

Mechanical behaviour of nanoparticles: Elasticity and plastic deformation mechanisms

CELINE GERARD* and LAURENT PIZZAGALLI

Institut Pprime-CNRS UPR3346, Université de Poitiers-CNRS-ISAE-ENSMA,
F86961 Chasseneuil Futuroscope Cedex, France

*Corresponding author. E-mail: celine.gerard@cnsr.pprime.fr

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Abstract. Nano-objects often exhibit drastically different properties compared to their bulk counterpart, opening avenues for new applications in many fields, such as in advanced composite materials, nanomanufacturing, nanoelectromechanical systems etc. As such, related research topics have become increasingly prominent in recent years. In this review on the mechanical behaviour of nanoparticles, the main investigation approaches are first briefly presented. The main results in terms of elasticity and plastic deformation mechanisms are then reported and discussed.

Keywords. Nanoparticle; elasticity; plasticity; size effect; dislocation

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1. Introduction

In the framework of material sciences, a nano-object refers to any structure whose dimension is at least one dimension smaller than few hundreds of nanometers. Depending on whether one, two or three dimensions are nanometric, one may consider nanofilms, nanoplaets, nanowires, nanotubes, or nanoparticles and nanograins, the ‘nano’-character being definitely higher in the case of a nanoparticle or a nanograin (three nanometric dimensions).

Nano-objects often exhibit properties that can be drastically different from their macroscopic counterparts, giving rise to a wide variety of new applications, among which are applications in micro/nanoelectromechanical systems or advanced composite materials. Nanoparticles provide effective options for the surface modification of a device, or to improve the quality of nanomanufacturing processes. For these applications, understanding the mechanical properties and deformation mechanisms is of critical importance. As such, research topics on the mechanical properties of nanoparticles have become increasingly popular in recent years [1].

In fact, specific properties of nanoparticles are often attributed to the large surface-to-volume ratio. The main difference between macroscale materials and nanostructures lies in the significant role of surfaces (or interfaces) for the latter: surface atoms experience a different local environment in density, coordination number, electronic density, etc. Structural modifications usually occur due to relaxation or reconstruction, both mechanisms leading to surface energy minimization, but also adding an extra contribution to surface stress. Surfaces and interfaces can have a strong impact on mechanical properties of nanostructures. For instance, in the plastic regime deformation mechanisms can be different in bulk and in nanostructures. The dislocation starvation process has been proposed to explain the first stages of plastic deformation in nanostructures [2]. Also, surfaces act as nucleation centres for dislocations [3]. This is also true for boundaries between nanograins, which can either emit or absorb dislocations [4], or favour other deformation mechanisms like twinning for instance [5]. Furthermore, surface diffusion may play an important role in the plastic deformation of nanostructures.

In addition to surfaces/interfaces, the mechanical behaviour of nanostructures is influenced by reduced dimensions [6]. In fact, the number of pre-existing defects which can act as sources for plastic deformation mechanisms scales with the volume of the nanostructure. This source exhaustion is often proposed as an explanation for the hardening in small nanostructures, as reported in many cases [7].

2. Method

In terms of experimental approaches, different testing methods have been developed. First experimental investigations were driven thanks to X-ray diffraction analysis (XRD) [8], then, nanoindentation with atomic force microscopy (AFM) [9,10] and *in-situ* compression under transmission electron microscopy (TEM) [11,12]. Finally, a few more recent studies have tried to investigate the deformation of nanoparticle due to synchrotron radiation [13], or under scanning tunnelling microscope [14]. But, the smallest sizes are rarely investigated due to the difficulties in manipulating, isolating and testing the corresponding nanoparticles. Furthermore, the results obtained are still controversial, and the possibility of technical artifacts opened to debate [9]. For instance, the fact that the elastic moduli measured with AFM may depend on the indentation depth is still under debate [10].

Theoretical approaches are complementary to the experimental ones for several reasons. First of all, it allows for investigating the smallest sizes, precisely the one which are hardly attainable experimentally. Furthermore, the investigated system being described at the atomic level, it is possible to follow the trajectories of all the atoms in the systems, which provides particularly useful indications, especially regarding plasticity phenomena like the nucleation and glide of dislocations.

One can divide molecular modelling approaches in two main classes, depending on whether the electronic structure is calculated or not [15]. In the first case, which may be tight-binding or density functional theory, the electronic structure is calculated and taken into account into the modelling. However, even though this approach provides accurate and reliable results, only very small nanostructures can be handled. In the second case, the electronic structure is not calculated. Only the forces between the atoms are considered. These forces are most commonly computed from empirical interatomic potentials, which

are usually fitted on known bulk material properties. This approach has the advantage of allowing investigation of nanoparticle dimensions within the reach of experimental approaches. On the other hand, it may be difficult to handle multicomponent systems since the corresponding potentials may not be available for all atomic interactions.

3. Main results

3.1 Elasticity

The last decade gave rise to a rather rich literature regarding elasticity of nanoparticles. Hardness and elastic moduli of particles are often reported to differ from their bulk counterpart, and to exhibit a size dependence. But there is still no agreement on the values and mechanisms, even for same range of sizes. Thus, elastic moduli are mentioned to be size-independent for 20 nm-Ni nanoparticles [16] and 10 nm-Fe nanoparticles [17]. The bulk modulus of the nanoparticle is reported to be higher than that of the bulk material for 9 nm-sized γ -Fe₂O₃ [8], 30 nm-sized gold and 10 nm-sized silver nanoparticles [18]; and for 1.6 to 6.2 nm ZnS nanoparticles the modulus increases when the size decreases [19]. On the contrary, Clark *et al* [20] concluded that the bulk modulus decreases with the size for 3 to 7 nm γ -Fe₂O₃ nanoparticles. For polymer-based systems, the compressive moduli of the 200 nm-sized polystyrene nanoparticles were found to be slightly less than those of the corresponding bulk materials due to the presence of hydrated ionic functional groups [21]. But, Paik *et al* [22] found that the elastic modulus of polypropylene (PP) nanoparticles was higher than that of the bulk counterpart.

Several hypotheses have been suggested to explain this discrepancy. One concerns the definition of the nanoparticle size. First of all, Masadeh *et al* [23] mentioned that the measurement of the size itself may sensibly differ depending on the technique used. Then, the definition of the nanoparticle volume is uncertain because the boundaries of the object are not clearly defined at the nanoscale. This aspect is of particular importance as both theoretical and experimental approaches require a volume (or cross-section) definition to calculate the elastic moduli. For instance, *ab-initio* approaches usually calculate the Young modulus in the framework of small strains theory (staying in the harmonic regime), and by considering

$$E = \frac{1}{V_0} \left. \frac{\partial^2 U}{\partial \varepsilon^2} \right|_{\varepsilon=0}, \quad (1)$$

where E is the Young modulus, V_0 is the volume at equilibrium and U is the total energy of the system. Another way to proceed, is to calculate the bulk modulus by fitting the Birch–Murnaghan EoS [24,25], which also requires determination of volume. A common definition of the volume is the geometric one such as the volume of a sphere or a cube, respectively for a spherical nanoparticle or cubic nanoprecipitate. Volume can also be defined as the sum of spherical overlapping atomic radii, such as covalent or van der Waals radii, though Van der Waals radii represent π -bond systems very poorly [26]. Finally, Wagner *et al* [27] proposed a different approach, by considering a volume definition based on the electron density. The idea was to consider as the nano-object volume, a volume chosen such that the average electron density of the nano-object matches that of the parent bulk material.

The changes of the lattice strain and the bond energies of nanoparticles due to the compressive stress were also proposed as possible causes for the strengthening and weakening of the mechanical properties of nanoparticles [28]. Qi *et al* [29] investigated the effect of passivation on the size dependence of the Young modulus, by comparing the (non-passivated) ‘pristine’ ZnO nanostructure with the H-passivated one. An opposite size effect is reported for the two structures. Cherian *et al* [30], based on first-principles calculations, also suggested that size dependence of the bulk moduli of several semiconductor nanoclusters may be partly correlated with the interaction with the passivant. Finally, Fereidoon *et al* [31] mentioned that surface treatment may strongly influence the results obtained on elastic moduli, and even the stability of phases [32].

The comparison between the results from theoretical approaches and experimental ones is delicate because they are often not addressing the same range of sizes. Many experimental investigations rely on AFM or TEM approaches. The size of the nanoparticle ranges from 10 to 100 nm [33,34]. A few more recent studies tried to investigate the deformation of metallic nanoparticles thanks to synchrotron radiation [13], or covalent one under scanning tunnelling microscope [14], reaching 3–8 nm-sized nanoparticles. On the other hand, approaches based on *ab-initio* simulations rarely reached sizes bigger than 3 nm [30,35,36]. This technical limitation regarding the size is also important with regard to the fact that some authors noticed a threshold effect around 15 nm in terms of size effect for phase changes [33], volumic expansion or elastic moduli [37].

In addition to the issue of size, it is noteworthy that most experimental approaches do not allow the checking of the potential presence of defects in the structure before applying the loading, whereas theoretical investigations are carried out on perfect crystalline structures.

3.2 Plasticity

The literature regarding the plastic deformation of a single nanoparticle is more recent and more limited. Most available results mainly tackle the size effect mostly due to nanoindentation [38–40]. *In-situ* TEM nanoindentation experiments showed direct evidence of the presence of dislocations in metal nanoparticles during deformation [41]. Recently, molecular dynamic simulations aiming at reproducing the experimental loading allowed to better analyse the dislocation processes in nanoparticles [42–44].

Gerberich *et al* described the response of a silicon nanosphere (20–50 nm) to a cyclic loading applied on compression due to nanoindentation [11,45–47]. Two main observations have been reported. First, loading curves exhibit some steps (figure 1), as noticed on gold [48], on silicon and tungsten [49] and on copper thin films [50]. Then, Gerberich *et al* [45,46] reported an inverse plasticity phenomenon after several cycles of loading. Note that these works used an approach that does not allow to check either the presence of any defects pre-existing in the nanoparticle, or the crystallographic orientation of the nanoparticle compared to the loading axis. Mook *et al* [11] and Deneen *et al* [47] proceeded then to nanoindentation testings performed under TEM to apply the loading and proceed to observations simultaneously. A cyclic loading is applied as in [45,46], but inverse plasticity is no more reported.

More recently, Mordehai *et al* [44] performed nanoindentation tests and molecular dynamic simulations on single-crystal gold faceted nanoparticles. Nanoparticle strength

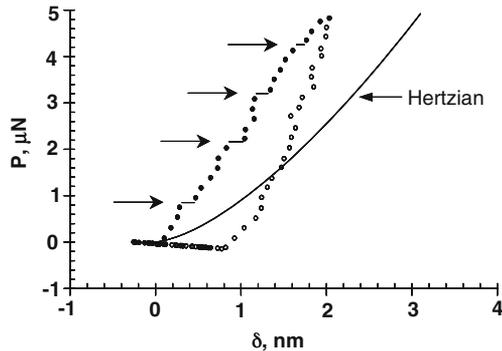


Figure 1. The load (P)–displacement (δ) curve of a 38.6 nm diameter silicon nanosphere showing staircase yielding events as noted by arrows. Solid points are loading while open points are unloading. An elastic Hertzian curve is also shown which underpredicts the experimental values (courtesy of Gerberich [45]).

is reported to be controlled by dislocation nucleation in the so-called dislocation starvation regime [51]. The observed dislocation activity under indentation is described as follows. Dislocations nucleate near the indenter, glide towards lateral particle facets, and produce surface steps as they are pushed along the facets. When dislocations exit the nanoparticle, point defects or small stacking fault tetrahedra may be left behind, but they disappear with the passage of next dislocation. It has to be noted that, contrary to the nanoindentation of the (001) surface of a bulk Au sample [52], no material pile-up (mesa formation) has been observed around the indenter. Furthermore, once the dislocation loop exits the particle, no dislocation debris is left behind within the particle, so that there is no phenomenon of dislocations interacting with debris, like in the bulk material. Similar observations have been reported in other materials like MgO nanoparticles (see [53]).

Bian and Wang [56] proposed another molecular dynamic study of deformation mechanisms, analysing in detail the very first steps of dislocation nucleations at the surface of a spherical nanoparticle of copper. The load–compression curve exhibits small abrupt load drops that are attributed to dislocation nucleations, in agreement with previous works by Mordehai.

The nucleation of dislocations from the surface is detailed as follows: Shockley partial dislocations nucleate from the contact edge. Then nucleated dislocation loops expand into four slip systems and the intersection of dislocation loops forms a pyramid hillock structure. On further compression, the load is transmitted through this pyramid hillock, its tip being a stress concentrator. As the compression goes on, a second bigger pyramid hillock is formed outside the small one, and new partial dislocations nucleate from the edge of this new hillock, being pinned at the tip of the hillock and at the surface of the nanoparticle. Dislocations then migrate towards the centre of the nanoparticle.

After this first stage of plasticity initiation, Bian and Wang suggested that with increasing compression, the deformation mechanism shifts to a deformation twinning process, which becomes the main hardening mechanism.

Nucleation of dislocations at the surface has also been reported in the compression of Ni_3Al nanocubes mainly due to molecular dynamic simulations [55]. The nucleation of the first partial Shockley dislocation is reported from the edge of the cube, giving rise

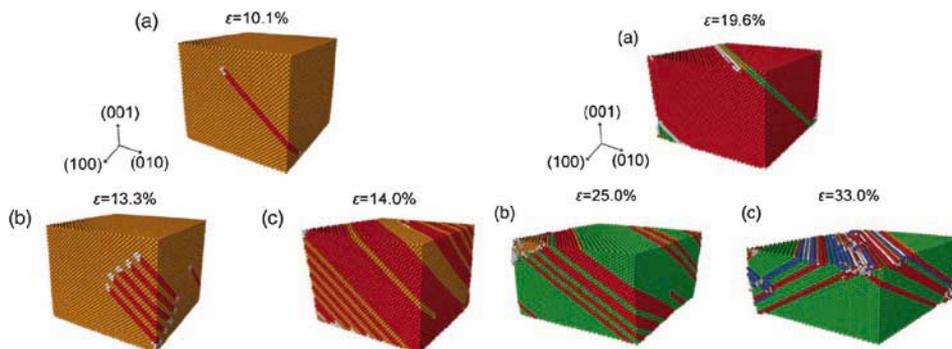


Figure 2. On the left: Dislocation activity during Stage 1 of deformation (ϵ). Atoms coloured in orange and red represent the perfect L12 structure and complex stacking faults environment. Atoms in white refer to other defects, e.g. dislocation cores. For the sake of clarity, surface atoms have been removed. On the right: Dislocation activity during Stage 2(a), (b) and Stage 3(c). Atoms coloured in green refer to the pseudotwin structure, whereas atoms coloured in blue belong to an antiphase boundary environment. The coordinate system refers to the original orientation of the sample (courtesy of Amodeo [55]).

to the formation of a pseudotwin structure which further deforms by Shockley partial dislocations (figure 2).

At last, a part of the literature on the plasticity of nanoparticles is specifically dedicated to twinned nanoparticles [54]. Internal boundaries, such as twin boundaries, have strong influence on the mechanical behaviour of nanomaterials [57]. Deng and Sansoz [58] reported that the yield stress of gold nanopillars is governed by the synergistic effects of sample diameter and spacing of twin boundaries. Li *et al* [59] also described a softening mechanism controlled by dislocation nucleation when the thickness of the spacing of twin boundaries is below a critical thickness.

4. Conclusion

Results presently available on the elasticity of nanoparticles, as well as on plastic deformation mechanisms, are still controversial. Nevertheless, perspectives are really promising. Impressive recent experimental developments allow one to better understand and discuss the potential artifacts, to handle and analyse the properties of smaller nanoparticles, and finally to get better comprehension and comparison with theoretical approaches, the size difference between systems investigated in experiment and simulations being now much reduced.

Regarding theoretical approaches, on the one hand, DFT approaches are progressively opened to bigger systems because of the increase of computational power and the development of new class of approaches [60,61]. On the other hand, classical molecular dynamic methods still suffer from their dependance to the reliability of the interatomic potentials. But the results obtained may either be confirmed due to modelling performed with other potentials, or compared to *ab-initio* simulations on smaller systems [62]. The

time-scale issue remains probably the most critical issue in molecular dynamics modelling simulations. Thus, a standard time-step in these simulations is about 1 fs. Then, molecular dynamics of large systems are performed at the deformation rate of 10^{-7}s^{-1} at the best, whereas experimental investigations are usually driven at rates in the range of 10^{-4} – 10^{-1}s^{-1} . Such a large difference can introduce many bias in the analysis of the plastic regime.

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