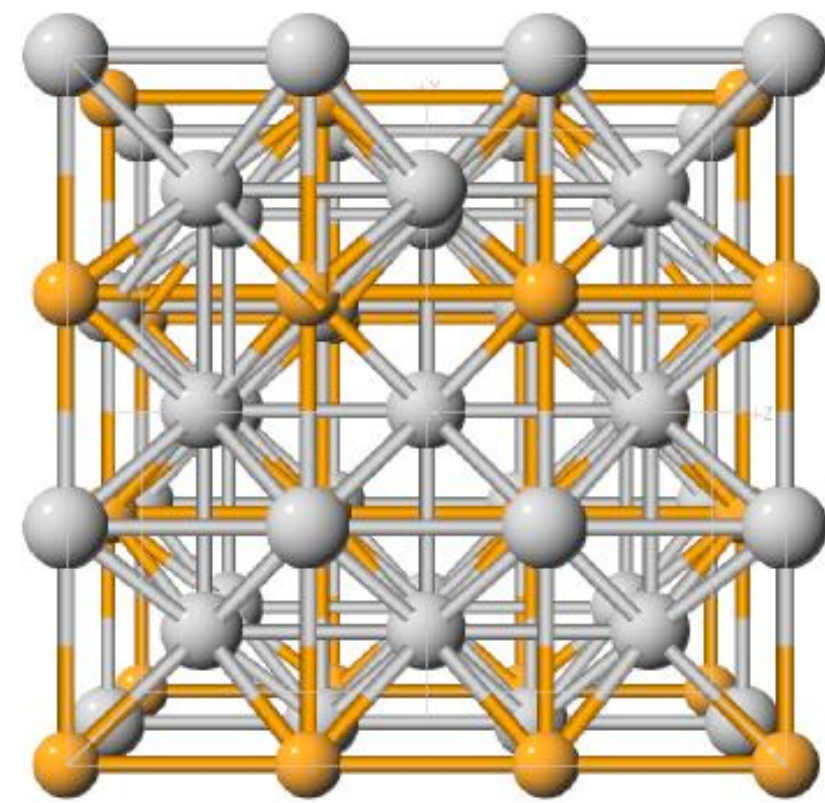


# Empirical Energy Models and Force Fields

Richard G. Hennig, University of Florida

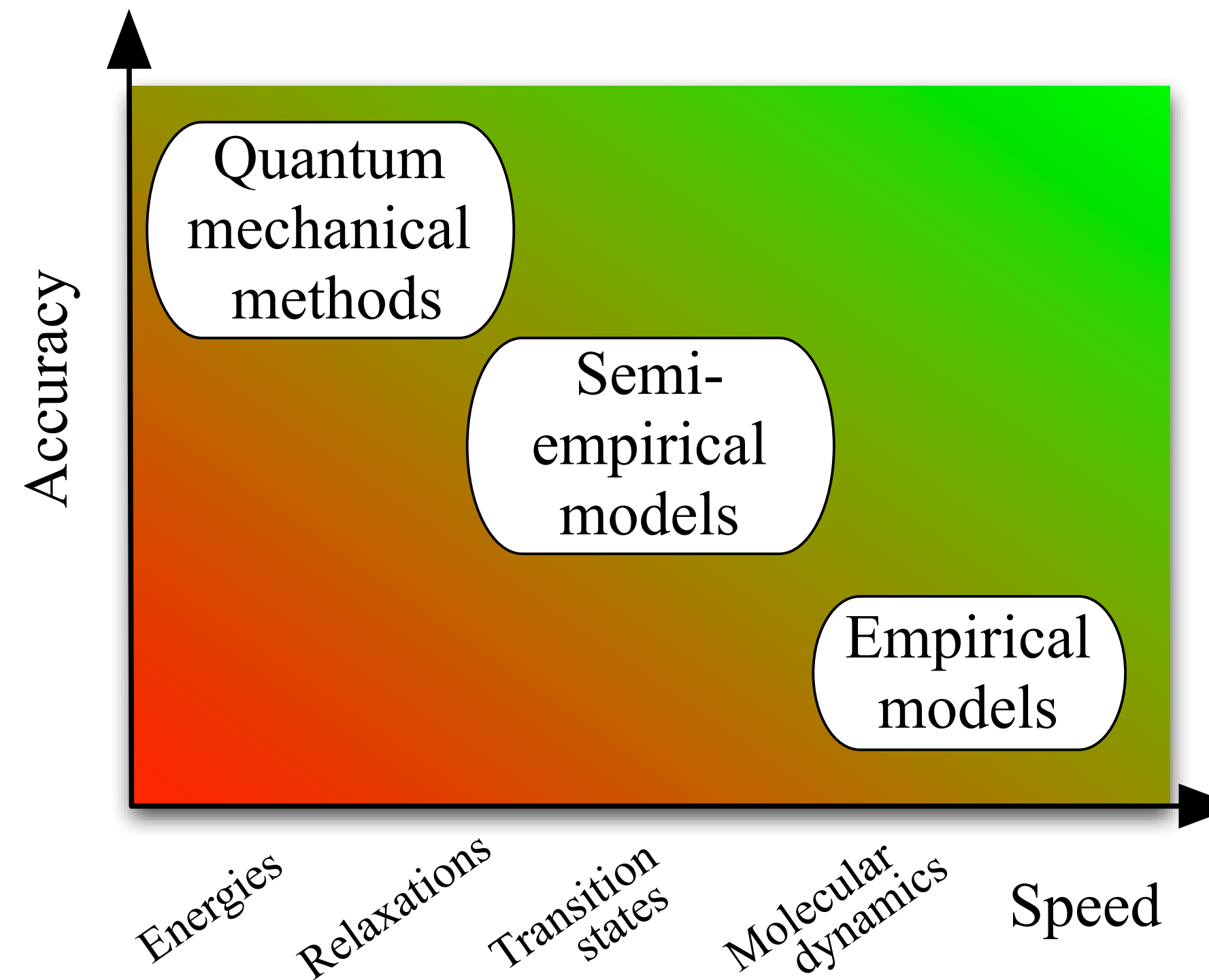


Atomic  
structure  $\{\mathbf{R}_i\}$

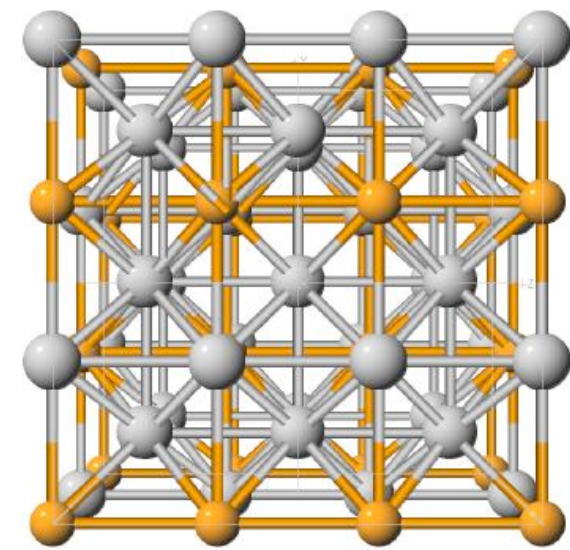
Energy model

Energy  $E(\{\mathbf{R}_i\})$

Hierarchy of energy models



# Born-Oppenheimer Approximation



Atomic structure  $\{\mathbf{R}_i\}$

Energy model

Energy  $E(\{\mathbf{R}_i\})$

- The electrons are much lighter than the nuclei ( $m_p/m_e \approx 1,800$ )
- Hence, for given nuclei position, the electrons are in their ground state  $\Psi_0$
- This approximation is known as the **Born-Oppenheimer approximation**
- However, for some materials and properties this approximation can fail
  - Hydrogen diffusion in materials by tunneling
  - Hydrogen phases at high temperature and pressure
  - He droplets
  - Superconductivity
  - Atomic gases at low temperatures  $\Rightarrow$  Bose-Einstein condensation
- Treat nuclei as classical particles and use the Born-Oppenheimer approximation

# Hierarchy of Energy Models

## Quantum mechanical methods

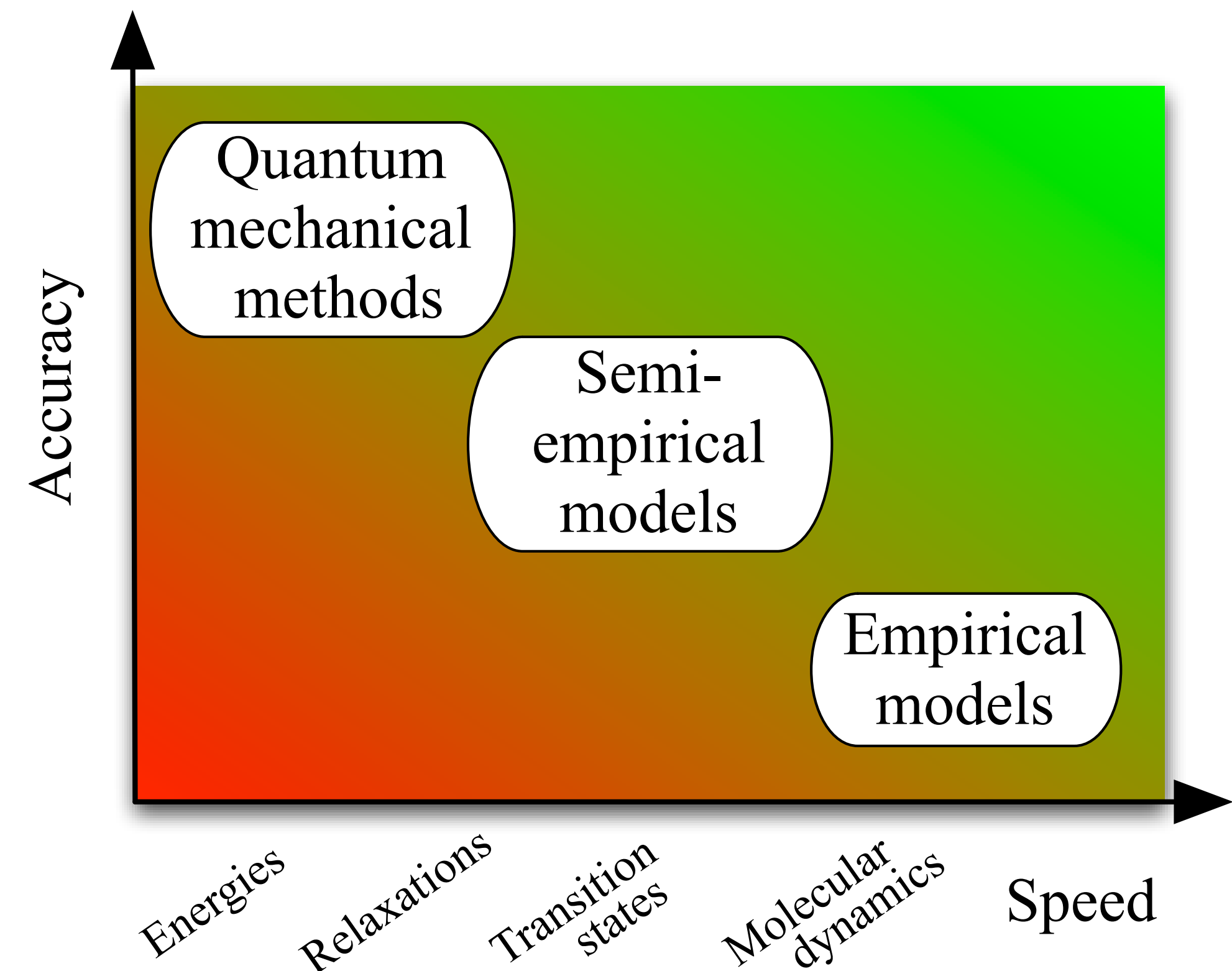
- Start from the many-body Schrödinger equation and make approximations
- Examples:
  - ▶ Quantum chemistry (Hartree-Fock, Coupled clusters, configuration interaction, ...)
  - ▶ Density-functional theory, GW approximation, random-phase approximation
  - ▶ Quantum Monte Carlo, dynamical mean-field theory, density matrix renormalization group

## Semi-empirical models

- Functional form motivated by quantum mechanics, neglecting difficult terms, fitted parameters
- Examples: Tight-binding, neglect of differential overlap

## Empirical models

- Functional forms with fitted parameters
- Examples: Pair potentials, many-body potentials, effective medium potentials





# Outline

---

## Choice of functional form of empirical potentials

- Motivated by types of chemical bonds relevant for specific material
- Increasing in complexity: pair potentials, pair functionals, many-body potentials, ...

## Optimization of empirical potential parameters

- Least-square optimization techniques using a fitting and testing database

## Validation strategies

- Obvious: Comparison with other available data
- Validation of energy landscapes using structure search methods

## Open questions

- How to select the optimal functional form of potential for a given material?
- How to choose an optimal data set for model parameter optimization?
- How to identify tradeoffs between conflicting model predictions?

# Common Features of Empirical Potentials

---

## Decomposition in atomic energies

- Energy is constructed as sum of local atomic energies

$$E = \sum_i \epsilon_i(\mathbf{R}_i)$$

- Locality of atomic interactions is known as near-sightedness in quantum chemistry

## General N-body expansion

$$E = \sum_i \Phi_1(\mathbf{R}_i) + \sum_i \sum_{j>i} \Phi_2(\mathbf{R}_i, \mathbf{R}_j) + \sum_i \sum_{j>i} \sum_{k>j} \Phi_3(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \cdots$$

# Pair Potentials

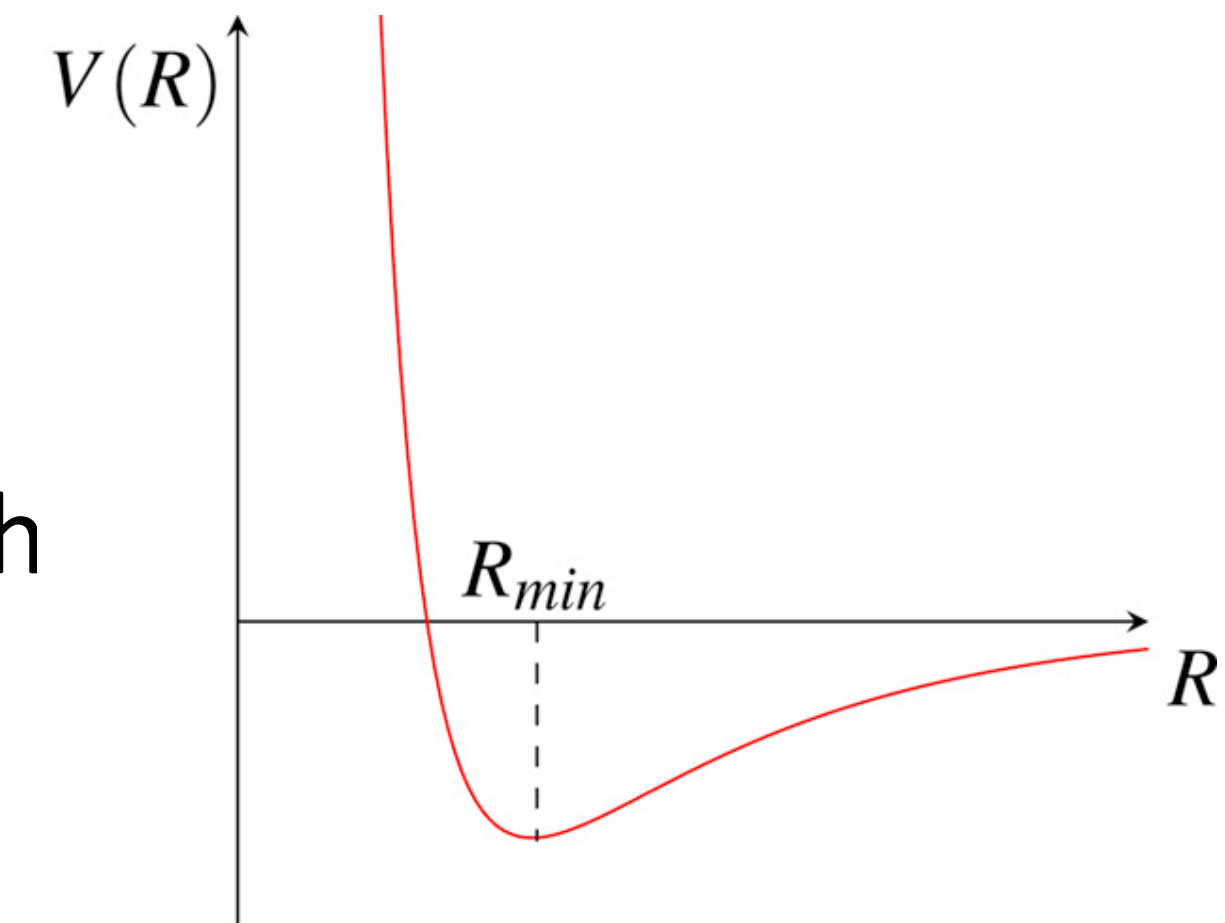
## Common features

- Approximation of only pairwise interaction
- Form of pair potential  $V(r)$ 
  - ▶ Repulsive at short distances, attractive at long distances
  - ▶ Usually applied with a cutoff
- Analytical forms of potentials are usually based on basic physics
- Physical relevance of parameters disappears when potentials are fitted
- Minimal set of parameters: energy scale and length scale

$$E = \frac{1}{2} \sum_{i,j} V(|\mathbf{r}_i - \mathbf{r}_j|)$$

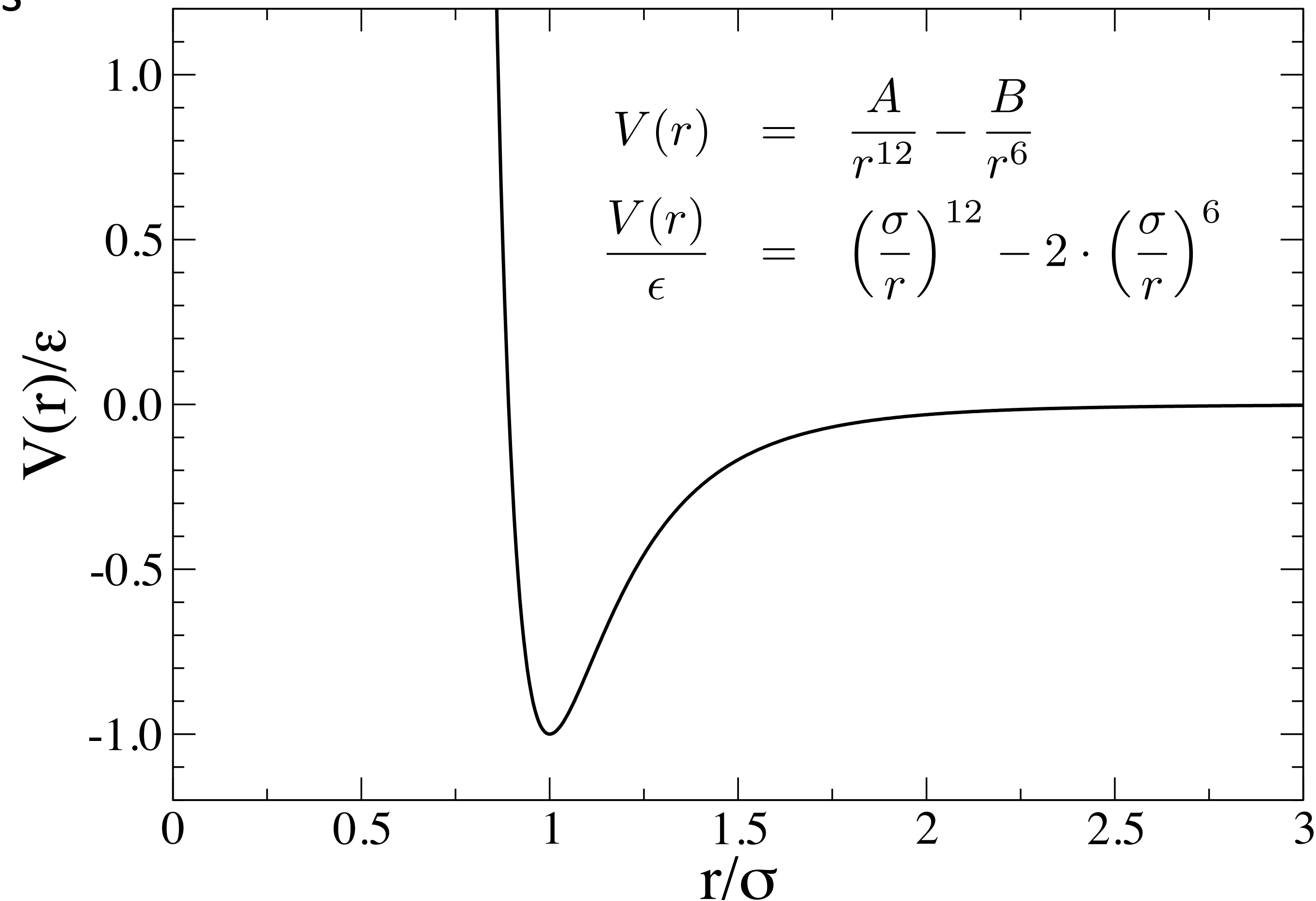
## Functional forms of potentials

- Many different functional forms have been developed and used
- Lennard-Jones, Buckingham, Morse, Coulomb, screened Coulomb, hard sph



# Lennard-Jones Potential

- Proposed in 1931 by John Lennard-Jones at Bristol University
- Attractive  $1/r^6$  term describes **van der Waals attraction**
- Repulsive  $1/r^{12}$  term chosen for **efficiency**



Sir John  
Lennard-Jones

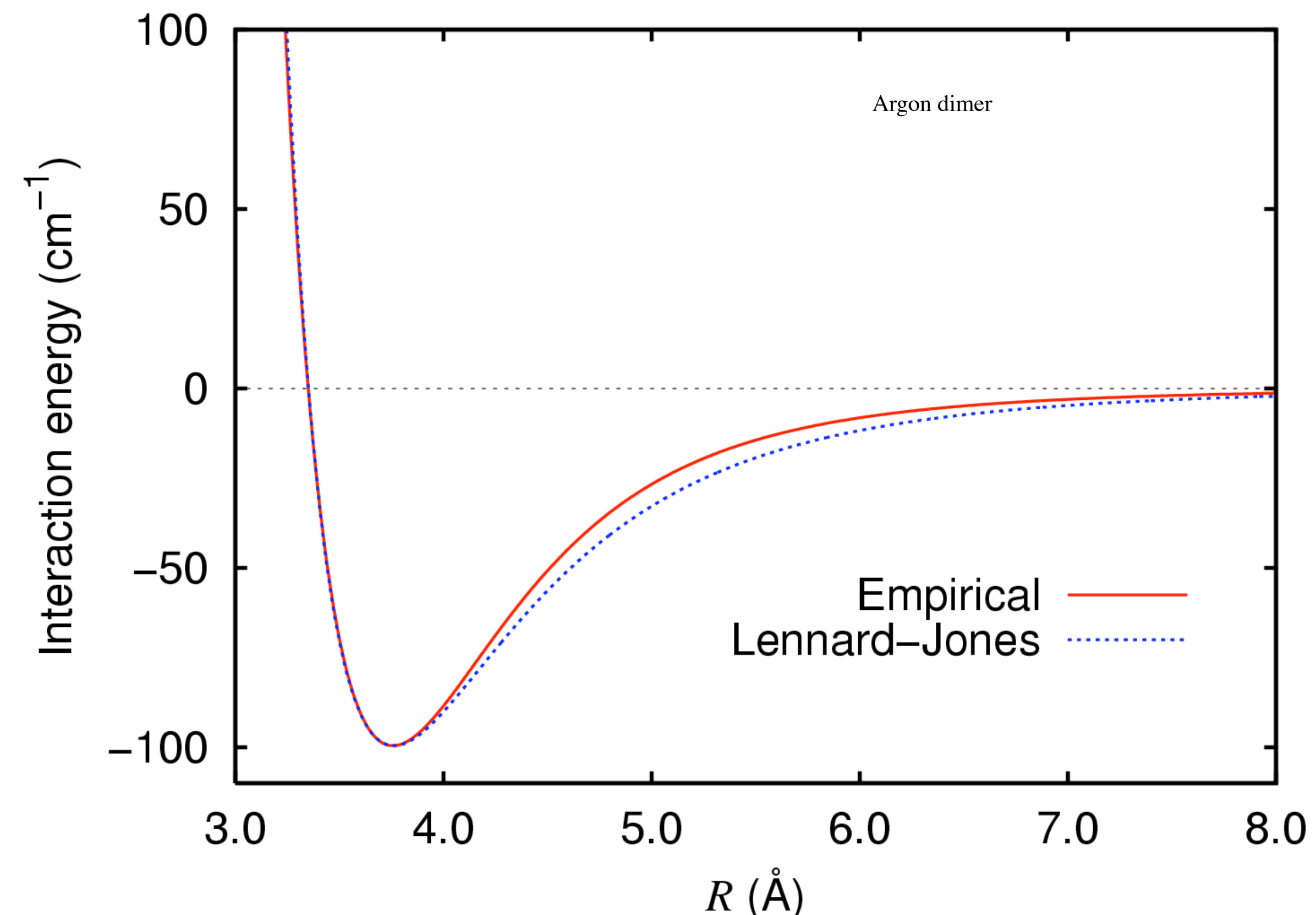
J. E. Lennard-Jones, *Cohesion*. Proc. Phys. Soc. 43, 461 (1931).

# Lennard-Jones Potential

- When expressing  $T$ ,  $p$ , and  $\rho$  in renormalized units all Lennard-Jones potentials are identical
  - ▶ Temperature  $\varepsilon/k_B$
  - ▶ Pressure  $\varepsilon/\sigma^3$
  - ▶ Density  $1/\sigma^3$
- If we set lattice parameter  $r_0 = \sigma$  and cohesive energy  $E_{\text{coh}} = \varepsilon$ , then all other properties such as elastic coefficients, melting point *etc.* are determined

⇒ There is only one Lennard-Jones material

The Lennard-Jones potential is really only applicable to **noble gases** (no bonding, only van der Waals attraction)





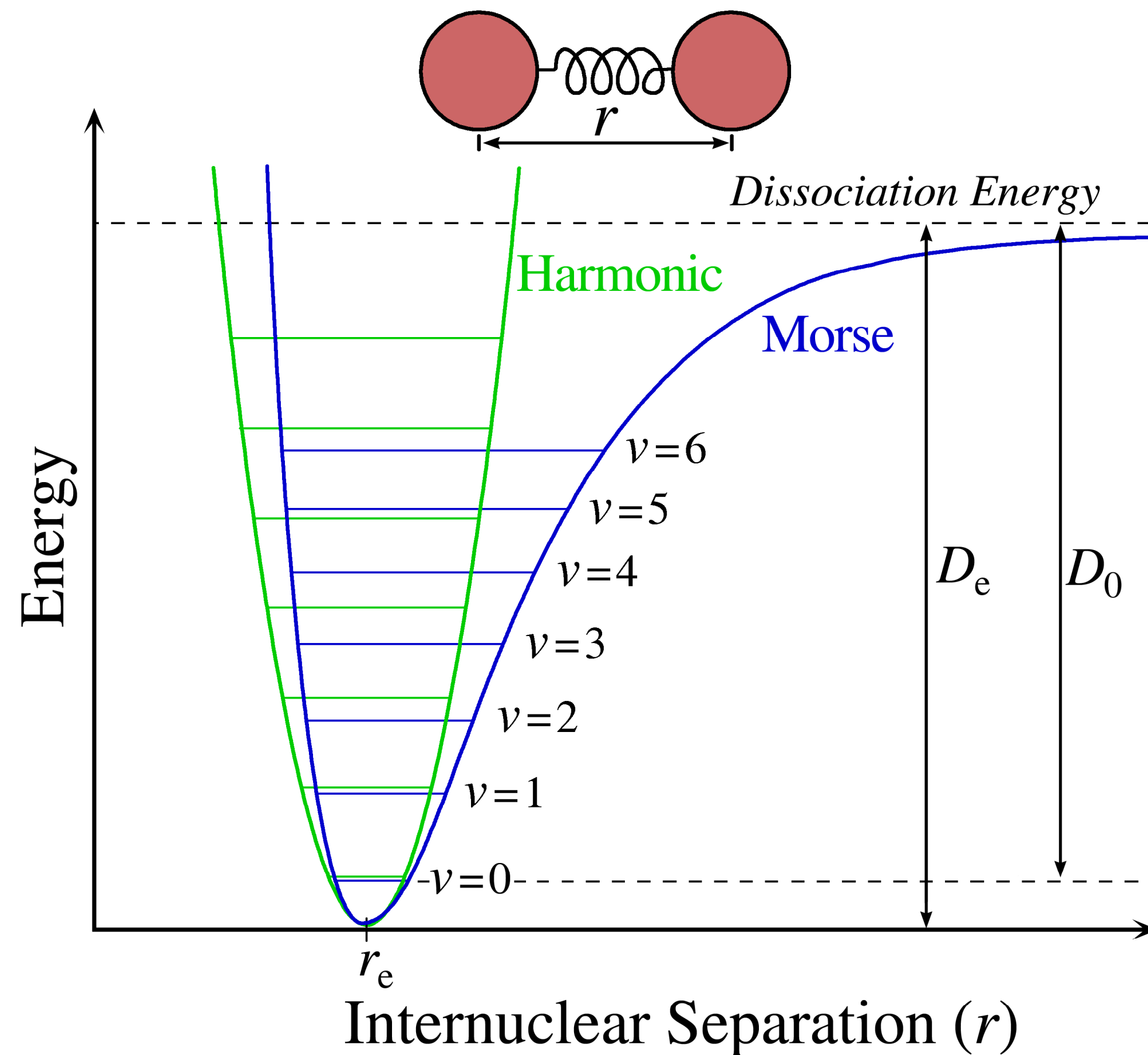
# Born-Mayer/Buckingham Potential

---

- Sometimes, the repulsive  $1/r^{12}$  term of the Lennard-Jones potential is too steep
- The Buckingham potential employs a softer repulsive potential

$$V(r) = A \cdot \exp(-B \cdot r) - \frac{C}{r^6}$$

# Morse Potential for Diatomic Molecules



Proposed by Morse in 1929 for the potential energy of a diatomic molecule

$$V(r) = D_e \left( 1 - e^{-\alpha(r-r_e)} \right)^2$$

# Bond Stretching in Methane

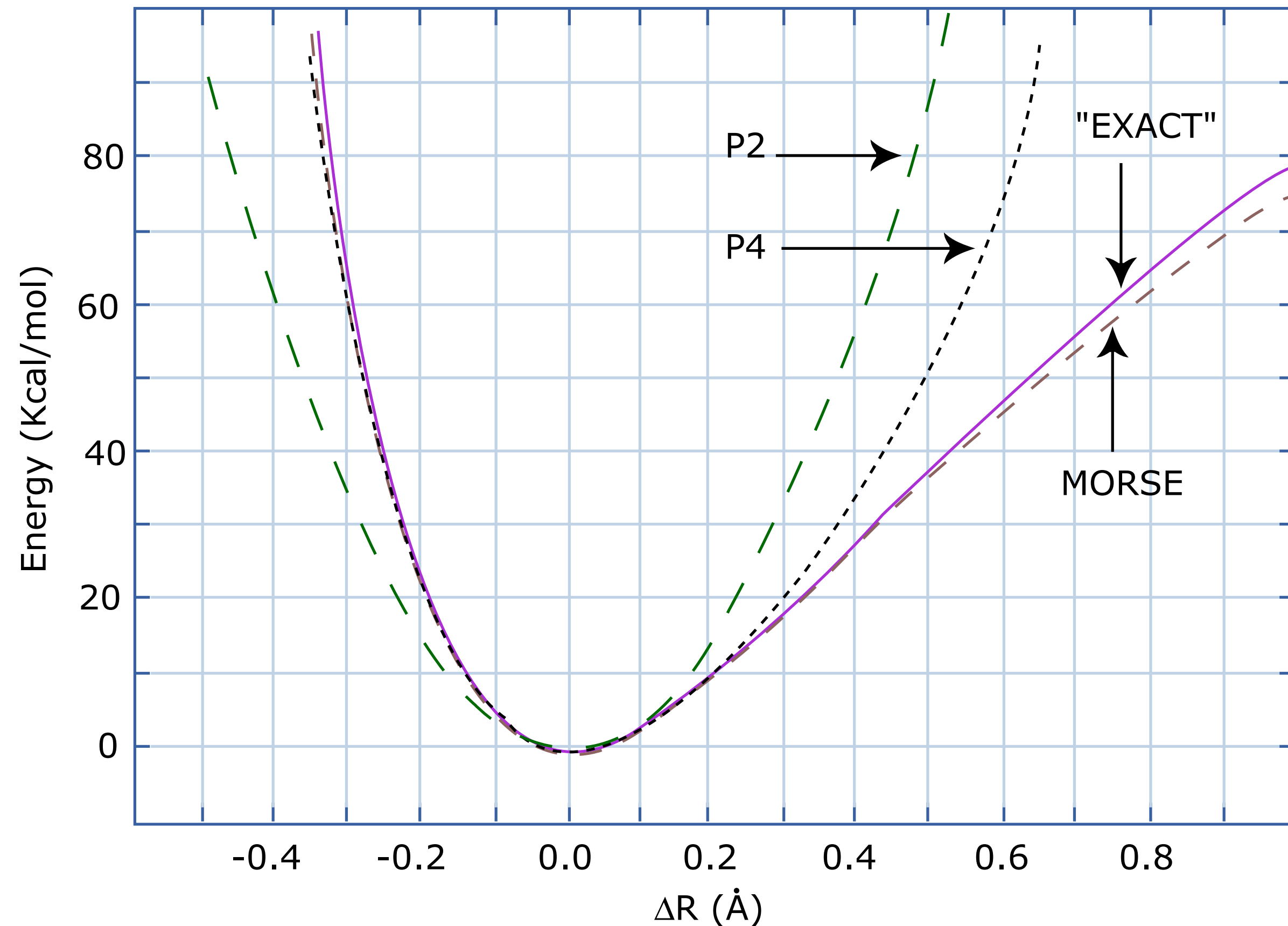
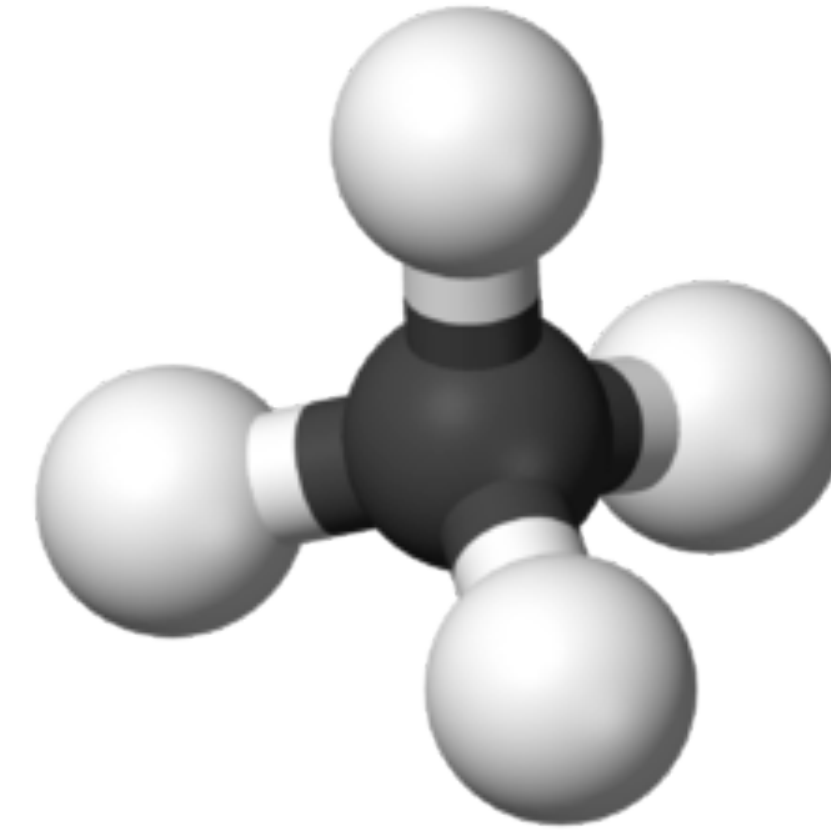


Figure by MIT OCW.

Morse potential highly accurate compared to harmonic (P2) and quartic (P4) potential.



$$V(r) = D_e \left( 1 - e^{-\alpha(r-r_e)} \right)^2$$

How far from equilibrium do we need the potential to be accurate?

- 1 kcal/mol corresponds to 43 meV or 503 K
- Potential needs to be accurate only close to the minimum

# Potentials for Charged Systems

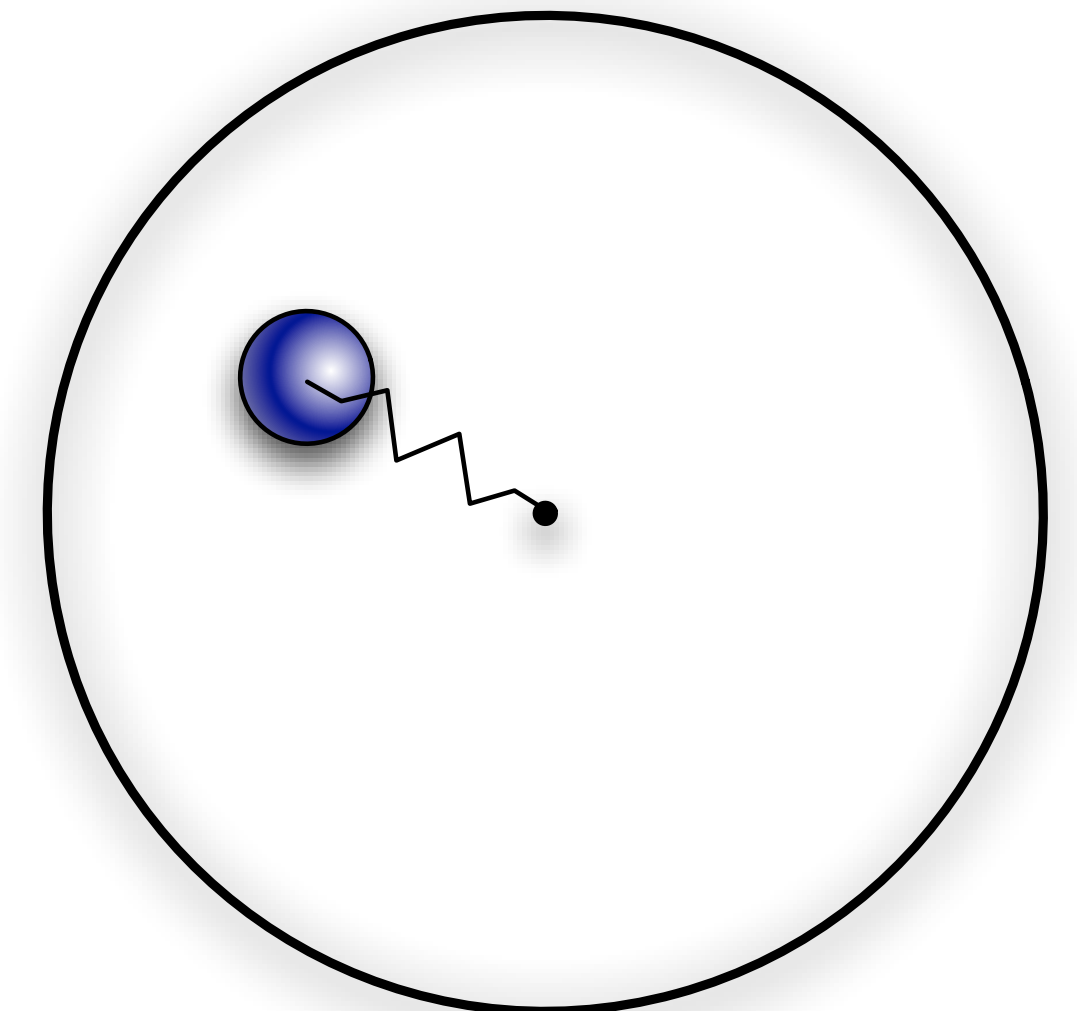
## Start with pair potentials with Coulomb interactions

- Buckingham plus electrostatic Coulomb term

$$V(r) = \underbrace{A \cdot \exp\left(-\frac{r}{B}\right) - \frac{C}{r^6}}_{\text{Buckingham}} + \underbrace{\frac{q_1 \cdot q_2}{r}}_{\text{Coulomb}}$$

## Include polarization of ions

- Electric field from other ions induces a dipole moment
- **Shell model**
  - ▶ Describe the ion core and the electron shell separately as two particles connected by a spring
  - ▶ Spring constant between core and shell corresponds to polarizability

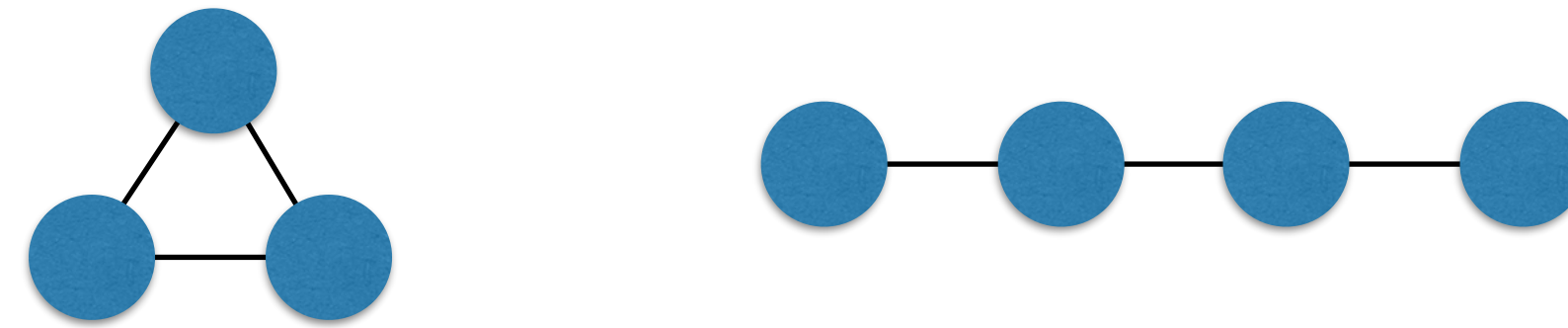




# Limitations of Pair Potentials

---

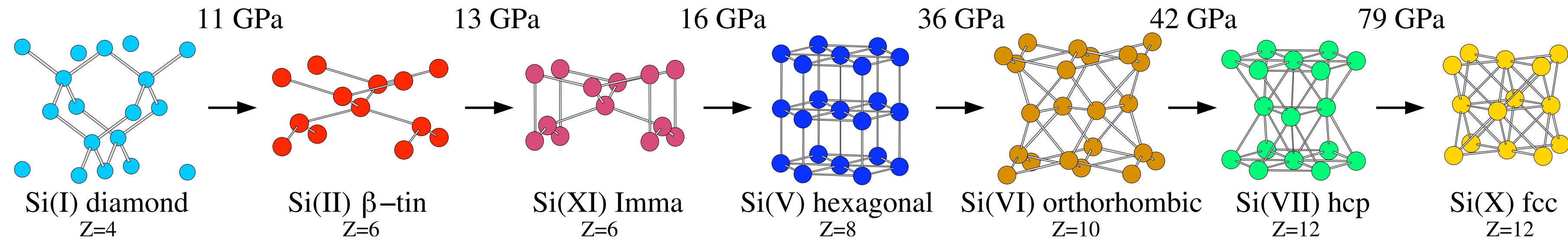
- Pair Potentials “count” bonds but do not take into account their organization  
⇒ Similar energy for a triangle of three atoms versus chain of four



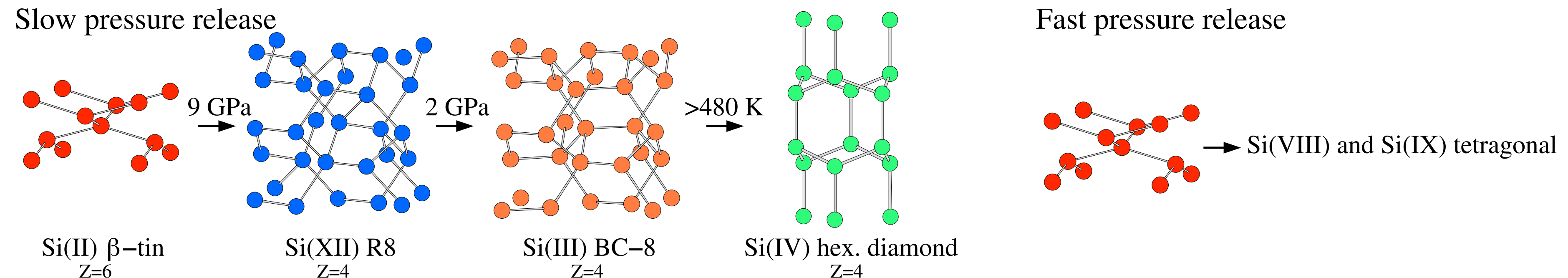
- Tendency to form close-packed structures such as bcc and hcp
  - Difficult to stabilize diamond-cubic structure of Si with pair potential
  - Silicon undergoes a series of structural phase transitions (from tetrahedral to  $\beta$ -tin to simple hexagonal to fcc) under pressure
  - Small energy differences between these structures
  - Cohesive energy nearly independent of coordination number

# Silicon Phases

## Compression



## Decompression



Under pressure silicon displays 12 crystal phases with a steady increase of coordination and a transition from insulating to metallic.

# Limitations of Pair Potentials

The assumption of a pair potential determines a variety of properties

<i>Crystal</i>	$E_{\text{coh}}/k_{\text{B}}T_{\text{m}}$	$E_{\text{vac}}/E_{\text{coh}}$	$C_{12}/C_{44}$
<i>Pair potential</i> Lennard-Jones	<b>13</b>	<b>~1</b>	<b>1</b>
<i>Noble gases</i>			
Ar	11	0.95	1.1
Kr	12	0.66	1
<i>fcc metals</i>			
Ni	30	0.31	1.2
Cu	30	0.37	1.6
Pd	25	0.36	2.5
Ag	27	0.39	2
Pt	33	0.26	3.3
Au	34	0.23	3.7

Ratio between  $E_{\text{coh}}$  and  $k_{\text{B}}T_{\text{m}}$  is about 30 in metals and 10 for pair potentials and noble gases

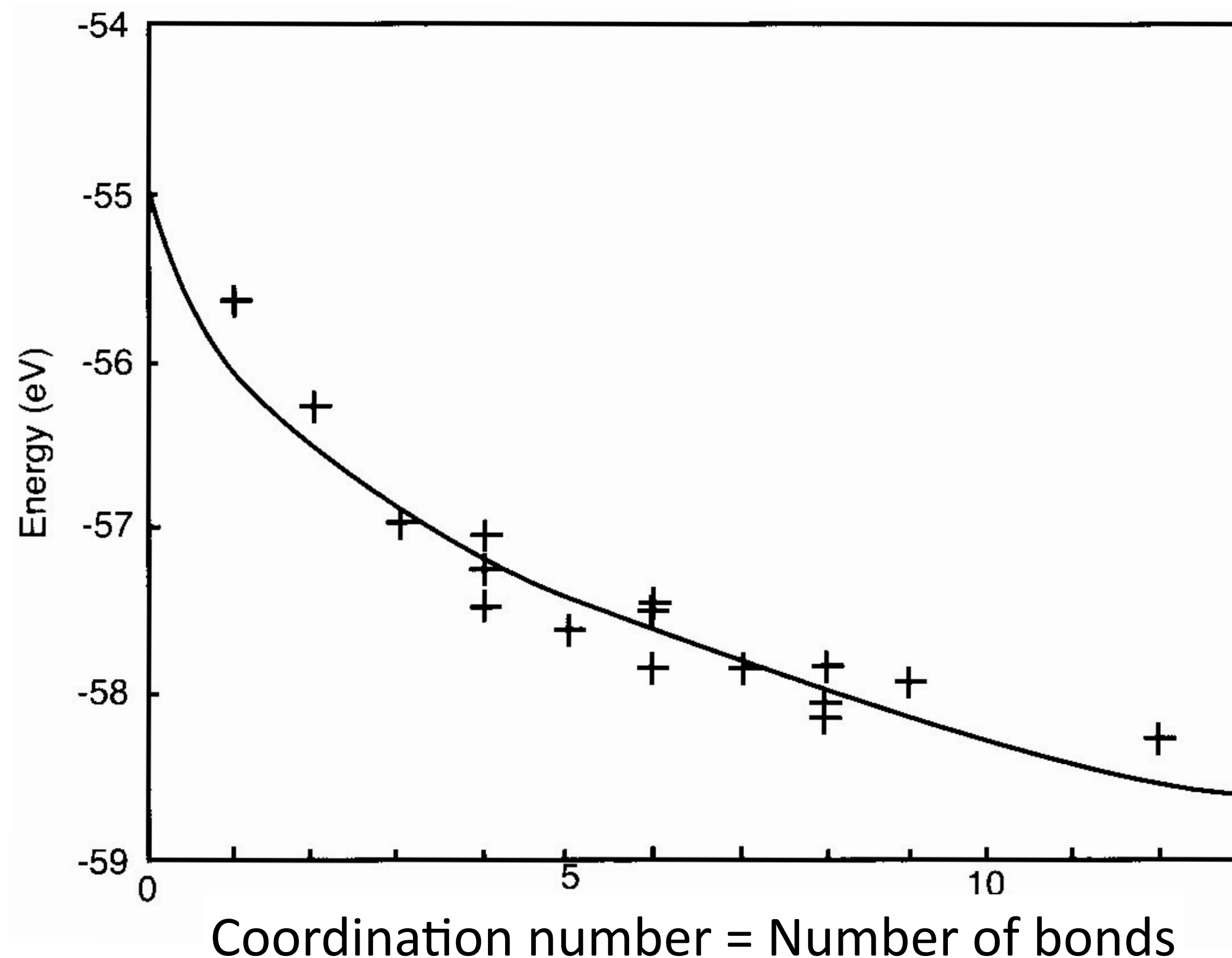
Ratio between the  $E_{\text{vac}}$  and the  $E_{\text{coh}}$  is between 1/4 and 1/3 in metals and about 1 in two-body systems (exactly 1 if relaxations are neglected)

Cauchy ratio  $C_{12}/C_{44} = 1$  for pair potentials. Deviations in metals are common.

# Environment Dependence of the Binding Energy

## Example: Cohesion in Al

- Energy per atom for a variety of Al structures
- The curve is fit to a function  $E = E_0 + \alpha Z^{1/2} + \beta Z$



## Lack of environment dependence in pair potentials

- One bond does not know about the others
- This is in contradiction with both experiments and accurate quantum mechanical calculations
  - ▶ For pair potentials:  $E \propto Z$
  - ▶ For metals:  $E \propto \sqrt{Z}$

**Bonding gets weaker as more atoms surround the central atom**



# Cohesive Energy and Vacancy Formation in Al

Remove a single atom and place it in bulk position somewhere else

## For pair potential $E \propto Z$

- Cohesive energy per atom:  
Each Al atom has 12 bonds and each bond is shared between two atoms

$$E_{\text{coh}} = \frac{12 \cdot E_{\text{bond}}}{2} = 6 \cdot E_{\text{bond}}$$

- Pair potentials – 12 bonds are broken and removed atom is placed in bulk

$$\begin{aligned}\Delta E_{\text{vac}} &= \underbrace{12 \cdot E_{\text{bond}}}_{\text{broken bonds}} - \underbrace{6 \cdot E_{\text{bond}}}_{\text{bulk}} \\ &= 6 \cdot E_{\text{bond}} = E_{\text{coh}}\end{aligned}$$

## For metals $E \propto \sqrt{Z}$

- Each of the neighboring atoms changes configuration number from 12 to 11
- Removed atoms is again placed in bulk

$$\Delta E_{\text{vac}} = 12 \cdot \left( c \cdot \sqrt{12} - c \cdot \sqrt{11} \right)$$

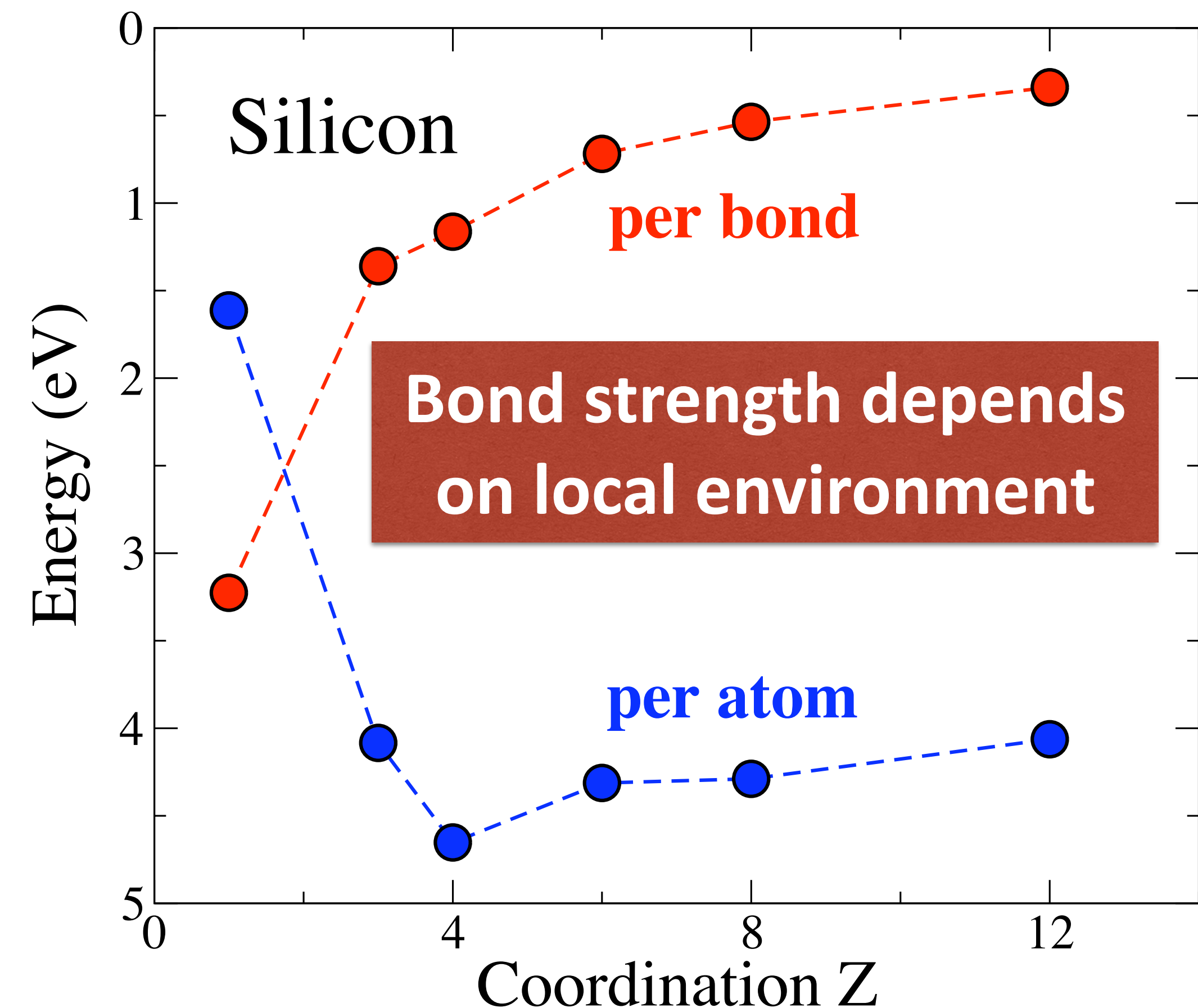
$$\frac{\Delta E_{\text{vac}}}{E_{\text{coh}}} = 12 \cdot \left( 1 - \frac{\sqrt{11}}{\sqrt{12}} \right) \approx 0.5$$

- Vacancy energy in metals lower than predicted by pair potentials

# Environment Dependence of the Binding Energy

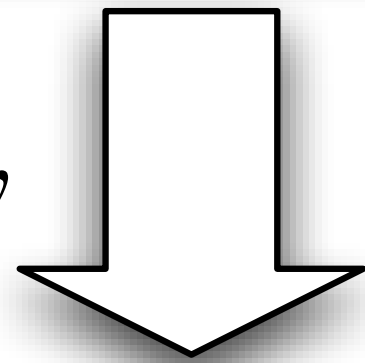
## Example: Cohesion in Si

- Cohesive energy has a maximum for 4-fold coordinated diamond structure
- Energy of each bond decreases with increased coordination number
- Bond strength depends on local environment
  - ▶ Either through **angular dependence** with other bonds
  - ▶ Or through dependence on number of other bonds, *e.g.* **bond-order**
- This limits the transferability of pair potentials
- Fitted for one particular coordination environment they can not be used without significant error for other coordination (*e.g.* fit to bulk but use on surface)
- Fitting to all environments simultaneously only “averages” the error
- Pair potentials cannot predict crystal structures in metals or covalent solids
- For example, the fcc-bcc energy difference requires four-body interactions



# How to Overcome Deficiencies of Pair Potentials

Pair  
potentials



*Non-linearity*

Pair  
functionals

- Include effect of other atoms on bond
- Energy as a non-linear function of coordination
- **Pair functionals** include effective medium potentials
- Include three-body terms (angular dependent forces) and four-body terms
- **Cluster potentials** include many-body terms
- **Cluster functionals** combine both

$$E = \sum_i \Phi_1(\mathbf{R}_i) + \sum_i \sum_{j>i} \Phi_2(\mathbf{R}_i, \mathbf{R}_j) + \sum_i \sum_{j>i} \sum_{k>j} \Phi_3(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \cdots$$

# Embedded Atom Potentials (EAM)

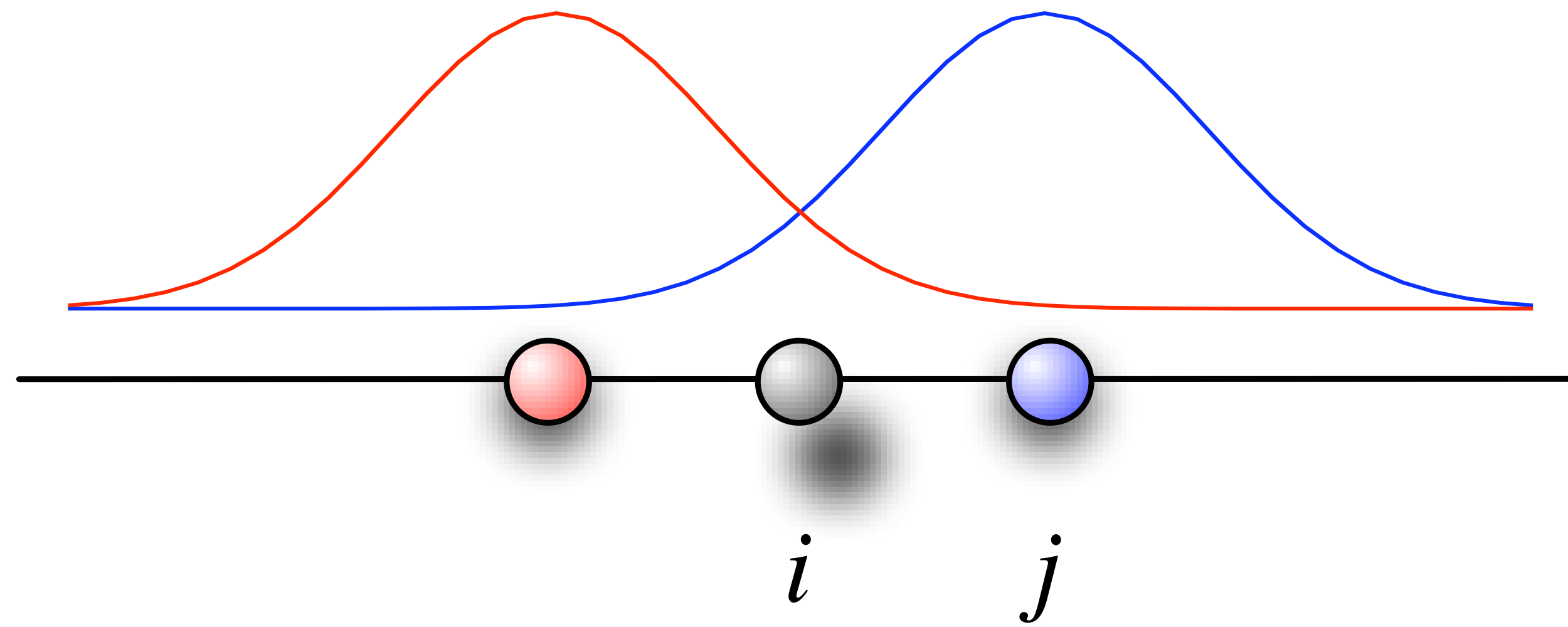
## Idea:

- Energy of an atom depends non-linearly on the surrounding atoms (number and distance)
- $E = f(\text{number of bonds})$  where  $f$  is a non-linear function  $\Rightarrow$  **Energy functionals**
- Use **electron density** as a measure of the surrounding atoms

$$E_{\text{coh}} = \underbrace{\sum_i F_i(\rho_i)}_{\text{Embedding energy}} + \underbrace{\frac{1}{2} \sum_i \sum_{j \neq i} V(R_{ij})}_{\text{Pair potential}}$$

- Use either analytic or tabulated embedding function
- Tabulated form computationally efficient, use of cubic splines
- Often the **embedding function** is fit to the equation of state (Energy versus volume)

$$\rho_i = \sum_{i \neq j} f(R_{ij})$$





# Embedded Atom Potentials (EAM)

---

## Physics Concept

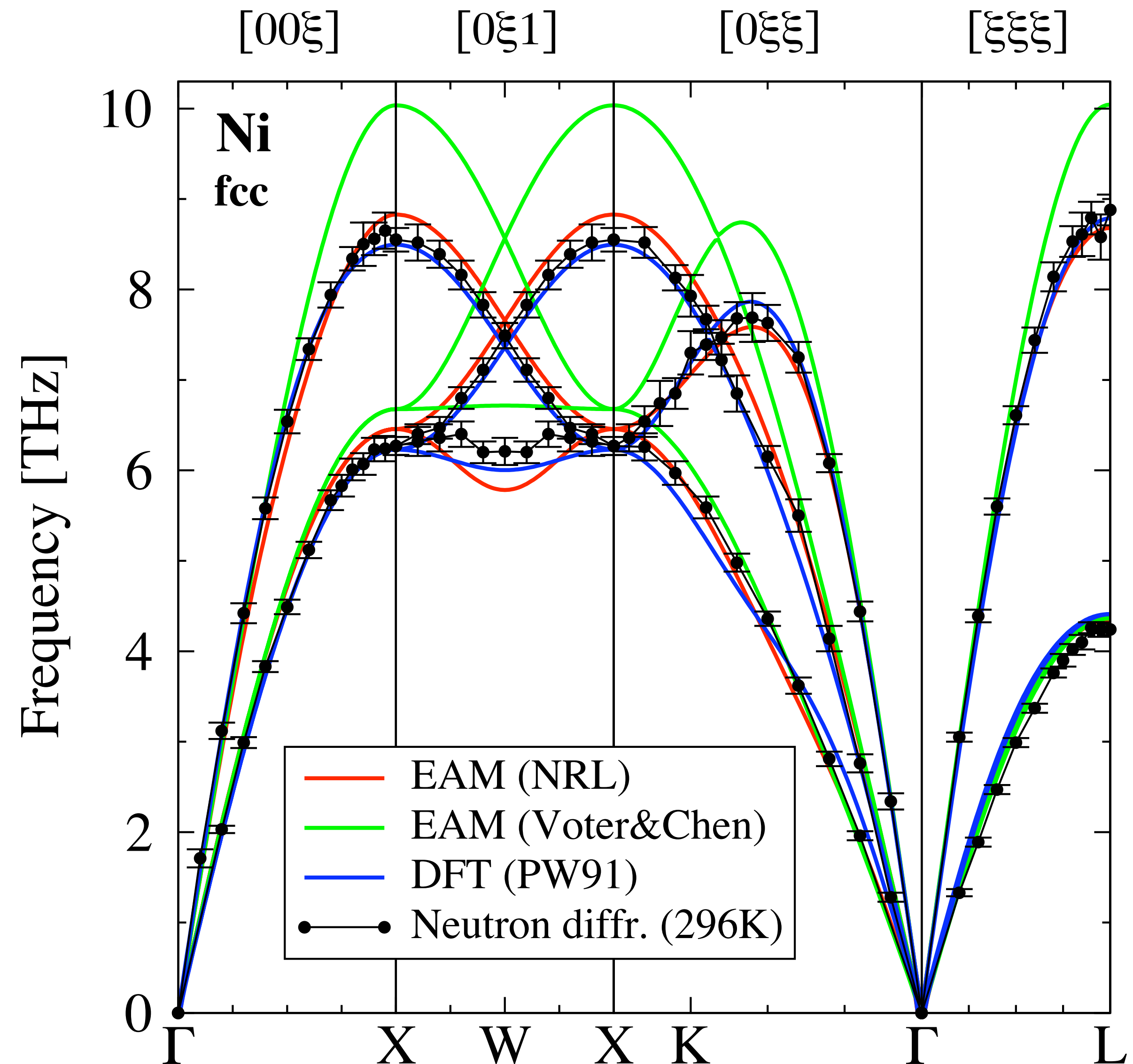
- Bonding energy (embedding energy) due to electron delocalization
- As electrons spread out more, their kinetic energy decreases
- When an impurity is put into a metal its energy is lowered because its electrons can delocalize into the solid
- The embedding density (electron density at the embedding site) is a measure of the number of states available to delocalize onto  
⇒ **Many body effect**

## Other effective medium theories

- EAM is similar to many other effective medium theories
- Other theories differ in the “non-linearity” used or the measure of “embedding density”
- Glue model (Ercollesi, Tosatti and Parrinello)
- Finnis-Sinclair Potentials
- Equivalent Crystal Models (Smith and Banerjee)

# Accuracy of EAM Potentials for Phonons

- Phonon dispersion for fcc Ni
- Importance of checking the accuracy of empirical potential models
- The NRL potential is very accurate while the Voter&Chen potential overestimates the frequencies

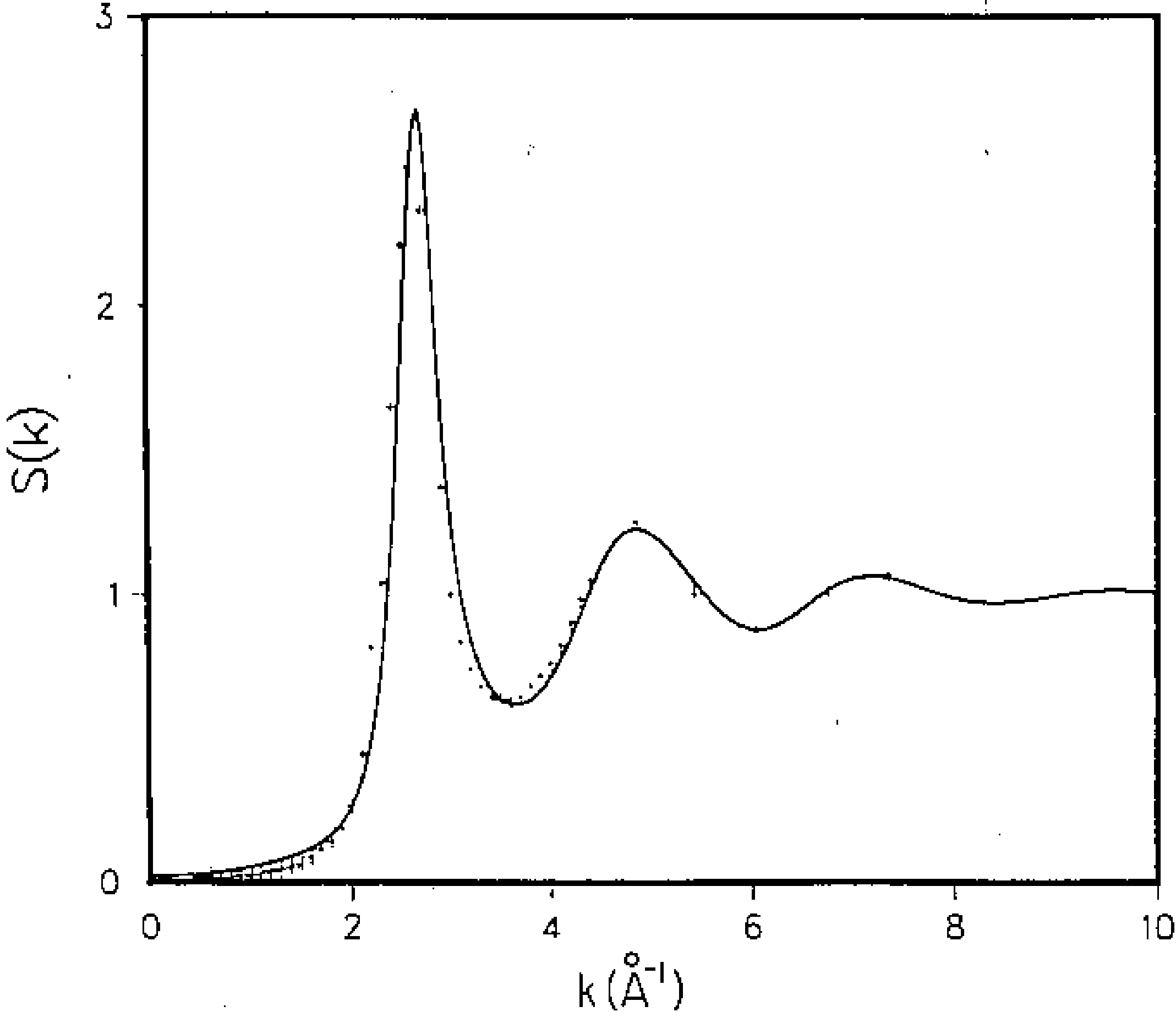


# Accuracy of EAM Potentials for Liquids

## Melting points

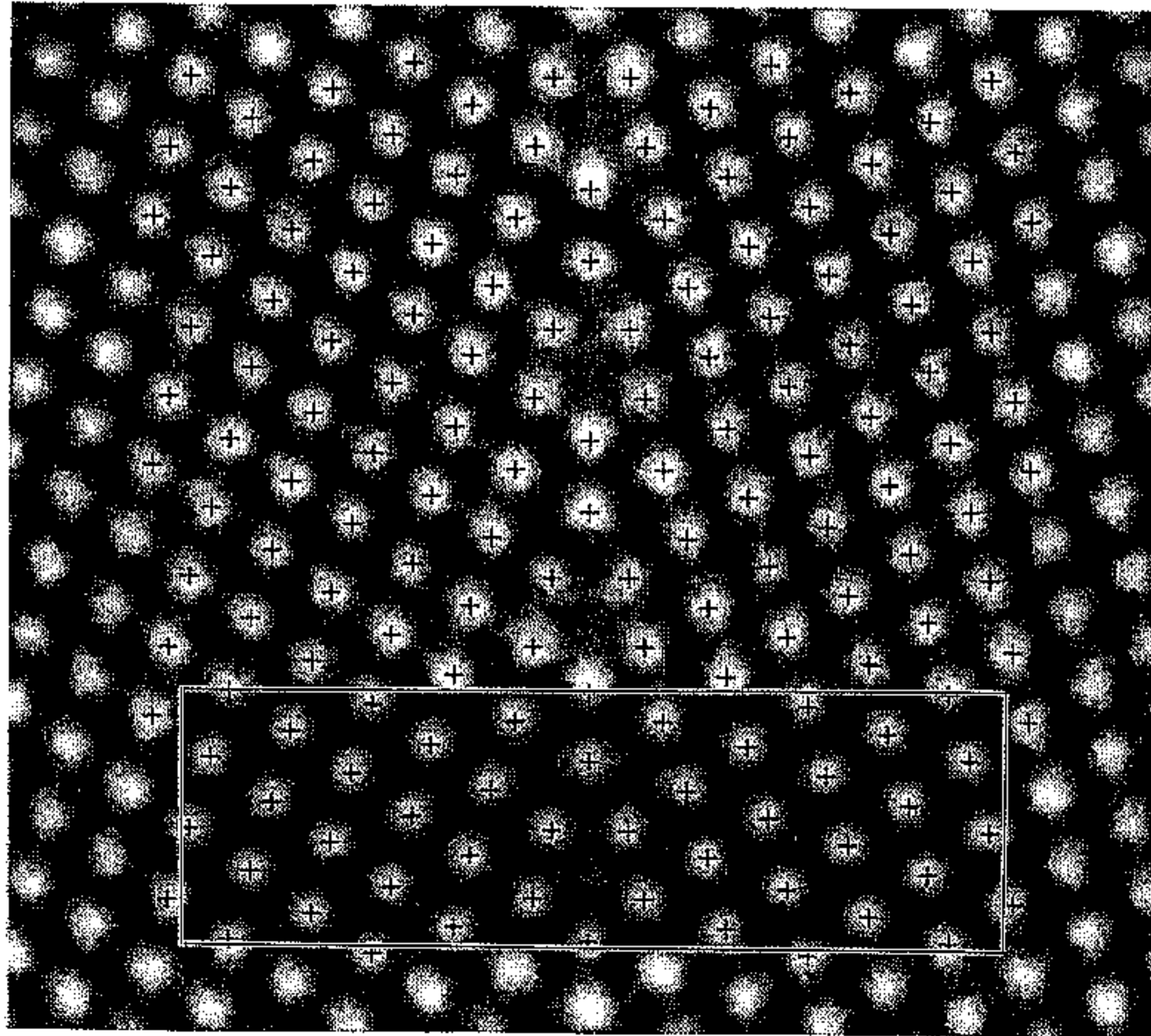
Element	EAM	Experiment
Cu	1340	1358
Ag	1170	1234
Au	1090	1338
Ni	1740	1726
Pd	1390	1825
Pt	1480	2045

Structure of liquid Ag at 1270 K. The solid line is from EAM simulations and the dots are experimental results.





# Accuracy of EAM Potentials for Grain Boundaries

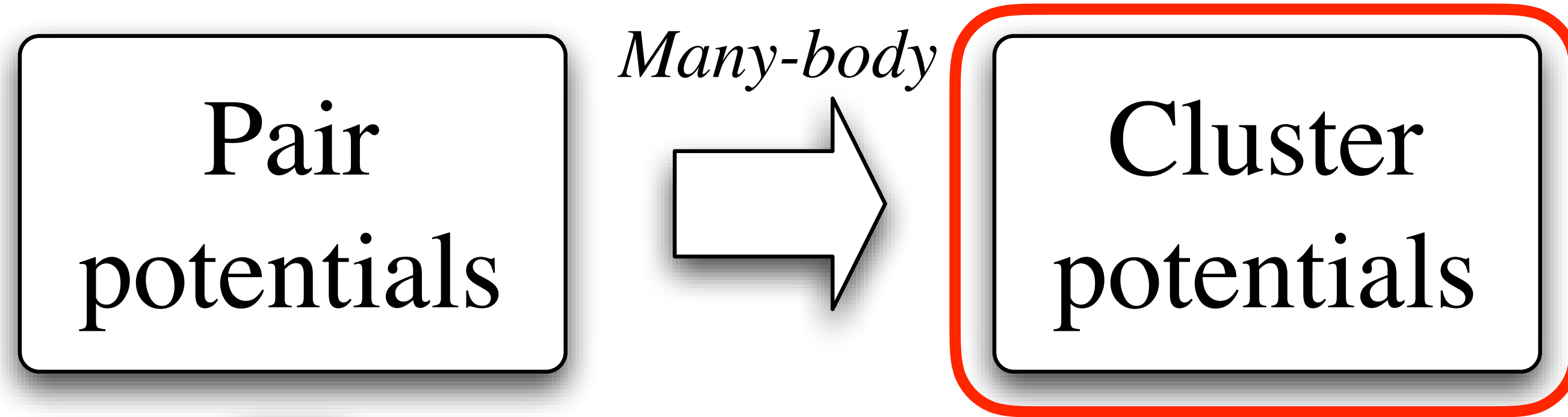


## Grain boundary in Al

- Comparison of theory and experiment for a grain boundary in Al.
- The high-resolution TEM image of tilt boundary is overlaid with an inset of the simulated structure predicted by an EAM potential



# Many-Body Potentials



- Expansion of energy in terms of clusters of atoms
- Two, three, and four-body and higher order terms

$$E = \frac{1}{2!} \sum_{i,j=1}^N V_2(\mathbf{R}_i, \mathbf{R}_j) + \frac{1}{3!} \sum_{i,j,k=1}^N V_3(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \dots$$

# Interactions in Many-Body Potentials

## Types of interactions of interactions considered

- Four common components of energy models describe
  1. Bond stretching
  2. Bond bending
  3. Bond rotation
  4. Electrostatic and non-bonding interactions

$$V(\{\vec{R}_i\}) = \underbrace{\sum_{\text{bonds}} \frac{k_i}{2} (l_i - l_{i,0})^2}_{\text{bond stretching}} + \underbrace{\sum_{\text{angles}} \frac{\kappa_i}{2} (\Theta_i - \Theta_{i,0})^2}_{\text{bond bending}} + \underbrace{\sum_{\text{torsion}} \frac{\chi_i}{2} [1 + \cos(n \cdot \omega - \gamma)]}_{\text{bond rotation}} + \underbrace{\sum_{i,j} \left( \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}^2} \right)}_{\text{electrostatics and dispersion}}$$

# Example: 3-Body Potential for Silicon

- Coordinates  $\mathbf{R}_i$ ,  $\mathbf{R}_j$  and  $\mathbf{R}_k$  can be replaced by  $\mathbf{R}_i - \mathbf{R}_j$ ,  $\mathbf{R}_k - \mathbf{R}_j$  and  $\theta_{ijk}$
- Tetrahedral coordination:
  - ▶ Bond angle of  $\theta_0 = 109.5^\circ$  and bond distance of 2.35Å

$$V(\{\vec{R}_i\}) = \underbrace{\sum_{\text{bonds}} \frac{k_i}{2} (l_i - l_{i,0})^2}_{\text{bond stretching}} + \underbrace{\sum_{\text{angles}} \frac{\kappa_i}{2} (\Theta_i - \Theta_{i,0})^2}_{\text{bond bending}}$$

- Possible choices are  $K(\theta - \theta_0)^2$  or  $K(\cos \theta_{ijk} + 1/3)^2$
- Stillinger-Weber potential

$$E = \frac{1}{2} \sum_{i,j=1}^N V(R_{ij}) + \sum_{i,j,k=1}^N g(R_{ij}) g(R_{kj}) \left( \cos \theta_{ijk} + \frac{1}{3} \right)^2$$

- Reproduces Si properties such as 2×1 reconstruction of Si(100) but not 7×7 reconstruction

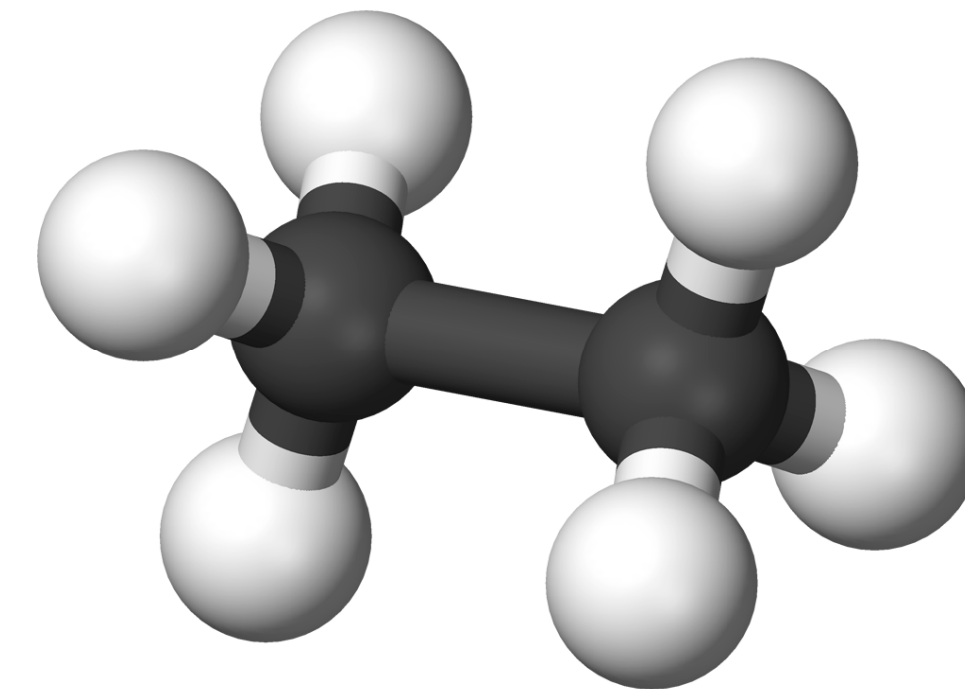
# Potentials for Organic Molecules

## Distinguish between *bonded* and *non-bonded* interactions

### (1) Ethane $\text{H}_3\text{C}-\text{CH}_3$

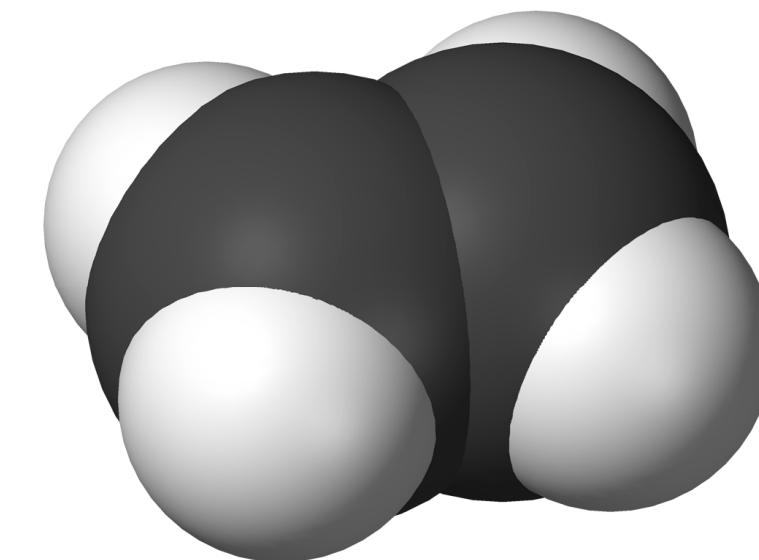
- Torsion of C—C bond
- Staggered versus eclipsed configuration has different energy
- Requires four-body potential

$$V_{\text{torsion}} = K \cdot \cos(3\theta)$$



### (2) Ethene $\text{H}_2\text{C}=\text{CH}_2$

- Double bond between C=C has different strength than single bond C—C in ethane
- Requires cluster functional or different potentials for  $\text{sp}$ ,  $\text{sp}^2$ , and  $\text{sp}^3$  carbon



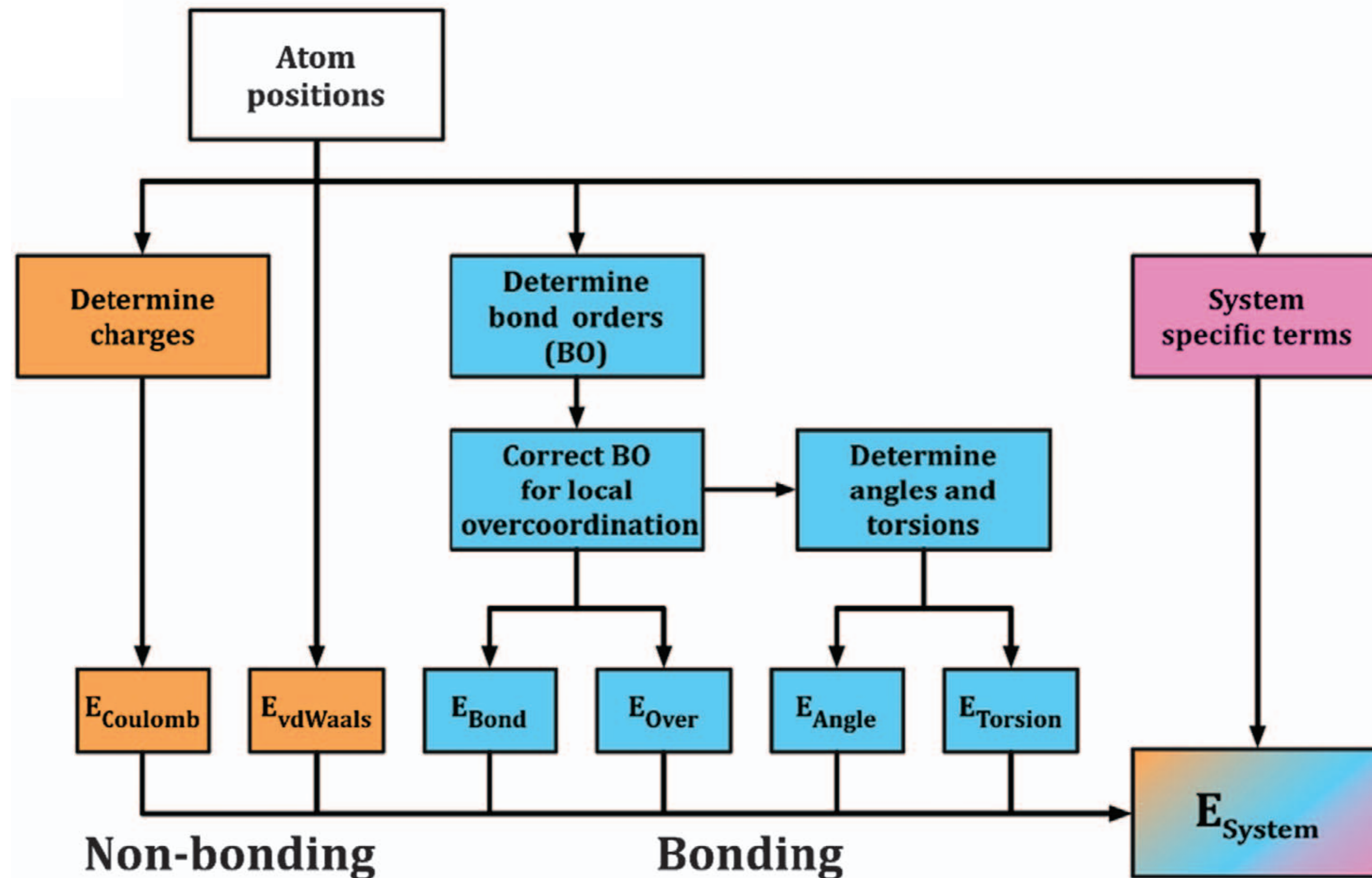
- Changes in coordination are done by changing the potential
- Examples: AMBER, CHARMM, MM3



# Reactive Force Field Potentials (COMB and ReaxFF)

- Sum of many-body and Coulomb terms
- Can handle bond breaking and formation

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{angle}} + E_{\text{tors}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} + E_{\text{Specific}}.$$

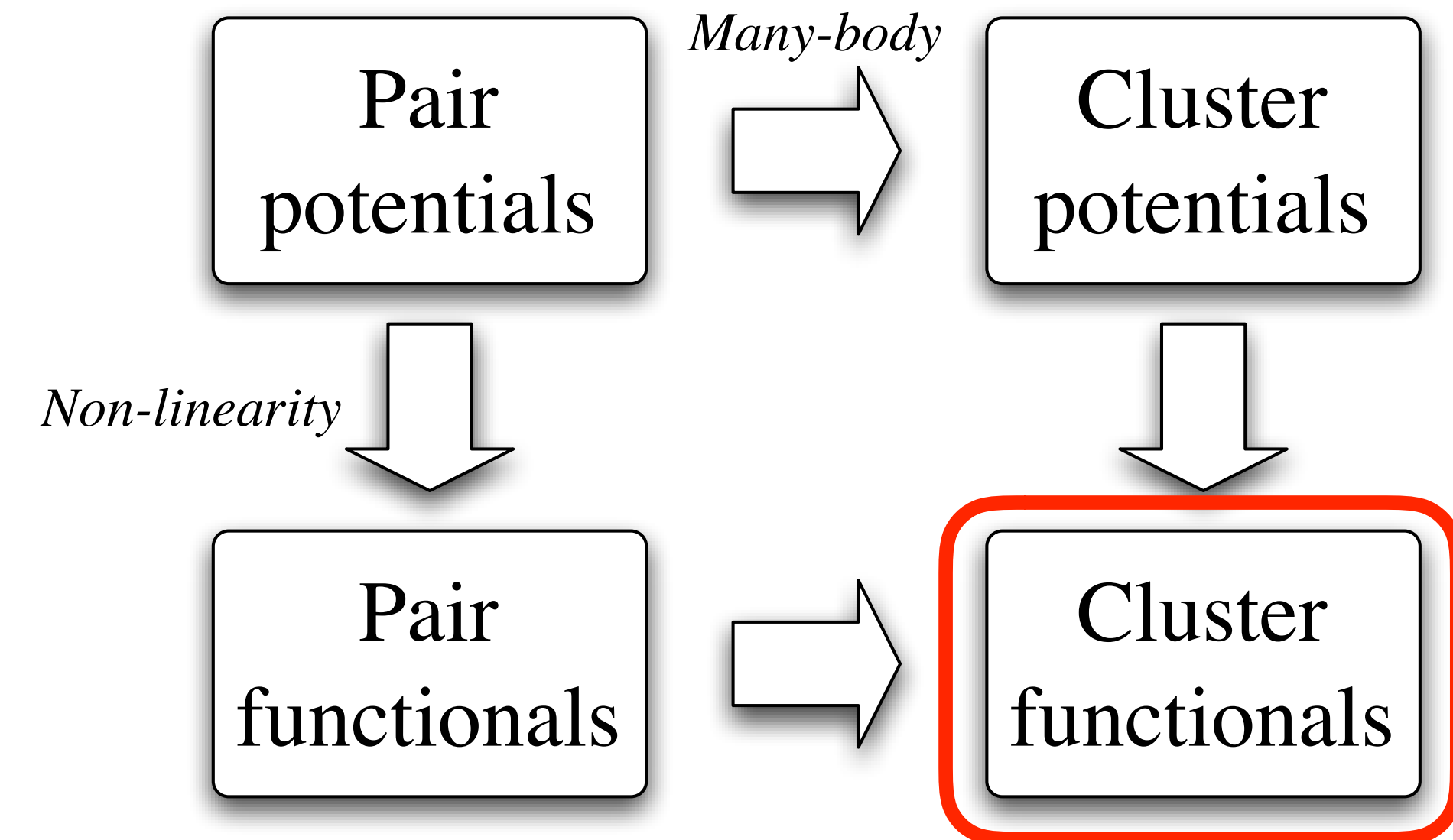


# Modified-Embedded Atom Potentials

- Similar form to EAM with modified density function

$$E_{\text{coh}} = \underbrace{\sum_i F_i(\rho_i)}_{\text{Embedding energy}} + \underbrace{\frac{1}{2} \sum_i \sum_{j \neq i} V(R_{ij})}_{\text{Pair potential}}$$

$$\rho_i = \sum_{j,k} f(R_{ij}) \cdot f(R_{ik}) \cdot g(\cos \theta_{ijk})$$



- Angular force terms particularly important for early transition metal elements and covalent bonded systems
- Applications of EAM to Si, Ti and refractory metals

# Recent Advances in Empirical Energy Models

## Gaussian Approximation Potentials developed by Bartók and Csányi

- Create database of various atomic configurations
- Decompose the energy of these configurations into sum of atomic energies
- For new configuration, determine the energy of each atom by using a function  $\epsilon(\mathbf{q}_i)$  of local atomic neighborhood structure, structure represented by  $\mathbf{q}_i$

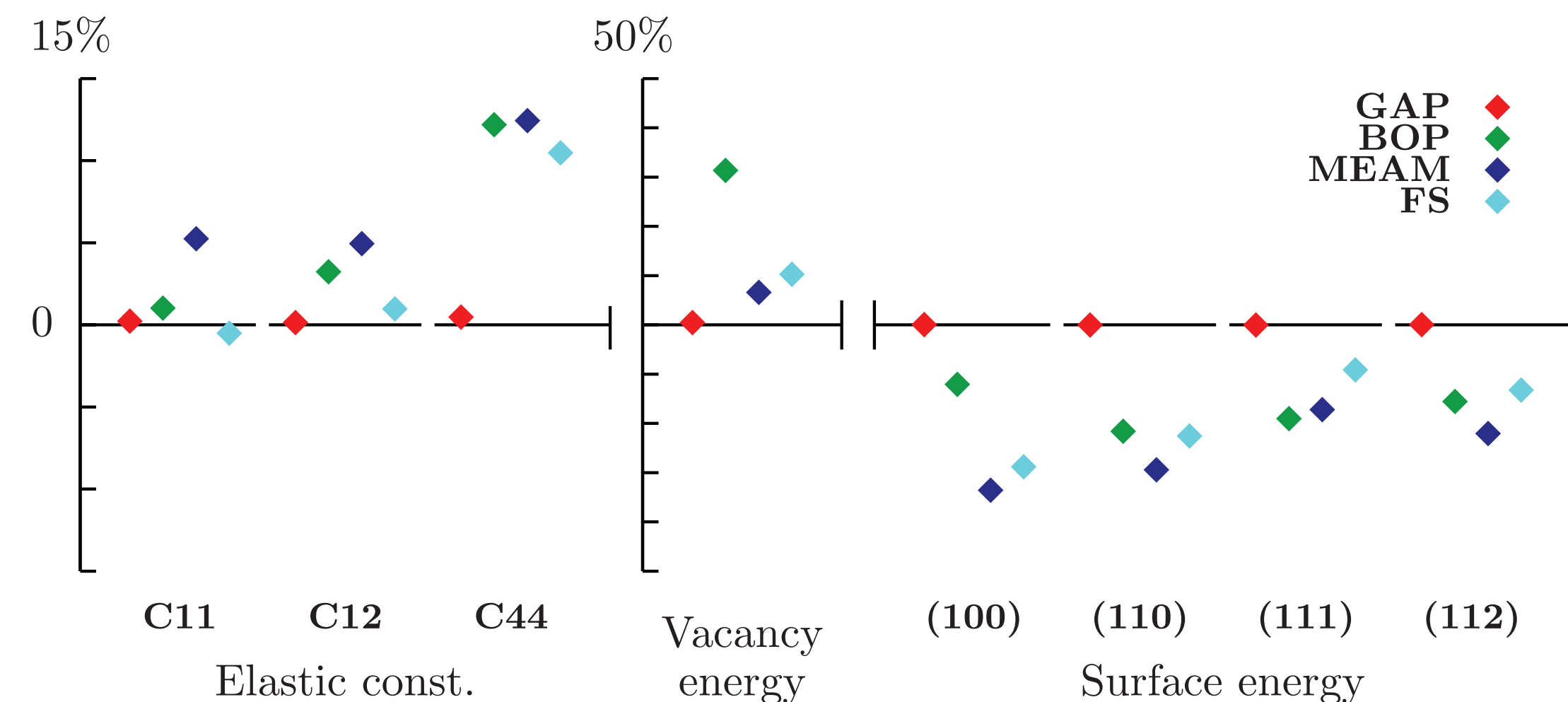
$$E = \sum_i \epsilon(\mathbf{q}_i)$$

- The energy function  $\epsilon(\mathbf{q}_i)$  is expanded in a basis set

$$\epsilon(\mathbf{q}) = \sum_j \alpha_j K(\mathbf{q}_j, \mathbf{q})$$

- The kernel  $K(q_j, q)$  measures the similarity between two different environments

### Example: Tungsten



**More on this and neural network potentials in Workshop III**

# Optimization of Model Parameters

---

## Data for optimization of potential parameters

- Properties of crystals, defects, liquids
  - ▶ Crystal structures and energy differences
  - ▶ Lattice constants, cohesive energy, equation of state
  - ▶ Elastic coefficients, phonon frequencies, and forces
  - ▶ Point defect structures and energies, surface energies, and relaxation

## Optimization methods

- Optimization using simulated annealing, parallel tempering, genetic algorithms, *etc.*
- Parameters usually lose the particular physical meaning of the analytic form
- It is crucial to test the transferability and accuracy of the potential on data that was **not** in the fit
- Empirical potentials have the tendency to lead to unexpected behavior in parts of phase space such as energy divergencies and unphysical roughness of landscape
- Fitting a potential is an art form and requires a lot of experience

⇒ **Clear need for improved methods**



# Evaluation of Empirical Potentials

---

## Comparison between potentials:

- Most potentials result in similar static properties
- Note, that they are often fit to static properties
- Problems usually occur for dynamics properties (forces, phonons) and defect properties

## For oxides

- In highly ionic oxides, qualitatively reasonable results can be expected with empirical potential models (+ electrostatic energy)
- Accuracy is mainly limited by the oxygen “breathing” effect
- The more covalent the oxide, the more difficult it will be to find potentials that reproduce the materials behavior in a wide range of environments
- Shell polarization is essential in low symmetry environments

## For metals

- Bond energy depends on the number of bonds already made to an atom
- This effect is absent in pair potentials, which are environment-independent
- Hence, whenever bond-breaking is involved, the result of a potential model should be interpreted cautiously

## For organic molecules

- Very good potentials have been fit to C-H and C-C bonds in various bonding arrangements (AMBER, CHARMM, MM3, MMFF94)
- These can be used to model conformational arrangements of polymeric systems (where *no bond-breaking* is involved)

# Validation of Empirical Energy Models

---

## Should at least use a testing dataset to estimate uncertainty

- Testing datasets of similar properties as fitting dataset
- Can also contain more expensive data such as:
  - ▶ Melting points
  - ▶ Thermal expansion
  - ▶ Thermal conductivity
  - ▶ Phase transition pressures
  - ▶ Rates
  - ▶ ...
- These require MD simulations and are less suitable for fitting database

# Validation of Empirical Energy Models

---

## Validation of energy landscapes

- Goal: Identify unphysical minima where the potential fails
- Strategy: Explore configuration space using global optimization methods
- Methods:
  - ▶ Simulated annealing, parallel tempering MD
  - ▶ Basin hopping
  - ▶ Evolutionary algorithms
  - ▶ ...

# Validation of Empirical Energy Models

## Example 1: Mo MEAM potential

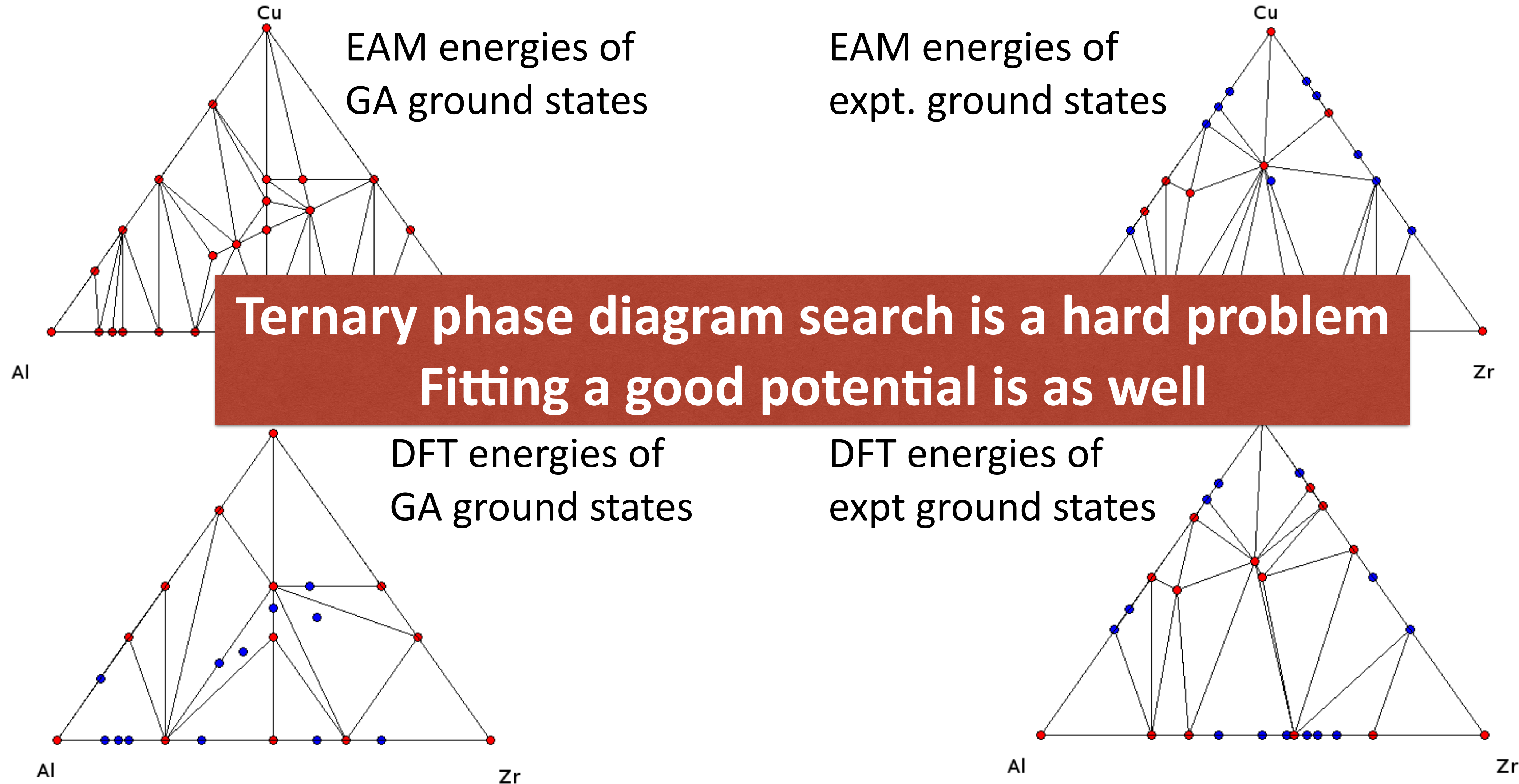
- Comparison of empirical potential with density-functional theory
- Modified embedded-atom model for Mo
- Perform GASP search with LAMMPS
- Calculate DFT energy of newly found structures
- Potential reproduces the ground state and all low-lying minima
- Provides confidence in accuracy of the potential

	MEAM <sup>a</sup>	GGA-PBE <sup>a</sup>	Exp.
$E_{\text{coh}}$ (eV/atom)	6.82	6.25	6.82 <sup>b</sup>
$a$ (Å)	3.167	3.169	3.147 <sup>c</sup>
$B$ (GPa)	253	263	270 <sup>d</sup>
$C_{11}$ (GPa)	441	462	479 <sup>d</sup>
$C_{12}$ (GPa)	158	163	165 <sup>d</sup>
$C_{44}$ (GPa)	96	102	108 <sup>d</sup>
$\Delta E_{\text{C2/m}}$ (meV/atom)	198	175	...
$\Delta E_{\text{Fddd-bcc}}$ (meV/atom)	242	231	...
$\Delta E_{\beta\text{W-bcc}}$ (meV/atom)	266	96	...
$a_{\beta\text{W}}$ (Å)	5.026	5.058	...
$\Delta E_{\text{Pmma-bcc}}$ (meV/atom)	269	233	...
$\Delta E_{\beta\text{Ta-bcc}}$ (meV/atom)	280	168	...
$a_{\beta\text{Ta}}$ (Å)	9.719	9.752	...
$c_{\beta\text{Ta}}$ (Å)	5.048	5.113	...
$\Delta E_{\omega\text{Ti-bcc}}$ (meV/atom)	332	404	...
$a_{\omega\text{Ti}}$ (Å)	4.616	4.681	...
$c_{\omega\text{Ti}}$ (Å)	2.595	2.572	...
$\Delta E_{\text{fcc-bcc}}$ (meV/atom)	391	418	...
$a_{\text{fcc}}$ (Å)	3.931	4.013	...
$\Delta E_{\text{hcp-bcc}}$ (meV/atom)	415	433	...
$a_{\text{hcp}}$ (Å)	2.743	2.765	...
$c_{\text{hcp}}$ (Å)	4.692	4.905	...



# Validation of Empirical Energy Models

## Example 2: Testing of Al-Cu-Zr EAM potential

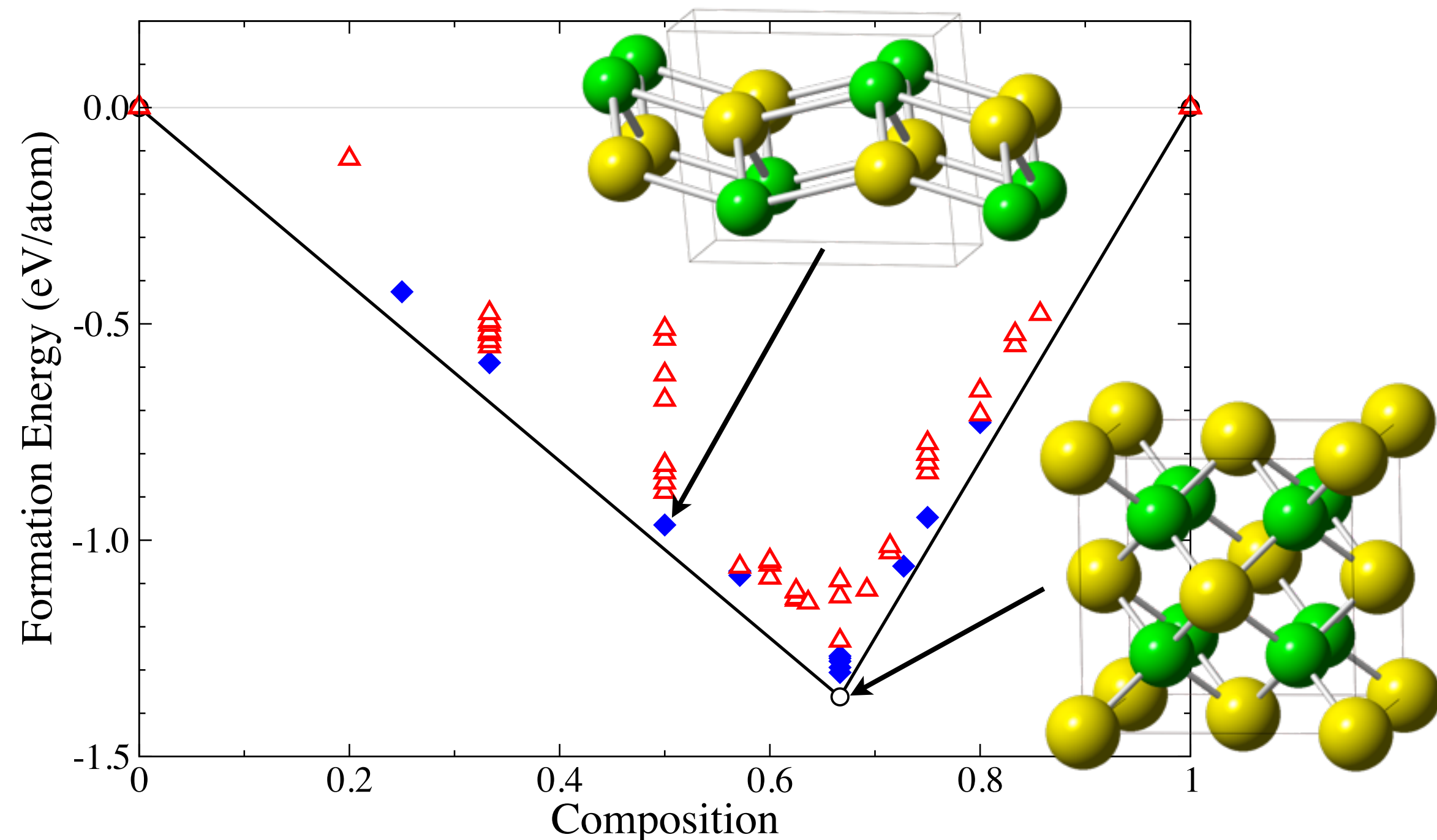


# Validation of Empirical Energy Models

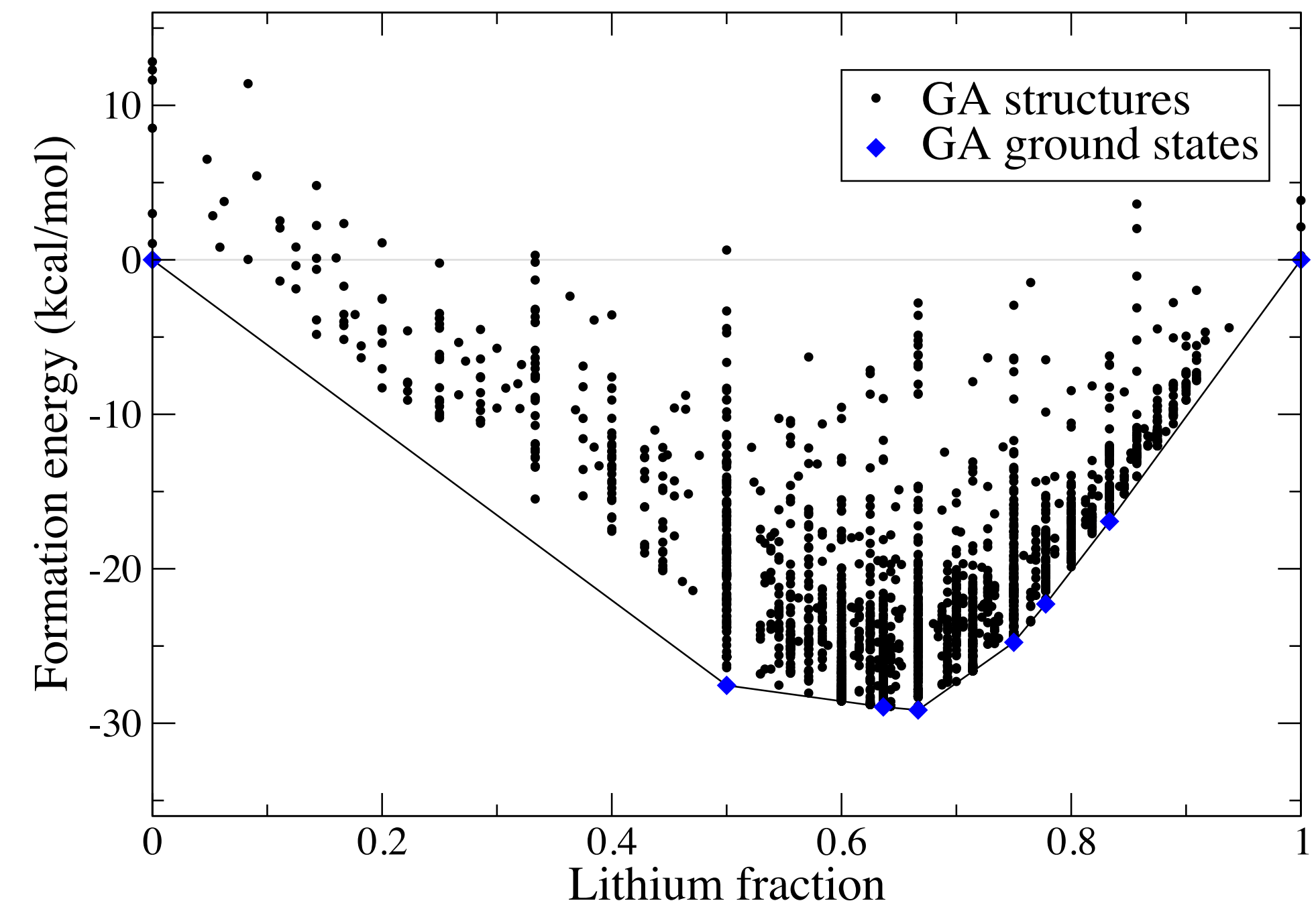
## Example 2: Li-S system

- Three ground state phases: Li, Li<sub>2</sub>S, S
- Li monosulfide, LiS, reported by Thomas and Jones in 1929
- ReaxFF potential fitting and evolutionary algorithm testing (van Duin *et al.*)
- Unphysical structure from first search were used in fit to improve potential

### Density-functional theory



### ReaxFF potential model





# Open Question

---

How should we select the optimal functional form of an energy model for a given materials system?

How should we choose a fitting data sets for parameter optimization that minimizes the errors on the model predictions?

How can we identify tradeoffs between conflicting model predictions for a given functional form of the model?

How can we effectively employ energy models as surrogate models for energy landscapes?