Further random results from random structure searching

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Locating the global minimum of a potential energy surface

Search method of choice depends on affordable number of energy evaluations
“Accurate” methods such as first principles DFT are required
Random searching algorithm for crystal structures

Generate a population of random structures and relax them:

Choose random unit cell translation vectors
Renormalize the volume to a reasonable range of values
Choose random atomic positions within the cell

May constrain the initial positions:

Fix the initial positions of some of the atoms (e.g., defect)
Insert molecules randomly (rather than atoms)
Choose a particular space group
The $I4_1/a$ and $C2/c$ structures of silane

Golden spheres: silicon atoms; white spheres hydrogen atoms


$I4_1/a$ has been found in experiments by Eremets et al.
When is H$_2$O not water?

“X-ray-induced dissociation of H$_2$O and formation of an O$_2$-H$_2$ alloy at high pressure”, Mao et al., Science 314, 636 (2006)

Pickard and Needs, unpublished
The $R\bar{3}m$ structure

Oxygen atoms in red and hydrogen atoms in white
When is $\text{H}_2\text{O}$ not water?

X-ray diffraction patterns from experiment of Mao et al. and groups A-H
Phase diagram of solid hydrogen


- Hydrogen atoms scatter X-rays weakly ⇒ Difficult for experiments
- Large zero point motion and small energy differences ⇒ Difficult for theory
- Perform structural search on static structures and add harmonic zero point energy (very poor approximation at very high pressures)
Phase diagram of solid hydrogen

Phase diagram of solid hydrogen

The $C2/c$ layered structure - Phase III?

$C'2/c$  

IR and Raman frequencies
Aluminum Hydride AlH$_3$ - Enthalpy

Pickard and Needs, unpublished
Aluminum Hydride $\text{AlH}_3$ - Structures

$Pnma$  
Insulating

$Pm\bar{3}n$  
Metallic
Aluminum Hydride AlH$_3$ - Bandstructures

$Pnma$

$Pm\bar{3}n$

Pickard and Needs, unpublished
Perspective

- The “simplest possible” random searching algorithm is useful for finding crystal structures
- Finding crystal structures may be simpler than we thought?