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Pressure-dependent Structure and Mechanics of Grafted Gold Nanoparticle Superlattices

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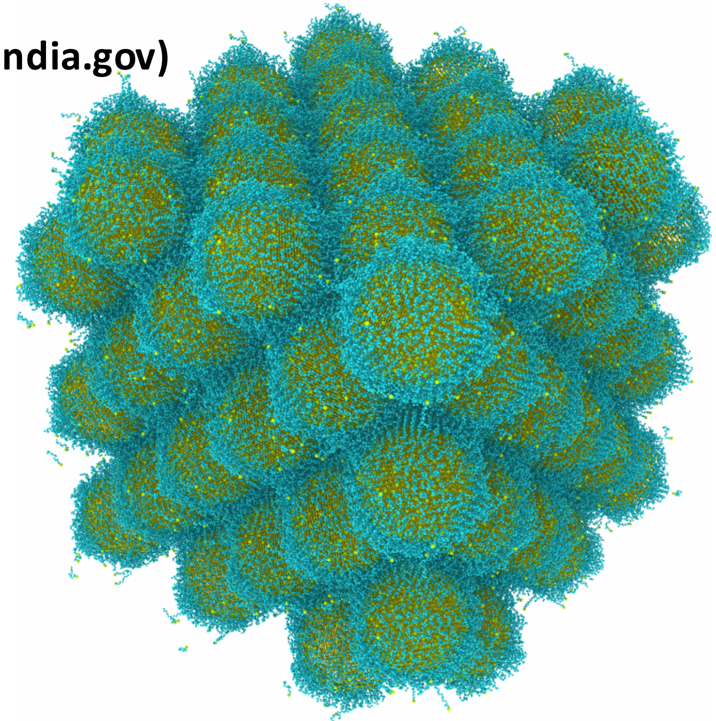

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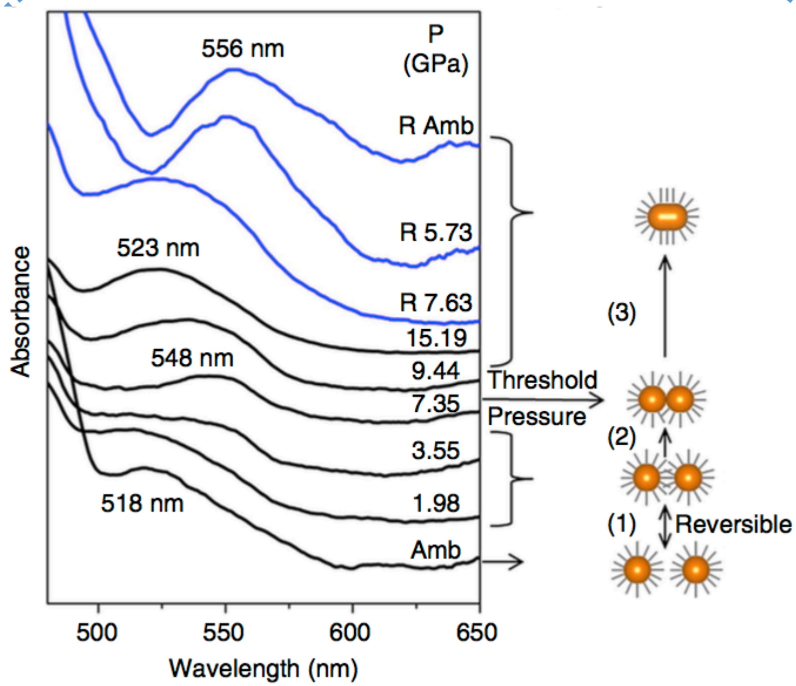
Nanoparticle Superlattices: Novel Applications

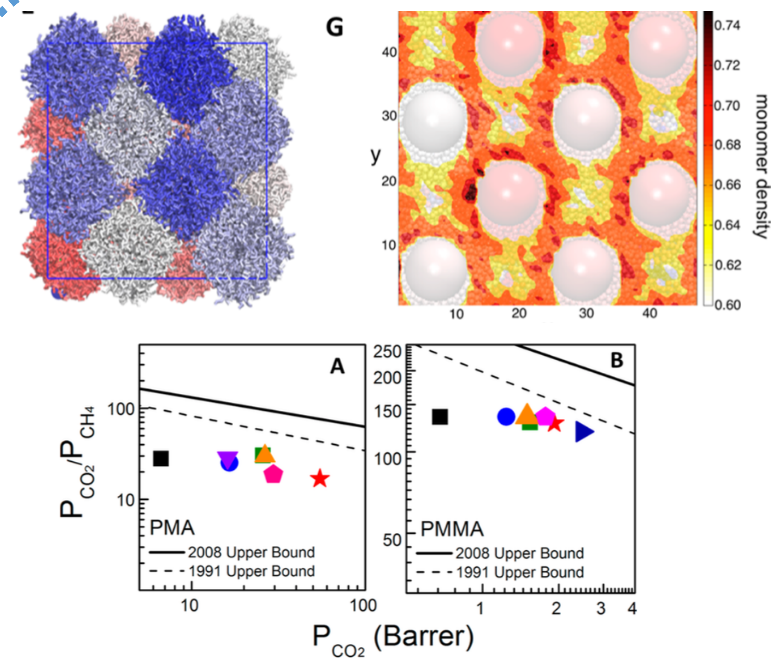
tunable optical properties



Li et. al., Nature Comm, 5, 4179 (2014)

- gold nanoparticle array are used in photonics with tunable optical properties: surface plasmon resonance
- pressure can reversibly increase/decrease inter-particle spacing, thereby allowing tunable photonics

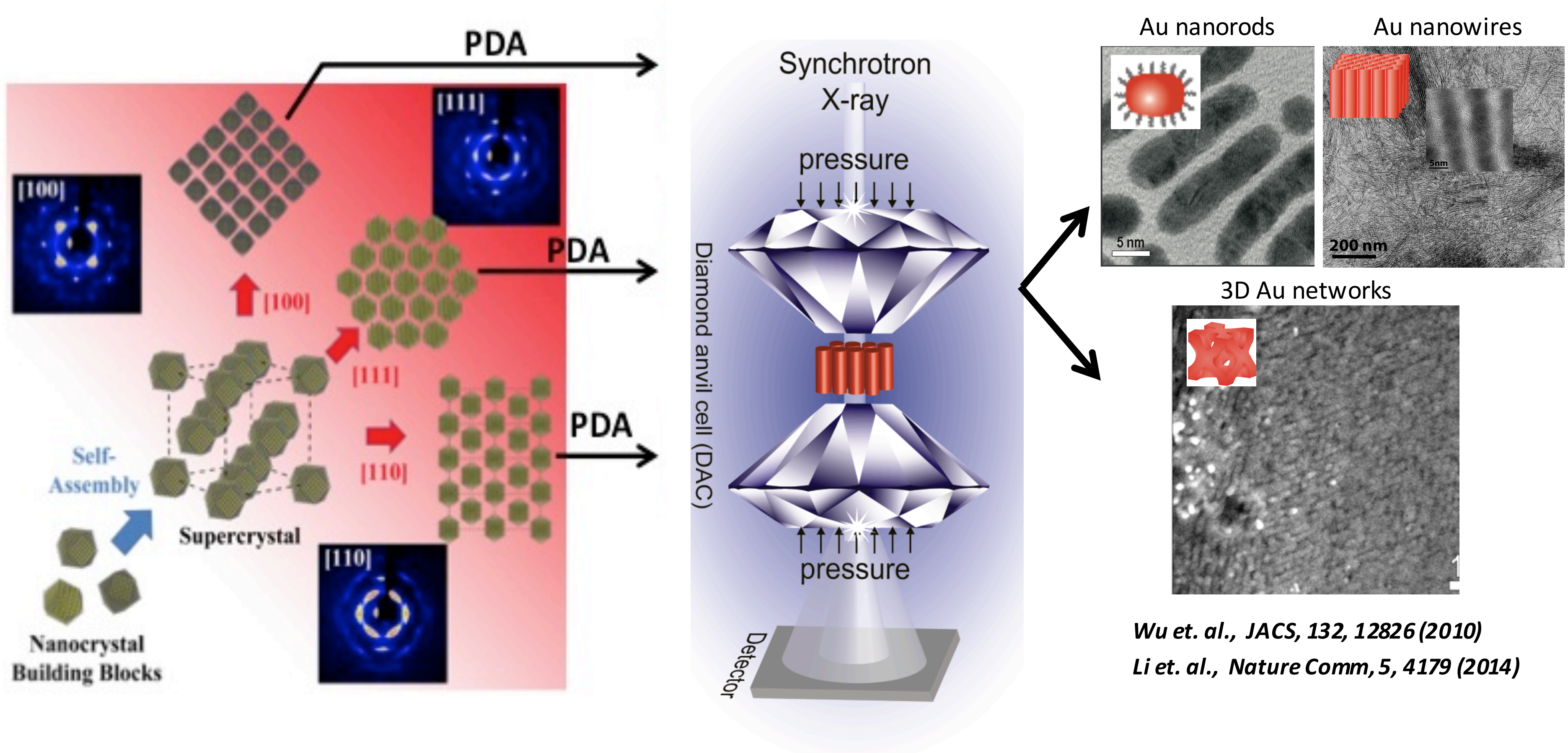
gas separation



Bilchak et. al., Macromolecules, 50, (2017)

- ligand grafted nanoparticle assemblies have a tunable complex pore structure for gas permeation
- changing ligand length and pressure provides control over the membrane permeability

Pressure-driven Nanostructure Fabrication

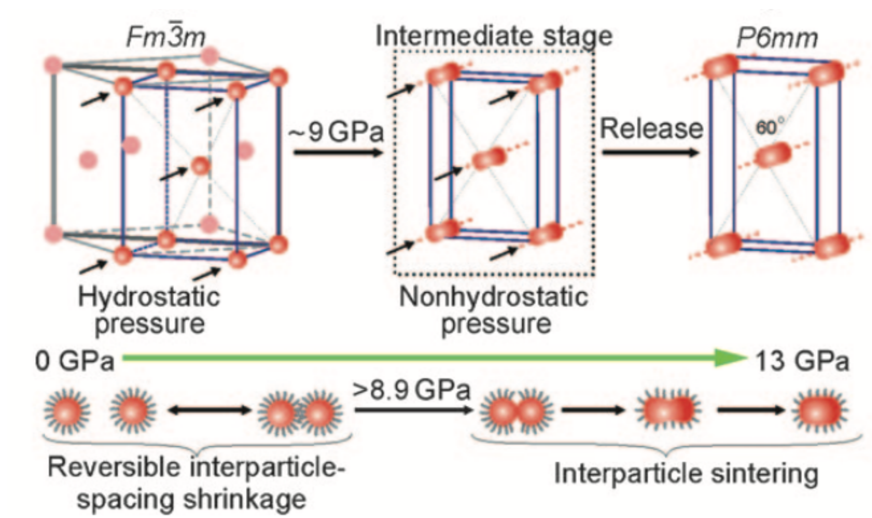


Wu et. al., JACS, 132, 12826 (2010)
Li et. al., Nature Comm, 5, 4179 (2014)

- a hydrostatically-stressed nanoparticle superlattice at 9GPa can be driven to generate 1D nanostructures (nanorods, nanowires) and 3D nanostructures (networks) by applying uniaxial stress along common crystal planes ([100], [111], [110])

Pressure-driven Nanostructure Fabrication: Outstanding Issues and Simulations

Proposed mechanism:



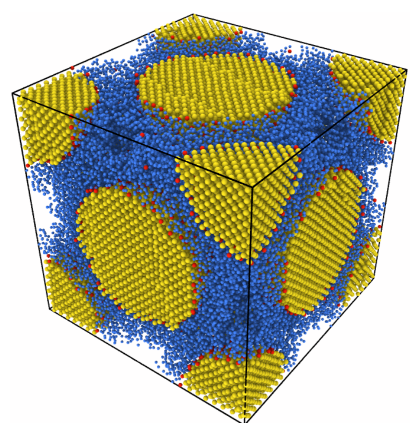
Wu et. al., Angw. Chem., 122, (2010)

- FCC superlattices of grafted Au nanoparticles compress reversibly up to hydrostatic pressure of ~ 9GPa
- beyond that threshold pressure, non-hydrostatic component (uniaxial) of stress drives irreversible sintering into nanowires, nanorods etc.

Outstanding issues:

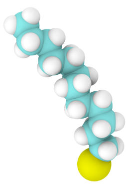
- is the hydrostatic pressure limit for deviatoric-stress driven sintering tunable based on ligand length, grafting density? For practical scalable manufacturing, can it be reduced?
- what are the mechanics and microstructural features of such FCC nanoparticle superlattices at high pressures (0-10 Gpa)? Can these insights help in achieving lower pressure sintering?

Simulation methods:

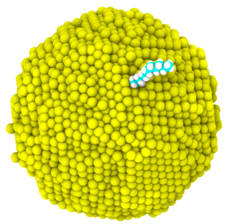


- ***prepare*** FCC super-lattice at ambient conditions
- ***compress*** the system by controlling pressure (NPH simulation method): 1 Gpa/ns
- ***characterize*** mechanics and microstructure at various pressures

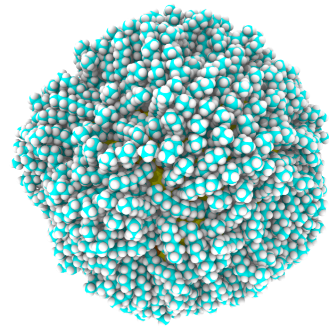
Nanoparticle Superlattice: Hierarchical Complexity



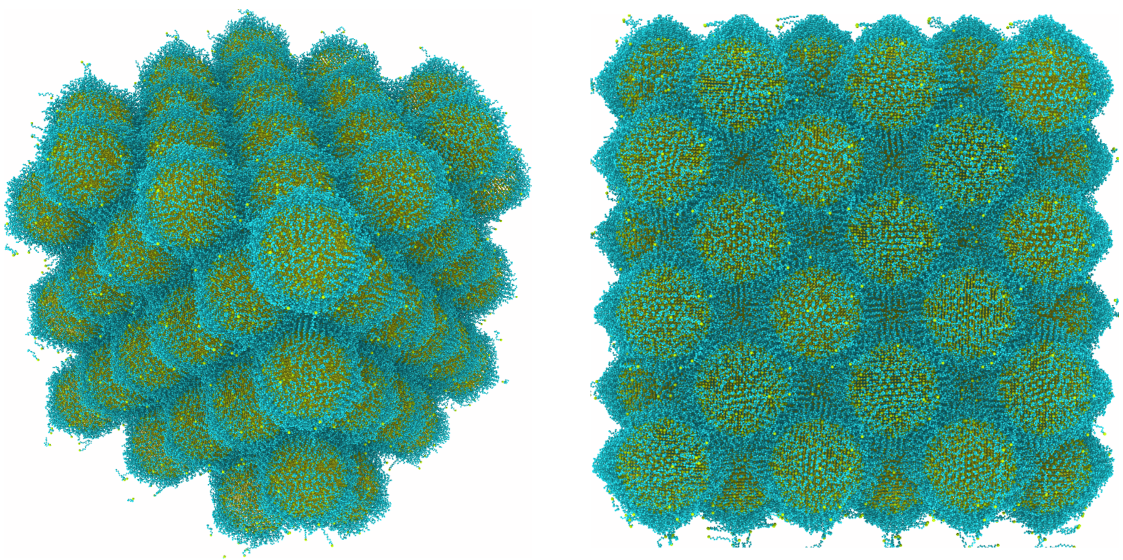
alkanethiol
$C_nH_{2n+1}S$



gold nanoparticle



alkanethiol-grafted
gold nanoparticle

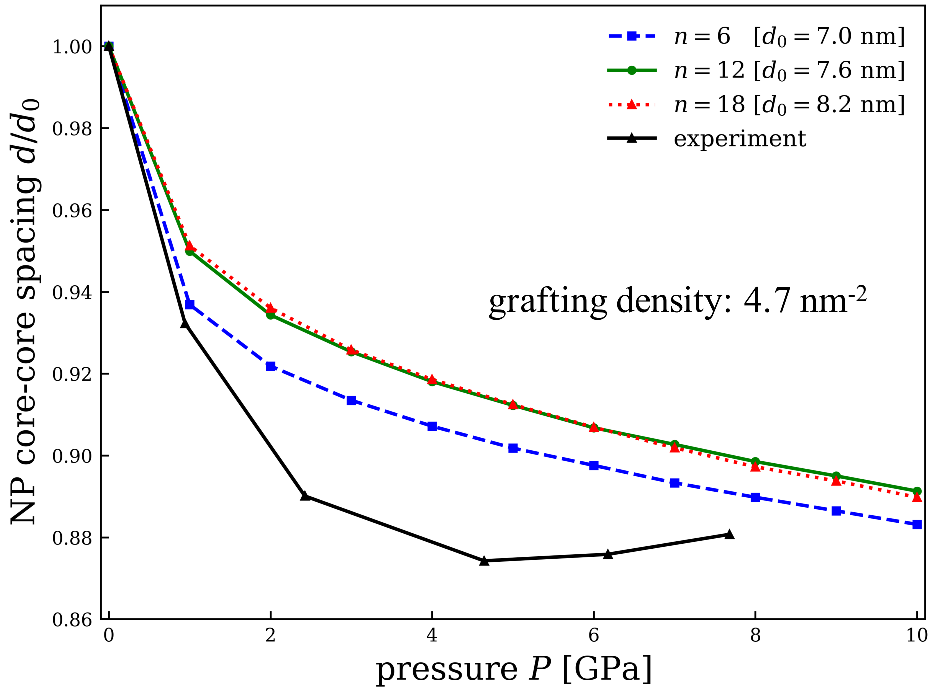


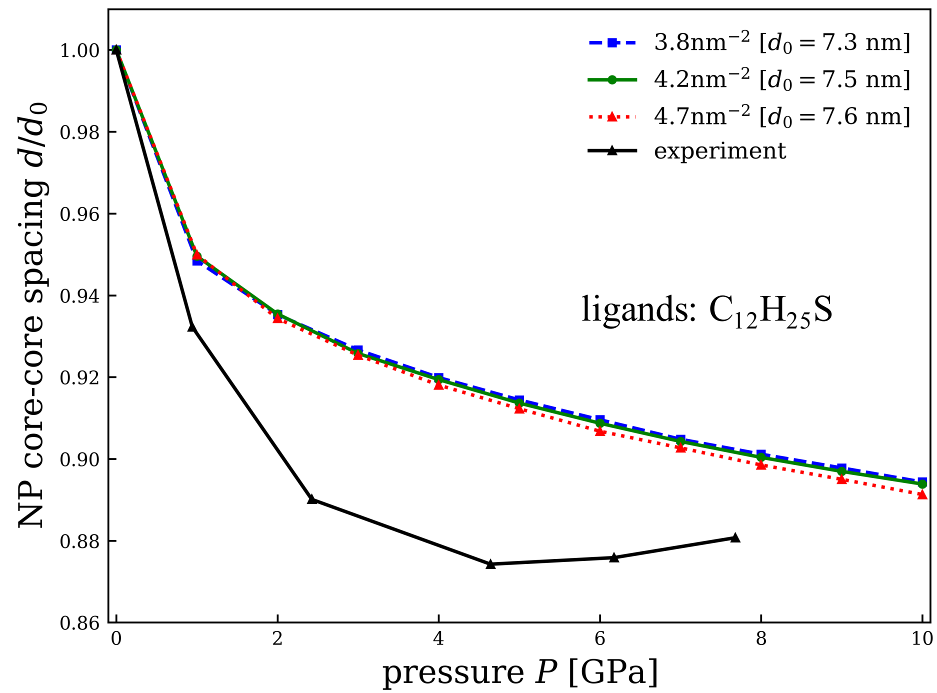
FCC superlattice of alkanethiol-grafted gold nanoparticles

Hierarchical complexity:

- **alkanethiols ligands**
  - $C_nH_{2n+1}S$
  - n = 6, 12, 18
  - exp-6 OPLS for hydrocarbons
    Jorgensen et. al., J. Am. Chem. Soc. 118, 11225 (1996).
- **gold core nanoparticle**
  - 5.9 nm solid gold core
  - cut from a FCC gold lattice
  - embedded atom method
    Foiles et. al, Phys Rev B, 33, 7983 (1986)
- **grafted nanoparticle**
  - mobile ligands with 2.4 kcal/mol binding strength using Morse potential
    Henz et. al., Langmuir, 24 (2008)
  - three grafting densities: 4.7, 4.2, 3.8 nm^{-2}
- **nanoparticle superlattice**
  - 4 and 96 nanoparticles in FCC superlattice

Hydrostatic Compression: Microstructure [Lattice Spacing]

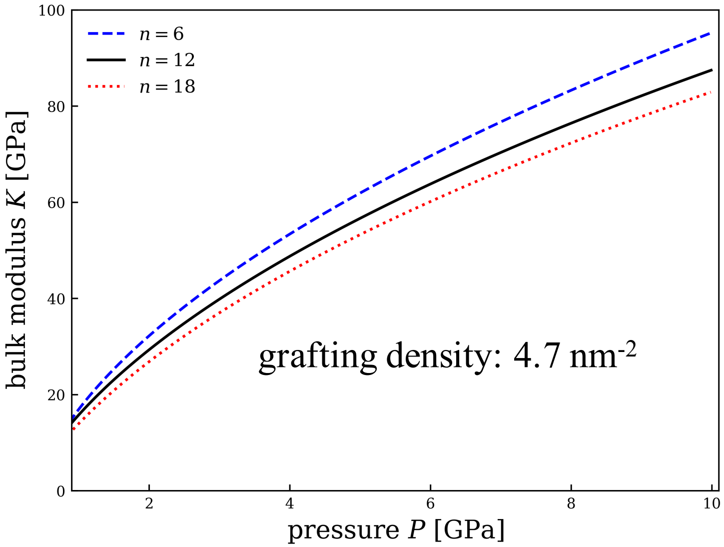


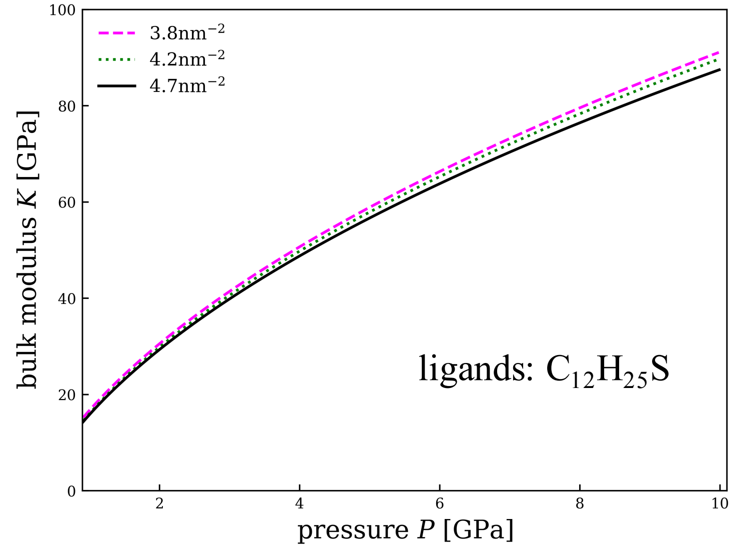


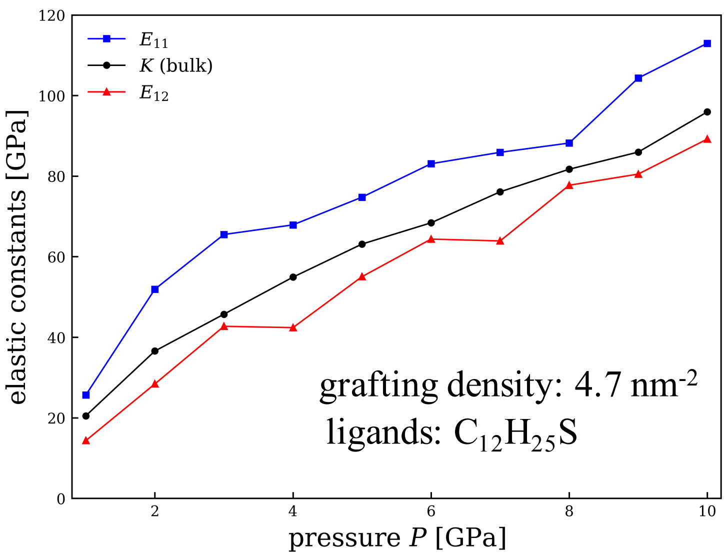
experiments ***[Wu et. al., Angwe. Chem., 122 (2010)]***: 5.2 nm gold NP with $C_{12}H_{25}S$. Results from d-spacing of first Bragg reflection in HP-SAXS. Ratio is the d-spacing ratio. Initial spacing: 7.3 nm

- ligand length plays a crucial role in NP-NP spacing in the lattice; insensitive to grafting densities, at least for moderately high densities (~ 80%)
- shorter ligands compress more resulting in larger reduction in NP-NP spacing in the lattice
- fcc lattice structure is maintained up to 10GPa in MD simulations; evidence of uniaxial stress component beyond ~8GPa in diamond anvil cell experiments

Hydrostatic Compression: Mechanics [Elastic Moduli]

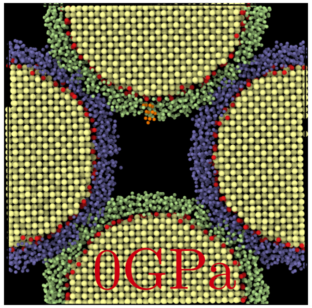


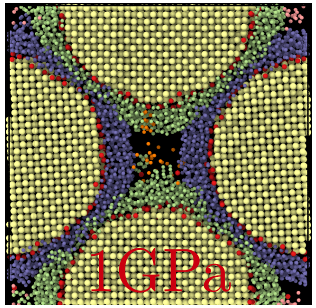


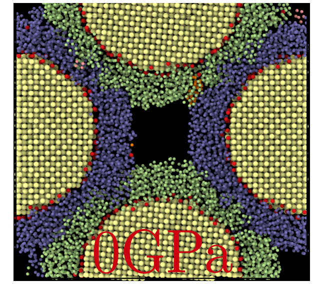


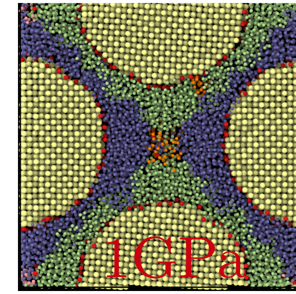
- bulk system depends on ligand length significantly; shorter chains' superlattices are more incompressible
- grafting density has negligible effect on compressibility
- elastic constants increase monotonically with hydrostatic pressure: stabilizing effect on the superlattice

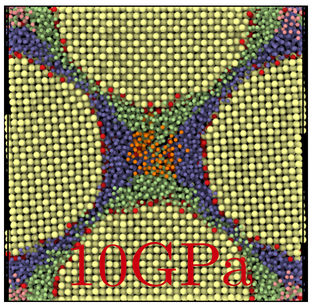
Hydrostatic Compression: Void Collapse



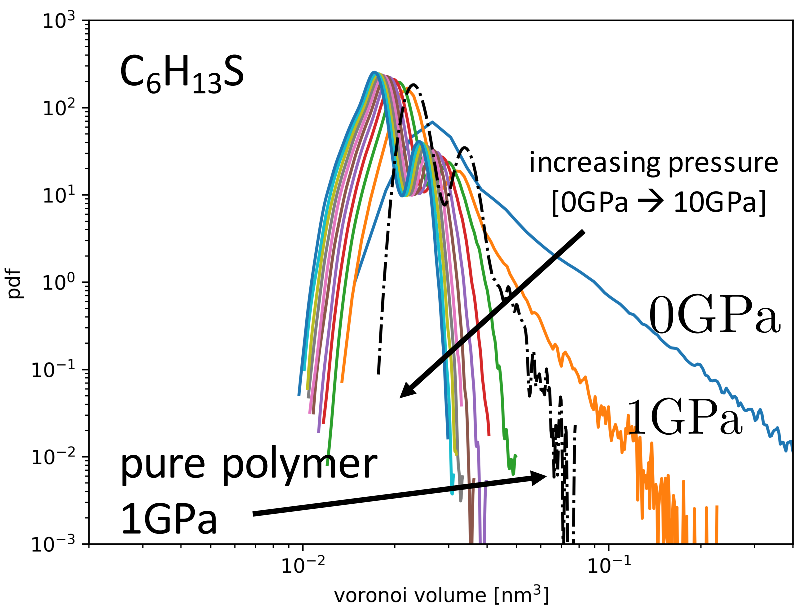


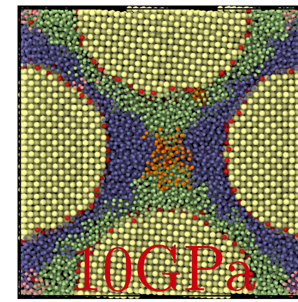


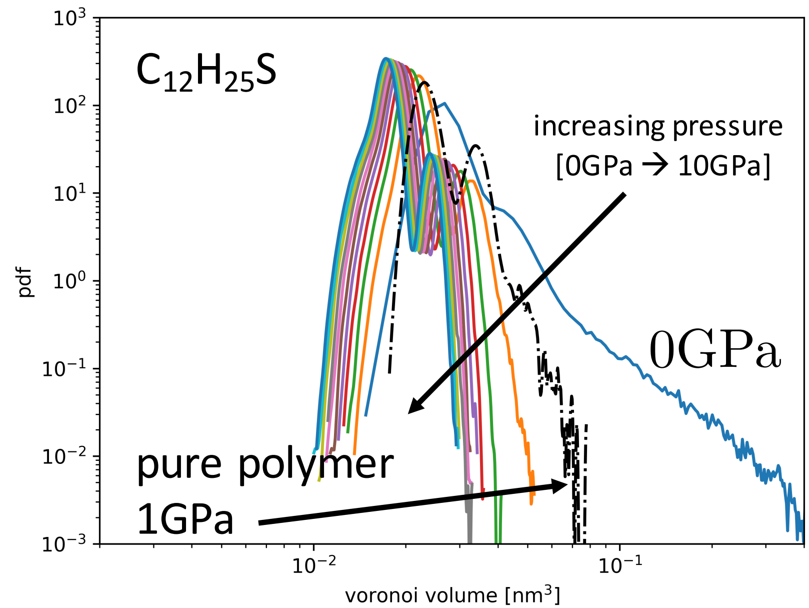




- voids at ambient pressure: larger for shorter chains
- voids collapse upon hydrostatic compression
- long tails (and no second peak) in voronoi free volume distribution







Hydrostatic Compression: Gold Core Sintering?

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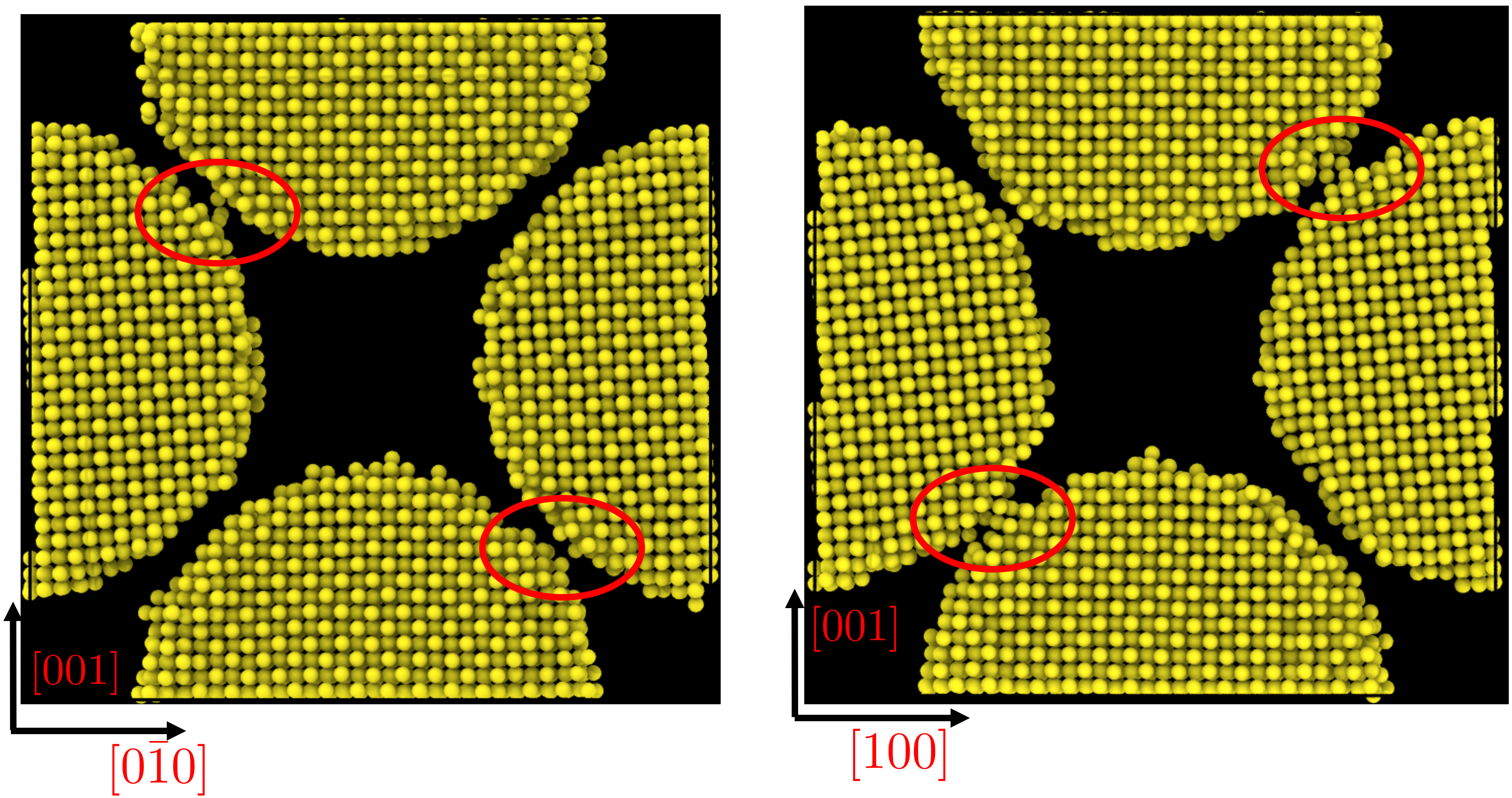

- evidence of gold-gold sintering at high pressure (15GPa) for short chains (C_6); not for longer
- does sintering preclude the formation of nanostructures? is there an upper limit of pressure?
- is there a limit on chain length beyond which sintering will never occur?
  [refer: **Li et. al., Nano Letters, 14, 4951 (2014)**]

Conclusions

1. FCC superlattices of polymer-grafted gold nanoparticles exhibit **reduced lattice spacing** upon hydrostatic **compression**; relative changes in microstructure/mechanics from ambient pressure are strongly **ligand-length dependent**

2. a systematic increase in elastic moduli upon hydrostatic compression is observed; **highest bulk compressibility** is observed for the **longest ligands**

3. **voids** are present within the microstructure at ambient pressures; these voids **collapse** at varying hydrostatic pressures depending on ligand length

4. for shortest ligands, evidence of gold core **sintering without deviatoric stress** is observed at high pressures

Future Work

1. check whether gold core sintering happens for all ligand lengths; if yes, then at what pressures?

2. perform deviatoric-stress-driven sintering simulations, and quantify the minimum hydrostatic stress required for sintering for various ligand lengths; correlate these findings with microstructural changes

3. investigate the role of core size, core orientation, superlattice structures (bcc, hcp) on stress-driven sintering into nanostructures