

Polymorphic Adaptation

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Abstract. Polymorphism, the ability of a substance to exist as multiple, different, crystalline solids is a subject of much interest in the fields of chemistry, pharmacy and crystallography. In some cases, polymorphs can be found to interconvert, usually in response to changes in the physical environment such as changes in temperature or pressure. The ability of structures composed of identical building blocks to interconvert is relevant to the field of architecture where architectural artefacts may require to respond to transient demands. Here we describe the phenomenon of polymorphism and the relevance to the architectural field, together with the development of a bespoke software plugin to allow polymorphic crystal structures to be used in design.

Keywords: Collaborative Design Research, Polymorphism, Digital Form Studies

1 Introduction

This paper illustrates the phenomenon of "polymorphism", a widely studied concept in the science of crystallography, and articulates the potential to utilize this phenomenon to design adaptive physical systems for architectural applications. The term polymorph is derived from the Greek words *πολυ* ("polu") which means many and *μορφη* ("morphē") which means form, thus translating as many forms. In crystallography, polymorphs are solid, crystalline substances with identical chemical composition but different atomic or molecular arrangements. Different polymorphs of the same substance often exhibit considerable variation in their physical properties. Polymorphism thus presents itself as an important principle as it illustrates that chemical composition alone is not enough to determine the physical properties of a crystalline substance, and highlights the significance of structure in relation to properties [1-4]. This paper discusses how the characteristic of polymorphic substances to exist in multiple forms (crystalline arrangements) and to transform from one form to another under certain conditions may find potential applications in design.

Architectural artefacts must often respond to transient demands. These demands could be environmental, in which a change in external temperature and humidity may require a corresponding change in architectural features to maintain comfortable internal ambient conditions. The demands could also be spatial or structural, in which the same space must serve different programmatic functions at different points in time, or they could be optical, where the same space requires modulation in its levels of transparency. This paper suggests that adapting and applying some of the principles of polymorphic transformations will help to address the above situations, by informing design research in the field of adaptive architecture in the following ways:

- by systematizing how designers understand the relationship between structure and physical properties;
- by interpreting the transformation from one (polymorphic) structure to another, for a variety of polymorphic geometries;
- by providing arrays of a variety of components that can be assembled into a variety of tectonic arrangements.

2 Polymorphism

An understanding of the geometric principles that underlie the arrangements of the building units (e.g. atoms, ions or molecules) in crystalline materials is key to understanding the phenomenon of polymorphism. In the fields of chemistry and crystallography, the spatial arrangements of the building units in crystal structures are rationalized through two fundamental principles – periodicity and symmetry [2]. It is the differences in spatial arrangements, and hence the differences in these two mathematical principles, that determine the varying physical properties of polymorphs.

Atoms and molecules in crystal structures inhabit space in regular arrays and exhibit long range periodic order. Crystal structures are typically represented in terms of a lattice, which is a geometrical abstraction of the actual structure. A lattice is made up of a collection of nodes, positioned at integral or specific fractional coordinates, with each node signifying the three-dimensional periodic replication of a structural motif, which represents a collection of atoms, ions or molecules. The repeating unit of the lattice defines the unit cell. The unit cell is an imaginary volumetric entity, which tiles space continuously when translated in three dimensions to build the lattice. For three-dimensional lattices, all unit cells are parallelepipeds. There are only seven different classes of parallelepiped that can tile three-dimensional space without gaps. These seven forms are defined as the seven crystal systems: *triclinic*, *monoclinic*, *orthorhombic*, *tetragonal*, *trigonal*, *hexagonal* and *cubic*. In a crystal system, the nodes may be located at only integer coordinates (termed primitive), or both at integer coordinates and well-defined fractional coordinates, in which case it becomes *centred*. Centring types include: base-centred (with nodes located at the cell corners and at the

centres of two parallel faces), face-centred (with nodes located at the cell corners and at the centres of all six faces), body-centred (with nodes located at the cell corners and at the centre of the cell), and rhombohedrally-centred (with nodes located at the cell corners and at two points along the longest diagonal, and arising only for the hexagonal crystal system). We note that only certain centring types occur within a given crystal system, and their combination yields the 14 Bravais lattices, which are the 14 different types of unit cell that are possible in three-dimensional space [5-8].

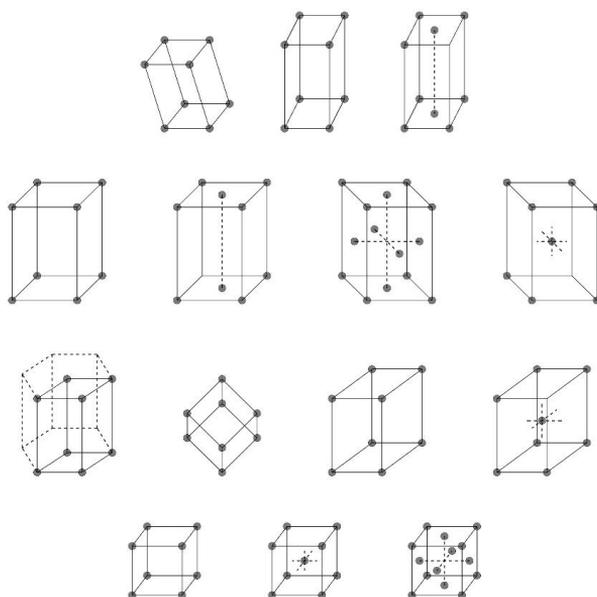


Fig. 1. Bravais lattices

Furthermore, within the unit cell, the positions of the constituent atoms and molecules are often related by a combination of symmetry elements, which include operations such as translation, reflection in mirror planes, rotation and inversion. Only certain combinations of these symmetry operations, in relation with the unit cell types, allow for the continuous tiling of space. Each allowed combination of symmetry operations defines a space group. In total, there are 230 space groups in three-dimensional space. The largest group of atoms within the unit cell which are not related to each other by any crystallographic symmetry operation is called the asymmetric unit. When the symmetry operations of the space group are applied to the asymmetric unit, the complete contents of the unit cell are generated [5].

Transformations between different polymorphic forms are often associated with a change in the Bravais lattice type and space group. For instance, shifting of certain atoms can result in a change of unit cell type – say from the *monoclinic* to the *tetragonal* crystal system, a change in unit cell dimensions along one or more axes, and/or a change in the number of atomic or molecular units per unit cell. These geometric transformations arise from changes in the nature of interatomic or intermolecular interactions, which are associated with alterations in interatomic or intermolecular distances and relative orientations of molecules. In turn, these structural changes are generally associated with changes in physical, mechanical, electromagnetic and optical properties.

The case of polymorphism in chemical elements is termed allotropy. For example, diamond and graphite are allotropes of the element carbon. It is interesting to note that these two materials exhibit very different physical properties and yet they are both constructed only from carbon atoms and hence have identical chemical composition. In graphite, the carbon atoms form hexagonal layers with weak interactions between adjacent layers, whereas in diamond, each carbon atom is bonded to four neighbouring carbon atoms in a tetrahedral arrangement [9].

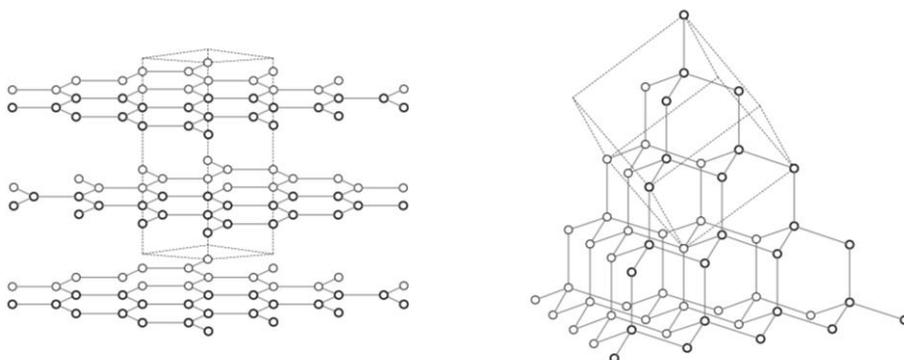


Fig. 2. (Left) Crystal structure of graphite, (Right) Crystal structure of diamond

Graphite has a hexagonal lattice (unit cell dimensions: $a = 2.46 \text{ \AA}$, $c = 6.71 \text{ \AA}$, where $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$) and space group $P6_3/mmc$. Diamond has a cubic lattice (unit cell dimension: $a = 3.56 \text{ \AA}$) and space group $Fd\bar{3}m$. The weak interactions between layers in graphite give rise to the softness of this material, while delocalization of electrons within each layer gives rise to the electrical conductivity and colour of graphite. On the other hand, the strength of the bonding in three dimensions gives diamond its hardness, high thermal conductivity and refractive qualities [10-11].

Under a specific set of physical conditions (i.e., temperature and pressure) only one polymorph of a substance is the *most* energetically (thermodynamically) stable form. All other polymorphs are less energetically stable than the stable form, and may be expected to undergo a polymorphic transformation into the more stable form. In some cases, however, the energetic barrier for this transformation is so high that the

polymorphic transformation is very slow. The diamond/graphite system represents an example of this type. Graphite is the stable polymorph under ambient conditions, and therefore, according to the laws of thermodynamics, all diamonds should transform to graphite. However, the energy barrier for the transformation from diamond to graphite is so high that no conversion of diamond to graphite occurs on normal human timescales.

3 Polymorphic Transformations

Polymorphism and polymorphic transformations represent a vast subject within the physical sciences. As an example of how such transformations may be relevant to design, we now discuss a specific classification of polymorphic transformations that is generally found for extended inorganic materials: reconstructive *versus* displacive transformations. Reconstructive transformations involve rearrangements that include breakage of bonds and creation of new bonds. Displacive transformations, on the other hand, involve only relative changes in positions of the atoms, for example through rotations or changes of bond lengths. While reconstructive transformations are typically slow (due to a high energy barrier) and often irreversible, displacive transformations are typically rapid (due to a low energy barrier) and often reversible [12-13].

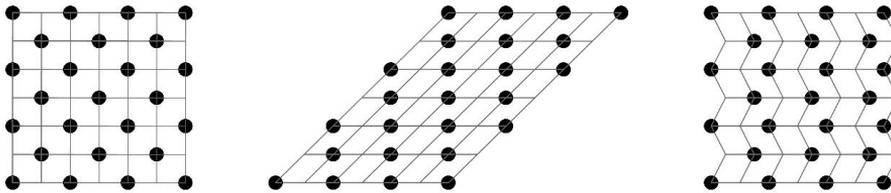


Fig. 3. Martensitic transformations: transformation of the structure on the left may produce the two structures on the right

A specific type of displacive transformation, observed for certain materials, is the martensitic transformation. It is found in metals, alloys and ceramics and has been used for applications in multiple fields. For instance, in some alloys such as nitinol (a nickel/titanium alloy), martensitic transformations lead to a *shape memory effect*, in which the sample can restore its original shape after deformation. This property leads to applications in medical and engineering devices, such as orthodontic files, and has been used to create new materials for actuation (such as ferroelectrics). Martensitic

transformations are also observed in life forms. The tail sheath of the T4 bacteriophage virus is constituted of protein molecules in regular arrays, the realignment of which causes the tail to expand and contract. On the other hand, similar transformations in bacterial flagella lead to various versions of left and right handed helical coiling. Because martensitic transitions are reversible, require low energy for actuation, and are often structurally continuous, they are potentially a very effective model for applications in the field of adaptive design [14-16].



Fig. 4. T4 Bacteriophage virus prior to and upon attachment to host cell.

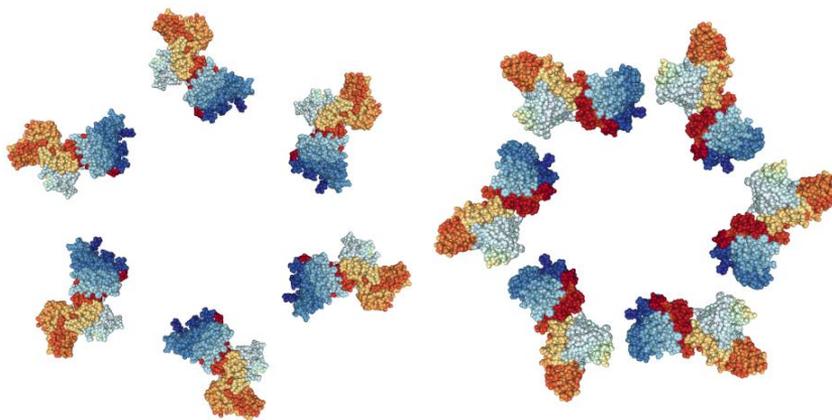


Fig. 5. gp18M protein from the tail of the T4 Bacteriophage virus in expanded and contracted form [17]

Another special category of crystallographic transformations, relevant to applications in adaptive physical systems, are transformations that result in mechanical changes.

For example, photomechanical crystals display changes in mechanical behaviour in response to the external stimulus of light [18-20]. Strictly speaking, many of these transformations are not polymorphic transformations, as the stimulus induces chemical changes in the crystal such that the molecular components are different before and after the transformation. In polymorphic transformations, on the other hand, the molecular components remain identical before and after the transformation. A variety of mechanical responses are known to arise in such crystals, including bending, twisting and cracking. In some cases, crystal explosions can even occur as a consequence of structural changes at the nanoscale generating extreme forces of stress and strain within the macroscopic crystal.

As an example, crystals of *cis*-4,4'-dibromo-octafluoroazobenzene are found to bend away from a source of blue light (with wavelength 457 nm) [18]. This bending is caused by a chemical transformation (in this case, a *cis-trans* isomerization). The two isomers of the molecule occupy different volumes of space in their respective crystal structures, with the *trans* isomer requiring a greater volume than the *cis* isomer. When the blue light is shone on the crystal, the *cis-trans* isomerization occurs mainly on the crystal face nearest to the light source, causing an anisotropic expansion of the crystal. Thus, the crystal face nearest to the light source expands more than the crystal face furthest from the light source, and the resultant anisotropic expansion of the crystal leads to the bending process observed.

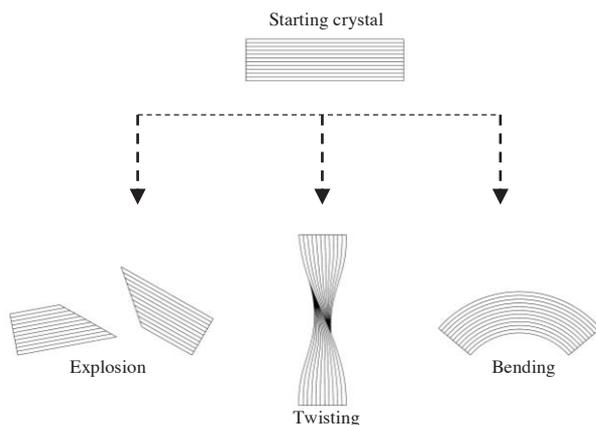


Fig. 6. Schematic diagram describing photomechanical phenomena in crystals

4 Interpretive Mapping of Transformations

In order to be able to translate the concepts of polymorphic transformations within the field of design, it is imperative to map the transformations between different polymorphic materials for any case documented in the fields of chemistry and crystallography. We note, however, that the actual physical mechanism of polymorphic transformations is often not well understood, and is the subject of much research. The pathway of the transformation may be expected to occur in different ways for different polymorphs, and different mechanisms are expected to be applicable in different cases. The types of interatomic and intermolecular forces that operate at the atomic/molecular scale in crystals are not necessarily the types of force that are relevant at a macro-spatial scale. The mechanism of transformation will, therefore, fundamentally differ at these contrasting scales, with transformations at the macro scale often having non-chemical interpretations.

To allow for the development of design applications, our research team has created a digital interface that simulates polymorphic structures, while allowing their geometries and transformations to be manipulated in real time through design criteria. This digital interface is part of a wider software application, which is the product of an ongoing research collaboration focusing on crystallographically inspired architecture. The collaboration brings together architects and scientists at Cardiff University and is funded by the Leverhulme Trust. The project proposes that crystal nano-structures possess valuable physical properties, and a multi-scale potential with possible design applications. It thus aims to make the wealth of information stored in crystallographic datasets available to the community of designers and architects, by developing a bespoke software application which offers a CAD based platform to study the structures and properties of crystalline materials. The bespoke software application embeds the principles of lattice types and space group symmetry to simulate the logic of crystalline arrangements and computes forms at various scales within this process. It begins by importing the asymmetric unit of a crystal structure, applies the symmetry operations of the space group to generate the contents of the unit cell, and translates the unit cell periodically in three-dimensional space to generate the crystal structure. *Rhino*, a widely used NURBS based platform, serves as the host environment, while *grasshopper* serves as its associated visual programming software and the plugin application is coded with *python* [5]. The component being developed on polymorphic transformations is embedded within this logic.

4.1 Component 1

The first approach to mapping polymorphic transformations is focused on the movement of individual atoms from the unit cell of the first polymorph to the unit cell of the second polymorph. As input, the component uses a Crystallographic Information File (denoted CIF). CIFs are standard text file formats which record various geometric properties of crystal structures, and are available in crystallographic databases such as the Cambridge Structural Database (CSD), the Protein Data Bank (PDB), and the Inorganic Crystal Structure Database (ICSD). The bespoke application reads the input file to plot the crystal structure within *rhino*. The atom positions are plotted as points or spheres, and the interatomic connections are modelled as lines. The polymorph component inputs two CIFs, for the first and second polymorphs, in such a way that their unit cells are aligned with each other in a structurally relevant way, and enlists atoms according to atom type within each structure. It then plots the trajectory of the nearest displaced atoms according to atom type, from the unit cell of the first polymorph to the unit cell of the second polymorph, and re-parameterizes the collective transition onto an input slider. Further, it records the changes in interatomic connections while the transformation occurs.

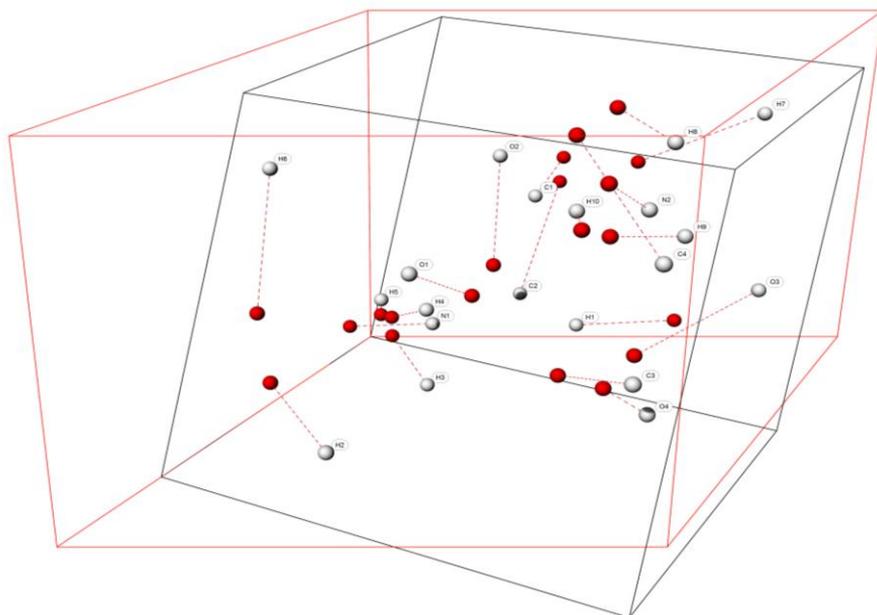


Fig. 7. Atomic positions in and displacement trajectories between two polymorphs of glycine

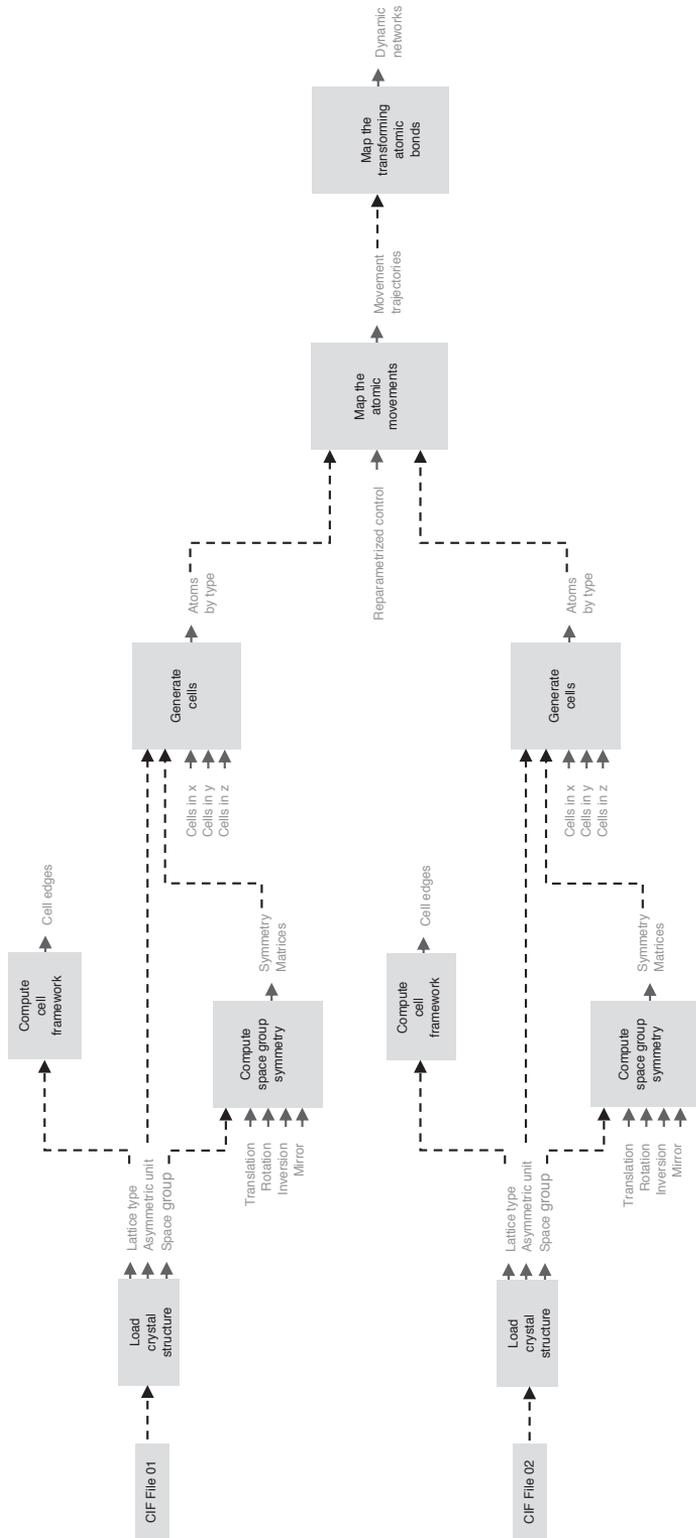


Fig. 8. Component 1 Workflow

4.2 Component 2

The second approach to mapping polymorphic transformations is derived from the concept of atomic nets and polyhedral units. For example, all the polymorphs of silica (chemical formula SiO_2) comprise SiO_4 tetrahedra, in which a silicon atom is located at the centre of the tetrahedron and an oxygen atom is located at each of the four corners of the tetrahedron, with each oxygen atom shared by two SiO_4 tetrahedra [21]. In the different polymorphs of silica, such as tridymite, cristobalite and the well-known mineral quartz, these tetrahedral motifs are arranged differently. The different structural arrangements correspond to different unit cells and different space groups, and give rise to differences in physical properties.

This component uses a CIF as input, and outputs a list of atom types. It then allows the user to specify the central and peripheral atoms for the polyhedral units. A library of observed interatomic distances allows the central atoms to connect only to those peripheral atoms that fall within the prescribed distance ranges. The networks between these peripheral atoms in a unit describe the faces of the polyhedron. The component then maps the trajectories through which the central atoms move and through which the orientations of the polyhedra change, on moving from the initial polymorph to the final polymorph.

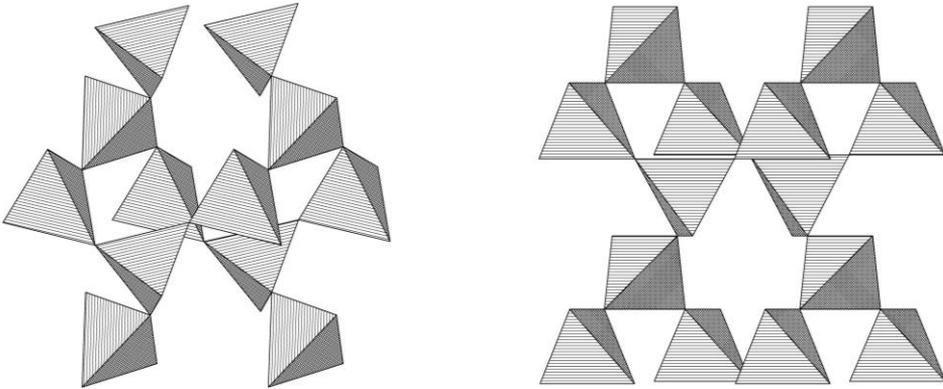


Fig. 9. Tetrahedral SiO_4 units in polymorphs of silicon dioxide (silica), generated with the bespoke component. (left) the alpha quartz polymorph of silica and (right) the beta quartz polymorph of silica

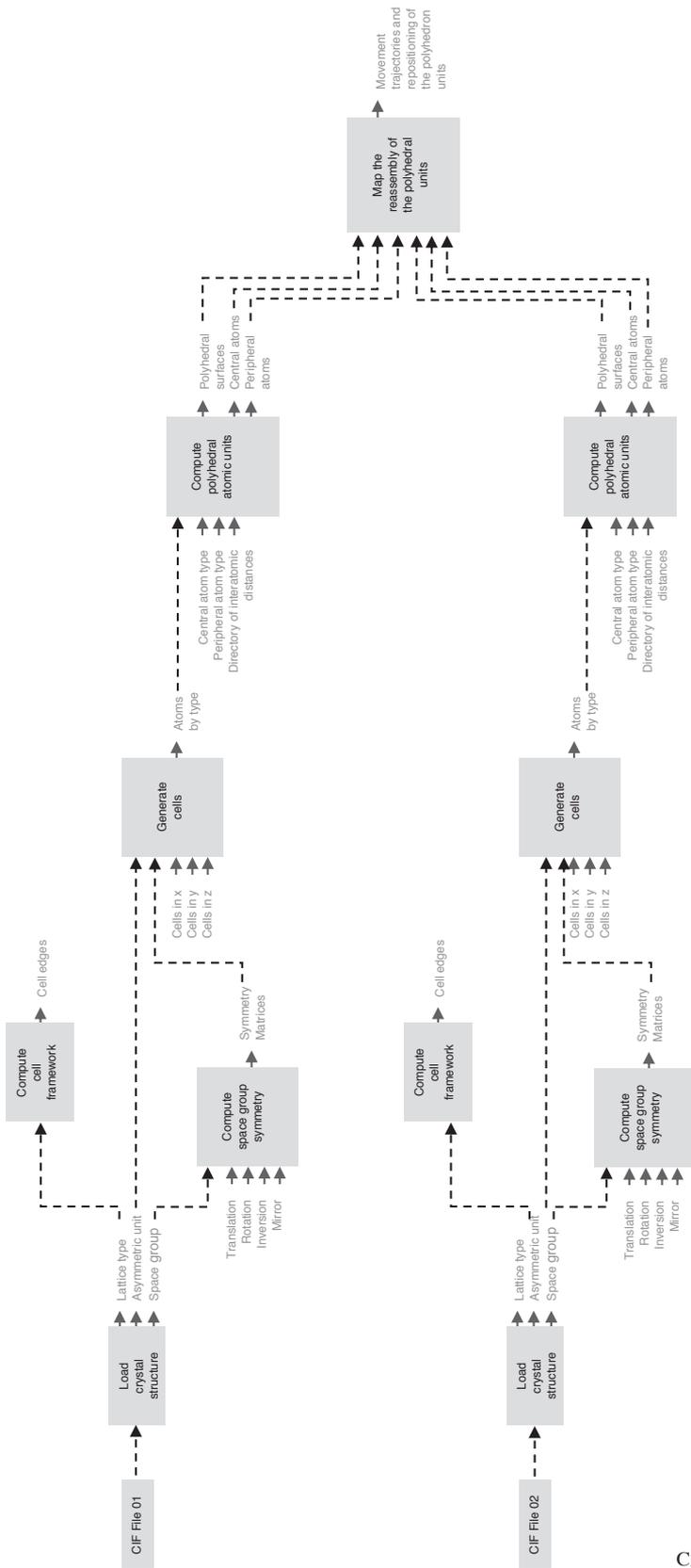


Fig. 10. Component 2 Workflow

4.3 The Application of Polymorphism in Design

As illustrated so far, polymorphism in chemistry has a geometric foundation. The concept of polymorphism is also used in fields such as biology (where its definition is genetic) and computer science (where its definition is based on data typologies). We believe that the concept of polymorphism can be applied further afield, and therefore we propose a geometric polymorphism derived from, but not restricted to, the principles that govern polymorphism in crystalline materials. This area of application would constitute a broader use for the concept of polymorphism, in which it is used as an instrument to develop new designs for structural and spatial configurations. Clearly, this application is inspired by the work of crystallographers and mathematicians in developing polyhedral assemblies as descriptors of crystal structures at the atomic level. The following definitions allow for the development of design principles based on polyhedral assemblies:

Local rules of component connection: Polyhedral components may connect face to face, edge to edge or vertex to vertex. Within these categories, further possibilities may arise based on the symmetries of the polyhedral components themselves. Some prominent types of coordination polyhedra are the tetrahedron and the octahedron. Figure 11 demonstrates a few connection types between two saddle polyhedral units [22] (the modular octahedral component here is derived from combining four irregular saddle tetrahedra).

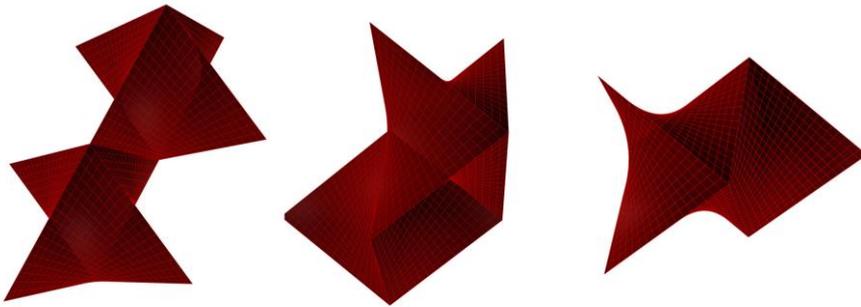


Fig. 11. Connection types between two saddle polyhedral units

Global strategies for polyhedral assembly: The arrangement of the polyhedral components and the directions of assembly further influence variations in the global structures obtained.

We have developed an interface with which designers are able to control parameters (such as component connection type, grid and component size, building units, and directions of assembly) to evolve a range of different structures from the same building blocks. This method facilitates a rule-based generative approach to work in coordination with the designer's intuitive control, and enables the development of a tectonic physical system with multiple combinatorial possibilities.

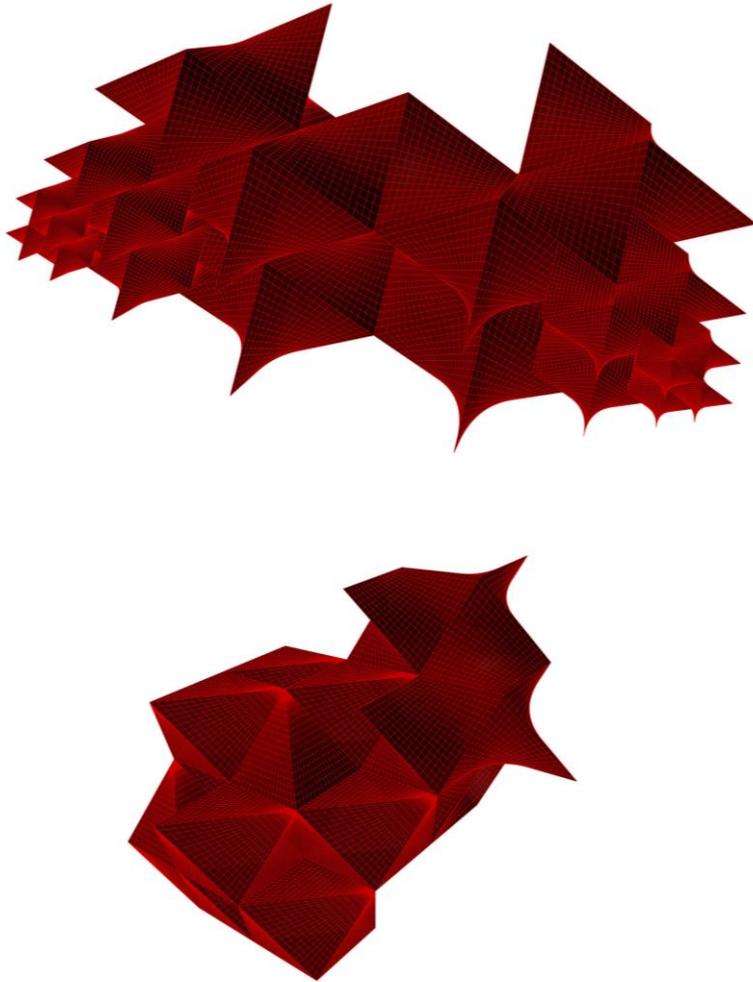


Fig. 12. Variable global structures developed from saddle and flat polyhedral units

5 Conclusions

From Gordon Pask's ideas of conversational machines in *Colloquy of Mobiles* in 1968 [23], to Philip Beesley's *Hylozoic Ground* in 2016 [24], the last few decades have witnessed considerable interest in the design and development of transformative physical systems. However, both the search for architectonic systems and the range of mechanical transitions explored so far remain somewhat incomplete and arbitrary.

The research described in this paper, on the other hand, aims to direct our understanding towards the fundamentals of adaptation through the phenomenon of polymorphism, where nature offers a model of structural transformations which lead to optimization of a number of properties, which are now discussed.



Fig. 13. 3D printed saddle polyhedral components

Structures: In the phenomenon of polymorphism, a substance is able to adopt more than one structural arrangement in the solid state (one of which is stable under a particular set of conditions while any others are metastable), with differing properties. An understanding of how nature arranges chemical components in space in multiple ways, and an understanding of the advantageous properties offered by each polymorphic structure, may provide a framework for developing component based architecture. Applications may be found within material, spatial or programmatic

aspects. For example, in the design of micro-latticed materials or building space-frames, a repertoire of alternative configurations may offer insight into the relationship between geometry, density, weight-transfer directionality and load-bearing capacity. In the design of modular housing units, it may offer a variable vocabulary which may be reassembled with distinctive programmatic or microclimatic advantages. The second approach in our bespoke software, derived from the concept of atomic nets and polyhedral units, opens up this realm of combinatorial possibilities in the development of components for tectonic arrays.

Transformations: With regard to the first approach for mapping polymorphism, which is focused on the movement of atoms from their positions in the initial polymorph to those in the final polymorph, displacive and martensitic transformations become more immediately relevant for applications in adaptive physical systems. In this category of transformations, atoms move in a directed, regular and concerted manner, resulting in substantial changes in the overall structural arrangement. Similarly significant structural rearrangements are also found in the context of biomolecules. In the T4 bacteriophage tail sheath or bacterial flagella discussed earlier, modest geometric changes at the molecular level induce advanced mechanical movements in the organism. Further development of these concepts by exploiting this component may lead to new geometrical arrangements for sensing and actuation in the design of objects and spaces.

Stimuli: Various environmental factors (e.g. temperature or pressure) can induce polymorphic transformations in crystalline materials. Multiple transformations can occur within a series of polymorphs in response to a changing stimulus, with each polymorph representing the most stable structure under a particular set of conditions. Studies of these phenomena may provide insight into developing feedback and conversation in the transformative process.

The bespoke interface developed in our research allows polymorphic geometries to be simulated and manipulated in real time, leading to interpretations on polymorphic transformations, and giving the user a degree of intuitive control. This research is thus intended as a foundational platform, which offers a digital interface for a global community of architects and designers to study polymorphism as a source from which to test previously unexplored possibilities within the field of adaptive design and component-based tectonic systems.

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References

1. Dunitz, J. D.: Phase transitions in molecular crystals from a chemical viewpoint, in *Pure Appl. Chem.* 63: 177-185 (1991)
2. Bernstein, J.: *Polymorphism in Molecular Crystals*, Oxford University Press: Oxford, U. K. (2002)
3. Ahn, S. Y.; Guo, F.; Kariuki, B. M.; Harris, K. D. M.: Abundant polymorphism in a system with multiple hydrogen bonding opportunities: oxalyl dihydrazide, in *J. Am. Chem. Soc.* 128: 8441-8452 (2006)
4. Williams, P. A.; Hughes, C. E.; Lim, G. K.; Kariuki, B. M.; Harris, K. D. M.: Discovery of a new system exhibiting abundant polymorphism: m-aminobenzoic acid, in *Cryst. Growth Des.* 12: 3104-3113 (2012)
5. Pineda, S., Arora, M., Williams, P. A., Kariuki, B. M., and Harris, K. D. M.: The grammar of crystallographic expression, in *Posthuman Frontiers: Papers for the ACADIA 2016 Conference* (2016)
6. Glusker, J. P., Trueblood, K.N.: *Crystal Structure Analysis - A Primer*, Oxford University Press, Oxford (1985)
7. Dunitz, J. D.: *X-ray Analysis and the Structures of Organic Molecules*, Verlag Helvetica Chimica Acta, Basel (1995)
8. Hahn, T. ed.: *International Tables for Crystallography, Volume A: Space Group Symmetry*, Springer Netherlands (2002)
9. Rossi, M.: How can graphite and diamond be so different if they are both composed of pure carbon? In *Scientific American* (2002). Retrieved January 30, 2017 from <http://www.scientificamerican.com/article/how-can-graphite-and-diam/>
10. Trucano P., Chen R.: Structure of graphite by neutron diffraction, in *Nature* 258: 136-137 (1975)
11. Straumanis M. E., Aka E. Z.: Precision determination of lattice parameter, coefficient of thermal expansion and atomic weight of carbon in diamond, in *J. Am. Chem. Soc.* 73: 5643-5646 (1951)
12. Carter, C. B., Norton, M. G.: *Ceramic Materials: Science and Engineering*, Springer, New York (2007)
13. Falk, W., James, R. D.: Elasticity theory for self-assembled protein lattices with application to the martensitic phase transition in bacteriophage T4 tail sheath, *Physical Review E* 73: 011917 (2006)
14. Bhattacharya, K., Conti, S., Zanzotto, G., Zimmer, J.: Crystal symmetry and the reversibility of martensitic transformations, in *Nature* 428: 55-59 (2004)
15. Leiman, P. G., Arisaka, F., Kanamaru, S., Raaij, M.J.V., Kostyuchenko, V.A., Aksyuk, A. A., Rossmann, M.G.: Morphogenesis of the T4 tail and tail fibers, in *Virology J.* 7: 355 (2010). Retrieved January 27, 2017 from <http://virologyj.biomedcentral.com/articles/10.1186/1743-422X-7-355>
16. Ohlson, G. B., Hartman, H.: Martensite and Life: Displacive Transformations as Biological Processes, in *J. Phys. Colloques* 43: C4-855-865 (1982)

17. Images of 3FOH and 3FOI. Aksyuk, A. A., Leiman, P. G., Kurochkina, L.P., Shneider, M. M., Kostyuchenko, V. A., Mesyanzhinov, V. V., Rossmann, M. G.: The tail sheath structure of bacteriophage T4: a molecular machine for infecting bacteria, in *EMBO J.* 28: 821-829 (2009). Created with NGL Viewer [Rose A.S., Hildebrand P.W.: NGL Viewer: a web application for molecular visualization, in *Nucl. Acids Res.* 43: W576-W579 (2015)]
18. Bushuyev, O. S.; Tomberg, A.; Friščić, T.; Barrett, C. J.: Shaping crystals with light: crystal-to-crystal isomerization and photomechanical effect in fluorinated azobenzenes, in *J. Am. Chem. Soc.* 135: 12556-12559 (2013)
19. Zhu, L., Al-Kaysi, R. O., Bardeen, C. J.: Reversible photoinduced twisting of molecular crystal microribbons, in *J. Am. Chem. Soc.* 133: 12569-12575 (2011)
20. Naumov, P., Sahoo, S. C., Zakharov, B. A., Boldyreva, E. V.: Dynamic single crystals: kinematic analysis of photoinduced crystal jumping (the photosalient effect), in *Angew. Chem. Int. Ed.* 52: 9990-9995 (2013)
21. Egon, W., Wiberg, N. and Holleman, A.F.: *Inorganic Chemistry*, Academic Press, San Diego (2001)
22. Heyring, C. B.: Useable Electromagnetic Blueprint of the Structure of Space, Patent No. US 20120141966 A1 (7th July 2012)
23. Haque, U.: The Architectural Relevance of Gordon Pask, in *Architectural Design* 77(4): 54-61 (2007)
24. Peters, T.: Life in Venice, in *Azure*, 86-91 (2010)