Etude des propriétés mécaniques aux échelles nanométriques par dynamique moléculaire ab initio à température finie

Laurent Pizzagalli
CNRS - Institut Pprime
Poitiers, France
Mechanical properties at small scales

Smaller is stronger
Very high strength values
Most studies concern 1D systems (nanopillars, whiskers)

Does strength keep increasing when dimensions are further reduced?
Experimentally challenging to explore smaller dimensions...
MD compression of nanoparticles

Kilymis et al., Acta Mat. 2018

Amodeo et al., Comptes Rendus Physique 2021


Shape dependency
Plateau or increase

Shape and material dependency
Mainly increases

Decrease!

MD calculations of small (< 10nm) systems are computationally cheap, but interatomic potentials are not necessarily reliable due to high strain, surfaces, electronic effects.
Accurate method for ultra-small systems

Car-Parrinello MD DFT coupled with classical ionic force fields (why ?)

\[
M_\alpha \ddot{R}_\alpha (t) = - \frac{\partial}{\partial R_\alpha (t)} E[\{\Psi(t), R(t)\}] + F_\alpha [R_\alpha(t), t]
\]

Pizzagalli, Phys. Rev. B 2020

Implemented in

DFT accuracy
Versatile and adaptable to polyatomic systems
Much more costly than classical MD

Investigation of mechanical properties of endofullerenes:

Pizzagalli, Phys. Chem. Chem. Phys. 2022
Implementation and performance on curta

Example: Si$_{147}$H$_{100}$:

1 run using 288 cores
1 iteration (ions + electrons): $\sim$2.5 s  → Efficient and fast MPI implementation

BUT

Strain rate is a critical factor in mechanical simulation (usually $10^{11}$ faster than in ‘normal’ experiments)
The timestep of the simulation is very small, lower than 1fs for Car-Parrinello MD

A large number of iterations is needed, about $3\times10^5$ for a single run, i.e. $\sim$200h for 288 cores (57600 h)
Segmentation is possible and easy if the run termination is well controlled.
Strength of Si/SiC quantum dots

Objectives:
Strength and elastic limit determination
Plasticity mechanisms

Si / SiC nanoparticles (quantum dots)
<001> and <111> orientations
Sizes: 1.1 - 1.8 nm

25 Ry cutoff
γ-point sampling
Ultrasoft pseudopotentials
Isolated nanoparticles in a PBC supercell
Ionic (300K) and electronic thermostats
Surface atoms saturated by H
MD Compression with two virtual flat punches
Si nanoparticle compression

$\text{Si}_{123} <001>$ compression

- Force / stress max. at $\varepsilon = 0.20$
- 1st energy max. at $\varepsilon = 0.26$
Si nanoparticle compression: softening

\[ \varepsilon = 0.20 \]

- Force (13.8 nN) and stress (30 GPa) maxima
- Energy inflexion point
- Elastic deformation (?)

\( \langle 001 \rangle \) softening: beginning of diamond → \( \beta \)-tin transition (shear softening) (Needs & Mujica Phys. Rev. B 1995)

No \( \beta \)-tin because deconfinement effect in nanoparticles (Chrobak et al, Nature Nanotechnology 2011)

Stress maximum does not imply plasticity !!!

No visible “plastic” deformation
Si nanoparticle compression: amorphization

\[ \varepsilon = 0.26 \]

- Energy maximum (20 eV)
- Force minimum
- Plastic deformation

Polyedral template matching analysis (Mahler Larsen et al, MSMSE 2016)

Elastic - plastic transition by amorphization
Low dimensions improve a-Si phase stability (Tolbert et al, PRL 1996)
SiC nanoparticle compression

SiC\textsubscript{141} <111> compression

Force / stress /energy max. at $\epsilon = 0.21$
Other “events” at $\epsilon = 0.26 / 0.37$
SiC nanoparticle compression: dislocation formation?

\[ \epsilon = 0.223 \quad \sigma = 100 \text{ GPa} \]
SiC nanoparticle compression: dislocation formation?

$\varepsilon = 0.223 \quad \sigma = 100 \text{ GPa}$

Concerted motion of 4 atoms

(111)
SiC nanoparticle compression: dislocation formation?

ε = 0.223  σ = 100 GPa

Concerted motion of 4 atoms

ε = 0.225

Point defects dipole BUT equivalent to the formation of a dislocation loop in (111) plane with \( \mathbf{b} // <110> \) (|\( \mathbf{b} \)|\( \leq \frac{1}{2} |110| \))
**SiC nanoparticle compression: dislocation formation?**

- Suggests homogeneous nucleation of dislocation is possible in nanoparticles of 1-2 nm
- Partial Burgers vector, in agreement with previous studies (Gutkin et al. Acta Mat. 2008, Miller et al. JMPS 2008)
- Loop expansion is prevented by large stress decrease

\[ \varepsilon = 0.223 \quad \sigma = 100 \text{ GPa} \]

\[ \varepsilon = 0.225 \]

\[ \varepsilon = 0.242 \quad \sigma = 57 \text{ GPa} \]

Point defects dipole BUT equivalent to the formation of a dislocation loop in (111) plane with \( b // <110> \) (\(|b| < \frac{1}{2}|110|\))

Concerted motion of 4 atoms

Suggests homogeneous nucleation of dislocation is possible in nanoparticles of 1-2 nm

Partial Burgers vector, in agreement with previous studies (Gutkin et al. Acta Mat. 2008, Miller et al. JMPS 2008)

Loop expansion is prevented by large stress decrease
### Plasticity mechanisms: summary

<table>
<thead>
<tr>
<th>Material</th>
<th>Orientation</th>
<th>Strain</th>
<th>Stress</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si - 123</td>
<td>&lt;001&gt;</td>
<td>0.26</td>
<td>30 GPa</td>
<td>Softening → Amorphization</td>
</tr>
<tr>
<td>Si - 148</td>
<td>&lt;111&gt;</td>
<td>0.195</td>
<td>30 GPa</td>
<td>Amorphization</td>
</tr>
<tr>
<td>SiC - 127</td>
<td>&lt;001&gt;</td>
<td>0.28</td>
<td>98 GPa</td>
<td>Amorphization</td>
</tr>
<tr>
<td>SiC - 172</td>
<td>&lt;001&gt;</td>
<td>0.30</td>
<td>134 GPa</td>
<td>NP rotation → Amorphization</td>
</tr>
<tr>
<td>SiC - 147</td>
<td>&lt;111&gt;</td>
<td>0.21</td>
<td>111 GPa</td>
<td>Dislocation-like → Amorphization</td>
</tr>
<tr>
<td>SiC - 122</td>
<td>&lt;111&gt;</td>
<td>0.25</td>
<td>119 GPa</td>
<td>Dislocation-like → Amorphization</td>
</tr>
</tbody>
</table>

**Amorphization the most common mechanism (might be related to the high deformation speed)**

Dislocation-like formation possible in small NP (but limited expansion due to stress release / low temperature)

“Grain” or surface-related mechanisms can be activated (nanoparticle rotation, surface crack)
Ultimate compressive stress

Stress increases when size decreases, up to the tiniest nanoparticles/quantum dots. Theoretical strength can be reached (exceeded?) in these systems, or Schmid law cannot be used.

\[ \tau(\text{Si}) = 9.1 \text{ GPa} \]
\[ \tau(\text{SiC}) = 31 \text{ GPa} \]

Schmid law: \( H \equiv \sigma = \tau/m \)

\[ m(<111>) = 0.272 \]
\[ m(<001>) = 0.408 \]

\( H(\text{Si}) = 22.2 \text{ GPa} <001> \)
\( = 33.3 \text{ GPa} <111> \)
\( H(\text{SiC}) = 76 \text{ GPa} <001> \)
\( = 114 \text{ GPa} <111> \)

(a) This work
(b) Kilymis et al, Acta Mat. 2018
(c) Hale et al, Comp. Mat. Sci. 2011
(d) Chrobak et al, Nat. Nanotech. 2011
(e) Valentini et al, PRL 2007
(f) Kilymis et al, Acta Mat. 2019
(g) Hong et al, Acta Mat. 2018
(h) Chen et al, Nat. Com. 2020
(j) Kayang et al, Appl. Phys. A 2021
(k) Shin et al, JACS 2012

L. Pizzagalli

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Conclusions

DFT molecular dynamics compression of Si/SiC nanoparticles

Several plasticity mechanisms (amorphization, dislocation, surface-related, grains) revealed

The homogeneous nucleation of dislocation is possible in very small systems

High yield stress and strain values, theoretical bulk strength is reached and even exceeded

Suggests that strength value increases up to the theoretical value (no plateau and no decrease): at least for covalent systems like Si/SiC

Todo next:
- Development of a similar approach using Born-Oppenheimer dynamics and application to metallic nanoparticles
- Time increase for one ionic iteration (but a slightly larger timestep can be used)
- Need for more computational resources....
Contact surface determination

What is the best approximation of the contact surface?
- Vergeles: overestimation, not suited for non-circular contact
- Convex hull ($S_0$): lower limit
- Convex hull + corrections: $S_1 = S_0 + w(n)\Sigma s_c$
- “Augmented” convex hull ($S_2$): upper limit

S1 appears as a reasonable “measure” of the contact surface area
NP rotation: a ‘grain’-like mechanism

SiC$_{172}$ $<001>$ compression

Max. stress corresponds to the rotation of the NP surface area: ‘grain’-like mechanism
Due essentially to a contact surface increase
No energy and force maxima: suggests that the deformation remains elastic
Limits at ultra small scales?

Han et al., Adv. Func. Mat. 2015

Wagner et al., Acta Mat. 2015

Beaber et al., Philos. Mag. 2011

Materials dependency?
Shape (material) dependency?
Extrinsic effects (coatings)?
Hardness/strength definition...

Plateau at low dimensions?

No plateau?

Many unanswered questions!!!
But experimentally challenging to explore smaller dimensions