

Introduction to interatomic potentials (I)

In order to use Molecular Dynamics or Monte Carlo methods we have to define the rules that are governing interaction of atoms in the system. In classical and semi-classical simulations these rules are often expressed in terms of potential functions. The potential function $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ describes how the potential energy of a system of N atoms depends on the coordinates of the atoms, $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$. It is assumed the electrons adjust to new atomic positions much faster than the motion of the atomic nuclei (Born-Oppenheimer approximation).

The forces in MD simulation are defined by the potential, $\vec{F}_i = -\vec{\nabla}_{\vec{r}_i} U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$

How to obtain the potential function for a particular system?

1. One can assume a functional form for the potential function and then choose the parameters to reproduce a set of experimental data. This gives so-called **empirical** potential functions (e.g. Lennard-Jones, Morse, Born-Mayer).
2. One can calculate the electronic wavefunction for fixed atomic positions. This is difficult for a system of many atoms. Different approximations are used and analytic **semi-empirical** potentials are derived from quantum-mechanical arguments (e.g. Embedded Atom Method (EAM) by Foiles, Baskes, and Daw, Glue Model by Ercolessi et al., bond-order potentials by Tersoff and Brenner, etc.).
3. One can perform direct electronic-structure (quantum-mechanics-based) calculations of forces during so-called **ab-initio** MD simulation (e.g., Car-Parrinello method using plane-wave pseudopotentials).

Introduction to interatomic potentials (II)

Going from QM to classical mechanics through the Born-Oppenheimer approximation

In Molecular Dynamics or Monte Carlo methods we use potential function U to describe interaction among atoms. But we know that in real materials the dynamics of atoms is controlled by the laws of quantum mechanics and the bonding is defined by the electrons that are not present in classical MD/MC. Is the use of the potential functions justified?

The Hamiltonian for a real material is defined by the presence of interacting nuclei and electrons:

$$H = \sum_i \frac{P_i^2}{2M_i} + \sum_\alpha \frac{p_\alpha^2}{2m} + \frac{1}{2} \sum_{ij} \frac{Z_i Z_j e^2}{|\vec{R}_i - \vec{R}_j|} + \frac{1}{2} \sum_{\alpha\beta} \frac{e^2}{|\vec{r}_\alpha - \vec{r}_\beta|} - \sum_{i\alpha} \frac{Z_i e^2}{|\vec{R}_i - \vec{r}_\alpha|}$$

where we can recognize the kinetic energy terms and coulombic interactions. In principle we should solve a Schrödinger equation $H\psi=E\psi$ and find the total wavefunction $\psi(\mathbf{R}_i, \mathbf{r}_\alpha)$ which tells us everything about the system. But... this is impossible and we should use approximations. In 1923 Born and Oppenheimer noted that electrons ($m_e=5.5 \cdot 10^{-4}$ amu) are much lighter than nuclei, and are moving much faster:

$$\frac{\omega_{el}}{\omega_n} \sim \sqrt{\frac{M}{m}} \sim 100$$

We can then consider electronic motion for fixed nuclei and factorize the total wavefunction as $\psi(\mathbf{R}_i, \mathbf{r}_\alpha) = \Xi(\mathbf{R}_i)\Phi(\mathbf{r}_\alpha, \mathbf{R}_i)$, where $\Xi(\mathbf{R}_i)$ describes the nuclei, and $\Phi(\mathbf{r}_\alpha, \mathbf{R}_i)$ depends parametrically on \mathbf{R}_i and describes the electrons. The problem then can be reformulated in terms of two separate Schrödinger equations: $H_{el}\Phi(\mathbf{r}_\alpha, \mathbf{R}_i)=U(\mathbf{R}_i)\Phi(\mathbf{r}_\alpha, \mathbf{R}_i)$ and $H_i\Xi(\mathbf{R}_i)=E\Xi(\mathbf{R}_i)$, where

$$H_{el} = \sum_\alpha \frac{p_\alpha^2}{2m} + \frac{1}{2} \sum_{ij} \frac{Z_i Z_j e^2}{|\vec{R}_i - \vec{R}_j|} + \frac{1}{2} \sum_{\alpha\beta} \frac{e^2}{|\vec{r}_\alpha - \vec{r}_\beta|} - \sum_{i\alpha} \frac{Z_i e^2}{|\vec{R}_i - \vec{r}_\alpha|} \quad H_i = \sum_i \frac{P_i^2}{2M_i} + U(\mathbf{R}_i)$$

The equation for the electronic problem $H_{el}\Phi(\mathbf{r}_\alpha, \mathbf{R}_i)=U(\mathbf{R}_i)\Phi(\mathbf{r}_\alpha, \mathbf{R}_i)$ gives the energy $U(\mathbf{R}_i)$ that depend parametrically on the coordinates of the nuclei, \mathbf{R}_i . Once found, $U(\mathbf{R}_i)$ enters $H_i\Xi(\mathbf{R}_i)=E\Xi(\mathbf{R}_i)$ which describes the motion of nuclei. The later equation does not include any electronic degrees of freedom, all the electronic effects are incorporated in $U(\mathbf{R}_i)$ that is called **interatomic potential**.

In classical MD we replace Schrödinger equation with Newton equation. As we discussed before, this replacement is justified when if the de Broglie thermal wavelength is much less than the smallest interatomic separation (this condition is justified for all atoms except for the lightest ones).

Introduction to interatomic potentials (III)

When choosing potentials one should consider the following characteristics:

Accuracy (reproduce properties of interest as closely as possible)

Transferability (can be used to study a variety of properties for which it was not fit)

Computational speed (calculations are fast with simple potentials)

The choice of the interatomic potential depends on the area of intended application, there are (almost) no “good” or “bad” potentials, there are potentials that are appropriate or inappropriate for a given problem. High accuracy is typically required in Computational Chemistry, computational speed is often critical in Materials Science (processes have a collective character and big systems should be simulated for long times).

Pair potentials vs. many-body potentials

The total energy of the system of N atoms with interaction described by an empirical potential can be expanded in a many-body expansion:

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_i U_1(\vec{r}_i) + \sum_i \sum_{j>i} U_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_{j>i} \sum_{k>j} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

U_1 – one-body term, due to an external field or boundary conditions (wall of a container).

U_2 – two-body term, or pair potential. The interaction of any pair of atoms depends only on their spacing and is not effected by the presence of other atoms.

U_3 – three-body term arise when the interaction of a pair of atoms is modified by the presence of a third atom.

Based on this expansion, we can loosely separate potentials into two classes: **pair potentials** (only U_2 is present) and **many-body potentials** (U_3 and higher terms are included).

We will also consider examples of many-potentials in which multi-body effects are included implicitly, through an environment dependence of two-body terms.

Short review of potentials used in MD and MC

The plan of this short review is as follows.

Pair Potentials (hard spheres, Lennard-Jones, Morse)

- for inert gases, intermolecular van der Waals interaction in organic materials;
- for investigation of general classes of effects (material non-specific).

Calculation of forces for a given pair potential function.

Relation between interatomic potentials and lattice properties: lattice energy, elastic constants, vacancy energy. Calculation of elastic constants for pair potentials. The limitations of pair potentials.

Potentials for metallic systems

Isotropic many-body pair-functional potentials for metals (the Embedded Atom, the Glue, the Effective Medium Models). The advantages and limitations of pair-functional potentials.

Angular-dependent many-body potentials for BCC metals

Potentials for ionic systems, ceramics

The Born model for sodium chloride, the shell model.

Potentials for covalently bounded systems

Angular-dependent many-body potential for Si (Stillinger-Weber)

Bond order potential by Tersoff for Si, GaAs, Ge

Reactive potential for different forms of carbon and hydrocarbons by Brenner

Molecular Mechanics potentials (Force-Field Methods)

Pair potentials

The total potential energy of the system of N atoms interacting via pair potential is:

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_i \sum_{j>i} U_2(r_{ij}) \quad \text{where} \quad r_{ij} = |\vec{r}_j - \vec{r}_i|$$

Commonly used examples of pair potentials:

Hard/soft spheres – the simplest potential without any cohesive interaction. Useful in theoretical investigations of some idealized problems.

$$U(r_{ij}) = \begin{cases} \infty & \text{for } r_{ij} \leq r_0 \\ 0 & \text{for } r_{ij} > r_0 \end{cases} \quad \text{- hard} \qquad U(r_{ij}) = \left(\frac{r_{ij}}{r_0} \right)^{-n} \quad \text{- soft}$$

Ionic – Coulomb interaction of charges, strong, long range repulsion or attraction. Is often added to other functional forms to account for charge-charge interaction or polarization.

$$U(r_{ij}) = \frac{q_i q_j}{r_{ij}}$$

Lennard-Jones – van der Waals interaction in inert gases and molecular systems. Often used to model general effects rather than properties of a specific material.

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

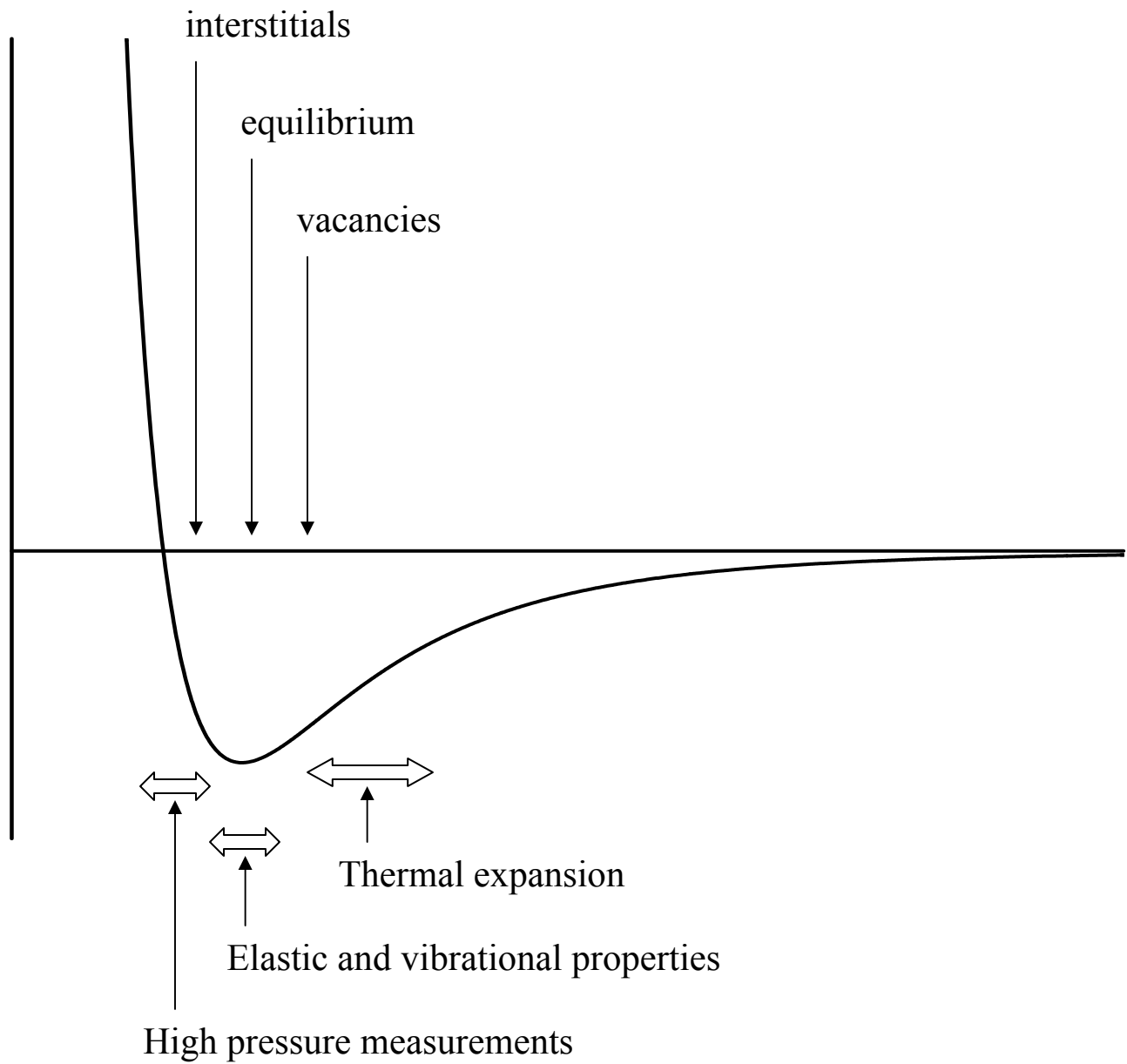
Morse – similar to Lennard-Jones but is a more “bonding-type” potential and is more suitable for cases when attractive interaction comes from the formation of a chemical bond. Proposed by P. M. Morse, Phys. Rev. **34**, 57, 1930. It was a popular potential for simulation of metals that have fcc and hcp structures. A fit for many metals is given by Girifalco and Weizer, Phys. Rev. 114, 687, 1959.

$$U(r_{ij}) = \epsilon \left[e^{-2\alpha(r_{ij}-r_0)} - 2e^{-\alpha(r_{ij}-r_0)} \right]$$

6-exp (Buckingham) potential – exp term (Born-Mayer) provides a better description of strong repulsion due to the overlap of the closed shell electron clouds, which is important in simulation of bombardment by energetic atoms or ions, etc.

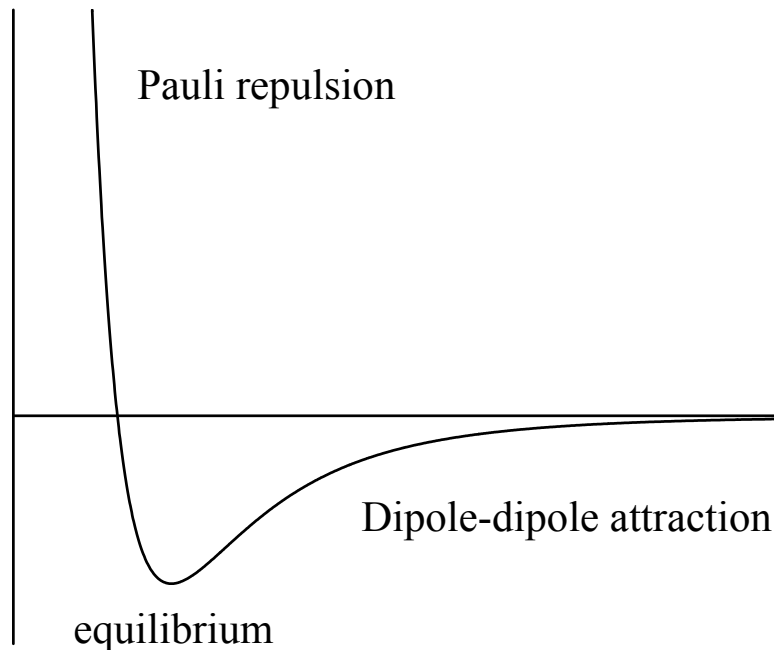
$$U(r_{ij}) = Ae^{-r_{ij}/R_{BM}} - B/r_{ij}^6$$

Fitting the parameters of the potential to experimental data



Lennard – Jones potential (I)

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$



The term $\sim 1/r_{ij}^{12}$ - the repulsion between atoms when they are brought close to each other. Its physical origin is related to the Pauli principle: when the electronic clouds surrounding the atoms starts to overlap, the energy of the system increases abruptly. The exponent 12 was chosen on a practical basis: Lennard-Jones potential is particularly easy to compute. In fact, on physical grounds an exponential behavior would be more appropriate. Exponential term for repulsion (Born-Mayer potential) is typically used in simulations where high-energy inter-atomic collisions are involved.

The term $\sim 1/r_{ij}^6$, dominating at large distance, constitute the attractive part and describes the cohesion to the system. A $1/r^6$ attraction describes van der Waals dispersion forces (dipole-dipole interactions due to fluctuating dipoles). These are rather weak interactions, which however are responsible for bonding in closed-shell systems, such as inert gases.

Lennard – Jones potential (II)

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

The potential provides a good description of van der Waals interaction in inert gases and molecular systems (Ar, Kr, CH₄, O₂, H₂, C₂H₄, etc.). Parameters are given in [J. Chem. Phys. 104 8627 (1996)]. Parameters for inert gases can be also found in Ashcroft-Mermin textbook. For example, Ar ($\epsilon = 0.0104$ eV, $\sigma = 3.40$ Å), Ne ($\epsilon = 0.0031$ eV, $\sigma = 2.74$ Å), Kr ($\epsilon = 0.0140$ eV, $\sigma = 3.65$ Å), Xe ($\epsilon = 0.020$ eV, $\sigma = 3.98$ Å).

Many-body effects in the interaction are present in inert gases as well and potentials more accurate than Lennard-Jones have been developed for rare gases. Many body effects can account for up to 10 % of total energy.

There was an attempt to parameterize Lennard-Jones potentials for metals [T. Halicioğlu and G. M. Pound, Phys. Stat. Sol. **30**, 619 1975], but it did not find any practical application. Another pair potential, by Morse, provides a better description of some of the properties of metals with fcc and hcp structure.

Lennard-Jones potential is also often used in simulations when the objective is to model a general class of effects and the only requirement is to have a physically reasonable potential. **→ the main reason for popularity of Lennard-Jones potential.** (e.g. an expensive billion atoms simulation of ductile failure of a FCC solid under tension, that we discussed before, was performed with Lennard-Jones potential).

Many studies on Lennard-Jones solids, liquids, surfaces, clusters have been performed. It is the potential of choice in studies when the focus is on fundamental issues, rather than on properties of a specific material.

Reduced Units

When a potential is simple and has only a few parameters, a set of reduced units is often used in simulations.

Advantage of using reduced units:

- Allows to apply results of a single simulation to different systems that can be described by the same potential with different parameters. This way one can avoid repeating practically the same simulation.
- Evaluation of the potential can be more efficient in reduced units.

Disadvantages of using reduced units:

- Makes interpretation of the results more difficult, physical meaning of the results is not immediately clear. For complex potential scaling of the parameters can be not trivial. I do not recommend using reduced units, but some researchers would recommend them, basically this is a question of taste.

Example: reduced units for Lennard-Jones.

$$U(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

Natural choice of length and energy units is σ and ε .

Then, the complete set of parameters of a system in reduced units can be chosen as

| | |
|-----------------|--|
| Length | $r^* = r/\sigma$ |
| Energy | $E^* = E/\varepsilon$ |
| Time | $t^* = t \times [\varepsilon/(m\sigma^2)]^{1/2}$ |
| Temperature | $T^* = k_B T/\varepsilon$ |
| Force | $F^* = F\sigma/\varepsilon$ |
| Frequency | $\nu^* = \nu \times [m\sigma^2/\varepsilon]^{1/2}$ |
| Pressure | $P^* = P\sigma^3/\varepsilon$ |
| Density | $\rho^* = \rho\sigma^3/m$ |
| Surface tension | $\gamma^* = \gamma\sigma^2/\varepsilon$ |
| etc. ... | |

In simulations where reduced units are used, the system is sometimes called “Lennard-Jonesium” and atoms are “Lennard-Jones atoms”...

“Lennard-Jonesium” have been studied extensively, and phase diagrams are known, e.g. Molecular Physics **37-5**, 1429, 1979, and simulation conditions targeted at investigation of a given phenomenon can be easily chosen.

Derivation of the force for pair potential

In MD simulation we need forces that are acting on the atoms. The forces are given by the gradient of the potential energy surface (the force on atom i is a vector pointing in the direction of the steepest decent of the potential energy): $\vec{F}_i = -\vec{\nabla}_{\vec{r}_i} U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$

Note, that $\vec{\nabla}_{\vec{r}_i}$ operates on the position \vec{r}_i of atom i . **Any change in the total potential energy that results from a displacement of atom i contributes to the force acting on atom i .** This is important to keep in mind when calculating forces for many-body potentials.

For a pair potential:
$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_i \sum_{j>i} U(r_{ij})$$

where
$$r_{ij} = |\vec{r}_i - \vec{r}_j| = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$

The force on atom i is
$$\vec{F}_i = -\vec{\nabla}_{\vec{r}_i} U(\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_N) = -\sum_{j \neq i} \vec{\nabla}_{\vec{r}_i} U(r_{ij}) =$$

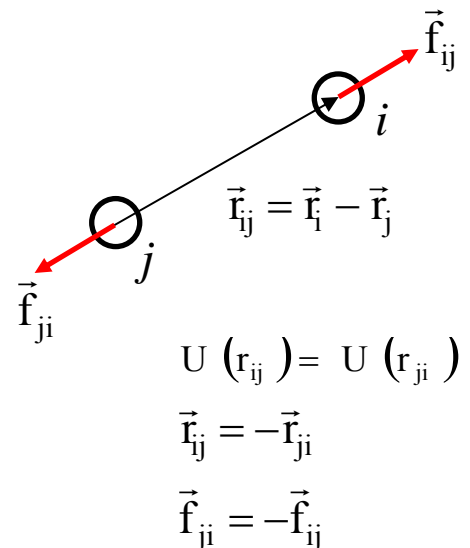
$$= -\sum_{j \neq i} \left(\hat{x} \frac{\partial}{\partial x_i} + \hat{y} \frac{\partial}{\partial y_i} + \hat{z} \frac{\partial}{\partial z_i} \right) U(r_{ij}) = -\sum_{j \neq i} \left(\hat{x} \frac{\partial r_{ij}}{\partial x_i} + \hat{y} \frac{\partial r_{ij}}{\partial y_i} + \hat{z} \frac{\partial r_{ij}}{\partial z_i} \right) \frac{dU(r_{ij})}{dr_{ij}} =$$

$$= -\sum_{j \neq i} \left(\hat{x} \frac{x_{ij}}{r_{ij}} + \hat{y} \frac{y_{ij}}{r_{ij}} + \hat{z} \frac{z_{ij}}{r_{ij}} \right) \frac{dU(r_{ij})}{dr_{ij}} = -\sum_{j \neq i} \left(\frac{\vec{r}_i - \vec{r}_j}{r_{ij}} \right) \frac{dU(r_{ij})}{dr_{ij}} = \sum_{j \neq i} \vec{f}_{ij}$$

For Lennard-Jones:
$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

$$\frac{dU(r_{ij})}{dr_{ij}} = 4\epsilon \left[-12 \frac{\sigma^{12}}{r_{ij}^{13}} + 6 \frac{\sigma^6}{r_{ij}^7} \right]$$

$$\vec{F}_i = -\sum_{j \neq i} 24 \frac{\epsilon \sigma^6 (\vec{r}_i - \vec{r}_j)}{r_{ij}^8} \left[1 - 2 \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$



Potential cut-off (I)

The potential functions like L-J have an infinite range of interaction. In practice a cutoff radius R_c is established and interactions between atoms separated by more than R_c are ignored. There are two reasons for this:

1. The number of pair interactions grows as N^2 . Example: Consider system of 3000 atoms. There are $N^2/2 = 4.5$ million pairs of atoms. Using a cutoff of 8-10 Å we can reduce a number of interacting neighbors for each atom to ~ 50 and we will have to evaluate force only $\sim 50N = 150$ thousand times.
2. The size of the system that can be simulated is finite, periodic boundary conditions are often used and we do not want an atom to interact with itself.

A simple truncation of the potential creates a jump in the potential at the cutoff distance. This can spoil the energy conservation or lead to unphysical behavior in simulations of the effects where contribution of far-away molecules is important (surface tension, stacking faults, etc.). To avoid this potential can be shifted:

$$U(r_{ij}) = \begin{cases} U(r_{ij}) - U(R_c) & r_{ij} \leq R_c \\ 0 & r_{ij} > R_c \end{cases}$$

For shifted potentials forces can have a jump at the cutoff. To avoid this, a smooth transition function that brings potential to zero can be added.

In any case, physical quantities (cohesive energy, total pressure etc.) are affected by the truncation and most modern potentials for real materials are designed with a cutoff radius in mind, and go to zero at R_c together with several first derivatives of the potential function.

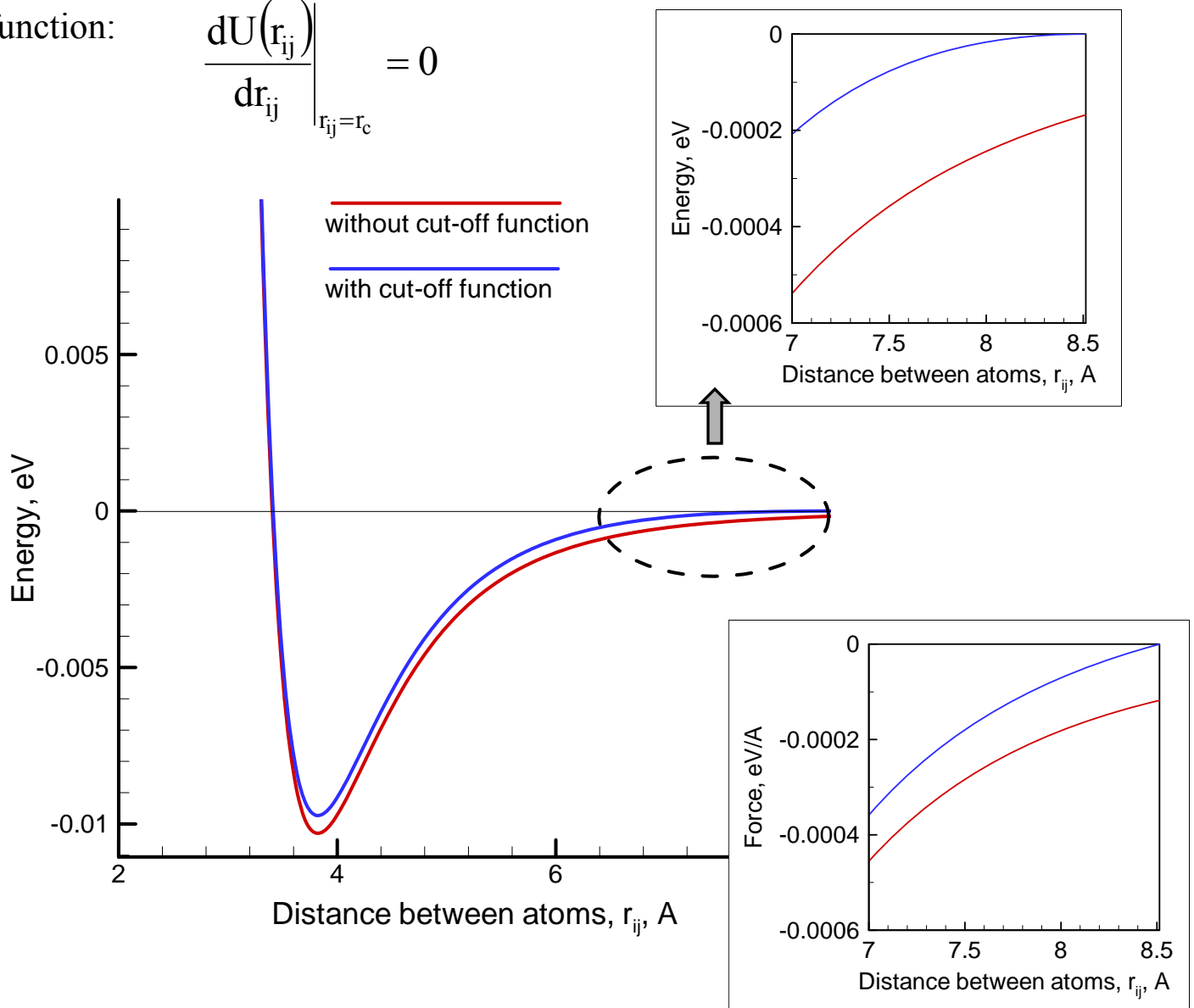
Potential cut-off (II)

Example: Lennard-Jones potential. Typical cut-off used is $r_c \sim 2.5 - 5.5\sigma$

$$U(r_{ij}) = 4\epsilon \left[\left\{ \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right\} + \underbrace{\left\{ 6 \left(\frac{\sigma}{r_c} \right)^{12} - 3 \left(\frac{\sigma}{r_c} \right)^6 \right\} \left(\frac{r_{ij}}{r_c} \right)^2 - \left\{ 7 \left(\frac{\sigma}{r_c} \right)^{12} - 4 \left(\frac{\sigma}{r_c} \right)^6 \right\}}_{\text{Cut-off function}} \right]$$

Cut-off function by S. D. Stoddard and J. Ford, Phys. Rev. A **8**, 1504, 1973.

With cut-off function: $U(r_c) = 0$
 $\left. \frac{dU(r_{ij})}{dr_{ij}} \right|_{r_{ij}=r_c} = 0$



Limitations of pair potentials

Many body effects are important in real materials.

Metals

Pair potentials **do not have environmental dependence** (e.g. atom in the bulk is too similar to the atom on the surface or near a defect site). In reality, the strength of the “individual bonds” should decrease as the local environment becomes too crowded due to the Pauli’s principle, but pair potentials do not depend on the environment and cannot account for this decrease.

Pair potentials **do not account for directional nature of the bond**. Covalent contributions (d orbitals) of the transition metals can not be described. Pair potentials work better for metals in which cohesion is provided by s and p electrons.

Quantitative problems:

The vacancy formation energy, E_v , is significantly overestimated by pair potentials ($E_v \sim E_c$ with pair potential, $E_v=0.25E_c$ for Au, $E_v=0.33E_c$ for Cu, where E_c is the cohesive energy).

The ratio between the cohesive energy and the melting temperature, T_m , is underestimated by as much as 2-3 times. Metals have some “extra cohesion” that is less effective than pair potential in keeping the system in the crystalline state.

Pair potentials do not describe the deviations from the Cauchy relation for elastic constants in cubic crystals ($C_{12} = C_{44}$ or $G = 3/5 B$). This issue is considered in the next two pages.

Semiconductors and other covalently bonded systems

Pair potentials favor close-packed structures whereas most of the covalently bond crystals have open structures. (Si forms diamond lattice with 4 neighbors and has several polytypes under pressure. Pair potentials are useless for such systems).

Potentials for organic or biomolecular systems have to account for many contributions to the potential energy coming from stretching, bending, torsion deformations of bonds and bond angles.

Relationship between pair potential and elastic constants (I)

The bonding energy density of the system of N atoms interacting via pair potential is:

$$E_b = \frac{1}{2N\Omega_a} \sum_{j \neq i} U(r_{ij}) \quad \text{where } \Omega_a \text{ is the average volume per atom}$$

In equilibrium, when the force acting on any particle is zero, the structure must be stable with respect to the application of a small *homogeneous* strain tensor $\epsilon_{\alpha\beta}$. Then the displacement vector for each interatomic distance, r_{ij} , is $u_{ij}^\beta = a_{ij}^\alpha \epsilon_{\alpha\beta}$ where a_{ij} is undeformed value of r_{ij} (that is, $\mathbf{u}_{ij} = \mathbf{r}_{ij} - \mathbf{a}_{ij}$). The elastic energy can be expanded into a Taylor series with respect to the small displacements:

$$E_b = \frac{1}{2N\Omega_a} \sum_{j \neq i} \left\{ U(r_{ij}) \Big|_0 + \frac{\partial U(r_{ij})}{\partial r_{ij}^\beta} \Big|_0 u_{ij}^\beta + \frac{1}{2} \frac{\partial^2 U(r_{ij})}{\partial r_{ij}^\beta \partial r_{ij}^\delta} \Big|_0 u_{ij}^\beta u_{ij}^\delta + \dots \right\}$$

where the evaluation is at the undeformed values of r_{ij} and summation is implied by repeated indices. Using $u_{ij}^\beta = a_{ij}^\alpha \epsilon_{\alpha\beta}$ we can rewrite this equation as

$$E_b(\epsilon) = E_b(0) + A_{\alpha\beta} \epsilon_{\alpha\beta} + \frac{1}{2} C_{\alpha\beta\gamma\delta} \epsilon_{\alpha\beta} \epsilon_{\gamma\delta} + \dots$$

where

$$A_{\alpha\beta} = \frac{1}{2N\Omega_a} \sum_{j \neq i} \frac{\partial U(r_{ij})}{\partial r_{ij}^\beta} \Big|_0 a_{ij}^\alpha \quad \text{- tensor of internal stresses. First invariant of this tensor } (A_{xx} + A_{yy} + A_{zz})/3 \text{ is the pressure. In equilibrium } A_{\alpha\beta} = 0.$$

$$C_{\alpha\beta\gamma\delta} = \frac{1}{2N\Omega_a} \sum_{j \neq i} \frac{\partial^2 U(r_{ij})}{\partial r_{ij}^\beta \partial r_{ij}^\delta} \Big|_0 a_{ij}^\alpha a_{ij}^\gamma \quad \text{- tensor of elastic moduli.}$$

Relationship between pair potential and elastic constants (II)

$$C_{\alpha\beta\gamma\delta} = \frac{1}{2N\Omega_a} \sum_{j \neq i} \left. \frac{\partial^2 U(\mathbf{r}_{ij})}{\partial r_{ij}^\beta \partial r_{ij}^\delta} \right|_0 \mathbf{a}_{ij}^\alpha \mathbf{a}_{ij}^\gamma \quad - \text{tensor of elastic moduli.}$$

For a pair potential:
$$\frac{\partial U(\mathbf{r}_{ij})}{\partial r_{ij}^\beta} = \frac{r_{ij}^\beta}{r_{ij}} \frac{dU(\mathbf{r}_{ij})}{dr_{ij}}$$

$$\frac{\partial^2 U(\mathbf{r}_{ij})}{\partial r_{ij}^\beta \partial r_{ij}^\delta} = \frac{r_{ij}^\beta r_{ij}^\delta}{r_{ij}^2} \left(\frac{d^2 U(\mathbf{r}_{ij})}{dr_{ij}^2} - \frac{1}{r_{ij}} \frac{dU(\mathbf{r}_{ij})}{dr_{ij}} \right) + \delta_{\beta\delta} \frac{1}{r_{ij}} \frac{dU(\mathbf{r}_{ij})}{dr_{ij}}$$

$$C_{\alpha\beta\gamma\delta} = \frac{1}{2N\Omega_a} \sum_{j \neq i} \left[\frac{1}{r_{ij}^2} \left(\frac{d^2 U(\mathbf{r}_{ij})}{dr_{ij}^2} - \frac{1}{r_{ij}} \frac{dU(\mathbf{r}_{ij})}{dr_{ij}} \right) \mathbf{a}_{ij}^\alpha \mathbf{a}_{ij}^\beta \mathbf{a}_{ij}^\gamma \mathbf{a}_{ij}^\delta + \delta_{\beta\delta} \frac{1}{r_{ij}} \frac{dU(\mathbf{r}_{ij})}{dr_{ij}} \mathbf{a}_{ij}^\alpha \mathbf{a}_{ij}^\gamma \right]$$

$A_{\alpha\gamma} = 0$

$C_{\alpha\beta\gamma\delta}$ is symmetric with respect to all changes of indices and using Voigt notation ($C_{11} = C_{1111}$, $C_{12} = C_{1122}$, $C_{44} = C_{2323}$, $C_{66} = C_{1212}$ etc.) we have *Cauchy relation* $C_{12}/C_{44}=1$ satisfied [Cauchy relation can be expressed as $G = 3/5 B$ for polycrystalline isotropic cubic crystals, where $G = 3/5 C_{44} + 2/5 \cdot 1/2(C_{11} - C_{12})$ and $B = 1/3(C_{11} + 2C_{12})$]. The Cauchy relation is often satisfied for van der Waals solids and ionic crystals. It is never valid for metals (e.g. C_{12}/C_{44} is 1.5 for Cu, 1.9 for Ag, 3.7 for Au). This means that for van der Waals and ionic solids the total energy may be reasonably well described by the pair potential approximation. But for metals pair interaction may be used to represent only part of the total energy.

This discrepancy can be corrected (e.g. V. Vitek in MRS Bulletin, February 1996, pp. 20-23) by adding a large density-dependent but **structure-independent** part $U(\Omega)$ to the pair interactions to describe the total bonding energy:

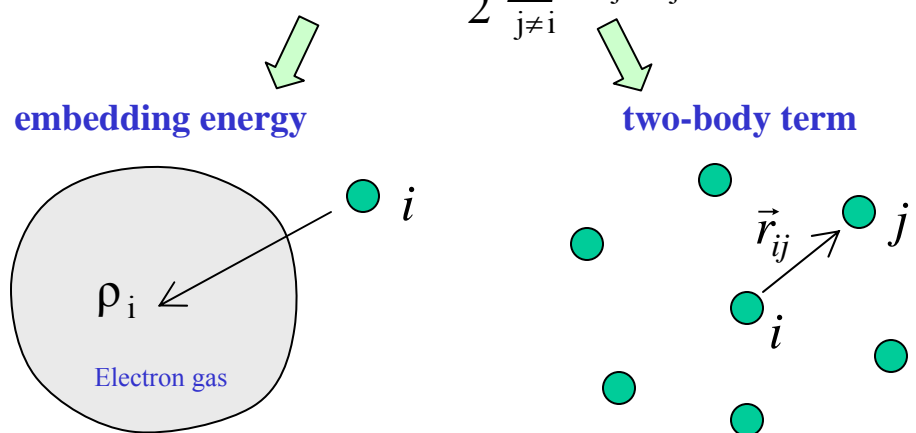
$$E_b = \frac{1}{2N\Omega_a} \sum_{j \neq i} U(\mathbf{r}_{ij}) + U(\Omega_a) \quad \text{where } \Omega_a \text{ is the } \mathbf{average} \text{ volume per atom.}$$

Although such potentials (sometimes called *pseudopotentials*) can provide a better description for the bulk properties of perfect crystals, they can not be used to study lattice defects where the assumption of homogeneous density is incorrect. We will not consider pseudopotentials in this course.

Embedded-atom and related methods for metallic systems (I)

As we discussed above, pair potentials, even with an additional density-dependent term cannot provide an adequate description of metallic systems. An alternative simple but rather realistic approach to the description of bonding in metallic systems is based on the **concept of local density** that is considered as the key variable. This allows one to account for the dependence of the strength of individual bonds on the local environment which is especially important for simulation of surfaces and defects.

Many methods, that have been proposed since early 1980s, have different names (e.g. embedded-atom method - EAM, effective medium theory, Finnis-Sinclair potential, the glue model, corrected effective medium potential - CEM, etc.) and are based on different physical arguments (e.g. tight-binding model, effective-medium theory), but result in a similar expression for the total energy of the system of N atoms:

$$E_{\text{tot}} = \sum_i E_i \quad E_i = F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(\mathbf{r}_{ij}) \quad \rho_i = \sum_{j \neq i} f_j(\mathbf{r}_{ij})$$


Interpretation and functional form of F , f , and ϕ depend on a particular method. From the point of view of effective medium theory or the embedded-atom method, the energy of the atom i is determined by the local electron density at the position of the atom and the function f describes the contribution to the electronic density at the site of the atom i from all atoms j . The sum over function f is therefore a measure of **local electron density** ρ_i . The **embedding energy** F is the energy associated with placing an atom in the electron environment described by ρ . **The pair-potential term** ϕ describes electrostatic contributions. The general form of the potential can be considered as a generalization of the basic idea of the Density Functional Theory – the local electron density can be used to calculate the energy.

Embedded-atom and related methods for metallic systems (II)

In addition to having different physical interpretations, the different methods differ in the way function are determined. Some authors derive functions and parameters from “first-principles” calculations, others guess the functions and fit parameters to experimental data... Results are usually rather similar.

The main advantage of these methods over pair potentials is the ability to describe the variation of the bond strength with coordination. Increase of coordination decreases the strength of each of the individual “bonds” and increases the “bond” length.

$$E_i = F_i \left(\underbrace{\sum_{j \neq i} f_j(\mathbf{r}_{ij})}_{\rho_i} \right) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(\mathbf{r}_{ij})$$

In order to use this potential in MD simulation we need to find the forces:

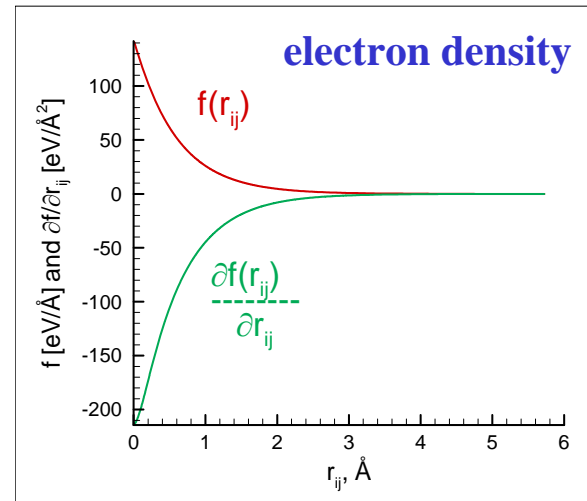
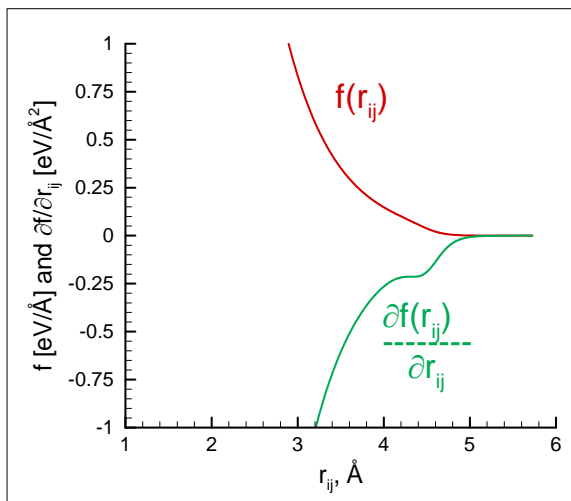
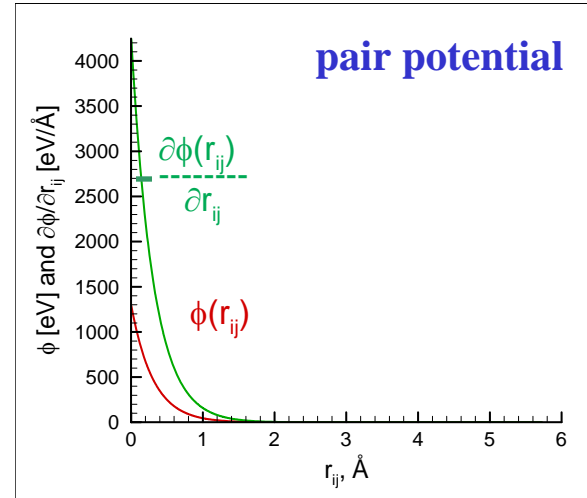
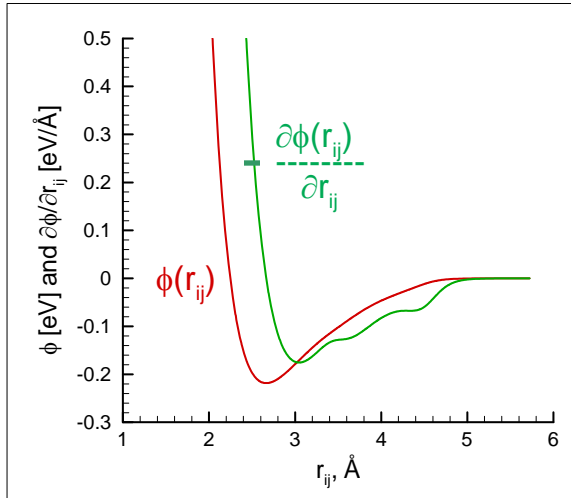
$$\begin{aligned} \vec{F}_i &= -\vec{\nabla}_{\vec{r}_i} E_{\text{Tot}} = -\vec{\nabla}_{\vec{r}_i} \sum_i E_i = -\vec{\nabla}_{\vec{r}_i} \left[F_i(\rho_i) + \sum_{j \neq i} F_j(\rho_j) + \sum_{j \neq i} \phi_{ij}(\mathbf{r}_{ij}) \right] = \\ &= -\sum_{j \neq i} \left[\frac{\partial F_i(\rho)}{\partial \rho} \bigg|_{\rho=\rho_i} \frac{\partial f_j(\mathbf{r})}{\partial \mathbf{r}} \bigg|_{\mathbf{r}=\mathbf{r}_{ij}} + \frac{\partial F_j(\rho)}{\partial \rho} \bigg|_{\rho=\rho_j} \frac{\partial f_i(\mathbf{r})}{\partial \mathbf{r}} \bigg|_{\mathbf{r}=\mathbf{r}_{ij}} + \frac{\partial \phi_{ij}(\mathbf{r})}{\partial \mathbf{r}} \bigg|_{\mathbf{r}=\mathbf{r}_{ij}} \right] \frac{(\vec{r}_i - \vec{r}_j)}{r_{ij}} \end{aligned}$$

Only inter-particles distances r_{ij} are needed to calculate energy and forces – the calculation is nearly as simple and efficient as with pair potentials. The EAM potential can be called an **environment-dependent pair potential**. The lack of explicit 3-body terms makes it challenging to design potentials for metals where covalent effects are important.

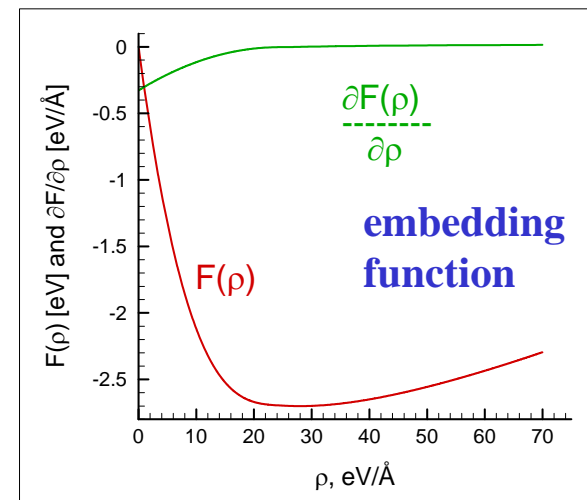
In so-called Modified EAM (MEAM) by Baskes or Extended EAM (EEAM) by R.A. Johnson, an angular dependence of the electron density function ρ have been introduced to account for the local symmetries in interatomic bonding. MEAM potentials have been developed for cubic [M.I. Baskes, Phys. Rev. B **46**, 2727 (1992)] and HCP metals [M.I. Baskes and R.A. Johnson, Model. Simul. Mater. Sci. Eng. **2**, 147 (1994)], covalent Si and Ge [Phys. Rev. B **40**, 6085 (1989)]. Some more recent developments by Baskes include fitting of MEAM for Ni [Mater. Chem. Phys. **50**, 152 (1997)], Lennard-Jones-based EAM [Phys. Rev. Lett. **83**, 2592, 1999].

Example of EAM potential: R.A. Johnson's potential for Ni (I)

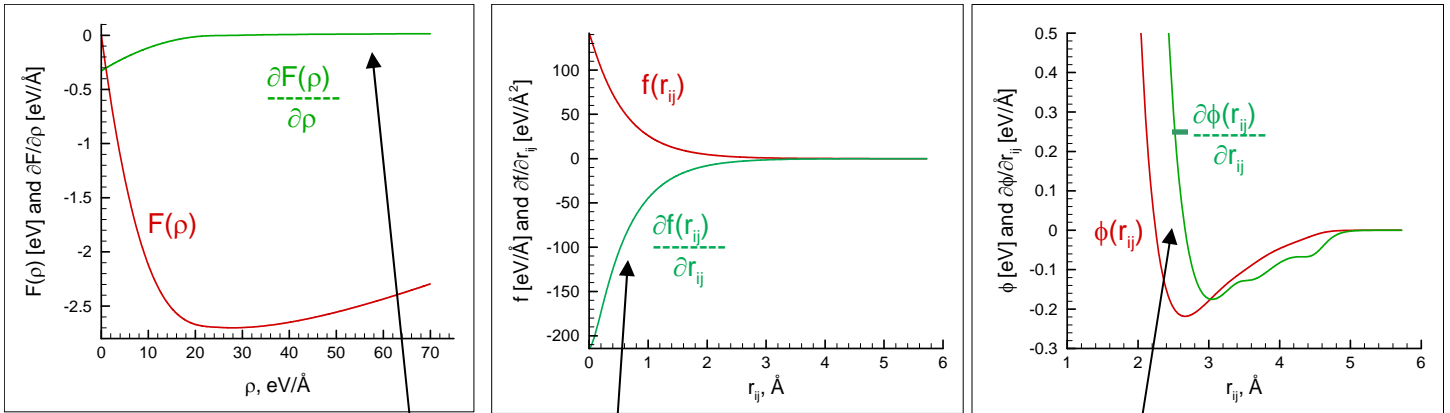
To define an EAM potential we have to define three functions, the embedding function $F(\rho)$, the pair potential $\phi(r_{ij})$, and electron density function $f(r_{ij})$. Below are these functions and their derivatives for Johnson's EAM with parameters for Ni.



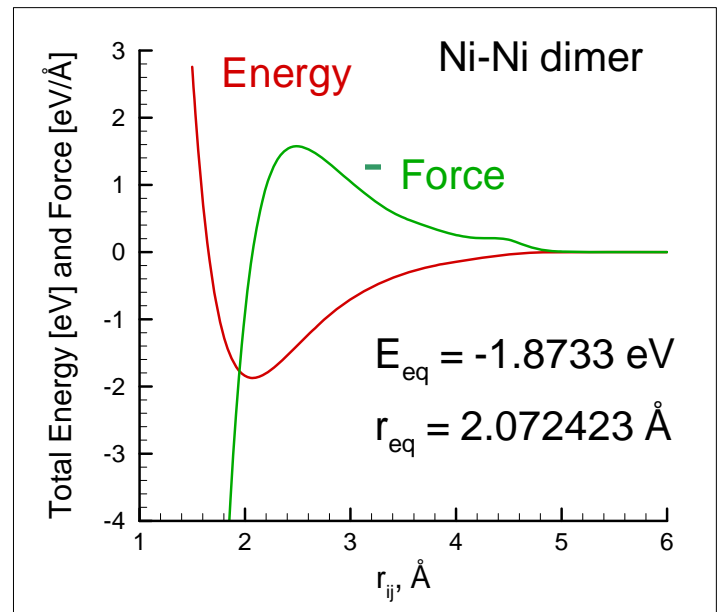
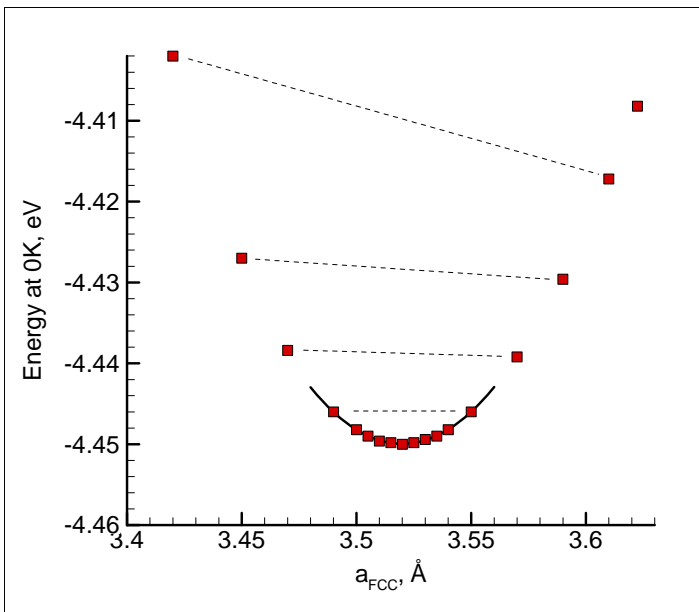
If $F(\rho)$ is a linear function of ρ , then we have just a pair potential. Many-body effects are related to the curvature of $F(\rho)$. For function F with a positive curvature and a positive decreasing f , the effective potential becomes more repulsive as the density increases. This trend is predicted by all the physical pictures that lead to this type of potential.



Example of EAM potential: R.A. Johnson's potential for Ni (II)



$$\vec{F}_i = - \sum_{j \neq i} \left[\frac{\partial F_i(\rho_i)}{\partial \rho_i} \frac{\partial f_j(r_{ij})}{\partial r_{ij}} + \frac{\partial F_j(\rho_j)}{\partial \rho_j} \frac{\partial f_i(r_{ij})}{\partial r_{ij}} + \frac{\partial \phi_{ij}(r_{ij})}{\partial r_{ij}} \right] \frac{(\vec{r}_i - \vec{r}_j)}{r_{ij}}$$



equilibrium distance in FCC = $a_{\text{fcc}}/\sqrt{2} = 2.49 \text{ \AA}$ \gg equilibrium distance in a dimer = 2.07 \AA

Embedded-atom and related methods for metallic systems (III)

Below are some of the examples of EAM-type potentials:

FCC metals:

“Sandia” (National Lab.) **EAM** by Daw, Baskes, Foiles: [S.M. Foiles, Phys. Rev. B **32**, 3409 (1985)]; [S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986)]; [M. S. Daw, S. M. Foiles, and M. I. Baskes, Mat. Sci. Rep. **9**, 251-310 (1993)] – the most popular potential, provide a good description of Au, Cu, Pd, Ag, Pt, Ni, Al as well as some of the alloys. The functions do not have an analytical form, are given as a table of data points that result from fitting to experimental data. Spline interpolation is used to evaluate the functions.

R. A. Johnson’s potential for most FCC metals [Phys. Rev. B **37**, 3924 (1988)] and their alloys [Phys. Rev. B **39**, 12554 (1989)] – simple and convenient analytical form.

“Glue” potentials by Ercolessi et al. [Ercolessi and Adams, Europhys. Lett. **26**, 583 (1994)]; [Phys. Rev. Lett. **57**, 719 (1986)]; [Phil. Mag. A **58**, 213 (1988)] – Similar to EAM, choice of analytical functions is partially based on DFT. The embedding function is called in this method “glue function”. Good description of Au and Al.

Cleri-Rosato potentials based on the second-momentum approximation of the tight-binding method. Potential was parameterized for Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, Al, Pb [Phys. Rev. B **48**, 22 (1993)] and alloys [Mazzone et al., Phys. Rev. B **55**, 837 (1997)].

Corrected effective medium (CEM) potential by DePristo et al. [Surf. Sci. **310**, 425 (1994)]; [Intl. Rev. Phys. Chem. **10**, 1 (1991)] – the embedding functions are fit not only to bulk properties but also to properties of a dimer (the Sandia EAM tends to overpredict bonding in dimers).

Voter and Chen potentials for Al and Ni [Mater. Res. Soc. Symp. Proc. **82**, 175 (1987)] and Ag [SPIE Proc. **821**, 214 (1987)] as well as for Ni₃Al alloy [Scr. Metall. **20**, 1389 (1989)]. Also used some of the dimer properties along with the bulk properties.

Embedded-atom and related methods for metallic systems (IV)

The development of EAM-type potentials for BCC and HCP metals is more difficult and the progress in this direction is slower.

HCP metals:

In fitting potentials for HCP metals one should make sure that HCP structure has lower energy as compared to FCC one and that the experimental c/a ratio, that often deviates from the ideal value of $\sqrt{8/3}$ is reproduced. Moreover, there are 5 independent elastic constants to fit to in HCP as compared to 3 in cubic metals. Examples of the reported potentials:

Oh and Johnson developed potentials for HCP metals Mg, Ti, Zr [J. Mater. Res. **3**, 471 (1988)]

Cleri and Rosato parameterized their potential for Ti, Zr, Co, Cd, Zn, Mg [Phys. Rev. B **48**, 22 (1993)].

Pasianot and Savino developed a potential for Hf, Ti, Mg, Co [Phys. Rev. B **45**, 12704 (1992)].

BCC metals:

A potential for a BCC metal should predict an energetic stability of a more “open” (not close-packed) BCC structure. BCC structure cannot be described by a pair potential. Examples of popular potentials for BCC metals are

Finnis-Sinclair potentials for Fe, V, Nb, Ta, Mo, W [Phil. Mag. A **50**, 45 (1984)]; [Phil. Mag. A **56**, 15 (1987)].

Oh and Johnson developed potentials for BCC metals Li, Na, K, V, Nb, Ta, Cr, Mo, W, Fe [J. Mater. Res. **4**, 1195 (1989)].

To learn about recent extensions of EAM see notes by Prof. Robert A. Johnson

Stillinger – Weber potential for silicon

Stillinger - Weber potential is one of the first potentials for diamond lattices (e.g. Si, GaAs, Ge, C). It was introduced in 1985 [Phys. Rev. B **31**, 5262-5271] and gained significant popularity since then. Description of the bonding in Si requires that the potential predicts the diamond lattice (each atom has four neighbors in a tetrahedral arrangement) as the most stable atomic configuration. Directional bonding is introduced in the Stillinger-Weber potential through an explicit three-body term of the potential energy expansion:

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_i \sum_{j>i} U_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_{j>i} \sum_{k>j} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

$$U_2(r_{ij}) = A \left(B r_{ij}^{-p} - r_{ij}^{-q} \right) \exp \left[\frac{c}{(r_{ij} - r_c)} \right]$$

The first term in this expression has a Lennard – Jones form, the second term is a cutoff function that smoothly terminates the potential at a distance r_c . The three – body part of the potential is given as

$$U_3(r_{ij}, r_{ik}, r_{jk}) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj})$$

where θ_{jik} is the angle centered on atom i and h is a function with three parameters, λ, γ, β :

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp \left[\frac{\gamma}{r_{ij} - r_c} + \frac{\gamma}{r_{ik} - r_c} \right] \left(\cos(\theta_{jik}) - \beta \right)^2$$

This is probably the simplest approach designed to maintain the tetrahedral angle of the Si crystal structure. If the value of β is $\cos(109.47^\circ) = -1/3$ then the diamond lattice is the energetically favorable structure.

Stillinger – Weber potential for Silicon

Stillinger - Weber potential has gained big popularity and was used in numerous studies. The main advantage of this potential is its simplicity and fairly realistic description of crystalline silicon. However, it has certain serious limitations or **transferability problems**:

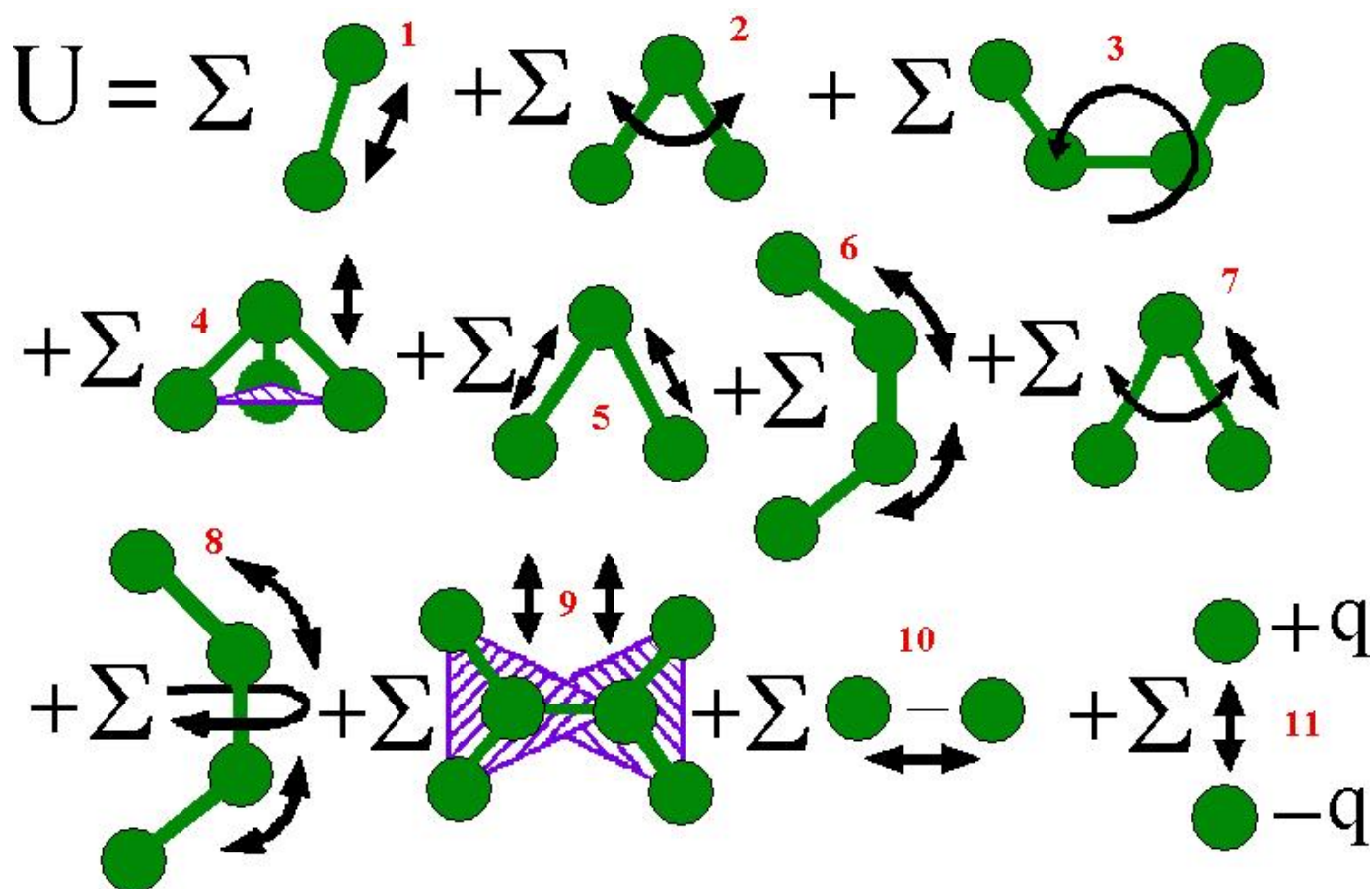
The three-body term defines only one equilibrium configuration. It is difficult to extend it to an element such as carbon, that can have equilibrium angles of 180° , 120° , and 109.47° . Moreover, the build-in tetrahedral angle causes problem in many situations: the coordination in liquid silicon is too low, surface structures are not correct (surface relaxation cannot be reproduced), energy and structure of small clusters cannot be reproduced correctly.

More realistic, so-called bond-order potentials, have been developed for group IV elements (Si, Ge, C) based on the concept of **bond strength dependence on local environment** (Tersoff-Abell potential for Si & Ge, Brenner potential for C).

See notes by Prof. Robert A. Johnson on Tersoff potential

Force fields for organic materials

Most of the potentials used in large-scale simulations of organic and bio-organic systems (proteins, polymers, etc.) are based on ideas similar to what we discussed for Stillinger – Weber potential: potential is defined through geometrical parameters such as bond-lengths and bond angles. The potentials for organic systems are typically much more complex as compared to Stillinger – Weber potential, and have many more parameters that are chosen based on experiments or other calculations. The potential energy can have the following (and more) terms:



Picture adapted from http://www.ncsc.org/training/materials/Software_Release/foundations/camd_md/

1. Bond stretching term; 2. Angle term; 3. Torsion term; 4. Out of plane term; 5. Bond - Bond term; 6. Angle - Angle term; 7. Bond - Angle term; 8. Angle - Angle - Torsion term; 9. Out of plane - Out of plane term; 10. Non bonded term; 11. Electrostatic term; etc....

Advantages: simple, intuitive, well-developed (commercial packages are available)

Drawbacks: bonding among atoms is fixed during simulation, chem. reactions are excluded

University of Virginia, MSE 4592/6270: Introduction to Atomistic Simulations, Leonid Zhigilei

MSE 627 References for Interatomic Potentials

Reviews

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4. D. W. Brenner, The art and science of an analytical potential, *Phys. Stat. Sol. B* **217**, 23-40 (2000) – review with strong accent on bond-order potential for carbon materials.
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Covalently bonded systems, semiconductors

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