loaded through hole in mounting. Both Right: The corresponding atomistic models of structures. (b) Sample loaded on tensile testing apparatus, secured by clevis pins. It can be seen that sample is loaded in a way to guarantee a uniform loading in the desired direction. Additionally, the loading mitigates moments out of plane.

The samples displayed in Figure 24 are tested in the direction perpendicular to that of the mounting bars. The results of the testing are visualized in Figure 25, which clearly shows...
that the $1/n$ scaling law of Young’s modulus is maintained. The fits shown in Figure 25 are of the form of a $1/n$ scaling with no additional fitting parameters. It is constructive to note that for the higher-allotropes, the larger scale of the sample may affect the measured stress due to imperfections of the experiment given the loading configuration. Such an imperfection is that of a moment introduced by the metal bar on the load cell by out of plane motion, which is inevitable, given the length of the bar and the softness of the substrate, leading for example to creep effects. In the case of the smallest samples for each loading condition, there was a finite engineering stress at the point of zero strain, which was not the case for the three larger samples. This could be related to the relatively high values for the scaling law. In general the desired scaling law and therefore suggest the validity of the olog in the context of a real system.
Figure 25: Results of tensile test with scaling behavior. Young's modulus measured using tensile testing compared with the theoretical $Y = ax^{-1}$ scaling that is seen in the
original work for a) Reclined Chair loading direction and b) Zig-Zag loading direction. We note a general very good agreement between the data and the theoretical curves, based on the use of a single parameter. (Fitting done using the autofit function within the curve-fitting toolbox in MATLAB.)

To show that the results here have implications beyond those of Young’s modulus, we extend beyond the original analysis. To do this, we devised a twisting experiment which is simultaneously performed in a molecular model as well as a an abstracted 3-D printed sample, equivalent to those used in the previous section for testing of Young’s modulus. We depict our experimental geometry in Figure 26. It should be noted that particular attention was paid to the selection of boundary conditions to be most similar to that of the tensile testing upon which the olog is best.

Figure 26: Schematic of twisting analysis. The twisting is performed in both experiment and modeling by fixing a region of atoms at the bottom of the sample. At the top of the sample, the region of the sample twisted along the y-axis through the middle of the sample. As can be seen in Figure 26, the sample was clamped along the x-axis and rotated about the y-axis. An intron was used to mount and put tension in the sample. The unique nature of this testing required a non-standard set up in which “lead-screw” type apparatus was
used. We note that during rotation, slightly more tension was applied in y but we deem this negligible in comparison with the dimensions of the sample. We state this explicitly as this was not accounted for in simulation.

![Image of twisting analysis](image)

**Figure 27: Result of twisting analysis.** Twisting is performed on both an atomistic and 3-D printer abstractive model. The top row shows twisting of the 3-D printed composite while the bottom row shows snapshot from the atomistic simulation. We see qualitative agreement throughout the twisting.

In **Figure 27**, we present the results of the molecular dynamics simulation and qualitative comparison with the 3-D printed specimens for the twisting analysis. The corresponding 3-D printed morphologies are depicted in **Figure 27** where we can see a similar morphology. With a more advanced instron, a stress-angle plot could be recorded but for proof of concept in this paper this is sufficient to show a point. With simulation, we present the results for our twisting analysis in **Figure 28**. Additionally, it should be noted that with no standard for twisting, there exists a considerable uncertainty in the values of angles in the experiment. The purpose of this analysis is to show the extension of our Olog into a new domain for these materials. Our results support this conclusion.
Figure 28: **Stress in Y as a function of angle for simulation.** Here we present the stress of the sample as a function of angle as calculated at LAMMPS. The sample breaks at its bottom as depicted in Figure 27.

6.5 Conclusions

The results here have implications beyond the scaling of Young’s modulus which was the scope of the original study. By expanding this analysis to twisting, we show here that if the constraints imposed by the olog are not violated, one can have an accurate description of the behavior of the system under deformation. Beyond mechanics, it is well known that for tight-binding systems, such as carbon, the symmetry changes during deformation have drastic implication on the electronic structure of these materials. Based on structural shifts we see during the testing of our 3-D-printed samples, we can make assertions about the electronic structure’s response to strain as well if we perform a tight-binding $^{14}$ calculation on a resulting geometry. We present a complex problem and a way to abstract
it through following a series of rules that ensure validity and finally explore calculations that can be done without violating the rules disclosed in the Olog.
Chapter 7: Conclusion and Future Work:

7.1 The mechanics of the extended graphynes

In this work we investigated the fracture of graphdiyne in a single direction, under quasi-static isolated conditions. We have seen an intricate combination of crack arrest and delocalized failure, forming a two-tiered fracture process as visualized in Figure 19F, and provided a detailed analysis of the fracture mechanism which we not is magnified by the specific loading condition which we take to be the extreme for this mechanism. These effects have been linked to the bulk stress strain behavior of the material and explain the saw-tooth behavior seen in Figure 19A. We also compared the results to those of graphene in order to understand the implications of heterogeneous bond strength on the mechanical performance and failure of two-dimensional carbon allotropes. As an emerging engineering material, which has been fabricated, graphdiyne’s failure must also be understood. More work is needed to assess the mechanism of failure of larger samples, and to explore experimental approaches to confirm the mechanism seen here. Other efforts could focus on the development of theoretical models to explain this phenomenon, which is reminiscent of leading and trailing dislocations that occur in certain lattices such as shown in Diao et al. 82.

7.2 Mapping from Atomistic Model to 3-D Printers

We have used ologs to effectively map a phenomenon seen at the atomistic length-scale and described in a model, to a macroscopic prototype whose mechanical features can be tested in bulk. This mapping is carried out by 3-D printer and is verified with a tensile
The subject of this study is the scaling of Young’s modulus in the extended graphynes with allotrope number. The production of samples and testing is done algorithmically to maximize reproducibility. This serves as an example to use mathematical abstraction to allow investigation including the scaling of an inherently molecular mechanism to the continuum length scale to enable experiments that would be impossible at the original length scale. New manufacturing processes such as 3-D printing reduce the latency between the laboratory and implementation. The work here provides a framework that is can accommodate the modern rate of growth while robust enough to ensure that desired information is not lost between the lab and the assembly line.

7.3 Future Work

Future work must address more complex systems and materials using the framework derived here. Scaling of Young’s modulus is an important first step in the use of ologs to realize a model in a new space, but other properties such as thermal, fracture, and optical properties must be translated as well. These systems will certainly have nuances and details that need to be address but the same framework of category theory can be applied. Additionally, future work must test the failure of 2-D carbon materials in application-driven environments such as on substrates and in the presence of solvents.

7.4 Closing remarks

In a world where computers have an ever-increasing role and data sharing becomes evermore prevalent, it becomes clear that collaborators and scientists must use all of the tools at their disposal to find the best solution to their problem. It is not necessarily who can incorporate the most information but rather those who incorporate it well. A future can be anticipated in which materials discovered can be quickly tested and optimized with computers and realized in the field through additive manufacturing and tailored for specific applications on a short time-frame. Although we have presented this here for 2-dimensional carbon, the same framework can be utilized in a myriad of applications
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**Figure 12:** Schematic of representative 3-D printer: At the top-left corner is a reservoir for the printed material. At the top-right corner there is a motor to drive motion in the X-Y plane, by moving the linear rails directly below the reservoir. Similarly for control of z motion, in the center left there is a Z-Motion lead-screw which is driven by a Z-motion motor on the bottom left. On the right side there is a heated nozzle from which material is extracted. In the bottom right corner rests the printed object that sits on a substrate. The substrate is often heated to ensure smoothness of printing.

**Figure 13:** Printed samples and view of inside of 3-D printer: On the left one can see 3-D printer head described. The silver-colored nozzles on the head are where the material comes out. Additionally there is massive amounts of electronics on the head to control and power motion. On the back one can see linear rail for motion in x and y. Samples are covered in solution and sit on top of heated surface.

**Figure 14:** Mounted 3-D printed geometries: In this we show geometries mounted before testing. We note holes for mounting to mitigate out of plane torsions.

**Figure 15:** Simple spring-network model representation of extended graphynes (A) Spring representation of acetylene links and aromatic carbons derived from mechanical simulation performed by Steven Cranford. The stiffness of a single segment is the sum of $k_0$ (the stiffness of the benzene ring) and $k_1$ (the stiffness of a single acetylenic link which constitutes the connection in the mesh).

**Figure 16:** Fracture mechanics of graphynes. Each graphyne sheet was subject to mode I fracture via the introduction of a crack/wedge. (A) Stress-strain results of each model. We note a near-linear stress versus strain behavior for each model, supporting the purely elastic results. In terms of critical stress (onset of fracture) we see failure events consistent with those predicted about by the linear spring model (with ultimate stresses decreasing from approximately 30 GPa for graphyne to less than 10 GPa for graphtriyne/graphtetrayne). (B) Visualizations of the failure indicate that, as anticipated, fracture initiates at the crack and propagates along a plane defined by the single-carbon bonds of the acetylene links (indicated by arrows). A pronounced shifting (e.g., geometric alignment) of the finite samples is observed in the higher allotropes ($n \geq 3, 4$), facilitating the observed “two-tier” effect. Figure reproduce from [40] with permission of Authors and Royal Society of Chemistry.

**Figure 17:** Structure of graphdiyne, geometry of model and application of boundary conditions. (A, B), The structure of graphdiyne contains aromatics of the sp$^2$ motif linked by sp$^1$ acetylene that consist of alternating triple and single bonds, where there are two triple and three single bonds. This is a distinct departure from the structure of graphene. (C), Geometry of the test specimen with relevant dimensions to complement description in methods section. The sample is loaded in the x-direction in mode I. This figure is reproduced from [49].

**Figure 18:** Stress-strain plot and connection with geometry: (A), Stress-strain curves for loading in the x-direction comparing graphene and graphdiyne. A “saw-tooth” behavior can be seen for graphdiyne. Our data shows the implications of the bond breaking mechanisms on the overall stress of this material. (B and D) and (C and E)
show principal stress distributions for graphene and graphdiyne, respectively. These materials are at a point near the first bond-breaking event. This figure is reproduced from [49].

**Figure 19:** Mechanism of failure in graphdiyne, visualized using principal stress distributions. The field plots are presented at different deformation states to show the propagation of the crack and to expose the delocalized failure mechanism. The respective strains are A=3.9%, B=4.2%, C=4.4%, D=4.5%, E=5.5%, and F=6.5%. We notice that the crack begins to propagate along the y-axis but almost immediately progresses along a diagonal. This causes a reorganization of stress concentration that deviates from the failure behavior of graphene that is directed along the axis of the initial crack (see also Figure 21). This figure is reproduced from [49].

**Figure 20:** Detailed view of the molecular mechanism of failure of graphdiyne, clearly revealing the two-tiered fracture process. The horizontal propagation occurs at a faster rate than that of the diagonal bonds such that the region of partial fracture grows as the system is loaded. We present here a closer view of the samples above at strains of A=3.9%, B=4.2%, C=4.4%, D=4.5%, E=5.5%, and F=6.5%, respectively. This figure presents the crack from the formation of a small group of delocalized voids to (E) and (F) in which several bonds are broken in isolation from the continuous crack. This figure is reproduced from [49].

**Figure 21:** Comparison of crack propagation for graphene and graphdiyne. Graphene (panels A and C) is shown at a strain of 17.2% while graphdiyne (panels B and D) is shown at a strain of 6.5%. The difference in direction in crack propagating is that graphene follows a path that is straight in the y-direction and graphdiyne’s propagates along a path that is diagonal to the vertical. Graphene experiences symmetric stress distributions about the crack and graphdiyne’s crack turns and re-centers itself along the diagonal. This figure is reproduced from [49].

**Figure 22:** Functorial translation between the atomistic structure and function of Graph-X and the macroscale printed material. Each aromatic is to be realized by a 3-D-printer as a vertex, and each acetylene is realized as an extruded edge.

**Figure 23:** Olog formalizing graph-X model from [40], used for 3-D printing. Graph-X is modeled as a symmetric graph, consisting of aromatics (A) and alkyne chains (C). Each chain has a length of 3 Å. An aromatic is considered a 2-D material sample (MS), each alkyne chain is realized as a 2-D material sample with either axial or orthogonal loading direction (MSL). All loaded 2-D material samples are characterized by a spring constant (K), and the aromatics are isotropic. 2-D material samples are given a 3-D representation using 1 Å cutoff around their surface (Vol, VolL). The commutative diagrams are shown in the upper right box. Note that a standard tensile test for 2-D materials does not yet exist, but any standard like the ASTM will suffice.

**Figure 24:** Geometries of Samples: 3-D Printed and Atomistic a) Printed samples with mounting. Samples are loaded through hole in mounting. Both Right: The corresponding atomistic models of structures. b) Sample loaded on tensile testing apparatus, secured by clevis pins. It can be see that sample is loaded in a way to guarantee a uniform loading in the desired direction. Additionally, the loading mitigates moments out of plane.
**Figure 25:** Results of tensile test with scaling behavior. Young’s modulus measured using tensile testing compared with the theoretical $Y = ax - 1$ scaling that is seen in the original work for a) Reclined Chair loading direction and b) Zig-Zag loading direction. We note a general very good agreement between the data and the theoretical curves, based on the use of a single parameter. (Fitting done using the autofit function within the curve-fitting toolbox in MATLAB.)

**Figure 26:** Schematic of twisting analysis. The twisting is performed in both experiment and modeling by fixing a region of atoms at the bottom of the sample. At the top of the sample, the region of the sample twisted along the y-axis through the middle of the sample.

**Figure 27:** Result of twisting analysis. Twisting is performed on both an atomistic and 3-D printer abstractive model. The top row shows twisting of the 3-D printed composite while the bottom row shows snapshot from the atomistic simulation. We see qualitative agreement throughout the twisting.

**Figure 28:** Stress in Y as a function of angle for simulation. Here we present the stress of the sample as a function of angle as calculated at LAMMPS. The sample breaks at its bottom as depicted in Figure 27.

**References**


