Random search
challenges and new directions

Chris J Pickard

University of Cambridge
Department of Materials Science and Metallurgy
Tohoku University
Advanced Institute for Materials Research
Joining the dots

\[(n-1)! = 50! \sim 3 \times 10^{64}\]

age of universe \sim 4 \times 10^{17} \text{ seconds}
Joining the dots

(n-1)! = 50! \sim 3 \times 10^{64}

age of universe \sim 4 \times 10^{17} \text{ seconds}
Joining the dots

Data from William Cook:

\[ y = -5.4933 + 2.8399 \times x \]

Reasonable random guess

Go “downhill” as far as you can

Do something - or nothing

Analyse and Repeat
Structure Prediction

What structure will a collection of atoms adopt?

Crystal

Point Defect

Interfaces

“All The Arrangement of Atoms in Space”
Jacobus Henricus van 't Hoff, 1898
Energy

Interpolative
Empirical or data driven

Extrapolative and predictive
First principles or theory driven
Smooth interactions

\[ H \Psi = -\frac{1}{2} \nabla^2 \Psi + V \Psi = E \Psi \]

Coulomb

\[ E_{ep} = -\frac{1}{r_{ep}} \]

Schroedinger
Smooth Landscapes
Smooth Landscapes
Smooth Landscapes

Deep basins are large
Basin Volumes

from Baranau and Ulrich Tallarek, Soft Matter, 2014, 10, 3826
Basin Volumes

Apollonian Gasket

a Fractal

Massen and Doye, PRE, 75, 037101 (2007)
Random Sampling

- Uniform distribution
  *exploration not exploitation*

- Intrinsically parallel

- Uncorrelated

- Clear when (not) to stop

- Robust and communicable
Being Sensible

When you don’t know anything:
rough volume, avoid overlap

Impose chemical ideas
molecules, fragments, distances, connectivity

Impose symmetry
space, wallpaper, point group

Use experimental data
lattice parameters
Empirical or First Principles?

Eight atoms of Silicon

DFT (2.5K)

REAXFF (5K)

Tersoff (5K)

Data-Driven Learning of Total and Local Energies in Elemental Boron

Deringer, Pickard, Csanyi, PRL, 2018

Learn entire energy landscape
Ab Initio Random Structure Searching

Superconducting hydrides
Physical Review Letters, 2006

Hydrogen is polar and “graphene”
Nature Physics, 2007

Ammonia is ionic

The end of water
Physical Review Letters, 2013
+ Martinez-Canales

Pickard & Needs, PRL 2006 and JPCM 2011
see also: basin/minima hopping, GA/EAs, particle swarms
Ab Initio Random Structure Searching

See also: basin/minima hopping, GA/EAs, particle swarms

Hydrogen is polar and "graphene"

Physical Review Letters, 2006


The end of water

Physical Review Letters, 2013

Pickard & Needs, PRL 2006 and JPCM 2011

Ammonia is ionic

Nature Physics, 2007

Superconducting hydrides
Ab Initio Random Structure Searching

see also: basin/minima hopping, GA/EAs, particle swarms

Hydrogen is polar and “graphene”
Nature Physics, 2007

Pickard & Needs, *PRL* 2006 and *JPCM* 2011

- Hydrogen Clathrate Structures in Rare Earth Hydrides at High Pressures: Possible Route to Room-Temperature Superconductivity

- Hydrogen Clathrate Structures in Rare Earth Hydrides at High Pressures: Possible Route to Room-Temperature Superconductivity
  - Max-Planck-Institut für Chemie, Hahn-Meitner Weg 1, 55128 Mainz, Germany

- Evidence for superconductivity above 260 K in lanthanum superhydride at megabar pressures
  - M. Ottaviani, M. Altieri, Ch. Staudacher, M. B. Ebner, T. J. rests, R.-J. Herbst
  - arXiv 2013
Ab Initio Random Structure Searching

Pickard & Needs, PRL 2006 and JPCM 2011

see also: basin/minima hopping, GA/EAs, particle swarms

Hydrogen is polar and "graphene"

Nature Physics, 2007
Ab Initio Random Structure Searching

Superconducting hydrides
Physical Review Letters, 2006

Hydrogen is polar and “graphene”
Nature Physics, 2007

Ammonia is ionic

The end of water
Physical Review Letters, 2013

Pickard & Needs, *PRL* 2006 and *JPCM* 2011

see also: basin/minima hopping, GA/EAs, particle swarms
Thomas-Fermi-Dirac
simplified 128 atoms ($V \sim L^{3.84}$)

Gamma Boron

Fixed Cell
AIRSS Example 2.3

Oganov et al *Nature* 2009
Random “sensible” structures

#VARVOL=11.8

#SPECIES=B%NUM=1,N%NUM=1

#SYMOPS=1
#NFORM=128

#MINSEP=1.0 B–B=2.6 N–N=2.6 B–N=1.6

KPOINTS_MP_SPACING 0.07

SYMMETRY_GENERATE
SNAP_TO_SYMMETRY

%BLOCK SPECIES_POT
%ENDBLOCK SPECIES_POT

%BLOCK EXTERNAL_PRESSURE
0 0 0
0 0
0
%ENDBLOCK EXTERNAL_PRESSURE
Beyond Crystals


{2H,3Li} complex in silicon
Morris, Grey, Needs & Pickard, 2014

Silicon(111) 3x3 reconstruction

Interfacial Materials

Ni$_3$InAs
Schusteritsch et al, 2015

Zirconium suboxide
Nicholls et al, 2015
Challenges
New directions

Allow the particles making up a structure to explore a higher dimensional physical space.

\[ d = d_0 + d_+ \]

Hyperspace          Normal space          Extra dimensions

\[ \bar{E}(\{\tilde{x}_i\}) = \tilde{E}(\{\tilde{x}_i\}) + \frac{1}{2} \mu \sum_{i} l_i^2 \]

Energy extended to hyperspace
Increasing penalty

\[ \mu = \mu_0 \beta^{n-1} \quad \mu_0 = 10, \ \beta = 1.001 \]

Toy example

\[ d = 1 + 1 \]
1. When $d_+ > 0$ the dependence on system and packing ($f$) is much reduced
2. Performance for LJ38 comparable to MH and EA ($-\log_{10}(p_e) = 3.1$)[1]
3. Adjusting parameters for LJ38 leads to $-\log_{10}(p_e) = 2.8$ (at cost of more GO steps)
4. Combining with Relax and Shake (RASH), for LJ55 $-\log_{10}(p_e) = 1.9$
5. **Reality check**: $-\log_{10}(p_e) = 5.8$ for LJ75 (RASH) while it is 4.4 for MH

**Acronyms**

**Random structure search - RSS**
**Geometry optimisation of structures from hyperspace - GOSH**
**Relax and shake - RASH**
Binary chain

\[ p_e = \frac{N_A!N_B!}{(N_A + N_B)!} \]
Binary cubes

---

Density of States

- $d=3+3$ (89/29K)
- $d=3+2$ (62/29K)
- $d=3+1$ (11/29K)
- $d=3+0$ (0/29K)

Energy

- $C_1$
- $O_h$
- $D_{3h}$

---

Legend:

- Green line: $d=3+3$ (89/29K)
- Blue line: $d=3+2$ (62/29K)
- Red line: $d=3+1$ (11/29K)
- Orange line: $d=3+0$ (0/29K)
Covalent bonds
Covalent bonds
Covalent bonds

\[ d = 3 + 0 \text{ (97/28K)} \]
\[ d = 3 + 1 \text{ (5092/28K)} \]
\[ d = 3 + 2 \text{ (6115/28K)} \]

\[ \mu_0 = 1, \beta = 1.001 \]
Conclusion

Random search is *better* than you would think.

Stochastic search and first principles approaches can *discover*

*Hyperspatial optimisation* provides promising new directions.

AIRSS package available from:

http://www.mtg.msm.cam.ac.uk/Codes/AIRSS

under the GPL 2.0 licence

Please direct queries to airss@msm.cam.ac.uk