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(R).*

V(R) determines the quality of result.

- But we don't know V(R)!
  - Semi-empirical approach: make a good guess and use experimental data to adjust it. (Evaluation is fast! But difficult to get accurate potential.)
  - 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 ions and electrons:

$$H = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i}\nabla_i^2 + \sum_{i<j} \frac{e_i e_j}{r_{ij}} + \text{external fields}$$
$$+ \text{symmetry and boundary conditions}$$

“Atomic units”: $\hbar = m_e = e = 1$

Energy in Hartrees=27.2eV=316,000K Lengths in Bohr radii= 0.529 A = 5.29 x10^{-9}cm

$$H = -\sum_{i=1}^{N_e} \frac{1}{2}\nabla_i^2 + \sum_{a=1}^{N_I} \frac{1}{2\left(M_a / m_e\right)}\nabla_a^2 + \sum_{a<b} \frac{Z_a Z_b}{r_{ab}} - \sum_{i,a} \frac{Z_a}{r_{ia}} + \sum_{i<j} \frac{1}{r_{ij}} + \text{external fields}$$
+symmetry and boundary conditions

Accuracy needed to address questions at room temp.: 100 K=0.3 mHa=0.01eV.

MANY DECIMAL PLACES! Solving this is difficult!

Born-Oppenheimer (1927) Approximation

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

$$H = H_e + H_N$$

electronic and nuclear parts

$$H_e = -\sum_{i=1}^{N_e} \frac{1}{2}\nabla_i^2 + \sum_{a<b} \frac{Z_a Z_b}{|R_a - R_b|} - \sum_{i,a} \frac{Z_a}{|R_a - r_i|} + \sum_{i<j} \frac{1}{|r_i - r_j|} \qquad H_N = -\sum_{a=1}^{N_I} \frac{1}{2\left(M_a / m_e\right)} \nabla_a^2$$

$$\Psi(r\,|\,R) = \psi(r\,|\,R)\phi(R)$$ variational trial function

$$H_e \psi(r\,|\,R) = E_{BO}(R)\psi(r\,|\,R)$$ $E_{BO}\left(R\right) =$ BO energy surface

$$\left(H_N + E_{BO}(R)\right)\phi(R) = E_{tot}\phi(R)$$

$$error(E_{tot}) \approx O\left(\frac{m_e}{m_I}\right)^{3/2} \quad \text{electronic energy} \leq 10^{-5}\, Ha$$

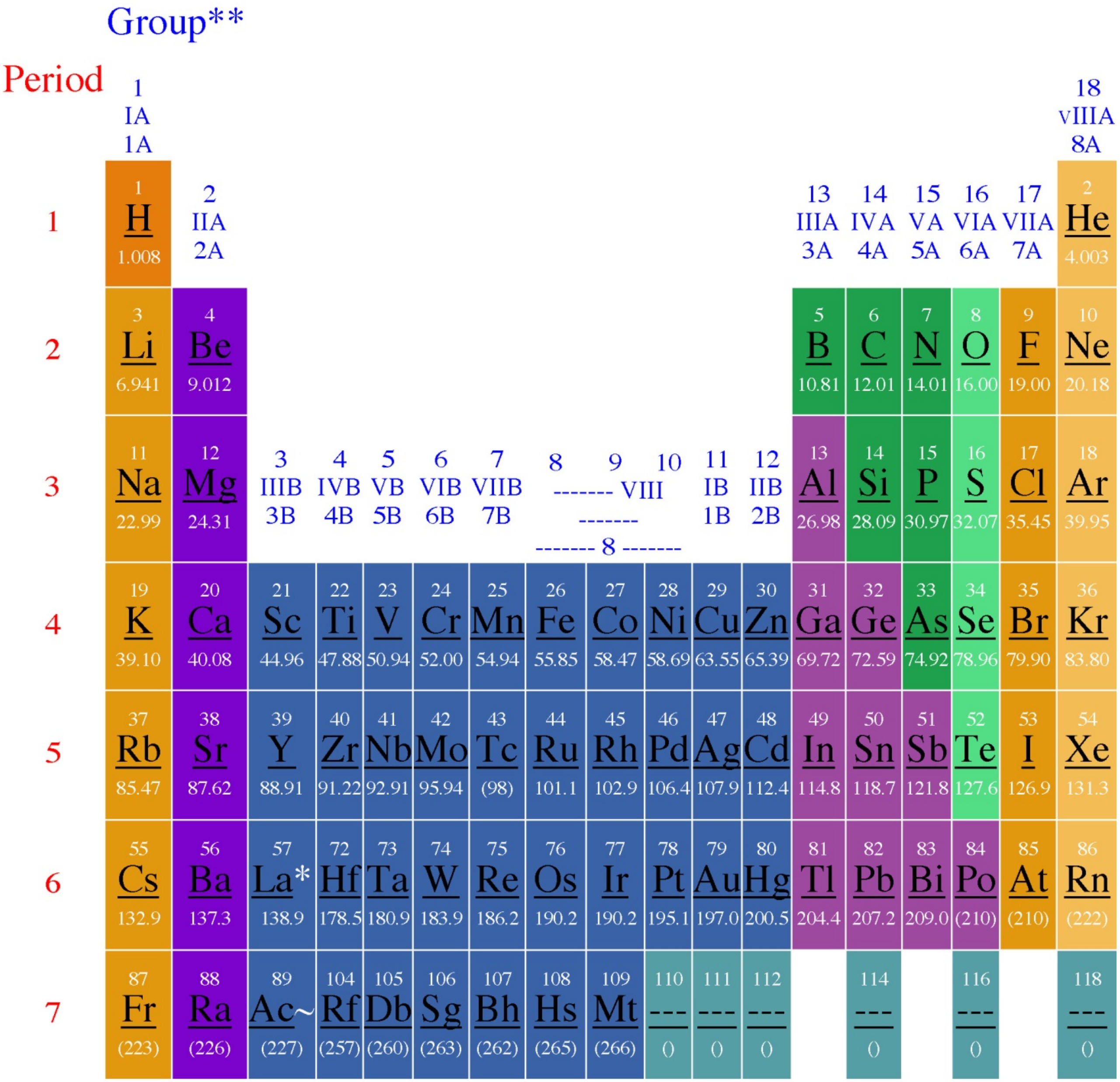
- *Eliminate the electrons and replace by an effective potential.*
- *Does not require classical ions (but MD assumes it) (see end of course)*

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
  - 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?**

Group**



Period	1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 ------- VIII ------- ------- 8 -------	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 vIIIA 8A
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.47	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 190.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac~ (227)	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 --- ()	111 --- ()	112 --- ()		114 --- ()		116 --- ()		118 --- ()

Atom-Atom potentials

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

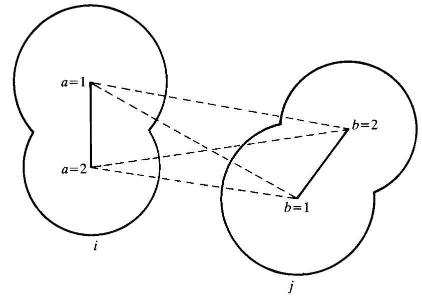


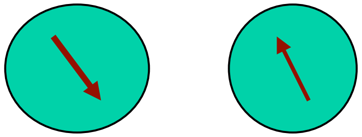
Fig. 1.6 An atom–atom model of a diatomic molecule.

- Total potential is the sum of atom-atom pair potentials
- Assumes molecules are rigid, in non-degenerate ground states. Interactions are weak so the internal structure is weakly affected by the environment.
- Geometry (steric effects) are important.
- Short-range effects-repulsion caused by cores: exp(-r/c)
- Perturbation theory as $r_{ij} >>$ 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)

$$C_6 = \int d\omega \alpha_A(\omega)\alpha_B(\omega)$$

Atomic systems

- Neutral rare gas atoms are the simplest atoms to find a potential for: attractive spheres.
  - Repulsion at short distances because of overlap of atomic cores.
  - Attraction at long distance do to the dipole-induced-dipole force. **Dispersion interaction is $c_6 r^{-6} + c_8 r^{-8} + \ldots$.**



  - 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 (e.g. Aziz potentials). 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.
  - Low density H_2 is almost like rare gas because angular degrees of freedom average out due to quantum effects. But H_2 has a much larger polarizability.

Lennard-Jones (2-body) potential

$$V(R) = \sum_{i<j} v(|r_i - r_j|) \qquad v(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

ε~ minimum

σ= wall of potential

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

Why these exponents: 6 and 12?

- There is only 1 LJ system!

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

•Reduced units:

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

–Lengths in σ : $x = r / \sigma$

–Time is mass units, pressure, density,..

See references on FS pgs. 51-54

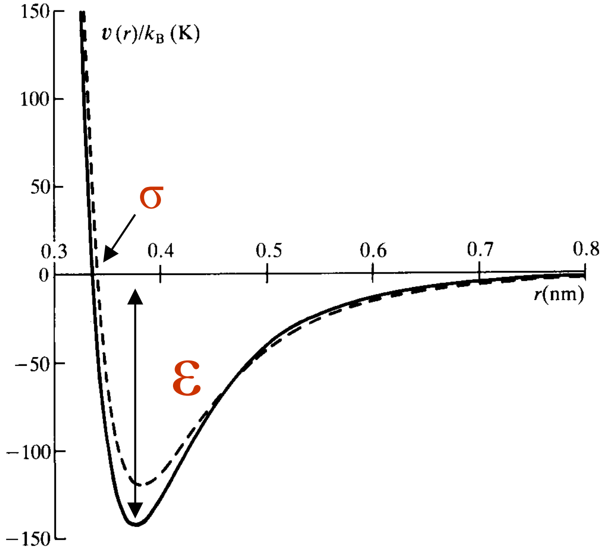


Fig. 1.3 Argon pair potentials. We illustrate the BBMS pair potential for argon (solid line) [Maitland and Smith 1971]. The BFW potential [Barker *et al.* 1971] is numerically very similar. Also shown is the Lennard-Jones 12–6 effective pair potential (dashed line) used in computer simulations of liquid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

Phase diagram of Lennard-Jones

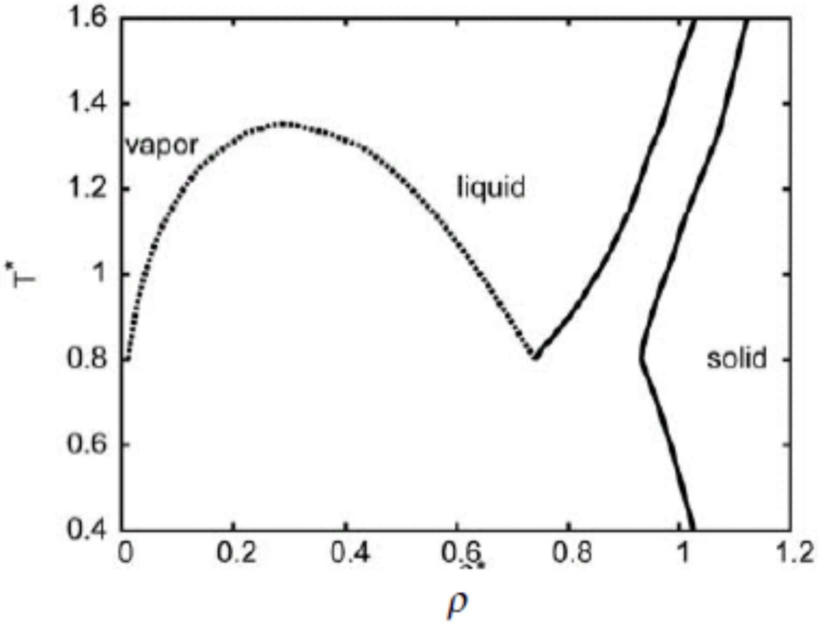
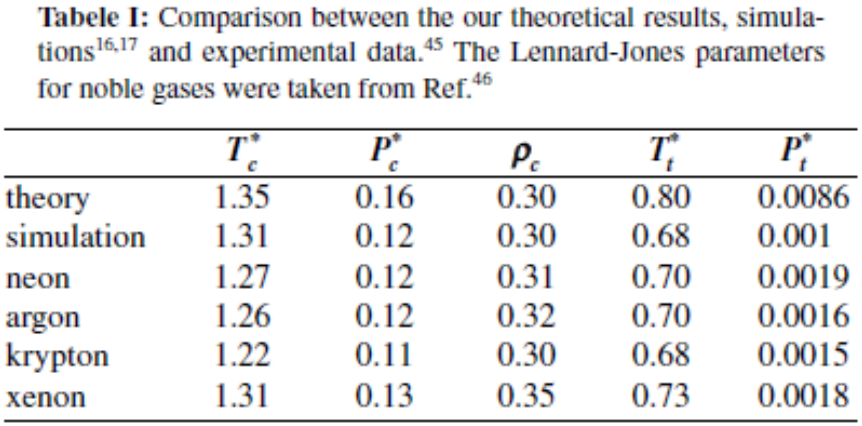


Figure 3: Phase diagram of the Lennard-Jones fluid: Reduced temperature as the function of the reduced density. The dashed line corresponds to the liquid-vapour coexistence line and the solid ones to solid-liquid and solid-vapour coexistence.



Tabele I: Comparison between the 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

A. Bizjak, T.Urbi and V. Vlachy *Acta Chim. Slov.* ***56****, 166–171 (2009)*

Comparison with experiment for rare gas solids

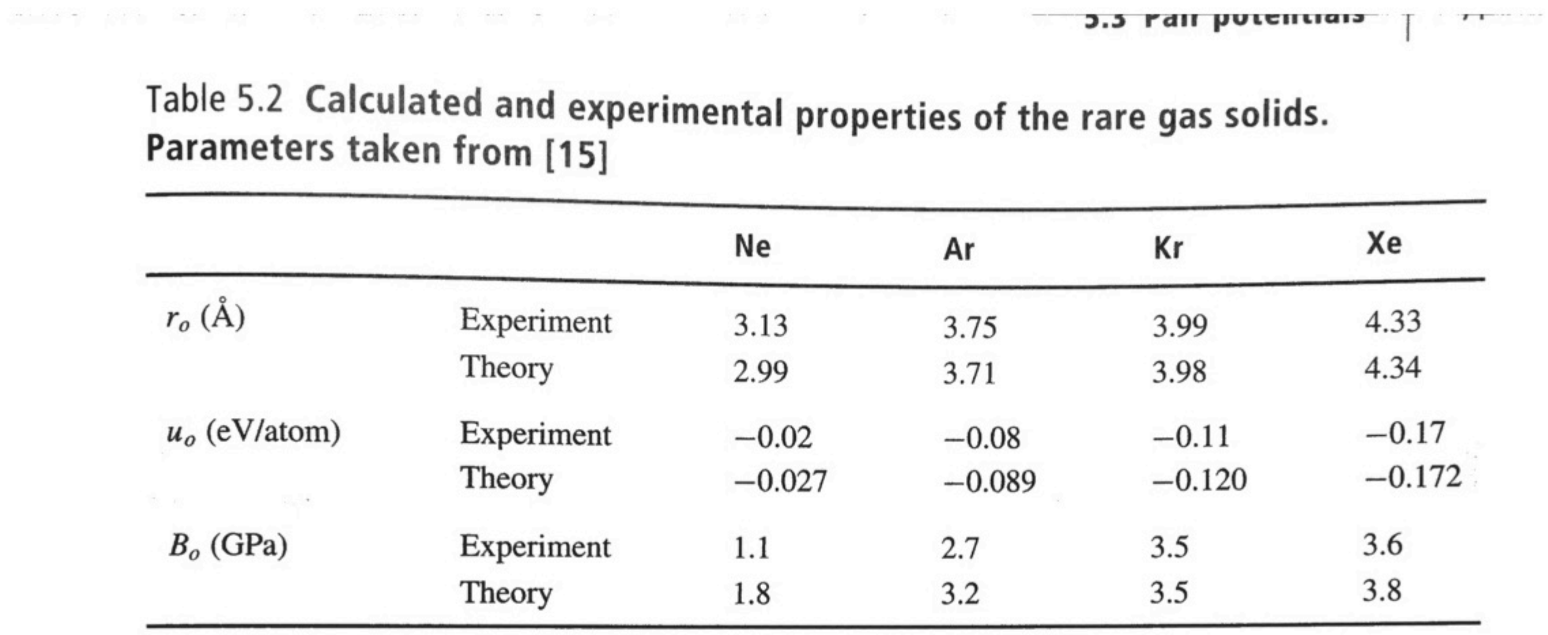


Table 5.2 **Calculated and experimental properties of the rare gas solids. Parameters taken from [15]**

		Ne	**Ar**	**Kr**	**Xe**
r_o (Å)	Experiment	3.13	3.75	3.99	4.33
	Theory	2.99	3.71	3.98	4.34
u_o (eV/atom)	Experiment	−0.02	−0.08	−0.11	−0.17
	Theory	−0.027	−0.089	−0.120	−0.172
B_o (GPa)	Experiment	1.1	2.7	3.5	3.6
	Theory	1.8	3.2	3.5	3.8

LJ Force Computation

```
! Loop over all pairs of atoms.
     do i=2,natoms
       do j=1,i-1
!Compute distance between i and j.
         r2 = 0
    do k=1,ndim
           dx(k) = r(k,i) - r(k,j)
!Periodic boundary conditions.
         if(dx(k).gt. ell2(k)) dx(k) = dx(k)-ell(k)
         if(dx(k).lt.-ell2(k)) dx(k) = dx(k)+ell(k)
           r2 = r2 + dx(k)*dx(k)
     enddo
```

```
!Only compute for pairs inside radial cutoff.
          if(r2.lt.rcut2) then
            r2i=sigma2/r2
            r6i=r2i*r2i*r2i
!Shifted Lennard-Jones potential.
            pot = pot+eps4*r6i*(r6i-1)- potcut
!Radial force.
            rforce = eps24*r6i*r2i*(2*r6i-1)
            do k = 1 , ndim
              force(k,i)=force(k,i) + rforce*dx(k)
              force(k,j)=force(k,j) - rforce*dx(k)
            enddo
          endif
        enddo
      enddo
```

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 ~N^2 iterations; reduce to ~N using neighbor tables.

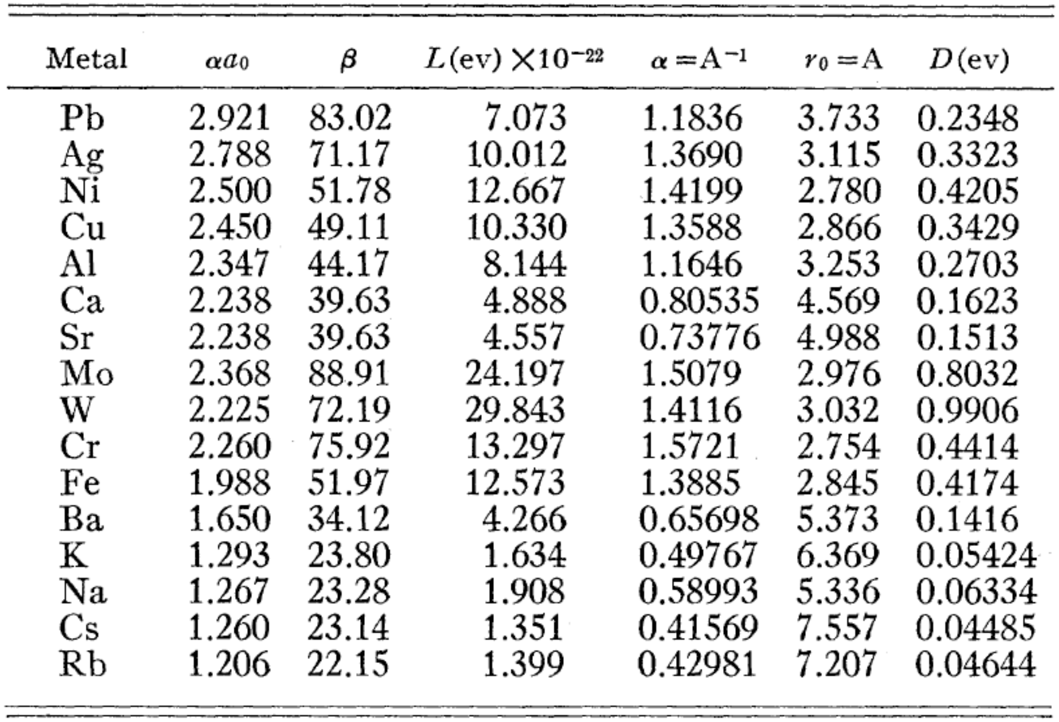
Morse potential

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

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

$$\left.\frac{dE}{dr}\right|_{r_0} = 0 \qquad B = -V\left.\frac{dP}{dV}\right|_{V_0} = V\left.\frac{d^2E}{dV^2}\right|_{V_0}$$

Morse potential: parameters



Metal	αa_0	β	L(ev) $\times 10^{-22}$	$\alpha = \text{A}^{-1}$	$r_0 = \text{A}$	D(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).

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
- Use cohesive energy and lattice constant (at T=0) to determine A and n

$$E_B = \frac{e_a}{d} + \frac{e_r A}{d^n} \qquad \frac{dE_B}{dd} = -\frac{e_a}{d^2} - \frac{n e_r A}{d^{n+1}} = 0$$

→ n=8.87 A=1500eV$^{8.87}$

- Now we need a check, say, the "bulk modulus".
  - We get 4.35 x 10^{11} dy/cm^2 Experiment = 2.52 x 10^{11} dy/cm^2
- You get what you fit for! Other properties might be wrong.

Various Other Empirical Potentials

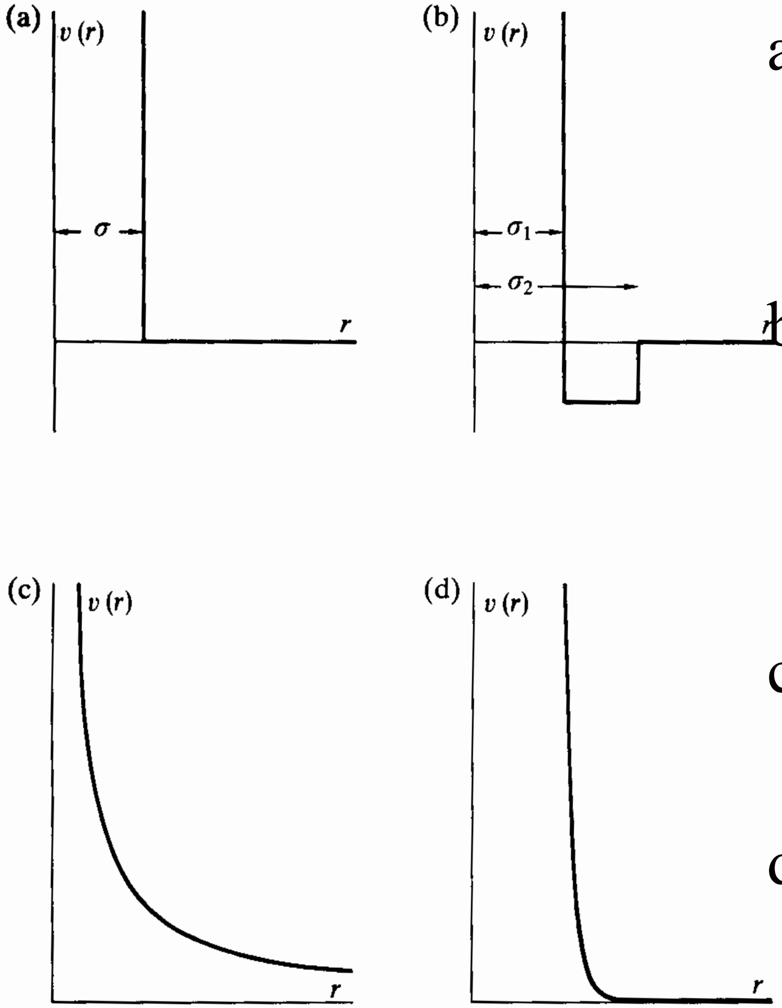


Fig. 1.4 Idealized pair potentials. (a) The hard-sphere potential; (b) The square-well potential; (c) The soft-sphere potential with repulsion parameter $\nu = 1$; (d) The soft-sphere potential with repulsion parameter $\nu = 12$.

a) Hard sphere -

simplest, first, no integration error using a specialized algorithm.

b) Hard sphere, square well

c) Coulomb (long-ranged), We will discuss later.

d) $1/r^{12}$ potential (short-ranged)

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. You need to provide a table of V(r) & dV(r)/dr.
- During computation, map interatomic distance to a grid and compute grid index and difference.
- Do table look-up and compute a (cubic) polynomial.
- Complexity is a memory fetch and a few flops/pair
- **Advantage**: Code is completely general-can handle any potential at the same cost.
- **Disadvantage**: some cost for memory fetch. Possible cache misses.

Failure of pair potentials

Property	Cu	Ag	Pt	Au	LJ
E_c/T_m	30	28	33	33	13
E_v/E_c	0.33	0.36	0.26	0.25	1
C_{12}/C_{44}	1.5	1.9	3.3	3.7	**1.000**

- 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

Metallic potentials (EAM)

- Have a 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 the Pauli principle.

$$\text{does } E \propto Z \text{ or } E \propto \sqrt{Z} \text{ for } Z = \text{coordination number ?}$$

- EXAMPLE: at a surface LJ potential predicts expansion but metals contract.
- Embedded Atom Model (EAM) or *glue models* work better.

Daw and Baskes, Phys. Rev. ***B 29****, 6443 (1984).*

- Use electron density as a fundamental parameter.

$$V(R) = \sum_{atoms} F(n_i) + \sum_{pairs} \phi(r_{ij}) \qquad n_i = \sum_j \rho\left(r_{ij}\right)$$

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

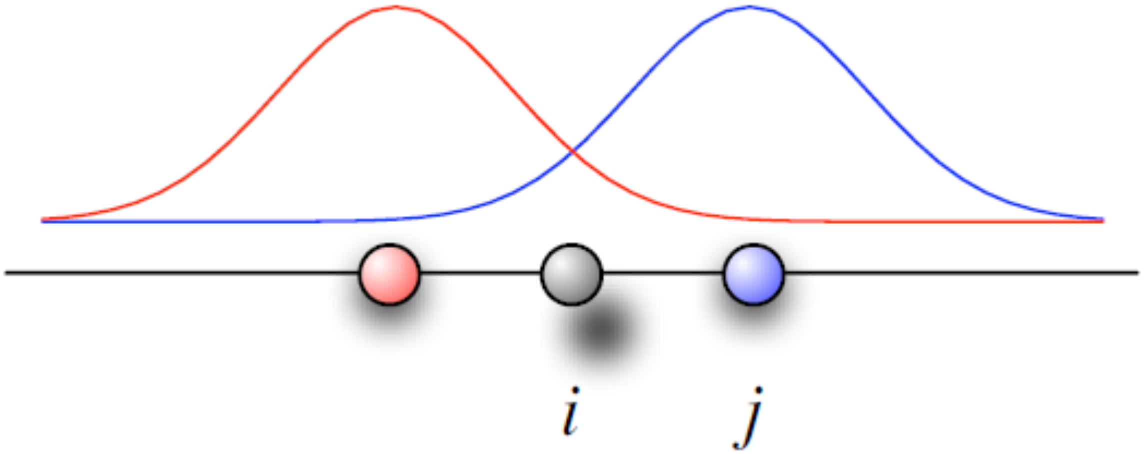
Embedded-atom potential

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

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

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

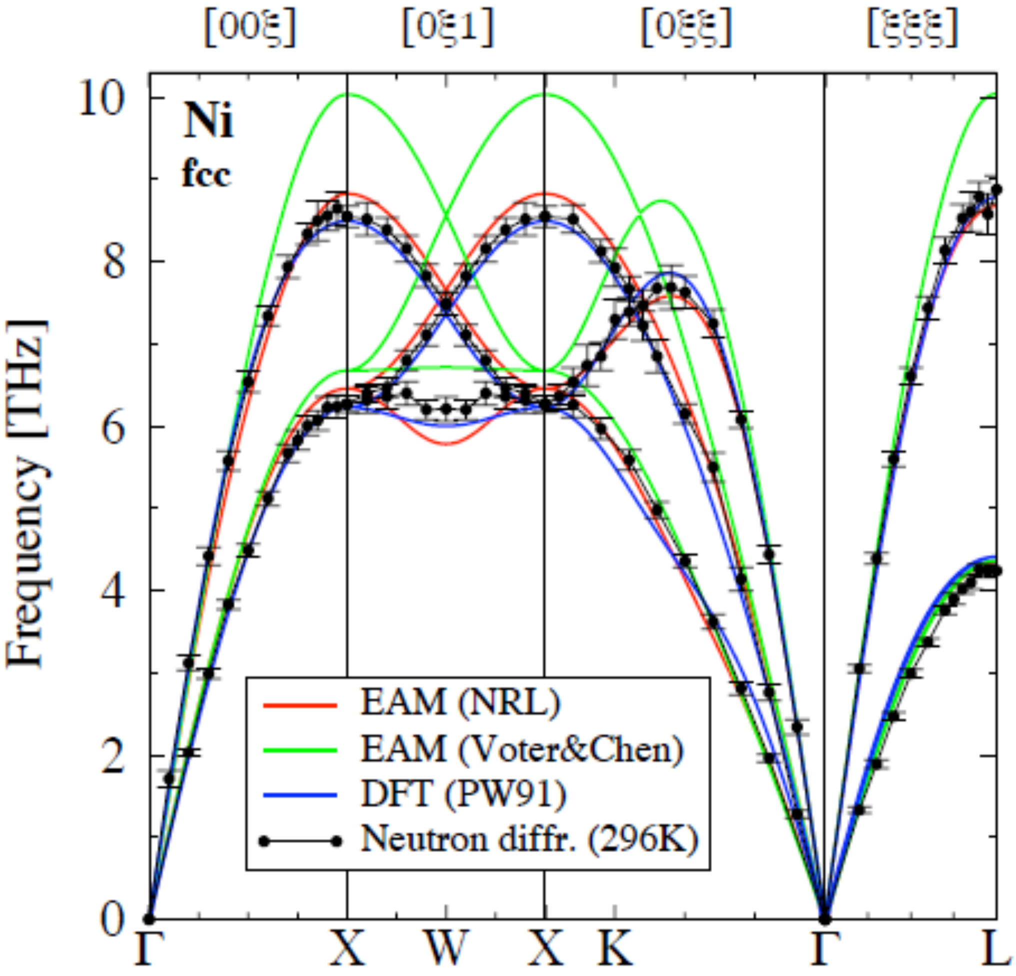


Accuracy of Embedded Atom Potentials

	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



Modified Embedded Atom Method

- Similar form to EAM with modified density function

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

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

- 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

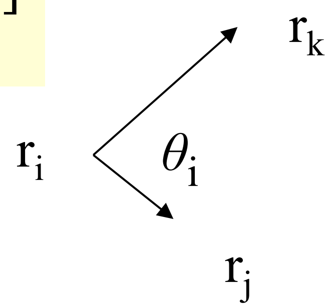
- Solid silicon cannot be described with a pair potential.
- Has open structure, with coordination 4!
- Tetrahedral bonding structure caused by the partially filled p-shell.
- Very stiff potential, short-ranged caused by localized electrons.
- ***Stillinger-Weber*** (Phys. Rev. **B 3**1, 5262, 1985) potential is fit from:
  lattice constant, cohesive energy, melting point, structure of liquid Si.

$$v_2 = (B/r^4 - A)e^{1/(r-a)}$$

for r<a

$$v_3 = \sum_{i,j,k} \lambda \mathrm{e}^{\gamma/(r_{ij}-a)+\gamma/(r_{ik}-a)}[\cos(\theta_i) + 1/3]^2$$

- Minimum at 109°



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: $v_n[1 - \cos(n\varphi)]$
  - All parameters taken from experiment.
  - Rules to decide when to use which parameter.
- Several *"force fields"* available
  - open source or commercial.

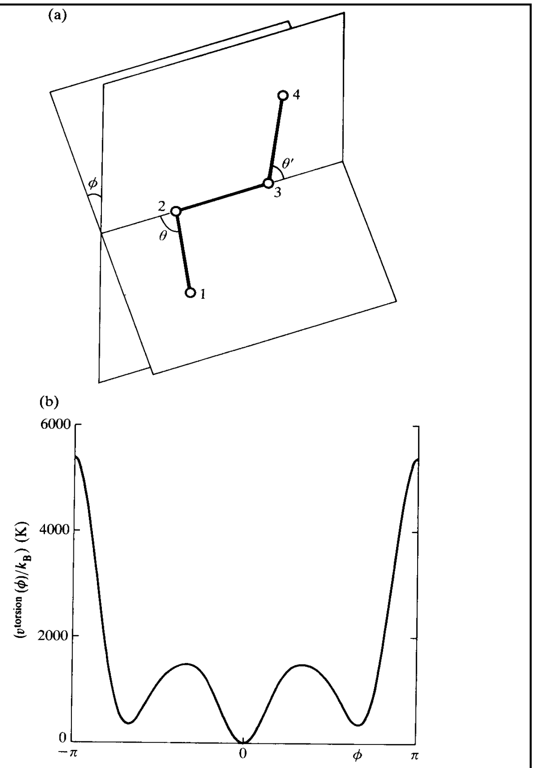
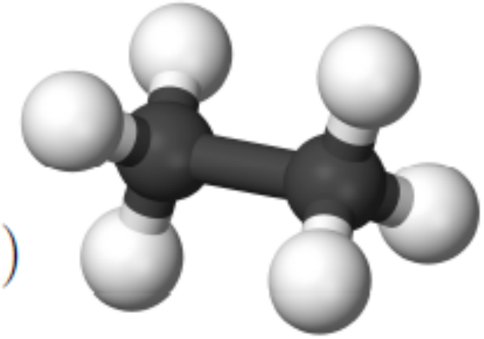


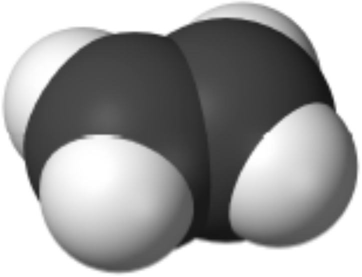
Fig. 1.8 (a) A model of butane [Ryckaert and Bellemans 1975]. (b) The torsional potential [Marechal and Ryckaert 1983].

More potentials for organic molecules

- Distinguish between bonded and non-bonded interactions



(1) Ethane $H_3C–CH_3$
  - 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 $H_2C=CH_2$
  - 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 = ±0.24) around it so it has a dipole moment
- Compare with phase diagram (melting and freezing), pair correlations, dielectric constant.
- But protons need a quantum description!

Mahoney & Jorgensen

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

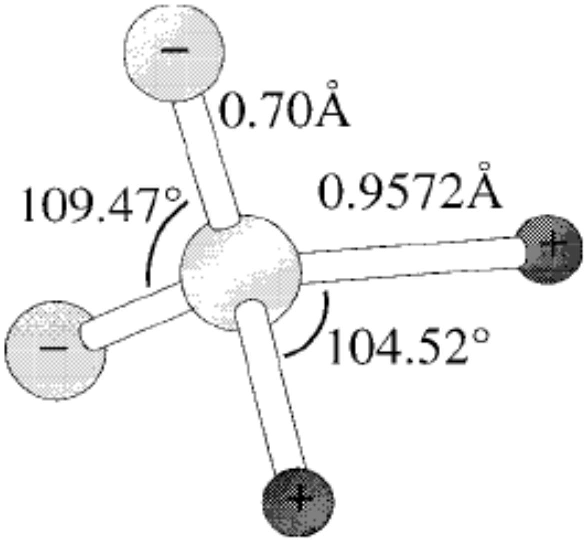


FIG. 1. TIP5P monomer geometry.

Potentials for Charged Systems

Start with pair potentials with Coulomb interactions

•Buckingham plus electrostatic Coulomb term

$$V(r) = Ae^{-r/B} + \frac{Q}{r} - Cr^{-6}$$

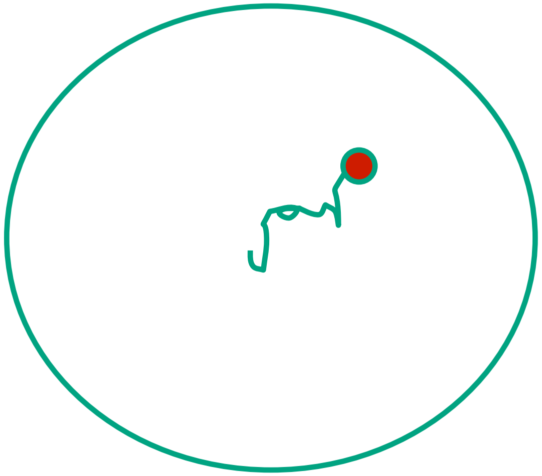
Include polarization of ions

•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

- The interaction is high dimensional function. It arises from quantum electronic effects 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 the potential.
- Do quantum chemical (SCF or DFT) calculations of snapshots. 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: sometimes the fine details of the potential are not important.

Summary of semi-empirical potentials

Potentials	Metals	Semi-conductors	Ionic materials	Polymers	Bio-materials	Organic materials	Noble Gases	Dimers
Lennard Jones							🟦	
Buckingham							🟦	
Morse								🟦
Embedded Atom	🟦							
Modified embedded atom	🟦	🟦						
Stillinger-Weber		🟦						
Amber				🟦	🟦	🟦		
Charmm				🟦	🟦	🟦		
MM3				🟦	🟦	🟦		
Buckingham + Coulomb			🟦					
Shell potentials			🟦					

Which potential 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 10^8atoms. 100fs or 10 ms)

Total error is the combination of:

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

- Can we use machine learning or neural network ideas to generate better semi-empirical potentials? Get lots of data from quantum calculations of snapshots and let the computer figure out the potential.