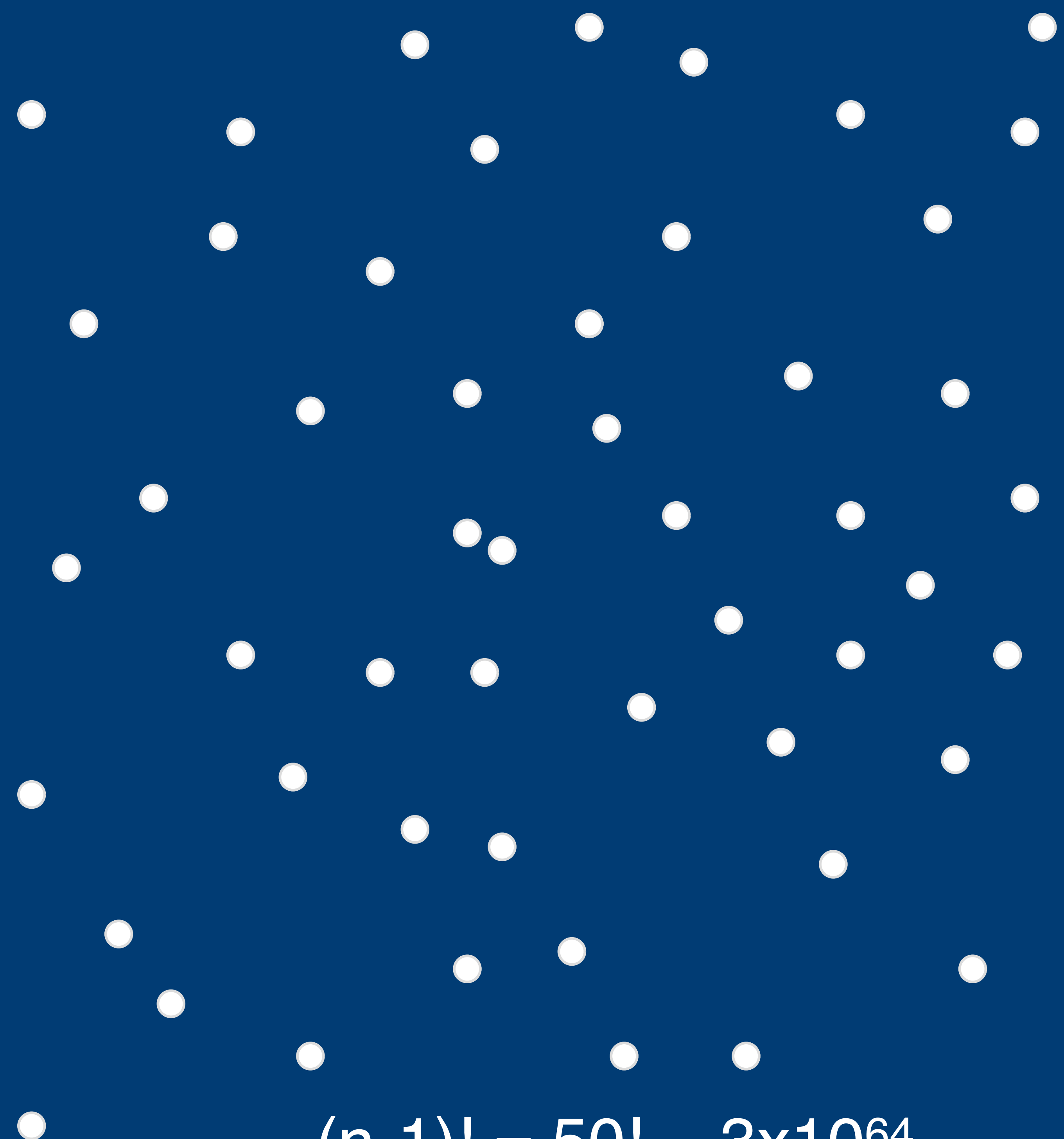
Random search

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



$(n-1)! = 50! \sim 3\times10^{64}$

age of universe ~ 4×10^{17} seconds

Joining the dots

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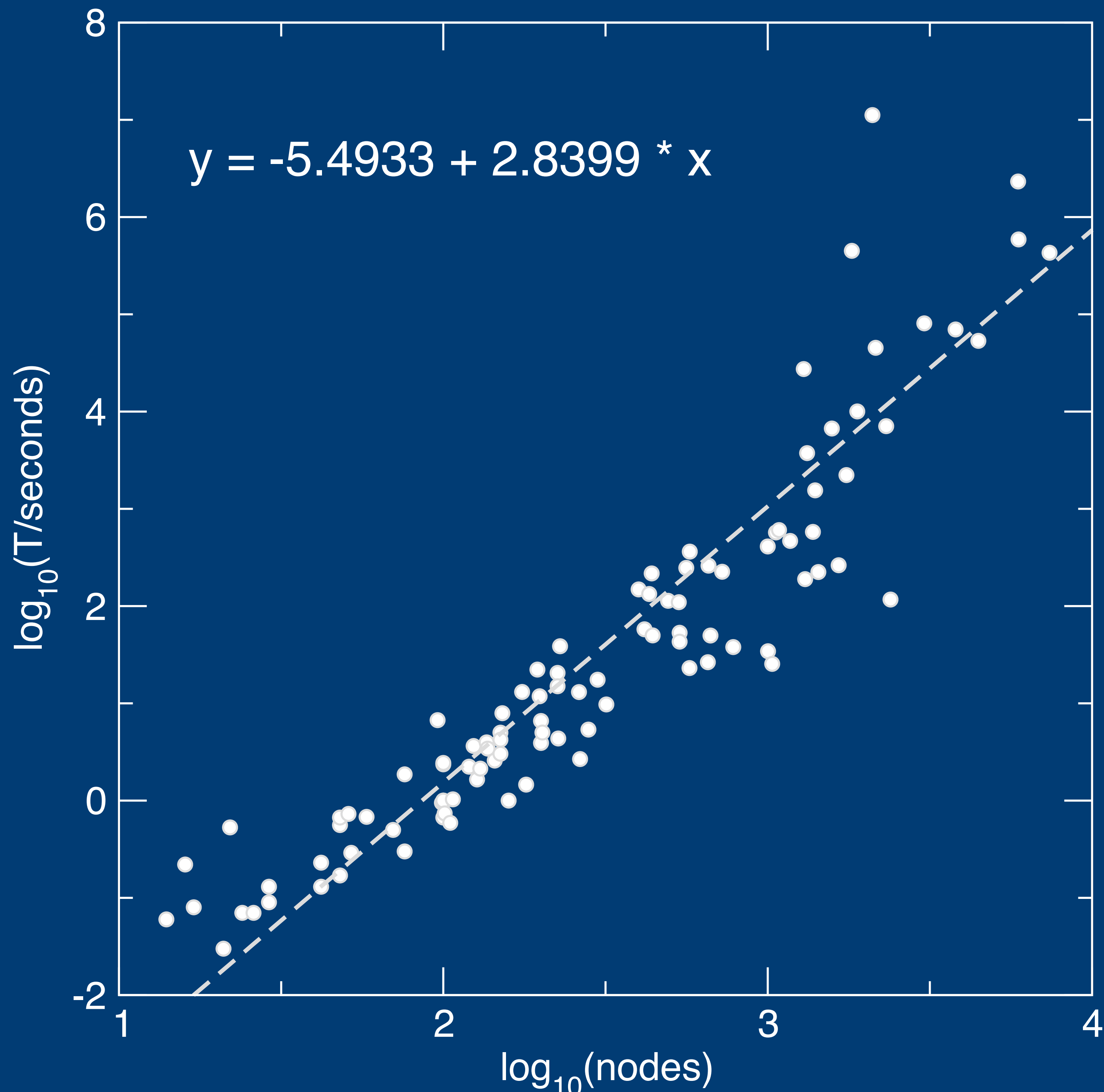
age of universe $\sim 4 \times 10^{17}$ seconds

Joining the dots



Reasonable random guess

Go “downhill” as far as you can

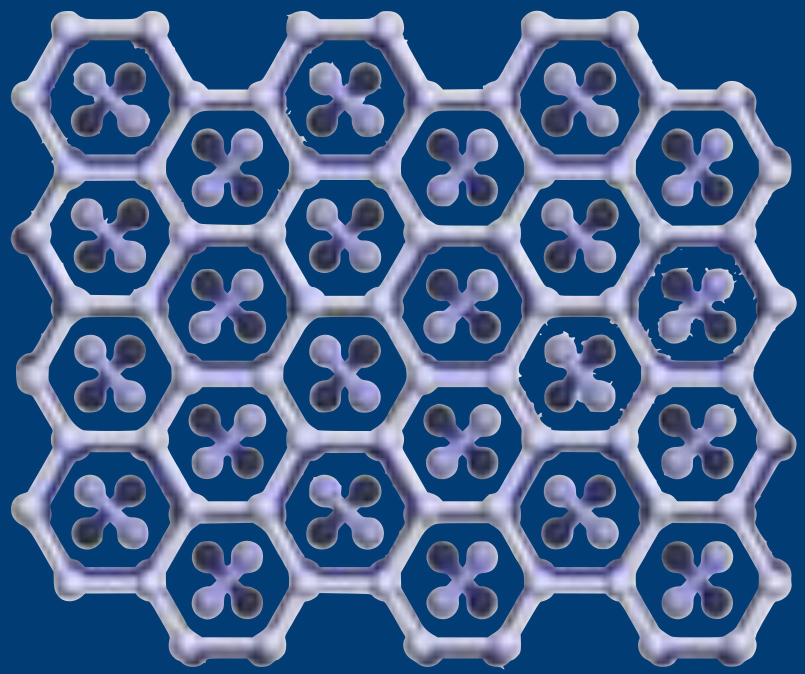
Do something - or nothing

Analyse and Repeat

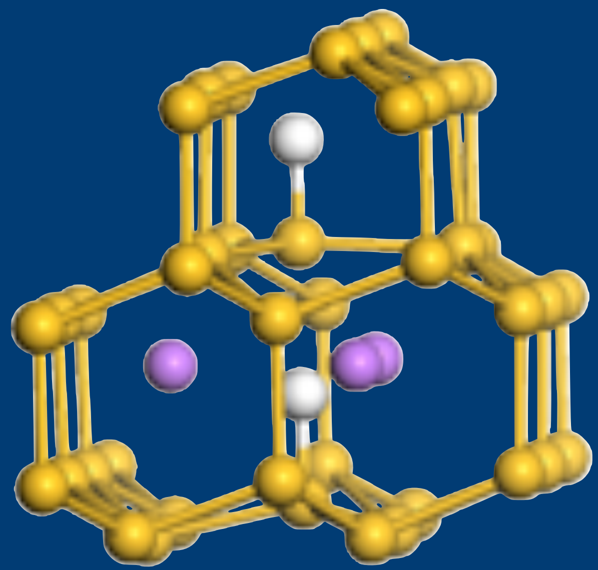
Data from William Cook:
http://www.math.uwaterloo.ca/tsp/concorde/benchmarks/bench99.html

Structure Prediction

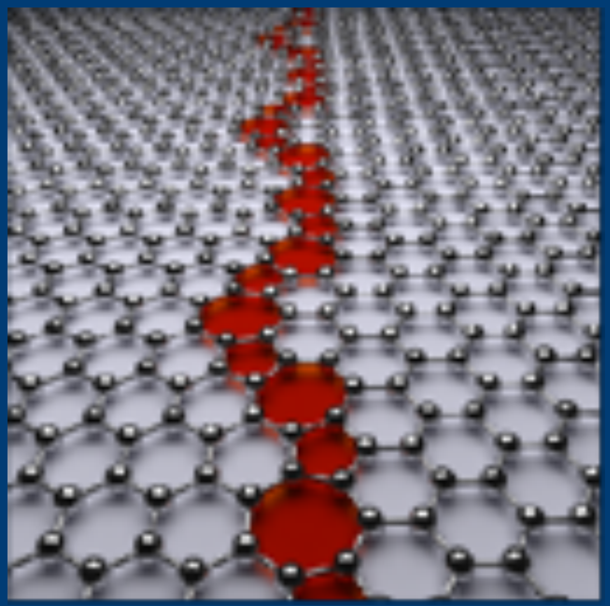
What structure will a collection of atoms adopt?



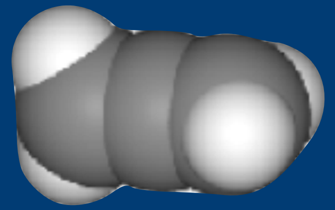
Crystal



Point Defect



Interfaces



Allene

"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

Periodic Table

Reference point: WIEN2k13.1 with basis LAPW/APW+lo and potential all-electron

Code: CASTEP9.0 with basis plane waves and potential OTFG CASTEP 9.0

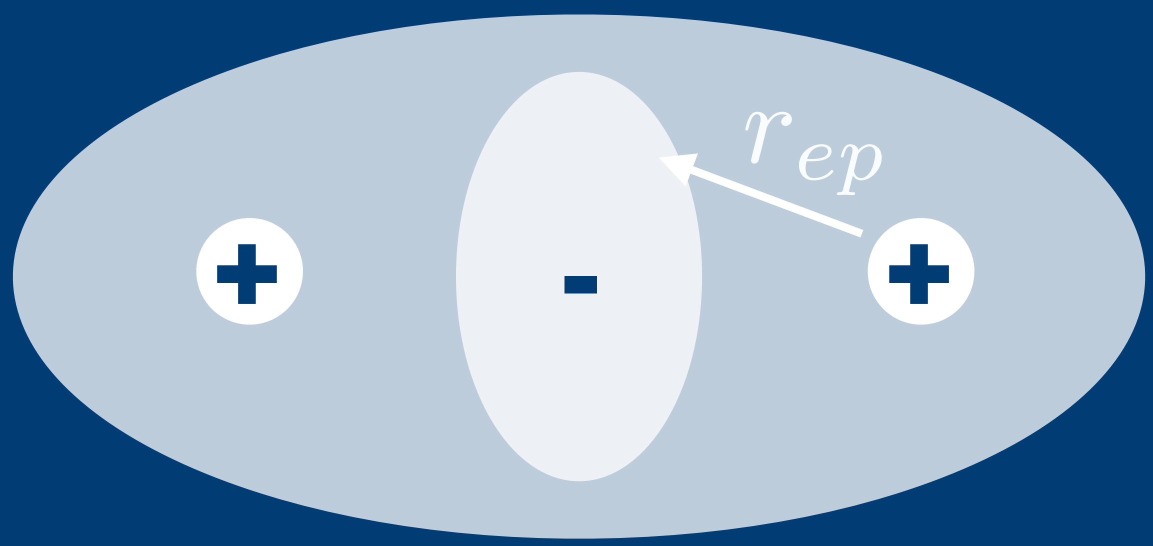
Maximum at Mn, Minimum at V

All values are in meV.

H 0.05																	He 0.03
Li 0.08	Be 0.26											B 0.81	C 0.37	N 0.66	O 1.17	F 0.52	Ne 0.16
Na 0.44	Mg 0.27											Al 0.11	Si 0.24	P 0.64	S 0.28	Cl 0.74	Ar 0.12
K 0.12	Ca 0.07	Sc 0.82	Ti 0.35	V 0.03	Cr 1.19	Mn 2.42	Fe 0.62	Co 0.44	Ni 0.28	Cu 0.51	Zn 0.40	Ga 0.06	Ge 0.18	As 0.35	Se 0.58	Br 0.11	Kr 0.04
Rb 0.21	Sr 1.23	Y 0.53	Zr 0.33	Nb 0.30	Mo 0.46	Tc 0.56	Ru 0.89	Rh 0.37	Pd 0.52	Ag 0.46	Cd 1.35	In 0.32	Sn 0.28	Sb 0.30	Te 0.08	I 0.77	Xe 0.11
Cs 0.13	Ba 0.11		Hf 0.36	Ta 0.85	W 1.05	Re 0.75	Os 0.35	Ir 0.23	Pt 0.24	Au 1.15	Hg 1.02	Tl 0.19	Pb 0.67	Bi 1.09	Po 1.03	At	Rn 0.13
Fr	Ra																
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu 0.54	
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Kurt Lejaeghere, et al., Reproducibility in density functional theory calculations of solids, Science 351 (6280), aad3000 (2016).

Smooth interactions



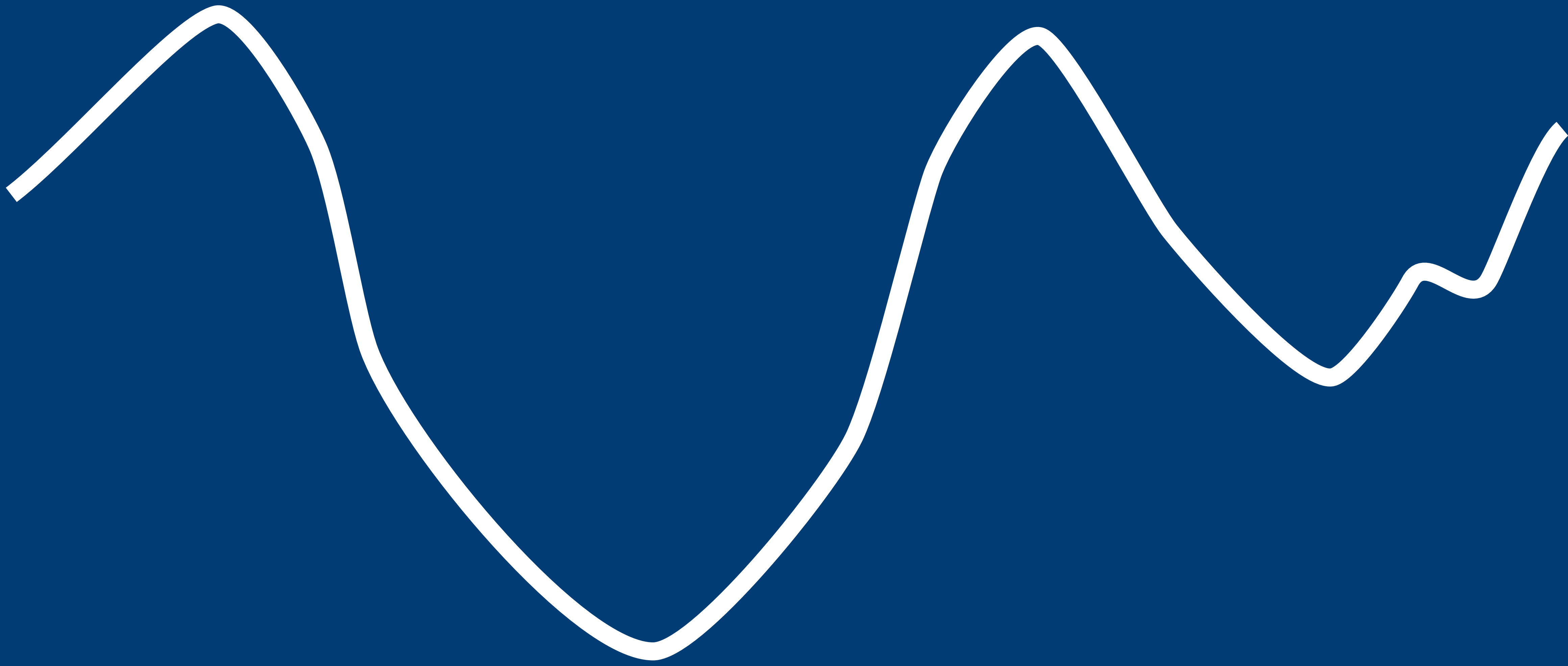
$$E_{ep} = -\frac{1}{r_{ep}}$$

Coulomb

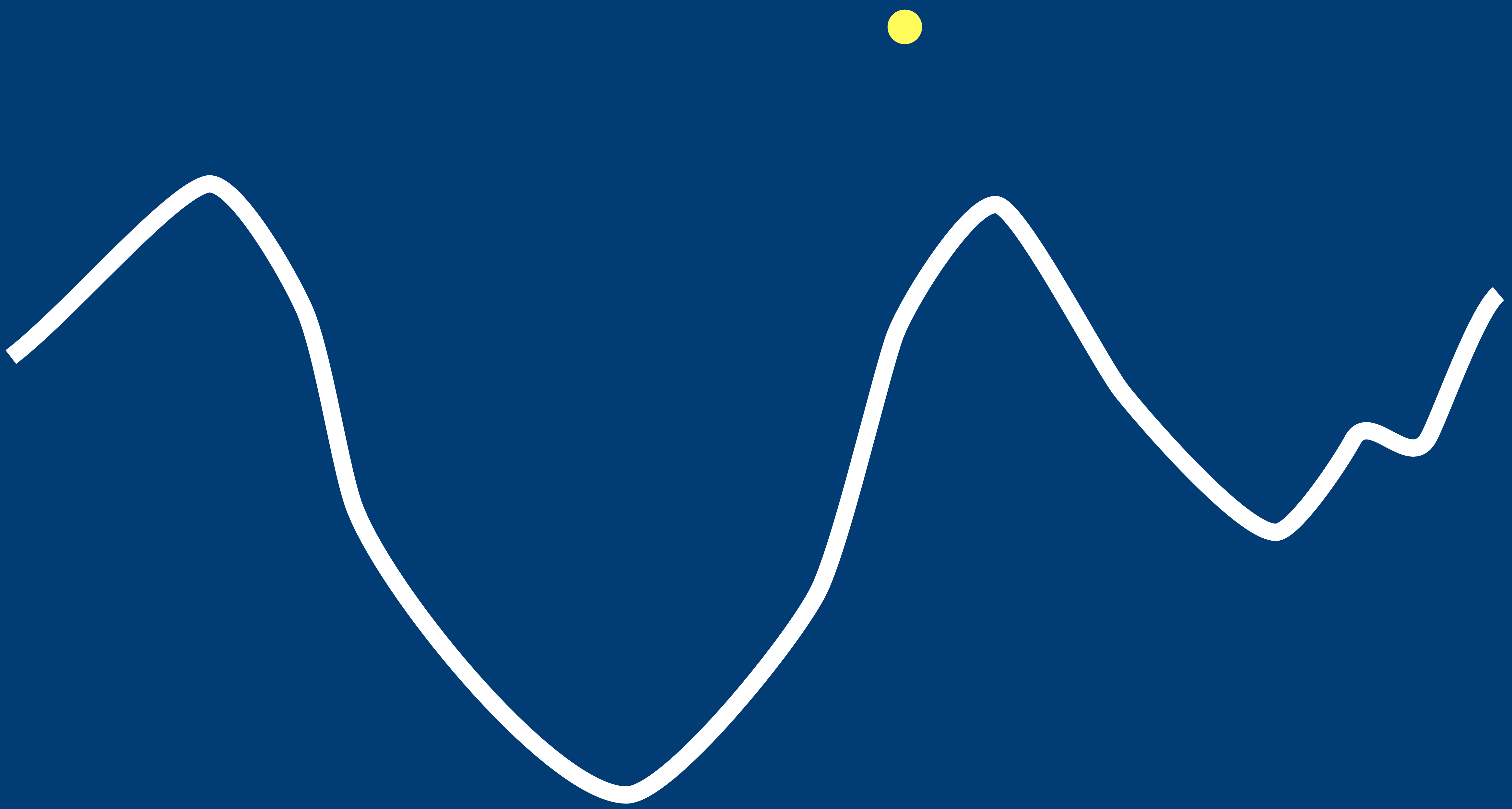
$$H\Psi = -\frac{1}{2}\nabla^2\Psi + V\Psi = E\Psi$$

Schroedinger

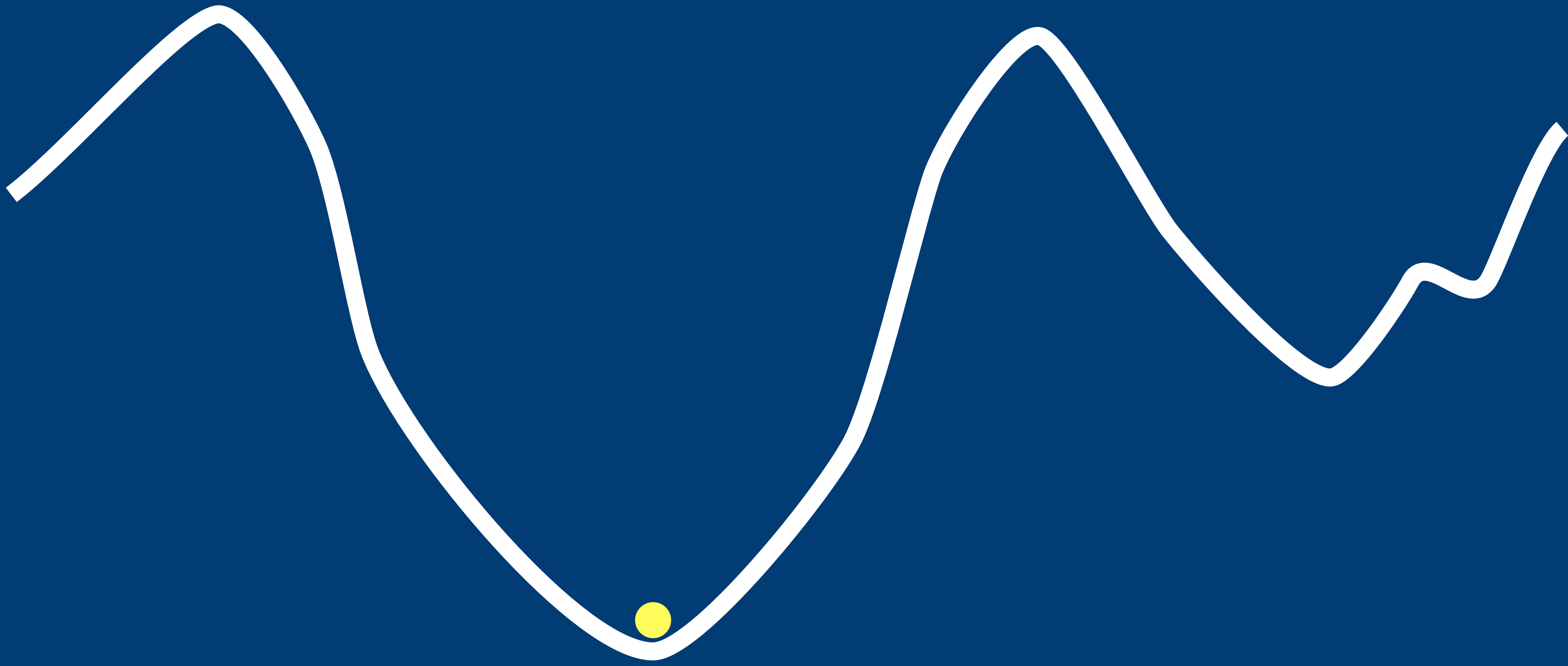
Smooth Landscapes



Smooth Landscapes

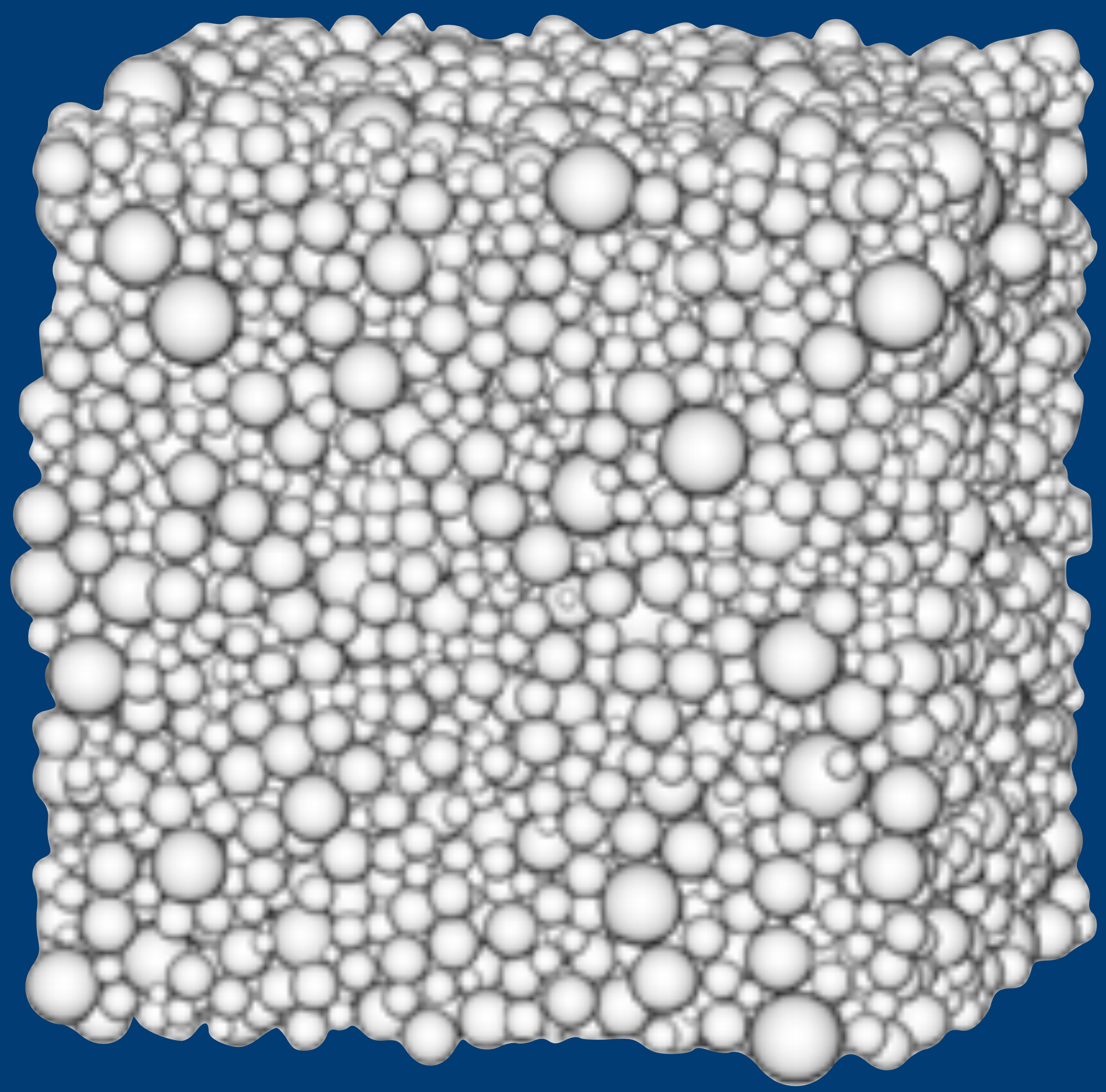


Smooth Landscapes

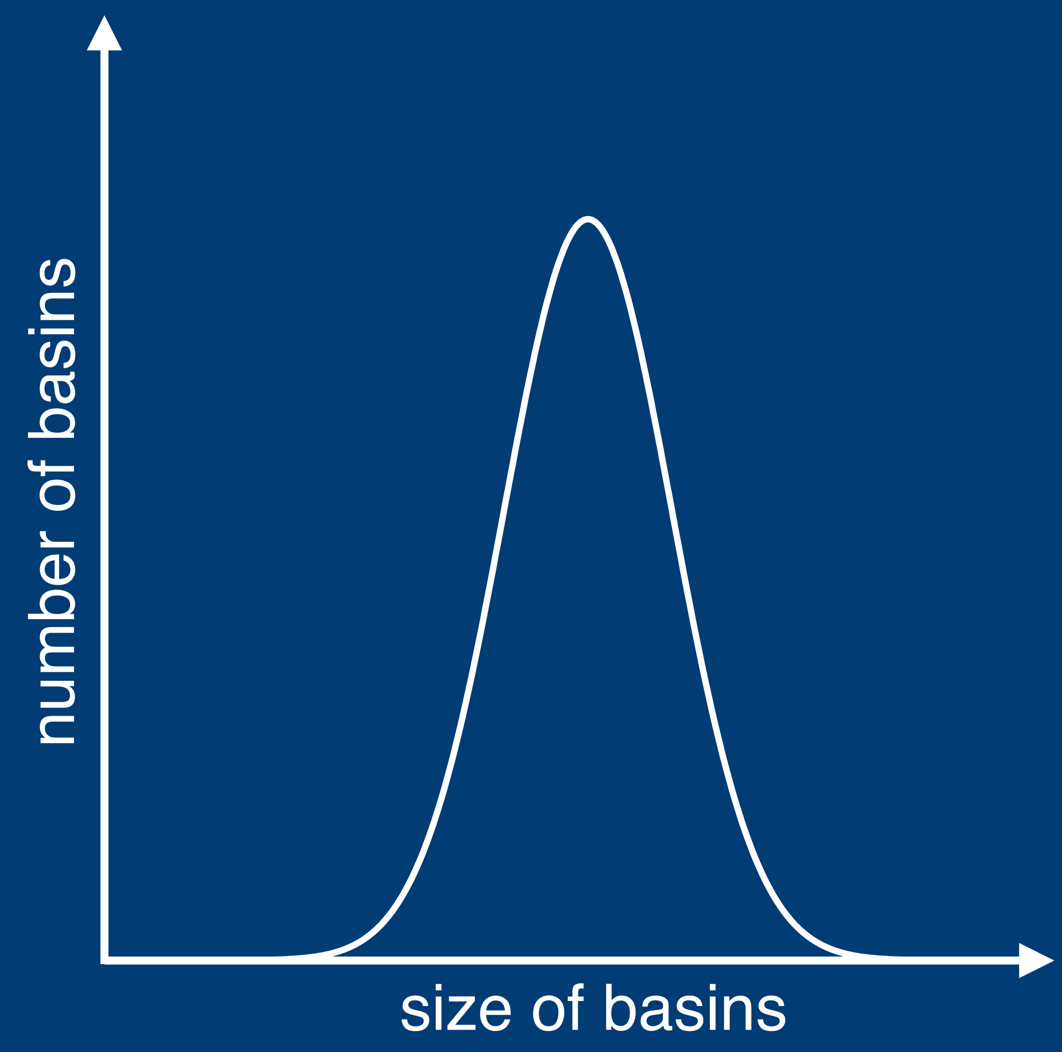


Deep basins are large

Basin Volumes

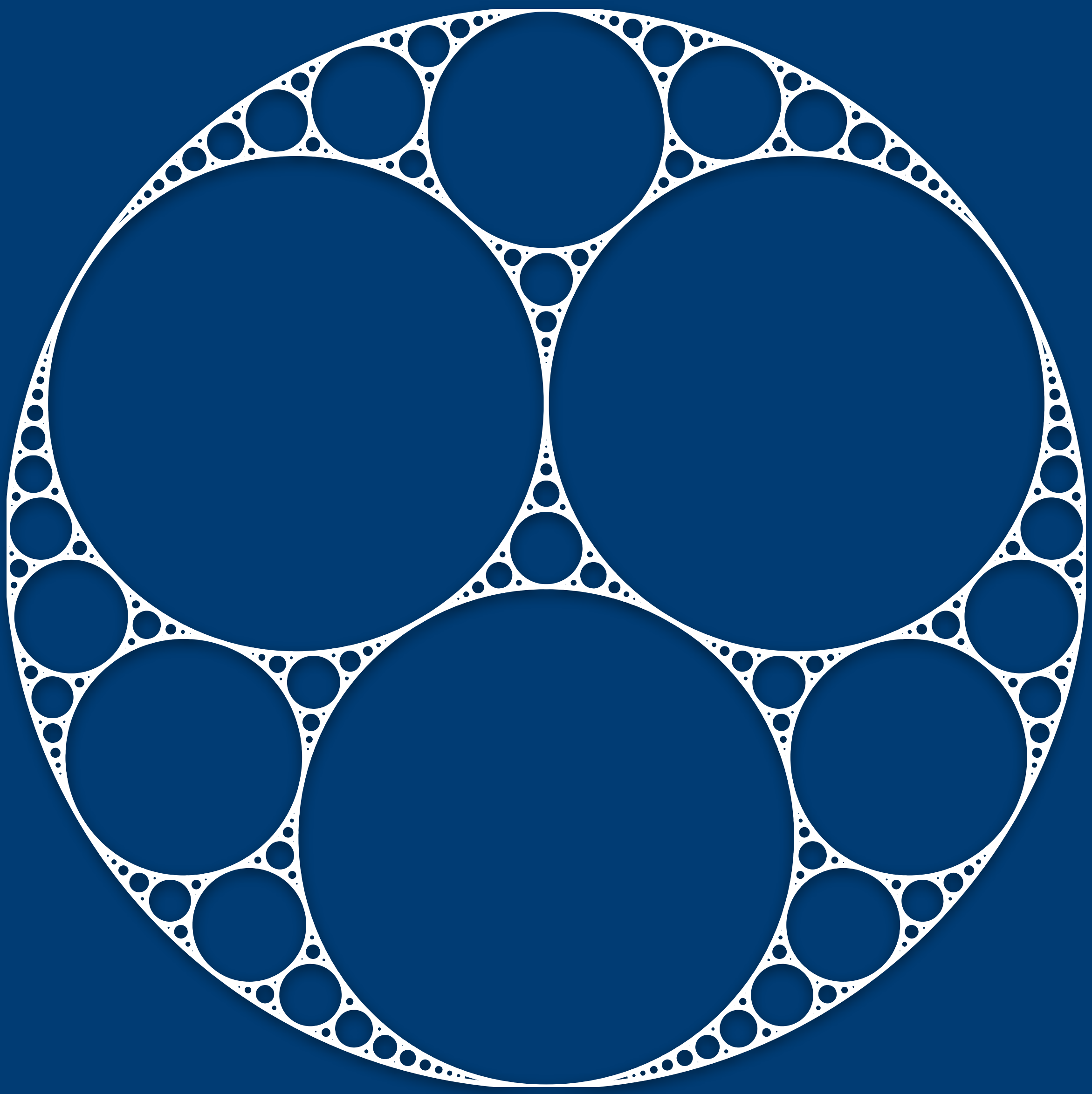


basin



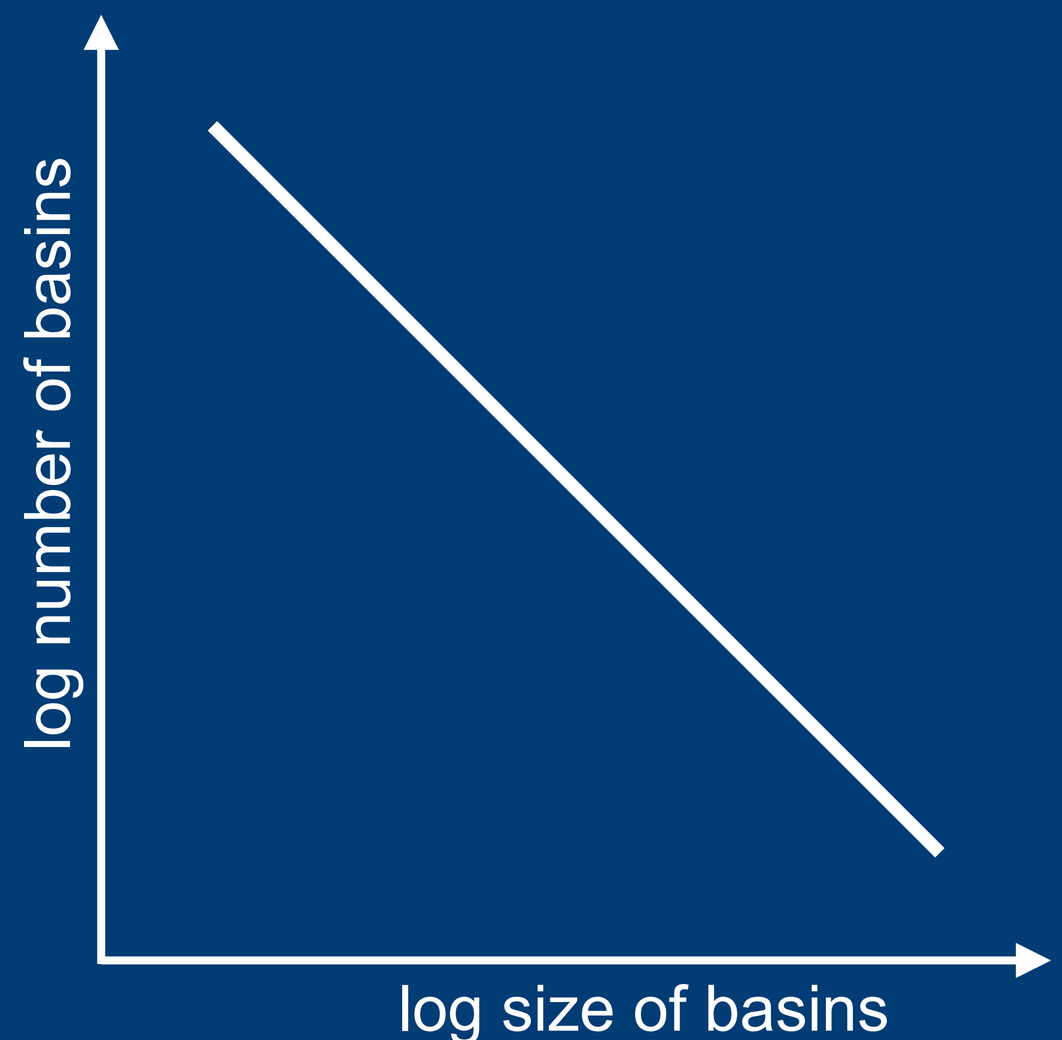
from Baranau and Ulrich Tallarek, Soft Matter, 2014, 10, 3826

Basin Volumes



Apollonian Gasket

a Fractal



Doye and Massen, J. Chem. Phys. 122, 084105 (2005)
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

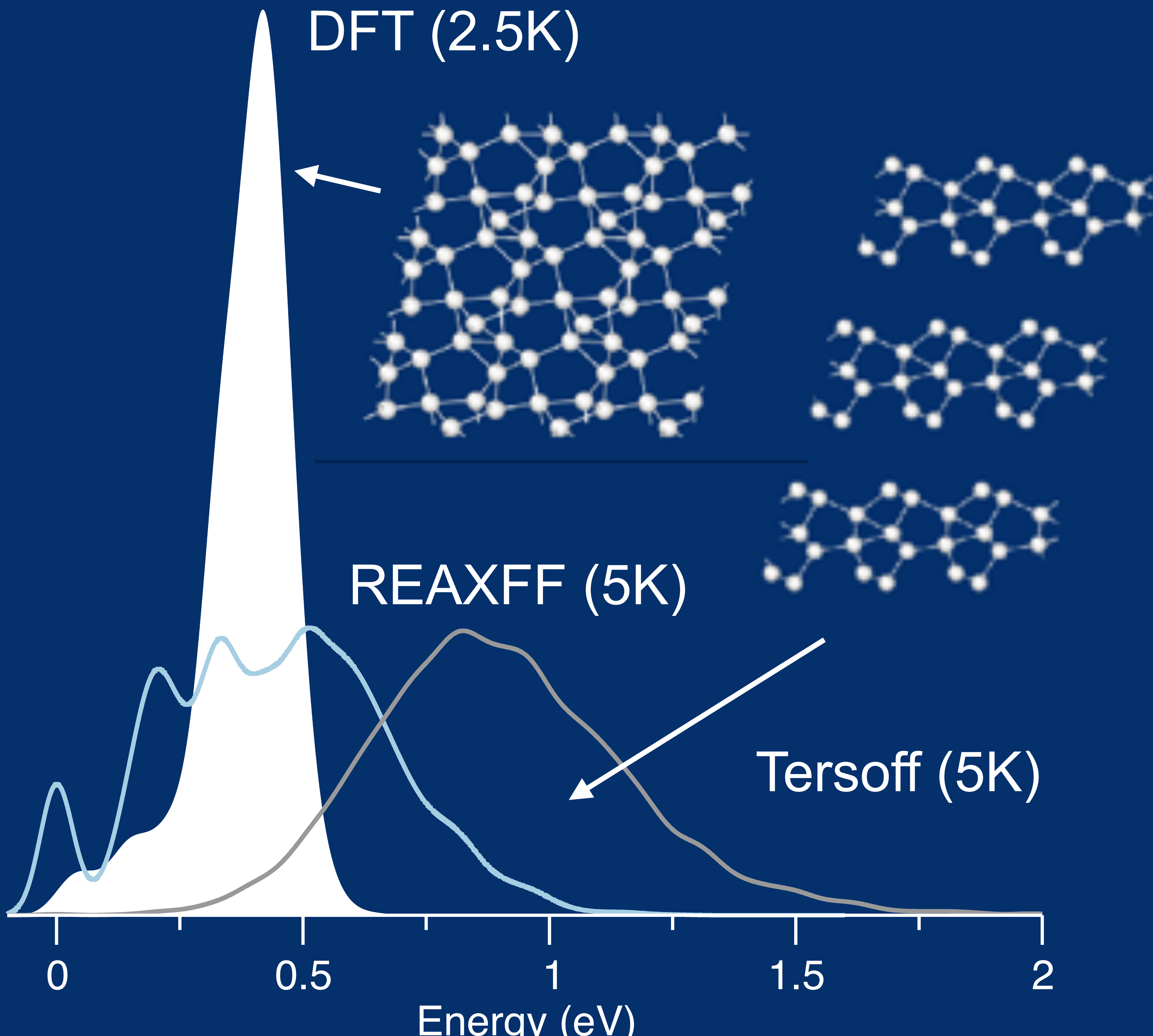
Impose chemical ideas
molecules, fragments, distances, connectivity

Impose symmetry
space, wallpaper, point group

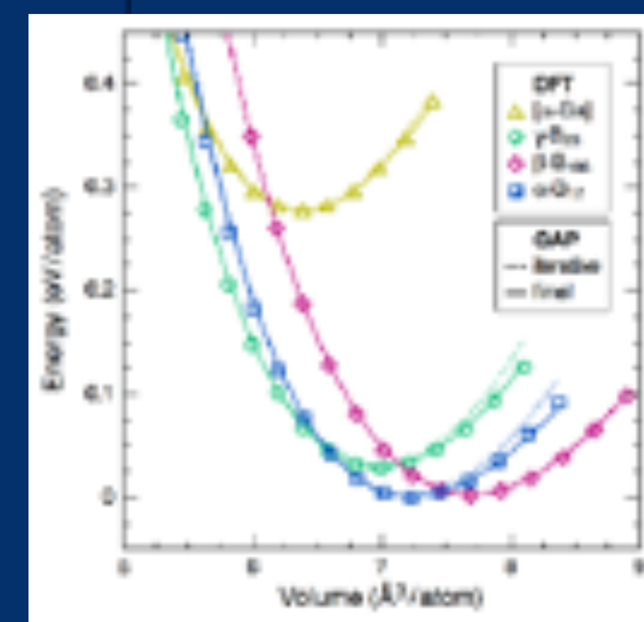
Use experimental data
lattice parameters

Empirical or First Principles?

Eight atoms of Silicon



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



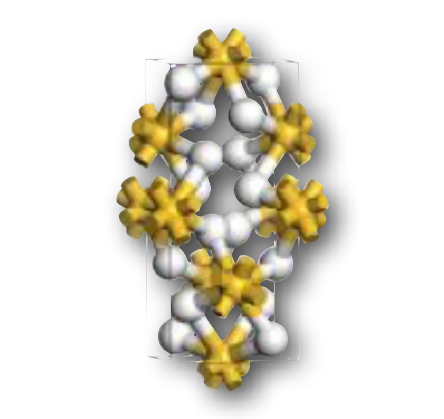
Deringer, Pickard, Csanyi, PRL, 2018

Learn entire energy landscape

Ab Initio Random Structure Searching

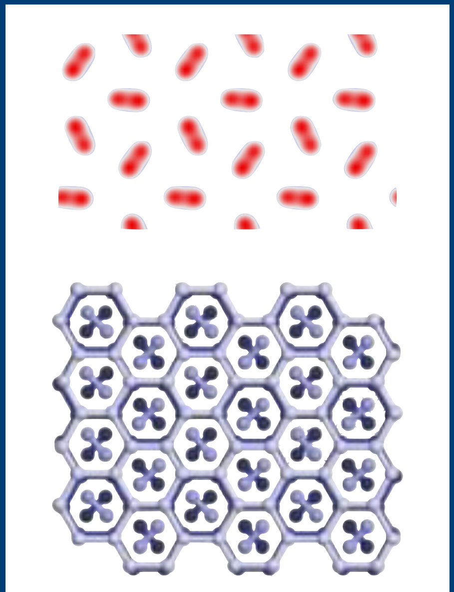
Superconducting hydrides

Physical Review Letters, 2006



Hydrogen is polar and "graphene"

Nature Physics, 2007



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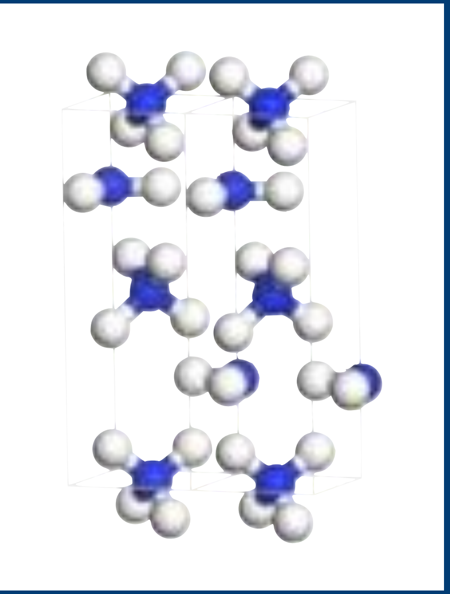
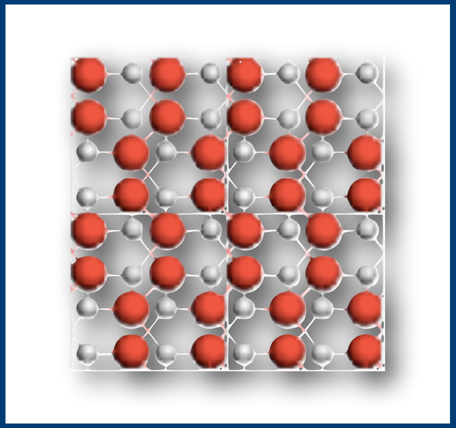


The end of water

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

rching


PRL 119, 107001 (2017) PHYSICAL REVIEW LETTERS week ending 8 SEPTEMBER 2017

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

Feng Peng, Ying Sun, Chris J. Pickard, Richard J. Needs, Qiang Wu, and Yanming Ma

(Received 11 May 2017; published 8 September 2017)

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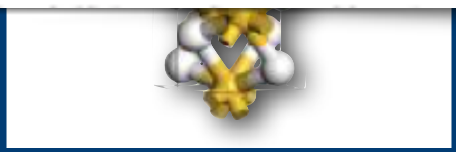

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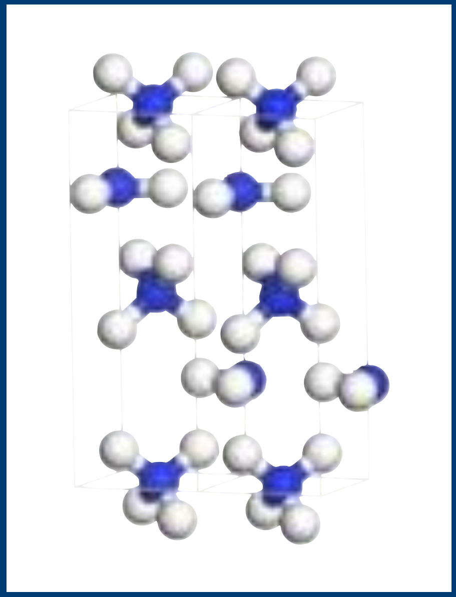

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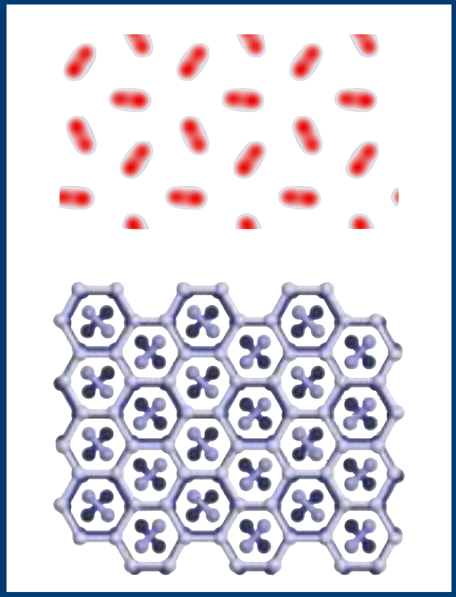

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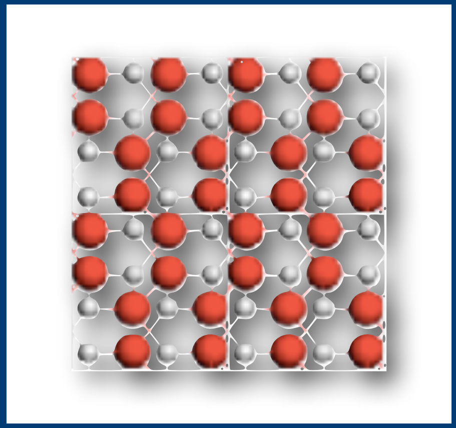

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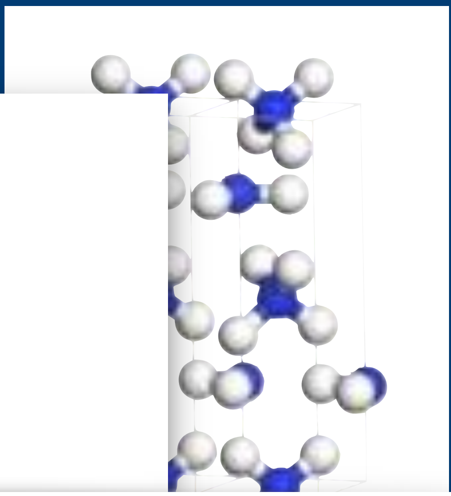
Physical Re...
20...

Superconductivity at 215 K in lanthanum hydride at high pressures

A. P. Drozdov, V. S. Minkov, S. P. Besedin, P. P. Kong, M. A. Kuzovnikov, D. A. Knyazev, M. I. Eremets

Max-Planck-Institut fur Chemie, Hahn-Meitner Weg 1, 55128 Mainz, Germany



Evidence for superconductivity above 260 K in lanthanum superhydride at megabar pressures

Maddury Somayazulu, Muhtar Ahart, Ajay K Mishra, Zachary M. Geballe, Maria Baldini, Yue Meng, Viktor V. Struzhkin, and Russell J. Hemley

Institute for Materials Science and Department of Civil and Environmental Engineering, The George Washington University, Washington DC 20052, USA
Geophysical Laboratory, Carnegie Institution of Washington, Washington DC 20015, USA
HPCAT, X-ray Science Division, Argonne National Laboratory, Argonne IL 60439, USA

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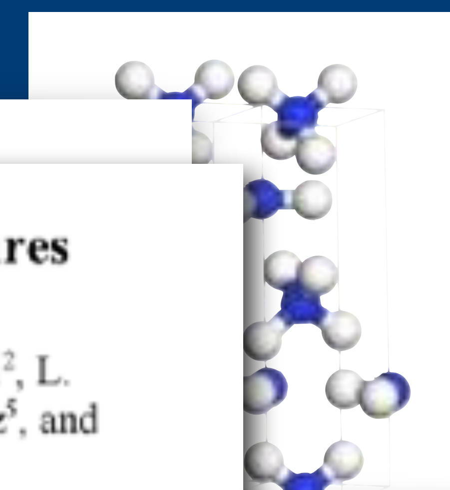
Physical Re...
20...

Superconductivity at 250 K in lanthanum hydride under high pressures

A. P. Drozdov[1], P. P. Kong[1], V. S. Minkov[1], S. P. Besedin[1], M. A. Kuzovnikov[1,6], S. Mozaffari[2], L. Balicas[2], F. Balakirev[3], D. Graf[2], V. B. Prakapenka[4], E. Greenberg[4], D. A. Knyazev[1], M. Tkacz[5], and M. I. Eremets[1]



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Ab Initio Random Structure Searching

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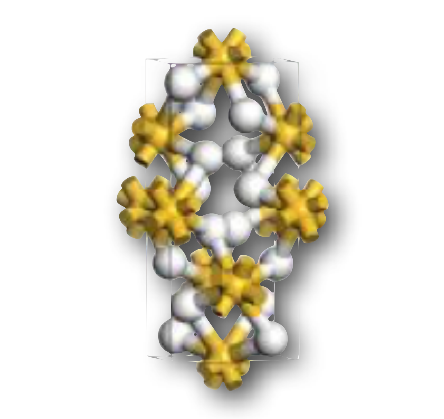

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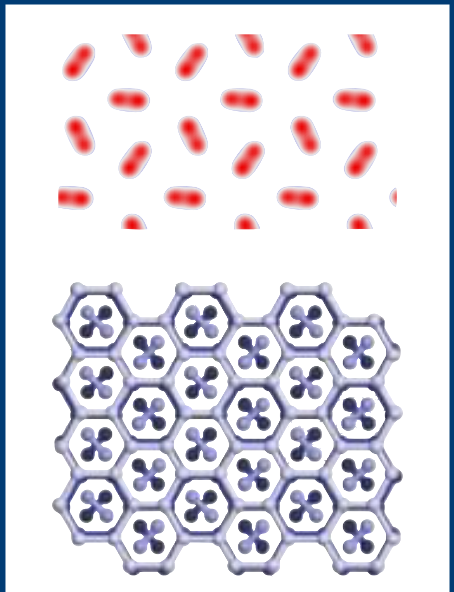

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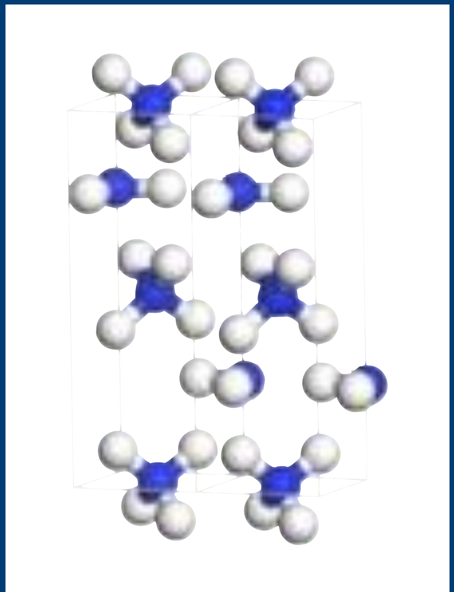

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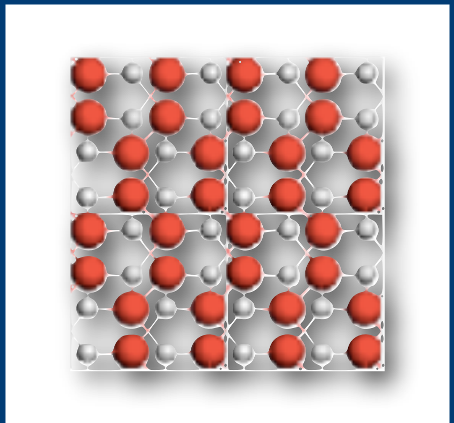

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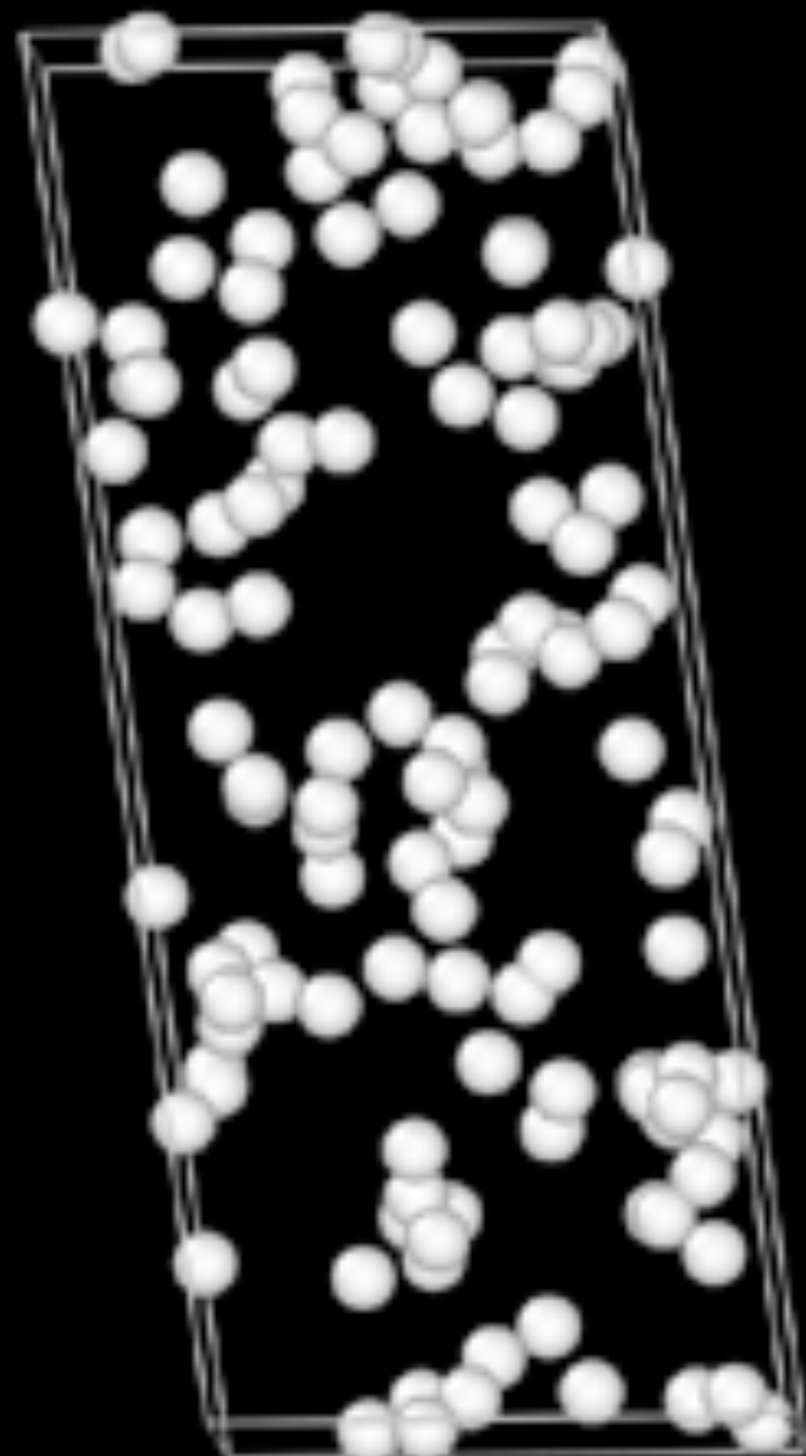
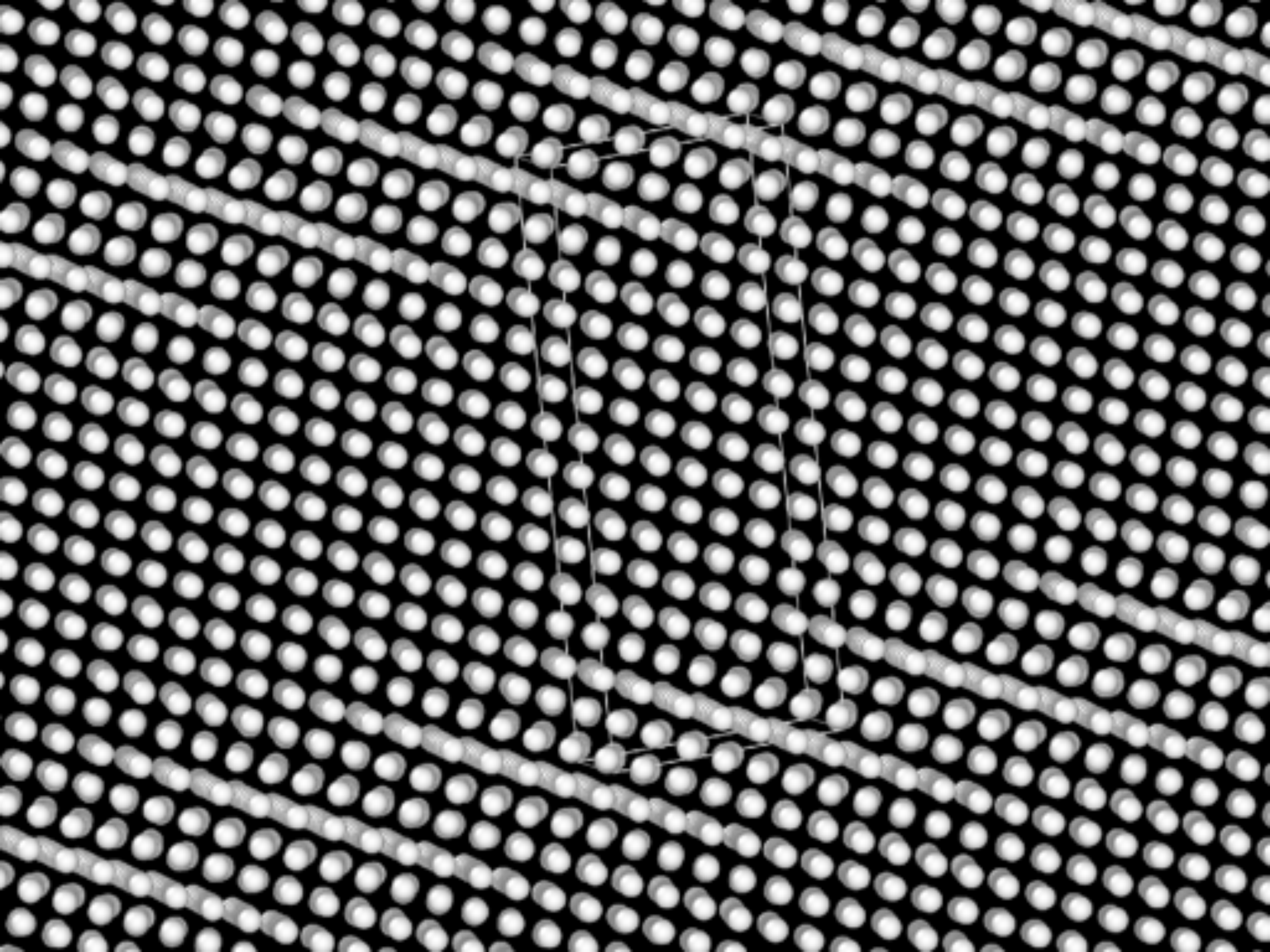


Thomas-Fermi-Dirac

simplified 128 atoms ($V \sim L^{384}$)

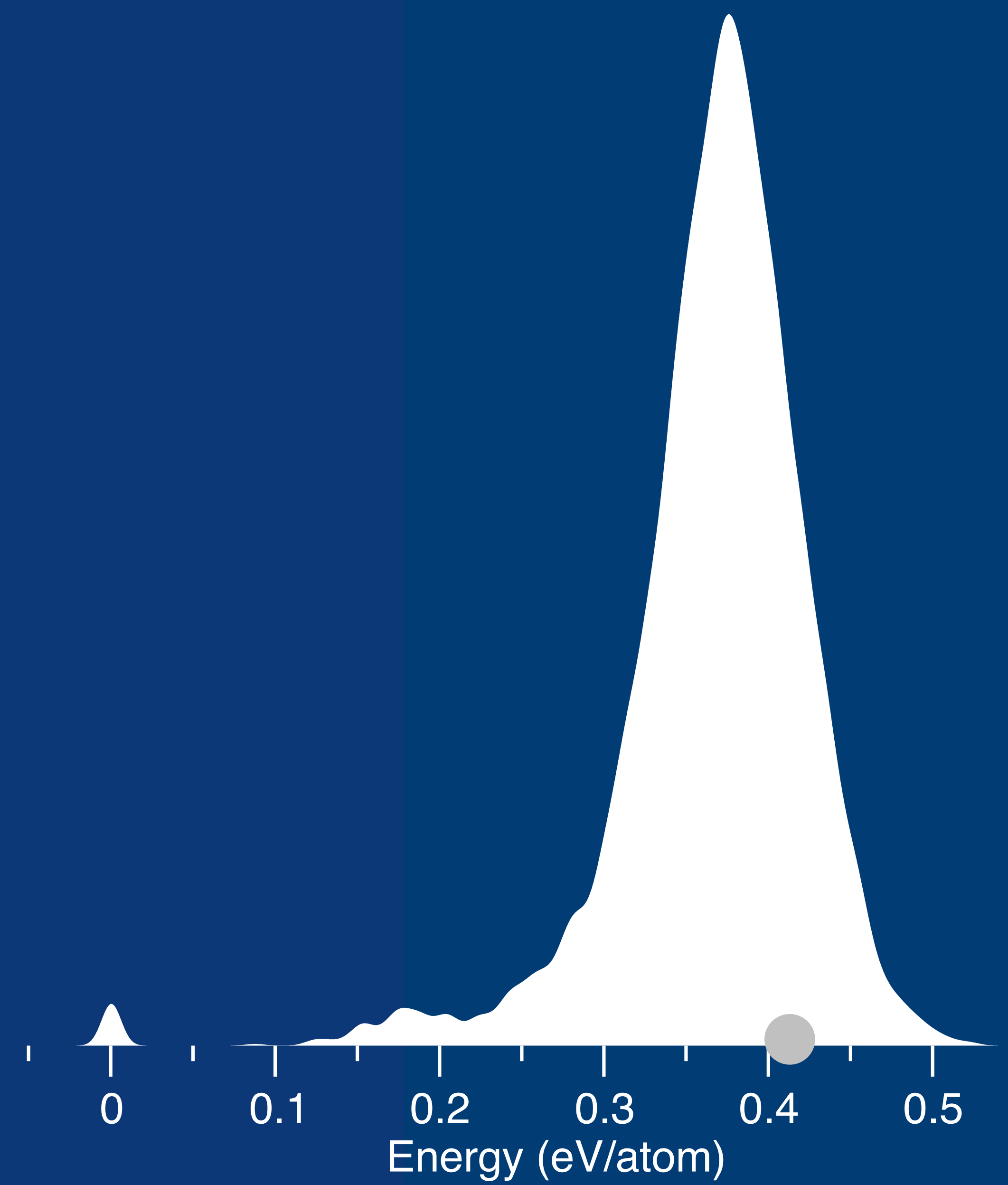
C.J. Pickard, *Physical Review Materials*, **2**, 013806 (2018)



Gamma Boron

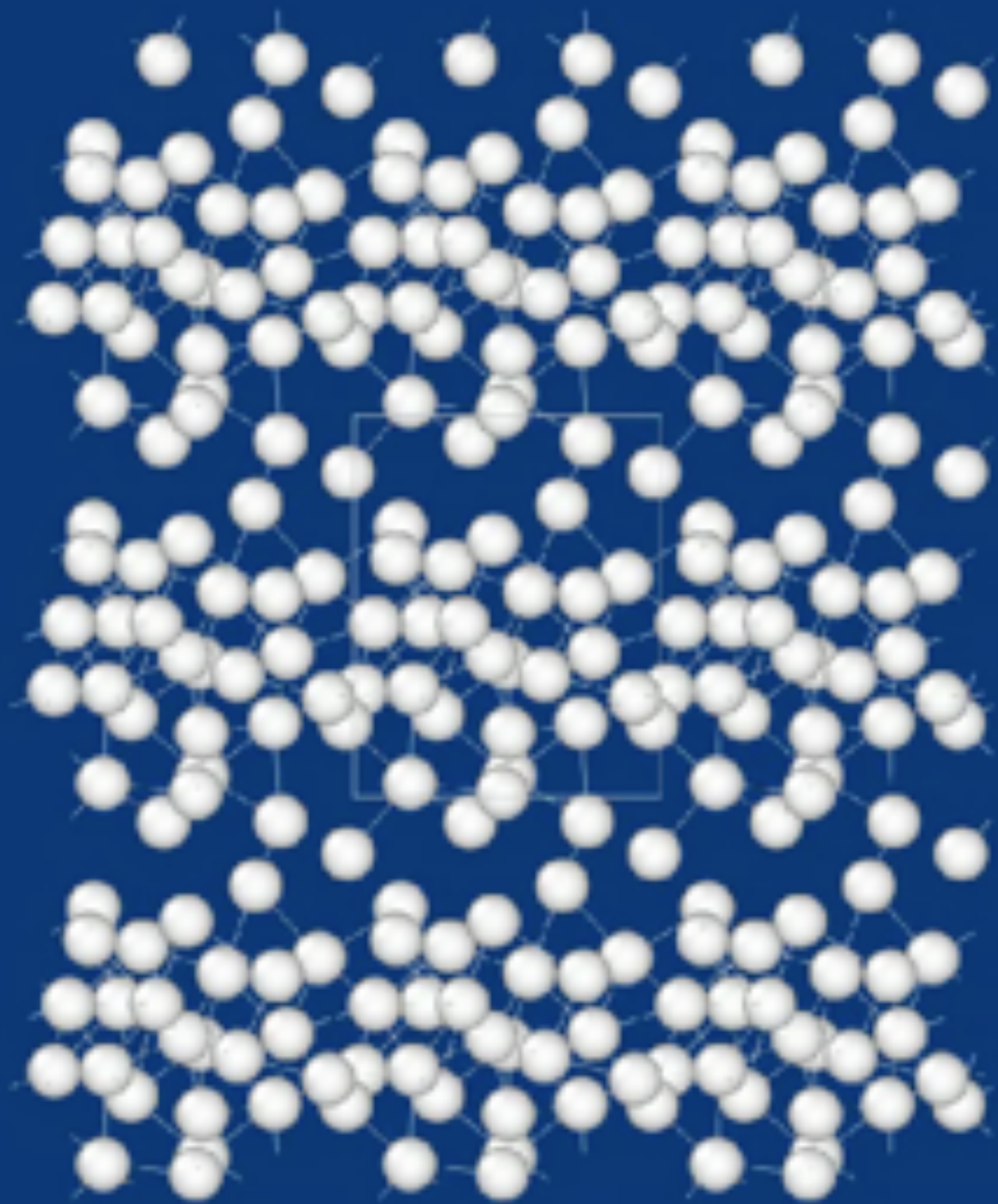
Fixed Cell

AIRSS Example 2.3



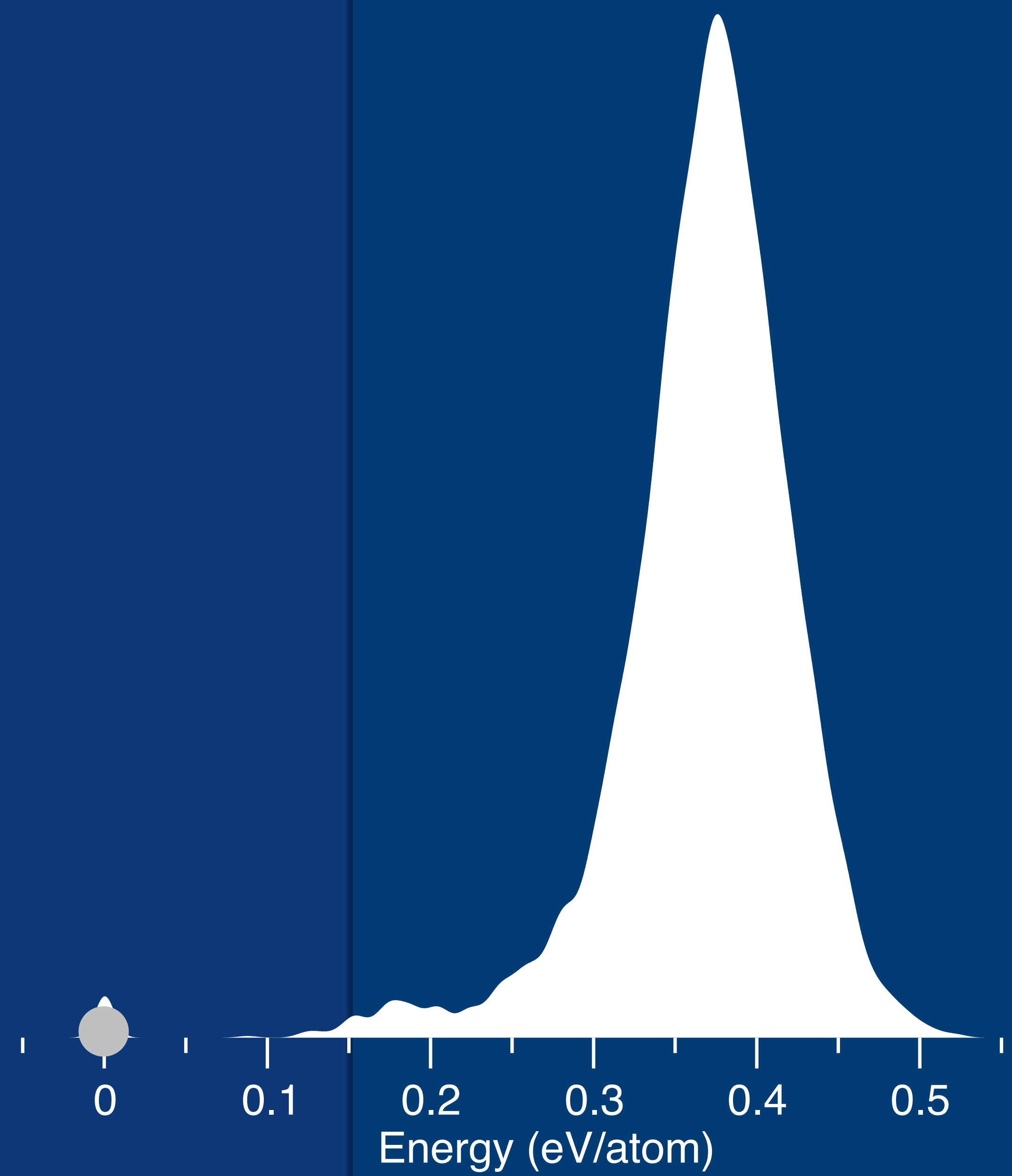
Oganov et al *Nature* 2009

Gamma Boron



Fixed Cell

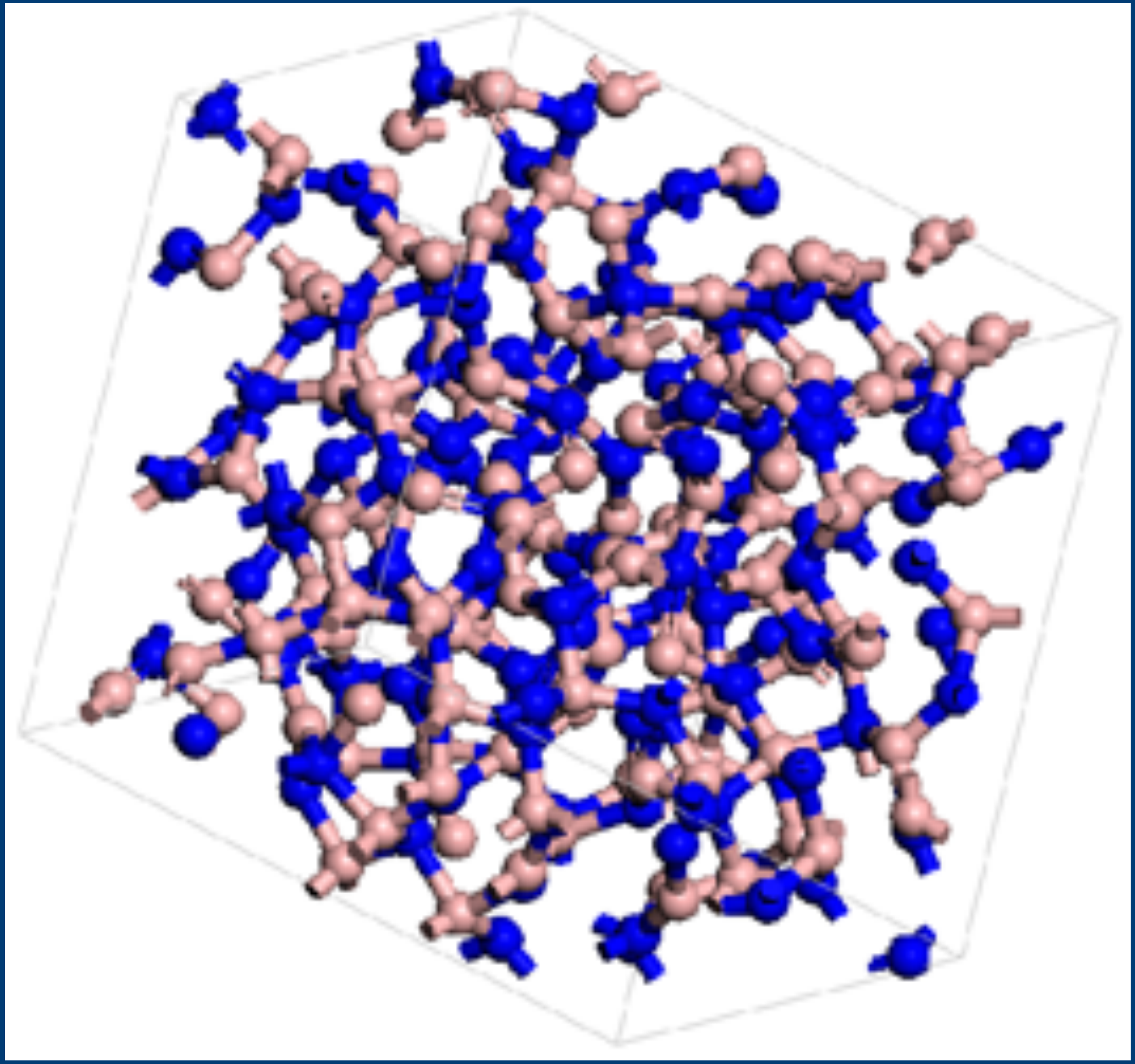
AIRSS Example 2.3



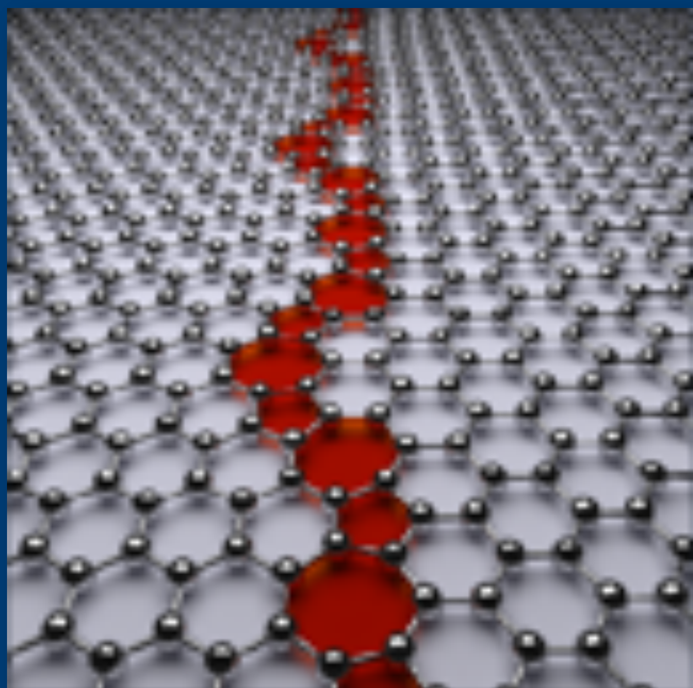
Oganov et al *Nature* 2009

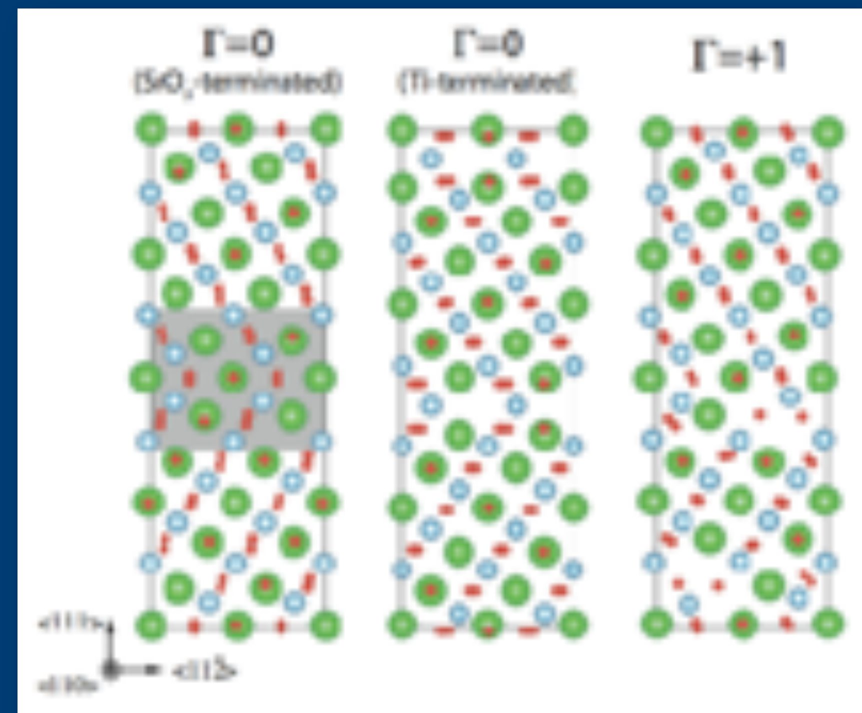
Random "sensible" structures

```
#VARVOL=11.8

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

#SYMMOPS=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
```

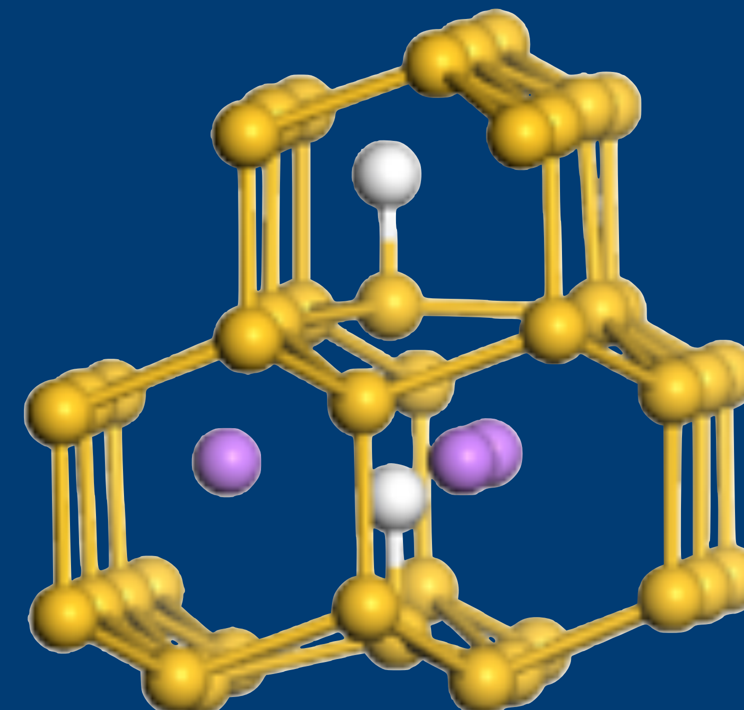


Beyond Crystals



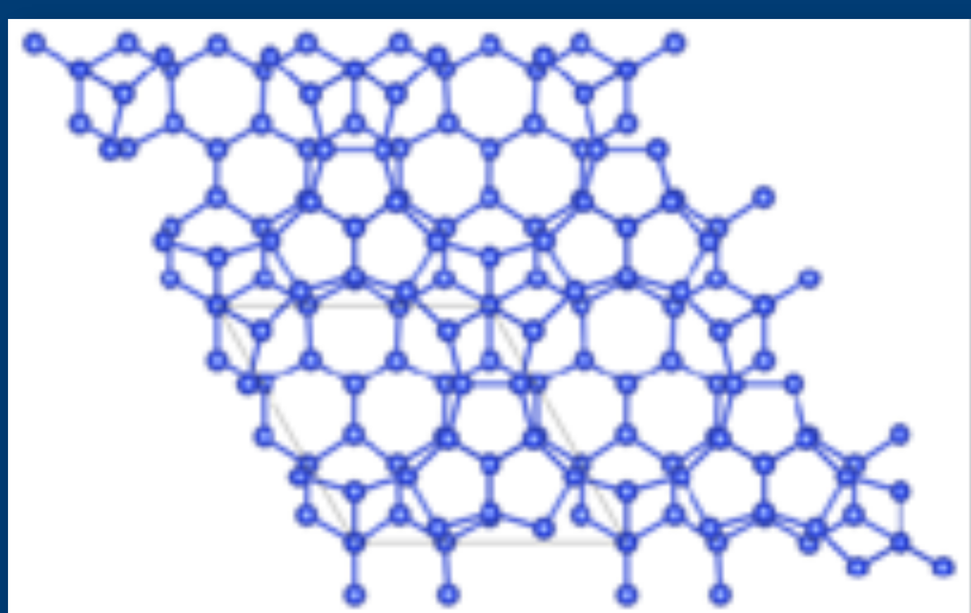


Schusteritsch & Pickard, "Predicting interface structures: From SrTiO3 to graphene", Physical Review B (2014)

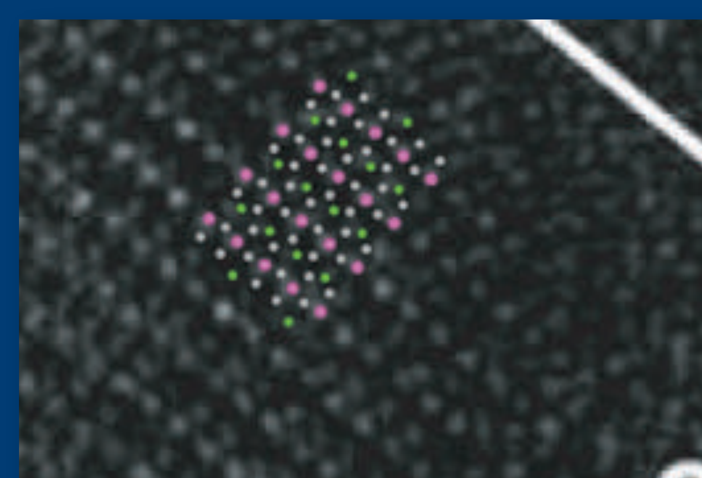


{2H,3Li} complex in silicon
Morris, Grey, Needs & Pickard, 2014

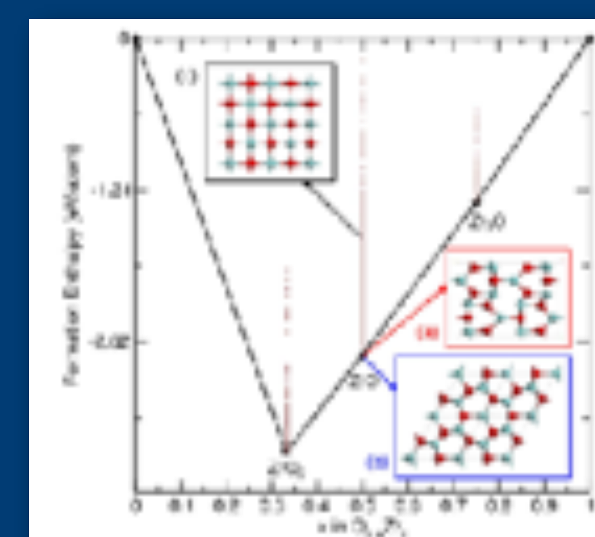
Interfacial Materials



Silicon(111) 3x3 reconstruction

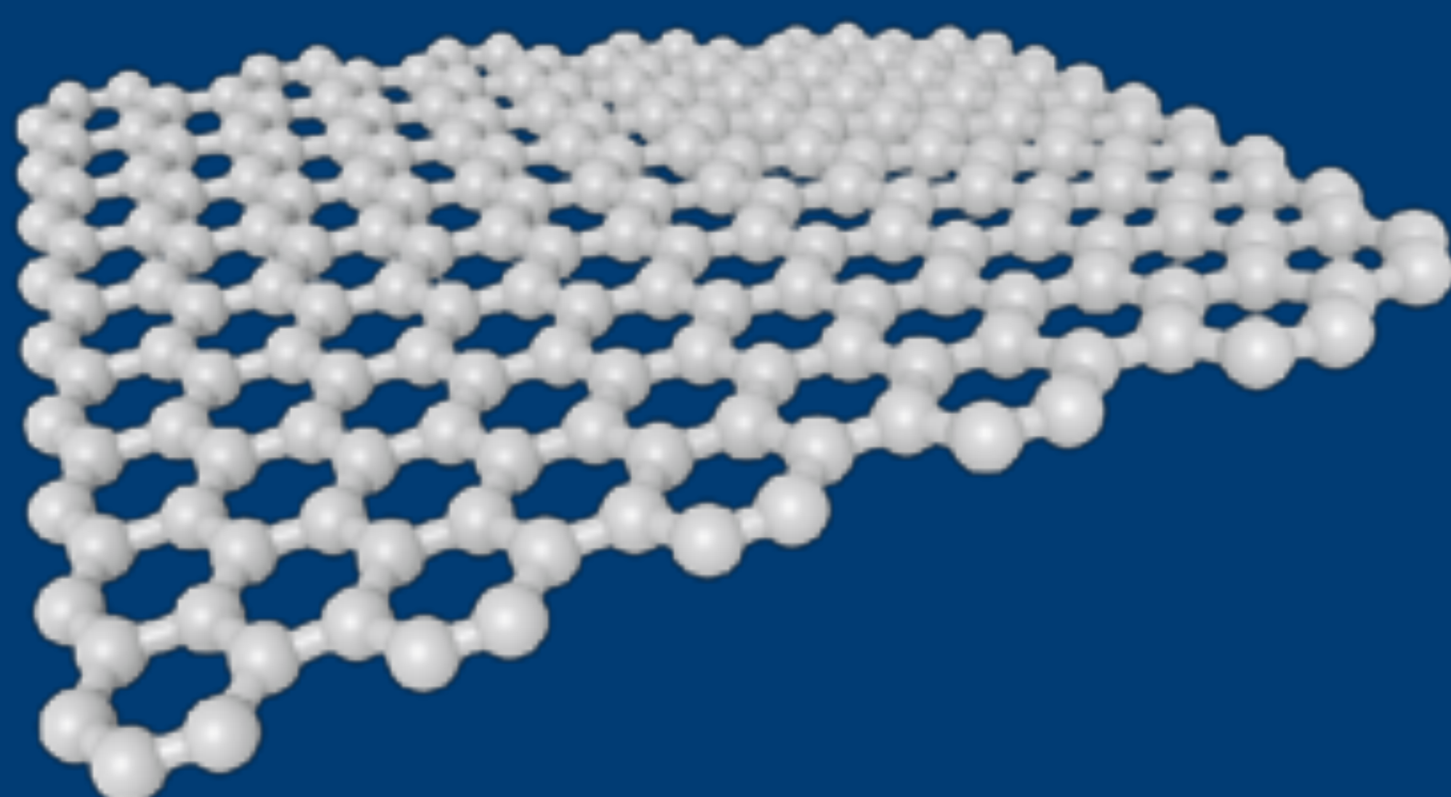


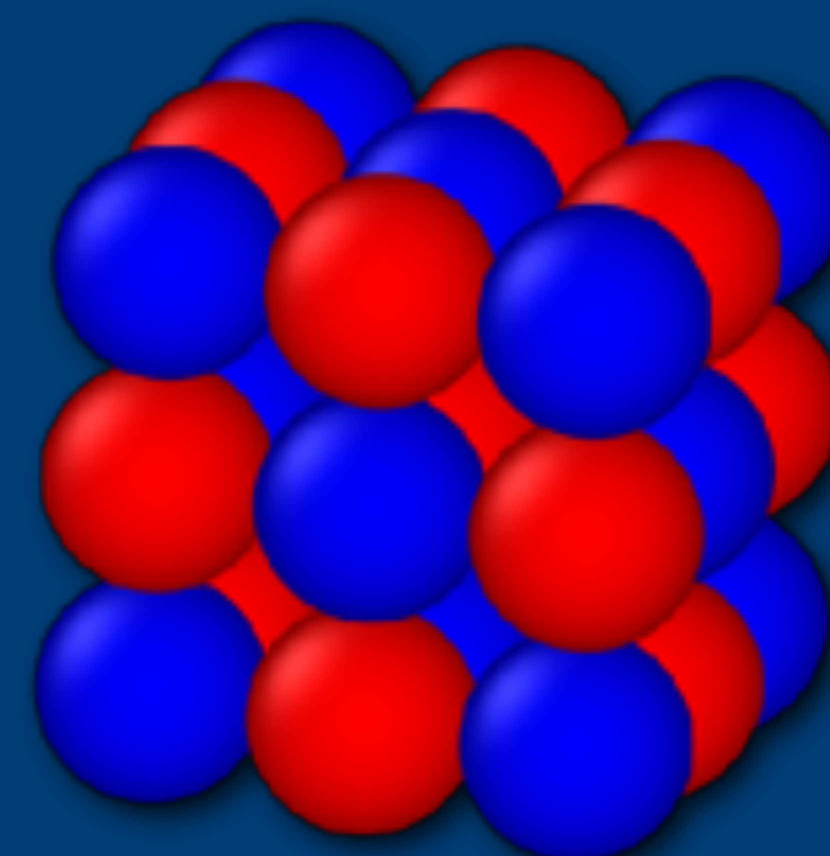
Ni_3InAs
Schusteritsch et al, 2015



Zirconium suboxide
Nicholls et al, 2015

Challenges





New directions

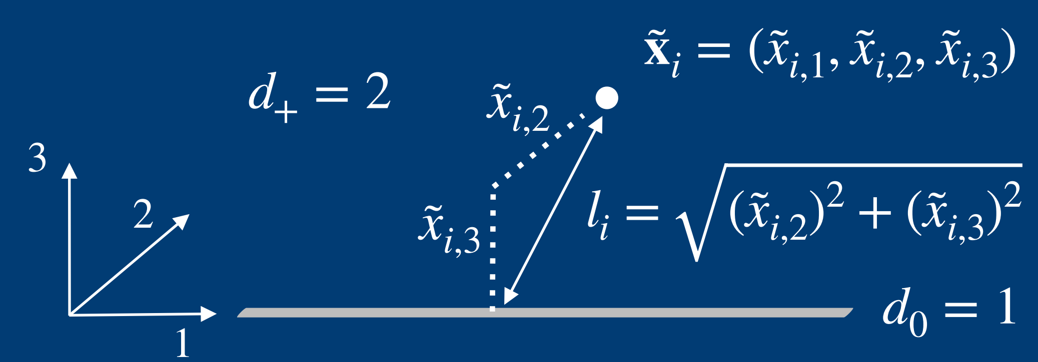
*Allow the particles making up a structure to explore a higher dimensional **physical** space.*

$$d = d_0 + d_+$$

Hyperspace | Normal space | Extra dimensions

$$\bar{E}(\{\tilde{\mathbf{x}}_i\}) = \tilde{E}(\{\tilde{\mathbf{x}}_i\}) + \frac{1}{2}\mu \sum_i l_i^2$$

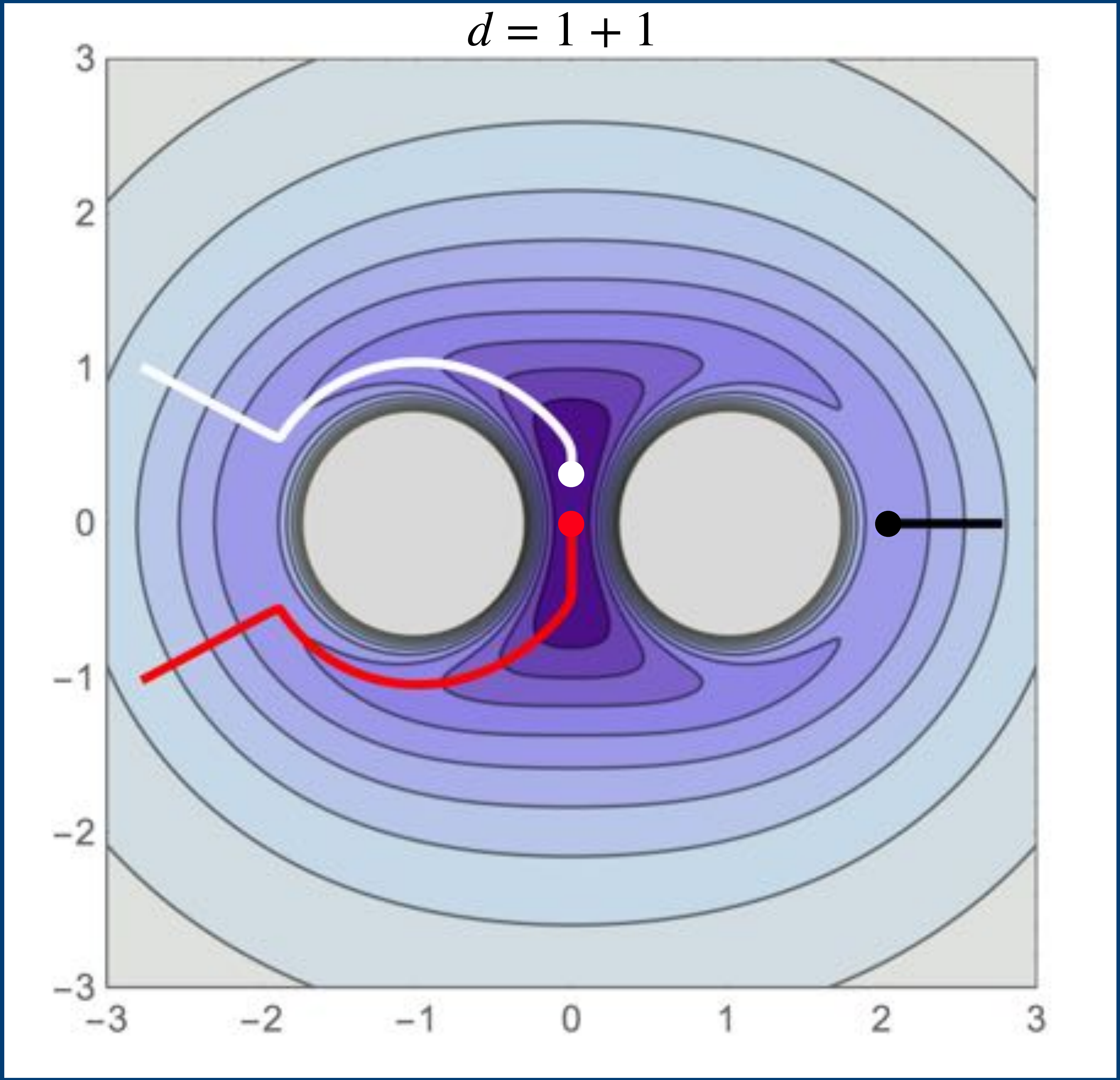
Energy extended to hyperspace | Increasing penalty



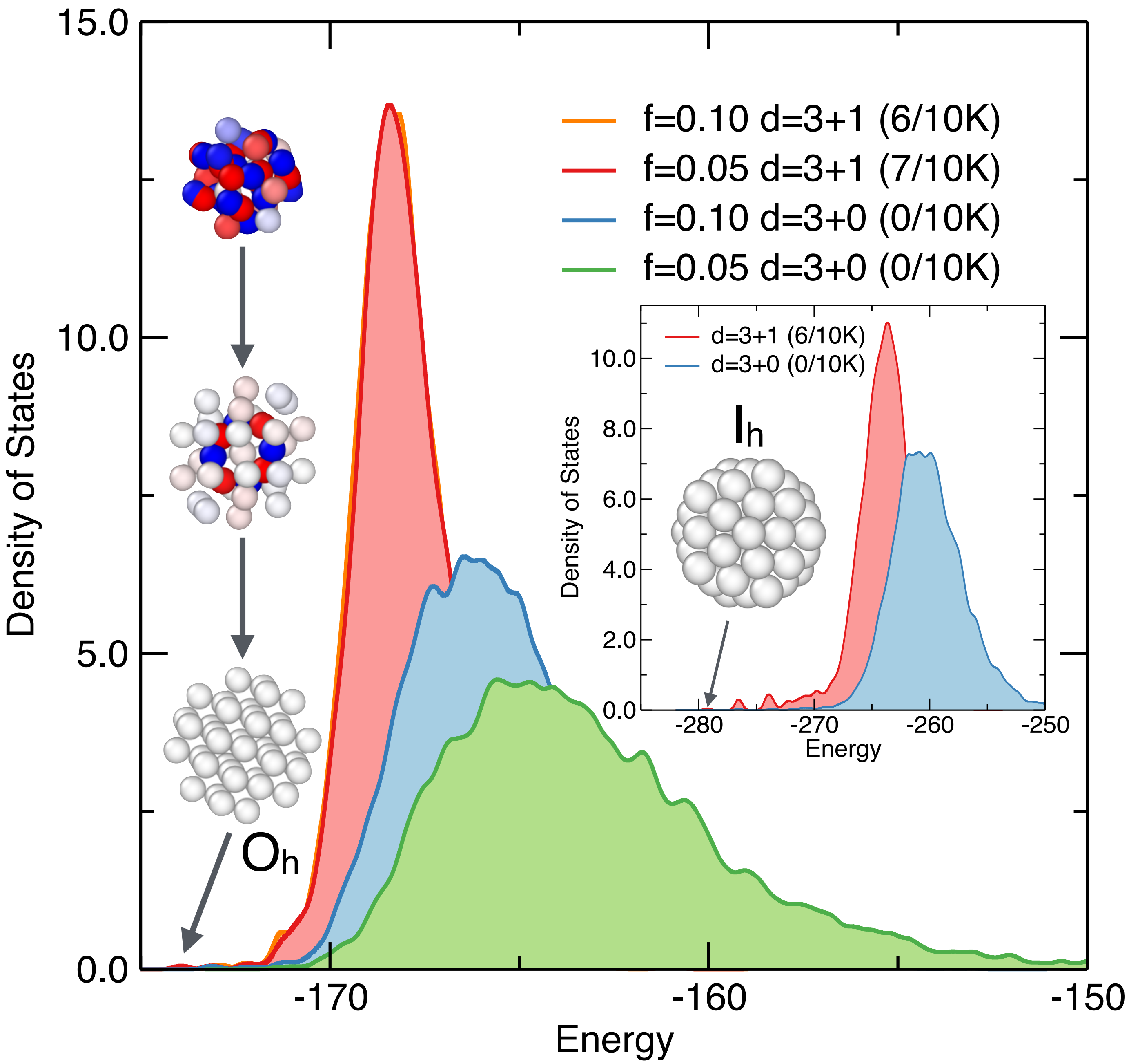
$$\mu = \mu_0 \beta^{n-1} \quad \mu_0 = 10,\ \beta = 1.001$$

C.J. Pickard, "*Hyperspatial optimization of structures*", PRB (to appear)

Toy example



Lennard-Jones Clusters

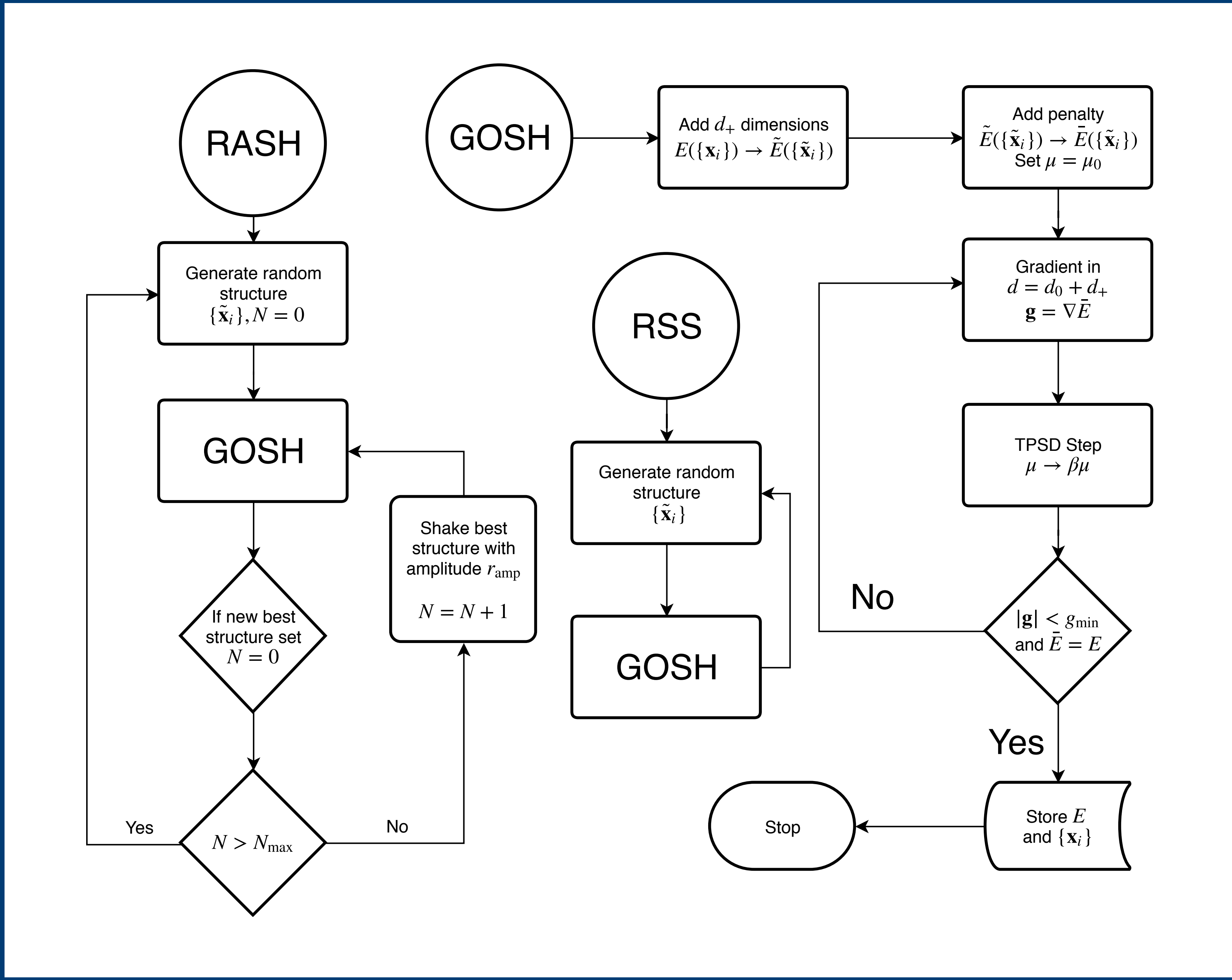


d	f	Num. of Lennard-Jones atoms (PG of GS)					
		37 (C_1)	38 (O_h)	39 (C_{5v})	47 (C_1)	55 (I_h)	69 (C_{5v})
3+0	0.05	4.5	6.0	4.4	4.6	5.6	7.0†
	0.10	3.8	5.0	3.8	4.1	4.8	6.5†
	0.20	3.2	3.9	3.1	3.5	3.6	5.9†
3+1	0.05	3.3	3.4	3.1	3.6	3.3	5.9†
	0.10	3.2	3.3	3.2	3.6	3.2	5.9†
	0.20	3.2	3.2	3.2	3.6	3.2	5.9†
3+2	0.10	3.5	3.8	3.2	3.7	3.3	5.8†

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

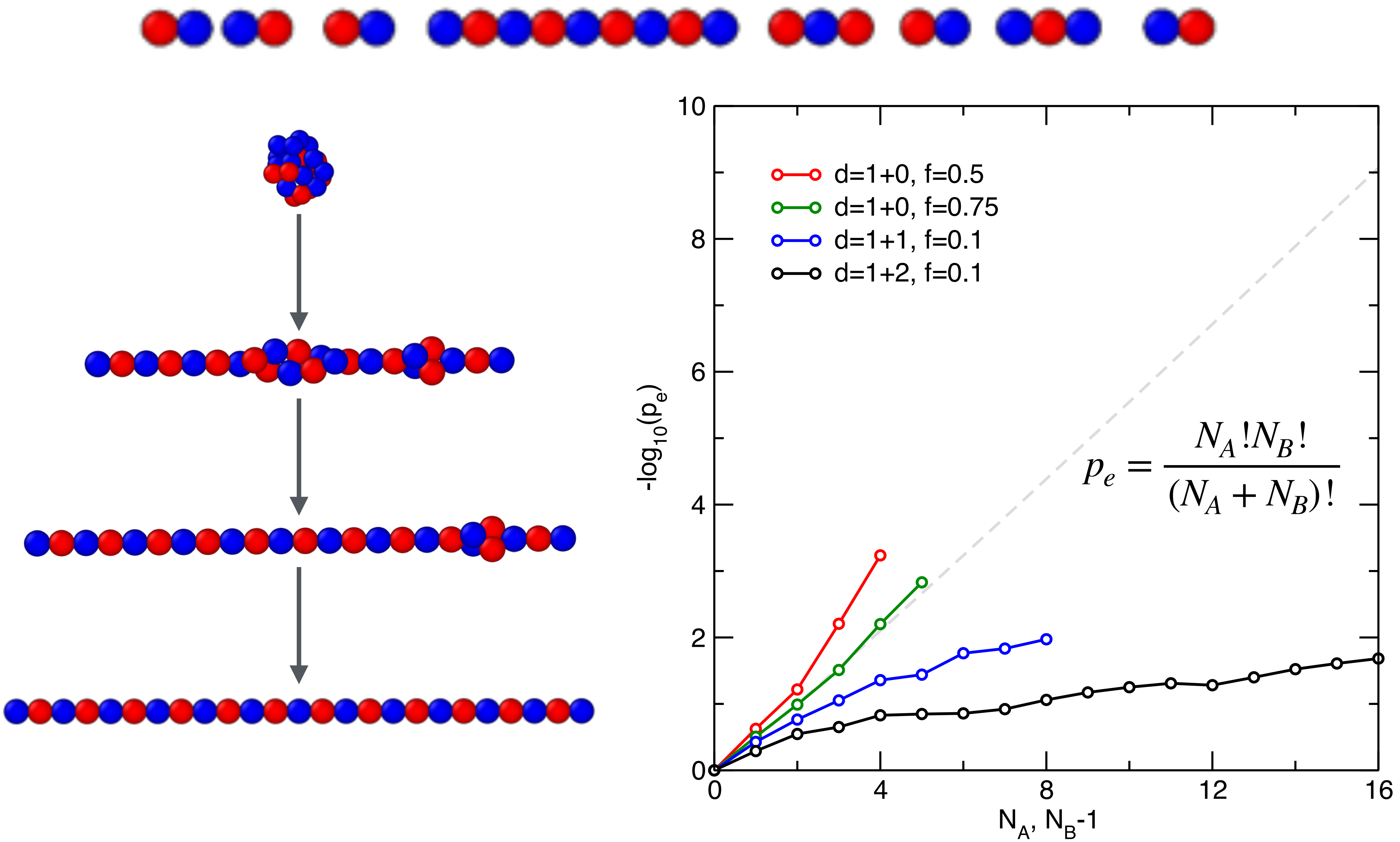
[1] S. E. Schönborn, S. Goedecker, S. Roy, and A. R. Oganov, J. Chem. Phys. **130**, 144108 (2009).

Acronyms

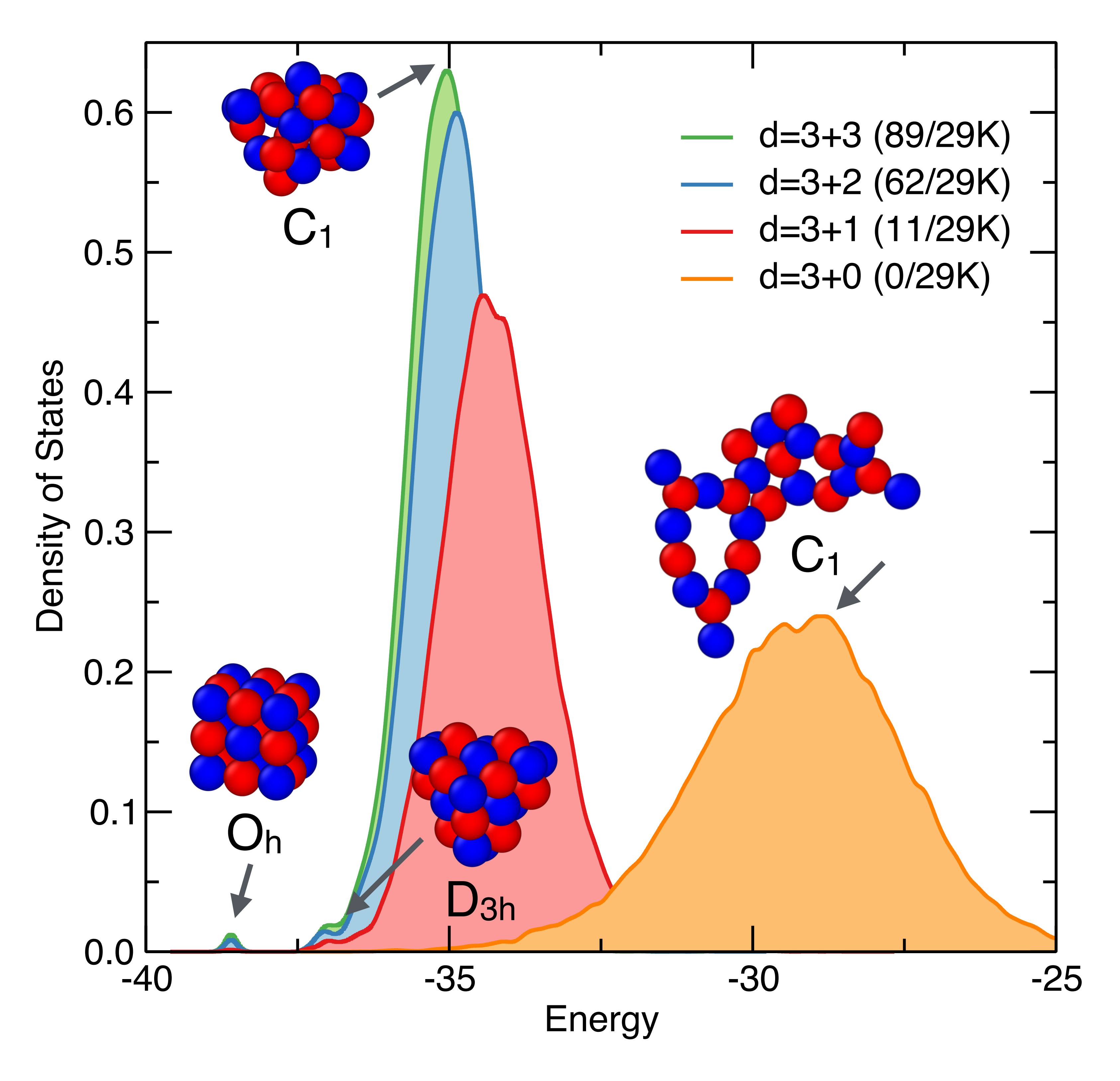


Random structure search - RSS
Geometry optimisation of structures from hyperspace - GOSH
Relax and shake - RASH

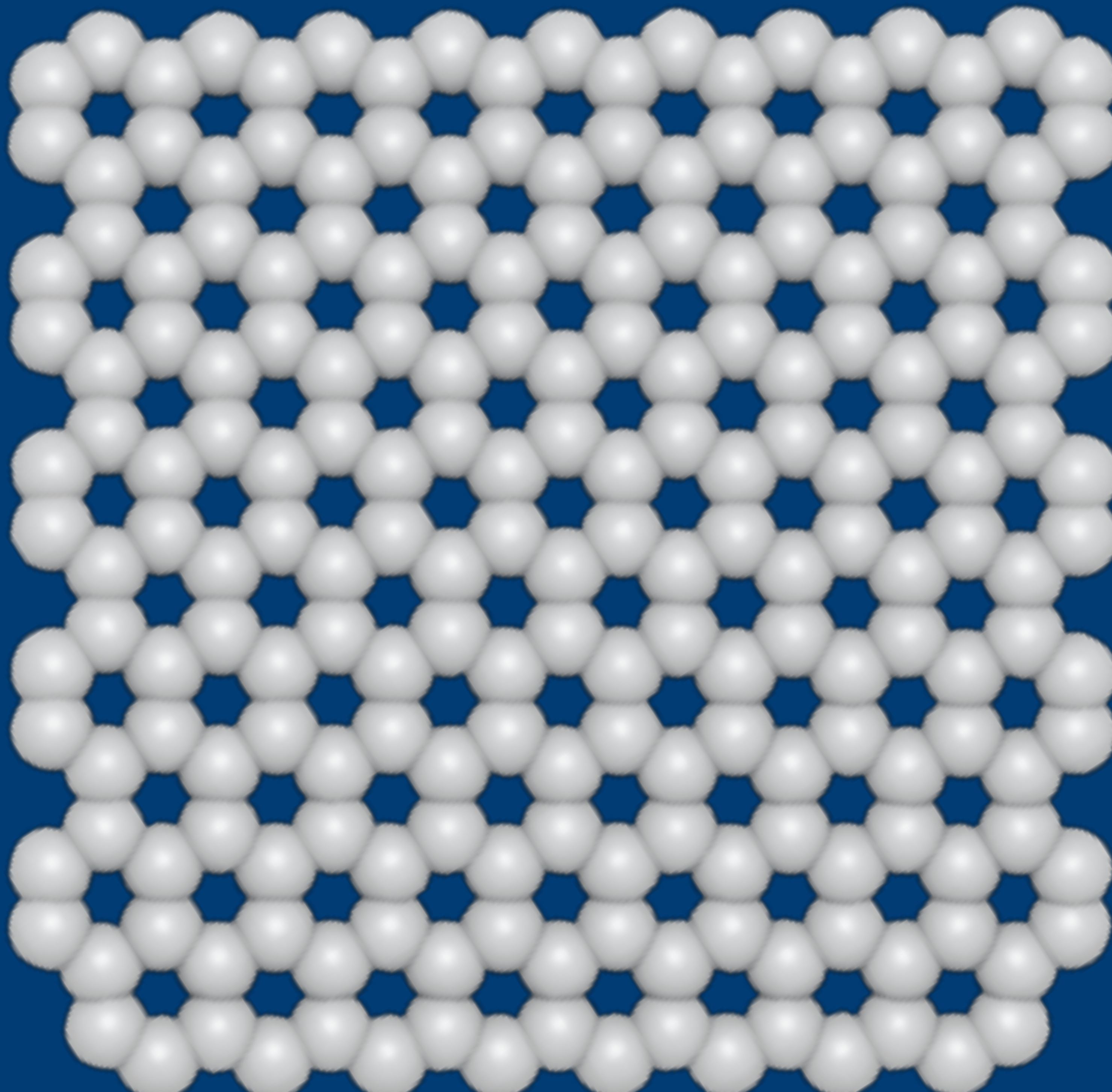
Binary chain



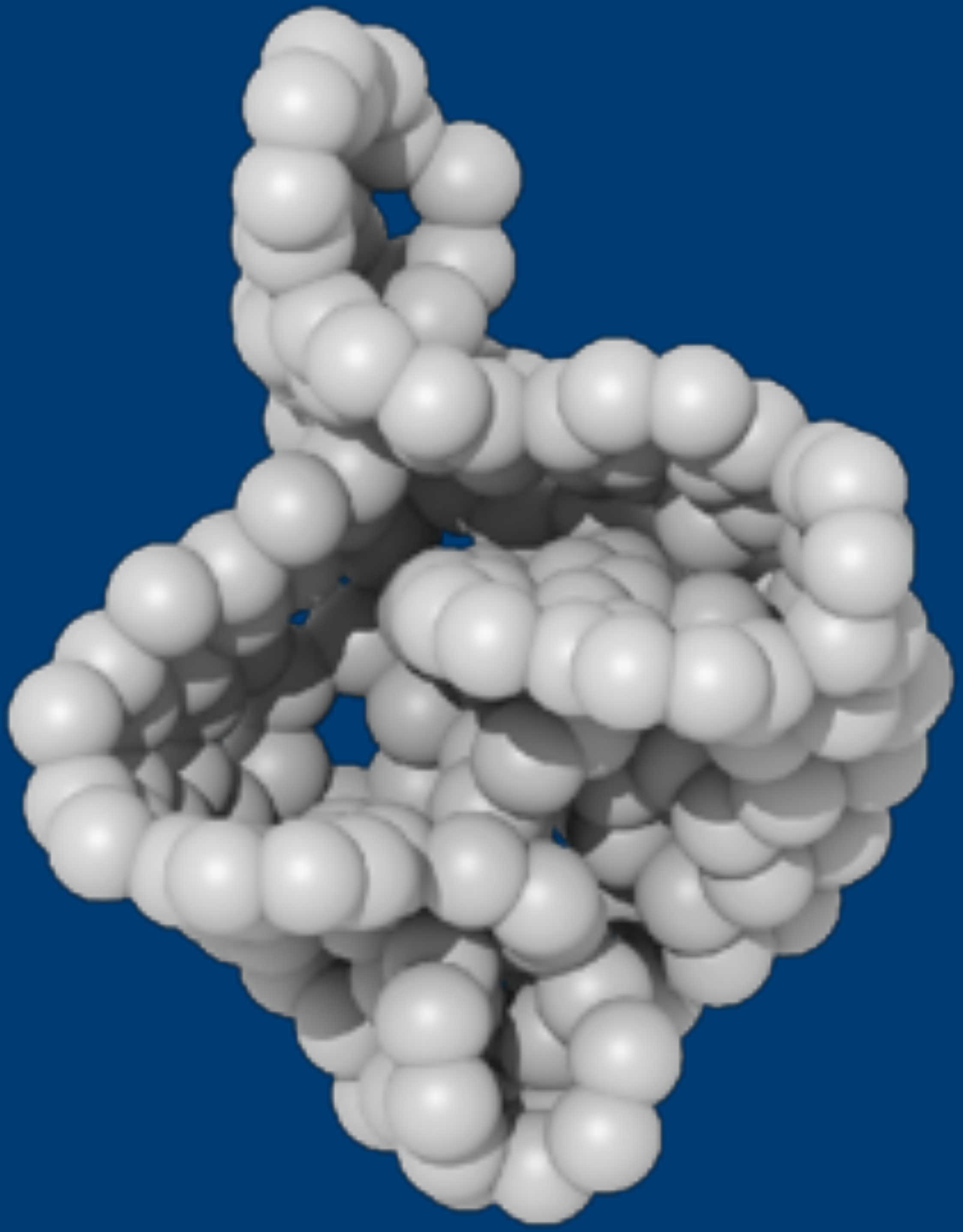
Binary cubes



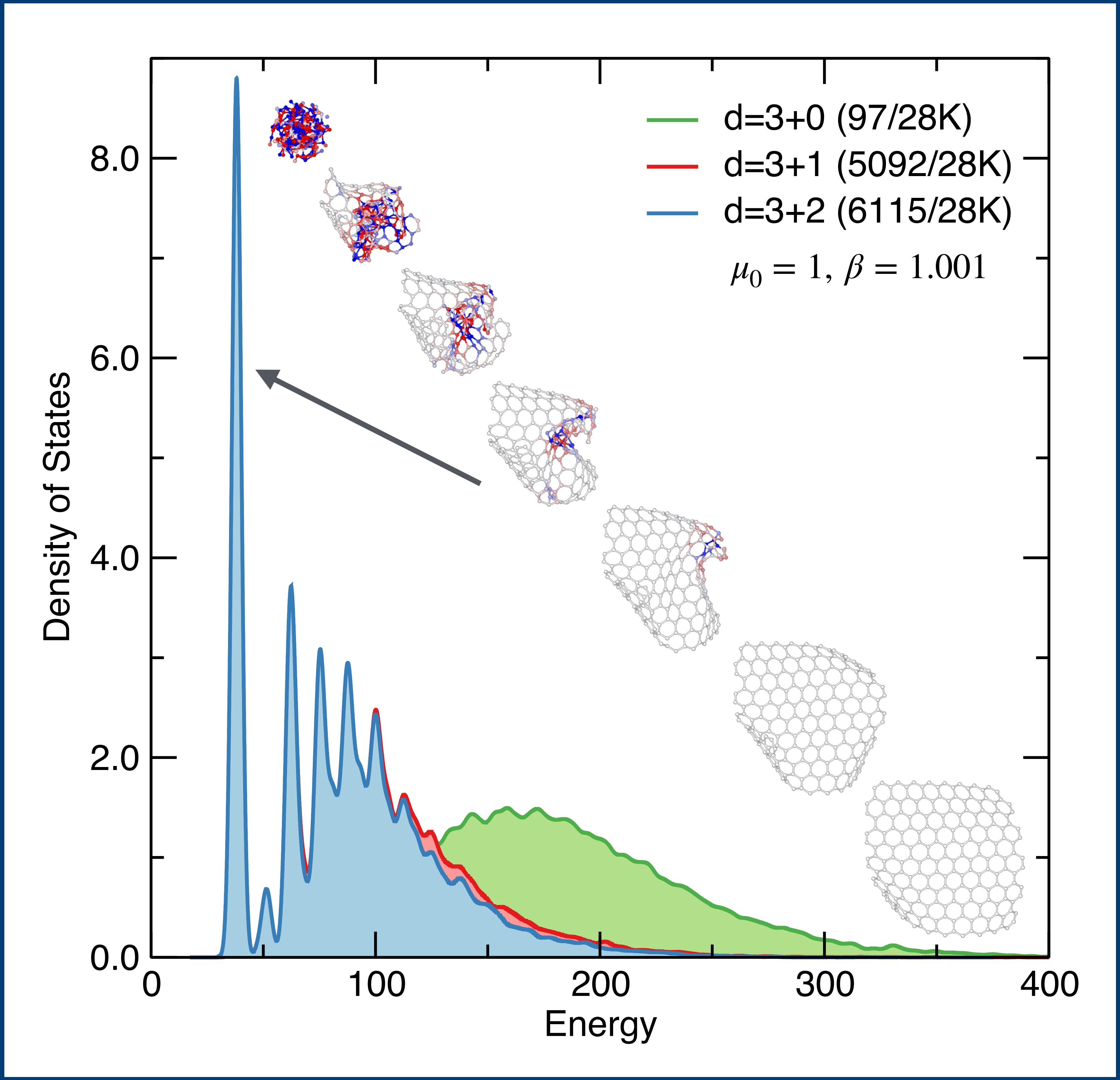
Covalent bonds

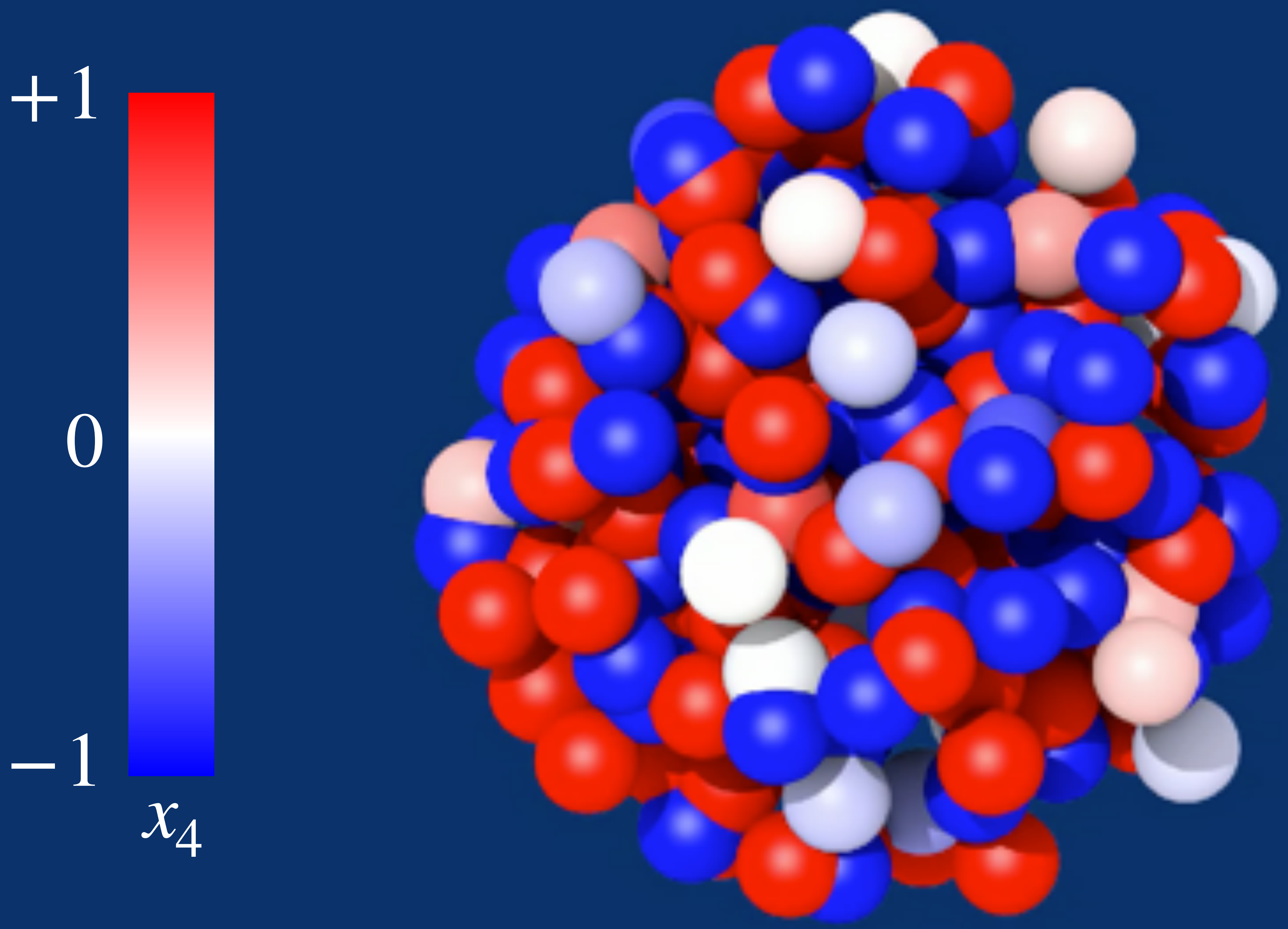


Covalent bonds

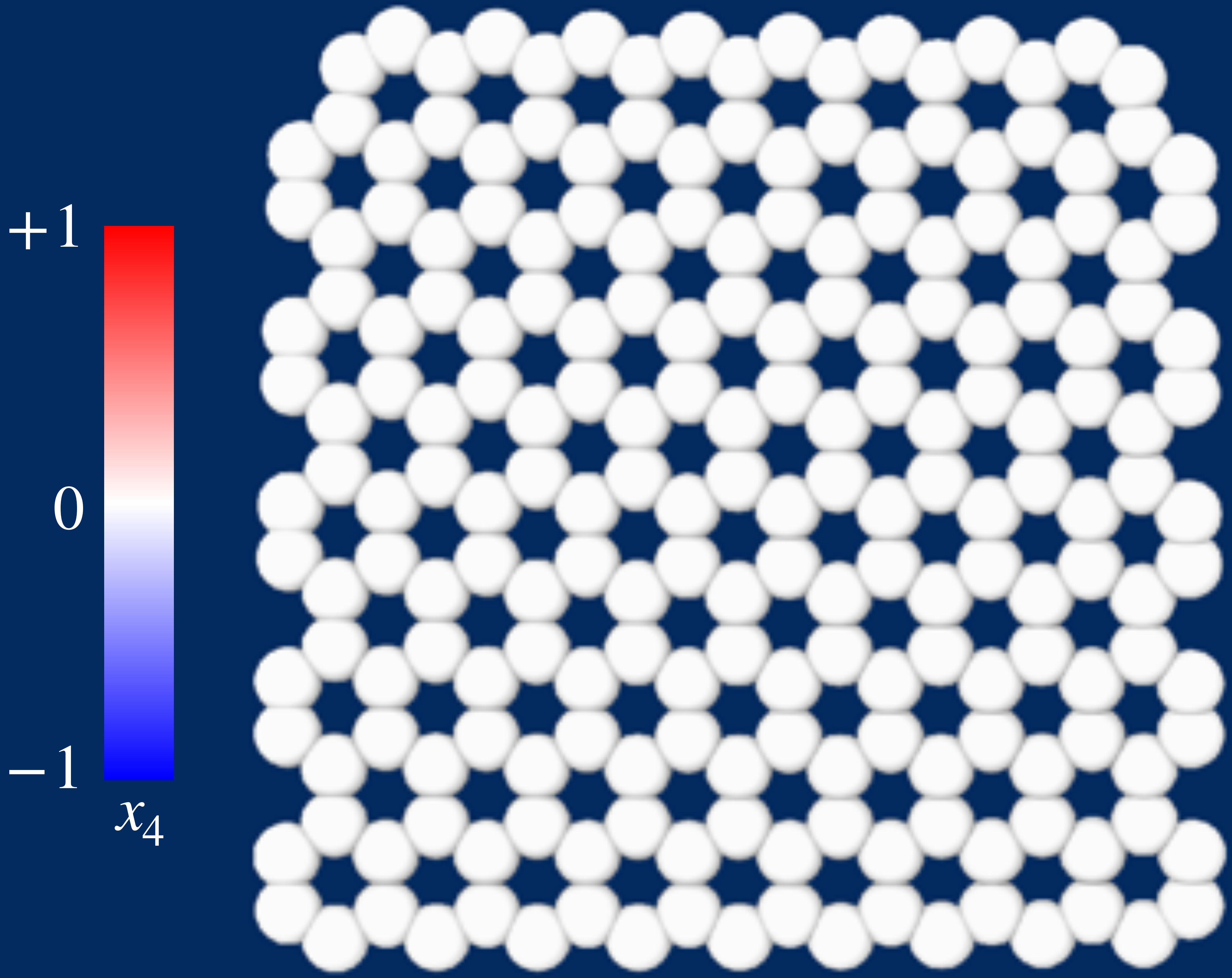


Covalent bonds





+1
0
−1
x_4


+1
0
−1
x_4

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