Hidden structure in amorphous solids

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Roadmap

• Methods & Models
• a-Si, a terse review
• a-Si, some new details
• Other materials (a-SiO₂, graphene, β-carotene)
• Discussion
Methods used

- Models: Mostly WWW-type for Si, “Decorate and Relax” for silica.
- Electronic structure, MD simulation -- carried out with SIESTA (local basis *ab initio* density functional code Ordejon, Artacho, and Soler).
Philosophy

• Study real materials using believable models (large and reproducing experiments). Possible for a few systems.

• Disorder intrinsic to atomistic model determines the off-diagonal matrix elements of the Hamiltonian, not a random number generator.
Long and short bonds in a-Si

- Good quality models of a-Si all possess *structural correlations*: Long and short bonds are spatially correlated (connected), *not random*.
- These connected *short* (long) bonds are responsible for the exponential *valence* (conduction) tails in CRN models.
- These structures are a novel form of medium-range order in a-Si.
Example: DTW-512

- A particularly good model of a-Si is the 512-atom computer model of Djordjevic, Thorpe and Wooten\(^1\), fabricated with WWW-method. *No electronic defects, well relaxed, realistic RDF and phonons.*
- FWHM of bond length distribution function is ~0.09Å. The bond lengths are normally distributed.
- Model is 100% fourfold.

Connectivity in DTW-512

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

Strong spatial correlation of long-long, short-short.
Tail states
Bondlength decomposition as function of energy

Messages: 1) valence tail from short; 2) conduction from long; 3) Defects add ‘noise’ – but the pattern is evident nevertheless; 4) Note the symmetry in B(E) about $E_f$, especially for $M_1$.

$M_1, M_2$ – WWW (DTW)
$M_3$-MD (Feldman)
$M_4$-ART (Mousseau)
$M_5$-WWW+xtal
$M_6, M_7$ – RMC (allowing defects)

Electron states near $E_f$

L: Conduction tail states
H: Valence tail states

• 70% of charge shown for each state
Connection to the band tails

- The 512-atom DTW model produces an exponential valence tail (red line):
  \[ \rho(E) \propto \exp(-|E - E_b|/E_U) \]
  \[ E_U \approx 110 \text{ meV (model)} \]
  \[ [\text{a-Si:H } \approx 50 \text{ meV valence } \]
  \[ \sim 25 \text{ meV conduction}] \quad \text{E. A. Schiff} \]
- These states have filamentary/connected topology.
- Damage the filaments, no longer exponential (blue).
The story so far…

• **Short bonds**
  o Tend to be spatially connected
  o Are responsible for the valence band tail
  o Tend to have a fractal dimension greater than 1. Some 3D character.

• **Long bonds**
  o Tend to be spatially connected
  o Are responsible for conduction band tail
  o Tend to be filamentary (1D)
Some new results on a-Si

• Examine topology of short (or long) bond network more closely
• How does the relaxed defect structure depend on how extreme the “defect nucleus” is?
Electrons: are defects ‘filament seeds’?

Electron hair: tail states (violet). The states ‘grow’ from surface of xtal inclusion in CRN.

DOS for c-Si with relaxed divacancy. Filaments are created. Sundari (2004) sees the effect with ion-bombarded c-Si before amorphization.
Decay of bond length anomaly from long or short bonds (*nuclei*)

Short-bond decay

Long-bond decay

Λ: distance from extreme (long or short) bond to normal bonds considering all paths – Λ is range of the strain field
Dependence of $\Lambda$ on shift from mean bond length
Defect radius $\Lambda$

- A crude measure, not well-defined near $\delta r=0$. Also quite “noisy”.
- There is no obvious trend for long bonds. *Longer bond defect center does not mean larger $\Lambda$.*
- For short bonds, tendency for shorter nucleus bond to imply longer $\Lambda$.
- In all cases, $\Lambda < 7\text{Å}$
Cluster size

Number of atoms participating in defect

Bond length of defect “nucleus”
Blobs and filaments: valence states

Other blobs and filaments: Lyman $\alpha$ emission from a giant galaxy ‘string’. Paul Francis, ANU, 2004

Blobs and filaments in solids, not space: J. Dong & DAD PRL 80 1928 (1998)
Si: conclusions

- Shorter bond ‘nuclei’ create clusters of short bonds; local densification. Long bonds, wispy filaments.
- Short bonds can nucleate locally dense regions with range up to ~7Å
- The observed $\Lambda$ is similar to range of density matrix (or most-localized Wannier functions). Does the electronic non-locality (measured by $\Lambda$) set the size of clusters?
- Might there be experimental signatures? SAXS, TEM, FEM
Si: speculations

- 3D Anderson model: at criticality states are multi-fractal with dimension $D \sim 1.3$
  
- Our models are too small to accurately compute $D$ but we surely have:
  
  Filaments: $D$ near 1 on the conduction side
  
  Clusters: $D$ closer to (smaller than) 3 on the valence side
  
  *We link such electronic information to the connectivity/structure of the network. $D$ is unknown for a real material!*

- This must be relevant to electrical conductivity (Kubo-Greenwood):

$$\sigma_{\alpha\alpha}(\omega) = \frac{2\pi e^2}{\Omega m^2} \sum_{ni} |\langle \psi_n | p_\alpha | \psi_i \rangle|^2 \frac{f_F(\varepsilon_i) - f_F(\varepsilon_n)}{\hbar \omega} \times \delta(\varepsilon_n - \varepsilon_i - \hbar \omega),$$

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

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\(^1\)T. Ohtsuk et al., Ann. Phys. 8 655 (1999)
Other materials

- Amorphous graphene
- Silica
- β-carotene
Amorphous graphene

with M. F. Thorpe and V. Kapko

• Graphene is current hot topic. Why not add something really interesting -- disorder.

• Simple cook and quench model with SIESTA.

• What is the structure? Blobs and filaments -- short bonds tend to densely cluster, long tend to be more extended in 1-D.
Amorphous Graphene

Aqua -- short bonds, green ‘normal’, black long
Graphene conclusions

• Somewhat like Si, short bonds tend to cluster in 2D, long bonds are more filamentary

• Short is again associated with valence, long with conduction (*caveat emptor* – the gap is zero so everything is rather extended).
a-SiO$_2$

- Start with 216-atom WWW model, decorate bond centers with O, rescale to density of a-SiO$_2$ and relax$^1$. Dead simple and produces a good 648-atom model. We further refined with SIESTA and highly optimized basis set.

- Nutshell: no nearest-neighbor bond length correlations. However: strong bond angle correlations (and second neighbor bond length correlations).

- Si-O bond length is practically constant.

Representative SiO$_2$ structures

Examples of short R$_{O-O}$ and long R$_{Si-Si}$ clusters in a-SiO$_2$ network. Grey sites represent the defect nuclei.
Defect size vs “nucleus” bond length

\[ N_{cl} \text{ as a function of second-neighbor distances. Vertical lines are mean-distances.} \]
Silica: discussion

- Small $R_{O-O}$ (small $\theta_{O-Si-O}$) leads to larger clusters with 3D character, of characteristic size $\sim 5\text{Å}$.
- Large $R_{Si-Si}$ – leads to more filamentary structures.
- Big variation in $R_{O-O}$ is a serious defect, as $\theta_{O-Si-O}$ lies near $\theta_T$. Variation in $R_{Si-Si}$ more common (since $P(\theta_{Si-O-Si})$ is broader, network “response” to nucleus is weaker).
Silica electrons: bond length decomposition of DOS

Valence tail: short O-O (small $\theta_{O-Si-O}$); Conduction tail: long Si-Si (large $\theta_{Si-O-Si}$)
Silica band edges

\( \alpha \): (from convolution of valence and conduction tails) experiment, around 400 meV (S. C. Cheng, 2005)

Thanks to M. Zhang
Silica electrons

• Valence edge: much weight on oxygen, conduction edge on silicon.

• Note the dramatic asymmetry in localization at tails (valence very localized, conduction barely localized\(^1\)).

\(^1\)Also seen by Sarnthein \textit{et al}., PRL 74 4682 (1995)
β-carotene $\text{C}_{40}\text{H}_{56}$

HOMO (purple) and LUMO (cyan) states correspond to short and long bonds, with mean bond length 1.36Å (1.44Å) for HOMO (LUMO).

Thanks to K. Odbadrakh & James Lewis, WVU.
Conclusions

- Short or long bonds are spatially self-correlated.
- Short or long bonds impact the DOS. In CRN models of a-Si, these create Urbach tails (short bonds, valence edge, long bonds conduction).
- We hope to aid in *engineering* the tails: knowing ‘where they come from’ is a start.
- Results for silica are understandable in same general framework. Seems to be some generality to this picture.