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Studies of Hydrogenated Amorphous Silicon

David A. DRABOLD
Ohio University
Clippinger Research Laboratories
Department of Physics & Astronomy
Athens, OH 45701-2979
U.S.A.

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D. A. Drabold, T. Abtew, F. Inam
Ohio University

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- N. Mousseau, P. A. Fedders (structural models)
- P. C. Taylor, collaboration on interpreting proton NMR measurements

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Roadmap

- Motivation
- Preliminaries: methods and material
- Dynamics of H in a-Si:H
- Light-induced effects (Staebler-Wronski effect)

Technological interest of a-Si:H

TFTs for displays

IR microbolometer
“night vision”

PV applications
Uni-solar

Preliminary: SIESTA

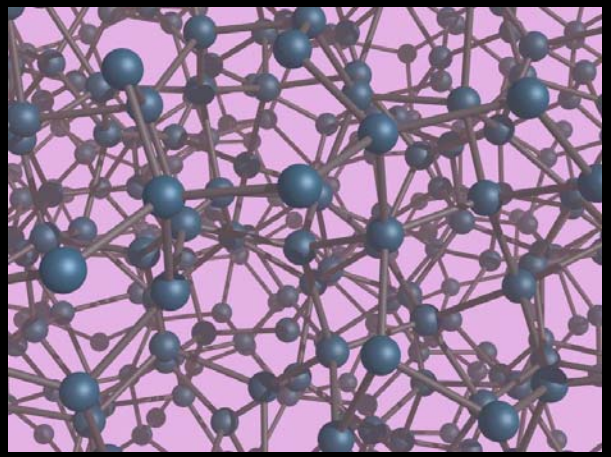
- All these calculations use DFT code SIESTA. Invented by several people here! *Powerful and flexible.*
- Computational approach:

  -standard SC Kohn-Sham (LDA or GGA)

  -norm-conserving pseudpotentials

  -atomic orbitals as basis, arbitrary multiple zeta, polarization orbitals *etc*.

Preliminaries: a-Si



WWW model:
continuous random network.
Mousseau/Barkema

R. Vink, *Thesis* (U. Utrecht) 2000

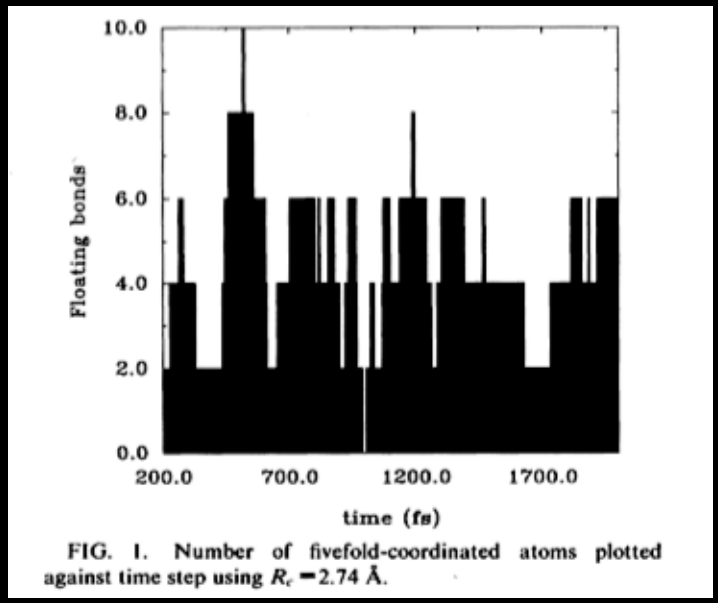


FIG. 1. Number of fivefold-coordinated atoms plotted against time step using $R_c = 2.74$ Å.

N_5(t): 5-fold atoms in 216 WWW cell, 300K.
Coordination Fluctuation: Similar for N_3(t)

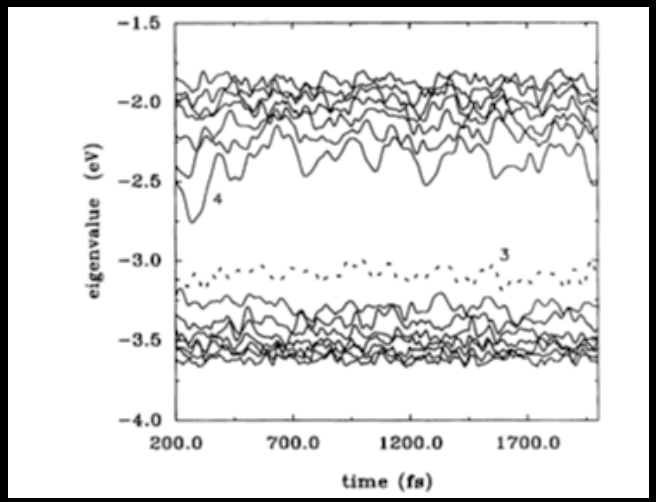
PRL **67** 2179 (1991)

“Coordination fluctuation”

- Involves the entire network.
- Conceptually reminiscent of Phillips/Thorpe floppy modes (though a-Si is certainly *overconstrained* in this language).
- The topology of amorphous network enables structural fluctuations not seen in comparable crystals.

Electronic consequence of thermal disorder

- At 300K as many as 10% of atoms have instantaneous coordination not 4! (PRL '91, unpub. 06)
- Vibrations *strongly* modulate eigenvalues near E_f:



E_f

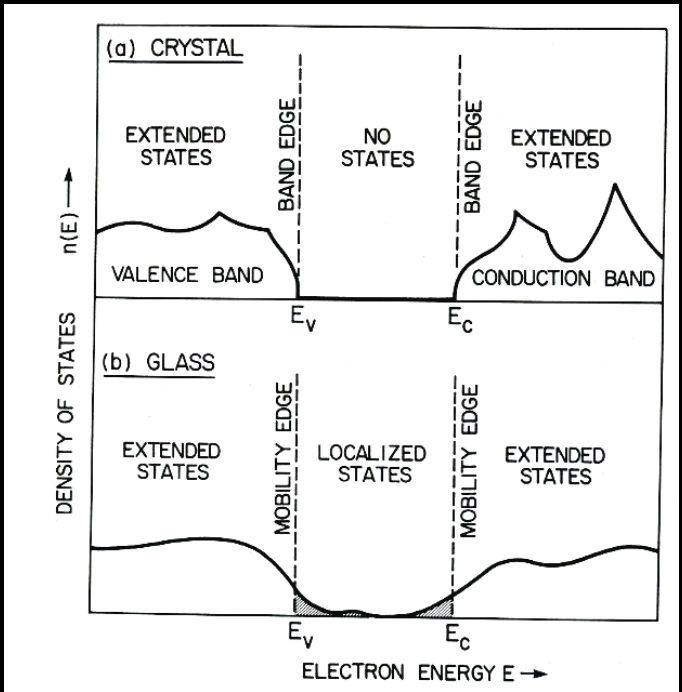
Structure of a-Si:H

- What about the H?
  - It exists in both isolated and clustered states (NMR).
  - Its existence is critical to device grade material.
  - It has a Jekyll-Hyde character: fixes dangling bonds, but player in light-induced degradation.

Models

- We use 138 atom cell with (12% H), reasonable proton NMR second moment (information about H-H distance). *(P. A. Fedders, unpub.)*
- Also use 64-atom defect free a-Si plus H or H_2 *(N. Mousseau ART or WWW).*

Elementary electronic structure



Disordered systems have extended states and localized states (both "band tail" and midgap).

R. Zallen, 1981

Thermal Simulations: H dynamics

- Two 5 ps runs with T=1000K MD, 138 atom cell, no electronic defects at t=0.
  - 1. Fully dynamic lattice
  - 2. Si lattice frozen
- Results in a nutshell:
  - Static Si sublattice: No H diffusion
  - Full simulation: significant H motion, short-time sampling of diffusion mechanism, one dominant.
  - Hints that H_2 plays a serious role on long time scales.

T. Abtew, F. Inam and DAD, PRL (*submitted)*

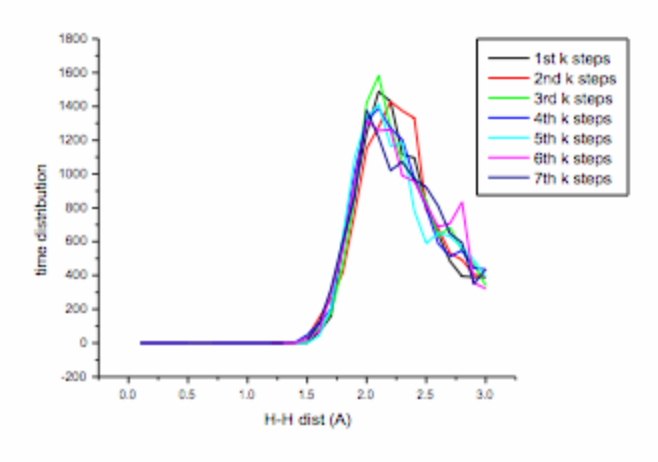
Some details

- Interesting features of a-Si:H involve electronic structure, transport, delicate energetics and H motion: *ab initio* method required.
- Accurate approximations required (polarization orbitals, GGA [PBE 96]).
  No surprise from work of van de Walle and Fedders.
- In our work we employ SIESTA, 5 ps runs, Δt=0.25 fs.

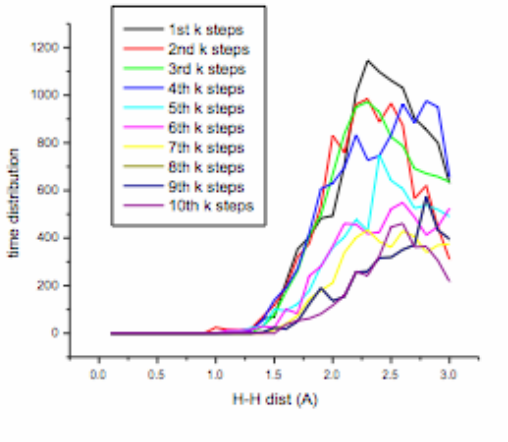
H motion depends upon local temperature

$$\rho(r) \propto \langle \sum_{i \neq j} \delta(r - r_{ij}(t)) \rangle$$

<>: thermal average



300K

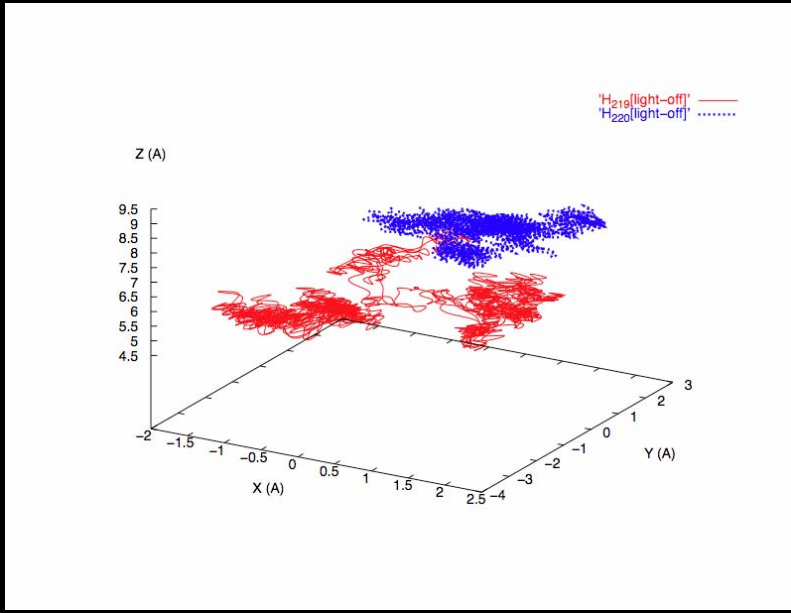


1000K

300K: little change in pair distances, 700C much more.

Hardly a surprise -- high T, more mobile H!

Diffusion

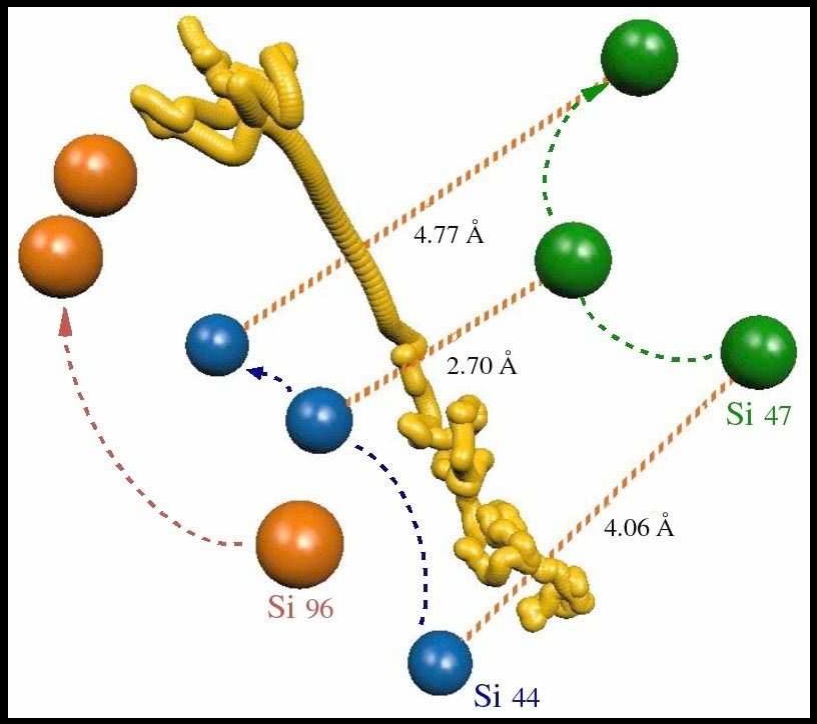


First glance: appears to be “Scher-Lax” hopping, trapping.

Motion of two H atoms (10ps, 300K)

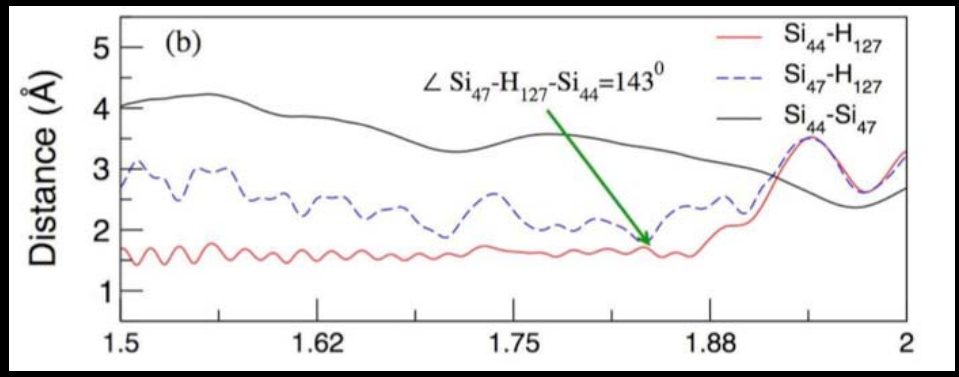
H dynamics: Fluctuating Bond Center Detachment "FBCD"

Converting bonded H to diffusing H

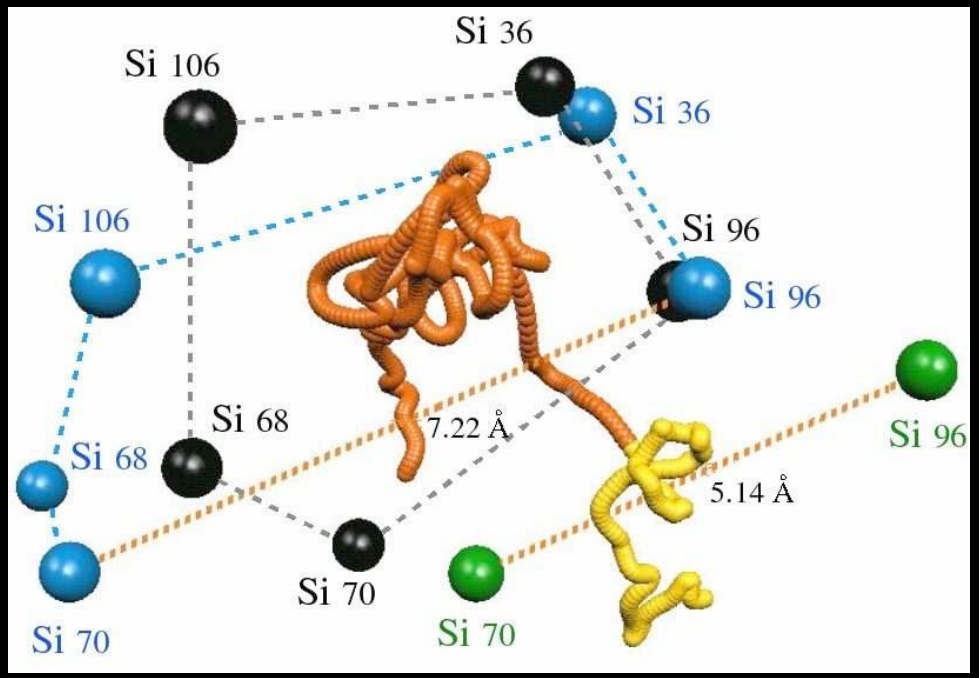


Explicit example. Yellow: path of H_{127}

1. H passivates DB on Si_{44}
2. H becomes BC when Si_{47} "transits"
3. BC H hops, bonds to Si_{96}



Interesting and rare: H_2 formation



Worms: Hydrogen
Yellow: H_{122}, Orange:H_2 (molecule)

- H Hops from BC(Si_{70}-Si_{96}); forms H_2
- H_2 hops to pentagonal center, diffuses.

Comment: rare, obviously. Yet a strong hint that H_2 may be key player for longer times (P. A. Fedders, 2000).

Statistics ?

- In 25 bond breaking events, 22 are FBCD.
- 3 are *Floating Bond Assisted* Diffusion.
- FBCD is more common and more general.

*Y. Su et al, PRL **88** 165503 (2002).*

Picture of H diffusion

- The FBCD mechanism generates free atomic H.
- Such H is quickly trapped by Si-Si bond center sites or other reactive sites such as dangling bonds.
- H in BC sites is driven to hop from motion of silicon network. Toy model shows that thermal fluctuations “squeeze” the BC H out.

H dynamics: conclusions

- “Coordination fluctuation”, a characteristic of “amorphous topology” at T>0 enhances FBCD diffusion mechanism, which dominates for short (several ps) times.
- Preliminary work suggests importance of H_2 (under study).
- FBCD provides free H (and dangling bonds!); hard to understand the energetics of breaking passivating H in other ways.

Light-induced effects

- A limiting factor in utilizing a-Si:H photovoltaics is light-induced device degradation. *Staebler-Wronski Effect -- ca. 20% reduction in PV efficiency due to light-induced trap formation.*
- The electron-lattice coupling plays a key role.
- A few key experiments:
  - NMR suggests that H-H distance of d=2.3±0.2Å created by light soaking (Su *et al*)
  - H motion is stimulated by light soaking (Isoya et al)
  - Defects (dangling bonds) are created by light soaking (Staebler-Wronski).
  - Its *very* nonlocal: “Up to 1000 H atoms are significantly displaced for each new light-induced defect” (Norberg ‘91)

Preliminary/Aside: Electron-lattice coupling is large for localized states

- Hellmann-Feynman theorem and harmonic approximation lead easily to expression for fluctuations in electronic eigenvalues:

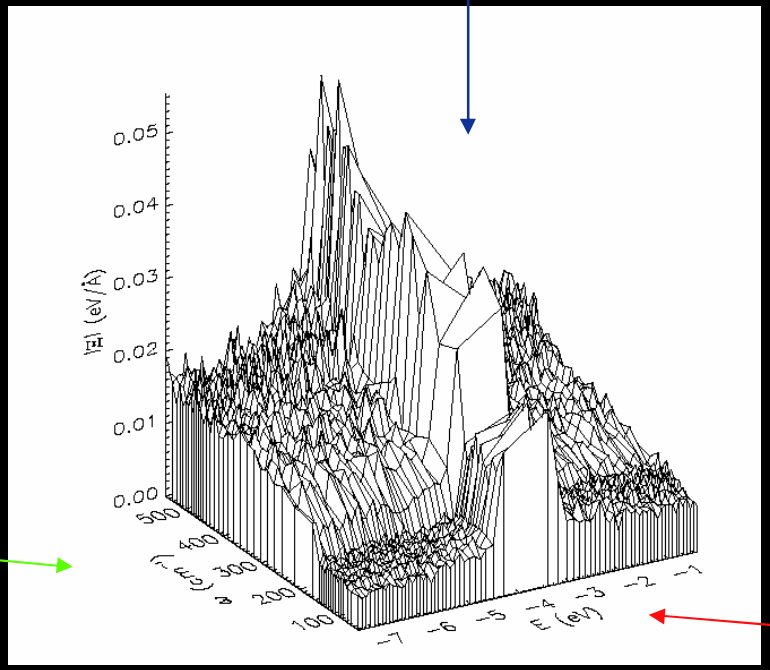
$$\langle \delta\lambda_n^2 \rangle = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau dt\, \delta\lambda_n^2(t) \approx \left(\frac{3\mathrm{k_B T}}{2\mathrm{M}}\right) \sum_{\omega=1}^{3\mathrm{N}} \frac{\Xi_\mathrm{n}^2(\omega)}{\omega^2},$$

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

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

E-Fermi

E-P coupling



Phonons

Electrons

216 atom WWW Model, SIESTA DZP

Atta-Fynn *et al*, PRB **69** 254204 (2004)

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

The coupling between electron n and phonon ω

Comments

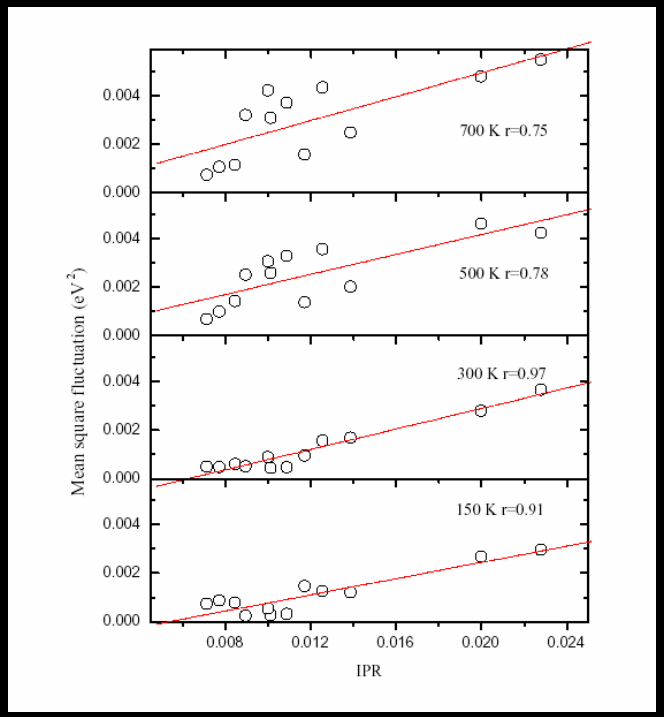
1. Large e-p coupling for localized states near the gap.
2. For *localized* states, simple algebra leads to the conclusion that:
   a) Ξ^2 [for eigenvalue n] ~ *IPR* [n]
   b) $\langle \delta\lambda^2 \rangle$ ~ IPR
3. Expect significant effects on conductivity.

IPR = inverse participation ration; simplest measure of localization

Thermal MD supports simple calculation

$\langle \delta\lambda^2 \rangle$ →

(T>0 property)



700K

500K

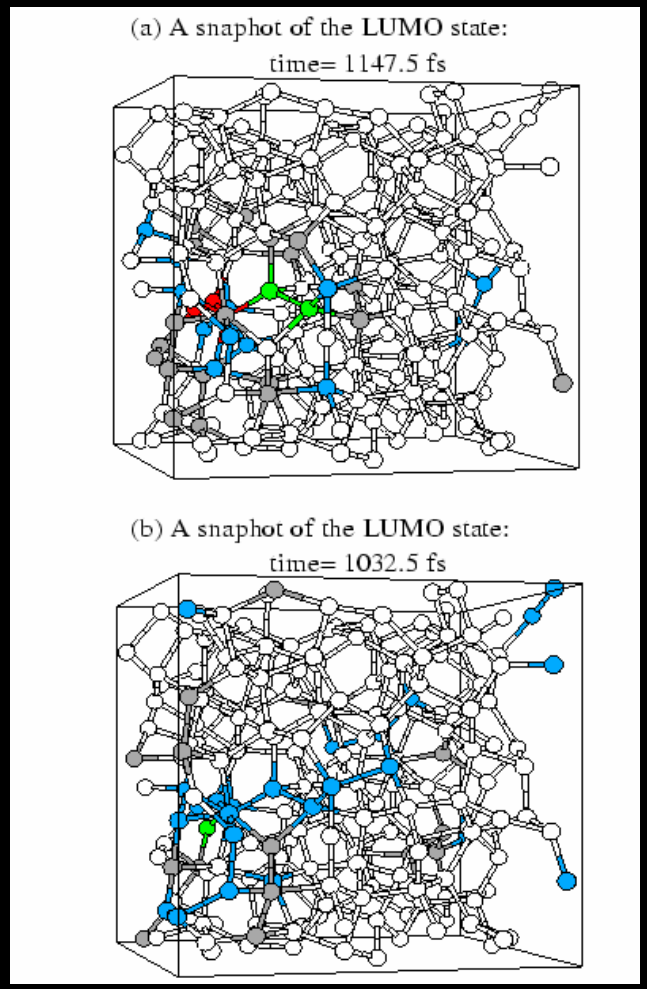
300K

150K

Localization (T=0 property)

Fits analytic result for low T

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



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[1] 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.

[1]J. Dong and DAD, PRL **80** 1928 (1998); J. Ludlam *et al*, JPCM **17** L321 (2005)**.**

Light: Discussion

- There is little certain about the theory of light-induced effects. Many models.
- Light-induced structural changes are mediated by the electrons (e-p coupling).
- Approach in two steps:

1. The sharply defined nature of the 2.3Å feature suggests the existence of a particular conformation. *Try to determine it.*
2. Consider local rearrangements due to changes in occupation of well-localized states.

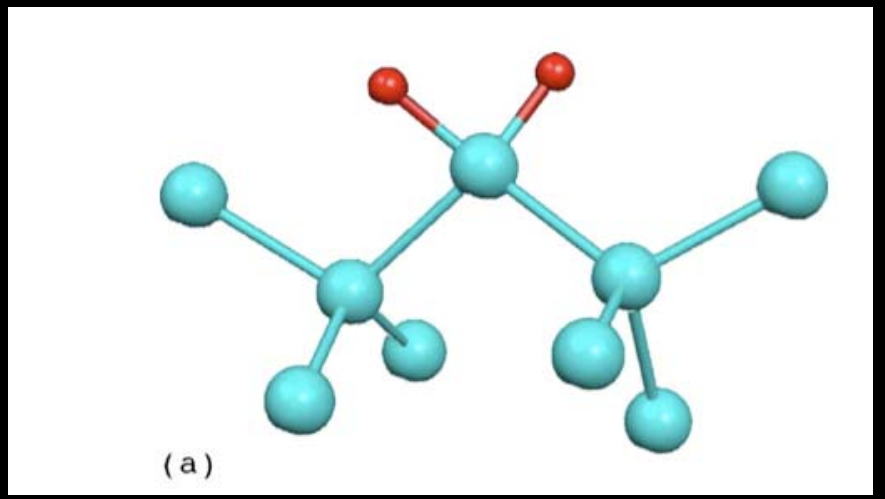
2.3Å separation: SiH_2 is a plausible answer

- We tried various possibilities. In the solid state, the simplest (SiH_2) produces a mean proton-proton separation of 2.39Å. DZP basis and PBE were required.
- SiH_2 was made surgically: H added at four different sites, dangling bonds passivated and the system annealed and relaxed. Starting point was Mousseau 64-atom defect-free cell.

Model *a*SiH–72

Configurations	H–H distance before relaxation (Å)	H–H distance after relaxation LDA (SZ) (Å)	LDA (DZP) (Å)	GGA (DZP) (Å)
1	1.61	2.39	2.35	2.34
2	2.20	2.59	2.51	2.46
3	2.35	2.34	2.33	2.32
4	3.29	2.56	2.47	2.44
Average		2.47	2.42	2.39

APL **86** 241916 (2005)



A direct approach?

- Since the electron-lattice coupling is large for localized states, occupation changes involving these states causes *local heating* near sites upon which the state is localized.
- Such heating is concentrated in defective part of system.
- *The plea: reasonable excited states, picosecond simulations on >100 atoms!*

Change charge states

- In small cell with simple Harris functional code, changed defect (DB) charge states and saw non-local changes in cell. Fedders, Fu, DAD PRL 68 1888 (1992)
- Have repeated this in a-Si:H with modern Hamiltonian and models, find enhanced H motion, defect creation and even SiH_2 formation.

Light-induced *vs* Thermal

does light just make heat?!

- Light
  - Creates protons separated by ~2.3Å (E)
  - Creates new defects, on average well separated from pre-existing dangling bonds (E)
  - SiH_2 in solid state seems to match NMR. (T/E)
  - Enhances H motion. (E)

- Heat

–Thermal motion “frees” some H from bond-saturation role. (T)

–There is substantial H diffusion in the network for 1000K. (T)

–SiH_2 is observed at high T, starting from system with only defect-passivating H (T).

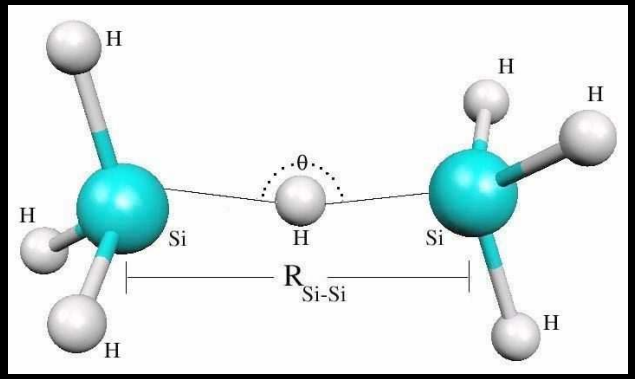
Discussion

- It is tempting to suppose that light-induced occupation change induces local heating and thus enhanced H diffusion, defect formation and SiH_2.
- More work is needed on the pathway to form SiH_2, associated energetics, also more accurate methods.

Conclusions

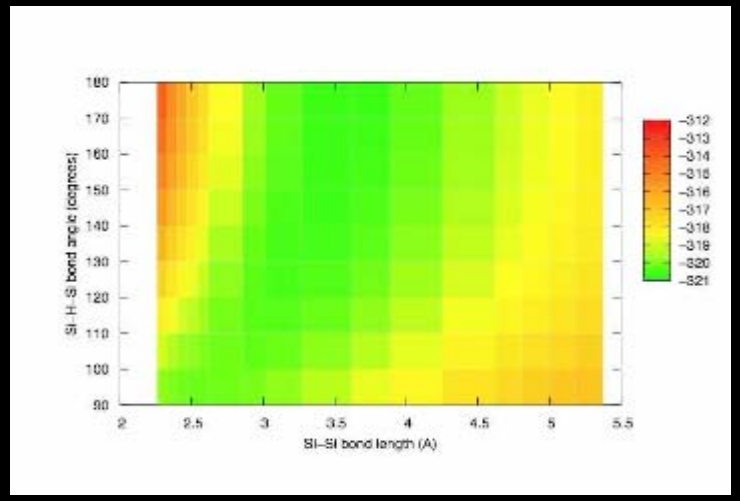
- H motion is an interesting story in a-Si:H -- driven by some unexpected mechanisms.
- It appears that SiH_2 may be a product of light exposure, further accurate and direct simulations are needed.

Toy model



Lets work out the energetics of BC H in the simplest model imaginable. Compute total energies as function of R and ∪. Si lattice motion modulates the energetics. Use SIESTA.

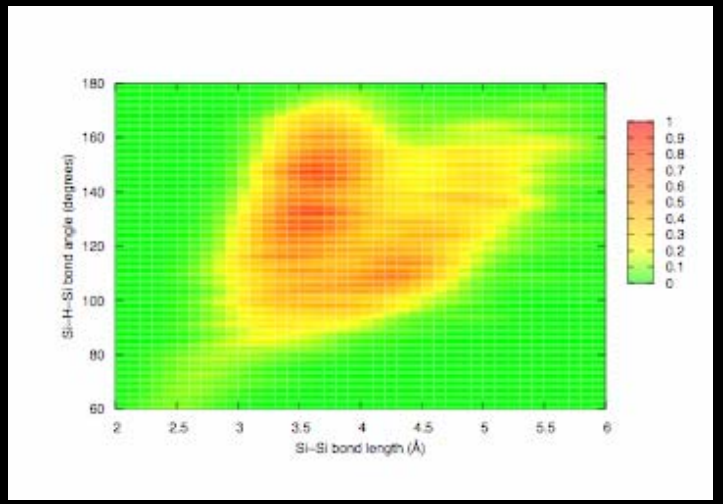
Toy model: results



U

R

Total energy of toy model. Green: most attractive. If Si-Si bonds become too short or long, H binding weakens. Network dynamics affects this!

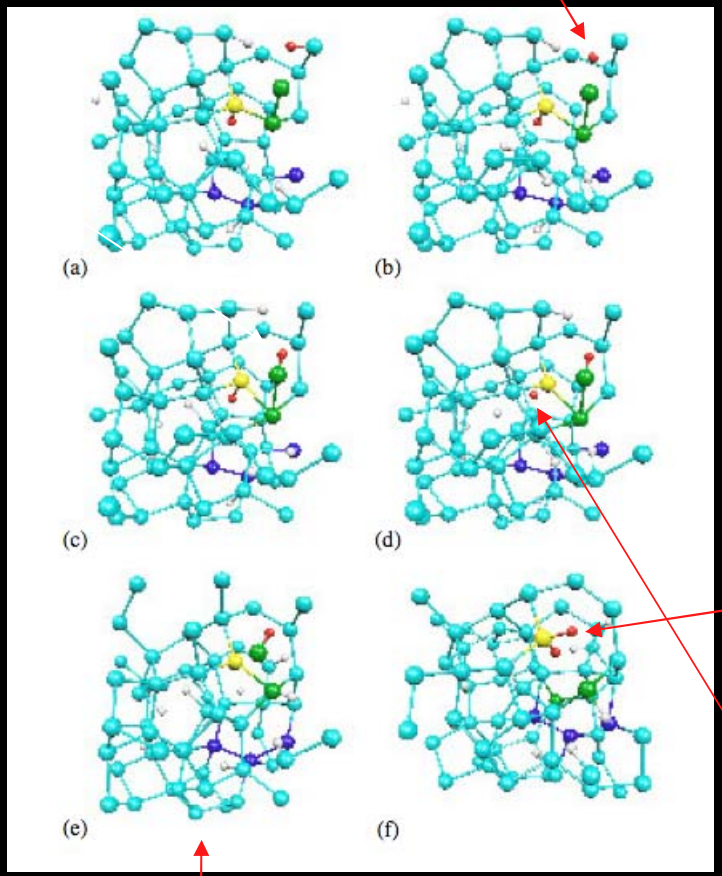


U

R

Temporal distribution for real MD run with 138-atom model. Note that the “real” system prefers configurations favorable to toy model.

Simulations in the light-excited state: an example



a.Original network
b.H dissociates, makes DB
c.Mobile H attaches to a DB
d.Other (red) H shifts
e.Rearrangements near defects
f.SiH_2 formed

SiH_2 -- final state

TA,DAD JPCM '06