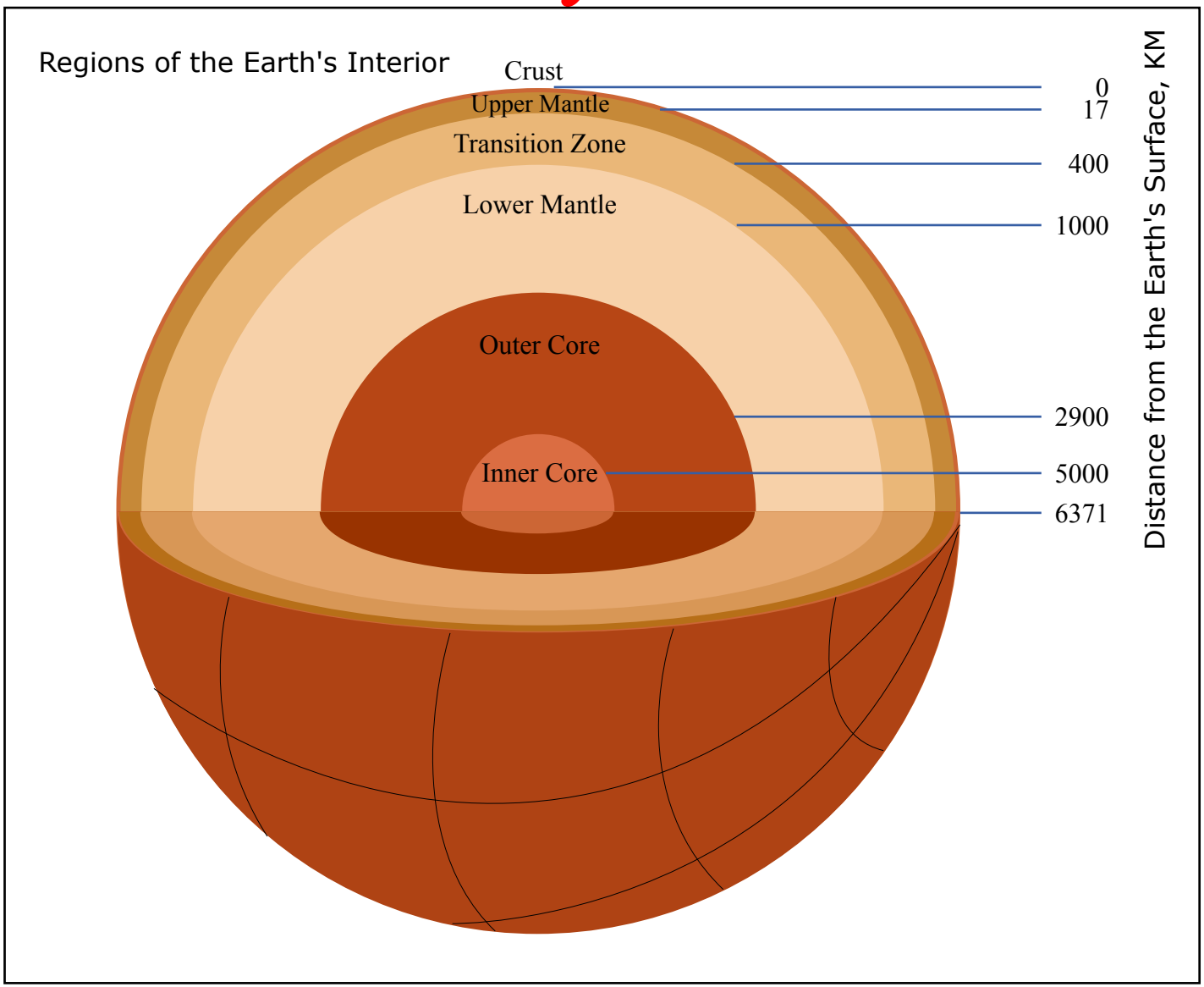
3.320: Final Lecture (May 10 2005)

JOURNEY TO THE CENTRE OF THE EARTH

Planetary Interiors



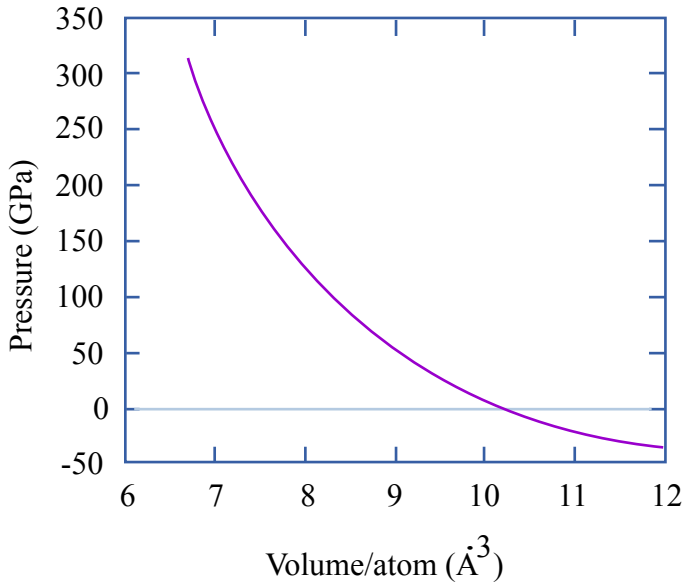
Alfe' and Gillan, Nature '98, '99, '00

Figure by MIT OCW.

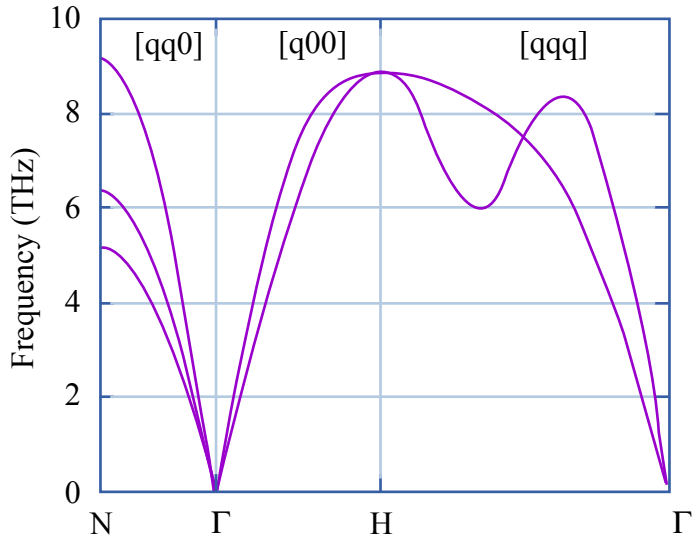
Earth's core

- 30% of mass of the planet
- Mainly iron (star nucleosynthesis) – the liquid outer core is slightly less dense (light impurities: S, O, Si, H ?)
- Pressure ranges 100-400 GPa, temperatures 3000-7000 K (?)
- Liquid-solid boundary: 330 Gpa (seismic waves)
- DAC: 300 GPa @ 300K, 200 Gpa @ 3700K

GGA-DFT Iron



Pressure as a function of atomic volume of hcp Fe.

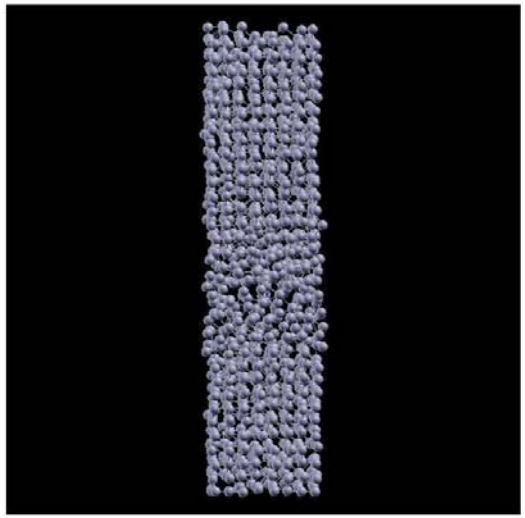


Phonon dispersion curves of ferromagnetic bcc Fe at Zero pressure along the [100], [110], and [111] directions.

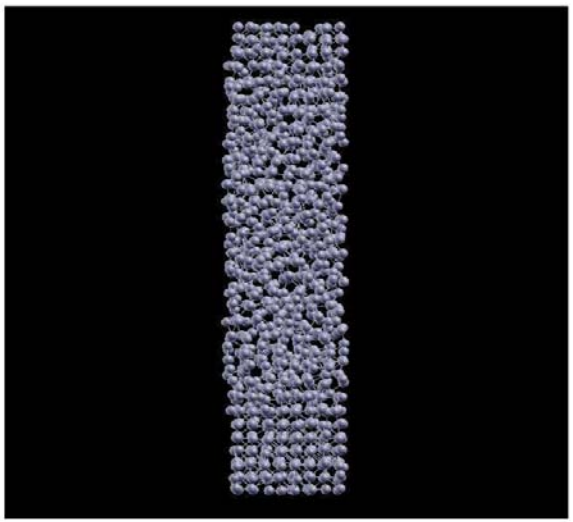
Figure by MIT OCW.

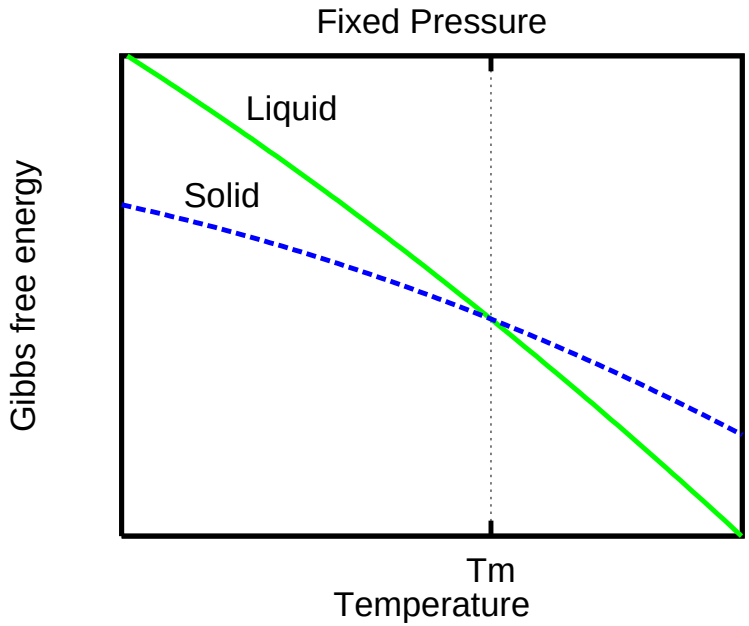
Melting Point

Initial T = 100 K, final T = 119.5 K.



Initial T = 130 K, final T = 120.9 K.





Thermodynamic integration (I)

$$\mathcal{U}(\lambda) = (1-\lambda)\mathcal{U}_I + \lambda\mathcal{U}_{II} \qquad Q(N,V,T,\lambda) = \frac{1}{\Lambda^{3N}N!}\int d\mathbf{r}^N \exp[-\beta\mathcal{U}(\lambda)].$$

$$\left(\frac{\partial F(\lambda)}{\partial\lambda}\right)_{N,V,T} = -\frac{1}{\beta}\frac{\partial}{\partial\lambda}\ln Q(N,V,T,\lambda) = -\frac{1}{\beta Q(N,V,T,\lambda)}\frac{\partial Q(N,V,T,\lambda)}{\partial\lambda}$$

$$= \frac{\int d\mathbf{r}^N (\partial\mathcal{U}(\lambda)/\partial\lambda)\exp[-\beta\mathcal{U}(\lambda)]}{\int d\mathbf{r}^N \exp[-\beta\mathcal{U}(\lambda)]} = \left\langle\frac{\partial\mathcal{U}(\lambda)}{\partial\lambda}\right\rangle_\lambda$$

Partitioning the free energy

$$F = -k_B T \ln\left\{ \frac{1}{N!\,\Lambda^{3N}} \int d\mathbf{R}_1 \ldots d\mathbf{R}_N \times \exp[-\beta U(\mathbf{R}_1, \ldots \mathbf{R}_N; T_{el})] \right\},$$

$$U(R_1,\ldots,R_N;T_{el}) = U(R_1^0,\ldots R_N^0;T_{el}) + U_{vib}^{harm}(R_1,\ldots,R_N;T_{el}) + U_{vib}^{anharm}(R_1,\ldots,R_N;T_{el})$$

Harmonic Term

$$F_{\text{harm}} = -k_B T \ln\left\{ \frac{1}{\Lambda^{3N}} \int d\mathbf{R}_1 \ldots d\mathbf{R}_N \times \exp[-\beta U_{\text{harm}}(\mathbf{R}_1, \ldots \mathbf{R}_N; T_{\text{el}})] \right\},$$

$$U_{\text{harm}} = \frac{1}{2} \sum_{ls\alpha, l't\beta} u_{ls\alpha} \Phi_{ls\alpha, l't\beta} u_{l't\beta} \quad \Rightarrow \quad F_{\text{harm}} = \frac{3k_B T}{N_{\mathbf{k}s}} \sum_{\mathbf{k}s} \ln(\beta \hbar \omega_{\mathbf{k}s})$$

Anharmonic Term

$$F_{\text{anharm}} = (F_{\text{vib}} - F_{\text{ref}}) + (F_{\text{ref}} - F_{\text{harm}}),$$

$$F_{\text{vib}} - F_{\text{ref}} = \int_0^1 d\lambda \, \langle U_{\text{vib}} - U_{\text{ref}} \rangle_\lambda^{\text{vr}},$$

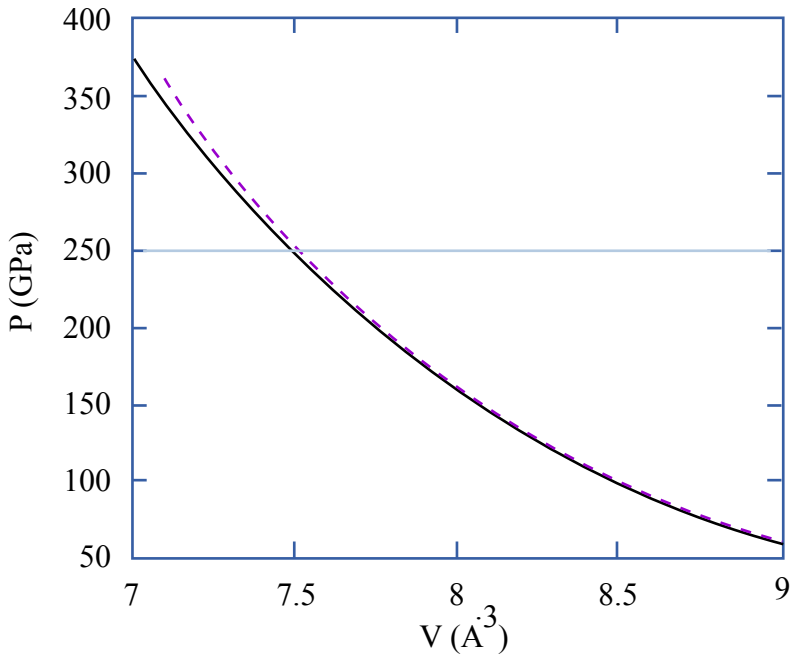
$$F_{\text{ref}} - F_{\text{harm}} = \int_0^1 d\lambda \, \langle U_{\text{ref}} - U_{\text{harm}} \rangle_\lambda^{\text{rh}}.$$

Reference System

$$U_{\mathrm{IP}} = \frac{1}{2} \sum_{I \neq J} \phi(|\mathbf{R}_I - \mathbf{R}_J|),$$

$$U_{\mathrm{ref}} = c_1 U_{\mathrm{harm}} + c_2 U_{\mathrm{IP}}.$$

Shock Hugoniot



Experimental and *ab initio* Hugoniot pressure p as a function of atomic volume V.

Figure by MIT OCW.

Taking the temperature…

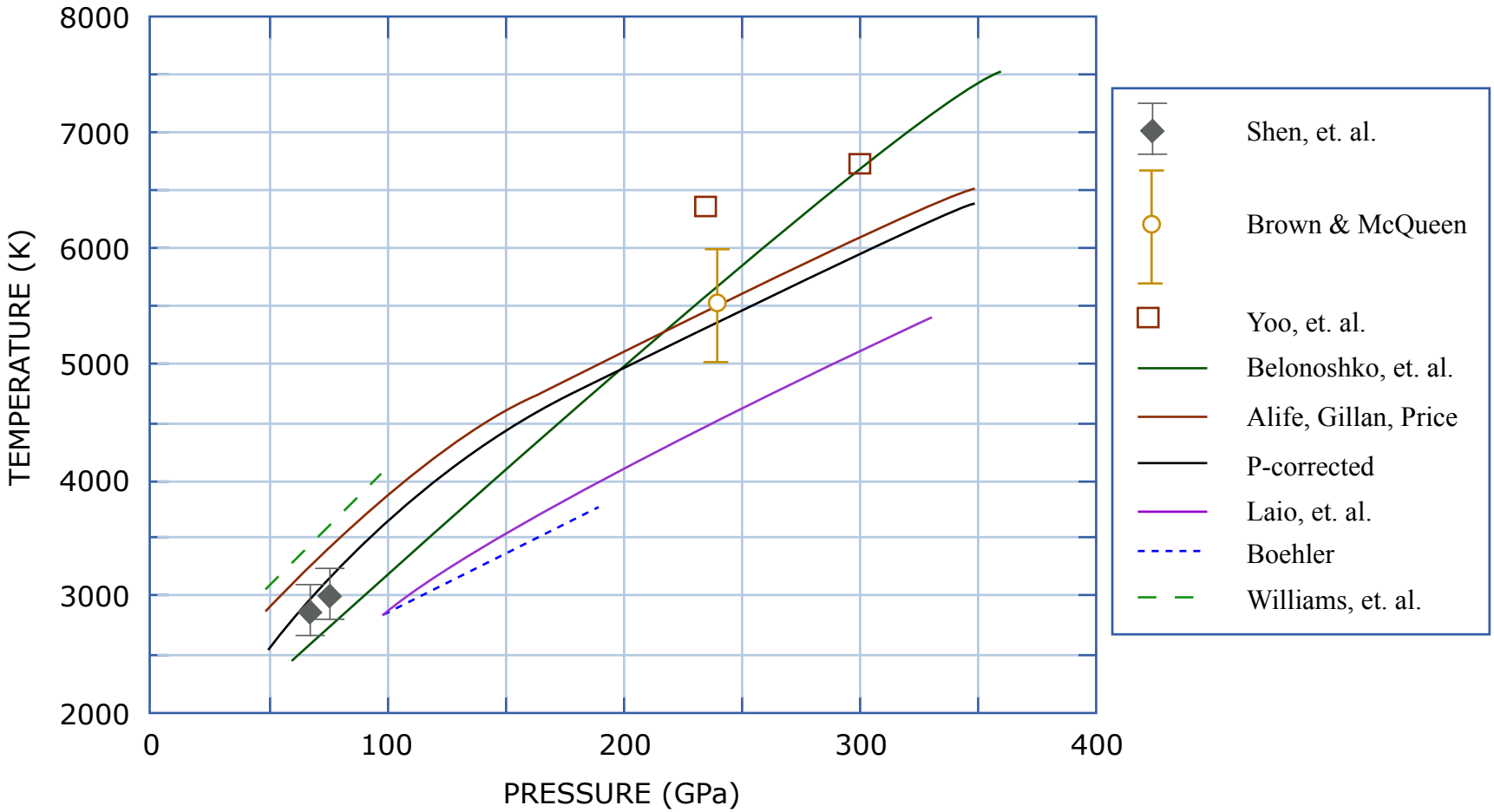


Figure by MIT OCW. After D. Alfe.

Force Matching Method

Laio et al, Science ‘00

Graph and diagram removed for copyright reasons.

Neptune and Uranus

Ancilotto et al, Science '97

- Middle ice layer: methane, ammonia, and water in solar proportions
- From 20 GPa/2000K to 600 Gpa/8000K

A rain of diamonds ?

Diagrams removed for copyright reasons.

Source: Figure 1 in Ancilotto, F., et al. "Dissociation of Methane into Hydrocarbons at Extreme (Planetary) Pressure and Temperature." *Science* 275, no. 5304 (Feb. 1997): 1288-1290 .

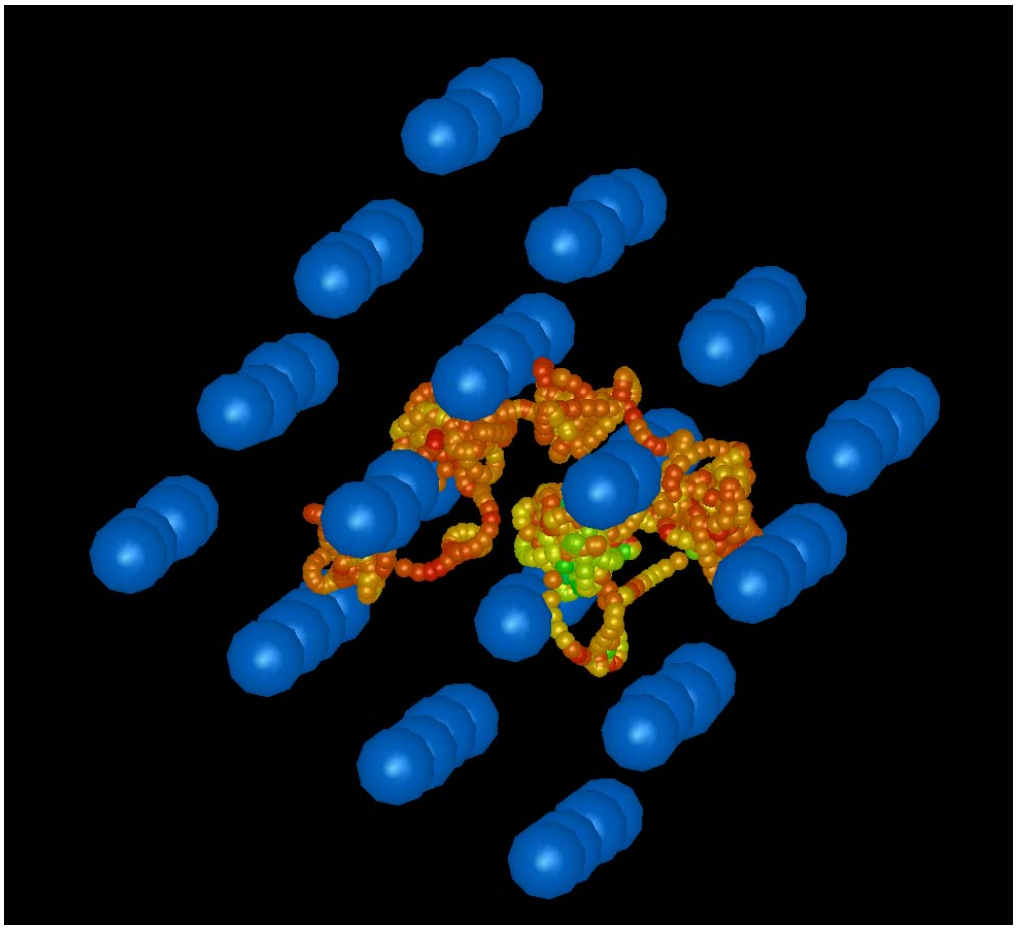
Image removed for copyright reasons.

From Benedetti et al, 1999.

Experimental confirmation that hydrocarbons and diamonds could both form methane at planetary conditions came from a diamond-anvil experiment at UC-Berkeley by Jeanloz et al.

Superprotonic Water

Cavazzoni et al, Science '99



Courtesy of Erio Tosatti. Used with permission.

Image removed for copyright reasons.

Scan of paper: Goncharov, A.F., et al. "Dynamic Ionization of Water under Extreme Conditions." *Physical Review Letters* 94 (April 1, 2005).

Pairing in dense alkali

Graph and diagram removed for copyright reasons.

Figure 5 in Neaton and Ashcroft, Nature 1999.

Lyrics for song "My Way" removed for copyright reasons.

3.320
Last Lecture
(May 10 2005)

Overview

Basic Techniques

DFT and Potentials

MD, MC

Often need to be combined in creative ways to get results

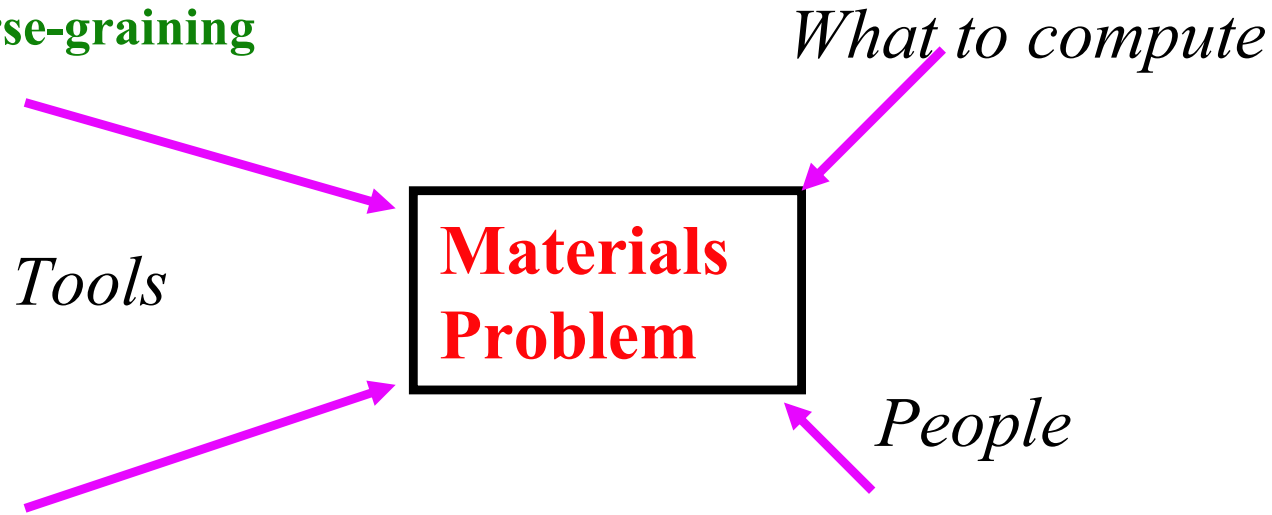
Issues: How to make impact ?

Methods: **DFT++**

DFT and Potentials
MD, MC
Coarse-graining

Knowledge:

Basic Science of your field



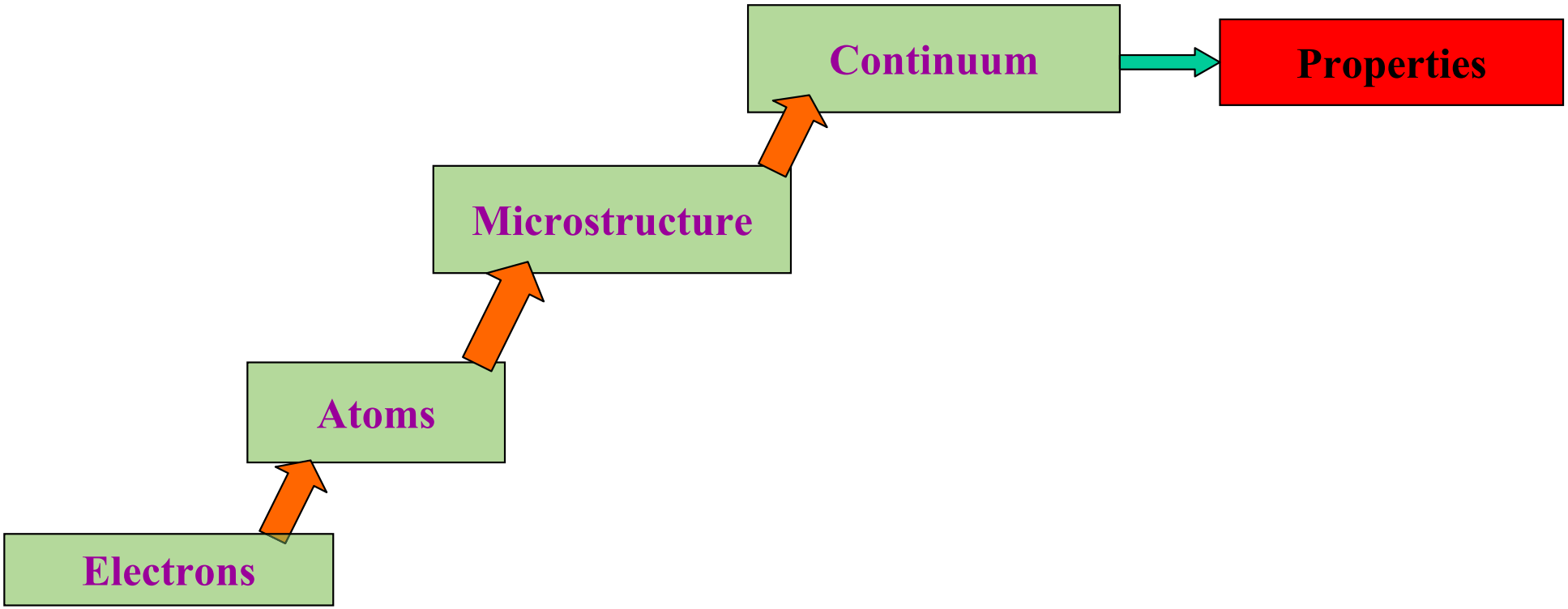
Dissemination

Publish, educate and code development.

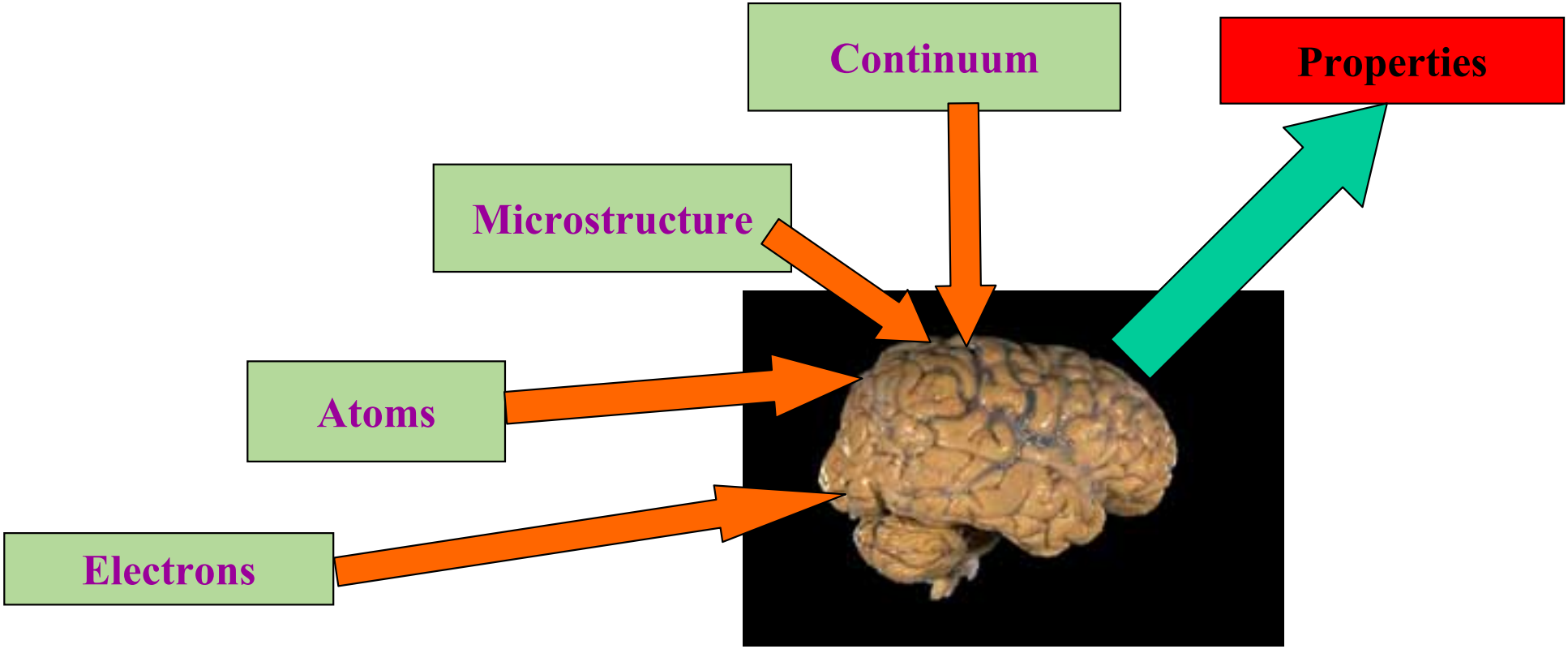
Education:

Computational Materials Science/Chemistry is still the step child in Educational Curricula

Theory of Properties: The Multi-Scale Materials View



Theory of Properties: A More Realistic View



Courtesy of NIH.

Computations should not substitute for lack of knowledge

Example: Intergranular Embrittlement of Fe

Observation: **P embrittles high strength steel**
B enhances intergranular cohesion

Can we study this with atomistic modeling ?

Rice-Wang theory

"Embritting tendency of solute depends on difference in segregation energy at grain boundary and free surface"

Calculate segregation energy for B and P at free surface and grain boundary

Intergranular Embrittlement of Fe

Rice-Wang theory

"Embritting tendency of solute depends on difference in segregation energy at grain boundary and free surface"

Diagram removed for copyright reasons.
Source: Wu, R., A. J. Freeman, and G. B. Olsen. *Science* 265 (1994): 376-380.

Calculate segregation energy for B and P at free surface and grain boundary

Intergranular Embrittlement of Fe

Graph and diagrams removed for copyright reasons.

R. Wu, A. J. Freeman, G. B. Olson, *Science* 265, (1994) 376-380 .

When you can not think through the relation between macroscopic behavior and "computable" properties on the atomic scale

Derive relation statistically -> data mining techniques

What if we can not bridge the gap between microscopic and macroscopic with theory ?

Microscopic

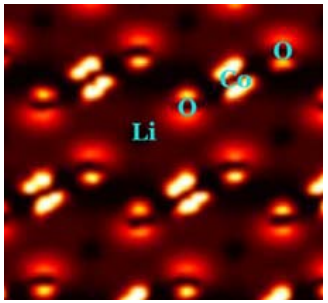
Macroscopic

Use large amounts of data for which macroscopic property is known

Photo of hands counting money removed for copyright reasons.

Correlate ?

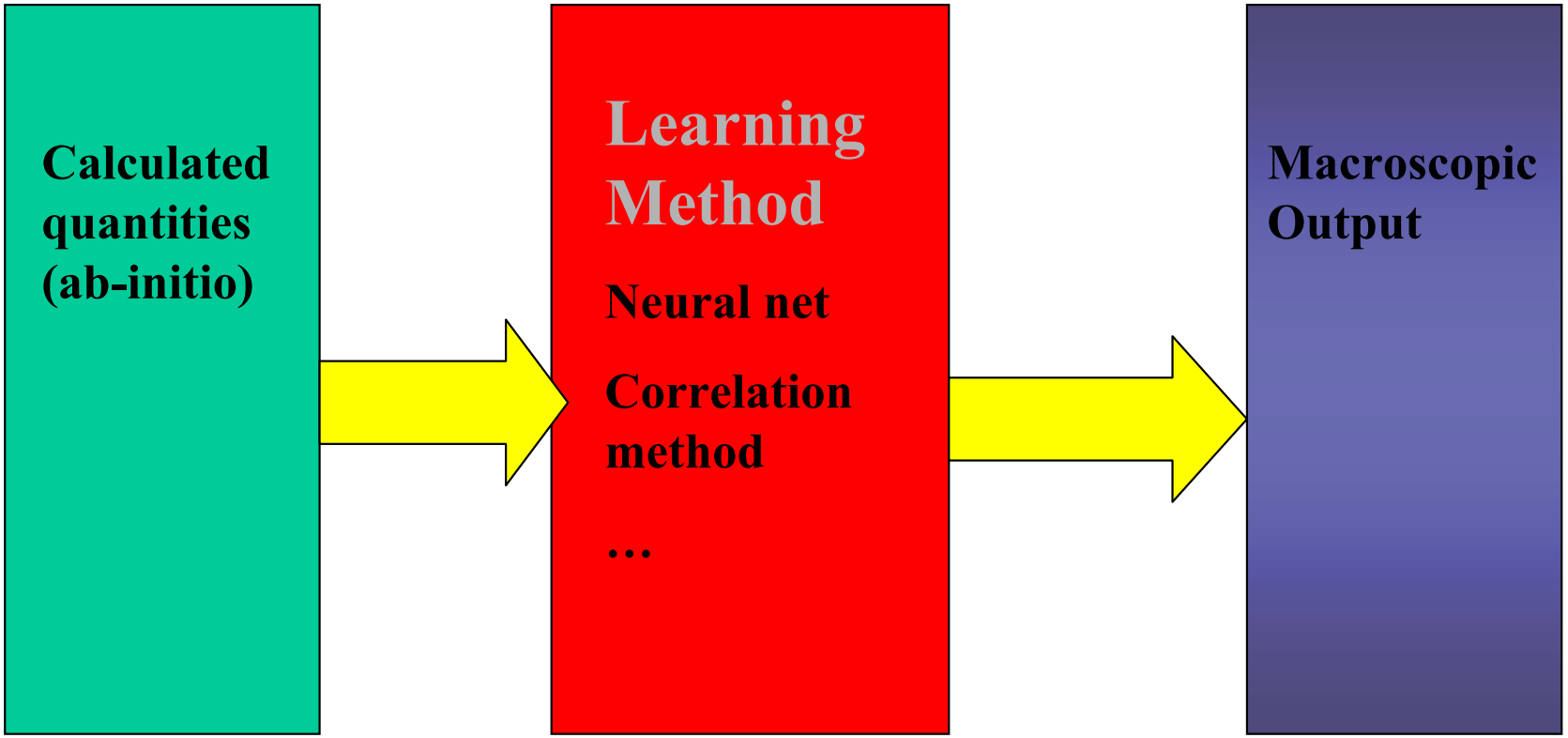
Properties



Electrons

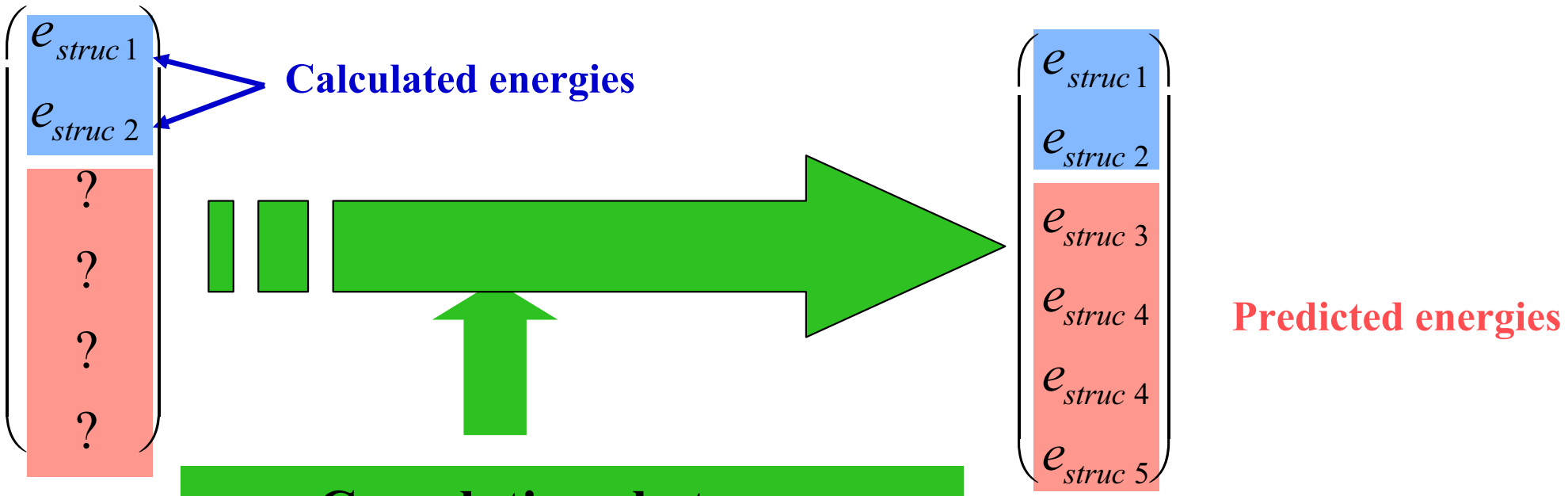
Makes it possible to deal with properties for which one has no microscopic theory or approach

Learning Methods



e.g QSAR in chemistry (Quantitative Structure Activity Relationship)

Example, can one predict stable crystal structures in a binary alloy from knowledge of only the energy of a few compounds



Correlations between structural energies extracted from database on other alloys

trained algorithm with ≈ 130 crystal structures in each of 80 binary alloys

Ag-Cd: Example

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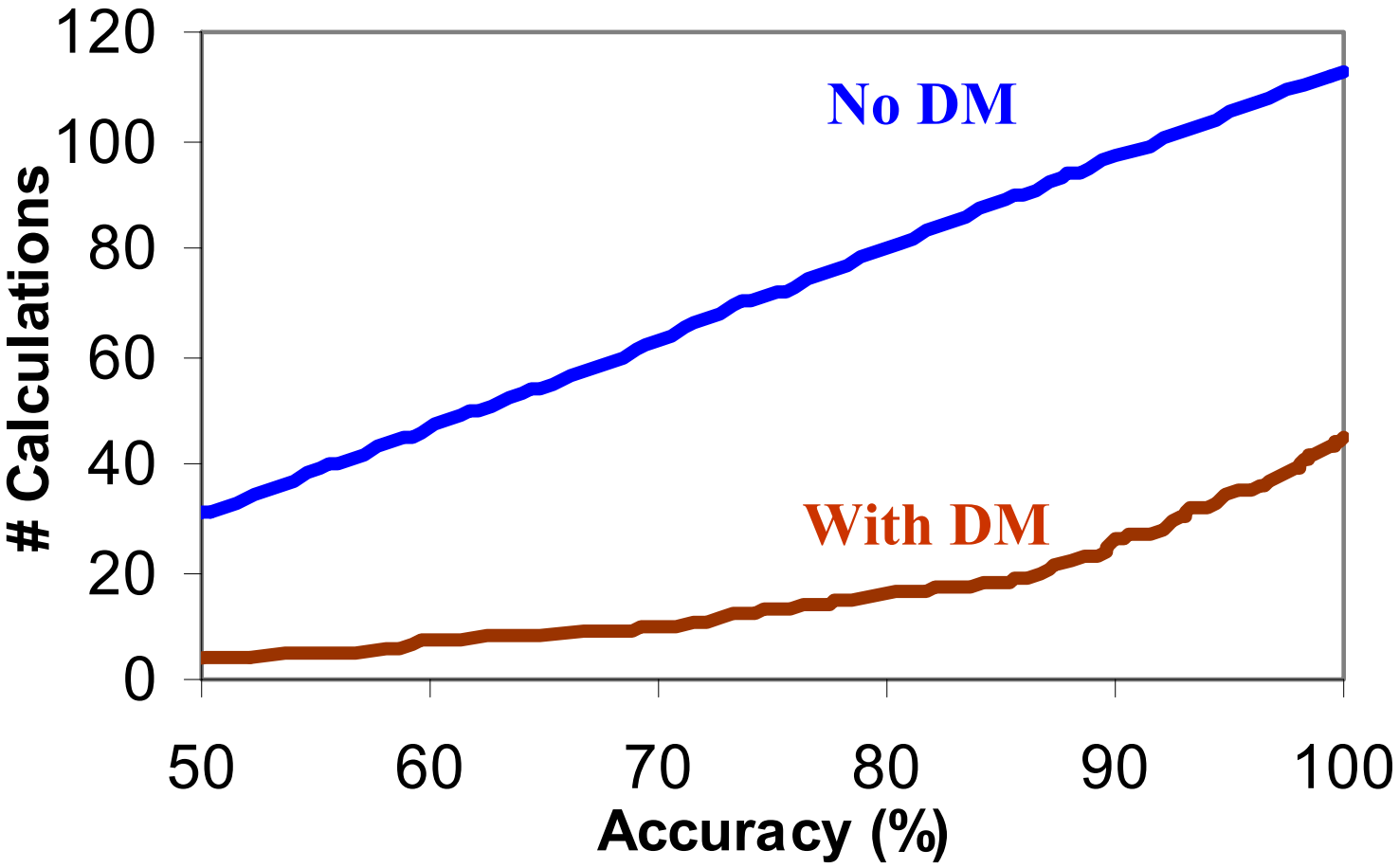
Test : Crystal Structure Prediction



~4x speedup from Data Mining

Design: Bandgaps

Standard First Principles Methods (LDA/GGA) underestimate band gaps

Example: Silicon

Figure removed for copyright reasons.

Calculated: 0.55 eV

Experimental: 1.1 eV

Can be fixed

With empirical pseudo potentials (not generally available) band gaps can be corrected by fitting to well-known semi conductors

GaAs **Si**

Figure removed for copyright reasons.

Then, can predict band gaps of mixtures and states of impurities

Figure removed for copyright reasons.

Figure removed for copyright reasons.

Can try to find composition and arrangement with "tuned" gap

Scan through milions of AlAs/GaAs superlattices to find one with maximal band gap

Figure removed for copyright reasons.

Thermoelectrics

Figure of merit

$$ZT \quad \frac{\sigma}{\kappa} S^2 T$$

Seebeck Coefficient

$CeFe_4P_{12}$

Want low thermal conductivity: Can be calculated, but tedious. Use qualitative guidelines:

Figure removed for copyright reasons.

Complex unit cells, "ratteling" ions to cause scattering of phonons

e.g. skutterudites

Thermoelectrics

Want semiconductors with high s and high S

$$S \quad \frac{e\tau}{3\sigma T}\int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon}\right) \; N(\varepsilon) \; v^2(\varepsilon)(\varepsilon-\varepsilon_o)$$

Can be calculated from band structures

Figure removed for copyright reasons.

Prediction of high thermo-electric performance

$La(Ru_{1-x}Rh_x)_4Sb_{12}$

Figure removed for copyright reasons.

from Fornari and Singh: Applied Physics Letters, Vol 74, 3666 (1999)

The future of modeling

What does more computing buy you ?

Doubling every two years

40 years -> 10^6 increase in performance

Figure removed for copyright reasons.

But, … scaling

Molecular Dynamics with potentials **O(N)**

DFT (LDA, GGA) **O(N^3 or $N^2\log(n)$)**

Hartree Fock **O(N^4)**

Method	Today (atoms)	+40 years
MD (potentials)	10^8 atoms	10^{14} atoms
LDA (N^3)	1000	100,000
LDA(N)	1000	10^9
HF +CI(N^6)	10	100

Scaling for length

$N = L^3$

Conclusion

Computational modeling is very powerful, but

Be Smart