On shape and elasticity: bio-sheets, curved crystals, and odd droplets

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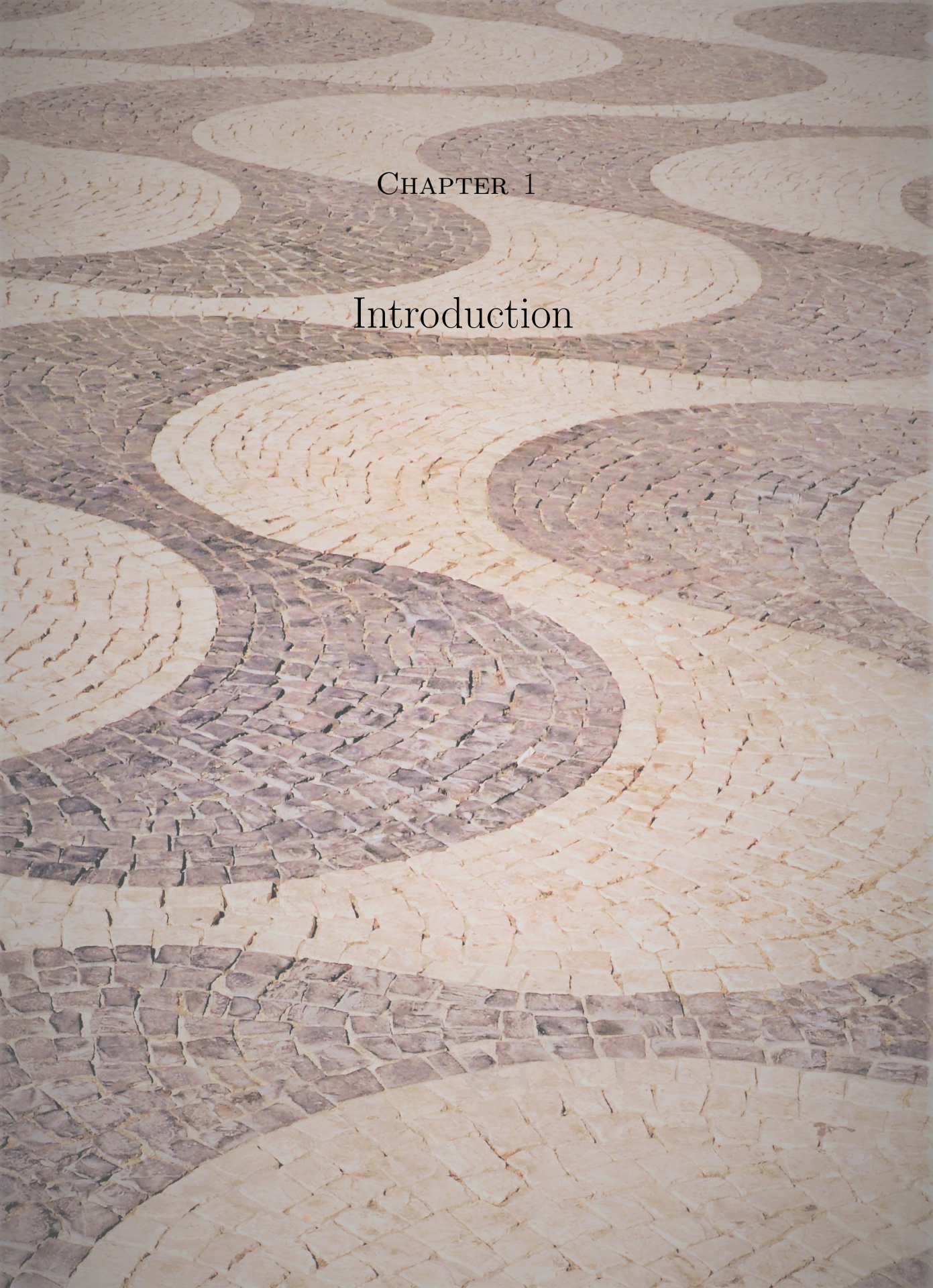

Chapter 1

Introduction

1.1 Elastic curved surfaces in soft condensed matter

Thin sheets, shells, surfaces, membranes, ribbons, films and *plates* typically describe three-dimensional condensed matter systems where one dimension, say the thickness, is much smaller than the width and the length. Think of paper, the interface of bubbles, plant leaves, fabric, cell membranes, and countless other examples from our macroscopic experience down to the micro and nanometer scale in soft and bio systems. Because they are thin, they characteristically display large deformations at the expense of small strain along the thickness [1, 2].

Thin systems are therefore a playground where geometry and physics meet. Due to the relative ease to deform out of plane, their shape is an expression of the mechanical forces at hand, and consequently of the internal interactions within the material and/or external ones with its surroundings. It is this interplay which explains why most suspended soap bubbles or liquid droplets are spherical, the shape of viruses, the wavy patterns in flowers, and even how some plants come back to life [3–6]. Conversely, reshaping the local geometry often affects the material's integrity and response. Harnessing the deformations can thus give birth to interesting applications, such as deployable structures or the booming field of metamaterials, branching into robotics [7–9]. In many biological systems, and in particular at the micrometer scale of living organisms, chemistry enters the game and causes the fascinating but incomprehensibly complicated interplay between geometry and mechanics to sit at the core of functionality, by directing essential processes that make us literally *alive* [10]. A broad example of this is protein folding, where conformational switches – basically a change in shape – drive, among others, cytoskeleton organization and fundamental aspects of the cell cycle.

In this thesis, we look at the connection between shape and mechanics in thin closed shells and open sheets, which we effectively consider as two-dimensional incompressible solids that we study in the framework of linear elasticity theory. In particular, we investigate shape deformations in the context of three soft matter systems which perhaps, depending on the reader, would not immediately be grouped together: single-layered crystals, micrometer emulsion droplets and assemblies of the ubiquitous bio-molecule tubulin. The goal is that, by the end of the chapter, their connecting thread will become clear.

1.1.1 Geometry and Topology

The relation between shape and mechanics is quantitatively explored through geometry. We model the thin shells and sheets as orientable two-dimensional surfaces. In other words, not only of vanishing thickness but also surfaces with a defined orientation such that it is clear what the "outside" normal is. The notion of *curvature* is straightforward when we think of a drawn line meandering on a piece of paper. For some point on it, the magnitude of the line curvature is the inverse of the radius of the osculating circle to that point, i.e. the one that follows the second derivative of the curve; and the sign is given in relation to the predetermined normal direction. We adopt the convention that if the circle curves away from the normal, the curvature

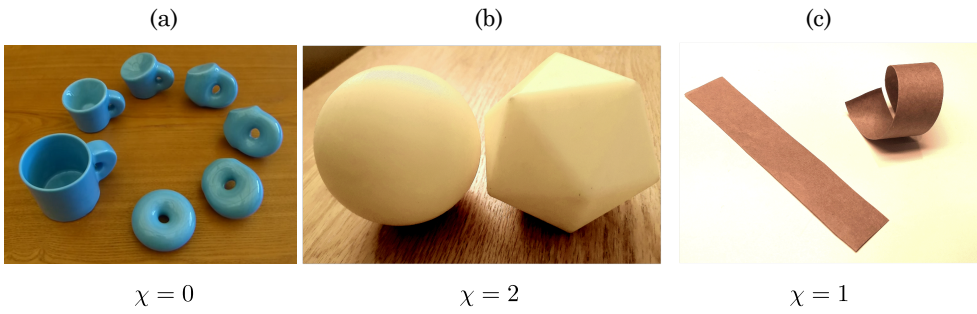

Figure 1.1: Two-dimensional orientable surfaces of different topologies. Shown are examples of three different topologies, with their corresponding Euler characteristic χ: (a) the staple example of a coffee mug deforming into a torus [11], (b) sphere and polyhedron (icosahedron) with spherical topology, (c) rectangular sheet curled into a helix. The first two are examples of closed surfaces, while the sheet is an open surfaces with boundaries. It is not possible to continuously deform a sphere or a sheet into a torus for example, without punching holes through the surfaces or gluing back some edges, respectively.

is positive. In a two-dimensional surface embedded in three-dimensional space, the extra dimension degenerates such a definition because, for starters, a surface has an infinite number of line projections. In the context of this work, two of the relevant measures of surface curvature are the *mean curvature* and the *Gaussian curvature*.

The mean curvature is an *extrinsic* measure of curvature, which depends on the embedding. In other words, it is related to the intuitive perception of curvature as how a plane escapes into the third dimension. The Gaussian curvature on the other hand, is an *intrinsic* measure, independent of the embedding. It is therefore less intuitive but we can think of it as reshaping that stretches or compresses the surface. For example, the inconvenience of having a flat world map that distorts the real size of countries towards the poles, comes from a sphere having constant Gaussian curvature, while we can easily roll that flat map and put it in a cylindrical container without ripping the paper. We distinguish between a surface *curving* or *bending* in space. Bending a paper sheet into a cylinder changes its extrinsic curvature but not the intrinsic one. Curving the flat map back to a globe requires also a change in the extrinsic Gaussian curvature.

Topology however, does not even distinguish between curving or bending as it describes objects at a level which is blind to continuous deformations of the surface. The surface can compress, stretch or twist, that, as long as it is not ruptured or glued together to other pieces, its topology is the same. The classical joke used to explain this is illustrated in Fig. 1.1a: *"a topologist is someone who cannot distinguish between a doughnut and a coffee mug"*. Furthermore, topology is concerned with global properties of surfaces and it characterizes the surface by integer identifiers such as the *Euler characteristic* χ. In 1758, Leonhard Euler was the first to note that the number of faces F, the number edges E and the number of vertices V of a convex polyhedron are related through a single constant, but the same is true for surfaces

that can be discretized through some poligonization, where in general

$$F - E + V = \chi\,. \tag{1.1}$$

This relation highlights how continuous deformations do not change the surface topology; stretching the edge lengths do not affect the Euler characteristic, but getting rid of some edges do. In Fig. 1.1, the coffee mug, as a closed surface (no boundaries) with one handle or hole, has an Euler characteristic $\chi = 0$. In contrast, a closed sphere Fig. 1.1b has no handles, thus it has $\chi = 2$ or *spherical topology*, but an open surface without holes but with boundaries like the ribbon in Fig. 1.1c has $\chi = 1$, or *disk topology*.

1.1.2 Mechanics of elastic surfaces

Continuum elasticity theory allows us to quantify the energetic cost of deforming a solid body from a rest configuration. If the relative deformations, or strain, are small we can use linear elasticity to calculate the retorting forces, or stress, generated in the body. However, because thin systems can have large plane deformations at little strain, our two-dimensional approximation gives rise to a separation between in-plane deformations and out-of-plane ones. Therefore, the elastic energy of sheets and shells has two different contributions: the stretching energy from stress generated by compressing or extending the surface, and the bending energy from deformations along the thin dimension. Bending and stretching of curved surfaces are coupled in a similar way as their extrinsic and intrinsic curvatures are. Furthermore, introducing Gaussian curvature to a surface undoubtedly introduces elastic stress.

1.2 Bending and spontaneous curvature

The resistance of thin sheets to bend can be experienced with a simple piece of flat paper. We can bend one of the sides towards the other to form a paper tube (without sharp folding, as this incurs in plastic deformations and we care about elastic behavior), but releasing the paper will have it spring back to its initial flat configuration. To roll it into a cylindrical shape that stays, we need to put a band around it or shove it in a container; it then stores some elastic energy. However, many of us have also experienced how after some time, a poster out of its cylindrical container or rolled gift wrapping paper would very much like to stay folded. With enough time, rearrangements at the molecular level result in an intrinsically bent state for the paper. If we flatten it and release it, now it springs back to its rolled configuration.

In general, the *spontaneous curvature* is the value of curvature that an unconstrained surface adopts when allowed to relax. It originates at the level of the constituents making up the material and their interactions. These can for instance generate states of pre-stress (like the sheet of paper) which drive specific shape deformations [13], even between multistable states which is the principle behind deployable structures [14]. Details in the molecular geometry and/or interactions can also drive the self-assembly of soft and bio membranes into specific shapes. For instance, different geometries and topologies are observed for liquid lipid vesicle and membranes which

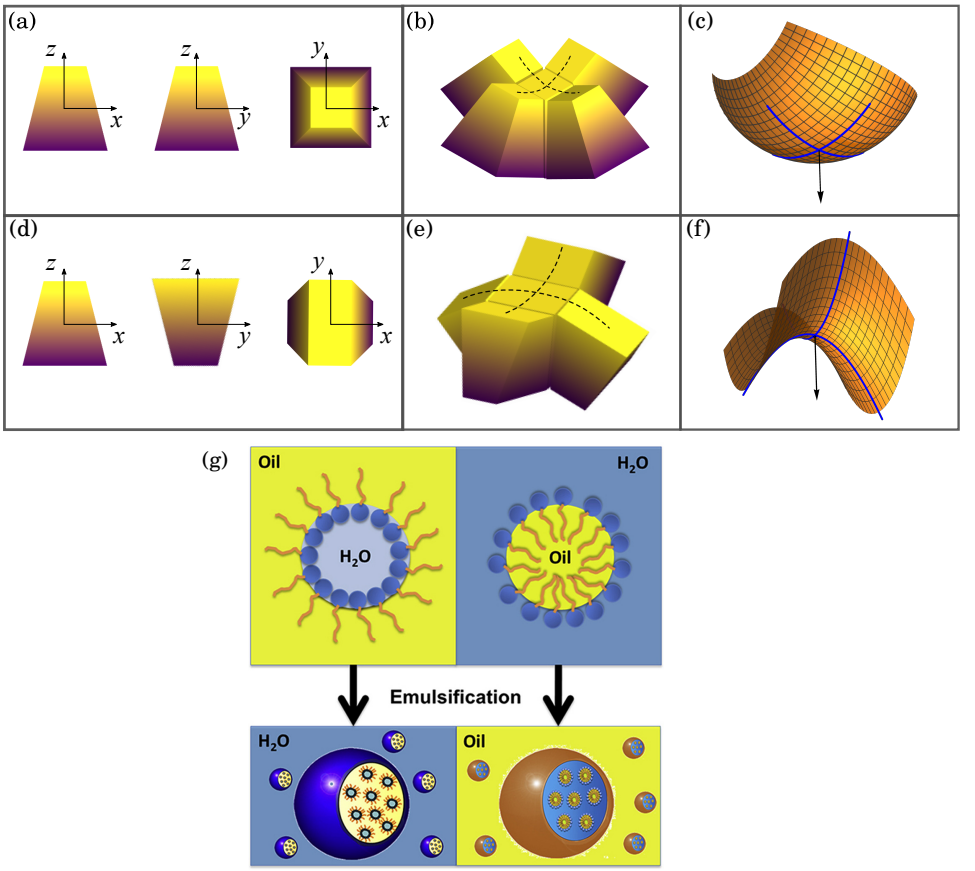

Figure 1.2: Spontaneous curvature. The top (a-c) illustrate spherical curving resulting in sphere-like closed shapes, while the bottom (d-f) illustrate hyperbolic curving resulting in saddle-like shapes. The projections in (a) and (d) reveal that the spherical deformation is from conical geometry along width and depth, while the hyperbolic one is conical along the width and inverted conical along the depth. (g) Surfactant molecules have an effective conical shape in both projections. Depending on the specific molecular shape and interactions of these amphilic molecules, the cone orientation will give rise to spherical curving but with either a positive or negative sign. This panel is an adapted reprint from Ref. [12]. We consider oil-in-water emulsions to be positively curved by convention.

can be described in terms of spontaneous curvature [10, 15–19]. We illustrate two simple scenarios of how assembly is affected by the effective shape of the building blocks in Fig. 1.2. Consider the stacking of conically shaped two-dimensional blocks (like the first projection in panel a). If done in a way that leaves no gaps, it produces a structure that bends with a characteristic radius of curvature (any of the projections in panel b) which depends on how conical they are, as opposed to the rectangular ones which form a straight structure. If the three-dimensional block is also conical on the perpendicular direction the assembly forms a spherical shape (panel c), but if the conical shape is inverted in the second projection (panel d), the oppositely oriented curvatures form a saddle-like assembly (panels e and f). Changes in external conditions can change the interactions and thus the effective shape of the molecular building blocks, and generate surface deformations like in biological membranes of cells or other components [19–21].

Another example of spherical assembly is the mixing of oil and water. *Microemulsions* are stable droplet mixtures of oil and water, stabilized by amphiphilic molecules called *surfactants*, which have effectively conical shapes. The specific surfactant geometry determines the spontaneous curvature which ultimately influences which phase, water or oil, forms the droplets [22](see Fig. 1.2g).

1.3 Hexagonal order on curved surfaces

A *crystal* is a solid whose constituents are organized in regular and periodically-repeated lattices, thus with characteristic translational and orientational order [23]. Crystalline monolayers endowed with spatial curvature are ubiquitous in hard and soft matter across a vast range of length scales: from nanoscopic twisted graphene sheets [24] to rafts of millimeter-sized soap-bubbles [25]. The *coordination number* z of a crystal is the number of nearest neighbors for a perfect lattice. Among all possible crystal structures in two dimensions, the *triangular lattice* with $z = 6$ is the most efficient arrangement of particles with isotropic interactions (see Fig. 1.3a,b). As such, its mechanical properties have been studied in a plethora of different systems, including the long-standing Thomson problem [26–28], viral capsids [4, 29], colloidosomes [30–35], Abrikosov vortices in thin-film superconductors [36], Pickering emulsions [35] and, more recently, in surfactant-stabilized emulsions [37, 38].

1.3.1 Topological defects

Consider first a triangular lattice on a flat plane, like the small patch drawn in Fig. 1.3b. In general, the complementary *Voronoi tessellation* of a triangulated surface describes the spatial partition in regions which are correspondingly closest to each lattice element as opposed to any other. In the case of a perfect triangular lattice these are regular hexagons.

Lattice defects break the crystalline order, and as such, introduce elastic stress from the departure of the ideal rest configuration [39]. Our work revolves around two types of point defects with unfortunately similar-looking names: disclinations and dislocations. If unfamiliar with these, it helps to think of the type of distortion they

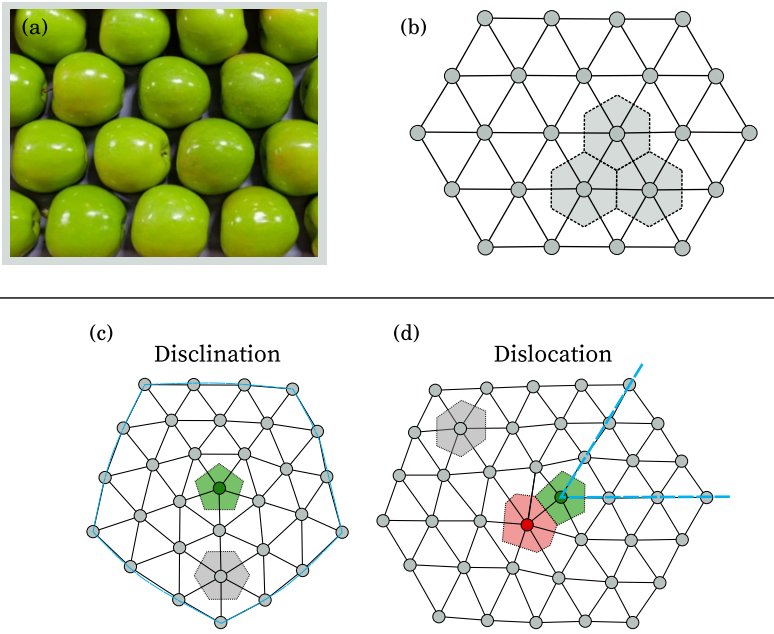

Figure 1.3: Hexagonal order and defects in a triangular lattice. (a) In two dimensions, particles with isotropic interactions such as spherical hard disks, but also apples, pack the most efficiently in a triangular lattice. (b) In a crystal without defects, each lattice element has six nearest neighbors, or coordination number $z = 6$. The Voronoi tesselation of a perfect triangular lattice corresponds to regular hexagons, like those in gray. (b) Isolated disclination in green has a coordination number $z = 5$. The shaded green area is the corresponding pentagonal Voronoi area. The deformation in the crystal orientational order introduced by the disclination expands throughout, visible from the overall pentagonal tendency of the batch shown (c) Isolated dislocations can be regarded as a tightly bound pair of disclinations, in this case a disclination of $z = 5$ and one of $z = 7$ in red. While the orientational order is preserve on a long scale, two additional lattice lines radiating from the dislocation (highlighted with blue dashed lines) distort the translational order.

cause in the crystal. *Disclinations* distort the orientational order. In a triangular lattice, they are points with $z \neq 6$, such as the green pentagon Fig. 1.3c (the original "dis-inclination" was coined by Frank [40] in the context of liquid crystals). The *topological charge* q of a defect, quantifies the breaking of bond orientational order, which for sixfold hexagonal order

$$q = 6 - z\,. \tag{1.2}$$

Dislocations on the other hand, can be visualized as two disclinations right next to each other which compensate the corresponding loss in the bond orientational order, for example the green pentagon with $q = 1$ and red heptagon with $q = -1$ in Fig. 1.3d. Consequently, they induced new lattices lines (in blue), distorting the translational order instead (the "dis-location" comes from sliding along such induced planes on 3D crystals [41]). Dislocations carry no topological charge, i.e. $q = 0$.

Although it is possible to perfectly tile flat space with hexagons, the same is not true for a curved surface. The typical layman's example is the outside of a soccer ball[1] requiring both hexagonal and pentagonal patches. It is mathematically impossible to have a spherical triangular lattice without disclinations, or in fact, any crystal of spherical topology. A fundamental connection between Gaussian curvature, topology and the breaking of order gives rise to *geometrical frustration* in curved crystals[2]. The topological constraint is expressed in Euler's formula

$$\sum_i q_i = 6\chi\,, \tag{1.3}$$

summing over all the lattice defects. Recall that $\chi = 2$ for a sphere, therefore explaining the twelve black pentagons on a soccer ball.

1.3.2 Dealing with stress

In actual triangular crystals, given the different possible ways to comply to the mathematical constraint, it is mechanics which dictates the number and position of defects since both disclinations and dislocations introduce in-plane elastic stress.

The stretching energy of a disclination scales with the square of its charge and the elastic distortion extends throughout the system size [44]. As a consequence, the simplest and most common distribution of the required defects on a sphere are twelve disclinations with $q = 1$, located at the vertices of an inscribed icosahedron as this maximizes their distance (see Fig. 1.4a). In a way, the regular icosahedron is the minimal realization of such a crystal of spherical topology. As a matter of fact, it is the geometry which deals with the distortion from the disclinations in the best possible way. To understand this, first imagine an isolated disclination on a very stiff crystal, or basically, a hexagonal piece of paper with a angular slice cut out[3]. Since the paper cannot be stretched to compensate for the angular loss, the alternative is to *buckle* it out of plane into a conical shape like the model in Fig. 1.4b. In general, shape deformations normal to the tangent plane serve as a relaxation process in surfaces subjected to local in-plane strains [5, 45]. This concept generalizes to a smooth and flexible two-dimensional crystal and it goes back to the fact that Gaussian curvature also breaks the orientational order but it can nonetheless compensate for the distortion caused by a disclination [39, 46]. A sharp regular icosahedron is the example of perfect curvature screening of a crystal with spherical topology. Buckling as a screening mechanism is common for crystals with low density of lattice defects [4, 47–49] and it explains why many viral capsids are icosahedral [42] (for example, Fig. 1.4d).

A second screening mechanism is the creation of dislocations around the disclination [43]. Back to our paper model (Fig. 1.4e, f), since a dislocation creates lattice lines, various next to one another can be visualized as pleats in the paper, which are

[1] Sure, or *football*, but this minimizes possible misinterpretations.

[2] A quick intuitive read on this is possible through Eq. (1.1), that connects a topological variable to a poligonization of space, which in turn would be distorted in the presence of intrisic curvature.

[3] Ref. [33] not only presents more visual explanations on the paper models, but provide templates of triangular lattices for those who want to try it out.

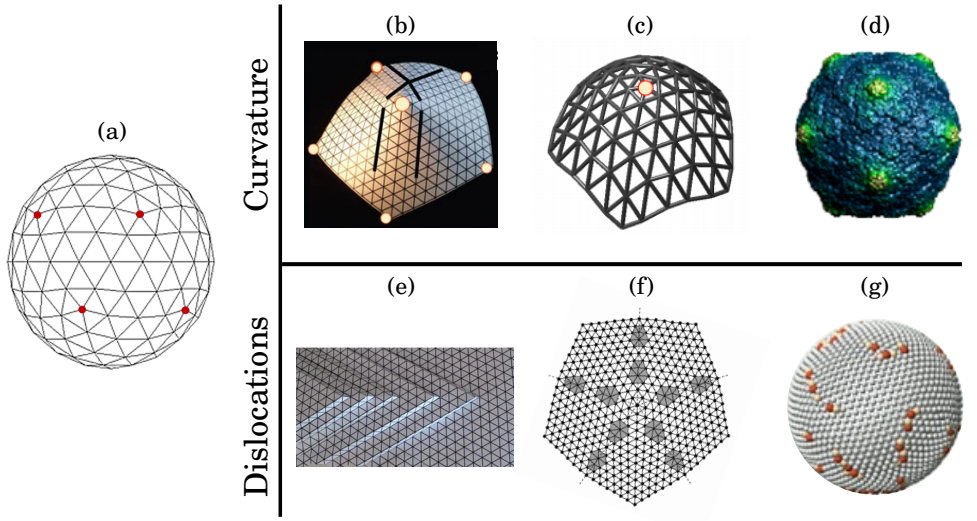

Figure 1.4: Accommodating topological defects. (a) Crystals of spherical topology are constrained to have disclinations. An isolated disclination with coordination number $z = 5$ in a triangular lattice can be accommodated by: (b, c) curving out of plane, but also by (e, f) introducing dislocations in its surroundings. (d) Viral capsids, with low number of lattice elements, show curvature screening, while (g) colloidal crystals, containing many more elements, have screening dislocation scars. Panels (b, c, e, g) were adapted from [33] with permission from Springer Nature. Panel (d) was adapted from [42]. Panel (f) was reprinted with permission from Ref. [43]; Copyright (1999) by the American Physical Society.

then able to compensate for the disclination slice [33]. On flat crystals, chains of dislocations, called *grain boundaries*, are known radiate away from large distortions [50]. On dense spherical crystals where the neighborhood around the disclination starts looking flat, dislocations chains also form radiating away from the topological disclinations (see Fig. 1.4g). Having no topological charge, arbitrarily many dislocations can be formed in the crystal without betraying Eq. (1.3). However, because of the Gaussian curvature of the surface, the chains, termed *dislocation scars*, terminate at some distance within the lattice [26, 30].

1.4 Inside this thesis...

We study the elasticity-driven shape deformations of closed and dense crystalline monolayers, oil-in-water microemulsions, and biological thin assemblies affected by protein conformational changes. By considering these systems as incompressible two-dimensional smooth surfaces, we establish a mechanical description based on continuum theory to quantify the bending and stretching energies, and further use three-dimensional computer modeling to investigate how elasticity in turn affects the system's geometry.

In **Chapter 2** we revisit the concepts introduced in the previous sections but in the framework of differential geometry and continuum elasticity, which are the stepping stones to the theoretical study of the mechanics of soft, thin solids. Differential geometry allows us the quantification of the local geometry, including intrinsic and extrinsic measures of the curvature. The rigorous mathematical description brings to light the connection between Gaussian curvature and in-plane deformations. With all the appropriate definitions in place, we present the continuum expressions for the bending energy and the stretching energy of an elastic surface. In the final section of this chapter, we detail how these can be translated for discretized surfaces, which are necessary if we are to make progress with more general shapes where analytical calculations are not possible.

1.4.1 Curved crystals

We look at two-dimensional triangular crystals of spherical topology, inevitably bound to have disclinations, and in particular, twelve $q = 1$ ones distributed on an icosahedral symmetry. As we saw, the crystal can counteract the in-plane distortions created by the disclinations, that is, by reshaping the surface around them either by increasing the local curvature (buckling), or by creating more defects. The former screening mechanism is often found in systems with a size comparable to the lattice spacing, while it switches to the latter in denser crystals, as most typically seen from viral capsids and pickering emulsions respectively [4, 30].

However, it was recently discovered that a much denser triangular crystal can be found at the interface of emulsion droplets with specific chemical compositions [37, 38, 51]. On these, a mixed monolayer of surfactants and alkanes freezes at temperatures higher than the freezing temperature of bulk oil and water, forming a nanometer thick crystal with hexagonal order. Among other fascinating aspects of this system is the

observation of the buckling screening mechanism into icosahedral shapes while in a size regime where dislocations scars should proliferate. Since these are micrometer sized droplets, not only is the actual lattice structure not possible to be resolved using microscopy but the crystal density makes it prohibitively difficult to study from a completely discrete perspective, as the predicted number of dislocations is very large [52].

In **Chapter 3**, we develop a continuum theory of dislocation screening for dense two-dimensional crystals of spherical topology based on previous calculations of the in-plane stress introduced by isolated disclinations and dislocations [39, 44, 52]. We build a general framework considering the discrete nature of disclinations and a continuous treatment of scars. This allows us to find an expression for the stretching energy for any crystal of spherical topology which is simple and also easy enough to implement for arbitrary geometries. Our results follow the size-scaling behavior previously seen for a growing number of dislocations. To understand how the curvature screening mechanism plays a role here, we apply our methodology to three geometries with varying local Gaussian curvature. We include a short analysis on the effect of finite temperature in the elastic energy and dislocation number.

For simplicity, in this chapter we focus on defect elasticity and its effect in the stretching energy, disregarding any bending cost. On the other hand, examples like a stiff piece of paper or liquid membranes have either infinite or zero stretching energy, so they have little interesting value in the deformations of flexible shells. In reality, most materials have finite values of elastic constants and their deformations are therefore also molded by a competition between in-plane stretching and out-of plane bending. The last two chapters explore this competition.

1.4.2 Odd droplets

It has been long understood that emulsion droplets are spherical since this is the closed surface which minimizes both the area and the bending energy functional [3]. However, Sloutskin *et al.* reported in 2005 the serendipitous observation of liquid droplets of oddly specific shapes: icosahedra and flat polyhedra such as hexagonal, triangular and rectangular platelets [53]. These are the same oil-in-water emulsion droplets with frozen interfaces mentioned above, which have been extensively studied ever since. The buckling of spheres into icosahedra immediately pointed to an interplay between crystal elasticity and surface tension from the liquid nature of the emulsion. Despite this model getting far in explaining many aspects of the deformations, none of the theoretical work done before could address relevant size-scaling observations.

In **Chapter 4** we introduce this soft matter system and expand on the characteristics that make it unique. Mechanically speaking, each droplet is a melting pot where crystal elasticity, the spontaneous curvature of surfactant molecules, surface tension, and buoyancy compete and cooperate, giving rise to the shape deformations. We focus on the two initial ones: the faceting of spherical droplets into icosahedra, and the further flattening to hexagonal platelets. We show that spontaneous curvature and buoyancy, which were left out in previous models, are actually key to account for the deformations, including the size-dependent behavior.

1.4.3 Bio-sheets

In **Chapter 5**, we go on to also explore the competition between bending and stretching but on a different topology: that of open sheets. The motivation comes from biology, and in particular from assemblies built from a small globular protein called *tubulin* which has been interestingly conserved through the ages in most living cells. In eukaryotic cells, *tubulin dimers* are mostly known for assembling into hollow single-layered cylindrical structures called *microtubules* (MTs): one of the main biopolymers making up the cytoskeleton and key to a myriad of cellular functions including cell motility [54, 55], morphogenesis [56], inter and intracellular transport [57, 58], and organizational roles during the different stages of the cell cycle [59]. As such, the dynamics and mechanics of these rigid cylindrical structures have been extensively studied. It is known that conformational changes in the tubulin dimers and changes in the inter-dimer interactions can give rise to bending moments akin to the presence of spontaneous curvature on a thin sheet.

Furthermore, tubulin, in a lego-like fashion can assemble into a zoo of other different shapes such as flat sheets, helical ribbons or curly ribbons, depending in numerous different environmental conditions but only empirically understood [60, 61]. Although intrinsic curvature in tubulin assemblies is widely explored in the context of MTs [62, 63], there has not yet been a connection to the polymorphic nature of tubulin structures in general. In that spirit, in this chapter we dive into the competition between stretching and bending in rectangular ribbons of varying flexibility, when subjected to different values of spontaneous curvature. Even in the simplest model, we show that mechanical anisotropy is key in explaining MT-like shapes and we provide further insight on how other shapes come to light.