

MODULE 3: Structures
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*“To those whose tracks we have followed and those who will follow ours”
– V.K. Pecharsky and P.Y. Zavalij*

LEARNING OBJECTIVES

1. Identify the three basic crystal structures
2. Describe a unit cell and a crystal lattice
3. Connect back to the crystal structure of graphene

BACKGROUND

One of the most interesting parts of materials science is that materials can form different crystal structures. You don't always think about how atoms and molecules arrange themselves, but this is a key concept to consider when picking a material. In Module 2, we saw the importance of considering different sizes in materials (and how their size may affect their materials properties). Now we will look at materials and their structures.

Now you may be thinking to yourself, or not, “there couldn't possibly be that many different materials structures to discuss...” but there are actually many combinations that can change a material's properties.

To begin, there are three types of crystal structures: crystalline, polycrystalline, and amorphous structures. Figure 1 shows the difference between the three types of structures. You can see that the atoms (circles) in the crystalline structure are neatly arranged in rows and columns, while the amorphous structure is disordered. The polycrystalline structure has several ordered regions that do not always line up where they meet. Generally, when studying different crystalline structures, we focus on crystalline solids.

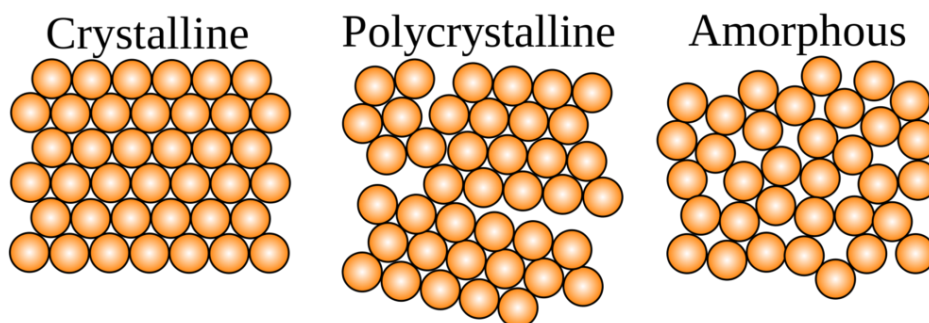


Figure 1. The three types of crystal structures: crystalline, polycrystalline, and amorphous [1].

An important factor for **crystallography** (the study of crystal structures) is how the atoms and molecules are bonded. On a very basic level, there are both repulsive and attractive forces affecting **chemical bonding** (like in ionic and covalent bonds). There are several types of chemical bonds: **ionic bonds**, **covalent bonds**, **metallic bonds**, and **secondary bonds**. The

elements' **electronegativity** is one important factor in the kind of bonds and structures formed in a material.

Now back to crystal structures. An important concept to understand is the unit cell and the crystal lattice. An ideal crystal, like the one pictured in Figures 1 and 2, has a periodic, or repeating, structure. We could describe the location of each of these atoms, or instead, we could use a smaller piece of the repeating structure. The larger structure is called a **lattice**, and the smaller repeating regions are **unit cells**. In a lattice, all **unit cells** are equal in their shape and content. Most significantly, if the location of atoms in a one-unit cell is known, then the structure of the whole crystal can be reconstructed by translating or shifting this unit cell along any direction. [2] Figure 2 shows an example of a construction of a lattice with several unit cells.

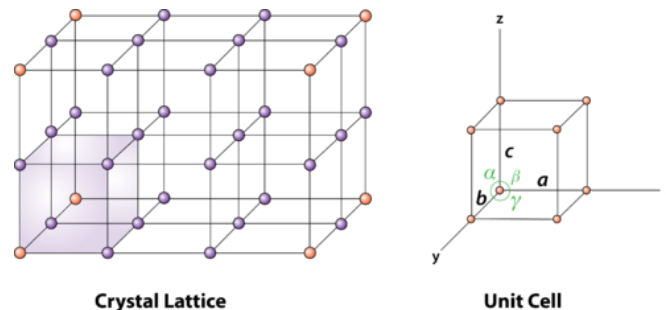


Figure 2. Example of the crystal lattice in comparison to a material's unit cell [3].

Since we have now discussed the crystal lattice and unit cells, we can dive into more specific crystal systems and lattice shapes. This module will only talk about three of these lattices: the **simple cubic (SC)**, **face-centered cubic (FCC)**, and **body-centered cubic (BCC)**. Figure 3 demonstrates the cubic crystal system of the three types of unit cells. In simple cubic, the atoms or ions are at the corners of the unit cell only. The face-centered cubic has atoms or ions at the corners and also has atoms or ions in the center of each of the faces of the unit cell. For the body-centered cubic unit cell, there is one atom or ion in the center of the unit cell in addition to the corner atoms or ions.

As I have previously mentioned, there are many different crystal structures. In this module, we focused on the most important information, but there is obviously a lot more content that could be covered. The thing is, to really truly understand materials you must understand crystal structures. Additional resources, simulations, and virtual activities are also available in the **ADDITIONAL RESOURCES** section of this module.

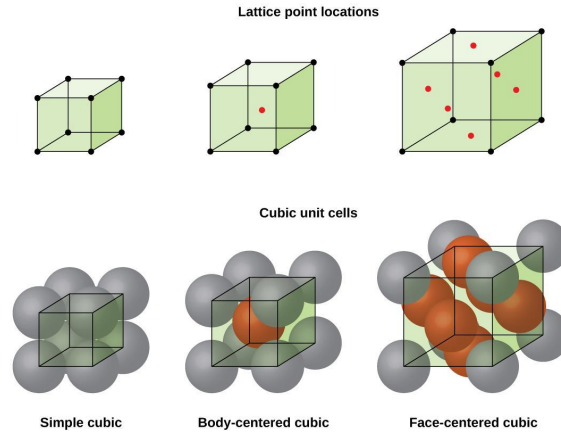


Figure 3. Simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) diagrams representing locations of their atoms within the lattice [4].

Let's connect this back to graphene and MODULE 1. Carbon is a light atom with six protons and six neutrons in its nucleus. The electrons are arranged with two electrons in the inner shell, and four electrons in the next shell (which can hold eight electrons). The simplest thing a carbon atom can do is share each of its four electrons with another carbon atom, forming four chemical bonds. Since there are four active electrons, each electron is partnered with a corresponding electron, belonging to another carbon atom. In this specific scenario, the crystal structure is extremely rigid and known as the diamond crystal structure (see Figure 4). Figure 4 shows the comprehensive shape for a carbon structure including diamond, graphene, graphite, and carbon nanotube structure.

Remember, graphite is the most common type of carbon. We can consider this to be our first form or type of carbon.

The second form of carbon that we can discuss is graphene. Graphene is a single, two-dimensional (2D) layer of carbon packed in a **hexagonal lattice**. As the name suggests, the lattice is based on a hexagon instead of the squares for the cubic structures, where each carbon atom is bonded to three other carbon atoms. We mentioned that carbon has four active electrons, but so far, we've only accounted for three of these. What happens to the fourth electron for each atom? Well, in a graphene sheet, the outer electrons do not just bond with a counterpart electron in a neighboring atom but rather form a sea of electrons within the material. Because of this, graphene can conduct electricity. It is the thinnest, strongest, and stiffest known material. It also can conduct heat faster than other materials and carry electricity with little resistance. This means that graphene has the potential to be used in many electronic applications such as replacing silicon chips and touchscreens. Think about the "sticky-tape experiment", why is it so easy to remove the sheets of graphene from one another to graphite? This is because of van der Waals bonding. This type of bonding is important for graphene because of the repulsion and attraction between the atoms. The repulsion makes it easier for the graphene to be pulled apart and made into sheets of graphite.

The third form of carbon is diamond. We know that in a diamond, all the atoms in the lattice are strongly held in a bond and that there are no "free" electrons. This is due to the fact that the electrons can move around freely like fluid, unlike in a diamond due to its structure. Also,

compared to diamond, graphite has a hexagonal shape similar to graphene. You may have also heard about a fourth form of carbon: carbon nanotubes. Connecting back to nanotechnology and size, carbon nanotubes are graphene sheets that are rolled up to form a long, thin tube. Current nanotechnology research is working to extend the length of carbon nanotubes beyond a few hundred nanometers in length. [5]

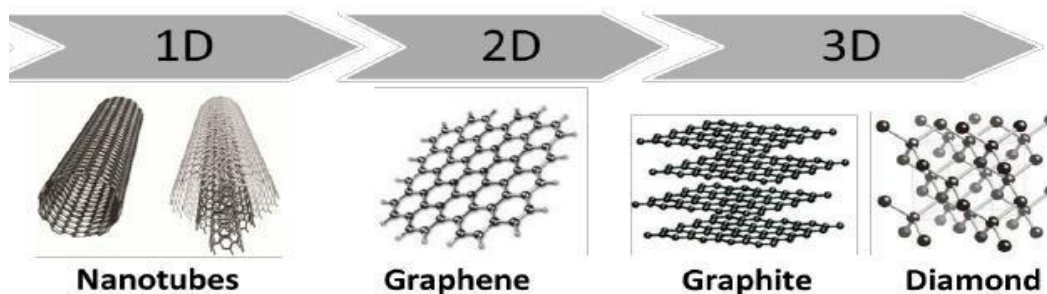


Figure 4. Structures of carbon [6].

REFERENCES

- [1] “The Solid State: Crystalline and Amorphous Solids,” *Toppr*.
<https://www.toppr.com/guides/chemistry/the-solid-state/crystalline-and-amorphous-solids/>
- [2] V.K. Pecharsky and P.Y. Zavalij. (2009) *Fundamentals of Powder Diffraction and Structural Characterization of Materials*. 2nd Ed. Springer.
- [3] Nguyen, Minh, Mandeep Singh. (2020). “Unit Cells,” *Lumen Learning, LibreTexts*.
<https://courses.lumenlearning.com/cheminter/chapter/unit-cells/>
- [4] Flowers, Paul, Klaus Theopold, Richard Langley, et al. “10.6 Lattice Structures in Crystalline Solids,” *Rice University, OpenStax*. <https://openstaxbc.ca/chemistry/chapter/10-6-lattice-structures-in-crystalline-solids/>
- [5] M. Miodownik. *Stuff Matters: Exploring the Marvelous Materials that Shape Our Man-Made World*. 1st Ed. Houghton Mifflin Harcourt Publishing Company. 2015.
- [6] Srivatsa, Thushar. (2017). “Graphene-Based surface coatings on ceramic membranes for water desalination”.

ACTIVITY

Draw the structure

Level of Difficulty: Intermediate

Note: The internet may be necessary for this activity

Instructions: We discussed three cubic crystal systems (SC, FCC, and BCC). Using the internet or the figures provided in this module's background, draw the three systems below in the space provided.

Simple Cubic	Face-Centered Cubic	Body-Centered Cubic

Crystal Viewer: Learning through Simulations

Level of Difficulty: Expert

Note: The internet is needed for this activity

<https://nanohub.org/tools/crystalviewer>

The purpose of this activity is to get familiar with using the nanoHUB website and getting into using virtual simulations. This is a good starting point for activities in later modules (like MODULE 4) that has a simulation.

Procedure:

It may be helpful to refer to Figure 5 when completing steps 1-4, to find the correct buttons to click.

1. Open the nanoHUB website and simulation tool: <https://nanohub.org/tools/crystalviewer>
2. There are two tabs when you open the Crystal Viewer: the "Crystal Viewer" and the "Bravais View." We will first begin looking at the "Bravais View."
3. While using the "Bravais View" tab, under "Crystals" select the first image which is the cubic crystal system.
4. Once the cubic crystal system is selected, you can then toggle between the three different Bravais lattices (the simple cubic, body-centered cubic, and face-centered cubic).

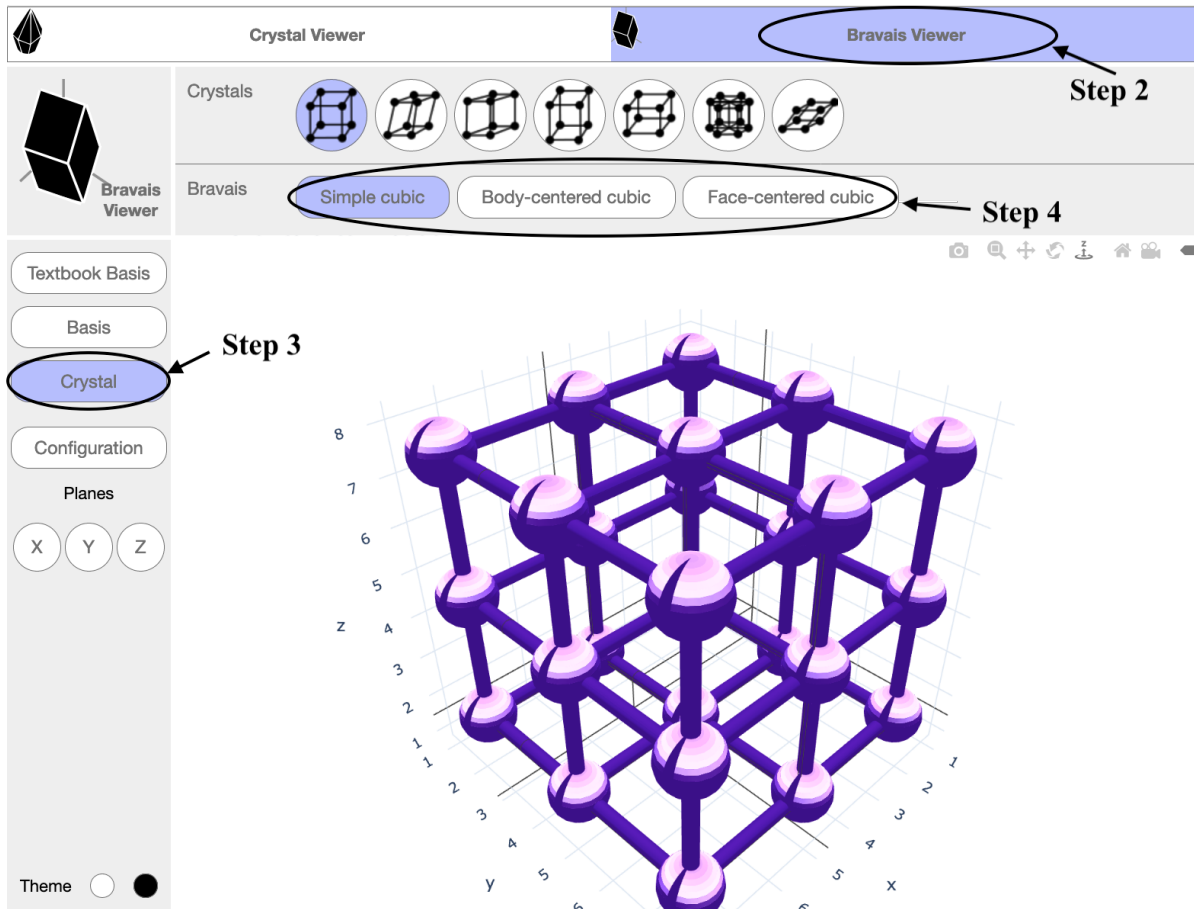


Figure 5. Procedure for steps 2-4.

- Next, change from the “Bravais View” to the “Crystal View.” We will only be using a few features of the “Crystal View,” but feel free to explore this amazing simulation tool!

We will again be looking at the simple cubic, body-centered cubic, and face-centered cubic features of the “Crystal View.” For this part of the simulation, the steps are shown in Figure 6.

- In the simple cubic tab, choose between the Cu, Al, Ag, and Au views.
- Draw one of the simple cubic structures. Note significant features.
- Change to the body-centered cubic tab.
- Draw the body-centered cubic structures. Note significant features.
- Change to the face-centered cubic tab. In the face-centered cubic tab, switch between the NaCl and SmSe crystals.
- Draw one of the face-centered cubic structures. Note significant features.

Note: The Crystal Viewer tool on nanoHUB offers various perspectives and vantage points of different crystal systems. This activity only explores a taste of what the simulation has to offer.

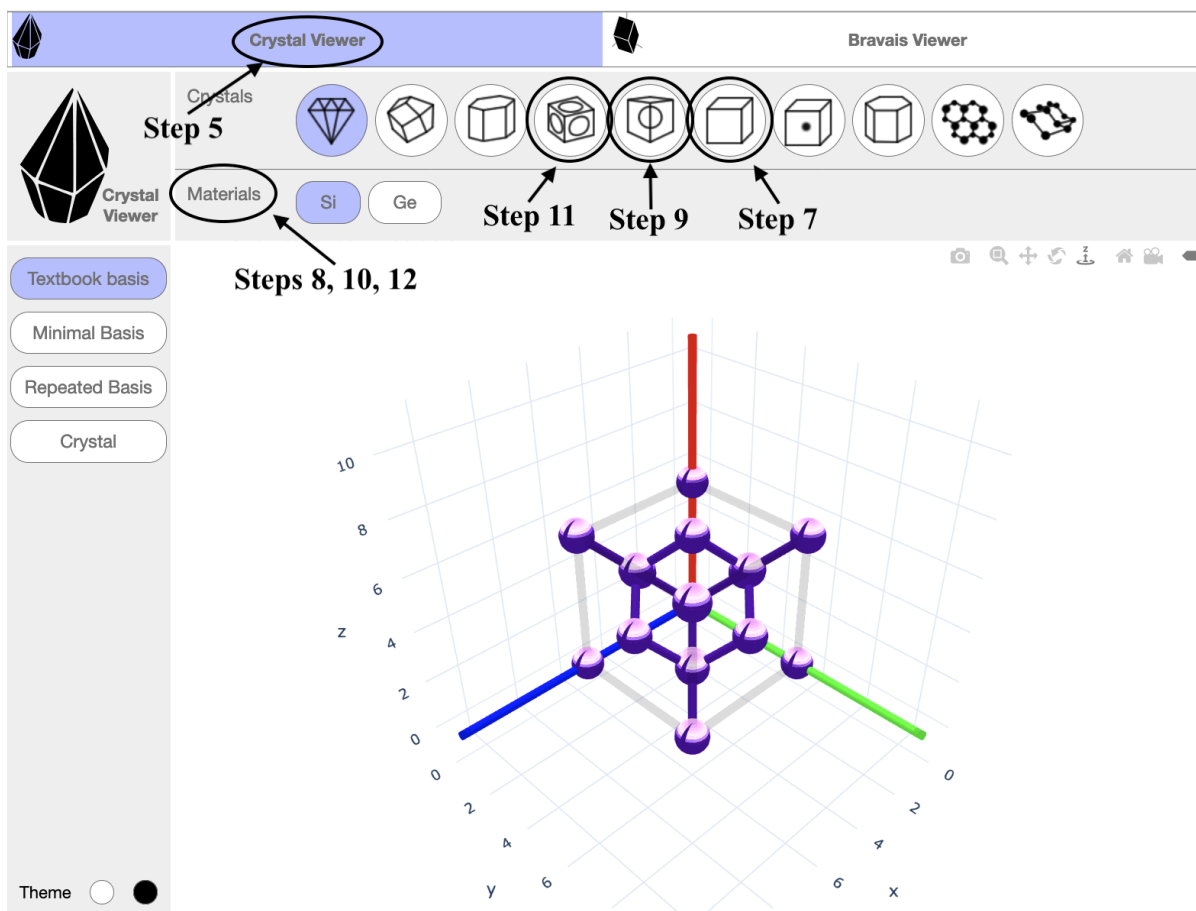


Figure 6. Shows the procedure for steps 6-10.

If you would like to see the shape of graphene using this simulation, you will have to use an older version of it, which can be found here: <https://nanohub.org/resources/3741?rev=336>. Follow the same process of the Crystal Viewer simulation in the Procedure above (but in “Crystal View,” select the graphene icon).

Questions:

- In step 7, is there a difference between the Cu, Al, Ag, and Au views? Why or why not?
- In step 9, is there a difference between the NaCl and the SmSe crystals? Why or why not?
- Compare the simple cubic, body-centered cubic, and face-centered cubic structures. What are key differences between the three?

ADDITIONAL RESOURCES

- Video on Unit Cells (The Organic Chemistry Tutor):
<https://www.youtube.com/watch?v=h-Xv9nsJLc>

CONCLUSION

In this module, the basics of crystal structures were investigated. The unit cell and the crystal lattice were described in order to discuss the cubic crystal systems (simple cubic, body-centered cubic, and face-centered cubic).

Key Takeaway: There is a lot to learn about crystal structures, and these are integral to our understanding of graphene.

“The edifice of science not only requires material, but also a plan. Without the material, the plan alone is but a castle in the air—a mere possibility whilst the material without a plan is useless matter.” – Dmitri Mendeleev, Chemist

APPENDIX

There were a lot of bonding terms in the BACKGROUND of this module, which are defined in this APPENDIX.

Now we will jump into the different bonds. Most likely, you have already heard (or learned) about some of these, especially if you have taken a chemistry class. To begin, an important concept of atomic interactions and bonding is **electronegativity**. **Electronegativity** is the tendency of an atom to attract a shared pair of electrons. This is related to the atomic number and the distance between the valence electrons from the atom's nucleus. **Valence electrons** are the electrons in the outermost shell, or energy level, of an atom.

There are three primary types of bonding [1]:

- **Ionic bonding:** valence electrons are transferred from one atom to the other to complete the outer electron shell. This creates positive and negative ions that are attracted.
- **Covalent bonding:** valence electrons from one atom are shared between two or more particular atoms.
- **Metallic bonding:** valence electrons are not associated with a particular atom or ion, but exist as an electron cloud around the centers of many ions.

Secondary interactions are also possible between atoms [2]:

- **Dipole-dipole interactions:** created when positive and negative centers exist, in other words, an asymmetrical distribution of electron charges within the electron cloud.
- **Hydrogen bonding:** considered a type of dipole-dipole interaction; exists between polar bonds containing a hydrogen atom that is normally covalently bonded to fluorine (F), oxygen (O), or nitrogen (N) atoms.
- **van der Waals interactions:** fluctuation-induced dipole bonds based on attraction and repulsion. The charge on the atom in motion is redistributed.

References

[1] CES Information Guide--Materials Science Engineering. (2006). "Atomic Bonding," *University of Washington*.

https://depts.washington.edu/matseed/ces_guide/bonding.htm#:~:text=There%20are%20three%20primary%20types,ionic%2C%20covalent%2C%20and%20metallic.&text=Definition%3A%20An%20ionic%20bond%20is,complete%20the%20outer%20electron%20shell.

[2] "Intermolecular Forces," *Lumen Learning*. <http://myweb.ncku.edu.tw/~cyylin/0802.pdf>