

Cite this: DOI: 00.0000/xxxxxxxxxx

Function from configurational degeneracy in disordered framework materials

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Received Date

Accepted Date

DOI: 00.0000/xxxxxxxxxx

The existence of correlated disorder in molecular frameworks is an obvious mechanism by which unusual cooperative phenomena might be realised. We show that the use of local-symmetry lowering approaches can allow ostensibly high-symmetry framework structures to harbour exotic disordered states often studied in the context of spin lattice models. These states exhibit strongly cooperative behaviour that might be exploited in anomalous mechanical, host/guest, and information storage behaviour. Our contribution focusses in particular on the concepts of (i) combinatorial mechanics, (ii) adaptive flexibility, and (iii) error-correcting data storage in framework materials.

1 Introduction

Molecular framework materials can host a variety of different types of disorder.^{1–6} A trivial example is the inclusion of disordered guest molecules—such as solvent or adsorbed gases—within a framework pore network. Alternatively, node or linker secondary building units (SBUs) may be disordered over multiple equivalent orientations; this is the case even in the paradigmatic IRMOF family that includes MOF-5.^{7,8} Frameworks once considered highly ordered are now known to support a range of defect structures, and the study of defects in metal–organic frameworks (MOFs) and related materials is itself a rapidly growing field. While the naïve expectation is that defects degrade material performance, there is now considerable interest in exploiting defective frameworks in catalytic, sorption, and electronic applications.^{4,6,9}

In this paper we propose some alternative applications of disordered framework materials. Rather than focusing on defective structures, we instead consider homogeneously disordered systems in which disorder is inherently strongly correlated.¹⁰ A recent review of such systems, including design rules for their synthesis, is given in Ref. 11. A central concept is that of local symmetry-lowering that propagates according to a set of local

rules. The two-in-two-out hydrogen bonding rules of ices are perhaps the best known example,^{12,13} but we will come to present a number of other examples of direct relevance to well-known framework materials. Common to all these systems is a large configurational degeneracy: the one framework can exist in a variety of different states with essentially identical energies.^{11,14,15} We use a combination of computation and theory to flag some ways in which this configurational degeneracy might be exploited in terms of novel and unexpected functional properties of disordered frameworks.

Figure 1 illustrates two simple examples of local symmetry-lowering approaches relevant to framework materials. The paddle-wheel SBU ordinarily possesses D_{4h} symmetry in its idealised form. Replacement of one linking dicarboxylate with a monodentate modulator (e.g. formate¹⁶) reduces the local symmetry to C_{2v} ; there are four equivalent ways in which this symmetry-lowering can take place, each of which can be represented by the orientation of a vector directed towards the modulator binding site. Simple connectivity arguments enforce correlation between modulator arrangements of neighbouring SBUs,³ and hence neighbouring vectors. Alternatively, the point symmetry of linkers might be reduced in a similar fashion. Our example here is that of azopyridine—its symmetry is C_{2h} , while that of its higher-symmetry parent 4,4'-bipyridine is D_{2h} . The two equivalent conformations of the R–N=N–R bridge correspond to a d -orbital-like quadrupole and its inverse. We will come to show how framework connectivity can again enforce strong correlations between the conformations (hence quadrupolar states) of nearby linkers.

The bulk of our study is divided into three parts. First, we consider the mechanical properties of some simple homogeneously disordered (procrystalline¹⁵) frameworks. Our key result is that

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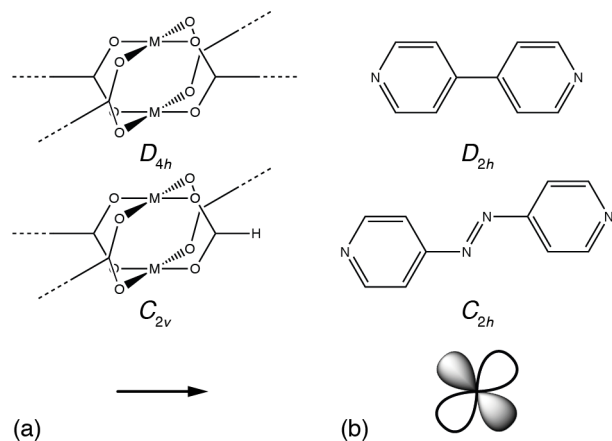


Fig. 1 Examples of local symmetry lowering of (a) node and (b) linker SBUs. In each case the high-symmetry parent is shown at the top, with the symmetry-lowered SBU below. The corresponding local degree of freedom is related to the irreducible representation associated with the symmetry lowering process. In the case of the modulated paddle-wheel (a) this degree of freedom can be considered as a vector oriented towards the monosubstituted carboxylate linker. In the case of the stepped linker (b) the relevant degree of freedom is a d_{xy} -like quadrupole oriented in the plane of the linker, the parity of which distinguishes a step ‘up’ and step ‘down’ from left to right.

the macroscopic mechanical response of these systems can be dominated by the contributions from small regions of the disordered network. Different external perturbations activate different localised motifs, to give what we term a ‘combinatorial’ mechanical response—we draw here on the language of dynamic combinatorial chemistry.^{17–19} Second, we develop a mapping between stepped columnar frameworks and two-dimensional ice models. Focusing on the specific case of square ice,²⁰ we argue that an ability to navigate the corresponding configurational landscape may allow switching between flexible and rigid framework states in response to guest adsorption/desorption. We term this functional property ‘adaptive flexibility’. And, third, we show how such mappings might be extended to establish a relationship between disordered frameworks and elements of the mathematical group \mathbb{Z}_2^n , on which a number of important error-correcting codes are based.²¹ Hence, in principle, disordered frameworks might find application in error-correcting data storage. Our paper concludes with a brief discussion of the implication of our study for future directions for the field.

2 Results and discussion

2.1 Combinatorial mechanics

Consider the hypothetical two-dimensional network structure represented in Figure 2(a). Its underlying topology is that of the square net, as realised in many paddle-wheel MOFs [Fig. 2(b)]. In the modified network, exactly one quarter of the linkers are missing—i.e. replaced by pairs of modulators—such that the node geometry is related to that illustrated in Fig. 1(a). So a physical realisation of this system might be a paddle-wheel MOF in which transition-metal dimers are linked by bridging dicarboxylates, and with one quarter of the bridging ligands substituted by monocarboxylate modulators. As such, each node is connected to

only three of its neighbours, and the positions of modulator pairs are correlated as inferred above. Despite this correlation, there is no unique way of propagating the arrangement of modulators (missing linkers), and indeed the system exhibits a macroscopic configurational entropy $S \simeq 0.29R$ related to that of domino tilings of the plane.^{15,22} As such, there is a strong thermodynamic driving force for physical realisations of this state to be disordered. Our interest is in the implications of the correlated linker vacancies on some mechanical properties of this network.

Our entry point was to determine the so-called rigid unit modes (RUMs) for the disordered network using the split-atom dynamical matrix method as implemented in the code CRUSH.^{23,24} The RUMs are those vibrational modes that propagate without significant distortion of the nodal coordination geometry. In the context of our hypothetical modulated paddle-wheel MOF, the RUMs would involve flexing of the bridging linkers without any distortion of the paddle-wheel geometry. This is known to be a low-energy deformation mode;^{25,26} hence, any such RUMs are likely to play an important role in their thermodynamic behaviour. We find a large number of RUMs and quasi-RUMs that are associated with ‘breathing’ and other distortions of the unconnected network voids [Fig. 2(c)] in addition to the single non-trivial RUM (alternating polyhedral rotations) allowed by the parent topology [Fig. 2(d)].²³ The number of (quasi-)RUMs grows quickly with system size, indicating that the flexibility of this disordered network can be understood in terms of localised degrees of freedom.

On the very simplest level, this analysis predicts an increased density of states in the low-energy phonon spectrum associated

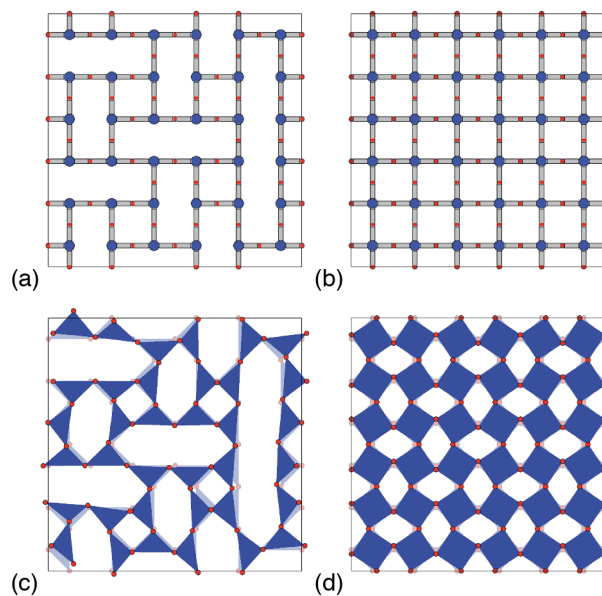


Fig. 2 (a) A homogeneously-disordered framework structure related to the square net (b), but with one linker missing at each node. Note that the nodal coordination environment corresponds to that of the modulated paddle-wheel shown in Fig. 1(a). (c) A representative (quasi-)RUM distortion for the framework shown in (a). This mode involves both polyhedral rotations and translations, and is allowed by distortions of the large cavities. (d) The only non-trivial RUM supported by the parent structure involves counter-rotation of neighbouring coordination polyhedra (e.g. paddle-wheels).

with dispersionless RUM phonon branches distributed throughout the Brillouin zone. Since each of these modes is volume-reducing (negative Grüneisen parameters), one expects an increased likelihood of negative thermal expansion (NTE) effects in the disordered framework.^{27,28} This is hardly surprising, given its reduced network connectivity. More subtle is the implication of the existence of low-energy distortion modes associated with *localised* structural motifs buried within the disordered network. Whereas the ordered parent network is mechanically uniform—by which we mean that the eigenvectors associated with its low energy distortions are distributed uniformly throughout the network—the disordered network contains regions with different mechanical responses.

We developed our understanding of this point by employing finite element models to determine how the disordered network responds to external (macroscopic) stress.²⁹ We generated a large network containing 400 nodes distributed across a 20×20 square grid, with each node connected to exactly three of its neighbours as described above. These connections were treated as beams with a finite bending stiffness. Node geometries were constrained to be rigid and periodic boundary conditions were applied. We then applied each of four uniaxial stresses, corresponding to expansion and compression along each of the two orthogonal in-plane directions. Our results are presented graphically in Figure 3. Here we colour beams according to the direction of their displacement under stress, and scale the beam thickness according to the magnitude of displacement. We make no attempt to carry out an exhaustive analysis of the corresponding distortion modes but instead note that the variation in colour and thickness throughout the configuration reflects the mechanical inhomogeneity discussed above.

Whereas most flexible frameworks exhibit a single dominant flexibility mechanism (the canonical example being the hingeing mode of wine-rack frameworks³⁰), we find that our disordered framework exploits different mechanisms when subjected to different stresses. Clearly the larger horizontal or vertical gaps in the structure play an important role (*cf* the unconventional mechanics of slit-perforated metamaterials²⁹), with their collective response mediated by the cooperative rotation of rigid square motifs. The presence of correlated disorder generates an ensemble of available mechanical responses. On application of an external stress, the system activates preferentially that subset of mechanical responses that allows greatest accommodation of the applied stress. In other words, different external perturbations amplifying a different set of mechanical motifs from amongst a library of available responses.

In this sense there is a conceptual parallel to the phenomenology of dynamic combinatorial libraries (DCLs).¹⁹ A given DCL represents an equilibrium mixture of small polymers with varying composition and structure. On exposure of the system to a ligand (*i.e.* external perturbation), the system adjusts to amplify the concentration of those polymers with optimal binding properties for that ligand; different ligands amplify different receptors. Hence we suggest the terminology ‘combinatorial mechanics’ to reflect the existence of an equivalent library of mechanical responses in homogeneously disordered network structures. From an appli-

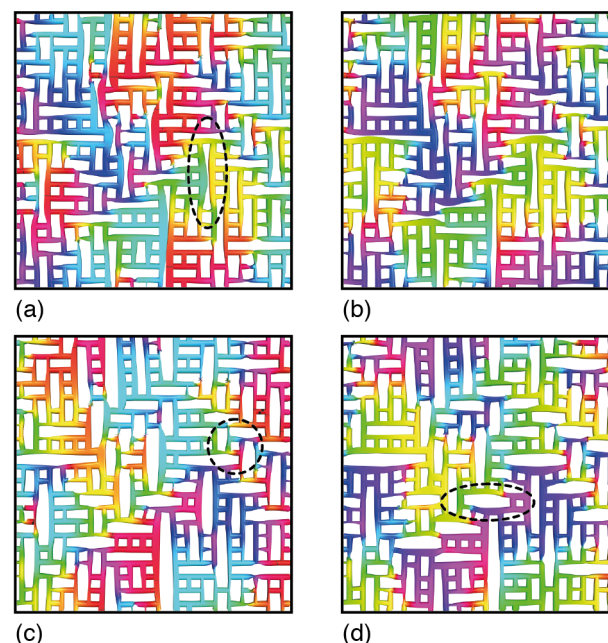


Fig. 3 Representations of framework displacements obtained using finite-element analysis calculations for an extended network of the type shown in Fig. 2(a): (a) compression along the horizontal axis, (b) compression along the vertical axis, (c) extension along the horizontal axis, and (d) extension along the vertical axis. The beams are coloured according to the displacement direction (here corrected for configuration drift), and their thickness reflects the magnitude of this displacement. Some representative distortion motifs are highlighted: vertical and horizontal pores allow accommodation of horizontal and vertical stresses, respectively. Correlated rotations of rigid square units help mediate the response.

cations perspective, we suggest this property will allow greater resistance to plastic deformation for a broad range of different stress scenarios.

2.2 Adaptive flexibility

The structures of a number of important metal–organic framework (MOF), covalent organic framework (COF), and hybrid inorganic–organic materials can be understood in terms of linked columnar or rodlike components [Fig. 4].^{31–33} Two well-known examples are the MIL-53 and DMOF families of MOFs, the structures of which are assembled from columns of either hydroxide-bridged cations or diamine-bridged ‘paddle-wheel’ clusters.^{34,35} In both cases these columnar components are linked by dicarboxylate (usually terephthalate) bridges. The canonical COF system COF-5 is also columnar, but in this case the columns are rigid stacks of hexahydroxytriphenylene (HHTP) molecules held together *via* particularly strong van der Waals forces and connected stack-to-stack by boronate ester linkages.³² Likewise the structures of a range of inorganic carboxylates—*e.g.* gallates, formates, and succinates—can also be viewed in similar terms.^{36–38} So a convenient geometric simplification of the structures of these different phases is in terms of linked periodic rods or columns. In principle there is a large number of framework topologies that can result from rod packings of this form.^{31,39} Nevertheless, em-

pirically, it seems that the canonical 2D nets—square, hexagonal, triangular, and kagome—are the most frequently observed in practice.^{31,33,40,41} We use the term ‘columnar framework’ to describe these particular 2D-net-derived systems.

Because each individual column of a columnar framework is periodic along its axis, and because the lattice on which the columns are arranged is also periodic in the two directions perpendicular to this axis, it seems natural to assume that these systems must be periodic in all three dimensions—*i.e.* they should be crystalline. Indeed this premise was exploited in Ref. 31 to enumerate rodlike MOF architectures *via* consideration of space group symmetries compatible with periodic rod packings.

However, this paradigm can break down in cases where neighbouring columns are shifted vertically with respect to one another. In a physical system, these shifts might originate as a strong constraint of the particular chemical component used to link columns—*e.g.* the naphthalenedicarboxylate bridge of DUT-8, which enforces a constant discrete displacement of neighbouring columns.⁴² Alternatively it may simply be the case that small continuous shifts are allowed by flexibility of the column–linker interaction and hence neighbouring columns may be displaced by varying amounts. This is the case for the boronate ester motif in COF-5, for example.^{32,43} Whatever the origin and particular form of these shifts, an important consideration is how they propagate in the bulk if connectivity is to be maintained.

Consider the case of a columnar framework with square channels, where the framework columns are connected by stepped linkers. On proceeding from column to column the system undergoes a vertical shift that is either positive or negative. Proceeding around the square channel, the requirement that we end up where we began implies that exactly two such shifts are positive and two are negative. We can capture this constraint formally by assigning to each linker its corresponding quadrupole

$$\mathbf{Q} \in \frac{c}{a} \left\{ \begin{bmatrix} 0 & 0 & \pm 1 \\ 0 & 0 & 0 \\ \pm 1 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \pm 1 \\ 0 & \pm 1 & 0 \end{bmatrix} \right\}, \quad (1)$$

where a, c are the lattice constants associated with the intercolumn separation and vertical repeat distance, respectively. Then

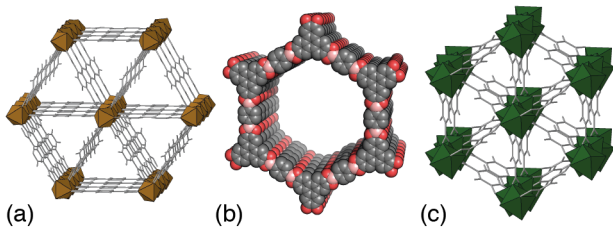


Fig. 4 Some representative columnar frameworks. (a) the MOF Iron(III) 1,4-benzenedipyrazolate⁴¹, (b) the covalent organic framework COF-5 (Ref. 32), and (c) the dense inorganic framework nickel(II) gallate.^{36,37} Each system can be considered in terms of periodic columns connected by flexible linkers.

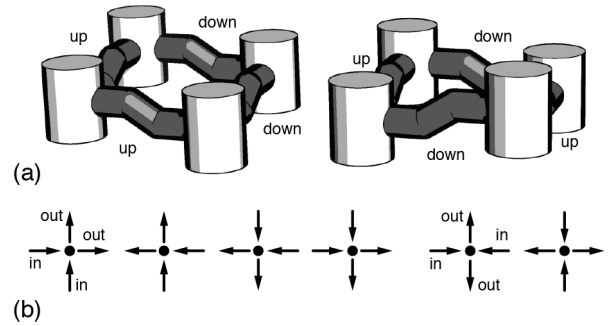


Fig. 5 In columnar frameworks with stepped linkers, the sense of each step orientation must be correlated around framework channels. (a) The two symmetry-inequivalent possibilities for square channels. The ‘up’/‘down’ senses shown here correspond to the vertical displacement direction as the channel is traversed in a clockwise sense. The requirement that the loop closes sensibly means that exactly two steps are up and two are down. Note that in the arrangement on the left, the two up steps follow one another; in the arrangement on the right, the step senses alternate. (b) The full six possibilities are shown here as pseudospin configurations. the central node (circle) corresponds to the framework channel, and the orientation of each pseudospin (in/out) maps to the corresponding linker step state (up/down).

the two-up-two-down constraint emerges from the path integral

$$\int_{\mathcal{C}} \Delta z \mathbf{Q} d\mathbf{S} = 0 \quad (2)$$

evaluated over the channel \mathcal{C} , where Δz is the magnitude of the vertical displacement associated with each step. Equation (2) has the form of Gauss’s law for a system free of topological charges (monopoles).^{*} We will return later to the point of what form these charges take for columnar frameworks and what application(s) they might have.

This analysis allows us to map the physically-accessible linker conformations onto the so-called ‘square ice’ model,^{20,44} itself originally developed to interpret the ferroelectric behaviour of potassium dihydrogen phosphate (KDP).^{45,46} Each square channel of our framework structure maps to a node of the ice model, and the two-up-two-down constraint of the former translates to the two-in-two-out rule of the latter [Fig. 5]. Once again, we note the existence of a macroscopic configurational entropy $S \simeq 0.19R$ for this system²⁰ which in turn implies that columnar frameworks with square channels and stepped linkers are thermodynamically predisposed to adopt ice-like correlated disorder. Having established this predisposition, we turn now to the question of how this type of disorder might be exploited *via* the concept of adaptive flexibility.

First, we address the issue of adaptivity. We use this term in a configurational sense; *i.e.* the viability of an appropriate columnar framework actually to sample the configurational space accessible to the square-ice model. Degenerate states in this model system are related to one another by the activation of successive ‘loop

^{*} While we present this equation in the context of stepped linkers with equal-magnitude steps, the same formalism holds for continuous shifts of arbitrary magnitude Δz .

moves',^{47,48} which in the context of columnar frameworks involve correlated inversion of the linker step orientation throughout closed cycles of the network structure. Hence adaptivity depends on the barrier height to step inversion; in the case of DUT-8 this barrier is estimated to be $ca\ 20\text{ kJ mol}^{-1}$, which is comparable in scale to the binding energies of adsorbates in many MOFs.⁴² Consequently, it is conceivable that host-guest interactions allow navigation of the square-ice configurational landscape, and these columnar frameworks might be considered adaptive.

Next, we address the issue of flexibility. The six possible linker configurations for a given channel result in one or other of two symmetry-inequivalent channel geometries [Fig. 5(a)]. *A priori* one can expect these two geometries to differ in terms of both (i) their affinity for various adsorbates, and (ii) their flexibility (*e.g.* propensity for large pore / narrow pore transitions).

Pulling these various strands together, we construct the following argument. Columnar frameworks connected by stepped linkers are inherently predisposed to adopt disordered states governed by well-understood local rules. In favourable cases, the adsorption of guest species within the framework channels may allow navigation of the corresponding configurational landscape: such systems may potentially reorganise their structure as a consequence of host/guest interactions. Pore geometries vary amongst these configurations such that the degree of framework flexibility will depend on the particular state favoured by a given adsorbate. Hence flexibility might be controlled—indeed switched on and off—by exploiting the configurational degeneracy of these disordered frameworks.

2.3 Error-correcting codes

Any system capable of adopting a number of distinguishable states can be used to store information.⁴⁹ The conventional approach is to build memory devices from non-interacting components, where information is stored in the state of each individual component. Clearly, storage capacity scales linearly with the number of components. In the various disordered frameworks we have discussed so far, the number of available states also scales linearly with system size; this is reflected in the finite (extensive) nature of the corresponding configurational entropies. Yet the configurational degrees of freedom of these systems are correlated and not independent, which we recently suggested allows for classical entanglement of the information associated with a given configuration.¹¹

Here we develop the related idea that disordered frameworks can adopt states directly related to those used in established error-correcting codes. To do this we establish a mapping between a variant of our square columnar framework model and the mathematical group \mathbb{Z}_2^n , which is the basis of a family of error-correcting codes.²¹ In order to do this, we need to define a group action on framework configurations. We emphasise from the outset that such an action is entirely fictitious—at no point will we suggest it is practical to perform the action on an physical pair of disordered frameworks. Nor will we present an algorithm for encoding information within a framework configuration. With these caveats in mind, our key result is simply that the configurational landscape

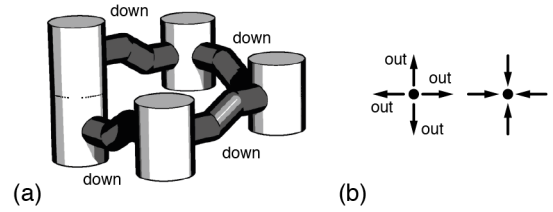


Fig. 6 (a) If the step size is exactly one quarter of the vertical repeat distance, then loop closure can involve translation by one unit cell repeat (either up or down). (b) The corresponding pseudospin configurations: all-in and all-out. In the context of the square-ice model these states are monopole charges.²⁰

accessible to a specific class of disordered frameworks is mathematically exploitable in error-correcting data storage.

Before presenting our mapping, we return to the path integral given in Eq. (2). Recall that the plain-speak implication of this integral is that, on traversing the stepped links surrounding a channel, we step up as many times as down. Consider, however, the peculiar case that each step height is exactly one quarter as large as the vertical repeat length along each column; in other words, $\Delta z = \frac{1}{4}$. In such a scenario, it is possible that each of the four links steps ‘up’ (or indeed each steps ‘down’): on traversing the links around a channel, we will have shifted vertically by exactly one unit cell [Fig. 6]. Mathematically, our possibilities are now

$$\int_{\mathcal{C}} \Delta z \mathbf{Q} d\mathbf{S} = \mathbf{0}, \pm \mathbf{c}. \quad (3)$$

Here, the two non-zero integrals correspond to topological charges of opposite parity. In the icelike mapping, these states correspond to the ‘all-in’ and ‘all-out’ pseudospin configurations. It is this very specific and peculiar system—for which there are a total of eight possible linker configurations around each square channel—that we will use in our error-correcting code mapping. Specifically, we claim that each disordered framework configuration satisfying Eq. (3) represents an element of a mathematical group, which we proceed to show is isomorphous to \mathbb{Z}_2^n .

In order to do this, we need to establish a group action, which we denote by the symbol $*$. We also identify a reference configuration e , which will come to play the role of identity in our group; the form of e is shown in Figure 7.[†] Given two configurations a, b , we form the new configuration $a * b$ as follows. For each linker in a we identify the corresponding linker in b . If these are in the same state (*e.g.* both ‘up’) then we assign to the new configuration $a * b$ the state of the corresponding linker in e . Alternatively, if the two linkers in a and b are in opposite states, then we assign to the new configuration $a * b$ the state opposite to that of the corresponding linker in e . An example of the outcome of this operation on two small configurations is shown explicitly in Figure 7, and the group action table for isolated nodes is given in Figure 8.

A number of results follow immediately from this action table. First, it is clear that the set of configurations is closed under this operation since each pair of possible column configurations

[†] Note that any configuration can play the role of identity; its choice is arbitrary.

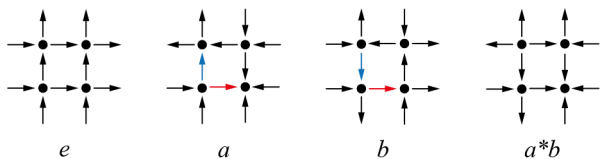


Fig. 7 A portion of the reference configuration e described in the text is shown on the left. Note that the pseudospin arrangement is identical at each node; this arrangement would extend throughout the configuration. The group action is illustrated with the arbitrary configurations a and b . At each linker (pseudospin) site, the corresponding state in the resultant configuration $a*b$ is taken from e if a and b are in the same state (e.g. red arrows), and is the opposite to that in e if a and b are in opposite states (e.g. blue arrows).

gives a valid configuration. Likewise, associativity is straightforwardly verified. The special reference configuration e satisfies $e*a = a*e = a$ for all configurations a (by design), and hence it behaves as the group identity. And, finally, we have the result that each element is its own inverse: $a*a = e$ for all a . Hence each of the four axioms of closure, associativity, identity, and invertibility hold and these disordered framework configurations form a group under the operation described. Moreover the property that each element of the group is its own inverse endows the group with the same structure as that of \mathbb{Z}_2^n (and, by analogy, to the corresponding field \mathbb{F}_2^n). Elements of \mathbb{Z}_2^n can be represented as n -digit binary codes. In our mapping, these codes would each be replaced by a single disordered framework configuration.

The error-correcting nature of \mathbb{Z}_2^n codes is such that one or more of the bits contained within a message can be erased/inverted and the original message nonetheless recovered.²¹ In the context of a disordered framework, the implication is that the information contained within a given configuration is tolerant to errors or variations in the column arrangements. This aspect of error-correction is distinct from the redundancy associated with delo-

calised information content already noted in Ref. 11.

3 Conclusions and future directions

Through these three examples we have attempted to demonstrate some ways in which the configurational degeneracy accessible to disordered framework materials might be exploited to give unconventional materials properties. In each case our analysis is as yet only very preliminary and one can envisage straightforwardly how the various strands might be developed in due course. A particular challenge will be devising synthetic strategies to realise suitable framework materials. In some cases (such as the columnar frameworks), it is possible that the disordered states we reference actually exist within already-well-known systems. Whereas there is no evidence as yet for the existence of strictly procristalline frameworks of the type described in Section 2.1, one potential opportunity is to exploit post-synthetic modification strategies to selectively remove a subset of linkers from a suitably-designed MOF.^{50,51}

The distinction between the effects of random and correlated disorder on the mechanical properties of disordered networks is an important and difficult problem. Our preliminary investigations have hinted that—for the one-quarter-missing-linker model of Fig. 2 at least—there is a meaningful difference in the Poisson’s ratios of the two cases. Experimental realisation of such networks would be particularly useful, and we note for completeness the evidence in other carboxylate MOFs for correlated disorder in modulator decorations.³ From a theory perspective, the interpretation of deformation mode eigenvectors presents its own significant challenge, shared more generally in the study of correlated phenomena in disordered media.⁵²

Our concept of exploiting configurational degeneracy in driving adaptive flexibility is conceptually related to the notion of ‘conformational mobility’ in MOFs.⁵³ Whereas the focus of Ref. 53 is on a configurational landscape with distinct local minima that allows interconversion between a small and finite number of crystalline polymorphs, the key point we are making here is that configurational degeneracy allows for switching between an arbitrarily large number of distinct disordered states, each with their own specific properties. We would argue that, in principle at least, this scenario allows for a much more adaptive system. Again, experimental realisation and validation are major challenges in this strand, but our own preliminary work in this area has led us to be optimistic regarding the likelihood of success in this regard.

Having established that disordered framework configurations offer a viable means of scalable and robust information storage, the clear challenge that remains is to determine a methodology for encoding arbitrary information in—and then re-extracting information from—such configurations. As yet, we know only that both processes are possible *in principle*. An ambitious development would be to attempt to use disordered frameworks not only as a vector for storing information, but also as a means of performing computations.

Conflicts of interest

There are no conflicts to declare.

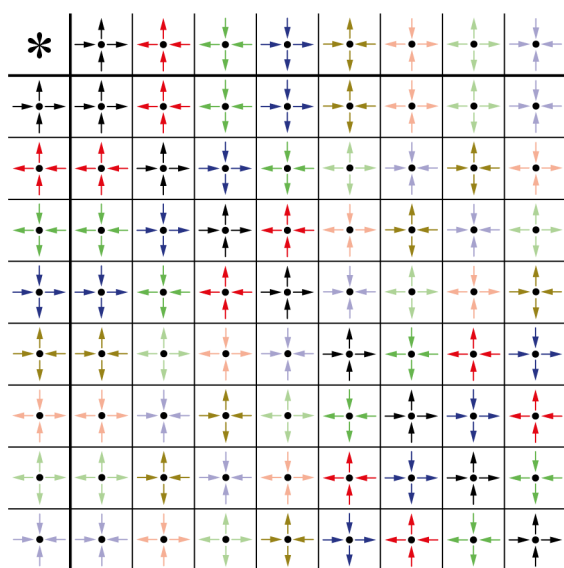


Fig. 8 The group action table for all possible node configurations. Note that the group is closed under the action and that each element is its own inverse. The black configuration behaves as the identity.

Acknowledgements

The authors gratefully acknowledge funding from the European Research Council (Grant 788144) to A.L.G., the Leverhulme Trust U.K. (Grant No. RPG-2015-292) to A.S. and A.L.G., the Royal Society to L.M. and J.N.G. and the German Research Foundation (DFG) to S. K. (Grant No. FOR2433).

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