

Interatomic Potentials

- Before we can start a simulation, we need the model!
- Interaction between atoms and molecules is determined by quantum mechanics:
 - Schrödinger Equation + Born-Oppenheimer approximation
 - BO: we can get rid of electrons and consider the effective interaction of nuclei – the “potential energy surface”, $V(q)$.

$V(q)$ determines the quality of result.
- But we don't know $V(q)$!
 - *Semi-empirical approach*: make a good guess and use experimental data to adjust it. (This is fast! May not reveal correct details, depends on V)
 - *Quantum chemistry approach*: compute the surface at a few points and fit to a reasonable form. (This is hard!)
 - *Ab initio approach*: do the QM calculations “on the fly” as the trajectory is being generated. Couple a quantum calculation of the electrons with a classical one of the nuclei. (Much more computer effort, but no analytic form needed.)

The electronic-structure problem

The non-relativistic Hamiltonian for a collection of charged particles:

$$H = - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i<j} \frac{e_i e_j}{r_{ij}} + \text{(external fields)}$$

"Atomic units": $\hbar = m_e = e = 1$

couples to individual particles

Energy in Hartrees = 27.2eV = 316,000K

Lengths in Bohr radii = 0.529Å = 5.29×10⁻⁹cm

$$H = - \sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 + \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \sum_{I=1}^{N_I} \frac{Z_I}{r_{iI}} - \sum_{I=1}^{N_e} \frac{m_e}{2M_I} \nabla_I^2 + \sum_{I<J} \frac{Z_I Z_J}{r_{IJ}} + \text{(external fields)}$$

electron KE+interaction

electron+ion

ion KE + interaction

couples to individual particles

Accuracy needed to address questions at room temp.:

100K = 0.3mHa = 0.01eV.

MANY DECIMAL PLACES!
difficult!

Solving this is

Born-Oppenheimer (1927) Approximation

- Make use of the fact that nuclei are so much heavier than electrons.
 - proton mass = 1836 electron mass. Electrons move much faster!
- Factor total wavefunction into ionic and electronic parts. (adiabatic approx)

$$H = \underbrace{-\sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 + \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \sum_{I=1}^{N_I} \frac{Z_I}{r_{iI}}}_{\text{electron Hamiltonian}} \underbrace{- \sum_{I=1}^{N_e} \frac{m_e}{2M_I} \nabla_I^2 + \sum_{I<J} \frac{Z_I Z_J}{r_{IJ}}}_{\text{ionic Hamiltonian}}$$

electron Hamiltonian

ionic Hamiltonian

$$\Psi(r_i, R_I) = \psi(r_i|R_I)\phi(R_I)$$

slow ions \approx frozen ions

$$H_e[R_I]\psi(r_i|R_I) = E_{\text{BO}}(R_I)\psi(r_i|R_I)$$

electronic **ground state**

$$(H_I + E_{\text{BO}}(R_I))\phi(R_I) = E_{\text{total}}\phi(R_I)$$

ions respond to electronic energy

electrons remain in **instantaneous ground state** in response to ion motion

$$\text{error}(E_{\text{total}}) \approx O\left(\frac{m_e}{M_I}\right)^{3/2} E_{\text{BO}} \leq 10^{-5} \text{Ha}$$

Does not *require* classical ions (though MD uses that).

Eliminate electrons from dynamics and replace by an **effective potential**.

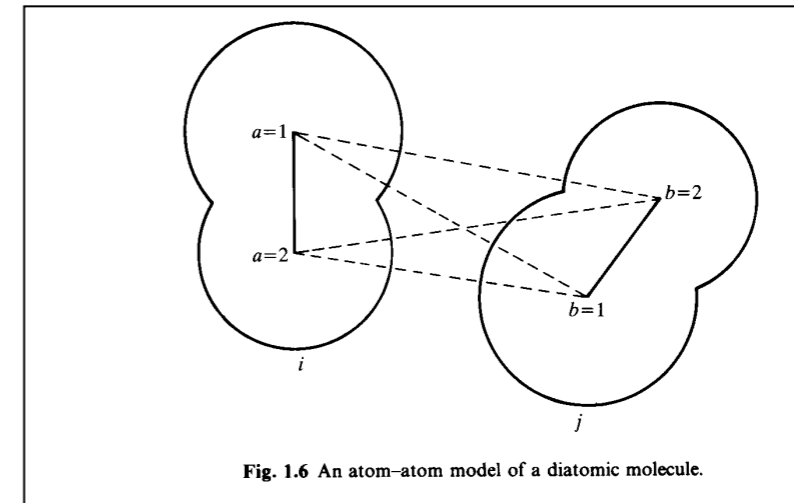
Semi-empirical potentials

- Assume a functional form, e.g., a 2-body or 3-body.
- Find some data from experiment.
- Use theory+simulation to determine parameters.

- What data?
 - Molecular bond lengths, binding energies
 - Atom-atom scattering in gas phase
 - Virial coefficients, transport in gas phase
 - Low temperature properties of the solid, cohesive energy, lattice constant, elastic moduli, vibrational frequencies, defect energies.
 - Melting temperature, critical point, triple point, surface tension,....
 - Point defects, surface energies, diffusion barriers
 - Random positions during molecular dynamics; liquid structure
- GIGO, i.e. "garbage in, garbage out"!
- Interpolation versus extrapolation: "transferability"
- Are results predictive?
- How much theory to use, and how much experimental data?

Atom-Atom potentials

$$V(r_i) = \sum_{i < j} v(|r_i - r_j|)$$

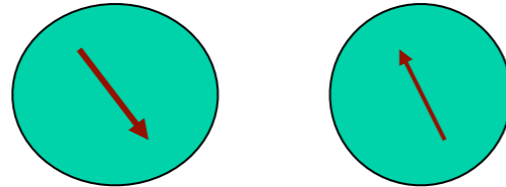


- Total potential is the sum of atom-atom pair potentials
- Assumes molecule is rigid, in non-degenerate ground state, interaction is weak so the internal structure is weakly affected by the environment.
- Geometry (steric effect) is important.
- Short-range effects-repulsion caused by cores: $\exp(-r/c)$
- Perturbation theory as $r_{ij} \gg$ core radius
 - Electrostatic effects: do a multipole expansion (if charged or have dipoles)
 - Induction effects (by a charge on a neutral atom)
 - Dispersion effects: dipole-induced-dipole (C_6/r^6)

Atomic systems

- Neutral rare gas atoms are the simplest atoms to find a potential for: little attractive spheres.
 - Repulsion at short distances because of overlap of atomic cores.
 - Attraction at long distance due to the dipole-induced-dipole force.

Dispersion interaction is $c_6 r^{-6} + c_8 r^{-8} + \dots$



- He-He interaction is the most accurate. Use all available low density data (virial coefficients, quantum chemistry calculations, transport coefficients,) Good to better than 0.1K (work of Aziz over last 20 years). But that system needs quantum simulations. Three-body (and many-body) interactions are small but not zero.
- Good potentials are also available for other rare gas atoms.
- H_2 is almost like rare gas from angular degree of freedom averages out due to quantum effects. But has a much larger polarizability.

Lennard-Jones (2-body) potential

$$V(r_i) = \sum_{i < j} v(|r_i - r_j|) \quad v(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad \begin{array}{l} \epsilon = \text{energy minimum} \\ \sigma = \text{wall of potential} \end{array}$$

- Good model for non-bonded, rare gas atoms
- Standard model for MD!

Why these exponents? 6 and 12?

- There is only 1 LJ system!

$$v(x) = 4(x^{-12} - x^{-6})$$

- Reduced units:

–Energy in ϵ : $T^* = k_B T / \epsilon$

–Lengths in σ : $x = r / \sigma$

–Time is mass units, pressure, density

See references on FS pgs. 51-54

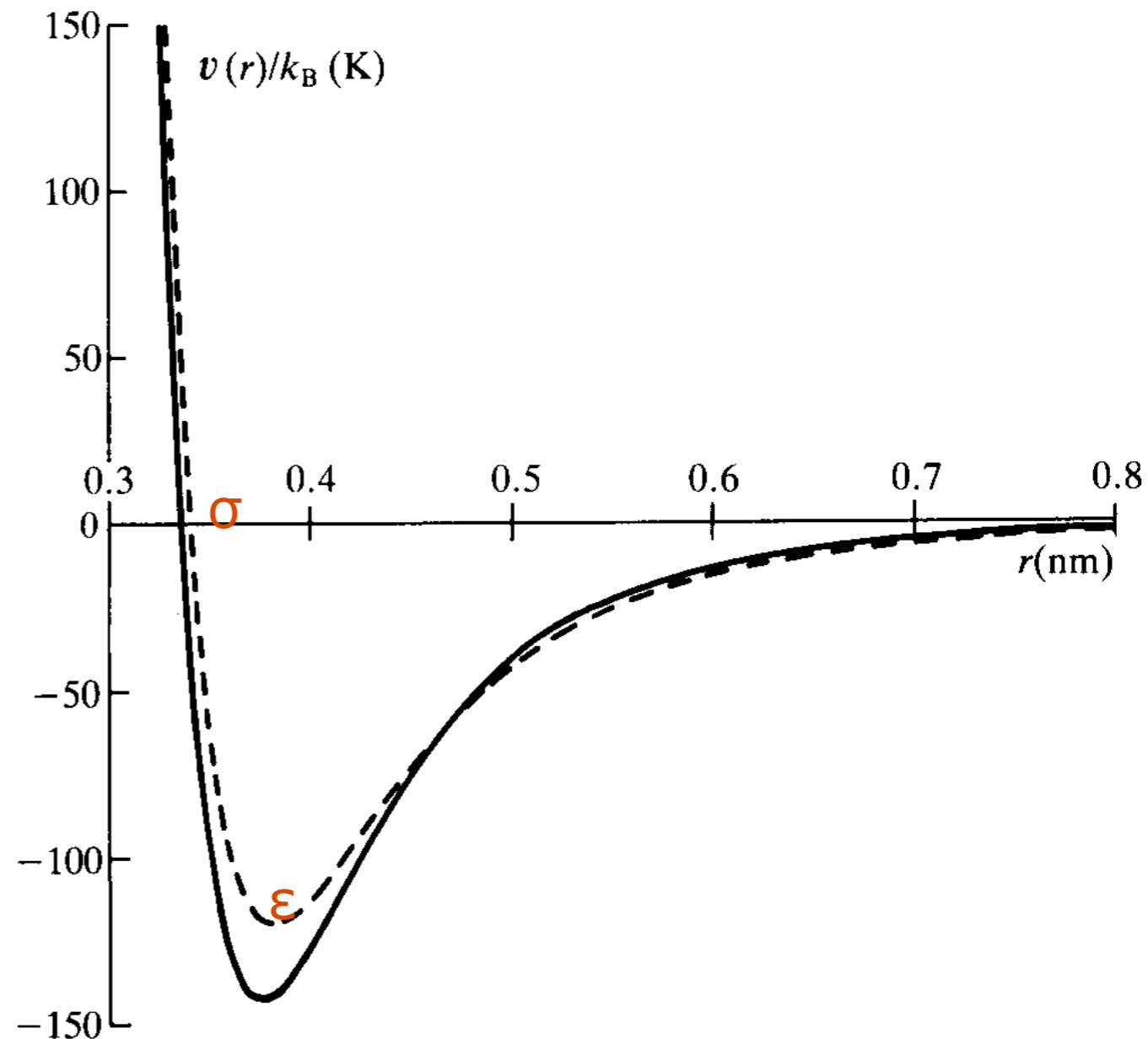


Fig. 1.3 Argon pair potentials. We illustrate the BBMS pair potential for argon [Maitland and Smith 1971]. The BFW potential [Barker *et al.* 1971] is numerically v. Also shown is the Lennard-Jones 12–6 effective pair potential (dashed line) used in simulations of liquid argon.

Phase diagram of Lennard-Jones

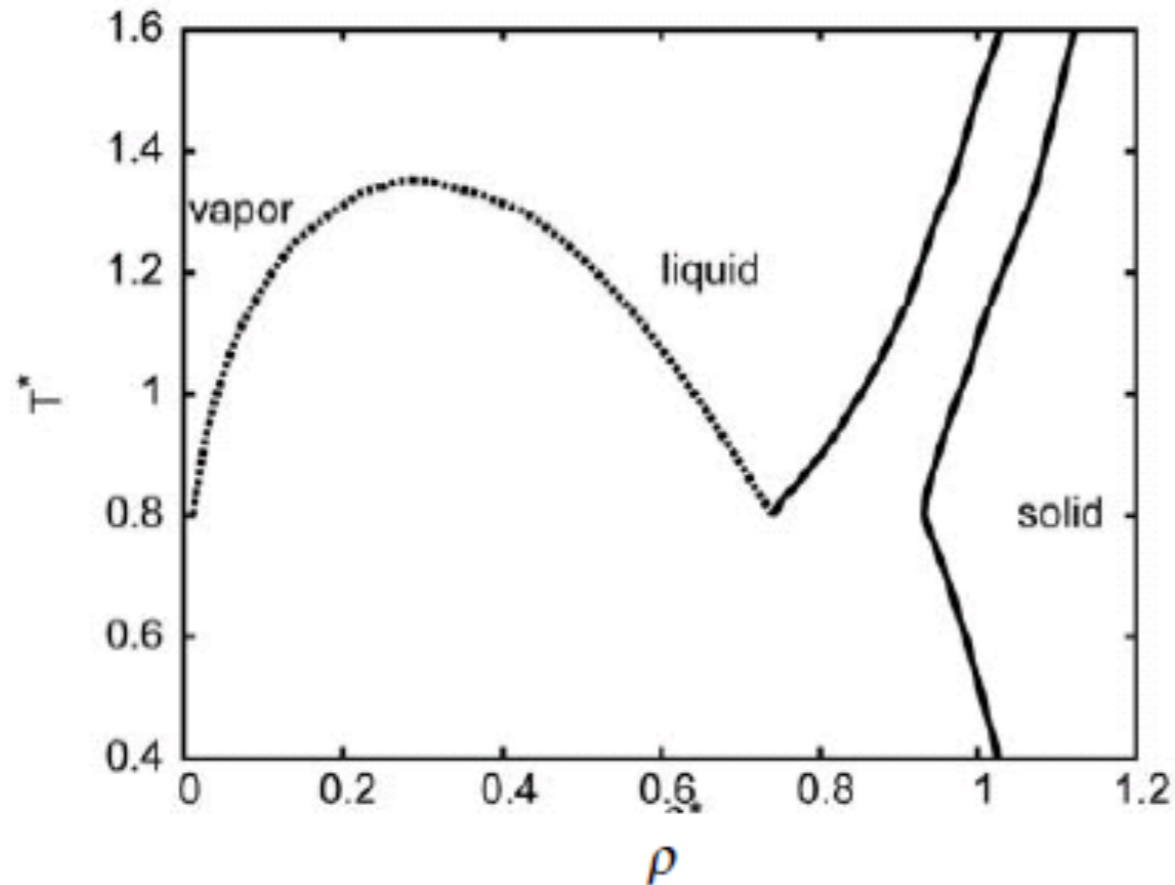


Figure 3: Phase diagram of the Lennard-Jones fluid: Reduced temperature as the function of the reduced density. The dashed line corresponds to the liquid-vapour coexistence line and the solid ones to solid-liquid and solid-vapour coexistence.

Table I: Comparison between our theoretical results, simulations^{16,17} and experimental data.⁴⁵ The Lennard-Jones parameters for noble gases were taken from Ref.⁴⁶

| | T_c^* | P_c^* | ρ_c | T_t^* | P_t^* |
|------------|---------|---------|----------|---------|---------|
| theory | 1.35 | 0.16 | 0.30 | 0.80 | 0.0086 |
| simulation | 1.31 | 0.12 | 0.30 | 0.68 | 0.001 |
| neon | 1.27 | 0.12 | 0.31 | 0.70 | 0.0019 |
| argon | 1.26 | 0.12 | 0.32 | 0.70 | 0.0016 |
| krypton | 1.22 | 0.11 | 0.30 | 0.68 | 0.0015 |
| xenon | 1.31 | 0.13 | 0.35 | 0.73 | 0.0018 |

Lennard-Jones Force calculation

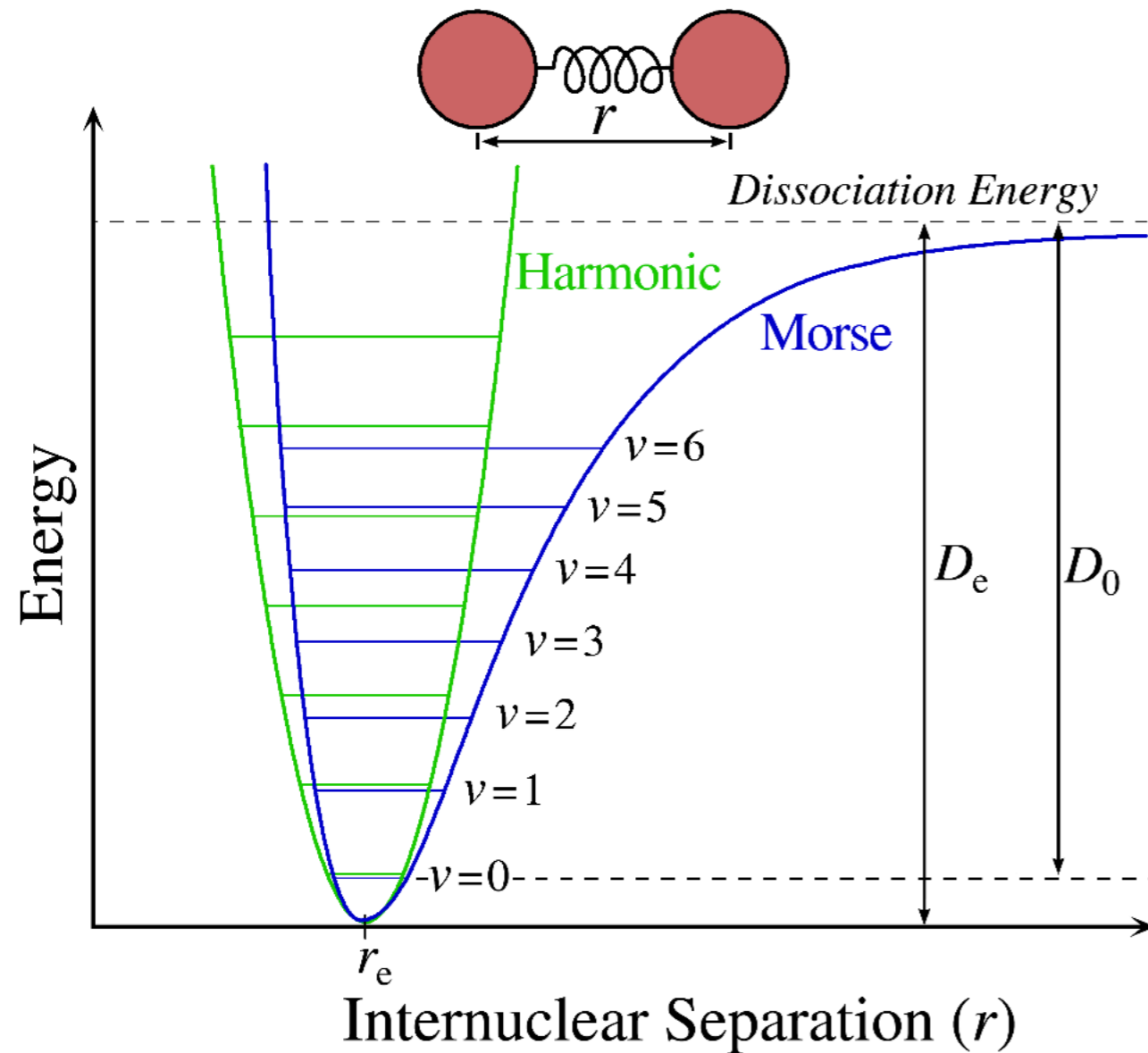
```
for i in range(Natoms):
    for j in range(i+1,Natoms):
        dx=x[i]-x[j]          # this will be a vector if x&y are array
        for d in range(3):    # more clever ways to do this?
            if dx[d]>L[d]/2:  dx[d] -= L[d]
            if dx[d]<-L[d]/2: dx[d] += L[d]
        r2 = sum(dx*dx)       # dx[0]*dx[0]+dx[1]*dx[1]+dx[2]*dx[2]
        if r2>rcutoff2: continue # outside of cutoff distance^2
        r2i = sigma/r2
        r6i = r2i**3
        pot += eps4*r6i*(r6i-1) - potcut
        rforce = eps24*r6i*r2i*(2*r6i-1)
        F[i] = F[i] + rforce*dx # F[i] and dx are vectors!
        F[j] = F[j] - rforce*dx
```

Note number of times through loops over atoms

Pair potential $\sim N^2$ iterations; reduce to $\sim N$ using neighbor tables.

Compare to *long range*: Ewald sums $\sim N^{3/2}$ but Fast Multipole $\sim N$ for large N

Morse potential: diatomic molecule



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

P. M. Morse, *Diatomic molecules according to the wave mechanics. II. Vibrational levels*. Phys. Rev. **34**, 57 (1929).

Morse potential

$$v(r) = \varepsilon \left[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right]$$

- Like Lennard-Jones but for bonded atoms
- Repulsion is more realistic - but attraction less so.
- Minimum at r_0 , approximately the neighbor position
- Minimum energy is ε
- An extra parameter “ a ” that can be used to fit a third property: **lattice constant** (r_0), **bulk modulus** (B) and **cohesive energy**.

$$\left. \frac{dE}{dV} \right|_{V_0} = 0$$

$$E_{\text{cohesive}} = -E(V_0)$$

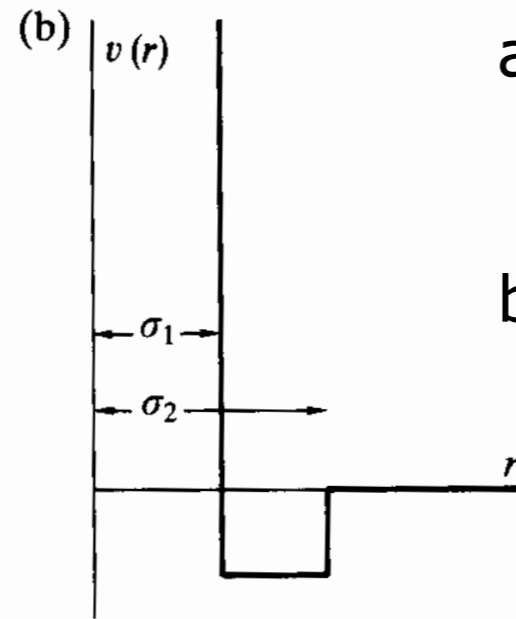
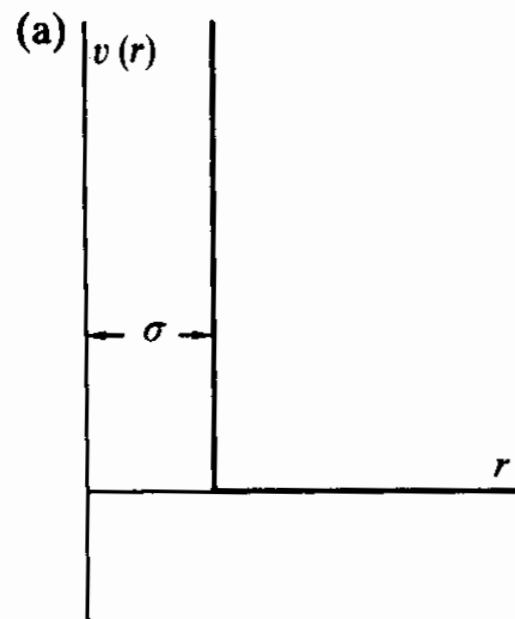
$$B = -V \left. \frac{dP}{dV} \right|_{V_0} = V \left. \frac{d^2E}{dV^2} \right|_{V_0}$$

Morse potential: parameters

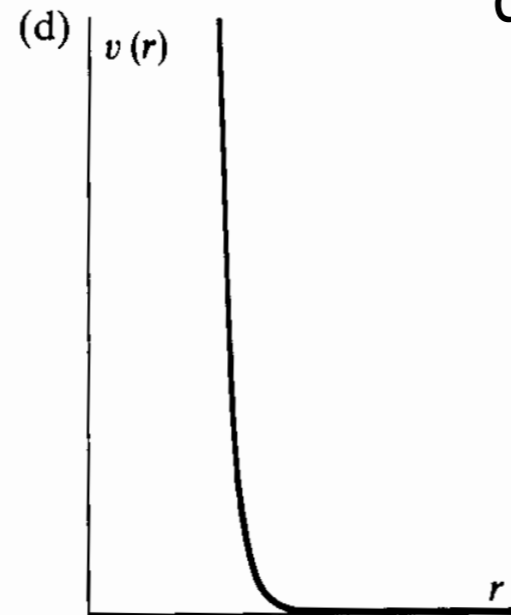
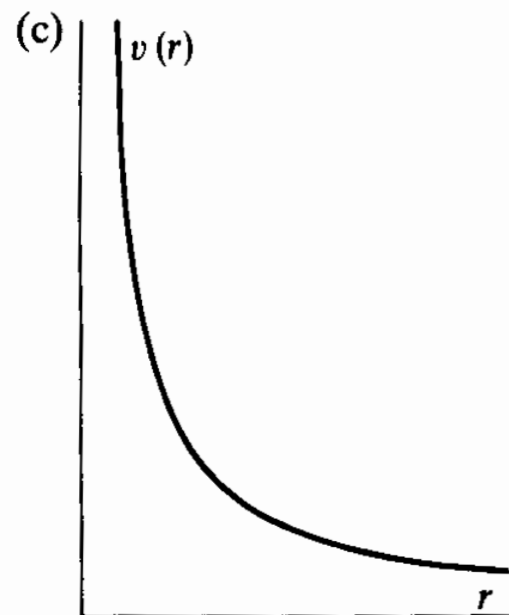
| Metal | αa_0 | β | $L(\text{ev}) \times 10^{-22}$ | $\alpha = \text{\AA}^{-1}$ | $r_0 = \text{\AA}$ | $D(\text{ev})$ |
|-------|--------------|---------|--------------------------------|----------------------------|--------------------|----------------|
| Pb | 2.921 | 83.02 | 7.073 | 1.1836 | 3.733 | 0.2348 |
| Ag | 2.788 | 71.17 | 10.012 | 1.3690 | 3.115 | 0.3323 |
| Ni | 2.500 | 51.78 | 12.667 | 1.4199 | 2.780 | 0.4205 |
| Cu | 2.450 | 49.11 | 10.330 | 1.3588 | 2.866 | 0.3429 |
| Al | 2.347 | 44.17 | 8.144 | 1.1646 | 3.253 | 0.2703 |
| Ca | 2.238 | 39.63 | 4.888 | 0.80535 | 4.569 | 0.1623 |
| Sr | 2.238 | 39.63 | 4.557 | 0.73776 | 4.988 | 0.1513 |
| Mo | 2.368 | 88.91 | 24.197 | 1.5079 | 2.976 | 0.8032 |
| W | 2.225 | 72.19 | 29.843 | 1.4116 | 3.032 | 0.9906 |
| Cr | 2.260 | 75.92 | 13.297 | 1.5721 | 2.754 | 0.4414 |
| Fe | 1.988 | 51.97 | 12.573 | 1.3885 | 2.845 | 0.4174 |
| Ba | 1.650 | 34.12 | 4.266 | 0.65698 | 5.373 | 0.1416 |
| K | 1.293 | 23.80 | 1.634 | 0.49767 | 6.369 | 0.05424 |
| Na | 1.267 | 23.28 | 1.908 | 0.58993 | 5.336 | 0.06334 |
| Cs | 1.260 | 23.14 | 1.351 | 0.41569 | 7.557 | 0.04485 |
| Rb | 1.206 | 22.15 | 1.399 | 0.42981 | 7.207 | 0.04644 |

L. A. Girifalco and V. G. Weizer, *Application of the Morse potential function to cubic metals*. Phys. Rev. **114**, 687 (1959).

Various Other Empirical Potentials



- a) Hard sphere - simplest, first, no integration error.
- b) Hard sphere, square well



- c) Coulomb (long-ranged) for plasmas
- d) $1/r^{12}$ potential (short-ranged)

Fig. 1.4 Idealized pair potentials. (a) The hard-sphere potential; (b) The square-well potential; (c) The soft-sphere potential with repulsion parameter $\nu = 1$; (d) The soft-sphere potential with repulsion parameter $\nu = 12$.

Fit for a Born potential

$$v(r) = \frac{Z_i Z_j}{r} + \frac{A}{r^n}$$

- Attractive charge-charge interaction
- Repulsive interaction determined by atom core.

EXAMPLE: NaCl

- $Z_i = \pm 1$ on simple cubic structure/alternating charges
- Need Madelung constant for cubic structure for total energy
- Use cohesive energy and lattice constant (at $T=0$) to determine A and n

$$E_{\text{bind}} = \frac{e_a}{a_0} + \frac{e_r A}{a_0^n} \quad \frac{dE_{\text{bind}}}{da_0} = -\frac{e_a}{a_0^2} - \frac{ne_r A}{a_0^{n+1}} = 0$$
$$n = 8.87 \quad A = 1500 \text{eV}\text{\AA}^{8.87}$$

- Now we need a check: bulk modulus.
 - We get $4.35 \times 10^{11} \text{ dyn/cm}^2$ **Experiment** = $2.52 \times 10^{11} \text{ dyn/cm}^2$
- You get what you fit for!

Arbitrary pair potential

- For anything more complicated than a LJ 6-12 potential you can use a table-driven method.
- In start up of MD, compute or read in a table of potential values:
 - $V(r)$, dV/dr on a table.
- During computation, map interatomic distance to a grid and compute grid index and difference
- Do table look-up and compute (cubic) polynomial.
- Complexity is memory fetch+a few flops/distance
- **Advantage:** Code is completely general—can handle any potential at the same cost.
- **Disadvantage:** some cost for memory fetch. (cache misses)

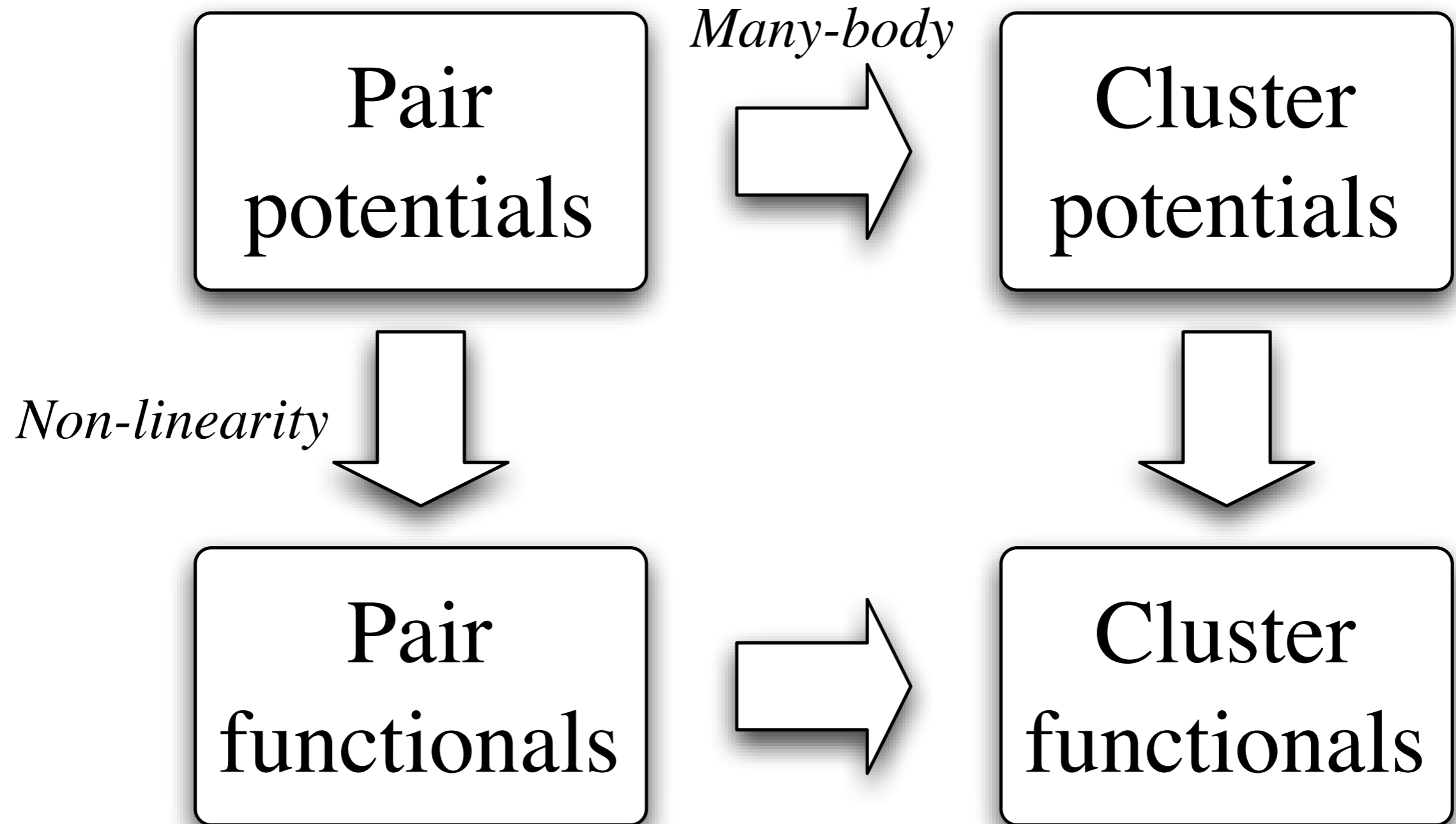
Failure of pair potentials

| Property | Cu | Ag | Pt | Au | Ar | LJ |
|-----------------|------|------|------|------|------|----|
| E_c/T_m | 30 | 28 | 33 | 33 | 11 | 13 |
| E_v/E_c | 0.33 | 0.36 | 0.26 | 0.25 | 0.95 | 1 |
| C_{12}/C_{44} | 1.5 | 1.9 | 3.3 | 3.7 | 1.1 | 1 |

- E_c =cohesive energy and E_v =vacancy formation energy
- T_m =melting temperature
- C_{12} and C_{44} are shear elastic constants.
 - A “Cauchy” relation makes them *equal* in a cubic lattice for *any pair potential*.
- Problem in metals: electrons are not localized!

[After Ercolessi, 1997]

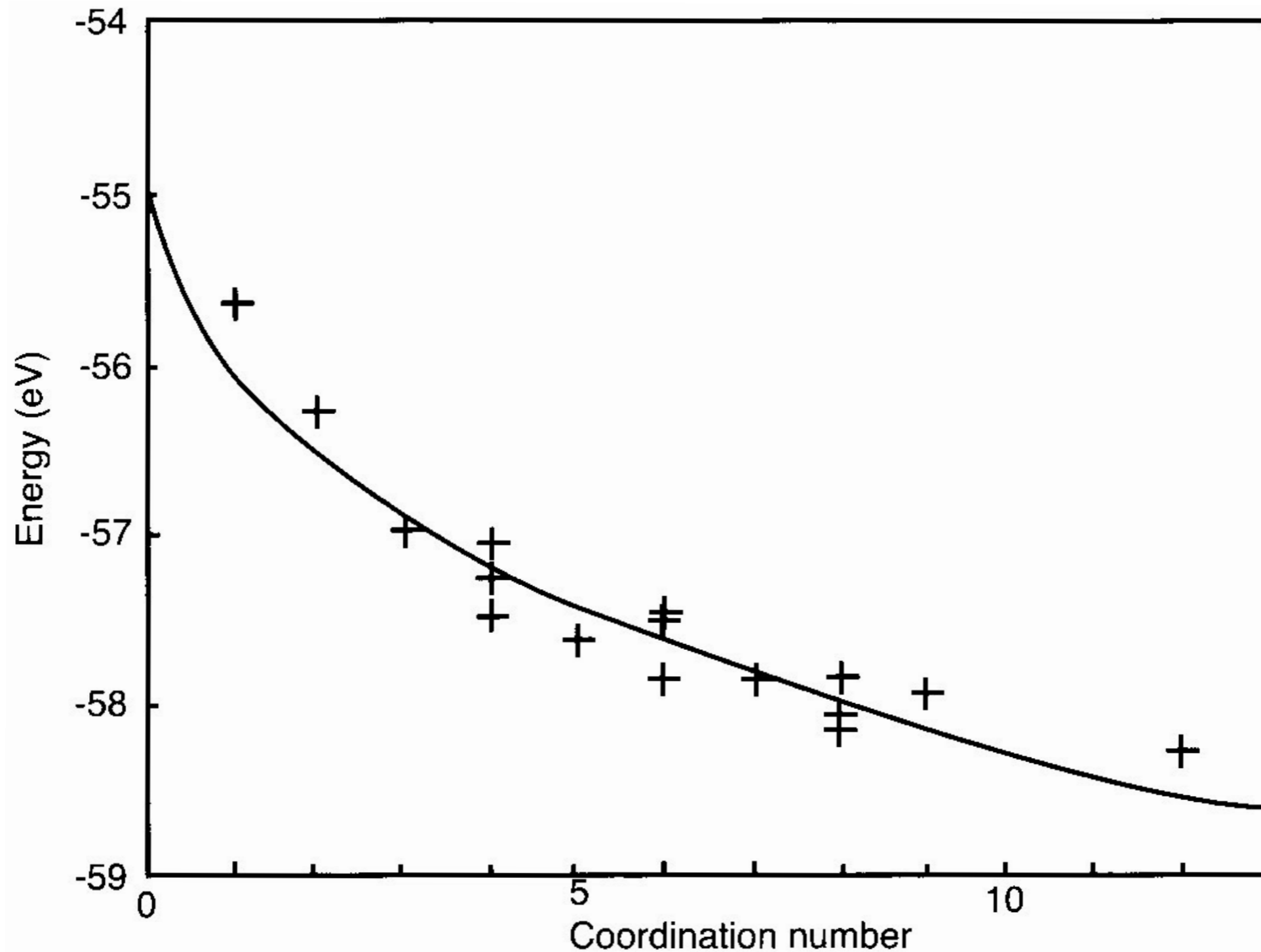
Overcoming deficiencies of pair potentials



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 $E = E_0 + a Z^{1/2} + \beta Z$



Metallic potentials

- Have an inner core + valence electrons
- Valence electrons are delocalized.
 - Hence pair potentials do not work very well. Strength of bonds decreases as density increases because of Pauli principle.

should $E \sim Z$ or $E \sim \sqrt{Z}$ for Z : coordination number?

- EXAMPLE: at a surface LJ potential predicts expansion but metals contract.
- Embedded Atom Model (EAM) or [glue models](#) work better.
Daw and Baskes, PRB **29**, 6443 (1984).

$$V = \sum_i F(n_i) + \sum_{i<j} \phi(r_{ij}), \quad n_i = \sum_j \rho(r_{ij})$$

- Three functions to optimize!
- Good for spherically symmetric atoms: Cu, Pb
 - Not for metals with covalent bonds or metals (Al) with large changes in charge density under shear.

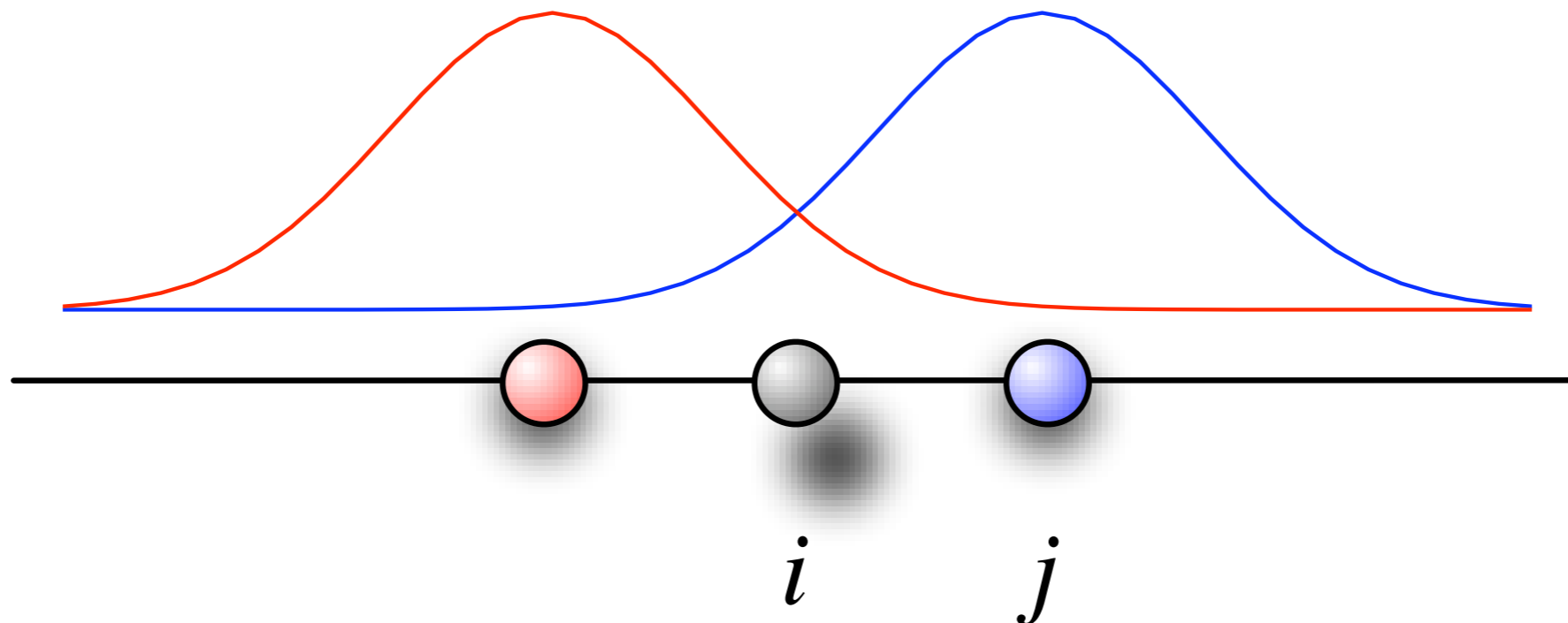
Embedded-atom potential

Idea:

- Energy of an atom depends *non-linearly* on the surrounding atoms (number and distance)
- Use electron density as a measure of the surrounding atoms

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

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



Accuracy of Embedded Atom Potentials

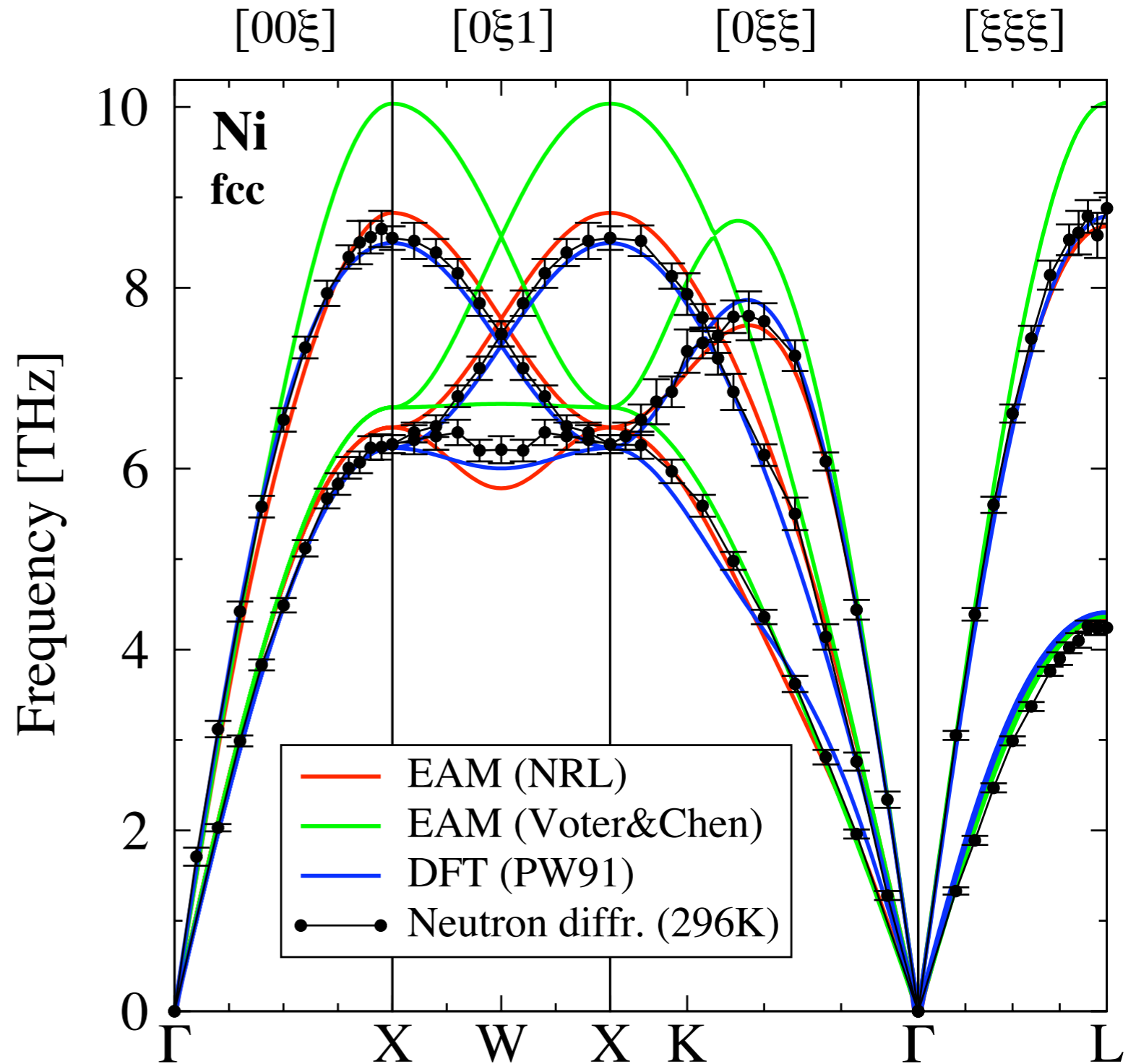
Linear thermal expansion
in units of $10^{-6}/K$

Activation energy for self-
diffusion in eV

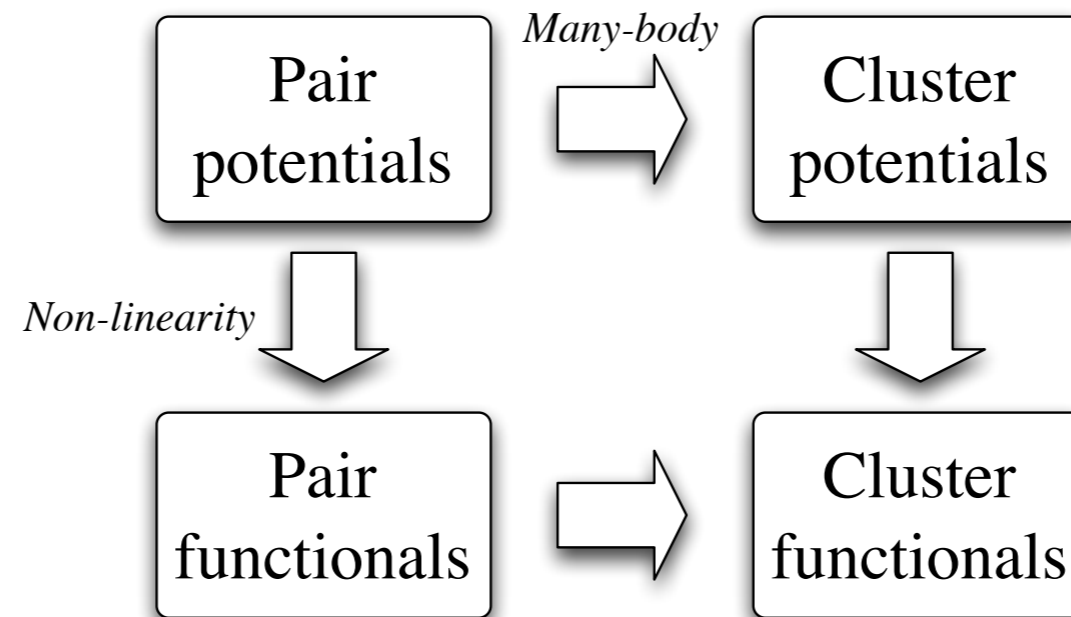
| Element | EAM | Experiment | EAM | Experiment |
|---------|------|------------|------|------------|
| Cu | 16.4 | 16.7 | 2.02 | 2.07 |
| Ag | 21.1 | 19.2 | 1.74 | 1.78 |
| Au | 12.9 | 14.1 | 1.69 | 1.74 |
| Ni | 14.1 | 12.7 | 2.81 | 2.88 |
| Pd | 10.9 | 11.5 | 2.41 | < 2.76 |
| Pt | 7.8 | 8.95 | 2.63 | 2.66 |

Accuracy of Embedded Atom Potentials

- 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



Many-Body Potentials



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

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

Modified Embedded Atom Method

- Similar form to EAM with modified density function

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

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

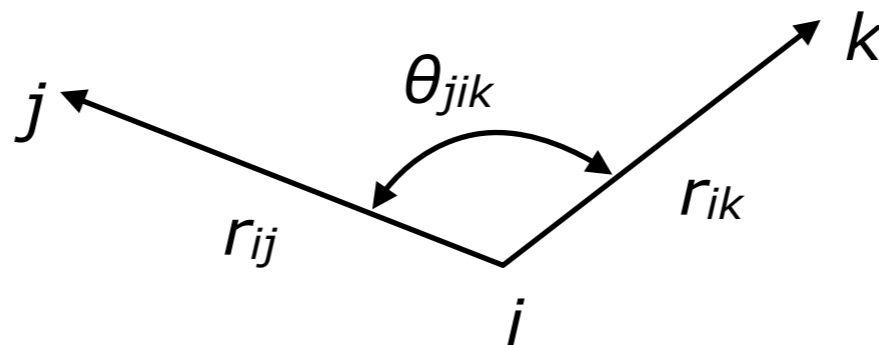
- Angular force terms particularly important for early transition metal elements and covalent bonded systems
- Applications of EAM to Si, Ti and refractory metals

Silicon potential

- Solid silicon can not be described with a pair potential.
- Has open structure, with coordination 4!
- Tetrahedral bonding structure caused by the partially filled p -shell.
- Very stiff potential, short-ranged caused by localized sp^3 electrons
- **Stillinger-Weber** (Phys. Rev. B **31**, 5262 (1985)) potential fit from:
Lattice constant, cohesive energy, melting point, structure of liquid Si

$$v_{\text{two body}} = \sum_{i < j} \left(B/r_{ij}^4 - A \right) \exp \left[\frac{1}{r_{ij} - a} \right] \quad \text{for } r < a$$

$$v_{\text{three body}} = \sum_{ijk} \lambda \exp \left[\frac{\gamma}{r_{ij} - a} + \frac{\gamma}{r_{ik} - a} \right] \left(\cos \theta_{jik} + 1/3 \right)^2 \quad \text{minimum at } 109^\circ$$



Hydrocarbon potential

- Empirical potentials to describe intra-molecular and inter-molecular forces
- **AMBER potential** is:
 - Two-body Lennard-Jones+ charge interaction (non-bonded)
 - Bonding potential: $k_r(r_i-r_j)^2$
 - Bond angle potential $k_a(\theta-\theta_0)^2$
 - Dihedral angle: $v_n[1 - \cos(n\phi)]$
 - All parameters taken from experiment.
 - Rules to decide when to use which parameter.
- Several “force fields” available
 - (open source/commercial).

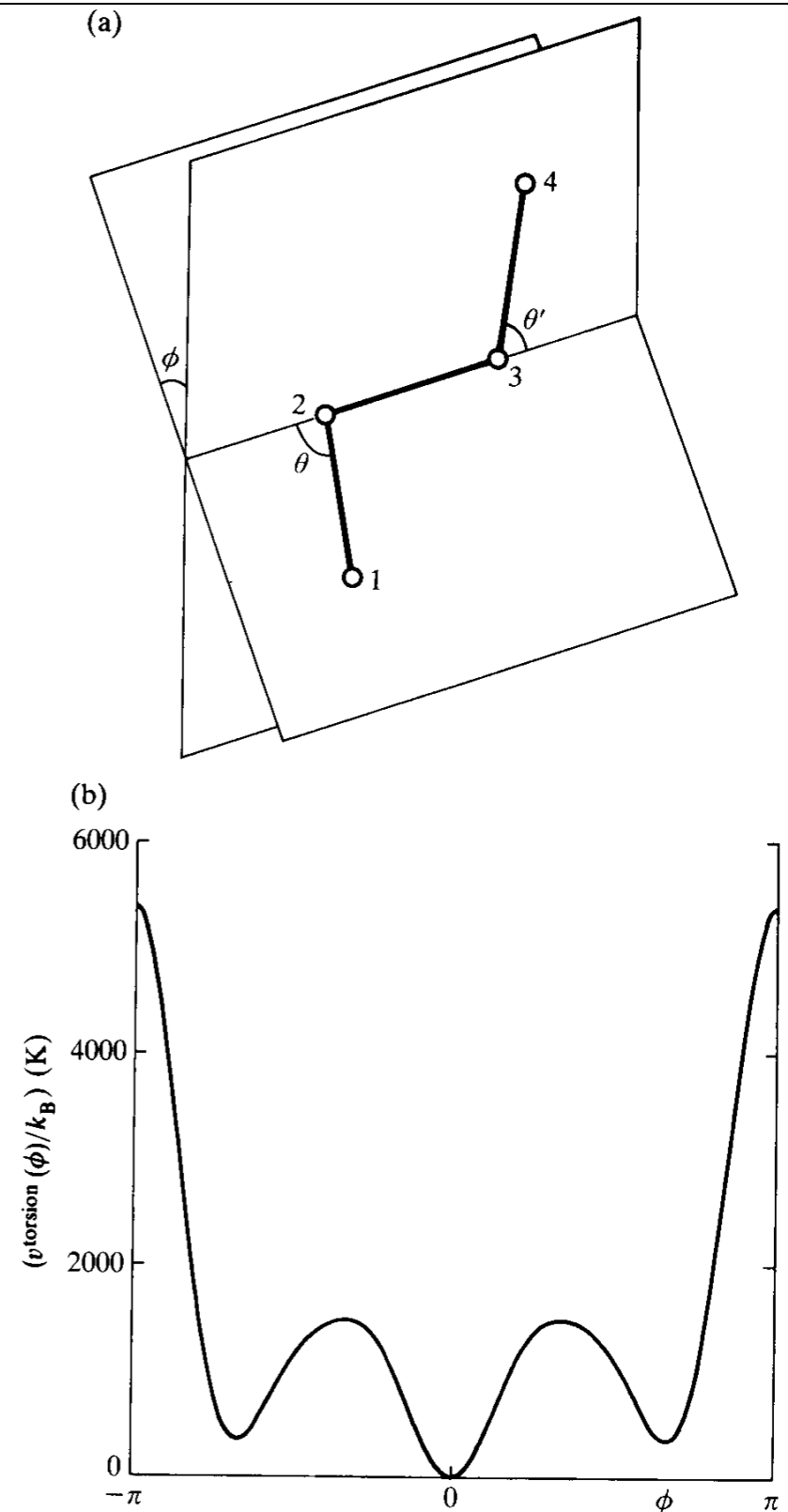


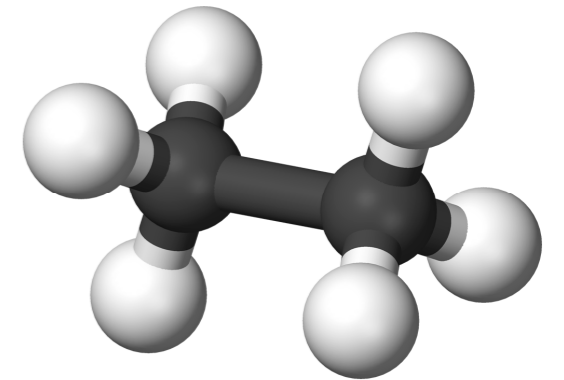
Fig. 1.8 (a) A model of butane [Ryckaert and Bellemans 1975]. (b) The torsional potential [Marechal and Ryckaert 1983].

More potentials for organic molecules

- Distinguish between bonded and non-bonded interactions

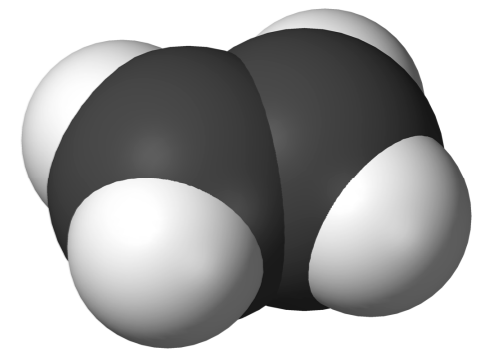
(1) Ethane $\text{H}_3\text{C}-\text{CH}_3$

- 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 sp , sp^2 , and sp^3 carbon



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

Water potentials

- Older potentials: **BNS,MCY,ST2**
- New ones: **TIP3P,SPC,TIP4P**
- **TIP5P**
 - Rigid molecule with 5 sites
 - Oxygen in center that interacts with other oxygens using LJ 6-12
 - 4 charges ($e = \pm 0.24$) around it so it has a dipole moment
- Compare with phase diagram (melting and freezing), pair correlations, dielectric constant

Mahoney &
Jorgensen

J. Chem. Phys., Vol. 112, No. 20, 22 May 2000

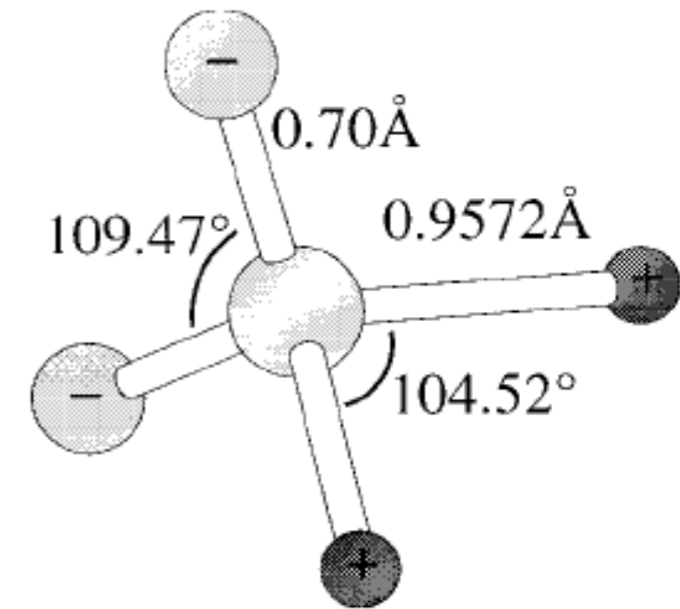


FIG. 1. TIP5P monomer geometry.

Potentials for Charged Systems

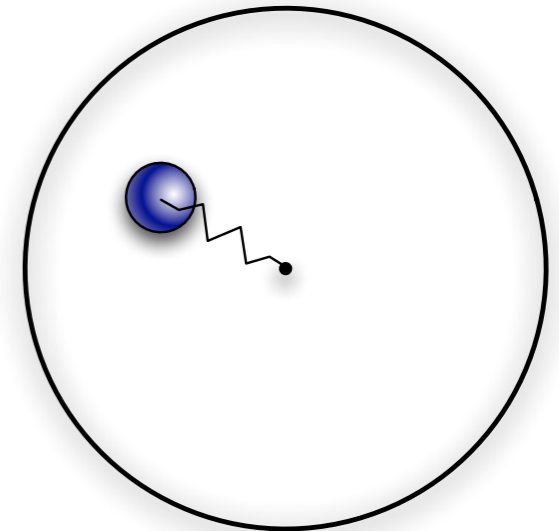
Start with pair potentials with Coulomb interactions

- 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



Problems with potentials

- Potential is highly dimensional function. Arises from QM so it is not a simple function.
- Procedure: fit data relevant to the system you are going to simulate: similar **densities** and **local environment**.
- Use other experiments to **test potential**.
- Do quantum chemical (SCF or DFT) calculations of clusters. Be aware that these may not be accurate enough.
- **No** empirical potentials work very well in an inhomogenous environment.
- This is the main problem with atom-scale simulations--they really are only suggestive since the potential may not be correct. **Universality helps (i.e., sometimes the potential does not matter that much)**

Which approach to use?

- Type of systems: metallic, covalent, ionic, van der Waals
- Desired accuracy: quantitative or qualitative
- Transferability: many different environments
- Efficiency: system size and computer resources
 - (10 atoms or 10^8 atoms. 100fs or 10ms)

Total error is the combination of:

- **statistical error** (the number of time steps)
- **systematic error** (the potential)

Sample input script to LAMMPS: 6×6×6 FCC LJ

```
units          lj          # use scaled LJ units
boundary       p p p      # periodic in all 3 directions
atom_style     atomic     # atoms have mass, position, velocity
lattice        fcc 1.0    # initialize atoms on an FCC lattice
region         box block 0 6 0 6 0 6 units lattice # expand
create_box     1 box      # make the box (supercell dimensions)
create_atoms   1 box      # fill up with atoms
pair_style     lj/cut 2.5          # define LJ type of interaction
pair_coeff     1 1 1.0 1.0 2.5    # set eps=sigma=1, cutoff=2.5
mass           1 1.0          # atomic mass
# generate initial velocities from a normal dist
velocity      all create 1.2 987654 rot yes dist gaussian
fix           fix1 all nve        # use constant N, V, E
thermo        10                # output thermo. info / 10steps
thermo_style  custom pe ke etotal temp      # what to output
dump          dump1 all atom 100 dump.out  # what to output
timestep      0.005              # timestep for run
run           1000                # how long to run
```