

8 Potential Functions

For integration of equations of motion, forces $\mathbf{f}_i = -\nabla_{\mathbf{r}_i}\mathcal{U}(\mathbf{r})$ are needed. Therefore we will need to study some parametrizations of $\mathcal{U}(\mathbf{r})$. Naturally these parametrizations are idealization of the reality, but should reflect the interactions in the system to be studied.

8.1 Constructing a Potential Function

- In MD simulations, interactions between particles are typically presented with potential functions or functionals with free parameters.
- The free parameters are fitted to experimental data or more accurate calculations.
- Another option is to directly use quantum mechanical models for calculating the forces on-the-fly.
- In these models, we apply the Born-Oppenheimer approximation to simplify the interactions (electrons are assumed to be **always** in the ground state), and the interaction strength depends only on the interatomic separation.
- As has already been pointed out, a typical way to construct a interatomic potential is to split it first in parts:

$$\mathcal{U}(\mathbf{r}) = \sum_i U_1(\mathbf{r}_i) + \sum_{i,j} U_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i,j,k} U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots \quad (8.1)$$

first term is external potential, second one is a two-particle term involving atoms i and j , and the third one is a three particle term for i , j and k .

- The field quantity related to this scalar is the force on atom i :

$$\mathbf{f}_i = -\nabla_{\mathbf{r}_i}\mathcal{U}(\mathbf{r}) \quad (8.2)$$

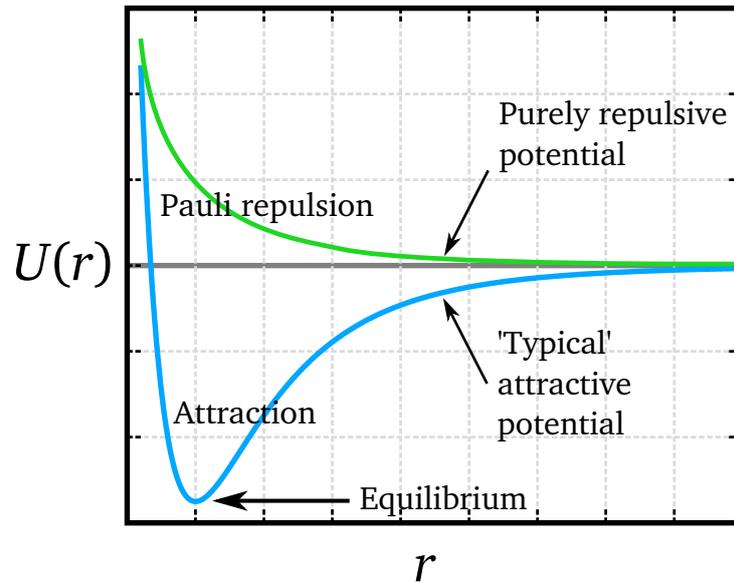
- **In chemistry**, it's common to directly describe the force without defining the corresponding potentials.
- Therefore, chemical interaction models are often referred to as **force fields**, even when they are not constructed this way.
- Other names for **analytic potentials** are **empirical potentials** or **classical potentials**.
- They are used in many fields – also outside MD simulations – with field-specific emphasis.

8.2 Interaction Models in Different Fields

- **Chemistry**; Accurate reaction rates and molecular energy transfer are the key points of interest → small systems and short times. The forces and integrators must be accurate.
- **Materials Science**; Solid state structures like surfaces, grain boundaries and interfaces are of interest as well as many-atom dynamics, like in crack motion. Systems can be large – $N \approx 10^6$ – and the forces are relatively accurate (from quantum mechanics). Simulation times below μs range.
- **Statistical Mechanics**; Correlated many body motion is the main emphasis, especially liquids. Systems are larger and times longer than above → simple interaction models.
- **Biochemistry/–physics**; The molecular structure and correlated motion (as in protein folding) require simple forces and long times.

8.3 Interatomic Interactions

- As we know by now, the potential energy function is (typically) of this shape:



- At very small interatomic separations Coulombic repulsion between the nuclei dominates.
- After this, Pauli rule and Coulombic interaction between the electrons of the two atoms are dominating contributors in the repulsion.
- Attraction between two atoms can be due to
 - Coulomb interaction
 - Covalent bonding
 - Metallic bonding
 - van der Waals interaction

8.4 Different Ways to Form Bonds

8.4.1 Ionic Bonding

Charge transfer occurs between two atoms which have a large difference in electronegativity: one of the atoms, typically a halogen, rips of an electron from the other one, typically an alkali metal.

- Due to the transferred electrons, one of the formed ions has a positive charge whereas the other one becomes negative.
- The ions attract each other via **Coulombic interaction**

$$\mathcal{U}(\mathbf{r}_i, \mathbf{r}_j) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

- For example e.g. NaCl
- Ionic bonding depends only on the distance between the atoms. Thus the angular relations play no role.

8.4.2 Covalent Bonding

- When two atoms have a similar electronegativity ¹², e.g. in the case of atoms of the same element, they can **share some of the electrons**.
 - the process is described by solving stationary Schrödinger equation for the electron system
- For example, in an oxygen dimer, O₂, two oxygen atoms (with six valence electrons each) will share four electrons between the atoms so that each *effectively* has a filled outermost electron level.
- In contrast to ionic bonding, due to spatially localized electrons, **covalent bond energetics depend on the angles between the atoms** (when more than two atoms are bonded with covalent bonds).

¹²Exactly the same electronegativity leads to non-polar covalent bonds, whereas differences in it lead to polar bonds.

8.4.3 Metallic Bonding

- In contrast to ionic and covalent bonds, a single *metallic bond* does not exist.
- Instead, **metallic bonding is collective in nature** and always involves a group of atoms.
- A metal is characterized by its electric conductivity which is due to **delocalization of electrons** in the material.
- Metallic bonding is a result of the **attraction between the delocalized electrons and ions** which are embedded in the *electron cloud* (or, free electron gas) of the the delocalized valence electrons.
 - Again, Quantum physics is needed for proper understanding.

8.4.4 Dipole Interactions (van der Waals)

- For noble gas atoms, the attraction arises from dipole interaction which is due to the perturbed charge densities of the two atoms involved in the bonding.
- Induced dipoles.
- High level correlated electron structure method needed for ab initio understanding.
- This interaction is weak, but still forms the basis for noble gas dimers and solids at low temperatures.
- For molecular systems, van der Waals interactions can play a role too.

8.5 Different Interatomic Potentials

Pair potentials: $\mathcal{U}(\mathbf{r}) = U_0 + \sum_{i,j} U_2(\mathbf{r}_i, \mathbf{r}_j)$

Pair functionals: $\mathcal{U}[F, \mathbf{r}] = \sum_{i,j} U_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_i F \left(\sum_j g_2(\mathbf{r}_i, \mathbf{r}_j) \right)$

Cluster potentials: $\mathcal{U}(\mathbf{r}) = U_0 + \sum_{i,j} U_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i,j,k} U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$

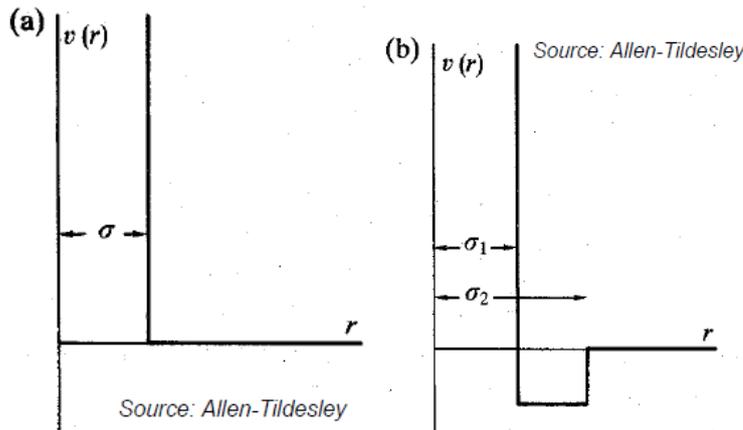
Cluster functionals: $\mathcal{U}[F, \mathbf{r}] = \sum_{i,j} U_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_i F \left(\sum_j g_2(\mathbf{r}_i, \mathbf{r}_j), \sum_{j,k} g_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \right)$

Real potentials are often combinations of the above. For most of the time we will focus on pair potentials. These are in idealization and can be parametrized to effectively reproduce the higher-body interactions

$$\mathcal{U}(\mathbf{r}) \approx \sum_i u_1(\mathbf{r}_i) + \sum_i \sum_{j>i} u_2^{eff}(r_{ij}) \quad (8.3)$$

8.5.1 Pair Potentials for atomic systems

Idealistic potentials can serve as the first approximation. Hard Sphere (HS) potential and Square Well (SW) potential are such models



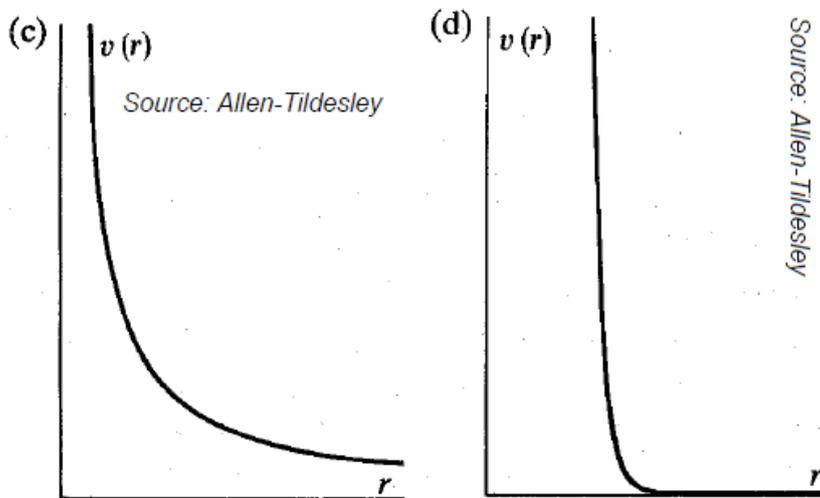
$$\mathcal{U}^{\text{HS}}(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r \geq \sigma \end{cases} \quad \mathcal{U}^{\text{SW}}(r) = \begin{cases} \infty, & r < \sigma_1 \\ -\epsilon, & \sigma_1 \leq r < \sigma_2 \\ 0, & r \geq \sigma_2 \end{cases} \quad (8.4)$$

- First ever MD potential
- Billiard-ball physics
- Works for packing problems

8.5.2 Soft Sphere Potentials

Soft sphere (SW) potentials become progressively harder with increasing parameter ν values. They contain no attractive part.

$$\mathcal{U}^{\text{SS}}(r) = \varepsilon \left[\frac{\sigma}{r} \right]^\nu \quad (8.5)$$



Potentials with $\nu = 1$ and $\nu = 12$ depicted.

8.5.3 Lennard-Jones potential

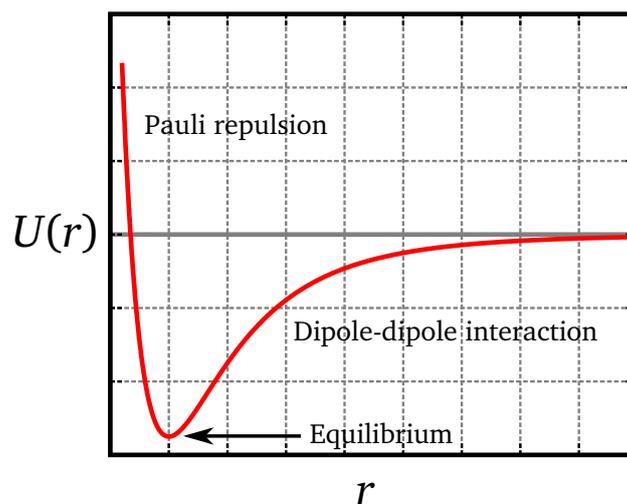
Lennard-Jones potential is probably the most famous pair potential describing van der Waals interaction. It can be used for simulation of real system like liquid noble gases.

- If the charge distributions of the atoms would be rigid, the cohesive energy would be zero.
- However, the atoms induce dipole moments in each other, and the induced moments cause an attractive interaction.

- Model calculations on coupled oscillators yield attractive interaction caused by the induced dipole moment (i.e., van der Waals dispersion interaction or London interaction) obeying the scaling law $\propto r^{-6}$.
- This is the principal attractive force in crystals of inert gases and many organic molecules.

However, we still need a repulsive part for the interaction.

- When two atoms (A & B) are brought together, at some point their charge densities will start to overlap.
- With increasing overlap, the potential energy will become positive due to Pauli exclusion principle.
- This principle says that two electrons can not have equal quantum numbers, which would happen if some of the electrons from atom B would occupy states in atom A (or the other way around).
- Therefore, those electrons must be excited to higher energy levels, which leads to increase in the overall energy of the system.
- The analytical problem becomes overly complicated for this case, but fitting to experimental data has shown that a repulsive potential of the form B/r^{12} describes it well enough while allowing easy computations ($2 \times 6 = 12 \dots$).



- Adding the terms up gives the functional form:

$$\mathcal{U}_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (8.6)$$

LJ works reasonably well for noble gases close to equilibrium. However, due to $\mathcal{U}(r) \propto r^{-12}$ it fails badly at **very** close interatomic separations (true behavior is $\mathcal{U}(r) \propto e^{-r}/r$).

The parametrization of LJ potential can be interpreted as follows

- Collision diameter σ

$$\mathcal{U}_{LJ}(r) > 0, r < \sigma$$

- Well depth ϵ at minimum.

$$\mathcal{U}_{LJ}(r_m) = -\epsilon$$

- For large distances $\mathcal{U}_{LJ}(r) \rightarrow 0, \quad r \rightarrow \infty$

Alternative parametrizations exist too

$$\mathcal{U}_{LJ}(r) = \epsilon \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right] \quad (8.7)$$

$$\mathcal{U}_{LJ}(r) = \left(\frac{A}{r^{12}} \right) - \left(\frac{C}{r^6} \right), \quad (8.8)$$

where $A = \epsilon r_m^{12} = 4\epsilon\sigma^{12}$ and $C = 2\epsilon r_m^6 = 4\epsilon\sigma^6$. In many cases we would like to get an estimate for LJ parameters between different atom types directly from the existing ones

- For CO, one needs C-C, O-O and C-O parameters.
- Lorentz-Berthelot mixing rules

$$\sigma_{AB} = \frac{1}{2}(\sigma_{AA} + \sigma_{BB}) \quad (8.9)$$

$$\epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}} \quad (8.10)$$

These rules are most successful when applied to similar species. However, they overestimate the well depth. Some force fields use geometric mean also for collision diameter.

Some other atomistic pair potentials

- General LJ potential

$$\mathcal{U}_{\text{LJnm}}(r) = k\varepsilon \left[\left(\frac{\sigma}{r} \right)^n - \left(\frac{\sigma}{r} \right)^m \right], \quad k = \frac{n}{n-m} \left(\frac{n}{m} \right)^{m/(n-m)}. \quad (8.11)$$

- Buckingham potential:

$$\mathcal{U}^{\text{Buck}}(r) = A \exp(-r/\rho) - C/r^6. \quad (8.12)$$

This potential tries to solve the problem of LJ at small separations, but remains finite at small interatomic distances. It contains three parameters A , ρ and C .

Obviously there are many other potential functions designed for different systems.

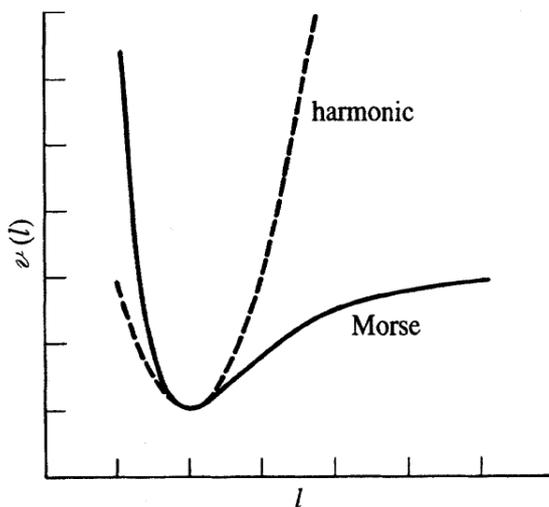
8.5.4 Morse Potential

A typical potential energy curve for a chemical bond is modeled quite usefully by a formula suggested by Morse

$$U(r) = D_e \{1 - \exp(-a(r - r_0))\}^2, \quad (8.13)$$

where D_e is the well depth, $a = \omega \sqrt{\mu/2D_e}$, ω is the frequency of bond vibration and μ is the corresponding reduced mass. In addition r_0 refers to minimum energy distance. The Morse potential

- has analytical solutions for the Schrödinger equation.
- decays faster than LJ \rightarrow less problems with cutoff.



The Morse potential has 3 parameters and can be used for wide range of models in equilibrium and close to dissociation.

- However, for molecular simulation close to energy minimum, simpler harmonic form can be adapted

$$U(r) = \frac{k}{2}(r - r_0)^2$$

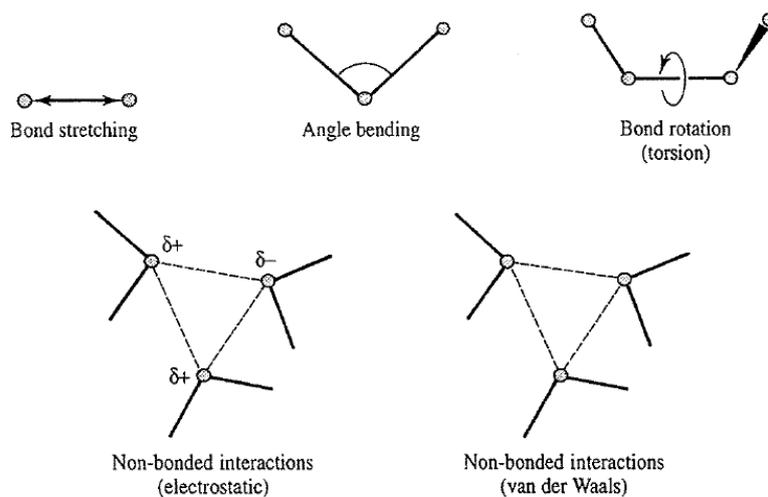
8.6 Potentials for molecular systems

For molecular systems the force field should take into account covalent bonding between certain atoms, angle bending, bond rotation, and intermolecular interactions: van der Waals and Coulombic. However, for most cases the system to be simulated is close to potential energy minimum. For such cases a general and widely used force field formula reads

$$U(\mathbf{r}) = \sum_{\text{bonds}} \frac{k_i}{2} (l_i - l_{i,0})^2 + \sum_{\text{angles}} \frac{n_i}{2} (\theta_i - \theta_{i,0})^2 + \sum_{\text{torsions}} \frac{V_n}{2} (1 + \cos(n\omega - \gamma))$$

$$+ \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right) \quad (8.14)$$

The interaction terms in the previous formula are illustrated below (source: Leach)



As the size of a molecule grows, the number of terms in (8.14) becomes large very soon. It is typical to have different parameters for atoms in different chemical environments, but still not optimize these for every different molecule. More detailed discussion on molecular force fields will follow. We will also touch the subject in the GROMACS exercises.

8.6.1 Generating potentials / force fields

Generating a force field is not a simple task and it is usually done by specialized experts. Molecular forcefields however may be applied to a variety of different molecules. Such force fields

- Should be transferrable
- are generated using existing data
 - QM calculations for a set of molecules
 - Known structures and their distribution
 - Thermodynamic properties
 - vibrational frequencies
- can be done in order from least important
 - van der Waals
 - electrostatics
 - torsional parameters

Generating a force field usually ends up in iterative procedure, as change in some parameters implies changes in others for the model to work.

Transferrability Some force fields are very specialized on a particular system (atom, molecule), possibly in a very wide range of conditions. Others, like

- AMBER, designed for proteins and nucleic acids
- OPLS, optimized parameters for liquid simulations
- GAFF, generalized amber force field

- CHARMM, and so on...

were designed for a variety of molecules. For such force fields the **ability to transfer parameters from molecule to another** is crucial. One has to be able to

- Get combined parameters from existing ones
- Generate missing parameters

It is useful to use as wide data set as possible to cover as many circumstances as possible. But as said, for us it is necessary to co-operate with experts if parametrization of new stuff is needed.

Ar & water In the excercises, we will get our hands on Ar and later on water. The forcefield that we will use for Ar is Lennard-Jones with

$$A = 4\epsilon_i\sigma_i^{12}[kJmol^{-1}nm^{12}] = 0.96960E - 05[kJmol^{-1}nm^{12}]$$

$$C = 4\epsilon_i\sigma_i^6[kJmol^{-1}nm^6] = 0.62220E - 02[kJmol^{-1}nm^6]$$

obtained from Gromacs forum. We are using GROMACS combination rule 1, meaning that we give these parameters in this format. Using combination rule 2 we would give $\sigma = 0.3405 \text{ nm} = 3.41 \text{ \AA}$ and $\epsilon = 1.00 \text{ kJ mol}^{-1} = 0.01 \text{ eV}$.

As another example, a 3-point rigid (with constraints) water molecule (TIP3P)¹³ force field has vdW only at O and

A (kJmol ⁻¹ Å ¹²)	C (kJmol ⁻¹ Å ⁶)	$l_{0,OH}$ (Å)	q_H (e)	q_O (e)	θ (deg)
2435.088×10^3	2489.48	0.9572	+0.4170	-0.8340	104.52
σ (Å)	ϵ (kJmol ⁻¹)	$l_{0,OH}$ (Å)	q_H (e)	q_O (e)	θ (deg)
3.15061	0.6364	0.9572	+0.4170	-0.8340	104.52

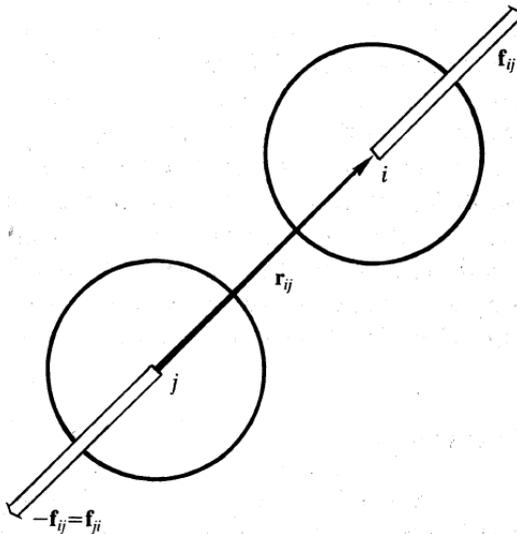
But naturally, for a real simulation we take the values from proper databases or articles, not relying on any lecture material.

¹³J. Chem. Phys. 79 (1983) 926-935

9 Calculating the Forces

In the former chapter we introduced some parametrizations for the $\mathcal{U}(\mathbf{r})$ and now are then facing the problem of evaluation the gradient $\mathbf{f}_i = -\nabla_{\mathbf{r}_i}\mathcal{U}(\mathbf{r})$ for each atom. Succeeding in this, we would know how to run an constant-NVE simulation!

- The potential should allow analytical derivatives (numerical are slow to evaluate)
- Potential is usually expressed in internal coordinates, and relative distances (like $U_2(\mathbf{r}_i, \mathbf{r}_j) = U_2(r_{ij})$)
- Positions in Cartesian coordinates \mathbf{r}_i
- For a pure pair potential U_{ij} , the force acting on atom i due to atom j is



$$\begin{aligned} \mathbf{f}_{ij} &= -\nabla_{\mathbf{r}_i} U_2(r_{ij}) = +\nabla_{\mathbf{r}_j} U_2(r_{ij}) = -\mathbf{f}_{ji} \\ &= -\left[\frac{\partial U_2}{\partial x_i} \hat{\mathbf{x}} + \frac{\partial U_2}{\partial y_i} \hat{\mathbf{y}} + \frac{\partial U_2}{\partial z_i} \hat{\mathbf{z}} \right], \end{aligned} \quad (9.1)$$

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j, \quad x_{ij} = x_i - x_j, \quad (9.2)$$

- To transform the force on atom i (caused by atom j) to our desired Cartesian coordinates, we need to apply the chain rule

$$\frac{\partial U}{\partial x_i} = \frac{\partial U}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_i}$$

- For a force $U_2(r_{ij})$ depending on

$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2},$$

we will have

$$\begin{aligned} \frac{\partial U}{\partial x_i} &= \frac{\partial U}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_i} \\ &= \frac{\partial U}{\partial r_{ij}} \times \frac{1}{2} \left((x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \right)^{-1/2} \times 2(x_i - x_j), \\ &= \frac{\partial U}{\partial r_{ij}} \times \frac{x_i - x_j}{r_{ij}} \end{aligned}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. Therefore we have

$$\mathbf{f}_{ij} = -\nabla_{\mathbf{r}_i} U(r_{ij}) = -\frac{\partial U}{\partial r_{ij}} \times \frac{\mathbf{r}_{ij}}{r_{ij}}$$

- Now for LJ potential we have

$$\frac{\partial U_{LJ}}{\partial r_{ij}} = \frac{24\epsilon}{r_{ij}} \left[-2 \left(\frac{\sigma}{r_{ij}} \right)^{12} + \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

And finally, for the LJ potential the force takes the form

$$\mathbf{f}_{ij}^{(LJ)} = (\mathbf{r}_i - \mathbf{r}_j) \frac{24\epsilon}{r_{ij}^2} \left[2 \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (9.3)$$

This equation emphasizes the value of a clever choice for a form of a potential function. For many potential formulations, the expressions for analytical derivatives are available. If one uses new functional forms, such formulas need to be derived from scratch. It is clear that we will gain little extra understanding when going to more laborous potentials.

9.1 Practical Implementation on Force Calculation

```

set all forces to 0.
for atom_i=1 to N-1
  for atom_j=i+1 to N (or apply the neighbor list to avoid double loop)
    if (r_ij <= rcut) (check the cutoff criterium)
      calculate f_ij
      add f_ij to total force to atom_i: f_i=f_i+f_ij
      add -f_ij to total force to atom_j: f_j=f_j-f_ij
    end
  end
end
end
end

```

- As stated above, analytical expressions for forces due to other terms in the molecular mechanics potential function have been published for most functional forms encountered in common force fields.
- These expressions can be complicated due to intramolecular terms: bonds, angles torsions (evaluated in terms of internal coordinates)
- Chain rule must be applied to these to transform to Cartesian coordinates
- In the end, that has to be just done and has been done as many MD codes exist

9.2 Many-body effects in empirical potentials

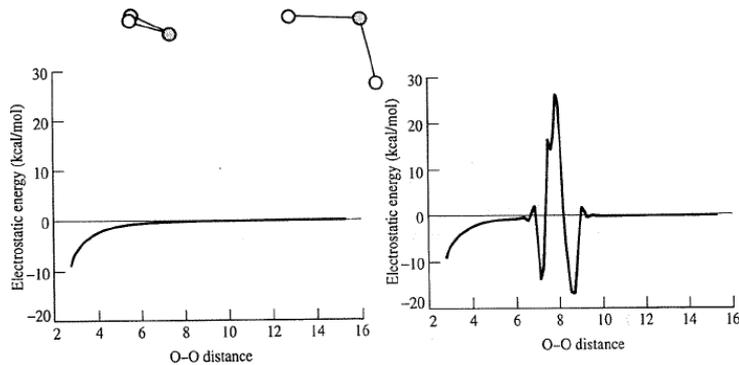
- For a pair potential, $U_{ij} = U_{ji}$ since the potential only depends on $r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_{ji}|$. This simplifies the force calculation.
- In the case of a many-body potential, things are more difficult, since $U_{ij} \neq U_{ji}$.
- When we have both two-body terms $U_{ij} = U_2(\mathbf{r}_i, \mathbf{r}_j)$ and three-body terms $U_{ijk} = U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$, the force (on atom i) becomes

$$\mathbf{f}_i = -\nabla_i \left[\sum_j (U_{ij} + U_{ji}) + \sum_{j,k} U_{ijk} \right]$$

Naturally this ruins good scaling because more elaborate summation takes place. Sometimes using 3-body potentials is a necessity, but otherwise we would like to avoid using them.

9.3 Group-based cutoff

Consider electrostatic interaction of two TIP3P water molecules draw away from each other. (Source: Leach)



- At certain points, atoms move out of r_c (8\AA).
- For TIP3P exclusion of hydrogen results the remaining OH to have $q_{tot} = -0.417e$.
- Naturally large artifacts are produced.
- It will be better to exclude the whole molecule at once.

The answer is to divide atoms to groups that have zero total charge and apply the cutoff to the whole group.

- Charge groups. That sum to q_{tot} (like the water molecule)
- For other type of interactions, hierarchy of groups to be identified can be listed based on behaviour at large r_{ij}
 - charge-charge $1/r_{ij}$
 - charge-dipole $1/r_{ij}^2$
 - dipole-dipole $1/r_{ij}^3$
 - dipole-quadrupole $1/r_{ij}^4$
 - charge-induced dipole $1/r_{ij}^5$
 - dipole-induced dipole $1/r_{ij}^6$

If neutral groups are chosen the next interaction will be $1/r_{ij}^3$. There are a couple of options how the cutoff should be applied

- include group-group interaction if any atom of the group is within cutoff
- define a marker atoms for groups for which cutoff condition is evaluated (needs rather small groups)

Evaluation of long-range electrostatics will be dealt with Ewald summation, a topic of coming lectures.

9.4 Modifications at Short and Large Distances

The potential we have chosen may have pitfalls in the close distances and near the cutoff radius.

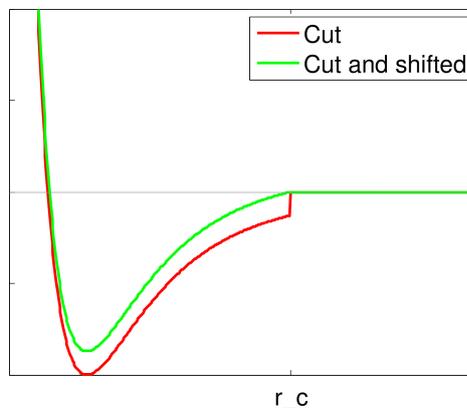
9.4.1 Potentials at Cutoff

At large separations (near the cutoff) problems may rise due to the potential not settling smoothly (continuous, continuous first derivative) to the value it has at infinite separation. Large enough cut-off (at least $r_c > 10 \text{ \AA}$) is one cure for the problem. Some tricks can be made as well.

Shifted potentials Truncation of a pair potential introduces a jump in $U_2(r)$

- Discontinuity at r_c violates energy conservation when molecules move in or out the cutoff regime.
- A simple solution to this is to shift the potential function by $U_c = U_2(r_c)$

$$U_2^{(s)}(r_{ij}) = \begin{cases} U_2(r_{ij}) - U_c & , r \leq r_c \\ 0 & , r > r_c \end{cases} \quad (9.4)$$



- The shift does not affect the forces for $r_{ij} < r_c$ and $r_{ij} > r_c$
- However, the shift affects total energy and need to be included in energy expression.
- Most importantly, $U_2^{(s)}(r_{ij})$ is not differentiable at $r_{ij} = r_c$ and the force is therefore discontinuous.
- Questionable physics may result

Shifted-force potential We can circumvent the problem by introducing additional term making the force continuous (derivative of the force discontinuous)

- The first approximation would be driving the potential to zero with linear term

$$U_2^{(sf)}(r_{ij}) = \begin{cases} U_2(r_{ij}) - U_c - \left(\frac{dU_2(r_{ij})}{dr_{ij}} \right)_{r_{ij}=r_c} (r_{ij} - r_c) & , r \leq r_c \\ 0 & , r > r_c \end{cases} \quad (9.5)$$

Now both $U_{12}^{(sf)}(r_c) = 0$ and $U_{12}^{(sf)'}(r_c) = 0$

- Shifted-force potential $U_2^{(sf)}$ now fulfils energy conservation and numerical stability in the evaluation of equations of motion.
- the discontinuity now appears in the derivative of the force
- Stricly speaking, the physics will not be the same as the linear term "tilts" the potential function
 - use two values for r_c and compare results
- In many modern potentials, the potential is defined with a proper first derivative at r_c .

Switching function The last method we describe is multiplying the potential with a switching function $S(r_{ij})$

$$U_2^{sw}(r_{12}) = S(r_{ij})U_2(r_{ij}),$$

where the switching function has properties

$$\begin{cases} S(r_{ij}) \rightarrow 1 & , r_{ij} \rightarrow 0 \\ S(r_{ij}) \rightarrow 0 & , r_{ij} \rightarrow r_c \end{cases} \quad (9.6)$$

In addition the switching function should

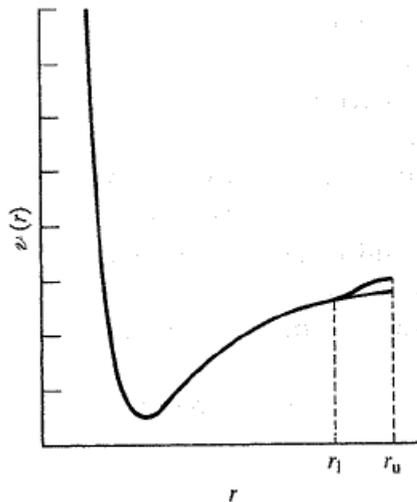
- Be close to 1 quite near r_c (potential not altered in crucial parts)
- Smoothly varying (minimize forces due to swithing, be differentiable)

We can now figure out a number of functions. Let us give additional requirements for the function

- To change from 1 to 0 between $[r_l, r_c]$ ($r_l < r_c$)

$$\begin{aligned} S(r_l) &= 1 & S(r_c) &= 0 \\ S'(r_l) &= 0 & S'(r_c) &= 0 \\ S''(r_l) &= 0 & S''(r_c) &= 0 \end{aligned} \quad (9.7)$$

- For example, a polynomial can be fitted
A switching function in action (Source: Leach)



- For molecules group based switching is the preferred option.

Even smooth-looking potential functions can have problematic forces (even if continuous). Rapid changes in slope imply large forces.

9.4.2 Repulsion close to nuclei

At very close internuclear separations, the electron clouds do not shield completely the nuclei. This causes the nuclei interacting directly with each other according to the r^{-1} Coulombic law. For systems where electronic shielding is reduced, potentials need to be modified accordingly. For simulation of biomolecules in normal conditions this is usually not a problem to be considered. For materials sciences this may not be the case.

Summary

- Different scientific disciplines have different requirements for the accuracy of potential energy functions and forces.
- The simplest interaction model is provided by **pair potentials**, which are simple functions of only one variable (interatomic distance r) and a few fitted parameters.
- Interatomic potentials are typically constructed of separate attractive and repulsive parts. Attraction depends on the material, repulsion arises from the Pauli rule and Coulombic repulsion.
- Because forces are direct derivatives of the potentials, \mathcal{U} must have a continuous first derivative for all r . This poses a problem at cutoff, since \mathcal{U} must be smoothly driven to zero.
- Most of the equilibrium potentials have wrong scaling at very short r so that they may have to be modified.