4D Printing: a Radical Shift in Additive Manufacturing

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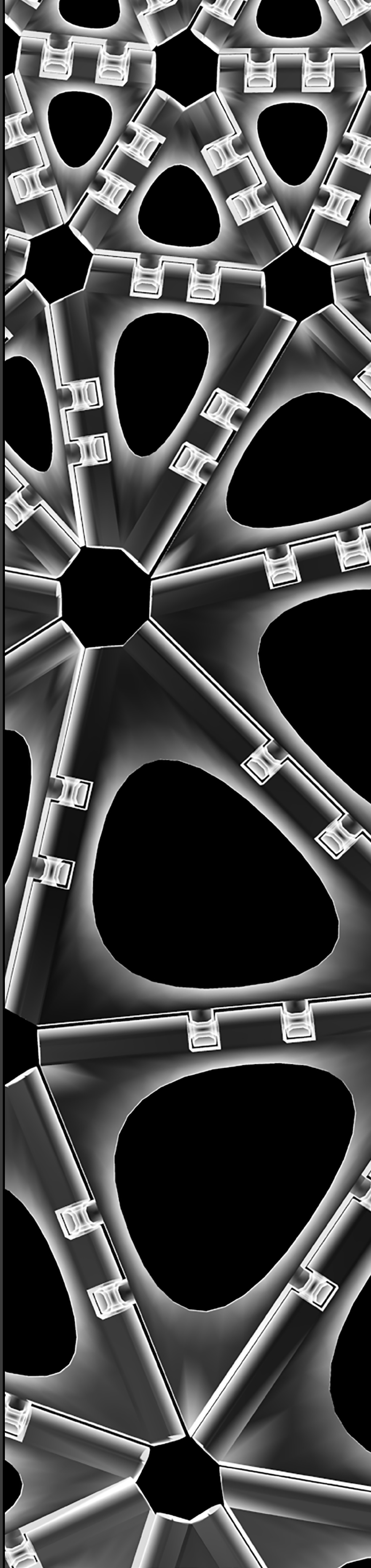
Academic year 2018 - 2019



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ABSTRACT

Additive manufacturing (AM) has been introduced since the late 1980s and although a considerable amount of progress, there is still a lot of research to be done in order to overcome the various manufacturing challenges. Recently, one of the actively researched areas lies in the additive manufacturing of smart materials and structures. Smart Materials (or Stimulus-Responsive Materials - SRM) are those materials that have the ability to change their shape and properties under the influence of an external stimulus (Temperature variation, light, humidity etc.). Taking advantages of these features, AM-fabricated components are able to alter their structure as a response to the applied stimuli from environment or through human interference. Hence, this gives rise to a new term called *"4D Printing"* to include the structural reconfiguration over time in AM processes. Despite being still in its infancy, this new field has attracted great interest since first conceptualization in 2013. 4D Printing is capable of achieving new ways of self-assembly, multi-functionality and self-repair, it can fabricate dynamic products with predictable adjustable shape, properties or functionalities.

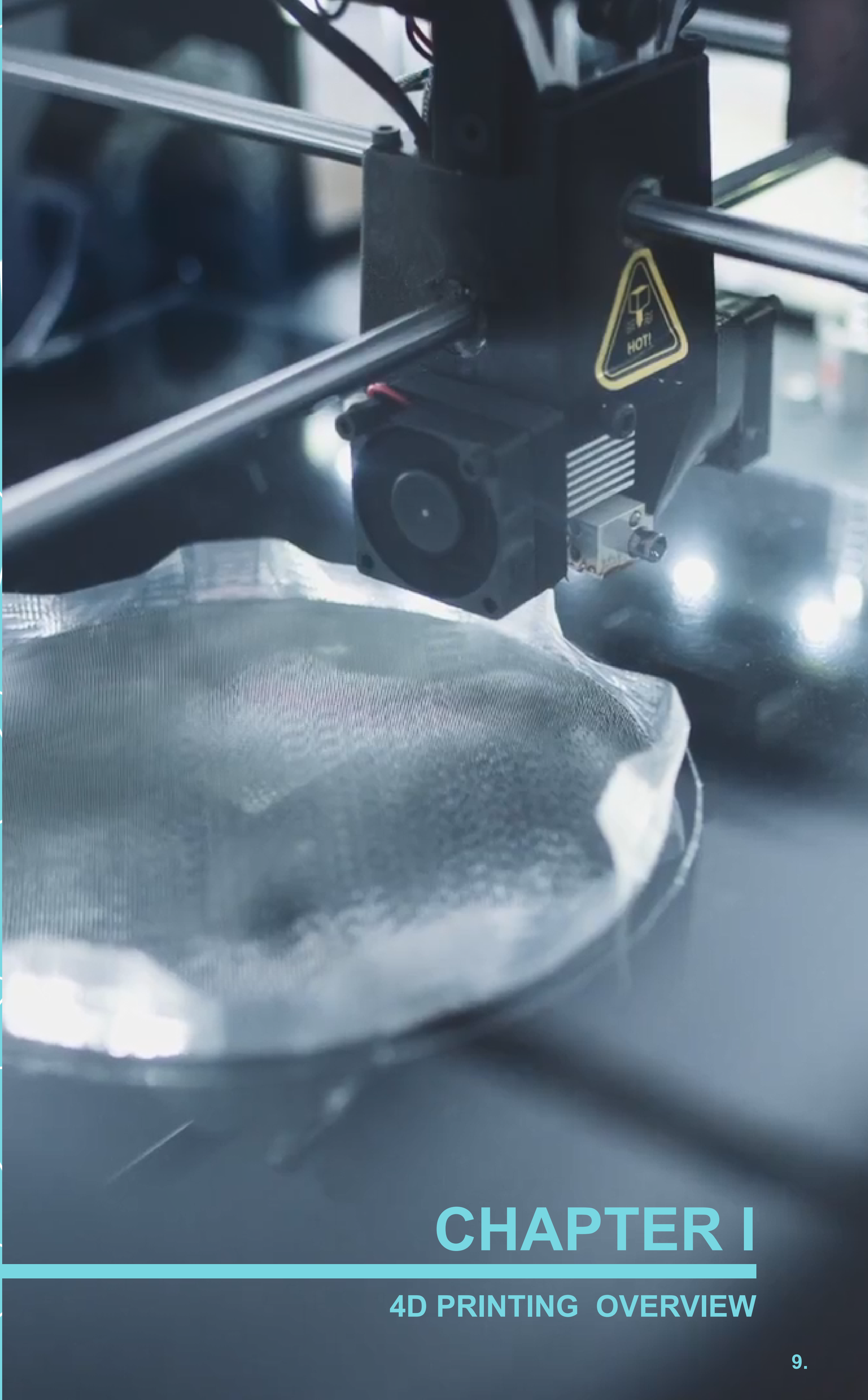
In this master thesis the major progresses of 4D Printing are reviewed in order to evaluate future directions of this new research field. After a brief overview of the state-of-the-art of 4D Printing technologies and smart materials, in the second chapter, principles, theoretical models and tools are presented, which are at the base of the design of 4D printed structures. Relevant benefits and limitations are discussed in the third chapter, considering manufacturing, materials features and design process. Moreover, some detailed case studies are analyzed in fourth chapter, while the final chapter is a general summary of the main challenges and outlooks with a overview of the future potential applications. According to the latest predictions, 4D Printing will take more than 10 years in its path to bring feasable results to mainstream reality.

Keywords: Additive manufacturing (AM), 3D Printing, 4D Printing, Smart Materials, Stimulus Responsive Materials (SRM), Shape Memory Materials (SMM), Active Origami

La produzione additiva (Additive manufacturing - AM) è stata introdotta alla fine degli anni ottanta e sebbene siano stati compiuti notevoli progressi, sono ancora necessarie molte ricerche per superare le varie sfide produttive. Recentemente, una delle aree in cui si sta concentrando la ricerca è la produzione additiva di materiali e strutture intelligenti. I materiali intelligenti (Smart Materials or Stimulus-Responsive Materials - SRM) sono quei materiali che hanno la capacità di cambiare la loro forma e le loro proprietà sotto l'influenza di uno stimolo esterno (variazione di temperatura, luce, umidità ecc.). Traendo vantaggio da queste caratteristiche, i componenti fabbricati con le tecniche additive sono in grado di alterare la loro struttura, come risposta agli stimoli applicati dall'ambiente o da interferenze umane. Questo dà origine a un nuovo termine chiamato *"Stampa 4D"* (4D Printing - 4DP) per includere nella produzione additiva la riconfigurazione strutturale nel tempo. Nonostante sia ancora alla sua infanzia, questo nuovo campo ha suscitato grande interesse sin dalla sua prima concettualizzazione nel 2013. La Stampa 4D infatti è in grado di raggiungere nuovi modi di auto-assemblaggio, multi-funzionalità e riparazione automatica, può fabbricare prodotti dinamici con forma, proprietà o funzionalità regolabili.

In questa tesi di laurea vengono esaminati i principali progressi della Stampa 4D per valutare le direzioni future di questo nuovo campo di ricerca. Dopo una breve panoramica dello stato dell'arte, delle tecnologie di Stampa 4D e dei materiali intelligenti; nel secondo capitolo sono presentati i principi, i modelli teorici e gli strumenti alla base della progettazione delle strutture 4D. I vantaggi e le limitazioni sono discussi nel terzo capitolo, considerando la produzione, le caratteristiche dei materiali e il processo di progettazione. Inoltre, alcuni casi studio sono presentati e analizzati nel quarto capitolo; mentre il capitolo finale è una sintesi delle principali sfide e prospettive, con una panoramica sulle potenziali applicazioni future. Secondo le ultime previsioni, la Stampa 4D impiegherà più di 10 anni nel suo percorso per portare risultati fattibili nella realtà mainstream.

Parole chiave: Produzione additiva, Stampa 3D, Stampa 4D, Materiali Intelligenti, Materiali a Memoria di Forma, Active Origami



CHAPTER I

4D PRINTING OVERVIEW

1.1 INTRODUCTION

Additive manufacturing (AM), commonly known as three-dimensional 3D printing or rapid prototyping (RP) is a series of various processes and technologies in which material is joined or solidified under computer control to create a three-dimensional object, using digital data from a 3D model [1]. It has been introduced in the late 1980s by Chuck Hull, inventor of the solid imaging process known as stereolithography (SLA), and Scott Crump, inventor of fused deposition modeling (FDM) and co-founder of Stratasys (One of the biggest manufacturer of 3D printers and 3D production systems for office-based rapid prototyping).
3D printing provided a new manufacturing route that could overcome the various limitations in processing materials by conventional methods. The main advantages of these technologies are based on the fast fabrication of mock-ups and prototypes for functional and design evaluation, allowing the experimentation with physical models of any complexity in a relatively short time. In this way, product designers can increase part complexity with little effect on lead time and cost.
Nowaday 3D printing has many different applications: it has been used to manufacture end-use products, 3D printed electronics, fashion and jewellery products, food design, healthcare products and living biological structures. There have been huge advancements in the area of additive manufacturing and there is still a lot of research work to be done in order to overcome the various challenges.

Over the past few years, the number of materials manufactured by 3D printing has increased by a large extent. One category of materials that has been in the spotlight recently are the so called Smart Materials (Also known as Stimulus-responsive Materials). Although Smart Materials are widely researched and used in practice, there is still disagreement on the definition. In general, Smart Materials can be defined as materials that can sense fluctuations in its external environment (Heat, light, humidity, magnetic field etc.) and generate a useful response by either changing their material properties or geometries [2]. Due to the ability of Smart Materials, the 3D fabricated components consisting of such materials would be able to evolve in a predefined manner. This gives rise to a new concept called “4D Printing” to include the structural reconfiguration over time (**Figure 1.1**).
4D Printing derives from the fast growth and interdisciplinary research of 3D Printing, Smart Materials, and Design [3]. Currently, 4D Printing is still in its infancy, but it has become an branch of additive manufacturing and attracts great interest from academia of different disciplines and industries. 4D Printing progresses made in research has allowed experiments in various fields of smart devices (Personal responsive products, adaptive infrastructure, space applications etc.). Methods based on self-folding and origami principles are used to design and produce different active origami structures, flats sheet automatically folds into a complicated 3D component under specific stimuli [4].

This thesis analyzes the impact that 4D Printing (4DP) is having and which will be its future role in the field of Design and Engineering. In the first chapter 4D Printing is presented with its main features. Hence, principles and methods of self-folding structures are reviewed, with theoretical models and design tools used to design 4D printed products. Furthermore in the third chapter advantage and disadvantages of 4D Printing are analyzed. In addition, some chase studies are also reviewed with the aim of giving a vision of the main innovations both from the technological and design point of view. At last, the summary of the main points covered in the thesis is given in the conclusion with an overview of the future potential applications and challenges.
The first chapter is a general presentation of 4D Printing, starting from definitions, first researches and the main differences compared to the 3D printing methods. In the second half of the chapter, the main printing technologies and smart materials are reported, with shape-shifting mechanisms and fields of application.
In last section an adapted diagram is showed, that is the summary of all the features of 4D Printing covered in this chapter.

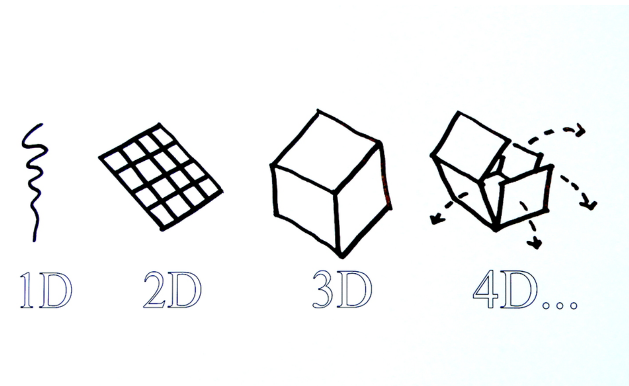


Figure 1.1 *Simple illustration of the 4D printing concept.*

1.2 DEFINITIONS

In order to differentiate 3D printing from 4D printing, the definition of 4D printing needs to be properly defined becouse it incorporates differences in definitions and characteristics.

4D Printing was initially defined by Skylar Tibbits (Director of the Self-Assembly Lab at the MIT) as 4D printing = 3D printing plus time, where the shape, property, or functionality of a 3D printed structure can change as a function of time. According to Tibbits: *"It entails multi-material prints with the capability to transform over time, or a customised material system that can change from one shape to another, directly off the print bed ... the fourth dimension described here as the transformation over time, emphasising that printed structures are no longer static, dead objects; rather, they are programmably active and can transform independently"* [5].

On the other hand, according to Eujin Pei (Programme Director for the BSc Product Design): *"4D printing is the process of building a physical object using appropriate additive manufacturing technology, laying down successive layers of stimuli-responsive composite or multi-material with varying properties. After being built, the object reacts to stimuli from the natural environment or through human intervention, resulting in a physical or chemical change of state through time"* [2]. The main difference between them is that Pei considered 4D printing to incorporate either a physical or chemical change of state while Tibbits et al. only considered shape changes.

Number of studies conducted on the technology has increased, so a more comprensive definition is presented. 4D Printing is capable of achieving self-assembly, multi-functionality and self-repair, it is time dependent, printer-indipendent and predictable, it can fabricate dynamic structures with adjustable shape, properties or functionality.

Zhong Xun Khooa, Joanne Ee Mei Teoh et al. review some examples of 3D printed smart materials/structures that are regarded as 4D printing [4]. On their paper based on the Tibbits and Pei definitions they give their definition of 4D Printing. According to them: *"We shall define 4D printing as an additive manufacturing process that integrates smart materials into the starting form of the printing material for 3D printed structures/components. After fabrication, the 3D object would respond in an intended manner to external stimuli from the environment or through human interference, resulting in a change in shape or physical properties over time."* [2].

1.3 ORIGIN AND FIRST RESEARCHES

4D Printing was initiated and termed by a research group at MIT directed by Skylar Tibbits (American designer/ computer scientist and founder of the Self-Assembly Laboratory in Massachusetts Institute of Technology). Collaborating with the Stratasys Materials Group, the researchers produced a composite polymer composed of highly hydrophilic elements (Hydro-reactive polymers) and non-active, rigid elements. Hydro-reactive parts of the printed chain swelled up to 150% in water, while the rigid elements set structure and angle constraints for the transformed chain. Tibbits printed a chain made with this composite polymer that would spell "MIT" when submerged in water (**Figure 1.3**). The results of these researches were presented for the first time at TED Conference in 2013 by Skylar Tibbits, with the name *"The emergence of 4D printing"* [6] (**Figure 1.2**).

Qi Ge et al. published the first research paper on 4D printing in 2013 by using the concept of printed active composites (PACs) where a printed sheet can transform into a complex configuration by using Shape Memory Materials (SMMs) [7]. Since then, 4D printing spurred great attention in research communities of smart materials and 3D printing.

Figure 1.2 *Skylar Tibbits's talk during TED Conference.*

Figure 1.3 *Transformation over time of the printed chain made of active composite polymers (from top to bottom).*

Qi Ge et al. based on their previous research on printed active composite materials, advance the 4D printing concept to the design and fabrication of active origami structures [8]. They print active composites with shape memory polymer fibers precisely printed in an elastomeric matrix and use them as intelligent active hinges to enable origami folding patterns. They develop a theoretical model to provide guidance in selecting design parameters such as fiber dimensions, hinge length, and programming strains and temperature. Using the model, several active origami components were designed and fabricated which assemble from flat polymer sheets, including a box, a pyramid, and two origami airplanes.

1.4 PERSPECTIVE AND OUTLOOK

4D printing has spurred great interest since its conception 5 years ago. Many different printing processes, materials, and actuation methods have been tested in this period. However, similar to many other emerging technologies, there are still many challenges facing the embryonic 4D printing for practical applications. While many of these challenges are the target for intensive research, 4D printing is still very young and needs a significant amount of efforts for future development.

Currently some perspectives and outlooks have been advanced. The *Gartner hype cycle* provides the evaluation of emerging technologies that will potentially connect with new business ecosystems over the next 5–10 years in five stages [9]. This hype cycle looks at emerging technologies and predicts the possibilities of these new technologies for practical applications with high competitive advantage. Along with other new technologies, such as smart robots, quantum computing and human augmentation, 4D printing is in the innovation triggering stage and the expectation would increase with time (**Figure 1.4**). Looking at the time, 4D printing will take more than 10 years to bring real results.

According to Xiao Kuang et al., 4D printing is a very active topic as indicated by the rapid growth in the number of publications (Searching by 4D printing and 3D printing of shape memory polymers (SMPs)) in the past 5 years (**Figure 1.5**) [3]. It is also noted that the citations increase more dramatically than the publications (**Figure 1.6**) [6]. Holding nearly 42% of the total publications, the United States is the most active country in this area with China and Singapore following behind. Thus, 4D printing research starts to be recognized in academia, which will generate further hype and interest in the years to come.

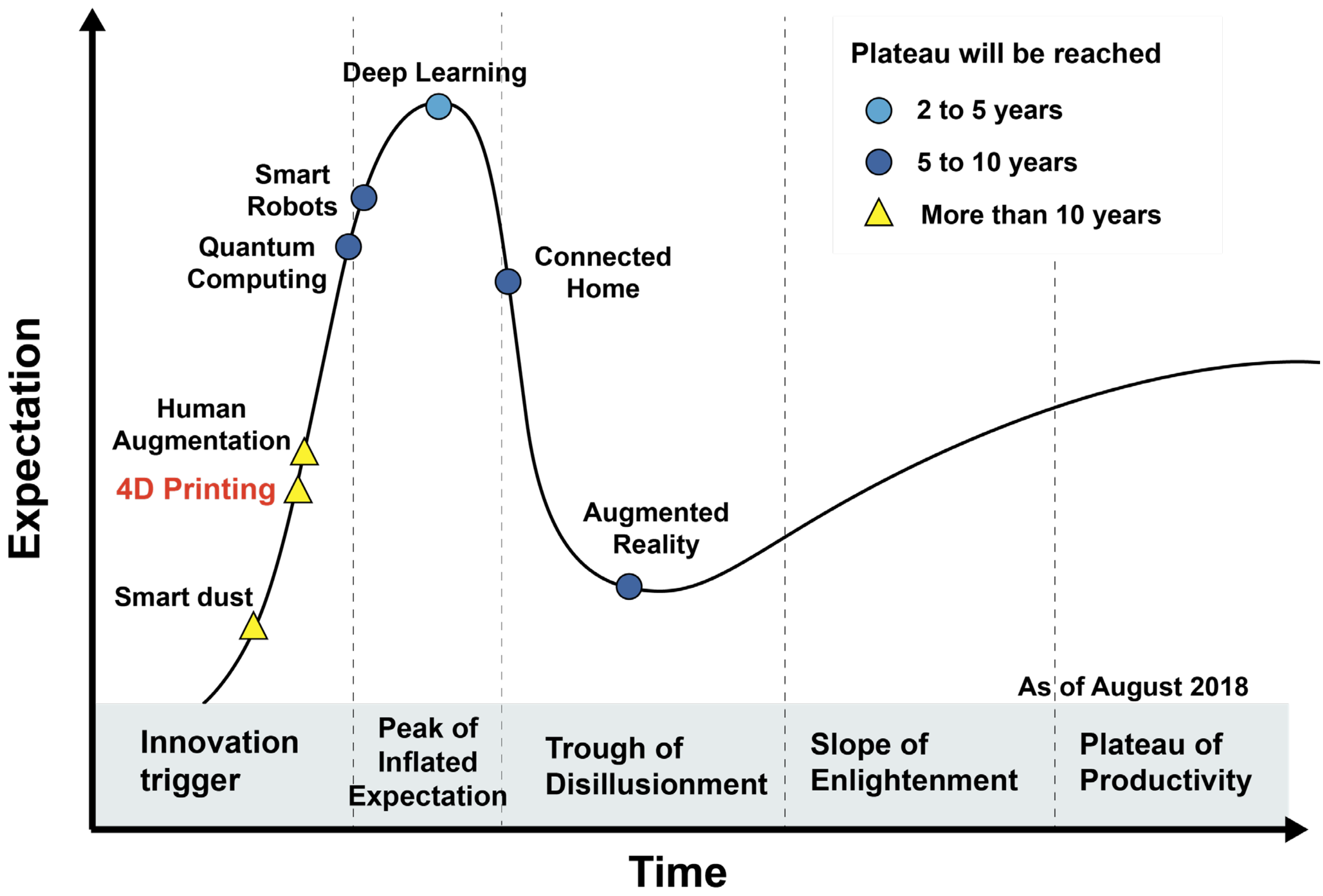


Figure 1.4 *Adapted Gartner hype cycle for emerging technologies (2018).*

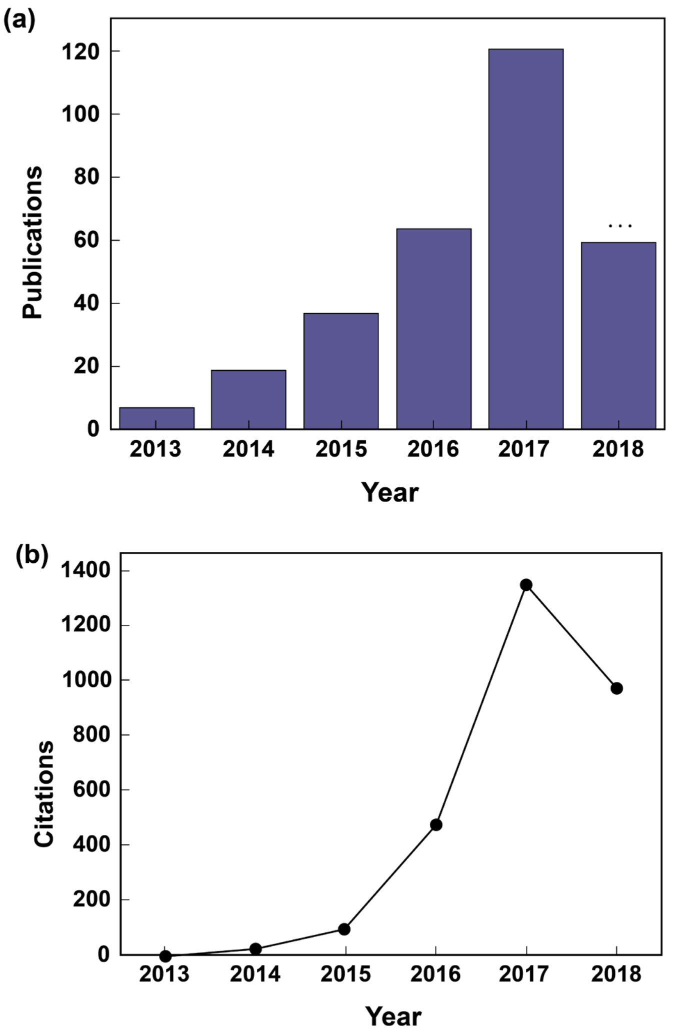


Figure 1.5 *The statistics data of publication on the topic of 4D printing or 3D printing of shape memory polymer from Web of Science.* **a)** *publications,* **b)** *citations in each year.*

1.5 DIFFERENCES BETWEEN 3D PRINTING AND 4D PRINTING

The adapted diagram from F. Momeni et al. illustrates the main differences between 3D printing and 4D printing [10] (**Figure 1.6**). As shown in the graph, 3D Printing and 4D Printing are characterized by different elements respectively.

On on hand, 3D Printing is about repeating a 2D structure, layer by layer in a print path, from the bottom to the top until a 3D volume is created. A large number of materials and additive processes are available, especially thanks to the great progresses made by the first 3D printing techniques. The differences between processes are in the way layers are deposited (material extrusion, vat photo-polymerization, powder bed fusion etc.) to print products and in the materials that are used. Objects printed with 3D Printing technology, are characterized by *Static Structure* with a certain rigidity. That means that 3D printed objects are going to keep their 3D shape in time once printed.

On the other hand, as it has already been mentioned, the big breakthrough about 4D Printing over 3D Printing is its ability to change shape over time. Objects printed with 4D Printing technology, are characterized by a *Smart Static Structure* that under the corresponding external stimulus it shifts to the another state called *Smart Dynamic Structure*.

Unlike 3D Printing, 4D printing is mainly characterized by five elements which enable predictable evolution of 4D printed structures [5]. These elements are:

3D Printer: Usually a 4D printed structure is created by combining several materials in the appropriate distribution. The differences in material properties, such as swelling ratio and thermal expansion coefficient, will lead to the desired shape-shifting behavior. Therefore, 3D printing is necessary for the fabrication of multi-material structures with simple geometry.

Stimulus: It is required to trigger the alterations of shape/property/functionality of a 4D printed structure. The stimuli that researchers have used in 4D printing include mainly water, heat, a combination of heat and light, and a combination of water and heat. The selection of the stimulus depends on the requirements of the specific application, which also determines the types of smart materials employed in the 4D printed structure.

Smart Material: Stimulus-Responsive Material is one of the most critical components of 4D printing. Smart Material are capable of transformation when there is a change in the environment and this coupling effect or interaction can result in a mechanical response due to *field-induced eigenstrain* (a deformation produced without external forces such as thermal expansion or phase change) in the smart material, or resulting in an indirect mechanical response due to a field-induced change in stiffness. The transformational characteristics of smart materials include self-sensing, responsiveness, shape memory, self-repair, self-adaptability, and multi-functionality.

Interaction mechanism: In some cases, the desired shape of a 4D printed structure is not directly achieved by simply exposing the smart materials to the stimulus. The stimulus needs to be applied in a certain sequence under an appropriate amount of time. For example, one of the main interaction mechanisms is constrained-thermo-mechanics. In this mechanism, the stimulus contains a 4-step cycle. First, the structure is deformed by an external load at a high temperature; second, the temperature is lowered while the external load is maintained; third, the structure is unloaded at the low temperature and the desired shape is achieved, fourth, the original shape can be recovered by theating the structure.

Mathematical Modeling: Mathematics is necessary for 4D printing in order to design the material distribution and structure needed to achieve the desired change in shape, property, or functionality. Mathematics provides the theoretical models to create algorithms, simulation programs and design tools that let to predict the shape evolution after printing over time and to avoid collisions between components of the structure during the self-assembly operation.

1.6 4D PRINTING TECHNOLOGIES

According to the American Society for Testing and Materials (ISO/ASTM 52900:2015), there are over 50 different AM technologies that can be classified into seven different categories: binder jetting, material jetting, material extrusion, vat photo-polymerization, powder bed fusion, energy deposition, and sheet lamination.

There are several 3D printing technologies suitable for processing smart materials for 4D printing listed below [3]. Since most 4D printing methods use polymers, either single material or multi-material, in this thesis it is provide a brief introduction on the 3D printing methods for polymers.

1.6.1 FFF and DIW (extrusion-based methods)

The most used 3D printing processes are extrusion-based methods, including fused filament fabrication (FFF or fused deposition modeling (FDM)) and direct ink writing (DIW) (**Figure 1.7**). Both methods form a 3D object depositing material in a layer-by-layer manner. The difference is that FFF melts a solid filament in a heating nozzle, whereas DIW deposits a viscous liquid “ink” that can be cured later. One of the main advantage of the extrusion methods is that they can print a wide range of materials. For example, a wide range of engineering thermoplastics can be printed by FFF, whereas DIW, assisted by a post-cure, can be used to print different thermosetting polymers.
The resolution of FFF and DIW is limited by the nozzle diameter, which is typically in the range of 100–200 μm. Another limitation of the extrusion-based method is the low printing speed, although a higher speed can be achieved when multiple nozzles are used. In general, it is difficult to print multiple materials by using the FFF method because different thermoplastics may have different printing temperatures, resulting in poor interface bonding between two different materials. DIW, on the other hand, can be used for multi-material printing if the two polymer resins are compatible with each other.
Much attention has been given especially to DIW in the printing of smart materials, method heavily utilized in meso- and micro-scales. For example, DIW has been used to print Hydrogels and Polymer nanocomposites

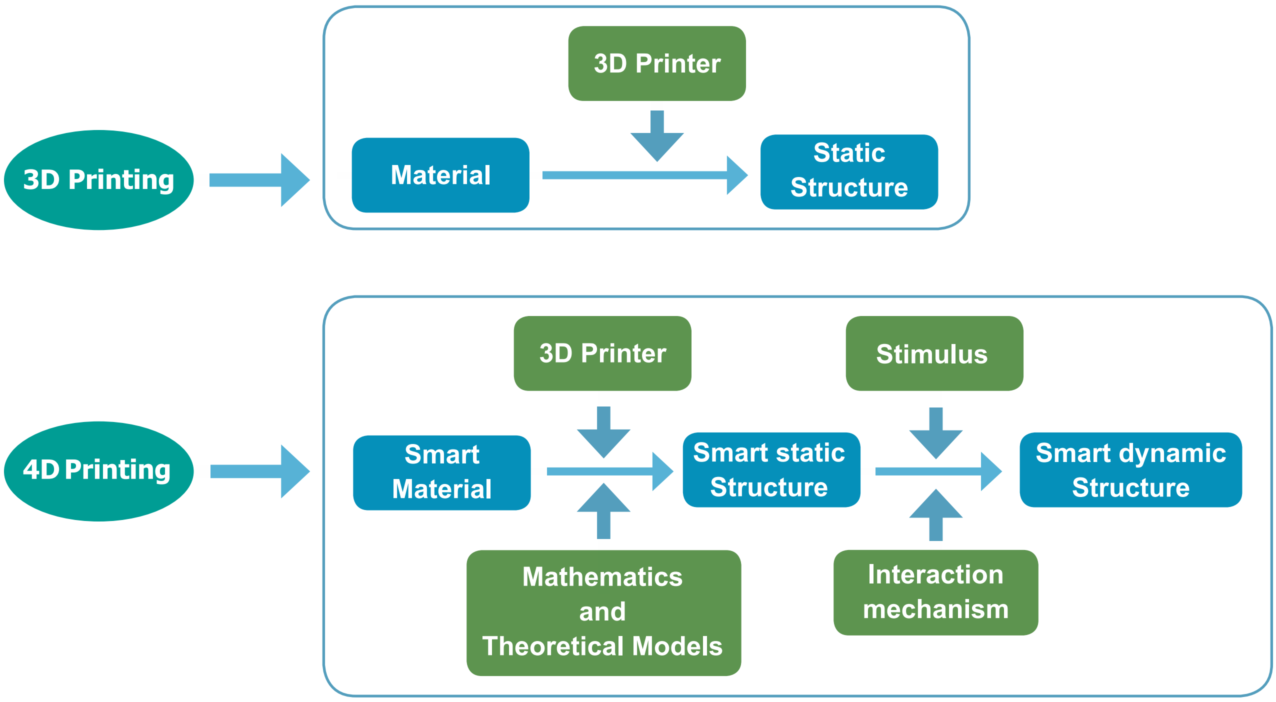


Figure 1.6 *The adapted F. Momeni et al.‘s diagram of the difference between 3D Printing and 4D Printing.*

consisting of a polymer matrix and nanoparticles including carbon based ones such as carbon nanotubes [3].

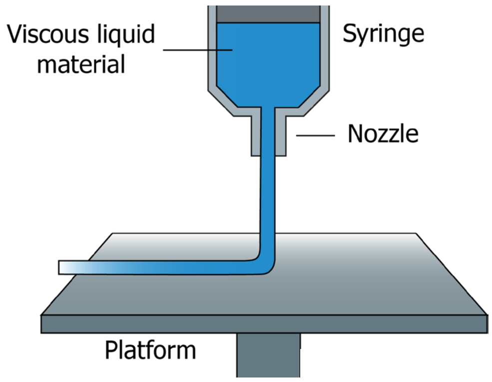


Figure 1.7 *Representation of* Direct Ink Writing (DIW) *3D printing.*

1.6.2 Inkjet (Material jetting)

Inkjet 3D printing is another popular method for polymer printing and it can use multiple printheads to simultaneously spray different photocurable liquid resins on the printing bed to form a layer followed by UV curing (PolyJet). This allows the easy fabrication of parts composed of multi-materials at a relatively high resolution (**Figure 1.8**). Typical in-plane resolution of an inkjet printer is ≈30–40 μm for single-material printing. However, the resolution drops quickly to 200–400 μm when multiple materials are printed [3].

Inkjet is also used to print biocompatible materials for medical applications, such as mouthguard, reproduction of study models, surgical guides for implant placement, sleep apnea appliances, orthodontic bracket guides, and try-in veneers [11].

The already mentioned Qi Ge et al. in their research used multi-material Inkjet printer Objet Connex 260 from Stratasys to print their Active materials and Active origami structures [7].

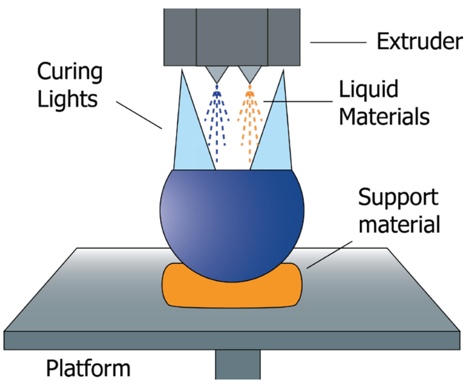


Figure 1.8 *Representation of PolyJet photopolymer (PPP) 3D printing.*

1.6.3 SLA, DLP and PμSL (vat photopolymerization)

Another method for 3D printing of polymers is the so-called vat photo-polymerization. A laser beam or a UV light can be used as a light source to induce photocuring, which is called stereolithography (SLA) and digital light processing (DLP), respectively.

DLP (Digital Light Processing) is a similar process to stereolithography since it is a 3D printing process that works with photopolymers. The major difference is the light source. DLP uses a more conventional light source, such as an arc lamp with a liquid crystal display panel, which is applied to the entire surface of the vat of photopolymer resin in a single pass, generally making it faster than SLA. It is becoming increasingly popular in recent years because it can cure a layer of resin at one time and thus can print parts very fast [3].

Highresolution (micro- and nanoscale) DLP can be achieved with optical lens systems called projection micro-stereolithography (PμSL) (**Figure 1.9**). PμSL adapts 3D printing technology for micro-fabrication. This technique allows for rapid photo-polymerization of an entire layer with a flash of UV illumination at micro-scale resolution. The mask can control individual pixel light intensity, allowing control of material properties of the fabricated structure with desired spatial distribution.

Materials include polymers, responsive hydrogels, shape memory polymers and bio-materials.

As already mentioned Qi Ge et al. [12] demonstrated the feasibility of PμSL printing some high resolution multimaterial shape memory polymer (SMP) architectures.

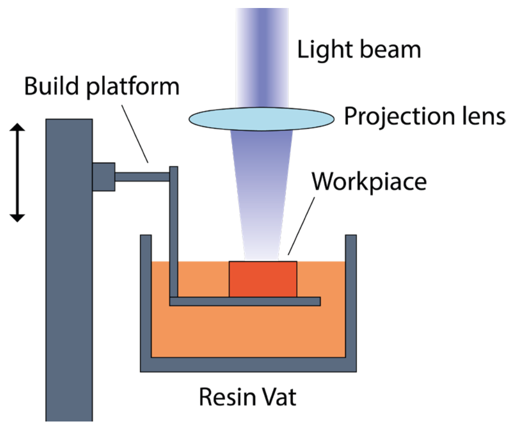


Figure 1.9 *Representation of* projection micro-stereolithography (PμSL) *3D printing.*

1.6.4 SLS, MJF (powder bed fusion–based methods)

The last major group of polymer 3D printing methods is the powder bed fusion–based methods, including selective laser sintering (SLS) and multijet fusion (MJF). MJF uses

two perpendicular carriages that work concurrently to process parts one applies a fresh layer of material across the work area, while the other prints functional agents. In a continuous pass, the carriage that prints the functional agents also provides the energy source needed to sinter the material (**Figure 1.10**).
MJF uses the absorption of infrared light as heat source after jetting the fusing agent, which is faster and cheaper than SLS technique by using a laser [3].

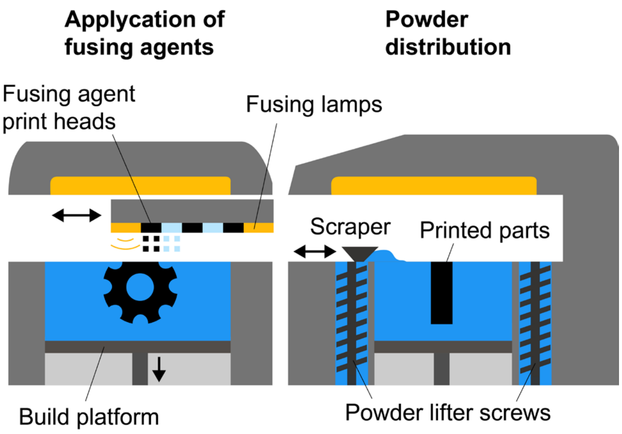


Figure 1.10 *Representation of* multi-jet fusion (MJF) *3D printing.*

1.7 SHAPE-SHIFTING MECHANISMS AND STIMULI

4D Structure can alter its shape, propierties, or functionality based on one or more stimuli. However, an interaction mechanism needs to be identified for which the printed smart structure can respond to stimulus in a appropriate way. The mechanisms can be divided into various categories. In this thesis, mechanisms from literature are organized and summarized as follow.

1.7.1 Hydro-mechanisms

In this mechanism, a smart printed structure consists of an expandable active material and a rigid material.
Water is utilized as the external stimulus so that the structure can undergo shape-shifting under water and so that it can return to its original shape after being dried (**Figure 1.11**) [10]. This mechanism is driven by the different swelling ratios between the active and rigid materials. The expansion of the smart material generates a force that leads to the shape change. When the expandable material is appropriately arranged with the rigid material, complex shape-shifting behavior can be achieved. The magnitude and the direction of the shape change depends on the spatial arrangements of the two materials.
Tibbits et al. used this type of mechanism in their first experiments on shape-shifting structures [5].

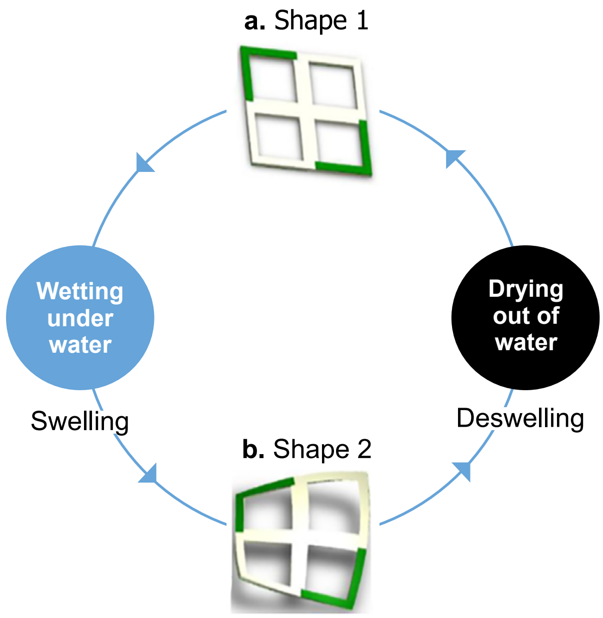


Figure 1.11 *Schematic illustration of the unconstrained-hydro-mechanics mechanism in 4D printing. The green parts represent expandable materials.*

1.7.2 Thermo-mechanisms

Two levels of temperature and one external load are required in this mechanism. One temperature is higher than the Critical Temperature (**Tc**) of the smart material, such as its Glass Transition Temperature or Crystal-Melt Transition Temperature (**Th>Tc**). The other temperature should be lower than the Critical Temperature (**Tl<Tc**). In this mechanism, the printed structure is heated to **Th** and the cycle starts at **Th** in the following order. First, the original structure is stretched at **Th** with certain amount of strain depending on specific applications. Then, under external stress,the structure is cooled to **Tl** while the strain remains unchanged. Next, the external stress is removed at **Tl**, and the desired temporary shape is obtained at the end of this step. Finally, the structure can be reheated to **Th** in a free stress condition to recover its original shape. In this mechanism, temperature is the external stimulus (**Figure 1.12**) [10]. Ge et al. applied this mechanism in their experiments [7] [8] [12].

Unlike the previous mechanism, the external load is not included in the cycle of the mechanism. Only the two temperatures are required. One is higher than critical temperature of the active material involved in the structure, and the other one is lower than the critical temperature. The printed structure is first heated to Th (**Figure 1.13**) [10]. The cycle then starts at Th and proceeds in the following manner. First, the original structure is cooled to Tl, where the desired shape is achieved at the end of this step. Then, the structure can be heated to Th to recover its original shape.

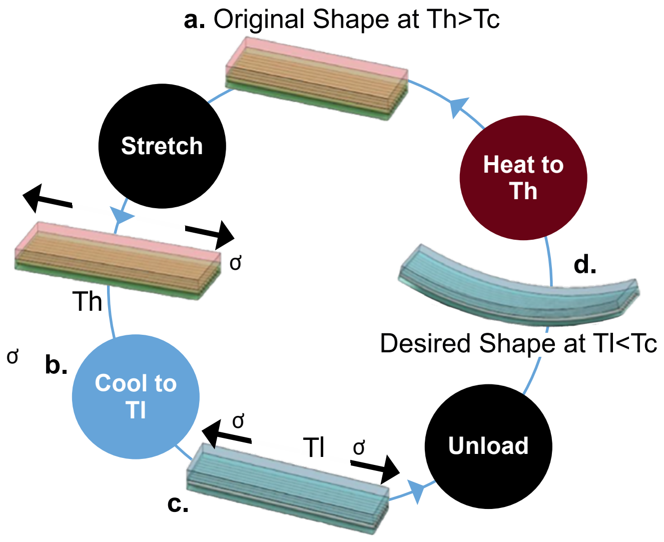


Figure 1.12 Adapted *schematic illustration of the constrained-thermo-mechanism in 4D printing.*

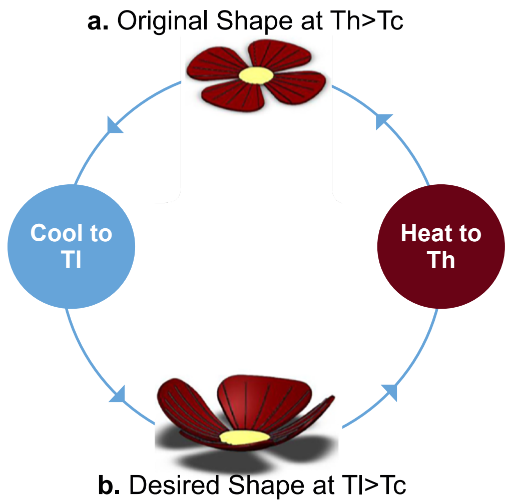


Figure 1.13 Adapted *schematic illustration of the uncontrained-thermo-mechanics in 4D printing.*

1.7.3 Photo-mechanisms

Light driven actuation can worked on the principle of radiative heating. Here, however, we consider actuation driven by micro-structural changes directly caused by light irradiation. Folding of polymer films with light was investigated by Ryu and coworkers **[13]**. The mechanism used for self-folding in their work was localized photo-induced stress relaxation. Straining the composited polymer sheet and subsequently irradiating it with light dissociates specific photoinitiators into free radicals that react with and cleave along the polymer backbone. Such events irreversibly rearrange the network connectivity and macroscopically result in stress relaxation that generates the folds. The authors were able to create folded arcs and a closed cube-shaped box using this self-folding approach.

In another mechanism, fibers were considered to be photo-responsive materials and the matrix was considered to be a thermo-responsive material. Researchers showed that the application of light, heat, or a conbination of both stimuli could yield printed structures with various morphologies. In their study, the gel has a lower critical solution temperature. The spiro benzopyran (SP) chromophres functionalize elastic fibers, which can be converted into a hydrophobic form when subjected to blue light, and recover its hydrophilic form in the dark environments. Different behavior under exposure to light or heat is a result of local and global response. Light can be used to non-invasively enable local shape-shifting behavior in specific regions of the structures. The original composite shrinks like an accordion when heated freely and bends like a caterpillar when subjected to blue light (**Figure 1.15**) **[10]**.

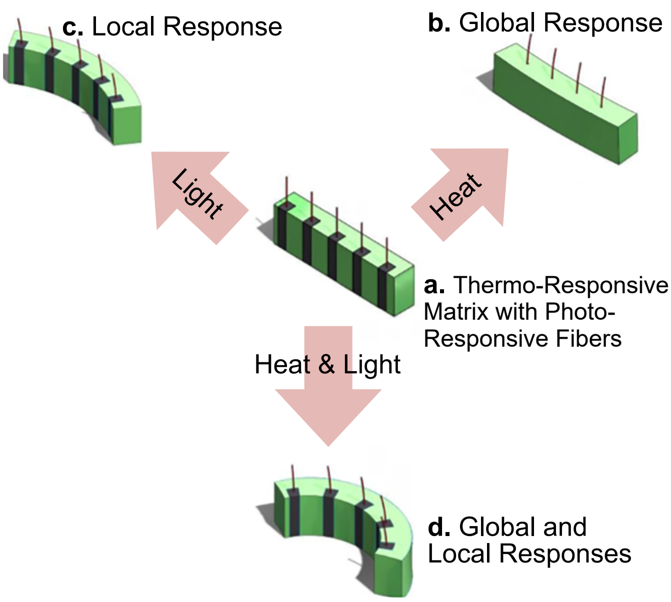


Figure 1.14 Adapted *schematic illustration of the uncontrained-thermo-photo-mechanism.*

1.7.4 Ph-mechanisms

This mechanism was demonstrated by Nadgotny et al. In this mechanism, a 4D Printed, ph responsive hydrogel can linearly swell at a specific ph level and then shrink at another designed ph level (**Figure 1.19**) **[14]**. This cycle is mainly conducted in an aqueous environment and is therefore suitable for the shape-shifting of hydrogels.
Many studies on ph-responsive hydrogels have been conducted in available literature. Nadgorny et al. provided ph-responsive hydrogels with a composition appropriate for printing, and enabled shape-shifting behavior with this mechanism **[10]**.

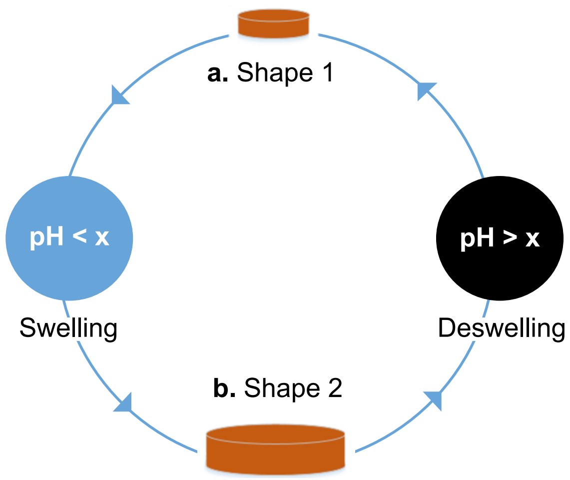


Figure 1.15 Adapted *schematic illustration of the unconstrained-ph-mechanism in 4D printing.*

1.7.5 Magnetic mechanisms

Yoonho Kim et al. report 3D printing of programmed ferromagnetic domains in soft materials that enable fast transformations between complex 3D shapes via magnetic actuation **[15]**. This approach is based on direct ink writing (DIW) of an elastomer composite containing ferromagnetic microparticles. By applying a magnetic field to the dispensing nozzle while printing, this reorient particles along the applied field to impart patterned magnetic polarity to printed filaments. This method allows to program ferromagnetic domains in complex 3D-printed soft materials, enabling a set of previously inaccessible modes of transformation, such as remotely controlled auxetic behaviours. Yoonho Kim et al. further demonstrate diverse functions derived from complex shape changes, including reconfigurable soft electronics, a mechanical metamaterial that can jump and a soft robot that crawls, rolls, catches fast-moving objects and transports a pharmaceutical dose (**Figure 1.16**). This case will be further analyzed in the fourth chapter.

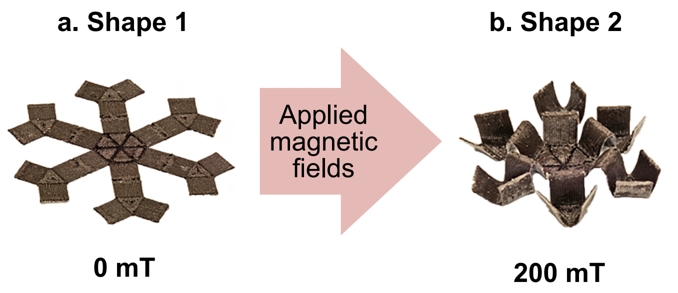


Figure 1.16 *Schematic illustration of the Unconstrained magnetic mechanics in 4D printing.*

1.8 SMART MATERIALS FOR 4D PRINTING

Smart materials can be classified as shape memory materials and shape-changing materials. Shape memory materials have the ability to recover to their original shape from a temporary shape when stimuli are applied and this is known as the shape memory effect (SME). Shape memory materials (SMMs) include shape memory alloys (SMAs), shape memory polymers (SMPs), shape memory gels (SMGs), shape memory ceramics (SMCs), and other shape memory hybrid (SMHs) materials. Shape-changing materials are materials that possess stimulus-induced behaviour, known as the shape-change effect (SCE). They morph in response to the stimuli and may return to its permanent shape when the stimuli are removed.

Shape memory polymers (SMPs) are more popularly used for 4D printing and they will be described in further detail in this paper.

In this section the major advances in 4D printing of polymeric materials are reviewed from the materials standpoint and their potential applications. The review is organized in the order of 4D printing by a single material, by multiple materials, and research activities on 4D printing of multifunctional materials.

1.8.1 Single Material

Simple way to achieve 4D printing is 3D printing a single smart material. The process usually needs to be based on the structure with a *gradient distribution* (Spatial variation of density in different location of the material). This anisotropy can generate shape-shifting behaviors such as bending and twisting, which is beyond linear expansion and contration. The most widely used single smart materials for shape shifting are the SMPs and liquid crystal elastomers (LCEs) **[3]**.

SMP (shape memory polymers): Predominantly polymeric materials that have an ability to revert back to its preprogrammed shape from a deformed (temporary) configuration when exposed to stimuli, such as heat or light. SMPs are preferred over the use of shape memory alloys (SMAs) as SMPs have a wide range of glass transition temperatures from − 70 to 100 °C, allowing their stiffness to be tailored **[22]**. SMPs have the potential to achieve a shape recovery property up to 400% of plastic strain, whereas SMAs are around 7–8%. SMAs are regarded disadvantageous due to complex manufacturing, higher costs, toxic, and with limited recovery.

For an SMP to achieve a shape-shifting behavior, it requires a *programming step* and a *recovery step*. In the programming step, the SMP is first deformed at a temperature above a *Transition Temperature* (**Tt**), then is cooled down to below **Tt**, and finally unloaded. Then the SMP is programmed (or fixed) in the deformed shape called *Temporary Shape*. Shape shifting is achieved through the *recovery step* where the SMP is heated to a temperature above Tt and the SMP recovers to its original shape due to the entropic elasticity. It is noted that the thermally triggered SMP can be achieved by direct heating or indirect heating via Joule heating, photo-thermal effect, and hysteresis effect, as well as remotely controlled by magnetic field.

Qi Ge et al. printed a refined and complex 3D printed structure Eiffel Tower with a single SMP using high resolution projection micro-stereolithography (PμSL) and a family of photo-curable methacrylate based copolymer networks [12]. Following the Shape Memory Cycle, a temporary bent shape was achieved by bending the Eiffel tower at 60 °C and removing the external load after cooling to 25 °C. After heating back to 60 °C, the bent Eiffel tower gradually recovered its original straight shape (**Figure 1.17**).

Figure 1.17 *3D printed SM Eiffel tower on a Singapore dollar that nonlinear large deformation SM behavior.*

LCE (liquid crystal elastomer): These materials are slightly crosslinked liquid crystalline polymer networks. These materials combine the entropy elasticity of an elastomer with the self-organization of the liquid crystalline phase. In liquid crystalline elastomers, the *mesogens* (or Liquid Crystal. It is a compound that displays liquid crystal properties) can either be part of the polymer chain (main-chain liquid crystalline elastomers) or they are attached via an alkyl spacer (side-chain liquid crystalline elastomers).
Side-chain or main-chain LCEs with liquid crystal molecules can undergo a large contraction along the direction of the mesogens (or nematic director) under external stimulus. These stimulus can be thermal or photo.

Yuan et al. demonstrated the potential of using LCEs in 4D printing to achieve reversible thermal actuation [18]. Kotikian et al. used the same strategy to achieve 3D printing of liquid crystal elastomeric actuators with spatially programmed nematic order in arbitrary form factors [16]. **Figure 1.18** shows the printed shapeshifting structures undergoing reversible 2D to 3D and 3D to 3D transformations.

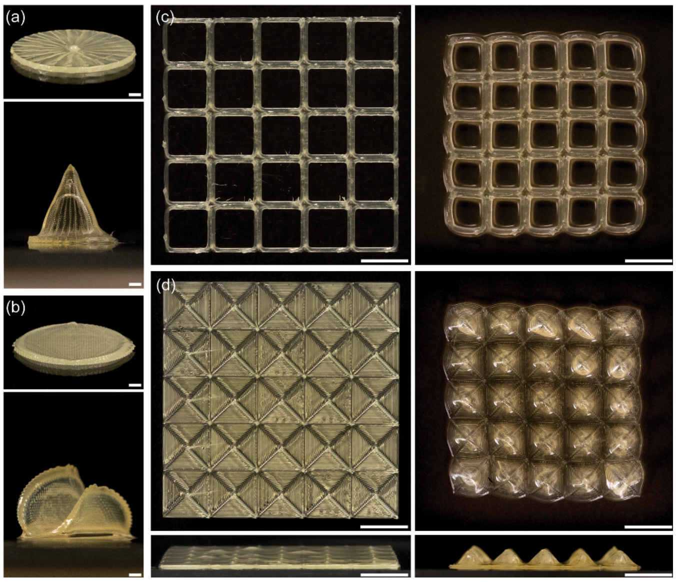


Figure 1.18 *Programmable shape morphing of LCE actuators from 2D to 3D (scale bars = 5 mm).*

1.8.2 Multimaterials and Composites

With components and multimaterials 3D printing has been explored to create components with locally controlled chemical compositions and mechanical properties. In a multimaterial structure, eigenstrains [4] (kind of strain/deformation produced without external forces) can be generated due to environmental stimuli; these eigenstrains are dependent on the relative positions and volume fractions of different materials and can drive the shape change of the structure. 3D printing has a advantage of offering the great flexibility of placing different materials at different spatial locations, and thus the opportunity of controlling the generation of eigenstrains and creating many innovative shape-shifting structures. In this section, it is summarized some widely used multimaterial systems, that are composite hydrogel and SMP composites.

Composite hydrogel: A group of polymeric materials, which hydrophilic structure renders them capable of holding large amounts of water in their three-dimensional networks [3]. Hydrogels are appealing materials for tissue engineering scaffold applications due to their hydrophilicity, which closely mimics highly hydrated natural biological tissues, thus increasing biocompatibility. However, hydrogels are limited by their mechanical weakness and compliance. There are two main categories that are Water-Responsive Composite Hydrogel and Thermal-Responsive Composite Hydrogel.

Tibbits et al. developed 4D printing by constructing a series of primitives (or hinges) with a rigid plastic base and a hydrophilic rubber (hydrogel) that swelled upon exposure to water by using a Connex Objet500 printer [5]. This hydrogel expansion induced the eigenstrain in the hinge and triggered a bending deformation. The folding angle of the printed active hinges could be precisely controlled by changing the spatial distribution of the two materials (the rigid plastic and the hydrogel). As shown in **Figure 1.19**, a 4D printed multimaterial strand could self-fold into a 3D cube.

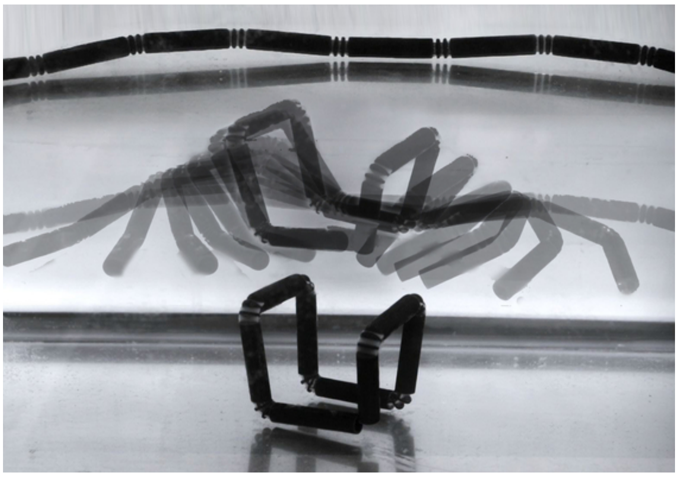


Figure 1.19 *Sequence showing the self-folding of a 4D printed multimaterial single strand into a 3D cube. Reproduced with permission.*

Multimaterial SMPs: Multimaterial 3D printing offers the opportunity to create digital materials that have different Tg values (or digital SMPs), which could be utilized for multiple shape shifting and sequential transformation. Mao et al. controlled the shape-changing sequences of 3D printed structures containing spatially distributed digital SMPs [3].

Qi Ge et al. demonstrates the printing of grippers with multiple SMPs that have the potential to function as microgrippers that can grab objects, or drug delivery devices that can release objects [12]. Compared to contemporary manufacturing approaches, Qi Ge et al.'s approach is simple and straightforward enabling stiffer grippers with thick joints made of SMPs (**Figure 1.20**). The capability of multimaterial fabrication enables to print the tips of the grippers with the materials different from the SMPs constructing the joints, and to design the stiffness of the tips based on that of the object to realize a safe contact.

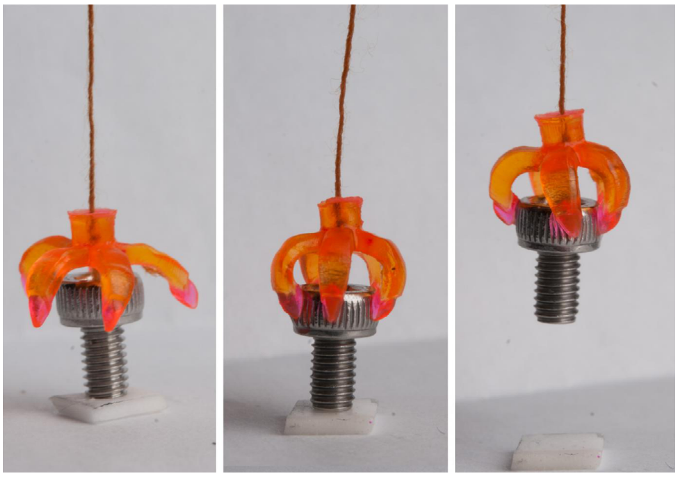


Figure 1.20 *A time-lapse of an SMP gripper developed for grabbing and releasing an object through heat transmission.*

SMP Composites: About Fiber-Reinforced Active Composites, one of the early works on SMP-based 4D printing was based on PAC introduced by Ge et al. [8].
The PAC was printed by the multimaterial 3D printer (Connex Objet260, Stratasys) consisting of glassy polymer fibers (VeroWhite) in a rubbery matrix (TangoBlack). The glassy polymer has a glass transition temperature of 60 °C and thus was used as an SMP. Ge et al. used a laminate composed of a pure rubber lamina and a composite lamina with parallel fibers in the rubber matrix. After the laminate was printed, it was heated, stretched, cooled, and released. After the release of the external stress at the low temperature, the composite turned into a complex temporary shape (**Figure 1.21**). Depending on the fiber distribution and orientation, various complex 3D configurations could be obtained, including bent, twisted, coiled, and folded shapes. The SMP composites could be used as smart hinges to enable active origami for creating complex 3D architectures.

Another variaton of SMP Composites is Bilayer SMP. A bilayer laminate strip was printed by Ding et al. using Connex3 Objet500 (Stratasys) with TangoBlack+ as the elastomer and VeroClear as the SMP [17]. After the printing and heating above the Tg (Glass Transition Temperature) of the SMP, the laminate bent into a new permanent shape.

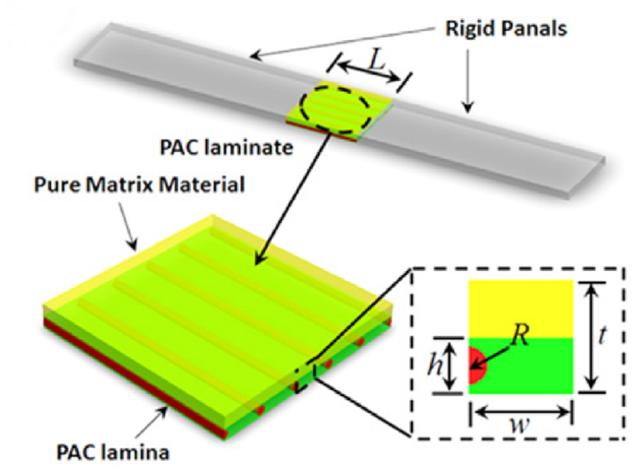


Figure 1.21 *Schematics of a PAC hinge and the thermo-mechanical programming steps.*

1.8.3 Multifunctional Materials

Recently, 4D printing concept has been expanded from its initial definition of shape shifting to including the function or property shifting. Printed functional objects, such as electronic devices, have been combined with the shape changing to achieve 4D printing of functional devices. Also some functional properties, such as optics or conductivity properties, can also evolve with the process of shape changing for functional 4D printing.
Third, the time-dependent functional properties, such as tissue maturation, degradability, self-healing, or color shifting for 3D printed constructs, can be broadly termed as 4D printing.

4D Bioprinting: It refers the printed 3D biocompatible materials or living cellular structures that evolve over time after printing. 4D bioprinting includes both the shape-shifting biomaterials and the maturation of engineered tissue constructs enabled by 3D printing.

Villar et al. [18] shows that a flower-shaped network constructed by printing two layers of droplets with different osmolarities self-folded spontaneously into a hollow sphere due to the swelling or shrinkage mismatch induced by the flow of water (**Figure 1.22**).

Kang et al. reported an integrated tissue–organ printer (ITOP) that can fabricate stable, human-scale tissue constructs of any shape [3]. the ITOP was shown to enable fabrication of mandible and calvarial bone, cartilage, and skeletal muscle. 4D bioprinting shows great potential for future biomedical applications, such as tissue engineering, drug delivery, and building functional organs that are suitable for transplantation and organ regeneration.

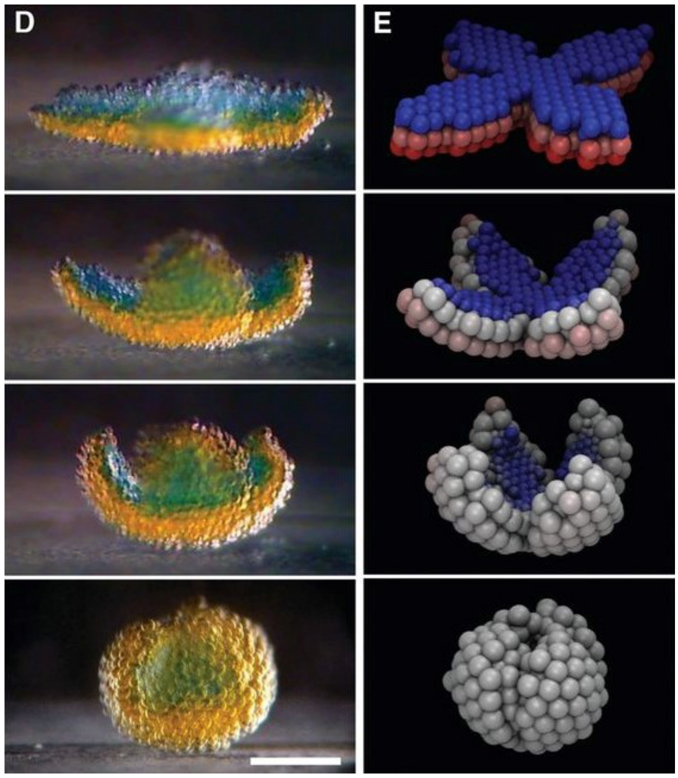


Figure 1.22 *The experiment related to 2D to 3D self-bending in which a flower-shaped network transforms into a hollow sphere.*

Self-Healing Materials: These materials have been fabricated to enable structural restoration and function recovery of materials so as to enhance reliability and extend the lifetime of material systems.
3D printing of self-healing materials, with the capability of crack healing after printing, has been investigated recently. Early in 2009, Hansen et al. used a dual ink deposition method to print interpenetrating microvascular networks, which were used to supply multiple healing agents encapsulated with a layer of thermoset coating [4]. Upon damages, capillary action drove the release of the healing agent into the crack, which could be polymerized for repeated and autonomous healing of mechanical damage.

Kuang et al. developed UV-assisted DIW printing to fabricate a semi-interpenetrating polymer network elastomer with complex structures as well as high strain SME and repeated self-healing capability [3]. The diffusion and re-entanglement of linear PCL chain in crack interfaces upon heating led to repeated crack healing. In addition, the high strain shape memory effect could assist large crack healing. Vitrimers (Class of plastics, which are derived from thermosetting polymers), or covalent adaptive networks, are able to change their network topology through bond exchange reactions and can be used for thermosets' self-healing and reprocessing. Bond exchange reactions are typically achieved by using different types of dynamic covalent bonds, such Diels–Alder (DA) reaction, transesterification, Schiff base chemistry, and disulfide metathesis.

Zhang et al. used a two-step polymerization strategy to develop 3D printed reprocessable thermosets that impart reshapeability, repairability, and recyclability into 3D printed structures [3]. They printed a rabbit statue and showed that the lost ears could be repaired by conducting the 3D printing of new material on the polished surface site. These recyclable and healable 3D printing methods contribute to alleviating environmental challenges associated with the continuous increase in consumption of 3D printing materials.

1.9 FIELDS OF 4D PRINTING

In this section are presented the main fields of application related to 4D Printing, an overview of the potentials and fields of interest concerning the use of smart materials.

1.9.1 Active Origami Structures

Origami, the ancient art of paper folding, has inspired the design and functionality of engineering structures for decades. The principles of origami are very general, it takes two-dimensional components that are easy to manufacture (sheets, plates, etc.) into three-dimensional structures. Recently, researchers have become interested in the use of active materials that convert various forms of energy into mechanical work to produce the desired folding behavior in origami structures. Such structures are termed "Active Origami Structures" and are capable of folding and/or unfolding without the application of external mechanical loads but rather by the stimulus provided by a non-mechanical field (thermal, chemical, electromagnetic). It is advantageous for many areas including aerospace systems, underwater robotics, small scale devices and smart packaging. This topic is explored deeply in the next chapter.

1.9.2 Dynamic/ Smart Devices

Researches on 4D Printing has focused on creating actuators made with smart materials for smart devices. This field incorporate products that have functions of sensing, actuation, and control in order to describe and analyze a situation, and make decisions based on the available data in a predictive or adaptive manner, thereby performing smart actions.
In most cases the “smartness” of the system can be attributed to autonomous operation based on closed loop control, energy efficiency, and networking capabilities. Smart systems typically consist of diverse components: Sensors for signal acquisition, Elements transmitting the information to the command-and-control unit, Command-and-control units that take decisions and give instructions based on the available information, Components transmitting decisions and instructions, Actuators that perform or trigger the required action.

1.9.3 Metamaterial

Metamaterials are nanocomposite structures made up of materials such as metals or plastics which are engineered by Metamaterial Technologies Inc.’s (MTI) scientists to exhibit properties not found in nature.
A “metamaterial” is commonly described as an assembly of multiple individual elements (which are sometimes referred to as meta-atoms). These meta-atoms are fashioned from conventional microscopic materials such as metals or plastics, but the materials are usually arranged in specific periodic patterns. Therefore, metamaterials gain their properties not from their composition, but from their exactingly-designed structures.
Their precise shape, geometry, size, orientation and arrangement gives them their smart properties capable of manipulating electromagnetic waves: by blocking, absorbing, enhancing, or bending waves, to achieve benefits that go beyond what is possible with conventional materials. Potential applications of metamaterials are diverse and include optical filters, medical devices, remote aerospace applications, sensor detection and infrastructure monitoring, smart solar power management, crowd control, radomes, high-frequency battlefield communication and lenses for high-gain antennas, improving ultrasonic sensors, and even shielding structures from earthquakes.

1.9.4 Tissue Engineering

Tissue engineering is the use of a combination of cells, engineering and materials methods, and suitable biochemical and physicochemical factors to improve or replace biological tissues. Tissue engineering involves the use of a tissue scaffold for the formation of new viable tissue for a medical purpose. While it was once categorized as a sub-field of biomaterials, having grown in scope and importance it can be considered as a field in its own.
Shida Miao, Wei Zhu et al. [19] deepened this topic in their paper showing a series of novel shape memory polymers with excellent biocompatibility and tunable shape changing effects were synthesized and cured in the presence of three-dimensional printed sacrificial molds, which were subsequently dissolved to create controllable and graded porosity within the scaffold.

1.9.5 Biomedicine

The application of 4D printing to biosciences and biomedicine has the potential to transform diseases' prevention, diagnosis and therapies, as well as post-surgical rehabilitation.
3D Printing is already being used to create objects and prosthesis in the medical field: many biocompatible materials are 3D-printed for orthopaedic applications (prosthetic hands, arms, jaws, legs, knees) and some objects have also been implanted in needy patients. The technique can have dental applications and be used for the making of hearing aids and general medical devices.
Also 3D bioprinting has been developed to effectively and rapidly pattern living cells and biomaterials, aiming to create complex bioconstructs. However, placing biocompatible materials or cells into direct contact via bioprinting is necessary but insufficient for creating these constructs. Recent developments in 4D bioprinting technology concern the uses of 4D bioprinting in tissue engineering and drug delivery. For exemple as already mentioned Villar et al. [20] have shown how 4D biopriting enables the precise control of the spatial distribution of different components that can self-unfold to encapsulate and realease drugs or cells in a programmable manner. Small oil drops encapsulating aqueus droplets, called "multisomes" can be printed in water. The aqueous droplets adhere to one another and form interface bilayers. interface bilayers. Upon changes in temperature or pH of the surrounding environment, the components in the driplets can be released. Another method also utilized differentially swelling polymeric hydrogel layers to form self-folding devices, anabling the directional encapsulation and release of therapeutics [20].

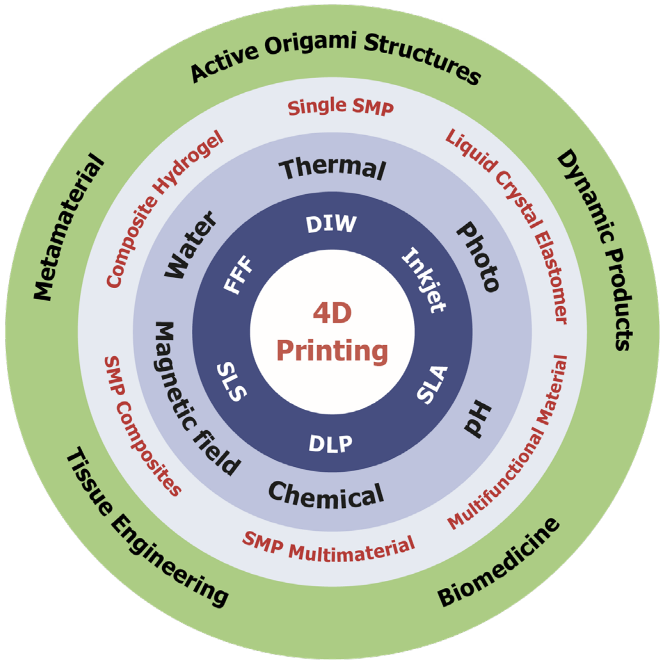


Figure 1.23 *Adapted The diagram of 4D printing made by Xiao Kuang et al.*

1.10 SUMMARY

The adapted diagram made by Xiao Kuang et al. is summary of all the of fields of 4D Printing covered in this chapter (**Figure 1.23**) [3]. 4D printing, referred to as 3D printing plus time, enables shape or function evolution with time after printing using different materials under the internal stimuli, such as the self-folding of a 4D printed flat sheet into a box. The elements and the categories involved in 4D printing are shown. 1) 3D printing technology: FFF, DIW, DLP, SLS, inkjet, and SLA. 2) The stimulus for 4D printing: thermal, photo, water, pH, chemical, and magnetic field. 3) Material systems for 4D printing: single SMP, liquid crystal elastomer, composite hydrogel, SMP composites, SMP multimaterial, and other multifunctional material. 4) Fields of 4D printing: active origami structures , dynamic/smart devices, metamaterial, tissue engineering, and biomedicine.

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CHAPTER II

DESIGN OF 4D PRINTED STRUCTURES

2.1 INTRODUCTION

In the previous chapter the main features of 4D Printing processes are presented, with a general overview of the main technologies and materials.
In the following chapter will be analyzed some of the main principles and methodologies in order to design and develop 4D printed structures. These principles of self-folding systems are provided by researchers and practitioners from this evolving area, which has led to applications ranging from smart devices to deployable space structures.

In the first sections are reported shape memory effects related to the SMPs and how these effects are used in development of 4D printed structures by *"direct 4D Printing"*. In the second section, tipical shape-shifting structures are showed such as active origami concepts and Self- Folding/Bending actuators. The following section is an overview of the mathematical models and the critical design drivers to select active materials for self-folding systems. Then fabrication and characterization of printed active composite hinges for origami structures from Qi Ge et al.'s researches are analyzed in details [1]. In last section there is a list of the main tools and softwares used to design specific 4D structures. As will be seen, modeling the geometries, determining interactions for shape-shifting states, and calculating the energy (from heat, shaking, pneumatics, gravity, magnetics, etc.) need the support and development of powerful softwares.

2.2 SHAPE MEMORY EFFECTS

As already mentioned in the previous chapter, the main characteristic of shape memory materials (SMMs) is the ability to recover to their programmed shape from a temporary shape when stimulus is applied. This is known as the shape memory effect (SME).

SMMs require two processes to form a complete *shape memory cycle*. The first step is to deform the material into a Temporary Shape through the *programming process*, followed by the *shape recovery process*. SMMs will remain constant in its Temporary Shape until the right optimum stimulus is applied to trigger the *"shape recovery process"*.
The rapidity of shape change from a Temporary Shape depends on the responsiveness of the material and the physical design of the geometrical part. The network elasticity of the SMM determines the "memory" of one or more shapes.
During the *shape memory cycle*, the polymer chain is being rearranged and *residual stress* can be built: the polymer chain is pulled and straight; it will be forced to keep the straight state (the state of Temporary Shape after Step 1 in **Figure 2.1**) after it quickly cools and solidifies. If we reheat the solidified material, it will *release the residual stress*, return its polymer chain to its chaotic, or low energy mode, and shorten along the printing direction.

The two significant factors that determine the shape memory effect of SMMs are the *strain recovery rate (Rr)* and the *strain fixity rate (Rf)*. The *strain recovery rate (Rr)* refers to the ability of the material to memorize its permanent shape, whereas the *strain fixity rate (Rf)* refers to the ability of the switching segments within the mechanical deformation.

This thesis is focused on the SMEs of SMPs (Shape Memory Polymers). There are tree main SMEs related to the SMPs that will be presented: one-way shape memory effect, two-way shape memory effect and three-way shape memory effect **[2]**.

2.2.1 One-Way Shape Memory Effect

The majority of SMPs have a one-way shape memory effect which is irreversible. When an external stimulus is applied, the deformation (temporary) shape will become a permanent shape. A programming step is needed for the object to return back to its temporary shape.
Figure 2.2 describes the process of the one-way shape memory effect where the SMP changes from its temporary shape (A) back to the permanent original shape (B) under an applied stimulus. In the programming process, the SMP is first heated above transition temperature to soften the material, so that a deformation force (e.g. loading) can be applied to the original shape. The predeformed shape is cooled under the load to a fixed temporary shape. When the unloaded fixed temporary shape is exposed to stimuli, in this case is heat, the original shape (B) is recovered **[24]** (**Figure 2.3**). In terms of heating, there are various types of thermal transition temperatures (Tt) that are associated

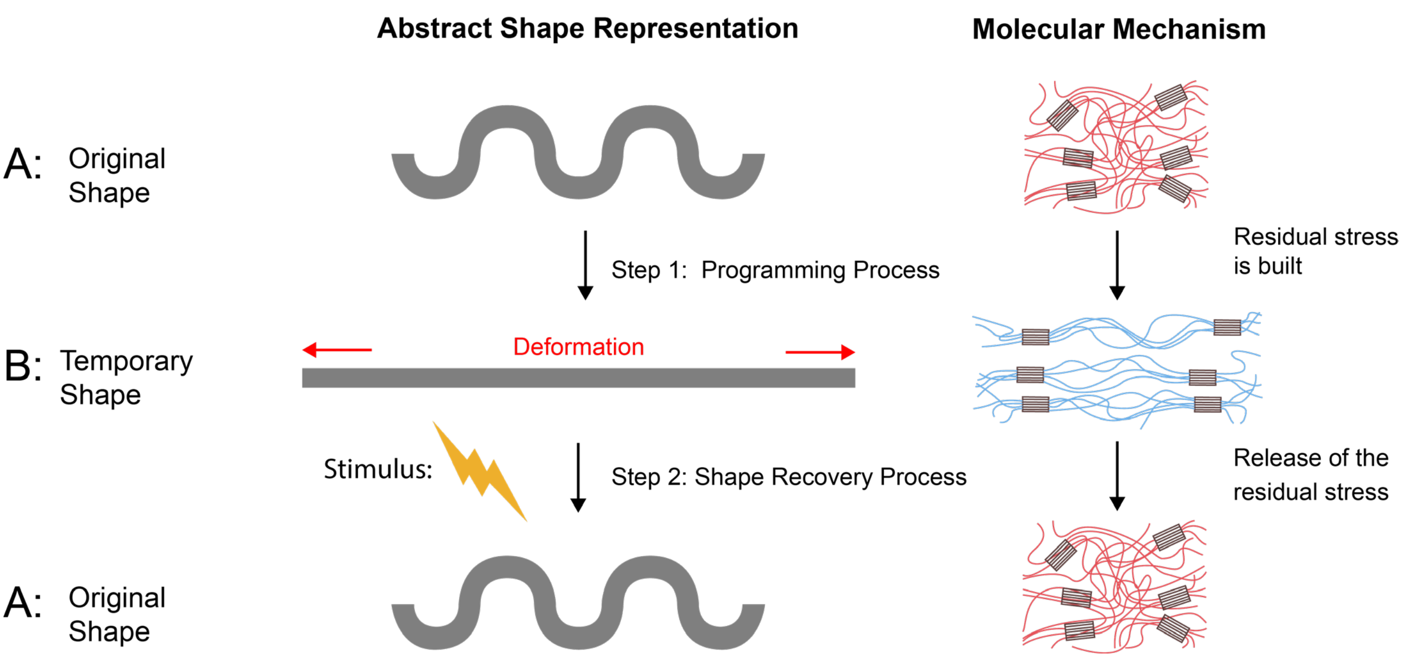


Figure 2.1 *Illustration of the Shape memory effect of printable* shape memory materials (SMMs).

with switching domains. It includes the melting transition (Tm), liquid crystalline transition (TLC), or glass transition (Tg). For the shape memory effect, the glass transition (Tg) temperature is usually considered.

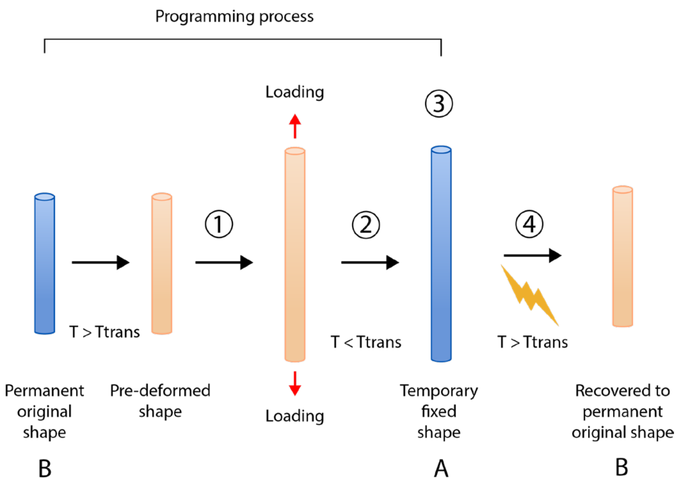


Figure 2.2 *Reprogramming procedure for a one-way shape memory effect.*

2.2.2 Two-Way Shape Memory Effect

SMP with two-way shape memory effect has the ability to remember two different shapes when exposed to stimuli. The material can change from a temporary shape back to its permanent shape and the change is reversible (**Figure 2.3**) [2]. This behaviour is neither mechanically nor structurally constrained, thereby allowing for multiple switching between encoded shapes without applying any external force. The two-way SME can be found in liquid crystalline elastomers and photo-actuated deformation polymers.

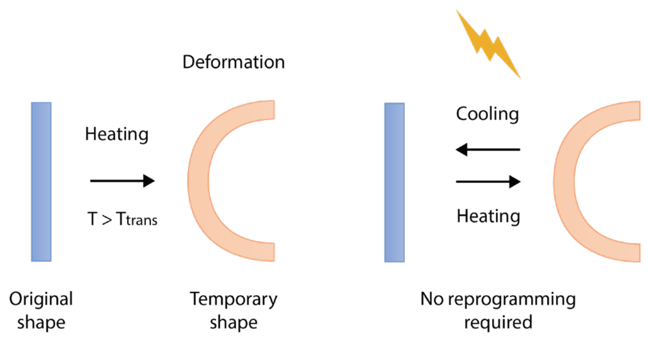


Figure 2.3 *Reprogramming procedure for a one-way shape memory effect.*

2.2.3 Three-Way Shape Memory Effect

The main difference between a one-way and three-way shape memory effect is that the three-way shape memory effect has one intermediate shape between its original and temporary shapes.

If there is more than one intermediate shape, then this is also known as a "multiple shape memory effect", achieved by combining multiple two-way shape memory polymers with different glass transition temperatures; or by heating a programmed shape memory polymer first above the glass transition temperature and then above the melting transition temperature of the switching segment. The threeway shape memory effect is shown in **Figure 2.4**, whereby there are two different thermal transition temperatures—Tlow,1 (70 °C) and Tlow,2 (0 °C). This is attributed to the two segregated crystalline domains in the original shape [2].

Li listed several methods to manage triple shape memory effects such as by blending, grafting, and blocking copolymers, SMP hybrids, or other polymer laminates [3]. A material with dual-SME is able to achieve one permanent shape and one temporary shape, whereas a triple-SME material can achieve one permanent shape and two temporary shapes.

The dual shape mechanism is achieved by assembling two components in the form of hard and soft segments within a single matrix.

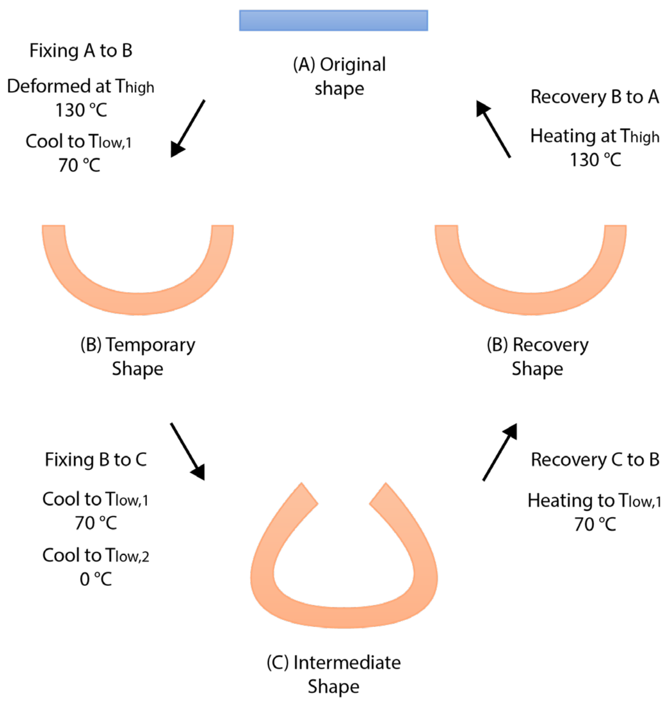


Figure 2.4 *Three-way shape memory effect.*

2.2.4 Direct 4D Printing

The approaches using SMPs for 4D printing typically involve a series of thermo-mechanical programming steps after printing, which could be tedious. Incorporating the internal stress during printing or heating step without applying external force for shape programming leads to the so-called "direct 4D printing" [4]. Ding et al. reported an SMP-based direct 4D printing process, where the eigenstrain was incorporated into the material during printing [21].

Byoungkwon An et al. converted this shortening effect upon reheating into a bending behavior for their project Thermorph [6]. They used Polylactide (PLA) as the active layer for their self-folding structures. As already seen in section 2.2, during the printing process, when PLA is being extruded, the polymer chain is pulled and straight creating residual stress inside the structure (the state of Temporary Shape in **Figure 2.5**) after it quickly cools and solidifies. If the solidified PLA is reheated, it will release the residual stress, polymer chains will shorten along printing direction, causing bending behavior in the active material (the state of Permanent Shape in **Figure 2.5**).
This technique can be used to print efficient actuators that do not need to be programmed during shape memory cycles.

2.3 TYPES OF SHAPE-SHIFTING STRUCTURES AND BEHAVIOURS

Shape-shifting structures and behaviours that researchers have explored tend to focus on simple forms and using a bilayer composite comprising of soft hyper-plastics and SMPs. Such geometric programming involves two or more active materials in which the desire to generate complex and multiple shapes from the same starting material can be achieved by programming the sequence of shape transformation with temporal control.
In this section, it is introduced the basic concepts of origami structures and a focus on the active self-folding structures more commonly applied in 4D printing.

2.3.1 Basic Origami Concepts

As already mentioned in Chapter 1.9, Origami is the Japanese art of paper folding in which desired shapes are achieved through the sequence of folding from a planar sheet. Its original purpose was not particularly utilitarian, but rather recreational and artistic.

In the mid-1970s, mathematicians discovered that an endless number of shapes could in theory be created using traditional origami (initially planar shape, only folds allowed) [7]. These discoveries enabled new approaches for manufacturing, assembling, and morphing of devices and structures based on origami principles.

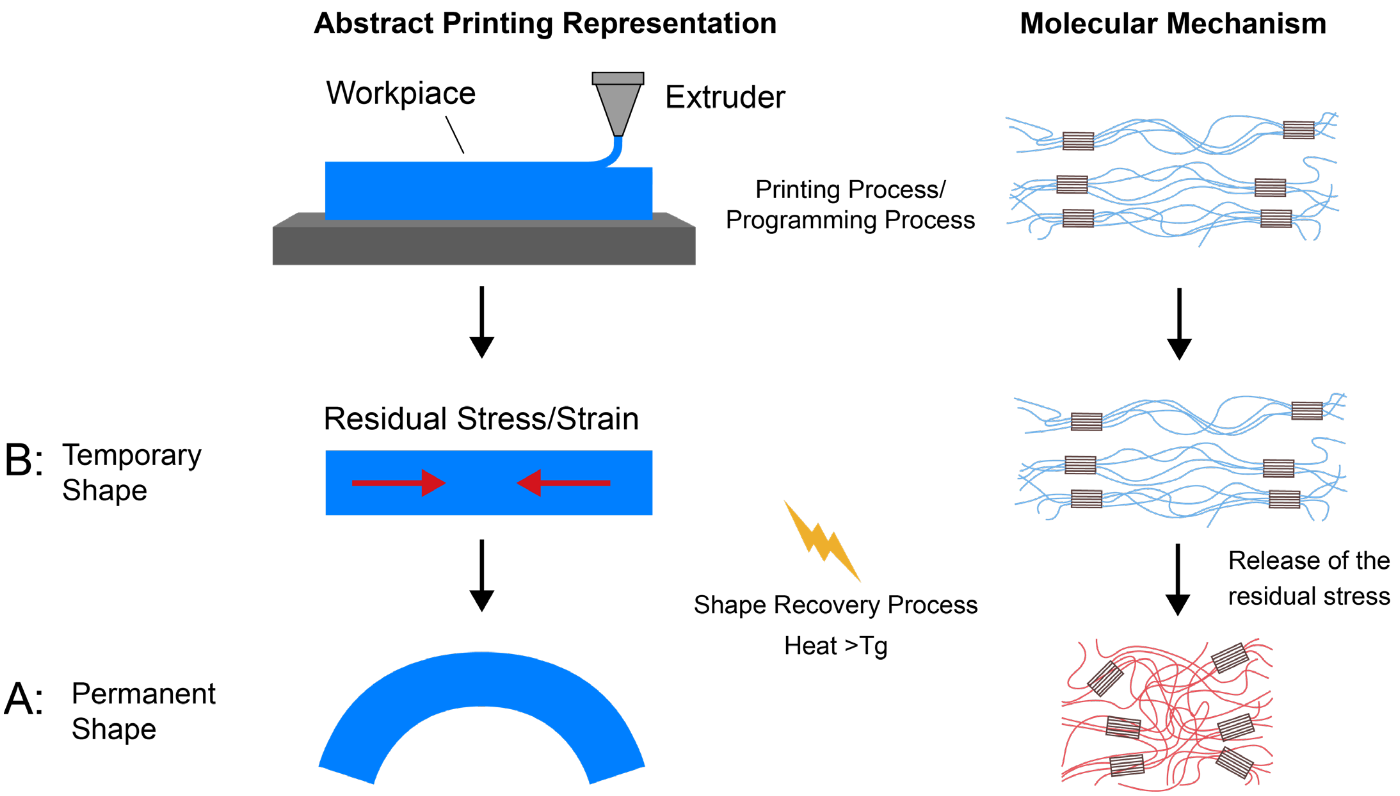


Figure 2.5 *Illustration of the direct 4D printing.*

This is evident in the increasing attention mathematicians, scientists, and engineers have given to origami theories and tools over the past four decades, which have inspired the design and functionality of engineering structures.
Origami offers engineers novel ways to fabricate, assemble, store, and morph structures. Potential advantages include the capability to compactly store deployable structures, the potential for structures to be reconfigurable, and a reduction in manufacturing complexity [8].

Researchers have become interested in the use of active materials that convert various forms of energy into mechanical work to produce the desired folding behavior in origami structures. Such structures are termed "*Active Origami Structures"* and are capable of folding and/or unfolding without the application of external mechanical loads but rather by the stimulus provided by a non-mechanical field.
More Recently, The field of active origami has been exposed to 4D printing thanks to the possibility of printing some smart materials using 3D printing. Originally Skylar Tibbits and his team introduced the 4D printing concept by printing simple active origami structures. Truncated octaheldron, cubes and tubes were printed and assembled from 2D to 3D through shape-shifting behaviors based on self-folding mechanisms [9]. This shape-shifting is enabled by the stress mismatch between rigid and active materials due to their different swelling ratios.

Certain basic origami concepts should be defined before introducing active self-folding structures.
In origami, a goal shape is obtained from an initially planar sheet exclusively through folding operations. For an idealized sheet with no thickness, a fold is defined as: *"any deformation of the sheet such that the in-surface distance between any two points in the sheet is preserved and self-intersection does not result"* [10]. Stretching and tearing are not permitted, bending is the essential deformation. For a sheet with non-zero thickness, a fold is defined as: *"any deformation of the sheet that preserves a continuous neutral surface (that neither stretches nor contracts) and prevents self-intersection"* [10].
In origami, the locations of localized folds on the sheet are formally called *"creases"* [11]. The creases, folding directions, folding magnitude, and folding sequence determine the ultimate shape of the structure.
Typically, creases are defined by their endpoints, formally called *"vertices"*. Sheet regions bounded by the creases are known as *"faces"*. To determine the fold direction of a crease, a *"mountain-valley"* assignment is typically used. For mountain folds, faces on either side of the crease can be thought of as rotating into the page, while for valley folds, they can be thought of as rotating out of it.

A crease pattern is a schematic that shows all the creases on a sheet required to fold a structure, typically with mountain-valley assignments. These concepts are depicted in **Figure 2.6**. Two parameters that describe the magnitude of a fold are the *folding angle* and the *radius of curvature* at the fold line. These parameters are shown schematically in **Figure 2.7**. In the view that a finite thickness sheet cannot provide sharp folds, it is assumed that a finite region centered at the fold is bent and has a radius of curvature R. The internal fold angle θi is the angle at the intersection of two line segments stretching collinearly with respect to the folding faces. The external fold angle θ e is defined as *180° − θi* [11].

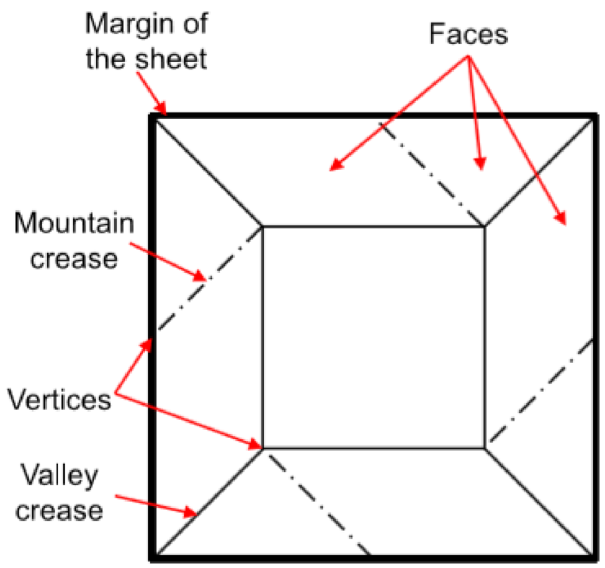


Figure 2.6 *Schematic of a pinwheel crease pattern illustrating various origami concepts.*

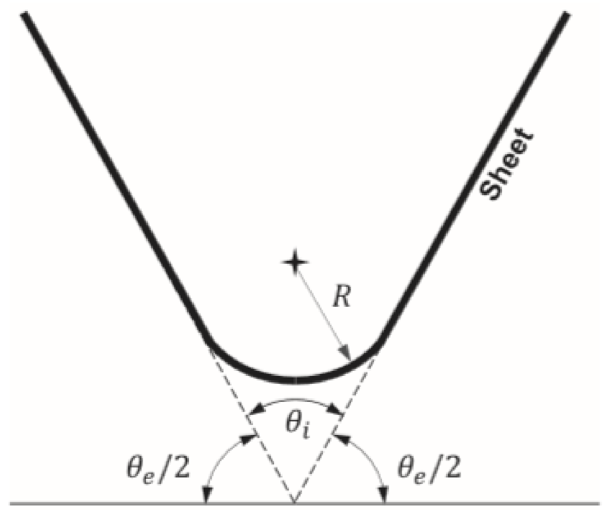


Figure 2.7 *Parameters that define the magnitude of a fold.*

2.3.2 Self- Folding and Bending Concepts

The term self-folding is a class of self-assembly mechanism that uses a shape transformation effect such as folding, curving or rolling from a printed patterned geometry.
Self-folding and bending structures are more commonly applied in 4D printing. A fold is a deformation in which the in-surface distance between any two points in the sheet is preserved without self-intersection. Bending is a global deformation associated with a smoother distributed curvature, whereas folding emphasises on localized deformation with sharp angles in a narrow hinge area. Most shape-shifting behaviour from 2D into 3D is achieved through bending that is caused by expansion or contraction of materials with different magnitudes in different directions.
Significant design parameters or drivers that need to be considered while designing active self-folding mechanisms include the selection of the folding mechanism, the size of the component and the type of material. It is also important to account for the *actuation strain*, *actuation stress*, and the capacity of generating and manipulating the desired field at the chosen location of the bend.

Concepts for generating individual folds using active materials are showed in **Figure 2.9**. The concepts are divided into two categories: *hinge type* and *bending type* [11].

Hinge Type: Most hinge-type active folds are associated with one of three local actuator concepts: variable length active rod or spring connected to the two faces joined by the hinge (*Extensional concept*) (**Figure 2.8(a)**), active torsional element at the hinge (*Torsional concept*) (**Figure 2.8(b)**), and active element with preset folded shape (*Flexural concept*) (**Figure 2.8(c)**).

The *extensional concept* uses the active material in a rod or spring form with its two ends attached to the faces connected by the hinge and the length of the active element controls the rotation of the hinge [11].

The *torsional concept* uses the active material as a torsional spring or a rod that provides twist at the hinge. The twist angle of the active material thus directly controls the rotation of the hinge [11].

In the *flexural concept*, the active material has been manufactured or trained to have a preset folded configuration but is then deformed to an initially flat configuration. Upon application of the activation field, the active material itself returns to its preset folded configuration and being bonded to the faces of the passive material, induces the local hinge to do the same [11].

All concepts can be further improved to allow for folding in both directions relative to the sheet normal by adding corresponding antagonistic active components. In the torsional concept, this can be achieved by installing two active elements that generate twist in opposite directions. For the extensional and flexural concepts, it can be achieved by pairs of active elements in opposition to each other (On opposite sides of the sheet for the extensional concept).

Bending Type: Other applications and approaches do not assume the existence of discrete hinge mechanisms but are rather based on direct local sheet bending caused by the actuation of the active material. Such concepts are shown in **Figure 2.8(d)** and **(e)**. Unlike the hinge type fold concepts, the direct bending approach (without hinges) may offer the advantage of massive foldability. In other words, folds can occur at any location or orientation to which the driving field is applied (unless mechanically restricted). In hinge type concepts, however, folds are restricted to structurally pre-determined hinge locations. It is refered to the concept of **Figure 2.8(d)** as *multi-layer* and that of **Figure 2.8(e)** as *single layer*.

The *multi-layer concept* considers self-folding using a two-layer laminate with one *passive layer* and one *active layer* (**Figure 2.8(d)**). A passive layer generates negligible mechanical work compared to the active layer under the application of the actuation inducing field. When such a field (thermal, magnetic, etc) is applied, the active layer is driven to deform, generally axially, while the passive layer is not. This difference in expansion or contraction between the two layers generates localized bending of the sheet [11].

This concept can be further expanded to allow for folds in both directions relative to the sheet normal in a manner similar to that employed for hinge-type folds. Specifically, three-layer designs with two opposing outer layers of active material separated by a passive material can be used.

The *single layer concept* considers self-folding via bending without hinges using a sheet with a single active layer subjected to a graded driving field (**Figure 2.8(e)**). Such a gradient generates a distribution of actuation strain through the sheet thickness, causing the sheet to bend. This design allows for folds in both directions relative to the sheet normal based on the direction of the driving field gradient. However, folding via this approach is generally more difficult as compared to the multi-layer concept since it is not practical to maintain gradients in some physical fields (e.g., temperature) at specific locations for a considerable period of time. It should be noted that folding using active materials is not restricted to the five concepts presented in this section [11].

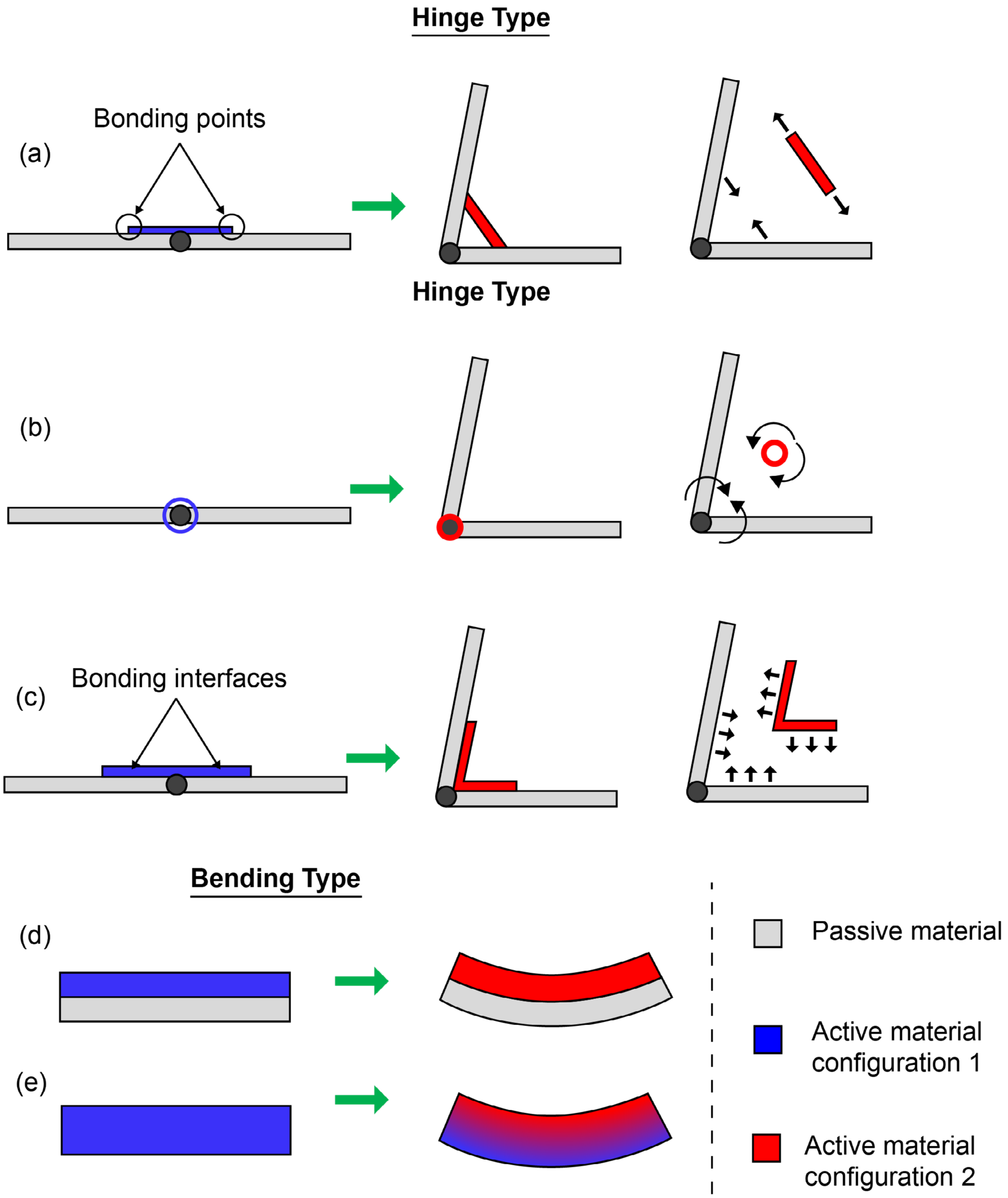


Figure 2.8 *.Basic active fold concepts. Hinge type:* **(a)** *extensional (variable length active rod or spring connected to the two faces),* **(b)** *torsional (active torsional element at the hinge), and* **(c)** *flexural (active element with preset folded shape). Individual simplified free body diagrams of the hinge-face structure and the active element are also shown. Bending type:* **(d)** *bilayer consisting of an active and a passive layer, and* **(e)** *single layer subjected to graded driving field.*

2.4 GEOMETRICAL PRIMITIVES

Byoungkwon An et al. in their paper propose a bi-layer structure for 4D printed structures: one layer of Thermopolyurethane (TPU) as the constrain layer and three layers of Polylactide (PLA) as the active layer. Together these four layers form an actuator upon reheating into a bending behavior for self-folding purpose [6].

By controlling the printing orientation and printing speed of the active layer (PLA) within the actuator, a wide variety of geometrical shapes can be created that can be folded from flat patterns (**Table 2.1**) [6].

For all the samples except those under the polyhedron fold category, Byoungkwon An et al. can plan the printing toolpath with the forward design flow in their software editor Thermorph (explained in the Fourth Chapter); all the samples of polyhedron fold are designed with the inverse design flow by importing the desired 3D models.

PLA and TPU were extruded through a 0.4mm nozzle. PLA was heated to 210 °C and TPU 230 °C. Layer thickness was 0.2mm. All the printed samples were triggered at 70 °C for ~2 minutes for their self-folding effects.

Straight Fold: The printing lines of the actuator are parallel to at least one of the geometry edges.

Angled Fold: The printing lines of the actuator are not parallel to any geometry edges.

Two-side Fold: Actuator layers are located on both sides of the geometry.

Circular Fold: The printing lines of the actuator are circular. Compared to some other thermoplastic based self-folding techniques, this technique has an advantage of printing curved creases with ease and flexibility.

Polygonal Fold: Lines fold into polygons. The narrow actuator is achieved by increasing the printing speed from commonly recommended PLA printing speed of 3000 mm/min to 9000 mm/min.

Polyhedron Fold: A series of polyhedrons are showed with related printing tool path. These were generated and printed quickly, with 15 - 30 minutes designing and printing time for each.

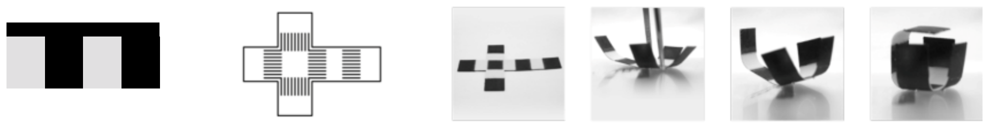
Name	PLA orientation	Printing layer instructions	Actuator layer instructions	Before heating	Self-folding in progress	After heating
Straight Fold	0°					
Angled Fold	45°					
Two side-Fold	0°					
Circular Fold	Follow the curve					
Polygonal Fold	0°					
Polyhendron Fold	0°, 90°					
	0°, 60° ,120°					
	0°, 60° ,120°					

Table 2.1 *Adapted table of the Geometric Primitives.*

TPU ■ PLA ■

2.5 MATHEMATICAL MODELS

Mathematical models are the basis of the tools and methods which are required to design 4D printed structures. These models define the approach for simulating and fabricating self-evolving structures which transform into a predetermined shape, changing property and function after fabrication.

Appropriate Mathematical models or theoretical models are necessary for the following reasons [12]:
- Predicting the final shape for a given material structure, material properties and stimulus properties.
- Predicting the shape evolution after printing over time.
- Avoid collisions between components of the structure during the self-assembly operation.
- Reducing the number of trial-and-error experiments.

Different modeling experiments were conducted to design complex self-evolving structures. Early experiments involve many repetitions for a specific structure to achieve the desired shape. For example, Tibbits et al. printed and repeated a series of experiments to identify the appropriate material structure needed to reach the desired shape [12]. Moreover, the aforementioned experimental study by Tibbits et al. was quantified with mathematical models developed by Raviv et al. [13], where the *spring-mass concept* was adopted, as shown in **Figure 2.9**.

An appropriate theroretical model for 4D printing consists of four major components [12]. The first is the final desired shape, which may include desired bending angle, length, volume, etc. The next is material structure, such as the volume fractions of fibers and the matrix, filament size, orientation, interfilament spacing, anisotropy. Equivalently the material structure can be described by the size, shape and spatial arrangement of the voxels. From the perspective of the printing process, the material structure depends on the print paths and nozzle sizes. Material properties makeup the third component, and they include shear modulus, Young's modulus, and the interactive properties associated with the stimulus, such as glass transition temperature and swelling ratio. The final component is the stimulus properties, such as the temperature value and light intensity.

4D printing mathematics can be divided into two categories according to Gladman et. [14] the forward problem and the inverse problem. The categories are defined below:

- Forward problem: Determination of the final desired shape given material structures, material properties, and stimulus properties.

- Inverse problem: Determination of the material structure or the print paths and nozzle sizes given the final desired shape, material properties, and stimulus properties.

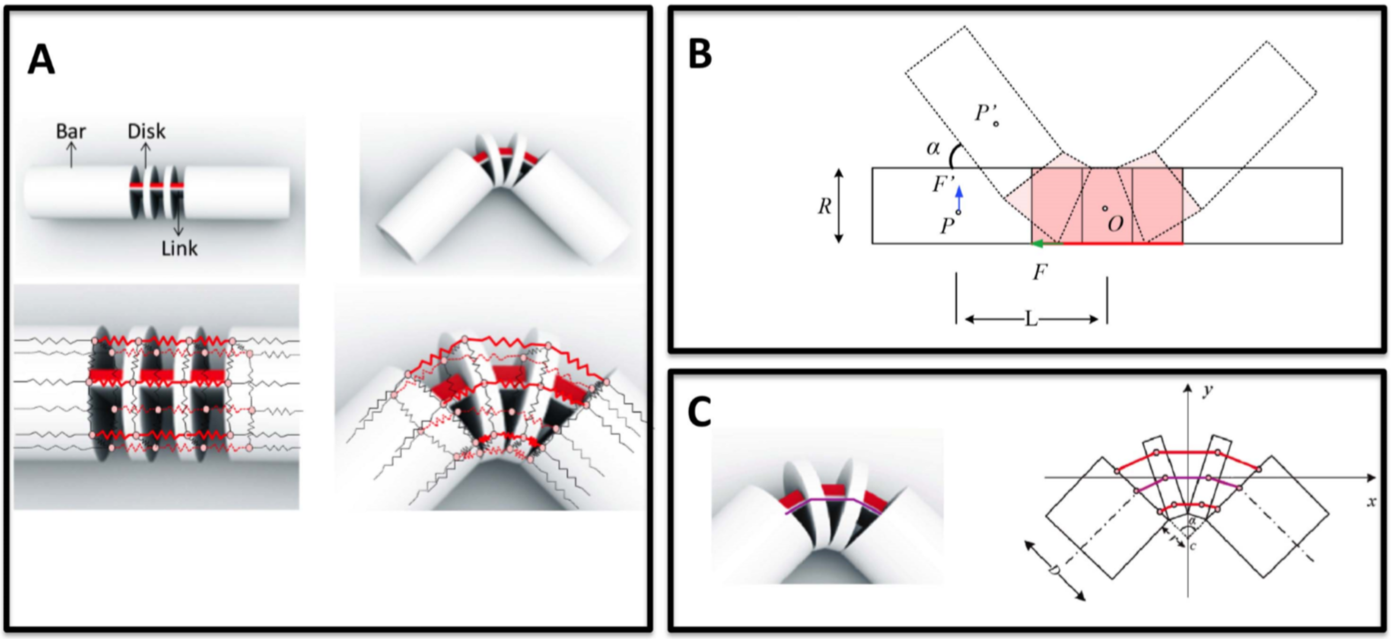


Figure 2.9 **(a)** *Renderings of an initial joint and its folding, with their corresponding spring-mass systems shown in the lower row. The lateral black springs represent the rigid bars and disks. The red springs represented the links that cause the joint to fold.* **(b)** *Variables in this schematic are used for calculation of stiffness coefficients.* **(c)** *Illustration of computing the joint length. Each joint is modeled using two disks, and the length of each inner limb is calculated according to its distance from the center of rotation. The center link (marked as purple) remains constant in time.*

2.6 FABRICATION OF PRINTED ACTIVE COMPOSITE HINGES

Qi Ge et al. fabricated active material hinges made by PAC (Polymeric Active Composite) using computer aided design (CAD) files that specify the complete 3D architecture of the fibers and matrix then printing them using a multi-material Inkjet 3D printer (Objet 260 Connex, Stratasys, Edina) [1].

The layer-by-layer printing process works by depositing droplets of polymer ink onto the building platform, wiping them into a smooth film, and ultraviolet (UV) photo-polymerizing the film. Once a layer is created, the platform moves down, and the next layer is printed. Several inkjet heads with separate material sources exist in the printing block, so multiple materials can be printed in each layer. In this process, each layer generally contains materials that constitute part of the matrix and part of the fibers. In addition, a hydrophilic gel is printed and used as a sacrificial material for the fabrication of complex geometries [5].

The result are PAC hinges consisting of composites with a matrix that is elastomeric over its desired operating temperature range of between room temperature and about 100°C and fibers that exhibit the shape memory effect (SME) over this temperature range.

Qi Ge et al. designed their PACs to have a matrix with a glass transition temperature (Tg) below 25°C and fibers exhibiting SME in the range 25°C–70°C. To this end, they make use of the digital materials that are available with Objet 3D printer. It provides two base materials: one is *Tangoblack*, a rubbery material at room temperature polymerized with a material ink containing urethane acrylate oligomer [5] and the other is *Verowhite*, a rigid plastic at room temperature polymerized with a material ink containing isobornyl acrylate [5]. Qi Ge et al. created hinges made by PACs consisting of Tangoblack as the matrix (Tg – 5°C) and a digital material (termed *Gray 60*) with Tg – 47°C.

PAC hinges are characterized experimentally by directly printing two-layer PAC laminates that are connected to inactive (rigid) panels [1]. These panels can be used as end tabs to apply mechanical loads (**Figure 2.10 (a)**). The PAC laminates consist of two layers: one layer of matrix-only material and one layer of a PAC lamina with a prescribed fiber size and spacing (figure **Figure 2.10 (a)**). Hinges function via a mechanism of programmed strain mismatch (eigenstrain) between the two layers that leads to constant curvature bending over the hinge region, resulting in the plates on each side rotating an angle of θ with respect to each other (**Figure 2.10 (b)**). The strain mismatch is created by *contrained-thermo-mechanics* of *one-way shape memory effect.*: stretching the hinge at an elevated programming temperature (**TH >Tg**) to a prescribed strain (ε_0), then cooling it to the usage temperature (**TL <Tg**) while maintaining the strain ε_0, and then releasing the load. Upon releasing the mechanical constraint, the hinge bends to an angle θ due to the combined effect of the entropic elasticity of the pure matrix material lamina and the shape memory effect of the PAC lamina. The hinge returns to its original flat shape after heating back to TH.

Qi Ge et al. characterize the hinge performance by its bending angle θ, which depends on the hinge materials (matrix and fiber thermo-mechanical constitutive behaviors), geometric parameters (hinge length L, and laminate/lamina configuration), and programming parameters (ε_0, TH, and TL) (**Figure 2.10 (b)**) [1].

In order to investigate the effects of these factors on hinge angle, Qi Ge et al. designed, fabricated, and carried out tests for a range of parameters including five different laminate/lamina configurations, three different programmed deformations (ε_0 - 10, 20, and 30%), and four different hinge lengths (L =2.5, 5.0, 7.5, and 10mm). All of the tests were done with TH =70°C and TL =25°C. The laminate configuration is defined by the thickness of the hinge **t** and the thickness of the PAC lamina **h** (**Figure 2.10**). The PAC lamina is characterized by the fiber volume fraction (v=πR^2/(2hw)), which it is controlled by varying the fiber radius R and the PAC lamina thickness h, while keeping the fiber pitch fixed at 2w=1mm.

Figure 2.11 shows hinge angles (measured at more or less 1 min after unloading) as a function of the programming stretch and hinge length, respectively, for various laminate/ lamina configurations. The results in **Figure 2.11(a)** are for hinges with L=5mm and those in **Figure 2.11(b)** for hinges with ε0=20%.

Figure 2.11 demonstrates behaviors that are been used to understand for the design of PAC hinges. For a fixed material and geometric configuration, the hinge angle decreases (the bending increases) with increasing programming stretch **Figure 2.11(a)**. This mismatch strain between the layers increases with applied stretch, and this drives increased bending. Furthermore, as the length L increases, the hinge angle decreases **Figure 2.11(b)**. As the strain mismatch results in approximately constant curvature over the length of the hinge, and so geometry dictates a larger curvature (or smaller hinge angle θ) as L increases.

In order to obtain parameters used for the mathematical models developed by Qi Ge et al., they also conducted a series of fundamental thermomechanical tests, including dynamic mechanical analysis (DMA) tests, uniaxial tensile tests, thermal strain tests, and stress relaxation tests. As described in their paper [5] , Qi Ge et al. developed a theoretical model of the behavior of a PAC hinge, and this allows to predict the result of hinge behavior beyond the range of parameters considered in their experiments.

Qi Ge et al. [1] created a number of examples that demonstrate how it is possible printing flat-plate structures consisting of PAC hinges directly connected to rigid plastic components of arbitrary shape then program the hinges to assemble the as-printed structure into a desired 3D configuration. Qi Ge et al. showed, composite hinges can be programmed to assume prescribed folding angles, and these depend on a set of material, geometrical, and programming parameters using their validated mathematical model to design the hinge parameters for a range of applications.

First they designed a box consisting of six sides connected by PAC hinges that is printed in a flat (unfolded) form as shown in **Figure 2.12(a)**. It shows the as-printed box (the flat plate), where the rigid sides are white and the hinges are black. The assembled box was created after biaxially stretching the as printed structure by 20% at TH, cooling to TL, and releasing the load. It assembles into the desired box shape (**Figure 2.12(b)**), with small deviations from the desired 90° angles, and these are likely due to inaccuracies in the straining process. **Figure 2.12(c)** and

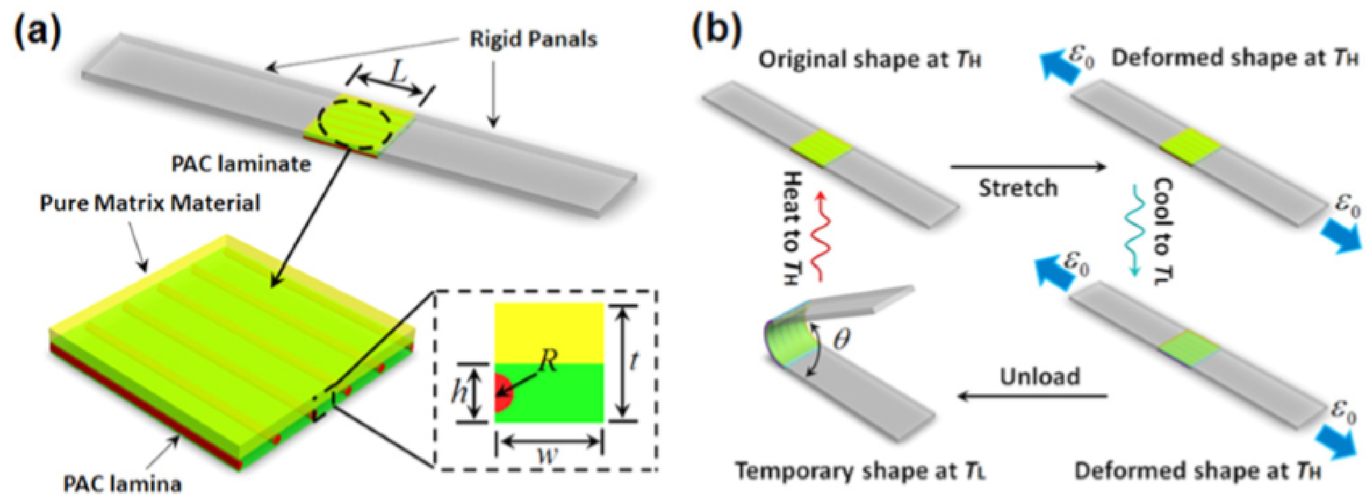


Figure 2.10 *Schematics of a PAC hinge and the thermo-mechanical programming steps.* **(a)** *Geometrical and material properties of a PAC hinge.* **(b)** *Thermo-mechanical programming steps to train a self-folding/unfolding PAC hinge.*

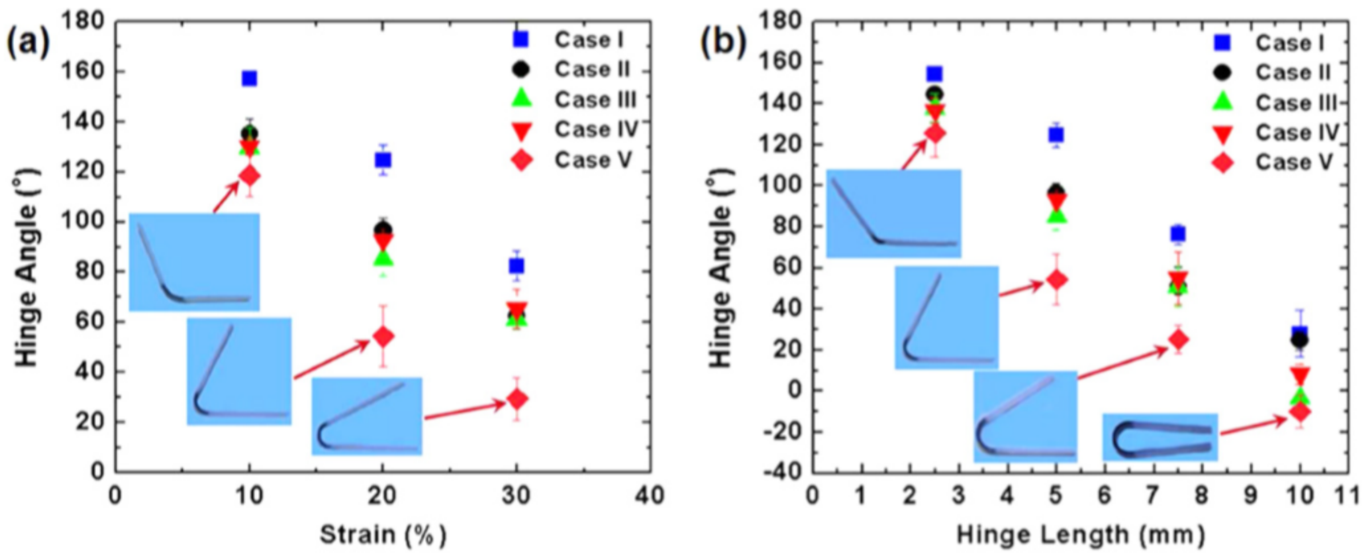


Figure 2.11 *The measured deformation of PAC hinges.* **(a)** *Hinge angle vs applied strain for 5mm long hinges with five different cross-section profiles.* **(b)** *Hinge angle vs hinge length for hinges with five different cross-section profiles pre-stretched by 20%.*

d show a similar structure, a five-sided 3D pyramid. Here the printed flat star shape plate consists of a square base with four triangular sides **Figure 2.12(c)** that are folded to 3D pyramids with 60° angles (**Figure 2.12(d)**).

It is possible also create complex 3D shapes with different hinge angles by printing hinges with different geometries [1]. **Figure 2.13 (a)** shows a flat triangle sheet that folds itself into an origami airplane with a 0° angle in the middle hinge that bends upward and 90° angles in the two side hinges that bend downward. The hinges are created by printing the bilayer composites with the fibers on the top layer for the 0° hinges and on the bottom for the 90° hinges. To simplify the loading process (allowing simply a 20% stretch), they printed the 90° hinges in **Figure 2.13 (a)** at an inclined angle relative to the base of the plane, but they maintained the fiber orientations parallel to the base (and the applied stretch, **Figure 2.13 (a)** inset). They created an even more sophisticated origami airplane by printing not only hinges with different lengths but also ones with different cross section profiles (**Figure 2.13 (b)**).

The use 3D printing of active materials to create components that controllably change their shape over time is not limited to the use of PAC hinges. In fact, it possible directly print 3D devices by strategically placing shape memory polymers at pivotal locations or throughout an entire structure. Then programing a temporary shape of arbitrary form that can be achieved by applying a prescribed mechanical loading at TH followed by releasing the constraints at TL. The components can then be returned to their complex original 3D shapes after heating back to TH. **Figure 2.14** shows such an example. Compared to the means of printing flat components with PAC hinges and then assembling them into 3D components, directly printing 3D components with SMPs allows the creation of complex 3D configurations that are potentially more precisely controlled, as they are printed directly in their permanent shapes. However, the direct printing requires longer manufacturing times and uses more material than printing flat components and assembling them. With the Objet printer used in this work, a 1mm (20mm×20mm×20mm box) thick structure takes roughly 10 mins to complete.

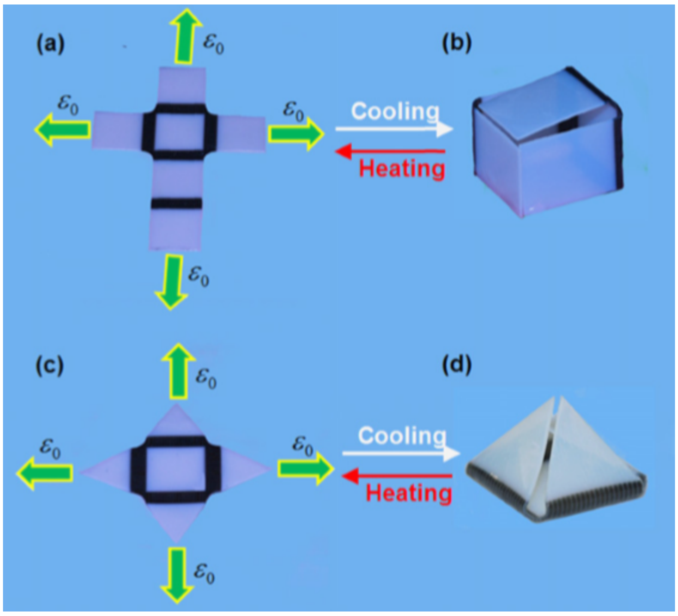


Figure 2.12 *Active origami box and pyramid. The printed flat cross shape in* **(a)** *assembles itself into a desired box shape in* **(b)** *after the programming steps.*

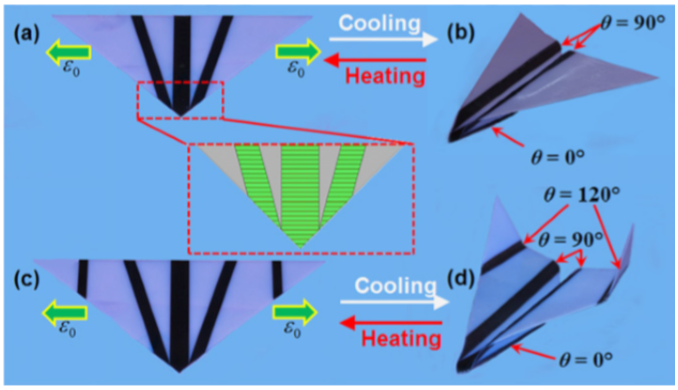


Figure 2.13 *Active origami airplanes. A flat triangle sheet with three hinges in* **(a)** *assembles itself into an origami airplane with a 0° angle in the middle hinge that bends upward and 90° angles in the two side hinges that bend downward in* **(b)**.

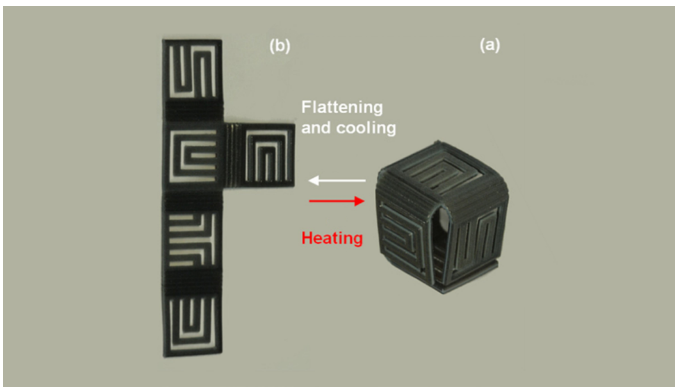


Figure 2.14 *A directly printed origami SUTD-CU box. An as-printed 3D SUTD-CU box in* **(a)** *was deformed into a flat form at TL in* **(b)**. *After heating back to TH, the structure recovers the 3D box shape.*

2.7 DESIGN TOOLS

The previous sections of this chapter have focused primarily on domain knowledge about fold concepts and the various drivers to design 4D printing structures.
In this section some of the main 4D printing design tools in support of design activities are reviewed. Design tools are objects, media, mainly computer programs, which can be used to design. They may influence the process of production, expression and perception of design ideas and therefore need to be applied skillfully.
Existing computer aided design can be used directly or extended for use in the analysis and design of active folds. However, the challenges of identifying crease patterns and fold sequencing require unique tools and methods and finding a way to control the sequence in which the structure will fold in a controlled manner. The design tools below come from different fields, some of them have been developed to design 4D printed structures, others are mainly used for origami models which can be adapted to deal with self-folding active products.

2.7.1 Project Cyborg

Project Cyborg by Autodesk is a software to simulate the 4D printed object's bending algorithm [15]. It is a platform capable of programming self-folding from nanoparticle to human-scale manufacturing. This software can simulate self-assemblies and programmable materials, specify the optimisation parameters for geometrical transformation, shape constraints, and the folding sequence.
Originally, Tibbits used this software that carries out complex self-assembly structures using one chain of feedbacks (**Figure 2.15**). Now, Project Cyborg allows for specific areas of a part, such as joints and hinges, can be assigned with the smart material properties and provide a visualisation of the object's bending process. This allows users to predict if folds will block another fold's path or improve bending efficiency.

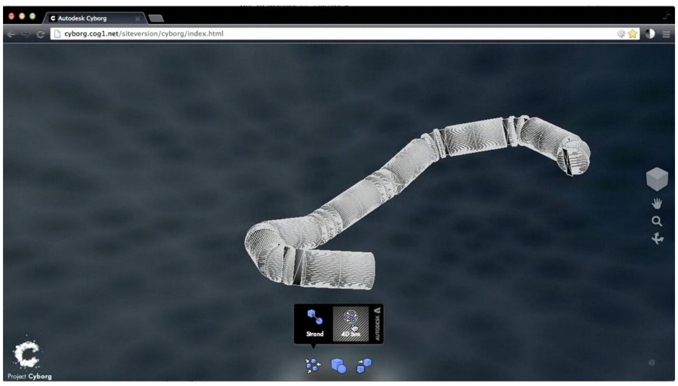


Figure 2.15 *Visualisation of the bending process of a chain of feedbacks with related hinges from Project Cyborg from Autodesk.*

2.7.2 Thermorph

Thermorph is a design editor to print flat thermoplastic composites using fused deposition modeling (FDM) and trigger them to self-fold into 3D with arbitrary bending angles [6] (**Figure 2.16**).
Byoungkwon An et al. have developed this novel method printing complex self-folding geometries. They have demonstrated that with a desktop fused deposition modeling (FDM) 3D printer, off-the-shelf printing filaments and a design editor, they can print different 4D printing structures. Thermorph is based on a new curved folding origami design algorithm, compiling given arbitrary 3D models to 2D unfolded models in G-Code. As a demonstration of the Thermorph platform, complex self-folding geometries (up to 70 faces) have been designed and printed, including 15 self-curved geometric primitives and 4 self-curved applications, such as chairs, the simplified Stanford Bunny and flowers. Compared to the standard 3D printing, this method can save up to 60 - 87% of the printing time for all shapes chosen.
Thermorph will be further detailed in the fourth chapter dedicated to case studies.

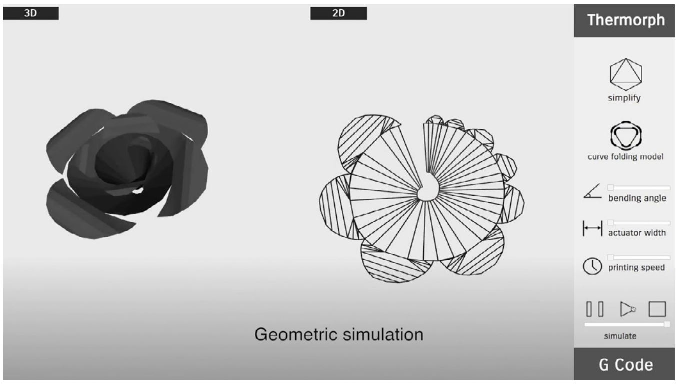


Figure 2.16 *The interactive design software for the self-folding rose to allow the shape exploration. It let simulate folding and specify parameters related to actuation parts.*

2.7.3 4DMesh

Similar to the Thermorph, 4DMesh is a method developed by Guanyun Wang et al. that combines shrinking and bending thermoplastic actuators with customized geometric algorithms to print 4D printing shells. With these tools, users can input CAD models of target surfaces and produce respective printable files [16].
Guanyun Wang et al. in their 4DMesh project push the practical uses of 4D printed self deployable structures, making efforts on material composition design, manufacturing procedure and design tools. Their aim is designing practical and suitable design tools to augment

the design potential of HCI (Human computer interaction). 4DMesh is based on two end-to-end inverse design approaches for 4D printing morphing mesh surfaces that are non-developable. The two methods utilize either shrinking or bending actuators that they designed and characterized.
The artifacts fabricated with the G-code and an FDM printer have the configuration of a mesh and can morph into an approximation of the target surface. To trigger 4DMeshes products, Guanyun Wang et al. submerge them into hot water.
This method has been envisioned to enable and democratize modular, personalized, and custom-made designs. By digitally sketching a surface and processing it with the algorithm, the artifacts can be manufactured easily and rapidly with an FDM 3D printer (**Figure 2.17**).

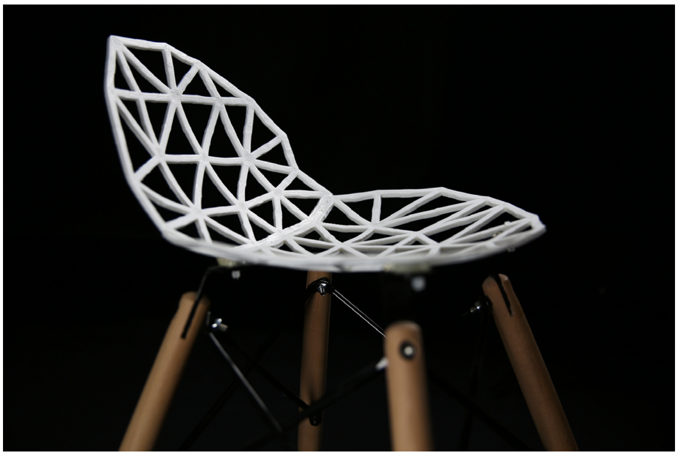


Figure 2.17 *Back support and seat realized by 4DMesh method.*

2.7.4 Kinematics

Another 4D printing tool, even if it was not born for this field of applications, is Kinematics by Nervous System Studio [15]. This project started in 2013 with the attempt was to print larger objects than the printer itself and to succeed without having to assemble small parts.
Kinematics is a system that creates complex, foldable forms composed of articulated modules. The system provides a way to turn any three-dimensional shape into a flexible structure using 3D printing. It combines computational geometry techniques with rigid body physics and customization.
The system has been used for clothing because of its advanced folding algorithm. First, a person's body is 3D scanned then imported into the program. Next, the user can alter the clothing by changing the clothing's shape and pattern. The custom designed clothing can be draped to show what it will look like on the individual or folded into a compact profile. That piece of clothing is 3D printed with the proportions specific to that individual. The object is made of small triangular hinged fragments that allow for movement and form (**Figure 2.18**). Typically, a dress is larger than the print bed of most 3D printers and would require multiple prints in order to be pieced together. In some cases, Kinematics allows the dress to be folded in a way that models the behaviour of how a person would fold the dress to fit the print volume of the 3D printer (**Figure 2.19**). Nervous System even developed with Kinematics an online platform on their website, in which users customize and order their own jewelry and clothes.

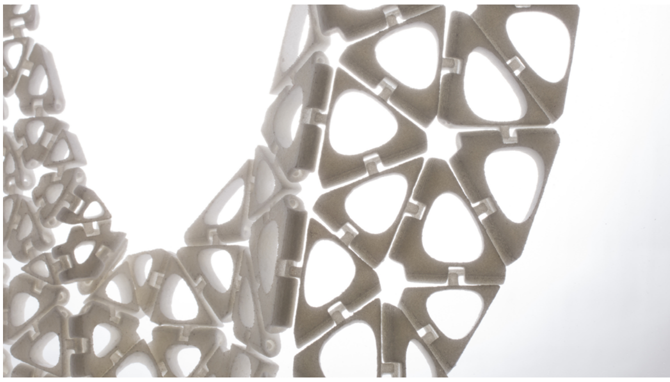


Figure 2.18 *A piece of triangular pattern of flexible hinges that can be customized in shape and dimension before printing.*

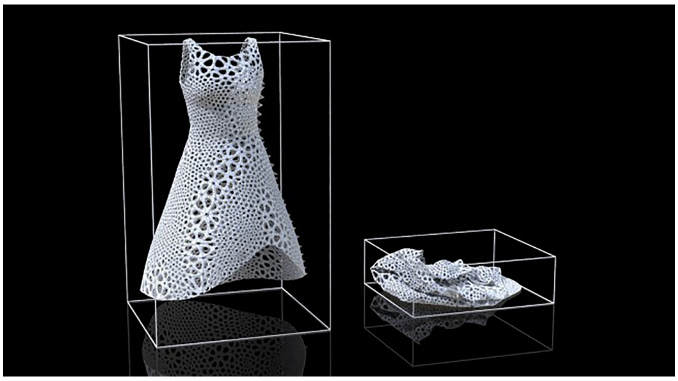


Figure 2.19 *A simulation of the Kinematics dressed folded and compressed into a compact form that will fit the build volume of a 3D printer.*

2.7.5 Origamizer

One of the ultimate challenge in computational origami design is to devise an algorithm that tells the best way to fold anything object. Tomohiro Tachi developed several software tools for origami design such as Origamizer (2008) in order to generate the crease pattern on a sheet of paper that folds to a given three-dimensional polyhedral mesh (**Figure 2.20**) [17].

Origamizer pattern folding software that can be used to create complex origami shapes through assigning nodes, edges, paths, polygons, vertices, and creases. The software is capable of generating crease patterns that can fold solid geometries into a complex polyhedral model with a designated number of seams.

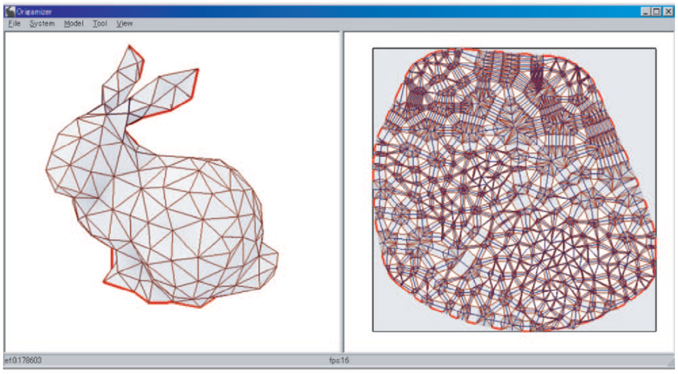


Figure 2.20 *Triangular hinged fragments that allow for flexibility and movement in the 3D printed structure from the linking of small rigid components.*

2.7.6 System Eos

Another origami computational interface called Eos that permits a user to fold sheets virtually as if they were folding paper by hand has been developed by Ida and coworkers (**Figure 2.21**) [20].
The software allows for visualization and interaction of origami constructions. Eos provides two methods for folding: the mathematical fold and the artistic fold. The former folding method is based on axiomatic definitions of origami folds. Such method requires fair knowledge of nomenclature and coding definitions for different folding options. The artistic fold method is more user-friendly and allows one to specify relatively straightforward folding features features such as whether fold is a Valley or a Mountain (types of origami foldings), which lines are to be folded, and to what angle they should be folded. This method is preferred for the creation of artistic origami.

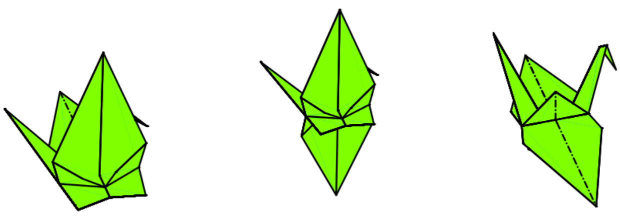


Figure 2.21 *Construction of Crane from Origami System Eos.*

2.7.7 TreeMaker

One of the most well known software packages for fold pattern design is Robert Lang's TreeMaker [19].
Lang described the theoretical foundation on which TreeMaker is based called *the tree method*. This method allows for the design of an origami base, which is defined as a no stretching transformation of the sheet into 3-space such that all facets remain flat. The base can be fully defined by the location of creases, their angles, and the orientation and location of each facet. The base is then folded and shaped into an origami model.
TreeMaker determines a crease pattern that results in the desired base via optimization methods. An example of the application of this algorithm is shown in **Figure 2.22**, where the tree graph of a bug is shown together with the computed crease pattern generated by TreeMaker.

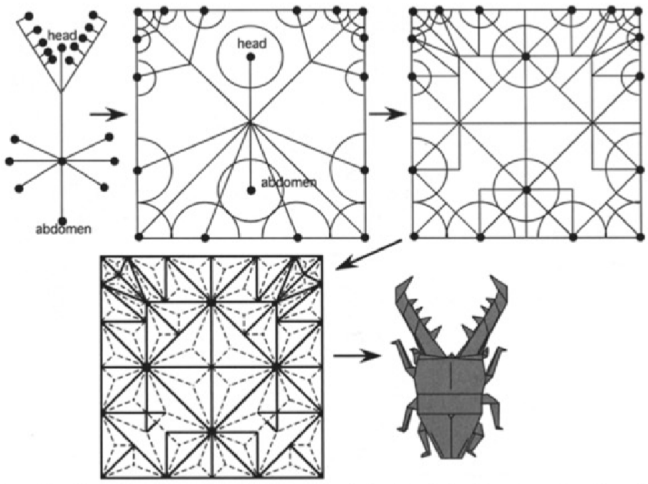


Figure 2.22 *Illustration of the tree algorithm using one of Meguro's bugs.*

2.7.8 Akleman's method

Akleman and coworkers developed a method to unfold a given convex polygonal shape into a one-piece planar developable surface [20].
The algorithm first triangulates (divides into triangles) the initial shape to guarantee that all faces of the shape are planar. A "dual mesh" is then constructed from the triangulated shape such that every face becomes a vertex and every original vertex becomes a face. A dual graph consisting of the edges and vertices of the dual mesh is then created along with an associated spanning tree that includes all vertices from the dual graph. Every vertex of the dual graph is then two-dimensionally thickened into a triangle and every edge of the spanning tree is two dimensionally thickened into a developable quadrilateral. The spanning tree is then unfolded into two-dimensional

planar shapes. The algorithm has been extended such that each two-dimensional planar shape can be further subdivided into smaller quadrilaterals and triangles for input into finite element software, which allows full mechanical analysis of the folding (or self-folding) process. An example of this procedure for the creation of a single-panel unfolding for a cube is shown in **Figure 2.23**. The feasibility of the algorithm was tested by considering the complete unfolding/re-folding process associated with a dome and a cube shapes.

Table 2.2 is a summary of the design tools reviewed in this section.

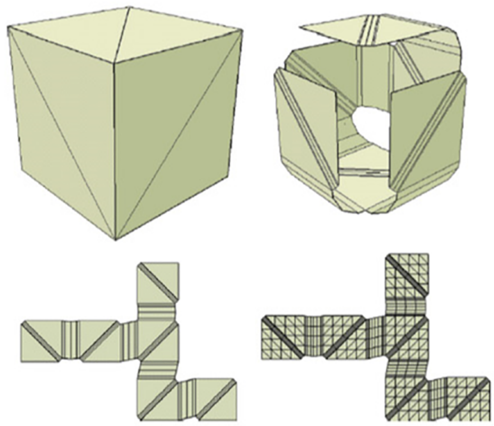


Figure 2.23 *Procedure to obtain a single-panel unfolding from a cube: initial mesh, spanning tree, unfolding, and refinement for finite element analysis.*

DESIGN TOOL	CONCEPT	APPLICATIONS	CURRENT UPDATE
Project Cyborg	4D Printing Software	Simulating transformation Specifying parameters	Project in development
Thermorph	4D Printing Software	Converting 3D/2D model into self-folding structures Simulating folding Specifying parameters Creating G-Code for 3DP	Prototype
4DMesh	4D Printing Method	Converting 3D model into self-folding structures Specifying parameters Creating G-Code for 3DP	Prototype
Kinematics	3D Printing System	Converting 3D model into patterned flexible structure Customization 3D printed in-place	Specific method of a Design Studio
Origamizer	Origami software	Generating the origami pattern for a given three-dimensional shape	Available
System Eos	Origami software	Virtually folding sheets to design origami structures	Available
TreeMaker	Origami software	Design of origami bases	Available
Akleman's method	Algorithm Origami Model	Generating the origami pattern for a given three-dimensional shape	Available

Table 2.2 *Summary and comparisation of the design tools.*

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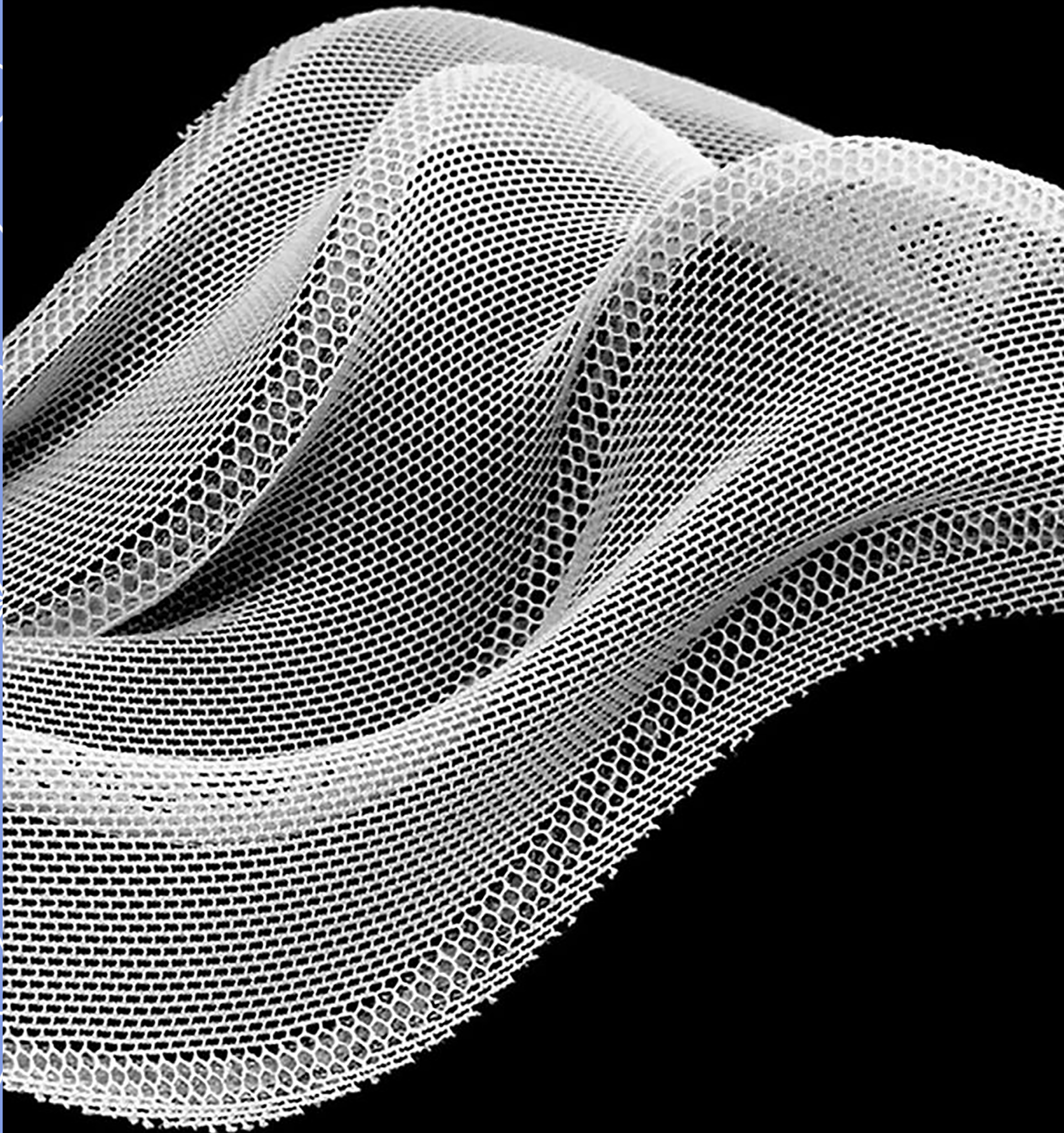

CHAPTER III

BENEFITS AND LIMITATIONS OF 4D PRINTING

3.1 INTRODUTION

Researchers have begun to explore the possibilities of 4D printing as an emerging technology as additive manufacturing technologies mature in parallel to growing knowledge of smart materials, available stimuli, mathematical modelling, and geometric programming.

In this chapter it is discussed advantages and disadvantages of 4D Printing, considering productive and design implications and which are the challenges and current limitations that researchers are facing to bring concrete results. In the first section, efficiency and productivity are considered, focusing on fast prototyping, printing time and saving in raw materials. In the following sections, limits of 4D Printing are classified into three main areas; technological limitation, material limitation and design limitation. Once these challenges are solved, this new technology will be hopefully simplified and applied in many different applications and industries.

3.2 PRODUCTION BENEFITS

3D printing has emerged as a revolutionary manufacturing technology for its advantages including fast prototyping, savings in raw materials, and design freedom in shape and structure, positioning it as an attractive and important manufacturing method for engineering and design applications. However 3D printing faces many challenges. For example, a critical drawback is the slow printing speed because of the “layer by layer” process. In addition, the advantage of raw material saving deteriorates when 3D printing is used for fabricating hollow or slender structures made of thin shells, plates, or trusses, since these structures typically require support materials or sacrificial printing materials. Most 3D printing technologies, such as Polyjet, fused filament fabrication (FFF), etc. require support materials to create overhanging structure during the printing process; selective laser sintering (SLS) emplys unsintered powder as support; and stereolithography (SLA) require a large vat of printing material. As a result, efficiently printing proper hollow or slender structures remains a challenge in 3D printing.

Recently, 4D printing has emerged as a method where a 3D structure can be printed and then transformed into a new and more complex shape when subjected to an environmental stimulus such as temperature, light or humidity. From a product manufacturing point of view, an attractive feature of 4D printing is the potential to realize a complicated 3D structure from a low-dimensional printed structure, such as 2D plate or 1D rod. This offers the significant advantages of saving both raw materials and manufacturing time.

As demonstrated recently by Zhen Ding et al., self-folding of active material structures can accelerate the fast prototyping of 3D objects by saving 60 - 87% of both printing time and material consumption.
Zhen Ding et al. **[1]** used in their research direct 4D printing of programmable 1D SMPs composite rods that can rapidly change into 3D structures. Complex permanent 3D shapes are achieved through design of the spatial layout of multiple materials in a 1D rod configuration, demonstrating the 4D printing method saves 70 - 90% printing time and printing materials compared with direct printing of 3D structures.
3D structures transformed from straight or curved 1D composite rods have considerable potential and offer advantages over conventional 3D printing technologies by reducing printing time as well as the amount of support material required. Zhen Ding et al. highlights this feature printing the buckyball in **Figure 3.1** **[1]**. The as printed structures are shown for both conventional 3D printing and 4D printing approach where the flat rod mesh is printed. As shown in **Figure 3.1 a** and **b**, each spatial component in the 3D buckyball has to be supported. It is clearly evident that a significantly larger amount of support material is needed in conventional 3D printing.
In contrast, the flat 2D buckyball mesh almost does not need any support, except some sacrificial materials set by the system to connect the model part with the build tray.

Table 3.1 compares the model and support material required for different structures, as well as the time required for both conventional Polyjet 3D printing and 4D printing of 1D rod structures **[1]**. 4D printing method offers significant reduction of both printing time and material consumption, bringing savings beyond 70% in the former and 90% in the latter in all three examples Zhen Ding et al. demonstrated. It should be noted that the supports consist of a combination of soft support material (gel) and rigid model material (Veroflex), which results in more model material being required for 3D printing than 4D printing. In addition, the post process required to remove the support material in conventional 3D printing for slender 3D structure can be time consuming, as a large amount of material has to be cleaned in a careful way to avoid breaking the slender model part. The time for this process in 4D printing is greatly reduced, but at the expense of needing to perform the heating process after printing to assemble the 3D structure. Additional savings in printing time could be achieved by strategic placement of multiple flat rods in a single print **[3]**.

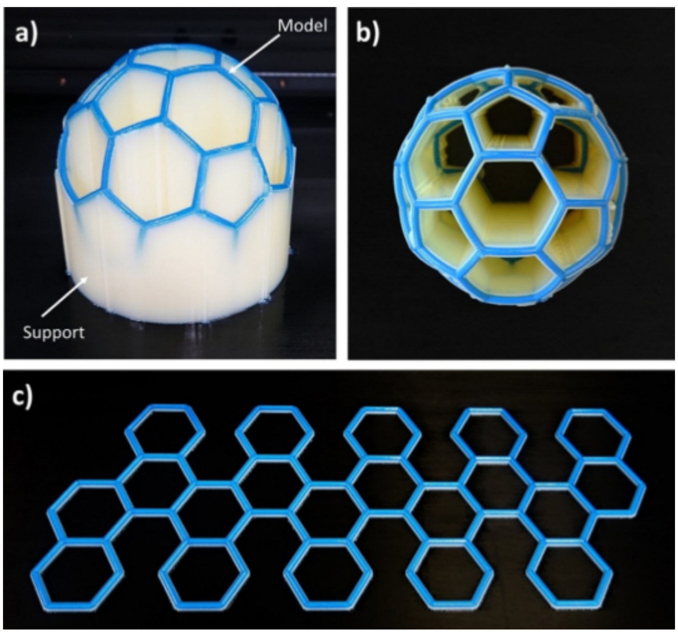

Figure 3.1 *The buckyball in conventional 3D printing* **a)** *and* **b)** *top view needs to be supported by a large amount of sacrificial material.* **c)** *The initially flat, 4D printed buckyball mesh consumes only little support material.*

Structure	4D/3D printing material and time consumption						Savings by 4D printing			
	Model material (g)		Support material (g)		Printing time (h)		Model material (%)	Support material (%)	Total material (%)	Printing time (%)
	4D	3D	4D	3D	4D	3D				
Cubic frame	28	93	14	179	3.3	13.9	70	92	85	76
Buckyball	36	145	24	316	3.3	17.2	75	92	87	81
Helix	26	95	13	148	3.3	12.0	73	91	84	73

Table 3.1 *Comparison of material and time needed for the 3D structure using the conventional Polyjet 3D printing and 4D printing methods.*

3.3 TECHNOLOGICAL LIMITS

In the future, 4D printing requires interdisciplinary research and technological advances in various fields, including hardware of 3D printing techniques, material science of smart materials, as well as novel design and modeling tools **[2]**.

First, *high-resolution*, *high-speed*, and *multi-material 3D printing technologies* are highly desirable to satisfy the production of materials and devices with multiscale complex geometries. These are the technological challenges that researchers are currently facing to bring concrete results of 4D printing. Unfortunately there are a limited number of 3D printing technologies that are suitable for 4D printing, as already seen in the first chapter. In the area of technological limitation, this is considered inadequate availability of 3D printing technologies **[2]**.

Even the most common printing processes of 4D printing do not completely meet the requirements and maintain a certain level of inadequacy.

For example, Polyjet printing, one of the most used forms of 4D printing, enables digital materials with widely tunable mechanical properties for SMPs and composites. However, polyjet printing has some drawbacks, including high equipment cost, stringent resin property requirement, and limited material choices. About the cost, Inkjet is perhaps the most commercially viable 3D printing approach for 4D printing devices, although at a price that is typically 10–100 times higher than FDM printers **[2]**.
However in order to truly master the field, there remain a number of significant challenges.

Alternatively, extrusion-based printing methods (FFF and DIW) are more versatile but have the limitations of slow printing speed, relatively low resolution, and sometimes poor interface.

Others 3D printing processes, stereolithography (SLA) and digital light processing (DLP) have strong potential to contribute to the future of 4D printing. For example, Yu Ying Clarrisa Choong et al. **[3]** and Tingting Zhao et al. **[4]** used stereolithography (SLA) to print components of shape memory polyurethane (SMPs) with high mechanical performance. Although products print with steligraphy are brittle and not suitable for mechanical efforts, unless they are made with the right combinations of composite materials (for example using Inkjet 3D printing with multiple printheads) that can be much more difficult and expensive to produce.

Another common limitation to current products made with 4D Printing are the limited scale dimension, which is beyond the limited space used in 3D printers, also due to the difficulty of dealing too large devices with external stimuli. For example, the application of the PμSL technique allows for producing shape-changing materials at the microscale, which is favored for some biomedical applications. However, printing using a PμSL system is limited by the chemistry the resin undergoes and by resin viscosity and its small (mm-scale) build area.

In the area of technological limitation, one of the challenges faced is the design of smart structures. One example of smart structure is the *antagonistic actuator* for soft robotics **[2]**. In order for the actuator to work, the membranes used have to be in a pre-strain state. However, currently there is no report on design to create a pre-strain membrane directly. At the current status, there is no 3D printing technology that is capable of directly fabricating a prestrain membrane. Therefore, in this example, the development of 4D printing are hampered by the lack of feasible design of smart structures and the available technology to fabricate the final component.

Table 3.2 is a summary of the main technological limits of 4D Printing related to 3D printing process, with a comparison between advantages and disadvantages.

PRINTER	ADVANTAGES	DISADVANTAGES
FFF, DIW	Wide range of materials.	Low printing speed. The resolution of FFF and DIW is limited by the nozzle diameter (100–200 μm). Difficult to print multiple materials.
Inkjet 3D	High resolution.	High equipment cost (Combinations of composite materials). Limited material choices (Stringent resin property requirement).
SLA, DLP, PμSL	High resolution. High printing speed.	High equipment cost. Limited to UV-curable substances. Laser could damage living cells.
SLS, MJF	Low cost. High printing speed. Wide range of materials.	Low resolution. Difficult to remove the solvent/ liquid binder.

Table 3.2 *Summary of the advantages and disadvantages of 3D printing processes related to 4D Printing.*

3.4 MATERIAL LIMITS

The challenge faced under the category of material limitation is related to the properties of the smart materials or smart composites. Mechanically robust materials with fast response speed are usually the desired properties for practical applications. Researchers have tried over time to reach these two goals, which can be reached through combinations of SMP or SMA composites.

For example, Veriflex is a fiber-reinforced composite that uses a shape memory polymer as the matrix. This allows the material to easily change shape above its activation temperature. At lower temperatures, the material maintains high strength and high stiffness. When heated, Veriflex will temporarily soften. It can then be reshaped and will harden in seconds, maintaining the new configuration. When reheated, Veritex will return to its original cured shape. This versatility allows for structures to be stowed and then later deployed to the operational shape.
The combinations of mechanically robust materials with fast response speed, could require a lot of effort and production costs from 3D printing process.
One example is the NiTi SMA [2]. As NiTi SMAs are extremely compositional sensitive, it requires great effort to fabricate NiTi components by both conventional and 3D printing methods without encountering problems such as micro-structural defects, oxidation and changes in the phase transformation behaviour. Besides, fabricating NiTi powders from NiTi ingot is expensive and normally results in significant waste of the materials. Hence, more research is required to overcome these constraints as these would hamper the developments of 4D printing. Additionally, during the SLM fabrication of NiTi SMA, the metallic alloy was subjected to complex thermal history such as rapid solidification, directional cooling, repeated melting and phase transformations. These factors would introduce complications to the evolution of micro-structures and properties that might not be found when the NiTi alloy was manufactured by conventional methods. Furthermore, the complications may even lead to unexpected failure of the components. Therefore, the lack of knowledge in the interaction between the smart materials and 3D printing technologies will pose a challenge to the progress of 4D printing.

Another challenge faced is the fundamental issue of fast mechanical degradation observed in multi-material printed parts during repeated thermo-mechanical cycling. Normally the components or materials made with active

material have a life cycle limited to the number of thermal cycles they can withstand before becoming unusable. This can become a major problem if you want to use 4D printing material for various applications that require a certain durability and longevity.
Yu Ying Clarrisa Choong et al. [3] has been focused on these aspects realizing a material can achieve a high curing rate and precise printing that are highly desired for SLA process. The mechanical strength of the printed parts is comparable statistically to industrial SMPs. An outstanding durability of 22 cycles was demonstrated to show its prolonged shape memory cycle life (**Figure 3.2**).

Moreover, as 4D printing is a relatively new research area, a lot of smart materials have not been explored yet. However, one thing we can expect in the near future is that the range and variety of printable smart materials will definitely increase, together with the improvements in the properties of printed components such as strength, durability and quality of surface finish.

Another limitation of 4D printing structures is the mechanical loading that usually have to be applied in order to pass from Permanent Shape to Temporary Shape. Future work will focus on realising 4D printed parts that eliminate the need for mechanical loading. For example, recent work by Mao [5] produced a multi-material layered composite with a reversible shape-changing effect. Each material reacts differently to the stimuli, thereby switching behaviours between two stable and stiff configurations without the need for mechanical loading. The controlled spatial distribution and temporal arrangements also determine the geometrical and temporal shape-change characteristics, mechanical stiffness, and load-carrying capacity for each configuration. The lower layer is made up of a hydrogel sandwiched between two columns of elastomers, while the top is placed with a layer of thermo-responsive SMP. Small holes are made within the elastomer layer to permit the flow of water, in which the design restricts the swelling of the hydrogel in the Z direction, allowing the shape change to only occur in the X–Y direction. In addition, the difference in stiffness between the elastomer and the SMP means that the strip bends inwards. More importantly, the thermo-sensitive SMP is carefully designed in such a way to regulate the sequence of time for the shape change to take place.

Table 3.3 is a summary of the material limits of 4D Printing are presented in this section.

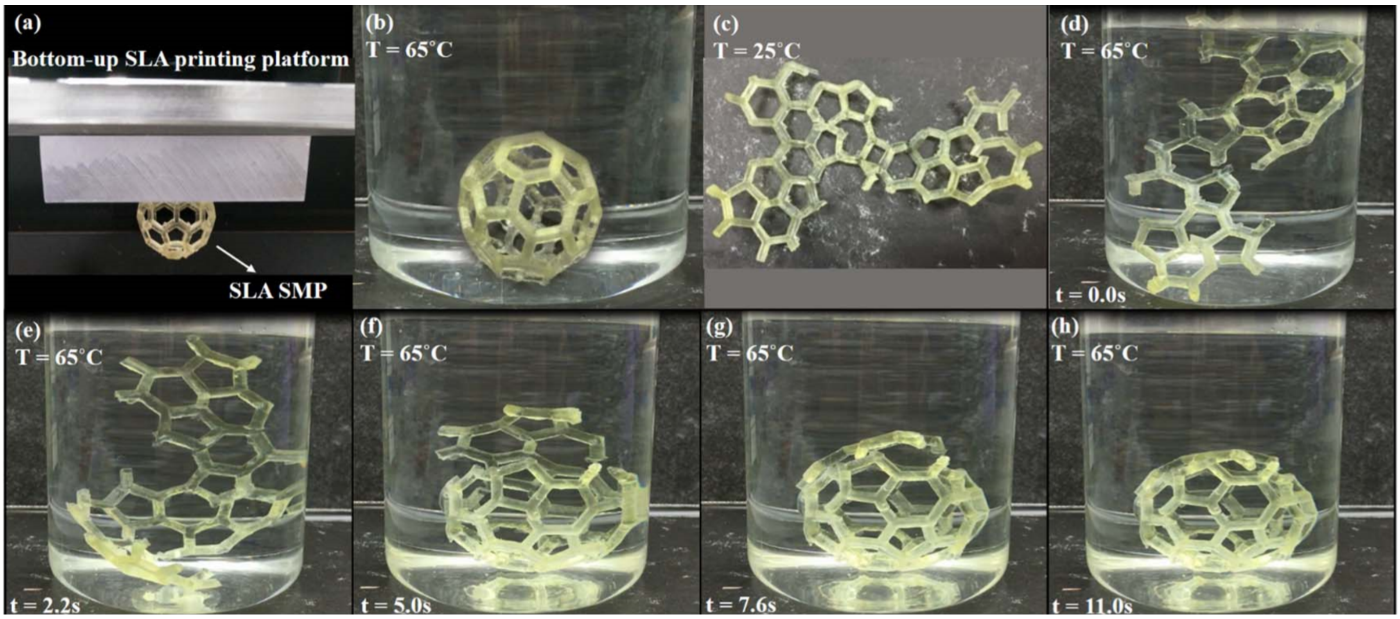

Figure 3.2 *SLA SMP Buckminsterfullerene (or C60 bucky-ball) in printing (in panel a),unfolded after printing (in panels b–c), and recovered its original bucky-ball shape by soaking at 65 °C of water (in panels c–h).*

	Need for mechanical loading to pass from Permanent Shape to Temporary Shape.	
Problems and defects during fabrication of Composites SMM.	**MATERIAL LIMITS**	A lot of smart materials have not been explored yet.
	Fast mechanical degradation during repeated thermo-mechanical cycling.	

Table 3.3 *Summary of the material limits of section 3.4.*

3.5 DESIGN LIMITS

Although the research on 4D design principles and folding structures has been extensive, multiple challenges and open questions remain.

As already mentioned, theoretical/mathematical models and design methodology are needed to accurately predict and optimize the shape shifting. Basically 4D printing by shape shifting involves two states of a part: the as-printed state and the as-transformed state [7]. A practical application of 4D printing will require the precise control of both states. A model-based design tool or mathematical model is needed to predict the transformed shape from the printed shape, or even more desirable to guide the design of the as-printed shape based on the target as-transformed shape.

Mathematical models used in 4D printing process can change based on a desired shape, material structure, material properties, and stimulus properties.
Evaluation of common active materials and self-folding structures for various fold concepts confirms that there is no dominant active material or mechanism for self-folding applications. Material and mechanism selection are application-dependent (e.g., dependent on the desired folding radii or angle, surrounding environment) [6]. This is a crucial point for designers of 4D structures, since the level of complexity requires an certain effort and deep specialized knowledges.

Another challenge is the need of increased understanding of the mechanics of folding in thick structures toward improved flat foldability. Even though multiple theories and software exist for the design and analysis of zero thickness folding structures, few exist for the development of folding structures with non-zero thickness. Thick origami folding is a challenging problem and has to be addressed for the development of applications that require compact storage in non-planar configurations (e.g., stacking of faces) and conventional origami structures where the thickness of the sheet is not several orders of magnitude below the characteristic length of the sheet.

Another need is the development of remote field-induced reconfigurable foldability [6]: every one of the active material-based folding or fold-like structures described herein relies on the imposition, local or global, of a single given physical field (e.g. thermal, magnetic, etc). Sheets are pre-engineered to respond in a single particular manner to such field application. Therefore, reconfigurability (i.e., from one morphed/ folded shape to another) under global fields becomes difficult, this may prevent the level of truly reconfigurable self-folding structures at the small scale or other situations where local field imposition becomes unfeasible. Thus, reconfigurability under global (remote) fields would be an important advancement. This could be accomplished by designing for multi-field actuation (e.g. thermal and electric, thermal and magnetic) or by allowing discrete folding regions to be tuned so as to respond to changes in a single global field type (e.g., as in changes in magnetic field frequency). Multi-field self-folding is being addressed by some researchers in both large and small scales but there is still much to be done in this area.

Table 3.4 is a summary of the design limits of 4D Printing are presented in this section.

	Theoretical/ mathematical models are needed to accurately predict the shape shifting.	
Limited understanding of the mechanics of folding in thick structures.	**DESIGN LIMITS**	There is no dominant active material or mechanism for self-folding applications.
	Difficult of reconfigurability through global fields instead of local fields.	

Table 3.4 *Summary of the design limits of section 3.5.*

CHAPTER 3. REFERENCES

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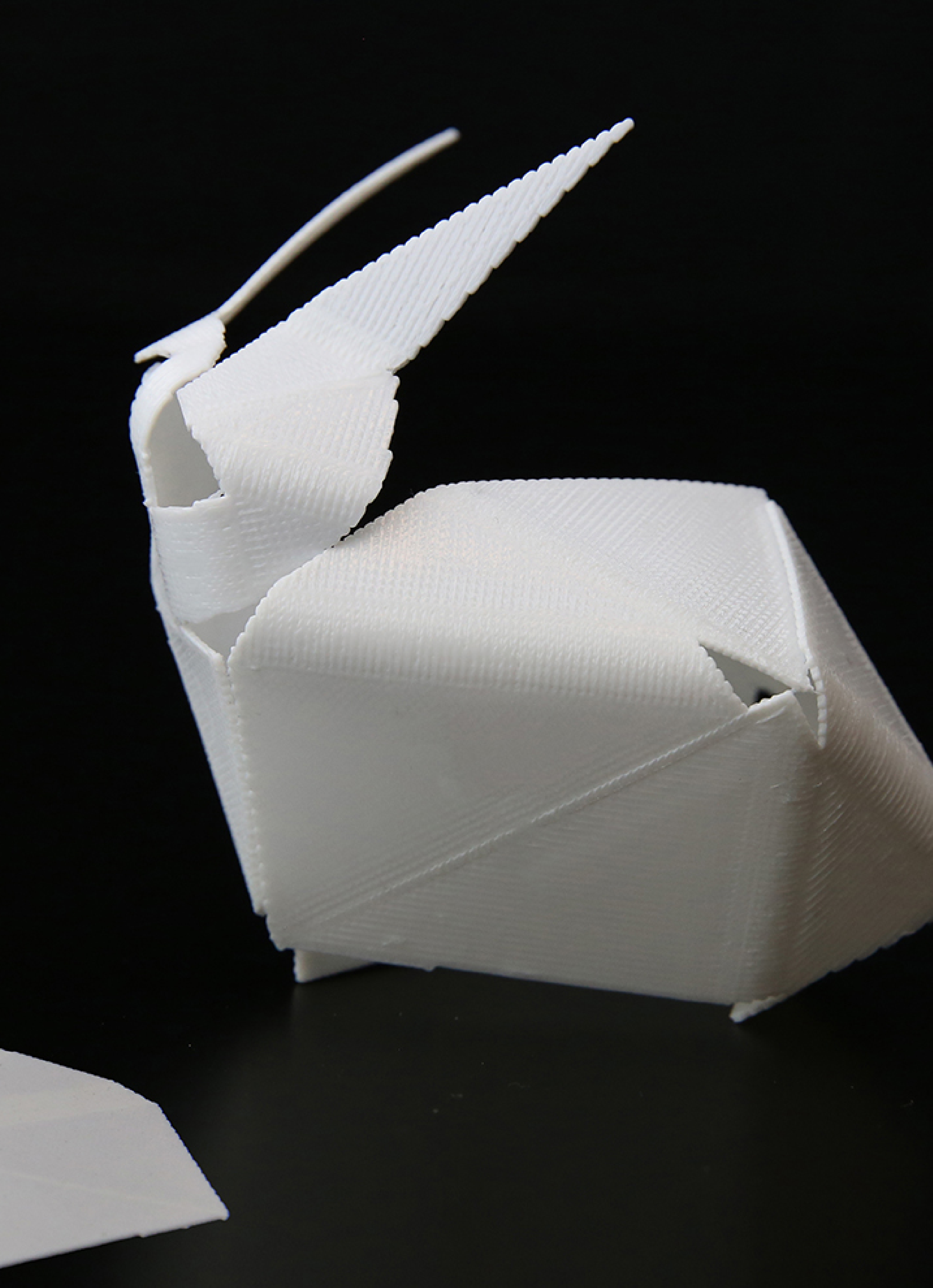

CHAPTER IV

CASES STUDIES

4.1 INTRODUCTION

After a general view of the methods and tools of 4D Printing and an analysis of the benefits and limitations, in this chapter four case studies are reported regarding possible applications that have been highlighted in the previous chapters: Design tools for 4D printing, specific 4D printing method for flexible devices, specific biomimetic 4D printing for flexible and biocompatible devices.

The first two cases studies, 4DMesh and Thermorph (Already seen in chapter 2.7) are design softwares for the development of 4D Printing products for rapid prototyping. These are projects that are still under development, however these represent the latest progress made in an important area such as design tools, essential for modeling the geometries, parameters and determining interactions for shape-shifting states.

The third one, Yoonho Kim et al.'s method, shows how to exploit properties of smart materials using a 3D printing process **[8]**. It is about 4D printing ferromagnetic devices used to create soft actuators and robots controllable by magnetic fields through global fields.

The fourth one case study, Sydney Gladman et al.'s method to produce biomimetic hydrogel composite orchids, shows potential alternative uses, presenting the most recent progress in the field biomimetic 4D printing to create products that mimic plants **[8]**.

4.2 THERMORPH: DEMOCRATIZING 4D PRINTING

As already mentioned in Chapter 2.7. Byoungkwon An et al. develop a novel editor of printing complex self-folding geometries Thermorph [1]. It is used to prototype hollow and foldable 3D shapes using fused deposition modeling (FDM), based on new curved folding origami design algorithm. An overview of the phases of Thermorph can be see in **Figure 4.1**.

Thermorph is a rapid prototyping system through self-folding mechanisms of shape memory thermoplastic, which introduce an end-to-end design pipeline to fold a variety of arbitrary 3D geometries from a flat sheet. Byoungkwon An et al. has proved that thair approach can save printing time and post-processing efforts for a lot of complex 3D geometry fabrication comparing to standard 3D printing approach, with the main promise of the work to achieve novel folding structures with readily available printing materials.

It is noteworthy that Byoungkwon An et al. set some criteria to make Thermorph as practical platform [1]:

- It should be an automated printing process, no pre- or post-processing.

- It should be on a desktop FDM printer to make this 4D printing technique readily accessible for researchers, hobbyists, makers and students.

- It should use off-the-shelf, low-cost and accessible printing filaments.

- While heat is generated by various energy sources and is deliberated by various media, such as air, microwave or water, Thermorph should be made of thermoplastic for its fitness as a general prototyping material.

- Thermorph should be an end-to-end approach, which means that users can input their desired 3D shape and see the printer printing it out automatically.

- Unlike most of the self-folding and 4D printing work which showcases a group of predesigned primitives and combinations of these primitives, Thermorph should be able to handle arbitrary 3D geometries.

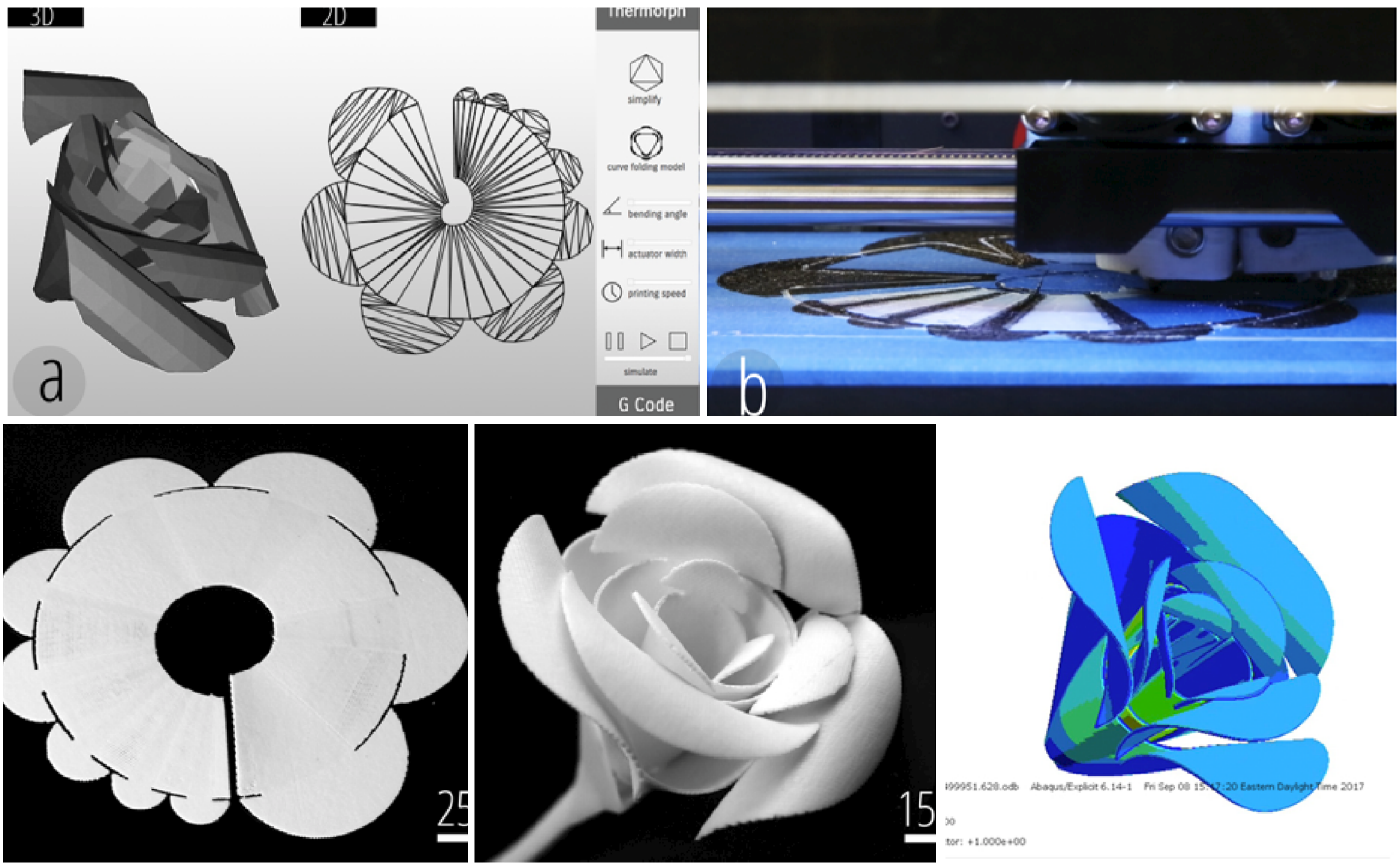

Figure 4.1 *Thermorph overview.* **(a)** *Design editor to define and simulate the self-folding composite;* **(b)** *the printing toolpath of a flat sheet is generated from* **(a)** *and printed on an FDM printer;* **(c)** *the printed flat sheet;* **(d)** *the flat sheet self-folds sequentially into a rose;* **(e)** *finite element based simulation of the self-folding rose.*

4.2.1 SELF-FOLDING MECHANISMS

Thermorph propose a bi-layer structure: one layer of Thermopolyurethane (TPU) as the constrain layer and three layers of Polylactide (PLA) as the active layer. Together these four layers form an actuator.

As already seen in chapter 2.2.4, Thermorph uses *"direct 4D printing"*, incorporating the internal stress during printing. When PLA is being extruded by FDM printer, the polymer chain is forced to keep the straight state after it quickly cools and solidifies. If the solidified PLA is reheat, it will release the residual stress, return its polymer chain to its chaotic and shorten along the printing direction. In this way it is not necessary applying external force after the printing process for shape programming.

Figure 4.2 shows two possible ways of printing Thermorph actuator to achieve both concave and convex folding. In case A, the PLA layer is printed firstly; and in case B, the TPU layer is printed firstly. Both cases can bend substantially upon being heated. However, case A has a bigger bending angle than case B. That is because that the active layer (the PLA layer) in case A is printed on a relatively cool substrate - blue tape on the printing bed, while case B has its active layer (the PLA layer) printed on a comparably warm substrate - the previous TPU layer. As a result, PLA in case A built a bigger *residual strain/ stress* comparing with case B.
Moreover, the different bending angles in both cases are due to another reason: the differences in the residual stress between the top and bottom sides of one single PLA layer. Upon heating, the bottom side shrinks more as it retains more stress due to the constraints of the printing bed or the existing layer below. As a result, one single PLA layer tends to bend downwards when reheated. In case A, both the stress in each single PLA layer and the global constrains of TPU cause the strip to bend downwards, thus both effects add up for a downward bending; however, in case B, two effects cause opposite bending directions, and so the final behaved bending angle is smaller than case A.

Byoungkwon An et al. conducted a quantitative analysis of the bending performance on both actuators (case A and B from **Figure 4.2**). All the samples contain a middle actuator part and two side face parts. The fold angle of a sample is defined by an excluded angle of the extension lines from two side faces (the excluded angle is 180° minus the included angle). As explained before, the actuator part is composed of three active layers (PLA) and one constrain layer (TPU).
Byoungkwon An et al. measured how the printing speed (**Figure 4.3**) and the length of the actuator (**Figure 4.4**) can affect the bending angle for both cases. The data is used to provide us not only a reference for the design, but also a quantitative material performance guideline for the software development.

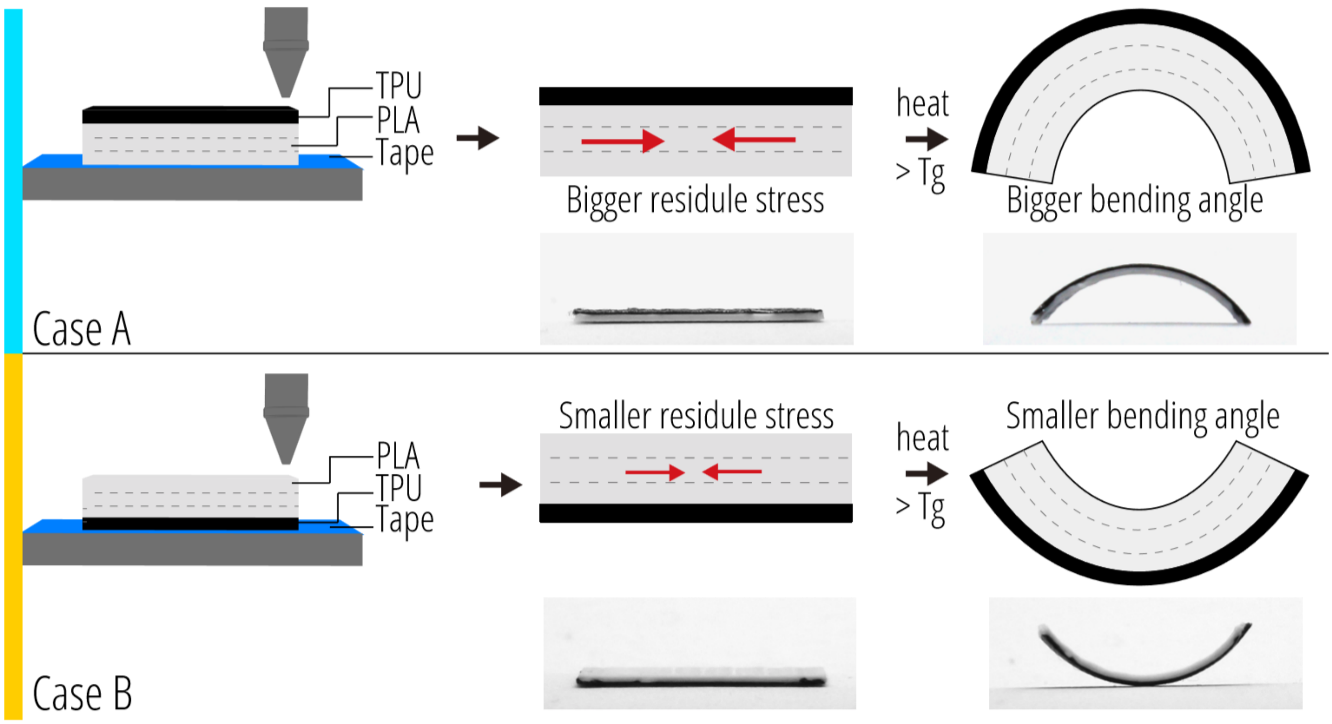

Figure 4.2 *Two printing orders of Thermorph material cause different bending directions and angles. Case A is with PLA layer (the active layer) printed firstly at the bottom; case B is with TPU layer (the constrain layer) printed firstly.*

Figure 4.3 shows that as the printing speed of the PLA layers is increased, the fold angle increases as well. This can be intuitively understood as that the faster the printing filament is pulled, the larger the residual stress is formed within the printing filament, and the more dramatically it will recover [1].

Figure 4.4 shows that the length of the actuator can be another very effective parameter to tune the bending angle. The bending angles measured for case A and B are used as a reference in Thermorph editor discussed in the following section [1].

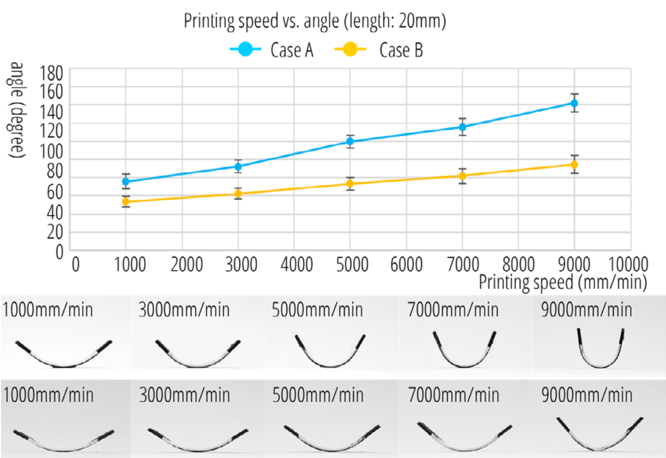

Figure 4.3 *The fold angle as a function of the printing speed of the PLA layers (the length and width of the PLA is 20mm and 10mm, respectively). The printing speed of the TPU was 1500mm/min.*

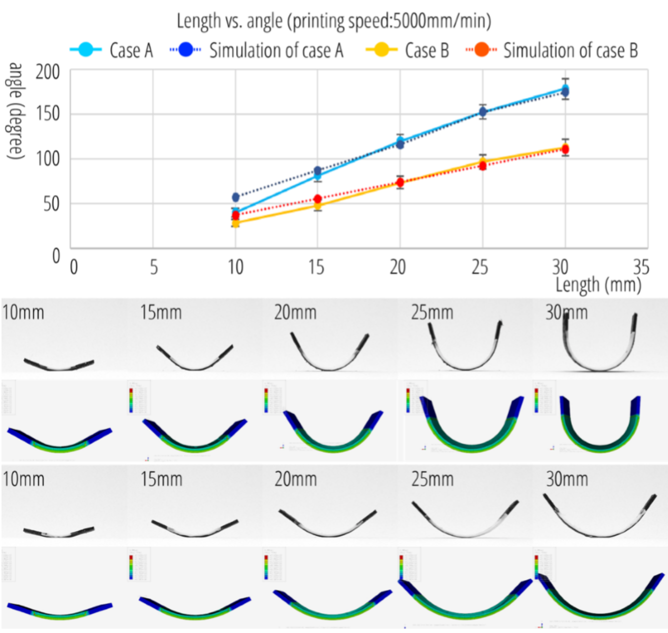

Figure 4.4 *The fold angle as a function of the actuator length (the width of each sample is 10mm). The printing speed of the TPU was 1500mm/min, PLA was 5000mm/min.*

4.2.2 THERMORPH USER INTERFACE

An interactive web-based design platform has been developed to help with the design, simulation and fabrication of Thermorph structures (**Figure 4.5**). The end-to-end pipeline allows users to start with a 3D model or 2D pattern, and end with a printed sheet that can self-fold into a desired 3D shape upon heating. The underlining pipeline is composed of five modules. Modeling, compiling and simulating modules are the backbones, while interactive editing and visualization modules provide the actual design environment.

The deterministic geometry algorithm providing mathematically guaranteed machine codes allows users to focus on the designs rather than hypothesize the right composite geometry for a desired transformation type.

Byoungkwon An et al. include two design flows: inverse and forward design flow. While the inverse design flow helps users who already have a desired 3D shape to fold into, the forward design flow enables users to define the folding angles and explore the possible folded shape before they finalize their design.

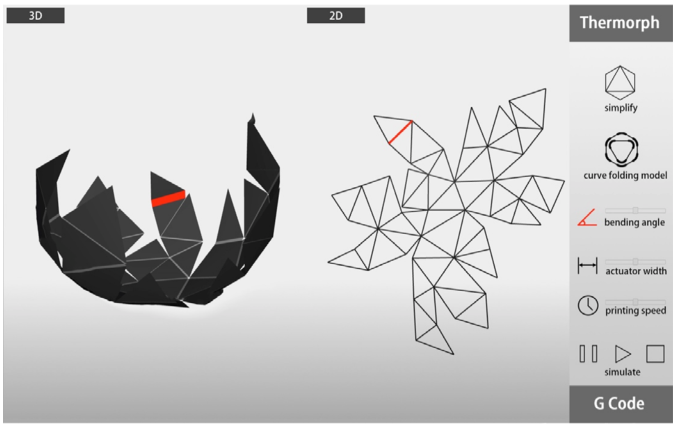

Figure 4.5 *Thermorph editor: an interactive web-based design, visualization and simulation tool.*

4.2.3 INVERSE DESIGN WALKTHROUGH

In this process (**Figure 4.6**), steps start by (a) importing a desired 3D model that we hope to print flat; (b) simplifying the mesh into a sharp folding origami model, the input mesh is simplified into a desired number of mesh faces; (c) unfold the mesh, which can be unfolded into a 2D origami pattern, each edge is associated with a fold angle and a fold sequence information; (d) converting the sharp folding origami pattern into a curved folding origami pattern, and this step integrates the actual Thermorph actuator mechanisms; (e) simulating folding, thus we can simulate how the 2D pattern can be folded back into the original simplified 3D mesh; (f) generating the printing toolpath, the G-Code, contains information of the actuator geometry on each folding hinges, printing toolpath, printing speed, material options etc. (g) printing the flat composite sheet; finally (h) triggering the self-folding with heat (hot water in this case) [1].

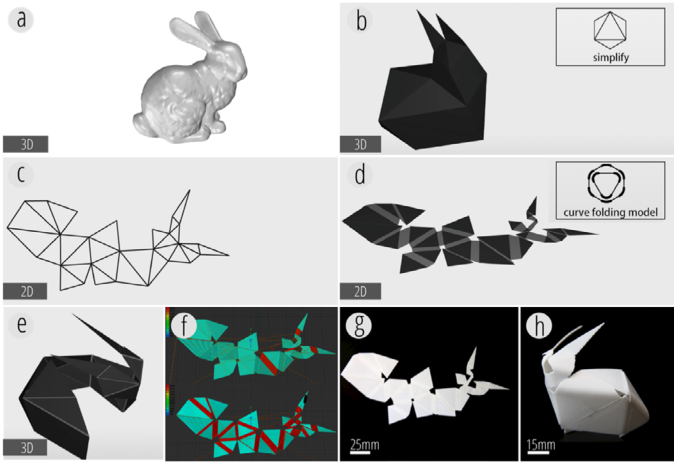

Figure 4.6 *Inverse Design walkthrough to create the self-folding Stanford bunny.*

4.2.4 FORWARD DESIGN WALKTHROUGH

Instead of importing a 3D mesh, steps start by **(a)** importing a 2D pattern with the desired folding hinge location, and select each hinge to define the desired folding angle; **(b)** simulating folding in real-time simultaneously with Step a, thus user can obtain real-time feedback on the final folded shapes; **(c)** adjusting the selected actuator length, while keep the folding angle consistent, which is to give users more flexibility to adjust the bending curvature from a sharp fold to a curved bend, and printing speed will be adjusted accordingly; **(d)** simulating the folding of the entire pattern; **(e, f, g)** follow the same steps of the inverse design flow [1] (**Figure 4.7**).

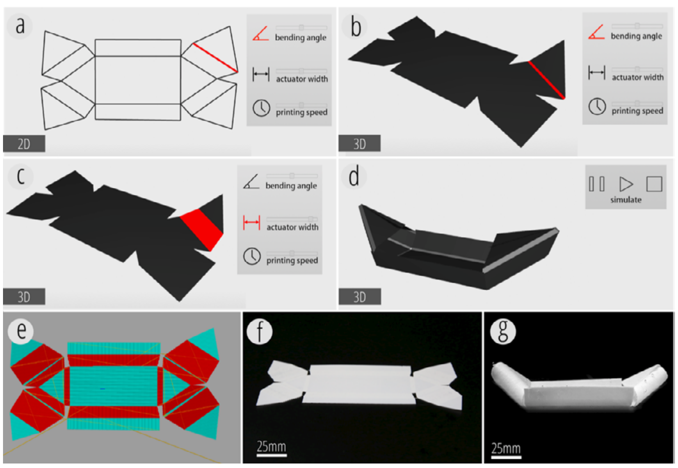

Figure 4.7 *Forward design walkthrough to create a self-folding boat.*

4.2.5 THERMORPH PIPELINE

Thermorph pipeline is a general design algorithm compiling an arbitrary 3D geometry into head motions of a 3D printer in G-Code format. **Figure 4.8** shows an overview of the pipeline with a pyramid as an example, composed of one square and four equilateral triangles.
It can be synthetically divided into the following steps:
- Step 1 Mesh Preparation for A Selected 3D Printer
- Step 2: Unfold Mesh and Calculate Fold Angles
- Step 3: Build Curve Origami Model
- Step 4: Generate G-Code for Printing

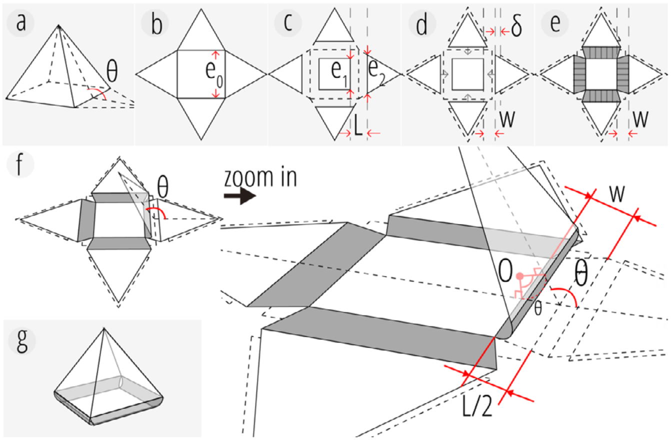

Figure 4.8 *Convert an origami pattern to a Thermorph printing pattern.* **(a)** *folded states of the development,* **(b)** *unfolded states of the development (a net representing traditional origami)* **(c-e)** *Converting process.* **(e)** *The thin lines of four actuation areas represent the direction of the curve, when it is triggered.* **(f)** *The curve origami model folds on its actuator. The angle of arc O is equal to the fold angle θ.* **(g)** *Thermorph's 3D geometry- the curved origami model, which is* **(e)***'s self-folded geometry.*

4.2.6 GENERATE G-CODE FOR PRINTING

The last step is to convert the printing pattern into G-Code. Considering that the bending direction is the same as the printing direction, when printing the actuator (the folding area), the toolpath should be perpendicular to the edges of the connected faces. While for faces between actuators, the printing direction does not matter.
In addition, to strengthen the connections between actuators and faces, we print the PLA layers of the actuator 1 mm longer on both sides connected to adjacent faces, so that there is a 1mm overlap for bonding.

4.2.7 APPLICATIONS

Byoungkwon An et al. detail four potential self-folding structures that can be manufactured by Thermorph.

Art - Self-folding Rose: A rose was created to illustrate a sequential deformation mechanisms in Thermorph system. Using forward design in the software editor, they improved the pattern design iteratively to achieve a rose shape with a spiral stem and several petals from one flat piece (**Figure 4.9**). However, to improve the aesthetic quality, they refined the geometry once the basic mechanisms were verified in Thermorph editor.
The structure was designed to allow the fold of the vertical stem part in a spiral direction, followed by the flipping motion of each petal. The folding angle can be computationally controlled by printing speed and the width of the actuators, which is simulated in a finite element model.

Transportation - Self-Folding Boat: Boat is another example for us to test out the forward design procedure in Thermorph editor as this example starts with a 2D pattern design as well (**Figure 4.10**). Users fold and simulate each hinge in the software to determine the desired folding state. In addition, through this example, envision that transportation tools can be self-assembled on site. The boat self-folded on the surface of hot water of 70 °C.

Furniture - Self-Folding Chair: Flat pieces of furniture can save shipping and packaging cost, and provide convenience for transportation. With this self-folding chair design (**Figure 4.11**), we envision the scenario of “baking a chair” - flatly packed IKEA piece can be baked into a chair, when no assembly is needed.

4.2.8 LIMITATIONS

Mismatch: The major reason for mismatching between the simplified 3D mesh and the printed model is gravity. To mitigate the influence, Byoungkwon An et al. chose the relatively centered face as the fixed face during the folding process, or purposely modified the printing speed from the theoretical calculation.

Mechanical strength: Current 1:100 chair is 0.8mm in thickness and can hold ~350g vertical load with < 5°

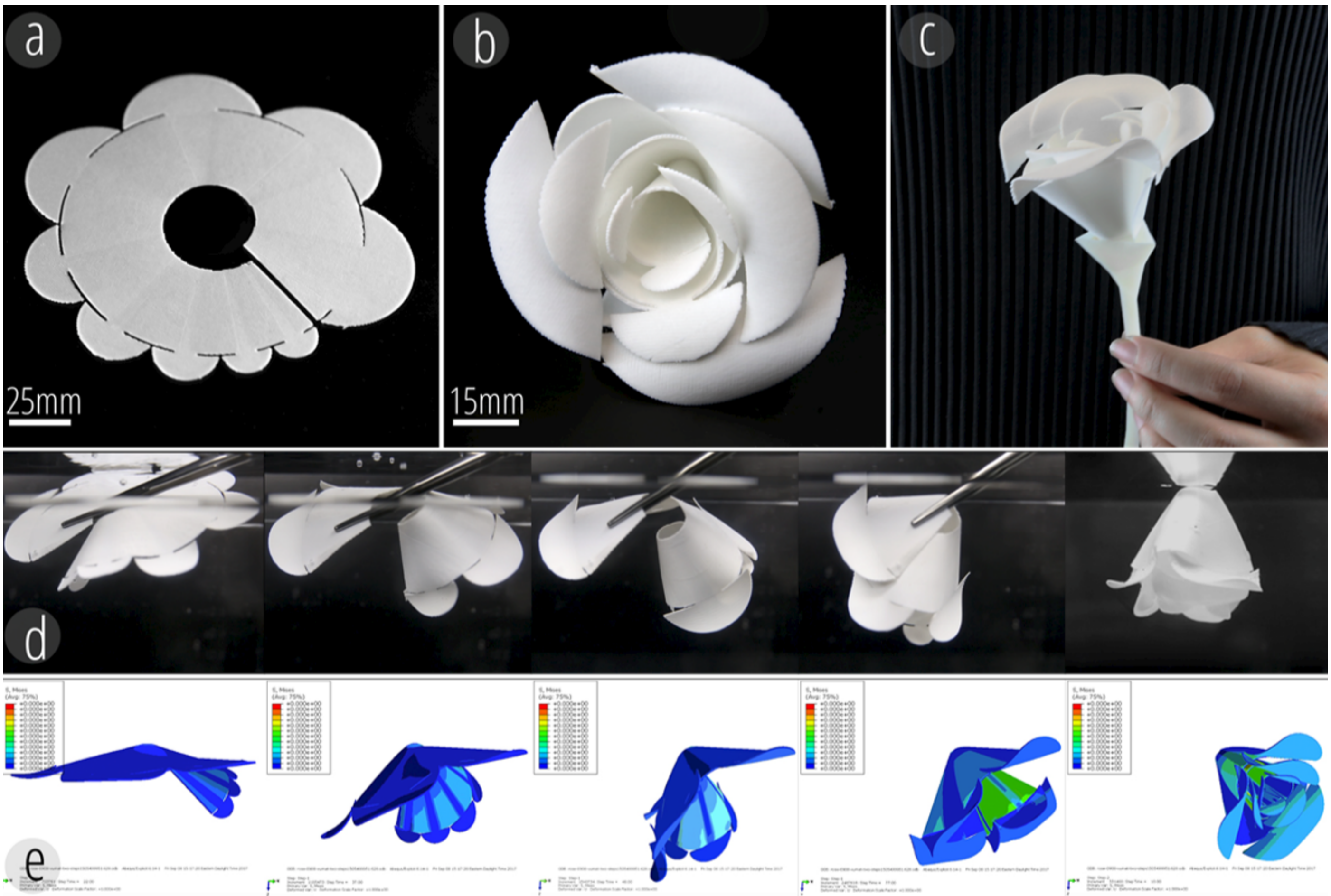

Figure 4.9 *Self-folding rose:* **(a)** *a 3D printed flat sheet (16x14.5cm);* **(b)** *3D rose after self-folding;* **(c)** *decorative rose as an art piece;* **(d)** *the sequential self-folding steps of the rose;* **(e)** *simulation of the self-folding steps.*

elastic deformation. If chair is modeled as a cantilever beam, for a 1:1 model that is capable of holding 50kg with 2° deformation, calculation gives a ~3mm thickness requirement [1].

Collision: as the bunny (**Figure 4.6**) had one collision on the right of the neck, it is oriented in a specific position to introduce some gravity effect to slow down the folding of the colliding faces; since the rose (**Figure 4.9**) collides if the outer petal folds faster than the inner ones, the outermost petal was fixed during the folding process. In the future, additional features will be explored to suggest the holding place and orientation during the folding process.

Scale: In the application examples, within the range of 25 - 225 cm2 all cases except the rose were scaled down to fit the bed. In the future, Thermorph's designers will explore the scale effect. They envision an on-site fabrication scenario, where flat pieces are printed and trigger them to self-assemble in the wild with natural energy - concentrated sunlight, hot springs, etc [1].

Figure 4.10 *Self-folding boat:* **(a)** *a printed flat sheet (17.1x7.4cm);* **(b)** *a self-folded boat in 3D;* **(c)** *the boat can self-fold and float on a hot water surface.*

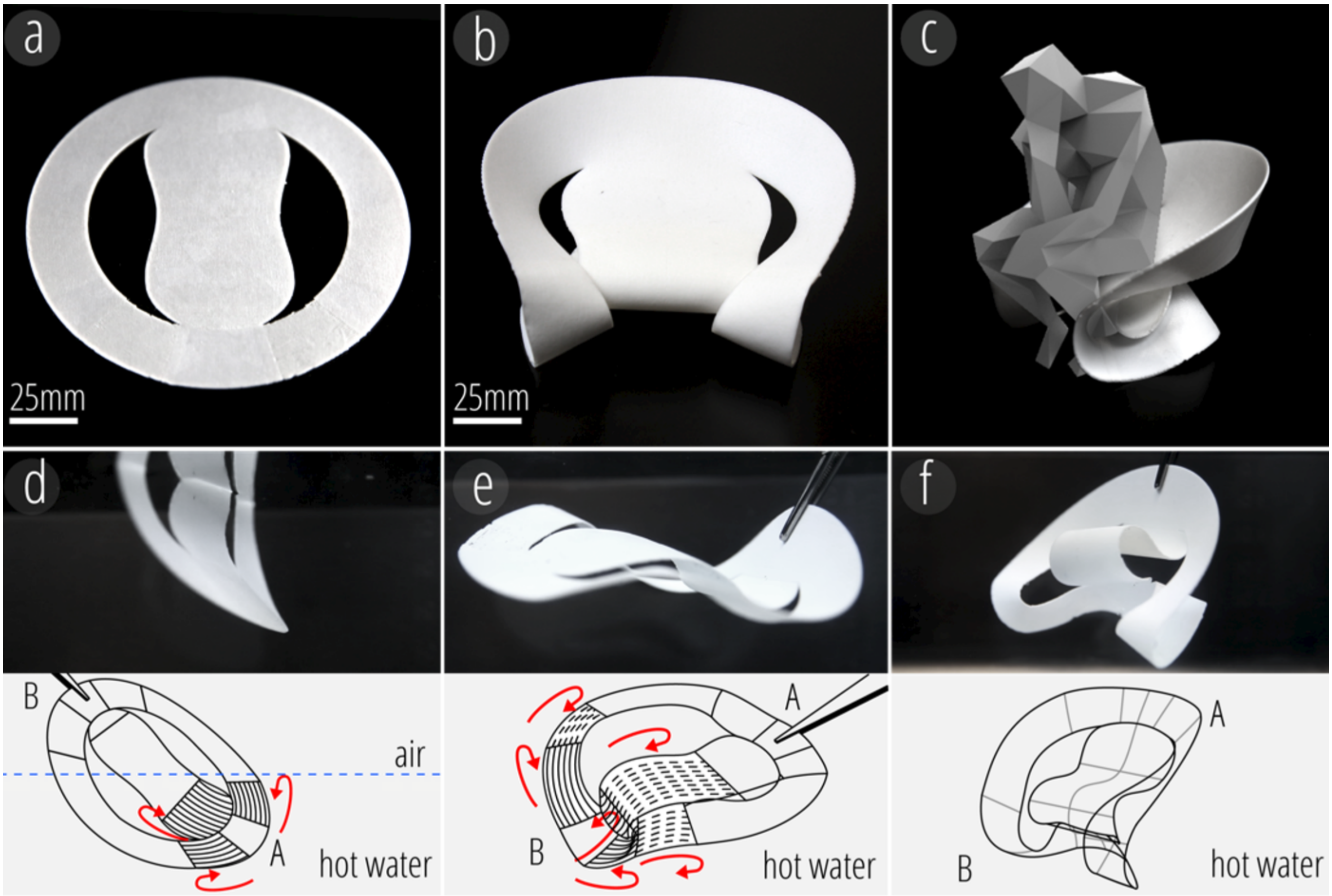

Figure 4.11 *Self-folding chair:* **(a)** *a printed flat sheet (14x14cm);* **(b, c)** *a 3D chair after self-folding;* **(d-f)** *the sequential folding steps. The chair is soft when heated and solidifies when it cools down.*

4.3 MATERIAL LIMITS 4DMESH: DESIGN TOOL FOR 4D PRINTING

4DMesh is a method developed by Guanyun Wang et al. [1] that combines shrinking and bending thermoplastic actuators with customized geometric algorithms to print 4D printing shells. As already reported in chapter 2.8, Guanyun Wang et al. in their 4DMesh project push the practical uses of 4D printed self deployable structures, making efforts on material composition design, manufacturing procedure and design tools. Their aim is designing practical and suitable design tools [1]. They share two end-to-end inverse design approaches to 4D printing morphing mesh surfaces that are non-developable. With 4DMesh, users can input CAD models of target surfaces and produce respective printable files.

Guanyun Wang et al. focus on non-developable surfaces that are often associated with mechanical performances, aerodynamics, ergonomics and unique aesthetics (organic and biomimetic architectures). These kind of shapes are hard to make with other manufacturing methods including laser cutting and CNC milling. In 3D printing, these surfaces often require extensive supporting structures that render the fabrication process inefficient. Also compared to flatly packed surfaces, non-developable structures take up more spaces for packaging and shipping. With their design tools and workflow, some of these challenges can be effectively tackled.

In **Figure 4.1** is showed a synthesis of 4D Mesh approach that starts from Basic Shape of Non-developable Surface, it goes through design methods and arrives to different applications.

Shell structures can be categorized into single or double curvature structures. Single curvature shell, or developable surface, is curved on one linear axis and is a part of a cylinder or cone; double curvature shell, or non-developable surface, is either part of a sphere or non-developable surface, is either part of a sphere or a hyperboloid of revolution. With this technique, it is possible self-deploy both developable and non-developable surfaces in mesh (**Figure 4.12**) [2].

4DMesh introduces two inverse design methods to produce morphing non-developable surfaces. These surfaces can be either a part of a sphere or a hyperboloid of revolution. The two methods utilize either *shrinking* or *bending actuators* that they designed and characterized (**Figure 4.12**).

Applications of the non-developable geometries are focused on ergonomic and aerodynamic designs, investigation of practical uses, customization and labour saving manufacturing (**Figure 4.12**). In particular, their structural strengths are quantified with both physical experiments and digital simulations.

The inverse design pipeline of 4DMesh produces artifacts by meshing and flattening the input surface, then generate the respective printing pattern and *G-code* according to the function assignment of each element. The artifacts fabricated with the G-code and an FDM printer have the configuration of a mesh and can morph into an approximation of the target surface.

4DMesh uses a commercially available PLA filaments (polymaker PolyMax PLA) and an FDM 3D printer (Stacker S4) with a 0.8 mm extrusion nozzle that works within 520x320x625 mm cubic space. The large-diameter nozzle accelerates the prototyping process while achieving the resolution required to program materials. To print artifacts faster and to ensure the print quality, it is choosed 5000 (mm/min) as printing speed and 0.2 mm as layer height base on the results from experiments.

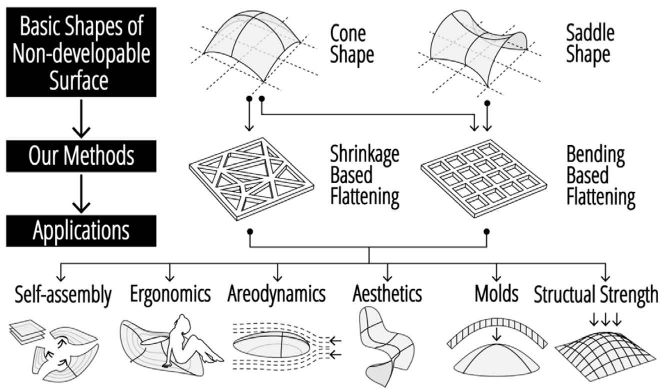

Figure 4.12 *Workflow preview.*

4.3.1 METHOD ONE: SHRINKAGE-BASED FLATTENING

Shrinkage elements are designed as a combination of two solid passive blocks at both ends with an actuator block at the center. In a layer of the shrinkage element, the printing path of the actuator block is parallel to the shrinking direction while the passive blocks have toolpaths that are perpendicular to it (**Figure 4.13a**). They vertically repeat the layers to achieve the desired height in the fabricated object. With this design, the overall shrinkage within an element can be controlled through modulation of the actuator length, or equivalently the actuator ratio such that longer the actuator, higher the shrinkage.

To characterize the performance with different printing parameters, it has been conducted a quantitative analysis of the shrinkage actuators. It is investigated the shrinkage ratio with respect to layer thickness as shown in **Figure 4.14** [2]. The shrinkage ratio here is the ratio between the final and initial lengths, where 1 represents no shrinkage and a smaller ratio indicates more shrinkage. The samples are printed 6 cm in length, 0.73 cm in width, and 0.4 cm in height. The shrinkage performance increases with decreasing layer thickness. In repetitive tests, they print these samples three times each and obtain consistent results on the same printer, but there may be differences depending on the machines used. In their work, it is selected the parameter with the high performance.

The algorithm that is used takes a target surface S as input and produces a flat pattern containing shrinkage actuators as G-code. The framework consists of four main steps: surface preprocessing, flattening, shrinkage actuator segmentation and G-code generation (**Figure 4.15**). In the process of meshing the surface, Quadric Edge Collapse Decimation (QECD) [2] is used to achieve a reasonable mesh density such that the wireframe object can be printed with conventional 3D printers. For flattening, it is used conformal mapping. This flattening approach mimics the shrinking process by distorting lengths while preserving angles. Although conformal mapping could result in both extension and shrinkage, they scale the flattened mesh to ensure that each element is extended when flattened and thus achieve the target shape, only shrinking when triggered. Next, they segment the mesh and place shrinkage actuators that satisfy the shrinkage requirement for each element. Finally, printing paths are created in the form of G-codes by connecting raster lines on the segmented pattern blocks and stacking them vertically. Toolpaths as G-codes are generated by rasterizing each segmented block in the flat pattern. Limited by the size of printer work area, to manufacture large surfaces, the mesh is divided into smaller pieces that fit the print bed when flattened.

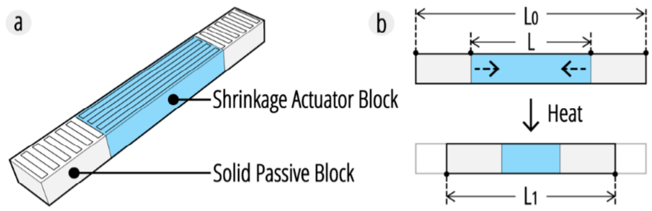

Figure 4.13 *Shrinkage actuator design.* **(a)** *Block assignments and printing toolpaths;* **(b)** *Actuation.*

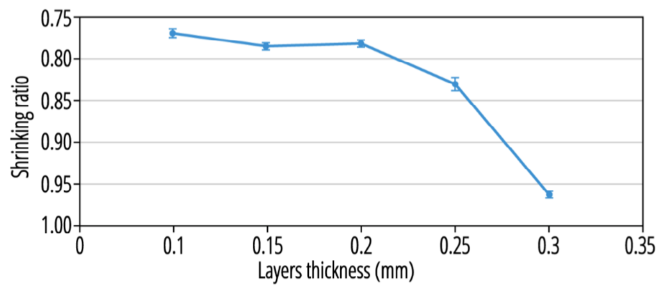

Figure 4.14 *Plot of shrinkage versus actuator layer thickness.*

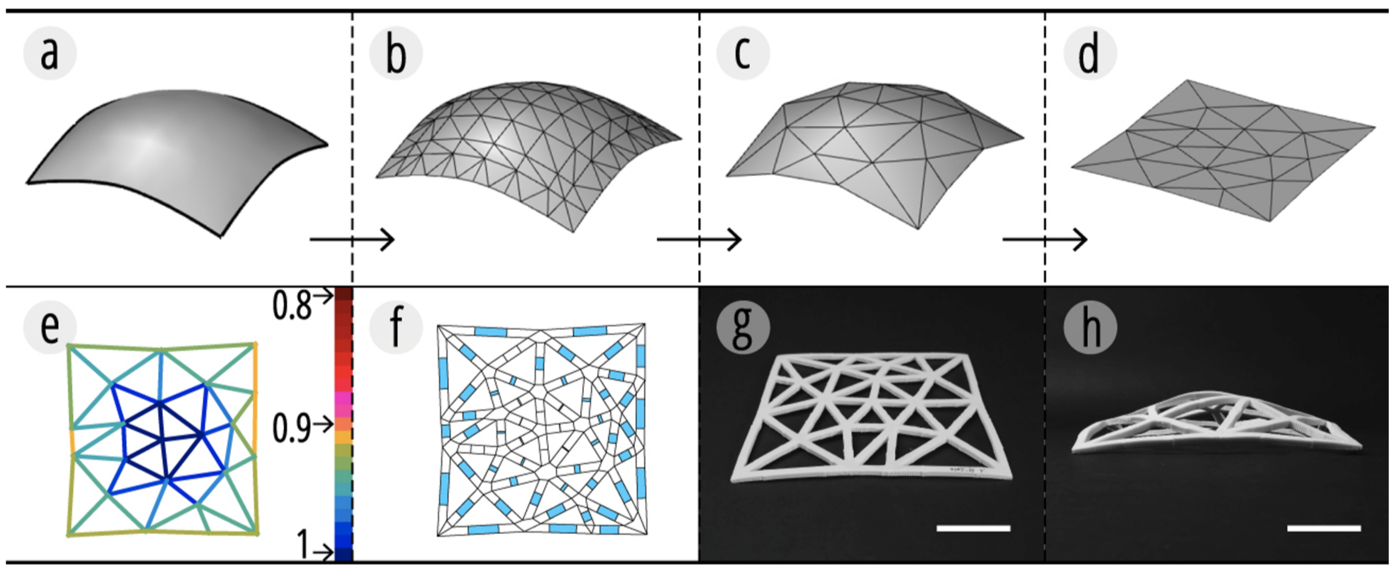

Figure 4.15 *Shrinkage actuator design.* **(a)** *Block assignments and printing toolpaths;* **(b)** *Actuation. Shrinkage-based flattening pipeline overview.* **(a)** *Target surface S;* **(b)** *Meshed S;* **(c)** *Simplified mesh M;* **(d)** *flattened Pattern Mf;* **(e)** *length distortion;* **(f)** *actuator assignments;* **(g)** *fabricated artifact;* **(h)** *triggered artifact. (Scale bar: 5 cm).*

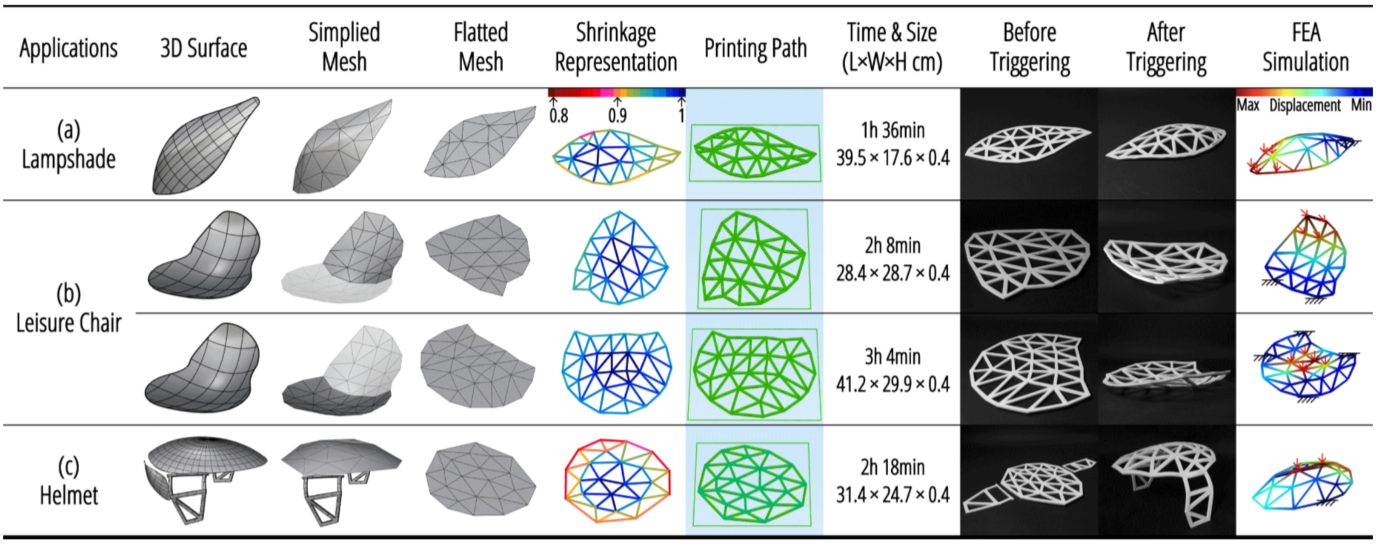

Figure 4.16 *Shrinkage-based method applications.*

4.3.2 APPLICATION EXAMPLES METHOD ONE

This method has been envisioned to enable and democratize modular, personalized, and custom-made designs. By digitally sketching a surface and processing it with the algorithm, the artifacts can be manufactured rapidly with an FDM 3D printer (**Figure 4.16**).
Some models that have been printed are showed in **Figure 4.17, Figure 4.18, Figure 4.19.**

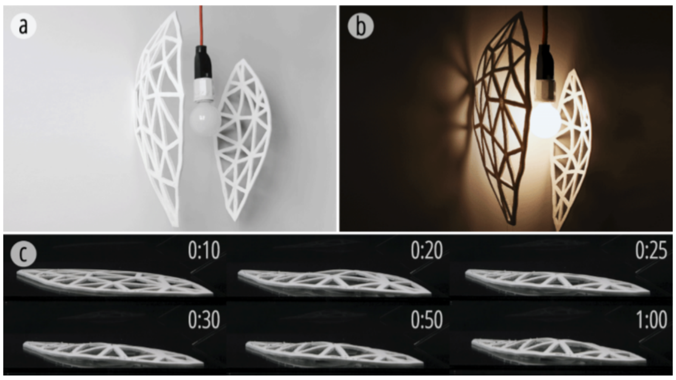

Figure 4.17 *Lampshade* **(a)** *without light,* **(b)** *with lights on, and* **(c)** *triggered transformation over time.*

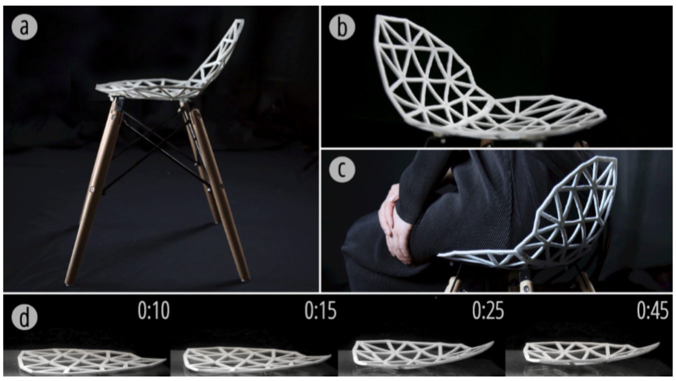

Figure 4.18 (a, b, c) *The triggered artifacts and serial transformation of* **(d)** *back support and* **(e)** *seat.*

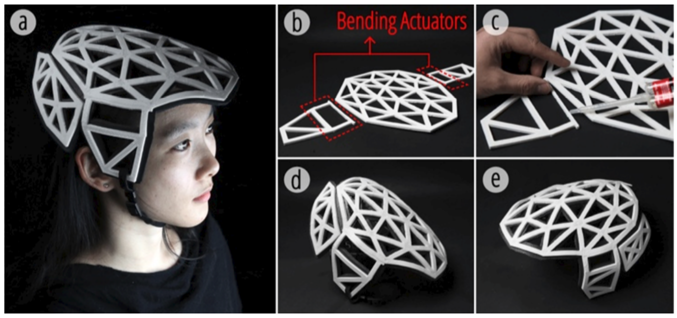

Figure 4.19 *Aerodynamic helmet.* **(a, d, e)** *The triggered and assembled helmet;* **(b)** *The printed flat pieces;* **(c)** *The preassembling process.*

4.3.3 METHOD TWO: BENDING-BASED FLATTENING

The design of bending elements is identical to the design of shrinkage elements, where the actuator block is placed in between two passive blocks. In the case of bending elements, certain layers of the actuator are substituted, either on top or at the bottom, with perpendicular constraint blocks creating a bi-component structure (**Figure 4.20**). This bicomponent structure causes differential length changes between layers and thus results in arc-like bending of the elements. Like the shrinkage elements, it is controlled the overall bending of each element by modulating the length of the bicomponent structure such that longer it is, the larger the bending angle.

As the previous method, quantitative analysis is conducted for bending actuators to characterize the relationship between printing/design parameters and the resulting bending performances. The samples are printed with the same dimensions as those used for the shrinkage actuators. As shown in **Figure 4.21**, it is considered the correlation between the number of actuator layers and the resulting performance, which is measured in bending angles per unit length of the bi-component structure. Bending angle of an element refers to the angular number difference between the tangent vectors at its two ends on the plane of the arc. Expectedly, as the number of actuator layers increases, bending performance improves. For a given surface mesh, the highest bending angle is identified within the mesh and select the number of actuator layers that can accommodate this value. Keeping the number of actuator layers constant for the mesh, the length of the bicomponent structures is adjusted to control the bending angle throughout the surface.

This algorithm takes a target surface S as input and produces a flat pattern containing bending actuators as G-code. The pipeline consists of four main steps: surface pre-processing, flattening, actuator segmentation, and G-code generation (**Figure 4.22**).

It is formulated this algorithm based on the Chebyshev Net Algorithm (CNA) [3] to convert and flatten NURBS surfaces into quad meshes. CNA is commonly adopted in models where torsion is absent and element lengths are invariant. To use CNA as a mesh flattening algorithm, it is modified to preserve surface outlines and to accommodate for edges of different lengths. The first feature requires preprocessing of the surface and the second requires CNA to take variable edge length as input when applied on plane.

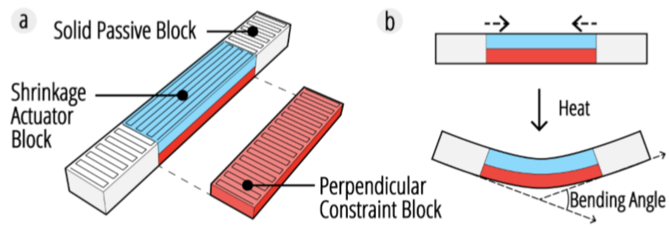

Figure 4.20 *Bending actuator design.* **(a)** *Block assignments and printing toolpaths;* **(b)** *Actuation.*

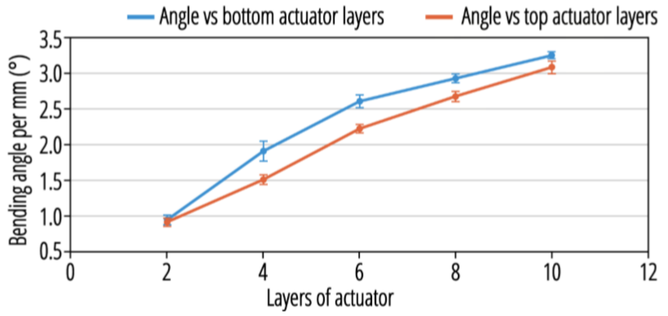

Figure 4.21 *Plot of bending performance (angle/mm) versus actuator layers.*

4.3.4 APPLICATION EXAMPLES METHOD TWO

Fruit Plate and Chairs Comparing to shrinkage-based flattening, this method allows for larger curvatures on the target and concurrent programming of concave and convex. Guanyun Wang et al. exploit this feature to design a fruit plate and two chair models (**Figure 4.24**).

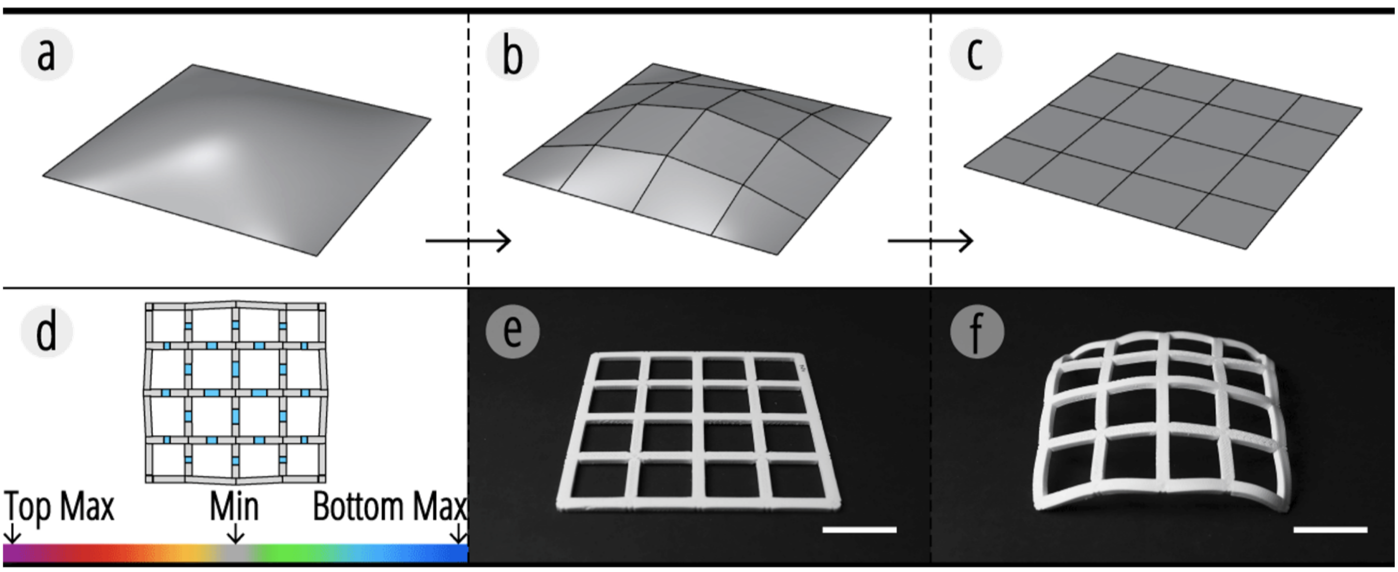

Figure 4.22 *Bending-based flattening pipeline overview.* **(a)** *Target surface S;* **(b)** *CNA meshed M;* **(c)** *Flattened mesh Mf;* **(d)** *Actuator assignments;* **(e)** *Fabricated artifact;* **(f)** *Triggered artifact.*

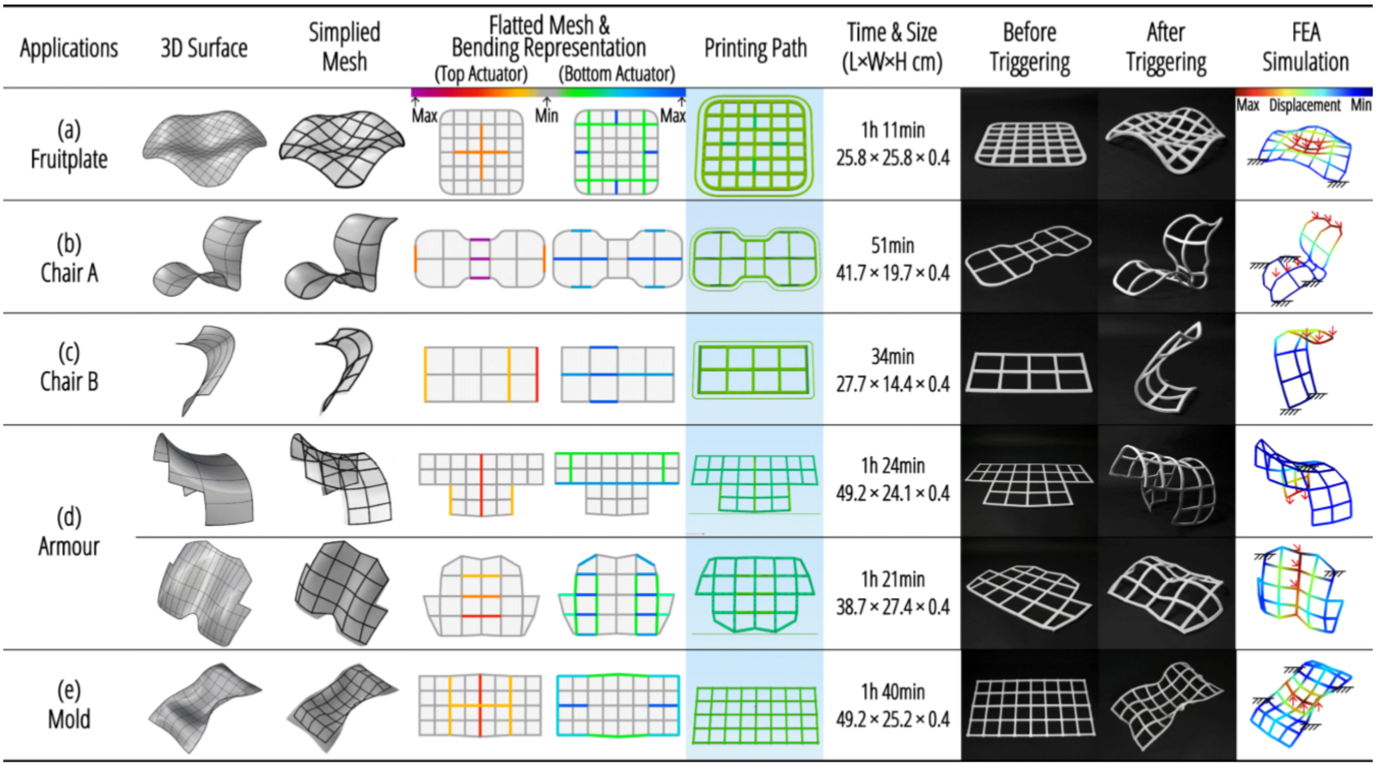

Figure 4.23 *Bending-based method applications.*

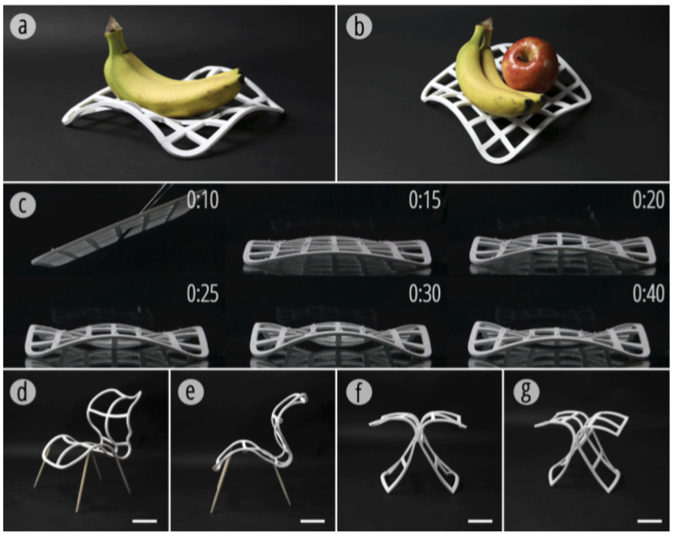

Figure 4.24 (a, b) *Triggered fruit plate and* **(c)** *its sequential transformation over time;* **(d, e)** *A scaled chair model;* **(f, g)** *A chair made of two segments.*

4.3.5 EDITOR

Guanyun Wang et al. implemented their algorithms in Rhinoceros 6 with Grasshopper and Human UI. Users can calibrate the system to their own printer and thermoplastics following their actuator characterization tests, and set parameters including beam width, height, standard length, and scaling to process their input geometry with either flattening method. The system estimates the printing time and outputs G-code files.

4.3.6 TRIGGERING METHOD

Hot water is the triggering method for 4DMeshes. The medium is heated up to 175°F, which is much higher than 149°F, the Glass Transition temperature of PLA, to minimize convection for a uniform trigger; allow sufficient transformation time before the temperature drops to 140°F, the re-solidify temperature of PLA. The artifacts are submerged and stay still underwater until the temperature reaches 140°F. For quantitative experiments on the actuator performances and triggering large pieces, sugar was added into the water to increase its density to around 1.25 g/mm3.

4.3.7 DIFFERENCES FROM THERMORPH

4DMesh is different from Thermorph in three aspects:

Scale: The improvement in scale is one of the critical achievements of 4DMesh, covering many challenges such as cubically growing gravitational effects, new global mesh structures, optimized inner structure and toolpath to decrease the weight and the printing time, alternative actuator types for controllable behavior at this scale, and altered triggering conditions.

Developability: Thermorph re-meshes non-developable surfaces into foldable shapes with flat faces, often requiring cuts into the geometry which weaken their mechanical strengths; in contrast, 4DMesh can flatten the geometry as a smooth surface without any cuts.

Material Usage: Instead of using two different materials in actuation mechanism, 4DMesh introduces morphing process along the beam using the print direction relative to the longitudinal axis to determine the out-of-plane bending direction, which can be achieved with a singular material.

4.3.8 LIMITATIONS

Surfaces: B can take on both developable and non-developable surfaces while A is limited to the former. Deploying conformal mapping on a developable surface is geometrically feasible but will not give shrinkage ratio locally. For A, while a conformal map can be found for any surface, the length distortions may fall beyond an achievable range. To solve this, Guanyun Wang et al. introduce segmentation to the surface to keep length distortions within achievable range. B can achieve larger curvatures but ignores torsion within elements and assumes that all joints are capable of free rotation. In reality, the deviations caused by these factors are absorbed by the plasticity of the material. Currently, B can achieve simultaneous concave and convex (e.g., a saddle shape), while A has a relatively arbitrary bending direction.

Maximum Curvature: The maximum Principal Curvature achievable with B is 0.022/mm. For A, the maximum curvature varies depending on the geometrical position: the surface center can be curved more than the edges due to curvature accumulation.

Mesh Density: For both methods, the higher the mesh density the more resembling the approximation is. B used arcs and gives a smoother surface but rebuilds the outline of the input. This method works well with surfaces of rectangular outlines and arbitrary curvatures. On contrary, A preserves the outline but requires a higher mesh density to approximate a surface well.

Printing Speed: A requires higher resolution of material programming and more time to manufacture. To produce a cone-shaped mesh of identical weights, A and B takes 166 and 137 minutes respectively.

Beam Design Parameters: 4DMesh is aimed on functional objects for daily use and therefore based the beam thickness (4 mm) on typical plastic chairs (3-5 mm) and the width (7.3 mm) on the nozzle diameter (0.8 mm) and resulting print quality of FDM 3D printer . While thinner beams minimize the size of joints (interfering less with transformation), the morphed artifacts cannot withstand as much load. Additionally, higher mesh density requires more printing time and more joints. 4DMesh provides print time estimates for users to balance between structural and fabrication efficiencies.

Transformation Accuracy and Reproducibility: 4DMesh methods exhibit good reproducibility in general. However, as the geometry scales up, the volume and the gravitational effect increase cubically, leading to controlling difficulty, transformational inaccuracy, and more mismatch between the actual transformation and simulation.

Other Limitations: There are many technical challenges faced in this research, including the limit of geometry, the effect of gravity, and the transformation precision. Current 4DMesh can only process surfaces that form no enclosure, have no periodic frame, and have no interior holes. To account for the precision of transformation and the effect of gravity, a rapid simulation tool is required. While high resolution finite element analysis does provide accurate results, the computational cost to compute large scale morphing structures is colossal. A fast simulation tool will also enable real-time iterative design with transformative materials. With increasing size, fabrication time may also become an issue.

4.4 PRINTING FERROMAGNETIC DOMAINS FOR SOFT MATERIALS

This project is mentioned in the first chapter about shifting mechanisms by magnetic fields (Chapter 1.7.5).
Magnetic fields offer a safe and effective manipulation method for biomedical applications, which typically require remote actuation in enclosed and confined spaces. With advances in magnetic field control, magnetically responsive soft materials have also evolved from embedding discrete magnets or incorporating magnetic particles into soft compounds to generating nonuniform magnetization profiles in polymeric sheets [4].
Yoonho Kim et al. developed 3D printing soft materials that enable fast transformations between complex 3D shapes via magnetic actuation. They printed diverse devices using Direct Ink Writing (DIW) of an elastomer composite containing ferromagnetic microparticles [4].

This composite ink for 3D printing consists of *magnetizable microparticles of neodymium–iron–boron (NdFeB) alloy* (**Fig. 4.25**) and fumed silica nanoparticles embedded in a silicone rubber matrix containing silicone catalyst and crosslinker. The fumed silica within the silicone resin serves as a rheological modifier to induce the mechanical properties required for direct ink writing including shear thinning and shear yielding. These properties ensure that the composite ink can be extruded through a micro-nozzle when pressurized and that the deposited inks maintain their shapes even when stacked up to form multiple layers. The composite ink is prepared first by mixing the non-magnetized NdFeB particles and the silica nanoparticles with the uncured elastomer matrix and then magnetized to saturation under an impulse field. The presence of yield stress in the composite ink helps to prevent the dispersed magnetized particles from agglomerating.
During the printing process, a magnetic field is applied along (or in reverse to) the flow direction of the ink via a permanent magnet or an electromagnetic coil placed around the dispensing nozzle (**Figure 4.25**). The applied field makes the magnetized NdFeB particles reorient along the field direction, imparting a permanent magnetic moment to the extruded ink filament. The magnetic polarities of the deposited inks can be tuned either by switching the applied field direction or changing the printing direction. Using this approach, a 3D structure can be encoded with intricate patterns of ferromagnetic domains depending on the magnetic polarities of the filaments that are arranged to construct the 3D structure. To avoid interference in the programmed domains of the printed structure by the applied field at the nozzle, a magnetic shield is used to attenuate the magnetic flux density under the nozzle tip (**Figure 4.25**). When the printing process is complete, the printed structure is cured at 120 °C for 1 h, during which the presence of yield stress in the uncured ink helps the programmed ferromagnetic domains to remain unaffected by thermal randomization of the aligned particles.

Yoonho Kim et al. present a set of two-dimensional planar structures that rapidly transform into complex 3D shapes under the applied magnetic fields of 200 mT as a result of the programmed ferromagnetic domains (**Figure 4.26**) [3].
In **Figure 4.27 a** and **d**, are showed two annular rings with the same geometry but different patterns of ferromagnetic domains to illustrate the effects of programmed domains on the macroscale response. Model-based simulation predicts that the two rings should yield different 3D morphologies under the same magnetic field applied perpendicularly to their planes. The second annulus encoded with alternating patterns that vary in magnitude gives a more complex undulating shape (**Figure 4.27e**) than does the first annulus (**Figure 4.27b**), whose alternating patterns are equidistant. The simulation results are in good agreement with experimental results (**Figure 4.27c**), further demonstrating that the model is capable of guiding the design of complex shape-morphing structures using programmed ferromagnetic domains.
When programmed with more intricate domain patterns, even a simple geometry can yield a complex 3D shape under an applied magnetic field. As an example, in **Figure 4.27g**, Yoonho Kim et al. design a simple rectangular structure with alternating oblique patterns of ferromagnetic domains to create a “Miura-ori pattern”. This untethered structure provides fast (in 0.3 s) and fully reversible folding and unfolding under magnetic actuation (**Figure 4.27i**), as predicted by the model (**Figure 4.27h**).

The capability to create complex shape changes allows to achieve diverse functions from different printed structures, as shown in **Figure 4.28** [4]. First, by combining electronic components and circuitry with annular rings structure in **Figure 4.28a**, a soft electronic device is printed.
This soft electronic device deforms into two different shapes depending on the direction of applied magnetic fields of 30 mT, and each mode of transformation yields a different electronic function. Yoonho Kim et al. further demonstrate the capability of interacting with an object based on the complex shape changes of the hexapedal structure shown in **Figure 4.28r**. Using the fast response upon magnetic actuation, the hexapedal structure quickly stops a fastmoving object (**Figure 4.28b**). When applying a magnetic field in the opposite direction to create a reversed shape, the hexapedal structure can catch a falling object and hold it against external disturbance and then release the object on demand by using the previous mode of transformation. When a rotating magnetic field is applied, the hexapedal structure can roll up its body

and move forwards and backwards by rolling-based locomotion. Harnessing the shape changes and motion, the hexapedal structure can carry an object with arbitrary shape such as a round or oblong pharmaceutical pill (**Figure 4.28c**) and release the pill on demand.

This printing method can be used as a fabrication platform that can be extended to multiple composite inks using different types of elastomer and hydrogel matrices and magnetic particles. By printing ferromagnetic domains in soft materials, new design parameters domain patterns, magnetization strength and actuation fields are introduced into the design and fabrication of shape-programmable soft materials. The remote actuation of such untethered, complex and fast shape-shifting soft materials based on magnetic fields suggests new possibilities for applications in flexible electronics, biomedical devices and soft robotics.

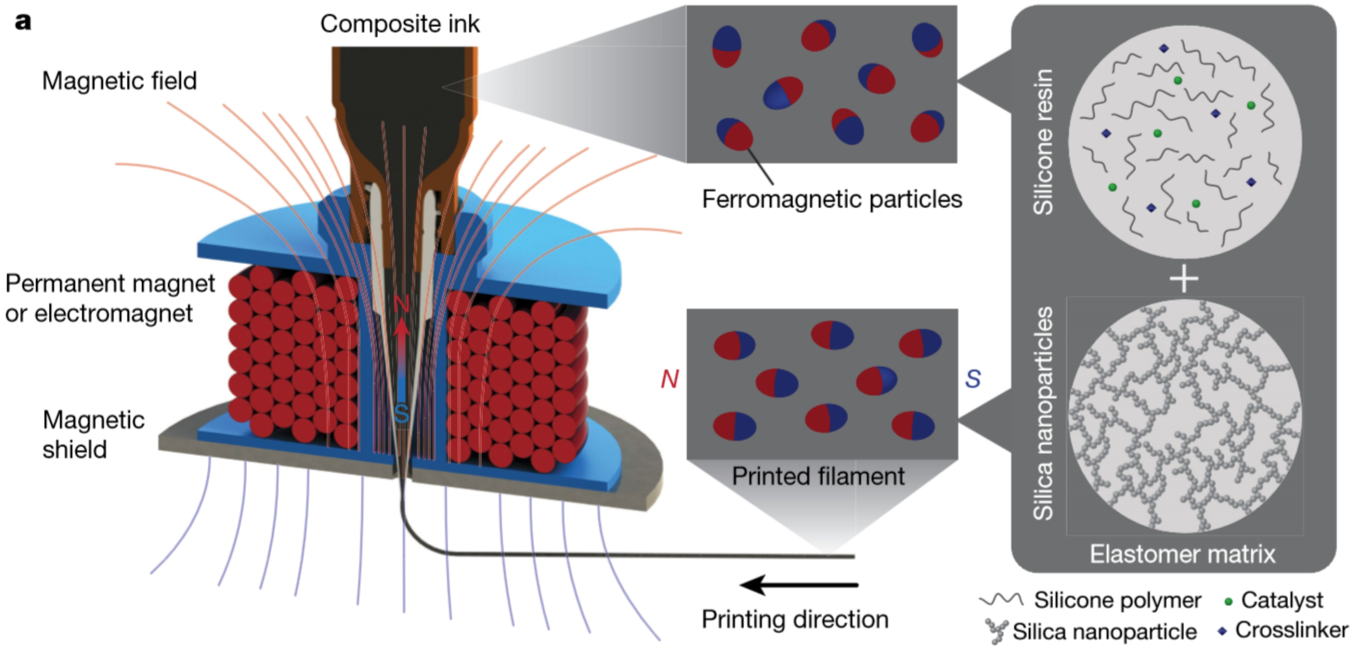

Figure 4.25 *Schematics of the printing process and the material composition. The ferromagnetic particles embedded in the composite ink are reoriented by the applied magnetic field generated by a permanent magnet or an electromagnet placed around the dispensing nozzle.*

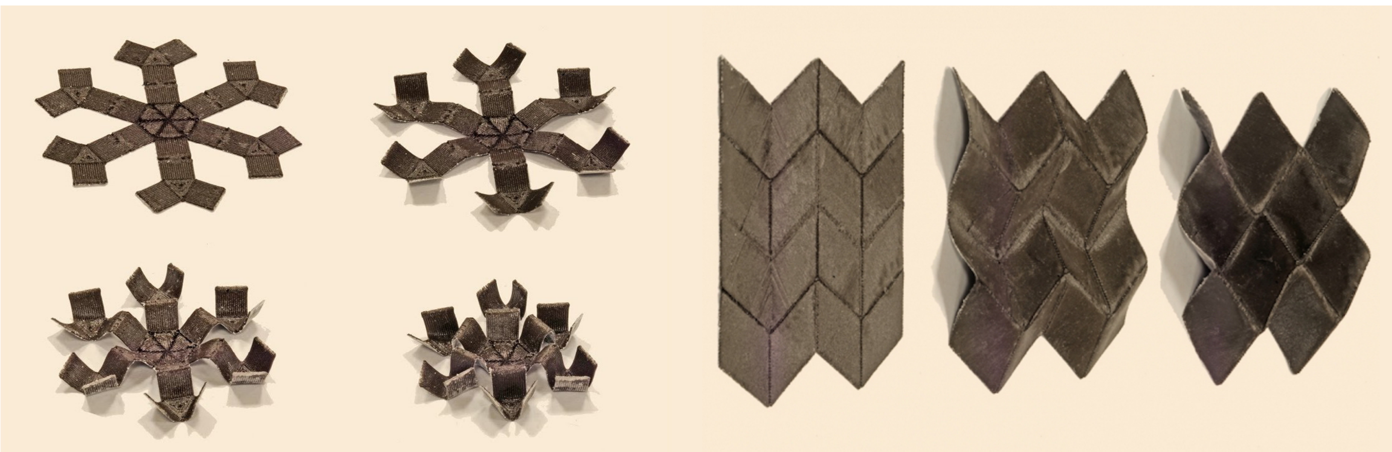

Figure 4.26 *Different transformation of Spiderlike Grabber (on the left) and Miura-ori fold (on the right). Actuation of the demonstrated structures is performed by applying magnetic fields of 200 mT perpendicular to the planes of the structures.*

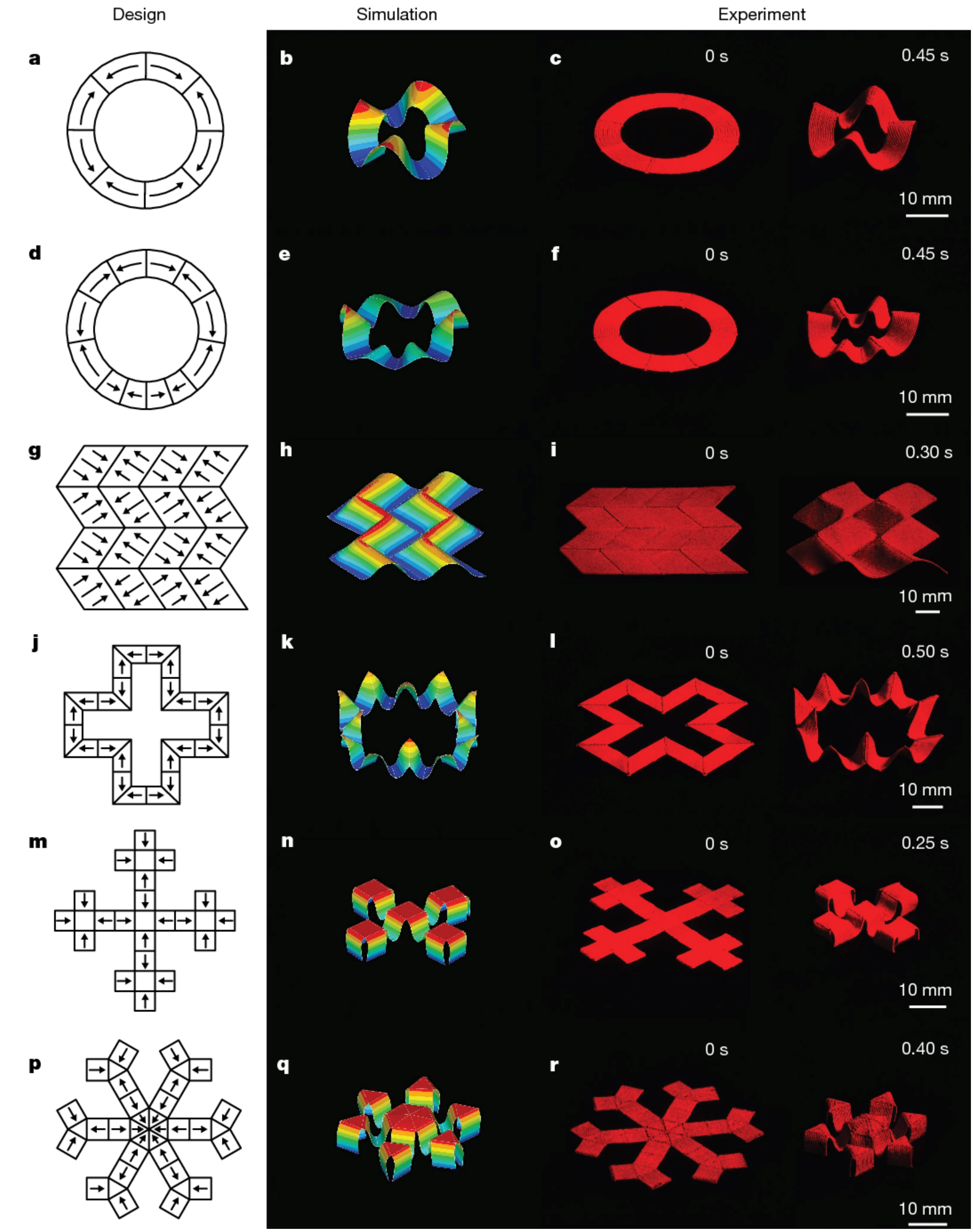

Figure 4.27 *Schematic designs, finite-element simulations and experimental results for an annulus encoded with alternating domains that are equidistant* **(a–c)***; an annulus encoded with alternating domains that vary in size* **(d–f)***; a Miura-ori fold encoded with alternating oblique patterns of ferromagnetic domains* **(g– i)***; a hollow cross encoded with alternating ferromagnetic domains along the perimeter* **(j–l)***; All of the demonstrated structures are printed with the elastomeric composite ink containing 20 vol% of magnetized NdFeB particles using a nozzle of diameter 410 μm under a magnetic field of 50 mT at the nozzle tip generated by a permanent magnet.*

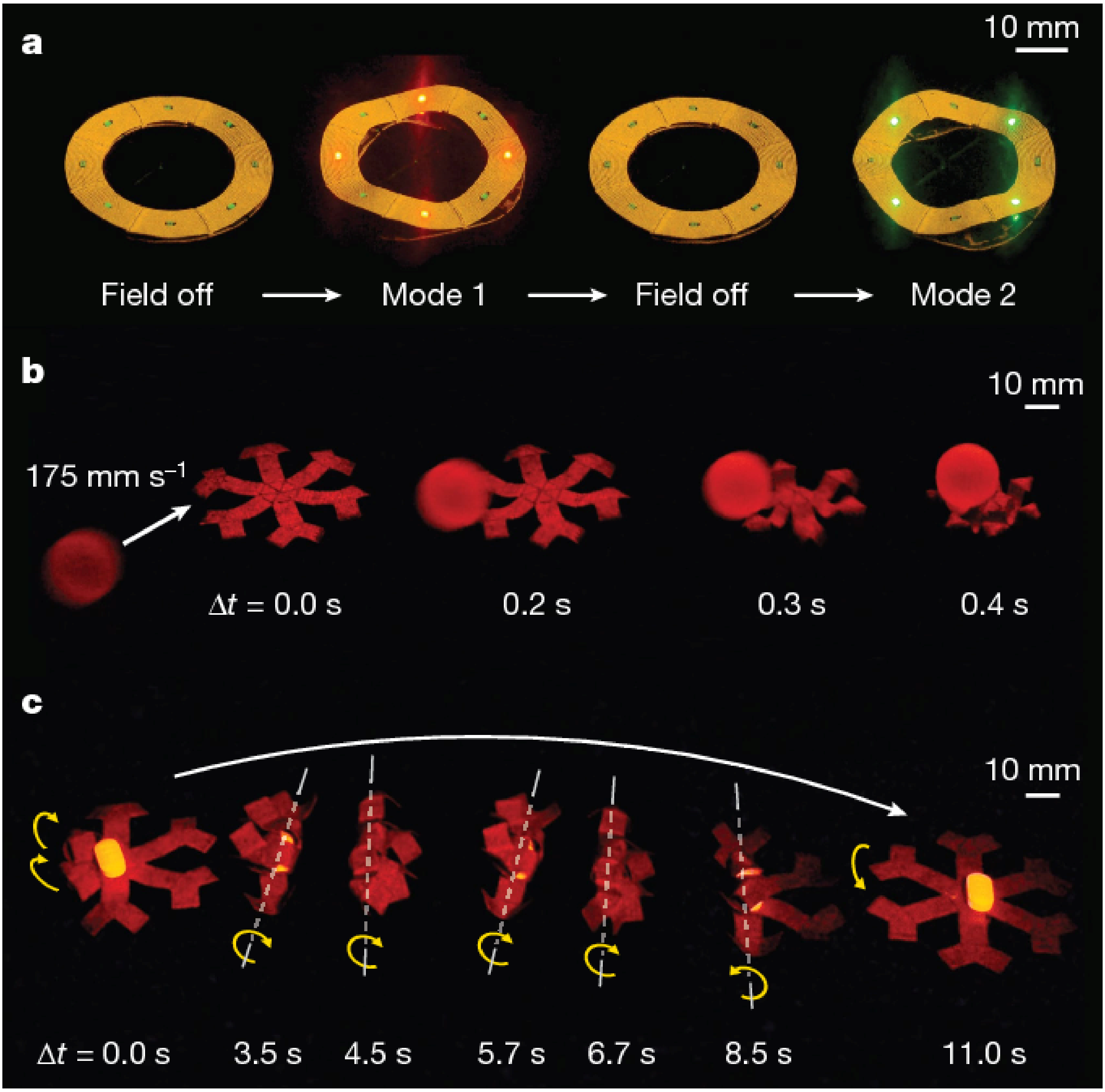

Figure 4.28 **a)** *A reconfigurable soft electronic device based on the annular ring structure exhibiting different electronic functions depending on the direction of an applied magnetic field of 30 mT.* **b)** *A hexapedal structure stopping and holding a fast-moving object (glass ball of diameter 18 mm and weight 8* **g)** *upon application of a magnetic field generated by a permanent magnet.* **c)** *A hexapedal structure wrapping an oblong pharmaceutical pill and carrying the pill using rolling-based locomotion under a rotating magnetic field generated by a permanent magnet.*

4.5 BIOMIMETIC 4D PRINTING

Plants exhibit hydration-trigged changes in their morphology due to differences in local swelling behaviour that arise from the directional orientation of stiff cellulose fibrils within plant cell walls [5]. Emerging pathways for mimicking these dynamic architectures incorporate materials that can respond to external stimuli, such as *shape memory alloys* and *swellable hydrogel composites*, and can be assembled by methods from 4D printing and self-folding origami. For example, recent efforts to create plant-inspired, shape-changing structures have employed differential swelling in *isotropic* (Solid material for which physical properties are independent of the orientation of the system) or composite bilayers and hinges. However, none of these approaches enable shape change using a single material patterned in a one-step process. Sydney Gladman et al. [5] develop a biomimetic hydrogel composite that can be 4D printed into programmable patterned bilayer structures, which are encoded with localized swelling anisotropy that induces complex shape changes on immersion in water.

This hydrogel composite ink is composed of stiff cellulose fibrils embedded in a soft acrylamide matrix, which mimics the composition of plant cell walls. The composite architectures are printed using a viscoelastic ink that contains an aqueous solution of *N-dimethylacrylamide*, *photoinitiator*, *nanoclay*, *glucose oxidase*, *glucose*, and *nanofibrillated cellulose (NFC)*. The constituents serve different purposes: the clay particles are a rheological aid, inducing the desired viscoelastic behaviour required for Direct Ink Writing (DIW); glucose oxidase and glucose minimize oxygen inhibition during the ultraviolet curing process by scavenging ambient oxygen, there by improving polymerization in the printed filamentary features (100µm to 1mm in diameter) to yield mechanically robusts tructures; the wood-derived cellulose fibrils serve as stiff fillers (E >100GPa). After printing under ambient conditions,the acrylamide monomeris photopolymerized and physically crosslinked by the nanoclay particles, producing a biocompatible hydrogel matrix that swells readily in water (**Figure 4.29**).

The efficacy of this biomimetic 4D printing (bio-4DP) method relies on the ability to deterministically define the elastic and swelling anisotropies by local control of the orientation of cellulose fibrils within the hydrogel composite. During printing, these fibrils undergo shear-induced alignment as the ink flows through the deposition nozzle, which leads to printed filaments with anisotropic stiffness, and, hence, swelling behaviour in the longitudinal direction (along the filament length, as defined by the printing path) compared to the transverse direction. Harnessing anisotropic swelling allows precise control over the curvature in bilayer structures.
Quantifying this requires a mathematical model for the mechanics of anisotropic plates and shells, which combines aspects of the Timoshenko model for thermal expansion in bilayers [6] with a tailored metric driven approach that employs anisotropics welling to control the embedding of a complex surface.

By combining patterns that generate simple curved surfaces, Sydney Gladman et al. created a series of functional folding flower architectures to demonstrate the capabilities of bio-4D Printing (**Figure 4.30**).
Inspired by flower opening/closing, they printed petals in a floral form (**Figure 4.31**) comprised of a bilayer lattice with a 90◦/0◦ configuration. As a control, they also printed an identical pattern using an ink devoid of micro-fibrils, and observe that it remains flat on swelling. When the petals are printed with the ink filaments oriented at −45◦/45◦ the resulting structure yields a twisted configuration; the resulting structures is characterized by broken top–bottom symmetry of the bilayer and thence differential swelling across the thickness. These constructs contain spanning filaments that are readily fabricated by direct writing of the viscoelastic composite ink. The interfilament spacing promotes rapid uptake of water through the filament radius (100µm), leading to shape transformations that occur on the order of minutes consistent with diffusion-limited dynamics. As an example of the versatility of bio-4D Printing, Sydney Gladman et al. mimic the complexity of the orchid *Dendrobium helix* by encoding multiple shape-changing domains. The print path is designed with discrete bilayer orientations in each petal. The resulting 3D morphology following swelling in water resembles the orchid (**Figure 4.30**) and exhibits four distinct types of shape change (three different petal types and the flower centre).

This 4D printing method relies on a combination of materials and geometry that can be controlled in space and time. This technique has potential as a platform technology, where the hydrogel composite ink design can be extended to a broad range of matrices (for example, liquid-crystal elastomers) and anisotropic fillers (for example, metallic nanorods) that when combined with flow-induced anisotropy allows to produce dynamically reconfigurable materials with tunable functionality. Through the control of printing parameters, such as filament size, orientation, and interfilament spacing, it is possible create bilayer architectures with programmable anisotropy that morph into given target shapes, predicted by model, on immersion in water [5].

About possible applications of this technique, according with Sydney Gladman: *"All together, owing to our biocompatible and flexible ink design, our study opens new avenues for creating designer shape shifting architectures for tissue engineering, biomedical devices, soft robotic sand beyond"* [5].

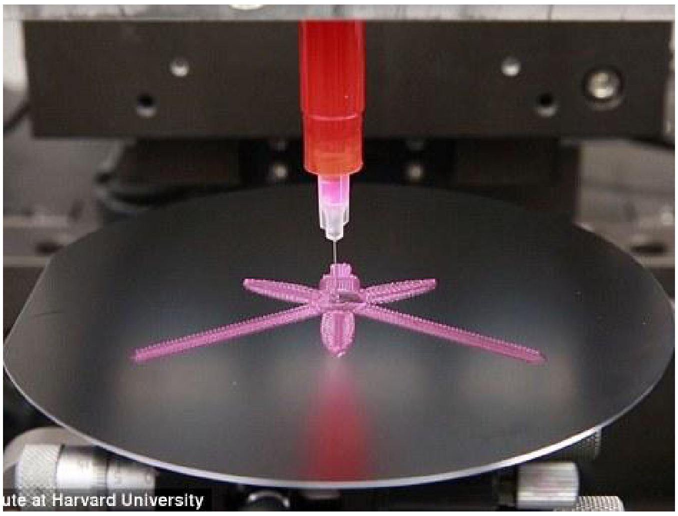

Figure 4.29 *The microscale printing process of orchid-shaped hydrogel composite structure.*

Figure 4.30 *Resulting swollen structure of a flower demonstrating a range of morphologies inspired by a native orchid, the "Dendrobium helix" swelling process.*

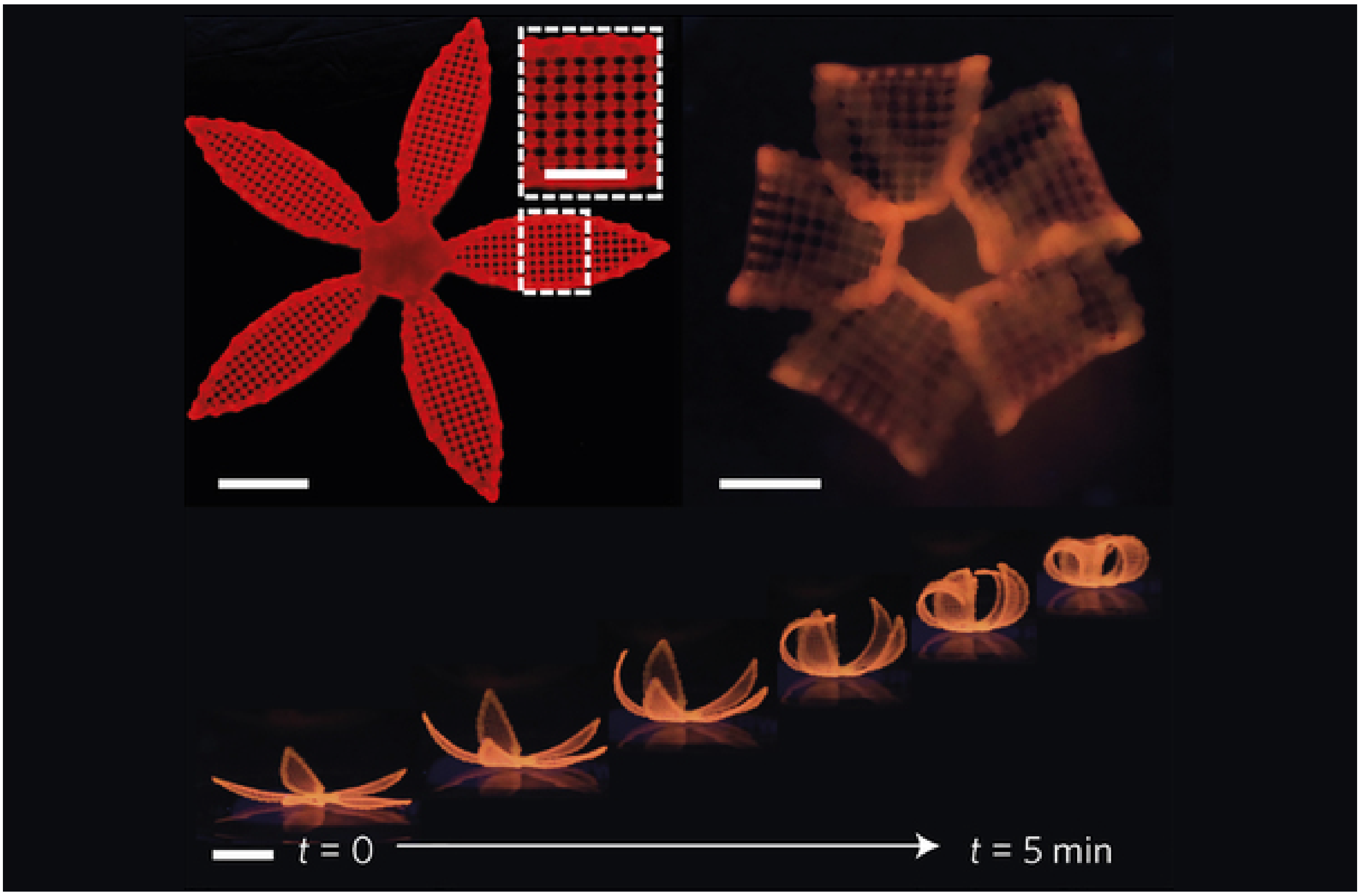

Figure 4.31 *Bilayers oriented with respect to the long axis of each petal, with time-transformation during the swelling process after its submersion in water (bottom panel).*

CHAPTER 4. REFERENCES

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CHAPTER V

CONCLUSION

5.1 POTENTIAL APPLICATIONS

4D printing adds time to 3D printing and thus has the advantages, as already mentioned, to fabricate intelligent devices enabled by the evolution of shape and functions of the printed smart materials.

The stimulus responsive shape-changing feature can be utilized to save space for storage and transportation [1]. Printed active origami products could assume a planar shape for the ease of transportation in limited space before they are activated at the designated time and location. Hence, this might help to decrease the logistic cost as the printed products can be stored as compactly as possible before activated to full volume and functionality.

For exemple, Guanyun Wang et al. with 4DMesh [2] and Byoungkwon An et al. with Thermorph [3] developed a method of combining shrinking and bending thermoplastic actuators with customized products. With their tools, users can input CAD models of target surfaces and produce respective printable files. The flat sheet printed can morph into target surfaces when triggered by heat. This system can save shipping and packaging costs, in addition to enabling customizability for the design of relatively large non-developable structures.

Moreover, at the Self-Assembly Lab of Skylar Tibbits [4], 4-D Eames Elephant has been printed out of programmable wood composite (**Figure 5.1**). By controlling the pattern of the wood grain, Athina Papadopoulou was able to 4-D print a flattened wooden elephant that sprang into its proper shape as it dried. Working with product designer Christophe Guberan, the team is now developing a series of product concepts around programmable wood.

One of the future applications in 4D printing lies in overcoming the limitation of requiring manpower to work in an extreme environments. There are scenarios where it is difficult to build, where current construction techniques do not work properly.

One such example is the fabrication of a 3D printed self-assembled satellite components with its hinges made of smart materials such as NiTi [5]. When the self-assembled satellite component is being manufactured on Earth, it could be designed to assume a compact structure before it is being launched. Once the satellite has been brought up to the outer space, the hinges would then open up and the satellite components will adopt a deployed structure either by solar heating or joule heating (**Figure 5.2**).

Another scenario is about adaptive infrastructure. An exemple is presented by Skylar Tibbits during his TED talk “The emergence of 4D printing” where he shows an underground pipes concept that change shape to help move water [6] (**Figure 5.3**).

Active Origami and 4D Printing has also inspired the manufacturing and design of robots. An example of application in robotics is shown in **Figure 5.4.** It shows a robot fabricated using an origami-inspired technique [1] whereby the structure starts as a planar sheet with embedded electronics and shape memory polymer (SMP) actuators, and then transforms under the application of heat into robot having origami wheels with variable size that are manipulated through internal actuators that drive their foldable outer shape to collapse or expand. By changing the size of the wheels, the robot can trade speed for the ability to move in smaller spaces.

Potential applications of 4D printing is related to the development of personal responsive products. Such products are able to react to the demands of the users or react to the physical conditions of the users such as body temperature, perspiration and biometric information. Furthermore, such products can be made more durable as well as they can be designed to adapt to environmental changes such as humidity level or moisture content, temperature, altitude and pressure.

An exemple of this application is a system called Active Textile Tailoring [7] developed by MIT’s Self Assembly Lab and MIT-born apparel company Ministry of Supply (**Figure 5.5**). It demostrates a new system for smart textiles in which fibers change shape and structure in response to heat and moisture, unlocking a new wave of customization of fit and aesthetic.

Others applications of active origami/ 4D printed structures may include: various space structures (e.g. solar panels telescope lenses ecc...), micro-mirrors, electronic components, foldcore-based structures for enhanced mechanical properties and impact resistance, micro-electromechanical systems (MEMS) and many others.

Figure 5.1 Eames Elephant made of programmable wood before and after shape-changing process.

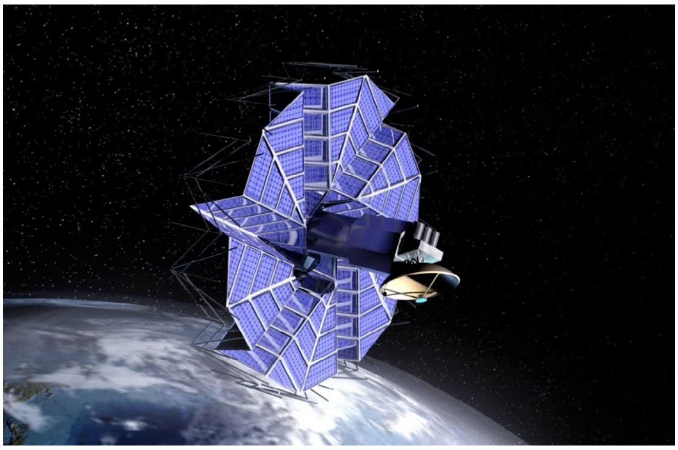

Figure 5.2 *NASA Solar Arrays for space inspired by origami principles.*

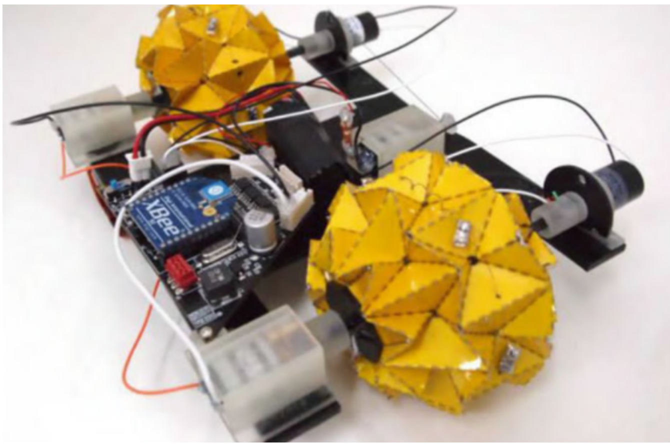

Figure 5.4 *Robot with variable size origami wheels. The size of the wheels can be manipulated through folding and unfolding, allowing moving in smaller spaces.*

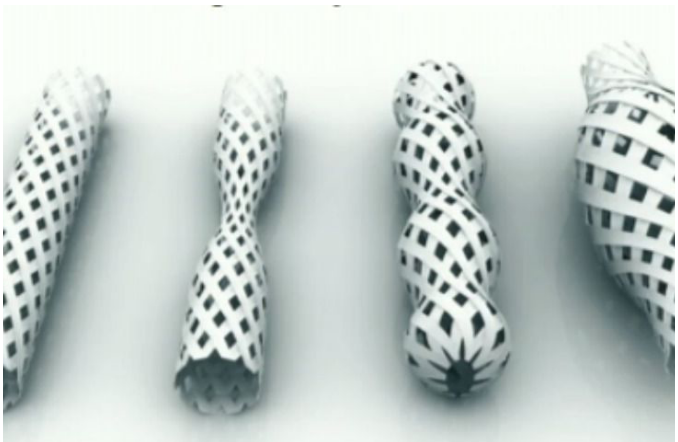

Figure 5.3 Underground pipes concept that change shape to help move water.

Figure 5.5 Demonstration of Active Textile that changes shape and structure in response to heat.

5.2 CHALLENGES AND FUTURE OUTLOOKS

In this thesis, 3D printing of smart materials, also known as 4D printing, has been analyzed and classified according to the printing technologies, shape-shifting mechanisms, material systems and potential fields of applications.
The term “4D printing” was coined in 2013 and since then has received a growing level of attention from various disciplines. The basis of the 4D printing process includes the 3D processes, external stimulus, responsive materials, interaction mechanisms and mathematical modeling. These properties enable changes in shape/property/functionality after printing, as a function of time.

From the engineering aspect, the 4D printing process enables fascinating applications that can hardly be achieved with conventional manufacturing processes. However, similar to many other emerging technologies, there are still many challenges that the embryonic 4D printing is facing for practical applications.

Considering efficiency and productivity point of view, 4D Printing offers advantages of saving both raw materials and manufacturing time. In addition, the post process required to remove the support material in conventional 3D printing can be time consuming, while the time needed in 4D printing is reduced, but at the expense of needing to perform the shape-shifting mechanisms after printing to assemble the 3D structure.

4D printing is still very young and needs a significant amount of efforts for future development, especially from the technological point of view. In the area of technological limitations, there is an inadequate availability of 3D printing technologies (high equipment cost, low mechanical propierties, relatively low resolution and limited material choices), limited scale dimension and the difficult of development of some smart structures.
It should also be considered the lack of knowledge in the interaction between some specific smart materials and 3D printing technologies, and the issue of fast mechanical degradation observed in multi-material printed parts during repeated thermo-mechanical cycling.

Different theoretical/mathematical models and design methodologies have been developed to accurately predict and optimize different shape shifting processes. This is a critical point in the 4D printing, since the level of complexity and require knowledges could be much higher than common 3D printing processes. For this reason, modeling the geometries, determining interactions for shape-shifting states (predicting the shape evolution shaking, pneumatics, gravity, magnetics, etc.) need the support and development of powerful and usable softwares which are starting to emerge (For exemple Thermorph, 4DMesh, Project Cyborg from Autodesk etc.).

In order to improve and maximize the potential applications of the 4D printing process, a large amount of multidisciplinary research needs to be conducted (Interdisciplinary research of 3D Printing, Smart Materials, and Design) [8]. According to future projections (Gartner hype cycle in Chapter 1.4), 4D printing will take more than 10 years in its path to bring feasable results to mainstream reality [9].

CHAPTER 5. REFERENCES

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