

Thinking in 3D Teachers' and Techs' Conference 2022





2022 Teachers' and Techs' Conference: Thinking in 3D

'Thinking 3D' is a new workshop inspired by the Bodleian Library exhibition of the same name, exhibited in the summer of 2020 and a talk by Dr Martin Galpin. This workshop uses this central theme to address four primary foci within the workshop:

- 1. Allotropes of Carbon
- 2. The use of Mathematics in Chemistry
- 3. Critical Evaluation of Modelling used in Chemistry
- 4. Fullerene Chemistry at the University of Oxford

The workshop is presented in a circus format, with classes divided into four teams of ideally 4-5 pupils each. This format illustrates the central advantage of our workshop; all three foci can be interconnected in many different ways, all under the central umbrella of thinking in three dimensions. We hope you may be able to apply some of the resources from this workshop to use in your lesson plans.

Contents:

Allotropes of Carbon	Background Information, Tarsia Puzzle, Files for 3D Printing Models (separate attachment)
Mathematics in Chemistry	Background Information, Proof of the Euler Characteristic, Proof of the 12-Pentagon Rule for Classical Fullerenes
Modelling in Chemistry	Information about iMolview Lite and ChemFord software, Sample Critical Questions
Fullerene Chemistry at Oxford	Current research with fullerenes and allotropes of carbon





Thinking in 3D Station Two Demonstration of the Euler Characteristic.

Focus One: Allotropes of Carbon

Key: Allow students to recognize the importance of shape to the structural properties of carbon.

In this activity, students are encouraged to connect the properties of allotropes of carbon to their structure. Three illustrative allotropes will be investigated: diamond, graphite/ graphene, and Buckminsterfullerene. The final activity in this station is a tarsia puzzle designed to test student retention of discussed concepts and pose a great challenge in problem solving skills!

Background Information:

Carbon is a chemical element found in the periodic table with the chemical symbol C. It belongs to group 14 of the periodic table and has a proton number of 6 and a mass of 12 g/mol.

The atoms in carbon can bond together is diverse ways resulting in the various allotropes of carbon.

Allotropes are different structural forms of the same element in the same physical state.

Some examples of different allotropes of carbon include graphite, diamond and Buckminsterfullerene. These allotropes have the same atomic unit but very different chemical and physical properties. Hence, we conclude these differences must be a result of structure.

Consider the properties of these allotropes in more detail.

Diamond is shiny, hard and highly transparent, in stark contrast to graphite. Diamond is the hardest naturally occurring material known. Diamond has an extended covalent lattice structure, with each carbon having four covalent bonds. Thus, the lattice has tetrahedral shaped connectivity around each carbon.

The strength of the covalent network is responsible for the high melting point of diamond. Significant energy is required to overcome these covalent bonds in the process of melting. Diamond has no free moving (delocalised) electrons therefore, it does not have a charge carrying medium. This makes diamond non-conducting and a very good insulator.

Graphite is dark and opaque. It is soft in nature and this is as a result of its structure. The pattern of bonding in graphite forms hexagonal shaped connectivity between carbons with three covalent bonds per carbon, which form layers in the extended structure. These layers overlap each other and are only weakly attracted to each other via intermolecular forces. Layers within graphite are therefore able to slide over each other which gives rise to the softness of graphite. This property is utilized with pencils, as when writing, sheets of graphite are scraped onto the paper.

Due to the strong covalent bonds between carbons within the sheets, graphite has a high melting point. Graphite also as free moving (delocalised electrons) which act as charge carriers giving graphite the ability to conduct electricity. A single sheet of graphite is known as graphene.

Fullerenes consist of single molecule caged structures formed by carbon units. This imposes a number of geometrical constraints on the fullerene if it is closed, which will be investigated in this workshop. However, there are also many partially open-cage shapes included in the family. The most famous and first discovered of fullerenes is buckminsterfullerene, C_{60} . This is the most energetically stable fullerene and is therefore most easily formed.

Both fullerene and graphite consist of carbon atoms covalently bonded to three other carbons, with a hybrid of single and double bonds. However, as the carbons are arranged to form a closed polygon in fullerenes, bonds are distorted from their ideal angles.

This changes the electrical properties of fullerene compared to graphene, as only fullerenes with 2n+2 carbons, where n is the number of carbons, are aromatic with electrons delocalized across the entire molecule. Also, as fullerenes have a molecular structure only held together by weak intermolecular forces, they have low melting points.



Challenge Card for Tarsia Puzzle Depicting from Left to Right: Diamond, Buckminsterfullerene and

Graphite

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Tarsia Puzzle:

Please find the Tarsia puzzle templates and solutions attached. Note different sections of the puzzle can be printed on different coloured paper to help the students arrange the pieces and divide the work. We suggest dividing into four smaller triangular puzzles which fit together to form the final product.



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3D Models Files for 3D Printing:

Please find in a separate folder the .stl files used for 3D printing of the carbon allotropes investigated throughout this focus. Models provide a great way for students to illustrate key structural characteristics and relate them to chemical properties! Other modelling suggestions for the allotropes of carbon include using molymod kits or encouraging students to use classroom supplies to model structure.



Students using Models of Buckminsterfullerene in Station 3 of 'Thinking 3D'

Focus Two: Mathematics in Chemistry

Proof and Introduction of the Euler Characteristic:

Key: Illustrate the challenge of representing 3D shapes in 2D and introduce the Euler Characteristic.

In this activity, students are introduced to the Euler characteristic and prove it using Cauchy's proof.

Background Information:

In understanding chemical shape, we must consider geometry which may impose confines on a structure and therefore affect behaviour. This point is best illustrated with fullerenes, which are subject to geometrical constraints of convex polyhedra.

Today, we have many ways of visualizing 3D objects, from physical models to virtual reality. However, 300 years ago it was a significant challenge to communicate 3D shapes, which inhibited geometrical advancement at the time.

In 1752, a mathematician called Euler, one of the most influential mathematicians of all time, noticed a peculiar characteristic about polyhedra. In attempting to classify polyhedra by their

geometrical properties, he noted that if he subtracted the number of edges from the number of vertices and added the number of faces, the result was consistently 2.

Having tested his hypothesis on a number of polyhedra, Euler now proposed his conjecture:

$$V - E + F = 2$$

Ultimately, Euler could not prove his result. However, mathematics is a highly collaborative field, and about 60 years later, in 1811, another mathematician Cauchy proposed a proof for Euler's conjecture.

First, Cauchy had the idea to represent 3D polyhedra as 2D <u>graphs</u>. Essentially, we are squishing polyhedra into the plane of the paper. This proof relies on a series of manipulations of the polyhedra. So, for each manipulation, importantly keep in mind, is this changing the total V - E + F?

To complete the proof, draw a generic map of a polyhedron. Now, add diagonal lines such that all faces are triangles. Confirm this does not change the total number of V-E+F. For every diagonal we add one edge and one face, so the total does not change.



Now begin removing border triangles such that the graph remains intact. This still does not change V-E+F as we remove two edges, a face and a vertex or one edge and one face. Note we must only remove *border* triangles for this to work!



Now if we continue this removal, we are left with a single triangle! For this triangle, V-E+F=2. As we have said throughout the proof, we have not changed the total V - E + F. Therefore, our original general polyhedra must have had a total factor of 2! This is Cauchy's proof, as it can be extended to any polyhedra which we can represent using a 2D map.



Proof and Introduction of the 12-Pentagon Rule:

Key: Illustrate properties of fullerenes structures we can deduct from their geometry and the Euler characteristic.

In this activity, students will apply the Euler characteristic to fullerenes. In doing so, they will show fullerenes must have an even number of carbons, contain 12 pentagons and have a general formula in terms of the number of hexagons. If there is time, they will be challenged to think about the connection between geometric feasibility and stability. Models are important tools in this activity, in particular to illustrate relations between geometric entities!

Background Information:

Geometric constraints are greatly important in fullerene chemistry, as they dictate the possible shapes we can construct. Classic fullerenes are generally considered to consist of only pentagonal and hexagonal faces. Within this criterion, we can use the Euler characteristic of 2 to derive a number of properties of classic fullerenes.

First, by considering that each carbon connects three edges of fused carbon rings, we realize we can express the number of edges in terms of the number of vertices. We must divide by 2 as each edge connects two vertices, so without this factor we would double count edges.

$$E=\frac{3V}{2}$$

As both the number of edges and the number of vertices are integers, we see from this relation that V must be an even number. An even or odd number (number of edges) times two *must* be an even number. Thus, the left-hand side of the below equation is always even. An odd number (3) times an odd number is always odd. Therefore, for the right-hand side of the below equation to be even, V *must* be an even number. That is, the number of carbons must be even.

$$2E = 3V$$

Now, consider the Euler factor of 2 (deduced in Activity 2):

$$V - E + F = 2$$

On substituting the first expression above for the number of edges in terms of the number of vertices:

$$V - E + F = 2$$
$$V - \frac{3V}{2} + F = 2$$
$$-\frac{V}{2} + F = 2$$
$$2 + \frac{V}{2} = F$$



Now, if we consider a fullerene to consist only of pentagons (P) and heptagons (H) then we can express the total number of faces in terms of hexagonal and pentagonal faces:

$$F = H + P$$

We can also express the total number of vertices in terms of hexagonal and pentagonal faces. A hexagonal face has six vertices and a pentagonal 5. Each vertex connects three faces, so we must divide this total by 3 to avoid triple counting.

$$V = \frac{5P + 6H}{3}$$

Therefore, we have the following three relations:

$$F = P + H$$
$$F = 2 + \frac{V}{2}$$
$$V = \frac{5P + 6H}{3}$$

Setting the first two equations for F equal to each other to eliminate F, then collecting like terms to eliminate V, and finally substituting the third relation for V reveals:

$$P + H = 2 + \frac{V}{2}$$

$$P + H = 2 + (\frac{5P + 6H}{3})/2$$

$$P + H = 2 + \frac{5P + 6H}{6}$$

$$P + H = 2 + \frac{5}{6}P + H$$

$$P - \frac{5}{6}P = 2 + H - H$$

$$\frac{P}{6} = 2$$

$$P = 12$$

That is, every classical fullerene has 12 pentagonal faces!



$$P + H = 2 + \frac{V}{2}$$
$$12 + H = 2 + \frac{V}{2}$$
$$H = \frac{V}{2} - 10$$

If we rearrange to solve for the number of vertices:

$$H = \frac{V}{2} - 10$$
$$\frac{V}{2} = H + 10$$
$$V = 2H + 20$$

Which is a general formula for geometrically feasible fullerenes, considering V is equal to the number of carbons.

However, just because the structure is geometrically feasible does not mean it is stable. Consider from our formula that the smallest possible formula is C_{20} . Yet, the first synthesized due to its increased stability relative to the rest of the series was C_{60} . Theoretical calculations of fullerenes have led to the development of the isolated pentagon rule, which states there is a greater energy cost to have two fused pentagons compared to a pentagon fused to a hexagon. C_{60} is the first fullerene in the series to have all pentagons only adjacent to hexagons, which plays a role in its increased stability.



Students completing 12-Pentagon Proof with demonstrator guidance.

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Focus Three: Critical Evaluation of Modelling in Chemistry

In this station of the workshop, the Chemistry Teaching Laboratory is grateful to use a departmental virtual reality set to illustrate critical themes in the comparison of different models used throughout the workshop, including: 2D models of 3D shapes with Schlegel diagrams, static 3D printed carbon allotrope models, and now virtual reality models.



Students interacting with VR in the Chemistry Teaching Laboratory

Other technology is easily accessible to model in chemistry. Two illustrative examples include iMolview Lite and ChemFord.



iMolview Lite:

iMolview Lite is freely downloaded from the App Store. It allows for interaction with generated models from its large library of chemicals. It also can be used for construction of specific molecules and includes protein and DNA structures.



ChemFord:

ChemFord uses AR (augmented reality) to model molecules. It is also freely downloadable from the App store. Trigger images can be found on the website: http://elforddaniel93.wixsite.com/chemford. The camera needs to be pointed at a trigger picture in order for the desired molecule to be displayed. The user may then interact with the molecule.

This software may also be used in other lessons, such as to introduce functional groups at the GCSE level or VSEPR at the A level.



Focus Four: Fullerene and Other Carbon Allotrope Chemistry at Oxford University

Key: Students will connect what they have been learning in the workshop to fullerene chemistry at Oxford.

In this activity, students will practice summarising information. Current research is used to illustrate the relevance of topics learned and to pique interest to cement important concepts into students' minds.

Background Information:

Fullerene chemistry is prominent across many research groups in Oxford.

The Compton group is interested in the electrochemistry of fullerenes. C₆₀ has interesting electrochemical properties as it can be both oxidized and reduced. That is, it can accept electrons to become negatively charged, or it can donate electrons to become positively charged. This is because the valence orbital of the fullerene molecule is partially filled and can either be filled completely or depleted of electrons.

The Compton group applied this electrochemistry to detect C_{60} nanoparticles. Nanoparticles are defined as being between 1 and 100 nanometres long. This is different from a sample of C_{60} as it is much smaller, and not visible to our eye. Nanoparticles are on the molecular scale. It has been reported that C_{60} nanoparticles are toxic to humans.

Hence, the Compton group hypothesized that they could detect C_{60} nanoparticles using their electrochemical properties. By using an electrode, the Compton group was able to catalyse a redox reaction of C_{60} and measure a voltage change, thereby allowing them to detect the nanoparticle of interest.



The Beer group is leading an investigation into the use of fullerenes in molecular machines. Molecular machines refer to molecules that are designed to respond in a mechanical way when stimulated by a specific input. Many molecular machines can be found in nature and biological examples include proteins which allow for movement, gene expression, and energy production.

Fullerenes are particularly suited to bind to host systems as their size can be easily manipulated. The Beer group focussed on designing large molecules to selectively interact with C_{60} and C_{70} fullerenes. C_{60} and C_{70} are both good electron acceptors, so the host cavity interacts with these molecules via a redox mechanism.

The Beer group aims to exploit this property of fullerenes in molecular machines by designing a mechanism which is stimulated by the fullerene interaction with the host cavity. Excitingly, the electronic interactions between the host and fullerene can be tuned to signal when an interaction has occurred. This can be used in sensing the fullerenes themselves, or in a larger molecular machine where the interaction of another detectable molecule causes the electrochemical charge transfer between the fullerene and host.



The Foord group also does significant work with carbon allotropes on surfaces. The Foord group utilizes carbon in the form of nanomaterials, which are defined as being on the scale of 1-100 nanometres. The group is particularly interested in nanodiamonds, graphene (a single sheet of graphite), nanotubes, and carbon onions (fullerenes nested inside of each other). These materials have a wide range of applications when applied to a thin film as they are porous, for a potential use as a sieve, and they can occupy high surface areas. The Foord group aims to investigate the potential use of these materials in battery electrodes.

In another vein of their research, the group investigates diamond nanoparticles. We know diamond is non-conducting, but on this scale in a thin film the layer can be modified to make the surface electrically conducting. This phenomenon has exciting potential applications in sensory devices whereby this current is detected.

Finally, the group investigates the interactions of these carbon nanomaterials with polymers. Interactions between carbon allotropes and polymers can be exploited to change properties of the polymer, such as modify its physical properties, electrical behaviour, and its interactions with other molecules.



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The Tsang group is interested in the cavity within fullerenes. Fullerenes can be separated based upon their size. Hence, a specifically sized fullerene can be isolated to give a known cavity size within the fullerene. Only ions of the right size are encapsulated within the fullerene. This allows the researchers to selectively bind ions by size.



In order to further trap the ion of interest, the Tsang group encapsulates it within a nano-carbon onion. A nano-carbon onion refers to a series of nested fullerenes, with the ion of interest in the centre. This has important applications in medical diagnosis. Radioisotopes are used as tracing agents to help doctors develop images of the body, which is in turn used to detect abnormalities. This works by using devices which detect the emitting gamma rays from the radioisotope. Trapping the radioisotope within a nano-carbon onion provides a suitable vehicle for the radioisotope.

The Tsang group is also particularly interested in carbon nanotubes as vehicles for catalysis or separation. They aim to use this material as a nanoscale "test tube.

Please find more information about current chemistry research at: http://www.chem.ox.ac.uk

Acknowledgements and copyright:

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