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”, \( V(R) \).
    \( V(q) \) 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. (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 ions and electrons:

\[
\begin{align*}
H &= -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i<j} e_i e_j r_{ij} + \text{external fields} \\
&\quad + \text{symmetry and boundary conditions}
\end{align*}
\]

“Atomic units”:

\( h = m_e = e = 1 \)

Energy in Hartrees=27.2eV=316,000K Lengths in Bohr radii= 0.529 A = 5.29 x 10^{-9}cm

\[
H = -\sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 + \sum_{a=1}^{N_i} \frac{1}{2(M_a/m_a) r_{ia}} \nabla_a^2 + \sum_{a<b} \frac{Z_a Z_b}{r_{ab}} - \sum_{i<j} \frac{Z_i Z_j}{r_{ij}} + \text{external fields} \\
&\quad + \text{symmetry and boundary conditions}
\]

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)*

\[
H = H_e + H_n \\
H_e = \sum_{i=1}^{N_e} \frac{1}{2} \sum_{j>i} Z_i Z_j \sum_{a} \frac{1}{R_a - r_{ij}} + \sum_{a} \frac{1}{r_{ii}} \\
H_n = \sum_{i=1}^{N_n} \frac{1}{2} \sum_{a} \left( \frac{M_a}{m_i} \right) r_{ii}^2
\]

\[\Psi(r \mid R) = \psi(r \mid R) \phi(R)\]  
**variational trial function**

\[H_e \psi(r \mid R) = E_{BO}(R) \psi(r \mid R)\]  
**BO energy surface**

\[\left( H_n + E_{BO}(R) \right) \phi(R) = E_{BO}(R) \phi(R)\]

\[\text{error}(E_{BO}) \approx O \left( \frac{m}{m_i} \right)^{3/2}\]  
**electronic energy \( \leq 10^{-5} \text{Ha} \)**

- **Does require classical ions** *(but MD assumes it)*
- **Eliminate the electrons 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
- 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?**

1/29/2013
Atom-Atom potentials

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

- 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 \( (C_6/r^6) \)

\[ C_6 = \int d\omega \alpha_A(\omega) \alpha_B(\omega) \]
Atomic systems

- Neutral rare gas atoms are the simplest atoms to find a potential for: 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 $c_6 r^{-6} + c_8 r^{-8} + \ldots$.
  - He-He interaction is the most accurate. Use all available low density data (virial coefficients, quantum chemistry calculations, transport coefficients, \ldots) 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

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

$$v(r) = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6$$

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

Why these exponents? 6 and 12?
- There is only 1 LJ system!
  $$v(x) = 4(12 - x^{-6})$$

Reduced units:
- Energy in $\varepsilon$: $T^*=k_B T/\varepsilon$
- Lengths in $\sigma$: $x=\sigma r/\sigma$
- Time is mass units, pressure, density,\ldots
See references on FS pgs. 51-54
Phase diagram of Lennard-Jones

![Phase diagram of Lennard-Jones](image)

Figure 3: Phase diagram of the Lennard-Jones fluid. Reduced temperature as a 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.


---

LJ Force Computation

```fortran
! 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) 
      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/r2i
      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
```

---

Table 1: Comparison between our theoretical results, simulations[40] and experimental data. The Lennard-Jones parameters for noble gases were taken from Ref.[36].

<table>
<thead>
<tr>
<th></th>
<th>(T^*_c)</th>
<th>(T^*_r)</th>
<th>(\rho^*_c)</th>
<th>(\rho^*_r)</th>
<th>(P^*_c)</th>
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<td>0.16</td>
<td>0.30</td>
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<td>0.12</td>
<td>0.30</td>
<td>0.68</td>
<td>0.001</td>
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<td>0.12</td>
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<td>0.70</td>
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<td>argon</td>
<td>1.26</td>
<td>0.12</td>
<td>0.32</td>
<td>0.70</td>
<td>0.0016</td>
</tr>
<tr>
<td>krypton</td>
<td>1.22</td>
<td>0.11</td>
<td>0.30</td>
<td>0.68</td>
<td>0.0015</td>
</tr>
<tr>
<td>xenon</td>
<td>1.31</td>
<td>0.13</td>
<td>0.55</td>
<td>0.73</td>
<td>0.0018</td>
</tr>
</tbody>
</table>
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

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

- 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 \( \varepsilon \)
- An extra parameter “a” that can be used to fit a third property: lattice constant \( (r_0) \), bulk modulus \( (B) \) and cohesive energy.

\[ \frac{dE}{dr} \bigg|_{r_0} = 0 \quad B = -V \frac{dP}{dV} \bigg|_{V_0} = V \frac{d^2E}{dV^2} \bigg|_{V_0} \]
Morse potential: parameters

<table>
<thead>
<tr>
<th>Metal</th>
<th>$u_0$</th>
<th>$b$</th>
<th>$L(\infty) \times 10^{-8}$</th>
<th>$a = A^{-1}$</th>
<th>$r_s = A$</th>
<th>$D_{rev}$</th>
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</thead>
<tbody>
<tr>
<td>Pb</td>
<td>2.921</td>
<td>83.02</td>
<td>7.073</td>
<td>1.1436</td>
<td>3.733</td>
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<td>Ag</td>
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<td>10.012</td>
<td>1.3900</td>
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<td>Al</td>
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<td>W</td>
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<td>1.4116</td>
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<tr>
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<td>Fe</td>
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<td>51.97</td>
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<tr>
<td>Ba</td>
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<td>4.266</td>
<td>0.65698</td>
<td>5.375</td>
<td>0.1416</td>
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<tr>
<td>K</td>
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<td>1.634</td>
<td>0.49762</td>
<td>6.369</td>
<td>0.08324</td>
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<td>Na</td>
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<td>23.28</td>
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<td>0.58993</td>
<td>5.536</td>
<td>0.06334</td>
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<tr>
<td>Cs</td>
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<td>0.41160</td>
<td>7.537</td>
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<td>22.15</td>
<td>1.399</td>
<td>0.42983</td>
<td>7.207</td>
<td>0.04644</td>
</tr>
</tbody>
</table>


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)

![Idealized pair potentials](image)

Fig. 1.4 Idealized pair potentials. (a) The hard-sphere potential. (b) The square-well potential. (c) The soft-sphere potential with repulsion parameter $s = 1$. (d) The soft-sphere potential with repulsion parameter $s = 12$. 1/29/2013
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
- Obviously $Z_i = \pm 1$ on simple cubic structure/alternating charges
- Use cohesive energy and lattice constant (at $T=0$) to determine $A$ and $n$

$$E_B = \frac{e^2}{4} + \frac{e}{d} A$$
$$\frac{dE_B}{dd} = -\frac{e}{d^2} - \frac{ne A}{d^{n+1}} = 0$$

$$\Rightarrow n = 8.87 \quad A = 1500eV^{[8.87]}$$

- Now we need a check, say, the “bulk modulus”.
  - We get $4.35 \times 10^{11} \text{dy/cm}^2$  
  - **Experiment** = $2.52 \times 10^{11} \text{dy/cm}^2$
- 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. e.g. $V(ri), dV/dr$ 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

- $E_c = \text{cohesive energy}$ and $E_v = \text{vacancy formation energy}$
- $T_m = \text{melting temperature}$

- $C_{12}$ 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

<table>
<thead>
<tr>
<th>Property</th>
<th>Cu</th>
<th>Ag</th>
<th>Pt</th>
<th>Au</th>
<th>LJ</th>
</tr>
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<tr>
<td>$E_c/T_m$</td>
<td>30</td>
<td>28</td>
<td>33</td>
<td>33</td>
<td>13</td>
</tr>
<tr>
<td>$E_v/E_c$</td>
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<td>0.36</td>
<td>0.26</td>
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<td>1</td>
</tr>
<tr>
<td>$C_{12}/C_{44}$</td>
<td>1.5</td>
<td>1.9</td>
<td>3.3</td>
<td>3.7</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Metallic potentials

- 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 Pauli principle.
  
    does $E \propto Z$ or $E \propto \sqrt{Z}$ 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.
  

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

- 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

\[ E_{\text{coh}} = \sum_i E_i(\rho_i) + \frac{1}{2} \sum_{i,j} V(R_{ij}) \]

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

Accuracy of Embedded Atom Potentials

<table>
<thead>
<tr>
<th>Element</th>
<th>EAM</th>
<th>Experiment</th>
<th>EAM</th>
<th>Experiment</th>
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</thead>
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<tr>
<td>Cu</td>
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<td>16.7</td>
<td>2.02</td>
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</tr>
<tr>
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<tr>
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<tr>
<td>Pd</td>
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<tr>
<td>Pt</td>
<td>7.8</td>
<td>8.95</td>
<td>2.63</td>
<td>2.66</td>
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</tbody>
</table>
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

\[ E_{\text{coh}} = \sum_i F_i(\rho_i) - \frac{1}{2} \sum_i \sum_{j \neq i} V(R_{ij}) \]

- Embedding energy
- 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 electrons.
- **Stillinger-Weber** (Phys. Rev. B 31, 5262, 1985) potential fit from:
  - Lattice constant, cohesive energy, melting point, structure of liquid Si
  - Stillinger-Weber potential:
    \[
    v_2 = \frac{B}{r^4} - A e^{\frac{1}{2}(r-a)} \quad \text{for } r<a
    \]
    \[
    v_3 = \sum_{i,j,k} \lambda e^{\gamma/(r_i-\alpha) + \gamma/(r_k-\alpha)} [\cos(\theta_i) + 1/3]^2
    \]
- 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: \( k_i (r_i - r_j)^2 \)
  - Bond angle potential \( k_j (\theta_i - \theta_j)^2 \)
  - 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).
More potentials for organic molecules

- Distinguish between bonded and non-bonded interactions

1. Ethane $\text{H}_2\text{C} \cdot \text{CH}_3$
   - Torsion of $\text{C} \cdot \text{C}$ bond
   - Staggered versus eclipsed configuration has different energy
   - Requires four-body potential $V_{\text{t} \text{o} \text{r} \text{s} \text{i} \text{o} \text{n}} = K \cdot \cos(3\theta)$

2. Ethene $\text{H}_2\text{C} \equiv \text{CH}_2$
   - Double bond between $\text{C} \equiv \text{C}$ has different strength than single bond $\text{C} \cdot \text{C}$ 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

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

Potentials for Charged Systems

Start with pair potentials with Coulomb interactions
• Buckingham plus electrostatic Coulomb term

\[ V(r) = A e^{-r/\beta} + \frac{Q}{r} - C r^{-6} \]

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

• 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 10 ms)

**Total error is the combination of:**
- **statistical error** (the number of time steps)
- **systematic error** (the potential)