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

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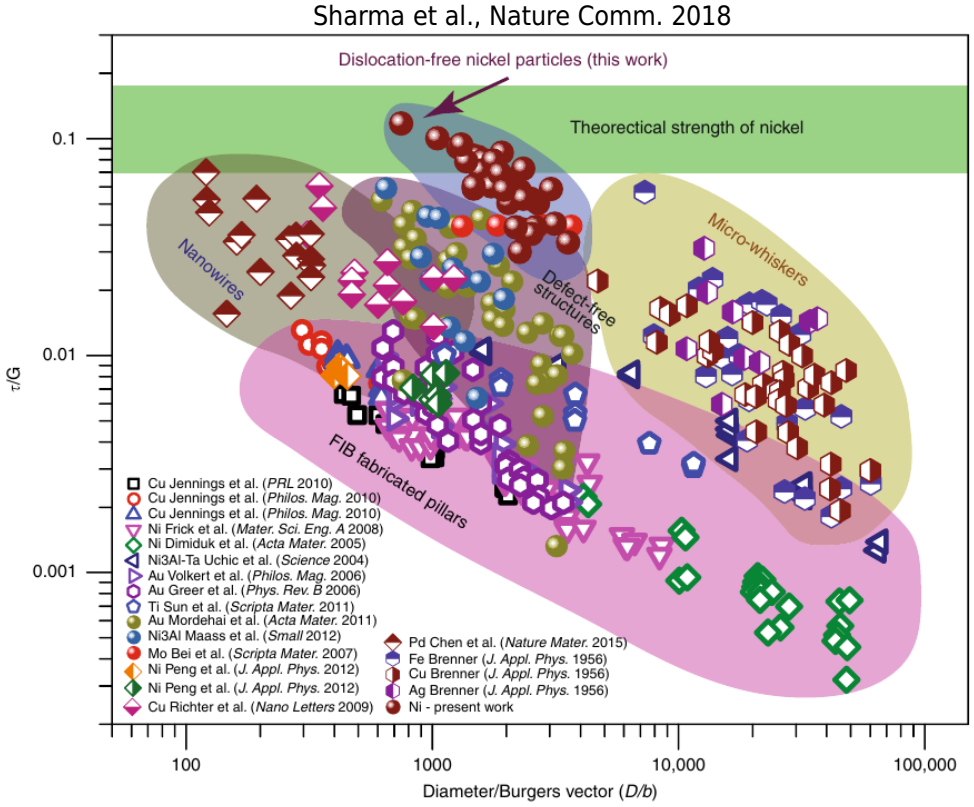
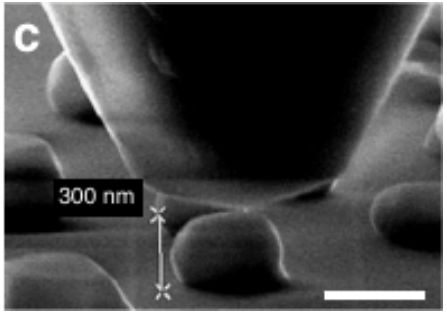
Mechanical properties at small scales

Sharma et al., Nature Comm. 2018



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

Sharma et al., Nature Comm. 2018



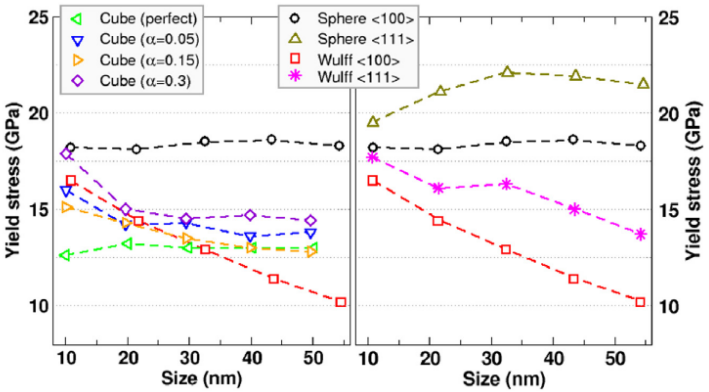
↓

Strength values even higher for nanoparticles
Reach theoretical strength values (Ni, Mo)

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

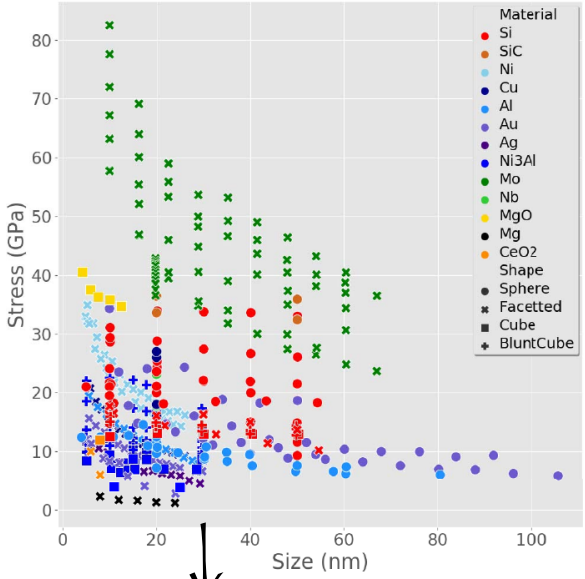
MD compression of nanoparticles

Kilymis et al., Acta Mat. 2018



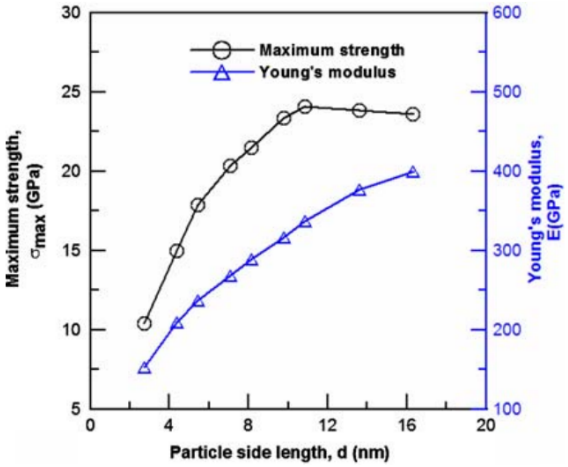
Shape dependency
Plateau or increase

Amodeo et al., Comptes Rendus Physique 2021



Shape and material dependency
Mainly increases

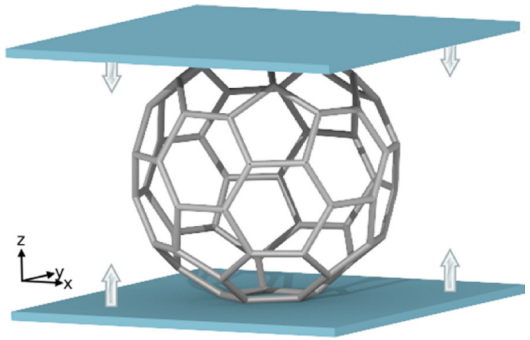
Fang et al., J. Nanopart. Res. 2009



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 ?)

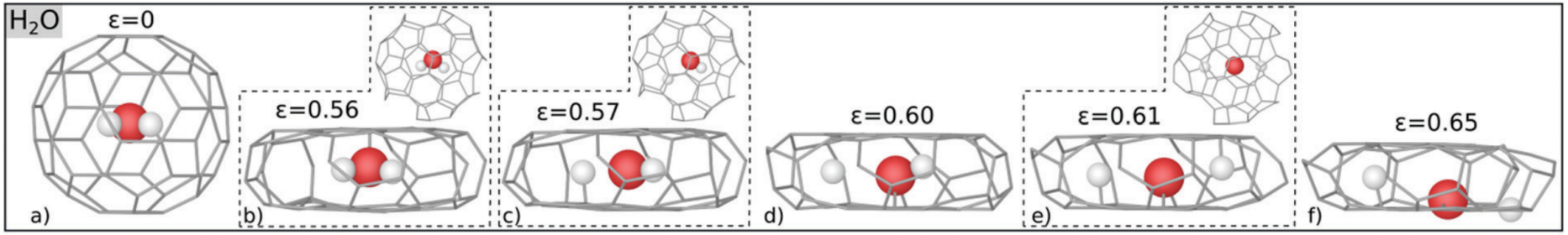
$$M_\alpha \ddot{\mathbf{R}}_\alpha(t) = -\frac{\partial}{\partial \mathbf{R}_\alpha(t)} E[\{\Psi(t)\}, \mathbf{R}(t)] + \mathbf{F}_\alpha[\mathbf{R}_\alpha(t), t]$$

Pizzagalli, Phys. Rev. B 2020

Implemented in QUANTUMESPRESSO

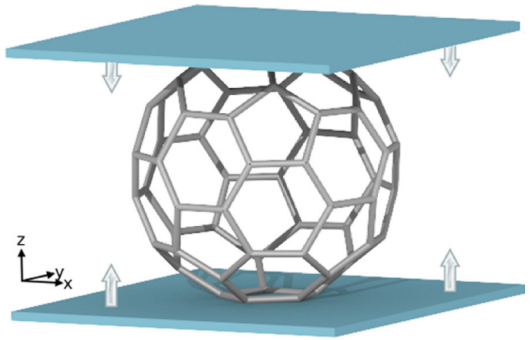
→ DFT accuracy
Versatile and adaptable to polyatomic systems
Much more costly than classical MD

Investigation of mechanical properties of endofullerenes:



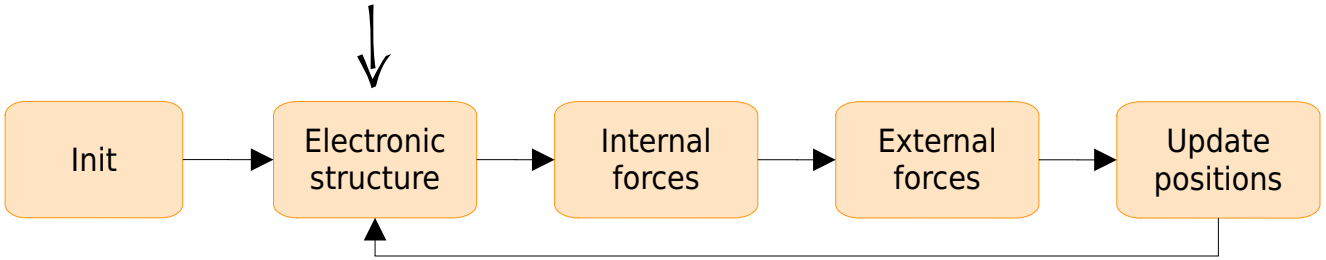
Pizzagalli, Phys. Chem. Chem. Phys. 2022

Implementation and performance on curta



Implemented in QUANTUMESPRESSO → Gitlab/github
Fortran

Computational effort essentially needed here



Example: $Si_{147}H_{100}$:

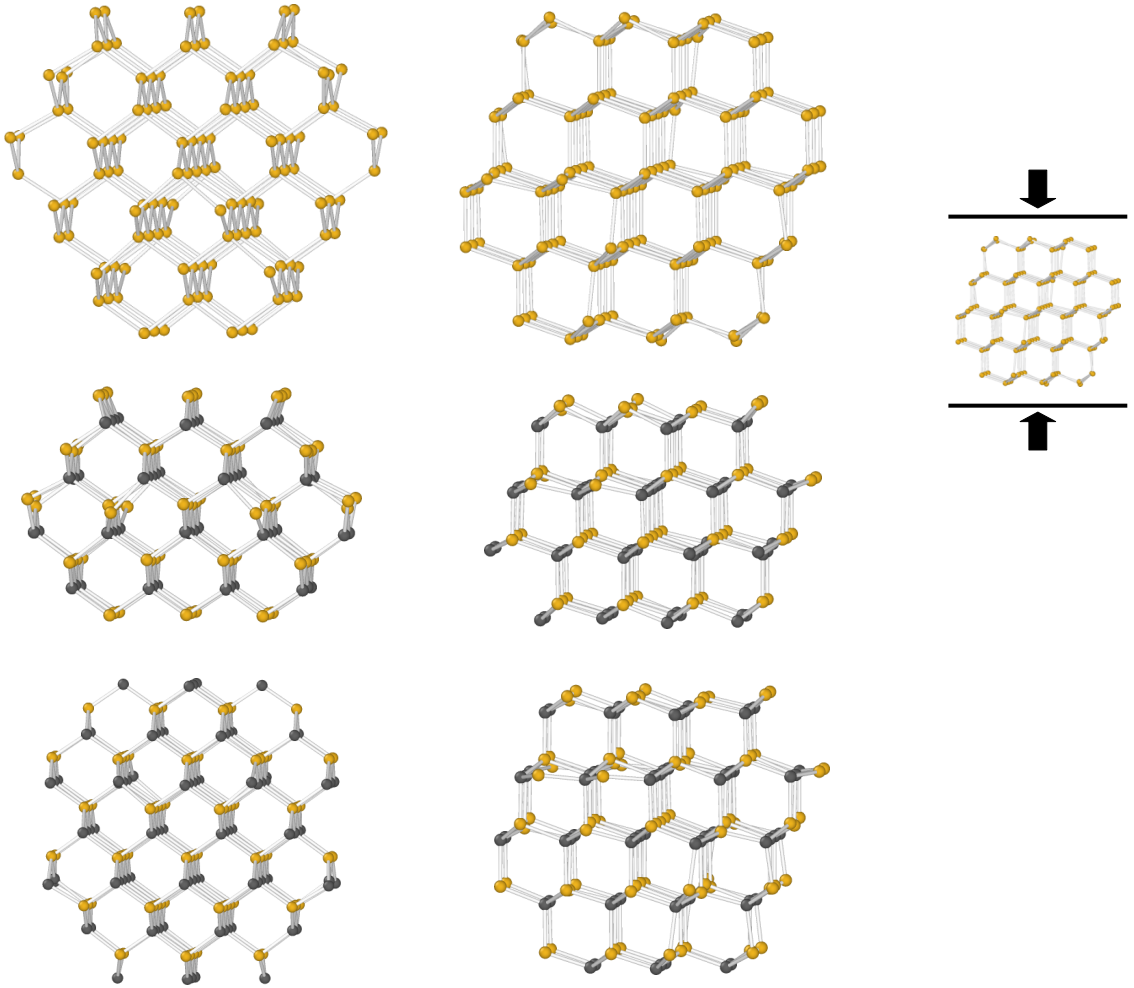
1 run using 288 cores
1 iteration (ions + electrons): ~2.5 s → Efficient and fast MPI implementation

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 $3x10^5$ for a single run, i.e. ~200h for 288 cores (57600 h)

Segmentation is possible and easy if the run termination is well controlled.

Strength of Si/SiC quantum dots



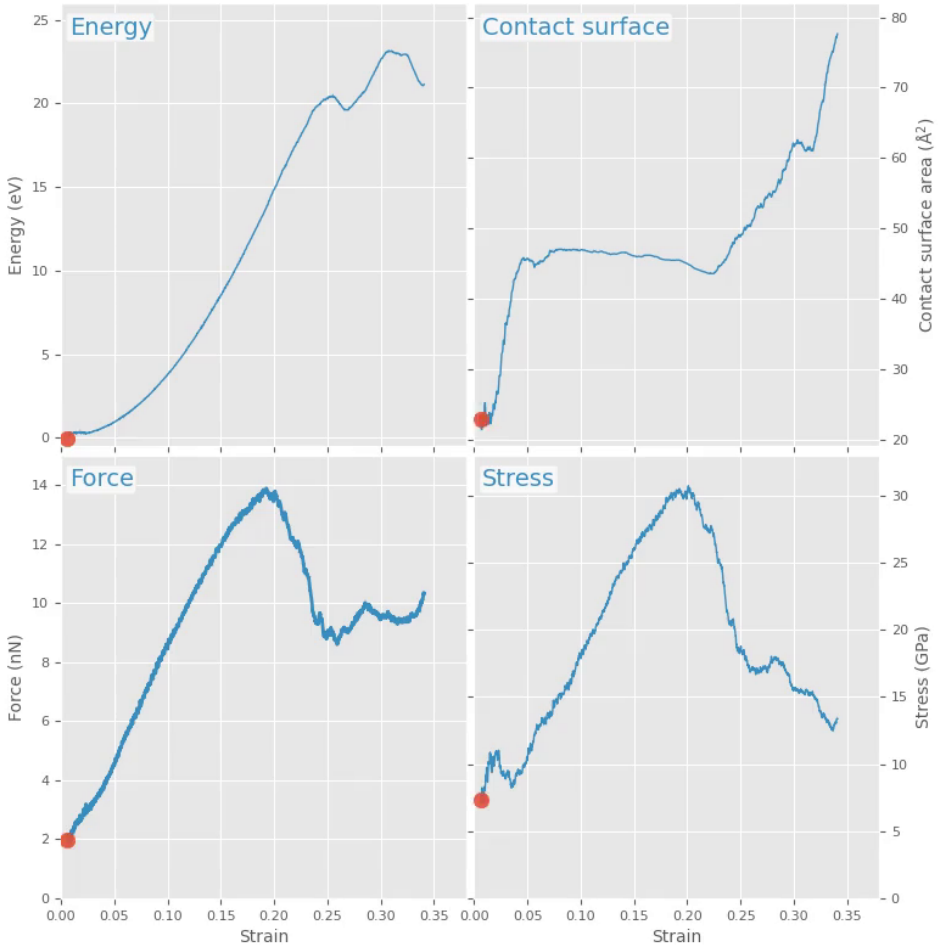
Si / SiC nanoparticles (quantum dots)
<001> and <111> orientations
Sizes: 1.1 – 1.8 nm

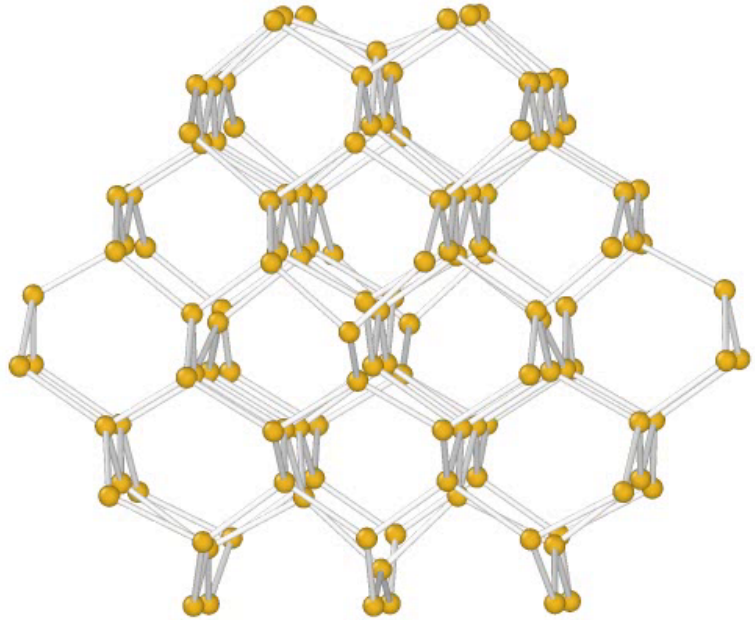
25 Ry cutoff
γ-point sampling
Ultrasoft pseudopotentials
Isolated nanoparticles in a PBC supercell
Ionic (300K) and electronic thermostats
Surface atoms saturated by H
MD Compression with two virtual flat punches

Objectives:
Strength and elastic limit determination
Plasticity mechanisms

Si nanoparticle compression

Si_{123} <001> compression

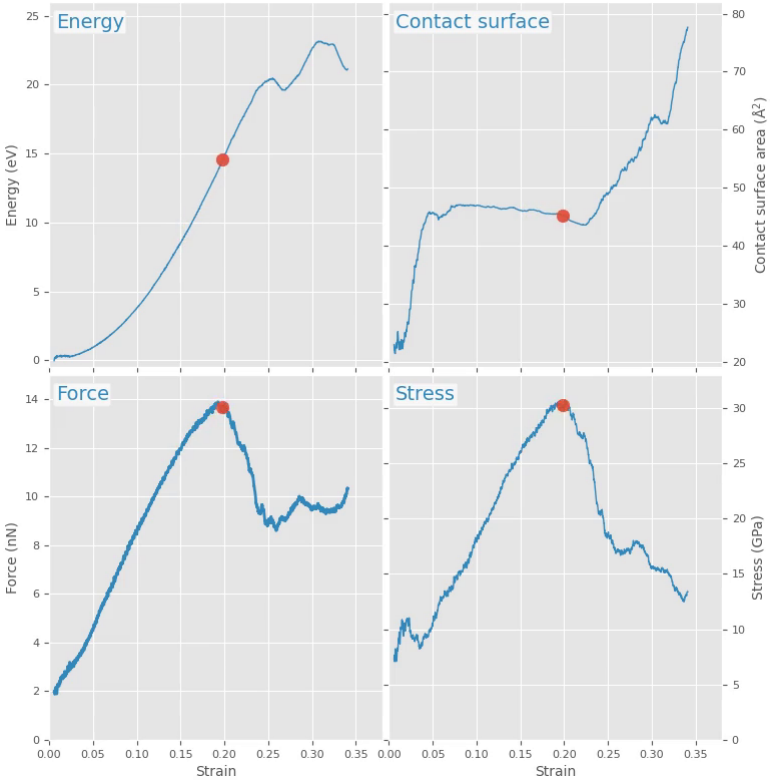




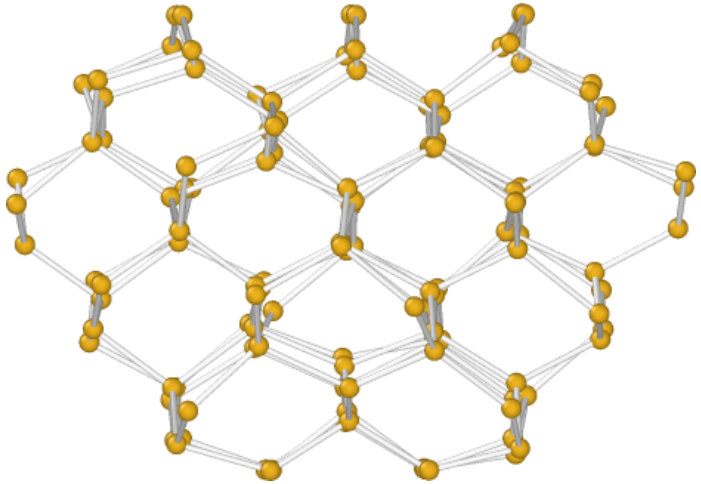
→ Force / stress max. at ε = 0.20
1st energy max. at ε = 0.26

Si nanoparticle compression: softening

ε = 0.20



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

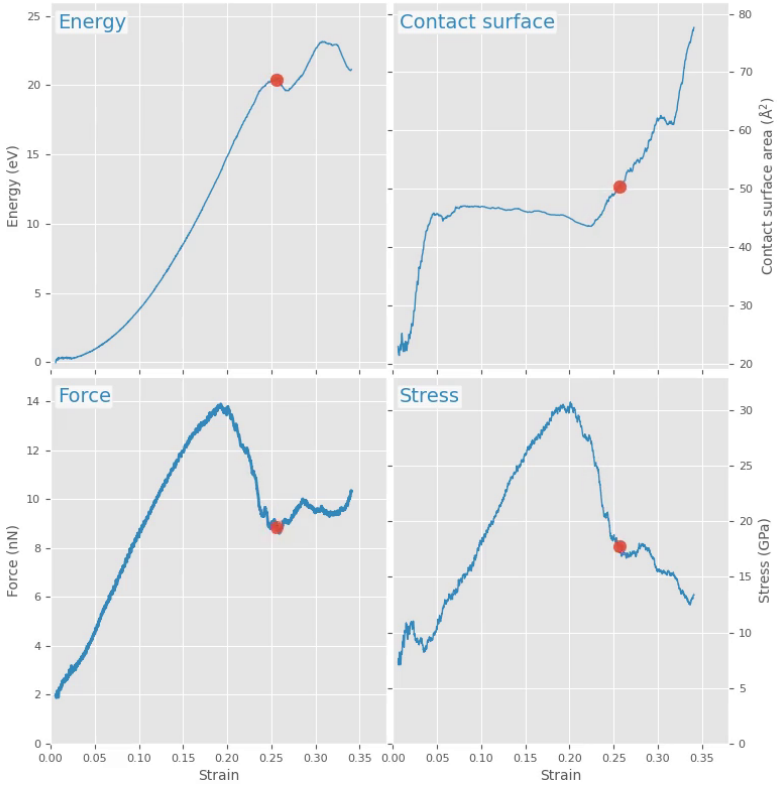


→ No visible “plastic” deformation

<001> softening: beginning of diamond → β-tin transition (shear softening) (Needs & Mujica Phys. Rev. B 1995)
No β-tin because deconfinement effect in nanoparticles (Chrobak et al, Nature Nanotechnology 2011)
Stress maximum does not imply plasticity !!!

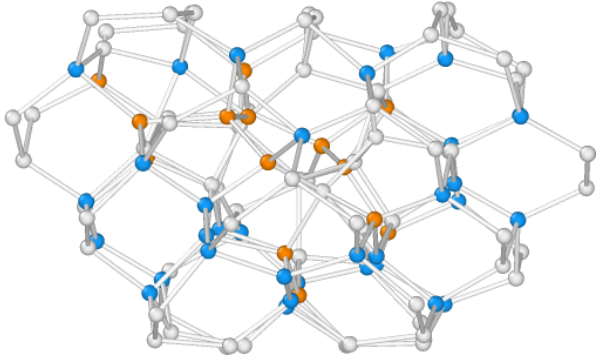
Si nanoparticle compression: amorphization

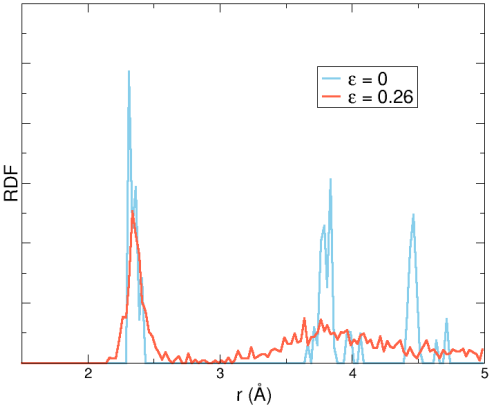
ε = 0.26



→ Energy maximum (20 eV)
Force minimum
Plastic deformation

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

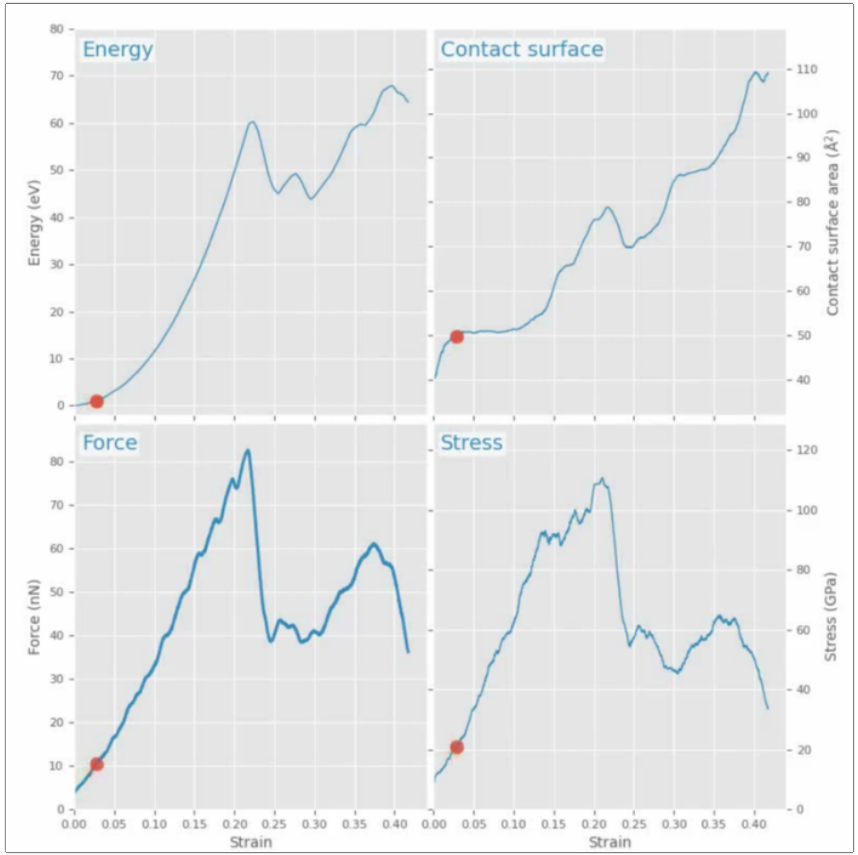


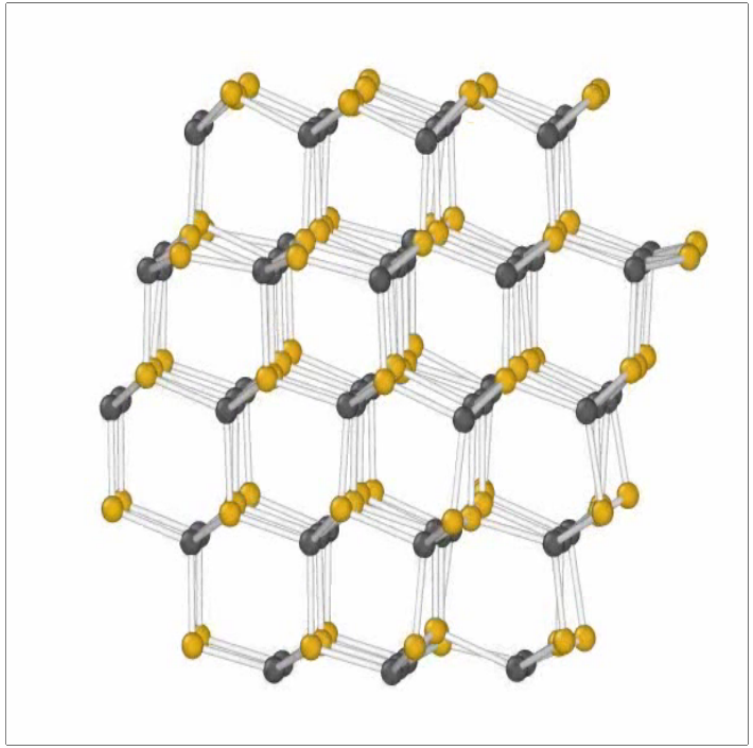


Elastic – plastic transition by amorphization
Low dimensions improve a-Si phase stability (Tolbert et al, PRL 1996)

SiC nanoparticle compression

SiC_{141} <111> compression

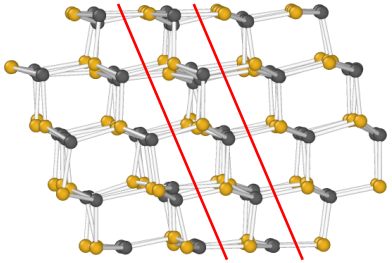


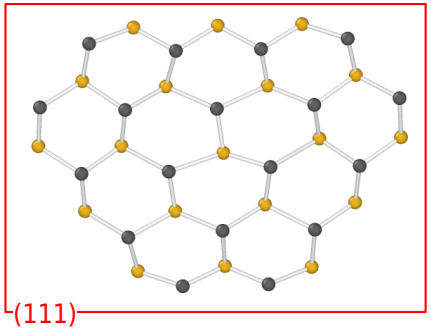


→ Force / stress /energy max. at ε = 0.21
Other “events” at ε = 0.26 / 0.37

SiC nanoparticle compression: dislocation formation?

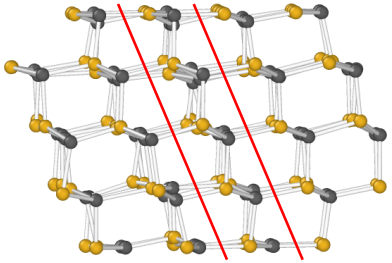
ε = 0.223 σ = 100 GPa

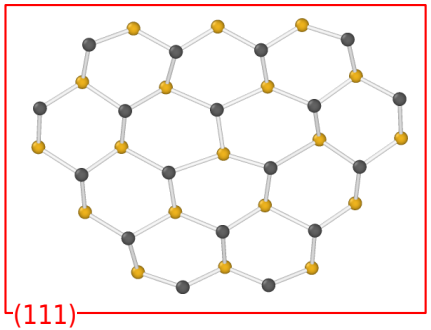




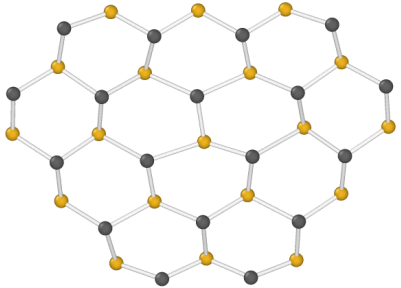
SiC nanoparticle compression: dislocation formation?

ε = 0.223 σ = 100 GPa





Concerted motion
of 4 atoms



SiC nanoparticle compression: dislocation formation?

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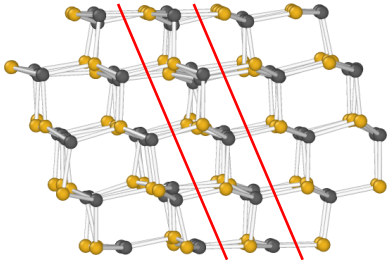
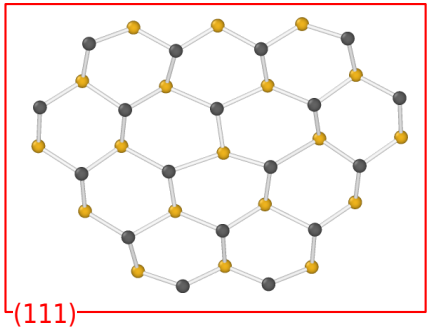
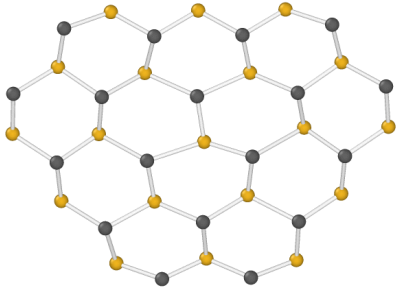
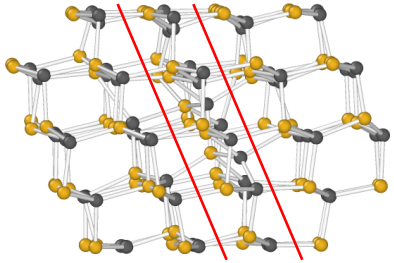


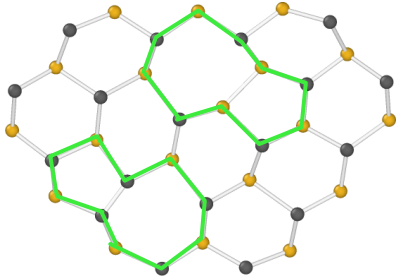


Concerted motion
of 4 atoms



ε = 0.225

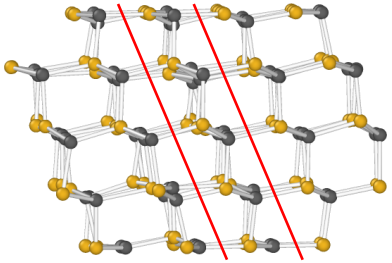


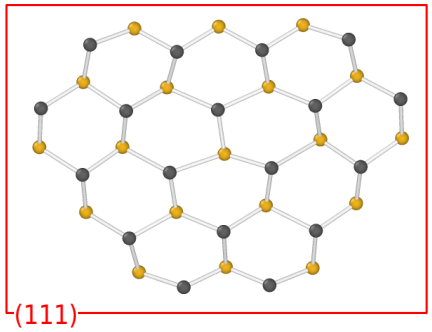


Point defects dipole
BUT equivalent to the formation
of a dislocation loop in (111) plane
with **b** // <110> (|b|<½|110|)

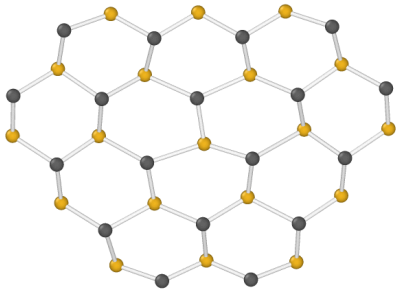
SiC nanoparticle compression: dislocation formation?

ε = 0.223 σ = 100 GPa

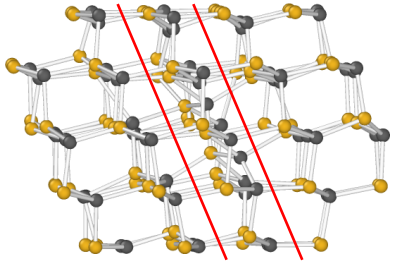


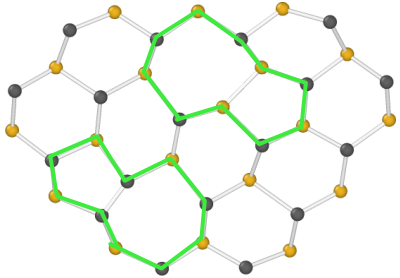


Concerted motion
of 4 atoms



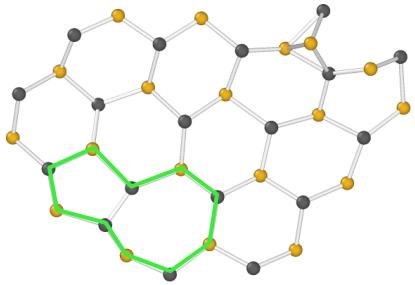
ε = 0.225





Point defects dipole
BUT equivalent to the formation
of a dislocation loop in (111) plane
with **b** // <110> (|b|<½|110|)

ε = 0.242 σ = 57 GPa

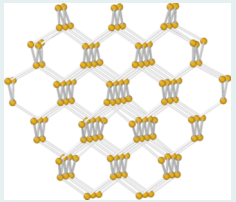
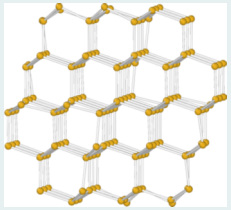
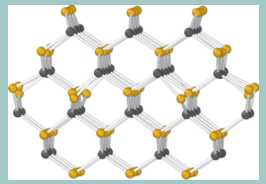
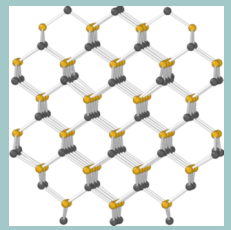
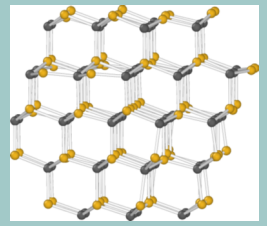
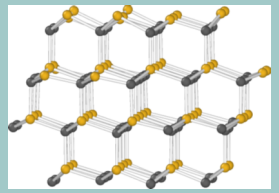


Suggests homogeneous nucleation of dislocation is possible in nanoparticles of 1-2 nm

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

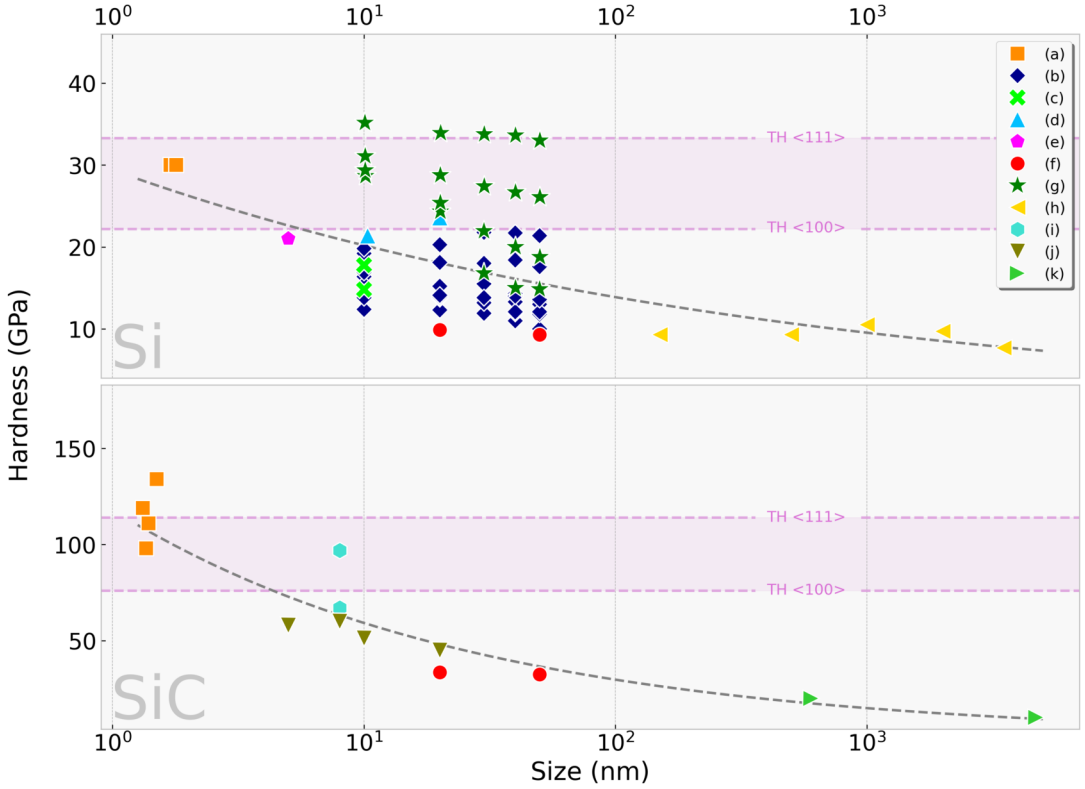
					
Si – 123 - <001>	Si – 148 - <111>	SiC – 127 - <001>	SiC – 172 - <001>	SiC – 147 - <111>	SiC – 122 - <111>
ε = 0.26 σ = 30 GPa	ε = 0.195 σ = 30 GPa	ε = 0.28 σ = 98 GPa	ε = 0.30 σ = 134 GPa	ε = 0.21 σ = 111 GPa	ε = 0.25 σ = 119 GPa
→ Softening → Amorphization	→ Amorphization	→ Amorphization	→ NP rotation → Amorphization	→ Dislocation-like → Surface crack → Amorphization	→ Dislocation-like → Amorphization

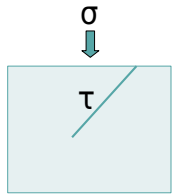
Amorphization the most common mechanism (might be related to the high deformation speed)

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





τ(Si) = 9.1 GPa
τ(SiC) = 31 GPa

Schmid law: H ≡ σ = τ/m

m(<111>) = 0.272
m(<001>) = 0.408

H(Si) = 22.2 GPa <001>
= 33.3 GPa <111>
H(SiC) = 76 GPa <001>
= 114 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
(i) He et al, J. Nano. Res. 2016
(j) Kayang et al, Appl. Phys. A 2021
(k) Shin et al, JACS 2012

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

Conclusions

DFT molecular dynamics compression of Si/SiC nanoparticles

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

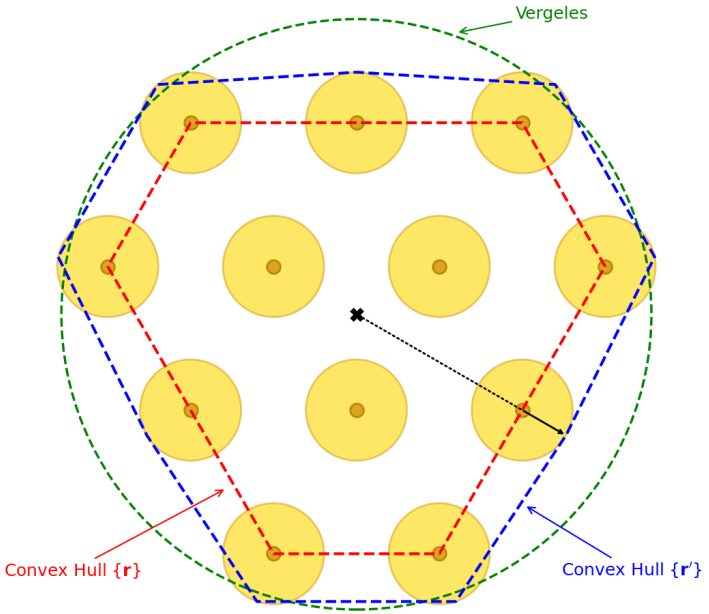
→ The homogeneous nucleation of dislocation is possible in very small systems

→ 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....

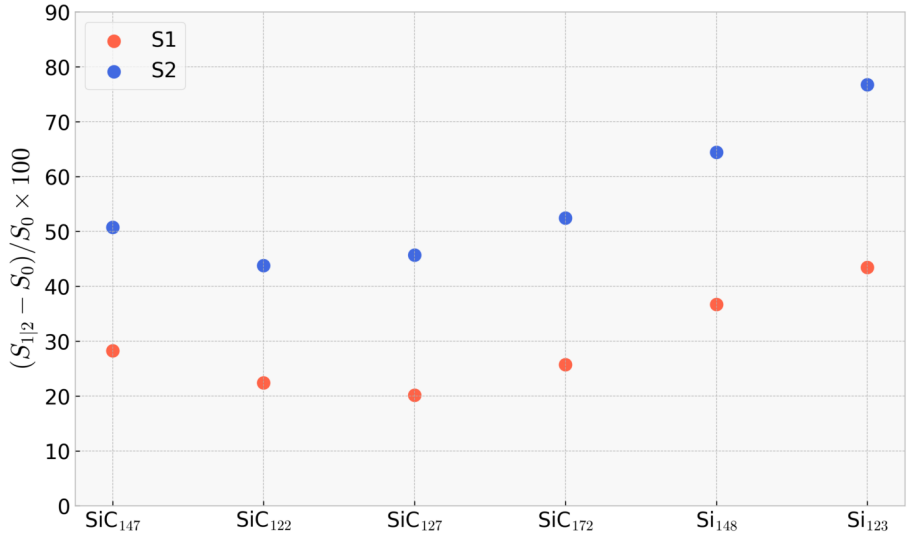
Contact surface determination



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

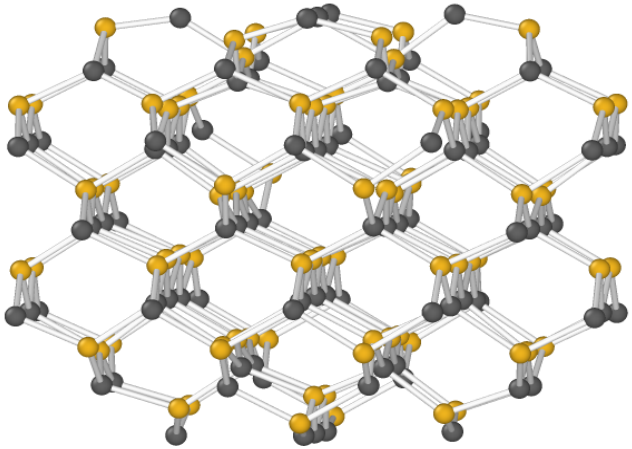
S1 appears as a reasonable “measure” of the contact surface area



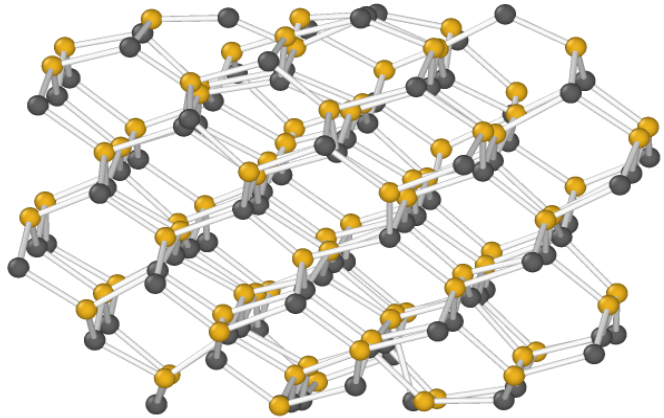
NP rotation: a ‘grain’-like mechanism

SiC_{172} <001> compression

ε = 0.234 σ = 134 GPa



ε = 0.291 σ = 97 GPa

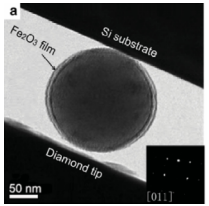


Max. stress corresponds to the rotation of the NP surface area: ‘grain’-like mechanism

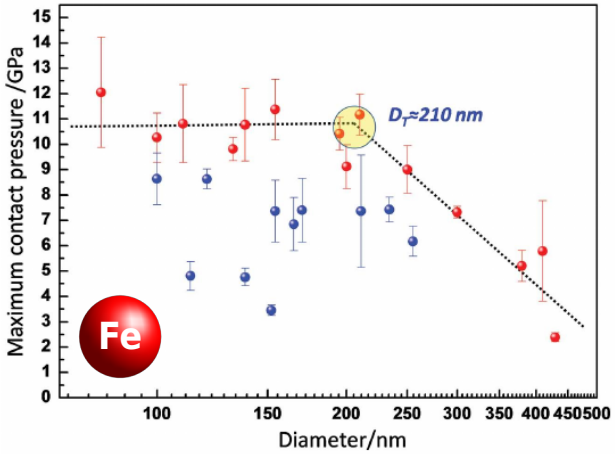
Due essentially to a contact surface increase

No energy and force maxima: suggests that the deformation remains elastic

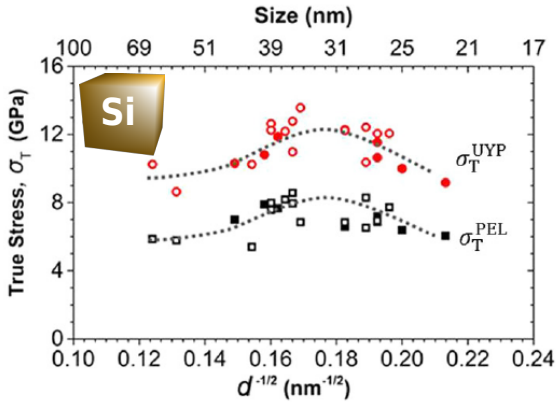
Limits at ultra small scales?



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

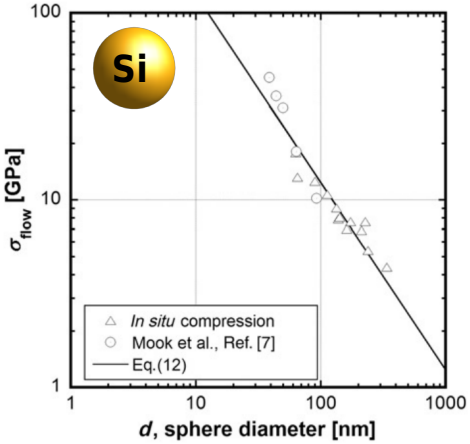


Wagner et al., Acta Mat. 2015



→ Plateau at low dimensions?

Beaber et al., Philos. Mag. 2011



→ No plateau?

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

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