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Nanoparticles under Pressure: Dynamic Assembly and Phase Transition Modeling and Experiments

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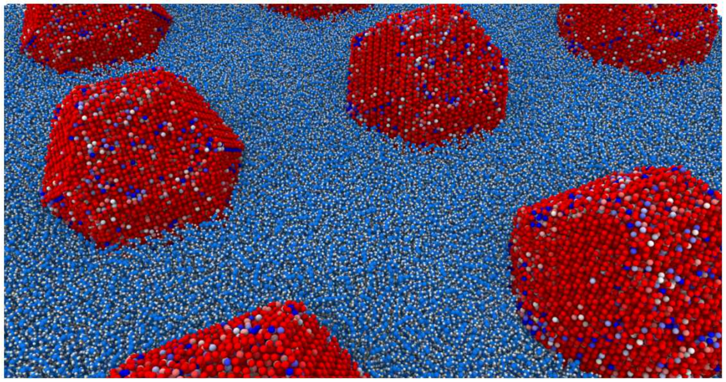

U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

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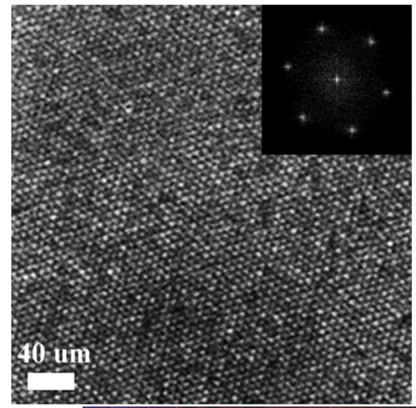
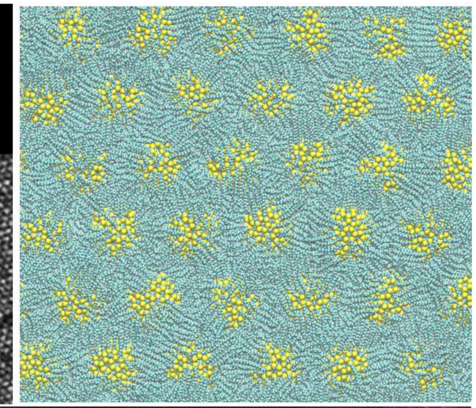
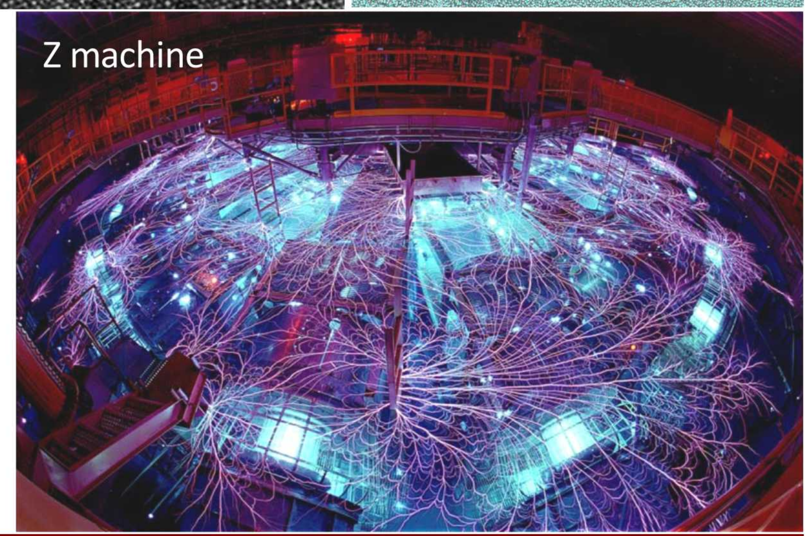
World-class resources at Sandia

- CINT
  - Nanoscale synthesis/experiment, analysis
  - Modeling thrust
- Super computing
  - Massive parallel computing resources
  - Software tools (LAMMPS)
- Pulsed power platform
  - World-class and unique pressure drivers
  - Shock and ramp waves to incredible states

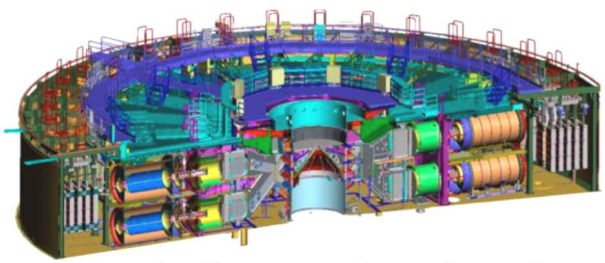




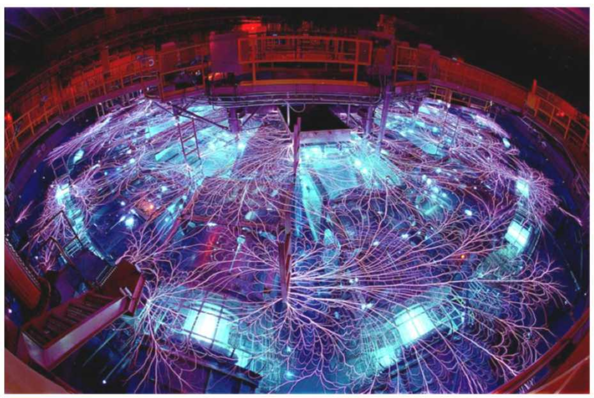


Magnetically-driven compression experiments

Z-machine at Sandia National Labs



33 m in diameter, 3 stories tall

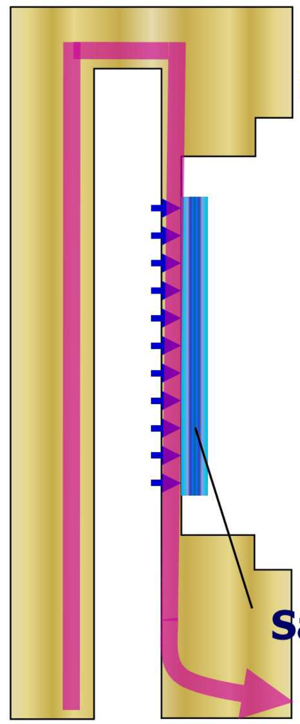


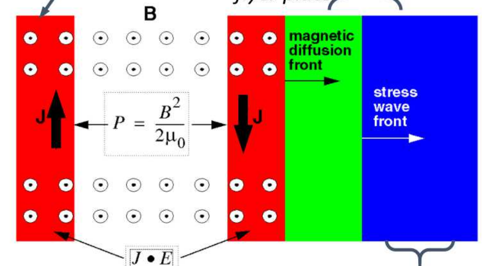
22 MJ stored energy
25 MA peak current
100-600 ns rise time

25 MA is the max current load of 160,000 homes

Veloce experiments allow:

- High-pressure shock-less studies





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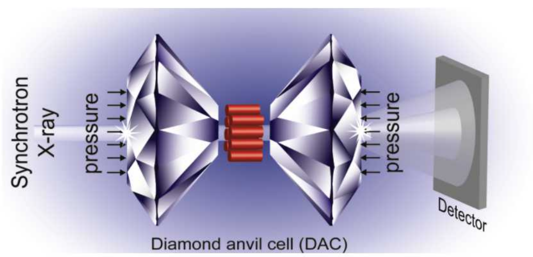
Pressure / compression drives

- Dynamic loading isn't just shock loading

Quasi-static

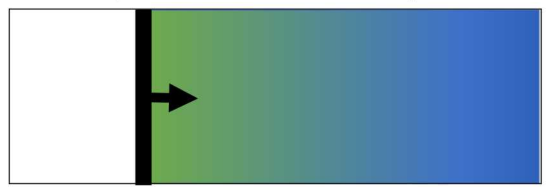


No rise in T

Hydrostatic or directional loading

Lower peak pressures

Ramp/Isentropic loading (invented on Z)

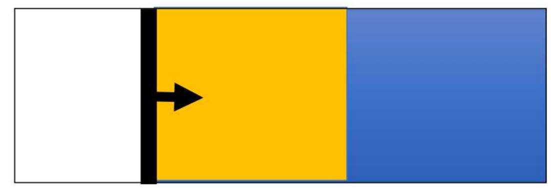


Minimal heating

High pressures

Uniaxial loading

Shock



Significant shock heating
100s to 1000s degrees

Constrained final states

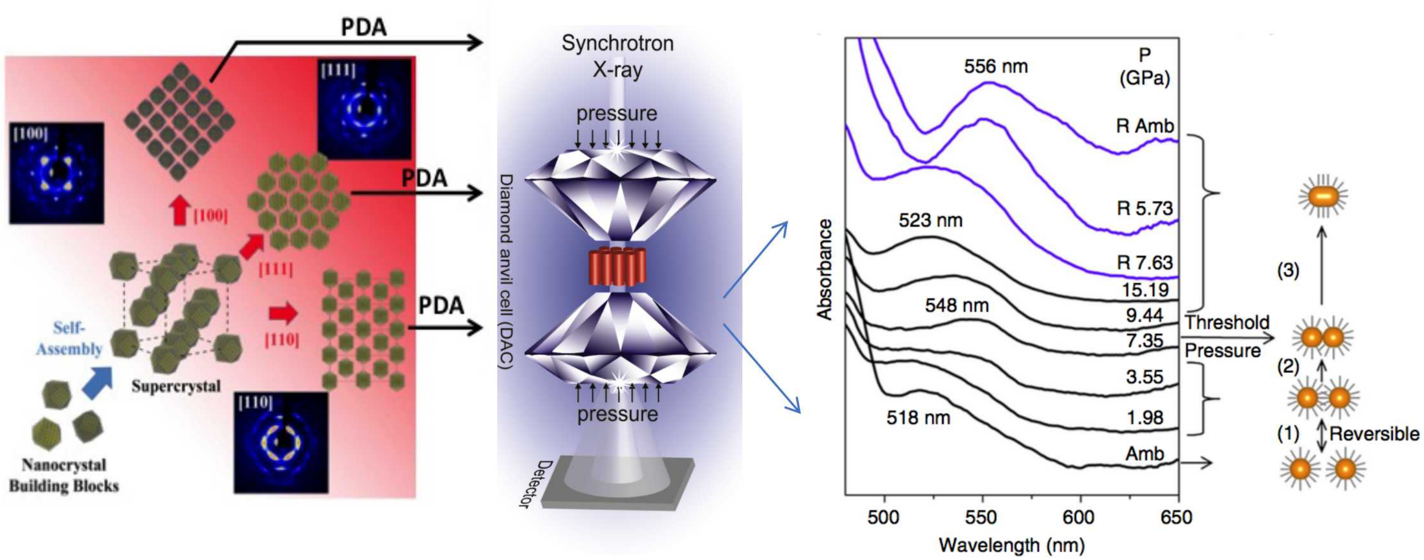
Uniaxial loading

Part I

Synthesis of unique gold nanostructures With dynamic loading on nanosecond time scales

Static pressure-driven assembly

Diamond anvil cells have been used to compress superlattice arrays of ligand coated gold nanoparticles



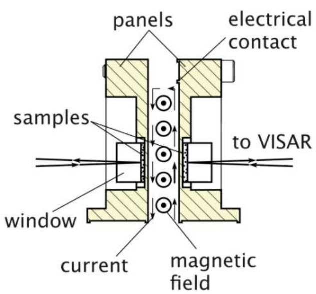
Above threshold pressure of approximately 8 GPa, nanoparticles consolidate into 1D and 3D (e.g., nanorods, nanowires, matrix, etc.)

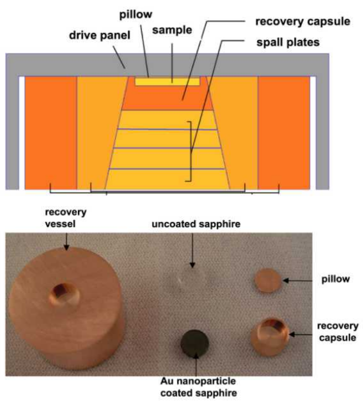
Surface plasmon resonance alters the optical scattering/absorption properties

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

Wu et al., JACS, 132, 12826 (2010)

Dynamic isentropic compression



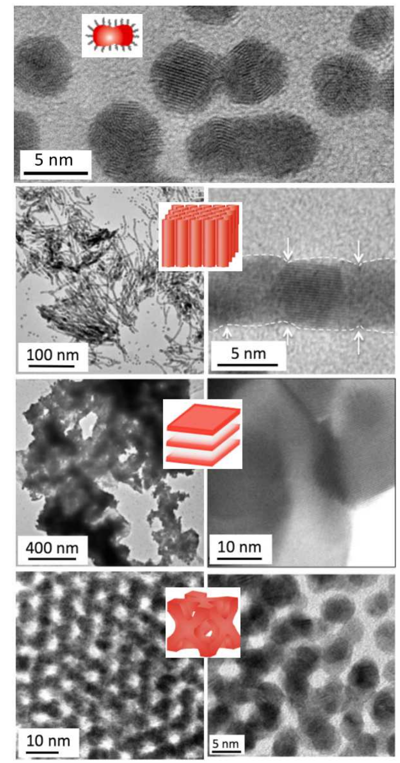


Nanosecond pressure-driven assembly (PDA) has been demonstrated using Magnetically-driven Dynamic Isentropic Compression (DICE) to produce mesoscale nanoparticle assemblies of several geometries.

- The Veloce driver was used to drive pressures to 12 GPa, producing several assembled mesostructures from dynamic uniaxial ramp waves.
- Veloce was fitted with a capture capsule to allow soft recovery of gold samples.

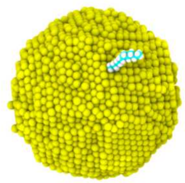
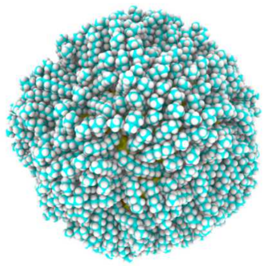
Chantrenne et al., AIP Conf. Proc 1195, 695 (2010)

The success of this dynamic compression experiment in producing a variety of gold nanostructures, without initial hydrostatic loading, and at nanosecond timescales challenged some assumptions. But, opened the door to using molecular simulations to better understand the link between loading, and particle/coating properties on the final structures.



Li, Bian, Lane, Salerno, Grest, Ao, Hickman, Wise and Fan, Nature Comm., 8, 14778 (2017)

MD approach: nanoparticle superlattice

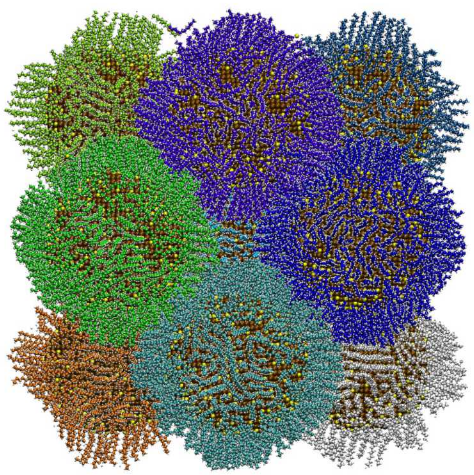
Hierarchical complexity

Coated Nanoparticle

- 5.9 nm diameter solid gold core
- Attach 515 hydrocarbon ligands $S\text{-}(CH_2)_{11}CH_3$
  - Full coverage at 4.7 chains per nm^2
  - Mobile ligands w/ 10 kcal/mol binding strength

Nanoparticle superlattice

- 96 nanoparticles in fcc lattice - 2.5 million atoms
- Core-core center separation of 7.6 nm



Heterogeneous hard/soft sample

Analogies to atomic systems

Complex NP interactions mediated by soft material

Interatomic potentials vetted for high pressure

- Embedded atom method (EAM) for gold cores,

Foiles et al, Phys Rev B, 33, 7983 (1986)

- Exp-6 modified OPLS for hydrocarbons
  - bonds, angles, dihedrals and coulomb

Jorgensen et al., J. Am. Chem. Soc. 118, 11225 (1996).
Siu et al., J. Chem. Theory Comput. 8, 1459 (2012).

- Morse interactions for sulfur-gold surface

Luedtke, Landman, J. Phys. Chem. b 102, 6566 (1998).

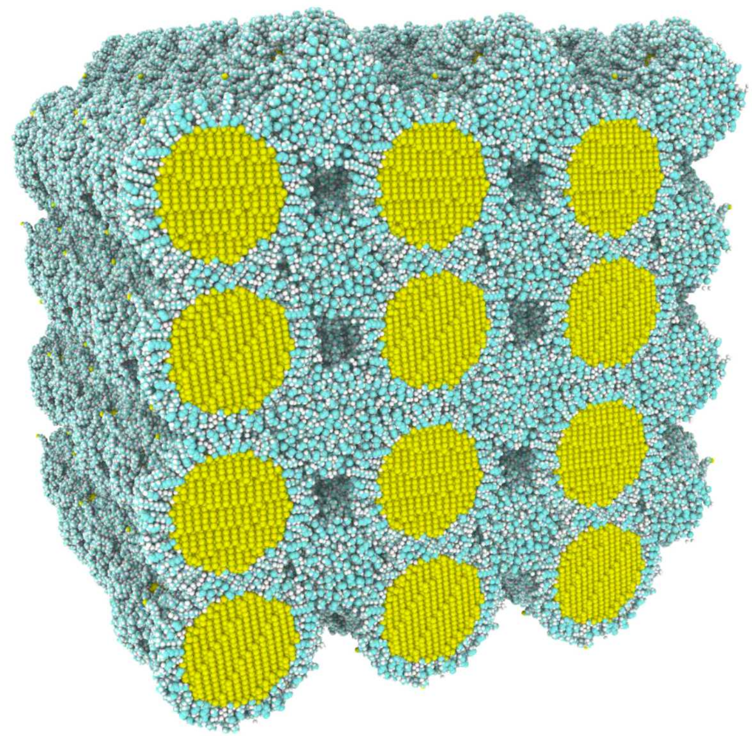
MD approach: dynamic loading

We load the superlattices uniaxially along three different orientation [100], [110] and [111]

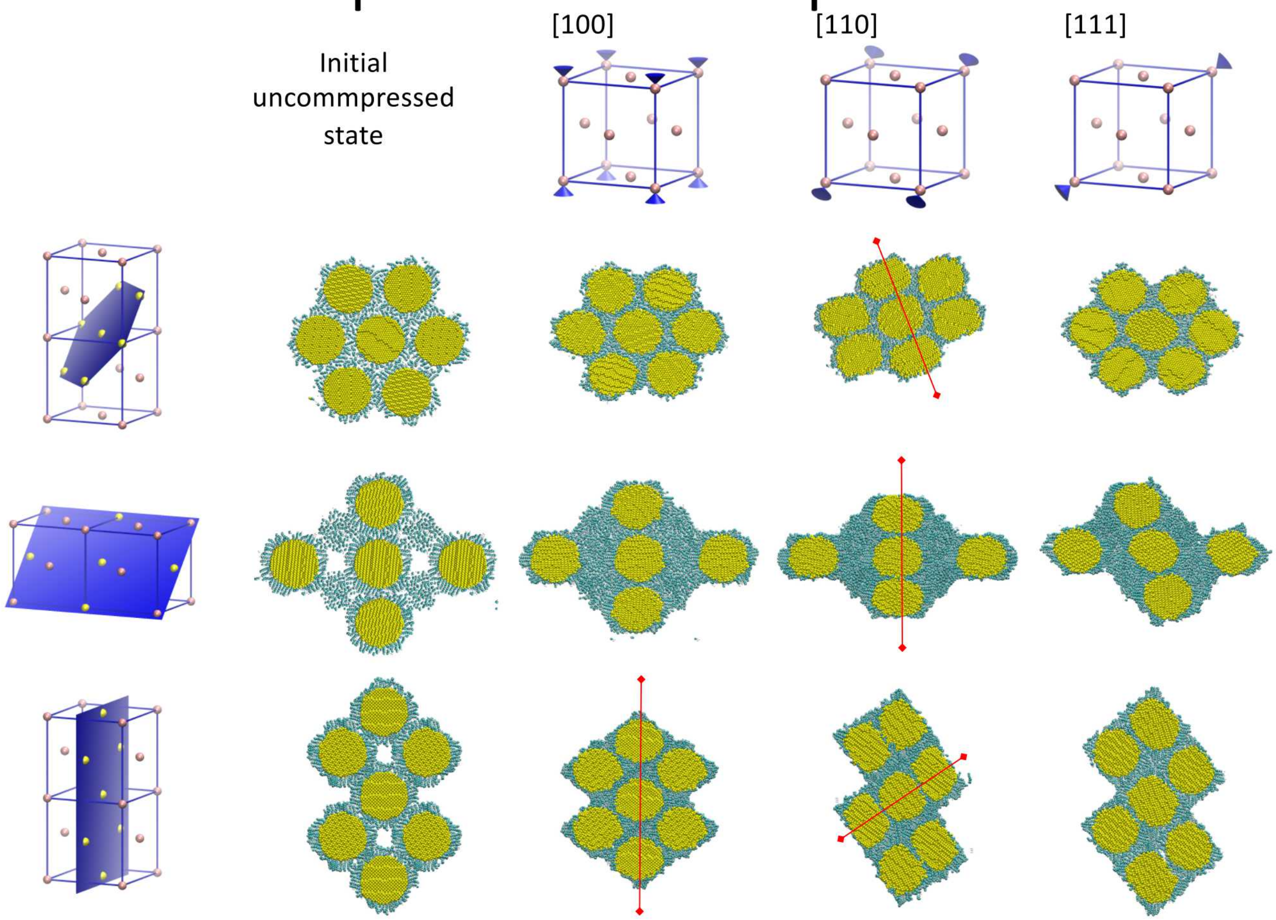
We initially used a Hugoniostat method, but then confirmed the results with isothermal ramp compression

Like hard spheres initial structures are not fully dense. As the loading progresses the ligands deform to fill space as pressure increases.

Ultimately, the gold cores contact and sinter to form continuous gold structures in 1D, 2D and 3D depending on compression orientation.



Orientation dependent response



Nearest Neighbor analysis

Initial fcc = 12

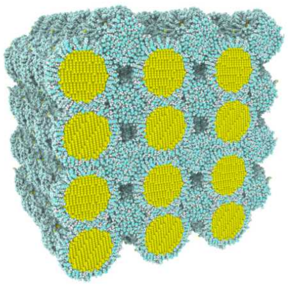
[100] -> 8

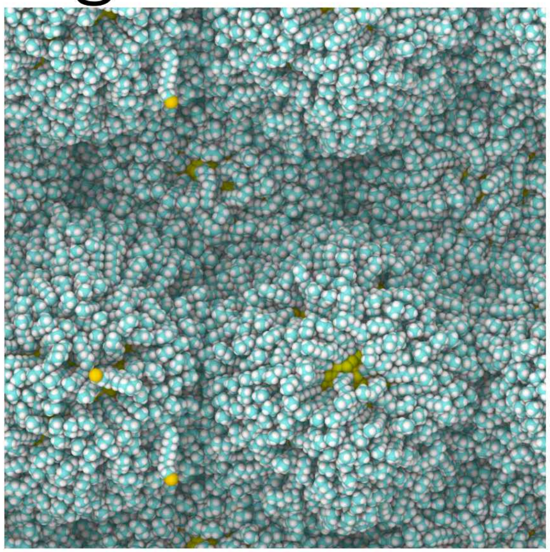
[110] -> 2

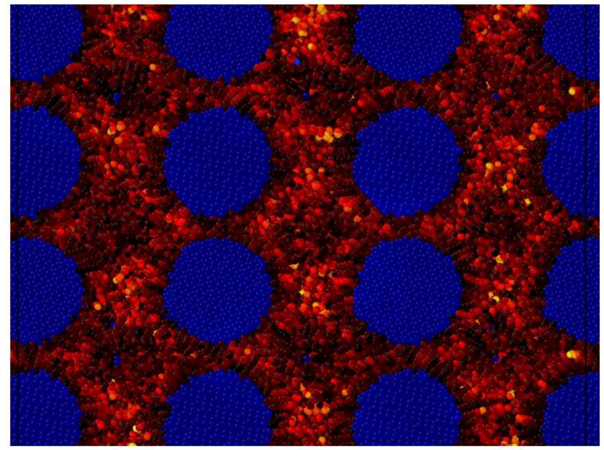
[111] -> 6

Li, Bian, Lane, Salerno, Grest, Ao, Hickman, Wise and Fan, Nature Comm., 8, 14778 (2017)

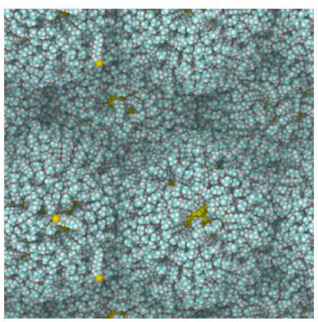
Ligand migration at contact points



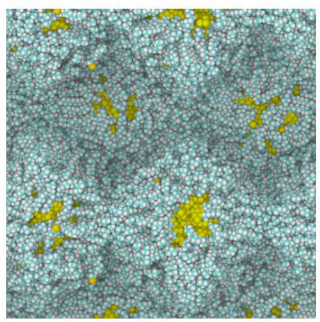




0 GPa



7.5 GPa



Ligands are pushed laterally from between the gold cores, but not pulled from the gold surface

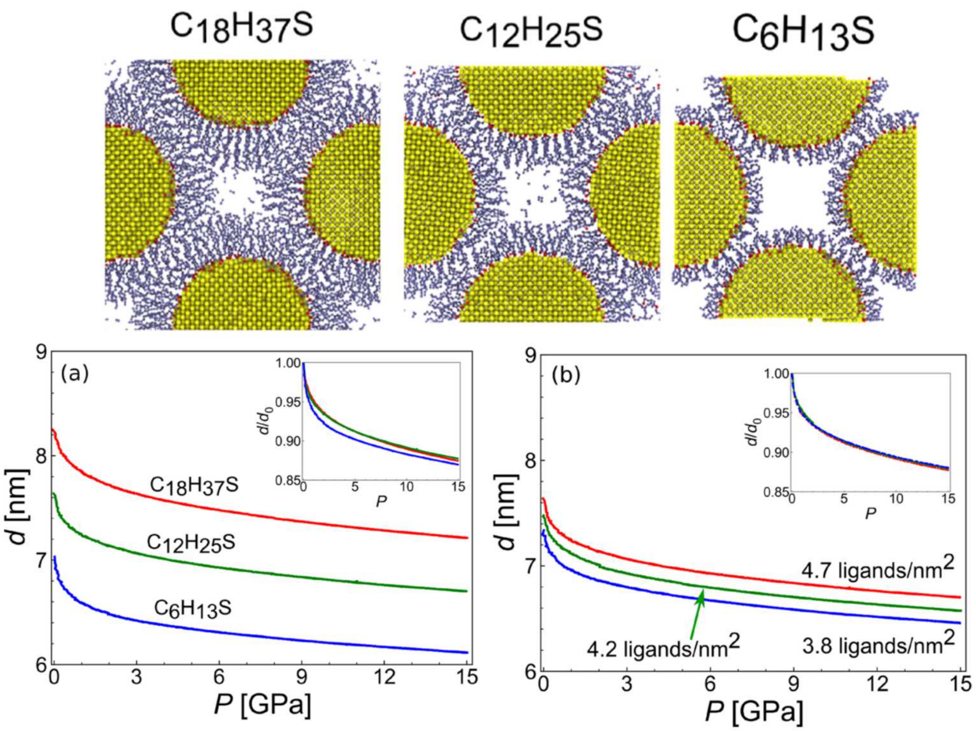
Some crystalline alignment is observed

At the highest pressures, the gold cores are also deformed, laterally

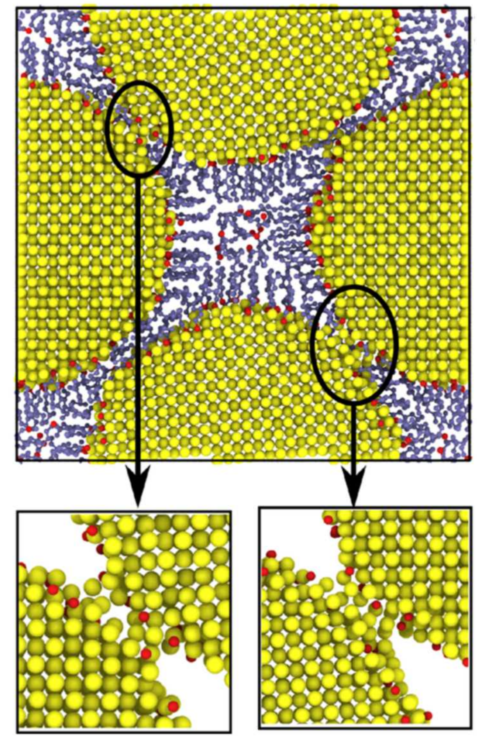
Lane, Salerno, Srivastava, Grest, Fan,
AIP Conf. Proc. 1979, 090007 (2018)

Further hydrostatic studies

In **Srivastava, et al., J. Phys. Chem. C 123, 17530 (2019)**, we report systematic study of moduli, and compaction processes as a function of chain length and grafting density under hydrostatic compression



Showed 3D sintering even in pure hydrostatic loading for the shortest chain lengths



Sintering conclusions and on-going work

- Our simulations reproduce the various sintered structures from experiments (1D, 2D and 3D) and unambiguously tie each structure to the initial orientations between loading and lattice.
- Significant deformation is seen in the ligand coatings in order to fill space. These vary significantly with loading direction.
- Significant surface mobility at contact points, but ligand chains are not pulled from the nanoparticle surfaces on these timescales.
- Uniaxial compression is key to sintering, for all but the shortest chain lengths.

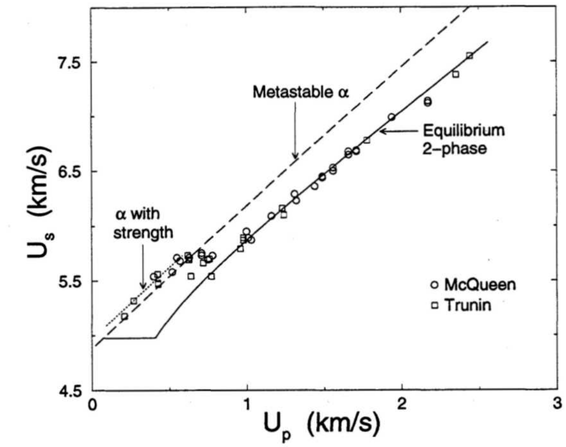
Part II

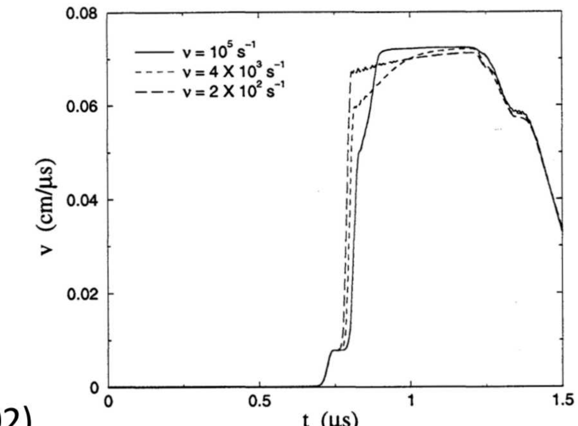
Dynamic phase transition in nanoparticle CdS

Motivation for transition kinetics

- Phase metastability in high-rate pressure-induced transitions is a daunting but important problem
- Depends on materials and nature of transitions
  - Materials microstructure
  - Orientation
- Improved understanding of the interplay between time and length scale in phase transitions.
- Using nanoparticle arrays as a model system

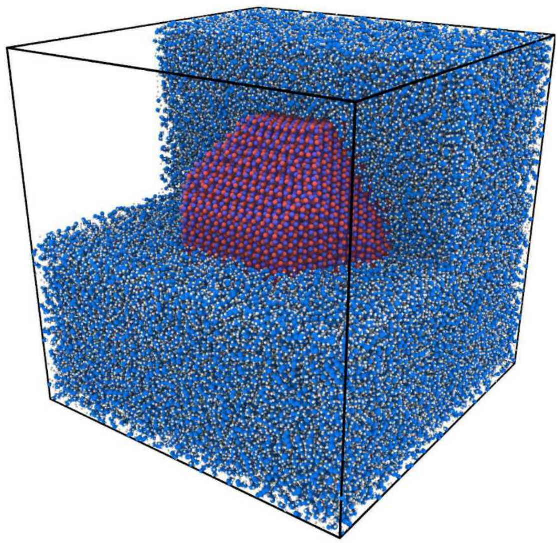
Titanium



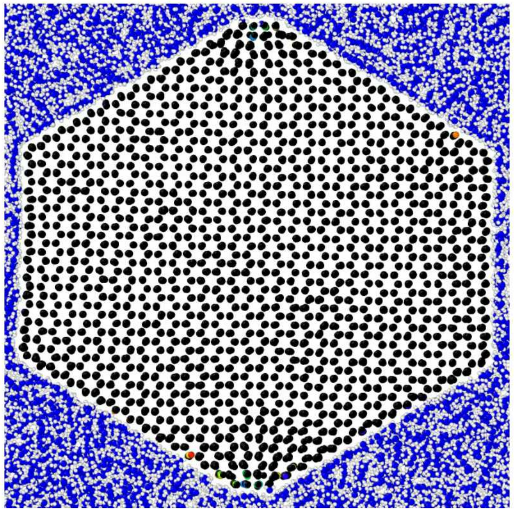


C. W. Greeff, D. R. Trinkle and R. C. Albers, SCCM (2002)

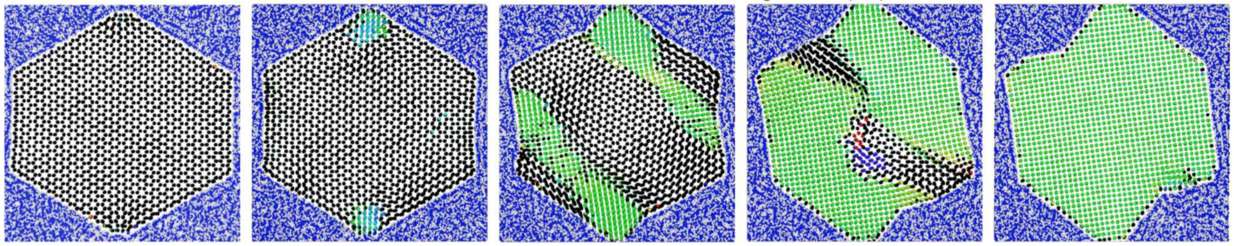
Modeling length scale effects



Nanoparticle compression is modeled with faceted CdS nanoparticles embedded in a decane pressure medium.

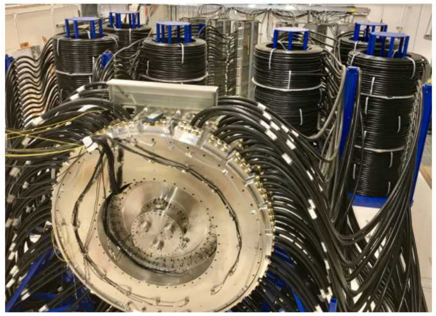


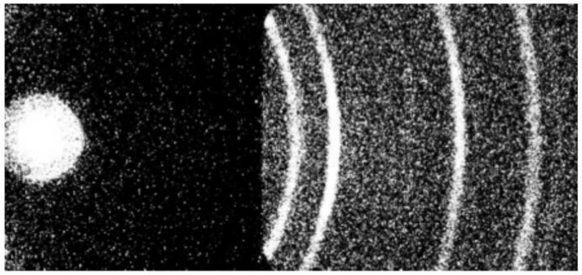
Transition mechanisms are difficult to separate in this geometry.



Broad project goals

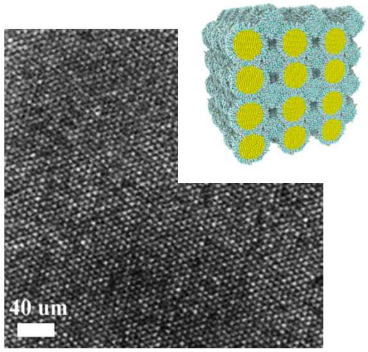
1. Careful control of loading and ramp profile:
   A pulsed power driver at Sandia, Thor.





2. Diagnostics for phase transition identification: Implement a platform-independent X-ray diffraction (XRD) diagnostic capable of analysis in a variety of materials, VISAR and PDV.

3. Careful control of length scale: Introduce a “synthetic material target” which allows for the careful control of length scale to study the combined effect of rate and scale on transition kinetics



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Control of rate: Thor driver, new diagnostic

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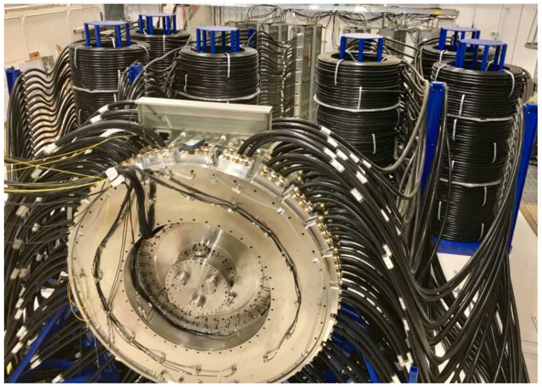
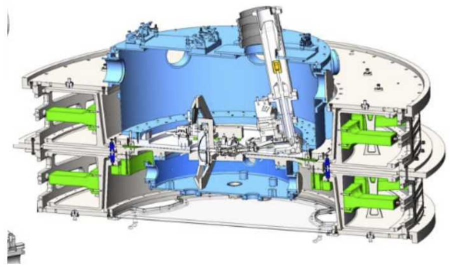
Thor is a pulsed-power accelerator similar to Z, which can drive ramp waves to **pressures of approximately 25 GPa** in its current 64 brick configuration.

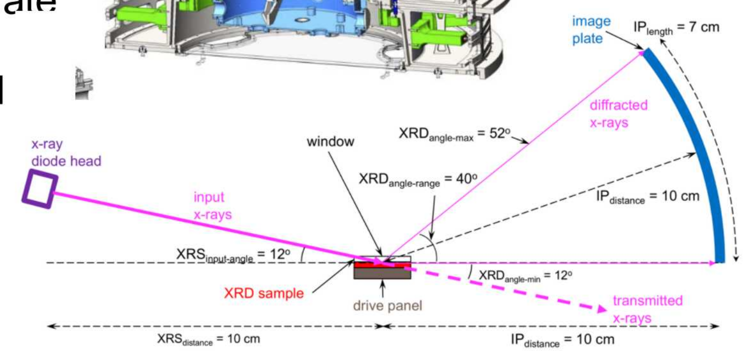


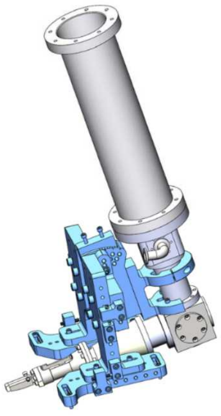
Thor can be configured like Z but with lower peak pressure, but better pulse shaping
Careful control of ramp profile

- Adding X-ray diffraction diagnostic to existing velocimetry (VISAR & PDV)

- NSTec Supersaver (x-ray diode) to generate line emission from molybdenum metal anodes.



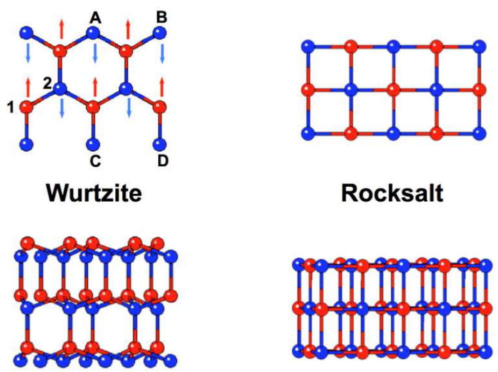




Specifications:
- 17.48 keV from Mo-K-α
- 20 – 30 ns duration flash
- Expect 10^8 to 10^9 photons incident on the diffraction sample
- Good penetration of 20-50 um, allows high-Z targets
- Image plate for most shots, could be replaced with CCD

Phase transition kinetics in CdS

Pressure-induced Cadmium Sulfide (CdS) phase transition from Wurtzite to Rocksalt at ~2-3 GPa



Highly-coordinated military rearrangement

Transition kinetics depend strongly on the crystal orientation

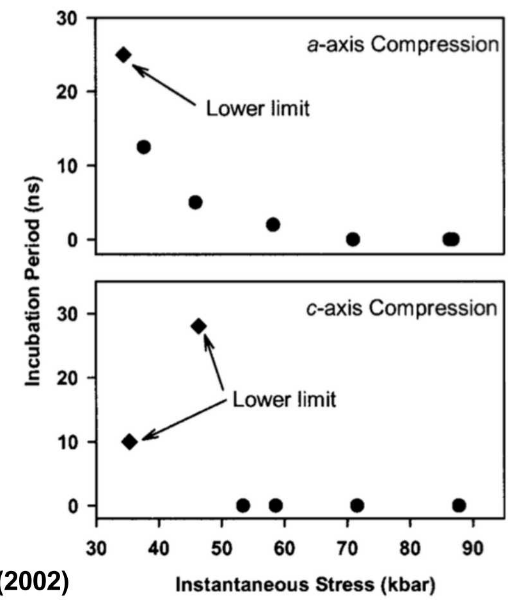
Measurements of the two-step transition, with fast, time-resolved spectroscopy showing the first step is sub-ns

Knudson, Gupta, Kunz. Phys. Rev. B, 59, 11704 (1999)
Knudson, Gupta. Phys. Rev. Lett., 81, 2938 (1998)

At higher pressures transitions are effectively immediate, but at lower pressures there is an "incubation" time for the transition which is different for different orientations.

In a-axis orientation, inelastic deformation is observed before the onset of the phase transition which may influence the mechanism

Second step in transition is delayed depending on peak stress



Knudson, Gupta, J. Appl. Phys. 91, 9561 (2002)

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Modeling motivation and methodology

Interatomic Potential for CdS (Rabani et al., 2012)

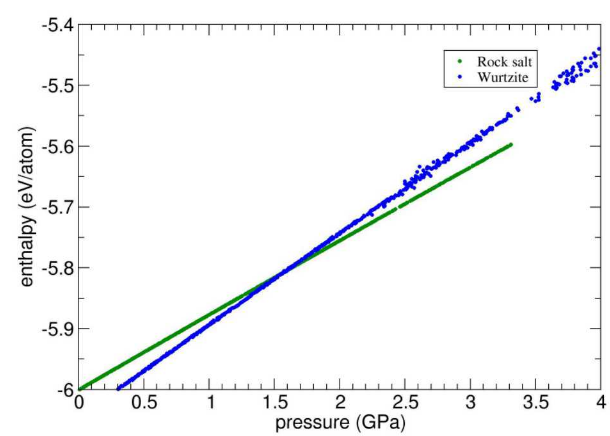
LJ-type with long-range electrostatics, fit to elastic constants

$$V_{ij} = \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right\}$$

	Exp.	MD	Δ
$P_{W\text{->}RS}$ (GPa)	2.5 - 3.2	1.6 - 3 - 11.5	
Wurtzite			
a (Å)	4.13	4.16	1%
c (Å)	6.70	6.59	2%
B (GPa)	65.0	55.2	-15%
Rock salt			
a (Å) P=0	5.44	5.43	0%

- Stable Wurzite and Rocksalt
- Potential predicts both phases and the dynamic transition

- Hugoniostat methodology to allow long-time simulations of shocked states (Ravelo et al., 2004)



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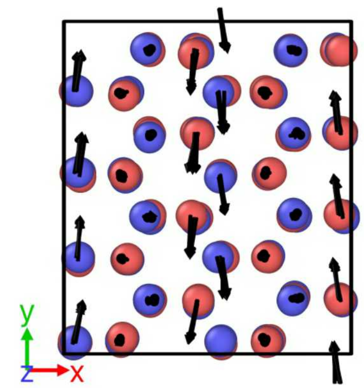
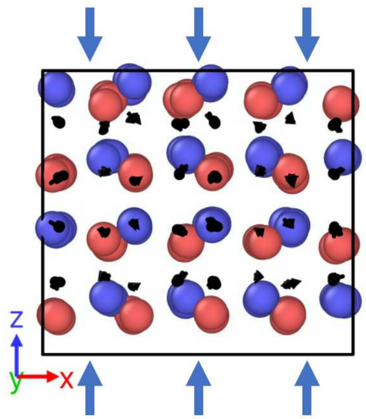
Orientation-dependent mechanisms c-axis

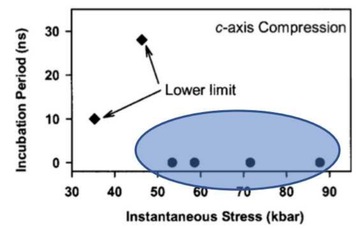
(High-pressure regime – shear activation)

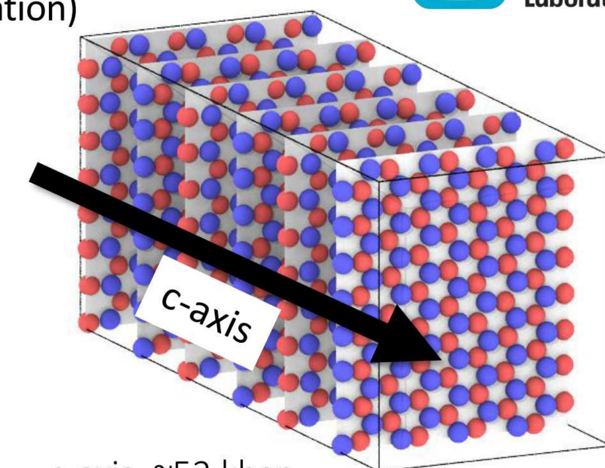
Solid-solid pressure-induced phase transitions have been studied in bulk geometries and for military (Martensitic) transformations in dS.

c-axis compression:



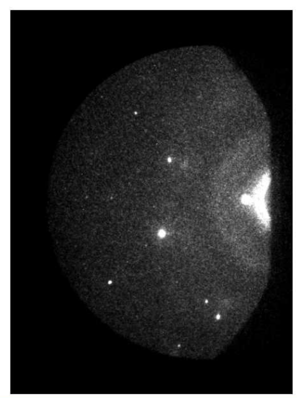




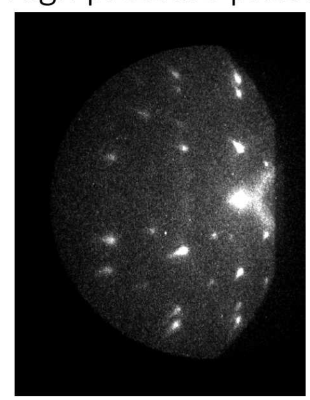


c-axis, ~52 kbar

Ambient phase



High pressure phase



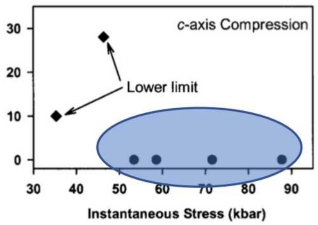
Knudson, DCS exps.

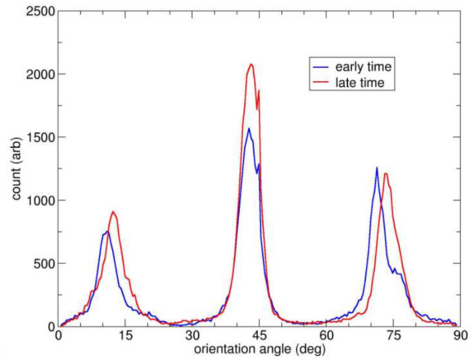
c-axis:

- alternating plane shift along y when compressed along z.
- no observed rate dependence
- final state rocksalt rotated 45 in x-y plane

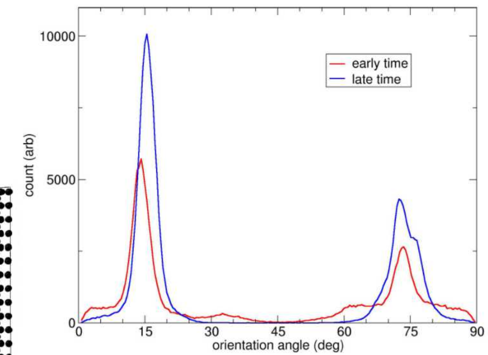
Displacement vectors show non-affine displacement

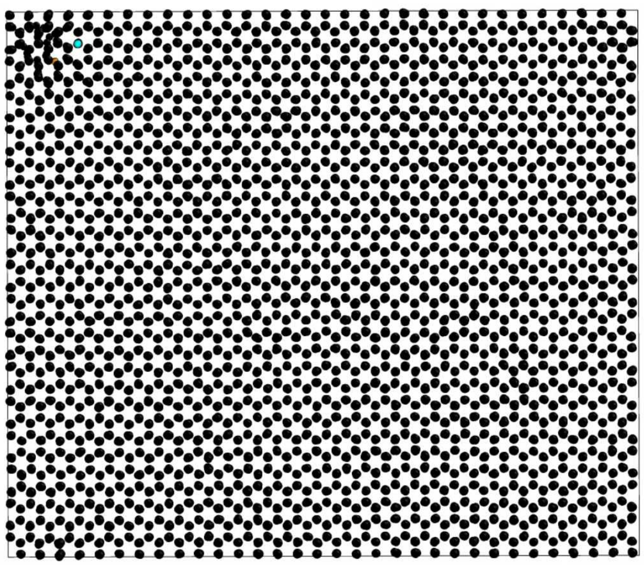
Orientation-dependent mechanisms c-axis



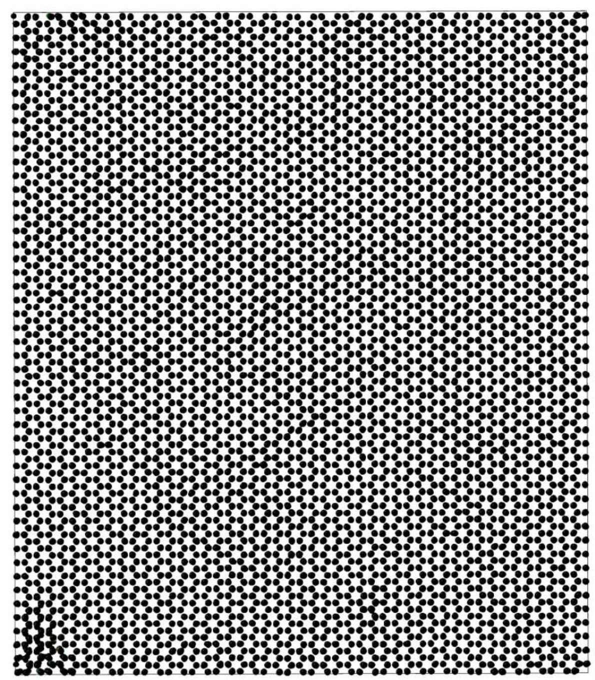


High-pressure regime – shear activation





Three orientations Identified and confirmed with experiment.



There is a local competition between between the orientations

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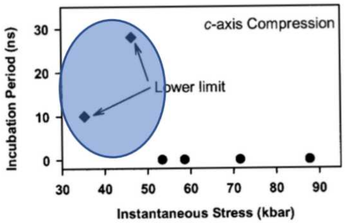
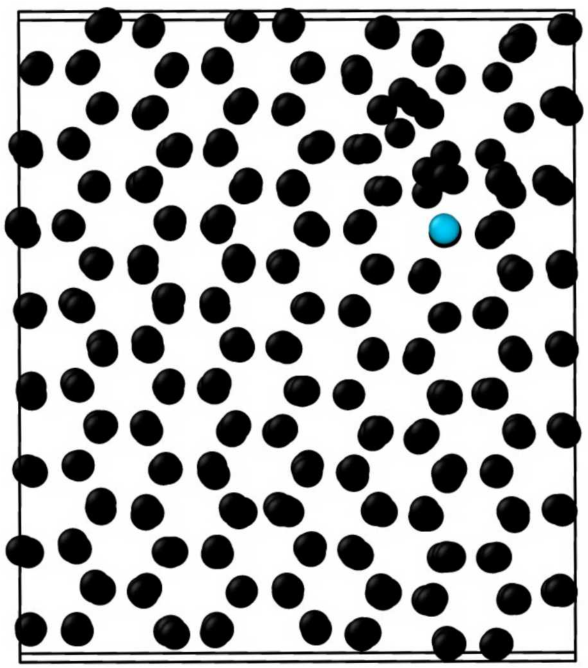
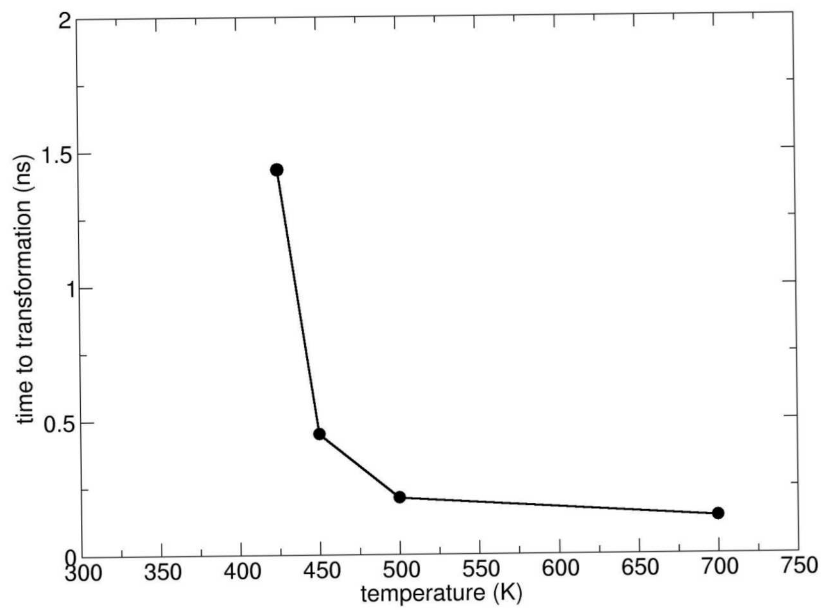
Orientation-dependent mechanism c-axis

Low-pressure regime – thermal activation



Sluggish "incubation" time followed by a rapid transition. Different mechanism and final orientations.



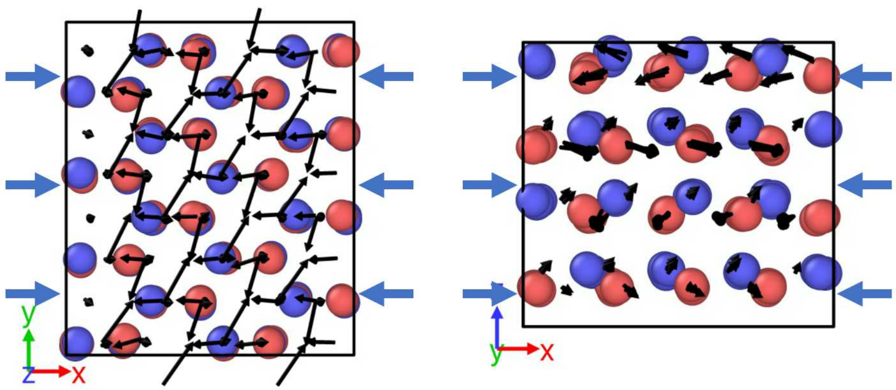


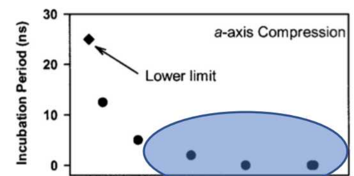
Orientation-dependent mechanisms a-axis

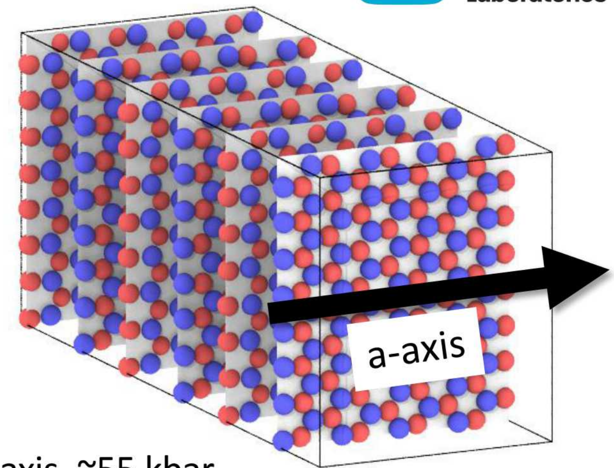
Sandia National Laboratories

Solid-solid pressure-induced phase transitions have been studied in bulk geometries and for military (Martensitic) transformations in CdS.

a-axis compression:



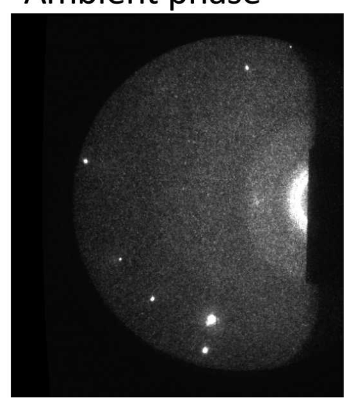




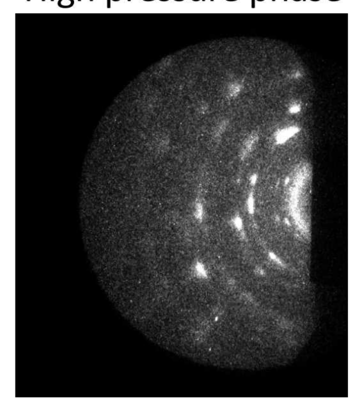
a-axis, ~55 kbar

- Diagonal alternating shifts of individual atoms when compressed along x.
- lower rates lead to lower transition pressure
- final state rocksalt rotated 9 degrees in x-z plane

Ambient phase



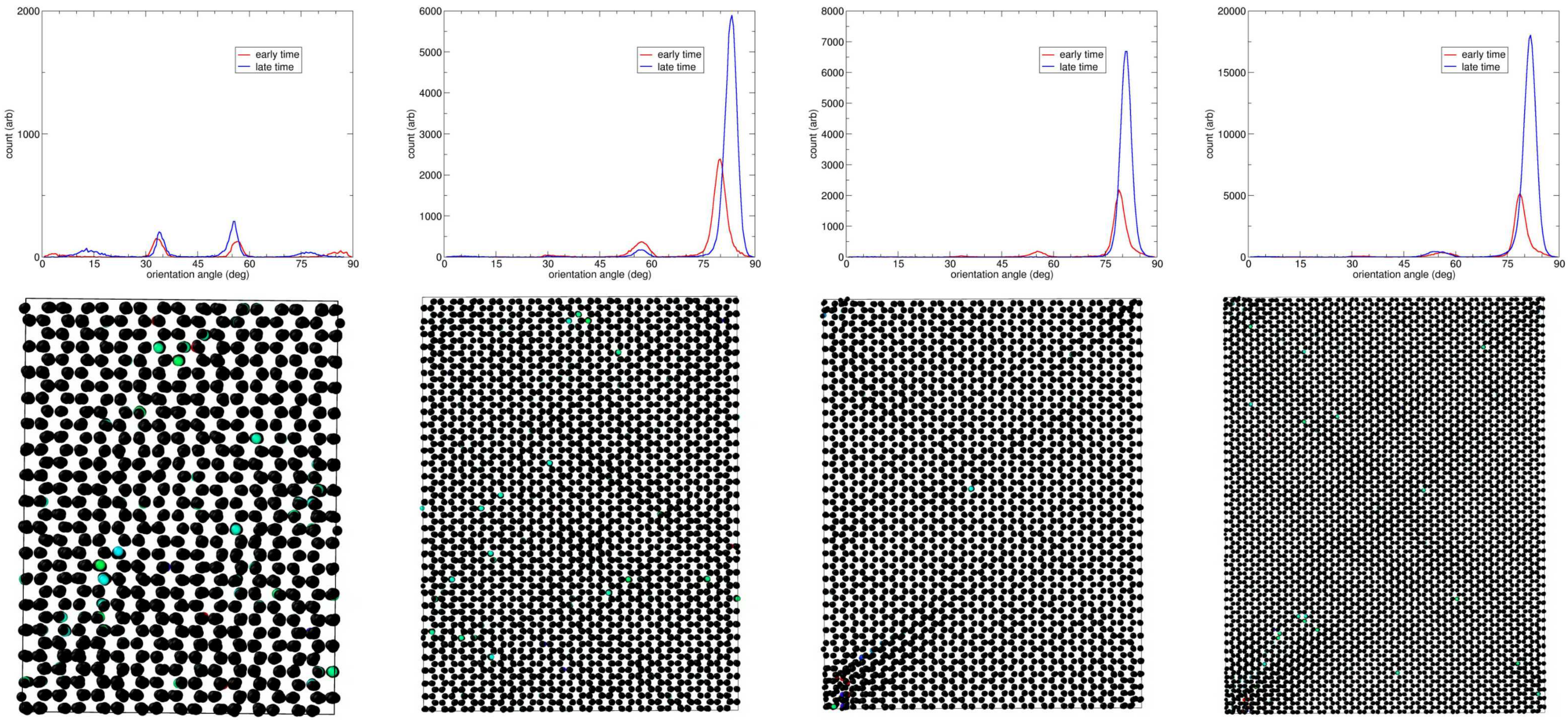
High pressure phase



Knudson, DCS exps.

Displacement vectors show non-affine displacement

Orientation-dependent mechanisms a-axis



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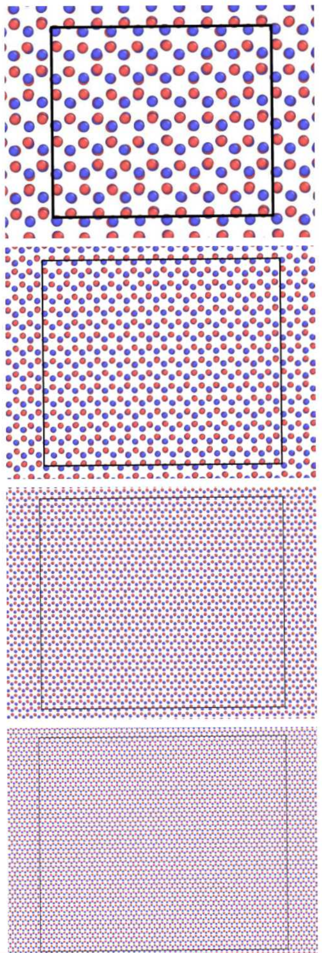
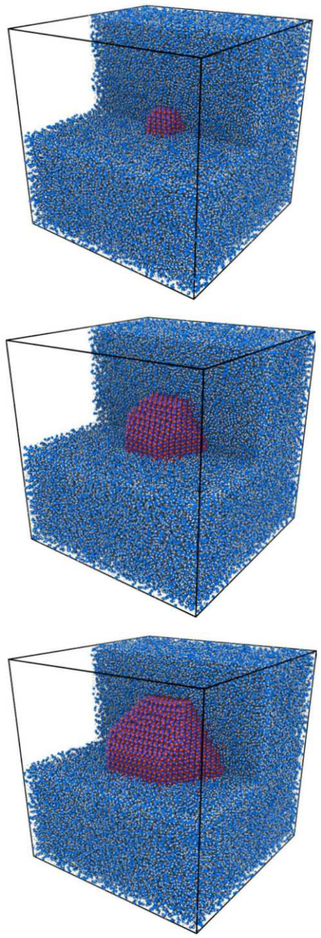
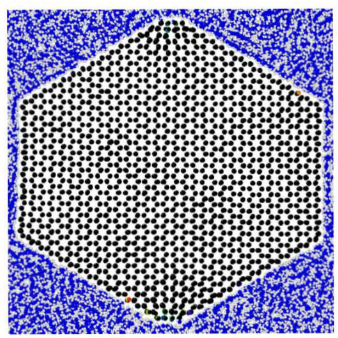
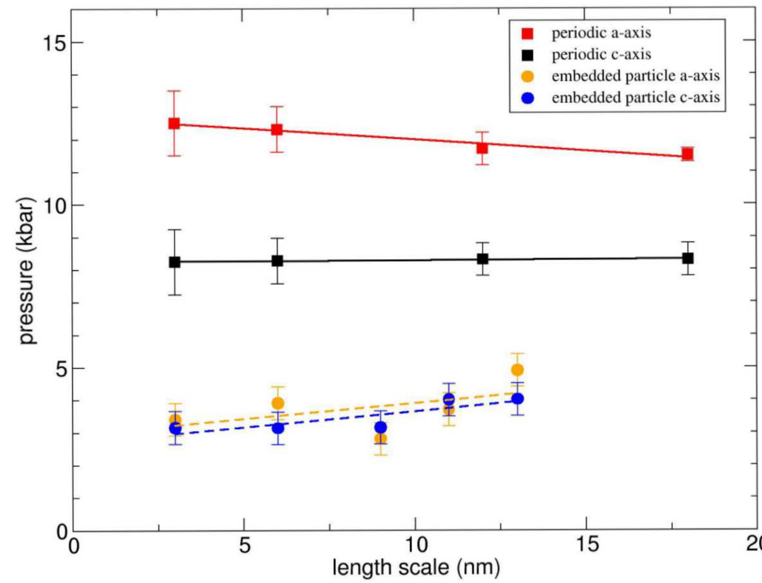
Modeling length scale effects





Length scale can be controlled with and without introducing surface. We see difference trends





Orientation pressure thresholds are reduced for cut nanoparticle which bodes well for randomly oriented films.

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Conclusions and direction

- We are conducting a combined experimental and modeling effort to explore the interplay between length and time scales in phase transitions within a carefully controlled model system
- We've identified transition mechanisms and orientations resulting from c-axis and a-axis compression in CdS
- Modeling results indicate different trends for homogeneous and surface nucleation as a function of length scale
- Future: Integration of experimental results and modeling

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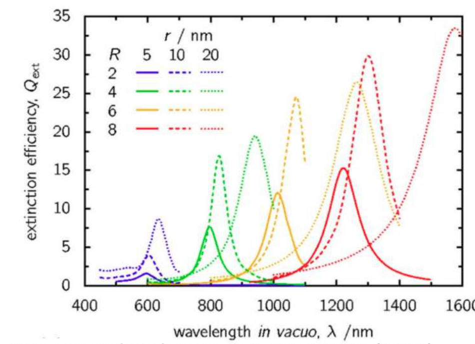
Properties of nanoparticle assemblies

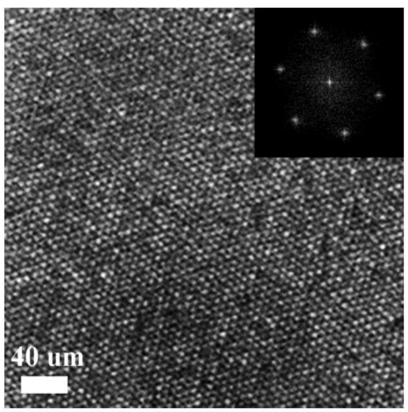
Nanostructured gold and gold nanoparticle arrays are used in photonic crystals and exhibit unique optical properties due to surface plasmon resonance (SPR).

Surface plasmon resonance alters the optical scattering/absorption properties
Applications: environment sensors, nanoelectronics and photonic materials.

In superlattices of spherical nanoparticles, SPR coupling gives absorption spectra which vary with inter-particle spacing, size, and shape.



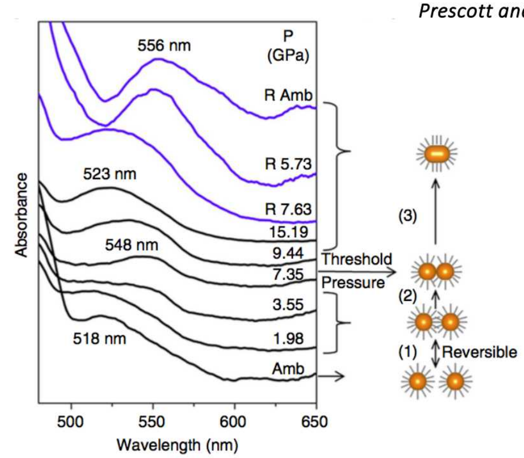
Prescott and Mulvaney, JAP, 99 123504 (2006)



Wu et al., JACS, 132, 12826 (2010)

Pressure-driven response

Below threshold pressure, the interparticle spacing and resulting surface plasmon coupling were systematically and reversibly tuned.



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

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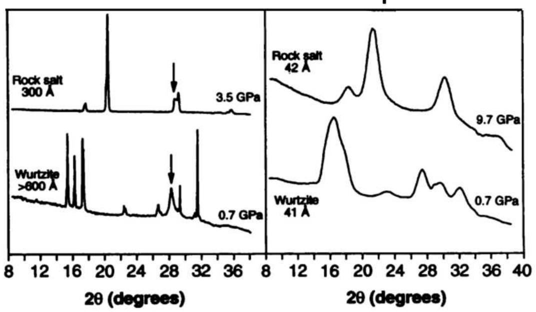
Control of length scale: “synthetic microstructures”

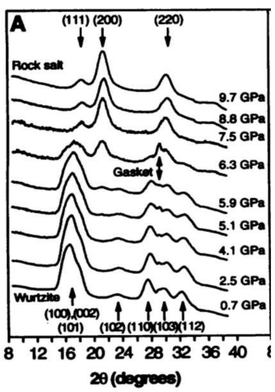
Bulk Nano spheres

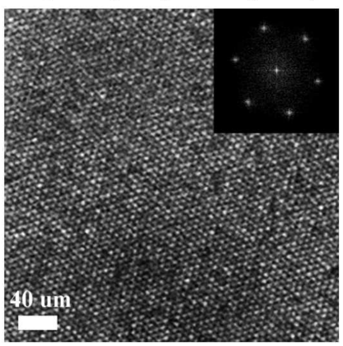


XRD data delineates the transition clearly

Tolbert, Alivisatos, Science, 265, 373 (1994)

Wu et al., JACS, 132, 12826 (2010)





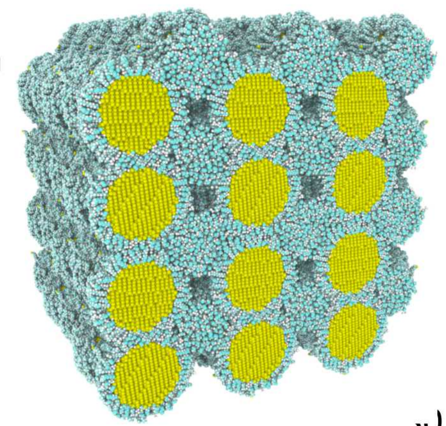
We can create a “synthetic microstructure” by leveraging the synthesis and assembly processes to create well-characterized films.

These nanoparticle films **mimic some aspects of grain structure** microstructure, but with better (monodisperse) size control.

- Coated spherical monodisperse particles
- Particles from 2 to 50 nm in diameter, initially
- Well-ordered fcc super lattice structures

A particle size dependence of the phase transition has been observed for very small particles

Dynamic compression has been validated with similar arrays of particles (gold), pressures up to 12 GPa were achieved.



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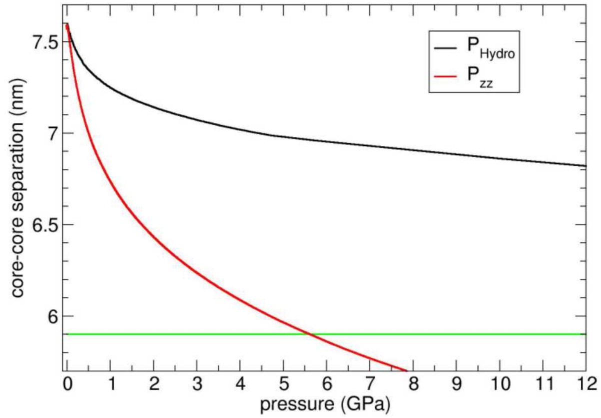
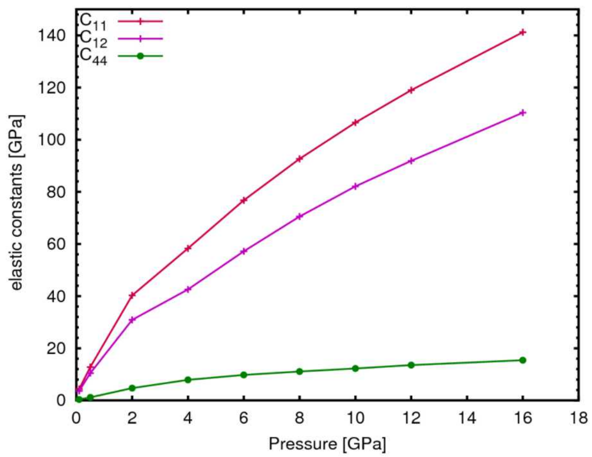
Uniaxial vs hydrostatic deformation



Ju Li et al. had previously shown that sintering requires a deviatoric stress component. We agree that sintering can't result from hydrostatic compression.

Li et al., Nano Letters, 14, 4951 (2014)

Hydrostatic pressures up to >15 Gpa, are reversible and do not lead to sintered nanostructures in simulations.



The elastic constants increase with applied hydrostatic pressure, which can stabilize the superlattice.

At our rates, we do not observe a need to overcoming a critical hydrostatic pressure before linear nanowires can be formed. However, this may be a result of our loading rates.

Control of final nanostructures?

What controls do we have on the symmetry and dimensionality of our final structures?

- Orientation of superlattice, loading direction, and perhaps even gold lattice
- Ligand density, length, and grafting strength
- Pressure thresholds and need for hydrostatic vs. uniaxial compression