Two-dimensional Mechanical Metamaterials with Unusual Poisson Ratio Behavior

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We design two-dimensional (2D) mechanical metamaterials that may be deformed substantially at little or no energy cost. Examples of such deformable structures are assemblies of rigid isosceles triangles hinged in their corners on the macro-scale, or polymerized phenanthrene molecules forming porous graphene on the nano-scale. In these and in a large class of related structures, the Poisson ratio $\nu$ diverges for particular strain values. $\nu$ also changes its magnitude and sign, and displays a shape memory effect.

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I. INTRODUCTION

There is growing interest in mechanical metamaterials, man-made structures with counter-intuitive mechanical properties [1]. Unlike in ordinary uniform materials, deformations in such metamaterials derive from the geometry of the assembly rather than the elastic properties of the components. This behavior is scale independent, covering structures from the macro- to the nanoscale. Most attention in this respect seems to be drawn by the Poisson ratio $\nu$ [2], the negative ratio of lateral to applied strain. Ordinary materials with typical values $0 < \nu < 0.5$ contract laterally when stretched, with unusually large values reported for cellular materials [3]. Auxetic metamaterials with $\nu < 0$, on the other hand, expand in both directions when stretched [3–7] leading to advanced functionalities [8, 9]. Auxetic systems with macroscopic components have been utilized for shock absorption in automobiles [10], in high-performance clothing [11–13], in bioprostheses [14] and stents [15] in medicine, and for strain amplification [16]. Auxetic 2D mechanical metamaterials with nanostructured components, some of which have been described previously [17–20], may find their use when precise micromanipulation of 2D structures including bilayer graphene is required [21].

Here we report the design of 2D mechanical metamaterials that may be deformed substantially at little or no energy cost. Unlike origami- and kirigami-inspired metamaterials, which derive their functionality from folding a 2D material into the third dimension [22–25], the structures we describe are confined to a plane during deformation. Such confinement may be achieved by a strong attraction to a planar substrate or in a sandwich geometry. Specifically, we consider infinite assemblies of rigid isosceles triangles hinged in their corners on the macro-scale [26] and polymerized phenanthrene molecules forming ‘porous graphene’ on the nano-scale. In these and in a large class of related structures, consisting of connected and near-rigid isosceles triangles, the Poisson ratio $\nu$ diverges at particular strain values. $\nu$ also changes its magnitude and sign, and displays a ‘shape memory’ effect in a specific range of deformations, meaning that this quantity depends on previously applied strain. Our corresponding results are scale invariant.

II. COMPUTATIONAL APPROACH

We have studied the electronic and structural properties as well as the deformation energy of polyphenanthrene dubbed ‘porous graphene’ using ab initio density functional theory (DFT) as implemented in the VASP code [27–29]. We represented this 2D structure by imposing periodic boundary conditions in all directions and separating individual layers by a vacuum region of 20 Å. We used projector-augmented-wave (PAW) pseudopotentials [30, 31] and the Perdew-Burke-Ernzerhof (PBE) [32] exchange-correlation functional. The Brillouin zone of the conventional unit cell of the 2D structure has been sampled by a $5 \times 3 \times 1$ $k$-point grid [33]. We used 500 eV as the electronic kinetic energy cutoff for the plane-wave basis and a total energy difference between subsequent self-consistency iterations below $10^{-4}$ eV as the criterion for reaching self-consistency. All geometries have been optimized using the conjugate-gradient method [34], until none of the residual Hellmann-Feynman forces exceeded $10^{-2}$ eV/Å.

III. RESULTS

A. Constructing a 2D mechanical metamaterial

Figure 1 depicts the macro-scale 2D mechanical metamaterial we consider, namely an infinite assembly of rigid
FIG. 1. Deformations in a 2D assembly of rigid isosceles triangles. (a) Adjacent triangles with opening angle \( \alpha \) and mutual orientation defined by the closing angle \( \beta \), hinged tip-to-corner, forming the primitive unit cell. The triangle height \( x_0 \) and the length \( y_0 \) of its base define the horizontal and vertical length scales. (b) Snap shots of the \( \alpha = 120^\circ \) triangle assembly for different values of \( \beta \). The conventional rectangular unit cell is twice the size of the primitive unit cell. (c) Contour plot of the Poisson ratio \( \nu_{xy} \), as a function of \( \alpha \) and \( \beta \). The dotted red line highlights behavior of the \( \alpha = 120^\circ \) triangle assembly. (d) Poisson ratio \( \nu_{xy} \) as a function of \( \beta \) in the \( \alpha = 120^\circ \) system. (e) Changes in the scaled width \( x/x_0 \) and height \( y/y_0 \) of the conventional unit cell for \( \alpha = 120^\circ \) caused by changing the angle \( \beta \).

isosceles triangles hinged in the corners and described using periodic boundary conditions. There are two identical triangles with different orientation in the primitive unit cell of the lattice, as seen in Fig. 1(a). The conventional unit cell, shown in Fig. 1(b), is rectangular and twice the size of the primitive unit cell. The deformation behavior of such constrained lattices of polygons including rectangles [35] and connected bars, some of which display a Poisson ratio that changes sign, value, and even diverges, has been described and classified earlier [26, 36].

In our system, structural changes are regulated by the only independent variable, the angle \( \beta \). The full range of \( \beta \) is \( 0 \leq \beta \leq \alpha + 180^\circ \) for \( \alpha \leq 60^\circ \) and \( 0 \leq \beta \leq 270^\circ - \alpha/2 \) for \( \alpha \geq 60^\circ \). Since there is no energy involved when changing \( \beta \), the structure maintains its geometry after deformation. Snap shots of the triangle assembly and the conventional unit cell at different values of \( \beta \), shown in Fig. 1(b), illustrate the unusual flexibility of the system. The movie of the continuous shape change is provided in Video 1 in the Appendix.

For a system of triangles aligned with the Cartesian coordinate system as shown in Fig. 1(a), we can determine the strain in the \( y \)-direction in response to strain applied along the \( x \)-direction. The negative ratio of these strains is the Poisson ratio \( \nu_{xy} \), which is given by

\[
\nu_{xy} = -\frac{dy/y}{dx/x}
\]

\[
= \frac{\cos(\frac{\alpha}{2}) \sin(\frac{\beta}{2}) - 3 \sin(\frac{\alpha}{2}) \cos(\frac{\beta}{2})}{\cos(\frac{\alpha}{2}) \cos(\frac{\beta}{2}) + 3 \sin(\frac{\alpha}{2}) \sin(\frac{\beta}{2})} \tan\left(\frac{\alpha + \beta}{2}\right)
\]

Dependence of \( \nu_{xy} \) on \( \alpha \) and \( \beta \) is presented as a contour plot in Fig. 1(c). Several aspects of this result are noteworthy when inspecting the behavior of \( \nu_{xy}(\beta) \) for a constant value of the opening angle \( \alpha \). With the exception of \( \alpha = 60^\circ \) describing equilateral triangles [37, 38], \( \nu_{xy} \) changes magnitude and sign with changing \( \beta \). Presence of the tangent function in Eq. (1) causes \( \nu_{xy} \) to diverge to \( \pm \infty \) for \( \beta_{\text{crit}}(\nu_{xy}) = 180^\circ - \alpha \), with \( \beta_{\text{crit}}(\nu_{xy}) = 60^\circ \) for \( \alpha = 120^\circ \). For \( \alpha > 60^\circ \), \( \nu_{xy} \) changes sign twice across the full range of \( \beta \) values, as shown in Fig. 1(d) for \( \alpha = 120^\circ \). The condition for the divergence of \( \nu_{xy} = 1/\nu_{xy} \), describing strain in the \( y \)-direction in response to strain applied in the \( y \)-direction, is \( \tan(\beta_{\text{crit}}(\nu_{xy})/2) = 3 \tan(\alpha/2) \). For \( \alpha = 120^\circ \), \( \nu_{xy} \) will diverge at \( \beta_{\text{crit}}(\nu_{xy}) = 158.2^\circ \).

Maybe the most unexpected aspect of our result is the ‘shape memory’ effect displayed by both \( \nu_{xy} \) and \( \nu_{yx} \).
if the angle $\beta$ becomes a hidden variable in the system. To explain what we mean, we first inspect the $(x(\beta)/x_0, y(\beta)/y_0)$ trajectory given by

$$
\frac{x}{x_0} = 2 \left[ \tan \left( \frac{\alpha}{2} \right) \cos \left( \frac{\beta}{2} \right) + \sin \left( \frac{\beta}{2} \right) \right], \quad (2)
$$

$$
\frac{y}{y_0} = 3 \sin \left( \frac{\beta}{2} \right) + \cot \left( \frac{\alpha}{2} \right) \cos \left( \frac{\beta}{2} \right). \quad (3)
$$

The $(x(\beta)/x_0, y(\beta)/y_0)$ trajectory, describing the changing shape of the unit cell, is shown for $\alpha = 120^\circ$ in Fig. 1(e), and for other values of $\alpha$ in Fig. 4 in the Appendix section. The sign of the slope of the trajectory, opposite to the sign of $\nu_{xy}$ and $\nu_{yx}$, changes twice as the structure unfolds with increasing $\beta$. Regions of positive and negative $\nu_{xy}$ and $\nu_{yx}$, delimited by the above-mentioned critical values $\nu_{xy}$ and $\nu_{yx}$ for $\beta_{\text{crit}}(\nu_{xy})$ and $\nu_{yx}$ for $\nu_{yx}$, are distinguished graphically in Fig. 1(e). For any $x$ in the range $3.46 < x/x_0 < 4.00$, there are two different values of $y$ associated with different values of $\beta$ and different signs of $\nu_{xy}$. Similarly, for any $y$ in the range $2.75 < y/y_0 < 3.06$, there are two different solutions for $x$ associated with different values of $\beta$ and different signs of $\nu_{yx}$.

Let us now consider a macroscopic piece of ‘material’ consisting of hinged triangles, which are so small that their mutual orientation cannot be made out. With no information about the deformation history, the material may exhibit either a positive or a negative Poisson ratio. The only way to change the material so that it would exhibit a definite positive or negative sign of the Poisson ratio is to subject it to a sequence of deformations. Assume that this material is first stretched to its maximum along a given direction such as $x$. Subsequent stretching along a direction normal to the first will result in a positive, subsequent compression in a negative Poisson ratio. We may say that the system retains a memory of previous deformations.

What happens microscopically can be clearly followed in Fig. 1(e). Even though the value of $\beta$ is hidden, we know that it becomes $60^\circ$ for maximum stretch along $x$ and $158.2^\circ$ for maximum stretch along $y$. Subsequent deformation normal to the first direction then dictates the sign of $\nu$. This behavior derives from the nonlinearity in the system and, in some aspect, parallels the behavior of shape memory alloys.

B. Porous graphene as a 2D mechanical metamaterial

Whereas macroscopic triangular assemblies with various values of $\alpha$ will find their use in particular applications, we turn our interest to 2D nanostructures that can be formed by coordination chemistry and macromolecular assembly. Microstructures including col-
To the isoenergetic model system of Fig. 1. Our DFT-PBE calculations indicate only small structural distortions of the phenanthrene molecules, which nevertheless break their initial mirror symmetry.

In Fig. 2(c) we compare changes in the scaled height $y/y_0$ for the assembly of triangular and for porous graphene. The corresponding changes in the scaled height $y/y_0$ are shown in Fig. 2(d) in the same range of $\beta$ values. Interestingly, $x(\beta)/x_0$ reaches its maximum at $\beta_{\text{crit}}(\nu)$ for both systems, whereas $y(\beta)/y_0$ increases monotonically with increasing $\beta$. According to the definition of the Poisson ratio $\nu=(d y)/(d x)$, $\nu_{xy}$ diverges at $\beta_{\text{crit}}(\nu_{xy}) = 60^\circ$ in the triangular assembly, as seen in Fig. 1(d). Similarly, $\nu_{zy}$ diverges at $\beta_{\text{crit}}(\nu_{zy}) = 70^\circ$ in porous graphene, as shown in Fig. 2(e). The slope of $x(\beta)/x_0$ changes sign at $\beta_{\text{crit}}$, resulting in $\nu_{zy} < 0$ for $\beta < \beta_{\text{crit}}(\nu_{zy})$ and $\nu_{zy} > 0$ for $\beta > \beta_{\text{crit}}(\nu_{zy})$ in both systems.

The energy investment $\Delta E$ associated with deforming the polyphenanthrene structure is shown in Fig. 2(f). Our results were obtained by optimizing the structure for selected values of the angle $\beta$ that defines the relative orientation of the two inequivalent phenanthrene molecules in the unit cell. With $\beta \approx 70^\circ$ representing the structural optimum, we found that changing $\beta$ by $\pm 10^\circ$ required $\Delta E < 3$ eV per unit cell, corresponding to an energy investment of only $\approx 50$ meV per C atom, about 1% of the bond breaking energy. Thus, the polyphenanthrene structure is rather soft and represents a valid counterpart to the isoenergetic model system of Fig. 1.

Phenanthrene is a tricyclic organic molecule with a 3.36 eV wide DFT-PBE gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). When polymerized to the 2D polyphenanthrene structure depicted in Fig. 2(b), the HOMO broadens to the valence and the LUMO to the conduction band. This is seen in Fig. 3(a), which depicts the band structure and the density of states of the optimum geometry of polyphenanthrene with $\beta = 70^\circ$, with the Brillouin zone shown in the inset. Our DFT-PBE results indicate that the fundamental band gap $E_g$ is reduced from the molecular value to 1.75 eV in the equilibrium structure of the layer, but still does not vanish for $55^\circ < \beta < 80^\circ$. The gap is near-direct due to the flatness of bands, and decreases from 1.9 eV at $\beta = 55^\circ$ to 1.7 eV at $\beta = 80^\circ$. We should remember that Kohn-Sham eigenvalues in all DFT calculations including ours do not correctly represent the electronic structure and typically underestimate the band gaps.

The decrease of $E_g$ and its dependence on $\beta$ upon polymerization is caused by the presence of covalent C-C bonds that connect individual phenanthrene molecules elastically and electronically. Unfolding of the polyphenanthrene structure with increasing angle $\beta$ rotates individual phenanthrene molecules and modifies the bonding at the connection between adjacent monomers, causing the electronic structure to depend on $\beta$. The range of deformations in polyphenanthrene is smaller than in triangular assemblies due to the steric hindrance caused by hydrogen termination. In absence of planar
confined, phenanthrene molecules rotate out-of-plane at large tensile strain values not considered here.

IV. DISCUSSION

Elastic response of materials is commonly described by elastic constants constituting the elastic matrix, which describe stress-strain relationships and thus contain energy in their dimension. The Poisson ratio is fundamentally different. It is a dimensionless quantity that describes deformations induced by strain, independent of the energy cost. According to its definition in Eq. (1), it depends on the choice of the coordinate system. The trace of the strain matrix, however, which describes the fractional change of the area induced by the mechanism, is independent of the choice of coordinates and could couple naturally to external fields such as pressure.

We believe that changes in pore size caused by the deformation of the 2D unit cell may find their use in tunable sieving in a layered system [45, 46], including application in desalination membranes. 2D mechanical metamaterials may also find unusual applications in micro-manipulation. In particular, a 2D layer in partial contact with an in-plane junction of 2D metamaterials with different values of ν, including ν > 0 and ν < 0, may experience a torque normal to the plane when in-plane strain is applied at the junction of the 2D systems. Also the observation of strain–related electronic structure changes in polyphenanthrene opens new possibilities. Since polyphenanthrene and a wide range of porous graphene structures can be viewed as a system of covalently connected quantum dots, in-layer strain may be used to tune the coupling between such quantum dots and thus change the electronic structure of the system.

V. SUMMARY AND CONCLUSIONS

In summary, we have designed 2D mechanical metamaterials that may be deformed substantially at little or no energy cost. Unlike origami- and kirigami-based mechanical metamaterials that derive their functionality from folding a 2D material to the third dimension, the structures we design are confined to a plane during deformation. In reality, such confinement may be achieved by a strong attraction to a planar substrate or in a sandwich geometry. On the macro-scale, the structures we describe are assemblies of rigid isosceles triangles hinged in their corners. Their nanoscale counterpart are molecules such as phenanthrene that may be polymerized using coordination chemistry or macromolecular assembly to form specific geometries with a porous graphene structure. In these and in a large class of related structures, consisting of connected and near-rigid isosceles triangles confined to a plane, the Poisson ratio ν diverges for particular strain values. ν also changes its magnitude and sign, depending on the applied uniaxial strain, and displays a shape memory effect with respect to the deformation history.

VI. APPENDIX

A. Deformation behavior in 2D isosceles triangle assemblies

Video 1. Unfolding of a 2D assembly of α = 120° isosceles triangles with changing angle β.

As discussed earlier, for a given value y of the unit cell height in a 2D assembly of isosceles triangles with α > 60°, we can find two different values x of the unit cell width, with the two structures displaying opposite signs of ν. Similarly, we can find two different values y for a given value of x, with the two structures displaying opposite signs of ν. This unusual behavior results from the presence of a hidden variable, the relative triangle orientation β, and causes ν to depend not only on the overall sample shape, but also the history of the system. The unfolding of an assembly of triangles with α = 120° and its history dependence has been characterized by the x − y trajectory in Fig. 1(e) in the range of accessible β angles. The unfolding process of the α = 120° triangle assembly is depicted in Video 1.

x − y trajectories for several values of α are shown in Fig. 4. The particular shape of these x − y trajectories indicates that also for opening angles other than α = 120° discussed above, the value and sign of ν may depend on sample history. Only in the specific case of equilateral triangles with α = 60°, discussed in the following, the

FIG. 4. Changes in the scaled width x/x₀ and height y/y₀ of the conventional unit cell for different values of the opening angle α as a function of the closing angle β. The relevant quantities are defined in Fig. 1.
y − x trajectory in Fig. 4 is linear and ν is history independent.

B. Deformations in a 2D assembly of rigid equilateral triangles

We mentioned above that the behavior of α = 60° triangle systems, depicted in Fig. 5, is unique among the 2D assemblies of corner-sharing isosceles triangles. As discussed in the main manuscript and above, the Poisson ratio changes drastically for triangle systems with opening angle α other than 60°. While hinged equilateral triangles gradually unfold when β increases, as seen in Video 2, the width x of the unit cell remains proportional to its height y, resulting in a constant, β-independent Poisson ratio $\nu_{xy} = -1$, as noted earlier [37, 38]. For the particular angle $\beta = 120°$, the structure of the assembly resembles the Kagomé lattice.

![Video 2. Unfolding of a 2D assembly of $\alpha = 60°$ equilateral triangles with changing angle $\beta$.](image)

FIG. 5. Deformations in a 2D assembly of rigid equilateral triangles. (a) Adjacent triangles with mutual orientation defined by the closing angle $\beta$, hinged at the corners, forming the primitive unit cell. The triangle height $y_0$ and the length $x_0$ of its base define the horizontal and vertical length scales. (b) Snap shots of the triangle assembly for different values of $\beta$. The conventional unit cells of width $x$ and height $y$ are indicated.

C. Deformations of 2D polyphenanthrene

Changes in the 2D polyphenanthrene structure as a function of $\beta$ are shown in Video 3. The structural changes resemble those shown in Video 1 for the assembly of $\alpha = 120°$ rigid triangles.

![Video 3. Unfolding of a 2D polyphenanthrene structure dubbed 'porous graphene' with changing angle $\beta$.](image)

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