Inverse and hybrid approaches for disordered solids

DAVID DRABOLD, PARTHA BISWAS, D. K. LIMBU, R. ATTA-FYNN, D. TAFEN, ANUP PANDEY, BISHAL BHATTARAI, RAJENDRA THAPA

Logic…

Modeling as a problem of inference

E. T. Jaynes
1922-1998

1) Conventional approach: Do your best simulation (big cell, fancy interactions, long simulation times, etc). *This is very different from the way the material was really made!* Compare to experiment, hope for the best. Write the paper.
2) There may be other information that would improve the realism of the simulation -- experimental, chemical or other information not included. *Why not use it in making the model?!*

Modeling paradigms and imposing *a priori* information

1) **Simulation**: Implement your best calculation (big cell, fancy interactions, long time evolution, *etc*). *Hope* that the results look like experimental ones.
2) **Information:** Try to invert the experimental data.
3) **Merge the two**: carry out simulation but impose the *a priori* (possibly experimental) information as part of the simulation.

D A Drabold, EPJB **147** 1 (2009).

Reverse Monte Carlo

Kaplow, McGreevy *et al.*

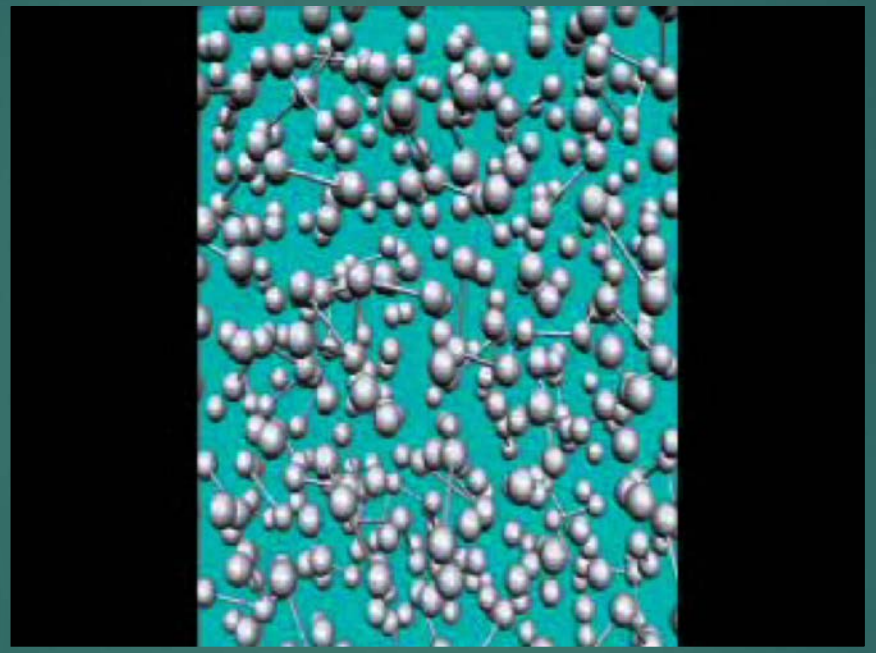
- **Information paradigm**. *What does experiment imply about the structure?*
- "Reverse Monte Carlo": put atoms in a supercell, move at random with Monte Carlo, keep moves if closer to experiment, accept with Metropolis probability if worse.
- Result: matches experiment by construction, but diffraction data **alone** is **insufficient** to produce a chemically realistic model. *Still, it is a clever idea -- **use the information you have**!*

RMC: Discussion

- Promising ***if*** additional information (constraints) are employed.
- Flexible, enables inclusion of *a priori* information.
- Constraints are tricky: we are imposing information, but we are potentially imposing errors – *the model is only as good as the information employed*!

RMC: order from chaos

RMC on a-Si (diffraction plus bond angle constraint)



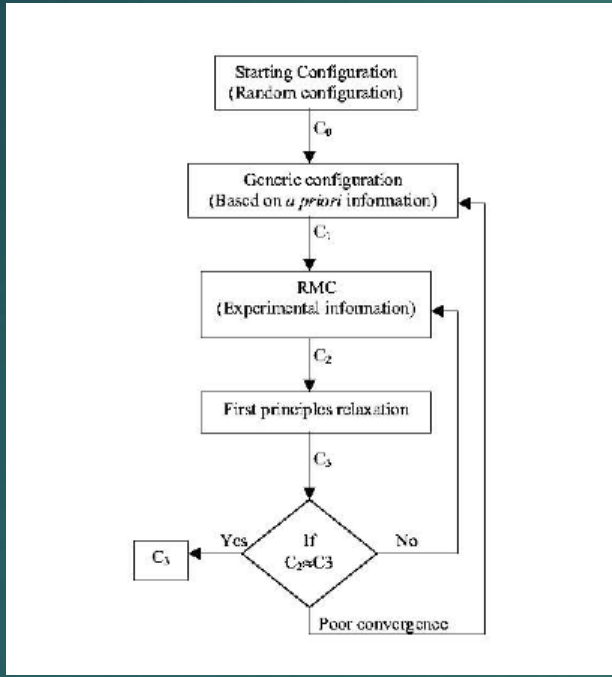
Credit: **Partha Biswas (about 2005)**

Experimentally Constrained Molecular Relaxation (ECMR)

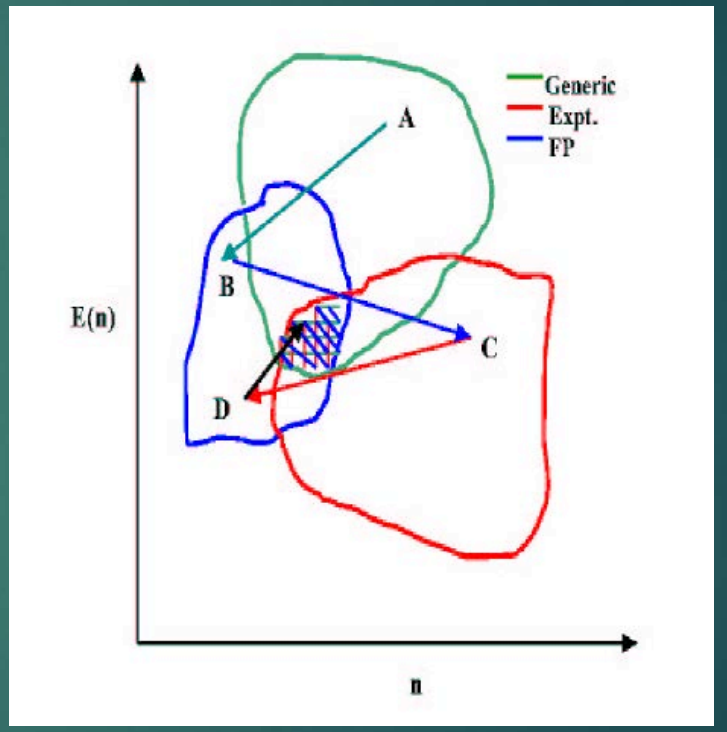
- We want to include experimental data in MD: **merge RMC and molecular dynamics modeling.**
- Start from "experimentally realistic" subspace, self-consistently iterate between RMC and first principles relaxation.

P. Biswas, *et al.,* J. Phys. Cond. Matt. **16**, S5173 (2004); PRB **71** 054204 (2005)

ECMR: *implementation*



Flow chart for ECMR



Cartoon suggesting ECMR convergence

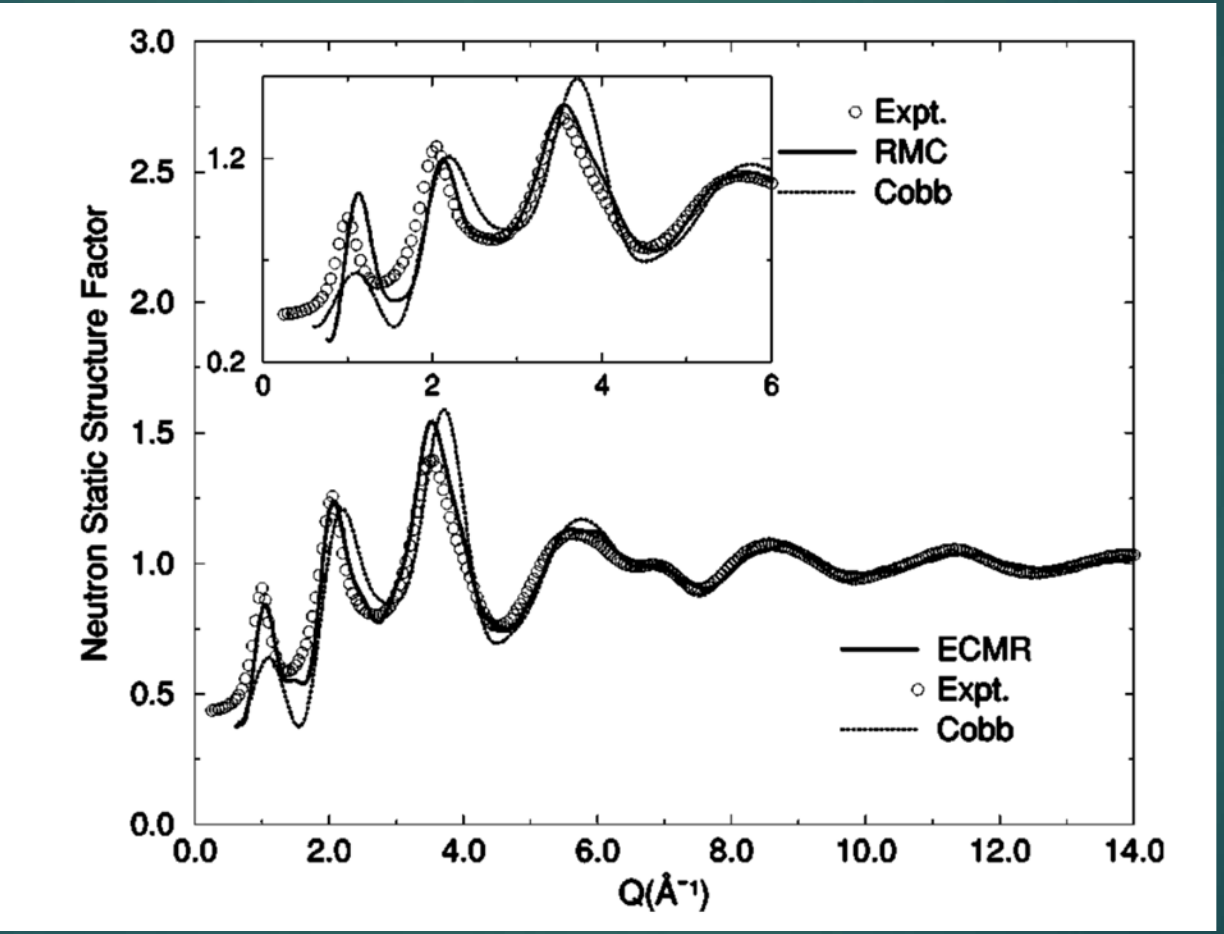
ECMR & $GeSe_2$

- $GeSe_2$: Classic chalcogenide glass, hard to model well, especially first sharp diffraction peak.
- Lets try ECMR:

Experimental input: Petri and Salmon partial structure factors.

Hamiltonian: Density functional, minimal basis, supercell with 648 atoms in unit cell.

ECMR: g-$GeSe_2$ results



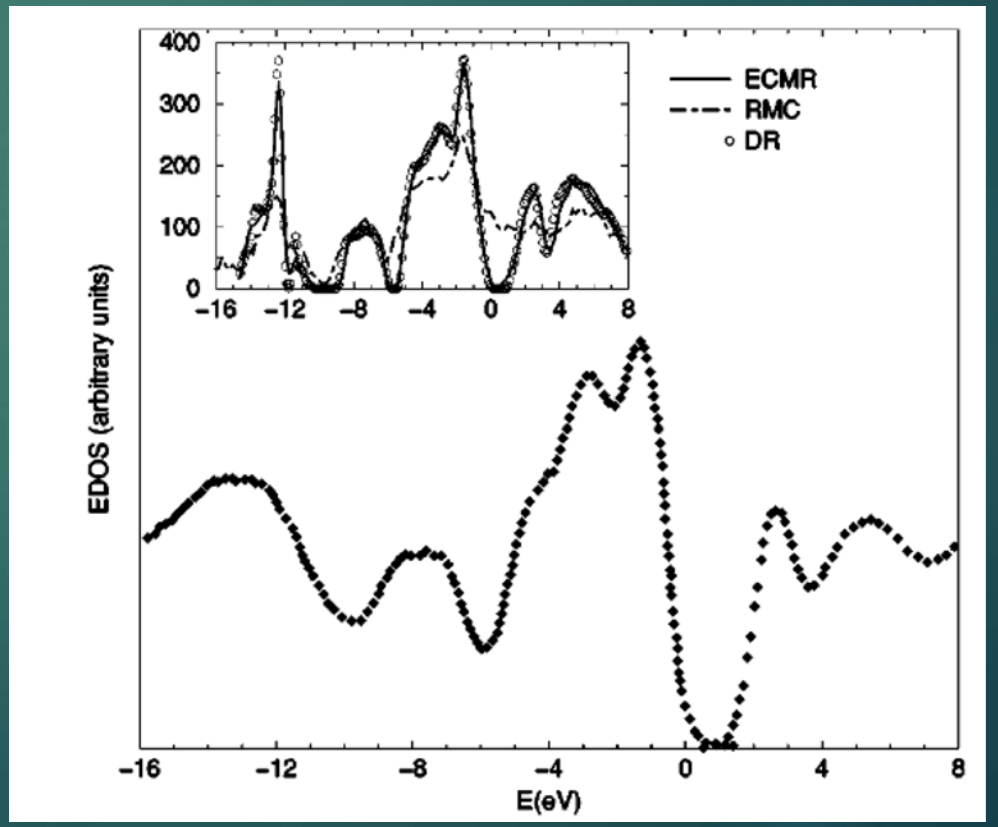
Static structure factor

Electronic structure: density of states

Note: a valid structural model **must** have a realistic electronic DOS.

$GeSe_2$ →

Expt: XPS - Bergignat *et al* PRB (1988), IPES- Hosokawa *et al*, JPCM (1994)



ECMR: improving the convergence

- ECMR is great – *if it converges*!
- Rather than doing a sequence of full relaxations, perform partial inversions, followed by partial relaxations.
- Iterate THAT!
- Seems to be more robust than ECMR.

Beyond ECMR: Force Enhanced Atomic Refinement (FEAR)

- Start with random model (assume density is known)
- Repeat to these two steps convergence:

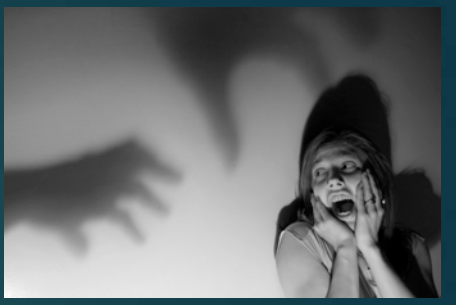
-- Obtain N accepted moves from RMC [drives model toward experiment]

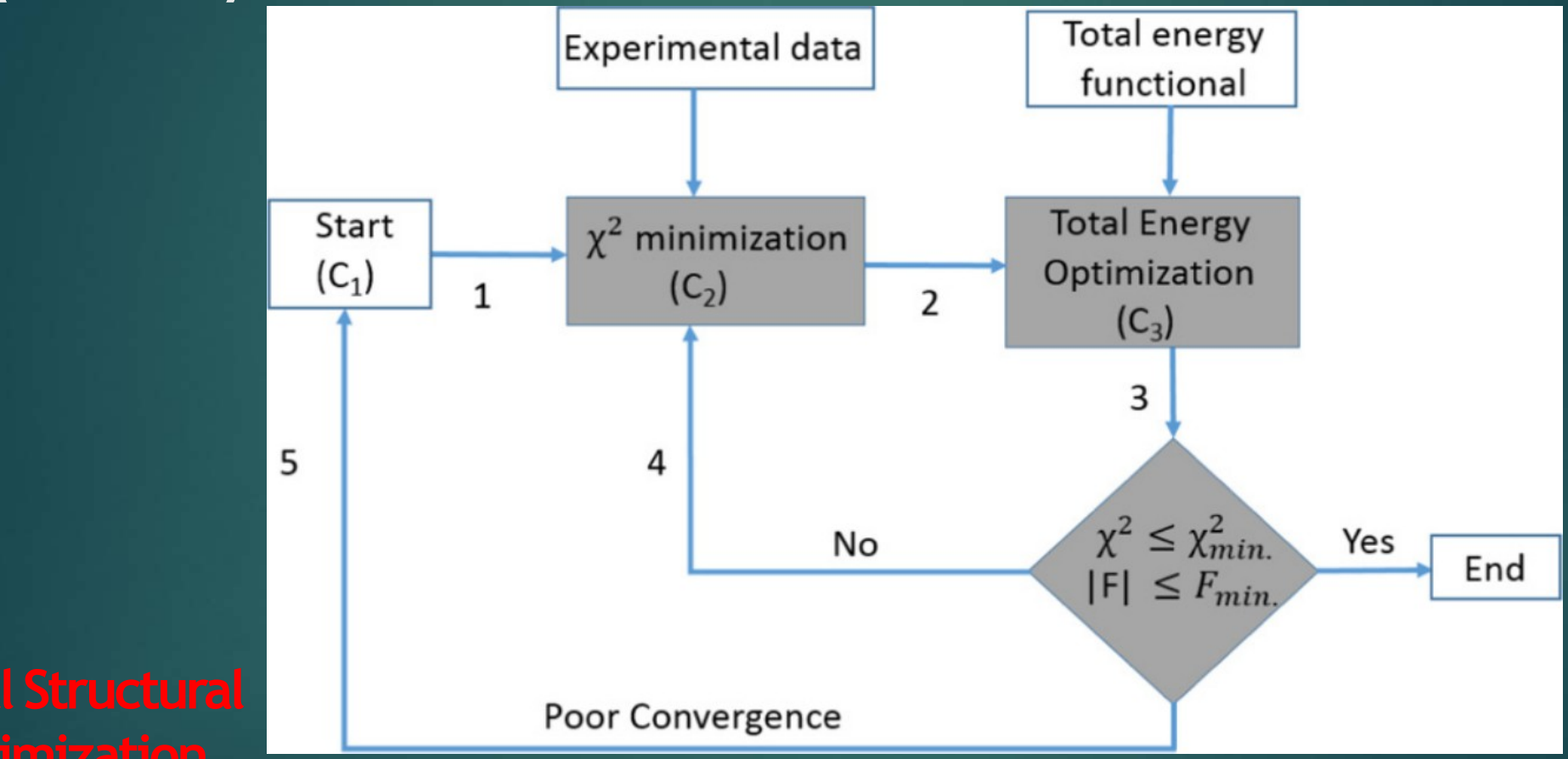
-- Take M conjugate gradients steps with energy functional [enforce chemistry]

Typically N~100, M~1-5. Always N>>M.

A. Pandey, B. Bhattarai, P. Biswas, DAD

Force Enhance Atomic Refinement (FEAR)





Partial Structural minimization

Partial Energy minimization

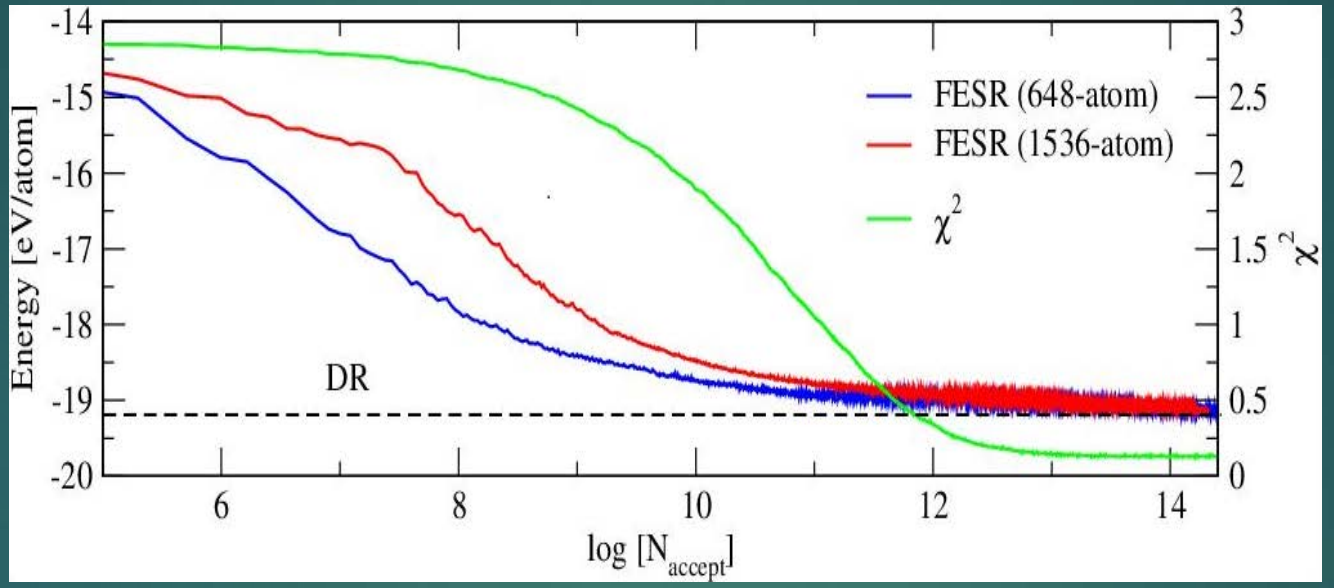
Pandey et. al, Phys.RevB 94, 235208 (2016)

Example: FEAR for amorphous SiO_2

- Adopt 648-atom, 1536-atom models.
- Use the van Beest (BKS) potential (PRL, 1990). Start with **random** coordinates.
- After 100 successful RMC moves, move all the atoms along van Beest gradient – only one step, *not a full minimization*.
- *Repeat previous until convergence (fit and force) is achieved.*
- Need about 30,000 force calls

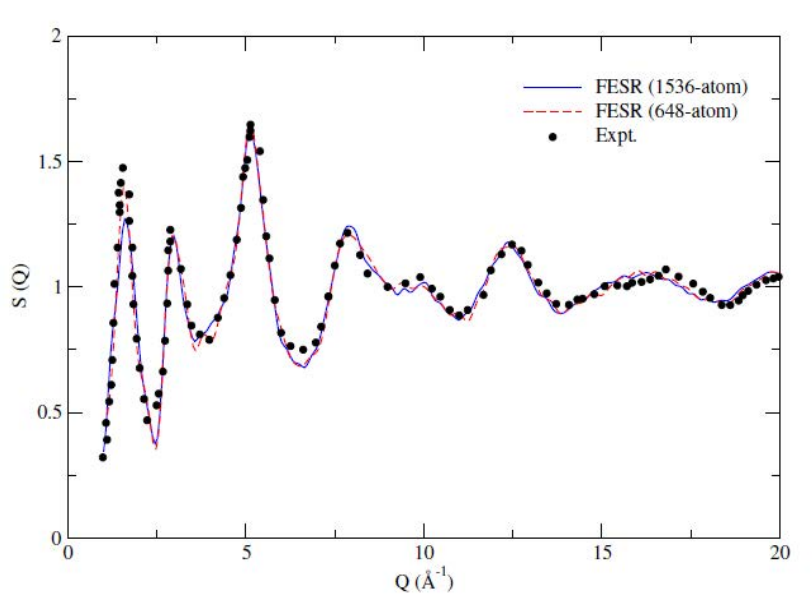
A. Pandey, P. Biswas, DAD Phys Rev B 92 155205 (2015)

FEAR of silica

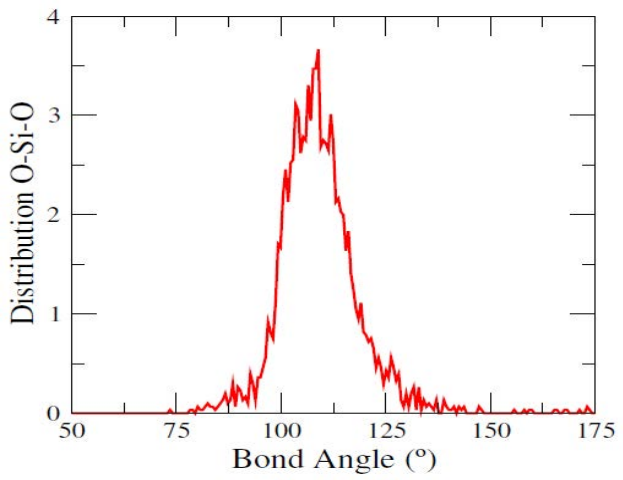


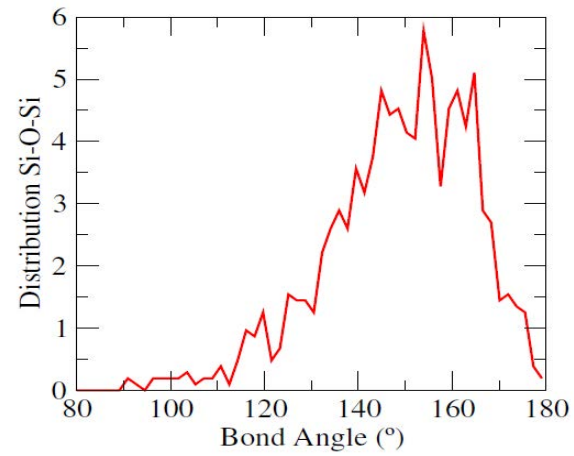
FEAR: minimization of error vs. experiment and total energy.

Results: silica



Peak position (Å)			
atom-atom	FESR	MD	Expt.
Si-Si	3.15	3.10	
Si-O	1.62	1.62	1.610± 0.050
O-O	2.64	2.64	2.632± 0.089





Bond Angle (°)				
	FESR	MD	Expt.	DR
O-Si-O	109.5 (15.6)	109.6 (10)	109.5	109.5 (9)
Si-O-Si	154.3 (27.8)	142.0 (25)	144 (38)	140 (25)

Ab initio FEAR – use DFT (VASP or SIESTA) as energy functional

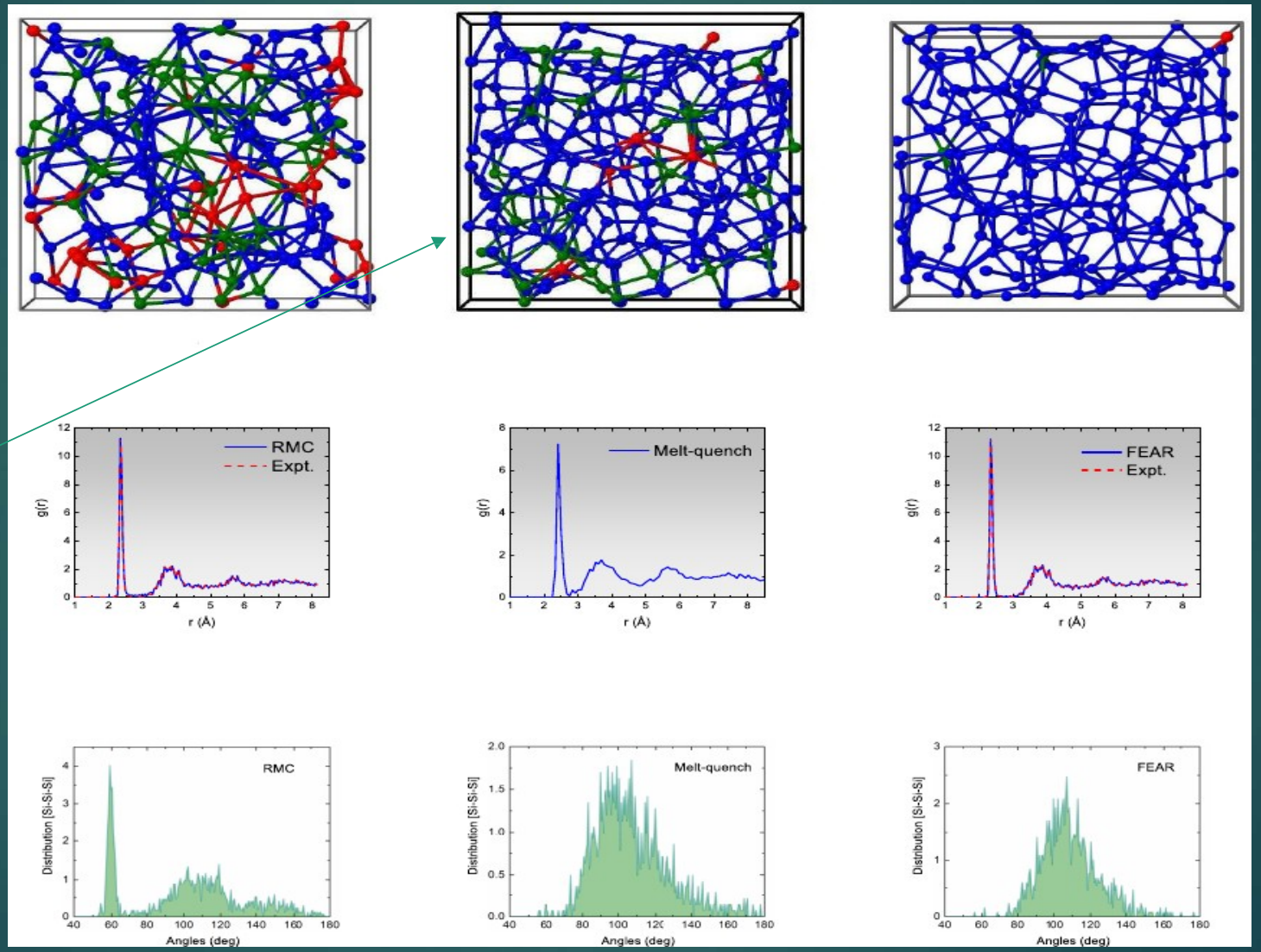
Key to making a general method – to structurally invert a very wide range of materials from diffraction – need general accurate interatomic interactions to unbiased provide chemical information.

First example: silicon and SIESTA

RMC Melt Quench FEAR

RMC

Melt-Quench



Blue: 4-fold
Green, Red are coordination defects

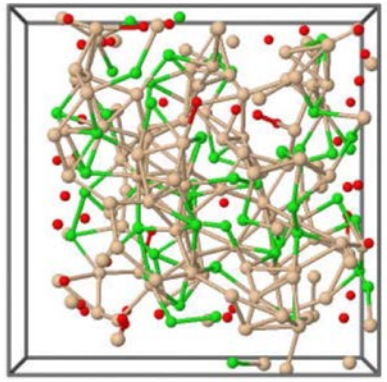
FEAR

Pandey et. al, Scientific reports 6, 33731 (2016), JNCS J. Non-Cryst. Sol 492 27 (2018).

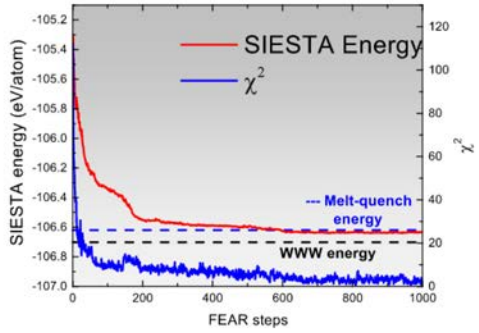
FEAR: a-Si animation and details

Force-enhanced Atomic Refinement:

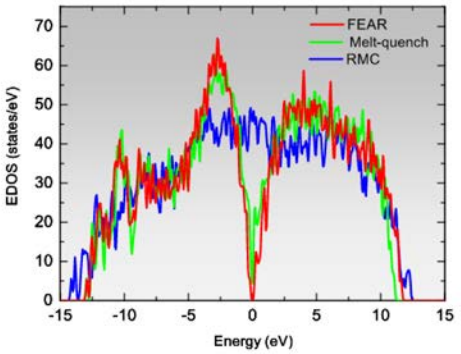
Evolution of 216-atom model amorphous Si starting from random initial configuration with beige sphere representing (correctly coordinated) four-fold atoms, green over-coordinated and red under-coordinated.



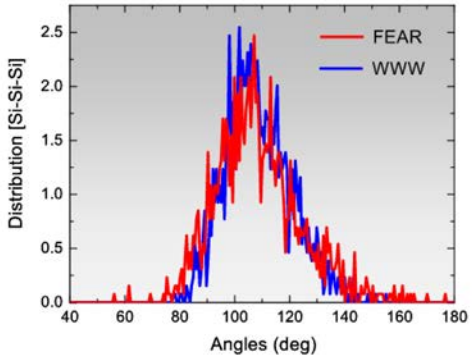
RED : Si (<4) GREEN : Si (>4) BEIGE : Si (=4)



a)



b)



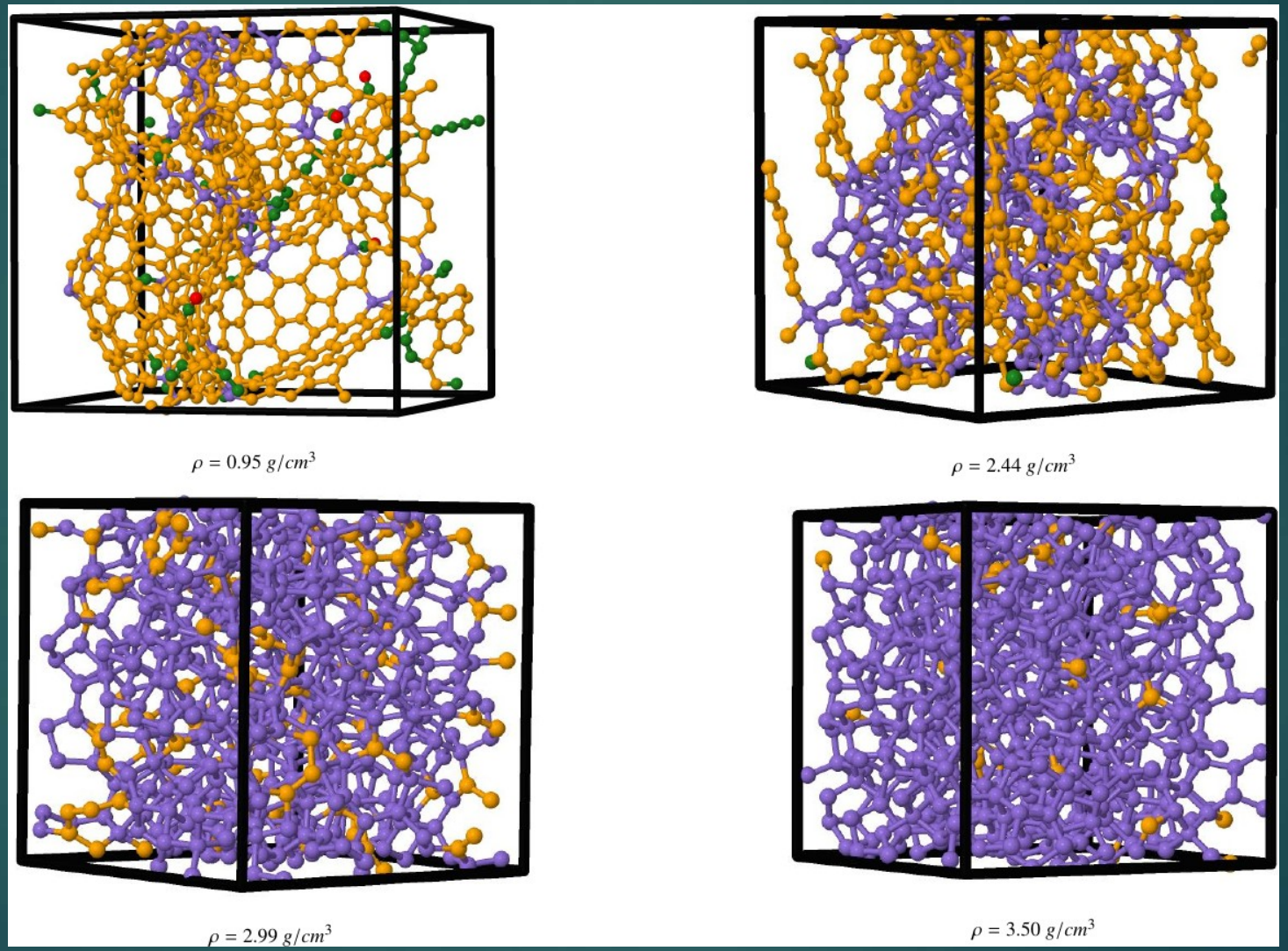
c)

Example: Amorphous carbon across densities

- Hard: Carbon happily sp^3, sp^2 or even sp bonds. Need a good potential.
- Wealth of experiments to check against.
- We carry this out with largish models (up to 800 atoms), SIESTA as energy functional. Then relax final models with VASP (little change).

Amorphous Carbon across densities

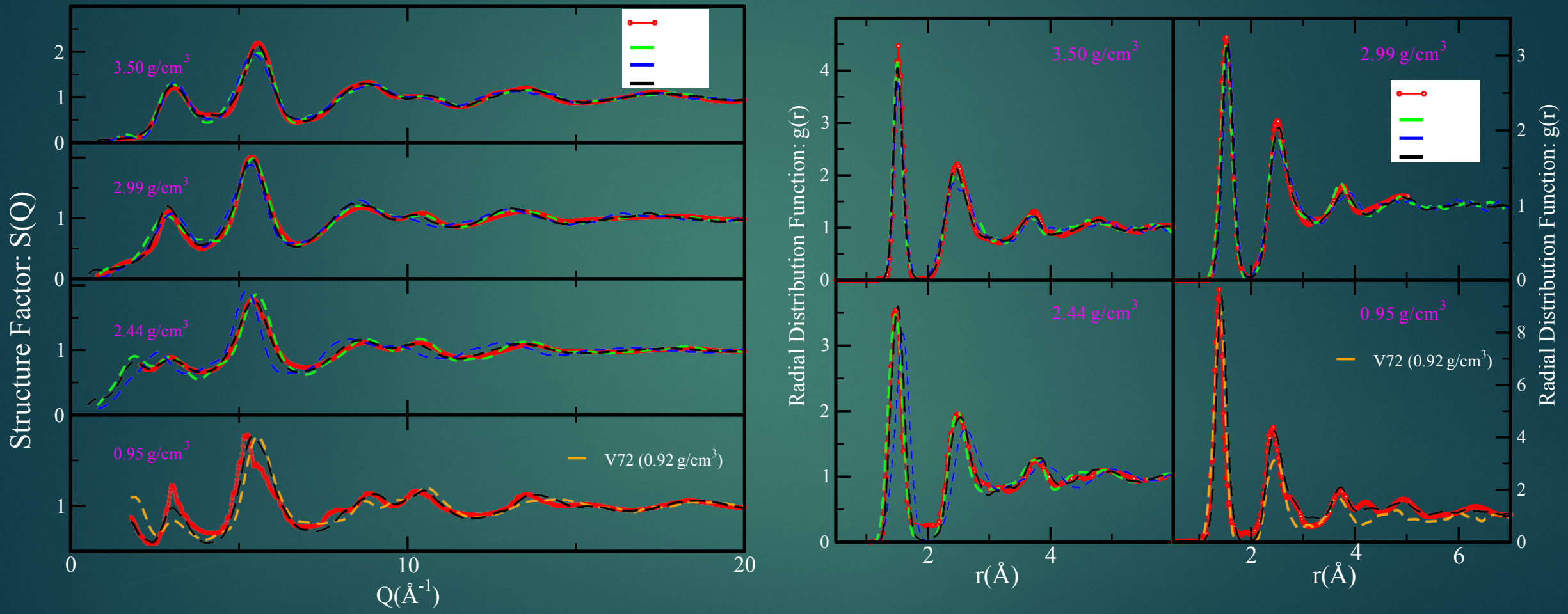
648 atoms



Purple (sp^3), Orange (sp^2), Green (sp)

Bhattaraii, Pandey & DAD, Carbon, 131 168 (2018)

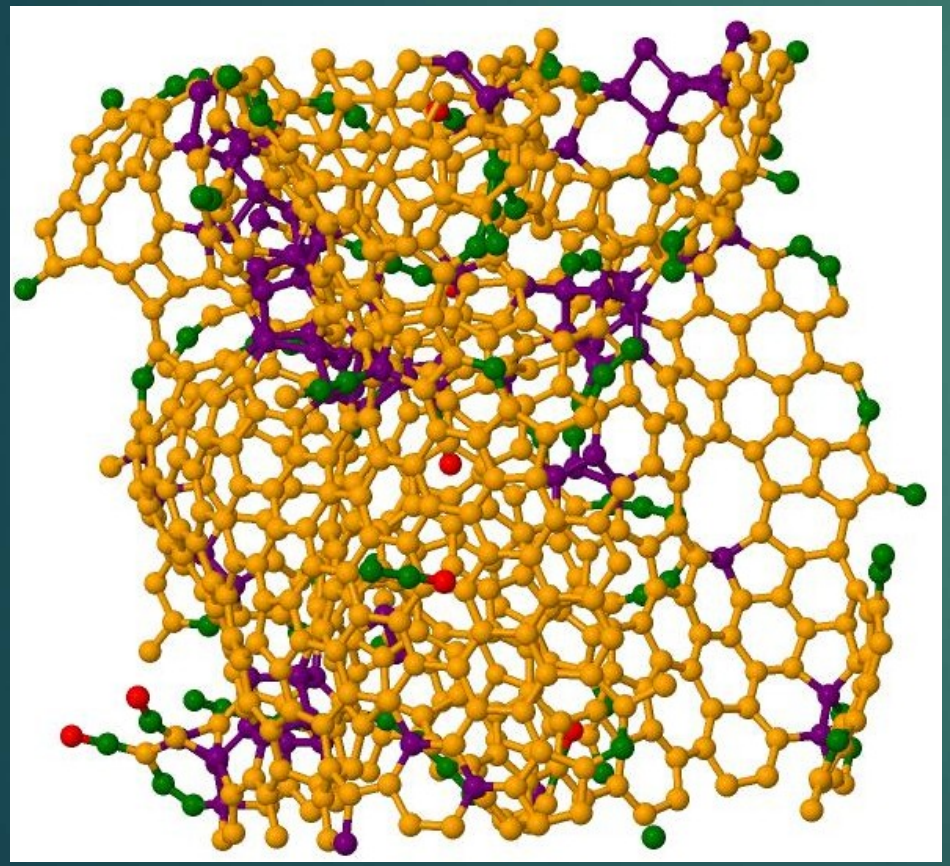
Amorphous Carbon

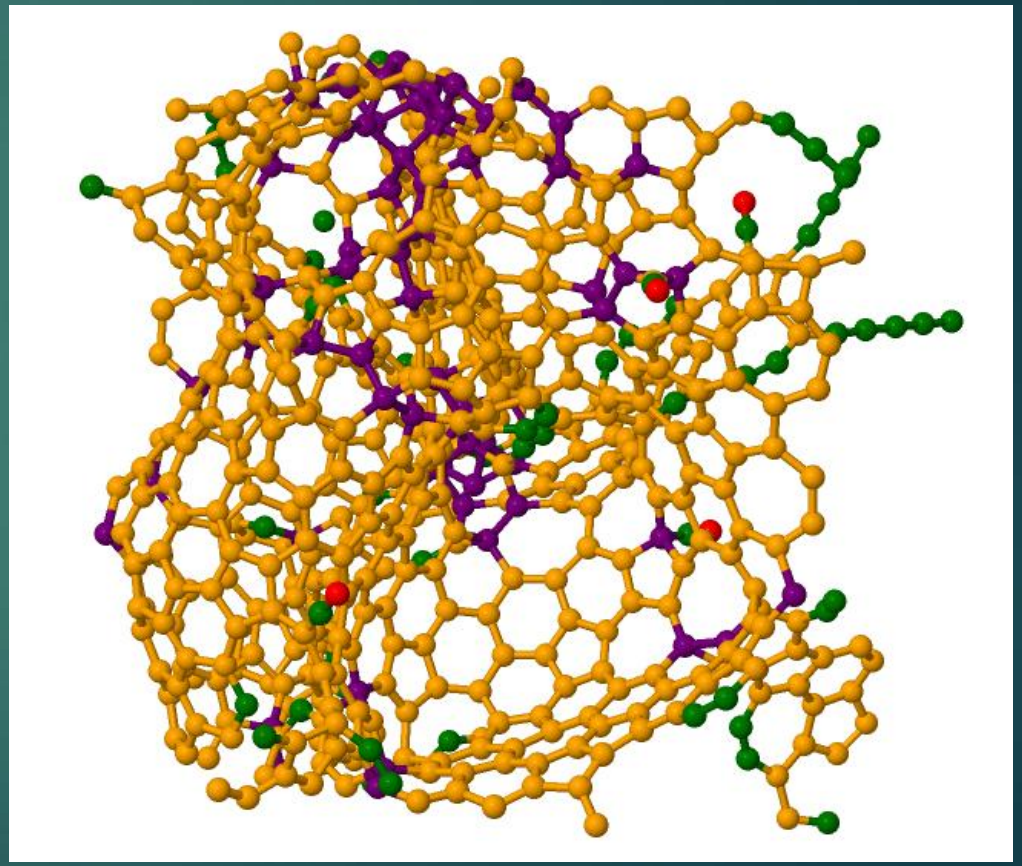


Bhattarai et. al, Carbon (2018)

Low density (0.95 gm/cc) FEAR Carbon (800-, 648-atom models)

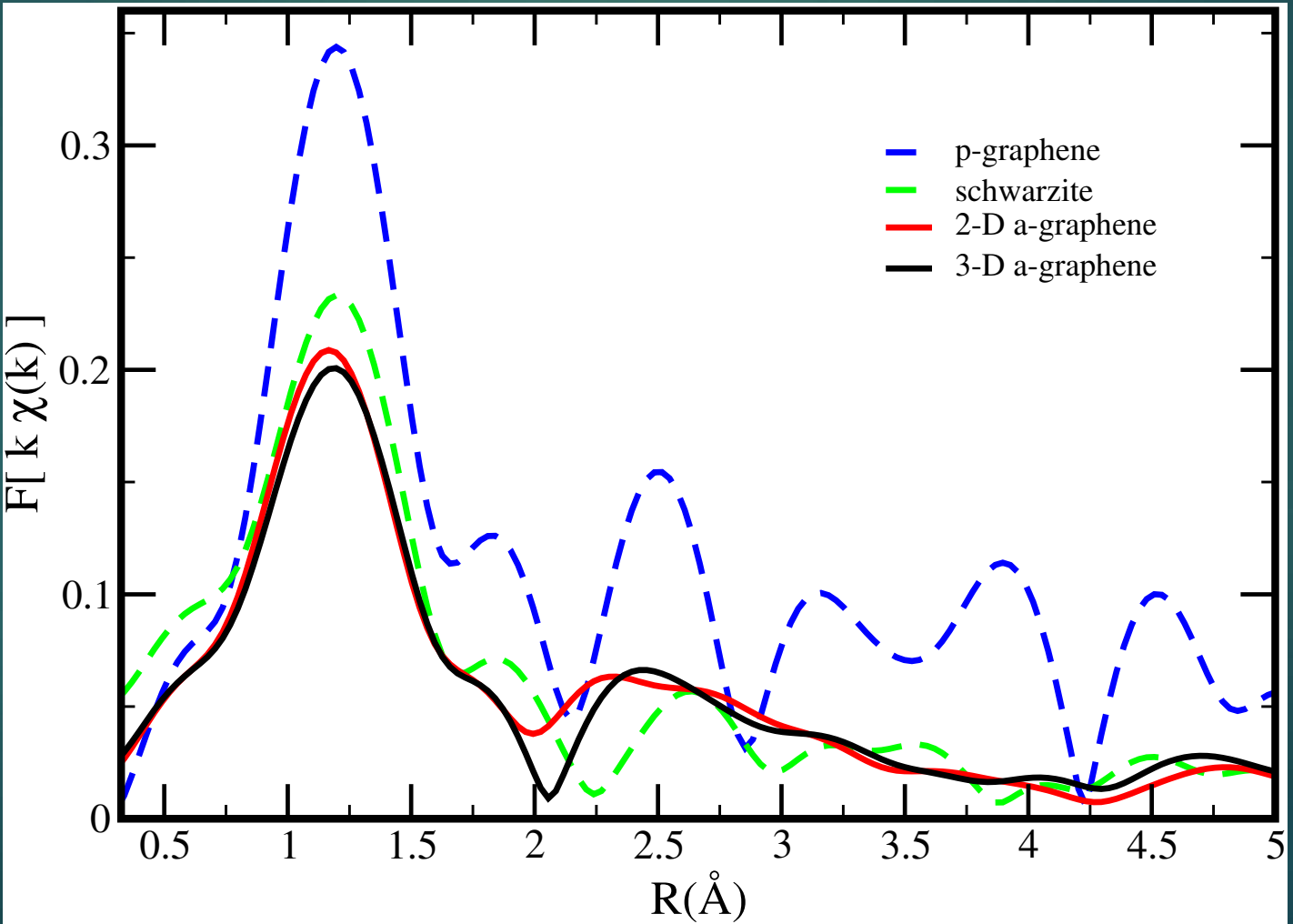
Purple (sp^3), Orange (sp^2), Green (sp)





Bhattarai et al, PCCP, 2018

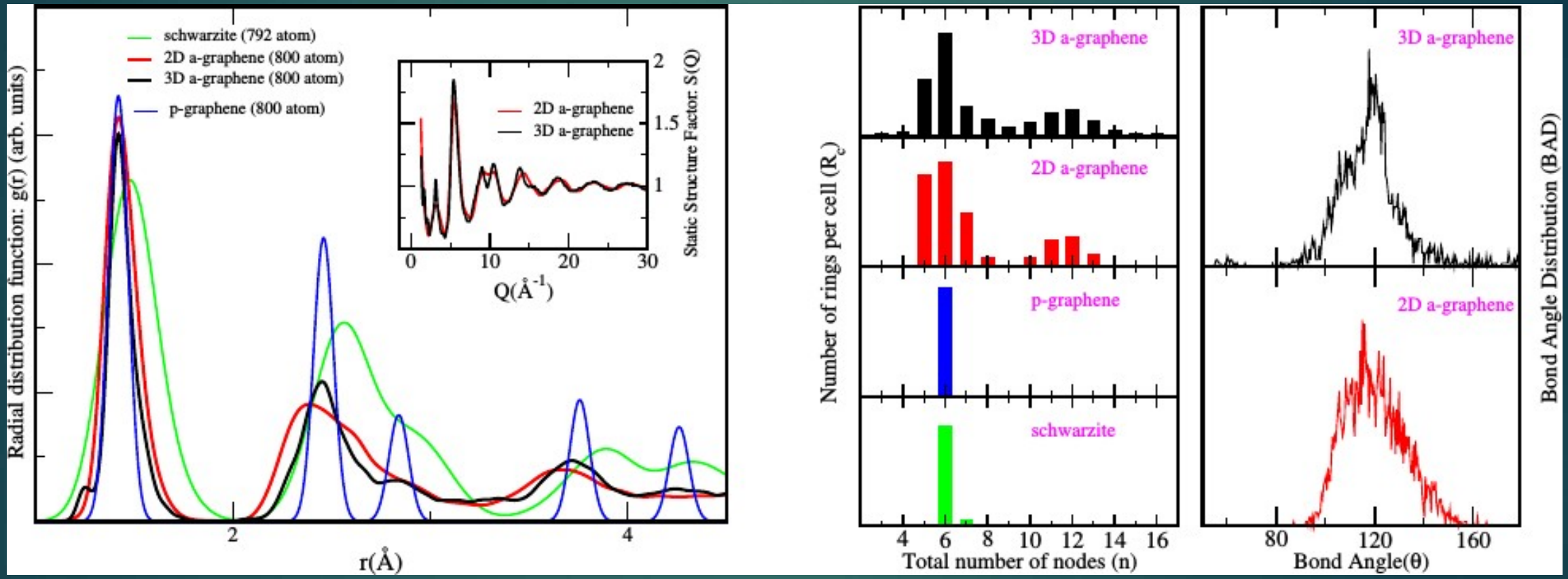
A prediction: EXAFS of 0.95gm/cc a-C. Fairly small differences…



Comment

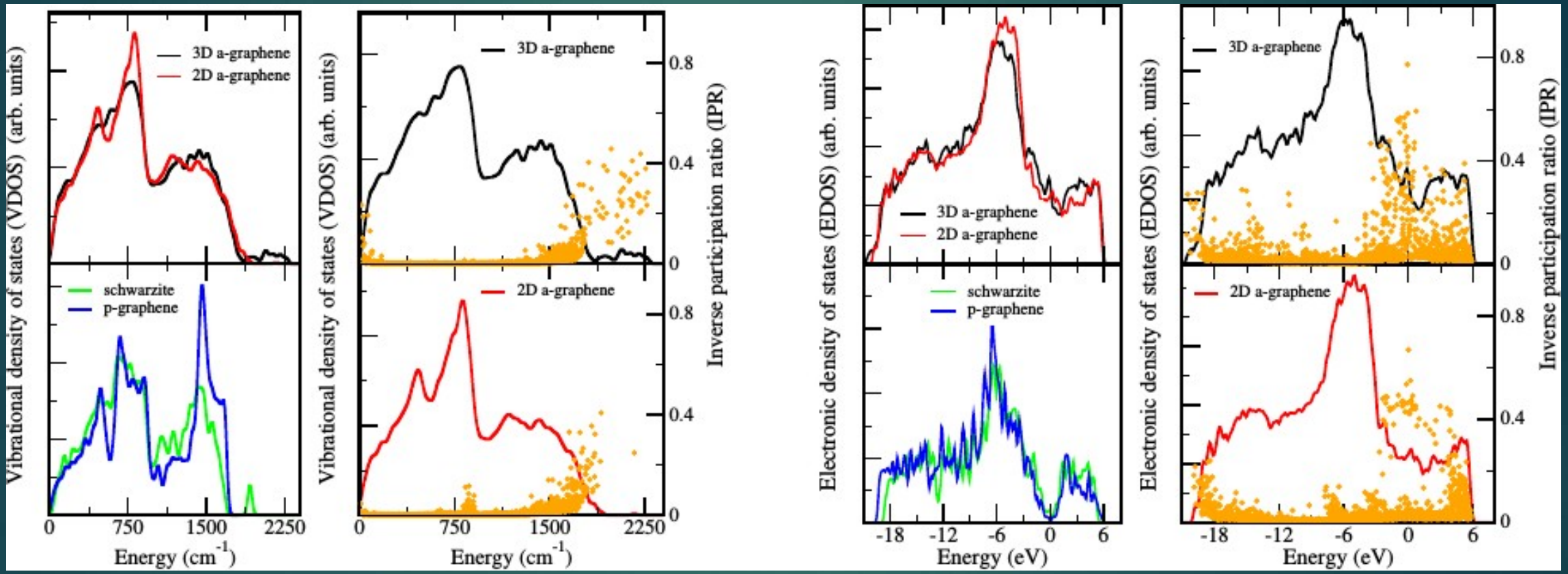
- **Amorphous C with density near 1 gm/cc is a form of three-dimensional graphene: warped, wrapped sp^2 sheets including ring disorder (pentagons, hexagons, heptagons) and also with sp and sp^3 defects.**

Structural Comparison

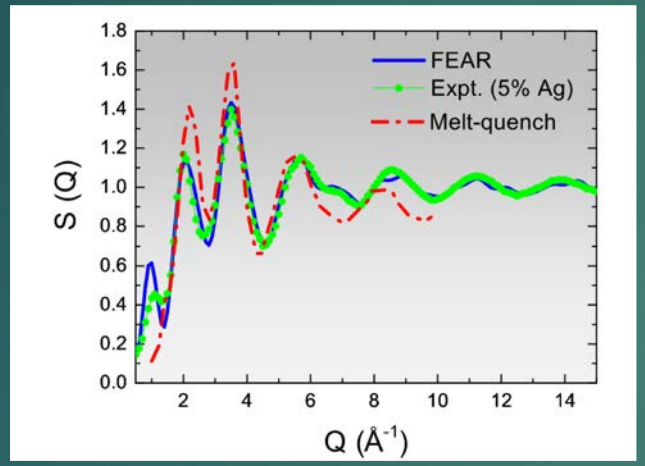


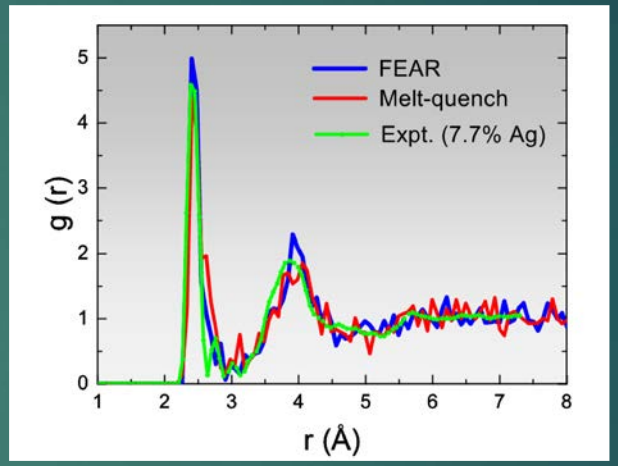
Bhattarai et. al, PRL submitted (2018)

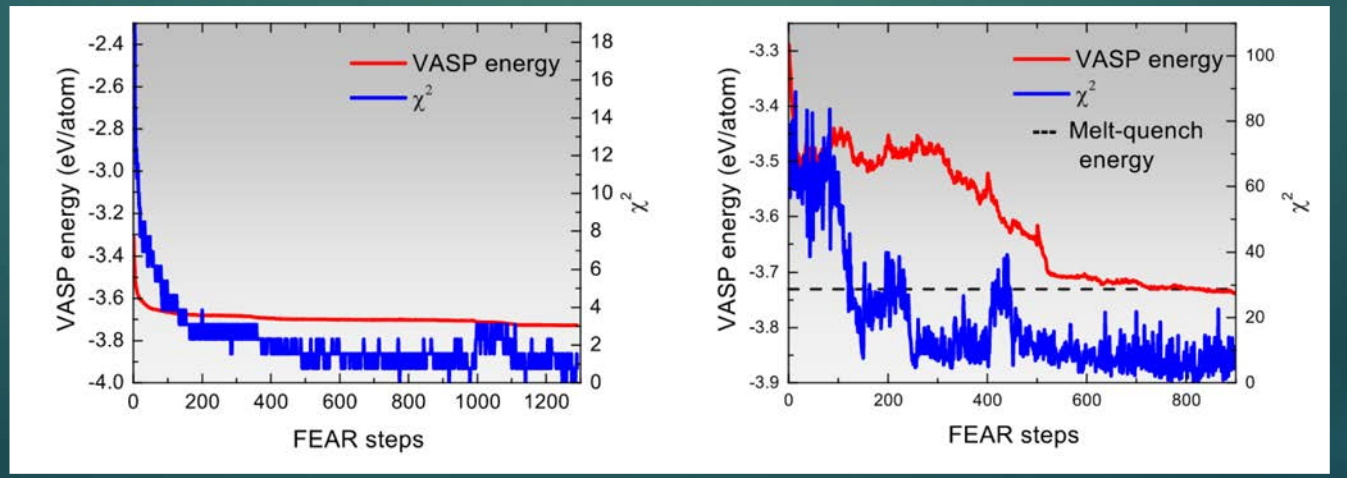
Electronic and Vibrational Properties



FEAR: Ag-doped chalcogenides, $[(GeSe_3)_{1-x}Ag_x$ x=0.05,0.077] data: Zeidler and Salmon (Bath) VASP, A. Pradel group (Montpellier)







Conclusion (FEAR)

- Efficient: Fewer calls to force code.

- Robust convergence: Really works [a-Si, a-C (0.95-3.5 gm/cc), GeSeAg materials]. We're trying a metallic glass, fiddling with EXAFS too -- $Pd_{40}Ni_{40}P_{20}$ (nothing to report yet!). Used empirical pots, tight-binding, SIESTA and VASP. Routinely produces (slightly) lower total energies than a reasonable melt quench.

- Easy: if you know RMC and VASP, this is essentially a shell script.

- It is GENERAL.