



HAL
open science

Tuning Elastic Properties of Metallic Nanoparticles by Shape Controlling: From Atomistic to Continuous Models

Matteo Erbi, Hakim Amara, Riccardo Gatti

► **To cite this version:**

Matteo Erbi, Hakim Amara, Riccardo Gatti. Tuning Elastic Properties of Metallic Nanoparticles by Shape Controlling: From Atomistic to Continuous Models. 2023. hal-04025590v1

HAL Id: hal-04025590

<https://hal.science/hal-04025590v1>

Preprint submitted on 12 Mar 2023 (v1), last revised 28 Feb 2024 (v2)

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Tuning Elastic Properties of Metallic Nanoparticles by Shape Controlling: From Atomistic to Continuous Models

Matteo Erbi¹, Hakim Amara,^{1,2,*} and Riccardo Gatti^{1,†}

¹*Laboratoire d'Etude des Microstructures, ONERA-CNRS, UMR104,
Université Paris-Saclay, BP 72, Châtillon Cedex, 92322, France*

²*Université de Paris, Laboratoire Matériaux et Phénomènes Quantiques (MPQ), F-75013, Paris, France*

(Dated: March 12, 2023)

Understanding and mastering the mechanical properties of metallic nanoparticles is crucial for their use in a wide range of applications. In this context, we use atomic-scale (Molecular Dynamics) and continuous (Finite Elements) calculations to investigate in details gold nanoparticles under deformation. By combining these two approaches, we show that the elastic properties of such nano-objects are driven by their size but, above all, by their shape. This outcome was achieved by introducing a descriptor in the analysis of our results enabling to distinguish among the different nanoparticle shapes studied in the present work. In addition, other transition-metal nanoparticles have been considered (copper and platinum) using the aforementioned approach. The same strong dependence of the elastic properties with the shape was revealed, thus highlighting the universal character of our achievements.

I. INTRODUCTION

Metallic nanoparticles (NPs) are fascinating objects with unique properties that differ significantly from their bulk counterparts due to their high surface area to volume ratio. Consequently, many nanoparticle-based technology approaches are foreseen in different fields such as catalysis, medical or optics applications¹. However, NPs can be subjected to mechanical constraints, whatever their domain of use, leading to structural modifications or even irreversible changes that can drastically affect their intended application². In this context, understanding the structural modifications of small-sized metallic NPs induced by elastic deformations is crucial. Yet, this must be addressed by taking into account that the physics at the nanoscale is particular, especially for NPs whose diameter is smaller than around 10 nm. Typical examples include the dependence on the size of the melting temperature³ or surface energy⁴ in case of pure NPs as well as the order-disorder transition temperature for bimetallic nanoalloys⁵.

Regarding the mechanical properties of metallic materials, an increase in strength is commonly observed when the characteristic microstructural length scale is reduced^{6,7}. This mainly concerns systems with a minimal size of the order of a hundred nanometers where three regimes have been highlighted. In case of plastic deformations: the nanometer regime (~ 100 nm and below), an intermediate regime (between 100 nm and approximately $1 \mu\text{m}$), and a bulk-like regime⁸. However, the study of the mechanical properties of NPs of a few nanometers is much more complex. From an experimental point of view, in situ Transmission Electron Microscopy nanoindentation is a suitable tool for addressing this issue as it provides real-time monitoring of the deformation⁹⁻¹². Although powerful, these techniques are rather cumbersome limiting their use for systematic studies and often require a numerical support. Indeed, different theoretical

models based on analytical calculations have been proposed to characterize the structural properties of NPs under elastic deformation^{13,14}. Despite being attractive on a purely formal point of view, these models are not really adapted to NPs since they do not take explicitly into account their finite shape i.e. the prevalent role of the surfaces, the vertices and the edges that lead to specific structural properties. More specifically, the nature of the different surface sites should not be ignored, especially since as the size decreases, the contribution of facets, which are predominant for large dimensions, decreases in favour of vertices and edges. In order to obtain an atomic-scale view, in which the surface sites are clearly treated, computer simulations are generally considered very useful tools to investigate the mechanical properties of NPs. Among the possible techniques¹⁵⁻¹⁷, molecular dynamics (MD) simulations are the most widespread as they enable to precisely characterize the elastic and plastic mechanisms of NPs under deformation whose sizes are close to the experiments¹⁸⁻²¹.

Surprisingly, there is no exhaustive study regarding the effects of size and shape on the elastic properties of NPs. Most of the previously published works concerned uniaxial compression along a specific orientation for fairly large NPs (above 10 nm) whose shape is rarely observed (cubic, spherical, truncated spherical, ...). However, these studies are incomplete to better understand and predict the properties of metallic NPs under elastic deformation. To address this issue, different sizes (ranging from 4 to 25 nm) and shapes (truncated-cube, cuboctahedra and Wulff) of NPs, close to those experimentally observed, are investigated using complementary approaches, i.e. MD and Finite elements (FE). Thanks to these approaches, the elastic deformations during nanoindentation along the (111) and (001) facets are analyzed. NPs of three different metal (Au,Cu,Pt) will be considered to draw conclusions as general as possible.

II. METHODOLOGY

A. Nanoparticles

Nanoparticles are systems of finite size that cannot be considered as simple fragments of a crystalline solid thus adopting structural arrangements that differ from the those of bulk²². In this context, Wulff established a well known rule to describe the equilibrium forms of free polyhedral crystals²³ that has been extended to supported systems²⁴. Among all the possible identified structures, we focus our study on morphologies that are observed experimentally, i.e. truncated cube, cuboctahedral and Wulff shapes (see Fig. 1a). Note that the particular case of icosahedral NPs, common for small aggregates, is not considered here since the icosahedral arrangement is unstable for particles larger than 4-5 nanometers. As seen

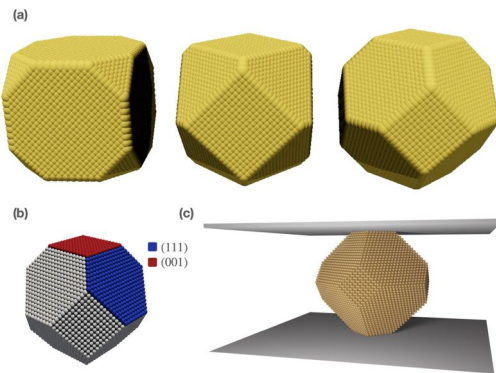


FIG. 1. (a) Truncated cube, cuboctahedral and Wulff structures (b) (001) and (111) facets present at the surface of the NPs. (c) Schematic representation of the indentation of the NP where plane indenters are imposed.

in Fig. 1b, the shapes addressed in the present work are based on the face-centered cubic (FCC) lattice, leading to the presence of outer facets of (111) and (001) orientations. To highlight size effects, NPs with diameters (d) ranging from 4 to 25 nm range (around 10^2 to 10^6 atoms, respectively) are taken into account. More precisely, d is defined as following:

$$d = 2 \cdot \left(\frac{3V_{eff}}{4\pi} \right)^{1/3}$$

with V_{eff} being the effective volume of a sphere equal to the exact volume of the considered nanoparticle. The size is strictly related to the number of atoms of the NP and allows us a more methodical study of different shapes at same size. Lastly, different transition metal elements (Au, Cu and Pt) are considered to generalize as much as possible our conclusions on the elastic properties.

In the following, the NPs deformation procedure using plane indenters (see Fig. 1c) is detailed from atomistic

and continuous approaches.

B. Atomistic calculations - Molecular Dynamics

The MD simulations are carried out using the open source Large-scale Atomic/Molecular Massively Parallel Simulators (LAMMPS) package²⁵. To study nanoindentation of NPs, we apply the methodology successfully adopted in Ref. 18,20,21,26. In this study, we explore Au, Cu and Pt NPs at the atomic level by using a specific N -body inter-atomic potential derived from the second moment approximation of the tight-binding scheme (TB-SMA).^{27,28} The accuracy of TB-SMA models depends

	Lattice parameter	Cohesive energy	B	C'	C ₄₄
SMA (Au)	4.08	-3.81	165	16.0	44.5
Experiments (Au)	4.08	-3.81	166	16.0	45.0
SMA (Cu)	3.63	-3.39	154	23.0	54.5
Experiments (Cu)	3.62	-3.50	142	24.0	75.0
SMA (Pt)	3.98	-5.53	220	35.0	100
Experiments (Pt)	3.92	-5.86	288	52.0	77.0

TABLE I. Comparison of our TB-SMA model with experimental data: lattice parameters (\AA)²⁹ cohesive energies (eV/at),²⁹ bulk modulus and elastic moduli (GPa)³⁰ for Au, Cu and Pt in a FCC structure.

critically on the validity of the database to which the parameters of the potentials are fitted. Here, we summarize only the crucial points of the TB-SMA potential and refer the reader to the Ref. 31-33 for more details. In particular, the parameters of the TB-SMA potentials are obtained by fitting on the experimental values of the lattice parameter, the cohesive energy, and the elastic moduli (bulk modulus and the two shear moduli) for a FCC structure as seen in Table I. Such approach is then perfectly adapted to deal with large systems (~ 1000 to 10000 atoms) and to reproduce the main energetic properties of transition and noble metals. Using this approach, it is interesting to note that we are able to distinguish the different surface sites, i.e. vertices, edges and facets. Obviously, with increasing size the contribution of the vertices and edges, which are preponderant for small sizes, decreases in favour of the facets.

To model NPs compression via the nanoindentation procedure, the Verlet algorithm with a timestep of 1 fs combined with the Nose-Hoover thermostat at 0.01 K is used for the integration of equations of motion in the NVT canonical ensemble. The size of the supercell in the all directions is large enough to avoid artefacts due to interaction between images caused by periodic boundary conditions. Prior to compression, the NPs are relaxed at 0.01 K until convergence of the total energy (a relative error of $\epsilon_r = 10^{-5}$ has been considered) to get the equilibrium configuration. As seen in Fig. 1c, the indenter and substrate are simulated with two rigid infinite planes, parallel to the (001) or (111) facet of the NP. The effect

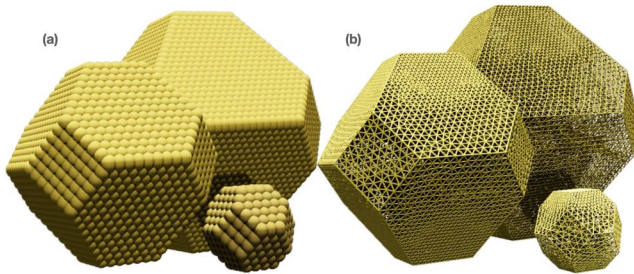


FIG. 2. (a) NP of different sizes revealing the surface sites i.e. vertices, edges, (001) and (111) facets. (b) Typical meshes used in FE calculations where the mesh is more refined on the surface sites.

of an indenter is implemented by introducing in the MD simulation fictitious repulsive forces to be integrated. In the present simulations, we used a quadratic repulsive force: $F(r) = -K(r - R)^2$ with $K = 1000 \text{ eV} \cdot \text{\AA}^{-3}$ and R corresponding to the indenter position in agreement with previous works^{18,26}. During the simulation we use two moving indenters (bottom and top plane in Fig. 1c), each of them applying a strain rate of about $3 \cdot 10^7 \text{ s}^{-1}$ which corresponds to an indenter velocity of roughly 0.06 to $0.6 \text{ m} \cdot \text{s}^{-1}$. As stated in the Ref.¹⁸, the velocity has to be less than the speed of sound in the considered material to allow the atoms to reorganise before a new displacement is imposed.

C. Continuous modeling - Finite Element

In our continuous approach, indentation has been modeled using FE method assuming a linear elastic material. Within this framework, the stress acting on a system is directly proportional to its deformation and can be expressed by the Hooke's law so that $\sigma = E \cdot \epsilon$, where σ and ϵ are, respectively, the second order stress and strain tensor and E is the elastic constant third order tensor. In FE calculations, the linear elastic problem can be solved by computing the mechanical equilibrium, using the Hooke's law, in a discrete domain (here the NP), imposing the proper boundary conditions. In this study, we used an open source FE code named FEniCS³⁴ where second order partial differential equations and a variational approach are adapted to handle a linear elastic problem. The continuous domain is discretised in a three dimensional mesh, where the solution, the displacement field, is computed at the nodes (see Fig. 2a). It is worth noting that the generation of an accurate mesh is a fundamental step for obtaining results comparable with atomistic simulations. With this purpose, the meshes are refined until the results converge by means of a linear iterative solver. Similar to atomic-scale MD studies, a displacement is applied as a boundary conditions, to mimic a rigid indenter, at the top surface of the NP while the bottom surface is fixed. A non uniform mesh is generated with more points

on the regions near the contact surfaces (i.e. the top and the bottom surfaces), where more heterogeneous stress field is expected, as seen in Fig. 2a. Moreover, the resolution of the continuous equations implies to consider the proper elastic constants of the studied system. In this case, the cubic symmetry of the bulk FCC crystal imposes that only three independent elastic constants are expected (c_{11} , c_{12} and c_{44}). To ensure consistency with the MD simulations, the values considered here are those calculated at the atomic scale from the TB-SMA potentials (see Table I), using anisotropic formulation of the Hooke's law.

III. GOLD NANOPARTICLES

The elastic properties of gold NPs calculated by the two previous approaches are now compared macroscopically and locally. First, the true stress true strain curves are investigated to identify the overall mechanical properties. In a second step, the stress maps are calculated to have a local insight of the elastic deformations of NPs.

A. Stress - strain curves

We first examine the mechanical response of NPs under deformation by means of stress-strain curves. Figure 3 shows a typical example of this analysis for a given size and shape of Au NP. Regarding the MD simulations,

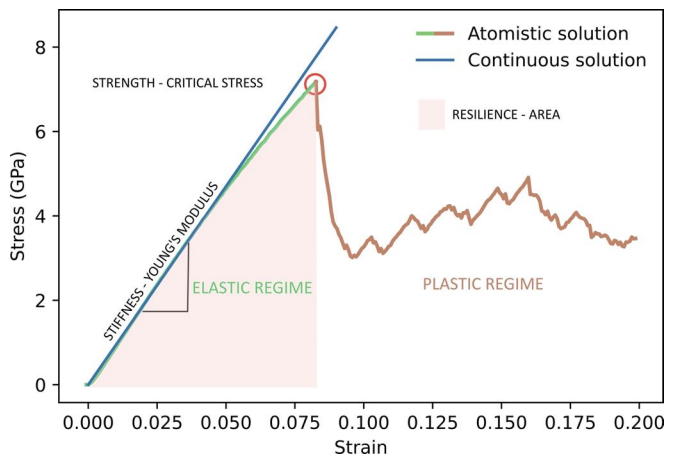


FIG. 3. Typical stress-strain curve. Comparison between the continuous solution and the atomistic one.

the characteristics common to all the calculated results show two main regimes. During the very early stages of the loading, the stress variation is initially linear corresponding to an elastic regime. Then, the stress has a peak value, which defines the yield point corresponding to the largest stress that the NP can handle. Above this point, a meaningful reduction of the stress is noticed, which indicates that the plastic deformation has been

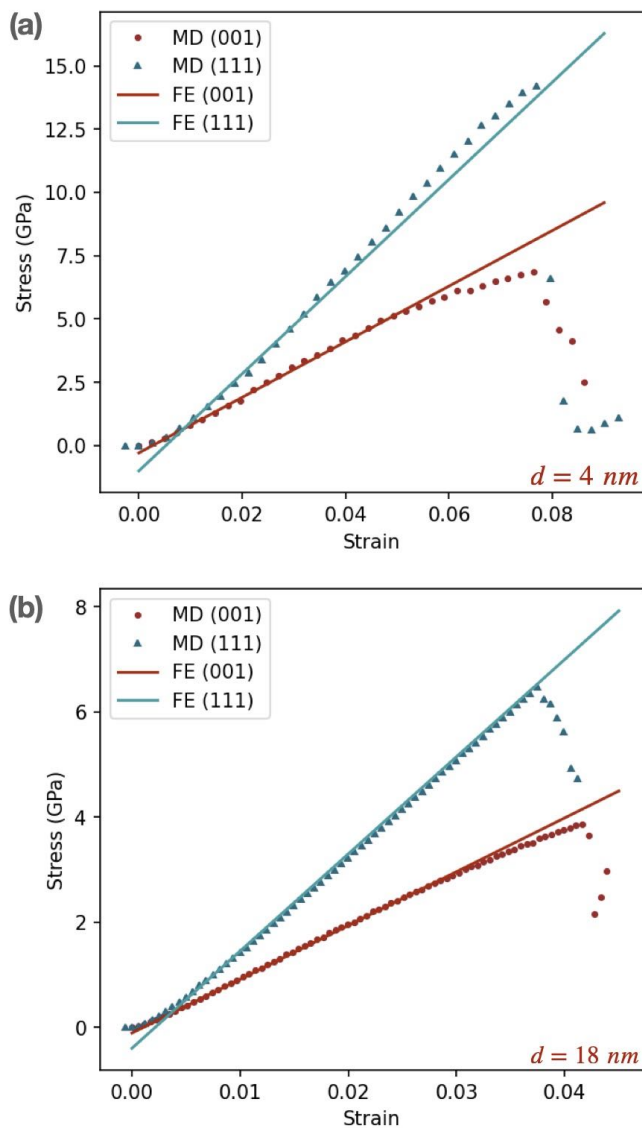


FIG. 4. Compressive stress as a function of strain of Wulff-shaped NP of different sizes: (a) 4 nm and (b) 18 nm. Comparison between FE and MD calculations with indentation on (001) and (111) facets.

activated. More precisely, the emergence of plasticity in NPs results from the heterogeneous nucleation of dislocations from the contact surfaces^{18,20,26}. In the case of FE calculations, it can be noticed that only the elastic part is probed since FE formulation is based on the Hooke's law (see Fig. 3). By focusing on the initial deformation process, elastic properties can be extracted. To this purpose, it is therefore necessary to determine a macroscopic quantity to analyze the global behavior of the NP under elastic deformation. As done in previous works^{18,20,26}, we define an average value named the true stress compression equal to the ratio between the force applied by the indenter and the surface contact area (A). At the atomic level, A is not a well defined concept. As a result, many

approaches exist but all of them follow the same recipe³⁵. Firstly, we need to identify the atoms in contact with the indenter. In our case, all atoms at a distance lower than 1 Å from the considered indenter. It is noteworthy that no significant differences are reported by slightly varying this parameter. Then, A is determined by computing a Delaunay triangulation of the points defined by the coordinates of atom centers at each indenter displacement. Consequently, the true stress strain in MD calculations can be obtained, since the indenter position is a known quantity. From FE calculations, the true strain stress is an easy accessible data. The only difficulty lays in the force calculation which is not straightforward and this has to be done by computing the reaction force generated by the NP on the surface where the displacement is imposed.

To highlight elastic size effect, the mechanical responses of NPs of different diameters d are considered. Figure 4 depicts the stress-strain curves of a small ($d = 4$ nm) and larger ($d = 18$ nm) Wulff NPs nanoindented with plane indenter on the (001) and (111) facets. In the case of MD simulations, deviation from linearity in the elastic regime is observed for the small NP as seen in Fig. 4a. This trend is found for all particles below 5-6 nm in agreement with previous calculations^{19,20,36} where the influence of surfaces on the mechanical behavior inside small NPs is emphasized. For the larger NPs, a linear trend is observed in the elastic regime until plastic deformation, whatever the facet considered (see Fig. 4b). Obviously, finite elements fail to reproduce the deviation from the linear regime observed for small particles (intrinsically, no deviation from linearity can be observed). In contrast, the agreement between MD and finite elements for larger particles is quite remarkable proving that a linear elasticity framework can be used to model mechanical properties at the nanoscale. Besides, plastic behaviour can be noticed in MD results: the critical yield stress (σ_C) can be extracted since it corresponds to the maximum value before a drop, corresponding to dislocation nucleation events. As already discussed in¹⁸, increasing the NPs size implies a reduction in the critical stress according to the following equation: $\sigma_C = \alpha \cdot d^{-B}$ where α and B are fitted values. We found that for the (001) and (111) facets, B is equal to 0.461 and 0.523, respectively. The second value is in good agreement with the 0.530 ± 0.013 found by Feruz *et al.* for Wulff structure¹⁹. Note that so far only (111) facets were considered in the literature. Hence, we show here that this size-dependent strength can also be extended to (001) facets. A more detailed analysis on the onset of plasticity in FCC metal NPs will be presented in a future work.

To better analyse the elastic behaviour of NPs, effective Young modulus (E_{eff} i.e. $\Delta\sigma/\Delta\epsilon$) are extracted from the stress-strain curves for all NP sizes. The results for indentation on both facets are presented in Fig. 5. Above 5 nm, it can be observed that MD and FE calculations provide very similar results with extremely low errors. This is not so surprising for large particles since

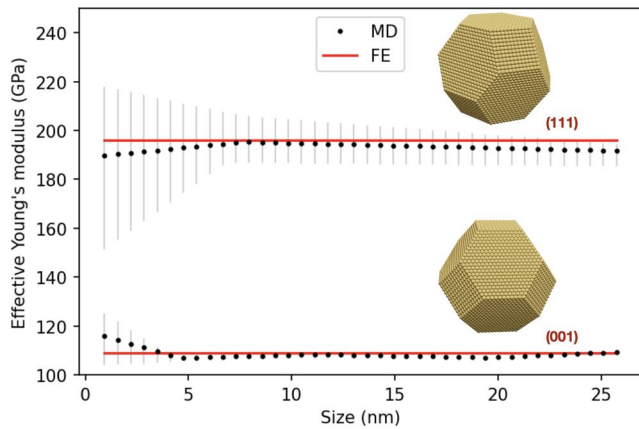


FIG. 5. Effective Young modulus as a function of the size for Wulff-shaped gold nanoparticles. Comparison between continuous and atomistic calculations with indentation on (001) and (111) facets.

finite elements reproduce the elastic domain very well as revealed in Fig. 4b. For smaller particles, it is clear that the deviation from linearity already discussed in Fig. 4b is not reproduced with FE calculations. Furthermore, the parameter E_{eff} is also difficult to be defined for small Nps. For this reason an error bar is introduced that consider different possible linear fit for the elastic part of a given nanoparticle stress-strain curve. Due to the deviation from linearity using MD calculations, E_{eff} values for small NP have larger error bars than the large ones. Nevertheless, when comparing results from FE and MD calculations even for small NPs, the global slope of the curve is rather correct enabling to get effective Young modulus values in agreement between both approaches. As the size of the nanoparticles increase the value of the effective Young modulus for both (001) and (111) indentation converges to a plateau³⁷, while the $E_{eff}^{(111)}$ is larger than $E_{eff}^{(001)}$, as expected in anisotropic media ($E^{(111)} > E^{(001)}$ for bulk), the value of the plateau depends on the shape of the NP, as it will be highlighted in section IV.

B. Stress Map

In the previous section we discussed the mechanical properties of NPs from a global point view via the stress-strain curve. Here we want to analyse local elastic properties, by the means of stress maps, comparing MD and FE outcomes. In order to highlight the similarities between the two simulation approaches, the surface contraction peculiar to transition metals³⁸ reproduced in atomistic simulations is neglected. Therefore, we took as reference state (no stress in the NP) the atomic positions after relaxation steps. Concerning the FE approach, the displacement fields is computed at each node of the mesh for an imposed indentation depth.

From this displacement field, the stress is computed and by interpolation is projected on the mesh nodes. Obviously, the mesh size is crucial to achieve robust results. Therefore, the mesh was refined until the convergence of stress values. In Fig. 6, the stress distributions obtained from MD and FE calculations are presented in case of small (6 nm) and large (20 nm) NPs. This corresponds to nanoindentations on a (001) facet (on the left) and on a (111) facet (on the right) at 2.5% strain, in a linear regime. Concerning the (001) indentation, stress is concentrated in two conical regions, close to the plane indenters. For all the components of the stress field, the maximum value is observed at the corners as already discussed in^{18,26}. If we observe the ZZ component, the stress field is negative due to the compression imposed by the applied loading and we can notice that with the presence of free surfaces, the stress decrease rapidly moving from the top or the bottom surface to the center of the nanoparticle. Remarkably, FE and MD calculations give very similar results for both NP sizes: the values for stress tensor components computed with the two approaches are very close, with differences less than 5 %. Such common features were also obtained for a nano-indentation on the (111) facets, for any particle sizes and shapes. The only dissimilarity with (001) indentation is that the stress distribution is more homogeneous in the z direction. This is because the plane indenters has a larger contact area, indeed for Wulff structures (111) surfaces are wider than (001).

Studying nanoindentation of a Wulff Au nanoparticle, we have shown both finite elements and atomistic simulations are perfectly adapted to capture the elastic properties on both a local (stress map) and a global (stress-strain curve) viewpoint. The agreement between the two different approaches is good, notably for NPs with diameter above 5 nm. It is then tempting to think that such features are mainly driven by the shape of the particle and not by atomistic features such as the presence of specific surface sites (edges, vertices > surface arrangement).

IV. SHAPE EFFECTS

To highlight shape effect on the elastic properties, the mechanical responses of different Au NPs are considered. In Fig. 7, the calculated effective Young modulus for various NP shape as a function of size are presented. First, we can notice that the general observation of section III A for Wulff shape NPs are valid also for truncated-octahedra and truncated cubes: for NPs larger than 5 nm the value of E_{eff} converge to a plateau and no visible size effect is observed. In the case of the truncated-octahedron, there is a stronger variation of the E_{eff} values for small size NPs (< 5 nm) in MD calculations, from ~ 200 to ~ 175 GPa. For larger particles, E_{eff} reaches a constant value around 175 GPa. Again, FE approach is not able to reproduce such a size depen-

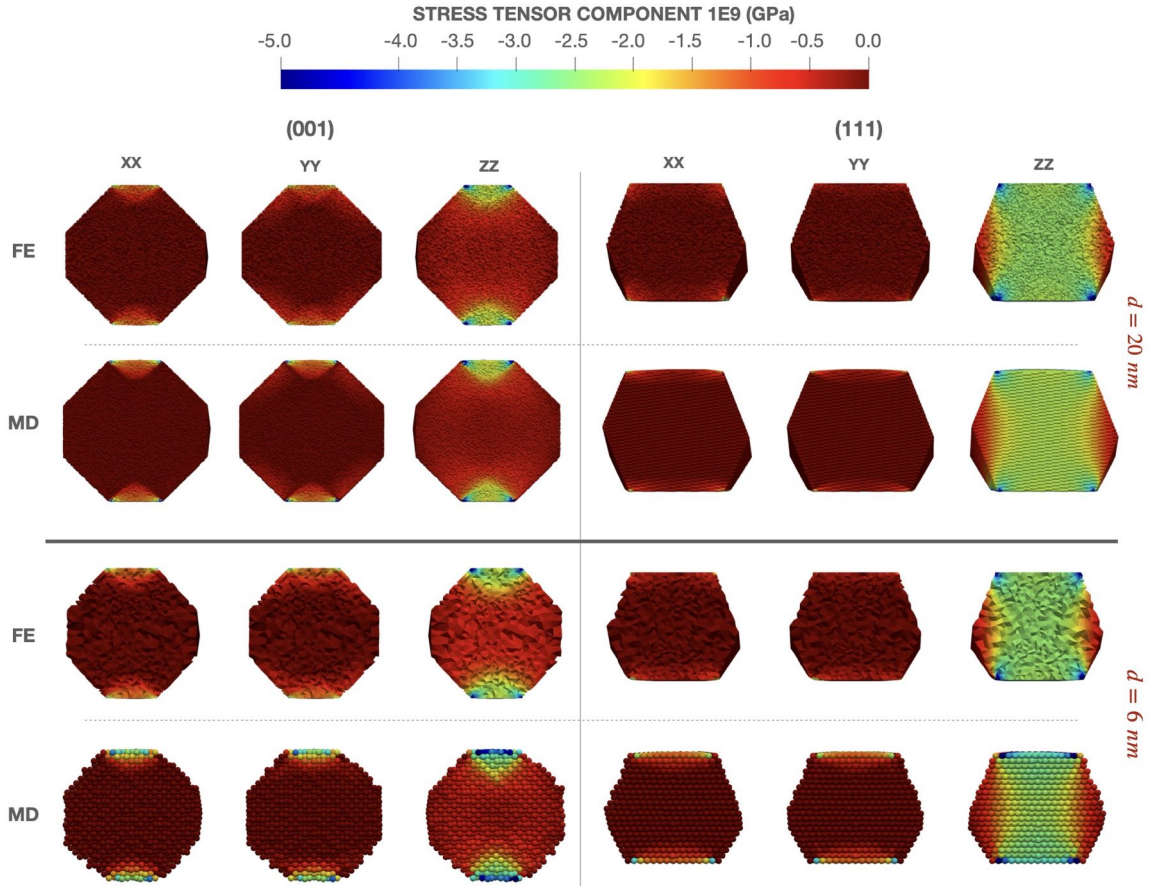


FIG. 6. Stress maps calculated with MD and FE approaches for Wulff-shaped gold nanoparticles of (top) 20 nm and (bottom) 6 nm diameter NPs and by imposing nanoindentation on (001) and (111) facets.

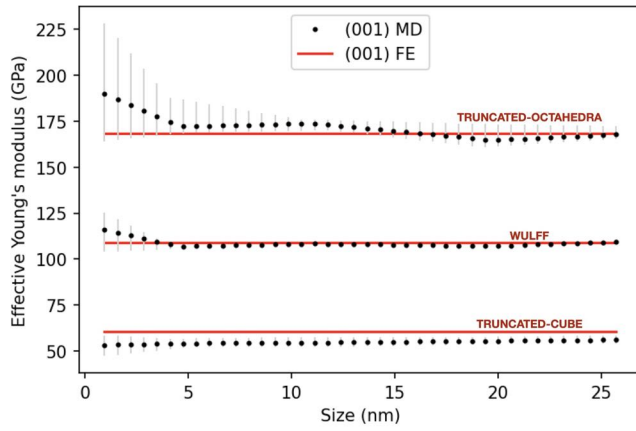


FIG. 7. Effective Young modulus as a function of the size for gold nanoparticles with different shapes. Comparison between continuous and atomistic calculations with indentation on (001) facets.

dence, suggesting that the role of specific surface sites cannot be neglected in small NPs. On the other hand,

the agreement between FE and MD for larger particles is quite remarkable. More interestingly, a strong shape effect is observed in Fig. 7, where the E_{eff} plateau value changes depending on the shape. Indeed, wide differences are obtained ranging from ~ 50 GPa (truncated cube) to ~ 175 GPa (truncated octahedra). To further emphasise the observed shape effect, we introduce a descriptor G to classify the shape of the NPs with respect to the ratio between (001) and (111) facets:

$$G = \frac{8 \cdot A_{(111)}}{6 \cdot A_{(001)}}, \quad (1)$$

where $A_{(111)}$ and $A_{(001)}$ are the area of the (111) and (001) facets, respectively. The factors 8 and 6 correspond to the number of free surfaces. From this descriptor, it is then possible to clearly distinguish the different shapes considered in our study (see Fig. 8). Moreover, two limiting cases are also identified: the cube and the octahedron with $G = 0$ and $G = \infty$, respectively. At a given NP size (here 20 nm), Fig. 8b depicts the variation of the effective Young modulus for different shapes. Again, a very good agreement is found between FE and MD calculations. A maximum difference of about

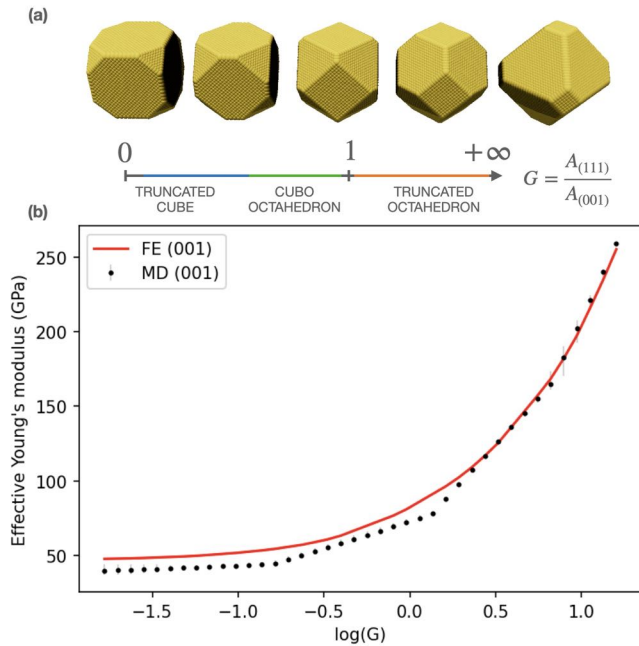


FIG. 8. (a) The descriptor G introduced to discriminate the different shapes of NP. (b) Effective Young modulus as a function of the shape for gold nanoparticles. Results correspond to an indentation on (001) facets for a 20 nm diameter NP.

4% is revealed and corresponds to the truncated-cube shapes. Such deviation is due to the non linearity of the stress-strain curves in approaching a cubic system (for cubes a very large elastic deformation of about 10% is observed before the plastic onset, so non-linear behaviour is observed in MD simulations). Very interestingly, a significant variation of the order of 200 GPa can be observed between the two limiting shapes. This considerable effect illustrates that the influence of the NP shapes on the elastic properties is huge for a 20 nm nanoparticle.

To generalize, E_{eff} computed values in function of different shapes (G descriptor) and of NP sizes ranging from 4 to 25 nm is presented in Fig. 9 in a bi-dimensional map for MD simulations (left panel) for FE simulation (right panel). On one hand, no size effect is identified (above 5nm). Indeed, the variation of the E_{eff} with the size of the NP is negligible, never exceeding few GPa for a given NP shape. On the other hand, significant variation of the effective young's modulus are remarked with NP shape. From truncated-cube to truncated-octahedron structures, a difference of about 150 GPa on the effective young's modulus is reported. Here again, we can note that the agreement between the atomistic and finite element calculations is remarkable whatever the shape and size of the NP.

All the results presented so far concern nano-indentation on (001) facets. Meanwhile, the same conclusions have been achieved by investigating the defor-

mation mechanisms on (111) facets (see Sec. I. of the Supplemental Materials). It is important to stress that our analysis show that the shape, not the size, of the gold NPs has a wide impact on its macroscopic measured elastic properties.

V. GENERALIZATION TO OTHER SYSTEMS

In the previous sections, the investigations were focused on gold NPs. To generalize our conclusions, the analysis of the elastic properties of NPs has been extended to other metals, such as Cu and Pt. The calculated effective Young modulus are presented in Fig. 10 for different sizes and shapes in case of Au, Co and Pt by imposing nanoindentation on (001) facets. More results can be found in Sec. II and III of the Supplemental Materials for Cu and Pt, respectively. Whatever the material considered, we first see that the finite elements reproduce the atomistic calculations for NP sizes exceeding 5 nm. For smaller diameters, the differences are fairly notable for Cu and Pt (< 40 GPa) but minor for Au NPs (< 15 GPa). Beyond this limit, no size effect is reported with a constant value for E_{eff} . More interestingly, it can be seen that the elastic properties vary strongly with the shape of the particle. As shown in Fig. 10b, significant variations of the elastic properties are highlighted whatever the transition metals. Indeed, E_{eff} varies of hundreds of GPa moving from small value to large value of G . For the nanoindentation of the (111) facet, the same trend is observed, and the same conclusions can be drawn for Cu and Pt, as seen in Sec. IV and V of the Supplemental Materials, respectively.

VI. CONCLUSION

In this work, we have presented an extensive study on elastic deformations of metallic nanoparticles with different shapes and sizes, imposing a mechanical loading via nano-indentation on (001) and (111) facets. By combining atomistic and continuous calculations, no size effect is revealed for nanoparticles with a diameter of larger than 5 nm. More interestingly, we have shown that the elastic properties of NPs are highly driven by the shape of the particle, finding that the ratio between (111) and (001) is a suitable descriptor to address this shape dependence. These results were achieved by nanoindenting Au, Cu and Pt NPs, showing that our conclusion can be applied to different transition metal nanoparticles. Thanks to this study, we can state that controlling the shape of nanoparticles can be viable path for the engineering of a new class of nano-objects with unique and targeted mechanical properties.

SUPPLEMENTAL MATERIAL :

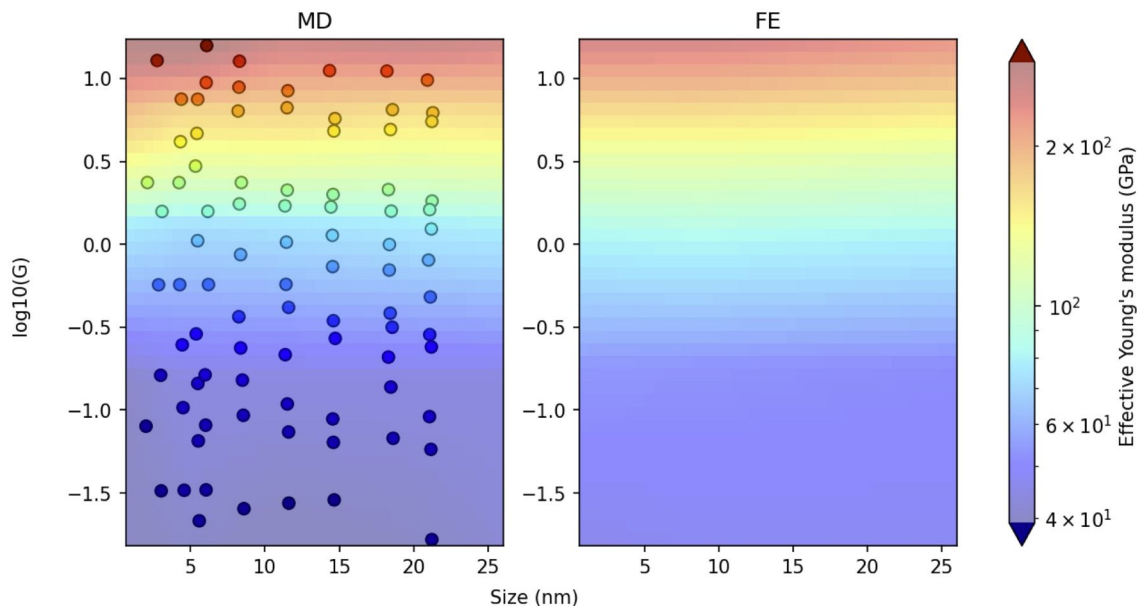


FIG. 9. Effective Young modulus as a function of the size and shapes for gold nanoparticles plotted on a bi-dimensional map. Comparison between atomistic (on the left) and continuous (on the right) calculations for an indentation on (001) facets.

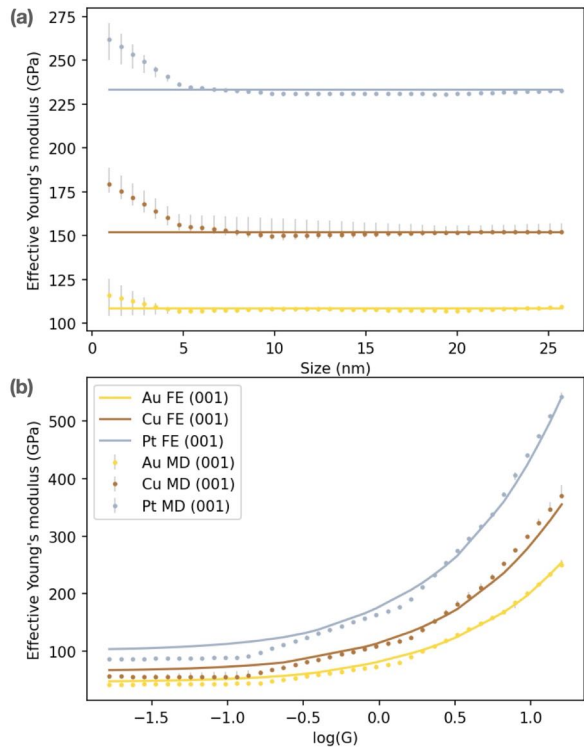


FIG. 10. (a) Effective Young modulus as a function of the size for Au, Cu and Pt Wulff nanoparticles. (b) Effective Young modulus as a function of the shape for Au, Cu and Pt nanoparticles of 20 nm. Comparison between continuous and atomistic calculations with indentation on (001) facets.

TUNING ELASTIC PROPERTIES OF METALLIC NANOPARTICLES BY SHAPE CONTROLLING: FROM ATOMISTIC TO CONTINUOUS MODELS

Sec. I. Elastic properties of Au nanoparticles under (111) deformation

All the results concerning the elastic properties of gold nanoparticles for nanoindentation on (111) facets are presented in the Fig. 11, 12 and 13.

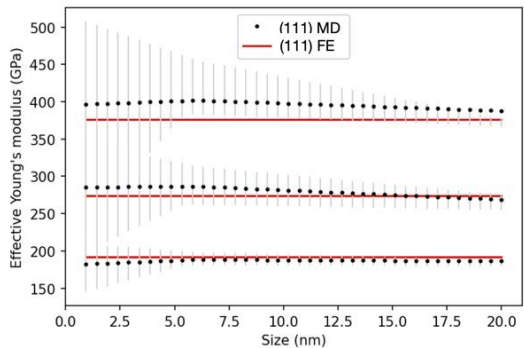


FIG. 11. Effective Young modulus as a function of the size for Au nanoparticles with different shapes. Comparison between continuous and atomistic calculations with indentation on (111) facets.

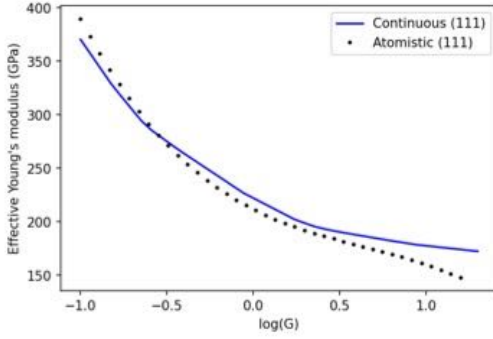


FIG. 12. Effective Young modulus as a function of the shape for gold nanoparticles. Results from continuous and atomistic calculations correspond to an indentation on (111) facets for a 20 nm diameter NP.

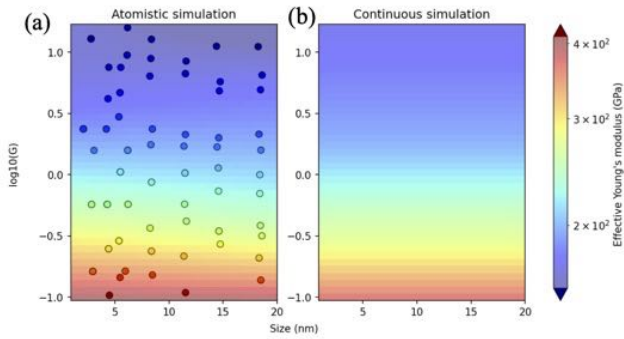


FIG. 13. Effective Young modulus as a function of the size and shapes for gold nanoparticles in a map form. Comparison between (a) atomistic and (b) continuous calculations with indentation on (111) facets.

Sec. II. Elastic properties of Cu nanoparticles under (001) deformation

More results concerning the elastic properties of Copper nanoparticles for nanoindentation on (001) facets are presented in the Fig. 14 and 15.

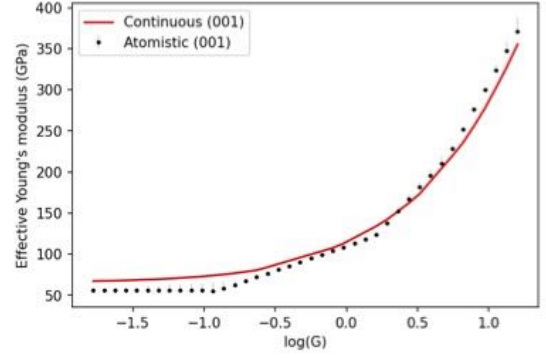


FIG. 14. Effective Young modulus as a function of the shape for copper nanoparticles. Results from continuous and atomistic calculations correspond to an indentation on (001) facets for a 20 nm diameter NP.

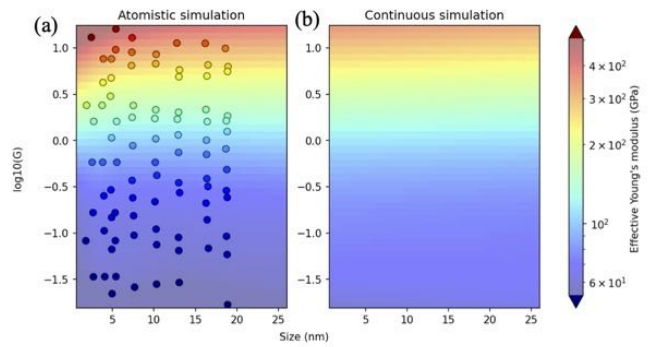


FIG. 15. Effective Young modulus as a function of the size and shapes for copper nanoparticles in a map form. Comparison between (a) atomistic and (b) continuous calculations with indentation on (001) facets.

Sec. III. Elastic properties of Pt nanoparticles under (001) deformation

More results concerning the elastic properties of Platinum nanoparticles for nanoindentation on (001) facets are presented in the Fig. 16 and 17.

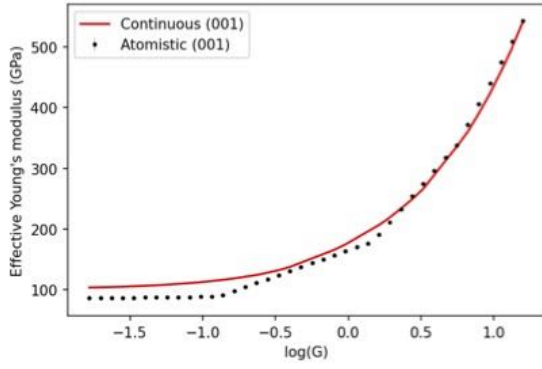


FIG. 16. Effective Young modulus as a function of the shape for platinum nanoparticles. Results from continuous and atomistic calculations correspond to an indentation on (001) facets for a 20 nm diameter NP.

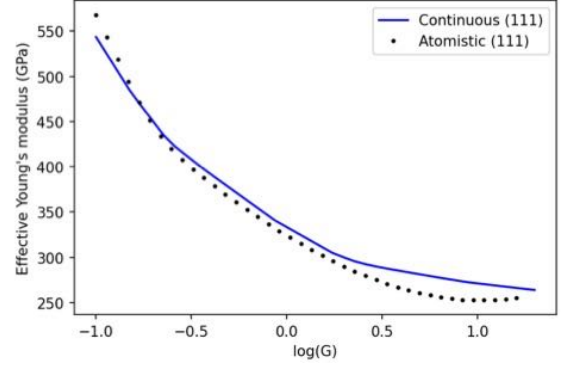


FIG. 18. Effective Young modulus as a function of the shape for copper nanoparticles. Results from continuous and atomistic calculations correspond to an indentation on (111) facets for a 20 nm diameter NP.

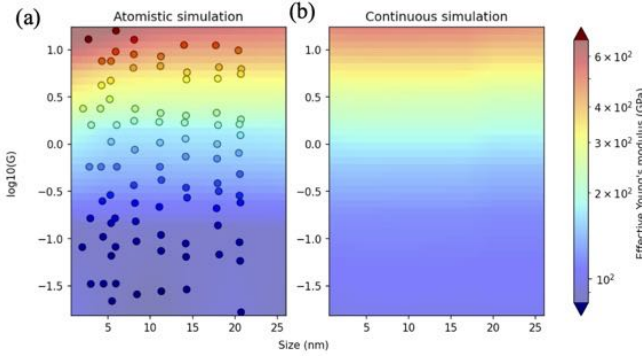


FIG. 17. Effective Young modulus as a function of the size and shapes for platinum nanoparticles in a map form. Comparison between (a) atomistic and (b) continuous calculations with indentation on (001) facets.

Sec. IV. Elastic properties of Cu nanoparticles under (111) deformation

All the results concerning the elastic properties of Cu nanoparticles for nanoindentation on (111) facets are presented in the Fig. 18 and 19

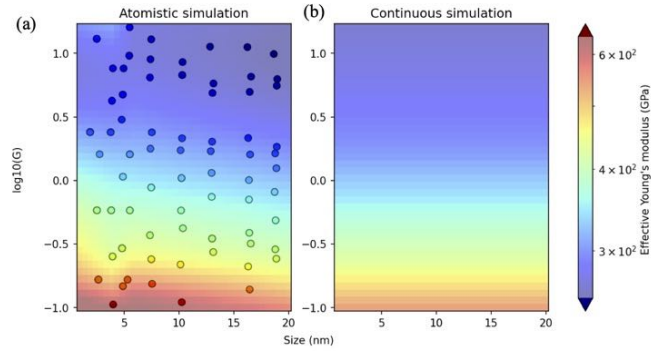


FIG. 19. Effective Young modulus as a function of the size and shapes for copper nanoparticles in a map form. Comparison between (a) atomistic and (b) continuous calculations with indentation on (111) facets.

Sec. V. Elastic properties of Pt nanoparticles under (111) deformation

All the results concerning the elastic properties of Pt nanoparticles for nanoindentation on (111) facets are presented in the Fig. 20 and 21

ACKNOWLEDGMENTS

H.A. thanks C. Ricolleau for fruitful discussions.

* hakim.amara@onera.fr

† riccardo.gatti@onera.fr

¹ L.-B. He, L. Zhang, L.-P. Tang, J. Sun, Q.-B. Zhang, and L.-T. Sun, "Novel behaviors/properties of nanometals induced by surface effects," *Mater. Today Nano.* **1**, 8–21 (2018).

² D. Guo, G. Xie, and J. Luo, "Mechanical properties of nanoparticles: basics and applications," *J. Phys. D: Appl.*

Phys. **47**, 013001 (2013).

³ Ph. Buffat and J-P. Borel, "Size effect on the melting temperature of gold particles," *Phys. Rev. A* **13**, 2287–2298 (1976).

⁴ H. Amara, J. Nelayah, J. Creuze, A. Chmielewski, D. Alloyeau, C. Ricolleau, and B. Legrand, "Effect of size on the surface energy of noble metal nanoparticles from analytical and numerical approaches," *Phys. Rev. B* **105**, 165403

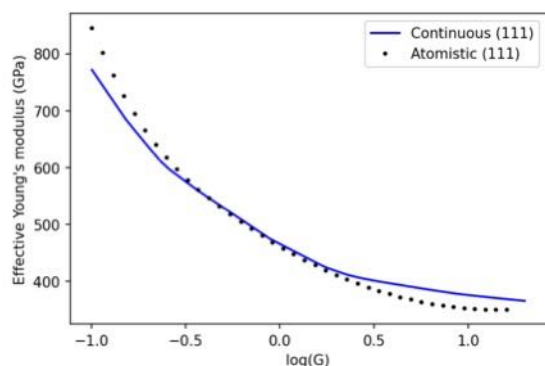


FIG. 20. Effective Young modulus as a function of the shape for platinum nanoparticles. Results from continuous and atomistic calculations correspond to an indentation on (111) facets for a 20 nm diameter NP.

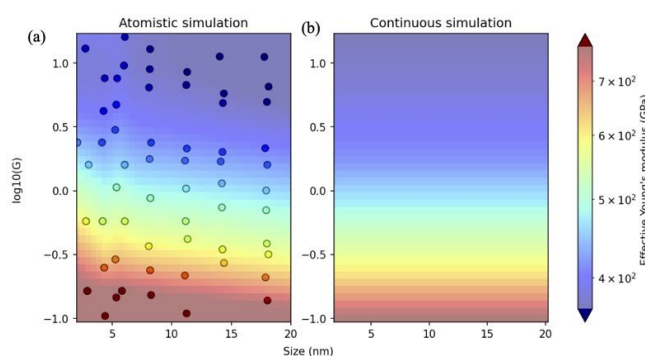


FIG. 21. Effective Young modulus as a function of the size and shapes for platinum nanoparticles in a map form. Comparison between (a) atomistic and (b) continuous calculations with indentation on (111) facets.

(2022).

- ⁵ D. Alloyeau, C. Ricolleau, C. Mottet, T. Oikawa, C. Langlois, Y. Le Bouar, N. Braïdy, and A. Loiseau, "Size and shape effects on the order-disorder phase transition in CoPt nanoparticles." *Nat. Mater.* **8**, 940–6 (2009).
- ⁶ M. D. Uchic, D. M. Dimiduk, J. N. Florando, and W. D. Nix, "Sample dimensions influence strength and crystal plasticity," *Science* **305**, 986–989 (2004).
- ⁷ B. Wu, A. Heidelberg, and J. J. Boland, "Mechanical properties of ultrahigh-strength gold nanowires," *Nat. Mater.* **4**, 525–529 (2005).
- ⁸ O. Kraft, P. A. Gruber, R. Mönig, and D. Weygand, "Plasticity in confined dimensions," *Annu. Rev. Mater. Res.* **40**, 293–317 (2010).
- ⁹ J. Deneen, W. M. Mook, A. Minor, W. W. Gerberich, and C. B. Carter, "In situ deformation of silicon nanospheres," *J. Mater. Sci.* **41**, 4477–4483 (2006).
- ¹⁰ C.E. Carlton and P.J. Ferreira, "In situ tem nanoindentation of nanoparticles," *Micron* **43**, 1134–1139 (2012).
- ¹¹ M. Legros, "In situ mechanical TEM: Seeing and measuring under stress with electrons," *C. R. Phys.* **15**, 224–240 (2014).
- ¹² J. A. de la Rosa Abad, A. Londoño Calderon, E. M. Bringa, G. J. Soldano, S. A. Paz, U. Santiago, S. J. Mejía-Rosales, M. J. Yacamán, and M. M. Mariscal, "Soft or hard?

- investigating the deformation mechanisms of Au-Pd and Pd nanocubes under compression: An experimental and molecular dynamics study," *J. Phys. Chem. C* **125**, 25298–25306 (2021).
- ¹³ S. Cuenot, C. Frétiigny, S. Demoustier-Champagne, and B. Nysten, "Surface tension effect on the mechanical properties of nanomaterials measured by atomic force microscopy," *Phys. Rev. B* **69**, 165410 (2004).
 - ¹⁴ M. Shaat, "Size-dependence of young's modulus and poisson's ratio: Effects of material dispersion," *Mech. Mater.* **133**, 111–119 (2019).
 - ¹⁵ R. Cherian, C. Gerard, P. Mahadevan, Nguyen Thanh Cuong, and Ryo Maezono, "Size dependence of the bulk modulus of semiconductor nanocrystals from first-principles calculations," *Phys. Rev. B* **82**, 235321 (2010).
 - ¹⁶ L. Pizzagalli, "Finite-temperature mechanical properties of nanostructures with first-principles accuracy," *Phys. Rev. B* **102**, 094102 (2020).
 - ¹⁷ J. Amodeo and L. Pizzagalli, "Modeling the mechanical properties of nanoparticles: a review," *C. R. Phys.* **22**, 35–66 (2021).
 - ¹⁸ D. Mordehai, S. W. Lee, B. Backes, D. J. Srolovitz, W. D. Nix, and E. Rabkin, "Size effect in compression of single-crystal gold microparticles," *Acta Mater.* **59**, 5202–5215 (2011).
 - ¹⁹ Y. Feruz and D. Mordehai, "Towards a universal size-dependent strength of face-centered cubic nanoparticles," *Acta Mater.* **103**, 433–441 (2016).
 - ²⁰ D. Kilymis, C. Gérard, J. Amodeo, U. V. Waghmare, and L. Pizzagalli, "Uniaxial compression of silicon nanoparticles: An atomistic study on the shape and size effects," *Acta Mater.* **158**, 155–166 (2018).
 - ²¹ J. A. de la Rosa Abad, E. M. Bringa, S. J. Mejía-Rosales, and M. M. Mariscal, "On the mechanical response in nanoalloys: the case of NiCo," *Faraday Discuss.* **242**, 23–34 (2023).
 - ²² C. R. Henry, "Morphology of supported nanoparticles," *Progr. Surf. Sci.* **80**, 92–116 (2005).
 - ²³ G. Wulff, "Zur Frage der Geschwindigkeit des Wachstums und der Auflösung der Krystallflächen," *Z. Kristallogr.* **34**, 449 (1901).
 - ²⁴ R. Kaischew, *Arbeitstagung Festkörper Physik* (Dresden, 1952) p. 81.
 - ²⁵ S. Plimpton, "Fast parallel algorithms for short-range molecular dynamics," *J. Comput. Phys.* **117**, 1–19 (1995).
 - ²⁶ S. Roy, R. Gatti, B. Devincere, and D. Mordehai, "A multiscale study of the size-effect in nanoindentation of Au nanoparticles," *Comput. Mater. Sci.* **162**, 47–59 (2019).
 - ²⁷ F. Ducastelle, "Module élastique des métaux de transition," *J. Phys. (Paris)* **31**, 1055 (1970).
 - ²⁸ V. Rosato, M. Guillopé, and B. Legrand, "Thermodynamical and structural properties of f.c.c. transition metals using a simple tight-binding model," *Philos. Mag. A* **59**, 321 (1989).
 - ²⁹ C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1995).
 - ³⁰ G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregates Properties* (MIT, Cambridge, 1971).
 - ³¹ L. Delfour, J. Creuze, and B. Legrand, "Exotic behavior of the outer shell of bimetallic nanoalloys," *Phys. Rev. Lett.* **103**, 205701 (2009).
 - ³² A. Chmielewski, J. Nelayah, H. Amara, J. Creuze, D. Alloyeau, G. Wang, and C. Ricolleau, "Direct Measurement

- of the Surface Energy of Bimetallic Nanoparticles: Evidence of Vegard's Rulelike Dependence," *Phys. Rev. Lett.* **120**, 025901 (2018).
- ³³ A. Front and C. Mottet, "Stress effect on segregation and ordering in Pt-Ag nanoalloys," *J. Phys.: Condens. Matter* **33**, 154006 (2021).
- ³⁴ M. S. Alnæs, J. Blechta, J. Hake, A. Johansson, B. Kehlet, A. Logg, C. Richardson, J. Ring, M. E. Rognes, and G. N. Wells, "The FEniCS Project Version 1.5," *Archive of Numerical Software* **3**, 9–23 (2015).
- ³⁵ T. D. B. Jacobs and A. Martini, "Measuring and Understanding Contact Area at the Nanoscale: A Review," *Appl. Mech. Rev.* **69**, 060802 (2017).
- ³⁶ J. Amodeo and K. Lizoul, "Mechanical properties and dislocation nucleation in nanocrystals with blunt edges," *Mater. Des.* **135**, 223–231 (2017).
- ³⁷ P. Armstrong and W. Peukert, "Size effects in the elastic deformation behavior of metallic nanoparticles," *J. Nanopart. Res.* **14** (2012), 10.1007/s11051-012-1288-4.
- ³⁸ R. P. Gupta, "Lattice relaxation at a metal surface," *Phys. Rev. B* **23**, 6265–6270 (1981).