Spatial correlations in amorphous networks and their electronic consequences: an emerging theory of the Urbach tail

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Roadmap

• Background/preliminaries; Anderson model
• Calculation of electron states for real systems and a simple picture of Anderson transition.
• The Urbach problem: where do exponential band tails come from?
• Principle of nearsightedness for disordered systems [if time allows]
Materials

• a-Si: Important PV material, key TFT material, micobolometer (IR imaging “night vision” devices).
• a-Si is simplest system with topological disorder, theoretically tractable, wealth of experiments.
• Credible models exist, close agreement with structural, electronic/optical and vibrational measurements.
• Briefly: a-SiO$_2$, beta carotene.
Preliminary: Disorder and water waves

Water waves with obstacles; left periodic obstacles, commensurate frequency to yield “Bragg reflection”, note that pattern is extended in space. Right: disordered obstacles, standing waves – localization!

Lindelof et al. 1996
Q. How does disorder in atomic coordinates affect the electron states?

**Crystalline Si (diamond)**
- Translational periodicity
- Bloch states

**Amorphous Silicon**
- Short-range order, no L.R.O.
- $k$ not a “good” quantum number
Models of disorder

Anderson Model (1958)

\[ H = \sum_I |I><I| E_I + \sum_{IJ} |I><J| S_{IJ} \]

\( E_I \) are random, “diagonal” disorder. Fact -- enough variation in \( E_I \) -- all states localized!

Topological (bond length/angle) disorder

\[ H = \sum_I |I><I| E_I + \sum_{IJ} |I><J| S_{IJ} \]

\( S_{IJ} \): Computed from realistic model.

Anderson model: disorder uncorrelated site-to-site; our case – spatial correlations induce correlations in matrix elements.
Anderson model

*Left*: A localized eigenstate in 1D (Kramer/MacKinnon)

*Right*: 3D critical eigenstate (15.6M sites; Roemer)
Anderson model

- Disorder causes electron amplitude to be unevenly distributed.
- The more severe the disorder, the stronger the fluctuations.
- Sufficient disorder can produce electron states disconnected from the rest of the network: localized states.
- Details depend on dimensionality, electron energy and other factors.
- The model has impact beyond condensed matter physics – even ball lightning is explained with the Anderson model!
Approach for a real material

• Compute electronic states around the gap for big and realistic models of a-Si\textsuperscript{1}, and study the nature of the localized (midgap) to extended (in the band) transition. [4096 atoms model, periodic BC]

• Employ unholy amalgam of tight-binding, maximum entropy, shift and invert Lanczos techniques.

\textsuperscript{1}B. Djordjevic, M. F. Thorpe and F. Wooten, PRB 52 5685 (1995)
A priori expectations

from R. Zallen
Evolution of electron states in a-Si.  PRL 80 1928 1998
Interpretation

• Structural irregularities or defects “beyond the mean” exist.
• 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”]
• If many such resonant defects overlap, one has “electronic connectivity”. This is Mott’s mobility edge.

“Resonant Cluster Proliferation” Model
Calculation for large system

• Model: Barkema and Mousseau WWW-type: 100,000 atoms. Excellent RDF, fourfold, quite tetrahedral.

• Hamiltonian: Kwon et al. orthogonal tight-binding model, maximum entropy tricks to compute the DOS (ask me...)

DAD and O. F. Sankey, PRL 70 3631 (1993); DAD EPJB 68 1 (2009); K. Bandypoadhyay et al, PRE 71 057701 (2005)
I. Kwon et al, PRB 49 7242 (1994)
Density of states: reconstruction from moments

Maxent form:
find $\Lambda_i$ to match moments

$$\rho(E) = \exp(-\sum_{i=0}^{107} \Lambda_i E^i)$$

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

$E_U=200$ meV (valence)

$E_U=96$ meV (conduction)
Comments

• 100,000 atom model gives the same exponential band tails as the 4096-atom model, and reasonably close to experiment.

• It is no mean feat for the maxent function to produce a simple exponential at band edges:

\[ \exp(-\sum_{i=0}^{107} \Lambda_i E^i) \approx \exp(-\lambda E); E \in Tail \]

These models produce quite exponential tails
“Universality” and structure of eigenstates

- Disorder comes in many shapes and sizes.
- **electrons**, Anderson models (diagonal and off-diagonal); “real” disorder from topologically disordered network.
- **vibrations** “Substitutional”; Force constant disorder on a FCC lattice; Topological disorder (a-silica) with long-range (Coulomb) interactions; (a-Si)10,000 atom

The qualitative nature of the localized-extended transition is similar for all these systems.

Do the correlations in matrix elements matter?

• The Anderson model gets the qualitative features right: islands, resonant mixing etc around spectral gaps.

• Off-diagonal and diagonal disorder seem to make no qualitative difference

• But the Anderson model misses important phenomena, nevertheless!

Answer: Yes – the correlations matter.
The Urbach tail problem

• Urbach\textsuperscript{1} noted exponential (not Gaussian) band tails for impure crystals in 1953. Rather ubiquitous (particularly in systems with disorder). Question is: why exponential? *Interesting because nearly universal.*


• This has been carefully studied in amorphous Si. Exponential tails measured separately for each band edge\textsuperscript{2}.

\textsuperscript{1}F. Urbach, PRB 92 1324 (1953)
\textsuperscript{2}S. Aljishi *et al.*, PRL 64 2811 (1990)
Simulations

• We employ SIESTA for these calculations (local basis *ab initio* DFT code).

• We relax point defects in 512-atom supercell model of c-Si; compute electronic DOS.

• We do the same for 512-atom Djordjevic *et al* WWW model of a-Si. Similar results for similar models (Barkema-Mousseau).
Defective xtal and ion-bombarded diamond Si;

- Experiment\(^1\): ion-damaged diamond exhibits an exponential tail.
- Simulation\(^2\): relaxed divacancy in 512-atom cell forms exponential tail.
- Relaxing divacancy yields strain field involving many atoms. *The beginning of the Urbach tail?*

\(^2\)Y. Pan, F. Inam, M. Zhang, DAD, PRL 100 206403 (2008)
Exponential tails in a-Si

We obtain exponential valence tail:

\[ \rho(E) \propto \exp\left(-\frac{|E - E_b|}{E_U}\right) \]

\[ E_U \sim 110\text{meV (DFT)} \]

\[ 170-240\text{meV (expt)} \]

And: gently jumble the atoms and the exponential edge disappears
So what does it mean?

- Evidently, the structures giving rise to the exponential tails are present. In a nutshell, we find
  - conduction tail: due to 1-D filaments of long bonds.
  - valence tail: due to 3-D clusters of short bonds ‘nucleated’ by a particularly short bond.

Bond length decomposition of density of states

\[ Q(n,r) \]

- $r_{bl} = 2.35 \text{ Å}$
- $r_{bl} = 2.25 \text{ Å}$
- $r_{bl} = 2.45 \text{ Å}$

- valence
- $|\text{gap}|$
- conduction
Filaments and clusters

- Electron filaments
- Structural filaments

Fig. 2. (A) 1%, (B) 2%, (C) 3%, (D) 4%, (E) 5% and (F) 8% shortest (dark) and longest (light) bonds of model M1.

Pan, Zhang, DAD JNCS 354 3480 (2008)
Bond-bond correlation functions

Pair correlations for 4% longest and shortest bonds.

Long correlated with long short with short!

Pan, Zhang, DAD JNCS 354 3480 (2008)
How does the system recover from a local strain?
What about short/long-bond dynamics

- The filament/cluster structures fluctuate for $T>0$.
- The creation and formation of these structures determines the thermal broadening of the tails.
T>0: so what?

- Fluctuations in two parts: random and part associated with regions of the network ‘prone’ to connected short (or long) bonds.
- We detect correlations in the dynamics too: not just single anomalous bonds – they come in correlated groups.
- Will help to understand (T-dependent) photoemission experiments.
a-Si: conclusions

- Shorter bond ‘nuclei’ create clusters of connected short bonds; local densification. Long bonds, wispy filaments. Short; valence tail, long; conduction tail.
- Short bonds can nucleate locally dense regions with range up to ~7Å
- 3D Anderson model: at criticality states are multi-fractal with dimension $D \approx 1.3$\(^1\)
- Our models are too small to accurately compute $D$ but we surely have:
  - **Filaments**: $D$ near 1 on the conduction side
  - **Clusters**: $D$ significantly higher than for the valence side

*We link such electronic information to the connectivity/structure of the network. $D$ is unknown for a real material — and varies asymmetrically about $E_f$.*

\(^1\)T. Ohtsuk *et al.*, Ann. Phys. 8 655 (1999)
a-Si: continued

• This must be relevant to electrical conductivity (Kubo formula):

\[
\sigma_{\alpha\alpha}(\omega) = \frac{2\pi e^2 \hbar}{\Omega m^2} \sum_{ni} |\langle \psi_n | p_a | \psi_i \rangle|^2 \frac{f_F(\epsilon_i) - f_F(\epsilon_n)}{\hbar \omega} \times \delta(\epsilon_n - \epsilon_i - \hbar \omega),
\]

\(\sigma\) is determined by transitions between occupied/unoccupied states with specific topological character (blob to filament etc.)

• A thermal average must provide information about T-dependence of \(\sigma\) and the tailing.

• There are interesting T>0 features of the filaments that we don’t yet fully understand.
a-Silica

- Silica tails: small $\theta_{O\text{-Si-O}}$ (valence), large $\theta_{\text{Si-O-Si}}$ (conduction).
- Strain recovery is much faster than silicon.

F. Inam, J. Lewis, DAD PSS(a) 207 599 (2010)
Silica – link to electrons
Carotene-\( \beta \) \( \text{C}_{40}\text{H}_{56} \)

Mean HOMO bond length 1.36Å, mean LUMO bond length 1.44Å. HOMO is on the short double bonds.

Long and short bonds even in simple organic molecule
Conclusion

• We have a clearer understanding of the limitations of the Anderson model
• The Urbach tails are associated with networks of connected long and short bonds in a-Si.
• Break the connections, break the Urbach tail!
• There are hints that the observation is applicable to systems other than Si.
Local formulation of quantum mechanics: disorder

- Quantum mechanics can be formulated locally in space using the density matrix or Wannier functions. Valuable new insights.

Questions:
- How local is local?
- How are insulators different than metals?
- How does structural disorder affect the decay?
Density matrix: gauge of electronic nonlocality

\begin{equation}
\rho(x,x') = 2 \sum_{n \text{ occ}} \psi_n^*(x) \psi_n(x')
\end{equation}

W. Kohn: density matrix \( \rho \) is localized by destructive wave-mechanical interference.

*This decay is a fundamental property of the material (and structure).*

*This decay sets the range of inter-atomic interactions: key for accurate, efficient modeling.*

*Does disorder significantly modify this decay?*

Example: Aluminum

Metal: **power law** decay. Simple free electron gas calculation gives same DM as DFT! *Slow decay because of Gibbs ringing from cutoff at Fermi surface.*
Insulators (c-Si and a-Si)

Insulators: exponential decay!
Wannier functions for disordered systems

Diamond


a-Si
Wannier functions

- Wannier functions: great computational advantages, and utility for transport and polarization calculations\(^1\)
- Think of them as the *solid state analog of the chemical bond*
- Long range decay of these is similar for c-Si and a-Si, and similar to decay of density matrix.

\(^{1}\)Especially due to D. Vanderbilt and coworkers “*Maximally-localized WF*”
Local formulation: conclusions

Asymptotically: $\rho(x, x') \sim \exp(-\gamma|x - x'|)$

For c-Si, we get $\gamma = 0.49/\text{Å}$ for c-Si and $0.45/\text{Å}$ for a-Si; not far from Kohn’s estimate: $\gamma = (2E_gm/\hbar^2)^{1/2}$ from a simple argument in 1D!

This expression also works approximately for diamond and silica.

So for a-Si: gross features of electronic structure need $\sim 5$-$6\text{Å}$; 1% accuracy, something exceeding $10\text{Å}$.

Fancy estimate: Taraskin, Elliott and Drabold, PRL 88 196405 (2002)
Locality, continued

- Does the electronic non-locality (measured by $\Lambda$) set the size of valence clusters?
- Decay for amorphous and (locally similar) crystalline phases close [in Si, SiO$_2$, C], despite no long range order for the former.
- Convenient alternative basis to use for quantum mechanical calculations; view as chemical bond in the solid state.