1

Incremental Developments of Processes, Machines and Materials

"When things are arranged so that description through using the senses allows us to easily imagine them, we say that they are well-ordered. Otherwise, we say that they are not well-ordered or confused. As the things which we can easily imagine are more pleasant than the others, Man therefore prefers order to confusion, as though, outside of our imagination, order were something found within Nature". [SPI 94]

"Knowledge… is not a series of coherent theories converging towards an ideal conception. It is not a gradual march towards the truth. Rather it is an ever-greater ocean of mutually incompatible (and perhaps immeasurable) options. Each singular theory, each fairy tale and each myth being part of this collection, forces the others to a state of greater flexibility. All of this contributes, via this rivalry to the development of our awareness". [FEY 79]

"Our post-modern societies seem to be characterized by a so-called 'dual loss': that of tradition and the certainties of pre-modernity. This is based, on the one hand around respect for the past, and that of the modernity myths anchored within a positive view of the future, and in faith in progress. On the other hand, it is based upon a Promethean concept of Man". [GUY 14]

"Bergson defined the laugh as the 'superimposition of the mechanical upon the living'. Likewise we could say of industry that it is the superimposition of machinery upon organic concepts, and it longs to become natural. The same can be said of digital being affixed to machinery". [MUS 14]

"The second stage is to divide each of the difficulties which I will look at into as many fragments as possible, and as may be required to best resolve these difficulties. The third stage is to put my thoughts into order, starting with the simplest and easiest subjects to understand to go up little by little, as if by degrees, to the most complex knowledge". [DES 92]

"It is important that we do not conceal our uncertainties. This awareness of the frailty of given structures is consubstantial to the scientific approach". [BAR 16]

"Make the present moment more intense so as to make the moment profitable in the extreme. We thus escape the routine of a life which is limited in space and time, such could be the sense of this present imprisoned within the moment". [KHE 10]

"The capitalist economy is not and does know not how to be stationary". [SCH 11/99]

"The entire issue lies within this opposition between gradual and disruptive innovations. Should innovation extend current cycles, support existing structures and make our way of life sustainable? Alternatively should it even open up radically new routes, substitute new technologies for those inherited from the past and revolutionize our societies? Owing to this ambivalence, the rhetoric of technological innovation takes the form of a paradoxical injunction: 'Let everything change, so that nothing changes!' As humans we recognize that this is hardly a stimulating approach'". [KLE 15]

"However, within many management teams, the appetite for, or the tolerance of risk, are perceived as interesting esoteric topics of conversation. This is especially the case for researchers and academics. However it has no actual bearing on their daily activities in terms of strategies, and no impact upon their decision-making processes". [LOU 17]

1.1. Introduction

The myth of the so-called "industrial revolution", promised for additive manufacturing, arises when the question concerns new technology creation. However, these myths have their significance. They permit the creation of the given movements and membership of those movements. Nevertheless, any production system only truly has direction if it is both explained and questioned at regular intervals. It can thus maintain a standard of technological excellence relative to a determined future view, preferably a technological view, for the purposes of this chapter. If we consider the innovation market, several principles are at work [GUZ 95, CAR 98]:

– an initial aspect corresponds to the principal of assimilation depending upon the success of a given new product, or identified as such (the launch of new products on traditional markets, or attacking new markets with advanced products, which have simply been re-tailored). Success can lead to the stabilization of ways of thinking and modes of action;

– a second aspect is linked to the principle known as plurality, which assumes that a new element (product, process or another aspect) can only be assimilated if it is integrated within a given existing set (linked with the notion of technological rupture);

– the principle of alignment stipulates that technical skills induced by a technical or organizational change should not exceed (in terms of training, hiring and other outlays) the maximum cost already agreed within the business in other circumstances;

– the principle of transfer to others is aimed at making the initial research and development effort profitable;

– the principle of expectation is linked to a response to demand without the business seeking to propose a given offer. Indeed, often the creative offer is only generally included because it flows from a technological innovation that disrupts the course of events.

These observations evidence accelerated production of new products using well-mastered methodologies. Under these conditions, there can be a connection between research temporalities and that of the company managing such research. This is so, as long as scientific "laboratory" expertise is effectively present and it is a question of "genuine" innovation.

Chapter 3 of Volume 1 of this series set out the majority of current technologies for additive manufacturing. We can imagine, within a world undergoing rapid development, that these few technologies grouped together by the authors within the 3D printing technology categories 3, 4 and 7 are only a small share of all publications and patents since 1984. However, doing everything possible may not necessarily lead to an industrial application, and several criteria come into play. These are criteria that range from types of obstructions on the part of interested businesses having a strong presence in the field to the purchase of start-ups and little promotion of entrepreneurship favoring the academic world. There are also difficulties in financing with the so-called "Death Valley crossing" and other factors. Moreover, not all ideas, even if their concept is proved, can be applied. This chapter therefore integrates an area in which there is a place for uncertainty with particular projects. This includes some ideas that are nearly at the end of the transition between research and application, with others still remaining at the stage of "academic" feasibility.

Intentional risk-taking by the inventor involves not siding too much with the fear of seeing the seeds of creative and original ideas killed too soon. Ideas should not be shelved before they have demonstrated their capacity to aid additive manufacturing in its development, "biodiversity" or abundance. If we take mechanical manufacturing into account, the number of modes of manufacture largely exceed the current 3, 4 and 7 technologies "acknowledged" in additive manufacturing. However, a personal choice criterion (which may be subject to criticism on the part of the reader) has been retained. This concerns the ability of ideas to emerge from forms of continuation of activities stemming from the sole "knowledge of prior art/knowledge". It is thus the case that this chapter does not describe how we may increase the size of a 3D machine to build houses (except perhaps for the "material" component), produce a 3D machine functioning on solar energy and with sand as the material, or spatialize a 3D machine.

Notwithstanding this, not taking this aspect into account does not mean that these activities are completely eliminated; after all, they are even considered by some to be industrious or exotic. It is simply that the development of such a machine takes time, necessitating a number of so-called "DIY (Do It Yourself) scientists". It also necessitates that technological, prescriptive and financial constraints, which are often difficult to surmount, are taken into account. What we note is that increasingly refined mechanisms and control procedures are being implemented all the time. These operations continue on a "business as usual" basis. Moreover, by being located upstream, no doubt fewer inertial constraints are experienced. However, clearly this is not the objective of this chapter.

Within a broad view, creativity, which conditions innovation, may be considered as the capacity to either provide or find original solutions to adjustment problems. In fact, every human being is confronted with such problems. The creative approach begins with the acknowledgment of a given problem [FOR 02]. From there, stakeholders become involved in a divergence process, which will finally perhaps end with convergence, in the form of a new solution to the problem. "Creativity and then innovation, is therefore 'doing' derived from 'being'" [ANZ 88]. Innovation covers the aspects stated below. These are discussed by Schumpeter [SCH 04, SCH 11/99]; Gaglio [GAG 11a]; Larédo and Mustar [LAR 03]; Lesourne *et al.* [LES 04]; OCDE [OCD 05]; Ecrin [ECR 05]; Kuhlmann [KUH 01] and other works, they are:

– new goods or the same goods equipped with new and distinct original properties;

– new production methods with new potential markets;

– the opening up of new markets;

– conquering a source of raw materials, which has not yet been exploited;

– the creation of a new organization, such as the creation of a monopoly situation;

– an innovation assuming the emergence of new social practices within the wake of the new product [ALT 10];

– an innovation making the assumption that we are capable of imagining how it will be carried out for members of society [CHA 11];

– an innovation calls into question long-established positions and secure income. It upsets certainties and adaptations [GAG 11a].

Should not we consider creative innovation as governed, both by the search to discover fundamental principles on the one hand and by ideas stemming from divergent thought, and systemic research and development on the other, likely to favor the creation of economic and social value? If it is thus, these fields should have particular characteristics: one aspect is openings and the other is deepening understanding. Let us consider together what the author has selected as potential openings. We understand that these are essentially the foremost aspects of this list, mainly coming within the supply logic, and which are targeted below. Essentially, on the one hand, it is possible to evoke linear progress being predictable and not entirely used in every case. On the other, we may evoke a more spontaneous, reticular and chaotic innovation.

1.2. Undertaking non-layered stereolithography

The concept devised by the Institut Battelle in the 1970s [ADA 68, ADE 71, MCG 84] was the concept of the manufacture of three-dimensional (3D) objects within transparent fluids using multi-photon absorption. The principle used at that time involved the exploitation of two-photon and multi-photon absorption, such as that shown in Figure 1.1. In this figure, incident photons are shown by their $h\nu$ energy, where h is Planck's constant and ν is the frequency of radiation. During that point in this particular field's development, sequential absorption was defined as follows: a chromophore absorbs the wavelength λ_1 (corresponding to the frequency ν_1 with the formula $\lambda = C/\nu_1$, where C is the velocity of light in a vacuum), which has a given lifespan (ranging from a few nanoseconds up to an hour). A second photon emitted at λ_2 allows conversion to a higher excited electronic state, leading to the fragmentation of the substance (or by energy transfer from a given acceptor). Thus, compared to the description in the previous volume concerning energizing a photon from a radical or ionic polymerization reaction, the formation of given species, which will initiate polymerization, occurs within a sequential or simultaneous two-photon process (see Figure 1.2).

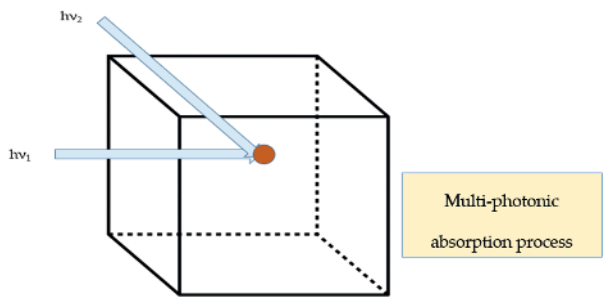

Figure 1.1. *Principle of two-photon simultaneous or sequential absorption*

In Figure 1.2, the principle of simultaneous absorption is shown on the right-hand side. Light beams are displaced within a transparent medium (which is generally not as simple to achieve when the thickness of the given medium to be penetrated is of the order of a few dozen centimeters). In principle, we might

envisage carrying out a local-scale conversion of the medium. This process might include species involved in energizing, inhabiting an excited precursory electronic state. This may occur by either sequential absorption, necessitating the transition through an intermediate electronic excited state [JIA 14], or simultaneous absorption.

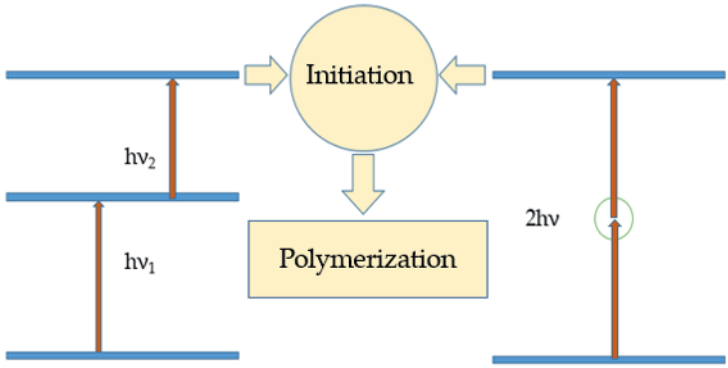

Figure 1.2. *Two-photon sequential absorption (left) and simultaneous absorption (right)*

To go further back in time, the access to picosecond lasers, or better yet femtosecond lasers, was not envisaged even though the photochemistry of two-photon processes had already been studied. This explains the origin of the patents proposed at the beginning of this section. Several possibilities might be mentioned at this point. These are photon absorption to inhabit an electronic singlet state, transition to a triplet state (with a lifespan which is potentially longer than that for a singlet state) and absorption of a second photon to change from inhabiting this state to that of a triplet reactive state. An example of the latter is acridine, referred to by Lewandowka-Andralojc *et al.* [LEW 12] and Kellmann and Tfibel [KEL 82]. Similarly, there is also the formation of a triplet state transferring its energy to another triplet, which itself absorbs a photon to create a reactive state (e.g. the acridine–rhodamine 123 couple). The significance of this system is that if linear transformation translates by a non-radiative return without a marked chemical transformation, there is a benefit. It is that the system can be reversible at low light intensities. On the contrary, triplet–triplet absorption allows for the chemical transformation of the medium, with apparent opportunities in terms of spatial

resolution. The reader who is interested in this field may benefit from referring to several works. These include Bensasson and Land [BEN 71] who found coefficient values for increased molecular extinction coefficients for triplet–triplet transitions, with complements derived from Bagdasaryan *et al.* [BAG 72/73]. With regard to other substances, Nielsen *et al.* [NIE 98]; Brinen *et al.* [BRI 72]; Malval *et al.* [MAL 07, MAL 11]; Singh-Rachford and Castellano [SIN 09], and with regard to biacetyl (which has a lifespan of the high triplet at room temperature, of the order of 1 ms (as Almgren demonstrated in [ALM 67])), Land [LAN 68] is worth consulting. However, to deal with the question of sequential absorption, other than the choice of the right photochemical initiator, raises the issue of bringing together two beams within a parallelepipedic vessel (see Figure 1.1).

Simulations were undertaken, aiming to be completed within a plane, having a given number of voxels limited to a quarter circle. The two beams are considered to be perpendicular, of the same amplitude and, for simplicity, emitting the same wavelength ($\nu_1 = \nu_2$). They also have the same rate of absorption for all substances, taking part in single-photon absorption or sequential absorption. They therefore have a maximum flow for the parts subject to irradiation and nil for the non-polymerization zones. Through the selection of a six-step beam, Figure 1.3 shows the distribution of light for a given section by using false colors. In this case, the red area shows weakest intensities and the dark green area, the highest intensities. We can observe from this figure that where single-photon processes are involved, the quarter circle being produced is not visible and that the optimum position available is a square zone (green), which leads to polymerization.

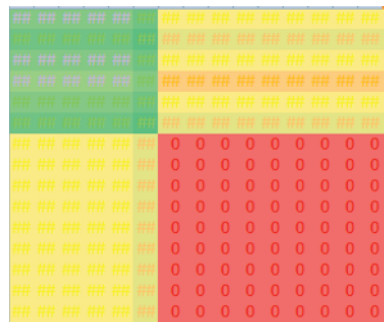

Figure 1.3. *R = 6 and the addition of photon flows. For a color version of the figure, see www.iste.co.uk/andre/printing2.zip*

The three diagrams in Figure 1.4 show the distributions using so-called “false colors” (on the same bases as those used above) for two-photon, three-photon and four-photon absorptions.

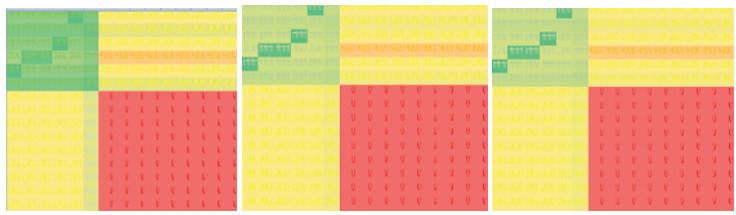

Figure 1.4. *Two-photon absorption (left); three-photon absorption (center) and four-photon absorption (right). For a color version of the figure, see www.iste.co.uk/andre/printing2.zip*

For these examples, the contrast (the dark green/yellow relationship) varies with the degree of multi-photon process. The results are 2.6, 5 and 6.8 for the two-photon, three-photon and four-photon processes, respectively. This is achieved with a very modest number of voxels. This technically non-exploitable situation has led scientists in this field to work in layers (see Chapter 3 of Volume 1).

Figure 1.5 shows the same phenomena for a four-photon process but for the case of R = 13. The size of the mesh is therefore appreciably reduced by a factor of 2, compared to that shown in Figure 1.4. It is worth noting that the contrast which was 6.8 decreases to 2 when the value of R is doubled (from 6 to 12). Under these conditions involving the intersection of two parallel and orthogonal beams in relation to each other, it is unrealistic to be able to produce an object with an accurate resolution using this process. This situation would be further accentuated if we were to take into account the third dimension of the space.

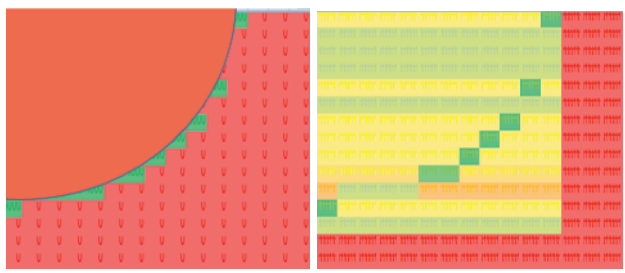

Figure 1.5. *Four-photon absorption; R = 12 (with the left-hand side diagram showing what is envisaged would happen with the quantification effect). For a color version of the figure, see www.iste.co.uk/andre/printing2.zip*

1.2.1. *Optimizing the light supply within a single-photon process*

Under these conditions, it was not necessary to find multi-photon absorption systems. Hence, at the time, the use of continuous lasers is necessary to "shape" the

finish resin. By choosing such a principle, the transfer of issues so as to make the process operational, relying upon the implementation of layers, appeared fairly quickly as a decisive factor in optimizing the process.

Besides the so-called "simple" methods mentioned in Chapter 3 of Volume 1, several solutions were attempted to avoid undergoing the stage involving layers. These are described below.

1.2.2. *Transparent window*

Figure 1.6 shows the principle where a window, which is transparent to photons, is placed on an object in the course of its construction. This is done by mechanically imposing a layer between the object and the transparent window.

The process enables us to realize polymerization. However, the problem of polymer adhesion on the window, or the extremity of a given fiber optic, cannot be solved simply by using optical glass plates. This leads us to use flexible strippable materials or strive for another solution. The choice of such existing materials in the form of films allows for the effective production of a given object. However, the manufacturing time is longer than when using a skimmer (and in addition, it produces a lot of waste).

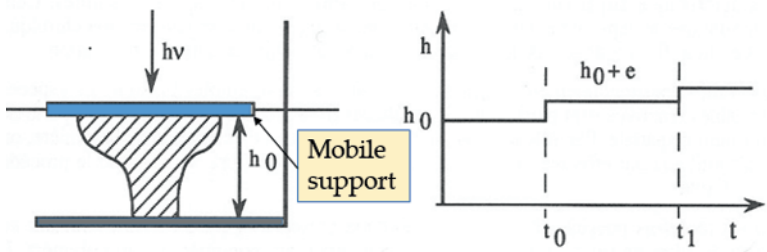

Figure 1.6. *Stereolithography using a transparent window*

1.2.3. *Gaseous interface*

The principle of such a procedure is shown in Figure 1.7. The basic concept is to protect the extremity of the optical fiber or the irradiation system by separating them using a gas bubble from the resin undergoing the polymerization process Although this system operates effectively, its size limits its displacement within the resin. This is particularly the case when the resin is extremely viscous. Once again, this

potentially misguided "good idea" does not allow us to invalidate the basic process by adding successive layers of stereolithography.

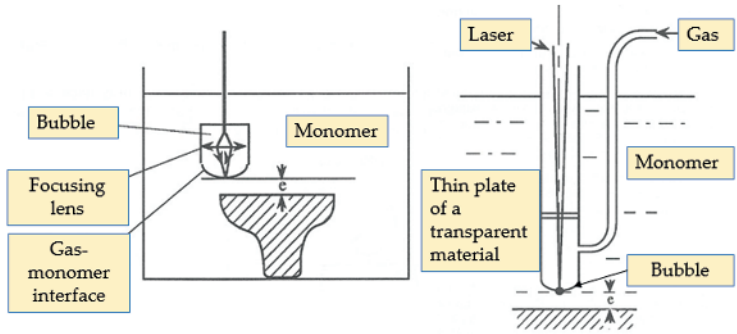

Figure 1.7. *Gas–resin interface (fiber optic (left) and direct irradiation (right))*

1.2.3.1. *Screw system*

A solution was proposed to avoid the use of layers by "screwing" the part being constructed within the appropriate resin. Instead of representing an object by the standard x, y and z coordinates, the part being printed is then defined by cylindrical coordinates (ρ, θ and z). In such a case, z is the height of the object undergoing light treatment, θ is the angle and ρ is the modulus (see Figure 1.8).

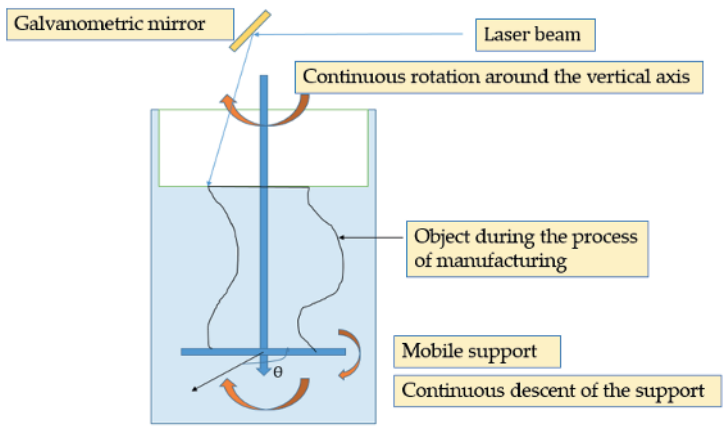

Figure 1.8. *"Screw" process*

With this patented system, André *et al.* [AND 91a, AND 91b] stated that it is no longer deemed necessary to use two rotating galvanometric mirrors positioned with two degrees of freedom if the angular speed of rotation of the falling object is constant. It was concluded that a single galvanometric mirror suffices. This system definitely avoids the waiting periods linked to the creation of layers; however, it is not sufficiently general in nature. In particular, although it allows for the manufacture of workpieces such as busts, it does not easily allow for the production of complex parts (see Figure 1.9).

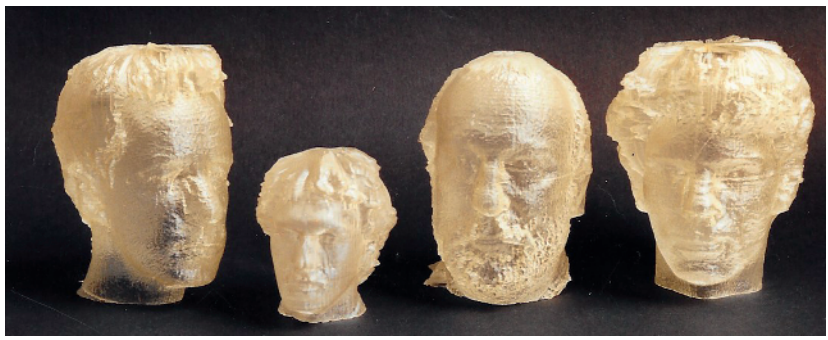

Figure 1.9. *Three-dimensional portraits of four of the inventors of the patent that is associated with this particular system (from left to right: Nonnenmacher, Schaeffer, André and Brullé)*

1.2.3.2. *The so-called "good idea"*

Recently, Tumbleston *et al.* [TUM 15] have proposed a very clever improvement of the stereolithography process. They exploited a constraint connected to the presence of oxygen, a classic inhibitor of radical chain polymerizations (see Volume 1 of this series). In their process, which is termed CLIP (continuous liquid interface production), by saturating the resin, this gaseous inhibitor in the vicinity of the light entry, the transparent surface which makes up the interface with the monomer, stays in contact with a liquid and not with a polymer. There is therefore no longer bonding, as has been previously mentioned. Although the concept of transforming a defect falls within divergent (and indeed very clever) thinking, all the same it has been necessary to produce a complex membrane, which is both transparent to light and porous to oxygen.

Figure 1.10 shows the process that has now been developed by Carbon 3D Inc. Irradiation happens through a continuous sequence of UV images, which are generated by a digital light projector. There are no layers to produce because it suffices to "pull" the object toward the top, to the extent that the interface between

the entry window and the object is not, under normal use conditions, polymerizable. This opportunistic variable assumes the use of fairly fluid resins (the reaction of which is highly sensitive to oxygen) to allow both the transfer of oxygen within the reactant fluid and the limiting of mechanical constraints between the object under construction and the light entry window connected with a given resin viscosity. It is, however, highly attractive thanks to the significant time gain made possible. Fabulous [FAB 16] stated this to be seven times faster, as alluded to by André [AND 17] and Alex [ALE 16]. Scupteo [SCU 16] propounded that the resolution may be 75 µm. Also in this work, the author sets out a comparison between stereolithography and the CLIP process. An example part produced by this process is shown in Figure 1.11 [MAG 15].

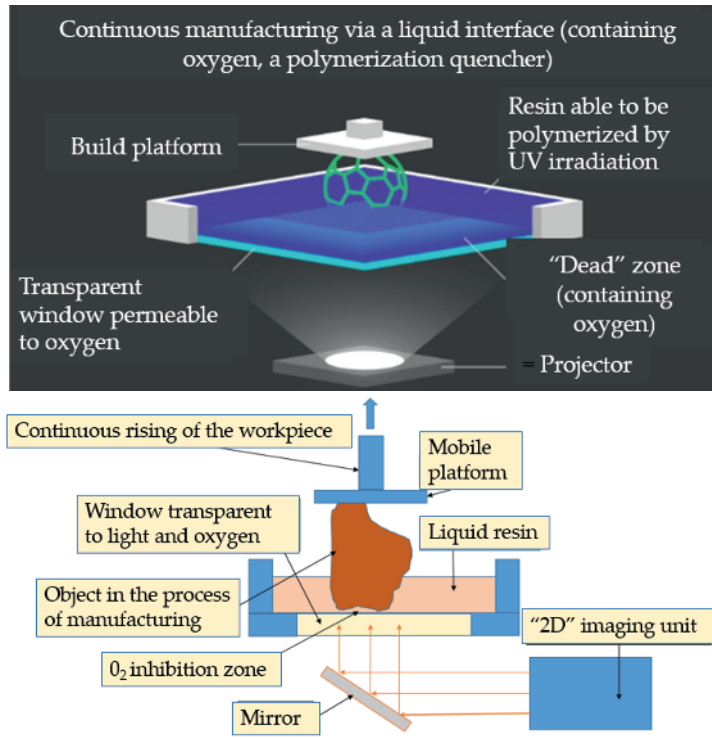

Figure 1.10. *Stereolithography according the 3D Carbon process ([TUM 15, WHE 15]; reproduced with kind permission from Carbon3D)*

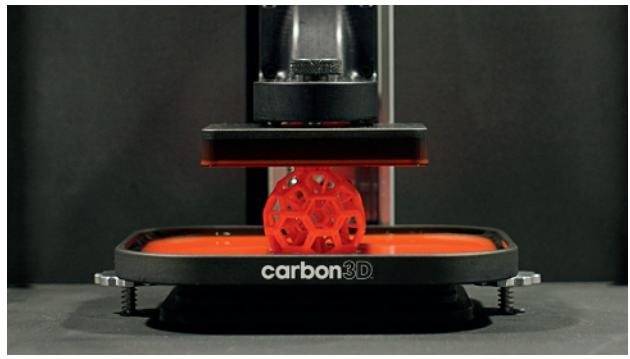

Figure 1.11. *Example part produced using the CLIP process [ALE 15]*

1.2.4. *Simultaneous two-photon absorption*

Returning to the issue of irradiation, instead of using two parallel orthogonal beams, it appears conceivable to focus such beams. The author also thinks that it is conceivable to examine whether there is a possibility of having an acceptable contrast within the vicinity of their crossing point. To do this, the effect of light concentration was examined for focusing a beam at ± 45° (still working within a two-dimensional environment), leading to digital results that are more promising than those shown in Figure 1.4. This is the case because, under these conditions, the contrast (of the order of 50 under the simulation conditions) comes very close to the expected result (see Figure 1.12).

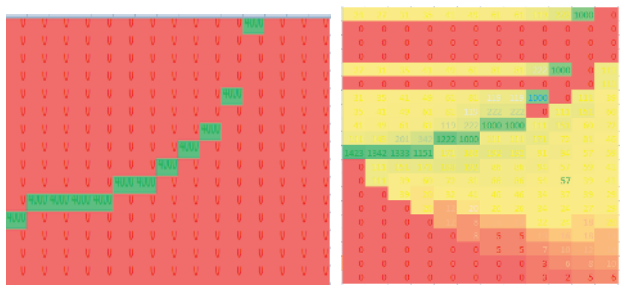

Figure 1.12. *Effect of focusing the beam (2D) (left, the control; right, simulation result). For a color version of the figure, see www.iste.co.uk/andre/printing2.zip*

When dealing with the focus of three-dimensional irradiation, the contrast is accentuated. It is greater than 100 between the green and orange zones. Yet, as was shown in Chapter 3 of Volume 1, photochemical polymerization is at the threshold,

as Figure 1.13 shows, resuming this chapter's theme. Under these conditions, if we know how to absorb light at the focal point, it becomes possible to reach a state of liquid transformation being solid without undergoing implementation of the layering process. Areas with low levels of irradiation do not contribute to photo-polymerization, provided they are situated within zone I shown in this figure. However, the issue is then one of 3D printing, so we might say that the term "additive manufacturing" is therefore no longer required!

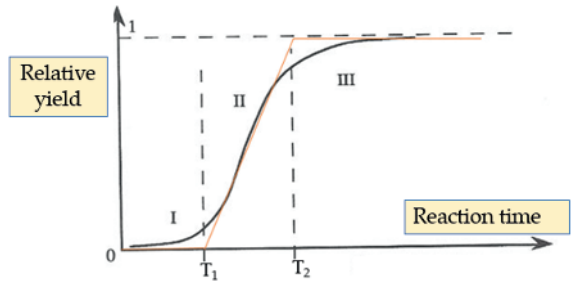

Figure 1.13. *Kinetic polymerization curve type (a point resumed from Chapter 3 of Volume 1) Relative yield*

1.2.4.1. *"Aides-memoires" on simultaneous two-photon absorption and its energizing potential*

The process of simultaneous absorption, shown in Figure 1.2, which is discussed here, was originally considered in 1931 by Gœppert-Mayer. Two-photon absorption (TPA) is the simultaneous absorption of two photons of either identical or different frequencies with the aim of exciting a molecule in a given electronic state (commonly the ground state) to reach a higher-energy excited electronic state. The energy difference between these two states is equal to the sum of the energies of the two photons. Simultaneous two-photon absorption is a third-order process, which is several degrees of magnitude weaker than the absorption of the so-called "linear" photon absorption defined in Volume 1. It differs from linear absorption because it is proportional to the square of the given light intensity, which undergoes a nonlinear process (see [ZHO 15]). This involves very high flow densities and hence the use of pulse light sources (for the most part, picosecond or femtosecond sources) in such instances.

It is worth repeating that single-photon absorption obviously follows, within non-diffused media, the Beer–Lambert law. Locally, for a given concentration (c), the absorbed light intensity (Ia) at the distance x is proportional to the product c. $\exp(-\alpha.c.x)$, where x is the distance within the vat of the light input window, c is the concentration of the absorber and α is a coefficient called the molecular extinction coefficient. F(0) is the flow at the vat entry. It is expressed as:

$$Ia = \alpha.c.F(0).\ \exp(-\alpha.c.x)$$

For a given two-photon process, in making the reasonable hypothesis that the absorption is modest except within the vicinity of the focus point [SAL 07], the flow density is approximately equal to:

$$F(x,t) = F(0,t).\ R^2/(x+a)^2$$

where R is the photon entry beam in the vat, which has a parameter linked to both the light diffraction and the quality of the focus. Then, Ia is defined by:

$$Ia = dF(x)/dx = \beta.c.F(0,t)^2.R^4/(x+a)^4$$

where β is the equivalent of α for a given TPA. These use increased flux densities (>MW/cm^2) so that the responses of the various mediums are not proportional to the sources that produced them (see [TAO 09]). Several light sources may be used simultaneously to achieve this objective. However, it is also conceivable to focus a laser beam on a point in the space such as that which was applied in this simple calculation. We note that for a Gaussian pulse, only a very small part of the power emitted will be used for the actual absorption part of the process (much lower than 1%), which offers a decisive advantage, in terms of spatial resolution.

It can be observed that, if we take into consideration a two-photon process, the nonlinear system with which it is associated will translate into a better spatial resolution than that of the incident beam. This is markedly lower than the square of the radial power density, because it is necessary to have exceeded the consumption threshold of quenchers, as indicated in Figure 1.13. In order to be able to excite an initiator molecule by two-photon excitation, it is necessary that the photons are concentrated both spatially and in time. Indeed, in order for an electron with electronic orbitals lower than the initiator to move to an excited higher electronic state, it must receive a second photon quasi-simultaneously. It is from this excited state that unstable species, which are responsible for polymerization, are produced during a dissociative process. Consequently, we cannot normally use a continuous laser but one or more pulse laser(s). Indeed, by compressing the photons, both spatially and temporally, the likelihood of two-photon excitation is increased. The

consequence of this type of illumination is that excitation is generally confined to the immediate vicinity of the given focal plane (which is the desired outcome). Figure 1.14 shows, in qualitative terms, that the gain in spatial resolution is a function of the square of flow density, as shown by the red curve.

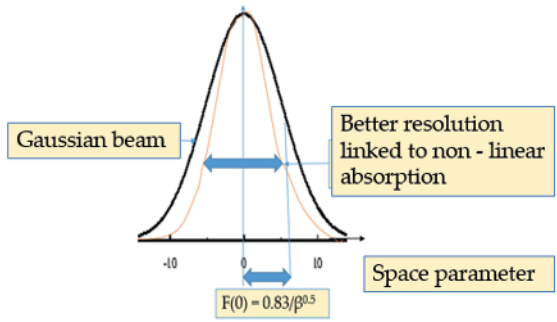

Figure 1.14. *Gain in spatial resolution induced by the TPA process. For a color version of the figure, see www.iste.co.uk/andre/printing2.zip*

With duration of a pulse ($\tau = 140 \times 10^{-15}$ s), repetition frequency (T = 80 MHz) and average power ($P_{average}$ = 3W), for peak power, we obtain $P_{peak} = 1.7 \times 10^6$ W, which corresponds to the magnitude at which two-photon absorption may lead to electronic excitation of the initiator. These approximate data define the framework of one of the constraints to be satisfied so that there is a possibility of two-photon absorption.

However, taking into account generally exothermic polymerization reactions and the non-radiative relaxation linked to the deactivation of the excited state created by TPA, there can be a local (and temporary) increase in temperature. This may locally induce a change in the refractive indices of the polymerizable liquid and solid polymer. Under these conditions, we should have object shapes to construct that are adapted to avoiding the problems mentioned above. In addition, it may be necessary to work within spatial and/or chemical conditions under which these phenomena are not preponderant and likely to be masked. This objective can be reached if we want to create, for example, small objects, a task which is well adapted to commercial picosecond lasers and microscopes.

Kannan *et al.* [KAN 01] and Belfield *et al.* [BEL 99, BEL 00] gave examples of values calculated for β from experimental data for two-photon absorption coefficients. Selimis *et al.* [SEL 15] suggested that molecules which have a "good" two-photon absorption output are often compounds from the benzophenone family (see, e.g. Woodward *et al.* [WOO 02]). Other substances have been discussed in several publications (Kim and Cho [KIM 09]; Devi *et al.* [DEV 15]; Liu *et al.*, [LIU 10, LIU 11]; Moura and Simas [MOU 10]; Terenziani *et al.* [TER 08]; Lee *et al.*, [LEE 04, LEE 08]; Chakrabarti and Ruud [CHA 09] and other authors). These are chiefly chemical compounds containing the so-called "aromatic" groups. It is in respect of these that we demonstrated in Chapter 3 of Volume 1 the potential for the formation, with a high quantum yield, of free radicals likely to initiate radical chain polymerization reactions.

COMMENT 1.– Practical uses for initiators:

Von Raumer *et al.* [VON 97] mentioned in the case of benzophenone the possibility of reactions between triplets leading to reactive species within this compound family. The production of these electronic states indeed falls within a one-photon process. However, the bi-molecular reaction between triplets induces a nonlinear process that may be exploited. Varadan *et al.* [VAR 01] moreover suggested using this type of initiation method in respect of the micro-stereolithography laser. In fact, it is actually possible for the benzophenone to take on its singlet state, and before decomposing into free radicals, it goes through the triplet state, which indeed absorbs a third photon, which then decomposes the molecule into free radicals. Thus, the process of initiation can be a little more complex than the author introduced in the previous sections. The development of the picosecond and/or femtosecond pulse laser sources might allow this concept to be demonstrated.

COMMENT 2.– Values of β:

Taouri [TAO 09] stated that the β coefficient values (β), which link a given power density (I) and absorption (dI/dx) through the relationship:

$$dI/dx = -\beta.I^2$$

are included between 0.04 and 0.4 10^{-8} cm.W^{-1}. This result means that for values in the range of Gigawatts per square centimeter, the probability of absorption is of the order of 0.004–0.04 for a layer crossing a distance of 0.1 mm. If, as for a sequential absorption, we want to produce 10^{-3} mole.l^{-1} of given reactive species (in the case of benzophenone) within a single voxel, we require energy availability of the order of some 2×10^{-7} J. For a pulse excitation duration of 0.5 ps, with an energy per pulse of 2 mJ and a repetition rate of 100 kHz, the firm Amplitude Systèmes® proposed an

"8 W" laser emitting at 1,030 nm. The power for the pulse duration is then 4 GW, which corresponds to an absorption of the order of 0.04 over a pulse duration (using a rectangular hypothesis), or at 10^{-3} J/pulse in the given voxel if the radiation is concentrated around 0.1 × 0.1 mm^2. This arrangement, as a consequence, leads to the potential transformation of 100–200 molecules of monomer per voxel following simultaneous two-photon absorption. From this approximate calculation, it is found that a commercial material is appropriate. This is chosen slightly by chance from the arsenal available on the market. However, according to its average increased power and the duration of its pulses, this leads to the possibility of inhabiting, by a single process, the excited electronic state, which is responsible for the polymerization sought using acrylic monomers. It is therefore conceivable, with a repetition frequency of the order of 10 kHz, to have a low average power available which is commercially accessible (but keeping the short duration of the pulses) to transform a liquid resin into a solid without any difficulty.

COMMENT 3.– Thermal effects:

Taking data from Lee *et al.* [LEE 08] by way of example, the following elements arise:

– an excitation at 780 nm; an average power of 100 MW and a frequency rate of 100 MHz, which correspond to a pulse of 10^{-9} J per pulse of 1 per second;

– absorption: 10^{-12} J per pulse (yield estimated at 1%);

– heat loss: 5×10^{-13} J per pulse (estimated at 5%).

With a heat capacity of 0.4 $cal.g^{-1}$, we are able to calculate the initial temperature rise, or $\Delta\theta = 10^2$ °C (with a very rapid temporal decrease around the voxel). Moreover, as Maruo and Ikuta [MAR 02] have already shown, using one-photon absorptions, initiations focusing upon a microscope lens could be photo-thermic. There is no reason for the same to apply with two-photon absorptions. Thus, this simplistic calculation shows that within micro-manufacturing, we have to take account of these temperature effects at least so as to avoid them.

We now examine, in a simplistic and approximate way, the typical average heat transfer time at the surface, for a distance of 1 mm, which is of the order of 10 s, according to the laws of Fick or Fourier (with a thermal diffusion coefficient of the order of 10^{-3} $cm^{2}.s^{-1}$). Alternatively, when expressed in another way, between two laser pulses, or 10 ns, heat transfer occurs over distances of the order of 15 nm. This result shows that with pulses every 10 ns, heat transfer at the surface has no time to take effect. We are therefore working under two-photon absorption conditions in which the local temperature may be superior to the average of that of the fluid

situated a long distance from the nano-object in the course of construction. However, to the best of the author's knowledge, this phenomenon has not yet been commented upon by authors involved in the development of the process.

1.2.4.2. *Experimental manufacturing*

Taking into account the resolution potentialities, which are significantly lower than 1 µm, with the difficulty of producing stereolithographic layers, this principle of two-photon absorption (TPA) has particularly been used to produce objects with a very small size. At the point where the beam focuses, TPA is effective and is followed by polymerization. The movement in space of the given support (or in a reciprocal manner, the entire laser beam/lens device) allows, without the reactant fluid moving, little by little, the manufacture of a given object. Figure 1.15 illustrates the principle of this form of micro-fabrication.

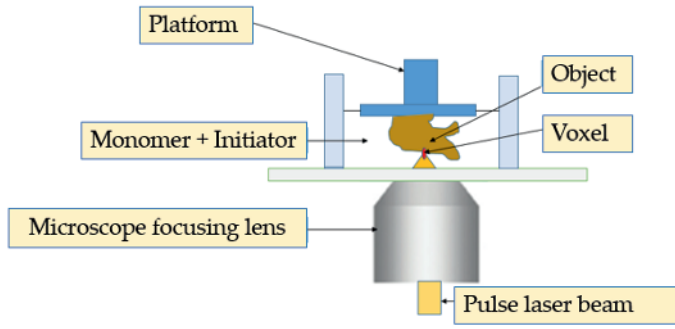

Figure 1.15. *Principle of two-photon stereolithography*

According to Park *et al.* [PAR 05, PAR 09a, PAR 09b]; Narayan *et al.* [NAR 10]; Chen *et al.* [CHE 12] and Ovsianikov *et al.* [OVS 11], through multi-photonic absorption, it is possible to have an excellent resolution available in this type of process. This is indicated in Figure 1.16. The number of other publications around this theme is still modest, but slowly the technology is developing (see, e.g. Lee *et al.* [LEE 04]; Al-Abaddi *et al.* [AL 12]; Jiang *et al.* [JIA 14, JIA 16]; Zhao *et al.* [ZHA 06]; Lim *et al.* [LIM 11]; Narayan *et al.* [NAR 10]; Xing *et al.* [XIN 15a, XIN 15b]; Jin *et al.* [JIN 14]; Engelhardt *et al.* [ENG 11]; Yokohama *et al.* [YOK 03]; Sun and Kawata [SUN 04]; Marder *et al.* [MAR 07]; Duan *et al.* [DUA 04]; Houbertz *et al.* [HOU 03]; Ovsianikov *et al.* [OVS 08]; Niesler and Werner [NIE 14]; Niesler and Hermatschweiler [NIE 15] and many others).

COMMENT 1.– Effects linked to initiation precision:

Waller and von Freymann [WAL 16] showed that two-photon-initiated precision can enable the production of micro-heterogeneous structures, allowing them to indirectly measure free-radical diffusion coefficients in the polymer material. This knowledge may be exploited to create spatially resolved refractive index structures.

COMMENT 2.– Induced birefringence:

Mendonca *et al*. [MEN 07] wrote that there is the possibility of inducing a given birefringence with the colorant, known as Disperse Red13, dissolved in PMMA (poly methyl methacrylate), which is linked to two-photon isomerization in polarized light to determine angular speed. After this treatment, through analysis in direct light, using a traditional one-photon polarized process, it is possible, within a volume of polymer, to observe a 3D image.

COMMENT 3.– Coupled effects:

By using two-photon absorption, Lim *et al*. [LIM 11] showed that we can exploit, simultaneously, 3D manufacturing and laser ablation that, taking into account the instantaneous forms of power, may occur. However, the shape of given objects should remain fairly simple to avoid the difficulties mentioned above. Other methods might be mentioned in exploiting the light-induced conversion of materials (insolubilization) (see [BRA 11]).

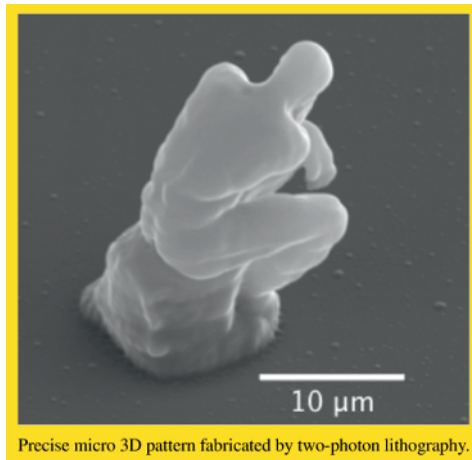

Figure 1.16. *Multi-photon micro-stereolithography [PAR 09a, PAR 09b]*

COMMENT 4.– Holography and 3D printing:

Daqri, an American company, developed a 3D printing technology. This uses lasers to transform a photosensitive monomer into a polymer. However, instead of creating a shape layer by layer, this technology allows for the printing of a small object within a single stage, owing to holography [MEL 17, CON 17, GEO 17].

1.2.4.3. *Manufacturing time and voxel size*

We can devise the hypothesis of a voxel size 0.1 μm (such a voxel being assumed to be spherical, which is far from the case in reality) and then presume that each pulse (taking the data already used in the calculation produced in Comment 3) allows for the polymerization of the given voxel. As a consequence, we can then produce an object of volume 1 mm^3 by 10^{12} pulses, or ~10^4 s provided that the displacement system operates correctly. Alternatively, such a displacement system can last for a few hours. All of these conditions are considered acceptable for scientific works.

Yet what should we make of a complete part of 1 dm^3? The time would actually be, using this resolution of 0.1 μm, of the order of 10^{10} s or approximately 250 years. We put forward here, for the first time in this volume, a major issue, a type of "Heisenberg principle" applied to additive manufacturing. If we want to arrive at a short production time T, we must accept a level of precision linked to a modest voxel size V. Perhaps, it is thus necessary to propose a law (albeit very empirical) relating to shape:

Production time × Size of voxel =/= Constant

The issue is therefore no longer the quality in terms of resolution (100 μm often constitutes, for industrial parts, an acceptable compromise), which, in the preceding example, would give a production time of a few hours. Furthermore, 3D technology with TPA should be able to explore the possibility of a variable resolution taking advantage of the perspective of focus and the instantaneous power of the laser source. Thus, for what constitutes the internal part of the object (indeed the large part of it), there would be the possibility of using a poor resolution and producing the given object, step by step, by exploiting the potentialities of multi-photon absorption in terms of resolution. This aspect would, in principle, constitute significant added value when compared to current such production. At present, the majority of printing technologies have a fixed-value resolution.

To reach this objective, for a given distance z, there are solutions available to use Δz and Δzz, with, for example Δz = 4.Δzz. The perimeter of the object at the *area* z is polymerized several times with maximum precision (Δzz), followed by core polymerization with average precision Δz. Figure 1.17 illustrates this principle.

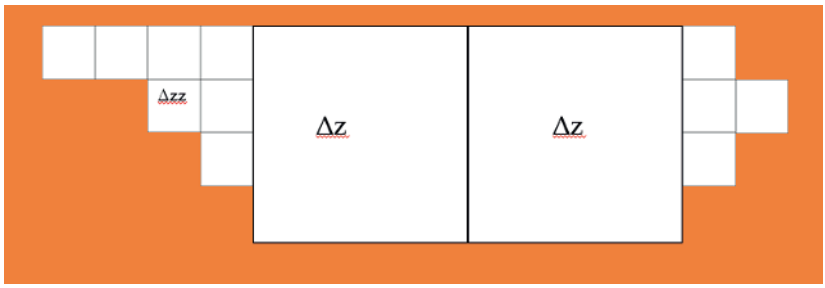

Figure 1.17. *Principle of the significance of resolution change*

Further on, the data used previously and by devising the hypothesis that we can rapidly change the laser beam focus system, if we want to produce, in one phase, the voxel with a size Δz, it is appropriate to have a pulse energy available that is 64 times that used previously (4^3). This would be an average power of 6.4 W, which is (still) commercially attainable. However, if we want to use a relationship Δz/Δzz of 10, we attain average power results, of the order of 100 W. This starts to pose a problem.

Nevertheless, this trend is worth bearing in mind. It should, as long as we find the "good idea", which is readily applicable, break down a highly significant barrier in additive manufacturing. This is manufacturing time.

1.2.4.4. *Analysis of innovations using photo-polymerization*

The partially historic approach described in section 1.2 starts from the acknowledgement that the time taken to create layers in the process of stereolithography may be prohibitive, despite numerous incremental innovations. It has already been technically possible to replace laser beams and their galvanometric mirrors with less expensive sources using irradiation mechanisms for an entire surface. However, the creation of layers to overcome the part being constructed sometimes remains a problem.

"Obvious" solutions have been both proposed and tested with mediocre success for various reasons explained in the paragraphs of this section. The transformation

from a stereolithographical limit (oxygen) into an advantage in order for a highly original process to emerge, the aptitudes of which in terms of material usage and precision have to be explored further.

On the contrary, the exploitation of the nonlinear two-photon absorption process effectively avoids the production of layers. However, although the precision of objects is noteworthy, the manufacturing duration does not, in the end, compensate for the time taken to create layers. Even if we deal with "nanofabrication", it is therefore necessary to be content with compromise, the development of manufacturing mechanisms dedicated to a specific application. A relevance of this approach discussed here is indeed to show, for a particular technology, that the significance of the notion of additive generalist manufacturing apparatuses will be less and less limited.

1.3. Challenging the notion of layers

The Cartesian concept of orderly add-ons was a significant cultural element for the engineer in producing a given object using a rational approach. Moreover, the transition by way of cylindrical coordinates described above did not last long. Can we not rephrase the question in seeking to produce complex objects by other means? This paragraph approaches two possibilities, which are based on different principles, but which may require the fundamentals of additive manufacturing, within certain niche applications.

1.3.1. *Addition of prefabricated structures*

If we are able to assemble autonomous voxels of different sizes, as with a game of Lego® ([SOO 15]; see Figure 1.18), it is thus possible to produce complex three-dimensional structures. This is according to a principle that is intermediate between collaborative robots and "intelligent/smart" matter, which is mentioned in Volume 3 [CAM 14]. The objective of additive manufacturing without any loss of material (we recall the difference with traditional factory-based processes), with the concept of manufacturing with the so-called "right-material", should be retained. It is a matter of assembling components on the basis of "Robotic Building Construction by Contour Grafting" [KOS 04, KOS 14] or by doing so through techniques involving significant reductions. The "builder" is replaced by a robot, which uses the results of a CAD project. Koshnevis used a computer-controlled crane and a gantry to rapidly create desired buildings in the future at lower cost, requiring less material and using less time and workforce than those required for traditional construction methods. He

considered that this technology will make it possible to construct large-scale architectural objects (see also Koshnevis *et al.* [KOS 06]).

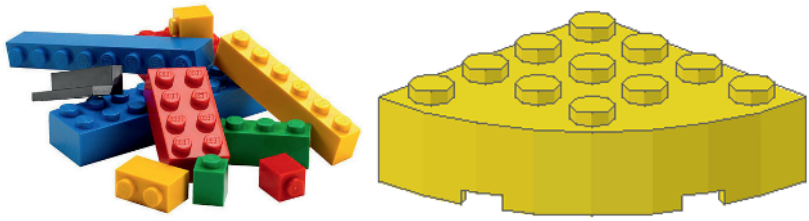

Figure 1.18. *Interlocking using "Lego" constructions*

To reach this objective, the following are appropriate:

– from a given stock of voxels (see. Figure 1.19) to be able to move "a basic brick" (even several) to the part being constructed (e.g. with the aid of a robot system (see [MAN 13]). Perhaps, if we are capable of it, by morphogenesis [BIO 95, THÉ 95, RAM 02], traditional gripper systems may be envisaged or more sophisticated means [BOH 00];

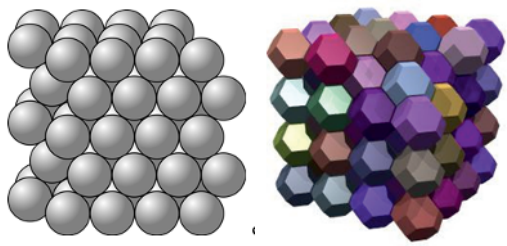

Figure 1.19. *Possible examples of voxels and their assemblies*

– to have isotropic materials (if we want to create optical experiments). The process described here allows us to avoid the issues of anisotropy produced by $2^1/_2$-D manufacturing and is henceforth considered conventional [SHA 14]. Moreover, it allows us to largely avoid the problems of aging and distortion, which intervene in traditional processes [MAN 07];

– these various voxels can be produced in one or indeed several materials with different properties (whether an insulator, conductor or numerous other properties);

– being able to link the voxels to the structure in the course of construction by different processes (electrostatic, thermal, photo or radiochemical bonding, magnetic attraction, mechanical fastening, "bio-inspired" assembly (LEMA project [LEM 13], and others);

– if necessary, to provide, whether locally or not, information within one or several voxels by different routes (optical, electromagnetic and other means) allowing for facilitated tracking or future tracking (see e.g. Meyer *et al.* [MEY 01]);

– equally, on the surface of each voxel it is possible to produce molecular grafting or a specific deposit allowing for surface reactivity, bonding or a form of adapted wettability (see, e.g. CEA [CEA 05]);

– Chapter 3 of Volume 1 showed the need to have available supports in respect of component parts, which are not yet supported, in the case of a process of transferring from a liquid to a solid or even from a powder to a solid. Within the process succinctly described here, there is no possibility to put in place such components. This leads production outside of the main three-dimensional structures, which can be added, within a future stage, onto the part under construction. This technique indeed therefore applies to complex structures, which themselves are partially hollow. Figure 1.20 shows the means to produce objects from sub-elements also using prefabricated components;

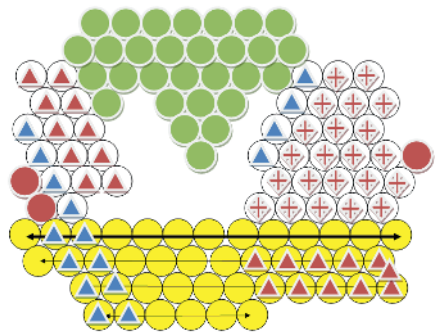

Figure 1.20. *Production (in 2D) of an object from sub-elements, some of which are pre-fabricated and stored in the so-called "library". This takes the form of a line of five circles each with a red triangle and its blue counterpart with four components. The yellow base can be advantageously produced from pre-fabricated components inside out. This is the same with the green component or that represented by the red crosses [SHI 03]. It is therefore by optimizing the procedure involving associated elements produced separately and by adding simple components (the red disks) that we can construct a given object. For a color version of the figure, see www.iste.co.uk/andre/printing2.zip*

– a methodology was developed by Vanek *et al.* [VAN 14] to define the zones of the given object being produced in the form of components, of variable and separate sizes (see the pictures in Figure 1.21). As the lower part of this figure shows, regarding the choice of shape (equilateral triangle or square), the basic components may induce different shapes to represent the same object for a given voxel size;

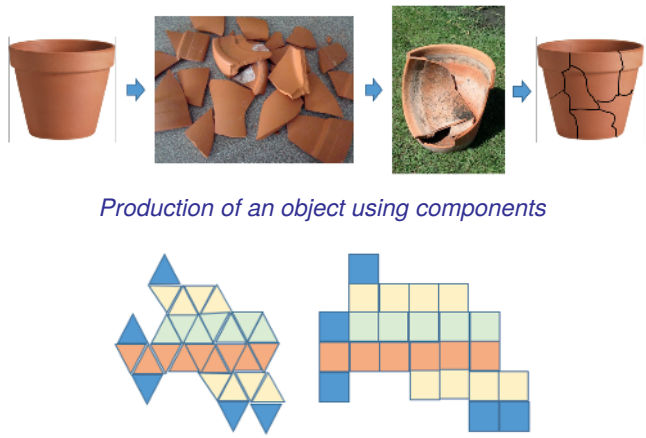

Figure 1.21. *Principle of segmentation and the production of an object using components and a given set of components (see. Vanek et al. [VAN 14]). For a color version of the figure, see www.iste.co.uk/andre/printing2.zip*

– exploiting a different path consists of either using solely appropriately shaped components or in combination with the previous item, which can be discarded at the end of production. This may be completed by means of either dissolution or meltdown (see Figure 1.22). It should be stressed that it is not necessary to fill all of the space, which can be emptied within a subsequent stage [STR 13]. The exception is where the researcher proceeds voxel by voxel within a simplified automated process;

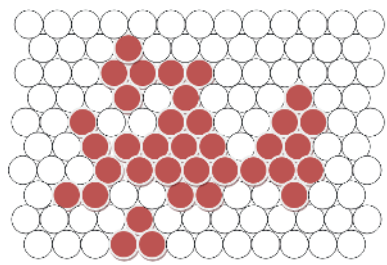

Figure 1.22. *Inclusion of solubilized support components (in red). For a color version of the figure, see www.iste.co.uk/andre/printing2.zip*

– on this basis, there is scope for the availability (even to save time during construction) of a library of sub-objects (including the choice of materials and shapes). Figure 1.23, which is more realistic, allows us to illustrate the concept [DEL 13];

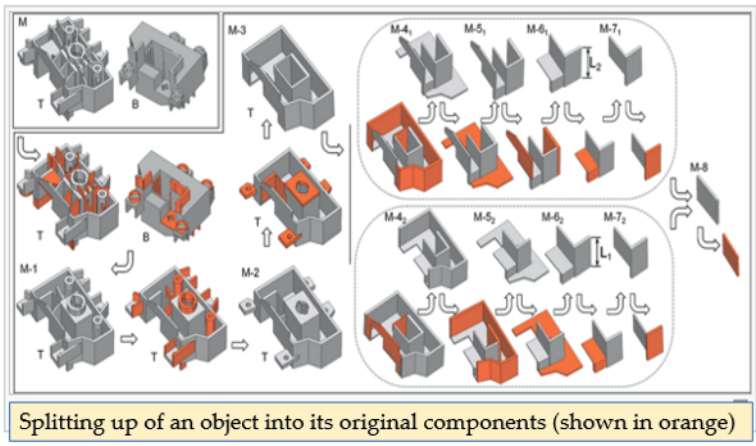

Figure 1.23. *Breaking up a given object into its core components (in this instance known as "original" components) under "creative commons". For a color version of the figure, see www.iste.co.uk/andre/printing2.zip*

– the bonding between components can usefully be produced with the help of a monomer of the same nature as that used previously to produce the elementary voxel. Thus, for example, by the illustration of the process through precise photochemical reticulation within a given area, it is possible to bring two or more voxels into contact and interlock them. Other techniques of the welding variety may be used with metals;

– within a prior stage, the component (which is not subject to volume withdrawals as generally happens in the field of stereolithography with the majority of uncharged monomers and with powder materials) may see its rigidity strengthened. This may happen through the wetting of the latter within a monomer bath, the moistening properties, which are adapted to the size of given voxels [BER 12]. A means envisaged for components made up of a spherical assembly consists of placing the object within a vat. In this vat, we can create a vacuum, allowing for, within a future phase, the introduction of the transformable fluid, from bottom to top, so that it can reach all of the accessible space within the given component. After discharge of the excess fluid, a reticulation/polymerization process can be carried out, allowing for the filling of the inter-voxel space (see Figure 1.24);

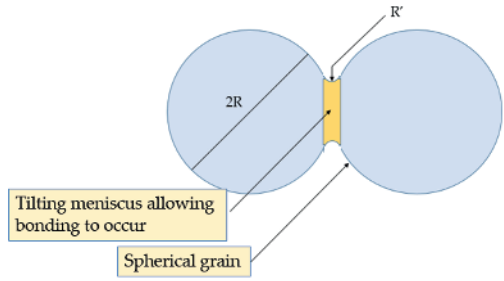

Figure 1.24. *Diagram of fluid distribution between two spheres [ANO 15]*

– it is possible to associate this process with that which is henceforth considered to be the more "standard" of additive manufacturing, particularly stereolithography (with necessary adaptations). This is able to generate structures which are finer than those of the voxels used in the process; and

– it is possible to envisage, as takes place with the Stratoconception® methods [CIR 15], subsequent substractive machining of the part so that its surface complies with the desired specification.

COMMENT 1.– Production time:

Although it is acknowledged that to have a time T to position a voxel at a given point in space, to produce a cube of a side containing n voxels, it is therefore necessary to have a time equal to T.n. Therefore, the higher the resolution sought, the longer the time to produce the component will be (with T = 1 s, a cube of 10 × 10 × 10 voxels will necessitate 1,000 s, whereas 100 × 100 × 100, about 250 h). Seeking the means to reduce T is therefore, as always, a necessity either by taking advantage of T itself (as within laser stereo-photolithography with reference times of the order of 10^{-3} s) or through more collaborative approaches (an example being computer-controlled mask irradiation). However, one of the major interests besides the possible choice of multi-materials is the possibility of producing objects with dimensions which comply with the instructions determined by the designer (e.g. avoiding the problem of withdrawals and tensions within parts) with a more limited number of object construction components (voxel systems of various shapes and sizes).

COMMENT 2.– Modeling:

As has already been shown, there are numerous ways to produce a complex component from an elementary voxel (or from prefabricated parts). The system is normally inadequately conditioned and imposes the following additional constraints:

– minimization of the time to produce a given component;

– knowledge of stocks of pre-fabricated components;

– accessible space for the production of sub-components;

– the selection (or non-selection) of given supports (voxels which may be non-reactive and, for example, solubilized);

– etc.

In such production (which is already at the stage of simulation), it may be necessary to detect un-cooperative situations operating between the various components (e.g. the impossibility of introducing a sub-object across the entire construction) and trying to delete them by re-organizing the programming [BON 94]. For example, it seems that it is possible to apply two approaches to lead the particular robot to place a component (whether unique or pre-fabricated) in a given position by avoiding collisions:

– analysis of trajectory planning (finding a trajectory to resolve the given problem) and monitoring (controls, which, in fact, produce the given trajectory). This approach may call upon CAD resources; and

– "behavioral" analysis, which should allow obstacles to be avoided while heading toward the given aim (an evasive strategy).

The overall movement of the robot is then obtained by means of structure cooperation between these two approaches (both anticipated and "reactionary"). The system resolution may also be influenced by other non-geometric factors: color, present information, material, texture, storage errors and predictable behaviors (the rigidity and fragility of a prefabricated component, e.g. linked with its prehension). It seems that taking into account all of these risk elements is particularly complicated. In a similar work, Ponche *et al.* [PON 12] showed the various stages involved in defining calculation procedures used in exploiting a layered process.

This may serve as a basis to produce the modeling of a construction process in which we would add the various components shown above.

1.3.2. *Proof of concept*

For a given "rustic" proof of concept (or "straw mattress corner"), 10 mm glass beads were bonded together using a bond of the "cyanolite®" variety to constitute three families of components of one, three and nine spheres. An example of these is shown in Figure 1.25.

Figure 1.25. *"Components of the library of sub-parts to produce a given object"*

These various components are bonded with each other as the two following figures (Figures 1.26 and 1.27) indicate:

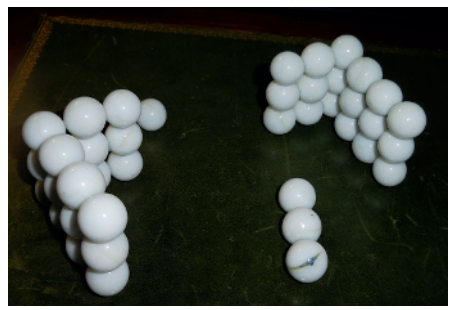

Figure 1.26. *Partial assembly*

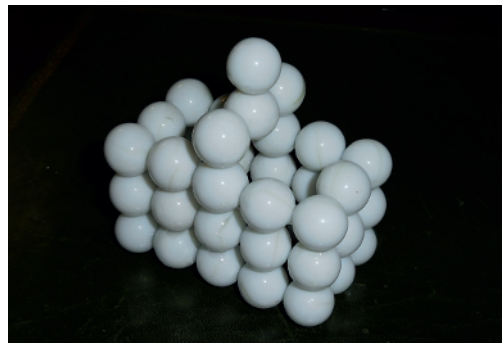

Figure 1.27. *Final assembly*

The use of a library of components therefore allows (and it is fairly obvious) for the production of three-dimensional objects by different means to standard additive manufacturing methods. Development may be necessary to allow for optimization between the number of components available and the main component to produce, by optimizing time-savings through moving construction components using a robotic transport device. One solution may be to combine additive manufacturing and machining determined within space, a little in the manner suggested by Maxey [MAX 15]. With the principle of carrying out preform production, it is possible to manufacture, either layer by layer or as a whole, with the necessary machining to achieve production as per the geometric instructions. This allows us to take into account the complexity of the object at the same time as optimizing the quantity of material used for production. Either way, this little working table area "tweaks" amount to a proof of concept, which it may prove judicious to explore.

1.3.3. *Synthesis*

Table 1.1 pulls together all of the elements to be mastered to develop this process (classed as + for "easy", = "achievable", – "existence of a barrier", – – "sticking point") with relevant commentaries.

Theme	Accessibility	Comments
Voxel	+	
Choice of materials	+	
Production of components taking the form of wires and sheets	+	
Robotization	-	Accessible space and principle of voxel prehension
Precision	--	The smaller the voxel size, the greater the chances of the construction time linked to physical movement in the manufacturing process becoming prohibitive
Optimized storage	-	Complex issue
Breaking up the object to create stored components	-	Ditto
The bonding of components	=	Various types of processes are accessible: welding, bonding and others
General principle	++	

Table 1.1. *Components to master to develop the process*

The issues to deal with stem from the author's skill set. Feasibility may even be produced by assembling identical volumes of given components in order to obtain a particular shape. However, it seems difficult to produce an instrumental mock-up of a device without the aid of automation experts (see the following chapter).

1.4. Optical-quality surface finish

It is common to produce an object with surface imperfections and then to treat its surface accordingly. The aim of this section is to show that it is possible to

disregard this process by exploiting either the physicochemical properties of the material or indeed certain aspects of the process.

1.4.1. *Glasses lenses and contact lenses*

Several companies have embarked upon the niche of glasses printed in 3D, personalizing the shape of the glasses to make them perfectly tailored and comfortable as per individual requirements. This is unlike glasses manufactured by large-scale production. Although producing frames according to customer specifications depends on knowledge of additive manufacturing technologies, which is standard nowadays, the production of marketed optics is a recent innovation. The Dutch company, LuXeXcel [LUX 16], has proposed to print an entire pair of 3D glasses, including the lenses. It has also committed to print usable 3D contact lenses using this method.

According to Allard [ALL 15], this involves a stereolithography process by, means of depositing a resin material, at the end of the operation, which spreads out across the component under construction. After the process of polymerization, this allows us to achieve a sufficient level of transparency. The principle involved in such production is shown in Figure 1.28 (see also the first part of Volume 1 of this series). It is obvious that date issues around the treatment of the anti-UV surfaces and durability have not been studied within this field.

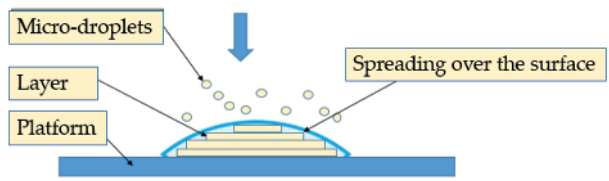

Figure 1.28. *Principle of producing a lens with optical features*

1.4.2. *Microlenses*

This is another interesting concept stemming from Lu's thesis work [LU 06]. It uses the influence of incident light flows across a given surface to modify the depth of polymerization. Knowing the influence of the threshold effect linked to the presence of inhibitors, complex shapes can be produced. By using the so-called "gray wedge", Figure 1.29 shows diagrammatically what may be obtained as a

component made from a polymer material. It will be noted that the "gray wedge" uses a homogeneous, light-absorbing material, the transmission of which, independent of wavelength, is a function of the thickness of the material that it passes through. By adapting an additional parameter, the exposure time and the shape of microlenses may be fairly flexible.

In his work, Lu [LU 06] used this principle to produce sets of microlenses. This is an example of mass batch-processed manufacturing, made possible thanks to an increased number of "gray wedges" (see also [HUN 05]).

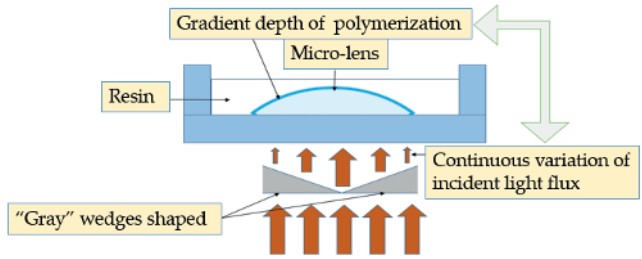

Figure 1.29. *Use of "gray wedges" to produce microlenses*

Other similar technologies could be used (see, e.g. [HUN 05]).

1.4.3. *Direct lens manufacture [AND 91a, AND 94]*

Rather than envisaging a production in several stages as was set out in Volume 1, it may be interesting to examine whether it is possible to calibrate a liquid voxel by giving it the form of an optic lens. It is then a matter of a principle of confinement in relation to the reactive part. The example shown in Figure 1.30 explains the concept. A cylindrical container is set to rotate at a constant angular speed, so that the liquid in it forms a vortex, which is normally a revolutionary paraboloid. Although this liquid is denser than the resin (immiscible) placed above, it constitutes the base of a type of mold. Thus, by irradiating the resin after hydrodynamic stabilization, we are able to produce an optical component.

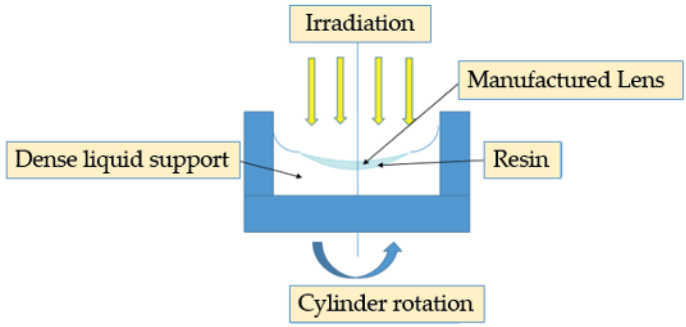

Figure 1.30. *Principle of production of a lens on a vortex with a single voxel*

As has already been discussed in Chapter 3 of Volume 1, the effects linked to interfacial tension may play a determining role in the shape and focal distance of the lens.

– There will be low interfacial tension in the face of inertia forces. The lens takes on a concave–convex shape (see Figure 1.30);

– when the tension forces across interfaces predominate and, in particular, at low rotational speeds, the shape taken on is biconvex; and

– by using two immiscible liquids, the resin voxel may be placed between the two fluids, which can allow the exploitation of the various parameters of influence. Such parameters are:

– the size of the rotating reactor,

– the volume of the voxel,

– the densities of the immiscible fluids,

– the interface tensions, and

– the rotational speed.

Figure 1.31, produced by André and Corbel [AND 94], illustrates the potentiality of this process.

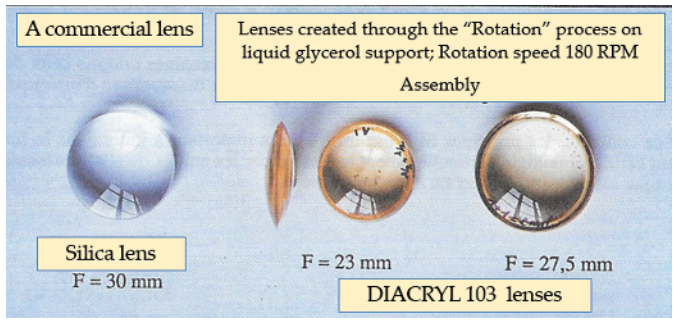

Figure 1.31. *Example of production of optical lenses using this process*

Brullé, in his thesis (completed in [BRU 92]), showed that it was possible to produce support fluids for resin voxels, by using phenomena other than rotation. He discussed the levitation of a given volume of resin, the molding on the surface of a ferromagnetic fluid subjected to a suitable magnetic field and other such cases. The limits of what is possible are therefore, even for a fairly specific application niche, fairly broad.

1.4.4. *Multi-mode optical fiber*

Yves Brullé showed that it was possible to resume Reynolds's experiment, as shown in Figure 1.32. The experiment relates to a liquid monomer containing a photochemical initiator flowing out at low velocity, surrounded by the flow from the same monomer at the same temperature, but not containing any initiator. When the two fluids meet, the light causes the polymerization of the central zone comprising the core of an optical fiber. At the crossing point of these two fluids, an initiator concentration gradient is established, leading to a polymerization gradient. Correspondingly, this translates optically, in practice, into an index gradient. Thus, in a single operation, within a continuous process, it is possible to produce the core and the sheath for a multi-mode optical fiber. The proof of this concept was demonstrated and patented [AND 91b].

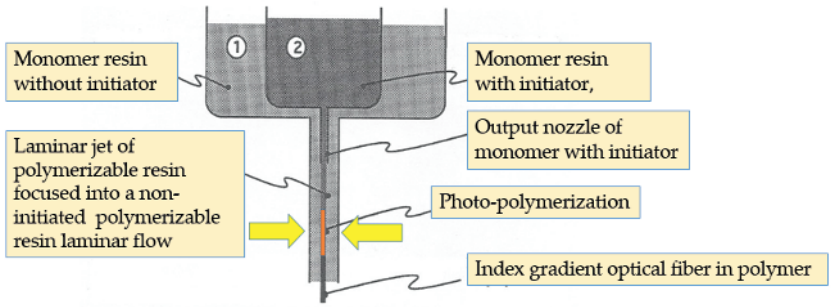

Figure 1.32. *Production of multi-mode optical fibers by photo-polymerization*

We note from these descriptions that it is the location of the voxel which defines the object and not the location of a form of energy (which is light in this situation, but it may also have had the ability to take on other energy forms).

1.5. Cold-cast metal 3D printing

In what has been shown throughout this work, there is indeed a need that is widely expressed by the manufacture of metal products. Certainly, several of the techniques shown in Chapter 3 of Volume 1 already allow for such production, but these go through several stages and a given number of works try to show that we may hope to achieve more with current "metal" processes, which are already broadly operational. These works are succinctly described below (see also [LUC 16]).

1.5.1. *Electrolytic deposition*

Research by LEPMI (*Electrochimie et Physicochimie des Matériaux et des Interfaces*, which translates as "Electrochemistry and physicochemistry of materials and Interfaces" laboratory [LEP 15]) has a particular emphasis. It deals with electro-crystallization of cold metals and their growth in relation to their respective electrochemical, chemical or physical properties. The objectives of such research aim to improve the superficial or structural properties of materials produced by electrochemistry (structural materials) or to confer new properties upon them (functional materials). The following diagram, shown in Figure 1.33, depicts the various modes of electrochemical synthesis for metallic phases from an electrolyte liquid, both globally and synthetically.

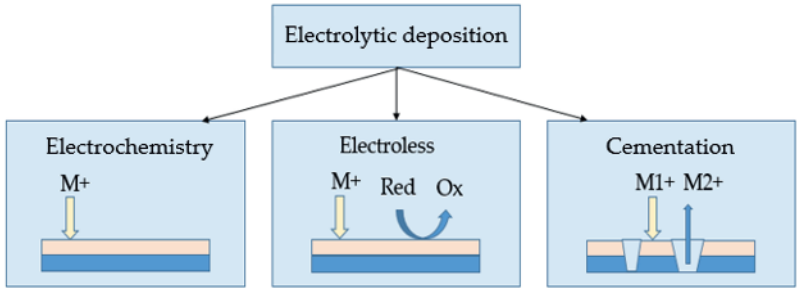

Figure 1.33. *Electrolytic deposit methods*

There are two major stages leading to the production of a metal phase from a liquid phase. As a first step, species of the liquid phase are adsorbed across the surface before their partial or total reduction. On the given surface, these adsorbed species may be diffused across the surface, before finding a given insertion site (for growth) or to create a new germ (nucleation). In both these cases, a phase change in species is seen with an electron exchange (the phenomenon known as electro-crystallization). According to LEPMI, there is a particular case of crystal growth given by deposits (UPD – Under Potential Deposition). The deposit obtained is generally of the thickness of the order of a few atomic monolayers. This situation is therefore not easily adaptable to additive manufacturing (perhaps apart from aspects of nanofabrication, which will be dealt with in this particular volume).

Other metal deposit methods also exist, such as "dynamic chemical plating" (DCP) developed to produce cold metal cast deposition (however with an absence of spatial resolution). This occurs by reacting in an aqueous solution of metallic salts with a reducer, such as KBH_4 (potassium borohydride). However, growth is very modest (of the order of 30 μm/h^{-1}, according to Stremsdoerfer [STR 03]). This type of process will not therefore be described in further detail in this book.

A more promising means was proposed by Seol *et al.* [SEO 15] aiming for metal deposition owing to droplets containing a metallic ion, the conversion into metal of which may be induced by an energy source, such as an electric current. This process, which uses pure metallic ions, is described in Figure 1.34. There remain some issues to be resolved. These include the positioning of the given drop in line with aspects of surface tension and wettability. There are also issues concerning the complex shape of the object and the speed of metal deposition.

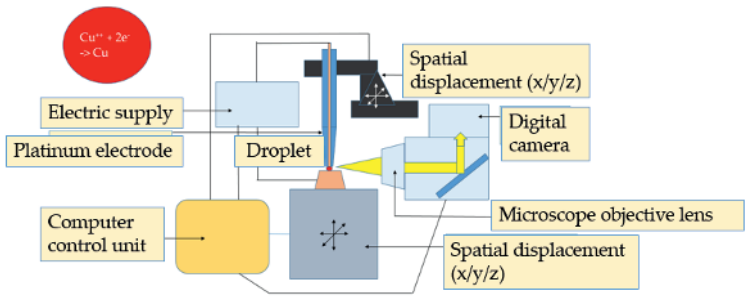

Figure 1.34. *Electroplating process by Seol et al. [SEO 15]*

In the conditions for the use of a given micropipette, the flow is perfectly controlled and regulated by the IT unit. Figure 1.35 illustrates the potential of the given technology (examples are bridge manufacture and micrometer resolution).

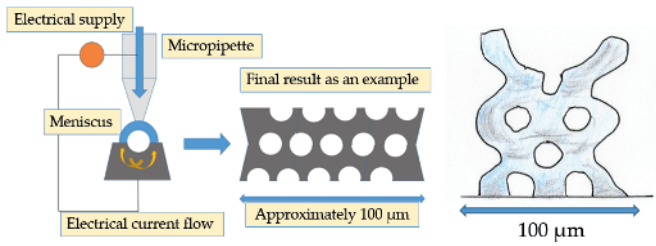

Figure 1.35. *Complex components likely to be produced by electroplating and design similar to an experiment by Seol et al. [SEO 15]*

Evidence suggests that this proof of concept has potential applications useful in micro-engineering.

NOTE.–

Concerning direct electrolytic deposits, on the micrometer or sub-micrometer scale, Brant and Sundaram [BRA 16] showed that it was possible to deposit metal through electrolysis, owing to the fine nature of a given electrode. Both of them, taking into account the nature of the technology, posed the issue of the shape of objects, which ought instead to have a shape that is close to convex. This should thus also have possible solutions to offset this disadvantage (also see [BRA 15, KAD 05, SUN 15] on this subject).

1.5.2. *Metallic ink*

In recent articles, [SHA 15, VIC 16, LUC 16, SHE 15], the creation of a start-up business in Israel called "Xjet" was referred to. This was intended to be capable of producing metal objects from metallic nanoparticles included within an "adequate" solution. By themselves settling upon the component being constructed, the nanoparticles would accumulate so as to make up a continuous metallic medium. The object being produced is constructed layer by layer, with a thickness of less than 2 μm followed by the evaporation of the support liquid (at 300 °C) so as to only leave metallic particles which are sintered at a later stage. The Xjet site is no more informative than this, but industrialization of the process seems to be near. If this was the case, a certain number of laser-based processes could most likely lose their appeal as long as the cost of the device is affordable to the consumer.

1.5.3. *Laser processes*

Stemming from the older works of Bohandy *et al*. [BOH 86], who had shown the possibility of depositing the metal in the form of thin sheets by excimer laser excitation, Zenou *et al.* [ZEN 15a, ZEN 15b] used pulse lasers to produce micro-machining for simple objects of a small size. The principle used by these authors is shown in Figure 1.36. The LIFT (laser-induced forward transfer) process, which serves as their basis [ALL 06, ALL 16, YUN 16] is based on irradiation and ejection, by a single pulse, from a layer of material laid beforehand upon a transparent substrate. The respective absorption coefficients of the layer and the substrate depend on the laser beam wavelength. According to these properties and the laser flow density, the process of various light–material interactions becomes relevant (whether thermal ablation of the material or mechanical ejection subject to high-intensity pressure waves). The process may be broken down into three phases: ablation, transfer and deposition. The LIFT process allows for local deposition and with a large spatial pixel resolution (using voxels) from a substrate on which the material was deposited beforehand as a thin film. This process may be recommended so as to exploit the potential of insoluble compounds, which cannot be deposited by more conventional processes such as ink jet printing [ALL 16, PAP 16, YU 15].

Zenou *et al*. [ZEN 15a, ZEN 15b] relied upon a variant of the LIFT process. The metallic material lies upon a transparent substrate within thin layers. The laser beam liquefies the metal or the alloy, and the molten zone is transferred to the receptor and solidifies. For the "LISAT" (laser-induced self-alloying transfer) part, which the

article by Zenou *et al.* [ZEN 15a, ZEN 15b] involves, the process is identical, but they use several metallic layers in place of a single one. The resolution is of the order of a single micrometer, with modest growth speeds linked to the reduced voxel size.

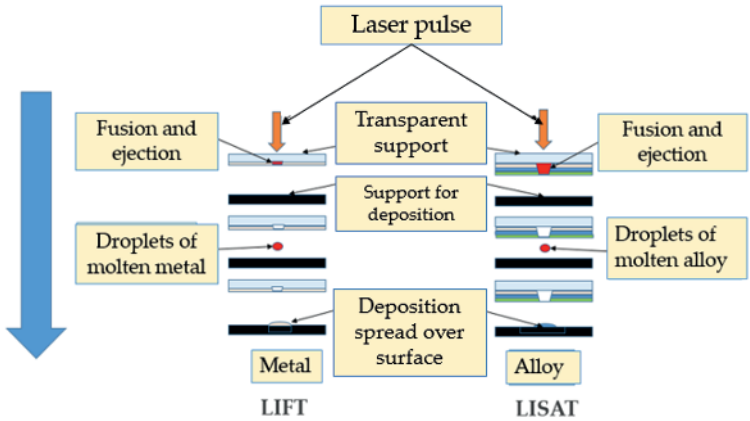

Figure 1.36. *LIFT and LISAT processes*

NOTE 1.–

In a spirit akin to this, Murr [MUR 16] set out a system for the deposition of metallic droplets, which are deflected owing to an electric potential of an oscilloscope type (in the manner of a "cell sorter" used in biology (see e.g. [HER 02]). The American company Vader Systems, according to Lucas [LUC 16], uses aluminum and its alloys to supply a machine in the form of a wire. This is heated in a chamber at a temperature of 750 °C. The liquefied metal is then directed via an electromagnetic field. "The projected drops, traveling at a rate of 1,000 µm/s, have a minimum size of 200 µm." Figure 1.37 shows the principle of the process. We should remember that this mechanism only allows for the manufacture of convex components and that its purpose is more micro-technology oriented. Designed with a print head capable of ejecting metallic drops at temperatures reaching 1,800 °C, caused by an electromagnetic force, this system may project silver, tin and/or copper. However, it does not quite fall under the section title, even if it is an innovative process.

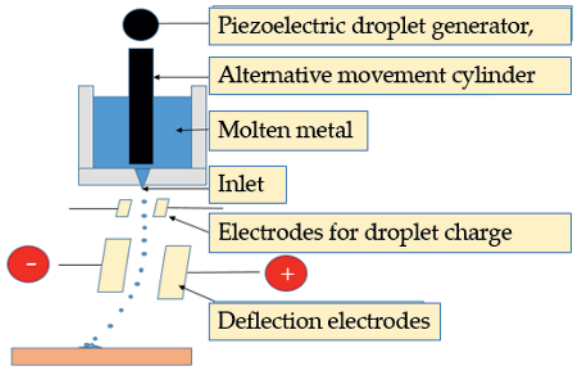

Figure 1.37. *Deposition of molten metal by electrical deflection determined on the given surface*

NOTE 2.–

On a similar basis to the method used in Note 1, there is a method which was invented in 1934 termed "electro-spinning". It consists of the deposition of a guided charged polymeric material through an intense electric field. By controlling the given field strength, it is possible to move the particular impact across a given surface and to, step by step, produce a given object [LEE 15, TEO 05].

1.5.4. *Photochemistry*

By giving "control" back to chemists, it is possible to find simple plating processes, as Ikeda *et al.* proposed in [IKE 01]: It is possible to use the oxidation–reduction (redox) properties of titanium oxide, irradiated by moderate levels of UV, to enable production of a copper-plated deposit. The copper-plated deposit produced has an electrical conductivity surface, which is sufficient for electrolytic deposition, allowing for an increase in the thickness of the metallic layer (see also Akamatzu *et al.* [AKA 05] with a slightly different process). Other metals can be deposited from this TiO_2 coupling as well as metallic ions: platinum, gold and palladium (see [MAI 11]).

1.5.5. *Silver metal*

Recently, the INM – Leibnitz Institute of New Materials [INM 16] published its works on the use of nanoparticles, containing silver oxide, which upon receipt of appropriate light energy, manufactures a type of latent image (see the traditional photography processes). This occurs using a silver salt bath that allows for the release of silver metal atoms. It also allows for the production of conductive layers, without any form of post-treatment being applied.

The article by Nie *et al.* [NIE 12] illustrates decomposition of silver citrate in the presence of a complexing agent 1,2-diamino-propane. This may be carried out with solvents such as methanol and isopropanol. These allow for the adjustment of viscosity and surface tension. They thus favor deposition at temperatures above 130 °C on the positron emission tomography (PET) surfaces. These authors showed an example of the application for the production of a circuit, which is usable within an RF (radiofrequency) antenna. The resolution may reach about 100 µm. Other compounds such as silver(I)-2-[2-(2-methoxyethoxy) ethoxy]-acetate were used by Jahn *et al.* [JAH 10]. It was thus possible to sequentially deposit from metallic silver. The latter is produced by thermal decomposition at approximately 250 °C.

With "inks" containing silver, the use of YAG lasers (488 and 515 nm) allows for the thermal conversion of the deposited material (continuous power densities are of the order of 10–150 kW.cm^{-2}) with resolutions that may reach 5 µm for silver (Aminuzzaman *et al.* [AMI 09]; see also [LEE 13]) and a few dozen nanometers for copper [LEE 14]. However it does not occur, strictly speaking, in photochemistry. Sakamato *et al.* [SAK 09], in an article targeting the photochemical production of metallic nanoparticles, set out two main mechanisms of metal atom production (see Figure 1.38).

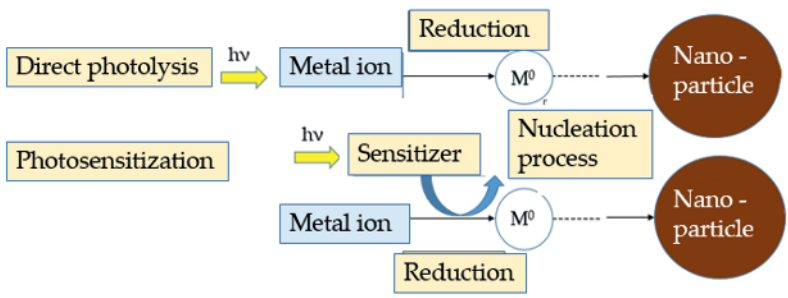

Figure 1.38. *Metallic atom photochemical production*

The first mechanism corresponds to photolysis of silver chlorate in an alcoholic medium. This is illustrated by Figure 1.39 (see also [AKA 03]). Reactions of the same nature have also been published for other metals such as nickel [PLY 92], platinum [GRI 92, GRI 91] and gold [MAL 01] using the principle of metallic deposition shown in Figure 1.39. The reduction mechanisms for the respective elements are then as follows:

– For silver:

$Ag^{+} + RH$ --- $h\nu$ -→ $Ag^{0} + H^{+} + R.$

$Ag^{+} + R.$ ----------→ $Ag^{0} + H^{+} + R'$

$Ag^{0}xn$ ----------→ $(Ag^{0})n$ (Nucleation)

– For gold:

$AuCl_4 - h\ \nu \rightarrow 2AuCl_3 + 2Cl_0$

$2AuCl_3 - \rightarrow AuCl_4 + AuCl_2$

$AuCl_2 - \rightarrow Au + Cl_0 + Cl^{-}$

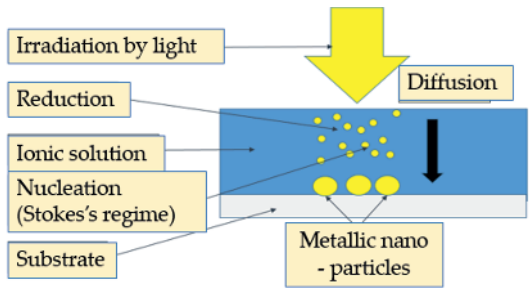

Figure 1.39. *Metal photochemical deposition*

The second mechanism uses, for example, chromophore absorption from the benzophenone family, which will react with a metallic ion, by means of reduction of the given ion leading to metal. Other chromophores may be used in this process, such as pyrene, thionine, titanium oxide and other such chromophores. In $2^{1}/_{2}$-D printing, the resolution is a few dozen micrometers.

It is a question of surface depositions, but with possibilities for the spatial resolution of convex objects. Furthermore, as nucleation occurs with Stokes' flow, the process occurs slowly, which, for standard industrial applications, may not be very worthwhile.

1.5.5.1. *Two-photon systems*

The general principle of this type of conversion induced by pulsed lasers is shown in Figure 1.40 [SAK 08, SAK 09]. This can apply to structures which are $2^{1}/_{2}$-D or 3D as long as the substrate is transparent to radiation types (see also [LIU 16]).

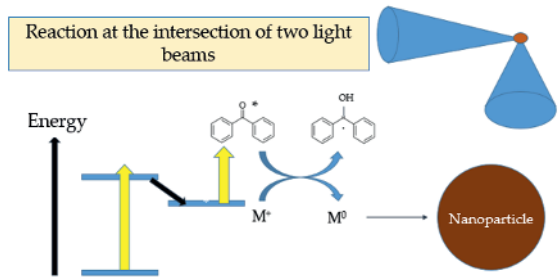

Figure 1.40. *Two-photon photo-reduction located within a given space*

Various examples may be found in specialist works in the field. With a femtosecond laser, films of polyvinylpyrrolidone (PVP) containing silver ions (silver nitrate) have been proposed by Maruo and Saeki [MAR 08]. This leads to the production of metallic silver, which conducts electricity. Figure 1.41 by Tanaka *et al.* [TAN 06] shows a doorway produced from silver in water.

Figure 1.41. *Approximate design of a conducting micrometer "doorway"*

Wu *et al.* [WU 00] produced this type of conversion by using a porous silica gel into which silver nitrate in an aqueous solution is introduced (through pores of 0.2 nm). With the help of a pulsed laser (120 fs, 800 nm) producing 5 $TW.cm^{-2}.pulse^{-1}$, metallic silver is produced within a 3D structure in a spectroscopy cell. Other examples can be found within field resources (see e.g. Soukoulis and Wegener [SOU 11]; Baldacchini *et al.* [BAL 05]; Park *et al.* [PAR 09a, PAR 09b]; Tosa *et al.* [TOS 08]; Terzaki *et al.* [TER 11]; Shukla *et al.* [SHU 10] and other works).

COMMENT.–

In the work published by Lenhart *et al.* [LEN 11], gold is the metal considered to have the most complex chemistry for preparation of a deposit with a usable fluid, having an "inject-printing" system. In order to reach the same objective, other compounds may be used, such as $[AuO_2CCH_2(OCH_2CH_2)_2OCH_3.(^nBu_3P)]$, containing 34.2% gold by mass [SCH 13].

Similarly, it is possible to use lasers such as excimer lasers (e.g. KrF) to convert a polyimide. The process involves initial thermal degradation and the formation of carbon atoms followed by a re-arrangement on a supra-molecular scale. This leads to the production of a graphitic polycrystalline electrical conductor network [QIN 01].

1.5.6. *Conducting polymers*

There are very few works related to the deposition of conducting polymers. However, we can cite the use of poly-pyrrole within some applications [ZHA 14, DES 97, AMB 16, LE 15, SEO 08, MUR 15, KIM 11]. A deposit conductor production principle is shown in Figure 1.42, taken from Kim *et al*. [KIM 11].

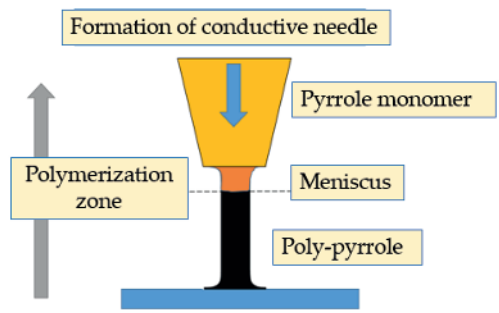

Figure 1.42. *Production of polypyrrole needles*

It is worth repeating that conductive polymers have appropriate electrical properties, as indicated in Table 1.2 [DES 97]. Research works could therefore be undertaken to test the relevance of the producing 3D objects containing non-metallic conductor components.

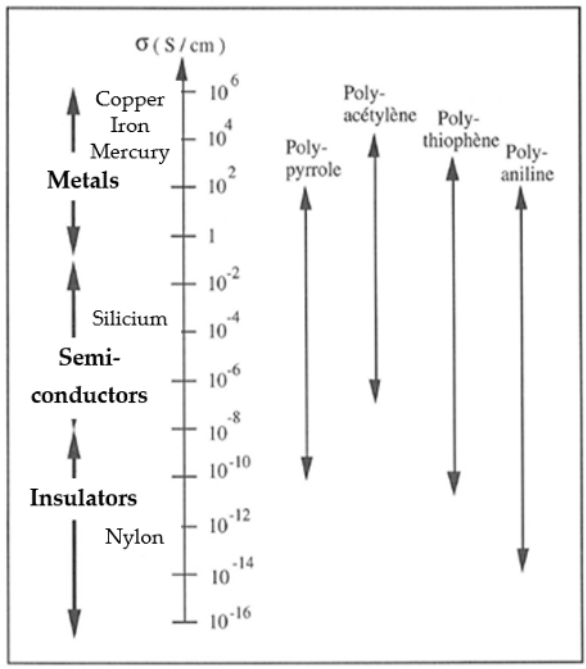

Table 1.2. *Comparison of the conductivities of various components including polymer conductors*

COMMENT.–

It is detrimental to the field that these metallic deposition processes receive insufficient attention from scientists and technologists. This is because it is already possible to produce connectors, which simply lack the conductor component. This is the subject of what might be termed a minor incremental research exercise carried out by Prodways (a French 3D machine manufacturer) to give a level of functionality to a particular 3D object [PRO 17]. This is shown in Figure 1.43.

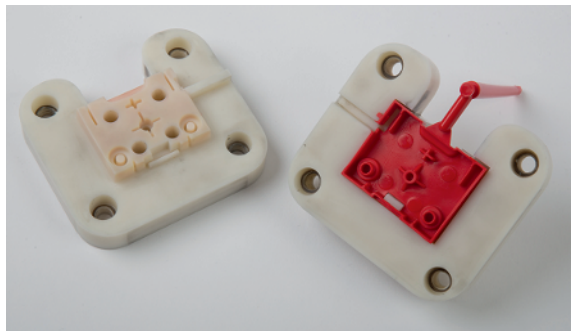

Figure 1.43. *Connector support [PRO 17] ©Prodways and ©Hamilton de Oliveira)*

1.6. Colored objects

By using several vats containing photo-polymerizable resins, associated with organic colorants of varying colors, it had already been possible to produce colored objects using stereolithography as early as 1992 [AND 92]. The system was complicated by the presence, between each given vat, of a solvent bath to eliminate the resin located around the object during construction, followed by a drying process before immersion within the vat containing the next color. Each layer might necessitate several colors, the position of which was defined by the computer used. Figure 1.44 shows some examples produced which are the precursors to 3D color photographs. Although, the proof of concept had been demonstrated, the transition from vat to vat was fairly tedious with the necessity to check the resin level within each vat and other factors. That having been said, apart from aspects relating to actual color changes, the mechanism worked. Despite this, there was, however, a considerable increase in the production time of a component by a factor of the order of between 5 and 10.

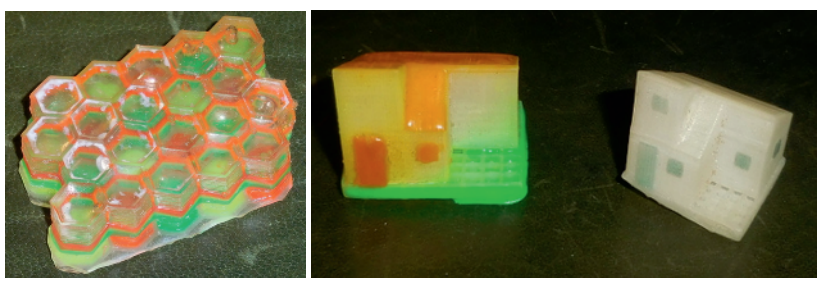

Figure 1.44. *Colored objects produced by the process of stereolithography. For a color version of the figure, see www.iste.co.uk/andre/printing2.zip*

We have had to wait a few years for the new 3DP process developed at the MIT (Massachusetts Institute of Technology in Boston, USA). The process, called 3DP (three-dimensional printing) or BJ (binder jetting), consists of the spreading of a fine layer of composite powder over a given platform. The print head will then deposit adhesive drops, which may or may not contain color. By combining drops when they contain color, we then obtain the desired color to produce a 3D color reproduction. This process is now industrialized.

Within this chapter, it has proved worthwhile to consider whether or not there exist alternative technologies, allowing for discussion of an object during its construction. The first example is fairly standard, corresponding to light irradiation by a pulsed source (the YAG laser type) powered by a given semiconductor material, such as titanium oxide (TiO_2). The light flow allows for a change in the stoichiometry of the given oxide leading to a corresponding change from white to gray or even black according to the following process (see Figure 1.45).

TiO_2 (white) + Nonlinear light absorption -> TiO_{2-x} (black)

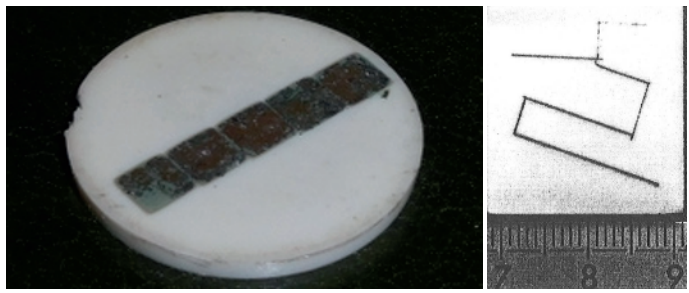

Figure 1.45. *Pulsed irradiation stemming from YAG laser across a polymer containing titanium oxide (the right-hand side image is from Desprez [DES 97])*

On the basis of this principle, it is possible, either during manufacture or at the end of this, to irradiate, using a pulsed laser, the surface of the given object. This allows, in this example, for the provision of information around components, which contain semiconductor materials such as titanium oxide.

Crespo-Monteiro *et al.* [CRE 13], in their production, made this simple process more sophisticated. The photo-catalytic properties of this semiconductor allow us to modify the absorption spectrum of metallic nanoparticles and, as a result, alter the color of the material. These reversible color changes (photochromism) result from variations in the distribution of nanoparticle sizes, due to oxidation mechanisms

within the material. The reduction of Ag(I) ions in this process is thermodynamically more favorable across particles that are already formed than with those formed from isolated sub-particles. With the mobility of ionic silver being large within these porous matrices, the use of lower light intensities (typically of the order of a few to few hundred milliwatts per square centimeter ($mW.cm^{-2}$)) tends to favor the growth of individual nanoparticles to the detriment of the actual quantity of such particles. They give rise to fairly large distributions ranging from several nanometers to a few dozen nanometers. According to the distribution of the given sizes obtained, the film has an absorption band, which is more or less extensive in terms of visibility, being orange, brownish or grayish.

Works of the same type have already been published on other systems. Ocana and Calatayud [OCA 16] experimented with titanium metallic surfaces, Penide *et al.* [PEN 15, PEN 16], aluminum, Mangaiyarkarsai *et al.* [MAN 05] over lenses containing silver ions. Depending upon the conditions, it is possible to go from black and white through to color.

With organic aromatic materials from the diarylethene family, Mori *et al.* [MOR 11] used a principle of multi-photon absorption with a femtosecond laser (35 fs; 1.28 μm) with energies lower than 1 nJ/pulse. The result obtained is the green colorization of the dye. They also showed that it is possible to erase the color by returning to the original color. This is due to a two-photon process, which brings back the initial material. A diagram of the reaction is shown in Figure 1.46.

Figure 1.46. *Multi-photon process of reversible colorization from 1,2-bis(5-{N,N-bis(4-methylphenyl)aminophenyl}-2-methylthiophenyl-3)-3,3,4,4,5,5-hexafluorocyclopentene (APT)*

COMMENT.–

The so-called super-resolution may come from the inhibition of radical production induced by a dual excitation, allowing us to go beyond the limits of diffraction [FOR 13]. There is therefore, as shown in Chapter 3 of Volume 1, the possibility of gaining resolution, owing to a link between chemistry and light absorption. These authors have applied this principle by using photo-chromatic

compounds not, in fact, allowing the production of objects but color images within a transparent matrix, consistent with Weis *et al.* [WEI 16].

Here, we have used a non-exhaustive approach to examine the possibility of adding colors to a 3D object produced by additive manufacturing. This overview analysis shows the possibilities that it would probably be necessary to look into in greater depth. These include the implementation of multi-color information for a given object in an even broader way to produce colored parts.

1.7. Conclusion

In this chapter, we have tried to show that there are numerous conceivable means to develop new 3D processes. These are increasingly specific and dedicated to particular, applications:

– from a localized transformation energy in the given space with specific physicochemical effects;

– linked to the form or the nature of this energy;

– by locating a particular voxel or by giving it a certain shape;

– or all of the above.

Within the list of proposals shown in this chapter, (which are probably not exhaustive), some processes are at a stage of actual industrialization. We might cite the case of 3D Carbon with its generic CLIP process. Others are aiming for high-added-value niches. Examples of these are optical lenses, microelectronics and other spheres. Works other than those revisiting stereolithography and a robotics system indeed focus upon microtechnological or nanotechnological aspects. We are still working within the standard paradigm of adding original material with energy source or material aspects, and/or physicochemical conversion of the given material. The essential barrier, linked to the manufacturing time, for a given quality in terms of precision and finding the "right material" remains an obstacle, which only the CLIP process can partially overcome. This particular research axis therefore seems to favor laying down the need to send the entire additive manufacturing concept back to the drawing board. However, no doubt it was necessary to travel this entire route to reach this conclusion.

Highly upstream spheres are not, however, legion, within this chapter. Moreover, we will not be interested, within the next chapter, in analyzing the reasons leading to this particular situation. We may suppose that, on the one hand, knowledge of reality and possibility, and, on the other hand, mastering ignorance of certain aspects, both

serve to stimulate innovation, particularly on an incremental basis. It is from the proximity to known aspects that validation arises. It is because we know reasonably well what we must obtain. To invent within a framework of thought, to conceptualize the incremental concept, we must not move too far from justifiable knowledge. We simply take a form of distance concerning the aspects that we already know. When the issue is somewhat up in the air, academic research, which has, in theory, considerable freedom should help us to envisage the appropriate response. Without wishing to be too verbose(!), it is what proves, to a degree, that which we are trying to prove.

In addition, within the context of the strong competition which European industry is currently experiencing, the purpose of this chapter may have been to prove our capacity to develop an innovative technological offer. This would allow manufacturers to address the challenges of competitiveness and differentiation. Moreover, by this means, we could enter, via additive manufacturing, into the era of the so-called FoF "factory of the future". Yet, probably the ambition of given socioeconomic backgrounds focusing upon additive manufacturing is still too reliant upon cost rationalization, deadlines and the product lifecycle for new products, the growth of diversity and the quality of conceivable products (e.g. aspects such as high-end, production speed, customization, size and high accuracy involved in such production).

Briefly, the suggestions here are probably too upstream relative to a more immediate demand. Does that prove that creative researchers, without any network and motivation, actually accomplish very little? These observations may largely reduce the significance that we must attach to single individual creativeness. According to Chanut-Guieu and Guieu, "If this is not managed within a given motivating organizational mechanism it risks in the end not being very productive" [CHA 14]. In this section, from available works in the field (manufacturers' driving forces rarely form the subject of such publications), the opportunity comes uniquely from the mind of the given researcher. Save for his/her imagination, he/she starts with nothing or virtually nothing within his/her disciplinary competence. He/she transforms a scientific opportunity on a "bottom–up" basis into an applicable action [SHA 61]. This carries with it the risk of undertaking "inapplicable applied research". This forms, at least in part, the subject of risk-taking, which should be sought within the research sphere.

Indeed, we always look from a given hypothesis, with a return, which unfortunately cannot achieve a form of unity. We should remember that there are two forms of thought: deductive thinking, which starts from a hypothesis to reach a result. The author has attempted to use this approach in this chapter. There is also inductive thinking, which makes given assumptions. The latter approach will be further explored in Volume 3. This thinking comes from forms of intuition, divergent thinking and a

willingness to simplify the world to formulate original promising concepts, which are breakthrough innovations [TEE 97, KEA 09, SAL 12]. It is then that we can explore other forms of uncertainty, those which do not rest upon a known issue. This is when nobody knows to ask the question because it is not (yet) being bandied about.

The initiatives described within this chapter already illustrate the possibility of going beyond the so-called "statuary" technologies set out in the previous volume. However, it must be noted that there are probably more concepts than actual economic successes to be expected in this branch of the field. Many of those set out are still at the proof-of-concept stage. The road is yet to be traveled before knowing whether the processes proposed can one day grapple with economic reality. However, for this to happen, the players in innovation must re-assert their will to try to explore the sphere. This is because they must understand that the hopes for long-term growth will be fulfilled. This is so even if the psychological warning shot may be harsh when a given process concept amounts to nothing. The El Dorado, which the researcher initially thought existed in this field, is not yet available, and the research group, or R&D department, must go through a phase of disappointment (which should be purely temporary).

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