Shape Entropy of a Reconfigurable “Isigami” Surface

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Disclinations in a 2D sheet create regions of Gaussian curvature whose inversion produces a reconfigurable surface with many distinct metastable shapes, as shown by molecular dynamics of a disclinated graphene monolayer. This material has a near-Gaussian “density of shapes” and an effectively antiferromagnetic interaction between adjacent cones. A ∼10 nm patch has hundreds of distinct metastable shapes with tunable stability and topography on the size scale of biomolecules. As every conical disclination provides an Ising-like degree of freedom, we call this technique Isigami.

Techniques arising from papercraft – origami and kirigami – inspire efforts to impart three-dimensional shapes to two-dimensional materials [1–13]. Origami and kirigami both work by imposing one-dimensional modifications (folds or cuts) into surfaces. Here we investigate an alternative method of shape control that inserts zero-dimensional objects – isolated disclinations – into an atomically thin sheet. Inversion of bistable conical disclinations provides a means to control the shape of the surface, with tunable topography down to the length-scale of protein secondary/tertiary structure and energy barriers against shape change that are tunable from below room temperature to values much larger. A tunable topography in a biologically relevant size regime suggests that reconfigurable shape-driven binding interactions may be possible with such sheets.

A disclination removes or adds a wedge of material in the lattice of a two-dimensional sheet, yielding a conical or hyperbolic local region; in a hexagonal lattice the least costly such defects are 5 and 7-member rings. Since a cone (in a continuum approximation) has a local C∞ symmetry for rotations about its apex, its mechanical states are anticipated to be particularly simple: just “up” and “down”, related by a local inversion. The reduced rotational symmetry of the saddle suggests more complex behavior, as it may be able to assume more than one in-plane orientation depending on the local mechanical environment. Here we investigate a sheet containing multiple disclinations balanced between positive and negative (i.e. asymptotically flat) and determine the multiplicity and character of the shape metastability thereby instilled in the 2D layer. Anticipating our conclusions, the sheet’s conformational freedom is dominated by Ising-like bistable cone degrees of freedom; hence we call this means of shape control Isigami.

To create such a surface, we begin with a so-called Haeckelite [14, 15] structure and “inflate” each ring with a penumbra of hexagons, similar to inflation of larger fullerenes from C60 [16, 17]. We choose a Haeckelite in which the pentagonal rings form a slightly deformed kagome lattice (Fig. 1) [18], speculating that this may cause mechanical frustration which brings the set of possible shapes closer to mutual degeneracy, since this surface has no obvious pairings of opposite disclinations. Other disclination patterns are also possible, and those formed by phase field crystal methods have been examined independently for their effect on sheet toughness in an interesting work by Zhang, Li and Gao [19]. We choose graphene as an archetype, since its mechanical response is reasonably well-studied and methods exist to functionalize the surface to control mechanical stiffness, interfacial energetics, and hydrophilicity [20–22]. Since the behavior described below is largely geometrical in origin, conclusions derived from graphene Isigami should generalize to other atomically thin two-dimensional materials.

We construct both periodic and finite-patch regions of material hosting twelve cones and twelve saddles on a kagome lattice as depicted in Fig. 1 and model the mechanical response using the AIREBO potential [23] as implemented in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator [24], as it is well-validated for the mechanical response of nanoscale sp² carbon [25–29]. We first examine a finite sheet whose disclinations are all separated by six hexagons (∼20 Å) from the nearest neighboring disclinations; the edges are terminated by hydrogen. This separation is large enough that even cones on the edge of the sheet have two well-defined metastable “up” and “down” orientations. Shape variance is most dramatic in a finite patch of material, as the periodic boundary constraint is absent. The patch is systematically forced into every possible set of cone orientations by mechanically inverting various sets of cones with external forces. To this end, a force of ±1.7 eV/Å is applied to the five atoms at the apices of various cones according to the desired up/down states and the system is then allowed to evolve for 500 femtoseconds while the atoms are constrained to move no more than 0.1Å each timestep. A constraint force is also applied evenly across every atom in the system to zero-out the net force. The structure is then relaxed either through a thermal bath at 300 K for 50 ps followed by a linear ramp anneal over 30 ps from 300 K to 3 K, or (for the periodic systems described below) through a shorter 1 ps thermal bath followed by a series of conjugate gradient minimizations where the unit cell geometry is allowed to relax during

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alternate optimization steps. These methods both produce well-converged energy minima (converged to less than 100 meV in systems with thousands of atoms), but the anneal method performs better for the finite patch in avoiding local minima.

For every initial choice of the twelve up/down cone configurations, the system relaxes into a distinct metastable shape, i.e. all $2^{12}$ nominal Isigami configurations are accessible. Fig. 2 shows some examples of these shapes, labeled by the cone configuration: the different shapes that are metastably assumed by the same sheet can be dramatically different. Several of these configurations, including the five highest in energy, were simulated at 800 K in an NPT ensemble for one nanosecond, with the sheet maintaining its original Ising state. This high-temperature “challenge” anneal was also applied to a subset of configurations that were repeated to create a larger $2 \times 2$ supercell patch, providing assurance that shape metastability is preserved for larger patch sizes as well.

Collapsing the reflection symmetry about the sheet midplane, we actually obtain $2^{11}$ distinct Isigami configurations for this 12-pentagon patch, with an additional approximate reflection symmetry about the short diagonal (broken very weakly by the detailed termination of the patch). Additional symmetries in the periodic case further reduce the number of symmetry-distinct configurations per unit area, but the conformational entropy of metastable Isigami states remains extensive.

As noted earlier, whereas cones naturally have two distinct conformations (i.e. up and down), the orientations of the principal axes of saddle-point disclinations do not naturally fall into a binary choice; depending on the states of nearby disclinations and other aspects of the local environment, a given saddle point disclination could have one, two or possibly more metastable axial orientations. We do in fact find certain conformations that have the same set of cone orientations (i.e. the same Isigami state) but visibly different overall shapes, sometimes differing by over an eV in energy and stable in shape up to at least 800 K over half a nanosecond. Fig. 3 depicts two such states. While we have not exhaustively quantified the frequency of these non-Ising states, our observations suggest that they contribute a number of configurations equivalent to roughly one additional Ising degree of freedom for a 12-cone sheet; i.e. they contribute only modestly to the overall configurational entropy. Although these non-Ising states do sometimes correspond to different orientations of the saddle disclinations, we do not find a simple rule governing their appearance, as reflected by the examples shown in Figure S5. Similar non-Ising states are seen in the larger $2 \times 2$ supercell patch. Simulations of this larger patch (and larger periodic systems) reveal a similarly pervasive metastability to Ising conformations, suggesting that the system has an extensive
conformational shape entropy. How are these states distributed in energy? The “density of shapes” (i.e. the number of shapes in a given energy range) for the finite 12-cone patch is strikingly close to Gaussian, as shown in Fig. 4. It is tempting to consider this outcome as an expression of the Central Limit Theorem for multiple nearly independent energetic contributions from different disclinations, but the stronger deviations from a Gaussian shape seen in a similarly-sized periodic patch argue against a simple application of this notion. It is likely that quasi-random finite-size effects in the finite patch, when combined with medium-range effectively many-body elastic interactions, generate a complexity sufficient to reproduce a roughly central-limit-like behavior.

Mechanical intuition suggests that nearby cones will have pair-wise antiferromagnetic interactions, since opposing up/down orientations produce compatible sidewall slopes – the prospects for generating a near-degeneracy of conformations with such an interaction was one motivation for choosing a frustrated kagome-like lattice for the disclinations [30]. In practice, we find that longer-range and many-body elastic interactions between disclinations are too strong to admit a strict frustration-derived degeneracy. While these non-idealities (and also non-Ising states) are sufficiently important that the sheet is not a simple nearest-neighbor antiferromagnet, the energies of different sheet configurations do reveal an overall nearest-neighbor antiferromagnetic trend, as the energy varies systematically with the number of oppositely-oriented nearest-neighbor cones for both the periodic-boundary and finite-patch cases (Fig. 5). The effective $J$ of this trend is proportionately smaller for a sheet with 1-hexagon separation between the 5-fold rings (Fig. S1). As noted in Supplementary Information, it was not possible to describe the sheet energetics with a simple cluster expansion; this was likely due in part to the long-range nature of elastic interactions amongst nearby cones (i.e. when even a single cone inverts, we see significant changes in shape across the entire patch, as shown in Figure S4) and in part to the presence of a modest number of additional states not fully specifiable by an Isigami state vector, as noted earlier.

These reconfigurable surfaces provide a means to access a multitude of distinct sheet topographies from a single patch of multiply disclinated 2D material: an obvious area of potential application for such an object is shape recognition and binding of biomolecules. Ideally, such a surface would have topography on the length scale of protein tertiary structure, a hydrophilic surface that does not denature delicate biomolecules, and a tunable barrier against shape change so that both dynamic ($\sim k_BT$) and static ($\gg k_BT$) regimes can be accessed. The $\sim 0.5$ nm inter-pentagon spacing of the sheet depicted in Fig. 6 provides topography on a biologically relevant length-scale, as demonstrated by the comparison to insulin, a small protein, in the same figure. The use of graphene oxide [31, 32] rather than hydrophobic bare graphene [33–35] could introduce the needed hydrophilicity, and perhaps also increased flexibility [36].

The question of barrier height control requires more detailed study. The inversion barriers of isolated graphene cones have been simulated previously [37]; the barrier height depends on the chemical character of the conical apex but is generally multiple electron volts for well-separated cones. Energy barriers against cone inversion will depend on the material of the sheet, the separation between conical disclinations, and also any structural modifications performed on the conical apices such as functionalization [37] to heighten the barrier or flattening to soften it (through grain boundaries that interconnect disclinations [38, 39]). We observe in the periodic sheets that the stability of the Ising and non-Ising states indeed varies with cone separation, and also that the barriers against inter-conversion of the non-Ising states are typically much lower than those between states with distinct Ising configurations. We monitored the energy along the cone inversion pathway for a few periodic sheets with different cone separations; although the distribution of inversion barriers could not be exhaustively quantified, the barriers all remained on the order of electron volts, likely lowered somewhat (compared to isolated cones) by irregularities in the local environment. The typical barrier height scales roughly linearly with the separation between pentagonal disclinations, being
Figure 5. The sheet energy as a function of the number of nearest-neighbor cone pairs which are oppositely-oriented for both free (left, blue) and periodic (right, orange) boundary conditions, with vertical axes shifted for clarity. The overall linear trend yields similar nearest-neighbor antiferromagnetic $J$'s for free ($-0.54$ eV) and periodic ($-0.56$ eV) cases. The large dispersion about the linear trend reflects contributions from longer-ranged or collective interactions and a modest admixture of non-Ising configurations. A wider range of antiferromagnetic pairings is accessible to the free-boundary case, due to a more forgiving boundary condition. Points are translucent to better reveal the overall density of configurations.

Around $1$ eV for a 1-hexagon separation and around $6$ eV for the 6-hexagon separation. At the 1-hexagon separation a significant fraction of the Isigami states destabilize (see Figure S2) while almost all of the non-Ising states disappear, where our criterion for stability is surviving the room-temperature anneal mentioned earlier.

Since most of the sheets considered above often have inversion barriers much greater than $k_BT$, we now consider a means to “thermalize” these barriers even at larger disclination separations: oxidizing the sheet and etching away the central five-membered ring and one or more surrounding rings to reduce the mechanical deformation associated with nucleating inversion, terminating the resulting apical multivacancy with hydrogen atoms. To this end, we oxidized a six-hexagon-separation periodic sheet by random placement of oxygen atoms equally onto upper and lower surfaces followed by a structural relaxation and subsequent removal of any unreacted oxygen, yielding a functionalized sheet with $12.6\text{ at}\%$ oxygen (Fig. S3). These simulations used a version of the REAXFF reactive force field [40–42] designed [43] to describe carbon, hydrogen and oxygen [44] and updated to more precisely describe chemical properties of C/H/O/N systems [45–48]. Neither the structural relaxation following etching (nor that which followed oxygenation) caused cone inversion, but during a subsequent molecular dynamics simulation at $800K$ we observe rapid ($\sim 1$ ns) spontaneous inversion of cones; we anticipate that a similar simulation without periodic boundary conditions would be at least as floppy. Although these simulations were performed in the gas phase, we anticipate that the qualitative conclusion of low, thermally accessible inversion barriers will be robust against the introduction of aqueous conditions. In constrast, the same system with intact (non-etched) apices shows no inversion over $1$ ns at $800$ K.

The richness and reconfigurability of shape at the nanometer scale is a signature element of biology, but one that is not so easily expressed in non-biological systems. Here we have described a strategy towards expressing richness of shape in inorganic materials by means of the non-planarity intrinsic to the Gaussian curvature of disclinations in a 2D sheet, so that a combinatorially large library of shapes can be expressed in a single sheet. As this approach is purely geometrical, it should apply to any atomically thin sheet, which could be more polar (e.g. hBN), more hydrophilic (graphene oxide [31, 32]) or stiffer [49] than graphene. The degree of metastability of this library of shapes is tunable from highly stable (multi-eV barriers) to potentially room-temperature reconfigurable (for tightly spaced disclinations in sheets that may also be intrinsically more flexible, possibly with apices removed). Possible applications for 2D shape reconfiguration and memory naturally center on those involving interaction with biological systems where, for example, diverse shape libraries could be created under shape-labile conditions and then selected for desired biological function under shape-conserving conditions. Outside the biological regime, the presence of disclinations (with associated geometrical phases [50]) and local strains (with associated pseudomagnetic fields [51–54]) may introduce
unusual and tunable electronic and plasmonic [55] properties as well. The behavior of a disclinated sheet on longer length scales, where linear arrays of disclinations could be organized to act in concert, may also be able to recover phenomena akin to more traditional fold-based origami wherein mean curvature plays a more prominent role.

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SUPPLEMENTARY MATERIAL

**Attempted cluster model:** The cones’ twisted kagome lattice has significant geometrical frustration under antiferromagnetic nearest-neighbor spin interactions, which motivates a study of whether our mechanical system can be similarly described, i.e. whether their energetics is dominated by nearest-neighbor pair-wise antiferromagnetic mechanical interactions, and whether the overall shape of the membrane can be described solely with Ising-like degrees of freedom for the conical disclinations. To assess this, we attempted to fit the energies of the periodic system with a Hamiltonian using cone clusters of various sizes [1]:

\[ H = \sum_{\alpha} J_{\alpha} \sum_{\alpha_m \in \alpha} \prod_{j \in \alpha_m} \sigma^{(j)} \]

We attempt to construct a Hamiltonian as a power series expansion in the mechanical Ising psuedospins of the system. We partition the cones into differing clusters (unique layouts of cones) \( \alpha \) with energies \( \pm J_{\alpha} \) dependent on the parity of the cluster’s cone states. Then for each cluster \( \alpha_m \) we assign the cones states \( \sigma^{(j)} = \pm 1 \), depending on their orientation. Our expansion includes only clusters with even numbers of cones: odd-numbered clusters are absent due to inversion symmetry. After the clusters are defined, the terms to the right of \( J_{\alpha} \) become a correlation matrix:

\[ \Pi_{\alpha k} = \sum_{\alpha_m \equiv \alpha} \prod_{j \in \alpha_m} \sigma^{(j)}_k \]

where \( k \) counts different shapes, and the unknown cluster coefficients \( J_{\alpha} \) are found as a solution to a linear system:

\[ E_k = \sum_{\alpha} J_{\alpha} \Pi_{\alpha k} \]

which is done by least squares minimization, using a singular value decomposition pseudoinverse.

As our initial model attempt produced results whose variations in energy, even for large cluster sizes, are very large, we made another attempt while ignoring the internal symmetries of our system, modeling each cluster as distinct. As an example, this means that every possible group of four cones is modeled as a unique cluster type with its own coefficient. Even then, this does not produce results with any close match to the data until we include six-cone clusters, and high accuracy with eight-cone clusters, at which point we have nearly
as many coefficients as unique states in the system. Presumably the reason why the cluster expansion fails is the presence of non-Ising states that fall outside of its purview, combined with a high degree of longer-ranged (and collective) elastic interaction due to the slow power-law falloff of elastic interactions with distance. There is an overall antiferromagnetic trend, as described in the main text, but it is swamped by effectively stochastic variations when one looks beyond the main trend.

| cluster types present | 2(pairwise) | 2,4 | 2,4,6 | 2-8 | 2-10 |
|-----------------------|------------|-----|-------|-----|------|
| total energy error (eV) | 29997 | 11940 | 3351 | 589 | 440 |
| median energy error (eV) | 1.76 | 1.09 | 0.58 | 0.16 | 0.0007 |
| number of clusters | 22 | 157 | 397 | 532 | 553 |

Table S1. Results of model fitting. The top row shows the total error in energy for fits with varying number of cluster types. A small percentage of data points were excluded from the fit due to errors in cone assignment. The middle row shows the median absolute error in energy for each state produced by the fit, and the bottom shows the total number of clusters used for each fit. A very large number of clusters is needed to obtain an accurate energetic description.
Figure S1. The energy for a 1-hexagon spacing version of the periodic cell studied in the main paper plotted against the number of oppositely-oriented nearest-neighbor cones: this is a 1-hexagon version of Figure 3 of the main text. A linear fit produces $J \sim -0.12$. Although this fit shows significantly more scatter than the six-hexagon-separation case shown in the main paper, the effective antiferromagnetic J does scale roughly with the separation between cones (i.e. the effective size of the cones). The Ising states of the most favorable shapes differ from those of the six-hexagon separation case, and certain Ising configurations at the smaller spacing are not metastable (i.e. relax into other configurations). The translucency of the points helps to show clustering around certain Ising states (more so than in the six-hexagon case).
Figure S2. Two images of a periodic-boundary 1-hexagon-separation sheet, before (left) and after (right) simulation at 300 K. The left state, which is stable at room temperature for a six-hexagon separation between disclinations, rapidly converts to a new metastable Ising configuration at this closer spacing. At one-hexagon separation, there are fewer metastable Ising states and easier interconversion between these states.

**Analysis of barrier height for cone inversion:** Approximate magnitudes for transition barriers were calculated within LAMMPS, using the AIREBO potential. A few selected structures covering a variety of local curvatures and total energies were chosen from the periodic lattice as a representative sampling. For each of these, one cone at a time was slowly moved from its original position to an inverted one. Two reference atoms in the sheet, one at the cone apex and one elsewhere in the sheet (and well-separated from the cone in question) were fixed in the direction perpendicular to the sheet plane to set vertical height as a reaction coordinate and explore minimally constrained inversions. Different choices for the fixed atom in the sheet produced fairly modest changes in overall barrier height. The typical inversion barrier is around 6 electron volts for the sheet with six hexagons of separation between apical disclinations and around 1 eV for the one-hexagon case. A more systematic sampling of barrier heights was complicated by the frequent inversion of a cone other than that specified by the apical fixed atom.

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Figure S3. NVT simulations of an oxidized sheet with cone apices etched away, in periodic boundary conditions. Panel (a) shows the sheet pre-relaxation, with apices removed and the new boundaries terminated with hydrogen. Panel (b) shows the same sheet post-relaxation. Panel (c) shows this sheet after 1 ns at 800 K: the black circles highlight a cone that spontaneously inverted under thermal excitation. The same sheet without etching does not invert under these conditions: etching the apices greatly reduces the kinetic barrier against inversion at this cone separation.

Figure S4. A $3 \times 3$ supercell of the periodic sheet studied, before and after the inversion of a single cone (circled). The topography of the sheet changes visibly over a region larger than the $1 \times 1$ patch studied (denoted with a dashed line), underlining the relatively long range of elastic interactions.
Figure S5. Four different cone orientations (top row) each with a candidate “plateau” motif bounded by three co-aligned adjacent cones, to explore if manipulation of the plateau region – while preserving the cone orientations – can generate non-Ising states. Three of these cases have non-Ising partners, but of different characters: the new metastable state is associated either with correlated or anti-correlated shifts of the plateau height or with deformations around but not on the plateau. The second case does not have an Ising partner, although it does have the candidate motif. All shapes shown are metastable under a combination of local relaxation and molecular dynamics at 300 K (similar to the method used in the main text). This diversity of behaviors reflects the absence of a simple rule for the presence or absence of non-Ising states.
Figure S6. Scripts provided elsewhere in Supplementary Information make use of the cone numbering scheme shown above, which differs from the streamlined version used in Fig. 3 of the main text.