上海交通大學
材料科学与工程学院
School of Materials Science and Engineering, SJTU

MSE6701H Multiscale Materials Modeling and Simulation

Lecture 03

Interatomic Potentials

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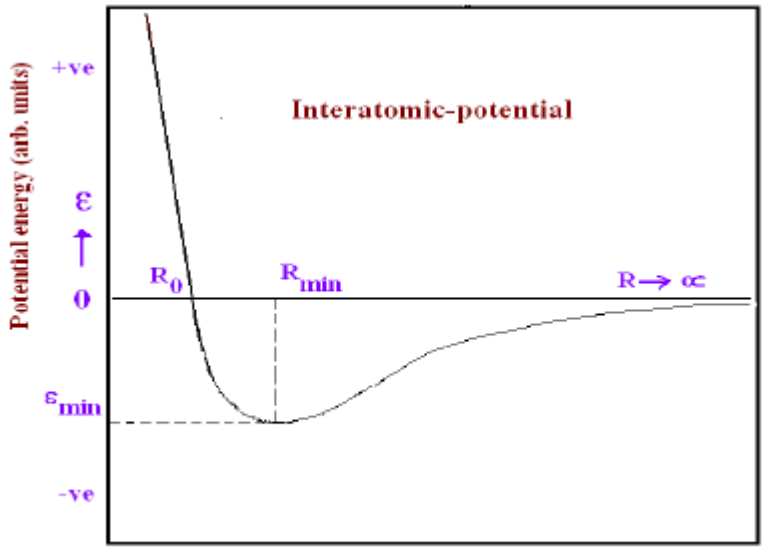
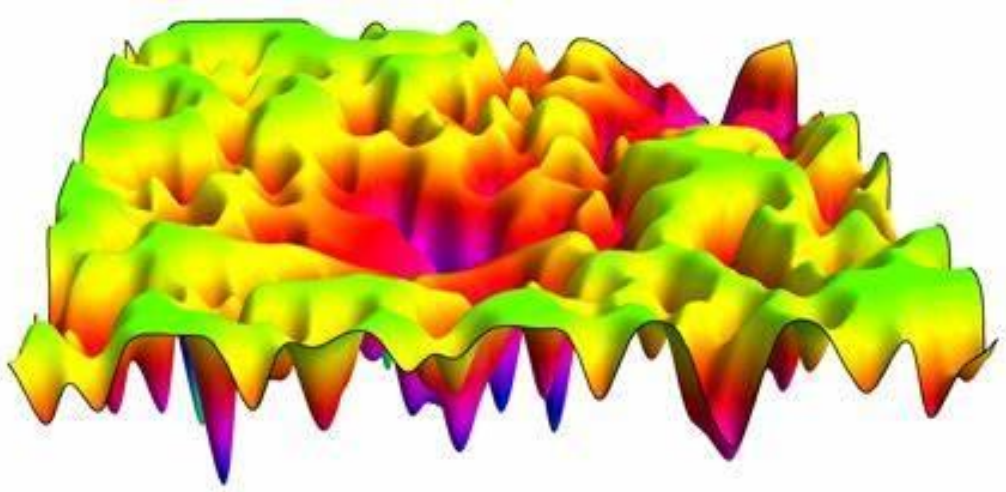
Molecular Dynamics Simulation

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

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

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





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 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

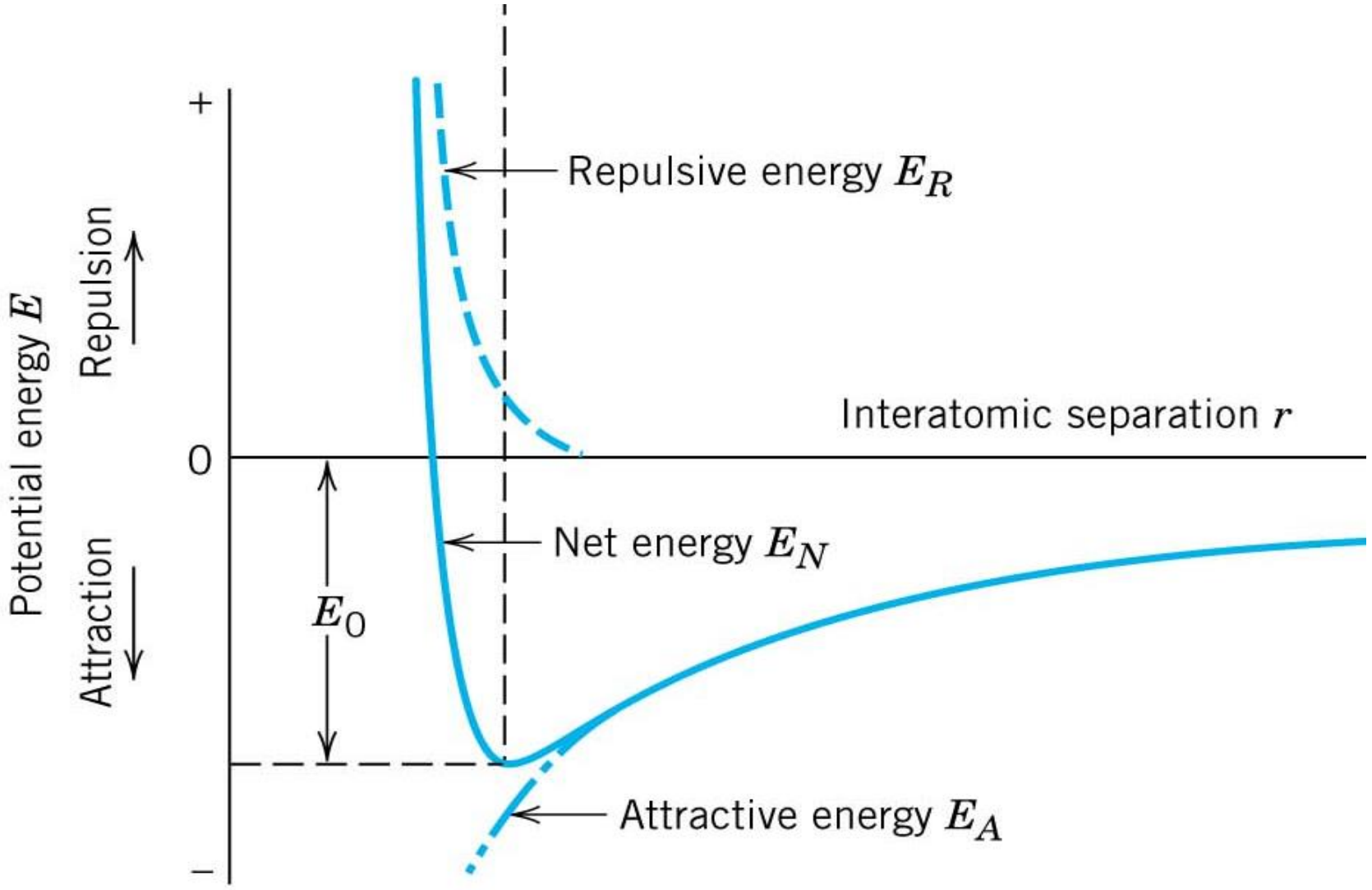
- Metallic bonding
- Covalent bonding
- Ionic bonding
- Dispersion (van-der-Waals interaction)
- …

More pragmatic approach
make it work!

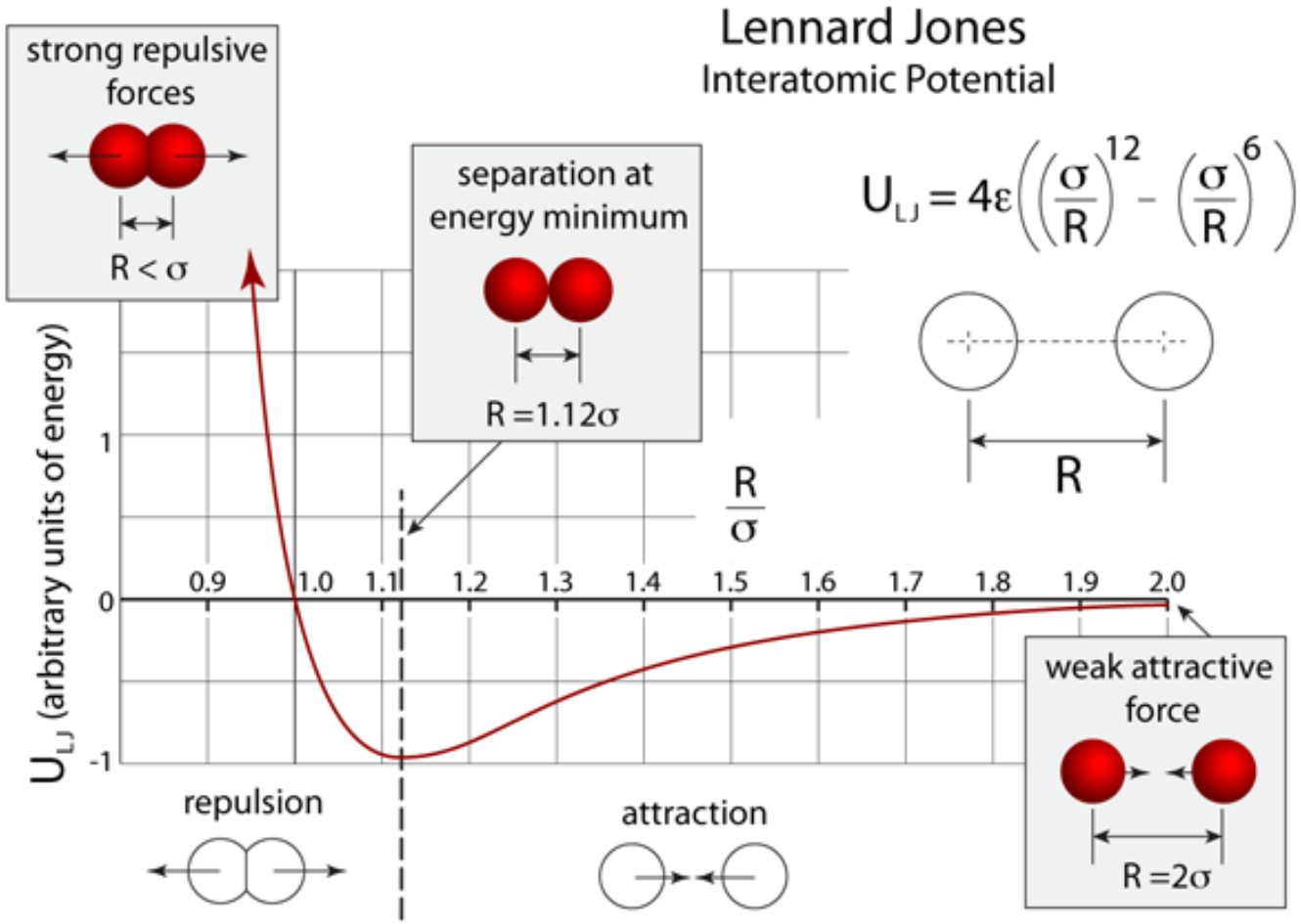
Force fields

- Non-reactive and reactive versions
- Non-bonded and bonded interactions

Pair potential



Lennard-Jones Potential



- 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**

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

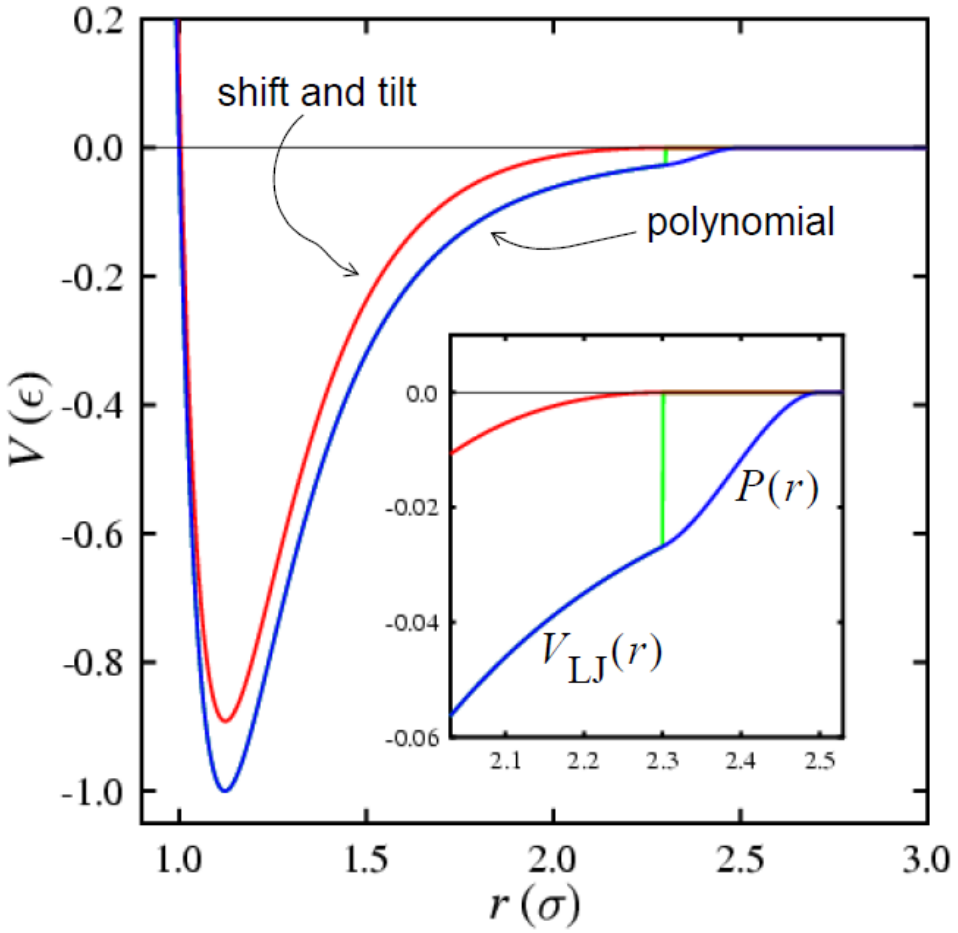
- **Shift**

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

- **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** $E(r) = \left(\frac{n}{n-m}\right)\left(\frac{n}{m}\right)^{m/(n-m)} \varepsilon \left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m\right]$ $r_{min} = \left(\frac{n}{m}\sigma^{n-m}\right)^{1/(n-m)}$

- **Buckingham**

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

- **Born-Mayer-Huggins**

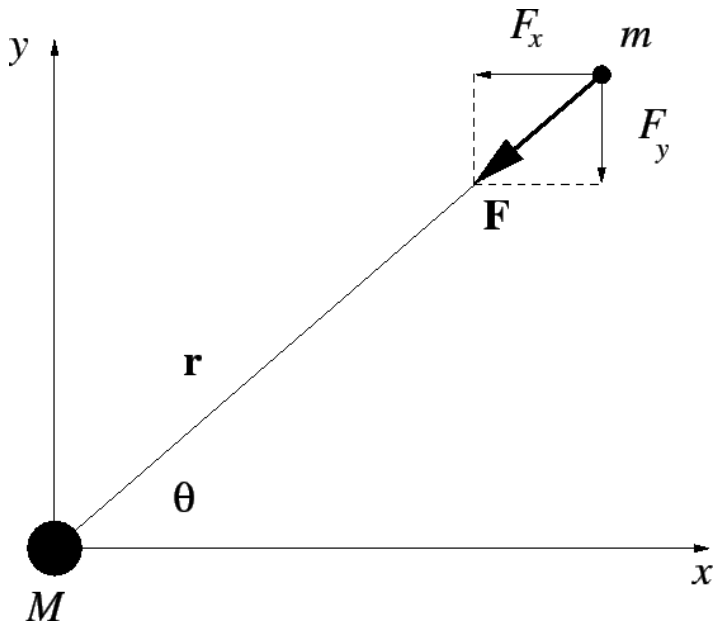
$$E = A\exp\left(\frac{\sigma - r}{\rho}\right) - \frac{C}{r^6} + \frac{D}{r^8} \quad r < r_c$$

- **Morse**

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

Central force potential

- Interaction depends on distance only
- Always favors simple structure, e.g., FCC, BCC
- Cauchy relation: $C_{12} = C_{44}$



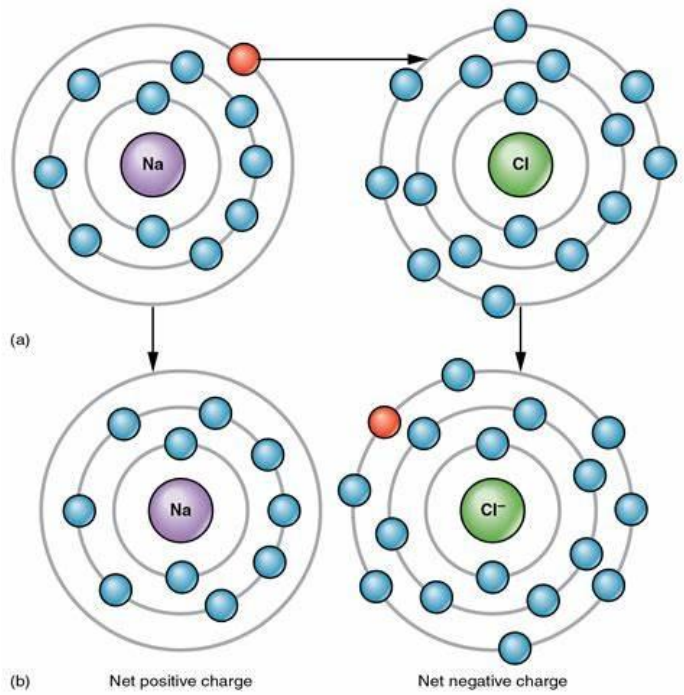
Material	c_{12}/c_{44}
"LJ"	1.00
Ar	1.12
Mo	1.54
Cu	1.94
Au	4.71
NaCl	0.99
Si	0.77
MgO	0.53
diamond	0.16

Potential for Ionic Materials

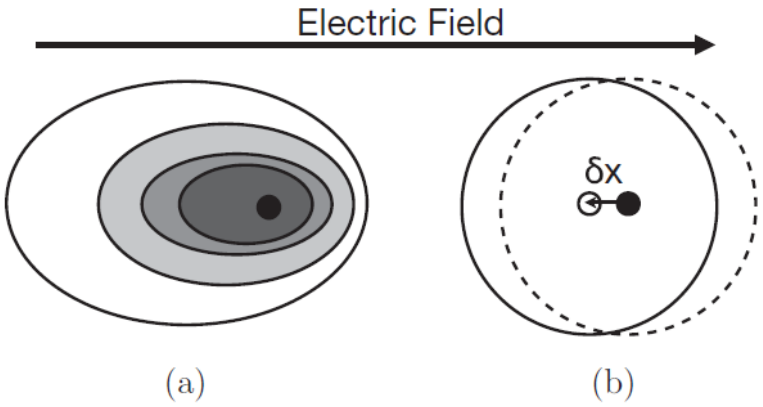
Pair + Coulombic

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

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



Problem: polarization

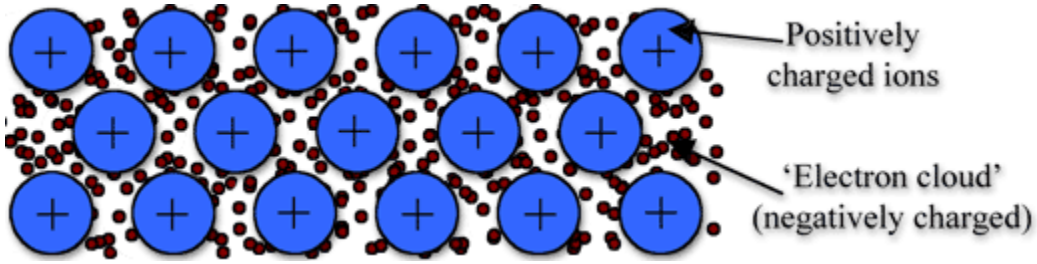


Solution: core-shell model

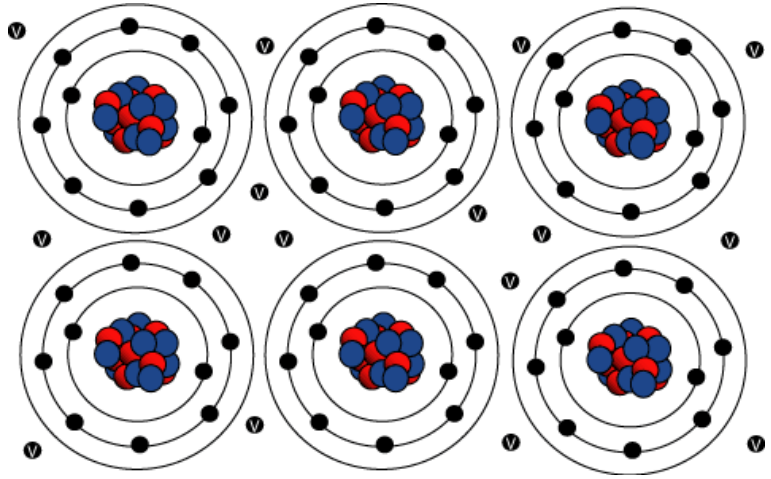
Potential for Metals

Embedded Atom Potential (EAM)

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



$$\rho_i = \sum_{j \neq i} f_j(r_{ij})$$ **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)

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

$$\rho_i = \sum_{j\neq i} f_j(r_{ij}) + \sum_{j\neq i} \sum_{k>j,k\neq i} g(r_{ij})g(r_{ik})\psi(\cos\theta_{jik})$$

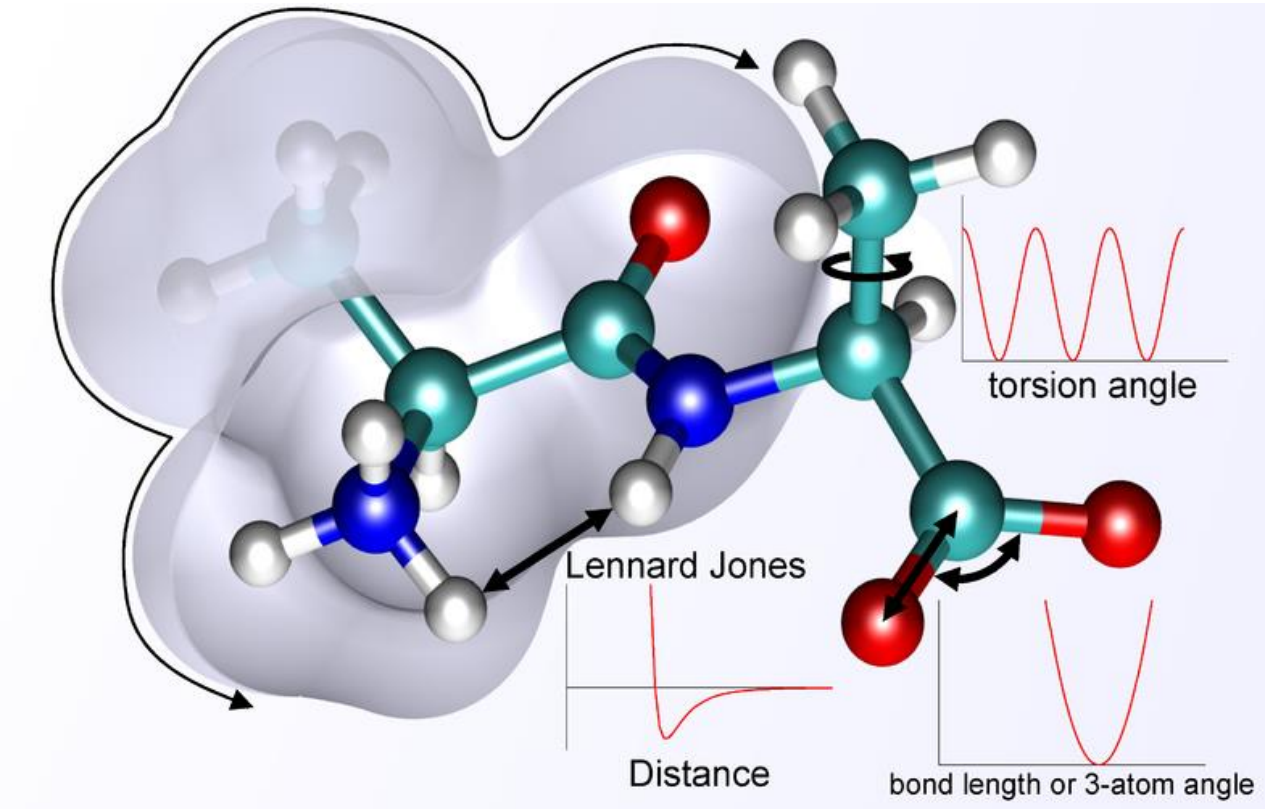
Using Rose function to construct the embedding function

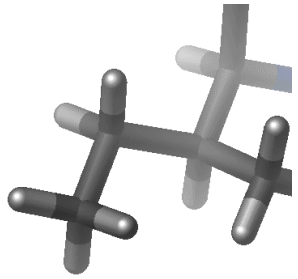
$$E(a^*) = -E_{\text{coh}} f(a^*)$$

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

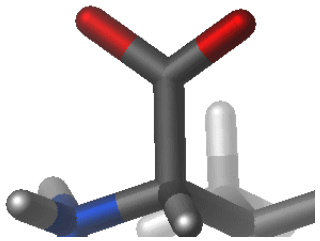
$$a^* = \left(\frac{a}{a_0} - 1\right)\left(\frac{E_{\text{coh}}}{9B\Omega}\right)^{-1/2}$$

Potential for polymers

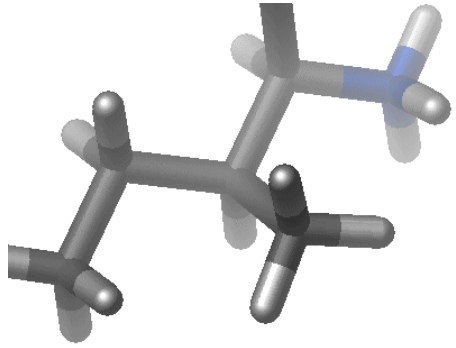




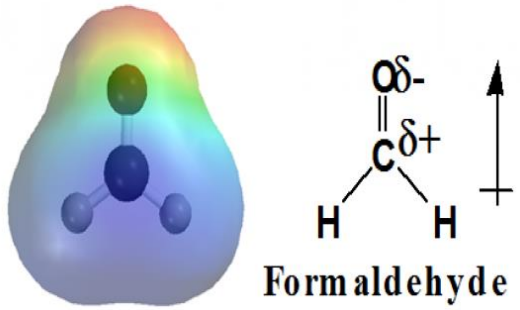
Bond length stretching



Bond angle bending



Dihedral torsion



Partial charges

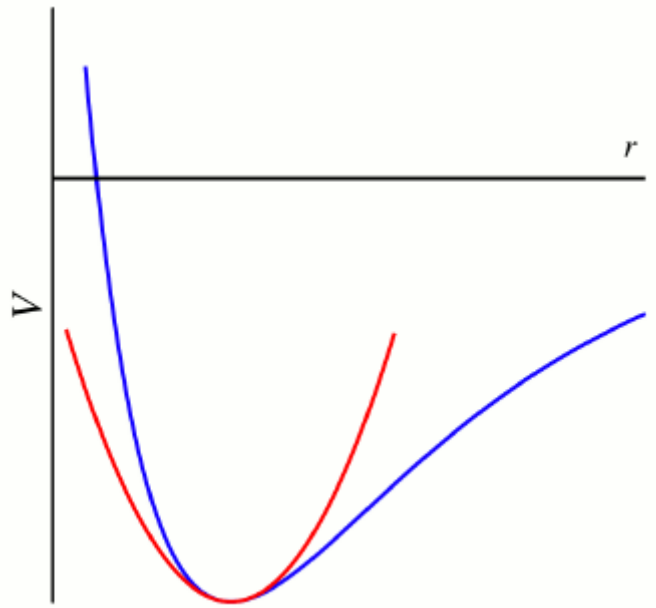
$$E_{\text{total}} = \sum_{\text{bonds}} \phi_b(r) + \sum_{\text{angles}} \phi_\theta(\theta) + \sum_{\text{dihedrals}} \phi_\psi(\psi) + \sum_{i<j} U_{LJ}(r_{ij}) + k \sum_{i<j} \frac{q_i q_j}{r_{ij}} + \cdots$$

Potential for polymers

Bond stretch

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

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



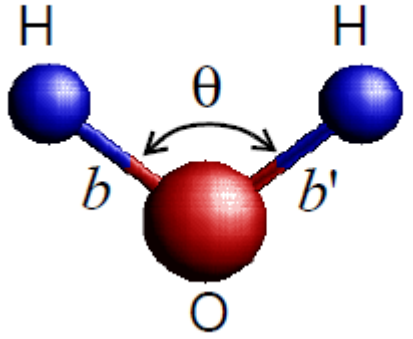
Morse potential, enable breaking at infinite distance

$$E_{\text{bond}} = \sum_{\text{bonds}} D_b\left[1 - e^{-\alpha(b-b_0)}\right]^2 = \sum_{\text{bonds}} D_b\left[e^{-2\alpha(b-b_0)} - 2e^{-\alpha(b-b_0)} + 1\right]$$

Potential for polymers

Bond bending

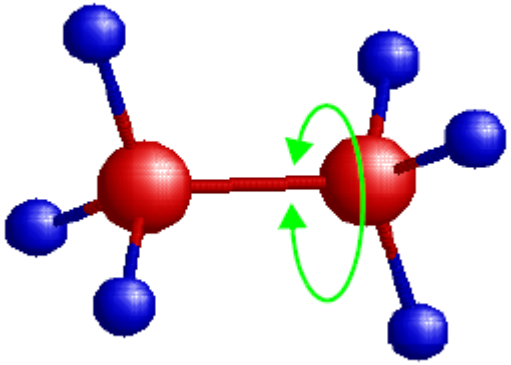
$$E_{\text{angle}} = \sum_{\text{angles}} \frac{1}{2} H_\theta (\theta - \theta_0)^2,$$



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

Bond torsion (Dihedral)

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

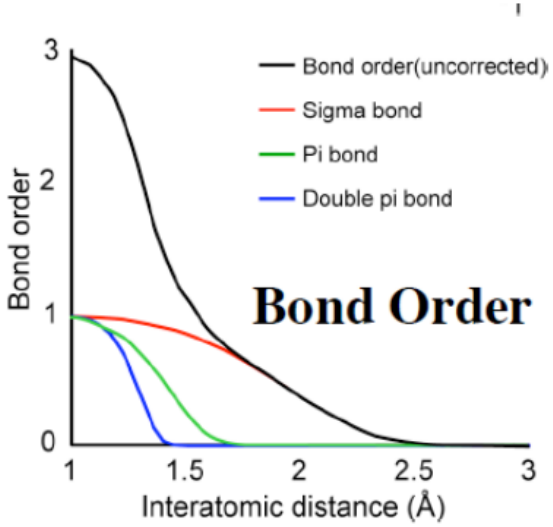


Reactive Force Fields

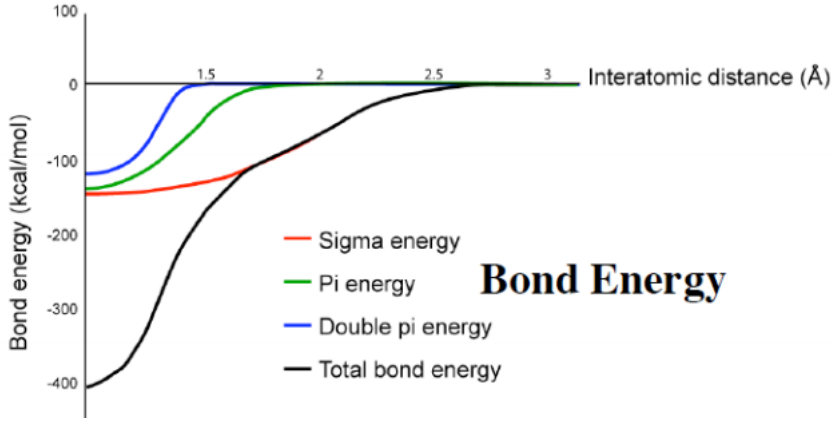
A bond-order/distance relationship

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

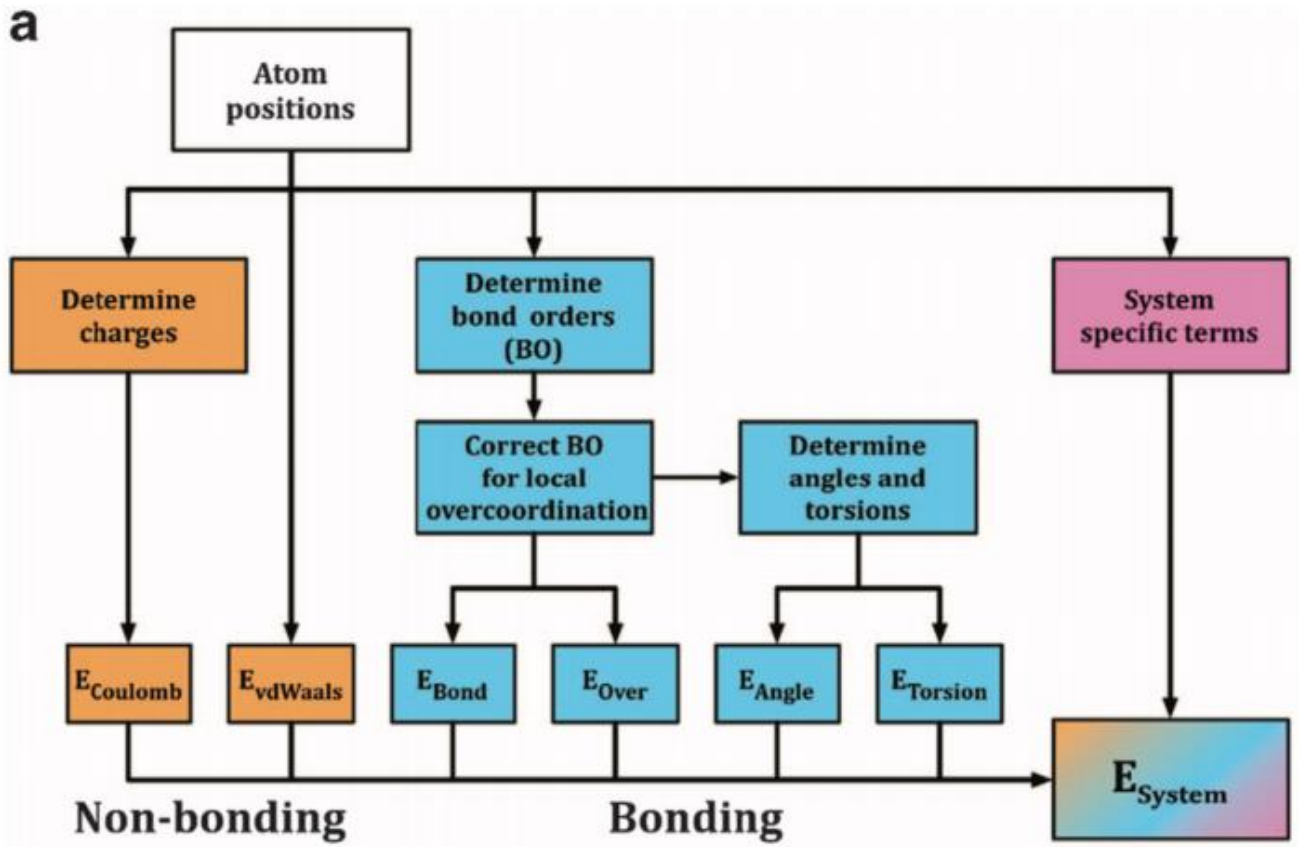
C-C bond order



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



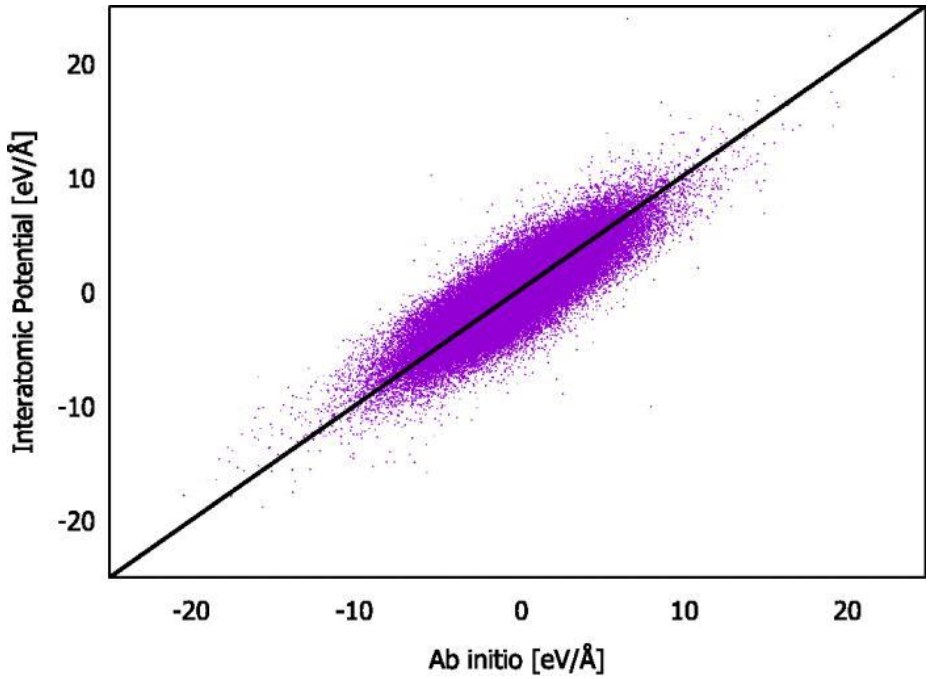
*Russo, Michael F., and van Duin, Adri. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **269** (2011): 1549-1554.

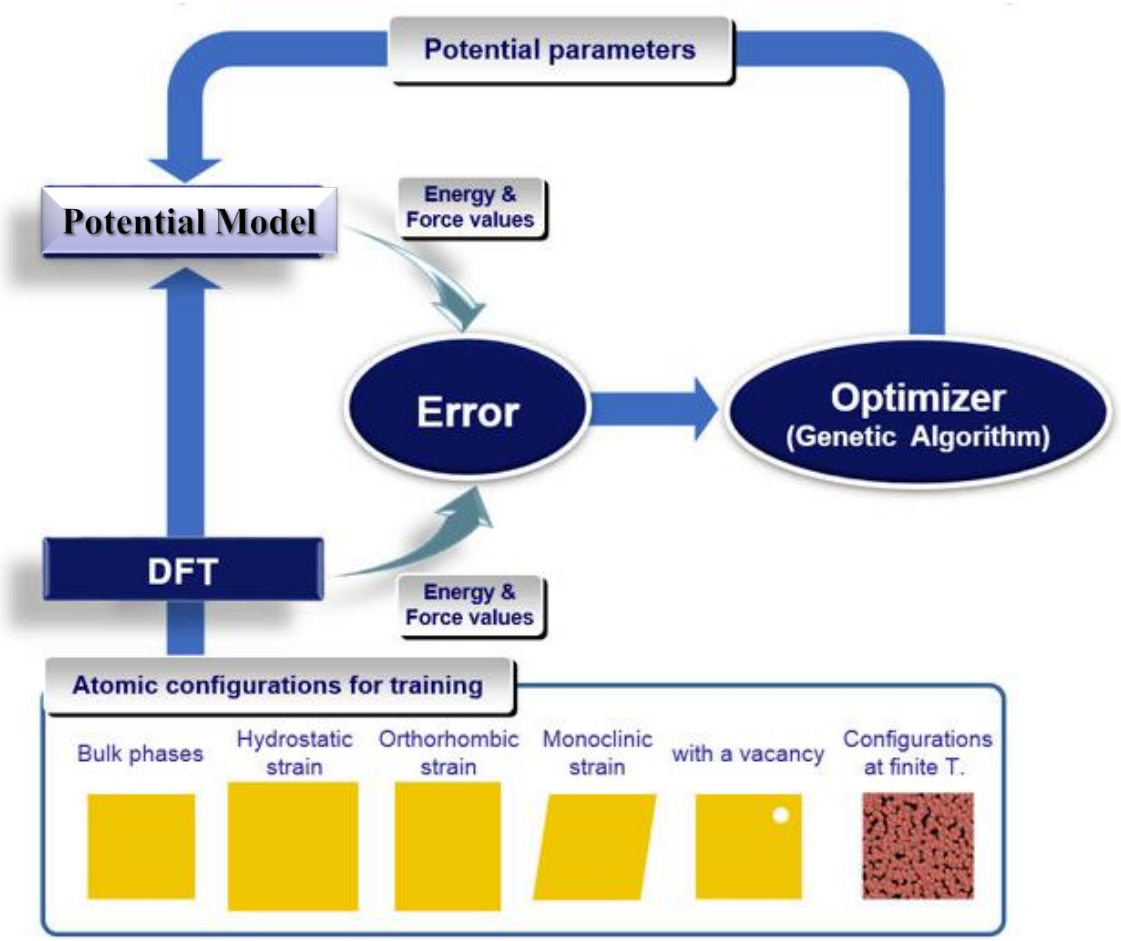


*Senftle, Thomas, *et al. npj Computational Materials* **2** (2016).

Potential Fitting

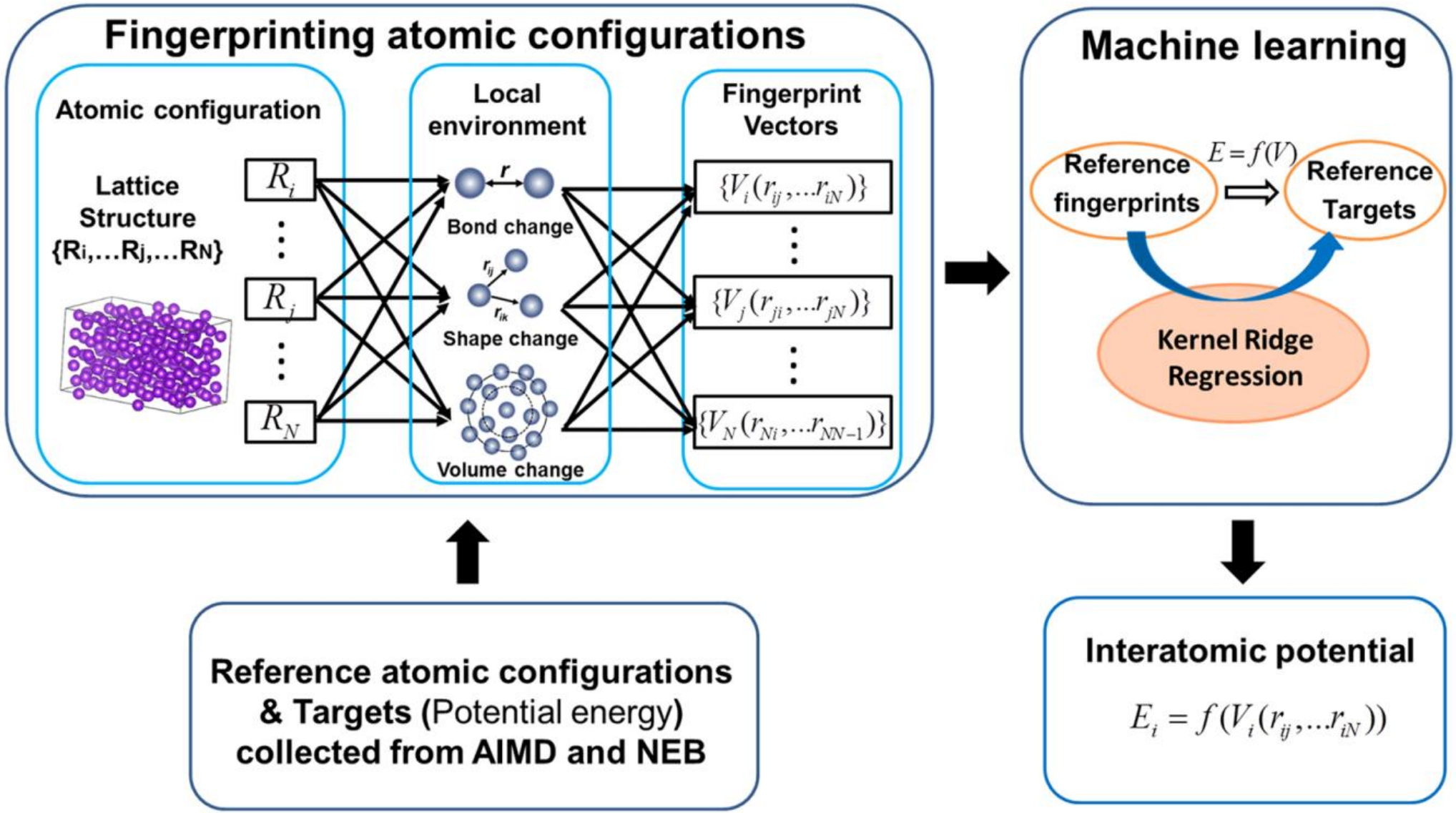
Physical property	Atom-level property
Crystal structure	Balance of atomic forces.
Cohesive energy	Potential energy at the equilibrium atom positions
Elastic constants $c_{\rho\sigma}$	Long-wavelength acoustic vibrations Elastic distortions of unit cell.
Equation of state $P(V)$	Compression or expansion of material
Neutron scattering	Phonon $\omega(\mathbf{k})$ in the Brillouin zone.





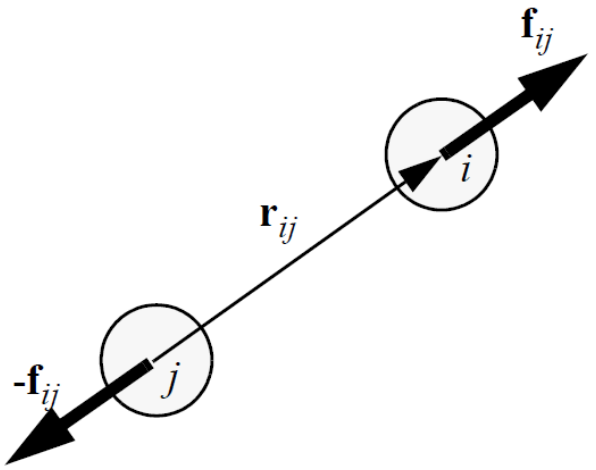
$$Error = \sum_{i}^{\text{property}} \sum_{j}^{\text{configuration}} \sum_{k}^{\text{run}} \sum_{l}^{\text{atom}} w_{ijkl} \frac{|p_{ijkl}^{\text{pot}} - p_{ijkl}^{\text{ref}}|^2}{\Delta_i}$$

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 $$\mathbf{f}_i = f_{x_i}\cdot\mathbf{x} + f_{y_i}\cdot\mathbf{y} + f_{z_i}\cdot\mathbf{z}$$

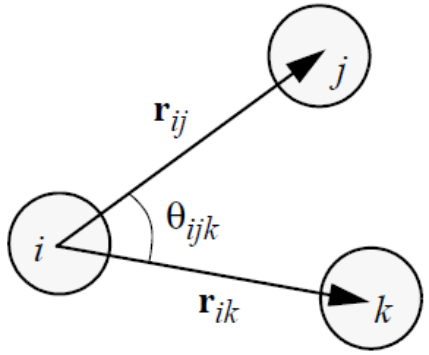
$$f_{x_i} = -\frac{\partial U}{\partial x_i} = -\sum_{j\neq i} \left.\frac{\partial \phi}{\partial r}\right|_{r=r_{ij}} \frac{\mathrm{d}r_{ij}}{\mathrm{d}x_i} = -\sum_{j\neq i} \phi'(r_{ij})\frac{x_{ij}}{r_{ij}}$$

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

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 = y[j][0] – y[i][0]; zij = z[j][0] – z[i][0];
    Apply_PBC(xij, yij, zij);
    rij = sqrt(xij*xij + yij*yij + zij*zij);
    if (rij < Rcut){
        dp = - partial_phi(rij);
        fij = dp / rij * [xij, yij, zij];
        f[i] += fij;      f[j] -= fij;
    }
}}
```

Force Evaluation (angular term)



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

LAMMPS cosine/squared angle style

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

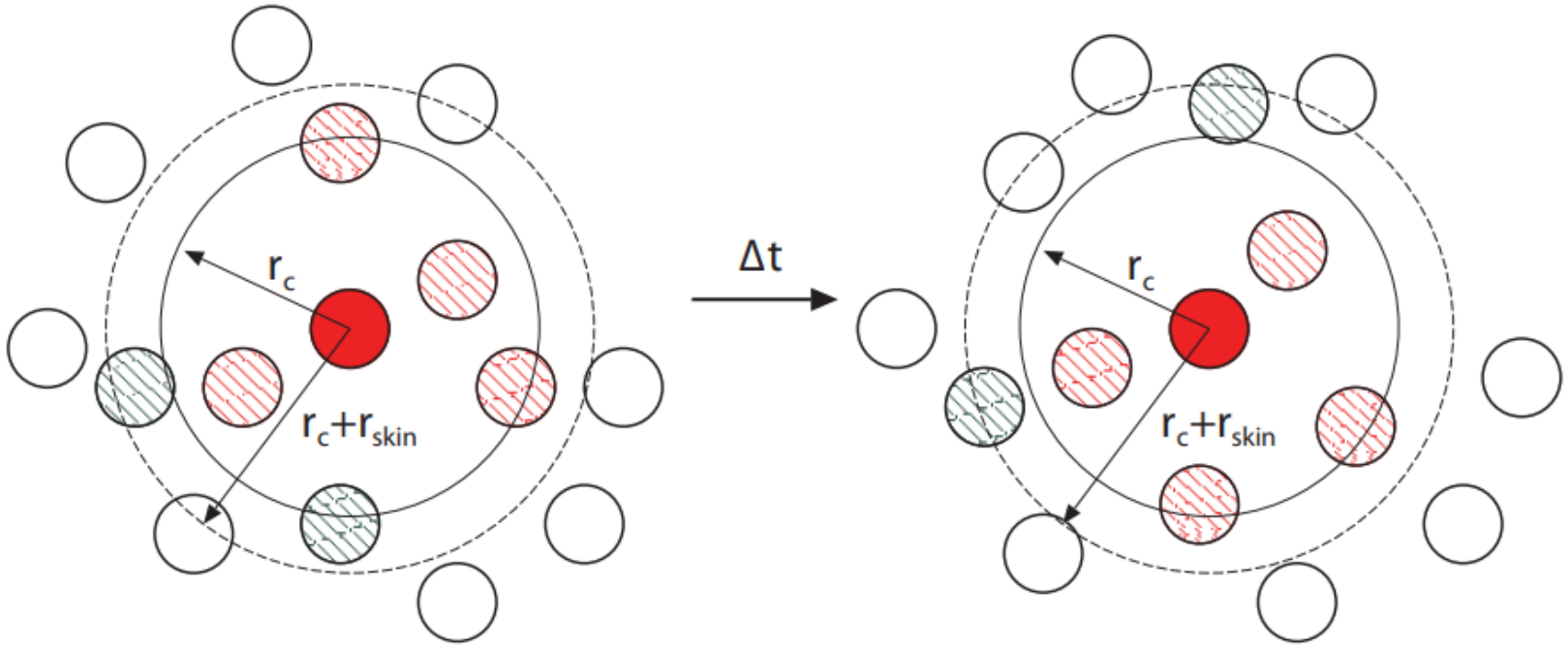
$$\mathbf{f}_i = -\frac{\partial E}{\partial \mathbf{r}_i} = -\frac{\partial E}{\partial \cos\theta}\frac{\mathrm{d}\cos\theta}{\mathrm{d}\mathbf{r}_i}$$

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

Neighbor list

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

$O(N^2)$

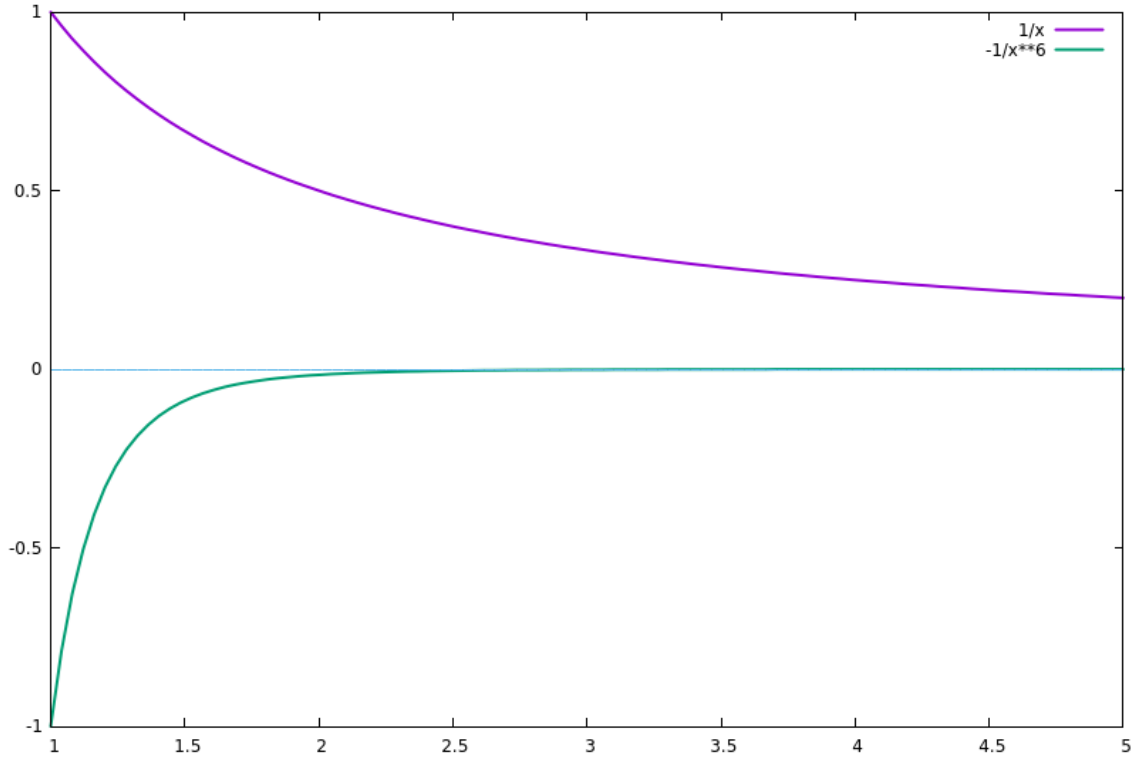



```
for (i = 0; i<N; ++i){
for (jj = 0; jj < num_nei[i]; ++jj){
    j = neighbor[i][jj];
    ….
    }
}}
```

$O(N)$

Long range interaction

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



Ewald sum method

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

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

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

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

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

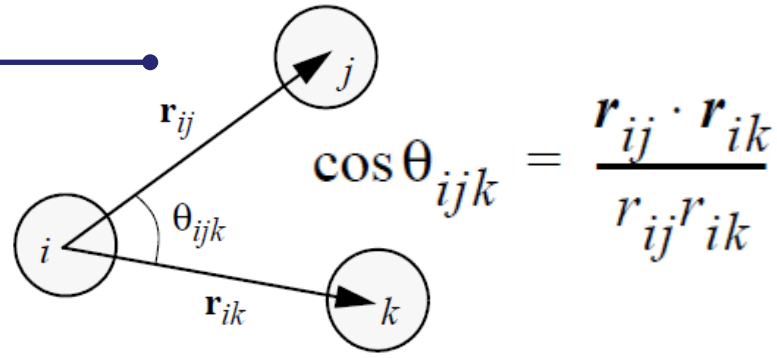
- **Ewald summation**
- **Field multipole method**
- **Particle-Particle/Particle-Mesh**
- **Random Batch Ewald**

https://math.sjtu.edu.cn/faculty/xuzl/RBE.pdf

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: Oct. 19, 2022

Next Lecture：

Molecular Statics & Temperature/Pressure Control