1

Getting Things Moving

> Manufacturing, but not action or speech, always involves means and ends; in fact, the category of means and ends derives its legitimacy from the sphere of making and manufacturing, where a clearly reasonable end, the final product, determines and organizes everything that plays a role in the process – the material, the tools, the activity itself, even the people who participate in it; all of them become mere means to the end and are justified as such. (Arendt 1972)

Warning

In the 16th century, in his treatise on magic, Giordano Bruno had, among other ideas, a certain notion of reactivity and consequently of adaptive materials. Thus, he wrote:

> If one resorts to the virtue of sympathy and antipathy of things, as when substances repel, transmute or attract other substances […], one rightly speaks of extra-natural magic. […] From these premises, it can be deduced that the magnet stone attracts by its very nature. Indeed, attraction is twofold: certain objects attract first of all by sympathy, as when parts move towards their whole, when what has a definite place joins its place… (Bruno 2020)

This chapter tries, however, to move away from any magical context by examining, as scientifically as possible, how by various stimulations a form can change spatially or in functionality, alone in a homogeneous way or by association with materials.

For a color version of all the figures in this chapter, see: www.iste.co.uk/demoly/4Dprinting2.zip.

1.1. Introduction

The introduction of additive manufacturing in the 1980s transformed the manufacturing industry. This technology, despite its success, still has some drawbacks, such as printing speed, surface finish of the final product and lack of fully functional materials (Manikandan et al. 2021). 4D printing uses smart or active materials to achieve a change in form or functionality. Materials that are sensitive to certain stimuli, the stimuli themselves and the time required for the change in state to occur are key research areas in 4D printing.

This chapter summarizes the developments in 4D printing, with a focus on the materials and methods used for the manufacture of 4D printed objects and structures. Smart or active printed structures can be disrupted in a custom manner by external stimulus such as water, heat, electricity, light and solvents with different pH values. Although printed structures exhibit self-healing, self-diagnosing, self-acting and self-sensing capabilities, etc., this chapter illustrates attractive possibilities and also highlights some difficulties. The field is not yet mature and still needs further research.

Innovations, such as new tools, devices and processes, can bring significant benefits to society by providing elements of comfort, means of medical treatment, etc., all in conditions of frugality imposed by a crying environmental need. Only then will innovations become inventions that can help the world's citizens live better, longer, healthier, more productive lives, and provide new ways to build, move, communicate, heal, learn and play. Understanding and clearly communicating the value of innovation (not the promises of it) can help decision-makers understand the benefits of supporting initiatives for their development. With 4D printing, we are at the beginning of a new scientific and technological adventure and the reality principle must be taken into account.

The Rand Corporation (2021) highlights three lessons:

– The impact of innovations goes beyond the direct effect of the invention itself; it can serve as an inspirational image for other fields.

– Success stories, which must be seen by the public, can help solve challenges facing society.

– But, it is not enough to create an invention that must meet the challenges of industrial application and manufacturing to satisfy a potential public demand.

> This is another book that all employees on the verge of burnout are snatching up and running to buy in their bookstores, like a crocodile rushing into a leather shop. (Vervisch 2020)

However, before reaching this stage, we must go beyond simple proofs-of-concepts (POCs). However, in Chapter 1 of Volume 1 we have shown a significant difficulty linked to the control of the deformation of complex shaped objects coming out of the basic origami. Methods of "successive approximations" have thus been proposed to reach a certain satisfaction in transformable devices, allowing for the adjustment of ends and means. If Lippmann (1937) wrote:

> Technical progress, experimental in nature, requires much trial and error […]. For these great centralized controls […] are not suitable for a system of production which can only make a profit by new invention if it is flexible, experimental, and competitive,

this is only true if one has properly circumscribed the subject to avoid wasting time.

In order to do this, we felt that it was important to start from the most robust bases possible, in order to attack a market that still expects little or nothing from 4D printing. One of the elements that has already been widely discussed (because it is essential) is the effect of a stimulation to transform cohesive matter – thus materials – (we are obviously not talking about chemistry, which could claim this definition, nor about cooking) by providing a new functionality and/or a deformation. We know from Tahon (2003) that, despite (or because of) an increasingly unstable demand, unless we change the business model, there will continue to be pressure to produce as quickly as possible, and the diversity of products will increase. It will also be a matter of being ready on time in 4D printing.

Thus, the purpose of this chapter is to provide an overview of the means, of whatever nature, which make it possible to reach this objective. On the basis of the proposals, it will then be possible to evoke exploitation paths of these means for 4D printing applications. It is at this (partial) price that we will know if it is really a potentially attractive "disruptive technology". The concept of disruption was introduced and argued by Christensen (1997) because he recognized that few technologies are intrinsically of a disruptive or continuative nature. It is, according to Bessen et al. (2020), their use that manifests a disruptive effect.

In André (2017), a chapter was devoted to 4D printing and transformation processes under stimulation. These data and presentations are re-used here with (legitimate) enrichments, following recently published work, as the background from four years ago is considered robust.

Box 1.1 *General note*

> It is true that the test of causality – the predictability of the effect, if all the causes are known – cannot be applied to the field […]. But this practical unpredictability is not proof of freedom; it simply means that we are never in a position to know all the causes that come into play. (Darwin 2020)

1.2. Actuators

2,000 years before our time, Sumer imagined that the gods created humans in the form of animated clay statues, so that they could work in their place (principle of intentionality). This is the active matter side. But this myth would be found, according to Couveinhes (2012), in the legend of the Golem: the clay creatures could be animated thanks to inscriptions, as well as by a scroll. There would thus be an association between active matter and information. The central question in this chapter is to know how these androids can move (and not why). According to Wikipedia (2021), an actuator is an object that transforms the energy supplied to it into a physical phenomenon that provides work, and modifies the behavior or the state of a system. To do this, the initial energy can be pneumatic, hydraulic, electrical, electromagnetic, mechanical, thermal, photochemical, chemical, biochemical, biological, etc., to finally transform into mechanical energy and provide work. The link sought is therefore the actuator or engine that connects matter to energy for practical actions.

Robots are platforms for the integration of advanced technologies: energy storage, support and active materials, information and acquisition, data processing and transmission, mechatronics, sensors, etc. These are autonomous systems for producing a service. “The convergence of advanced technologies and their increasing interoperability, resulting from dematerialization, make the robot a fertile ground for innovation, cost reduction, and new uses” (Roure and Arcier 2012).

Box 1.2. *Remark on robots*

Thus, an actuator is a device capable of producing (and reproducing) a physical phenomenon such as a displacement, heating, an emission of light, sounds and a change of functionality. It is a transformer of one form of energy into another.

1.2.1. *General information*

> Culture is nothing more than the transmission and sharing of representations that are temporal discretizations produced by the

> techniques of a given era. Telling is ultimately about organizing temporal discretizations in time. (Kaplan 2012)

While looking in the past for traces concerning actuators (before including them in additive manufacturing), we wished to give a quick overview on this aspect. While, a long time ago, industrial activity was focused on a centralized energy: windmill, water mill, etc., steam, the explosion engine and especially electricity allowed us to include or distribute engines and actuators in any object whatever its size, as a way to transform, at will, usable energy flows into spatiality. In classical technologies, discrete elements are integrated into each other to form a system that will operate a temporal change; with 4D printing, we hope to move from the "quantum" to the continuous, from an ancestral and robust technical know-how to a more innovative concept of a new mastery of matter. So, the possibility of repair in this new field imposes level maintenance integrated into the process itself of creating an object. We no longer replace elements: there is no need for skills, standardized modes of communication, disassembly, storage, maintenance, etc. This is a future that could, independently of the other performances associated with 4D printing, constitute a real disruptive leap in the technological functioning: we no longer repair, but we throw away! It would therefore be the "smart" use of the object that would paradoxically create value and not the object itself, which is becoming more or less invisible! Moreover, 4D objects are connected objects:

> [They] do not pose any problems as such, what challenges us is the extent to which we have become, willingly or not, connected subjects, and therefore disconnected. (de Brabandère 2017)

But this is another story, for later.

Technical and formal innovation has involved and combined, in one way or another, a theoretical reflection that is now mature with a creative practice that links different energies together. We do not seek to find, reveal the various stages, methods and stakes which led the designers to push back the limits of the discipline, develop, as well as innovate, renew and create new materials, tools or uses through the production of these machines of transfer and transformation of energy in this chapter. We wish to make a state of affairs that will serve to initiate the reflection on this setting in shape- or property-changing objects.

Indeed, this prior knowledge can reveal how traditional systems of action and their cultural practices can inform and consolidate research regarding 4D printing. Like the tendency to focus on spectacular cases, anticipating a pre-foundational dogma, the possible exclusion of cultural knowledge and traditional practices can impoverish 4D printing development. It is thus a question here of re-examining the question of the links between external stabilized knowledge concerning what "moves" or what induces "movement" to consider possible ramifications. It is not a question of reconstructing the modes of thought, the socio-cultural and scientific markers, the impact on the social recognition of the designers and manufacturers of actuators, as well as the types of production and transmission that have led to the establishment of this approach within developed societies, but to examine whether this immense field of knowledge can serve as a medium for the applicative development of 4D printing.

An invention begins with the association of at least two existing techniques (Kaplan 2012) to lead, in the sense of Simondon (2001), to what he calls a "concretization": here, 3D printing (André 2017b) and active matter. Initially, it is classically a juxtaposition of knowledge, but in time one can imagine a mutualization, a more complete integration (which is only rarely envisaged).

> Converging technologies (CTs) refer to the convergence towards a common goal of discoveries and techniques of fundamental science and technology: CTs are technologies and knowledge systems that complement each other in order to achieve a shared goal. Together or in isolation, [4D] technologies can contribute to this convergence. (Nordmann 2004)

Citton (2016) mentions hyper-objects in the field of complexity that can be applied to the 4D printing domain. He writes:

> Hyper-objects are nowhere isolable like classical objects because their existence is inter-objective: their mode of existence is constituted by relations between the things we identify as objects (e.g. a glacier, a water level, a harvest, a thermometer, etc.). Whether we call them "systems", "attractors", "networks", "entanglements", it does not matter: they exist and operate as a web of relations conditioning the behavior of the objects on which our attention is focused. […] Hyper-objects are viscous: they tend to stick to the beings whose existence is involved in theirs.

We will have to deal with it, like Captain Haddock in *Tintin*… if the theme keeps its promises. It is a thought of the adventure which,

> by the moving and complex order of the knowledge that it gets, invites us to face the novelty and the unforeseen. This relationship of transformation, made of tinkering, of adaptation to the circumstances and to the unforeseen, of forgetting the pre-established models and of ingenuity obliges, in any case, invents a specific mode of transmission, which is not of the order of the teaching of an abstract

> knowledge but of the learning of an ingenious know-how. (Faucheux and Forest 2011)

It is far from this present and potential future, the objective of this chapter which only envisages examining the links between known actuators and their possible penetration into 4D space, with an essential concept of “printability” because it is necessary to accept a humiliating defeat (to varying degrees) in regard to additive manufacturing. It is also to examine other more autonomous sources of inspiration, and even to imagine others. It is by the yardstick of the mastery of these elements that we will know if this boundary object or this hyper-object that is the result of 3D printing (which belongs, whatever we think, to the old world) will introduce itself into our daily life in a punctual or radical way.

> The only thing that counts is the process, for it is the process that lasts, not the goal, which is only an illusion of the traveler when he walks from peak to peak, as if the goal reached had a meaning. (Fourastié 1966)

But in relation to the theme of this chapter, the comments presented show a complementary partner, that of the sensor used to take information and which is also an energy interface like the actuator and the engine. So, if we combine these three elements, the scientific literature is particularly vast! Figure 1.1 illustrates the temporal evolution of the number of publications on the theme.

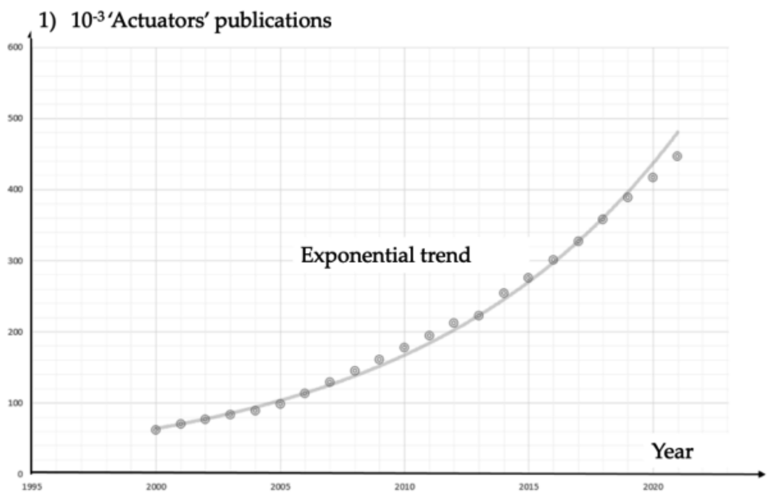


Figure 1.1. *Evolution of the number of publications on the theme of “Actuators” (according to the CNRS database)*

Like most sciences and other scientific fields, the number of publications is increasing very rapidly with exponential evolutions. But, after having recalled that the 4D printing paradigm emerged around the year 2013, it seemed interesting to us to consider at the same time, in the same approach, “Actuators” and “4D Printing” themes to examine the existence of a particular “academic pressure” on this association. Figure 1.2, which represents this data in relation to that corresponding to the main theme “Actuators”, illustrates the interest of the researchers on these associated themes in an obvious way.

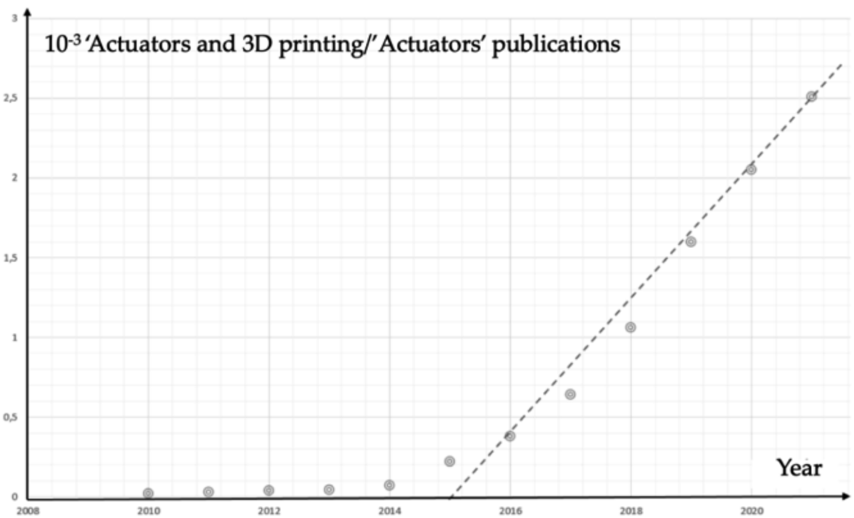


Figure 1.2. *Evolution of the number of publications on the themes of “Actuators” and “4D Printing” compared to the number of publications on the theme of “Actuators” (according to the CNRS database)*

Obviously, even if this composite theme remains modest in number of publications, the subject is very quickly associated with the production of 4D objects (dotted line extrapolated in 2015). There is thus an almost consubstantial link between both fields (4D and actuators).

1.2.2. *Different types of actuator*

> Philosophy begins in wonder. And at the end, when philosophic thought has done its best, the wonder remains. There have been added, however, some grasp of the immensity of things, some purification of emotion by understanding. (Whitehead 1968)

By engineering definition, an adaptive structure is

> a structure that can change its properties (mechanical, physical, electrical, etc.) or geometric form in response to changing environmental conditions. (Wagg et al. 2007)

In addition to the ability to move in multiple directions, some actuators have the ability to deform in any way. A concrete example comes from the bio-inspired actuator of a jellyfish's locomotion (Villanueva et al. 2010).

An actuator can be described as a mechatronic device that changes the mechanical state of a system by modulating an energy flow between the mechanical domain and another energy domain. Different types of actuators, according to Bréguet (1998), Vermes and Czigany (2020) and other more specific authors, are described in Table 1.1. To meet the specificities of 4D printing, the actuators, integrated or not, must satisfy the following: a resolution below a certain threshold, allowing a given stroke, depending on the application, a reasonable speed and a mechanical strength adapted to the objective, and the ability to be totally or partially integrable in the 4D device. Other performances may be of interest, such as active or passive control aspects, reproducibility, robustness, stability in a polluted environment and aging. A distinction is made between classical linear actuators (pneumatic, hydraulic and electric) (e.g. Joo and Sanders (2009)). Nonlinear aspects can come from several sources: large displacements (geometric nonlinearity), changes in contact status (contact nonlinearity) and nonlinear stress-strain relationships (material nonlinearity) (Lee 2012).

Nature	Comment
Hydraulic and pneumatic	In general, high energy density and very high stiffness Numerous on-off applications
Flexible fluidic	Application of a pressure on an anisotropic elastic structure Artificial muscles Origamis by elastomers
Electromechanical	High energy density linear or rotary engines High precision possible (step by step)
Electrostatic	Low power but can be used in parallel Dielectric elastomers (change in shape induced by electrical energy)
Deformation of materials	Ultrasonic actuators (piezoelectric vibration converted into motion), change in elasticity, change in electrical properties, etc.
	Inch-worm (displacement in a bore like a worm in its hole)
	Rotating inch-worm with bimetals
	Inertial actuators (a mass is moved away from another one

Deformation of materials (cont'd)	suddenly, then slowly brought closer)
	Stick and slip (one of the two masses is zero or negligible compared to the other)
	Electro-hydrostatic (avionics)
	Pyrotechnics (forcing by explosion of a membrane)
	Chemical reaction inducing a variation of volume or pressure
	Specific chemical absorption or adsorption
Modifications of 2D and 3D structures	Thermal expansion (bimetal and other amplifications) Structural reorganization; isomerization Electroactive polymers and electroactive ceramics, single or multilayer; resonances of piezoelectric elements Electrostriction, magnetostriction Shape memory alloys: reversible evolution between two crystalline states affecting the geometry Thermosensitive and photosensitive functional polymer actuators based on semi-crystalline polymers and/or liquid crystal polymers
Micro heat sources	Association of a heat-sensitive material with several heat sources
Integration of magnetic micro-sources	Association of a magneto-sensitive material with several magnetic sources
Modification of the bearing capacity	Drag and boundary layers: promote the laminar-turbulent transition of the boundary layer to delay separation and reduce recirculation zones; disorganization of sheared layers

Table 1.1. *Different types of actuator (non-exhaustive list)*

A liquid crystal is a state of matter that combines properties of an ordinary liquid and those of a crystallized solid. We express its state by the term "mesophase" or "mesomorphic state". Borshch et al. (2013) remind us that these are ordered structures (with an associated order parameter S). S goes from 0 for a completely absent structure to 1 for a crystal structure. The behavior of the system, at a macroscopic level, is given by a collective variable. The order parameter describes the behavior, that is the coordination of the various constituent elements of the organized system. If θ is the angle between two elongated molecules, then:

$$S = \frac{3\cos^2(\theta) - 1}{2}$$

The effect of a stimulus (of the same type as those sought in 4D printing) can change the interaction potentials between the constituent elements of liquid crystals and thus S. Figure 1.3, from Ge (2019), shows the classical forms of liquid crystals.

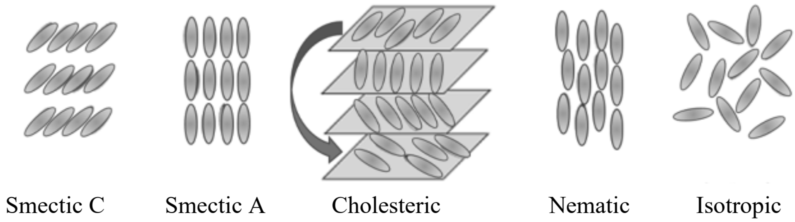


Figure 1.3. *Liquid crystals*

Box 1.3. *Liquid crystals*

1.2.3. *Amplification*

> About the laws of nature: "To say this to a physicist is to say to a tiger in search of prey that all flesh is grass." (Weinberg 1997)

4D printing can reproduce physico-mechanical changes over time in a controlled manner, allowing the transition from static to dynamic. By combining the ability of 4D printing to create dynamic morphological changes under certain stimuli and the possibility of creating biocompatible micro- or nano-robots based on elastomeric materials, biomedical applications can be envisaged (Hann et al. 2020). However, among the current challenges and limitations of these devices, is the issue of deformation amplitude. As in any system where mechanical elements are involved, this question of the amplitudes of displacements is often raised. When these are considered too modest in relation to the objective, mechanics have already developed relays that allow the movements to be amplified. It is in this field that we will find, for example, the bilayer or constrained systems, presented in Figures 1.4 and 1.5, which could be used in 4D printing.

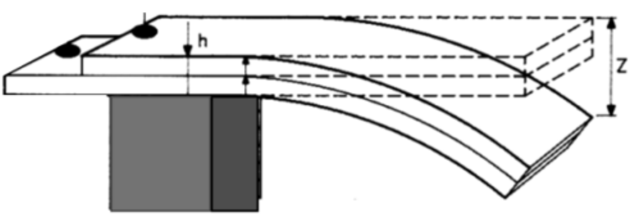


Figure 1.4. *Bilayer*

A bilayer, as its name indicates, is a device made of the juxtaposition of two cohesive blades of materials with different mechanical properties (e.g. different expansion coefficients). It is thanks to the different properties of these two materials that it will deform to achieve a mechanical action. Bilayer type elements allow for the generation of a bending moment or annular elements that will, using a shear mode, generate a displacement perpendicular to the element (Lambert et al. 2016). A 4D printing model is presented in Lee et al. (2019). For their part, Baran et al. (2017) propose multi-layer or multi-blade evolutionary systems.

Figure 1.5. *Displacement amplification under stress*

If Δl is the elongation, the height h reached is defined by $h = \sqrt{2l\Delta l}$, which corresponds to an amplified effect in spatial terms.

1.2.4. *Other modes of action from mechanics*

> The artist, taken in this highest sense, does not create only for the entertainment and instruction of his audience, he works solely and exclusively for the formation of his own existence. It is culture as Goethe understood it, as he opposed it to philosophy and science, it is this hard and rigorous task of knowledge that accompanied him all his life, forcing him to assimilate with a hunger never satisfied, all of the phenomena of life, and to metamorphose them to the true meaning of the word. (Broch 1985)

The discovery of new materials is an important part of our technological history. Manufacturers are increasingly using materials for high-tech sectors, as well as in more everyday areas; their objectives are to improve performance, lower the cost of manufacturing products and maintain or even improve reliability. The concept of "smart" materials and systems emerged in the early 1980s. They are capable of changing a characteristic such as shape, modulus, viscosity and transparency under stress (Elguesse 2015).

1.2.4.1. *Fluidic actuators*

> Before Koch, the bacillus had no real existence. (Latour 2020)

The first family of flexible fluidic actuators is based on the historical McKibben actuator, developed in the late 1950s. The basic principle of flexible fluidic actuators consists of a pressure applied on an anisotropic elastic structure. The basic configurations are shown in Figure 1.6.

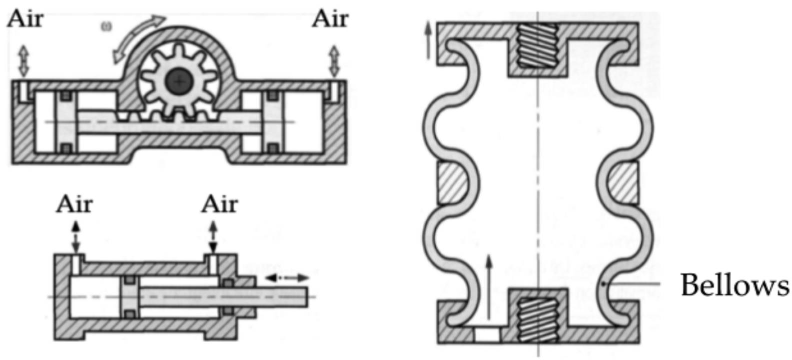


Figure 1.6. *Different types of fluidic actuator (see http://www.zpag.net/Tecnologie6s_Indistrielles/Verin.htm)*

A pneumatic actuator, as shown in this figure, consists of a cylinder containing a sliding piston with a fixed metal rod that transmits the mechanical energy generated by the pressure. For a double-acting cylinder, two compressed air supply ports are machined on either side of the piston. The commonly accepted advantages of these flexible fluidic actuators lie in high compliance (compliance is the opposite of stiffness), high efficiency of input pneumatic energy conversion, very low heating, low density and, most importantly, the absence of a magnetic part (Lambert et al. 2016). Since it involves the use of flexible materials, this type of actuator should advantageously be able to be used in 4D printing.

For Lambert et al. (2016), the characteristic elements to be considered are free elongation (without applied force), locking force (without displacement), and response time, developed stress (N/mm^2) as a function of actuator volume (mm^3), applied pressure (bar), dimensions, number of degrees of freedom, achieved performance, as well as indications on manufacturing choices (materials, processes), etc. (Huber et al. 1997; De Volder and Reynaerts 2010; Gorissen et al. 2011).

1.2.4.2. *Shape memory alloy (SMA)-based actuators*

Time is the modification of space. (Fourastié 1966)

Shape memory alloys (SMAs) are exploited for their thermomechanical properties, such as their hyperelasticity in the austenite state, plastic behavior in the martensite state and the shape memory effect controlled by temperature change (Simoneau 2013; Yuan et al. 2020). In mechanical applications, SMAs have the advantages of being clean and developing high stresses for low weights (Lambert et al. 2016). The principle of these active systems is observed in large families of alloys including copper (CuAlZn), nickel-titanium (NiTiNb) or AuCd (discovered in 1932) based alloys. These materials can evolve between two crystalline states affecting their geometry: the austenite state at high temperature (cubic mesh) and the martensite state at low temperature, the latter has a significantly flattened mesh, as shown in Figure 1.7.

The transition from both crystalline states occurs through a threshold temperature. According to Lambert et al. (2016) and Boni and Royer-Carfagni (2021), the stress experienced can be a uni-axial elongation when the SMA is a tensioned wire or bar (Mavroidis 2002). But, for a larger stroke, it is possible to use an SMA material in the form of a coil spring (Velazquez et al. 2008). When this spring is stretched or compressed, the material works primarily in torsion and the internal stresses are of the shear type (Sheng and Desai 2015). The beam network form can be useful when looking for an optimal trade-off between force and output stroke (Abadie et al. 2009).

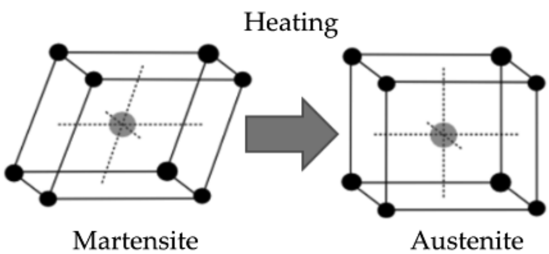


Figure 1.7. *Shape memory alloys*

Figure 1.8, from Lambert et al. (2016), represents the evolution of the martensite phase in the material as a function of temperature and for a given stress. This diagram accounts for the transformation hysteresis Y. The different transition temperatures are defined by considering that *As* and *Af* are respectively the thresholds of start and end of transformation from the martensite state to the austenite state, and *Ms* and *Mf* are those of the reverse transformation (Cianchetti 2013).

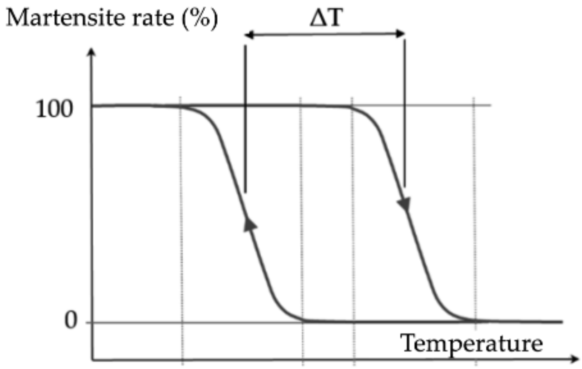


Figure 1.8. *Evolution of the martensite rate in the material as a function of temperature and for a given stress*

1.2.4.3. *Translation – rotation*

> Some ideas spread so well that, in different versions, they invade whole populations in a lasting way. Culture is made, in the first place, of these contagious ideas. It is also made up of all the behaviors […] and all the products […] whose presence in the shared environment of a human group allows ideas to spread. (Sperber 1995)

Ren et al. (2021) have taken up a system that transforms a stimulus-induced translation (electrochemical in their case) with a rotation (arm joint type). Figure 1.9 illustrates a working principle of such a biomimetic system.

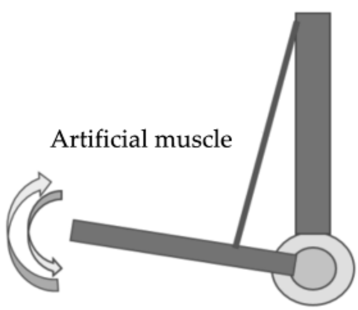


Figure 1.9. *Actuator transforming translation into rotation*

Relative to what is proposed by work from homogeneous processes, the nanofiber-containing "muscles" provide an isometric stress of 10.8 MPa (about

30 times what is achieved with skeletal muscle). Using the accumulated isometric stress, the wire muscles achieve a high contraction rate of 36.3% s^{-1}. The wire muscles can be grouped together to lift large masses and grasp real objects.

1.2.4.4. *Rotary engines*

Most engines that output mechanical power in the form of torque (rotary output) use crank-crank (translation-rotation) foundations with sequentially excited actuators.

1.2.5. *Remarkable properties*

> Philosophy […] must refuse the freedom indulged in by specialized thoughts that reject or exclude what is incompatible with their presupposition and that, if need be, boast of "scandalizing common sense". (Stengers 2020)

1.2.5.1. *General considerations*

> Time is the moving image of still eternity. (Morel 2020)
>
> All happiness is essentially poetry, and poetry means action; one hardly likes a happiness that falls to you, one wants to have done it. (Alain 1985)

Recall that an actuator is an operating component of a functional system that transforms the energy supplied to it into a physical phenomenon that provides work, transfers energy or modifies the behavior or state of a system. An associated effector can finalize the work by producing the expected effect. Among the properties of the actuators are a number of important elements, such as the response time or the elastic modulus.

– Response time is a measure of performance defined as the time between the end of a request to an actuator and the beginning of the response (see Figure 1.10). Latency is also expressed as a creep (or delay) function.

– Young's modulus, the modulus of elasticity or tensile modulus is the constant that relates the tensile stress and the onset of deformation of an isotropic elastic material. The law of elasticity is Hooke's law of the form: $\sigma = \varepsilon E$, where σ is the stress (in units of pressure), E is Young's modulus (in units of pressure) and ε is the relative (dimensionless) elongation. The international unit is therefore the pascal (Pa). However, because of the high values this modulus takes, it is usually given in mega-pascals (MPa).

Figure 1.10. *Concept of response time*

– Other criteria related to the material are presented in Figure 1.11 (Troyano et al. 2021) and others can be searched for, such as a nominal power (Watt), an action frequency (s^{-1}) and a torque to be transmitted (Newton.m or N.m). Additional elements resulting from their use in robotics concern aspects of impedances and mechanical admittances. These are stiffness or elasticity, mass or inertia, viscous friction or damping, dry or Coulomb friction and kinematic constraints (revolute, ball joint, etc.). The interested reader can find information on these aspects in Fauteux (2009). Indeed, the main elements such as the response time and the main mechanical properties will suffice to start a comparison between "traditional" actuators and 4D devices.

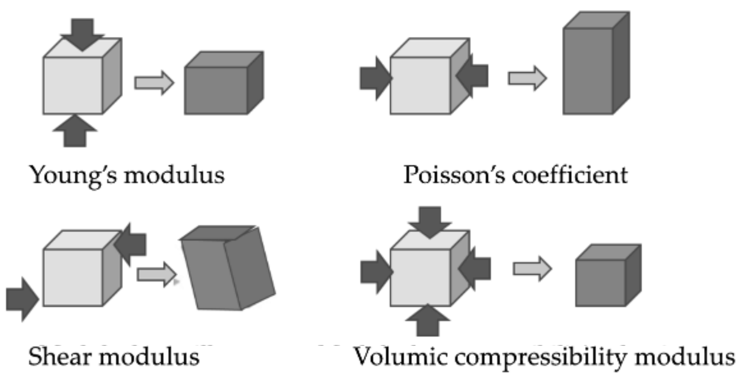


Figure 1.11. *Material characterization (E:Young's modulus; υ: Poisson's ratio; G: Shear modulus; K: volume modulus of compressibility)*

COMMENT ON FIGURE 1.11.– *The three moduli E, G and K allow for the characterization of the elastic behavior of an elastic material. These constants result from the existing relationship between a stress and the induced deformation:*

– $\sigma = \varepsilon E$, *where* σ *is the stress (in units of pressure), E is the Young's modulus (in units of pressure) and ε is the relative (dimensionless) elongation.*

– $\tau{:}\gamma G$, *where* τ *is the shear stress (in units of pressure),* G *is the shear or Coulomb modulus (in units of pressure) and* γ *is the shear angle (dimensionless).*

– $p = -K\frac{\Delta V}{V}$, *where* p *is the hydrostatic pressure exerted on the volume (unit of pressure),* K *is the volume modulus of compressibility (unit of pressure) and* $\frac{\Delta V}{V}$ *is the relative change in volume (dimensionless).*

If the deformation is elastic, there is partial compensation of this increase in volume by lateral contraction of the specimen (Δy and Δz) in directions perpendicular to the tension. The relative deformation in the y and z directions is then written (for a homogeneous material):

– $\varepsilon_y = \frac{\Delta y}{y_0}$ with υ, Poisson coefficient defined by $\upsilon = \frac{\varepsilon_y}{\varepsilon_x} = \frac{\varepsilon_z}{\varepsilon_x}$

– E, G, K and υ are related to each other by the relation $E = \frac{9KG}{(G+3K)} = 2G(1+\upsilon)$

– Temporal aspects must be taken into account with materials whose shape must evolve following a stress. Figure 1.12 (from Billon (2007)) represents the case of the deformation of a linear polymer after a first transition (not shown in the figure) from a completely disordered state, in thermodynamic equilibrium prior to the stimulation, to a change of order that favors the flow.

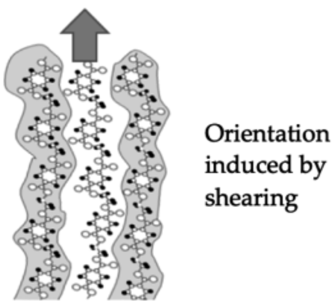


Figure 1.12. *Orientation of polymeric chains in the direction of flow*

Each "linear" chain has a free volume in which it can move by propagating local conformational changes. But, depending on the constraint exerted, the system that constitutes each polymer can be forced to adapt, for example by reducing the number of its Cis bonds relative to the Trans ones, thus prompting the transport phenomenon. These different movements have their own time scale. In polymers, the elasticity energy represents the energy storage resulting from the rotation around the bonds, the variation of the bond angles and finally the variation of the equilibrium distances between atoms. The elasticity energy is a contribution from intramolecular bonds (within a macromolecule) rather than from intermolecular bonds.

The macroscopic properties of polymers depend on their local architecture: monomers, nature of the chains and their rotational abilities, length of the chains, etc. (flexibility of the skeleton, capacity of cooperativity, physico-chemical and physical interactions, entanglements and disentanglements). The formulation of the polymer material involves additives, such as fillers or plasticizers (inter-chain interaction), nucleating agents (semi-crystalline organization (rate and size)) and blends. All of these interactions lead to different relaxation times that can be considered in global 4D printing.

Thus, for a viscoelastic fluid, there are two modes of deformation characterizing the viscoelastic behavior: (1) stress relaxation which consists of imposing a deformation step on the material and observing the evolution of the stress as a function of time and (2) creep which consists of imposing a stress step and then observing the evolution of the deformation as a function of time. Under viscoelastic conditions, these different parameters become functions of time and space.

An elastomer is made up of long molecular chains assembled, at rest in “balls”. These chains are linked together by cross-links, entanglements or polar bonds with mineral fillers. They form a 3D network. The mechanical properties of elastomers depend primarily on the length of the chains between the nodes of the network. The shorter this length (dense network), the more rigid the elastomer. When the material is extended or twisted, the molecular chains unfold and adopt a linear order which is achieved at the expense of the secondary bonds, the primary bonds remaining effective. The cessation of the extension-torsion stresses thus allows the molecular chains to return to their passive, folded and random configuration (elastic deformation), provided that the stresses have not broken the primary bonds, in which case the deformation becomes irreversible (passage into the plastic domain) (Mercier et al. 1999)

The deformation of a homogeneous polymer results from local changes of more or less cooperative conformations, which, from one to another, lead to global deformations.

> These local conformational changes are constrained by interaction energy terms (van der Waals or others) between unbound atoms (not bound by a covalent bond) and by torsion potentials on the valence

cones for bound atoms. The elementary processes of chain deformation. (Billon and Bouvard 2015)

The deformations of thermally activated macromolecules are time-dependent, dependent on the nature of the material (and its charges) and thermally dependent on their associated energies. “It also depends on the interchain organization through the conformational changes it favors and/or annihilates” (Billon and Bouvard 2015). Figure 1.13, from Pic (2009), recalls the effects of temperature on a polymer.

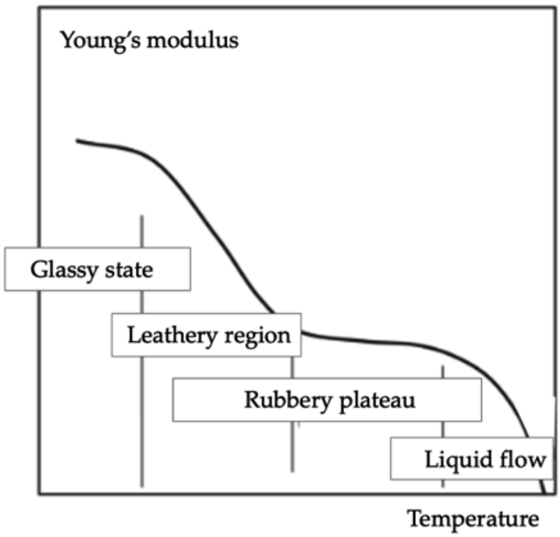


Figure 1.13. *Effects of temperature on the elasticity of a macromolecule*

These different parameters are defined under conditions where there is proportionality between the stress and the transformation. For too high stresses, the behavior may no longer be linear, with irreversibilities and performance losses (degraded processes and failures) (see Zhou et al. (2021)).

Evanescent memory: in viscoelastic materials, the deformations determined at the reference time depend on the entire history of mechanical stresses already experienced. According to Pic (2009), this type of material called “evanescent memory material” keeps the deformations undergone during its manufacture and during its use in its memory, but the effect of these constraints fades in the course of time (Lagache 2006).

Box 1.4. *Conditions on materials*

1.2.5.2. *Mechanical performance*

> He who finds what he is looking for generally does a good schoolboy's job; thinking about what he wants, he often overlooks the signs, sometimes minimal, that bring something other than the object of his predictions. The true researcher must know how to pay attention to the signs that will reveal the existence of a phenomenon that he does not expect. (Bourcier and Van Andel 2017)

Figure 1.14 (according to Liu et al. 2021a) depicting an Ashby diagram of compressive-density strength shows the range of possibilities depending on the inorganic materials used with very large dynamics.

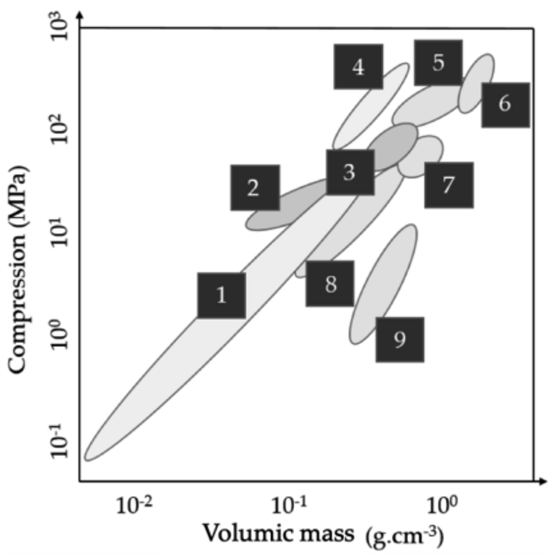


Figure 1.14. *Ashby diagram of inorganic materials (ceramics). 1: Hollow alumina nano-lattice; 2: SiOC micro-lattice; 3: SiOC honeycomb; 4: AlO/C_{23} nano-lattice; 5: AlO/C_{23} honeycomb polymer; 6: SiOC matrix and carbon nanotube matrix; 7: SiOC matrix and honeycomb carbon nanotube matrix; 8: AlO/C_{23} nano-lattice polymer; 9: SiC foam*

With respect to organic materials, Figure 1.15 shows that we are generally a long way away from the conditions achieved and illustrated in Figure 1.14. Most of the research efforts in the field of 4D printing are focused on smart (often soft) actuators with sensing and shape-changing capacities. They need to be observed through Key Performance Indicators (KPIs) and associated mechanical properties. Following the classification of actuators proposed by Zupan et al. (2002) and more specifically their derived characteristics, some attributes can be given special attention by designers and engineers, such as actuation stress, actuation deformation, actuation modulus, work output, work capacity, actuator efficiency and stroke work coefficient, in order to define the industrial specifications. In the present analysis, to measure and monitor the performance of 4D printed actuators with active materials, these attributes can also be derived and expressed in terms of material-properties (Karothu et al. 2020), such as Young's modulus, response time under stimulation, force generated and actuation efficiency (i.e. the ratio of mechanical work produced to energy absorbed during a complete cycle). Thus, Figure 1.15(a) represents the KPIs ranges for the main categories of active materials as used in 4D printing (Shape Memory Polymer – SMP, Shape Memory Alloy – SMA, Piezoelectric Polymer – PZT polymer, hydrogel, Ionic Polymer-Metal composites – IPMC and Liquid Crystal Elastomer – LCE).

Many studies have focused on characterizing active materials to provide relevant evidence for material selection (Huber et al. 1997; Song et al. 2016; Boyraz et al. 2018; Kim et al. 2019a; Decroly et al. 2020; Halabi et al. 2021). However, large disparities can be reported between the calculated/measured indicators which make it difficult for non-experts to use them. This can be explained in particular by the different measurement scales highlighting different temporalities, the customization and distribution of materials, the size of actuators, as well as the different material shaping processes studied over the last two decades. However, it should be noted that the current KPIs (shown in Figure 1.15(a)) are still low when compared to the performance of existing actuators (e.g. hydraulic and pneumatic) as used in industry. Most 3D printed active materials have notable weaknesses in terms of mechanical stiffness, actuation forces, actuation/recovery responses (e.g. thermoactive materials with large heating/cooling times due to Fourier's law of thermal conduction), changeability and even functional degradation of the material over multiple cycles.

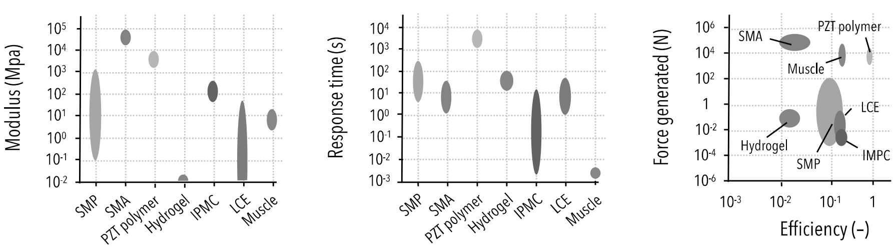


Figure 1.15(a). *KPIs of the main categories of active materials used in 4D printing: a) Young's modulus, b) response time once stimulated and c) forces generated and actuation efficiencies (from Demoly et al. (2021))*

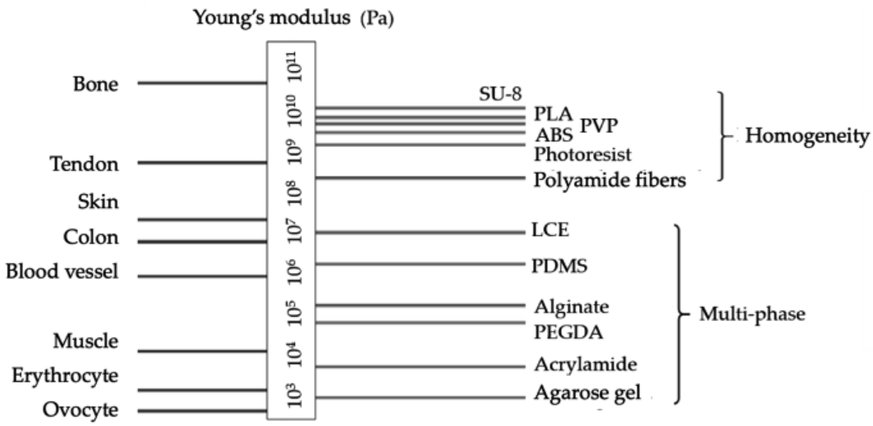


Figure 1.15(b). *Comparison of Young's moduli according to Adam et al. (2021)*

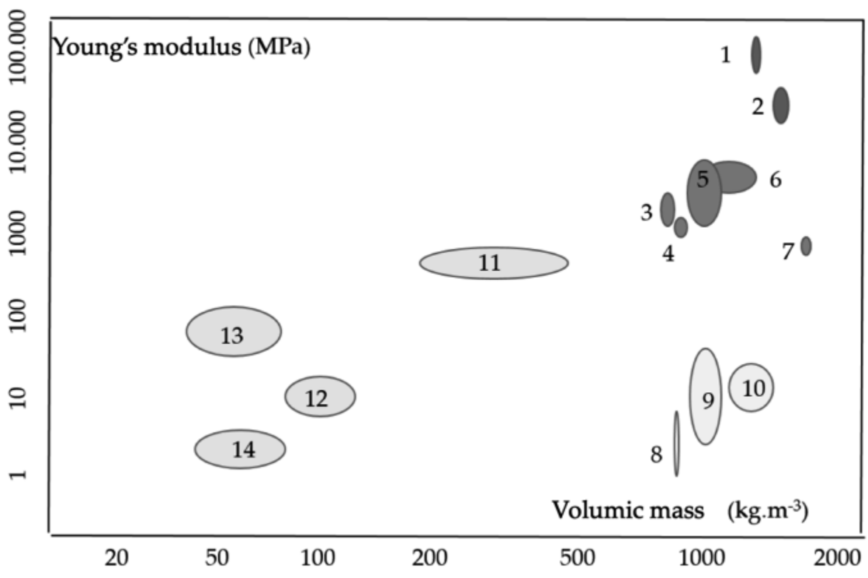


Figure 1.15(c). *Case of conventional polymers according to Lecomte-Beckers (2010). 1: Carbon fiber reinforced composites; 2: glass fiber reinforced polymers; 3: polypropylene; 4: polyethylene; 5 and 6: conventional polymers; 7: PTFE; 8: Butyl rubber and Isoprene; 9: rubber reinforced with carbon black; 10: silicone-based elastomers; 11: high-density rigid polymeric foams; 12: medium-density flexible polymeric foams; 13: low-density rigid polymeric foams; 14: low-density flexible polymeric foams*

Figure 1.16 of Hofman (2021) shows other highly differentiating criteria between Young's modulus and coefficients of thermal expansion. The same is true for the items shown in Figure 1.17 corresponding to mass torque relative to actuator speed (Babaei et al. 2021).

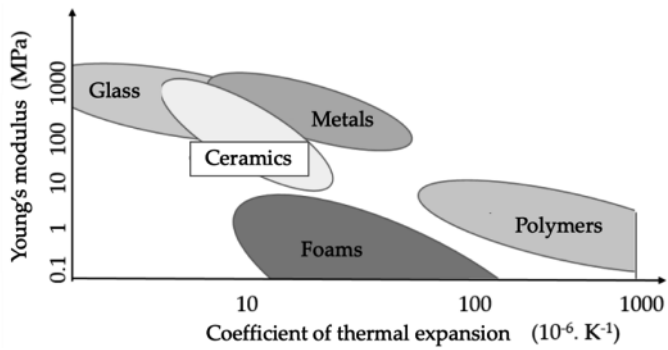


Figure 1.16. *Young's modulus – coefficient of thermal expansion relationship*

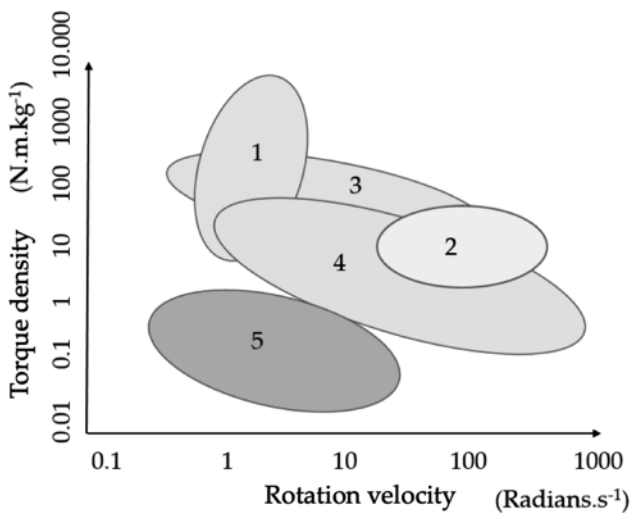


Figure 1.17. *Relationship between torque density and speed*

Considering the considerable dynamics to be taken into account, going from an established field for which rules exist to a very recent field still "boiling", we can imagine the difficulty that a designer may have to find "good" materials adapted to their problem.

1.2.5.3. *Actuator selection*

> The simulacrum is the identical copy of an original that never existed.
> (Baudrillard 1978)

Almost obviously, apart from the mechanical aspects (Young's modulus) and response time, other elements of choice can be considered. Depending on the use, the nature of the actuation (bending, elongation, deformation, etc.), the power in relation to the mass, the robustness, the durability, the frequency of use, etc., can be taken into account. In the same way (if only to prepare the next paragraph), the selection of materials can be a selection criterion: single-material system, multi-material, biocompatibility, biodegradability, etc.

Among some examples explaining this selection issue, Forget (2018) presents criteria for a pneumatic actuation with advantages: intrinsically compliant system; very dynamic movements; good control of the position/force of the joint, as well as its impedance/admittance; simplicity and lightness (good weight/power ratio); reduced price; pump relocation, etc. The disadvantages are the following: high pressures involved (risk of explosion); accurate modeling of the system difficult due to highly nonlinear behavior according to Alvarez Palacio (2020); friction losses; noise; each force/speed requirement requires different actuator sizing; pump sized for the "worst case", that is for the most powerful actuator; agonist-antagonist architecture imposing control of two variables per degree of freedom, making control more expensive in terms of computational power, etc.

In the case of an electric cable actuator also proposed by Forget (2018), using an electric engine and a ball screw/nut linkage used to drive a cable, the advantages would be as follows: well-documented and mastered electric engine control; reversible/transparent actuator, providing good perception of external forces from motor current, as well as good efficiency; use of a cable, providing flexibility that softens contact with the environment and providing an interface for estimating external forces (by measuring cable deflection); and the footprint is similar to a human muscle (exoskeletons and biomimetic systems). The disadvantages proposed by this author would be flexibility introduced by the cable, complicating the control of the system and reducing its bandwidth, and the presence of complex physical phenomena to identify and control.

For all that, these criteria need to be refined. We have chosen a single example from Abba (2012), related to the possible selection of engines for robotics.

Figure 1.18 shows that this selection based on efficiency and weight criteria is quite difficult to consider if it must interfere with the others presented above.

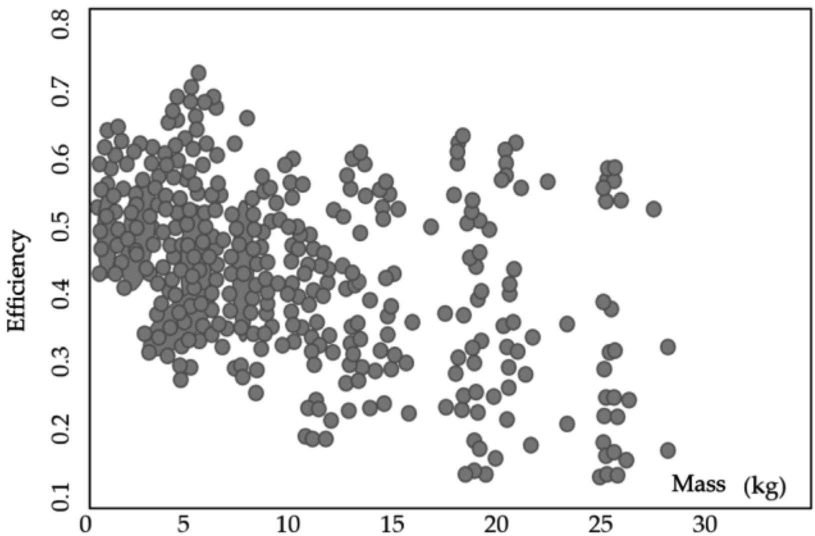


Figure 1.18. *Relation between efficiency and weight of a motorization in robotics (knees)*

1.3. Actuators and 4D printing

> Power establishes an asymmetrical relationship between the one or those who command and the one or those who obey. If it is not reduced to domination, the power relationship can engender a consent to obedience, but also the possibility of disobedience, the impatience of freedom, the horizon of insubordination. (Spector 2018)

NAP (2019b) reminds us that "soft matter" (Modes and Warner 2016; Nagel 2017; Smalyukh 2018) can be described as a material with low or zero elastic modulus and that this parameter can govern the ability of a material to resist deformation. This domain concerns polymers, colloids, foams, emulsions, etc. It corresponds to a mesoscopic scale (intermediate between the atomic and millimeter scales). The energies taken into consideration are adapted to easily accessible energy inputs, energies involved in 4D printing. NAP (2019b) also writes:

> Soft matter is often highly dissipative, disordered, entropy-dominated, far from equilibrium, and characterized by strong nonlinear and slow

> dynamic responses. Although these properties have been extensively studied over the past decades, our understanding of them is still incomplete.

In fact, independently of 4D printing, this field is growing rapidly and it seems wise to follow the current developments to consider profitable applications for the manufacturing field.

1.3.1. *General framework*

> To produce something new, one must certainly "doubt…". But also to be able to "doubt…", that is to say, to accept, at least temporarily, a badly supported, fragile and provisional knowledge. Beyond doubt, it is the risk of thought that we must assume. (Lévy-Leblond 2020)

In order to extend the application domain of the actuators presented in the previous section to 4D printing and then to partially unknown, dynamic or anthropogenic environments, the same or better, increased physical interaction capabilities are required. In this context, meeting the safety, robustness and versatility requirements of new 4D devices is a challenge.

If we had limited this book to homogeneous 4D printing, this volume of published information could have been greatly reduced by the addition of an essential discriminating criterion, that of "printability" (this will be mentioned later in this chapter). On the other hand, with heterogeneous 4D printing strategies, it is possible to introduce elements into a 4D device that are not necessarily realized by 3D printing (but with elements that are effectively mechanically linked together to constitute the object). For all that, we did not wish to widen the presentation too much by essentially limiting ourselves to the energetic material-stimulation relationships. Table 1.2 presents some works that may be of interest for combining additive manufacturing and actuators.

4D printing allows for the addition of active and reactive features in response to various external stimuli. The SMPs, which by selective absorption of light can produce a mechanical action, will often be mentioned (Hingoran et al. 2019; Zhang et al. 2019; Jeong et al. 2020). If, in principle, 4D printing can enable the fabrication of objects with complex geometries, the fine control of deformations with predefined responses is not yet optimal. We will later show that this difficulty is not unique to SMPs.

Energy	Subject and commentary	References	3D
Mechanical	Self-assembly of silk Pneumatic effects in elastomers	Elletro 2015 Di Natali et al. 2020; Lee and Bhattacharya 2021	N ?
Mechanical	Actuators made of SMA wires combined with a return element Valves Energy storage	Morellon 2010 Pal et al. 2020; Qian et al. 2020; Sweet et al. 2020	?
Mechanical	Haptic devices and electroactive actuators	Biet 2007; Kaneto 2016	N
Acoustic	Polymers	Adam et al. 2021	Y
Mechanical engineering	Transfer in metamaterials; origami	Mukhopadhyay et al. 2020; Novelino et al. 2020; Vangelatos et al. 2020	Y
Fluid mechanics	Reduction of drag in flows	Onal et al. 2017; Ott 2020	?
Piezoelectricity	Microsystems	Cueff 2011	N
Electro-activity; electrothermics	Polymers; hydrogels	Choi et al. 2020 Garces and Ayranci 2020	? Y
Electric field	Ionic polymers	Carrico et al. 2019; Narayan et al. 2021; Tyagi et al. 2021	?
Various	Micro-actuators	Bréguet 1998; Vermes and Czigany 2020	?
Various	Electro-activity and flexible fluidics	Lambert et al. 2016	Y
Magnetic	Deformation under magnetic field; nanoparticles	Whip 2016; Song et al. 2020; Zhang et al. 2021e	?
Electromechanical	MEMS	Li et al. 2020b	
Magneto-mechanical	Nanoparticles Elastomers	Glock et al. 2015; Golovin et al. 2015 Sindersberger et al. 2018; Zhang et al. 2019; Mirvakili et al. 2020	N ?

Di-electricity	Active polymers	Chortos et al. 2019	N
Chemistry	Chemical reaction producing a change in phase, volume, etc.	Suzumori et al. 2013	?
Chemistry; color change	Color change associated with the chemical environment	Lu et al. 2020; Nie et al. 2021	?
Chemistry: pH	Oriented polymers	Sarikaya et al. 2021	Y
Heat, photons	Heat and/or light sensitive materials; SMAs	Ge 2019; Du et al. 2020; Lee et al. 2020	?
Thermal effect	Deformation of organized liquid crystal structures	Zhang et al. 2020b	Y
Thermomechanics	Bilames	Cao et al. 2010; Baran et al. 2017	?
Photochemical effect	Molecular rotor	Bhatti et al. 2020; Kuenstler et al. 2020; Lan et al. 2020; Li et al. 2020a; Lu et al. 2020	?
Microwave	Liquid crystals	Wang et al. 2020d	?
Moisture; water	Absorption/desorption inducing volume change	Le Duigou 2017; Dai et al. 2020; Li et al. 2020a; Zhao et al. 2020; Piotrowska et al. 2021	?
Biology	Bio-printing	Nie and Takeuchi 2020	Y
Electricity	Dielectric muscles	Haghiashtiani et al. 2018; Qiu et al. 2019; Ghosh and Basu 2021	?
Autonomy	Autonomous chemical reactor	Hu et al. 2020	Y

Table 1.2. *Examples of energy transformers (Y: publications that consider the use of 3D printing; N: do not consider it; ? do not mention it)*

What this table shows is that in a top-down approach going from the main market (actuators) to the 4D aspect, the scientific field shows a weak interest in this last area, which remains quite confidential. Nevertheless, we find the classical effects presented in section 1.1 with originalities associated with active materials with stimulations presented in Figure 1.19 (Rastogi et al. 2019).

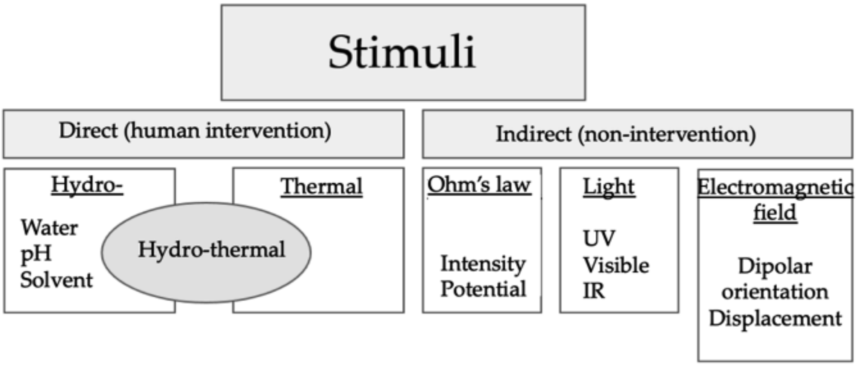


Figure 1.19. *Main stimulation modes in 4D printing*

For reasons associated with the resolution and/or the limited number of voxels, most authors have turned to the use of a transformable material to manufacture a polymer sensitive to a stimulus (heat, solvent, humidity, pH, light, mechanical, electromagnetic field, etc.) via an additive manufacturing process. Therefore, for the most part, there are classic additive manufacturing processes with so-called intelligent, active, informed or programmable materials. The underlying idea is to start from a given geometry so that it becomes a shape corresponding to an application through energy input. By playing on the spatial and amplitude distribution of a form of this energy (of these energies), there would also be the possibility of having an adaptive system like an actuator, a flexible robot, a structure evolving in time and perhaps in its functionalities (André 2017; Frenzel et al. 2017; Zarek et al. 2017; Kuang et al. 2019; Lehn 2002).

1.3.2. *Specificities linked to the manufacturing process*

> There are still dead generations that make prudish books […], books about the day, about hobbies, about travel. But not books that embed themselves in thought and speak about the black mourning of all life, the commonplace of all thought. (Duras 1993)

In the field of 4D printing, the main criterion is in the material itself, with processes that must "follow" to achieve the desired objective. We have recalled throughout this book one of the interests of additive manufacturing, which is that deposits of different materials located in the space constituting the 4D object are enabled. However, as shown in Figure 1.20, if at least two materials are used, several active associations can be retained (Du Plessis et al. 2021). Obviously, these structures have an effect on the behavior of 4D objects.

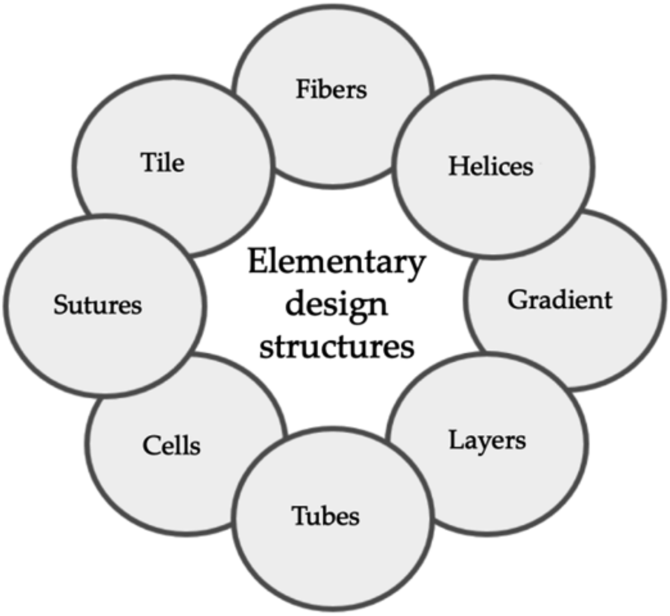


Figure 1.20. *Possible arrangements of multi-materials*

Natural structures are generally based on a limited number of repetitive structural design elements (Naleway et al. 2015), such as fibrous, helical, gradient, layered, tubular, cellular, sutured and tile. These structural design units are present in nature and can be used in 4D design, in connection with the search for the best performance (e.g. carbon fibers, already used for material reinforcement (Ahmed et al. 2020)). Helical structures improve fracture toughness by inducing curved crack paths. Cellular structures, tube, suture and tile designs can also improve performance (Du Plessis et al. 2021). What this figure basically shows is that the active component can be embedded in a supporting material, from a molecular homogeneity step to associations between objects of different natures and functionalities. One serves to support the action carried out by the other element. The "passive" component (effector) must have specific criteria in terms of weight, mechanical properties, etc. This is where metamaterials come into their own.

1.3.2.1. *Metamaterials*

> Design is a problem-solving activity without a fixed, directly applicable procedure. (Malhotra et al. 1980)

Metamaterials have origins dating back to the early 19th century (Veselago and Narimanov 2006). They are fabricated structures that can mimic the responses of known materials or possess new ones, some of which do not exist in nature (Engheta and Ziolkowski 2006). In particular, these organizations may have properties that are weakly related to the characteristics of their chemical constituents, but rather to the shapes given to these metamaterials (Liu and Zhang 2011). According to Saunders (2020), the origins of these organizations stem from the theoretical work of Veselago (1968) and later Pendry (2000) and Smith et al. (2000). Shelby et al. (2001) are said to have been the first to create such arrangements and demonstrate an interesting property such as a negative refractive index.

Furthermore, metamaterials have been developed and used for multiple purposes in many fields: morphing of aircraft structures, internal prostheses of implants, comfort of shoes and linings of helmets and cribs to reduce the risk of brain trauma in case of impact, etc. These new classes of metamaterials can be manufactured by additive manufacturing. At present, these materials are not stimulable (but this is being considered and is sometimes practiced) and can be used as effectors (Bristol University 2021).

Buckling, once considered the "ultimate" design failure, has been exploited in recent years to develop mechanical metamaterials with advanced features to create 3D structures with exploitable properties in 4D printing (Janbaz et al. 2019). The structural complexity of metamaterials is in principle unlimited, but most designs include periodic architectures that lead to materials with spatially homogeneous characteristics (Cui et al. 2010, 2014; Buriak et al. 2016; Coulais et al. 2016; Krödel et al. 2017; Jayashankar et al. 2019).

1.3.2.1.1. Metamaterials and their properties (based primarily on Kadic et al. 2019)

> The provincial cities, quietly sitting on their heritage, are not often associated with audacity and willingly leave the effervescence of feverish creations and polemics to the capitals. This fixed representation of a cultural life where everything that moves and sometimes disturbs is necessarily concentrated in a single extreme of free creativity, corresponding to the place in which powers and wealth are concentrated, is a very French fact. (Francfort 2007)

– Metamaterials are rationally designed composites, made up of custom-made building blocks, with average properties superior to those of their constituents.

– Metamaterials can be designed by computers (to avoid tedious trial and error procedures and excessive experimentation).

– Additive manufacturing can advantageously be used to physically create complex shapes.

– Although many 1D and 2D model architectures have been considered due to their ease of manufacture and reduced design complexity, the potential of the metamaterial concept is fully open to 3D microstructures and nanostructures.

– For Salari-Sharif et al. (2018), it is possible to combine the stiffness of metals or ceramics with the damping capabilities of rubber (damping properties).

– In electromagnetism and optics, they have remarkable properties (diamagnetism, paramagnetism up to optical frequencies, impedance matching, negative refractive indices, maximum electromagnetic chirality, perfect optical absorption, non-reciprocal propagation of electromagnetic waves without static magnetic fields, etc.).

– In acoustics and mechanics, they have full flexibility in elastic parameter matching, chiral mechanical behavior, sign reversal of effective static compressibility, negative dynamic mass density, non-reciprocal sound propagation, perfect broadband sound absorption at the fundamental limit imposed by causality and highly nonlinear, multi-stable and programmable properties of linear elastic constituents (see Dubourg (2015)).

– Thermal conductance is highly anisotropic, such as sign reversal of absolute mobility and Hall coefficient, highly anisotropic Hall tensors, giant magnetoresistances and thermoelectric power factors that are increased by an order of magnitude.

– 3D printers could enable thousands of different metamaterial properties from a small number of input materials.

Therefore, it is not only mechanical and actuation properties that can be of interest to researchers invested in 4D printing, since many functionalities can be envisaged. The emerging areas presented above constitute a roadmap for future research on metamaterials. In particular, extending the study of the mechanical behavior of metamaterials to the nonlinear range of deformations and to flexible metamaterials should receive attention in the next few years, as well as developing the manufacture of metamaterials containing active materials, such as those used in homogeneous 4D printing. Many possible designs of nonlinear flexible meta-materials yet to be discovered could present opportunities for novel applications using, in particular, additive manufacturing.

Figures 1.21 (Ion et al. 2016, 2018a, 2018b; Novak et al. 2016) and 1.22 (Kamru et al. 2020) illustrate on these bases, the possibility of realizing flexible structures that can be set in motion using external mechanical actuators. These structures can be made using additive manufacturing. The example in Figure 1.22 corresponds to a microstructure prevalent in the literature: originally realized in 1982 by Gibson and Ashby, according to Azoti (2012), in a 2D model, this simple shape is based on the hexagonal geometry of a conventional honeycomb structure. By defining an angular parameter, it is possible to reverse the orientation of the edges or struts of the geometry and thus define a "reentrant" geometry. Thus, contrary to the homogeneous 4D printing, we use wire structures or foams (and not a material in volume) with external actuations (let us recall however that the materials must be flexible to consider the deformation, but can only be inert).

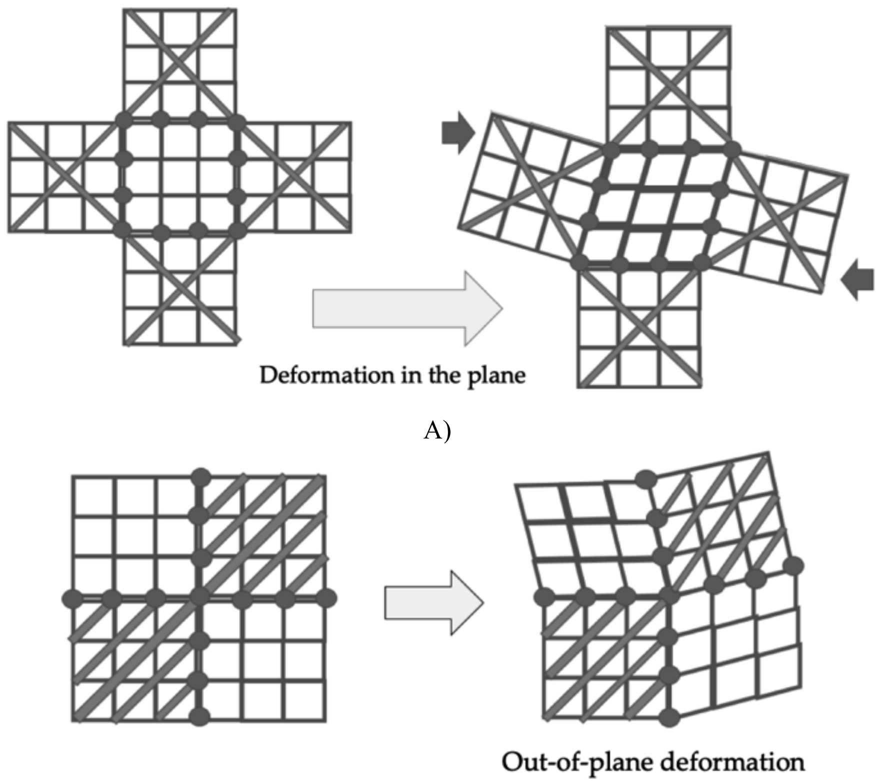


Figure 1.21. *Deformation of heterogeneous structures under the action of an external force (the red disks correspond to the attachment points between the different structures: A: planar deformation; B: spatial deformation from a planar structure)*

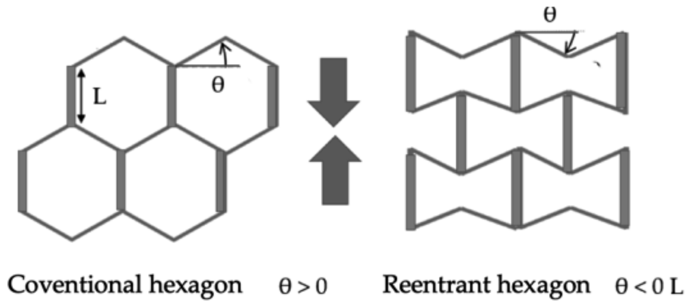
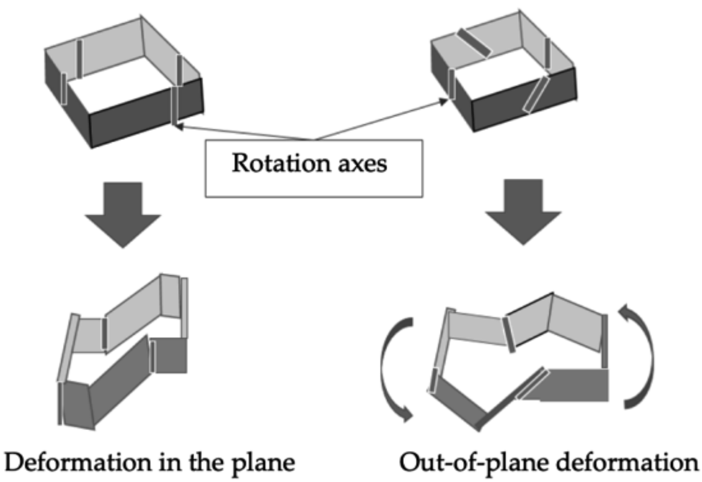
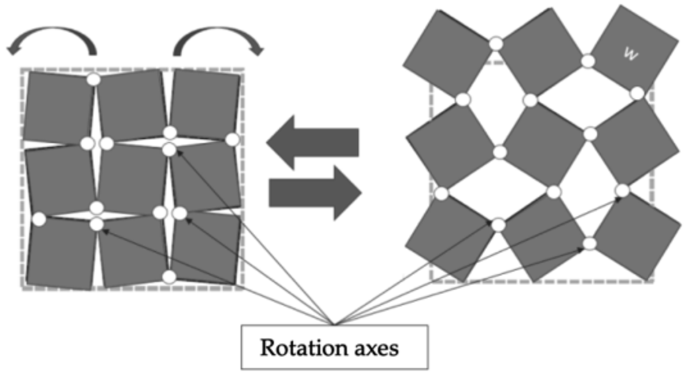


Figure 1.22. *Reentrant structure*

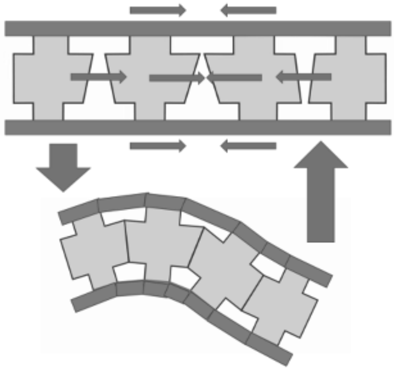
Other deformations can be considered, as shown in Figures 1.23 (Novak et al. 2016) and 1.24 (Kolken and Zadpoor 2017). The renewed interest in metamaterials is, in fact, associated with recent advances in additive manufacturing that allow for the manufacture of objects with complex nano/micro-architecture, potentially covering different spatial scales. Due to their rationally designed architecture, mechanical metamaterials exhibit unusual properties at the macro scale. These properties could be utilized for the development of materials with advanced functionalities, with applications in soft robotics (Jin et al. 2018), biomedicine, soft electronics, acoustic masking, etc. (Kolken and Zadpoor 2017).



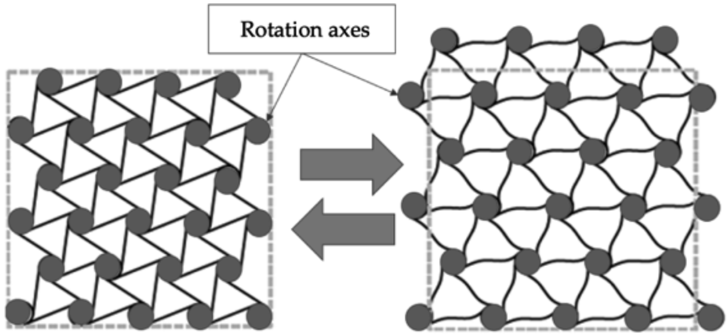
A)



B)



C)



D)

Figure 1.23. *Other examples of deformation: A): Multi-material system with a flexible joint; B): Flexible relationship between blocks; C): Bi-material (active, inert) system; D): Deformation of a chiral structure*

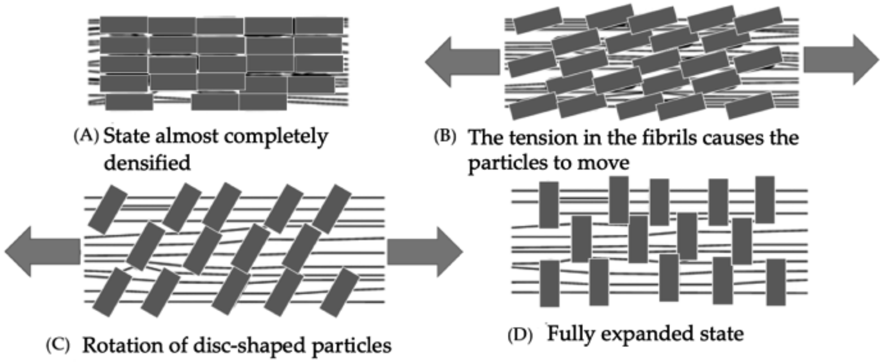


Figure 1.24. *Structural changes observed in a microporous PTFE (Poly-Tetra-Fluoro-Ethylene) foam subjected to tensile loading in the horizontal direction: A) Almost fully densified state; B) Tension in the fibrils causes displacement of the particles; C) Rotation of the particles into a disk shape (side view): D) Fully expanded state*

However, it should be remembered that such a structurally complex implementation can lead to geometric frustration (whereby local constraints cannot be satisfied everywhere), which can prevent coherent operation and consequently hinder the desired functionality. Regardless of this aspect, the literature abounds with 2D and 3D lattice structures. The interested reader can advantageously consult the following references: Bodaghi et al. (2017b), Martinez et al. (2017, 2018), Liu et al. (2018a, 2018c), Alison et al. (2019), Kadic et al. (2019), Yang et al. (2019), Callens et al. (2019), Wu et al. (2019) and Wang et al. (2020).

The shapes given to these metamaterials can be very complex (which is an area of excellence of additive manufacturing). In general, the mechanical properties of the metamaterials are programmed and fixed during the design and fabrication of the architecture, and do not change with changing environmental conditions or application requirements. However, according to Li et al. (2020c), while materials are of great research interest due to unusual mechanical responses and a wide range of deployment possibilities in plane and space, the cellular structure and nature of the constituent elements of materials that deform in bending or rotation generally still have relatively low stiffness. For these authors, this situation limits their applications when high stiffness, strength, hardness and energy absorption are desired simultaneously. They propose the use of auxiliary reticular structures as reinforcements, combining them with almost incompressible flexible materials to produce high-performance composites. However, in reality, as shown in Figure 1.25, since one does not seek to have a material suitable for additive and active manufacturing simultaneously, it is possible to cover a very wide range of densities and mechanical properties (Zadpoor 2016). But the debate remains open.

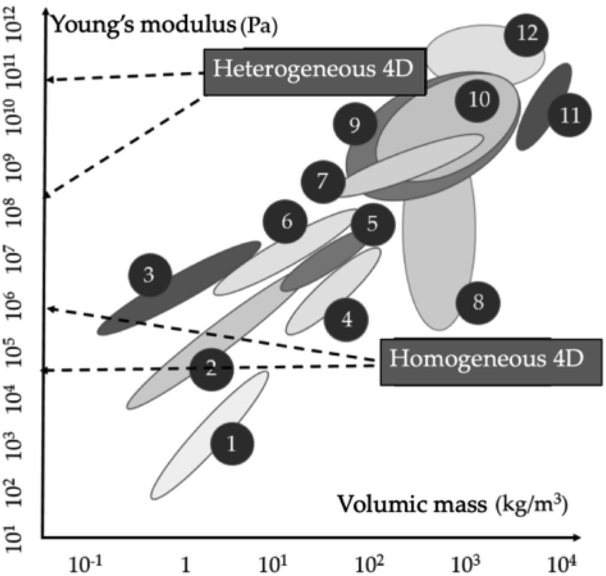


Figure 1.25. *Different ultralight and ultrarigid metamaterials using various types of repeating unit cells (see also Zheng et al. (2014)) – 1: graphene-containing elastomers; 2: ultralight metal micro-meshes; 3: hollow alumina-based lattices; 4: foams containing carbon nano-tubes; 5: acrylic foam; 6: solid acrylic; 7: solid alumina; 8: elastomers; 9: solid composite materials; 10: metals; 11: "hard" metal alloys; 12: industrial ceramics*

However, additive manufacturing technologies always play on an optimization between a precision or a resolution on the one hand and an object realization time on the other hand. On this observation, the definition of different metamaterial scales is limited. Yildizdag et al. (2019) recall that multiscale architectures are designed to achieve the desired macroscopic behavior by activating interactions between different length scales and coupling different physical mechanisms. Research perspectives are discussed by these authors in order to determine the most efficient methodology needed to design new metamaterials that optimally meet a functional specification. However, the number of spatial scales exploited is still modest.

Several examples of metamaterial structures can be found in the literature (Masters and Evans 1996; Schumacher et al. 2015; Jiang and Wang 2016; Boydston et al. 2018; Chen et al. 2018; Golaszewski et al. 2018; Ion et al. 2018a, 2018b; Jackson et al. 2018; Jiang et al. 2018; Mirzaali et al. 2018; Alison et al. 2019; Beli et al. 2019; Bodaghi and Liao 2019; Kadic et al. 2019; Lei et al. 2019; Yuan et al. 2019; Vangelatos et al. 2019; Zhao et al. 2019; Jing et al. 2020; Manna et al. 2020; Naify et al. 2020; Rafsanjani et al. 2020; Tao et al. 2020). Based on the examples presented in this list of publications, there is, as can be seen, a solid foundation for moving forward.

1.3.2.1.2. Auxiliary materials (meta-materials)

> The error committed by the scientist is the product of the haste of his desire, which decides to undertake an action when his understanding has not yet sufficiently weighed the parties involved. (Willmann 2010)

Lattice structures have specific geometric characteristics reported to have a negative Poisson's ratio (auxetic metamaterial), that is stretching induces expansion in the transverse direction, as illustrated in Figure 1.26 (Lim 2015; Saxena et al. 2016; Lei et al. 2019). Materials and structures with a negative Poisson's ratio obviously exhibit counterintuitive behavior (Ren et al. 2018).

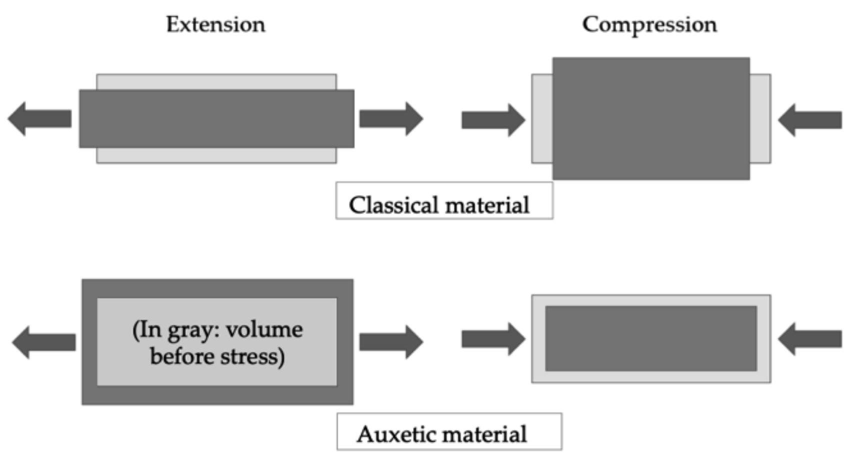


Figure 1.26. *Differences in the behavior of conventional and auxetic materials*

The Poisson's ratio ν is one of two mechanical properties used in the description of elastic and isotropic behavior of solid materials following the small strain approximation (Goldstein et al. 2009). In the case of tensile/compression mechanical tests, ν is defined by the negative ratio of transverse strain to axial strain. Its effect is of fundamental importance in the behavior of materials so that a variation in its value leads to significant changes in mechanical performance. In the case of isotropic materials, the value of ν is defined according to thermodynamic restrictions such as $-1 < \nu < 0.5$. Most materials have a positive ν coefficient. Therefore, these materials deform by a contracted or thinned cross-section when they are longitudinally stressed.

By analyzing the deformation mechanism associated with auxetic behavior, it is possible to show that the macroscopic behavior results from a structure-related effect due to a network of architectural or periodic reinforcements. Foams remain the preferred domain of auxetic materials (Lakes 1987). Thermoplastic (polyester, urethane), thermosetting (rubber, silicone) and metallic (copper) foams have been reported by Friis et al. (1988) as auxetic. It is found that, in all cases, the value of the Poisson's ratio varies with strain, and values approaching the –1 limit for isotropic materials have been reported in polymeric and metallic foams (Choi and Lakes 1992). As a result of this work, it has been possible to design stiffer materials for a wider range of applications. For example, in 1989, Caddock and Evans discovered a form of microporous PTFE (Poly-Tetra-Fluoro-Ethylene) foam exhibiting strongly anisotropic and strain-dependent behavior, such that a Poisson's ratio value as low as –12 was observed in one direction.

1.3.2.1.3. Voronoi diagrams and 4D printing

> The forms are passive insofar as they represent the actuality; they become active when they are organized in relation to the bottom, thus bringing the previous virtualities to the actuality. (Simondon 1997)

In mathematics, a Voronoi diagram or Dirichlet tessellation is a tessellation of the plane into cells (adjacent regions) from a discrete set of points called "seeds". Each cell encloses a single seed, and forms the set of points in the plane that are closer to this seed than to any other. The cell represents, as it were, the seed's "zone of influence". As shown in Figure 1.27, to generate a Voronoi diagram, only certain medians are used and not others: sites that are too far away are not taken into consideration; then the useful segments form a triangulation or partition of the plane known as the Delaunay diagram. In mechanics, a Delaunay triangulation structure is considered to minimize the squares of the areas of the triangles. Counting the outer boundaries, each site is inside a convex polygon. All points in this polygon are closer to the inner point than to all other points. This is an irregular honeycomb pattern. Voronoi diagrams can use more complex distance rules (power Voronoi network) (Delaunay 1934; Preparata and Shamos 1985; Okabe et al. 1992; Aurenhammer and Klein 2000; Baert 2003; Wormser 2008; Boissonnat 2010; Mitchell et al. 2018).

One design route is to spatially distribute materials with different properties within lattice structures to achieve desired mechanical properties. Advanced multi-material 3D printing techniques allow for the design and fabrication of multi-material cellular structures for which the elastic modulus and Poisson's ratio can be independently tuned in different directions (anisotropic) (Mirzaali et al. 2018). Seed distribution for additive manufacturing can be achieved by random Monte Carlo firing methods that allow for spatial coverage. In addition, it is possible to define the oriented probabilities of the variable density type (case A in Figure 1.28) or preferred orientations in Figure 1.28 (case B).

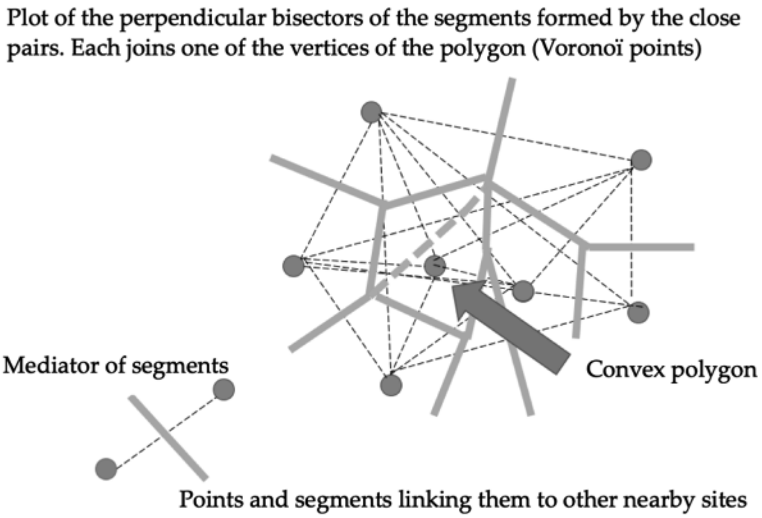


Figure 1.27. *Basics of Voronoi diagram construction*

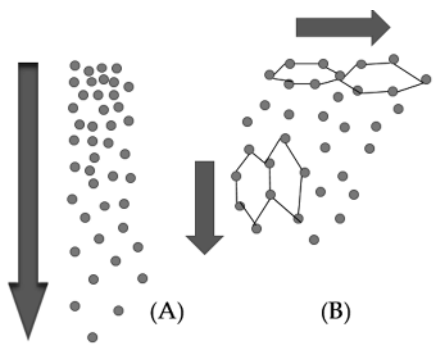


Figure 1.28. *Seed space coverage produced by random firing: A: variable density; B: variable orientation*

Lee et al. (2018) used Voronoi diagrams for tessellation applied to additive manufacturing. But, to the authors' knowledge, it is mainly Sylvain Lefebvre's team at INRIA (Martinez et al. 2018; Ray et al. 2018; Bedel et al. 2021) that has applied this type of scanning to the realization of deformable objects. Figure 1.29 represents some examples from this team, illustrating the possibility of creating structures, optimized relative to the desired effect, inhomogeneous of metamaterials with specific spatial functionalities.

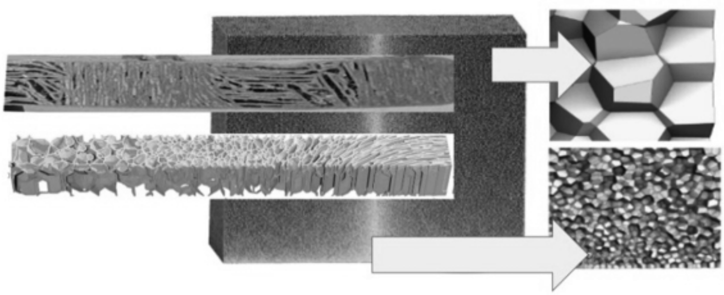


Figure 1.29. *Non-periodic metamaterials with optimized spatial functionality*

Figure 1.30, taken from Martinez et al. (2017) from the same team, using the hand as a mechanical actuator, illustrates the potential of auxetic foams shaped from Voronoi diagrams using 3D printing.

Figure 1.30. *“4D heterogeneous” application of auxetic systems*

Publications envision the use of additive manufacturing technologies to create auxetic structures (Schaffner et al. 2018; Bodaghi and Liao 2019; Kanu et al. 2019; Sadeqi et al. 2019; Rafiee et al. 2020). Recall that recent advances in multi-material 3D and 4D printing should be able to be further exploited to extend the design space beyond the now conventional geometries of metamaterials. It is then conceivable to combine different materials and various additive manufacturing technologies to create multifunctional objects that better meet application needs (with, for example, multi-scale and multi-material structures; see Liu et al. (2021b)). Apart from the possibility of incorporating multiple materials, it is envisaged by Zheng et al. (2016) to realize fractal structures of meta-materials. In their publication, they use seven scale changes, ranging from tens of nanometers to tens of centimeters. As a result, these micro- and nano-array materials can support more than 16,000 times their own weight and exhibit a quasi-linear scaling between the structure's density and its Young's modulus. In addition, the aspect ratio is increased.

Zadpoor (2016) reports that fatigue behavior studies of mechanical metamaterials have focused on static, quasi-static or specific types of dynamic behaviors of mechanical metamaterials. In the real situation of structural use of mechanical metamaterials, fatigue behavior studies should be conducted.

Box 1.5. *Functional fatigue*

1.3.2.1.4. Modeling of deformations

> Withdraw into yourself and look. And if you do not find yourself beautiful yet, act as does the creator of a statue that is to be made beautiful: he cuts away here, he smoothes there, he makes this line lighter, this other purer, until a lovely face has grown upon his work. So do you also: cut away all that is excessive, straighten all that is crooked, bring light to all that is overcast, labour to make all one glow of beauty and never cease chiselling your statue (Plotinus 2017)

Each structure and material combination leads to unique structural properties such as stiffness, Poisson's ratio and overall elasticity. The ideal input or bypass force distribution mechanism could be suggested for the design of guards using different shapes, thicknesses and auxiliary materials to reduce the risk of damage (Yang et al. 2018). Related to homogeneous 4D printing, there is the possibility of modeling displacements as a function of actuation amplitude and directivity (Weeger et al. 2019; Liu et al. 2020c; Weeger 2021).

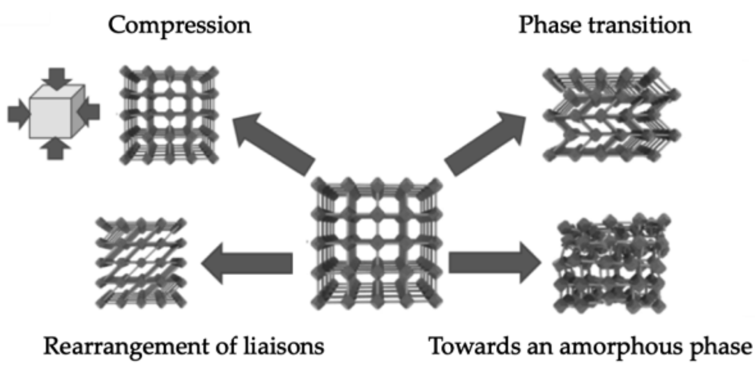


Figure 1.31. *Possible degradation of metamaterials under mechanical stress*

However, as it has already been specified, these deformations must remain within a linear behavior, in any case reversible. In the case of metal-organic material systems, Troyano et al. (2021) remind us (see Figure 1.31) of the possible irreversible fate of metamaterial structures, depending on the nature (and the amplitude) of the solicitation.

1.3.2.1.5. Some applications of metamaterials

Increasingly, metamaterials are associated in the literature with additive manufacturing and, in particular, with 4D printing. Table 1.3 gathers some recent references concerning these particular structures and applications.

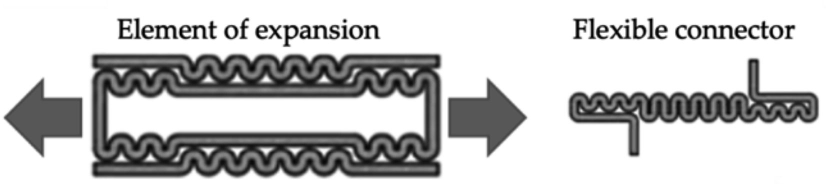


Figure 1.32. *Reconfigurable connector for medical applications*

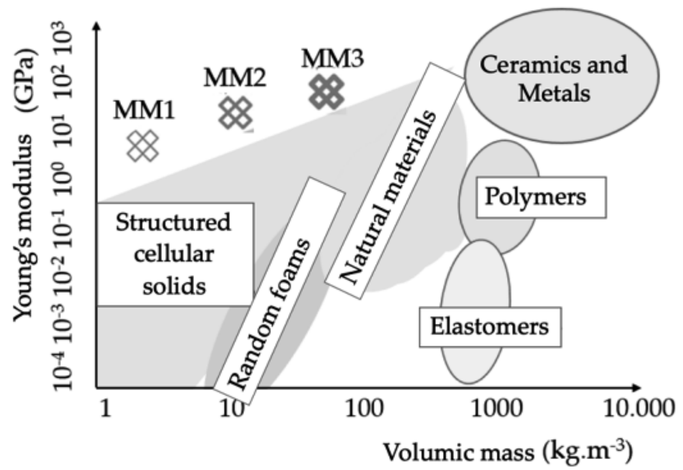


Figure 1.33. *Relationships between the form of metamaterials and mechanical performance (Metamaterials – MM1: density 0.001; MM2: density 0.01; MM3: density 0.1)*

Nature of the deformation	Comments	References
Reconfigurable connector	Stents (see Figure 1.32) Smart-robot (5 axes) Smart-sensor	Van Manen et al. 2021 Kim et al. 2019b; Zhang et al. 2021b Zhu et al. 2020
Active structure	Origami; kirigami; electromagnetic propulsion Ferromagnetic structures Electroactive polymers	Mousanezhad et al. 2017; Ning et al. 2018; Zhao and Kim 2019; Jin et al. 2020; Novelino et al. 2020; Chung et al. 2021; Guo et al. 2021; Li and Yin 2021; Ma et al. 2021; Zhang et al. 2021a Kim et al. 2018 Tyagi et al. 2021
Relationship between form and performance	Young's modulus (see Figure 1.33) Hierarchical architecture Compression-torsion Tensegrity Different configurations	Jenett 2020 Coulais et al. 2016; Ronellenfitsch et al. 2019; Surjadi et al. 2019 Wang and Liu 2020; Zhong et al. 2020; Goswami et al. 2021 Yin et al. 2020 Meng et al. 2020; Yang et al. 2020
Porous structures	Graphene-based structures	Zhang et al. 2018
Tunable performance	Shape memory polymers	Tao et al. 2020
Deformation and shape	Damping of acoustic waves, vibrations	Rocklin et al. 2017; Liu et al. 2020b; Wang et al. 2020; Xue et al. 2020
Pneumatics	Auxiliary structures	Zunker and Gonella 2021
Materials	Different organic materials Organometallic	Kuang et al. 2020 Hu et al. 2017b
Viscoelasticity	Viscoelastic materials	Dykstra et al. 2019

Table 1.3. *Metamaterials and applications*

1.3.2.2. *Notion of "printability"*

> I am convinced that half of what separates successful entrepreneurs from the non-successul ones is pure perseverance. (Jobs 2011)

Additive manufacturing enables complex parts that are true to their design to be manufactured in a single step. It aims to eliminate the need to assemble multiple components, train a new workforce or set up new equipment, while minimizing manufacturing time, wasted materials and energy. The available "library" of printable materials and the range of properties represented is growing, but needs to be expanded – for example, to include materials that have a variety of electrical and thermal conductivities, or that swell when they absorb a solvent, etc. (Overvelde 2019). But, even if at the beginning, the materials that are going to be used for the manufacture of a 4D object are compatible with each other, after their deposition or placement that is associated with an energy input, there is nothing to say that their behavior maintains cohesion between voxels of different origins – how then do we perform "tenacious" solidarizations (hence the interest or risk of working with heterogeneous 4D printing)? In the past, it was possible to use mechanical means such as rivets, weaving, felting, interlocking, glues and cements. We can push "open doors" with resins of the same family for 3D work using stereolithography (Katri et al. 2020), but there are very serious issues associated with this notion: problems related to the manufacturing process, the thicknesses involved with their internal tensions (Altenhofen et al. 2018), and also to the physico-chemical and mechanical interactions between the voxels. However, the consultation of craftsmen and industrialists in the trade reveals constants in the bonding operations: preparation of the surfaces to be assembled to promote the closeness between elements to be connected, using the largest possible contact surface (Wang et al. 2021b), playing as much as possible on the wettability of the adhesive so that it can spread in the area to be bonded, exploitation of the surface condition to promote adhesion (see Figure 1.34).

This technology has a weakness related to the bonding of the layers formed during the printing process. Gojzewski et al. (2020) defined a mapping of the contact Young's modulus across the layered structure with sub-micrometer resolution. They observed local depressions with values up to 30% of the maximum stiffness at the interface between consecutively deposited layers, indicating a local depletion of the macromolecular cross-linking density. Even with a single base material, differences in mechanical coefficients may exist, which may (or may not) favor voxel-to-voxel bonding and, consequently, printability…

Box 1.6. *Stereolithography*

For Freund et al. (2019), the factors influencing the interface strength between different materials are not well understood, so this complexity is rarely utilized, which hinders innovation. A systematic approach to identifying and quantifying the adhesion phenomena that influence interface strength is a necessary step if one wishes to move beyond proofs of concept. For this reason, these authors propose experiments adapted to certain lines of action, such as roller peel tests and peel strength of rigid and flexible materials. Polarity, mechanical locking and surface roughness associated with the design of 4D structures have a great influence on the interface strength of multi-material parts manufactured by extrusion (FFF technique). In this example, criteria that mainly affect the interface strength are deduced and design recommendations for creating functional parts with mismatched material combinations can be formulated.

In the case of bonding, direct adhesion between materials occurs rarely, only when the materials to be joined have completely smooth and clean surfaces that allow intimate contact between the materials at a very small distance. It is therefore not possible between two materials with rough surfaces since the contact area is greatly reduced. The use of a glue (or adhesive), applied between the two materials, will therefore allow the creation of a film that will ensure an intermediate and intimate contact between the two surfaces to be joined (see Figure 1.34 inspired by ISPA (2015)). Amorphous polymers present a structure without any particular arrangement. The chains of molecules are intermingled in a disordered manner. They are characterized by a glass transition temperature *Tg*. Above the *Tg*, the energy is high enough for the molecular chains to become disordered. In this case, the cooling conditions have no influence on the mechanical characteristics of the material. The processing can therefore be done more easily compared to semi-crystalline polymers. Amorphous polymers have weaker mechanical properties than semi-crystalline ones. The reinforcing fibers, of which the most used in the traditional materials are glass, carbon and aramid fibers, have a role of optimizing the properties, especially mechanical, of the material (but also of surface). The choice of the reinforcement is made according to the application and the required characteristics.

> On a practical level, positivism makes the programming of science assured, but horizontal: when an idea is truly new, one usually only has the most confused lights as to the means by which one may even conceive of verification by experiment. (D'Espagnat 2015)

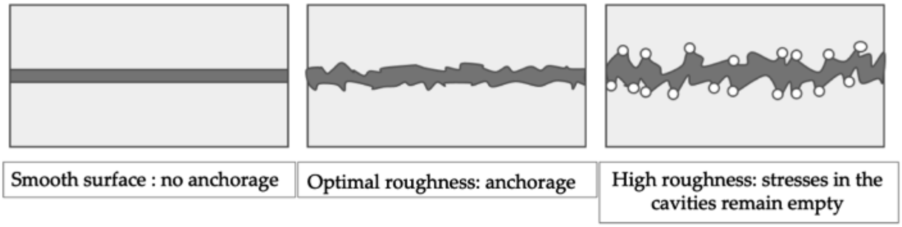


Figure 1.34. *Roughness and mechanical adhesion*

Alternatively, flexible composite 4D actuators can be manufactured by embedding SMA wires or fibers in flexible polymer matrices (Akbaria et al. 2021). This manufacturing method can be complex as it involves multi-material printing. Several solutions can be considered: deposition of a soft elastomeric layer on a more rigid layer of SMP, homogeneous or not (see Rodrigue et al. (2017)). Depending on the temperature, deformations of greater or lesser amplitudes can be achieved as preferred axes of action. If nonlinear finite element models can be used to predict the deformation of these actuators, nothing is said about the behavior in time of this type of hybrid actuator. Normally, a good adhesion between the passive and active elements is expected. However, if the expansion coefficients are very different (bimetal effect), nothing says that the two materials will keep a sufficient cohesion over time. This situation is even more critical when the two materials do not adhere to each other. It is in these conditions that the notion of "printability" can be introduced.

In the heterogeneous manufacturing processes discussed, we can have voxels of "reasonable" size that can be connected to each other by mechanical means (Demoly and André 2021b). However, this situation of classical (improved) mechanics no longer makes sense with voxels of sub-millimeter size and it is then necessary to examine whether the usable multi-materials are compatible with each other for fabrication and whether they will have a high number of actuations. Indeed, tensions between passive and active elements (which are responsible for the desired deformation) can lead to micro-fractures during use, which can be amplified during the loading/unloading time and cause the 4D performance to drop or even disappear.

Thus, this notion, which is not found in the work corresponding to "simple" actuators, seems here to be a primordial criterion in the definition of a good 4D actuator. One of the possible reasons is the small number of "multi-material" 3D machines (see Thomas (2021)).

Antoine Le Duigou (2019) reports on the advantage of using natural fibers such as those from flax, which he likens to nano-structured composites with very interesting mechanical properties for 4D applications. Flax fibers are composed of cellulose, hemicellulose and lignin for the most part. After suitable treatments, the moisture-active properties can be measured and lead to spectacular 4D demonstrations. Other natural fibers have similar properties (coconut, banana, wood, etc.).

Box 1.7. *Natural fibers*

1.3.2.2.1. Multi-material 3D machines

> When we are not in the grip of a theory, we are all capable of juggling multiple contextual, practical and semantic resources, according to the

> demands of situations, and we are not seized with dismay at the idea that these situations may matter to others in a different mode. On the contrary, it interests us, it enters our ruminations and activates our imaginations. (Stengers 2020)

Rafiee et al. (2020) point out that a limited number of 3D machines are suitable for using multiple materials (see their tables of commercially available multi-material 3D printers and their specifications for polymers and biomaterials). They present known results in a synthesis linking materials and processes without introducing adhesion criteria between voxels from different materials. However, at the end of their paper, they conclude with the following general points:

– Topological optimization can be used to propose new complex geometries that are easier to manufacture by 3D printing than by any other process. Although considerable progress has been made with multi-material 3D and 4D printing, the potential has not yet been fully explored.

– The mechanical performance of parts made by multi-material additive manufacturing is generally better than that of parts printed by single-material printing. The formation of voids between successive layers of printed parts can affect their mechanical performance due to a decrease in interfacial bonding between the printed layers. Different mechanical behavior under vertical tension or compression compared to that of the horizontal direction is another common challenge of 3D printing processes.

– The efficiency of the production of parts can be an area of research to explore with the mastery of post-processing methods adapted to the use of several materials.

– Most commercial multi-material 3D printers create parts from voxels of the same size. However, obviously, for a certain functionality and, in particular, mechanical strength (Young's modulus, elasticity), different sizes may be required.

– Future processes could tailor the microstructure properties of a 4D printed part to create more complex geometric transformations by strategically controlling the density and directionality of the deposited stimulus-sensitive materials. They can also improve the inter-material bonding of heterogeneous smart compositions, and even ignore active or non-active material properties.

In these senses, the development of multi-material 4D printing can be the object of decisive integrative research to accelerate the growth of the smart materials sector dedicated to this field. It is not just about serendipitous encounters or process modification (Muguruza et al. 2017; Toursangsaraki 2018).

1.3.2.2.2. Elements of "printability"

> Better to be Socrates dissatisfied than a fool satisfied. (Mill 1988)

> If you judge a fish on its ability to climb a tree, it will spend its life thinking it is stupid. (Vervisch 2020)

A literature review on this topic was conducted: out of more than 170,000 references on additive manufacturing, between 30 and 50 articles mention this problem without one or more generic paths being formulated. Obviously, the youth of 4D printing technology has not allowed this type of hindsight to generate all the hypotheses, validate them and propose practical solutions to designers (see, however, Mao and Anand (2018) and Ni et al. (2020)). Table 1.4 gathers the collected elements.

Elements of "printability"	Materials	References
Inter-diffusion between different voxels	Hydrogels	He et al. 2016
Shear effects	General framework	Peng et al. 2021
Polymer blend	Long and short chains	Zhang et al. 2021c
Linear polymers	Long chains	Zhang et al. 2020a
Surface condition	Interfaces between voxels	Freund et al. 2019
Bi-materials (improved electrical properties)	CNT and graphene polybutylene terephthalate (PBT) nano-composites	Gnanasekaran et al. 2017
Control of phase transitions	Liquid crystal elastomers (LCEs)	Saed et al. 2019
Temperature effects	Cracking of stressed polymers	Baek et al. 2021
3D CFD (Computational Fluid Dynamics) modeling	Liquid-liquid system	Urhal et al. 2020
Shear strength and thixotropic properties	Elastomer with magnetic field dependent rheology	Bastola et al. 2018
Damping effect	Foams	Montgomery et al. 2021
Viscosity and surface tension	UV resin loaded with metallic nanoparticles	Saleh et al. 2017
Collage	Binding between voxels	Frascio et al. 2020
The process itself	Metals and non-metals	Wang and Liu 2014
"Sandwich" structures	Various extruded polymers	Moises et al. 2020
Intermediate binder	Coated fibers	Bodkhe et al. 2020; Liu and Wei 2021
Fiber orientation Surface tension	Fiber filled polymers	Ma et al. 2019; Mantelli et al. 2019

Prioritization of deposits Time between layers	Polymers Cement	Teoh et al. 2017; Scalet 2020; Weng et al. 2021
Extrusion mode	Polymers	Baca and Ahmad 2020
Debinding and sintering	Metals, ceramics and polymers	Gonzalez-Gutierrez et al. 2018
Subtractive-additive coupling	Robotics	Mostafavi et al. 2019
Self-organization	General framework	Demoly and André 2021
Wave propagation	Crystals in a polymer matrix	Zhang and Wu 2021
Accession	Hydrogels	Li et al. 2021
Interfacial cohesion	Filaments	Lopes et al. 2018; Fernandez et al. 2019
Cohesion	Tensile tests	Kluczyński et al. 2021

Table 1.4. *Some elements collected on the "printability" aspect*

> Professionals are suspicious of amateurs. They are wrong. The latter get it wrong with less method. (Lemire 2015)

The exceptional abilities of geckos to adhere to various surfaces are largely credited to the large actual contact areas of the fibrillar and hierarchical structures of their feet. These special features regulate the essential structural compliance for each attachment and thus provide robust but reversible adhesions (Wang et al. 2013). Figure 1.35 (taken from Wang et al. (2019b)) illustrates the principle of such a system. It can be a torsional (Kang et al. 2017) or shear (Wang et al. 2013) detachment process.

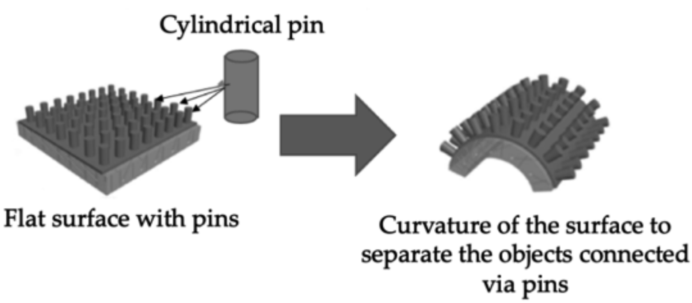


Figure 1.35. *Mechanical adhesion and de-adhesion*

Other methods have also been tested to change the adhesion values: temperature in Xu et al. (2018) and a magnetic field in Li et al. (2018). These biomimetic materials can therefore play an adhesion role and by different treatments see their bonding power transformed for the disassembly of the 3D object's constituent elements, an advantage relative to the case of using polymer adhesives and the maintenance of the adhesion material on the building blocks.

The adhesion of an interface could be activated and deactivated by the sole interaction between hydrophilic functional groups, introduced by surface oxidation, and the native AlO_{23} oxide on the aluminum surface (Khongtong and Ferguson 2004). This interaction also acts as a driving force (enthalpy) to stretch the chains to increase the entropy of the system, with functional groups being pulled away from the elastomer/aluminum interface, resulting in the weakening of adhesion. The basic science is developed in the paper, but practical solutions are not reached. The search for a follow-up to this work was not successful.

In the absence of cyclic processes, according to Zhang et al. (2020a), the use of inelastic dissipators often achieves strong adhesion (see Yang et al. (2019)). Good fatigue-resistant adhesion is proposed by Zhang et al. (2020a) using a particularly simple type of elastic heatsink consisting of long-chain polymers. Each polymer chain remains elastic before it breaks. When a single covalent bond in the chain breaks, the elastic energy stored in the entire chain dissipates, amplifying the adhesion energy by the number of links in the chain. They obtain adhesion and fatigue threshold energies that can reach 1,400 J/m^2 and 300 J/m^2, respectively. This fatigue threshold would be linearly proportional to the square root of the chain length, in agreement with the Lake and Thomas (1967) model. This fatigue resistant design could be advantageously extended to the association of voxels of different origins as long as a suitable 3D process is available.

Freund et al. (2019) proposed a set of criteria to consider when thinking about the adhesion of voxels to each other. This set, building on the work of Awaja et al. (2009) and Mohamed et al. (2015) is the subject of Figure 1.36 (see also Nguyen et al. (2018), Alief et al. (2019) and Ando et al. (2021)). These are elements that will need to be examined on a case-by-case basis in combination with others yet to be considered.

On the other hand, Zhao et al. (2021) used hydrogels, composed of non-covalently cross-linking 3D polymer networks and water. The fatigue behavior of these conventional materials in 4D printing was studied. With poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAA) gels with weak hydrogen bonding (called weak gels) and PVA/PAA-LiCl gels with strong hydrogen bonding (strong gels), they show that for fatigue damage of uncut samples, the weak and strong gels are amplified by fatigue for small deformations (rearrangement of the hydrogen bonds induced by stretching), but with fatigue damage effects in case of large deformations by the sliding of the polymeric chains, one over the other. For the fatigue failure of pre-cut samples, the weak and strong gels do not present any measurable fatigue threshold for these authors, but the strong gel can attenuate the growth of cracks. These results reveal that intrinsically weak non-covalent bonds cannot effectively increase the fatigue strength of physical hydrogels. More generally, Zhou et al. (2021) have practically investigated the effect of stresses on materials on fracture mechanisms. Zhang et al. (2015c) and Bai et al. (2019) had, on the other hand, studied the same phenomena of elastomeric materials splitting under stress.

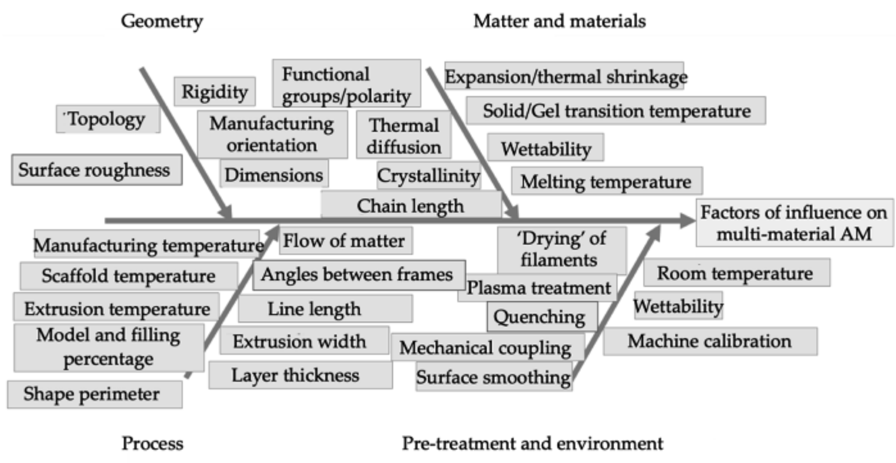


Figure 1.36. *Fishbone diagram of factors of influence concerning the interface strength of multi-material voxels*

Regardless of these more or less predictable, but disparate aspects, Melanie (2020) reports that optimization involves a printability analysis corresponding to the evaluation of the part before printing. The AMFG enterprise reportedly includes a feature in its software package that ensures that a part to be manufactured is truly suitable for 3D printing, whether in terms of stability, shape or resilience.

1.3.2.2.3. 4D printing and functionality

Throughout this book, we have been talking about the form and functionality given to a material that must be thought of as a complex but structured system. However, a further analysis of the literature shows very few references where the active material (apart from materials dissolved in printable media) is concerned with anything other than changes in form. However, Table 1.5 gives some examples of changes in functionality.

Change in functionality	References
Electromagnetic properties	Wu et al. 2020
Piezoelectricity	Nkomo 2018; Tang et al. 2021
Nanotechnology, color	Zhang et al. 2021
4D and power supply	Teng et al. 2021
Temperature sensitive color	Chen et al. 2021a

Table 1.5. *4D printing and feature changes*

1.3.2.2.4. A return to aspects of self-organization

> The truly good and wise man will bear all kinds of fortune in a seemly way, and will always act in the noblest manner that the circumstances allow. (Aristotle 2012)

An intentional artifact (related to the work of the engineer and/or designer) can be considered as a means of linking an "internal" environment, the substance, functioning and organization of the object itself, and an external environment, the surroundings in which it is implemented. If the two environments are in a compatible situation, the artifact meets the specifications. As Simon (2004) pointed out in another framework, knowledge of an artifact such as a machine:

> has an advantage over knowledge of nature, because it is based on valid prior foundations, the purposes of which will be deviated from with a certain amount of intentional novelty to give the projects intelligibility and openings to society.

This can be true for 4D printing of single-materials, we have just shown that it is not quite the same for associations of materials.

The term "self-organization" refers to the spontaneous/stimulated formation of a dynamic nature leading to forms of organization resulting from a set of homogeneous or non-interacting units. Self-organization results from large-scale structures based on microscopic chaotic motions and small-scale random fluctuations (Lebedev 2012). After placing energy in the right place at the right time in a given environment, the initial system under stress organizes itself to achieve a form, if possible sought by the experimenter (Moreno 2004). From a thermodynamic point of view, this "shaping" supposes that the transport of matter and energy between the system undergoing transformation is functionally constrained in the absence of external energy input. As the object changes, there is an appearance of causality (universal laws of physics), which can be represented by a kind of selection between several possible alternatives (Campbell 1974).

Thermodynamics describes the change of a system from an initial state to a final equilibrium state, without taking into account the transitions. In fact, it is the path and "distance" of the system from its final equilibrium that generates and maintains the structural complexity found in living organisms and sought to be replicated with "non-living" matter (Monteiro 2018). Dissipative structures are processes in which a fluctuation stabilizes to form a dynamic macroscopic configuration enabled by the flow of energy through the system under construction. These macroscopic structures require a continuous supply of energy of an amplitude adapted to its coherence:

> The term "self"-organization implies a spontaneous creation of order or organization rather than an agential identity capable of determining or constituting itself in a sense that implies functional plasticity. (Alvaro 2004)

It is basically to respect this comment by Bruter (Le Moigne 1994), who wrote: "The events shape with the time the object, it is above all to have pierced the secrets of its history, of the lineage of which it is, at the same time, the result and a projection".

> Even if, by some extraordinary chance, you were to stumble upon her, how would you know it was her, since you have never known her? (Socrates 2021)

> Order is only a random special case of disorder. (Schiffter 2019)

In Demoly and André (2021), we considered the possibilities of local manipulation of matter by different forms of energy, with this matter being activatable with the ultimate goal of realizing 3D shapes meeting industrial requirements. This field of "morphogenetic engineering", according to Doursat et al. (2013):

> explores the design, implementation, and control (directly, through programming, and/or indirectly, through learning or evolution) of complex system agents capable of autonomously and reproducibly giving rise to large, heterogeneous architectures that will support a desired set of functionalities, without depending on central planning or external control.

Indeed, it is necessary to control the parameters presented in Figure 1.37 in order to achieve an operating efficiency that enables the precise realization of a 3D object.

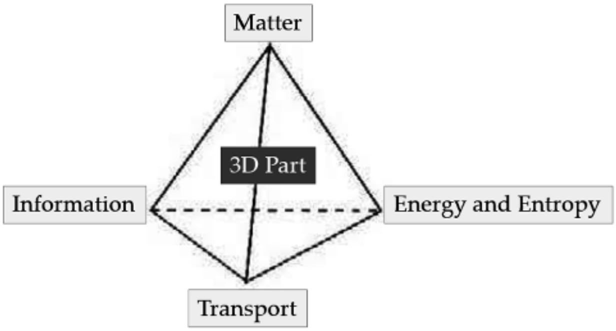


Figure 1.37. *Influence of self-organization parameters on additive manufacturing*

For those who study the intrusion of temporal and functional aspects in additive manufacturing, systems have been fully determined for a long time. But, as "self-organized" phenomena, they can become sensitive, far from equilibrium, to factors considered negligible near equilibrium. It is the intrinsic activity of the increasingly complex system, with its increasingly nonlinear behavior, that would determine how it is possible to describe its relationship with the environment, and that would generate the type of intelligibility that would be relevant for understanding its possible histories. In this chapter, it was not only a field of application with its constraints, but also a theoretical field to be attacked in order to solve the equation finality/means to achieve it in a robust way. However, the inability to master the inverse problems associated with the aspects of morphogenesis presented in this reflection could (should?) have closed the debate. There is no realistic solution today for the realization of precise 3D objects by self-organization, starting from a certain disorder to reach a desired order!

> Self-organization brought the idea that a stable and reproducible form can be the product of a balance of local rules and randomness. These are collective phenomena, since they are irreducible to one or more elements taken in isolation. (Petitgirard 2014)

On the other hand, in the situation considered here, we are trying to explain losses in performance that could originate from an order-disorder transition following a stimulation (which, obviously, is in line with the evolution of the entropy of a system). What we recalled is that in the case of systems with several degrees of freedom, not all attractors are equal: some aim for greater stability, others for greater growth potential. However, the dynamics involved do not necessarily lead to the most stable state: the system that follows the fastest path may reach local areas of stability. It is then possible that a certain reversibility of the processes is at work: the actuator does its job! But, after a certain number of actuations, this path will generally end with a global minimum of potential, and not with the local minimum (see Figure 1.38).

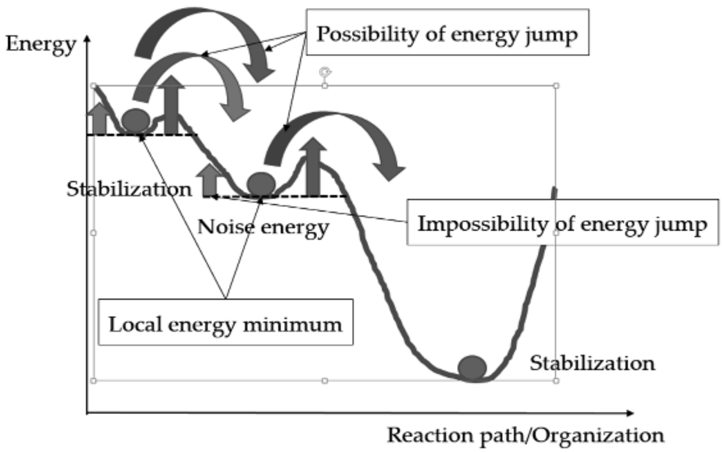


Figure 1.38. *Considered energy degradation processes*

> When some change occurs in nature, the quantity of action necessary for this change is the smallest possible. (Moreau de Maupertuis, cited in Lemire (2015))

One way to get the system out of a local minimum is to add a degree of indeterminacy to the dynamics, that is to give the system the possibility to make transitions to states other than the one that is the most "adapted" locally. It is at this level that the concept of "printability" takes on its full importance by preventing this degradation. This can be seen as preventing the injection of "noise" or random disturbances into the system, allowing new trajectories. In physics, this is usually the effect of external disturbances (e.g. vibrations or shocks in the system) or intrinsic indeterminacy (e.g. thermal or quantum fluctuations, or simply unknown factors that have not been incorporated into the state description).

The deeper the "valley" representing free energy, the harder it will be for a disturbance to move a system out of that valley. Therefore, noise will generally move the system out of the shallower valleys and into the deeper valleys (a form of determinism). However, a system subjected to noise will never really settle into a local or global minimum, because no matter what energy level it reaches, it can always be perturbed with the risk of reaching more energetic metastable states. The actuator will be unstable and probably of modest interest!

By considering polymers of different chain lengths (as found, for example, in natural rubber), Gros (2016) considers both the thermodynamics and the inhomogeneous entangled characters of the polymeric network. Polymeric chains orient and crystallize as the system deforms under stimulation (in this case mechanical or thermal). Crystallization under stress would occur from successive states of matter whose characteristics and threshold extensions of crystallization and melting depend on the initial chain length distribution. A scenario for the evolution of the chain network organization, with varying degrees of cross-linking, involves the critical and entanglement molar masses and the stress rate. Qualitatively, it is possible to go from an unstressed state to a deformed state, but the return to the initial situation is never total (hence the fatigue problems).

These broadly outlined elements can serve as an explanatory basis for undesired phenomena. But, for the practitioner, it is necessary to go further than this global explanation which can make people understand, but not solve problems which are likely to be critical in the near future.

1.3.2.2.5. Fatigue and return to equilibrium of high entropy materials: aging

> Top-down logic is not made to enrich knowledge and adapt it, but on the contrary to tighten and reduce it. Once the premises have been established, there is always one solution and one solution only, and this solution is imposed in the name of one principle and one principle only: consistency. At the end of the decision-making chain, the executors are then considered as a burden: they impede the limpid formal beauty of the process put in place. (Crozier and Tillette 2000)

In the spirit of what has been presented above, it is for example possible to deposit fibers of different materials included in oriented polymers in a shear field, as shown in Figure 1.39. The order parameter of these materials can then approach unity. The classical stimulation is the use of moisture to evolve the fibers in their medium (see Wang et al. (2018, 2020), Le Duigou et al. (2019, 2020a, 2020b), Zou et al. (2020), Armstrong et al. (2020), Cohades and Michaud (2020), Balla et al. (2020), Bernard et al. (2021) and Cera et al. (2021)). But, after several round trips, we can imagine that the fibers will slowly return to a more thermodynamically stable configuration, thus with an order parameter approaching zero. This phenomenon is probably associated with the creation of fractures/cracks in the support material… (Liu and Moran 2021). Internal shear occurs when the fibers slide over each other during deformation. To maximize strength and avoid failure through this creep process, the longest possible fibers with the highest realistic load density would probably be appropriate (NAP 2019a). Thus, 4D properties are likely a function of the number of cycles they are cycled through, without much citation of this in the literature, which is still in its infancy.

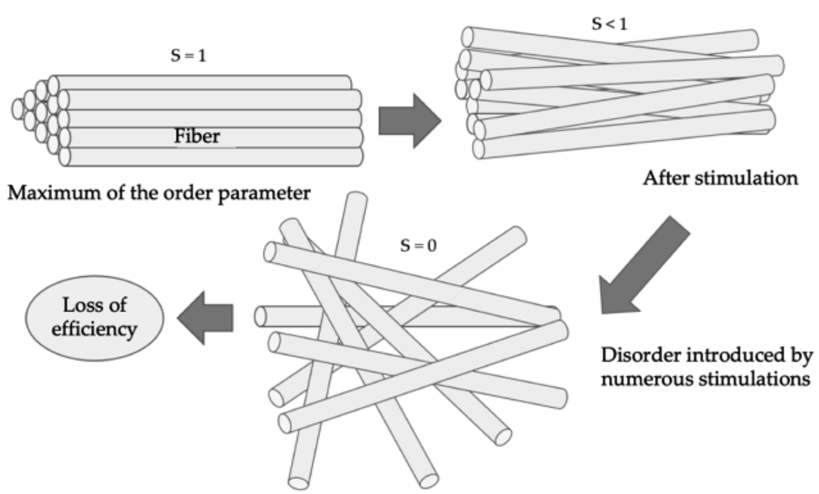


Figure 1.39. *Degradation of the 4D properties of fibers induced by the degradation of the S order parameter during use*

Zorzetto and Ruffoni (2019) remind us that helical fibers can form building blocks (already used by nature). These materials arranged in multiple layers lead to biological structures with good and durable mechanical properties. With synthetic structures combining fibers and fibrils, they show that the fracture strength can be improved if fibrils are oriented perpendicular to the applied load.

1.3.2.2.6. A hybrid “printable” 4D printing

> The numerical discretization of all movements in individualization makes it possible to sum, process, calculate, and model them by producing categorical attractors. (Stiegler 2004)

Sertoglu (2021) reports a recent process of depositing in a given shape a layer of a filler, possibly consisting of fibers, with a high filler density on a flat surface. In a second step, a liquid resin is deposited on the entire object under construction. What is not mentioned by this author is that this material has good activation properties by energy stimuli. A layer of charge is then deposited, etc. The difference with what is found in the scientific literature is that we “work backwards”, the charged areas constitute passive structures (because the charges present prevent any local deformation, while accepting global deformations), the areas without charges constitute the active areas. Moreover, it is possible to have free zones without elastomeric material, loaded or not. The principle of this 4D construction is shown in Figure 1.40.

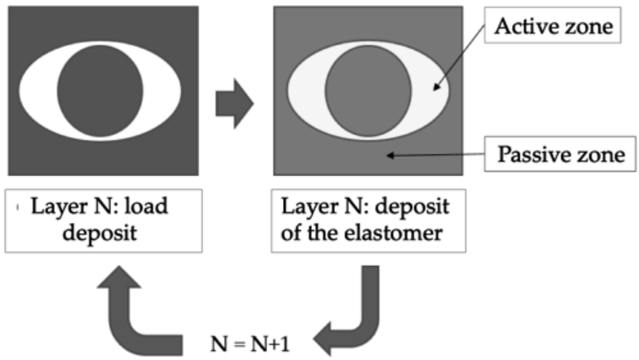


Figure 1.40. *4D "reverse" hybrid with passive loads*

1.3.2.2.7. A study path

Moore et al. (2020) proposed a stereolithography method to realize assemblies made of different materials. This technology, among others, can be exploited to realize composite prints allowing studies of aging, either under mechanical stimulation or under specific stimulation associated with at least one of the materials. This practical work has interest for real applications.

1.4. Stimulations of matter

> Culture concerns objects and is a phenomenon of the world; leisure concerns people and is a phenomenon of life […]. Culture is threatened when all objects and things in the world, whether produced by the present or by the past, are treated as pure functions of the vital process of society, as if they were only there to satisfy some need. (Arendt 1989)

We have tried to progress in this chapter from classical actuators to effectors, leaving behind the central question of energy-matter interactions which must manage the temporal evolutions of 4D objects in terms of form or functionality. We must be consistent with the title of the chapter: "Getting things moving"! However, these physical, physico-chemical and/or chemical interactions have already been approached, without being studied in depth. They will be only partially explored, so vast is this domain that they could constitute a whole library.

Box 1.8. *Stimuli-materials interactions*

4D printing involves the use of “smart” materials with possible changes in form or functionality via additive manufacturing processes. Stimulus-sensitive materials, stimuli and characteristic times required for the transformation to occur are key research areas (Manikandan et al. 2021). This chapter focuses on the materials and methods used to make adaptive structures. We will not revisit the most common processes used, which are stereolithography (SLA), fused filament fabrication (FFF), material jetting, selective laser melting and direct ink writing (DIW) (see for example Bodaghi et al. (2017a)).

One of the first goals is to try to get out of this opposition between the morphology of an artificial structure desired by the designer, designed digitally in advance and manufactured from one step to the next (current case of additive manufacturing) and a system that can develop over time thanks to the interactions between the different parts made up of informed materials of the structure, which we know generally leads to forms that are weakly structured enough to allow for evolutions. But is it possible? However, engrossed in the certainties of their scientific paradigms, a number of researchers are constantly ploughing the same furrow. What the authors wanted to do in this article was to approach the way of thinking like a detective or explorer by examining (no doubt with great naivety) whether it is possible to discover exceptions to the accepted laws, to reach the limit of the accepted theories (Lévy-Leblond 2020).

1.4.1. *Programmable matter*

> Perhaps the simplest way to symbolize the permanent form of our life is as follows: it is determined by the pressure exerted on us by objects and circumstances, by nature and society, as well as by the reactions of our freedom, which abolish this pressure or allow themselves to be violated by it, fight it or avoid it […]. This is perhaps the major complication of our life: what limits its spontaneity and oppresses its free upward aspiration is at the same time the indispensable condition for this aspiration to action to reach a visible expression, a creative activity of form. (Simmel 1990)

Molecular motors whose movement is induced by external energy inputs constitute an archetype of what can be programmable matter. As early as the 1950s, Richard Feynman predicted the development of molecular nano-machines, such as those made by Jean-Pierre Sauvage in 1983 when he invented a chemical method allowing two molecules in the form of rings to be intertwined, thus forming a chain named catenane (Collin et al. 2001; CNRS 2016). Through electrical or light stimulation it has been widely shown that it is possible to drive the rotation of a molecule in a controlled manner, similar to an engine. We can therefore consider these examples as already representative of what could be the programmable matter, which has been the object of interest of researchers for only a few years, without it being possible to identify a trend (linear or exponential) in the growing number of publications associated with the keyword “*programmable matter*” (see Figure 1.41). The total number of publications provided by the CNRS database is in the order of 1,000 (which should be compared to the 150,000–200,000 concerning additive manufacturing).

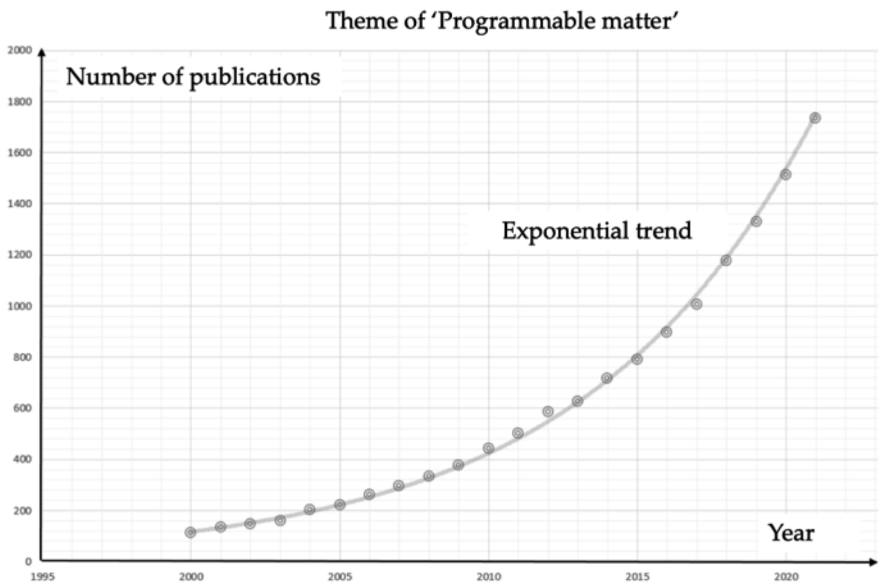


Figure 1.41. *Evolution of the number of publications under the theme of “programmable matter” (according to the CNRS database)*

By focusing on 4D printing, it seemed necessary to quickly examine this research field and then leave it to get closer to the concept of a connection between voxels, which effectively implies the notion of additivity. It is therefore necessary to have at least two molecules (or two voxels) in order to start talking about additive manufacturing. Indeed, the concept of programmable matter allows us to consider applications such as the remodeling of an object or to test different possibilities of actuation. According to Catry et al. (2020), this assembly can be realized in principle easily according to the needs of the designers. They propose several solutions based on self-reconfigurable modular robotics. A POC has been realized for a catome with links between voxels of electrostatic origin. However, if the shape is achieved, the mechanical strength of the realized structures can still be improved (see also Di Luna et al. (2017), Yue et al. (2018), Zakharov and Pismen (2019), Almethen et al. (2019), Yigit et al. (2019), Liu et al. (2020), Gastineau et al. (2020), Piranda and Bourgeois (2020), Qi et al. (2020), Dolev et al. (2020) and Yang et al. (2021b).

The basic principle is to associate elements, as shown in Figure 1.42 from Catry et al. (2020).

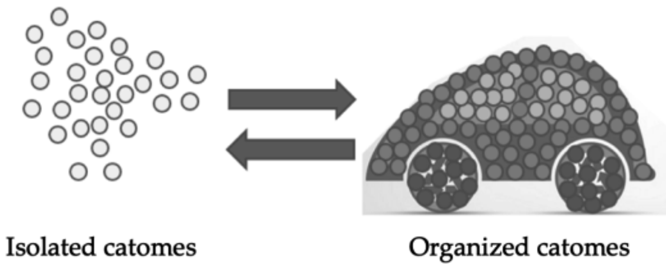


Figure 1.42. *Voxel after voxel association for realizing a possible evolving object*

1.4.1.1. *Starting from the material*

> Linking with others: "This question matters less for social endurance than for the partial interdependence between heterogeneous partners, the ontological choreography where each one needs not others in general, but some others, perhaps himself, where each time in his own mode, each one has to pass through others to accomplish himself". (Stengers 2020)

We have already mentioned Stéphane Leduc who, more than a century ago, wrote: "The elementary act of life is diffusion and osmosis" (see Thuillier (1980); see also Haudin et al. (2018)). The methods considered are often thought of as deterministic: the phenomena are controlled by laws, which must be discovered and applied as faithfully as possible. On this basis, it is possible to think that we will be able to control matter, in its most intimate elements, so that it transforms itself to achieve a given form and functionality. This is what was presented in the previous section.

Historically, DNA origami makes arbitrary shapes out of pieces of DNA. It was developed by Paul Rothemund, from Caltech, USA, in 2006. The chemical properties of the molecules that make up DNA, the nucleic bases, are well known. It is known that such and such a part binds to such and such another by "Watson–Crick" bonds, and from this principle, one can manage to model 2D or 3D structures. Rothemund's technique uses a long chain of DNA from a virus, with a linear and relatively uncomplicated structure, whose sequence is known exactly. Then, by computer, the precise places where the DNA molecule must be folded to arrive at the desired shape are located. We then synthesize small "pieces" that will link themselves exactly where we want them to, to "pin" the viral genome.

Only these "staples" need to be synthesized, the basic material being borrowed from nature, and the operations are therefore both less costly and less time consuming. These small staples will then, by the play of chemical bonds, cling to the scaffolding chain. Moreover, as these staples will also attract other molecules, they will bend the central DNA strand and give it a particular shape. It is from this folding that the original name DNA origami is derived. In Rothemund's publication (2006), images of variously shaped constructions that he made were presented. The most original are probably the world map, the snowflake and the smiling man. Of course, there are not only drawings that can be reproduced with DNA. Hao Yan's team has managed to create closed 3D shapes (Han et al. 2011; Sawyer 2011, and Figure 1.43).

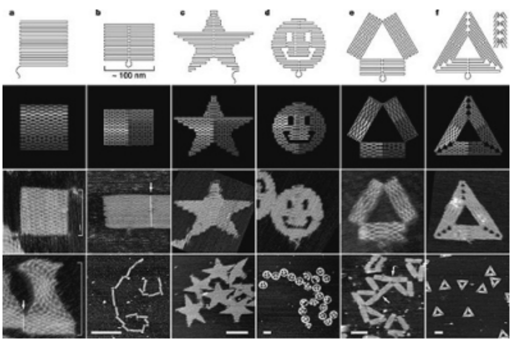


Figure 1.43. *DNA origami (nanometer size)*

Since then, nano-motors of a few nanometers (Dureuil 2013) with controlled direction of rotation have been developed:

> The rotor is made by five ferrocenes connected to a central phenyl, while a ruthenium in the center acts as a rotation axis. Finally, the whole assembly is lifted by three feet and tiols to grip the molecule to the surface. (Dureuil 2013)

These spectacular molecular machines are animated by movements under the action of an external stimulus (nano-motors, nano-elevators, nano-pins, nano-transporters). Their use, due to their extremely small size, raises the question of the energy input (stimulus) and its mechanical recovery. However, applications in drug delivery are currently being developed (Medina-Sanchez et al. 2018; Bandari et al. 2020). Other applications, shown in Figure 1.44, of these nanoscale entities are being considered by Julin et al. (2018), Woods et al. (2019) and Novotný et al. (2020).

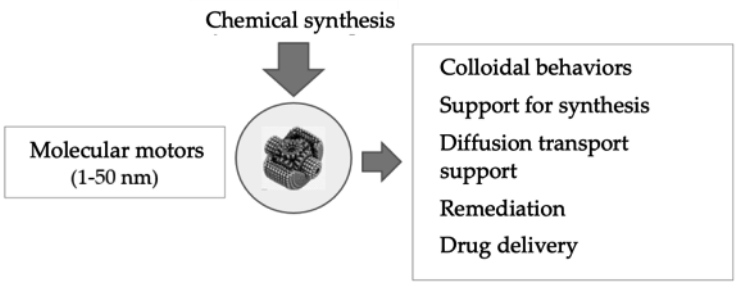


Figure 1.44. *Application areas of nano-machines*

Once science begins to understand how nature has selected certain forms and not others, both in the physical and biological worlds, it can seek to apply/transpose the corresponding mechanisms to solve engineering problems that are of interest in the manufacture of artifacts, tools or final objects. The wide variety of applications given to a generic form such as the manufacture of a functional object is not inspired by what nature does, and it is interesting to examine whether knowledge about “morphogenesis” can be used to achieve the desired form by (rather stimulated) self-organization (Baquiast 2004). As early as the 1950s, Richard Feynman predicted the development of nanomolecular machines, such as those of Jean-Pierre Sauvage, a recent Nobel Prize winner, who invented a chemical method to intertwine two ring-shaped molecules (called catenan). Figure 1.45, taken from Sauvage (2017), shows some examples of such systems.

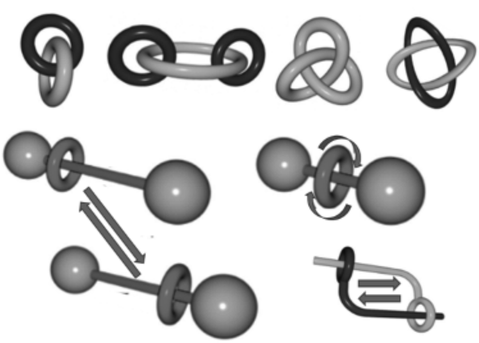


Figure 1.45. *Examples of molecular machines and their movements*

This is always a difficult problem in the case of linear systems which are generally ill-conditioned (see Mugnier (2008)), especially with noisy signals. This being the case, the stakes are high, as mastering the inverse problem can be an integral means of realizing an object from an easily realizable matrix whose deformation as a function of time or supplied energy could enable the realization of a complex-shaped object. Thus, according to Sussan (2011), it is now possible to create DNA Origami by computer. But it is already less satisfactory when we become interested in larger elements, since the number of chemical bonds to be considered increases with the power of three of the size (see, for example, Zentel (2020), Sanchez (2011) and Kotov (2017)). It does not yet seem possible to develop systems in which the object would be "entrusted" with a form of intentionality, thus, in the limit, leaving it the choice to look for what it needs to make itself, and thus pass self-organization with the selection of the necessary elements that it would extract from a "bank" for the construction of the final object.

However, these exciting aspects are still anecdotal (but more work needs to be done before we abandon this avenue). Another example is that of self-repairing cell growth, adapted to hydra, but not directly to humans. Turing (1952) showed how reactions between chemical substances coupled with a diffusion-reaction process of these substances could give rise to the appearance of specific structures or regularities (spots on a coat, shape of a shell, etc.). Will we ever be able to complete and experiment with his mathematical model of "reaction-diffusion equations" to create well-defined objects? The road does not exist yet, but… Besides, we have not, in Demoly and André (2021), found the right way!

Independently of this aspect linked to a spatial change induced by a stimulation, we find all the molecular chemistry which is largely out of the context of this work. However, and because the color change is mentioned in 4D applications, we have chosen to quickly present some photochemical reactions, including photochromic reactions. Photochromism corresponds to a reversible reaction of a chemical species between two forms, A and B, induced by light for the transition A -> B with a return B -> A, which can be photochemical or thermal. The transition between the two species can be manifested by various changes such as refractive index, solubility, viscosity, wettability of a surface or dielectric constants. This phenomenon can be observed in both organic and inorganic compounds (see, for example, Crano and Guglielmetti (1999), Dürr and Bouas-Laurent (2003), Irie et al. (2013) and Knyazhanskiy (2018)).

Moreover, nature, even if only via DNA or RNA knows how to dispose of information and is able to process it through chemical or biochemical pathways, within a reaction network (Dramé-Maigné et al. 2019). According to Ahmady (2017) "molecular computing" is defined as "the processing or storage of computer data using circuits or components made of living or non-living molecules, replacing traditional materials such as copper or silicon”. The idea is to use the properties of molecules: charge, structure, volume, polarity… to design new computing and storage models. Using these principles, it is in principle possible to:

> find a solution to a combinatorial search problem (using all combinations of molecules, and their hybridization, which realizes, in a way, a parallel computer), but it is also possible to create “logic gates” (“logic switches”, at the basis of computer science, such as AND, OR, XOR…) by relying on the links between DNA molecules. (VMF214 2017)

Many scientific studies explore the potential of molecular circuits to optimize modern technological tools. Examples of programming based on these principles have already been published (Pevzner 2010; Fujii and Rondelez 2013; Thubagere et al. 2017; Zadorin et al. 2017; Cherry and Qian 2018). Thus, with a small number of molecules or macromolecules in a network, these authors show the possibility of considering information processing through other routes than the current systems. If this field is clearly outside the authors’ competence, this vision fits perfectly into the “4D doctrine” and should be followed up (monitoring), and there should be joint reflections with information science specialists to increase the applicative potential of the field, which, moreover, could lead to a large gain in legitimacy.

1.4.1.2. *Starting from ordered voxels*

> Manufacturing differs from action in that it has a definite beginning and an end that can be fixed in advance. (Arendt 1989)

The current scientific context does not mean that the spontaneous complexity that was discussed above is abandoned, but that the engineer and/or designer is trying to regain control over autonomous phenomena that are difficult to control by accepting the manipulation of non-living matter and energy so that the initial forms adapt to their will. On the basis of KIS (“Keep It Simple”), publications either deal with deployable objects based on deformable origami, or with 3D objects containing matter that can be activated by different stimuli (pH, heat, light, electromagnetic field, etc.). We are therefore moving from a global approach to a more traditional methodology: creation of a 3D part using different methods, including additive manufacturing with active materials, followed by localized stimulation in space and time to change the 2D or 3D shape of an object.

1.4.1.2.1. Nanometric aspect

> A world transformed by the mind does not offer to the mind the same perspectives and the same directions as formerly; it imposes entirely new problems, innumerable enigmas. (Valery 1931)

More than 25 years ago, the advent of near-field microscopy changed the landscape of condensed matter research. Based on the detection of a signal from a short-range interaction between a fine probe (a tip) and the object of study (surface, nano-objects, etc.), these microscopies have not only enabled the observation of the nanoworld, but also permitted the nanostructuring of surfaces.

> Thus, in addition to their major role in surface physics and physicochemistry, these microscopies have become essential in many current research fields, such as molecular electronics, spintronics, superconductivity, nanostructure optics, nanoplasmonics, mesoscopic physics, etc. (INSP 2020; Tian et al. 2020)

But, for the most part, it is about moving atoms on the surface, rarely in volume.

1.4.1.2.2. Centimetric aspect

> Intellectual judgments are regulated by emotions, not dispassionate analysis, and the goal is to minimize threats to the "self". (Western et al. 2006)

It has just been shown that it is possible to chemically produce nanometric structures whose shape changes in the presence of a stimulus. But to reach centimetric dimensions, we can imagine the difficulty of chemically manufacturing a molecular or supramolecular assembly that would contain about 10^{22} atoms! So, it is possible to use elements of reasonable size that can be moved to achieve a given shape. These small robots are assembled and disassembled according to the programming that organizes their movements. This is how the cubes of Daniela Rus' team at MIT move to create real 3D structures, but still with a very limited number of voxels, as shown in Figure 1.46 (Gilpin et al. (2012); see also MIT (2019)).

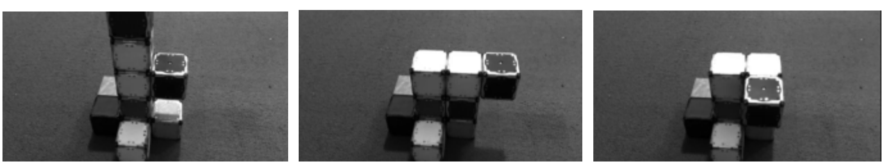


Figure 1.46. *Example of 4D printing using cubes (according to Sussan (2014))*

The technology for the programmed assembly of homogeneous or heterogeneous modular robots is still in the research stage (Fischer et al. 2014; Thomas et al. 2014; Bakarich et al. 2015; Bückmann et al. 2015; Crawford 2015; Li et al. 2015; Abtan 2019, etc.). Indeed, as soon as the number of robots increases, the programming of their movements must avoid collisions, while optimizing the travel times of each of the mobile entities (André 2017), whether for intra- or inter-reconfigurations (Tan et al. 2020).

1.4.1.3. *Origami*

> Evolution, it is said, calls for mutations that allow us to survive and adapt to a new environment, now described as unstable, complex, and uncertain, and in relation to which our societies are constantly accused of falling behind. (Stiegler 2019)

If it is interesting to examine how to use this knowledge on Turing's "morphogenesis" to reach the desired form by self-organization. The resolution of the inverse problem, applicable to the direct manufacturing of objects, remains to be done… (Demoly and André 2021). In this field where complexity reigns supreme, we return to the pillars from which we can advance: additive manufacturing, or even more simply, origami (see Tenzeris et al. (2016)). In the latter case, the folding areas are printed (in 2D) using an active material that will fold and unfold the origami, turning it into an externally activated robot (see Figure 1.47).

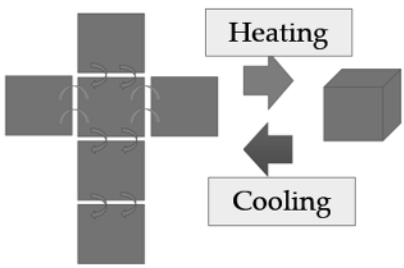


Figure 1.47. *Operating principle of a thermomechanical origami*

Recall that one of the advantages of additive manufacturing is that "complexity is free" (André 2017). So, the deposition of an active material that will promote the spatial transformation of an originally planar structure may not be homogeneous, thus orienting the deformation in privileged directions. To come back to 4D printing itself, the "simple" solution of the engineer can also consist of the use of an active mono- or multi-material assembly with an additive manufacturing medium associated with a system allowing the movement: SMA, external actuation by pressurized gas, stimulated boiling of a liquid included in the material matrix, etc. From an "esthetic" point of view, this is basically improved 3D (but it works, as shown by the experiments carried out over 30 years ago on shape memory actuators!). So, to achieve "exciting scientific 4D printing", you just need to involve at least one active material in the additive manufacturing process. Any 3D technology can be used as long as (1) the active material does not lose its properties during the fabrication process and (2) they have the ability to print multiple materials.

For example, researchers at MIT (Hardesty 2015) have produced a small robot prototype capable of amazing feats. Indeed, this machine is capable of adopting different shapes, moving, carrying loads… capabilities that hint at many future applications. Halfway between an origami and an actuator, this small robot is indeed capable of folding in on itself in order to adopt different shapes (Ranosa 2015). But this amazing contraption is also able to walk, swim and carry loads heavier than itself before self-destructing in acetone (see Figure 1.48). Other origami inspired systems have been published recently (see Schulz et al. (2017), Abtan (2019), Callens et al. (2019) and Liu et al. (2019)).

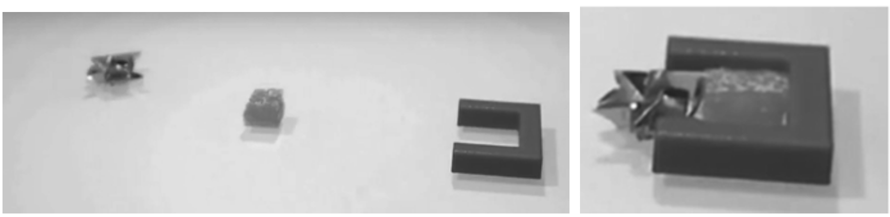


Figure 1.48. *Origami robot moving an object (from start to goal)*

> According to Hornyak (2019), robots without control by a CPU have been realized at MIT. The robots are connected by magnetic force and move by expanding or contracting. They use local measurement of light flux to decide when to start an expansion or contraction cycle, thus forcing the units to move in groups. This 2D extension can allow a “physical” simulation of the functioning of living cells.

Box 1.9. *Small robots*

1.4.2. *Materials for 4D printing*

> It seems to me, then, that knowledge is nothing else than the perception of the connection and propriety, or of the opposition and disconvenience which lies between two of our ideas. (Locke 2019)

Several methods can be selected in terms of reversible movements with different stimuli external to the 3D object (e.g. Sossou et al. (2019a, 2019b) and André (2017)):

– Polymers sensitive to moisture, heat: either the polymer absorbs water or loses it, its density changes with a possible shrinkage (swelling/contraction). There are also reversible systems sensitive to heat (SMPs) with changes in density.

– Photochemical muscles: irradiation induces internal rotations in the material (classic example of azobenzene), which contribute to modifying the geometry of the irradiated area, leading to deformations that depend on the luminous flux received; these can be reversible if photochromic materials are available (reversible transformation).

– With multi-material systems, it is possible to play on the difference in behavior of materials with a stimulation to produce "bilayer effects".

– With charged materials, an electromagnetic field can induce a charge orientation leading to a desired deformation of the 3D object, etc.

1.4.2.1. *Active materials*

> Unidirectional thinking is systematically favored by policy makers and their suppliers of mass information. Their discursive universe is full of assumptions which find their justification in themselves and which, repeated incessantly and exclusively, become hypnothic formulas, diktats. (Marcuse 1964)

We examine here how materials can be sensitive to a stimulus, independently of the additive manufacturing processes. Indeed, given the proposed manufacturing method, it is possible to introduce voxels in active materials into the object without them coming from additive manufacturing. The main information comes from: https://www.hisour.com/fr/electroactive-polymers-42852/.

Electroactive polymers, or EAPs, are polymers that exhibit a change in size or shape when stimulated by an electric field. The most common applications for this type of material are in actuators and sensors. A typical characteristic property of an EAP is that it will undergo a large amount of deformation while maintaining large forces (Bar-Cohen 2004; Lendlein 2010; Hu et al. 2012; Hager et al. 2015; Duduta et al. 2019; Lendlein and Gould 2019).

The majority of historical actuators are made from piezoelectric ceramic materials. Although these materials are capable of withstanding large forces, they typically deform only a fraction of a percent. In the late 1990s, it was demonstrated that some EAPs could exhibit up to 380% strain, which is far more than any ceramic actuator. One of the most common applications of EAPs is robotics in the development of artificial muscles (Maziz et al. 2017; Wang et al. 2017); thus, an EAP is often called an artificial muscle. EAP exhibiting a reversible transformation characteristic can have several configurations, but is generally divided into two main classes: dielectric (Du et al. 2015) and ionic (Carrico et al. 2019). Table 1.6 brings together the knowledge and properties of these materials. Figure 1.49, from Ganet-Mattei (2018), positions these compounds in a Young's Modulus-strain diagram.

Functionality	Comments
Electrostrictive polymers and dielectric elastomers	Actuation is caused by electrostatic forces between two electrodes that squeeze the polymer. Dielectric elastomers are capable of withstanding very high stresses and are basically capacitors that change capacitance when a voltage is applied, by allowing the polymer to compress in thickness and expand in surface due to the electric field.
Ferroelectric polymers and ferrofluids	They retain a permanent electrical polarization that can be reversed or switched in an external electric field. Ferrofluids are colloidal suspensions of ferromagnetic or ferrimagnetic nanoparticles of the order of 10 nm in size (Schärtl 2010; Kim et al. 2018).
Electrostrictive graft polymers	Electrostrictive graft polymers consist of flexible back chains with branched side chains. When an electric field is applied, a force is applied to each partial charge and causes the assembly to rotate. This rotation causes electrostrictive stress and deformation of the polymer.
LCEs	Synthesis of highly oriented elastomers leads to significant stress thermal actuation in the polymer chain direction, with temperature variation resulting in unique mechanical properties and potential applications as mechanical actuators.
Ionic polymers	The activation is caused by the displacement of ions inside the polymer (conducting polymers).
Electro-rheological fluid	Electro-rheological fluids change the viscosity of a solution with the application of an electric field. The fluid is a suspension of polymers in a liquid with low dielectric constant.
Ionic polymer-metal composite	Ionic polymer-metal composites act by electrostatic attraction between the cationic counter ions and the cathode of the applied electric field.
Stimuli sensitive gels	They are swellable polymer networks with volume phase transition behavior. These materials reversibly change their volume, optical, mechanical and other properties by small modifications of some physical (e.g. electric field, light and temperature) or chemical (concentrations) stimuli.
Stimulus sensitive materials	These are materials that are sensitive to light, humidity, temperature, etc. (see André (2017)). Produced in additive manufacturing, the objects are derived from so-called homogeneous 4D printing.

Table 1.6. *Stimulable materials*

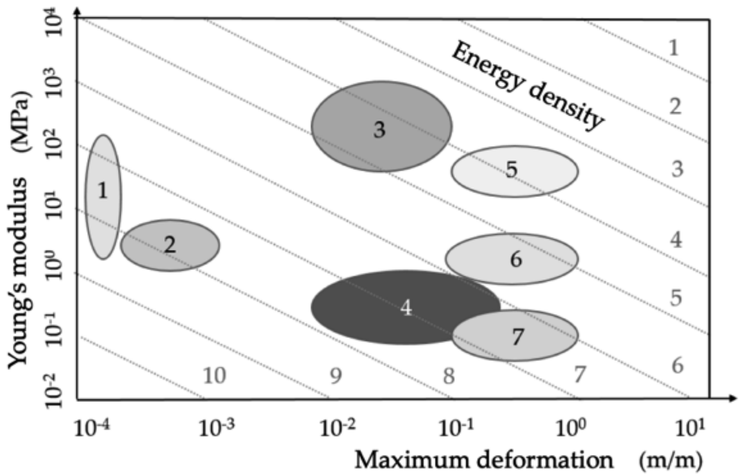


Figure 1.49. *Young's modulus-strain diagram (1: piezoelectric ceramic; 2: piezoelectric polymer; 3: shape memory actuator; 4: EAP; 5: hydraulic actuator; 6: pneumatic actuator; 7: solenoids) – Energy densities: 1: 10 GJ.m^{-3}; 2: 1 GJ.m^{-3}; 3: 100 MJ.m^{-3}; 4: 10 MJ.m^{-3}; 5: 1 MJ.m^{-3}; 6: 100 kJ.m^{-3}; 7: 10 kJ.m^{-3}; 8: 1 kJ.m^{-3}; 9: 100 J.m^{-3}; 10: 10 J.m^{-3}*

1.4.2.2. *Conventional materials used in homogeneous 4D printing*

> In 2007, when the iPhone came out, the CEO of Microsoft at the time said: this object has no industrial future. (Berry 2019)

4D printed materials must react to impose environmental changes: geometric deformations can be observed as soon as an external stimulus triggers the shape memory effect embedded in the material. Microscopic movements of the polymer chains then result in global changes of shape. Several modes of stimulation can be evoked to produce a 3D object by additive manufacturing and stimulation-induced shape changes (Chu et al. 2020).

1.4.2.2.1. Active polymers – photochemical muscles

One approach concerns the effect of light on the structure of a polymer like photochemical muscles (Yu et al. 2003; Nakano 2010; Yoshino et al. 2010; Jochum and Theato 2013; Khoo et al. 2015; Yu et al. 2015; Fang et al. 2017; Roppolo et al. 2017; Jin et al. 2018; Jung et al. 2020; Yoon and Bae 2020), as shown in Figure 1.50, extracted from Kuksenok and Balzs (2013). Irradiation induces internal rotations in the material, which contributes to changing the geometry of the irradiated area, leading to deformations that depend on the received flux. These can be reversible if photochromic materials are available (temporary, reversible transformation).

The full range of processes outside of photodegradation (Khim et al. 2014) can thus be exploited in 4D printing. Curvatures of polymeric fibers can be related to a non-homogeneous distribution of photo products (see Ge et al. (2016) and André (2017)). Different effects can be exploited (see Figure 1.51).

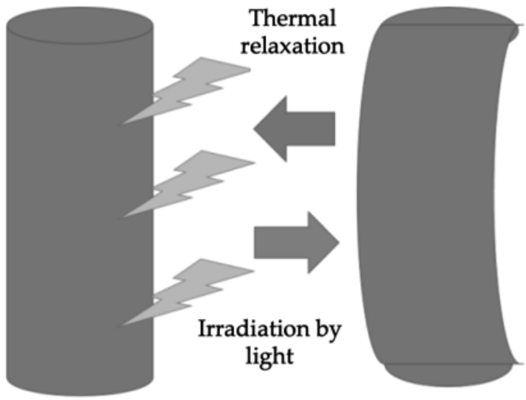


Figure 1.50. *Light-induced deformation of a photoshrinkable polymer cylinder*

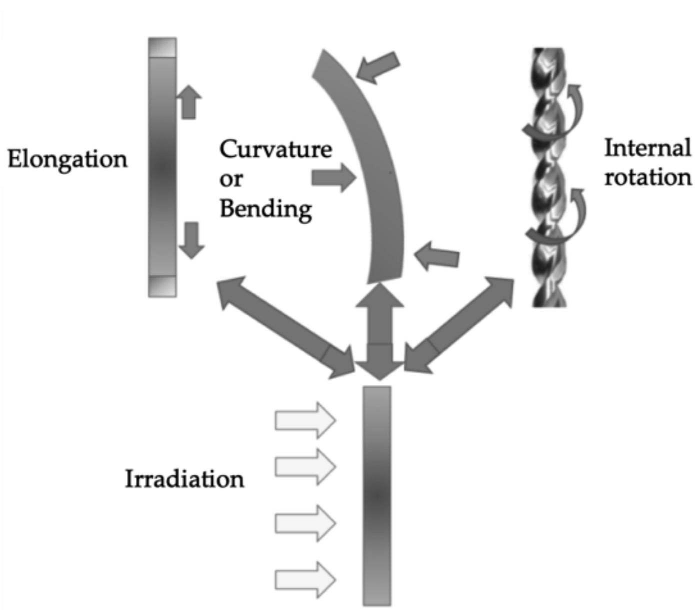
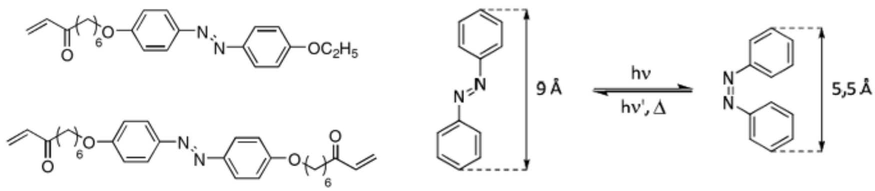


Figure 1.51. *Photomechanics of polymers*

Examples include Mahimwalla's (2013) thesis showing significant deformation of polymers containing azobenzene groups (see Figure 1.52 and Mahimwalla et al. (2012)). Upon irradiation, these groups change from Trans to Cis configurations depending on the wavelength used (see Figure 1.51). The effects are notable, as can be seen in Figure 1.52 (see also De Simone et al. (2015), Rosales et al. (2015), Liu et al. (2017) and Hagaman et al. (2018)).



a) b)

Figure 1.52. *a) Azobenzene-based polymers and b) sizes of the two isomers (Deloncle 2007). The Trans -> Cis transformation takes place in the mid-UV (300–400 nm), the return in the visible (between 400 and 500 nm)*

> To alleviate this sense of cognitive dissonance, in many cases, instead of acknowledging an error in judgment, one seeks to reframe one's views in a new way that justifies the old views. (Livio 2017)

The azobenzene molecule is generally in the Trans conformation, which can be considered uniaxial. When this molecule is exposed to visible light, it can undergo photoisomerization and change to the Cis conformation (see Figure 1.53). The molecule can then return to the Trans conformation following a thermally or optically induced transformation. Once this cycle is completed, the molecule can be in a new orientation. This process can be used to affect the macroscopic orientation of the molecules in a film. When linearly polarized light is used to activate the Trans -> Cis photo-reorientation cycle, only molecules whose electronic absorption transition moment is in the direction (or in the vicinity) of the polarization absorb light and undergo an orientation change. In this way, it is possible to reduce the number of molecules oriented parallel to the direction of polarization and increase the number of molecules oriented perpendicular to that direction (Rochon 2015).

These authors present rather dramatic results from Yamada et al. (2009), corresponding to the deformation of a polymer film induced, both by UV irradiation (Trans -> Cis transformation) at 366 nm (240 $mW.cm^{-2}$) and in the visible (λ > 540 nm and 120 mW.cm^{-2}) for the reverse transformation. Figure 1.54, kindly provided by Ge (2016), shows a reversible transformation of a polymer that deforms with temperature. Figure 1.56 by Cheng et al. (2010) complements the previous one: with a double layer of polymers, one of which contains azotolane that can undergo Cis -> Trans thermal and Trans -> Cis photochemical isomerization in the visible, it is possible to induce a temporary shrinkage of the irradiated film, followed by a return to the inital position after stopping the irradiation (see also Figure 1.56 by Zhang et al. (2015)). Other works may address this transformation principle (Ercole et al. 2010; Ilic-Slovanovic et al. 2011; Petr et al. 2015; Gao et al. 2016). As a side note, given the molecular structure of azobenzene and azotolane, it should be possible to take into account the orientation of the transition moments of these molecules placed in a polymeric system to make transformations in spatially resolved polarized light, to create for example programmable diffraction gratings (see above). Robotic applications are envisioned by Umedachi et al. (2013).

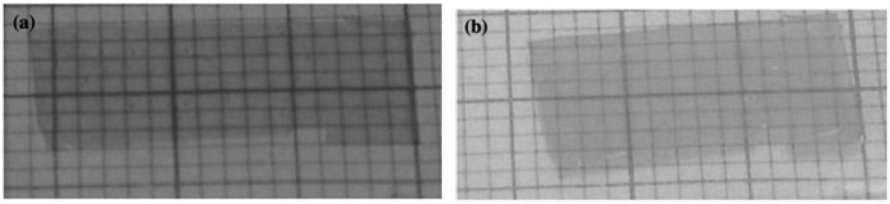


Figure 1.53. *Effect of irradiation on a polymer film containing azobenzene groups: a) before irradiation, b) immediately after according to Mahimwalla et al. (2013)*

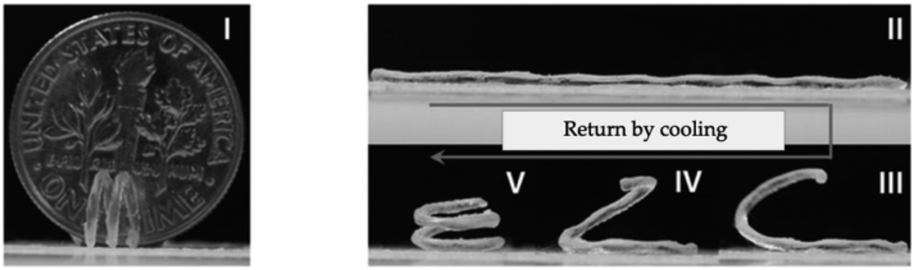


Figure 1.54. *Light-induced deformations of a polymer film (Ge 2016)*

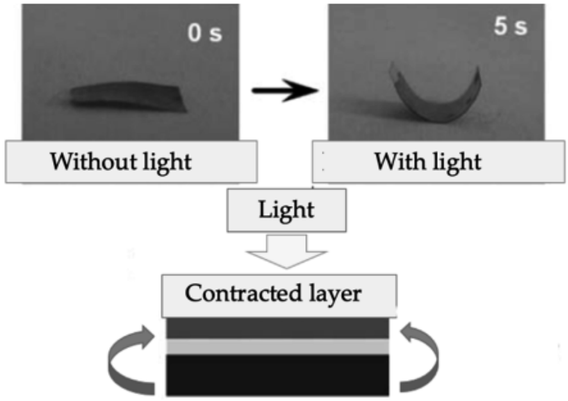


Figure 1.55. *Polymeric bilayer under light irradiation*

Such systems can be realized in additive manufacturing using various passive, yet highly elastic materials (e.g. with epoxy-based (monofunctional) and urethane-based (bifunctional) mixtures of aliphatic acrylic monomers published by Patel et al. in 2017).

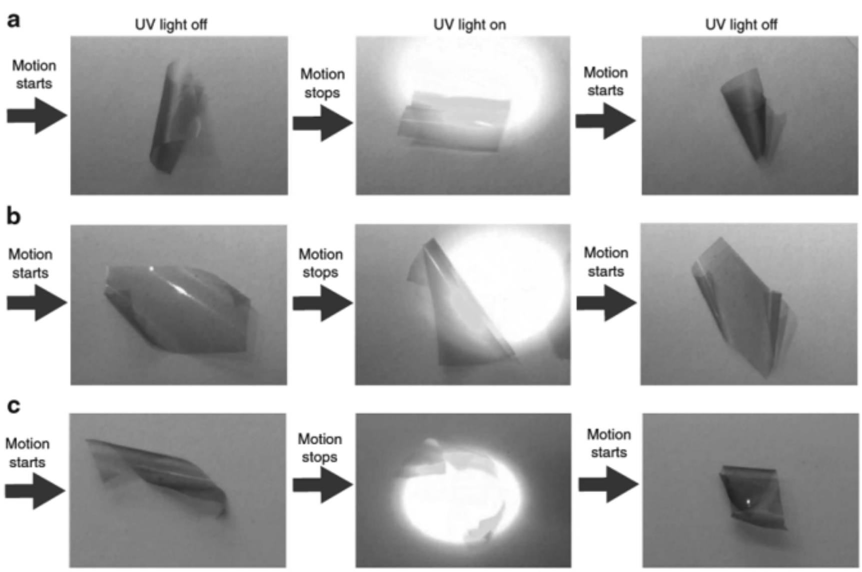


Figure 1.56. *Light-induced deformations of a polymer film according to Zhang et al. (2015)*

Another example from the work of Chen et al. (2016): active polymers, ready to respond to blue light stimulation (from an LED), containing tri-thiocarbonate (TTC) moieties with an accordion structure can be activated by organic catalysts. In the presence of light, monomers are formed (reverse process of polymerization), stretching the macromolecule. As the monomers are uniformly distributed throughout the structure, they impart new properties to the material, which then allows the shape of the object to be changed. This complex technique requires specific conditions of use.

1.4.2.2.2. Active polymers – thermal effects on polymers

> We no longer even understand how [objects] work, we have even become individually incapable of reproducing or repairing them. (Ariès 2010)

For Zhao et al. (2015), it is possible to have polymeric materials whose shape can depend either on temperature or on photochemical transformations. For these authors, it is a matter of finding reversible reactions affecting the space between molecules or macromolecules (see Figure 1.57) (see also Dutta and Cohn (2017), Zare et al. (2019), Zare et al. (2019), Yang et al. (2021a) and Aziz et al. (2021)).

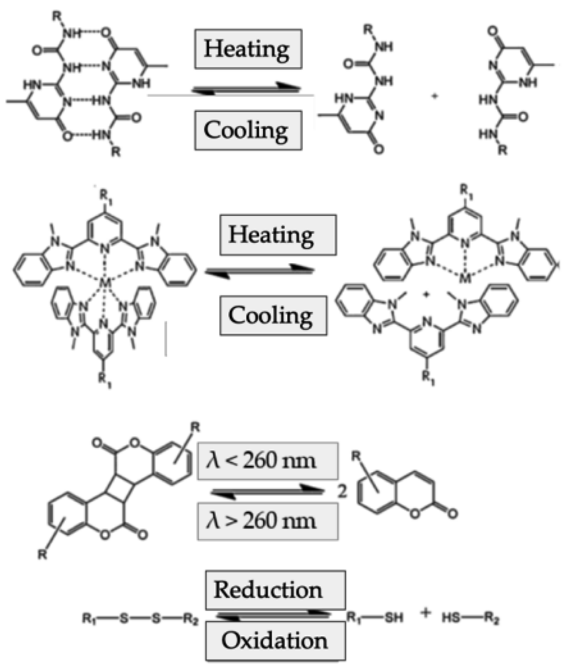


Figure 1.57. *Reversible systems with volume change*

An explanatory example is given in Figure 1.58, illustrating the shape change. Other examples are given in this review article on different active materials.

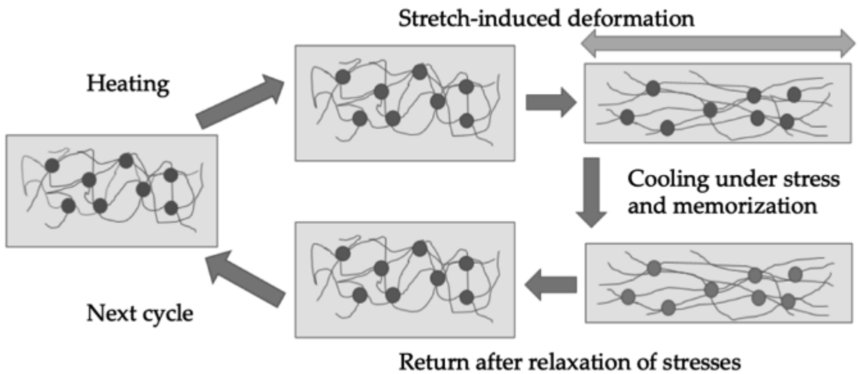


Figure 1.58. *Principle of thermally induced reversible deformations*

Inks made from hydrogels are capable of moisture- and temperature-induced deformation (André 2017). Le Duigou et al. (2016) used plant particles as a filler in a polymer (see also Gauss et al. (2021)). Oriented in the extrusion shear of this meltable polymer, they retain the memory of their orientation below the gel point of the material and can see their shape change in the presence of moisture (or heating). Finally, from an optimization standpoint Zhang et al. (2011) added carbon nanotube fillers to the heat- and light-sensitive (hydrogel) material, poly-(N-isopropylacrylamide) (pNIPAM), which facilitates heat transfer into the bulk of the material and light absorption on the surface. Han et al. (2012) exploited pH-induced transformations.

In Table 1.7, Rastogi et al. (2019) proposed liquid crystal transformations induced by photo-thermal effects (heating by light) (see also Rousseau (2008), Plucinsky et al. (2018), Roach et al. (2018) and Longo et al. (2019)).

The selection of materials is therefore very important when trying to define a target application. Pinho et al. (2020) consider that the chemistry responsible for the morphing effect of polymeric materials is not explicit enough, despite the growing number of articles published on this topic. They write: “For specific applications, only chemical modification of polymeric materials can achieve the characteristics required for 4D printing”. For electro-thermal effects, Chen et al. (2021b) show that the presence of carbon fibers increases the strength of the 4D printed composite, and also improves the recovery strength of the active form.

Properties/nature	Polymer	Elastomer	Network
Cross-linking	No	Low	Important
Change after stimulation	No	Approximately 5%	>90%
Shape memory	No	Yes	Yes
Glass transition temperature	200°C	25°C	Between 60°C and 100°C
Modulus of elasticity	>2 GPa	<100 MPa	Intermediate

Table 1.7. *Performance comparison of liquid crystals usable in 4D printing*

1.4.2.2.3. Active polymers – swelling effects in polymers

> We take as true what is credible, what we want to believe. However, we must sometimes inhibit our automatic beliefs in order to develop more logical, rational thinking. (Houdé 2019)

Other physical phenomena can be exploited to see a 3D object made of an environmentally sensitive material change shape: pH, presence of a solvent, etc. (Bakar and Djaider 2007; Liu et al. 2017, Lv et al. 2018; Abdelmohsen et al. 2019). The swelling of cross-linked polymer networks in the presence of a solvent is a well-known phenomenon (Ancla 2010; Bounouira 2015). In the latter case, shown in Figure 1.59, very noticeable changes in the shape of a 3D object can be observed.

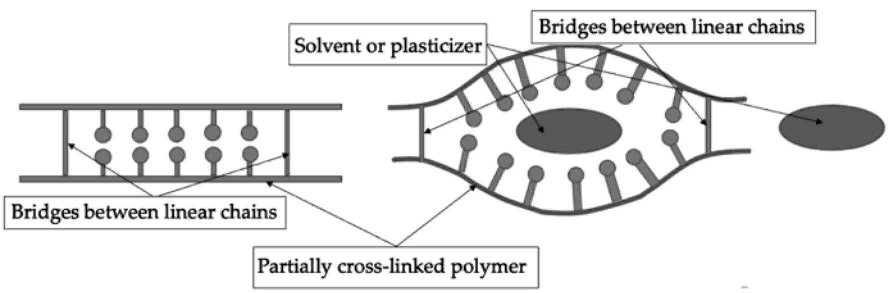


Figure 1.59. *Shape changes in the presence of a solvent*

With certain solvents, the chain sections between two cross-linking points unfold as in the case of linear chains, but this movement is limited by the existence of bridges. The phenomenon is therefore limited to swelling, which is more pronounced the lower the degree of cross-linking. The term hydrogel defines materials with a liquid and a solid component. They are composed of polymer chains assembled via the cross-linking process and can contain liquids such as water. Hydrogels can be used in additive manufacturing and have their shape change in the presence of a solvent (see also Oveissi et al. (2021)). Figure 1.60, from Curatolo et al. (2021), illustrates how a network can be deformed by the presence of micro-molecules or spheres.

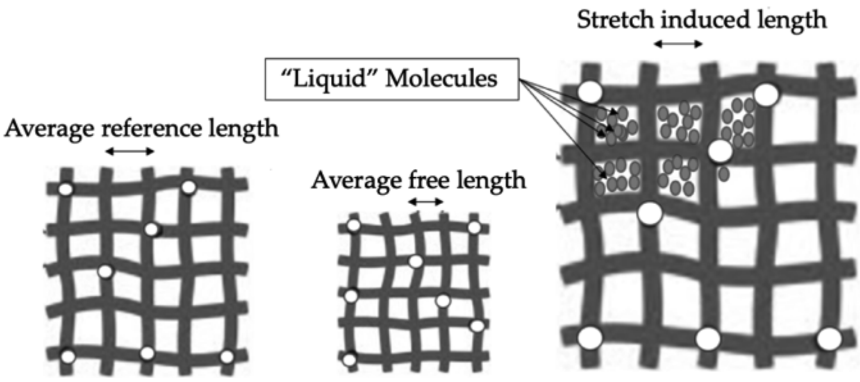


Figure 1.60. *Deformation of a network by the presence of active molecules or nanospheres*

Table 1.8, taken in part from Gao et al. (2016), gives indications on processable materials and on the processing methods applied in this area.

Type of material	Mechanism and comments	References
Polyethylene glycol; lipid bilayers	Contact with water	Villar et al. 2011, 2013; Jamal et al. 2013
Low transition temperature polymers (PNIPAAm; PCL); ceramic alumina	Transition temperature	Peppas et al. 2000; Bakarich et al. 2015; Wang et al. 2015
Magnetic materials	Precise positioning by locating the magnetic field	Kokkinis et al. 2015; Zhu et al. 2018; Wu et al. 2020
Polymers containing light isomerizable groups	Photochromes	Zhang et al. 2015

Table 1.8. *Different types of informed materials and associated mechanisms*

1.4.2.2.4. Electrochemical effects

> You don't know […] that there is life only in differences, difference of temperature, difference of potential. And if the same heat or the

same cold reigns everywhere in the universe, it is necessary to shake them so that the fire, the explosion, the Gehenna are born. We will shake them. (Zamiatin 2020)

Figure 1.61 schematically represents the effect of ion transport on polymer conformation, according to Kaneto (2016). Either ions are made to act and we can engage in 4D printing, or we have a means of dosing the ions (actuator/4D printing reciprocity).

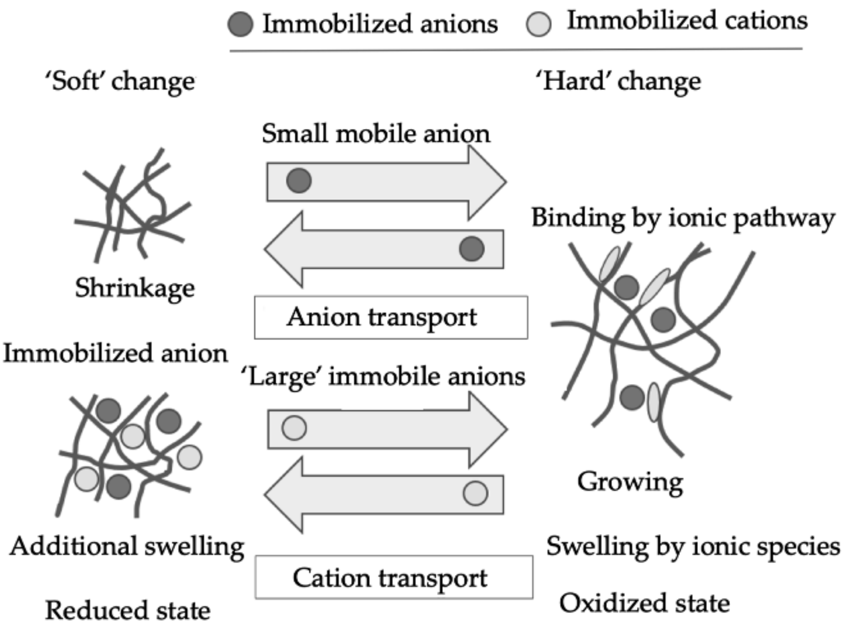


Figure 1.61. *Conformation/ion relationship: Acrylic type polymers are "welded" or rather cross-linked and in the 3D structure thus generated, the presence of ions disturbs the shape of the structure*

1.4.2.2.5. Biological and organic materials

Experience is the name everyone gives to their mistakes. (Wilde 2017)

Plants exhibit spontaneous curvature changes due to the orientation of cellulose, which undergoes anisotropic swelling in the presence of water. Gladman et al. (2016) mimicked this process with a hydrogel containing such rigid cellulose fibrils. They spontaneously align under shear as they flow through the printer's extruder nozzle, inducing anisotropies in swelling and elastic modulus. With positioning in bilayers, differential swellings can be achieved, resulting in a (calculable) curvature of the object. Using anisotropy in the material, Qe et al. (2016) showed in Figure 1.62 how it is possible to develop the shape of an object depending on the stimulation it receives.

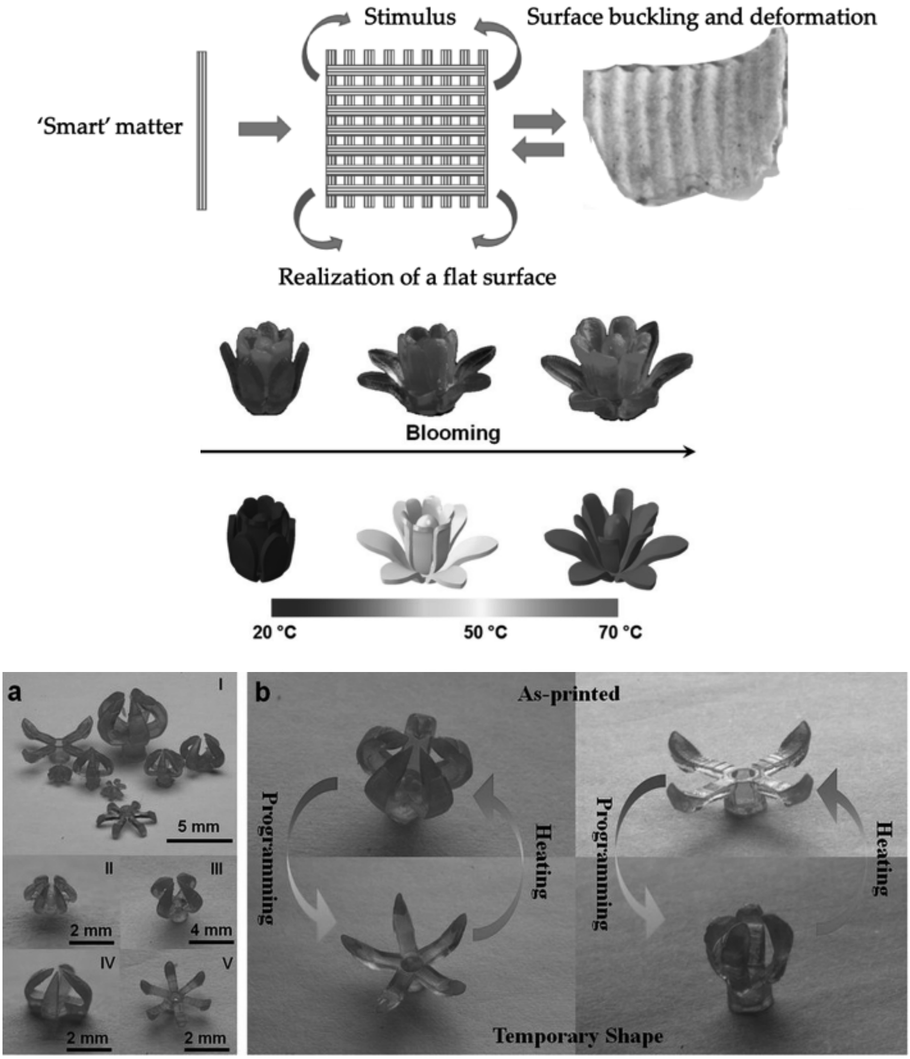


Figure 1.62. *The anisotropy of the material creates a curvature when the temperature changes (the same phenomenon could have been obtained with the swelling of bi-layers of cellulose loaded threads). Complex morphologies (here a flower) are generated with changes in the shapes of the objects*

Lind et al. (2017) used heart muscle cells that contract under the influence of electrical stimulation as an activatable material. Figure 1.63 illustrates the compression/expansion phenomenon to bend a plastic material (see also Jackson (2016)).

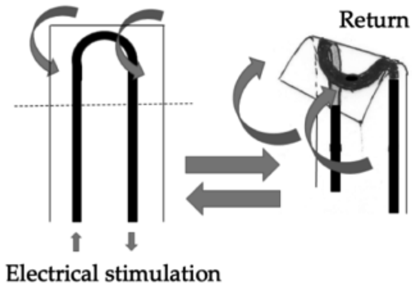


Figure 1.63. *Deformation induced by muscle cells*

1.4.2.3. *Elongation-Young's modulus relationship*

> Men are conscious of their desires and ignorant of the causes that determine them. (Spinoza 1955)

In his thesis, He (2021) relates this important aspect to design deformable assemblies in 4D printing. Figure 1.64 shows typical results with considerable variation depending on the materials and activation modes chosen.

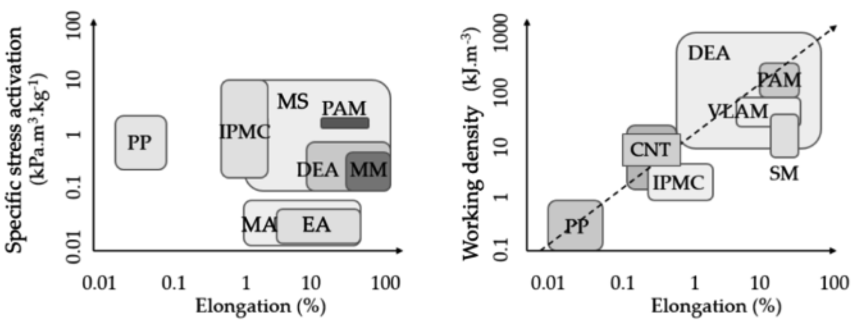


Figure 1.64. *Steady-state actuation performance of LCE-based vascular artificial muscle. Left: specific actuation stress as a function of strain of classically used materials and mammalian skeletal muscle. Right: working density as a function of strain (Abbreviations: PP: piezoelectric polymer; MA: magnetic actuator; EA: electrostatic actuator; MM: mammalian muscle; IPMC: ionic polymer-metal composite; MS: mammalian skeleton; CNT: carbon nanotube; DEA: dielectric elastomer actuator; PAM: pneumatic artificial muscle)*

1.4.2.4. *Some typical results*

> Dare I state here the greatest, most important, most useful rule of all education? It is not to save time, it is to lose time! (Rousseau 1995)

Kimionis et al. (2015) used both 3D printing and origami making for the manufacture of radio frequency (RF) antennas. An example of their demonstration that couples two emerging potentials in the same object can be found in Figure 1.65.

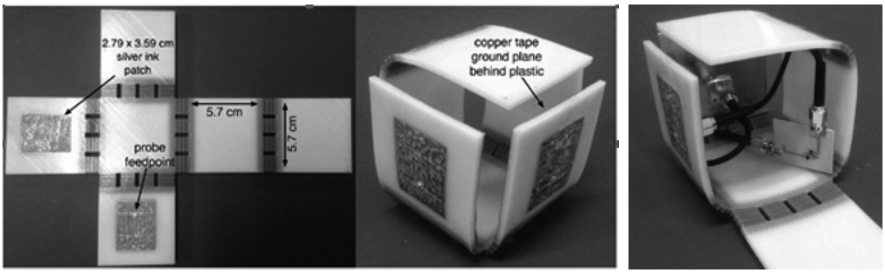


Figure 1.65. *An origami-based RF antenna realized by multi-material additive manufacturing (silver ink patch; probe feedpoint: copper tape ground plane behind plastic)*

Apart from origami, which can be temperature sensitive (Ge et al. 2014), more large-scale transformations can be achieved with light-sensitive polymeric materials. Another approach involves the effect of light on the structure of a polymer (Nakano 2010; Yoshino et al. 2010; Kuksenok and Balzs 2013; Gao et al. 2015; Petr et al. 2015; Patel et al. 2017; Shao et al. 2018; Jayashankar et al. 2019; Kriegman et al. 2019; Goo et al. 2020; MIT 2020): Irradiation induces internal rotations in the material, which contributes to changing the geometry of the irradiated area inducing deformations; these can be reversible if photochromic materials are available. Polymeric fiber bends can be related to the inhomogeneous distribution of photoproducts following either surface resolved illumination or tailored deposition, as illustrated in Figure 1.66 (Sossou et al. 2019a; see also Baker et al. (2016), Zhang et al. (2017b), Zolfagharian et al. (2018), Carrell et al. (2020) and Yuan et al. (2021)).

Another example is the significant deformation of polymers containing azobenzene groups (Mahimwalla et al. 2012; Mahimwalla 2013; De Simone et al. 2015; Rosales et al. 2015), that upon irradiation, change from Trans to Cis configurations. The effects are notable, with reversible shrinkages of over 20%. Using anisotropy in the material, Qe et al. (2016) showed in Figure 1.57 how the shape of an object can be made to change with the stimulation it receives.

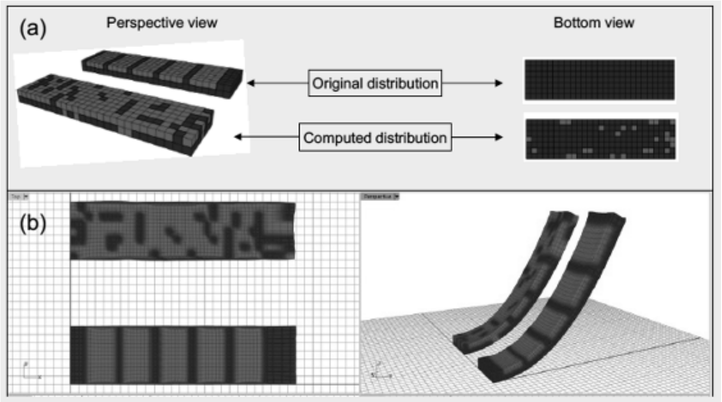


Figure 1.66. *Optimization of an active material deposit for a given deformation (Sossous et al. 2019a)*

Chen et al. (2019) performed 4D metal printing using a specialized machine. This is one of the first demonstrations of metal use with the publication by Lohmuller et al. (2019). Kim (2014), however, had already made prints with piezoelectric nanoparticles. But a reverse approach has already been attempted by implementing piezoelectric materials in structures to avoid deformations of various origins (Bent and Hagood 1997). With piezoelectric fibers in an epoxy matrix, orthotropic activation can be achieved using interdigitated electrodes, producing an electric field in the plane of the structure (in the direction of the fibers). If these advances in the field of smart materials have opened up new possibilities for active control of composite structures (Gakwaya 2006), it is conceivable to use these systems to perform heterogeneous 4D printing.

However, according to Reiser et al. (2019), the synthesis of industrially good inorganic materials remains a challenge. They show that current additive microfabrication techniques lead to a wide range of microstructures and mechanical, elastic and plastic properties. While this work provides practical guidelines for users of metal additive manufacturing methods, a high level of specialized materials expertise is required.

Dufaud et al. (2002) studied the effect of electric current on composites containing PZT ceramics with piezoelectric properties aimed at the realization of actuators. More recently, Martin et al. (2015) combined magnetic particles with photo-polymerizable resins that can be specifically oriented by changing the field amplitude and orientation. This realization where two forms of energy are coupled allows the realization of structures with singular magnetic properties, along with a possible reinforcement of the material by increasing the order of the elongated particles in the polymeric matrix. Catheters for neonatal applications have been realized on this principle.

Box 1.10. *Additional remarks*

1.4.2.5. *Transition between activation modes*

> Objectivity, associated with knowledge, relegates everything that does not belong to it, values and principles, to the side of subjectivity, belief, opinion, etc. (Roux 2011)

In André (2017a), dealing with emerging niches in 3D printing, different themes useful for the development of 4D printing were presented. These themes are presented in Table 1.9.

Theme	Comments
Doing chemistry	By chemical means, we can modify the structure of a macromolecule which, by reaction, can be deformed to create an object. However, given the number of links to be considered, these objects are limited to nanometric sizes (3D DNA; nano-machines, catenanes, etc.)
Self-organization	The example of the crystallization can be retained: if it was possible to guide the shape of the structure, it would be possible to reach in the time of the transfer of matter shapes answering the specifications Another example is bio-printing
Displacement of atoms	The development of near-field systems allows the displacement of atoms and the realization of 3D sub-nanometric structures
Nano-manufacturing	Additive-subtractive couplings
Swimming robots	Directed particles that gather to form an object (as long as the cohesion between these particles is assured). The number of possible particles remains modest because of the slowness of the movements
Robotic voxels	Programming the movement of voxels (autonomous robots) to create a 3D object whose shape can evolve over time. The size of the voxels and their number are factors that limit the development of this construction principle
4D origami	Foldable 2D structures can be generated by placing stimulable adaptive materials in the folds, allowing the fabrication of externally controlled centimeter-sized robots by external actuation

Table 1.9. *Other processes that may be of interest in 4D printing*

In this transition, it is possible to mention associations between electrical potential and physical chemistry. Figure 1.67 illustrates the principle of deformation (Narayan et al. 2021; see also Coltelli et al. (2021) with additional microfluidic effects).

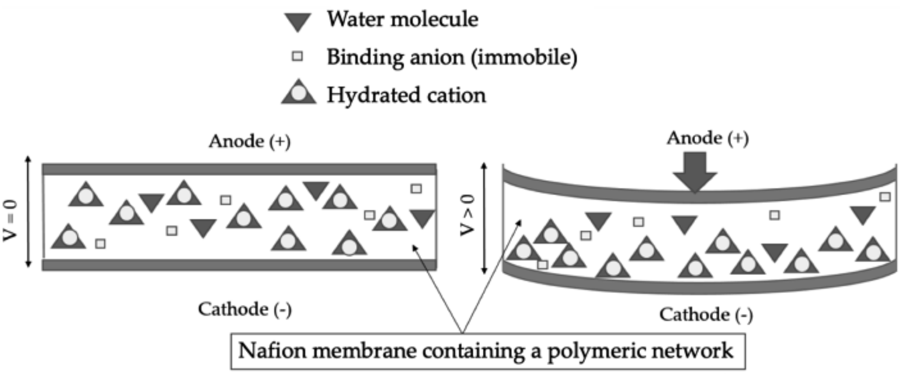


Figure 1.67. *Diagram of deformation under tension due to migration of hydrated cations*

Without returning to the construction of volumes atom by atom, the following sections deal with other ways than those related to chemical interactions exploiting the assistance of different types of energy sources. Furthermore, materials subjected to mechanical stress can undergo a change in their structures, properties and/or functions (Troyano et al. 2021). This mechano-reactivity can be exploited to trigger chemical transformations (Do and Friščić 2017). Poro-mechanics is devoted to modeling and predicting the deformation of porous materials in response to external loads. It could also be investigated in 4D printing.

1.4.3. *Activations by physical pathway*

> Within a limited rationality, the terms of reason become disjointed: losing their unity, they lose their meaning. It seems that rationality and finality do not pre-exist the facts which carry them and which one supposes that they bring (or peddle). (Lefebvre 1971)

We have already discussed the modes of activation of materials. While most of the work deals with the chemical methods just mentioned, there are other ways of physical origin, which can make them evolve in form or in functionality or, more simply, help them to move. These are the different elements that are recalled below.

1.4.3.1. *Mechanical effects*

1.4.3.1.1. Internal effects

Grossweiler et al. (2015) use polymers containing spiropyrans that are sensitive to mechanical stress, these deform and change color with a relaxation time of several minutes (see Figure 1.68). This type of material has enabled micro-clamps to be made.

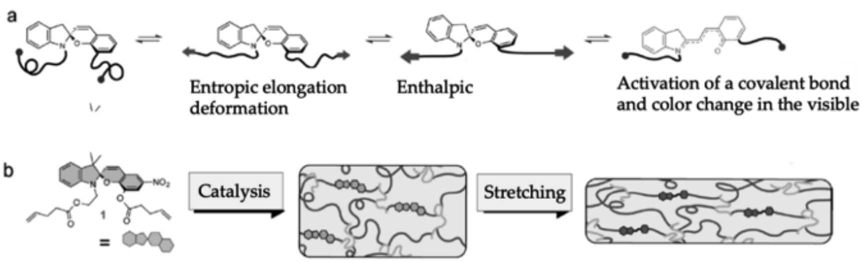


Figure 1.68. *Effect of mechanical stress on the chemical transformation of a spyropyran-based polymer*

Recall further that Vatankhah-Varnosfaderani et al. (2018) synthesized an elastomer composed of a central block, which has side chains extended by two terminal blocks grafted onto it (see Figure 1.69). The end blocks of these structures gather into nanoscale spheres, distributed in a matrix formed by the "pin-like" structures. The light interferes with this architecture according to the distance between the ends; a stretching of the material thus results in a change of color (chameleon effect). It is therefore possible to encode mechanical properties (elastomer) and optical properties in a single polymer, with modulation possibilities. By imposing a mechanical deformation on an object, it is therefore possible, in principle, to show where the areas of mechanical stress are located.

Qian et al. (2021) teach us that precise mechanochemical transformations in polymeric materials are poorly explored. Before the advent of mechanophores (synthetic force-sensitive molecules) few mechanosensitive functions were known in polymers (Nixon and De Bo 2020). Mechano-actuation has a directional parameter that, in turn, is coupled with the geometric attributes of the mechanophore through its points of attraction:

> thereby tuning the force responsiveness. In other words, by modulating the attachment points of a mechanophore in polymer

> chains, the force-induced reactivity of the mechanophore and the reactivity of the material vary significantly. (Church et al. 2014; Gossweiler et al. 2015; Stevenson and De Bo 2017)

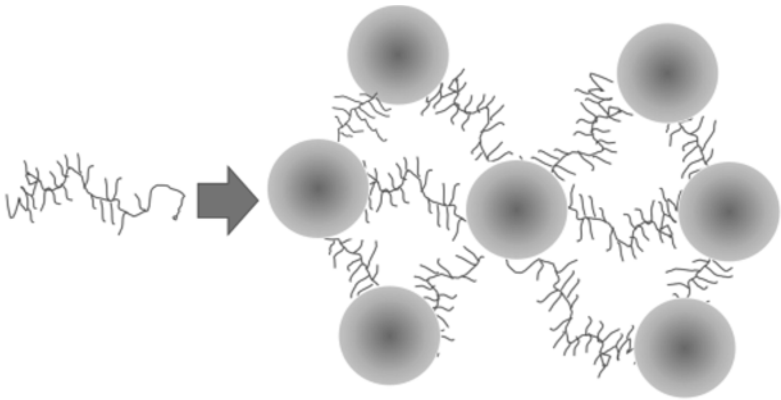


Figure 1.69. *Active structure of the chameleon type*

1.4.3.1.2. External effects

> Even in its most fortuitous forms, chance does not make the discovery: it is only the occasion. (Picard 1928)

These can be, as shown in Figure 1.70(a), simple and fairly traditional solutions of actuators made by additive manufacturing (Peele et al. 2015; see also Walters et al. (2010) with a pneumatic actuator principle using origami in Martinez et al. (2012)). In this figure, the left or right displacement depends on the difference in gas pressure between the two compartments of the actuator. Foldable systems whose fast internal swelling (compared to response times obtained with solid materials) leads to interesting shape changes like those in Figure 1.70(b) of Yuk et al. (2017) correspond to an object made in additive manufacturing, whose shape can be modified by the effect of hydraulic pressure. Recently, Sparrman et al. (2021) produced a study in this same field with flexible fluidic actuators (whose principle is based on the historical McKibben actuator) made with silicone polymers in 3D printing, with the possibility of operating them sequentially for complex deformations (application in soft robotics – see, for example, Franco et al. (2020)). Other (simultaneous) actuation devices are proposed by Shao et al. (2021) with magnetic actuation. In this last case, a change of scale is sought for applications in micro-robotics (millimeter size).

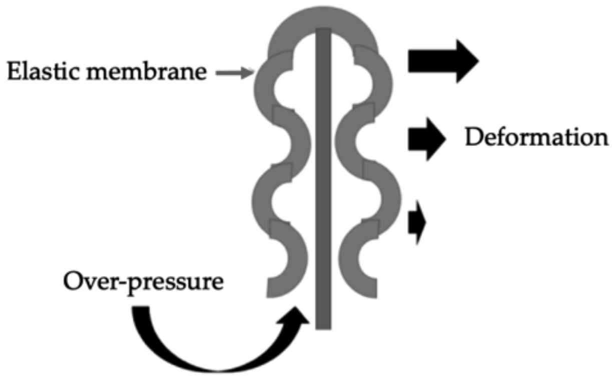


Figure 1.70a. *Principle of a pneumatic 3D actuator (André 2017)*

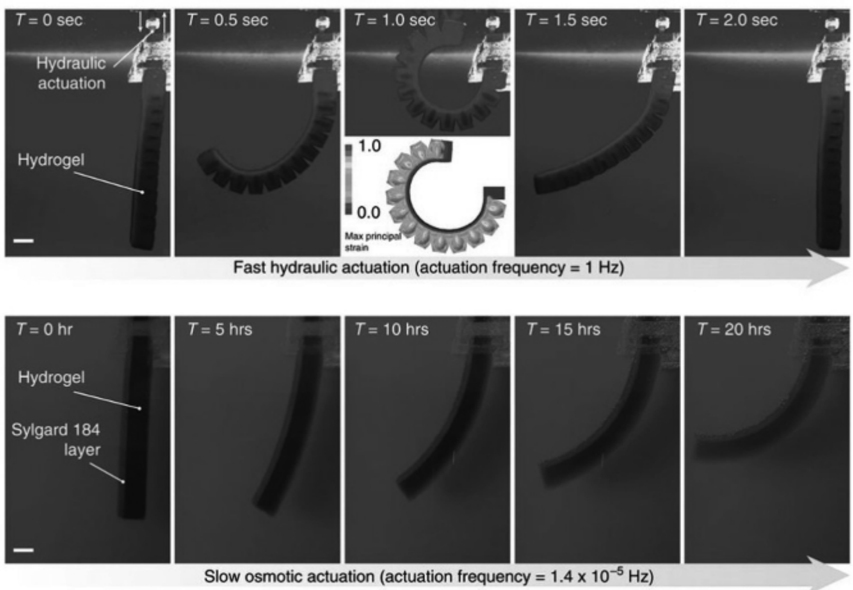


Figure 1.70b. *Hydraulic actuator (Yuk et al. 2017)*

1.4.3.2. *Physical changes*

> Any action is risky. But inaction is almost always more risky. There is no progress without risk. (Comte-Sponville 2015)

1.4.3.2.1. Macroscopic effects

MIT (2013) has shown that on simple examples, it is possible to "order" the material if only by visual recognition. This idea, illustrated in Figure 1.71, is based on the displacement of cylinders as used in two dimensions by carpenters to take the impression of a cornice, or as some toys to achieve three dimensions. If a numerical control is added to the displacement of each cylinder, it is possible to make the material "programmable" directly or indirectly. However, in these two examples that serve as an introduction to the subject, the material is inert. The idea is to go a little further in the process by "informing" the matter directly, at finer scales than the one in this figure.

Figure 1.71. *Reversible sculpture toy (Cdiscount 2017)*

Figure 1.72 with the idea from MIT (2013) shows the intrinsic complexity of such a system that will not be able to scale down due to the very large number of actuators that would need to be put together in a finite volume (voxel size problem to consider).

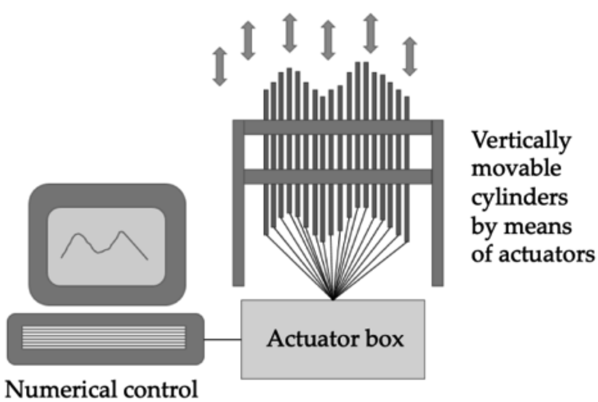


Figure 1.72. *MIT experimental setup (2013)*

1.4.3.2.2. Microscopic effects

> The necessity that all sciences be directed towards a useful goal, and that the point of coincidence of all their discoveries be the physical and moral prosperity of the French Republic. (Abbé Grégoire, quoted by Lévy-Leblond (2006))

A surfactant is a molecule with a hydrophilic head and a hydrophobic tail, the hydrophilic head being preferentially oriented toward the aqueous phase, unlike the hydrophobic tail. Thus, surfactants are generally positioned preferentially at the water/air or water/oil interfaces.

> Their presence stabilizes the interfaces, which implies a local decrease of the surface tension. As the presence of surfactants on a surface decreases the surface tension locally, it is possible to create a surface tension gradient. This results in a movement of fluids toward areas of higher surface tension. (Marques-Serra 2014), as illustrated in Figure 1.73

The addition of a surfactant (orange) causes a decrease in surface tension from γ_0 to γ, which induces to a deformation of the surface that leads to a flow of fluids (blue arrows) toward the areas of higher surface tensions γ_0 (André 2017).

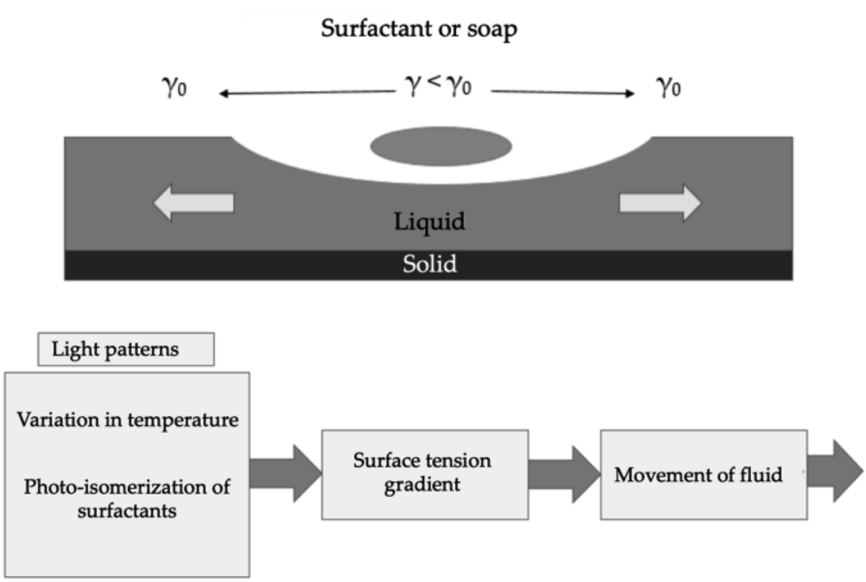


Figure 1.73. *Surfactant-induced deformation of a fluid*

If an active surfactant (e.g. containing azobenzene) is used, Trans-Cis isomerization is likely to change the surface tension, which may allow material flow. Under UV irradiation the concentration of Trans isomer decreases, which increases the surface tension. Depending on the light distribution, a surface tension gradient can be obtained with the possibility of having a photo-induced Marangoni effect. Thus, if a drop is deposited on a surface, it will be able to move on it by playing, as shown in Figure 1.74, on the changes of the surface tension induced by light (Shin and Abbott 1999).

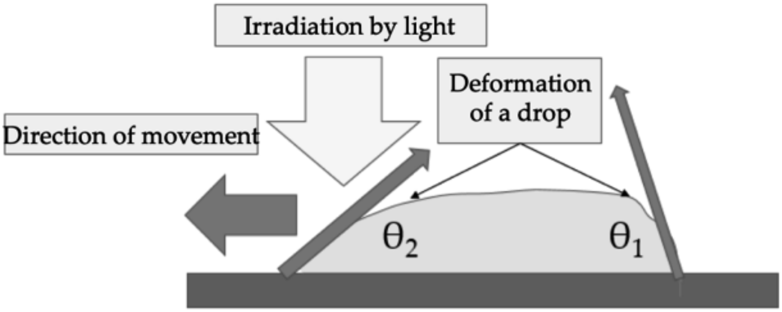


Figure 1.74. *Possibility of guiding the movement of a drop on a surface*

Considering the energies involved, if this technology enables droplets to move on a flat horizontal surface, it can only be considered with immiscible fluids of the same density (see swimming robots in section 1.4.4) for an application in additive manufacturing.

With Trans-BTHA, Shin and Abbott (1999) showed that the irradiation of hanging drops could cause their fall. From there, to consider a principle of rapid deposition of material by this process, there is only one step… (see Figure 1.75 representing the structural formula of the surfactant considered).

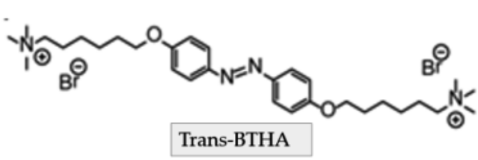


Figure 1.75. *Structural formula of the surfactant*

Box 1.11. *Influence of the surfactant*

1.4.3.3. *Deformation of metal parts*

> Scenario method: "[Kahn and Wiener's] method turns out to be fundamentally heuristic: they do not seek to know whether the hypotheses put forward are true or false, but rather to explore progressively, through them, problems that may arise". (Durance 2014)

1.4.3.3.1. Drops

As an initial example, the 3ders.org paper (2014) announced the possibility of rotating and moving droplets of a Ga/In/Se alloy melting at 10°C, floating (due to surface tension) on water via a magnetic field. Sheng et al. (2014) from the Chinese Academy of Sciences in Beijing were able to change the shapes, as well as the sizes of metal droplets. It will be interesting to see how we can access the third dimension, and then the fourth. Figure 1.76 illustrates the effect of an electric field (New Scientist 2015).

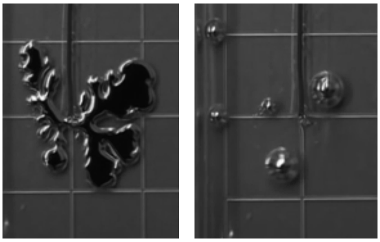


Figure 1.76. *Effect of an electric field (left) on the shape of alloy droplets*

1.4.3.3.2. Oriented magnetic architectures

Martin et al. (2015) have combined magnetic particles with photopolymerizable resins that can be specifically oriented by changing the field amplitude and orientation. This realization where two forms of energy are coupled enables the realization of structures with singular magnetic properties, along with a possible reinforcement of the material by increasing the order of the particles arrayed in the polymeric matrix. Catheters for neonatal applications have been realized on this principle.

1.4.3.3.3. Shape memory alloys

> Don't kid yourself, don't abuse yourself, with the understanding that you yourself are the easiest person to abuse. (Feynman 2000)

SMAs can be used (Ballandras et al. 1996) to realize actuators by heterogeneous 4D printing. These alloys have several properties that are new among metallic materials: the ability to keep an initial shape in memory and to return to it even after a deformation; the possibility to alternate between two previously memorized shapes when its temperature varies around a critical temperature; and a superelastic behavior allowing elongations without permanent deformation that are higher than those of other metals. Among the major SMAs are a variety of alloys with nickel and titanium as primary constituents in nearly equal proportions (Meier et al. 2012; Dadbakhsh et al. 2014). Although the name "nitinol" is actually only the name of one of these "quasi-equi-atomic nickel-titanium alloys", this name has become commonly used in the literature to refer to all of these alloys, which have very similar properties. To a lesser extent, some copper-aluminum-based alloys also possess shape memory properties (Wikipedia 2015). While these materials have not really been used in additive manufacturing, their application areas now span medicine, aerospace, automotive, women's clothing, eyewear, security and research… (Nimesis 2017). This development has long been limited by poor durability in their ability to return to their original shape (Chluba et al. 2015). However, everyone remembers a now classic example, that of Uri Geller's demonstration, in front of an astonished audience of the deformation of spoons made with such alloys by thermal effect (L'arrêt public gouverne MENT 2010). Several applications in additive manufacturing can be considered (keeping in mind small volume variations, but changes in shape that can be reasonable). In particular, as shown in Figure 1.77, SMAs have a specific advantage (relative to polymers), which is their good weight/power ratio, increasing their potential use as actuators by 4D printing.

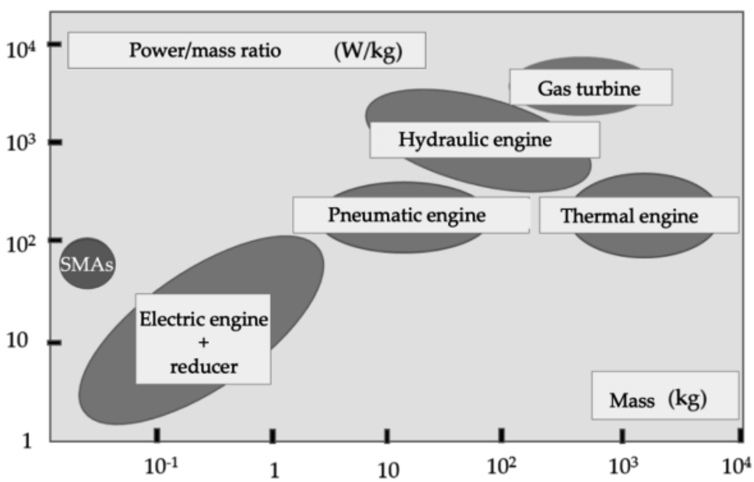


Figure 1.77. *Power/mass ratio of SMA linkages versus motors according to Patoor (2006)*

Example: It is possible to 4D print various structures made of composite filaments, for example polylactic acid (PLA) and PLA/FeO_{34}. The shape memory behaviors of 4D printed structures triggered by a magnetic field have been studied by Zhang et al. (2019). The printed structures can quickly recover their original shape. Furthermore, the structures activated by a magnetic field at 27.5 kHz have a uniform surface temperature around 40°C, which is consistent with a physiological operating temperature.

1.4.3.4. *Intermediate conclusion*

> For if I wish to speak the truth, I will have to talk in the way I've described. Whether it's the business of a philosopher to tell lies, I don't know, but it certainly isn't mine. (More 1997)

This section is partly taken from André (2017) with a modest update. Indeed, this domain stemming from physico-chemical interactions in matter seem to be of less concern to researchers than the more large-scale interactions between different forms of energy and matter (NAP 2019b). The original component of this recently emerged 4D domain to open up additive manufacturing to other application niches lies in the principle of informing matter to extract spatial functionality (rather than being part of spontaneous self-assembly). At this stage, while the photochemical muscles have already been the subject of work for many years, to the knowledge of the authors, the idea which consists of starting from a simple form, easily realizable by traditional techniques (i.e. molding and traditional machining) for after treatment by light (or any other form of energy localized in space and time), to obtain a complex object has not been emitted. It raises the question of having materials with high expansibility (remember that for SMAs, the difference between the two shapes is generally of the order of a few %), to be able to treat an inverse problem. Starting from a shape to be reached, what could be the initial shape?

In any case, while this path seems interesting, it would be advisable to begin studies on very simple objects to deduce laws. Obviously, it would be necessary to work on surfaces rather than volumes to simplify the situation. However, the number of influencing parameters to be taken into account may be high, leading not to a unique solution for a given spatial resolution, but to a set of solutions (and at the same time to the absence of solutions for too complex shapes). Thus, starting from a continuous material, the formation of a percolating medium, for example, could be problematic.

1.4.4. *A transition to 4D printing: swimming robots*

> Breakpoints reveal situations where the existence of unstable conditions makes it impossible to predict future events because our

> knowledge of the present state is only approximate and far from reality. (Goux 2014)

There is a possibility to move a droplet of inert matter by bringing an external energy onto it (see Sheng et al. (2014)). Based on this principle, tiny swimming robots containing iron oxide particles, bound together by chemical bonds, can move by magnetic force (Cheang and Kim 2016). In this paper, these particles are not intended to assemble to create an object, but, with a size on the order of a nanometer, this object must be able to move through the vasculature from an external magnetic field (see Rao et al. (2015), and Figure 1.78). Indeed, the swimming of robots is well controlled, as they move at low Reynolds number:

> Indeed, the Reynolds number of the flow is very small, on the order of 0.00001, whereas in usual flows (that we have to consider for a human swimming in water, for example) this number is typically on the order of 100,000. (Alouges 2012)

A swimming robot consisting of three spheres joined in a line has been studied by Alouges et al. (2008), Naja and Golestanian (2004) and Garcia (2013), where it is shown that it can indeed swim (slowly) in a 3D flow with low Reynolds number.

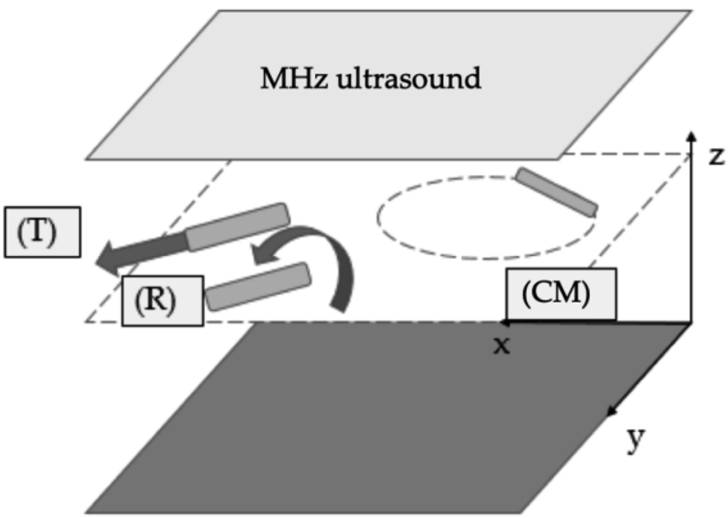


Figure 1.78. *Movement principle of swimming robots (different types: translation (T); rotation (R); circular movement (CM))*

Even if swimming robots can be considered as solid structures, they have their own energy for their movements or have a movement stimulated by an external energy. They are therefore systems exploring both space and time.

Box 1.12. *Swimming robots*

If the vision of the researchers is to transport drugs (cargo effect) or to use the swimming robots to clear blocked vessels (ice-breaking effect), it is possible to use, in a voxel, transformable matter which, in weightlessness, can be guided on an object under construction. The principle of this construction requires precise guidance of each robot considered as isolated from other robot-swimmers (otherwise, apart from the feasibility of precise control, these entities have density- and flow-dependent behavior, as shown by Lushia and Peskin (2013) and Liebchen et al. (2016)). In groups of swimming robots, using particles of varying sizes, it is possible to consider the construction of nanoscale or larger objects, via a "multi-voxel" principle, or even multi-material with voxels of various sizes (see Figure 1.79).

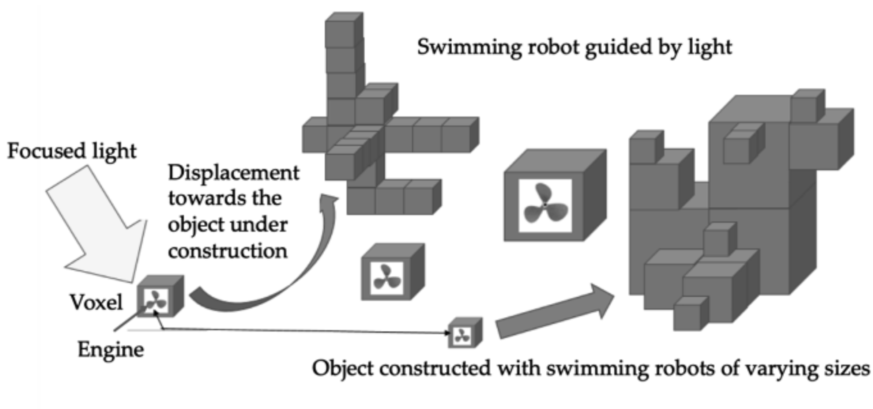


Figure 1.79. *Application of swimming robots to additive manufacturing, for example in light-induced polymerization*

Different guidance techniques can be considered, and they are presented in Table 1.10, widely inspired by Rao et al. (2015).

Principle of locomotion	Materials	Comments	References
Electrophoresis	Microspheres, bimetallic rods, fibers	Known mechanisms, self-generated electric field, sensitivity to the conductivity of the medium, high velocity > 100 $\mu m.s^{-1}$	Paxton et al. 2005; Wheat et al. 2010; Dou et al. 2016; Katuri et al. 2017; Brooks et al. 2019
Diffusio-phoresis	Heterogeneous voxel	Self-generated concentration gradient with enrichment of the carrier fluid with dissolved substances during the process (difficult to apply in additive manufacturing)	Howse et al. 2007; Ibele et al. 2009; Hong et al. 2010; Clement et al. 2016; Clement 2016
Thermo-phoresis	Nanoparticles	Gallium heated by NIR laser	Wang et al. 2021a
Separation	Colloid/ surfactant	Elimination of water molecules at the interface	Youssef et al. 2016
Chemo-taxicity	Gold nanoparticles	Glucose oxidase in the presence of glucose	He et al. 2019
Bubble propulsion	Elongated shapes	Catalysis of the decomposition of a reagent producing bubbles, but uncertain trajectory	Gibbs and Zhao 2009; Solovev et al. 2009; Wilson et al. 2012; Zhang et al. 2015a; Hu et al. 2017a; Patino et al. 2018
Electric field (1)	Micro-particles	Localized electrolysis of water producing bubbles, difficult precision and slow movements	Calvo-Marzal 2010; Loget and Kuhn 2011; Katuri et al. 2017; Rajonson et al. 2020
Electric field (2)	EAPS	Robot weighing about 100 g	Tang et al. 2017; Wang et al. 2019
Magnetic rotation	Flexible elongated shapes	Rotation of the swimmer in a magnetic field inducing locomotion, possible precision but slow speed	Ghosh and Fischer 2009; Gao et al. 2010, 2011; Peyer et al. 2012; Tottori et al. 2012; Li et al. 2016a; Shi et al. 2019; Wu et al. 2021
Ultrasound and acoustic waves	Metal particles Particles	Conversion of energy into motion, uncontrolled behavior, high speed Focus of the waves	Wang et al. 2012; Ahmed et al. 2016, 2017; Kong et al. 2019 Shapiro et al. 2021
Photochromy	Elongated shape	Spiropyrans or azobenzene are susceptible to light-induced Trans-Cis transitions resulting in flagellar movement	Huang et al. 2015; Stanton et al. 2015; Li et al. 2016b; Zhang et al. 2017a; Richard et al. 2018; Heckel and Simmchen 2019

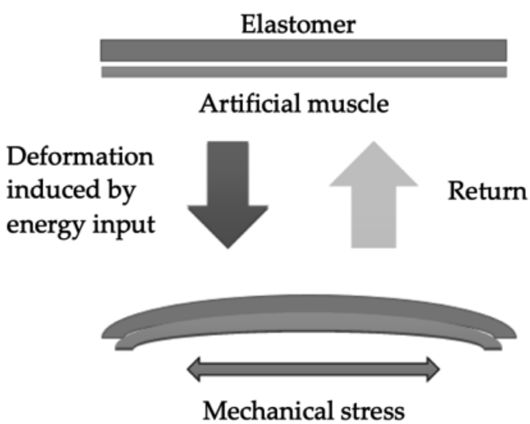
Table 1.10. *Different forms of propulsion for swimming robots*

For magnetic propellants, Li et al. (2016a, 2016b) give some indication of travel speeds by mode of action. These data are presented in Table 1.11.

Nature of the magnetic excitation	**Speed (µm.s^{-1})**	**Comments**
Internal oscillation of the particle	30.9	Fish-like movement
Oscillation	6-14.4	Sculling movement
Rotary feeder	18-40-180-250	Screw movement

Table 1.11. *Travelspeeds obtained by Li et al. (2016a)*

In the case of the Trans-Cis transformation of azobenzene related to a light-induced transformation, the engine is related to the voltage induced by the change in shape of the azobenzene in a sandwich structure, as shown in Figure 1.80. There is, with this type of device, a way to control the partial rotation of a flagellum attached to this engine, as shown in Figure 1.81 (Huang et al. 2015; see also Egunov et al. (2016)). If the stresses are not homogeneous in the different layers, a moment of force arises and the thin layers can then bend spontaneously under the action of external forces. Thus, by exploiting these stresses, a new “self-curling” material made with cross-linked Polydimethylsiloxane (PDMS), a transparent and biocompatible elastomer and silicone oil, can be realized.



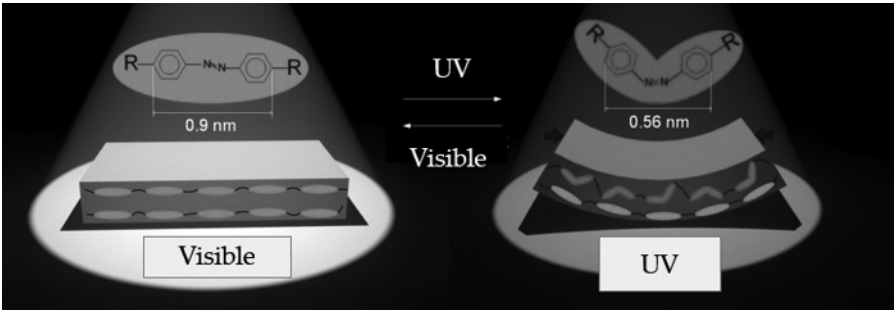


Figure 1.80. *Operating principle of the photochemical engine*

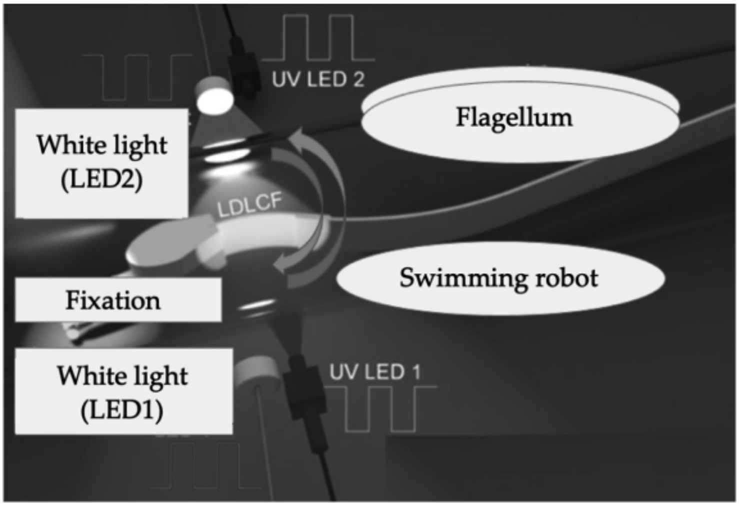


Figure 1.81. *Relationship between a photochemical engine and its flagellum*

In their publication, Khoo et al. (2015) performed a synthesis of applicable processes in terms of informed matter. A summary of their synthesis is shown in Table 1.12.

Materials and structures	Approximate resolution	Comments
Piezoelectric nanocomposites	5 μm	Production of electrical charges when stress is applied (and vice versa); the support material is a conventional acrylic polymer such as PEGDA
SMAs (NiTi)	/	Temperature-induced shape change (hysteresis problem to be taken into account)
SMPs	20 μm	Deformation of a bi-component system with different properties (bilayer effect) induced by temperature or light (heating)
Bimaterial system including a dielectric elastomer	30 +/– 10 μm	Electrical activation and bilayer effect
Polymeric composite and origami	45 +/– 15 μm	Temperature-induced movements

Table 1.12. *Some examples of informed materials applied in additive manufacturing*

1.4.5. *Current scientific offer and application specifications*

> We will simply note that the nature and size of the object studied, or the confrontation between adjacent objects, determine different levels of structuring of interdisciplinarity. (De Beaulieu 2006)

The current scientific context presents a particularly rich set of means to make shapes evolve or modify the functionalities of structures realized at least partially by additive manufacturing. It is therefore possible to think that the engineer and/or the designer have a large offer allowing them to regain control over the phenomena of manipulation of matter and energy so that the initial forms adapt, in the course of time, to their will(s). On the basis of KIS, publications deal either with objects that can unfold based on deformable origami – 2D printing followed by folding (Gillman et al. 2019), or with 3D objects containing massive amounts of matter that can be activated by different stimuli (pH, heat, light, electromagnetic field, mechanical, etc.). We are therefore moving, in principle, from a global approach to a more traditional methodology: creation of a 2D/3D part using different methods, including additive manufacturing with active materials, followed by localized stimulation in space and time to change the 2D or 3D shape of an object. Several methods can be selected in terms of reversible movements with different stimuli external to the 3D object (e.g. Ge et al. (2013), Sossou et al. (2019a, 2019b) and André (2017a)):

– Polymers sensitive to moisture, heat: either the polymer absorbs water or loses it, its density changes with a possible shrinkage (swelling/deflating). There are also reversible systems sensitive to heat (shape memory polymers) with changes in density.

– Photochemical "muscles": irradiation induces internal rotations in the material (classic example of azobenzene and derivatives), which contribute to modifying the geometry of the irradiated area, leading to deformations that depend on the luminous flux received; these can be reversible if photochromic materials are available (reversible transformation; bistability).

– With multi-material systems, it is possible to play on the difference in behavior of materials with a stimulation to produce "bimetal" or bimetal effects.

– With charged materials, an electromagnetic field can induce a charge orientation leading to a desired deformation of the 3D object, etc.

> I believe in evidence. I believe in observation, measurement, and reason when confirmed by independent observation. I can believe anything, no matter how strange and ridiculous, if there is proof. However, the stranger and more ridiculous the thing, the firmer and more solid the proof must be. (Asimov 1983)

Table 1.13 from the considerations presented in André (2017a) recalls the interests and limitations of homogeneous 4D printing. The knowledge of the synthetic results presented will then be used to consider prospective aspects regarding the scientific and technological developments of 4D printing.

While the offers of temporal evolutions are multiple, the following sections can, by the knowledge of the real and the possible, be the origin of certain difficulties, even frustrations because it is not always possible to satisfy the demand or the desire. This hiatus, which is quite general in this work, will be highlighted again with spectacular POC and applications that are not accessible (failure to meet "reasonable" industrial requirements). It is in this role of "shipwreckers" presented hereafter that we commit ourselves, defining by the conclusions to which it leads, a form of roadmap to follow if we do not wish to see a loss of interest from the socio-economy for this original technology.

4D printing	Comments
Advantages	- Sequential 2D process using a localized deposition of active material on a surface followed by folding leading to spectacular effects - Additive manufacturing process allowing an object to be manufactured *in a single step* and then to have more or less homogeneous actuation modes - Use of external stimulation modes to change the shape (see Figure 1.4) and/or the functionality of the object - Large number of stimulation modes (mechanical, heating, humidity, pH, light and other electromagnetic fields) - Large application domains (see Figure 1.5 for the use of 4D printing in terms of functionality) - Obvious spectacular aspect
Limitations	- Limited choice of active materials, with *very high deformation coefficients*, mainly polymers that must be *sufficiently elastic* to allow deformation and, consequently, with modest *mechanical properties* - Difficulty in locating the stimulation on the object - Anisotropy of the stimulation - *Size of the stimulation device* required to actuate the 4D object - *Long response time after stimulation*, incompatible with industrial uses - Stimulation energy that can damage the object - Anisotropy related to layer-by-layer fabrication mode - Durability - Modeling of volume deformations is difficult

Table 1.13. *Current advantages and limitations of 4D printing*

1.4.6. *Some constraints*

> Science discovers these laws of power, of motion, of transformation: industry applies them to the raw method, which the Earth provides us with in abundance, but which acquires its value only through knowledge. (Priestley 2015)

It is clear that the range of deformable systems is wide, without a specific path being favored today. In fact, reference is made to the POC in an emerging field which hides a certain number of scientific and technological problems to be solved. While the volume of the literature is rapidly increasing, the number of methods for deforming a macromolecule due to stimulation is limited to a few classical principles. Moreover, as the object is realized, the stimulus must reach the areas to be deformed, which for actuators may pose some space problems. This may be less constraining if the choice is turned to the use of light as a deformation stimulator (André 2018, 2018a; Li et al. 2019), as it is possible to selectively excite certain areas of the 3D object with great precision and distance. However, several problems, not mentioned in most of the literature on the topic, have emerged (and are mostly valid for other stimulation modes) (see André (2020a)).

1.4.6.1. *Mechanical strength (E: Young's modulus)*

In order to make an active object out of a single material, it is necessary that the material has a certain mechanical strength and also elastomeric properties to achieve a shape change. With Young's modulus of a few tens of MPa, classical in additive manufacturing, the forces necessary for a deformation of 1 mm of a bar of 1 cm, 0.1 mm thick and 1 mm wide are of the order of 2.10^{-4} N. Conventional polymer materials are therefore not suitable for deformation to realize an efficient actuator. Moreover, in the literature deformations are just shown, without too much mechanical or energetic potential associated with them (see, for example, Listek (2019)).

Young's modulus: Young's modulus, modulus of elasticity or tensile modulus is the constant that relates the tensile stress and the onset of deformation of an isotropic elastic material (linearity). Figure 1.82 (see: https://www.xr6805.fr/school/sti_web/rdm/deforme/deforme.htm) represents a beam resting on two supports with a concentrated load in the middle (see Thorin and Forêt (2013)).

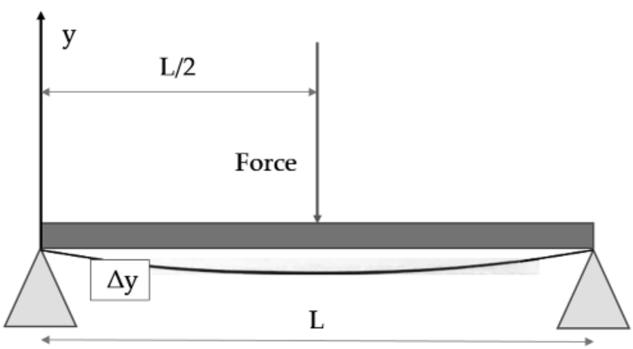


Figure 1.82. *Deformation of a beam as a function of its Young's modulus*

With F as the force exerted at the center, L as the length of the beam and E as the Young's modulus, the deflection Δy is expressed by: $\Delta y = \frac{FL^3}{48E}$. With conventional elastomers, a deformation Δy of 0.1 cm for a beam of size 1 cm (thickness and width: 0.1 cm) corresponds to an approximate load of 5×10^{-3} N. As for metal, the corresponding load is approximately 100–500 N.

1.4.6.2. *Quantum efficiency*

> I am just having fun. I was determined to do physics for fun, as I liked to do it. (Feynman 2000)

If we want to cause the rotation of a carbon-carbon or nitrogen-nitrogen double bond (case of compounds of the azobenzene family), it is necessary to absorb a photon of suitable energy (energies of the order of 400 kJ per mole or about 1 Megajoule/kg). But this process occurs with a quantum yield sometimes much lower than the unit. Regardless of the possibility of absorption on small elements (Beer-Lambert absorption law for a one-photon process), it is necessary that a large number of bonds are activated, which with a quantum yield of 0.5, for example, can lead to a very significant rise in local temperature. With a heat capacity of 2 J/g/°C, in the absence of energy transfer (conduction, convection, radiation), a temperature of 250°C can be reached! This critical situation raises the question of the choice of the light source's power, because the time associated with heat transfers can be a parameter to be considered.

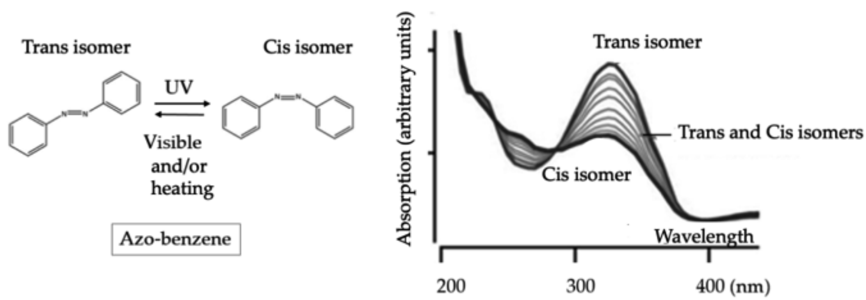


Figure 1.83. *Problems associated with light stimulation*

With one-photon light absorptions, the absorbed intensity follows a law of decreasing exponential in the simple cases, with more significant effects in the vicinity of the arrival of photons. It is then a complex nonlinear process whose modeling of the deformations remains difficult. Moreover, in the chemical system generally retained (which must be reversible) the compound Cis produced also absorbs (but less than the most stable compound, which is the Trans (see Figure 1.83)). It is the Trans-Cis passage which induces the deformation which is reversible by return of the Cis to the Trans, but the sharing of the incident photons is a factor of thermal rise of the medium. In reality, it is necessary to place ourselves in conditions where the thermal aspects can be neglected (small size actuators).

1.4.6.3. *Heat transfer (Fourier law)*

> The event is inseparable from the options to which it has given rise; it is that place constituted by often surprising choices that have modified customary distributions, groups, collectives, parties and communities, according to an unexpected division. (de Certeau 1994)

The materials selected in the literature are essentially polymers with low thermal conductivity. If heat is used to induce physical transformations of the object, the temperature must change in the mass of the material (which explains the choice of a stimulation by light). From an applicative point of view, the average characteristic time of heat transfer τ, inside the material assumed to be homogeneous, for a given distance d and a diffusion coefficient D_t, is defined by the following approximate law:

$$d = \sqrt{D_t \tau}$$

So with $D_t = 10^{-3}$ cm/s^2 for $d = 1$ cm, a heat transfer time of about 15 minutes!

> Fourier's law is a phenomenological law similar to Fick's law for the diffusion of matter or Ohm's law for electrical conduction. These three laws can be interpreted in the same way: the inhomogeneity of an intensive parameter (temperature, number of particles per unit volume, electric potential) causes a transport phenomenon that tends to fill the imbalance (thermal flow, diffusion current, electric current).

Box 1.13. *Fourier's law*

Lantada (2017) conducted an analysis of the response times of different active systems. Figure 1.84 from his synthesis confirms the considerations presented above. Given heat transfer coefficients about 100 times higher than for material transfers, strongly amplified effects are expected.

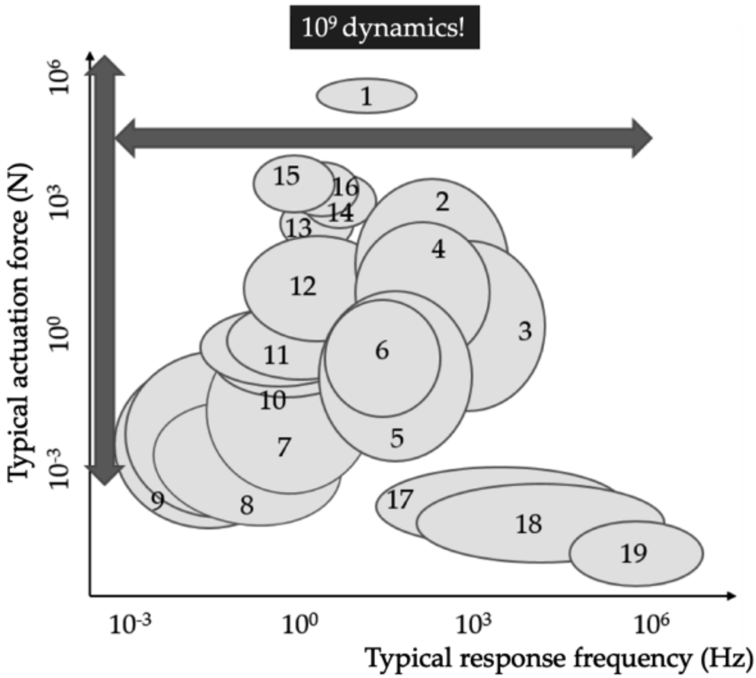


Figure 1.84. *Force-time response relationships in actuators: 1: magneto-resistive system; 2: biological muscles; 3: high-performance EAPs; 4: McKibben-type muscles; 5: SMP structures; 6: ceramic and polymer electroactive multilayers; 7: electroactive polymers; 8: hydroactive polymers; 9: shape memory foams; 10: SMPs; 11: ditto with fillers; 12: SMP + McKibben; 13: bi-metal; 14: tri-metal; 15: SMA; 16: SMA + Peltier effect; 17: MEMS; 18: magnet-MEMS; 19: NEMS*

1.4.6.4. *Material transfer (Fick's law)*

Material transfers are generally between 10 and 100 times slower than heat transfers. The possible effects will therefore be very slow. This is what happens, for example, when a deformation is induced by the pH, requiring the diffusion of H+ atoms in the solid material, or the transfer of a solvent inside a polymeric matrix. Therefore, with $D_m = 10^{-6}$ cm^2/s for $d = 1$ cm, a material transfer time is of the order of 10 days (but only 0.01 second for a distance of 1 µm). Apart from these "average time" aspects, which already illustrate a problem that is difficult to deal with, there are aspects related to the thicknesses crossed: for sensitive materials, the effect of humidity, for example, close to the arrival of water molecules, will start much earlier than for materials placed deeper. Moreover, delay phenomena can appear with active materials which have space-dependent material diffusion coefficients.

Moreover, over the course of time, micro-fractures can appear within the material(s), significantly modifying the transport processes or the diffusion coefficients.

Within these two time-consuming areas are internal elements that are largely related to materials. These consume internal energy or extract energy from stimuli to move/deform and generate forces for spatial change of passive structures. Non-equilibrium effects are related to creep as in linear polymers or filaments.

> The interplay between activity and conformational degrees of freedom gives rise to new structural and dynamic features of individual polymers, as well as interacting assemblies. (Winkler and Gompper 2020)

The properties of active materials depend on the coupling of the stimulated process with the conformational degrees of freedom of macromolecular structures associated with the coupled presence of local steric and hydrodynamic interactions that result in "time-consuming" conformational and dynamic properties. These two antagonistic effects probably play a role in the response time of the active structures and in the maintenance in time of their mechanical actuation properties; for the moment, the literature is, on this problem, relatively silent. It would undoubtedly be useful to examine the importance of the flexible modes corresponding to conformational fluctuations in connection with intra-macromolecular interactions.

1.4.6.5. *Manufacturing anisotropy*

> Disruption is not a fad, not a trend, it is our new paradigm. (Mallard 2018)

If an object is made by stereolithography (for the moment with 1 photon), the light arriving on the surface to be polymerized is more absorbed at the surface than at depth (André 2017). The part present toward the surface is thus more polymerized (or even rigidified) than the areas located deeper. Under these conditions, the elasticity of materials, active or not, depends on spatial parameters. If we try to use actuation modes exploiting light (case of azobenzene type compounds, for example), the photons can contribute simultaneously to a hardening of the resins and to the desired deformation. This situation is thus not, a priori, the most recommendable! In other modes (molten wire in particular), it is the anisotropy of the deposit that leads to the desired deformation effect.

It is therefore not possible to separate the manufacturing process from the desired 4D effect. Moreover, these examples show the difficulty of a good programming of the relations amplitude of the stimulation – an effect on the changes of form and/or the functionality.

1.4.6.6. *Other problems*

> One must be willing to scuttle in order to comply with the requirement imposed by the disruptors […]. But to scuttle, you need a vision. (Mallard 2018)

Not mentioned here are other problems that would have to be considered: that of the mathematical control of deformations (considered for massive materials as very difficult by Weeger et al. (2019) and Ding et al. (2019)), of the optimal design, nor of the response time and local amplitudes of the stimulations in the active material, nor of the footprint of the stimulus generating system. Figure 1.80 illustrates one of the difficulties of exploiting 4D printing: knowing the properties of the materials under stimulation, how and where to position the active voxels in an inert supporting material, how to calculate the local flows in time and space of energetic stimulation (advantageously using light?) for a 3D object to move from one shape to another, from one functionality to another? This work is beginning to be approached in simple model situations. At best, it only concerns grid structures, as shown in Figure 1.85.

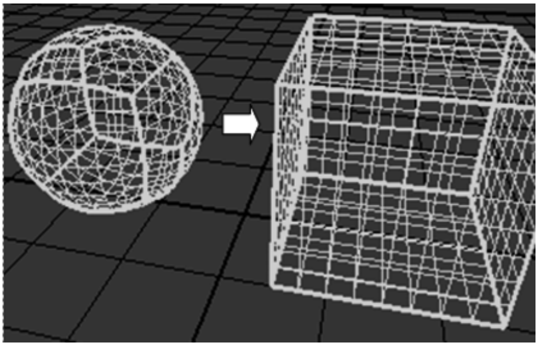


Figure 1.85. *The issue of modeling shape change by stimulation: the "possible" case of a structure composed of segments*

These elements define real limits to the development of 4D printing. For example, for low response times, it would be necessary to produce very small objects, or perhaps to use optical (stereolithography technique) or electromagnetic (wire fusion process) stimulations, for which we know how to have time bases adapted to the demand. In any case, these technological constraints are areas of research to be conducted to push 4D printing toward an industrial technology.

1.5. And tomorrow?

> Scientists founded, beyond the production of knowledge, systems of action that influence nature and society, systems of value that inspire norms and ideals, systems of representation on which discourses and postures of authority are based. (Rasmussen 2015)

The most common liquid crystals are formed by amphiphilic molecules. The specific forces involved in these crystals are thought by NAP (2019b) to be atypical (Davidson et al. 2015; Zhou 2017). This results in unusual conformations and functionalities (Jeong et al. 2015). For example, the ferro-nematic liquid crystal phase (a liquid exhibiting long-range ferromagnetic order coexisting with nematic order) was created by dispersing ferromagnetic nano-disks with magnetic moments normal to their flat planes in a conventional nematic. After further treatments, the magnetic excitations are overdamped and would not exhibit the dispersion observed in the traditional way. It is with such modes of action that new ways of using liquid crystals have opened up, in particular for chemical and gas sensors. These advances are based on the disruption of liquid crystal orientations at the liquid crystal/solid or liquid crystal/air interface, caused by the product to be measured. If this type of behavior has not, to the authors' knowledge, been directly exploited for 4D printing, it is not the case for elastomeric crystals.

In another domain, granular materials are aggregates of individually solid grains that interact with their neighbors via contact forces. Their properties do not depend significantly on temperature and they do not explore the many internal configurations of systems in thermal equilibrium (they are non-ergodic). One of the most remarkable properties of granular materials is their ability to change from a fluid to a solid state by simply applying pressure or, equivalently, by increasing the volume fraction of the constituent particles. Moreover, according to their radial distribution function (for mono-dispersed hard spheres) the space can be filled with a variable number of spheres, as illustrated in Figure 1.86 (in statistical mechanics, the radial distribution function, classically noted g(r), describes, in a particle system, how the density varies as a function of the distance from a reference particle). In fact, between materials and their forms, there are, independently of the modes of stimulation, an infinite number of possibilities. Let us recall Friedman (2018) who wrote: "I do not know reality, but it seems to me that it cannot be faced otherwise than by the image". 4D printing makes us see, so it is an excellent laboratory to try.

NAP (2019b) shows that non-spherical and same-sized particles with more exotic shapes can jam under their own weight. This area falls under random architecture (Keller and Jaeger 2016), but, to the authors' knowledge, has not yet been applied in 4D printing.

Figure 1.86. *Density related to regular stacks of spheres (according to http://villemin.gerard.free.fr/Wwwgvmm/Geometri/SpheEmpi.htm)*

Thus, regardless of the form (e.g. metamaterials) the exploration of systems that can evolve under the influence of stimulation is probably not complete. It would be interesting to examine whether transitions linked to regular voxel stacks (heterogeneous or hybrid 4D) can be at the origin of original 4D printing, provided that we have first solved the questions of printability.

How do we know that we will find the right threesomes between materials, local and global forms (3D printing) and stimuli that meet the specifications in this almost infinite (and largely unexplored) world? Will we have to develop anticipatory thinking on new possibilities of action, using a complex analysis of weak signals? Or will we have to work with trial and error methods? Perhaps the future will tell us.

> According to Schoemaker et al. (2012): a weak signal is “isolated information that, at first glance, is akin to background noise, but when studied through another analytical framework, or linked to other information, can ultimately be understood as part of an important informational pattern for the organization”.

Box 1.14. *Weak signals*

> [Universities] do the basic research that large companies no longer do and assume the risks and part of the cost of that work. (Lécuyer 2015)

> Engineering is also, in its own way, about working your way through the space of all possible solutions to a problem, climbing from solution to solution, each better than the last, until you reach the optimal solution. (Benyus 2017)

> Science is in fact entering a transitional phase. It was historically anchored in Cartesian principles of duality and reductionism defined by empirical facts that can be apprehended by the senses. (Vinardi 1980)

1.6. References

3ders.org (2014). Chinese test self-forming liquid metal seeing a Terminator like future [Online]. Available at: http://www.3ders.org/articles/20140304-chinese-test-self-forming-liquid-metal-seeing-a-terminator-like-future.html [Accessed 5 May 2022].

Abadie, J., Chaillet, N., Lexcellent, C. (2009). Modeling of a new SMA-micro-actuator for active endoscopy applications. *Mechatronics*, 19, 437–442.

Abba, G. (2012). Comparaison des actionneurs [Online]. Available at: https://sam.ensam.eu/bitstream/handle/10985/9238/LCFC_RAPP_2012_ABBA;sequence=1.

Abdelmohsen, S., Adriaenssens, S., El-Dabaa, R., Gabriele, S., Olivieri, L., Teresi, L. (2019). A multi-physics approach for modeling hygroscopic behavior in wood low-tech architectural adaptive systems. *Computer-Aided Design*, 106, 43–53.

Abtan, A.A. (2019). Design and fabrication of origami elements for use in a folding robot structure. PhD Thesis, University of Leeds [Online]. Available at: http://etheses.whiterose.ac.uk/26458/1/Akeel%20Abtan%20Thesis%20Final%20V.pdf.

Adam, G., Benouhiba, A., Rabenorosoa, K., Clévy, C., Cappelleri, D.J. (2021). 4D printing: Enabling technology for micro-robotics applications. *Advances in Intelligent Systems*, 2000216.

Ahmady, S. (2017). Vers une informatique moléculaire ? [Online]. Available at: https://www.anthropotechnie.com/vers-une-informatique-moleculaire/.

Ahmed, D., Baasch, T., Jang, B., Pane, S., Dual, J., Nelson, B.J. (2016). Artificial swimmers propelled by acoustically activated flagella. *Nano Letters*, 16, 4968–4974.

Ahmed, D., Baasch, T., Blondel, N., Läubli, N., Dual, J., Nelson, B.J. (2017). Neutrophil-inspired propulsion in a combined acoustic and magnetic field. *Nature Communications*, 8, 770.

Ahmed, Z., Biffi, A., Hass, L., Bos, F., Salet, T. (2020). 3D concrete printing – Free form geometries with improved ductility and strength. *RILEM Book-series*, 28, 741–756.

Akbaria, S., Sakhaei, A.H., Panjwani, S., Kowsaric, K., Ge, Q. (2021). Shape memory alloy based 3D printed composite actuators with variable stiffness and large reversible deformation. *Sensors and Actuators A: Physical*, 321, 112598.

Alain (1985). *Propos sur le Bonheur*. Gallimard, Paris.

Alief, N.A., Utomo, M.S., Kartika, I., Whulanza, Y. (2019). Geometric and mechanical performance of multi-material fused deposition modelling. *IOP Conferences Series: Materials Science and Engineering*, 557, 012022.

Alison, L., Menasce, S., Bouville, F., Tervoort, E., Mattich, J., Ofner, A., Studart, A.R. (2019). 3D printing of sacrificial templates into hierarchical porous materials. *Scientific Reports*, 9, 409.

Almethen, A., Michail, O., Potapov, I. (2019). Pushing lines helps: Efficient universal centralized transformations for programmable matter. arXiv: 1904.12777v1.

Alouges, F. (2012). La natation dans le miel ou l'Hélium liquide : un problème de contrôle linéaire et sans drift [Online]. Available at: http://smai.emath.fr/canum2012/resumesPDF/alouges/Abstract.pdf.

Alouges, F., De Simone, A., Lefebvre, A. (2008). Swimming at low Reynolds number at optimal strokes: An example. *Journal of Nonlinear Science*, 18, 277–302.

Altenhofen, C., Luu, T.H., Grasser, T., Dennstädt, M., Mueller-Roemer, J.S., Weber, D., Stork, A. (2018). Continuous property gradation for multi-material 3D-printed objects. *Solid Freeform Fabrication 2018: Proceedings of the 29th Annual International Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference* [Online]. Available at: https://www.cuttlefish.de/assets/publications/urn_nbn_de_0011-n-512629-10.pdf.

Alvarez Palacio, J.M. (2020). Control of an ultra-lightweight inflatable arm driven by fabric pneumatic actuators. PhD Thesis, École Nationale Supérieure d'Arts et Métiers, Paris.

Alvaro, M. (2004). Auto-organisation, autonomie et identité. *Revue internationale de philosophie*, 228, 135–150.

Ando, M., Birosz, M., Jeganmohan, S. (2021). Surface bonding of additive manufactured parts from multi-colored PLA materials. *Measurement*, 169, 108583.

André, J.C. (2017a). Impression 3D : niches applicatives porteuses. *Techniques de l'Ingénieur*, Ref. BM7970 V1.

André, J.C. (2017b). *From Additive Manufacturing to 3D/4D Printing 1: From the First Concept to the Present Applications*. ISTE Ltd, London, and John Wiley & Sons, New York.

André, J.C. (2017c). *From Additive Manufacturing to 3D/4D Printing 2: Improvement of the Present Technologies and Constraints*. ISTE Ltd, London, and John Wiley & Sons, New York.

André, J.C. (2017d). *From Additive Manufacturing to 3D/4D Printing 3: Breakdown Innovations: Programmable Matter; 4D Printing and Bio-Printing*. ISTE Ltd, London, and John Wiley & Sons, New York.

Arendt, H. (1972). *Le corail de la vie*. Éditions Payot & Rivages, Paris.

Arendt, H. (1989). *La crise de la culture*. Poche, Paris.

Ariès, P. (2010). *La simplicité volontaire contre le mythe de l'abondance*. La Découverte, Paris.

Aristotle (2012). *Aristotle's Nicomachean Ethics*. University of Chicago Press, Chicago.

Armstrong, C.D., Todd, N., Alsharhan, A.T., Bigio, D.I., Sochol, R.D. (2020). A 3D printed morphing nozzle to control fiber orientation during composite additive manufacturing. *Advanced Materials Technology*, 6, 2000829.

Asimov, I. (1983). *The Roving Mind*. Prometheus Books, New York.

Aurenhammer, F. and Klein, R. (2000). Voronoi diagrams, C5. In *Handbook of Computational Geometry*, Sack J. and Urrutia, G. (eds). Elsevier Science Publishing, New York.

Aziz, S., Villacorta, B., Naficy, S., Salahuddin, B., Gao, S., Baigh, T.A., Sangian, D., Zhu, Z. (2021). A microwave powered polymeric artificial muscle. *Applied Materials Today*, 23, 101021.

Azoti, W.L. (2012). Conception et amélioration des propriétés amortissantes des composites auxétiques basées sur l'utilisation des outils de la micromécanique. Thesis, Université de Lorraine [Online]. Available at: http://docnum.univ-lorraine.fr/public/DDOC_T_2012_0218_AZOTI.pdf.

Baca, D. and Ahmad, R. (2020). The impact on the mechanical properties of multi-material polymers fabricated with a single mixing nozzle and multi-nozzle systems via fused deposition modeling. *The International Journal of Advanced Manufacturing Technology*, 106, 4509–4520.

Baek, K., Chung, I., Shin, H., Cho, M. (2021). Multiscale study for the temperature effect on the mechanical properties and fatigue crack growth rate of polyamide 66. *Extreme Mechanics Letters*, 43, 101154.

Baert, A.E. (2003). Réseaux cellulaires de Voronoï [Online]. Available at: https://isdm.univ-tln.fr/PDF/isdm13/isdm13a113_baert.pdf.

Bai, R., Yang, J., Suo, Z. (2019). Fatigue of hydrogels. *European Journal of Mechanics – A/Solids*, 74, 337–370.

Bakar, M. and Djaider, F. (2007). Effect of plasticizers content on the mechanical properties of unsaturated polyester resin. *Journal of Thermoplastic Material*, 20, 53–64.

Bakarich, S.E., Gorkin III, R., in het Panhuis, M., Spinks, G.M. (2015). 4D printing with mechanically robust, thermally actuating hydrogels. *Macromolecular Rapid Communication*, 36, 1211–1217.

Baker, A.B., Wass, D.F., Trask, R.S. (2016). 4D sequential actuation: Combining iono-printing and redox chemistry in hydrogels. *Smart Materials and Structures*, 25, 10LT02.

Balla, V.K., Dattatreya Tadimeti, J.G., Kate, K.H., Satyavolu, J. (2020). 3D printing of modified soybean hull fiber/polymer composites. *Materials Chemistry and Physics*, 254, 123452.

Ballandras, S., Calin, M., Zissi, S., Bertsch, A., André, J.C., Bourjault, A., Hauden, D. (1996). Actionneurs miniatures à alliages à mémoire de forme fabriqués par micro-stéréo-photolithographie. *J. Phys. III France*, 6, 1759–1774.

Bandari, V.K., Nan, Y., Karnaushenko, D., Hong, Y., Sun, B., Striggow, F., Karnaushenko, D.D., Becker, C., Faghih, M., Medina-Sánchez, M. et al. (2020). A flexible microsystem capable of controlled motion and actuation by wireless power transfer. *Nature Electronics*, 3, 172–180.

Baquiast, J.P. (2004). La morphogénèse [Online]. Available at: http://www.automatesintelligents.com/echanges/2004/jan/morphogenese.html.

Bar-Cohen, Y. (2004). *Electroactive Polymer (EAP) Actuators as Artificial Muscles: Reality, Potential, and Challenges*. SPIE, Bellingham.

Baran, I., Cinar, K., Ersoy, N., Akkerman, R., Hattel, J.H. (2017). A review on the mechanical modeling of composite manufacturing processes. *Archives on Computational Methods in Engineering*, 24, 365–395.

Bastola, A.K., Paudel, M., Li, L. (2018). Development of hybrid magnetorheological elastomers by 3D printing. *Polymer*, 149, 213–228.

Baudrillard, J. (1978). *Le système des objets*. Gallimard, Paris.

Bedel, A., Coudert-Osmont, Y., Martínez, J., Islam Nishat, R., Whitesides, S., Lefebvre, S. (2021). Closed space-filling curves with controlled orientation for 3D printing [Online]. Available at: https://hal.inria.fr/hal-03185200/document.

Beli, D., Fabro, A.T., Ruzzene, M., Arruda, J.R.F. (2019). Wave attenuation and trapping in 3D printed cantilever-in-mass metamaterials with spatially correlated variability. *Scientific Reports*, 9, 5617 [Online]. Available at: https://www.nature.com/articles/s41598-019-41999-0.

Bent, A.A. and Hagood, N.W. (1997). Piezoelectric fiber composites with interdigitated electrodes. *Journal of Intelligent Marterial, Systems and Structures*, 8, 903–919.

Benyus, J. (2017). *Biomimétisme : quand la nature inspire des innovations durables*. Rue de l'Échiquier, Paris.

Bernard, S.S., Suresh, G., Srinivasan, T., Srinivasan, S., Kaarmugilan, N., Naveed, L.M., Kiranmouli, N., Mahalakshmi, C.S. (2021). Analyzing the mechanical behavior of sisal fiber reinforced IPN matrix. *Materials Today: Proceedings*, 45, 569–572.

Berry, M. (2019). L'hyper-puissance de l'informatique. In *Les promesses de la science*, Chauvière, F. (ed.). Flammarion, Paris.

Bessen, J., Denk, E., Kim, J., Righi, C. (2020). Declining industrial disruption. Research Paper, 20–28 [Online]. Available at: https://ssrn.com/abstract=3682745 and http://dx.doi.org/10.2139/ssrn.3682745.

Bhatti, M.R.A., Bilotti, E., Zhang, H., Varghese, S., Verpaalen, R.C.P., Schenning, A.P.H.J., Bastiaansen, C.W.M., Peijs, T. (2020). Ultra-high actuation stress polymer actuators as light-driven artificial muscles. *ACS Applied Materials and Interfaces*, 12, 33210–33218.

Biet, M. (2007). Conception et contrôle d'actionneurs électro-actifs dédiés à la stimulation tactile. Thesis, Université de Lille [Online]. Available at: https://ori-nuxeo.univ-lille1.fr/nuxeo/site/esupversions/ddfa21ea-890d-4b48-9182-78bd18dfdcf5.

Billon, N. (2007). Comportement mécanique des polymères [Online]. Available at: http://mms2.ensmp.fr/mat_paris/deformation/transparents/Amphi_Deformation_Polymeres_2007.pdf.

Billon, N. and Bouvard J.L. (2015). Propriétés et comportement mécanique des polymères thermoplastiques. *Techniques de l'Ingénieur*, Ref. AM3115.

Bodaghi, M. and Liao, W.H. (2019). 4D printed tunable mechanical metamaterials with shape memory operations. *Smart Materials and Structures* [Online]. Available at: http://irep.ntu.ac.uk/id/eprint/36143/1/13638_Bodaghi.pdf.

Bodaghi, M., Damanpack, A.R., Liao, W.H. (2017a). Adaptive metamaterials by functionally graded 4D printing. *Materials & Design*, 135, 26–36.

Bodaghi, M., Damanpack A.R., Hu G.F., Liao W.H. (2017b). Large deformations of soft metamaterials fabricated by 3D printing. *Materials & Design*, 131, 81–91.

Bodkhe, S., Vigo, L., Zhu, S., Testoni, O., Aegerter, N., Ermanni, P. (2020). 3D printing to integrate actuators into composites. *Additive Manufacturing*, 35, 101290.

Boissonnat, J.D. (2010). Convex hulls, Voronoi diagrams and Delaunay triangulations. Winter School on Algorithmic Geometry, ENS-Lyon [Online]. Available at: http://www.ens-lyon.fr/LIP/Arenaire/ERGeoAlgo/JDB-ens-lyon-I.pdf.

Boni, C. and Royer-Carfagni, G. (2021). Equilibrium of bi-stable flexural-tensegrity segmental beams. *Journal of the Mechanics and Physics of Solids*, 152, 104411.

Borshch, V., Kim, Y.K., Xiang, J., Gao, M., Jákli, A., Panov, V.P., Vij, J.K., Imrie, C.T., Tamba, M.G., Mehl, G.H. et al. (2013). Nematic twist-bend phase with nanoscale modulation of molecular orientation. *Nature Communications*, 4, 2635.

Bounouira, F. (2015). Les gels, aspects théoriques et applications. Pharmacy Thesis, Université Mohammed V de Rabat, Morocco [Online]. Available at: http://ao.um5.ac.ma/xmlui/bitstream/handle/123456789/14759/P%2007-2015.pdf?sequence=1&isAllowed=y.

Bourcier, D. and Van Andel, P. (2017). *C'est quoi la sérendipité ?* Le courrier du livre, Paris.

Boydston, A.J., Cao, B., Nelson, A., Ono, R.J., Saha, A., Schwartz, J.J., Hrasher, C.J. (2018). Additive manufacturing with stimuli-responsive materials. *Journal of Material Chemistry*, A6, 20621.

Boyraz, P., Runge, G., Raatz, A. (2018). An overview of novel actuators for soft robotics. *Actuators*, 7, act7030048.

Bréguet, J.M. (1998). Actionneurs "stick and slip" pour micromanipulateurs. EPFL Thesis, Lausanne.

Bristol University (2021). £2M ERC grant awarded to Professor Fabrizio Scarpa from the Bristol Composites Institute [Online]. Available at: https://www.bristol.ac.uk/engineering/news/2021/fabrizio-scarpa-erc-grant.html.

Broch, H. (1985). James Joyce et le temps présent. In *Création littéraire et connaissance*, Broch, H. (ed.). Gallimard, Paris.

Brooks, A.M., Tasinkevych, M., Sabrina, S., Velegol, D., Sen, A., Bishop, K.J.M. (2019). Shape-directed rotation of homogeneous micro-motors via catalytic self-electrophoresis. *Nature Communications*, 10, 495.

Bruno, G. (2020). *De la magie*. Allia, Paris.

Bückmann, T., Kadic, M., Schittny, R., Wegener, M. (2015). Mechanical metamaterials with anisotropy and negative effective mass density tensor made from one constituent material. *Physics Status Solidi*, 252B, 167–174.

Buriak, I.A., Zhurba, V.O., Vorobjov, G.S., Kulizhko, V.R., Kononov, O.K., Rybalko, O. (2016). Metamaterials: Theory, classification and application strategies (review). *Journal of Nano- and Electronic Physics*, 8, 04088.

Caddock, B.D. and Evans, K.E. (1989). Microporous materials with negative Poisson's ratios – Microstructure and mechanical properties. *Journal of Physics D: Applied Physics*, 22, 1877.

Callens, S.J.P., Tümer, N., Zadpoor, AA. (2019). Hyperbolic origami-inspired folding of triply periodic minimal surface structures. *Applied Material Today*, 15, 453–461.

Calvo-Marzal, P., Sattayasamitsathit, S., Balasubramanian, S., Windmiller, J.R., Dao, C., Wang, J. (2010). Chemical sensing based on catalytic nano-motors: Motion-based detection of trace silver. *Chemical Communications*, 46, 12082–12083.

Campbell, D.T. (1974). Downward causation in hierarchically organized biological system. In *Studies in the Philosophy of Biology*, Ayala, F. and Dobzhansky, T. (eds). University of California Press, Berkeley.

Cao, J., Fan, W., Zhou, Q., Sheu, E., Liu, A., Barrett, C., Wu, J. (2010). Colossal thermal-mechanical actuation via phase transition in single-crystal VO2 micro-cantilevers. *Journal of Applied Physics*, 108, 083538.

Carrell, J., Gruss, G., Gomez, E. (2020). Four-dimensional printing using fused-deposition modeling: A review. *Rapid Prototyping Journal*, 5, 855–869.

Carrico, J.D., Hermans, T., Kim, K.J., Leang, K.K. (2019). 3D-printing and machine learning control of soft ionic polymer-metal composite actuators. *Scientific Reports*, 9, 17482.

Catry, R., Mohand-Ousaid, A., Rakotondrabe, M., Lutz, P. (2020). Presentation, modeling and experiments of an electrostatic actuator based catom for programmable matter. *Actuators*, 9, 43.

CDiscount (2017). Jouet magique avec impression forme 3D [Online]. Available at: http://www.cdiscount.com/juniors/jeux-de-societe-cartes/jouet-magique-avec-impression-forme-3d/f-12079-gen6922263311393.html.

Cera, L., Gonzalez, G.M., Liu, Q., Choi, S., Chantre, C.O., Lee, J., Gabardi, R., Choi, M.C., Shin, K., Parker, K.K. (2021). A bioinspired and hierarchically structured shape-memory material. *Nature Materials*, 20, 242–249.

Cheang, U.K. and Kim, M.J. (2016). Fabrication and control of simple low Reynolds number micro-swimmers. *Applied Physics Letters*, 109, 034101.

Chen, M., Zhong, M., Johnson, J.A. (2016). Light-controlled radical polymerization: Mechanisms, methods, and applications. *Chemical Review*, 116(17), 10167–10211.

Chen, T., Bilal, O.R., Lang, R., Daraio, C., Shea, K. (2018). Autonomous deployment of a solar panel using an elastic origami and distributed shape memory polymer actuators. arXiv:1810.08978v1.

Chen, X., Liu, X., Ouyang, M., Chen, J., Taiwo, O., Xia, Y., Childs, P.R.N., Brandon, N.P., Wu, B. (2019). Multi-metal 4D printing with a desktop electrochemical 3D printer. *Scientific Reports*, 9, 3973.

Chen, D., Liu, Q., Geng, P., Tang, S., Zhang, J., Wen, S., Zhou, Y., Yan, C., Han, Z., Shi, Y. (2021a). A 4D printing strategy and integrated design for programmable electroactive shape-color double-responsive bionic functions. *Composites Science and Technology*, 208, 108746.

Chen, H., Zhang, F., Sun, Y., Sun, B., Gu, B., Leng, J., Zhang, X. (2021b). Electro-thermal shape memory behavior and recovery force of four-dimensional printed continuous carbon fiber/poly-lactic acid composite. *Smart Materials and Structures*, 30, 025040.

Cheng, F., Zhang, Y., Yin, R., Yu, Y. (2010). Visible light induced bending and unbending behavior of crosslinked liquid-crystalline polymer films containing azotolane moieties. *Journal of Material Chemistry*, 20, 4888–4896.

Cherry, K.M. and Qian, L. (2018). Scaling up molecular pattern recognition with DNA-based winner-take-all neural networks. *Nature*, 5, 370–376.

Chluba, C., Ge, W., Lima de Miranda, R., Strobel, J., Kienle, L., Quandt, E., Wuttig, M. (2015). Ultralow-fatigue shape memory alloy films. *Science*, 348, 1004–1007.

Choi, J.B. and Lakes, R.S. (1992). Non-linear properties of metallic cellular materials with a negative Poisson's ratio. *Journal of Materials Science*, 27, 5375–5381.

Choi, M.Y., Shin, Y., Lee, H.S., Kim, S.Y., Na, J.H. (2020). Multipolar spatial electric field modulation for freeform electroactive hydrogel actuation. *Scientific Reports*, 10, 2482.

Chortos, A., Hajiesmaili, E., Morales, J., Clarke, D.R., Lewis, J.A. (2019). 3D printing of interdigitated dielectric elastomer actuators. *Advanced Functional Materials*, 1907375.

Christensen, C.M. (1997). *The Innovator's Dilemma*. Harvard Business School Press, Boston.

Chu, H., Yang, W., Sun, L., Cai, S., Yang, R., Liang, W., Yu, H., Liu, L. (2020). 4D printing: A review on recent progresses. *Micromachines*, 11, 796.

Chung, H.J., Parsons, A.M., Zheng, L. (2021). Magnetically controlled soft robotics utilizing elastomers and gels in actuation: A review. *Advances in Intelligent Systems*, 3, 2000186.

Church, D.C., Peterson, G.I., Boydston, A.J. (2014). Comparison of mechanochemical chain scission rates for linear versus three-arm star polymers in strong acoustic fields. *ACS Macro Letters*, 3, 648–651.

Cianchetti, M. (2013). Fundamentals on the use of shape memory alloys in soft robotics. In *Interdisciplinary Mechatronics*, Habib, M.K. and Davim, J.P. (eds). ISTE Ltd, London, and John Wiley & Sons, New York.

Citton, Y. (2016). Accélérer notre attention collective aux hyper-objets. In *Accélération !*, de Sutter, L. (ed.). PUF, Paris.

Clément, E. (2016). The microfab/microlab (MiFaMiLab) platform at ESPCI. Paper, Nanoscale 3D Printing Workshop, Singapore, 1–2 December.

Clément, E., Lindner, A., Douarche, C., Auradou, H. (2016). Bacterial suspensions under flow. *European Physics Journal – Special Topics*, 225, 2389.

CNRS (2016). Jean-Pierre Sauvage, un Nobel pour les machines moléculaires [Online]. Available at: https://lejournal.cnrs.fr/articles/jean-pierre-sauvage-un-nobel-pour-les-machines-moleculaires.

Cohades, A. and Michaud, V. (2018). Shape memory alloys in fiber-reinforced polymer composites. *Advanced Industrial and Engineering Polymer Research*, 1, 66–81.

Collin, J.P., Dietrich-Buchecker, R., Sauvage, J.P. (2001). Vers des machines et des moteurs moléculaires. *Actualité Chimique*, 6(247), 27–32.

Coltelli, M.A., Catterlin, J., Scherer, A., Kartalov, E.P. (2021). Simulations of 3D-printable biomimetic artificial muscles based onmicrofluidic microcapacitors for exoskeletal actuation and stealthy underwater propulsion. *Sensors and Actuators*, A325, 112700.

Comte-Sponville, A. (2015). *La France 3.0 – Agir, espérer, réinventer*. Odile Jacob, Paris.

Coulais, C., Teomy, E., de Reus, K., Shokef, Y., van Hecke, M. (2016). Combinatorial design of textured mechanical metamaterials. *Nature*, S35, 529–535.

Couveinhes, P. (2012). Editorial. In *Les robots : nouveaux concepts, nouveaux usages*, Roure, F. and Arcier, L. (eds). Annales des Mines – Réalités industrielles, Paris.

Crano, J.C. and Guglielmetti, R.J. (1999). *Organic Photochromic and Thermochromic Compounds: Main Photochromic Families*. Plenum Publishing Co., New York.

Crawford, M. (2015). 4D printing, the next level of additive manufacturing [Online]. Available at: https://www.asme.org/engineering-topics/articles/manufacturing-processing/4d-printing-next-level-additive-manufacturing.

Crozier, M. and Tillette, B. (2000). *Quand la France s'ouvrira*. Fayard, Paris.

Cueff, M. (2011). Micro-actionneurs piézo-électriques. Thesis, Université de Grenoble [Online]. Available at: https://tel.archives-ouvertes.fr/tel-00716847/document.

Cui, T.J., Smith, D., Liu, R. (2010). *Metamaterials – Theory, Design, and Applications*. Springer Verlag, New York.

Cui, T.J., Qi, M.Q., Wan, X., Zhao, J., Cheng, Q. (2014). Coding metamaterials, digital metamaterials and programmable metamaterials. *Light: Science & Applications*, 3, e218.

Curatolo, M., Nardinocchi, P., Teresi, L. (2021). Mechanics of active gel spheres under bulk contraction. *International Journal of Mechanical Sciences*, 193, 106147.

D'Espagnat, B.L. (2015). *A la recherche du réel : le regard d'un physicien*. Dunod, Paris.

Dadbakhsh, S., Speirs, M., Kruth, J.P., Schrooten, J., Luyten, J., Van Humbeeck, J. (2014). Effect of SLM parameters on transformation temperatures of shape memory nickel titanium parts. *Advanced Engineering Materials*, 16, 1140–1146.

Dai, L., Ma, M., Xu, J., Si, C., Wang, X., Liu, Z., Ni, Y. (2020). All-lignin-based hydrogel with fast pH-stimuli responsiveness for mechanical switching and actuation. *Chemistry in Materials*, 32, 4324–4330.

Darwin, C. (2020). *Le corail de la vie*. Rivages Poche, Paris.

Davidson, Z.S., Kang, L., Jeong, J., Still, T., Collings, P.J., Lubensky, T.C., Yodh, A.G. (2015). Chiral structures and defects of lyotropic chromonic liquid crystals induced by saddle-splay elasticity. *Physical Review*, E91, 050501.

De Beaulieu, J.L. (2006). Itiniréraires de palynologues, pratiques pluridisciplinaires d'une expérience d'interface. In *L'interdisciplinarité dans les sciences de la vie*, Leguay, J.M. (ed.). INRA, Paris.

De Brabandère, L. (2017). *Homo Informatix*. Le Pommier, Paris.

De Certeau, M. (1994). *La prise de parole et autres écrits politiques*. Le Seuil, Paris.

De Simone, A., Gidoni, P., Noselli, G. (2015). Liquid crystal elastomer strips as soft crawlers. *Journal of Mechanics and Physics of Solids*, 84, 254–272.

De Volder, M. and Reynaerts, D. (2010). Pneumatic and hydraulic micro-actuators: A review. *Journal of Micromechanics and Microengineering*, 20, 4.

Decroly, G., Toncheva, A., Blanc, L., Raquez, J.M., Lessinnes, T., Delchambre, A., Lambert, P. (2020). Programmable stimuli-responsive actuators for complex motions in soft robotics: Concept, design and challenges. *Actuators*, 9, act9040131.

Delaunay, D. (1934). Sur la sphère vide – A la mémoire de Georges Voronoï. *Izvestia Akademia Nauk SSSR – Otdelenie Matematicheskii i Estestvennyka Nauk*, 7, 793—800.

Deloncle, R. (2007). Dendrimères phosphorés à motifs azo-benzène : vers des matériaux photo-adaptatifs. Thesis, Université Paul Sabatier, Toulouse.

Demoly, F. and André, J.C. (2021a). Is order creation through disorder in additive manufacturing possible? *Cogent Engineering*, 1889110.

Demoly, F. and André, J.C. (2021b). Projet de protection industrielle. Confidentiel.

Demoly, F., Dunn, M.L., Wood, K.L., Qi, H.J., André, J.C. (2021). The status, barriers, challenges, and future in design for 4D printing. *Materials & Design*, 212, 110193.

Di Luna, G.A., Flocchini, P., Santoro, N., Viglietta, G., Yamauchi, Y. (2017). Shape formation by programmable particles. In *Leibniz International Proceedings in Informatics*, Aspnes, J., Bessani, A., Felber, P., Leitão, J. (eds). Schloss Dagstuhl, Leibniz-Zentrum für Informatik, Dagstuhl Publishing, Leibniz.

Di Natali, C., Sadeghi, A., Mondini, A., Bottenberg, E., Hartigan, B., De Eyto, A., O'Sullivan, L, Rocon, E., Stadler K., Mazzolai, B. et al. (2020). Pneumatic quasi-passive actuation for soft assistive lower limbs exoskeleton. *Frontiers in Neuro-robotics*, 14, 31.

Do, J.L. and Friščić, T. (2017). Mechano-chemistry: A force of synthesis. *ACS Central Science*, 3, 13–19.

Dolev, S., Narayanan, R.P., Scheideler, C. (2020). Towards synchronizing radio communication of in-vivo nano-robots. *Nano Futures*, 4, 035008.

Dou, Y., Cartier, C.A., Fei, W., Pandey, S., Razavi, S., Kretzschmar, I., Bishop, K.J.M. (2016). Directed motion of metallo-dielectric particles by contact charge electrophoresis. *Langmuir*, 32, 13167–13173.

Doursat, R., Sayama, H., Michel, O. (2013). A review of morphogenetic engineering. *Natural Computing*, 12, 517–535.

Dramé-Maigné, A., Estevez-Torres, A., Galas, J.C., Génot, A., Rondelez, Y. (2019). Programmer avec des molécules : pourquoi et comment ? In *Inventer l'avenir. L'ingénierie se met au vert*, Meireles-Masbernat, M., Nicolas, L., Slaoui, A. (eds). CNRS, Paris.

Du, F.P., Ye, E.Z., Yang, W., Shen, T.H., Tang, C.Y., Xie, X.L., Zhou, X.P., Law, W.C. (2015). Electroactive shape memory polymer based on optimized multi-walled carbon nanotubes/polyvinyl alcohol nanocomposites. *Composites*, B68, 170–175.

Du, Z., Zhou, X., Ye, P., Zeng, X., Gan, C.L. (2020). Shape-memory actuation in aligned zirconia nanofibers for artificial muscle applications at elevated temperatures. *ACS Applied Nano-Materials*, 3, 2156–2166.

Du Plessis, A., Babafemi, A.J., Paul, S.C., Panda, B., Tranf, J.P., Broeckhoven, C. (2021). Biomimicry for 3D concrete printing: A review and perspective. *Additive Manufacturing*, 38, 101823.

Dubourg, A. (2015). Intégration de structures absorbantes acoustiques innovantes au sein d'une turbo-soufflante. Master's Thesis, Université de Montréal [Online]. Available at: https://publications.polymtl.ca/2045/1/2015_ArnaudDubourg.pdf.

Duduta, M., Hajiesmaili, E., Zhao, H., Wood, R.J., Clarke, D.R. (2019). Realizing the potential of dielectric elastomer artificial muscles. *Proceedings of the National Academy of Science USA*, 116, 2476–2481.

Dufaud, O., Marchal, P., Corbel, S. (2002). Rheological properties of PZT suspensions for stereo-lithography. *Journal of the European Ceramic Society*, 22, 2081–2092.

Durance, P. (2014). Herman Kahn et la méthode des scénarios : histoire d'une idée. In *La prospective stratégique en action*, Durance, P. (ed.). Odile Jacob, Paris.

Duras, M. (1993). *Ecrire*. Gallimard, Paris.

Dureuil, A. (2013). Des nano-moteurs pour des courses de nano-voitures… [Online]. Available at: https://www.info-chimie.fr/des-nano-moteurs-pour-des-courses-de-nano-voitures,46270.

Dürr, H. and Bouas-Laurent, H. (2003). *Photochromism: Molecules and Systems*. Elsevier, Amsterdam.

Dutta, S. and Cohn, D. (2017). Temperature and pH responsive 3D printed scaffolds. *Journal of Material Chemistry*, B5, 9514–9521.

Dykstra, D.M.J., Busink, J., Ennis, B., Coulais, C. (2019). Viscoelastic metamaterials. arXiv:1904.11888v1.

Egunov, A.I., Korvinkb, J.G., Luchnikov, V.A. (2016). Polydimethylsiloxane bilayer films with an embedded spontaneous curvature. *Soft Matter*, 12, 45–52.

Elguesse, I. (2015). Etude et application des composites à base des matériaux intelligents : (cas des matériaux piézo-électriques et des alliages à mémoire de forme). Thesis, Université de Rabat [Online]. Available at: http://thesesenafrique.imist.ma/bitstream/handle/123456789/1730/THESE_ELGUESSE.pdf?sequence=1.

Elletro, H. (2015). Le treuil élasto-capillaire : de la soie d'araignée aux actionneurs intelligents. Thesis, Université Pierre et Marie Curie, Paris.

Engheta, N. and Ziolkowski, R.W. (2006). *Metamaterials*. John Wiley & Sons Inc., Hoboken.

Ercole, F., Davis, T.P., Evans, R.A. (2010). Photo-responsive systems and biomaterials: Photochromic polymers, light-triggered self-assembly, surface modification, fluorescence modulation and beyond. *Polymer Chemistry*, 1, 37–54.

Fang, L., Chen, S., Fang, T., Fang, J., Lu, C., Xu, Z. (2017). Shape-memory polymer composites selectively triggered by near-infrared light of two certain wavelengths and their applications at macro-/microscale. *Composites Sciences & Technology*, 138, 106–116.

Faucheux, M. and Forest, J. (2011). Stimulating a creative rationality to stimulate innovation. *Creativity and Innovation Management*, 20, 207–212.

Fauteux, P. (2009). Conception d'un actionneur adapté à l'interaction physique dans un contexte de robotique. Mechanical engineering Master's Thesis, Université de Sherbrooke [Online]. Available at: https://introlab.3it.usherbrooke.ca/mediawiki-introlab/images/b/b2/MemoireFauteux.pdf.

Fernandez, P., Pelayo, F., Avila, D., Beltran, N., Blanco, D. (2019). Failure analysis of bi-material FFF parts. *8th Manufacturing Engineering Society International Conference Procedia Manufacturing*, 41, 571–578.

Feynman, R.P. (2000). *Vous voulez rire Monsieur Feynman ?* Odile Jacob, Paris.

Fischer, J., Thiel, M., Wegener, M. (2014). Matter made to order. *IEEE Spectrum*, 51, 34–58.

Forget, F. (2018). Modélisation et contrôle d'actionneurs pour la robotique humanoïde. Thesis, Université de Toulouse [Online]. Available at: http://thesesups.ups-tlse.fr/4279/1/2018TOU30342.pdf.

Fouet, M. (2016). Micro-fluidique 3D et actionneurs magnétiques : de leur intégration à la préparation d'échantillons biologiques. Thesis, Université de Toulouse [Online]. Available at: http://thesesups.ups-tlse.fr/3102/1/2016TOU30036.pdf.

Fourastié, J. (1966). *Essais de morale prospective*. Gonthier, Paris.

Francfort, D. (2007). Du bon usage provincial de la provocation ou comment dépatrimoinaliser "l'histoire culturelle". In *Culture de la provocation – réflexions indisciplinaires*, Francfort, D. (ed.). Presses Universitaires de Nancy.

Franco, E., Tang, J., Garriga Casanovas, A., Rodriguez y Baena, F., Astolfi, A. (2020). Position control of soft manipulators with dynamic and kinematic uncertainties. *IFAC PapersOnLine*, 53, 9847–9852.

Frascio, M., de Sousa Marques, E.A., Camilo Carbas, R.J., Martins da Silva, R.F., Monti, M., Avalle, M. (2020). Review of tailoring methods for joints with additively manufactured adherents and adhesives. *Materials*, 13, 3949.

Frenzel, T., Kadic, M., Wegener, M. (2017). Three-dimensional mechanical metamaterials with a twist. *Science*, 358, 1072–1074.

Freund, R., Watschke, H., Heubach, J., Vietor, T. (2019). Determination of influencing factors on interface strength of additively manufactured multi-material parts by material extrusion. *Applied Sciences*, 9, 1782.

Friedman, Y. (2018). *L'ordre compliqué et autres fragments*. Editions de l'Eclat, Paris.

Friis, E.A., Lakes, R.S., Park, J.B. (1988). Negative Poisson's ratio polymeric and metallic foams. *Journal of Materials Science*, 23, 4406–4414.

Fujii, T. and Rondelez, Y. (2013). Predator-prey molecular ecosystem. *ACS Nano*, 7, 27–34.

Gakwaya, M. (2006). Compensation des deformations induites thermiquement dans les matériaux composites à l'aide d'un piezo-composite. Thesis, Université Laval, Quebec [Online]. Available at: https://www.collectionscanada.gc.ca/obj/s4/f2/dsk3/QQLA/TC-QQLA-23590.pdf.

Ganet-Mattei, F. (2018). Fabrication additive de matériaux électroactifs pour applications à la mécatronique. Thesis, Université de Lyon [Online]. Available at: https://tel.archives-ouvertes.fr/tel-02124607/document.

Ganet-Mattei, F., Le, M.Q., Capsal, J.F., Lermusiaux, P., Petit, L., Million, A., Cottinet, P.J. (2015). Development of a smart guide wire using an electrostrictive polymer: Option for steerable orientation and force feedback. *Nature: Scientific Reports*, 5, 18593.

GAO (2015). 3D printing: Opportunities, challenges and policy; implications of additive manufacturing [Online]. Available at: http://www.gao.gov/assets/680/670960.pdf.

Gao, W., Sattayasamitsathit, S., Manesh, K.M., Weihs, D., Wang, J. (2010). Magnetically powered flexible metal nanowire motors. *Journal of the American Chemical Society*, 132, 14403–14406.

Gao, W., Sattayasamitsathit, S., Orozco, J., Wang, J. (2011). Highly efficient catalytic microengines: Template electro-synthesis of polyaniline/platinum micro-tubes. *Journal of the American Chemical Society*, 133, 11862–11864.

Gao, B., Yang, Q., Zhao, X., Jin, G., Ma, Y., Xu, F. (2016). 4D bio-printing for biomedical applications. *Trends in Biotechnology*, 34, 746–756.

Garces, I.T. and Ayranci, C. (2020). Active control of 4D prints: Towards 4D printed reliable actuators and sensors. *Sensors and Actuators*, A301, 111717.

Garcia, M. (2013). Hydrodynamique de micro-nageurs. Thesis, Université de Grenoble [Online]. Available at: https://tel.archives-ouvertes.fr/tel-00952771/document.

Gastineau, N., Abdou, W., Mbarek, N., Togni, O. (2020). Leader election and local identifiers for 3D programmable matter. arXiv:2010.09286v1.

Gauss, C., Pickering, K.L., Muthe, L.P. (2021). The use of cellulose in bio-derived formulations for 3D/4D printing: A review. *Composites Part C*, 4, 100113.

Ge, F. (2019). Study of soft polymer actuators driven by an order-disorder phase transition. PhD Thesis, Sherbrooke University [Online]. Available at: https://savoirs.usherbrooke.ca/bitstream/handle/11143/16043/Ge_Feijie_PhD_2019.pdf?sequence=11&isAllowed=y.

Ge, Q., Qi, J., Dunn, M.L. (2013). Active materials by four dimensions printing. *Applied Physical Letter*, 103, 131901.

Ge, Q., Sakhaei, A.H., Lee, H., Dunn, C.K., Fang, N.X., Dunn, M.L. (2016). Multi-material 4D printing with tailorable shape memory polymers. *Scientific Reports*, 6, 31110.

Ghosh, A. and Basu, S. (2021). Soft dielectric elastomer tubes in an electric field. *Journal of the Mechanics and Physics of Solids*, 150, 104371.

Ghosh, A. and Fischer, P. (2009). Controlled propulsion of artificial magnetic nano-structured propellers. *Nano Letters*, 9, 2243–2248.

Gibbs, J.G. and Zhao, Y.P. (2009). Autonomously motile catalytic nano-motors by bubble propulsion. *Applied Physics Letters*, 94, 163104.

Gilpin, K., Knaian, A., Rus, D. (2012). Robot pebbles: One centimeter modules for programmable matter trough self-disassembly [Online]. Available at: http://cba.mit.edu/docs/papers/10.05.knaian.ICRA.pdf.

Gladman, A.S., Matsumoto, E.A., Nuzzo, R.G., Mahadevan, L., Lewis, J.A. (2016). Biomimetic 4D printing. *Nature Materials*, 15, 413–418.

Glock, S., Canal, L.P., Grize, C.M., Michaud, V. (2015). Magneto-mechanical actuation of ferromagnetic shape memory alloy/epoxy composites. *Composites Science and Technology*, 114, 110–118.

Gnanasekaran, K., Heijmans, T., van Bennekom, S., Woldhuis, H., Wijnia, S., de With, G., Friedrich, H. (2017). 3D printing of CNT and graphene-based conductive polymer nanocomposites by fused deposition modeling. *Applied Materials Today*, 9, 21–28.

Gojzewski, H., Guo, Z., Grzelachowska, W., Ridwan, M.G., Hempenius, M.A., Grijpma, D.W., Vancso, G.J. (2020). Layer-by-layer printing of photopolymers in 3D: How weak is the interface? *ACS Applied Materials and Interfaces*, 12, 8908−8914.

Golaszewski, M., Grygoruk, R., Giorgio, I., Laudato, M., Di Cosmo, F. (2018). Metamaterials with relative displacements in their microstructure: Technological challenges in 3D printing, experiments and numerical predictions. *Continuum Mechanical Thermodynamics* [Online]. Available at: https://doi.org/10.1007/s00161-018-0692-0 or https://www.researchgate.net/profile/Ivan_Giorgio/publication/326015487_Metamaterials_with_relative_displacements_in_their_microstructure_technological_challenges_in_3D_printing_experiments_and_numerical_predictions/links/5b8a47c892851c1e123fabd8/Metamaterials-with-relative-displacements-in-their-microstructure-technological-challenges-in-3D-printing-experiments-and-numerical-predictions.pdf.

Goldstein, R., Gorodtsov, V., Lisovenko, D. (2009). About negativity of the Poisson's ratio for anisotropic materials. *Doklady Physics*, 54, 546–548.

Golovin, Y.I., Gribanovsky, S.L., Golovin, D.Y., Klyachko, N.L., Majouga, A.G., Master, A.M., Sokolsky, M., Kabanovb, A.V. (2015). Towards nanomedicines of the future: Remote magneto-mechanical actuation of nanomedicines by alternating magnetic fields. *Journal of Control Release*, 10, 43–60.

Gonzalez-Gutierrez, J., Cano, S., Schuschnigg, S., Kukla, C., Sapkota, J. (2018). Additive manufacturing of metallic and ceramic components by the material extrusion of highly-filled polymers: A review and future perspectives. *Materials*, 11, 840.

Goo, B., Hong, C.H., Park, K. (2020). 4D printing using anisotropic thermal deformation of 3D-printed thermoplastic parts. *Materials & Design*, 188, 108485.

Gorissen, B., De Volder, M., De Greef, A., Reynaerts, D. (2011). Theoretical and experimental analysis of pneumatic balloon micro-actuators. *Sensors and Actuators*, A168, 58–65.

Gossweiler, G.R., Kouznetsova, T.B., Craig, S.L. (2015). Force-rate characterization of two spiropyran-based molecular force probes. *Journal of the American Chemical Society*, 137, 6148–6151.

Goswami, D., Zhang, Y., Liu, S., Abdalla, O.A., Zavattieri, P.D., Martinez, R.V. (2021). Mechanical metamaterials with programmable compression-twist coupling. *Smart Materials and Structures*, 30, 015005.

Goux, C. (2014). La prospective est inhérente à l'Homme. In *La prospective scientifique en action*, Durance, P. (ed.). Odile Jacob, Paris.

Gros, A. (2016). Modélisation de la cristallisation sous tension du caoutchouc naturel. Thesis, Ecole Centrale de Nantes.

Grossweiler, G.R., Brown, C.L., Hewage, C.B., Sapiro-Gheiler, E., Trautman, W.J., Welshofer, G.W., Craig, S.L. (2015). Mechano-chemically active soft robots. *ACS Applied Materials and Interfaces*, 7, 22431–22435.

Guo, X., Ni, X., Li, J., Zhang, H., Zhang, F., Yu, H., Wu, J., Bai, Y., Lei, H., Huang, Y. et al. (2021). Designing mechanical metamaterials with kirigami-inspired, hierarchical constructions for giant positive and negative thermal expansion. *Materials Science and Engineering – Advanced Materials*, 33, 2004919.

Hagaman, D.E., Leist, S., Zhou, J., Ji, H.F. (2018). Photo-activated polymeric bilayer actuators fabricated via 3D printing. *ACS Applied Materials and Interfaces*, 10, 27308−27315.

Hager, M., Bode, S., Weber, C., Schubert, U. (2015). Shape memory polymers: Past, present and future developments. *Progress in Polymer Science*, 49, 3–33.

Haghiashtiani, G., Habtour, E., Park, S.H., Garde, F., McAlpine, M.C. (2018). 3D printed electrically-driven soft actuators. *Extreme Mechanical Letters*, 21, 1–8.

Halabi, J.M., Ahmed, E., Sofela, S., Naumov, P. (2021). Performance of molecular crystals in conversion on light to mechanical work. *Proceedings of the National Academy of Science*, 118, e2020604118.

Han, D., Pal, S., Nangreave, J., Deng, Z., Liu, Y., Yan, H. (2011). DNA origami with complex curvatures in three-dimensional space. *Science*, 332, 342–346.

Han, X.J., Dong, Z.Q., Fan, M.M., Liu, Y., Li, J.H., Wang, Y.F., Yuan, Q.J. (2012). pH-induced shape-memory polymers. *Macromolecular Rapid Communications*, 33, 1055–1060.

Hann, S.Y., Cui, H., Nowicki, M., Zhang, L.G. (2020). 4D printing soft robotics for biomedical applications. *Additive Manufacturing*, 36, 101567.

Hardesty, L. (2015). Centimeter-long origami robot [Online]. Available at: http://news.mit.edu/2015/centimeter-long-origami-robot-0612.

Haudin, F., Brau, F., De Wit, A. (2018). La chimie génératrice de forme : végétation métallique et jardins chimiques [Online]. Available at: https://www.openscience.fr/La-chimie-generatrice-de-forme-vegetation-metallique-et-jardins-chimiques.

He, Q. (2021). Bioinspired liquid crystal elastomer (LCE) based soft actuators with multimodal actuation. PhD Thesis, University of California, San Diego [Online]. Available at: https://escholarship.org/content/qt5x7434qw/qt5x7434qw.pdf.

He, Y., Yang, F.F., Zhao, H.M., Gao, Q., Xia, B., Fu, J.Z. (2016). Research on the printability of hydrogels in 3D bio-printing. *Scientific Reports*, 6, 29977.

He, Q., Ji, Y., Lin, X., Wu, Z., Wu, Y., Gao, W. (2019). Macroscale chemotaxis from a swarm of bacteria-mimicking nano-swimmers. *Angewandte Chemie, International Edition*, 58, 12200–12205.

Heckel, S. and Simmchen, J. (2019). Photocatalytic BiVO4 micro-swimmers with bimodal swimming. *Advanced Intelligent Systems*, 1, 1900093.

Hingorani, H., Yuan-Fang Zhang, B., Zhang, S.A., Ge, Q., Hingorani, H., Yuan-Fang, Z., Biao, Z., Serjouei, A. (2019). Modified commercial UV curable elastomers for passive 4D printing. *International Journal of Smart and Nano Materials*, 10, 225–236.

Hofman, J. (2021). FlexTECH: Taking the next step with "Printed Electronics". PhD Thesis, Delft University of Technology [Online]. Available at: https://repository.tudelft.nl/islandora/object/uuid:3182a136-65ba-4068-ad59-caf5b7e28c5c.

Hong, Y., Diaz, M., Córdova-Figueroa, U.M., Sen, A. (2010). Light-driven titanium-dioxide-based reversible microfireworks and micromotor/micropump systems. *Advanced Functional Materials*, 20, 1–9.

Hornyak, T. (2019). Particle robots work together to perform tasks – Clusters of decentralized units could be used in search and rescue operations or drug delivery [Online]. Available at: https://www.scientificamerican.com/article/particle-robots-work-together-to-perform-tasks/.

Howse, J., Jones, R., Ryan, A., Gough, T., Vafabakhsh, R., Golestanian, R. (2007). Self-motile colloidal particles: From directed propulsion to random walk. *Physical Review Letters*, 99, 048102.

Hu, J., Zhu, Y., Huang, H., Lu, J., (2012). Recent advances in shape memory polymers: Structure, mechanism, functionality, modeling and applications. *Progress in Polymer Science*, 37, 1720–1763.

Hu, L., Wang, N., Miao, J., Grüber, G. (2017a). Investigation of temperature dependency on the propulsion of disklike nanoswimmers. *Procedia Technology*, 27, 48–50.

Hu, Q., Sun, X.Z., Parmenter, C.D.J., Fay, M.W., Smith, E.F., Rance, G.A., He, Y., Zhang, F., Liu, Y., Irvine, D. et al. (2017b). Additive manufacture of complex 3D Au-containing nanocomposites by simultaneous two-photon polymerization and photo-reduction. *Scientific Reports*, 7, 17150.

Hu, X., Karnetzke, J., Fassbender, M., Drücker, S., Bettermann, S., Schroeter, B., Pauer, W., Moritz, H.U., Fiedler, B., Luinstra, G. et al. (2020). Smart reactors – Combining stimuli-responsive hydrogels and 3D printing. *Chemical Engineering Journal*, 387, 123413.

Huang, C., Lu, J.A., Tian, X., Wang, Y., Yu, Y., Liu, J. (2015). Miniaturized swimming soft robot with complex movement actuated and controlled by remote light signals. *Scientific Reports*, 5, 17414.

Huber, J.E., Fleck, N.A., Ashby, M.F. (1997). The selection of mechanical actuators based on performance indices. *Proceedings of the Royal Society (London)*, A453, 2185–2205.

Ibele, M., Mallouk, T.E., Sen, A. (2009). Schooling behavior of light-powered autonomous micro-motors in water. *Angewandte Chemie International Edition*, 48, 33083312.

Ilic-Stojanovic, S., Nikolic, L., Nikolic, V., Petronic, S., Stankovic, M., Mladenovic-Ranisavljevic, I. (2011). Stimuli-sensitive hydrogels for pharmaceutical and medical applications. *Facta Universitatis*, 9, 37–56.

INSP – Institut des Nanosciences de Paris (2020). Microscopie en champ proche [Online]. Available at: http://www.insp.jussieu.fr/-Microscopie-en-champ-proche-.html.

Ion, A., Frohnhofen, J., Wall, L., Kovacs, R., Alistar, M., Lindsay, J., Lopes, P., Chen, H.T., Baudisch, P. (2016). Metamaterial mechanisms. *Proceedings of the UIST'16* [Online]. Available at: https://hpi.de/fileadmin/user_upload/fachgebiete/baudisch/projects/metamaterial/metamaterial-mechanisms/2016UIST_Metamaterial_Mechanisms__authors_copy_.pdf or https://hpi.de/baudisch/projects/metamaterial-mechanisms.html.

Ion, A., Kovacs, R., Schneider, O.S., Lopes, P., Baudisch, P. (2018a). Metamaterial textures [Online]. Available at: https://www.researchgate.net/profile/Alexandra_Ion/publication/324669839_Metamaterial_Textures/links/5af18eedaca272bf4255bef2/Metamaterial-Textures.pdf.

Ion, A., Wall, L., Kovacs, R., Baudisch, P. (2018b). Digital mechanical metamaterials [Online]. Available at: https://www.researchgate.net/profile/Alexandra_Ion/publication/314263173_Digital_Mechanical_Metamaterials/links/5a0313b3a6fdcc6b7c9c2e1b/Digital-Mechanical-Metamaterials.pdf.

Irie, M., Yokoyama, Y., Seki, T. (2013). *New Frontiers in Photochromism*. Springer, Tokyo.

ISPA – Institut Supérieur de Plasturgie d'Alençon (2015). Méthodes d'assemblage de thermoplastiques renforcés fibres courtes ou longues [Online]. Available at: https://www.nae.fr/wp-content/uploads/2018/04/EB_Assemblage_TP.pdf.

Jackson, B. (2016). Futurist Ray Kurzweil makes 3D printing predictions [Online]. Available at: https://3dprintingindustry.com/news/futurist-ray-kurzweil-reiterates-3d-printing-predictions-100504/.

Jackson, J.A., Messner, M.C., Dudukovic, N.A., Smith, W.L., Bekker, L., Moran, B., Golobic, A.M., Pascall, A.J., Duoss, E.B., Loh, K.J. et al. (2018). Field responsive mechanical metamaterials. *Science Advances*, 4, eaau6419.

Jamal, M., Kadam, S.S., Xiao, R., Jivan, F., Onn, T.M., Fernandes, R., Nguyen, T., Gracias, D.H. (2013). Bio-origami hydrogel scaffolds composed of photo-crosslinked PEG bilayers. *Advanced Healthcare Materials*, 2, 1142–1150.

Jayashankar, D.K., Gupta, S.S., Stella, L.Y.N., Tracy, K. (2019). 3D printing of compliant passively actuated 4D structures. *Solid Freeform Fabrication 2019: Proceedings of the 30th Annual International Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference Reviewed Paper* [Online]. Available at: http://utw10945.utweb.utexas.edu/sites/default/files/2019/082%203D%20Printing%20of%20Compliant%20Passively%20Actuated%204D%20Str.pdf and https://3dprint.com/262342/4d-printing-singapore-researchers-pair-compliant-mechanisms-chitosan-biopolymers/.

Jenett, B.E. (2020). Discrete mechanical metamaterials. PhD Thesis, MIT [Online]. Available at: https://bej.pages.cba.mit.edu/home/Jenett-PhD-MAS-2020b.pdf.

Jeong, J., Kang, L., Davidson, Z.S., Collings, P.J., Lubensky, T.C., Yodh, A.G. (2015). Chiral structures from achiral liquid crystals in cylindrical capillaries. *Proceedings of the National Academy of Sciences USA*, 112, E1837–E1844.

Jeong, H.Y., Woo, B.H., Kim, N., Jun, Y.C. (2020). Multicolor 4D printing of shape-memory polymers for light-induced selective heating and remote actuation. *Scientific Reports*, 10, 6258.

Jiang, Y. and Wang, Q. (2016). Highly-stretchable 3D-architected mechanical metamaterials. *Scientific Reports*, 6, 34147 [Online]. Available at: https://www.nature.com/articles/srep34147.

Jiang, W., Yan, L., Ma, L., Fan, Y., Wang, J., Feng, M., Qu, S. (2018). Electromagnetic wave absorption and compressive behavior of a three-dimensional metamaterial absorber based on 3D printed honeycomb. *Scientific Reports*, 8, 4817 [Online]. Available at: https://www.nature.com/articles/s41598-018-23286-6/.

Jin, B., Song, H., Jiang, R., Song, J., Zhao, Q., Xie, T. (2018). Programming a crystalline shape memory polymer network with thermoand photo-reversible bonds toward a single-component soft robot. *Science Advances*, 4, eaao3865.

Jin, L., Forte, A.E., Deng, B., Rafsanjani, A., Bertoldi, K. (2020). Kirigami-inspired inflatables with programmable shapes. arXiv:2007.07312v1.

Jing, L., Li, K., Yang, H., Chen, P.Y. (2020). Recent advances in integration of 2D materials with soft matter for multifunctional robotic materials. *Materials Horizons*, 7, 54.

Jobs, S. (2011). *iSteve – Intuitions, sagesse et pensées de Steve Jobs*. G.W. Beahm, Paris, and M. Lafon, Paris.

Jochum, F.D. and Theato, P. (2013). Temperature and light-responsive smart polymer materials. *Chemical Society Review*, 42, 7468–7483.

Joo, J.J. and Sanders, B. (2009). Optimal location of distributed actuators within an in-plane multi-cell morphing mechanism. *Journal of Intelligent Material Systems and Structures*, 20, 481–492.

Julin, S., Nummelin, S., Kostiainen, M.A., Linko, V. (2018). DNA nanostructure-directed assembly of metal nanoparticle superlattices. *Journal of Nanoparticles Research*, 20, 119.

Jung, K., Corrigan, N., Ciftci, M., Xu, J., Seo, S.E., Hawker, C.J., Boyer, C. (2020). Designing with light: Advanced 2D, 3D, and 4D materials. *Advanced Materials, "Special Issue: Materials Science in Australia*", 32, 1903850.

Kadic, M., Milton, G.W., van Hecke, M., Wegener, M. (2019). 3D metamaterials. *Nature Reviews – Physics*, 1, 198–210 [Online]. Available at: https://openaccess.leidenuniv.nl/bitstream/handle/1887/72015/Kadic_Hecke_2019_T.pdf?sequence=1.

Kamru, H., Zulifqar, A., Hu, H. (2020). Deformation behavior of auxetic woven fabric based on re-entrant hexagonal geometry in different tensile directions. *Textile Research Journal*, 90 [Online]. Available at: https://doi.org/10.1177/0040517519869391

Kaneto, K. (2016). Research trends of soft actuators based on electroactive polymers and conducting polymers. *Journal of Physics: Conference Series*, 704, 012004 [Online]. Available at: https://iopscience.iop.org/article/10.1088/1742-6596/704/1/012004/pdf.

Kang, O.H., Lee, S.H., Yun, J.H., Yi, H., Kwak, M.K., Lee, S.R. (2017). Adhesion tunable bio-inspired dry adhesives by twisting. *International Journal of Precision Engineering and Manufacturing*, 18, 1433–1437.

Kanu, N.J., Gupta, E., Vates, U.K., Singh, G.K. (2019). An insight into biomimetic 4D printing. *RSC Advances*, 9, 38209.

Kaplan, F. (2012). *La métamorphose des objets*. FYP, Paris.

Karothu, D.P., Halabi, J.M., Li, L., Colin-Molina, A., Rodriguez-Molina, B., Naumov, P. (2020). Global performance indices for dynamic crystals as organic thermal actuators. *Advanced Materials*, 32, 1906216.

Katuri, J., Ma, X., Stanton, M.M., Sánchez, S. (2017). Designing micro and nano-swimmers for specific applications. *Accounts in Chemical Research*, 50, 2–11.

Keller, S. and Jaeger, H. (2016). Aleatory architectures [Online]. Available at: https://arxiv.org/ftp/arxiv/papers/1510/1510.05721.pdf.

Khatri, B., Frey, M., Raouf-Fahmy, A., Scharla, M/V., Hanemann, T. (2020). Development of a multi-material stereo-lithography 3D printing device. *Micro-machines*, 11, 532.

Khim, T., Zhu, L., Al-Kaysi, R.O., Bardeen, C.J. (2014). Organic photomechanical material. *ChemPhysChem*, 15, 400–414.

Khongtong, S. and Ferguson, G.S. (2004). Tunable glue: Rubber elasticity control of adhesion interface at polymer/metal. *Walailak Journal of Science & Technology*, 1, 23–28.

Khoo, Z.X., Mei Teoh, J.E., Liu, Y., Chua, C.K., Yang, S., An, J., Leonga, K.F., Yeong, W.Y. (2015). 3D printing of smart materials: A review on recent progresses in 4D printing. *Virtual and Physical Prototyping*, 10, 103–122.

Kim, H.Y. (2014). Effect of mechanical stretching on the maturation of 3D fascicle-like muscle tissue. PhD Thesis, MIT, Boston.

Kim, Y., Yuk, H., Zhao, R., Chester, S.A., Zhao, X. (2018). Printing ferromagnetic domains for untethered fast-transforming soft materials. *Nature*, 558, 274–279.

Kim, J., Kim, J.W., Kim, H.C., Zhai, L., Ko, H.U., Muthoka, R.M. (2019a). Review of soft actuators materials. *International Journal of Precision Engineering and Manufacturing*, 20, 2221–2241.

Kim, Y., Parada, G.A., Liu, S., Zhao, X. (2019b). Ferromagnetic soft continuum robots. *Science Robotics*, 4, eaax7329.

Kimionis, J., Isakov, M., Koh, B.S., Georgiadis, A., Tentzeris, M.M. (2015). 3D-printed origami packaging with inkjet-printed antennas for RF harvesting sensors. *IEEE Transactions on Microwave Theory and Techniques*, 63, 4521–4532.

Kluczyński, J., Śnieżek, L., Kravcov, A., Grzelak, K., Svoboda, P., Szachogłuchowicz, I., Franek, O., Morozov, N., Torzewski, J., Kubeček, P. (2020). The examination of restrained joints created in the process of multi-material FFF additive manufacturing technology. *Materials*, 13, 903.

Knyazhanskiy, M. (2018). *Esipt Photochromism: The Development of the Modern Views*. XLibris US, New York.

Kokkinis, D., Schaffner, M., Studart, A.R. (2015). Multimaterial magnetically assisted 3D printing of composite materials. *Nature Communications*, 6, 8643.

Kolken, H.M.A. and Zadpoor, A.A. (2017). Auxetic mechanical metamaterials. *RSC Advances*, 7, 5111–5129 [Online]. Available at: https://pubs.rsc.org/en/content/articlehtml/2017/ra/c6ra27333e.

Kong, D., Nishio, K., Kurosawa, M.K. (2019). A novel approach to swimmer actuation via leaky surface acoustic wave. *IEEE 32nd International Conference on Micro Electro Mechanical Systems (MEMS)*, Seoul, 27–31 January.

Kotov, N.A. (2017). Self-assembly of inorganic nanoparticles: Ab ovo. *Journal Exploring the Frontiers of Science*, 119, 66008.

Kriegman, S., Walker, S., Shah, D., Levin, M., Kramer-Bottiglio, R., Bongard, J. (2019). Automated shapeshifting for function recovery in damaged robots [Online]. Available at: https://arxiv.org/pdf/1905.09264.pdf.

Krödel, S., Li, L., Constantinescu, A., Daraio, C. (2017). Stress relaxation in polymeric micro-lattice materials. *Materials and Design*, 130, 433–441.

Kuang, X., Roach, D.J., Wu, J., Hamel, C.M., Ding, Z., Wang, T., Dunn, M.L., Qi, H.J. (2019). Advances in 4D printing: Materials and applications. *Advanced Functional Materials*, 29, 1805290.

Kuang, X., Roach, D.J., Hamel, C.M., Yu, K., Qi, H.J. (2020). Materials, design, and fabrication of shape programmable polymers. *Multifunctional Materials*, 3, 032002.

Kuenstler, A.S., Clark, K.D., de Alaniz, J.R., Hayward, RC. (2020). Reversible actuation via photo-isomerization-induced melting of a semi-crystalline poly-(azo-benzene). *ACS Macro Letters*, 9, 902–909.

Kuksenok, O. and Balazs, A.C. (2013). Modeling the photo-induced reconfiguration and directed motion of polymer gels. *Advances in Functional Materials*, 23, 4601–4610.

L'arrêt public gouverne MENT (2010). Portrait d'un charlatan [Online]. Available at: http://legosanstrique.blogspot.fr/2010_08_01_archive.html.

Lake, G.J. and Thomas, A.J. (1967). The strength of highly elastic materials. *Proceedings of the Royal Society of London*, A300, 108–119.

Lambert, P., Renaud, P., Szewczyk, J. (2016). Actionneurs non-conventionnels pour la robotique [Online]. Available at: https://hal.archives-ouvertes.fr/hal-02145907/document.

Lan, R., Sun, J., Shen, C., Huang, R., Zhang, Z., Ma, C., Bao, J., Zhang, L., Wang, L., Yang, D. et al. (2020). Light-driven liquid crystalline networks and soft actuators with degree-of-freedom-controlled molecular motors. *Advanced Functional Materials*, 30, 2000252.

Lantada, A.D. (2017). Systematic development strategy for smart devices based on shape-memory polymers. *Polymers*, 9, 496.

Latour, B. (2020). *Science, orgueil et préjugés*. EPFL Press, Lausanne.

Le Duigou, A. (2017). Actionneurs Bio-Composites hygromorphes : nouvelle fonctionnalité pour les fibres végétales [Online]. Available at: https://hal.archives-ouvertes.fr/hal-01623678/document.

Le Duigou, A. (2019). Les fibres de lin : du renforcement des composites aux structures bio-inspirées. In *Inventer l'avenir – L'ingénierie se met au vert*, Meireles-Masbernat, M., Nicolas, L., Slaoui, A. (eds). CNRS, Paris.

Le Duigou, A., Castro, M., Bevan, R., Martin, N. (2016). 3D printing of wood fiber bio-composites: From mechanical to actuation functionality. *Materials & Design*, 96, 106–114.

Le Duigou, A., Keryvin, V., Beaugrand, J., Pernes, M., Scarpa, F., Castro, M. (2019). Humidity responsive actuation of bioinspired Hygromorph BioComposites (HBC) for adaptive structures. *Applied Science Manufacturing*, A116, 36–45.

Le Duigou, A., Chabaud, G., Matsuzaki, R., Castro, M. (2020a). Tailoring the mechanical properties of 3D-printed continuous flax/PLA bio-composites by controlling the slicing parameters. *Composites Part B*, 203, 108474.

Le Duigou, A., Correa, D., Ueda, M., Matsuzaki, R., Castro, M. (2020b). A review of 3D and 4D printing of natural fibers bio-composites. *Material Design*, 94, 108911.

Le Moigne, J.L. (1994). *La théorie du système général : théorie de la modélisation*. PUF, Paris.

Lebedev, S. (2012). Order from disorder. *Nature Physics*, 8, 785–786.

Lecomte-Beckers, J. (2010). Rhéologie des matériaux polymères [Online]. Available at: http://dhaouadiramzi.e-monsite.com/medias/files/ch-6.pdf.

Lécuyer, C. (2015). Manager l'innovation. In *Histoire des sciences et des savoirs*, Pestre, D. (ed.). Le Seuil, Paris.

Lee, H.H. (2018). *Finite Element Simulations with ANSYS Workbench 19*. SDC Publications, New York.

Lee, A.Y., An, J., Chua, C.K., Zhang, Y. (2019). Preliminary investigation of the reversible 4D printing of a dual-layer component. *Engineering*, 5, 1159–1170.

Lee, J., Sroda, M.M., Kwon, Y., El-Arid, S., Seshadri, S., Gockowski, L.F., Hawkes, E.W., Valentine, M.T., de Alaniz, J.R. (2020). Tunable photo-thermal actuation enabled by photo-switching of donor–acceptor stenhouse adducts. *ACS Applied Materials and Interfaces*, 12, 54075–54082.

Lee, V. and Bhattacharya, K. (2021). Actuation of cylindrical nematic elastomer balloons. *Journal of Applied Physics*, 129, 114701.

Lefebvre, H. (1971). *Vers le cybernanthrope*. Denoël, Paris.

Lehn, J.M. (2002). Toward self-organization and complex matter. *Science*, 295, 2400–2403.

Lei, M., Hong, W., Zhao, Z., Hamel, C.M., Chen, M., Lu, H., Qi, H.J. (2019). 3D printing of auxetic metamaterials with digitally reprogrammable shape. *ACS Appl. Mater. Interfaces* [Online]. Available at: https://www.researchgate.net/profile/Haibao_Lu2/publication/333460880_3D_Printing_of_Auxetic_Metamaterials_with_Digitally_Reprogrammable_Shape/links/5db3eab2299bf111d4c98a7e/3D-Printing-of-Auxetic-Metamaterials-with-Digitally-Reprogrammable-Shape.pdf.

Lemire, L. (2015). *Ces savants qui ont eu raison trop tôt*. Taillandier, Paris.

Lendlein, A. (2010). *Shape-Memory Polymers*. Springer, Berlin/Heidelberg.

Lendlein, A. and Gould, O. (2019). Reprogrammable recovery and actuation behavior of shape-memory polymers. *Nature Reviews Materials*, 4, 116–133.

Lévy-Leblond, J.M. (2006). *La vitesse de l'ombre : aux limites de la science*. Le Seuil, Paris.

Lévy-Leblond, J.M. (2020). *Le tube à essais. Effervesciences*. Le Seuil, Paris.

Leydier, M. (2010). Méthodes complémentaires pour l'étude de verres et liquides fondus sur grands instruments : structure et dynamique. Thesis, Université d'Orléans [Online]. Available at: https://tel.archives-ouvertes.fr/tel-00623032/document.

Li, Y. and Yin, J. (2021). Architected kirigami metamorphosis [Online]. Available at: https://arxiv.org/ftp/arxiv/papers/2103/2103.15763.pdf.

Li, Q., Fuk, G., Moulin, E., Maaloun, M., Raviso, M., Kulic, I., Foy, J.T., Guiseppone, N. (2015). Macroscopic contraction of a gel induced by the integrated motion of a light-driven molecular motors. *Nature Nanotechnologies*, 10, 161–165.

Li, T., Li, J., Zhang, H., Chang, X., Song, W., Hu, Y., Shao, G., Sandraz, E., Zhang, G., Li, L. et al. (2016a). Magnetically propelled fish-like nano-swimmers. *Small*, 12, 6098–6105.

Li, W., Wu, X., Qin, H., Zhao, Z., Liu, H. (2016b). Light-driven and light-guided micro-swimmers. *Advanced Functional Materials*, 26, 3164–3171.

Li, X., Peng, Z., Yang, Y., Chen, S. (2018). Tunable adhesion of a bio-inspired micro-pillar arrayed surface actuated by a magnetic field. *Journal of Applied Mechanics*, 18, 1420.

Li, C., Iscen, A., Sai, H., Sato, K., Sather, N.A., Chin, S.M., Álvarez, Z., Palmer, L.C., Schatz, G.C., Stupp, S.I. (2020a). Supramolecular–covalent hybrid polymers for light-activated mechanical actuation. *Nature Materials*, 19, 900–909.

Li, H., Ruan, Y., You, Z., Song, Z. (2020b). Design and fabrication of a novel MEMS relay with low actuation voltage. *Micro-machines*, 11, 171.

Li, T., Liu, F., Wang, L. (2020c). Enhancing indentation and impact resistance in auxetic composite materials. *Composites Part B: Engineering*, 198, 108229 [Online]. Available at: https://www.sciencedirect.com/science/article/abs/pii/S1359836820332790.

Li, Q., Zhang, P., Yang, C., Duan, H., Hong, W. (2021). Switchable adhesion between hydrogels by wrinkling. *Extreme Mechanics Letters*, 43, 101193.

Liebchen, B., Cates, M.E., Marenduzzo, D. (2016). Pattern formation in chemically interacting active rotors with self-propulsion. *Soft Matter*, 12, 7259–7264.

Lim, T.C. (2015). *Auxetic Materials and Structures*. Springer, Singapore.

Lind, J.U., Busbee, T.A., Valentine, A.D., Pasqualini, F.S., Yuan, H., Yadid, M., Park, S.J., Kotikian, A., Nesmith, A.P., Campbell, P.H. et al. (2017). Instrumented cardiac micro-physiological devices via multi-material three-dimensional printing. *Nature Materials*, 16, 303–308.

Lippmann, W. (1937). *The Good Society*. Little, Brown & Company, Boston.

Liu, Y. and Moran, B. (2021). Crack tip fields in a neo-Hookean sheet reinforced by nonlinear fibers. *Journal of Mechanics and Physics of Solids*, 152, 104406.

Liu, J. and Wei, X. (2021). Enhancing the impact performance of reinforced composites through fiber hybridization – A hybrid dynamic shear-lag model. *Extreme Mechanics Letters*, 46, 101352.

Liu, Y. and Zhang, X. (2011). Metamaterials: A new frontier of science and technology. *Chemical Society Reviews*, 40, 2494.

Liu, Y., Xu, B., Sun, S., Wei, J., Wu, L., Yu, Y. (2017). Humidity and photo-induced mechanical actuation of cross-linked liquid crystal polymers. *Advanced Materials*, 29, 1604792.

Liu, J., Ou, H., Zeng, R., Wei, W., He, J., Zhou, J., Wei, W., Long, K., Wen, G., Xie, Y.M. (2018a). Miura-ori tube metamaterial with tunable dynamic property. arXiv, 1903.10282.

Liu, Q., Nian, G., Yang, C., Qu, S., Suo, Z. (2018b). Bonding dissimilar polymer networks in various manufacturing processes. *Nature Communications*, 9, 846.

Liu, X., Furrer, D., Kosters, J., Holmes, J. (2018c). Vision 2040: A roadmap for integrated, multiscale modeling and simulation of materials and systems. NASA/CR-2018-219771.

Liu, J., Tian, L., Qiao, Y., Zhou, S., Patil, A.J., Wang, K., Li, M., Mann, S. (2020a). Hydrogel-immobilized coacervate droplets as modular micro-reactor assemblies. *Angewandte Chemie – International Edition*, 59, 6853–6859.

Liu, K., Hand, L., Hua, W., Ji, L., Zhu, S., Wan, Z., Yang, X., Wei, Y., Dai, Z., Zhao, Z. et al. (2020b). 4D printed zero Poisson's ratio metamaterial with switching function of mechanical and vibration isolation performance. *Materials and Design*, 196, 109153.

Liu, T., Liu, L., Zeng, C., Liu, Y., Leng, J. (2020c). 4D printed anisotropic structures with tailored mechanical behaviors and shape memory effects. *Composites Science and Technology*, 186, 107935.

Liu, G., Zhang, X., Chen, X., He, Y., Cheng, L., Huo, M., Yin, J., Hao, F., Chen, S., Wang, P. et al. (2021a). Additive manufacturing of structural materials. *Materials Science and Engineering: R: Reports*, 145, 100596.

Liu, Y., Zheng, G., Letov, N., Zhao, Y.F. (2021b). A survey of modeling and optimization methods for multi-scale heterogeneous lattice structures. *Journal of Mechanical Design*, 143, 040803.

Livio, M. (2017). *Fabuleuses erreurs – de Darwin à Einstein*. CNRS, Paris.

Locke, J. (2019). *An Essay Concerning Human Understanding*. Wenworth Press, London.

Loget, G. and Kuhn, A. (2011). Electric field-induced chemical locomotion of conducting objects. *Nature Communications*, 2, 535.

Lohmuller, P., Favre, J., Kenzari, S., Piotrowski, B., Peltier, L., Laheurte, P. (2019). Architectural effect on 3D elastic properties and anisotropy of cubic lattice structures. *Materials & Design*, 182, 108059.

Longo, S.J., Cox, S.M., Azizi, E., Ilton, M., Olberding, J.P., St Pierre, R., Patek, S.N. (2019). Beyond power amplification: Latch-mediated spring actuation is an emerging framework for the study of diverse elastic systems. *Journal of Experimental Biology*, 222 [Online]. Available at: https://jeb.biologists.org/content/222/15/jeb197889.full.

Lopes, L.R., Silva, A.F., Carneiro, O.S. (2018). Multi-material 3D printing: The relevance of materials affinity on the boundary interface performance. *Additive Manufacturing*, 23, 45–52.

Lu, D., Zhu, M., Wu, S., Lian, O., Wang, W., Adlam, D., Hoyland, J.A., Saunders, B.R. (2020). Programmed multi-responsive hydrogel assemblies with light-tunable mechanical properties, actuation, and fluorescence. *Advanced Functional Materials*, 30, 1909359.

Lushia, E. and Peskin, C.S. (2013). Modeling and simulation of active suspensions containing large numbers of interacting micro-swimmers. *Computers & Structures*, 122, 239–248.

Lv, C., Sun, X.C., Xia, H., Yu, Y.H., Wang, G., Cao, X.W., Li, S.X., Wang, Y.S., Chen, Q.D., Yu, Y.D. et al. (2018). Humidity-responsive actuation of programmable hydrogel micro-structures based on 3D printing. *Sensors and Actuators*, B259, 736–744.

Ma, G., Li, Z., Wang, L., Wang, F., Sanjayan, J. (2019). Mechanical anisotropy of aligned fiber reinforced composite for extrusion-based 3D printing. *Construction & Building Materials*, 202, 770–783.

Ma, J., Zang, S., Feng, H., Chen, Y., You, Z. (2021). Theoretical characterization of a non-rigid-foldable square-twist origami for property programmability. *International Journal of Mechanical Sciences*, 189, 105981.

Mahimwalla, Z. (2013). Characterization of photo-induced photo-mechanical responses in azo-benzene polymers. PhD Thesis, McGill University, Montreal.

Mahimwalla, Z., Yager, K., Mamiya, J.I., Shishido, A., Priimagi, A., Barrett, C. (2012). Azo-benzene photo-mechanics prospects and potential applications. *Polymer Bulletin*, 69, 967–1006.

Malhotra, A., Thomas, J.C., Caroll, J.M., Miller, L.A. (1980). Cognitive processes in design. *International Journal of Man-Machines Studies*, 12, 119–140.

Mallard, S. (2018). *Disruption : préparez-vous à changer le monde*. Dunod, Paris.

Manikandan, N., Rajesh, P.K., Harish, V. (2021). An analysis of the methods and materials for 4-dimensional printing. *Materials Today Proceedings*, 38, 2167–2173.

Manna, R.K., Shklyaev, O.E., Stone, H.A., Balazs, A.C. (2020). Chemically controlled shape-morphing of elastic sheets. *Materials Horizons*, 7, 2314.

Mantelli, A., Levi, M., Turri, S., Suriano, R. (2019). Remanufacturing of end-of-life glass-fiber reinforced composites via UV-assisted 3D printing. *Rapid Prototyping Journal*, 26, 981–992.

Mao, Y. and Anand, L. (2018). A theory for fracture of polymeric gels. *Journal of the Mechanics and Physics of Solids*, 115, 30–53.

Marcuse, H. (1964). *One-Dimensional Man*. Beacon Press, Boston.

Martin, J.J., Fiore, B.E., Erb, R.M. (2015). Designing bioinspired composite reinforcement architecture via 3D magnetic printing. *Nature Communication*, 6, 8641.

Martinez, R.V., Fish, C.R., Chen, X., Whitesides, G.M. (2012). Elastomeric origami: Programmable paper-elastomer composites as pneumatic actuators. *Advanced Functional Materials*, 22, 1376–1384.

Martinez, J., Song, H., Dumas, J., Lefebvre, S. (2017). Orthotropic k-nearest foams for additive manufacturing. *ACM Transactions on Graphics, Association for Computing Machinery*, 7, 121:1–121:12.

Martinez, J., Hornus, S., Song, H., Lefebvre, S. (2018). Polyhedral Voronoi diagrams for additive manufacturing. *ACM Transactions on Graphics, Association for Computing Machinery, Proceedings of SIGGRAPH 2018*, 37 [Online]. Available at: https://hal.inria.fr/hal-01697103/file/paper.pdf.

Masters, I.G. and Evans, K.E. (1996). Models for the elastic deformation of honeycombs. *Composite Structures*, 35, 403–422.

Mavroidis, C. (2002). Development of advanced actuators using shape memory alloys and electrorheological fluids. *Research in Nondestructive Evaluation*, 14, 1–32.

Maziz, A., Concas, A., Khaldi, A., Stålhand, J., Persson, N.K., Jager, E. (2017). Knitting and weaving artificial muscles. *Science Advances*, 3, e1600327.

Meier, H., Haberland, C., Frenzel, J. (2012). Structural and functional properties of NiTi shape memory alloys produced by Selective Laser Melting. In *Innovative Developments in Virtual and Physical Prototyping*, Bártolo, P. (ed.). Taylor and Francis Group, London.

Mélanie, R. (2020). Pourquoi combiner l'intelligence artificielle et l'impression 3D ? [Online]. Available at: https://www.3dnatives.com/intelligence-artificielle-et-impression-3d-06012020/#!

Meng, L., Shi, J., Yang, C., Gao, T., Hou, Y., Song, L., Gu, D., Zhu, J., Breitkopf, P., Zhang, W. (2020). An emerging class of hyperbolic lattice exhibiting tunable elastic properties and impact absorption through chiral twisting. *Extreme Mechanics Letters*, 40, 100869.

Mercier, J.P., Zambelli, G., Kurz, W. (1999). *Introduction à la science des matériaux*. Presses Polytechniques et Universitaires Romandes, Lausanne.

Mill, J.S. (1988). *L'utilitarisme*. Champs Classiques, Paris.

Mirvakili, S.M., Sim, D., Hunter, I.W., Langer, R. (2020). Actuation of untethered pneumatic artificial muscles and soft robots using magnetically induced liquid-to-gas phase transitions. *Science Robotics*, 5, eaaz4239.

Mirzaali, M.J., Caracciolo, A., Pahlavani, H., Janbaz, S., Vergani, L., Zadpoor, A.A. (2018). Multi-material 3D printed mechanical metamaterials: Rational design of elastic properties through spatial distribution of hard and soft phases. *Applied Physics Letters*, 113, 10.1063/1.5064864.

MIT (2013). Amazing technology invented by MIT – Tangible media [Online]. Available at: https://www.youtube.com/watch?v=lvtfD_rJ2hE and https://www.youtube.com/watch?v=lCARHatJQJA&feature=iv&src_vid=lvtfD_rJ2hE&annotation_id=annotation_4171896729.

MIT (2019). MIT researchers upgrade self-transforming robot blocks: The jumping, spinning and flipping M-Blocks achieve better communication and coordination [Online]. Available at: https://www.roboticsbusinessreview.com/research/mit-researchers-upgrade-self-transforming-m-blocks/.

MIT (2020). MIT scientists made a shape-shifting material that morphs into a human face [Online]. Available at: https://arstechnica.com/science/2020/01/just-change-the-temperature-to-make-this-material-transform-into-a-human-face/.

Mitchell, N.P., Nash, L.M., Hexner, D., Turner, A.M., Irvine, W.T.M. (2018). Amorphous topological insulators constructed from random point sets. *Nature Physics* [Online]. Available at: https://par.nsf.gov/servlets/purl/10065111.

Modes, C. and Warner, M. (2016). Shape-programmable materials. *Physics Today*, 69, 32.

Moises, D., Lopez, B., Ahmad, R. (2020). Tensile mechanical behavior of multi-polymer sandwich structures via fused deposition modelling. *Polymers*, 12, 651.

Monteiro, M.J. (2018). Order from disorder through dissipation of free energy. *Nature Nanotechnology*, 13, 771–772.

Montgomery, S.M., Hilborn, H., Hamel, C.M., Kuang, X., Long, K.N., Qi, H.J. (2021). The 3D printing and modeling of functionally graded Kelvin foams for controlling crushing performance. *Extreme Mechanics Letters*, 43, 101323.

Moore, D.G., Barbera, L., Masania, K., Studart, A.R. (2020). Three-dimensional printing of multicomponent glasses using phase-separating resins. *Nature Materials*, 19, 212–217.

More, T. (1997). *Utopia*. Dover Publications, New York.

Morellon, E. (2010). Développement d'actionneurs en alliage à mémoire de forme pour un prototype d'aile d'avion adaptative. Electronics Master's Thesis, Ecole de technologie supérieure, Montreal [Online]. Available at: https://espace.etsmtl.ca/id/eprint/280/.

Moreno, A. (2004). Auto-organisation, autonomie et identité. *Revue internationale de philosophie*, 58, 135–150.

Mostafavi, S., Kemper, B.N., Du, C. (2019). Materializing hybridity in architecture: Design to robotic production of multi-materiality in multiple scales. *Architectural Science Review*, 62, 424–437.

Mousanezhad, D., Kamrava, S., Vaziri, A. (2017). Origami-based building blocks for modular construction of foldable structures. *Scientific Reports*, 7, 14792.

Mugnier, L. (2008). Introduction aux problèmes inverses : application à l'imagerie optique à haute résolution en astronomie. In *Des données à l'objet : le problème inverse*, Léna, P. (ed.). EDP Sciences/CNRS, Paris [Online]. Available at: http://laurent.mugnier.free.fr/ftp/SupOpt/methodesPhy-LM.pdf.

Muguruza, A., Bonada Bo, J., Gómez, A., Minguella-Canela, J., Fernandes, J., Ramos, F., Xuriguera, E., Varea, A., Cirera, A. (2017). Development of a multi-material additive manufacturing process for electronic devices. *Procedia Manufacturing*, 13, 746–753.

Mukhopadhyay, T., Ma, J., Feng, H., Hou, D., Gattas, J.M., Chen, Y., You, Z. (2020). Programmable stiffness and shape modulation in origami materials: Emergence of a distant actuation feature. *Applied Materials Today*, 19, 100537.

Nagel, S.R. (2017). Experimental soft-matter science. *Reviews of Modern Physics*, 89, 025002.

Naify, C.J., Ikei, A., Rohde, C.A. (2020). Locally programmable metamaterial elements using four-dimensional printing. *Extreme Mechanics Letters*, 36, 100654.

Naja, A. and Golestanian, R. (2004). Simple swimmer at low Reynolds number: Three linked spheres. *Physical Review*, E69, 062901.

Nakano, H. (2010). Direction control of photomechanical bending of a photochromic molecular fiber. *Journal of Material Chemistry*, 20, 2071–2074.

Naleway, S.E., Porter, M.M., McKittrick, J., Meyers, M.A. (2015). Structural design elements in biological materials: Application to bio-inspiration. *Advanced Materials*, 27, 5455–5476.

NAP – National Academy Press (2019a). High-entropy materials, ultra-strong molecules, and nanoelectronics: Emerging capabilities and research objectives. *Proceedings of a Workshop* [Online]. Available at: http://nap.edu/25106.

NAP – National Academy Press (2019b). Frontiers of materials research: A decadal survey [Online]. Available at: http://nap.edu/25244.

Narayan, S., Stewart, E.M., Anand, L. (2021). Coupled electro-chemo-elasticity: Application to modeling the actuation response of ionic polymer–metal composites. *Journal of the Mechanics and Physics of Solids*, 152, 104394.

New Scientist (2015). Liquid metal brings shape-shifting robot a step closer [Online]. Available at: https://www.newscientist.com/article/dn27127-liquid-metal-brings-shape-shifting-robot-a-step-closer/.

Nguyen, N.A., Bowland, C.C., Naskar, A.K. (2018). A general method to improve 3D-printability and inter-layer adhesion in lignin-based composites. *Applied Materials Today*, 12, 138–152.

Ni, X., Chen, C., Li, J. (2020). Interfacial fatigue fracture of tissue adhesive hydrogels. *Extreme Mechanics Letters*, 34, 100601.

Nie, M. and Takeuchi, S. (2020). 3D bio-fabrication using living cells for applications in bio-hybrid sensors and actuators. *ACS Applied Bio-Materials*, 3, 8121.

Nie, M., Huang, C., Du, X. (2021). Recent advances in color-tunable soft actuators. *Nanoscale*, 13, 2780–2791.

Nimesis (2017). Exemples d'applications [Online]. Available at: http://www.nimesis.com/faq/exemples-dapplications/.

Ning, X., Wang, X., Zhang, Y., Yu, X., Choi, D., Zheng, N., Kim, D.S., Huang, Y., Zhang, Y., Rogers, J.A. (2018). Assembly of advanced materials into 3D functional structures by methods inspired by origami and kirigami: A review. *Advanced Materials Interfaces*, 5, 1800284.

Nixon, R. and De Bo, G. (2020). Three concomitant C-C dissociation pathways during the mechanical activation of an N-heterocyclic carbene precursor. *Nature Chemistry*, 12, 826–831.

Nkomo, N.Z. (2018). A review of 4D printing technology and future trends. *11th South African Conference on Computational and Applied Mechanics SACAM 2018*, Vanderbijlpark South Africa, 17–19 September [Online]. Available at: https://www.researchgate.net/profile/Nkosilathi-Nkomo/publication/328162917_A_Review_of_4D_Printing_Technology_and_Future_Trends/links/5bbe0179a6fdccf2978f17d4/A-Review-of-4D-Printing-Technology-and-Future-Trends.pdf.

Nordmann, A. (2004). *Technologies convergentes. Façonner l'avenir des sociétés européennes*. Commission Européenne, Luxembourg.

Novak, N., Vesenjak, M., Ren, Z. (2016). Auxetic cellular materials: A review. *Journal of Mechanical Engineering*, 62, 485–493.

Novelino, L.S., Ze, Q., Wu, S., Paulino, G.H., Zhao, R. (2020). Untethered control of functional origami micro-robots with distributed actuation. *Proceedings of the National Academy of Sciences*, 117, 24096–24101.

Novotný, P., Wang, H., Pumera, M. (2020). Nano-robots: Machines squeezed between molecular motors and micro-motors. *Chemistry*, 6, 867–884.

Okabe, A., Boots, B., Sugihara, K. (1992). *Spatial Tessellations: Concepts and Applications of Voronoi Diagrams*. John Wiley & Sons, Chichester.

Onal, C.D., Chen, X., Whitesides, G.M., Rus, D. (2017). Soft mobile robots with on-board chemical pressure generation. *Robotics Research*, 525–540 [Online]. Available at: https://groups.csail.mit.edu/drl/wiki/images/8/81/Onal-ISRR-2011.pdf.

Ott, S. (2020). Caractérisation dynamique d'actionneurs fluidiques, et identification expérimentale des mécanismes dynamiques d'interaction jet couche limite induits. Thesis, Université Polytechnique des Hauts de France, Valenciennes [Online]. Available at: https://tel.archives-ouvertes.fr/tel-02886215/document.

Oveissi, F., Fletcher, D.F., Dehghani, F., Naficy, S. (2021). Tough hydrogels for soft artificial muscles. *Materials & Design*, 203, 109609 [Online]. Available at: https://www.sciencedirect.com/science/article/pii/S0264127521001623.

Overvelde, J.T.B. (2019). How to print multi-material devices in one go. *Nature*, 575, 289–290.

Pal, A., Goswami, D., Martinez, R.V. (2020). Elastic energy storage enables rapid and programmable actuation in soft machines. *Advanced Functional Materials*, 30, 1906603.

Patel, D.K., Sakhaei, A.K., Layani, M., Zhang, B., Ge, Q., Magdassi, S. (2017). Highly stretchable and UV curable elastomers for digital light processing based 3D printing. *Advanced Materials*, 28(15), 1606000.

Patino, T., Arqué, X., Mestre, R., Palacios, L., Sanchez, S. (2018). Fundamental aspects of enzyme-powered microand nano-swimmers. *Accounts in Chemical Research*, 51, 2662–2671.

Paxton, W.F., Kistler, K.C., Olmeda, C.C., Sen, A., St Angelo, S.K., Cao, Y., Mallouk, T.E., Lammert, P.E., Crespi, V.H. (2004). Catalytic nano-motors: Autonomous movement of striped nano-rods. *Journal of the American Chemical Society*, 126, 13424–13431.

Peele, B.N., Wallin, T.J., Zhao, H., Sheperd, R.F. (2015). 3D printing antagonistic system of artificial muscle using projection stereo-lithography. *Bio-inspiration & Bio-mimicry*, 10, 055003.

Pendry, J.B. (2000). Negative refraction makes a perfect lens. *Physical Review Letters*, 85, 3966–3969.

Peng, B., Li, Q., Feng, X.Q., Gao, H. (2021). Effect of shear stress on adhesive contact with a generalized Maugis-Dugdale cohesive zone model. *Journal of the Mechanics and Physics of Solids*, 148, 104275.

Peppas, N.A., Bures, P., Leobandung, W., Ichikawa, H. (2000). Hydrogels in pharmaceutical formulations. *European Journal of Pharmacy & Bio-pharmacy*, 50, 27–46.

Petitgirard, L. (2014). Les lectures scientifiques du changement et de l'incertitude : une perspective historique. In *La prospective scientifique en action*, Durance, P. (ed.). Odile Jacob, Paris.

Petr, M., Helgeson, M.E., Soulages, J., McKinley, G.H., Hammond, P.T. (2015). Rapid viscoelastic switching of an ambient temperature range photo-responsive azo-benzene side chain liquid crystal polymer. *Polymer*, 54, 2850–2856.

Pevzner, P.A. (2010). *Bio-Informatique Moléculaire : une approche algorithmique*. Springer, Paris.

Peyer, K.E., Qiu, F., Zhang, L., Nelson, B.J. (2012). Movement of artificial bacterial flagella in heterogeneous viscous environments at the microscale [Online]. Available at: https://infoscience.epfl.ch/record/180951/files/Kathrin-Nelson_Movement__Microscale_2012.pdf.

Pic, A. (2009). Les matériaux élastomériques [Online]. Available at: https://orthodfr.edpsciences.org/articles/orthodfr/pdf/2009/01/or0908.pdf.

Picard, J. (1928). *Essai sur les conditions positives de l'invention dans les sciences*. Felix Aléau, Paris.

Pinho, A.C., Buga, C.S., Piedade, A.P. (2020). The chemistry behind 4D printing. *Applied Materials Today*, 19, 100611.

Piotrowska, R., Hesketh, T., Wang, H., Martin, A.R.G., Bowering, D., Zhang, C., Hu, C.T., McPhee, S.A., Wang, T., Park, Y. et al. (2021). Mechanistic insights of evaporation-induced actuation in supramolecular crystals. *Nature Materials*, 20, 403–409.

Piranda, B. and Bourgeois, J. (2020). Datom: A deformable modular robot for building self-reconfigurable programmable matter. arXiv: 2005.03402v1.

Plotinus (2017). *The Six Enneads*, translated by Mackenna, S. and Page, B.S. CreateSpace Independent Publishing.

Plucinsky, P., Kowalski, B.A., White, T.J., Bhattacharya, K. (2018). Patterning non-isometric origami in nematic elastomer sheets. *Soft Matter*, 14, 3127–3134.

Preparata, F.P. and Shamos, M.I. (1985). *Computational Geometry: An Introduction*. Springer Verlag, New York.

Priestley, J. (2015). *Histoire des sciences et des savoirs*. Le Seuil, Paris.

Qi, S., Guo, H., Fu, J., Xie, Y., Zhu, M., Yu, M. (2020). 3D printed shape-programmable magneto-active soft matter for biomimetic applications. *Composites Science and Technology*, 188, 107973.

Qian, J.Y., Hou, C.W., Li, X.J., Jin, Z.J. (2020). Actuation mechanism of micro-valves: A review. *Micro-machines*, 11, 172.

Qian, H., Purwanto, N.S., Ivanoff, D.G., Halmes, A.J., Sottos, N.R., Moore, J.S. (2021). Fast, reversible mechanochromism of regioisomeric oxazine mechanophores: Developing in situ responsive force probes for polymeric materials. *Chem*, 7, 1080–1091.

Qiu, Y., Zhang, E., Plamthottam, R., Pei, Q. (2019). Dielectric elastomer artificial muscle: Materials innovations and device explorations. *Accounts in Chemical Research*, 52, 316–325.

Rafiee, M., Farahani, R.D., Therriault, D. (2020). Multi-material 3D and 4D printing: A survey. *Advanced Sciences*, 7, 1902307.

Rafsanjani, A., Bertoldi, K., Studart, A.R. (2020). Programming soft robots with flexible mechanical metamaterials [Online]. Available at: https://arxiv.org/ftp/arxiv/papers/1906/1906.00306.pdf.

Rajonson, G., Poulet, D., Bruneau, M., Teboula, V. (2020). Comparison of time reversal symmetric and asymmetric nano-swimmers oriented with an electric field in soft matter. *Journal of Chemical Physics*, 152, 024503.

Rand Corporation (2021). Measuring the value of invention: The impact of Lemelson-MIT Prize winners' inventions [Online]. Available at: https://www.rand.org/content/dam/rand/pubs/research_reports/RRA800/RRA838-1/RAND_RRA838-1.pdf.

Ranosa, T. (2015). MIT tiny origami robot can fold itself and self-destruct: Perfect profile for future microsurgeon? [Online]. Available at: http://www.techtimes.com/articles/56678/20150530/mit-tiny-origami-robot-can-fold-itself-and-self-destruct-perfect-profile-for-future-microsurgeon.htm.

Rao, K.J., Li, F., Meng, L., Zheng, H., Cai, F., Wang, W. (2015). A force to be reckoned with: A review of synthetic micro-swimmers powered by ultrasound. *Small*, 11, 2836–2846.

Rasmussen, A. (2015). Sciences et guerres. In *Histoire des sciences et des savoirs*, Pestre, D. (ed.). Le Seuil, Paris.

Rastogi, P., Njuguna, J., Kandasubramanian, B. (2019). Exploration of elastomeric and polymeric liquid crystals with photo-thermal actuation: A review. *European Polymer Journal*, 121, 109287.

Ray, N., Sokolov, D., Lefebvre, S., Lévy, B. (2018). Meshless Voronoi on the GPU. *ACM Transactions on Graphics. Association for Computing Machinery* [Online]. Available at: https://hal.inria.fr/hal-01927559/file/voroGPU.pdf.

Reiser, R., Koch, L., Dunn, K.A., Matsuura, T., Iwata, F., Fogel, O., Kotler, Z., Zhou, N., Charipar, K., Piqué, A. et al. (2019). Metals by micro-scale additive manufacturing: Comparison of micro-structure and mechanical properties. arXiv: 1912.03581v1. [Online]. Available at: https://www.researchgate.net/publication/337856016_Metals_by_micro-scale_additive_manufacturing_comparison_of_microstructure_and_mechanical_properties.

Ren, X., Das, R., Tran, P., Ngo, T.D., Xie, Y.M. (2018). Auxetic metamaterials and structures: A review. *Smart Materials and Structures*, 27, aaa61c [Online]. Available at: https://iopscience.iop.org/article/10.1088/1361-665X/aaa61c/meta.

Ren, M., Qiao, J., Wang, Y., Wu, K., Dong, L., Shen, X., Zhang, H., Yang, W., Wu, Y., Yong, Z. et al. (2021). Strong and robust electrochemical artificial muscles by ionic-liquid-in-nanofiber-sheathed carbon nanotube yarns. *Small*, 17, 2006181.

Richard, C., Simmchen, J., Eychmüller, A. (2018). Photocatalytic iron oxide micro-swimmers for environmental remediation. *Zeitschrift für Physikalische Chemie*, 232, 747–757.

Roach, D.J., Kuang, X., Yuan, C., Chen, K., Qi, H.J. (2018). Novel ink for ambient condition printing of liquid crystal elastomers for 4D printing. *Smart Materials and Structures*, 27, 125011.

Rochon, P. (2015). Description des intérêts actuels en matière de recherche [Online]. Available at: http://www.rmc.ca/fr/physique/dr-paul-rochon-bsc-phd-peng-professeur.

Rocklin, D.Z., Zhou, S., Sun, K., Mao, X. (2017). Transformable topological mechanical metamaterials. *Nature Communications*, 8, 14201.

Rodrigue, H., Wang, W., Han, W.H., Kim, T.J., Ahn, S.H. (2017). An overview of shape memory alloy-coupled actuators and robots. *Soft Robotics*, 4, 3–15.

Ronellenfitsch, H., Stoop, N., Yu, J., Forrow, A., Dunkel, J. (2019). Inverse design of discrete mechanical metamaterials. arXiv:1802.07214v2.

Roppolo, I., Chiappone, A., Angelini, A., Stassi, S., Frascella, F., Pirri, C., Ricciardi, C., Descrovi, E. (2017). 3D printable light-responsive polymers. *Materials Horizons*, 4, 396–401.

Rosales, A.M., Mabry, K.M., Nehls, E.M., Anseth, K.S. (2015). Photo-responsive elastic properties of azo-benzene-containing poly-(ethylene-glycol)-based hydrogels. *Bio-macromolecules*, 16, 798–806.

Rothemund, P.W.K. (2006). Folding DNA to create nanoscale shapes and patterns. *Nature*, 440, 297–302.

Roure, F. and Arcier, L. (2012). Avant-propos. In *Les robots : nouveaux concepts, nouveaux usages*. Annales des Mines – Réalités industrielles, Paris.

Rousseau, J.J. (1995). *L'Emile, ou de l'éducation*. Folios-Essais, Paris.

Rousseau, I.A. (2008). Challenges of shape memory polymers: A review of the progress toward overcoming SMP's limitations. *Polymer Engineering Science*, 2075–2089.

Roux, M. (2011). *J'ai demandé un rapport*. Flammarion, Paris.

Sadeqi, A., Nejad, H.R., Owyeung R.E., Sonkusale, S. (2019). Three dimensional printing of metamaterial embedded geometrical optics (MEGO). *Microsystems & Nanoengineering*, 5, 16.

Saed, M.O., Ambulo, C.P., Hyun, K., Rohit, D., Vyom, R., Kyle, S., Siddiqui, D.A., Cue, J.M.O., Stefan, M.C., Shankar, M.R. et al. (2019). Molecularly-engineered, 4D-printed liquid crystal elastomer actuators. *Advanced Functional Materials*, 29, 1806412.

Salari-Sharif, L., Ryan, S.M., Pelacci, M., Guest, J.K., Valdevit, L., Szyniszewski, S. (2018). Damping of selectively bonded 3D woven lattice materials. *Scientific Reports*, 8, 14572.

Saleh, E., Woolliams, P., Clarke, B., Gregory, A., Greedy, S., Smartt, C., Wildman, R., Ashcroft, I., Hague, R., Dickens, P. et al. (2017). 3D inkjet-printed UV-curable inks for multi-functional electromagnetic applications. *Additive Manufacturing*, 13, 143–148.

Sanchez, C. (2011). Chimie des matériaux hybrides [Online]. Available at: https://www.college-de-france.fr/media/clement-sanchez/UPL5460438176618849830_sanchez.pdf.

Sarikaya, S., Garde, F., Auletta, J.T., Kavosi, J., Langrock, A., Mackie, D.M., Naraghia, M. (2021). A-thermal artificial muscles with drastically improved work capacity from pH-responsive coiled polymer fibers. *Sensors and Actuators B: Chemical*, 335, 129703.

Saunders, R. (2020). Metamaterials using additive manufacturing technologies. Naval Research Laboratory, Washington [Online]. Available at: https://apps.dtic.mil/sti/pdfs/AD1103255.pdf.

Sauvage, J.P. (2017). From chemical topology to molecular machines (Nobel Lecture). *Angewante Chemie, International Edition*, 56, 11080–11093.

Saxena, K.K., Das, R., Calius, E.P. (2016). Three decades of auxetics research – Materials with negative Poisson's ratio: A review. *Adv. Eng. Mater.*, 18, 1847–1870.

Scalet, G. (2020). Two-way and multiple-way shape memory polymers for soft robotics: An overview. *Actuators*, 9, 10.

Schaffner, M., Faber, J.A., Pianegonda, L., Rühs, P.A., Coulter, F, Studart, A.R. (2018). 3D printing of robotic soft actuators with programmable bioinspired architectures. *Nature Communications*, 9, 878.

Schärtl, W. (2010). Current directions in core–shell nanoparticle design. *Nanoscale*, 2, 829–843.

Schiffter, F. (2019). Le desperado en espadrilles. In *Gaston, un philosophe au travail*, Latour, B., Chabot, P., Feertchak, S., Schiffter, F., Citton, Y., Jeantet, A. (eds). Philosophie Magazine, Paris.

Schoemaker, P.J.H., Day, G., Snyder, S.A. (2012). Integrating organizational networks – Strategi radars and scenarios planning. *Technological Forecasting and Social Change*, 80, 815–824.

Schulz, A., Sung, C., Spielberg, A., Zhao, W., Cheng, R., Grinspun, E., Rus, D., Matusik, W. (2017). Interactive robogami: An end-to-end system for design of robots with ground locomotion. *The International Journal of Robotics Research*, 36, 1131–1147.

Schumacher, C., Bickel, B., Rys, J., Marschner, S., Daraio, C., Gross, M. (2015). Microstructures to control elasticity in 3D printing. *ACM Transactions on Graphics*, 34, 136 [Online]. Available at: https://core.ac.uk/download/pdf/77926908.pdf.

Sertoglu, K. (2021). Impossible objects and Owens Corning set to develop fiberglass composites for 3D printing [Online]. Available at: https://3dprintingindustry.com/news/impossible-objects-and-owens-corning-set-to-develop-fiberglass-composites-for-3d-printing-190430/.

Shao, H., Wei, S., Jiang, X., Holmes, D.P., Ghosh, T.K. (2018). Bioinspired electrically activated soft bi-stable actuators. *Advanced Functional Materials*, 28, 1802999.

Shao, G., Ware, H.O.T., Huang, J., Hai, R., Li, L., Sun, C. (2021). 3D printed magnetically-actuating micro-gripper operates in air and water. *Additive Manufacturing*, 38, 101834.

Shapiro, J.M., Drinkwater, B.W., Perriman, A.W., Fraser, M. (2021). Sonolithography: In-air ultrasonic particulate and droplet manipulation for multiscale surface patterning. *Advanced Materials Technologies*, 6, 2000689.

Shelby, R.A., Smith, D.R., Schultz, S. (2001). Experimental verification of a negative index of refraction. *Science*, 292, 77–79.

Sheng, J. and Desai, J. (2015). A novel meso-scale SMA-actuated torsion actuator. *IEEE/RSJ International Conference on Intelligent Robot and Systems*, Hamburg, 28 September–2 October.

Sheng, L., Zhang J., Liu J. (2014). Diverse transformations of liquid metals between different morphologies. *Adv. Mater.*, 26, 6036–6042.

Shi, S., Chen, Y., Yao, X., Zhang, M. (2019). Lightweight evolution strategies for nanoswimmers-oriented in vivo computation. *IEEE Congress on Evolutionary Computation (CEC)* [Online]. Available at: https://ieeexplore.ieee.org/abstract/document/8790356.

Shin, J.Y. and Abbott, N.L. (1999). Using light to control dynamic surface tensions of aqueous solutions of water soluble surfactants. *Langmuir*, 15, 4404–4410.

Simmel, G. (1990). *Michel Ange et Rodin*. Rivages, Paris.

Simon, H.A. (2004). *Les sciences de l'artificiel*. Folio-Essais, Paris.

Simondon, G. (1997). *L'individuation psychique et collective*. Aubier, Paris.

Simondon, G. (2001). *Du mode d'existence des objets techniques*. Aubier, Paris.

Simoneau, C. (2013). Modélisation de matériaux composites adaptatifs munis d'actionneurs en alliage à mémoire de forme. Mechanical Engineering Master's thesis, Montreal [Online]. Available at: https://espace.etsmtl.ca/id/eprint/1177/1/SIMONEAU_Charles.pdf.

Sindersberger, D., Diermeier, A., Prem, N., Monkman, G.J., Sindersberger, D., Diermeier, A., Prem, N., Monkman, G.J. (2018). Printing of hybrid magneto active polymers with 6 degrees of freedom. *Materials Today Communications*, 15, 269–274.

Smalyukh, I.I. (2018). Liquid crystal colloids. *Annual Review of Condensed Matter Physics*, 9, 207–226.

Smith, D.R., Padilla, W.J., Vier, D.C., Nemat-Nasser, S.C., Schultz, S. (2000). Composite medium with simultaneously negative permeability and permittivity. *Physical Review Letters*, 84, 4184–4187.

Socrates (2021). *Vivre et revivre encore*. Editions de l'Aube, La Tour-d'Aigues.

Solovev, A., Mei, Y., Bermúdez Ureña, U., Huang, G., Schmidt, O.G. (2009). Catalytic microtubular jet engines self-propelled by accumulated gas bubbles. *Small*, 5, 1688–1692.

Song, S.H., Lee, J.Y., Rodrigue, H., Choi, I.S., Kang, Y.J., Ahn, S.H. (2016). 35 Hz shape memory alloy actuator with bending-twisting mode. *Scientific Reports*, 6, 21118.

Song, H., Lee, H., Lee, J., Choe, J.K., Lee, S., Yi, J.Y., Park, S., Yoo, J.W., Kwon, M.S., Kim, J. (2020). Reprogrammable ferromagnetic domains for reconfigurable soft magnetic actuators. *Nano Letters*, 20, 5185–5192.

Sossou, G., Demoly, F., Belkebir, H., Qi, H.J., Gomes, S., Montavon, G. (2019a). Design for 4D printing: A voxel-based modeling and simulation of smart materials. *Materials & Design*, 175, 107798.

Sossou, G., Demoly, F., Belkebir, H., Qi, H.J., Gomes, S., Montavon, G. (2019b). Design for 4D printing: Modeling and computation of smart materials distributions. *Materials & Design*, 181, 108074.

Sparrman, B., du Pasquier, C., Thomsen, C., Darbari, S., Rustom, R., Laucks, J., Shea, K., Tibbits, S. (2021). Printed silicone pneumatic actuators for soft robotics. *Additive Manufacturing*, 40, 101860.

Spector, C. (2018). Pouvoir, peur et terreur. In *De quoi avons-nous peur ?* Birnbaum, J. (ed.). Gallimard, Paris.

Sperber, D. (1995). *La contagion des idées*. Odile Jacob, Paris.

Spinoza, B. (1955). *Œuvres*. Gallimard, Paris.

Stanton, M.M., Trichet-Paredes, C., Sanchez, S. (2015). Applications of 3D printing for micro-swimmers and bio-hybrid robotics. *Lab-on-Chip*, 15, 1634–1637.

Stengers, I. (2020). *Réactiver le sens commun – Lecture de Whitehead en temps de débâcle*. Les empêcheurs de penser en rond, Paris.

Stevenson, R. and De Bo, G. (2017). Controlling reactivity by geometry in Retro-Diels-Alder reactions under tension. *Journal of the American Chemical Society*, 139, 16768–16771.

Stiegler, B. (2004). *De la misère symbolique*. Champs Essais, Paris.

Stiegler, B. (2019). *Il faut s'adapter – sur un nouvel impératif politique*. NRF Essais – Gallimard, Paris.

Surjadi, J.U., Gao, L., Du, H., Li, X., Xiong, X., Fang, N.X., Lu, Y. (2019). Mechanical metamaterials and their engineering applications. *Advanced Engineering Materials*, 21, 1800864.

Sussan, R. (2011). L'origami ADN assisté par ordinateur : vers une nanotechnologie de garage ? [Online]. Available at: http://www.internetactu.net/2011/05/10/lorigami-adn-assiste-par-ordinateur-vers-une-nanotechnologie-de-garage/.

Suzumori, K., Wada, A., Wakimoto, S. (2013). New mobile pressure control system for pneumatic actuators, using reversible chemical reactions of water. *Sensors and Actuators*, A201, 148–153.

Sweet, E., Mehta, R., Xu, Y., Jew, R., Lin, R., Lin, L. (2020). Finger-powered fluidic actuation and mixing via MultiJet 3D printing. *Lab-on-Chip*, 20, 3375–3385.

Tahon, C. (2003). *Evaluation des performances des systèmes de production*. Hermès/Lavoisier, Paris.

Tan, N., Hayat, A.A., Elara, M.R., Wood, K.L. (2020). A framework for taxonomy and evaluation of self-reconfigurable robotic systems. *IEEE Access*, 8, 13969–13986.

Tang, Y., Qin, L., Li, X., Chew, C., Zhu, J. (2017). A frog-inspired swimming robot based on dielectric elastomer actuators. *IEEE/RSJ International Conference on Intelligent Robots and Systems (IROS)*, Vancouver.

Tang, Y., Dai, B., Su, B., Shi, Y. (2021). Recent advances of 4D printing technologies toward soft tactile sensors. *Frontiers in Materials*, 8 [Online]. Available at: https://doi.org/10.3389/fmats.2021.658046.

Tao, R., Xi, L., Wu, W., Li, Y., Liao, B., Liu, L., Leng, J., Fang, D. (2020). 4D printed multi-stable metamaterials with mechanically tunable performance. *Composite Structures*, 252, 112663.

Teng, X., Zhang, M., Mujumdar, A.S. (2021). 4D printing: Recent advances and proposals in the food sector. *Trends in Food Science & Technology*, 110, 349–363.

Tenzeris, M.M., Bahr, R.A., Papadopoulos, A.D., Glytsis, E.N. (2016). Multi-domain modeling of 3D printed, nanotechnology and morphing/origami-based RF modules. *Microwave Symposium (IMS), IEEE MTT-S International*. doi: 10.1109/MWSYM.2016.7540101.

Teoh, J.E.M., An, J., Chua, C.K., Lv, M., Krishnasamy, V. (2017). Hierarchically self-morphing structure through 4D printing. *Virtual and Physical Prototyping*, 12, 61–68.

Thomas, B. (2021). Quelles sont les caractéristiques de l'imprimante 3D multi-matériaux d'Infotech ? [Online]. Available at: https://www.3dnatives.com/infotech-imprimante-3d-multi-materiaux-231220203/#!

Thomas, C., Tibbits, S., Banning, G. (2014). The programmable world. *Scientific American*, 311, 60–65.

Thorin, A. and Forêt, G. (2013). Calcul des structures : introduction au calcul de structures élastiques linéaires [Online]. Available at: https://cel.archives-ouvertes.fr/cel-01122394/document.

Thubagere, A.J., Thachuk, C., Berleant, J., Johnson, R.F., Ardelean, D.A., Cherry, K.M., Qian, L. (2017). Compiler-aided systematic construction of large-scale DNA strand displacement circuits using unpurified components. *Nature Communications*, 8, 14373.

Thuillier, P. (1980). *Le petit savant illustré*. Le Seuil, Paris.

Tian, Y., Demirel, S.E., Hasan, M.M.F., Pistikopoulos, E.N. (2018). An overview of process systems engineering approaches for process intensification: State of the art. *Chemical Engineering and Processing Process Intensification*, 133, 160–210.

Tottori, S., Zhang, L., Qiu, F., Krawczyk, K.K., Franco-Obregon, A., Nelson, B.J. (2012). Magnetic helical micro-machines: Fabrication, controlled swimming, and cargo transport. *Advanced Materials*, 24, 811–816.

Toursangsaraki, M. (2018). A review of multi-material and composite parts production by modified additive manufacturing methods [Online]. Available at: https://arxiv.org/ftp/arxiv/papers/1808/1808.01861.pdf.

Troyano, J., Legrand, A., Furukawa, S. (2021). Mechano-responsive porosity in metal-organic frameworks. *Trends in Chemistry*, 3, 254–265.

Turing, A. (1952). The chemical basis of morphogenesis. *Philosophical Transactions of the Royal Society London*, B237, 37–72.

Tyagi, M., Spinks, G.M., Jager, E.W.H. (2021). 3D printing micro-actuators for soft micro-robots. *Soft Robotics*, 8, 19–27.

Umedachi, T., Vikas, V., Trimmer, B.A. (2013). Highly deformable 3D printed soft robot generating inching and crawling locomotion with variable friction legs. *IEEE/RSJ International Conference on Intelligent Robots & Systems (IROS)*, 4590–4593.

Urhal, P., Mansour, G., Kyratsis, P., Tzetzis, D. (2020). A novel printing channel design for multi-material extrusion additive manufacturing. *MATEC Web Conference – 7th International Conference of Materials and Manufacturing Engineering (ICMMEN 2020)*, 318, 01024.

Valéry, P. (1931). *Regards sur le monde actuel*. Gallimard, Paris.

Van Manen, T., Janbaz, S., Jansen, K., Zadpoor, A.A. (2021). 4D printing of reconfigurable metamaterials and devices [Online]. Available at: https://assets.researchsquare.com/files/rs-182664/v1_stamped.pdf.

Vangelatos, Z., Gu, G.X., Grigoropoulos, C.P. (2019). Architected metamaterials with tailored 3D buckling mechanisms at the microscale. *Extreme Mechanics Letters*, 33, 100580.

Vangelatos, Z., Zhang, Z., Gu, G.X., Grigoropoulos, C.P. (2020). Tailoring the dynamic actuation of 3D-printed mechanical metamaterials through inherent and extrinsic instabilities. *Advanced Engineering Materials*, 22, 1901586.

Vatankhah-Varnosfaderani, M., Keith, A.N., Cong, Y., Liang, Y., Rosenthal, M., Sztucki, M., Clair, C., Magonov, S., Ivanov, D.A., Dobrynin, A.V. et al. (2018). Chameleon-like elastomers with molecularly encoded strain-adaptive stiffening and coloration. *Science*, 359, 1509–1513.

Velazquez, R., Pissaloux, E., Hafez, M., Szewczyk, J. (2008). Tactile rendering with shape memory alloy pin-matrix. *IEEE Transactions on Instrumentation and Measurement*, 57, 1051–1057.

Vermes, B. and Czigany, T. (2020). Non-conventional deformations: Materials and actuation. *Materials*, 13, 1383.

Vervisch, G. (2020). *Peut-on réussir sans effort, ni aucun talent ? Les mirages du mérite*. Poche, Paris.

Veselago, V.G. (1968). The electrodynamics of substances with negative epsilon and mu. *Soviet Physics USPEKHI*, 10, 509.

Veselago, V.G. and Narimanov, E.E. (2006). The left hand of brightness: Past, present and future of negative index materials. *Nature Materials*, 5, 759–762.

Villanueva, A.A., Joshi, K.B., Blottman, J.B., Priya, S. (2010). A bio-inspired shape memory alloy composite (BISMAC) actuator. *Smart Materials and Structures*, 19, 025013.

Villar, G., Heron, A.J., Bayley, H. (2011). Formation of droplet networks that function in aqueous environments. *Nature Nanotechnology*, 6, 803–808.

Villar, G., Graham, A.D., Bayley, H. (2013). A tissue-like printed material. *Science*, 340, 48–52.

Vinardi, L. (1980). L'art et les quatre faces de la connaissance. In *Prospective sur le XXème siècle*, Villoldo, A. and Dychtwald, K. (eds). Editions du Rocher, Monaco.

VMF214 (2017). L'essor de l'informatique moléculaire : une rupture capacitaire pour la défense [Online]. Available at: https://vmf214.net/2017/05/18/lessor-de-linformatique-moleculaire-une-rupture-capacitaire-pour-la-defense/.

Wagg, D., Bond, I., Weaver, P., Grisweel, M. (2007). *Adaptive Structures Engineering Applications*. John Wiley & Sons, New York.

Walters, P., Rossiter, J., McGoran, J. (2010). Smart materials and novel actuators: Creative applications in art and design [Online]. Available at: http://www.uwe.ac.uk/sca/research/cfpr/research/3D/research_projects/smart_materials_novel_actuators.html.

Wang, L. and Liu, J. (2014). Compatible hybrid 3D printing of metal and nonmetal inks for direct manufacture of end functional devices. *Science China Technological Sciences*, 57, 2089–2095.

Wang, L. and Liu, H.T. (2020). 3D compression–torsion cubic mechanical metamaterial with double inclined rods. *Extreme Mechanics Letters*, 37, 100706.

Wang, W., Castro, L.A., Hoyos, M., Mallouk, T.E. (2012). Autonomous motion of metallic micro-rods propelled by ultrasound. *ACS Nano*, 6, 6122.

Wang, Z., Gu, P., Wu, X. (2013). A gecko-inspired double-sided adhesive. *Physical Chemistry, Chemical Physics*, 47, 20764.

Wang, X., Sun, Y., Peng, C., Luo, H., Wang, R., Zhang, D. (2015). Transitional suspensions containing thermosensitive dispersant for three-dimensional printing. *ACS Applied Materials and Interface*, 7, 26131–26136.

Wang, L., Nurzaman, S., Iida, F. (2017). *Soft-Material Robotics: Foundations and Trends in Robotics*. Now Publishers Inc., Boston.

Wang, Q., Tian, X., Huang, L., Li, D., Malakhov, A.V., Polilov, A.N. (2018). Programmable morphing composites with embedded continuous fibers by 4D printing. *Material Design*, 155, 404–413.

Wang, S., Huang, B., McCoul, D., Li, M., Mu, L., Zhao, J. (2019a). A soft breaststroke-inspired swimming robot actuated by dielectric elastomers. *Smart Materials and Structures*, 28, 045006.

Wang, Y., Lai, H., Cheng, Z., Zhang, H., Zhang, E., Lv, T., Liu, Y., Jiang, L. (2019b). Gecko toe pads inspired in situ switchable super-hydrophobic shape memory adhesive film. *Nanoscale*. doi: 10.1039/c9nr00154a.

Wang, Q., Li, Z., Zhang, Y., Cui, S., Yang, Z., Lu, Z. (2020a). Ultra-low density architectured metamaterial with superior mechanical properties and energy absorption capability. *Composites*, B202, 108379.

Wang, Q., Yang, Z., Lu, Z., Li, X. (2020b). Mechanical responses of 3D cross-chiral auxetic materials under uniaxial compression. *Materials & Design*, 186, 108226.

Wang, W., Ouaras, K., Rutz, A.L., Li, X., Gerigk, M., Naegele, T.E., Malliaras, G.G., Huang, Y.Y.S. (2020c). Inflight fiber printing toward array and 3D optoelectronic and sensing architectures. *Science Advances*, 6, eaba0931.

Wang, X., Wang, Y., Wang, X., Niu, H., Ridi, B., Shu, J., Fang, X., Li, C., Wang, B., Gao, Y. et al. (2020d). A study of the microwave actuation of a liquid crystalline elastomer. *Soft Matter*, 16, 7332–7341.

Wang, D., Gao, C., Si, T., Li, Z., Guo, B., He, Q. (2021a). Near-infrared light propelled motion of needlelike liquid metal nanoswimmers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 611, 125865.

Wang, Z., Song, P., Pauli, M. (2021b). State of the art on computational design of assemblies with rigid parts. *Eurographics*, 40, In press [Online]. Available at: https://diglib.eg.org/bitstream/handle/10.1111/cgf142660/v40i2pp633-657.pdf.

Weeger, O. (2021). Numerical homogenization of secnd gradient linear elastic constitutive models for cubic 3D beam-lattice metamaterials. *International Journal of Solids and Structures*, 224, 111037.

Weeger, O., Boddeti, N., Yeung, S.K., Kaijima, S., Dunn, M.L. (2019). Digital design and nonlinear simulation for additive manufacturing of soft lattice structures. *Additive Manufacturing*, 25, 39–49.

Weinberg, S. (1997). *Le rêve d'une théorie ultime*. Odile Jacob, Paris.

Weng, Y., Li, M., Zhang, D., Tan, M.J., Qian, S. (2021). Investigation of interlayer adhesion of 3D printable cementitious material from the aspect of printing process. *Cement and Concrete Research*, 143, 106386.

Western, D., Blagov, P.S., Horenski, K., Kelts, C., Hamman, S. (2006). Neural bases of motivated reasoning – An IMRI study of emotional constraints on partisan political judgement. *Journal of Cognitive Neurosciences*, 18, 1947–1958.

Wheat, P.M., Marine, N.A., Moran, J.L., Posner, J.D. (2010). Rapid fabrication of bimetallic spherical motors. *Langmuir*, 26, 13052–13055.

Whitehead, A.N. (1968). *Modes of Thought*. The Free Press, New York.

Wikipedia (2015). Alliage à mémoire de forme [Online]. Available at: https://fr.wikipedia.org/wiki/Alliage_%C3%A0_m%C3%A9moire_de_forme.

Wikipedia (2021). Actionneur [Online]. Available at: https://fr.wikipedia.org/wiki/Actionneur.

Wilde, O. (2017). *Fabuleuses erreurs – de Darwin à Einstein*. CNRS, Paris.

Willmann, F. (2010). Présentation. In *La science-fiction : entre Cassandre et Prométhée*, Willmann, F. (ed.). Presses Universitaires de Nancy, Nancy.

Wilson, D.A., Nolte, R.J., van Hest, J.C. (2012). Autonomous movement of platinum-loaded stomatocytes. *Nature Chemistry*, 26, 268–274.

Winkler, R.G. and Gompper, G. (2020). The physics of active polymers and filaments. *The Journal of Chemical Physics*, 153, 040901 [Online]. Available at: https://aip.scitation.org/doi/10.1063/5.0011466.

Woods, D., Doty, D., Myhrvold, C., Hui, J., Zhou, F., Yin, P., Winfree, E. (2019). Diverse and robust molecular algorithms using reprogrammable DNA self-assembly. *Nature*, 567, 366–372.

Wormser, C. (2008). Generalized Voronoi diagrams and applications. PhD Thesis, Université de Nice Sophia Antipolis [Online]. Available at: https://tel.archives-ouvertes.fr/tel-00410850/document.

Wu, W., Hu, W., Qian, G., Liao, H., Xu, X., Berto, F. (2019). Mechanical design and multifunctional applications of chiral mechanical metamaterials: A review. *Materials & Design*, 180, 107950 [Online]. Available at: https://www.sciencedirect.com/science/article/pii/S0264127519303880.

Wu, H., Zhang, X., Ma, Z., Zhang, C., Ai, J., Chen, P., Yan, C., Su, B., Shi, Y. (2020). A material combination concept to realize 4D printed products with newly emerging property/functionality. *Advanced Science*, 7, 1903208.

Wu, J., Jang, B., Harduf, Y., Chapnik, Z., Avci, O.B., Chen, X., Puigmartí-Luis, J., Ergeneman, O., Nelson, B.J., Or, Y. et al. (2021). Helical klinotactic locomotion of two-link nanoswimmers with dual-function drug-loaded soft polysaccharide hinges. *Advanced Science*, 2004458.

Xu, Q., Wu, X., Wang, Z., Hu, T.S., Street, J., Luo, Y., Xia, Z. (2018). Temperature-induced tunable adhesion of gecko setae/spatula and their bio mimics. *Materials Today: Proceedings*, 5, 25879–25893.

Xue, R., Cui, X., Zhang, P., Liu, K., Li, Y., Wu, W., Liao, H. (2020). Mechanical design and energy absorption performances of novel dual scale hybrid plate-lattice mechanical metamaterials. *Extreme Mechanics Letters*, 40, 100918.

Yamada, K., Sone, J., Chen, J. (2009). Three-dimensional photochemical microfabrication of conductive polymers in transparent polymer sheet. *Optical Review*, 16, 208–212.

Yang, C., Vora, H.D., Chang, Y. (2018). Behavior of auxetic structures under compression and impact forces. *Smart Materials and Structures*, 27, aaa3cf [Online]. Available at: https://iopscience.iop.org/article/10.1088/1361-665X/aaa3cf/meta.

Yang, J., Bai, R., Chen, B., Suo, Z. (2019). Hydrogel adhesion: A supramolecular synergy of chemistry, topology, and mechanics. *Advanced Functional Materials*, 30(2), 1901693.

Yang, N., Chen, C.W., Yang, J., Silverberg, J.L. (2020). Emergent reconfigurable mechanical metamaterial tessellations with an exponentially large number of discrete configurations. *Materials and Design*, 196, 109143.

Yang, J., Wang, Z., Zhao, G. (2021a). Investigation into output force performance of an ionic polymer artificial muscle based on freeze-drying process. *Sensors and Actuators*, A321, 112427.

Yang, P., Fang, Y., Yuan, Y., Meng, S., Nan, Z., Xu, H., Imtiaz, H., Liu, B., Gao, H. (2021b). A perturbation force based approach to creasing instability in soft materials under general loading conditions. *Journal of the Mechanics and Physics of Solids*, 151, 104401.

Yigit, B., Alapan, Y., Sitti, M. (2019). Programmable collective behavior in dynamically self-assembled mobile micro-robotic swarms. *Advanced Science*, 6, 1801837.

Yildizdag, M.E., Tran, C.A., Barchiesi, E., Spagnuolo, M., Dell'Isola, F., Hild, F. (2019). A multi-disciplinary approach for mechanical metamaterial synthesis: A hierarchical modular multiscale cellular structure paradigm. In *State of the Art and Future Trends in Material Modeling*, Altenbach, H. and Öchsner, A. (eds). Springer, Cham [Online]. Available at: https://hal.archives-ouvertes.fr/hal-02916966/file/metamaterial_synthesis.pdf.

Yin, X., Gao, Z.Y., Zhang, S., Zhang, L.Y., Xu, G.K. (2020). Truncated regular octahedral tensegrity-based mechanical metamaterial with tunable and programmable Poisson's ratio. *International Journal of Mechanical Sciences*, 167, 105285.

Yoon, J. and Bae, S. (2020). Performance evaluation and design of thermo-responsive SMP shading prototypes. *Sustainability*, 12, 4391.

Yoshino, T., Kondo, M., Mamiya, J., Kinoshita, M., Yu, Y.L., Ikeda, T. (2010). Three dimensional photo-mobility of crosslinked azo-benzene liquid crystalline polymer fiber. *Advanced Materials*, 22, 1361–1363.

Youssef, M., Hueckel, T., Yi, G.R., Sacanna, S. (2016). Shape-shifting colloids via stimulated dewetting. *Nature Communications*, 7, 12216.

Yu, Y., Nakano, M., Ikeda, T. (2003). Photo-mechanics: Directed bending of a polymer film by light. *Nature*, 425, 145.

Yuan, S., Chua, C.K., Zhou, K. (2019). 3D-printed mechanical metamaterials with high performance of energy absorption. *Advanced Materials Technology*, 4, 1800419 [Online]. Available at: https://dr.ntu.edu.sg/bitstream/10356/141556/3/3D%20printed%20mechancal%20metamaterials%20with%20high%20performance%20of%20energy%20absorption%20Manuscript.pdf.

Yuan, C., Wang, F., Qi, B., Ding, Z., Rosen, D.W., Ge, Q. (2020). 3D printing of multi-material composites with tunable shape memory behavior. *Materials & Design*, 193, 108785.

Yuan, C., Wang, F., Rosen, D.W., Ge, Q. (2021). Voxel design of additively manufactured digital material with customized thermomechanical properties. *Materials and Design*, 197, 109205.

Yue, Y., Smith, B., Chen, P.Y., Chantharayukhonthorn, M., Kamrin, K., Grinspun, E. (2018). Hybrid grains: Adaptive coupling of discrete and continuum simulations of granular media. *ACM Transactions Graphics*, 37, 283.

Yuk, H., Lin, S., Ma, C., Takaffoli, M., Fang, N.X., Zhao, X. (2017). Hydraulic hydrogel actuators and robots optically and sonically camouflaged in water. *Nature Communications*, 8, 14230.

Zadorin, A.S., Rondelez, Y., Gines, G., Dilhas, V., Urtel, G., Zambrano, A., Galas, J.C., Estevez-Torres, A. (2017). Synthesis and materialization of a reaction-diffusion French flag pattern. *Nature Chemistry*, 9, 990–996.

Zadpoor, A.A. (2016). Mechanical meta-materials. *Materials Horizons*, 3, 371–381.

Zakharov, A.P. and Pismen, L.M. (2019). Programmable filaments and textiles. arXiv:1903.

Zamiatine, E. (2020). *Nous-autres*. Gallimard, Paris.

Zare, M., Prabhakaran, M.P., Parvin, N., Ramakrishna, S. (2019). Thermally-induced two-way shape memory polymers: Mechanisms, structures, and applications. *Chemical Engineering Journal*, 374, 706–720.

Zarek, M., Mansour, N., Shapira, S., Cohn, D. (2017). 4D printing of shape memory-based personalized endoluminal medical devices. *Macromolecular Rapid Communications*, 38(2), 1600628.

Zentel, R. (2020). Polymer coated semiconducting nanoparticles for hybrid materials. *Inorganics*, 8, 20.

Zhang, W. and Xu, J. (2021). Toward understanding solitary wave propagation in composite-cylinders-based 1D granular crystals. *Extreme Mechanics Letters*, 43, 101156.

Zhang, X., Pint, C.L., Lee, M.H., Scubert, B.E., Jamshidi, A., Takei, K., Ko, H., Gillies, A., Bardhan, R., Urban, J.J. et al. (2011). Optically and thermally-responsive programmable materials based on carbon nanotube-hydrogel polymer composites. *Nano Letters*, 11, 3239–3244.

Zhang, J., Yao, Y., Sheng, L., Liu, J. (2015a). Self-fueled biomimetic liquid metal mollusk. *Advanced Materials*, 27, 2648–2655.

Zhang, L., Liang, H., Jacob, J., Naumov, P. (2015b). Photo-gated humidity-driven motility. *Nature Communications*, 6, 7862.

Zhang, T., Lin, S., Yuk, H., Zhao, X. (2015c). Predicting fracture energies and crack-tip fields of soft tough materials. *Extreme Mechanics Letters*, 4, 1–8.

Zhang, K., Fraxedas, J., Sepulveda, B., Esplandiu, M.J. (2017a). Photo-chemically activated motors: From electro-kinetic to diffusion motion control. *ACS Applied Materials and Interfaces*, 9, 44948–44953.

Zhang, Q., Wommer, J., O'Rourke, C., Teitelman, J., Tang, Y., Robison, J., Lin, G., Yin, J. (2017b). Origami and kirigami inspired self-folding for programming three-dimensional shape shifting of polymer sheets with light. *Extreme Mechanics Letters*, 11, 111–120.

Zhang, Q., Zhang, F., Xu, X., Zhou, C., Lin, D. (2018). Three-dimensional printing hollow polymer template-mediated graphene lattices with tailorable architectures and multifunctional properties. *ACS Nano*, 12, 1096–1106.

Zhang, F., Wang, L., Zheng, Z., Liu, Y., Leng, J. (2019). Magnetic programming of 4D printed shape memory composite structures. *Manufacturing*, 125, 105571.

Zhang, W., Gao, Y., Yang, H., Suo, Z., Lu, T. (2020a). Fatigue-resistant adhesion I. Long-chain polymers as elastic dissipaters. *Extreme Mechanics Letters*, 39, 100813.

Zhang, Y., Wang, Z., Yang, Y., Chen, Q., Qian, X., Wu, Y., Liang, H., Xu H., Wei Y., Ji Y. (2020b). Seamless multi-material 3D liquid-crystalline elastomer actuators for next-generation entirely soft robots. *Science Advances*, 6, eaay8606 [Online]. Available at: https://advances.sciencemag.org/content/advances/6/9/eaay8606.full.pdf.

Zhang, M., Shahsavan, H., Guo, Y., Pena-Francesch, A., Zhang, Y., Sitti, M. (2021a). Liquid-crystal-elastomer-actuated reconfigurable microscale kirigami metastructures. *Advanced Material*, 33(25), 2008605, Forthcoming [Online]. Available at: https://onlinelibrary.wiley.com/doi/10.1002/adma.202008605#.YJ_Fl9P41MA.linkedin.

Zhang, T., Yang, L., Yang, X., Tan, R., Lu, H., Shen, Y. (2021b). Millimeter-scale soft continuum robots for large-angle and high-precision manipulation by hybrid actuation. *Advances in Intelligent Systems*, 3, 2000189.

Zhang, W., Hu, J., Yang, H., Suo, Z., Lu, T. (2021c). Fatigue-resistant adhesion II: Swell tolerance. *Extreme Mechanics Letters*, 43, 101182.

Zhang, W., Wang, H., Wang, H., Chan, J.Y.E., Liu, H., Zhang, B., Zhang, Y.F., Agarwal, K., Yang, X., Ranganath, A.S. et al. (2021d). Structural multi-colour invisible inks with submicron 4D printing of shape memory polymers. *Nature Communications*, 12, 112.

Zhang, Y., Wang, Q., Yi, S., Lin, Z., Wang, C., Chen, Z., Jiang, L. (2021e). 4D printing of magneto-active soft materials for on-demand magnetic actuation transformation. *ACS Applied Materials and Interfaces*, 13, 4174–4184.

Zhao, X. and Kim, Y. (2019). Soft micro-bots programmed by nano-magnets. *Nature*, 575, 58–59.

Zhao, Q., Qi, H.J., Xie, T. (2015). Recent progress in shape memory polymer: New behavior, enabling materials, and mechanistic understanding. *Progress in Polymer Science*, 49–50, 79–120.

Zhao, Z., Yuan, C., Le, M., Yang, L., Zhang, Q., Chen, H., Qi, J., Fang, D. (2019). Three-dimensionally printed mechanical metamaterials with thermally tunable auxetic behavior. *Physical Review Applied*, 11, 044074.

Zhao, Z., Hwang, Y., Yang, Y., Fan, T., Song, J., Suresh, S., Cho, N.J. (2020). Actuation and locomotion driven by moisture in paper made with natural pollen. *Proceedings of the National Academy of Sciences*, 117, 8711–8718.

Zhao, X., Wu, J., Zhou, Y., Pan, Y., Lu, T., Song, X., Hu, J. (2021). Fatigue behaviors of physical hydrogels based on hydrogen bonds. *Extreme Mechanics Letters*, 46, 101320.

Zheng, X., Smith, W., Jackson, J., Moran, B., Cui, H., Ye, J., Fang, N., Rodriguez, N., Weisgraber, T., Spadaccini, C.M. (2016). Multiscale metallic metamaterials. *Nature Materials*, 15, 1100–1106.

Zhong, R., Fu, M., Chen, X., Zheng, B., Hu, L. (2019). A novel three-dimensional mechanical metamaterial with compression-torsion properties. *Composite Structures*, 226, 111232.

Zhou, S. (ed.) (2017). Elasticity, viscosity, and orientational fluctuations of a lyotropic chromonic nematic liquid crystal disodium cromoglycate. In *Lyotropic Chromonic Liquid Crystals*. Springer, Cham.

Zhou, Y., Hu, J., Zhao, P., Zhang, W., Suo, Z., Lu, T. (2021). Flaw-sensitivity of a tough hydrogel under monotonic and cyclic loads. *Journal of the Mechanics and Physics of Solids*, 153, 104483.

Zhu, P., Yang, W., Wang, R., Gao, S., Li, B., Li, Q. (2018). 4D printing of complex structures with a fast response time to magnetic stimulus. *ACS Applied Materials and Interfaces*, 10, 36435–36442.

Zhu, Z., Park, H.S., McAlpine, M.C. (2020). 3D printed deformable sensors. *Science Advances*, 6, eaba5575.

Zolfagharian, A., Kaynak, A., Khoo, S.Y., Kouzani, A. (2018). Pattern-driven 4D printing. *Sensors and Actuators A: Physical*, 274, 231–243.

Zorzetto, L. and Ruffoni, D. (2019). Wood-inspired 3D-printed helical composites with tunable and enhanced mechanical performance. *Advanced Functional Materials*, 29, 1805888.

Zou, S., Therriault, D., Gosselin, F.P. (2020). Spider-web-inspired, transparent, impact-absorbing composite. *Cell Reports Physical Science*, 1, 100240.

Zunker, X. and Gonella, S. (2021). Soft topological lattice wheels. *Extreme Mechanics Letters*, 46, 101344.

Zupan, M., Ashby, M.F., Fleck, N.A. (2002). Actuator classification and selection – The development of a database. *Advanced Engineering Materials*, 4, 933–940.