MSE6701H Multiscale Materials Modeling and Simulation

Lecture 07

Interatomic Potentials

Lingti Kong (孔令体)

Shanghai Jiao Tong University
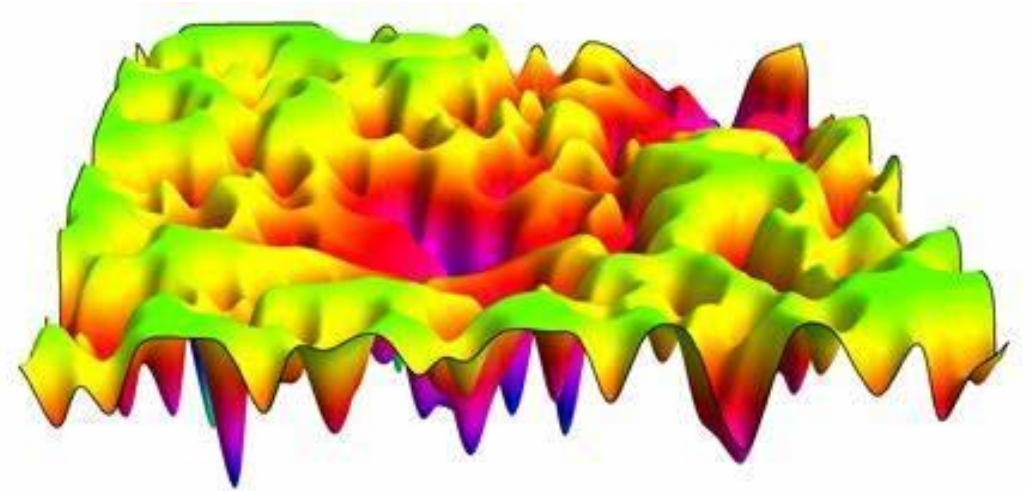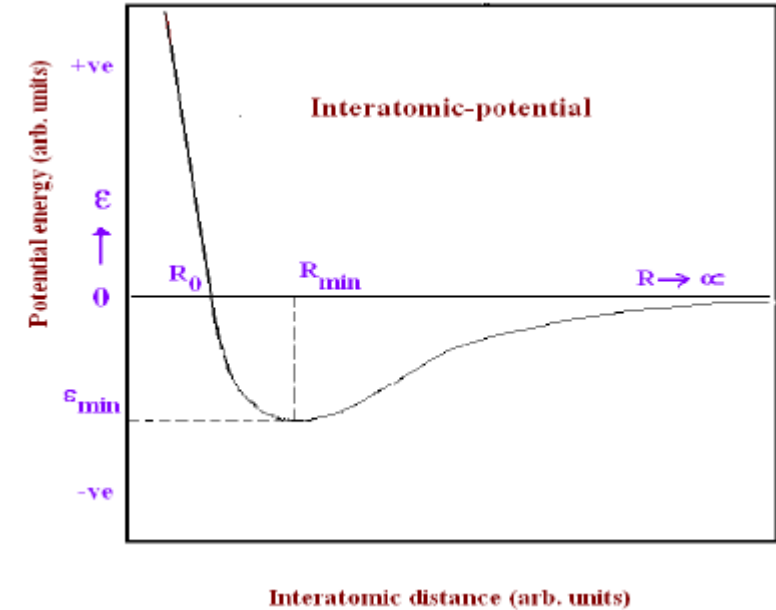
Molecular Dynamics Simulation

$$f = ma = m\ddot{r}$$

$$U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$

$$\vec{f}_i = -\frac{\partial U}{\partial \vec{r}_i} = -\sum_{j \neq i} \frac{\partial U}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \vec{r}_i}$$

Potential is vital to MD.

Bonding in Materials

Material	Primary bonding	Minor bonding
Metals	Metallic	Covalent; physical
Ceramics	Ionic; covalent	physical
Polymer	Covalent; physical; hydrogen	
Rare gas	Physical	

Energy of a system

Total interaction energy of N interacting particles:

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \sum_{i=1}^{N} \phi_1(\mathbf{r}_i) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \phi_2(\mathbf{r}_i \mathbf{r}_j)$$

$$+ \frac{1}{6} \sum_{i=1}^{N} \sum_{j \neq i} \sum_{k \neq i,j} \phi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \cdots$$

$$+ \frac{1}{N!} \sum_{i=1}^{N} \sum \cdots \sum_{i_n} \phi_n(\mathbf{r}_i, \mathbf{r}_j, \cdots, \mathbf{r}_n)$$

Potential Energy:

$$U = \Phi - \Phi_1 = \Phi_2 + \Phi_3 + \Phi_4 + \cdots + \Phi_n$$

Potential vs. Force field

Physics ← Used to be a cultural divide → **Chemistry**

More fundamental approach
ambition is to derive
general functional forms
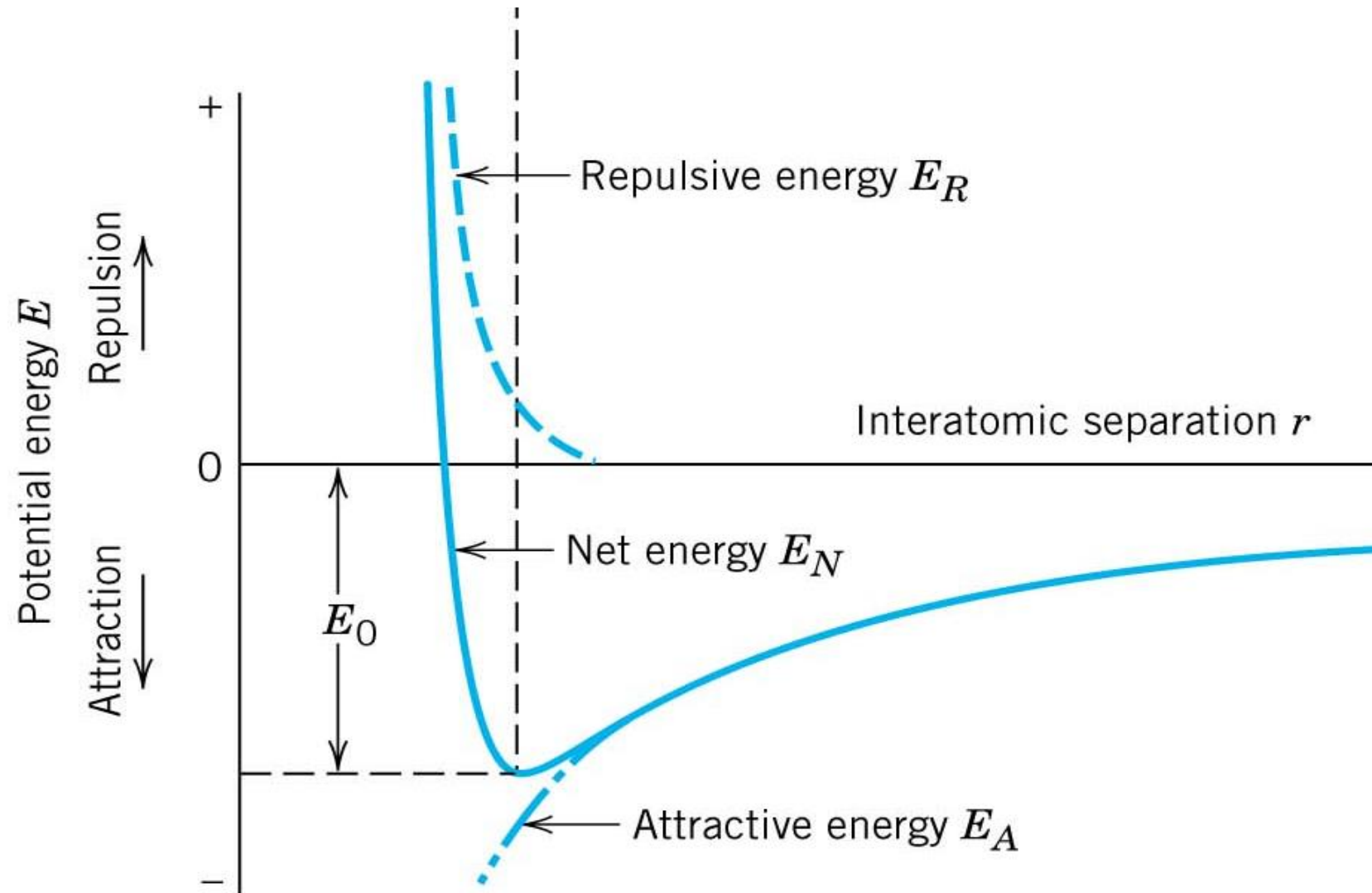(at least it used to be)

Potentials represent

- Metallic bonding

- Covalent bonding

- Ionic bonding

- Dispersion (van-der-Waals interaction)

- …
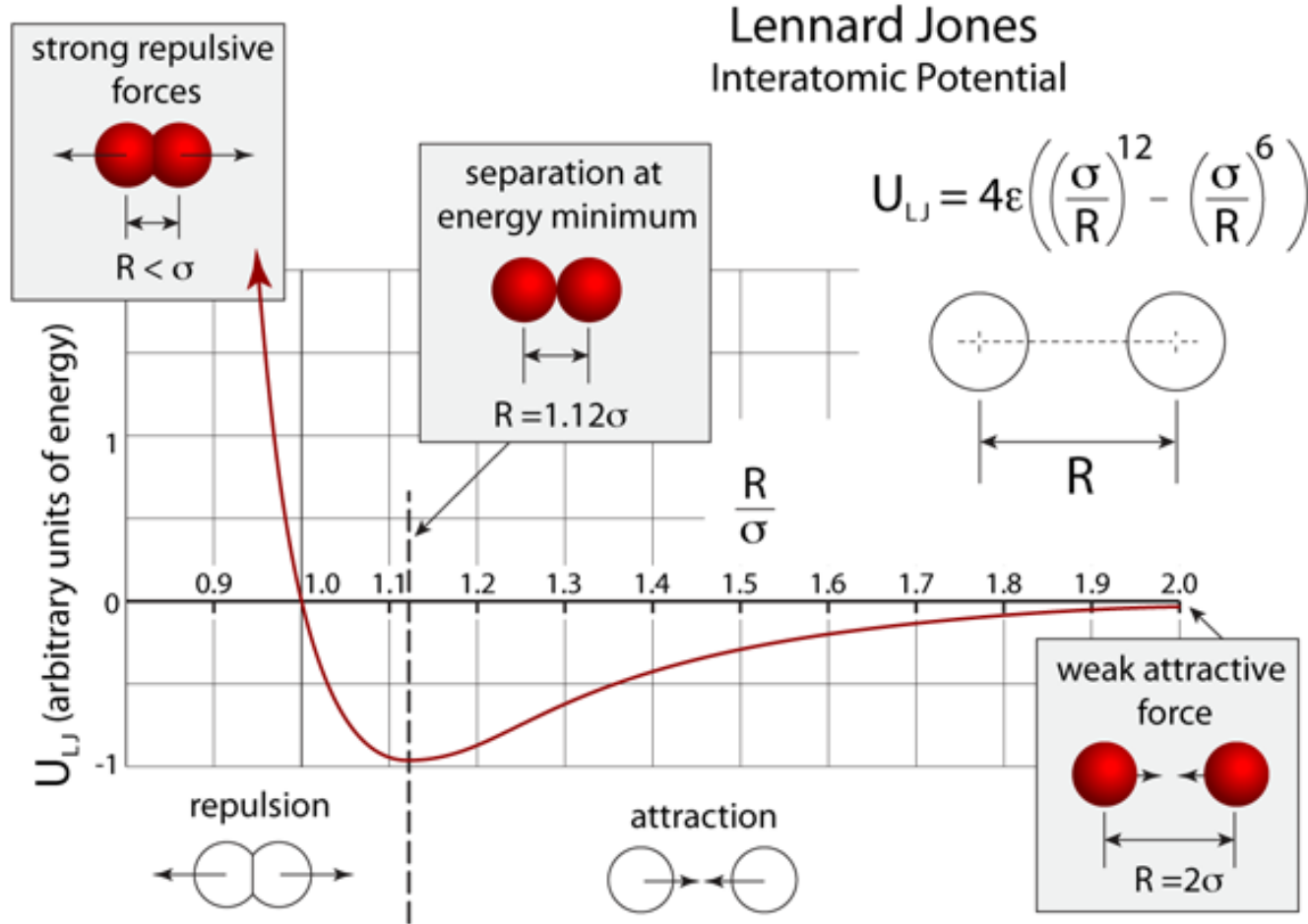
More pragmatic approach
make it work!

Force fields

- Non-reactive and
  reactive versions

- Non-bonded and
  bonded interactions

Pair potential

Lennard-Jones Potential

Lennard Jones Interatomic Potential

strong repulsive forces

$R < \sigma$

separation at energy minimum

$R = 1.12\sigma$

$\dfrac{R}{\sigma}$

R

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

weak attractive force

$R = 2\sigma$

repulsion

attraction

- Approximate

- Popular model pot.

- Good for rare gas

- Physical interaction

Table 5.1 Values of the Lennard-Jones parameters for the rare gases [32]

	Ne	Ar	Kr	Xe
ϵ (eV)	0.0031	0.0104	0.0140	0.0200
σ (Å)	2.74	3.40	3.65	3.98

http://atomsinmotion.com/book/chapter5/md

Lennard-Jones Potential

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

- **Truncation**

$$E(r) = \begin{cases} U_{LJ}(r), & \text{if } r < r_c \\ 0, & \text{if } r \geq r_c \end{cases}$$

- **Shift**

$$E(r) = \begin{cases} U_{LJ}(r) - U_{LJ}(r_c), & \text{if } r < r_c \\ 0, & \text{if } r \geq r_c \end{cases}$$
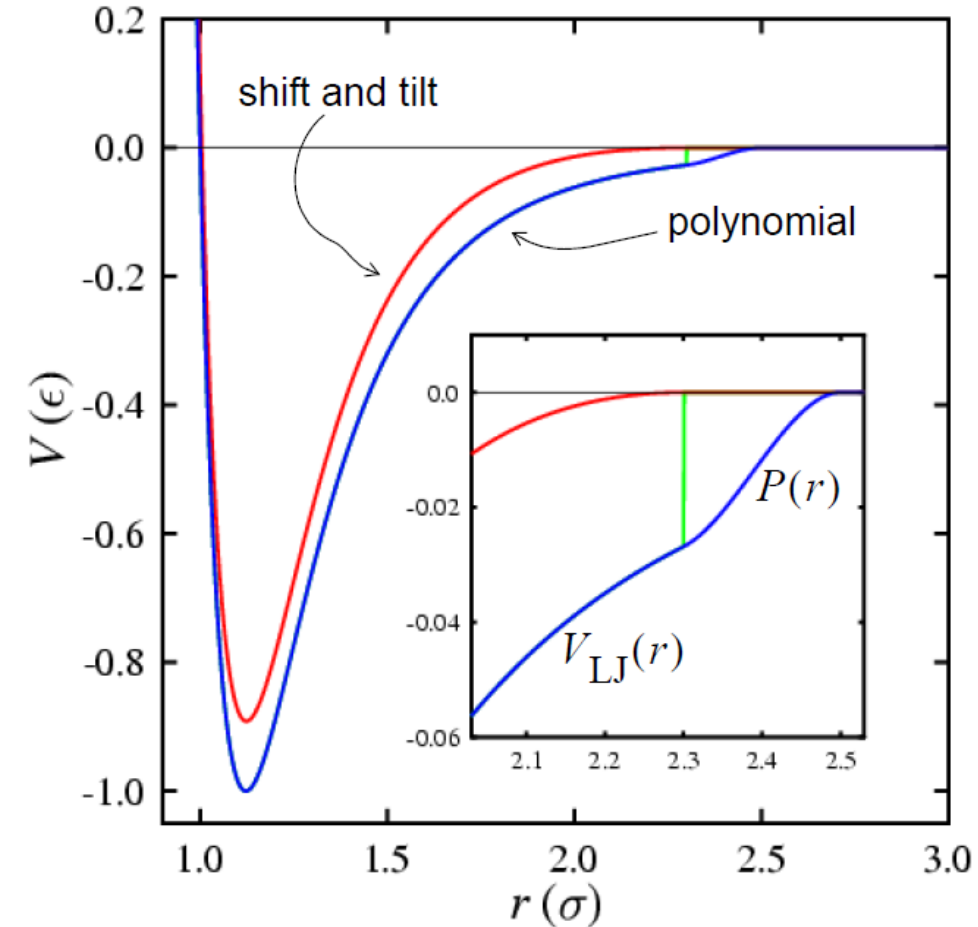
- **Shift and tilt**

$$E(r) = \begin{cases} U_{LJ}(r) - (r - r_c)U'_{LJ}(r_c) - U_{LJ}(r_c), & \text{if } r < r_c \\ 0, & \text{if } r \geq r_c \end{cases}$$

- **Tail (polynomial fit)**

$$E(r) = \begin{cases} U_{LJ}(r), & \text{if } r < r_c \\ P(r), & \text{if } r_c \leq r \leq r_c + \Delta r_c \end{cases}$$

$P(r_c) = U_{LJ}(r_c), P'(r_c) = U'_{LJ}(r_c); P(r_c + \Delta r_c) = 0, P'(r_c + \Delta r_c) = 0.$

Lennard-Jones Potential

Mixing rules

- **Geometric**

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$
$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$$

- **Arithmetic**

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$
$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$$

- **Sixth-power**

$$\epsilon_{ij} = \frac{2\sqrt{\epsilon_i \epsilon_j}\,\sigma_i^3 \sigma_j^3}{\sigma_i^6 + \sigma_j^6}$$

$$\sigma_{ij} = \left(\frac{1}{2}(\sigma_i^6 + \sigma_j^6)\right)^{\frac{1}{6}}$$

Other pair potentials

- **Mie**

$$E(r) = \left(\frac{n}{n-m}\right)\left(\frac{n}{m}\right)^{m/(n-m)}\varepsilon\left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m\right]$$

- **Buckingham**

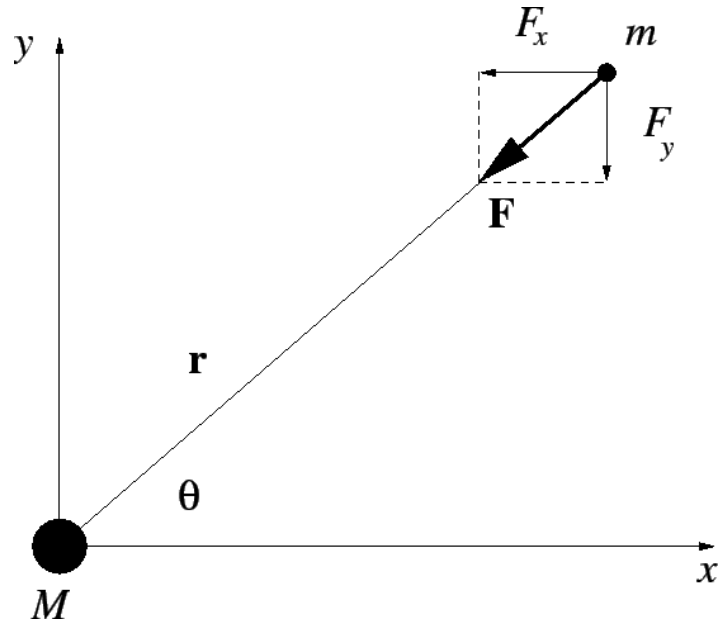$$E(r) = A\exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6}$$

- **Born-Mayer-Huggins**

$$E(r) = A\exp\left(\frac{\sigma-r}{\rho}\right) - \frac{C}{r^6} + \frac{D}{r^8}$$

- **Morse**

$$E(r) = D_0\left[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\right]$$

Central force potential

- **Interaction depends on distance only**

- **Always favors simple structure, e.g., FCC, BCC**

- **Cauchy relation: $C_{12} = C_{44}$**

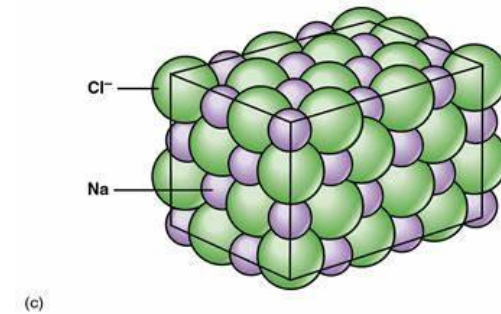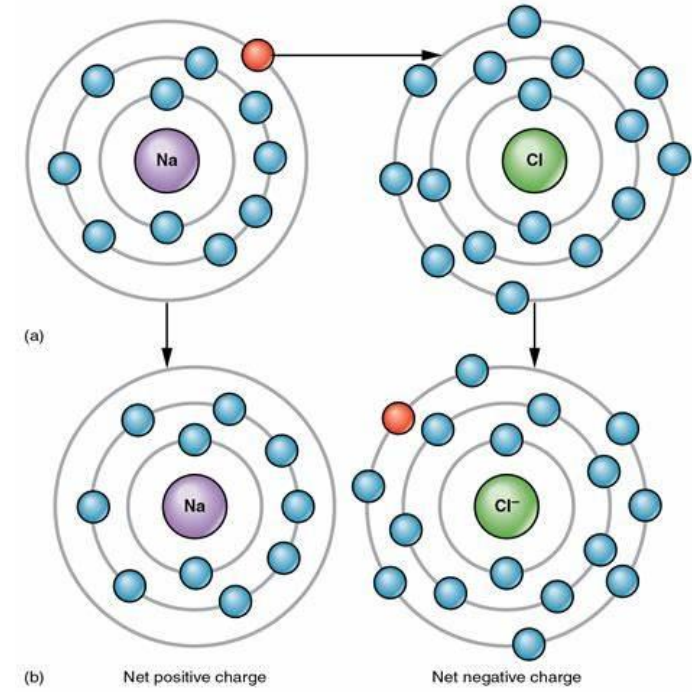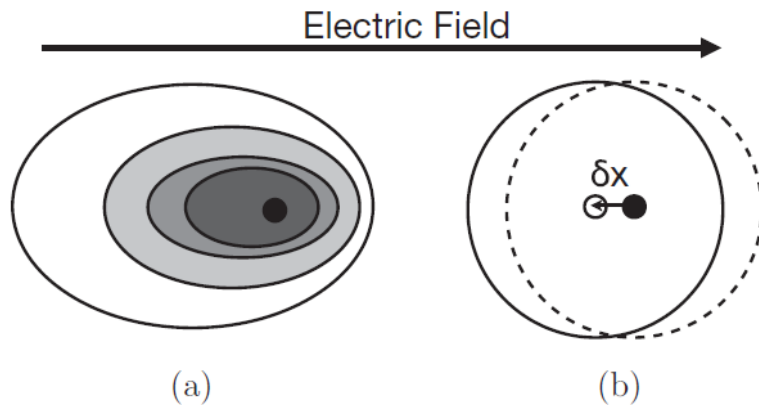| Material	c_{12}/c_{44}
"LJ"	1.00
Ar	1.12
Mo	1.54
Cu	1.94
Au	4.71
NaCl	0.99
Si	0.77
MgO	0.53
diamond	0.16

Potential for Ionic Materials

Pair + Coulombic

$$E = \sum_{i<j} \phi(r_{ij}) + k \sum_{i<j} \frac{q_i q_j}{r_{ij}}$$

$$E = \sum_{i<j} \phi(r_{ij}) + \sum_{i<j, j<k} \phi'(\theta_{jik}) + k \sum_{i<j} \frac{q_i q_j}{r_{ij}}$$

Problem: polarization

Electric Field

(a)   (b)

Solution: core-shell model

(a)

(b)   Net positive charge   Net negative charge

(c)   Cl⁻   Na

Potential for Metals

Embedded Atom Potential (EAM)

Positively charged ions

'Electron cloud' (negatively charged)

$$E_{\text{total}} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_i \sum_{j \neq i} \phi_{ij}(r_{ij})$$

$$\rho_i = \sum_{j \neq i} f_j(r_{ij})$$ **Total electron density at _i_.**

$f_j(r_{ij})$ **Electron density contributed by _j_ at _i_.**

$F_i(\rho_i)$ **Embedding energy for atom _i_.**

$\phi_{ij}(r_{ij})$ **Pair interaction.**
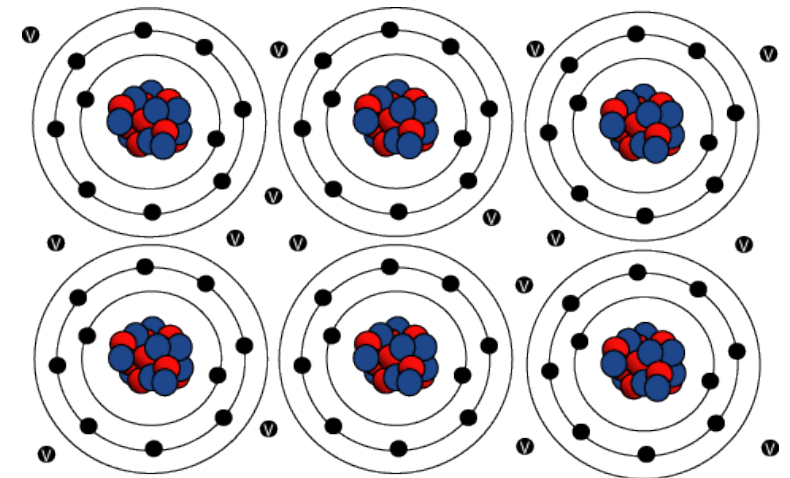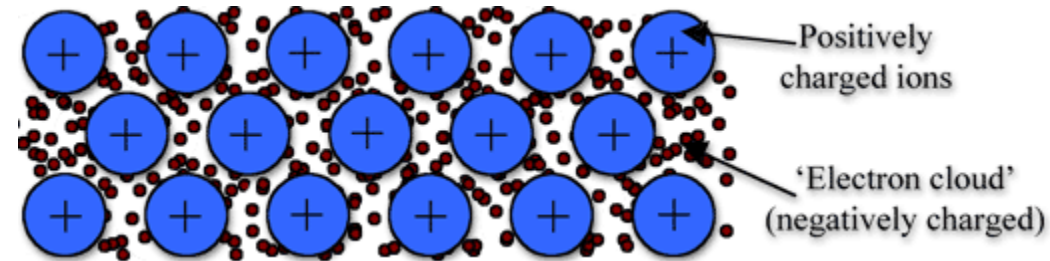
Potential for Metals

Modified EAM (MEAM)

$$E_{\text{total}} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_i \sum_{j \neq i} \phi_{ij}(r_{ij})$$

$$\rho_i = \sum_{j \neq i} f_j(r_{ij}) + \sum_{j \neq i} \sum_{k > j, k \neq i} g(r_{ij}) g(r_{ik}) \psi(\cos \theta_{jik})$$
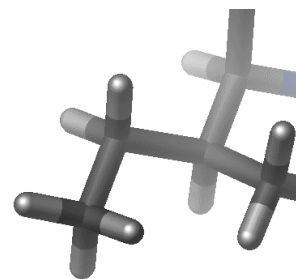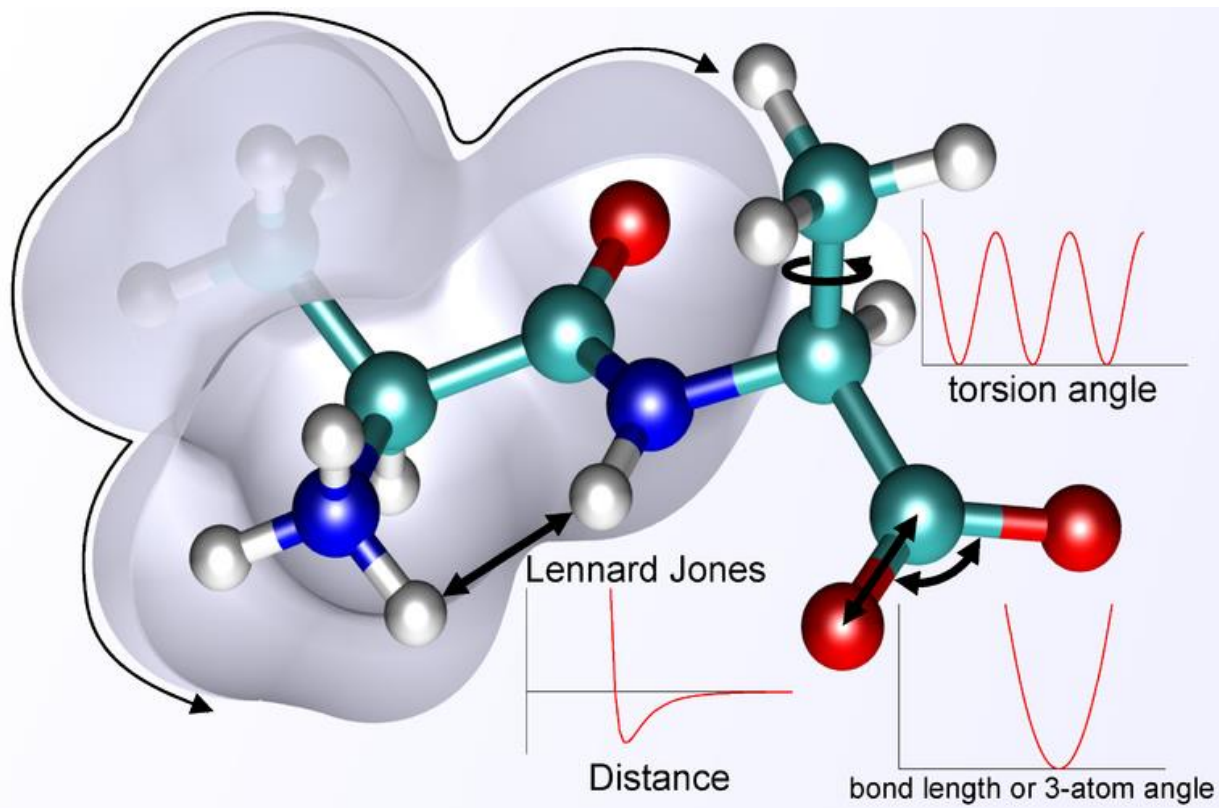
Using Rose function to construct the embedding function
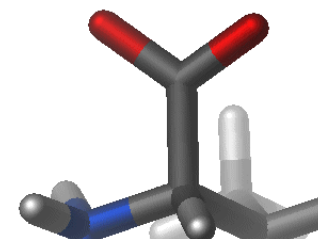
$$E(a^*) = -E_{\text{coh}} f(a^*)$$

$$f(a^*) = (1 + a^*) e^{-a^*}$$

$$a^* = \left(\frac{a}{a_0} - 1\right) \left(\frac{E_{\text{coh}}}{9B\Omega}\right)^{-1/2}$$
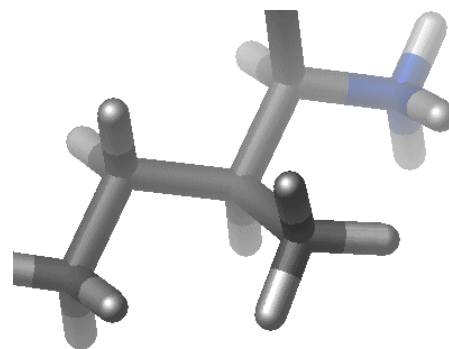
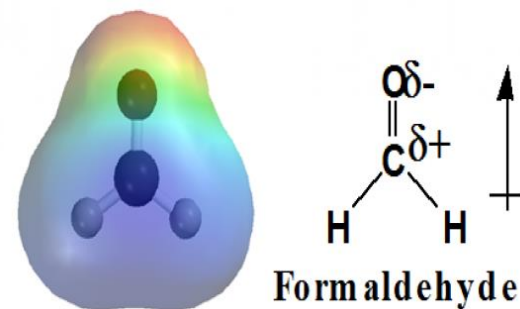# Potential for polymers (Force fields)

Bond length stretching
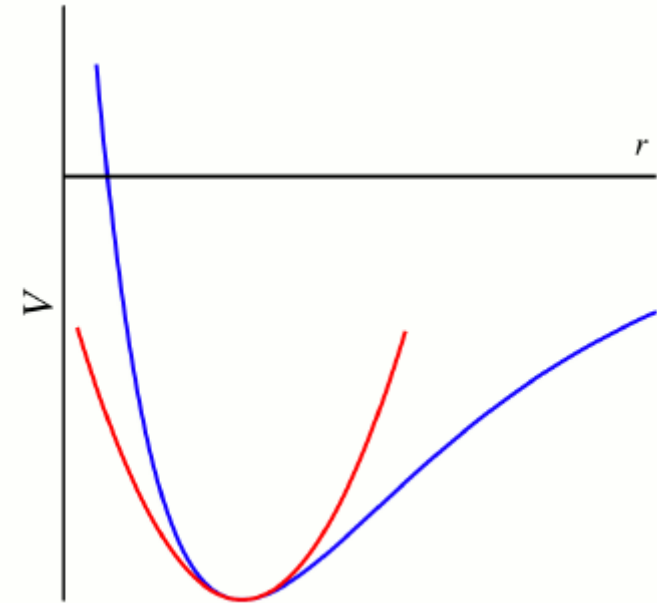
Bond angle bending

Dihedral torsion

Partial charges

$$E_{\text{total}} = \sum_{\text{bonds}} \phi_b(r) + \sum_{\text{angles}} \phi_\theta(\theta) + \sum_{\text{dihedrals}} \phi_\psi(\psi) + \sum_{i<j} U_{LJ}(r_{ij}) + k \sum_{i<j} \frac{q_i q_j}{r_{ij}} + \cdots$$

Potential for polymers

Bond stretch

$$E_{bond} = \sum_{bonds} \frac{1}{2} k_b (b - b_0)^2$$

$$E_{bond} = \sum_{bonds} K_2 (b - b_0)^2 + K_3 (b - b_0)^3 + K_4 (b - b_0)^4$$

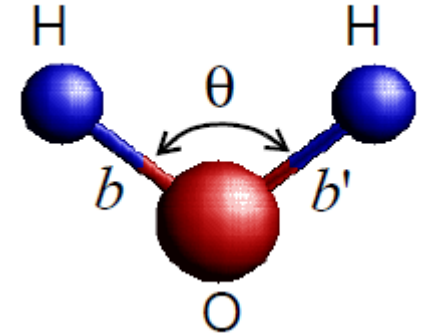**Morse potential, enable breaking** at infinite distance

$$E_{bond} = \sum_{bonds} D_b \left\{ 1 - e^{-a(b - b_0)} \right\}^2 = \sum_{bonds} D_b \left\{ e^{-2a(b - b_0)} - 2e^{-a(b - b_0)} + 1 \right\}$$
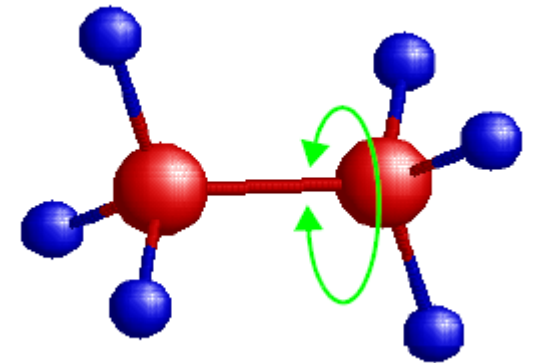
Potential for polymers

Bond bending

$$E_{angle} = \sum_{angles} \frac{1}{2} H_\theta (\theta - \theta_0)^2 ,$$

$$E_{angle} = \sum_{angles} H_2 (\theta - \theta_0)^2 + H_3 (\theta - \theta_0)^3$$

Bond torsion

$$E_{torsion} = V_1(1 + \cos(\phi)) + V_2(1 + \cos(2\phi)) + V_3(1 + \cos(3\phi))$$
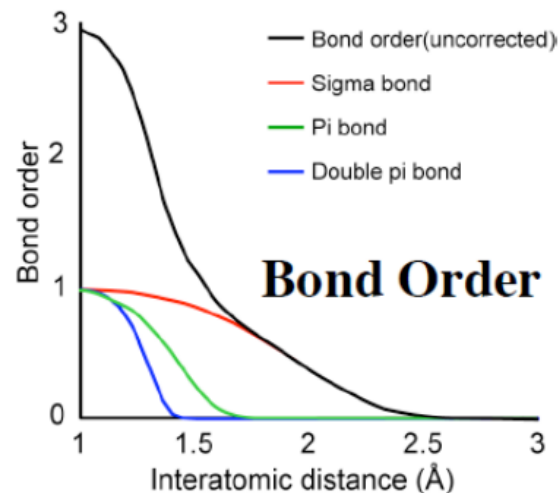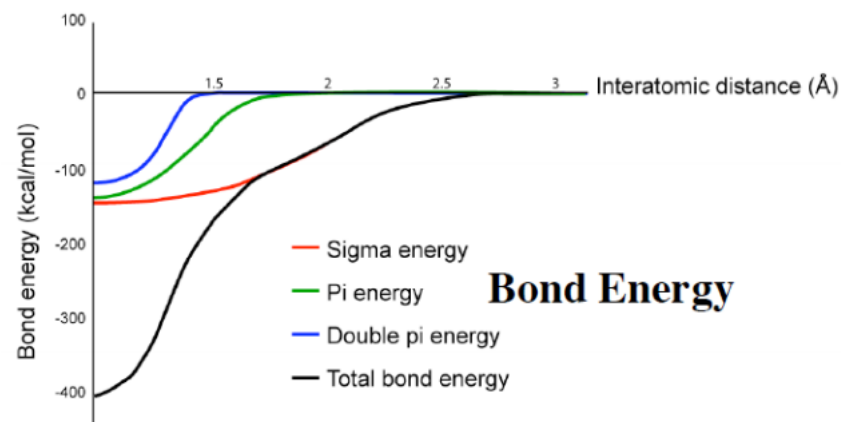
Reactive Force Fields

A bond-order/distance relationship

$$BO'_{ij} = \exp\left[p_{bo,1} \cdot \left(\frac{r_{ij}}{r_o^\sigma}\right)^{p_{bo,2}}\right]$$
$$+ \exp\left[p_{bo,3} \cdot \left(\frac{r_{ij}}{r_o^\pi}\right)^{p_{bo,4}}\right]$$
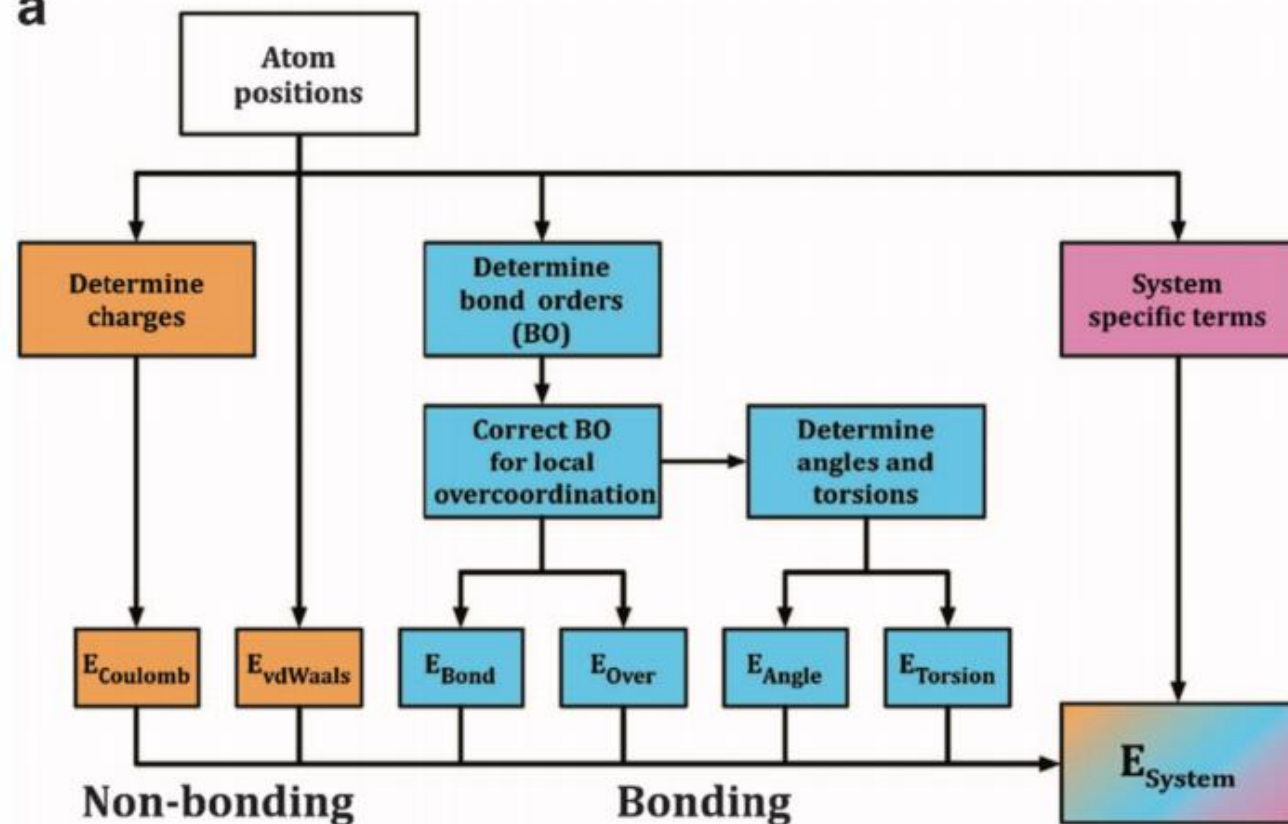$$+ \exp\left[p_{bo,5} \cdot \left(\frac{r_{ij}}{r_o^{\pi\pi}}\right)^{p_{bo,6}}\right]$$

$$E_{bond} = -D_e^\sigma \cdot BO_{ij}^\sigma \cdot f(BO_{ij}^\sigma) - D_e^\pi \cdot BO_{ij}^\pi - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}$$

C-C bond order

Bond Order

- Bond order(uncorrected)
- Sigma bond
- Pi bond
- Double pi bond

Bond Energy

- Sigma energy
- Pi energy
- Double pi energy
- Total bond energy

Senftle, Thomas, et al. npj Computational Materials 2 (2016).

*Russo, Michael F., and van Duin, Adri. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **269** (2011): 1549-1554.

Potential Fitting

Physical property	Atom-level property
Crystal structure	Balance of atomic forces.
Cohesive energy	Potential energy at the equilibrium atom positions
Elastic constants $c_{\rho\sigma}$	Long-wavelength acoustic vibrations Elastic distortions of unit cell.
Equation of state $P(V)$	Compression or expansion of material
Neutron scattering	Phonon $\omega(\mathbf{k})$ in the Brillouin zone.
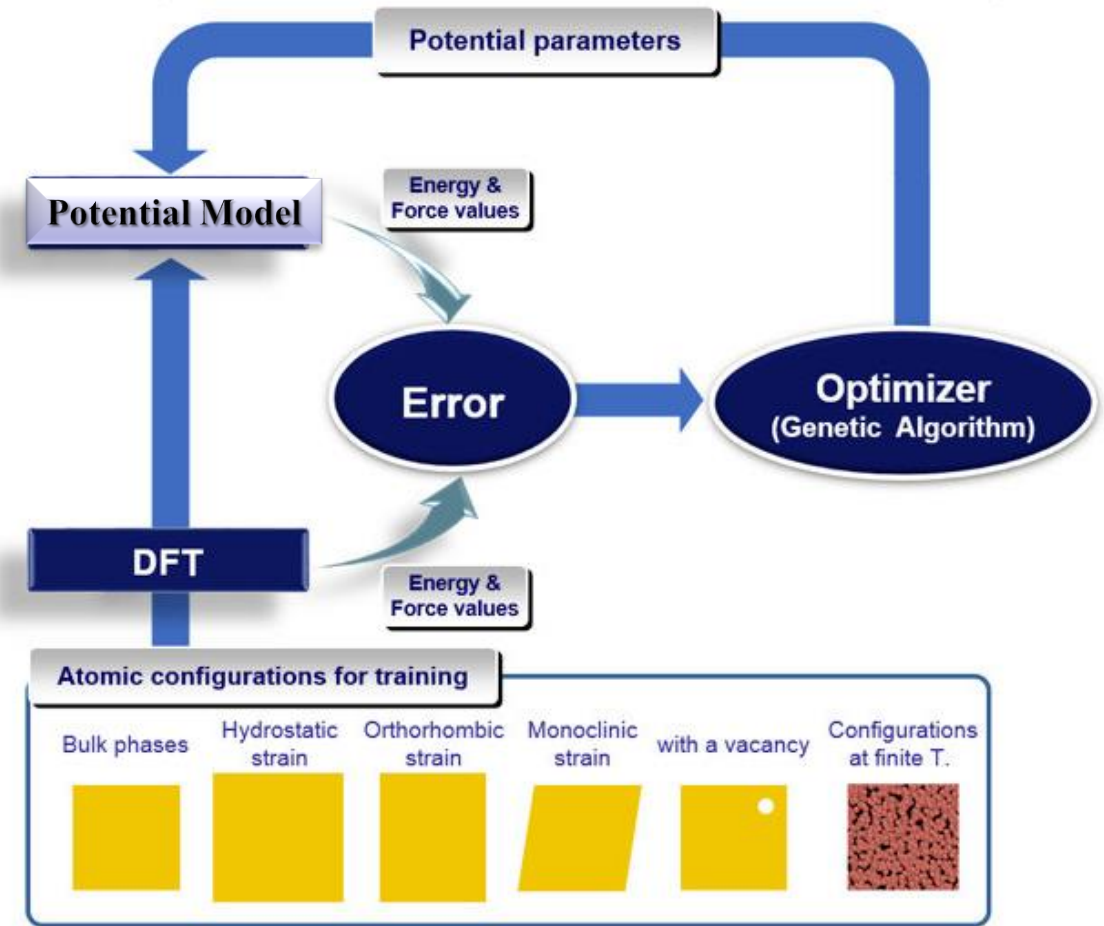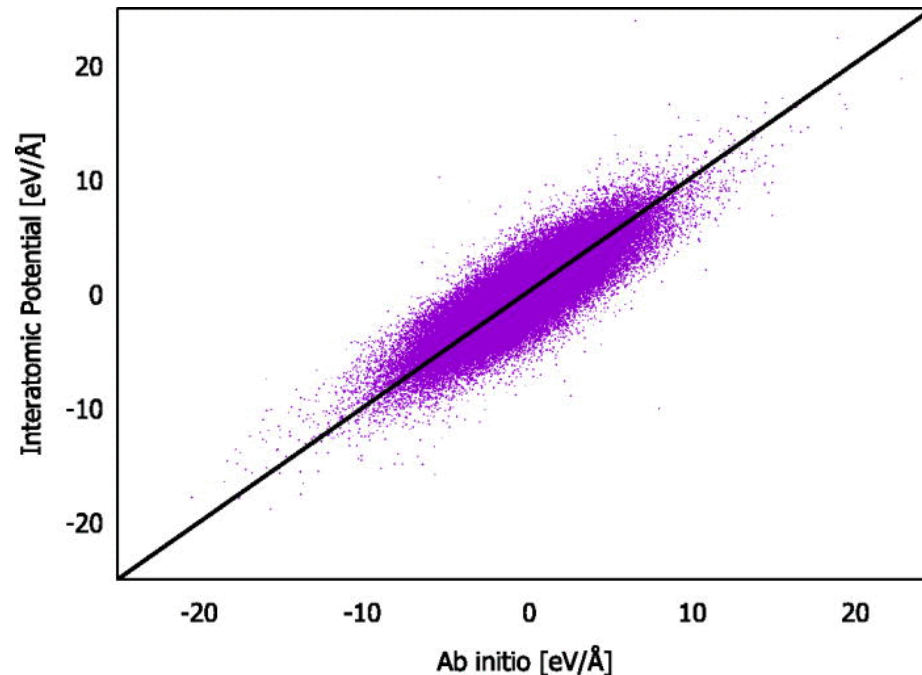
$$Error = \sum_{i}^{\text{property}} \sum_{j}^{\text{configuration}} \sum_{k}^{\text{run}} \sum_{l}^{\text{atom}} w_{ijkl} \frac{|p_{ijkl}^{\text{pot}} - p_{ijkl}^{\text{ref}}|^2}{\Delta_i}$$
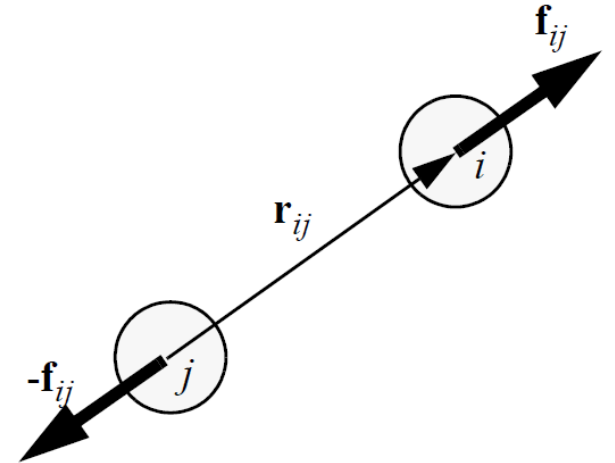
Machine learning empirical potentials
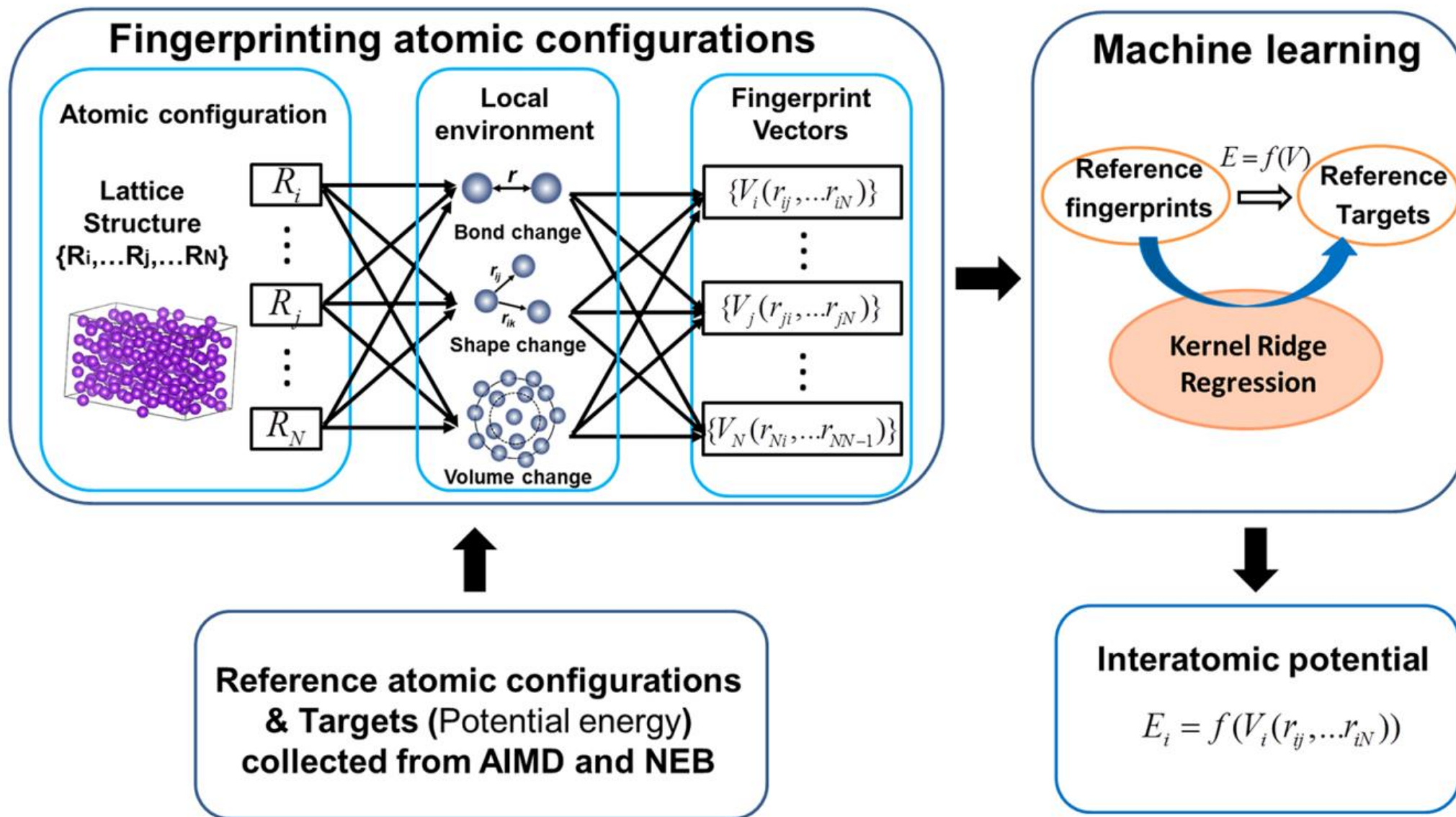
Force Evaluation (pair potential)

Total energy

$$U = \frac{1}{2} \sum_i \sum_{j \neq i} \phi(r_{ij})$$

Distance

$$\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r_i} = x_{ij}\mathbf{x} + y_{ij}\mathbf{y} + z_{ij}\mathbf{z}$$

$$x_{ij} = x_j - x_i$$

Force

$$\mathbf{f_i} = f_{x_i} \cdot \mathbf{x} + f_{y_i} \cdot \mathbf{y} + f_{z_i} \cdot \mathbf{z}$$
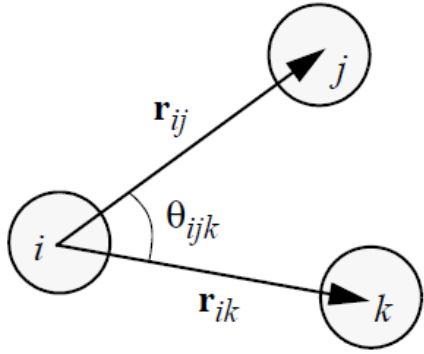
$$f_{x_i} = -\frac{\partial U}{\partial x_i} = -\sum_{j \neq i} \left.\frac{\partial \phi}{\partial r}\right|_{r=r_{ij}} \frac{\mathrm{d}r_{ij}}{\mathrm{d}x_i} = -\sum_{j \neq i} \phi'(r_{ij})\frac{x_{ij}}{r_{ij}}$$

$$\mathbf{f}_i = -\sum_{j \neq i} \phi'(r_{ij})\frac{\mathbf{r}_{ij}}{r_{ij}}$$

Force Evaluation (pair potential)

```
for (i = 0; i < N; ++i) f[i] = 0.;

for (i = 0; i<N-1; ++i){

for (j = i+1; j<N; ++j){

    xij = x[j][0] – x[i][0]; yij = x[j][1] – x[i][1]; zij = x[j][2] – x[i][2];

    Apply_PBC(xij, yij, zij);

    rij = sqrt(xij*xij + yij*yij + zij*zij);

    if (rij < Rcut){

        dp = - partial_phi(rij);

        fij = dp / rij * xij;

        f[i] += fij;      f[j] -= fij;

    }

}}
```

Force Evaluation (angular term)

LAMMPS cosine/squared angle style

$$\cos\theta_{ijk} = \frac{\boldsymbol{r}_{ij} \cdot \boldsymbol{r}_{ik}}{r_{ij} r_{ik}}$$

$$E = K(\cos\theta - \cos\theta_0)^2$$

$$\mathbf{f}_i = -\frac{\partial E}{\partial \mathbf{r}_i} = -\frac{\partial E}{\partial \cos\theta}\frac{\mathrm{d}\cos\theta}{\mathrm{d}\mathbf{r}_i}$$

$$\frac{\mathrm{d}\cos\theta_{ijk}}{\mathrm{d}\mathbf{r}_i} = \left[\frac{\cos\theta}{r_{ij}^2} - \frac{1}{r_{ij}r_{ik}}\right]\mathbf{r}_{ij} + \left[\frac{\cos\theta}{r_{ik}^2} - \frac{1}{r_{ij}r_{ik}}\right]\mathbf{r}_{ik}$$
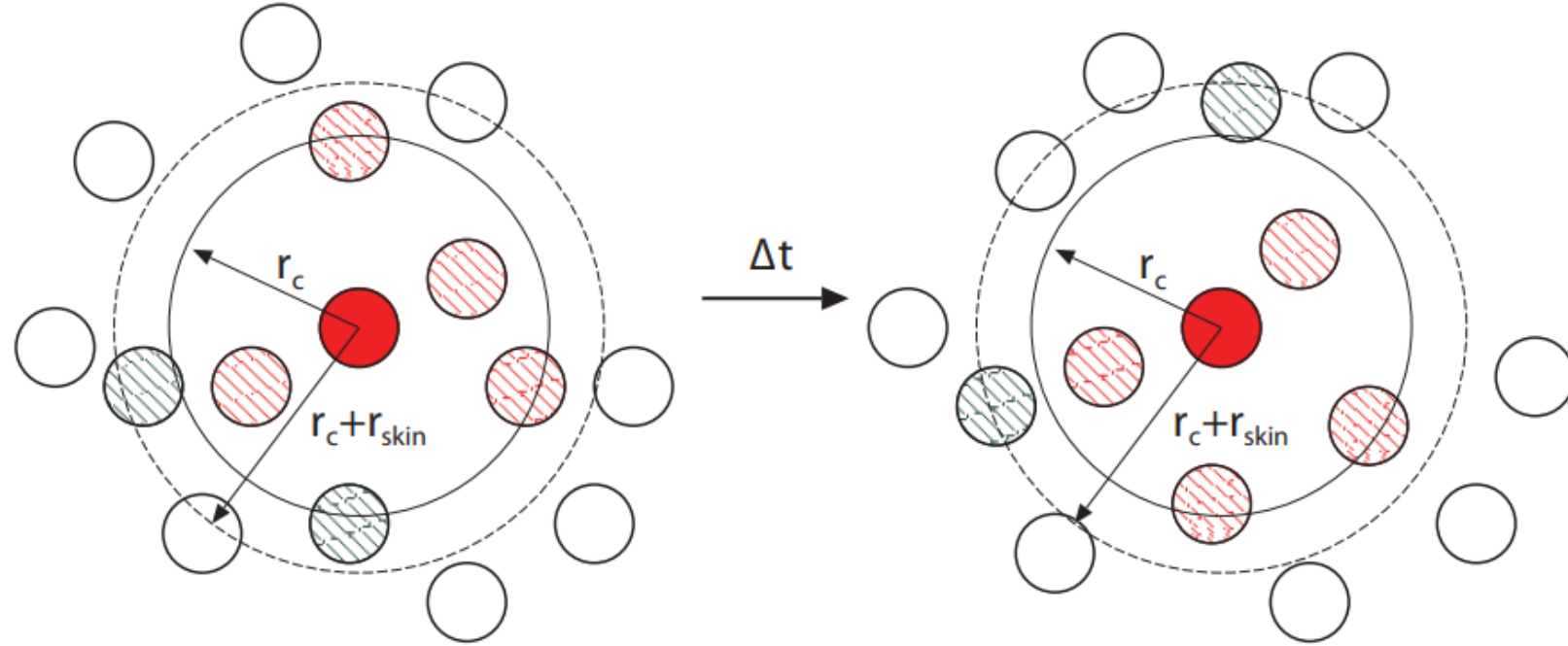
Neighbor list

```
for (i = 0; i<N-1; ++i){
for (j = i+1; j<N; ++j){

    ....
    }            O(N²)

}}
```

```
for (i = 0; i<N; ++i){
for (jj = 0; jj < num_nei[i]; ++jj){

    j = neighbor[i][jj];

    ....
    }
                O(N)
}}
```

Long range interaction

$$E_{Coulombic}(r) = \frac{kq_iq_j}{r}$$
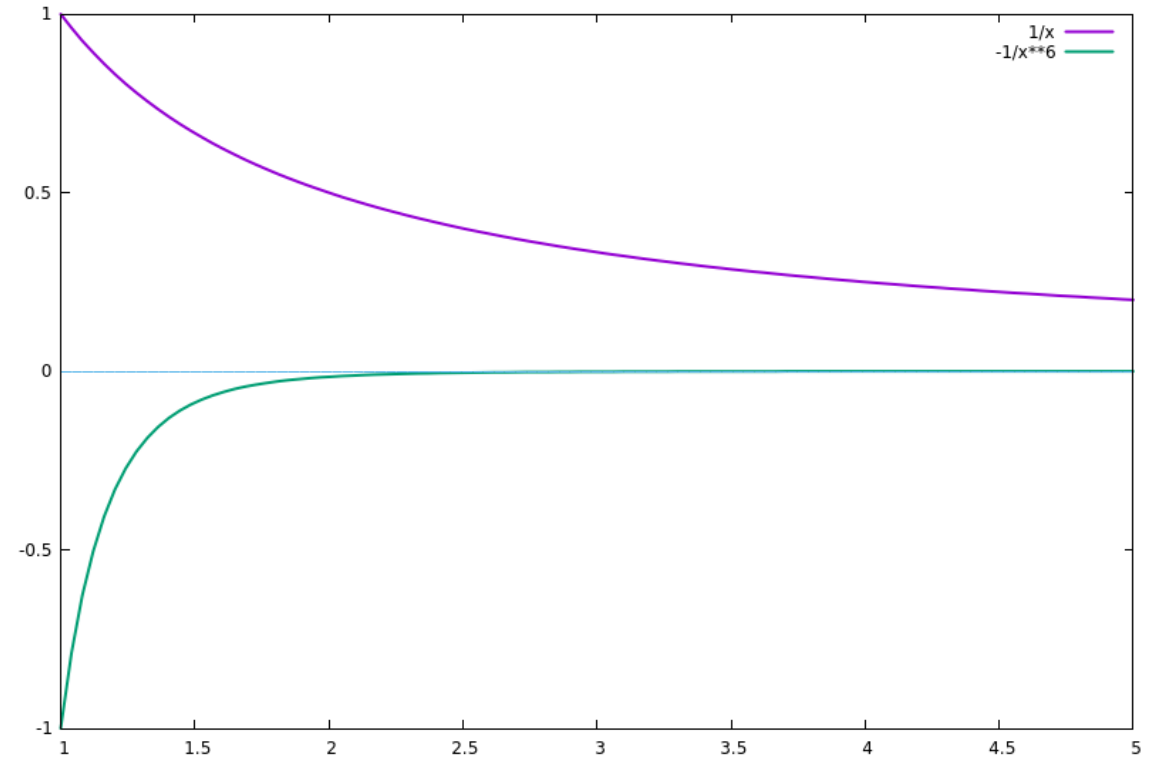
Ewald sum method

$$U = U^{(r)} + U^{(k)} + U^{(self)} + U^{(dipolar)}$$

$$U^{(r)} = \frac{1}{2}\sum_{i}^{N}\sum_{j}^{N}\sum_{\mathbf{n}\in\mathbb{Z}^3}^{\dagger} q_iq_j \frac{erfc(\alpha|\mathbf{r}_{ij}+\mathbf{n}L|)}{|\mathbf{r}_{ij}+\mathbf{n}L|}$$

$$U^{(k)} = \frac{1}{2L^3}\sum_{\mathbf{k}\in\mathbb{K}^3,\mathbf{k}\neq 0}\frac{4\pi}{k^2}\exp\left(-k^2/4\alpha^2\right)\sum_{i}^{N}\sum_{j}^{N}q_iq_j\exp(-i\mathbf{k}\cdot\mathbf{r}_{ij})$$

$$U^{(self)} = -\frac{\alpha}{\sqrt{\pi}}\sum_{i}^{N}q_i^2$$

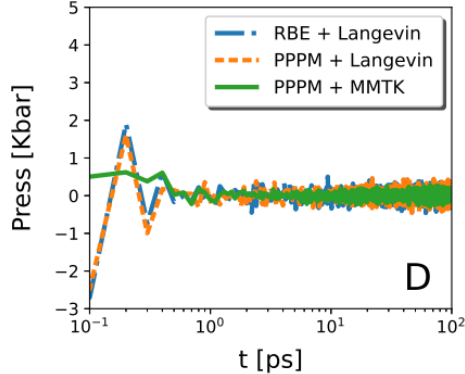$$U^{(dipolar)} = \frac{2\pi}{(1+2\epsilon')L^3}\left(\sum_{i}^{N}q_ir_i\right)^2$$
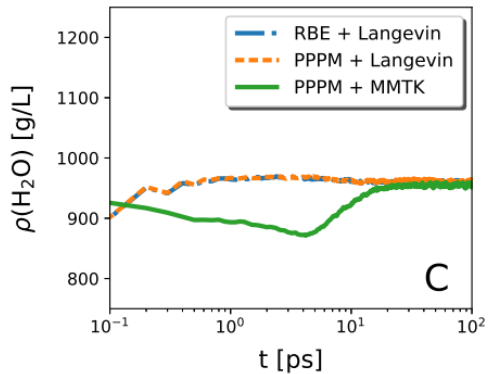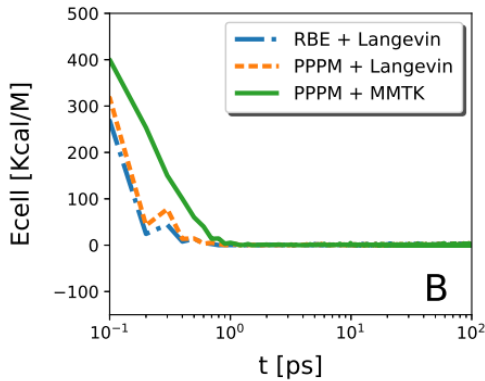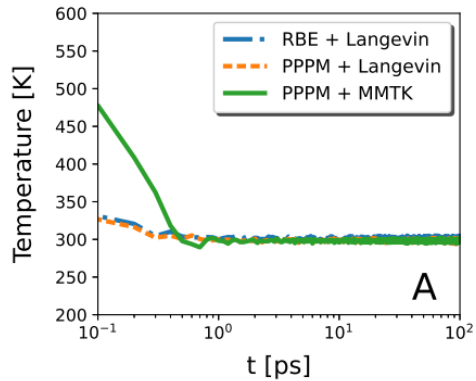

- **Ewald summation**
- **Field multipole method**
- **Particle-Particle/Particle-Mesh**

Random Batch Ewald
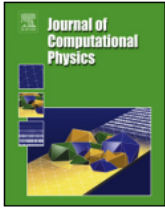
Random Batch Methods (RBM) for interacting particle systems

Shi Jin [a], Lei Li [a,*], Jian-Guo Liu [b,c]

[a] School of Mathematical Sciences, Institute of Natural Sciences, MOE-LSC, Shanghai Jiao Tong University, Shanghai, 200240, PR China
[b] Department of Mathematics, Duke University, Durham, NC 27708, USA
[c] Department of Physics, Duke University, Durham, NC 27708, USA

A random batch Ewald method for charged particles in the isothermal-isobaric ensemble

Jiuyang Liang, Pan Tan[3], Liang Hong[2,3], Shi Jin[1,2], Zhenli Xu[1,2], and Lei Li[*1,2]

[1]School of Mathematical Sciences, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China
[2]Institute of Natural Sciences and MOE-LSC, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China
[3]School of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China

https://arxiv.org/abs/2110.14362

	Number of CPU Cores							
	100		500		1000		2000	
	Kspace	Total	Kspace	Total	Kspace	Total	Kspace	Total
RBE P=200	2.20e-4	1.92e-3	8.27e-5	5.96e-4	5.87e-5	4.30e-4	4.76e-5	3.77e-4
RBE P=500	4.92e-4	2.19e-3	1.75e-4	7.24e-4	1.20e-4	4.99e-4	8.71e-5	4.16e-4
PPPM	6.83e-4	2.38e-3	5.83e-4	1.16e-3	7.82e-4	1.22e-3	9.88e-4	1.32e-3

Summary on Empirical Potentials

Potentials	Metals	Semi-conductors	Ionic Materials	Polymers	Noble Gases	Dimers
Lennard Jones					√	
Buckingham					√	
Morse	√					√
EAM	√					
MEAM, ADP	√	√				
Stillinger-Weber		√				
Amber/CHARMM				√		
Buckingham + Coulumb			√			
Core-Shell			√			
ReaxFF	√	√	√	√	√	√
Machine Learning	√	√	√	√	√	√

Potential Selection
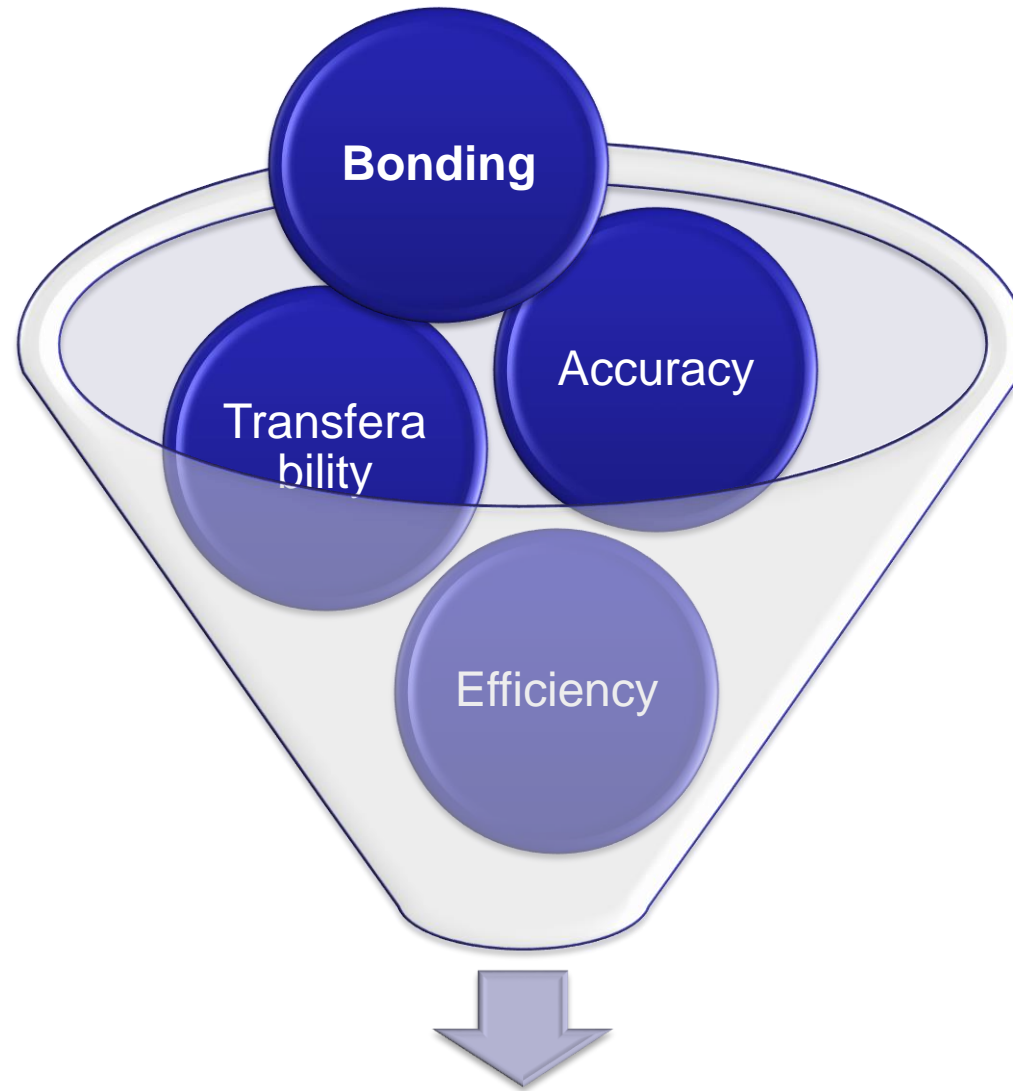
Empirical Potential

Homework

① **For a three body interaction described by**

$$E = K(\cos\theta - \cos\theta_0)^2$$

$$\cos\theta_{ijk} = \frac{\boldsymbol{r}_{ij} \cdot \boldsymbol{r}_{ik}}{r_{ij} r_{ik}}$$
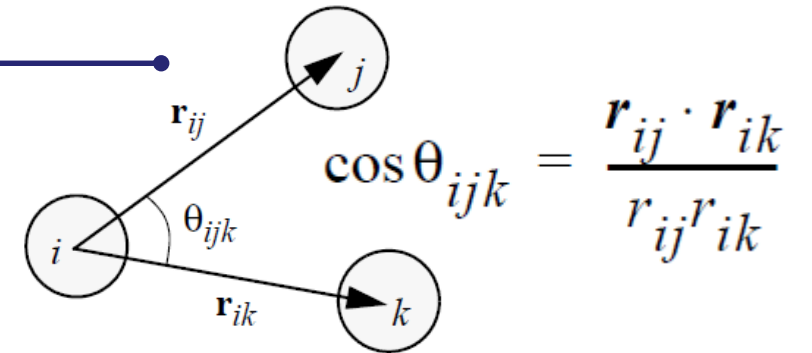
  derive the expression for the force on atom i, j, and k, respectively.

② **Extend your previous code on 1D harmonic chain into 3D FCC LJ case.**
   a) **Same programming language as last homework;**
   b) **2D array needed to store the positions, velocities, forces, …**

● Due: Nov. 24, 2021

Next Lecture：

Molecular Statics by Prof. Liu GS