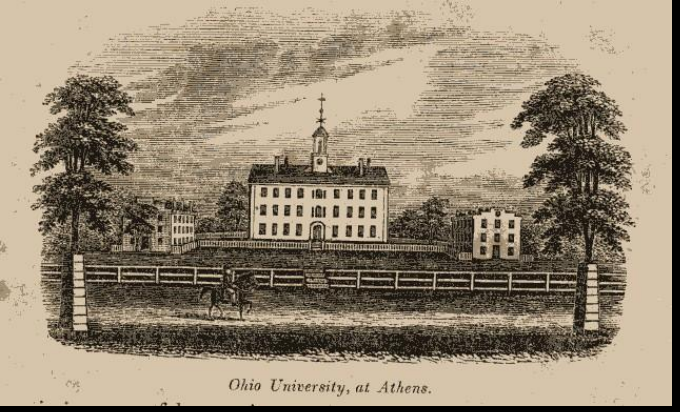


Simulations of Hydrogenated Amorphous Silicon

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

Ohio University

ICTP January, 2007

Acknowledgements

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

Funding: ARO/MURI and NSF

Roadmap

- Motivation
- Structure of network
- Coordination fluctuation
- 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”

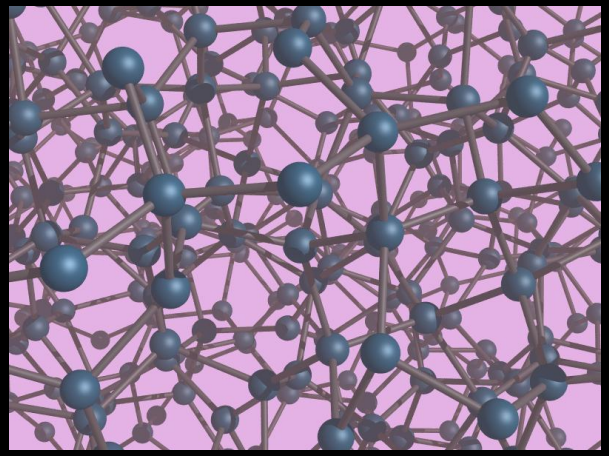
$

Its cheap

PV applications

Uni-solar

Preliminaries: a-Si



WWW model:
continuous random network

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

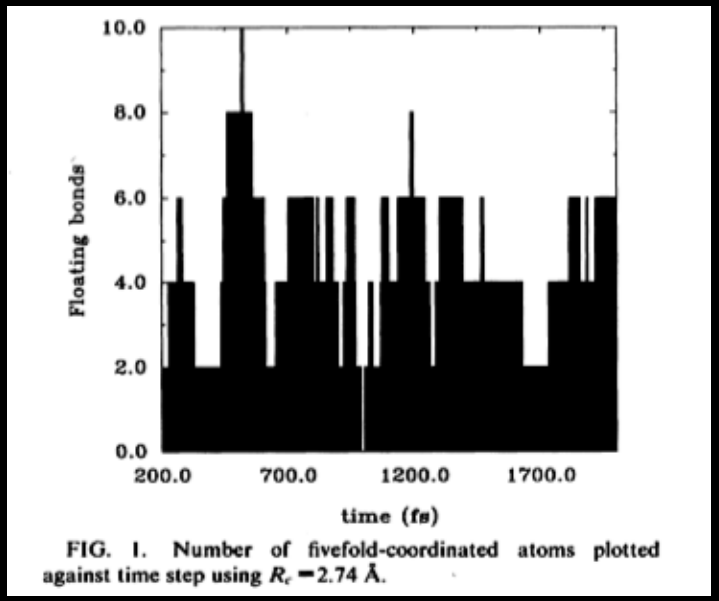


FIG. 1. Number of fivefold-coordinated atoms plotted against time step using $R_c = 2.74$ Å.

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

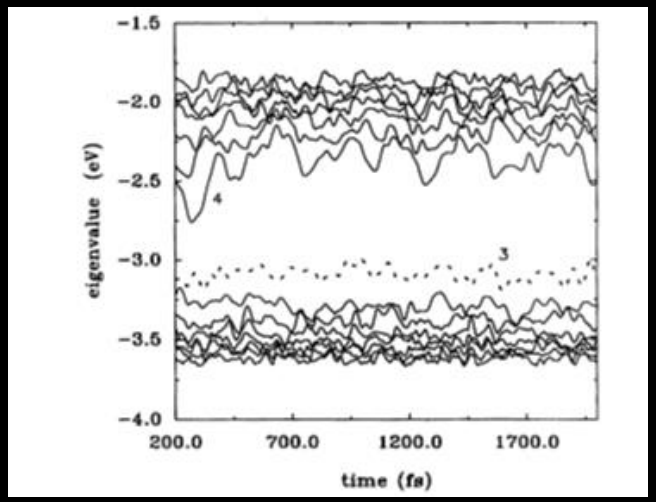
PRL **67** 2179 (1991)

“Coordination fluctuation”

- Involves the entire network.
- Conceptually reminiscent of Thorpe’s floppy modes (though a-Si is certainly *overconstrained* in Thorpe’s 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[1]! (PRL '91)
- Such fluctuations modulate eigenvalues near E_f:



E_f

[1]confirmed in recent calculations: TA,DAD (2006)

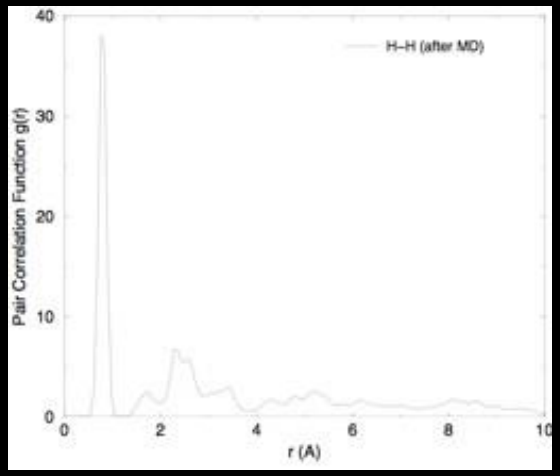
Structure of a-Si:H

- Best models of a-Si are from WWW method: Monte Carlo with special “bond-switching” moves and Keating springs. Such models agree with structural, dynamical, and optical experiments. *Mousseau showed that WWW moves are “real”.*
- What about the H?
  - It exists in both isolated and clustered states (NMR).
  - Its existence is critical to device grade material.
  - 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), state free optical gap. (P. A. Fedders, unpub.)
- Also use 64-atom defect free a-Si plus H or H_2 (N. Mousseau *ART or WWW*).

H pair correlation function



H-H pair correlations

Not experimentally measured, but appears to be reasonable, and proton NMR second moment is acceptable (both clustered and dispersed H).

Thermal Simulations

- 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)*

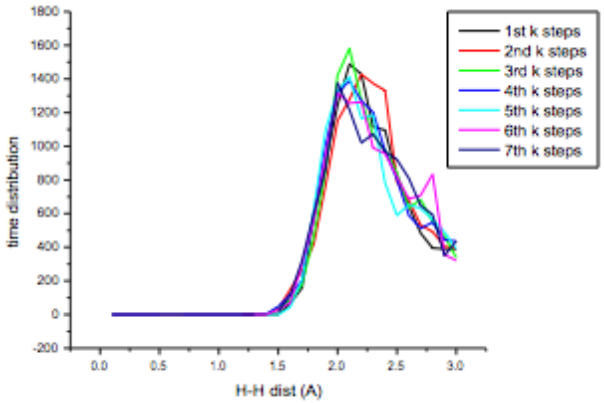
Some details

- 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, ⊗t=0.25 fs.

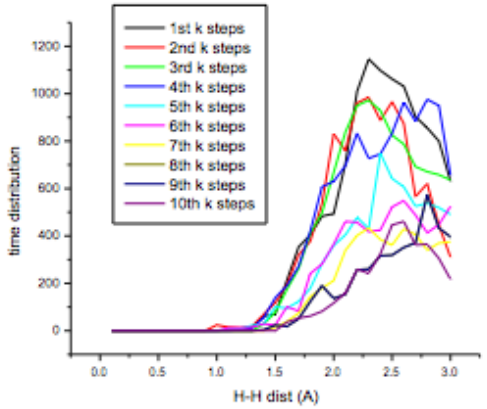
H motion depends upon local temperature

$$\rho(r) = \left\langle \sum_{i \neq j} \delta[r - r_{ij}(t)] \right\rangle$$

<>: thermal average



300K

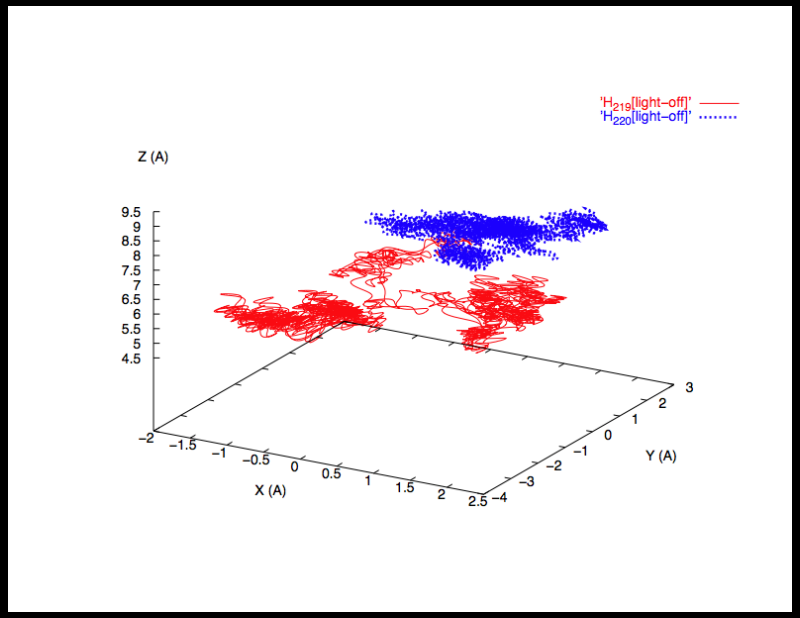


1000K

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

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

Diffusion

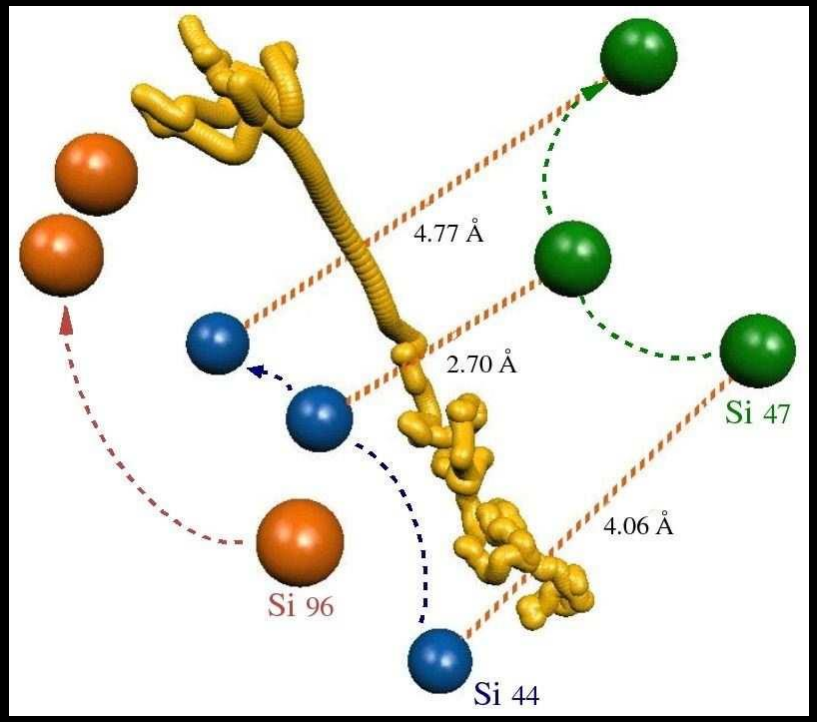


First glance: appears to be “Scher-Lax” hopping, trapping.

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

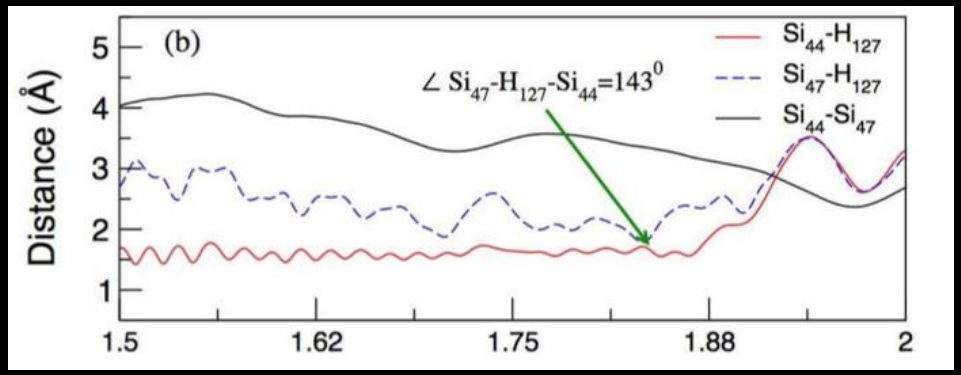
H dynamics: Fluctuating Bond Center Detachment "FBCD"

Converting bonded H to diffusing H

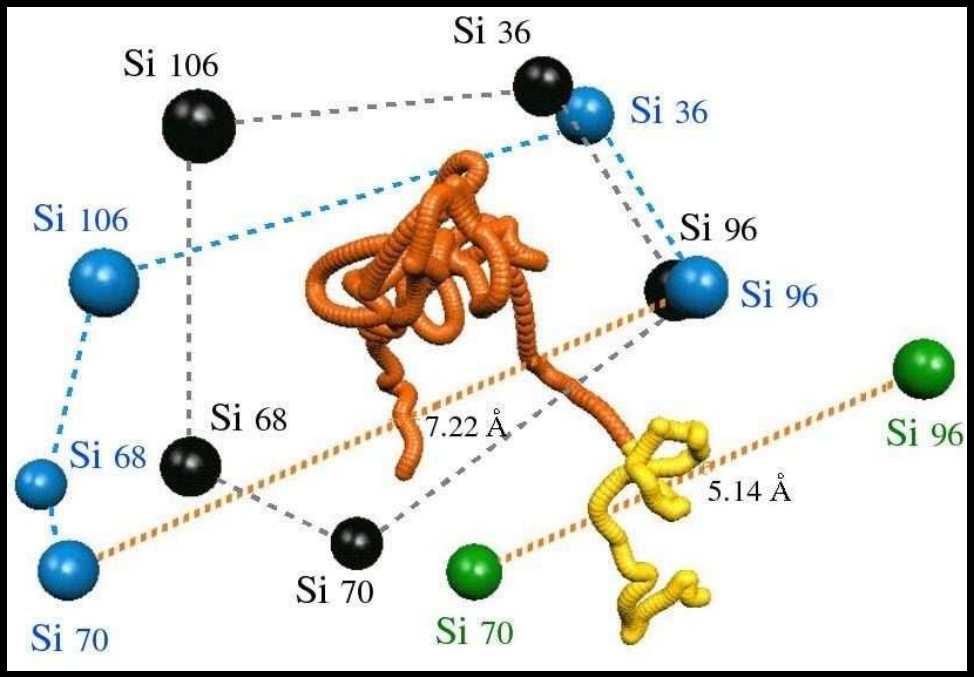


Explicit example. Yellow: path of H_{127}

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



Fun but 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 Su/Pantiledes Floating Bond assisted Diffusion.
- FBCD is more common and more general.

*Y. Su and S. Pantelides, PRL **88** 165503 (2002).*

H dynamics: conclusions

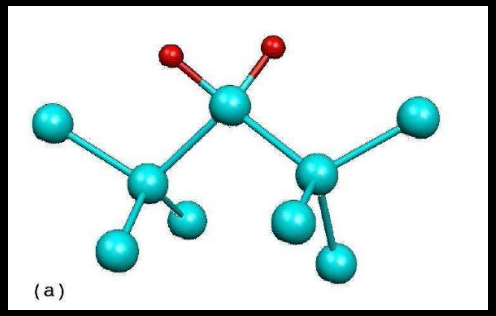
- Motion of Si “sublattice” critical to driving H motion. Toy model substantiates this. F. Buda *et al.* PRL **63** 294 (1989).
- “Coordination fluctuation”, a characteristic of “amorphous topology” at T>0 enhances FBCD diffusion mechanism, which dominates for short (several ps) times.
- Preliminary 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

- Key limiting factor in utilizing a-Si:H photovoltaics is light-induced device degradation. *Staebler-Wronski Effect*
- 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).

Experimental hint: The mysterious 2.3Å

- Taylor: proton NMR shows preferential creation of inter-H separation of 2.3Å
- Its sharply defined, and reproducible: hard to believe its not from a well-defined conformation.
- Fact: Simplest possibility, SiH_2 has about the H-H distance (DZP+PBE required)!



d_{HH}=2.39Å averaged over several conformations.

TA,DAD, P. C Taylor APL **86** 241916 (2005)

Background: Electron-phonon coupling is large for localized states

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

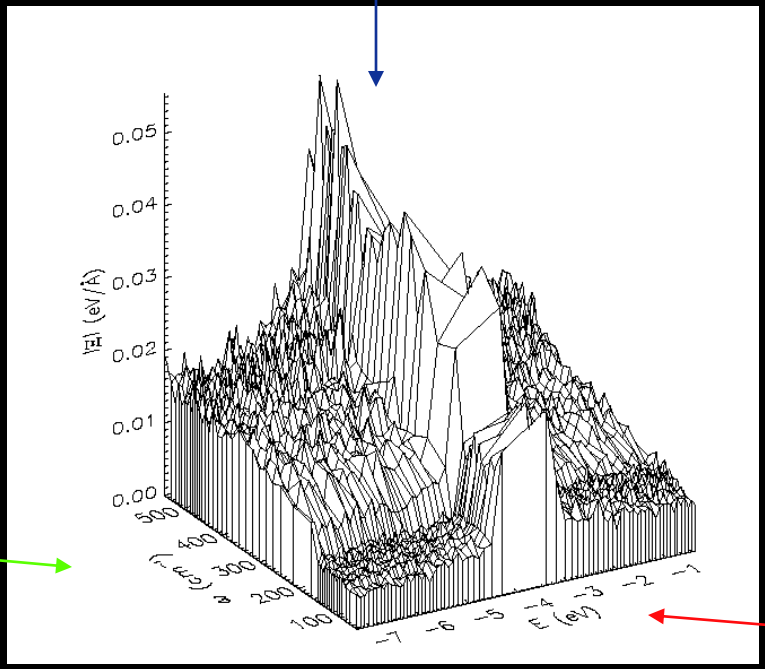
$$\langle \delta\lambda_n^2 \rangle = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau dt\, \delta\lambda_n^2(t) \approx \left(\frac{3k_B T}{2M}\right) \sum_{\omega=1}^{3N} \frac{\Xi_n^2(\omega)}{\omega^2},$$

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

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

Interpretation

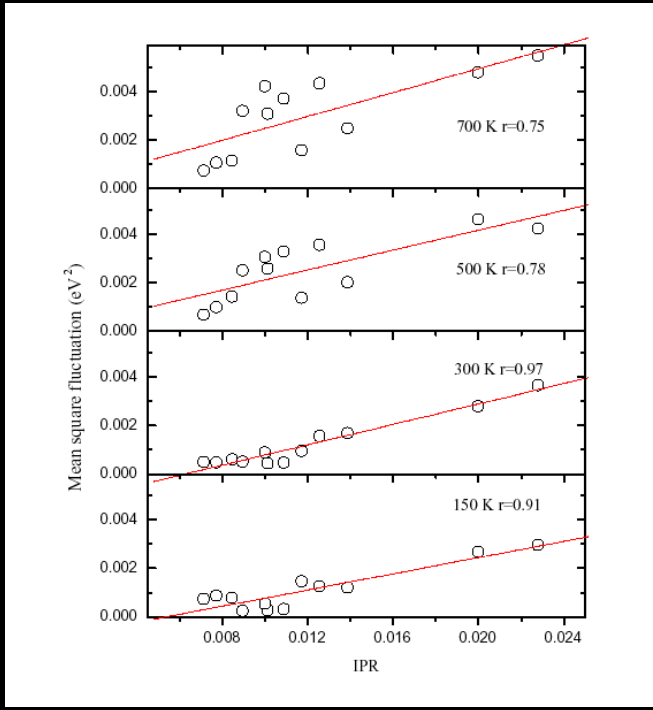
1. Large e-p coupling for localized states near the gap.
2. For localized states, simple algebra leads to the conclusion that:
   a) Ξ^2 [for eigenvalue n] ~ IPR [n]
   b) $\langle \delta\lambda^2 \rangle$ ~ IPR

IPR = inverse participation ration; simplest measure of localization

Thermal MD supports simple calculation

$\langle \delta\lambda^2 \rangle$ →

(T>0 property)



700K

500K

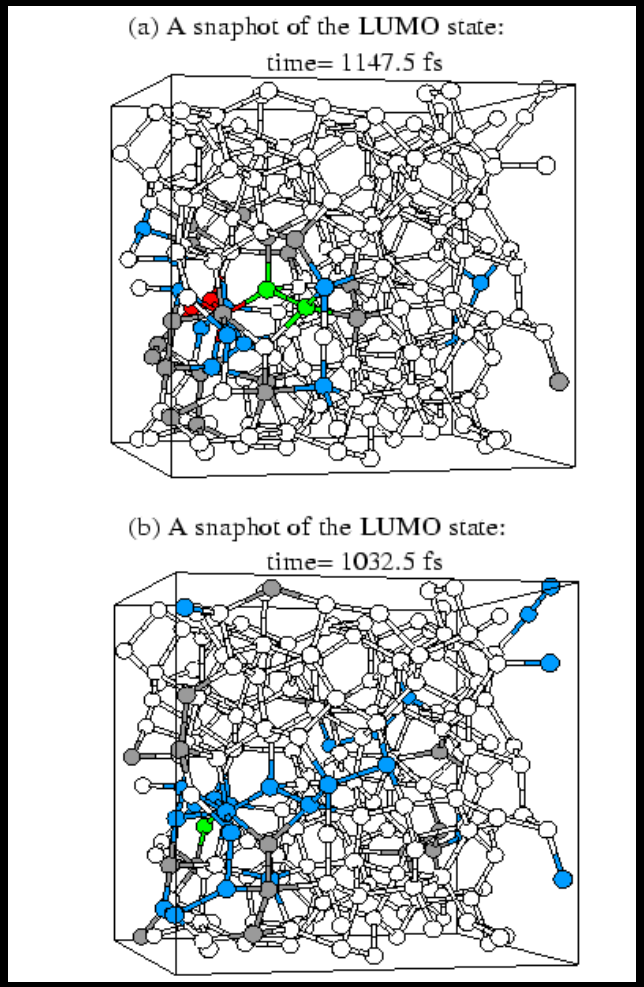
300K

150K

Fits analytic result for low T

Localization (T=0 property)

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).

A simple, direct approach to light-induced changes

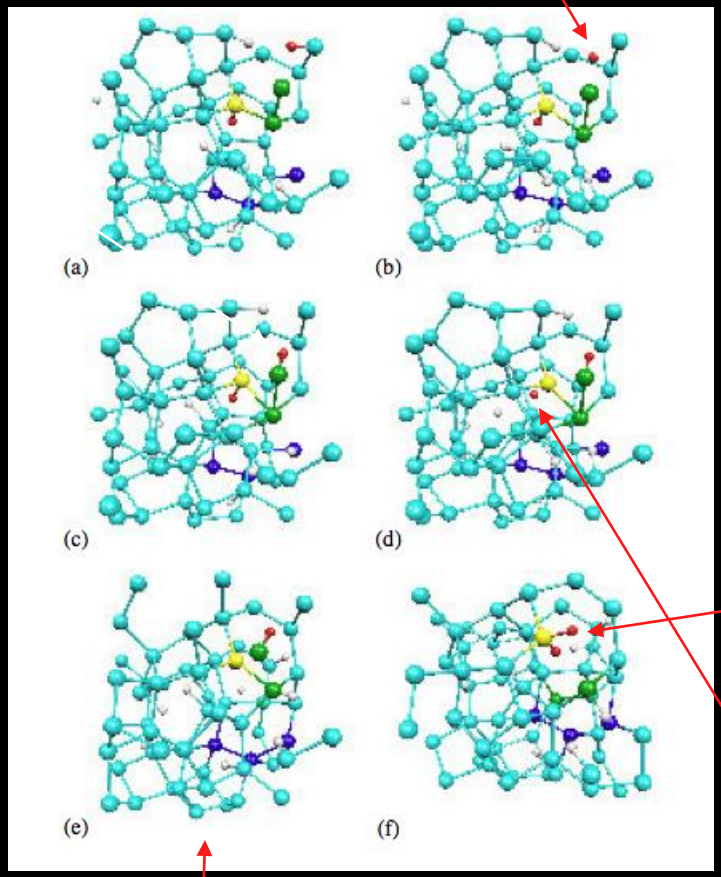
- It is *difficult* to do this right (time dependence, EM field, real excited states, lots of atoms…)
- We use unoccupied Kohn-Sham orbitals; Hellmann-Feynman forces associated with occupation change modify the dynamics.
- Has been helpful in a-Si, a-Se, g-As_2Se_3
- Simulation times are **short**: *ca.*10 ps

Logic

Change the charge state of a well-localized defect. If we add an electron and the highest occupied state is n, then for Hamiltonian *H*, The change in the interatomic force is a Hellmann-Feynman derivative:

$$\Delta F_\alpha = < n+1 | -\partial H / \partial R_\alpha | n+1 >$$

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

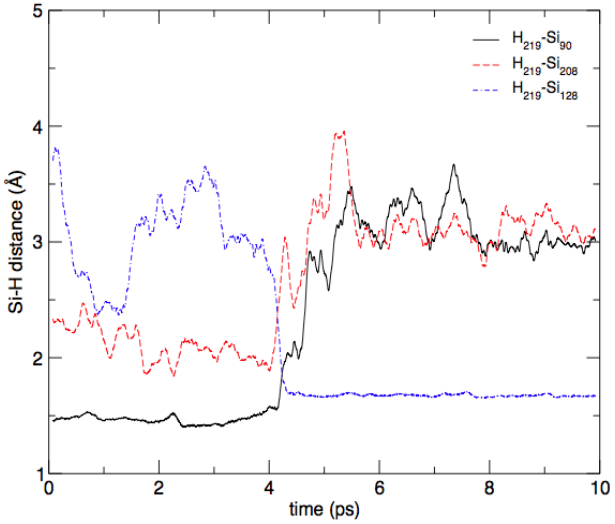
Comments on procedure

- Only expect this to work if *localized* states are involved (electron-phonon coupling is large for localized states). Network is “locally heated” near defects causing localized states (Zhang and DAD, PRL 2000, Li and DAD PRL 01).
- FBCD is induced by Si lattice motion. *Anything* inducing this (including local heating from electron suffering occupation change) causes increased H diffusion (as experiments of Isoya *et al*.).

Discussion

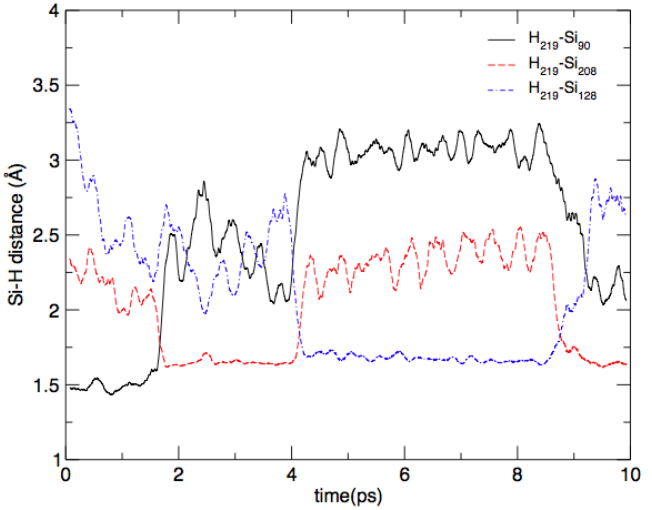
- In light-excited state, enhancement of SiH_2 formation.
- Same effect in 223 atom cells, similar approximations.

Trapping, diffusion: ground and excited states



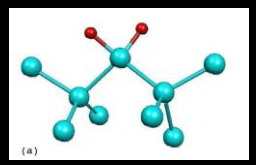
Ground state:
One BB event

Excited state:
Four BB events



Light-induced *vs* Thermal

- Light
  - Creates protons separated by ~2.3Å (E)
  - Creates new defects, on average well separated from pre-existing dangling bonds (E)
  - Dark anneal required to get rid of defects (E)
  - "excited state" MD leads to SiH_2 (T)



•Heat

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

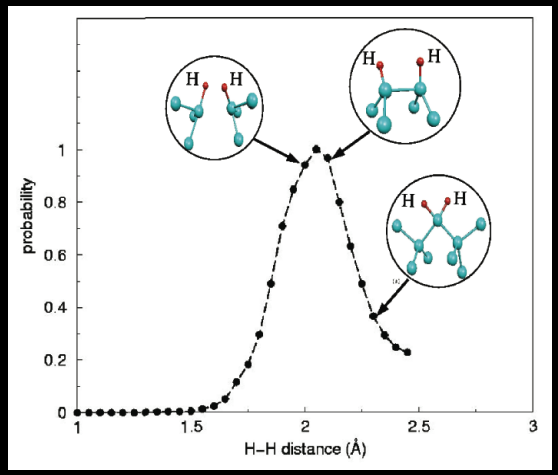
–There can be substantial H diffusion in the network for 1000K. (T)

–Light causes "local heating" near defective parts of network. (T)

So what?

- SiH_2 rare at 300K, not uncommon at 1000K.
- “pre-existing” [non-light-induced] proton-proton distance smaller (~1.8Å). [Taylor] *Other* dihydride conformations:

Distribution of configurations



Radical conjecture: **Light makes SiH_2**. Other dihydrides are associated with the ground state. SiH_2 is a signature of the Staebler-Wronski effect. Note: unproven, but evidence is consistent with the idea.

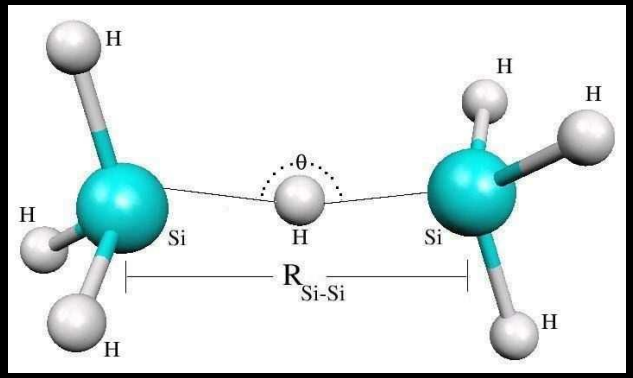
Discussion/Questions

- Local heating from changing charge state of localized states enhances motion, increases likelihood of FBCD events.
- Can fs optical spectroscopy validate/annihilate “coordination fluctuations”? *(C. Taylor).*
- **WHY** is SiH_2 formed in the excited state? *Chemistry of excited state* or *local heating and preferred SiH_2 energetics?*

Conclusions

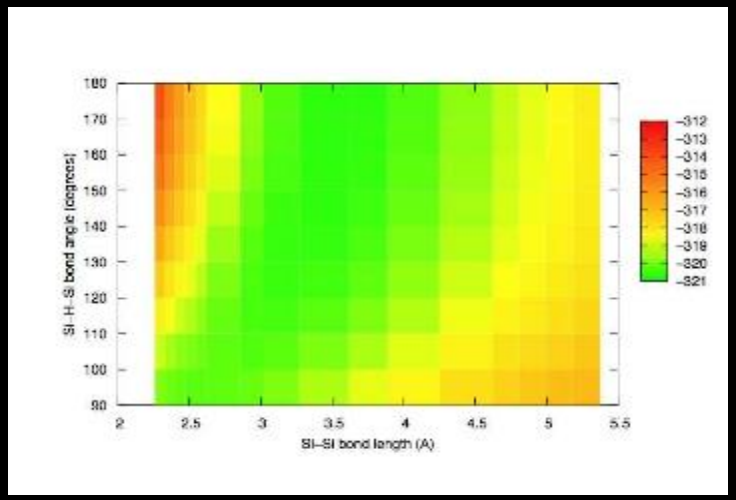
- H motion is an interesting story in a-Si:H -- driven by some unexpected mechanisms.
- a-Si:H is a completely different story than diamond, at least for short times.
- Perhaps the role of light is to preferentially create SiH_2!

Toy model



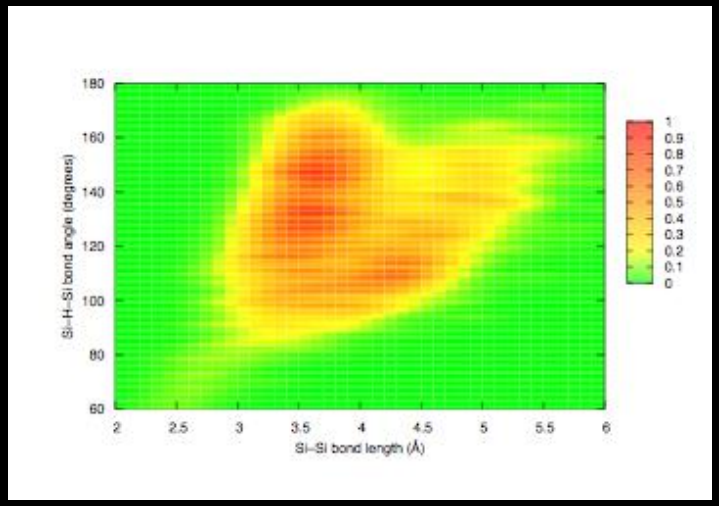
Lets work out the energetics of BC H in the simplest model imaginable. Compute total energies as function of R and $\cup$. Si lattice motion modulates the energetics. Use SIESTA.

Toy model: results



U

R



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!

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