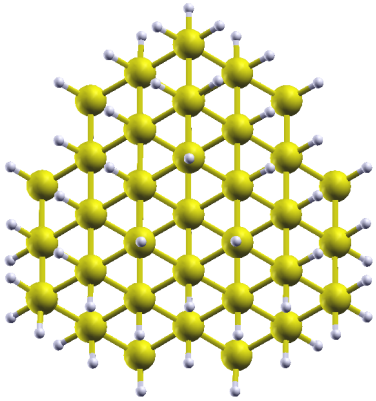
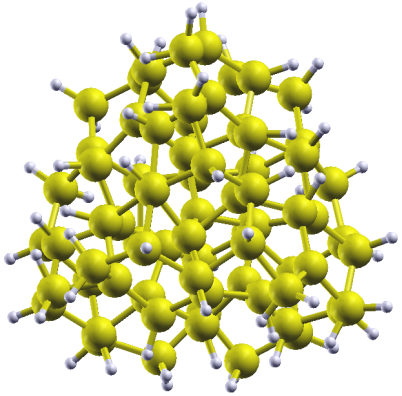
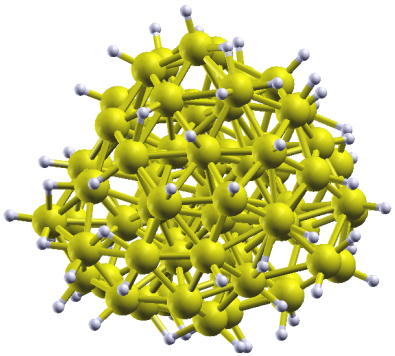
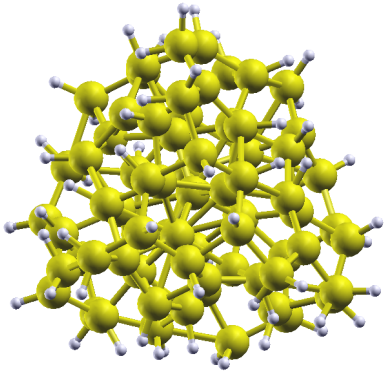




Pressure-induced structural transformations in nanomaterials: a linear-scaling DFT investigation

Niccolò Corsini[1], Peter Haynes[1], Carla Molteni[2] & Nicholas Hine[3]
Imperial College London[1], King's College London[2] & Cambridge University[3]

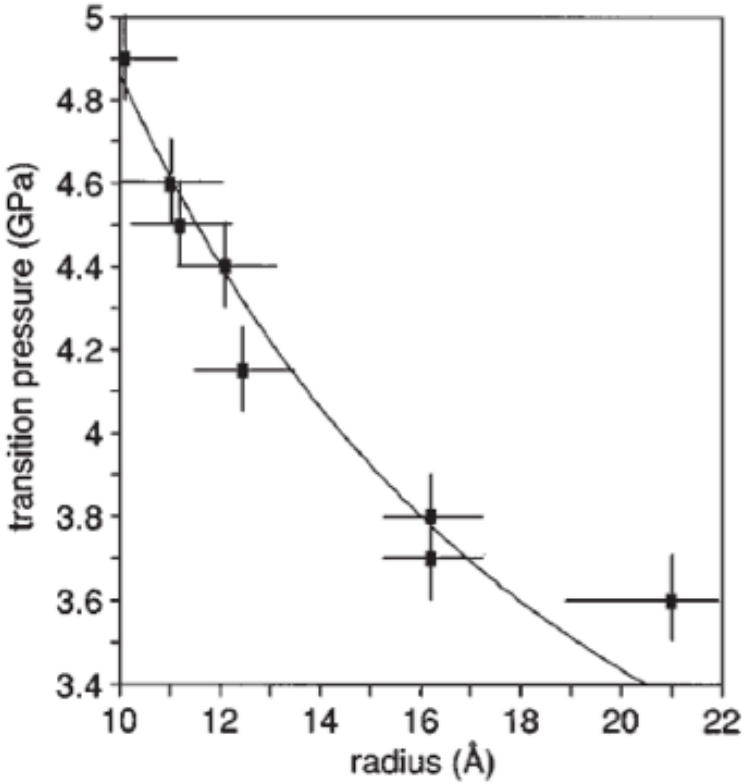




Available on J. Chem. Phys. **139**, 084117 (2013)

Motivation

- Nanocrystal size and surface add extra dimensions to phase diagram



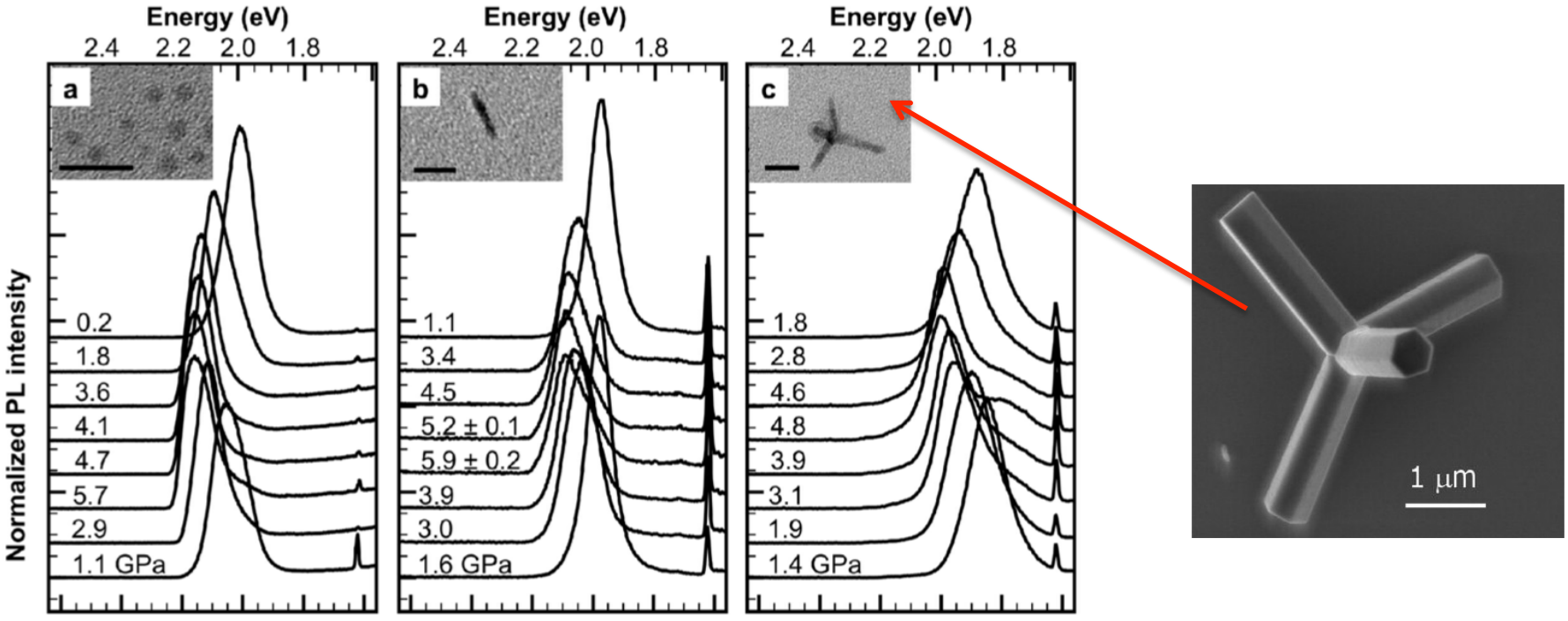
← CdSe WZ/RS nanocrystals

Tolbert and Alivisatos, J Chem. Phys. 102, 4642 (1995)

Motivation

- Nanocrystal size and surface add extra dimensions to phase diagram
- Ideal model for kinetics of solid-solid transformation
- CdSe/CdS nanocrystal display tunable optical properties
- Can use as nanoscale pressure sensors

CdS/CdSe dots, rods & tetrapods

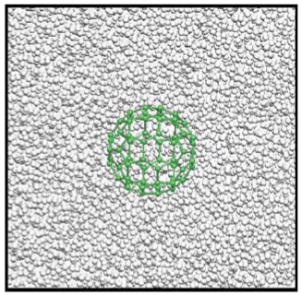


Choi et al, Nano Letters 9.10, 3544-3549 (2009)

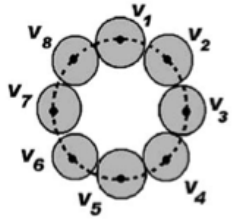
Finite systems under pressure

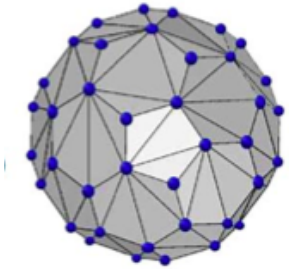
- Two approaches for finite systems :

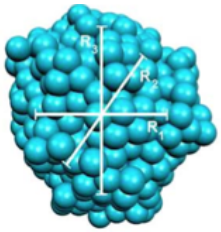
  1) Explicitly describing the pressure transmitting solvent



2) Introduce a PV term after defining volume as a function of atomic coordinates



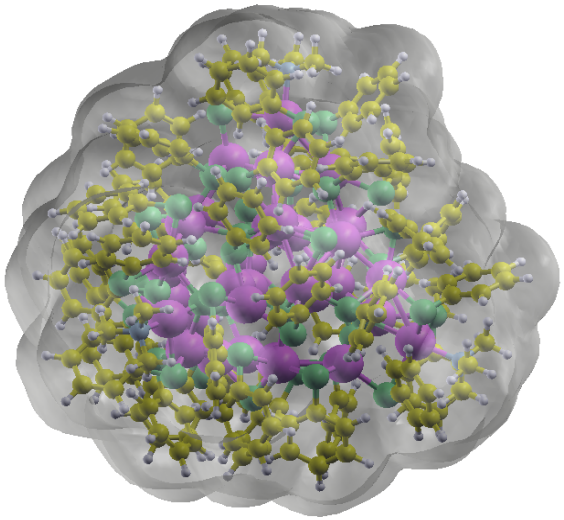




NON PERIODICITY => V DEFINITION NOT UNIQUE

Pictures taken from S. E. Baltazar et al, Comput. Mater. Sci., 2006, 37, 526

Electronic enthalpy method



•Natural to use electronic density to define volume of complex structures

• DFT self-consistent minimization of enthalpy H

$$H[\rho] = U[\rho] + PV_{\mathrm{e}}[\rho]$$

•Electronic volume defined as the interior of a charge isosurface of α density cutoff value

$$V_{\mathrm{e}} = \int \theta(\rho(\mathbf{r}) - \alpha) dr^3$$

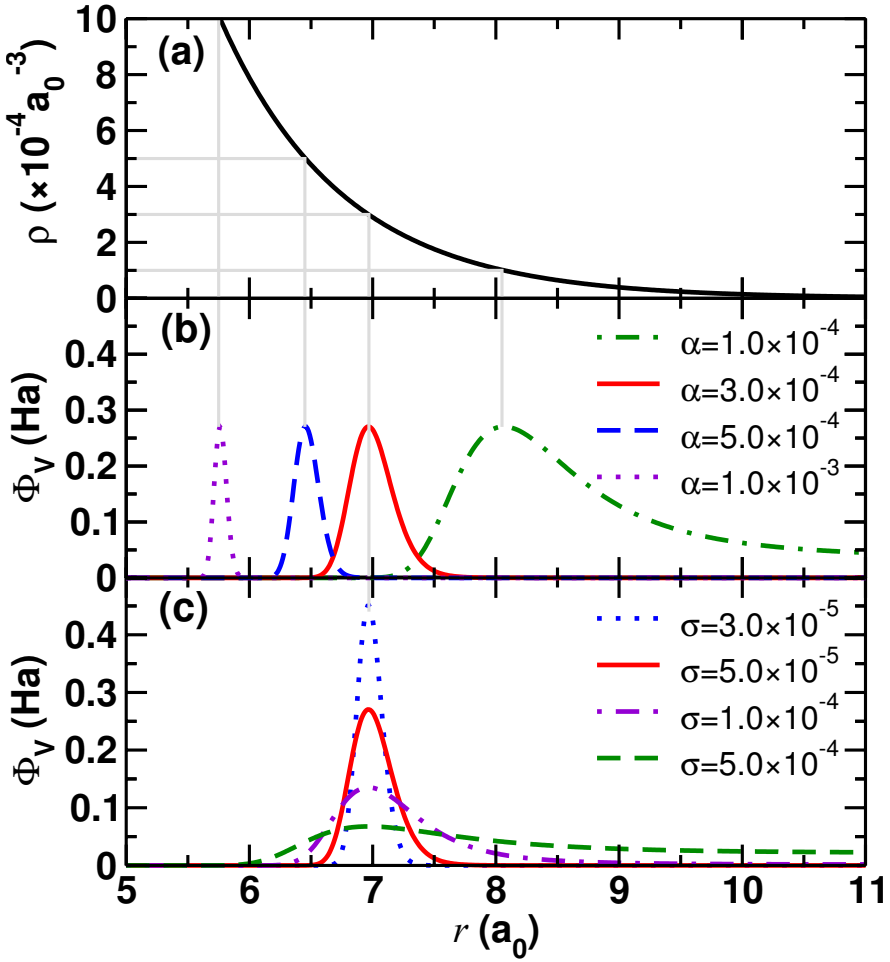
• Step function is smeared by σ for numerical reasons

M. Cococcioni et al, PRL 14, 145501 (2005)

Advantages

- Potential contribution due to PV is simple

$$\Phi_V(r) = P\frac{\delta V_{\mathrm{e}}}{\delta\rho}\Big|_{\rho=\rho(r)} = \frac{P}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(\rho(\mathbf{r})-\alpha)^2}{2\sigma^2}\right)$$



Advantages

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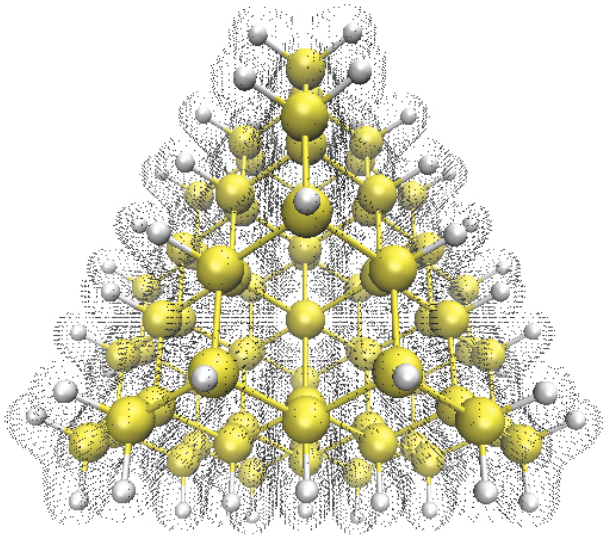
- Pressure field acts directly on electrons

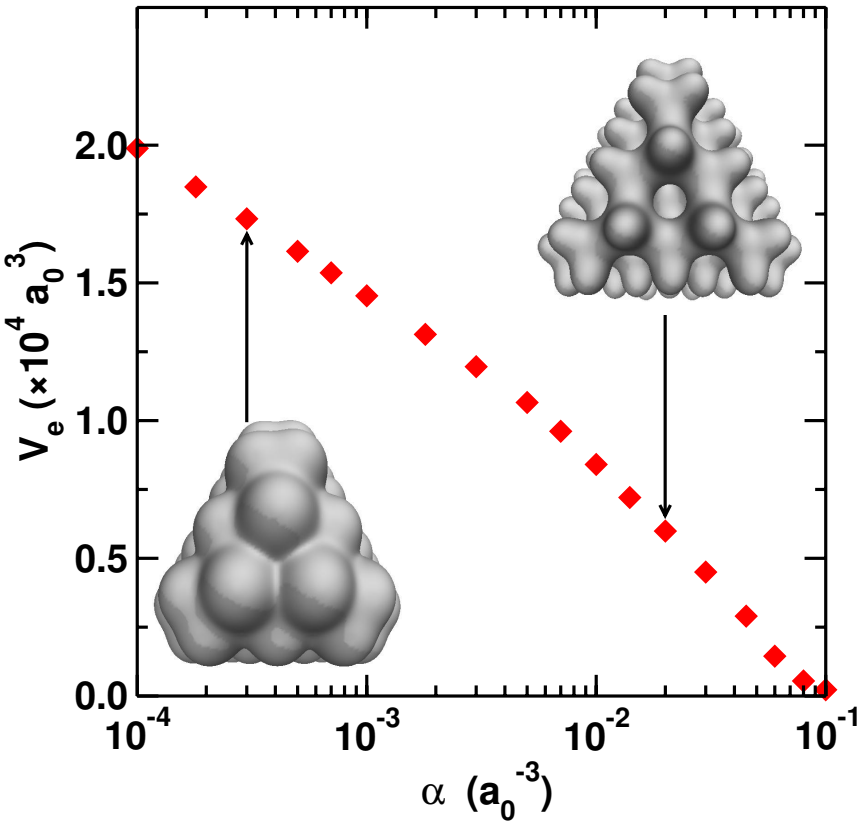
- No need for equilibration with pressurizing medium.

- Efficient compared to other *ab initio* methods

- Gives a homogeneous description of the solvent-nanocrystal interface with α defining the excluded volume of solvent and σ the range/intensity of interaction



$Si_{71}H_{60}$



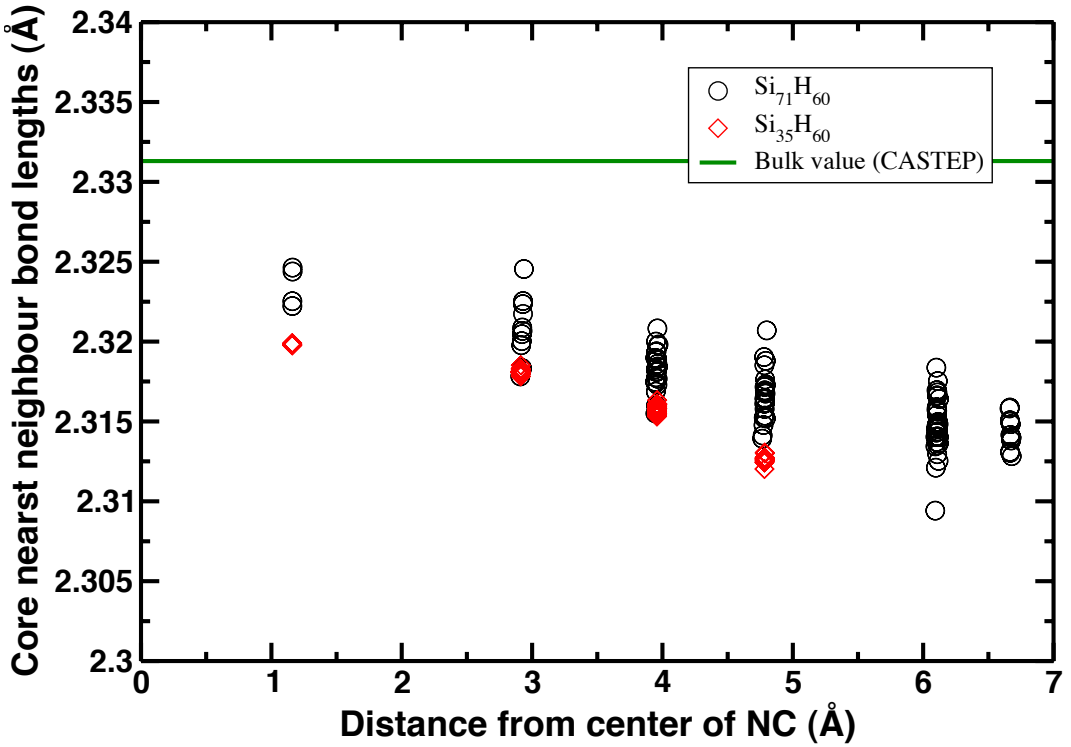
- α needs to be sufficiently large to avoid describing voids and calibrated to correspond to a realistic excluded volume

- σ has to be tuned and needs to be sufficiently large for the potential to be accurately integrated on the grid

Calibration

•If α and σ were chosen correctly, the effective pressure felt inside the nanocrystal should match the input pressure

•Exploit the fact that the core has very similar bond lengths and symmetry compared to the bulk and by virtue of nearsightedness principle similar elastic properties

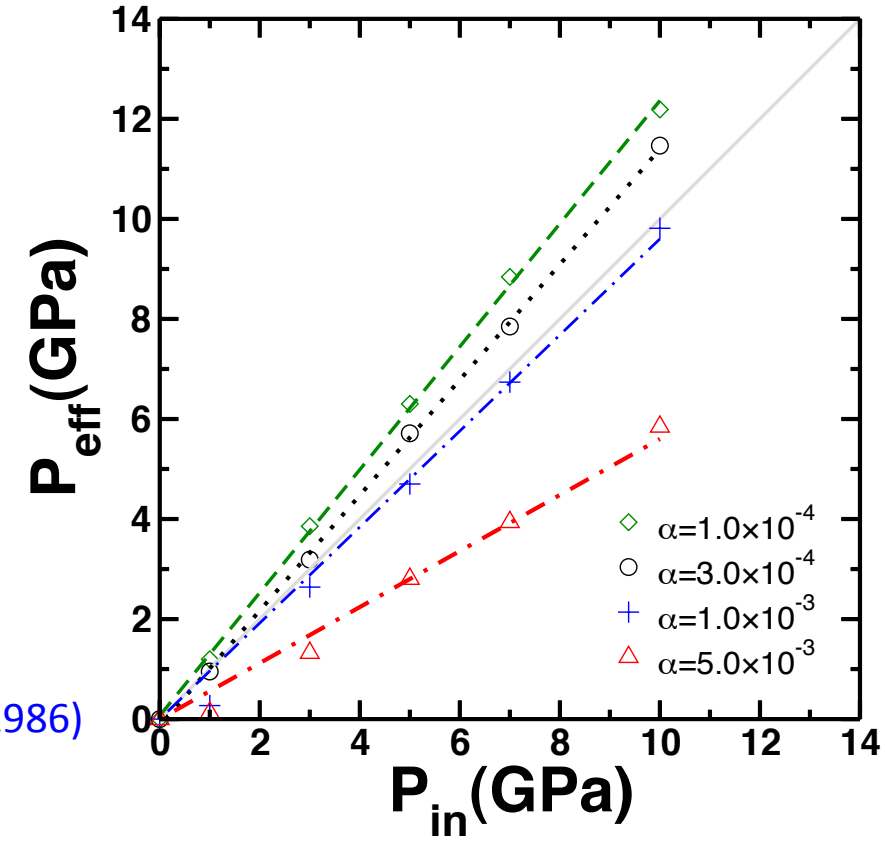


Calibration

•Calibration on $\mathrm{Si_{71}H_{60}}$ matching the applied pressure to an effective pressure[1] estimated from the compression of bulk-like nearest neighbor bond length

$$P_{\mathrm{eff}} = 3B_0\left(\frac{a}{a_{eq}}\right)^{-2}\left(1-\frac{a}{a_{eq}}\right)\exp\left[-\frac{3}{2}(B_0'-1)\left(\frac{a}{a_{eq}}-1\right)\right]$$

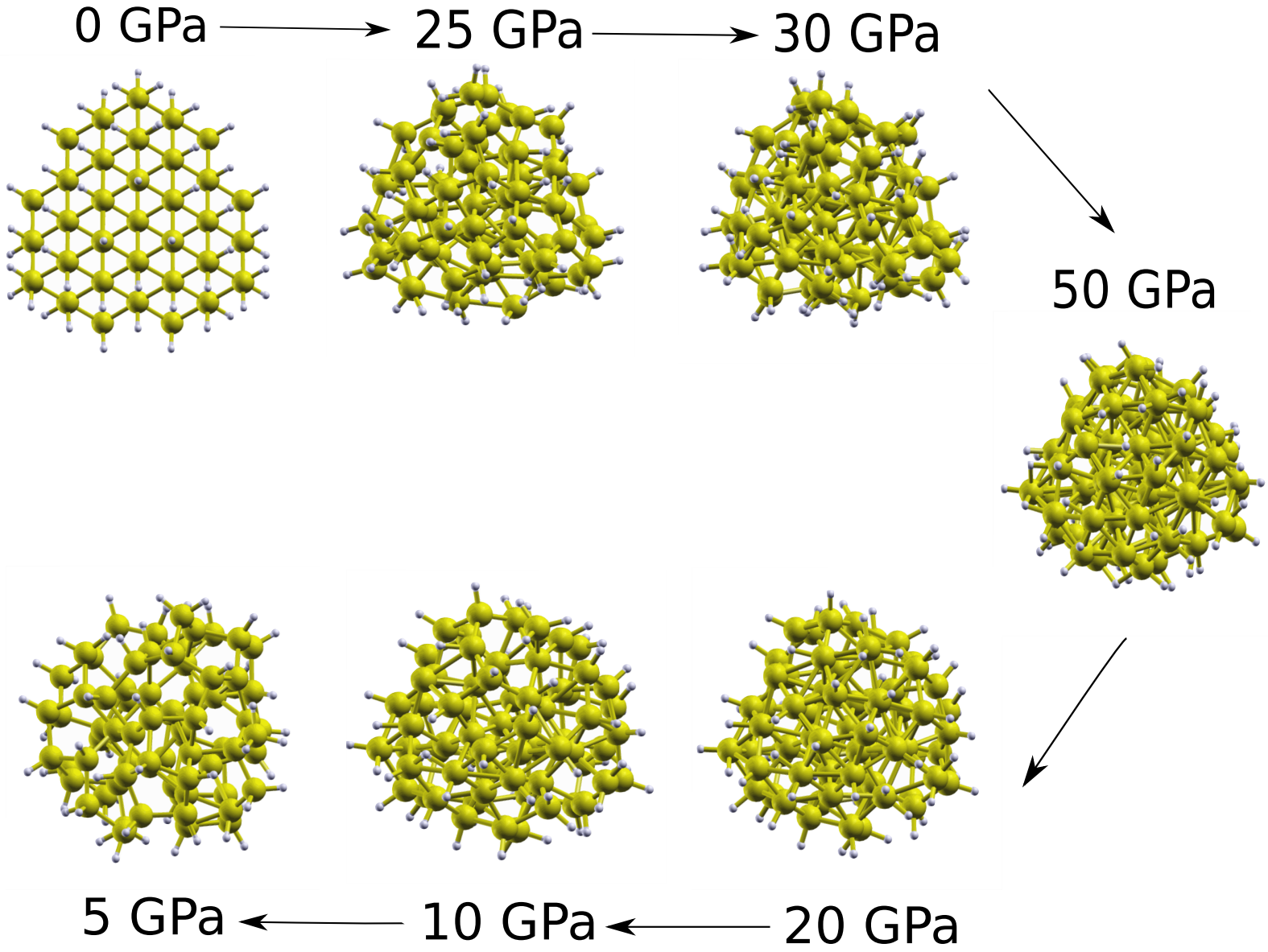
SIMULATION DETAILS
-Linear-scaling DFT[2] (www.onetep.org)
-CAPZ LDA
-Norm-conserving pseudopotentials
-800 eV cutoff
- Quasistatic geometry relaxation

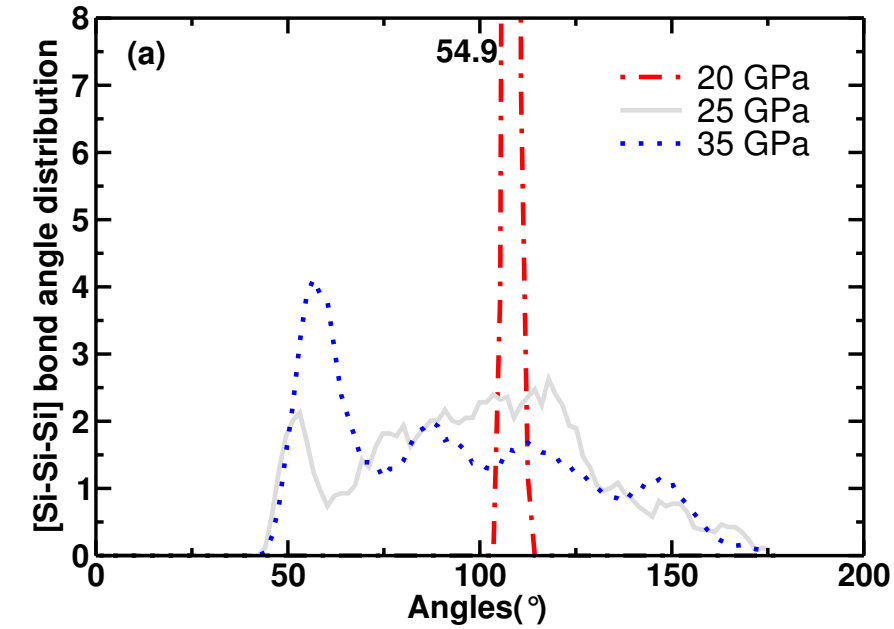


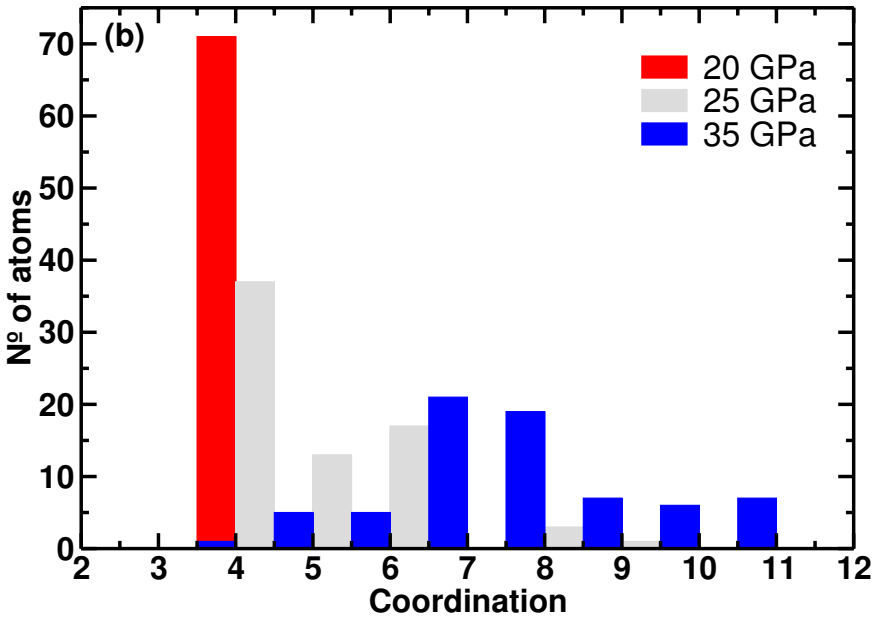
[1] Vinet et al, J. Phys. C: Solid State Phys. 19, L467 (1986)

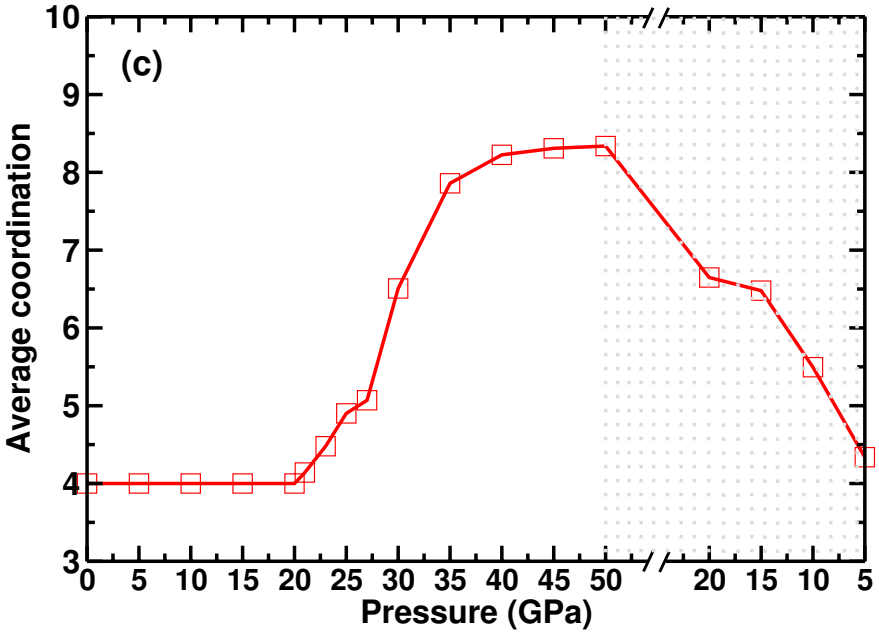
[2] Skylaris et al, J. Chem. Phys. 122, 084119 (2005)

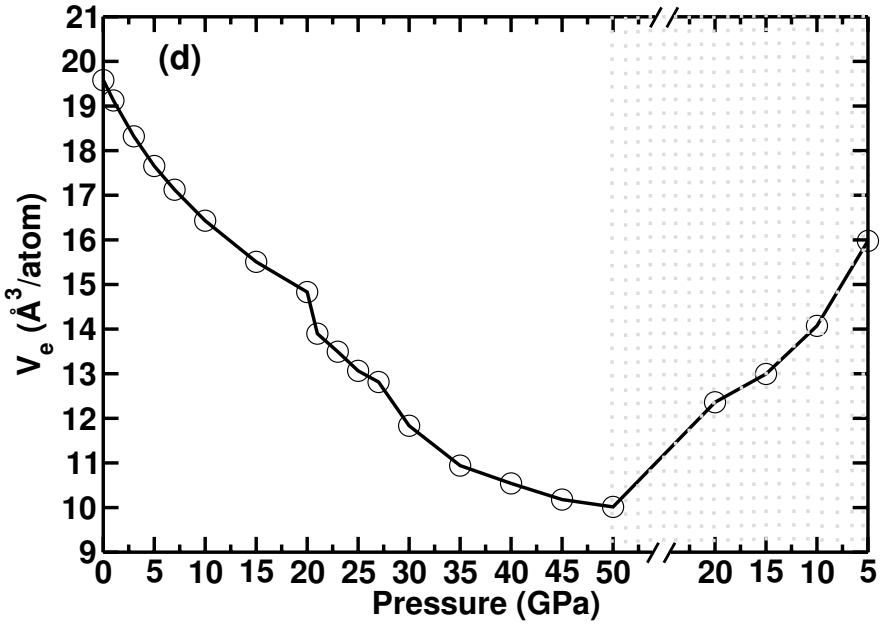
Pressure-induced amorphization



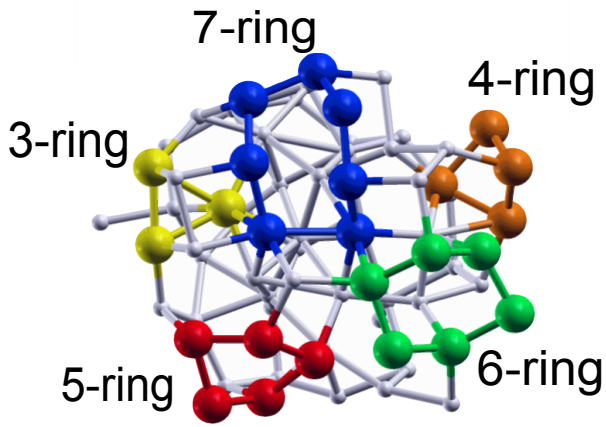

(a)
54.9
20 GPa
25 GPa
35 GPa
[Si-Si-Si] bond angle distribution
Angles(°)


(b)
20 GPa
25 GPa
35 GPa
Nº of atoms
Coordination


(c)
Average coordination
Pressure (GPa)

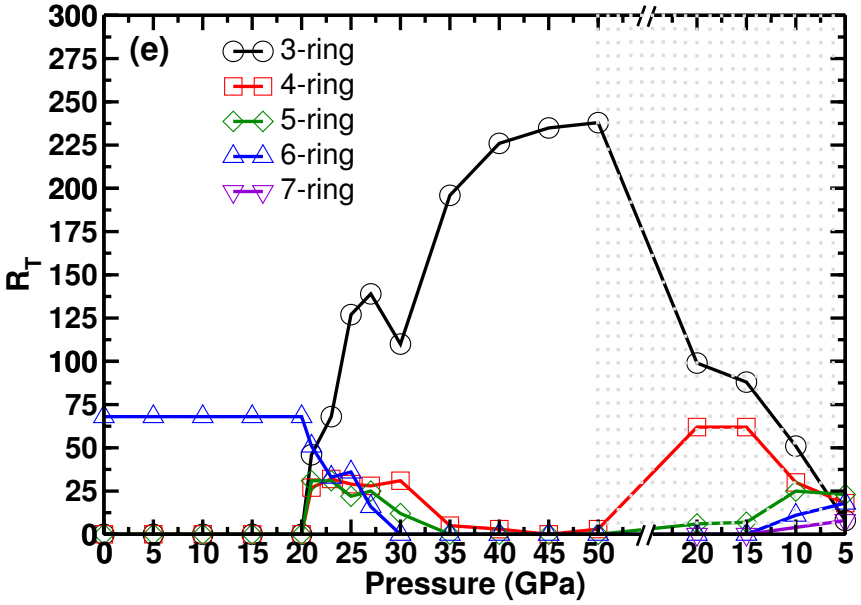

(d)
V_e (Å^3/atom)
Pressure (GPa)

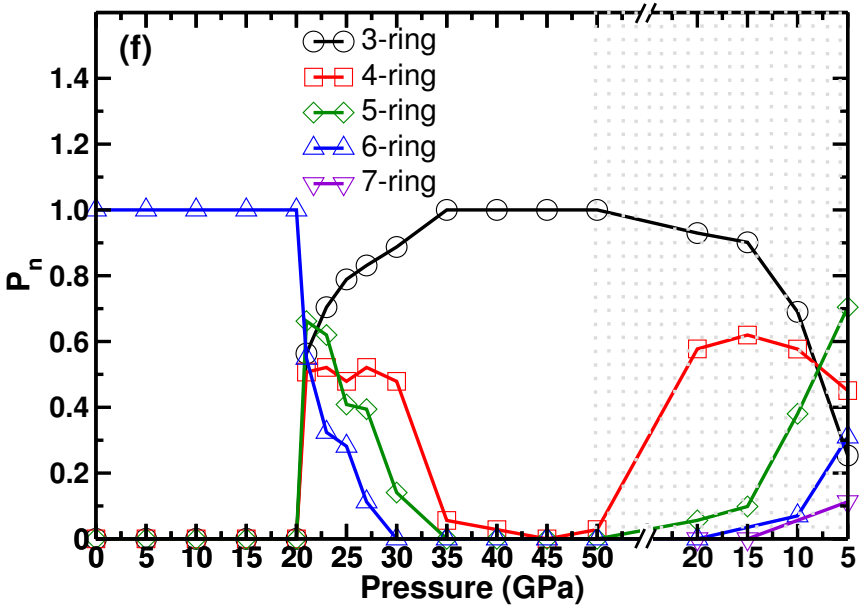
- Use ring statistics to track changes in covalent Si network



- Polyamorphic transformations between 3 types of amorphous structures: HDA, VHDA and LDA (upon decompression)

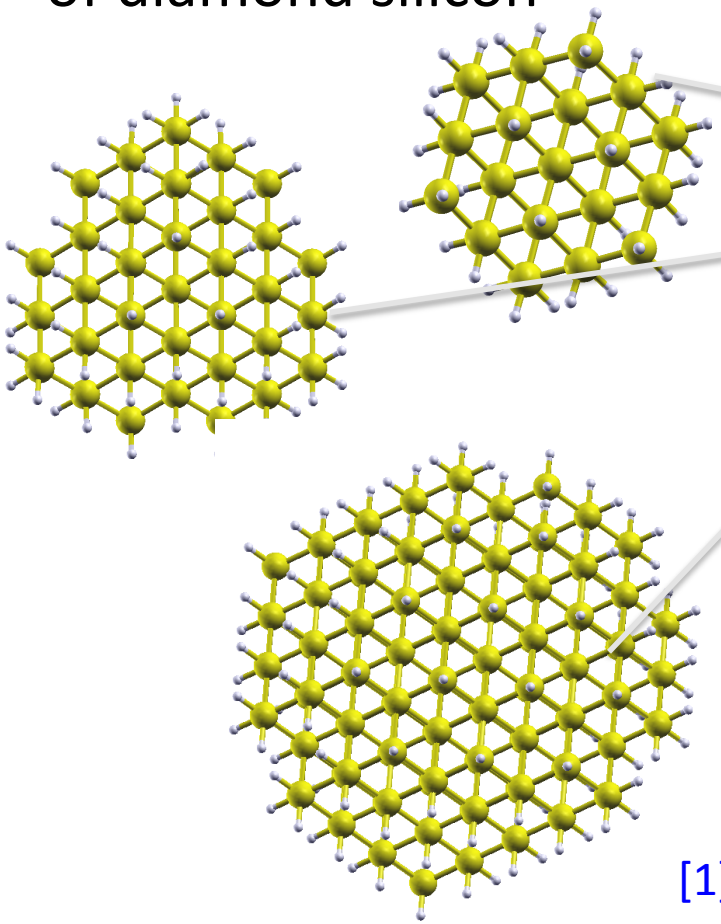
- Consistent with results obtained using explicit solvents

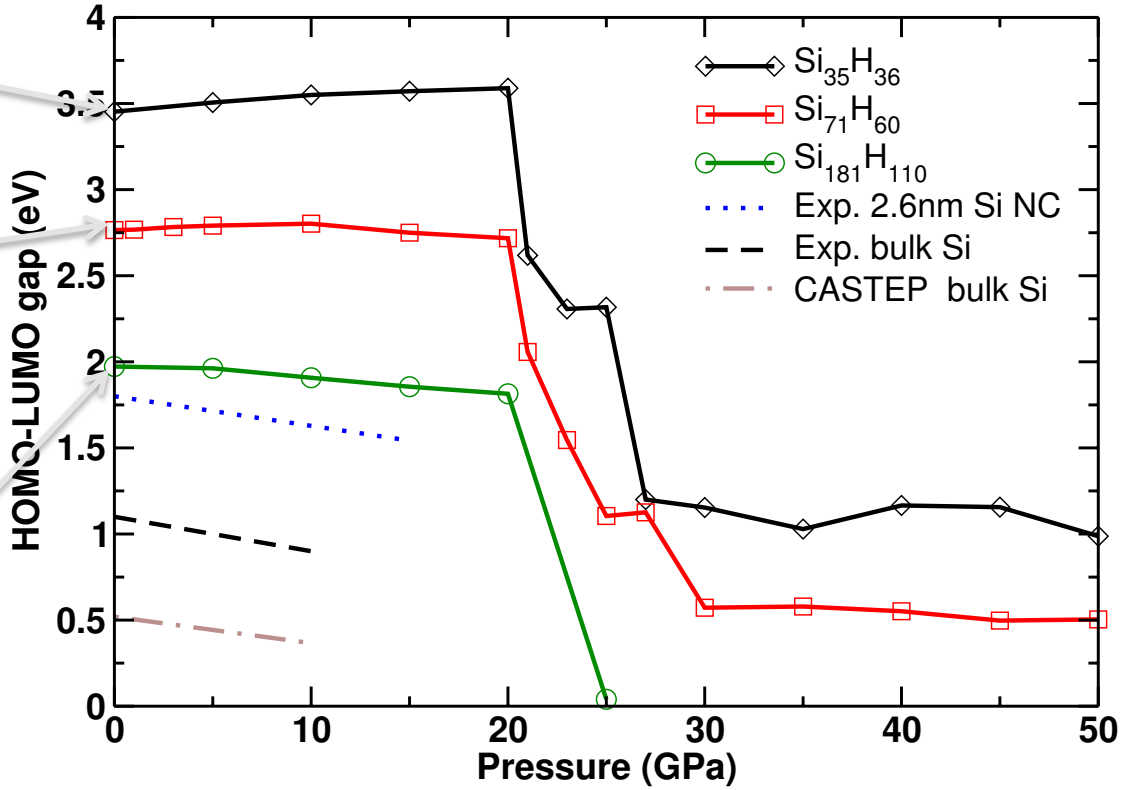




Size-dependence

- Dramatic change of the HOMO-LUMO gap with pressure
- Qualitative agreement with experiment[1] for larger nanocrystal
- Competition between quantum confinement and pressure coefficient of diamond silicon





[1] Hannah et al, Nano Letters 12, 4200 (2012)

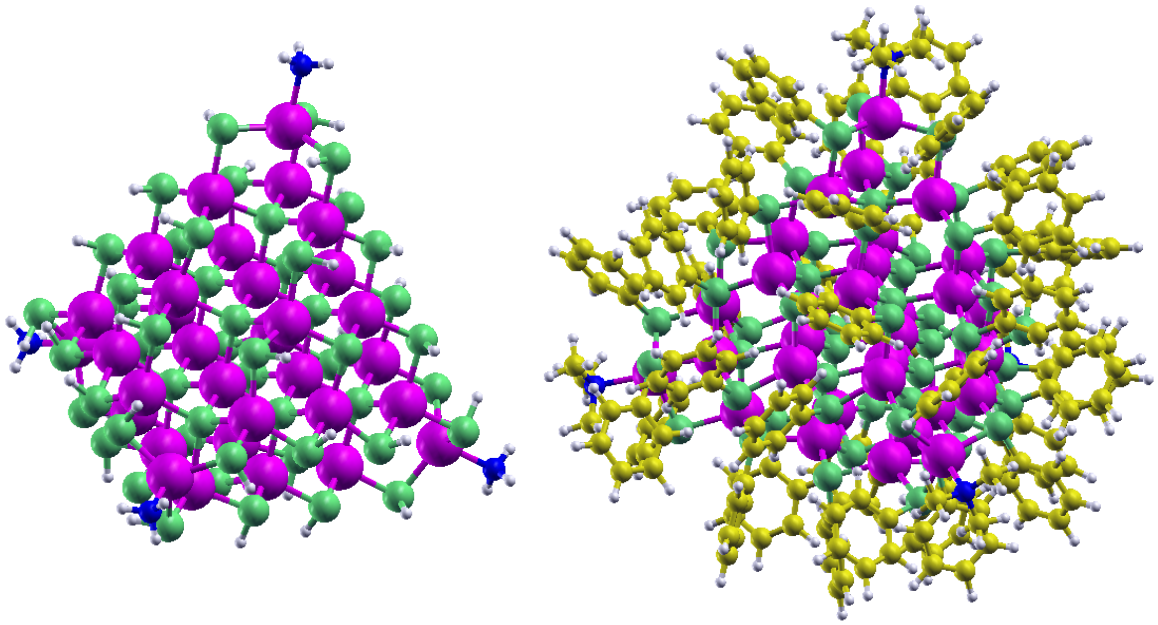
II-VI pressure sensors?

- CdS nanocrystals with a zincblende core passivated with H and phenyl groups taken from experiment[1]

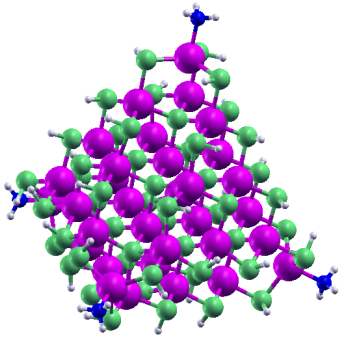
- Interested in the effect of surfactants on the structural and optical properties under pressure

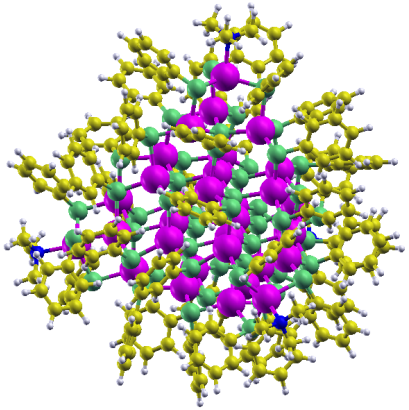
$Cd_{32}S_{50}H_{36}(NH_3)_4$ $Cd_{32}S_{14}(SC_6H_5)_{36}(N(CH_3)_3)_4$

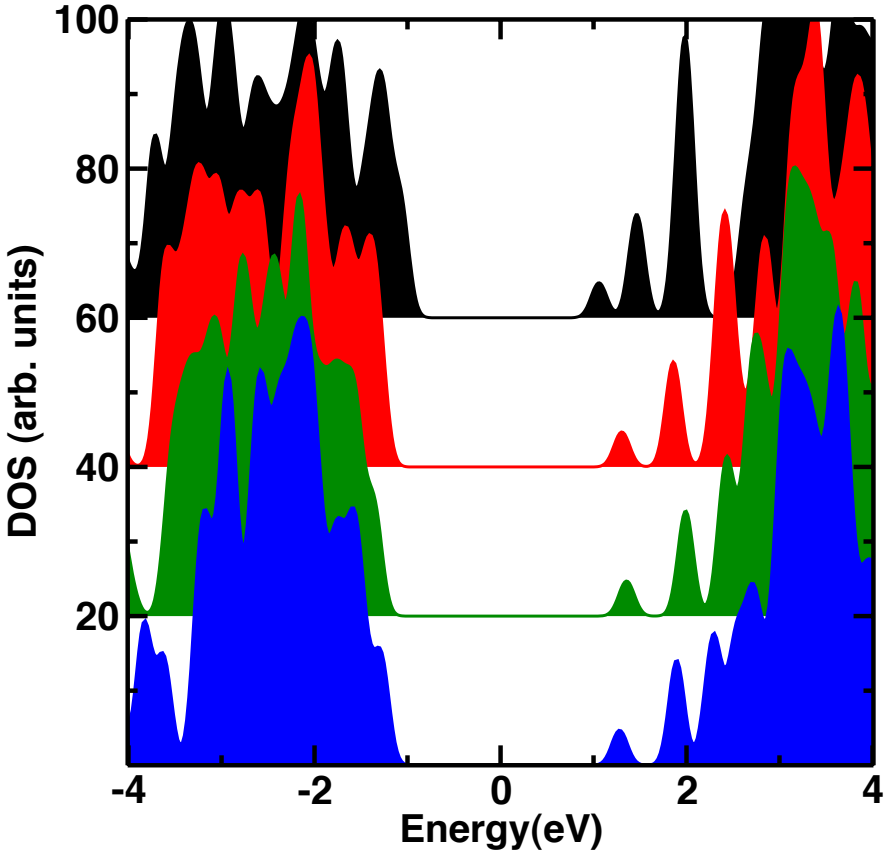
SIMULATION DETAILS:
- Blöchl PAW[2] in ONETEP
- PW92 LDA
- Scalar-rel. RRKJ projectors
- Extra 'd' partial wave for S
- 2 partial waves/ l channel
- 800 eV
-Quasistatic geometry relaxation

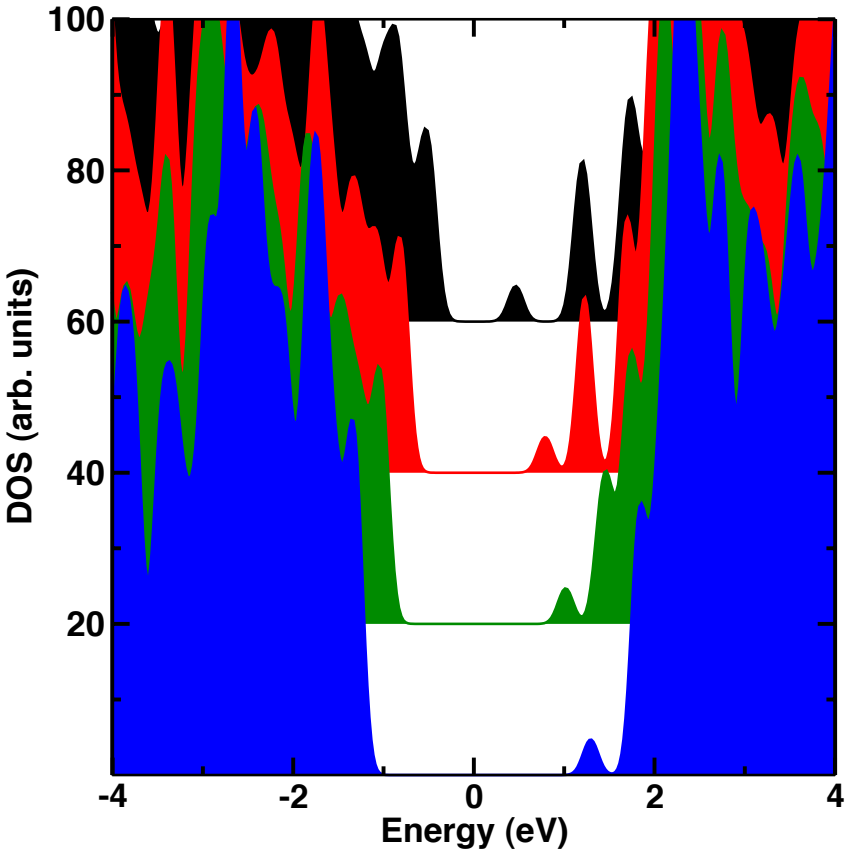


[1] Herron et al, Science 259(1993), 1426-1428; [2] Blöchl, Phys. Rev. B 50, 17953 (1994)

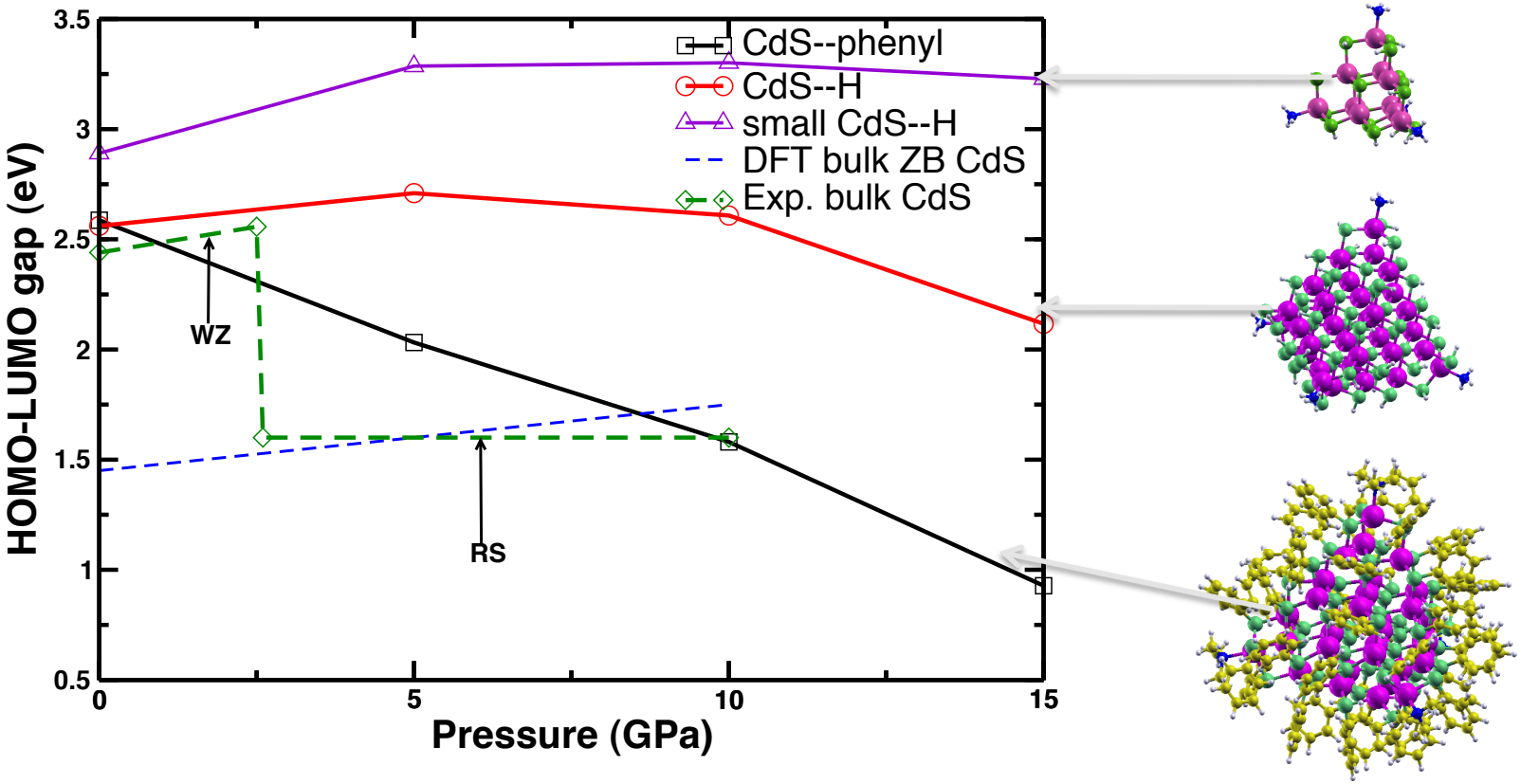








0 GPa → 5 GPa → 10 GPa → 15 GPa



•Complex interplay between electronic and structural effects: quantum confinement, pressure coefficients, hybridization, surface distortions, …

•Appearance of a mid-gap state (LUMO) due to the core

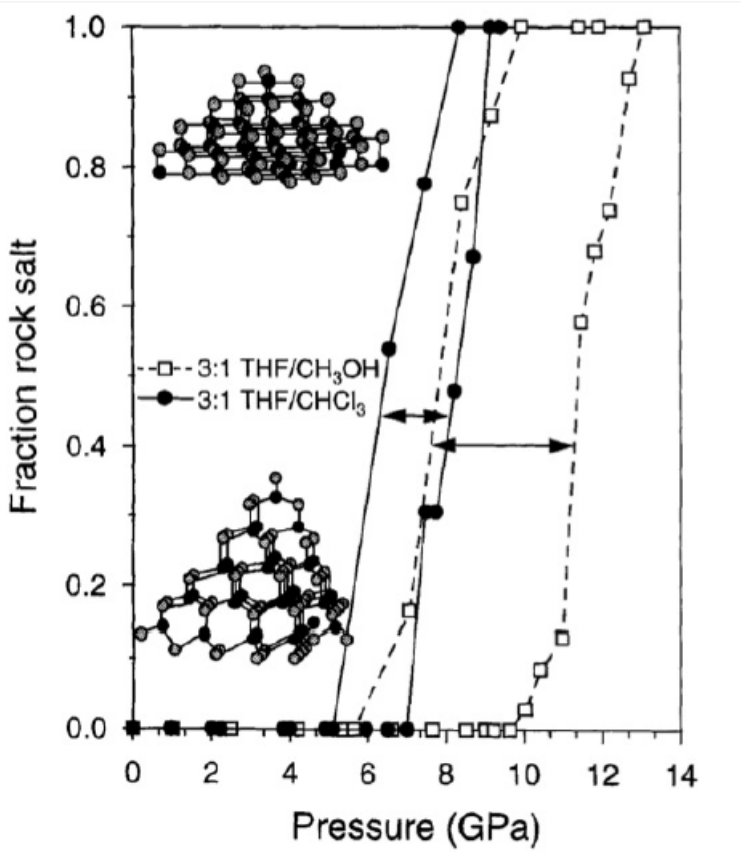
•Similar to CdSe but no consensus in the literature on origin

Puzder et al, PRL 92.21 (2004), 217401

Work in progress

- Study kinetics of WZ/ZB →RS transformation in nanocrystals

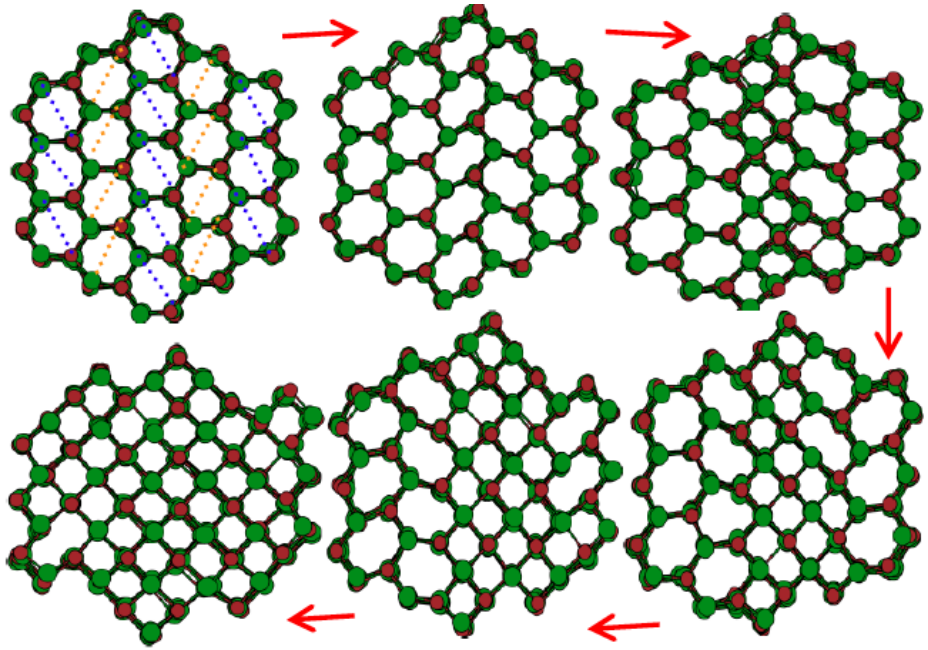
- Want to understand effect of surfactants and solvent on structural transformation



C. Chen, A. B. Herhold, C. S. Johnson, A. P. Alivisatos, Science 276, 398 (1997).

Work in progress

- Long timescales involved too expensive for ab initio treatment
- Use classical MD combined with metadynamics to accelerate free energy landscape exploration
- Do ab initio calculations on MD snapshots



$Cd_{216}S_{216}$
P=1.75 GPa
T= 300K
w=5meV
d=0.02

Summary

- Electronic enthalpy method is natural and efficient to simulate finite systems under pressure
- Need to calibrate terms defining the volume
- Gives similar results to explicit solvents
- Combined with linear-scaling DFT allows to investigate realistic nanocrystals under pressure
- Zincblende CdS nanocrystal is a candidate for pressure sensing
- Surfactants important in determining structural and optical response

Acknowledgments

- Now available on J. Chem. Phys. **139**, 084117 (2013)
- Collaborator: Andrea Greco
- Useful discussions: Francesco Mauri
- Funding: EPSRC grant #EPG036888/1
- Compute resources: Imperial HPC and HECToR
- ONETEP developers

Imperial College London

EPSRC Engineering and Physical Sciences Research Council

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