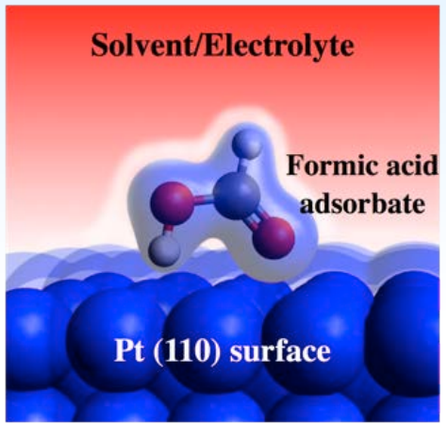
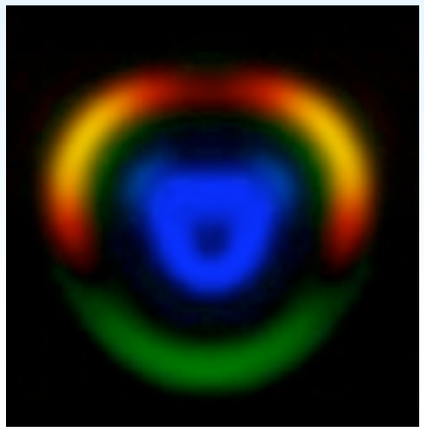
Computational Methods for Structure Prediction and Solid/Liquid Interfaces for Energy Materials

Richard G. Hennig, Cornell University

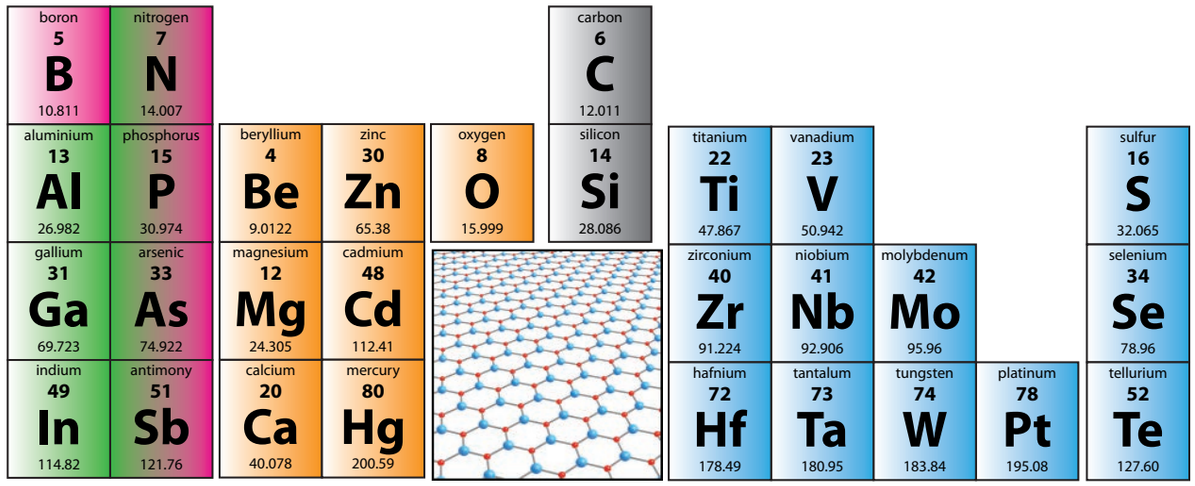


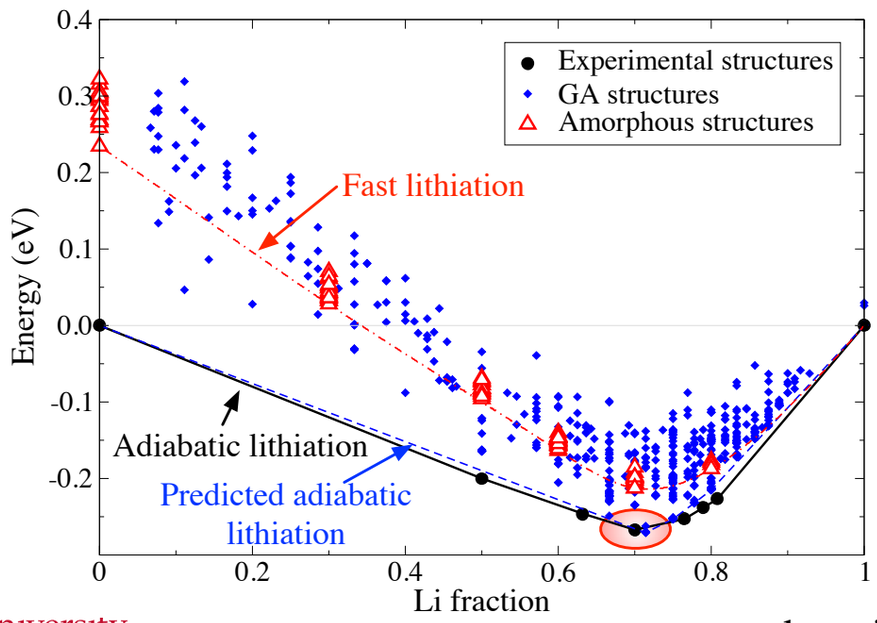


Ab initio methods for solid/liquid interfaces

http://vaspsol.mse.cornell.edu

Data mining for novel 2D materials





Genetic algorithm for structure predictions

http://gasp.mse.cornell.edu

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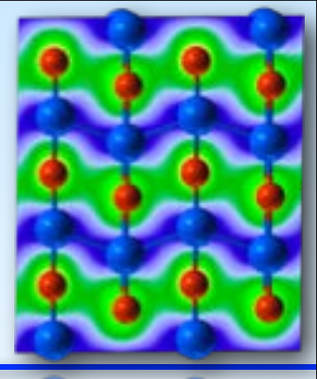
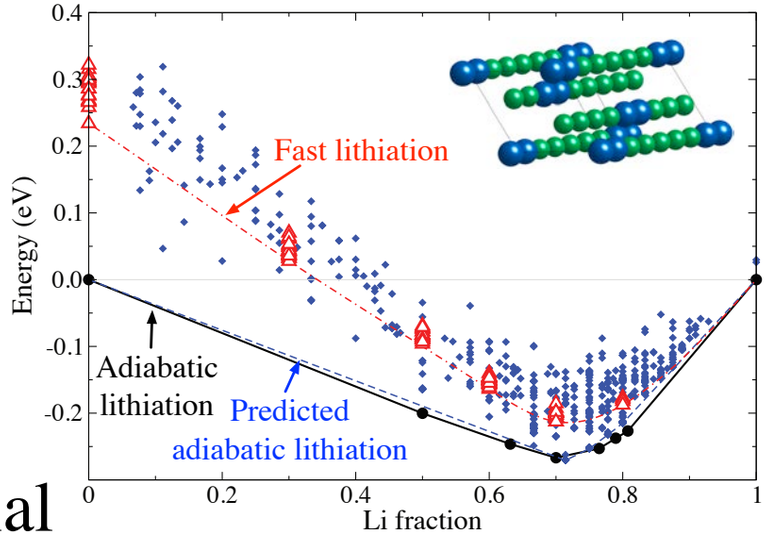
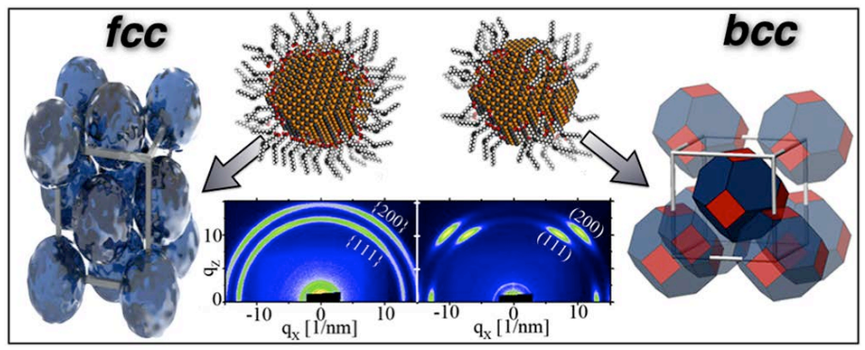


How can we predict the formation of novel compounds, their structure, composition, and stability?
How can we include solvation effects for surfaces?

- Prediction of compound formation and phase diagrams from quantum mechanics and genetic algorithms
  - GASP code for structure prediction
  - Application to materials for energy applications Li-Si and Li-S
  - Testing of the accuracy of empirical potentials
- Solvation included in DFT and QMC through external potential
  - Application to semiconducting and metallic nanocrystals
  - Desorption of ligands in polar solvents





Nature 451, 445 (2008), PRB 87, 184114 (2013), Phys. Rev. B 87, 184114 (2013),
J. Phys.: Condens. Matt. 25, 495401 (2013),
ACS Nano 6, 2118 (2012), JACS 133, 3131 (2011), Phys. Rev. B 85, 201102 (R) (2012)

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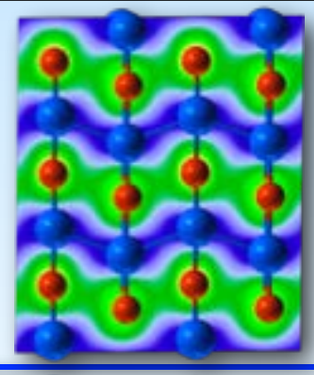
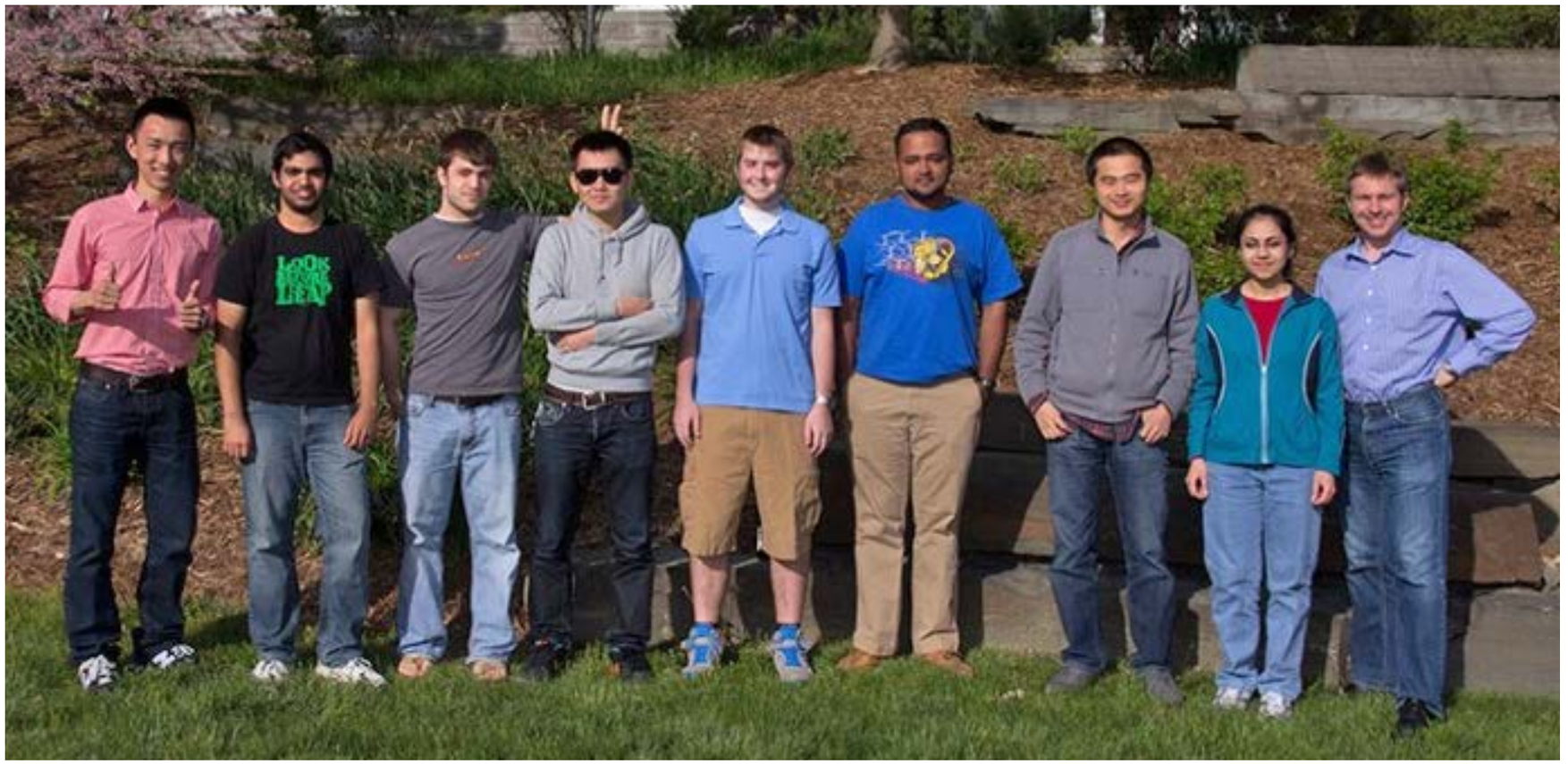


Acknowledgement

- Genetic algorithm development: W. Tipton, B. Revard, S. Wenner, A. Sanchez
- Battery materials: W. Tipton, C. Bealing, K. Matthew, M. Blonsky
- Solvation model and nanocrystals: K. Mathew, C. Bealing, H. Mera, K. Schwarz, K. Letchworth-Weaver, R. Sundarama, T. Arias

- Financial support by EMC², CCMR, NSF-CAREER
- Computational resources provided by XSEDE, Teragrid, CCNI



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The Energy Landscape

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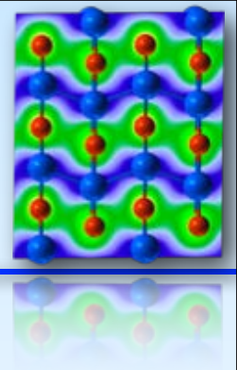
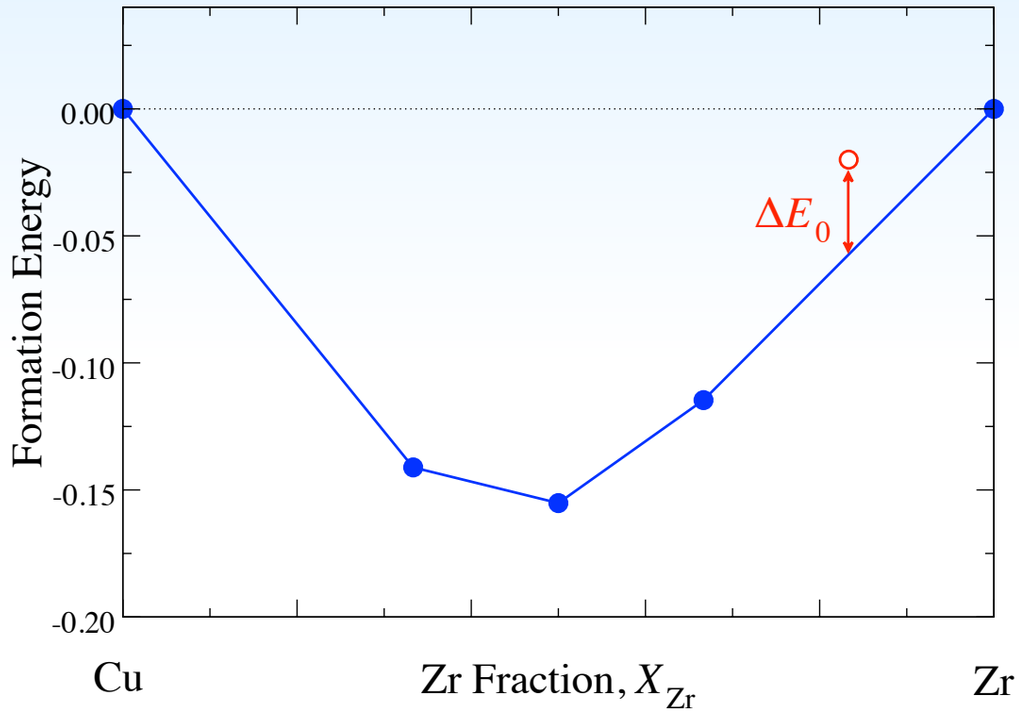
Minimum Free Energy Principle



Computational structure prediction based on optimization

- Stable structure ⇒ Lowest free energy
- Minimize the (free) energy
- Stability against competing phases



Energy methods

Interpolative
(Semi-)empirical methods

Extrapolative and predictive
First-principles or *ab-initio* methods

- Density-functional theory offers balance of speed and accuracy
- Pseudopotentials and plane-wave basis (VASP)

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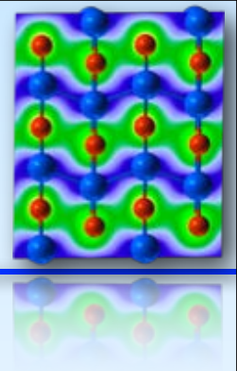
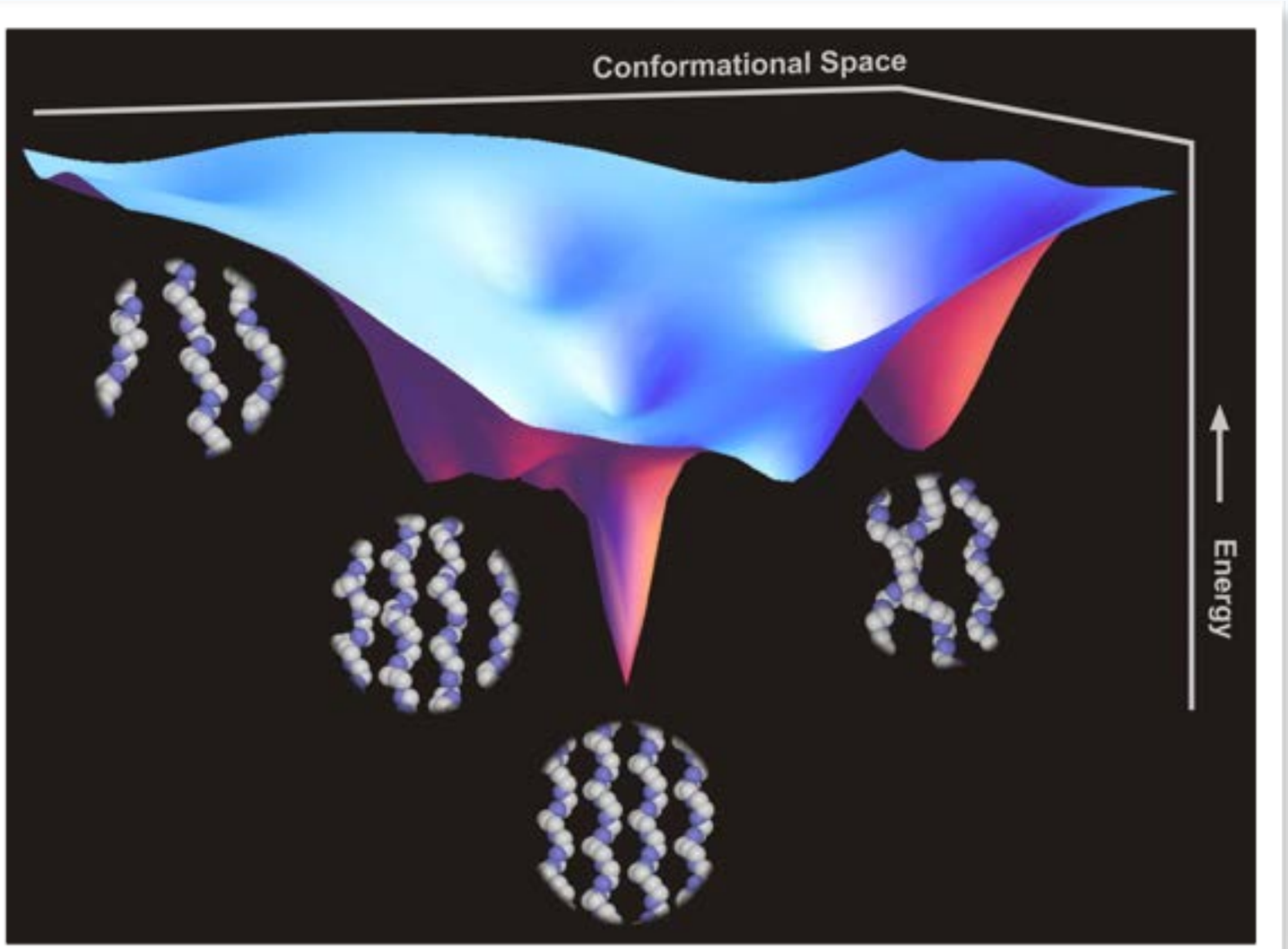
General Features of the Energy Landscape



Bell–Evans–Polanyi principle

- Highly exothermic chemical reactions have low activation energies
- Low-energy basins are expected to occur near other low-energy basins
- These regions are referred to as **'funnels'**



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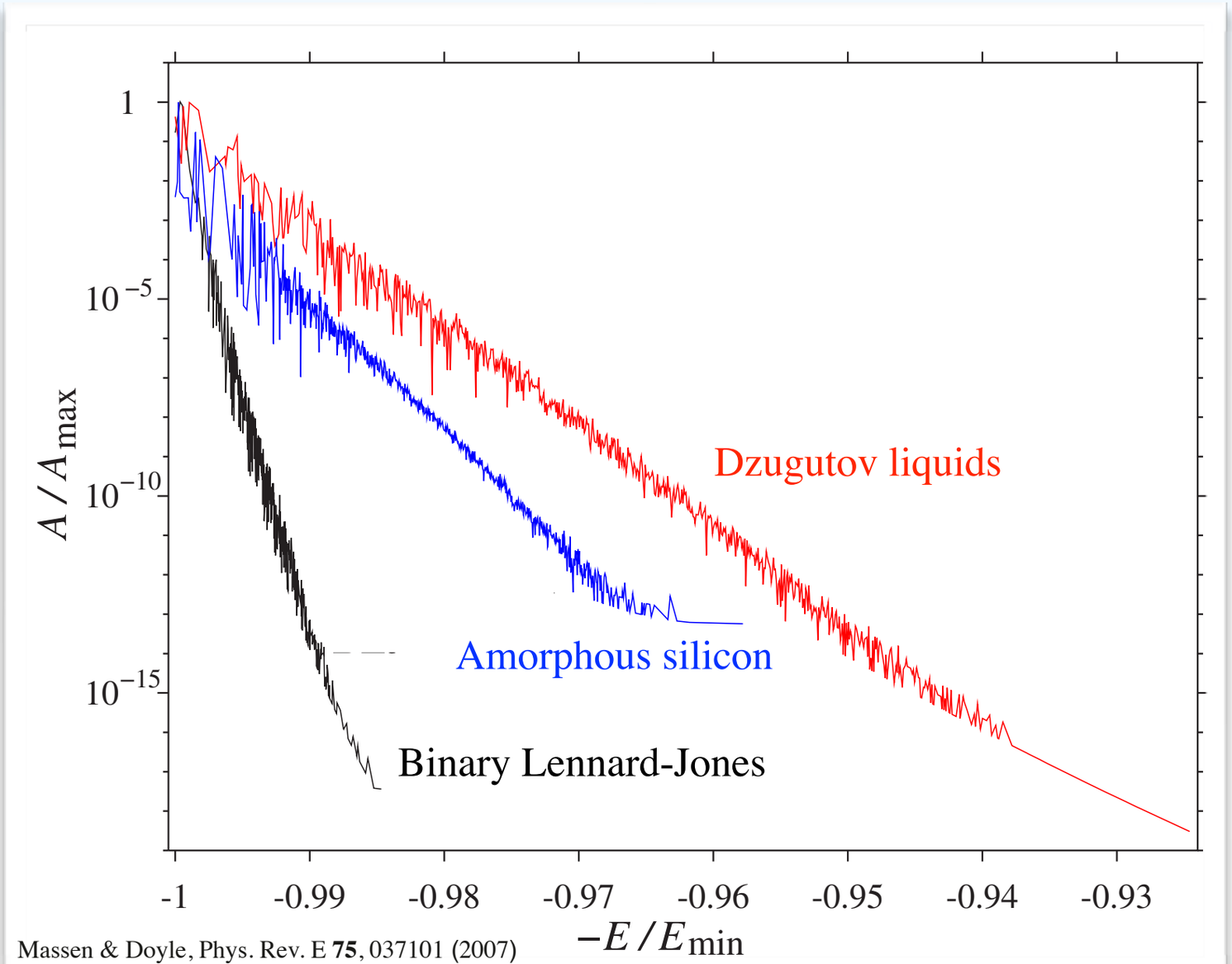
General Features of the Energy Landscape

Probability distribution of energies of local minima

- Basins with lower-energy minima have larger hyper-volumes
- Related to similar elastic constants, vibrational frequencies for different structures
- Power law probability distribution of these hyper-volumes
- Order in the arrangement of basins of different sizes
- Smaller basins filling gaps between larger ones



Massen & Doyle, Phys. Rev. E **75**, 037101 (2007)

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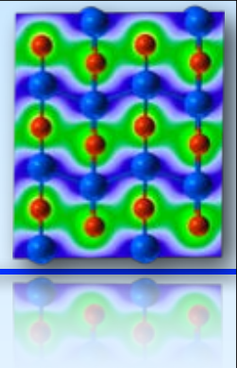
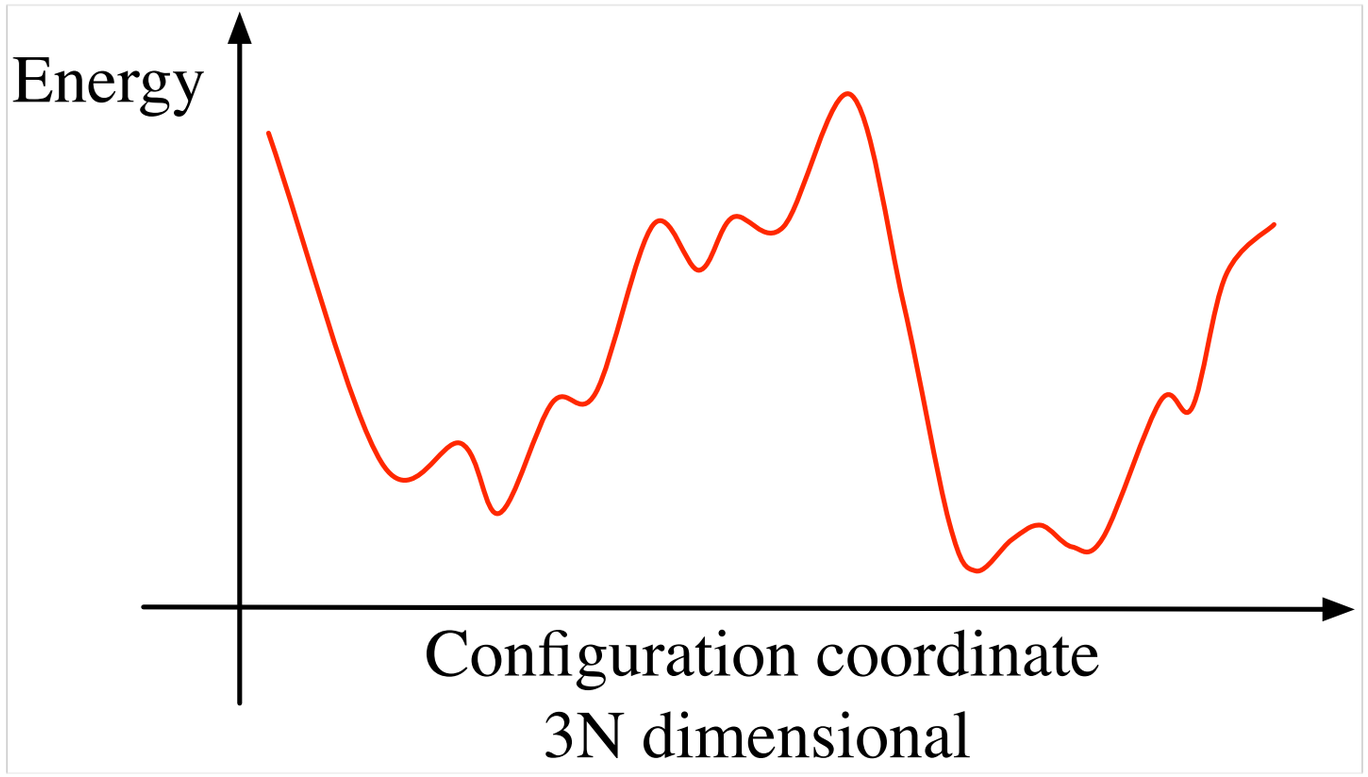
Illustration of Energy Landscape



- 1D and 2D cuts through 3*N*-dimensional configuration space
- Not a good representation of the distribution of basins in 3*N* dimensions



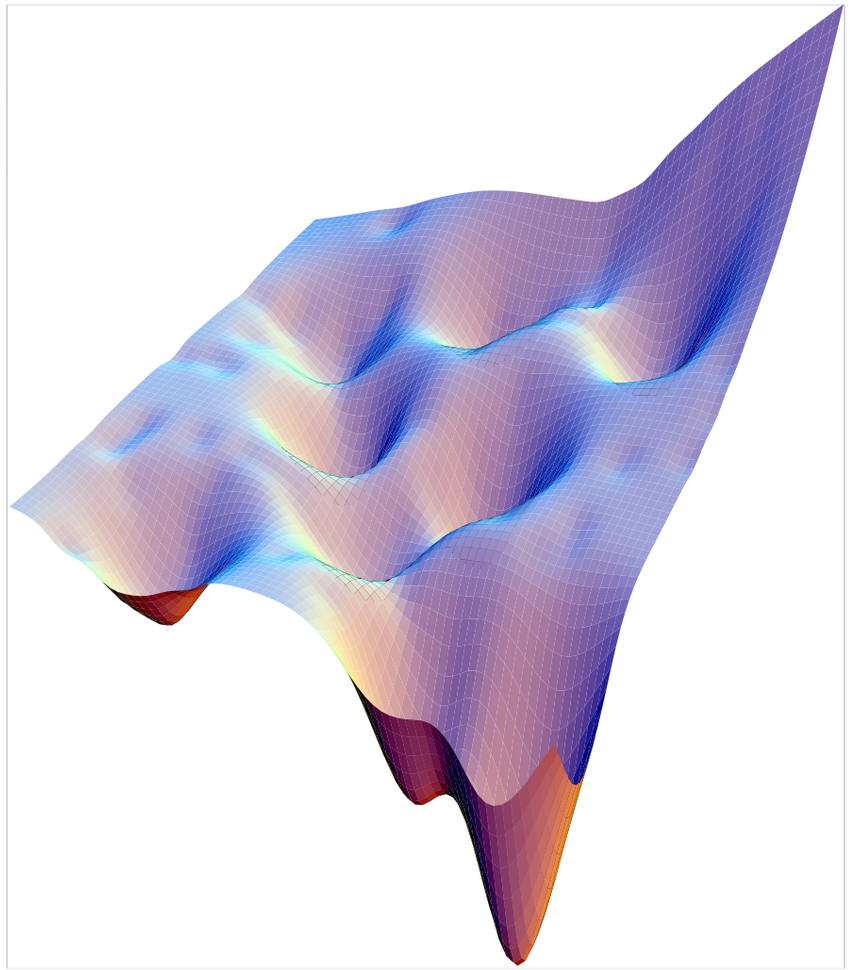


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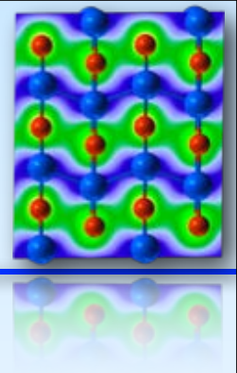
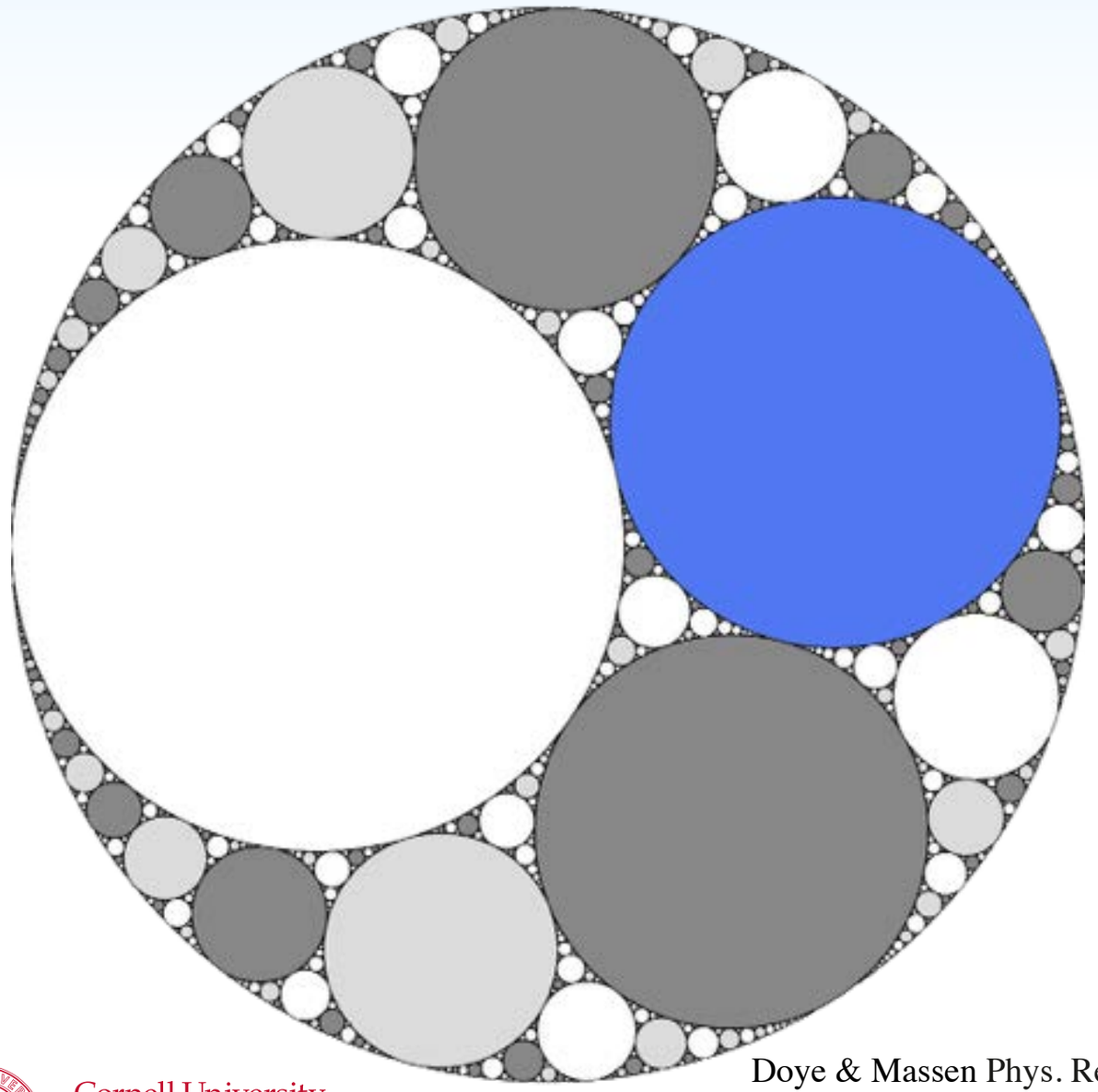
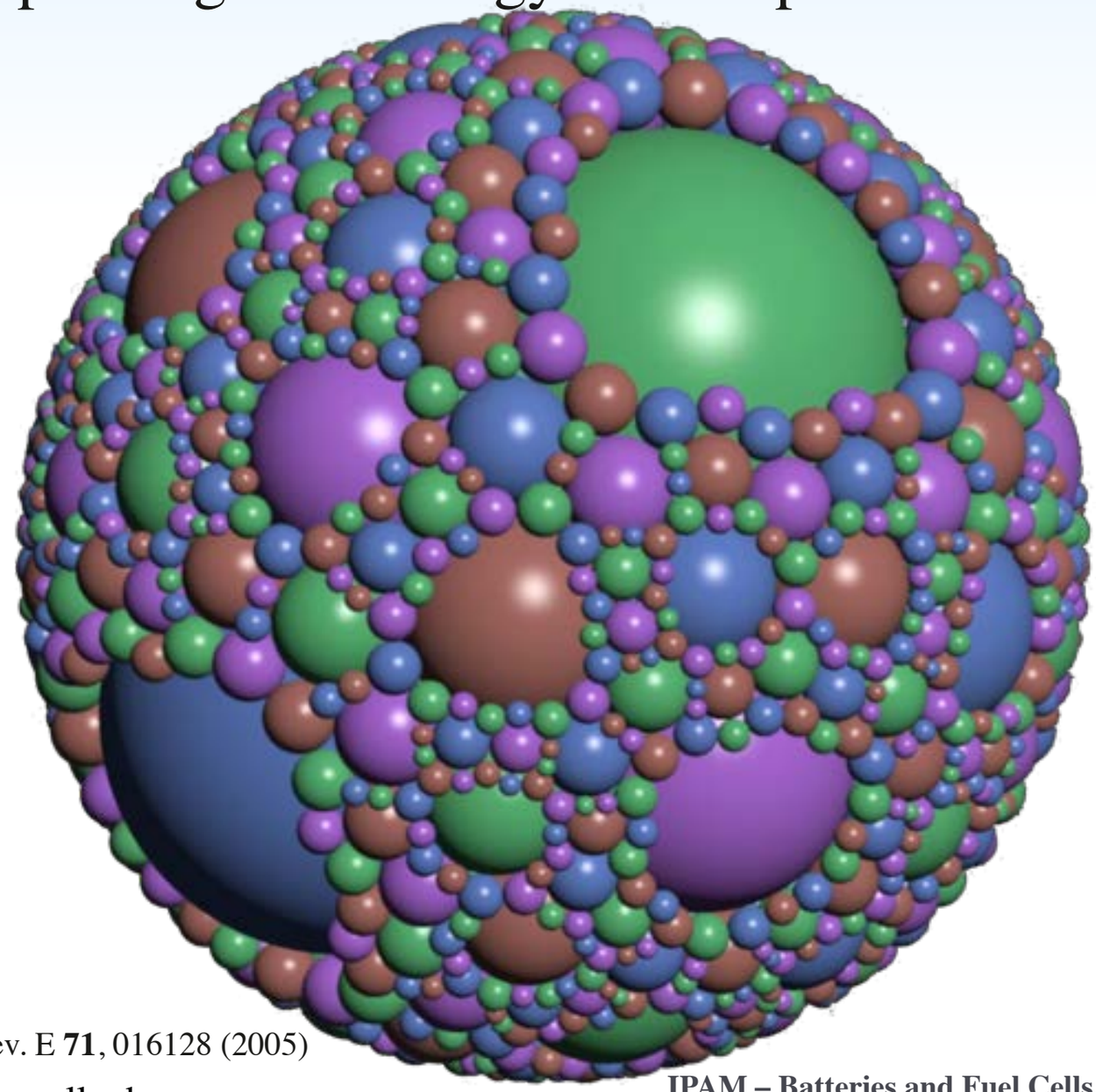
Illustration of Energy Landscape



- 1D and 2D cuts through $3N$-dimensional configuration space
- Not a good representation of the distribution of basins in $3N$ dimensions
- Similarities between Apollonian sphere packings and energy landscapes





Doye & Massen Phys. Rev. E **71**, 016128 (2005)

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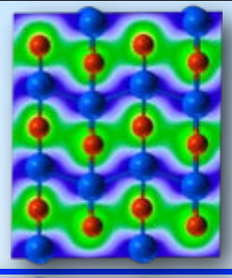
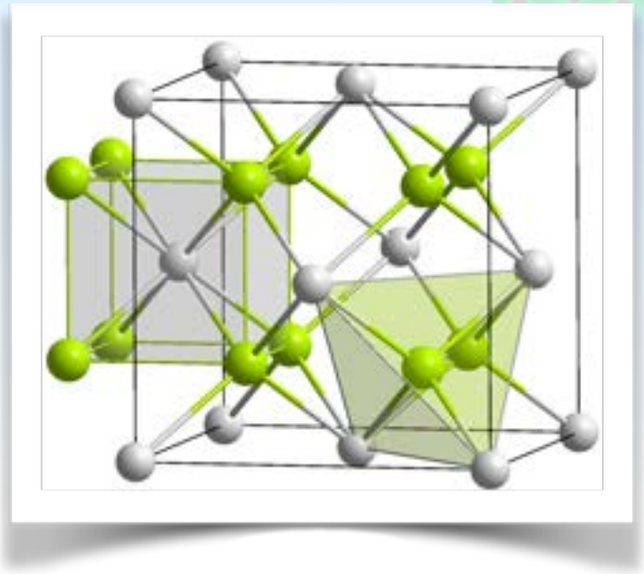
Symmetry and Structural Motifs



The Rule of Parsimony: *"The Number of essentially different kinds of constituents in a crystal tends to be small."* (Linus Pauling 1929)

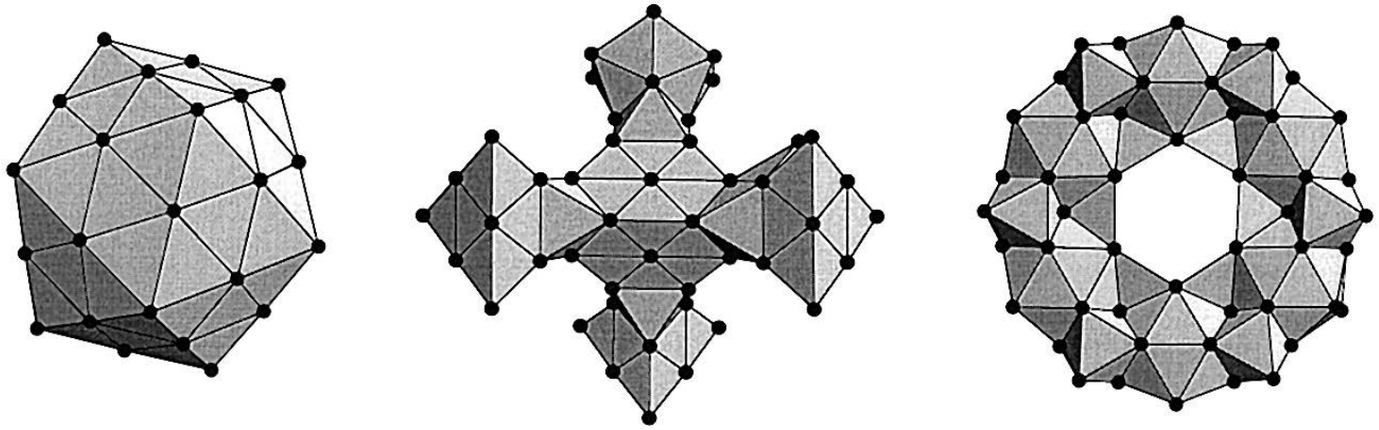


Correlation between energy and symmetry

- Low (and high) energy minima tend to correspond to symmetrical structures
- High symmetry of low-energy minima supported by the ubiquity of crystals

Example: 55-atom Lennard-Jones clusters (D. Wales '98)

Lowest energy Two highest energy



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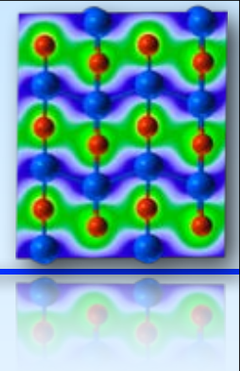
Frequency of Space Group Symmetries



For small organic molecules

- 75% of about 30,000 compounds occur in only five space groups
- 29 space groups only have one entry and 35 space groups none at all

Space Group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1$	$C2/c$
Frequency	36%	14%	12%	7%	7%

Inorganic systems show different space group frequencies

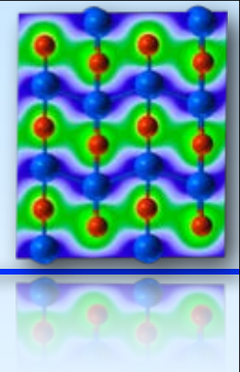
- 67% of about 100,000 compounds occur in only 24 space groups

Space Group	*Pnma*	$P2_1/c$	$Fm\bar{3}m$	$Fd\bar{3}m$
Frequency	7.4%	7.2%	5.6%	5.1%
Examples	Fe_3C, $CaTiO_3$	ZrO_2	Cu	C, Cu_2Mg

- Note: bcc is not one of the top 24 space groups

Some space groups are much more common than others in crystals

Specific Features of the Energy Landscape



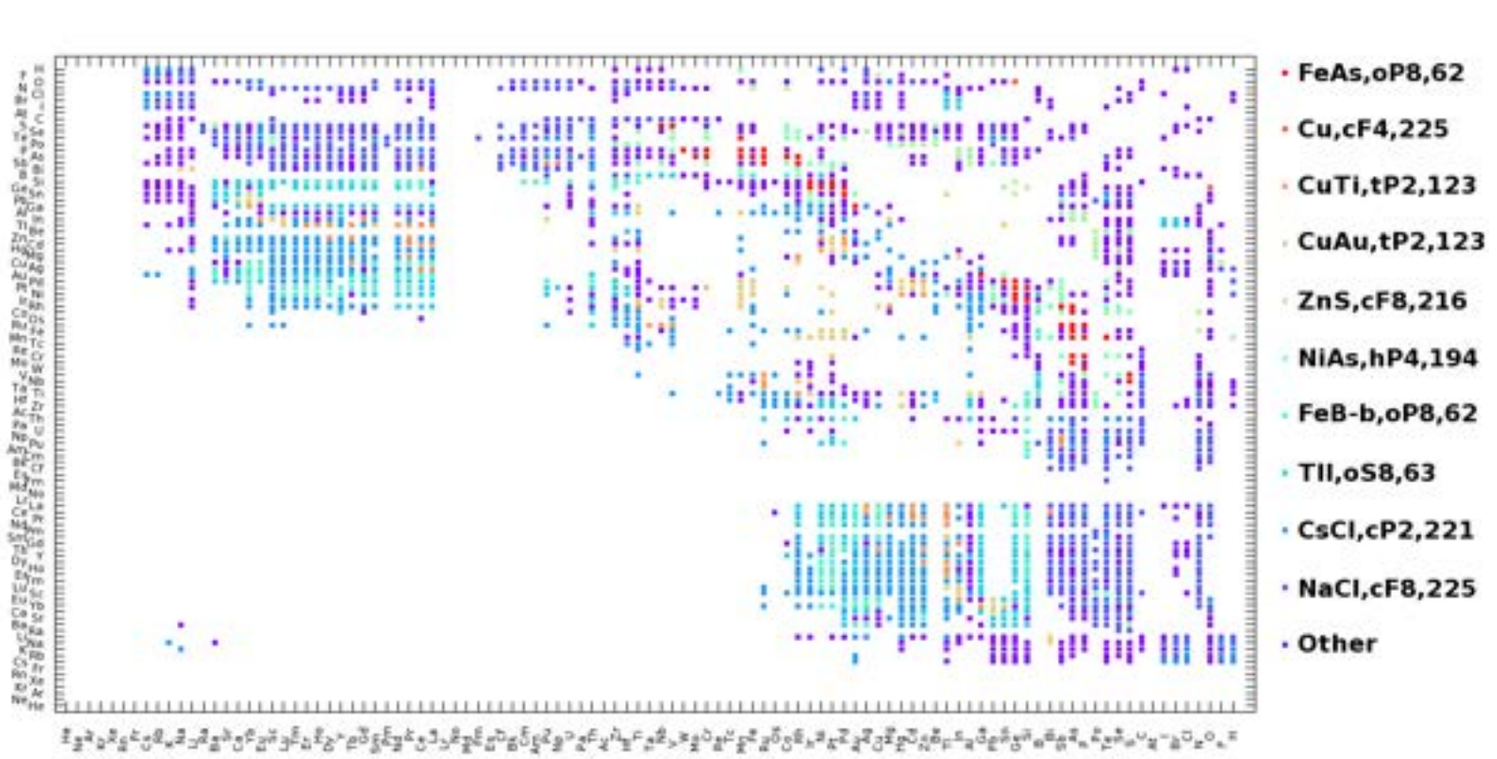
Chemical considerations

- Know a great deal about the chemistry of the systems we study
- Know which atomic types prefer to bond to one another
- Approximate bond lengths
- Likely coordination numbers of the atoms

Resulting empirical rules

- Hume-Rothery rules
- Laves rules for intermetallics
- Pauling rules for ionic materials
- Pettifor structure maps

...



E. Tasci http://www.emresururi.com/physics/?p=63

Crystal Structure Prediction is Hard: NP-Hard

NATURE VOL. 335 15 SEPTEMBER 1988

Crystals from first principles

John Maddox (1988)

A new calculation of the polymorphs of silica appears to have broken new ground in deriving crystal structure from chemical composition. But X-ray crystallographers need not worry — yet.

ONE of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition. Who, for example, would guess that graphite, not diamond, is the thermodynamically stable allotrope of carbon at ordinary temperature and pressure? Solids such as crystalline water (ice) are still thought to lie beyond mortals' ken.

Yet one would have thought that, by now, it should be possible to equip a sufficiently large computer with a sufficiently large program, type in the formula of the chemical and obtain, as output, the atomic coordinates of the atoms in a unit cell.

- Determining the global minimum of an energy landscape is an NP-hard problem
- NP-hard: Non-deterministic polynomial-time hard

  "*If a problem is NP-hard, no one in their right mind should believe it can be solved in polynomial time*" (Jeff Erickson, CS UIUC)

- For other NP-hard problems, see G. Viglietta: "Gaming is a hard job, but someone has to do it!" arXiv:1201.4995v3 (2012)

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Materials Discovery by Genetic Algorithms

The GASP Code for Structure Prediction

Will Tipton, Ben Revard, Stewart Wenner, Andy Sanchez, Richard G. Hennig

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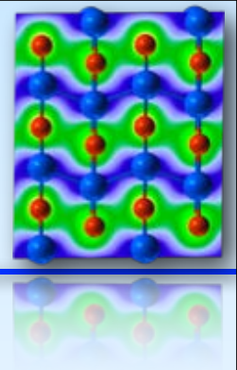
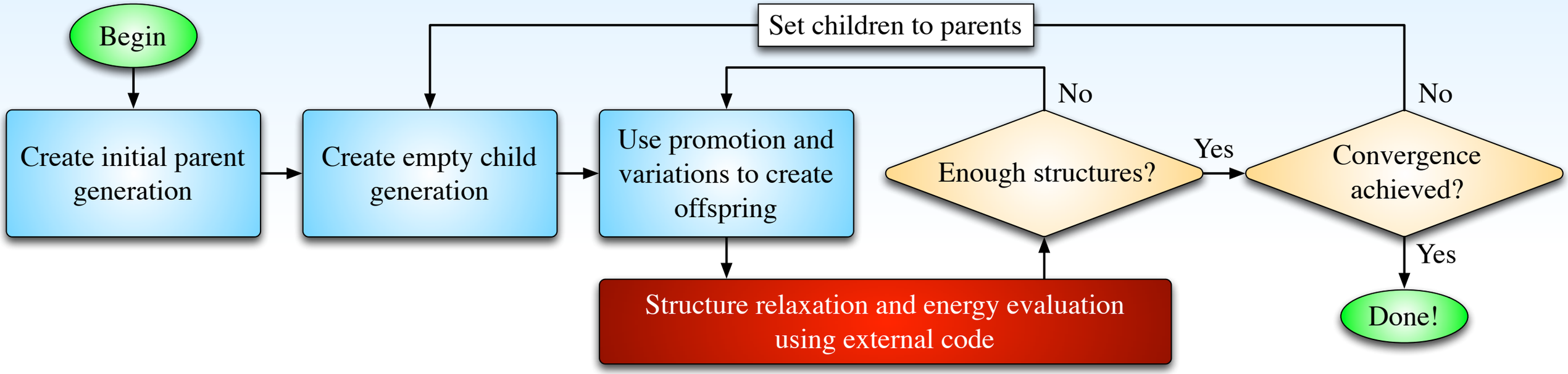
November 4-8, 2013 • Los Angeles, CA

Evolutionary Structure Search

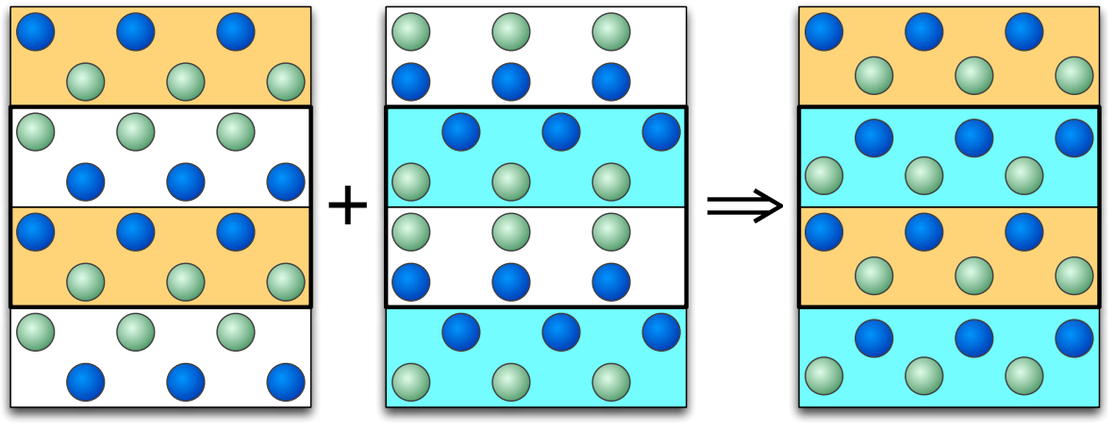


Genetic algorithm



Choice of genetic operators is important

- Selection
- Crossover
- Mutation



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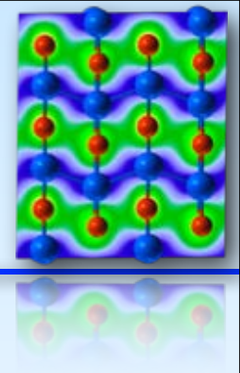
Genetic Algorithm For Structure and Phase Prediction – GA.S.P.



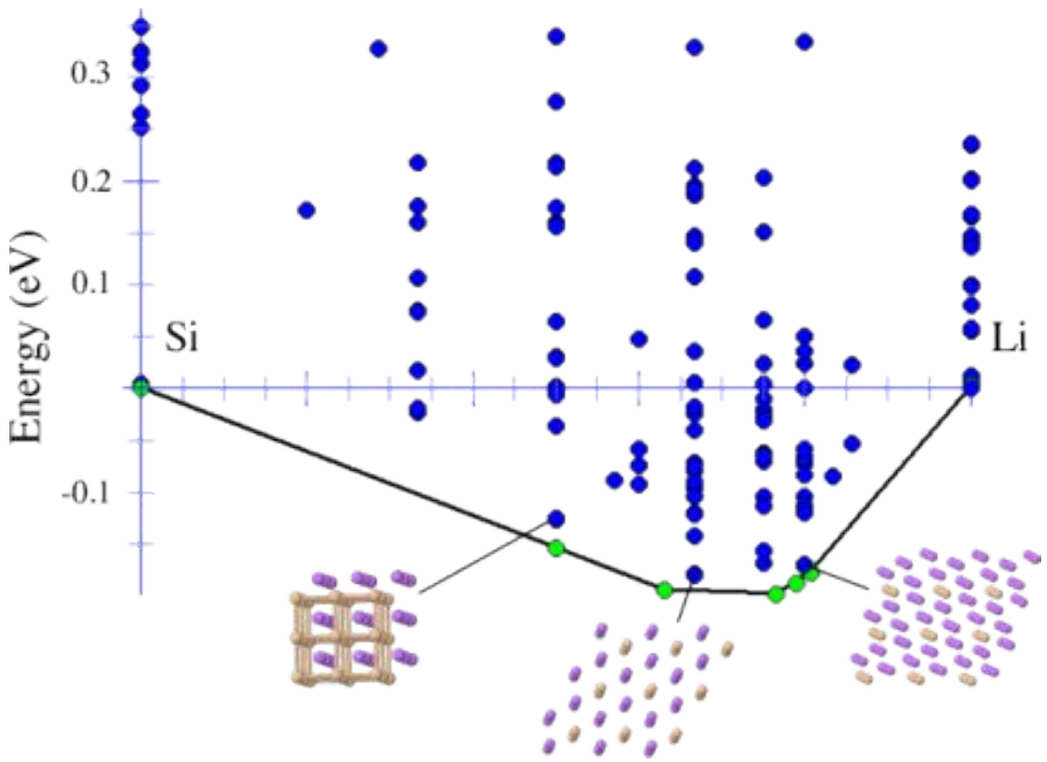
Features

- Predict **ground states**, **metastable states** and **phase diagrams**
- Search for **crystal structures, molecular crystals, molecules** and **clusters**

DFT	Semiempirical	Empirical
VASP, Gaussian, JDFT	MOPAC	LAMMPS, GULP, OHMMS

Composition-Space Search

- Convex hull of energy vs. composition
- Use formation energy as objective function
- **Grand canonical search** for all phases in multi-component phase diagram



Freely available

- Website: http://gasp.mse.cornell.edu/
- Examples, tutorials and manual

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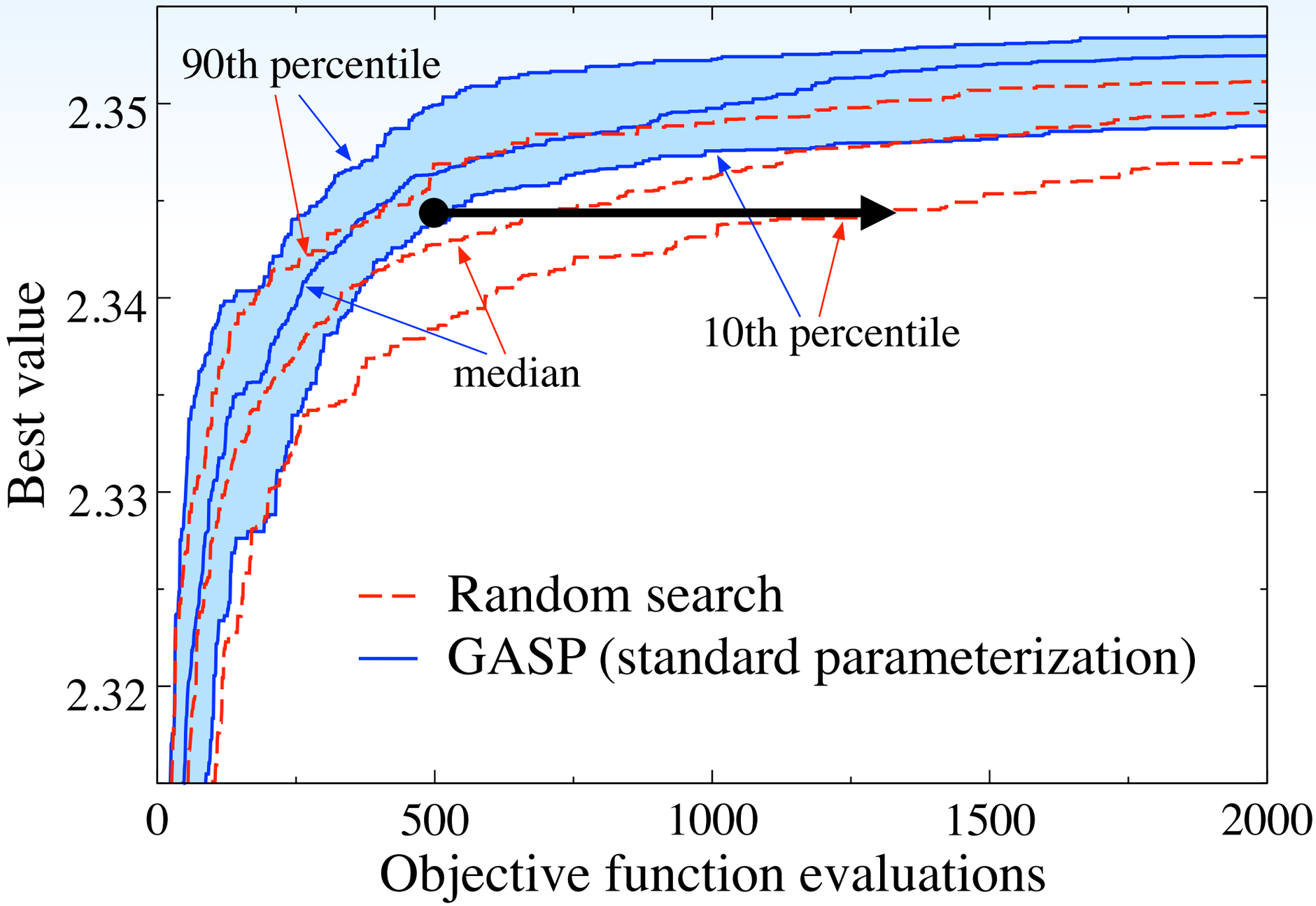
Efficiency of Genetic Algorithm

Efficiency compared to random search

- Random search requires 2-3x more structure relaxations
- Genetic algorithm learns from previous structures



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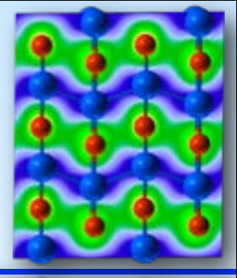
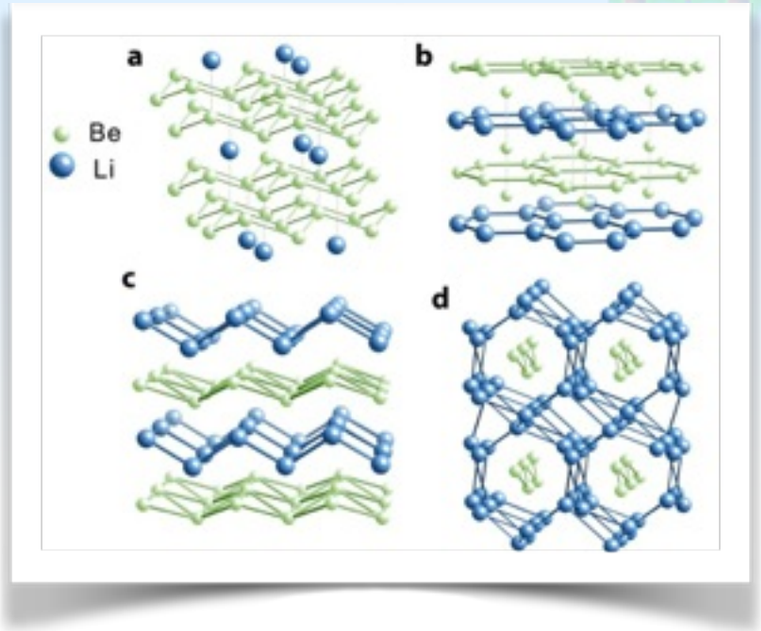
Successes of Structure Search



Lithium-Beryllium

- Immiscible at ambient conditions
- 4 compounds forming under pressure

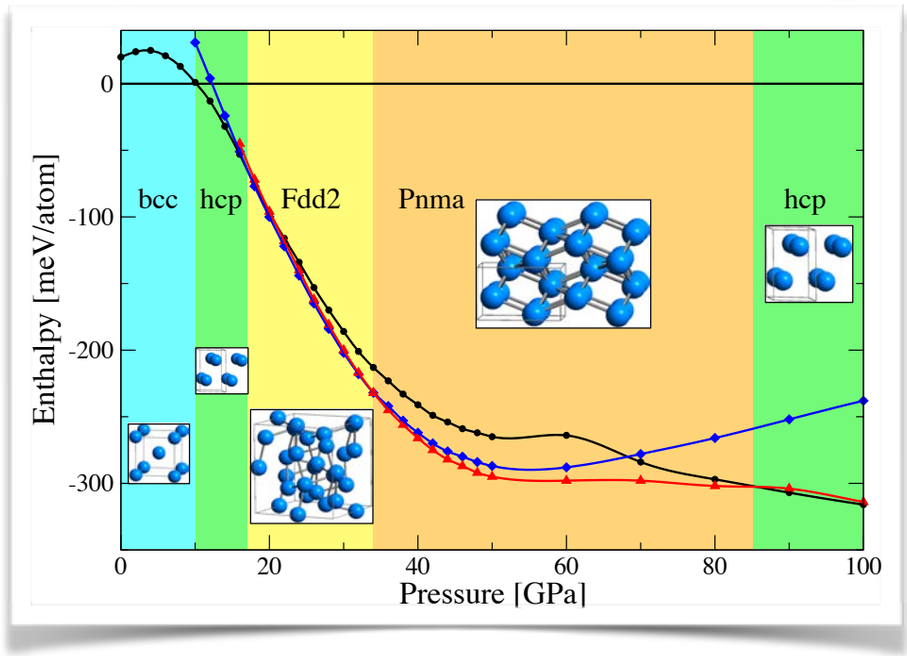
  Nature 451, 445 (2008)



Europium under pressure

- Prediction of crystal structure of superconducting Europium

  Phys. Rev. B 83, 104106 (2011)



Accuracy of empirical potentials

- Use genetic algorithm to verify accuracy of empirical energy models

  Phys. Rev. B 85, 214121 (2012)

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Prediction of Compound Formation

Li-Si and Li-S: Promising Battery Electrode Materials

Will Tipton, Clive Bealing, Michael Blonsky, Kiran Matthew, Richard G. Hennig

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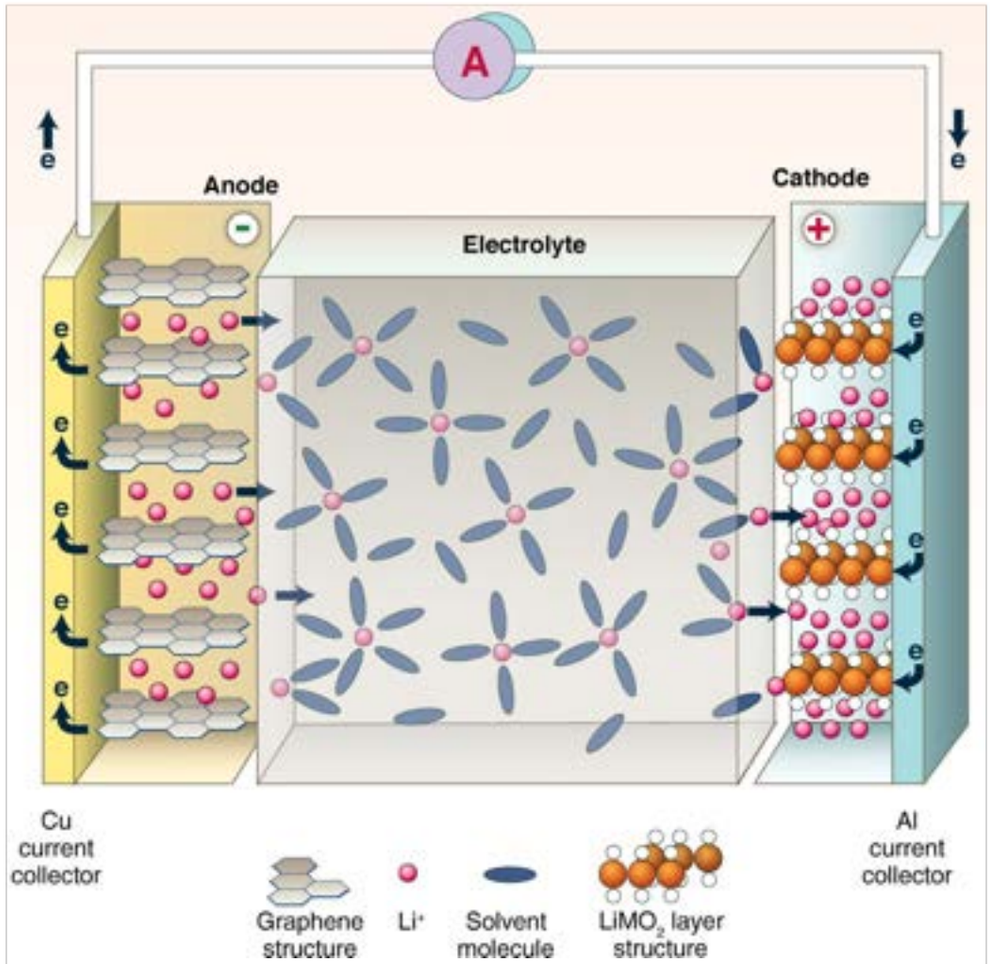
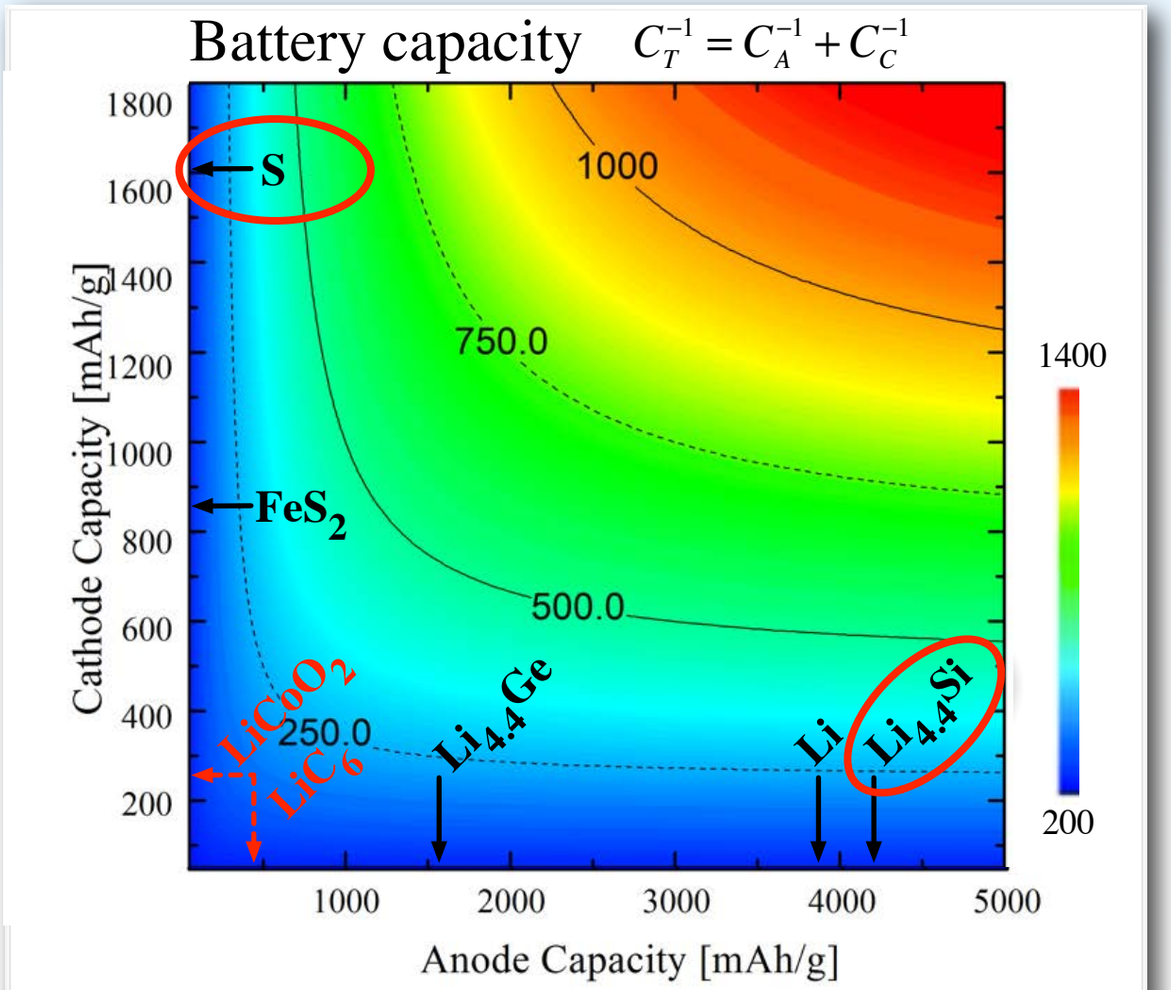
Li-Ion Batteries



Dunn *et al.* , Science 334, 928 (2011)

Anode	Cathode
LiC_6	$LiCoO_2$
<370 mAh/g	**120-150 mAh/g**

Current materials do not meet demand for high-performance batteries



If Li_6Si charge capacity exceeds Li_6C charge capacity **more than tenfold**, why don't we use Si-anodes?

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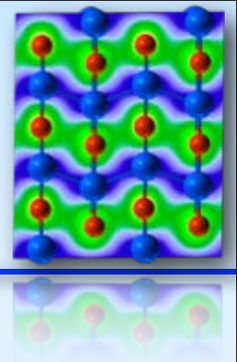
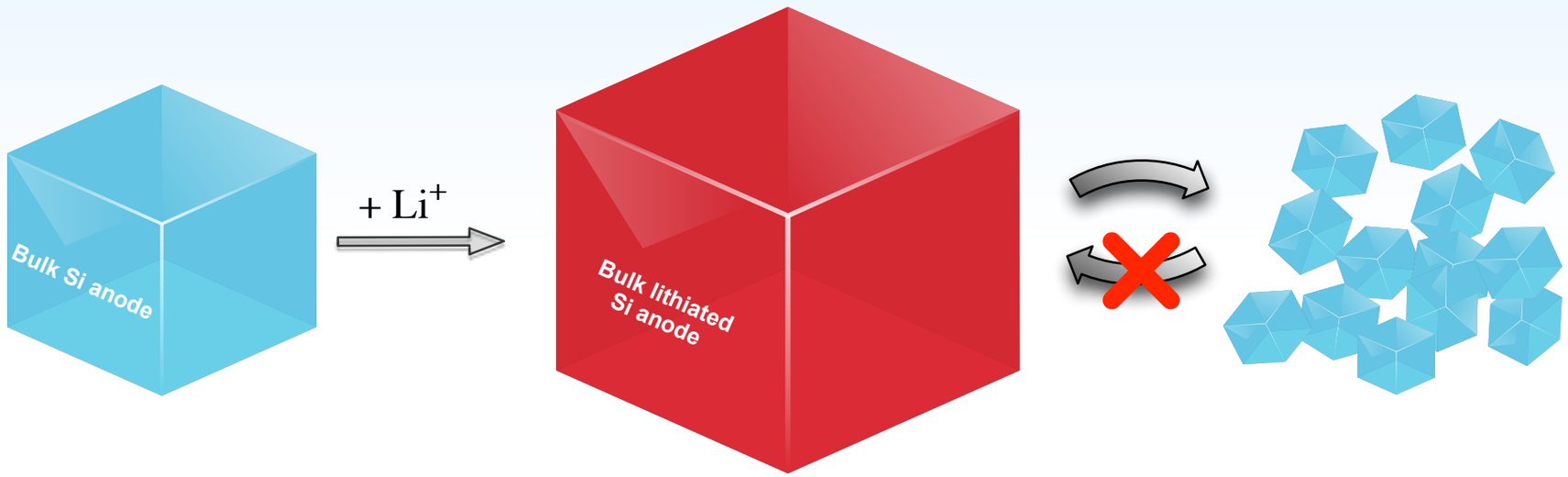
Li-Si Battery Anodes



- Charge-discharge cycles is accompanied by immense volume changes (300%) and resulting mechanical stresses



Park et al. *Nano Lett* 9, 3844 (2009)

- Experimental solution: Si nanowires and nanotubes
- Park *et al*.: Charge capacity of 3247 mAh/g
- c-Si becomes a-Li_xSi during lithiation and remains so after delithiation

How is the energy density affected by amorphization of structures?
Could small unit cell metastable crystal structures play a role?

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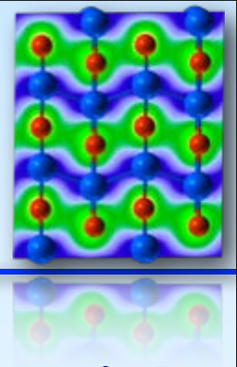
Energy Model and Amorphous Structures



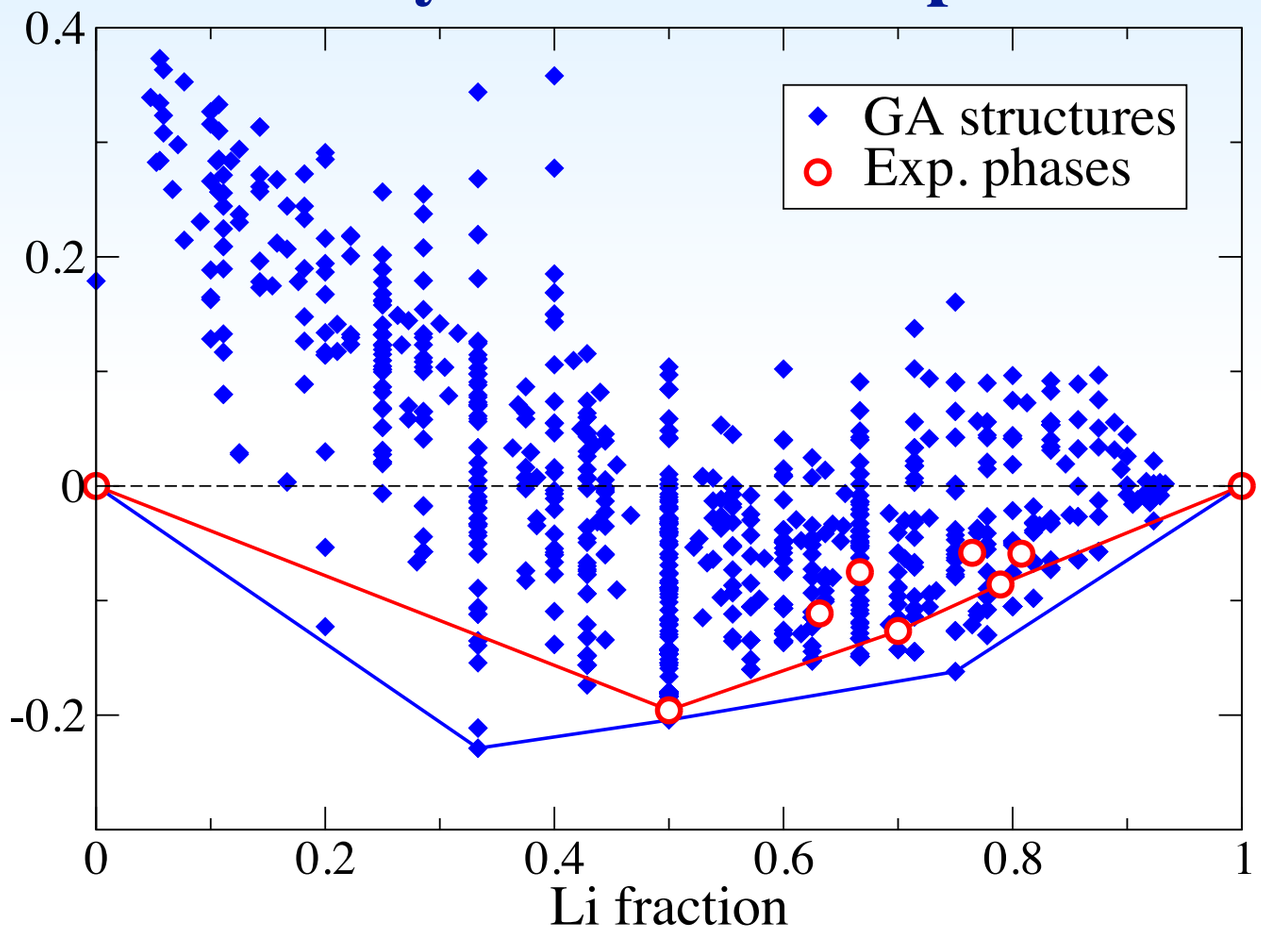
Energy methods

Interpolative
(Semi-)empirical methods

Extrapolative and predictive
First-principles or *ab-initio* methods

- **Density-functional theory offers balance of speed and accuracy**
- Pseudopotentials and plane-wave basis (VASP)
- Amorphous structures from melt/quench approach

Accuracy of Li-Si EAM potential



EAM insufficient for thermodynamics and kinetics

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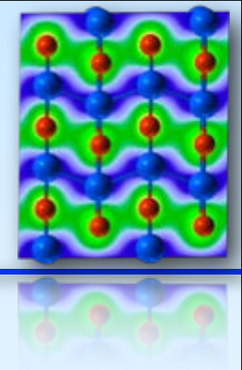
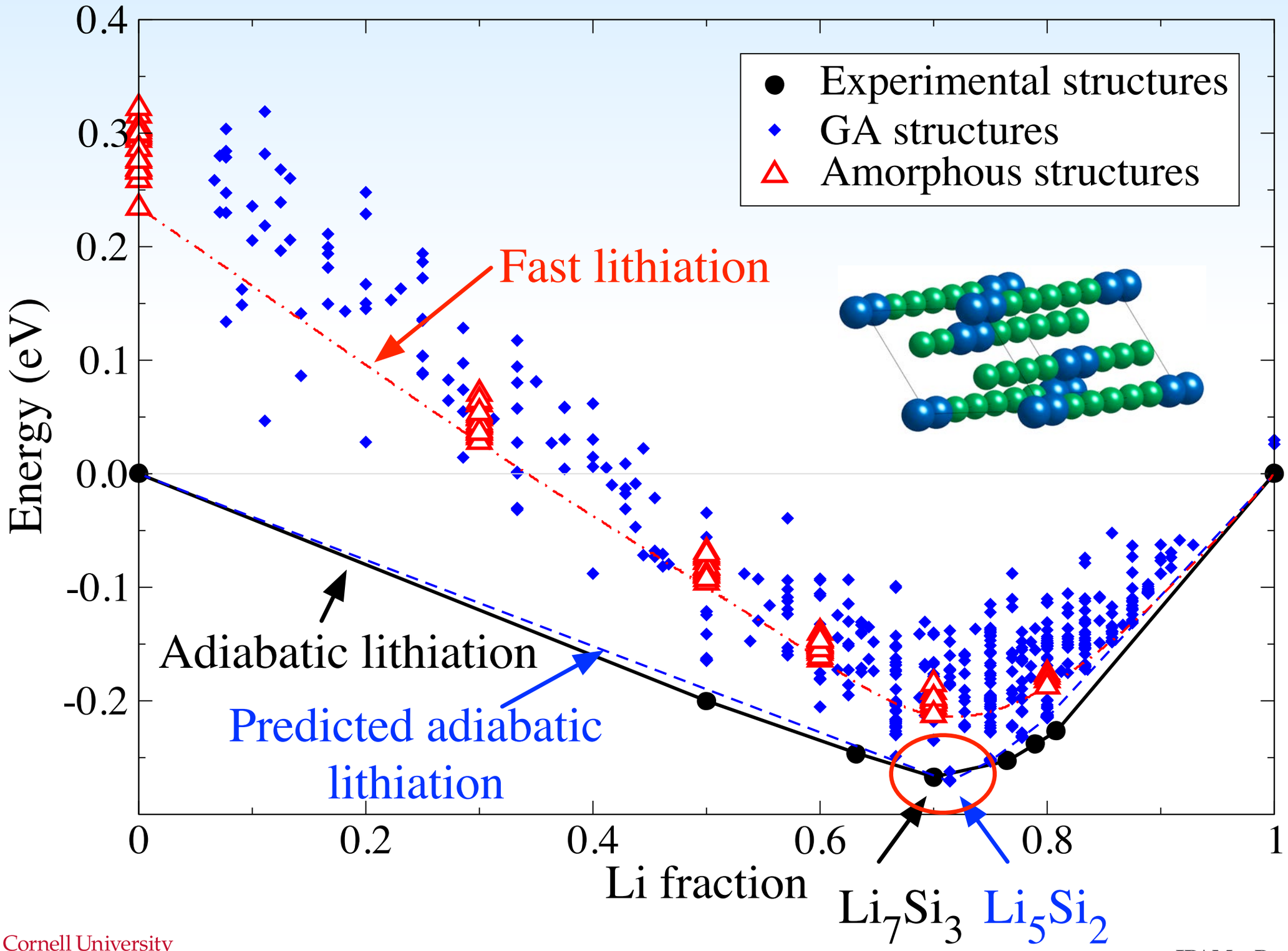
Li-Si Structure Search





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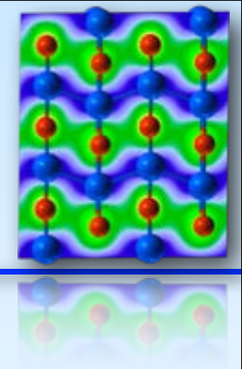
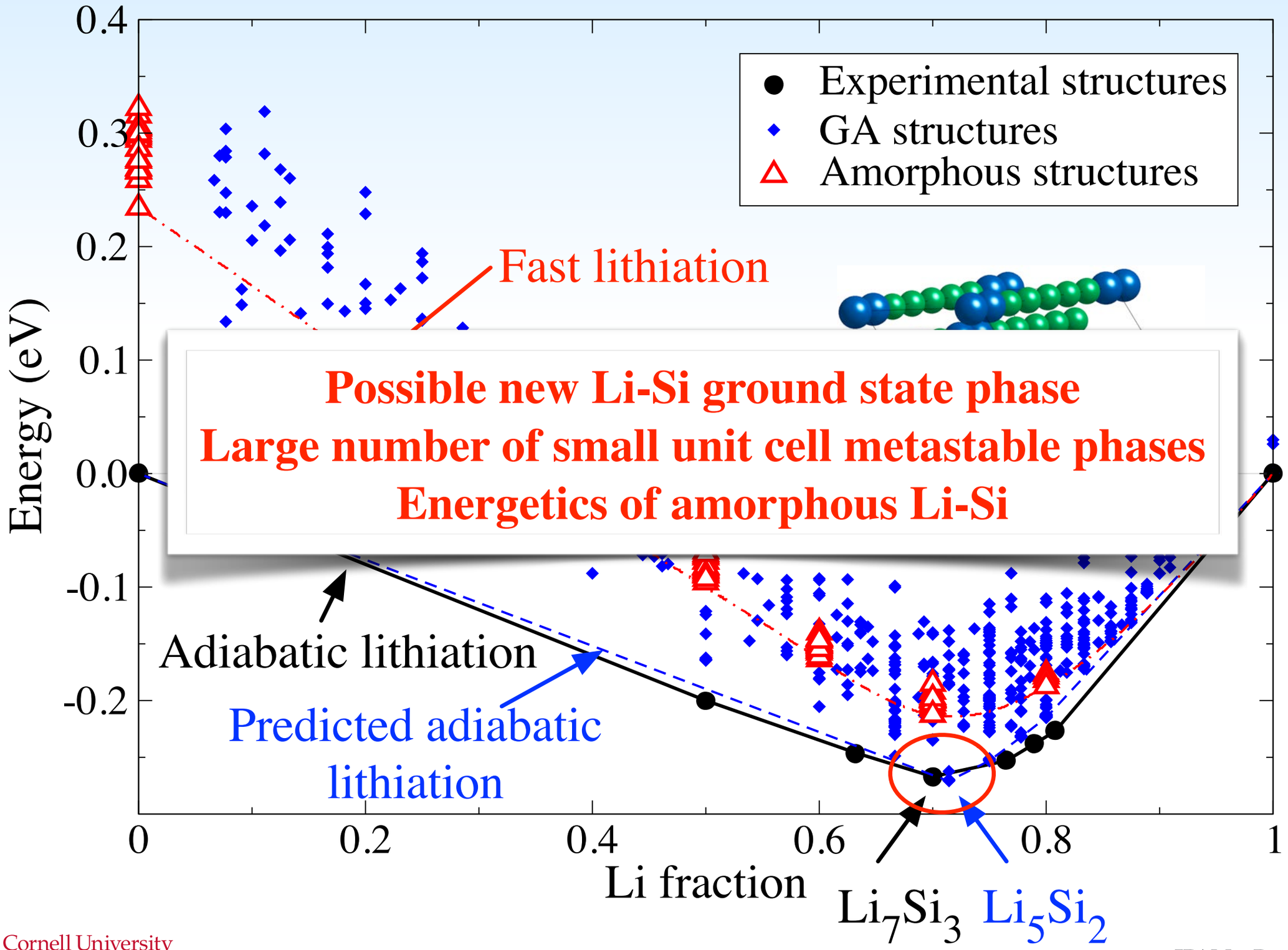
Li-Si Structure Search





Possible new Li-Si ground state phase
Large number of small unit cell metastable phases
Energetics of amorphous Li-Si

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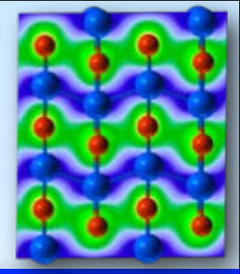
The Li_5Si_2 and Li_7Si_3 Phases



Experimental refinement

- Li_7Si_3 same structure as Li_5Si_2 phase
- High vacancy concentration on Li 1(b)
- About 1 vacancy per 3 unit cells in Li_7Si_3

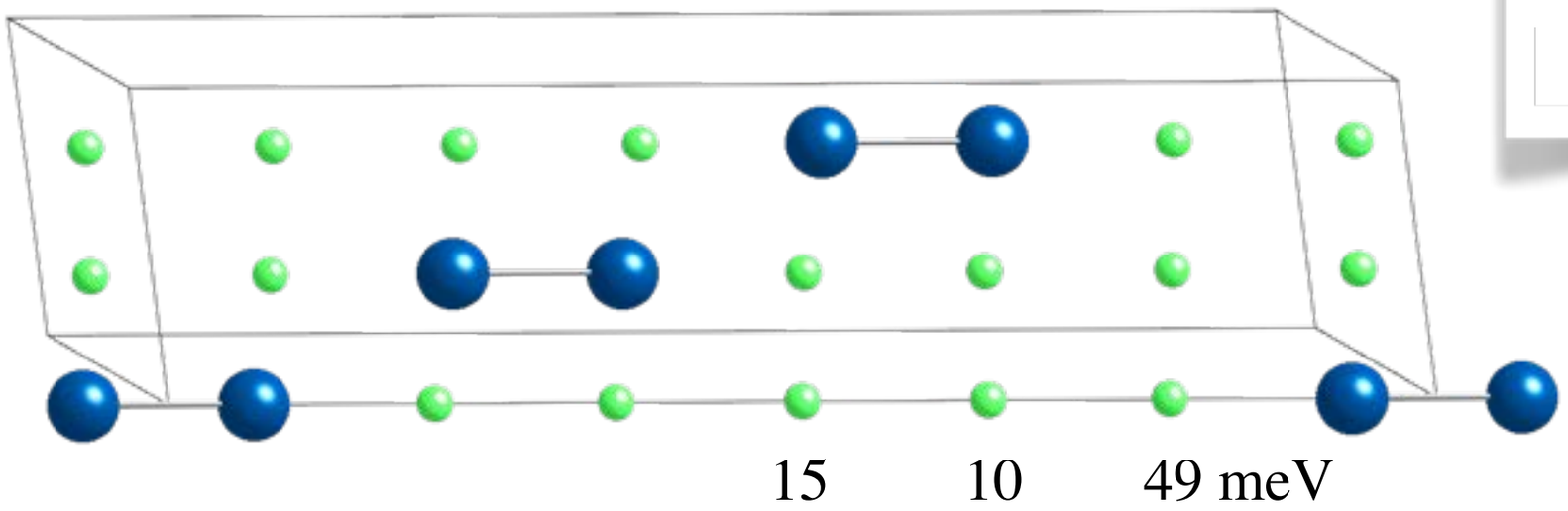
No. 166, R-3m, a = 4.39 Å, c = 17.92 Å			
Si 2(c)	0	0	0.067
Li 2(c)	0	0	0.353
Li 2(c)	0	0	0.21
Li 1(b)	0	0	1/2

Atom	Lage	SOF	x	y	z
Si	6c	1.00	0	0	0.06439(6)
Li1	6c	1.00(2)	0	0	0.3522(6)
Li2	6c	0.95(2)	0	0	0.2082(5)
Li3	3b	0.80(4)	0	0	1/2

Refinement: v. Schnering, Z. Metallkde. 71, 357 (1980)

Vacancies

- Very low formation energy explains high concentration at room temperature



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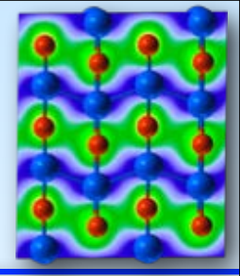
The Li_5Si_2 and Li_7Si_3 Phases



Experimental refinement

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Si 2(c)	0	0	0.067
Li 2(c)	0	0	0.353
Li 2(c)	0	0	0.21
Li 1(b)	0	0	1/2

Unusual large vacancy concentration expected to results in extremely high Li mobility

Vacancies

- Very low forr
  concentration at room temperature

			x	y	z
			)	0	0.06439(6)
			)	0	0.3522(6)
Li2	6c	0.95(2)	0	0	0.2082(5)
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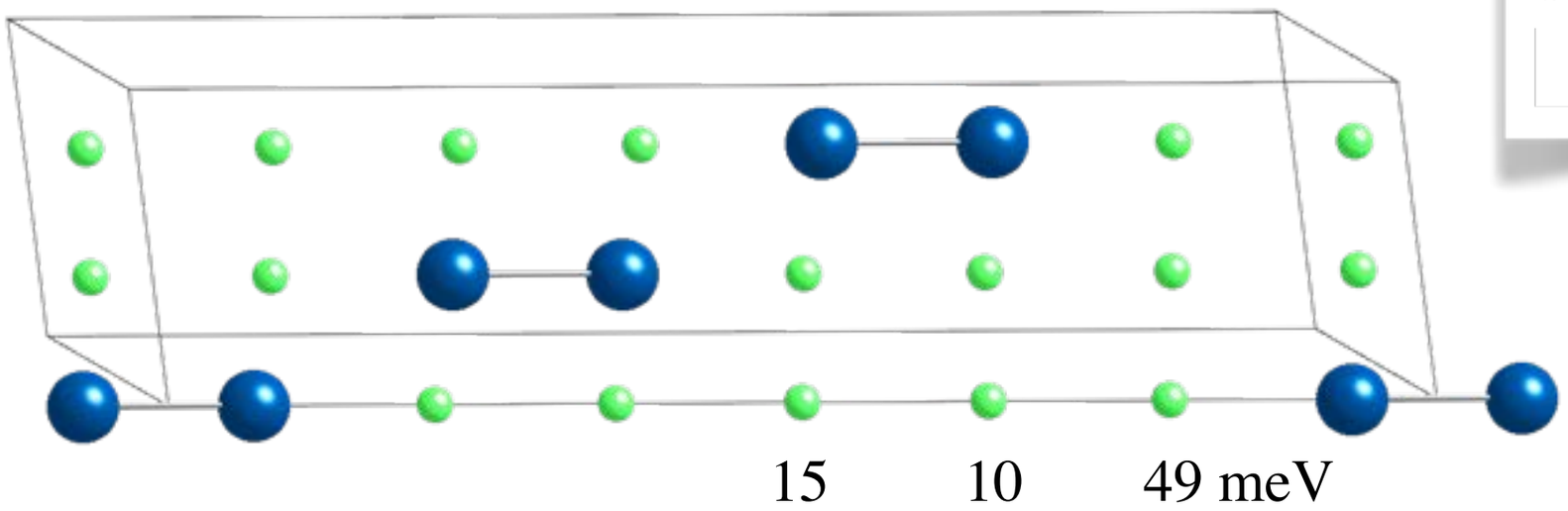

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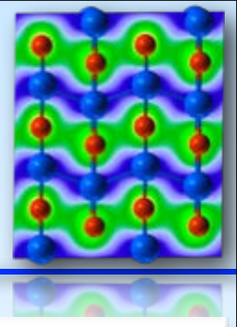
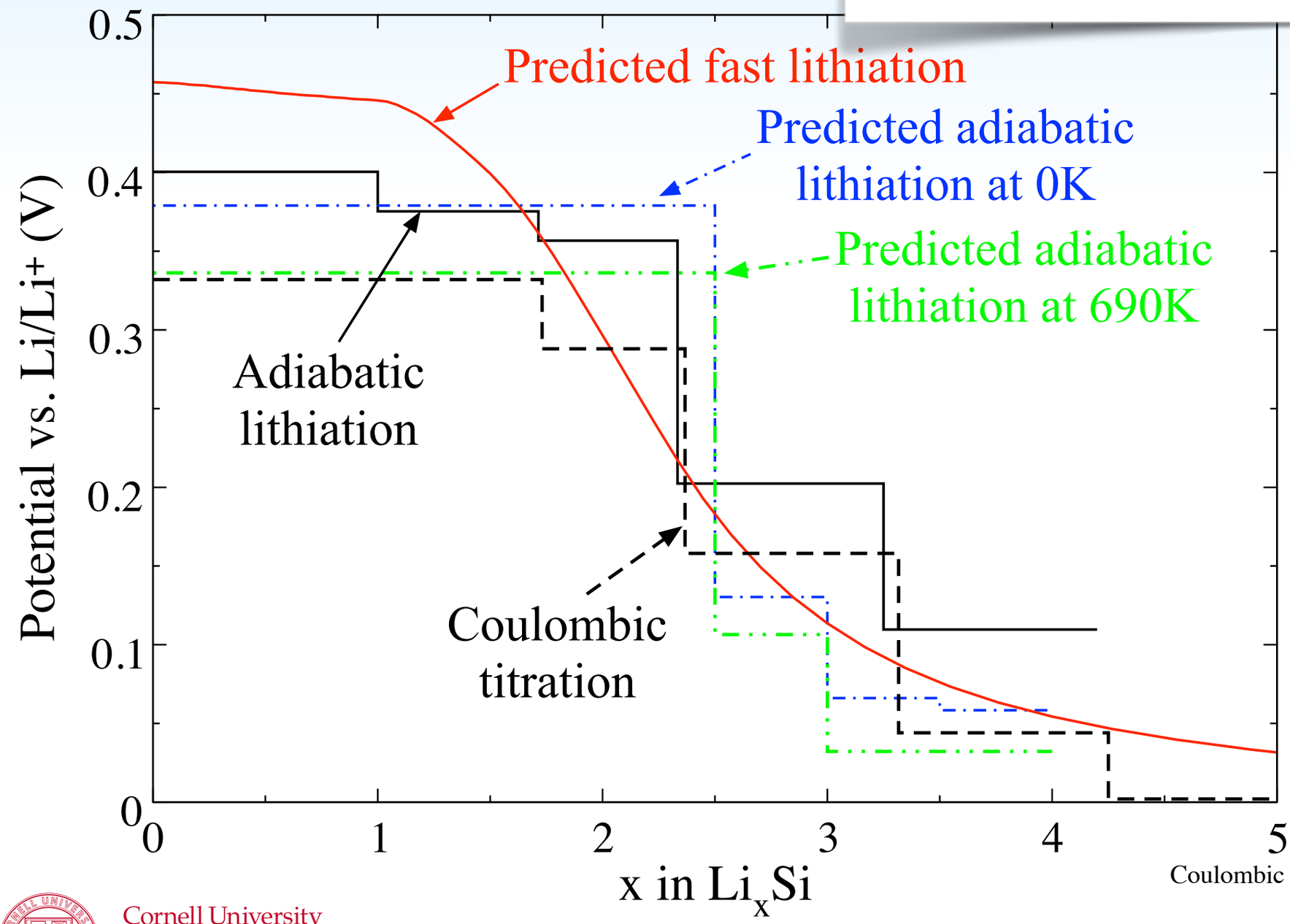
Voltage Dependence of Li-Si Anodes



Good agreement of predicted voltages with titration

Similar voltages for metastable structures and for amorphous structures



Phys. Rev. B 87, 184114 (2013).

Coulombic Titration: Wen et al. J. Sol. State Chem. 37, 271 (1981)

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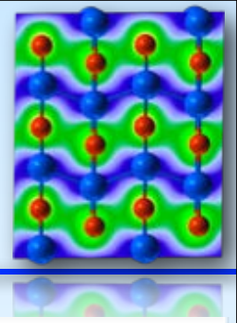
Voltage Dependence of Li-Si Anodes



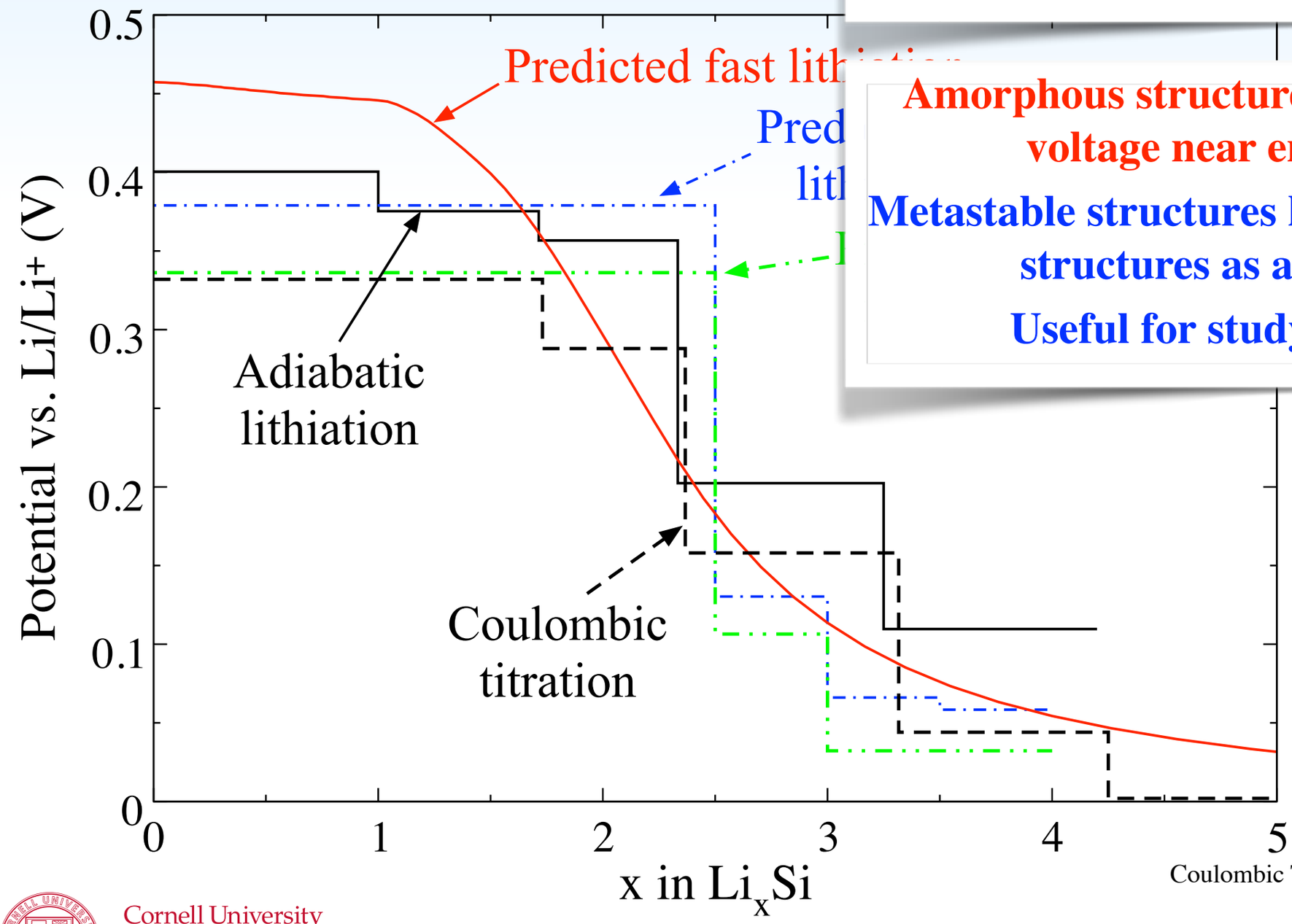
Good agreement of predicted voltages with titration

Similar voltages for metastable structures and for amorphous structures

Amorphous structures slightly reduce operating voltage near end of discharge cycle

Metastable structures have similar energy and local structures as amorphous structures

Useful for study of lithiation kinetics



Phys. Rev. B 87, 184114 (2013).

Coulombic Titration: Wen et al. J. Sol. State Chem. 37, 271 (1981)

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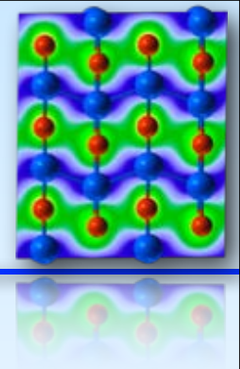
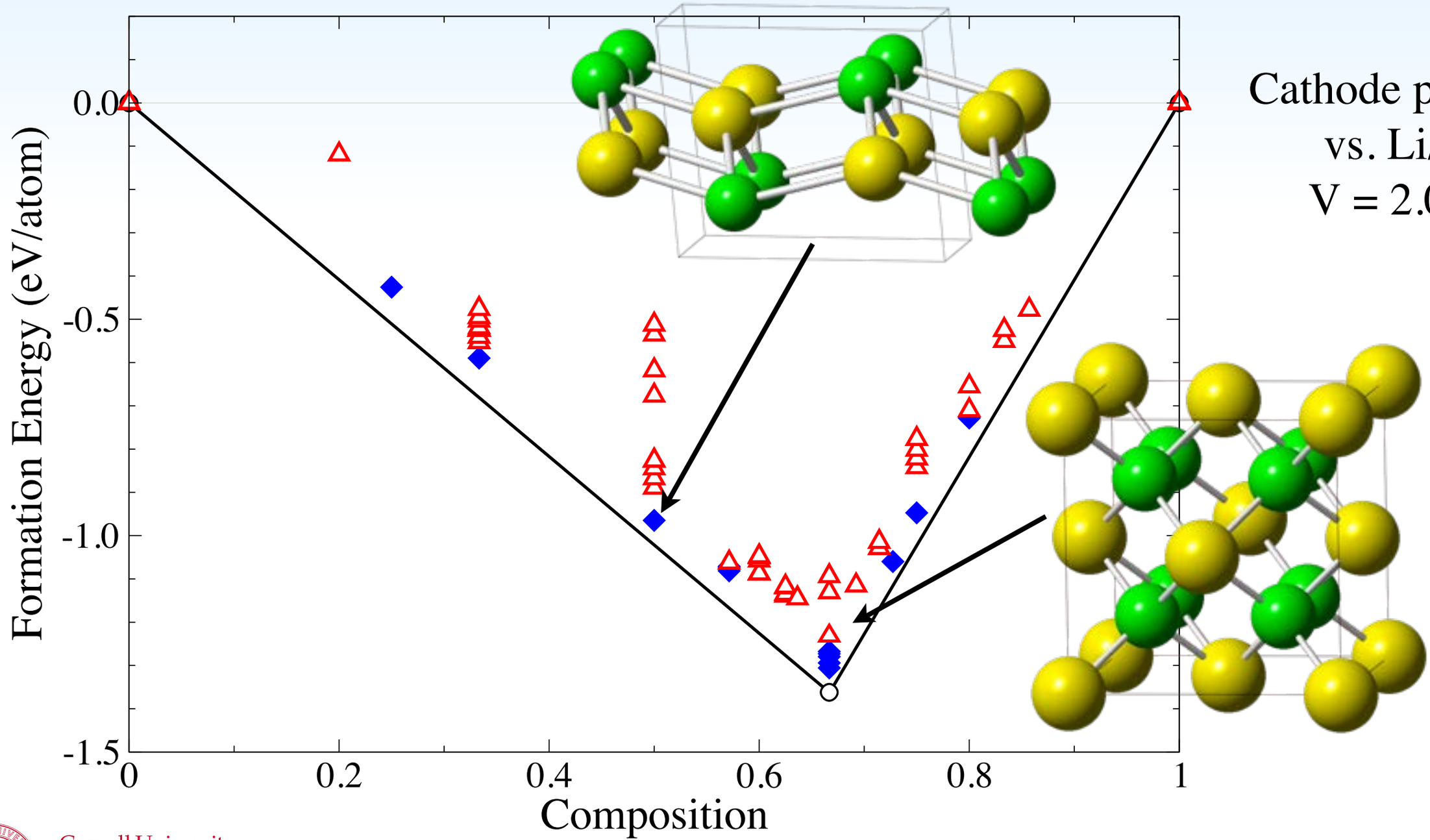
Li-S Structure Search



Li monosulfide reported by Thomas and Jones in 1929

GASP finds potentially metastable Li_2S_2 structure



Cathode potential
vs. Li/Li^+
V = 2.04 V

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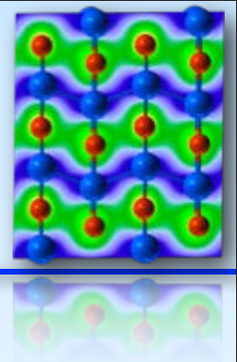
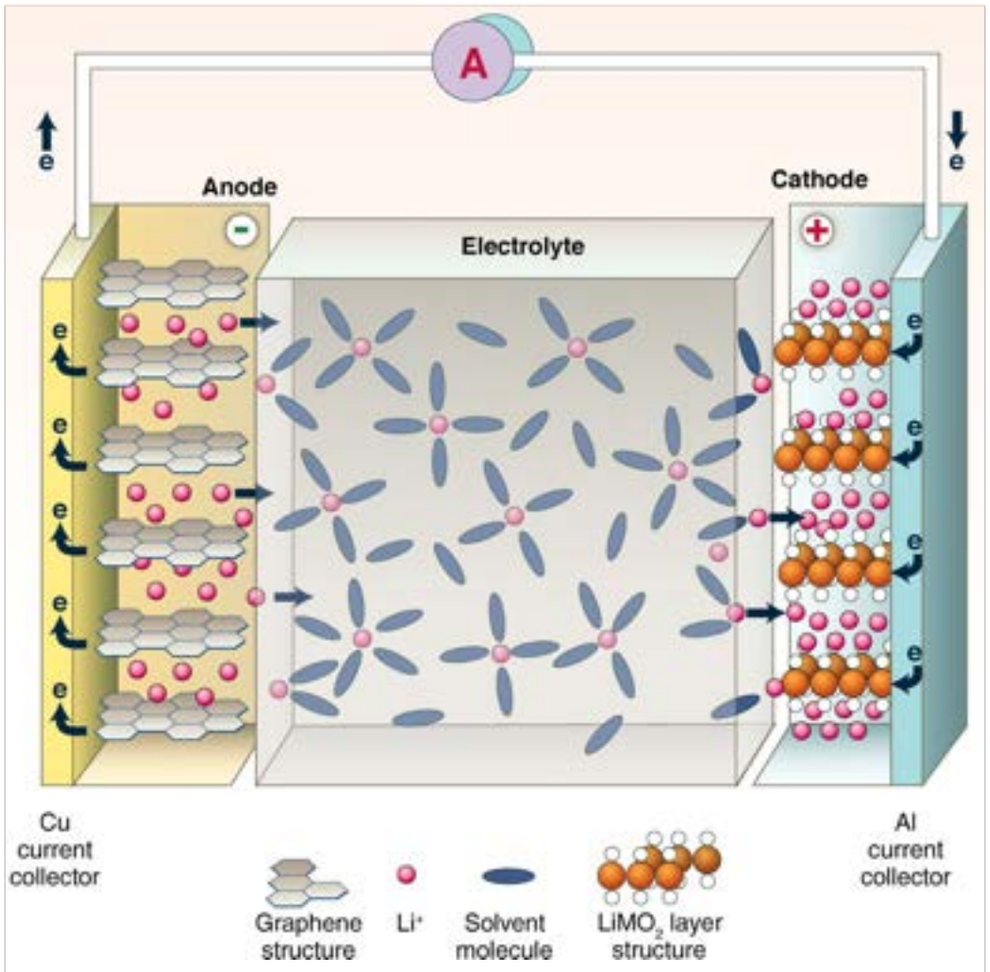
Li-ion Anode and Cathode Performance





Dunn *et al.* , Science 334, 928 (2011)

	Anode	Cathode
	$Li_{4.4}Si$	Li_2S
Charge capacity	**4,200 mAh/g**	**1,670 mAh/g**
Potential vs. Li/Li^+	**0.4 V**	**2.0 V**
Charge capacity	913 mAh/g	
Energy density	**1.5 Wh/g**	

Anode	Cathode
LiC_6	$LiCoO_2$
<370 mAh/g	**120-150 mAh/g**

Current commercial Li-ion batteries:
3.6 V, 70 mAh/g and **230 mWh/g**
(includes electrolyte and case)

Lot's of room for improvement for future Li-ion batteries

Data from http://www.panasonic.com/industrial/batteries-oem/oem/lithium-ion.aspx

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Ab initio methods for solid/liquid interfaces

Katie Schwarz, Kiran Matthew, Ravishankar Sundararaman, Kendra Letchworth-Weaver, Tomas Arias, Richard G. Hennig

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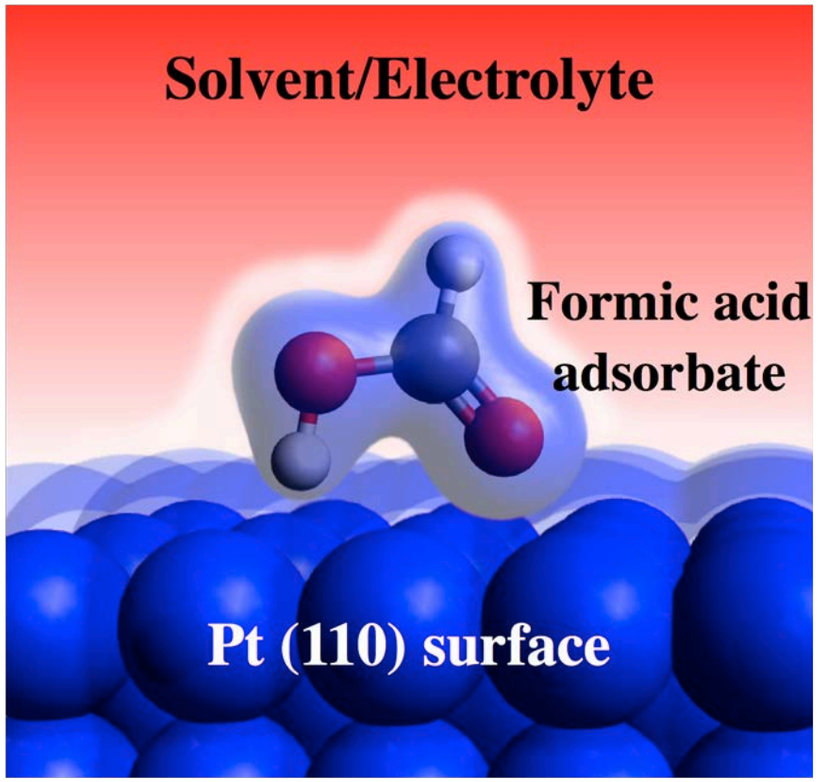
Importance of Solvent Effects

Motivation

- Energetics of chemical processes differ in vacuum and solution
- Importance of solvent effects in catalysis and electrochemistry
- Applications to energy technologies:
  Fuel cells and batteries
- Example:
  - Nucleophilic substitution (S_N2) reaction

$$Cl^- + CH_3Cl \rightarrow CH_3Cl + Cl^-$$

  - Hydration effects lower transfer rate by **20 orders of magnitude**



Solvation effects important for applications to energy technologies

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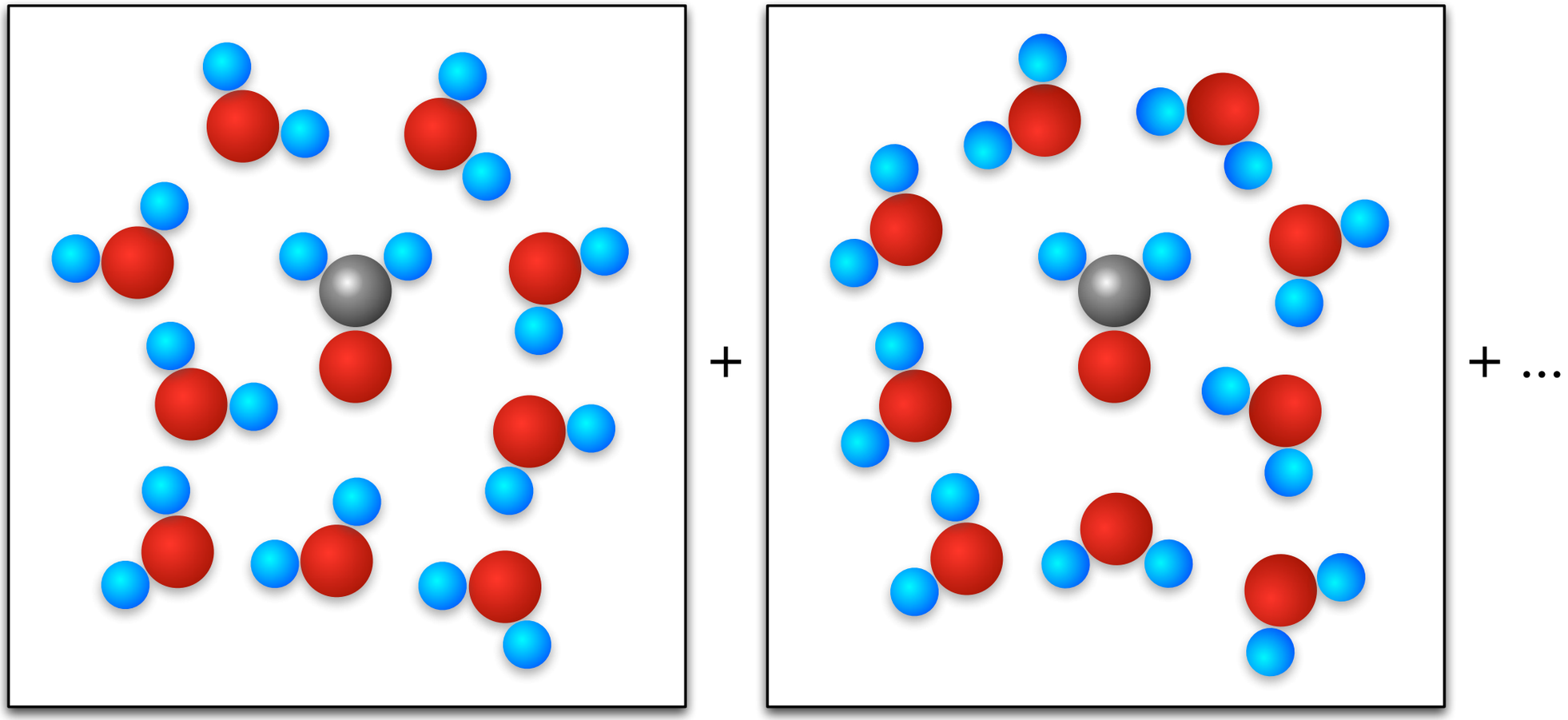
Why an Implicit Solvation Model?

Motivation

- Explicit solvation calculations require **many electrons** and **multiple nuclear configurations** of the solvent



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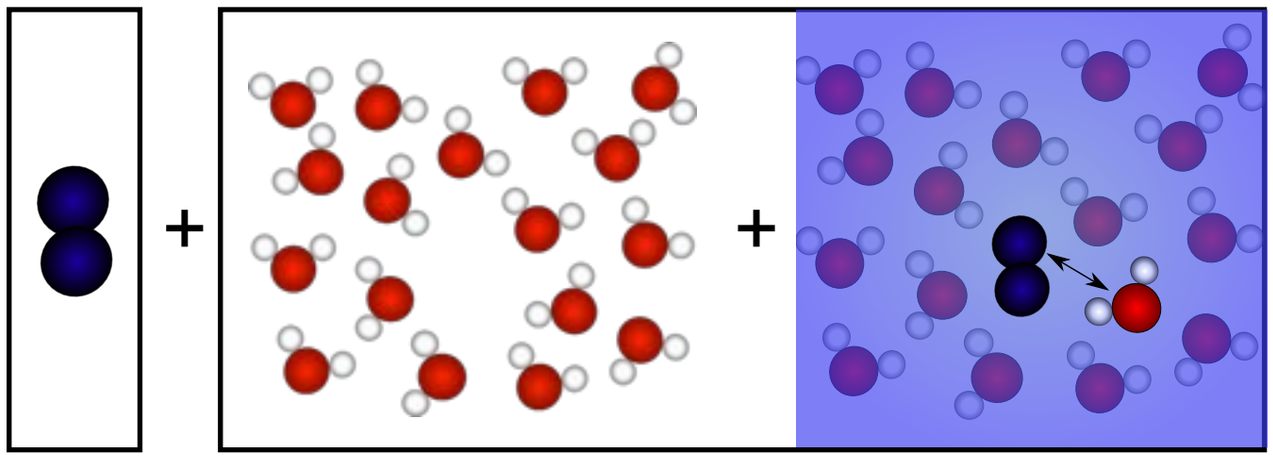
Joint Density Functional Theory

- Variational Principle of JDFT[1] - A is an exact free energy functional minimized by the fluid density N_α and electron density n

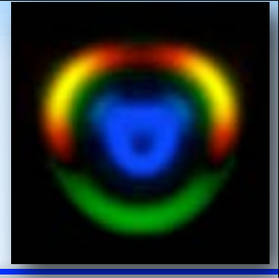
$$A[n,\{N_\alpha\}] = \underbrace{A_{\mathrm{HK}}[n]}_{\text{Electrons}} + \underbrace{\Omega_{\mathrm{lq}}[\{N_\alpha\}]}_{\text{Liquid}} + \underbrace{\Delta A[n,\{N_\alpha\}]}_{\text{Coupling}}$$



- The liquid and coupling terms are microscopically improvable
- Flexible, the model works with any electron basis set and can be used for surfaces and molecules

[1] S. Petrosyan, J.F. Briere, D. Roundy, and T. Arias, Phys. Rev B. 75, 205105 (2007)

Joint Density Functional Theory



- Combine terms related to the solvation into a single term

$$A[n, \{N_\alpha\}] = \underbrace{A_{\mathrm{HK}}[n]}_{\text{Electrons}} + \underbrace{\Omega_{\mathrm{lq}}[\{N_\alpha\}] + \Delta A[n, \{N_\alpha\}]}_{A_{\mathrm{solv}}}$$

solute electron density

average solvent site density

- Variational derivative with respect to the exact electron density *n*

$$\frac{\delta A}{\delta n} = \frac{\delta A_{\mathrm{HK}} + A_{\mathrm{env}}}{\delta n}$$

yields the usual Euler-Lagrange equation for the isolated electronic system with an **additional external potential**

$$V_{\mathrm{solv}}\left[n, \{N_\alpha\}\right] \equiv \left.\frac{\delta A_{\mathrm{solv}}\left[n, \{N_\alpha\}\right]}{\delta n}\right|_{N_\alpha}$$

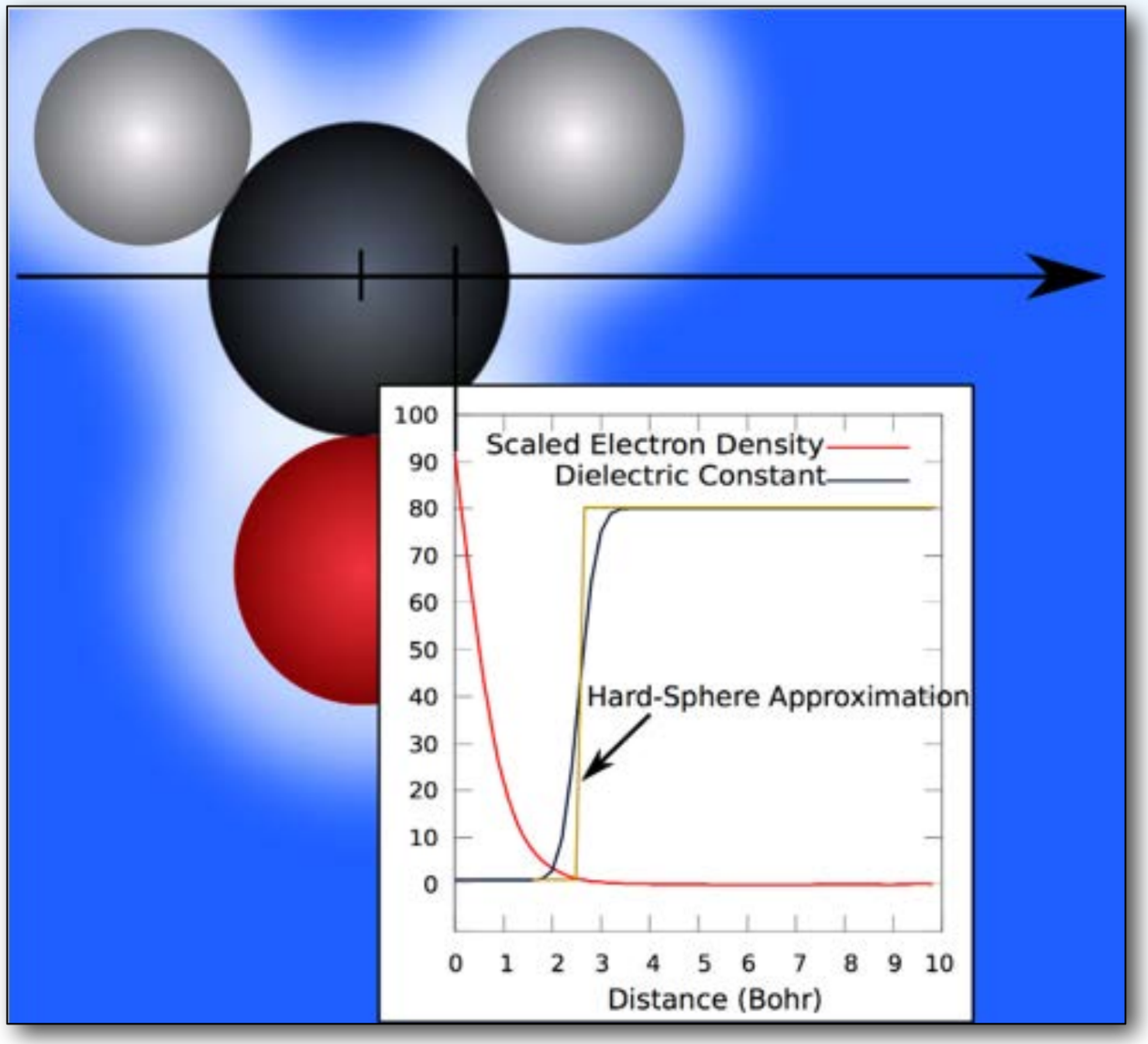
- Thermodynamic state of the system is given by **self-consistent solution** for which the electron density yields back the same potential

Simple Approximation for A_{env}

Linear dielectric continuum model

- Fluid and coupling modeled by dielectric continuum
- Dielectric constant determined by local electron density $n(r)$
- Switches smoothly from vacuum value at high density to value of liquid at low electron density
- Potential determined by modified Poisson equation

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \phi = -4\pi n(\mathbf{r})$$



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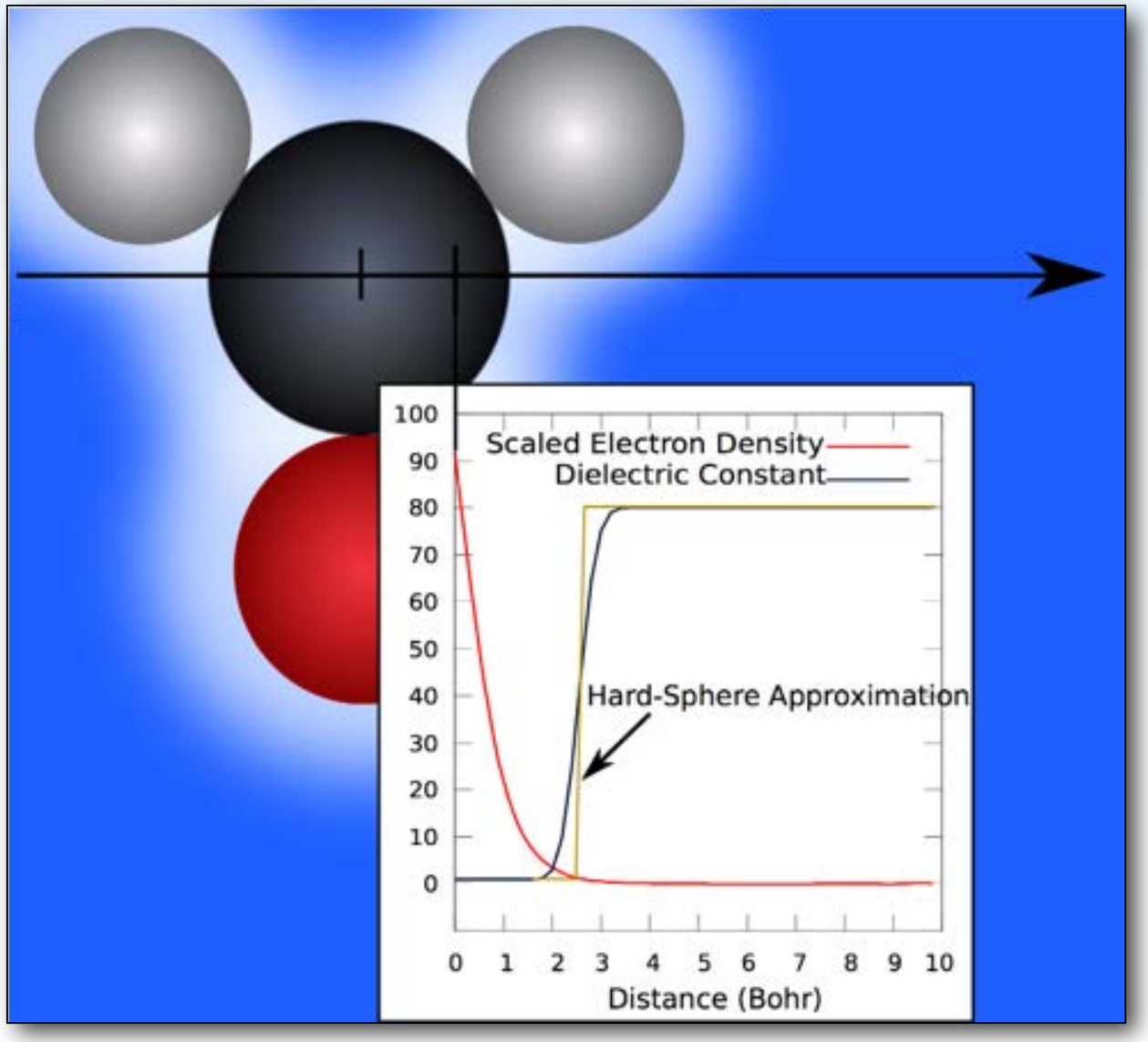
Linear Dielectric Continuum Model

- Similar to Fattebert and Gygi,
  Int. J. Quantum Chem., 93, 139 (2003)
- Hard Sphere approximation by Amovilli, Filippi and Flores and others
  J. Chem. Phys. 129, 244106 (2008),
  J. Phys. Chem. B 110(51) (2006)



Advantages of our model

1) **Microscopically improvable:**
   Part of larger theoretical framework
2) **Ab initio:** Cavity forms itself from the electron density
3) **Flexible:** Model works with any electron basis set and can be used for surfaces and molecules

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Linear Dielectric Continuum Model

Approximations

$$A_{\mathrm{solv}}[n] \equiv \min_{\{N_\alpha\}} \left(\underbrace{\Omega_{\mathrm{lq}}[\{N_\alpha\}]}_{=0} + \Delta A[n, \{N_\alpha\}] \right)$$

$$= \frac{1}{2} \int (n - N_\alpha) \left[\left(-\frac{\nabla \cdot \epsilon(n) \nabla}{4\pi} \right)^{-1} - \left(-\frac{\nabla^2}{4\pi} \right)^{-1} \right] (n - N_\alpha) d^3 r$$

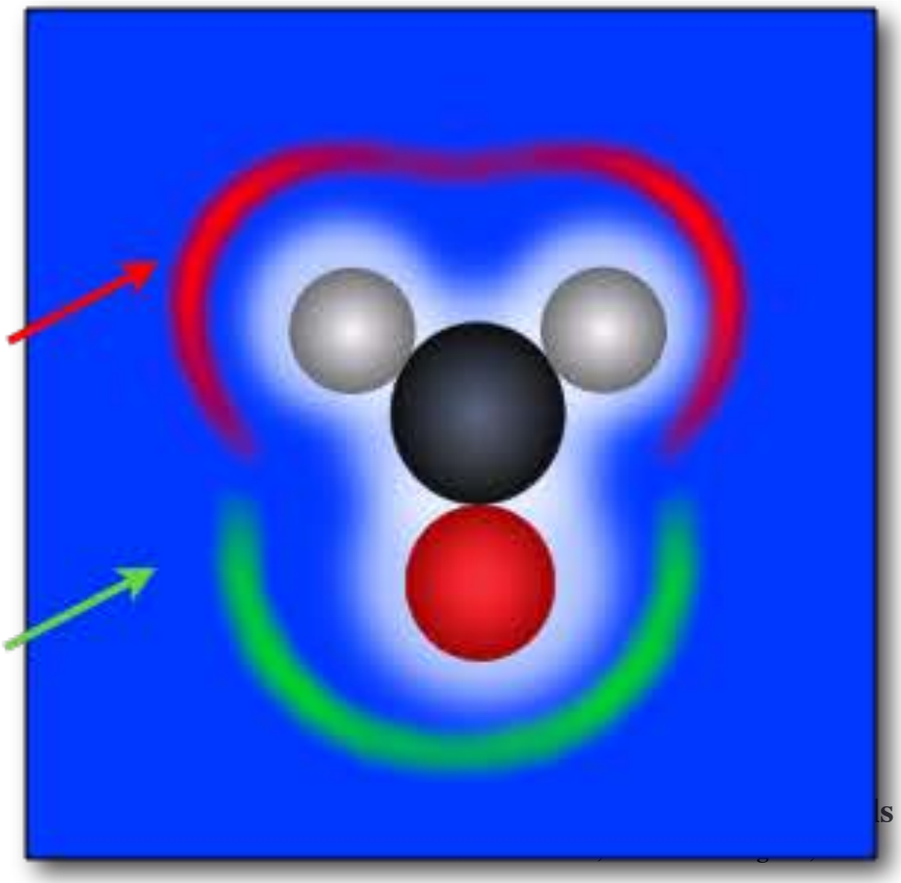
$$V_{\mathrm{solv}}[n] = -\phi_{\mathrm{Hartree}} + \phi + \mathcal{O}(10^{-2}) \approx \phi_{\mathrm{bound}}$$

Cavitation and dispersion

$$A_{\mathrm{cav}} = \tau \int dr |\nabla S|$$

Negative bound charge

Positive bound charge



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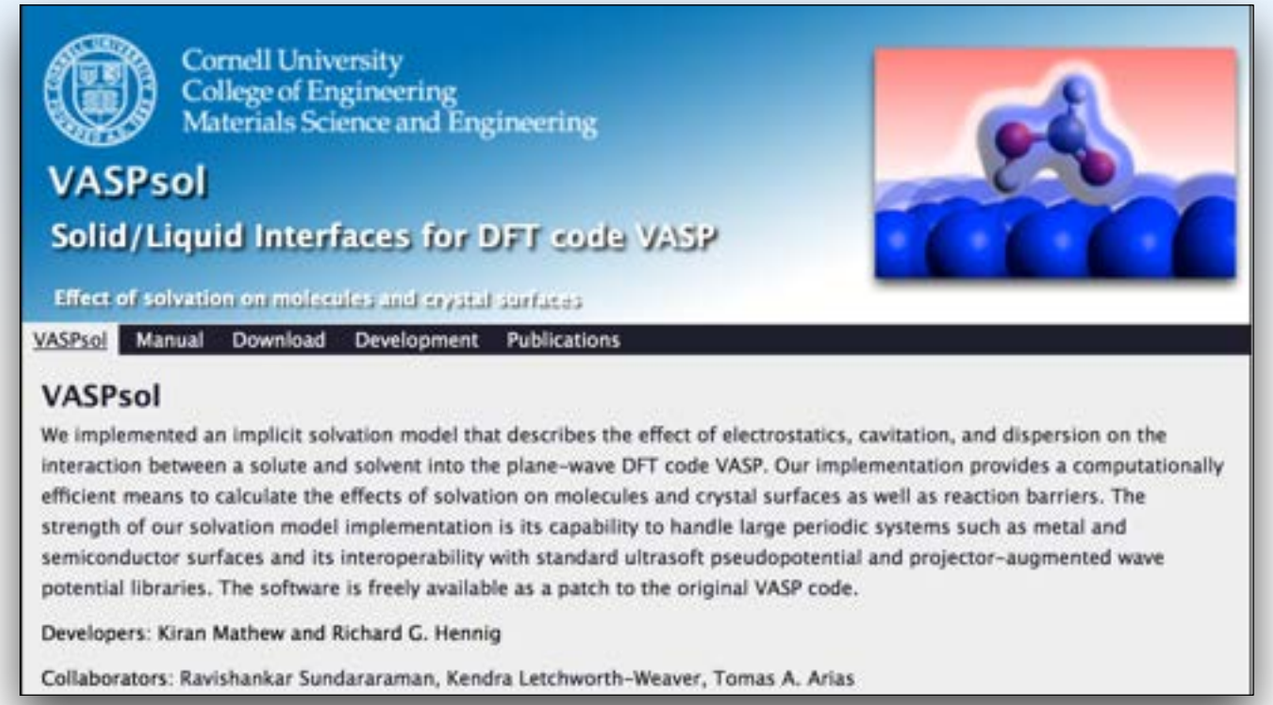
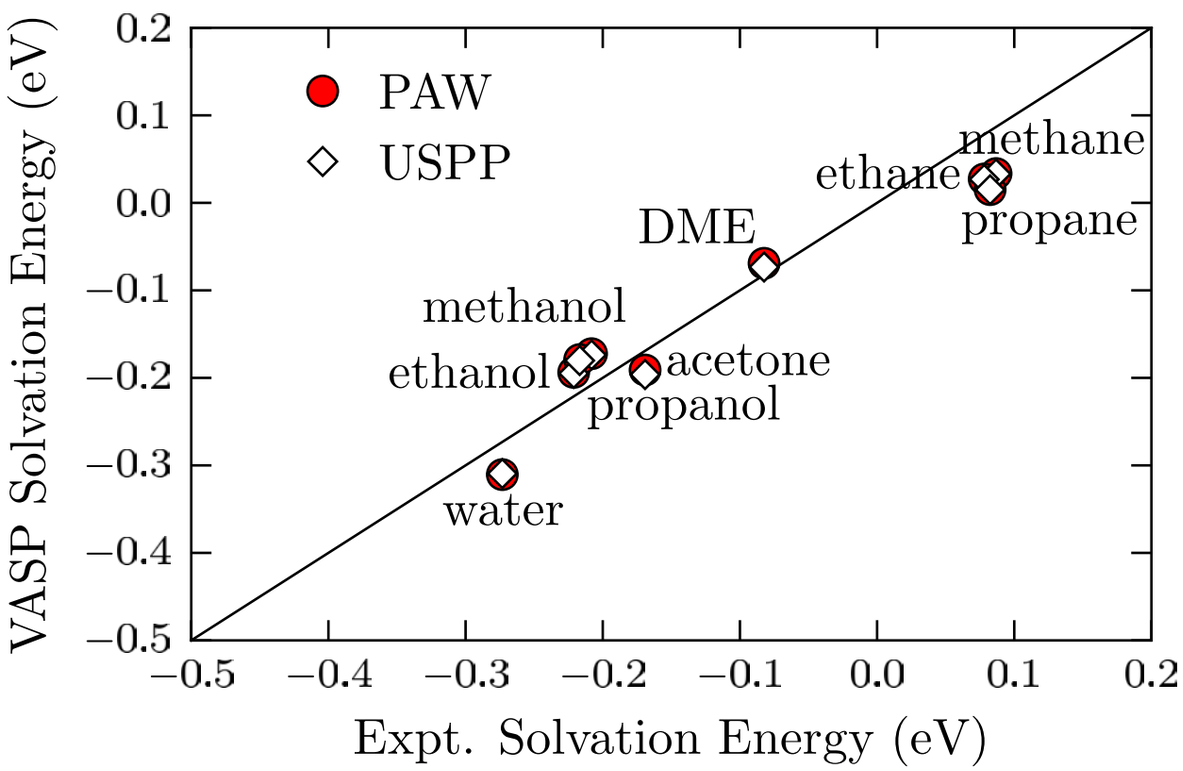
Implementation into VASP

VASP Solvation Module

- Iterative solution of modified Poisson equation

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \phi = -4\pi n(\mathbf{r})$$





Freely available at
http://vaspsol.mse.cornell.edu

Good agreement with experimental solvation energies of small molecules

http://arxiv.org/abs/1310.4242

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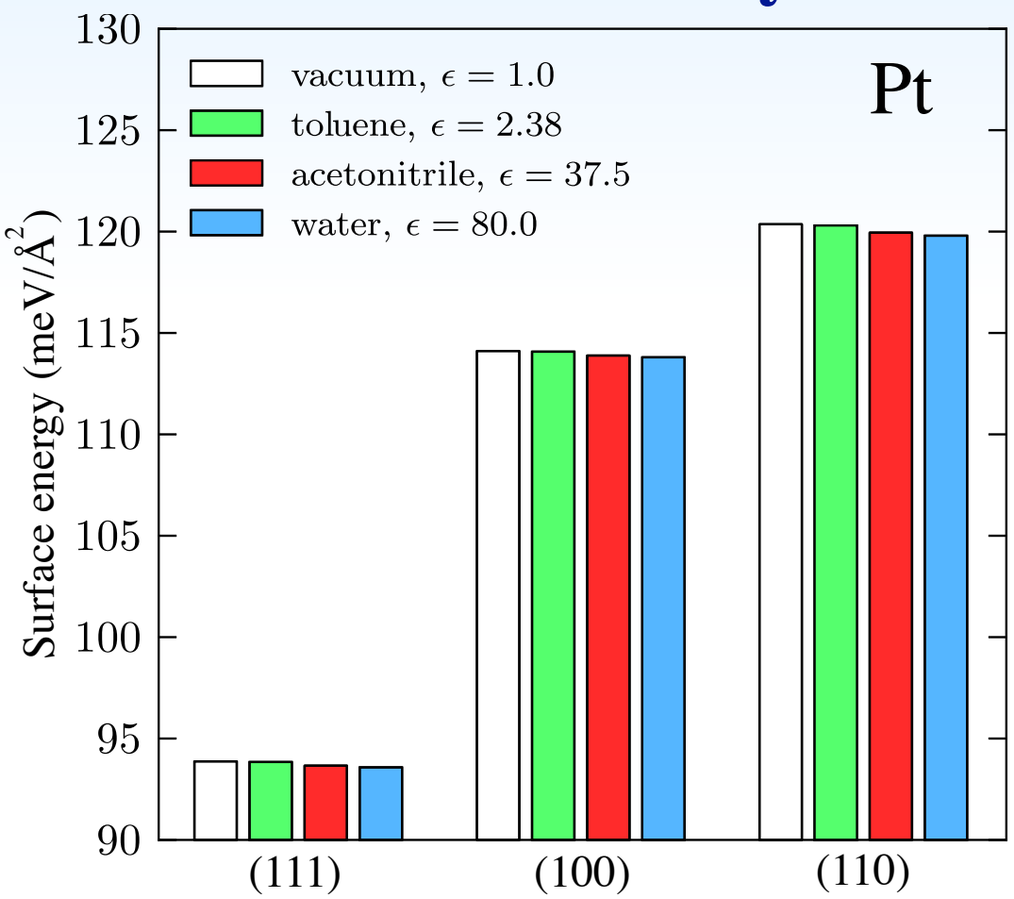
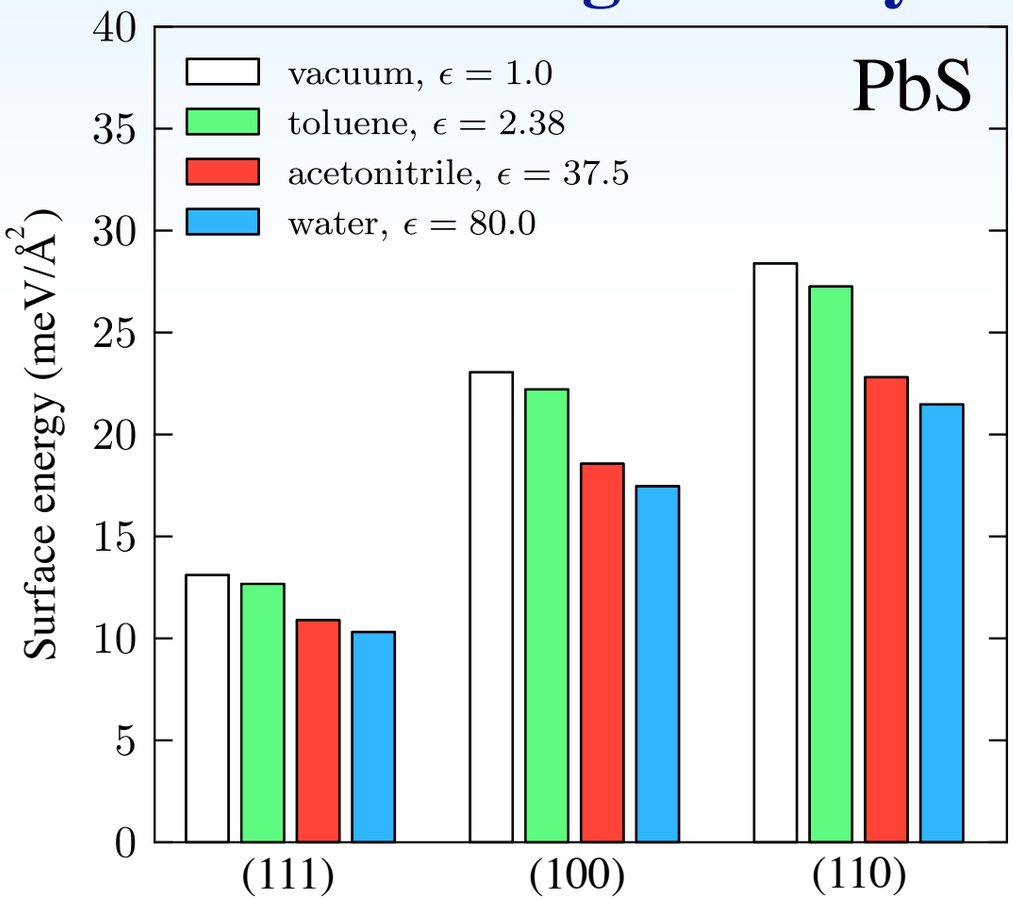
Application to Nanocrystal Facets

Metallic nanocrystals



Semiconducting nanocrystals



Significantly higher surface energies for metallic nanoparticles than semiconducting ones.

Larger effect of solvation for semiconducting nanoparticles due to polar nature of bonding.

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Control of Ligand Adsorption through Polar Solvents

Hilda Mera, Clive Bealing, Richard G. Hennig

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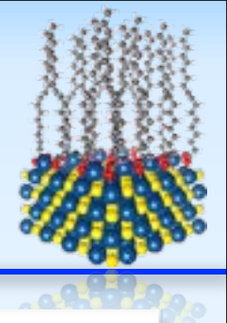
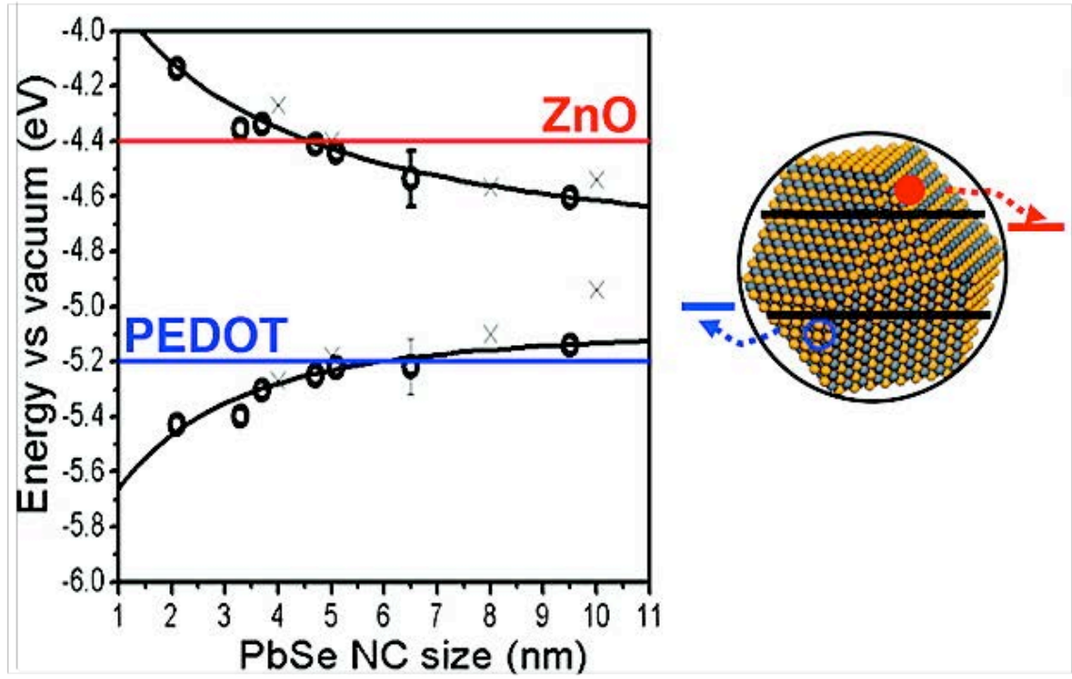
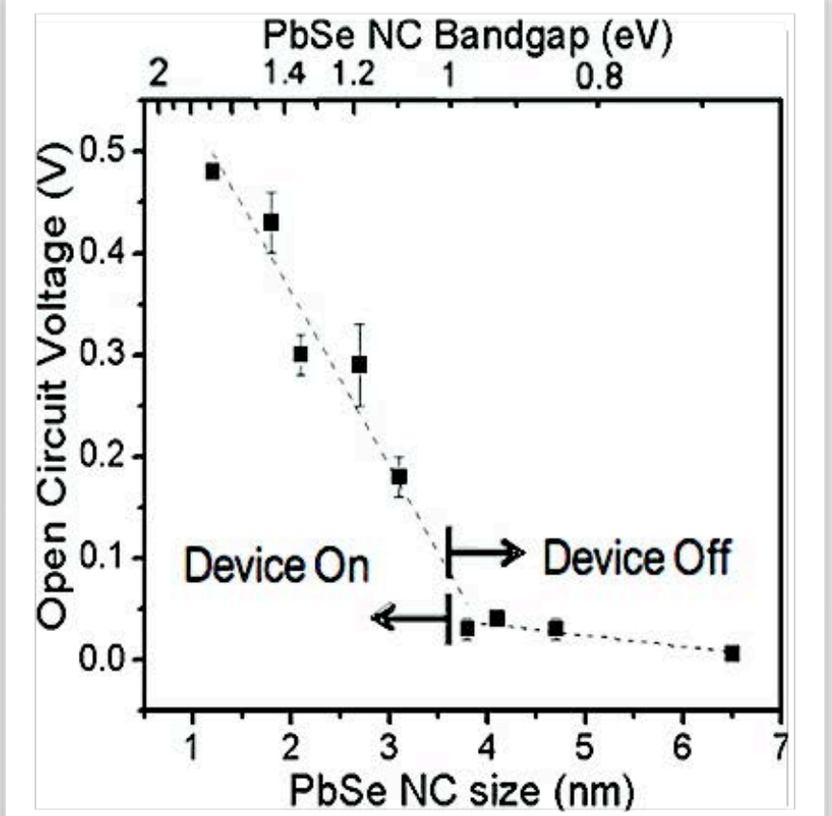
Importance of Lead-Salt Nanocrystals



- Promising candidates for photovoltaics
- Electronic and optical properties tunable through size
- Large exciton radius in PbSe of 46 nm
  ⇒ Energy gap tunable 1.4 – 0.4 eV





- Extension of solar energy conversion to near-infrared region
- Efficiency of excitonic solar cells of 3.4%

Nano Lett. 9, 3749 (2009)

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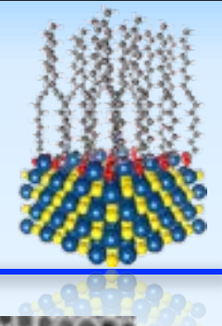
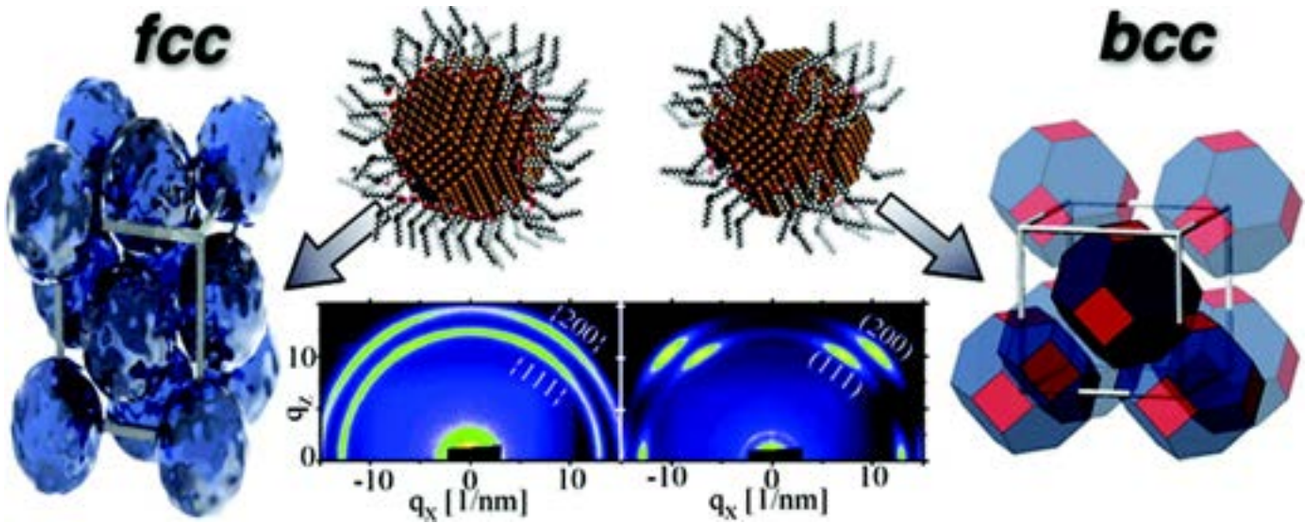
Importance of Lead-Salt Nanocrystals



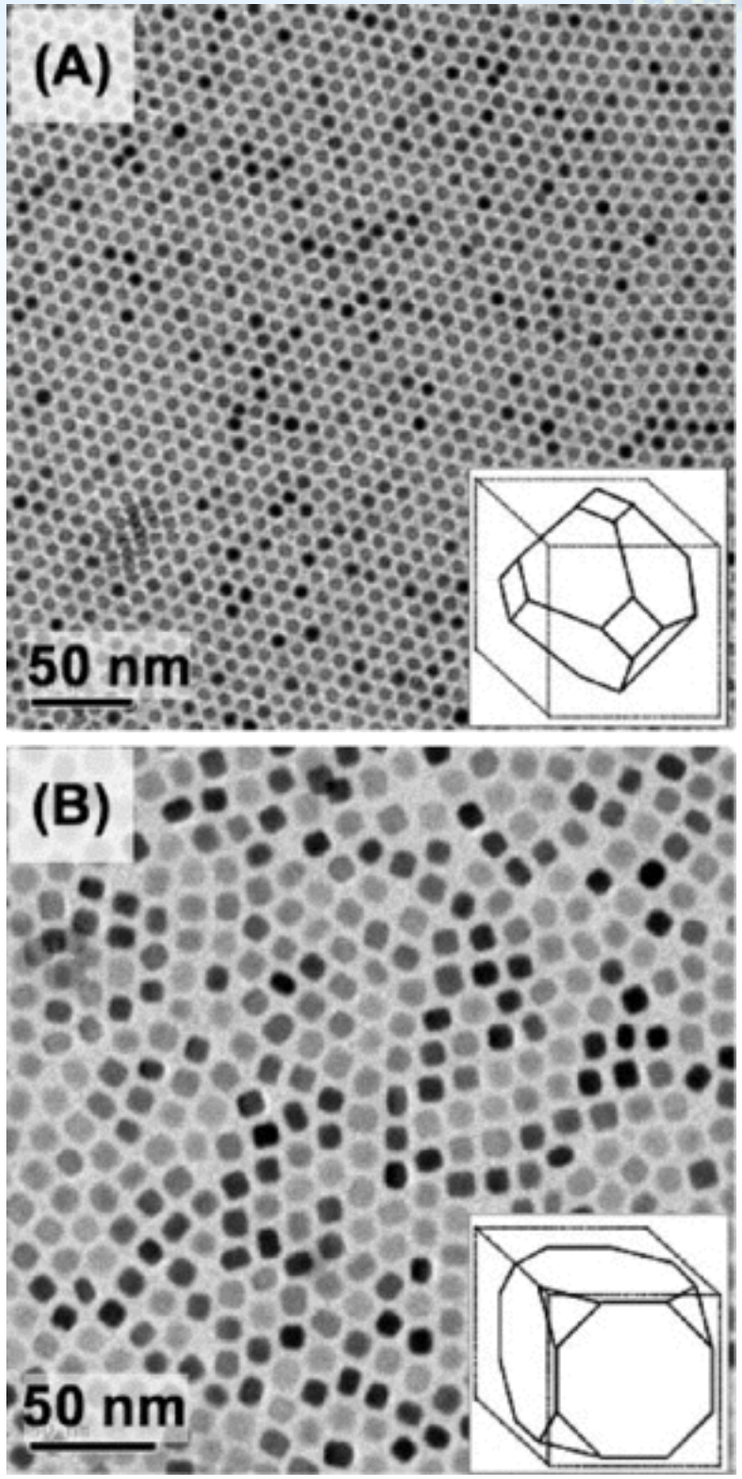
- Size and shape tunable in synthesis
- Nanocrystals stabilized by ligands like oleic acid
- Ligand loss of PbS nanocrystals

  ⇒ Transformation from *fcc* to *bcc* superlattice



JACS, **133**, 3131 (2011)

Importance of control of size, shape and composition of individual nanocrystal, and tunability of nanocrystal assembly



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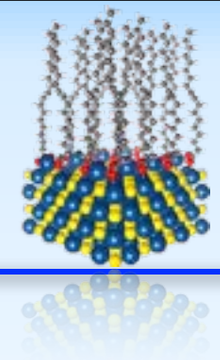
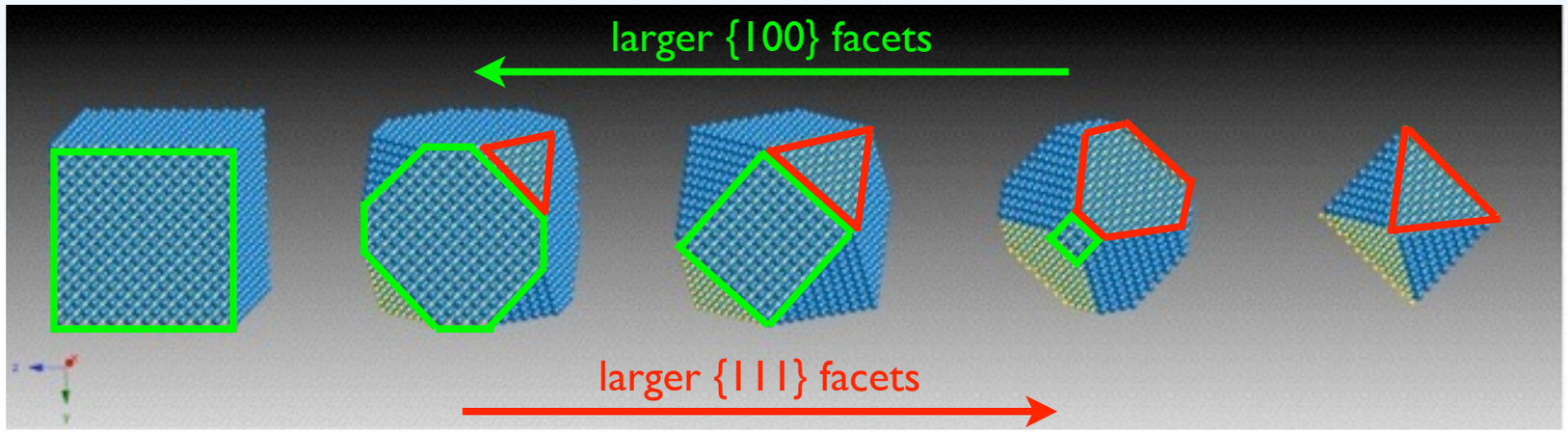
Nanocrystal Shape



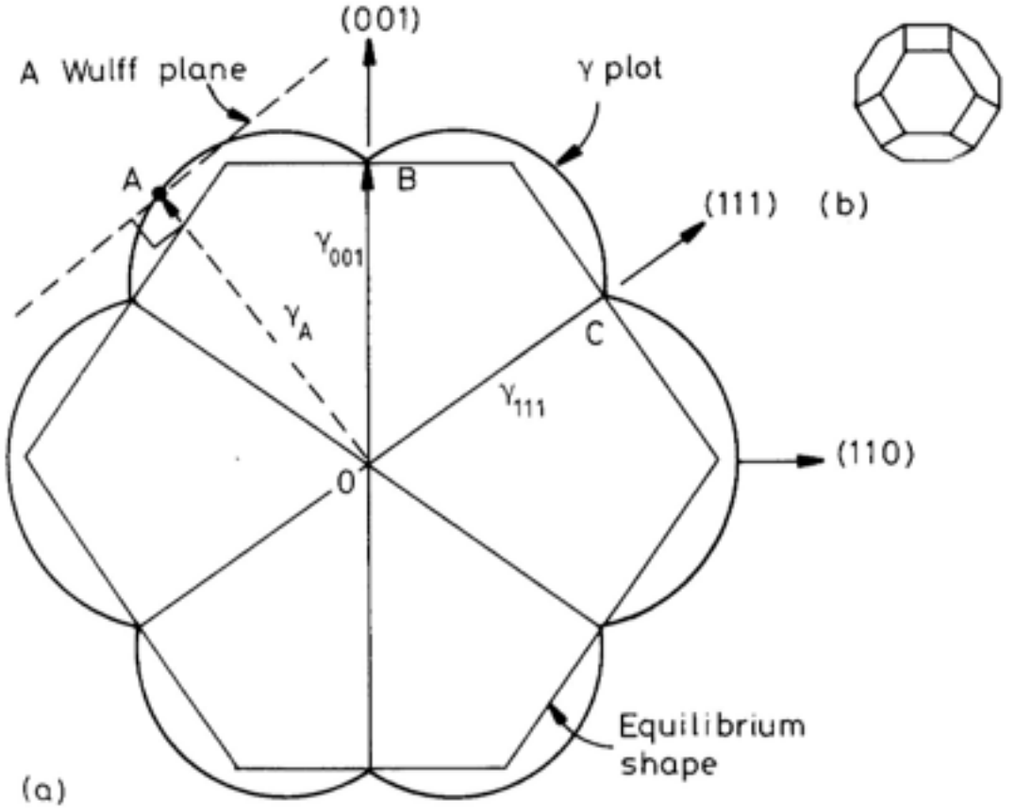
- Shape of nanocrystal core determined by size of {100} and {111} facets



- Facet sizes related to surface energies $\sigma_{\{hkl\}}$ of the facets $\{hkl\}$
- Equilibrium shape of nanocrystal given by minimum of Gibbs energy

$$\min \sum_i A_i \cdot \gamma_i$$

- Simple geometric construction by Wulff



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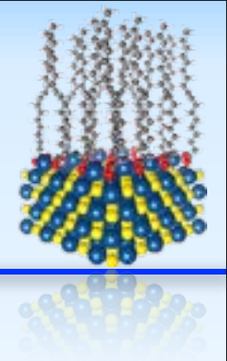
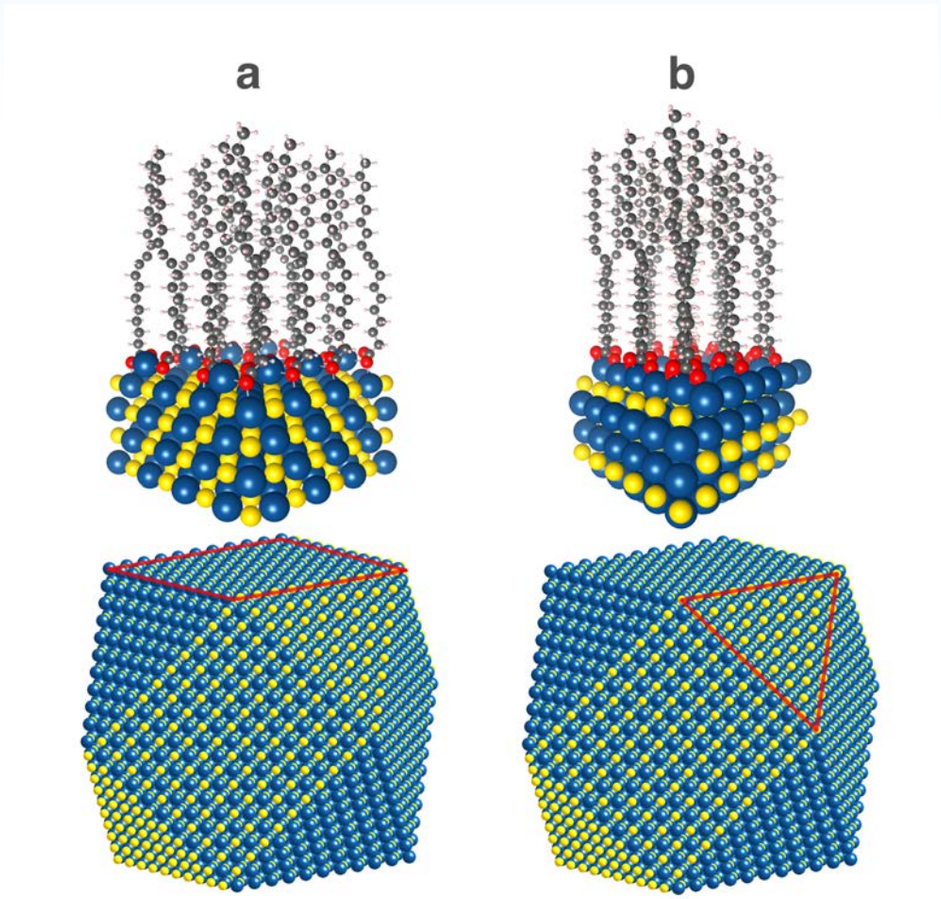
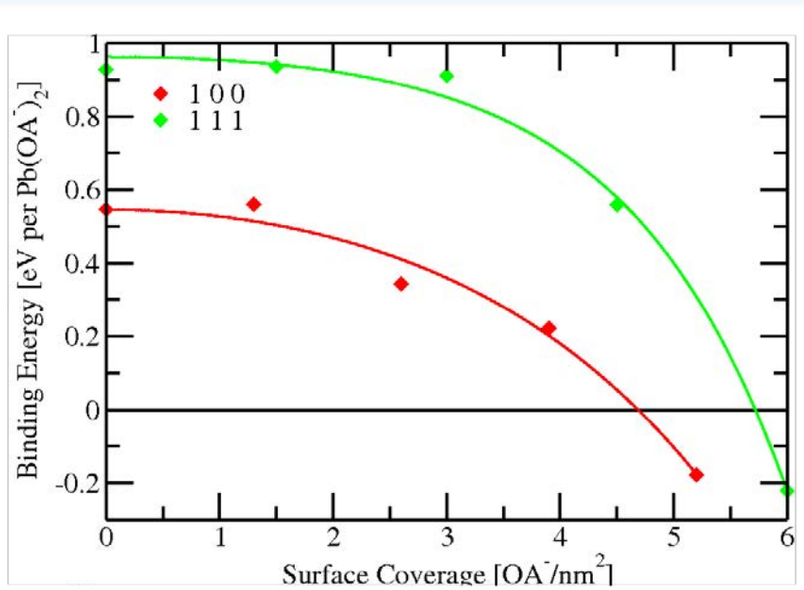
Ligand Binding and Surface Energies



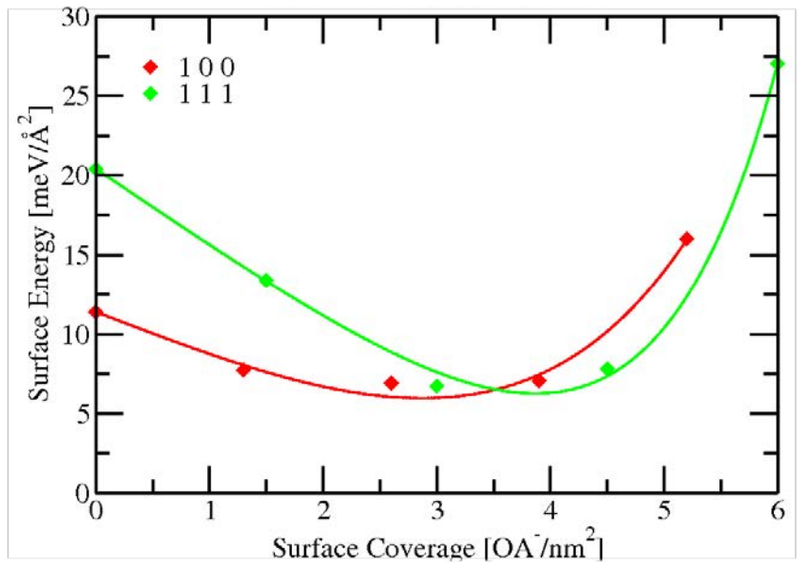
- Binding energies obtained through DFT (VASP)
- vdW interactions between ligands neglected



DFT binding energy decreases with coverage



Minimum in surface energy at 3 to 4 OA^-/nm^2



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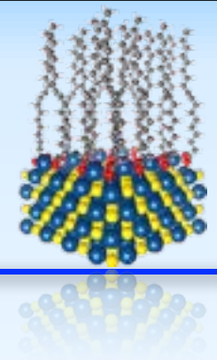
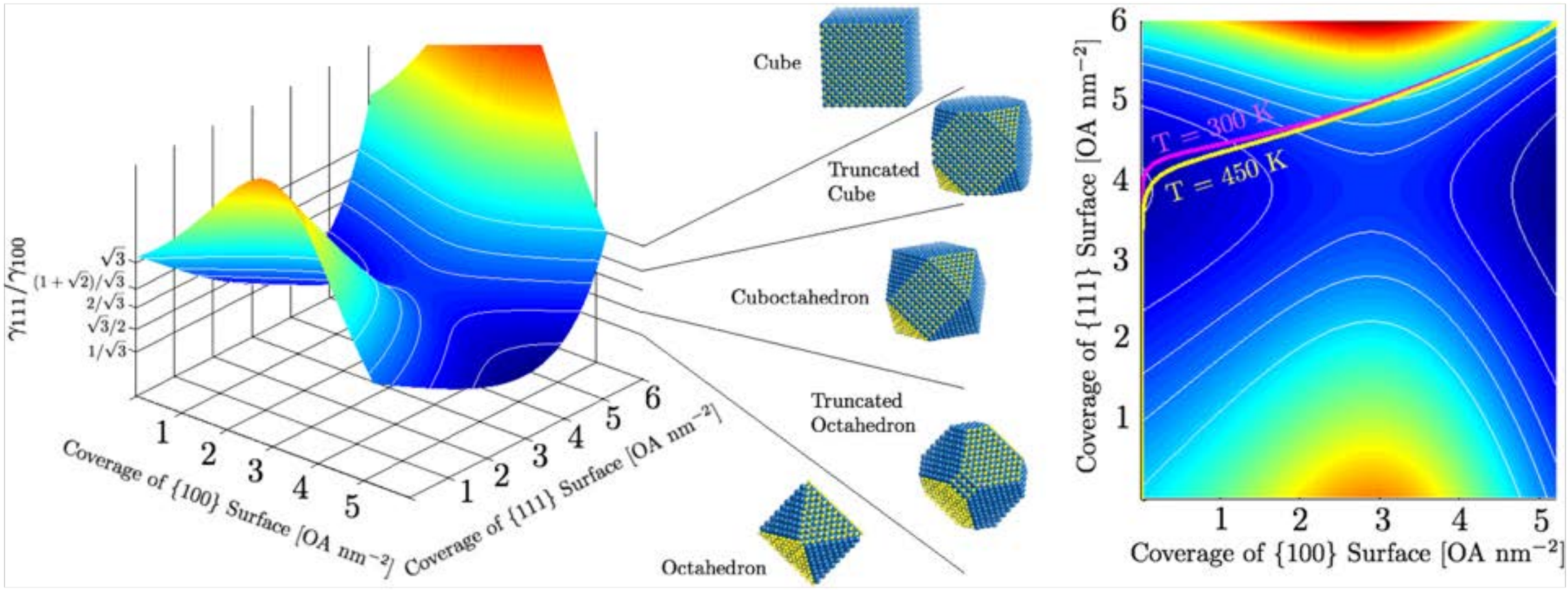
Predicted Nanocrystal Shapes



Wulff construction and equilibrium ligand coverage

- Ratio of the surface energies $\gamma_{111}/\gamma_{100}$ determines the equilibrium shape
- Isotherms for equilibrium coverage of facets show that
  Shape can be tuned through ligand concentration during synthesis



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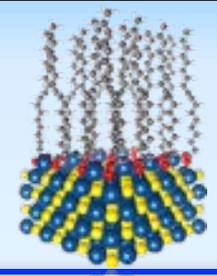
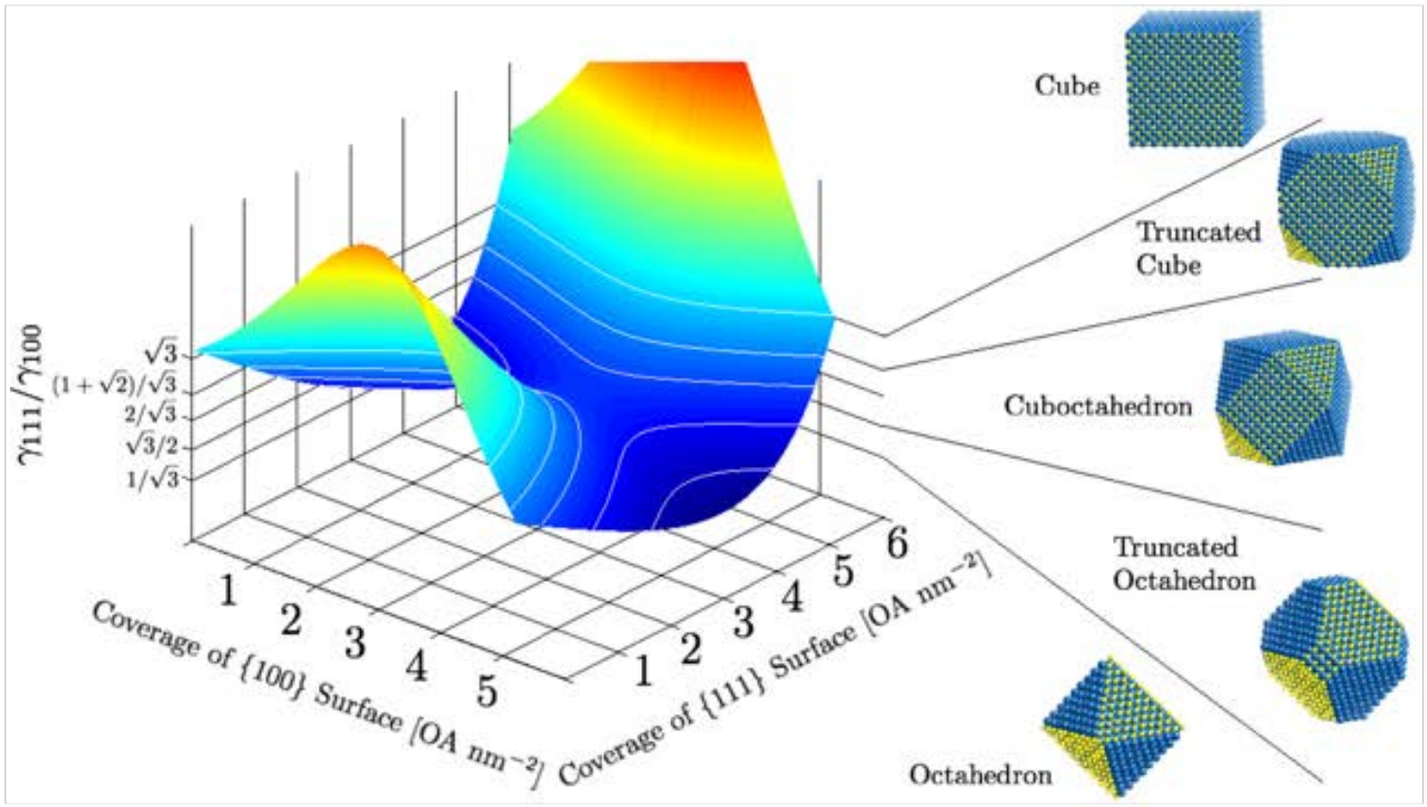
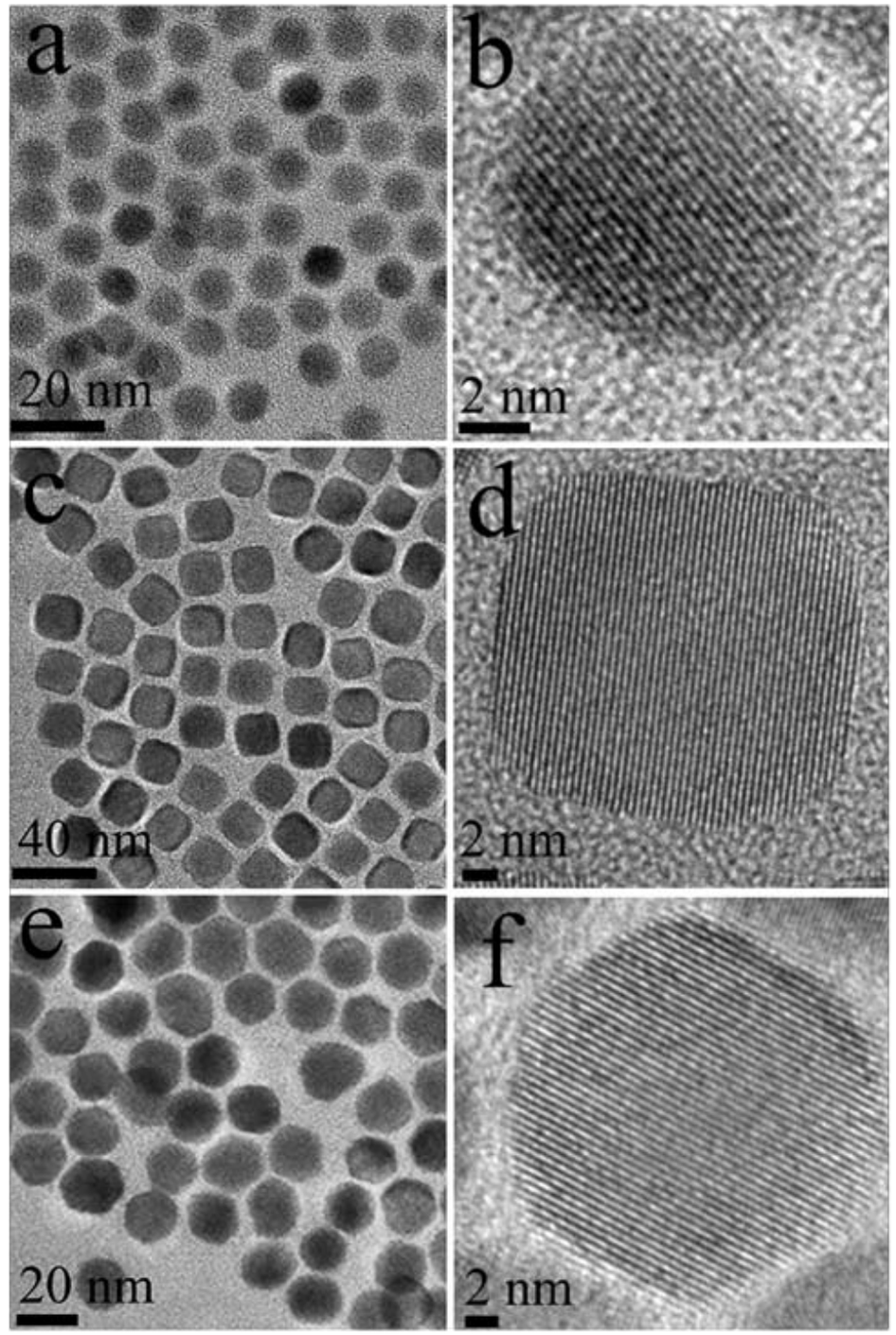
Experimental Confirmation



Li *et al*. *Cryst*. *Eng*. *Comm*. 12, 1127 (2010)

- Changing the amount of oleic acid and oleyamine with the same reaction time 1 min





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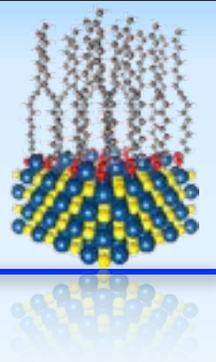
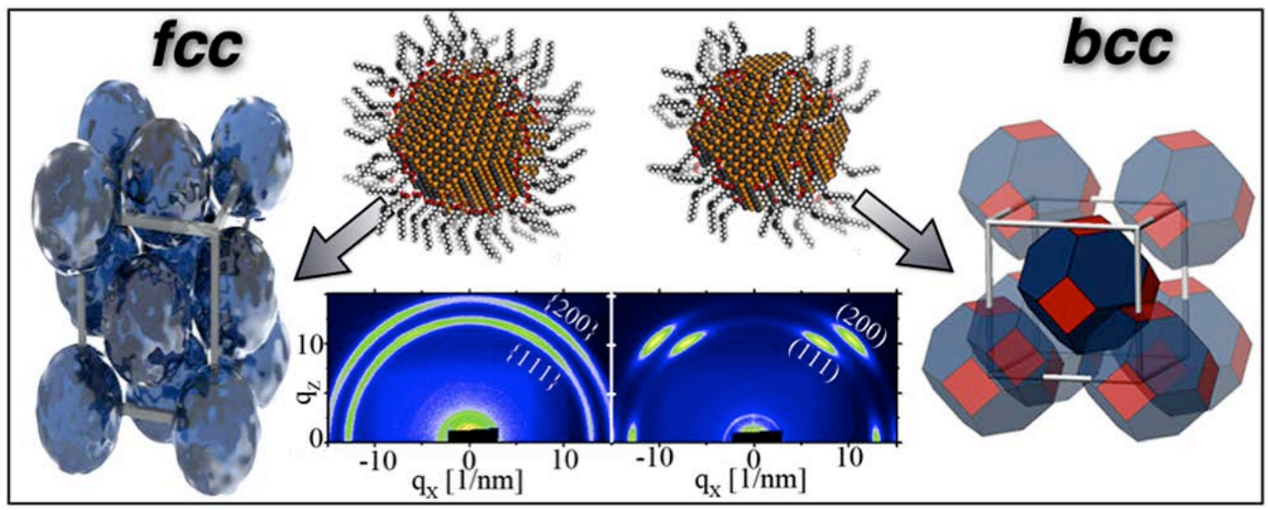
Nanocrystal Assembly



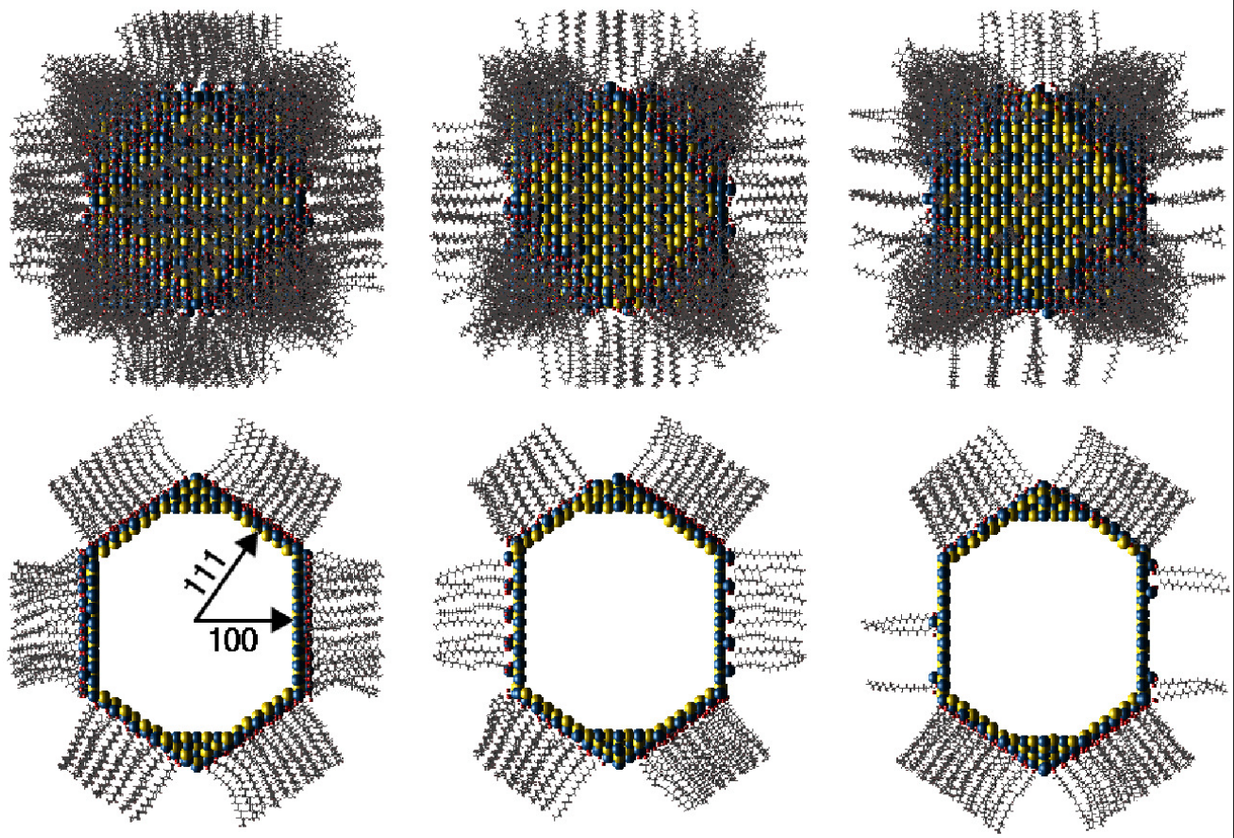
Aging of nanocrystals changes ligand coverage

- Ligands binding weaker on {100} than {111}
- Reduced coverage of {100} when aging in ligand poor condition
- Resulting change in "effective shape" from nearly spherical to preferred interactions in {111} direction
- Change in assembly

  ⇒ **Transformation from fcc to bcc**



JACS 133, 3131 (2011)



ACS Nano 6, 2118 (2012)

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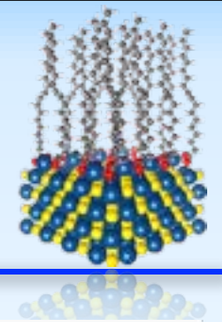
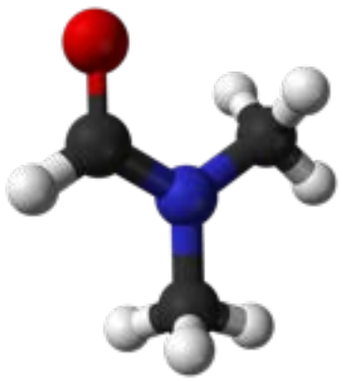
Ligand Desorption

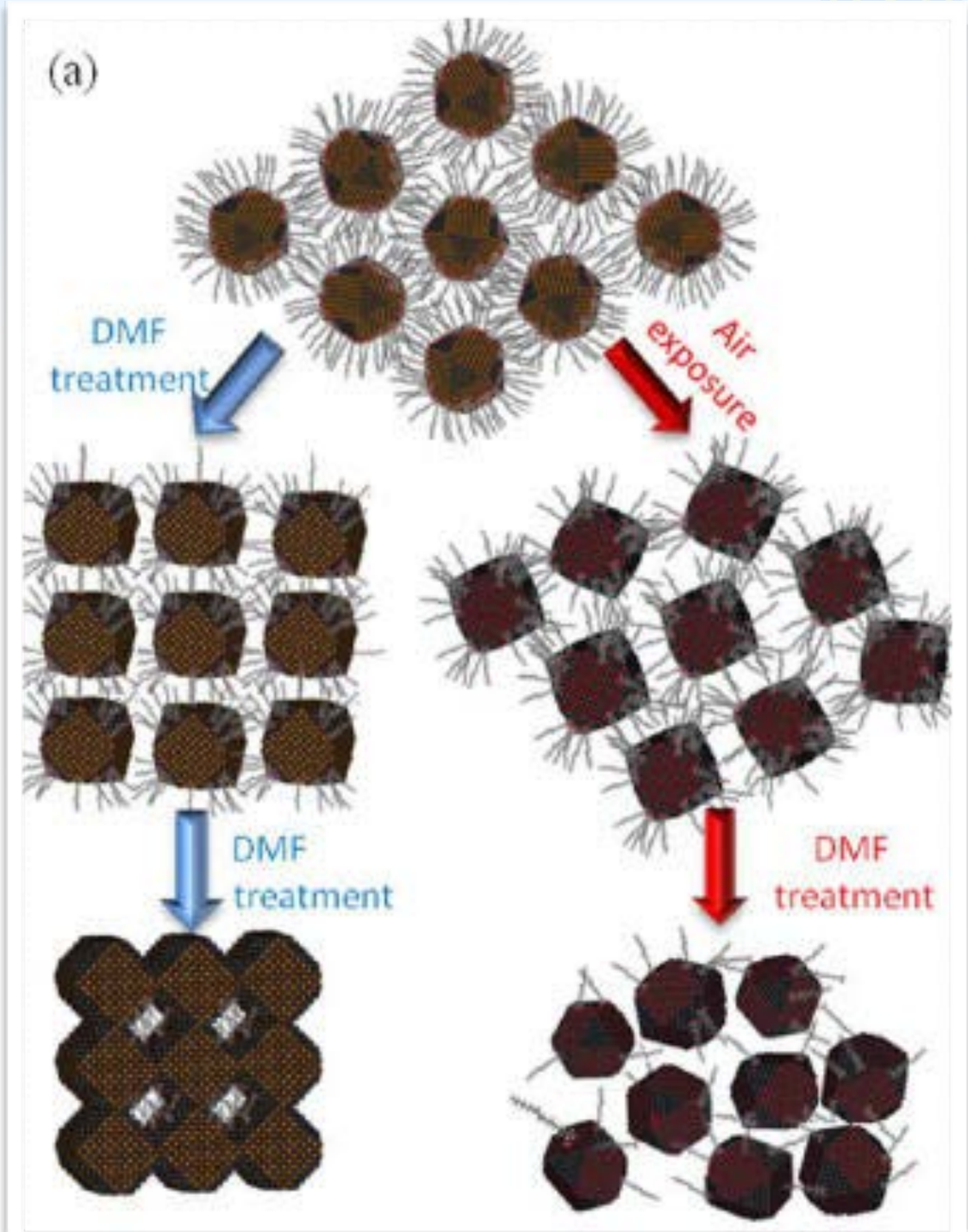


Solvent treatment can desorb ligands from nanocrystal surfaces

- Desorption of oleic acid ligands from PbSe surfaces after treatment with dimethylformamide (DMF, $\varepsilon_{DMF} = 37$)
- Hypothesis:
  Polar solvent reduces ligand binding energy



Dimethylformamide



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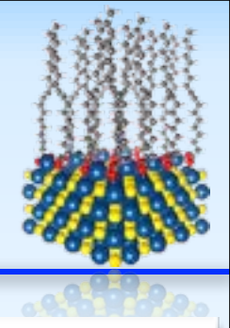
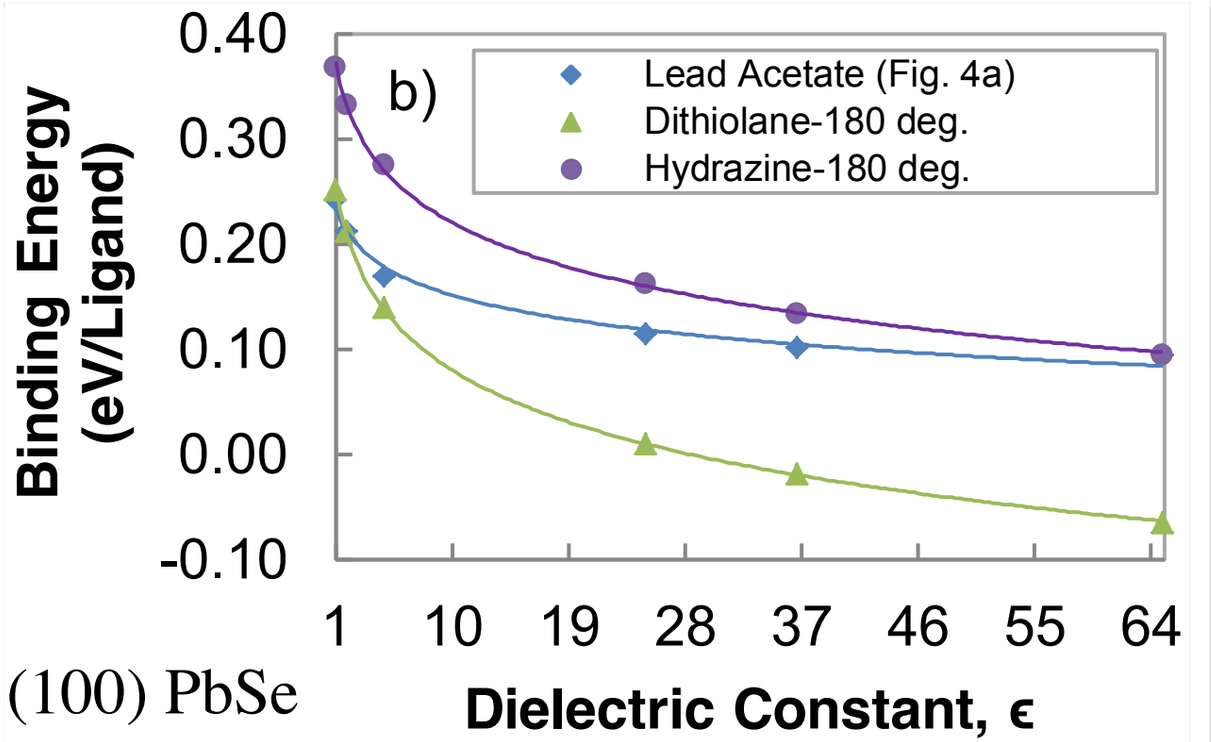
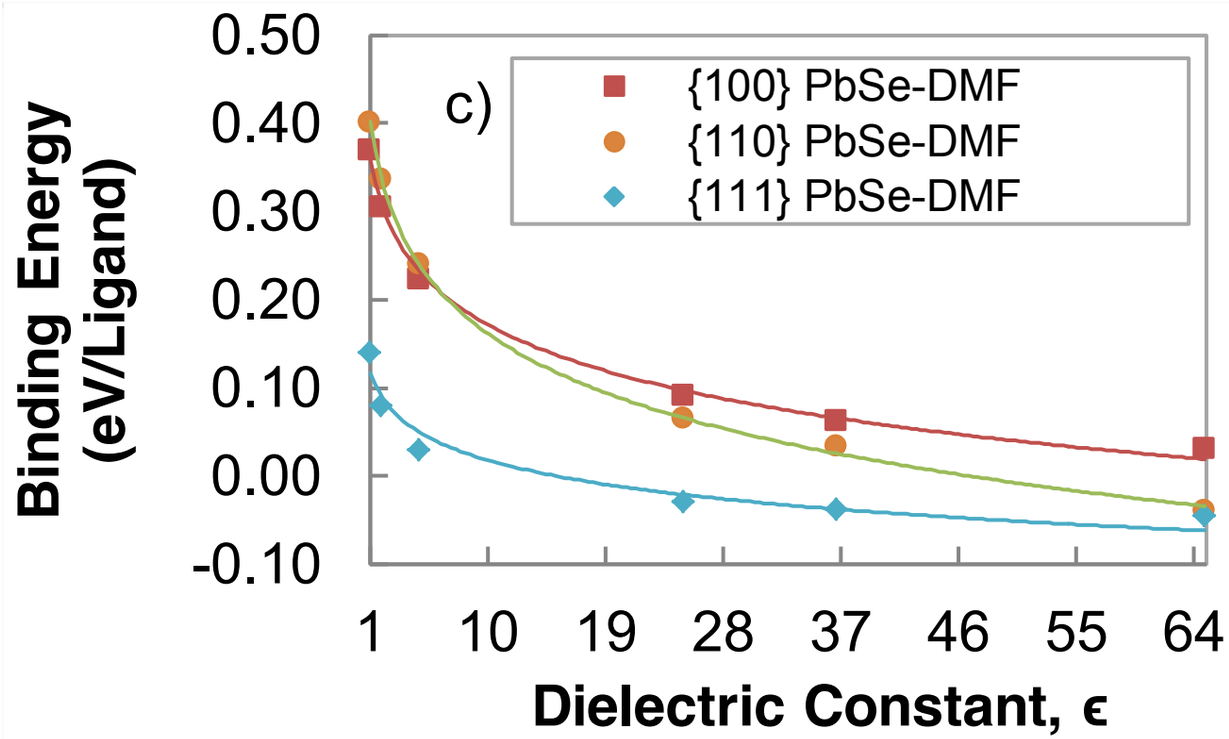
Solvent Effect on Ligand Binding





(100) PbSe



- Increasing electrostatic screening due to solvent reduces the energy of isolated surface, solvated ligand molecules and ligands adsorbed on surface
- Observe Reduction in ligand adsorption energy with permittivity ε
- High $\varepsilon_{DMF} = 37$ reduces adsorption by 75%, sufficient for desorption
- Preferential desorption of ligands on specific facets possible

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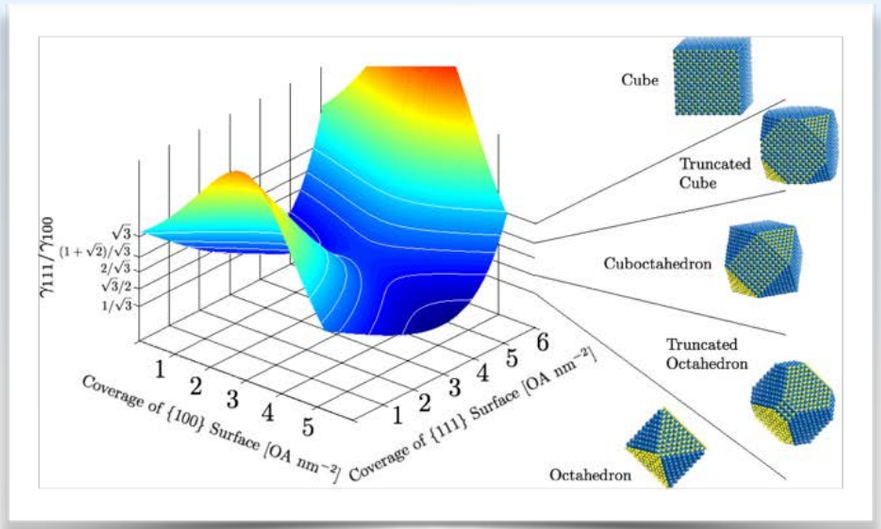
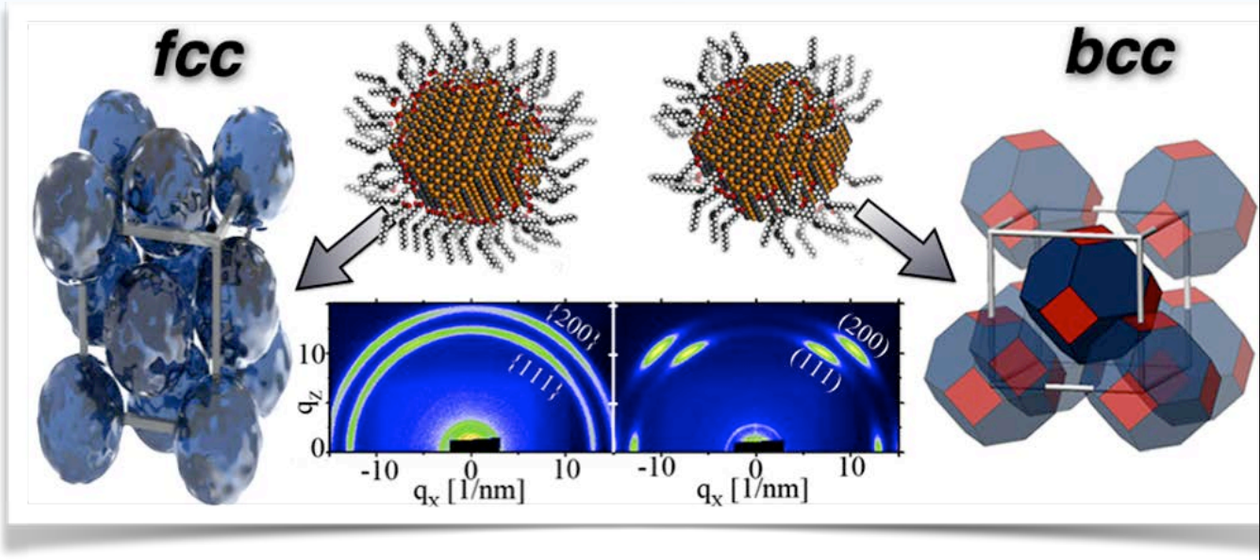
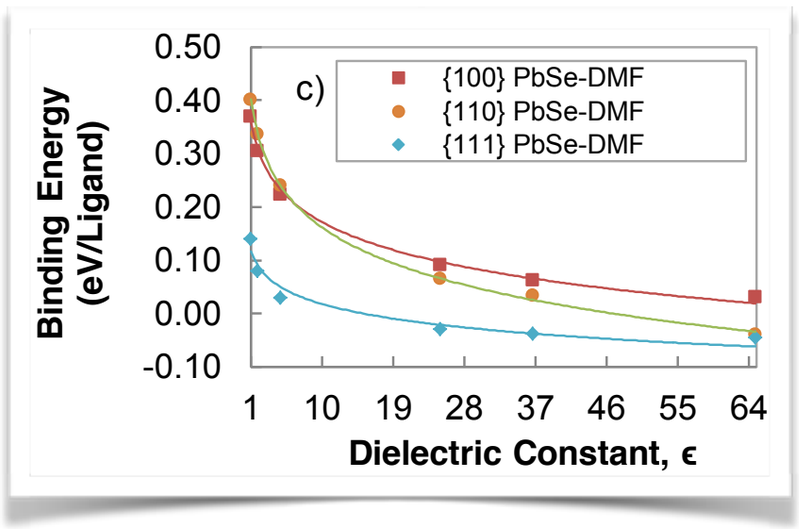
Complexity of Nanocrystal/Ligand/Solvent Systems



Shape control of nanocrystals core by modification of ligand coverage

Anisotropic ligand coverage nanocrystals leads affects assembly





Desorption of ligands by solvent screening

Design of nanocrystal shape, assembly and functionalization

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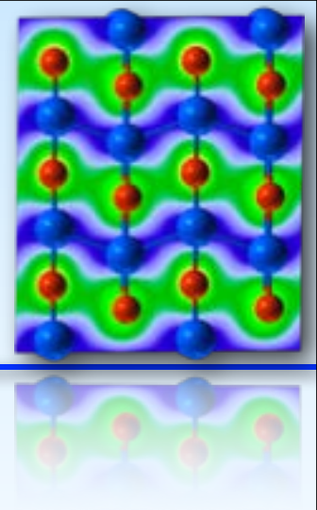
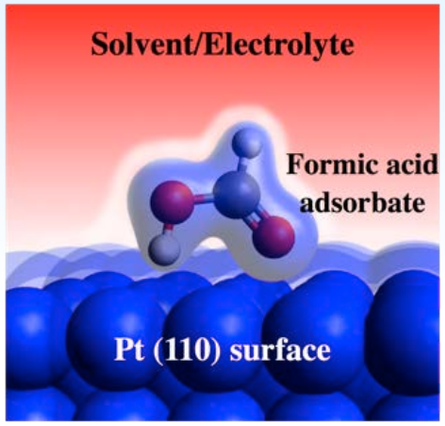
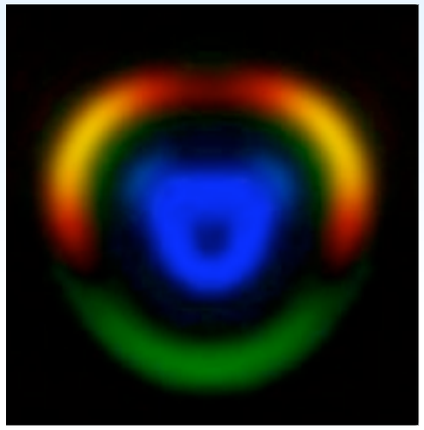
Computational Methods for Structure Prediction and Solid/Liquid Interfaces for Energy Materials

Richard G. Hennig, Cornell University







Ab initio methods for solid/liquid interfaces

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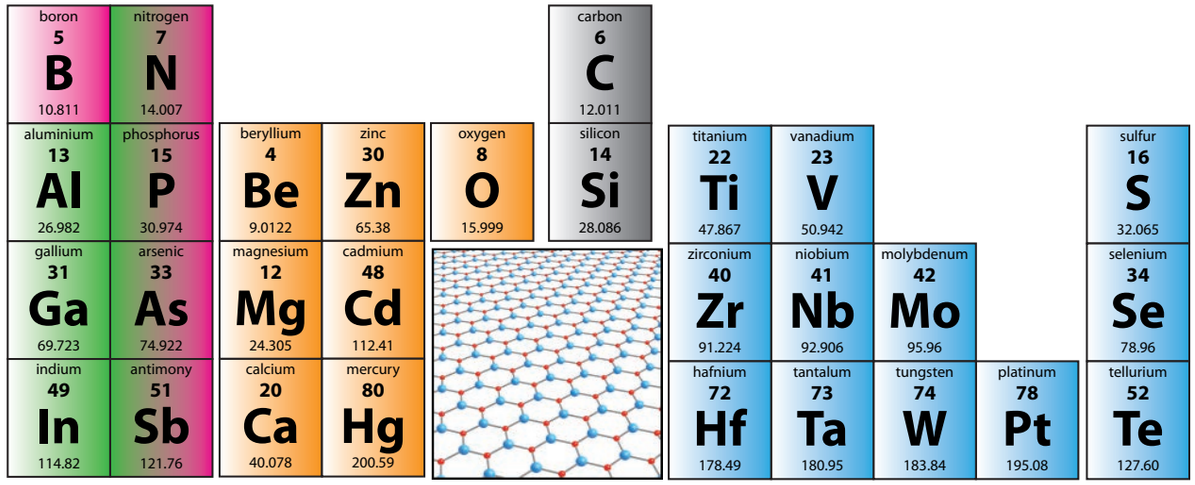
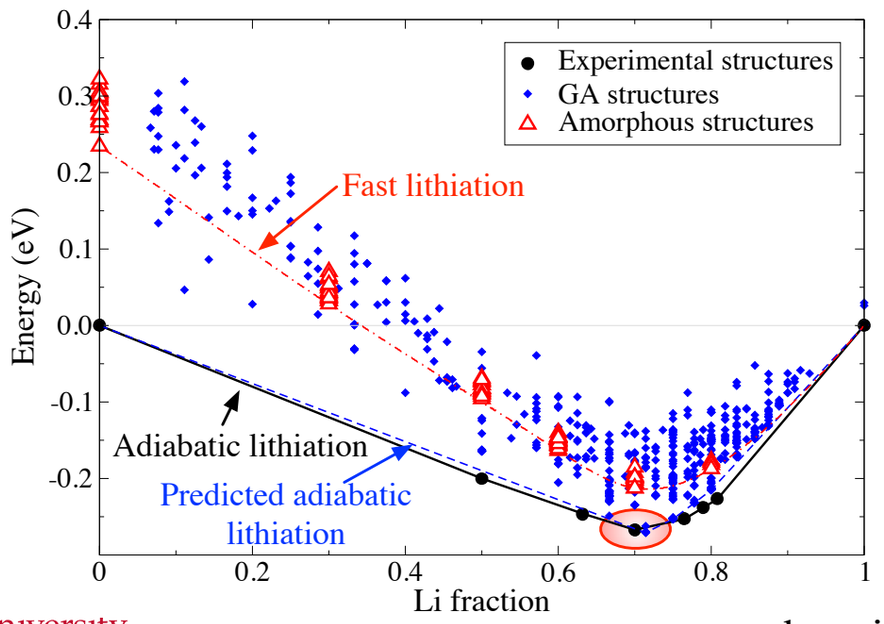
Data mining for novel 2D materials





Genetic algorithm for structure predictions

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