From ion-hammering to ion-shaping: an historical overview

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Abstract. The objective of this article is to summarize the research activity carried out within the field of amorphous materials submitted to swift heavy-ion irradiation since the opening of the GANIL facilities. In particular, this review focuses on two experimental observations which have created excitement in the swift heavy-ion community for several years: the ion-hammering and the ion-shaping processes. However, this article is neither a comprehensive review nor a tutorial. Indeed, its prime purpose is to give an historical overview of these two phenomena, putting the accent on how a new phenomenon is addressed by the scientific community and how through a difficult trial-and-error approach unsolved problems favor the issue of a coherent description of the phenomenon.

1. Introduction

I was asked by the committee for the 30 years of interdisciplinary research at GANIL to write an historical review of the study of the effects induced in glassy systems by swift heavy ions. In particular, amongst the large amount of existing experimental results I was asked to overview two phenomena: the anisotropic plastic deformation and the elongation of embedded nano-particles along the the beam direction. However, instead of giving a account of the experimental facts and theoretical predictions in chronological order, I will take this opportunity to describe how, in my humble opinion, a new phenomenon is addressed by the scientific community.

The explosive development of a new research field is almost always associated with the development of a new instrumental technique that allows new ideas to be checked. It is easier to study a phenomenon if the proper instrumentation to observe it is available. However, posing the right questions and giving the right answers is not always the path researchers follow when they are facing a new phenomenon. Usually, a complex and slow trial-and-error process will after years of research activity converge toward a coherent, but often not unanimously accepted, description of this new observation within the scientific community. In my opinion there exists an heuristic recursive schema that can be generally applied to describe how a new observation is first treated, then integrated and finally exploited by the researchers. This process can be schematically summarized into three main steps:

i) the dawn of a new physics or of the required technical and social background conditions,

ii) the discovery of a new phenomenon and the first steps toward a phenomenological description of it,

iii) from phenomenological to quantitative models and potential applications.

In the following, the ion-hammering and the ion-shaping phenomena will be reviewed within this empirical framework.
2. The historical background
The physics of swift heavy ions is tightly related to the physics of ion tracks, which in turn is the physics of how the energy deposited by an impinging charged particle is transferred to both electronic and atomic sub-systems.

The first experimental observations of the ion tracks in materials dates back to the late fifties with the works of Young [1] and Silk and Barnes [2]. These seminal works opened the door to a stimulating research activities in a variety of fields spanning from nuclear physics, to radiation dosimetry and interplanetary science. Earlier observations pointed out that an ion track is mainly due to inelastic processes, i.e. the radiation-induced excitation and ionization of the target atoms. However, owing to the limited power of the existing accelerators, these studies were mostly restricted to insulators and organic materials. Meanwhile, two different models were proposed to account for the existing experimental results. A model based on the concept of a Coulomb explosion [3], and a model based on the concept of a thermal spike [4]. The former assumes that the track core is always solid and that shear stress, whose magnitude approaches the ideal shear strength, is generated. The latter assumes that the track core is transiently fluid. The issue which one of the two approaches is more adapted to describe the track formation has a longstanding history that has its importance in this historical overview. At this point of this historical overview, what is possible to say is that till the early 1980s, the Coulomb explosion model was considered as the more appropriate one. The reason is threefold: i) at that time the thermal-spike models were not sufficiently developed to provide useful predictions, ii) the experimental fact that it is difficult to generate tracks in materials having a large Young’s modulus was nicely accounted for by the criterion that tracks form only when the stress resulting from Coulomb explosion surmounts the yield strength of the material and iii) it was implicitly assumed that the mechanism leading to the track formation does not hold in electric conductors.

As mentioned above, science often progresses by technological steps and the physics associated to swift heavy ion irradiation does not make an exception to this rule. Although, since its discovery in the early 1960s, an important deal of effort has been devoted to rationalizing the physics underlying the track formation, a real breakthrough took place around 1980, with the advent of large accelerator facilities (GANIL-Caen, GSI-Darmstadt and VICKSI-Berlin). Indeed, the access to these new large-power accelerators allowed the researchers to plan systematic experiments in regions of much higher excitation and ionization densities. This technological progress led to the dawn of the novel research activity described hereafter.

3. The discovery of the ion-hammering effect
The reason why tracks were not formed in metals was still an open issue in the early 1980s. It was often claimed that it was due to the high density of free electrons that quickly spread out the deposited energy and screen in a very short time the charge of the ionized atoms along the ion path. It is thus natural that, as soon as the large accelerator facilities became available to the research community, these materials were among the first ones to be investigated. Among them a particular focus was put onto metallic glasses. Indeed, they were seen as suitable radiation-resistant materials, as their disordered structure was supposed to prevent the irradiation growth by easily absorbing the radiation-induced disorder.

It was therefore with surprise that the first irradiation experiments on unstressed metallic glasses revealed large macroscopic deformations, figure 1a). The first experimental observation was reported in 1983 by Klaumünzer et al in a Pd$_{80}$Si$_{20}$ metal glass irradiated with 360 MeV Kr ions at the VICKSI accelerator in Berlin [5]. The irradiated sample was observed to undergo macroscopic changes at constant volume and without appreciable modifications in its microscopic structure. It was quite soon evident that this unknown phenomenon was different from all the deformation processes already observed in crystals, i.e. swelling, irradiation creep and irradiation growth. However, in analogy to the dimensional changes observed in anisotropic metals, see e.g. [6], it was first named growth. At this point, it is worth noticing that often the name given to a new phenomenon changes as the understanding of the phenomenon evolves. As the growth mechanisms that are active in crystalline and amorphous metals are totally
different, the name was subsequently changed to anisotropic deformation or plastic flow and finally to ion-hammering. The latter terminology conveniently highlighted the role played by each impinging ion: i.e. sample deforms in a manner as each ion would act like a little hammer.

3.1. The first experimental results: searching for a key parameter

During the ion-hammering process the sample dimensions perpendicular to the ion beam, $b$, are observed to grow whereas the sample dimension parallel to the ion beam, $a$, are observed to shrink in such a way that the mass density remains unaltered. In particular, it was observed that, above an incubation fluence, $\Phi_C$, the strain, $\varepsilon=\Delta b/b$, linearly scales with the irradiation fluence, $\Phi$, such that the following empirical relationship holds:

$$\frac{\Delta b}{b_0} = A (\Phi - \Phi_C)$$

(1)
where \( b_0 \) is the initial width of the sample. The coefficient \( A \) represents the strain rate, or the rate at which the ion-hammering occurs. It is characterized by the slope of the time-dependent deformation curve, figure 1b), and it is defined as \( \dot{\varepsilon} = \frac{d\varepsilon}{d\Phi} \). In the literature it has also been called the growth rate or the deformation yield.

In an early paper, Klaumünz er pointed out that equation (1) can be also obtained by considering the continuity equation \( \dot{\rho} + \rho \nabla \cdot \vec{v} = 0 \), where \( \rho \) is the mass density and \( \vec{v} \) is the velocity of any sample point [7].

Quite soon, the deformation yield became the key parameter to unveil the mechanisms underlying the ion-hammering phenomenon. Indeed, it provided a powerful tool to qualitatively categorize the large amount of available experimental results [5, 7–12], figure 2a–c). Indeed, it allowed to show that the growth rate was directly related to the electronic stopping power, \( S_e \). Moreover, it was shown that the deformation yield depends on irradiation temperature, on the electronic stopping power and the stress state of the target. The deformation yield is maximal at low temperature and decreases as soon as thermally activated atomic rearrangement are possible. Below the track generation threshold, \( A \) is small and decreases roughly exponentially with decreasing \( S_e \). Above the track generation threshold, \( A \) increases linearly with \( S_e \). Moreover, the deformation yield increases linearly with an externally applied stress. Finally ion-hammering was not observed in materials which remain crystalline during irradiation.

However, the study of the ion-hammering did not remain limited to metallic glasses. Indeed, soon after its discovery, it became clear that the ion-hammering was an universal phenomenon occurring not only in metallic glasses but in all amorphous materials, [12], such as dielectrics like SiO\(_2\) [13] or semiconductors like a-Si [14]. Again, the behavior of the amorphous material upon swift heavy ion irradiation could be classified on the basis of the deformation yield. It has been observed that \( A \) roughly scales with the glass transition temperature and the high-temperature coefficient of linear thermal expansion but not with the elastic properties of the materials [15].

### 3.2. The first steps toward a phenomenological description

Early experiments pointed out that the deformation yield was directly related to the electronic stopping power. Thus, the first phenomenological interpretations turned out to be focused on how local order modification is efficiently transformed into a macroscopic deformation.

At that time the dominating model for track formation was the Coulomb explosion model. Thus, the first phenomenological interpretations were (cognitively) biased by this approach [7, 9, 10]. For example, Hou et al. stated that "the constitutive atomic rearrangements are probably shear transformations induced by transient stresses which attend the ion explosion spikes in the wake of the fast ions" [9]. Audouard et al. proposed a two-hit model where the driving force for the atomic motion is the pressure induced by a shock wave. Thus, the macroscopic deformation results from the accumulation of the damage produced by the ion-induced compression waves [10].

In 1990 Hou et al. suggested that microscopically each ion acts like an hammer [9]. The macroscopic deformation is due to the accumulation of local plastic strains triggered by energy deposited by the ion into the electronic sub-system. The authors proposed to define the deformation yield per ion as: \( A = \varepsilon \pi R^2 \), where \( \varepsilon \) is the irreversible local radial strain and \( \pi R^2 \) the track cross-section. This simple relationship helps to qualitatively quantify the ion-hammering induced by a single ion impact. As the deformation yield, \( A \), is in the range \( 10^{-14}-10^{-15} \) cm\(^2\), for a track radius of \( R=3 \) nm, it follows that the \( \varepsilon = 10^{-2}-10^{-13} \). Besides, considering that the deformation time is of the order of 1 ps, the strain rate must be in the range \( 10^8-10^{10} \) s\(^{-1}\).

In 1991 Klaumünzer and Benyagoub published the first phenomenological model describing the ion-hammering phenomenon [16], figure 3. The authors used continuum mechanics to describe the dimensional changes of the sample upon irradiation by a strain tensor. In particular, they succeeded in
Figure 3. Dimensional changes of a vitreous silica thin film irradiated at 120 K with 360 MeV Xe ion. The experimental data for the ion-hammering are recorded for two irradiation geometries: i) $\theta=0^\circ$ and ii) $\theta=45^\circ$. Adapted after [13].

accounting for the ion-hammering when the irradiation angle was changed. In a cartesian coordinate system in which the z-axis is along the sample normal and the y-axis coincides with the tilt axis the deformation tensor, $\overline{A}$, reads:

$$\overline{A} = A(T,S_e,\sigma) \begin{pmatrix}
1 - 3\sin^2\theta & 3\sin\theta\cos\theta & 0 \\
0 & 1 & 0 \\
3\sin\theta\cos\theta & 0 & 1 - 3\cos^2\theta
\end{pmatrix}$$  (2)

where $A(T,S_e,\sigma)$ denotes the deformation yield per ion.

3.3. From phenomenological to quantitative models

The first attempts to interpret the ion-hammering process were based on the Coulomb explosion model, e.g [7, 17]. However, its predictive power remained quite limited and none of these phenomenological approaches was able to give an analytical expression for the deformation yield. Besides, it was observed that when mechanical stress is present, creep rates scale linearly with the applied stress [10, 18, 19]. Thus, the radiation creep in amorphous materials must be described as a Newtonian flow with an effective fluidity proportional to the ion flux. As the shock mechanism is beyond linear elasticity, Coulomb explosion approach turned out to be incompatible with a creep phenomenon which is linear in stress [20]. Meanwhile, using Auger and convoy electron spectrosopies, Schiwietz et al. demonstrated that in
metals electrical space charges are virtually neutralized within femtoseconds such that the occurrence of a repulsive Coulomb force of sufficient strength and lifetime is an unlikely process [21–26].

With the time the interest of the SHI community for this approach therefore gradually faded way and the thermal-spike models underwent a renaissance. This change of paradigm was especially due to Toulemonde and Dufour [27] and Szenes [28]. In the thermal-spike models the target solid is divided into two subsystems: the electronic (e) and the atomic (a) ones. The model states that the energy of the projectile is deposited into the electronic subsystem where it becomes thermalized within $10^{-15}$ sec. The energy is then transferred to cold atoms through an electron-phonon interaction, and a thermal equilibrium is reached after about $10^{-13}$ sec. Within this framework, the thermal evolution of both the electronic and the atomic subsystems can be described by numerically solving the following coupled differential equations:

\[
C_e(T_e) \frac{\partial T_e}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r K_e(T_e) \frac{\partial T_e}{\partial r} \right] - g(T_e - T_a) + A_e(r,t)
\]

(3)

\[
C_a(T_a) \frac{\partial T_a}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r K_a(T_a) \frac{\partial T_a}{\partial r} \right] + g(T_a - T_e)
\]

(4)

Within the thermal-spike approach, the ion-track is defined as the cylindrical region exceeding the melting temperature of the material. This useful definition allowed theoretical predictions and experimental observations to be compared directly. This is probably the main reason why the Coulomb explosion approach was discarded in favor to the thermal-spike approach.

However, thermal-spike models alone were not sufficient to give an insight into the ion-hammering phenomenon. Indeed, the critical issue was tightly related to the development of a relationship relating the ion-track to the build-up of a localized strain state around it. Otherwise stated, an analytical description of the deformation yield, $A$, was necessary. The main problem toward this goal was the definition of an amorphous track in an amorphous material. Indeed, if in a crystal the concept of track deformation yield, $A$, was necessary. The main problem toward this goal was the definition of an amorphous track in an amorphous material. Indeed, if in a crystal the concept of track definition allowed theoretical predictions and experimental observations to be compared directly. This is probably the main reason why the Coulomb explosion approach was discarded in favor to the thermal-spike approach.

The underlying idea was to use Eshelby’s classical theory of elastic inclusion [33], to describe an ion-track as a visco-elastic inclusion. Nowadays, this approach is known as the effective-flow-temperature approach (EFTA) and the basic ideas of the model are described hereafter:

The formation of an ion-track is associated to the melting of a cylindrical region around the ion path, whose extension is characterized by the flow temperature $T^*$. Stresses are generated by the thermal expansion of this cylindrical molten region. The EFTA model states that the principal stresses in the direction normal and parallel to the ion beam are different, i.e. $\sigma_{11}=\sigma_{22}\neq\sigma_{33}$. Thus, a shear stress emerges. The latter can be completely relaxed if its life-time, $\tau_s$, is shorter than the duration of the thermal spike, $\tau_{TS}$. However, the duration of the thermal-spike process is shorter than the shear stress relaxation time, such that upon rapid cooling the strain increment freezes-in. The resulting strained track represents the basic mesoscopic defect responsible for the ion-hammering. The overall effect is due to the sum of all the frozen-in viscous strains produced by the individual ion impacts.

The EFTA model gives an analytical expression for both the deformation yield, $A$, and the steady-state the in-plane stress, $\sigma_1$:

\[
A = 0.427 \frac{1 + \nu}{5 - 4\nu} \alpha S'\nu \frac{C_L}{\rho}
\]

(5)

\[
\sigma_1 = -1.16 \frac{1 + \nu}{1 - \nu} G_m \alpha (T^* - T_0)
\]

(6)

where $\alpha$ is the coefficient of linear thermal expansion, $S'\nu$ the fraction of the stopping power that has been converted into heat, $\rho$ the target density, $\nu$ the Poisson number and $G_m$ the high-frequency shear
Figure 4. Comparison between the experimentally determined slopes of the deformation yield $\partial A / \partial S_e$ and the predicted theoretical values calculated from equation 5 using $S'_e = f(S_e - S_{e0})$, with $f=0.5$ (dashed line) and $f=1$ (solid line). Adapted after [11].

The analytical expression for the deformation yield allowed experimental values and theoretical estimations to be directly compared [11, 35, 36]. One example is given in figure 4 where the experimental and the theoretical slopes of the deformation yield, i.e. $\partial A / \partial S_e$, are clearly correlated for a wide variety of amorphous materials.

3.3.1. Constitutive equations for the ion-hammering. In the first version of the EFTA model, the shear stress is instantaneously relaxed, conversely frozen, at $T^*$. To avoid this unphysical assumption, in 1998 Trinkaus succeeded in obtaining the complete constitutional equation describing ion hammering at low temperature [11, 32]:

$$\frac{d\varepsilon_{ij}}{dt} = A_{ij} \frac{d\Phi}{dt} + \frac{1}{2\mu} \frac{d}{dt} \left[ \sigma_{ij} - \frac{\nu}{1+\nu} \sigma_{kk} \delta_{ij} \right] + \frac{s_{ij}}{2\eta}$$  \hspace{1cm} (7)

The first term describes the unconstrained anisotropic deformation process. The second term represents the time-dependent elastic behaviour of the material, i.e. it corresponds to Hooke’s law for isotropic elastic media, where $\sigma_{ij}$ are the non-hydrostatic capillarity stresses and $\mu$ and $\nu$ the shear modulus of the liquid. However, in the EFTA model instantaneous shear stress relaxation occurs for $T>T^*$ and instantaneous freezing for $T<T^*$. The incorporation the time-dependence of the relaxation process is due to van Dillen et al. in a paper published in 2006 [34].
Figure 5. Damage cross-sections as a function of $S_e$ for quartz and vitreous silica. Full squares and open circles are experimental results, whereas open triangles and solid line represent the model calculations according to Eq. 7. Adapted after [11].

The third term describes the inelastic behavior of the material, i.e., the macroscopic irradiation-induced Newtonian viscous flow. Here, $s_{ij}=(\sigma_{ij}-1/3 \sigma_{kk}\delta_{ij}$ are the deviatoric stresses and $\eta=(d\Phi/dt)^{-1}$ is the ion-flux-dependent shear viscosity.

For example, the use of equation (7) allows to reproduce the damage cross-section in quartz and vitreous silica as a function of the stopping power $S_e$, figure 5.

4. The irradiation science strays into the nano-world

A change of the viewpoint in the swift heavy ion community started to develop since the late nineteens with the growing interest of the scientific community for the nanoworld: there's plenty of rooms at the bottom [37].

The emergence of nanotechnology started in the early 1980s mainly driven by two factors. On one hand, the publication of the Drexler’s book “Engines of creation: the coming era of nanotechnology”, who helped to popularize the concept of nanoscience as a mean to assemble the matter at the nanoscale [38]. On the other hand, two breakthrough technical advancements: the invention of the scanning tunneling microscope in 1981 and that of the atomic force microscope in the same year. Under the impulse of this scientific excitement, other techniques and approaches to the nanoscale went into a rapid growth process. Just to mention a few examples: the continuous development of the techniques associated to the transmission electron microscopy, photo-lithography, electron-beam lithography, and colloidal chemistry.

The swift heavy ion community was hit by this new scientific wave starting from the late 1990s. Indeed, if a lot of work has been done to understand the ion-matter interaction in the regime of pure
Figure 6. Tin oxide grains: (a) non-irradiated sample, and (b) after irradiation with 4.6 MeV.u⁻¹ Pb ions at a fluence of $5 \times 10^{12}$ cm⁻². The arrow indicates a small grain which partially disappears after irradiation. Adapted after [40].

electronic energy deposition, most of the experiments have been performed either on macroscopic samples or polycrystalline samples with a mean grain size exceeding a micrometer. At that time, it became clear that one way to obtain a deeper insight into the swift-heavy ion-matter interaction was to reduce the size of the target. Among these pioneering works, we can mention the cubic to monoclinic phase transformation observed in Y₂O₃ sub-micrometric powders [39] and the irradiation of Tin oxide nanograins [40], figure 6a-b).

4.1. The ion-hammering at the nanoscale

In a series of seminal papers published between 2000 and 2006, Polman’s group demonstrated that the ion-hammering was not only limited to macroscopic samples but it was effective even at the nanoscale, figure 7. In particular, exploiting the development of the colloidal chemistry, Snoeks et al [41, 42] and van Dillen et al. [43–46], extended the work of Cartz et al. to sub-micrometer silica particles [47]. Indeed, in 1981 Cartz et al. discovered that ion-amorphized silicate micro-particles (<5 μm) undergo an irradiation creep process when irradiated with 3 MeV Kr ions.

The value of these works is twofold. On one hand, this novel approach allowed to investigate the ion-hammering at the nanoscale. On the other hand, it introduced a novel paradigm in the study of the swift-ion irradiation phenomena. The ion-beam became a tool to sculpt the matter at the nanoscale paving the way to more applied research topics (the fabrication of track-etched membranes is another example of this novel approach). The combination of chemical synthesis and ion-irradiation techniques rendered it possible to produce a new class of colloidal ellipsoids of continuously variable shape. Soon after the publication of these results, it was demonstrated that the ion-hammering of colloidal silica nanoparticles was successfully described by the EFTA model [49].

We have seen that for an unconstrained amorphous thin film, the experimental data can be modeled by introducing the rate-of-strain tensor, e.g. $A_{ij}^0 = d\varepsilon_{ij}/d\Phi$. The solution of this equation in the direction perpendicular to the ion beam is an exponential function of the fluence:

$$L(\Phi) = L_0 \exp(A_0 \Phi).$$ (8)

This equation states that the ion-hammering is an insaturable process, figure 8b). However, when the thin film is replaced by a nanoparticle, capillarity stresses, which are related to the curvature radius of the nanoparticle, must be considered. This corresponds to the second and third terms of equation (7).
Figure 7. Scanning electron microscopy images of a) non-irradiated silica colloids and b) after 4 MeV Xe irradiation at a fluence of $3 \times 10^{14}$ cm$^{-2}$, at an angle of 45° relative to the surface normal, at 90 K. Adapted after [41].

For large nanoparticles, capillarity forces are small and the deformation kinetics is still given by Eq. (8). However, as pointed out by Klaumünzer [49] when the curvature radius is reduced, capillarity stresses becomes important and the two previous terms must be considered. As the signs for the ion-hammering and for the capillarity forces are opposite, ion hammering should be, in principle, balanced by viscous flow. The slowing down of the ion-hammering process when the colloidal size was reduced was first put in evidence by van Dillen et al [46], figure 8c). In 2011 Rizza et al. [50] showed that the deformation yield at the nanoscale is not longer constant but that it becomes a function of the irradiation fluence, i.e. $A \rightarrow A(\Phi)$. Furthermore, they show that it vanished for large irradiation fluences, i.e. $A \rightarrow 0$. Otherwise stated, the ion-hammering saturates, figure 8a-c).

5. The discovery of the ion-shaping

Motivated by these novel observations, D’Orléans, Stoquert and collaborators decided to study how the properties of embedded metallic nanoparticles were modified when submitted to a sustained swift heavy ion irradiation. In line with the approach developed by Polman’s group, the ion beam was used as a tool to modify the properties of embedded nanoparticles. Indeed, in a series of articles published over 2003-2004, D’Orléans et al. [51–53] reported that Co nanoparticles embedded in a silica matrix changed shape, from spheres to rods, under the influence of swift heavy-ion irradiation. Interestingly, while van Dillen’s experiments show that the silica colloids become oblate, i.e. the deformation is normal to the beam direction, in D’Orléans’s experiments the metallic nanoparticles become prolate, i.e. the major axis of the elongated nanoparticles was aligned parallel to the incident ion direction. The ion-shaping process was discovered.

This surprising finding has rapidly attracted the attention of an important number of groups worldwide [54–87]. The effect has been reproduced in many systems, and in general the results indicate that within a wide range of metals, the nano-particles can become elongated under suitable irradiation conditions.

It is interesting to note that in the first paper of D’Orléans et al [51] the deformation of the Co nanoparticles was not particularly highlighted in the title: “Irradiations of implanted cobalt nanoparticles in silica layers”. However, in their following paper the term of anisotropic deformation was introduced [52]: Anisotropy of Co nanoparticles induced by swift heavy ions. The same years, the same terminology was adopted by Roorda et al [80] and Penninkhof et al [82]. In 2007, Schmidt et al [77] first introduced the term ion-shaping to describe the ion-deformation of crystalline Ge NPs embedded in a silica matrix. Nowadays, this term has been accepted by the community and currently indicates the irradiation-induced transformation of spherical nanoparticles into prolate nanostructures (e.g. [61, 62]).
Figure 8. a) Bright-field micrographs showing the deformation of colloidal silica NPs (100 nm) as a function of the irradiation fluence. The ion beam is normal to the plane, ⊗. b) The dashed line shows the exponential growth behavior for free anisotropic plastic deformation given by equation 8 with $A_0=6.2 \times 10^{-16}$ cm$^2$ ion$^{-1}$. c) Evolution of the normalized transverse diameter of the NPs ($L(\Phi)/D_0$) as a function of the ion fluence. $D_0$ is the NP diameter. Circles are experimental data from [50] and triangles from [46]. Adapted after a) [50], b) [46] and c) [50].

Figure 9. Ion-shaping of Co NPs embedded in silica matrix. Adapted after a) [51], b) [52] and c) [52].
Hereafter, the experimental and theoretical developments will be described separately. Although this method of presenting the subject is somewhat arbitrary, it allows to focus on the difficult journey followed by the researchers to reach a coherent description of the phenomenon. We could describe this journey as a succession of ephemeral truths. First a brief summary of the experimental knowledge acquired over the last decade on the ion-shaping phenomenon will be given. Then, the intellectual efforts made to obtain an insight into the ion-shaping phenomenon will be described. In fact, in the present stage of knowledge, a coherent theoretical description of the ion-shaping process is still lacking.

5.1. The accumulation of experimental results
The fact that the deformation yield is a key parameter in the ion-hammering process emerged rapidly. However, it less obvious that there exists a similar unique key-parameter for the ion-shaping process. To put it simply, the ion-shaping is basically the transformation of a sphere of diameter $D$ into a cylinder of width $W$ and length $L$. Thus, a great deal of effort has been made to correlate these quantities to both the irradiation conditions and the thermodynamic properties of both the matrix and the embedded NPs.

In the first part, the studies on nanocomposite thin films will be summarized. In the second part we will briefly describe the research activity on core-shell colloidal NPs.

5.1.1. Ion-shaping in nanocomposite thin films
Right from the early experiments on, it has become clear that the ion-shaping depended on the NP dimension [51, 52, 63, 64]. In particular, three different deformation regimes were identified. NPs smaller than about 8-10 nm do not deform. However, they are observed to grow under irradiation, most likely through a process akin to Ostwald ripening where larger particles grow at the expense of smaller ones [51, 52, 64, 65]. NPs in the range 10-20 nm deform into nanorods and nanowires whose main axis is aligned with the direction of the beam. Finally, until 2009 the consensus in literature was that NPs larger than about 20 nm could not be deformed upon irradiation. It is however worth noticing that their deformation had been clearly observed in TEM micrographs, but not recognized as such, see e.g. figure 3a) in [51], figure 4 in [66] or figure 2 in [67]. The previous statement was justified by the fact that the thermal-spike simulations indicated that the threshold size for melting was about 20 nm [51, 63].

It was not until 2009 before the fact that ion-shaping was not limited to NPs smaller than 20 nm became explicitly noticed [62, 64, 68]. In particular, they were observed to evolve toward facetted-like morphologies [68]. At this point one is really entitled to wonder why a whole community had accepted for several years the paradigm that NPs larger than 20 nm were not deformable despite the contrary evidence in the published TEM images which clearly indicated the opposite. The source of the problem has a twofold origin.

The first reason is inherent to the technique used to prepare the pristine sample, i.e. the ion-beam synthesis (IBS) technique. While IBS is well suited to fabricate nanocomposite materials, the broad size distribution of the embedded NPs makes it difficult to give a clear correlation between the initial NP size and its final morphology. Within the framework of the ion-shaping phenomenon, this problem was solved by Rizza et al. by introducing a novel fabrication method where nearly mono-dispersed colloidal nanoparticles are sandwiched between two silica layers [69]. By using this novel approach, the correlation between the initial size of a NP and its final morphology could be clearly established, figure 10. This allows to show that four different size-dependent regimes exist during the ion-shaping process:

- NPs smaller than about 10 nm remain spherical in shape.
- NPs in the range 10-30 nm transform continuously into nanorods and nanowires.
- When the NP size is further augmented (30-70 nm), an increasing refractoriness to deformation is observed. These NPs take longer times to be ion shaped and reveal a tendency to evolve toward faceted configurations.
- Finally, larger NPs (>70-80 nm) are not noticeably deformed even at the highest irradiation fluence.
The second reason is that dominating models may cognitively bias the interpretation of the experimental results. We have already seen this at work in section 3.2 for the application of Coulomb explosion model to the interpretation of the ion-hammering effect. The reason is that with time the dominant becomes more and more simply accepted on the basis of trust (this is especially true for the experimentalists). This point will be described in more detail in the next section.

Returning to physics, it was observed that for NPs larger than the threshold size, the ion-shaping proceeds through two regimes [62, 70]: i) for low irradiation fluences, the ion-shaping is an individual process where each spherical NP progressively transformed to a rodlike shape of fixed width independent of length. However, when the width of the nanorod/nanowire approaches a critical value, morphological instabilities appear and the NP becomes subject to breakup [70, 71] and dissolution [72]. The rate of dissolution increases with ion energy or equivalently with electronic stopping power, demonstrating that the dissolution process is not mediated by ballistic interactions. ii) for large irradiation fluences, the maximum length of the unbroken NWs has been observed to depend on the initial density of the embedded NPs, indicating that a collective growth process is active where more than one NP contributes to the elongation process. These experimental observations indicate that when the inter-particle distance is sufficiently small to permit solute diffusion upon irradiation between, the single NP deformation must be considered as a simplistic approximation and a more complicated dynamical process must be taken into account.

The fragmentation of the elongated NPs is related to the minimum sustainable width W of the NW and can be interpreted in terms of a Rayleigh-like instability under irradiation [70]. Ridgway et al have shown that the maximum width of an elongated NP scales with the electronic stopping power, $S_e$ [61, 64, 74], i.e. it is limited by the diameter of the molten ion track within the host matrix. On the other
Figure 11. TEM micrographs of a) non-irradiated gold core (14nm) surrounded by a 72nm thick silica shell, b) after irradiation with 30MeV Se ions at an angle of 45° to the normal at a fluence of $2 \times 10^{14}$ cm$^{-2}$. Adapted after [80].

hand, the minimum width is governed by the energy density per atom required for vaporization of the metal [74].

Systematic investigations on both the energy, $S_r$, and the fluence, $\Phi_r$, thresholds have been performed by Dawi et al. using Rutherford backscattering (RBS) spectrometry [75]. It is deduced that above $S_r$, the deformation rate linearly scales with the electronic stopping power, $S_e$, and inversely scales with the NP size such that three size-dependent sub-domains can be identified: i) for Au NPs in the range 15-30 nm $S_r$ is found to be between 3 and 4 keV.nm$^{-1}$. Thus above the value of $S_e \sim 2$ keV.nm$^{-1}$ necessary for the silica matrix to be deformed upon irradiation [13, 35]. ii) $S_r$ is observed to increase up to 5.5-6 keV.nm$^{-1}$ when the dimension of the NPs is increased to 40-50 nm iii) Finally, for 80 nm NPs the threshold is observed to range between 7 and 8 keV.nm$^{-1}$. The threshold fluence for deformation, $\Phi_r$, has been observed to range between $10^{13}$ and $10^{14}$ cm$^{-2}$ [52, 62, 63, 75], i.e. close to the fluence necessary to complete the compaction of the silica matrix [35]. However, Amekura et al. have shown by optical analysis that the ion-shaping can be induced without overlaps of ion tracks, thus below $\Phi_r$ [76]. Furthermore, the amplitude of the process has been observed to decrease with the deposited energy, $S_e$, and to increase with the NP size [62, 75].

Finally, Ge NPs embedded in SiO$_2$ show either prolate or oblate deformation depending on the NP size [77–79].

5.1.2. Ion-shaping of core-shell nanoparticles. In parallel to the investigation of the ion-shaping process in nanocomposite thin films, the study of the ion-shaping in metallo-dielectric core-shell colloidal micro-to-nanoparticles has developed, motivated by the explosive development of the field of plasmonics.

In a series of articles published over 2004-2006 [80–82] it is shown that in Au-core/silica-shell colloids, the silica shell expands perpendicular to the ion beam, while the metal core deforms along the ion beam direction, provided the silica shell thickness is large enough (> 40 nm), figure (11). Besides, metal deformation was observed to occur above an electronic energy loss threshold in the silica of about 3.3 keV.nm$^{-1}$.

The negative counterpart, i.e. silica-core/gold-shell colloids, was also studied [83, 84]. Here, the anisotropic deformation was attributed to the ion-hammering of the silica core, counteracted by the mechanical constraint of the metal shell. At constant fluence, an increase of the metal shell thickness reduces the deformation, while the addition of an extra silica shell results in deformation rates that approach the deformation rates of silica.
Figure 12. a) Schematic diagram for the swift-heavy-ion-matter interaction for (a) bulk silica, (b) bulk gold, and (c) gold NPs confined within a SiO$_2$ matrix. b) Time-line of the thermal evolution for a 20 nm Au NP embedded within a SiO$_2$ matrix irradiated with a 74-MeV Kr ion. Simulations have been run considering an ion hitting the NP at the pole. Time evolutions are shown for the electronic temperature, the lattice temperature and the fraction of the NP that reach a temperature exceeding the melting temperature, i.e. the molten fraction. c) The size-vs-shape diagram used to rationalize the ion-beam-shaping process for all the NP sizes. Four temperature-dependent regions can be defined (see text). Adapted after [69].

5.2. Toward a phenomenological description

Since its discovery, the ion-shaping has been extensively studied by many groups worldwide. Below we discuss the early discussions of the elongation mechanism, although no definitive mechanism to explain it has been proposed up to now.

The explanation of a new phenomenon is always a complicate task and the first attempts are often done in the light of the knowledge already acquired elsewhere. The case of the ion-shaping has not been an exception to this rule. The first phenomenological model was proposed by D’Orléans at al in 2003 [51, 52] and it is largely based on the idea proposed by Berthelot et al [40] in their study on the fragmentation of tin oxide (SnO$_2$) powder irradiated with swift heavy ions. That is, when the energy deposited by a swift heavy ion is sufficient to melt an embedded NP large shear forces are generated. The latter are due the thermal expansion of the molten NP that is constrained by the surrounding solid matrix. In particular, simulations reported in the D’Orléans paper [52], indicate the existence of a temperature gradient between the insulating matrix and the embedded NP. The latter generates a thermal pressure which drives the elongation of the molten NP through a creep mechanism. As described in the following, this idea was recently revisited and refined by Leino et al [85].

On the basis of the results obtained in core-shell systems, Roorda et al. proposed in 2004 an indirect deformation mechanism where the melting of the NPs is not considered [80]. Here, the ion-shaping is driven by the in-plane mechanical stress, that is generated by the ion-hammering of the silica shell, and acts on the radiation-softened Au NP. This mechanism favors the flow of the metallic species towards the out-of-plane direction, i.e. along the direction of the ion beam. This mechanism has been extended to nanocomposite thin films.

The explanations proposed by D’Orléans et al. and by Roorda et al. are based on two completely different scenarios. In the first one, the melting of the metallic NPs is a necessary condition for the ion-shaping to be active. In the second one, the privileged mechanism is the creep of a solid (radiation-softened) NP enhanced by an in-plane mechanical stresses.

In a paper published in 2006 Klauhmüner tried to answer the question whether or not the melting of the NP is an inevitable conclusion for the ion-shaping [86]. First, deformation mechanisms based dislocations or grain boundary diffusion were rejected. Then, the velocity of radial shrinkage of a void, representing the most deformable passive cluster, i.e. $1.4 \times 10^{-13}$ ms$^{-1}$, was compared to the experimentally measured radial shrinkage for a cobalt NP, which is about $10^{-12}$ ms$^{-1}$. The larger shrinkage rate measured for the metallic NPs indicates that the passive deformation mechanism must
be discarded and that the NP must play an active role in the deformation process, i.e. it must melt and it is thus subjected to a large thermal pressure.

Interestingly, in this paper the following statement is reported "Particles with dimensions larger than 20 nm are expected not to melt". We have already mentioned that this assertion was in contrast with the available experimental results but in agreement with the simulation results based on the thermal-spike model. As pointed out by Klumünzer [11] although the existing TS models were successfully used to describe a large amount of SHI experiments, nonetheless they were based on a series of drastic approximations. Among them, three can be mentioned in this context: till 2008 i) the simulation of the thermal evolution of composite systems was not possible. In particular, due to the used boundary conditions, the diffusion of the heat through the metal/dielectric interface was not allowed. ii) TS models were based on a bi-dimensional approximation, and iii) in dielectric matrices, target electrons were considered to behave like a free electron gas. However, this approximation is only valid when the temperature exceeds the temperature which corresponds to the band-gap energy according to $T > T_g = k_B/E_g$.

To make progress towards a coherent description of the ion-shaping phenomenon it was necessary to overcome these limitations.

In 2008 Awazu et al. extended the thermal-spike model to account for the thermal evolution of a nanocomposite material [63]. The latter is simulated by two cylindrical regions centered at the ion trajectory, where the inner one represents the metal nanoparticle, and the outer one the silica matrix. The energy of the swift heavy ion is first deposited into the electronic sub-system of the metal nanoparticle. Then, it diffuses to peripheral electrons by electron-electron interactions and to the lattice by electron-phonon coupling, crossing the materials boundary at the metal-silica interface. The model maintains all the approximations used in the standard thermal-spike model [27]. Thus, only two-dimensional simulations are performed where only the heat flow in the plane normal to the ion beam is taken into account. However, spatial energy distribution has been modified to account for the presence of two materials around the ion path. The model tried to find a correlation between the ion-shaping and the melting of the nanoparticles. The main result is that the melting (and thus the shaping) only occurs for NPs smaller than 25 nm. Despite the improvement, the code failed thus in accounting for the deformation of large NPs.

The main problem with the classical, two dimensional, TS models is that they only provide a binary solution for the thermal evolution of the irradiated NP. Indeed, above 10 nm, NPs can only be either in a solid or in a molten phase. However, the reality has turned out to be slightly more complicated.

In this sense, a real breakthrough has been achieved by Khomenkov, Dufour and collaborators, [87]. Indeed, in a paper published in 2012, they introduced several major improvements to the existing TS codes. The first one concerns the implementation of the code in three dimensions and for a real nanocomposite material, i.e. the code allows to simulate all the NP shapes, where only coaxial cylinders were allowed in the Awazu’s model. Secondly, following the work of Daraszewicz and Duffy [88], they extended the TS model to insulators. Indeed, the number of electrons involved in the thermal process, $n_e$, is considered to be proportional to the electronic temperature, $T_e$ as long as $T_e$ is lower than the band-gap temperature, $T_g$. Thirdly, the heat diffusing through the matrix/metal interface is explicitly taken into account.

Abandoning the oversimplified idea that the electrons in insulators behave like in metals and allowing the heat to diffuse through the matrix/metal interface, has proved to be the key parameters to unveil the mechanism behind the ion-shaping process observed for larger NPs.

A phenomenological description of the physics behind the simulation results is obtained by using the schematic diagram of figure 12a). Silica possesses a low electronic thermal conductivity, $K_e$, and a high value for the electron-phonon coupling constant, $g$. Thus, the energy deposited remains spatially localized within the ion trajectory where it is rapidly thermalized, resulting in a narrow and hot ion track. In contrast to silica, gold possesses a high value for the electronic thermal conductivity and a weak electron-phonon coupling. Thus, the deposited energy is swiftly smeared out over the electronic
Figure 13. Elongation of Au nanocrystals in silica from Molecular Dynamic simulations. Each image shows a cross section of the simulation cell 50 ps after the ion impacts. The lower left image shows an experimental TEM image at an intermediate dose, and the lower right image shows the simulated shape after three non-overlapping impacts. Adapted from [85].
subsystem while it is only weakly coupled to the atomic subsystem. This results in a rapid increase of the electronic temperature but in a limited augmentation of the lattice temperature. The case for the Au NPs embedded within a silica matrix leads to an interesting effect. The energy transferred to the electrons of a Au NP diffuses rapidly outwards to the surface. When this energy reaches the Au/SiO₂ interface, it is transferred to the electrons of the neighboring silica matrix. Here, the large electron-phonon coupling results in the formation of a hot silica layer. Thus, the dielectric matrix acts as a barrier for the diffusion of the electronic energy, allowing, at the same time, its transformation into heat. Then, in a further stage the heat diffuses back toward the center of the NP. Thus, we can conclude that the irradiation-induced heating of a gold NP (high $K_e$, low $g$) confined within a silica matrix (low $K_e$, high $g$) can be seen as an indirect mechanism wherein both the NP and the surrounding matrix participate in the process. Due to this indirect-heating mechanism, the temperature profile within the NP becomes strongly size dependent, figure 12b). In particular, complete melting is observed for NP diameters up to 30 nm. For larger sizes, the efficiency of the process decreases and the molten region no longer reaches the core of the NP such that it remains solid. Thus, NPs are only partially molten upon irradiation. Furthermore, The thickness of the liquid layer is observed to decrease with the NP size. 

In a companion paper published in 2012 Rizza et al. give a rational description of the ion-shaping mechanism [69]. First, a matrix-like diagram is built to correlate the final ion-beam-shaped morphology to both the initial NP size and the irradiation fluence, figure 10. In a second step, 3DTS simulations are used to obtain the dependence of the vaporized/molten fraction on the initial NP size, figure 12c). Finally, the direct comparison between experimental results and simulations permits to obtain a precise characterization of four deformation regimes.

- Completely vaporized NPs (0-10 nm) remain spherical in shape upon irradiation.
- Completely molten NPs (10-35 nm) transform into nanorods and subsequently, for increasing fluence, into nanowires.
- Partially molten NPs (35-70 nm) transform into facetted NPs and subsequently, for increasing fluence, into nanowires.
- Very large NPs (>70 nm) do not melt and do not deform, or their deformation rate is very low.

The extension of each regime depends on both the NP composition and the irradiation parameters, such as the ion energy and the irradiation fluence.

Although, the papers of Dufour et al [87] and Rizza et al [69] represent a step forwards towards the comprehension of the ion-shaping mechanism, the fundamentals of the deformation process remain to be elucidated.

In this sense, an important insight has come from the work of Leino et al. published in 2014 [85]. Here, molecular dynamics simulations were used in conjunction with the inelastic (2D) thermal-spike model to include the electronic excitations of the swift heavy ions. The simulations predict that the elongation is caused by a dynamic crystal-liquid-crystal phase transition of the metal particle accompanied by a flow of the liquid phase into an under-dense track core in the silica matrix. The latter has been experimentally observed by Kluth et al. [89]. NPs whose minor axis is smaller than the diameter of the under-dense track expand more isotropically and are not elongated, which leads to a saturation of the width of the crystals. The results imply that both the formation of an under-dense track in the silica matrix and the shape-conserving crystallization of the molten cluster between ion impacts are necessary prerequisites to explain the elongation of metallic NPs by swift heavy-ion impacts.

6. Open problems, perspectives and challenges for the future

In this short historical overview, the evolution of the theoretical comprehension of two discoveries, the ion-hammering and the ion-shaping processes, has been traced from the first tentative steps to the state-of-the-art description of the phenomenon. I have tried to show how this cognitive process is not linear and that back and forth oscillations are a necessary part of the maturation process. Nowadays, both
phenomena have become versatile tools to shape the matter at the nanoscale. Indeed, both can be applied in nanofabrication methods allowing to control both the shape and the spatial orientation of dielectric nanocolloids and metallic NPs embedded within a dielectric matrix. However, they suffer from two main limitations: the radiation effect is size-dependent and the energy delivered by the impinging ions (either in the nuclear or electronic stopping regimes) scales with the length of the ion path. Thus, for more advanced applications a better control of the initial conditions is necessary. Those conditions include the spatial, size and depth distributions of the NPs. A possible issue is to replace the commonly used preparation technique, i.e. the ion-beam synthesis, by a preparation method based on colloidal chemistry or electron beam lithography. In this way a model system can be obtained that consists in a pattern of spatially mono-dispersed NPs confined to a unique plane. This model system can be used to obtain NP configurations that are barely realizable with the conventional bottom-up (i.e. the colloidal chemistry) or top-down (i.e. the electron beam lithography) nanofabrication techniques.

To conclude this review we discuss some possible applications:

The ion-hammering phenomenon is theoretically well described by the EFTA model [32]. The scope of possible practical applications remains however limited. The combination of techniques based on chemical synthesis and ion irradiation renders it possible to fabricate a new class of colloidal ellipsoids of continuously variable shapes with potential applications as photonic band-gap crystals [45], removable templates for the fabrication of macro-porous materials or masks for lithographic patterning [90].

Although the ion-hammering phenomenon is still waiting for a coherent description, the potential applications are instead very attractive. This is in part due to the plasmonic properties of the the ion-shaped NPs. As a spherical NP can be ion-shaped into the NW whose length can be as long as 400-500 nm, the corresponding plasmon resonances can range from the visible to the near-mid infrared. Thus, a broadband region of the optical spectrum can be explored. Hereafter two promising applications are shortly described:

A plasmon-based biosensor is based on the fact that, when a bio-molecular binding event occurs close to the surface of a noble metal nanostructure, the refractive index of the immediate environment surrounding the nanostructure becomes modified [91, 92]. A possible scheme for a sensor that would be able to detect low concentrations of molecules could be based on the idea that the tips of the ion-shaped NPs are situated either slightly below sample surface or touching it. This way, bio-molecular interactions at the surface of the nano-structures may lead directly to changes in the local refractive index; these changes can than be monitored via the wavelength shift of the LSPR peak.

Another potential application is in the field of plasmonic meta-materials [93–95]. Here tailor made nanocomposites - combinations of metallic and dielectric materials- can be designed such as to obtain optical properties that do not occur in nature. Hyperbolic meta-materials are a sub-class of plasmonic meta-materials displaying hyperbolic (or indefinite) dispersion [96]. This dispersion occurs when one of the principal components of the electric effective tensor has the opposite sign of the other two principal components. Such anisotropic structured materials exhibit distinctive properties, including a strong enhancement of spontaneous emission, a diverging density of states, a negative refraction index and enhanced super-lensing effects. Arrays of spatially oriented ion-shaped NPs may display such a hyperbolic behavior.

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