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

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Motivation

- Nanocrystal size and surface add extra dimensions to phase diagram

\[ \text{CdSe WZ/RS nanocrystals} \]

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

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

Electronic enthalpy method

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

• DFT self-consistent minimization of enthalpy $H$

\[ H[\rho] = U[\rho] + PV_e[\rho] \]

• Electronic volume defined as the interior of a charge isosurface of $\alpha$
density cutoff value

\[ V_e = \int \theta(\rho(\mathbf{r}) - \alpha) d\mathbf{r}^3 \]

• Step function is smeared by $\sigma$ 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_e}{\delta \rho} \bigg|_{\rho=\rho(r)} = \frac{P}{\sigma \sqrt{2\pi}} \exp \left( -\frac{(\rho(r) - \alpha)^2}{2\sigma^2} \right)
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- Pressure field acts directly on electrons

- No need for equilibration with pressurizing medium.

- Efficient compared to other \textit{ab initio} methods

- Gives a homogeneous description of the solvent-nanocrystal interface with \( \alpha \) defining the excluded volume of solvent and \( \sigma \) the range/intensity of interaction
• \( \alpha \) needs to be sufficiently large to avoid describing voids and calibrated to correspond to a realistic excluded volume

• \( \sigma \) has to be tuned and needs to be sufficiently large for the potential to be accurately integrated on the grid
Calibration

• If $\alpha$ and $\sigma$ 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 $\text{Si}_{71}\text{H}_{60}$ matching the applied pressure to an effective pressure $^{1}$ estimated from the compression of bulk-like nearest neighbor bond length

$$P_{\text{eff}} = 3B_0 \left( \frac{a}{a_{eq}} \right)^{-2} \left( 1 - \frac{a}{a_{eq}} \right) \exp \left[ -\frac{3}{2} (B'_0 - 1) \left( \frac{a}{a_{eq}} - 1 \right) \right]$$

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

Pressure-induced amorphization

0 GPa → 25 GPa → 30 GPa

5 GPa ← 10 GPa ← 20 GPa

50 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

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

\[
\text{Cd}_{32}\text{S}_{50}\text{H}_{36}(\text{NH}_3)_4 \quad \text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}(\text{N(CH}_3)_3)_4
\]

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

0 GPa $\rightarrow$ 5 GPa $\rightarrow$ 10 GPa $\rightarrow$ 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 $\rightarrow$ RS transformation in nanocrystals

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

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
- $T=300K$
- $w=5$ meV
- $d=0.02$
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
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