Pointing the mathematical microscope at the practical and exotic

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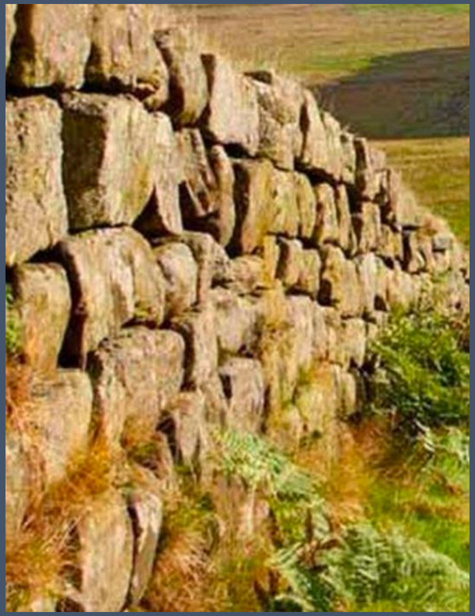
It’s about breaking down barriers

Devices, experiments



Atomistic understanding

History: realistic atomistic modeling of materials

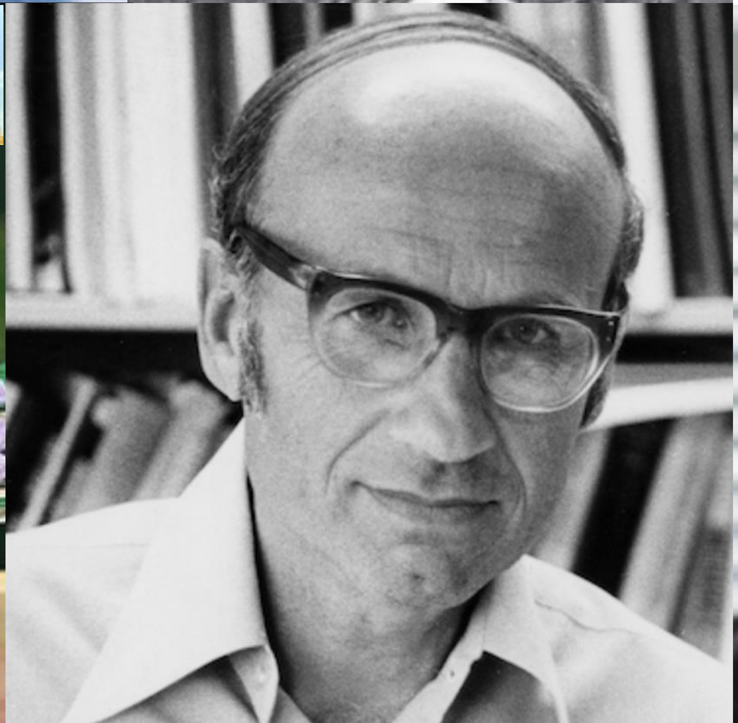
$$\left(\frac{-\nabla^2}{2}+V_{\mathrm{n}}(\mathbf{r})+V_{\mathrm{H}}(\mathbf{r})+V_{\mathrm{xc}}\left[\rho(\mathbf{r})\right]\right)\phi_i(\mathbf{r})=E_i\phi_i(\mathbf{r})$$

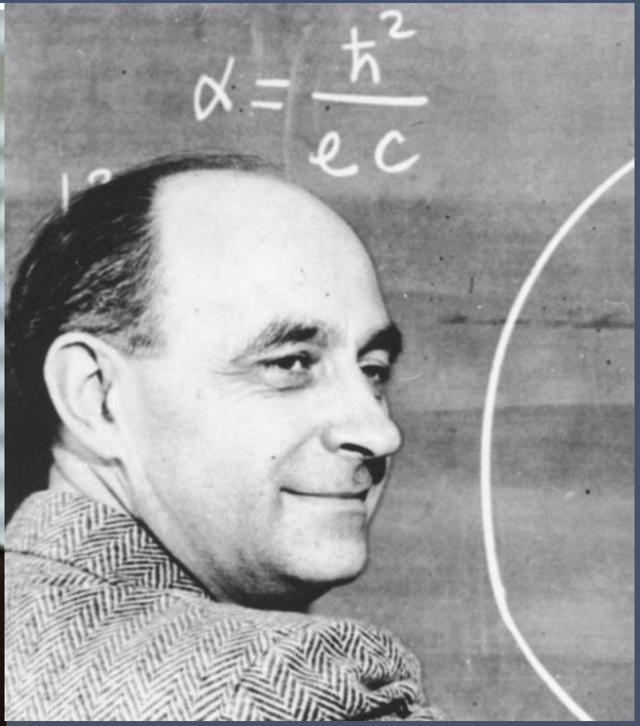
Ingredients: (tongue in cheek…)

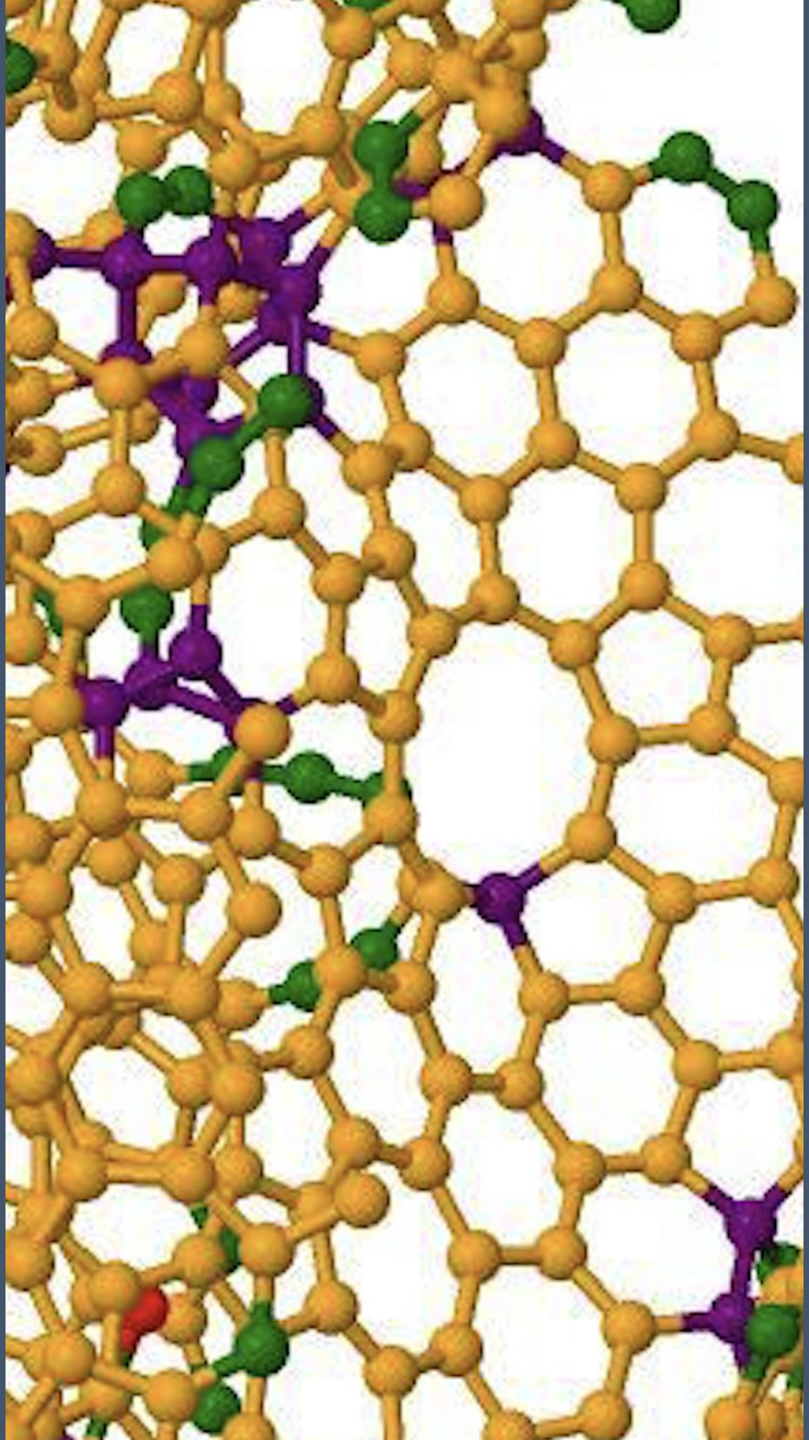
Single-particle theory (density functional) , clever computational science, and fast computers

Big advance over analytic theory for many problems

Some heroes of the mathematical microscope







The mathematical microscope has blossomed and matured.

- Computation and prediction of structure
- Dynamics of atoms
- Charge and heat transport
- Magnetic properties
- Prediction of spectroscopic signatures of matter: optical, Raman, UV, NMR, EPR….

Now to a time of ordinary men…

- Examples of the development and use of quantum simulation
- Physically Unclonable Function
- Machine Learning for interatomic potentials: see a fairly exotic phase transition

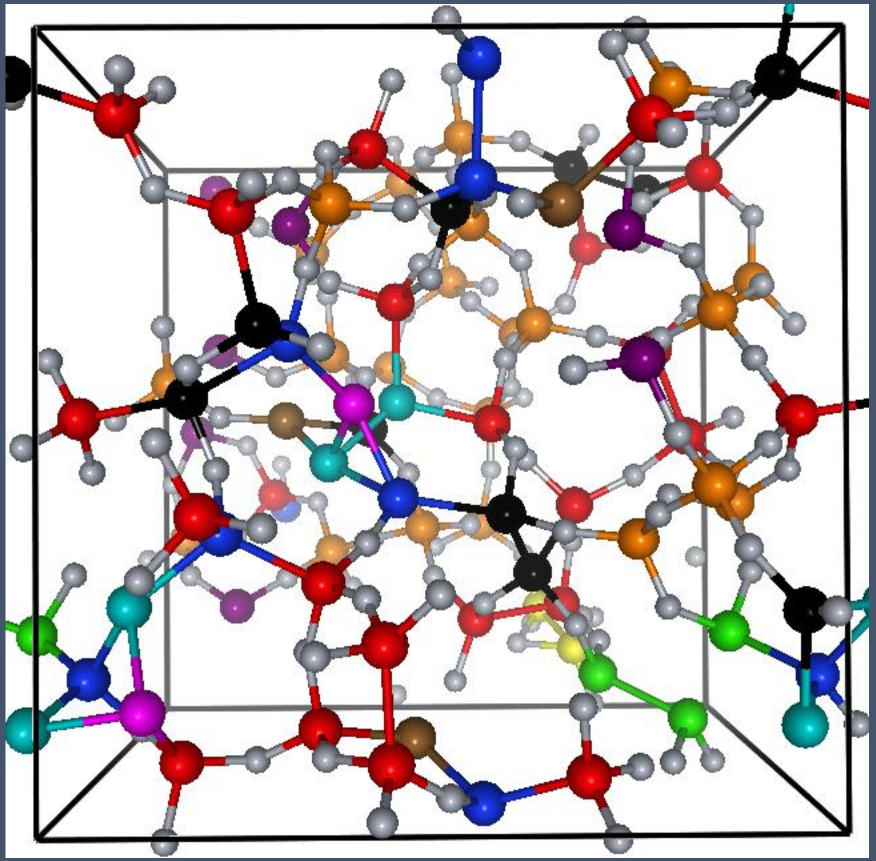
Physically Unclonable Function (PUF): a silicon suboxide realization

- Concept: Find an observable that depends upon some intricate and non-reproducible physical feature. Various ideas are afloat.
- Key application: computer security (unique keys/identifiers)
- We work on PUFs based upon electronic conduction in amorphous silicon suboxides (designed and built by M.N.K.) . We show in atomistic detail how these devices function.
- Two preliminaries: (1) What’s the structure of these materials and (2) what are the microscopic mechanisms of electronic conduction?

Amorphous silicon suboxides: structure

- Start with a-SiO_2 (silica glass).
- Now deplete some O: Consider SiO_x for *0<x<2*. Of course *x=2* is a-SiO_2 and *x=0* is a-Si.
- As O is removed from SiO_2, we are left with Si pining for O.
- Depending on x, we get a menagerie of defective Si sites (colored atoms)

a-$SiO_{1.3}$



K. Subedi, Ohio

Disorder is your friend: electronic conduction in amorphous Si suboxides

- Suppose we pick the DC conductivity as the observable. We need to compute the conduction path and see how it varies among different realizations.
- Harness the power of *entropy – disorder* -- to make a practical device.

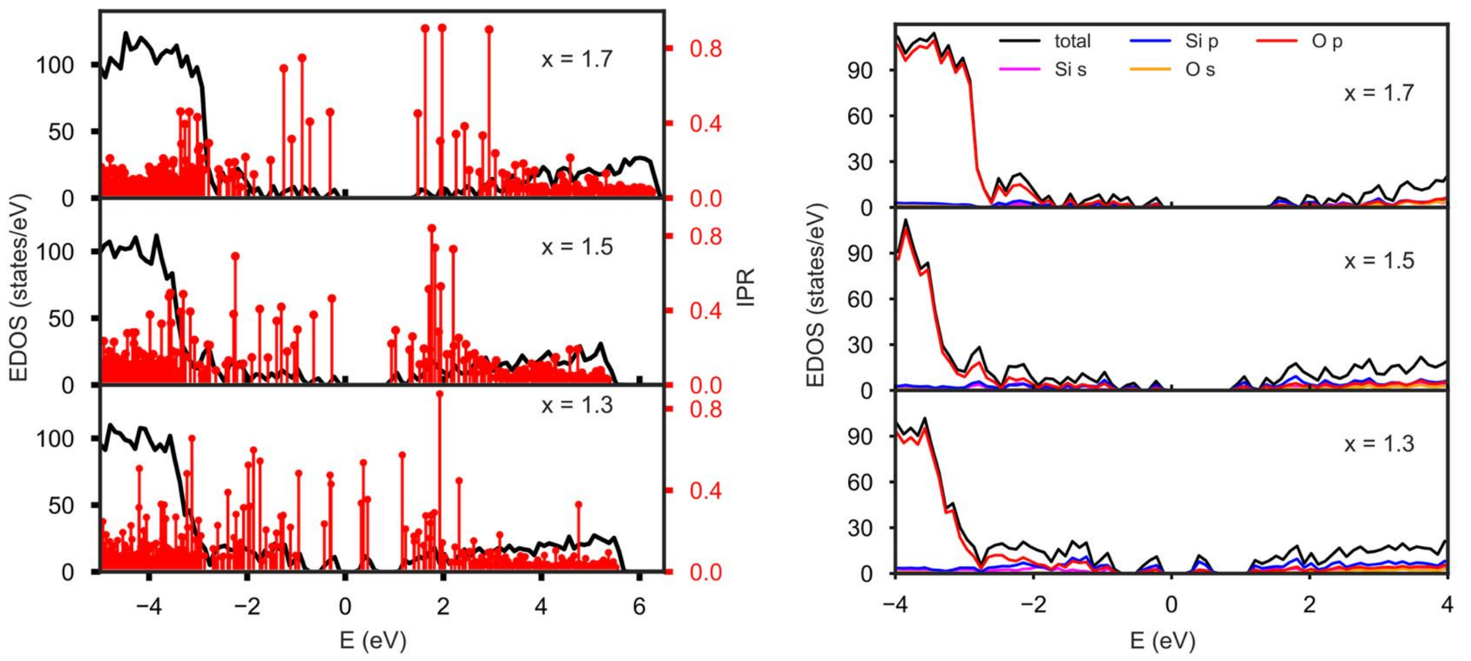


Figure 2: LEFT: Electronic density of states (EDOS) and the inverse participation ratio (IPR) for a-SiO_x models. RIGHT: Projected EDOS onto each orbital of each atomic species

The private life of electrons in the suboxides

Spatial information about conduction in materials

Q: How to compute the conductivity from wavefunctions, electronic eigenvalues *etc*?

A: The Kubo-Greenwood Formula (Kubo, 1957; Mott in the sixties)

- Once we have the computer models of material, we have everything needed.
- Great: but where did that conductivity "come from"? *What components of the network contributed*?

$$\sigma_{\mathbf{k}}(\omega) = \frac{2\pi e^2}{3m^2\omega\Omega} \sum_{i,j} \sum_{\alpha} [f(\epsilon_{i,\mathbf{k}}) - f(\epsilon_{j,\mathbf{k}})] \times |\langle \psi_{j,\mathbf{k}} | p^{\alpha} | \psi_{i,\mathbf{k}} \rangle|^2 \delta(\epsilon_{j,\mathbf{k}} - \epsilon_{i,\mathbf{k}} - \hbar\omega).$$

Subedi, Prasai, Kozicki, DAD PRM 2019

Spatial decomposition: a few tedious slides

1. Reduce the clutter, define:

$$g_{ij}(\mathbf{k},\omega) = \frac{2\pi e^2}{3m^2\omega\Omega}[f(\epsilon_{i,\mathbf{k}}) - f(\epsilon_{j,\mathbf{k}})]\delta(\epsilon_{j,\mathbf{k}} - \epsilon_{i,\mathbf{k}} - \hbar\omega).$$

2. Rewrite the conductivity:

$$\sigma = \sum_{i,j,\alpha} g_{ij} \int d^3x \int d^3x' [\psi_j^*(x) p^\alpha \psi_i(x)][\psi_i^*(x') p^\alpha \psi_j(x')]$$

3. Declutter again. Define:

$$\xi_{ij}^\alpha(x) = \psi_i^*(x) p^\alpha \psi_j(x)$$

Tedium (continued)

4. Approximate the integrals as sums on a discrete grid in real space

$$\sigma \approx h^6 \sum_{x,x'} \sum_{i,j,\alpha} g_{ij} \xi_{ji}^{\alpha}(x) (\xi_{ji}^{\alpha}(x'))^*$$

(exact as h → 0)

5. Spatially decompose σ:

$$\Gamma(x, x') = \sum_{i,j,\alpha} g_{ij} \xi_{ji}^{\alpha}(x) \left(\xi_{ji}^{\alpha}(x')\right)^*$$

Γ is Hermitian, positive semi-definite matrix. Sum on grid points gives σ.

6. Spatially projected conductivity:

$$\zeta(x) = |\sum_{x'} \Gamma(x, x')|$$

Discrete real-space decomposition of conductivity

Spectral decomposition: Γ is Hermitian, diagonalize in position representation:

$$\hat{\Gamma} = \sum_\mu |\chi_\mu\rangle \Lambda_\mu \langle\chi_\mu|$$

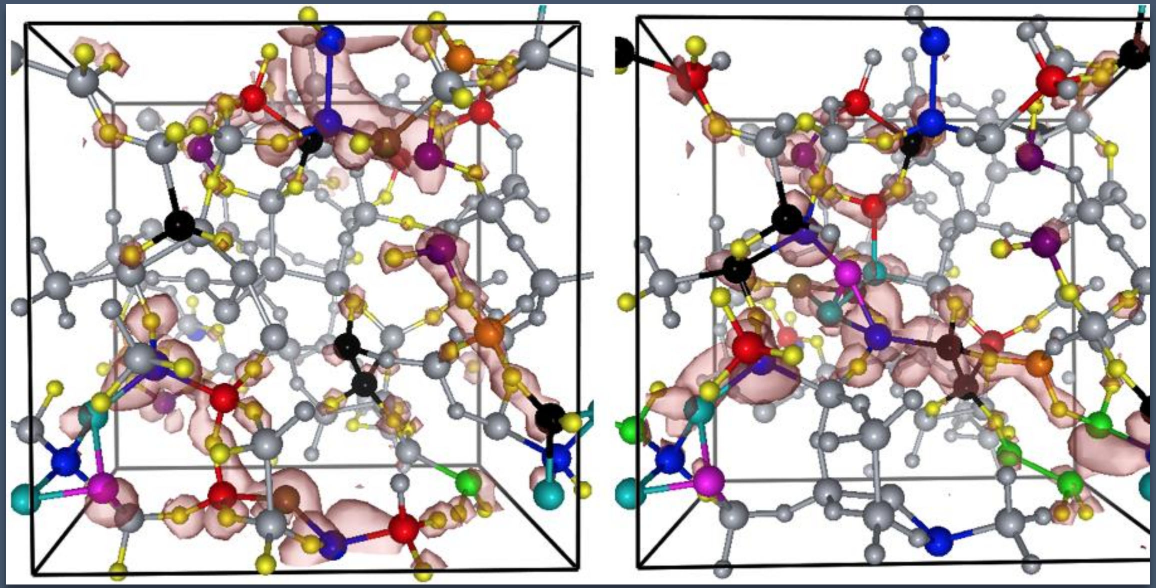
Λ has units of conductivity, so diagonalize Γ and:

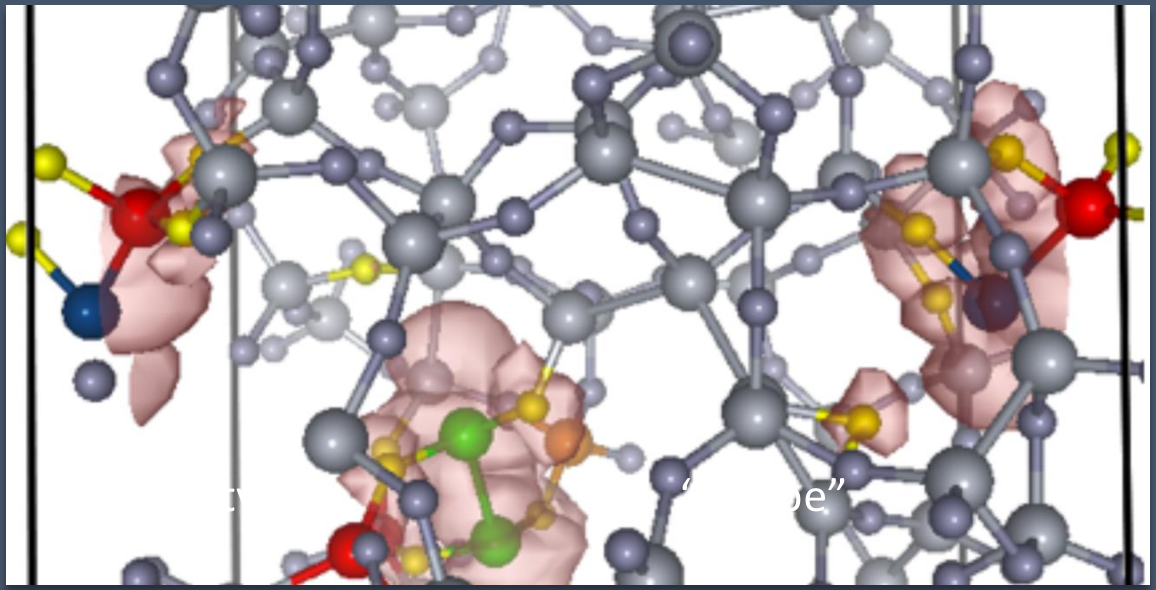
$$\sigma = \sum_\mu \Lambda_\mu + \sum_{x,x',x\neq x'} \sum_\mu \Lambda_\mu \chi_\mu(x)\chi_\mu^*(x')$$

We have *"eigenmodes of conductivity": percolation paths from a diagonalization.*

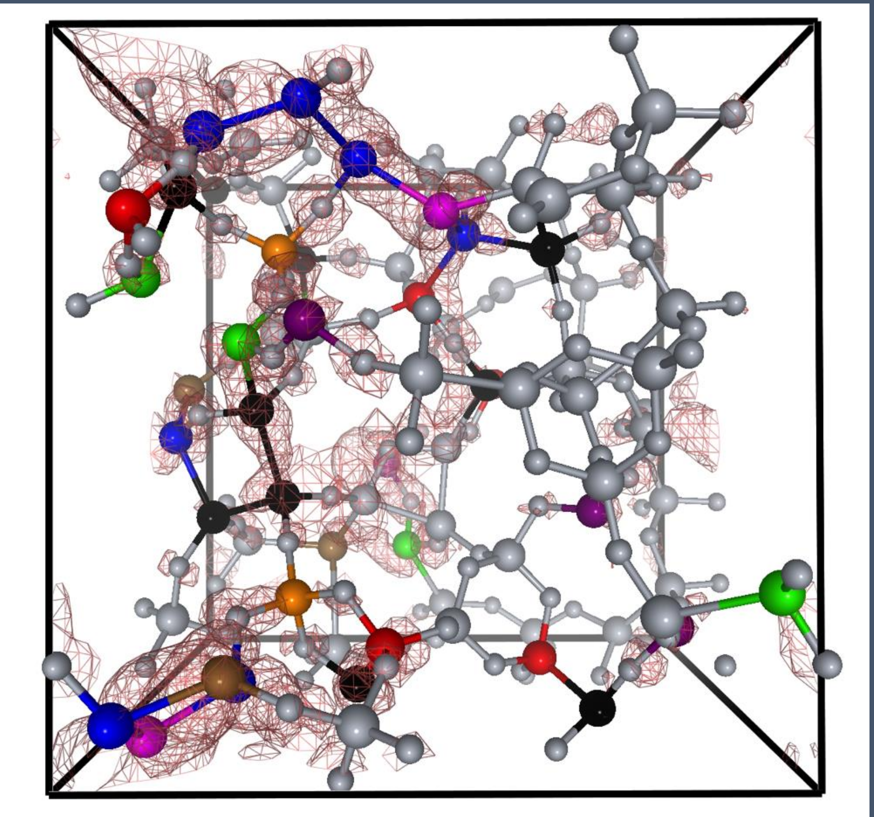
So what does this say about suboxides?

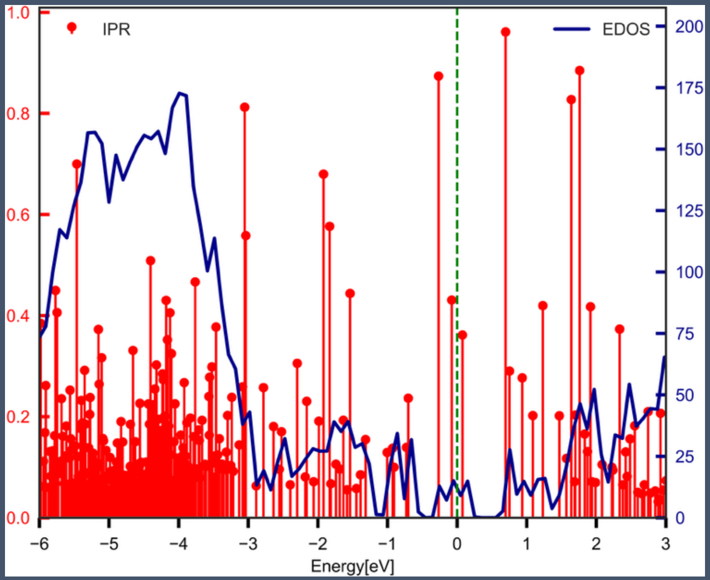
- The undulating pinkish blob is the projected conductivity. It clearly lies upon defective Si sites.
- Top: *x=1.3* n-type (left) and p-type (right). Note the space-filling conducting paths.
- Bottom *x=1.7*: Si defects less common; disconnected localized blobs (and much smaller s)

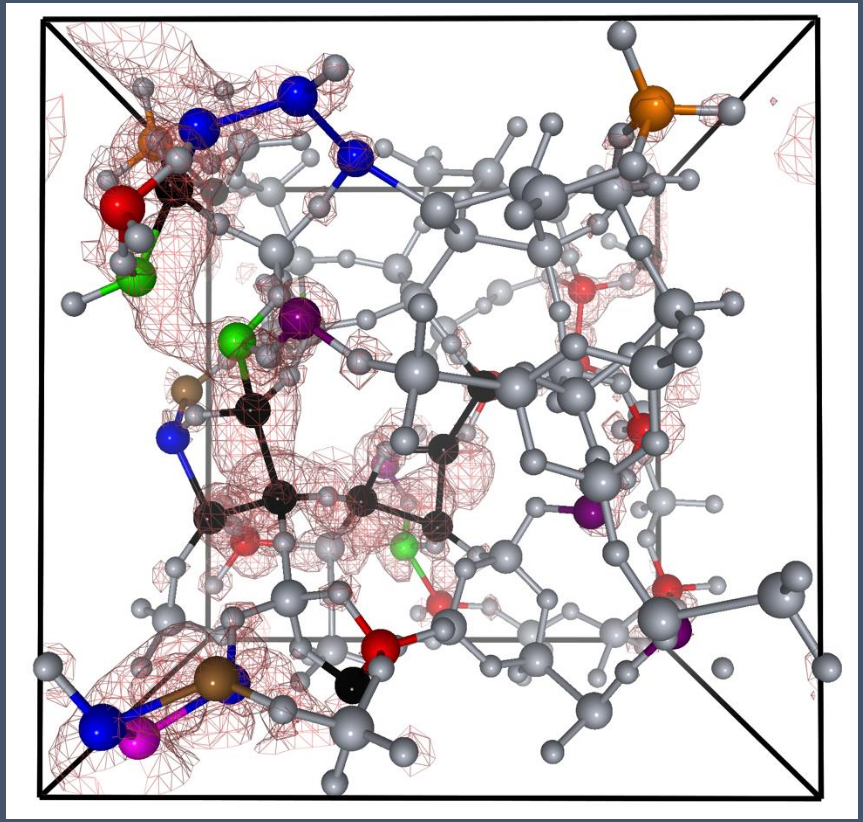




Do it all for a different model (*x=1.3*)





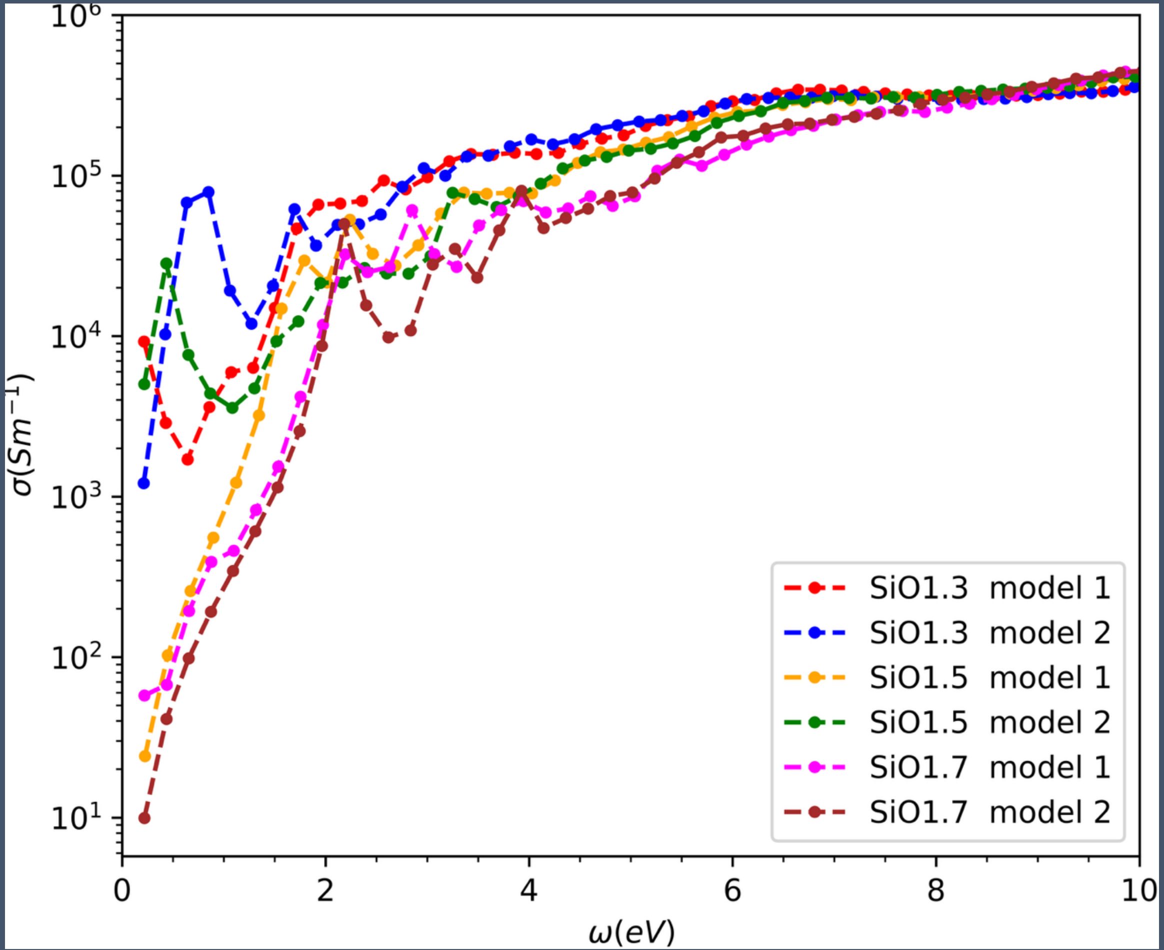


p-type

n-type

AC conductivity (extracted from VASP)

The AC and DC conductivity are model/sample dependent.



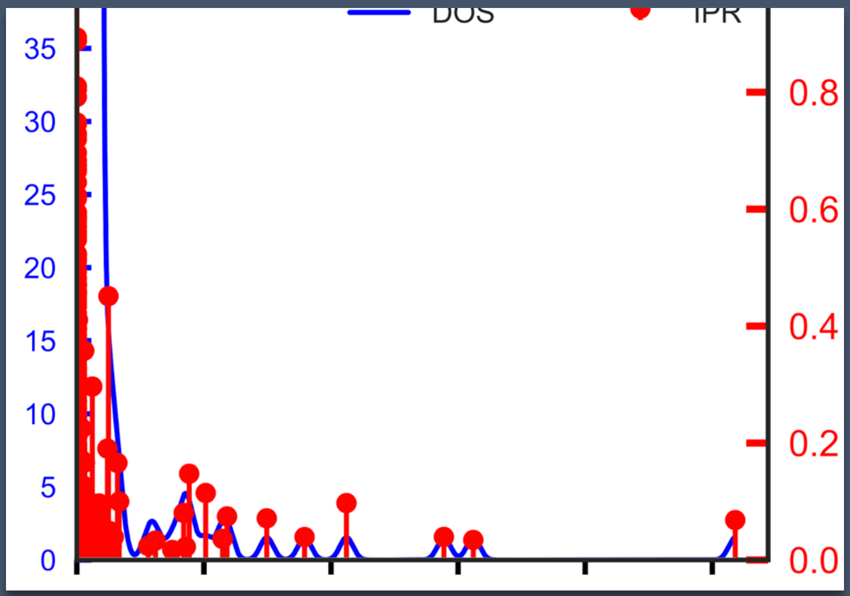
Spectral decomposition of Γ: "n-type", $SiO_{1.3}$ and FCC aluminum.

dim(Γ)=64000: only ~20 modes (of 64000) contribute much to σ!

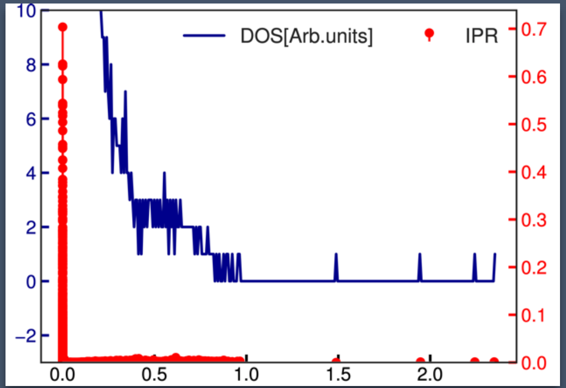
- The "diagonalization" result is the same as the result for $\zeta(x)$.
- Interesting things to study: a spectral tail forms near Λ=0 for delocalized/metallic conduction.

n-type $SiO_{1.3}$

$\rho(\Lambda)$



Λ (S/cm)

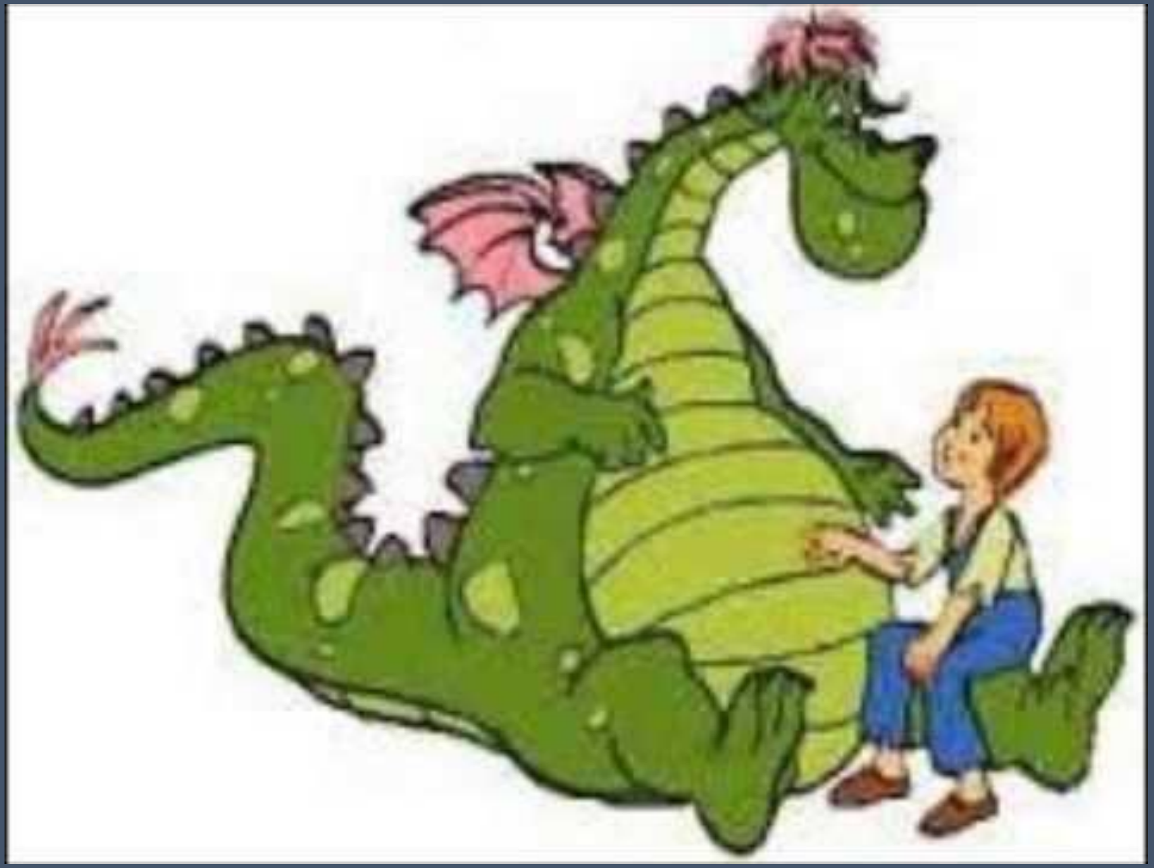


Aluminum

Conclusions about PUF

- The detailed conduction paths will never be exactly reproduced in amorphous materials.
- Experimentally (MNK) there is a big dispersion in the measured conductivities for identically prepared devices. Now we see why.
- More to be done:

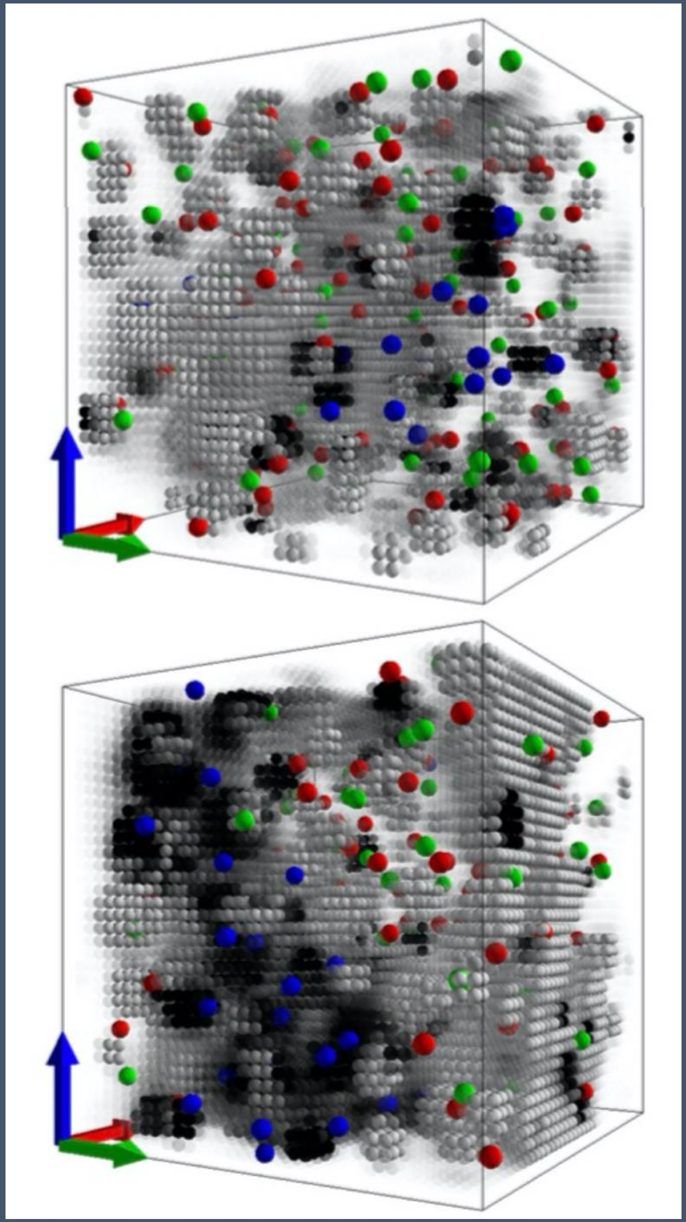
Spectral decomposition of conductivity, numerically correct conductivity, localized-delocalized (Anderson) transitions *etc.*



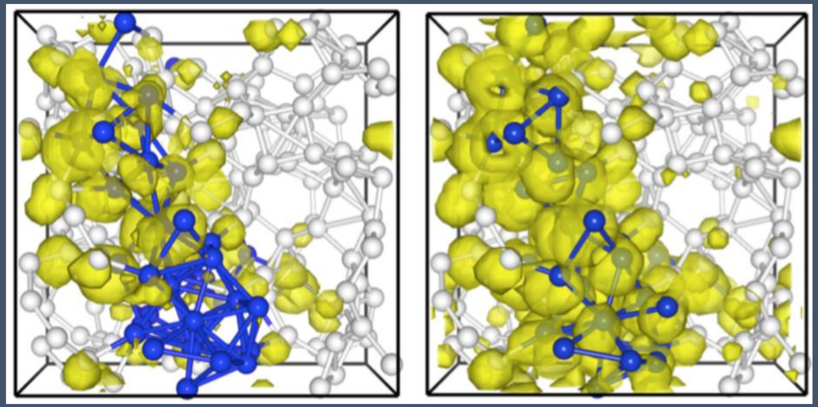
PUF(F) the Magic Dragon

Another Kozicki device: Conducting Bridge RAM

- Add Cu, Ag… to an amorphous insulator or semiconductor. Electrochemically control the conductivity: CBRAM
- At right :conduction through amorphous alumina with Cu (blue atoms)



Top: a-Al_2O_3+10% Cu, bottom 20% dark smog is scalar field $\zeta(x)$.



Results for 20% Cu, left with 20 eigenvectors, right: all.

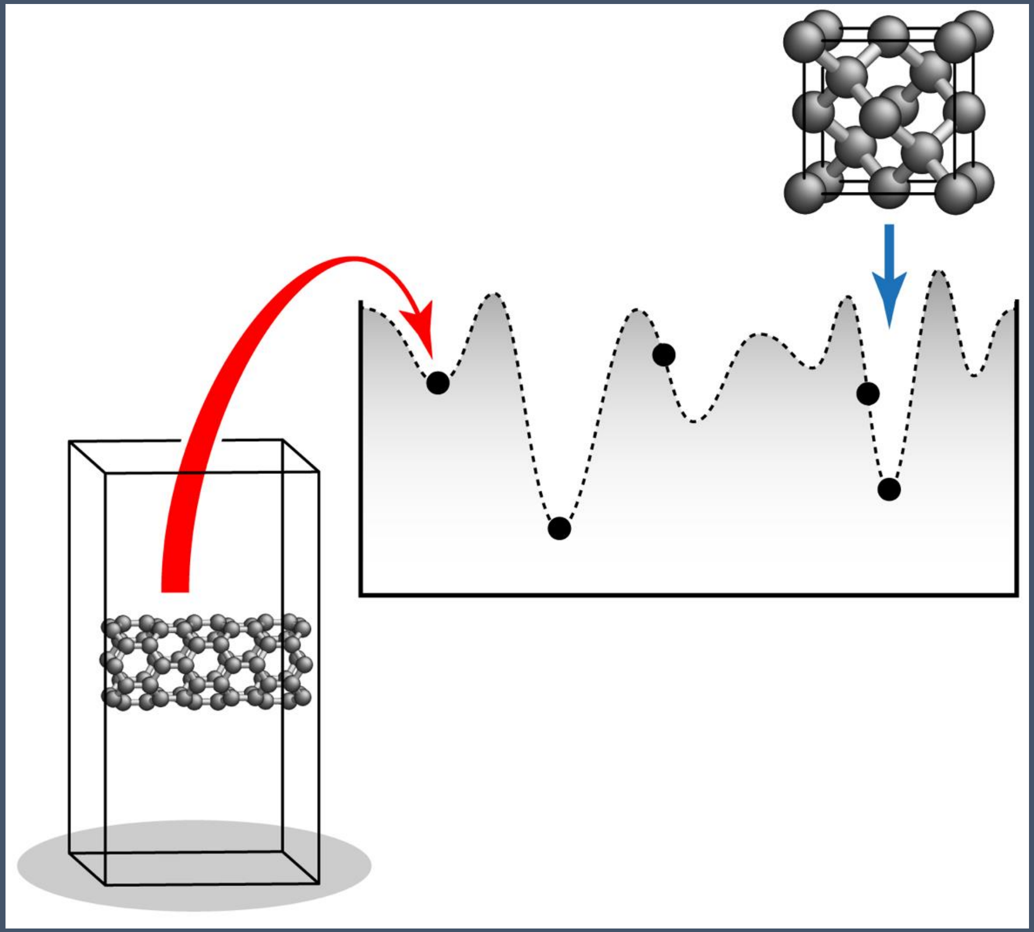
PSS RRL 800238 (2018)

Accurate large-scale simulations of Si: representing the energy landscape

- Silicon is hard to model well. Well known that liquid and disordered phases are well modeled only with DFT.
- Furio Ercolessi had an idea in the early 90's: why not fit a parametrized functional form for an interatomic potemtial to ab initio data? "Force-Matching method". Clever, but impossible to find a good fit.
- Nowadays: non-parametric approaches and "**Machine Learning**".
- **Csanyi, Bartok and Deringer** have pioneered a successful new approach: "Gaussian Approximation Potential" (GAP).

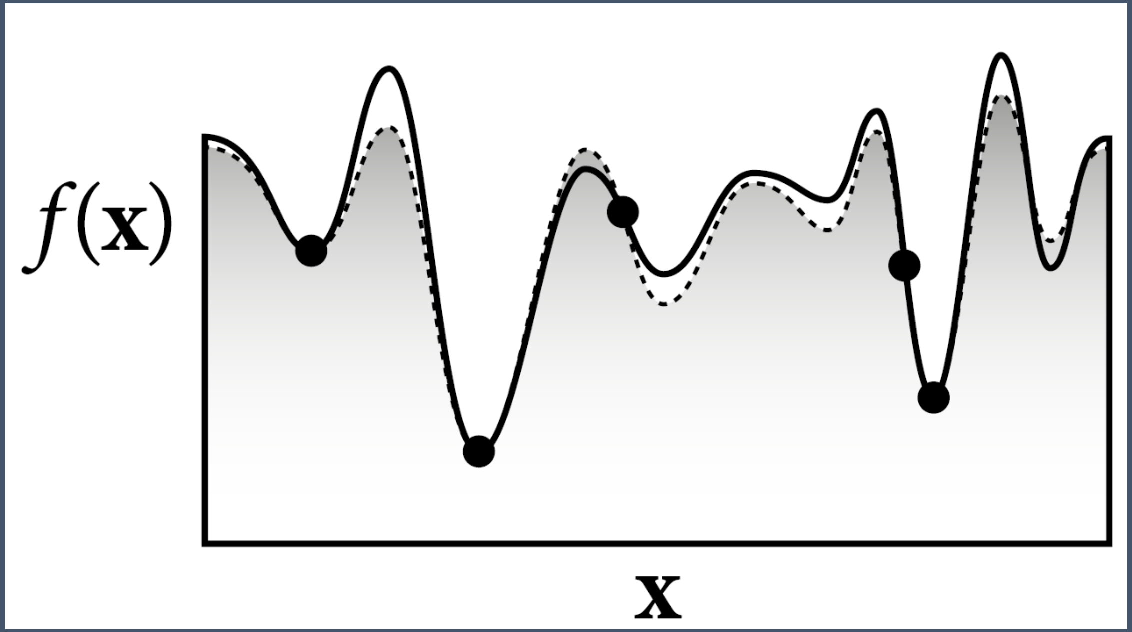
PRX 8 041048 (2018), PRL 104 136403 (2010); Adv. Mats. 31 1902765; several others.

Atomic-scale materials modelling:
Machine learning as an emerging approach



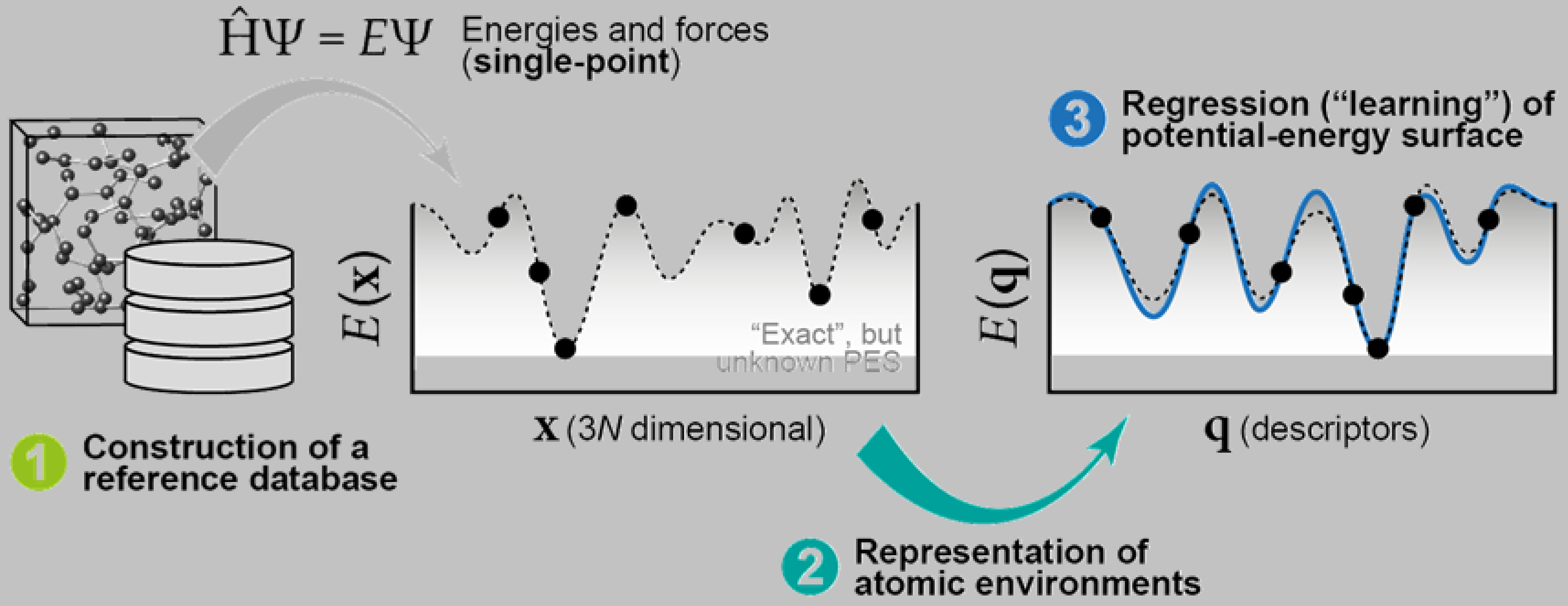
Quantum-mechanically accessible,
but only at selected points!

Atomic-scale materials modelling:
Machine learning as an emerging approach



Approximate an unknown function
(*here:* the potential energy surface)
based on data alone

Atomic-scale materials modelling:
Machine learning as an emerging approach

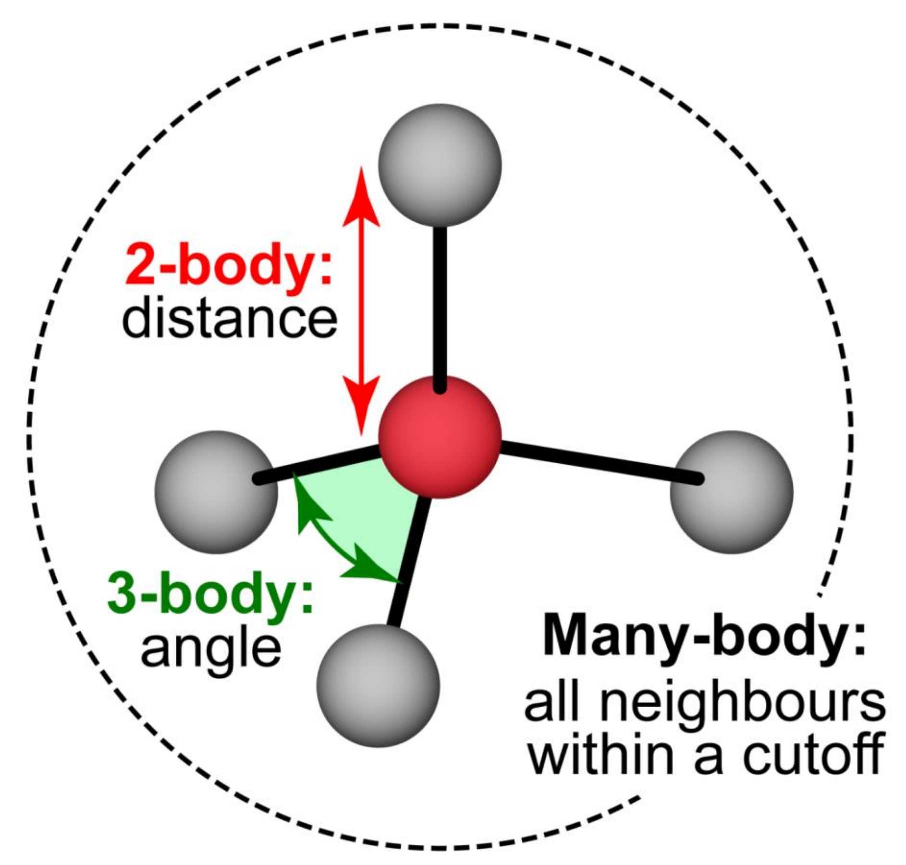


Courtesy Dr. Volker Deringer

A machine-learned potential for silicon

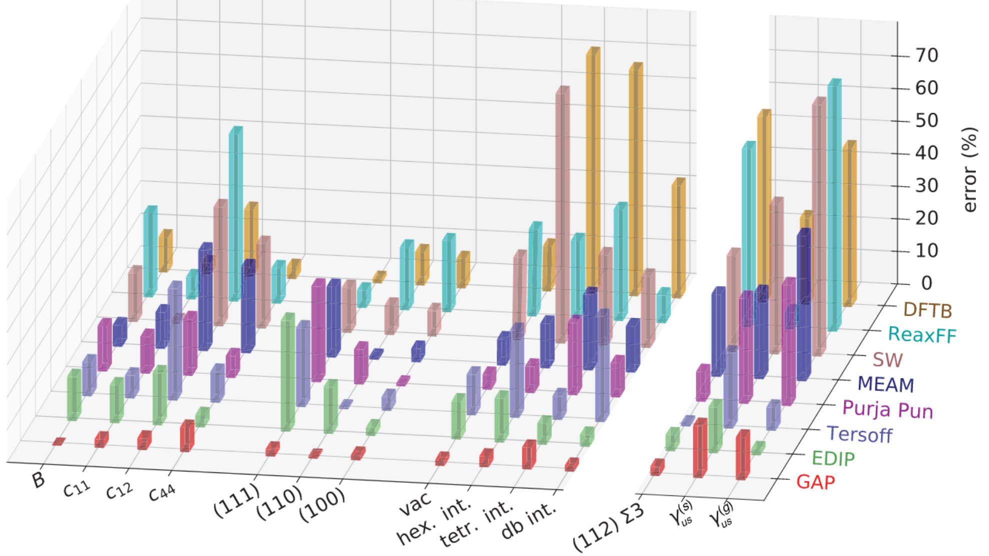
Gaussian approximation potential

- (GAP) framework: a kernel (*similarity*) based machine-learning method.
- New approach here: **combine** suitable structural descriptors.
- Provides meaningful local (site) energies.
- NB: calculations are **not** "cheap", but **are** linear scaling.



V. L. Deringer, G. Csányi, *Phys. Rev. B* **2017**, *95*, 094203

Tests (just a few of *many*)

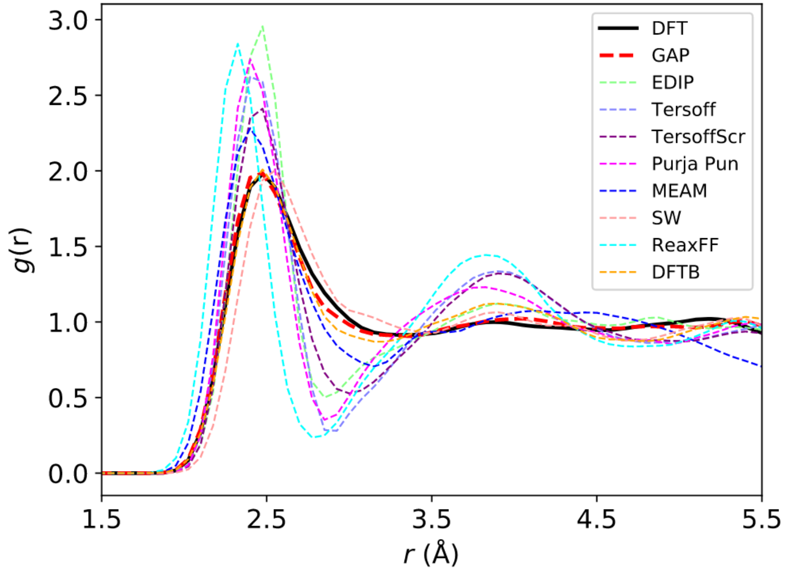


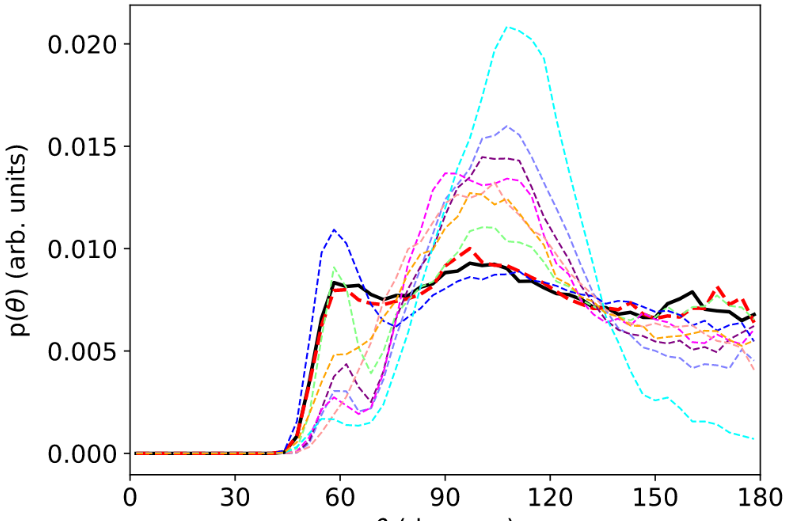
Model	Elastic props. / GPa				Surfaces / J/m^2			Point defects / eV				Planar defects / J/m^2		
	B	c_{11}	c_{12}	c_{44}	(111)	(110)	(100)	vac	hex. int.	tetr. int.	db int.	(112) Σ3	$\gamma^{(s)}_{us}$	$\gamma^{(g)}_{us}$
DFT reference	88.6	153.3	56.3	72.2	1.57	1.52	2.17	3.67	3.72	3.91	3.66	0.93	1.61	1.74
							Relative error [%]							
GAP	0	-3	4	-8	-2	-1	-2	-2	-3	-7	-2	3	-16	13
EDIP	14	12	16	-4	-34	-14	-3	-12	14	6	-4	5	-14	-2
Tersoff	10	-7	34	-10	-24	-0	4	13	27	-7	32	-1	-23	10
Purja Pun	14	11	17	7	-29	-11	1	5	8	-22	-10	9	-32	37
MEAM	7	-11	31	-26	-22	-1	4	-8	-14	-23	-14	25	-26	45
SW	14	-1	36	-26	-14	9	8	-27	77	28	22	30	-46	77
ReaxFF	26	7	51	-11	-5	19	-23	28	24	34	8	55	5	75
DFTB	11	4	21	-4	1	10	10	15	74	69	35	57	27	49

FIG. 1. Comparison of percentage errors made by a range of interatomic potentials for selected properties, with respect to our DFT reference. Those on the left of the break in the axis are interpolative, i.e., well represented within a training set of the GAP model: elastic constants (bulk modulus B, stiffness tensor components C_{ij}), unreconstructed (but relaxed) surface energies [(111), (110), and (100) low-index surfaces], point-defect formation energies (vacancy and hexagonal, tetrahedral, and dumbbell interstitials); while the planar defects to the right are extrapolative: (112) Σ3 symmetric tilt grain boundary and unstable stacking-fault energies on shuffle plane $\gamma^{(s)}_{us}$ and glide plane $\gamma^{(g)}_{us}$. The first row in the corresponding table shows reference quantities computed with the DFT (units indicated in the header row).

Bartok et al.
PRX 8 041048
(2018)

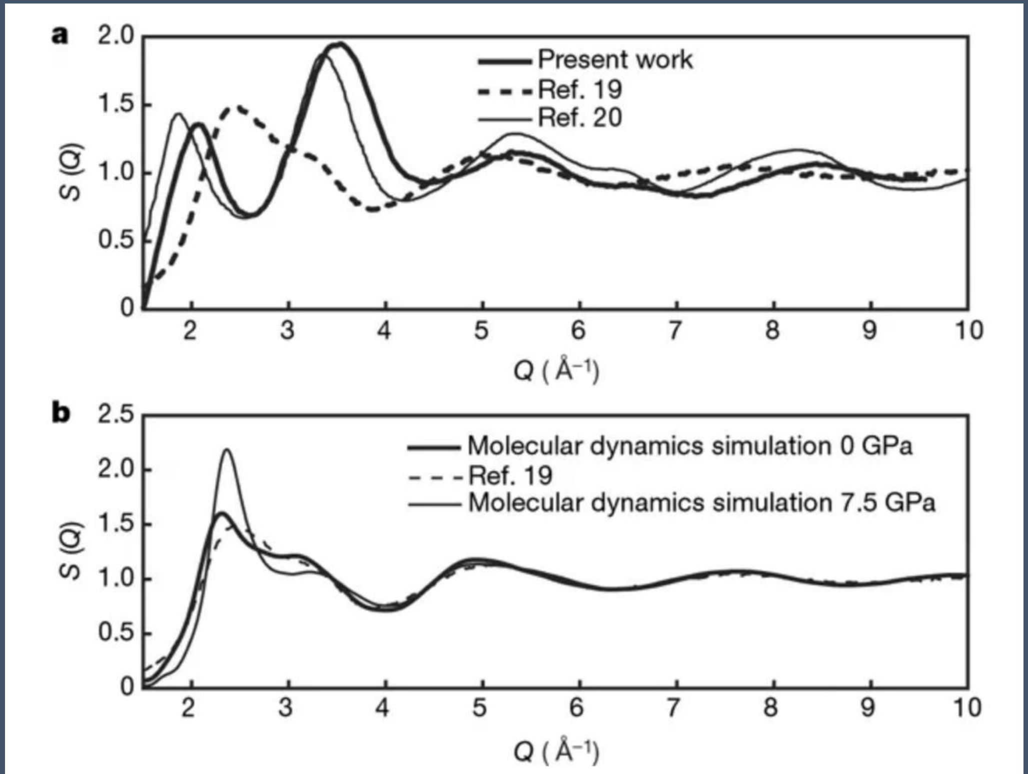
liquid





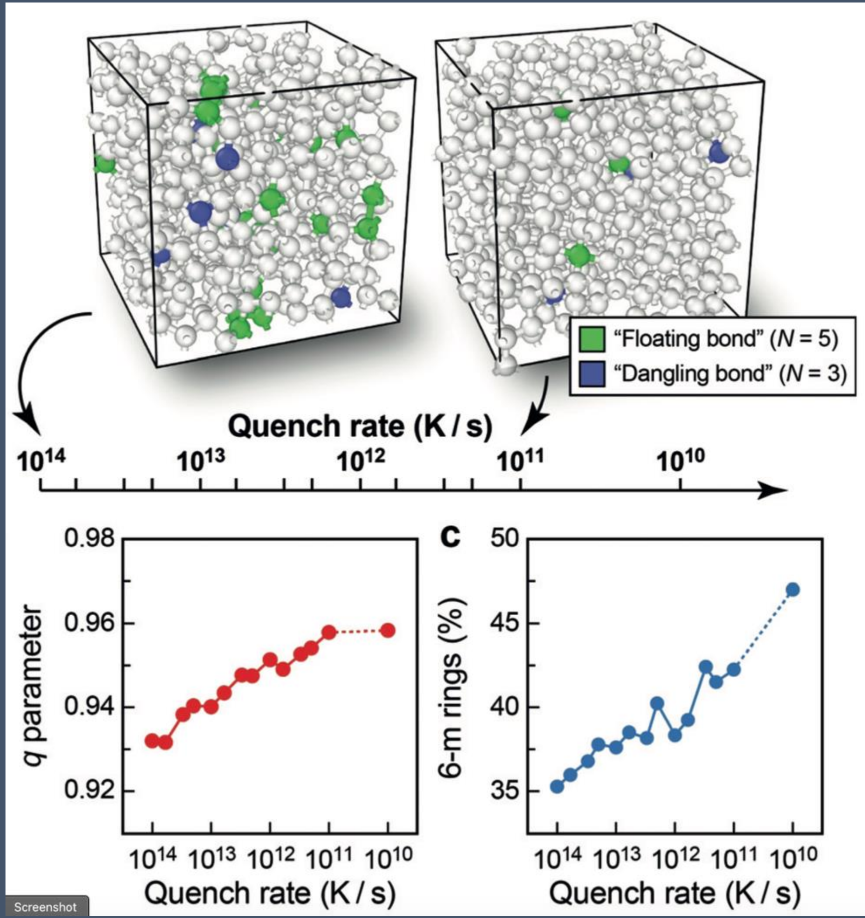
Liquid to amorphous transition

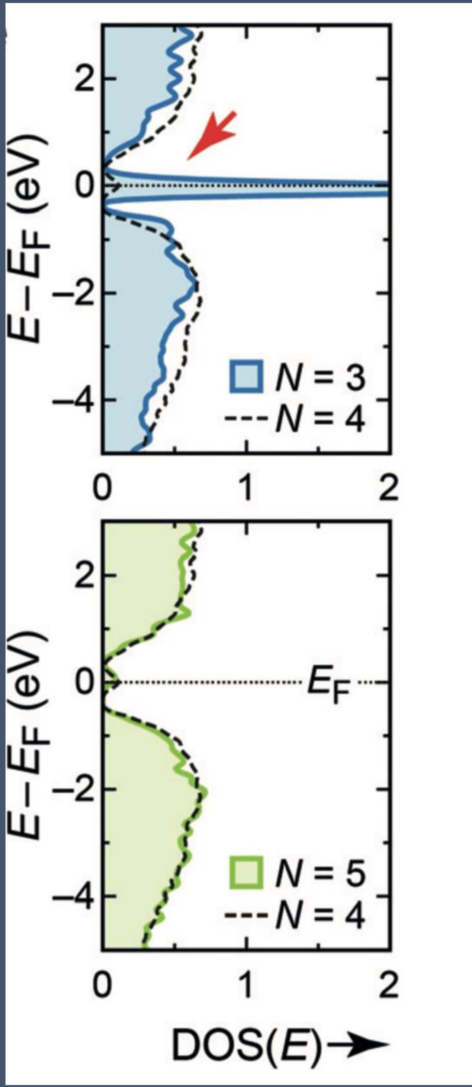
- Fact: Liquid Si is a ~6-fold coordinated metal, amorphous silicon a tetrahedral semiconductor. To my knowledge nobody has made a-Si by quench from the melt (Angell however has done it for Ge!)
- Train GAP for liquid configurations.
- We show that slow enough quenches of the liquid with GAP produces models of a-Si consistent with experiment.



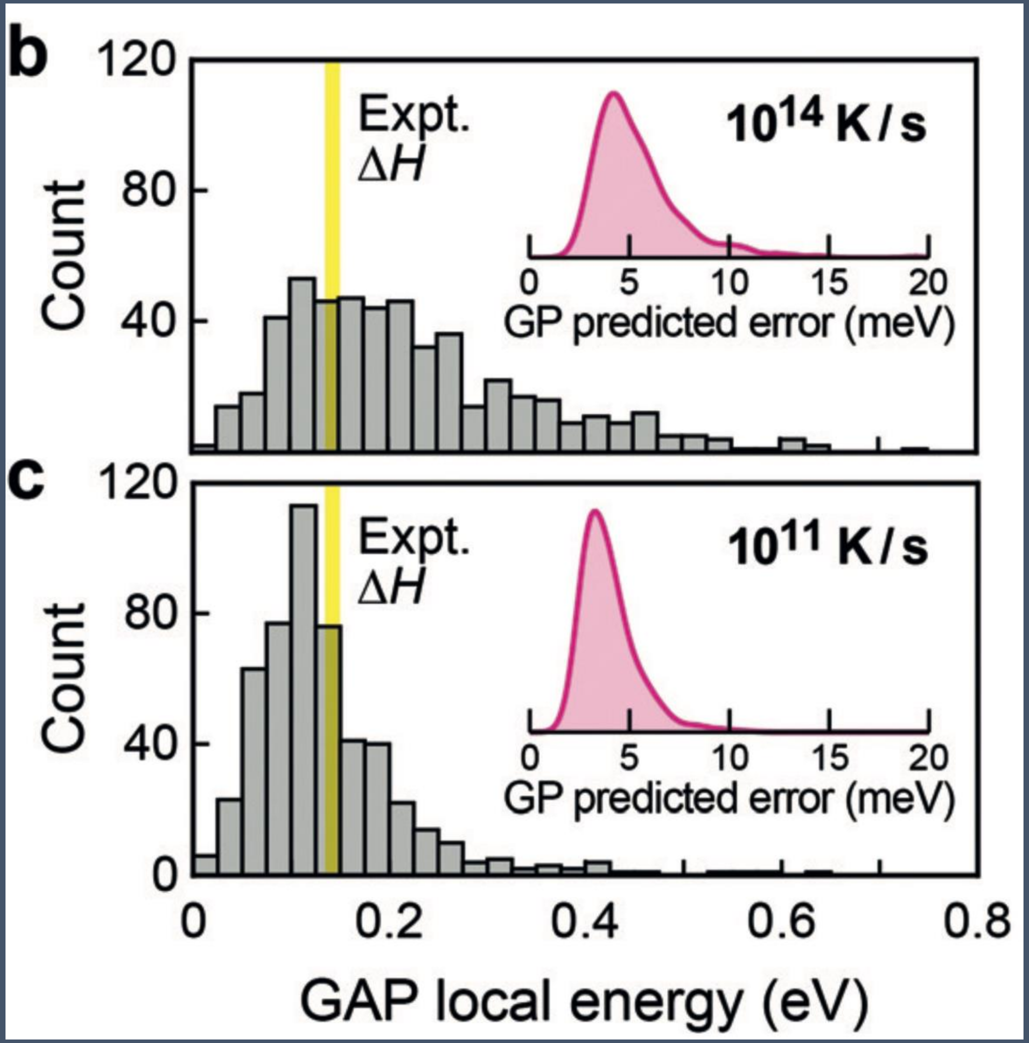
Bhatt *et al.*, Nature (2007).

Take 4096 atoms, and quench the liquid….
Sloooowly…….





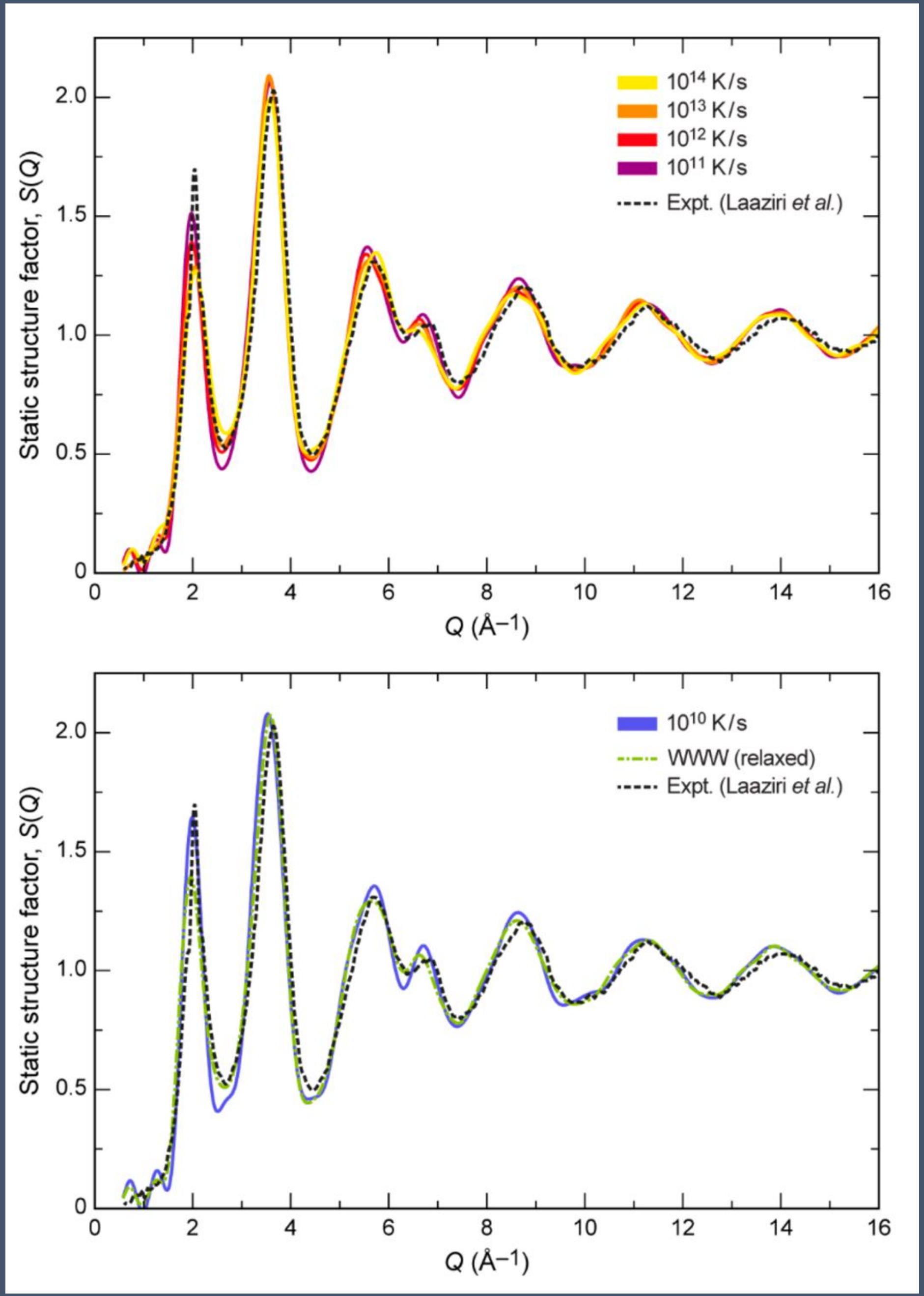
N. Bernstein, B. Bhattarai, G. Csanyi, DAD, S. R. Elliott Angew. Chem 131 7131 (2019)



Distribution of local energies (a fringe benefit of GAP)

10^{11}K/s system *slightly below* best WWW a-Si[1]

1. B. R. Djordjevic, M. F. Thorpe, F. Wooten PRB 52 5685 (1995)



Comparison to diffraction measurements on a-Si (Laaziri *et al.*)

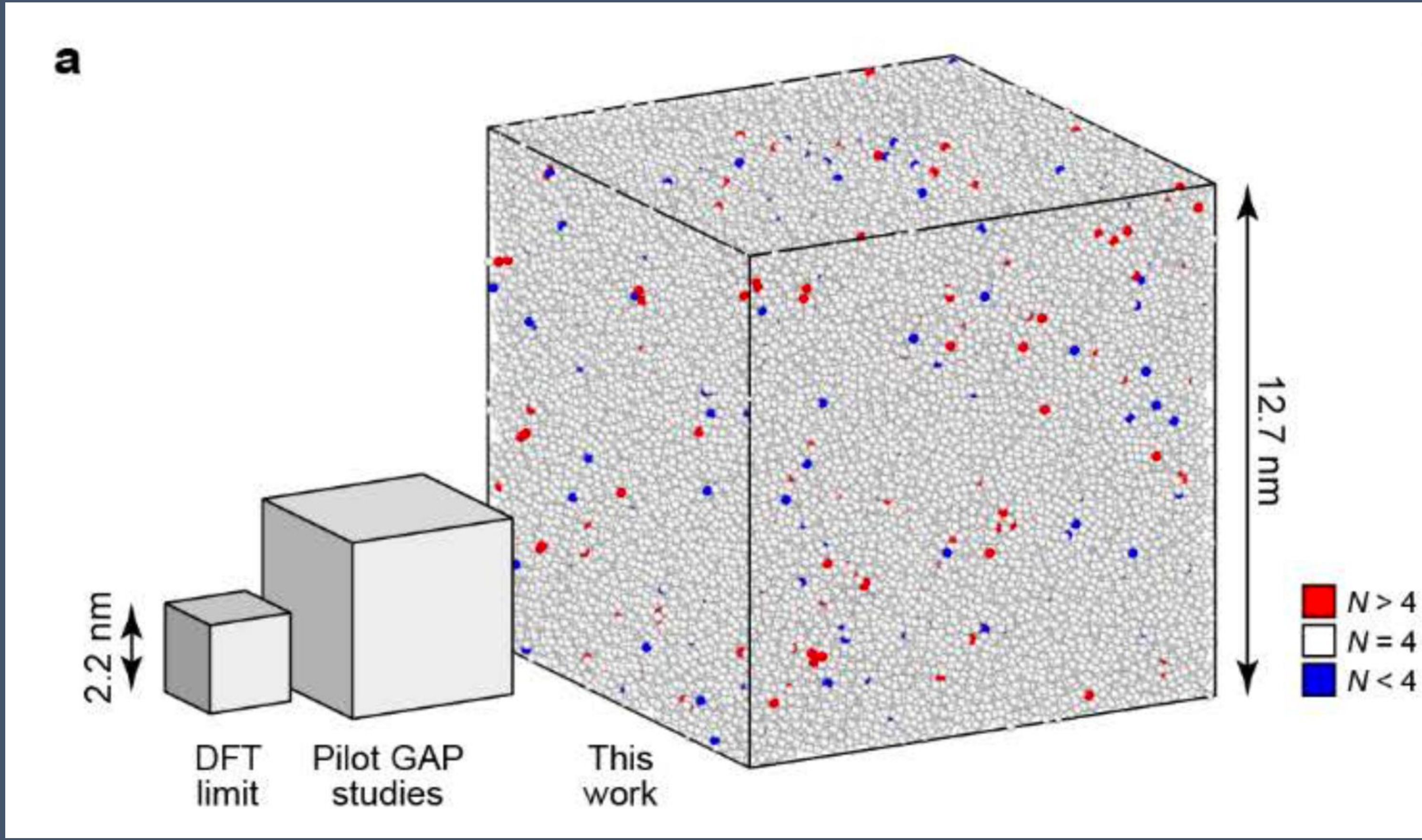
100,000 atoms with DFT-like accuracy

- GAP is linearly scaling (albeit with big prefactor). Linear scaling opens up some new realms for inquiry.

(1) Track liquid to amorphous transition

(2) Squeeze the liquid, compare to experiments

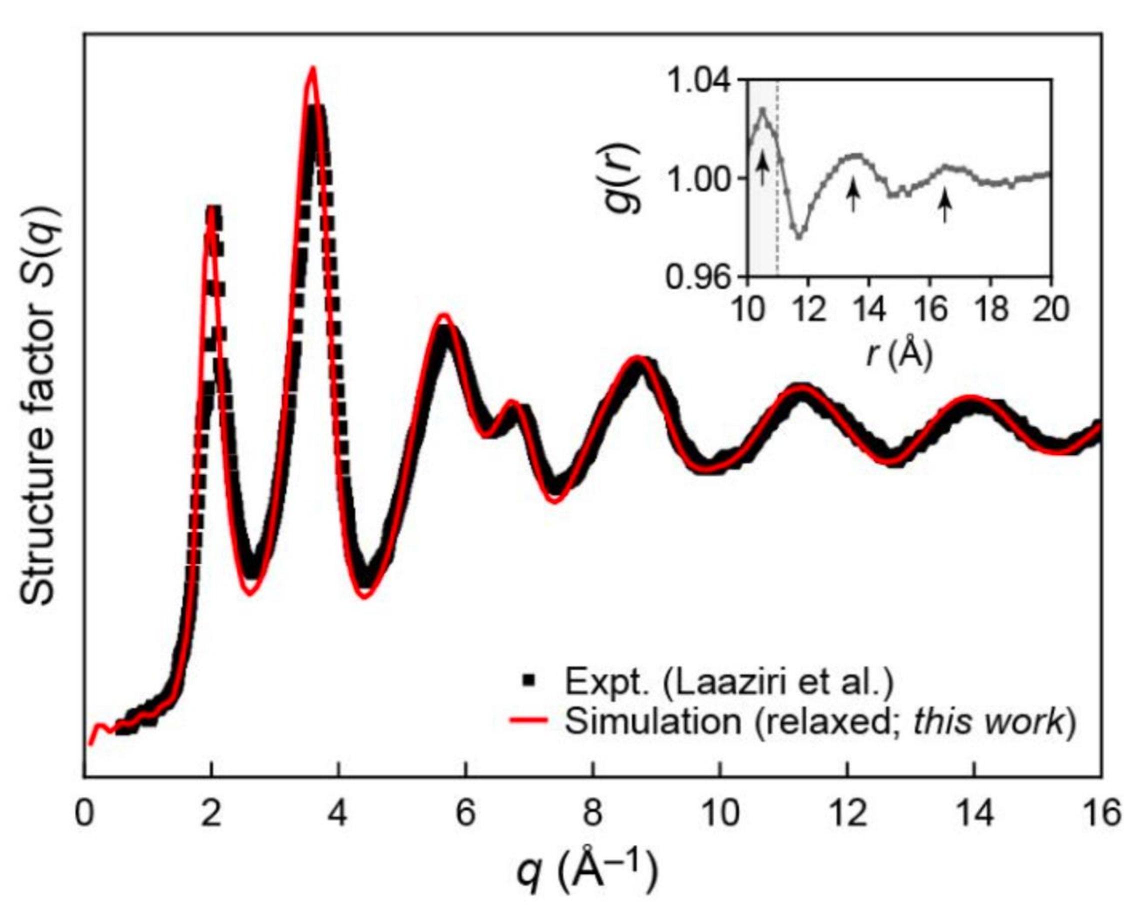
(3) Squeeze the solid, track the phase transitions. *n.b. needed to 'train' for such configurations*.

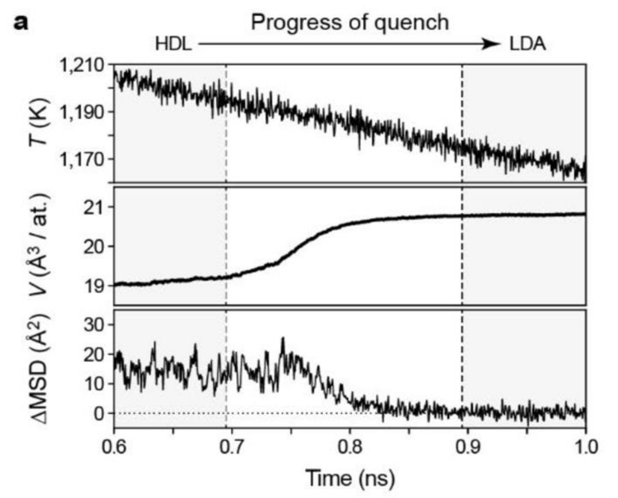


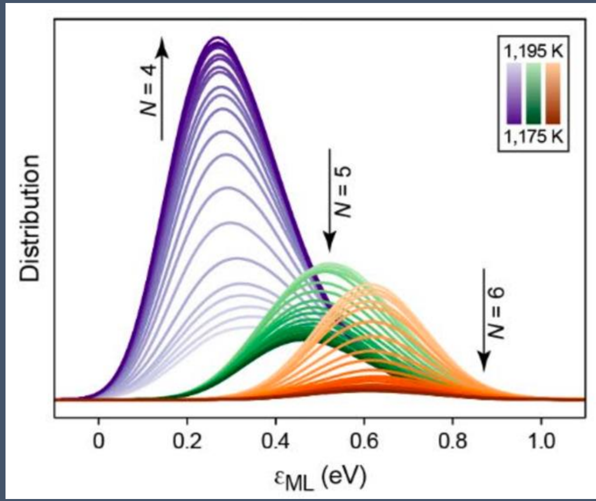
V. L. Deringer, N. Bernstein, G. Csanyi, M. Wilson, DAD, S. R. Elliott. Submitted to Nature; arxiv.org/1912.07344

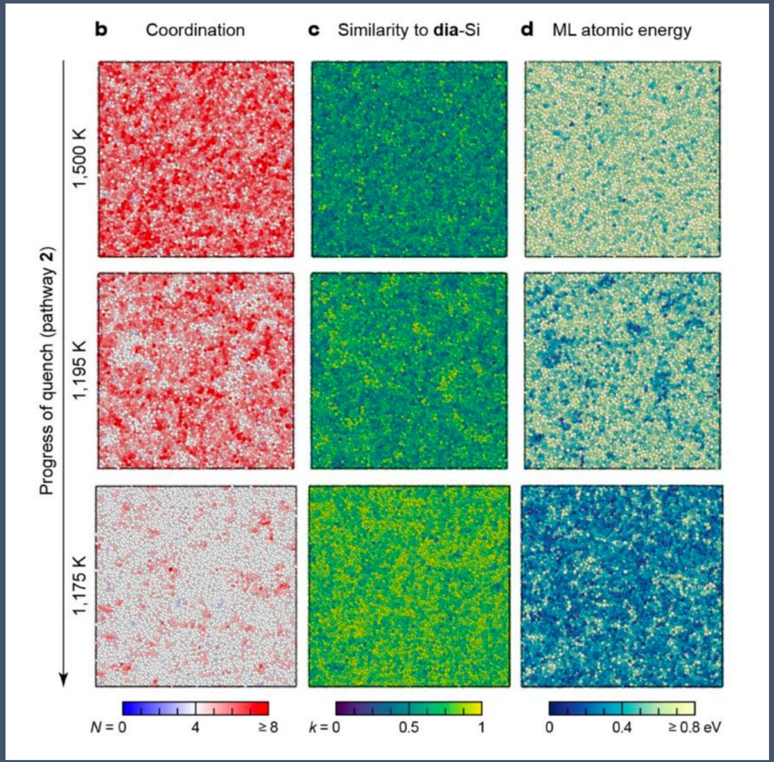
Quench the liquid to make a-Si (zero pressure)

- Similar S(q) to ideally tetrahedral model of Thorpe and coworkers.
- Statistically similar to 4096-atom mode, as expected.







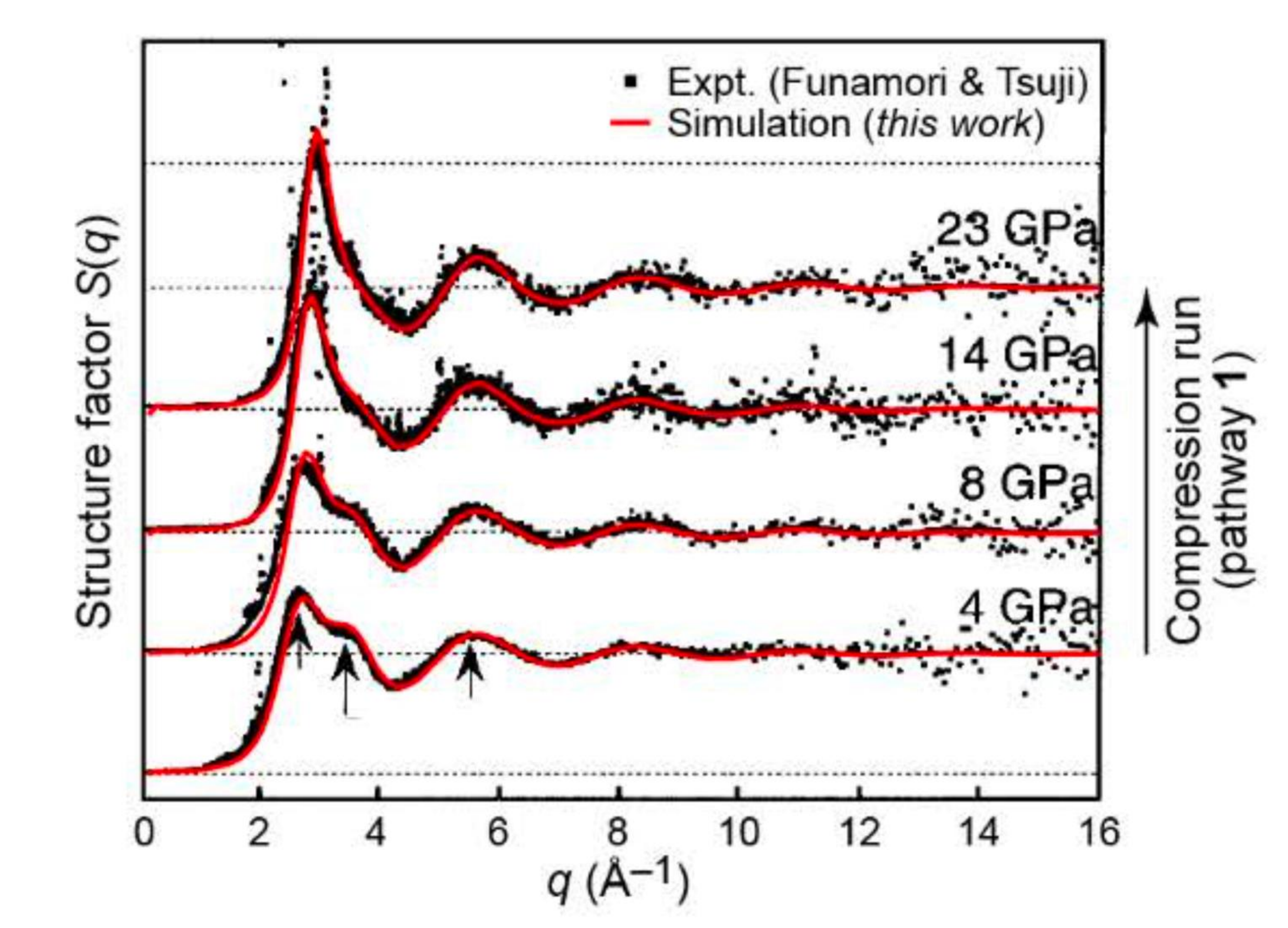


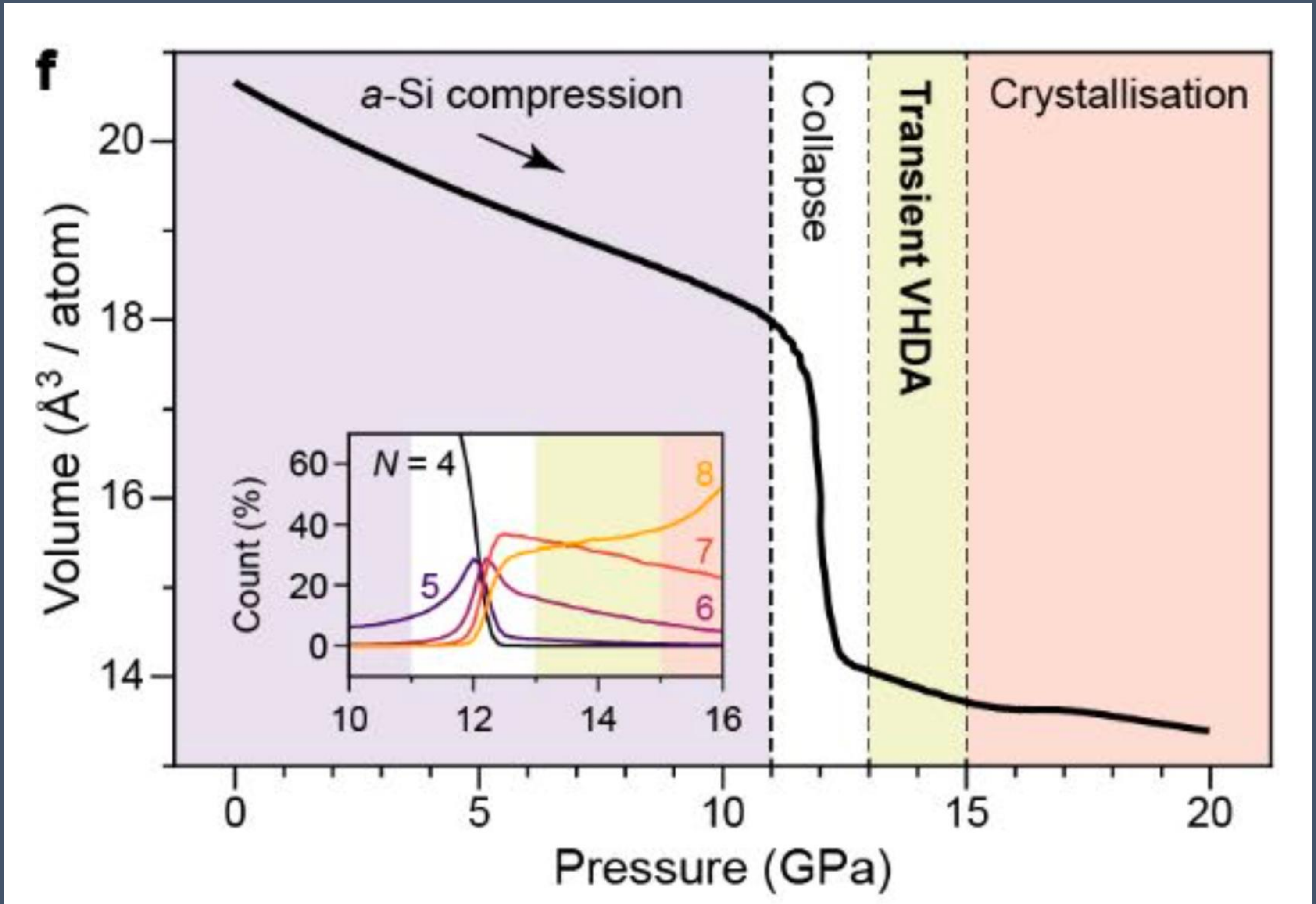
Structural evolution through the quench (500K, 10^{11} K/s)

High Pressure: 100,000-atom models

- **First**, we squeeze the liquid (T=1500K). Partly to check GAP, ensure we have all the conformations required. Compare to experiments.
- **Then** we squeeze a-Si (0.1 GPa/ps and T=500K).

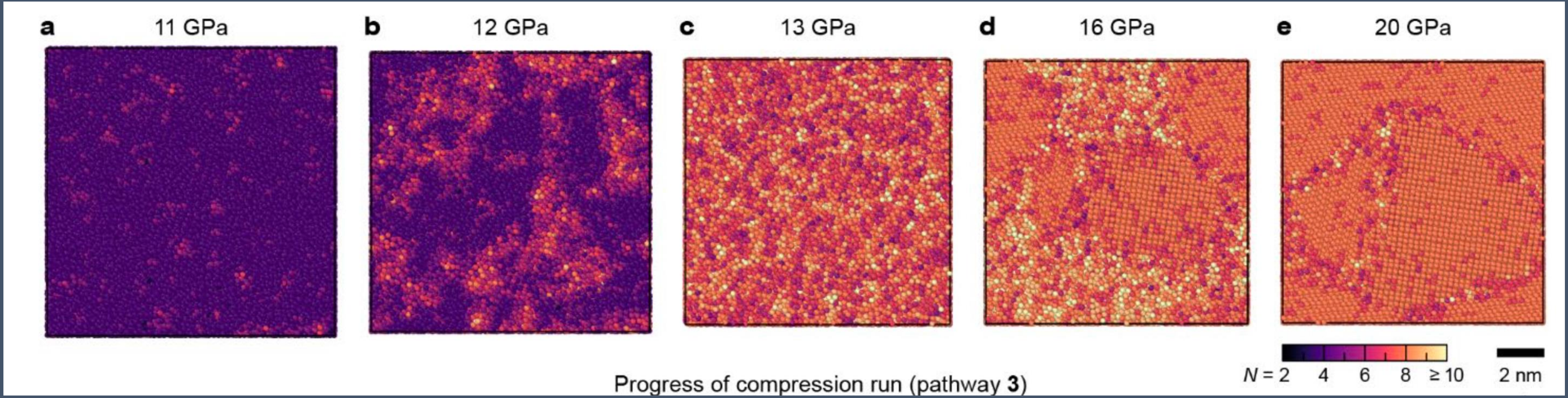
Squeeze the liquid: theory and experiment.



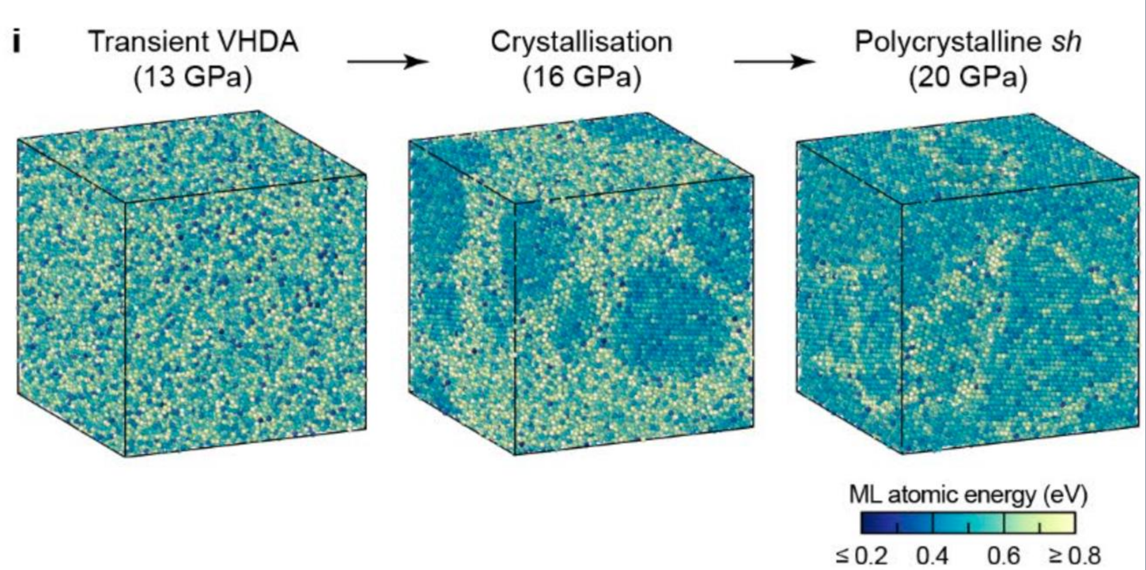


Squeeze a-Si: Results

Phase change: characterization

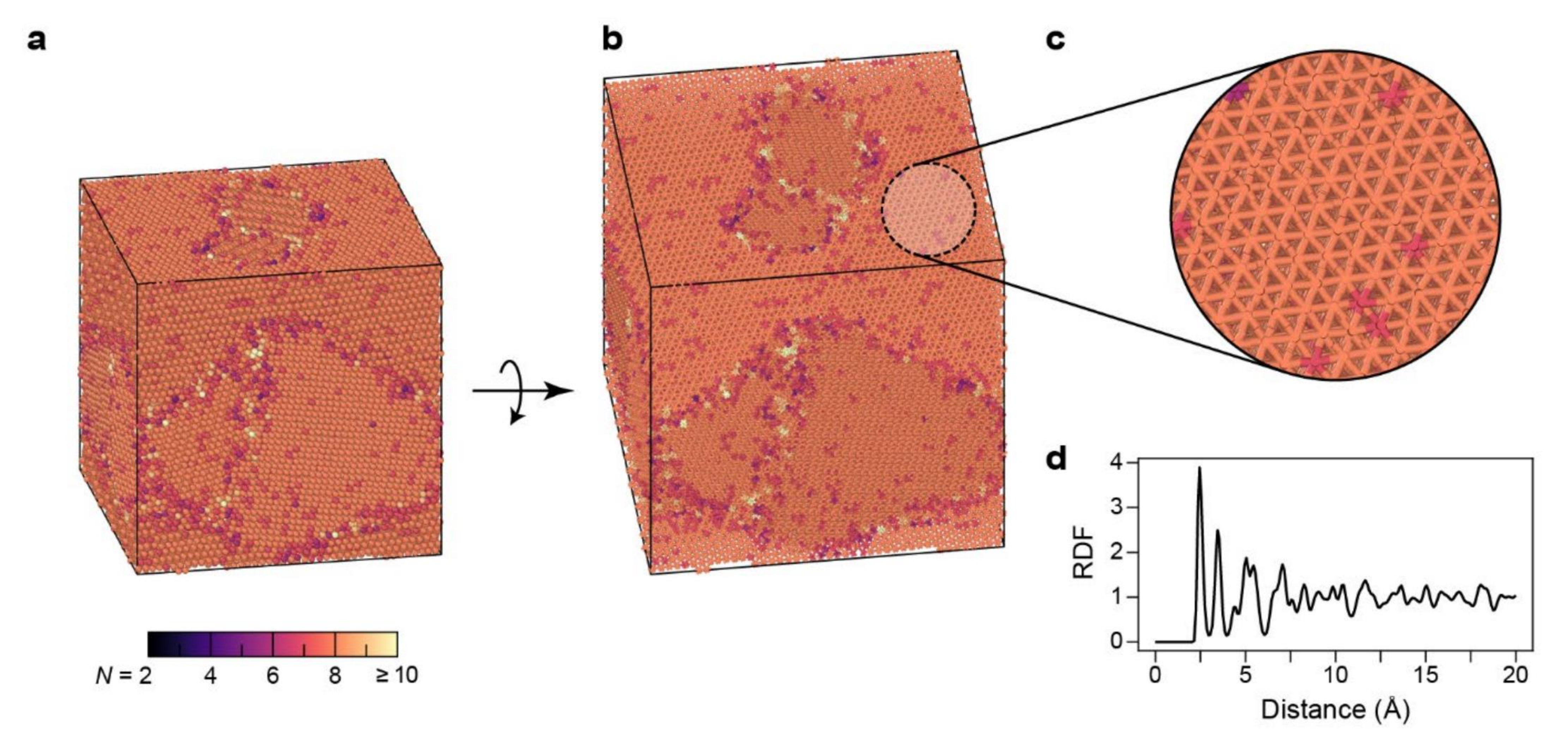


coordination



Local energy

Close up of crystallized phase



High pressure: discussion

Proceeds as follows:

(1) Some initial co-existence of High Density Amorphous (HDA) phase and low density amorphous: “Polyamorphism”.

(2) Abrupt collapse into highly disordered VHDA phase around 11 GPa. VHDA is transient, crystallization (to simple hexagonal phase) occurs at 15-16 GPa.

(3) So we have multistep crystallization originating in a precursor transient VHDA phase. **Not** direct HDA to simple hexagonal as previously believed.

(4) The crystallization does **not** occur in 1000-atom models, even up to 50 GPa. Small cell too dependent on stochastic effects?

Electronic structure

- Use orthogonal tight binding Hamiltonian (Kwon et al. PRB 1994). Four orbitals per site.
- dim(H)=400,000
- Method of DAD and Sankey (PRL 1993) to compute density of states. Ingredients:

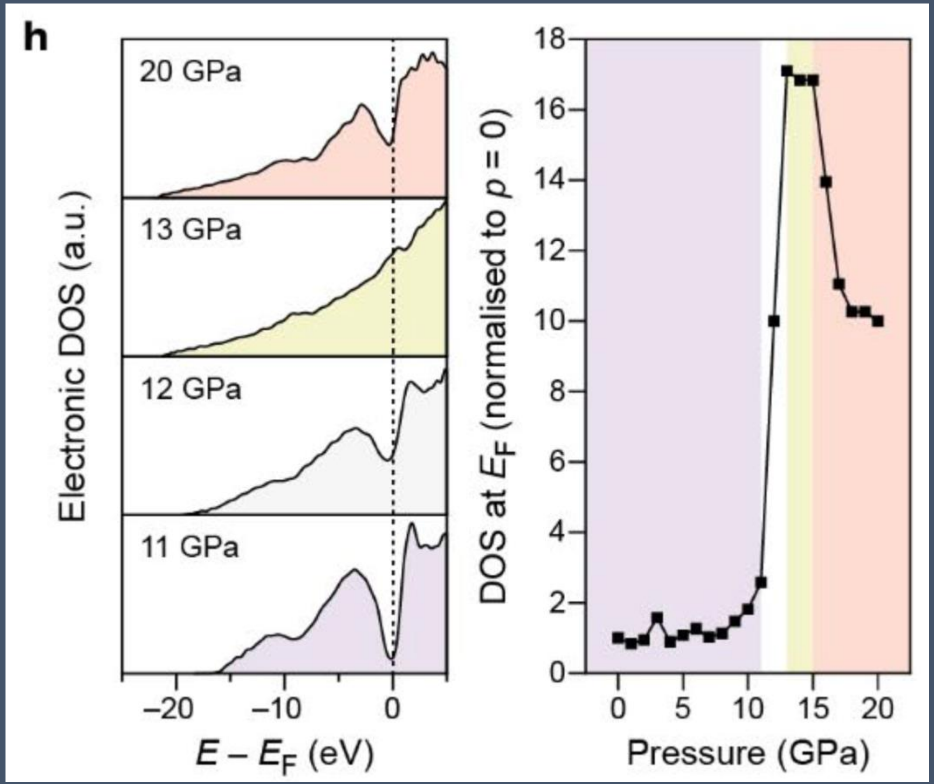
(1) Sparse matrix methods

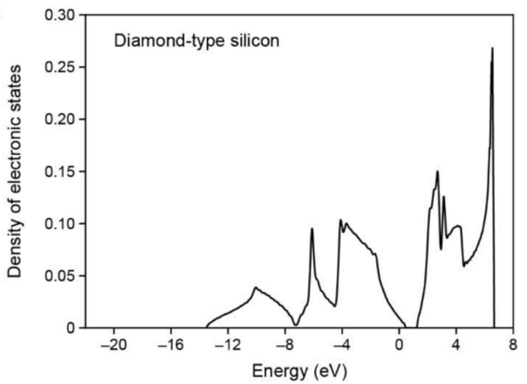
(2) Order-N computation of (many) moments of the spectral density of states

(3) Maximum-entropy reconstruction of the density of states from moments

Results: electrons

- Snapshots of the system through the pressurization run: examine the electronic density of states.
- Metallicity tracked by DOS(E_f).
- System “goes metallic” above 10 GPa, drops off some with s-h crystallization.
- Very High Density Amorphous DOS is **very** similar to 1500K liquid at similar pressure.
- *Caveat emptor*: Simple Hamiltonian, fit to some high-pressure configurations. Conduction states leave something to be desired.



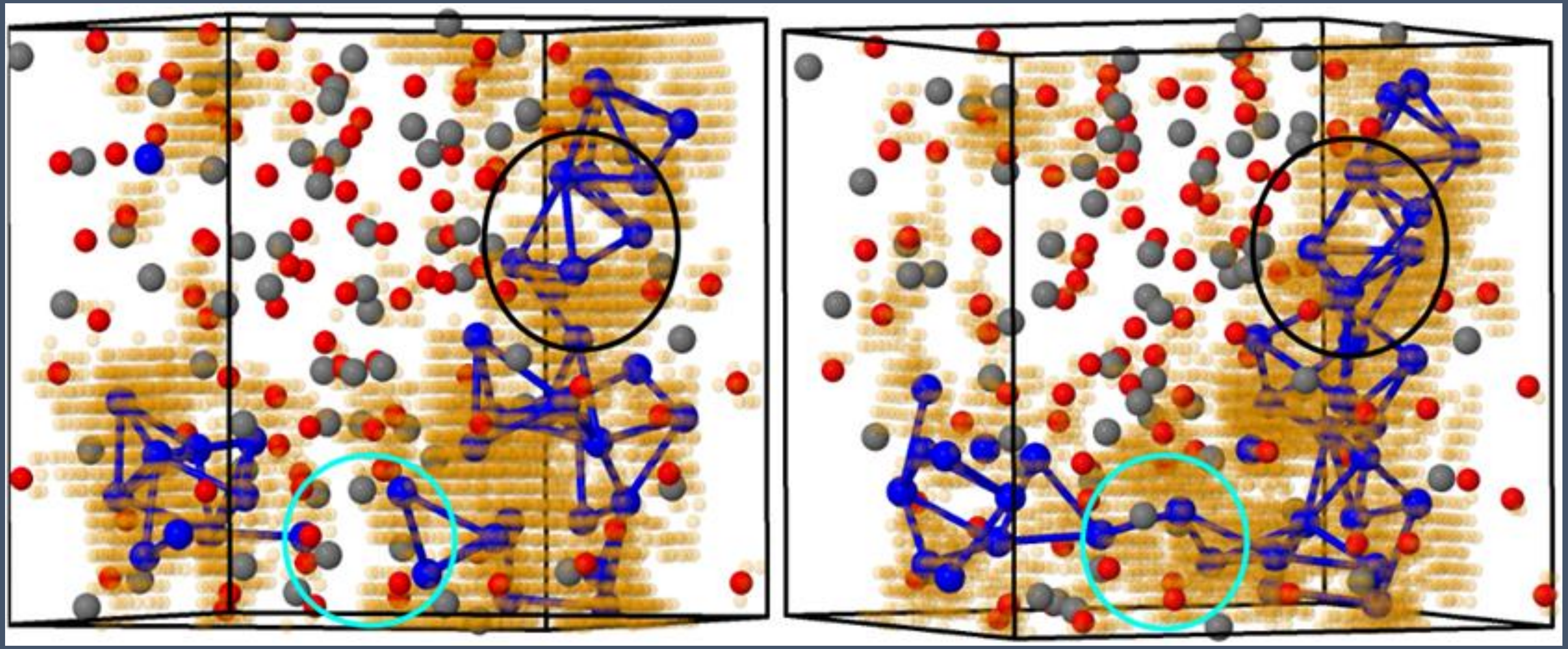


2.1 million-atom fragment of diamond (same method)

Conclusion: GAP/Silicon/Pressure

- Machine Learning techniques are emerging as a meaningful tool in simulation. Opens some new doors.
- Squeeze a-Si: Abrupt collapse into a transient high density/coordination state. Then rapid crystallization to simple hexagonal phase. Does not happen in 1000-atom cell!
- Lots of new frontiers: now we are looking at surfaces. Collaborators are working on Carbon, GeSbTe (phase change memory) materials, others.

How does the conduction change with fluctuations?



Large gap

Small gap

Electronic conductivity contrast of 10^4 between these two configurations.

GAP: comments from a cheerleader, not an expert

- Given a very large sampling of accurate (DFT) computations of forces for an “adequately diverse and representative” set of configurations, GAP estimates the forces by fitting/interpolating from its library of configurations.
- If ever the devil is in the details, it is in building ML potentials:

1) How many configurations are enough?
2) Have we sampled all salient environments?
3) How do we represent a local environment?
4) Error estimation is built in – if there is nothing close in the database, demand a new DFT calculation.
5) When this is done properly, it is **not cheap**. For less than 200 atoms, cheaper to use planewave DFT! **But, it is order N.**