Interatomic potentials

Computational Material Science
Lecture 3

Last time

- Often simulations require summing over various objects. For instance one can calculate the potential (cohesive) energy of a crystal summing the contribution of all atoms.

- Crystalline solids are held together by interatomic forces. Each material is characterized by different type of bonds that involve pairs of atoms, triplets,…, and electrons.

- The simplest interaction between atoms is that between rare-gas solids, because they have closed shells and their electrons do not contribute much to the bonding.

- The Lennard-Jones potential was introduced to model the cohesive energy of such solids. Due to its simplicity and flexibility it was then applied to many more solid types.

Today: how do we model solids?

Interatomic potentials

- Pair potentials:
   - Lennard-Jones potential
   - Mie potential
   - Morse potential
- The Coulomb potential for ionic solids
- The EAM potential for metals

- Cut-offs for long and short-ranged potentials

Periodic boundary conditions

Learning goals:
Capability of selecting the correct potential to study a given material
Awareness of main strengths and limitations of interatomic potentials
Capability of writing a computer program to calculate the cohesive
energy of a crystalline solid on a periodic unit cell

The Lennard-Jones potential

While developed to model closed-shell atoms it has been used to model almost anything….

Goal: create a potential to describe the interaction energy $\Phi(r)$ between two spherical atoms distant r (input) which can be valid for many materials
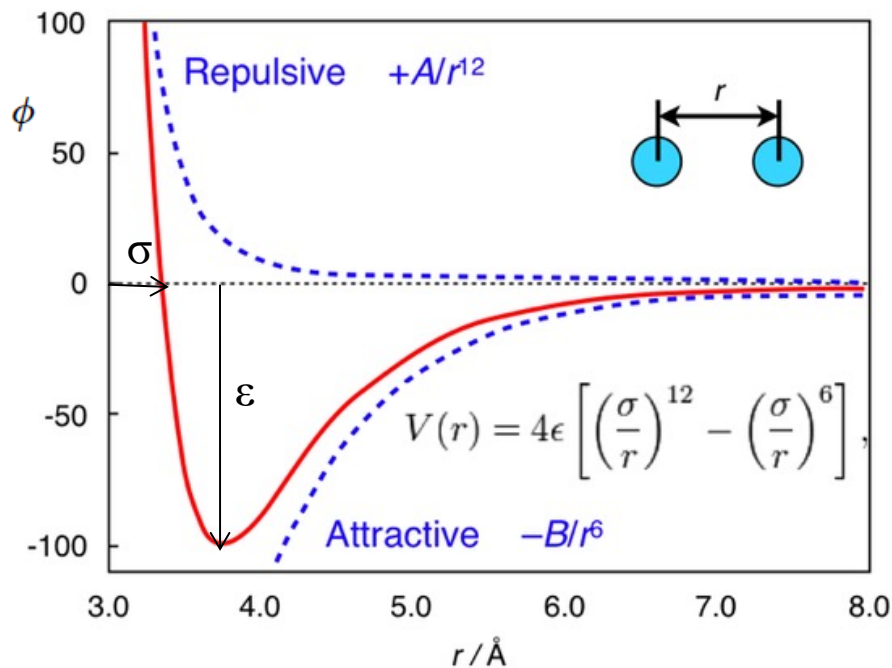
$$\phi(r) = \frac{B}{r^{12}} - \frac{A}{r^6}$$

The potential is rewritten as:

$$\phi(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

$$\sigma = (B/A)^{1/6} \qquad \phi(\sigma) = 0$$
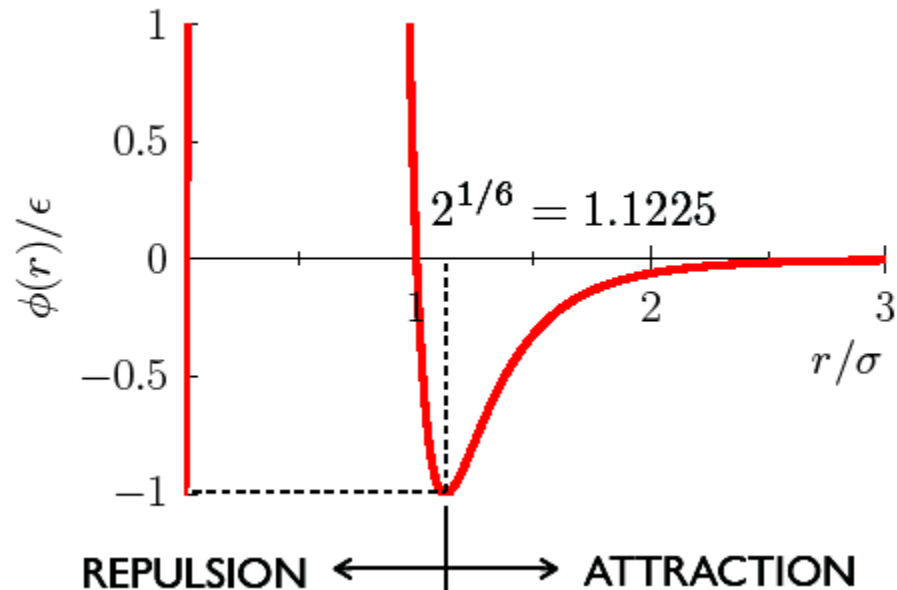
$$\epsilon = A^2/4B$$

absolute value of the minimum
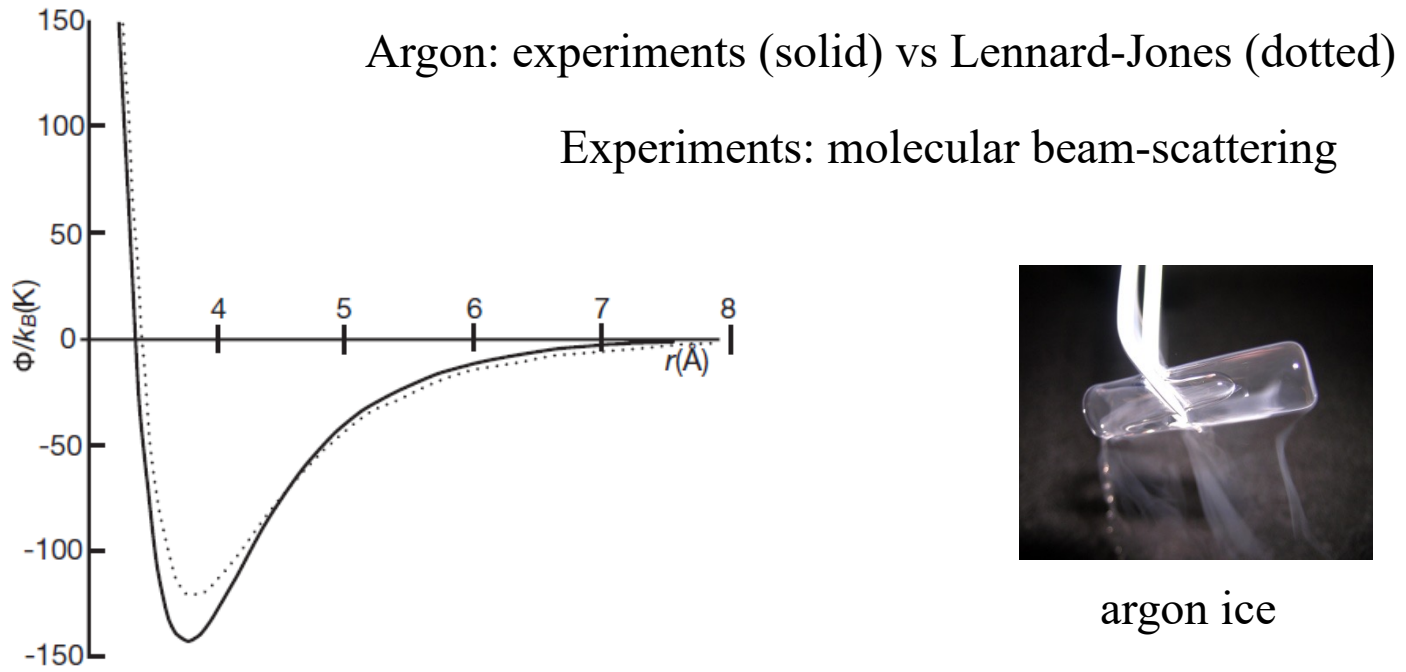
σ, ε are material constants!

4

Reduced units

For calculations, handy to use scaled (or reduced) units: $\phi^* = \phi/\epsilon$ and $r^* = r/\sigma$

$$\phi^*(r^*) = 4\left(\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right)$$

Comparison to experimental values

Argon: experiments (solid) vs Lennard-Jones (dotted)

Experiments: molecular beam-scattering

argon ice

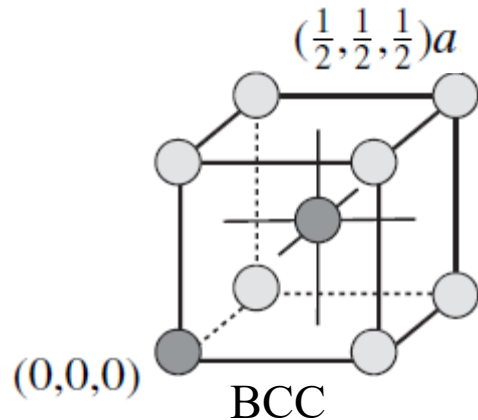|	Ne	Ar	Kr	Xe
ϵ (eV)	0.0031	0.0104	0.0140	0.0200
σ (Å)	2.74	3.40	3.65	3.98

Weak bonds, low melting points
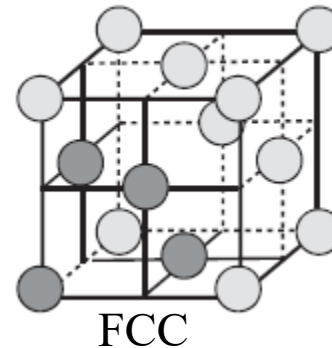
Calculation of cohesive energy

0K cohesive energy for solids:
The basic structure is cubic (simple cubic, FCC, BCC)

$$U_{cell} = \frac{1}{2} \sum_{\mathbf{R}} \sum_{i=1}^{n} \sum_{j=1}^{n}{}' \phi_{ij}(|\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i|)$$
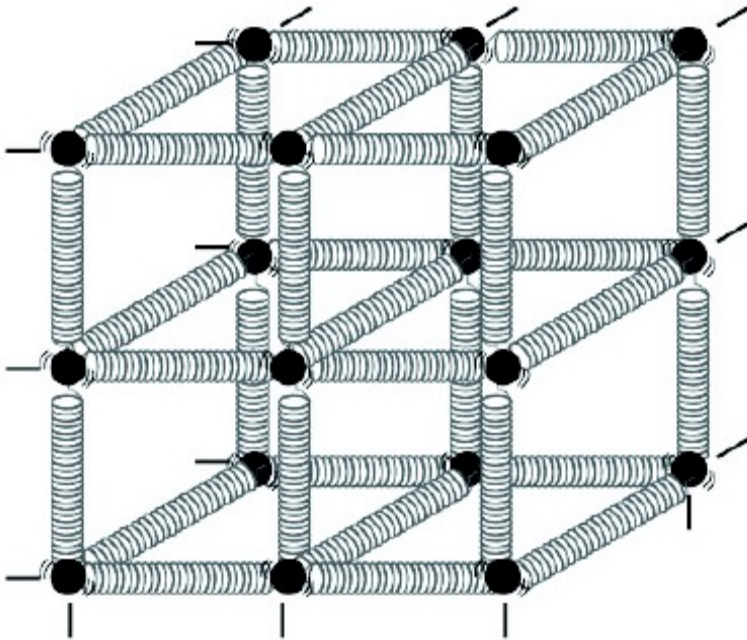

$(\frac{1}{2},\frac{1}{2},\frac{1}{2})a$

$(0,0,0)$

BCC

Fe, Cr, Mo, Ce, W

FCC

Ag, Au, Cu, Ni, Ar

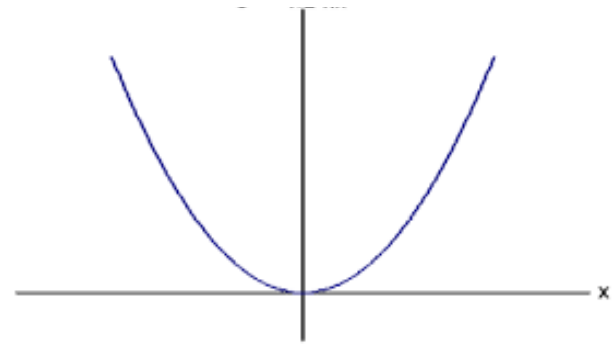$(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0)a$, $(\frac{1}{2},0,\frac{1}{2})a$, and $(0,\frac{1}{2},\frac{1}{2})a$

Atomic Model

Spring-ball model for the illustration of elastic behaviour of solids.

Potential energy of a spring:

$$U = 1/2 kx^2$$

Thermal expansion

o The atomic distance is defined as the distance between the centers of the bonded atoms.

o Strong bonds have short distances

o Distance between primary bonds are 0.1-0.2 nm

o The interatomic distance is constant at 0K.

o If temperature increases so does the interatomic distance, while the atoms vibrate

o Ceramic materials have a deep and narrow well: strong bonds and small thermal expansion
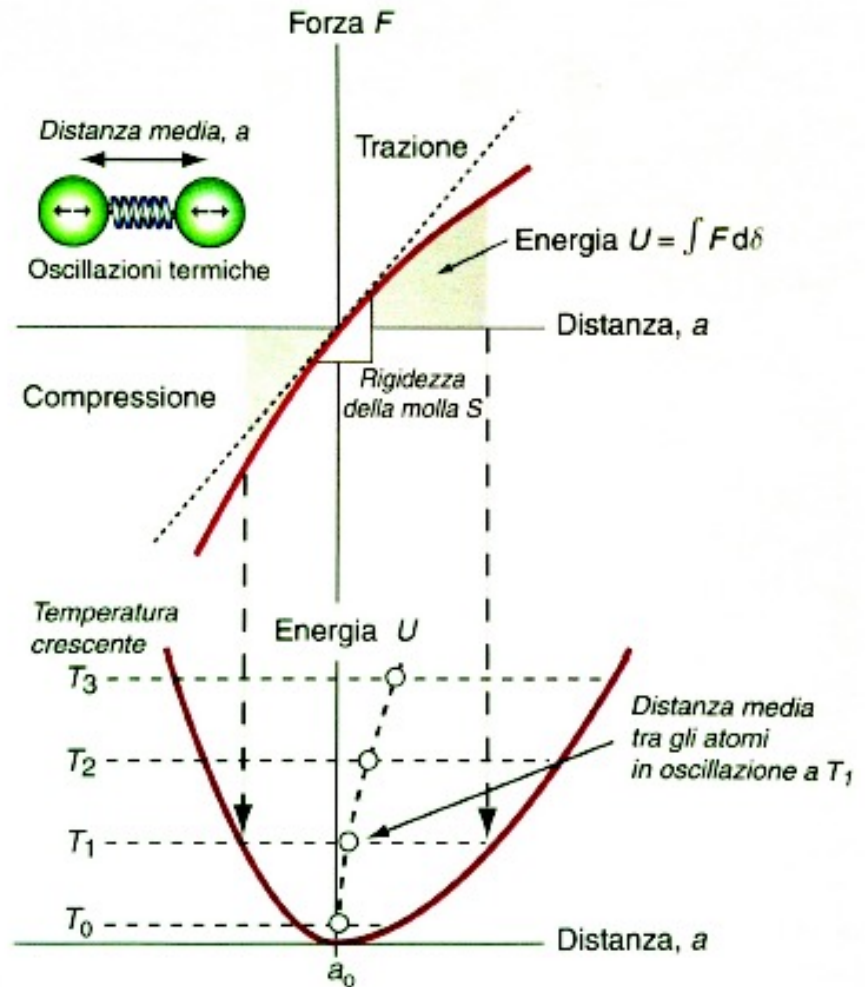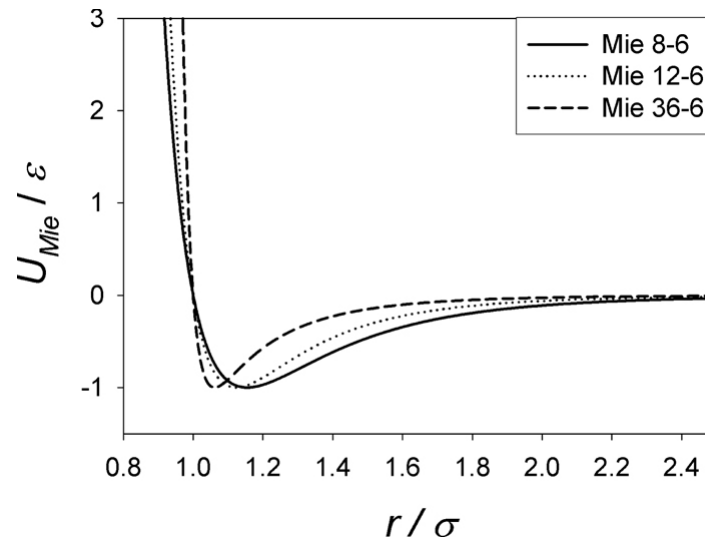
The Mie Potential

Improvements to the Lennard-Jones potential can be made by making the exponents 12 and 6 in the Lennard Jones potential adjustable parameters

$$\phi_{mn}(r) = \frac{\epsilon}{m-n}\left(\frac{m^m}{n^n}\right)^{\frac{1}{m-n}}\left(\left(\frac{\sigma}{r}\right)^m - \left(\frac{\sigma}{r}\right)^n\right)$$

The Mie potential has four parameters and is therefore more flexible than the L-J. The lattice sums for potentials in the form $1/r^n$ are obviously valid also for the Mie potential.

The Morse potential

▸ Another widely used pair potential is the **Morse potential.**

▸ Published in 1929 by Prof. Philip M. Morse

  • Morse, P. M., *Phys. Rev.*, **34**, 57 (1929)

▸ Developed as a simple model for anharmonicity effects in the quantum mechanics of diatomic molecules (reproduces allowed energy levels observed experimentally).
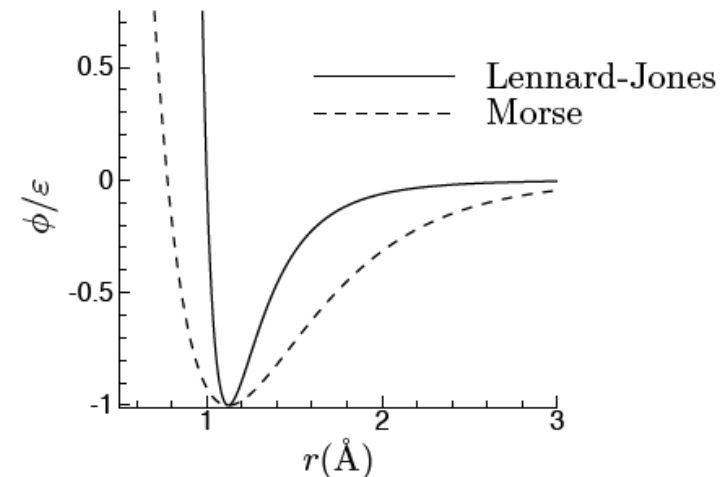
▸ Functional form:

$$\phi(r) = \varepsilon \left[\left(1 - e^{-(r - r_\epsilon)/\sigma} \right)^2 - 1 \right]$$

  • Three fitting parameters (ε, σ, r_ε):
    ε = energy scale (sets cohesive energy)
    σ = well width (sets bond stiffness)
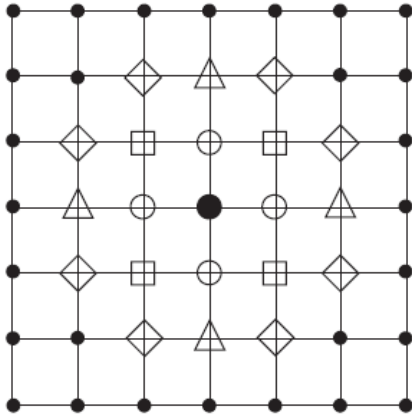 r_ε = location of minimum (sets equilibrium spacing)

Prof. Philip Morse

Reprinted with permission, AIP Emilio Segré Visual Archives.

Shells of neighbors

$$U_{cell} = \frac{1}{2} \sum_{\mathbf{R}} \sum_{i=1}^{n} \sum_{j=1}^{n}{}' \phi_{ij}(|\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i|)$$

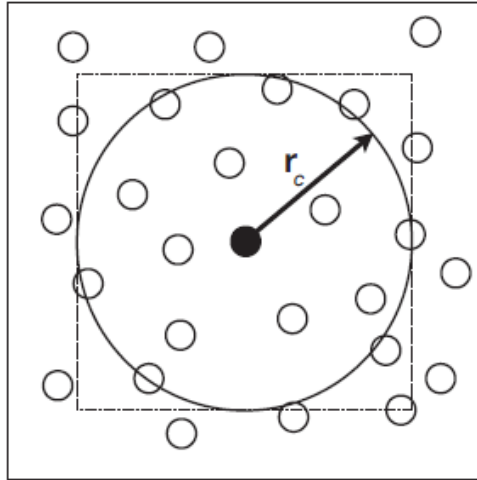$$\sum_{\mathbf{R}} = \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty}$$

First four neighbor shells in a square lattice: nearest neighbors are denoted by a ○, next-nearest neighbors by □, the third neighbor shell by △, and the fourth shell by a ◇.

$$\mathbf{R} = a(n_1 \hat{x} + n_2 \hat{y})$$

$$U_{cell} = 4\Phi(a) + 4\Phi(\sqrt{2}a) + 4\Phi(2a) + 8\Phi(\sqrt{5}a) + \cdots$$

Then you'll need to divide by 2.

Cut-offs

The interaction terms, $\phi(r)$, decrease with distance.

Finite range potential: if r is large, then the value of ϕ is sufficiently small that we can truncate the sum at some cutoff distance r_c, with only small to moderate error.

Cutoff:

We exclude all interactions between objects whose separations are greater than r_c.

What is the error?

Error using a cutoff

We can estimate the error by counting the number of atoms in a shell of width δr at distance r from the origin, assuming the volume of the shell to be the surface area of a sphere times the width δr:

$$4\pi r^2 \rho \, \delta r \qquad\qquad \rho=\text{density of atoms in the shell}$$

The net contribution to the interaction energy of the objects in that shell is

$$\delta U \approx 4\pi r^2 \rho \, \phi(r) \, \delta r$$

integrating over all the interactions now excluded from the sum through the introduction of a cutoff distance:

$$\Delta U \approx 4\pi\rho \int_{r_c}^{\infty} r^2 \phi(r) dr$$

This estimate of the error can also be used as an analytical correction to the potential calculated using the cut-off

Error for short-ranged potentials

The cut-off can be used for short-ranged potentials and the error can ba calculated by substituting the potential function in

$$\Delta U \approx 4\pi\rho \int_{r_c}^{\infty} r^2 \phi(r)dr$$

Many interatomic potentials have the form: $\phi(r) \propto 1/r^n$

Short range

$$\Delta U \approx 4\pi\rho \int_{r_c}^{\infty} r^{2-n}dr = \frac{4\pi\rho}{3-n}r^{3-n}\Big|_{r_c}^{\infty} = \frac{4\pi\rho}{n-3}r_c^{3-n} \qquad \text{as long as } n \geq 4.$$

when $n = 3$ the integrand goes as $1/r$, whose integral is $\log(r)$, which diverges at infinity.

The integral also diverges for $n < 3$.

Implementation:

We only want to calculate $\quad U_{cell} = \dfrac{1}{2} \sum_{R} \sum_{i=1}^{n} \sum_{j=1}^{n}{}' \phi_{ij}(|\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i|)$

for atoms distant from the atom of interest less than the cutoff.

In practice, one wants to avoid the computational inefficiency of calculating the distance from the atom of interest to all other atoms at every time increment.

It is customary to construct a neighbor list for each atom that is then updated during the simulation. One starts by making a list of atoms distant r_u-r_c from atom i.
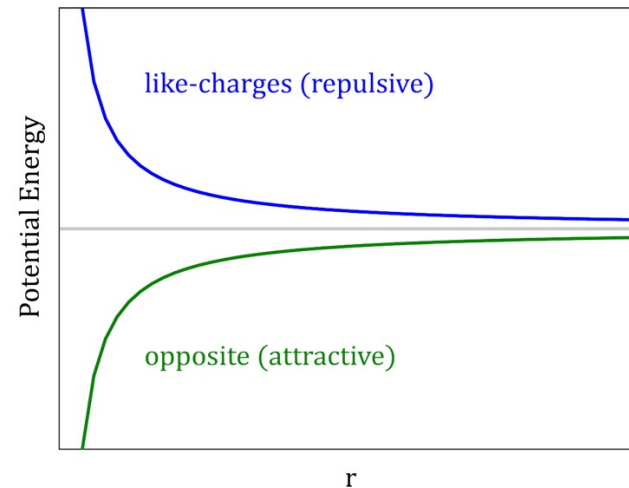If no atoms move more than r_u-r_c there is no need for an update.
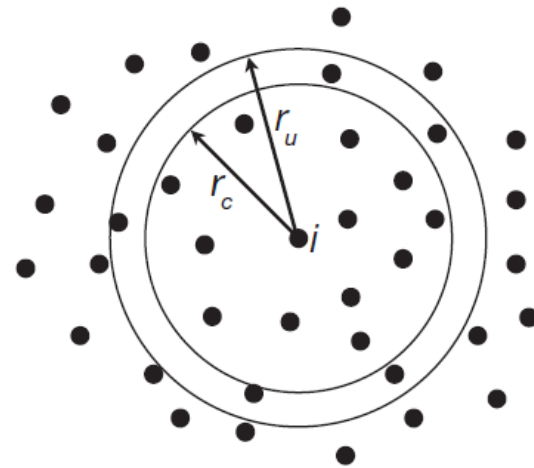
Long-ranged potentials

$$1/r^n \text{ with } n \leq 3$$

A good example of a long ranged potential is an ionic solid. Its properties are governed by electrostatic interactions of the form
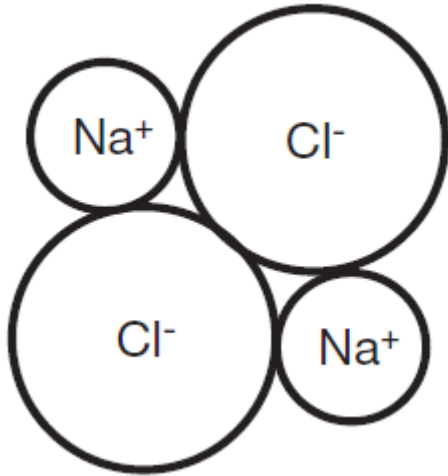
$$q_i q_j / r_{ij}$$

Let's consider the evaluation of the electrostatic energy.
Suppose we have N point charges in a periodically repeating unit cell, then the total electrostatic potential energy is:

like-charges (repulsive)

Potential Energy

opposite (attractive)

r

$$U_e = \frac{1}{2} \sum_{\mathbf{R}} \sum_{i=1}^{n} \sum_{j=1}^{n}{}' \frac{q_i q_j}{|\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i|}$$
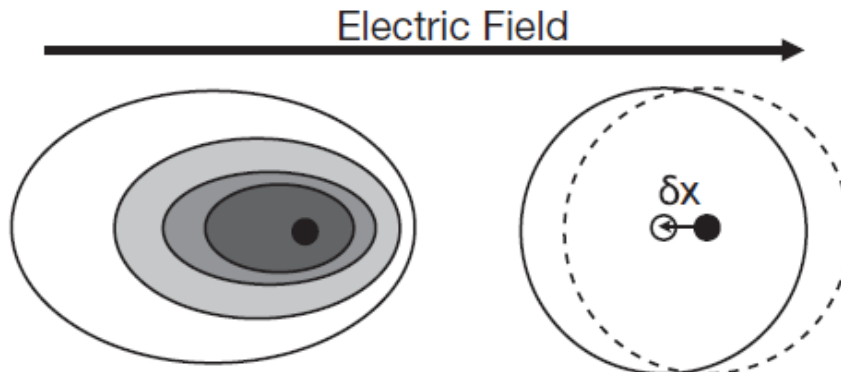
Ionic solids

Na⁺ Cl⁻ Cl⁻ Na⁺

Ionic solids consist of closed-shell ions with little charge in the interstitial region.

$$U = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \left(\phi_{ij}(r_{ij}) + k\frac{q_i q_j}{r_{ij}} \right)$$

electrostatic (Coulomb) interaction

$$\phi(r) = A e^{-\alpha r} - \frac{C}{r^6}$$ Born-Meyer

Electric Field →

Ionic systems have large electric field
→Distortion of the electronic distribution

δx

shell model representation binding energy
1/2kδx²

The Born-Meyer potential

- The Born-Mayer potential is a pair potential which describes ionic crystals well.
  - Ionic bonding is obtained when combining alkali, alkali-earth and some transition metals with group VI and VII elements, e.g. NaCl.

- Published in 1932 by Max Born and Joseph Mayer:

  - Born, M. and Mayer, J. E., Z. Physik, **75**, 1 (1932)
  - Born, M. and Mayer, J. E., J. Chem. Phys., **2**, 252 (1934)

- Functional form:
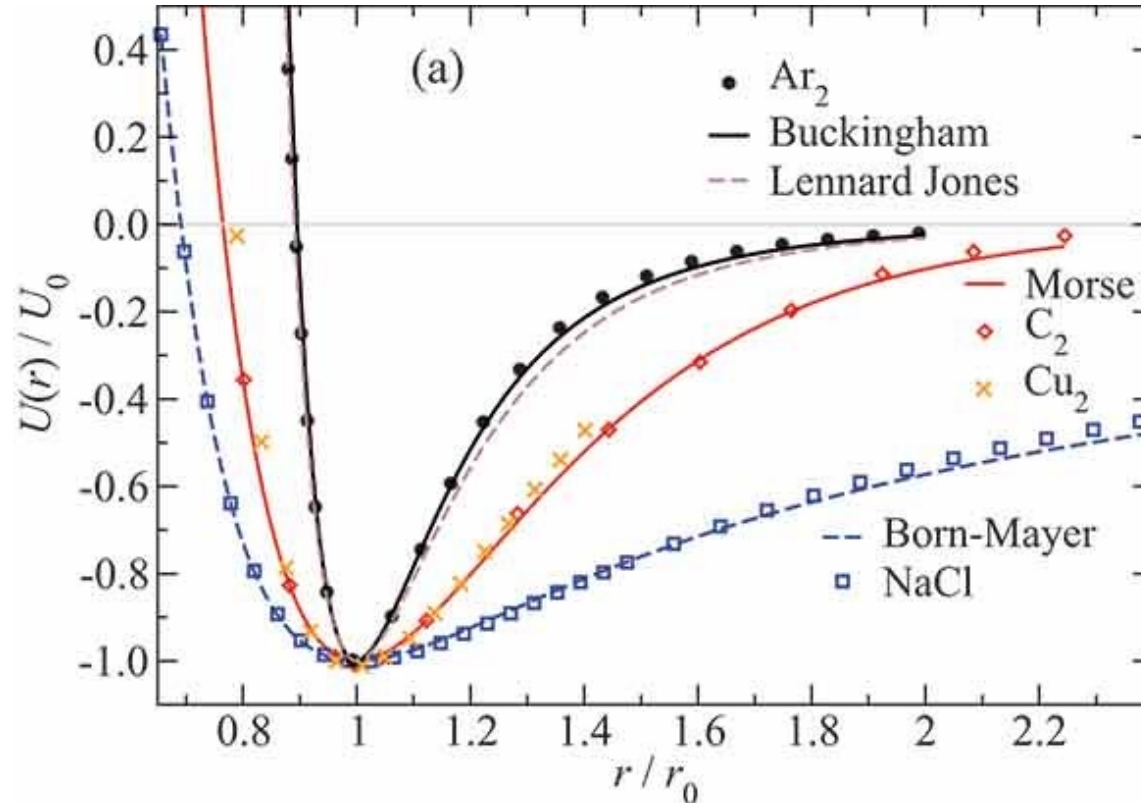
Max Born
Wikipedia (public domain)

$$\mathcal{V} = \frac{1}{2} \sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}}^{N} \frac{Z^{\alpha} Z^{\beta} e^2}{r^{\alpha\beta}} + \frac{1}{2} \sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}}^{\text{near}} A_{\alpha\beta} \left(1 + \frac{Z^{\alpha}}{z^{\alpha}} + \frac{Z^{\beta}}{z^{\beta}} \right) \exp\left[(\sigma^{\alpha} + \sigma^{\beta} - r^{\alpha\beta})/\rho^{\alpha\beta} \right]$$

Coulomb   short-range repulsive term

where Z = atomic number of an ion

e = electron charge

z = number of electrons in outer shell

$\sigma, A, \rho =$ fitting parameters that depend on the ionic species

# How good is the agreement with QC calculations?

This is the comparison of the pair potentials with quantum chemical calculations of the cohesive energy of a few diatomic molecules: Ar_2, C_2 and Cu_2

Spherically truncated Coulomb potential

This is a simple approximate method for Coulombic interaction to cut-off a long-ranged potential:

Use cut-off + approximation of the neglected terms
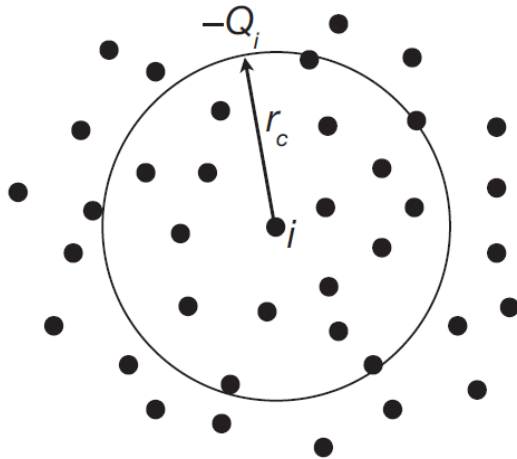
Correction: the overall system must be charge neutral. So if the charge inside the cut-off is:

$$Q_i = \sum_{j}^{r_{ij}<r_c} q_j$$

The net charge of the remaining atoms in the system must be $-Q_i$.

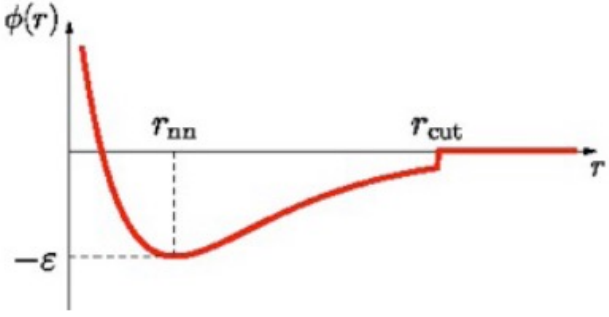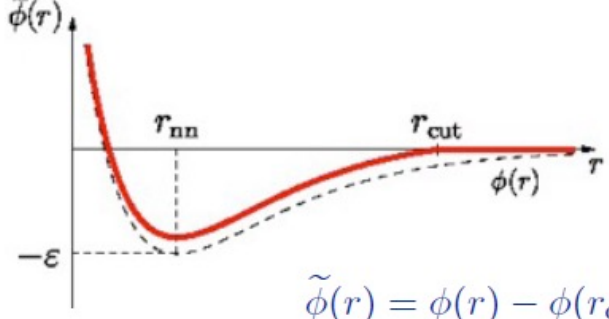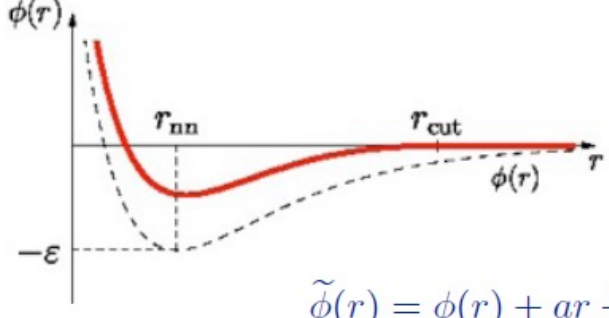$$E_{coul} = \sum_{i=1}^{N} \left(\sum_{j \neq i}^{r_{ij}<r_c} \frac{q_i q_j}{r_{ij}} - \frac{q_i Q_i}{r_c} \right)$$

Issues with cut-offs

QUESTION:

How does the potential energy curve looks like if one uses a cutoff, without correcting terms?

|		
Discontinuous cutoff		• Energy and gradient (force) discontinuous at cutoff. • Can cause convergence problems in static calculations. • Can cause loss of energy conservation in dynamic calcs.
Shifted cutoff	$$\tilde{\phi}(r) = \phi(r) - \phi(r_{\text{cut}})$$	• Energy continuous; gradient (force) discontinuous at cutoff. • Can cause convergence problems in static calculations. Discontinuity in elastic properties
Smoothed cutoff	$$\tilde{\phi}(r) = \phi(r) + ar + b$$	• Energy and gradient (force) continuous at cutoff. • Changes shape of potential everywhere, so is essentially a new potential.

Take home messages

- We model solids by using interatomic potentials, obtained by an educated guess on how the interaction between atoms should be.

- While pair potentials like Lennard-Jones work well for rare gases, we need progressively more fancy potentials for more complicated systems, like ionic solids, metals and covalent solids, for which charges, electron clouds or directionality of the bonds are important.

- It is often desirable to cut-off potentials at large distances to limit computational time. Short-ranged potentials are easily cut and do not need a compensation for what is cut out. Long-ranged potential cannot be simply cut.

FCC repeating unit
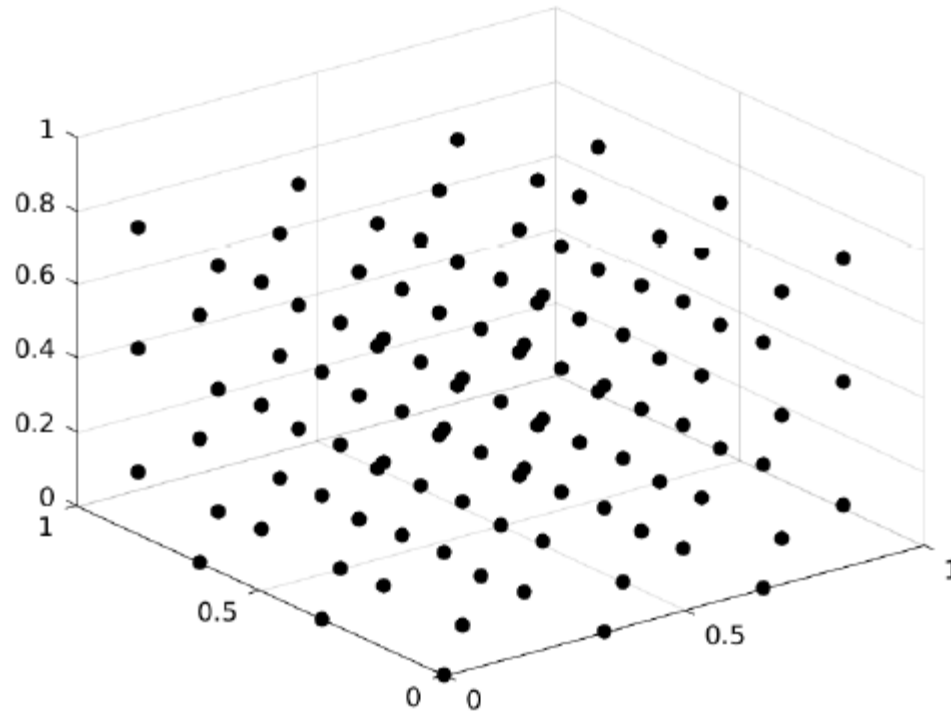
Write a MatLab function to calculate the energy per atom of the FCC (and BCC) crystal you created last time using the Lennard-Jones potential for a couple of values of the lattice constant.

Check that the outcome is reasonable. What should you do?

Check how many atoms you need for a converged result.

$$\phi(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right)$$

$$\phi^*(r^*) = 4 \left(\left(\frac{1}{r^*} \right)^{12} - \left(\frac{1}{r^*} \right)^{6} \right)$$

Cell energy: latsum.m

```matlab
% compute energy of the unit cell with Lennard-Jones potential
function[ucell]= latsum(a,s)
ucell=0;
nc=2;
a=1
[s,i1]=fccmke(nc);
n=i1;
for i = 1:n
    for j=1:n
        xij = s(j,1)-s(i,1);
        yij = s(j,2)-s(i,2);
        zij = s(j,3)-s(i,3);
        dist = a*nc*sqrt(xij^2+yij^2+zij^2);
        if dist>0
            phi=4*(1/dist^(12)-1/dist^6); % Lennard-Jones in reduced units
        else
            phi=0;
        end
        ucell = ucell + phi;
    end
end
ucell = ucell/2;
ucell = ucell/n; %lattice energy per atom (in reduced units)
```

Assignment 2

Calculate the potential energy for various values of the lattice constant and plot the energy as a function of the distance. What value of *a* gives the minimum of the potential energy?

Assignment 2

Lennard Jones potential

Min=(1.55,-6.0655)
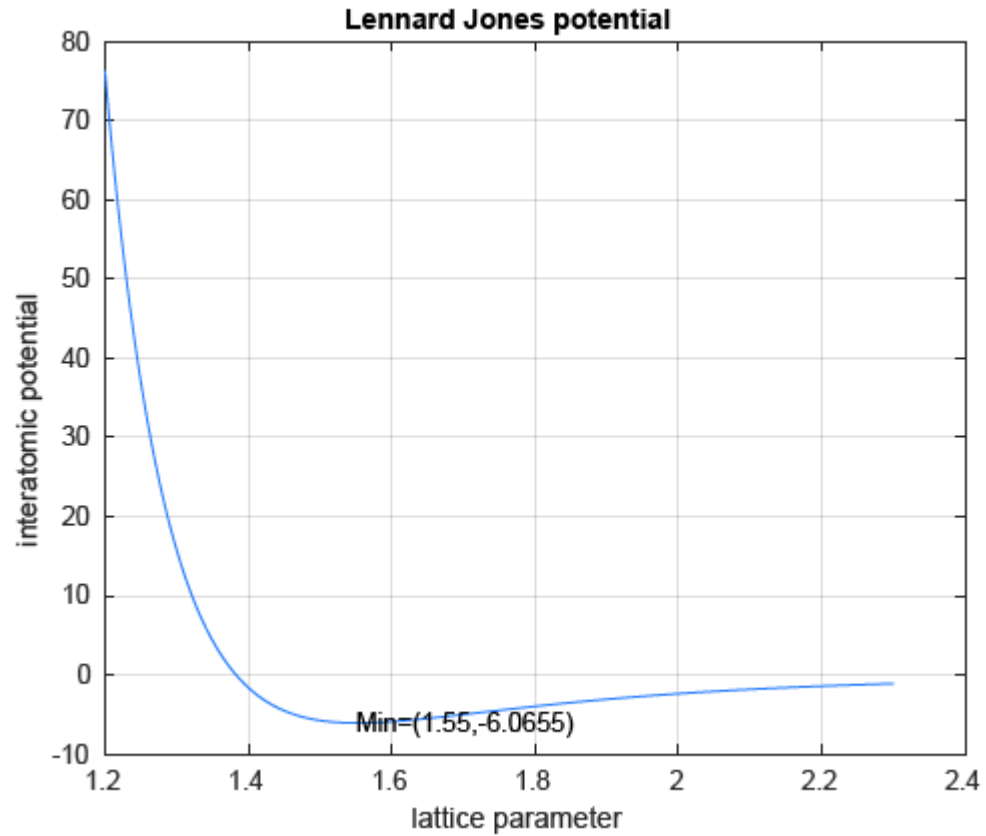
```matlab
function[ucell]= latsum(n,s)
nc=5;
amin=1.2;
amax=2.3;
step=0.005
nsteps=round((amax-amin)/step)+1
[s,i1]=fccmke(nc);
n=i1;
m=0;
ucell=zeros(nsteps,1);
for a=amin:step:amax
    m=m+1;
    b(m)=a;
    for i = 1:n
        for j=1:n
            xij = s(j,1)-s(i,1);
            yij = s(j,2)-s(i,2);
            zij = s(j,3)-s(i,3);
            dist = a*nc*sqrt(xij^2+yij^2+zij^2);
                if dist>0
                phi=4*(1/dist^(12)-1/dist^6); %(Lennard-Jones)
                else
                phi=0;
                end
        ucell(m) = ucell(m) + phi;
        end
    end
    ucell(m) = ucell(m)/2; %because I am double counting contributions
    ucell(m) = ucell(m)/n; %lattice energy per atom (in reduced units)
end
plot(b,ucell)
```

In class assignment 3

Introduce a cut-off value for the potential.
Check what is the effect of different cut-off distances on the results.

Lattice energy using a cut-off

```
function[ucell]= latsum(a,rc,s)
ucell=0;
nc=5
a=1
rc=20
[s,i1]=fccmke(nc);
n=i1;
for i = 1:n-1
    for j=i+1:n
        xij = s(j,1)-s(i,1);
        yij = s(j,2)-s(i,2);
        zij = s(j,3)-s(i,3);
        dist = a*nc*sqrt(xij^2+yij^2+zij^2);
        if dist <= rc
            phi=4*(1/dist^(12)-1/dist^6);
        else
            phi=0;
        end
        ucell = ucell + phi;
    end
end
ucell = ucell/n;
```

In class assignment 4

Apply to the code periodic boundary conditions.

Periodic boundary conditions

```
function[ucell]= latsum(a,rc,c,s)
ucell=0;
nc=5;
a=1;
c=3;
rc=20;
[s,i1]=fccmke(nc);
n=i1;
for i = 1:n
    for j=1:n
        for k=-c:c
            for l=-c:c
                for m=-c:c
                    xij = k + s(j,1)-s(i,1);
                    yij = l + s(j,2)-s(i,2);
                    zij = m + s(j,3)-s(i,3);
                    dist = a*sqrt(xij^2+yij^2+zij^2);
                    if dist>0 & dist<=rc
                        phi=4*(1/dist^(12)-1/dist^6);
                    else
                        phi=0;
                    end
                    ucell = ucell + phi;
                end
            end
        end
    end
end
ucell = ucell/2;
ucell = ucell/n;
```

Calculate the cohesive energy of a crystal of NaCl. The cohesive energy is made by the sum of a pair potential (use Lennard-Jones here) and of a Coulomb potential. The contribution of the charge outside of the cut-off to the Coulomb potential should be included:

$$U_{Coul} = k \sum_{i=1}^{N} \left(\frac{1}{2} \sum_{j \neq i}^{r_{ij} < r_c} \frac{q_i q_j}{r_{ij}} - \frac{q_i Q_i}{r_c} \right) \qquad Q_i = \sum_{j \neq i}^{r_{ij} < r_c} q_j$$

TABLE 1: Parameters of the Lennard-Jones Interactions

atom	σ (Å)	ϵ (kJ/mol)
Na	3.33	0.012
Cl	4.42	0.493
Na−Cl	3.84	0.076