1.021, 3.021, 10.333, 22.00 : Introduction to Modeling and Simulation : Spring 2012

Part II – Quantum Mechanical Methods : Lecture 11

A Bit More Solar PV, Some V&V and a Few Concluding Thoughts

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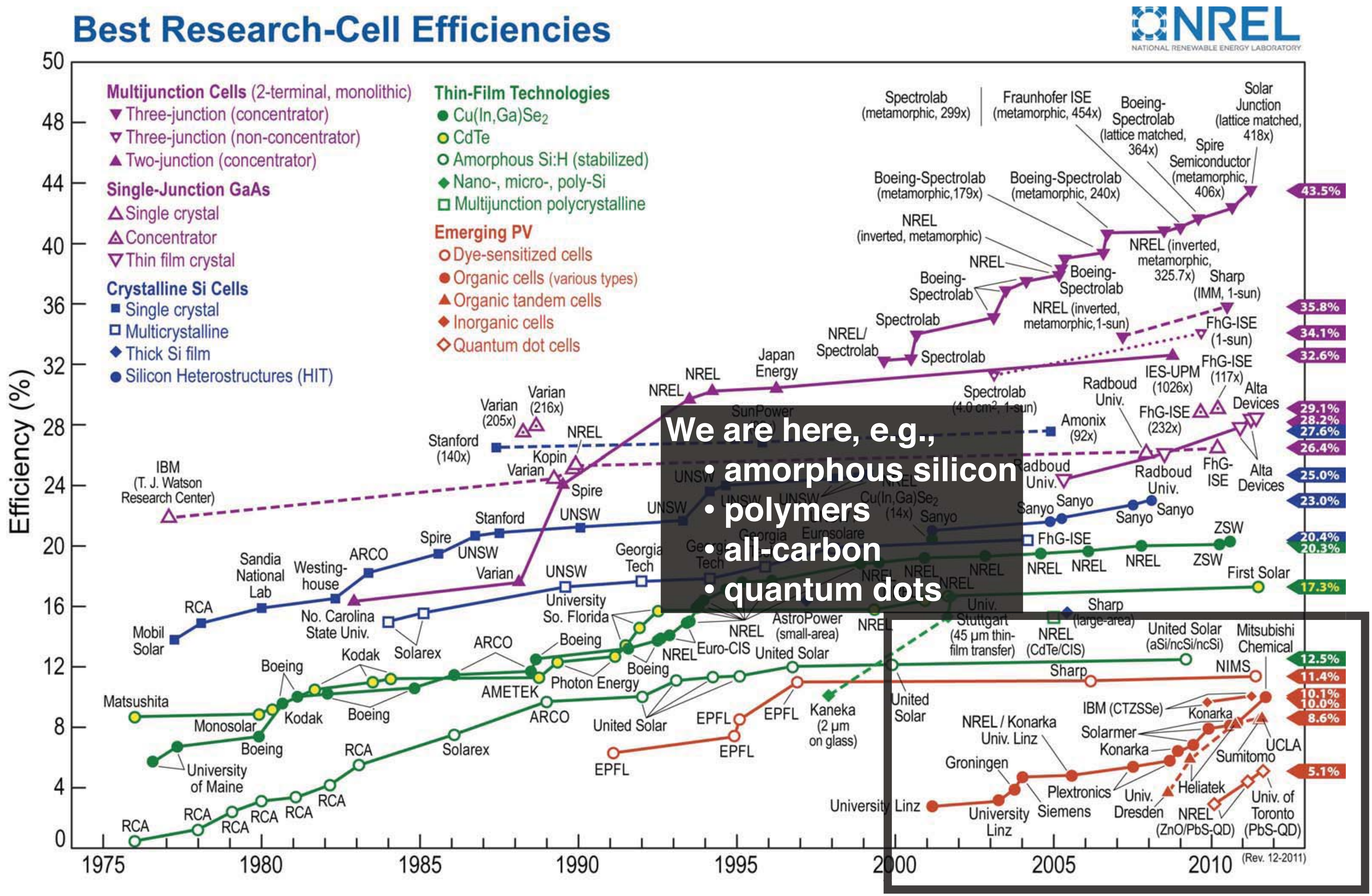
Part II Topics

1. It’s a Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. From Many-Body to Single-Particle; Quantum Modeling of Molecules
4. Application of Quantum Modeling of Molecules: Solar Thermal Fuels
5. Application of Quantum Modeling of Molecules: Hydrogen Storage
6. From Atoms to Solids
7. Quantum Modeling of Solids: Basic Properties
8. Advanced Prop. of Materials: What else can we do?
9. Application of Quantum Modeling of Solids: Solar Cells Part I
10. Application of Quantum Modeling of Solids: Solar Cells Part II
11. Some PV, Some V&V and Some Concluding Thoughts

Outline

- Some more PV
- Verification and Validation
- A few more thoughts

Comparison of PV Technologies



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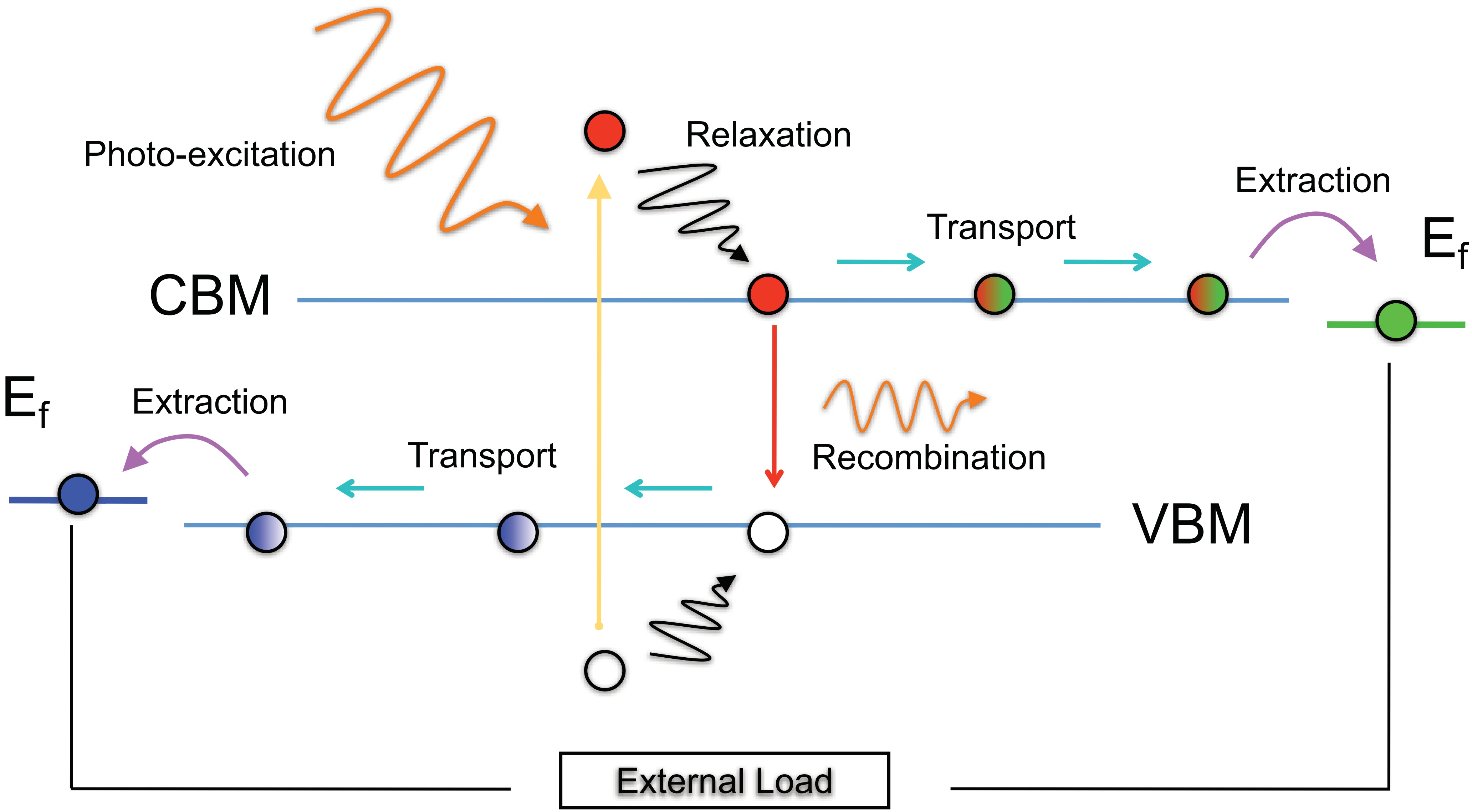
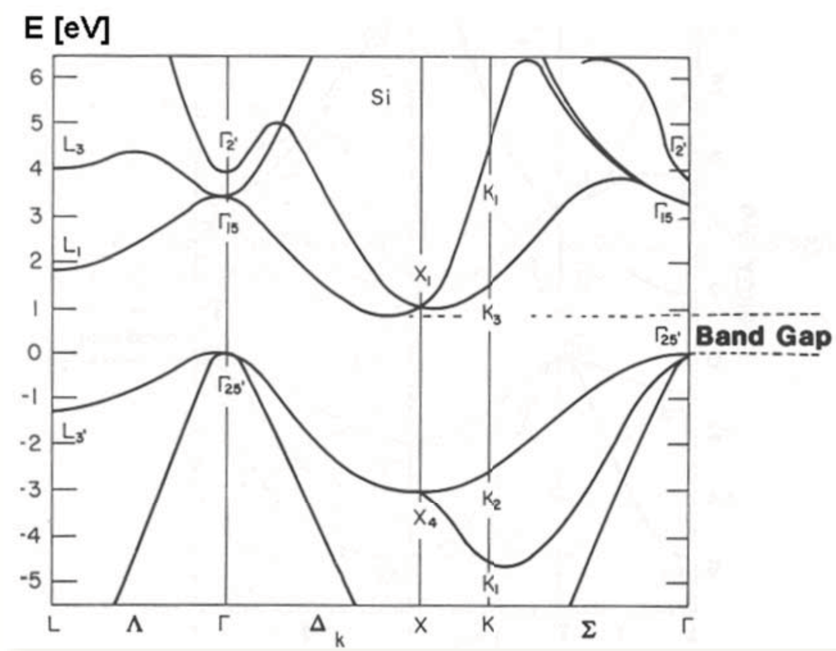
Fundamental Processes Involved in Solar Photovoltaics: Electron's View



Crystalline Silicon Solar PV (80% of current market)

- Light Absorption
  - Band Gap
  - Band Structure



- Electron/Hole Transport
  - Electron/Hole Mobilities

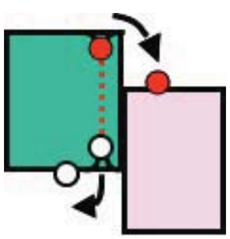
$$\sigma = e^2\tau \int \frac{d\mathbf{k}}{4\pi^3}\left(-\frac{\partial f}{\partial E}\right)\mathbf{v}(\mathbf{k})\mathbf{v}(\mathbf{k})$$

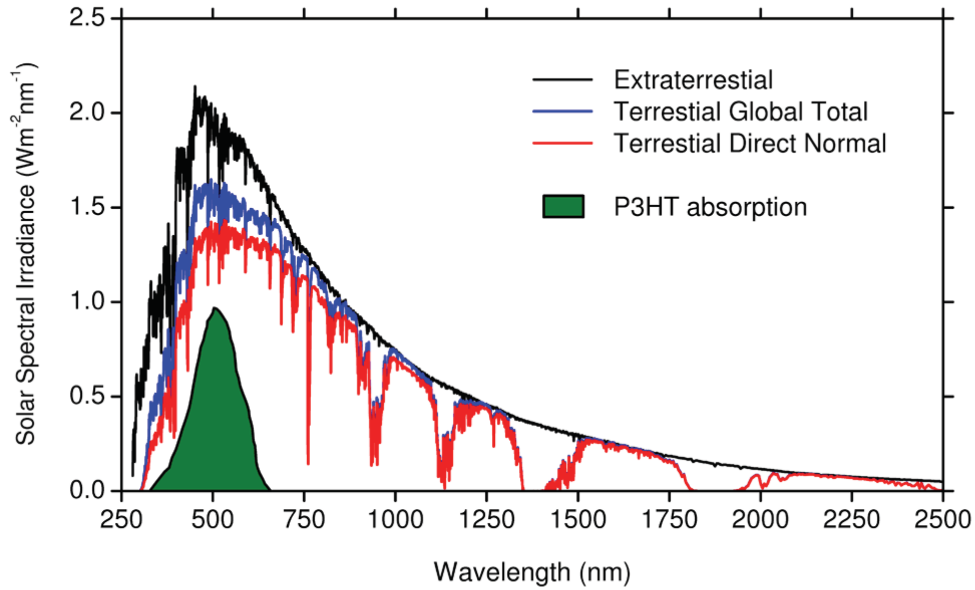
Amorphous Silicon Solar PV (3% of current market)

- Light Absorption (is actually pretty good)
- Electron-Hole Separation (also not a problem)
- Electron/Hole Transport (Holes are Slow!)
  - Hole Mobilities
  - Hole Traps: from total energy differences ($E_{neutral}$-$E_{charged}$)

Organic Solar PV

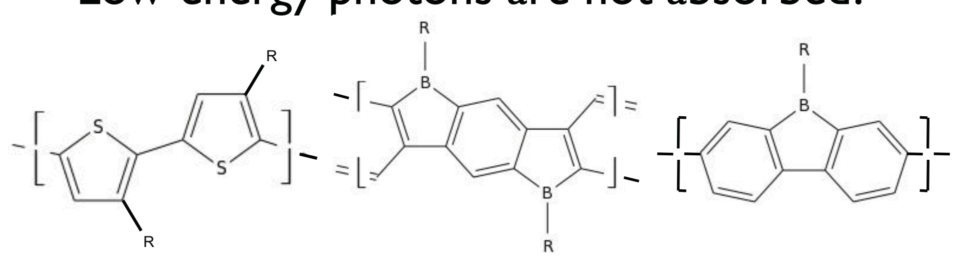
- Light Absorption (need to capture more of the solar spectrum)
  - Band gap
- Electron-Hole Separation
  - Orbital energies





Poly(3-hexylthiophene) (P3HT): $E_{g,exp}$ = 2.1 eV

Low-energy photons are not absorbed!



Egap = Eo   Egap = 0.55Eo   Egap = 1.1Eo

Dye Sensitized Solar PV

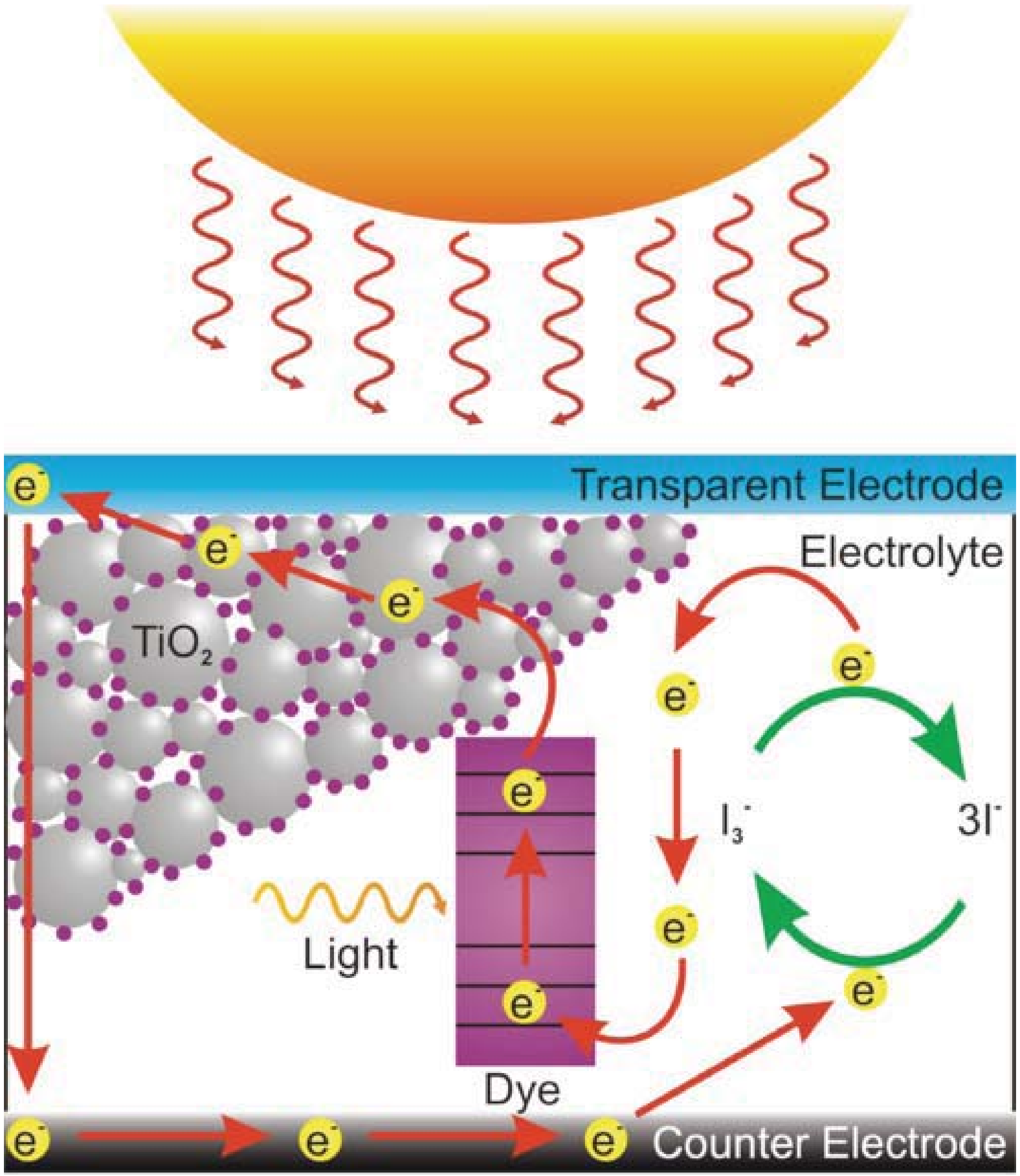


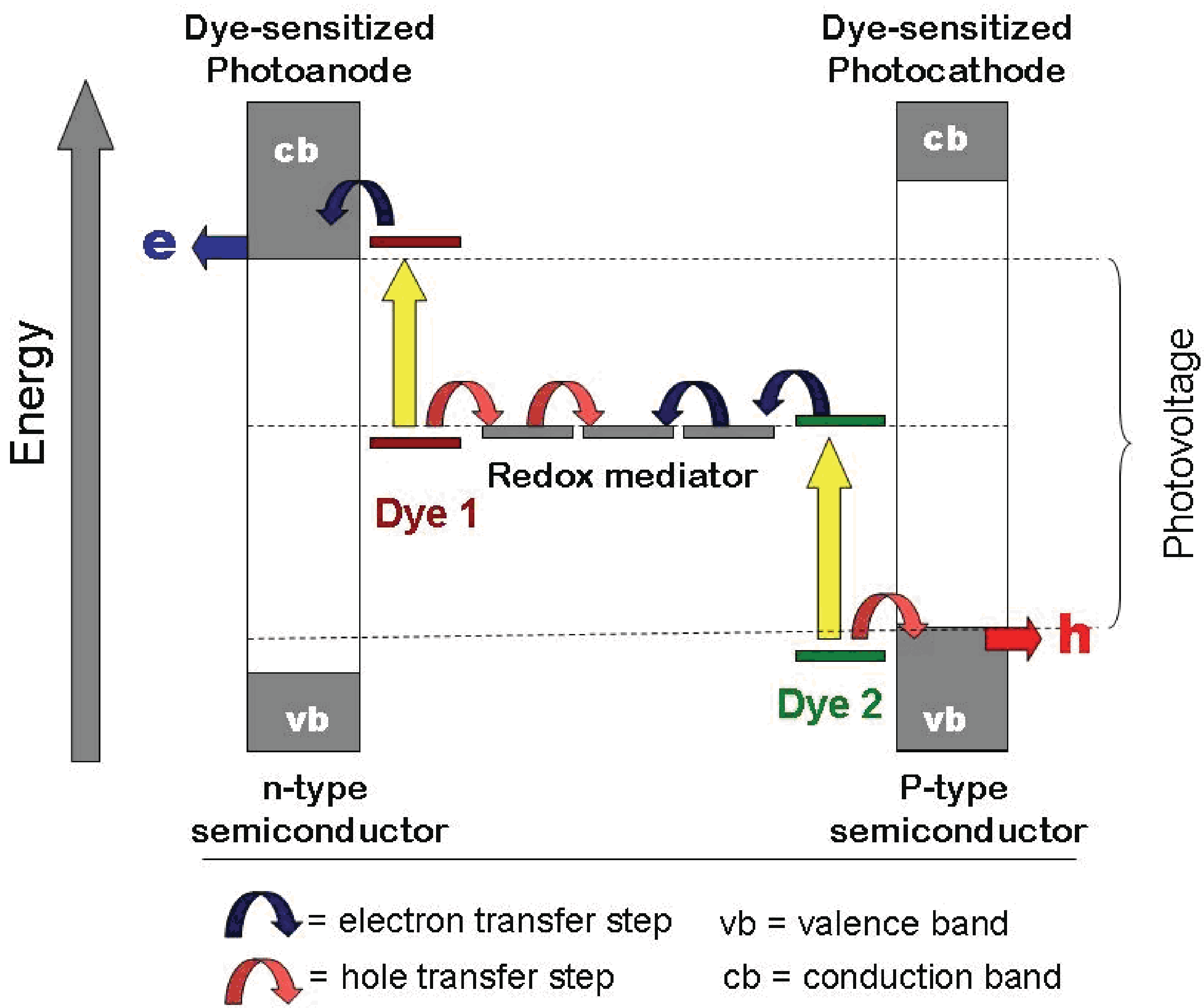
Image in the public domain. Via M. R. Jones on Wikimedia Commons.

Gratzel and O'Regan
(Nature, 1991)

Made up of 3 active materials:

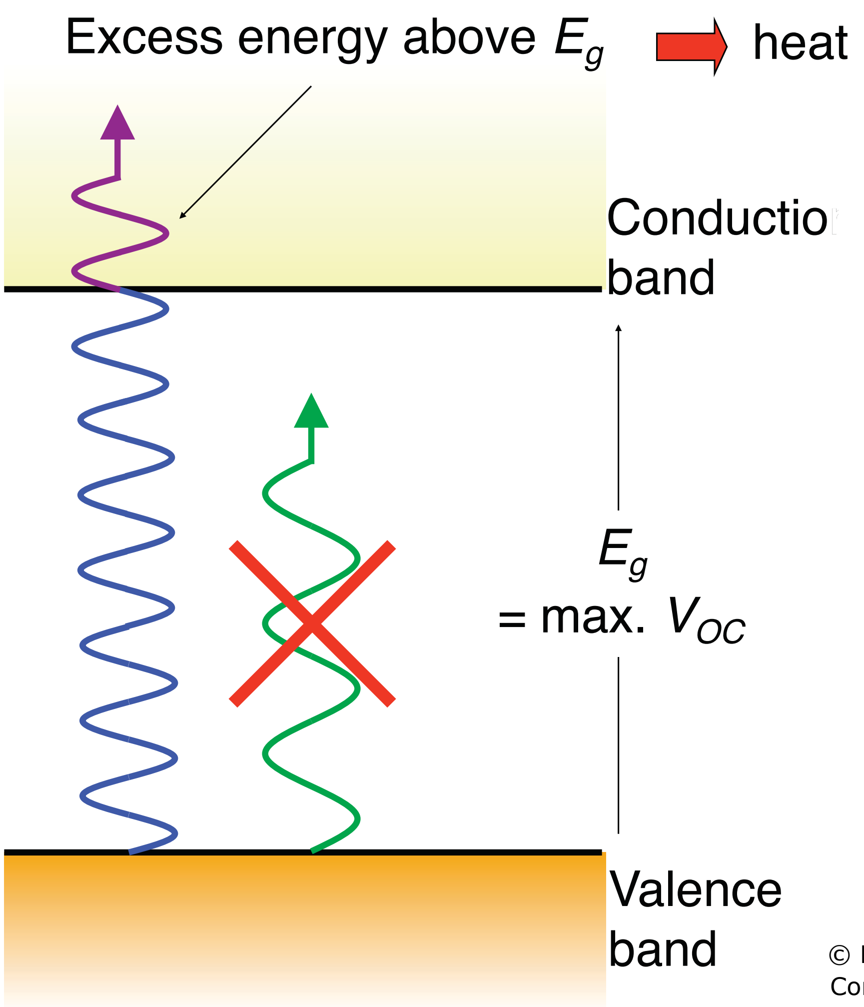
- Dye absorbs light.
- TiO_2 nanoparticles with very large surface area take electron.
- Liquid electrolyte delivers new electron from cathode to dye.

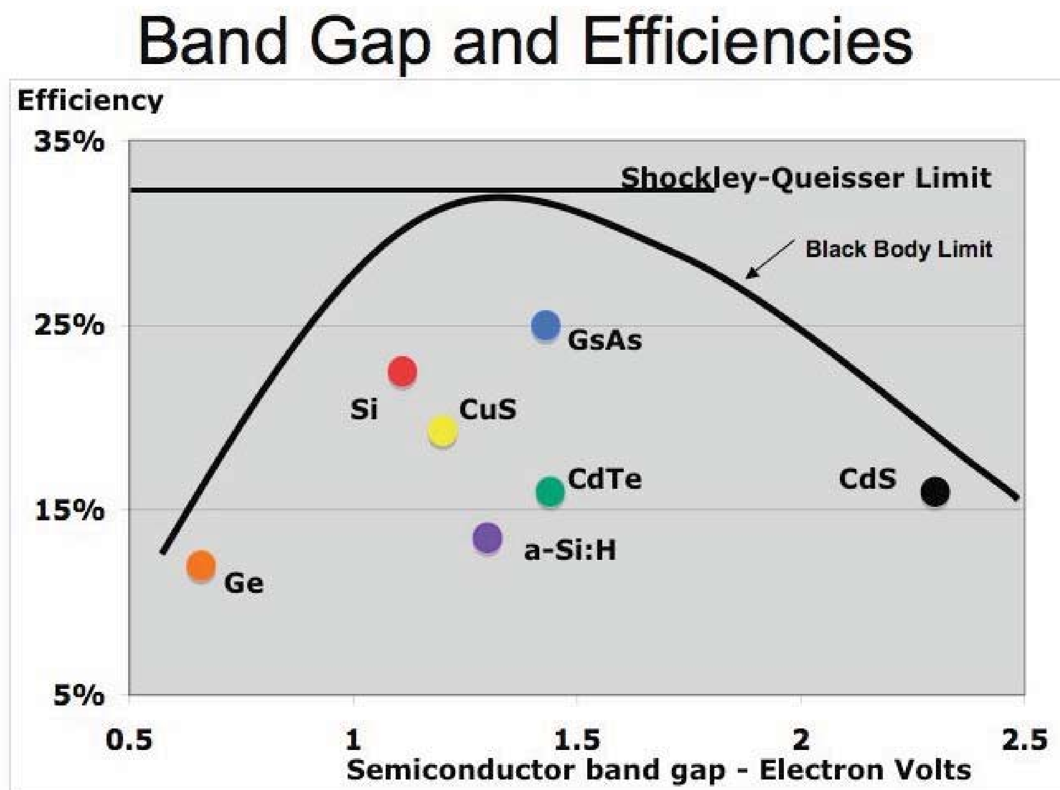
Dye Sensitized Solar PV



- Biggest problem is a liquid electrolyte.
- Relative energy levels of TiO2 and dye also key.

Going High Efficiency: Fundamental Limits





Source: DOE, Lewis Group at Caltech

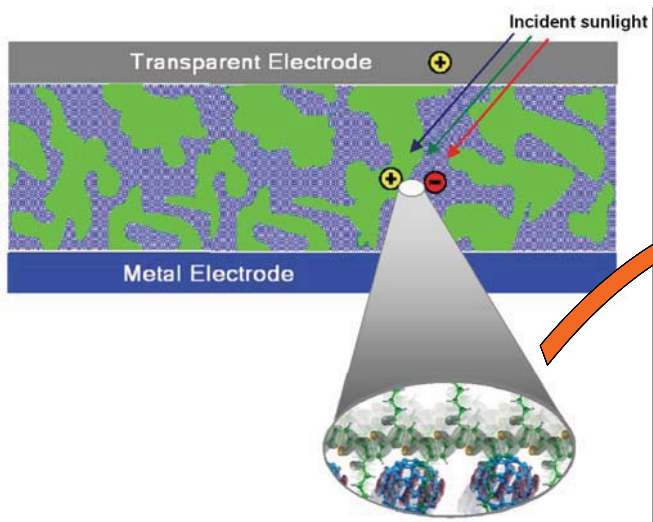
As band gap increases, the maximum open circuit voltage increases, but the fraction of the solar spectrum absorbed decreases.

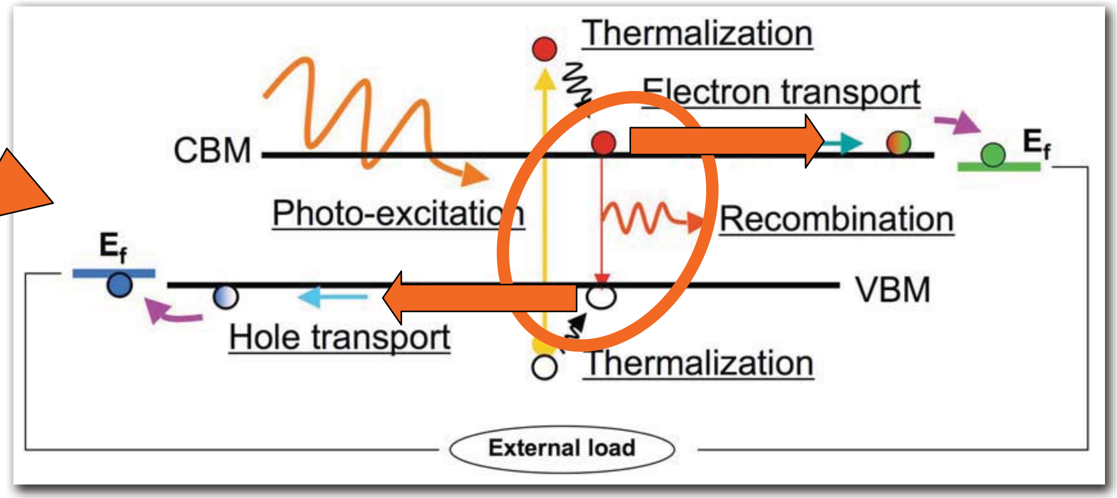
Multi-Junction Solar PV

Figures removed due to copyright restrictions. See http://www.nexpw.com/technology_tm.html.

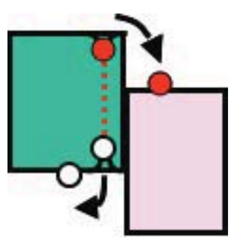
- Light Absorption
  - Band gaps
- Conductivity Across Interfaces
  - Band gaps, Band structures

Key Mechanism in Organic Solar PV: Charge Separation at the Interface





Charge separation at this interface is highly efficient*:
--Why?



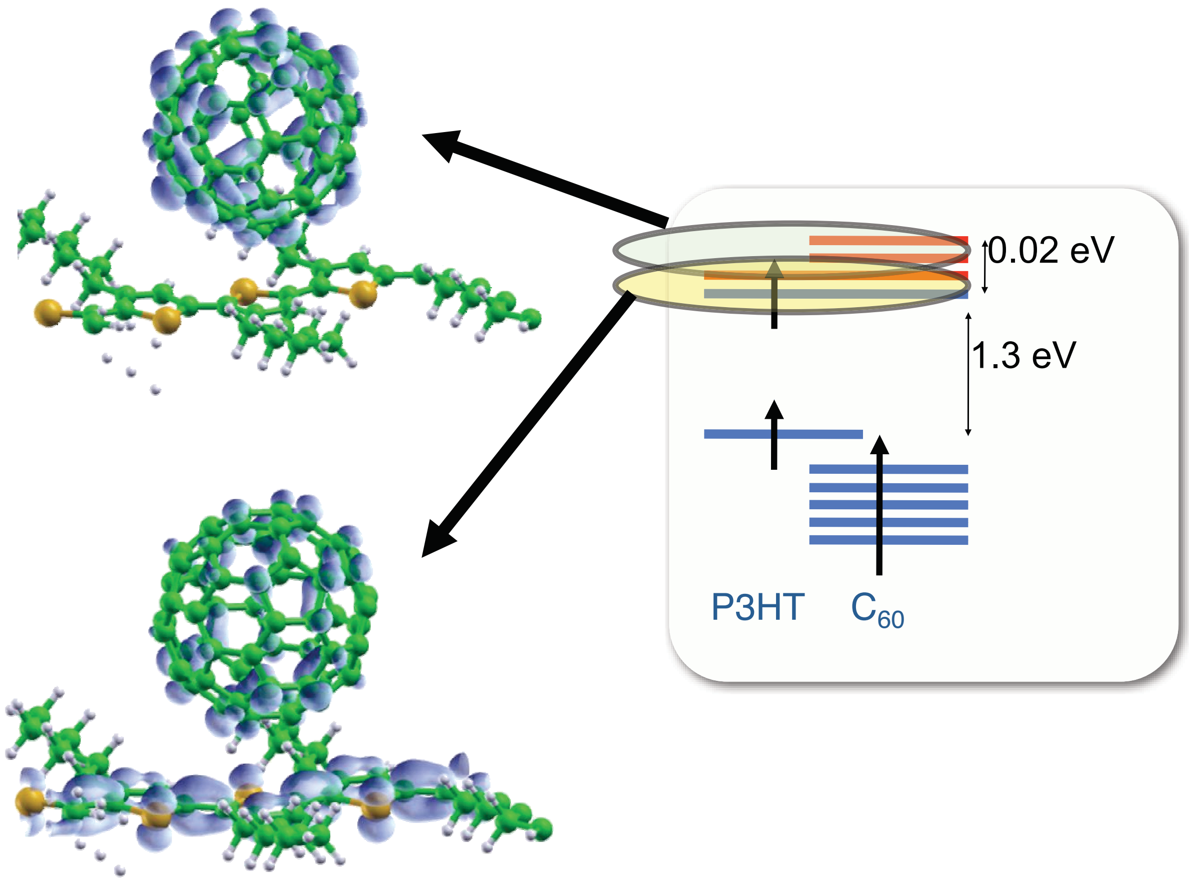
What is the detailed mechanism for this picture?

* N. S. Sariciftci et al., *Science,* 1992, *258*, 1474
B. Kraabel et al., *JCP,* 1996, 104, 4268
C. J. Brabec. et al, *CPL*, 2001, 340, 232

Excited State

Charge separated state: essentially degenerate with bridge state.

Bridge state forms: hybridization of P3HT π^* state and C60 t_{1u} state.



Y. Kanai and JCG, NanoLett 2007

CNT/P3HT: Metallic CNT

Carbon nanotubes instead of C60? Very little success thus far.*

Figures removed due to copyright restrictions. See Figures 4 and 5 in *Nano Letters* 8, no. 3 (2008).

E_f near P3HT π^* state

- Large charge transfer to the metallic CNT (~0.3 electron)
- Fermi level just above P3HT HOMO state
- No interface states are formed, so no E_f pinning
- Small built-in potential (0.06 eV), junction-induced exciton dissociation highly unlikely

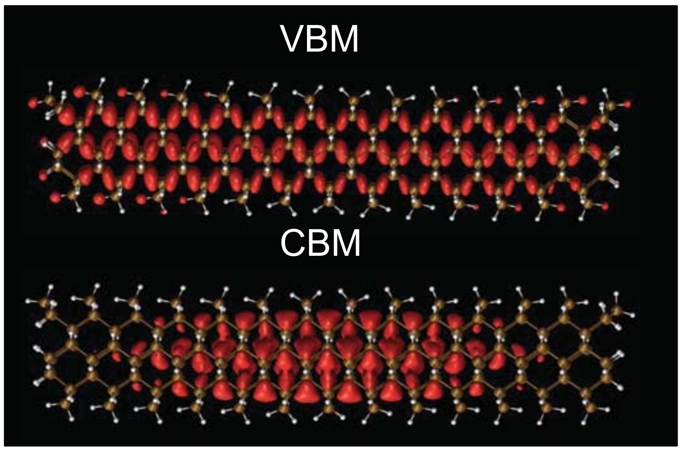
CNT/Polymer solar cells unlikely to work well with mixed CNT distribution.

*e.g. Kymakis, E. et al. *Rev. Adv. Mater. Sci.* 2005, 10, 300

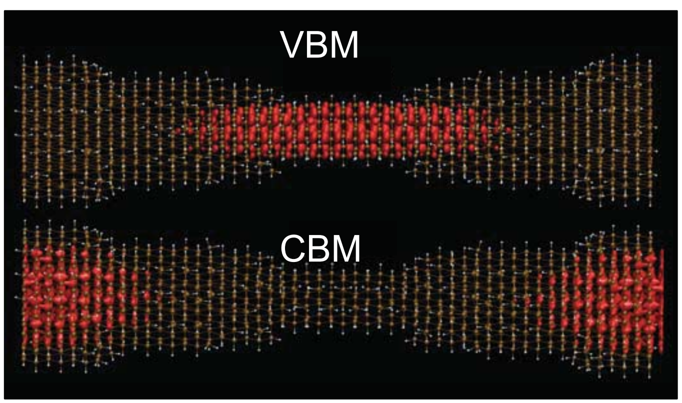
Y. Kanai and JCG, NanoLett (2008).

Using Computational Quantum Mechanics to Design New Mechanisms

Straight Wire

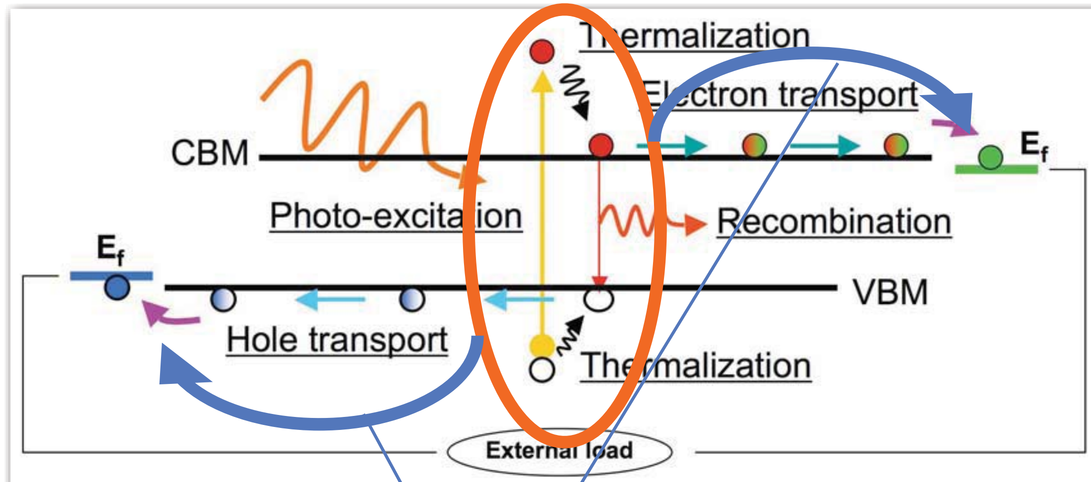


Tapered Wire

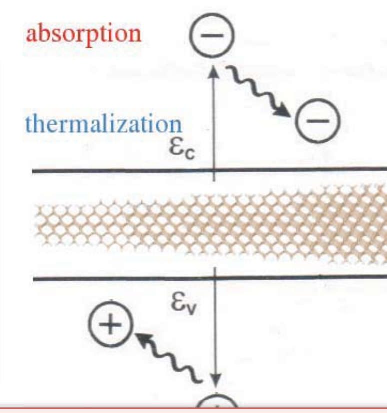


Axial charge redistribution due to quantum confinement

What could this mean for a solar cell?



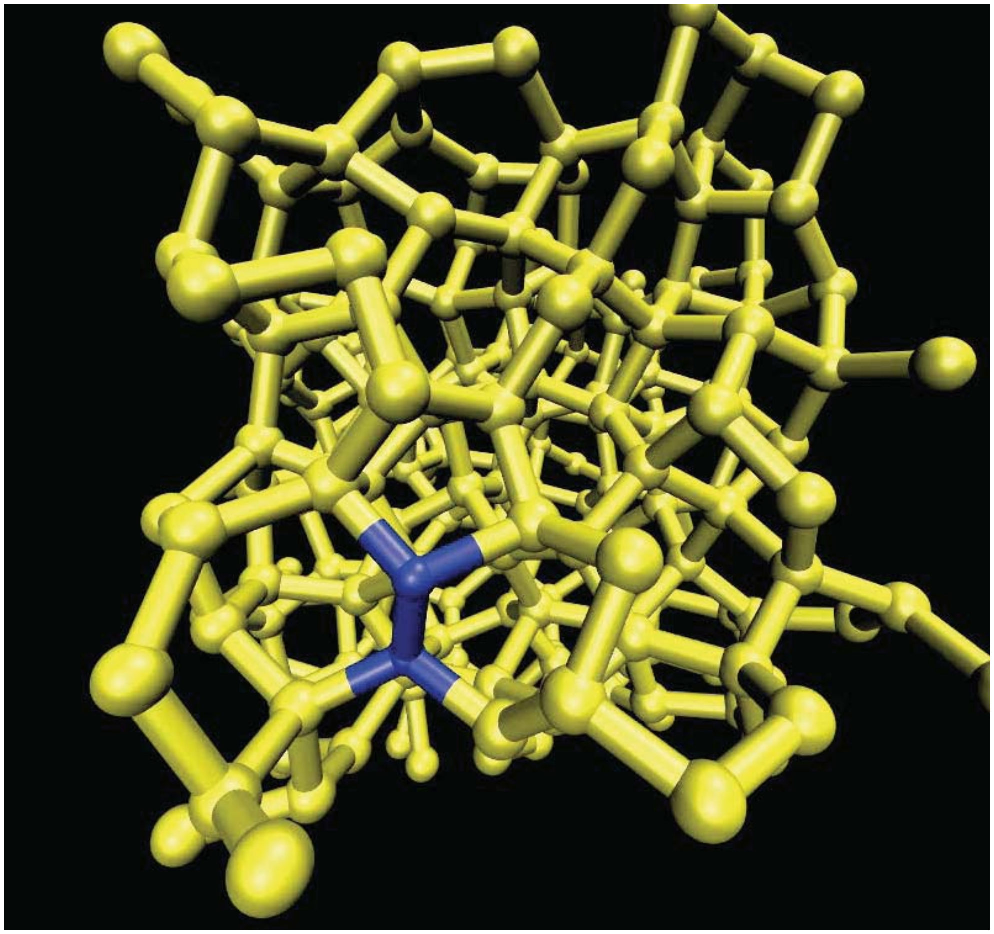
Electron/hole charge separation through thermalization?

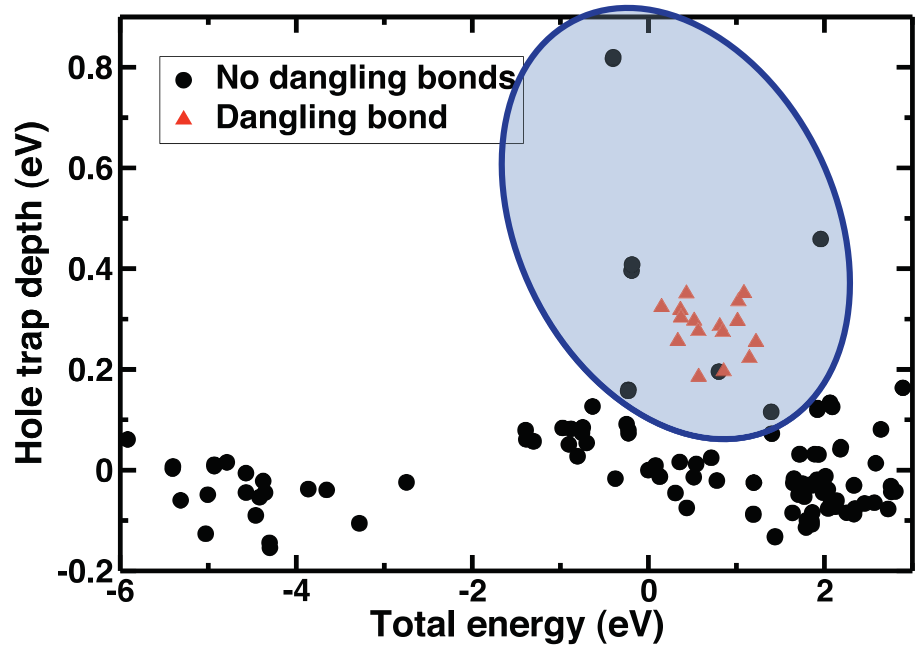


Majo po ential ad an age: no doping needed!

Z. Wu, J. B. Neaton, and JCG, PRL 100, 246804 (2008); Nanoletters (2009)

Amorphous Silicon PV: The Slow Holes



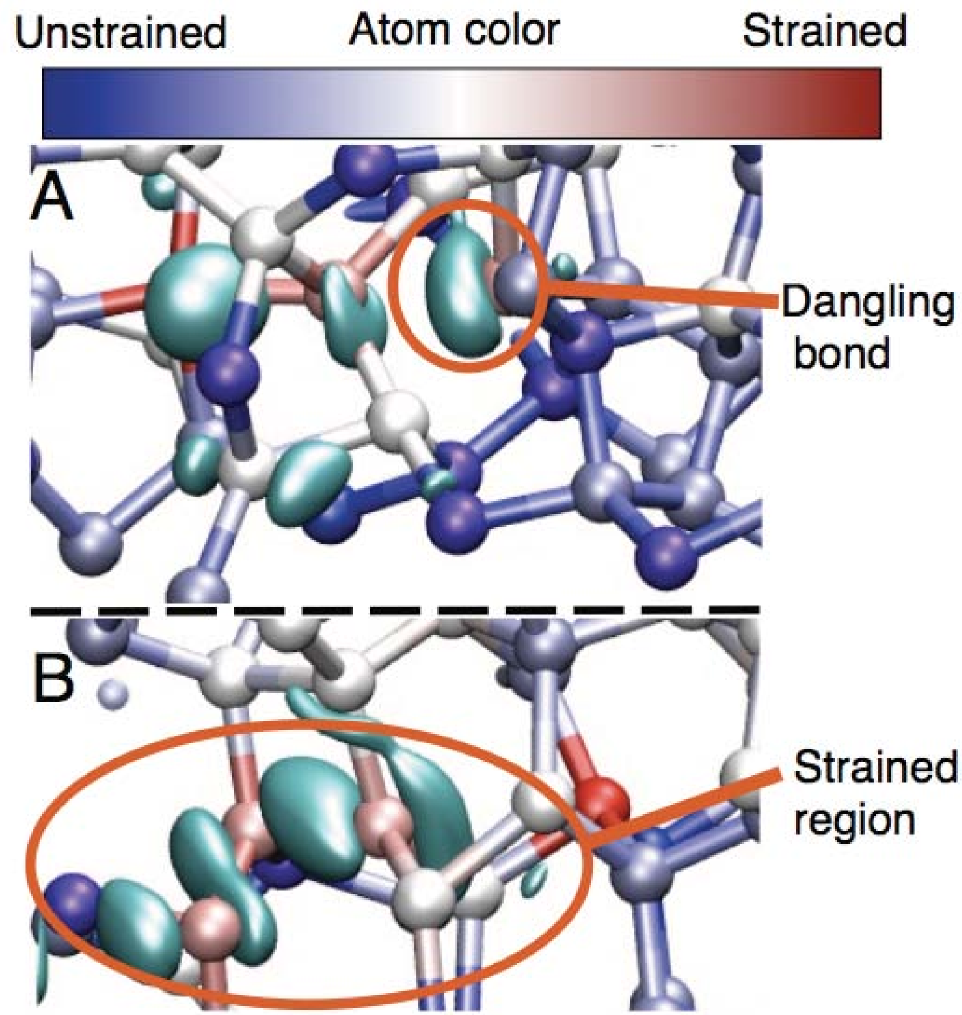


This type of bond switch can be as bad for hole mobility as dangling bonds.

Hole Traps: Dangling Bond vs. Strain

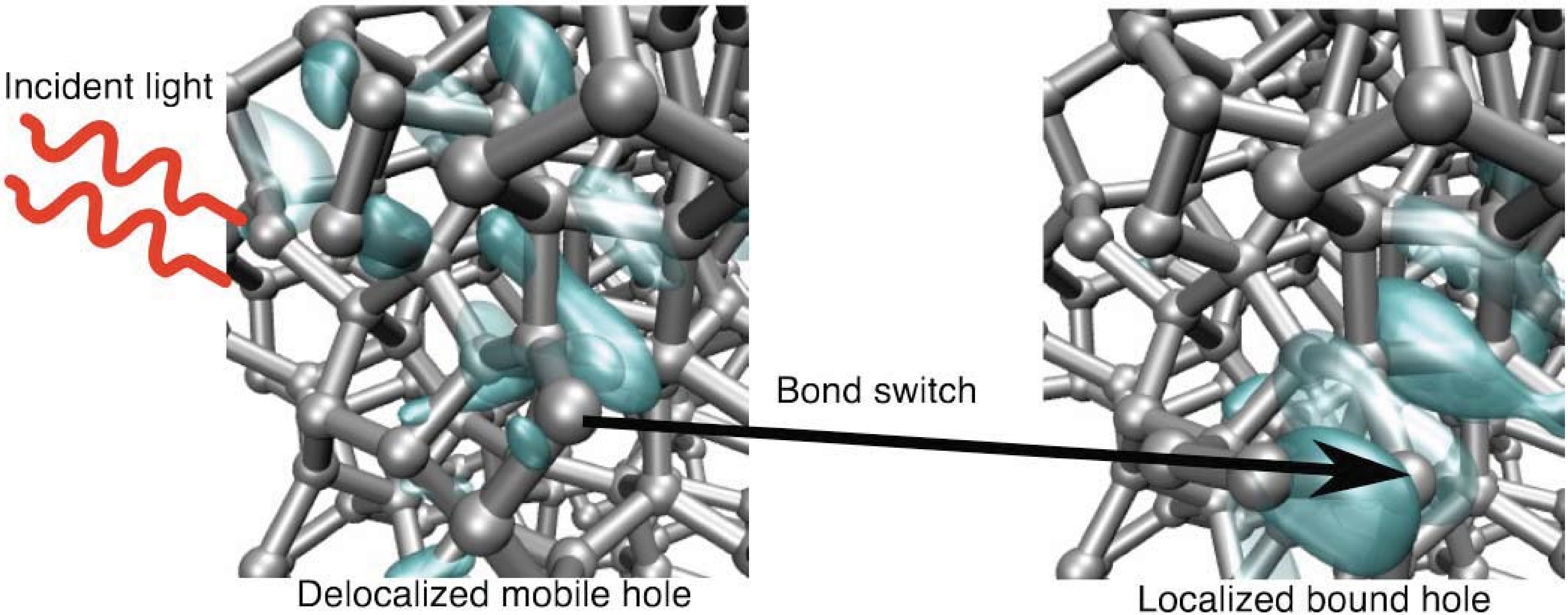
Dangling bond hole trap

Strain-only hole trap (stronger)



L.K. Wager and JCG, Phys. Rev. Lett. 101, 265501 (2008).

New Microscopic Picture of Holes in a-Si

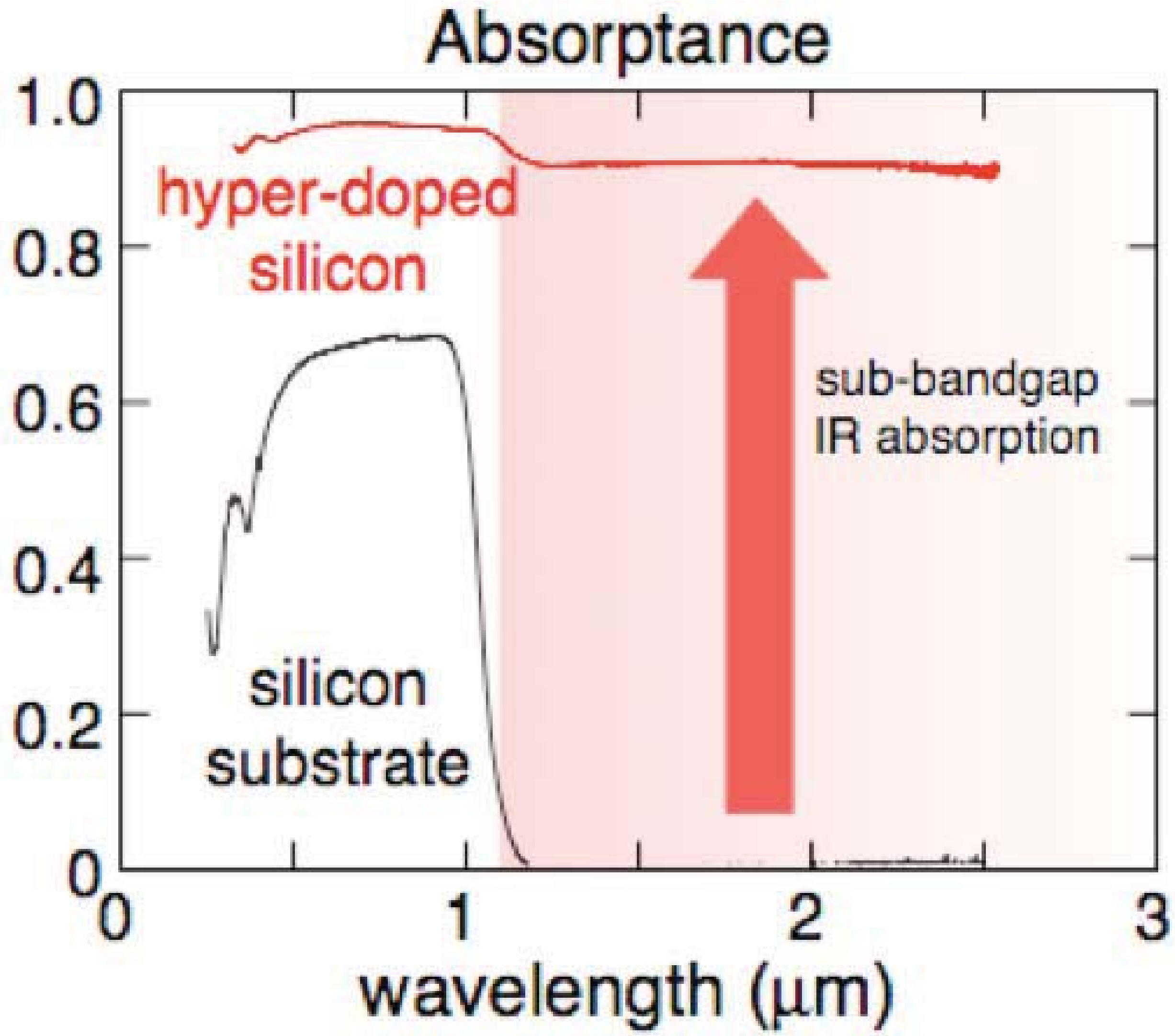


Computational quantum mechanics shows that pressure can mitigate these traps!

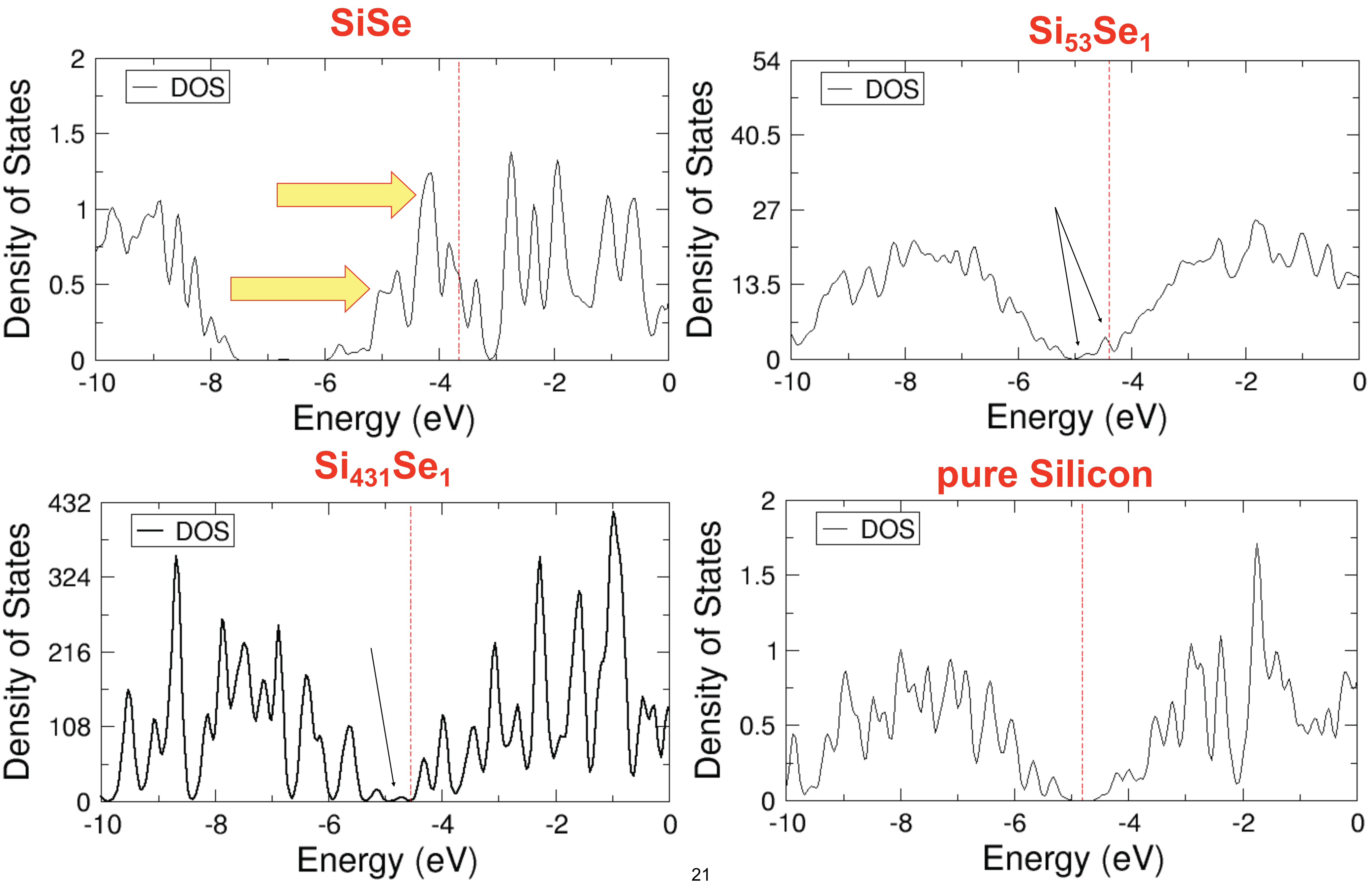
L.K. Wager and JCG, Phys. Rev. Lett. 101, 265501 (2008).

Another Thin-Film PV Example: Hyper-Doped Silicon

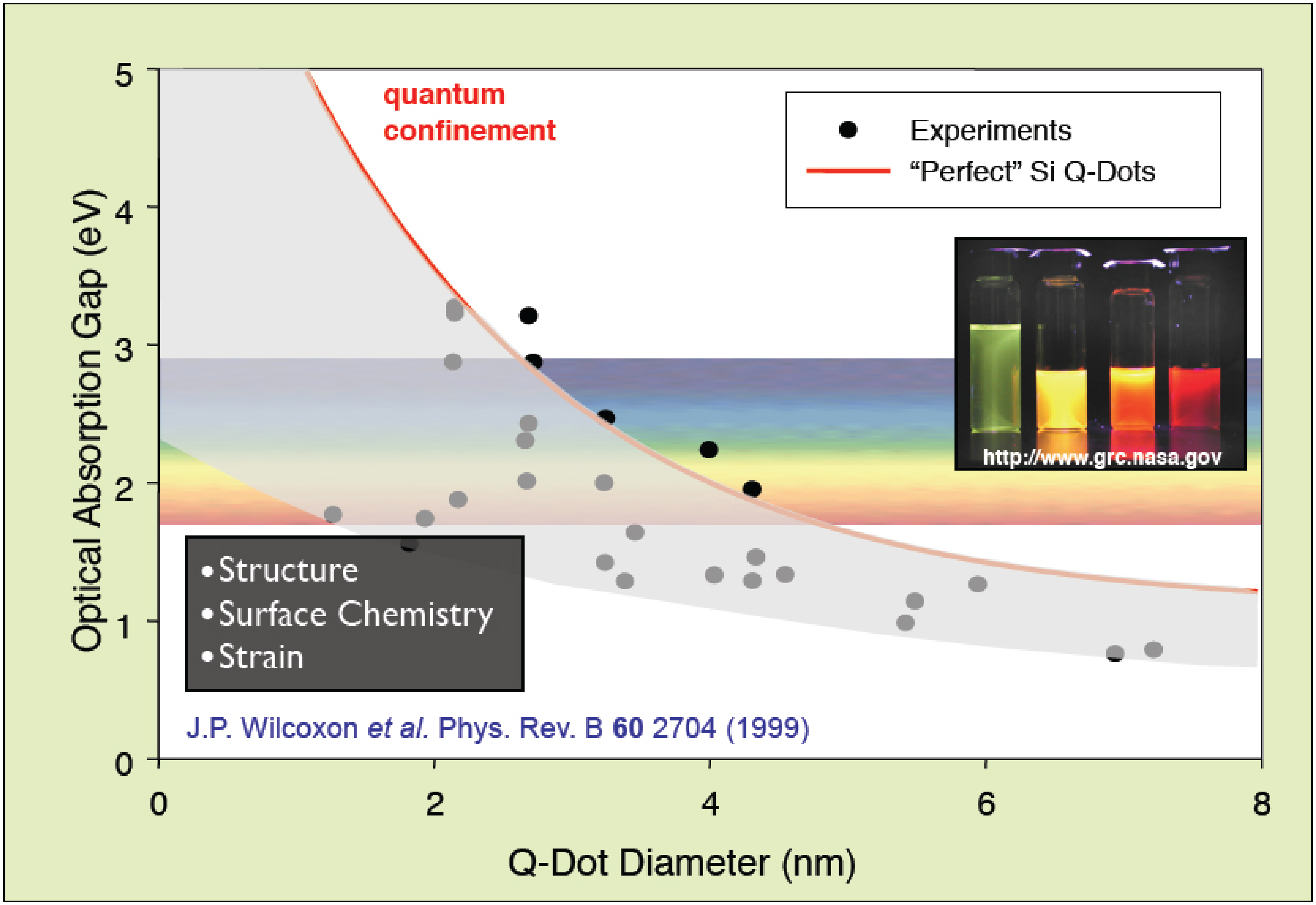
- Silicon doped with chalcogen atoms (sulfur, selenium, tellurium) to non-equilibrium concentrations.
- Strong optical response at photon energies where silicon is typically transparent.
- Promise as a photovoltaic material?



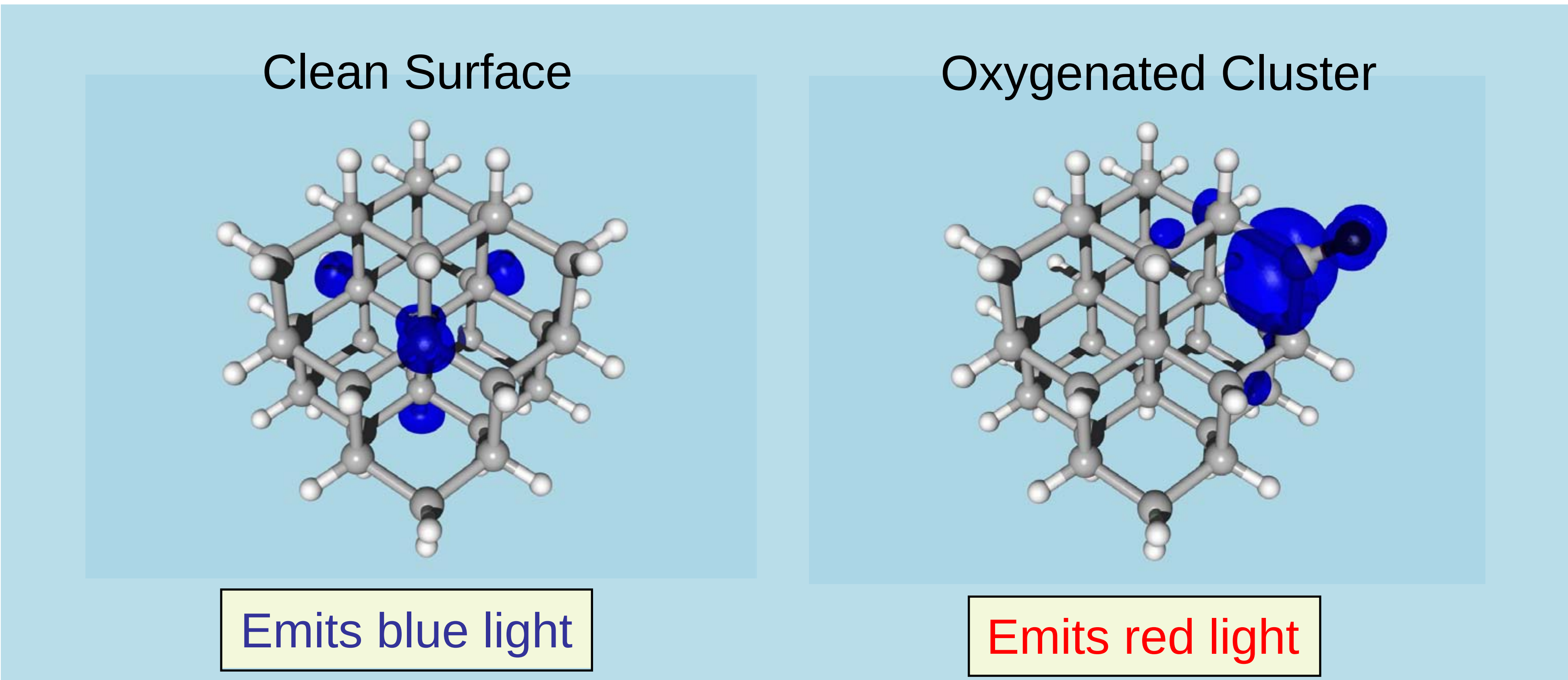
Evolution of Density of States



Needing to Know Structure and Chemistry



Needing to Know Structure and Chemistry



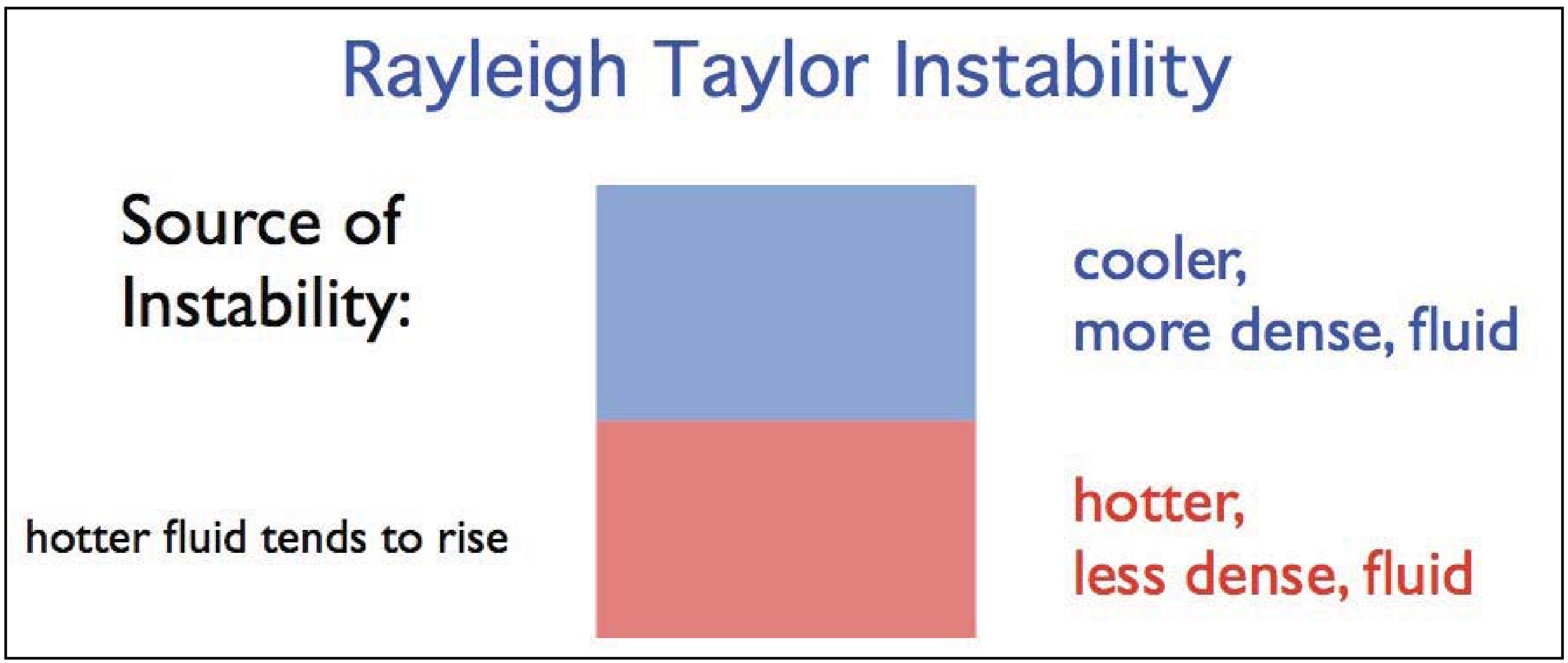
A. Puzder *et al.* Physical Review Letters, **88** 097401 (2002)

Validation

How do we know when a simulation is right?

Example: Rayleigh-Taylor Instability

From Leo P. Kadanoff, "The Good, the Bad, and the Awful Scientific Simulation and Prediction"



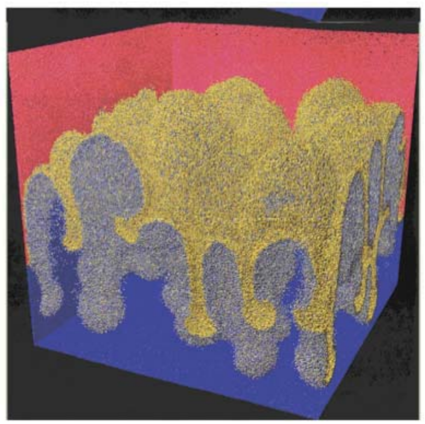
Example: Rayleigh-Taylor Instability

- Idea: occurs anytime a dense, heavy fluid is accelerated into a light fluid or lesser density
- Slight perturbations to plane parallel interfaces are unstable …fingers grow into sets of inter-penetrating fingers
- Observed in weather inversions, salt domes, star nebulae
- How to model this process? Requires solving hydrodynamics equations.

Example: Rayleigh-Taylor Instability

The Raleigh Taylor Instability.

Small deviations from perfect surface flatness triggers an instability. The two fluids penetrate into one another. Analysis (dimensional and RG arguments) suggest a penetration distance

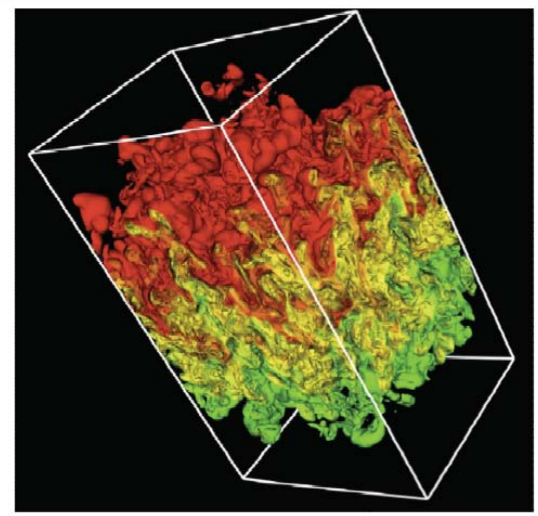


$$h = \alpha A g t^2$$

with A being the Atwoods number (density contrast) and α being dimensionless---and also Universal (!?).

Kai Kadau...Berni Alder, "Nanohydrodynamics simulation of R-T Instability", '04. $1.3 \cdot 10^8$ particles

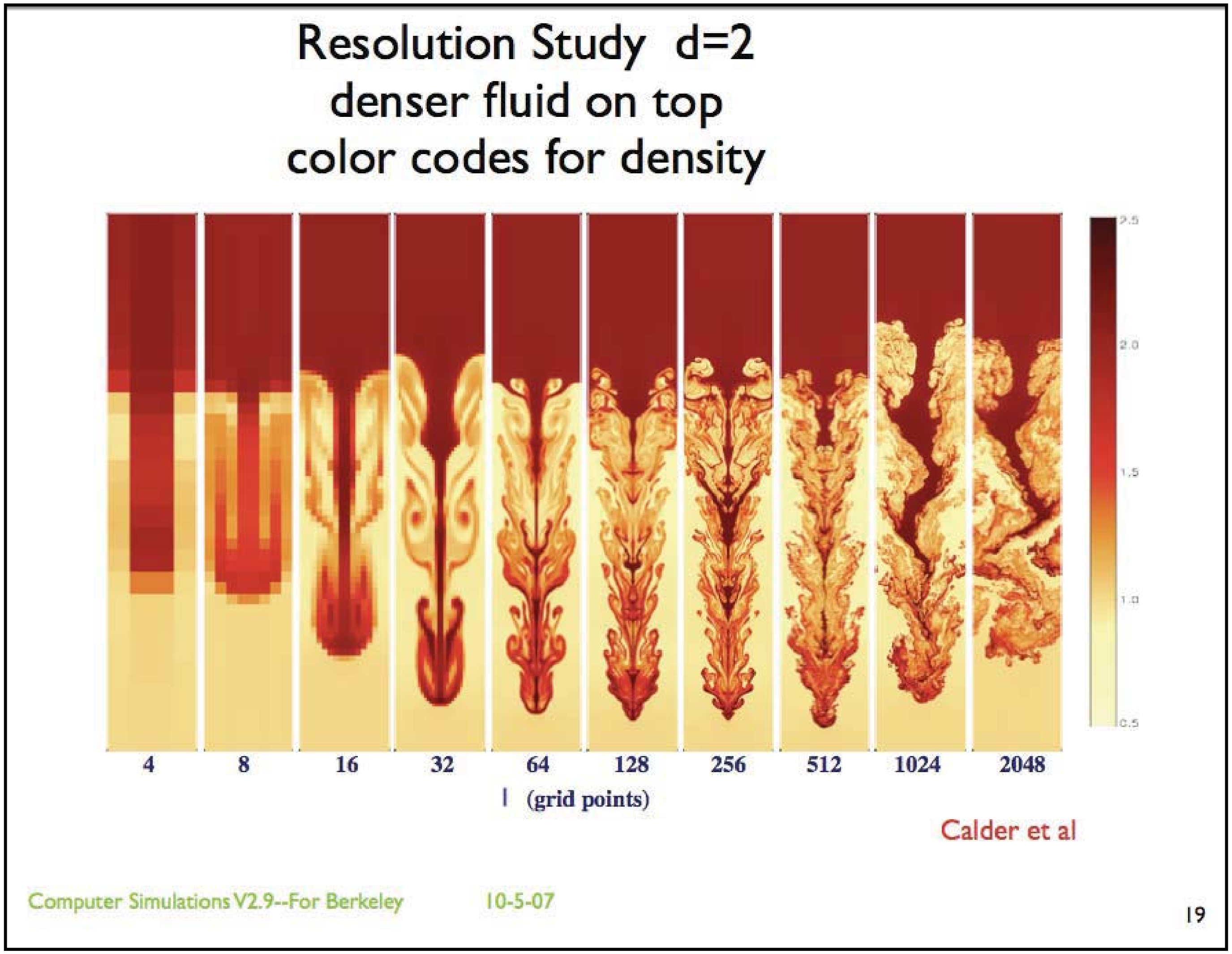
$$h = \alpha A g t^2$$



About 15 groups have measured or calculated α. Their results are important for us (a DOE supported astrophysics group) because the instability occurs on the surface of an exploding star.

Fluid Mechanics Simulation of RT instability. "On Validating an Astrophysical Simulation Code". A. C. Calder, et al. Astrophys.J.Supp. **143** 201-230 (2002). The value of α differs from previous picture by a factor of two.

Example: Rayleigh-Taylor Instability



Validation and Verification

Verification and validation (V&V) are processes that help to ensure that models and simulations are correct and reliable.

Verification: "Did I build the thing right?"

Have the model and simulation been built so that they fully satisfy the developer's intent?

Validation: "Did I build the right thing?"

Will the model or simulation be able to adequately support its intended use? Is its fidelity appropriate for that?

after Dale Pace

We've learned a lot!

Some of the key remaining challenges

The electron correlation problem. *Only seriously affects a fraction of materials, but that fraction tends to contain interesting physics and technological potential. At this point there is no logical follow-up on LDA/GGA*

Some of the key remaining challenges

The time-scale problem. *Short (MD) and long (thermo) is not a problem. Intermediate is a problem. e.g. phase transformations.*

Some of the key remaining challenges

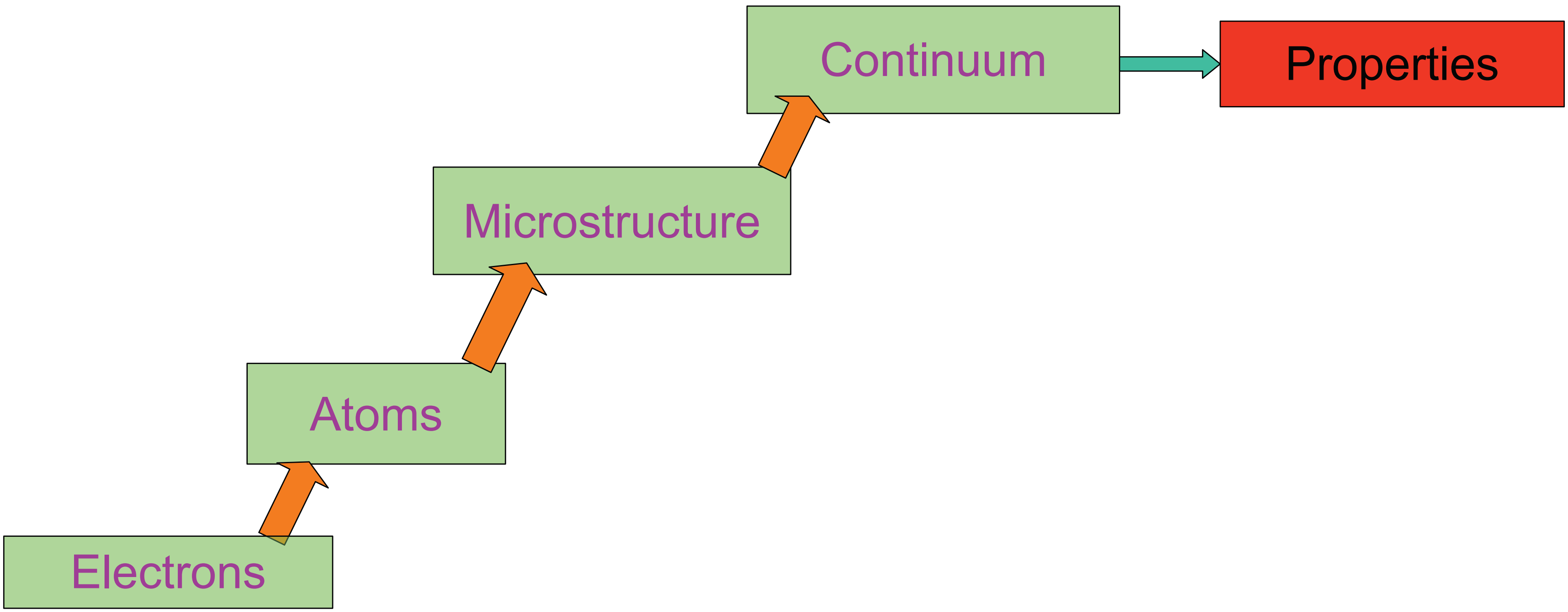
The knowledge problem. *To study an engineering property/behavior with atomistic-scale modeling, one needs to understand somewhat what controls that property (in order to include the relevant boundary conditions).*

e.g. If a property is controlled by impurities then intrinsic calculations will be irrelevant (Si conductivity).

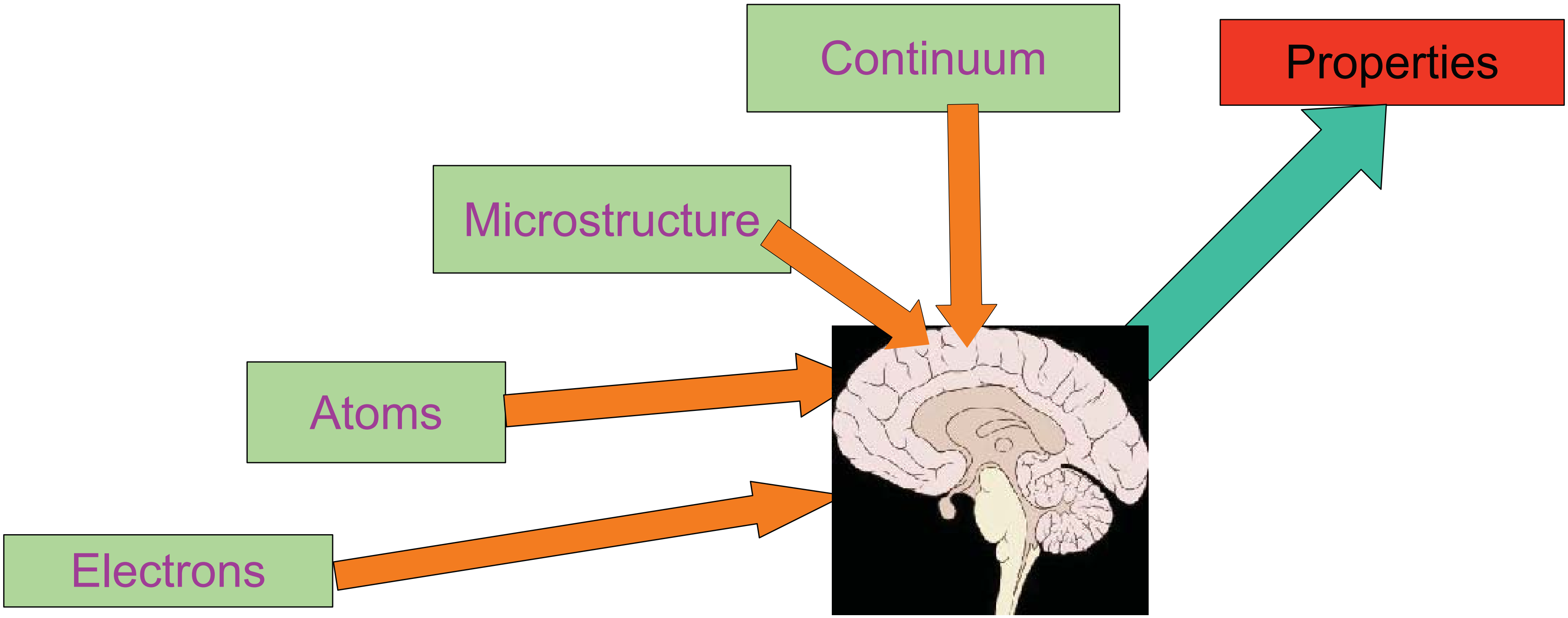
Some of the key remaining challenges

The structure problem. *Even though the structure-property relation is a key tenet of Materials Science, we have only very limited ability to predict structure (crystal structure, amorphous, microstructure, …)*

Theory of Properties: The Multi-Scale Materials View



Theory of Properties: The Multi-Scale Materials View



Computations should not substitute for lack of knowledge

Computational modeling is very powerful, but **be smart!**

3.021J / 1.021J / 10.333J / 18.361J / 22.00J Introduction to Modelling and Simulation
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