Developing and Fitting Reactive Empirical Potentials to Enable Atomic-Scale Simulations

Susan B. Sinnott

Department of Materials Science and Engineering
Penn State University

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Understanding Many-Particle Systems with Machine Learning Tutorials
IPAM, UCLA

Computational Materials Science

- Calculate energies and forces on atoms
  - **Quantum mechanics** – first principles approach with minimal approximations
  - **Empirical approach** - mathematical equations with parameters fit to quantum mechanical and experimental data to describe materials; called **potentials**
- Predict future dynamical or thermodynamic states with simulations
  - Explicit dynamical information – **molecular dynamics**
  - Evolution of the system to thermodynamic minimum – **Monte Carlo**

Molecular Dynamics Simulations

The Idea: Integrate

$$F_i(t) = ma_i(t)$$

$$F_i(t) = md^2r_i(t)/dt^2 = -dU(r^N)/dr_i$$

numerically to predict the responses of atoms to external forces with time. Several different numerical integrators are available.

The good news:

Can predict the motion of atoms under practically any conditions

The bad news:

Can only follow the motion for a few ps using traditional approach

More good news:

Accelerated methods allow one to overcome this limitation

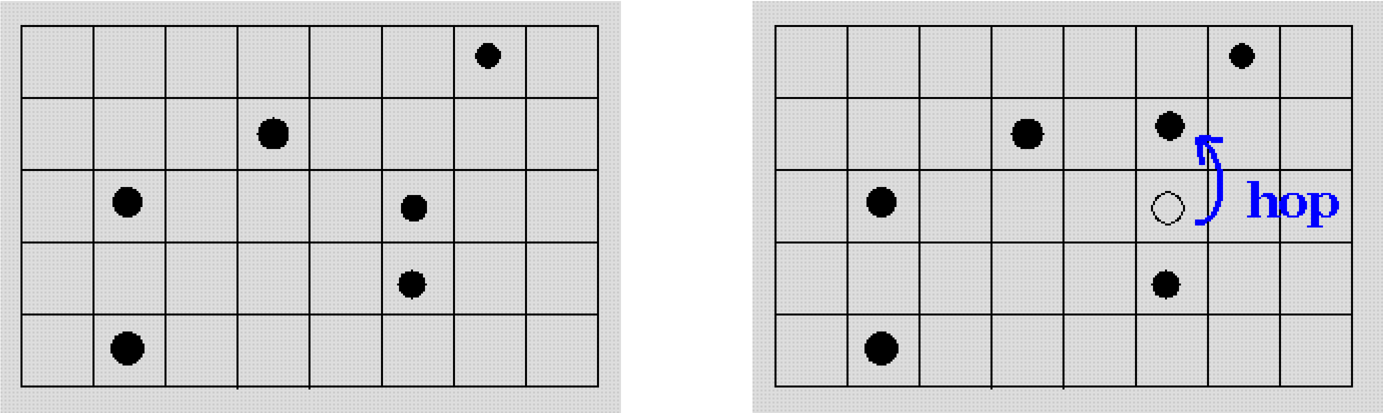
More bad news:

Accelerated methods are not very broadly applicable

Monte Carlo Simulations

The Idea:

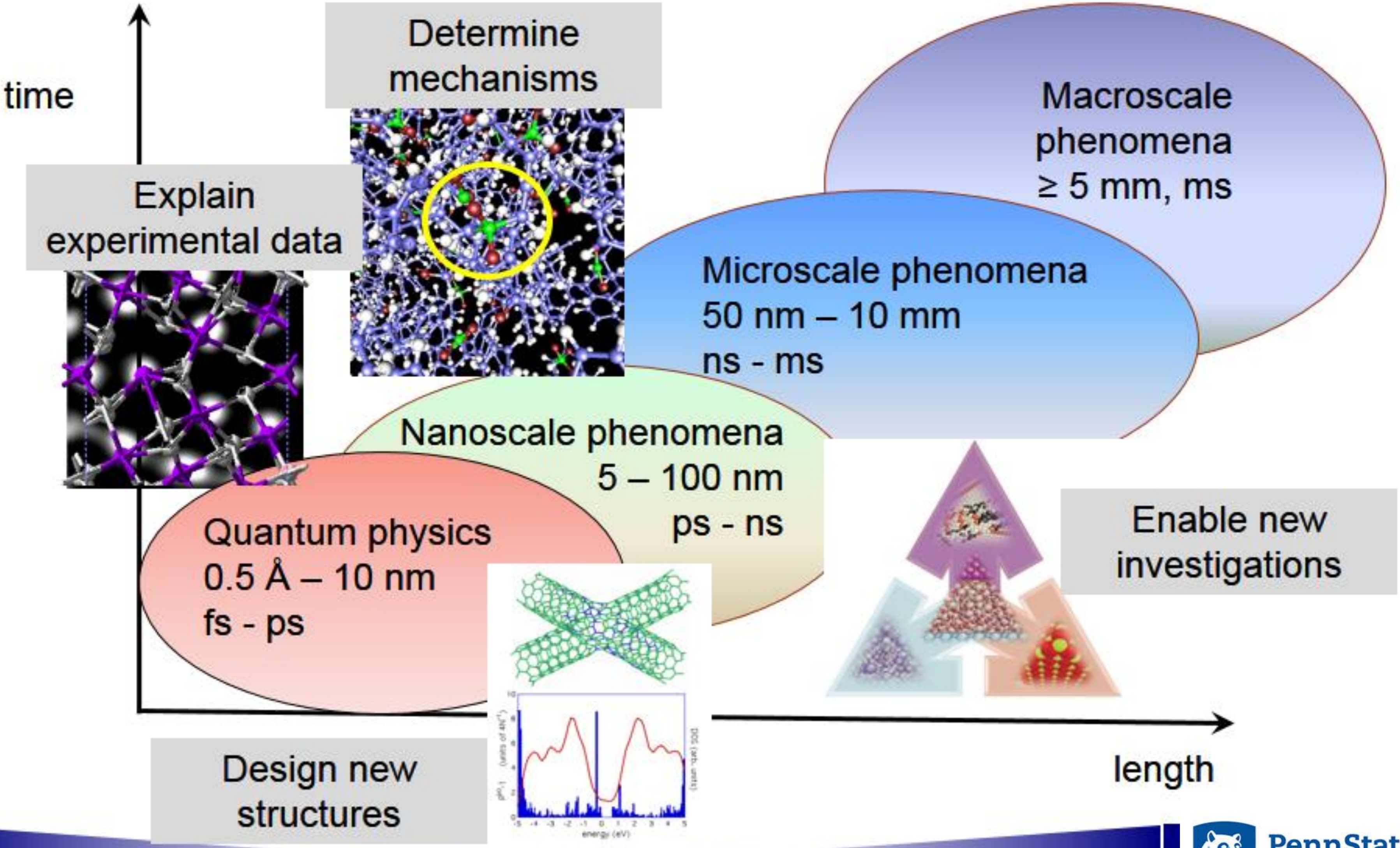
Calculate the energy for two configurations of interest



If the 2nd configuration is lower in energy accept it and consider the next variation in configuration. If not then check with a random number generator (roll the dice). Depending on the outcome, the 2nd configuration may or may not be accepted.

30+ Years of Potential Evolution

Computational Materials Science and Engineering



time

Determine mechanisms

Explain experimental data

Macroscale phenomena
≥ 5 mm, ms

Microscale phenomena
50 nm – 10 mm
ns - ms

Nanoscale phenomena
5 – 100 nm
ps - ns

Quantum physics
0.5 Å – 10 nm
fs - ps

Enable new investigations

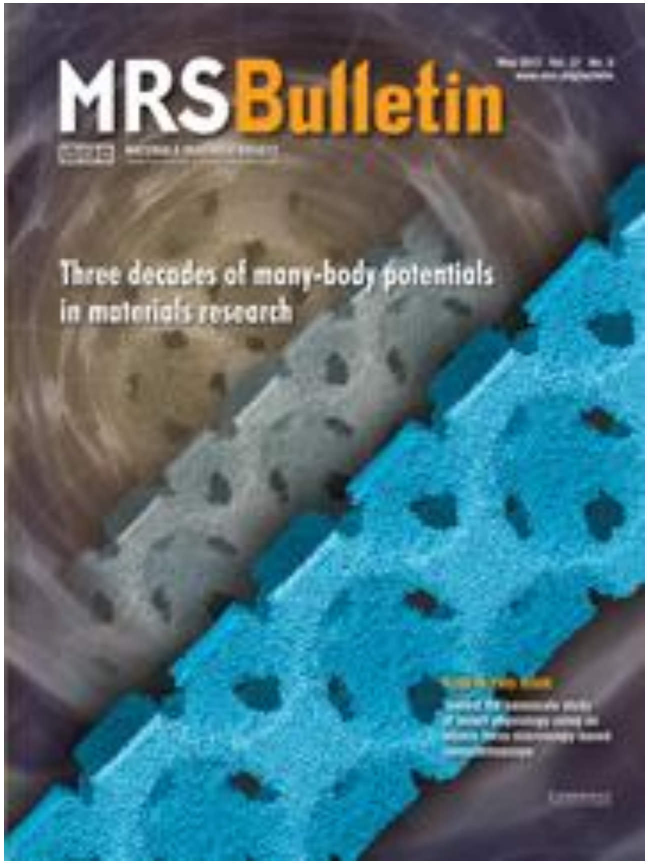
Design new structures

length

Reactive Materials Modeling at the Atomic Scale

- Electronic-structure level
  - High fidelity methods available:
    - Quantum chemical approaches
    - Density functional theory (DFT)
  - Off-the-shelf codes widely available
  - Wide-spread understanding of strengths and limitations
- Atomic-scale level
  - Many-body, realistic potentials have been available for over 30 years
  - Ideal for examining systems under extreme environments
  - Necessary to investigate chemistry + microstructure + mechanics + mechanisms + …..
  - Physics-based model development
- Inform microscale and mesoscale models
- Explain experimental observations

33 Years of Many-Body Atomic-Scale Potentials (Reactive Force Fields)



May 2012 issue

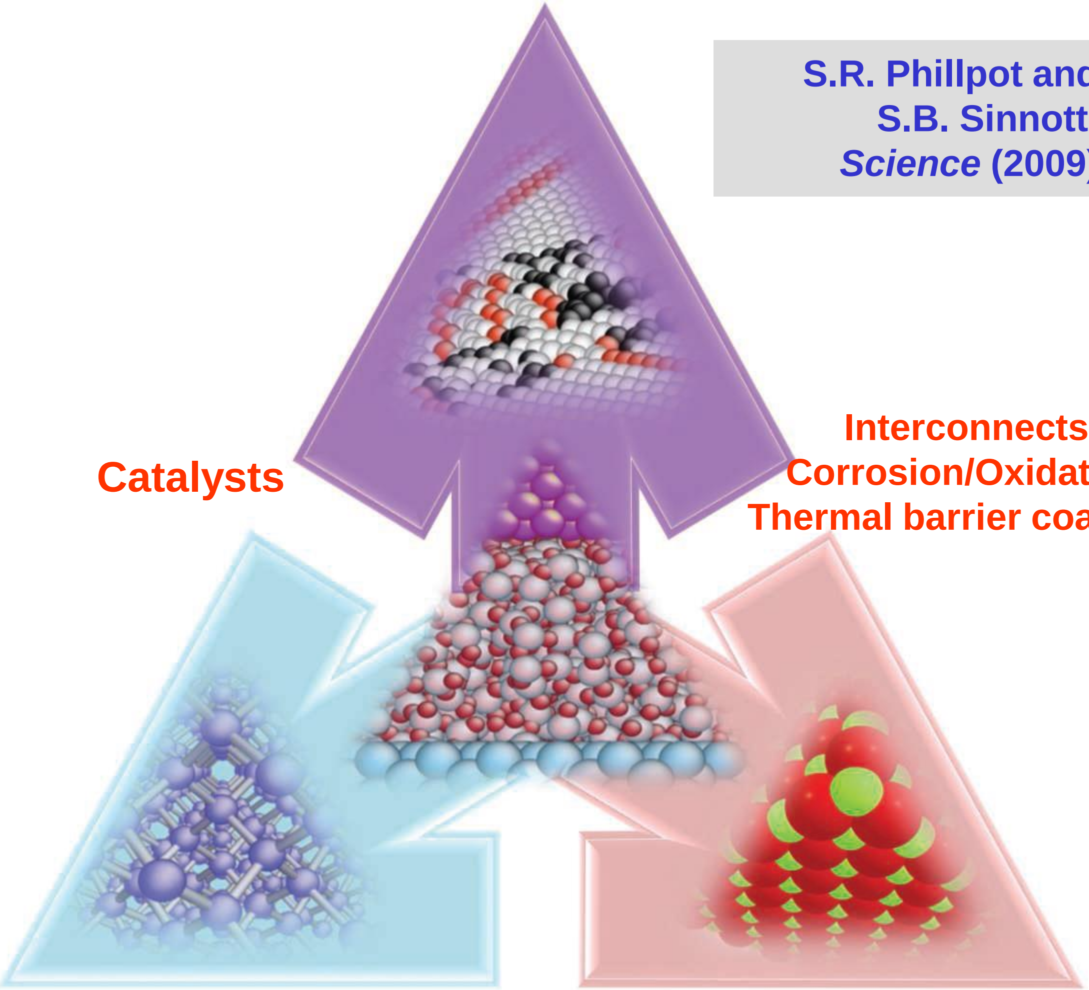
Historically developed for materials with specific types of chemical bonds

- Tersoff potentials for Si
  - Brenner or REBO potential for C,H + O,F,S,….
  - AIREBO
- EAM potentials for metals
  - MEAM for metals and oxides
  - EAM+ES for metals and oxides
- Rigid ion (Buckingham) potentials for ionically bound materials

Used to examine phenomena at the atomic and nanometer scale and develop a qualitative, mechanistic understanding

Multicomponent Systems

- Inherent to many applications
- Challenging for:
  - First-principles electronic structure methods (large systems, lacking usual symmetry)
  - Atomic-scale methods because of their heterogeneous nature
- This need spurred the development of ***next generation potentials:*** **Charge Optimized Many-Body (COMB)**, ReaxFF, EAM+ES, and a few others



Metallic

S.R. Phillpot and S.B. Sinnott, *Science* (2009)

Catalysts

Interconnects
Corrosion/Oxidation
Thermal barrier coating

Covalent

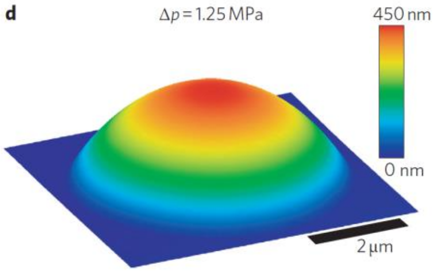
Bone/biocomposites
Aqueous biological systems

Ionic

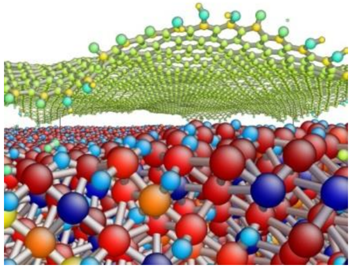
Selective Applications of COMB3

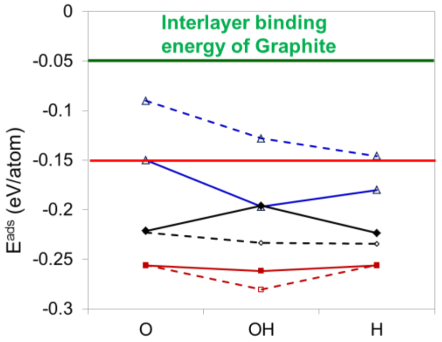
Graphene on Metal Oxides

G/SiO_2



G/Cu_2O

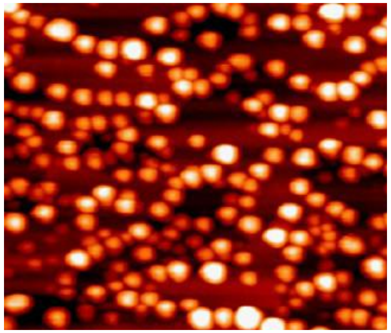




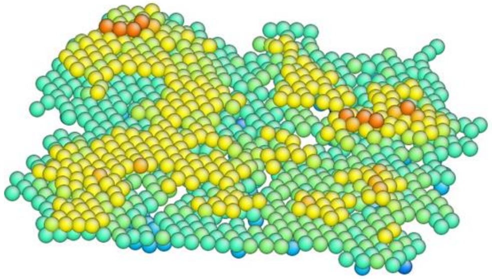
Ultra-strong adhesion

Heterogeneous Catalysts

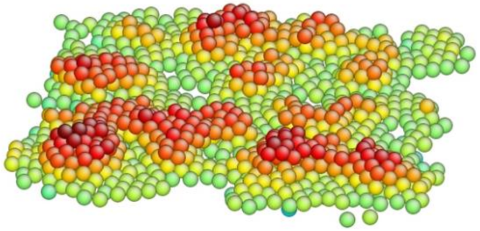
Cu/ZnO



Cu/Cu

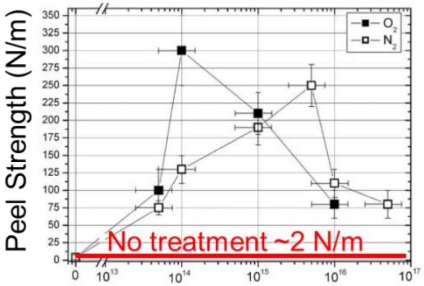


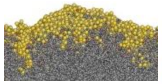
Cu/ZnO



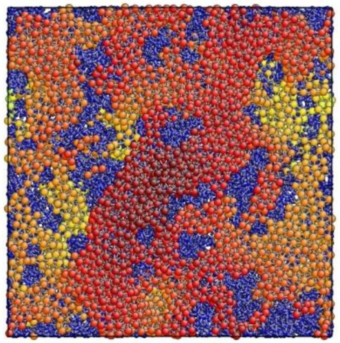
Growth mechanisms

Metallization of Polystyrene

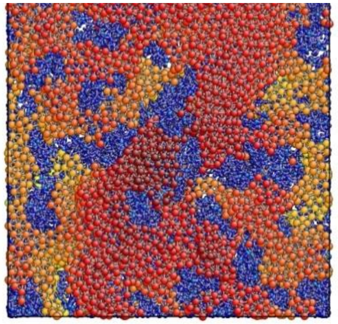




Cu/PS



Cu/PSO



Organic-inorganic chemistry

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Functional Form of the COMB3 Potential

$$E_T = \sum_i \left\{ \begin{array}{l} E_i^{Self}(q_i) + \frac{1}{2}\sum_{j\neq i}\left[V_{ij}^{short}\left(r_{ij}, q_i, q_j\right) + V_{ij}^{Coul}\left(r_{ij}, q_i, q_j\right)\right] \\ +B_i(q_i) + C_i\left(r_{ij}, \theta_{ijk}\right) + E^{polar}\left(q_i, r_{ij}\right) + E^{vdW}(r_{ij}) \end{array} \right\}$$

- **Self energy**: ionization energies and electron affinities; includes penalty function to capture change in self-energy due to the field from the ionic lattice
- **Short-range interactions**: reactive bond-order potential
- **Coulomb interactions**: Coulomb integral over the charge densities
- **Charge and angular correction terms**
- **Polarization**: Atomic polarizabililty for organic systems
- **van der Waals energy**

S.R. Phillpot and S.B. Sinnott, Science (2009)
T. Liang et al., Materials Science and Engineering R (2013)

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Functional Form of COMB3 Potential

General formalism:

$$E_T = \sum_i \left[E_i^S(q_i) + \frac{1}{2}\sum_{j\neq i} V_{ij}\left(r_{ij}, q_i, q_j\right) + B_i(q_i) + C_i(r_{ij}, \theta_{jik}) \right]$$

Self energy: fit to atomic ionization energies and electron affinities

$$E_i^S\left(q_i\right) = \chi_i q_i + J_i q_i^2 + K_i q_i^3 + L_i q_i^4$$

Penalty function to capture change in self energy due to field of ionic lattice

$$E_i^{field}(r, q_j) = \sum_{j\neq i}^{NN} \left(\frac{\rho_1 q_j}{r_{ij}^5} + \frac{\rho_2 q_j^2}{r_{ij}^5} \right)$$

$$V_{ij}(r_{ij},q_i,q_j) = f_c(r_{ij})\cdot A_{ij}(q_i,q_j)\cdot e^{-\lambda_{ij}\cdot r_{ij}} - f_c(r_{ij})\cdot b_{ij}\cdot B_{ij}(q_i,q_j)\cdot e^{-\alpha_{ij}\cdot r_{ij}} + q_i\cdot J_{ij}(r_{ij})\cdot q_j$$

Short range interactions: Bond-order type potential that was made charge dependent

A change in the partial charge on an atom affects the effective ionic radius, which influences the short-range repulsion and attraction

$$A_{ij}(q_i,q_j) = A_{ij}\cdot \exp\left[\lambda_i D_i(q_i) + \lambda_j D_j(q_j)\right]$$ →repulsive

$$B_{ij}(q_i,q_j) = B_{ij}\cdot B^*_{ij}(q_i,q_j)\cdot \exp\left[\alpha_i D_i(q_i) + \alpha_j D_j(q_j)\right]$$ →attractive

Bond order term, *b*$_{ij}$, includes many-body effects

$$b_{ij} = \left[1 + \left(\beta_i \sum_{k\neq i,j} \xi_{ijk}\, g\left(\theta_{jik}\right)\right)^{n_i}\right]^{-1/(2n_i)}$$

$$\zeta_{ijk} = f_{S_{ik}}\, e^{\left[\alpha_{ij}^{m_i}\left(r_{ij}-r_{ik}\right)^{m_i}\right]}$$ → symmetry function

$$g\left(\theta_{jik}\right) = 1 + c_i^2/d_i^2 - c_i^2/\left[d_i^2 + \left(h_i - \cos\theta_{jik}\right)^2\right]$$ → angular function

$$V_{ij}(r_{ij},q_i,q_j)=f_c(r_{ij})\cdot A_{ij}(q_i,q_j)\cdot e^{-\lambda_{ij}\cdot r_{ij}}-f_c(r_{ij})\cdot b_{ij}\cdot B_{ij}(q_i,q_j)\cdot e^{-\alpha_{ij}\cdot r_{ij}}+q_i\cdot J_{ij}(r_{ij})\cdot q_j$$

Long range interactions: Coulomb electrostatics

Spherical charge distribution: 1*s*-type Slater orbital

$$J_{ij}(r_{ij})=n_{ij}\int d^3r_i\int d^3r_j\;\rho_i(r_i,q_i)\rho_j(r_j,q_j)/r_{ij}$$

Treats long range interactions with Wolf summation

$$\rho_i(r_i,q_i)=q_i\frac{\xi_i^3}{\pi}\exp\left(-2\xi_i\left|r-r_i\right|\right)$$

Polarization term:

$$E^{Polar}[q_i,r_{ij}]=\sum_i\frac{\vec{\mu}_i^{\,2}}{2\alpha_i}+\sum_i\vec{\mu}_i\cdot\vec{E}_i^{\,q}+\tfrac{1}{2}\sum_i\sum_{j\neq i}\vec{\mu}_iT_{ij}\vec{\mu}_j$$

Wolf et al. J. Chem. Phys. 110 (1999)

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Fitting COMB3 Potentials

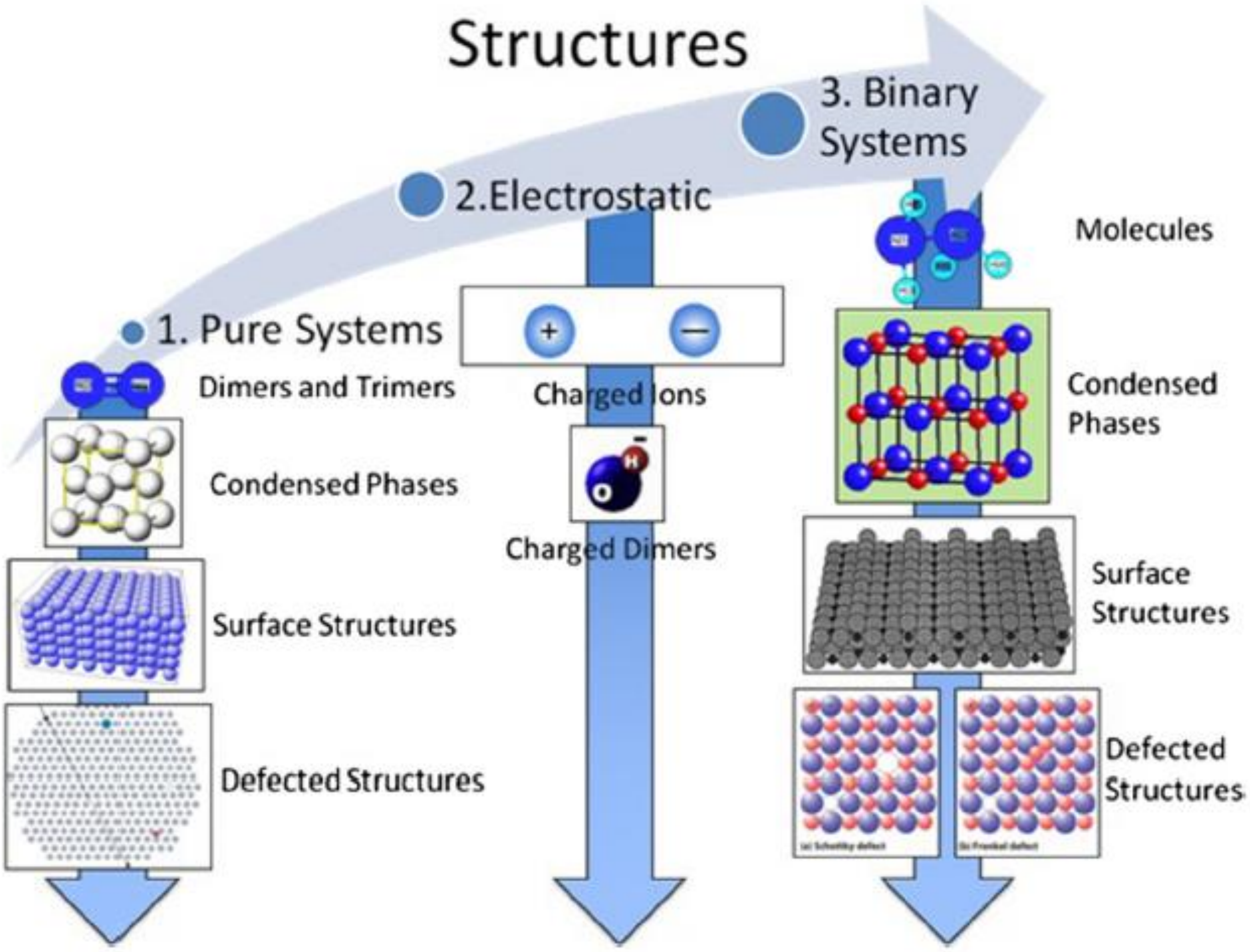
- POSMat program automates parameterization process
- Much human involvement in decision making process, which is still a “black art”
- Fitting database typically includes
    - lattice constants
    - cohesive energies
    - energy versus volume for multiple phases
    - bulk modulus
    - elastic constants
    - surface energies
    - point defect formation energies
    - stacking faults
    - others

Database from DFT and/or experiment; we use the numbers we “trust the most”; fit according to the **Rules of Finnis and Tersoff.** Database depends on:

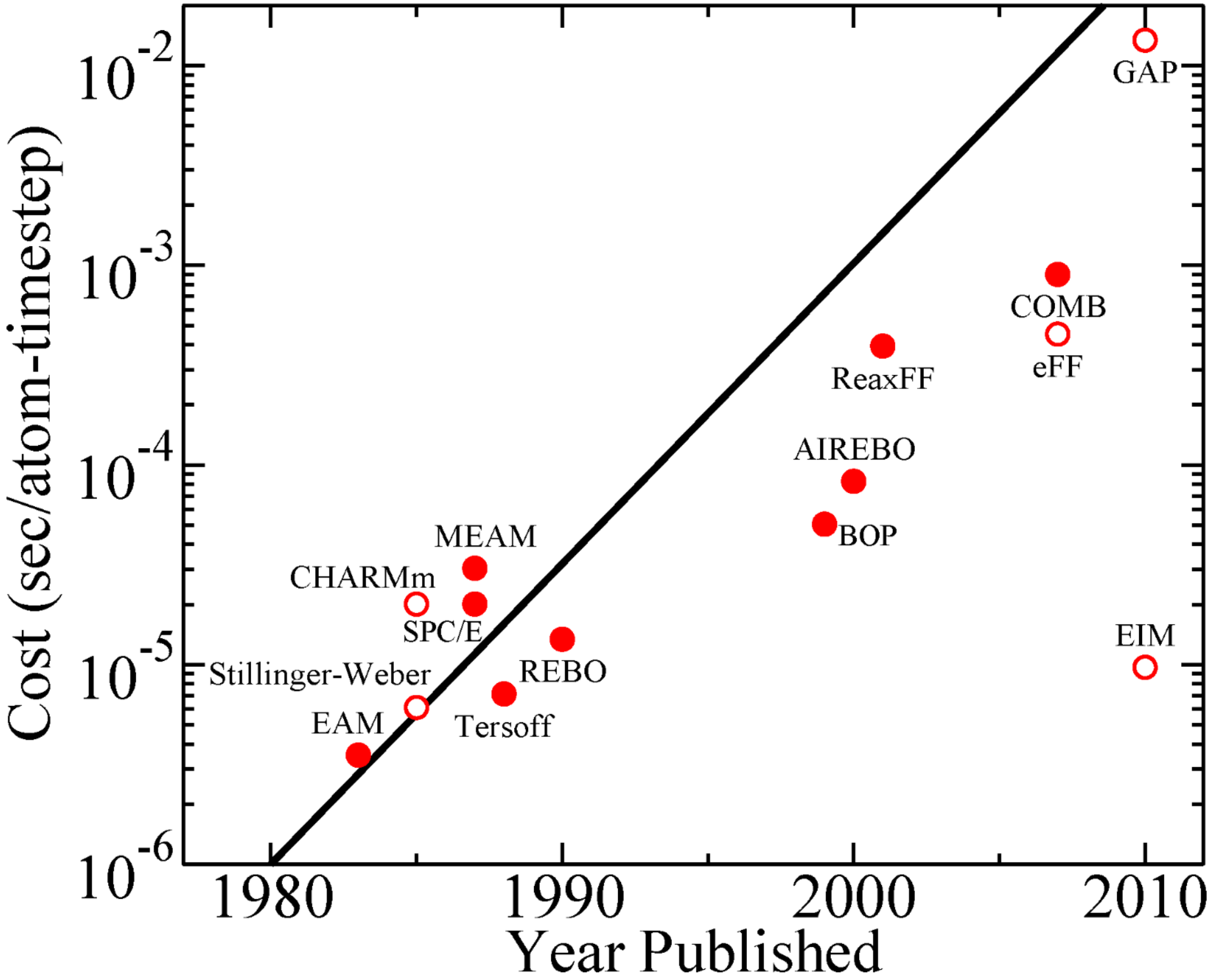
- ☐ material type (metallic, ionic, molecular)
- ☐ application (structural versus catalysis)

Martinez et al., *Current Opinion in Solid State & Materials Science* **17** (2013)

Automating the Fit



Cost of Potentials in LAMMPS



DFT calculations for systems 2 orders of magnitude smaller in size are 5 orders of magnitude more computationally expensive

Plimpton and Thompson, MRS Bulletin **37** (5) 513 (2012)

COMB and ReaxFF

COMB3:

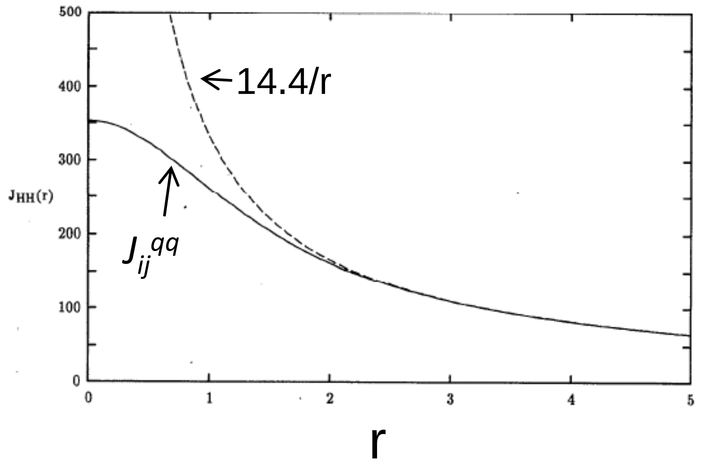
- Charge density function, ρ
- Core charge, Z
- Coulomb integrator, J^{qq}, J^{qz}
- DirectSum

$$f(|\mathbf{r}-\mathbf{r}_i|) = \xi_i^3 \pi^{-1} \exp(-2\xi_i |\mathbf{r}-\mathbf{r}_i|)$$

$$\rho_i(\mathbf{r};q_i) = Z_i \delta(|\mathbf{r}-\mathbf{r_i}|) + (q_i - Z_i) f_i(|\mathbf{r}-\mathbf{r_i}|)$$

$$J_{ij}^{qq} = \left[\rho_i | \rho_j\right] = \int d^3r_1 \int d^3r_2 \frac{\rho_i(\mathbf{r}_1)\rho_j(\mathbf{r}_2)}{r_{12}}$$

$$E^{qZ}[\{q\},\{r\}] = \sum_i \sum_{j>i} \left(q_i J_{ij}^{qz} q_j + q_j J_{ji}^{qz} q_i\right)$$



ReaxFF:

- Point charge
- No core charge
- Shielded Coulomb
- Tap function

$$-\mathrm{Tap} \cdot C \sum_{j \neq i}^{N} \frac{q_j}{\left[r_{ij}^3 + (1/\gamma_{ij})^3\right]^{1/3}}$$

~1/r -> Coulomb catastrophe when r is infinitely small

- Both 1/r at long distance
- To avoid Coulomb catastrophe at short distance
  - Coulomb integrator over charge density in COMB3
  - Shielding parameter γ in ReaxFF

COMB and ReaxFF

~ 1/r -> does not converge at infinitely long distances; the Ewald Summation method is costly

COMB3 uses Direct Sum

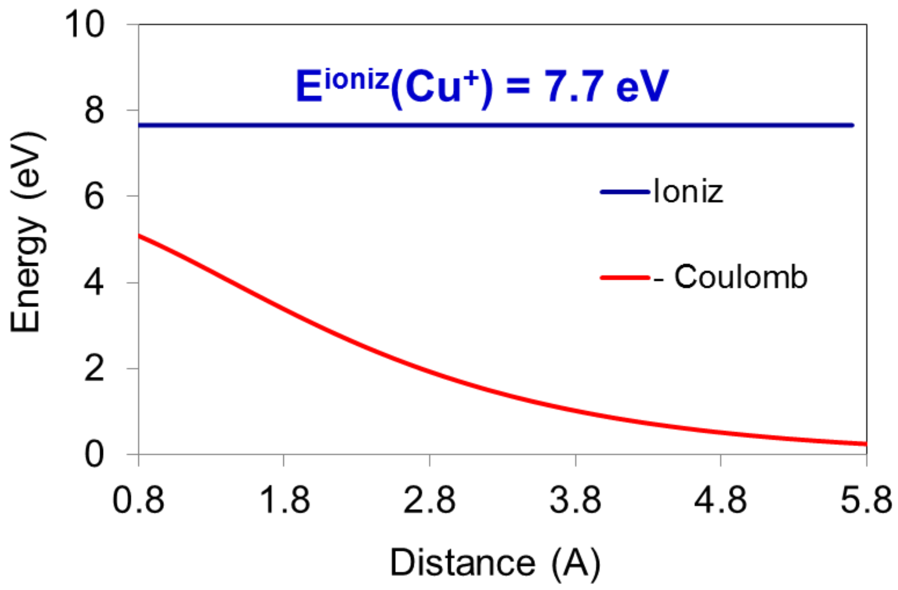
- Coulomb cutoff
- Design for crystals
- Underestimate the Coulomb in molecules

ReaxFF uses the Taper Function

$$- \mathrm{Tap} \cdot C \sum_{j \neq i}^{N} \frac{q_j}{\left[r_{ij}^3 + (1/\gamma_{ij})^3 \right]^{1/3}}$$

- Coulomb cutoff
- The Taper function can adjust the strength of Coulomb interactions

Coulomb + Ionization



- Energy minima at infinitely short distances
- No charge transfer

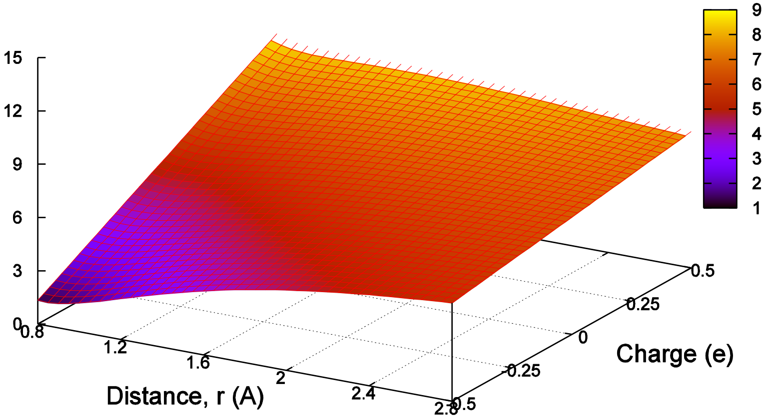
COMB and ReaxFF

Coulomb + Ionization -> underestimates charge transfer

COMB3 adds field effects

$$F_i^{Field}(r_{ij}, q_j) = \frac{1}{4\pi\varepsilon_o}\sum_{j\neq i}^{NN}\left(\frac{P^X q_j}{r_{ij}^3} + \frac{P^J q_j^2}{r_{ij}^5}\right)$$

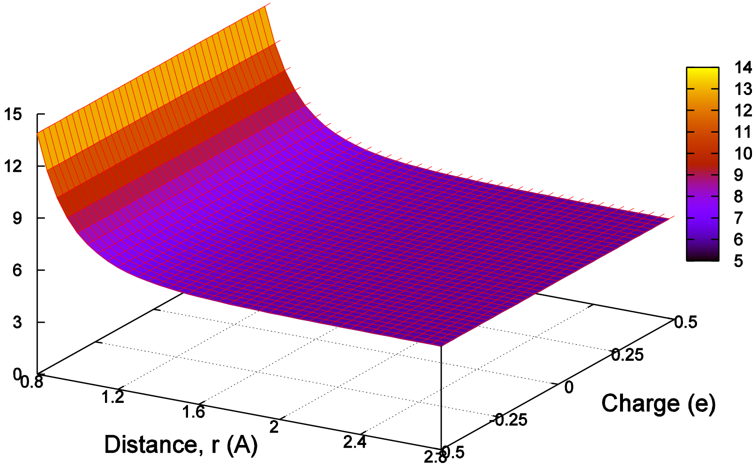
Electonegavitity



ReaxFF modifies the ionization energy curve

$$\chi_i^0 q_i + \frac{1}{2}J_i^0 q_i^2$$

Self-Coulomb



- COMB3 still underestimates charge transfer
- Original version of ReaxFF may have large residual charge in the case of bond dissociation; being resolved via integration with ACKS2 method

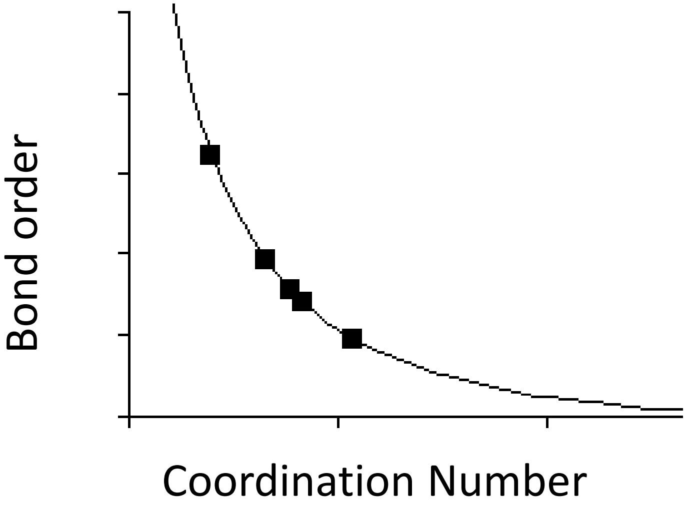
Short Range Bond Order Differences

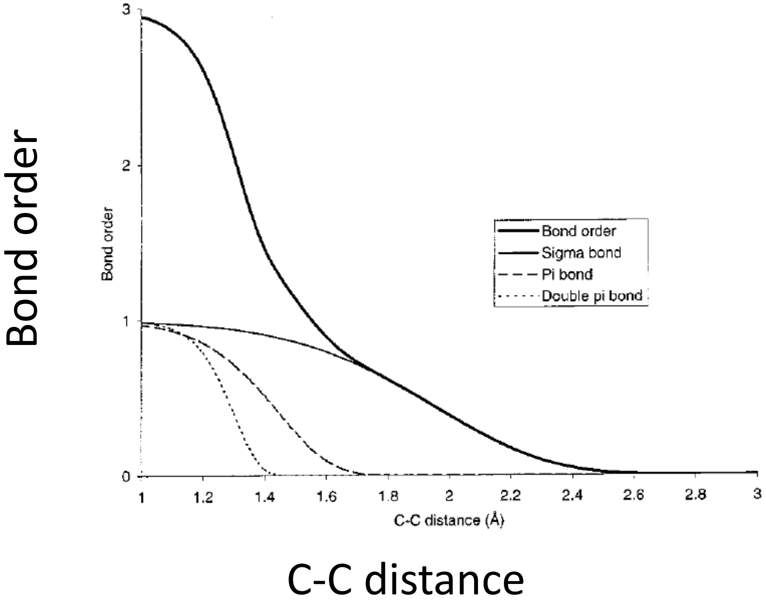
COMB3:

- Abell-Tersoff-Brenner
- Bond order evaluated based on CN, bond angle, torsion …
- Bond order scales the pairwise attraction
- Uses Tersoff cutoff function

ReaxFF:

- The bond order is first evaluated from bond length
- All other energy terms can be scaled by a bond order
- No cutoff function is used



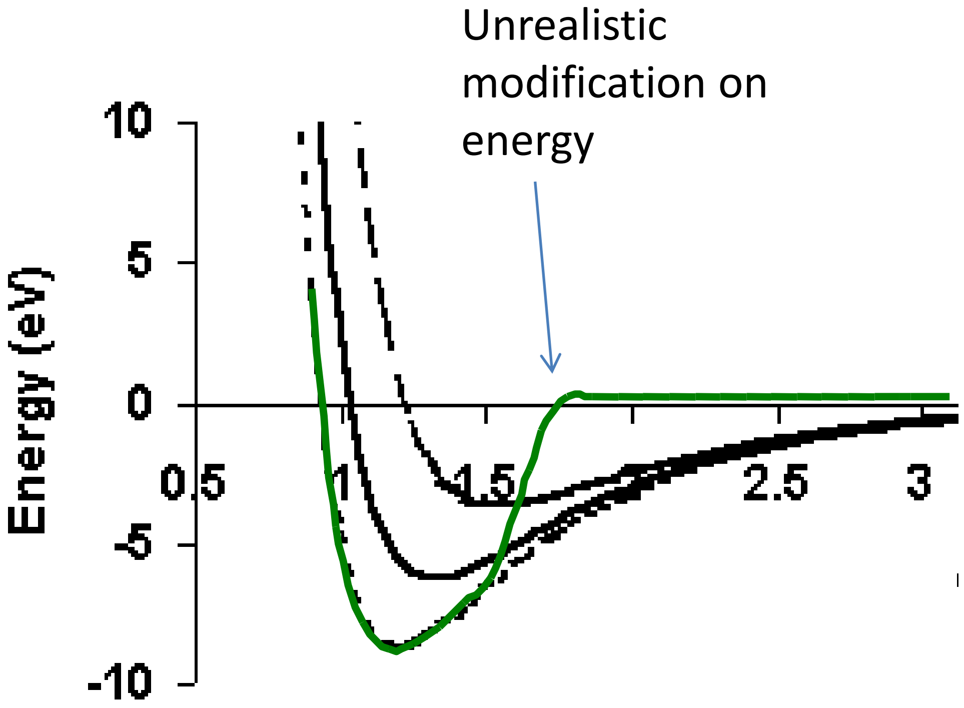


- Bond order in COMB3 is not directly related to distance
- CN increase -> increased electron-electron repulsion -> increased bond length

COMB3 and ReaxFF

Cutoff Function

Unrealistic energy and forces inside cutoff region for COMB3



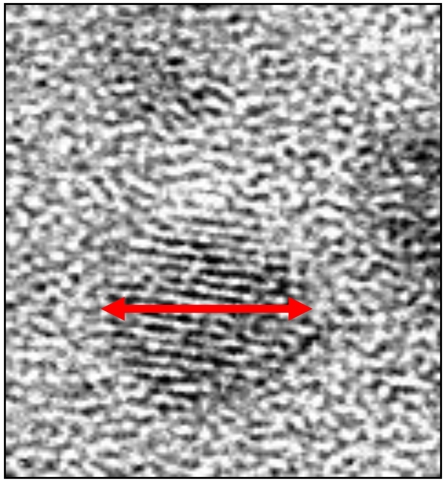
Parameterization

- COMB3 is more focused on crystals than molecules since DirectSum works better.
- ReaxFF can do a better job for transition states since there is no cutoff on short-range interaction.

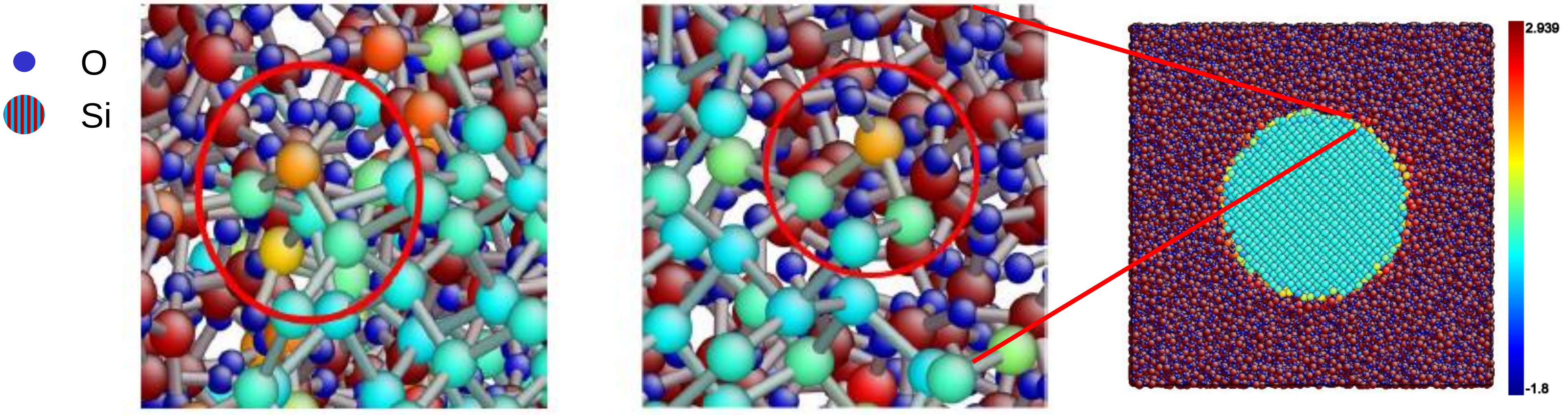
T. Liang et al., Annual Rev. Mater. Res. **43** (2013)
Y. K. Shin et al., MRS Bulletin **37** (2012)

Example: Si Nanocrystals Embedded in a-SiO_2

- Si nanocrystals (NCs) emit visible light and the extent of the emission depends on the
  - Size of the Si-NC
  - Structure of the Si-NC/a-SiO_2 interface
    - Silanone bonds (Si=O double bond)



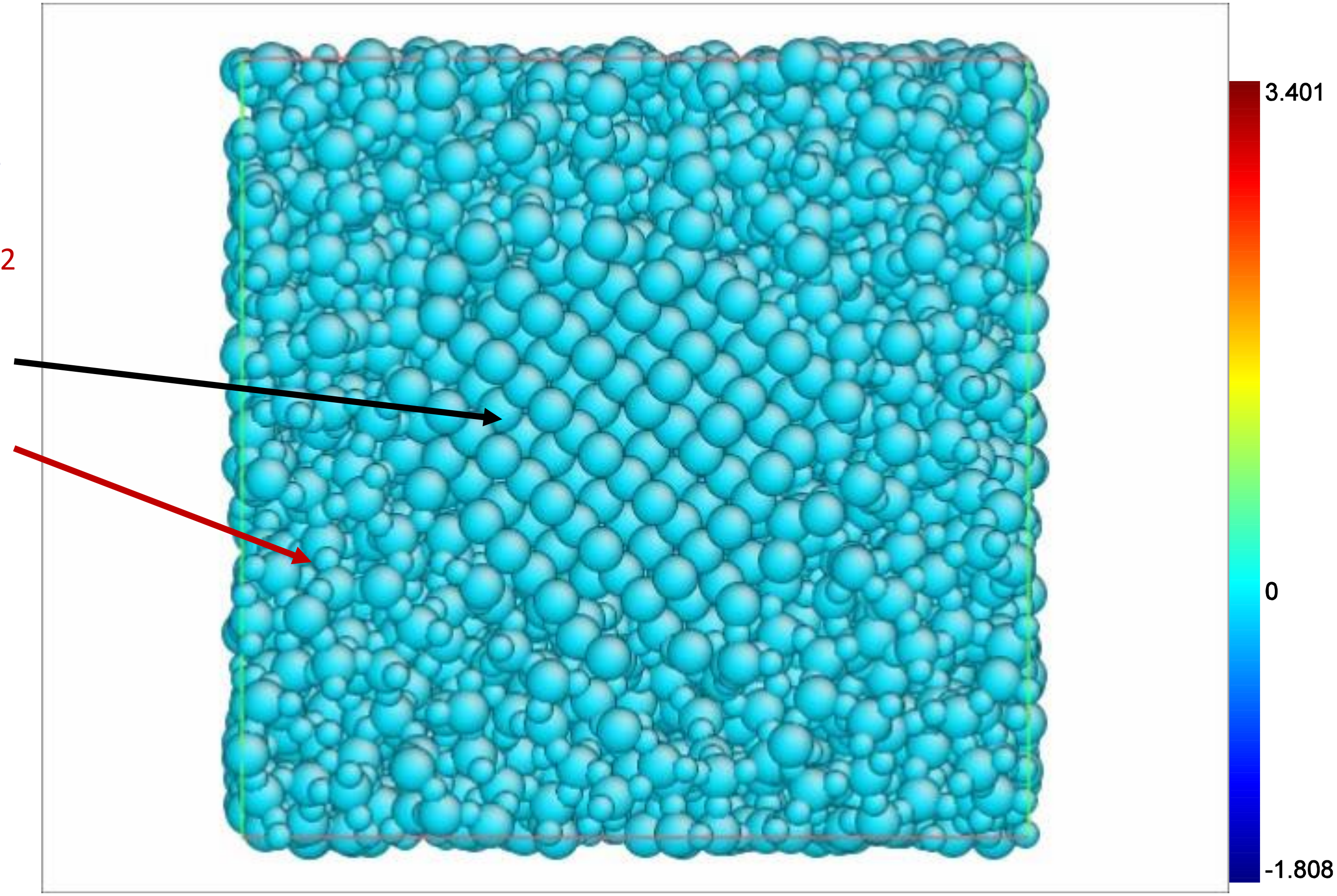
10 nm in diameter



In collaboration with Flyura Djurabekova and Kai Nordlund at the University of Helsinki

F. Djurabekova, M. Backholm, M. Backman, O. H. Pakarinen, J. Keinonen, K. Nordlund, **T.-R. Shan**, B. D. Devine, and S. B. Sinnott, ***Nucl. Instr. Meth. Phys. Res. B*** 268 19 3095 (2010).

Variable Charge Equilibration



Si-NC

a-SiO_2

Ti-C Parameterization

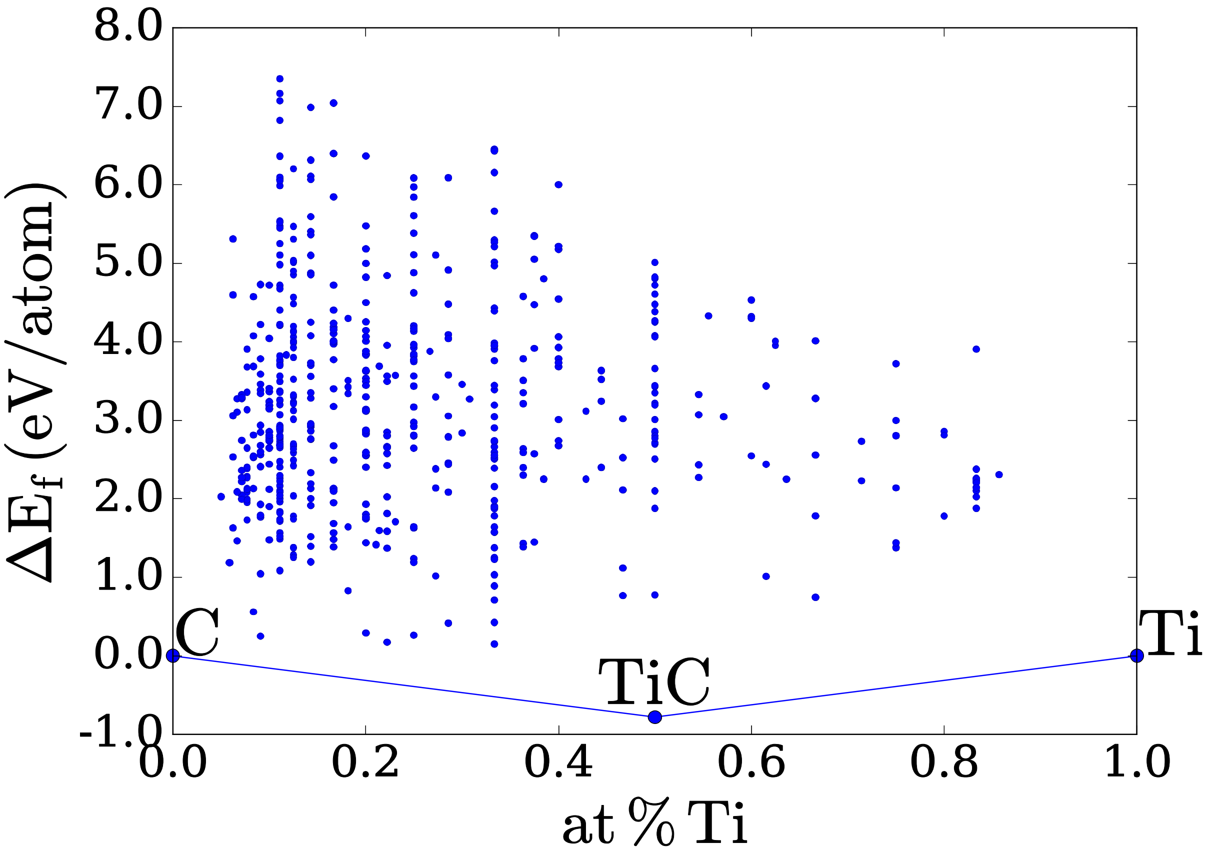
- Parameterize a COMB3 potential for TiC
- Exhibits satisfactory bulk, surface and point defect properties for the ground state structure of bulk TiC
- Also optimize for molecular Ti-C-O-H interactions such as occur in molecular systems such as Ti-$(OC_3H_7)_4$ or TTIP

	TARGET	COMB3
a (Å)	4.33[a]	4.34
ΔH_f (eV)	-1.56[b]	-1.52
B (GPa)	241[c]	262
C_{11} (GPa)	500[c]	504
C_{12} (GPa)	113[c]	144
C_{44} (GPa)	175[c]	204

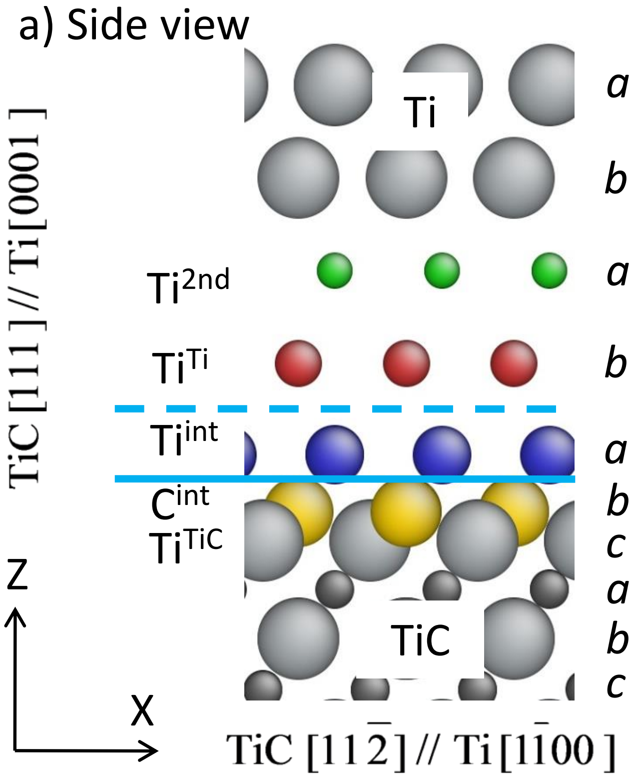
	TARGET	COMB3
V_{Ti} (eV)	14.38[d]	5.39
V_C (eV)	5.91[d]	18.45
Ti_i (eV)	12.47[d]	22.35
C_i (eV)	8.89[d]	16.16
$\gamma_{(001)}$ (J/m^2)	2.3[e]	3.6

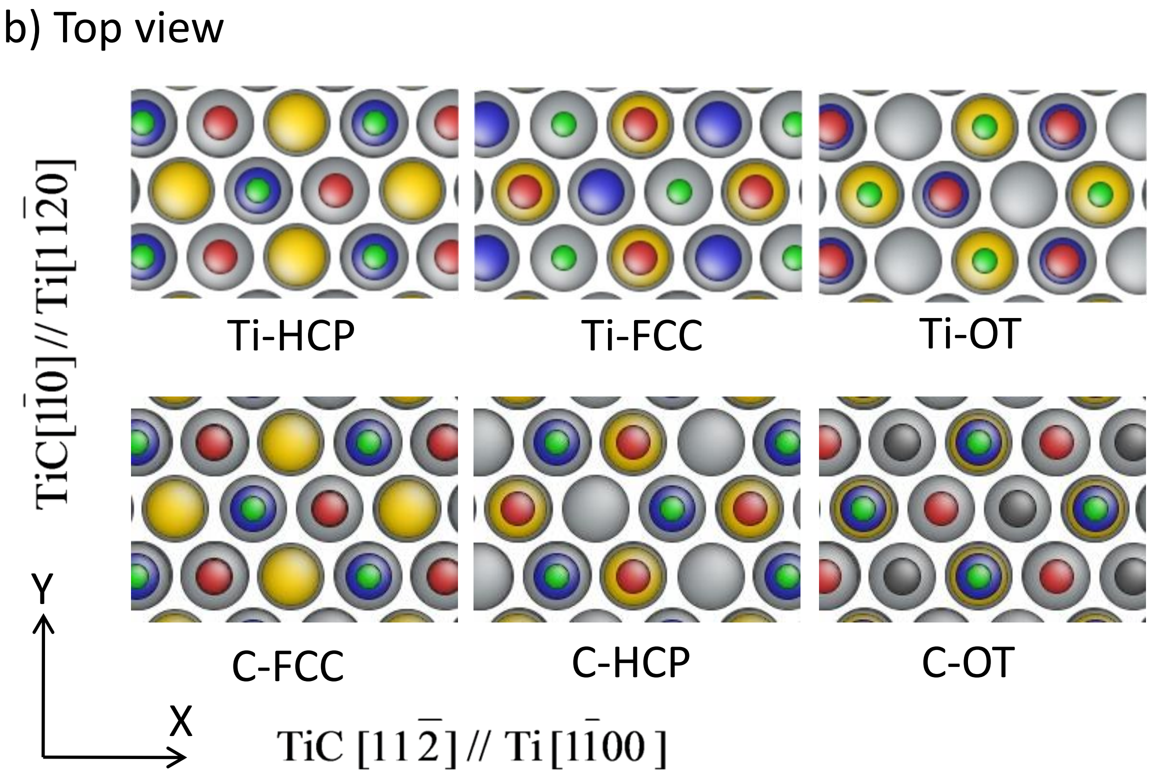
a. J.L. Murray, *OH: ASM International* (1987)
b. L.F.S. Dumitrescu LFS, *Z. Metallkd* (1999)
c. G. Simmons, *Cambridge: MIT Press* (1971)
d. T. Liang et al. (under revision)
e. A. Arya, *J. Chem. Phys.* (2003)

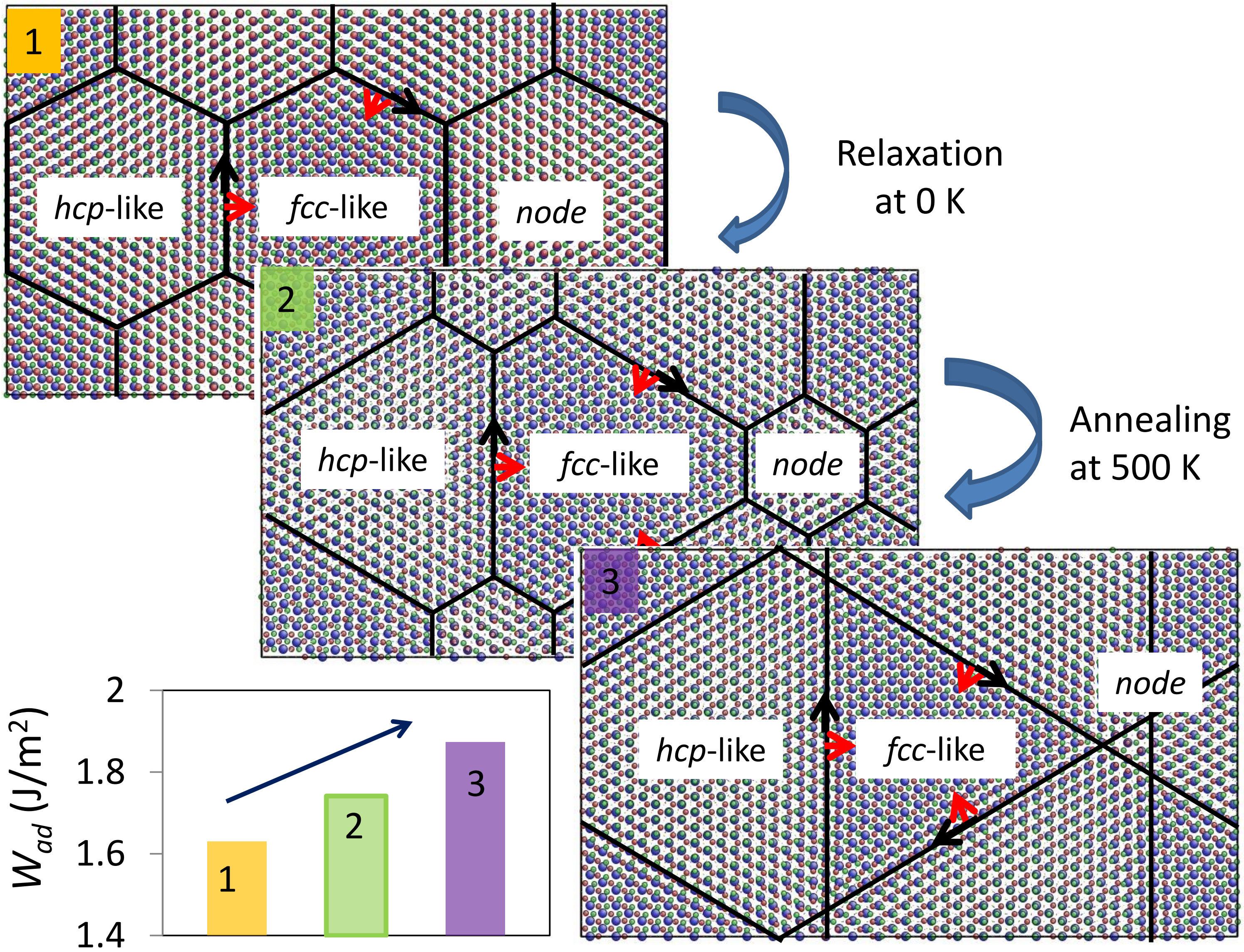
Genetic algorithm to investigate predicted phases



Ti/TiC Interfaces







Relaxation
at 0 K

Annealing
at 500 K

Challenges and Solutions for Materials Modeling

- Big-picture challenges:
  - What is the role of theory/computational modeling in the design, processing, and application of materials?
  - How do we integrate the latest computational approaches with experimental data to improve predictability?
  - To what extent are computational methodologies available that are applicable to the *physics of interest* in actual systems (materials, length and time scales)?
  - How do we ensure the next generation of scientists and engineers can work in this new paradigm?
- What is needed:
  - Natural workflow from discovery codes to predictive software
  - Tight integration between processing, characterization, and computational approaches
  - Accurate error bars for the results of theoretical/computational method results
  - Widespread dissemination of software with robust documentation