Electronic transport and the origin of Urbach tails in amorphous silicon

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Collaborators

Serge Nakhmanson, Peter Fedders, Jianjun Dong, Jon Ludlam, Sergei Taraskin, Stephen Elliott (older work on band tails, electron-lattice couplings)

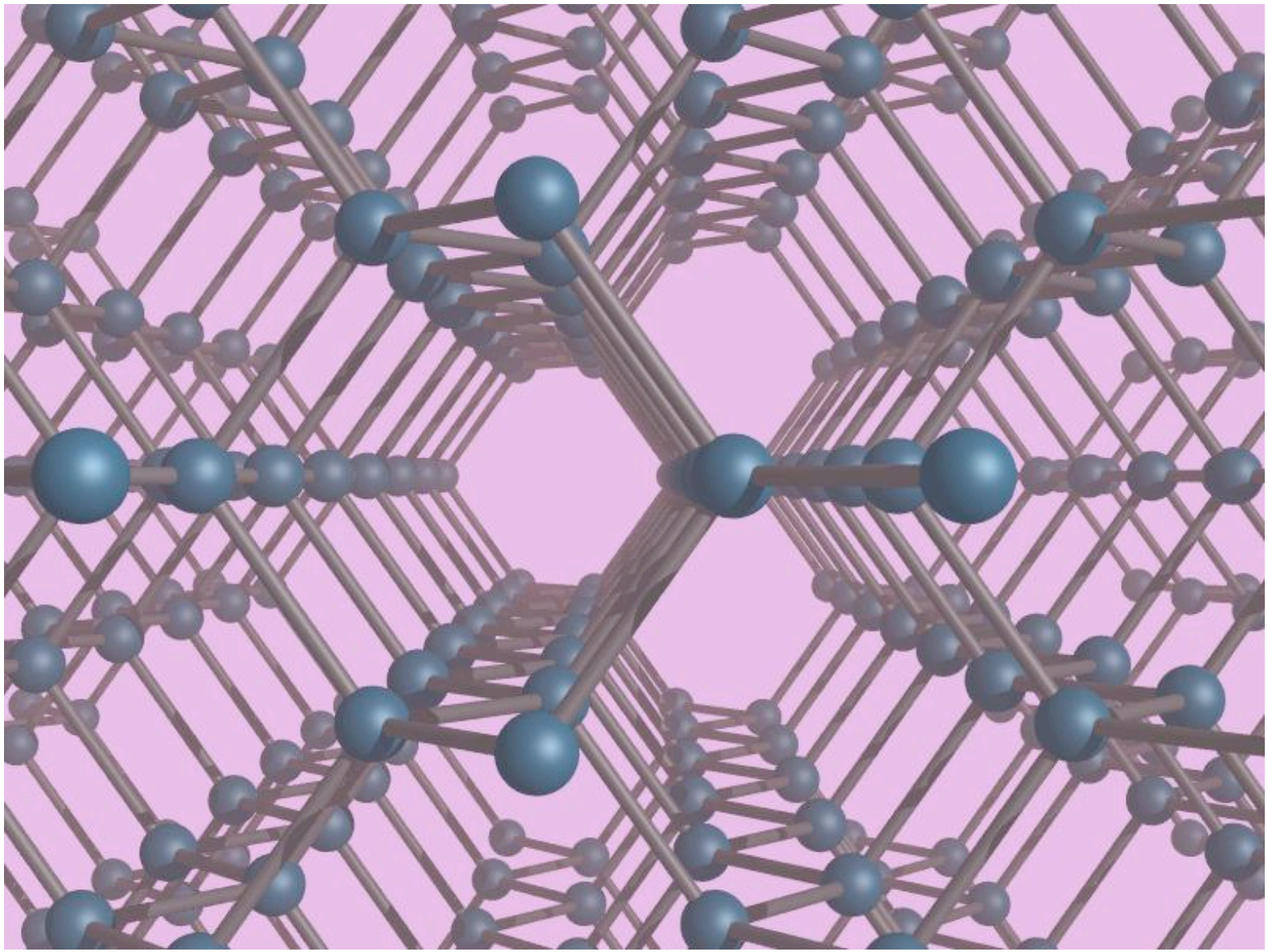
F. Inam, Y. Pan, M. Zhang (Urbach problem)

T. Abtew (transport)

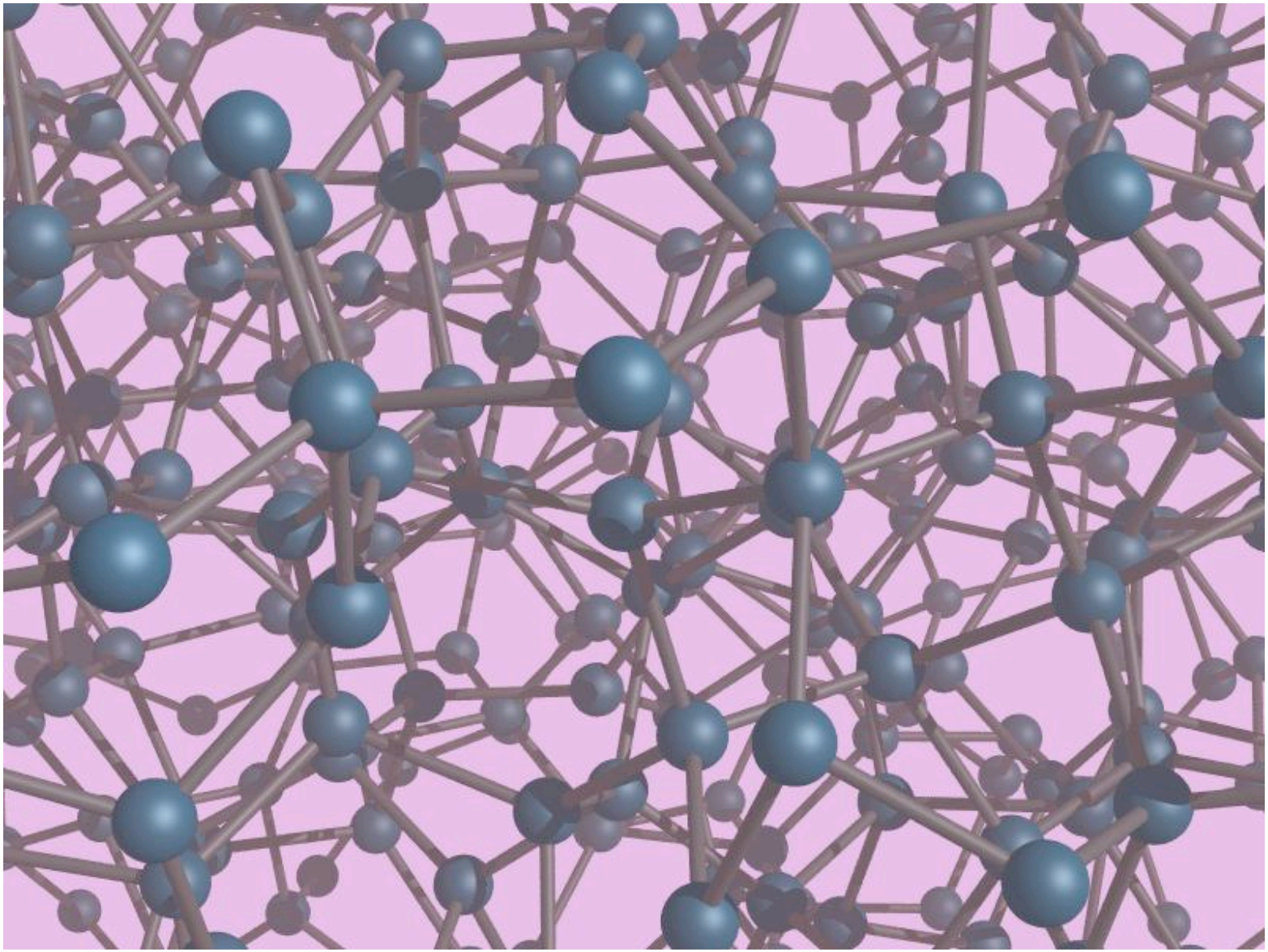
Pertinent questions

- How does the disorder affect electron states?
- What microstructures give rise to exponential “Urbach” tails observed in defective crystals and disordered systems?
- How useful is the linear response theory (Kubo-Greenwood formula) in amorphous materials?

We know about electron states in this (diamond):

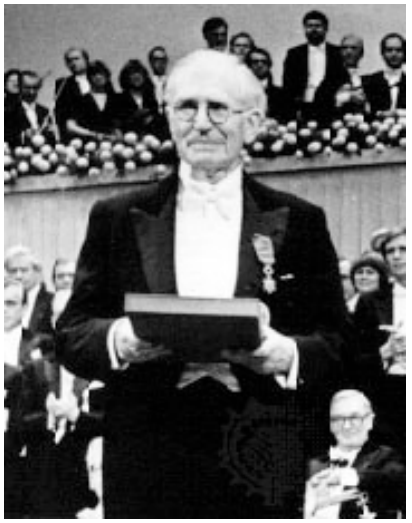


But what are electron states like in *this* (a-Si)?



History: Electron Localization from disorder

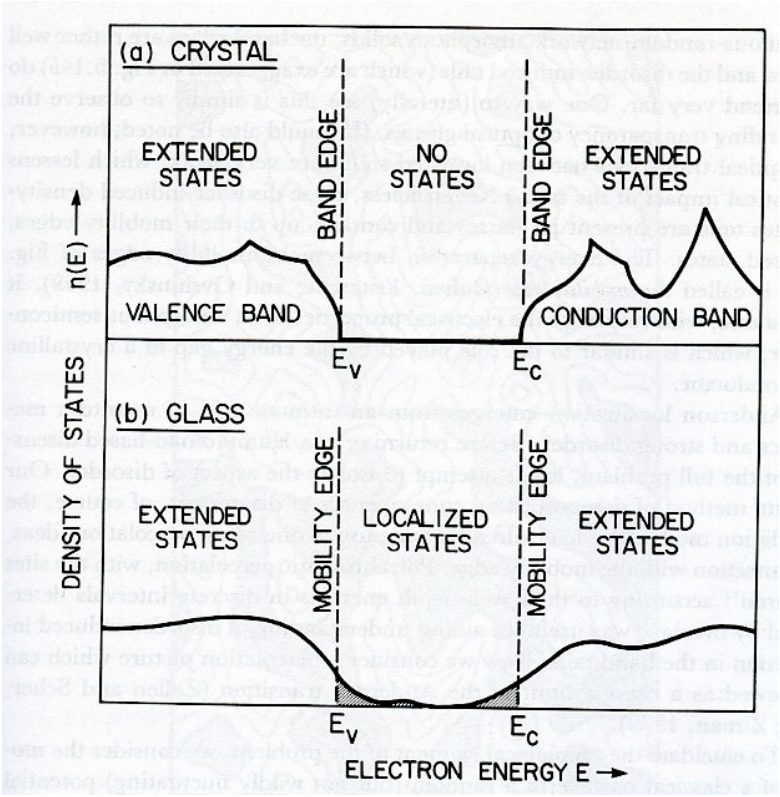
P. W. Anderson



Sir N. F. Mott

"*There is an extensive literature calculating the position of the mobility edge with various simple models, but it has not yet proved possible to do this for a "continuous random network" such as that postulated for* SiO_2, As_2Se_3, *amorphous Si or any amorphous material where the coordination number remains the same as in the crystal. This problem is going to be quite a challenge for the theoreticians - but up till now we depend on experiments for the answer...*" [From Mott's Nobel lecture, 1977]

The classic view



from R. Zallen

Tight-binding model of disorder

Anderson model (1958)

$$H = \sum_{i=1}^{n} \varepsilon_i |i\rangle\langle i| + \sum_{\substack{i,j=1 \\ (i \neq j)}}^{n} V |i\rangle\langle j|$$

Here, ε_i are random. The disorder is diagonal only. Sufficient variation in ε_i makes all states localized!

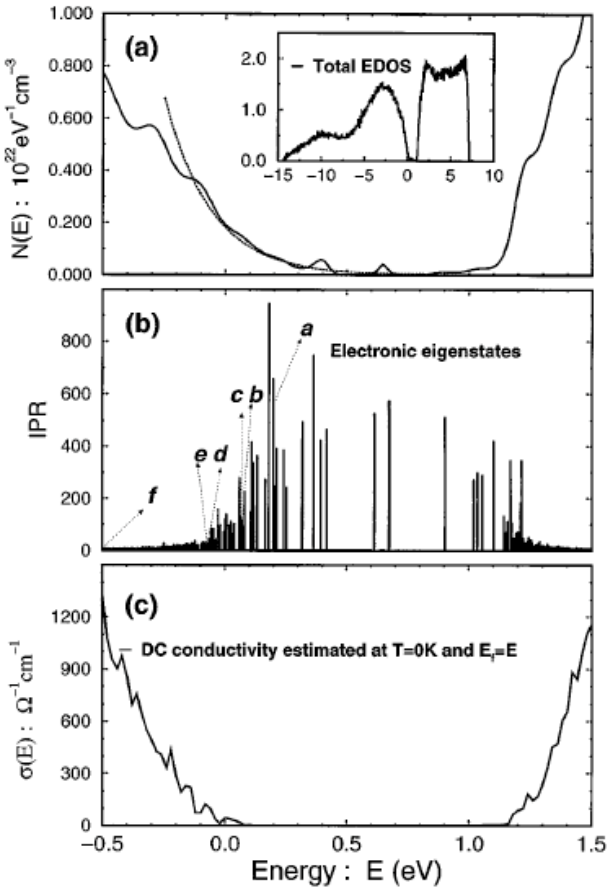
In what follows, we have disorder in $V \rightarrow V_{ij}$, not ε_i (just s or p atomic energies). Topological disorder modulates V; we compute the electronic consequences of this disorder.

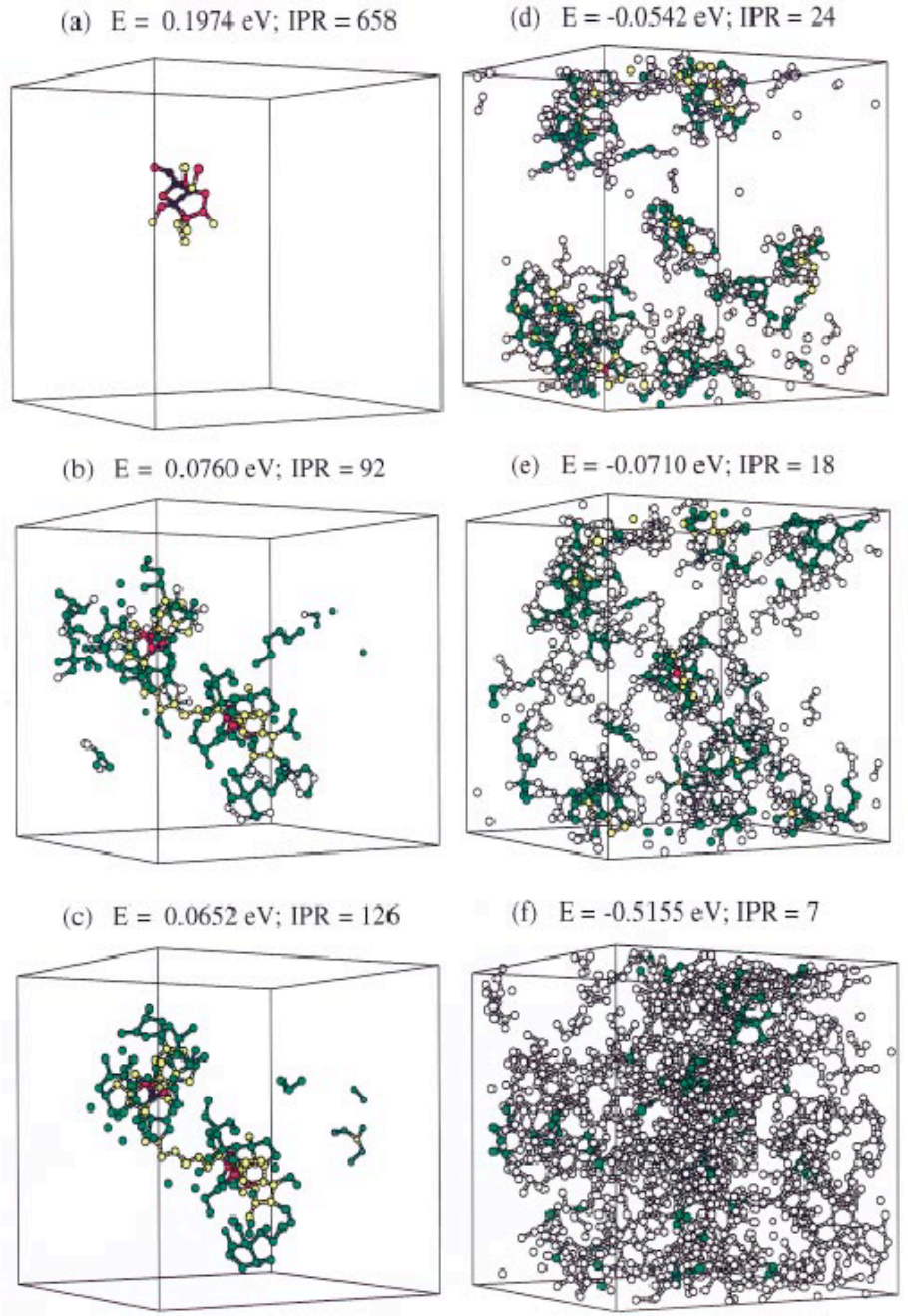
Computing the electronic consequences of static disorder

- We compute electronic eigenstates around the gap for realistic models[1] of a-Si, and study the nature of the localized (midgap) to extended (in the band) transition.

How: Use 4,096 and 10,000 atom models of a-Si, tight-binding Hamiltonian, maximum entropy and shift&invert Lanczos to compute the states.

[1] Djordjevic, Thorpe and Wooten "DTW" hereafter; Barkema and Mousseau





Evolution of electron states
In a-Si. PRL **80** 1928 1998

Interpretation

- Structural irregularities exist in the network. (Example: a dangling bond site, a strained site, a strained complex, a crystallite etc)
- If "bad enough" these induce localized wave functions.
- If two such defects are spatially near and have similar energies, system eigenstates will be mixtures. "States *b* and *c*" [clue: Symmetric and anti-symmetric linear combinations of *b* and *c* yield single "**islands**" connected by filaments]
- If many such resonant defects overlap, one has "electronic connectivity". This is Mott's *mobility edge*.

“Resonant cluster proliferation”

In midgap-band tail region (where states are localized), write the Hamiltonian in “island representation”:

$$\mathbf{H} = \sum \varepsilon_\zeta |\zeta\rangle\langle\zeta| + \sum |\zeta\rangle \xi_{\zeta\vartheta} \langle\vartheta|$$

Here, $|\zeta\rangle$ is localized “island state” as above, with energy ε_ζ, $\xi_{\zeta\vartheta}$ is intercluster coupling from embedding islands in amorphous environment.

Hückel Ansatz: $\xi_{\zeta\vartheta} \sim \langle\zeta|\vartheta\rangle(\varepsilon_\zeta+\varepsilon_\theta)/2$

“Add network topology in perturbation theory”

$$|\Psi_\zeta\rangle = |\zeta\rangle + \sum_{\varphi\neq\zeta} \xi_{\zeta\varphi}/(\varepsilon_\zeta - \varepsilon_\varphi) |\varphi\rangle$$

Small denominator -- resonance - strong mixing

Island representation: direct construction

- Start with most local states (midgap)
- Moving toward L-D threshold, extract the most localized objects from which the states could be built (maximize the IPR).
- We "decomposed" about 100 eigenstates for a-Si model with 10,000 atoms.

$$\psi_{loc} = \sum_{i(islands)} a_i \sigma_i \qquad \sigma_i = \sum_{E(loc.states)} b_E \psi_E$$

eigenvectors

islands

Island properties

- Islands decay exponentially.
- From midgap until LD transition, localization length increases modestly from ~0.6 Å to about 1.2 Å.

Thus, island decay length does not diverge at LD transition, but number of islands becomes large (*resonant cluster proliferation*)

Extension to other forms of disorder

- Disorder comes in many shapes and sizes.
- For electrons, we look at:

Anderson models (diagonal and off-diagonal), "real" disorder from topologically disordered network.

Other disorder (continued)

- Vibrations

"Substitutional" Force constant disorder on a FCC lattice

Topological disorder (a-silica) with long-range (Coulomb) interactions.

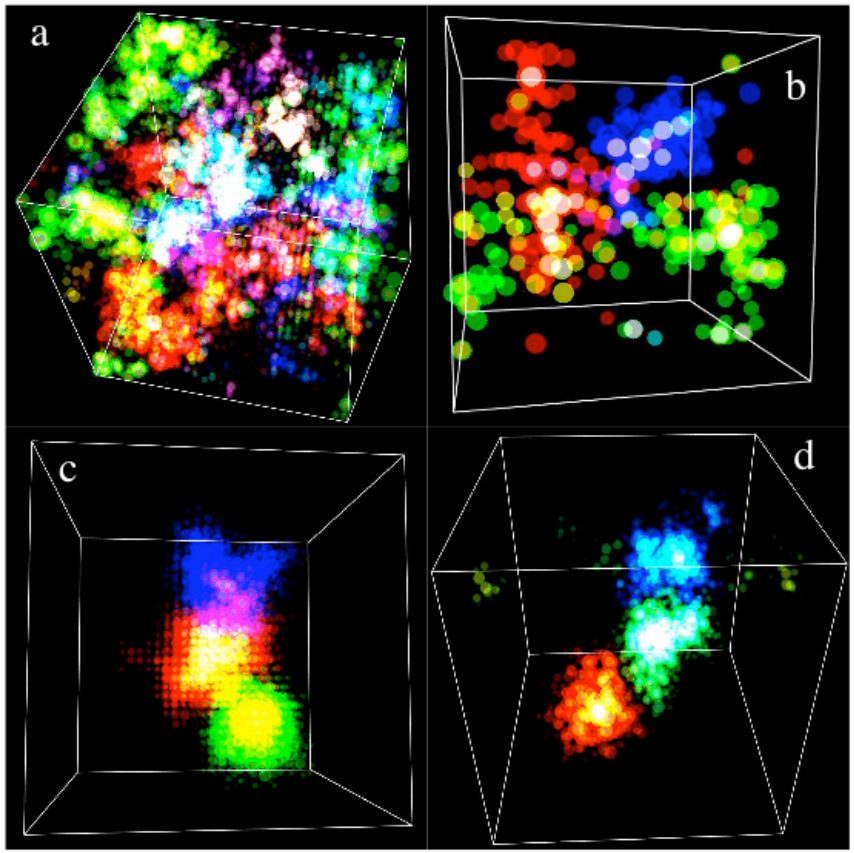
Topological disorder: 10,000 atom a-Si model

Bottom line: **the qualitative nature of the localized-extended transition is similar for all these systems.**

Ludlam, Taraskin, Elliott, DD -- JPCM **17** L321 2005

Universality: three adjacent-energy eigenstates

Anderson model, W/V=16.5 (all states localized).



Vitreous silica vibes note white centers

FCC lattice with force constants selected from uniform dist of width (W/V=2)

Vibrational evecs for 10K atom model of a-Si.

The Urbach tail problem

- Urbach[1] noted exponential (not Gaussian) tails for impure crystals in 1953. Rather ubiquitous (particularly in systems with disorder). Question is: why exponential? *Interesting because nearly universal.*
- Old important problem -- various models: Halperin-Lax, Cohen *et al*, Dow-Redfield. *Very different models*.
- This has been carefully studied in amorphous Si. Aljishi *et al*, PRL 1990. *Find: exponential tails at valence and conduction edges, conduction tail far more T-dependent than valence tail.*

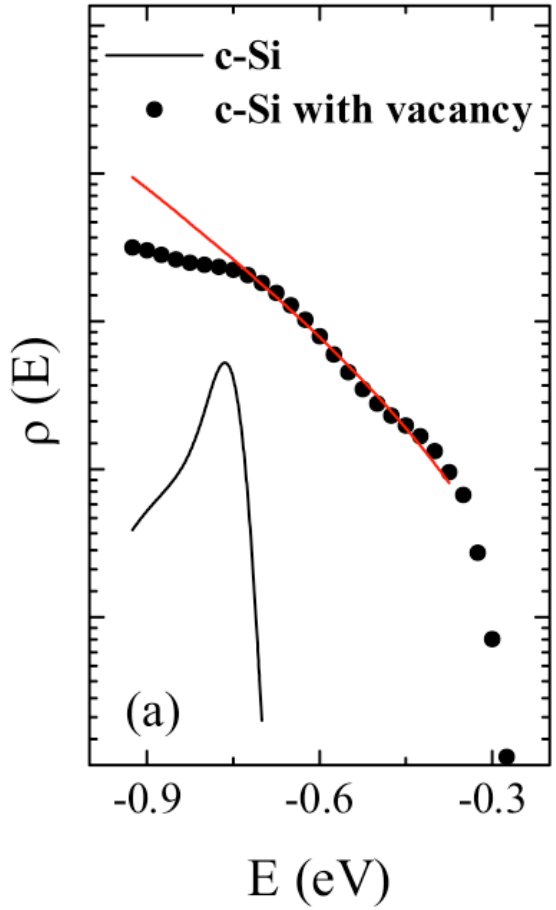
[1]F. Urbach, Phys. Rev. **92** 1324 (1953)

Simulations

- We employ SIESTA for these calculations (local basis *ab initio* DFT code). *Large systems and extensive* ***k****-sampling required.*
- We relax point defects in 512-atom supercell model of c-Si; compute electronic DOS.
- We do the same for 512-atom DTW model of a-Si.

Ion-bombarded diamond Si

- Experiment[1]: ion-damaged diamond exhibits an exponential tail for energies well below that required to amorphize.
- Simulation[2]: relaxed di-vacancy in 512-atom cell yields exponential tail.



[1]S. Sundari Nuc. Inst. Meth. B **215** 157 (2004)
[2]Y. Pan *et al*, PRL **100** 206403 (2008)

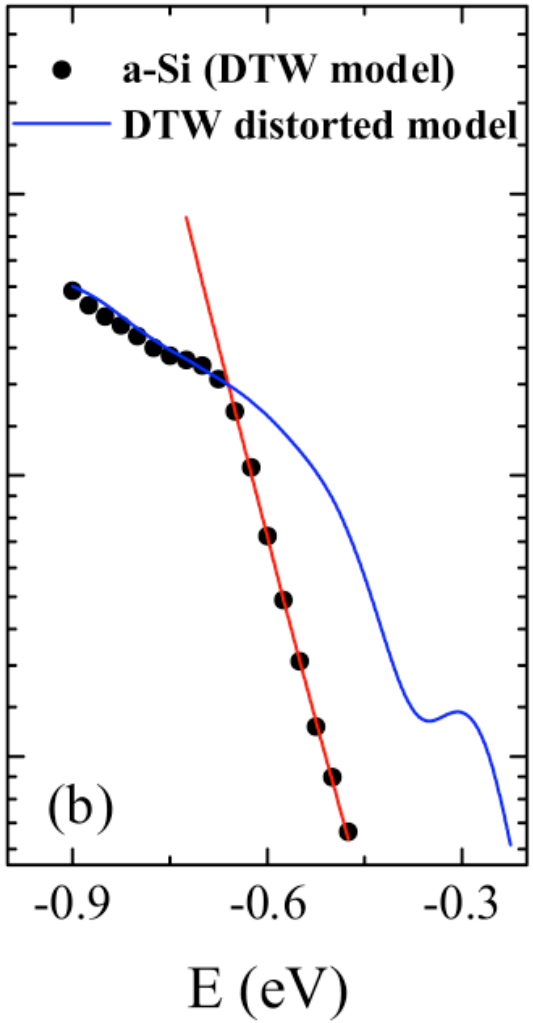
We find exponential tails in good models of a-Si

- Using 512-atom DTW models, obtain exponential valence tail:

$\rho(E) \propto \exp(-|E - E_b|/E_U)$

E_U~110meV *(theory)*

E_U~170-240meV *(expt)*

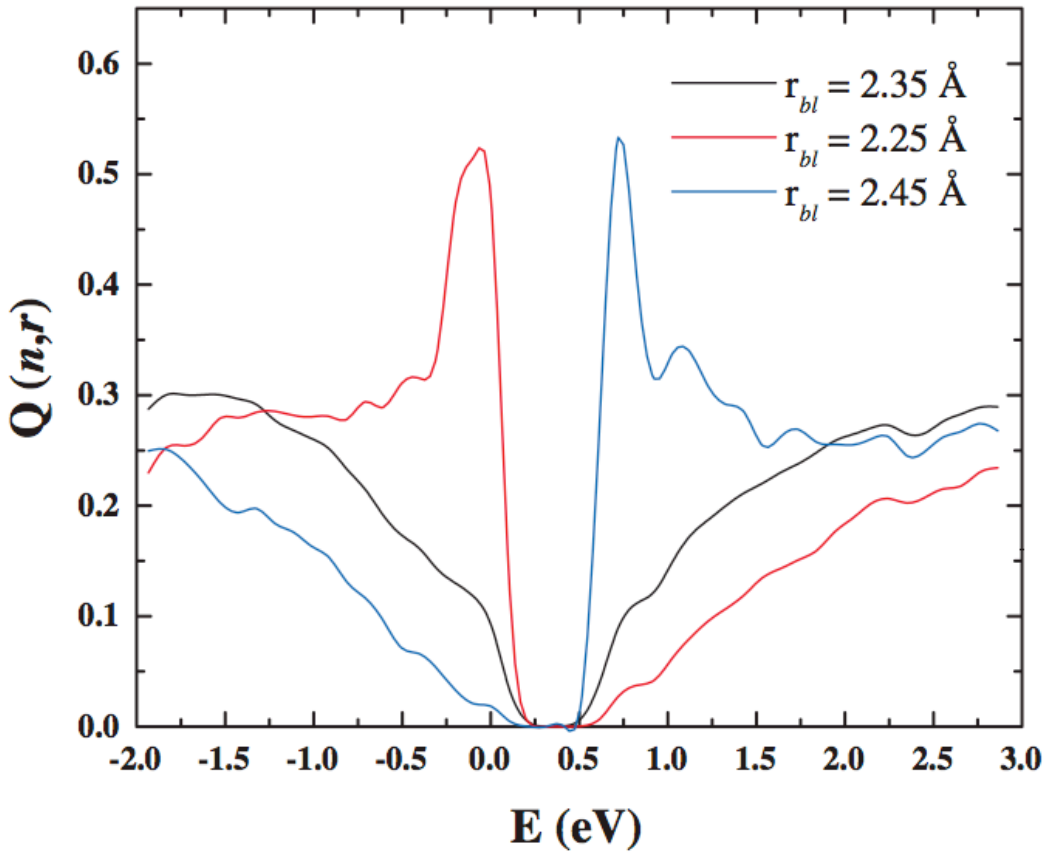


So what does it mean?

- Obviously, the structures giving rise to the exponential tails are present.
- We can look at the topology of the band tail states.

  In a nutshell, we find that tail eigenstates in the most realistic models are on 1-D filaments of long and short bonds we name *electron filaments* (long bonds, conduction; short bonds, valence). There are also *structural filaments* of long and short bonds present in the models.

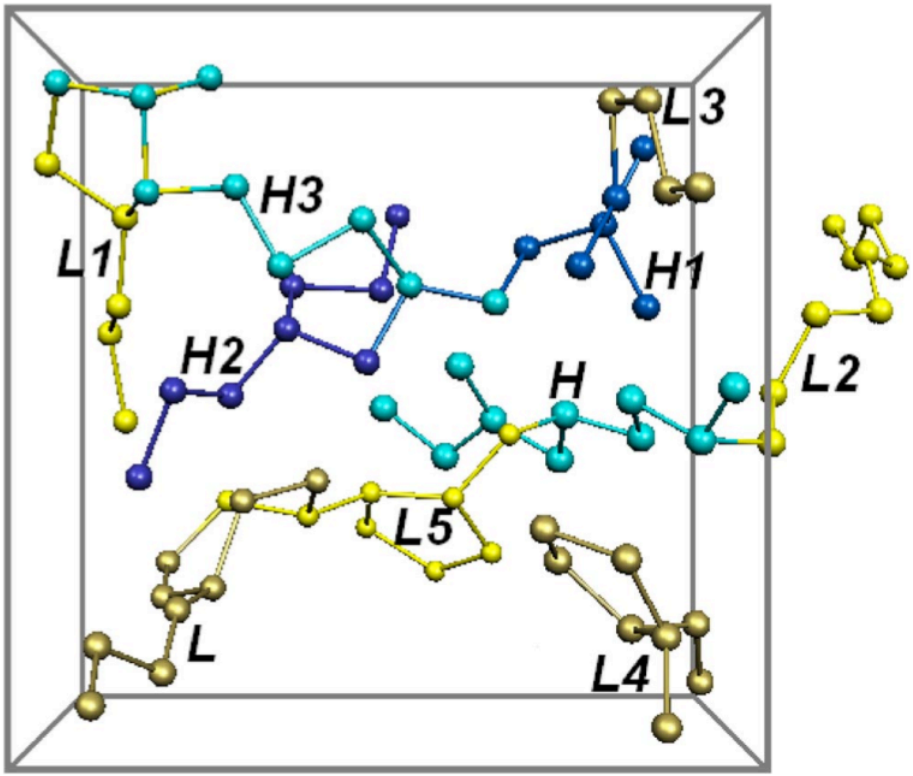
Spectral consequences of long and short bonds



valence gap conduction

Two filament systems

- Electron filaments
- Structural filaments



PRL **100** 206403 (2008)

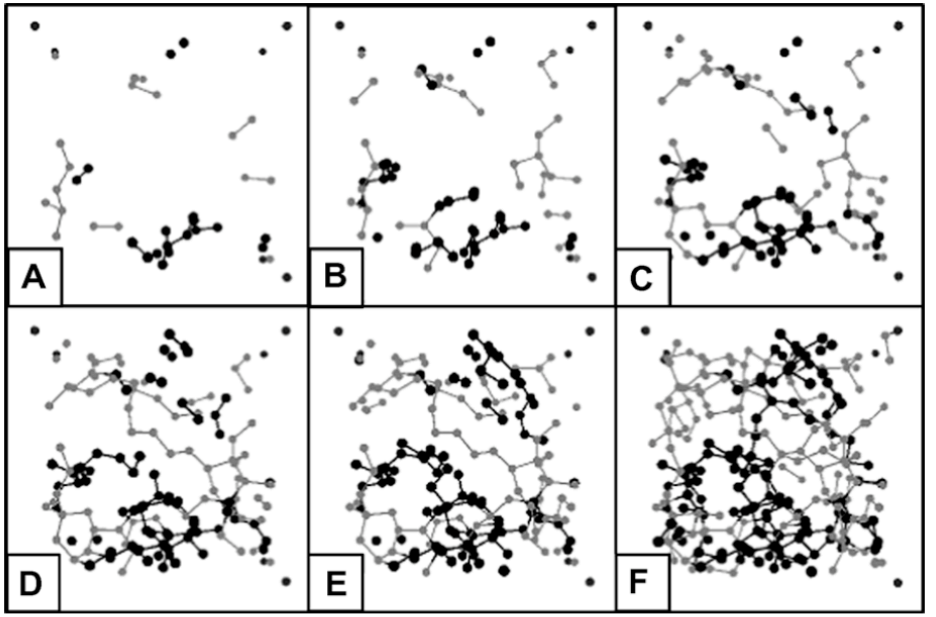


Fig. 2. (A) 1%, (B) 2%, (C) 3%, (D) 4%, (E) 5% and (F) 8% shortest(dark) and longest (light) bonds of model M_1.

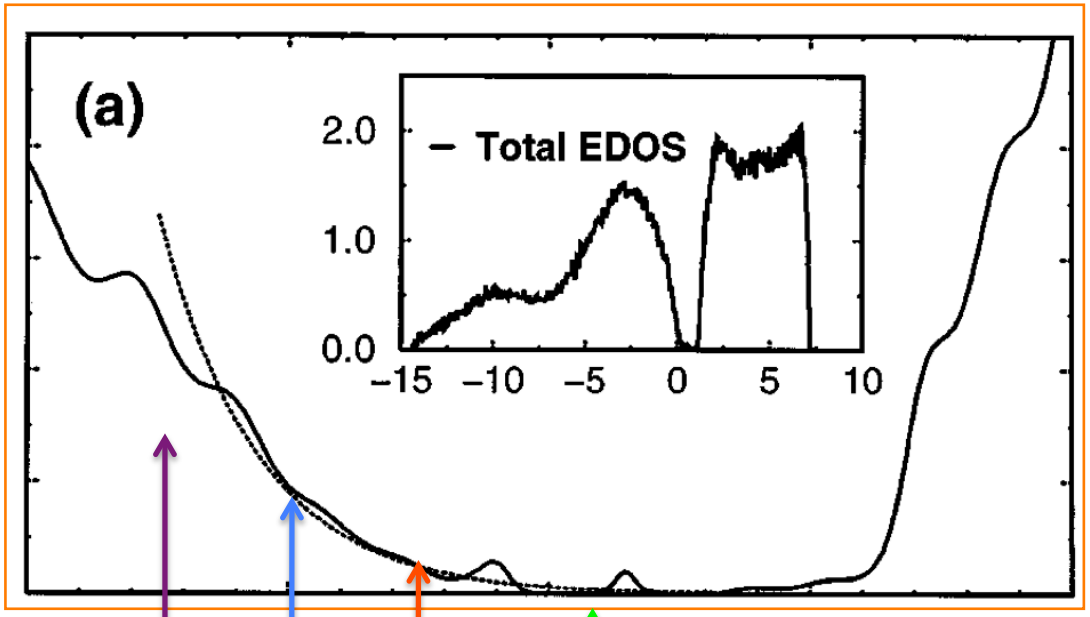
JNCS **354** 3480 (2008)

Comments on Urbach

- Electron filaments strongly overlap the structural filaments
- Destroy the filaments and the tail is no longer exponential
- Have extended the calculations to 100,000 atoms and tight binding, still exponential.
- Filaments appear as consequence of structural relaxation.
- Generality uncertain, certainly relevant to more than a-Si.

Conclusion: qualitative nature of the localized to extended transition

A cartoon depicting the character of the states near the gap



islands

filaments

Extended states

mid-gap (**very** localized)

Conclusion: T=0

- Mid-gap states: highly localized.
- Moving toward bands from midgap, eigenstates are composed initially of filaments, then islands.
- Islands arise from network defects and energy eigenfunctions are mixtures of the cluster states if clusters are resonant and overlapping.
- Urbach edges, at least nearest mid-gap, arise from filaments of long and short bonds in a-Si.

Localized Electrons + Phonons

- Move an atom (phonon) – the *electron-phonon coupling* gauges how the electron energies/states change with this deformation.
- Importance: Key to transport, device applications, theory of localization.
- Large coupling in amorphous systems: localized electron states and a floppier network; crystals are dull because all states are extended!

*PRB **69** 254204 (2005); JNCS **266** 156 (2000).*

Sensitivity of electron energy to particular phonon

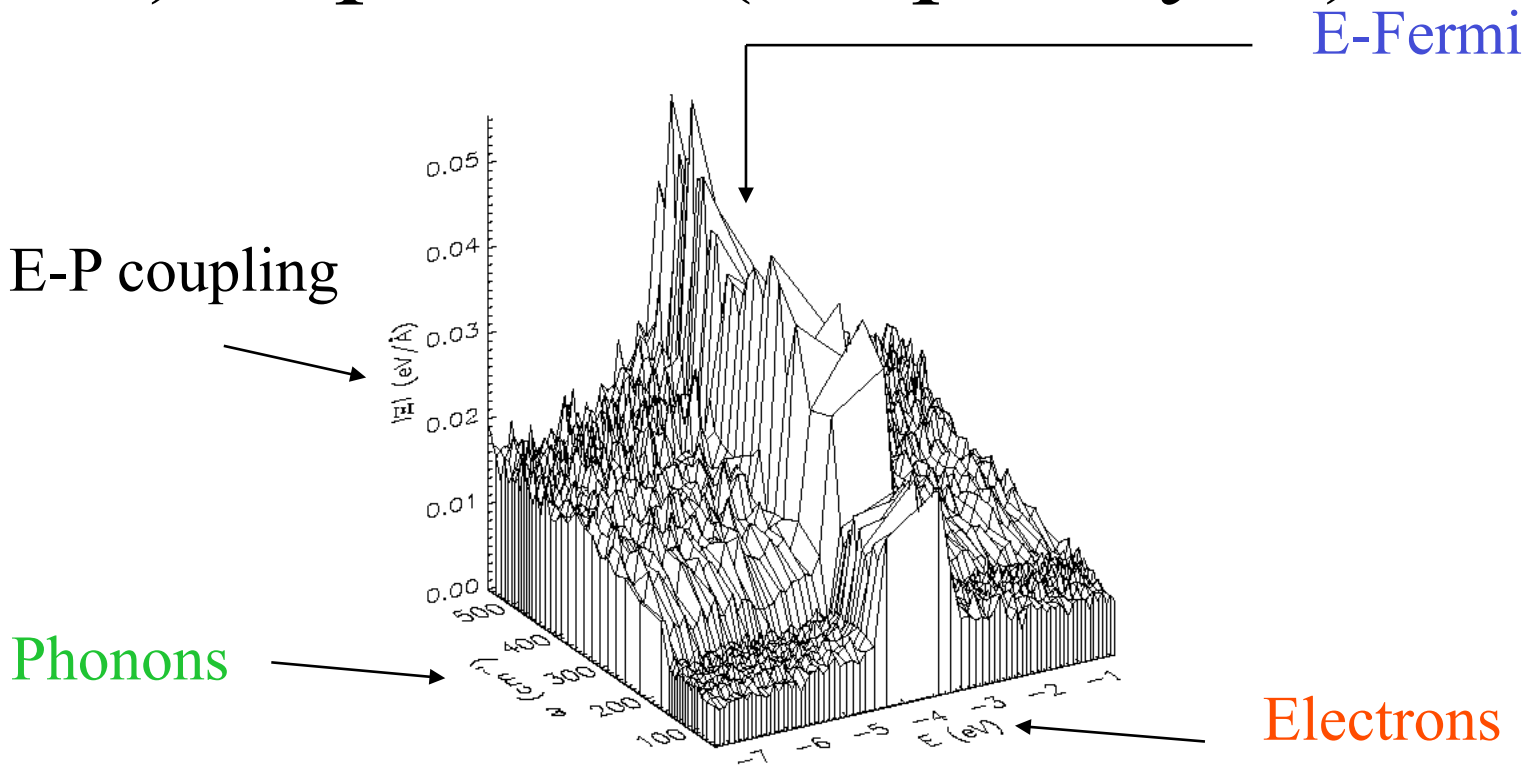
- Hellmann-Feynman theorem and harmonic approximation with classical lattice dynamics leads easily to fluctuations in electron energy eigenvalue $\langle \delta\lambda^2 \rangle$:

$$\langle \delta\lambda_n^2 \rangle = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau dt\, \delta\lambda_n^2(t) \approx \left(\frac{3k_B T}{2M} \right) \sum_{\omega=1}^{3N} \frac{\Xi_n^2(\omega)}{\omega^2},$$

$$\Xi_n(\omega) = \sum_{\alpha=1}^{3N} \langle \psi_n | \frac{\partial \mathbf{H}}{\partial \mathbf{R}_\alpha} | \psi_n \rangle \, \chi_\alpha(\omega).$$

We call Ξ the electron-phonon coupling

How sensitive is electron (energy E) to phonon (frequency ω)?



$\Xi_n(\omega) = \sum_\alpha \langle\psi_n|\partial H/\partial R_\alpha|\psi_n\rangle\ \chi_\alpha(\omega)$

Couple electron n (energy E) and phonon ω

Interpretation

1. Large electron-phonon coupling for localized states near the gap.

2. For localized states, simple algebra leads to the conclusion that:

a) Ξ^2 [electron eigenvalue n] ~ IPR [n]

b) $<\delta\lambda^2>$ ~ IPR

IPR = inverse participation ration; measure of localization

Why this is interesting: direct correlation between a **static property** (IPR) and **dynamic property** – adiabatic variance of the electron eigenvalues near E_f.

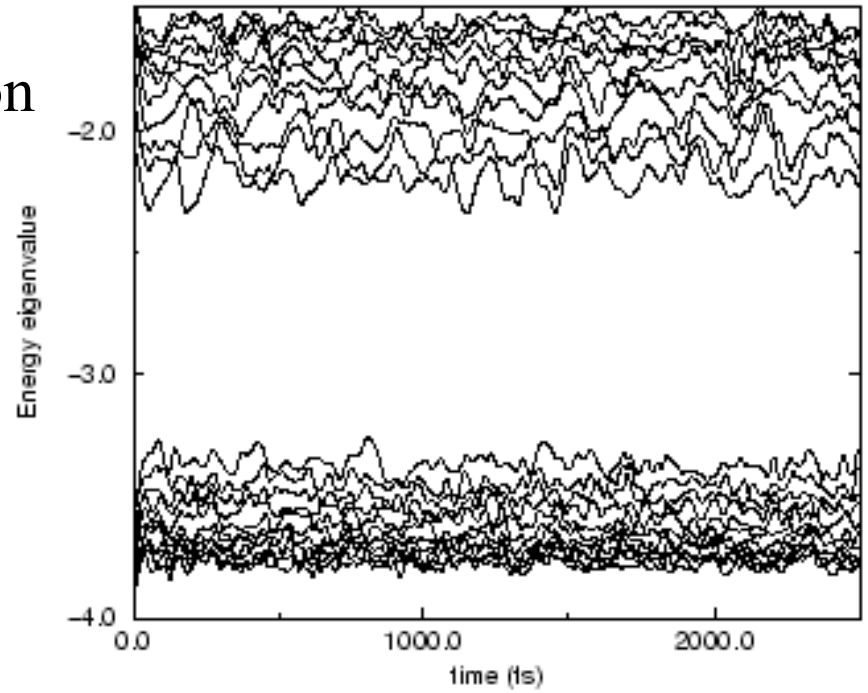
Now add thermal disorder directly! (track jiggling Kohn-Sham eigenvalues in thermal MD)

- Electrons near Fermi level are localized.
- Localized states have a large electron-lattice coupling.
- How do electronic energies and states change in thermal simulation?

Thermal fluctuations in electron energies (spaghetti plot)

Conduction band

Valence Band



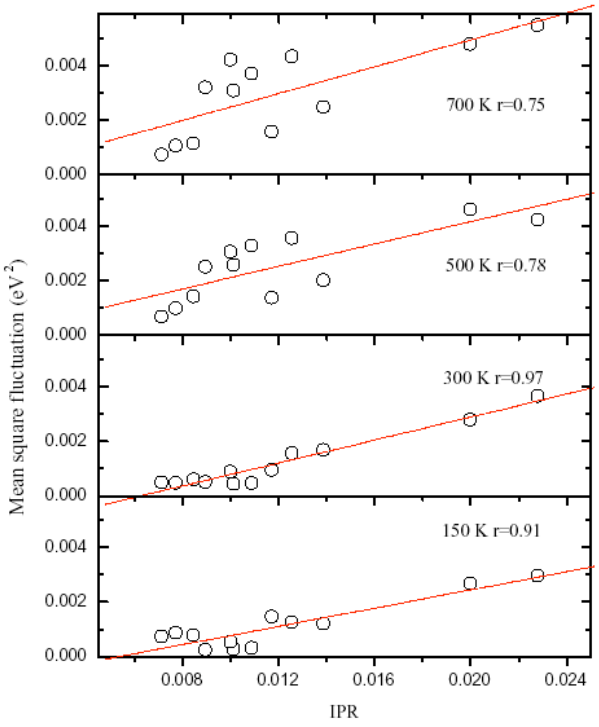
Thermal simulation
T=300K, E_f~-3.0eV

States near gap fluctuate by *tenths* of eV >> kT !

Correlation between localization and thermal fluctuation from MD

$\langle \delta\lambda^2 \rangle$ ⟶

(T>0 property)



700K

500K

300K

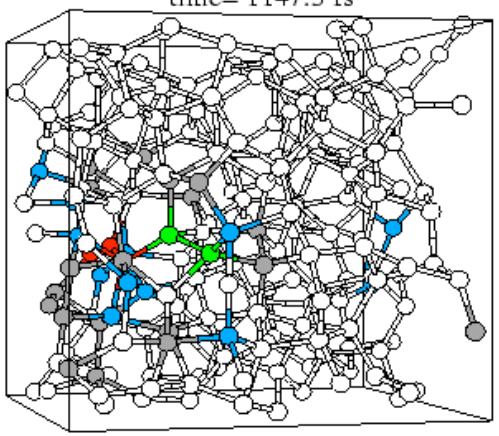
150K

Fits analytic result for low T

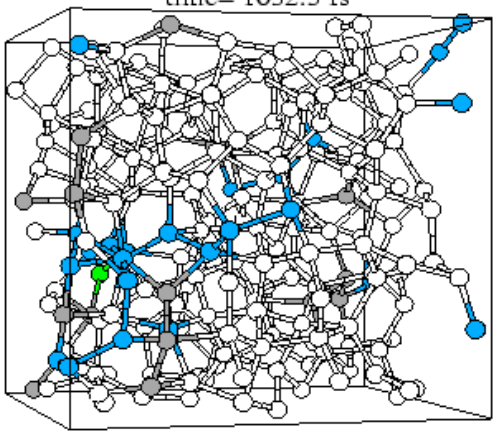
Localization (T=0 property)

Thermal motion modulates the eigen*states* (charge density) too!

(a) A snaphot of the LUMO state:
time= 1147.5 fs



(b) A snaphot of the LUMO state:
time= 1032.5 fs



The same eigenstate at two different instants of time (separated by ~100 fs!)

DAD and P. A. Fedders PRB **60** R721 (1999)

Why the big charge fluctuations?

Resonant cluster argument:

1. Eigenvalues in gap are sensitive to thermal disorder.
2. Thermal disorder can tune cluster energies into resonance; then there is strong mixing between clusters; eigenstates change dramatically.

Electrical conductivity

- Electronic conduction is key in applications.
- High “Temperature Coefficient of Resistance” (TCR) makes a-Si:H an ideal material for IR imaging (night vision) applications.
- We compute the conductivity using linear response theory “the Kubo formula”.

Large temperature coefficient of resistance in a-Si, *why*?

- *In an adiabatic picture*, thermal disorder strongly modulates electronic energy eigenvalues and eigenstates.
- The conductivity depends critically on these quantities. We routinely compute all of these.
- 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: $$\sigma \propto \lim_{\omega \to 0} \frac{1}{\omega} \overline{\sum_{ik} (f_i - f_k) |< \psi_i \mid p \mid \psi_k >|^2 \, \delta(E_k - E_i - \hbar\omega)}$$

$\omega : frequency$
$\psi : wavefunction$
$E : energy\_eigenvalue$
$p : momentum\_operator$
$bar : thermal\_average$

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

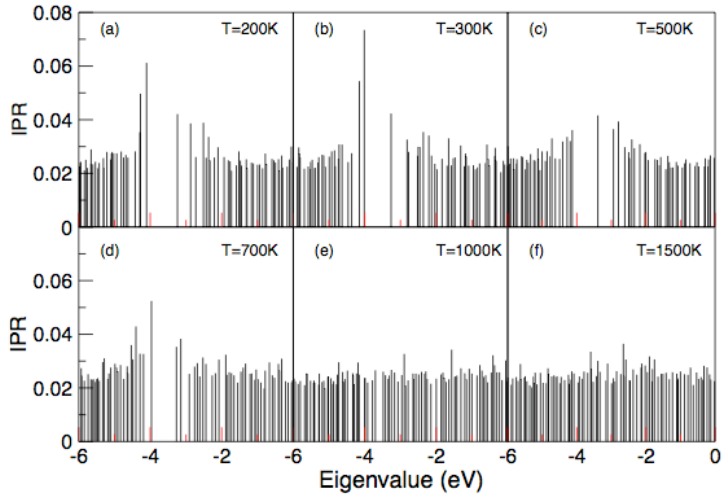
We have carried this out

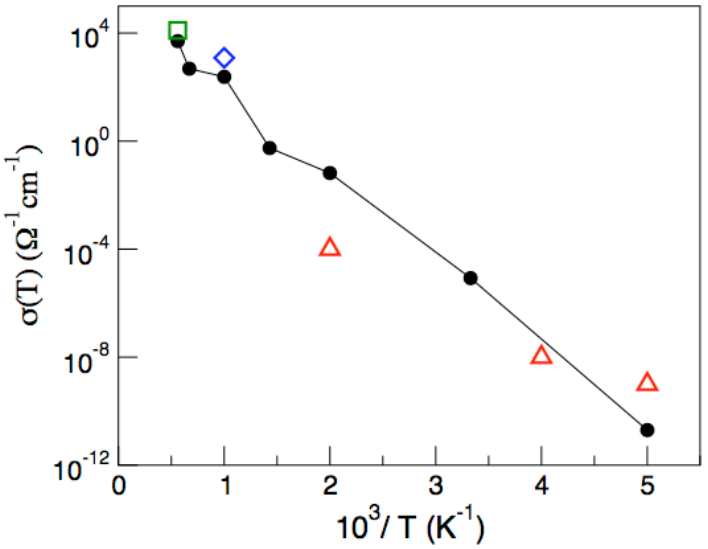
- System needs to be well equilibrated.
- Small systems (*ca* 64 atoms) and simple approximations (minimal basis set) appear to work rather well.
- Calculations: average Kubo formula over many configurations at various T.

Abtew *et al.*, Phys Rev B **76,** 045212 (2007)

Results from Kubo study

a-Si (intrinsic material)



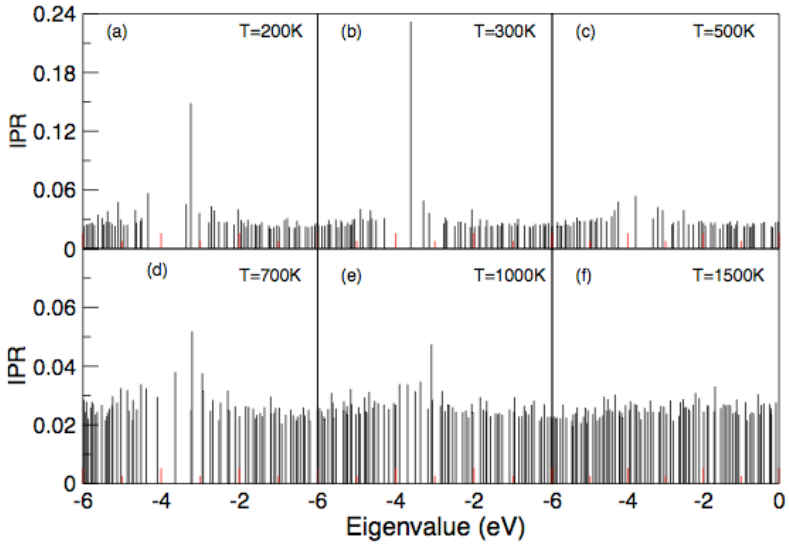


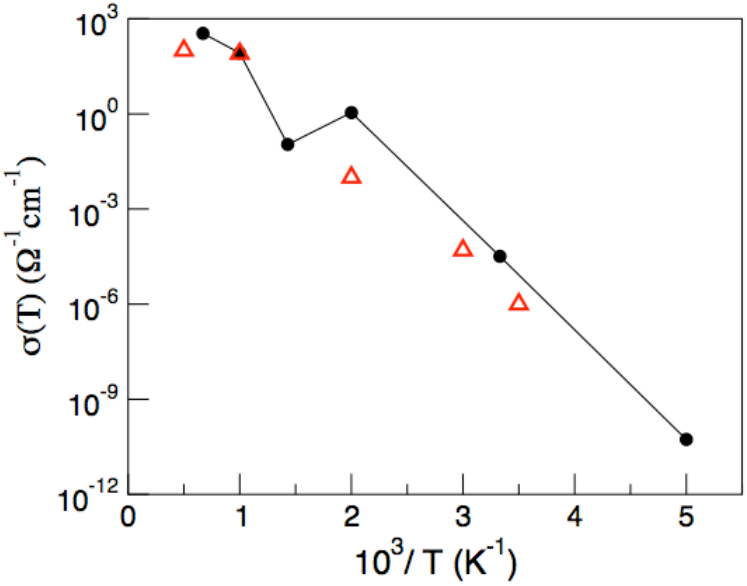
IPR [measure of localization] as function of temperature

DC Conductivity (black line)
Open symbols, experiments

T-dependent conductivity

a-Si:H (intrinsic)





IPR

Conductivity

Interpretation

- Low-T, states are very localized in the gap. Higher T, they become more extended (hence better able to conduct). Also, gap shrinks with temperature, and not just from melting (still solid at 1000K).
- Decent agreement with experiment, don't know yet if the kink for a-Si:H at ~700K is "real". Close to a "metallic transition".

Doping: Meyer-Neldel Rule†

- Meyer-Neldel rule (MNR) is the observation that pre-exponential factor and activation energy are correlated: $\sigma_0=\sigma_{00}\exp(AE_a)$ for conductivity.

This holds for many materials, even with different mechanisms for the conductivity, and the constant $E_a \sim 15\ eV^{-1}$. As it is nearly universal it is interesting.

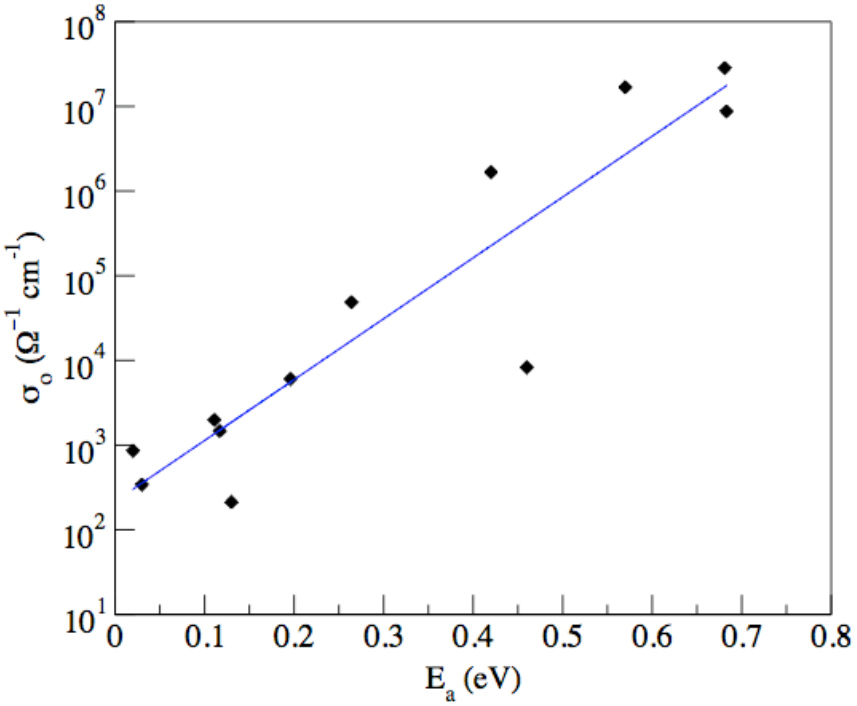
There are several explanations offered for this.

†W. Meyer and H. Neldel, Z. Tech. Phys. **12** 588 (1937).

Meyer-Neldel: Procedure

- For several Fermi level positions “sample doping”, compute $\sigma(T)$. Slope is E_a and intercept is DC conductivity.
- Then, plot MNR prefactor σ_0 vs. E_a. We get a straight line with some scatter, and the right slope (ca. 15/eV):

MNR from first principles



$\sigma_0=\sigma_{00}\ \exp(E_a/E_{MNR})$ E_{MNR}=0.060eV (best fit).

This is quite close to experiment.

MNR: interpretation

a work in progress!

- Empirically our thermally-averaged Kubo formula simulations pick up the correct T-dependence and the MNR. *Therefore, the physical mechanism underlying MNR is "in" the simulations.*
- We suppose that the MNR arises from the increasing E-P coupling for tail and gap states.
- Not a priori obvious that pathetic little 64 atom cells should pick up these effects.
- *Maybe* we have the "universal" explanation *(time will tell!)*

Details, Abtew *et al*. JNCS **354** 2909 (2008)

Conclusions (T>0, Transport)

The electron-lattice coupling is large for localized electron states.

The Kubo formula appears to provide reasonable estimates of T-dependence of the electrical conductivity in a key amorphous material

The Meyer-Neldel “compensation law” arises from the strong energy dependence of the electron-lattice coupling. No Meyer-Neldel relation if no localized states.