



Ohio University, at Athens.



DISORDER ON THE NANOSCALE: AB INITIO SIMULATIONS OF AMORPHOUS MATERIALS

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MOTIVATION

- To link experiment and theory convincingly and as directly as possible, via computer models.
- To design materials with sought after properties.

Personal opinion: neither experimentalists nor theorists succeed by themselves in our field – it's all about working together.

INTERLUDE: SCHRODINGER ON “APERIODIC CRYSTALS”

The non-physicist cannot be expected even to grasp—let alone to appreciate the relevance of—the difference in ‘statistical structure’ stated in terms so abstract as I have just used. To give the statement life and colour, let me anticipate, what will be explained in much more detail later, namely, that the most essential part of a living cell—the chromosome fibre—may suitably be called *an aperiodic crystal*. In physics we have dealt hitherto only with *periodic crystals*. To a humble physicist’s mind, these are very interesting and complicated objects; they constitute one of the most fascinating and complex material structures by which inanimate nature puzzles his wits. Yet, compared with the aperiodic crystal, they are rather plain and dull. The difference in structure is of the same kind as that between an ordinary wallpaper in which the same pattern is repeated again and again in regular periodicity and a masterpiece of embroidery, say a Raphael tapestry, which shows no dull repetition, but an elaborate, coherent, meaningful design traced by the great master.



E. S. “What is Life” (lectures in Dublin from 1942). p. 3 of the 1962 CUP reprint

PLAN OF LECTURE

- Computer simulations of materials.
- Applications: silver-doped chalcogenide materials, phase-change memory materials, some modeling of amorphous graphene and thermal imaging (night vision) materials.

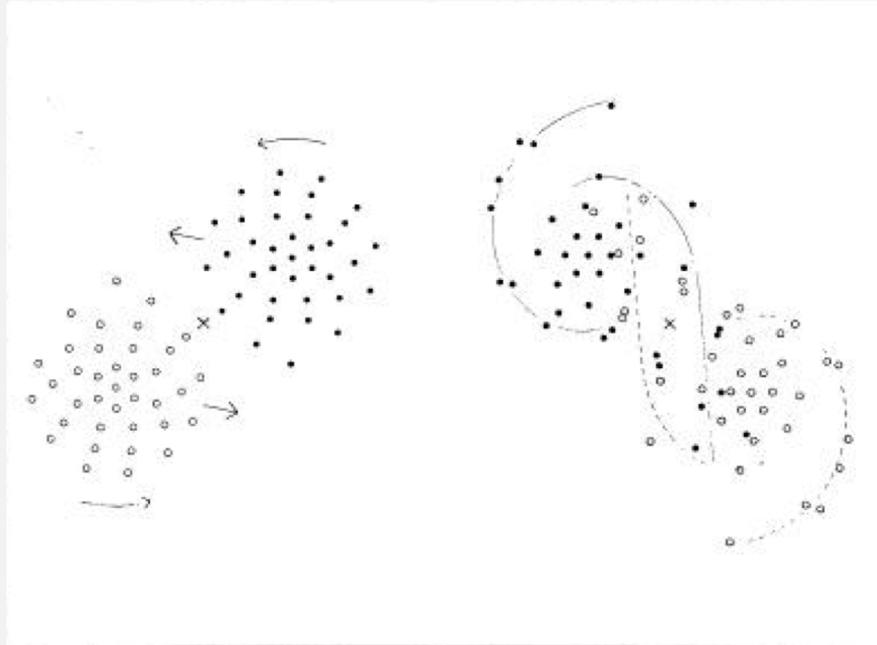


THE FIRST MD SIMULATION

Erik Holmberg (1908-2000), an astronomer at Uppsala, performed the first MD simulation to simulate galaxy collisions in 1941:

Starting with two “galaxies” (each with 37 “stars” represented by lamps), he simulated a galaxy-galaxy collision by attaching Se photocells to measure light intensity (which falls off like $1/r^2$, as does the gravitational force), evolved lamp coordinates according to equations of motion and optically inferred forces!

RESULTS: GALAXY MERGER



MD: CONDENSED MATTER (HEROIC AGE)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 55, NUMBER 7 1 OCTOBER 1971

Molecular Dynamics Study of Liquid Water*

ANEESUR RAHMAN

Argonne National Laboratory, Argonne, Illinois 60439

AND

FRANK H. STILLINGER

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974

(Received 6 May 1971)

A sample of water, consisting of 216 rigid molecules at mass density 1 gm/cm^3 , has been simulated by computer using the molecular dynamics technique. The system evolves in time by the laws of classical dynamics, subject to an effective pair potential that incorporates the principal structural effects of many-body interactions in real water. Both static structural properties and the kinetic behavior have been examined in considerable detail for a dynamics "run" at nominal temperature 34.3°C . In those few cases where direct comparisons with experiment can be made, agreement is moderately good; a simple energy rescaling of the potential (using the factor 1.06) however improves the closeness of agreement considerably. A sequence of stereoscopic pictures of the system's intermediate configurations reinforces conclusions inferred from the various "run" averages: (a) The liquid structure consists of a highly strained random hydrogen-bond network which bears little structural resemblance to known aqueous crystals; (b) the diffusion process proceeds continuously by cooperative interaction of neighbors, rather than through a sequence of discrete hops between positions of temporary residence. A preliminary assessment of temperature variations confirms the ability of this dynamical model to represent liquid water realistically.

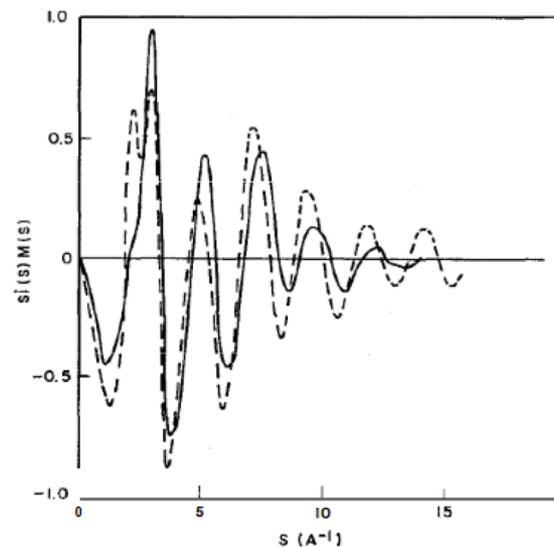


FIG. 7. Theoretical (solid line), and experimental (dotted line), x-ray scattering intensities for liquid water. The latter are taken from Narten, Ref. 29, and refer to 25°C .

THE ROAD TO ACCURATE INTERACTIONS

- Many papers appeared from the sixties to date using empirical potentials.
- Much has been gained: physical understanding and important lore (ensembles and many important technical details of simulation).
- Many current topics require better potentials. *Enter Quantum Mechanics*

“THE UNDERLYING PHYSICAL LAWS NECESSARY FOR THE MATHEMATICAL THEORY OF A LARGE PART OF PHYSICS AND THE WHOLE OF CHEMISTRY ARE THUS COMPLETELY KNOWN, AND THE DIFFICULTY IS ONLY THAT THE EXACT APPLICATION OF THESE LAWS LEADS TO EQUATIONS MUCH TOO COMPLICATED TO BE SOLUBLE. IT THEREFORE BECOMES DESIRABLE THAT APPROXIMATE PRACTICAL METHODS OF APPLYING QUANTUM MECHANICS SHOULD BE DEVELOPED, WHICH CAN LEAD TO AN EXPLANATION OF THE MAIN FEATURES OF COMPLEX ATOMIC SYSTEMS WITHOUT TOO MUCH COMPUTATION”. (P. A. M. DIRAC, 1929)

$$i\hbar \partial \psi / \partial t = H(t) \psi$$

$$\hat{H}(\{\vec{r}_i\}, \{\vec{R}_\nu\}, t) = \hat{T}_e + \hat{V}_{e-e} + \hat{T}_N + \hat{V}_{N-N} + \hat{V}_{e-N} + \hat{H}_{ext}$$

$$\hat{T}_e = \sum_{i=1}^{NZ_a} \frac{p_i^2}{2m}, \quad \hat{T}_N = \sum_{\nu=1}^N \frac{P_\nu^2}{2M} \quad \dots \text{kinetic energies}$$

$$\hat{V}_{e-e} = \frac{1}{2} \sum_{i \neq j}^{NZ_a} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \quad \hat{V}_{N-N} = \frac{1}{2} \sum_{\nu \neq \mu}^N \frac{Z_a^2 e^2}{|\vec{R}_\nu - \vec{R}_\mu|}, \quad \hat{V}_{e-N} = - \sum_{i=1}^{NZ_a} \sum_{\nu=1}^N \frac{Z_a e^2}{|\vec{r}_i - \vec{R}_\nu|}$$

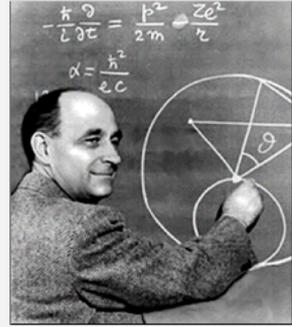
... potential energies

Kohn argues that it does not even make sense to compute the many-body wave function for more than ca. 100 electrons. The “exponential wall”.





THE INSIGHT



- **Thomas/Fermi:** Electron density determines energy: Ground state energy = $F[\rho]$ (input: electron density; output: energy of inhomogeneous electron gas)
- **Density functional theory** (Slater, Kohn, Hohenberg, Sham) Solve *single-particle* Schrödinger equation, potential is approximately known and depends upon the charge density. Mathematical structure of Hartree equations.

Dirac understood much of this: “This means that the whole state of the atom is completely determined by this electric density; it is not necessary to specify the individual three-dimensional wave functions that make up the total electric density. Thus one can deal with any number of electrons by working with just one matrix density function.” P.A. M. Dirac *Math. Proc. Cambridge Philos. Soc.* **26**, 376–385 (1930). Thanks to R. O. Jones *RMP* **87**, 897 (2015) for rediscovering this!



THE FORMULATION

- Current practical “first principles” materials theory is all based upon the **independent electron approximation and DFT in some form.**
- These methods **fail** for strongly-correlated systems (when interactions beat the delocalization from the kinetic energy).
Examples: 3d, 4d transition metals, Ce, Sm, Eu etc. Need techniques to handle correlation.

DFT IS ACCURATE AND USEFUL

- Cohesive energies tend to be a bit high (LDA overbinds) typically a 10% effect.
- Can extend to spin polarized case: “Local Spin Density Approximation” (LSDA)
- For improvements in energetics, use “generalized gradient corrections”. Some of the best are somewhat empirical.
- Modern “hybrid functionals” can help to estimate optical gaps, a weakness of DFT.

AB INITIO MD IN A SLIDE

$$\left\{ \frac{-\hbar^2}{2m} \nabla^2 + V_{ext}(x) + V_{Hartree}(\rho[x]) + V_{xc}(\rho[x]) \right\} \psi_i = \lambda \psi_i$$

Adopt pseudopotentials, pick a representation:

$$|\psi_i\rangle = \sum_{\vec{G} \neq 0} a_G^i |\vec{G}\rangle$$

PLANE WAVES

$$|\psi_i\rangle = \sum_{\mu} a_{\mu}^i |\mu\rangle$$

LOCAL ORBITALS

Diagonalize (obtain $\{\psi\}$), compute the density matrix $\rho_{\mu\nu}$. Then:

$$E_{bs} = \text{Tr}(\rho H)$$

$$n(\vec{R}) = \langle \vec{R} | \hat{\rho} | \vec{R} \rangle$$

$$F_{bs}^{\alpha} = -\nabla_{\alpha} E_{bs}$$

The quantity F_{bs} is the difficult, non-local part of the interatomic force

AB INITIO CODES AVAILABLE

- These days, you download or buy them. They are now complex and mature.
- Codes:
 - VASP “Vienna ab initio simulation package” plane wave/\$\$
 - SIESTA (local orbital DFT), freely available
 - FIREBALL (local orbital DFT)
 - ABINIT plane wave DFT, freely available
 - (many others)

TECHNICAL DETAILS

- **Local orbitals:** basis is incomplete, *be careful to check that you have enough orbitals*, but can be very fast. Born-Oppenheimer dynamics, usually using full diagonalization.
- **Plane waves:** memory hog, but reliable basis.
- Both are powerful with advantages and problems.

ONCE WE HAVE THE TOTAL ENERGY AND FORCE....

- MD simulation: $\mathbf{F}=\mathbf{ma}$ – it is easy to numerically integrate the equations of motion for the ions, generate atomic trajectories.
- Monte Carlo: Move atoms according to random process, find suitable conformations (energy minima).
- Other tools of classical simulation available.

WHAT CAN WE TACKLE? AN EXAMPLE FOR SCHRODINGER

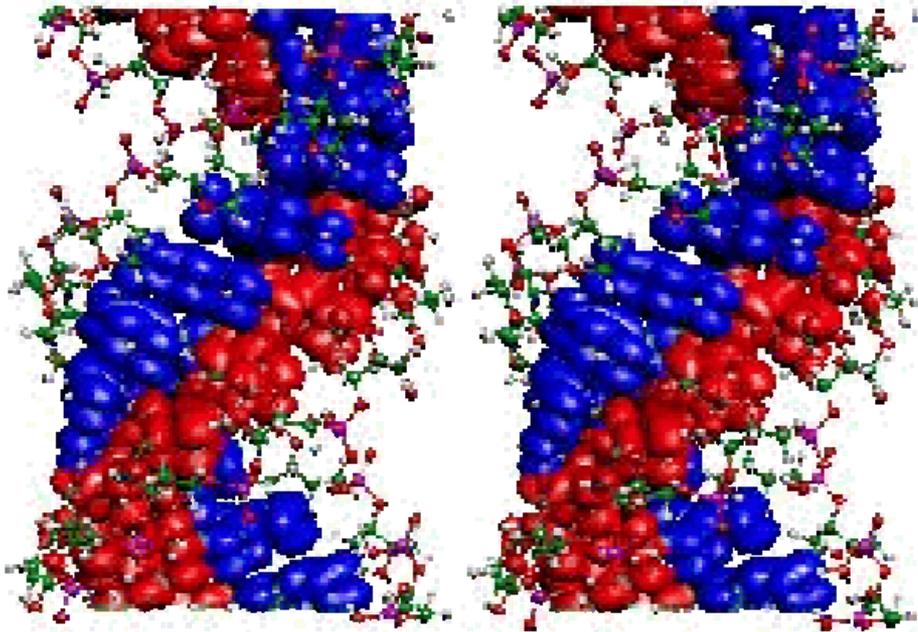


FIG. 2: (Color stereogram) Surfaces of constant density ($1.5 \cdot 10^5 e^-/\text{\AA}^3$) for the states corresponding to the lowest unoccupied band (red), and highest occupied band (blue) of the ordered pGpC structure. The graphs were produced with Molekel [64].

There is wide interest in DNA as a conductor. This is a simulation showing those states which could be involved in conduction. ~ 1000 atoms. Local basis order N approach used.

Artacho *et al* SIESTA

DIRECT SIMULATION OF A GLASS

Quench from Melt:

Molecular dynamics (simulated atomic dynamics)

Traditional: melt, equilibrate liquid, quench, anneal.

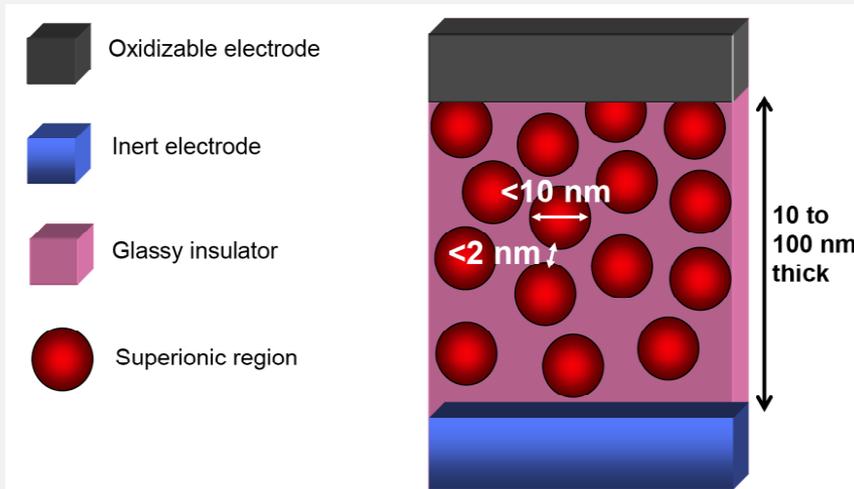
Not very realistic – time and length scales very different from experiment, but it works for chemically ordered glass forming materials.



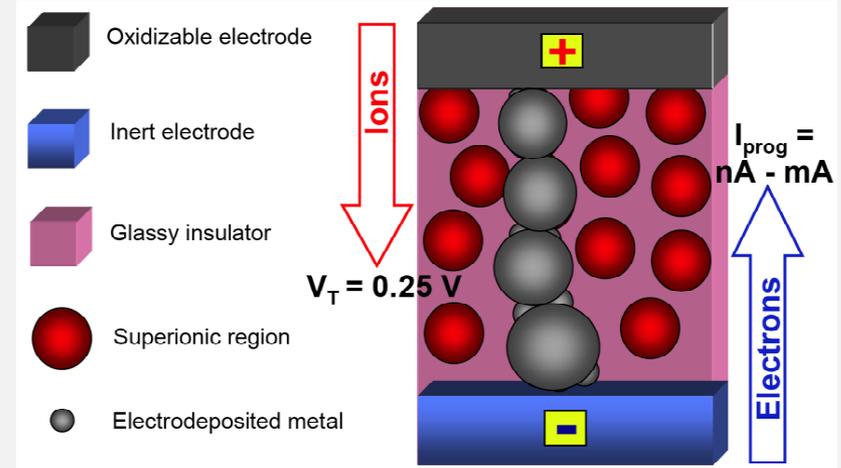
Glass a' la Computer

1. Build a cell (with ~ 200 atoms) and periodic boundary conditions with the atoms you want.
2. Cook/anneal -- form an equilibrated liquid a bit above T_m .
3. Simulate quenching it -- remove kinetic energy "dissipative dynamics" until motion is arrested.
This is the model of the glass!
4. This works surprisingly well for good glass formers, and quite *badly* for non-glasses (eg a-Si, etc)

PROGRAMMABLE METALLIZATION CELL OR “CONDUCTING BRIDGE” MEMORY



High resistance state (Ag exists in the form of ions).



The cell is biased to grow metallic Ag filaments between cathode (bottom electrode) and oxidizable (Ag) anode (top). The resistance is nearly zero, because of the metallic filament.

Illustrations courtesy M. Mitkova, Boise State
 M. N. Kozicki, Arizona State University

THE BASIC IDEA

- Silver ions in S or Se glasses move quickly through the glass.
- The cell has two states, one with nearly zero (electrical) resistance and one with nearly infinite resistance. The “0” and “1” states....
- It is easy to change from one state to the other.
- Switching time is ~ 10 nanoseconds (0.00000001 seconds!).
- Devices have been grown on ~ 10 nanometers (0.00000001 m) scale.

OUR PROBLEM: WHAT IS HAPPENING AT THE ATOMIC LEVEL?

- We make the first realistic models of the silver-doped glasses.
- We study the dynamics of the silver in detail.
- We discover atomic-level processes hard/impossible to infer from experiment.

APPROACH

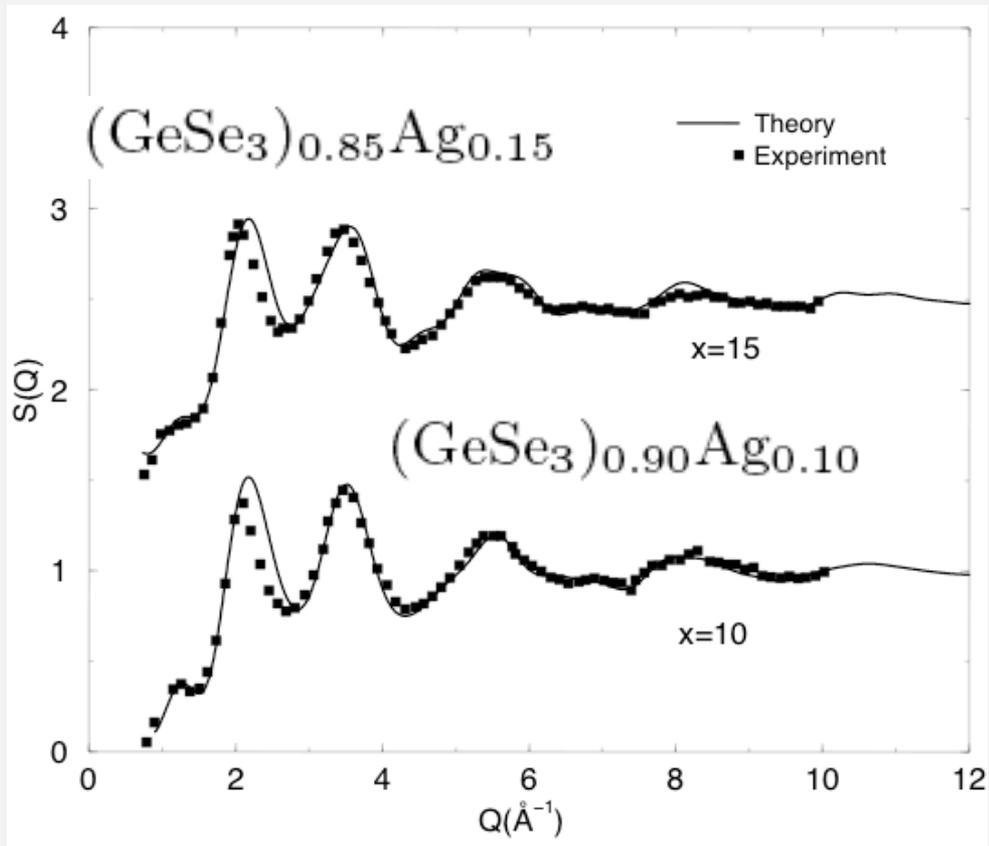
- Use Fireball local orbital MD, subsequently with plane wave DFT.
- Cook and quench in conventional way, forming models of $a\text{-(GeSe}_3\text{)}_9\text{Ag}_1$ and $a\text{-(GeSe}_3\text{)}_{.85}\text{Ag}_{.15}$

D. N. Tafen, M. Mitkova and DAD Phys. Rev. B **72** 054206 (2005),

F. Inam & DAD Phys. Rev. B **79** 100201R (2009).

Prasai and DAD Phys Rev B **83** 094202 (2011).

GESE:AG MODELS (240 ATOMS)



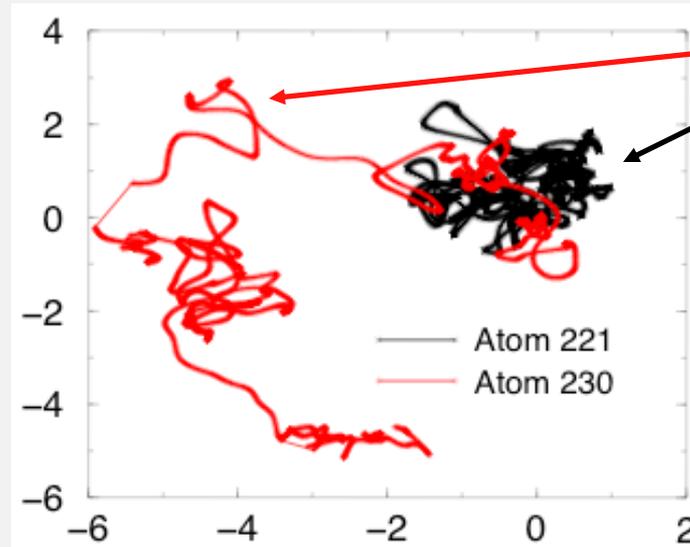
Static structure factors.

Experiment:

A. Piarristeguy, J. Non-Cryst. Sol. **332**, 1 (2003).

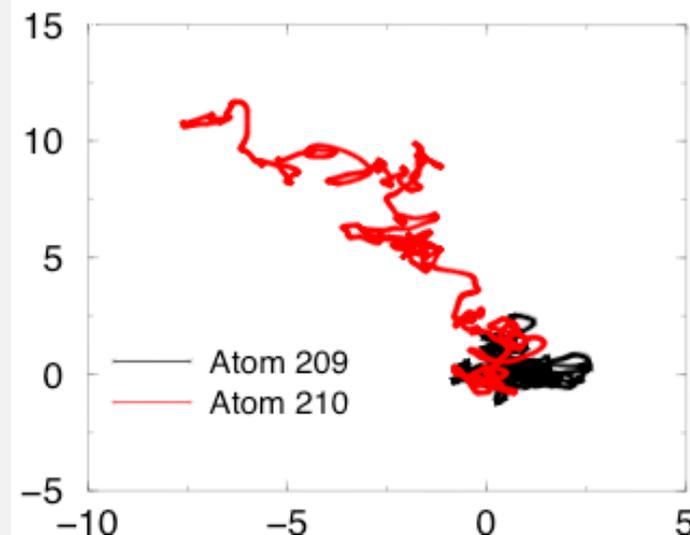
AG HOPPING FROM THERMAL MD

Thermal MD, constant T, 20 ps, *ab initio* interactions, 1000K.



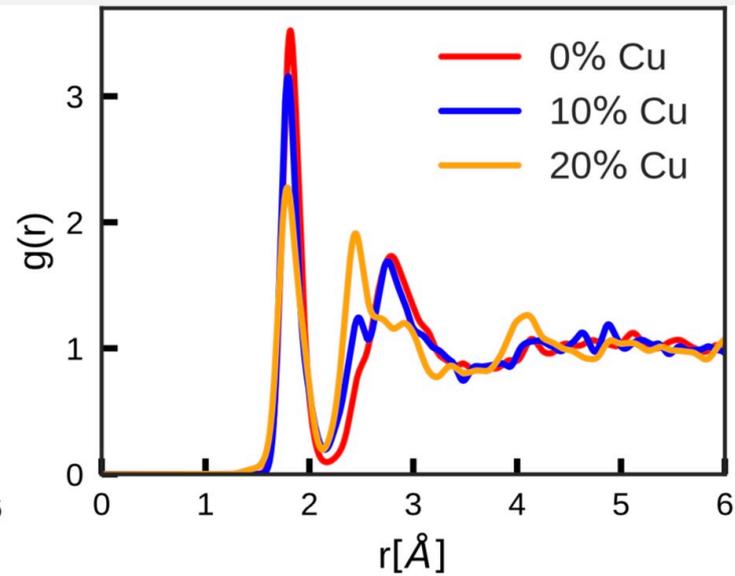
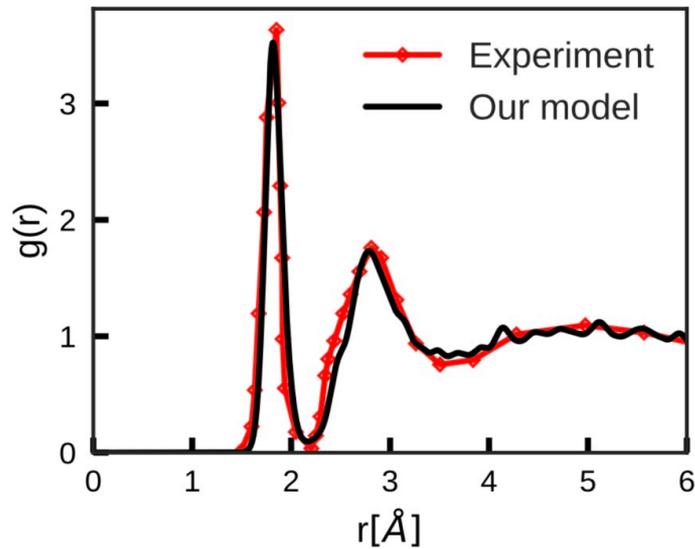
Most diffusive Ag atom
Least diffusive Ag atom

$(\text{GeSe}_3)_{0.90}\text{Ag}_{0.10}$



$(\text{GeSe}_3)_{0.85}\text{Ag}_{0.15}$

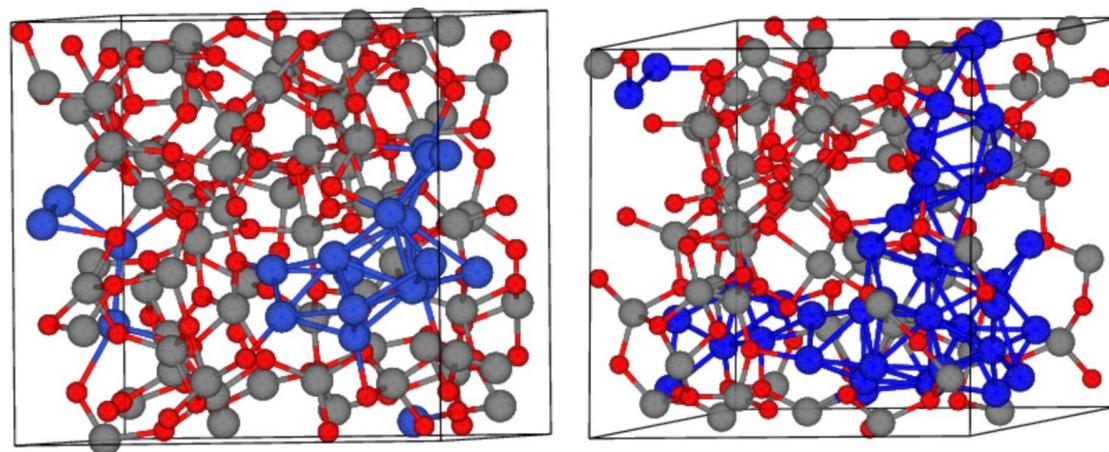
ANOTHER CBRAM SYSTEM: $\text{Al}_2\text{O}_3 + \text{Cu}$ (~ 200 ATOMS, VASP)



Left: alumina: model and experiment¹ Right: $g(r)$ for 0, 10%, 20% Cu

¹P. Lamparter, R. Kneip, Physica B 234-6 405 (1997).

CU CLUSTERS IN Al_2O_3



Space-filling Cu cluster
for 20% broken for 10%.

**Cu clustering in
Alumina, not in chalcs.**

FIG. 2. Cu atoms (blue), O (red) and Al (grey) in $(\alpha-Al_2O_3)_{.9}Cu_{.1}$ (top) and $(\alpha-Al_2O_3)_{.8}Cu_{.2}$ (bottom). Note that the Cu clusters in the oxide matrix. Periodic boundary conditions are employed throughout.

COMPUTATION OF CONDUCTION PATHS

- For Cu-doped alumina and a Ag-doped GeSe_3 , we compute the path of the conduction from the Kubo-Greenwood formula. Details next lecture (if time allows!)

BADER PROJECTION OF CONDUCTION ONTO ATOMIC SITES

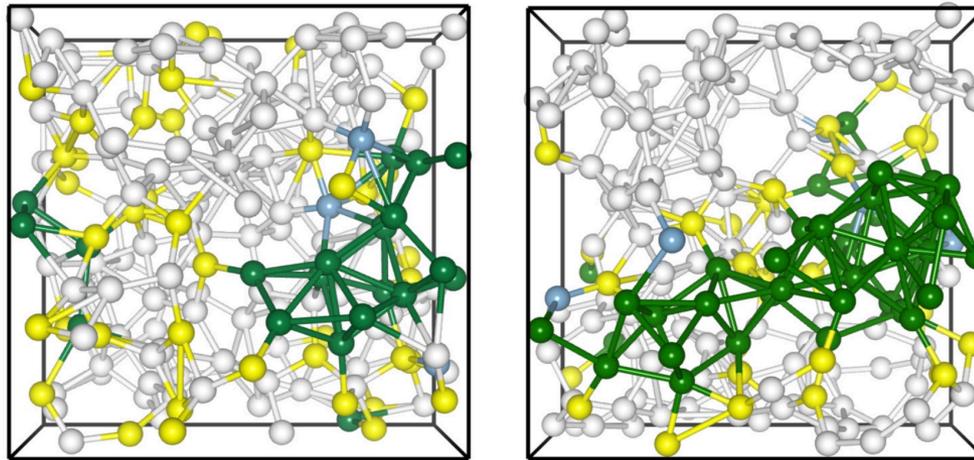


FIG. 4. Bader projection of SPC $\zeta(\mathbf{x})$ of oxides. Left: $\text{Al}_2\text{O}_3:\text{Cu}, 10\%$. Right: $\text{Al}_2\text{O}_3:\text{Cu}, 20\%$. The atoms with color represent the atoms with 95% of SPC[20]. Color nomenclature is green:Cu, yellow:O, blue:Al

INFERENCES

- There are *trapping defects*. Trap model is successful with relaxation data.
- There is free volume (reduced local density) for rapid diffusers.
- Some goals: provide the microscopic parameters for the trapping model, elucidate the microscopic (and dynamic) nature of the traps.
- Direct and realistic simulation of atomic diffusion: accessible with MD time scales (picoseconds).
- Cu (and Ag) cluster in alumina host, do *not* from the chalcogenide host. We compute/compare the conduction pathway.

And now
for something
completely different...



PHASE CHANGE MATERIALS

- GeSbTe alloys are famous “phase change” materials: because of controlled rapid switching between amorphous and crystalline phases, of interest since Ovshinsky in the 1960s.
- Now the basis of commercial FLASH memory devices.
- *What can we say about this?*

THE CHALLENGE OF CRYSTALLIZATION

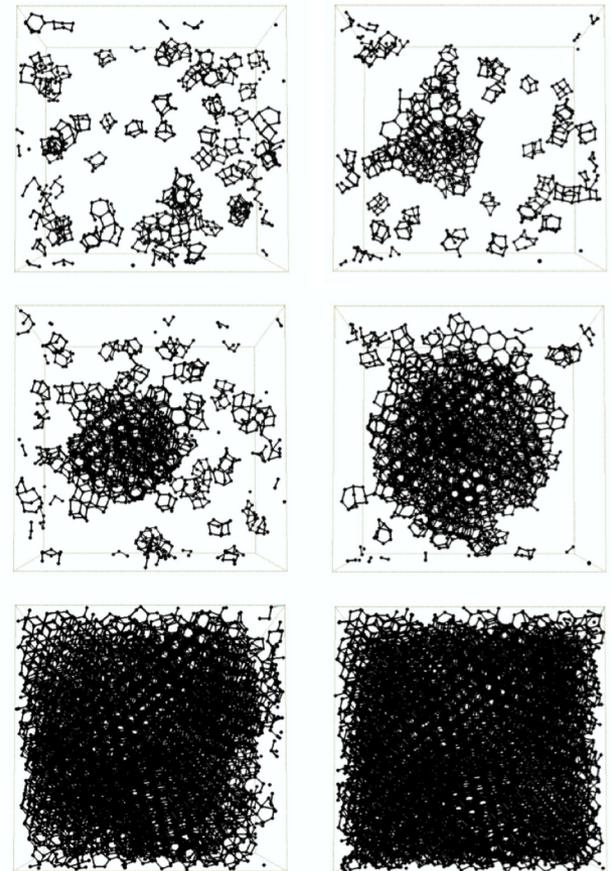
- The intrinsic time scale of these simulations is set by the MD time step: about 10^{-15} sec.
- Crystallization is devilishly hard – requiring typically *nanoseconds*¹, suggesting the need for millions of steps.

¹ P. Beaucage and N. Mousseau, PRB 71 094102 (2005)

CRYSTALLIZATION OF SI (FROM LIQUID)

“Evolution of nucleation and crystallization during the liquid-crystal phase transition of SW Si at 1250K and 2.32 g/cm³. The configurations show atoms that belong only to crystalline structures at 0, 0.58, 0.86, 1.15, 1.44, and 1.73 ns”

“Thus, the critical cluster size should be around 175 atoms for Si at 1250 K, in agreement with the estimate of Uttormark *et al.*”



NOW IS THE WINTER OF OUR DISCONTENT...

- Chemistry of GST is more complex than elemental silicon.
- There are no credible empirical interatomic potentials.
- Beware size artifacts: these simulations use periodic boundary conditions, and calculations have shown that small cells crystallize faster.
- It would seem that we are in the “large, long-time, chemically complex” regime.



THE CAMBRIDGE CRYSTALLIZATION

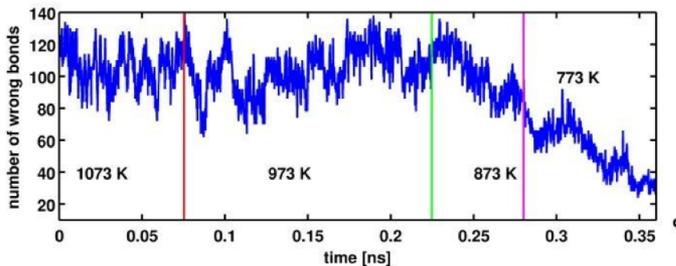
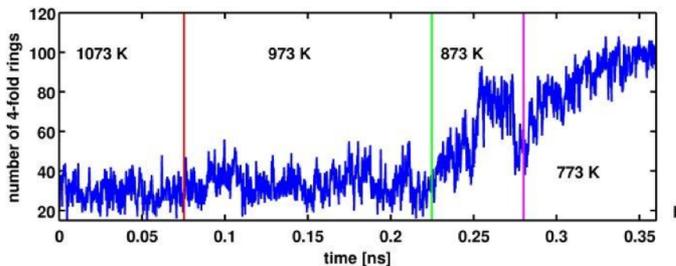
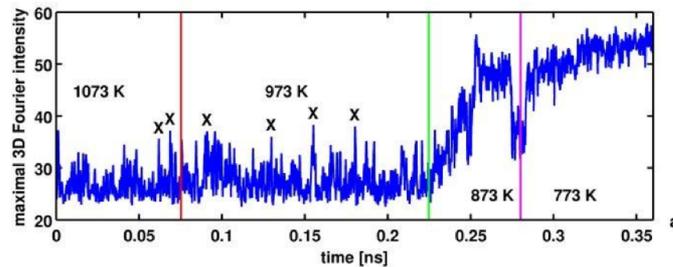
Microscopic origin of the fast crystallization ability of Ge–Sb–Te phase-change memory materials, J. Hegedüs & S. R. Elliott, Nat. Mats. (2008):

Here, we describe for the first time how the entire write/erase cycle for the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ composition can be reproduced using ab initio molecular-dynamics simulations. Deep insight is gained into the phase-change process; very high densities of connected square rings, characteristic of the metastable rocksalt structure, form during melt cooling and are also quenched into the amorphous phase. Their presence strongly facilitates the homogeneous crystal nucleation of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. As this simulation procedure is general, the microscopic insight provided on crystal nucleation should open up new ways to develop superior phase-change memory materials, for example, faster nucleation, different compositions, doping levels and so on.

HEGEDUS AND ELLIOTT RECIPE

- VASP *ab initio* MD code
- 63-90 atom models for GST-225, 124 (now much improved much improved and extended, esp. by Wuttig, Jones, Akola *et al.*)
- Cubic cells + periodic-boundary conditions
- Constant volume
- Quenching from melt + heating amorphous

E&H: THE EMERGENCE OF ORDER AMORPHOUS → CRYSTALLINE



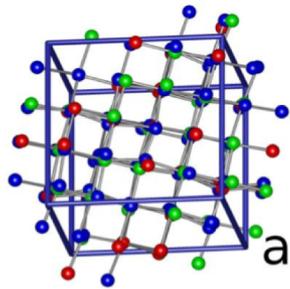
Long range order: Maximum
3D Fourier intensity.

Rocksalt building blocks

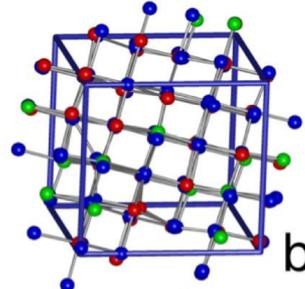
Wrong bonds

Simulated Crystallization

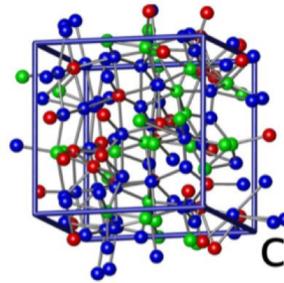
a) GST-225
(slow liquid-quenched)



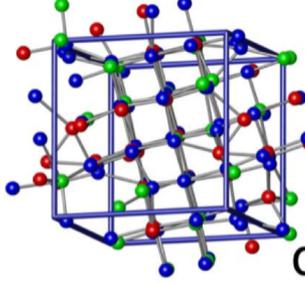
b) GST-124
(slow liquid-quenched)



c) a-GST-225
(fast liquid-quenched)

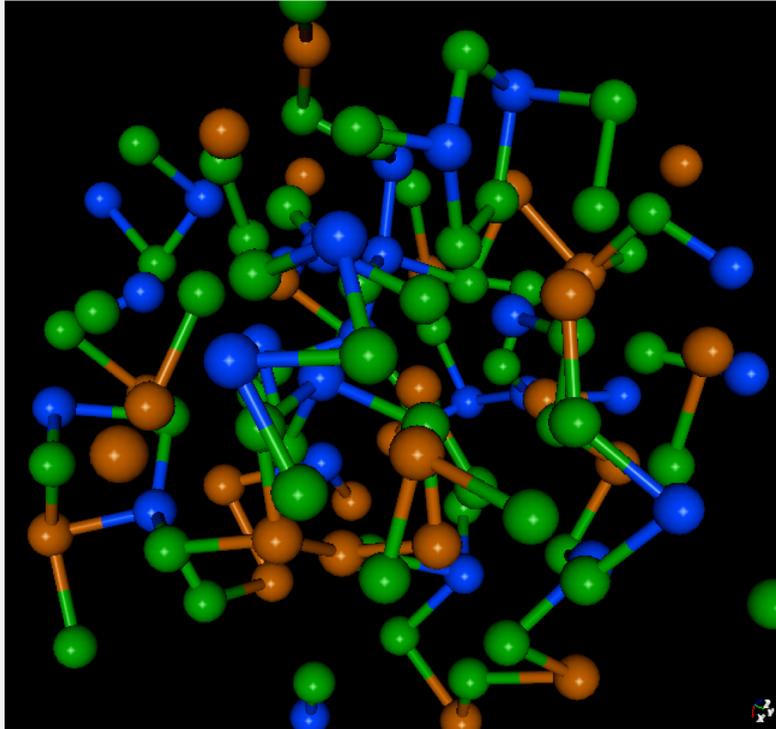


d) GST-225
(amorphous-annealed)



Ge= green; Sb= red; Te= blue

A-GST(225) \rightarrow C-GST(225) [THE MOVIE]

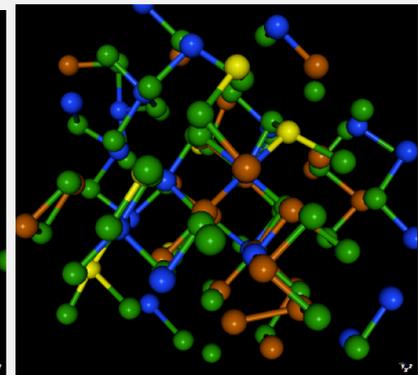
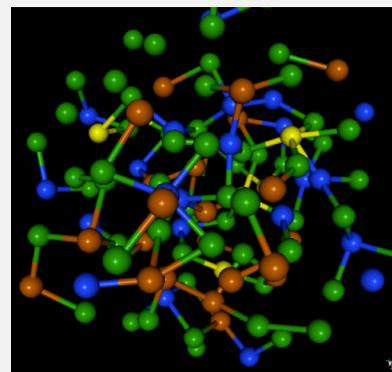


Ge: blue, Sb: orange, Te: green

The heart of the problem is DYNAMICS.
650K anneal: 340 ps depicted here.

A video showing the process of
crystallization in 225.

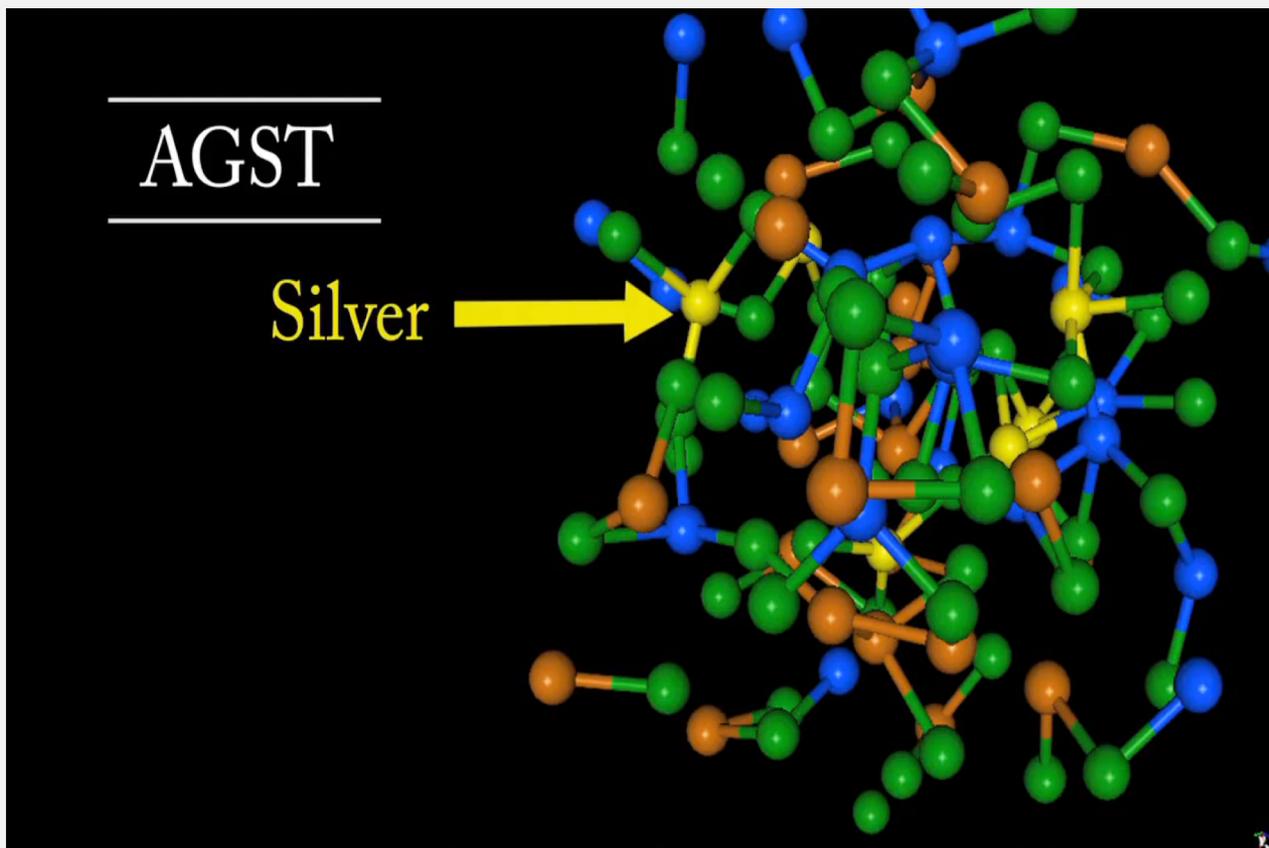
Snapshots near the beginning and near the end



H&E: SUMMARY

- A direct MD simulation of important physical process.
- The N.M. paper opened up the field. Many interesting subsequent studies along these lines.
- Implications beyond immediate interests – a realistic simulation of nucleation, the first *ab initio* simulation of crystallization.
- Now verified and improved by several groups!

225+AG: DYNAMICS



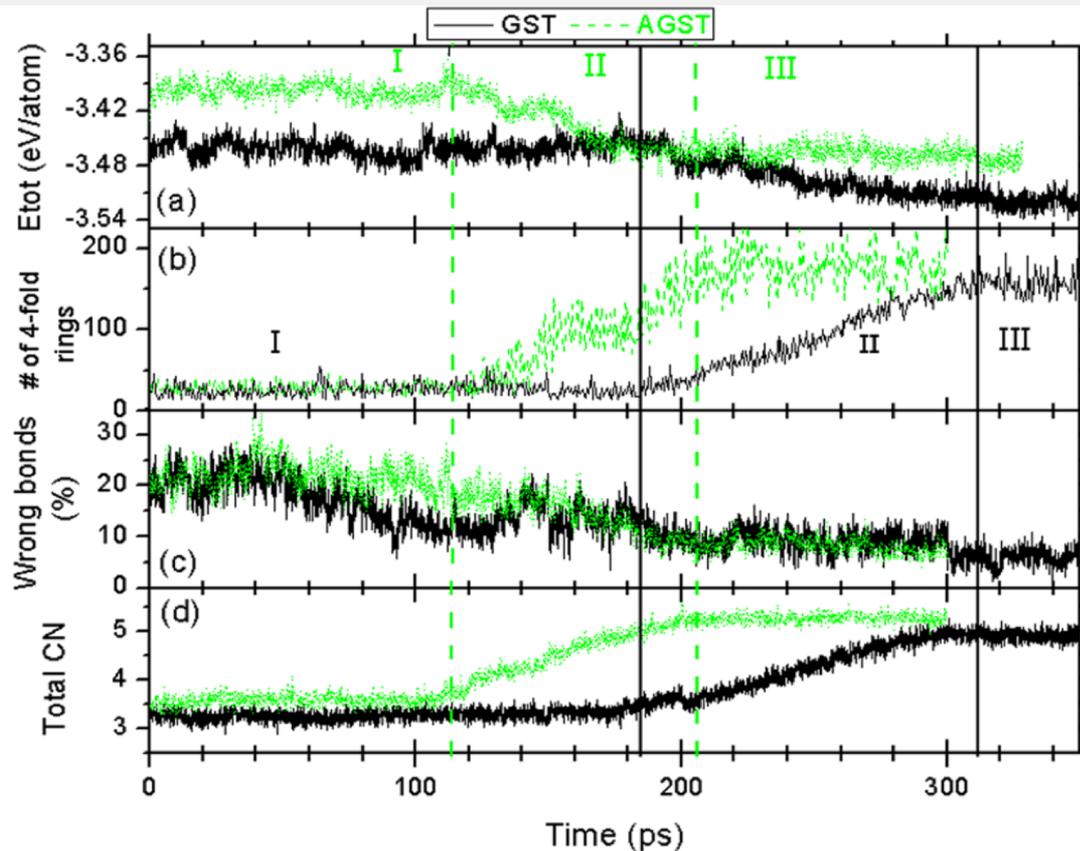
CRYSTALLIZATION COMPARED

| ← Crystallize → |

| ← Incubation → |

| ← Stabilization → |

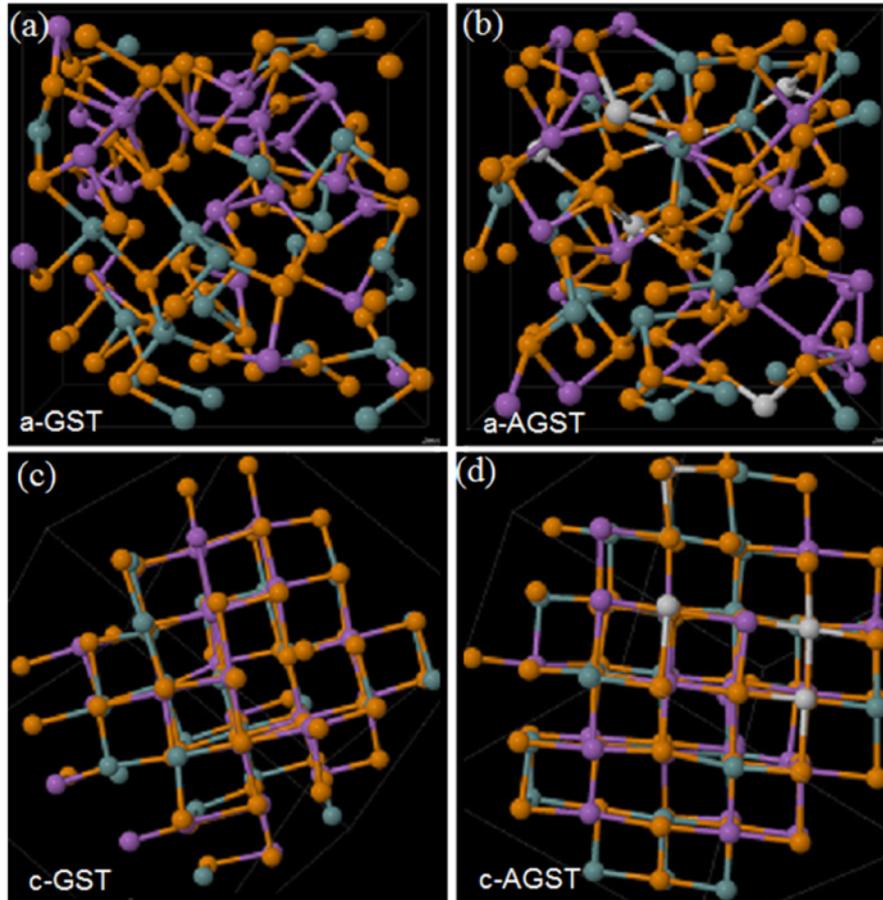
Nomenclature of H&E



WHAT DOES IT MEAN?

- Ag enters matrix substitutionally!
- Three repetitions suggest somewhat faster crystallization for Ag-doped GST (~ 200 ps) vs ~ 320 ps.
- The conductivity contrast is maintained, appears to be thermally stable.

BEFORE AND AFTER: RELAXED



Color definitions: orange-Te, green-Ge, purple-Sb, and gray-Ag.

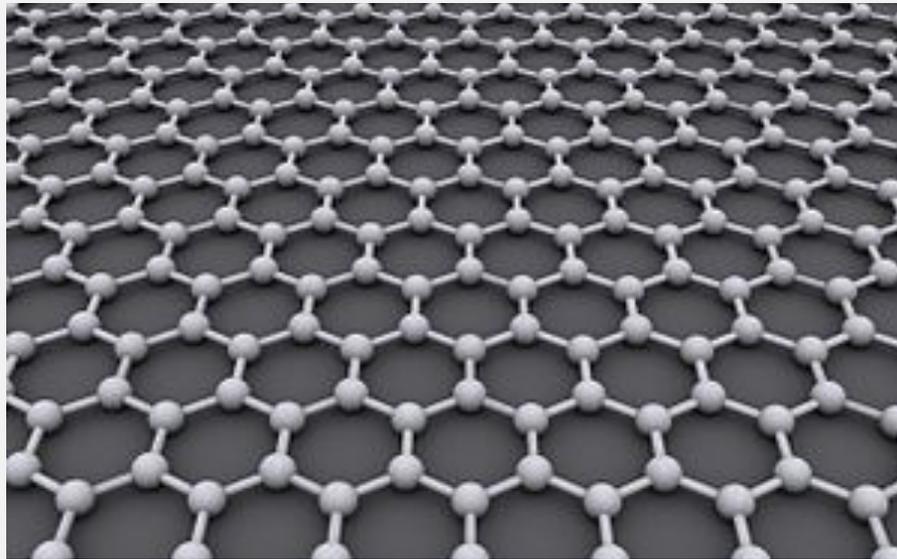
And now
for something
completely different...



AMORPHOUS GRAPHENE

- Graphene is a 2D network; perfect honeycomb lattice,
- Ideal semimetal,
- Carriers have astronomical mobilities, all kinds of devices are imagined,
- So what about disorder, in this material?

CRYSTALLINE GRAPHENE



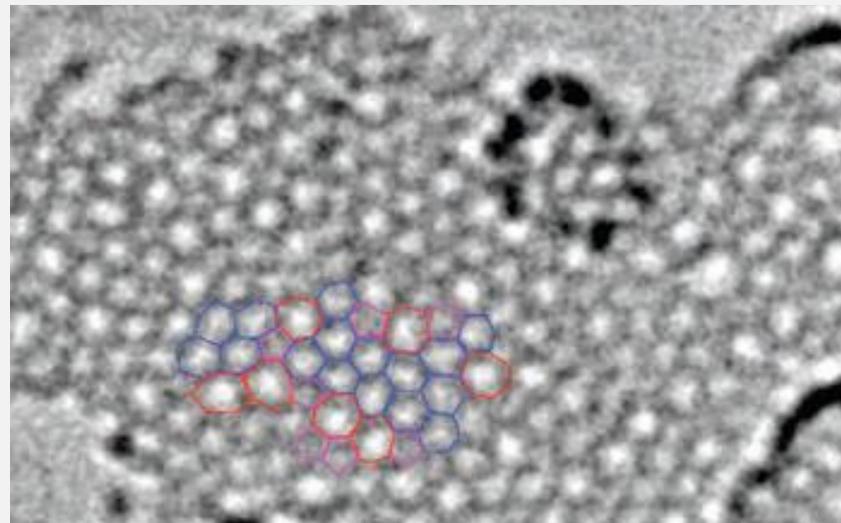
So what about amorphous graphene!?

Evidently, a “good” CRN model of a-G should maintain 3-coordination: honeycomb peppered with 5/7-member rings

AMORPHOUS GRAPHENE EXISTS



Giants Causeway
(N. Ireland)



Rings

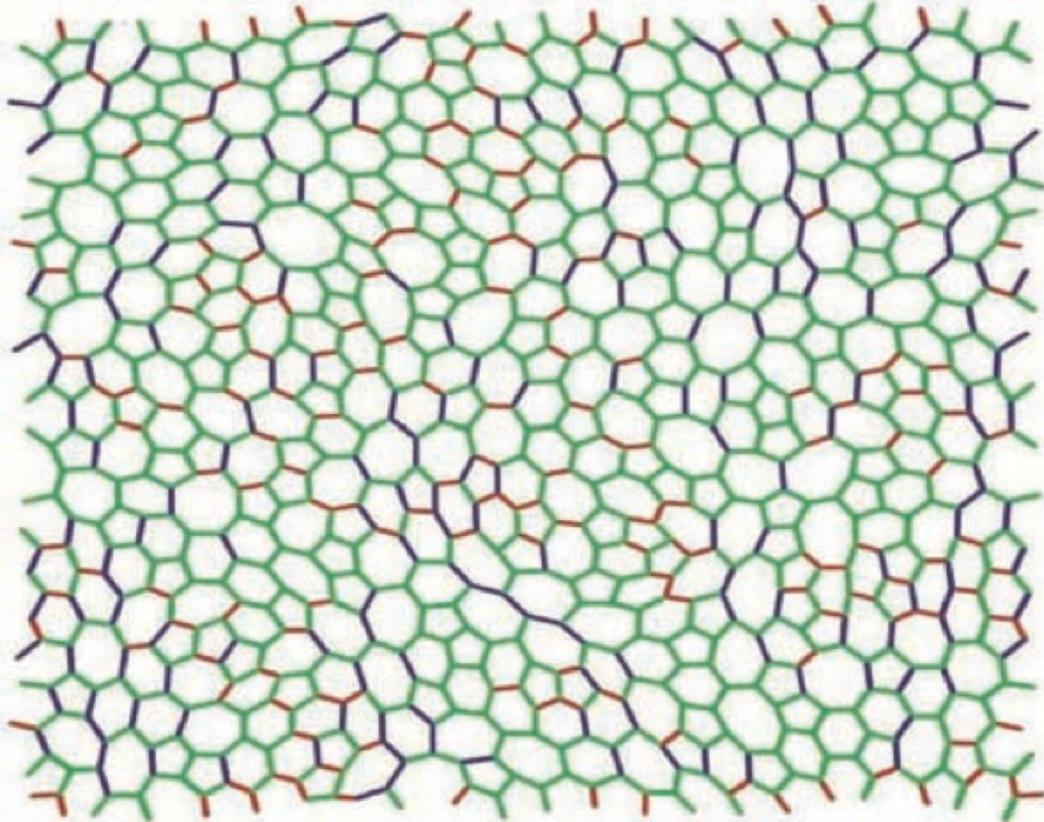
Five – purple

Six- blue

Seven-red

ex- Geim et al.

HE/THORPE MODEL (1985)



- 800 atoms
- periodic BC
- Three-fold
- 34% pentagons
- 38% hexagons
- 24% heptagons
- 5% octagons

+ subsequent work by DAD, Mark Wilson, M. F. Thorpe

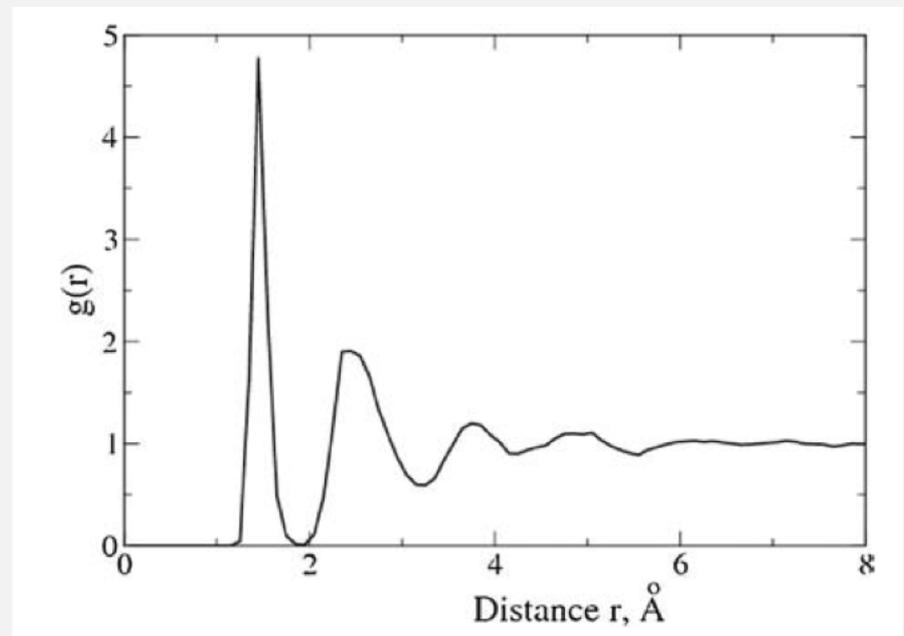
SOME QUESTIONS ABOUT A-G

- What are the energetics of such a network?
- Is the electronic structure near the Fermi level basically preserved as in a-Si?
- How would odd-member rings affect transport?
- Does the stuff remain flat?

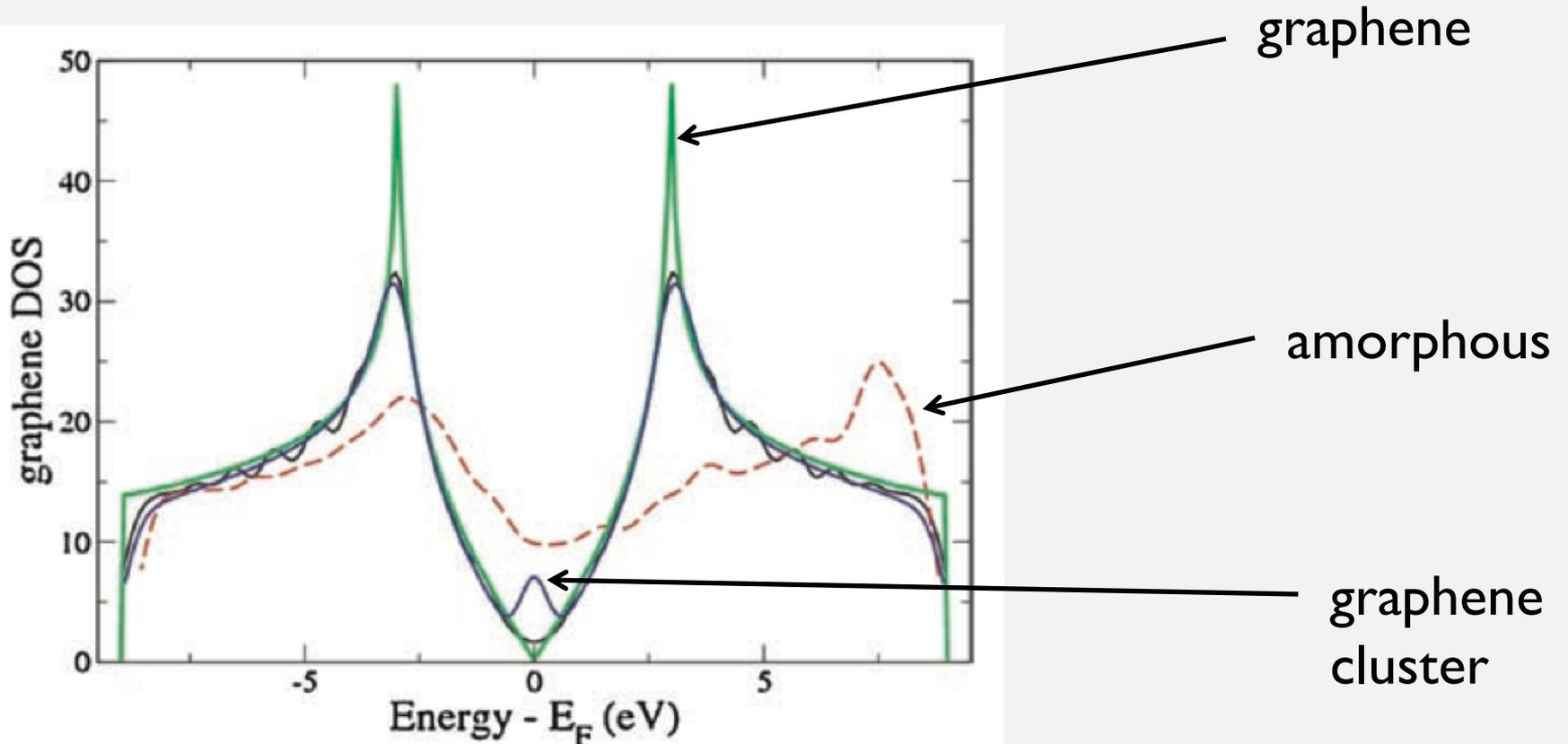
A FEW DETAILS

- Model was made with WWW bond switching
- Since mean ring size is 6, Euler's theorem implies it may exist as flat 2D structure with some local distortions

- Sensible $g(r)$



ELECTRONIC DOS (Π, Π^* BANDS)



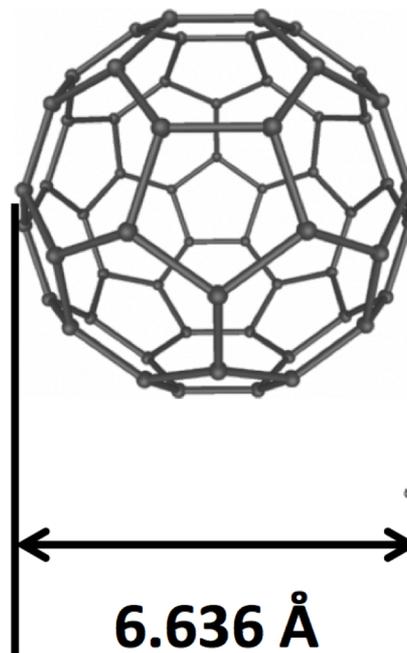
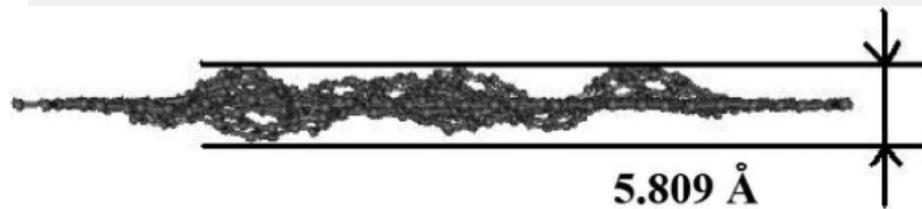
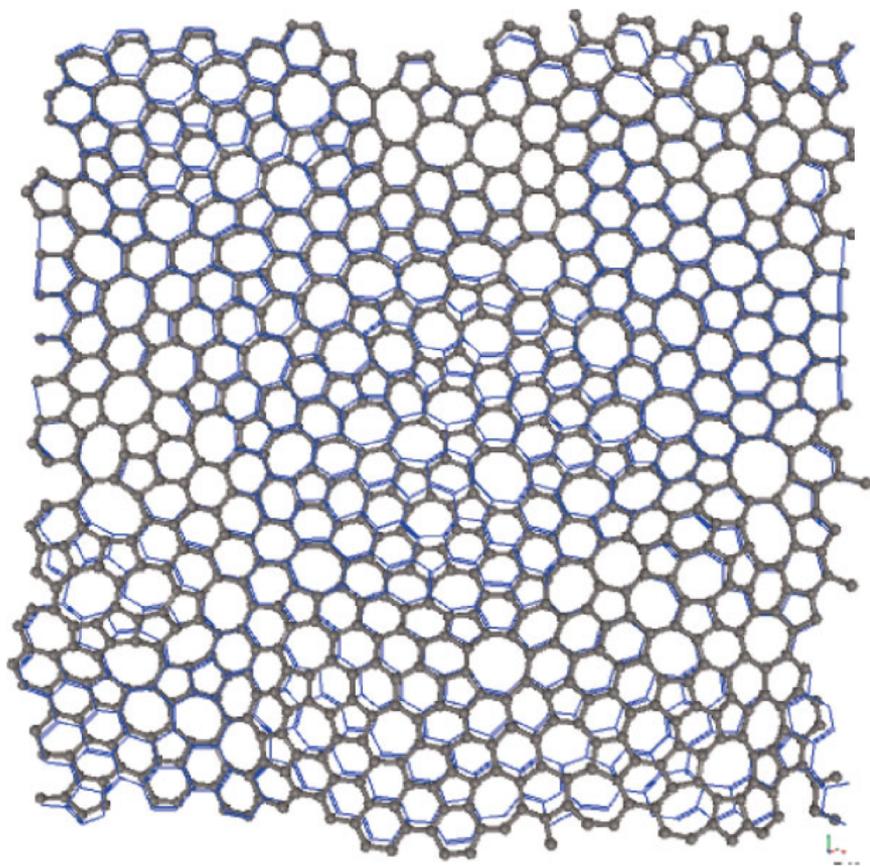
ELECTRONIC STRUCTURE

- Semi-metallic character completely ruined.
- A very different story than say, a-Si, where similar local connectivity preserves the gap.
- Somewhat surprising – “ring disorder” has a drastic effect on the DOS.
- Ring disorder diabolical for applications.

ENERGETICS AND STABILITY

- Relax coordinates in 2-D with ab initio code (SIESTA), no topological change: already a nice local energy minimum.
- Tiny (~ 0.01 eV/atom) relaxation energy.
- BUT relaxation with any breaking of planar symmetry leads to puckering: **pentagons induce curvature.**

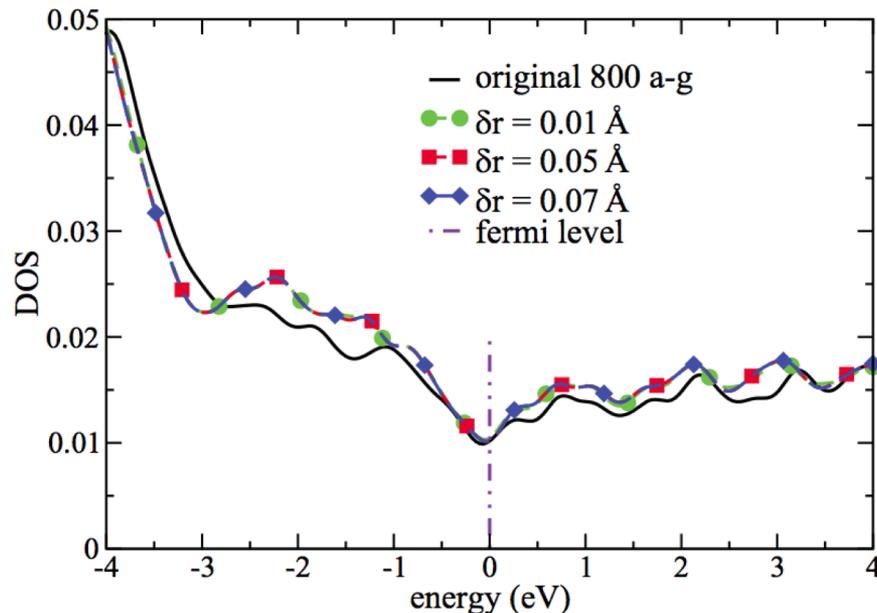
PUCKERING



Top view: grey puckerred; blue flat

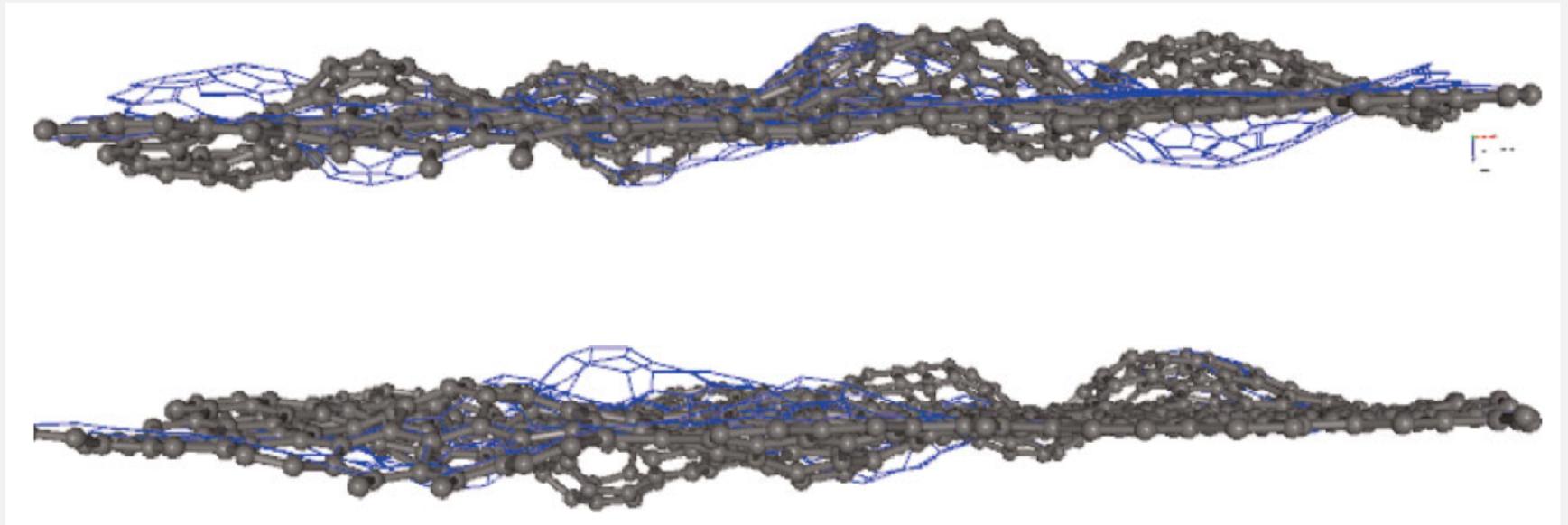
CONSEQUENCES OF PUCKERING

- Relaxation energy: ~ 0.1 eV/atom (fairly independent of ring statistics etc)
- Pentagonal rings induce undulations in the sheet (~ 6 Å top to bottom; much like Buckyballs (BB diameter ~ 6.6 Å))
- Alas, puckering does not cure the evils of the DOS



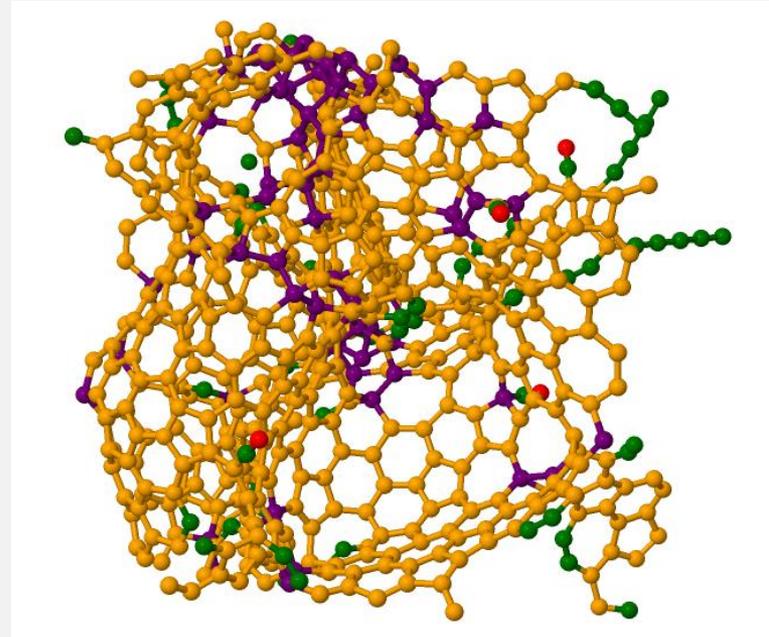
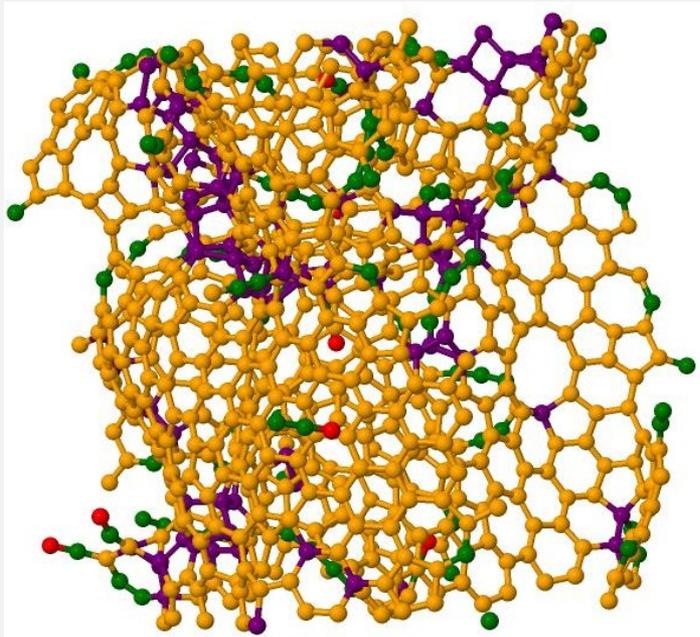
PLANAR SYMMETRY BREAKING

- Vary initial conditions, then relax -- obtain different minima. For example:



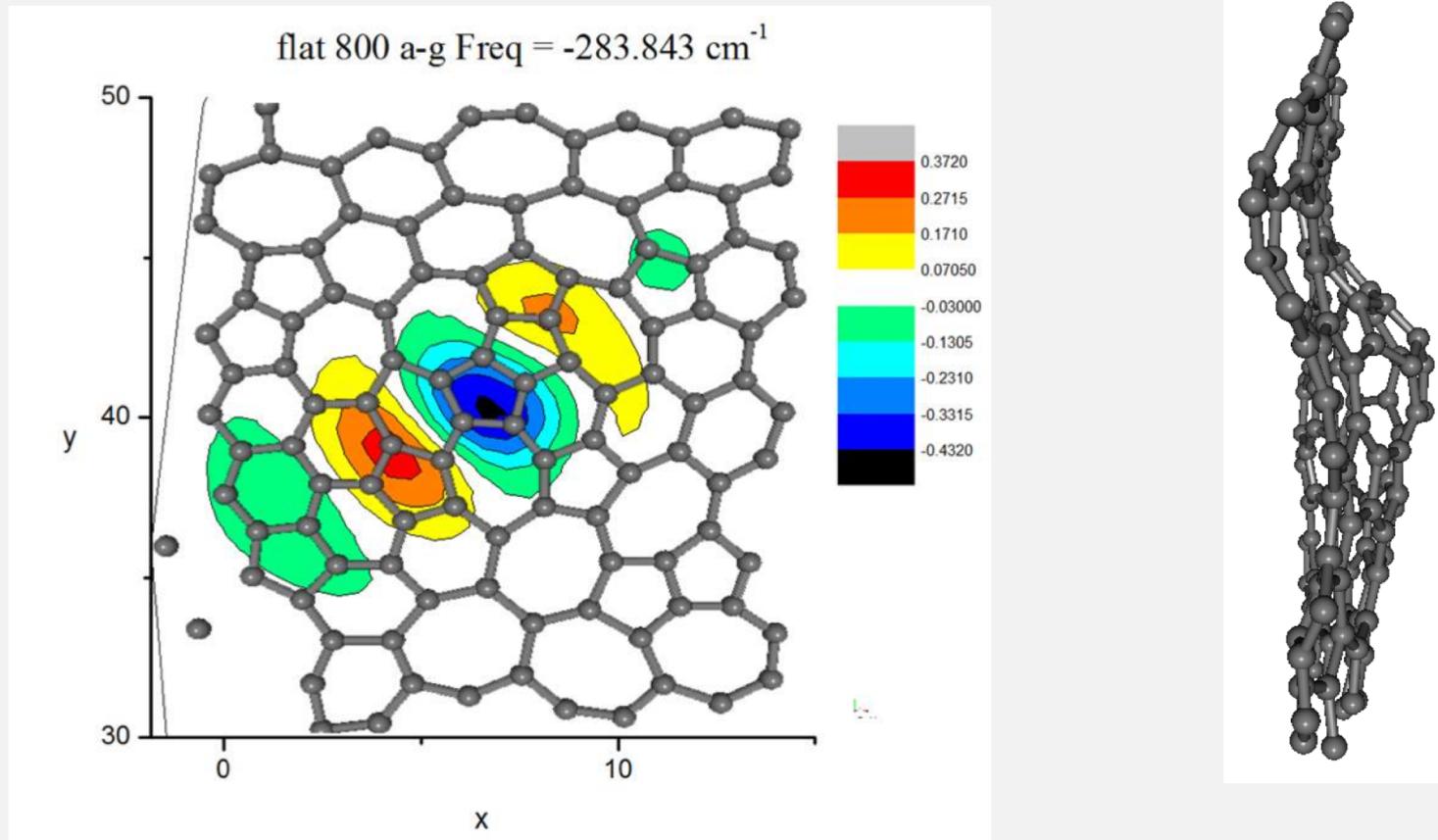
LOW DENSITY (0.95 GM/CC) FEAR CARBON (800-, 648- ATOM MODELS)

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



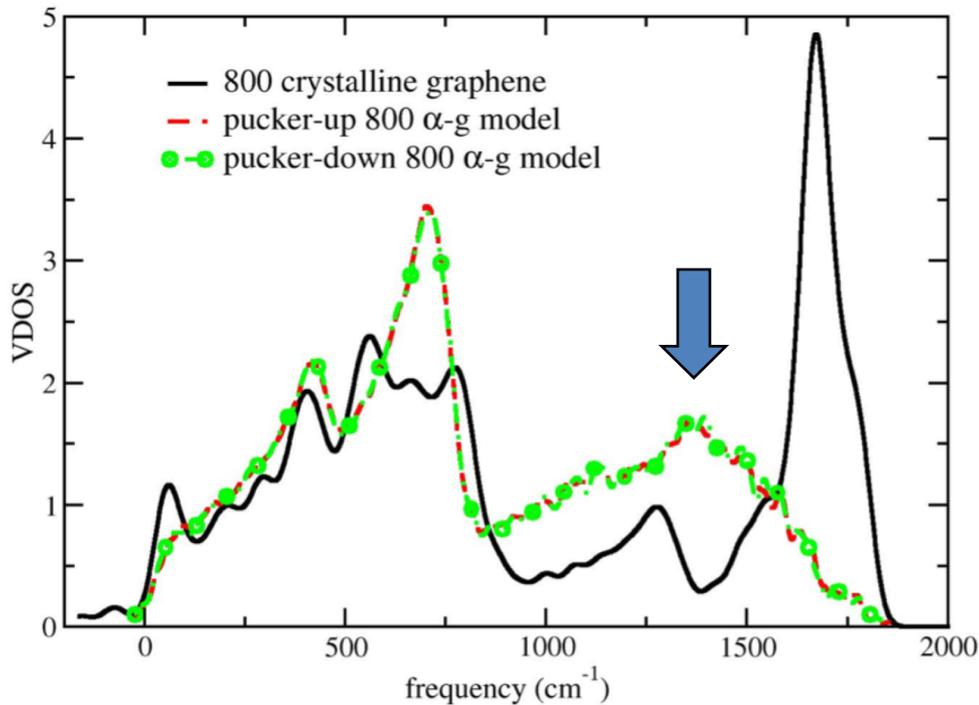
3D phases of a-G from *ab initio* inference “FEAR”:
Carbon **131** 168 (2018), PCCP **20** 19546 (2018)

VIBRATIONS: SOME $\Omega^2 < 0$ FOR FLAT CASE



Left: Imaginary-frequency mode loc. on pentagon;
Right: Relaxed structure near localization centre.

VIBRATIONAL SPECTRA: CRYSTALLINE AND AMORPHOUS



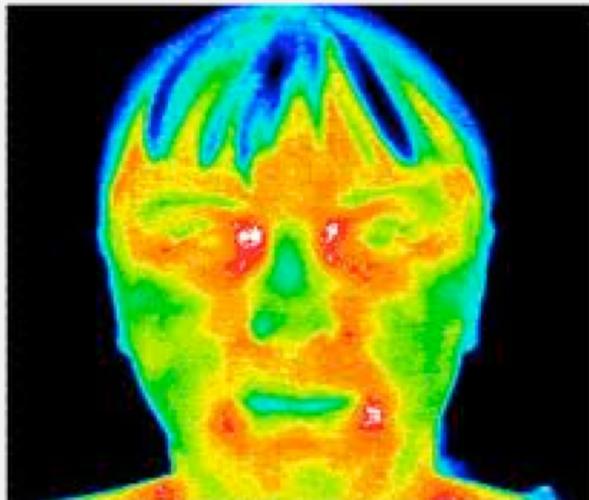
A “vibrational smoking gun” at 1350 cm^{-1} . Raman signature?

Distinct puckering states: virtually no effect

CONCLUSIONS

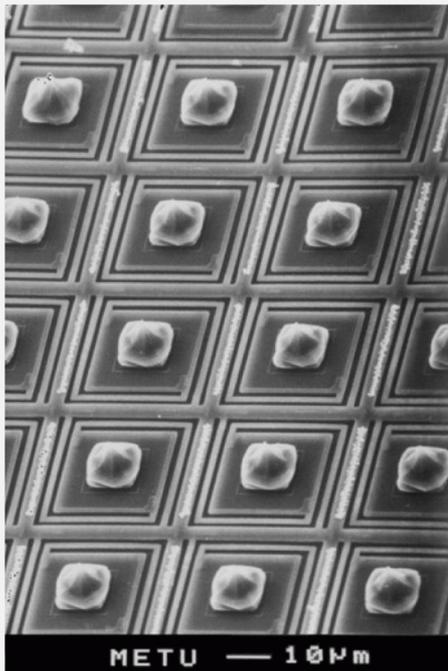
- a-G exists
- Unsupported film will pucker: potato chip topography
- Exquisite electronic DOS of crystal is ruined by topological disorder
- A potential vibrational signature of disorder

And now another application... Thermal imaging!



Thermal Imaging in a nutshell

Idea: probe the temperature pixel by pixel to get thermal image. Strategy: find material whose resistivity changes a lot with small change in T “high TCR”.



Micrograph of microbolometer at focal plane

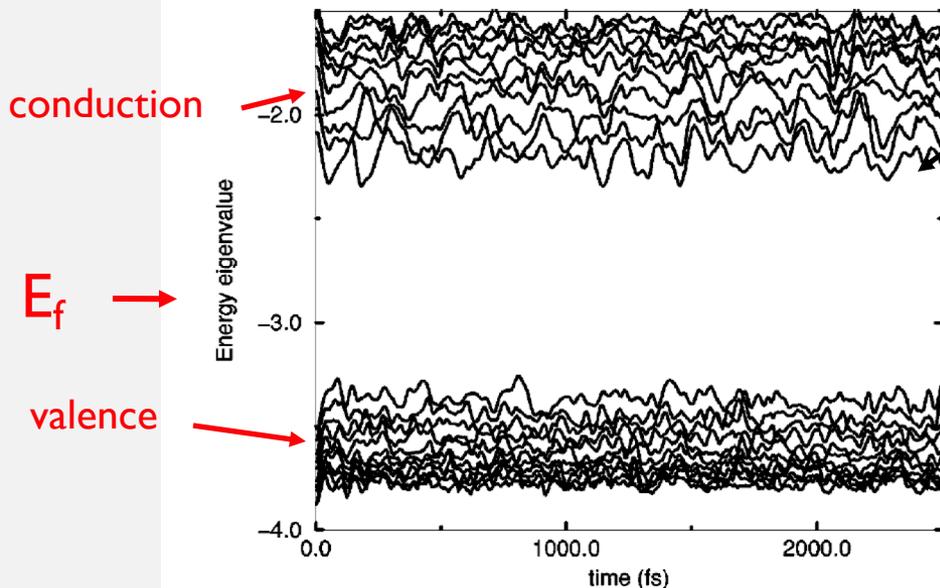
THE KEY IS A HIGH RESOLUTION T-SENSITIVE ARRAY

- Fact: doped a-Si:H and VO_x are the best focal plane materials.
- Materials physics question: what determines the temperature coefficient of resistivity (TCR), and why these materials?
- $T > 0$ means moving atoms: so we estimate conductivity as function of temperature!

SCIENCE OF TCR

States near gap are localized, sensitive to lattice vibrations. Consider **Amorphous Si**.

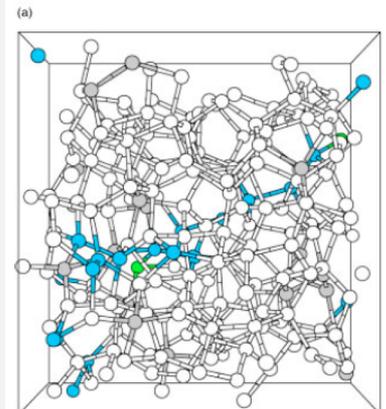
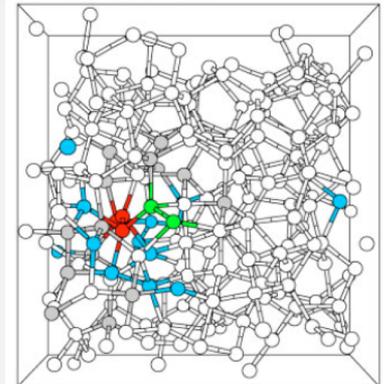
Simulation of network dynamics reveals that the electron eigenvalues and eigenfunctions near E_f are sensitive to phonons, and vary by tenths of eV at 300K, an energy scale larger than kT .



Simulation time (in fs= 10^{-15} s)

Thermal eigenvalue fluctuations, 300K
Large for localized States (DAD, PRL 1991)

States conjugate to fluctuating eigenvalues vary considerably (same state separated by 100fs)
DAD (Phys Rev B 2000)



LARGE TCR, WHY?

- In an adiabatic picture, thermal disorder strongly modulates electronic energy eigenvalues and eigenstates.
- The conductivity depends critically on these quantities. We use these quantities, obtained from believable atomistic models to estimate the T-dependence of the conductivity.
- Disorder (thus localization) amplifies the electron-lattice coupling, enhances T-dependence of conductivity.

ESTIMATING THE CONDUCTIVITY

Thus, DC conductivity may be computed as the zero frequency limit. To include the motion of the lattice (thus temperature dependence), we average over the motion of the atoms from a simulation.

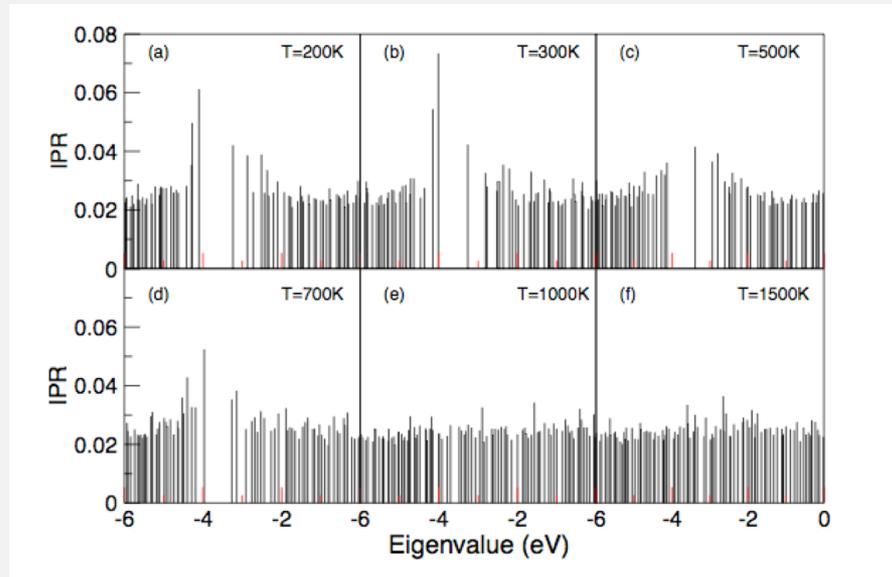
DC conductivity:
$$\bar{\sigma}_{\alpha\alpha}(\varepsilon) = \frac{2\pi e^2 \hbar}{\Omega m^2} \sum_{ni} \overline{|\langle \psi_n^t | p_\alpha | \psi_i^t \rangle|^2 \delta(\varepsilon_n^t - \varepsilon) \delta(\varepsilon_i^t - \varepsilon)}$$

We compute all this for credible structural models. Main T-dependence is in the thermal (trajectory) average!

WE HAVE CARRIED THIS OUT

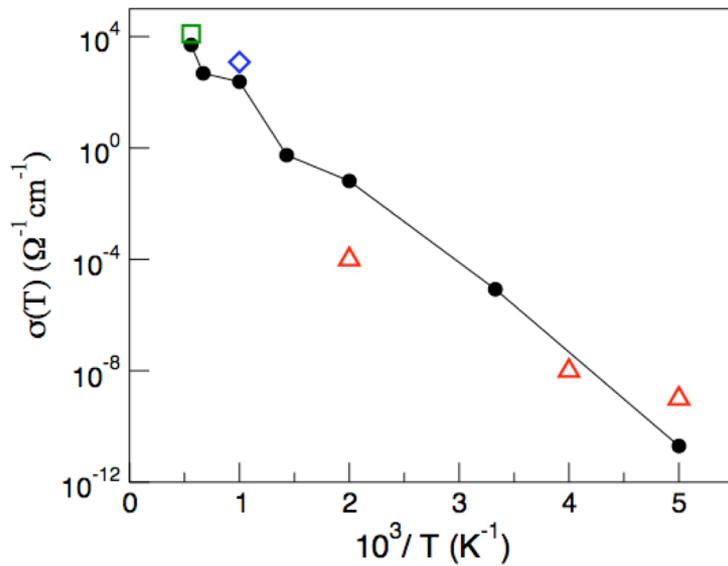
- System needs to be well equilibrated.
- Small systems (*ca* 216 atoms) and simple approximations (minimal basis set) appear to pick up the observed effects.
- Calculations: average Kubo formula over many configurations at various T.

RESULTS FROM KUBO STUDY A-SI (INTRINSIC MATERIAL)

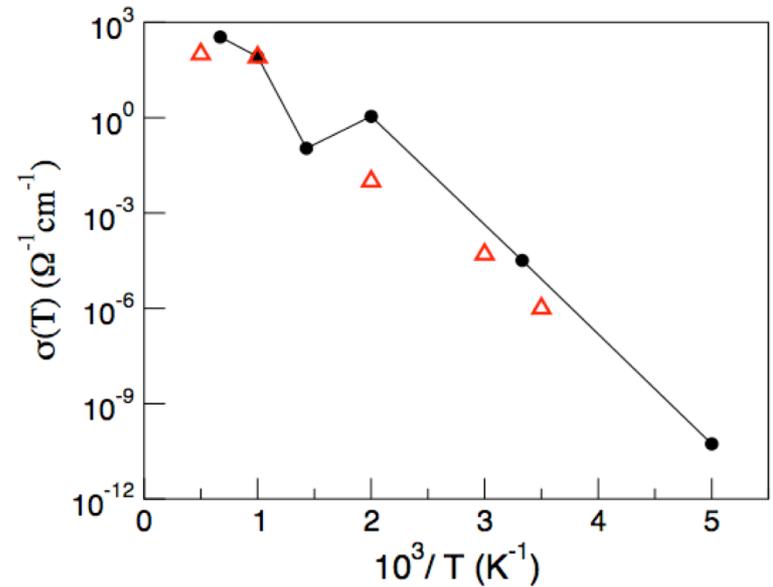


IPR [measure of localization]
as function of temperature

T-DEPENDENT CONDUCTIVITY



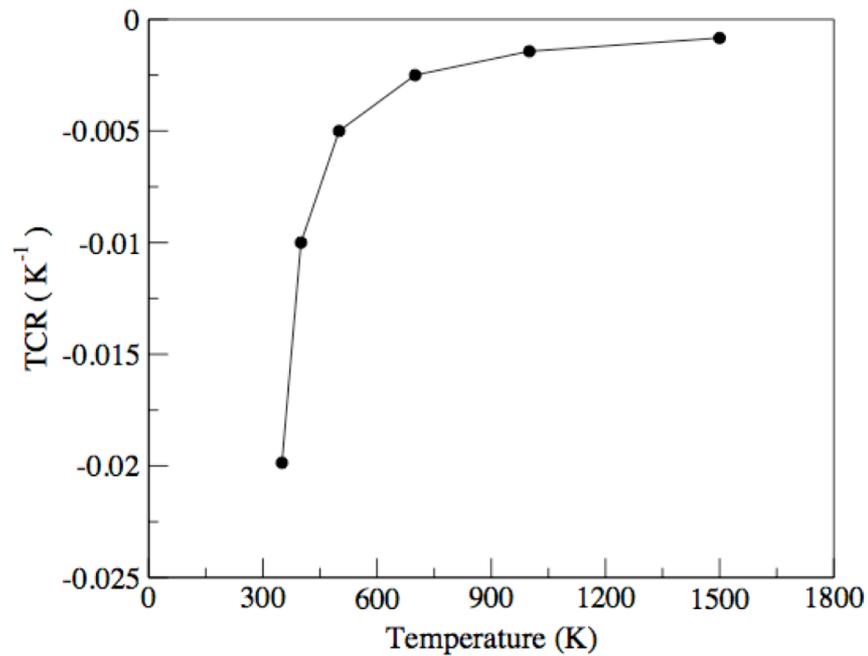
a-Si



a-Si:H

Symbols: experiment; connect-the-dots: calculation

TCR



$$TCR = \frac{1}{\rho_o} \frac{\rho - \rho_o}{T - T_o}$$

Note: TCR ~ -2.0%/K
Expt: -(2.0-5.0)%/K

SO WHAT DOES IT MEAN?

- The high TCR of a-Si is due to the high sensitivity of the states near the Fermi level to thermal distortions.
- Official buzz words: The electron-phonon coupling is large for localized states around the gap. Thermal effects are *amplified*.
- Shift the Fermi level into these thermally fluctuating states and the conductivity (resistivity) varies greatly with T!

ANOTHER EXAMPLE: PRESSURE-INDUCED PHASE TRANSITION IN A-SI

Ingredients:

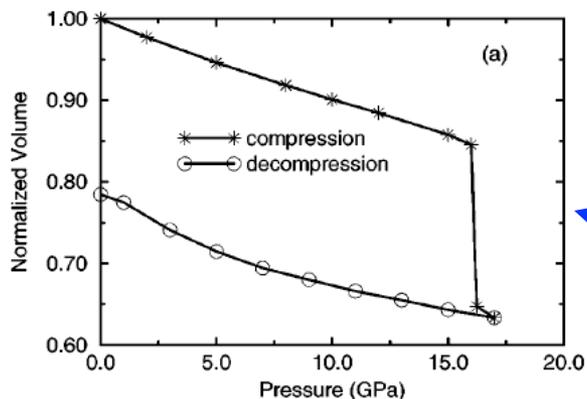
- Constant pressure MD simulation, Sankey Hamiltonian (local basis LDA).
- 216 atom models of a-Si from Mike Thorpe (ASU): highly realistic models of a-Si.

Approach:

- Simulate applied pressure and track the structural response.

RESPONSE TO PRESSURE: FIRST ORDER TRANSITION?

AB INITIO SIMULATIONS OF FIRST-ORDER . . .



Volume vs. Pressure
abrupt collapse

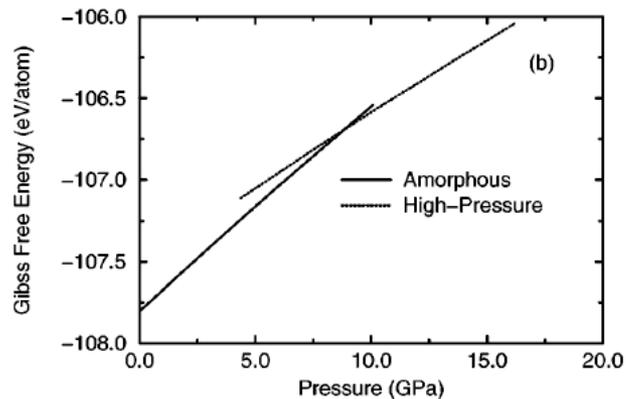
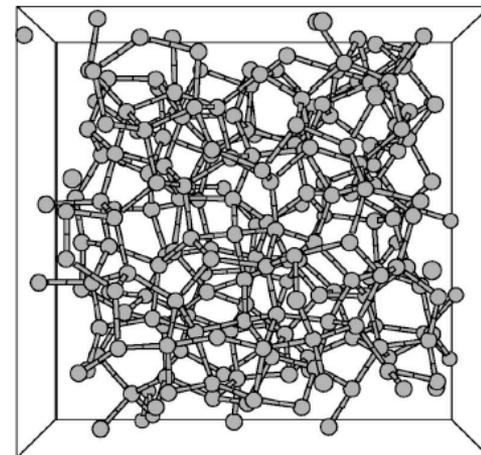


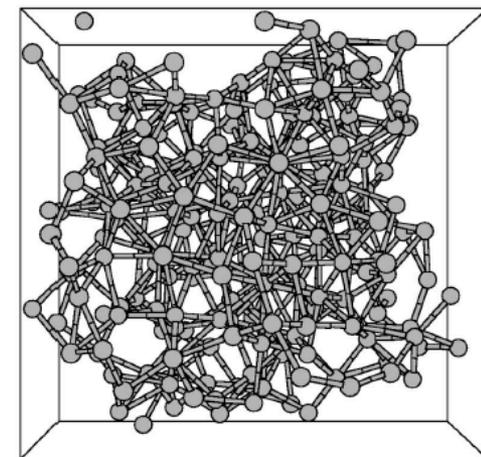
FIG. 1. (a) The normalized volume of *a*-Si to the zero-pressure measured volume. At 16.25 GPa, the volume drops suddenly, indicating pressure-induced phase transition. (b) Gibbs free energy of amorphous and high pressure phase cross near 9 GPa implying a transition.

a-Si, P=0



(a)

High pressure
metallic phase
16 GPa



(b)

ELECTRONIC STRUCTURE AND PRESSURE. *HOW THE INSULATOR-METAL TRANSITION OCCURS*

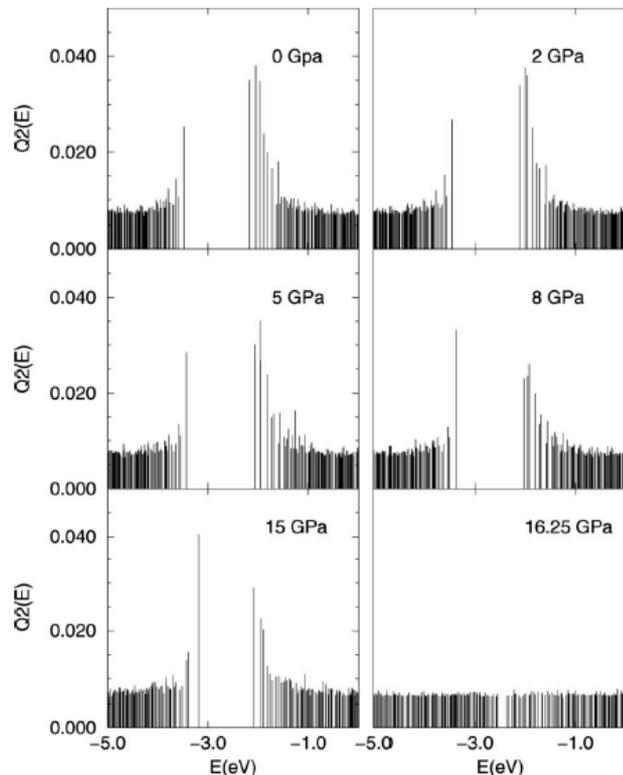


FIG. 6. Electronic eigenstates in the band gap region. The position of vertical bars represents the eigenvalues of the electronic eigenstates and height of the bars is the spatial localization $Q_2(E)$. The Fermi level lies in the middle of the band gap. Note the abrupt delocalization of tail states at 16.25 GPa.

Localization (Inverse Participation Ratio) and pressure. Note the abrupt delocalization of band tails at critical pressure and collapse of the gap