Short Course on Molecular Dynamics Simulation

Lecture 2:
Potential Energy Functions

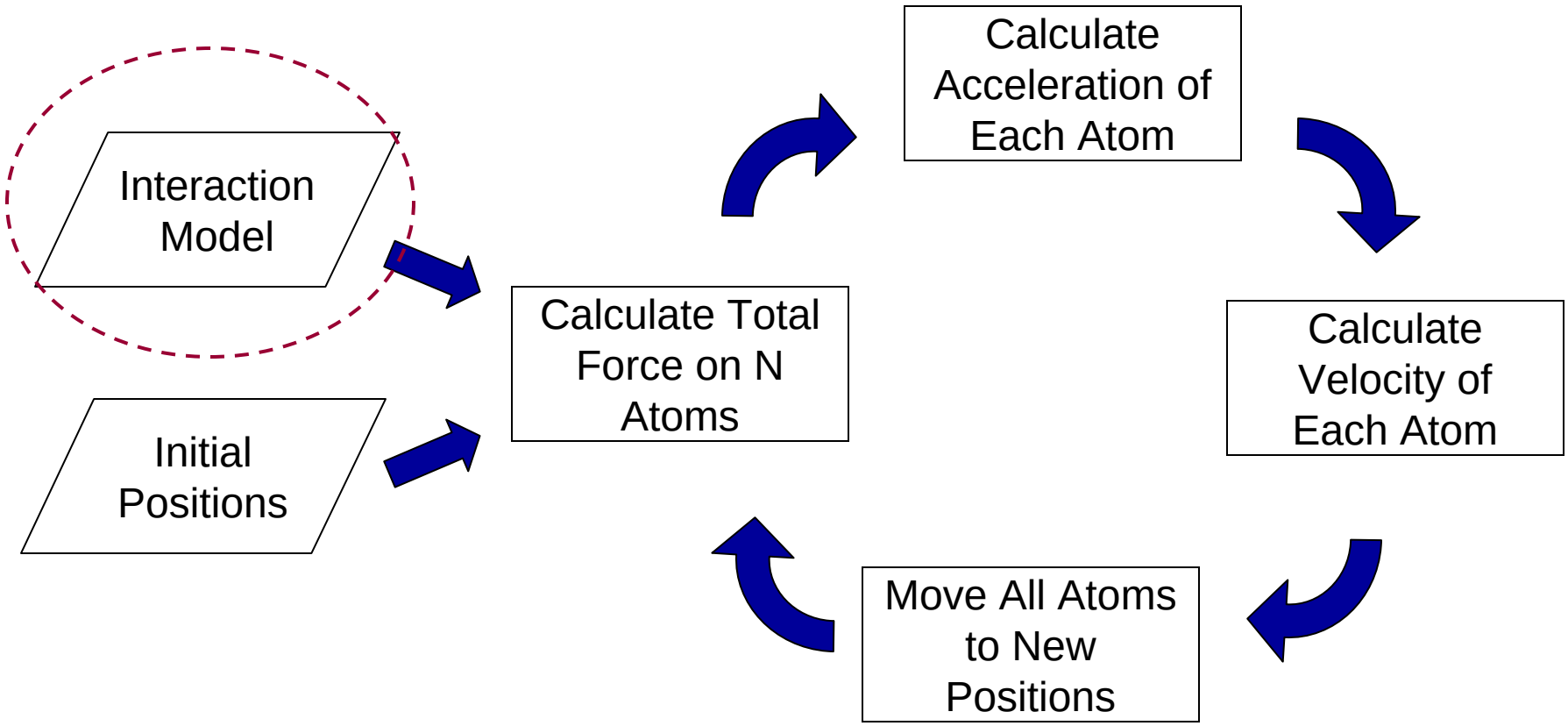
Professor A. Martini
Purdue University

High Level Course Outline

1. MD Basics
2. Potential Energy Functions
3. Integration Algorithms
4. Temperature Control
5. Boundary Conditions
6. Neighbor Lists
7. Initialization and Equilibrium
8. Extracting Static Properties
9. Extracting Dynamic Properties
10. Non-Equilibrium MD

MD Basics

- Process summary

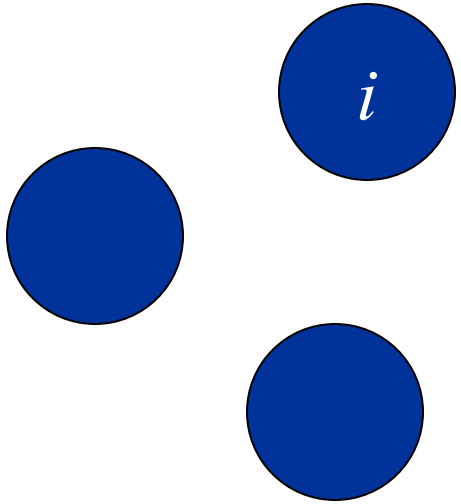


Interaction Models

$$ma = F$$

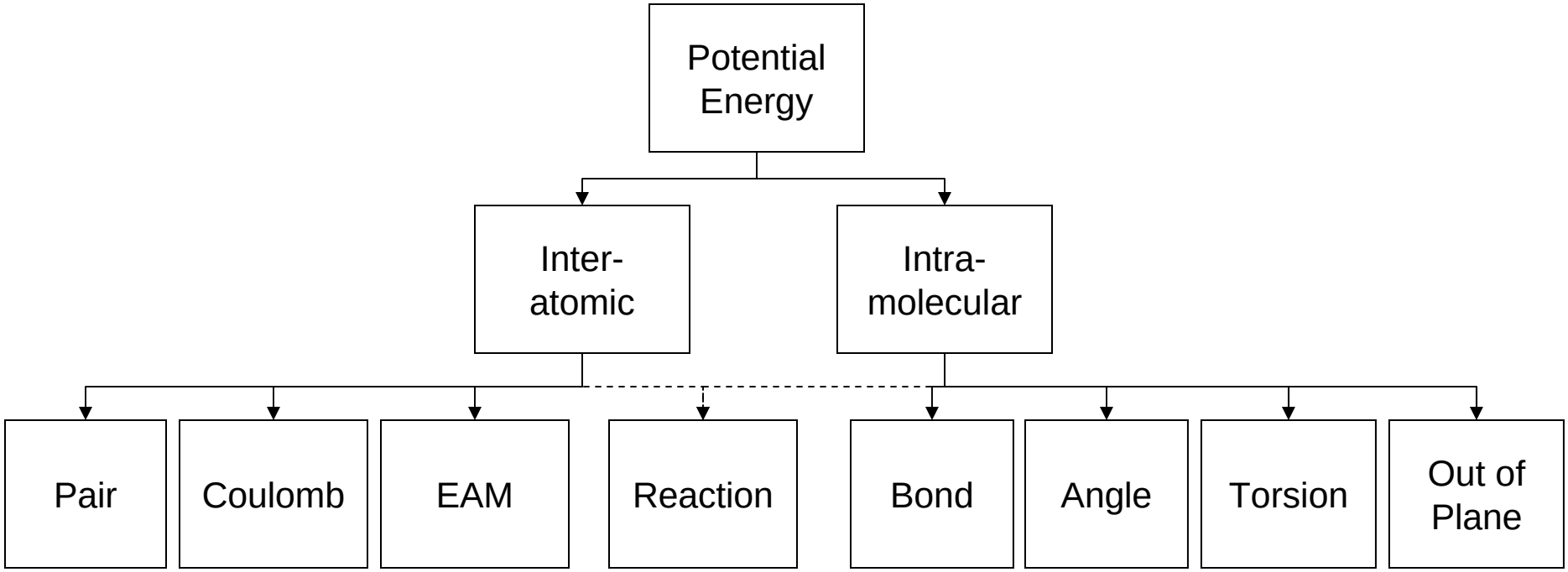
$$a = \frac{dv}{dt} \qquad v = \frac{dr}{dt}$$

$$F = \frac{dU}{dr}$$



Interaction force is the spatial derivative of the potential energy

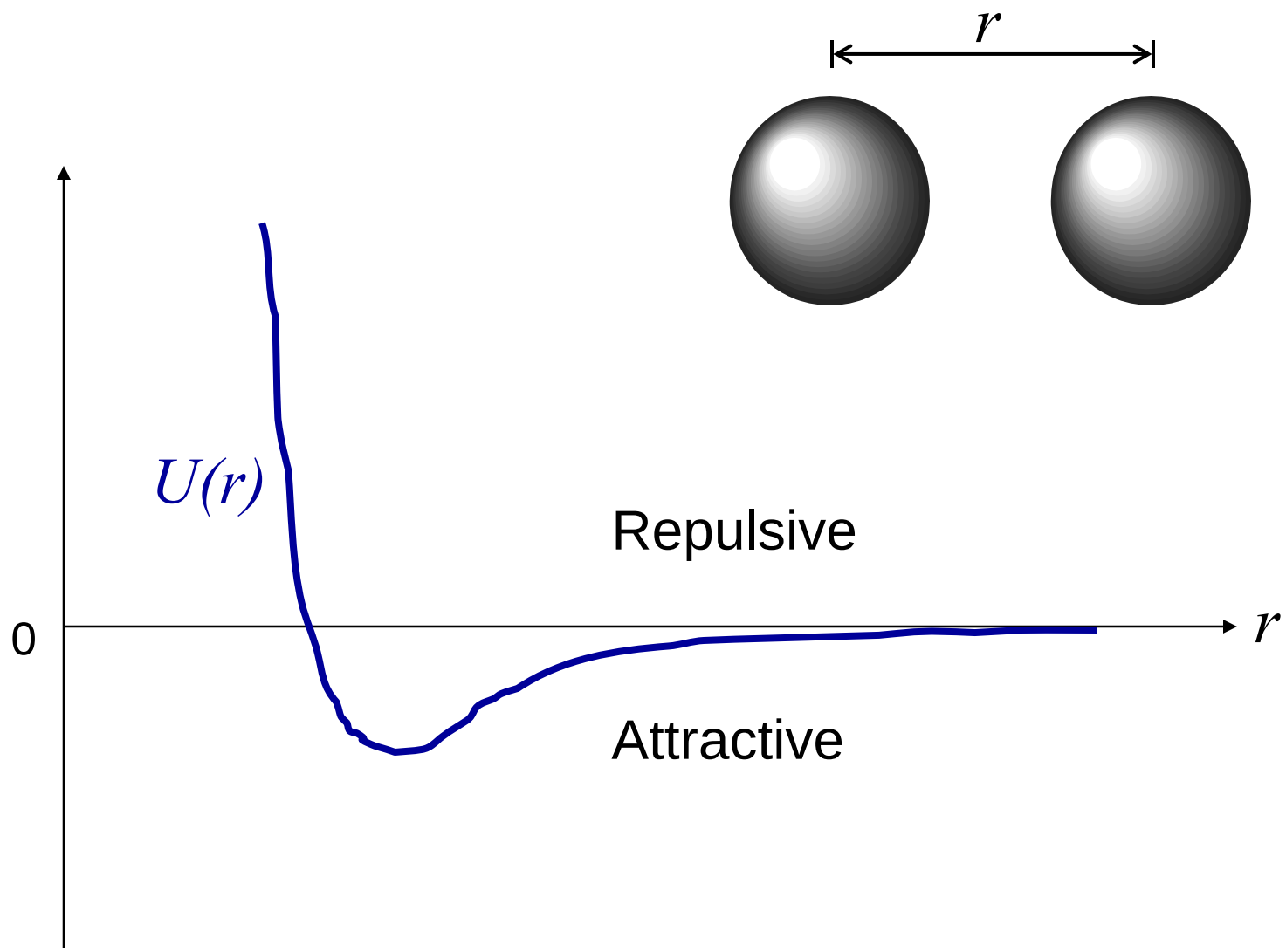
Interaction Models



Pair Potentials

- Pair potentials – van der Waals interactions
  - Attraction
    - Act at long distances
    - Dispersive forces
    - Due to instantaneous dipoles that arise during the fluctuations in the electron cloud
  - Repulsion
    - Act at short distances
    - Exchange forces or overlap forces
    - Overlap of electron clouds such that nuclei are less well shielded by electrons

Pair Potentials



Pair Potentials

- Pair potentials
  - General Form

$$U(r) = k\varepsilon\left(\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m\right) \qquad k = \frac{n}{n-m}\left(\frac{n}{m}\right)^{m/(n-m)}$$

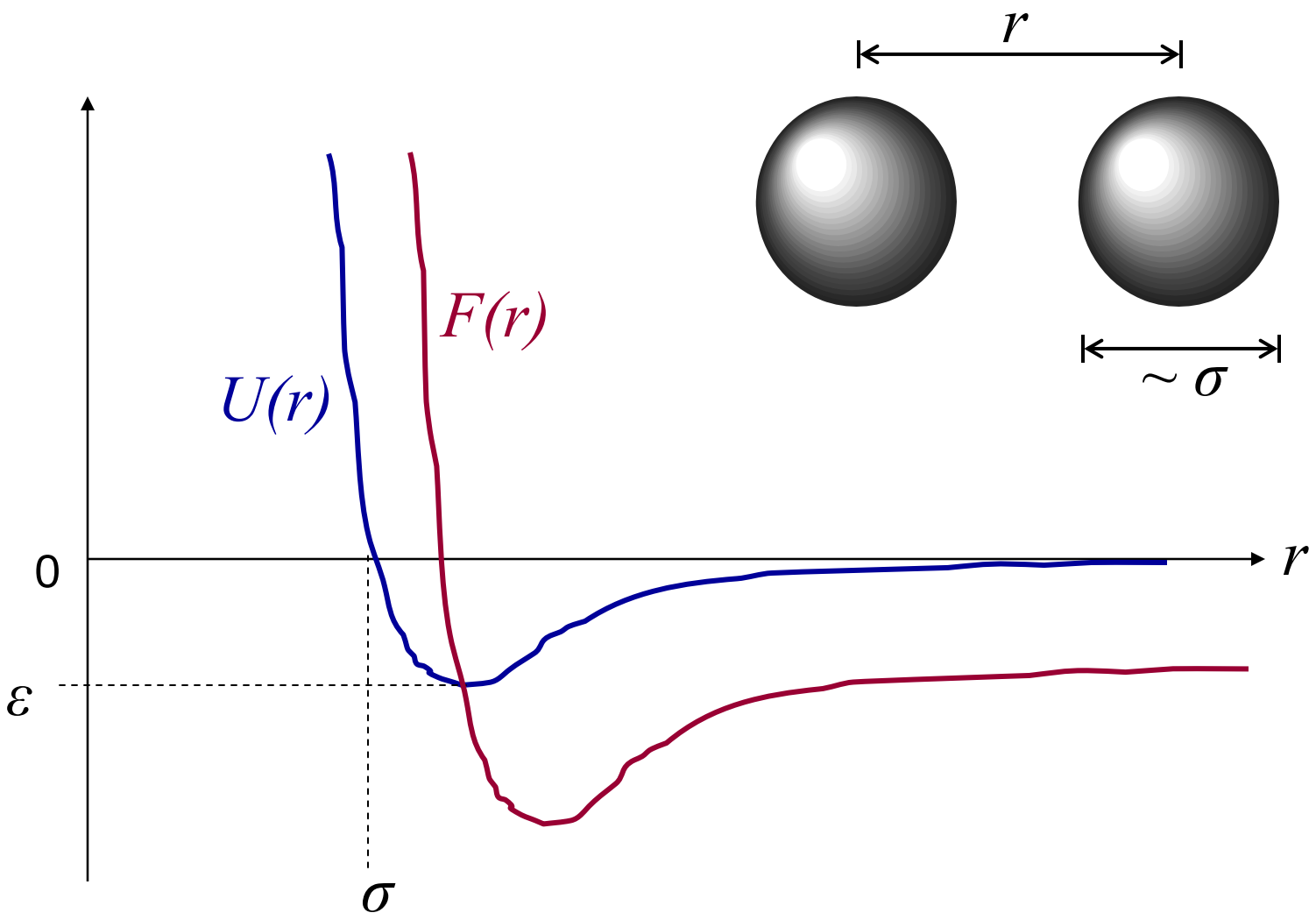
Repulsive Attractive

  - Lennard-Jones (n=12, m=6)

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

$$F_{LJ}(r) = -\frac{dU(r)}{dr} = 24\frac{\varepsilon}{\sigma}\left(2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7}\right)$$

Pair Potentials



Pair Potentials

- Truncation
  - The Lennard-Jones force (and similar models) decays rapidly with distance
  - Significant computation time can be saved by neglecting pair interactions beyond a cut-off

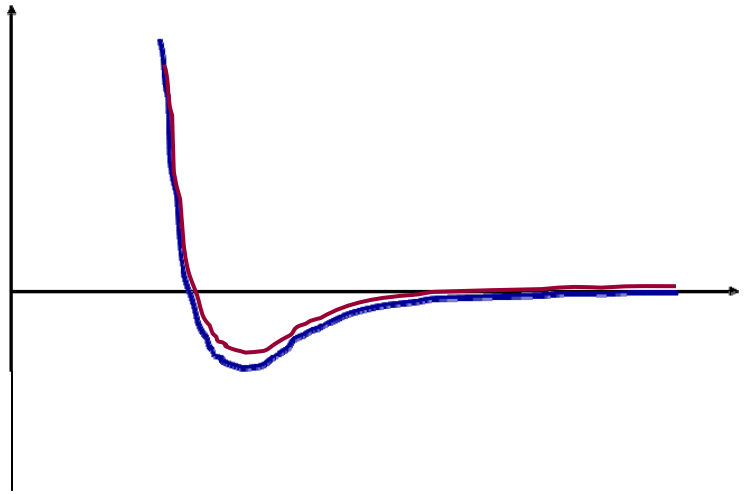
$$U_{LJ,t}(r) = \begin{cases} 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) & r \le r_c \\ 0 & r > r_c \end{cases}$$

  - Commonly, r_c = 2.5 σ

Pair Potentials

- Truncated and shifted
  - The potential energy vanishes at the cut off radius
  - No discontinuity → no impulsive force

$$U_{LJ,t-s}(r) = \begin{cases} U_{LJ}(r) - U_{LJ}(r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$



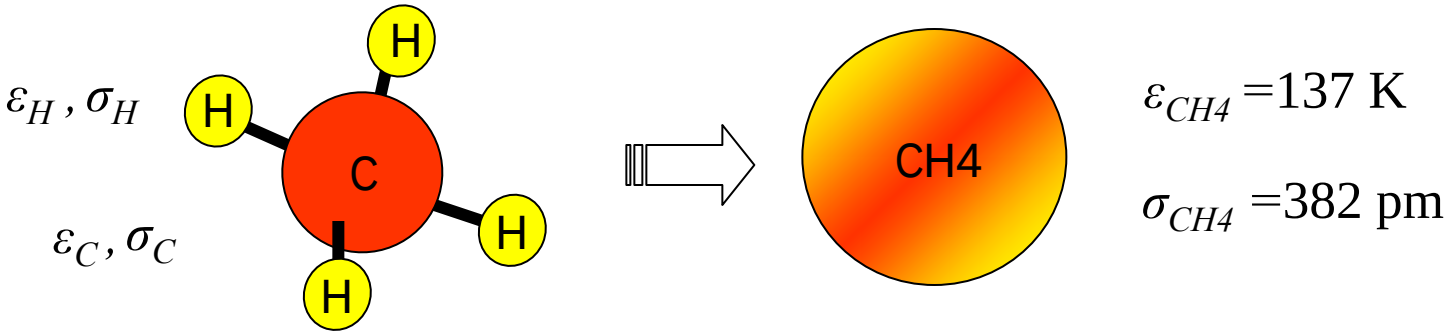
  - Shift must be taken into account in all post-processing calculations

Pair Potentials

- Typical values of LJ constants

Atom	ε/k_B (K)	σ (pm)
He	10.22	258
Ne	35.7	279
Ar	124	342

- The united atom model



Pair Potentials

- Combination rules
  - Relate LJ parameters for an unlike pair (i-j) to the parameters of two like pairs (i-i and j-j)

1. $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ $\qquad$ $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$

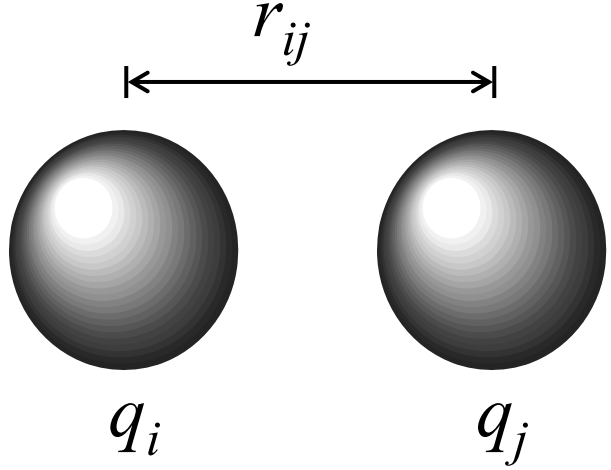
2. $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ $\qquad$ $\sigma_{ij} = \dfrac{\sigma_i + \sigma_j}{2}$

3. $\varepsilon_{ij} = \dfrac{2\sigma_i^3 \sigma_j^3 \sqrt{\varepsilon_i \varepsilon_j}}{\sigma_i^6 + \sigma_j^6}$ $\qquad$ $\sigma_{ij} = \left(\dfrac{\sigma_i^6 + \sigma_j^6}{2} \right)^{1/6}$

Coulombic Interactions

- Coulombic interactions
  - Included if electrostatics between atoms are significant
  - Atomic charges q_i and q_j

$$U_{coulomb} = \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}}$$



Coulombic Interactions

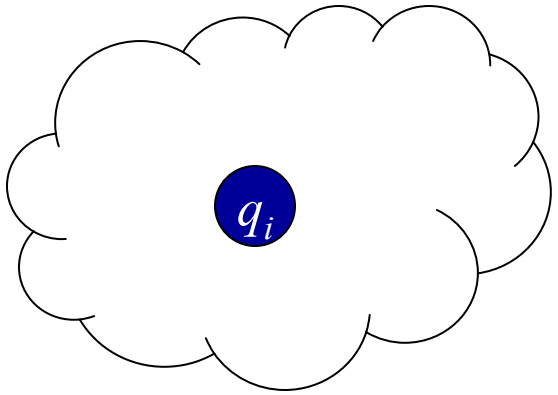
- In general, the contribution of the tail of a truncated potential is

$$U^{tail} = \frac{N\rho}{2}\int_{r_c}^{\infty} U(r) 4\pi r^2 dr$$

- Coulombic force decays slower than r^{-3}
- Methods for calculating the long-range contributions
  - Ewald summation
  - Fast multipole methods
  - Particle-mesh-based methods

Coulombic Interactions

- Ewald sums
  - Assume every particle i with charge q_i is surrounded by a diffuse charge distribution of opposite sign

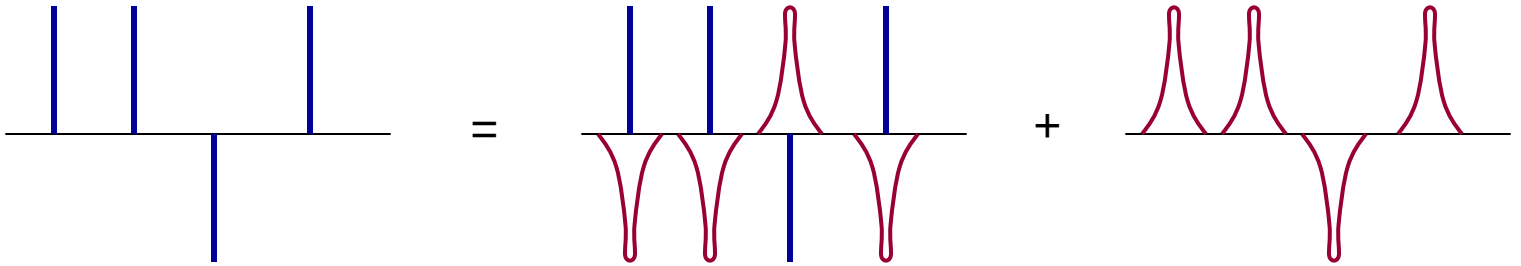


  - Electrostatic potential due to i is exclusively due to the fraction of q_i that is not screened by the cloud
  - This fraction rapidly decays to zero

Coulombic Interactions

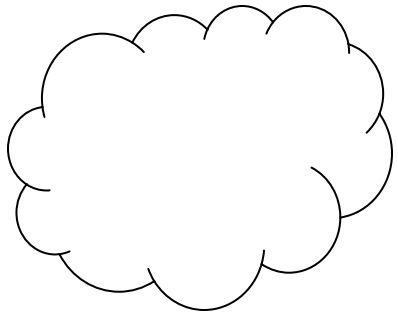
- Contribution to the electrostatic potential due to a set of screened charges can be found by direct summation because it decays rapidly with distance
- But we want to evaluate the contribution from *point* charges, not *screened* charges
- So we correct for the screening clouds by introducing a smooth, compensating charge density

point charges = (point charges + screening cloud) + compensating cloud



Coulombic Interactions

- Compensating charge distribution surrounding i is a Gaussian of width $\sqrt{2/\alpha}$



$$\rho_{Gauss}(r) = -q_i(\alpha/\pi)^{\frac{3}{2}} \exp\left(-\alpha r^2\right)$$

- Finally

$$U_{Coulomb} = \frac{1}{2V}\sum_{k\neq 0}\frac{4\pi}{k^2}\left|\rho(k)\right|^2 \exp\left(-k^2/4\alpha\right)$$

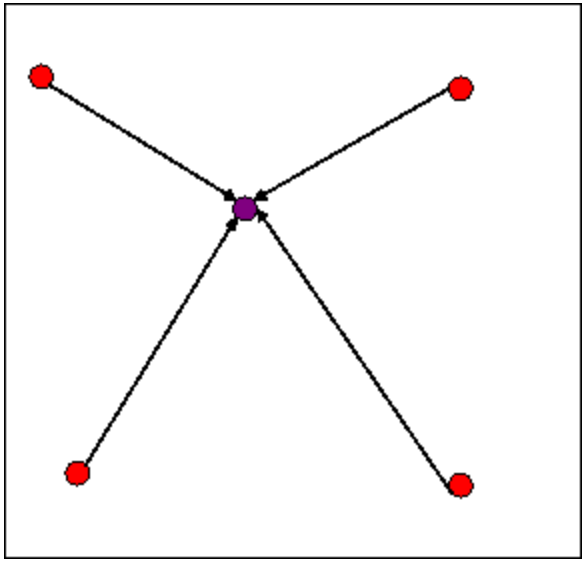
$$-(\alpha/\pi)^{\frac{1}{2}}\sum_{i=1}^{N} q_i^2$$

$$+\frac{1}{2}\sum_{i\neq j}^{N}\frac{q_i q_j \, erfc\left(\sqrt{\alpha} r_{ij}\right)}{r_{ij}}$$

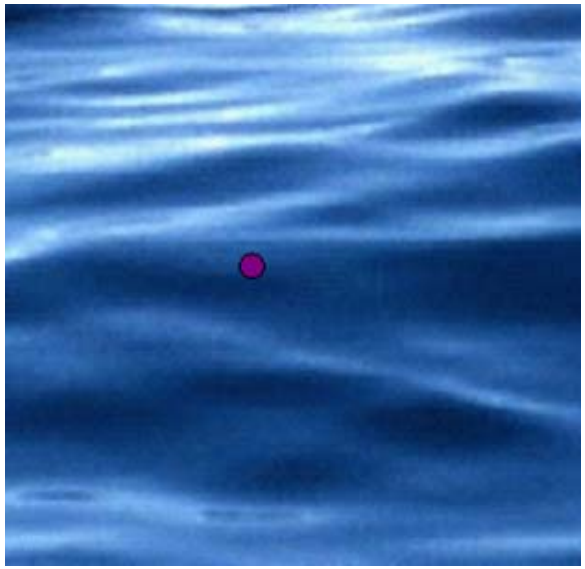
Embedded Atom Model

- Metals have ionized atom cores with a “sea” of delocalized valence electrons

Pair Potential



Electron Sea



Embedded Atom Model

- Model formulation

$$E_{total} = \sum_i F(\rho_i) + \frac{1}{2} \sum_{i,j(i \neq j)} \phi(r_{ij}) \qquad \rho_i = \sum_j f(r_{ij})$$

  - ρ_i : electron density at atom i
  - $F(\rho_i)$: embedding function
  - $\varphi(r_{ij})$: pair potential between atoms i and j
  - $f(r_{ij})$: electron density function at atom i due to atom j

- Three look-up tables

r_{ij}	$f(r_{ij}) - -electron density function$
ρ_i	$F(\rho_i) - -embedding fuction$
r_{ij}	$\phi(r_{ij}) - -pair potential function$

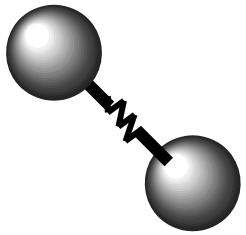
Reactive Potentials

- Some potentials model chemical reactions
  - Bond formation
  - Bond disassociation
- Common examples
  - Tersoff
  - REBO (reactive empirical bond order)
- Models developed for
  - Silicon
  - Carbon
  - Oxygen
  - Hydrogen

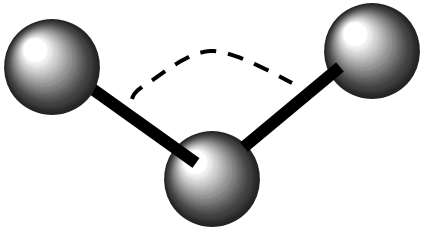
Intramolecular Interactions

- For multi-atomic molecules, models describe the behavior of covalent bonds

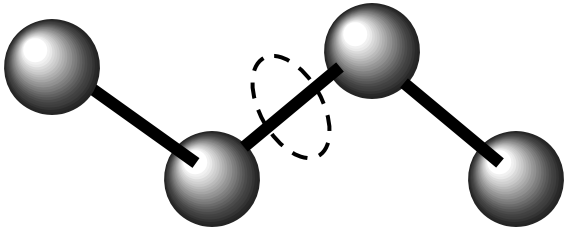
Bond



Angle



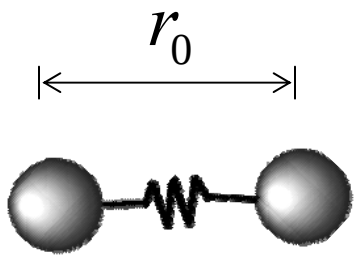
Torsion



Intramolecular - Bond

- Bond stretching models
  - Harmonic bond model where k is the "spring constant"

$$U_{bond} = \frac{k}{2}\left(r - r_0\right)^2$$



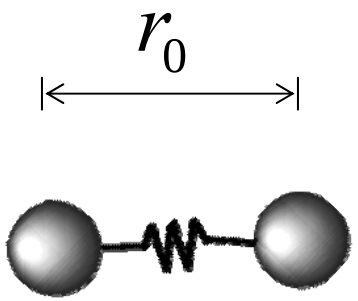
  - What is r_0
    - Reference bond length – value of bond when all other terms in the force field are zero
    - Equilibrium bond length – value when other terms contribute

Bond	r0 (A)	K (kcal/mol/A^2)
C-C	1.523	317
C=C	1.337	690

Intramolecular - Bond

- Bond stretching models
  - Morse bond potential where D is the potential well depth, α is a stiffness constant, and r_0 is the equilibrium bond distance
  - Better handling of large displacements

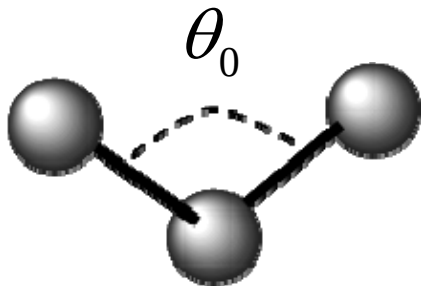
$$U_{bond} = D\left[1 - e^{-\alpha(r - r_0)}\right]^2$$



Intramolecular - Angle

- Bond angle models
  - Harmonic angle model

$$U_{angle} = k(\theta - \theta_0)^2$$



  - Cosine angle models

$$U_{angle} = k[1 + \cos(\theta)]$$

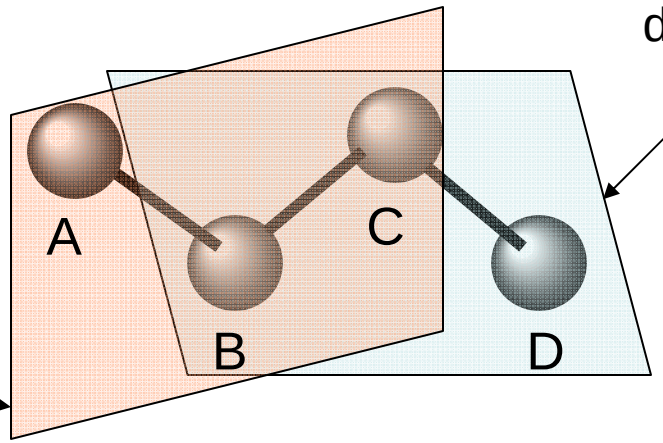
  - For all of these, k is energy constant and θ_0 is the equilibrium angle

Intramolecular - Torsion

- Torsion models (dihedrals)
  - Harmonic torsion angle

$$U_{torsion} = k\left[1 + d\cos\left(n\phi\right)\right]$$

ϕ is the angle between Plane 1 and Plane 2



Intramolecular – Out of Plane

- Out of plane models
  - The least common of the intramolecular potentials
  - Describes energy associated with the displacement of atoms out of their equilibrium plane
  - Relevant only to parts of molecules where atoms are known to lie in the same plane

$$U_{oop} = kh^2$$