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Auxetic behaviour from rotating rigid units

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Auxetic materials exhibit the unexpected feature of becoming fatter when stretched and narrower when compressed, in other words, they exhibit a negative Poisson's ratio. This counter-intuitive behaviour imparts many beneficial effects on the material's macroscopic properties that make auxetics superior to conventional materials in many commercial applications. Recent research suggests that auxetic behaviour generally results from a cooperative effect between the material's internal structure (geometry setup) and the deformation mechanism it undergoes when submitted to a stress. Auxetic behaviour is also known to be scale-independent, and thus, the same geometry/deformation mechanism may operate at the macro-, micro- and nano- (molecular) level. A considerable amount of research has been focused on the 're-entrant honeycomb structure' which exhibits auxetic behaviour if deformed through hinging at the joints or flexure of the ribs, and it was proposed that this 're-entrant' geometry plays an important role in generating auxetic behaviour in various forms of materials ranging from nanostructured polymers to foams. This paper discusses an alternative mode of deformation involving 'rotating rigid units' which also results in negative Poisson's ratios. In its most ideal form, this mechanism may be constructed in two dimensions using 'rigid polygons' connected together through hinges at their vertices. On application of uniaxial loads, these 'rigid polygons' rotate with respect to each other to form a more open structure hence giving rise to a negative Poisson's ratio. This paper also discusses the role that 'rotating rigid units' are thought to have in various classes of materials to give rise to negative Poisson's ratios.

1 Introduction

Auxetic[1] materials exhibit the very unusual property of becoming wider when stretched and thinner when compressed, in other words they exhibit a negative Poisson's ratio, ν [1]. Although this property is not observed in most everyday materials, materials with a negative Poisson's ratio are thermodynamically stable, and in fact, the classical theory of elasticity states that it is possible for isotropic three-dimensional materials to exhibit Poisson's ratios within the range $-1 \le \nu \le +\frac{1}{2}$. Two-dimensional isotropic systems [2] can exhibit Poisson's ratios within the range $-1 \le \nu \le +1$, whilst the Poisson's ratios can have any positive or negative values in certain directions for anisotropic materials.

Negative Poisson's ratios were first reported for single crystalline iron pyrites in the first half of the 20th century [3]. This phenomenon was attributed to twinning defects in the pyrite crystals and was regarded as an anomaly. This was followed by some other isolated reports of this unusual behaviour, such

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[1] The word auxetic was originally proposed by Professor K. E. Evans in 1991 and is derived from the Greek word auxetos, meaning "that may be increased".

as the report of negative Poisson's ratio in metallic alloys [4]. However, in the late 1980's, the study of materials exhibiting negative Poisson's ratios became more established and since then, negative Poisson's ratios have been predicted, discovered or deliberately introduced in several classes of naturally occurring and man-made materials including foams [5–9], polymers [1, 10–14], composites [15, 16], gels [17, 18], laminates [19], metals [20], silicates [21–25] and zeolites [26, 27].

Various two and three dimensional theoretical models and structures which can lead to negative Poisson's ratio have also been proposed including, two and three-dimensional 're-entrant' systems [1, 28–32], models based on rigid 'free' molecules [33–35], chiral structures [9, 36, 37], composites [38] and fractal structures [39].

It was found that in most of these cases, the negative Poisson's ratios can be described in terms of models based on the geometry of the system (in the case of materials, the geometry of material's internal structure) and the way this geometry changes as a result of applied loads (deformation mechanism). An important feature that has emerged from research in this field is that the Poisson's ratio does not depend on scale. Deformation can take place at the nano- (molecular), micro- or even at the macro- level – the only requirement is the right combination of the geometry and the deformation mechanism. This is particularly significant as it gives researchers a simplified approach towards the design of new molecular-level auxetic materials by making it possible to first design auxetic macrostructures and then downscale these to the molecular level so as to produce nanostructured materials that mimic auxetic macrostructures (the 'downscaling technique').

The first molecular-level auxetic material designed in this way was the 'reflexyne' polyphenylacetylene networks (see Fig. 1a) proposed by Evans et al. [1]. These networks were designed in a way so as to mimic the two-dimensional dove-shaped re-entrant unit deforming by hinging (changes in the angle θ) of the ribs forming the network (see Fig. 1b). As illustrated in Fig. 1b, stretching of this non-traditional honeycomb will result in an increase in the angle θ which causes the cells to expand in both the loading and transverse directions with the effect that the structure exhibits a negative Poisson's ratio. For this structure and deformation mechanism, auxetic behaviour can be obtained for any combination of the geometric parameters (l, h, θ) provided that the angle θ is within the range $0° < \theta < 90°$. (If the angle is larger than 90°, the structure will revert back to the conventional honeycomb and hence have a positive Poisson's ratio.) The re-entrant honeycomb also exhibits auxetic behaviour when deformation is by flexure of the ribs [28, 32]. Molecular modelling studies have confirmed the auxeticity in the reflexyne networks, hence showing that the downscaling technique was successful [1].

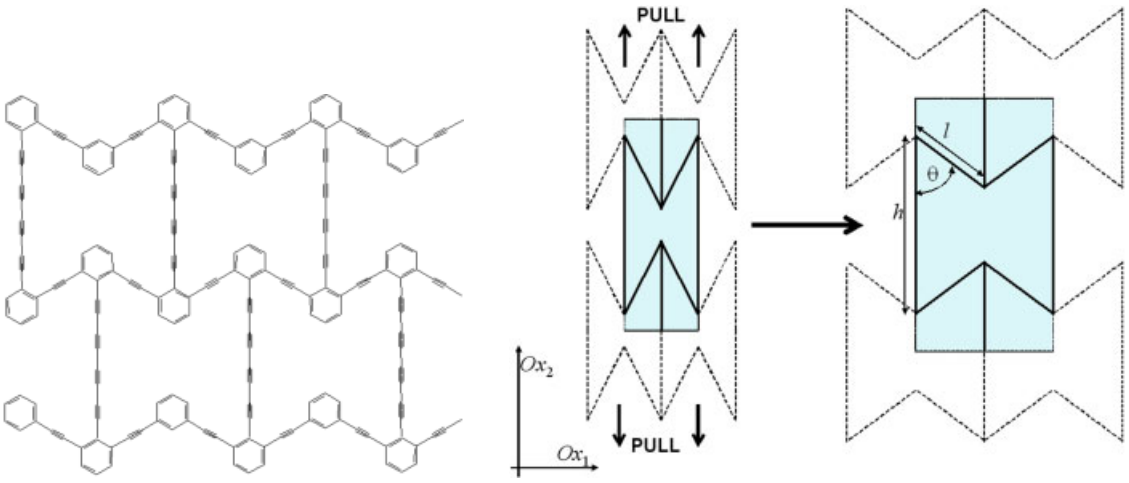

Fig. 1 (a) Auxetic reflexyne molecular system proposed by Evans [1], and (b) the idealised re-entrant structure deforming though hinging.

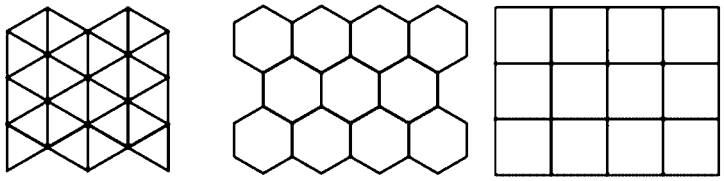

Fig. 2 Regular {3, 6}, {4, 4} and {6, 3} tessellated structures.

The re-entrant geometry (see Fig. 1b) has also been used to explain the auxetic effect in various other classes of materials including foams [5–7] and microporous polymers [40–42] thus confirming the important role of the re-entrant geometry and hinging/flexing deformation mechanism for attaining negative Poisson's ratios.

This paper discusses an alternative mechanism for achieving negative Poisson's ratios, namely one where non re-entrant rigid units rotate with respect to each other to produce more open structures when stretched.

1.1 Two dimensional space filling auxetics made from 'rotating' regular polygons

Johannes Kepler (1571–1630) has shown in his book *Harmonice Mundi* (1619) 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 (see Fig. 2). This is due to the requirement that the q internal angles of such p-sided regular polygons meeting at any one vertex must be a factor of 2π. In other words, it is required that $p, q \in \mathbb{N}$ must satisfy the equation:

$$\left(1-\frac{2}{p}\right)\pi = \frac{2\pi}{q}, \quad p, q \in \mathbb{N}, \tag{1}$$

i.e.,

$$(p-2)(q-2) = 4, \qquad p, q \in \mathbb{N}, \tag{2}$$

for which the only factors are $\{p, q\} = \{3, 6\}, \{4, 4\}$ and $\{6, 3\}$.[2]

If these tessellated polygons were to be transformed into structures where different adjacent polygons are connected together through simple hinges at the vertices, then q (the number of polygons meeting at any one vertex) must also be even since a hinge connects two (and only two) vertices. Thus, the only two hinged space filling structures that may be built using regular polygons are those involving equilateral triangles [13], and squares [14, 27, 43, 44] as illustrated in Fig. 3. Figure 3 visually suggests that if these systems deform solely through hinging (i.e., relative rotation of the polygons), they are geometrically constrained to exhibit negative Poisson's ratio of –1, a property which is only true for systems where the triangles or squares remain rigid. In fact, it has been shown that the Poisson's ratios of systems constructed from squares where the squares are allowed to deform will be dependent on the relative rigidity of the squares with respect to the rigidity of the hinges [27, 43, 45].

2 Two dimensional auxetics made from 'rotating' non-regular polygons

Planar structures exhibiting negative Poisson's ratios from relative rotation of rigid units are not restricted to the cases in Fig. 3 where the rigid units are regular shapes. It may be shown that the equilat-

[2] These regular tessellations are usually denoted by $\{p, q\}$ where p is the number of sides in the polygon and q is the number of corners meeting at any one vertex, i.e., the tessellations made from the equilateral triangle, the square and the regular hexagon are denoted by {3, 6}, {4, 4} and {6, 3} respectively (see Fig. 2).

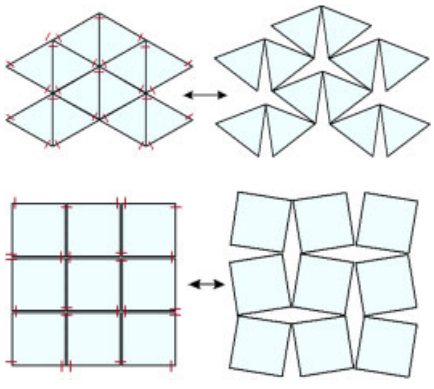

Fig. 3 (a) 'Rotating triangles' structure obtained from the {3, 6} tessellation and (b) the 'rotating squares' structure obtained from the {4, 4} tessellation.

eral triangles in Fig. 3a may be replaced by scalene triangles [27], (see Fig. 4a) whilst the 'rotating squares' model in Fig. 3b may be generalised by replacing the squares by irregular quadrilaterals where the unit cell must have a P2 two-dimensional space-group symmetry[3] (see Fig. 4b). If one was to also include the third dimension, then other more complex auxetic structures can be constructed.

For simple structures/deformation mechanisms the magnitude of the Poisson's ratio can be easily identified from a visual analysis of various conformations of the structure. For example, one may easily deduce that the 'regular rotating rigid unit' structures in Fig. 3 have in-plane Poisson's ratios of –1 (i.e., the structures maintain their aspect ratio). However, when the geometry of the structures is more complex, as in the cases illustrated in Fig. 4, the magnitude of the Poisson's ratio and hence the extent of auxeticity cannot be easily determined from a simple visual analysis. Furthermore, it can be shown that for these more general structures, the Poisson's ratios are not constant but depend on the direction of loading (i.e., the structure is anisotropic) and change as the structures change shape when loaded (i.e., the Poisson's ratios are strain/geometry dependent).

This problem may be addressed by deriving analytical equations for the Poisson's ratios (and the other in-plane mechanical properties, if a stiffness constant is assigned to the hinges) in terms of the structure's geometrical parameters. In this way, one may construct the full 3×3 compliance matrix S defined by $\varepsilon = S\sigma$ from which one may calculate the in-plane Poisson's ratio for loading in any direction.

In this paper we shall be deriving such analytical expressions for the 3×3 compliance matrix S of a simplified form of the 'rotating quadrilaterals' system in Fig. 4 where the quadrilaterals are rigid rectangles. This derivation will illustrate how the Poisson's ratio will be dependent on the shape of the system and on the direction of loading to the extent that from the same structure one may change the sign of the

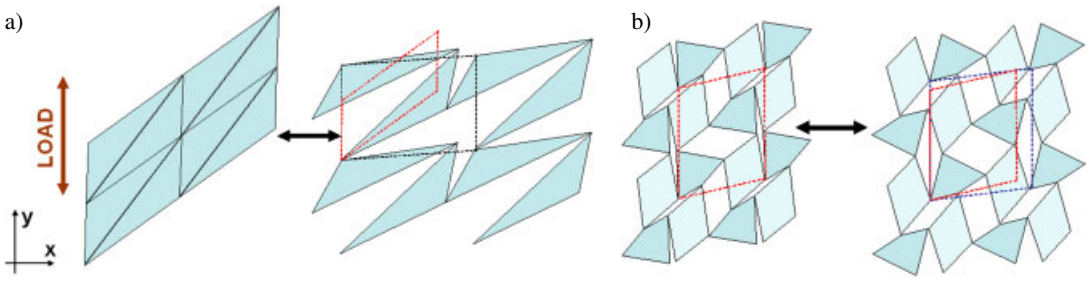

Fig. 4 General forms of the regular 'rotating triangles' (a) and 'rotating squares' (b) systems.

[3] In this generalised system, the unit cell is a parallelogram (containing four hinged quadrilaterals) where the symmetry inside this unit cell there is a rotation over 180 degrees. This means that in the general case, inside each unit cell there are two copies of two non-identical quadrilaterals arranged in such a way that one can identify a 2-fold axis of rotation. Note that this system may be such that it does not fully close to cover the whole plane.

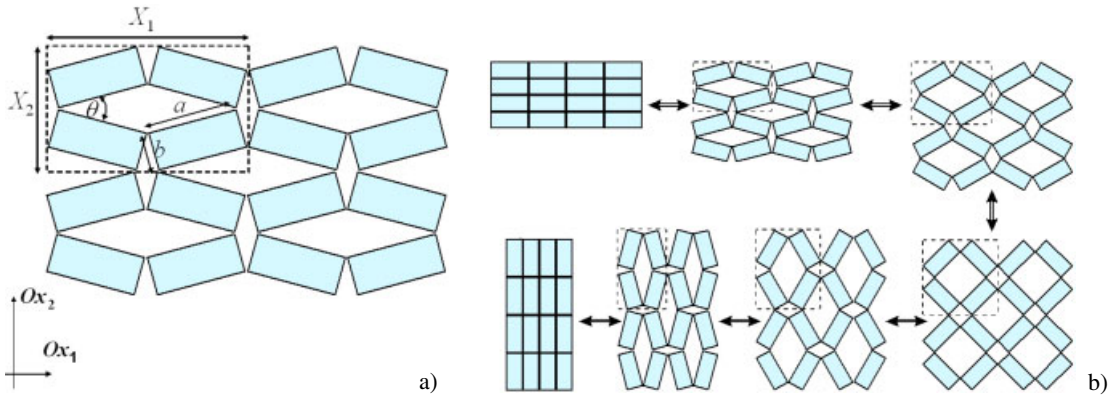

Fig. 5 'Rotating rectangles' structure composed of rectangles of size ($a \times b$).

Poisson's ratio from positive to negative or *vice-versa* simply by changing the relative orientation of the rectangles in the undeformed form. It should be noted that the derivation presented here represents the idealised scenario where the rectangles are perfectly rigid and do not deform. If such deformations were to be allowed, then the values of the Poisson's ratio would also become dependent on the relative rigidity of the rectangles with respect to the rigidity of the hinges.

2.1 Modelling the in-plane properties of the 'rotating rectangles' structure

Consider a two dimensional tessellation built with rigid rectangles of side lengths a, b hinged at their corners and aligned in the Ox_{12} plane as shown in Fig. 5a. Let the angle between two such rectangles be θ. The shape of the structure for various values of θ is shown in Fig. 5b. These different configurations may be obtained from one another through loading in an Ox_i direction. Figure 5b visually suggests that the structure is auxetic in the Ox_{12} plane for some, but not all, values of θ.

A rectangular unit cell may be used to describe this tessellation where the cell sides are parallel to the Ox_1 and Ox_2 axis. In this case, the unit cell exhibits a PMM symmetry (where the PMM group is a subgroup of P2) and contains four a-b rectangles (i.e., rectangles of side lengths a and b) as shown in Fig. 5. The projections of the unit cell in the Ox_i directions are given by:

$$X_1 = 2\left[a\cos\left(\frac{\theta}{2}\right) + b\sin\left(\frac{\theta}{2}\right)\right], \quad X_2 = 2\left[a\sin\left(\frac{\theta}{2}\right) + b\cos\left(\frac{\theta}{2}\right)\right], \tag{3}$$

where if we assume that the structure deforms solely by relative rotation of the rectangles, then a and b are constants and hence X_i are functions of the single variable θ, i.e., $X_i = X_i(\theta)$.

We shall assume that the stiffness of the structure (and hence the Young's moduli) may be related to the stiffness of the hinges, that is, a stiffness which opposes changes in the angles θ. In particular, we shall assume that the hinges satisfy the equation:

$$M = K_h(\delta\theta), \tag{4}$$

where M is the moment applied to the rectangles, $\delta\theta$ is the angular displacement due to M, and K_h is the spring constant for the hinge.

2.2 Hinged rectangles – The on-axis mechanical properties

If the structure may only deform through relative rotation of the rigid rectangles, then the structure is geometrically not allowed to shear. This results in an infinite on-axis shear modulus ($G_{12} = \infty$) and a

value of zero for the five elements of compliance matrix which are associated with shearing. The compliance matrix for this system is hence of the form:

$$S = [S_{ij}] = \begin{bmatrix} \frac{1}{E_1} & -\frac{\nu_{21}}{E_2} & 0 \\ -\frac{\nu_{12}}{E_1} & \frac{1}{E_2} & 0 \\ 0 & 0 & 0 \end{bmatrix}, \tag{5}$$

where ν_{ij} represent the Poisson's ratios (or more precisely the Poisson's functions) in the Ox_{ij} plane for loading in the Ox_i direction, defined by:

$$\nu_{ij} = (\nu_{ji})^{-1} = -\frac{\mathrm{d}\varepsilon_j}{\mathrm{d}\varepsilon_i} \qquad i, j = 1, 2\,, \tag{6}$$

whilst E_i are the Young's moduli for loading in the Ox_i directions given by:

$$E_i = \frac{\mathrm{d}\sigma_i}{\mathrm{d}\varepsilon_i} \qquad i = 1, 2\,, \tag{7}$$

where $\mathrm{d}\sigma_i$ and $\mathrm{d}\varepsilon_i$ are infinitesimally small stresses and strains for loading in the Ox_i directions respectively.

2.2.1 The Poisson's ratios

The infinitesimally small strains $\mathrm{d}\varepsilon_i$ in the Ox_i directions may be defined by:

$$\mathrm{d}\varepsilon_i = \frac{\mathrm{d}X_i}{X_i}\,, \tag{8}$$

and since $X_i = X_i(\theta)$,

$$\nu_{21} = (\nu_{12})^{-1} = -\frac{\mathrm{d}\varepsilon_1}{\mathrm{d}\varepsilon_2} = -\frac{\mathrm{d}X_1/X_1}{\mathrm{d}X_2/X_2} = -\frac{\mathrm{d}X_1/\mathrm{d}\theta}{\mathrm{d}X_2/\mathrm{d}\theta}\,\frac{X_2}{X_1}\,. \tag{9}$$

Differentiating Eq. (3) we obtain:

$$\frac{\mathrm{d}X_1}{\mathrm{d}\theta} = -a\sin\left(\frac{\theta}{2}\right) + b\cos\left(\frac{\theta}{2}\right), \qquad \frac{\mathrm{d}X_2}{\mathrm{d}\theta} = a\cos\left(\frac{\theta}{2}\right) - b\sin\left(\frac{\theta}{2}\right), \tag{10}$$

i.e., from Eq. (3) to (11) we obtain:

$$\nu_{21} = (\nu_{12})^{-1} = \frac{a^2\sin^2\left(\frac{\theta}{2}\right) - b^2\cos^2\left(\frac{\theta}{2}\right)}{a^2\cos^2\left(\frac{\theta}{2}\right) - b^2\sin^2\left(\frac{\theta}{2}\right)}. \tag{11}$$

2.2.2 The on-axis Young's moduli

The work done by each unit cell due to the changes in the inter-rectangle angles from θ to $\theta + \mathrm{d}\theta$ that accompany a small strain is given by:

$$W = N\left[\tfrac{1}{2}K_h(\mathrm{d}\theta)^2\right] = 8\left[\tfrac{1}{2}K_h(\mathrm{d}\theta)^2\right], \tag{12}$$

where N is the number of hinges per unit cell, which in this case is equal to eight. (One unit cell contains four rectangles, each rectangle has four vertices, and two vertices contribute to one hinge) and K_h is the stiffness constant of the hinges as defined through Eq. (4).

Also, since, $X_i = X_i(\theta)$ the work done per unit volume due to an infinitesimally small strain $\mathrm{d}\varepsilon_i$ for loading in the Ox_i direction ($i = 1, 2$) is given by:

$$U = \frac{1}{2} E_i (\mathrm{d}\varepsilon_i)^2 = \frac{1}{2} E_i \left(\frac{\mathrm{d}X_i}{X_i} \right)^2 = \frac{1}{2} E_i \left(\frac{1}{X_i} \frac{\mathrm{d}X_i}{\mathrm{d}\theta} \right)^2 (\mathrm{d}\theta)^2 . \tag{13}$$

Form the principle of conservation of energy:

$$U = \frac{1}{V} W , \tag{14}$$

where V is the volume of the unit cell given by (assuming a unit thickness in the third dimension):

$$V = X_1 X_2 . \tag{15}$$

Thus from Eq. (13) to Eq. (16) we have:

$$\frac{1}{2} E_i \left(\frac{1}{X_i} \frac{\mathrm{d}X_i}{\mathrm{d}\theta} \right)^2 (\mathrm{d}\theta)^2 = \frac{1}{X_1 X_2} 8 \left[\frac{1}{2} K_h (\mathrm{d}\theta)^2 \right], \tag{16}$$

and hence the Young's moduli E_i ($i = 1, 2$) are given by:

$$E_i = 8 K_h \frac{X_i^2}{X_1 X_2} \left(\frac{\mathrm{d}X_i}{\mathrm{d}\theta} \right)^{-2} \qquad i = 1, 2 , \tag{17}$$

i.e.:

$$E_1 = 8 K_h \frac{X_1}{X_2} \left(\frac{\mathrm{d}X_1}{\mathrm{d}\theta} \right)^{-2} = 8 K_h \left(\frac{\left[a \cos\left(\frac{\theta}{2}\right) + b \sin\left(\frac{\theta}{2}\right) \right]}{\left[a \sin\left(\frac{\theta}{2}\right) + b \cos\left(\frac{\theta}{2}\right) \right] \left[-a \sin\left(\frac{\theta}{2}\right) + b \cos\left(\frac{\theta}{2}\right) \right]^2} \right),$$

$$E_2 = 8 K_h \frac{X_2}{X_1} \left(\frac{\mathrm{d}X_2}{\mathrm{d}\theta} \right)^{-2} = 8 K_h \left(\frac{\left[a \cos\left(\frac{\theta}{2}\right) + b \sin\left(\frac{\theta}{2}\right) \right]}{\left[a \sin\left(\frac{\theta}{2}\right) + b \cos\left(\frac{\theta}{2}\right) \right] \left[a \sin\left(\frac{\theta}{2}\right) - b \cos\left(\frac{\theta}{2}\right) \right]^2} \right). \tag{18}$$

These equations for the Poisson's ratios and Young's moduli satisfy the thermodynamic requirements given by:

$$\frac{\nu_{ij}}{E_i} = \frac{\nu_{ji}}{E_j} \; |\nu_{ij}| \le \sqrt{\frac{E_i}{E_j}} . \tag{19}$$

Plots of E_i and ν_{ij} vs. θ for a rectangle measuring $(a \times b) = (1.5 \times 1.0)$ with $K_h = 1$ are given in Fig. 6.

2.3 Special case: Hinged squares – The on-axis mechanical properties

If the rectangles were to be replaced by squares of side length a, then the equations for the Poison's ratios (Eq. (12)) and Young's moduli (Eq. (19)) simplify to:

$$\nu_{21} = \nu_{12} = -1 , \tag{20}$$

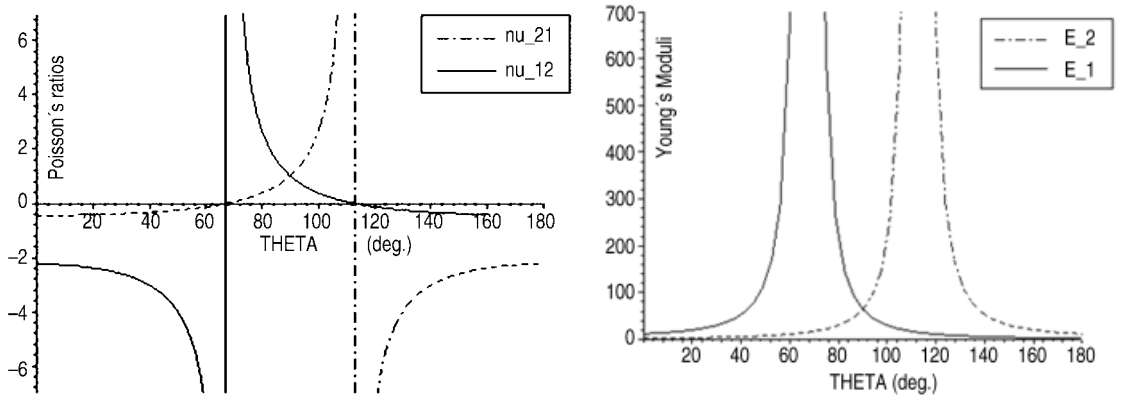

Fig. 6 Plots of (a) the Poisson's ratios and (b) Young's moduli of the rotating rectangles structure where $(a \times b) = (1.5 \times 1)$ and $K_h = 1$.

$$E = E_1 = E_2 = K_h \frac{8}{a^2}\left[\cos\left(\frac{\theta}{2}\right) - \sin\left(\frac{\theta}{2}\right)\right]^{-2} = K_h \frac{8}{a^2}\frac{1}{[1-\sin(\theta)]}, \tag{21}$$

and hence the compliance matrix $\boldsymbol{S}$ simplifies to:

$$S = \begin{pmatrix} \frac{1}{E_1} & -\frac{\nu_{21}}{E_2} & 0 \\ -\frac{\nu_{12}}{E_1} & \frac{1}{E_2} & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{E}\begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{22}$$

2.4 The off-axis mechanical properties

The equations for the Poisson's ratios, Young's moduli and compliance matrices derived above give the in-plane mechanical properties for loading in the Ox_1 or the Ox_2 directions. The equivalent expressions for loading in any arbitrary direction in the Ox_1–Ox_2 plane (in particular, $Ox_1(\zeta)$, the direction which is at an angle $+\zeta$ to Ox_1 direction) may be obtained by using standard axis transformation techniques [46] to obtain:

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

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

$$G_{12}^{\zeta} = \left[\frac{\cos^4(\zeta) + \sin^4(\zeta)}{G_{12}} + 2\cos^2(\zeta)\sin^2(\zeta)\left(\frac{2}{E_1} + \frac{2}{E_2} + \frac{4\nu_{12}}{E_1} - \frac{1}{G_{12}}\right)\right]^{-1}, \tag{23}$$

which in this particular case of the rotating rectangles (since $s_{33} = 1/G_{12} = 0$):

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

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

$$G_{12}^{\zeta} = \left[2\cos^2(\zeta)\sin^2(\zeta)\left(\frac{2}{E_1} + \frac{2}{E_2} + \frac{4\nu_{12}}{E_1}\right) \right]^{-1}, \tag{24}$$

whilst for the case when the rigid rectangles are replaced by rigid squares:

$$E_1^{\zeta} = E_1 = E_2 = E,$$

$$\nu_{12}^{\zeta} = -1,$$

$$G_{12}^{\zeta} = \infty. \tag{25}$$

One should note that the equations would assume a more complex form if the requirement that the rectangles/squares remain rigid is relaxed. For example, it has been shown that if the squares do not remain rigid, then the Poisson's ratio in Eq. (26) will become a function of ζ (i.e., the direction of loading) and of the relative rigidity of the squares with respect to the rigidity of the hinges as discussed elsewhere [27] and [45].

3 The analysis of the 'rotating rectangles' model

The expressions derived above suggest that the mechanical properties of these systems, including the Poisson's ratio are dependent on the geometry of the structures. The equations also suggest both positive and negative Poisson's ratios may be obtained from the same structure, where the sign of the Poisson's ratios depends on the particular combination of the geometric parameters (a, b, θ).

In particular, as discussed above, for a structure where the geometry is dependent on a single variable (= θ), the Poisson's ratios ν_{ij} are given by:

$$\nu_{ij} = -\frac{\mathrm{d}\varepsilon_j}{\mathrm{d}\varepsilon_i} = -\frac{\mathrm{d}X_j/\mathrm{d}\theta}{\mathrm{d}X_i/\mathrm{d}\theta}\frac{X_i}{X_j} \qquad i, j = 1, 2, \tag{26}$$

and for negative Poisson's ratios, we require:

$$\frac{\mathrm{d}X_j/\mathrm{d}\theta}{\mathrm{d}X_i/\mathrm{d}\theta}\frac{X_i}{X_j} > 0. \tag{27}$$

Since the unit cells are always positive (i.e., $X_i/X_j > 0$ for all values of θ), this requirement reduces to the requirement that the two derivatives $\mathrm{d}X_1/\mathrm{d}\theta$ and $\mathrm{d}X_2/\mathrm{d}\theta$ have the same sign (both positive or both negative), i.e., for this particular case, for negative Poisson's ratios it is required that either:

$$-a\sin\left(\frac{\theta}{2}\right) + b\cos\left(\frac{\theta}{2}\right) > 0, \qquad a\cos\left(\frac{\theta}{2}\right) - b\sin\left(\frac{\theta}{2}\right) > 0$$

or:

$$-a\sin\left(\frac{\theta}{2}\right) + b\cos\left(\frac{\theta}{2}\right) < 0, \qquad a\cos\left(\frac{\theta}{2}\right) - b\sin\left(\frac{\theta}{2}\right) < 0 \tag{28}$$

i.e., for $\theta \in (0, \pi)$:

$$\frac{b}{a} > \tan\left(\frac{\theta}{2}\right), \qquad \frac{a}{b} > \tan\left(\frac{\theta}{2}\right) \cdots \Rightarrow \cdots 0 < \theta < 2\tan^{-1}\left[\min\left(\frac{a}{b}, \frac{b}{a}\right)\right]$$

or:

$$\frac{b}{a} < \tan\left(\frac{\theta}{2}\right), \qquad \frac{a}{b} < \tan\left(\frac{\theta}{2}\right) \cdots \Rightarrow \cdots 2\tan^{-1}\left[\max\left(\frac{a}{b}, \frac{b}{a}\right)\right] < \theta < \pi\,. \tag{29}$$

The Poisson's ratios are positive for the other values of $\theta \in (0,\pi)$, i.e.:

$$2\tan^{-1}\left[\min\left(\frac{a}{b}, \frac{b}{a}\right)\right] < \theta < 2\tan^{-1}\left[\max\left(\frac{a}{b}, \frac{b}{a}\right)\right]. \tag{30}$$

This means that irrespective of the size of the rectangle, if we load the fully closed structure ($\theta = 0$) the structure is initially auxetic until θ reaches the value of $2\tan^{-1}\left[\min\left(\frac{a}{b}, \frac{b}{a}\right)\right]$ where the Poisson's ratio becomes positive and remains positive until θ is $2\tan^{-1}\left[\max\left(\frac{a}{b}, \frac{b}{a}\right)\right]$ when it becomes negative again and remains negative until $\theta = \pi$, a conformation were the structure is once again fully closed. The region of positive Poisson's ratio may be decreased by decreasing the difference between *a* and *b*, and in the limit when *a* = *b* (i.e., the rectangle is a square), the Poisson's ratio will be negative for all values of θ and equal to –1.

The nature of the transitions from negative to positive Poisson's ratios and vice-versa is also interesting. Referring to the definition of the Poison's ratio ν_{ij} in Eq. (28), since $X_i > 0$ for all values of θ, the changes in the sign of the Poisson's ratios must occur at the points when one of the two the derivatives $\mathrm{d}X_i/\mathrm{d}\theta$ are equal to zero. Furthermore, whilst a change in any of the two derivatives results in a change of the sign of the Poisson's ratio, the way that this change is accomplished is dependent on which of the two derivatives is equal to zero.

In particular, if we consider the changes in sign of ν_{21}, we will find that:

– When the change arises from $\mathrm{d}X_2/\mathrm{d}\theta = 0$, then the Poisson's ratio will vary asymptotically since $\mathrm{d}X_2/\mathrm{d}\theta = 0$ is in the denominator of the Poisson's ratio. This means that at the point when $\mathrm{d}X_2/\mathrm{d}\theta = 0$, the value of the Poisson's ratio is not defined (division by 0), and as ν_{21} approaches this point from the left, the Poisson's ratio will tend to $-\infty$ whilst as ν_{21} approaches this point from the right, the Poisson's ratio will tend to $+\infty$ (see Fig. 6). This point is also accompanied by $E_2 \to \infty$ since $(\mathrm{d}X_2/\mathrm{d}\theta = 0)^2$ is also part of the denominator of the expression for E_2 and corresponds to a point where further stretching in the Ox_2 direction will not result in any further change in θ. (Further changes in θ may be produced by stretching in the orthogonal direction.)

– When the change arises from $\mathrm{d}X_1/\mathrm{d}\theta = 0$ (part of the numerator of the Poisson's ratio), then the Poisson's ratio changes sign gradually and continuously by passing through $\nu_{21} = 0$. This change in sign of ν_{21} will not be echoed in the Young's modulus E_2 and the structure continues to deform smoothly.

One should also note that it is possible that both the derivatives are simultaneously zero, in which case the structure is locked (i.e., cannot be deformed any further by stretching in either the Ox_1 or the Ox_2 direction). This special case is only encountered when the 'rotating rectangles' are 'rotating squares' where both derivatives are simultaneously zero when $\theta = \pi/2$ (the fully open structure).

4 Discussion

In this paper we have presented a new concept for generating negative Poisson's ratios, namely one in which the auxetic effect is the result of relative rotation of rigid units. This new concept is not only interesting as it does not require the existence of 're-entrant' features in the structure (which have almost

Table 1 On-axis Poisson's ratios in the (001) plane of the SiO_2 equivalent of the THO zeolite framework as predicted by various force-field models [27].

force-field	on-axis ν_{xy}	on-axis ν_{yx}
Burchart force-field	–0.55	–0.55
BKS force-field	–0.33	–0.53
universal force-field	–0.33	–0.40
CVFF force-field	–0.46	–0.46

become a characteristic of auxetic structures), but also this novel mechanism can be used to explain the auxeticity in various classes of materials including foams (microstructured auxetics) and molecular systems such as zeolites or silicates (nanostructured auxetics, see for example, [13, 14, 27, 47].

4.1 Rotating rigid units in nanostructured auxetics

In a recent study through force-field based molecular modelling experiments, it was shown that various zeolite frameworks exhibit negative Poisson's ratios, and in the majority of these cases, the auxeticity was the result of deformation mechanisms which can be trivially explained in terms of a 'rotating squares' or 'rotating triangles' model [26, 27, 43].

For example, force-field based simulations on the SiO_2 equivalent of the THO zeolite framework have predicted negative Poisson's ratios in the (001) plane (ν_{xy} and ν_{yx}), a result which can be obtained using a variety of different force-fields as illustrated in Table 1. The molecular structure of this zeolite is such that when viewed down the [1] direction (the *Z* direction), the atoms of the framework form a geometric pattern which reproduces the 'rotating squares' model described here. Force-field based molecular modelling experiments have confirmed that when this zeolite is loaded in the [100] direction (the *X* direction), the 'squares' will rotate relative to each other in a way which mimics the 'rotating squares' deformation mechanism (see Fig. 7).

This behaviour is possible because the molecular structure of THO is such that the framework is composed of inter-locked six membered rings which produces 'cage-like' structures. The interlocked rings provide the rigidity required together with the essential 'square' geometry when projected onto the (001) plane. Adjacent 'cage-like' structures are connected by flexible Si–O–Al bonds (or Si–O–Si bonds in the case of the all-silica equivalents) which may act as hinges as illustrated in Fig. 8.

We have also observed similar behaviour in other zeolite frameworks including EDI, NAT, APD and ATT, where in each case the nanostructure is such that one may observe the 'rotating squares' mechanism operating in some particular plane of the zeolite giving rise to negative Poisson's ratios in that plane.

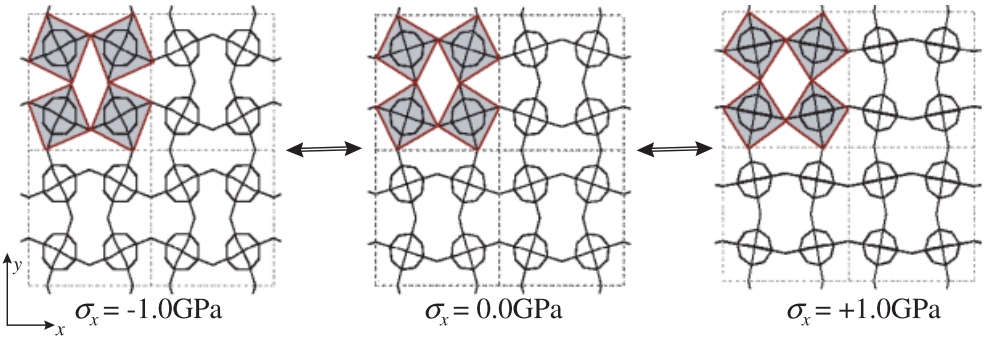

Fig. 7 (001) plane of THO at loads of –1.0 GPa, 0.0 GPa, and +1.0 GPa in the *X*-direction ([100] direction). As illustrated, the geometry may be trivially described in terms of highlighted 'rotating squares'.

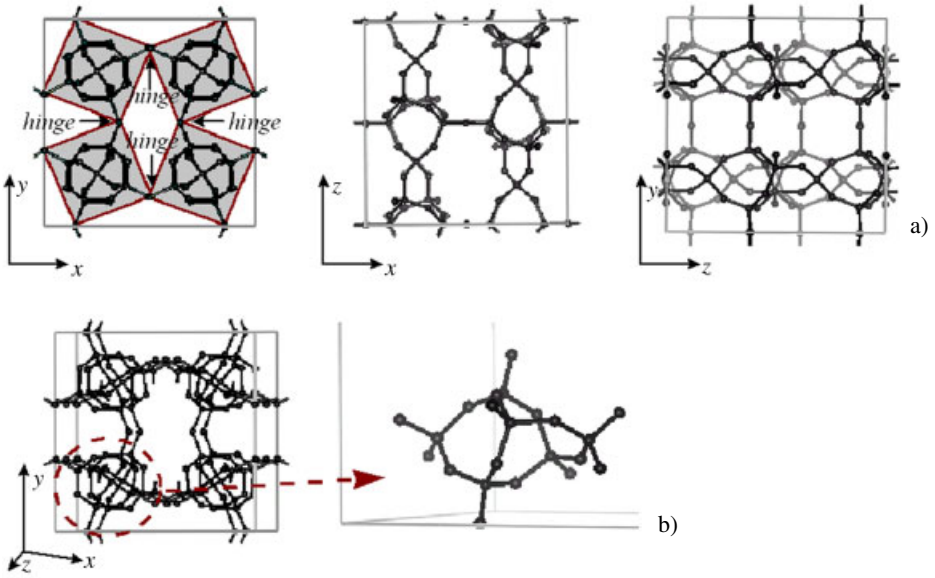

Fig. 8 Molecular structure of THO: (a) An illustration of the atomic configuration of the THO framework as seen down the *Z*, *Y* and *X* axes, and, (b) the atomic configuration of THO viewed at an angle with the *Z* axis with a zoomed illustration of a single cage-like unit which behaves as a 'rigid square'.

Negative Poisson's ratios were also predicted in the zeolites ABW and JBW and this time the auxeticity was due to a 'rotating triangles' mechanism [26].

More recently it was also proposed that the rotating squares model can be used to explain the auxetic behaviour in single crystalline materials belonging to the KH_2PO_4 family of the D_{2d} point group which have positive elastic compliance constant s_{12} [44]. It has also been shown through force-field based simulations that the experimentally observed auxeticity in the (010) and (100) planes of the naturally occurring silicate α-cristobalite may be explained in terms of 'rotating rectangles' where the rectangles are the two-dimensional projection of the three dimensional SiO_2 tetrahedral framework [47].

We have also proposed various theoretical polymeric networks which were designed in a way so as to mimic the 'rotating squares' or the 'rotating triangles' systems. In particular, we have shown that the molecular-level equivalent of the 'rotating triangles' macrostructure may be constructed using phenyl rings connected together through acetylene chains from the 1, 2, 3, 4 positions of the ring (see Fig. 9a). Force-field based simulations on these systems have confirmed that such systems exhibit negative Poisson's ratios, an effect which results from flexure of the acetylene chains that has the effect of allowing the 'molecular triangles' to rotate relative to each other (see Fig. 9b). Such man-made molecular level auxetics are highly desirable as they can be designed to have specific mechanical properties with the results that one may produce materials tailor-made for specific applications.

4.2 Rotating rigid units in microstructured auxetics

Another class of materials for which 'rotating rigid units' mechanisms are likely to play a very important role in generating auxetic behaviour are the auxetic foam materials produced from conventional foams through a combined triaxial compression/heat treatment process as described in [9].

Various attempts have been made to explain the experimentally observed auxetic behaviour of foams produced through this process. For example it has been proposed [5–7] that the auxetic effect is due to the presence of 're-entrant deformation mechanisms' which requires that the compression/heat treatment process described above would convert the 'Y' shaped joints to 'arrow shaped' joints, i.e., changes in the

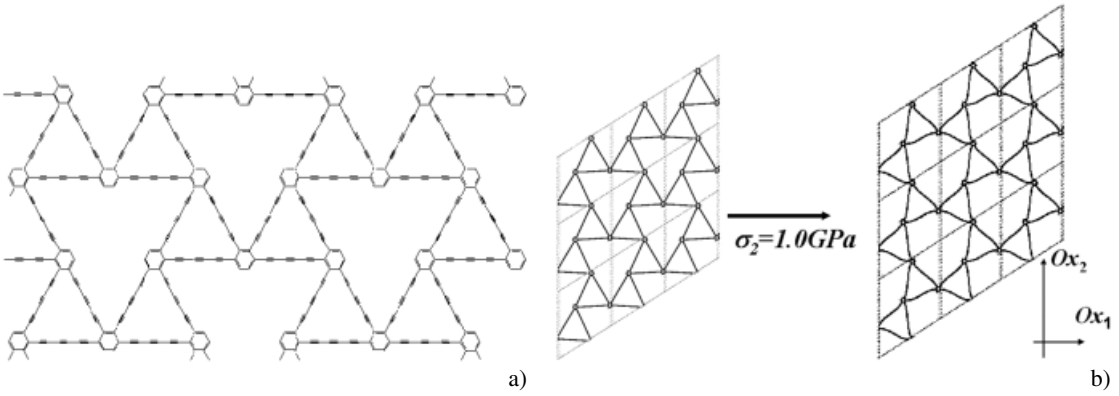

Fig. 9 (a) An illustration of the idealised structure of the proposed polyphenlyacteytlene 'rotating triangles' molecular structure made with acetylene chains containing 6 carbon atoms, and (b) the minimum energy conformations at different loads of the polyphenlyacteytlene networks made with acetylene chains containing 16 carbon atoms. The conformations were obtained using the molecular modelling package Cersius using the Dreiding force-fields [48].

microstructure of the foams must be concentrated at the joints. However, one may argue that this is unlikely given that one usually observes that the ribs of open cell foams are slightly thicker in the proximity of the joints than at the centre of the ribs. This means that it is more likely that changes in the microstructure during the compression/heat treatment process will conserve the 'geometry at the joints' and the major deformations will occur along the length of the ribs which can buckle (the foam is being subjected to, typically, a 28.6% compressive strain along each axis during the conversion process) with the effect the 'rigid joints' rotate relative to each other. This generates a foam with a microstructure that contains the necessary features which make it possible for the 'rotating rigid units' mechanism to operate and generate the experimentally observed auxetic behaviour. An illustration of this is given in Fig. 10 which shows how a conventional 'idealised 2D foam' can be converted through the compression/heat treatment process into an auxetic form where the auxeticity is achieved through 'rotating rigid units' (in this case 'rotating squares').

5 Conclusion

In this paper we have show that auxetic behaviour may be achieved from rigid units which rotate relative to each other. We have shown that in general, for such systems the extent of auxeticity depends on the actual geometry of the system and the direction of loading.

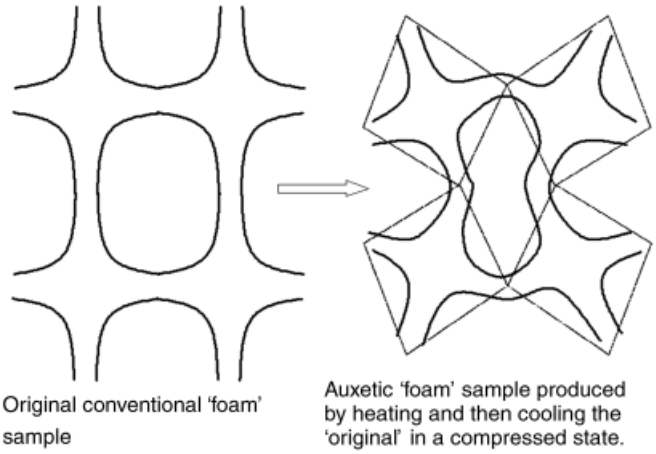

Fig. 10 An illustration of how a conventional 'idealised 2D foam' can be converted through the compression/heat treatment process into an auxetic form where the auxeticity may be achieved through 'rotating squares'.

This dependence has been illustrated through analytical modelling for the particular case of a system made from rotating rectangles. We have also shown that these mechanisms may play a very important role in generating auxetic behaviour in real systems including foams and molecular-level auxetics. This is particularly significant and we envisage that like the 're-entrant mechanism', this new mechanism will lead to the production of new materials and structures which exhibit negative Poisson's ratio behaviour.

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