Auxetic Behaviour and Other Negative Thermo-Mechanical Properties from Rotating Rigid Units

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Auxetics exhibit the anomalous property of expanding laterally when uniaxially stretched, that is, exhibit a negative Poisson's ratio, a property which arises from: (i) the presence of specific geometric features within the nano/macro structure of the material and (ii) amenable deformations in response to the applied stimulus. This work explores how ancient symmetrical aesthetic artefacts have been transformed to functional auxetics through mechanism that have ripened the field of "mechanical metamaterials" and "architected materials" in the last decades. In particular, it looks at the important role and various implementations, both in 2D and 3D, of 'rotating rigid units' which range from 'rotating squares' to much more complex renditions at various scales of structure. The role of rotating rigid units to generate negative thermal expansion and negative compressibility is also delved into.

Keywords: Auxetic, negative Poisson's ratio, negative thermal expansion, negative linear compressibility, mechanical metamaterials, architected materials

1. Introduction

Our innate desire to innovate and create functional yet aesthetically pleasing constructs seem to have found a natural home in the field of auxetics [1] and other systems exhibiting 'negative' thermo-mechanical properties. These marvels in design and functionality, often describable through highly elegant models and architectures, respond to external stimuli of mechanical stress and/or heat in a manner which defies common expectation of how materials should behave. Such 'negative' systems, defined in Figure 1, which have been at the core of what we now call "mechanical metamaterials" and "architected materials", expand laterally (get fatter) when uniaxially stretched (negative Poisson's ratio, or auxetic [1]) rather than shrink [1–41] expand rather than contract in at least one direction when subjected to a compressive hydrostatic pressure (negative linear compressibility) [12,42–50] or shrink rather than expand when heated (negative thermal expansion) [12,51–99]. Apart from being fascinating from an academic perspective, these anomalous 'negative' materials are known to be useful in various practical applications. For example, auxetics (see various recent reviews and monographs [100,101,110,111,102–109] are potentially superior to conventional materials in applications as diverse as sport [112], [113] textiles [26], filtration [114] [115], and medicine [116,117].

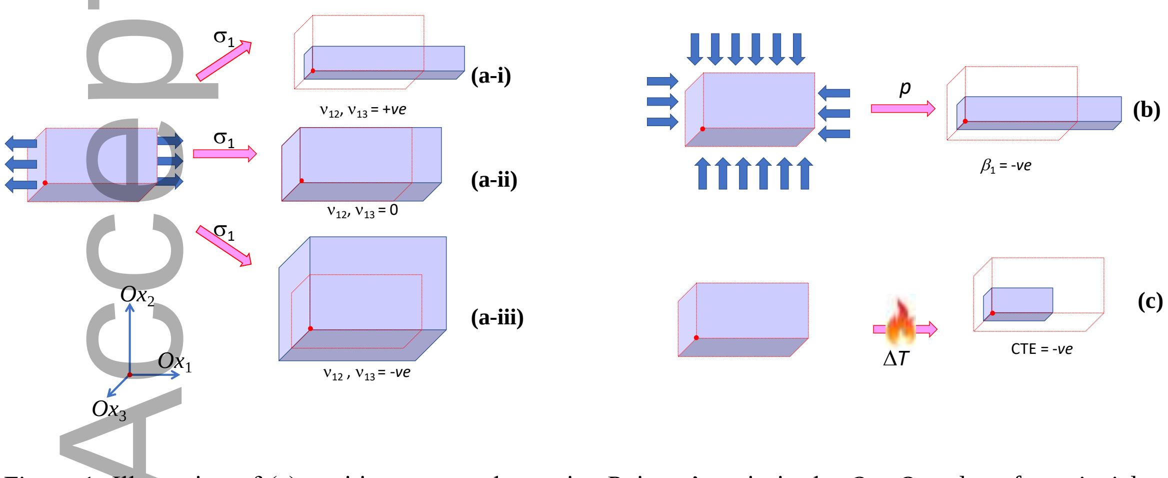


Figure 1: Illustration of (a) positive, zero and negative Poisson's ratio in the Ox_1-Ox_2 plane for uniaxial stretching in the horizontal Ox_1 direction; (b) negative linear compressibility in the Ox_1 direction when the system is subjected to an increase in pressure p; (c) negative thermal expansion. Note that in the context of anomalous properties, a zero Poisson's ratio (or compressibility / thermal expansion) present their own unique niche interest.

Current understanding is that the manifestation of such negative behaviour, in particular negative Poisson's ratio, requires the presence of features within the nano/macro structure of the material (i.e. an appropriate 'geometry'), and that the deformations in response to the applied stimulus are amenable (i.e. an appropriate 'deformation mechanism'). As a result, over the last decades, the field has developed in a manner where scientists look at materials from a 'geometry / deformation mechanism' perspective, where modelling and experimental work are normally used in tandem to unlock the secrets for making the perfect 'negative material'.

This article is being published on the 30th anniversary of the coining of the term 'auxetic' [1], and on the 60th anniversary of the establishment of *Physica Status Solidi*, which has been a natural home for many articles in the area of 'auxetics and related systems' with the publication of various special issues on this topic (starting in 2005 [118]). It focuses on what may broadly be defined as 'rotating rigid units' mechanisms, i.e., on systems where the overarching cause of the 'negative behaviour' is the presence of sub-units within the systems which, to a considerable extent, behave as rigid units that rotate relative to each other as a result of an externally applied stimulus. The 'rigid units' in crystalline naturally occurring or man-made materials such as zeolites [119–125] or metal oxides [7,8,126–128], are often recognisable through some very distinct, highly symmetric and aesthetically elegant motifs, nature's own way of achieving functionality gracefully.

Arguably, the most prominent of these motifs is the design shown in Figure 2 which features squares connected through their vertices in a manner where one square connects to four other squares in a space filling manner. This construction produces the pattern which was immortalised centuries ago through a mosaic which adorned the floor of the entrance of a Roman Villa discovered at the site of Daphne, a popular holiday resort used by the wealthy citizens and residents of Antioch. The artisans of the time were obviously unaware that nature had preceded them and that their creation existed in the tiniest of scales in a multitude of materials which were yet to be discovered, or, that centuries later, their design would be studied so extensively.

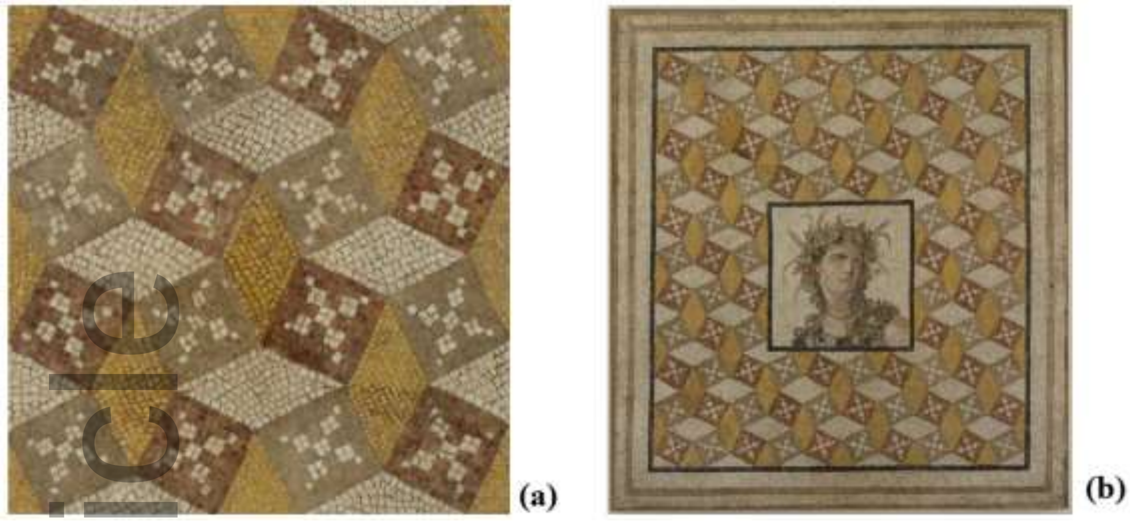


Figure 2: The ‘rotating squares’ motif as constructed in the 2nd Century AD to cover the floor of the entrance of a Roman Villa discovered at the site of Daphne, where (a) shows just the ‘rotating squares’ motif and (b) shows the full mosaic. This masterpiece in design is now displayed at the Metropolitan Museum in New York City, USA. Image adapted from https://www.metmuseum.org/art/collection/search/253565.

2. Early Work

From a historical perspective, the development of the ‘rigid unit mode’ (RUM) / ‘quasi Rigid Unit Mode’ (qRUM) terminology and approach is attributable to Martin Dove and co-workers who researched extensively on this topic and used it to explain various phenomena in real materials since the early 1990s. Some of the concepts used in this formulations date back even further. Worth mentioning is the 1864 work by James C Maxwell [129] which studies the behaviour of systems made from struts connected by pins. Maxwell noted that systems made from connected objects on which constraints are applied (for example the Eiffel Tower, bridges, etc.) will be “rigid if the number of constraints, C, exceeds the number of degrees of freedom, F, and has some degree of flexibility if F> C”, an approach “now used by engineers routinely in the design of flexible systems” [130]*. Other early work which could be seen as a precursor to the development of the RUM / qRUM approach is that of H.D. Megaw who in 1973 [131] described the α to β phase transition of the silicate quartz in terms of “coupled rotation of relatively rigid corner sharing SiO_4 tetrahedra” – quoted from J.S.O. Evans, Review [51].

*It is as a result of this work that it can be concluded that the triangle is a rigid body whilst the square would need an additional constraint to make it rigid, e.g. adding a diagonal element.

One of the earliest applications of this model by Dove and co-workers was to study distortions in the crystal structure of framework silicates to achieve a phase transition. [98,132]. The basic requirements for this model, as described when applied to silicates, is that the molecular frameworks should be characterised by having tetrahedral units which "are fairly stiff and any significant deformation will carry a high energy penalty" as well as "normal modes of motion that are allowed to propagate without the tetrahedra having to deform as part of the motion" – quoted directly from Dove *et al.* Mineralogical Magazine, 2000 [133]. Since then, the model has been extensively applied to the study of negative thermal expansion. As stated by Dove *et al.* [133], the RUMs idea as applied to negative thermal expansion (NTE) is "best illustrated with a two-dimensional representation of the network of linked octahedra in the cubic perovskite structure", see Figure 3. As shown in Figure 3 [64], [67], the rocking coupled rotations of the polyhedral as a result of thermal motions (termed as 'rigid unit modes', or 'floppy modes') can be easily envisaged as low energy vibrational modes of the structure which causes a net reduction in the size (linear dimension / area / volume) of the structure. Note that this model is rather similar, from a geometric perspective, to the 'rotating squares' model used in the field of auxetics [18] and, as noted by J.S.O. Evans [51], "*This may be thought of as a 2-D slice through the perovskite structure. Individual tetrahedra or octahedra of such a framework are, in general, relatively stiff, … but are typically joined by relatively "loose" hinges*; *… being as much as 100 times weaker than the stiffness of individual polyhedra*". Also worth mentioning in this regard is what is depicted in Figure 3b [93], which represents cristobalite and tridymite as linked tetrahedral models where the RUM approach is employed showing co-operative rotations of the tetrahedra resulting in NTE. This system, from a geometric perspective, has strong similarities with the auxetic 'rotating triangles' [134]. Apart from the relative simplicity yet highly elegant explanation of NTE through the RUM approach, what is remarkable is the large variety of NTE materials which can be represented by this model, as detailed in various reviews on the topic [51] [90] [88] [130].

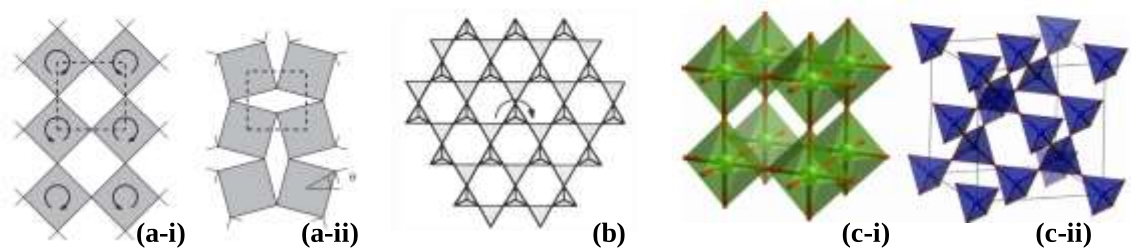


Figure 3: (a) The RUM model as applied to a 2D projection of the perovskite model where (a-i) represents the more open low temperature form and (a-ii) represents the less open, thus smaller, form due to thermal 'rocking'. Image taken from Welche, Heine and Dove [64] (b) An alternative RUM implementation, this time shown projections as connected traingles, Image taken from Pryde *et al.* [93]. (c) Some examples of simple crystalline materials exhibiting NTE through RUMs, (c-i) represents ReO_3 (c-ii) represents β-cristobalite. Image taken from Dove and Fang [90].

In a parallel development, the 1990s also saw the first reports where a negative Poisson's ratio started to be attributed to rotating rigid units. In fact, the Yeganeh-Haeri, Weidner and Parise [126] work on negative Poisson's ratio in α-cristobailite speaks of "rotations of SiO_4 tetrahedra as the structure is compressed" whilst the work by Keskar and Chelikowsky [128] states that it is possible to "demonstrate that the rigidity of the SiO_4 tetrahedral units is intimately related to the occurrence of negative Poisson ratios in crystalline forms of silica." However, studies on the role of rotating rigid units for generating auxetic behaviour became more mainstream following the report by Grima, Alderson and Evans [131] that negative Poisson's ratio in a number of zeolite frameworks could be explained through 'rotating squares' or 'rotating triangles' models, where these models were representing 2D projections of the 3D zeolitic framework. Here it should be mentioned that at that time, the field of auxetics was still at its infancy and the world still needed to be convinced that negative Poisson's ratio is indeed achievable. The manifestation of auxeticity through the 'rotating squares' mechanism, which could be easily rendered as a physical construct as a demonstration model, seemed to have helped in the mainstreaming and to spur the growth of this field of science.

3. The 'Rotating Rigid Squares' Mechanism and its Negative Poisson's ratio Properties

The 'rotating squares' mechanism was first formally reported by Grima and Evans [18], and can be considered as a revaluation and simplification of the seminal work carried out earlier by Sigmund, who proposed a system developed through topology optimisations [25]. This simplification can be considered as a product of lateral thinking; the process of viewing things and solving problems through methods which can be considered indirect and creative [135], a method which has been extensively applied to the field of auxetics [9]. In the work by Grima and Evans [18], and work published independently in parallel by Ishibashi and Iwata [136], the structure resulting in the rotating mechanism, given in Figure 4b, was explained as a two-dimensional arrangement (or three-dimensional structure projecting into this two-dimensional arrangement) of square rigid units which can rotate from their connected corners. This mechanism was found to manifest the highest possible negative Poisson's ratio for a two-dimensional isotropic structure, a value of −1.

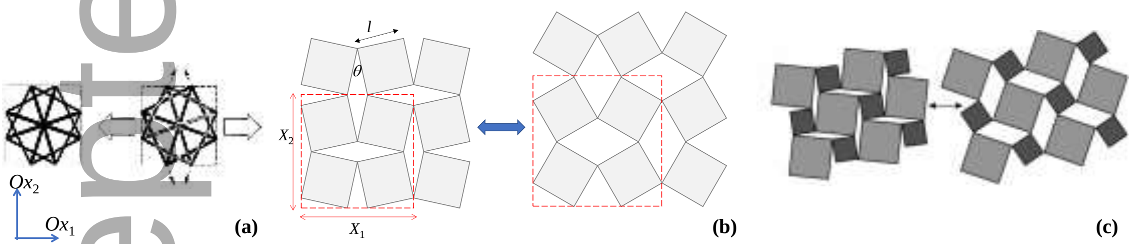


Figure 4: (a) The model proposed by Sigmund [25]; (b) the rotating squares model as proposed by Grima and Evans ([18] and (c) a variation proposed by Grima and Evans [18] made from different sized rigid squares.

The statement that the Poisson's ratio of the rotating squares system is −1 was formally backed up through analytical modelling, starting with the structural features of the structure, in particular the unit cell side lengths in terms of the squares in the cell and their arrangement within, which lengths were given as:

$$X_1 = X_2 = 2l\left[\cos\left(\frac{\theta}{2}\right)+\sin\left(\frac{\theta}{2}\right)\right], \tag{8}$$

where X_1 and X_2 are the side lengths of the unit cell, l is the side length of a square, and θ is the smaller angle between two squares (see Figure 4b). The Poisson's ratio was then found by the theoretical application of infinitesimally small strains, since the Poisson's ratio ν_{ij} (or more precisely the Poisson's function) in the Ox_i-Ox_j plane for loading in the Ox_i direction can be expressed as follows:

$$\nu_{ij} = \left(\nu_{ji}\right)^{-1} = -\frac{\mathrm{d}\varepsilon_j}{\mathrm{d}\varepsilon_i}, \qquad (i,j = 1,2) \tag{9}$$

where $\mathrm{d}\varepsilon_i$ and $\mathrm{d}\varepsilon_j$ are infinitesimally small strains in the Ox_i and Ox_j directions respectively. These strains may be written in terms of X_i, the unit cell side lengths, as:

$$\mathrm{d}\varepsilon_i = \frac{\mathrm{d}X_i}{X_i} \quad i = 1,2, \tag{10}$$

This resulted in a function where the Poisson's ratio was expressed in terms of structural features, which was then rearranged by using the relationship $X_i = X_i\left(\theta\right)$, since θ is the only variable, to get:

$$\nu_{21} = \left(\nu_{12}\right)^{-1} = -\frac{\mathrm{d}\varepsilon_1}{\mathrm{d}\varepsilon_2} = -\frac{\mathrm{d}X_1/X_1}{\mathrm{d}X_2/X_2} = -\frac{\mathrm{d}X_1/\mathrm{d}\theta}{\mathrm{d}X_2/\mathrm{d}\theta}\frac{X_2}{X_1} \quad i = 1,2. \tag{11}$$

By then differentiating the unit cell length equations (eq. 8) for this structure and substituting in equation 11, the on-axis Poisson's ratio was then expressed in mathematical form and determined to always be a value of −1, i.e.:

$$\nu_{21} = \left(\nu_{12}\right)^{-1} = -1 \tag{12}$$

This means that the lateral dimension is always increasing by the same amount by which the direction being stretched is increasing, i.e. maintains the aspect ratio. The on-axis Young's modulus, the property which reports the stiffness of a material or structure, was also expressed in terms of an equation by deriving it using the conservation of energy approach, which was first applied to thermo-mechanical metamaterials by Prall and Lakes [137]. This further shows the diversity of mathematical modelling, as many different methods may be used in order to achieve the same result, some making use of simpler, or more elegant, methods.

Grima and Evans [18] also showed that this system, if it behaves in an ideal way, does not shear and that the mechanisms can operate with a Poisson's ratio value of −1 in all directions, i.e. with the system being isotropic in plane. They further explained that for such idealised behaviour to be manifested, the units from which the structure is constructed must be fully rigid, as explained above, thus permitting an amenable deformation mechanism which allows for the opening and closing of the structure to be completely uniform upon application of stresses. In this same work, it was also theorised that the same behaviour (auxetic behaviour) can be expected from a structure of rotating rigid triangles as well as a structure of two different sized rigid squares connected in an alternating fashion (see Figure 4c). [18] This work therefore also acts as a precursor study for rotating rhombi and parallelogram mechanisms, which will be discussed in the forthcoming section.

Apart from more complex work which is discussed below, worth mentioning is the fact that although most of the work has looked at 'rotating squares' in a manner where the rigid unit is indeed a square, it is obvious that for the models to apply, what needs to really behave as a 'rigid square' is the profile between the corners (the hinges). Thus, for example, the square may be replaced by a rigid cross, or some other design as illustrated in Figure 5. Note that such system can be space filling or non-space-filling, with the non-space systems benefiting from reduced weight and tend to be highly aesthetically pleasing. Note also the flexibility in design means that such systems (or their pores) can be precisely designed for specific practical applications. An interesting demonstration of this concept is the system constructed from connected arcs to produce 'curly', more aesthetically pleasing, sub-units. [138]

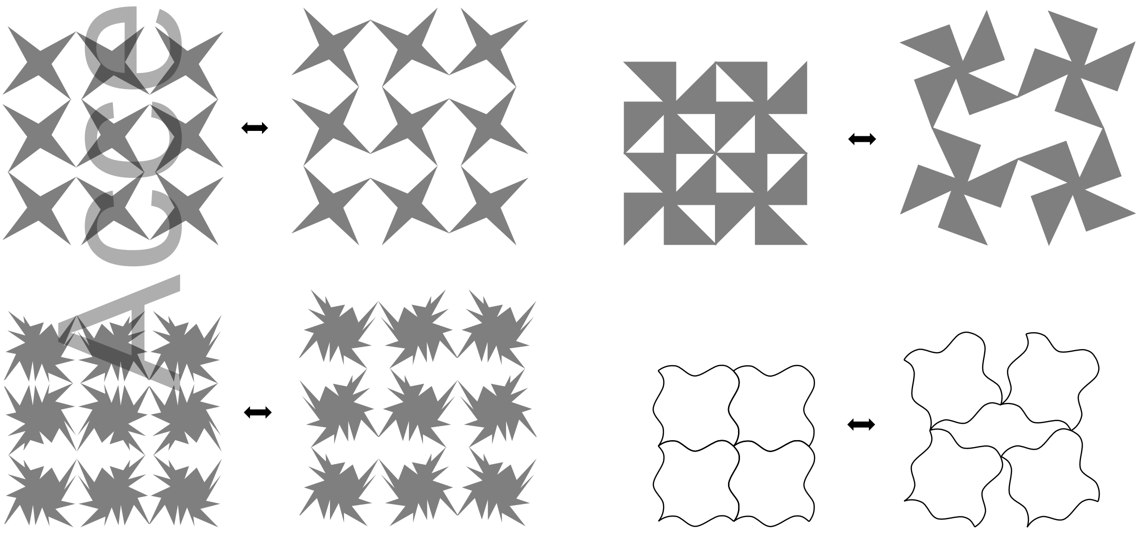


Figure 5: An illustration which shows that the important requirement for the 'rotating squares' mechanism to operate is that the actual shape traced by the four 'hinges', which connect one rigid unit to the ones adjacent, is in the shape of a square. This means that all the systems depicted above can be considered as 'rotating squares' and all exhibit Poisson's ratio of -1.

4. On the importance of Rigidity: 'Rotating Non-Rigid Squares'

One of the earliest natural developments of the 'rotating rigid squares' mechanism was to relax the rigidity requirements. Although in theory this could be done in a number of ways, systematic studies reported so far have only focused on two ways of relaxing the rigidity requirements.

The first of such models was inspired by the fact that simulations on the hypothetical SiO_2 equivalent of the zeolite Thomsonite (THO), a framework which projects into the (001) plane with the aforementioned 'rotating squares' like geometry (see Figure 6a) was not found to exhibit the idealised Poisson's ratio of -1 in the (001) plane [119]. Instead, the Poisson's ratio was found to be dependent on the direction of loading and was always more positive than -1, with maximum auxeticity being demonstrated on-axis. On closer inspection, it was shown through force-field based simulations that the unit which projected as 'squares' in the (001) did not actually retain their square profile perfectly upon uniaxial stretching and instead were found to elongate to become more rectangle like. It was also observed that the lengths of the diagonals changed much less that the lengths of sides of the 'squares'. Based on these observations obtained from molecular modelling, Grima [139] proposed a more advanced model for the 'rotating squares' where the rigid squares were replaced by their diagonals, which were permitted to pivot (against resistance) around each other. A rather similar model of rotating non-rigid squares was also proposed by Aleksey A. Vasiliev and co-workers [140]

Analytical modelling of this more complex system revealed that the effect of having semi-rigid units does in fact act as expected and increases the Poisson's ratio value to a more positive one than −1 (i.e. less auxetic), which fitted the profile of the Poisson's ratio of Thomsonite rather well. In the formal publication of this work, Grima *et al.* [141] argue that while the property of auxeticity is generally discussed as advantageous when maximised, there may be situations where maximisation of the negative Poisson's ratio property might not be the principle aim, but rather a structure which has a specific value of this negative property. Therefore, this study suggested using semi-rigid unit structures to the advantage of a designer / manufacturer, by seeing this normally undesired property as a possible way of fine tuning the property of the system, by increasing or decreasing the rigidity, so as to produce the desired result. The study also suggested that since real materials can all be considered to be semi-rigid in nature to some extent, this model is a better illustration of how the rotating squares model would work in real applications.

More specifically, the properties for semi-rigid rotating squares systems were also determined analytically by following the same method as above, with adaptations to make up for the semi rigid nature of the squares being made by considering a system where the solid squares (see Figure 6b) were replaced by their diagonals (see Figure 6c) where the diagonals of the same square where connected through a hinge at their centres [141]. In this model, derived with the aim of replicating the behaviour of the SiO_2 equivalent of the THO zeolite framework, see Figure 6, the angles between diagonals were permitted to change, but their lengths were assumed to be constant. It was found that the on-axis Poisson's ratio, for the systems oriented as shown in Figure 6, can be expressed, in the limit of zero strain, as:

$$\nu_{21} = (\nu_{12}) = -\left[1 + 4\left(\frac{k_\psi}{k_\phi}\right)\right]^{-1} \tag{13}$$

and, at non-zero strain, when the system starts deforming as:

$$\begin{aligned}\nu_{21} = (\nu_{12}) &= -\left[1 + 4\left(\frac{k_\psi}{k_\phi}\right)\right]^{-1} \left\{\frac{\cos\left(\frac{\psi_1}{2}\right)\sin\left(\frac{\psi_2}{2}\right)}{\sin\left(\frac{\psi_1}{2}\right)\cos\left(\frac{\psi_2}{2}\right)}\right\} \\ &= -\cot\left(\frac{\psi_1}{2}\right)\tan\left(\frac{\psi_2}{2}\right)\left[1 + 4\left(\frac{k_\psi}{k_\phi}\right)\right]^{-1}\end{aligned} , \tag{14}$$

where k_ψ and k_ϕ are constants relating to angles ψ and ϕ, which are the angles as defined in Figure 6c. Other mechanical properties of the system were also determined analytically in this work in order to have a more comprehensive understanding of the mechanism being studied, including the calculation of the off-axis Poisson's ratio which was found to range from the maximal 'auxeticity' on-axis where the Poisson's ratio can range from mostly –1 when the squares are rather rigid, to +1 when the squares are very flexible, see Figure 6d [141].

Here it should be mentioned that, recognizing that axes in structures are generally artificial and are applied to aid the researcher, an off-axis analysis is rather important for real life applications as many times a structure being applied cannot always be in the on-axis position. In most practical applications or studies, it may well be that a structure cannot be considered to be perfectly aligned unless extra effort is put in to ensure it. An area where such an off-axis analysis is of particular use is when considering crystal structures, since in this case, the orientation of the motif in the analytical study may not necessarily correspond to the crystal lattice vectors. This was the case for the zeolite Natrolite where the major axis of the 'rotating semi-rigid squares' model corresponded to 45° off-axis in the crystal lattice. It is also important to mention that alongside this work on rotating semi-rigid units, one should also look at the highly fundamental work on the non-dissimilar tetramer systems carried out in parallel by Tretiakov and Wojciechowski [142,143] where common features, including but not limited to auxeticity and symmetry, should be noted.

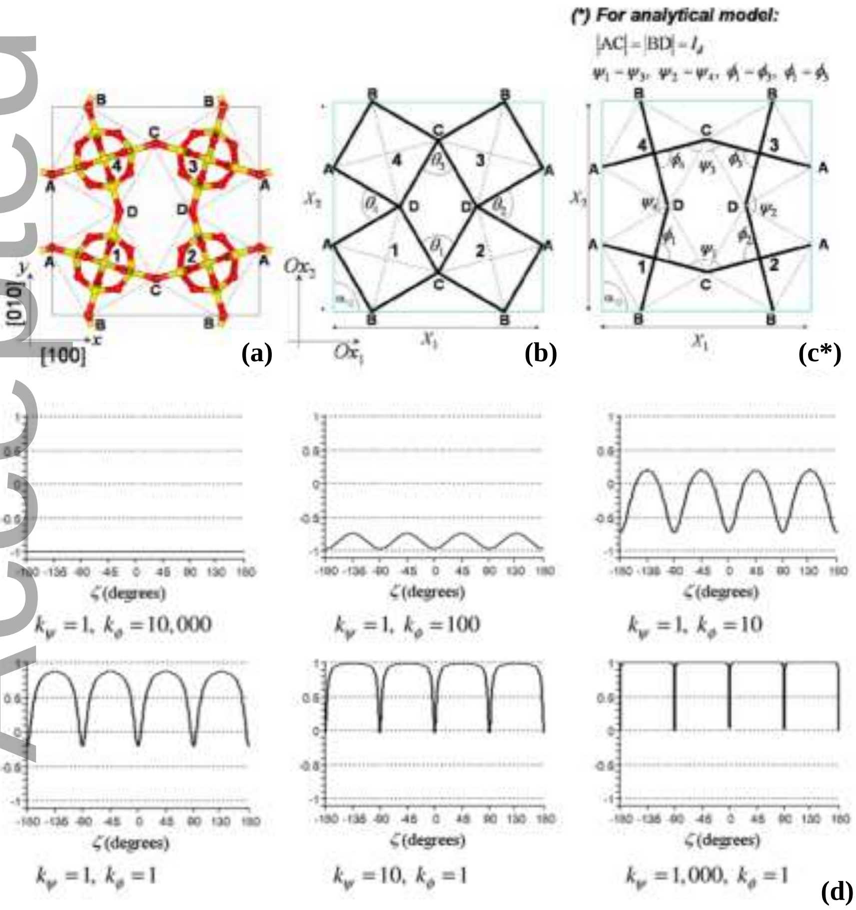


Figure 6: (a) The SiO_2 equivalent of THO as viewed in the (001) plane; (b) its description in terms of 'rotating rectangles' and; (c) the model of 'semi-rigid squares' where the squares are replaced by their

diagonals (d) The off-axis Poisson's ratio afforded by this structure for various combinations of k_φ and k_ψ with ψ = 145°. Adapted from [141].

A second form of 'non-rigid' adaptation of the 'rotating squares' mechanism has also been studied by Grima *et al.* [144] where the original geometry is retained, but the rotational motion is jammed thus favouring deformations of the squares themselves. In this case, the 'non-rotating' squares system was built in a manner which permits deformation in a stretching manner through sliding in the directions of the lengths of the squares, hence called "stretching squares", rather than operating as rotating squares (see Figure 7a).

The study by Grima *et al.* [144] investigates two types of 'non-rotating' square structures, referred to as Orientation I and Orientation II (see Figure 7b), which can be related to the orientation used for studying Type I and Type II rotating rectangles, which will be discussed later. It was found, through analytical modelling, that the stretching sides adaptation was highly anisotropic and had provided the structure with a negative or zero Poisson's ratio in-plane, as evident in Figure 7c,d, depending on the direction of stretching (or the orientation of the structure) or the angle between the squares. In fact, when stretching on-axis in Orientation II, the Poisson's ratio is always zero, whilst for loading on-axis in Orientation I, the Poisson's ratio is at its most negative value and dependent on the angle between the squares.

In a second paper on this topic, by Attard *et al.* [145], stretching and rotations of the square were allowed to take place concurrently where it was shown that the mechanical properties, including the Poisson's ratio, were dependent on the relative extents of stretching and hinging, the size of the square and the angle between the squares. It was thus suggested that this may be used to design systems with pre-desired Poisson's ratio values.

It was pointed out in such work that this, once again, helps give a better understanding of how real-life materials and structures would act, since true rigid units would be nearly impossible to achieve, and it is far more likely that a range of mechanisms will be operating at once, albeit some more predominantly than others. It is still important to consider these lesser effects when applying structures and mechanisms however, as certain applications are extremely sensitive and ignoring them could be catastrophic. [145] [144]

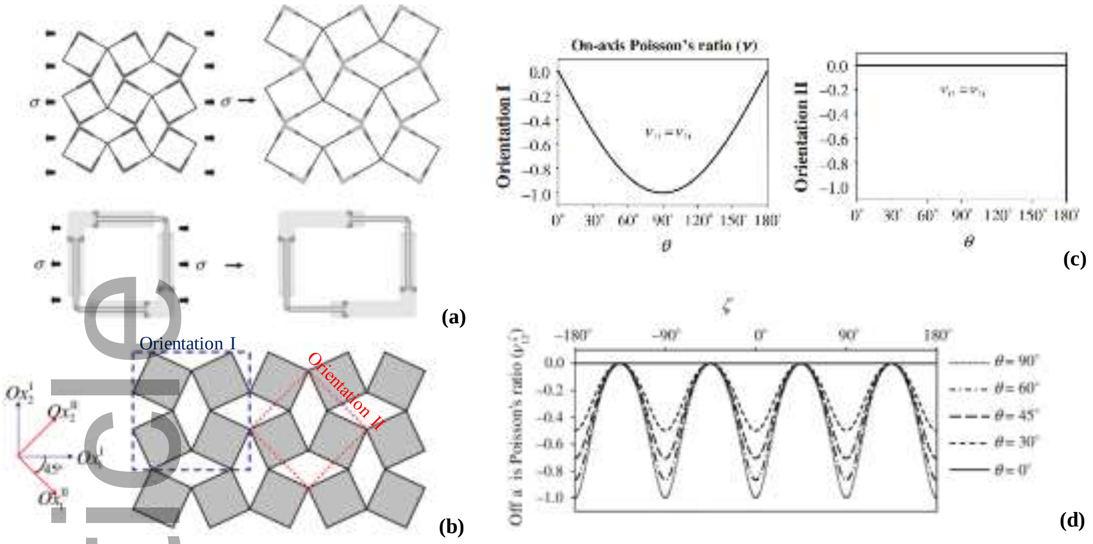


Figure 7: (a) The concept of 'stretching squares'; (b) The definition of the two simplest unit cells / orientations (Orientation I and II); (c) The on-axis Poisson's ratios for Orientation I and II, highlighting that Orientation II has a Poisson's ratio of zero, irrespective of the angle between the squares; (d) the off-axis in-plane Poisson's ratios where ζ=0º corresponds to Orientation I. Note that in this diagram, θ is the angle between the squares whilst ζ refers to the 'off-axis' angle. Figure adapted from [144].

5. On the importance of Shape: Rotating Polyhedra

5.1 The 'Rotating Rectangles' (Elongated Squares) Mechanism

In one of the more cited papers on auxetics published in *Physica Status Solidi b*, “Auxetic behaviour from rotating rigid units”, Grima, Alderson and Evans first mentioned the possibility of the existence of rotating irregular quadrilateral systems, a structure here termed a general model for the rotating squares system. [146] To some extent, this opened a whole new concept related to irregularity in rotating rigid unit mechanisms, which could possibly increase the applications one may have for such systems. The approach taken in this paper was to start by recognising that “the only space filling structures that may be built using regular polygons are those involving equilateral triangles and squares” (see Figure 8a, a result which was deduced from Johannes Kepler’s (1571–1630) book *Harmonice Mundi* [147] that “the only three regular *p*-sided polygons that can be tessellated to cover a plane in a space filling manner to from regular tessellations are the equilateral triangle, the square and the regular hexagon” and that “the number of polygons meeting at any one vertex must also be even since a hinge connects two (and only two) vertices”). It was then formulated that if one would relax the requirement of using ‘regular polygons’, far more general and complex structures could be obtained (see Figure 8b).

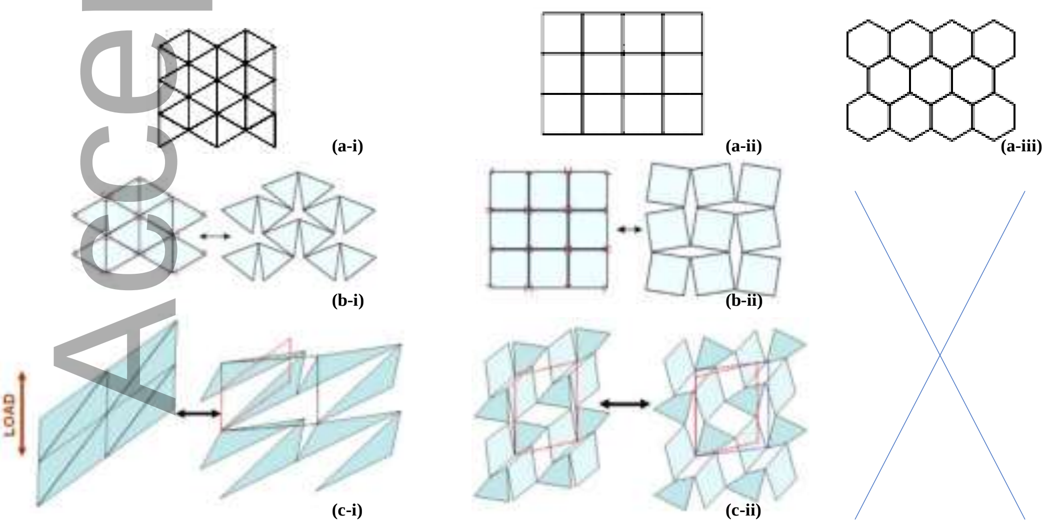


Figure 8: The evolution leading to generic rotating rigid units, shown in (c). These were conceived by noting that, as shown in (a), only the equilateral triangle, square and regular hexagon can tessellate in a space filling manner, and as shown in (b) of these, only the triangles and squares have an even number of polygons meeting at a common vertex and thus only these two can be used to construct ‘rotating rigid unit’ auxetics. Adapted from Grima *et al.*. [146].

The most obvious first evolutionary step if one had to discuss the effect of shape of the rigid unit on the Poisson's ratio is to replace the 'squares' in the original studies by Grima *et al.* [18,139,148,149] by a slightly more general rigid unit, such as 'rectangles'. Unlike the squares, the geometry of which is defined by just one geometric parameter (normally, the side length), the shape and size of rectangle needs to be defined by two parameters, normally the length of two non-equal sides ($a \times b$).

Two important studies on rotating rectangles carried out by Grima, Alderson and Evans [150] [146] looked at what was later termed as the 'Type I Rotating Rectangles'. These studies were conducted through the use of analytical models where the rotating rectangles structure described in the aforementioned work was carefully analysed and a model was produced to determine the mechanical properties in relation to the structural conformation (i.e. structural features such as the lengths of the rectangle sides). It was determined that the on-axis Poisson's function of the system oriented as shown in Figure 9, can be reported as follows:

$$\nu_{21} = (\nu_{12})^{-1} = \frac{a^2 \sin^2\left(\frac{\theta}{2}\right) - b^2 \cos^2\left(\frac{\theta}{2}\right)}{a^2 \cos^2\left(\frac{\theta}{2}\right) - b^2 \sin^2\left(\frac{\theta}{2}\right)}, \tag{15}$$

where a is the longer side and b is the shorter side of a rectangle in the structure as shown in Figure 9a, and θ is the angle between two long sides of two adjacent rectangles. This was found by following the same method used in the study described above, using the Poisson's function equation in (11) and inputting the differentiated unit cell length equations. It is important to note that in this case the Poisson's ratio was not found to be −1, a feature which can be attributed to symmetry differences to that of the structure of the rotating squares. In fact, an analysis of equation (15) suggests that the on-axis Poisson's ratio may be positive or negative, as shown in Figure 9b, where positive Poisson's ratio is manifested at intermediate values of θ within the range from 0^o to 180^o, more specifically within the range:

$$2\tan^{-1}\left[\min\left(\frac{a}{b},\frac{b}{a}\right)\right] < \theta < 2\tan^{-1}\left[\max\left(\frac{a}{b},\frac{b}{a}\right)\right]. \tag{16}$$

This, apart from showing that the systems where θ tends to 0º or 180º is always auxetic on axis whilst the system with θ = 90º always has postive on-axis Piosson's ratio, suggests that higher aspect ratios of the rectangles correspond to a wider θ-range of non-auxetic behaviour.

The Young's modulus was also calculated using an energy conservation approach. The equations obtained for Poisson's ratio and Young's modulus were then used to plot these properties for different angles of θ (i.e. for different configurations of the structure, from completely closed, up to completely open) (see Figure 9b) where it was confirmed that the system could exhibit a wide range of negative and positive on-axis Poisson's ratio values which were dependent on the shape of the rectangles (*a*,*b*) and the angle θ. In the same studies, Grima *et al.* also determined the off-axis properties for the rotating rectangles model by analytical modelling where it was shown that the off-axis equations for Young's modulus, E_1^{ζ}, Poisson's ratio, ν_{12}^{ζ}, and shear modulus, G_{12}^{ζ}, determined using techniques described by Nye (Nye, 1957), were respectively found to be:

$$E_1^{\zeta} = \left[\frac{\cos^4(\zeta)}{E_1} + \frac{\sin^4(\zeta)}{E_2} - 2\frac{\nu_{12}}{E_1}\cos^2(\zeta)\sin^2(\zeta) \right]^{-1}, \tag{17}$$

$$\nu_{12}^{\zeta} = -E_1^{\zeta}\cos^2(\zeta)\sin^2(\zeta)\left(\frac{1}{E_1} + \frac{1}{E_2}\right), \tag{18}$$

$$G_{12}^{\zeta} = \left[2\cos^2(\zeta)\sin^2(\zeta)\left(\frac{2}{E_1} + \frac{2}{E_2} + \frac{4\nu_{12}}{E_1}\right) \right]^{-1}, \tag{19}$$

where ζ is the angle at which the structure is loaded relative to its principal axis; and E_1 and E_2 are the Young's moduli for directions 1 and 2 respectively. A comparison was also made to the rotating rigid squares structures, where the properties in this case would simply be $E_1^{\zeta} = E_1 = E_2 = E$, $\nu_{12}^{\zeta} = -1$, and $G_{12}^{\zeta} = \infty$ due to increased symmetry in the properties of the structure [18].

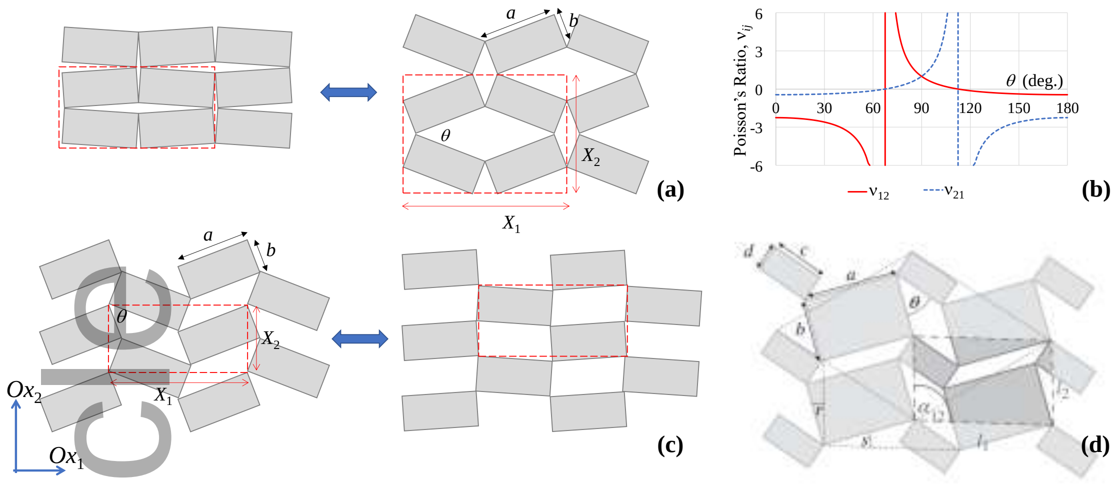


Figure 9: (a) The Type I Rotating rectangles which can exhibit both positive and negative Poisson's ratio, as shown in (b) for a = 1.5, b =1; (c) The Type II Rotating rectangles which is isotropic with Poisson's ratios of –1 for any shape of rectangles; and (d) The more generic system made from two sets of rectangles. Image adapted from [151].

As more studies on the vast field of thermo-mechanical metamaterials were carried out, different connectivity of the rectangles, as well as different constructions of the model, for the manifestation of auxeticity began to come to light. One study [152], looked at rectangles connecting at their corners in such a way that the empty spaces produced by the built structure are in the form of a rectangle when fully open, also known as the ($a \times b$) sides model, a structure which became known as the Type II rotating rectangles (see Figure 9c). In this work, the previously mentioned rotating rectangles with sides connected to form squares in the empty spaces when fully open, also referred to as the ($a \times a$) or ($b \times b$) sides model, were given the label Type I rotating rectangles due to their earlier discovery. [152] One should note that a characteristic difference of these two types of structures is that while the Type II rotating rectangles system has spaces which are all equal in shape, size and area at any level of 'openness' of the structure, like the behaviour of the rotating squares model, this does not hold true for the Type I system. This difference is evident in analogous symmetrical arguments which can be made for these systems, where, through further research, it was found that the Type II system has properties which are more similar to the rotating squares system than the Type I system does. In particular, it was found that for the Type II systems, using the approach described above, the he Poisson's function simplifies to:

$$\nu_{21} = (\nu_{12})^{-1} = -1, \tag{22}$$

which Poisson's ratio properties are even exhibited off-axis. This further shows the robustness of analytical modelling in the formulation of results and conclusions for such systems. Even though the rotating square and Type II rotating rectangle structures are not exactly alike, the symmetrical similarities are conveyed through the results obtained, which come through as a Poisson's ratio of −1 in all directions for both structures. These findings greatly increased the versatility and applicability of this type of mechanism, where for example, it was shown that this model could be used to explain auxetic behaviour in α-cristobalite.

A later more generalised study [151] on rotating rectangles focused on systems which were made from two sets of different sized rectangles, '$a \times b$' and '$c \times d$' where the alignment used in the analytical modelling was similar to that used to formulate the Type II model, see Figure 9d. This more complex model, which unfortunately lost the elegance of the simpler Type I and Type II models where all the rectangles were of the same size, was able to show a number of interesting characteristics. First and foremost, it was shown that when using a structure which does not have the symmetry relationships described earlier, the Poisson's ratio of −1 is lost. This was shown analytically using the method described above, where it was found that the on-axis Poisson's ratio function, for the systems oriented as shown in Figure 9d, can be expressed as:

$$\nu_{12} = \left(\nu_{21}\right)^{-1} = \frac{-bd\left[ab + cd + \sin(\theta)(ad + cb)\right]\cos(\theta)}{\left[ad^3 + cb^3 + bd\sin(\theta)(ad + cb)\right]\cos(\theta)}, \quad \text{for } 0° \leq \theta \leq 180°,\ \theta \neq 90° \tag{23}$$

where a, b, c, and d are side lengths of the rectangles and θ is the smallest angle between the rectangles. It was also shown that in the general case, these systems could shear upon loading on-axis. However, the true power of this model was the many systems it could represent, simply by assigning specific relationships between a,b,c and d. For example, by letting $a = b = c = d$ one would get the standard rotating squares whilst by letting $a = b$ and $c = d$, one would get a system made from two non-equally sized squares (similar to the projection of the auxetic $BAsO_4$ in the (001) plane [7]), which, for idealised systems made from rigid squares, would also show Poisson's ratios of –1. Similarly, by letting $c = b$ and $d = a$ one would get the Type I rectangles whilst by letting $c = a$ and $d = b$ one would get the Type II rectangles. Other interesting relationships emerged, where for example, in cases where *bc*/*d* = *a*, the Poisson's ratio gives a value of −1, otherwise the values are always higher than −1. [151].

One should also note that these systems were studied for other properties, including negative compressibility [153]; and negative thermal properties [79]. In fact, for example, apart from being auxetic, these structures have also been well studied for their negative linear compressibility (NLC) property, a property which is directly related to the Young's modulus and Poisson's ratio of a material. It was found that both the rotating squares and the Type II rotating rectangles are not expected to exhibit NLC due to having an isotropic negative Poisson's ratio. On the other hand, the Type I rotating rectangles system, which as mentioned above could exhibit positive Poisson's ratios, was found to have regions of NLC. The on-axis compressibility in the Ox_1 and Ox_2 directions, for the systems oriented as shown in Figure 9a, were found to be:

$$\beta_L[Ox_1] = \frac{(a^2+b^2)\cos(\theta)}{8K_h}\left(\frac{a\tan\left(\frac{\theta}{2}\right)-b}{a+b\tan\left(\frac{\theta}{2}\right)}\right), \quad (24)$$

$$\beta_L[Ox_2] = \frac{(a^2+b^2)\cos(\theta)}{8K_h}\left(\frac{a-b\tan\left(\frac{\theta}{2}\right)}{b+a\tan\left(\frac{\theta}{2}\right)}\right), \quad (25)$$

where *a* is the length of the longer side of the rectangle, *b* is the length of the shorter side of the rectangle and θ is the angle of aperture between the rectangles. Plots of these equations, which confirm NLC, are shown in Figure 10. The off-axis compressibility, measured at an angle ζ to the Ox_1 axis was found to be:

$$\beta_L[\zeta] = \frac{\cos(\theta)\left[(-a^4+b^4)\cos(2\zeta)+(a^2+b^2)^2\cos(\theta)\right]}{8K_h\left[2ab+(a^2+b^2)\sin(\theta)\right]}\left(\frac{a\tan\left(\frac{\theta}{2}\right)-b}{a+b\tan\left(\frac{\theta}{2}\right)}\right), \quad (26)$$

where K_h is the stiffness constant of the hinge connecting the rectangles.

In terms of negative thermal expansion (NTE), an analytical model for the Type I rotating rectangles, derived using the same protocol as formulated for squares by Heine, Welche and Dove [67], was able to show that this system may exhibit a more pronounced negative thermal expansion, which property becomes more enhanced as the rectangles become more elongated [79].

It should be noted that the 'rotating rectangles model' provides an excellent connection between rotating rigid unit mechanisms and the wine-rack mechanisms which is well known for its NLC and NTE characteristics and is one of more widely used structural models for explaining NLC and NTE in a wide range of materials [43,82,86,154–158]. In fact, as the aspect ratio of the rectangles becomes extreme, i.e. using pencil-like rigid units rather than square-shaped ones, the system starts to increasingly resemble the wine-rack model. This, once again, highlights the usefulness of studying such negative properties from the point of view of idealised geometry-based models, and emphasises the need to look at these thermo-mechanical properties in an holistic comprehensive manner.

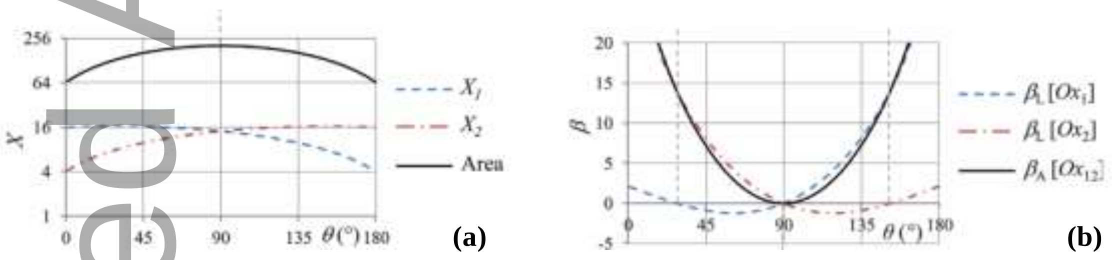


Figure 10: (a) The unit cell dimensions and area of the unit cell for a Type I rectangle with a = 8, b = 2, (b) the linear on-axis compressibility and the area compressibility (in arbitrary units). Note that although there are values of θ which correspond to NLC, the area compressibility (which for 2D systems would be the equivalent of the volume compressibility) is never negative. Image adapted from [153].

Work continues to be carried out on these systems to this day, including other work which has not been discussed here. This includes work on hierarchical systems of rotating squares, which have shown that the system in the higher hierarchical levels takes precedence in operation [27]; adaptations of systems by means of using attractive and repulsive forces or changing the resistance at the rotation point in order to fine tune the desirable properties [159] [160]; and numerous other past and ongoing projects around the globe. It must also be said that, in analogy to the 'rotating squares' variations illustrated in Figure 5, it is possible to replace the polygons with other, possibly more aesthetically pleasing ones, or ones specifically designed for particular practical applications.

5.2 The 'Rotating Rhombi' (Sheared Squares) Mechanisms

Following from the work on rotating rectangles, Grima and co-workers considered 'rhombi' [161], which are also a slightly more general rigid unit when compared to squares. In fact, like 'rectangles', the shape and size of rhombi can be defined by just two parameters, normally the length of sides, *a*, and one of the interior angles, ϕ (rhombi are simply 'sheared squares' where 90° square internal angles are now ϕ and 180°-ϕ).

In the main published work carried out on rotating rhombi, titled "Auxetic behaviour from rotating rhombi", the possible systems that can be constructed from equal sized rhombi were categorised into two; Type α and Type β systems, which were defined as follows: "in 'Type α rotating rhombi' the obtuse angle of a rhombus always connects to an acute angle of an adjacent rhombus, while in 'Type β rotating rhombi' adjacent rhombi have their like angles connected to each other" (See Figure 11a and b respectively). Analytical models were then produced for each of the models using the same methods described above, where it was found that the Type β systems had an isotropic Poisson's ratio of -1 while the Type α systems were not isotropic. This feature can once again be attributed to certain symmetries and to the way the pores open up. Specifically, the in-plane Poisson's ratio equation for Type α systems oriented as shown in Figure 11(a-i), was given as:

$$\nu_{12} = (\nu_{21})^{-1} = \tan\left(\frac{\theta-\phi}{2}\right)\tan\left(\frac{\theta+\phi}{2}\right), \tag{27}$$

where θ is the small angle between rhombi and ϕ is the interior angle of the rhombus. As shown in Figure 11a-ii, this expression of the Poisson's ratios simplifies to $\nu_{12} = -1$

when $\phi = 90^o$, as the rhombi would become squares, and, the Poisson's ratio is negative for half of the 'θ-ϕ' angle combinations (the shaded region in Figure 11a-ii).

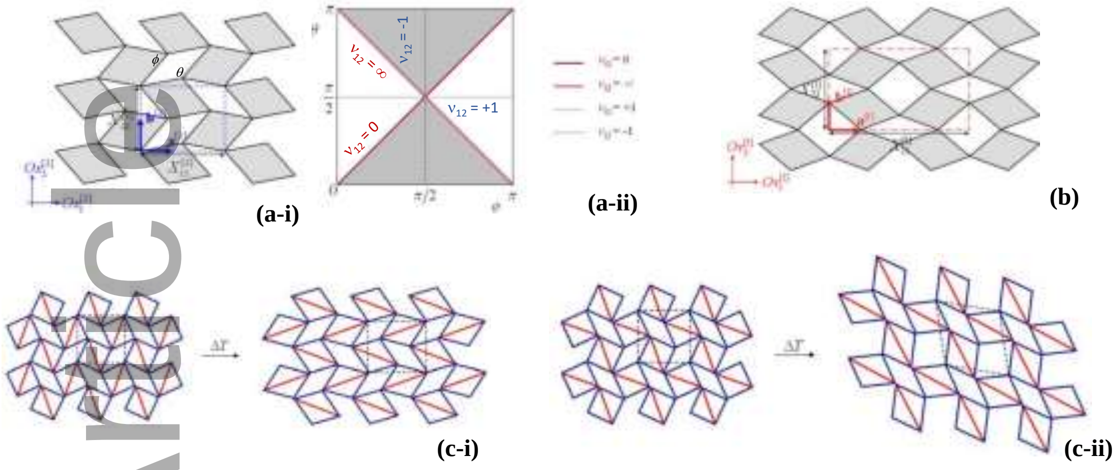


Figure 11: (a-i) The Type α Rotating Rhombi and (a-ii) their Poisson's ratio ν_{12}; (b) The Type β Rotating Rhombi which exhibit a Poisson's ratio of –1; (c) temperature sensitive systems which change their conformation when heated (red material expands more when heated than blue material). As a result of the different manner of placing the diagonals, the system (c-i) becomes Type α Rhombi, i.e. have shape/temperature dependent Poisson's ratio whilst the system in (c-ii) becomes Type β Rhombi, i.e. have shape/temperature independent properties with Poisson's ratio always –1. Image adapted from [161].

In the same study, an investigation was also carried out to determine the effect of temperature on systems made from 'smart' squares which become rhombi when heated. More specifically, the systems were modelled from pin-jointed rods where the material used to form the sides of each rhombus had a different thermal expansion coefficient to the rods used to make the diagonals. It was found that while the properties of the systems resulting in β type structures were unaffected by temperature (see Figure 11c-ii), the α type structures were affected and so that their Poisson's ratio could be considered to be temperature dependent (see Figure 11c-i). [161] This compliments the work which was done on the potential of such systems to exhibit negative thermal expansion, where once again, it was shown that the Type α rhombi had a potential to optimise NTE [79].

Apart from negative Poisson's ratio properties, Type α rhombi systems were also found to exhibit NLC, a property which is possible because the Poisson's ratio could also be positive. [153] It was determined analytically that the equations for the compressibility in the Ox_1 and Ox_2 directions, for the systems oriented as shown in Figure 11a-i, and the off-axis compressibility are:

$$\beta_L[Ox_1] = \frac{a^2\cos(\theta)}{4K_h}\cot\left(\frac{\phi+\theta}{2}\right), \tag{28}$$

$$\beta_L[Ox_2] = \frac{a^2\cos(\theta)}{4K_h}\tan\left(\frac{\phi-\theta}{2}\right), \tag{29}$$

$$\beta_L[\zeta] = \frac{1}{8K_h}\frac{a^2\cos(\theta)\left[\cos(\theta)+\cos(\phi)\cos(2\zeta)\right]}{\sin\left(\frac{\phi+\theta}{2}\right)\cos\left(\frac{\phi-\theta}{2}\right)}, \tag{30}$$

A plot of the on-axis compressibility is shown in Figure 12 below, which clearly shows that negative linear compressibility is exhibited on-axis for a quarter of the 'θ-ϕ' angle combinations. Note that this corresponds to half of the 'θ-ϕ' angle combinations which give positive Poisson's ratio since in the other half, the Poisson's ratio was not high enough to result in a lateral contraction to result in NLC.

Note that Type β rhombi cannot exhibit NLC due to an isotropic negative Poisson's ratio property, similar to that of Type II rectangles. [153]

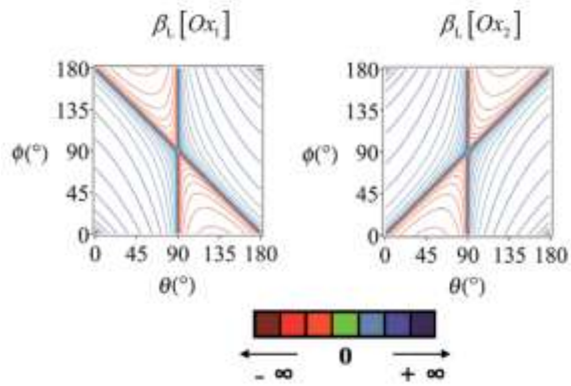


Figure 12: The on-axis compressibility for the Type α rhombi. Image adapted from [153].

5.3 The 'Rotating Parallelograms' (Elongated-Sheared Squares) Mechanisms

Originally suggested in the paper which first studied the rotating squares mechanism analytically [18], rotating parallelograms are the systems in the next higher level of complexity following the rotating rectangles and rotating rhombi [162,163]. In fact, a parallelogram can be considered as a more generic form of a rectangle (a sheared rectangle) or a more general form of rhombus (an elongated rhombus). Thus, following the study of the properties of the rotating rectangles and rotating rhombi, the next evolutionary step was to discuss ‘rotating parallelograms’, the shape of which rigid unit needs to be defined by three geometric parameters, normally the length of two non-equal sides (a, b), and the internal angle, ϕ. Due to this added generality, their development has led to a much better understanding of how modifications of such mechanisms can allow for fine tuning of the highly desirable auxetic property in structures. While not a vast amount of work has been done on these systems, the structures have been described, categorised, and analytical models have been produced for them.

For the rotating parallelograms case, a study, which defined the different types of systems as Iα, Iβ, IIα, and IIβ (a nomenclature combining that of rotating rectangles with rotating rhombi, see Figure 13), found that type IIβ systems have a Poisson’s ratio of −1 in all directions of loading, while this is not the case for the other systems. The other systems do, however, exhibit anomalous Poisson’s ratio properties as they have a negative Poisson’s ratio values for certain conformations. [162]. The expressions for the on-axis Poisson’s ratios, for the systems oriented as shown in Figure 13 were also derived. Off-axis properties can also be obtained using established techniques as exemplified elsewhere [164].

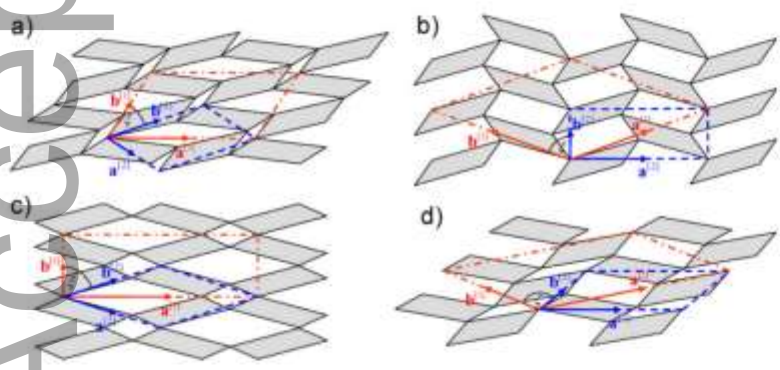


Figure 13: The four possible networks that can be constructed from parallelograms: (a) Type Iα; (b) Type IIα (c) Type Iβ and (d) Type IIβ, where (a) and (b) are space filling whilst (c) and (d) are not. Of these four systems, it is only the Type IIβ which exhibits Poisson’s ratios of –1. The figure also shows the two possible orientations / unit cells with unit cells for Orientation 1 shown in a red dash-dot-dash line whilst that for Orientation 2 shown in a blue dash line. Image adapted from [162].

5.4 Other 'simple' Rotating Rigid Units Mechanisms in 2D

Apart from systems made from polygons having four corners which are topologically equivalent to rotating squares, other mechanisms involving shapes with more and less corners have also been studied. A well-studied mechanism of this type is the 'rotating rigid triangles' model. Here, in its simplest form, triangles, equilateral or otherwise, are connected at their corners to form the structure shown in Figure 14a. This structure was first disclosed in 1999 as a model for explaining the auxetic behaviour in a number of nanomaterials [148,149]. Following this initial report, the system made from triangles was first formally reported to operate in such a manner in the work which originally reported the rotating squares mechanism back in 2000 by Grima and Evans [18], and was then re-mentioned in some more depth by the same authors in a subsequent paper that same year [134]. In the second paper, it was reported that upon application of a uniaxial stress in the principle axes for a regular equilateral model, the response produced is similar to that of the rotating squares model, where the Poisson's ratio is −1. This can be attributed to the regularity and symmetry of the model, in analogy to the auxetic trimer systems pioneered by Wojciechowski *et al.* [165,166].

In this same paper, the authors also implemented the model as a molecular level nanonetwork in the form of a poly(phenyl)acetylene structure (see Figure 14b, i.e. a structure made from benzene bound to acetylene chains, with different lengths of links [134] where it was confirmed through molecular modelling software that these nano-networks mimic the behaviour of the rotating triangles model and exhibit negative Poisson's ratios.

However, apart from the other mention in the Grima, Alderson and Evans [167] paper (*vide supra*), full analytical modelling of the 'rotating equilateral triangles' as well as more generic forms of it were only reported years later. In the first of such publications, Grima and Evans [168] have shown that rotating fully rigid equilateral triangles are isotropic in-plane with a Poisson's ratio of –1 irrespective of the size of the triangles. It was however also shown that, had the triangles been scalene, as shown in Figure 14c, the loss of symmetry would result in anisotropy and a geometry-dependent Poisson's ratio. In fact, Grima *et al.* [169] showed through analytical modelling that systems built from scalene rigid triangles, which deform through relative rotations of such triangles, can exhibit a very wide range of Poisson's ratio values, both positive and negative, the magnitude of which depends on the shape of the scalene triangles and the angles between them. Furthermore, in analogy to the work on rotating rhombi [161], the work also explored designs where the triangular units have sides made from materials which respond to temperature differently. As a result, they were able to show that the system could be designed to exhibit temperature-dependent Poisson's ratios. Unfortunately, the mathematical model of the more generic system is rather complex (for example, the system shears when uniaxially loaded on-axis) and the model lacks the mathematical elegance in other simpler models. In fact, the true beauty of this model is the various specific cases of this model which can be considered, such as the system made for two sets of non-equal sized equilateral triangles which also exhibits Poisson's ratios of -1.

In another study which builds on this work, Zhou, Yang and Zhang [170] also showed that this generic system can exhibit negative linear compressibility in some directions, for specific triangle shapes and angles between triangles. This result was in line with the findings in other systems exhibiting high positive Poisson's ratio values as discussed by Attard *et al.* [153]

Before this later development, Dudek *et al.* [53] also reported work they performed which modelled a different 'unimode' 'rotating triangles' system (Figure 14d-iii). This system, which had earlier been suggested by Milton [21] (Figure 14d-i), was analysed through analytical modelling for its mechanical (and thermal expansion) properties where it was shown that "these unimode systems exhibit positive Poisson's ratios irrespective of size, shape and angle of aperture, with the Poisson's ratio exhibiting giant values for certain conformations". This showed in an explicit manner that not all rotating rigid unit systems need to be auxetic. It was also shown that NLC was exhibited whenever the Poisson's ratio in that direction exceeded +1.

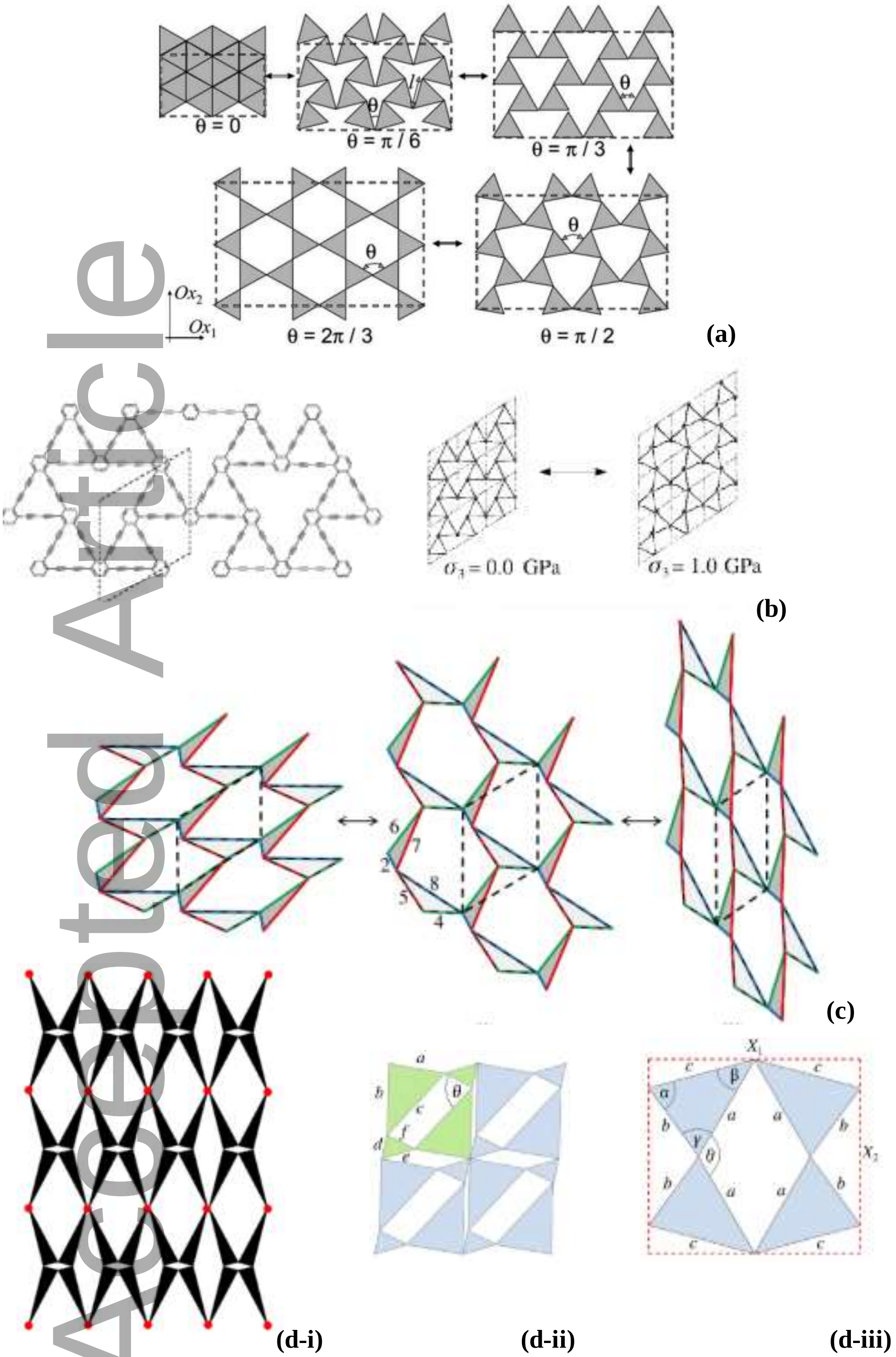


Figure 14: (a) The 'original' rotating triangles model by Grima & Evans (taken from [168]); (b) its implementation as a nano-network [134] (c) The generic form studied by Grima *et al.* [169] for its Poisson's ratio properties and by Zhou, Yang and Zhang [170] for its NLC properties (Image taken from [169]; (d-i) the implementation by Milton [21], (d-ii) the generalisation of Milton's model as suggested by Dudek *et al.* [53] and (d-iii) the system modelled by Dudek et al.

6. More Complex Implementations of Rotating Rigid Units in 2D

In addition to the systems mentioned above, the concept of inducing auxeticity in 2D as a result of planar plate-like units which rotate relative to each other has been further developed and implemented in a number of other systems.

One of the more elegant extensions of the work on 'rotating squares' was the proposal of a hierarchical structure where the 'rotating squares' (hierarchical level *n*) are made from other 'rotating squares' (hierarchical level *n*-1), and so on, until reaching the most basic original 'rotating squares' (hierarchical level 0). This concept, pioneered by Gatt *et al.* [27] is illustrated graphically in Figure 15 for a three-level hierarchical system. Simulations on this model not only confirmed the auxetic characteristics, but also suggested that the manner of opening upon stretching can be controlled through design, thus permitting some rather smart applications such as in drug delivery. [27]

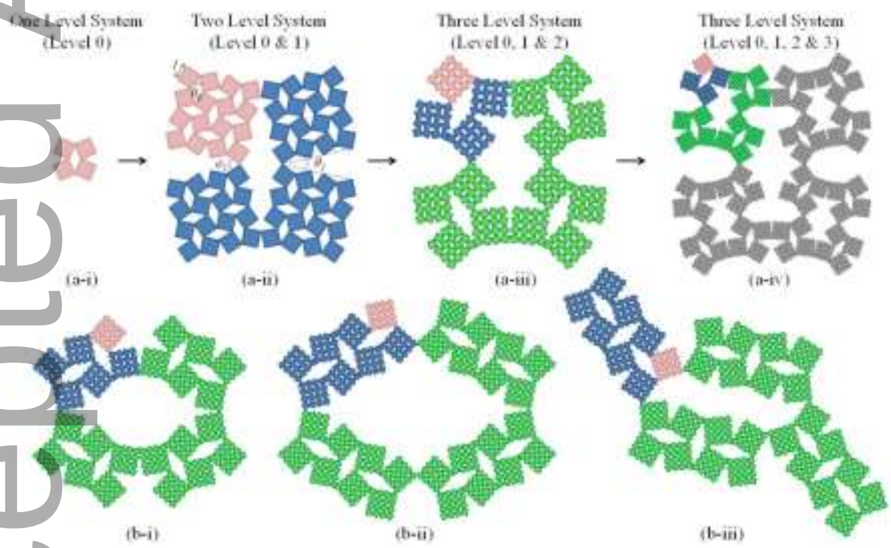


Figure 15: The hierarchical 'rotating squares', where (a) shows a three-Level hierarchical 'rotating squares' system, where all the levels are approx. square-shaped; (b) shows how variation can be introduced at higher level where in this case Level 3 is rectangular rather than square shaped. (Image taken from Gatt *et al.* [27]).

Another conceptual system evolving from rotating units is based on the well-studied idea of perforated systems where perforations are made in a sheet to create the pores, leaving a network of connected rotating units, in contrast to systems produced by directly building a system from individual units. These perforations can be done in many different shapes and forms, resulting in a production method which allows for versatile modifications of the rotating unit systems. One example is the perforation of a sheet material in order to produce a system which mimics the rotating squares system.

[20,171] This can also be done for other two-dimensional mechanisms for negative Poisson's ratio, such as rotating rectangles [172], rotating parallelograms [172], and rotating triangles [20] [173], which have also been studied. Perforated sheets have been found to successfully mimic the properties, albeit not to the same extent, of the respective idealised systems. This is because the resultant perforated systems have the inclusion of these rigid (or semi-rigid) units connected at their corners as necessary for operation. [20] Work has also been carried out on the removal of shapes to form the structures with anomalous properties. This includes the removal of ellipse shapes [174] and star shapes [28]. A graphical survey of such perforated structures is provided in Figure 16. Note that the robustness of the underlying mechanism was amply demonstrated when it was shown that auxeticity is retained even if the system is irregular or disordered to some extent [175].

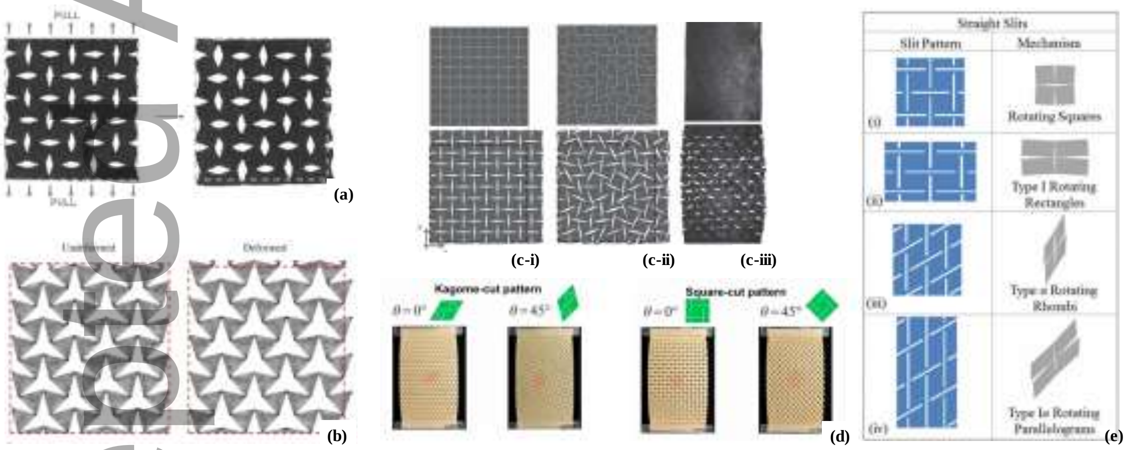


Figure 16: A graphical survey of 'perforated structures' with a special focus on those based on rotating rigid units: (a) shows the original report of a perforated system meant to mimic rotating squares [20] (b) shows the equivalent triangles model [173]; (c) slits, ordered (c-i) and disordered (c-ii) together with a prototype (c-iii) [175] (d) various models built by Shan *et al.* [176] tested for isotropicity (e) sheets with slits meant to mimic rotating squares, rectangles and parallelograms [177].

Another very smart implementation of the 'rotating squares' was the one proposed by Bertoldi and co-workers who looked at compressive deformations of 2D sheet-like structures having periodically arranged circular holes which, upon uniaxial compression, change their profile to become elliptical thus permitting the formation of the 'rotating squares' profile with its associated auxetic properties (see Figure 17a). This well cited work by Bertoldi and co-workers [178] may be, to some extent, regarded as a most practical implication of the proposal that had been made earlier by Grima, Alderson and Evans [167] for transforming similar conventional cellular system to auxetic forms (see Figure 17b).

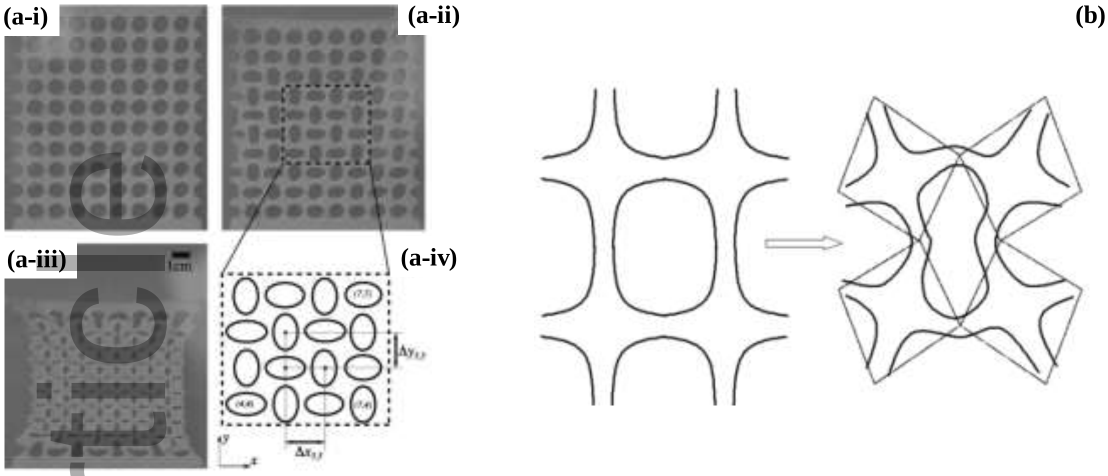


Figure 17: (a) Bertoldi *et al.* [178] model, where (a-i) shows the initial unstrained structure, (a-ii) shows the same structure under 6% uniaxial compression, where the 'rotating squares' motif becomes evident; (a-iii) shows sample under 25% compression and (a-iv) shows a schematic diagram of the central region shown in (a-ii). (b) Grima, Alderson and Evans [167] model which shows a similar concept of transformation, this time induced by biaxial compression (used as an explanation for the for conversion process), an idea originally proposed by Grima in his doctoral thesis [139].

7. Rotating Units in Three Dimensions

Apart from such two-dimensional systems, there have also been attempts to produce rotating rigid units which exist in three-dimensions, where, as noted elsewhere, different aspects need to be considered [179,180]. Pioneering work in this respect is the work involving 'rotating tetrahedra' which, as noted above, were inspired by crystalline systems such as α-cristobalite which are known to exhibit auxetic behaviour [115,126,128,181].

Other early work was carried out by Gaspar *et al*. [182], where a 3D system, which was not made from rotating rigid units but rather of a connected nodes model, was studied for its auxetic properties and its Poisson's ratio was determined analytically for different planes. More recently, work on 3D rotating rigid unit auxetic structures was carried out by Attard and Grima, [183] where a system based on the hexagonal rotating rigid-units system was designed (see Figure 18) and studied analytically. The system was found to have a Poisson's ratio in the Ox_1-Ox_2 plane; Ox_1-Ox_3 plane; and Ox_2-Ox_3 plane of:

$$\nu_{12} = \left(\nu_{21}\right)^{-1} = -\frac{X_1}{X_2} \frac{a_2 \cos\left(\frac{\theta}{2}\right)}{b_2 \cos\left(\frac{\theta}{2}\right) - a_2 \sin\left(\frac{\theta}{2}\right)}, \tag{32}$$

$$\nu_{13} = \left(\nu_{31}\right)^{-1} = -\frac{X_1}{X_3} \frac{a_2 \cos\left(\frac{\theta}{2}\right)\left(b_3 \cos\left(\frac{\varphi}{2}\right) - c_3 \sin\left(\frac{\varphi}{2}\right)\right)}{c_3 \cos\left(\frac{\theta}{2}\right)\left(b_2 \cos\left(\frac{\theta}{2}\right) - a_2 \sin\left(\frac{\theta}{2}\right)\right)}, \tag{33}$$

$$\nu_{23} = \left(\nu_{32}\right)^{-1} = -\frac{X_2}{X_3} \frac{\left(b_3 \cos\left(\frac{\varphi}{2}\right) - c_3 \sin\left(\frac{\varphi}{2}\right)\right)}{c_3 \cos\left(\frac{\varphi}{2}\right)}, \tag{34}$$

where X_1, X_2 and X_3 are the defined unit cell parameters; a_i, b_j and c_k i,j,k = 1,2,3 are the edges of the three-dimensional cubic / cuboidal units; and θ and φ are the angles between the cubes / cuboids, respectively. Alternatively, the Poisson's ratio was determined by taking a 2D section of the Ox_1 vs Ox_2 plane, and the same Poisson's ratio result was found, showing the robustness of the analytical methods employed.

A later suggested model was that by Luotoniemi, where a hypercube system colloquially known as the jitterbox was produced as an auxetic mathematical artwork, a perfect example of the links between art, mathematics, and material science. [184] These show the variety that can be achieved from these structures, both when studying them, or choosing to apply them where they may have a practical purpose. Future studies aiming to apply them may choose to take advantage of this variety by creating new systems with a similar theoretical background in order to truly tailor to the consumer who requires it.

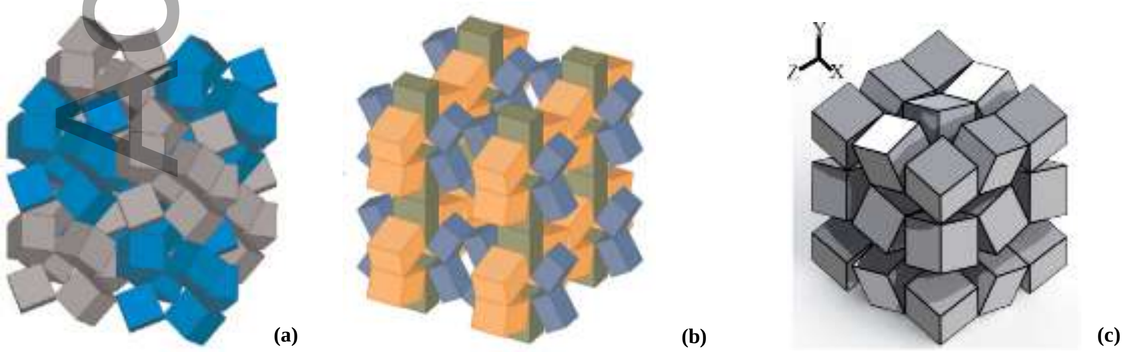


Figure 18: Three examples of rotating rigid polyhedra (a) corner sharing 'rotating cuboids' [183], (b) edge sharing 'rotating cuboids' [183], (c) edge and corner sharing 'rotating cuboids' [185] as first published in

Journal of Mechanics of Materials and Structures in Vol. 13 (2018), No. 1, published by Mathematical Sciences Publishers.

In addition to the systems which makes use of rotating three-dimensional polyhedral to generate the auxetic effect, one should also mention three very smart ways how to transform 2D rotating rigid unit auxetics to 3D. The first involves a simple transformation where the plane of the structure is given a 3D profile, such as turning it to a tube / cylinder. This approach was found to be rather useful in the design and manufacture of 3D tubular auxetics (see Figure 19) and a more detailed discussion on the properties of such finite-sized tubular stent-like auxetic structures is available elsewhere [117].

The second, development was proposed by Farrugia and co-workers in 2007 at 4th International Workshop on Auxetics and Related Systems (Malta) who proposed a novel mechanism which is very similar to that found in traditional 'push drill tools' to convert rotational motion to linear motion and vice-versa. In the very recent formal publication of this concept, Farrugia and co-workers propose and demonstrate that this mechanism can be used to connect parallel sheets of 'rotating squares' to convert them from two-dimensional to three-dimensional auxetics, as shown in Figure 20a [22]. Another rather similar idea was proposed by Duan and co-workers [186] who published what they term as a 'novel 3D NPR material design method based on the tension-twist coupling effects' which essentially combines parallel layers of rotating-squares through ligaments which twist as the squares rotate upon stretching forcing an increase in the separation between the squares, i.e. achieve auxeticity in 3D (see Figure 20b).

More recently, Grima-Cornish *et al.* [17] proposed a modification to the basic rotating-squares system to transform it from 2D to 3D. This modification builds on the fact that one of the diagonals of rhombic pores within the rotating squares model actually gets shorter as the rotating squares are pulled open, and thus can be used as the trigger for what they terms as a 'triangular elongation mechanism' (TEM) which can cause an increase in out-of-plane projection when the 'rotating squares' model is stretched open. This combined 'rotating squares' and 'triangular elongation mechanism' was studied through analytical modelling and through a simple physical prototype (see Figure 20c) which confirmed that this system can indeed exhibit auxetic behaviour in 3D.

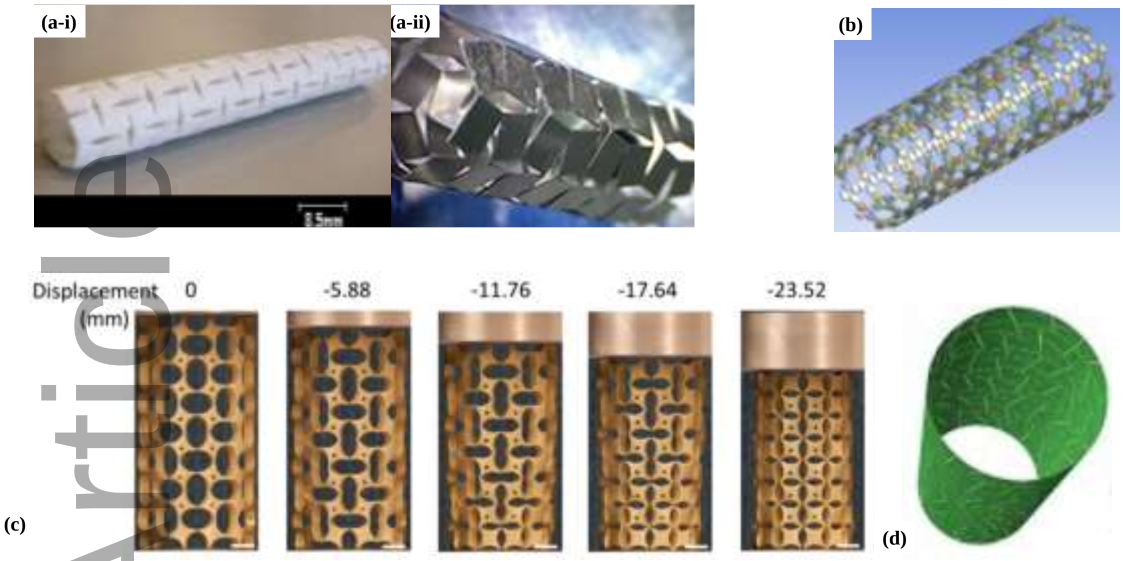


Figure 19: A graphical survey of some of the proposed 3D tubular/cylindrical auxetics made from 2D sheets of 'rotating polygons': (a) systems based on the 'rotating squares' where (a-i) shows a polyurethane tubular system, manufactured by Ali, Busfield and Rehman [116] and (a-ii) shows a femtosecond laser-cut auxetic metallic expanded tubular structure, manufactured by [187]; (b) shows a tube based on a hierarchical design as proposed by Gatt *et al.* [27] (c) shows experimental work by Ren *at al.* [188] on tubes with elliptical perforations which mimic the 'rotating squares' motif. (d) a cylindrical structure based on the system with irregular slits [177] as propped by Ren *et al*. [189]. A more detailed discussion on such finite-sized tubular stent-like auxetic structures is available elsewhere [117].

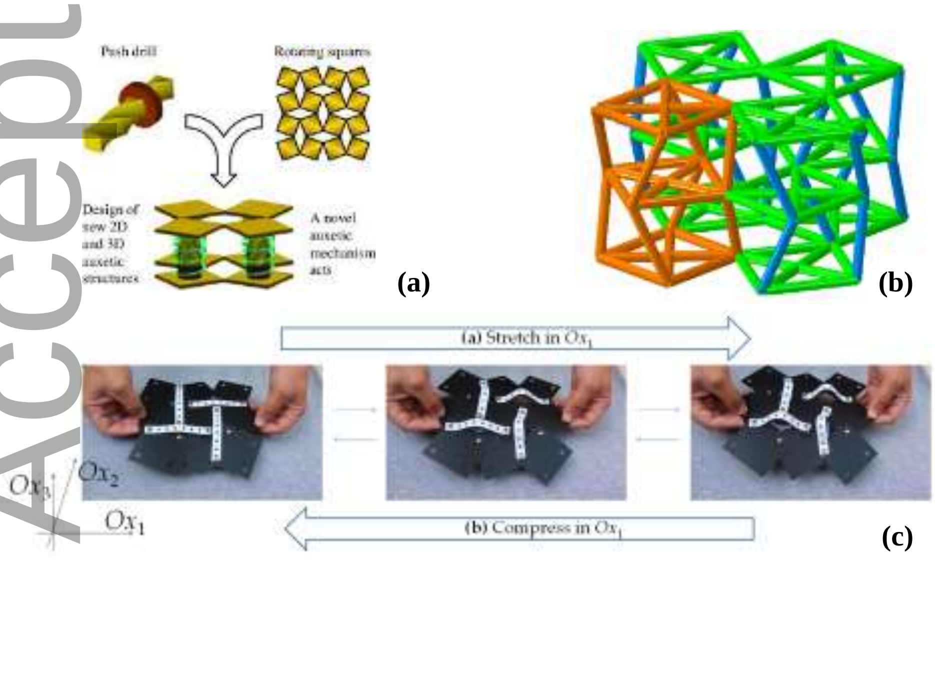


Figure 20: (a) Farrugia's push-drill mechanism and its use to convert 2D systems to 3D [22], (b) The 'tension-twist' idea applied to rotating squares [186] and (c) the more recent mechanism proposed by Grima-Cornish *et al.* for converting the 2D rotating-squares model to 3D through the use of the 'triangular elongation mechanism' (TEM) as illustrated through a prototype [17].

8. Applications and Implementations

Although as detailed above, the main initial investigative tool for ‘rotating rigid unit’ mechanisms was analytical modelling, research and development of these model systems does not terminate with the formulation of a set of expressions and mathematical relationships. Instead, it seems that rigorous mathematical analysis left ample space for imagination and creativity and the modelling work was followed by a number of other studies and projects where the focus was on application. Since the very onset, the analytical investigation by Grima and Evans [18] described above, was complimented with additional studies which also give examples of materials and structures where this model may be applied. The materials which were suggested at the onset to deform through such mechanisms include the hypothetical SiO_2-like THO zeolite framework. This nano-scale system was first reported as auxetic and featuring this ‘rotating squares’ motif in an earlier work by the researchers back in 1999 in ‘The 4th International Materials Chemistry Conference’ [148,149]. This was later formally published in the following year [119] where other zeolite frameworks, including EDI, NAT, and ADD, were also mentioned. The ‘mechanisms’ of these materials were described in terms of their cage like structures, which project as squares into a particular plane when viewed from the correct angle. In the same work, zeolites featuring the rotating triangles geometry when viewed down particular faces, also discussed above, were also reported. [119] Such a study shows the importance of the above discussed analytical models developed for the mechanisms found to be acting in these structures. With these models in place, one can now understand better the reason for, and how to fine-tune, the anomalous properties present in these materials due to the incorporated rotating rigid unit mode structures.

Furthering the work carried out on semi-rigid rotating squares, and the suggestion that real applications will follow this model rather than the more idealised version, it was also suggested that nanoscale materials which were discussed in terms of rotating squares, such as certain zeolite structures, will likely follow this model too. Here one should mention how experimental work was carried out in tandem with modelling work to provide a more complete picture of how nature achieves negative Poisson's ratio at the nano-scale. An important development was the experimental characterisation of the zeolite Natrolite by Sanchez-Valle *et al.* [124] who reported the full set of elastic constants of natrolite which were obtained experimentally through a Brillouin scattering study on a single-crystal of this material, and the interpretation of these constants by Grima et al. [122] who confirmed their earlier predictions of negative Poisson's ratio (see Figure 21a). In terms of modelling, one should mention a series of papers by Grima and co-workers which attempted to show real life applications of rotating squares at the nanoscale and simulate/predict the nano-scale deformations that result when materials are stretched

In addition to naturally occurring zeolites, the rotating squares motif has also been implemented at the nanoscale in man-made materials. The first reported successful attempt at this was the work by Suzuki and co-workers [190] who reported how they used self-assembly to achieve coherently dynamic two-dimensional protein crystals which not only clearly feature the 'rotating squares' motif (see Figure 21b), but were reported to be auxetic.

It should also be mentioned that not all synthetic auxetic materials which feature the rotating squares motif in one of their crystallographic planes were specifically designed with the scope to be auxetic. A case in point is $BAsO_4$; a crystalline material with an $I\bar{4}$ space group, first reported by Schulze in the 1930s [191], which has been recently shown to be auxetic in the (001) plane [7,8,192]. In this material (see Figure 21c), auxetic behaviour arises from relative rotation of tetrahedra that project in the (001) auxetic plane as rotating semi-rigid squares. This material is particularly interesting since it arguably represents one of the simplest possible manners how the rotating squares motif may be implemented into real materials where the squares are projections of single BO_4 or AsO_4 tetrahedra.

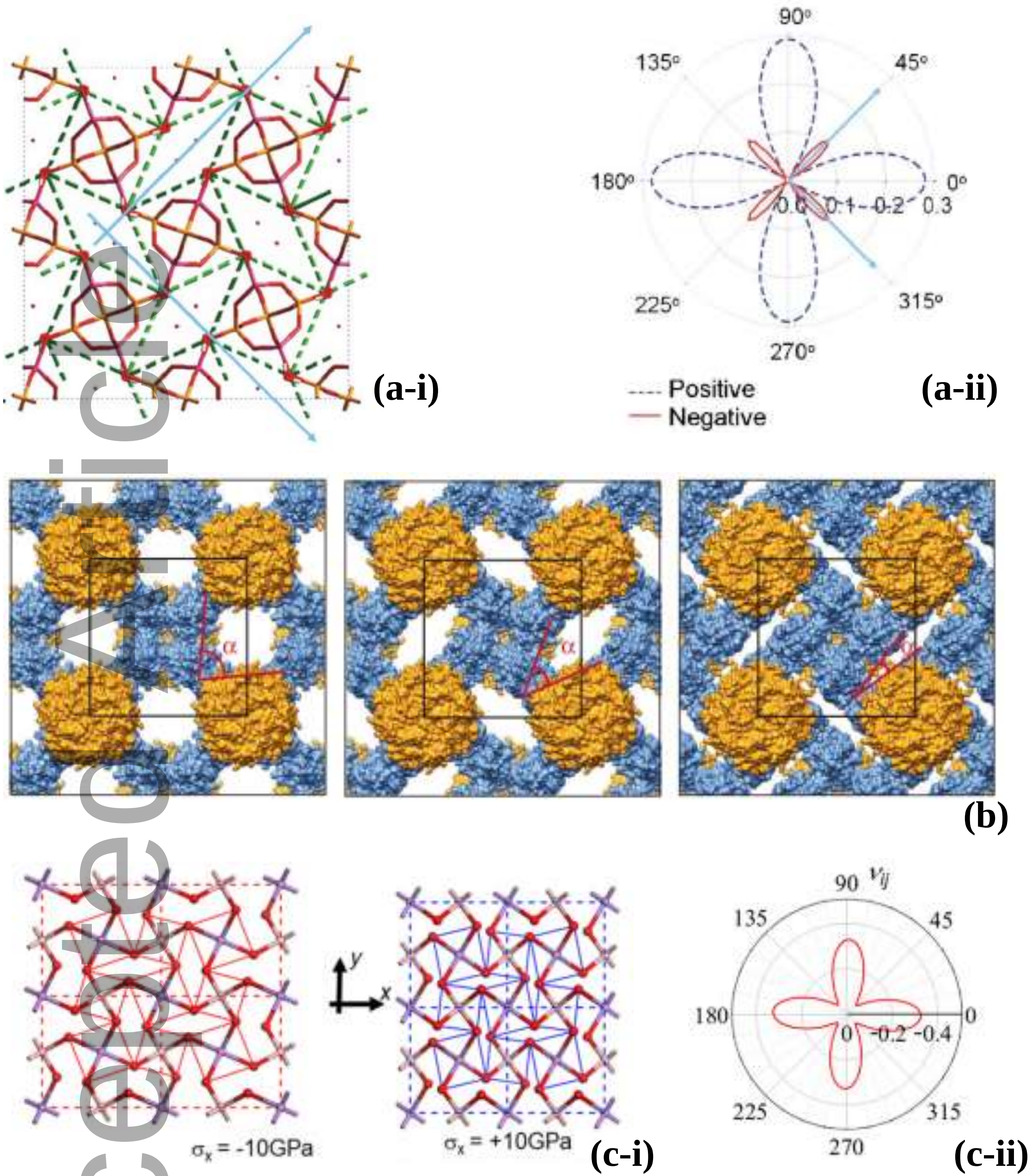


Figure 21: (a) (i) The structure of the zeolite Natrolite as viewed in the (001) with the 'rotating squares' motif highlighted and (ii) the profile of the Poisson's ratio as experimentally measured and analysed (adapted from [122]) where maximum auxeticity being measured off-axis, which correspond to the major axis of the projected squares; (b) The two-dimensional auxetic protein crystals featuring the 'rotating squares' motif, synthesised and characterised by Suzuki et al. (adapted from [190]); (c-i) the (001) plane of $BAsO_4$ as simulated under different uniaxial loads to illustrate the auxetic 'rotating squares' mechanism, and (c-ii) the in-plane Poisson's ratio of $BAsO_4$, as simulated through DFT simulations with maximum auxeticity being measured on axis, which correspond to the major axis of the squares (Image adapted from [7].

Moving up a few scales, macroscale applications for these rotating rigid unit mechanisms have also been suggested, and range over a number of applicatory fields. An important application that should be mentioned at the 'micro to millimetre' scale is the role of rotating rigid units in explaining the transformation process of auxetic foams.

The first mention of the application of this model to foams was made by Grima in his doctoral thesis [139], an idea which was formally published some years later by Grima, Alderson and Evans [167] (*vide supra*, Figure 17b) and further expanded in Grima *et al.* [193]. This work used a modelling approach to simulate what might be happening in foams, where, according to Grima and co-workers, the ‘joints’ in open-cell foams are much more rigid when compared to the cell walls connecting them and thus may be treated as semi-rigid units which can rotate relative to each other (see Figure 22). History has it that this latter hypothesis was confirmed as one of the main mechanisms leading to auxeticity in such materials, alongside the more established (at that time) ‘re-entrant mechanism’ [194].

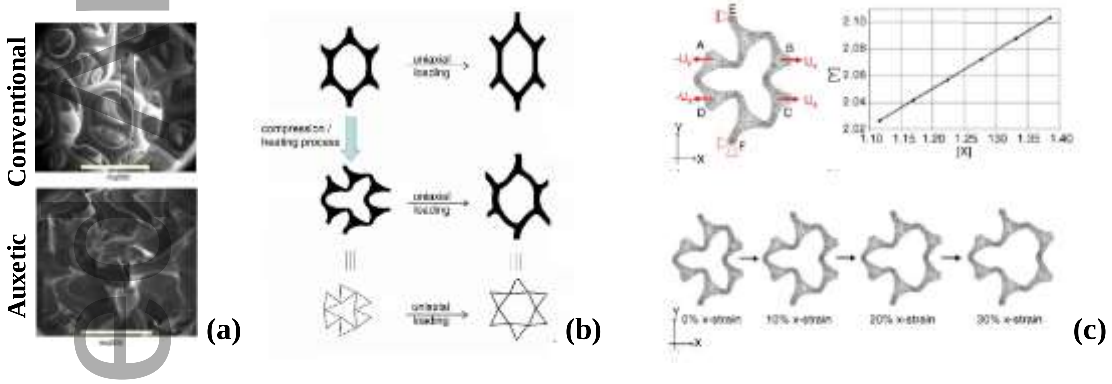


Figure 22: (a) Images of the microstructure of conventional and auxetic foams; (b) an idealised representation of the transformation through a 2D hexagonal cell and (c) a simulation of the deformation (through finite elements modelling) confirming auxeticity through a rotation mechanism (Image adapted from [193]).

Another very interesting and useful application of auxetics, which is very applicable at various scales of structure, is that of smart filtration and drug delivery, where the focus is on the change of pore size upon stretching. The idea being elaborated in this work is that as the systems are stretched, the pore size increases thus allowing larger particles to filter through, or, permitting a higher flow rate. These concepts have been thoroughly studied by Attard, Casha and Grima [195] who computed the filtration properties of various rotating rigid unit systems and derived mathematical expressions for the pore radius (which measured the particle size that can pass through a pore) and the ‘space coverage’ (which predicts the rate of flow of particles with a much smaller dimension than the pore), see Figure 23. Through this work, which compliments earlier claims that such prototypes can be used for smart drug delivery (Grima, 2009), the authors were able to show that "these systems offer a wide range of pore sizes and space coverage, both of which can be controlled through the way that the units are connected to each other, their shape and the angle between them". More relevant to the present discussion is the analysis of the shape of the pore size of various systems, which they present in table form (see Table 1 below).

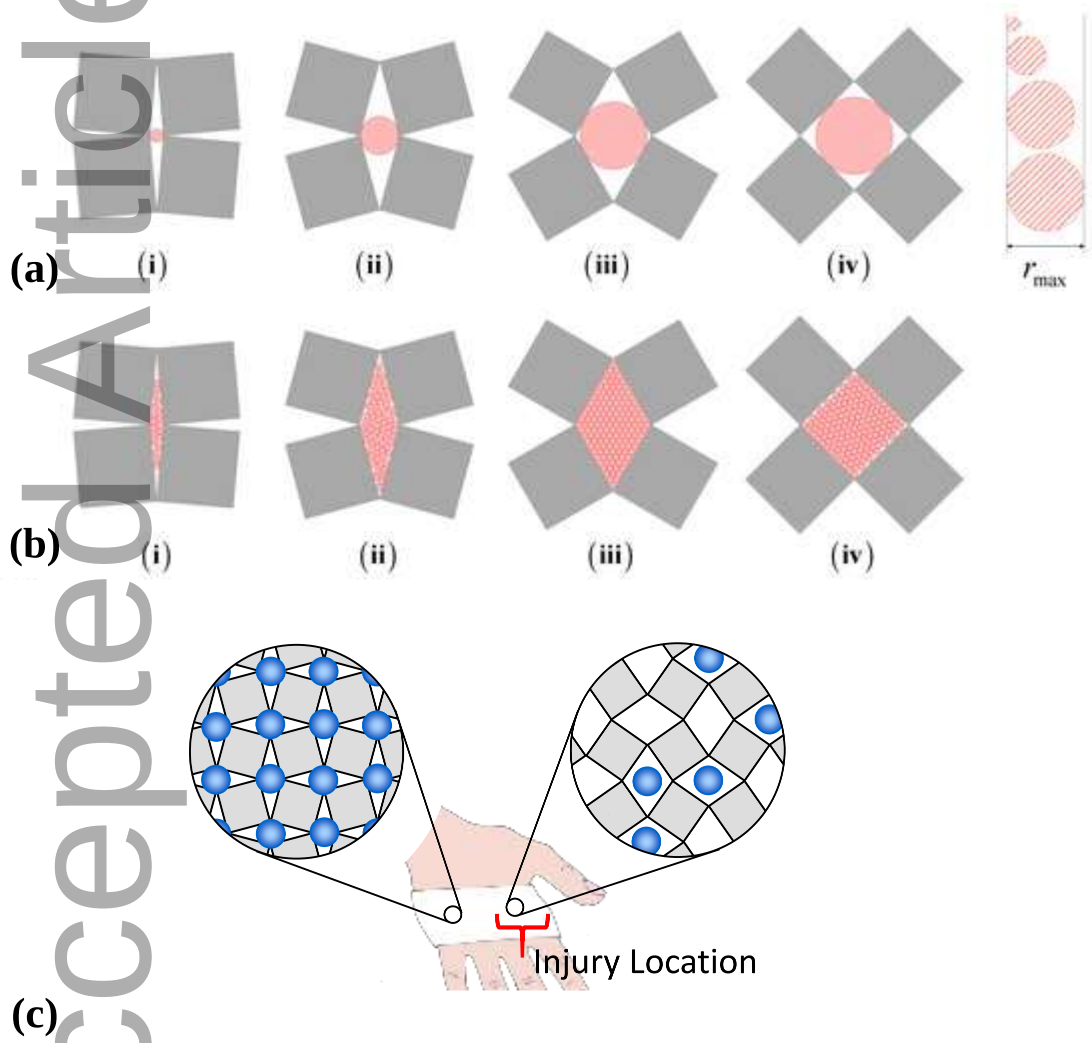
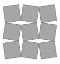
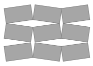
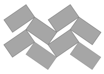
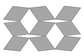
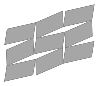
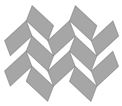
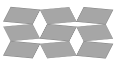
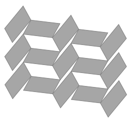


Figure 23: The concept of (a) pore-radius and (b) space coverage as applied to rotating squares, taken from [195] and (c) the proposed application of these systems for smart drug delivery where the medication is only released where and when it is needed.

Table 1: An analysis of the pore shape as presented by Attard, Casha and Grima [195]. Note that for all these systems, for a given structure, the pores are either in the shape of a parallelogram or a rhombus, the side lengths of which are dictated by the size of the rigid units (i.e. fixed in lengths) but their internal angles, and hence their diagonal length are variable. Moreover, for some systems, the pores could be all of the same shape and size (i.e. congruent) or same shape but different size (i.e. similar). Note also that not all systems are space-filling when the systems are fully contacted, in which case a pore would always exist.

Quadrilateral		**Pore shape**	**Congruent**	**Similar**	**Space filling**
Squares		Rhombus	Yes	Yes	Yes
Type I rectangles		Rhombus	No	Yes	Yes
Type II rectangles		Parallelogram	Yes	Yes	Yes
Type α rhombi		Rhombus	Yes	Yes	Yes
Type β rhombi		Rhombus	No	No	No
Type Iα parallelograms		Rhombus	No	Yes	Yes
Type IIα parallelograms		Parallelogram	Yes	Yes	Yes
Type Iβ parallelograms		Rhombus	No	No	No
Type IIβ parallelograms		Parallelogram	No	No	No

One example of a suggested macroscale application is in stents for medical use. In procedures requiring for oesophageal stents [196], it has been shown that rotating rigid units could be employed for their auxetic properties with the expectation that once it reaches the desired position, a deformation induces a mechanism which would increase the size of the stent radially and consequently longitudinally, therefore making the insertion less invasive and the implementation range higher. Similar medical applications which incorporate these structures have also been suggested, such as oesophageal stents for a person who may have a collapsed oesophagus. Here, the principle is the same, and it was found that semi-rigid units would probably make better candidates as produced samples failed early when fully rigid samples were used. [117] [116] Rotating units mechanisms have also been suggested for the use of skin grafts, due to the ability of the structure to be stretched in a manner which can be considered better to this application, i.e. when stretched it increases in dimension in all directions, rather than stretching undesirably in a manner which reduces the length of the side lateral to the one being stretched. [27]

Suggested applications for rotating rigid units also exist in the sports sector, where new ways to incorporate these structures are still being developed. One example of where these structures have already been applied is in the Nike Free Running shoe range (see Figure 24), in what they call the Flyknit sole, where the shoe sole was made to expand, increasing the surface area of contact upon contact with the ground, and therefore reducing the impact force. [197].

A look at some of the currently known applications of 'rotating rigid units' must mention the use of these models as an inspiration to various furniture, household and fashion items where the aesthetically pleasing aspect of these systems, combined with their functionality, can result in high-end products such as expandable tables [198], bookshelves [199], chairs[200], etc. (see Figure 25). Whilst due credit needs to be given to the researchers who developed the original mathematical models, and who many a times would have spoken about such potential uses at various conferences, the actual implementation and practical use of their theoretical work by designers and manufacturers is truly commendable.

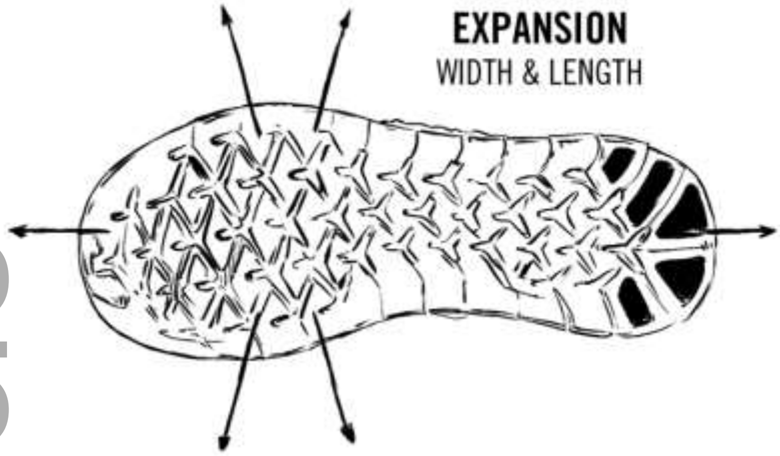


Figure 24: The Nike Inc. FlyKnit auxetic sole (Nike Inc., 2016, https://news.nike.com/news/nike-free-2016-running-training; as on 10th June 2021)

(a)

(b)

Figure 25: Some of the practical applications of rotating rigid unit auxetics: (a) auxetic table [198]; (b) auxetic chair [200].

9. Conclusion

This work has described some of the recent developments that have been made on 'rotating rigid unit' systems, that is, mechanisms involving the relative rotation of rigid or semi-rigid units, resulting in structures which have an array of interesting properties including negative Poisson's ratio (the main focus of this review), high positive Poisson's ratios leading to negative linear compressibility, as well as negative thermal expansion.

It was shown that over the last decades, following the report of auxetic behaviour resulting from 'rotating rigid squares', the theoretical work progressed in two directions: (i) relaxing the constraint that the squares are rigid, and (ii) retaining the rigidity but using 'deformed squares' either in the form of 'elongated squares' (i.e. rectangles); sheared squares (i.e. rhombi) or 'elongated and sheared squares' (i.e. paralellograms). In parallel to this, a number of materials have been discovered and found to operate by this mechanism. A number of constructs have also been specifically designed to manifest auxetic behaviour via 'rotating rigid units', both in two and three dimensions, rendering it as one of the most prominent mechanisms for achieving 'negative behaviour' at various scales of structure.

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The important role of 'rotating rigid units' in the field of "mechanical metamaterials" and "architected materials" is explored. In particular, this review delves into various implementations of this mechanism, ranging from 'rotating squares' to much more complex renditions, to generate negative Poisson's ratios (auxetic behaviour), negative thermal expansion and/or negative compressibility.

James N. Grima-Cornish is a science graduate of the University of Maltawith a passion for the arts and culture. His main fields of interest include molecular systems and metamaterials having negative and anomalous mechanical properties, which he investigates by means of analytical and computer simulations, and physical experiments. Currently, his research is focused on the development of novel structures and materials having anomalous thermo-mechanical properties. In 2019 he was awarded the Physical Crystallographer Group Award by the British Crystallographic Association and the Auxetics Young Researchers Award.In 2020 he was awarded the Malta Intellectual Property Emergent Innovator Award.

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