Some exceptional linkages, their continuum limit, and isometric deformations from helicoids to ruled Möbius bands

Eliot Fried

Mechanics and Materials Unit
Okinawa Institute of Science and Technology

Contibutors: Vikash Chaurasia, Martín F. Conde, Johannes Schönke

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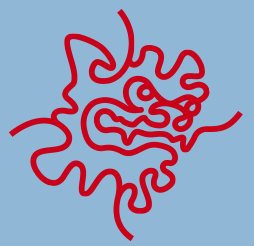

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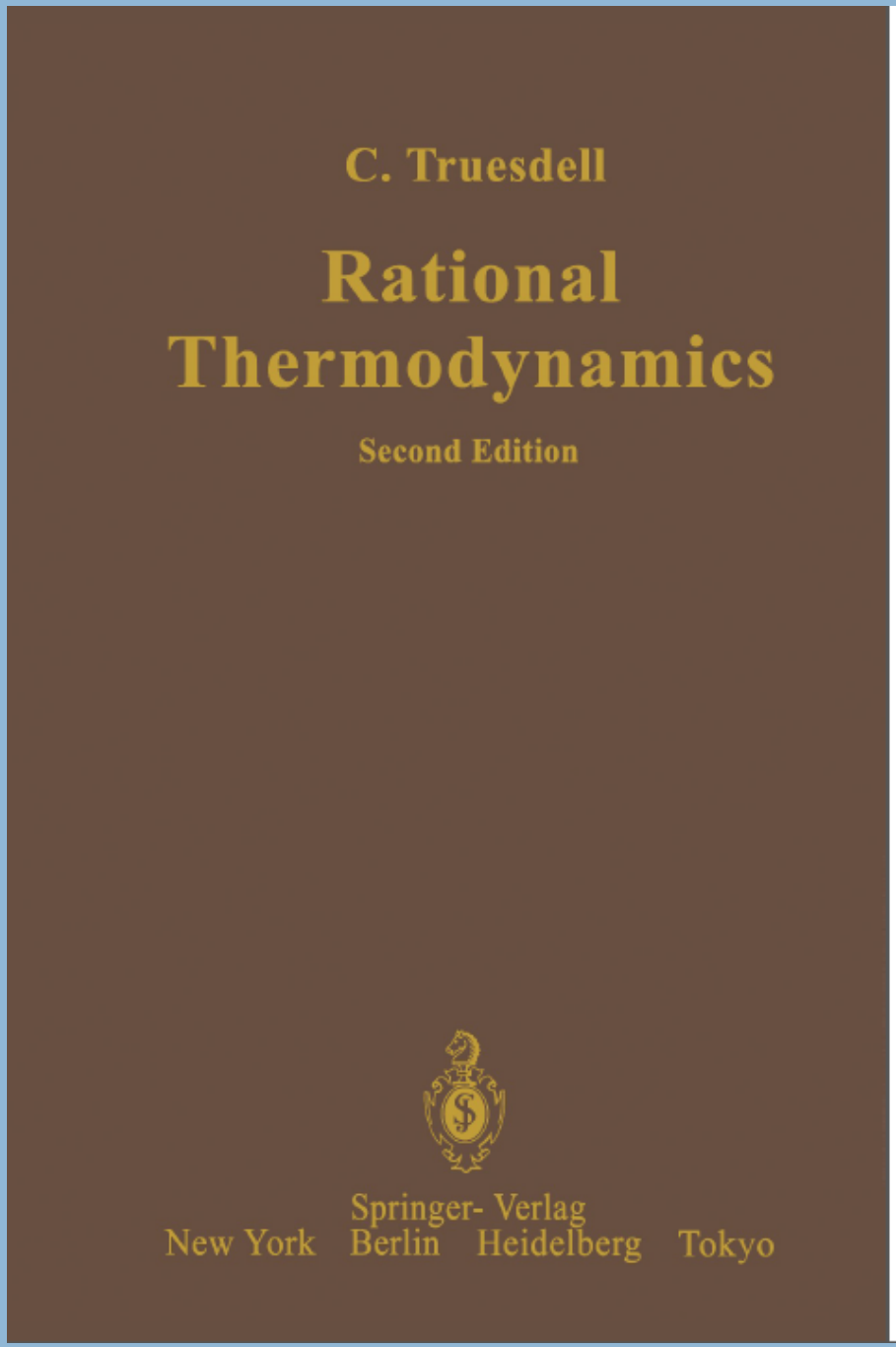

C. Truesdell

Rational Thermodynamics

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mechanics" or "material science" in its title, we find a chapter on thermodynamics, but that chapter presents a curious contrast with the same author's pages, earlier in the book, on pure mechanics. There the reader is faced by mappings, fields of vectors and tensors, Jacobians, differential invariants, perhaps even Christoffel symbols and affine connections; of course he is presumed familiar with calculus as calculus has been taught for the last fifty years. He can understand dynamical equations in tensorial form:

$$\operatorname{div} \mathbf{T} + \rho\mathbf{b} = \rho\ddot{\mathbf{x}} \qquad \text{or} \qquad T^{km}{}_{,m} + \rho b^k = \rho\ddot{x}^k. \tag{1.2}$$

He is informed, in each case, what the dependent and independent variables are, he is presented with explicit differential equations and boundary-value problems, he is shown many special solutions in concrete cases and is directed to grand tomes where he can find thousands more such solutions not given in the book he is reading, and often he is told about some major problems still unsolved and is challenged to solve them himself. The same reader of the same book then reaches the chapter on thermodynamics, where he is faced with the "axiom"

$$T\,dS \geqq \delta Q. \tag{1.3}$$

He is told that dS is a differential, but not of what variables S is a function; that δQ is a small quantity not generally a differential; he is expected to believe not only that one differential can be bigger than another, but even that a differential can be bigger than something which is not a differential. He is loaded with an arsenal of words like piston, boiler, condenser, heat bath, reservoir, ideal engine, perfect gas, quasi-static, cyclic, nearly in equilibrium, isolated, universe—words indeed familiar in everyday life, doubtless much more familiar than "tangent plane" and "gradient" and "tensor", which he learned to use accurately and fluently in the earlier chapters, but words that never find a place in the mathematical structure at all, words the poor student of science is expected to learn to hurl for the rest of his life in a rhetoric little sharper than a housewife's in the grocery store. The mathematical structure, in turn, is slight. There are no general equations to be solved, no boundary-value or initial-value problems set, no general theorems characterizing classes of solutions. The examples or exercises require no more than calculating partial derivatives or integrals of given functions or their inverses and plugging numbers into the results. The references cited lead to other books containing just the same material, perhaps otherwise explained and ordered, but no broader or clearer in concept, and equally unmathematical. No problems, in the sense that the word "problem" has in the theories of mechanics or electromagnetism or optics or heat conduction, are solved. Neither are any open problems stated. The reader must presume that thermodynamics is an exhausted as well as exhausting subject, with nothing left to be done.

As if to emphasize the difference between mechanics and thermodynamics, even the notations of calculus change from one to the other. Not only do differentials replace derivatives, but even derivatives look different, *e.g.*,

$$\frac{\delta^{\text{rev}}Q}{dV} = T\left(\frac{\partial S}{\partial V}\right)_p, \tag{1.4}$$

The difference is not merely formal (note the three different ds). It represents a difference of logic. In some books the chapter on thermodynamics contains a laborious geometrical explanation of the partial derivative, although partial derivatives required not even a definition to justify their abundance in the earlier chapters on mechanics. In paraphrasing his old thermodynamics text, after having paraphrased sections from perhaps still older treatises on continuum mechanics, our interdisciplinary compiler-author has forgotten that thermodynamics books are written for a different class of readers, and he reproduces vague, descriptive, and unmathematical wordplay which he himself would not for a moment tolerate in his own chapter on elasticity.

The difference is that thermodynamics never grew up. While aspects of mechanics were developed, applied, generalized, and recast by nearly every distinguished mathematician from ARCHIMEDES to G. D. BIRKHOFF, the unfortunate who reads about thermodynamics even today is made to follow KELVIN's preference for differentials, which KELVIN himself maintained in mechanics as well but hydrodynamicists and elasticians have long since abandoned, and to suffer over again the insecurity CLAUSIUS seems to have felt whenever he used calculus. For example, our poor reader is expected to believe that something different can come out of a line integral if the line is approximated by infinitesimal adiabats and isotherms, in defiance of the fundamental theorem of integral calculus.

In this lecture I will show you that classical thermodynamics can be stated precisely and learned, just as classical mechanics is stated precisely and learned. There are problems to be solved in thermodynamics. We can state these problems, and we can solve them in important special cases; more general ones remain to be studied. The range of intended application of classical thermodynamics is to homogeneous systems, namely, bodies that can be described sufficiently by functions of time only. A standard example is furnished by a mixture of fluids in a beaker sufficiently stirred that there are no differences of temperature, concentrations, or other parameters from point to point at any given time. Opening at random a recent and widely used book[1] on physical chemistry, I found an elegant diagram of just such a beaker, called a "stirred flow reactor", which is sketched in Figure 1. According to the author, "the reactants

[1] Since the example is selected as being typical, not for criticism of any particular author, I do not cite the book quoted.

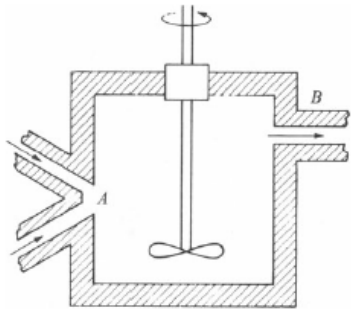

Figure 1. Stirred flow reactor.

enter the vessel at A, and stirring at 3,000 rpm effects mixing within about a second." He tells us that the product mixture is removed at B at a rate exactly balancing the feed, and that after a steady state is attained, the composition of the mixture in the reactor remains unchanged as long as the composition and rate of supply of reactants are unchanged. The numerical values, irrespective of the size of the vessel and of what be the reactants, seem intended to help us keep our feet firmly on the ground of empirical science. I cannot help wishing to see some of my classically thermodynamic friends try the experiment with asphalt as one ingredient and nitroglycerin as the other. Were some mathematician to dream up this apparatus, his colleagues in the natural sciences would rise with condescending smiles or scathing comments on persons who live in the clouds, but in fact it seems to furnish the standard way to connect classical thermodynamics with the world of experience, although, of course, conditions need not be steady in the theory we shall consider now. This theory describes the same situations, though possibly unsteady, as those for which classical thermodynamics is intended. If the one is applicable, so is the other. All quantities I shall write down will be functions of time, not varying in space, and a dot will denote the time derivative.

I shall draw parallels to classical mechanics. In this instance, "classical mechanics" will mean the Newtonian mechanics of finite systems of mass-points, called "bodies".

Any branch of mathematical physics is constructed in terms of:

1. A list of *primitive quantities*, not defined except by mathematical properties laid down for them.
2. *Definitions* of other quantities in terms of the primitives.
3. *General axioms* stated as mathematical relations satisfied by the primitives and the defined quantities.

4. Proved *theorems* referring to:
   a. The theory as a whole, or
   b. Mathematically defined special cases.

The axioms are regarded as *general principles* or *physical laws*: They refer to all systems covered by the theory. Particular systems may be selected and studied at random, but it is more useful to specify them by *constitutive relations* intended to represent important classes of systems. The entire class of constitutive relations is delimited by *constitutive axioms*, which are concrete, mathematical statements in terms of the variables entering the general axioms. The general principles express properties *common* to all systems, while the constitutive relations formalize *diversities* among the systems allowed by the general principles. It should be unnecessary to remark that the choice of primitives, definitions, and axioms is not unique, and that any given theory may be constructed in infinitely many different but equivalent ways. (This fact, however, should not be taken as a license, as often it is, especially in thermodynamics, to present a physical theory in a merely suggestive form, with no mathematical structure at all.)

Table 1 contains a possible list of primitives, axioms, and constitutive equations for classical mechanics and classical thermodynamics. The table merely describes the two theories, not pretending to supply a formal axiomatic development of either.

I will now explain the entries. The "classical mechanics" described here is a fairly special one; easily it could be generalized so as to include variable masses, frictional forces, and multiple interactions, but I have kept it special so that every line will be understood without question by anyone who has studied mechanics in any standard book. The system of thermodynamics outlined, on the other hand, is more general than the usual ones for homogeneous processes, and in form it will surely be unfamiliar. This lecture is devoted to presenting it, though not in the order of the entries. To the few mathematical supplements necessary, I will adjoin simple explanations such as are given in a beginning course in mechanics so as to help the student relate the symbols to everyday experience. At the same time, I will recast the mathematical structure into a more elaborate but more familiar one by introducing appropriate definitions and proving some easy theorems.

Classical thermodynamics refers to only one whole body $\mathscr{B}$, not an infinite system of subbodies, so we need not write the argument $\mathscr{B}$ any more. At each time, the body is assigned a real number called the *temperature*. This number is a measure of how hot the body is. Instruments for measuring it are called "thermometers" or "thermocouples". Experiments show that whatever such instrument be used, there is a temperature below which no body can be cooled. This least possible temperature depends on the thermometer used but not on the bodies whose temperature it mea-

1. Background
   - Nonorientable hydrocarbon rings: *Möbius annulenes*
   - Underconstrained nonorientable linkages: *Möbius kaleidocycles*
2. Isometric deformations from circular helicoids to Möbius bands
3. Isoenergetic and isometric everting motions of Möbius bands
4. Generalization of the Möbius kaleidocycles
5. Summary
6. Outlook

Nonorientable hydrocarbon rings

Tetrahedron Letters No.29, pp. 1923–1928, 1964. Pergamon Press Ltd.
Printed in Great Britain.

HÜCKEL MOLECULAR ORBITALS OF MÖBIUS-TYPE CONFORMATIONS OF ANNULENES

E.Heilbronner
Laboratorium für organische Chemie der Eidg. Technischen Hochschule, Zürich
(Received 1 June 1964)

The different conformations of a π-electron system can be specified by listing the twist angles $\omega_{\mu\nu}$ between all pairs of bonded atomic orbitals (AOs) ϕ_μ, ϕ_ν. The resonance integral $\beta_{\mu\nu}$ of a twisted π-bond is given by (1)

$$\beta_{\mu\nu} = \beta \cos \omega_{\mu\nu}$$

β being the standard resonance integral for a pair of parallel AOs. It is usually assumed that the total π-electron energy has an absolute maximum for the coplanar system (all $\omega_{\mu\nu} = 0$ or π). Any conformation with one or more angles $\omega_{\mu\nu}$ different from zero or π would then have a smaller π-electron energy, assuming that the interatomic distances between pairs of bonded AOs remain constant. We shall show that, according to Hückel molecular orbital (HMO) theory this may not necessarily be so.

The higher members of the annulenes $(CH)_n$ (2) are presumably present in solution in a variety of non-planar conformations. Among these conformations, there are some where the π-orbital is twisted into a möbius strip. Such conformations can be obtained with standard molecular models (Dreiding or Stuart - Briegleb) without introducing any apparent bond angle or steric repulsion strain when $n > \sim 20$. The topological equivalent of such a Möbius type conformation is shown in fig. 1.

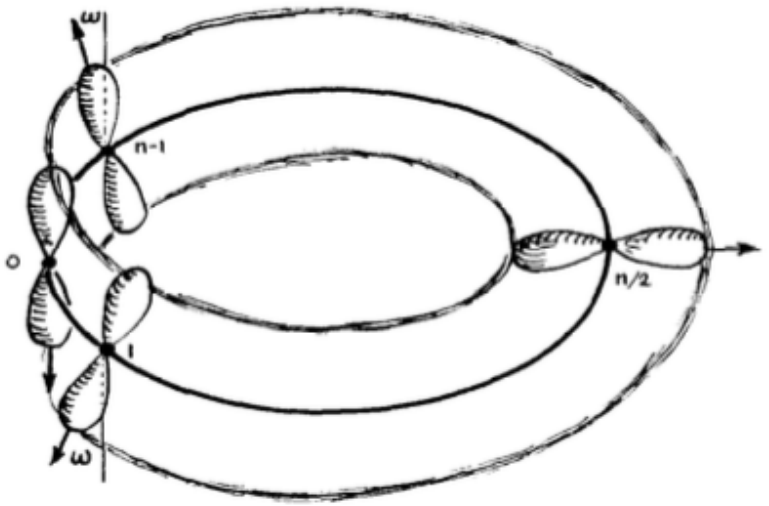

Figure 1

Triply twisted Möbius annulene

ARTICLES
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nature chemistry

Design and synthesis of the first triply twisted Möbius annulene

Gaston R. Schaller[1], Filip Topić[2], Kari Rissanen[2]*, Yoshio Okamoto[3], Jun Shen[4] and Rainer Herges[1]*

As long as 50 years ago theoretical calculations predicted that Möbius annulenes with only one π surface and one edge would exhibit peculiar electronic properties and violate the Hückel rules. Numerous synthetic attempts notwithstanding, the first singly twisted Möbius annulene was not prepared until 2003. Here we present a general, rational strategy to synthesize triply or even more highly twisted cyclic π systems. We apply this strategy to the preparation of a triply twisted [24]dehydroannulene, the structure of which was confirmed by X-ray analysis. Our strategy is based on the topological transformation of 'twist' into 'writhe'. The advantage is twofold: the product exhibits a lower degree of strain and precursors can be designed that inherently include the writhe, which, after cyclization, ends up in the Möbius product. With our strategy, triply twisted systems are easier to prepare than their singly twisted counterparts.

Most objects in our everyday lives exhibit two sides: in and out, or front and back. Möbius bands are exceptions. Any band with an odd number of twists has one side and one edge. Ribbons with an even number of twists (including zero) exhibit two sides. Unfortunately, sidedness is not an intrinsic topological parameter because its definition requires the object to be embedded in a surrounding space. Orientability is an intrinsic property, and therefore is used frequently to describe the topology of objects[1–3]. An object is said to be non-orientable if a chiral shape drawn onto the surface can be transformed into its mirror image simply by moving it over the surface. This seems trivial, but, for instance, the Fisher formula of D-lactic acid drawn onto a Möbius band is transformed into the structure of L-lactic acid by shifting it once around the ribbon. If our universe were non-orientable it would be possible to convert D-lactic into L-lactic acid by simply moving a sample around in space (see Supplementary Fig. 1). Other examples of non-orientable objects are the Klein bottle, Boy's surface, the Roman surface and the Crosscap (see Supplementary Fig. 2). The peculiar properties of non-orientable surfaces have attracted and inspired mathematicians, as well as artists, musicians and authors. Interest in chemistry started in 1964 when Edgar Heilbronner predicted that Möbius annulenes, being aromatic with $4n$ electrons, would violate the Hückel rules[4]. The 180° twist induces strain in the π system and reduces π overlap. Heilbronner concluded that therefore only [n]annulenes with a ring size larger than $n = 20$ would be stable. This forethought was confirmed recently by theoretical calculations[5–10]. Using a systematic generation procedure, and by subsequent energy calculations of several hundred thousand [n]annulene isomers of ring sizes $n = 8$–24, we can prove that there are numerous Möbius annulenes (about 50% of all structures); however, there is no Möbius global minimum among the uncharged [n]annulenes[11–14]. Obviously, the energy gain through Möbius aromaticity is overcompensated by the strain imposed by the twist. Unfortunately, the numerous higher-energy local-minimum structures are kinetically unstable. They would immediately 'untwist' and release strain energy, even at low temperatures, to form the more stable Hückel structures. The first Möbius annulene synthesis, therefore, used a strategy to stabilize the strained part of the Möbius ring by a suitable molecular framework[15–17]. Meanwhile, a number of Möbius-extended porphyrins have been synthesized that have a stability similarly enhanced by steric constraints[18–21].

Results and discussion

Topological design. Given the tremendous problems in synthesizing singly twisted Möbius systems, triply twisted annulenes seem to be rather out of reach. On realistic inspection, strain and reduced π overlap loom. Moreover, a simple synthetic analysis adds further implications to the heap of obstacles. From a naive point of view one could propose a cyclotrimerization of three singly twisted precursors or, alternatively, the cyclization of a triply twisted starting structure (Fig. 1a). However, as soon as one leaves this rather low level of abstraction, and dares to translate the rather simple-minded picture into real chemistry, one gradually realizes that the situation is fairly hopeless. How to stabilize a 180°, or even a 540°, twist in a linear π system—by substitution or a molecular rack? Even if one could do so, a simple cardboard model reveals that a twisted band would never bend. Hence, the ends of the bands would not find each other for cyclization. Anyhow, putting aside all the above concerns, if the target structure (against all odds) could form, it would be tremendously strained.

In this quandary, hope comes from topology. It is an everyday-life experience (telephone cord, garden hose) that twisted bands wind around themselves to release strain. Topologists call this phenomenon the projection of 'twist' into 'writhe' (Fig. 1b).

Whereas a twist (T_w) is straightforward to define (it is just the sum of the dihedral angles of the vectors normal to the π plane)[22,23], the topological parameter 'writhe' (W_r) is less obvious, at least in its precise mathematical definition. Writhe is defined as the double Gaussian integral over a closed curve C in three-dimensional (3D) Euclidean space $\mathbf{R}^3$ (ref. 24):

$$W_r = \frac{1}{4\pi}\int_C\int \frac{(\mathrm{d}\mathbf{r}_2 \times \mathrm{d}\mathbf{r}_1)\cdot \mathbf{r}_{12}}{|\mathbf{r}_{12}|^3}$$

$\mathbf{r}_1$, $\mathbf{r}_2$: points passing along C. $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$.

[1]Institute for Organic Chemistry, University of Kiel, Otto-Hahn Platz 4, 24098 Kiel, Germany, [2]Department of Chemistry, Nanoscience Center, University of Jyväskylä, PO Box 35, 40014 Jyväskylä, Finland, [3]Nagoya University, 1E Miyahigashi-cho, Showa-ku, Nagoya 466-0804, Japan, [4]College of Materials Science and Chemical Engineering, Harbin Engineering University, 145 Nantong Street, Harbin 150001, China. *e-mail: rherges@oc.uni-kiel.de; kari.t.rissanen@jyu.fi

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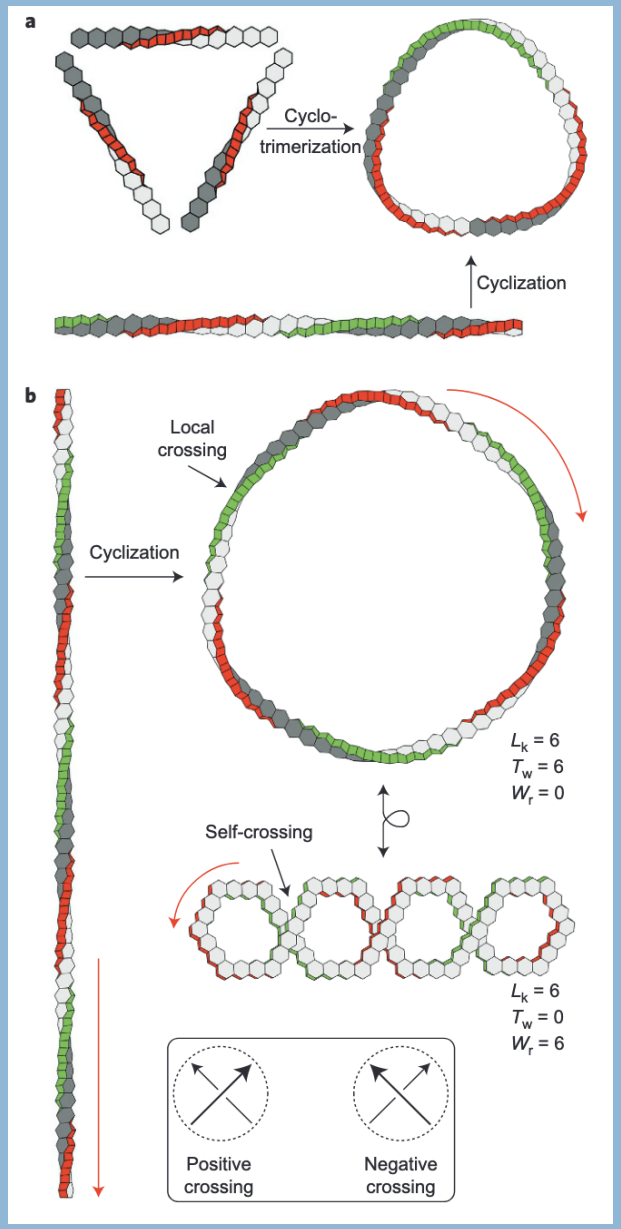

Underconstrained nonorientable linkages

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Single degree of freedom everting ring linkages with nonorientable topology

Johannes Schönke[a,1] and Eliot Fried[a,1]

[a]Mathematics, Mechanics, and Materials Unit, Okinawa Institute of Science and Technology Graduate University, Onna, Okinawa 904-0495, Japan

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Linkages are assemblies of rigid bodies connected through joints. They serve as the basis for force- and movement-managing devices ranging from ordinary pliers to high-precision robotic arms. Aside from planar mechanisms, like the well-known four-bar linkage, only a few linkages with a single internal degree of freedom—meaning that they can change shape in only one way and may thus be easily controlled—have been known to date. Here, we present "Möbius kaleidocycles," a previously undiscovered class of single-internal degree of freedom ring linkages containing nontrivial examples of spatially underconstrained mechanisms. A Möbius kaleidocycle is made from seven or more identical links joined by revolute hinges. These links dictate a specific twist angle between neighboring hinges, and the hinge orientations induce a nonorientable topology equivalent to the topology of a 3π-twist Möbius band. Apart from having many technological applications, including perhaps the design of organic ring molecules with peculiar electronic properties, Möbius kaleidocycles raise fundamental questions about geometry, topology, and the limitations of mobility for closed loop linkages.

spatial linkages | single degree of freedom | deployable structures | topology | nonorientability

Linkages have been known since antiquity (1, 2). They can be found in nature, as in the powerful jaw mechanism of the parrotfish and the mammalian knee joint (3), in the vertebrate skull (4), in the raptorial appendages of the mantis shrimp (5), and in countless gadgets and machines (6). The latter range from simple manual tools (like bolt cutters) to deployable structures (like umbrellas, foldable camping gear, solar panels for spacecraft, and portable architecture) to intricate components of robots and prosthetic devices.

Designers of deployable structures have considerable interest in adopting notions derived from rigid origami as described, for example, by You (7) or Chen et al. (8). This design principle takes advantage of the folding and unfolding of structures made from flat rigid bodies connected by revolute hinges as exemplified by the famous folding of Miura (9). The resulting constructions belong to the general class of mechanisms made from rigid bodies connected by joints. You and Chen (10) note that all such mechanisms, which they call "motion structures," combine a small set of fundamental building blocks: scissor-like elements, the Sarrus linkage, the Bennett linkage, and the Bricard linkage. Each of these linkages has one degree of freedom and except for the first, is overconstrained in the sense that it can move, although a simple mobility analysis dictates otherwise.

We present a class of ring linkages (also known as closed loop kinematic chains) that are fundamentally different from all previously known types. These linkages can have an unlimited number (greater than or equal to seven) of identical rigid bodies joined by hinges but still have only a single degree of freedom; an example is shown in Fig. 1. Except for the one with seven hinges, each of these objects is underconstrained, meaning that it has fewer degrees of freedom than a simple mobility analysis would suggest. Since they are rings and share the topology of a 3π-twist Möbius band, these linkages can be called "Möbius kaleidocycles." They may serve as building blocks of deployable structures and other machines, but beyond that, they have fascinating properties that raise many questions in mechanical engineering, physics, chemistry, and mathematics. Below, we describe the construction of Möbius kaleidocycles, discuss their distinct features, and sketch potential applications.

Classical and Möbius Kaleidocycles

Classical Kaleidocycles. A classical six-hinged kaleidocycle (K6) is a closed ring of six identical tetrahedra, the opposing edges of which serve as hinges. This object can be identified as the trihedral version of a general linkage invented by Bricard (11) in 1927, which is a closed loop kinematic chain consisting of six links connected by revolute hinges (and is known as a "6R Bricard linkage"). Fig. 2, *Upper* shows a paper model of a conventional K6 and a 3D printed realization of a 6R Bricard linkage that is kinematically equivalent to the paper model. A K6 possesses a single internal degree of freedom manifested by a cyclic everting motion, during which different tetrahedral faces are periodically exposed while a threefold rotational symmetry is preserved. In applications, the single degree of freedom affords controllability and is, therefore, a desirable property. Detailed kinematic analyses of a K6 are in, for example, Arponen et al. (12) and Fowler and Guest (13).

A classical eight-hinged kaleidocycle is made like six-hinged ones but with eight tetrahedra. This object is nevertheless markedly different from its six-hinged counterpart. It has two internal degrees of freedom; in any configuration, it can move in at least two independent directions as shown in Fig. 2, *Lower*.

Significance

Linkages are the basic functional elements of any machine. Known established linkages with a single degree of freedom, which facilitates control, have so far consisted of six or fewer links. We introduce "Möbius kaleidocycles," a class of single-degree of freedom ring linkages containing nontrivial linkages having less mobility than expected. Möbius kaleidocycles consist of arbitrarily many (but at least seven) identical hinge-joined links and may serve as building blocks in deployable structures, robotics, or chemistry. These linkages are chiral and have a nonorientable topology equivalent to 3π-twist Möbius bands. Other than technological promise, Möbius kaleidocycles pose a myriad of intriguing questions in mechanical engineering, physics, and various areas of mathematics, especially topology.

Author contributions: J.S. and E.F. designed research, performed research, and wrote the paper.

The authors declare no conflict of interest.

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[1]To whom correspondence may be addressed. Email: johannes.schoenke@oist.jp or eliot.fried@oist.jp.

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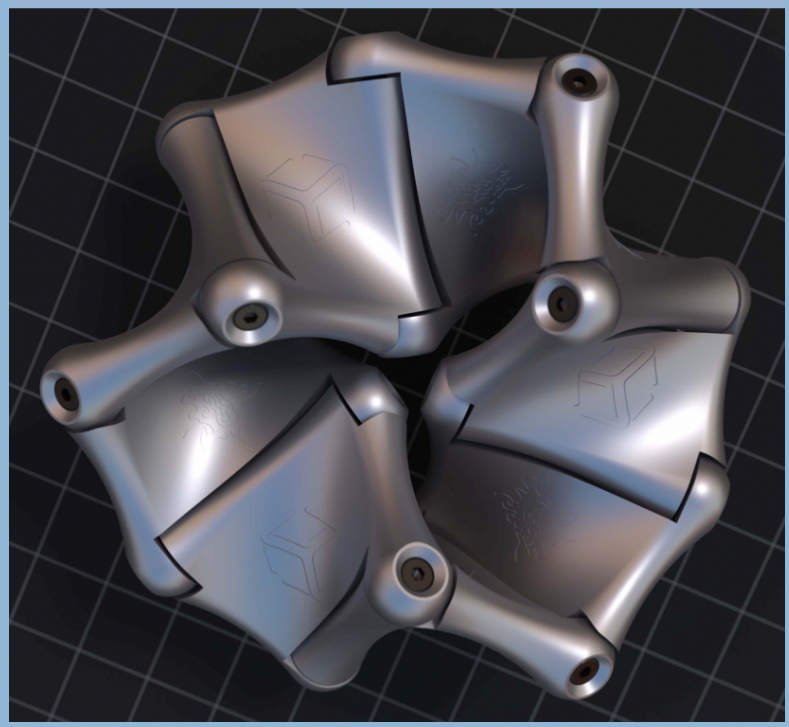
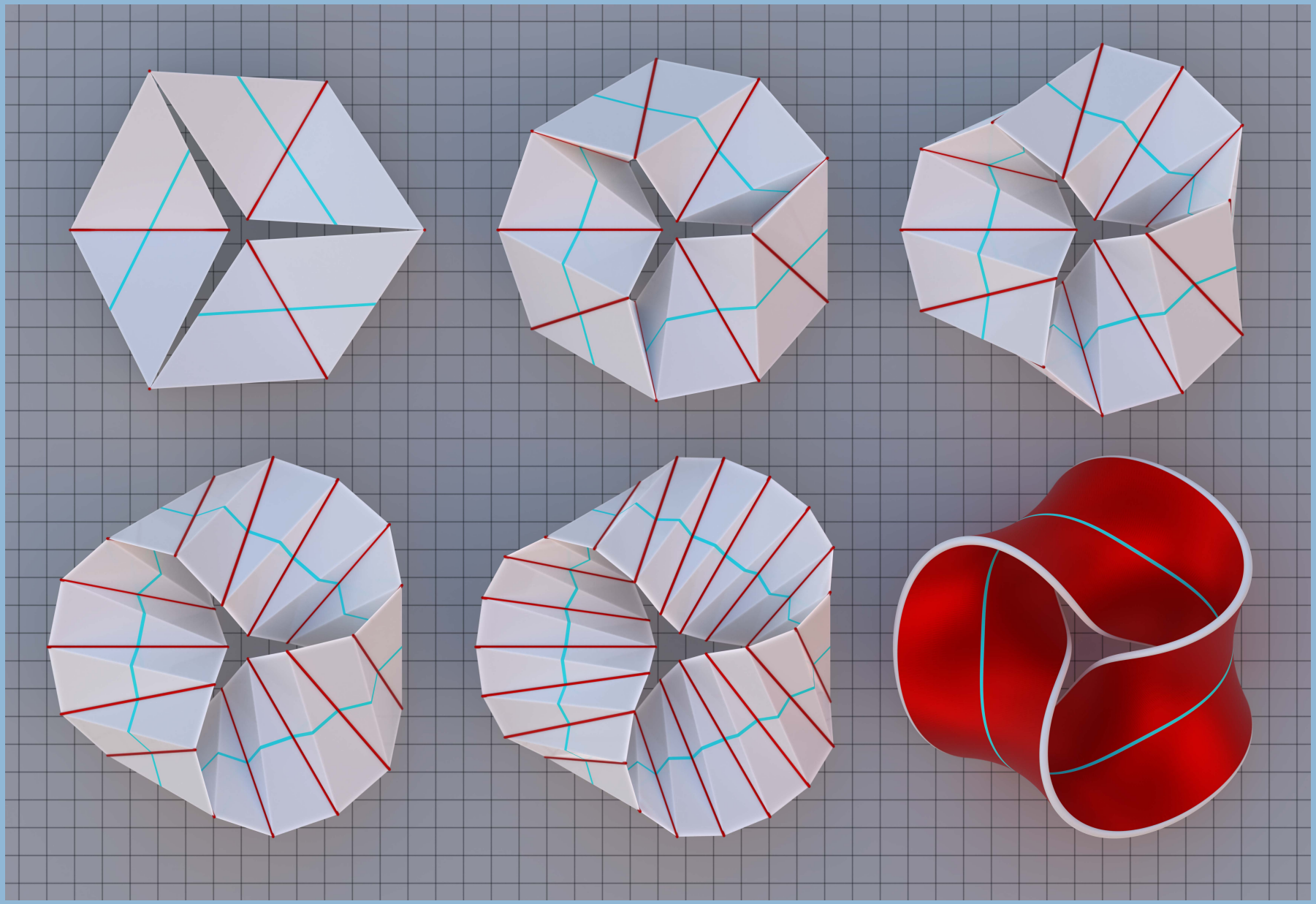


Critical twist angle

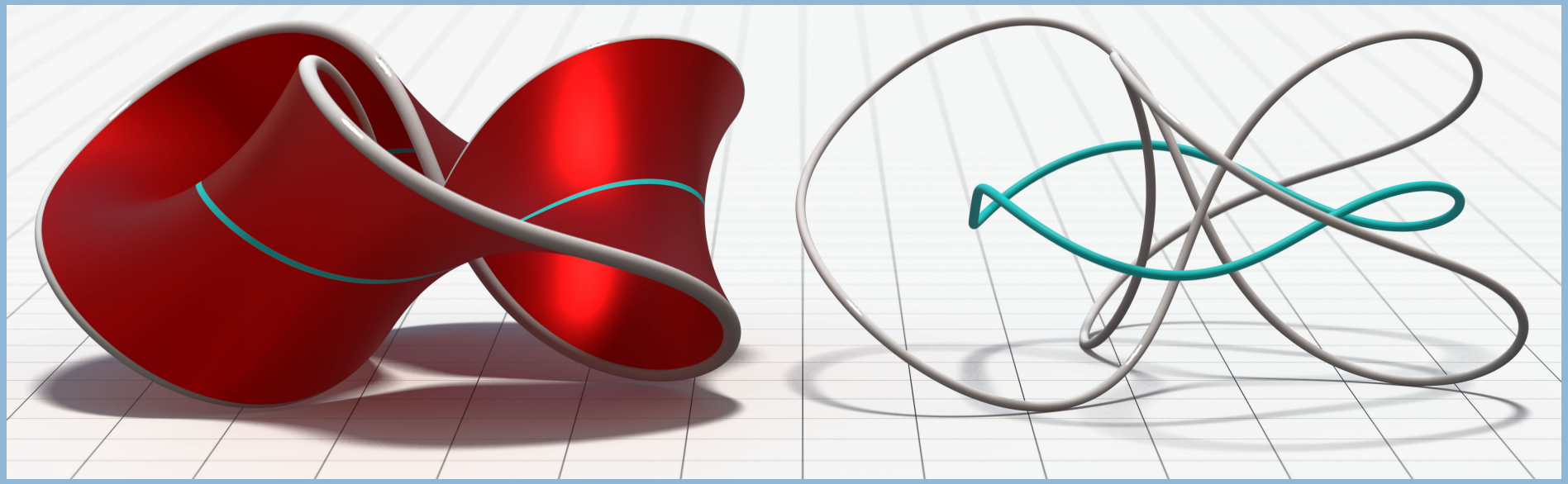
- A chain of $N \geq 7$ identical twisted connected by revolute hinges can be closed into a nonorientable linkage only if the twist angle $\theta \in (0, \pi/2]$ of the links obeys $\theta \geq \theta_c(N) > 0$.
- Each linkage so obtained is topologically equivalent to a Möbius band with three half twists.
- For $\theta = \theta_c(N)$, closing the chain generates $N - 7$ self stresses, leaving only one of the $N - 6$ internal degrees of freedom expected from the Chebyshev–Grübler–Kutzbach mobility criterion.
- For $N \geq 8$, the linkage with $\theta = \theta_c(N)$ thus has "exceptional" mobility.
- For $\theta = \theta_c(N)$, an everting motion afforded by the surviving internal degree of freedom.

Click here for visualization.

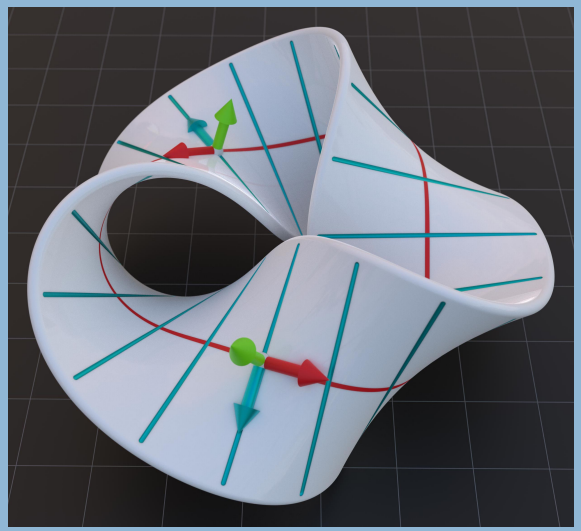
Limit surface



Properties of the limit surface



- Surface is a ruled Möbius band with three half twists and three-fold rotational symmetry.
- Midline is a geodesic and has uniform torsion.
- Rulings are parallel to the unit binormal of the midline.
- Edge is a trefoil knot.



Truesdell's on kinematics

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special cases of certain purely kinematical theorems valid for arbitrary media. Let no one contend, however, that I have merely derived the old results in a new way. Rather, circulation-preserving motions afford but the simplest and most elegant applications of some parts of the general theory, a theory constructed in the hope that it will prove useful in understanding the behavior of complicated media whose dynamical response is more elaborate than that represented by the classical laws of viscosity. All dynamical statements I have relegated to parenthetical sections, appendices, or footnotes, not in a foolish attempt to diminish their physical importance, but rather to let the argument course freely, uninterrupted by merely interpretative remarks, and to leave the propositions free for application to such special dynamical situations as may be of interest either now or in the future—for I cannot too strongly urge that a kinematical result is a result valid forever, no matter how time and fashion may change the "laws" of physics.

Questions

- *Can the limit surface of the Möbius kaleidocycles be obtained by subjecting a circular helicoid to an isometric, chirality preserving deformation and, if so, is that deformation stable?*

- *Do circular helicoids admit isometric, chirality preserving deformations to stable Möbius bands with more than three half twists and/or knots?*

Kinematics

- Parametrization $\hat{\boldsymbol{x}}$ of a helicoid $\mathcal{H}$ of pitch $p \neq 0$, axis $\mathcal{A}$ of length ℓ, and radius a:

$$\hat{\boldsymbol{x}}(s,v) = s\boldsymbol{e}_1 + v\left(\cos\frac{2\pi s}{p}\boldsymbol{e}_2 + \sin\frac{2\pi s}{p}\boldsymbol{e}_3\right),$$

$$\boldsymbol{e}_i \cdot \boldsymbol{e}_j = \delta_{ij},$$
$$\boldsymbol{e}_i \times \boldsymbol{e}_j = \epsilon_{ijk}\boldsymbol{e}_k.$$

- Parametrization $\hat{\boldsymbol{y}}$ of a ruled Möbius band $\mathcal{B}$:

$$\hat{\boldsymbol{y}}(s,v) = \boldsymbol{d}(s) + v\boldsymbol{g}(s),$$

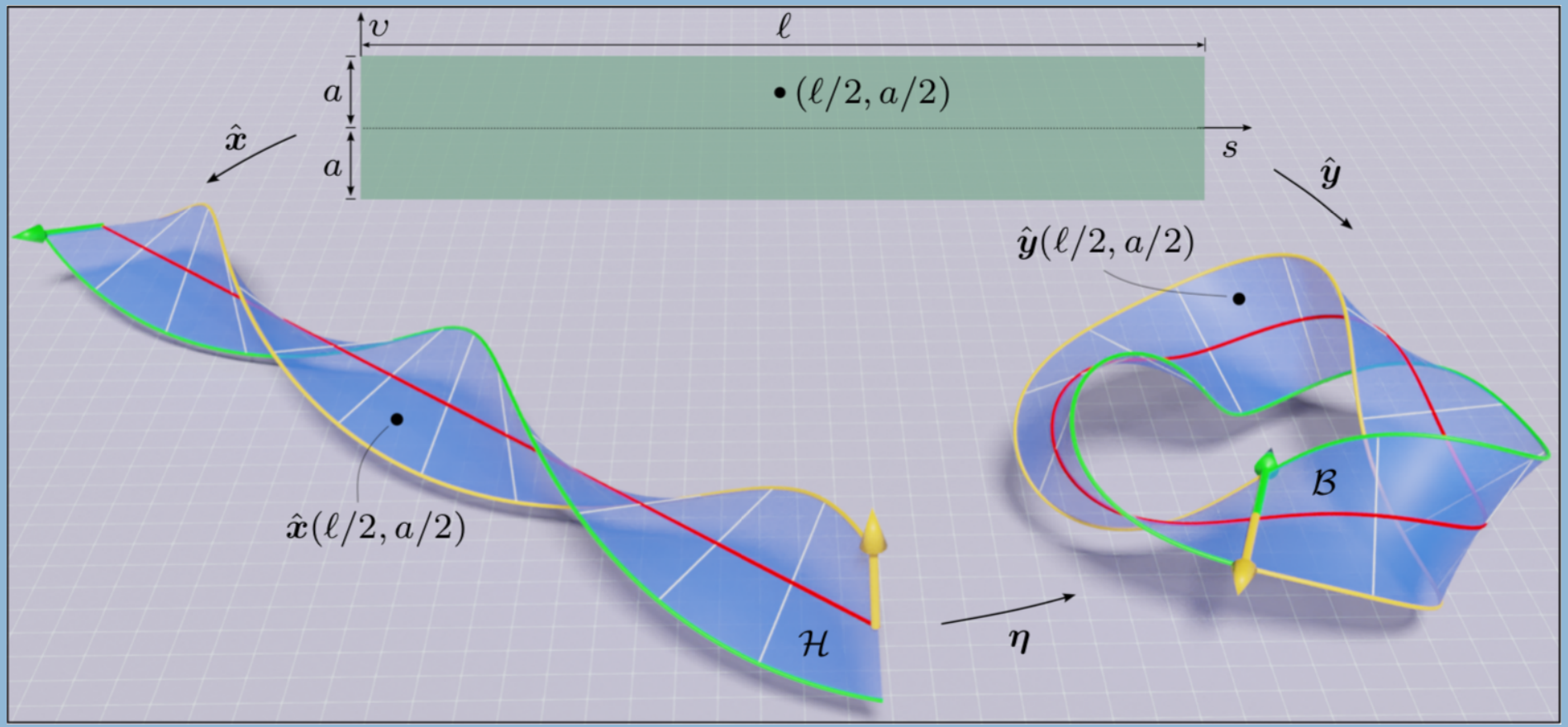
$$|\dot{\boldsymbol{d}}| = 1, \qquad |\boldsymbol{g}| = 1,$$

$$\boldsymbol{d}(0) = \boldsymbol{d}(\ell), \qquad \dot{\boldsymbol{d}}(0) = \dot{\boldsymbol{d}}(\ell), \qquad \ddot{\boldsymbol{d}}(0) = \ddot{\boldsymbol{d}}(\ell), \qquad \dddot{\boldsymbol{d}}(0) = \dddot{\boldsymbol{d}}(\ell),$$

$$\boldsymbol{g}(0) = -\boldsymbol{g}(\ell).$$

- Deformation $\boldsymbol{\eta}$ from $\mathcal{H}$ to $\mathcal{B}$:

$$\hat{\boldsymbol{y}}(s,v) = \boldsymbol{\eta}(\hat{\boldsymbol{x}}(s,v)), \qquad 0 \le s \le \ell, \quad |v| \le a.$$



Results of requiring that $\boldsymbol{\eta}$ be isometric

- The midline $\mathcal{C}$ of $\mathcal{B}$ must be a geodesic of $\mathcal{B}$.

- The torsion τ of $\mathcal{C}$ must be constant and is given by the pitch p of $\mathcal{H}$ through

$$\boxed{\tau = \frac{2\pi}{p}.}$$

- The rulings of $\mathcal{B}$ must be parallel to the unit binormal $\boldsymbol{b}$ of $\mathcal{C}$.

- Up to a rigid transformation, the parametrization $\hat{\boldsymbol{y}}$ of $\mathcal{B}$ is completely determined by $\boldsymbol{b}$:

$$\boxed{\hat{\boldsymbol{y}}(s,v) = \frac{p}{2\pi}\int_0^s \boldsymbol{b}(\zeta)\times\dot{\boldsymbol{b}}(\zeta)\,\mathrm{d}\zeta + v\boldsymbol{b}(s),} \qquad 0 \le s \le \ell, \quad |v| \le a.$$

Enter kinetics: Bending energy

- Suppose that each $\mathcal{H}$ is homogeneous, isotropic, and elastic.
- Since $\boldsymbol{\eta}$ is isometric, the energy ψ, per unit area, stored in bending $\mathcal{H}$ to $\mathcal{B}$ depends at most on the mean curvature H of $\mathcal{B}$.
- If ψ is quadratic in H, then, since $\mathcal{H}$ is minimal,

$$\boxed{\psi = 2\mu H^2,} \qquad \mu > 0.$$

- For the above choice of ψ, the total bending energy E of $\mathcal{B}$ has the dimensionally reduced form

$$\boxed{E = \frac{\alpha \ell^3}{8\pi^2\nu^2}\int_0^\ell |\ddot{\boldsymbol{b}}|^2 \,\mathrm{d}s - 2\alpha\pi^2\nu^2,}$$

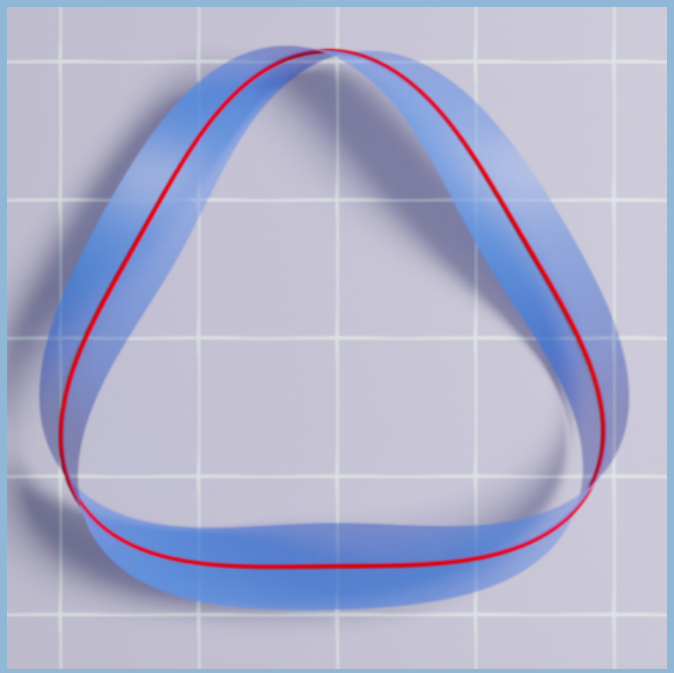
$$\alpha = \frac{\mu p}{\pi \ell}\,\mathrm{arcsinh}\,\frac{2\pi a}{p}, \qquad \nu = \frac{\ell}{|p|}.$$

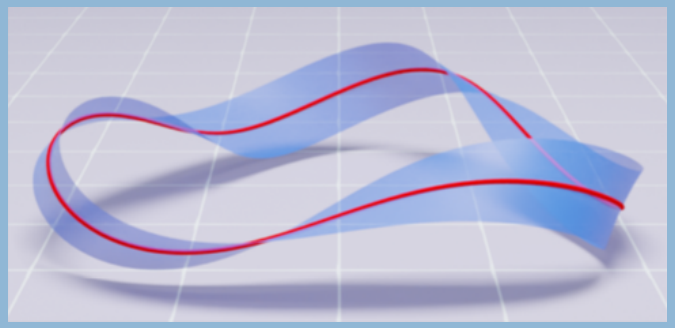
- Minimize $F = E/\alpha$ subject to:

$$\boxed{|\boldsymbol{b}| = 1,} \qquad \boxed{|\dot{\boldsymbol{b}}| = \frac{2\pi\nu}{\ell},} \qquad \boxed{\int_0^\ell \boldsymbol{b}\times\dot{\boldsymbol{b}}\,\mathrm{d}s = \boldsymbol{0}.}$$

Solution of the constrained variational problem

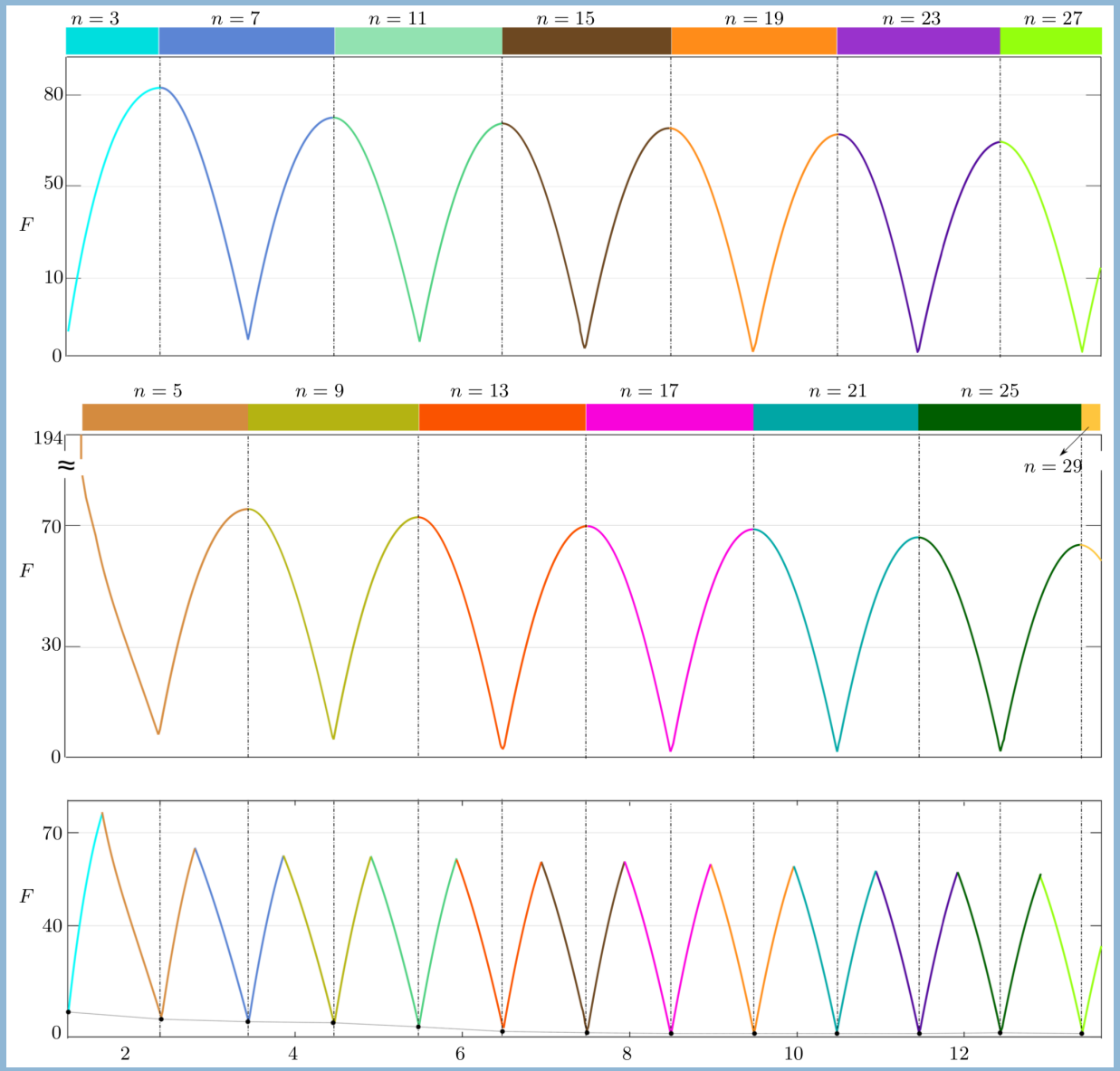
- Seek stable solutions starting with $\nu = 10^{-2}$, increasing ν by increments of 10^{-2}.
- First stable solution found, for $\nu \approx 1.29$, is identical to the limit surface of the Möbius kaleidocycles.



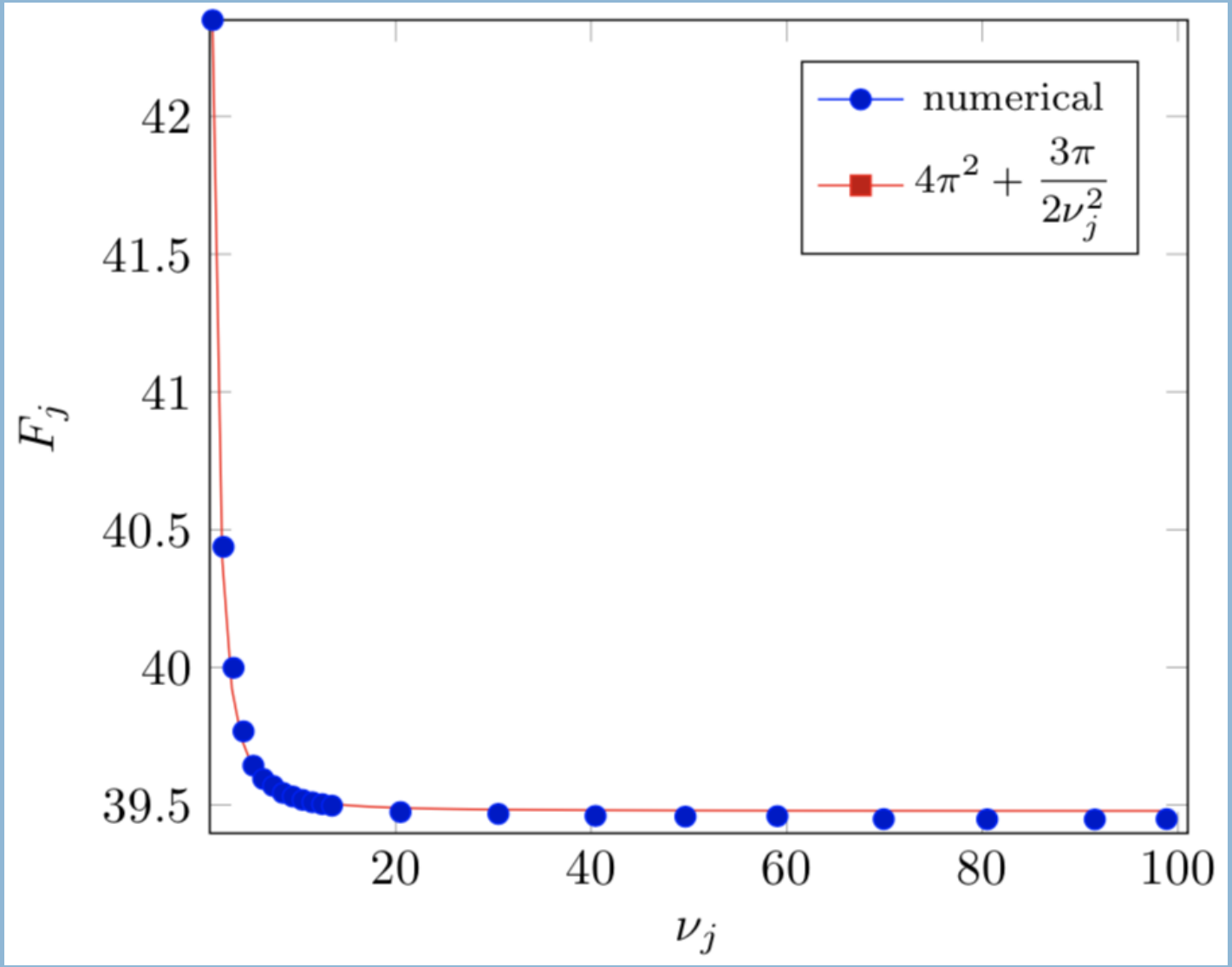


- Two stable solutions found for $\nu \geq 1.40$.
- Each solution is approximated to machine precision.

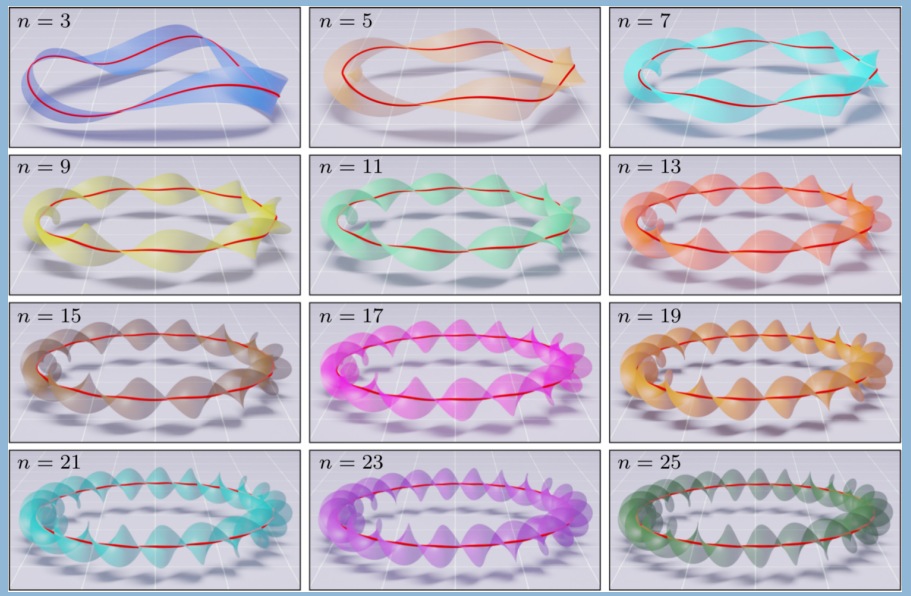
$F = E/\alpha$ versus ν for stable solutions



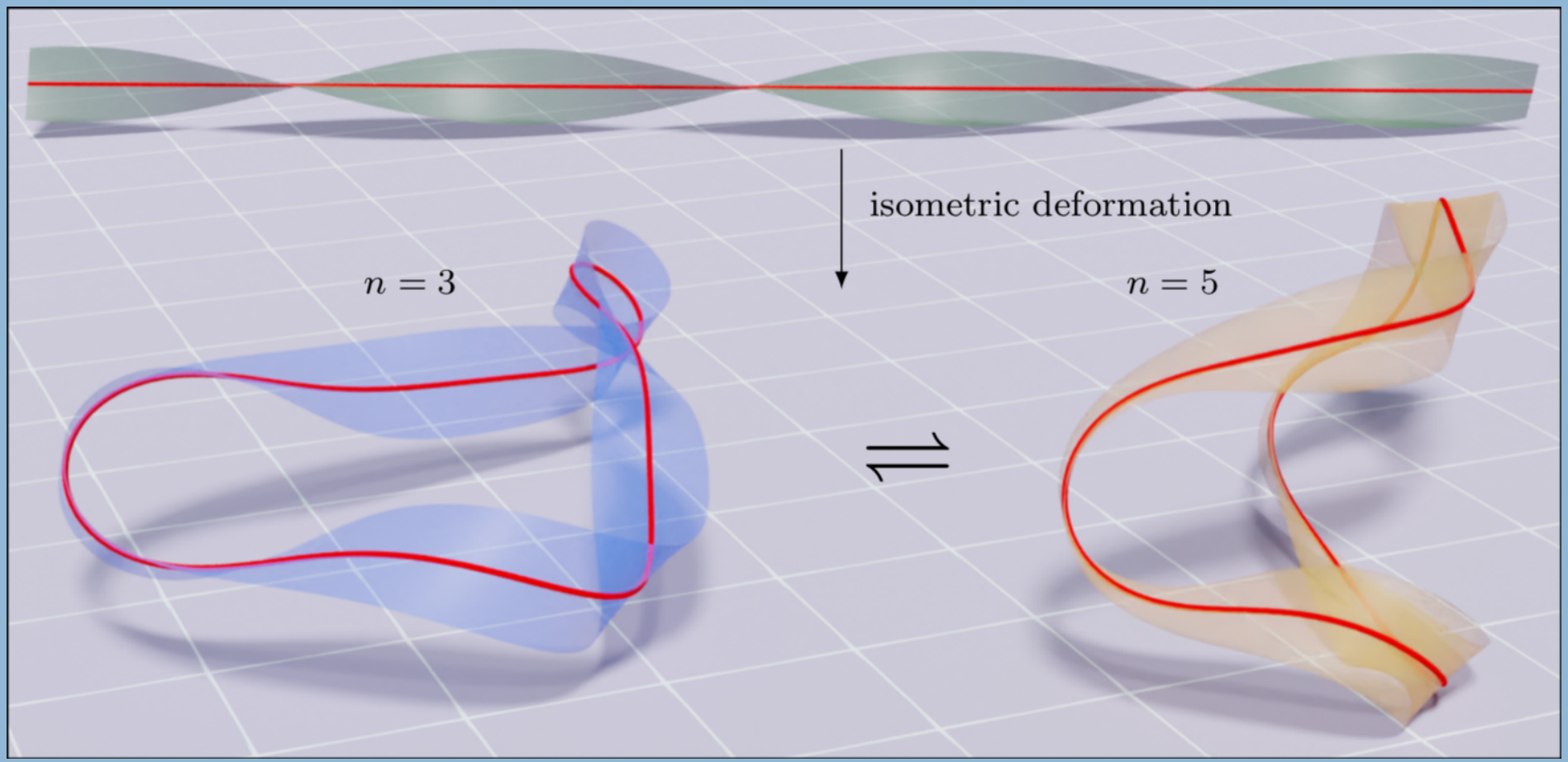
F versus ν for valley points of the lower envelope



Valley points exhibit rotational symmetry



Topological transitions at peak points



Isoenergetic and isometric everting motions of stable Möbius bands

- Consider a one-parameter ($t \geq 0$) family of deformations

$$\hat{\boldsymbol{y}}(s,\upsilon,t) = \frac{p}{2\pi}\int_0^s \boldsymbol{b}(\zeta,t)\times\boldsymbol{b}_\zeta(\zeta,t)\,\mathrm{d}\zeta + \upsilon\boldsymbol{b}(s,t), \qquad \begin{array}{c} 0\leq s\leq \ell,\\ |\upsilon|\leq a,\end{array}$$

where $\boldsymbol{b}$ satisfies the constraints

$$|\boldsymbol{b}| = 1, \qquad |\boldsymbol{b}_s| = \frac{2\pi\nu}{\ell}, \qquad \int_0^\ell \boldsymbol{b}\times\boldsymbol{b}_s\,\mathrm{d}s = \boldsymbol{0},$$

the antipodal junction conditions

$$\boldsymbol{b}(0,\cdot) = -\boldsymbol{b}(\ell,\cdot), \qquad \dot{\boldsymbol{b}}_s(0,\cdot) = -\boldsymbol{b}_s(\ell,\cdot),$$

$$\dot{\boldsymbol{b}}_{ss}(0,\cdot) = -\boldsymbol{b}_{ss}(\ell,\cdot), \qquad \dot{\boldsymbol{b}}_{sss}(0,\cdot) = -\boldsymbol{b}_{sss}(\ell,\cdot),$$

together with properly defined initial data $\boldsymbol{b}_0 := \boldsymbol{b}(\cdot,0)$.

- By the constraints $|\boldsymbol{b}| = 1$, $\boldsymbol{b} \cdot \boldsymbol{b}_t = 0$ and, thus, since $\boldsymbol{b}$, $\boldsymbol{b}_s$, and $\boldsymbol{b} \times \boldsymbol{b}_s$ are orthogonal, there exist scalar-valued quantities U and V such that

$$\boxed{\boldsymbol{b}_t = U\boldsymbol{b}_s + V\boldsymbol{b} \times \boldsymbol{b}_s.}$$

- Seek solutions of the form

$$\boxed{\boldsymbol{b}(s,t) = \boldsymbol{\beta}(s + ct),} \qquad c = \text{constant}.$$

- By the antipodal junction conditions, $\boldsymbol{\beta}$ must be periodic with period

$$\boxed{T = \frac{2\ell}{c}.}$$

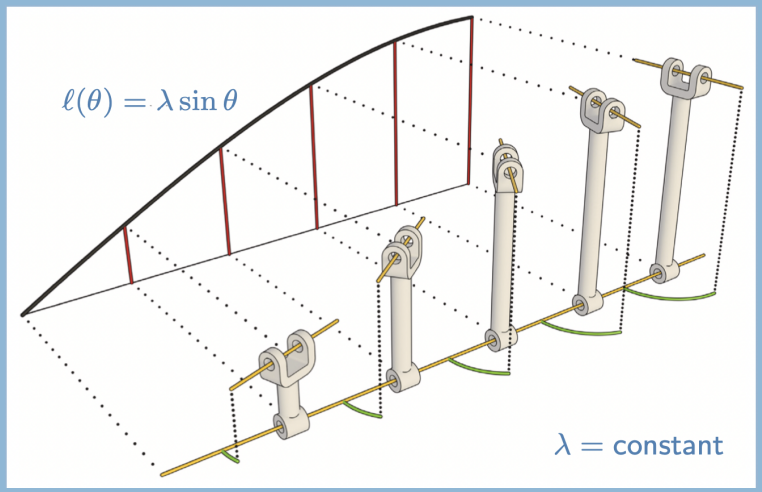
- Since $\boldsymbol{b}_s$ and $\boldsymbol{b} \times \boldsymbol{b}_s$ are orthogonal, U and V must satisfy

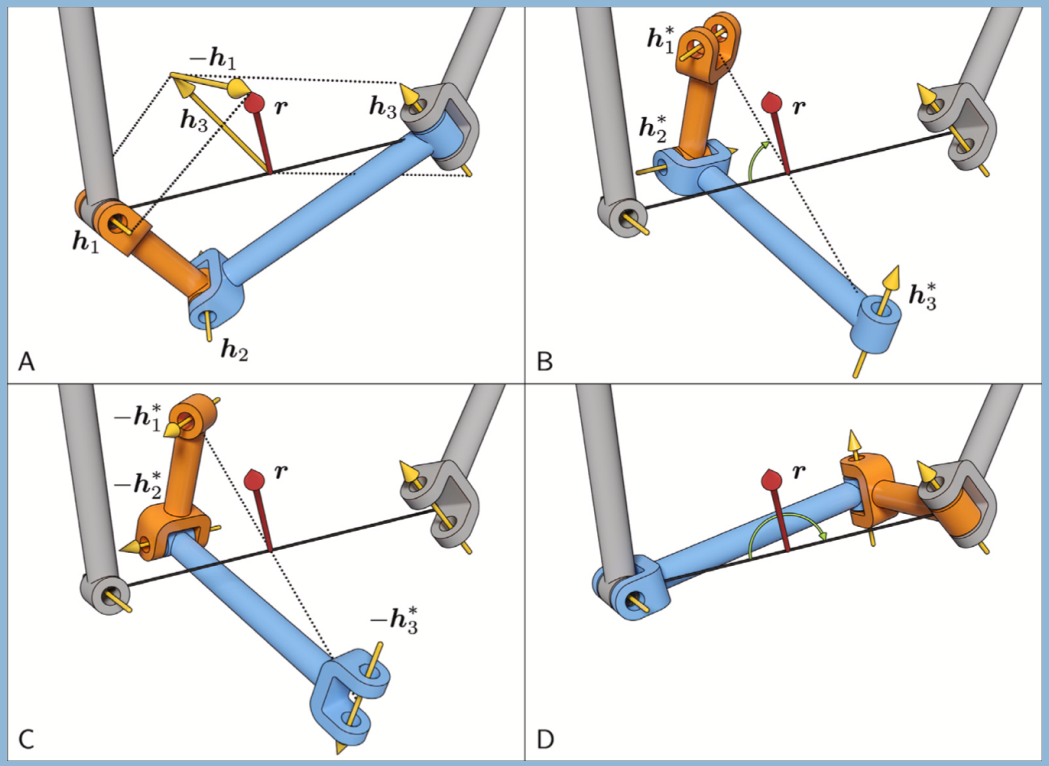
$$\boxed{U = c} \qquad \text{and} \qquad \boxed{V = 0.}$$

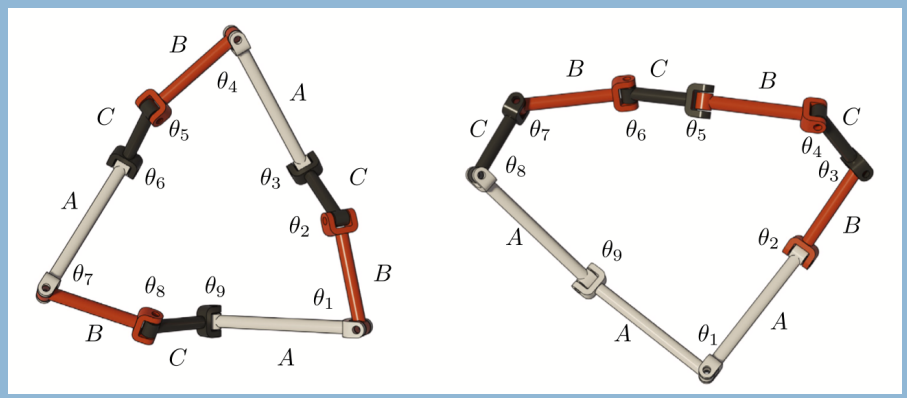
- If $\boldsymbol{b}_0$ is a minimizer, then $F_t = 0$.

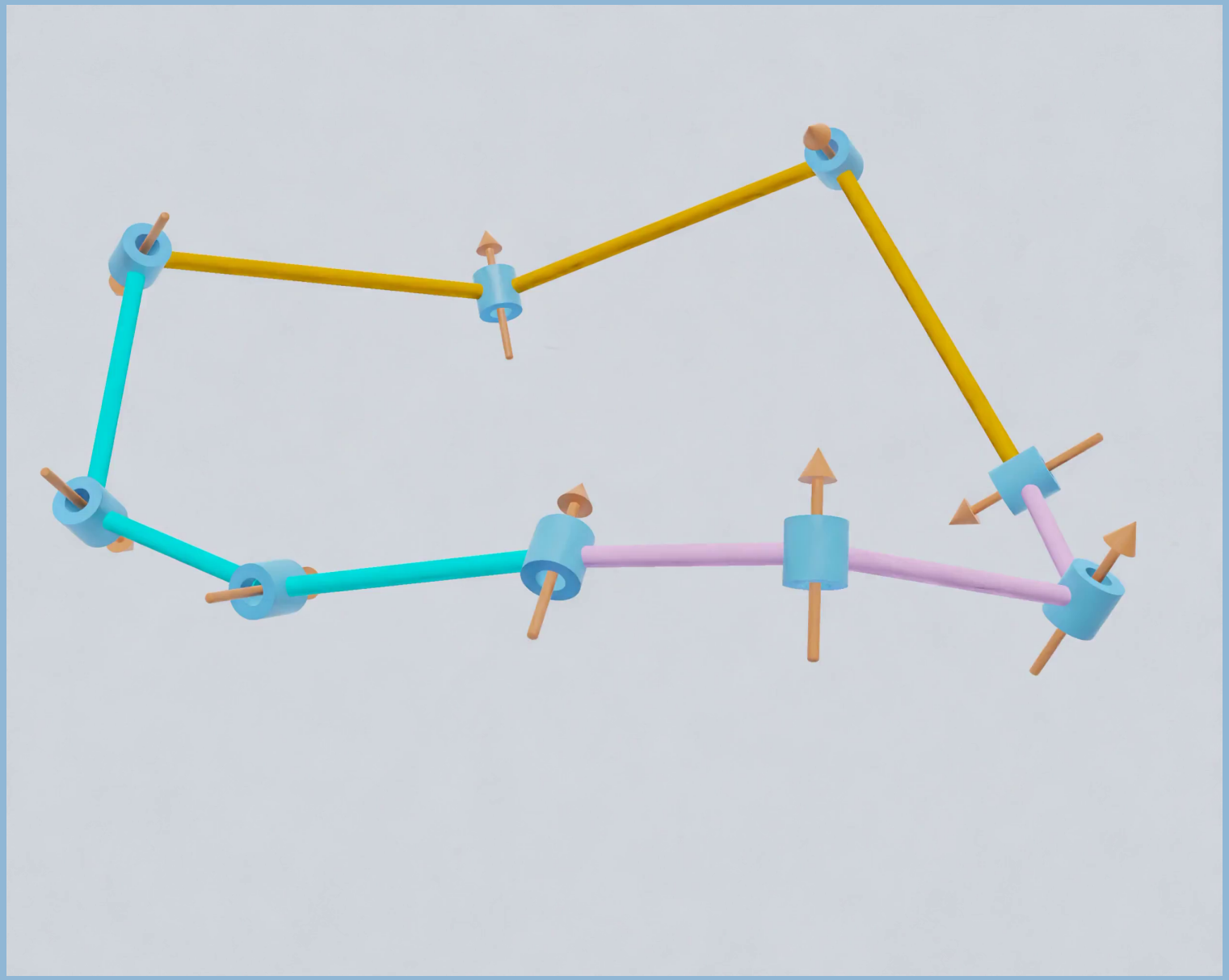
Click here for visualization.

Underconstrained linkages with exchangeable links







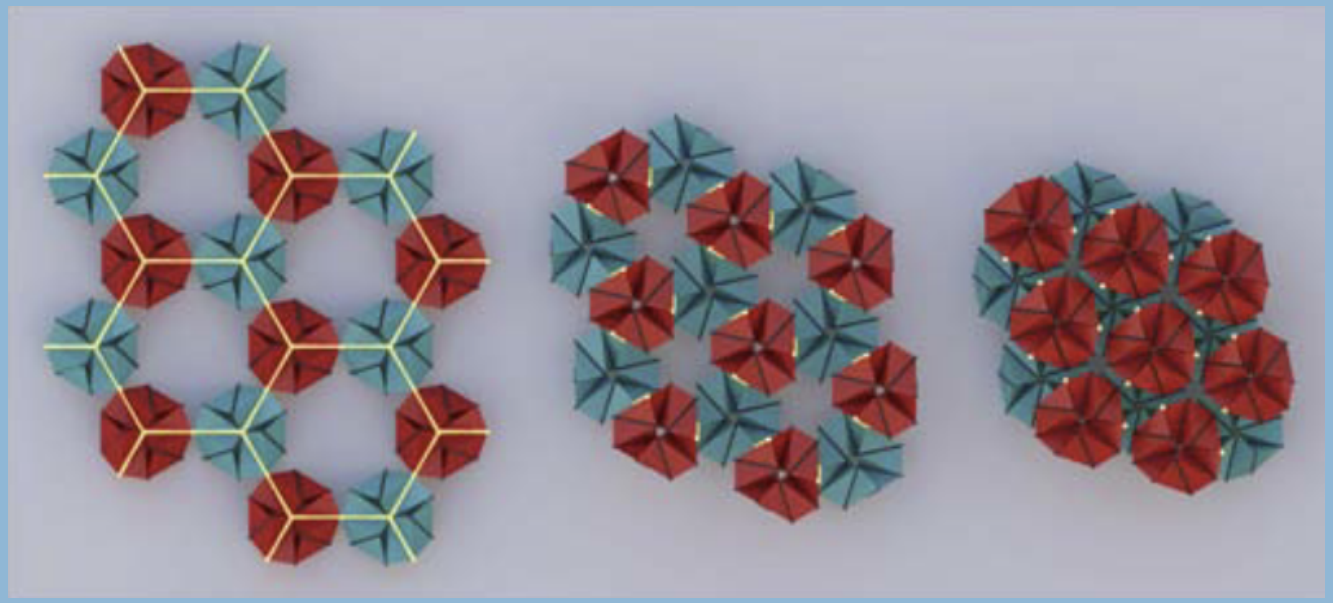


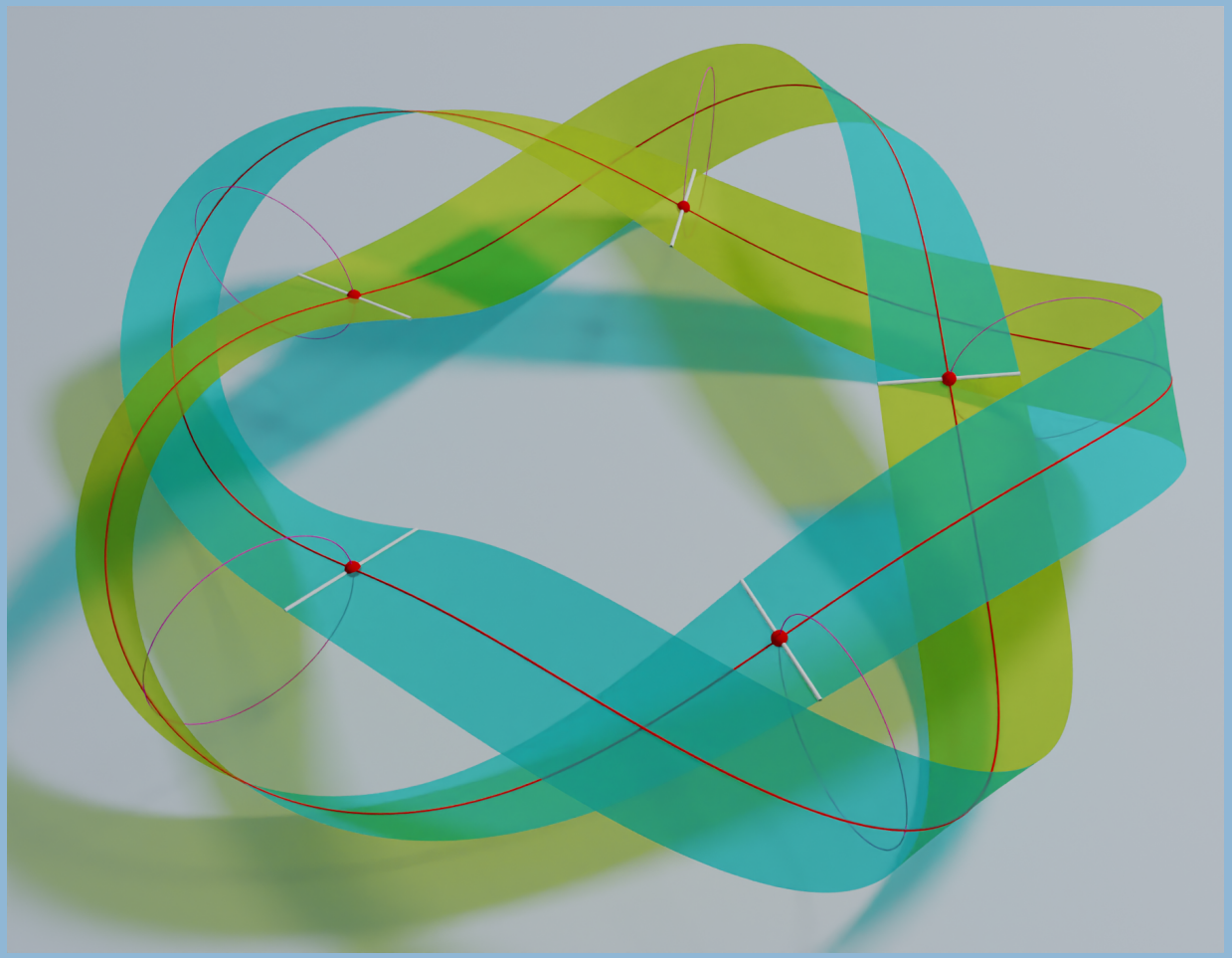
Everting motion of the $N = 9$ hinged ABCABCABC linkage.

Summary

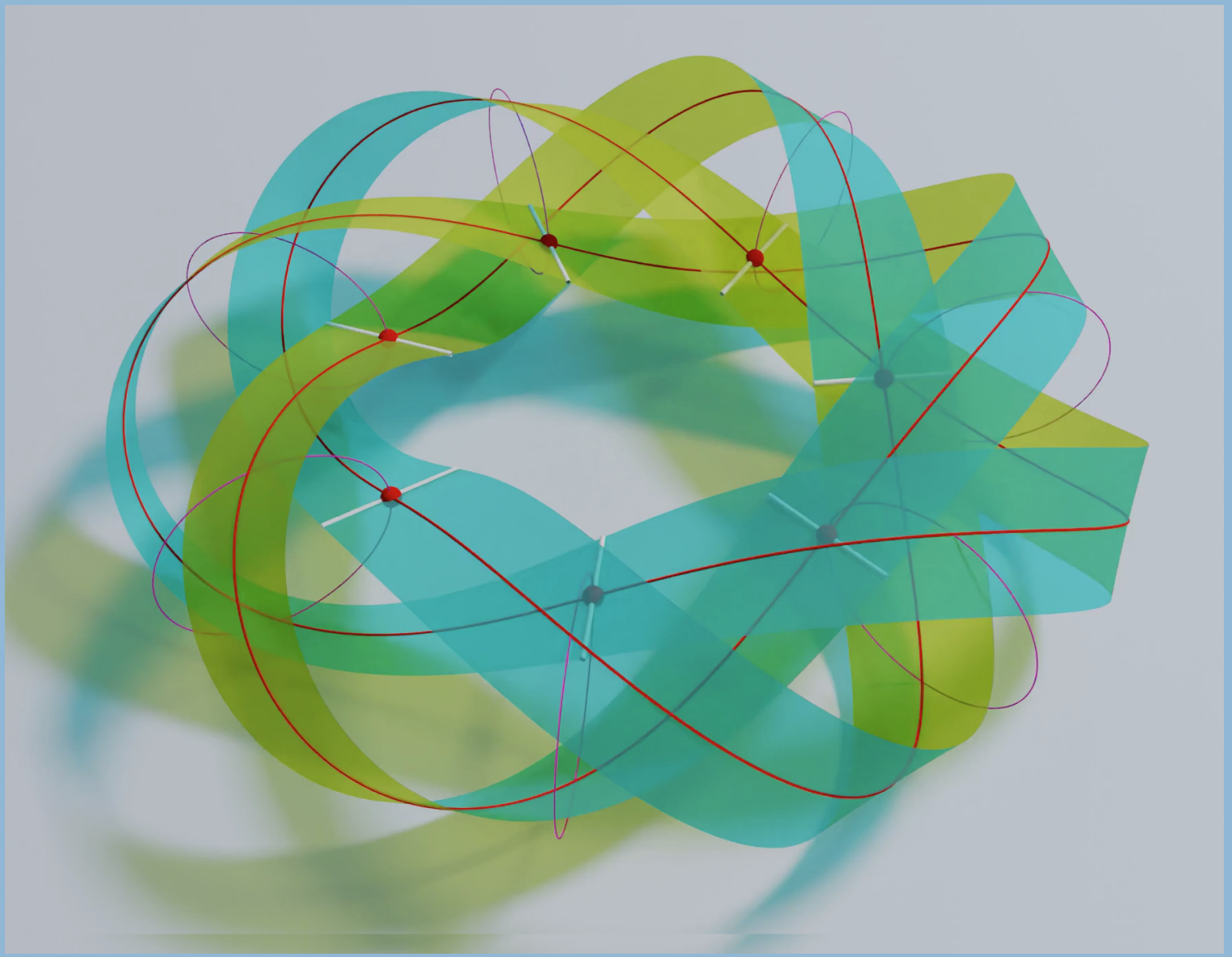
- Each $\mathcal{H}$ with $\nu = 1.29$ or more turns can sustain at least one isometric, chirality preserving deformation into a stable Möbius band.
- The choice $\nu = 1.29$ corresponds to the limit surface of the Möbius kaleidocycles.
- Valley points of the lower envelope of F versus ν yield energetically optimal stable Möbius bands with $n = 2k + 1$, $k = 1, 2, \ldots,$ half twists and n-fold rotational symmetry.
- Stable solutions obtained for choices of ν that do not correspond to valley points do not possess rotational symmetry.
- Topological transitions are possible at the peak points of the lower envelope of F versus ν.
- Stable solutions provide initial data for isoenergetic and isometric everting motions.
- Left- and right-handed energetically optimal solutions can be combined to construct deployable structures.
- Knotted solutions exist but are saddle points of the bending energy.

Deployable structures





Everting motion of a pentafoil Möbius knot ($n = 5$ half twists).



Everting motion of a septafoil Möbius knot ($n = 7$ half twists).

Outlook

- Use findings to develop guidelines for designing and synthesizing molecular Möbius bands...
- Explore the existence of threshold values of ν above which three or more stable solutions exist...
- Establish a rigorous basis for the empirical lower bound of F...
- Fabricate underconstrained nonorientable linkages with five or more half twists and/or knots...
- Explore whether knotted solutions can be stabilized by incorporating other physical effects...
- Study the quantum mechanical properties of optimal Möbius bands...

$$i\hbar\frac{\partial\Phi}{\partial t} = -\frac{\hbar^2}{2m}(\Delta + H^2 - K)\Phi$$

Thanks for listening! Questions?

Amphiphilic bilayers

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ARTICLE

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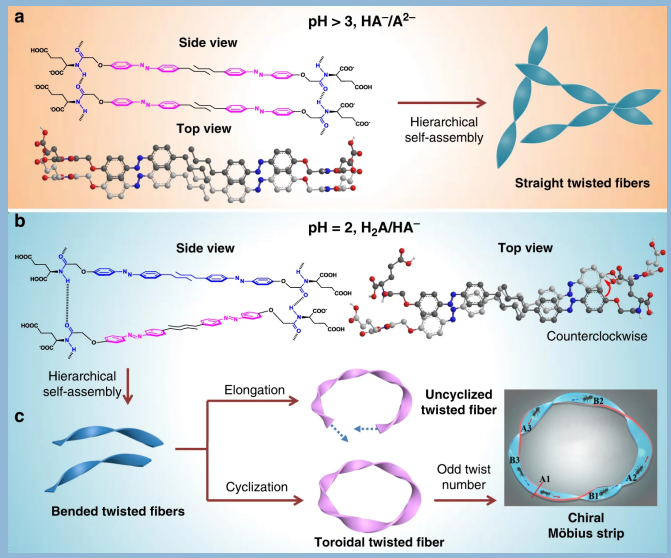
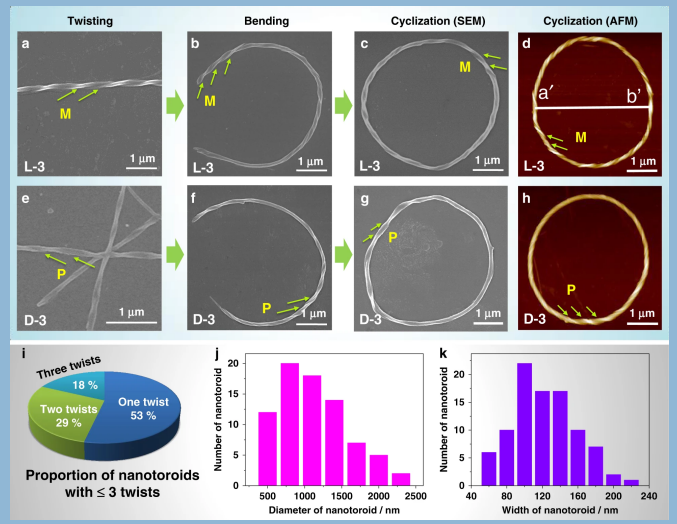
Self-assembled Möbius strips with controlled helicity

Guanghui Ouyang [1,2,6], Lukang Ji[1,3,6], Yuqian Jiang[4], Frank Würthner [2✉] & Minghua Liu [1,5✉]

Different from molecular level topology, the development of supramolecular topology has been limited due to a lack of reliable synthetic methods. Here we describe a supramolecular strategy of accessing Möbius strip, a fascinating topological object featured with only a single edge and single side. Through bending and cyclization of twisted nanofibers self-assembled from chiral glutamate amphiphiles, supramolecular nano-toroids with various twist numbers were obtained. Electron microscopic techniques could clearly identify the formation of Möbius strips when twist numbers on the toroidal fibers are odd ones. Spectroscopic and morphological analysis indicates that the helicity of the Möbius strips and nano-toroids stems from the molecular chirality of glutamate molecules. Therefore, *M*- and *P*-helical Möbius strips could be formed from L- and D-amphiphiles, respectively. Our experimental results and theoretical simulations may advance the prospect of creating chiral topologically complex structures via supramolecular approach.

[1] Beijing National Laboratory of Molecular Sciences, CAS Key Laboratory of Colloid, Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. [2] Institut für Organische Chemie and Center for Nanosystems Chemistry, Universität Würzburg, Am Hubland, Würzburg 97074, Germany. [3] College of Chemistry and Materials Science, Hebei Normal University, Shijiazhuang 050024, China. [4] Key Laboratory of Nanosystem and Hierarchical Fabrication, Chinese Academy of Sciences, National Center for Nanoscience and Technology, Beijing 100190, China. [5] University of Chinese Academy of Sciences, Beijing 100049, China. [6]These authors contributed equally: Guanghui Ouyang, Lukang Ji. ✉email: wuerthner@uni-wuerzburg.de; liumh@iccas.ac.cn





Carbon nanobelts

nature synthesis

ARTICLES

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Synthesis of a Möbius carbon nanobelt

Yasutomo Segawa[1,2,3,4]✉, Tsugunori Watanabe[3], Kotono Yamanoue[3,5], Motonobu Kuwayama[3,5], Kosuke Watanabe[1,4], Jenny Pirillo[6], Yuh Hijikata[6] and Kenichiro Itami[3,4,5]✉

Technologies for the creation of topological carbon nanostructures have greatly advanced synthetic organic chemistry and materials science. Although simple molecular nanocarbons with a belt topology have been constructed, analogous carbon nanobelts with a twist—more specifically, Möbius carbon nanobelts (MCNBs)—have not yet been synthesized owing to their high intrinsic strain. Here we report the synthesis, isolation and characterization of a MCNB. Calculations of strain energies suggest that large MCNBs are synthetically accessible. Designing a macrocyclic precursor with an odd number of repeat units led to a successful synthetic route via *Z*-selective Wittig reactions and nickel-mediated intramolecular homocoupling reactions, which yielded (25,25)MCNB over 14 steps. NMR spectroscopy and theoretical calculations reveal that the twist moiety of the Möbius band moves quickly around the MCNB molecule in solution. The topological chirality that originates from the Möbius structure was confirmed experimentally using chiral HPLC separation and circular dichroism spectroscopy.

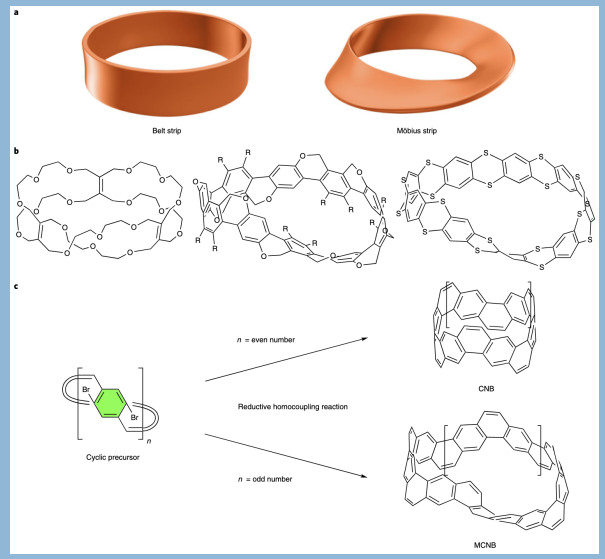
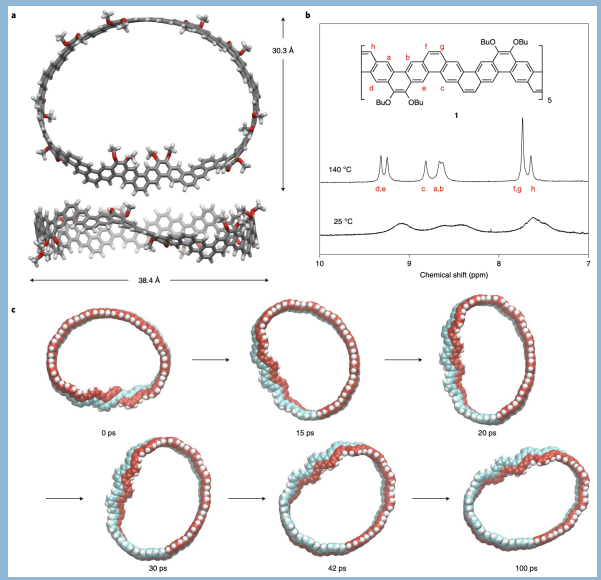
Organic chemists have striven to realize a wide variety of structural features on the molecular scale in nanocarbons. For example, nanocarbons with spherical, sheet-like, cylindrical or other exotic structures are usually obtained as mixtures on applying a high energy to the appropriate carbon sources[1–4]. In this context, molecular nanocarbon science, with which such substructures are created in a precisely controlled fashion, has attracted substantial attention, given that this approach is fundamentally able to circumvent the problem of the formation of such nanocarbon mixtures[5,6].

The history of the development of molecular nanocarbon science can be classified in terms of topology. Cycloparaphenylene, which was first proposed in the 1930s, is a ring-shaped molecular nanocarbon that represents a partial structure of carbon nanotubes[7–10]. Although cycloparaphenylenes were initially difficult to synthesize due to their high intrinsic strain energies, several synthetic methods, such as those reported since 2008 by Jasti, Itami and Yamago and their co-workers[11–13], have enabled the creation of molecular nanocarbons that exhibit non-trivial topologies, such as cages[14–17], catenanes and knots[18,19]. The next breakthrough in this research field was the synthesis of a carbon nanobelt (CNB) achieved by our group in 2017[20]. The fully fused, belt-shaped topology of CNBs creates two non-convertible faces, that is, the inner and outer faces. Since then, the synthetic chemistry of CNBs and related belt-shaped arenes has been intensively investigated worldwide in the context of the bottom-up construction of carbon nanotube substructures[21,22] as well as in the creation of new functional molecular nanocarbon materials.

The CNB structural feature of irreducible inner and outer faces can be extended to aromatic molecules with the topology of a Möbius strip, which is the simplest example of a non-orientable surface (Fig. 1a). Möbius-type molecules are found in nature[23] and have been of interest in synthetic organic chemistry, as demonstrated by the successful preparation of a non-conjugated Möbius-type double-stranded molecule by Walba et al. in 1982 (Fig. 1b, left)[24]. Aromatic single-stranded molecules with Möbius aromaticity were realized by Herges and co-workers in 2003[25], and Möbius aromaticity was further investigated by Grażyński and co-workers[26] and Osuka and co-workers[27,28]. Despite several examples of single-stranded Möbius molecules[29–33], double-stranded aromatic molecules with a Möbius topology still remain limited due to the difficulties associated with their synthesis. As shown in Fig. 1b, saturated linkers (–CH_2O–) or chalcogen atom linkers (–S–) are necessary to reduce the strain caused by the Möbius topology (Fig. 1b, centre and right)[34,35]. Even though Möbius-type CNBs have been theoretically proposed since the 1990s[36–38], a synthetic methodology to introduce Möbius topology to fully fused and fully conjugated all-sp^2 carbon structures still remains to be developed in molecular nanocarbon science.

Results and discussion

Here we report the synthesis, isolation and optical analysis of a Möbius carbon nanobelt (MCNB), that is, a fully fused CNB with a twist. The key to the synthesis of such MCNBs is a modification of our previously reported synthetic strategy for CNBs[19,39]. As shown in Fig. 1c, (*n*,*n*)CNBs (*n* = 6, 8 and 12, where (*n*,*n*) is the chiral index of the corresponding carbon nanotubes) were synthesized via a reductive homocoupling reaction using cyclic molecules that consisted of dibromoparaphenylene and *cis*-ethenylene precursors[19,39]. The important feature of this method is that a CNB can be generated when the number of repeat units is even, whereas an MCNB can be obtained when the number is odd. This is a simple but powerful method for the synthesis of a complex Möbius topology from highly symmetric precursors.

Strain energy calculation. The target size of the MCNB was determined using density functional theory (DFT) calculations. We found that MCNBs have a higher strain energy than CNBs of the same size (for details, see Supplementary Fig. 1), and that the strain of the MCNBs is mainly induced during the final bond-formation step. Figure 2a,b shows the hypothetical homodesmotic reactions using (*n*,*n*)MCNBs, (*n*,*n*)CNBs and their corresponding precursors (pre(*n*,*n*)MCNBs and pre(*n*,*n*)CNBs), based on which the strain induced in the final bond-formation step (ΔH_{FBF} (kcal mol^{-1})) was estimated. *Cis*-stilbene and phenanthrene were used as reference

[1]Institute for Molecular Science, Myodaiji, Okazaki, Japan. [2]Department of Structural Molecular Science, SOKENDAI (The Graduate University for Advanced Studies), Okazaki, Japan. [3]JST, ERATO, Itami Molecular Nanocarbon Project, Nagoya University, Nagoya, Japan. [4]Graduate School of Science, Nagoya University, Nagoya, Japan. [5]Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Nagoya, Japan. [6]Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Japan. ✉e-mail: segawa@ims.ac.jp; itami@chem.nagoya-u.ac.jp