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 \( U(r_1, r_2, \ldots, r_N) \) describes how the potential energy of a system of \( N \) atoms depends on the coordinates of the atoms, \( r_1, r_2, \ldots, r_N \). 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, \( \bar{F}_i = -\nabla_{\bar{r}_i} U (\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N) \)

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:

$$H = \sum_i \frac{p_i^2}{2M_i} + \sum_\alpha \frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} \sum_{ij} \left( \frac{Z_i Z_j e^2}{|\vec{R}_i - \vec{R}_j|} + \frac{\epsilon^2}{|\vec{r}_\alpha - \vec{r}_\beta|} - \sum_{i\alpha} \frac{Z_i e^2}{|\vec{R}_i - \vec{r}_\alpha|} \right)$$

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 $\psi(\vec{R}_i, \vec{r}_\alpha)$ which tells us everything about the system. But... this is impossible and we should use approximations. In 1923 Born and Oppenheimer noted that electrons ($m_e = 5.5 \times 10^{-4}$ 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 $\psi(\vec{R}_i, \vec{r}_\alpha) = \Xi(\vec{R}_i) \Phi(\vec{r}_\alpha; \vec{R}_i)$, where $\Xi(\vec{R}_i)$ describes the nuclei, and $\Phi(\vec{r}_\alpha; \vec{R}_i)$ depends parametrically on $\vec{R}_i$ and describes the electrons. The problem then can be reformulated in terms of two separate Schrödinger equations: $H_{el}\Phi(\vec{r}_\alpha; \vec{R}_i) = U(\vec{R}_i)\Phi(\vec{r}_\alpha; \vec{R}_i)$ and $H_i \Xi(\vec{R}_i) = \Xi(\vec{R}_i)$, where

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

The equation for the electronic problem $H_{el}\Phi(\vec{r}_\alpha; \vec{R}_i) = U(\vec{R}_i)\Phi(\vec{r}_\alpha; \vec{R}_i)$ gives the energy $U(\vec{R}_i)$ that depend parametrically on the coordinates of the nuclei, $\vec{R}_i$. Once found, $U(\vec{R}_i)$ enters $H_i \Xi(\vec{R}_i) = \Xi(\vec{R}_i)$ which describes the motion of nuclei. The later equation does not include any electronic degrees of freedom, all the electronic effects are incorporated in $U(\vec{R}_i)$ 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 total energy of the system of $N$ atoms with interaction described by an empirical potential can be expanded in a many-body expansion:

$$U(r_i, \ldots, r_N) = \sum_i U_1(r_i) + \sum_i \sum_{j>i} U_2(r_i, r_j) + \sum_i \sum_{j>i} \sum_{k>j} U_3(r_i, r_j, r_k) + \ldots$$

- $U_1$ – 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-body potentials in which multi-body effects are included implicitly, through an environment dependence of two-body terms.
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 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:

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

Commonly used examples of pair potentials:

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

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

**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.

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

**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.

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

**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.

$$ U(r_{ij}) = A e^{-r_{ij}/R_{BM}} - B/r_{ij}^6 $$
Fitting the parameters of the potential to experimental data

- interstitials
- equilibrium
- vacancies

- Thermal expansion
- Elastic and vibrational properties
- High pressure measurements
Note on nonlinear behavior of material described by a harmonic potential

The material described by the harmonic pair potential can exhibit, somewhat counterintuitively, a nonlinear behavior. For, example, let’s consider the propagation of strong acoustic waves.

For a 1D chain of particles interacting via a harmonic (parabolic) potential, the dependence of the elastic energy density on strain is also ideally parabolic. Consequently, the propagation of waves in the 1D chain is perfectly linear and does not result in the generation of higher frequency harmonics or other nonlinear effects.

In a bulk 3D crystal described by the harmonic pair potential, however, the anharmonic quadratic terms in the stress-strain dependence do appear due to purely structural reasons and the sign of these terms is opposite to the one in the material described by the LJ potential. Namely, the tensile deformation leads to the effective stiffening of the material described by the harmonic potential while the material softens under tension if the LJ potential is used. This contrasting behavior makes it possible to perform an exploration of the effect of the sign of the acoustic nonlinearity on the evolution of acoustic wave profiles with simple and computationally efficient pairwise potentials.

Shugaev et al.,
*J. Appl. Phys.* **128**, 045117, 2020
Note on nonlinear behavior of material described by a harmonic potential

Evolution of the surface acoustic wave profile simulated with Lennard-Jones potential:

The SAW profile for the lateral strain after shock formation in the material with harmonic (parabolic) interaction potential. Pronounced asymmetrical increase in the strain magnitude is well visible, but in contrast to the “soft” nonlinearity of the LJ potential the stronger cusp is formed at the upper part of the shock, and the shock itself appears at the descending branch in the SAW profile.

Shugaev et al., *J. Appl. Phys.* **128**, 045117, 2020
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 start 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.
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 ($\varepsilon = 0.0104$ eV, $\sigma = 3.40$ Å), Ne ($\varepsilon = 0.0031$ eV, $\sigma = 2.74$ Å), Kr ($\varepsilon = 0.0140$ eV, $\sigma = 3.65$ Å), Xe ($\varepsilon = 0.020$ 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.
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 \(\sigma\) and \(\varepsilon\).

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**: \(T^* = k_BT/\varepsilon\)
- **Force**: \(F^* = F\sigma/\varepsilon\)
- **Frequency**: \(\nu^* = \nu\times[\sigma^2/\varepsilon]^{1/2}\)
- **Pressure**: \(P^* = P\sigma^3/\varepsilon\)
- **Density**: \(\rho^* = \rho\sigma^3/m\)
- **Surface tension**: \(\gamma^* = \gamma\sigma^2/\varepsilon\)

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): 

$$\vec{F}_i = -\nabla_{\vec{r}_i} U(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$$

Note, that $\nabla_{\vec{r}_i}$ 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: 

$$U(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \sum_{i} \sum_{j>i} U(\vec{r}_{ij})$$

where 

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

The force on atom $i$ is 

$$\vec{F}_i = -\nabla_{\vec{r}_i} U(\vec{r}_1, ..., \vec{r}_i, ..., \vec{r}_N) = -\sum_{j \neq i} \nabla_{\vec{r}_i} U(\vec{r}_{ij}) =$$

$$= -\sum_{j \neq i} \left( \frac{\partial}{\partial x_i} x_{ij} + \frac{\partial}{\partial y_i} y_{ij} + \frac{\partial}{\partial z_i} z_{ij} \right) U(\vec{r}_{ij}) = -\sum_{j \neq i} \left( \frac{\partial \vec{r}_{ij}}{\partial x_i} + \frac{\partial \vec{r}_{ij}}{\partial y_i} + \frac{\partial \vec{r}_{ij}}{\partial z_i} \right) \frac{dU(\vec{r}_{ij})}{dr_{ij}} =$$

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

For Lennard-Jones: 

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

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

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

University of Virginia, MSE 4270/6270: Introduction to Atomistic Simulations, Leonid Zhigilei
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 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 $r_c \sim 2.5 – 5.5 \sigma$

\[
U(r_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] + \left\{ 6 \left( \frac{\sigma}{r_c} \right)^{12} - 3 \left( \frac{\sigma}{r_c} \right)^{6} \right\} \left( \frac{r_{ij}}{r_c} \right)^2 - \left\{ 7 \left( \frac{\sigma}{r_c} \right)^{12} - 4 \left( \frac{\sigma}{r_c} \right)^{6} \right\}
\]


With cut-off function:

\[
U(r_c) = 0
\]

\[
\left. \frac{dU(r_{ij})}{dr_{ij}} \right|_{r_{ij}=r_c} = 0
\]

![Graph showing energy and force vs. distance between atoms with and without cut-off function](image)
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 cannot 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.
The bonding energy density of the system of N atoms interacting via pair potential is:

$$E_b = \frac{1}{2 N \Omega a} \sum_{j \neq i} U \left( r_{ij} \right)$$

where $\Omega_a$ 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 $\varepsilon_{\alpha\beta}$. Then the displacement vector for each interatomic distance, $r_{ij}$, is $u_{ij}^\beta = a_{ij}^\alpha \varepsilon_{\alpha\beta}$ where $a_{ij}$ is undeformed value of $r_{ij}$ (that is, $u_{ij} = r_{ij} - a_{ij}$). The elastic energy can be expanded into a Taylor series with respect to the small displacements:

$$E_b = \frac{1}{2 N \Omega a} \sum_{j \neq i} \left\{ U \left( r_{ij} \right)_0 + \frac{\partial U \left( r_{ij} \right)}{\partial r^\beta_{ij}} v^\beta_{ij} + \frac{1}{2} \frac{\partial^2 U \left( r_{ij} \right)}{\partial r^\beta_{ij} \partial r^\delta_{ij}} v^\beta_{ij} v^\delta_{ij} + \ldots \right\}$$

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

$$E_b \left( \varepsilon \right) = E_b \left( 0 \right) + A_{\alpha\beta} \varepsilon_{\alpha\beta} + \frac{1}{2} C_{\alpha\beta\gamma\delta} \varepsilon_{\alpha\beta} \varepsilon_{\gamma\delta} + \ldots$$

where

$$A_{\alpha\beta} = \frac{1}{2 N \Omega a} \sum_{j \neq i} \frac{\partial U \left( r_{ij} \right)}{\partial r^\beta_{ij}} a^\alpha_{ij}$$

- tensor of internal stresses. Negative first invariant of this tensor $-(A_{xx}+A_{yy}+A_{zz})/3$ is pressure.

In the absence of external forces, at equilibrium $A_{\alpha\beta} = 0$

$$C_{\alpha\beta\gamma\delta} = \frac{1}{2N \Omega a} \sum_{j \neq i} \frac{\partial^2 U \left( r_{ij} \right)}{\partial r^\beta_{ij} \partial r^\delta_{ij}} a^\alpha_{ij} a^\gamma_{ij}$$

- tensor of elastic moduli.
Relationship between pair potential and elastic constants (II)

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

For a pair potential:

\[ \frac{\partial U(r_{ij})}{\partial r_{ij}^\beta} = \frac{r_{ij}^\beta}{r_{ij}} \frac{dU(r_{ij})}{dr_{ij}} \]

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

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

\[ A_{\alpha\gamma} = 0 \]

\( C_{\alpha\beta\gamma\delta} \) 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 \( G = 3/5 \left( C_{11} + C_{12} \right) + 2 / 5 \left( C_{11} - C_{12} \right) \) and \( B = \frac{1}{3} \left( C_{11} + 2C_{12} \right) \)]. 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 elastic constants 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:

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

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.
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:

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

Interpretation and functional form of $F$, $f$, and $\phi$ 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 $\rho_i$. The embedding energy $F$ is the energy associated with placing an atom in the electron environment described by $\rho$. The pair-potential term $\phi$ 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.

\[
E_i = F_i \left( \sum_{j \neq i} f_j (r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \varphi_{ij} (r_{ij})
\]

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

\[
\vec{F}_i = -\nabla \vec{r}_i E_{Tot} = -\nabla \vec{r}_i \sum_i E_i = -\nabla \vec{r}_i \left[ F_i (\rho_i) + \sum_{j \neq i} F_j (\rho_j) + \sum_{j \neq i} \varphi_{ij} (r_{ij}) \right] =
\]

\[
= -\sum_{j \neq i} \left[ \frac{\partial F_i (\rho)}{\partial \rho} \bigg|_{\rho=\rho_i} \frac{\partial f_j (r)}{\partial r} \bigg|_{r=r_{ij}} + \frac{\partial F_j (\rho)}{\partial \rho} \bigg|_{\rho=\rho_j} \frac{\partial f_i (r)}{\partial r} \bigg|_{r=r_{ij}} + \frac{\partial \varphi_{ij} (r)}{\partial r} \bigg|_{r=r_{ij}} \right] \left( \vec{r}_i - \vec{r}_j \right)
\]

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.

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 $\rho$, than 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)

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

Equilibrium distance in FCC = \(a_{FCC}/\sqrt{2} = 2.49\) Å >> equilibrium distance in a dimer = 2.07 Å
Example of EAM potential: R.A. Johnson’s potential for Ni (II)

$$\bar{F}_i = - \sum_{j \neq i} \left[ \frac{\partial F_i(\rho_i)}{\partial \rho_i} \frac{\partial f_j(r_{ij})}{\partial r_{ij}} + \frac{\partial F_j(\rho_j)}{\partial \rho_j} \frac{\partial f_i(r_{ij})}{\partial r_{ij}} + \frac{\partial \phi_{ij}(r_{ij})}{\partial r_{ij}} \right] \frac{\left( \vec{r}_i - \vec{r}_j \right)}{r_{ij}}$$
Example of EAM potential: R.A. Johnson’s potential for Ni

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


**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 Ni$_3$Al 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


**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

University of Virginia, MSE 4270/6270: Introduction to Atomistic Simulations, Leonid Zhigilei
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:

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

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

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

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

where \( \theta_{ijk} \) is the angle centered on atom i and h is a function with three parameters, \( \lambda, \gamma, \beta \):

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

This is probably the simplest approach designed to maintain the tetrahedral angle of the Si crystal structure. If the value of \( \beta \) 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 flexible, 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:

\[ U = \sum U_{1} + \sum U_{2} + \sum U_{3} + \sum U_{4} + \sum U_{5} + \sum U_{6} + \sum U_{7} + \sum U_{8} + \sum U_{9} + \sum U_{10} + \sum U_{11} + q + (-q) \]


Advantages: simple, intuitive, well-developed (commercial packages are available)
Drawbacks: bonding among atoms is fixed during simulation, chem. reactions are excluded

Picture adapted from http://www.ncsc.org/training/materials/Software_Release/foundations/camd_md/
Stillinger – Weber potential for silicon

\[ U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \sum_i \sum_{j > i} U_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \sum_{j > i} \sum_{k > j} U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + ... \]

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

\[ U_3(\mathbf{r}_{ij}, \mathbf{r}_{ik}, \mathbf{r}_{jk}) = h(\mathbf{r}_{ij}, \mathbf{r}_{ik}, \theta_{jik}) + h(\mathbf{r}_{ji}, \mathbf{r}_{jk}, \theta_{ijk}) + h(\mathbf{r}_{ki}, \mathbf{r}_{kj}, \theta_{ikj}) \]

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

Force calculation:

\[ \vec{F}_i = -\nabla_{\mathbf{r}_i} U(\mathbf{r}_1, ..., \mathbf{r}_i, ..., \mathbf{r}_N) = -\sum_{j \neq i} \nabla_{\mathbf{r}_i} U_2(\mathbf{r}_{ij}) - \sum_{j \neq i} \nabla_{\mathbf{r}_i} U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \]

Force from the two-body term:

\[ F_{2i} = -\sum_{j \neq i} \nabla_{\mathbf{r}_i} U_2(\mathbf{r}_{ij}) = -\sum_{j \neq i} \left( \frac{x_{ij}}{r_{ij}} + \frac{y_{ij}}{r_{ij}} + \frac{z_{ij}}{r_{ij}} \right) \frac{dU_2(\mathbf{r}_{ij})}{dr_{ij}} \]

\[ F_{2i} = -\sum_{j \neq i} \frac{(\mathbf{r}_i - \mathbf{r}_j)}{r_{ij}} \frac{dU_2(\mathbf{r}_{ij})}{dr_{ij}} \]

\[ \frac{dU_2(\mathbf{r}_{ij})}{dr_{ij}} = \frac{A}{\sigma} \left\{ -B p \left( \frac{r_{ij}}{\sigma} \right)^{-p-1} + q \left( \frac{r_{ij}}{\sigma} \right)^{-q-1} \right\} \exp \left[ (r_{ij} - r_c)^{-1} \right] - U_2(\mathbf{r}_{ij}) \frac{\sigma}{(r_{ij} - r_c)^2} \]
Stillinger – Weber potential for silicon

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

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

Force from the three-body term:

\[ F_{3i} = -\sum_{j \neq i \atop k \neq j} \nabla_{r_i} U_3 (r_i, r_j, r_k) = -\sum_{j \neq i \atop k \neq j} \left\{ \left( \frac{x_{ij}}{r_{ij}} + \frac{y_{ij}}{r_{ij}} + \frac{z_{ij}}{r_{ij}} \right) \frac{dU_3}{dr_{ij}} + \left( \frac{x_{ik}}{r_{ik}} + \frac{y_{ik}}{r_{ik}} + \frac{z_{ik}}{r_{ik}} \right) \frac{dU_3}{dr_{ik}} \right\} \]

\[ F_{3i} = -\sum_{j \neq i \atop k \neq j} \left( \frac{(\vec{r}_i - \vec{r}_j)}{r_{ij}} \frac{dU_3}{dr_{ij}} + \frac{(\vec{r}_i - \vec{r}_k)}{r_{ik}} \frac{dU_3}{dr_{ik}} \right) \]

\[ \cos \theta_{ijk} = \frac{r_{ij}^2 + r_{ik}^2 - r_{jk}^2}{2r_{ij}r_{ik}} \]

\[ \frac{\partial \cos \theta_{ijk}}{\partial r_i} = \frac{dx_{ij}}{r_{ij}} \left[ \frac{1}{r_{ik}} - \cos \theta_{ijk} \right] \left[ \frac{1}{r_{ij}} - \cos \theta_{ijk} \right] \]
MSE 627 References for Interatomic Potentials

Reviews

2. MRS Bulletin, Volume 37, Issue 05, May 2012 - Special issue on interatomic potentials

Metals


Ionic Solids, Ceramics

MSE 627 References for Interatomic Potentials

Covalently bonded systems, semiconductors


A few examples for organic and Bio-organic type potentials


