Introduction to Molecular dynamics

Complete lecture notes for self-studies

Professor Kai Nordlund and University lecturer Antti Kuronen 1999 - 2015

- The idea of the course is to teach the students the basics of atom-level computer simulations, which are widely used in materials and atomic physics, chemistry and biology.
  - The course deals with 2 basic simulation types: molecular dynamics (MD) and structural optimization (by using conjugate gradients (CG) and genetic algorithm (GA) methods).
- Course material home page: http://www.acclab.helsinki.fi/~knordlun/moldyn/

Exercises

- Questions and exercises are provided among the materials
- Many of the exercises involve writing subroutines or full computer programs.
-
- The programs are provided either in Fortran90 or C.
  - Linux (or other Unix) is the preferable environment.

Computer environment

- For exercises you need an computer environment with C or Fortran compiler.
- Good non-commercial (i.e. free) alternatives are the GNU compilers.
  - They can be easily installed in any Linux distribution.

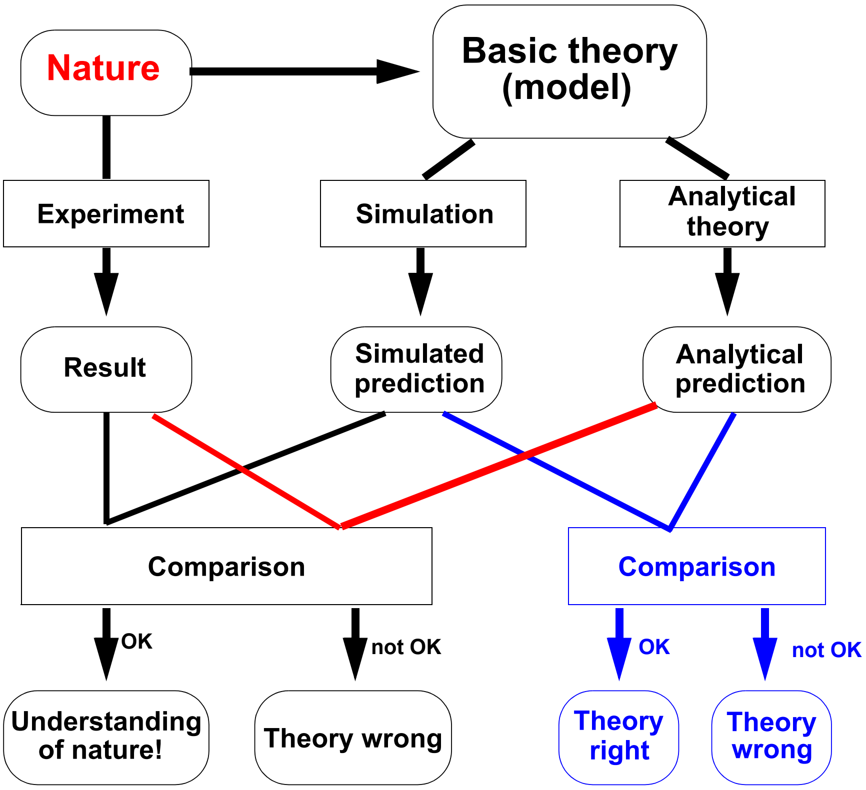
Contents

Literature

- Lecture notes
  - Will appear on the web a bit before the lecture (http://www.physics.helsinki.fi/courses/s/atomistiset/lecturenotes/).
  - The web page also has links to similar courses elsewhere in the world.

- As background information you can use e.g.:
  - M. P. Allen, D. Tildesley: *Computer simulation of Liquids* (Oxford University Press, Oxford,1989)
    - **The classical simulation textbook everybody refers to.**
    - Statistical mechanics approach.
  - D. Frenkel, B. Smit: *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd edition (Academic Press, 2001)
    - Statistical mechanics approach.
    - Note that the 1st edition has quite a few printing errors.
    - Book home page (http://molsim.chem.uva.nl/frenkel_smit/) has exercises and case studies.
  - R. Phillips: *Crystals, defects and microstructure : modeling across scales* (Cambridge University Press, 2001)
    - A nice textbook on computational methods in materials research in general; from atomistics to elastic continuum.
    - Includes a chapter on interaction models.
  - A. R. Leach: *Molecular modelling: Principles and applications*, 2nd edition (Prentice Hall, 2001)
    - In addition to simulation methods includes also nice chapters on interaction models (classical and quantum mechanical).
    - Molecular mechanics and force fields.

Computer simulations in physics



- Simulation can bridge the gap between theory and experiment.
- Sometimes only choice (theory too complicated).
- Sometimes simulation impossible: not enough computer capacity.
- Also comparison between analytical theory and simulation: if both are based on the same basic theory (e.g. Newtons laws), but analytical theory uses approximations, simulation can be a perfect way to test the approximation.

Atomistic simulation: What is it?

- Model where the basic object is (roughly) a spherical object.
  - This object can be an
    - atom
    - molecule
    - nanocluster
    - a particle in a fluid
    - a planet or a part of a galaxy
  - On this course, we almost always talk about “atoms”, but in many cases the algorithms are such that the “atom” could be almost any of the above.
- Application areas:
  - atom movement in equilibrium: thermodynamics
  - nonequilibrium phenomena: irradiation, material heat or pressure processing, phase transitions, nucleation, surface growth (thin film deposition)
  - properties of lattice defects
  - nanostructures: $N_{\text{atoms}} \sim 10^4 - 10^9$: can be simulated!
  - interactions inside a molecule: vibration, rotation, protein folding
  - intermolecular interactions
  - chemical reactions

And what is it not?

- Continuum modelling (e.g. Finite Element Modelling, FEM)
- Fixed lattice or grid model
  - Although here the limit is sometimes hard to draw.
  - Modeling of amorphous materials using continuous random networks: bond-switch simulations.
- Particle physics
- Electronic structure calculation (for fixed positions of nuclei)
  - But these are often used as basis for atomistic simulation: *ab initio* MD.
- Since the basic object is an atom, and a computer memory is limited, atomistic simulations are always somehow size limited.
  - Hence usually simulating macroscopic (mm size and up) objects is usually out of the question.
  - 100 million atoms is doable: quick estimate of what physical system size this corresponds to:
    - E.g. silicon: volume/atom $v = \frac{(5.43\,\text{Å})^3}{8\text{ at.}} = 20.0\frac{\text{Å}^3}{\text{at.}}$

$$V(10^8\text{ atoms}) = 2.0\times10^9\,\text{Å}^3$$

$$\text{cube edge} = \sqrt[3]{2.0\times10^9}\,\text{Å} = 1260\,\text{Å} = 0.126\,\mu\text{m}$$

- Time scale of normal MD limited to tens of nanoseconds (but more about that later).

Important types of atomistic simulations

- Molecular dynamics (**MD**)
  - Simulate the dynamic atom motion based on some interaction model.

- Monte Carlo (**MC**)
  - MC is in the broadest sense any simulation which uses random numbers.
  - Even most MD simulations do use random numbers, but they are still conventionally not considered true MC simulations.
  - There are a few varieties of MC which are often used for atomistic simulations. The most important are maybe:
    - Metropolis MC (**MMC**)
      - Simulate a thermodynamic ensemble, energy minimization by simulated annealing.
    - Kinetic MC (**KMC**)
      - Simulation of activated processes (e.g. diffusion)
  - The MC courses deal with all this. (http://beam.acclab.helsinki.fi/~eholmstr/mc/)

- Structural optimization
  - Find the equilibrium state of of an atomistic system based on some interaction model: energy minimization.
  - Global vs. local minimum: simulated annealing.
  - Conjugate Gradient (**CG**) method
    - An efficient way to find a local minimum.
    - Can also be used for atoms.
  - Genetic algorithms (**GA**)
    - Sometimes an efficient way to find a global minimum.
    - Can also be used for atoms.
  - Minimum energy path determination

- Binary collision approximation (BCA)
  - In nuclear and ion beam physics (and almost nowhere else)
  - Event-driven simulations in general (e.g. interaction of electron and photon radiation with matter)

How to present atomistic data

- There exist about a zillion different file formats for presenting atom positions.
  - An example: how should we present the coordinates?
    - For 8 Cu atoms in the corners of the unit cube
    - Trivial format 1 “x y z”:

```
0.0 0.0 0.0
1.0 0.0 0.0
0.0 1.0 0.0
0.0 0.0 1.0
1.0 1.0 0.0
1.0 0.0 1.0
0.0 1.0 1.0
1.0 1.0 1.0
```

- No information about time (for a dynamic system)
- Trivial format 2: “x y z t”

```
0.0 0.0 0.0 3.0
1.0 0.0 0.0 3.0
0.0 1.0 0.0 3.0
0.0 0.0 1.0 3.0
1.0 1.0 0.0 3.0
1.0 0.0 1.0 3.0
0.0 1.0 1.0 3.0
1.0 1.0 1.0 3.0
```

- Downside of both formats: All file has to be read in before we know how many atoms there are.

From program `babel`:

```
alc       -- Alchemy file
bgf       -- BGF file
bmin      -- Batchmin Command file
box       -- DOCK 3.5 box file
bs        -- Ball and Stick file
c3d1      -- Chem3D Cartesian 1 file
c3d2      -- Chem3D Cartesian 2 file
caccrt    -- Cacao Cartesian file
cache     -- CAChe MolStruct file
cacint    -- Cacao Internal file
cdct      -- ChemDraw Conn. Table file
contmp    -- Conjure Template file
csr       -- MSI Quanta CSR file
cssr      -- CSD CSSR file
diag      -- DIAGNOTICS file
dock      -- Dock Database file
dpdb      -- Dock PDB file
feat      -- Feature file
fhz       -- Fenske-Hall ZMatrix file
gamin     -- Gamess Input file
gcart     -- Gaussian Cartesian file
gotmp     -- Gaussian Z-matrix tmplt
gr96A     -- GROMOS96 (A) file
gr96N     -- GROMOS96 (nm) file
gzmat     -- Gaussian Z-matrix file
hin       -- Hyperchem HIN file
icon      -- Icon 8 file
idatm     -- IDATM file
m3d       -- M3D file
maccs     -- MDL Maccs file
macmod    -- Macromodel file
macmol    -- Mac Molecule file
mdl       -- MDL Molfile file
micro     -- Micro World file
miv       -- MolInventor file
mm2in     -- MM2 Input file
mm2out    -- MM2 Ouput file
mm3       -- MM3 file
mmads     -- MMADS file
mol       -- Sybyl Mol file
mol2      -- Sybyl Mol2 file
mopcrt    -- Mopac Cartesian file
mopint    -- Mopac Internal file
pcmod     -- PC Model file
pdb       -- PDB file
psc       -- PS-GVB Cartesian file
psz       -- PS-GVB Z-Matrix file
report    -- Report file
sdf       -- MDL Isis SDF file
smiles    -- SMILES file
spar      -- Spartan file
tinker    -- Tinker XYZ file
torlist   -- Torsion List file
unixyz    -- UniChem XYZ file
wiz       -- Wizard file
xed       -- XED file
xyz       -- XYZ file
```

How to present atomistic data

- In this course we use the **XYZ standard format**.
  - First line has number of atoms at this time
  - Second line is comment
  - Then come the coordinates of the atoms with the element symbol as the 1st column.

```
 8
Molecule name or comment or whatever (Might, however, be used by some applications.)
Cu 0.0 0.0 0.0 320.0
Cu 1.0 0.0 0.0 310.0
Cu 0.0 1.0 0.0 305.0
Cu 0.0 0.0 1.0 280.0
Cu 1.0 1.0 0.0 290.0
Cu 1.0 0.0 1.0 320.0
Cu 0.0 1.0 1.0 310.0
Cu 1.0 1.0 1.0 320.0
```

  - The fifth column can also hold other information, or be empty.

  - It is a very good idea to include useful information on the second line (a non-standard feature), e.g.

```
 8
Frame number 1 3.0 fs boxsize 3.0 3.0 3.0
Cu 0.0 0.0 0.0 320.0
Cu 1.0 0.0 0.0 310.0
...
```

How to present atomistic data

- For dynamic information, the info for each time can simply be put after each other in the same file:

```
 2
Frame number 1 0.0 fs boxsize 3.0 3.0 3.0
Cu 0.0 0.0 0.0 320.0
Cu 1.0 0.0 0.0 310.0
 2
Frame number 1 2.0 fs boxsize 3.0 3.0 3.0
Cu 0.1 0.0 0.0 330.0
Cu 1.1 0.1 0.0 300.0
 2
Frame number 1 4.0 fs boxsize 3.0 3.0 3.0
Cu 0.2 0.1 0.0 340.0
Cu 1.2 0.1 0.0 290.0
...
```

- For very large simulation systems this text format may become too inefficient (both from the point of view of space and time).
  - Binary formats exist, but are not standardized at all...

Visualization of atomic data

- Visualization is fun but also useful.
- Plot each atom as a sphere, either statically or dynamically.
- Plot bonds between atoms: ball-and-stick model.
- As with file formats, there are about a zillion programs which can do that.
- One much used visualization program is **RasMol**. It is

  \+ free and open source (easy to modify for your needs)
  \+ works at least in Linux, Unix, Windows, and Mac
  \+ fast
  \+ supports many of the most common chemistry formats, including XYZ
  \+ can produce publication-quality output
  \- poor at adding text to the graphics
  \- can not draw much else than atoms, bonds and protein backbones
  \- no perspective transformation

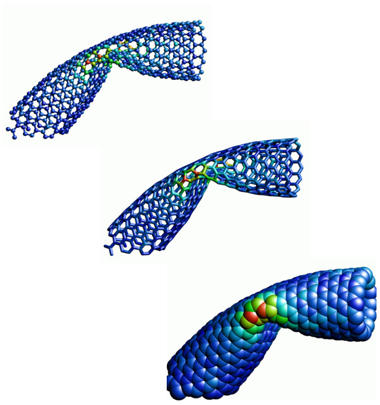
  - Home page: http://rasmol.org/

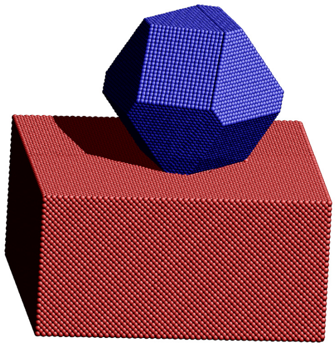
Visualization of atomic data

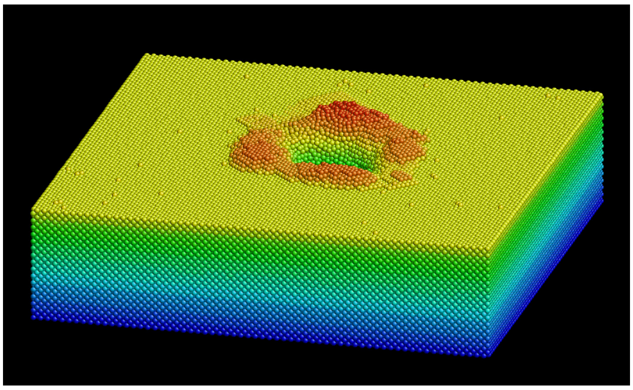
- Useful Rasmol commands (see also http://www.physics.helsinki.fi/courses/s/atomistiset/refcardUS.pdf):

`load xyz file`	Read in a file
`write gif image.gif`	Store an image in the gif format
`write ppm image.ppm`	Store an image in the ppm format
`write ps image.ps`	Store an image in the ps format
`zap`	Remove all data, needed before new load command
`quit`	
`wireframe <on/off/value>`	Adjust bond width
`spacefill <on/off/value>`	Adjust atom size
`spacefill temperature`	Get atom size from column 5 in XYZ file
`zoom 150`	Zoom display, default=100
`set ambient <value>`	Ambient light strength
`set specular on`	Use a nice 3D shade on atoms
`set specpower <value>`	Remove the 3D shade
`set shadows on/off`	Use/don't use atom shadowing (slow)

When started, rasmol reads the file `~/.rasmolrc` for initial settings.

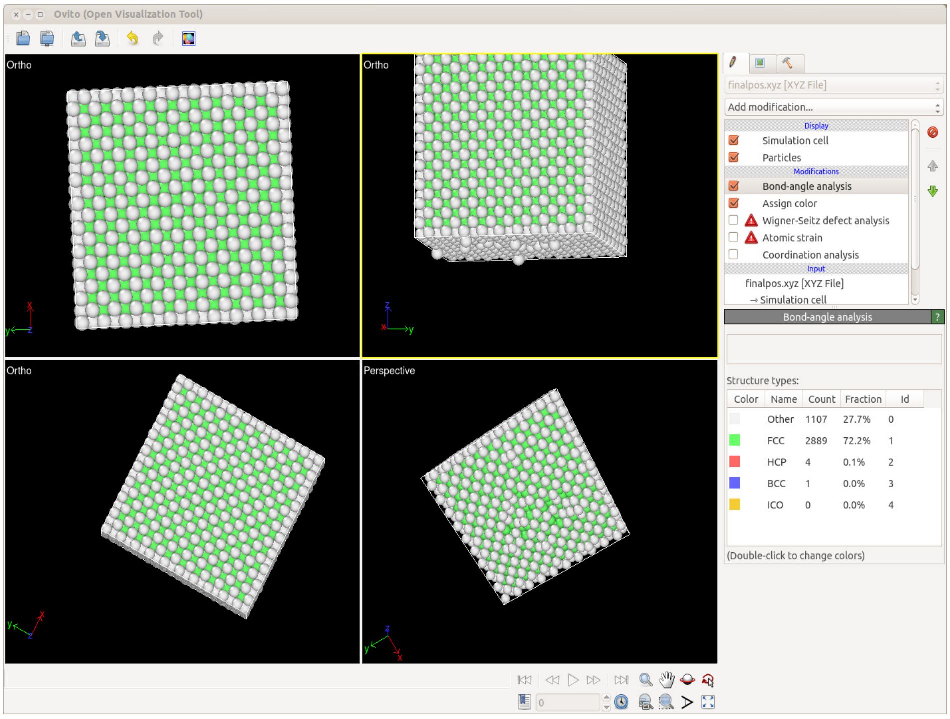






Ovito

- Ovito is a very powerful software for atom (not molecule) visualization **and analysis**
- Maintained and developed by Alex Stuchowski of the TU Darmstadt
- It has a very nice graphical user interface and many very advanced modern analysis methods
- Filters for selecting only parts of atoms
- Available for Unix/Linux, Windows and Mac OS X
- Very quick guide to get started for XYZ files:
  - Start ovito
  - From top right corner, select “Import data” button
    and then open an XYZ file
  - In “File column mapping” set (at least)
    - Column 1: Particle Type
    - Column 2: Position X
    - Column 3: Position Y
    - Column 4: Position Z
    - Column 5: Particle Type
  - After this the atoms should display
  - Analysis options in menus on right
- Can be scripted via python
- http://www.ovito.org/



finalpos.xyz [XYZ File]

Add modification...

Display
☑ Simulation cell
☑ Particles

Modifications
☑ Bond-angle analysis
☑ Assign color
☐ Wigner-Seitz defect analysis
☐ Atomic strain
☐ Coordination analysis

Input
finalpos.xyz [XYZ File]
→ Simulation cell

Bond-angle analysis

Structure types:

Color	Name	Count	Fraction	Id
⬜	Other	1107	27.7%	0
🟩	FCC	2889	72.2%	1
🟥	HCP	4	0.1%	2
🟦	BCC	1	0.0%	3
🟨	ICO	0	0.0%	4

(Double-click to change colors)

“Quick and dirty” command line animation tool: dpc

- A simple way to make animations is to use program `dpc` by Kai Nordlund
- It reads XYZ files that have many frames concatenated.
- `dpc` is available from the course web page
  - Compile it according to instructions
  - Run it by command: `dpc`
  - Basic usage for XYZ files:

```
dpc xyz erase sort 2 3 4 5 moviefile.xyz
```

    - “`2 3 4`” tells that the x, y- and z- info is taken from columns 2, 3 and 4.
    - “`5`” does not mean anything for XYZ, but must still be there.
    - All options are between “`dpc`” and “`2 3 4 5`”

- The program is not as flexible as `rasmol`, but it is very fast (it is written under plain `Xlib`)

- Help is given by command `dpc` with no options.

- Most important options

`s 600 800`	Window size
`sd 600 600`	Draw area size
`x 0 83`	x limits
`y 0 65`	y limits
`z 37.8 43.6`	Color (z) limits
`m 1`	Form of atoms: 0 rect, 1-4 circle
`d 4`	Dot size
`gifdump`	Make gif file dump of each window frame

Making presentation animations

- To make animations for the web or a presentation:
  - Use `rasmol, ovito` or `dpc` to make a separate a bitmap image of every single time step.
    - Each image should be stored with a name having the frame number encoded; e.g. `frame001.png`, `frame002.png`, ...
  - Make an animation from these separate frames by using any animation program (many of them available freely; e.g. `ffmpeg`).
  - With new versions of ffmpeg a typical atom animation can be made using something like:

```
ffmpeg -framerate 2 -i dpcdump%3d.png -qmax 5 -b 1800k -dframes 1 test.wmv
```

“Quick and dirty” data-analysis: awk

- Swiss army knife of Unix: `awk` (or `gawk`)
  - A lot can be done using simple ‘one-liners’.
  - Example: we have a XYZ file:

```
2632
Time (fs)       74500
C       3.14286         5.13682         9.99465         -7.30347
C       3.54844         3.00536         11.1538         -4.55679
C       4.20179         5.13682         12.1936         -7.30347
C       5.07013         3.00536         13.0619         -4.55679
C       6.10993         5.13682         13.7152         -7.30347
C       7.26903         3.00536         14.1208         -4.55679
C       8.48933         5.13682         14.2583         -7.30347
C       9.70963         3.00536         14.1208         -4.55679
```

  - And want to check the potential energy (5th column or so-called temperature column) distribution:

```
cat file.xyz |
gawk ’$1=="C" {i=int(10*$5+0.5); e[i]++} END {for (i in e) print i/10,e[i]}’|
sort -n | xgraph
```

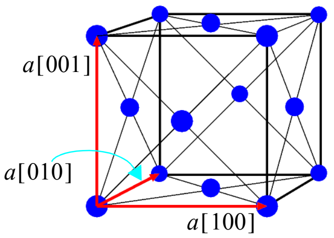
- Quick and dirty plotting: `xgraph`
  - This is also installed on mill at `/usr/local/bin`.
- These tools reduce the need to build C or F90 programs or to launch Matlab for every small task.

Other visualization programs

- **OpenDX**
  - A commercial IBM program package which was later made open source
  - Philosophy
    - build a network of modules through which data flows
    - data analysis and visualization in the same program package
  - Home page: http://www.opendx.org/
- **VMD**
  - More features than in RasMol.
  - Slows down for large systems.
  - Home page: http://www.ks.uiuc.edu/Research/vmd/
- And many many more...

Molecular dynamics 2015

Exercises 1 to chapter 1: Visualization



The face-centered cubic (FCC) lattice structure is as follows: a lattice has an number of cubes next to each other. Each cube has an atom in each corner, and in addition there is an atom on the center of each side of the cube. One cube is called the unit cell, and it thus has 4 atoms in total (Why only 4?). By displacing the atoms a bit it is possible to make a cube which has four atoms inside it.

FCC is one of the two close-packed structures in 3D, the other one is hexagonal close packed (HCP). The statement that FCC and HCP are the tightest ways of packing spheres in 3D is called the Kepler conjecture. All physicists know it's true but mathematicians only recently have been able to prove it (http://mathworld.wolfram.com/KeplerConjecture.html).

1. **(12 p)** Write a program which creates a 3-dimensional Cu FCC-lattice and prints it out in the XYZ format. As input the program should read the size of the system in unit cells in each direction (x, y, z). Coordinates of the atoms in the XYZ file should be in Å. Make a figure out of a $4 \times 4 \times 4$ system and visualize this with `rasmol, ovito or dpc`[1] so that at least three sides of the cube are visible. The lattice constant of Cu (side length of unit cell) is $a = 3.62$ Å.

2. **(8 p)** Modify your program so that you can visualize the (111) surface of the Cu FCC lattice. You can do this either by cutting the cube in the right direction or building the system from unit cells with the right orientation (i.e. a unit cell with one side in the (111) plane; it is possible, we come to that later in the lectures). Check that you get the right symmetry in the (111) plane (hexagonal).

The exercises are returned by emailing the source code creating atoms and one `rasmol`-picture/exercise in the gif format.

For additional information about crystal structures and notation see any solid state physics textbook, e.g. Kittel or Ashcroft and Mermin. Shortly, plane (111) is the the plane that is perpendicular to the vector $[111] = \mathbf{i} + \mathbf{j} + \mathbf{k}$. Here the unit vectors are oriented along the edges of the cube depicted above.

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[1] Or whatever visualization program you use.

Basics of molecular dynamics

- The basic idea of molecular dynamics (MD) simulations is to calculate how a system of particles evolves in time.
  - The method was first used by Alder and Wainwright in 1957 to calculate properties of many-body systems. They called the particles *molecules*.
    - There is an interesting parallel to classical mechanics here. The two-body motion problem was solved by Newton way back then. The three-body problem was solved by a Finnish guy, Sundman, in the early part of the last century - but the solution is utterly impractical ($10^{8000000}$ terms needed in a series expansion).

- The N-body problem, $N > 3$, can not be solved analytically. MD can also described to be a numerical way of solving the N-body problem. The solution is of course never exact, but if done properly it can be done arbitrarily accurately.

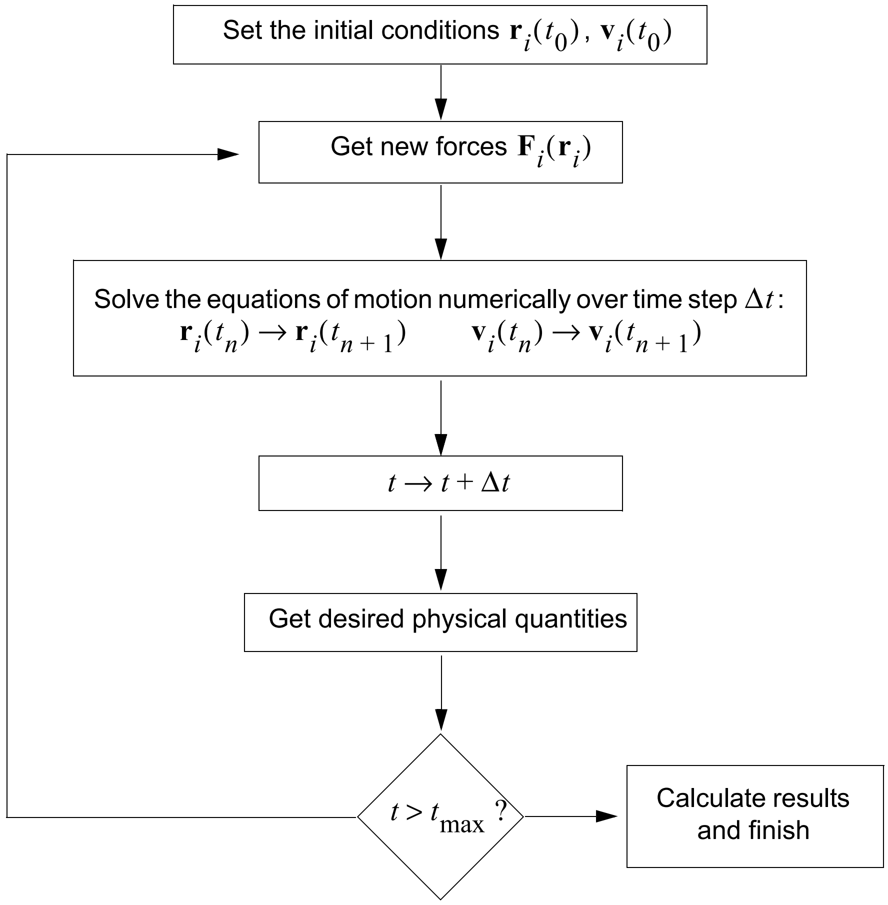
- Consider a set of atoms at positions $\mathbf{r}_i$ and some interaction model which gives us the potential energy of the system $V(\{\mathbf{r}_i\})$

- In Newtonian mechanics we then get:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i\ , \qquad \frac{d}{dt}(m_i\mathbf{v}_i) = \mathbf{F}_i = -\nabla_i V = -\nabla_i\left[\sum_j V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{j,k} V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots\right]$$

- By solving the above set of equations numerically we can derive $d\mathbf{r}$ over some short time interval dt.

Basic MD algorithm (slightly simplified)



Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Solve the equations of motion numerically over time step Δt:
$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1})$ $\mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$

$t \rightarrow t + \Delta t$

Get desired physical quantities

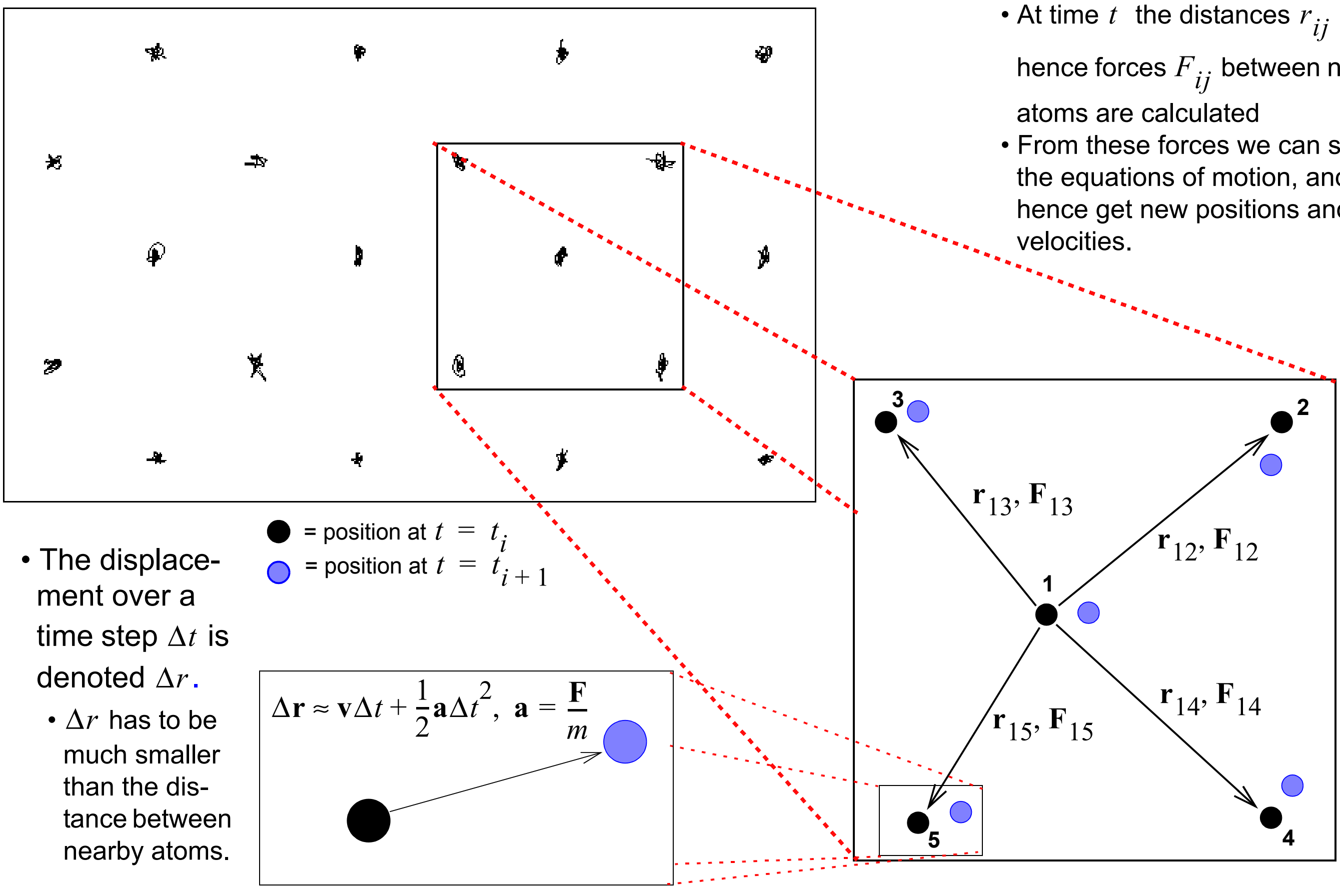
$t > t_{\max}$?

Calculate results and finish

An alternative view

- MD-simulation of thermal motion over 100 time steps

- Zoom in on 2 time steps (5 atoms):
  - At time t the distances r_{ij} and hence forces F_{ij} between nearby atoms are calculated
  - From these forces we can solve the equations of motion, and hence get new positions and velocities.



● = position at $t = t_i$
● = position at $t = t_{i+1}$

$$\Delta\mathbf{r} \approx \mathbf{v}\Delta t + \frac{1}{2}\mathbf{a}\Delta t^2, \quad \mathbf{a} = \frac{\mathbf{F}}{m}$$

- The displacement over a time step Δt is denoted Δr.
  - Δr has to be much smaller than the distance between nearby atoms.

General considerations

- The above was the simplest possible example, the so called microcanonical or NVE ensemble. This means that the approach preserves the number of atoms N, the volume of the cell V and the energy E. Other ensembles will be dealt with later on in the course. But the NVE ensemble is the most natural one in that it is the true solution of the N-body problem, and corresponds to the real atom motion.

- First MD simulations:
  - Hard spheres: B. J. Alder, T. E. Wainwright: *Phase transition for a Hard Sphere-System,* J. Chem. Phys. **27** (1957) 1208
  - Continuous potentials: J. B. Gibson, A. N. Goland, M. Milgram, G. H. Vineyard: *Dynamics of Radiation Damage*, Phys. Rev. 120 (1960) 1229.

- State-of-the-art (2015):
  - Of the order of 10 000 000 000 atoms can be done on many large supercomputers
  - In Finland: CSC Cray (louhi.csc.fi): some 100 000 000 atoms with a realistic potential easily possible for thousands of time steps.

- If all N atoms interact with all atoms, one has to in principle calculate N^2 interactions. This is prohibitively expensive for millions of atoms.

General considerations

- Fortunately, in practice most atomic interactions decrease rapidly in strength as $r \to \infty$. In that case it is enough to calculate only interactions to nearby atoms.
  - E.g. in diamond-structured semiconductors (Si, Ge, GaAs...) atoms have 4 covalent bonds, so the calculation can be reduced to 4 neighbours => 4 N interactions.

  - In metals atoms more than ~ 5 Å far can usually be neglected => about 80 N interactions

  - In ionic systems the interaction $V \propto 1/r$, i.e. decreases very slowly. It can not be cut off, but there are smart workarounds.

Early MD simulations

Phase Transition for a Hard Sphere System

B. J. Alder and T. E. Wainwright
University of California Radiation Laboratory, Livermore, California
(Received August 12, 1957)

A CALCULATION of molecular dynamic motion has been designed principally to study the relaxations accompanying various nonequilibrium phenomena. The method consists of solving exactly (to the number of significant figures carried) the simultaneous classical equations of motion of several hundred particles by means of fast electronic computors. Some of the details as they relate to hard spheres and to particles having square well potentials of attraction have been described.[1,2] The method has been used also to calculate equilibrium properties, particularly the equation of state of hard spheres where differences with previous Monte Carlo[3] results appeared.

The calculation treats a system of particles in a rectangular box with periodic boundary conditions.[4] Initially, the particles are in an ordered lattice with velocities of equal magnitude but with random orientations. After a very short initial run[1,2] the system reached the Maxwell-Boltzmann velocity distribution so that the pressure could thereafter be evaluated directly by means of the virial theorem, that is by the rate of change of the momentum of the colliding particles.[1,2] The pressure has also been evaluated from the radial distribution function.[5] Agreement between the two methods is within the accuracy of the calculation.

A 32-particle system in a cube and initially in a face-centered cubic lattice proceeded at about 300 collisions an hour on the UNIVAC. For comparison a 96-particle system in a rectangular box and initially in a hexagonal arrangement has been calculated, however only at high densities so far. No differences in the pressures can be detected. It became apparent that some long runs were necessary at intermediate densities, accordingly the IBM-704 was utilized where, for 32 particles, an hour is required for 7000 collisions. Larger systems of 108, 256, and 500 particles can also conveniently be handled; in an hour 2000, 1000, and 500 collisions, respectively, can be calculated. The results for 256 and 500 particles are not now presented due to inadequate statistics.

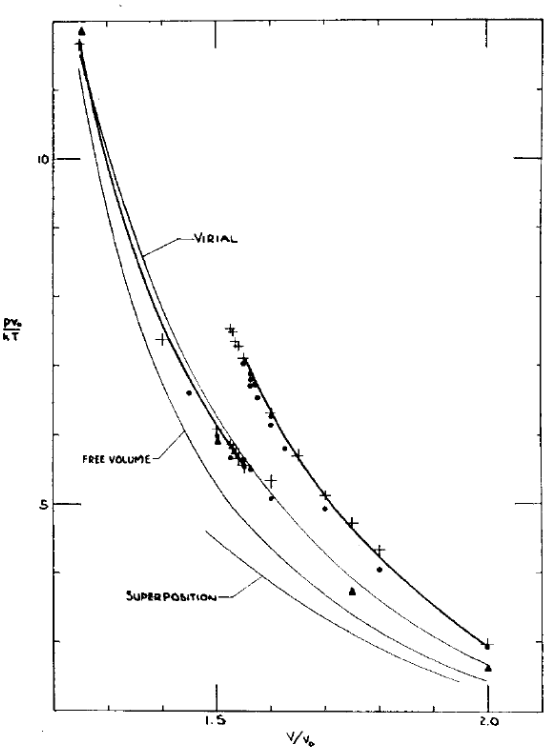


Fig. 1. The equation of state of hard spheres. The heavy solid curve represents Alder and Wainwright's[3] 108 molecule results; +, their 32 molecule results. ● and ▲ represent the present and previous[1] Monte Carlo results. Virial = five term virial expression.[1] Superposition = reference 5.

Early MD simulations

PHYSICAL REVIEW VOLUME 120, NUMBER 4 NOVEMBER 15, 1960

Dynamics of Radiation Damage*

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Brookhaven National Laboratory, Upton, New York
(Received July 14, 1960)

Radiation damage events at low and moderate energies (up to 400 ev) are studied by machine calculations in a model representing copper. Orbits of knock-on atoms are found and the resulting damaged configurations are observed to consist of interstitials and vacancies. Thresholds for producing permanently displaced atoms (i.e., interstitials) are about 25 ev in the ⟨100⟩ direction, 25 to 30 ev in the ⟨110⟩ direction, and around 85 ev in the ⟨111⟩ direction. Collision chains in the ⟨100⟩ and ⟨110⟩ directions are prominent; at low energies the chains focus, at higher energies they defocus. Above threshold, the chains transport matter, as well as energy, and produce an interstitial at a distance. The range of ⟨110⟩ chains has been studied in detail. Localized vibrational modes associated with interstitials, agitations qualitatively like thermal spikes, ring annealing processes, and a higher energy process somewhat like a displacement spike have been observed. Replacements have been found to be very numerous.

The configurations of various static defects have also been studied in this model. The interstitial is found to reside in a "split" configuration, sharing a lattice site with another atom. The crowdion is found not to be stable, and Frenkel pairs are stable only beyond minimum separations, which are found to be very much dependent on orientation.

Purely repulsive potential was used:

$$V(r) = V_0 e^{-\beta r}$$

cohesion: inward force on border atoms

- By current standards, both features extremely questionable...
- But for 1960, very impressice feat!

500 atoms on IBM 704:
1 minute/time step

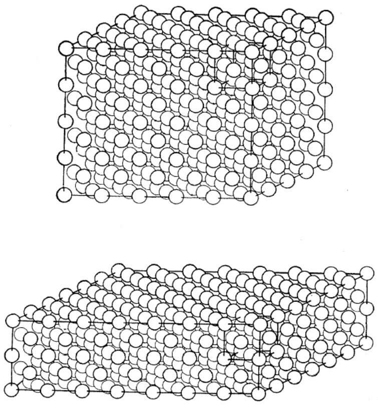


Fig. 1. Two of the sets of atoms used in the calculations. Set A is above, Set B is below.

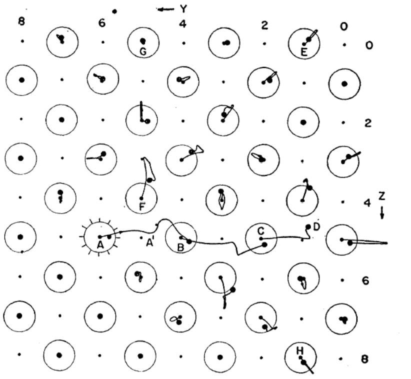
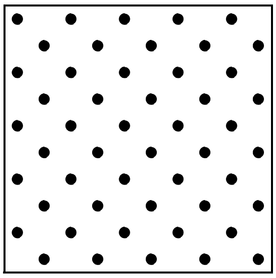


Fig. 6. Atomic orbits produced by shot in (100) plane at 40 ev. Knock-on was at *A* and was directed 15° above −*y* axis. Large circles give initial positions of atoms in plane; small dots are initial positions in plane below. Vacancy is created at *A*, split interstitial at *D*. Run to time 99. (Run No. 12).

Simulation cell

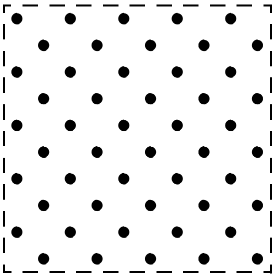
- In practice in most cases the atoms are arranged in a orthogonal **simulation cell** which has a size $S_x \times S_y \times S_z$.
  - It is also perfectly possible to use a simulation cell with axes than are not orthogonal.



- Problem: what should we do with the atoms at the borders.

  1. Nothing: "free" boundaries

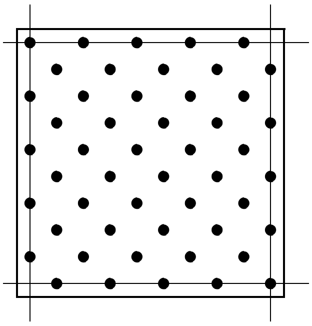
     - This works fine if we want to deal with e.g. a molecule, nanocluster or nanotube in vacuum.
     - If we want to describe a continuous medium, this does not work: the atoms are left "hanging" on the surface as if they would be on the surface.



Simulation cell

2. Fix the boundary atoms:

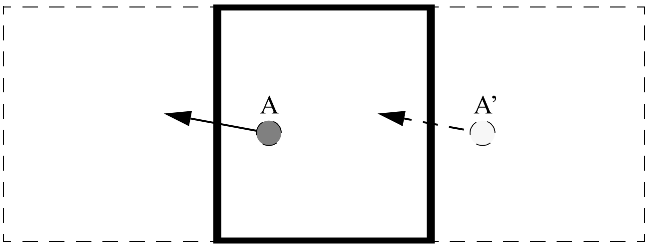
- Completely unphysical, this should be avoided if possible. Sometimes it is needed and with a fairly large "sacrificial" region next to the fixed ones can be perfectly OK.



3. Periodic boundary conditions

- To implement this **very** important boundary condition two things have to be done

1. An atom which **passes over the cell boundary** comes back on the other side:



Simulation cell

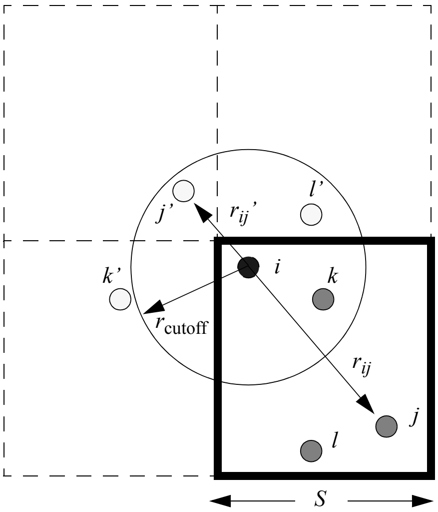
- In practice this can be implemented as follows (Fortran 90) (note that atomic coordinates are between $-S_x/2$ and $S_x/2$):

```
!x          : particle coordinate
!periodicx  : = true periodic, false free
!xsize      : MD cell size (S_x)

  if (periodicx) then
      if (x <  -xsize/2.0) x = x + xsize
      if (x >=  xsize/2.0) x = x - xsize
  endif
```

- Similarly for y and z

2. When **distances between atoms** are calculated, the periodic boundaries have to be taken into account:



- The solid box is the simulation cell, with atoms i, j, k and l. Because of the periodic boundaries, all atoms have image atoms in the repeated cells, for instance j', k', l'.

- When we want to get the distance between atom i and j, which distance should we use?

- Because here $r_{ij} > r_{ij}'$, we use for the distance between atoms i and j the vector r_{ij}'.

Simulation cell

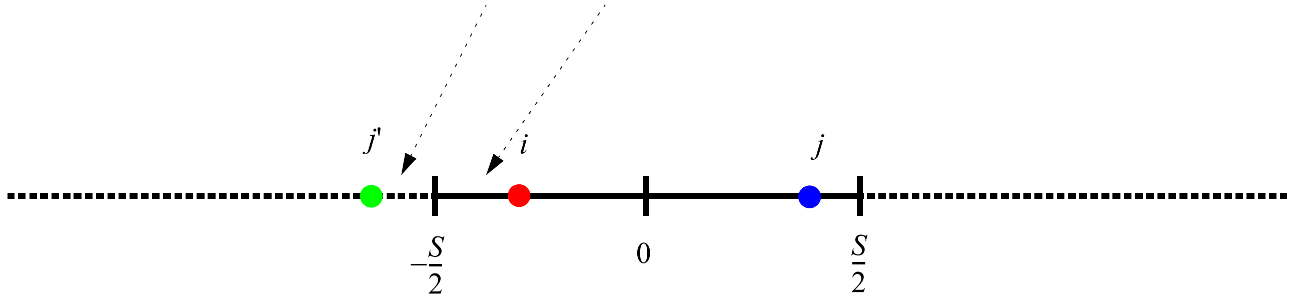
- As a pseudo-algorithm (Fortran 90) in the *x* dimension:

```
if (periodicx) then
    dx = x(j) - x(i)
    if (dx >   xsize/2.0)  dx = dx - xsize
    if (dx <= -xsize/2.0)  dx = dx + xsize
endif
```

and similarly for y and z

- Example in 1D

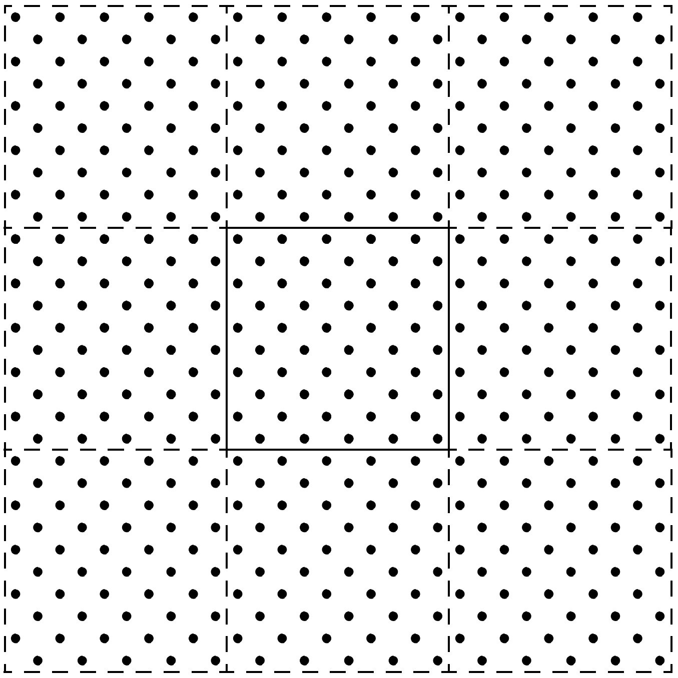
$$x_j - x_i \rightarrow x_{j'} - x_i = -\left[\left(\frac{S}{2} - x_j\right) + \left(\frac{S}{2} + x_i\right)\right] = x_j - x_i - S$$



- Note that if the maximum distance by which atoms can interact r_{cutoff} > *xsize/2* the atom *i* should actually interact both with atom *j* and *j'* . To prevent unphysical double interactions we need to have *xsize* > 2 r_{cutoff}

Simulation cell

- Thus we get a system where the simulation cell has an infinite number of image cells in all directions, and a model of an infinite system.



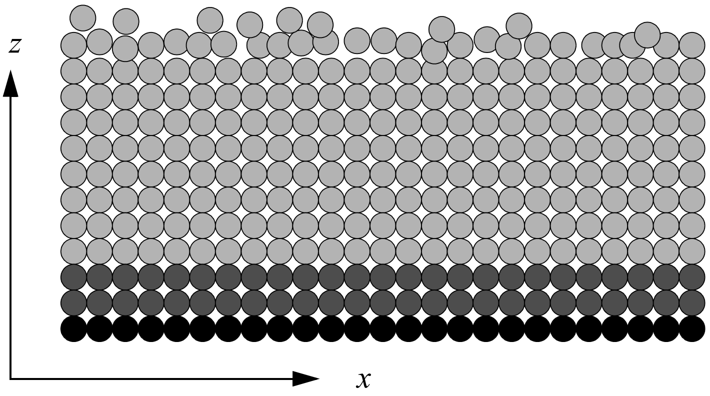
- However, be careful!
  - Periodicity brings an artificial interaction over the simulation cell borders.
  - For instance, a strain field arising from a point source, which is infinite, will obviously be distorted at the periodic borders. Examples:
    - A single vacancy (one missing atom) in Si: in quantum mechanical calculations at least some 200 atoms are required to get the energy reliably [Puska 1998 Phys. Rev. B]
    - And for instance a 5 nm Co cluster in Cu: about 10^6 atoms needed to get the strain energy reliably.
  - Upper limit for the phonon wavelength.
  - To test this: simulate with different N and monitor the convergence.
    - In general, this kind of ***size scaling test*** is very important in any simulations done for a finite-size system aiming to mimic any real much larger system

Simulation cell

- Simulating surfaces:
  - periodic boundaries only in x- and y-directions
  - free surface:
  - the bottom either:

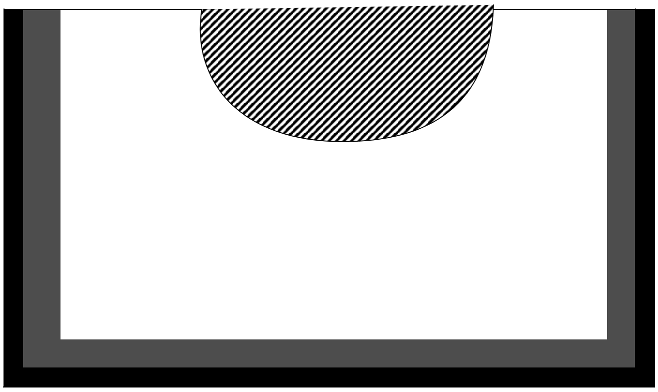
    a) free: simulation of a free-standing thin foil with two surfaces

    or b) fixed to model a bulk below:
    - very bottommost atoms fixed
    - a few atom layers above fixed layers damped with e.g. a temperature control algorithm



Simulation cell

- Simulation of energetic processes:
  - In a simulation where a lot of energy is brought into the MD cell in a local region, the energy has to be scaled out from the system to model a much cooler 'heat bath' in a realistic system.
  - The energetic processes may also introduce a lot of momentum into the cell, which could cause the entire cell to move.
  - Solution: fix all boundary atoms except at the surface, and do T scaling in a few atom layers above these, as above.



  - Here also: watch out the finite-size effects! Do some ***size-scaling tests***!

Initial conditions: creating atoms

- For cubic lattices (FCC, BCC, SC, DIA) it is easy to create the lattice. For instance FCC:

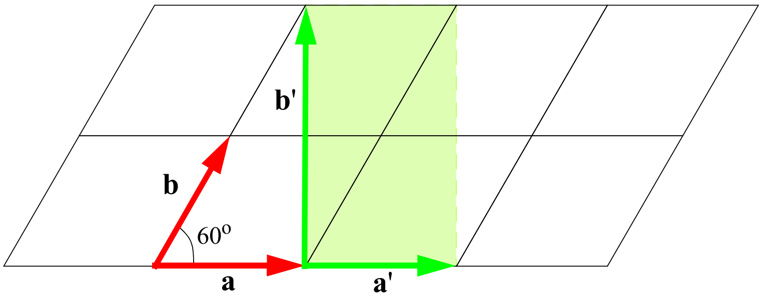
```
basis(1,1)=0.0;    basis(1,2)=0.0;    basis(1,3)=0.0;
basis(2,1)=0.5;    basis(2,2)=0.5;    basis(2,3)=0.0;
basis(3,1)=0.5;    basis(3,2)=0.0;    basis(3,3)=0.5;
basis(4,1)=0.0;    basis(4,2)=0.5;    basis(4,3)=0.5;
offset(1)=0.25;    offset(2)=0.25;    offset(3)=0.25;
nbasis=4;
n=0;
do i=0,nx-1
   do j=0,ny-1
      do k=0,nz-1
         do m=1,nbasis
            n=n+1
            x(n)=-xsize/2+(i+offset(1)+basis(m,1))*a
            y(n)=-ysize/2+(j+offset(2)+basis(m,2))*a
            z(n)=-zsize/2+(k+offset(3)+basis(m,3))*a
         enddo
       enddo
    enddo
enddo
```

Coordinates between $-\frac{S}{2}$ and $\frac{S}{2}$

To refresh your memory:

FCC : face centered cubic
BCC : body centred cubic
SC: simple cubic
DIA: diamond
HCP: hexagonal close-packed

- The HCP lattice is also very common, but not orthogonal in the conventional representation.
  - Because in the HCP structure $\mathbf{a} = \mathbf{b}$, and because $\cos 60° = 1/2$, the HCP lattice can be transformed into an equivalent orthogonal representation. Now the new unit cell (shaded area) corresponds to two of the conventional HCP unit cells.



Initial atom velocities

- How do we set the cell temperature to a desired value?
  - We have to generate initial atom velocities which correspond to the ***Maxwell-Boltzmann distribution*** (which is surprisingly well valid even in crystals):

$$\rho(v_{i\alpha}) = \left(\frac{m_i}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{1}{2} m_i v_{i\alpha}^2 / k_B T\right); \quad \alpha = x, y, z.$$

  - This is just a Gaussian function with suitable scaling, and exactly correct within an ideal gas model for atom velocities
  - We usually also want to set the total momentum of the cell to zero to prevent the entire cell from starting to move:

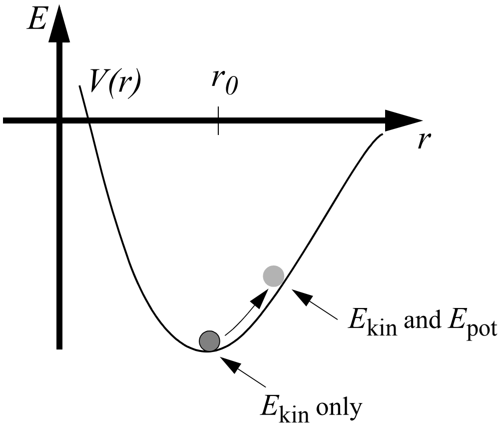
$$\mathbf{P} = \sum_{i=1}^{N} m_i \mathbf{v}_i$$

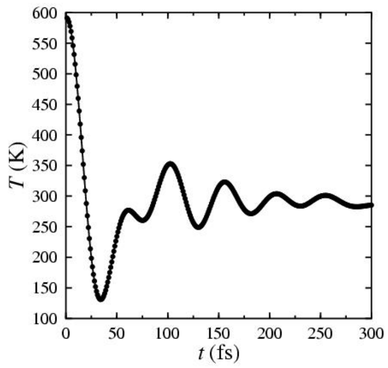
  - So in practice all this can be achieved with the code fragment on the right:

Note: $\exp\left(-\frac{v_{i\alpha}^2}{2\sigma^2}\right)$, $\sigma^2 = \frac{k_B T}{m_i}$

```
sigma2v=sqrt(kB*2*T/(m*u))/vunit
do i=1,n
      vx(i)=sigma2v*gaussrandom(iseed)
      vy(i)=sigma2v*gaussrandom(iseed)
      vz(i)=sigma2v*gaussrandom(iseed)
      vxtot=vxtot+vx(i)    ! If all atoms have the same mass,
      vytot=vytot+vy(i)    ! it is enough to scale the total v
      vztot=vztot+vz(i)    ! to zero
enddo
vxtot=vxtot/n
vytot=vytot/n
vztot=vztot/n
do i=1,n
      vx(i)=vx(i)-vxtot
      vy(i)=vy(i)-vytot
      vz(i)=vz(i)-vztot
enddo
```

Initial atom velocities





- Note the ***factor of 2***: if the simulation is started from perfect lattice sites, or bound equilibrium positions in a molecule, half of the initial kinetic energy will be changed to potential energy after a while.

- It is also possible to get realistic initial random displacements.
  - This can be derived from the Debye model: the thermal displacement in the direction of the axis i is a Gaussian distribution of the form

$$w(\delta_i, T) = [2\pi\sigma]^{-1/2} e^{-\delta_i^2/2\sigma^2} \text{ where}$$

$$\sigma = \frac{20.89}{\sqrt{3}\Theta_\text{D}}\sqrt{\frac{T}{A}}\text{Å} \text{, where } 20.89 = \sqrt{\frac{9\hbar^2}{k_B u}}\text{Å}\sqrt{\text{K}}$$

Θ_D = Debye temperature of the material, A = Atomic mass

  - The initial position can now be obtained with Gaussian-distributed random numbers as above.
  - Note, however, that this ***does not*** account for quantum mechanical zero-point vibrations which give additional displacements near 0 K.

Generating random numbers

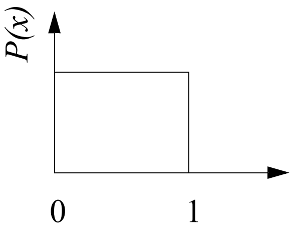
(This topic is dealt with in much more detail on the Monte Carlo simulation course)

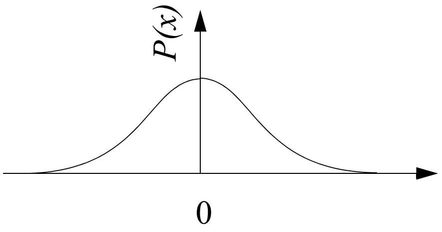
- Almost all kinds of simuations in physics use random numbers somewhere. As we saw above, MD simulations need them at least for initial velocity generation.

- Computer-generated random numbers are of course not truly random, but if they have been generated with a good algorithm, they start to repeat each other only after a very large (e.g. 10^{20}) number of iterations. If the number of random numbers used in the entire simulation is much less than the repeat number, the algorithm *probably* is good enough for the application.

- Random numbers can be generated for different distributions. This means that if we generate a large number of numbers and make statistics out of them, they will eventually approach some distribution.

- The most common is of course an even distribution in an interval, another very common is Gaussian-distributed numbers:





Generating random numbers

- Evenly distributed random numbers:
  - Many programming languages offer their own random number generator (e.g. in ANSI-C **rand()**). A good rule-of-thumb regarding these is:

    Never use them for anything serious !

    - The reason is simply that the language standard only specifies that the generator has to be there, not that it works sensibly. Since there are no guarantees it does (there are famous examples of the opposite) it should not be used
  - Most random number generators are based on modulo-arithmetics and iteration. In the simplest possible form:

    $$I_{j+1} = aI_j \pmod{m}$$

  - Park and Miller 'minimal standard'-generator: $a = 16807$, $m = 2^{31} - 1$
  - In the beginning the number I_0 i.e. the **seed number** is chosen randomly.
    - This can be done e.g. by using the current system time.

Generating random numbers

- One practical implementation (Fortran90):

```
real function uniformrand(seed)
    implicit none
    integer :: seed,IA,IM,IQ,IR,MASK
    real :: ran0,AM
    integer :: k

    parameter (IA=16807,IM=2147483647,AM=1.0/IM)
    parameter (IQ=127773,IR=2836,MASK=123459876)

    seed=ieor(seed,MASK)
    k=seed/IQ
    seed=IA*(seed-k*IQ)-IR*k
    if (seed < 0) seed=seed+IM
    uniformrand=AM*seed
    seed=ieor(seed,MASK)

    return

   end function uniformrand
```

- The repeat interval for this routine ~ $2.1 \cdot 10^9$
- This routine is easily good enough if for instance it is only needed for the choice of random numbers in the beginning of an MD simulation.
- In a long Monte Carlo integration where random numbers are used all the time, the repeat interval may be reached, after which continued running will not improve on the results (and for instance the error estimate of the result will be calculated outright wrong).
- More on this topic for instance from the book: Press, Teukolsky, Vetterling, Flannery: **Numerical Recipes** in C/Fortran, 2nd. ed., chapter 7.
- The book is on-line in its entirety (see http://www.nr.com/).
- But see also: "Why not use Numerical Recipes?", http://math.jpl.nasa.gov/nr/ and the reply to this: http://www.nr.com/bug-rebutt.html

Generating random numbers

- To generate Gaussian random velocities we need to be able to generate Gaussian-distributed random numbers.
  - How to do this is dealt with in great detail in Numerical Recipes chapter 7.2. Here we only present the most efficient accurate algorithm for this:

1° Obtain two evenly distributed random numbers v_1 and v_2 between -1 and 1, then calculate $w = v_1^2 + v_2^2$

2° If $w \geq 1$ return to step 1°

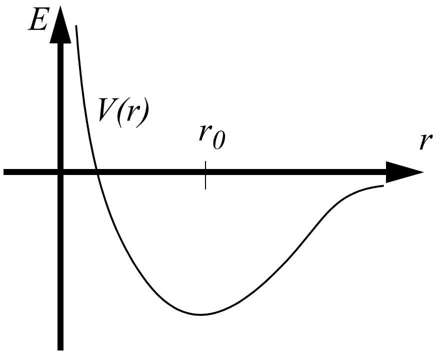
3° Calculate $r = \sqrt{-2 \log w}$

4° Calculate $x = rv_1 / \sqrt{w}$ and $y = rv_2 / \sqrt{w}$

5° Return x and on next step y

Choosing the MD time step

- Depends on the integration algorithm used, but not too strongly.
- The change in the atom position in the potential used should not be too strong.
- A practical, rough rule-of-thumb: the atoms should not move more than 1/20 of the nearest-neighbour distance.



- Thermal velocity of atoms (Maxwell-Boltzmann distribution):

$$E_{\mathrm{rms}} = \frac{3}{2}k_B T = \frac{1}{2}mv^2 \Rightarrow v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m}}$$

  - But the distribution continues much beyond this.
  - Rough estimate of the time step needed: 300 K Cu ($m = 63.55\mathrm{u}$):
  - $5v_{\mathrm{rms}} = 0.017$ Å/fs
  - Nearest-neighbour distance 2.55 Å => $\Delta t = \frac{2.55/20}{0.017}$ fs $= 7.5$ fs
- In practice for stability $\Delta t \leq 4$ fs.

Choosing the MD time step

- In pure MD there is no way to increase the time step above ~ 10 fs in atom systems at ordinary temperatures (77 K and up).
  - If we would want to simulate a process which, say, takes 1 s, we would need at least 10^{14} time steps!
- This gives an easy way to estimate the order-of-magnitude of the upper limit for the time scale MD can handle in a given time:
  - Most realistic classical MD interatomic potentials require at least of the order of 100 flops/atom/time step.
  - Say our time step is 1 fs, and we want to simulate a 10000 atom system.
  - Hence we need 10^6 flops/time step. To get to 1 ns = 10^9 fs we would need 10^{15} flops. Assuming 1 Gflop/s processor, the simulation would thus require $10^{15}/10^9$ seconds = 10^6 s i.e. about 11 days. To get to 1 µs would require some 30 years on this processor.
- Hence we see that ordinary MD is restricted to $\leq$ 100 ns processes in most practical uses.

Choosing the MD step

- In ordinary equilibrium MD Δt is usually constant throughout simulation
  - But if the maximum velocity of atoms changes a lot during the simulation, it is best to use a variable time step, which increases as the maximum velocity decreases.
  - Simulations of energetic processes [K. Nordlund, Comput. Mater. Sci. 3, 448 (1995)]:

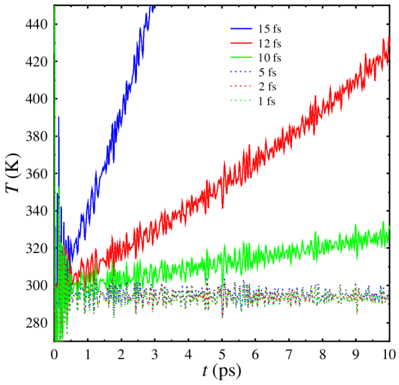
$$\Delta t_{n+1} = \min\left(\frac{k_t}{v_{\max}}, \frac{E_t}{F_{\max} v_{\max}}, c_{\Delta t}\Delta t_n, t_{\max}\right)$$

k_t	maximum movement distance/time step (e.g. $0.1\,\text{Å}$)
E_t	maximum allowed energy change/time step (e.g. 300 eV)
$c_{\Delta t}$	prevents too large sudden changes (e.g. $c_{\Delta t} = 1.1$)
$v_{\max}$	maximum atom speed in system
$F_{\max}$	maximum force on any atom in system
$t_{\max}$	time step once heat bath T has been reached

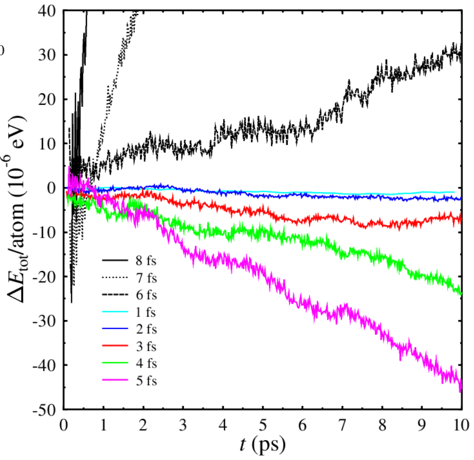
- The example values above have been found to work well for binary collisions up to 1 GeV in many materials.

Choosing the MD step

- What happens if Δt is too long?
  - The energy is not conserved.
  - For instance solid copper (FCC lattice, $a = 3.615\text{Å}$, EAM potential, code `parcas`) NVE simulation at 300 K:
  - Hence the real criterion for selecting the time step becomes energy conservation: for every:
    - new kind of system
    - new kind of process simulated
    - new material
    - new interaction potential
  - ***For every new system, one needs to check that energy is conserved 'well enough' by some test simulations, before starting the real production runs.***



Temperature



Change in total energy

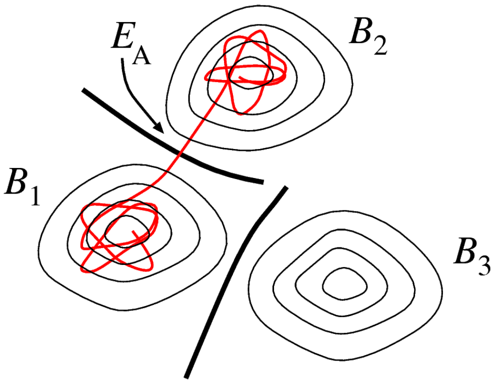
Acceleration methods

- Speeding up MD
  - This can be achieved at least in some cases where we are interested in transitions induced by thermally activated processes, i.e. processes which follow a behaviour of the type

$$\upsilon = \upsilon_0 e^{-E_A / k_B T}$$

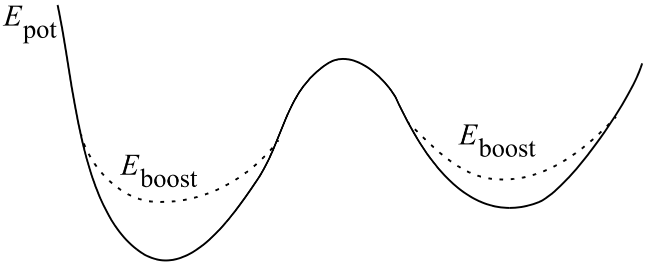
  where υ is the rate of the process occurring.

  - System spends most of its time in local potential energy minima B_i (basins).
  - Every once in a while it gets enough kinetic energy to go over the barrier E_A: rare events.
  - Acceleration: increase υ by increasing the probability for barrier crossing.
  - Modify E_A or T (??)



Acceleration methods

- Art Voter has presented so called Hyperdynamics [A. F. Voter, *J. Chem. Phys.* 106 (1997) 4665; *Phys. Rev. Lett.* 78 (1997) 3908]. It can in some cases speed up MD by a factor of the order of 100-1000, in others not at all.
  - In this method, Δt does not increase, but the potential well is made shallower so that the probability of processes with a large activation energy increases. The error which is thus formed is compensated by transition state theory (which is beyond the scope of this course).
  - The method is well suited for cases where we have to overcome a high potential energy barrier in an ordered system, e.g. vacancy and adatom diffusion. But if the energy barrier is low (e.g. interstitial migration in metals) or if we have numerous local energy minima close to each other, like in most amorphous and liquid systems, the method is useless.

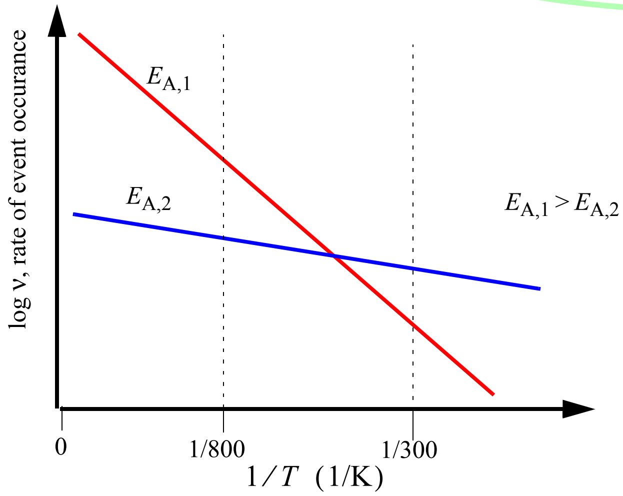


Acceleration methods

- Temperature accelerated dynamics (TAD)
  - There is of course always is the Arrhenius extrapolation method: if we know that in our system there is only one single activated process occurring, and nothing else, we can simulate at higher T and then extrapolate the Arrhenius-like exponential $\exp(-E_A/k_BT)$ to lower T to know the rate or time scale at lower T.
  - A smart extension to Arrhenius extrapolation is Art Voter's **TAD** method [e.g. Sorensen, *Phys. Rev. B* 62 (2000) 3658; a review of Voters methods is given in *Ann. Rev. Mater. Res.* 32 (2002) 321]
  - To understand the idea in this, let us consider a system with exactly 2 activation energies (this is just a tutorial example, the method works in principle for any number of activation energies). We want to simulate what the system does at 300 K, but the processes are so slow nothing happens there. So we will use a higher T, say 800 K.

Acceleration methods

- Let us then assume that the Arrhenius plot of the system looks as follows:



$$\upsilon = \upsilon_0\, e^{-E_A/k_BT} \Rightarrow \log\upsilon = \log\upsilon_0 - \frac{E_A}{k_BT}$$

- Now when we simulate at 800 K, event type 1 will occur much more frequently than type 2. But we want to know the behaviour at 300 K, so this is wrong. The idea in TAD is to recognize *every* transition that occurs, determine its activation energy, and then leave out the events that would not occur at the lower T. In our example, this means that (almost) only events of type 2 would be accepted.

Acceleration methods

- In principle this is an excellent idea, but in practice one needs thousands of force evaluations to recognize a transition barrier. Hence the difference between the rates of occurrance needs to be very large for a significant gain to be achieved. But the gain can be huge (Example: simulating growth of Cu (001) surface at 77 K the speedup factor is 10^7 !)

- Like hyperdynamics, if there are lots of shallow minima TAD tends to get stuck and never really gets anywhere.

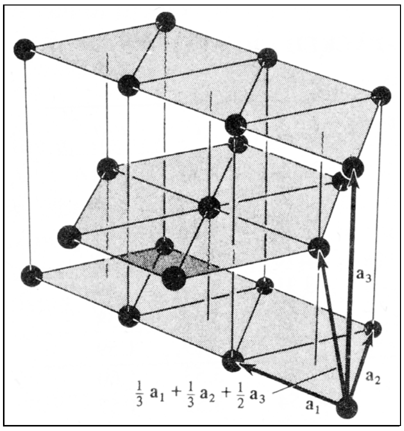
- TAD is developing rapidly towards wider applicability, so it will be interesting to follow the progress

- As of 2015, Hyperdynamics, TAD and other similar-in-spirit acceleration methods have found many applications in close-to-equilibrium simulations, typically such involving diffusion and an underlying crystal structure. In completely disordered, inhomogeneous systems (such as bio-systems) and far-from-equilibrium simulations, no atom-based acceleration method has found wide applicability.
  - In biosystems, coarse-graining, i.e. replacing single atoms with larger objects describing e.g. part of a molecule, can often give major speedups. These are beyond the scope of this coarse.

Molecular dynamics 2015

Exercise 2 to chapter 2: Random numbers etc.

1. (6 p) Modify your program of exercise 1 to construct a hexagonal close-packed (HCP) structure (using an orthorhombic unit cell; i.e. cell that has all three lattice vectors orthogonal with each other[1]). Using a visualization program demonstrate the (small) difference between the face centered cubic (FCC) and HCP structures: the different stacking order of (111) crystal planes. *Hint: the primitive unit cell depicted on the right contains two atoms, while the non-primitive orthorhombic cell contains four atoms.*



HCP

unit cell (non-orthorhombic)

$\mathbf{a}_1 = a\mathbf{i}$

$\mathbf{a}_2 = a/2\mathbf{i} + \sqrt{3}a/2\mathbf{j}$

$\mathbf{a}_3 = \sqrt{8/3}a\mathbf{k}$

basis
(atoms in the unit cell)

$\mathbf{b}_1 = 0$

$\mathbf{b}_2 = \frac{1}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3$

2. (7 p) Write subroutines which generate random numbers with an even and a Gaussian distribution. Generate 1 million Gaussian-distributed random numbers (with the standard deviation $\sigma = 1$ and mean $\mu = 0$), make a histogram of their distribution with a bin width of e.g. 0.01 and the *area* normalized to unity and make a plot. Also generate the same Gaussian distribution

$$f(x) = [2\pi]^{-1/2} e^{-x^2/2}$$

analytically and plot in the same figure as the random plot.

Return the code and the figure as pdf, postscript or png, jpeg, or the like.

3. (7 p) Equipartition theorem states that[2]: *Every degree of freedom of a body that contributes a square term of a coordinate or momentum to the total energy has a mean energy of* $k_B T/2$ *in that degree of freedom.* Based on this explain why the temperature drops by a factor 2 in the beginning of the simulation[3]. Would you expect the factor be 2 also at very high temperatures?

---

[1] Lecture notes, chapter 2, page 15.

[2] G. W. Wannier: *Statistical Physics* (Dover, New York, 1966), ch. 4-5.

[3] Lecture notes, chapter 2, page 17.

Constructing a neighbour list

- In MD simulations (and actually many other applications) one of the central operations is the calculation of distances between atoms.
  - In MD this is needed in the energy and force calculation.

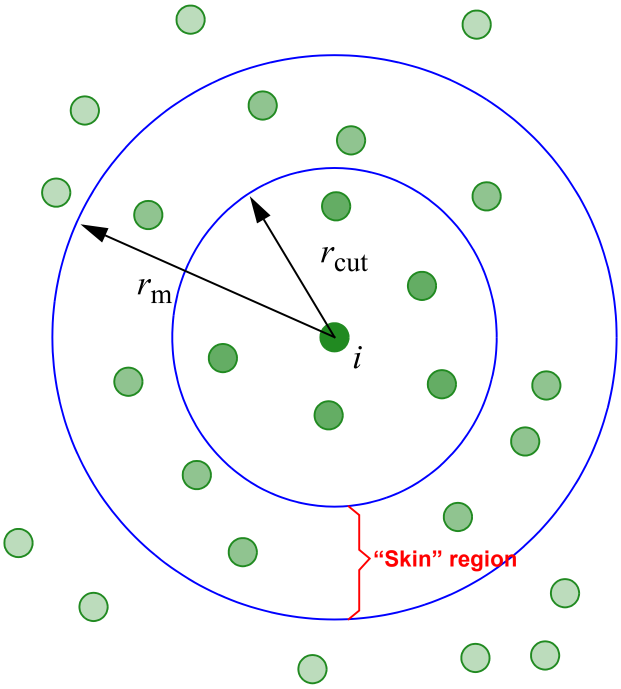
- Trivial calculation of distances between atoms:

```
do i=1,N
    do j=1,N
        if (i==j) cycle
        dx=x(j)-x(i);
        dy=y(j)-y(i);
        dz=z(j)-z(i);
        rsq=dx*dx+dy*dy+dz*dz
        r=sqrt(rsq)
    enddo
enddo
```

  - This algorithm is $O(N^2)$, i.e. very slow when $N \to \infty$.
  - But in practice we know the atoms move < 0.2 Å/time step. So a large fraction of the neighbours remain the same during one time step, and it seems wasteful to recalculate which they are every single time.

Constructing a neighbour list

- **Solution:** Verlet[1] neighbour list:



  - Make a list which contains for each atom *i* the indices of all atoms *j* which are closer to *i* than a given distance r_{m}. $r_{\text{m}} > r_{cut}$, the cutoff distance of the potential
  - The list is updated only every N_{m} time steps.
  - r_{m} and N_{m} are chosen such that

$$r_{\text{m}} - r_{\text{cut}} > N_{\text{m}} \bar{v} \Delta t,$$

where $\bar{v}$ is a typical atom velocity and Δt the time step

---

[1] Loup Verlet, *Phys. Rev.* **159** (1967) 98.

Constructing a neighbour list

- An even better way to choose when to update the interval: after the neighbour list has been updated, keep a list of the maximum displacement of all atoms:
  - Make a separate table `dxnei(i)`
  - When you move atoms, also calculate `dxnei(i)=dxnei(i)+dx`
  - Calculate the **two** maximal displacements of all atoms:

```
drneimax=0.0; drneimax2=0.0
do i=1,N
    drnei=sqrt(dxnei(i)*dxnei(i)+dynei(i)*dynei(i)+dznei(i)*dznei(i))
    if (drnei > drneimax) then
        drneimax2=drneimax
        drneimax=drnei
    else
        if (drnei > drneimax2) then
            drneimax2=drnei
        endif
    endif
enddo
```

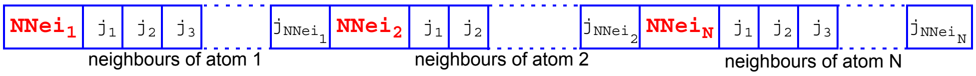
  - Now, when $(\texttt{drneimax+drneimax2}) > r_\mathrm{m} - r_\mathrm{cut}$ the neighbour list has to be updated.

  - When the update is done, do `dxnei(i)=0.0`

  - This alternative has two major advantages: the simulation does not screw up if one atom suddenly starts to move much faster than the average, and if the system cools down, the neighbour list update interval keeps increasing.

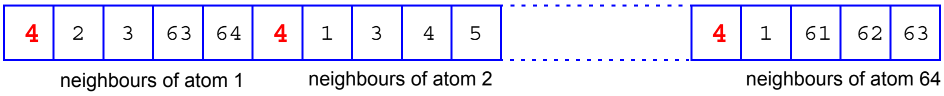
Constructing a neighbour list

- In practice the neighbour list can look e.g. like the following:



  - Here **$\texttt{NNei}_\texttt{i}$** is the number of neighbours of atom `i`.
  - $\texttt{j}_1$, $\texttt{j}_2$, ... are the indices of neighbouring atoms (different for different atoms).

  - So, if we would have a 64 atom system, where every atom has 4 neighbours, the neighbour list could look like this:



Constructing a neighbour list

- A practical implementation of creating the list:

```
nlistbeg=1
do i=1,N
    nnei=0
    do j=1,N
        if (i==j) cycle
        dx=x(j)-x(i)
        dy=y(j)-y(i)
        dz=z(j)-z(i)
        rsq=dx*dx+dy*dy+dz*dz
        if (rsq <= rskincutsq) then
            nnei=nnei+1
            nlist(nlistbeg+nnei)=j
        endif
    enddo
    nlist(nlistbeg)=nnei                    ! Write in number of i's neighbours into list
    nlistbeg=nlistbeg+nnei+1                ! Set starting position for next atom
enddo
```

Periodic boundaries omitted for brevity. See lecture02 for how to include them in the dx, dy, dz calculations.

- With the neighbour list, we can achieve a savings of a factor N_m in calculating the distances to neighbours.
- But even using the neighbour list, our algorithm is still $O(N^2)$.

Constructing a neighbour list

- Remedy: linked list / cellular method
- Using a linked list and cellular division of the simulation cell, we can make the algorithm truly $O(N)$:
  - Let's divide the MD cell into smaller subcells: $M \times M \times M$ cells
  - The size of one subcell *l* is chosen so that

$$l = \frac{L}{M} > r_\mathrm{m},$$

where L = the size of the MD cell, and r_m is as above.

  - Now when we look for neighbours of atom i we only have to look through the subcell where i is, and its neighbouring subcells, but not the whole simulation cell. For instance if atom i is in cell 13:

21	22	23	24	25
16	17	18	19	20
11	12	13	14	15
6	7	8	9	10
1	2	3	4	5

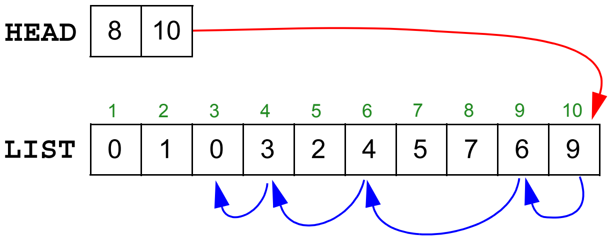
The average number of atoms in a subcell is $N_\mathrm{c} = N/M^3$.

$\Rightarrow$ We have to go through $27NN_\mathrm{c}$ atom pairs instead of $N(N-1)$.

  - For some interaction potentials (symmetric ij pairs) it is actually enough to calculate every second neighbour pair (e.g. $i > j$) whence the number of pairs is further reduced by a factor of 2.

Constructing a neighbour list

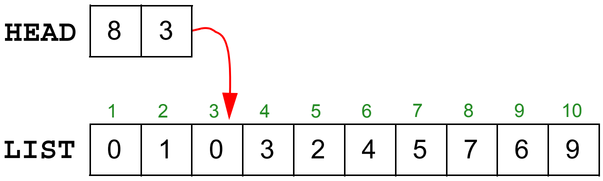
- A practical implementation:
  - array **HEAD**:
    - size = M^3
    - contains pointers to the table **LIST**
    - tells where the neighbours in subcell m start
  - array **LIST**:
    - size = N
    - element j tells where the next atom index of atoms in this cell is



- So the example below means that subcell 2 contains atoms 10, 9, 6, 4, and 3
- This representation is indeed enough to give all the atoms in all cells.
- A two dimensional array would of course also work, but would require much more memory, or dynamic allocation, both of which are less efficient.

Constructing a neighbour list

- Building the list:
  - assume a cubic case:
  - MD cell `size = size(3)`
  - size of subcell =`size()/M`
  - MD cell centered on origin



```
do i=1,N
    head(i) = 0
enddo
do i=1,N
        icell = 1 +  int((x(i)+size(1)/2)/size(1)*M)  &
                     int((y(i)+size(2)/2)/size(2)*M)  * M &
                     int((z(i)+size(2)/2)/size(3)*M)  * M * M
        list(i) = head(icell)
        head(icell) = i
enddo
```

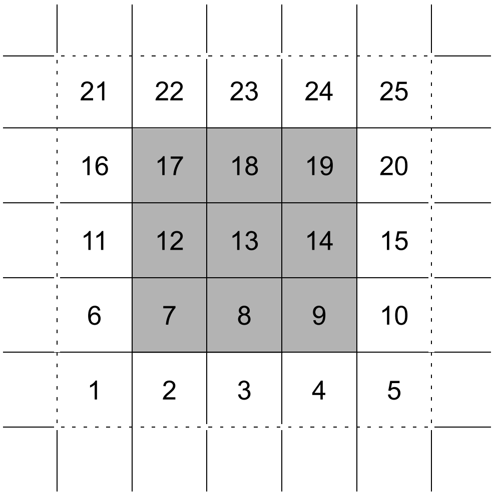
  - So the list **LIST** is filled in reverse order to the picture above.
  - The above algorithm requires periodic boundaries. If the boundaries are open, an atom may get outside the cell borders, and the **icell** may point to the wrong cell.

Constructing a neighbour list

- To account for possibly open boundaries properly things get a bit trickier:
  - MD Cell size `size(3)`
  - MD cell centered on origin
  - Number of cells in different dimensions `Mx, My, Mz`
  - Cell range `0` – `Mx-1` and same in y and z

```
do i=1,N
    dx=x(i)+size(1)/2
    ! Check that we are really inside boundaries
    if (periodic(1) == 1 .and. dx < 0.0) dx=dx+size(1)
    if (periodic(1) == 1 .and. dx > size(1)) dx=dx-size(1)
    ix=int((dx/size(1))*Mx)
    ! If not periodic, let border cells continue to infinity
    if (periodic(1) == 0) then
        if (ix < 0) ix=0
        if (ix >= Mx) ix=Mx-1
    endif
    (and same thing for y and z)
    icell=(iz*My+iy)*Mx+ix
    list(i)=head(icell)
    head(icell)=i
enddo
```

- So the subcells at open boundaries continue out to infinity:



Constructing a neighbour list

- Usually the linked list (**`LIST`**, **`HEAD`**) is used to generate a Verlet list
  - Decoding a linked list into a Verlet-list, as pseudocode:
  - Cell size `size(3)`
  - Number of cells `Mx, My, Mz`

```
do i=1,N
    do (Loop over 27 neighbouring cells: inx iny inz)
        icell=(inz*My+iny)*Mx+inx
        ! Get first atom in cell
        j=head(icell)
        do
            if (j==0) exit ! exit from innermost loop
            (get distance r between atoms i and j)
            if (r <= rneicut) then
                (accept neighbour)
            endif
            j=list(j)
        enddo
    enddo
enddo
```

MD code `mdmorse`

- A simplified MD code **`mdmorse`** has been written for this course:
  - **`mdmorse`** simulates atom motion in a variety of metals (but only one metal at a time) with a simple Morse pair potential model.

$$V(r) = D[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}]$$

  - The code has a Verlet neighbour list (but not a linked list) and the equations of motion are solved with the velocity Verlet method.
  - The code is given in Fortran90 and C.
- The code can be downloaded from the course web page.
  - The code has the input parameter and output routines included.
  - Physically interesting subroutines have been removed from the code, so it does not work.

  - During the course exercises, you get the task of writing the missing subroutines.
  - Solutions will be provided and explained during the exercise sessions.
  - You may either use your own or the provided solutions afterwards.

Structure of the `mdmorse` code

- Program files:

`main.f90`	Main program
`inout.f90`	Miscellaneous input and output stuff
`modules.f90`	Global variables
`physical.f90`*	Calculating T and E, and random number generators
`neighbourlist.f90`*	Getting the neighbour list
`solve.f90`*	Solving the equations of motion
`forces.f90`*	Calculating the forces
`Makefile`	Makefile (If you have used Unix or Linux systems you should know how to **`make`** programs.)

  - Files marked with * contain the subroutines which are to be filled up during the exercises
- C version: **`*.c`** → **`*.f90`**
  `modules.f90` → **`global.h`**
- Compiling the code:

```
make
```

  - This has been tested to work at least on Linux systems with a GNU compilers (`gfortran` and `gcc`).
  - You may have to change the compiler command in **`Makefile`**.

Structure of the `mdmorse` code

- Input files (file names are hardcoded):

`mdmorse.in`	Miscellaneous parameters
`atoms.in`	Atom coordinates in XYZ format

- Running the program:

`./mdmorse` (or if you don't want to disturb other users **`nice ./mdmorse`**)

- Should be done in the same directory where the input files are.

- Output files:

`standard output`	T, E, P and other interesting output
`atoms.out`	Atom coordinates at regular intervals

- Note also that during the program running, the code writes out a large number of atom coordinates to a file `atoms.out`, which may grow very large.

Structure of the `mdmorse` code

- Input file `mdmorse.in`

```
 Sample input file for mdmorse md program
 File format: -identifier, then value. Rest is arbitrary comments
 Lines which do not begin with "-" are all ignored

Identifier     | Value

-initialT       600.0     Initial temperature

-desiredT     300.0        Variables for temperature control
-btctau       0.0          If btctau=0 no effect

-bpctau       0.0          Variables for pressure control
-bpcbeta      7.0e-4       If bpctau=0 no effect
-desiredP     0.0

-mass           63.546       For Cu

-xsize          18.126900793    Box size in each dimension
-ysize          18.126900793
-zsize          18.126900793

-periodicx      1               1 = periodic, 0 = non
-periodicy      1
-periodicz      1

-morseDe        0.3429       Morse potential parameters for Cu
-morsealpha     1.3588
-morseRe        2.866

-rpotcut        5.0          Potential cutoff
-rskincut       6.0          Neighbour list cutoff, must be > rpotcut

-nupdate        5               Number of steps between neighbour list updates

-nmovieoutput   100             Interval between atom movie output

-deltat         2.0          Time step in simulation in fs
-tmax           10000.0     Total simulation time
```

Structure of the `mdmorse` code

- Input file `atoms.in`
    - The file is a normal XYZ atom coordinate file:

```
500
FCC cell made by makeFCC with a= 3.615 n= 5 5 5
Cu      -8.13375      -8.13375      -8.13375
Cu      -6.32625      -6.32625      -8.13375
```

...and so forth the remaining 498 atom coordinates....

```
Cu       6.32625       8.13375       8.13375
Cu       8.13375       6.32625       8.13375
```

- Note that the cell is centered on the origin.

Structure of the `mdmorse` code

- Standard output (for the working code; F90 version):

```
 --------------- mdmorse V1.0 --------------------

Read in parameter -initialT        value  1000.00
Read in parameter -desiredT        value  2500.00
Read in parameter -btctau          value  300.000
Read in parameter -bpctau          value  3000.00
Read in parameter -bpcbeta         value 0.700000E-03
Read in parameter -desiredP        value  0.00000
Read in parameter -mass            value  63.5460
Read in parameter -xsize           value  18.1269
Read in parameter -ysize           value  18.1269
Read in parameter -zsize           value  18.1269
Read in parameter -periodicx       value  1.00000
Read in parameter -periodicy       value  1.00000
Read in parameter -periodicz       value  1.00000
Read in parameter -morseDe         value 0.342900
Read in parameter -morsealpha      value  1.35880
Read in parameter -morseRe         value  2.86600
Read in parameter -rpotcut         value  7.00000
Read in parameter -rskincut        value  8.00000
Read in parameter -nupdate         value  5.00000
Read in parameter -nmovieoutput    value  100.000
Read in parameter -deltat          value  5.00000
Read in parameter -tmax            value  50000.0
Using periodics (1=on, 0=off) 1 1 1
Morse potential parameters: De alpha Re     0.342900     1.358800     2.866000
Movie output selected every     100 steps

Reading in     500 atoms described as FCC cell made by makeFCC with a= 3.62538
 Initial atom temperature is    1970.4541462944828
Neighbour list update found    176.00     neighbours per atom
ec       5.000   1890.175     0.24432    -3.48740    -3.24307
bpc       5.000      26.025014  5956.400065997    18.127    18.127    18.127
Outputting atom movie at t =      5.000
ec      10.000   1652.943     0.21366    -3.45507    -3.24141
bpc      10.000      33.853085  5956.635315608    18.127    18.127    18.127
ec      15.000   1318.804     0.17047    -3.40893    -3.23846
bpc      15.000      43.555081  5956.937997643    18.128    18.128    18.128
```

Structure of the `mdmorse` code

- And so on. Here most things are self-explanatory.
  - The "`ec`" and "`bpc`" lines contain the physically most interesting stuff in the following format:

	time(fs)	T (K)	E_{kin}/at.	E_{pot}/at.	E_{tot}/at.	P(kbar)	*(energies in eV)*
`ec`	`4.000`	`594.069`	`0.07538`	`-3.03868`	`-2.96330`	`163.82195`	

	time(fs)	b_x(Å)	b_y(Å)	b_z(Å)	V(Å^3)	P(kbar)	$\mu_{\mathrm{Berendsen}}$
`bpc`	`4.000`	`18.132452`	`18.132452`	`18.132452`	`5961.69346`	`163.82195`	`1.00015`

- Output file `atoms.out`
  - This file is in the XYZ format, but with the exception that column 5 contains the atom potential energy:

```
500
mdmorse atom output at time       2.000 fs boxsize      18.1269     18.1269     18.1269
Cu    -9.053407   -9.061041   -9.048299  -3.085270
Cu    -7.236810   -7.239921   -9.048988  -3.033905
Cu    -7.241191   -9.049845   -7.246436  -3.035222
Cu    -9.038484   -7.238137   -7.241429  -3.031141
.
.
.
```

Structure of the `mdmorse` code

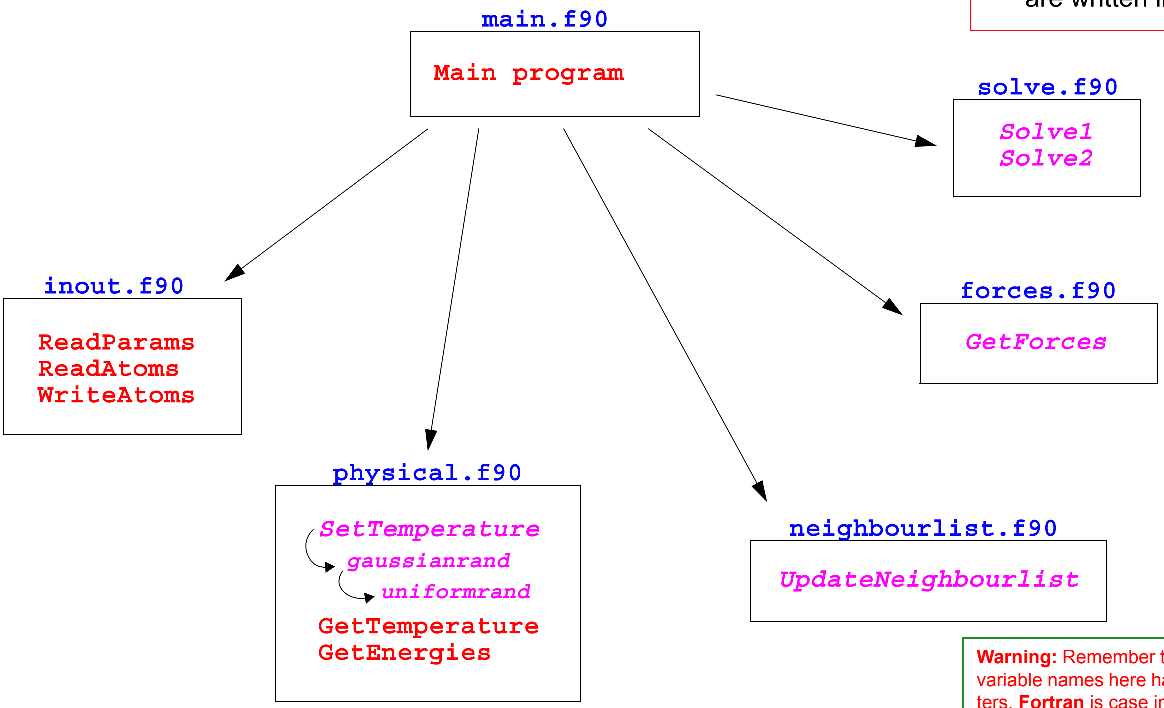
- Testing the incomplete code:
  - Even though the code is not complete, it should compile and run in the intermediate stages.
  - The output should look something like:

```
Reading in      500 atoms described as FCC Cu; boxsize      18.1000     18.1000
Initial atom temperature is   0.000000000000000
Neighbour list update found   0.26928E+06 neighbours per atom
ec       2.000      0.000     0.00000     0.00000     0.00000     0.00000
Outputting atom movie at t =       2.000
ec       4.000      0.000     0.00000     0.00000     0.00000     0.00000
```

  - I.e. the number of neighbours is nonsense, and the temperature is 0.
  - When you start doing the exercises, this should change and interesting things will start to happen.

- Structure of the program

Routines printed in *magenta*
are written in exercises.



`main.f90`

Main program

`solve.f90`

Solve1
Solve2

`inout.f90`

ReadParams
ReadAtoms
WriteAtoms

`forces.f90`

GetForces

`physical.f90`

SetTemperature
gaussianrand
uniformrand
GetTemperature
GetEnergies

`neighbourlist.f90`

UpdateNeighbourlist

Warning: Remember that although routine and variable names here have small and capital letters, **Fortran** is case insensitive. I.e. symbols

SetTemperature
settemperature

refer to same routine (or variable).

Molecular dynamics 2015

Exercises 3 to chapter 3: `mdmorse`: Setting initial temperature, building neighbourlist

You can obtain the `mdmorse` code from the course web page:

http://www.acclab.helsinki.fi/~knordlun/moldyn/mdmorse/

1. (8p) Complete the subroutine `SetTemperature()` in `physical.f90/.c` in the code `mdmorse`. This also requires completing the subroutine generating Gaussian random numbers. You may use your solutions of the previous excercises as help.

Check your code by compiling and running `mdmorse`. The routine `GetTemperature()` (which is already provided) should return about twice the input value `initialT.`

2. (12 p) Complete the subroutine `UpdateNeighbourlist()` in `neighbourlist.f90/.c` in `mdmorse.` The subroutine should generate a Verlet neighbour list taking account of the periodic boundary conditions. You do not need to use a linked list.

Hint: when the subroutine in the end outputs the number of neighbours, the answer should be 176.00 with the input files provided in the program distribution.

When coding keep the subroutine parameters as they are given. This makes it easy (for the lecturer) to test them in the original code.

Return the source files `physical.f90/.c` and `neighbourlist.f90/.c`. and the relevant parts of the output (standard output).

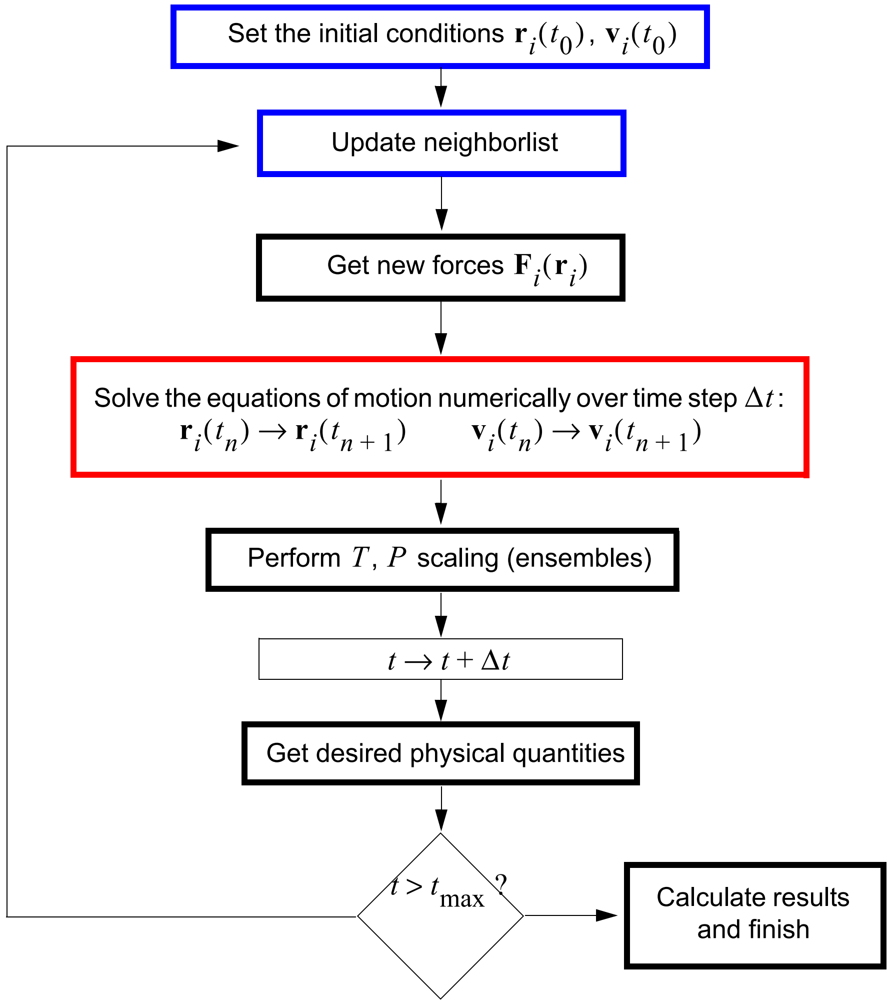
When returning subroutines to the code for the exercises, the minimum requirement is that each subroutine returned compiles on a standard Unix/Linux system with

```
gfortran -c filename.f90,
```

or in C

```
cc -c filename.c
```

Subroutines which do not compile, give 0 p.



Solving the equations of motion

[Main source: Allen-Tildesley]

- In MD, what we really want to do is solve the equations of motion of N atoms (or particles in general) interacting via a potential V

- Lagrange equations of motion:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0;$$

$$L(\mathbf{q}, \dot{\mathbf{q}}) = K(\mathbf{q}, \dot{\mathbf{q}}) - V(\mathbf{q}, \dot{\mathbf{q}})$$

$\mathbf{q}$ = generalized coordinate

- By using the cartesian coordinates

$$q_i = r_i$$

$$K(\dot{\mathbf{r}}) = \sum_i \frac{1}{2} m_i \dot{r}_i^2,$$

$$V = V(\mathbf{r}),$$

we get the familiar (Newtonian) form

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i,$$

where $\mathbf{f}_i = \nabla_{\mathbf{r}_i} L = -\nabla_{\mathbf{r}_i} V$ is the force acting in atom i

Solving the equations of motion

- We can also start by considering the Hamiltonian equations of motion

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i},$$

where $p_i = \frac{\partial L}{\partial \dot{q}_i}$ is the generalized momentum

and $H(\mathbf{q}, \mathbf{p}) = \sum_i \dot{q}_i p_i - L(\mathbf{q}, \dot{\mathbf{q}})$ the Hamiltonian function (we assume that $\dot{q}_i$ can be given as a function of $\mathbf{p}$)

- If V does not depend on the velocities, we get quickly back to the familiar form

$$H(\mathbf{q}, \mathbf{p}) = K(\mathbf{p}) + V(\mathbf{q})$$

and if we again use cartesian coordinates the equations of motion will be:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = -\nabla_{\mathbf{r}_i} V = \mathbf{f}_i$$

- So we have two alternatives:
  1. Solve a system of $3N$ 2nd order ODE's ($m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i$) derived from the Lagrangian or Newtonian formalism
  2. Solve a system of $6N$ 1st order ODE's derived from the Hamiltonian formalism

Numerical solution of equations of motion

- Finite difference method: from a system configuration (atom positions, velocities etc.) at time t we calculate the configuration at time $t + \delta t$
  - δt can be constant or variable
  - initial conditions $\mathbf{r}(0)$, $\mathbf{v}(0)$ have to be known (initial value problem)

- As an example a predictor-corrector -algorithm:
  - Use a Taylor series to **predict** the system configuration at time $t + \delta t$ using the small deviation δt:

$$\mathbf{r}^{\mathrm{p}}(t+\delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t) + \frac{1}{2}\delta t^2 \mathbf{a}(t) + \frac{1}{6}\delta t^3 \mathbf{b}(t) + \ldots$$

$$\mathbf{v}^{\mathrm{p}}(t+\delta t) = \mathbf{v}(t) + \delta t \mathbf{a}(t) + \frac{1}{2}\delta t^2 \mathbf{b}(t) + \ldots$$

$$\mathbf{a}^{\mathrm{p}}(t+\delta t) = \mathbf{a}(t) + \delta t \mathbf{b}(t) + \ldots$$

$$\mathbf{b}^{\mathrm{p}}(t+\delta t) = \mathbf{b}(t) + \ldots$$

Equations of motion not (yet) used.

  - $\mathbf{v}$, $\mathbf{a}$ and $\mathbf{b}$ are higher time derivatives of $\mathbf{r}$:
    $\mathbf{v}$ = velocity, $\mathbf{a}$ = acceleration and $\mathbf{b}$ = the time derivative of acceleration.

Numerical solution of equations of motion

- We can instead of $\mathbf{b}$ also use information from previous time steps:

$$\{\mathbf{r}(t), \mathbf{v}(t), \mathbf{v}(t-\delta t), \mathbf{v}(t-2\delta t)\}$$

or $\{\mathbf{r}(t), \mathbf{v}(t), \mathbf{a}(t), \mathbf{a}(t-\delta t)\}$

  - **Correction** step: we now have $\mathbf{r}^{\mathrm{p}}$, from which we can get the forces

    $\mathbf{F}_i(\mathbf{r}^{\mathrm{p}}{}_i)$ at $t+\delta t$

    $\Rightarrow$ accurate corrected accelerations $\mathbf{a}^{\mathrm{c}}(t+\delta t)$

    $\Rightarrow$ error in accelerations $\Delta\mathbf{a}(t+\delta t) = \mathbf{a}^{\mathrm{c}}(t+\delta t) - \mathbf{a}^{\mathrm{p}}(t+\delta t)$

Equations of motion now used.

  - Using this known error, one can calculate corrected positions, velocities and so on

$$\mathbf{r}^{\mathrm{c}}(t+\delta t) = \mathbf{r}^{\mathrm{p}}(t+\delta t) + c_0\Delta\mathbf{a}(t+\delta t)$$

$$\mathbf{v}^{\mathrm{c}}(t+\delta t) = \mathbf{v}^{\mathrm{p}}(t+\delta t) + c_1\Delta\mathbf{a}(t+\delta t)$$

$$\mathbf{a}^{\mathrm{c}}(t+\delta t) = \mathbf{a}^{\mathrm{p}}(t+\delta t) + c_2\Delta\mathbf{a}(t+\delta t)$$

$$\mathbf{b}^{\mathrm{c}}(t+\delta t) = \mathbf{b}^{\mathrm{p}}(t+\delta t) + c_3\Delta\mathbf{a}(t+\delta t)$$

  - The constants c_i depend on how many derivatives of $\mathbf{r}$ we include and the degree of the equation, etc.
  - The correction can also be iterated in principle; but not sensuble in MD: calculating the forces expensive $\Rightarrow$ use an algorithm requiring only *one evaluation of the force* per time step (one correction)
  - If the correction is not iterated, an obvious choice is $c_2 = 1$.

Numerical solution of equations of motion

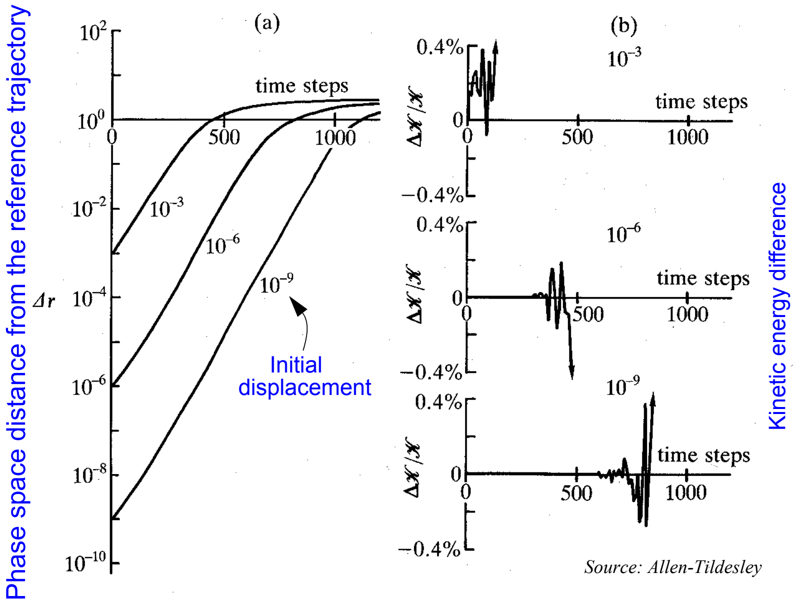
- Thus we reach the following approach to solving the MD equations of motion:
  (a) predict $\mathbf{r}$, $\mathbf{v}$ and $\mathbf{a}$ for the time $t+\delta t$ using the present values of the same variables
  (b) calculate forces and hence $\mathbf{a} = \mathbf{f}/m$ from the new $\mathbf{r}$
  (c) correct the predicted $\mathbf{r}$, $\mathbf{v}$ and $\mathbf{a}$ etc. using the new $\mathbf{a}$

- Requirements for a good MD algorithm

(a) fast	(not that important)
(b) takes little memory	(important)
(b) allows a long time step δt	(important)
(c) reproduces the correct path	(see below)
(d) conserves energy (and is reversible: $\delta t \to -\delta t \Rightarrow$ back to original state)	(very important)
(f) easy to implement	(not that important)
(g) only one force evaluation/time step	(important for complex V)

Numerical solution of equations of motion

- Fulfilling (c) completely is *not possible*: any small deviation somewhere will grow exponentially with time. Since all computers have limited floating-point precision, a small round-off error will eventually grow to a large difference (Lennard-Jones system; in reduced units $\rho^* = 0.6$, $T^* = 1.05$):



Source: Allen-Tildesley

- A reversible algorithm has in principle no drift in energy, except for that induced by numerical inaccuracies.

Common algorithms

- In the following we present some of the most common MD algorithms:

- **Verlet**
  - Derived from the following two Taylor series:

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \delta t\mathbf{v}(t) + \frac{1}{2}\delta t^2\mathbf{a}(t) + \ldots$$

$$\mathbf{r}(t-\delta t) = \mathbf{r}(t) - \delta t\mathbf{v}(t) + \frac{1}{2}\delta t^2\mathbf{a}(t) + \ldots$$

  - Sum them up and rearrange:

$$\mathbf{r}(t+\delta t) + \mathbf{r}(t-\delta t) = 2\mathbf{r}(t) + \delta t^2\mathbf{a}(t)$$

$$\Rightarrow \mathbf{r}(t+\delta t) = 2\mathbf{r}(t) - \mathbf{r}(t-\delta t) + \delta t^2\mathbf{a}(t)$$

  - So we have an algorithm which essentially does: $\{\mathbf{r}(t), \mathbf{a}(t), \mathbf{r}(t-\delta t)\} \to \{\mathbf{r}(t+\delta t), \mathbf{a}(t+\delta t)\}$.

  - However, the velocities are missing; these can be calculated from

$$\mathbf{v}(t) = \frac{\mathbf{r}(t+\delta t) - \mathbf{r}(t-\delta t)}{2\delta t}.$$

  - The error per iteration $O(\delta t^4)$; in the velocities $O(\delta t^2)$.
  - Memory requirement: $9N$.
  - Numerical problems, fluctuates heavily

Common algorithms

• Leap-frog

- Mathematically equivalent with Verlet (not numerically)

$$\left\{\mathbf{r}(t),\, \mathbf{a}(t),\, \mathbf{v}\left(t-\frac{1}{2}\delta t\right)\right\} \to \left\{\mathbf{r}(t+\delta t),\, \mathbf{a}(t+\delta t),\, \mathbf{v}\left(t+\frac{1}{2}\delta t\right)\right\}$$

$$\mathbf{v}\left(t+\frac{1}{2}\delta t\right) = \mathbf{v}\left(t-\frac{1}{2}\delta t\right) + \delta t\,\mathbf{a}(t)$$

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \delta t\,\mathbf{v}\left(t+\frac{1}{2}\delta t\right)$$

- Velocity

$$\mathbf{v}(t) = \frac{1}{2}\left[\mathbf{v}\left(t-\frac{1}{2}\delta t\right) + \mathbf{v}\left(t+\frac{1}{2}\delta t\right)\right]$$

  for energies etc.

- Advantage: explicit $\mathbf{v}$.

- Memory requirement $9N$.

- But still velocities at different time than the positions.

Common algorithms

• Velocity Verlet

- Eliminates the half-step velocity problem

$$\{\mathbf{r}(t),\, \mathbf{v}(t),\, \mathbf{a}(t)\} \to \{\mathbf{r}(t+\delta t),\, \mathbf{v}(t+\delta t),\, \mathbf{a}(t+\delta t)\}$$

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \delta t\,\mathbf{v}(t) + \frac{1}{2}\delta t^2\,\mathbf{a}(t)$$

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t) + \frac{1}{2}\delta t[\mathbf{a}(t) + \mathbf{a}(t+\delta t)]$$

- If we would eliminate $\mathbf{v}$ we would get back to normal Verlet
- This can also be considered to be a simple predictor-corrector-algorithm: (same as three stage Gear with $\mathbf{r}$ correction $= 0$):

  1. Predictor stage:

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \delta t\,\mathbf{v}(t) + \frac{1}{2}\delta t^2\,\mathbf{a}(t)$$

$$\mathbf{v}^{\mathrm{p}}\left(t+\frac{1}{2}\delta t\right) = \mathbf{v}(t) + \frac{1}{2}\delta t\,\mathbf{a}(t)$$

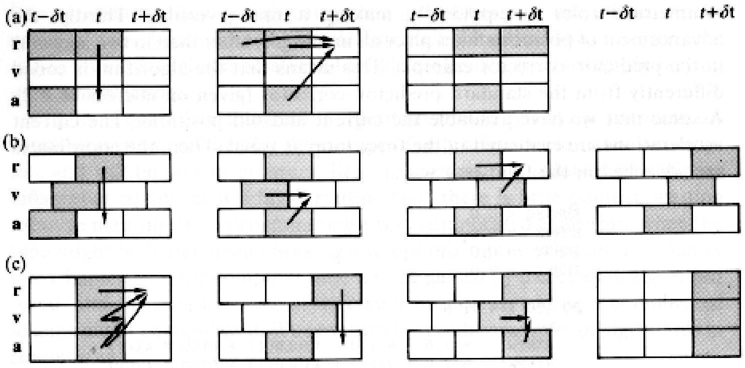
  2. Corrector stage:

$$\mathbf{v}^{\mathrm{c}}(t+\delta t) = \mathbf{v}^{\mathrm{p}}\left(t+\frac{1}{2}\delta t\right) + \frac{1}{2}\delta t\,\mathbf{a}(t+\delta t)$$

- Memory requirement $9N$.

Common algorithms

- Schematic illustration of the progress of different Verlet algorithms:



Verlet

Leap-frog

Velocity-Verlet

Source: Allen-Tildesley

- Velocity Verlet is a very popular algorithm because it is simple, reversible, yet reasonably accurate.

Common algorithms

- Velocity Verlet as pseudocode:

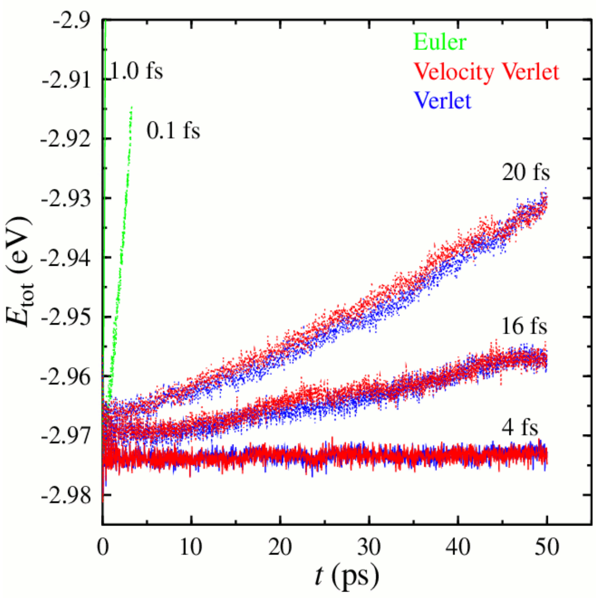
```
do i=1,N
    x(i)=x(i)+deltat*vx(i)+0.5*deltat**2*ax(i)
    vx(i)=vx(i)+0.5*deltat*ax(i)
    ((and same for y and z))
enddo

((get new forces F and accelerations ax(i)))

do i=1,N
    vx(i)=vx(i)+0.5*deltat*ax(i)
    ((and same for y and z))
enddo
```

- Comparison of performance
  - 500 Cu atoms at 300 K
  - Euler: $\mathbf{r}(t+\delta t) = \mathbf{r}(t)+\delta t\,\mathbf{v}(t)$

    $\mathbf{v}(t+\delta t) = \mathbf{v}(t)+\delta t\,\mathbf{a}(t)$



Common algorithms

- Beeman algorithm (D. Beeman, *J. Comp. Phys.* 20 (1976) 130.)
  - Equivalent with Verlet if $\mathbf{v}$ eliminated, but velocity more accurate

$$\{\mathbf{r}(t), \mathbf{v}(t), \mathbf{a}(t), \mathbf{a}(t-\delta t)\} \rightarrow \{\mathbf{r}(t+\delta t), \mathbf{v}(t+\delta t), \mathbf{a}(t+\delta t)\} :$$

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t) + \frac{2}{3}\delta t^2 \mathbf{a}(t) - \frac{1}{6}\delta t^2 \mathbf{a}(t-\delta t)$$

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t) + \frac{1}{3}\delta t \mathbf{a}(t+\delta t) + \frac{5}{6}\delta t \mathbf{a}(t) - \frac{1}{6}\delta t \mathbf{a}(t-\delta t)$$

  - Memory requirement $12N$

Common algorithms

- **Ion irradiation physics**
  - Initially $E_{\max} \sim 1 - 100\ \mathrm{keV}$;
  - In the end $E_{\max} \sim k_{\mathrm{B}}T \Rightarrow$ variable time step
  - Let us mark $\mathbf{r}_n = \mathbf{r}(t_n)$; $\mathbf{r}_{n+1} = \mathbf{r}(t_n + \delta t)$
  - **Smith & Harrison** (*Computers in Physics* **3** (1989) 68):

$$\{\mathbf{r}_n, \mathbf{v}_n, \mathbf{a}_n, \mathbf{a}_{n-1}\} \rightarrow \{\mathbf{r}_{n+1}, \mathbf{v}_{n+1}, \mathbf{a}_{n+1}\} :$$

  - Taylor : $\mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{v}_n\delta t_n + \mathbf{a}_n\frac{\delta t_n^{\ 2}}{2} + \mathbf{a}'_n\frac{\delta t_n^{\ 3}}{6} + O(\delta t_n^{\ 4})$
  - Estimate $\mathbf{a}'_n = \frac{\mathbf{a}_n - \mathbf{a}_{n-1}}{\delta t_{n-1}} + O(\delta t_{n-1})$

Time step ratio

$$R = \frac{\delta t_n}{\delta t_{n-1}}$$

$\Rightarrow$ Predictor for positions:

$$\mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{v}_n\delta t_n + [(3+R)\mathbf{a}_n - R\mathbf{a}_{n-1}]\frac{\delta t_n^{\ 2}}{6} \quad (1)$$

Velocity:

$$\mathbf{v}_{n+1} = \mathbf{v}_n + \mathbf{a}_n\delta t_n + \mathbf{a}'_n\frac{\delta t_n^{\ 2}}{2} + \mathbf{a}''_n\frac{\delta t_n^{\ 3}}{6} + O(\delta t_n^{\ 4})$$

Common algorithms

- Force calculation from $\mathbf{r}_{n+1}$:

$$\Rightarrow \mathbf{a}'_n = \frac{\mathbf{a}_{n+1} - R^2\mathbf{a}_{n-1} + (R^2-1)\mathbf{a}_n}{\delta t_n(1+R)}$$

$$\mathbf{a}''_n = 2R\left[\frac{\mathbf{a}_{n+1} - R\mathbf{a}_{n-1} + (R+1)\mathbf{a}_n}{\delta t_n^{\ 2}(1+R)}\right]$$

- Let's insert these into the Taylor series of $\mathbf{v}_{n+1}$:

$$\Rightarrow \mathbf{v}_{n+1} = \mathbf{v}_n + \left[\frac{(3+2R)\mathbf{a}_{n+1}}{1+R} + (3+R)\mathbf{a}_n - \frac{R^2\mathbf{a}_{n-1}}{1+R}\right]\frac{\delta t_n}{6} \quad (2)$$

- Algorithm:
  - (a) calculate new positions $\mathbf{r}_{n+1}$ using equation (1)
  - (b) calculate new accelerations $\mathbf{a}_{n+1}$
  - (c) calculate velocities using equation (2)

[(d) correct the positions using

$$\mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{v}_n\delta t_n + \left[\frac{(2+R)\mathbf{a}_{n+1}}{1+R} + (4+R)\mathbf{a}_n - \frac{R^2\mathbf{a}_{n-1}}{1+R}\right]\frac{\delta t_n^{\ 2}}{12}$$

but this demands two force evaluations per time step]

- Memory $12N$, error $O(\delta t_n^{\ 4})$.
- With a constant time step this reduces to the fairly simple form.

$$\Rightarrow \quad \mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{v}_n\delta t_n + [4\mathbf{a}_n - \mathbf{a}_{n-1}]\frac{\delta t_n^{\ 2}}{6}, \qquad \mathbf{v}_{n+1} = \mathbf{v}_n + [5\mathbf{a}_{n+1} + 8\mathbf{a}_n - \mathbf{a}_{n-1}]\frac{\delta t_n}{12}$$

Common algorithms

- Six-value (fifth-order predictor) Gear algorithm (Gear5). This is quite often used in MD[1].
  - Using the notation: $\mathbf{r}_i = \dfrac{\mathbf{r}^{(i)}(\delta t)^i}{i!}$, where $\mathbf{r}^{(i)} = \dfrac{\partial^i}{\partial t^i}\mathbf{r}$

we get the **predictor** $\mathbf{r}_i^{\mathrm{p}}$:

$$\begin{bmatrix} \mathbf{r}_0^{\mathrm{P}}(t+\delta t) \\ \mathbf{r}_1^{\mathrm{P}}(t+\delta t) \\ \mathbf{r}_2^{\mathrm{P}}(t+\delta t) \\ \mathbf{r}_3^{\mathrm{P}}(t+\delta t) \\ \mathbf{r}_4^{\mathrm{P}}(t+\delta t) \\ \mathbf{r}_5^{\mathrm{P}}(t+\delta t) \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 1 & 2 & 3 & 4 & 5 \\ 0 & 0 & 1 & 3 & 6 & 10 \\ 0 & 0 & 0 & 1 & 4 & 10 \\ 0 & 0 & 0 & 0 & 1 & 5 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{r}_0(t) \\ \mathbf{r}_1(t) \\ \mathbf{r}_2(t) \\ \mathbf{r}_3(t) \\ \mathbf{r}_4(t) \\ \mathbf{r}_5(t) \end{bmatrix}$$

- Note that the triangle is simply a Pascal's triangle matrix.
- For 2nd order (Newtonian) equations of motion, error term is $\delta\mathbf{r}_2 = \mathbf{r}_2 - \mathbf{r}_2^{\mathrm{p}}$.

---

[1] G. W. Gear, *Numerical initial value problems in ordinary differential equations,* (Prentice-Hall, Englewook Cliffs, NJ, USA) 1971; Allen-Tildesley

Common algorithms

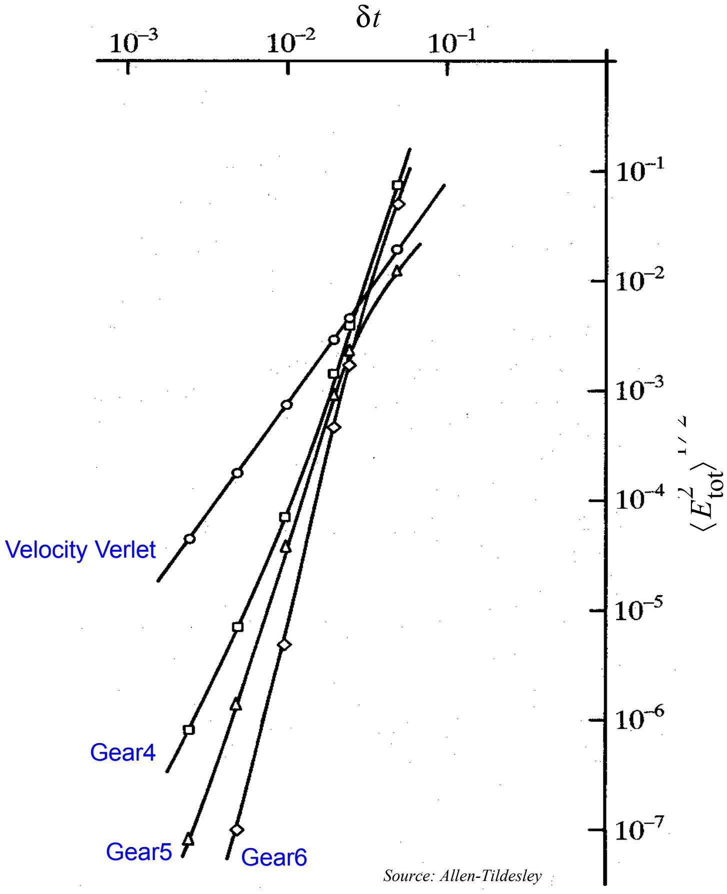
- Corrector: $\mathbf{r}_n^c = \mathbf{r}_n^P + \alpha\delta\mathbf{r}_2$, $\alpha = \begin{bmatrix} 3/16 \\ 251/360 \\ 1 \\ 11/18 \\ 1/6 \\ 1/60 \end{bmatrix} = \begin{bmatrix} 0.1875 \\ 0.6972 \\ 1.0000 \\ 0.6111 \\ 0.1667 \\ 0.0167 \end{bmatrix}$

- Note that if the forces may depend on the velocities, we should have $\alpha_0 = 3/20$ instead.

Common algorithms

- The fluctuations in energy of different algorithms as a function of the time step is illustrated on the right (Lennard-Jones system; in reduced units $\rho^* = 0.6$, $T^* = 1.05$)

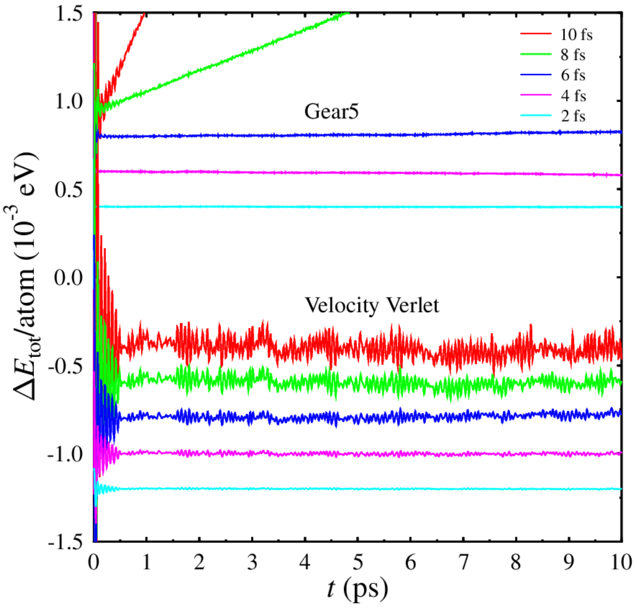
  - So the ‘better’ algorithms have much less fluctuations for very short timesteps.

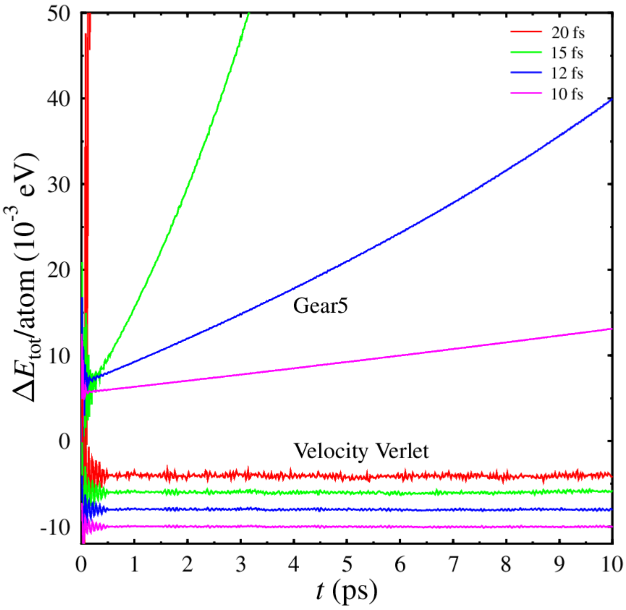


Source: Allen-Tildesley

Common algorithms

- Another illustration of this: a 10 ps simulation of a 4000 atom Cu lattice at 300 K. Potential = EAM





Curves are shifted in y direction in order to make the figures clearer.

Newer algorithms

- Tuckerman, Berne and Martyna developed around 1990 new reversible MD-algorithms using a Trotter factorisation of Liouville propagators.
  - The method is theoretically very well motivated, and it can be used to derive e.g. the Verlet algorithms [Tuckerman *et al.*, *J. Chem. Phys.* **97** (1992) 1990.]
  - It can also be used to derive a predictor-corrector-type algorithm which is comparable to Gear4 in accuracy but is also time reversible [Martyna and Tuckerman, *J. Chem. Phys.* **102** (1995) 8071.]
- So, what algorithm should one use?
  - A quick solution which works well with short time steps: **velocity Verlet**.
  - If one wants minimal oscillations in the total energy: **Gear5**.
  - If one wants great accuracy and minimal energy drift, it is worth looking into **Tuckerman’s method**.

Molecular dynamics 2015

Exercises 4 to chapter 4: `mdmorse`: solving the equations of motion
r

1. (12 p) Write the subroutine **`Solve1`**, which does the predictor part of the solution of the equations of motion with the velocity Verlet-algorithm.

Add also periodic boundary condition control in the code. That is, if the variable `periodic%x` (or `periodic.x` in the C version) is set to a nonzero value, the atoms which move outside the cell in the x dimension should be correctly returned inside it, and same for y and z.

3. (8 p) Write the subroutine **`Solve2`**, which does the corrector part of the velocity Verlet solution of the equations of motion.

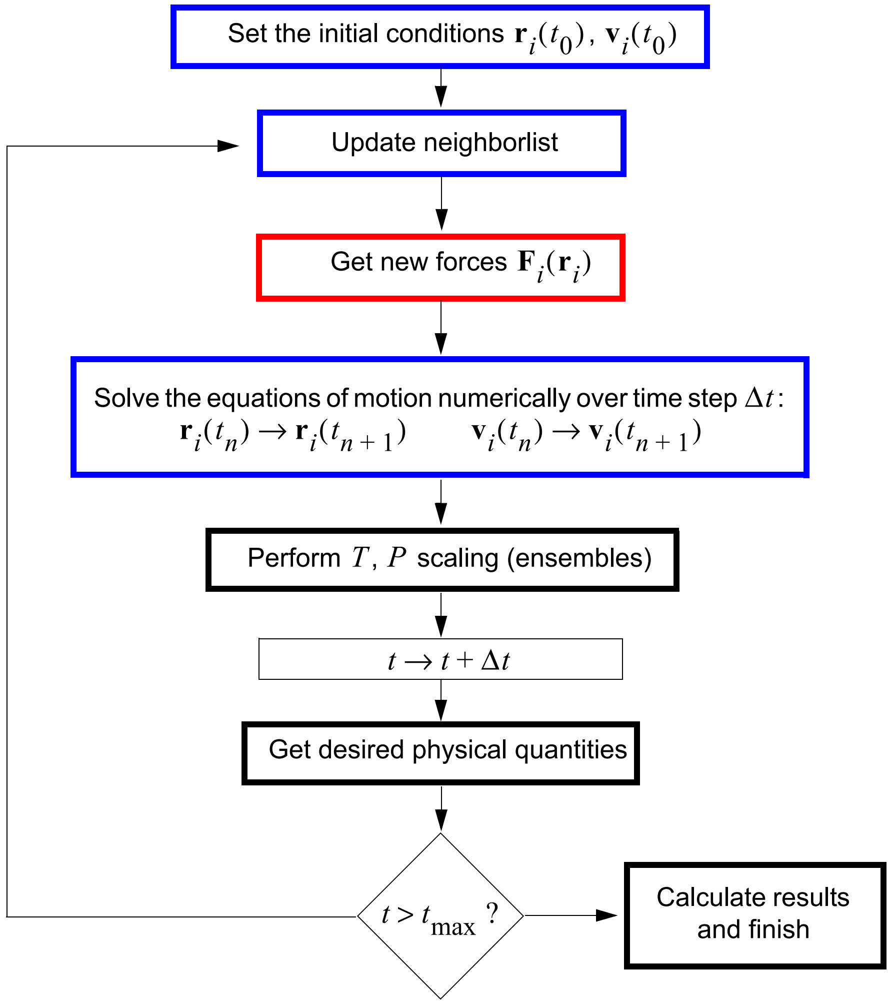
Return the exercises as the file `solve.f90/.c` and some output that shows that the code works (e.g. screen dump of `dpc` output).

If you solve this exercise right, and have a working solution to the exercise 3, the atoms will start moving when you run `mdmorse`. But since the force calculation is not yet implemented, the atoms will move in straight paths.

You can animate the motion on with `dpc`:

```
dpc cube 9.1 xyz erase sort 2 3 4 5 atoms.out
```

More info on `dpc` in the first lecture notes or by giving the command `dpc` without any arguments.



Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Solve the equations of motion numerically over time step Δt:
$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1})$ $\quad$ $\mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$

Perform T, P scaling (ensembles)

$t \rightarrow t + \Delta t$

Get desired physical quantities

$t > t_{\max}$?

Calculate results and finish

Calculating the forces between atoms

- The forces between atoms can be calculated in many different ways
  - This lecture:
    - classical potentials.
    - pair potentials, many-body potentials
  - Quantum mechanics
- A classical potential can be written in the form:

$$V = \sum_i V_1(\boldsymbol{r}_i) + \sum_{i,j} V_2(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_{i,j,k} V_3(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k) + \ldots$$

  - V is the total potential energy of an N atom system.
  - In principle all sums loop from 1 to N
  - V_1: **single particle potential**: external forces
  - V_2: **pair potential** which only depends on the distance between atoms r_{ij}
    - direct dependence on the *vectors* $\mathbf{r}_i$, $\mathbf{r}_j$ => dependence on the choice of the origin
  - V_3: **three-body potential** which may have an angular dependence
    - depends only on three variables, i.e. $V_3 = V_3(r_{ij}, r_{ik}, \theta_{ijk})$
  - **Four-body potentials**, even five-body terms: chemical and biological applications

Calculating the forces between atoms

- V_2 and V_3 enough to describe the basic mechanical and structural properties of most elements and simple compounds
- In order that things would not be too straightforward, in many cases a environment-dependence (i.e. implicit three-body term) is embedded into the two-body term V_2. We will give examples on these later.
- All terms which are not pure single particle or pair potentials are called **many-body** terms.

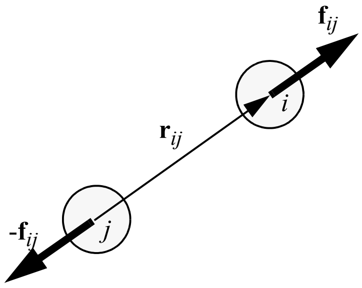
Calculating the forces between atoms

- Classification of empirical interatomic potentials [A. E. Carlsson, *Solid State Physics: Advances in Research and Applications*, **43** (1990) 1]
  - Pair Potential $V = \sum_{i,j} V_{\mathrm{P}}(r_{ij})$
  - Pair Functional Potential $V = \sum_i V_{\mathrm{PF}}(\rho_i)$, $\rho_i = \sum_{j \neq i} f(r_{ij})$

    If $f(r) = ar$
    ⇒ back to pair potential
  - Cluster Potential $V = \sum_{i \neq j \neq k} V_{\mathrm{CP}}(r_{ij}, r_{ik}, r_{jk})$

    Only clusters of three atoms here
  - Cluster Functional Potential $V = \sum_i V_{\mathrm{CF}}(\rho_i)$, $\rho_i = \sum_{\substack{j,k \\ i \neq j \neq k}} g(r_{ij}, r_{ik}, r_{jk})$
  - Real potentials often combinations of these: e.g. EAM for metals $V = \sum_i V_{\mathrm{PF}}(\rho_i) + \sum_{i,j} V_{\mathrm{P}}(r_{ij})$

Force calculation for pair potentials



- Pure pair potential $V(r_{ij})$. The force acting on atom i from atom j

$$\mathbf{f}_{ij} = -\nabla_{\mathbf{r}_i} V(r_{ij}) = -\nabla_{\mathbf{r}_{ij}} V(r_{ij}) = -\left[\frac{\partial V}{\partial x_{ij}}\hat{\mathbf{x}} + \frac{\partial V}{\partial y_{ij}}\hat{\mathbf{y}} + \frac{\partial V}{\partial z_{ij}}\hat{\mathbf{z}}\right],$$

($\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ unit vectors)

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j,\ x_{ij} = x_i - x_j \text{ etc.},\ \frac{\partial V}{\partial x_{ij}} = \frac{\mathrm{d}V}{\mathrm{d}r}\frac{\partial r_{ij}}{\partial x_{ij}},\quad \frac{\partial r_{ij}}{\partial x_{ij}} = \frac{x_{ij}}{r_{ij}}$$

$$\Rightarrow \mathbf{f}_{ij} = -\left[\frac{\mathrm{d}V}{\mathrm{d}r}\right]_{r = r_{ij}} \times \frac{\mathbf{r}_{ij}}{r_{ij}}$$

- To be precise ∇ operates on the position $\mathbf{r}_i$ of atom i. (Makes a difference for many-body potentials.)
- Cut-off radius r_c: atom pairs with $r_{ij} > r_\mathrm{c}$ do not interact, $r_\mathrm{c} \approx \text{a few Å}$.

Force calculation for pair potentials

- In case the potential extends to infinity, an analytical correction can be made to the energy, and other quantities of interest:

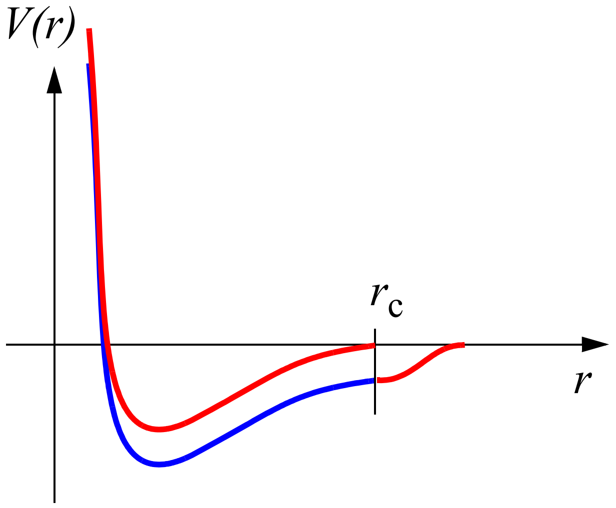
$$V_\mathrm{tot} = V_2 + V_\mathrm{corr} = E_c + 2\pi N\rho \int_{r_\mathrm{c}}^{\infty} r^2 V(r) dr$$

where ρ is the atom density of the system.

  - This obviously assumes that when $r > r_\mathrm{c}$ the atom density is constant everywhere, and thus does not work when for example a surface is present.

Force calculation for pair potentials

- Discontinuity at r_c ⇒ jumps in energy
  - Solution: take the potential to zero in $[r_c, r_c + \Delta r]$
    - potential and the force are continuous (3rd order polynomial) or
    - displace the potential, as the zero point of V is arbitrary but this changes the value of V_{tot}
  - Many modern potentials are in fact defined so that they have a well-defined cutoff r_c where V and at least the first derivative are ≡ 0.



Force calculation for pair potentials

- Example: cut-off of Lennard-Jones potential

$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

- Shift and tilt the potential: $V(r)$ and $V'(r)$ continuous at r_c:

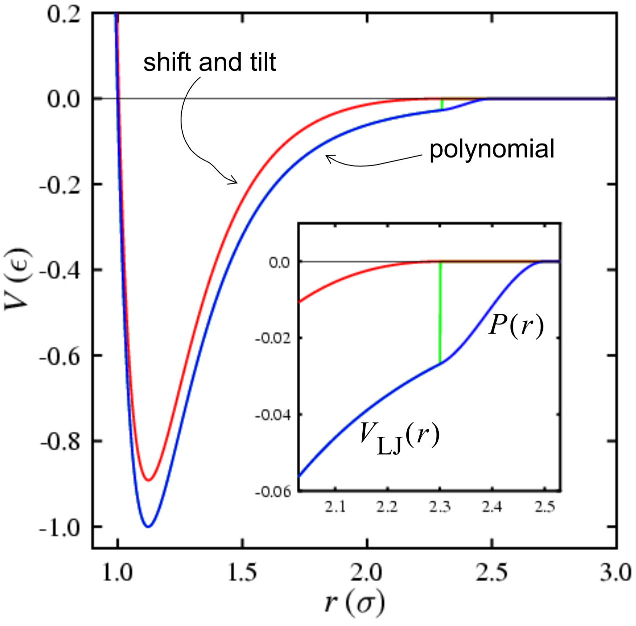
$$V(r) = V_{LJ}(r) - (r - r_c)V'_{LJ}(r_c) - V_{LJ}(r_c)$$

  - Problem: may change the potential at smaller r values

- Fit a polynomial $P(r) = ar^3 + br^2 + cr + d$ from $[r_c, r_c + \Delta r_c]$:

$$\begin{cases} P(r_c) = V_{LJ}(r_c) \\ P'(r_c) = V'_{LJ}(r_c) \\ P(r_c + \Delta r_c) = 0 \\ P'(r_c + \Delta r_c) = 0 \end{cases}$$

$r_c = 2.3$ Å $\Delta r_c = 0.2$ Å

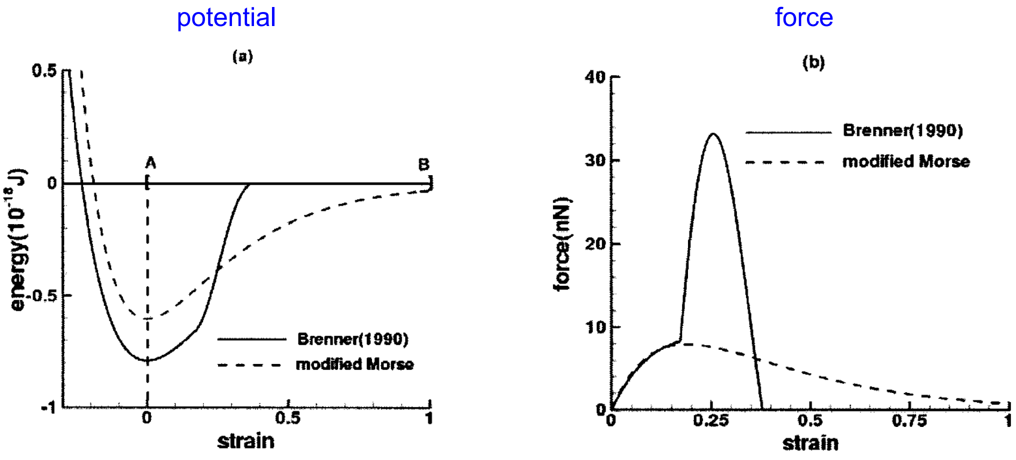


Force calculation for pair potentials

- Problem: high forces may result (see below)
- Brenner potential for carbon (Well, this is not a pair potential):

- Potential quickly to zero; doesn't look too bad

- However: huge forces; effect seen in fracture simulations
  (see also M. Sammalkorpi *et al.*, *Phys. Rev. B* **70** (2004) 245416.)



T. Belytschko *et al.*, *Phys. Rev. B* **65** (2002) 235430.

Force calculation for pair potentials

- Force calculation without periodic boundaries or neighbour list:

```
do i=1,N
   do j=1,N
    if (i==j) cycle
    rijx = rx(j)-rx(i)
    rijy = ry(j)-ry(i)
    rijz = rz(j)-rz(i)
    rijsq = rijx**2+rijy**2+rijz**2
    rij = sqrt(rijsq)
    if (rij < rcut) then
      V = (Potential energy per atom)/2
      dVdr = ...derivative of potential energy with respect to its only argument r...
      a = -dVdr/m/2.0 ! Unit transformations may be needed. Note the factor 1/2!!
      ax(i) = ax(i)-rijx/rij*a ! The application on both
      ax(j) = ax(j)+rijx/rij*a ! i and j ensures that
      ay(i) = ay(i)-rijy/rij*a ! Newton's third law is
      ay(j) = ay(j)+rijy/rij*a ! fulfilled
      az(i) = az(i)-rijz/rij*a
      az(j) = az(j)+rijz/rij*a
    endif
  enddo
enddo
```

Force calculation for pair potentials

- Use of Verlet neighbour list (cf. lecture 3):

```
startofineighbourlist=1
do i=1,N
  nneighboursi=neighbourlist(startofineighbourlist)
  do jj=1,nneighboursi
    j=neighbourlist(startofineighbourlist+jj)
    rijx = rx(j)-rx(i)
    rijy = ry(j)-ry(i)
    rijz = rz(j)-rz(i)
    rijsq = rijx**2+rijy**2+rijz**2
    rij = sqrt(rijsq)
    if (rij < rcut) then
      V = (Potential energy per atom)/2
      dVdr = ...derivative of potential energy with respect to its only argument r...
      a = -dVdr/m/2.0 ! Plus unit transformations ! Note the factor 1/2!!
      ax(i) = ax(i)-rijx/rij*a
      ax(j) = ax(j)+rijx/rij*a
      ay(i) = ay(i)-rijy/rij*a
      ay(j) = ay(j)+rijy/rij*a
      az(i) = az(i)-rijz/rij*a
      az(j) = az(j)+rijz/rij*a
    endif
  enddo
  startofineighbourlist=startofineighbourlist+nneighboursi+1
enddo
```

Force calculation for pair potentials

- Note that in the sum above every interaction is counted twice:

```
do i=1,N
   do j=1,N
        if (i==j) cycle
        ...
```

  - That is, e.g. interaction 1-3 is counted both as 1-3 and 3-1. Hence the factor 1/2 in front of the potential energy summation and forces (this actually depends on the exact definition of the potentials, some already have a factor of 1/2 in front).

- A straightforward solution:

```
do i=1,N-1
   do j=i+1,N
        ...
```

  (either in constructing the neighbour list or forces) reduces the calculation time to one half.

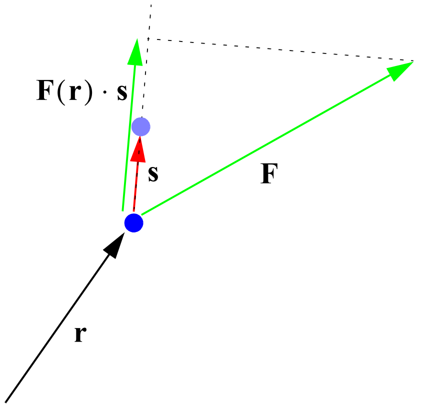
  - *For some many-body potentials this does not work.*

- $V(r)$ often is defined to give the total energy for a *pair* of atoms. When one wants the potential energy per *atom* one thus may have to include one more factor of 1/2. But this additional factor is not needed in the force calculation since the force always affects both atoms (Newton’s III law).

- Note that the sign conventions in defining r_{ij} in the literature may vary.

Force calculation for pair potentials

- One practical way of checking that you have correctly derived the forces from the potential energy and that all signs and factors of ½ are OK in you potential implementation:
  1. Calculate E_{pot} at 0 K and compare with an analytical prediction for some simple system, e.g. a dimer or perfect lattice.
  2. Simulate a two-atom system starting from a very small distance, so that E_{pot} is very large, much larger than the equilibrium energy per atom (say 10000 eV). When you run the simulation with a very small time step the atoms should explode outwards from each other so that the final E_{kin}/atom is the same as the original E_{pot}/atom. If you are uncertain what a 'very small' time step is, keep decreasing it until the answer doesn't change.
  3. Another good test: numerical derivation of potential energy:



Move one atom in direction $\hat{\mathbf{s}}$ amount Δs.

Directional derivative of the potential (assume $|\hat{\mathbf{s}}| = 1$):

$$\frac{\partial V(\mathbf{r})}{\partial \hat{\mathbf{s}}} = \lim_{h \to 0} \frac{V(\mathbf{r} + h\hat{\mathbf{s}}) - V(\mathbf{r})}{h} = \nabla V(\mathbf{r}) \cdot \hat{\mathbf{s}} = -\mathbf{F}(\mathbf{r}) \cdot \hat{\mathbf{s}}$$

Computed from potential energy as $\Delta V / \Delta s$

Computed from forces as $F_x s_x + F_y s_y + F_z s_z$

Force calculation for a three-body potential

- For a pure pair potential for an interaction between atoms i and j $V_{ij} = V_{ji}$ because $V(r_{ij}) = V(r_{ji})$ and hence also $\nabla_i V_{ij} = \nabla_i V_{ji}$ as described above. This symmetry simplifies the force calculation.

- For a three-body potential things get trickier because V_{ij} may not = V_{ji}. To get the force $\mathbf{F}_i$ acting on an atom i one instead has to calculate

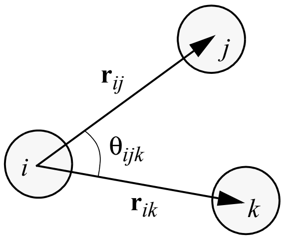
$$\boldsymbol{F}_i = -\nabla_i \left[\sum_j (V_{ij} + V_{ji}) + \sum_j \sum_k V_{jki} \right] = -\left[\sum_j (\nabla_i V_{ij} + \nabla_i V_{ji}) + \sum_j \sum_k \nabla_i V_{jki} \right]$$

- Many practical three-body potentials have been written such that

$$V_3(r_{ij}, r_{ik}, \theta_{ijk}) = V_3(r_{ij}, r_{ik}, \cos\theta_{ijk})$$

i.e. all angular information is in a cosine term.

Force calculation for a three-body potential



- In this case one can utilize the following equalities:

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

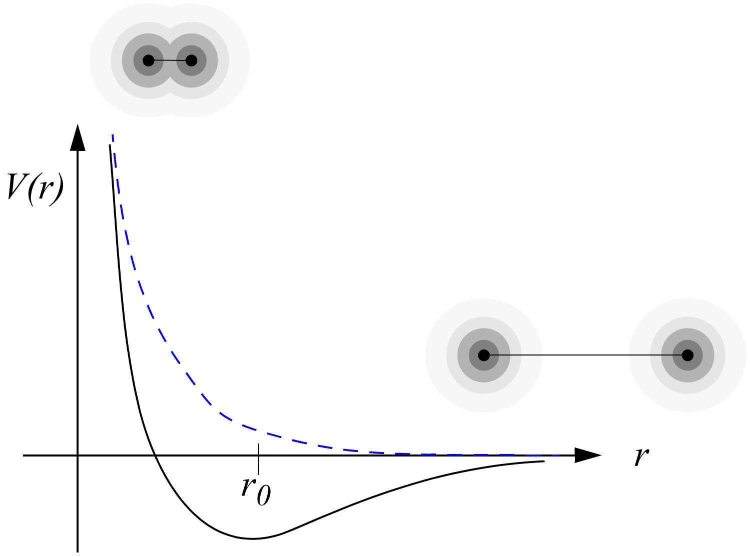
$$\nabla_i\cos\theta_{ijk} = \nabla_i\left(\frac{\boldsymbol{r}_{ij}\cdot\boldsymbol{r}_{ik}}{r_{ij}r_{ik}}\right) = \ldots\ldots = \left[\frac{\cos\theta_{ijk}}{r_{ij}^2} - \frac{1}{r_{ij}r_{ik}}\right]\boldsymbol{r}_{ij} + \left[\frac{\cos\theta_{ijk}}{r_{ik}^2} - \frac{1}{r_{ij}r_{ik}}\right]\boldsymbol{r}_{ik}$$

that is, no need to evaluate cos function.

- In many-body potentials there are often symmetries which can be used to reduce the number of operations needed in the force calculation even more.

The physical/chemical origin of interactions

- Qualitatively a two-atom interaction looks like the following:



- The minimum, i.e. equilibrium distance, is r_0.
- At small separations there is a strong repulsion. Just below r_0 this derives primarily from the Pauli rule preventing electrons being in states with the same quantum numbers, and from the electron-electron repulsion, whereas when the nuclei are very close to each other, the Coulombic repulsion between the nuclei dominates completely.
- At larger distances there may be an attraction, which can have different reasons: van der Waals attraction, Coulomb attraction, a covalent bond, (due to pairing of valence electrons) or metallic bonding
- Potential may also be purely repulsive

- A few examples (1 bohr = 0.53 Å)

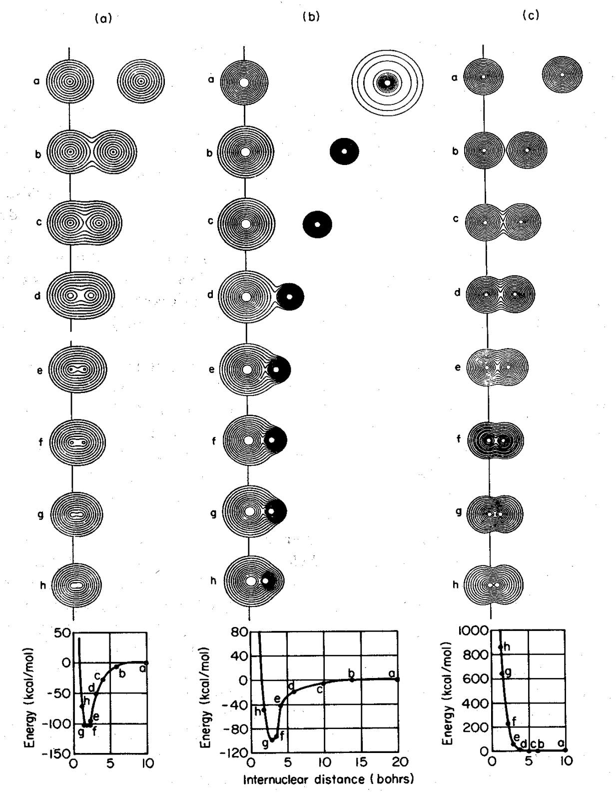
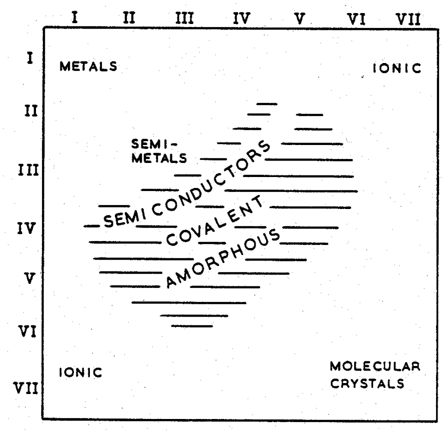
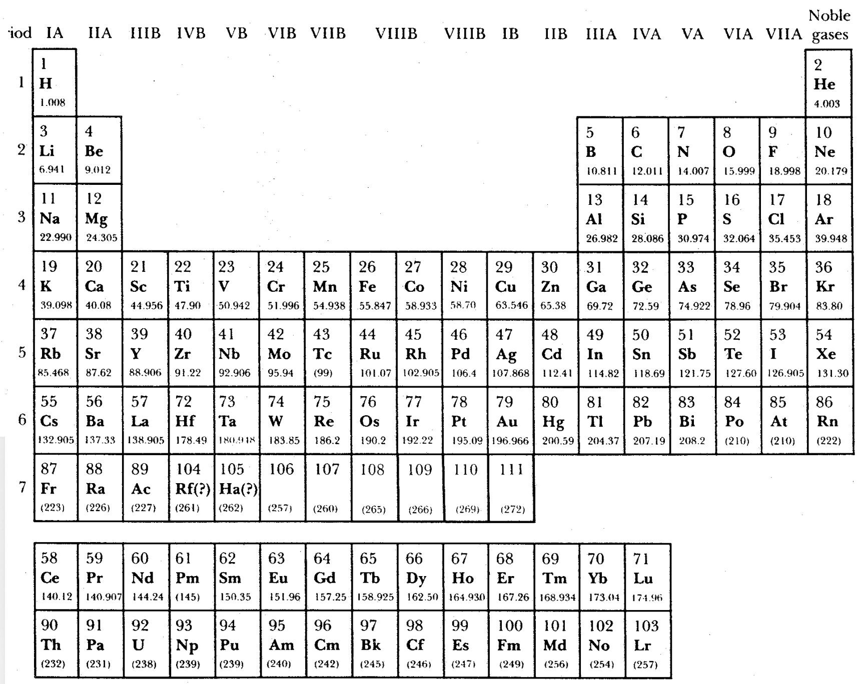


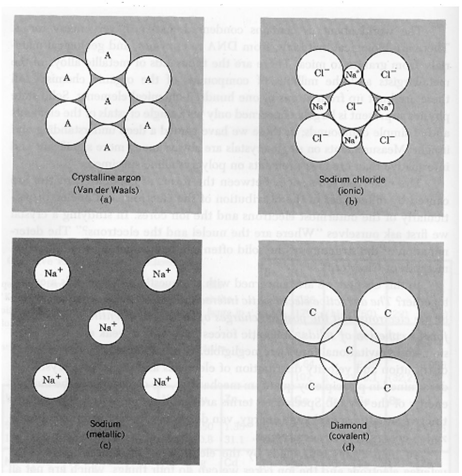
Fig. 1.2. Electron density distribution contours generated by computer solution of the Schrödinger equation for interactions in three atomic systems (a) H_2, (b) LiF, and (c) He_2. At the bottom is plotted the potential energy of interaction at the different stages of the process a–h. The separation is in atomic units. (After Wahl [3].)

- Overview of bonding expected in different cases, and illustration of electron distributions [Kittel, Introduction to Solid State physics]

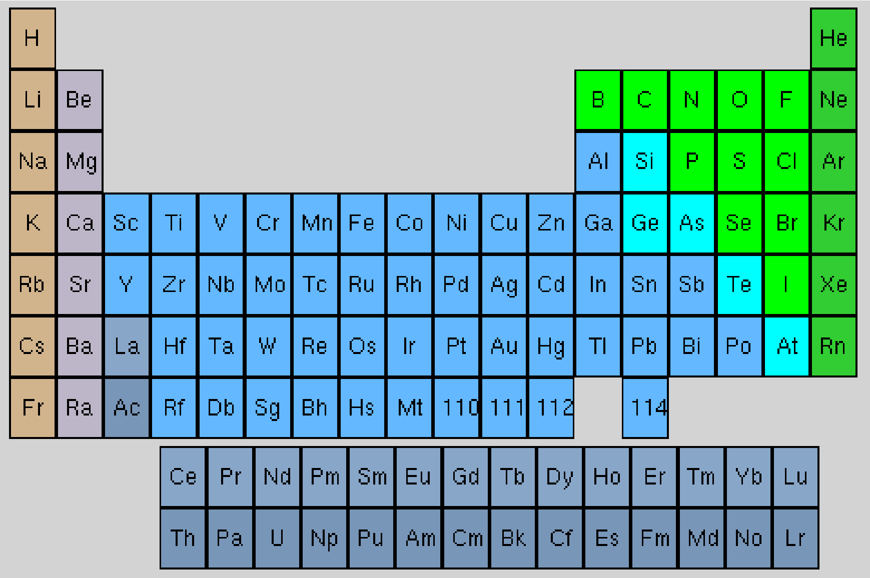




iod	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB		VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble gases
1	1 **H** 1.008																	2 **He** 4.003
2	3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.179
3	11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.064	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.098	20 **Ca** 40.08	21 **Sc** 44.956	22 **Ti** 47.90	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.70	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
5	37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.22	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (99)	44 **Ru** 101.07	45 **Rh** 102.905	46 **Pd** 106.4	47 **Ag** 107.868	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.69	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.905	54 **Xe** 131.30
6	55 **Cs** 132.905	56 **Ba** 137.33	57 **La** 138.905	72 **Hf** 178.49	73 **Ta** 180.918	74 **W** 183.85	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.09	79 **Au** 196.966	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.19	83 **Bi** 208.2	84 **Po** (210)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf(?)** (261)	105 **Ha(?)** (262)	106 (257)	107 (260)	108 (265)	109 (266)	110 (269)	111 (272)							
	58 **Ce** 140.12	59 **Pr** 140.907	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.35	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.925	66 **Dy** 162.50	67 **Ho** 164.930	68 **Er** 167.26	69 **Tm** 168.934	70 **Yb** 173.04	71 **Lu** 174.96				
	90 **Th** (232)	91 **Pa** (231)	92 **U** (238)	93 **Np** (239)	94 **Pu** (239)	95 **Am** (240)	96 **Cm** (242)	97 **Bk** (245)	98 **Cf** (246)	99 **Es** (247)	100 **Fm** (249)	101 **Md** (256)	102 **No** (254)	103 **Lr** (257)				



- So for the pure elements we get the familiar division:



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	110	111	112		114				
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Idealized potentials for theoretical and qualitative studies

- Hard sphere: $V^{\mathrm{HS}}(r) = \begin{cases} \infty, r < \sigma \\ 0, r \geq \sigma \end{cases}$

- First MD simulations were carried out with this potential.

- The equations of motion reduce to calculating where the next collision occurs: true billiard ball physics
  - Applications in packing problems

- Square well:

$$V^{\mathrm{SW}}(r) = \begin{cases} \infty, r < \sigma_1 \\ -\varepsilon, \sigma_1 \leq r < \sigma_2 \\ 0, r \geq \sigma_2 \end{cases}$$

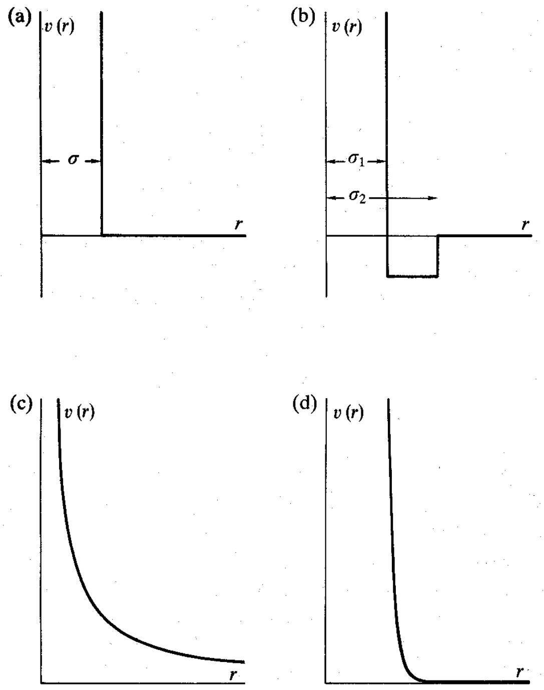


Fig. 1.4 Idealized pair potentials. (a) The hard-sphere potential; (b) The square-well potential; (c) The soft-sphere potential with repulsion parameter $\nu = 1$; (d) The soft-sphere potential with repulsion parameter $\nu = 12$.

Source: Allen-Tildesley

- soft sphere: $V^{\mathrm{SS}}(r) = \varepsilon\left[\frac{\sigma}{r}\right]^{\nu}$

“Realistic” pair potentials

- Lennard-Jones (LJ)

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

  - The attractive $1/r^6$ - term can be derived from the dipole-dipole interaction, or as the interactions between two oscillators (QM) [Kittel, *Introduction to Solid State Physics*, 7th edition, p. 62]. It is also known as the Van der Waals or London interaction.
  - The repulsive term $1/r^{12}$ chosen for convenience.
  - Also other exponents used; notation for any two exponents A and B is LJ (A-B) potential.
  - ε and σ are usually chosen by fitting into experimental data. σ gives the equilibrium distance ε the cohesive energy.
  - A few Lennard-Jones-parameters for gases [Ashcroft-Mermin s. 398]:

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

  - Very weak interaction: e.g. $V_{\mathrm{min}} = -3.1\ \mathrm{meV}$ for Ne.
  - LJ (12-6) potentials have proven to be good for noble gases (filled electron shells ⇒ almost always neutral) close to equilibrium. But they are obviously terrible for very small r ($r \le 1$ Å) since the true interaction is about e^{-r}/r and not $1/r^{12}$.

“Realistic” pair potentials

  - LJ potentials have been, and are used a lot, for instance in molecular modelling, in many cases even in systems where there is no physical motivation to using the LJ functional form. But if the fit is good for some purpose, using it may still be justified as long as the limitations are kept in mind.

- Reduced units
  - If a potential only has a couple of parameters, evaluating it can be really efficient in reduced units
  - Also, in reduced units the results are always the same, so the results can be transferred to different systems with straightforward scaling.
  - For instance for the Lennard-Jones-potential:

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad \text{[or any } V(r) = \varepsilon f(r/\sigma)\text{]}$$

⇒ Natural length unit = σ
natural energy unit = ε

$$\Rightarrow V^*(x) = 4[x^{-12} - x^{-6}]$$

“Realistic” pair potentials

- other units:

$$t^* = t/[(m\sigma^2)/\varepsilon]^{1/2}$$
$$\rho^* = \rho\sigma^3$$
$$T^* = k_B T/\varepsilon$$
$$P^* = P\sigma^3/\varepsilon$$
$$\mathbf{f}^* = \mathbf{f}\sigma/\varepsilon$$
$$v^* = v/[\varepsilon/m]^{1/2}$$

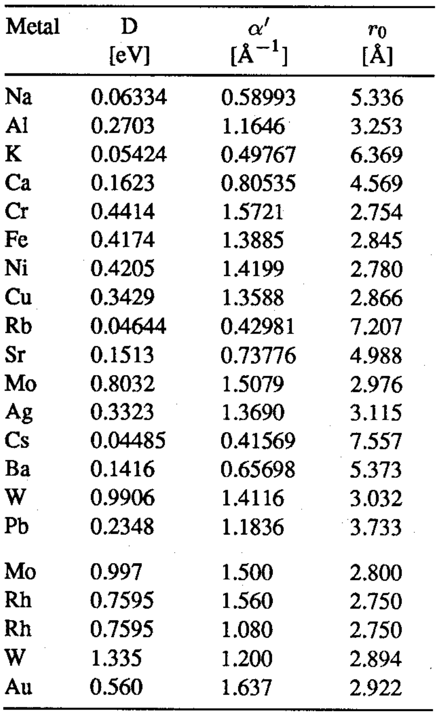
- Reduced units were very popular when one had to save CPU time in every single multiplication, and when potentials were still as simple as LJ.

“Realistic” pair potentials

- Morse potential
  - Simple metals (sp-metals, e.g. Na, Mg, Al; and metals with the fcc- or hcp-structure), are at least to some extent describable with a pair potential
  - A popular choice: the Morse potential [P. M. Morse, *Phys. Rev.* **34** (1930) 57.]:

$$V(r) = De^{-2\alpha(r-r_0)} - 2De^{-\alpha(r-r_0)}$$

  - Designed originally to describe vibrations in molecules.
    - The Schrödinger equation happens to have an analytical solution for this functional form.
  - Efficient to evaluate, in the form above only one exponential function needs to be evaluated.
  - Decays faster at large r than Lennard-Jones: less problems with cut-off.
  - A fit for many metals [Girifalco and Weizer, *Phys. Rev.* **114** (1959) 687.]
  - Works decently for being a pair potential.

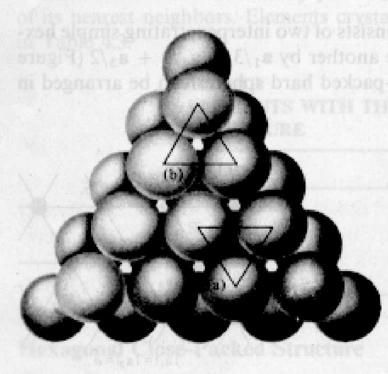


Metal	D [eV]	α' [Å^{-1}]	r_0 [Å]
Na	0.06334	0.58993	5.336
Al	0.2703	1.1646	3.253
K	0.05424	0.49767	6.369
Ca	0.1623	0.80535	4.569
Cr	0.4414	1.5721	2.754
Fe	0.4174	1.3885	2.845
Ni	0.4205	1.4199	2.780
Cu	0.3429	1.3588	2.866
Rb	0.04644	0.42981	7.207
Sr	0.1513	0.73776	4.988
Mo	0.8032	1.5079	2.976
Ag	0.3323	1.3690	3.115
Cs	0.04485	0.41569	7.557
Ba	0.1416	0.65698	5.373
W	0.9906	1.4116	3.032
Pb	0.2348	1.1836	3.733
Mo	0.997	1.500	2.800
Rh	0.7595	1.560	2.750
Rh	0.7595	1.080	2.750
W	1.335	1.200	2.894
Au	0.560	1.637	2.922

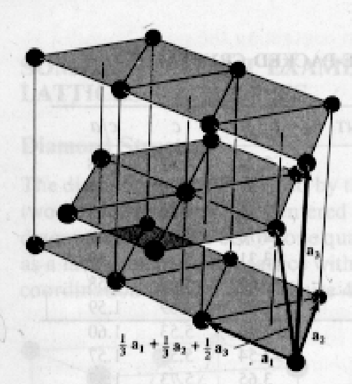
Girifalco and Weizer, *Phys. Rev.* **114** (1959) 687.

“Realistic” pair potentials

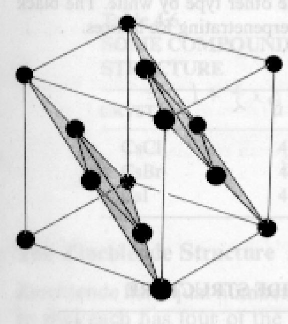
- An ordinary pair potential has a close-packed structure as the ground state. (usually either “face-centered cubic”, FCC or “hexagonal close packed”, HCP).



HCP

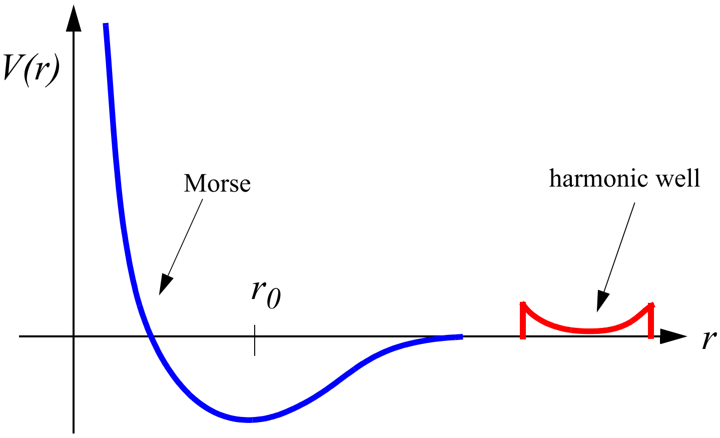


FCC



“Realistic” pair potentials

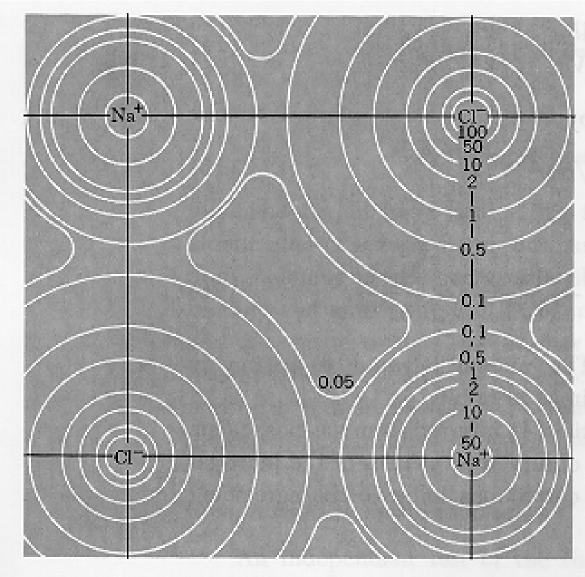
- A pair potential can thus not describe well elements with other structures than FCC or HCP. But this doesn’t mean people haven’t tried:
  - Diamond lattice: open structure, four nearest neighbours, very far from close packed.
  - Still, it is actually possible to make diamond stable locally with a pair potential, but this will become rather pathological (Mazzone potential for Si, [*Phys. Stat. Sol (b)* **165** (1991) 395.]):



  - Does actually work close to perfect lattice.
  - But what happens when atoms leave the harmonic well due to e.g. a high temperature?
    - System will collapse to close-packed structure => applicability of potential extremely limited
  - Unfortunately this is not uncommon regarding interatomic potentials: one has to be very critical of any new potential! Even well-respected physicists have presented potentials which have some very pathological features...

“Realistic” pair potentials

- Ionic compounds
  - Different ions, between which the electron density is very small. The ions have filled electron shells, and are thus unlikely to change their electron configuration
  - An extreme examples: NaCl:
  - A pair potential approximation works quite well, and potentials abound in the literature, as there is much experimental data available for the alkali halides which can be used in potential fitting.
  - Potentials typically contain a short-range (SR) term and the Coulomb interaction:



$$V(r_{ij}) = V_{SR}(r_{ij}) + \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{ij}}$$; z_i = ion charges

- V_{SR}: repulsive force between electrons packed closely together and an attractive van der Waals (vdW) interaction

---

“Realistic” pair potentials

- Most common forms for the short range potential:

Buckingham: $V_{SR}(r) = Ae^{-r/\rho} - \frac{C}{r^6}$

Born-Huggins-Mayer: $V_{SR}(r) = Ae^{-B(r-\sigma)} - \frac{C}{r^6} - \frac{D}{r^8}$

Morse: $V_{SR}(r) = De^{-2\alpha(r-r_0)} - 2De^{-\alpha(r-r_0)}$

- $1/r^6$-term comes from the dipole-dipole interaction (again)
- The repulsion is usually significant only for nearest neighbours, and the vdW interaction for next-nearest neighbours. Frequently for instance in oxides the only interaction assumed between cations is their Coulombic repulsion.

Fitting of potential parameters

- In almost all classical potentials there is a number of free parameters, e.g. in Lennard-Jones 2 (ε and σ), Morse 3 (D, α, r_0) etc.
  - An extreme example: the ReaxFF model for hydrocarbons: A.C.T. van Duin *et al.*, *J. Chem. Phys. A* **105** (2001) 9396.

$$E_{\mathrm{system}} = E_{\mathrm{bond}} + E_{\mathrm{over}} + E_{\mathrm{under}} + E_{\mathrm{val}} + E_{\mathrm{pen}} + E_{\mathrm{tors}} + E_{\mathrm{conj}} + E_{\mathrm{vdWaals}} + E_{\mathrm{Coulomb}}$$

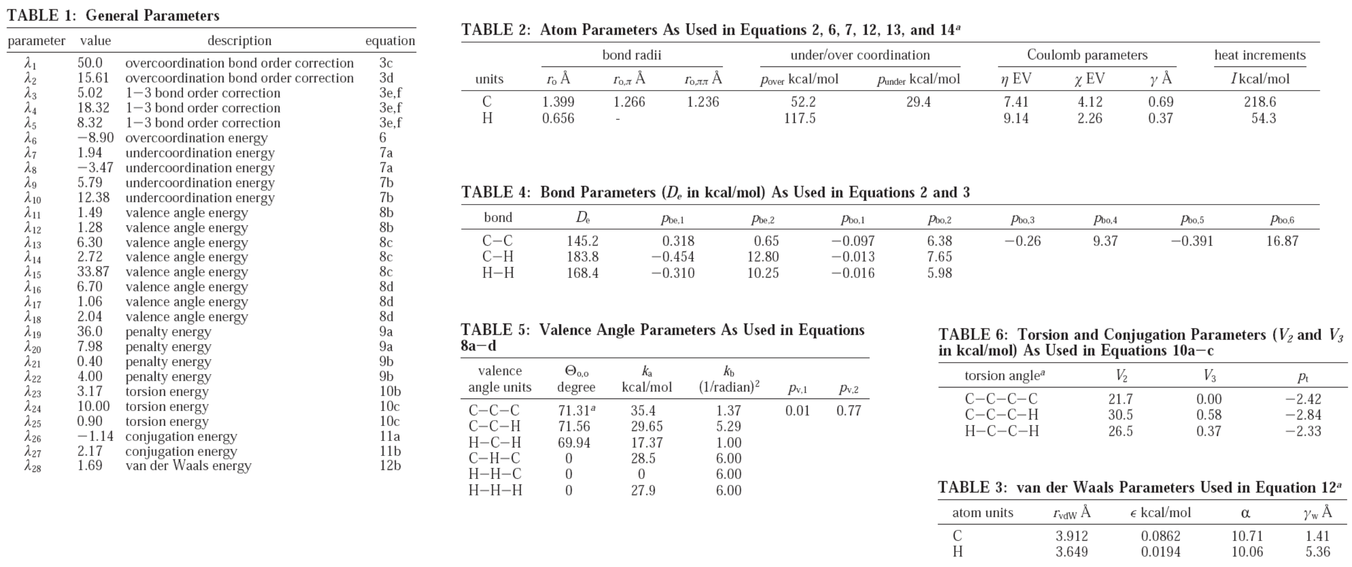


TABLE 1: General Parameters

parameter	value	description	equation
λ_1	50.0	overcoordination bond order correction	3c
λ_2	15.61	overcoordination bond order correction	3d
λ_3	5.02	1−3 bond order correction	3e,f
λ_4	18.32	1−3 bond order correction	3e,f
λ_5	8.32	1−3 bond order correction	3e,f
λ_6	−8.90	overcoordination energy	6
λ_7	1.94	undercoordination energy	7a
λ_8	−3.47	undercoordination energy	7a
λ_9	5.79	undercoordination energy	7b
λ_{10}	12.38	undercoordination energy	7b
λ_{11}	1.49	valence angle energy	8b
λ_{12}	1.28	valence angle energy	8b
λ_{13}	6.30	valence angle energy	8c
λ_{14}	2.72	valence angle energy	8c
λ_{15}	33.87	valence angle energy	8c
λ_{16}	6.70	valence angle energy	8d
λ_{17}	1.06	valence angle energy	8d
λ_{18}	2.04	valence angle energy	8d
λ_{19}	36.0	penalty energy	9a
λ_{20}	7.98	penalty energy	9a
λ_{21}	0.40	penalty energy	9b
λ_{22}	4.00	penalty energy	9b
λ_{23}	3.17	torsion energy	10b
λ_{24}	10.00	torsion energy	10c
λ_{25}	0.90	torsion energy	10c
λ_{26}	−1.14	conjugation energy	11a
λ_{27}	2.17	conjugation energy	11b
λ_{28}	1.69	van der Waals energy	12b

TABLE 2: Atom Parameters As Used in Equations 2, 6, 7, 12, 13, and 14[a]

	bond radii			under/over coordination		Coulomb parameters			heat increments
units	r_o Å	$r_{o,\pi}$ Å	$r_{o,\pi\pi}$ Å	p_{over} kcal/mol	p_{under} kcal/mol	η EV	χ EV	γ Å	I kcal/mol
C	1.399	1.266	1.236	52.2	29.4	7.41	4.12	0.69	218.6
H	0.656	-		117.5		9.14	2.26	0.37	54.3

TABLE 4: Bond Parameters (D_e in kcal/mol) As Used in Equations 2 and 3

bond	D_e	$p_{\mathrm{be},1}$	$p_{\mathrm{be},2}$	$p_{\mathrm{bo},1}$	$p_{\mathrm{bo},2}$	$p_{\mathrm{bo},3}$	$p_{\mathrm{bo},4}$	$p_{\mathrm{bo},5}$	$p_{\mathrm{bo},6}$
C−C	145.2	0.318	0.65	−0.097	6.38	−0.26	9.37	−0.391	16.87
C−H	183.8	−0.454	12.80	−0.013	7.65				
H−H	168.4	−0.310	10.25	−0.016	5.98				

TABLE 5: Valence Angle Parameters As Used in Equations 8a−d

valence angle units	$\Theta_{o,o}$ degree	k_a kcal/mol	k_b (1/radian)^2	$p_{v,1}$	$p_{v,2}$
C−C−C	71.31[a]	35.4	1.37	0.01	0.77
C−C−H	71.56	29.65	5.29		
H−C−H	69.94	17.37	1.00		
C−H−C	0	28.5	6.00		
H−H−C	0	0	6.00		
H−H−H	0	27.9	6.00		

TABLE 6: Torsion and Conjugation Parameters (V_2 and V_3 in kcal/mol) As Used in Equations 10a−c

torsion angle[a]	V_2	V_3	p_t
C−C−C−C	21.7	0.00	−2.42
C−C−C−H	30.5	0.58	−2.84
H−C−C−H	26.5	0.37	−2.33

TABLE 3: van der Waals Parameters Used in Equation 12[a]

atom units	r_{vdW} Å	ϵ kcal/mol	α	γ_w Å
C	3.912	0.0862	10.71	1.41
H	3.649	0.0194	10.06	5.36

Fitting of potential parameters

- Two main approaches to develop a potential exist:

  1. Derivation from so called *ab initio* (quantum mechanical) calculations

  2. Fit to empirical and/or *ab initio* data

  - Although the previous approach is better motivated physically, in practice the latter approach, or a combination of the two, often works better.

- A good classical potential is one which with a small number of free parameters can describe a wide range of properties well (usually 5-20 % accuracy in condensed matter physics is considered to be “well”, since experiments seldom are much more accurate than this).

- A related concept is that a good potential should be **transferable**, which means that it should be able to describe properties of other states of the material than those it was originally fitted to.

Fitting of potential parameters

- Regarding fitting the parameters in a potential of type 2, there are two opposite extreme approaches:

  1. ***“Blind fitting” :*** choose a functional form and a set of data to which the parameters are fit. Then use some fitting routine to obtain a best fit to all the data.

  2. ***“Parameter choice by hand”:*** use reliable experimental or *ab initio* data of crucial data to set as many potential parameters as possible exactly, then fit only the remaining (if any) parameters. For instance, the equilibrium separation, binding energy and vibration frequency for a dimer can be used to fix all the 3 Morse potential parameters.

  - A pure approach 1 is dangerous in that quantities which are outside the original parameter set may obtain completely pathological values.
    - Example: some Si bulk potentials predict that the Si dimer is non-bonding.

  - Also, if some potential parameter happens to be insensitive to all quantities in the data set, the fit may give ridiculously small or large values for it, which may cause trouble elsewhere.

  - To obtain transferable potentials, approach 2 is thus usually to be preferred. On the other hand, if optimal precision in a limited set of systems (say, elastic properties of a perfect bulk crystal) is desirable, approach 1 may still be the better way to go.

  - Most authors use approaches somewhere between 1 and 2.

Fitting of potential parameters

- A functional form can sometimes be derived from experimental equations of state $P(V)$. Example: solid Ne and Ar:

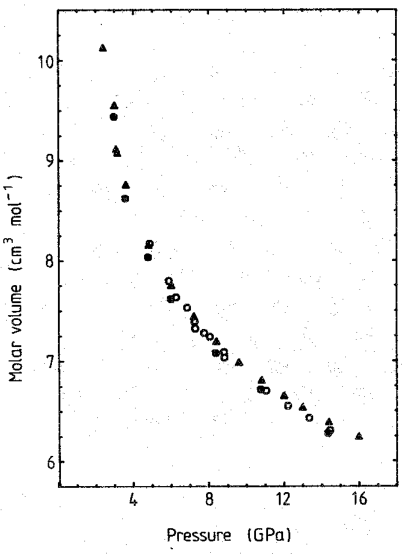


Figure 5. Pressure–volume isotherms of Ne at 293 K. ○, experimental data (after [19]); ●, CPMD (Lennard-Jones 6–12); ▲, CPMD (Siska *et al* [21]).

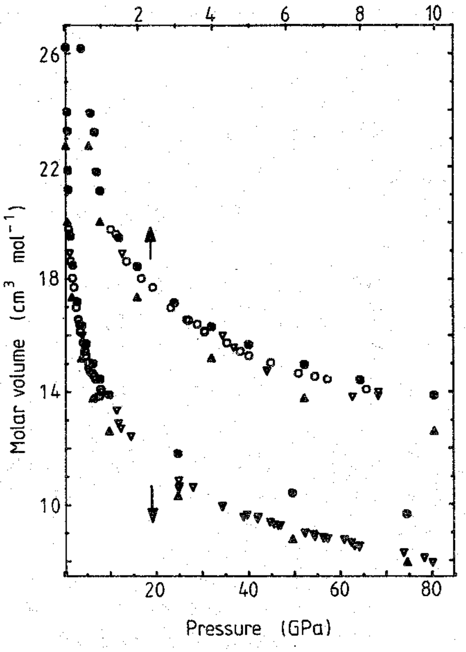


Figure 6. Pressure–volume isotherms of Ar at 293 K. The upper isotherm is in the pressure region 0 to 10 GPa and the lower one in the region 0 to 80 GPa. ○, experiment (after [19]); ▽, experiment (after [20]); ●, CPMD (Lennard-Jones 6–12); ▲, CPMD (exp–6 [20]).

Fitting of potential parameters

- Here is a short list of macroscopic, physical, properties which can and often are used to derive or fit interatomic potentials:

	Physical property	Atom-level property
mechanical	Crystal structure	Balance of atomic forces.
	Cohesive energy	Potential energy at the equilibrium atom positions
	Elastic constants $c_{\rho\sigma}$	Long-wavelength acoustic vibrations Elastic distortions of unit cell.
	Equation of state $P(V)$	Compression or expansion of material
	Neutron scattering	Phonon $\omega(\mathbf{k})$ in the Brillouin zone.
electric	Dielectric constant ε_∞	Electronic polarizability
	Dielectric constant ε_0	Polarizarization of electrons and lattice; long-wavelength optical vibration modes;
	Infrared absorption	Long-wavelength vibrations with a dipole moment.
	Raman scattering	Long-wavelength vibrations which change the polarizability.

  - Out of these, the first five depend purely on the mechanical properties of the material, and are relevant to almost all solids. The latter four involve electric properties and may or may not be relevant depending on what kind of materials and properties are studied.

Fitting of potential parameters

- **Crystal structure**:
  - The equilibrium crystal structure should be stable if one wants to describe any process where large atom displacements may occur (melting, surfaces, deposition, etc. etc.).
  - In equilibrium the force acting on every atom in the unit cell i should vanish:

$$\sum_j \mathbf{f}_{ij} = 0$$

  - Here the potential is only tested at a few r_{ij} values. (The smaller the crystal symmetry, the more values.)
  - Any potential has a minimum potential energy configuration, or many configurations with the same energy.
  - Example: Tersoff potential for Si [J. Tersoff, *Phys. Rev. B* **38** (1988) 9902.]

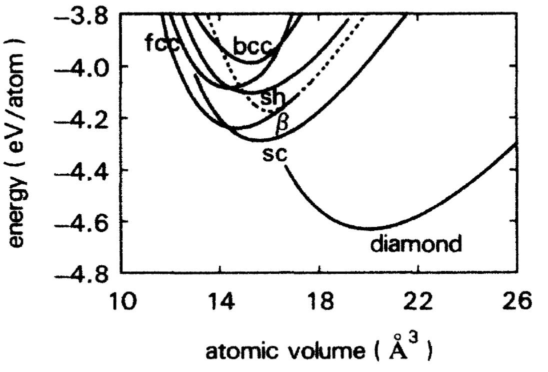


FIG. 3. Calculated cohesive energy vs volume per atom of silicon in the diamond, simple cubic (sc), β-tin (β), simple hexagonal (sh), bcc, and fcc structures. For β-tin, the dotted curve shows the result of the potential as given in Table I, while the solid curve results from taking $R=2.75$ Å and $D=0.1$ Å, as discussed in text.

Fitting of potential parameters

- Local stability is easy to achieve in a classical potential. But global stability (that is, that the real crystal structure is indeed the global minimum of the potential) may be surprisingly difficult.

- Even well-known authors make mistakes. For instance, the first Si potential of Tersoff [Tersoff, *Phys. Rev. Lett.* **56** (1986) 632.] was well motivated, well derived, and published in the best journal in physics. But the formation energy of the vacancy turned out to be negative, which means it did not have the right ground state structure...

- A good way to test the minimum energy: start from random atom positions, and quench the cell slowly enough so that it crystallizes. If the structure is the correct one, it probably is indeed the ground state. Unfortunately doing this may take forever.

- Another test: simulate a liquid and solid in equilibrium at the melting point, and check that the solid remains stable and the liquid recrystallizes to the same structure on slight cooling below T_{melt}.

Fitting of potential parameters

- **Cohesive energy** (E_{coh} = energy difference between free atoms and the solid):
  - Directly related to the potential minimum energy level
  - Often easy to get right exactly.

- **Elastic constants**[1] $c_{\rho\sigma}$
  - Related to deformation in the material

$$\mathbf{R}(\mathbf{r}) = \mathbf{r}' - \mathbf{r} = u_1(\mathbf{r})\hat{\mathbf{x}} + u_2(\mathbf{r})\hat{\mathbf{y}} + u_3(\mathbf{r})\hat{\mathbf{z}}$$

and to the external stress (pressure) σ:

$$\sigma_\rho = \sum_\sigma c_{\rho\sigma} e_\sigma$$

  - Voigt notation for ρ- and σ-indexing: $xx \to 1$, $yy \to 2$, $zz \to 3$, $yz \to 4$, $zx \to 5$, $xy \to 6$
  - Here the strain (crystal distortion) components e_{ij} are

$$e_{ii} = \frac{\partial u_i}{\partial x_i} \quad ; \quad e_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$$

---

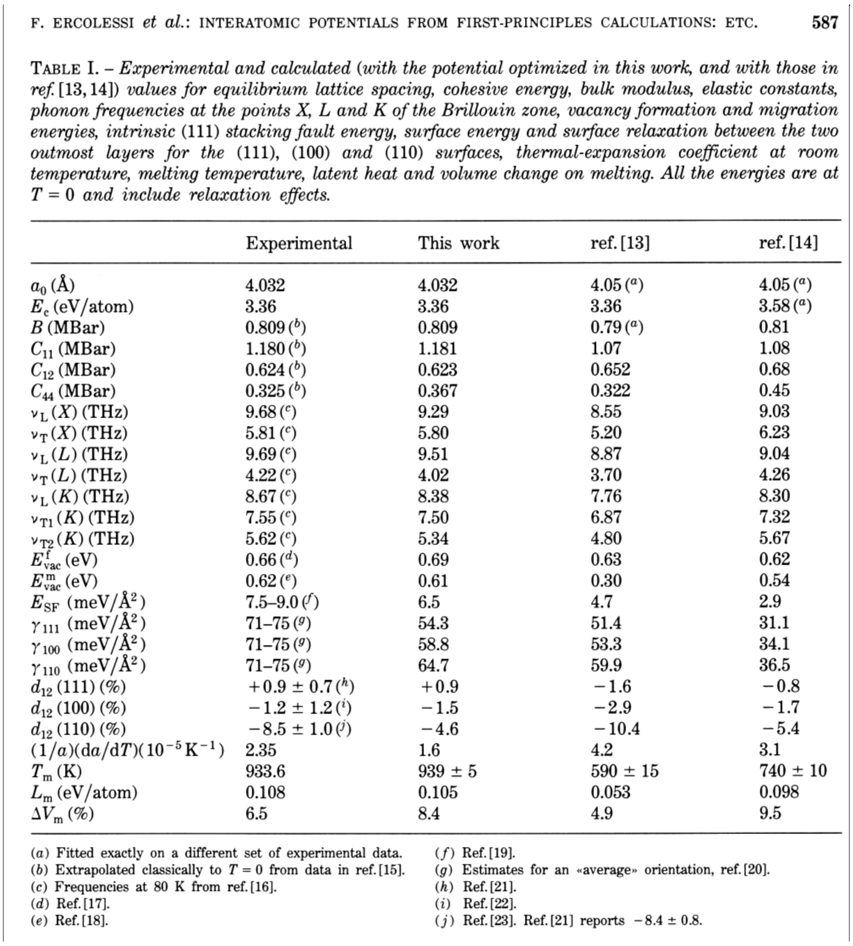
[1] See e.g. Kittel, *Introduction to solid state physics*, 7th edition, ch. 3.

Fitting of potential parameters

- The stress component σ_{ij} is the force which acts on the plane with the normal x_j in the direction x_i
- In principle there are 36 stress and strain components, but their number reduces to much smaller numbers in practice.
- For instance in a cubic crystal there are only three independent elastic constants $c_{11} = c_{xxxx}$, $c_{12} = c_{xxyy}$ and $c_{44} = c_{xyxy}$.

- Particularly important if there are deformations (compression, shear, melting) in the simulations. Also related to defect properties and the melting point ⇒ if we get the elastic constants about right we are already on a good way to a good potential.

- An example of an (unusually) good fit: F. Ercolessi, J. B. Adams, *Europhys. Lett.* 26 (1994) 583.



F. ERCOLESSI *et al.*: INTERATOMIC POTENTIALS FROM FIRST-PRINCIPLES CALCULATIONS: ETC. **587**

TABLE I. – *Experimental and calculated (with the potential optimized in this work, and with those in ref.* [13, 14]) *values for equilibrium lattice spacing, cohesive energy, bulk modulus, elastic constants, phonon frequencies at the points X, L and K of the Brillouin zone, vacancy formation and migration energies, intrinsic* (111) *stacking fault energy, surface energy and surface relaxation between the two outmost layers for the* (111), (100) *and* (110) *surfaces, thermal-expansion coefficient at room temperature, melting temperature, latent heat and volume change on melting. All the energies are at* $T = 0$ *and include relaxation effects.*

	Experimental	This work	ref. [13]	ref. [14]
a_0 (Å)	4.032	4.032	4.05 (a)	4.05 (a)
E_c (eV/atom)	3.36	3.36	3.36	3.58 (a)
B (MBar)	0.809 (b)	0.809	0.79 (a)	0.81
C_{11} (MBar)	1.180 (b)	1.181	1.07	1.08
C_{12} (MBar)	0.624 (b)	0.623	0.652	0.68
C_{44} (MBar)	0.325 (b)	0.367	0.322	0.45
$\nu_L(X)$ (THz)	9.68 (c)	9.29	8.55	9.03
$\nu_T(X)$ (THz)	5.81 (c)	5.80	5.20	6.23
$\nu_L(L)$ (THz)	9.69 (c)	9.51	8.87	9.04
$\nu_T(L)$ (THz)	4.22 (c)	4.02	3.70	4.26
$\nu_L(K)$ (THz)	8.67 (c)	8.38	7.76	8.30
$\nu_{T1}(K)$ (THz)	7.55 (c)	7.50	6.87	7.32
$\nu_{T2}(K)$ (THz)	5.62 (c)	5.34	4.80	5.67
E^{f}_{vac} (eV)	0.66 (d)	0.69	0.63	0.62
E^{m}_{vac} (eV)	0.62 (e)	0.61	0.30	0.54
E_{SF} (meV/Å^2)	7.5–9.0 (f)	6.5	4.7	2.9
γ_{111} (meV/Å^2)	71–75 (g)	54.3	51.4	31.1
γ_{100} (meV/Å^2)	71–75 (g)	58.8	53.3	34.1
γ_{110} (meV/Å^2)	71–75 (g)	64.7	59.9	36.5
d_{12} (111) (%)	$+0.9 \pm 0.7$ (h)	$+0.9$	-1.6	-0.8
d_{12} (100) (%)	-1.2 ± 1.2 (i)	-1.5	-2.9	-1.7
d_{12} (110) (%)	-8.5 ± 1.0 (j)	-4.6	-10.4	-5.4
$(1/a)(da/dT)(10^{-5}\,K^{-1})$	2.35	1.6	4.2	3.1
T_m (K)	933.6	939 ± 5	590 ± 15	740 ± 10
L_m (eV/atom)	0.108	0.105	0.053	0.098
ΔV_m (%)	6.5	8.4	4.9	9.5

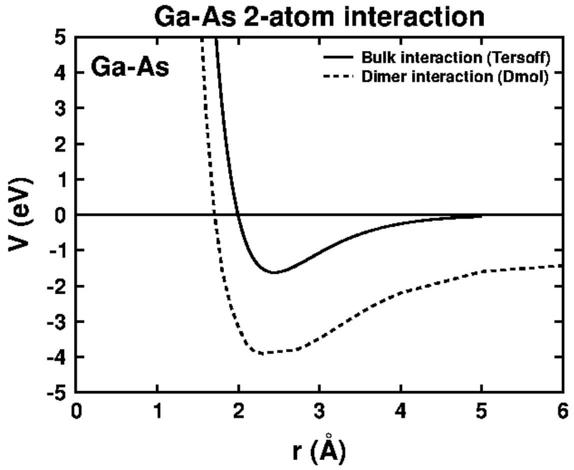
(*a*) Fitted exactly on a different set of experimental data.
(*b*) Extrapolated classically to $T = 0$ from data in ref. [15].
(*c*) Frequencies at 80 K from ref. [16].
(*d*) Ref. [17].
(*e*) Ref. [18].
(*f*) Ref. [19].
(*g*) Estimates for an «average» orientation, ref. [20].
(*h*) Ref. [21].
(*i*) Ref. [22].
(*j*) Ref. [23]. Ref. [21] reports -8.4 ± 0.8.

Weaknesses of pair potentials

- A pair potential can never describe well the directional properties of covalent bonds. For instance in the diamond/zincblende structure (C, Si, Ge, α-Sn, many compound semiconductors) the ideal angle between bonds = 109.47^{o} . Similarly, in almost all molecules the directional properties of covalent bonds is of crucial importance.
- Also longer-range angular dependence is completely neglected. For instance in the structure of polymers torsional terms are important. Also, recent calculations of BCC metals have shown that 4-particle interactions are about 50 % of the bond.
- Pair potentials also do not account for the environmental dependence. They predict that the strength of the two-atom bond is as strong in a dimer as inside a material, which almost never is true.

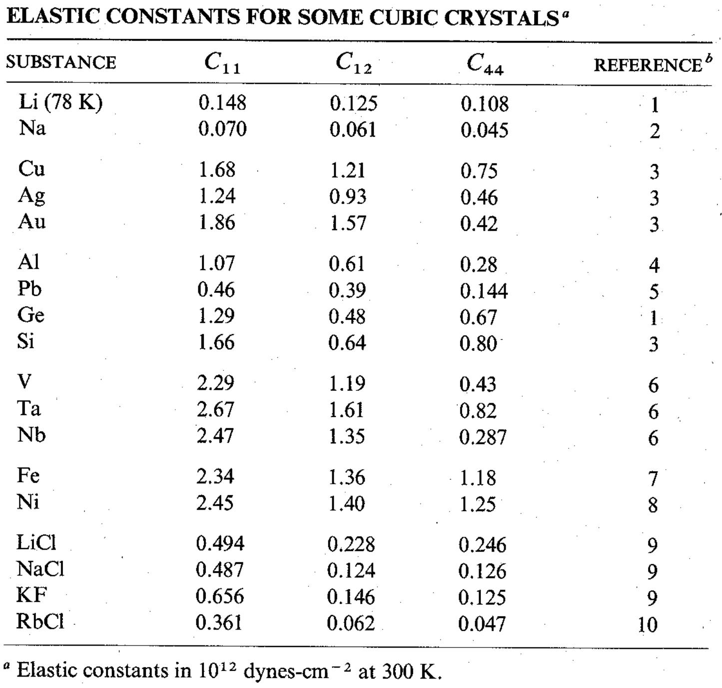
Weaknesses of pair potentials

- For instance the Ga-As interaction:



Weaknesses of pair potentials

- Moreover, a pair potential always predicts that the elastic constants $c_{12} = c_{44}$ for cubic crystals. but in reality:
- Also, vacancy formation energies are often completely wrong in pair potentials (see below).
- Pair potentials also usually give bad surface properties.
- *Summa summarum:* the pair potential approximation:
  - may work well close to equilibrium structure in many materials
  - is good for noble gases
  - is rather good for ionic compounds such as alkali halides
  - is rather bad for FCC and HCP metals
  - is terrible for covalently bonded materials



ELASTIC CONSTANTS FOR SOME CUBIC CRYSTALS[a]

SUBSTANCE	C_{11}	C_{12}	C_{44}	REFERENCE[b]
Li (78 K)	0.148	0.125	0.108	1
Na	0.070	0.061	0.045	2
Cu	1.68	1.21	0.75	3
Ag	1.24	0.93	0.46	3
Au	1.86	1.57	0.42	3
Al	1.07	0.61	0.28	4
Pb	0.46	0.39	0.144	5
Ge	1.29	0.48	0.67	1
Si	1.66	0.64	0.80	3
V	2.29	1.19	0.43	6
Ta	2.67	1.61	0.82	6
Nb	2.47	1.35	0.287	6
Fe	2.34	1.36	1.18	7
Ni	2.45	1.40	1.25	8
LiCl	0.494	0.228	0.246	9
NaCl	0.487	0.124	0.126	9
KF	0.656	0.146	0.125	9
RbCl	0.361	0.062	0.047	10

[a] Elastic constants in 10^{12} dynes-cm^{-2} at 300 K.

Source: Ashcroft-Mermin

- But for all these groups much better, and only slightly slower, models exist. These will be described later on this course.

Weaknesses of pair potentials

- Simple estimate of vacancy formation energy using pair potentials:

$$E^{\mathrm{f}}_{\mathrm{vac}} = E_{\mathrm{tot}}(\mathrm{vacancy}, N) - E_{\mathrm{tot}}(\mathrm{perfect}, N)$$

  - nearest neighbor pair potential, energy/bond= $V(r_{\mathrm{nn}}) \equiv \phi$
  - no relaxation
  - fcc structure ⇒ 12 neighbors

$$E_{\mathrm{tot}}(\mathrm{vacancy}, N) = \frac{1}{2}[(N-12)12\phi + 12(12-1)\phi] = 6(N-1)\phi$$

$$E_{\mathrm{tot}}(\mathrm{perfect}, N) = \frac{1}{2}N12\phi = 6N\phi$$

$$\Rightarrow E^{\mathrm{f}}_{\mathrm{vac}} = -6\phi = -E_{\mathrm{coh}}$$

  - However, ab initio calculations[1]:

Element	$\lvert E_{\mathrm{coh}} \rvert$ (eV)	$E^{\mathrm{f}}_{\mathrm{vac}}$ (eV)
V	5.31	2.1 ± 0.2
Nb	7.57	2.6 ± 0.3
W	8.90	4.0 ± 0.2

  - Relaxation: only minor effect (far less than 1 eV).

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[1] A. E. Carlsson, *Solid State Physics: Advances in Research and Applications,* **43** (1990) 1.

Molecular dynamics 2015

Exercises 5 to chapter 5: `mdmorse`: calculating the forces

1. **(12 p)** Write the subroutine **`GetForces()`** in the file **`forces.f90/.c`** in `mdmorse`. It should calculate the interaction between atoms with the Morse potential with the input parameters `morseD`, `morsealpha`, `morser0` giving the parameter values. Use the neighbour list created previously. The resulting subroutine should output the accelerations in the array `a(i)` and the potential energies in the array `Epot(i)`. The units are as described in `main.f90/.c`.

2. (**8p**) Using subroutines written for the previous exercises (your own or the official solutions on the web page) , and the **`GetForces()`** routine you should now have a working MD code. Demonstrate that the code works by

   (a) Running it with the test inputs for 10 ps. After the initial 50 fs, the total energy (column 6 on the "`ec`" output lines) should fluctuate or drift less than 0.01 eV over 10 ps with a time step `deltat` of 2 fs. The temperature (column 3) should fluctuate less than about 100 K from the average around 600 K.

   (b) Running it as above, but with a free surface in all dimensions. Now the temperature and energy will be different, but the total energy should still be conserved within about 0.02 eV after the first 1 ps. Describe what happens.

   Be careful not to use too small `nmovieoutput`, so that you don't fill up the disk!

   Return the exercise as the file `forces.f90` and a plot of the total energy vs. time and the temperature vs. time for cases (a) and (b).

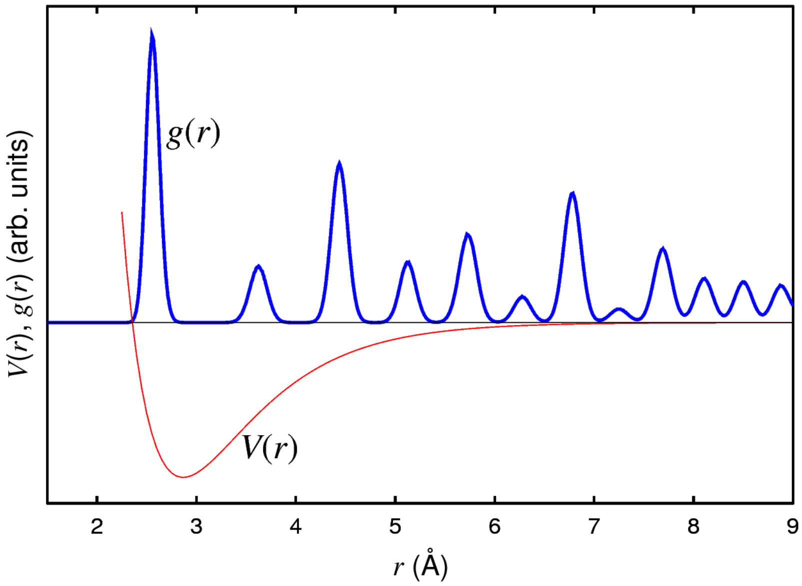
   After passing these tests your code is probably correct. (*But you can never be absolutely sure...*)

Molecular dynamics 2015

Exercises 6 to chapter 5: `mdmorse` : effect of cut-off radius and time step

1. (**10p**) Simulate a Cu fcc system with periodic boundary conditions and at temperature of 300 K for 10 ps using `mdmorse`. Do the simulations with the following values for the potential cut-off radius (`rpotcut` in `mdmorse`): $r_c = 4.0, 4.5, 5.0, 6.0, 8.0$ Å . Investigate the energy conservation by calculating the average fluctuation[1] in total energy. Remember to skip say 200 timesteps from the beginning of the simulation when calculating the averages. Why do the fluctuations behave as they do as a funtion of r_c? *Hint:* See the figure below, where the pair correlation function $g(r)$ of Cu at 300 K is plotted. Also plotted is the Morse potential used in the simulations.

Hints: Check that the temperature really is 300 K from your simulation output; no hassle with the infamous factor of two. For all simulations set the neighbourlist cut-off radius (`rskincut`) to 1 Å larger than the potential cut-off. The default value of `MAXAT*MAX-NEIGHBOURS` (100000) in `modules.f90/global.h` should be sufficient.



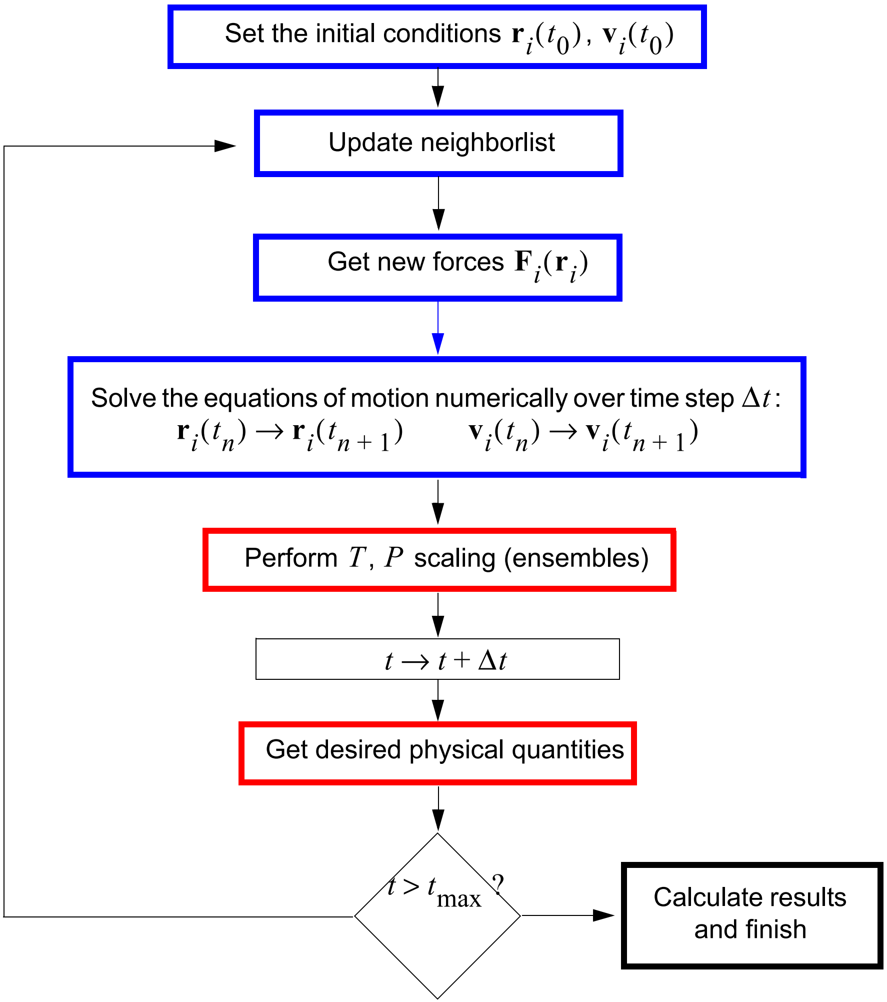
2. (**10p**) Check the effect of the time step `deltat` on energy conservation in the code `mdmorse`. Use time steps of 1, 3, 10, 30 and 100 fs to simulate thermal motion in Cu at 300 K over 10 ps. Plot the total energy as a function of time for each time step in the range in which it still behaves sensibly. What happens with the atoms for the largest time steps?

Return the appropriate figures and answers to the questions.

Remember that data visualization is your friend. Never just calculate the final results without first checking how the system configuration looks like (`dpc` and `rasmol`) and how the temperature and energies behave as a function of time.

---

[1] Variance or the like.



Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Solve the equations of motion numerically over time step Δt:
$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1}) \qquad \mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$

Perform T, P scaling (ensembles)

$t \rightarrow t + \Delta t$

Get desired physical quantities

$t > t_{\max}$?

Calculate results and finish

Theory behind atomistic simulations

[*main source: Allen-Tildesley*]

- An atomistic simulation (MD or MC) gives atom positions and velocities $\{\mathbf{q}_i, \mathbf{p}_i\}$
- $\{\mathbf{q}_i, \mathbf{p}_i\}$ (or in cartesian coordinates $\{\mathbf{r}_i, \mathbf{p}_i\}$) $\Rightarrow$ macroscopic quantities (This is what statistical physics is all about!)
- system Hamiltonian $H(\mathbf{q}, \mathbf{p})$
- equations of motion: $\dot{q}_k = \frac{\partial}{\partial p_k} H(\mathbf{q}, \mathbf{p}) \quad \dot{p}_k = -\frac{\partial}{\partial q_k} H$
- N particles $\Rightarrow$ the system state at any given time is a point Γ in a $6N$-dimensional **phase space**.
  - The evolution of the system from one point Γ to another is determined by the MD equations of motion or a Metropolis Monte Carlo simulation.

Theory behind atomistic simulations

- One point in phase space $\{\mathbf{q}_i, \mathbf{p}_i\} = \Gamma$

- Measured (macroscopic) quantity A_{obs} corresponding to (microscopic) physical quantity $A = A(\Gamma)$ from MD simulations ***as a time average:***

$$A_{\text{obs}} = \langle A \rangle_t = \langle A(\Gamma(t)) \rangle_t = \lim_{t_{\text{obs}} \to \infty} \frac{1}{t_{\text{obs}}} \int_0^{t_{\text{obs}}} A(\Gamma(t))dt$$

  - All practical simulations are of course over discrete steps, so the integral has to be rewritten

$$A_{\text{obs}} = \langle A \rangle_t = \frac{1}{\tau_{\text{obs}}} \sum_{\tau=1}^{\tau_{\text{obs}}} A(\Gamma(\tau))$$

and because an MD simulation often fluctuates strongly in the beginning, we skip the first, say, 100 time steps:

$$A_{\text{obs}} = \frac{1}{\tau_{\text{obs}} - 100} \sum_{\tau=101}^{\tau_{\text{obs}}} A(\Gamma(\tau))$$

Relation between simulations and statistical physics

- In MD a time average gives the experimental quantity A.
  - However: in statistical physics we use **ensembles**
    - a set of points Γ in phase space
    - the likelihood of system being in the $d\Gamma$ neigborhood of point Γ is given by the probability distribution $\rho(\Gamma)d\Gamma$
  - $\rho(\Gamma)$ depends on external conditions: (constant) NVE, NVT, NPT:

    e.g. with $\rho_{NVE}(\Gamma)$

    or generally, for any ensemble, $\rho_{\text{ens}}(\Gamma)$.

- In statistical physics the time average is replaced by an ensemble average (**why?**)
  - go through **all** the points $\{\mathbf{q}_i, \mathbf{p}_i\}$ in the ensemble phase space.
- In a Monte Carlo simulations the time average is replaced by going through a **large set** of points in phase space (using a Markov chain):

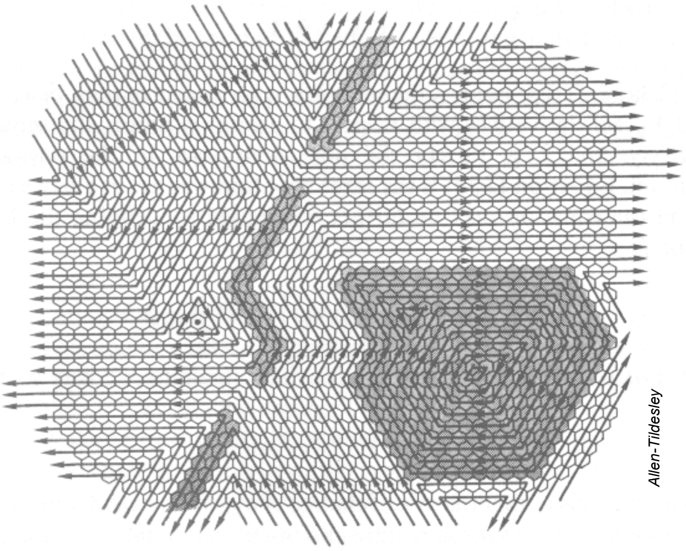
$$A_{\text{obs}} = \langle A \rangle_{\text{ens}} = \sum_{i=1}^{N_{\text{sim}}} A(\Gamma_i)\rho_{\text{ens}}(\Gamma_i)$$

- If $\rho_{\text{ens}}(\Gamma)$ is independent of time (thermodynamic equilibrium), and the system is **ergodic**

$$\langle A \rangle_t = \langle A \rangle_{\text{ens}}$$

Ergodicity

- In an ergodic system a long enough simulation will go through all points in phase space $\{\mathbf{q}_i, \mathbf{p}_i\}$.
- An example of a *non-ergodic* system (each hexagon represents one point phase space $\{\mathbf{q}_i, \mathbf{p}_i\}$):
  - In the darker area, the simulation moves in a close path, and can never get out of this area ⇒ the simulation does not test all of phase space, i.e. is non-ergodic.
  - In case there would be a single path which would go through the whole system, the system would be ergodic.



- Is it possible to prove that some system is ergodic? Not in the general case, and even for a given system it is usually very difficult in practice.
- In practice the system may not only have regions which are impossible to reach, but also regions which are surrounded by a high potential energy barrier so that reaching them in a finite simulation may be very unlikely (such a barrier is illustrated by the grey thin regions in the figure). This may distort the simulation averages badly.

Ergodicity

- A practical example:
  - Simulate diffusion in Cu at high temperature, around the melting point. In equilibrium the lattice has, say, 10 vacancies which cause diffusion at a rate of e.g. 1 atom/1 ps. Hence in a 100 ps simulation one gets about 1000 atom jumps, which appears to give a good time average of the diffusion constant.

    But: about once in a ns a Frenkel pair, that is a pair of one vacancy and one atom at an interstitial position, may be created. Because the interstitial moves very much faster than the vacancy, it can cause thousands of atom jumps before it recombines with some vacancy. Because the interstitial causes a huge lot of diffusion, its presence can completely change the diffusion constant which would have been obtained in 100 ps.

    So the system must be simulated for tens of ns's to get a reliable estimate of the diffusion coefficient - and if one does not realize the possibility of Frenkel pair formation, one would probably never notice this in a single 100 ps simulation. [Nordlund and Averback, *Phys. Rev. Lett.* **80** (1998) 4201]

  - ***To get reliable results one not only has to burn away computer time, but also understand the physics in the system well!***

Ergodicity

- Sometimes (in MC simulations) it is useful to use a weighting function $w_{\text{ens}}(\Gamma)$ to weight the ensemble and speed up getting the desired results:

$$\rho_{\text{ens}}(\Gamma) = \frac{w_{\text{ens}}(\Gamma)}{Q_{\text{ens}}}$$

$$Q_{\text{ens}} = \sum_{\Gamma} w_{\text{ens}}(\Gamma) \qquad \text{(partition function)}$$

$$\langle A \rangle_{\text{ens}} = \frac{\sum_{\Gamma} w_{\text{ens}}(\Gamma) A(\Gamma)}{\sum_{\Gamma} w_{\text{ens}}(\Gamma)}$$

  - MC integration: the flatter the function, the faster it is to obtain a precise average
  - Q_{ens} will depend on the macroscopic properties of the system.
  - Connection to thermodynamics: $\Psi_{\text{ens}} = -\ln Q_{\text{ens}}$ = thermodynamic potential
- In practice: set up the MC simulation Markov chain such that it generates points according to the desired weighting function.
  - A simple choice: $w_{\text{ens}}(\Gamma) = \rho_{\text{ens}}(\Gamma)$
  - How this is achieved in practice will be dealt with in the MC course.

Ergodicity

- So, to summarize the purpose of equilibrium simulations can be stated as:
  - go through phase space as efficiently as possible to get averages which correspond to experimentally observable quantities A_{obs}
  - molecular dynamics: $\langle A \rangle_t$
  - Monte Carlo: $\langle A \rangle_{\text{ens}}$ (importance sampling)
- In MD only the NVE ensemble is obtained by solving the ordinary Newton/Lagrange/Hamiltonian equations of motion. For the other ones, one has to generate equations of motion which behave according to the desired ensemble $\rho_{\text{ens}}(\Gamma)$

The most important ensembles

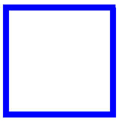
[*source: L.E. Reichl, A Modern Course in Statistical Physics*]

- As in thermodynamics, the ensembles are denoted by letters which indicate which physical quantities are conserved. The names are also the same.

1. Microcanonical (NVE)
2. Canonical (NVT)
3. Isothermal-isobaric (NPT)
4. Grand canonical (μVT)

- Here N is the number of atoms, V the system volume, T the temperature, P the pressure, and μ the chemical potential [cf. e.g. Mandl “Statistical physics” chapters 2 and 11].

- **Microcanonical: NVE constant (isolated)**



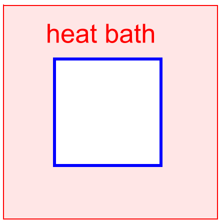
$$\rho_{NVE}(\Gamma) = \delta(H(\Gamma) - E)$$

$$Q_{NVE} = \sum_{\Gamma} \delta(H(\Gamma) - E) = \frac{1}{N!}\frac{1}{h^{3N}} \int d\mathbf{r}\, d\mathbf{p}\, \delta(H(\mathbf{r},\mathbf{p}) - E)$$

- Thermodynamical potential is the entropy: $\frac{S}{k_B} = \ln Q_{NVE}$.
- The δ function selects the states Γ where the total energy = E.
- Natural for MD in the sense that the total energy is conserved.

The most important ensembles

- **Canonical: NVT constant (closed but not heat-isolated)**



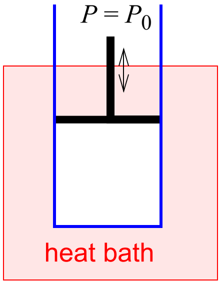
$$\rho_{NVT}(\Gamma) \propto \exp(-H(\Gamma)/k_B T)$$

$$Q_{NVT} = \sum_{\Gamma} \exp(-H(\Gamma)/k_B T) = \frac{1}{N!}\frac{1}{h^{3N}} \int d\mathbf{r}\, d\mathbf{p} \exp(-H(\mathbf{r},\mathbf{p})/k_B T)$$

- Thermodynamical potential is the Helmholtz free energy:

$$\frac{A}{k_B T} = -\ln Q_{NVT}, \quad A = E - ST$$

- **Isothermal-isobaric: NPT constant**



$$\rho_{NPT}(\Gamma) \propto \exp((-H(\Gamma) + PV)/k_B T)$$

$$Q_{NPT} = \sum_{\Gamma} \exp((-H(\Gamma) + PV)/k_B T) =$$

$$\frac{1}{N!}\frac{1}{h^{3N}}\frac{1}{V_0} \int d\mathbf{r}\, d\mathbf{p} \exp((-H(\mathbf{r},\mathbf{p}) + PV)/k_B T)$$

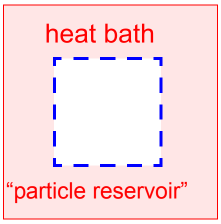
- Thermodynamical potential the Gibbs free energy:

$$\frac{G}{k_B T} = -\ln Q_{NPT}, \quad G = E - TS + PV$$

- In MD the volume has also to be made variable.

The most important ensembles

- **Grand canonical: μVT constant**



$$\rho_{\mu VT}(\Gamma) \propto \exp((-H(\Gamma)+\mu N)/k_B T)$$

$$Q_{\mu VT} = \sum_{\Gamma, N} \exp((-H(\Gamma)+\mu N)/k_B T) =$$

$$\sum_N \frac{1}{N!}\frac{1}{h^{3N}} \exp(-\mu N/k_B T) \int d\mathbf{r}\, d\mathbf{p} \exp(-H(\mathbf{r},\mathbf{p})/k_B T)$$

  - Thermodynamic potential is the grand potential:

$$\frac{-\Omega}{k_B T} = -\ln Q_{\mu VT}, \quad \Omega = E - TS - \mu N = -PV$$

  - Now the number of atoms is changing: we have to have an algorithm to add or remove particles [not trivial in most practical (condensed matter) systems].

- In the thermodynamic limit (system size $N \to \infty$) all the ensembles are equivalent (but the fluctuations around the average may not be).

Calculating thermodynamical quantities

- **Internal energy**, that is, total energy (in the `mdmorse` code `Etot`):

$$E = \langle H \rangle = \langle K \rangle + \langle U \rangle = \langle \sum_i \frac{|\mathbf{p}_i|^2}{2m_i} \rangle + \langle U(\mathbf{q}) \rangle$$

  - $U(\mathbf{q})$ is obtained directly from the potential energy calculation.

- **Temperature**

$$E_{kin} = \langle K \rangle = \frac{3}{2} N k_B T \quad \Rightarrow \quad T = \frac{2K}{3Nk_B} = \frac{1}{3Nk_B} \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{m_i}$$

  - So, on the average there is $k_B T/2$ of energy per degree of freedom, as the classical equipartition theorem predicts.

Calculating thermodynamical quantities

- **Pressure** (refer to Hamiltonian equations of motion):
  - Generalized equipartition theorem for atom positions:

$$\left\langle q_k \frac{\partial H}{\partial q_k} \right\rangle = k_{\mathrm{B}} T \quad \Rightarrow \quad -\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot (\nabla_{\mathbf{r}_i} U) \right\rangle = \frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i^{\mathrm{tot}} \right\rangle = -Nk_{\mathrm{B}} T;$$

- Divide the force into two components: $\mathbf{f}_i^{\mathrm{tot}} = \mathbf{f}_i^{\mathrm{ext}} + \mathbf{f}_i$

external pressure: $\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i^{\mathrm{ext}} \right\rangle = -PV$

internal virial: $W = -\frac{1}{3}\sum_{i=1}^{N} \mathbf{r}_i \cdot (\nabla_{\mathbf{r}_i} U) = \frac{1}{3}\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i$

$\Rightarrow \frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i \right\rangle + \frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i^{\mathrm{ext}} \right\rangle = -Nk_{\mathrm{B}} T$ which can be rewritten $\langle W \rangle - PV = -Nk_{\mathrm{B}} T$

$\Rightarrow$ desired pressure $PV = Nk_{\mathrm{B}} T + \langle W \rangle$

Calculating thermodynamical quantities

- Pair interaction $V(r)$ and periodic boundaries:

$$W = -\frac{1}{3}\sum_{i}\sum_{j>i} w(r_{ij}) ; \qquad w(r) = r_{ij}\frac{\mathrm{d}}{\mathrm{d}r_{ij}}V(r_{ij});$$

- Calculation in the force routine:

```
! dVdr is the derivative of V, i.e. the force
virial=virial+dVdr*(dx/r*dx+dy/r*dy+dz/r*dz)
```

• Calculating thermodynamical quantities

- **Thermodynamic potentials** (free energies)
  - Quantities which depend on the entropy
  - Energy/potential differences can be ‘easily’ calculated by integrating over a reversible path:

$$\left(\frac{A}{Nk_\mathrm{B}T}\right)_2 - \left(\frac{A}{Nk_\mathrm{B}T}\right)_1 = \int_{\beta_1}^{\beta_2}\left(\frac{E}{Nk_\mathrm{B}T}\right)\frac{d\beta}{\beta} = -\int_{T_1}^{T_2}\left(\frac{E}{Nk_\mathrm{B}T}\right)\frac{dT}{T}$$

$$\left(\frac{A}{Nk_\mathrm{B}T}\right)_2 - \left(\frac{A}{Nk_\mathrm{B}T}\right)_1 = \int_{\rho_1}^{\rho_2}\left(\frac{PV}{Nk_\mathrm{B}T}\right)\frac{d\rho}{\rho} = -\int_{V_1}^{V_2}\left(\frac{PV}{Nk_\mathrm{B}T}\right)\frac{dV}{V}$$

  - So one has to calculate a thermodynamic average for a large number of intermediate steps, then integrate over the path.
  - Calculating absolute values with the Frenkel-Ladd method:
    - Construct a potential energy which is dependent on a parameter λ: $U = U(\mathbf{r}, \lambda)$

Calculating thermodynamical quantities

$$\Rightarrow \frac{\partial A}{\partial\lambda} = -k_\mathrm{B}T\frac{\partial}{\partial\lambda}\left[\ln\int d\mathbf{r}\exp(-U(\mathbf{r},\lambda)/k_BT)\right]$$

$$= \frac{\int d\mathbf{r}\frac{\partial V}{\partial\lambda}\exp(-U/k_BT)}{\int d\mathbf{r}\exp(-U/k_BT)}$$

$$= \langle\frac{\partial U}{\partial\lambda}\rangle$$

- Construct U so that for $\lambda = \lambda_0$ the absolute value of A can be calculated analytically or numerically: e.g. an ideal gas or a harmonic lattice.
  - Then get the absolute value of A for any λ using:

$$A(\lambda) - A(\lambda_0) = \int_{\lambda_0}^{\lambda}\langle\frac{\partial U}{\partial\lambda}\rangle d\lambda$$

Calculating thermodynamical quantities

- Real potential function, for which we want A, is U_0
  - construct $U = U(\mathbf{r}, \lambda)$ to interpolate between U_0 and a harmonic lattice (Einstein's model) with

$$U(\mathbf{r}, \lambda) = U_0(\mathbf{r}) + \lambda \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{i0})^2$$

$$\Rightarrow \quad A(\lambda = 0) = A(\lambda) - \int_0^{\lambda} \langle \frac{\partial U}{\partial \lambda} \rangle d\lambda'$$

- At large values of λ we have harmonic lattice: e.g. Helmholtz free energy is:

$$A(\lambda) = \frac{3N\hbar\omega}{2} - 3Nk_B T \ln(1 - e^{-\hbar\omega/k_B T}) + O(1/\lambda)$$

and hence the free energy for our 'real' system U_0 is $A(\lambda = 0)$ and can be calculated by integrating over $(\partial U)/(\partial\lambda)$.
[Frenkel-Ladd, *J. Chem. Phys.* **81** (1984) 3188]

Calculating thermodynamical quantities

• Response functions

- How does the system react to a change in some thermodynamic variable?
- Some of the most important response functions:

constant volume heat capacity	$C_V = \left(\frac{\partial E}{\partial T}\right)_V$
constant pressure heat capacity	$C_P = \left(\frac{\partial H}{\partial T}\right)_P$
thermal expansion coefficient	$\alpha_P = V^{-1}\left(\frac{\partial V}{\partial T}\right)_P$
isothermal compressibility	$\beta_T = -V^{-1}\left(\frac{\partial V}{\partial P}\right)_T$
bulk modulus	$B = 1/\beta_T$
thermal pressure coefficient	$\gamma_V = \left(\frac{\partial P}{\partial T}\right)_V$

- Because $\alpha_P = \beta_T \gamma_V$ it is enough to get one of these three coefficients

Calculating thermodynamical quantities

- How can one get these from simulations?
  - Direct simulation
    - E.g. heat capacity C_V can be obtained by doing simulations at different temperatures, thus obtaining $E(T) \Rightarrow$

$$C_V(T) = \left(\frac{\partial E}{\partial T}\right)_V$$

  - From the fluctuations in the system (remember from basic thermodynamics that for a finite-sized system of N atoms, there ***should be*** fluctuations of the order of $\sqrt{N}$ in thermodynamic quantities such as T and P!)
    - E. g. C_V from a single simulation in the canonical ensemble:

$$\langle \delta H^2 \rangle_{NVT} = k_B T^2 C_V$$ (H is the momentaneous enthalpy)

  - Because $\langle \delta K \delta U \rangle_{NVT} = 0$, C_V can be separated into a kinetic and potential energy part:

$$\langle \delta H^2 \rangle_{NVT} = \langle \delta U^2 \rangle_{NVT} + \langle \delta K^2 \rangle_{NVT}$$

  - Kinetic energy part: $\langle \delta K^2 \rangle_{NVT} = \frac{3N}{2}(k_B T)^2 = \frac{3N}{2\beta^2}$ $\Rightarrow$ ideal-gas heat capacity $C_V^{\text{id}} = \frac{3}{2}Nk_B$.

Calculating thermodynamical quantities

- By combining these we get

$$\langle \delta U^2 \rangle_{NVT} = k_B T^2 \left(C_V - \frac{3}{2}Nk_B\right)$$

  - So we can calculate C_V solely from the fluctuations of the potential energy.
  - Similar fluctuation identities can also be derived for many other response functions (see e.g. Allen-Tildesley chapter 2.5.)
  - These identities really depend on the ensemble used.
    E.g. in the microcanonical ensemble:

$$\langle \delta K^2 \rangle_{NVE} = \langle \delta U^2 \rangle_{NVE} = \frac{3}{2}Nk_B^2 T^2 \left(1 - \frac{3Nk_B}{2C_V}\right)$$

Calculating thermodynamical quantities

- **Structural quantities**
  - Pair correlation function

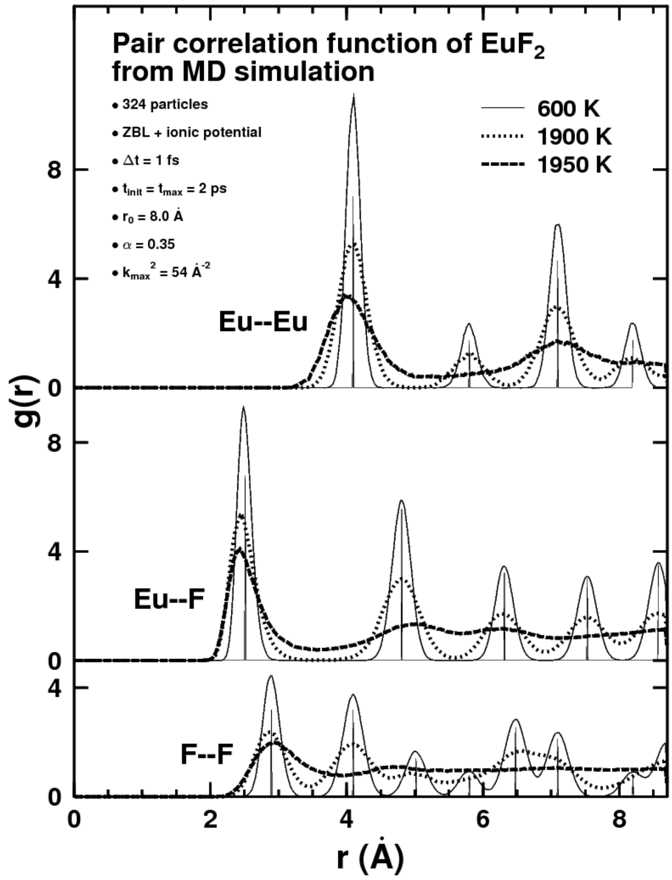
$$g_2(\mathbf{r}_i, \mathbf{r}_j) = g_2(r_{ij}) = g(r)$$

which tells at what distances atoms are from each other.

  - It can be calculated as

$$g(r) = \rho^{-2}\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r}_i)\delta(\mathbf{r}_j - \mathbf{r})\rangle$$
$$= \frac{N^2}{V^2}\langle \sum_i \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_{ij})\rangle$$

  - $g(r)$ gives information on the structure of the material. For instance melting:



Calculating thermodynamical quantities

- In practice it is of course not handy to use a delta function on a computer. So what is done instead is to collect statistics of what atom distances exist in some finite interval Δr:

```
integer :: stat(0:10000)

do i=0,10000
    stat(i) = 0
enddo

binwidth=0.01
do i=1,N
   do j=1,N
    if (i==j) cycle
    dx=x(j)-x(i)
    dy=y(j)-y(i)
    dz=z(j)-z(i)
    rsq=dx*dx+dy*dy+dz*dz
    r=sqrt(rsq)
    ir = int(r/binwidth+0.5)
    if (ir > 10000) ir=10000
    stat(ir) = stat(ir) + 1
   enddo
enddo
```

- Note: no boundary condition checks.

- The normalization factor $4\pi r^2 \Delta r$ can be added afterwards, when printing the statistics.

- In practice if N is small (say 100 or less) the statistics will be poor $\Rightarrow$ time averaging.

Calculating thermodynamical quantities

- $g(r)$ is also useful because the average of any pair function can be given in the form:

$$\langle a(\mathbf{r}_i, \mathbf{r}_j)\rangle = \frac{1}{V}\int d\mathbf{r}_i d\mathbf{r}_i g(\mathbf{r}_i, \mathbf{r}_j) a(\mathbf{r}_i, \mathbf{r}_j) \text{ or}$$

$$\langle A\rangle = \langle \sum_i \sum_{j>i} a(r_{ij})\rangle = \frac{1}{2}N\rho\int_0^\infty a(r)g(r)4\pi r^2 dr$$

- E.g. the energy (pair interaction $V(r)$) $E = \frac{3}{2}Nk_B T + 2\pi N\rho\int_0^\infty V(r)g(r)r^2 dr$

  or the pressure $PV = Nk_B T - \frac{2}{3}\pi N\rho\int_0^\infty w(r)g(r)r^2 dr$

Calculating thermodynamical quantities

- Structure factor in reciprocal $\mathbf{k}$-space (Fourier transformation of positions):

$$\rho(k) = \sum_{i=1}^{N} \exp(i\mathbf{k}\cdot\mathbf{r})$$

- The square of $\rho(k)$ gives the structure factor $S(k)$:

$$S(k) = N^{-1}\langle\rho(k)\rho(-k)\rangle,$$

  which can be measured with x-ray or neutron scattering

- This quantity can be shown to be related to $g(r)$ through a 3-dimensional Fourier transform:

$$S(k) = 1 + \rho\hat{g}(k) = 1 + 4\pi\rho\int_0^\infty \frac{\sin kr}{kr} g(r)r^2 dr$$

- Because $g(r)$ is a measurable quantity, it is often useful in testing how realistic a potential energy function is in describing some structure, especially a liquid or amorphous phase.

- However, this test is actually not all that sensitive to the detailed structure.

Calculating thermodynamical quantities

- Transport coefficients
  - The correlation between any two quantities A and B is

$$c_{AB} = \frac{\langle \delta A \delta B \rangle}{\sigma(A)\sigma(B)}$$
$$\sigma^2(A) = \langle \delta A^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2 \quad ;$$
$$\delta A = A - \langle A \rangle$$
$$0 \le c_{AB} \le 1$$

  - The time dependent correlation function $c_{AB}(t)$: A and B at different times, e.g. $A(t)$ and $B(0)$
  - Autocorrelation function $c_{AA}(t)$
  - Correlation time $t_A = \int_0^{\infty} c_{AA}(t) dt$
  - These give information on
    - the dynamics of the material
    - transport coefficients
    - can be related to experimental spectra by Fourier transformations

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Calculating thermodynamical quantities

- Transport coefficients: system response to an external disturbance $\rho(t) = \rho_{\mathrm{ens}} + \delta\rho(t)$
  - For instance diffusion coefficient: particle flux ↔ concentration gradient.
  - $\rho(t) \rightarrow$ time dependent averages.
  - Comparison to transport equations → transport coefficients.
  - Coefficients usually of the form $\gamma = \int_0^{\infty} \langle \dot{A}(t)(\dot{A}(0)) \rangle dt$
  - For a large time there also always exists an Einstein relation

$$2t\gamma = \langle (A(t) - A(0))^2 \rangle$$

Calculating thermodynamical quantities

- Some transport coefficients for the NVE-ensemble:
  - Diffusion constant $$D = \frac{1}{3}\int_0^\infty \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle dt$$
    - Simple form to evaluate: $$2tD = \frac{1}{3}\langle (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2 \rangle$$
  - Thermal conductivity $$\lambda_T = \frac{V}{k_B T^2}\int_0^\infty \langle j_i^\varepsilon(t) j_i^\varepsilon(0) \rangle dt,$$

$$2t\lambda_T = \frac{V}{k_B T^2}\langle (\delta\varepsilon_\alpha(t) - \delta\varepsilon_\alpha(0))^2 \rangle \text{, where}$$

$$\delta\varepsilon_\alpha = \frac{1}{V}\sum_i r_{i\alpha}(\varepsilon_i - \langle \varepsilon_i \rangle);$$

$$j_i^\varepsilon = \frac{\partial \delta\varepsilon_\alpha}{\partial t};$$

$$\varepsilon_i = \frac{p_i^2}{2m_i} + \frac{1}{2}\sum_{i \neq j} V(r_{ij})$$

Algorithms for simulating ensembles

[most material from Allen-Tildesley ch. 7.4]

- **Pure NVE**: see lectures 2-5
- **NVE-scaling** or constraint methods:
  - Often even in an NVE simulation one does some simple tricks to control temperature and/or pressure. This gives something of an NVT or NVP and NVE hybrid: T and P fluctuate, and the system does not behave as a true NVT or NVP ensemble in the thermodynamic sense. But on average T and P have the desired value. In true NVT or NPT algorithms it is possible to have T and P have exactly the desired value, and the simulation directly corresponds to the thermodynamic ensembles.
- **Temperature scaling**
  - Trivial scaling: force during every time step the system temperature to be exactly T. This may be a rather severe perturbation of the atom motion especially if there are only a few atoms. It suppresses the normal T fluctuations, and does still not correspond to a true NVT ensemble. But the error in ensemble averages usually is $O(1/N)$ so with a large number of atoms one may get away with it.

Algorithms for simulating ensembles

- The Berendsen method: essentially a direct scaling but softened with a time constant. [Berendsen *et al. J. Chem. Phys.* 81 (1984) 3684].
  - Coupling to heat bath, Langevin dynamics: $m\dot{v} = F - m\gamma v + R(t)$
  - Global coupling + ***local noise***
  - Replace the local noise by its average behvior in $\frac{\mathrm{d}E_\mathrm{k}}{\mathrm{d}t}$

$$\Rightarrow \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_\mathrm{bath} = 2\gamma(T_0 - T)$$

$$\Rightarrow m\dot{v} = F + m\gamma\left(\frac{T_0}{T} - 1\right)v$$

  - Let T_0 be the desired temperature, Δt the time step of the system and $\tau_T = 1/2\gamma$ the time constant of the control.

    In the Berendsen method in order to change the temperature in one timestep by $2\gamma\Delta t(T_0 - T) = \frac{\Delta t}{\tau_T}(T_0 - T)$ all atom velocities are scaled at every time step with a factor λ, where

$$\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T}\left(\frac{T_0}{T} - 1\right)} \quad \text{(*)}$$

  - Note: if $\tau_T > 100\Delta t$ then the system has natural thermal fluctuations about the average.

Algorithms for simulating ensembles

- The derivation above lacks a factor 2[1].
- Let's write the temperature behavior as $\frac{dT}{dt} = \frac{1}{\tau_T}(T_0 - T)$. From this we can solve $T(t)$ as

  $T(t) = T_0 + (T_i - T_0)e^{-t/\tau_T}$, where $T_i = T(0)$ is the initial temperature.
- On the other hand when we scale velocity $v \rightarrow \lambda v$ the change in the internal energy is $\delta E = (\lambda^2 - 1)\frac{3}{2}Nk_\mathrm{B}T$,
- Now the heat capacity is $C_V = \frac{\delta E}{\delta T}$. From this and from the differential equation of the temperature we get

  $\frac{\delta T}{\delta t} = \frac{1}{\tau_T}(T_0 - T) \Rightarrow \delta T = \frac{\delta t}{\tau_T}(T_0 - T)$.
- From the definition of heat capacity we obtain $C_V = \frac{\delta E}{\delta T} = \dfrac{(\lambda^2 - 1)\frac{3}{2}Nk_\mathrm{B}T}{\frac{\delta t}{\tau_T}(T_0 - T)}$.
- By solving λ from this we get $\lambda^2 = \frac{2C_V\delta t}{3k_\mathrm{B}N\tau_T}\left(\frac{T_0}{T} - 1\right) + 1$.
- Let's make the bold assumption that the heat capacity is given by the Dulong-Petit law: $C_V = 3Nk_\mathrm{B}$

---

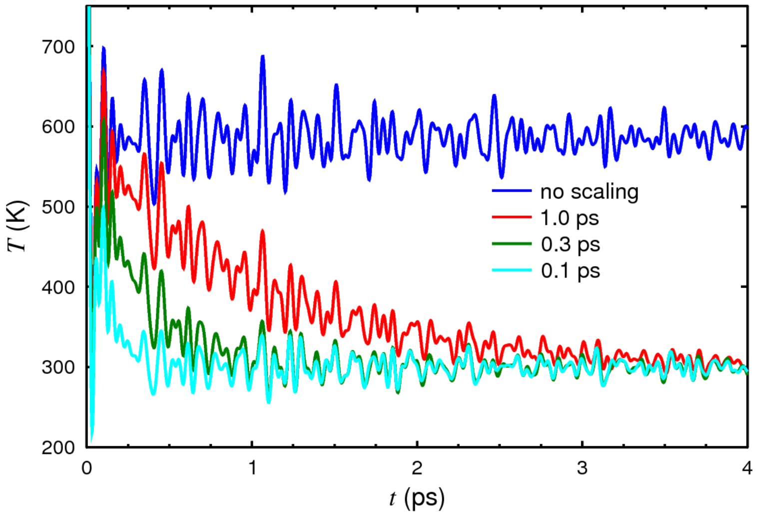
[1] Ideas for this derivation are from Kalevi Kokko's lecture notes at http://vanha.physics.utu.fi/opiskelu/kurssit/XFYS4416/

Algorithms for simulating ensembles

- Finally we obtain the expression for λ:

$$\lambda^2 = \frac{2\delta t}{\tau_T}\left(\frac{T_0}{T} - 1\right) + 1 . \quad \textbf{(**)}$$

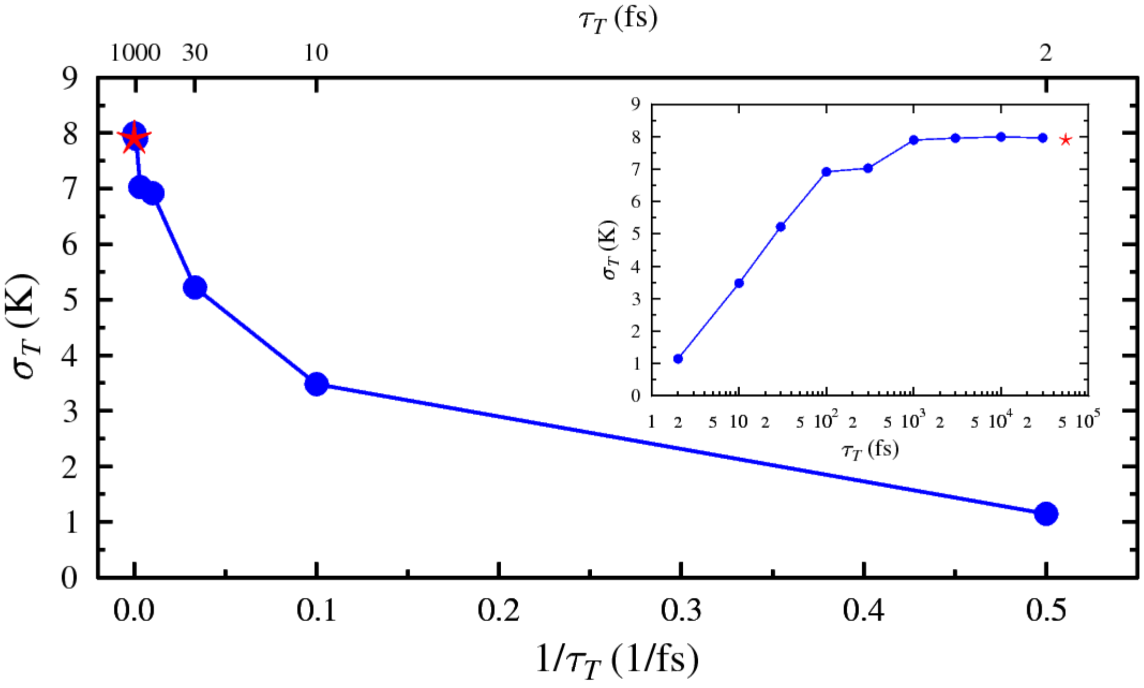
- As we shall see in exercise 7, this is the right expression in the sense that it reproduces the behavior dictated by the equation $\frac{dT}{dt} = \frac{1}{\tau_T}(T_0 - T)$.
- Effect of parameter τ_T on time development of T



FCC copper
Morse potential

Algorithms for simulating ensembles

- ... and on T fluctuations



simulation time = 50ps

first 10ps skipped

★ : simulation for $\tau_T = \infty$, i.e. no temperature control

Algorithms for simulating ensembles

• Pressure scaling (Berendsen)

- Pressure is put to a desired value by changing the cell size.
  - If the desired pressure is P_0 and τ_P is the time constant, the scaling factor is

$$\mu = \sqrt[3]{1 - \frac{\beta \Delta t}{\tau_P}(P_0 - P)}$$

where β is the isothermal compressibility of the system = 1/bulk modulus.

  - β only occurs in the division over the time constant τ_P it is just a factor which makes the typical time constant values roughly independent of the material.
  - Scaling implemented by changing all atom positions x and the system size S every time step

$$x(t + \Delta t) = \mu x(t)$$
$$S(t + \Delta t) = \mu S(t)$$

  - Also the system volume V changes:

$$V(t + \Delta t) = \mu^3 V(t)$$

  - Pressure scaling done after the solution of the equations of motion
  - $\tau_P > 100 \Delta t$

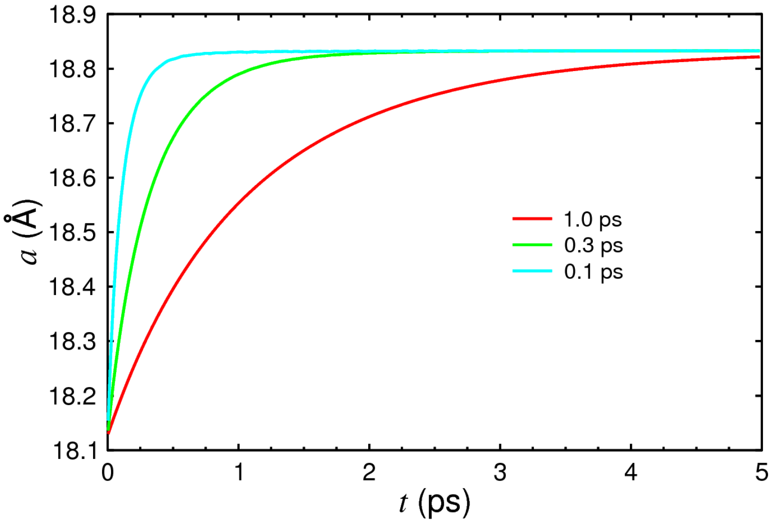
Algorithms for simulating ensembles

- Another (better) way to derive μ:
  - We want $\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{1}{\tau_P}[P_0 - P(t)]$ **(*)**
  - Volume scaling $V \rightarrow \mu^3 V$. Definition of compressibility: $\beta = -\frac{1}{V}\frac{\partial V}{\partial P} \Rightarrow \frac{\partial P}{\partial V} = -\frac{1}{V\beta}$.
  - Now $\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{\mathrm{d}P}{\mathrm{d}V}\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{1}{V\beta}\frac{(\mu^3 - 1)V}{\Delta t} = \frac{1 - \mu^3}{\beta \Delta t}$.
  - From this and **(*)** we get $\frac{1 - \mu^3}{\beta \Delta t} = \frac{1}{\tau_P}[P_0 - P(t)]$, from which we solve μ:

$$\mu^3 = 1 - \frac{\beta \Delta t}{\tau_P}[P_0 - P(t)]$$

Algorithms for simulating ensembles

- Effect of parameter τ_P



- The Berendsen scaling can be used to control T and P. If the system is in equilibrium the total energy E should still be conserved, but if phase transitions, such as melting occur, E does not necessarily stay conserved until equilibrium is reached again.

- In the Berendsen method P, T, V and E_{pot} all fluctuate, and because the time constants τ have to be fairly large it can take quite a while to reach a desired pressure or temperature.

- But in equilibrium and with large enough time constants, the method gives quite realistic fluctuations in T and P. And it is almost as trivial to implement as direct scaling. Hence it is much to be preferred over direct scaling.

Algorithms for simulating ensembles

- True NVT algorithms

- **The Andersén method** [H. C. Andersén, *J. Chem. Phys.* **72**, 2384 (1980)].
  - Give the atom with some probability a new velocity which corresponds to a desired heat bath temperature T_0
  - Physical interpretation clear: connection to external heat bath
  - Suitable for calculating thermodynamic averages, but not for looking at atomic processes in detail, since the random velocity is obviously an unphysical perturbation on the motion of a single atom.

- **Nosé-Hoover-method** [W. Hoover, *Phys. Rev. A* **31**, 1695-1697 (1985).]
  - A fictional degree of freedom s which has its own kinetic and potential energy is added to the system, and this degree of freedom controls the temperature. The system total energy, i.e. Hamiltonian:

$$H = \sum_i \frac{\boldsymbol{p}_i}{2m_i} + V(\boldsymbol{q}_i) + \frac{Q}{2}p_s^2 + qkT\ln s$$

where p_s is the momentum associated with the degree of freedom.

Algorithms for simulating ensembles

- Now the Hamiltonian equations of motion become:

$$\frac{d\boldsymbol{q}_i}{dt} = \frac{\boldsymbol{p}_i}{m_i}; \qquad \frac{d\boldsymbol{p}_i}{dt} = -\frac{dV}{d\boldsymbol{q}_i} - p_s\boldsymbol{p}_i, \qquad \frac{dp_s}{dt} = \left(\sum_i \frac{\boldsymbol{p}_i}{m_i} - gkT\right)/Q$$

- These can be solved with some suitable algorithm.
- Q is a fictional mass related to the extra degree of freedom, which describes the rate at which the temperature changed.
  - Nosé suggested $Q \sim gk_B T$ where g is the number of degrees of freedom in the system, typically $6N$. For large Q the connection to the heat bath weakens, and for small Q the energy E may oscillate too much.

- **Nosé-Hoover chains** [Tobias, Martyna, Klein, J. Phys. Chem. **97** (1993) 12959]
  - Also control the new degree s of freedom with another Nosé-Hoover-algorithm and so forth, i.e. form a chain of these.
  - At least in simulations of proteins this can give a very good temperature control.
  - “Massive” Nosé-Hoover-chain: add a Nosé-Hoover thermostat chain to every degree of freedom (!)
    - Advantage: as Nosé-Hoover, but in addition very efficient in equipartitioning the energy and thus getting the system into equilibrium. Disadvantage: even more coding

---

Algorithms for simulating ensembles

- True NPT algorithms
- **Andersén pressure control** [H. C. Andersén, *J. Chem. Phys.* **72**, 2384 (1980)]
  - The cell size V a dynamic variable, but the system shape may not change. The size is controlled by a fictional piston which has a mass Q (in units of m/l^4). The kinetic and potential energy of the piston are:

$$E_{\mathrm{kin}\,V} = \frac{1}{2}Q\dot{V}^2 \quad \text{and} \quad E_{\mathrm{pot}\,V} = PV$$

and if the atom positions $\mathbf{r}$ and velocities $\mathbf{v}$ are written in reduced units s such that $r = V^{1/3}s$ and $v = V^{1/3}\dot{s}$ we get the equations of motion

$$\ddot{\boldsymbol{s}} = \frac{\boldsymbol{f}}{mV^{1/3}} - \frac{2}{3}\dot{\boldsymbol{s}}\frac{\dot{V}}{V}$$

$$\ddot{V} = \frac{P_t - P}{Q}$$

where f are the forces acting on atoms, P_t is the momentaneous pressure and P the desired pressure.

Algorithms for simulating ensembles

- **Parrinello-Rahman-pressure control** [Parrinello and Rahman, *J. Appl. Phys.* 52 (1981) 7182]
  - This method also allows a variable simulation cell shape, that is, the angles between the axes do not have to be 90°.
  - The cell size and shape is given by vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$. If we form a 3×3-matrix $\mathbf{h}$ out of these the atom positions $\mathbf{r}$ can be written in the form
$\mathbf{r} = \mathbf{h}\mathbf{s}$.

    where $\mathbf{s}$ is an ordinary vector.
  - The equations of motion can be derived to be:

$$\ddot{s}_i = -\sum_j \frac{dV}{dr}\frac{1}{m_i r_{ij}}(s_i - s_j) - \frac{\dot{\mathbf{G}}}{\mathbf{G}}\dot{s}$$

$$W\ddot{\mathbf{h}} = (\mathbf{P} - p\mathbf{I})\sigma - \mathbf{h}\Sigma$$

    where $\mathbf{G} = \mathbf{h}^{\mathrm{T}}\mathbf{h}$, σ is a tensor which defines reciprocal space, and $\mathbf{P}$ is the generalized 3×3 pressure tensor:

$$\mathbf{P} = \frac{1}{V}\left[\sum_i m_i \mathbf{v}_i \mathbf{v}_i - \sum_i \sum_{j > i} \frac{1}{r_{ij}} \frac{\mathrm{d}u}{\mathrm{d}r_{ij}} \mathbf{r}_{ij} \mathbf{r}_{ij}\right].$$

Algorithms for simulating ensembles

- The diagonal elements of $\mathbf{P}$ are the pressures in x, y and z, the other elements are shear elements.
- The hydrostatic “ordinary” pressure $P = (\mathrm{tr}\mathbf{P})/3 = (P_{11} + P_{22} + P_{33})/3$.
- Σ is a quantity which depends on the external pressure tensor $\mathbf{S}$:

$$\Sigma = \mathbf{h}_0^{-1}(\mathbf{S} - p)\mathbf{h}_0^{\mathrm{T}-1}\Omega_0$$

  where $\mathbf{h}_0$ and Ω_0 are the original (reference) shape and volume of the system.
- W is a fictional “mass” which is used to control the rate of change of the pressure (compare with Q in the NVT algorithms above).

Algorithms for simulating ensembles

- This allows us to simulate a system which changes shape, for instance a cubic to hexagonal phase transformation.

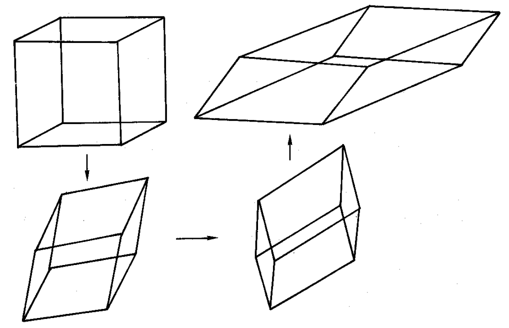
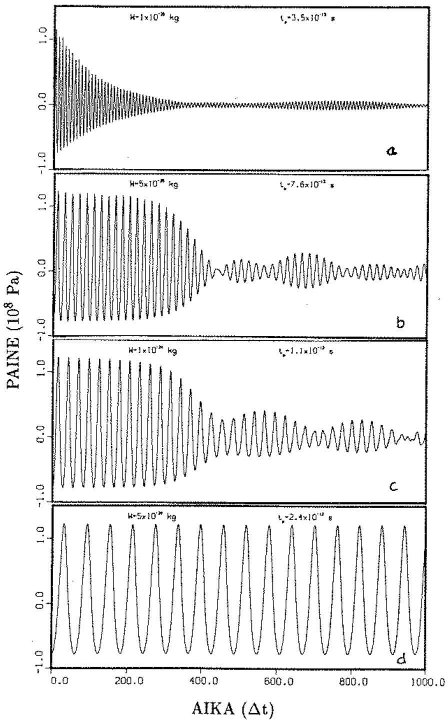


Fig. 7.3 Changing box-shape.

Source: Allen-Tildesley

- An example of the effects of the mass parameter Q:A Lennard-Jones-system (Ne); T=0.1 K; constant pressure-MD:



by Hannu Häkkinen

Kuva 4.1 *Massaparametrin W vaikutus paineen fluktuaatioihin. Aika–askeleen Δt pituus on eri ajoissa vaihdellut välillä 30 – 40 fs. t_p on painevärähtelyn lyhimmän jakson pituus.*

Algorithms for simulating ensembles

- µVT-methods
  - Chemical potential µ stays constant, number of atoms fluctuates
  - Rarely used in MD, more often in MC simulations where it is more natural to add and remove atoms from the system.
    - An alternative to adding or removing atoms is to add or remove “control volume”.
  - In condensed matter simulations the problem is that just adding an atom on a random place can easily lead to completely unphysical configurations.
  - Also adding or removing control volume without distrorting the system state too much may be tricky.
  - If you need this, see e.g. [Lynch, Pettitt: *J. Chem. Phys.* **107** (1997) 8594] or [Heffelfinger, *J. Chem. Phys.* **100** (1994) 7548].

Algorithms for simulating ensembles

- What T and P control to use?

- For T or P scaling: Berendsen is fast to implement, and does work well provided the time constants are large enough.

- If one wants accurate T control or needs to do NVT thermodynamic averaging, one of the Nosé-Hoover methods is probably best

- For orthogonal box *NPT* simulations: Andersén

- If one wants needs to deal with shear pressure or changes in crystal structure ⇒ Parrinello-Rahman

Other types of MD simulations

- **Non-equilibrium MD (NEMD)**
  - Any MD simulation of a system which is not in thermodynamic equilibrium.
  - Usually some perturbative term is added to the equations of motion.
  - For instance for simulating viscosity, heat conductivity and atomic diffusion there are special NEMD algorithms.
  - At its simplest, the perturbation can be an external force acting on some of the atoms.
  - The external force heats the system up, which can be compensated by temperature control.

- **Brownian dynamics or Langevin dynamics**
  - Random forces are let to act on some atoms some of the time. This can be useful e.g. in speeding up infrequent events.
  - This can also correspond to e.g. a large protein molecule in a liquid solvent. If the protein atoms do not react with the solvent atoms, and the solvent atoms are not interesting in themselves, their effect on the protein can be thought to reduce to random Langevin forces.

Other types of MD simulations

• Multiple time step methods

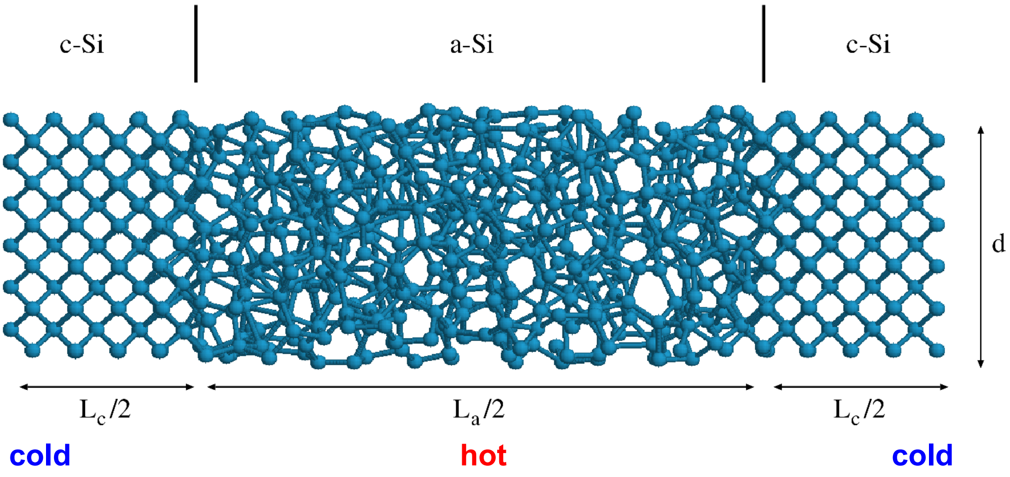
- In these methods the simulation is sped up by using different time steps for different atoms or parts of the system.
- A simple example of where this may be useful: a molecule which has light and much heavier particles. The light particles move much faster, so their motion can be simulated with a short time step Δt_1 and the heavy ones with a longer time step Δt_2.
- Another possibility: count near interactions acting on atom *i* with a short time step Δt_1 and those farther away with a longer one Δt_2. In here, we assume the movement of the atoms far away is so small that they do not move significantly with respect to atom i during the shorter time Δt_1.

• MD far from equilibrium

- Many processes of modern interest involve physical interactions which occur very far from thermodynamic equilibrium.
- E.g. two nanoparticles colliding in vacuum, or an energetic ion from an accelerator hits a material.
  - In both cases very violent interactions occur over ps timescales, and the surrounding medium does not have time to equilibrate the system into anything close to thermodynamic equilibrium during the time when the interesting processes occur.
- Simulating such a system is simple: simply use ordinary NVE with no T or P scaling.
  - But watch out for possible finite size effects!

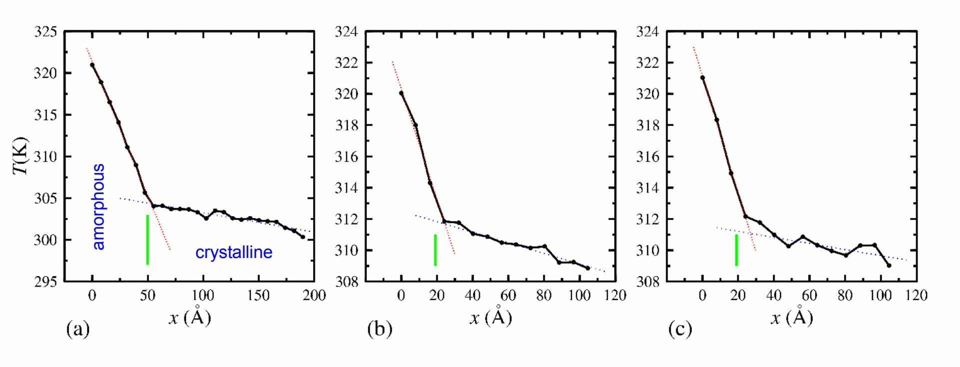
Other types of MD simulations

- An example of NEMD: heat conduction in crystalline and amorphous Si [von Alfthan *et al.*, *MRS Symposium Proceedings,* 703 (2002) V6.2.1]
- Straightforward way: impose a T gradient $\Rightarrow$ heat flux $J \Rightarrow k = -J/\frac{\mathrm{d}T}{\mathrm{d}x}$.
  - Problems: large fluctuations in $J \Rightarrow$ large dT/dx needed.



Other types of MD simulations

- Another way [Müller-Plathe, *J. Chem. Phys.* **106** (1997) 6082.]: impose heat flux by exchanging particle velocities between hot and cold parts of the system
  - Flux 'exact', controlled by exchange interval
- dT/dx's for different simulation system sizes: (a) $L_c = 296\ \text{Å}$, $L_a = 100\ \text{Å}$, $d = 32\ \text{Å}$ (b) $L_c = 187\ \text{Å}$, $L_a = 38\ \text{Å}$, $d = 16\ \text{Å}$ (c) $L_c = 187\ \text{Å}$, $L_a = 38\ \text{Å}$, $d = 32\ \text{Å}$



System	k_a (W/mk)	k_c (W/mk)
(a)	0.93	13
(b)	0.85	9
(c)	0.80	15

- Results for c-Si size dependent, moreover experimental $k_c = 160\ \text{W/mK}$!
  - Phonon mean free path in c-Si ~ 1000 Å
- Results for k_a reasonable.
- No thermal boundary resistance observed.

Molecular dynamics 2015

Exercises 7 to chapter 6: `mdmorse` : T control
return date Wed 29.10., exercise session Fri 31.10. *(Note the exceptional times due to mid-term break.)*

1. (10p) Simulate the distribution of the velocity v of atoms in Cu at 300 K. Make a histogram of the velocities obtained, and compare with the analytical Maxwell-Boltzmann distribution [see e.g. Mandl, Statistical Physics, 2nd ed., equation 7.59a]. Plot the simulated and analytical distribution in the same figure, both using a linear and logarithmic scale on the y axis. Comment on the agreement of the two distributions.

Hint: use the actual (rather than desired) average temperature of your simulation run in the comparison.

Return the exercises as the plots or data requested (in ps or png format) and an answer to the questions asked.

2. (10 p) Implement Berendsen temperature control into `mdmorse`.

Use the readin parameters `btctau` and `desiredT` for this. The first one is the temperature control time constant, and the second one the desired temperature towards which the temperature is taken. Implement the change so that the control is not performed at all if `btctau=0.`

Test the control by simulating morse Cu with the default inputs but using

`desiredT=0.0, initialT=300.0` and `btctau=1000.0.`

How long does it take until the cell temperature has decreased below 10 K? How about when running with `btctau=100.0`?

Return the exercise as the modified subroutines and answers to the questions.

Molecular dynamics 2015

Exercises 8 to chapter 6: `mdmorse` : P control

1. (12 p) Implement Berendsen pressure control into `mdmorse`.

Use the read-in parameters `bpctau`, `desiredP` and `bpcbeta` into the code. The first one is the pressure control time constant τ_P, the second one the desired pressure P, towards which the pressure is controlled, and the third one the compressibility β (1/bulk modulus) of the material. Implement the change so that the control is not used at all if `bpctau=0`. Implement a pressure/virial calculation in the force routines, and then the control in the main routine. Use kbar as the external pressure unit.

Return the modified subroutines. Mark the pressure-related modifications in the code with comments with the string “`bpc`”.

Test your code in the following way: Set $T = 300\ \mathrm{K}$ and $P = 0$. Find the equilibrium box size for the system by simulating 10 ps and using $\tau_T = 300\ \mathrm{fs}$ and $\tau_P = 300\ \mathrm{fs}$. Then perform two simulations where the box size (in file `mdmorse.in`) and the coordinates of atoms (in file `atoms.in`) are scaled 2% up and down (i.e. scaled by 1.02 and 0.98) from the equilibrium values you obtained from the first simulation. If your code works then all the three simulations should yield the same final box size and the instantaneous pressure fluctuating around zero. If your system explodes try using a longer time constant τ_P.

Return figures of the box size and instantaneous pressure as a function of time for all three simulations.

2. (8 p) Determine the thermal expansion coefficient of our copper model near NTP by simulating the system in constant pressure $P = 1\ \mathrm{atm} = 0.001013\ \mathrm{kbar}$[1] and at temperature range 200-400 K for 10-20 ps. Use the canonical value 5.0 Å for cut-off radius. Remember that the thermal expansion coefficient (in constant pressure) is defined by

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P .$$

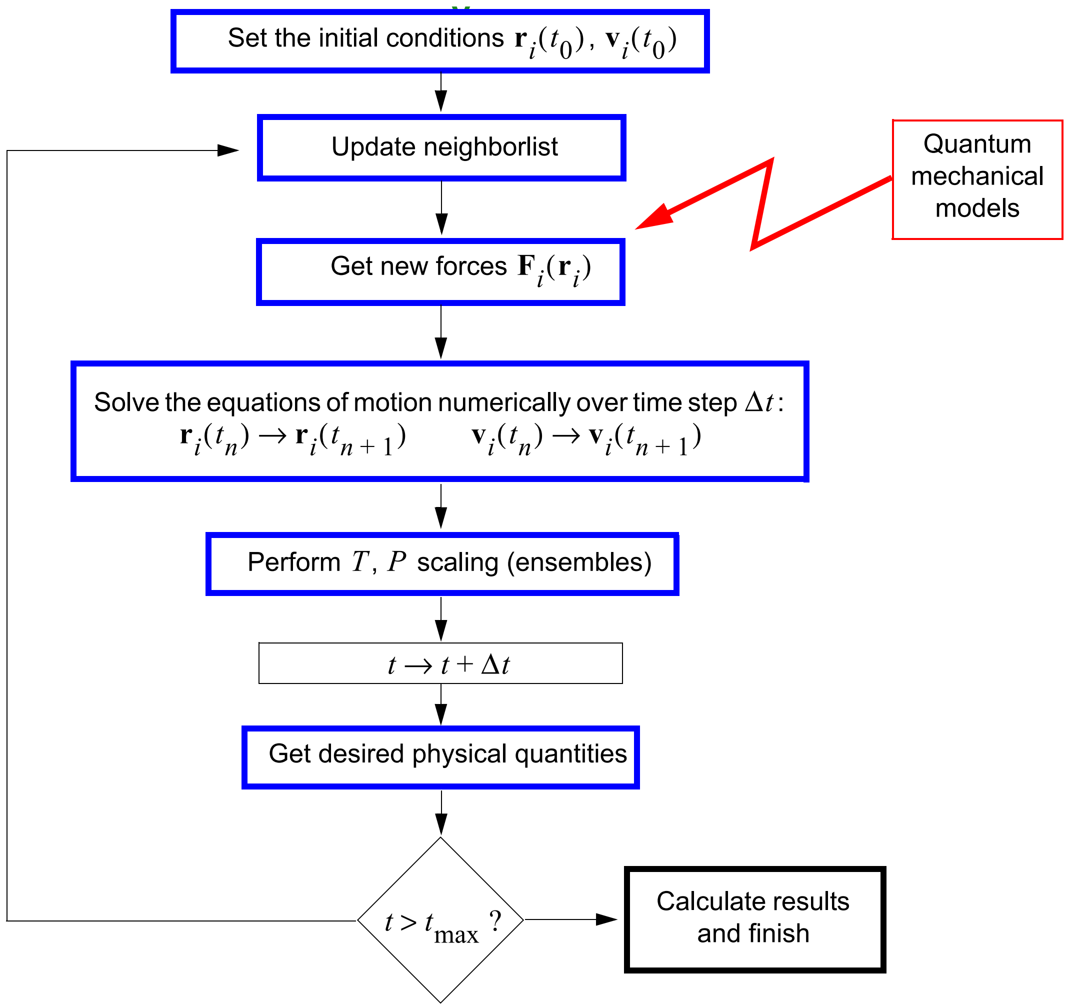
As always, when calculating averages from simulation data check how many points you have to skip from the beginning before starting to collect the average by plotting e.g. the system volume as a function of simulation time.

Compare your result to the literature value.

Return the curve $a_0(T)$ as a figure, explanation how you got α_P and of course its value.

---

[1] Well, the results for $P = 0$ and $P = 1\ \mathrm{atm} = 0.001013\ \mathrm{kbar}$ are practically the same.



Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Quantum mechanical models

Solve the equations of motion numerically over time step Δt:
$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1})$ $\mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$

Perform T, P scaling (ensembles)

$t \rightarrow t + \Delta t$

Get desired physical quantities

$t > t_{\mathrm{max}}$?

Calculate results and finish

Atomistic interaction models

- The true interaction energy between N nuclei and I electrons could be obtained by solving the Schrödinger equation for the system comprising the $N + I$ bodies.
  - Assumes: interactions between the nucleons neglected
  - This is also assuming relativistic effects can be ignored
  - Time-dependent Schrödinger equation: dynamics without MD alogrithm

Almost always true

Not always true for heavy elements

- But solving the full equation is extremely expensive computationally, and hence one always has to resort to various levels of approximation
- Term "***ab initio***" or "***first principles***" much used in this context to mean methods ***with no empirical input***
  - But may have several, even dubious, approximations!
  - semi-empirical= some empirical input used in choice of parameters or model

Model	Type	Scaling	N_{max}
Full solution of Schrödinger equation	quantum mechanical, *ab initio*	$O(e^N)$	1
HF (Hartee-Fock)	quantum mechanical, *ab initio*	$O(N^{4-8})$ $O(N)$	50
DFT (density functional theory	quantum mechanical, not always *ab initio*	$O(N^3)$ $O(N)$	1000
TB (Tight-binding)	quantum mechanical (often semiempirical)	$O(N^3)$ $O(N)$	1000 10000
MBP (Many-body potential)	classical, semiempirical	$O(N)$	10^8
PP (Pair potential)	classical, semiempirical	$O(N)$	10^9

Atomistic interaction models

- $O(N)$ variants of all classes of methods
  - The quantum mechanical $O(N)$ methods new $\Rightarrow$ work (so far) well only in a limited set of problems

- Prefactor in the efficiency, i.e. the factor A in $\text{speed} = A \times N^x$ for an $O(N^x)$ method.
  - A rule-of-thumb:

$$A_{\text{MBP}} = 3 \times A_{\text{PP}}$$
$$A_{\text{TB}} = 100 \times A_{\text{MBP}}$$
$$A_{\text{DF or HF}} = 100 \times A_{\text{TB}}$$

- Quantum mechanical models (HF and DFT): ~ 100 atoms $\Rightarrow$ e.g. small molecules, bulk properties of common phases, and point defect properties.

- TB, a ***minimal quantum mechanical*** model works well in a few materials (e.g. C, Si, Ge) but is problematic in many others.

- Classical models: possible to simulate very large systems, such as large protein molecules, 2- and 3-dimensional defects, whole nanoclusters, surface growth, grain boundaries etc.
  - No information on the electronic properties of the material.

Atomistic interaction models

- This chapter is a short overview on the methods; more information on other, specialized courses on the subject
  - ***A huge topic in itself! Mainly outside the scope of this course***

- Literature:
  - R. Phillips: *Crystals, Defects and Microstructures*, (Cambridge University Press, 2001), Chapter 4
  - A. Sutton: *Electronic Structure of Materials*, (Oxford Science Publications, 1996)
  - M. Finnis: *Interatomic Forces in Condensed Matter*, (Oxford Series in Materials Modelling, 2003)
  - R. M. Martin: *Electronic Structure: Basic Theory and Practical Methods*, (Cambridge University Press, 2004)

- There is a large number of review articles. A good one for those who do DFT calculations but are not quite experts in the field is

  Designing meaningful density functional theory calculations in materials science—a primer
  Ann E Mattsson et al. *Modelling Simul. Mater. Sci. Eng.* **13** (2005) R1-R31.

Overview of quantum mechanical models

- A system of N nuclei and I electrons with coordinates $\mathbf{r}_n$ $(n = 1\ldots N)$ and $\mathbf{r}_i$ $(i = 1\ldots I)$:
- **Schrödinger equation**

  $$H\Psi = E\Psi$$

  - Hamiltonian operator H

$$H = -\sum_{n=1}^{N}\frac{\hbar^2}{2M_n}\frac{\partial^2}{\partial\mathbf{r}_n^2} - \sum_{i=1}^{I}\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}_i^2} + \frac{1}{2}\sum_{i=1}^{I}\sum_{j=1}^{I}\frac{e^2}{|\mathbf{r}_{ij}|} \qquad (7.1)$$

$$+\sum_{n=1}^{N}\sum_{i=1}^{I}\frac{Z_n e^2}{|\mathbf{r}_{ni}|} + \frac{1}{2}\sum_{l=1}^{N}\sum_{n=1}^{N}\frac{Z_n Z_l e^2}{|\mathbf{r}_{nl}|}$$

$$= T_\mathrm{n} + T_\mathrm{e} + V_\mathrm{ee} + V_\mathrm{ne} + V_\mathrm{nn}$$

  - Here:
    - T_n and T_e are the kinetic energies of the nuclei and electrons, respectively.
    - V_ee, V_ne and V_nn are the electron-electron, electron-nucleus and nucleus-nucleus Coulomb interactions ⇒ Schrödinger equation.

      $(T_\mathrm{n} + T_\mathrm{e} + V_\mathrm{ee} + V_\mathrm{ne} + V_\mathrm{nn})\Psi = E\Psi$ (7.2)
    - Ψ is the total wavefunction of the full nucleus-electron system.

Born-Oppenheimer approximation

- For any given configuration of the nuclei one can assume that the electrons find their ground state before the atoms move significantly.
  - Classical simulations also based on the Born-Oppenheimer approximation: interatomic potentials do not depend on the atom motion.
- Mathematically: the wavefunction Ψ is separated into a product

  $$\Psi \approx \psi(n, \mathbf{r}_i)\eta(n),$$

  - $\psi(n, \mathbf{r}_i)$ is the electron wave function, which is a function of the positions of the electrons $\mathbf{r}_i$ and the positions of the nuclei n
  - $\eta(n)$ is the wave function of the nuclei.
  - $\psi(n, \mathbf{r}_i)$ fulfills the wave equation

  $$\{T_\mathrm{e} + V_\mathrm{ee} + V_\mathrm{ne}\}\psi(n, \mathbf{r}) = E_\mathrm{e}(n)\psi(n, \mathbf{r}) \qquad (7.3)$$

  where V_ne is the nucleus-electron potential of the original Hamilton operator.

  - Solution of this gives the electronic total energy of the system as a function of the positions of the nuclei.
    - Can also be used to give the forces acting between atoms ⇒ atom motion can be simulated using the classical MD algorithm (*ab initio* MD)

Hartree-Fock methods

- In the Schrödinger equation (7.3) the most difficult part is the electron-electron interaction

$$V_{\mathrm{ee}} = \sum_i \sum_j \frac{e^2}{|\mathbf{r}_{ij}|}$$

- The basic solution in **Hartree-Fock** (as well as in DFT) is to create some sort of ***average*** **electron density** with which every electron interacts independently:

$$V'_{\mathrm{ee}} = \sum_i V_i^{\mathrm{av}}$$

- Pauli exclusion principle: a Slater determinant of one-electron wave functions

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \ldots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \ldots & \phi_2(\mathbf{r}_N) \\ . & . & . & . \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \ldots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

Hartree-Fock methods

- Hence the Schrödinger eq. for electrons reduces to an equation to get a one-electron wave function ϕ_i:

$$\sum_i (T_{\mathrm{e},\,i} + V_{\mathrm{ne},\,i} + V_i^{\mathrm{av}})\Psi(x_1, x_2, \ldots, x_n) = E\Psi(x_1, x_2, \ldots, x_n)$$

$$(T_{\mathrm{e},\,i} + V_{\mathrm{ne},\,i} + V_i^{\mathrm{av}})\phi_i(x_1) = \hat{F}\phi_i(x_1) = \varepsilon_i\phi_i(x_1)$$

where $\hat{F}$ is the so called Fock-operator. The equation is the so called **Hartree-Fock equation.**

- Thus the new central problem becomes to find a good form for the average potential V_i^{av}.
  - Iteration: initial guess for the wave functions ϕ_i, plugged into the equation, solving to get a new ϕ_i , and keeping on iterating until the solution does not change any more, i.e. until a **self-consistent field** has been found (HF-SCF).

- The eigenvalues of the energy have a clear physical interpretation: ionization energy of the electron

- The SCF method fulfills the variational principle:

  - The eigenvalue of every inaccurate wave function is larger than that of the most accurate one.
  - So the smallest found energy is also the ‘most correct’ one.

Hartree-Fock methods

- The molecular orbital (MO) of every electron ϕ_i is written as a sum over atomic orbitals (LCAO - Linear Combination of Atomic Orbitals):

$$\phi_i = \sum_\mu C_{i\mu}\chi_\mu$$

- In the most straightforward approach the **basis functions** χ_μ can be so called Slater type orbitals (**STO**)

$$\chi = R(r)Y_{lm}(\theta, \phi), \begin{cases} R_{1s} = N_1 e^{-\zeta r} \\ R_{2s} = R_{2p} = N_2 r e^{-\zeta r} \end{cases}$$

which somewhat resemble orbitals of the hydrogen atom:

$$\psi_{nlm}(r, \theta, \phi) \propto e^{-\alpha r/2}(\alpha r)^l L_{n-l-1}^{2l+1}(\alpha r) Y_l^m(\theta, \phi), \quad \alpha = 2Z/na_0, \quad a_0 = \hbar^2/me^2.$$

- Integrating these STO orbitals is numerically difficult, however.

Hartree-Fock methods

- Computationally it is much more favourable to use Gaussian-type orbitals **(GTO)**

$$\chi^{\mathrm{GTO}}(r) = e^{-\alpha r^2}$$

because a product of two Gaussians is a Gaussian:

$$e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2} e^{-\beta|\mathbf{r} - \mathbf{R}_B|^2} = K_{AB} e^{-\gamma|\mathbf{r} - \mathbf{R}_C|^2},$$

$$\gamma = \alpha + \beta,$$

$$\mathbf{R}_C = \frac{\alpha\mathbf{R}_A + \beta\mathbf{R}_B}{\alpha + \beta},$$

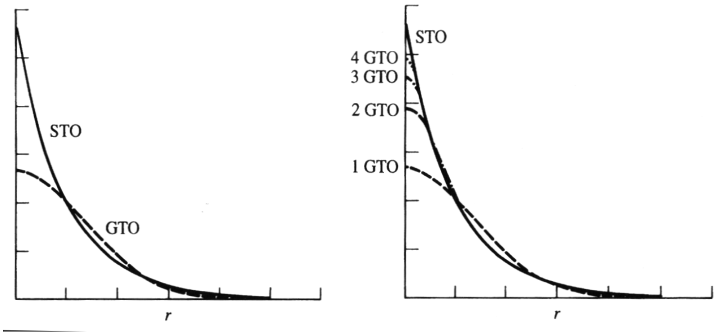
$$K_{AB} = \left[\frac{2\alpha\beta}{\pi(\alpha + \beta)}\right]^{3/4} e^{-\frac{\alpha\beta}{\gamma}|\mathbf{R}_A - \mathbf{R}_B|^2}$$

- But real electron wave functions are not Gaussian in shape ⇒ use a sum of GTO’s to describe the wave function:

$$\chi^{\mathrm{STO}} = \sum_v k_v \chi_v^{\mathrm{GTO}}$$

Hartree-Fock methods

- An example of an STO and how it can be approximated with one or more GTO's. One GTO only is not very good, but 4 GTO's already are quite close.



A.R.Leach, Molecular Modelling

- The most popular basis function sets $\{\chi\}$ are the Gaussian functions developed by the group of J. A. Pople (Nobel prize in chemistry 1998):
  - In the so called **minimal basis set** there is one orbital for two core electron orbitals, and one orbital for each valence electron. Every STO is replaced by a sum of N GTO-functions (STO-nG). The most common minimal set is the STO-3G set.
  - To improve on the results the basic approach is to increase the size of the basis sets. In the so called "Double Zeta" set there are twice as many orbitals as in the minimal set. If the doubling is made only with valence electrons (which are usually the most interesting ones) one obtains the "Split Valence" set of basis functions.
  - In the so called 3-21G set the first row elements have 3 GTO's for 1s electrons, 2 GTO's for 2s, 2p and so forth electrons, and the extra valence electrons are described by one GTO. This set is quite popular nowadays.
  - Other even larger basis sets: 6-31G, sets which have polarization functions, etc. etc.

Hartree-Fock methods

- Limitations of the basic Hartree-Fock method

  - The method does not at all account for electron correlation, that is, the correlation between the momentaneous motion between electrons. This energy is usually only of the order of 1 % of the total, but can sometimes be comparable to the total binding energy of the system and hence quite significant. Several methods have been developed to take this into account:

    - In the Configuration Interaction (CI) method a linear combination out of Slater determinants is formed. This is a very good approach, but unfortunately also very slow.

    - In Møller-Plesset perturbation theory a perturbation series is made out of the error in the correlation energy. The most popular approach is MP2, which takes into account the lowest-order correction.

    - In Multiconfiguration SCF (MCSCF) a small CI term is included in the HF iteration.

Density functional theory

- **Density functional theory** (**DFT**) is one of the most widely spread method to calculate electronic structure in materials.
  - Because it is computationally more efficient than HF, it has become especially popular among solid state physicists who need many atoms to describe a solid.

- Starts with the Schrödinger equation for electrons

$$\left\{-\sum_{i=1}^{I}\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}_i^2}+\sum_{i=1}^{I}\sum_{j=1}^{I}\frac{e^2}{|\mathbf{r}_{ij}|^2}+V_{\mathrm{ne}}\right\}\Psi(n,\mathbf{r}) = E_{\mathrm{e}}(n)\Psi(n,\mathbf{r}) \qquad \text{or}$$

$$\sum_i(T_{\mathrm{e}}+V_{\mathrm{ee}}+V_{\mathrm{ext}})\Psi = E\Psi$$

where V_{ext} is the so called external potential acting on the electrons due to the nuclei.

- The basic idea of DFT: instead of manybody wavefunction $\Psi(\{\mathbf{r}_i\})$ use electron density $n(\mathbf{r})$
  - Only need to calculate a scalar function of one vector variable not I vectors

Density functional theory

- DFT is based on the Hohenberg-Kohn theorems [Hohenberg and Kohn, *Phys. Rev.* 136 (1964) B864]:

Theorem I: For any given set of electrons which are in an external potential V_{ext}, this potential is determined uniquely, except for a trivial additive constant, from the electron density $n(\mathbf{r})$.

Corollary I: Because the system Hamiltonian is thus fully determined short of an energy shift, the electron density can be used to fully derive the many-particle wave function and thus all desired system properties.

Theorem II: It is possible to define a universal *functional* for the energy $E[n]$ depending on the electron density $n(\mathbf{r})$. The true ground state energy is the global minimum of the energy functional, and the density $n(\mathbf{r})$ which minimizes the functional is the exact ground state density.

Corollary II: The functional $E[n]$ is enough to determine the true ground state energy and electron density. Excited states must be determined by other means.

Density functional theory

- **Kohn-Sham ansatz** [W. Kohn and L. J. Sham, *Phys Rev.* **140** (1965) A1133]
  [see http://www.fysik.dtu.dk/~bligaard/wwwdirectory/phdthesis/phdproject.pdf]

  - The idea of the *ansatz* is that the original, complicated Hamiltonian can be replaced by another Hamiltonian function which is easier to solve. This effective Hamiltonian describes *non-interacting "electrons"* in a system which is *assumed* to have the same density as the true system with interacting electrons.
  - To put it in another way: We assume that there exists a system of non-interacting electrons that produce the same electron density $n(\mathbf{r})$.

  - The orbitals $\psi_i(\mathbf{r})$ of the non-interacting electrons are called Kohn-Sham orbitals.

- Apply Hohenberg-Kohn variational principle to the Kohn-Sham orbitals ⇒ the Kohn-Sham orbital equations

$$E[n] = T_0[n] + \frac{1}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}\, d^3\mathbf{r}' + \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E_{\text{xc}}[n],$$

Note that the *Hartree atomic units* are used here: $e = m = \hbar = 4\pi\varepsilon_0 = 1$

where $T_0[n]$ in now the kinetic energy of *non-interacting* electrons.

  - All the problematic terms are collected under $E_{\text{xc}}[n]$:

    error in the kinetic energy: $T[n] - T_0[n]$

    error in the Coulomb interaction between electrons: $E_{ee} - \frac{1}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}\, d^3\mathbf{r}'$

    correlation and exchange energies (quantum mechanical effects).

Density functional theory

- What we have gained here is that the above terms in E_{xc} are (usually) small corrections and can be calculated in an approximative way.

- The variational principle gives then

$$\frac{\delta E[n]}{\delta n} = 0 \Rightarrow \left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

where i runs over all electrons, ε_i is the Kohn-Sham eigenvalue of electron i, and the effective one-particle potential is:

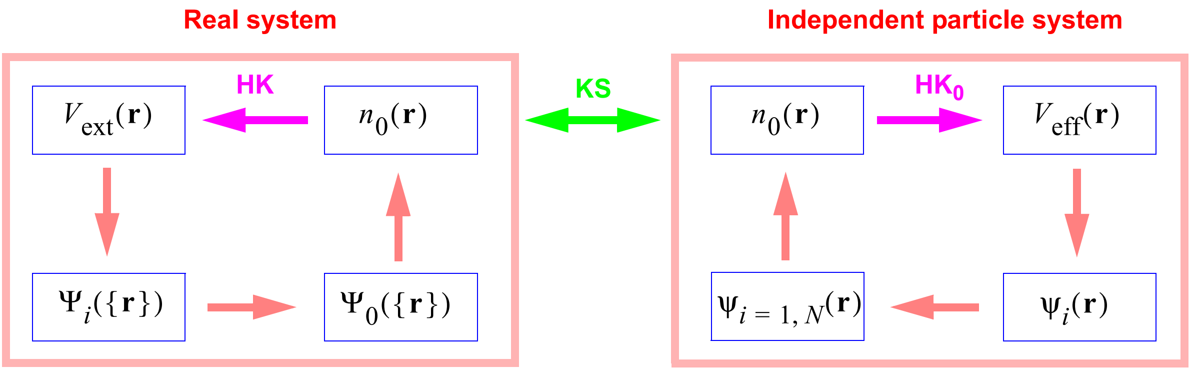
$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \phi_{\text{e}}(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

- Here V_{ext} is the external potential and

$$\phi_{\text{e}}(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \qquad n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

Density functional theory

- Pictorially this can be presented as[1]



Real system

HK

$V_{\text{ext}}(\mathbf{r})$

$n_0(\mathbf{r})$

$\Psi_i(\{\mathbf{r}\})$

$\Psi_0(\{\mathbf{r}\})$

KS

Independent particle system

HK$_0$

$n_0(\mathbf{r})$

$V_{\text{eff}}(\mathbf{r})$

$\psi_{i\,=\,1,\,N}(\mathbf{r})$

$\psi_i(\mathbf{r})$

---

[1] Adapted from R. M. Martin, *Electronic Structure: Basic Theory and Practical Methods*, (Cambridge University Press, 2004), Fig. 7.1

Density functional theory

- If the exchange-correlation energy is known, these equations can be solved by self-consistent iteration
  - Note, however, that the Kohn-Sham orbitals and their eigenvalues ε_i do not have a clear physical interpretation. There is no guarantee that they have any relation to real electron energies and wave functions, but it appears that they are in fact a surprisingly good approximation of the real electron properties.

- Local density approximation (LDA)

  - So far the DFT approach has not made any approximations.

    - To obtain the exchange-correlation functional $E_{\text{xc}}[n]$ the **local density approximation, (LDA)** is used:

$$E_{\text{xc}}[n] = \int d\mathbf{r}\, n(\mathbf{r})\varepsilon_{\text{xc}}([n], \mathbf{r}) \quad ,$$

where $\varepsilon_{\text{xc}}(n(\mathbf{r}))$ is the exchange and correlation energy of a **homogeneous electron gas** per one electron.

  - The exchange functional can be as simple as (Dirac LDA)

$$E_{\text{x, Dirac}}^{\text{LDA}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int n(\boldsymbol{r})^{4/3} d\boldsymbol{r}$$

Density functional theory

- Once an exchange and correlation energy for a homogeneous gas is introduced (several exist), the equations can be solved with an iteration process:
  1) Start with some $V_{\text{eff}}(\mathbf{r})$.
  2) Calculate the one-electron wave functions $\psi_i \Rightarrow$ new density $n(\mathbf{r})$
  3) New $n(\mathbf{r}) \Rightarrow$ new $V_{\text{eff}}(\mathbf{r})$.
  4) Repeat steps 2 and 3 until we have obtained a self-consistent solution.

- Spin in the exchange and correlation term: **local spin density approximation, LSDA**.
- DFT-LDA results compared with experimental data:
  1) Generally too large cohesive energies for solids
  2) Too large total energies for atoms
  3) Too small energy gaps for many semiconductors (LDA actually predicts zero gap for Ge!).
  4) Unstable for negative ions and gives a too diffuse electron density.
- To improve on the accuracy of DFT people have introduced exchange-and-correlation functionals which also depend on the variation of the electron density:

  $E_{\text{xc}}[n(\mathbf{r}), dn(\mathbf{r})]$.

  - There are numerous of these so called Generalized Gradient Approximations (GGA).
    - In practice there are a large number of GGA's around, and people choose one which for some reason has been "found to work well" in their system. This gives a semi-empirical character to the methods, i.e. they are not pure *ab initio*
- The DFT solution method does not restrict the way we express the Kohn-Sham wave functions.
    - Below are given two nowadays common ways to build the **basis sets** used in DFT calculations: plane waves and atomic-type orbitals.

Plane-wave methods

- In plane-wave methods the basic algorithms are as in DFT but:

- The outer valence electrons are described as a sum of plane waves:

Search for wave functions → search for coefficients

$$\psi = \sum_{l}^{N_l} f_l(\mathbf{K}_l) e^{-i\mathbf{K}_l \cdot \mathbf{r}}$$

where the wave vectors $\mathbf{K}_l$ are chosen to that they have the same periodicity as the simulation cell.

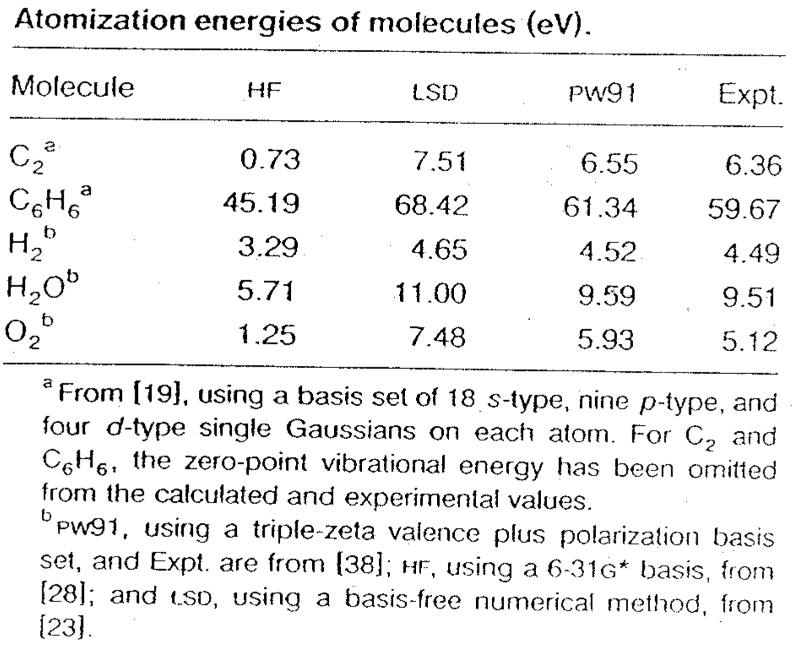
- Any shape of the electron wave functions can in principle be described with this sum provided ***the sum has enough terms*** N_l.

- Names of some common plane wave methods:
  - APW = Augmented Plane Wave
  - LAPW = Linear APW
  - FLAPW = Fully LAPW
  - SAPW = Spline APW
  - OPW = Orthogonal Plane Wave

- The main measure of the accuracy of plane-wave methods is the number of plane waves used to describe the system.

Plane-wave methods

- Examples of results of DFT / plane-wave calculation results:



Atomization energies of molecules (eV).

Molecule	HF	LSD	PW91	Expt.
C_2[a]	0.73	7.51	6.55	6.36
C_6H_6[a]	45.19	68.42	61.34	59.67
H_2[b]	3.29	4.65	4.52	4.49
H_2O[b]	5.71	11.00	9.59	9.51
O_2[b]	1.25	7.48	5.93	5.12

[a] From [19], using a basis set of 18 *s*-type, nine *p*-type, and four *d*-type single Gaussians on each atom. For C_2 and C_6H_6, the zero-point vibrational energy has been omitted from the calculated and experimental values.

[b] PW91, using a triple-zeta valence plus polarization basis set, and Expt. are from [38]; HF, using a 6-31G* basis, from [28]; and LSD, using a basis-free numerical method, from [23].

LCAO methods

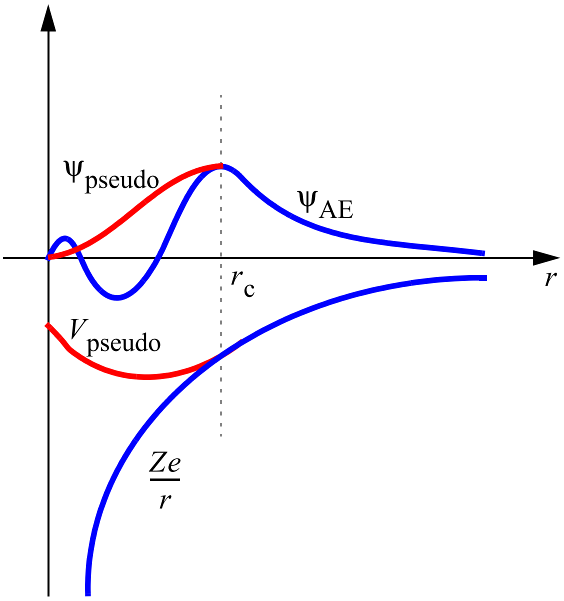
- In the **LCAO** (Linear Combination of Atomic Orbitals) method the basis set consists of orbitals **localized around each atom** in the system.
  - Compare with plane waves that are as non-localized as possible.
  - Orbitals can be obtained from quantum mechanical atomic calculations. (Or pseudo-atomic; see below)
  - The accuracy is not so straightforward to adjust as in the plane wave method.

Pseudopotentials

- In most cases the filled inner electron shells of atoms do not have any effect on the behavior of the system.
- The idea is to remove the core electrons and the strong nuclear potential and replace them with a weaker pseudo-potential.
- Outside some cut-off radius r_c the pseudo wavefunctions and the pseudopotential are indentical to those of the real atom..

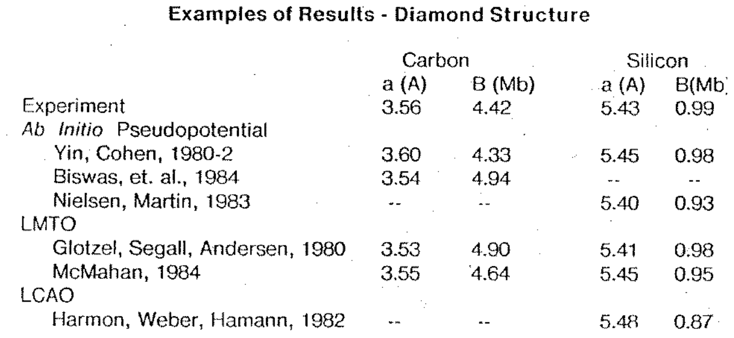
- The counterpart to pseudopotential methods are the **all electron methods.**

- Pseudopotentials are commonly used with DFT calculations both with planewaves and atomic type orbitals.



Pseudopotentials

- Results for the lattice constant a and bulk modulus B for C and Si:



Examples of Results - Diamond Structure

	Carbon		Silicon	
	a (A)	B (Mb)	a (A)	B(Mb)
Experiment	3.56	4.42	5.43	0.99
Ab Initio Pseudopotential				
Yin, Cohen, 1980-2	3.60	4.33	5.45	0.98
Biswas, et. al., 1984	3.54	4.94	--	--
Nielsen, Martin, 1983	--	--	5.40	0.93
LMTO				
Glotzel, Segall, Andersen, 1980	3.53	4.90	5.41	0.98
McMahan, 1984	3.55	4.64	5.45	0.95
LCAO				
Harmon, Weber, Hamann, 1982	--	--	5.48	0.87

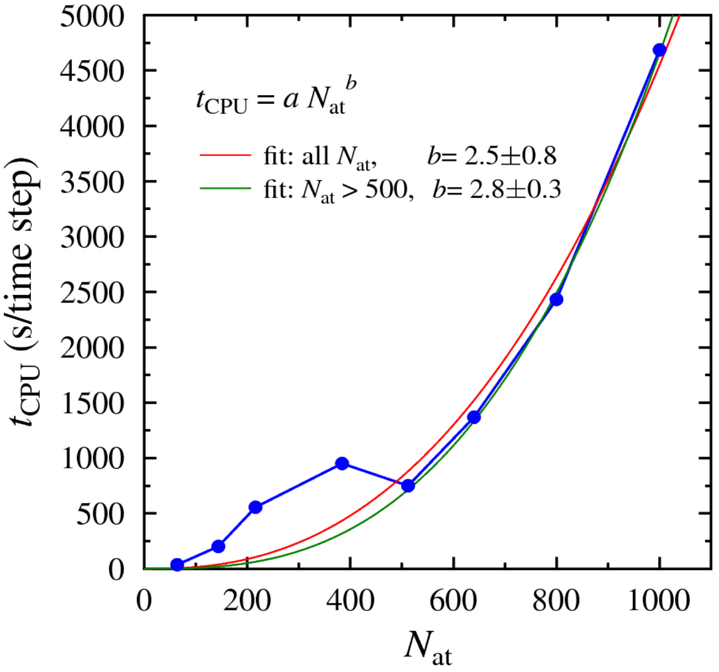
- So it is quite possible to obtain the quantities to an accuracy ~ 1 %.

- **Car-Parrinello MD**

- The Car Parrinello method [R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985)] is a method where the electron and atom motion is updated at the same time. The method has become very popular because it is highly efficient and can also be parallelized well.

Example of scaling of a DFT calculation

- CPU time usage of a SIESTA[1] calculation:
  - Si with simple SZ basis set.
  - CPU time for one energy calculation (~ time step).
  - Simulations by E. Holmström.



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[1] **S**panish **I**nitiative for **E**lectronic **S**imulations with **T**housands of **A**toms.

Commercial HF and DFT programs

- In practice, a large fraction of modern HF, DFT- and empirical simulations are carried out with commercial codes.
  - In commercial codes, the algorithms are typically 5-15 years or old. This is a mixed blessing: the state-of-the art methods may not be available, but on the other hand the algorithms in there are usually well tested. Roughly speaking especially the methods favoured by chemists have moved over to commercial codes, whereas physicists tend to stick to their own or non-commercial codes.
  - The commercial codes have flashy and easy-to-use graphical user interfaces. This is good in one sense, but also makes the risk to do **garbage in–garbage out** kinds of simulations very large. So don’t blindly start using a commercial code, you should understand its inner workings and the physics in there first!

Commercial HF and DFT programs

- **HF-codes:**
  - Gaussian The code deriving from Poples work. Very popular and versatile code. Nowadays also a DFT version is part of the package.
  - TurboMole

- **DFT-codes**
  - CASTEP Plane-wave DFT code, commercial
  - DMol^3 DFT code based on numerical basis sets, rather than Gaussian Sets
  - VASP Semi-commercial plane-wave DFT code developed in Vienna. Very widely used. http://cms.mpi.univie.ac.at/vasp/
  - Quantum Espresso http://www.quantum-espresso.org/ Open Source, Free
  - GPAW Python-based code, under active development. Real-space, scales well. https://wiki.fysik.dtu.dk/gpaw/
  - SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms)
    - Home page: http://www.uam.es/departamentos/ciencias/fismateriac/siesta/
    - A fully self-consistent $O(N)$ DFT code. Uses LCAO basis sets.
    - Source code available, can be used as a force routine in your MD code (*parcas_siesta!*)
    - *Free for academic use.*

- **Other important stuff**
  - InsightII The graphical user interface of Accelrys Inc., from which most codes of Accelrys and some non-commercial codes such as DMol and Gaussian can be run. http://www.accelrys.com
- See also **http://electronicstructure.org/**

Tight-binding methods

[Main source: Foulkes *et al.*, *Phys. Rev. B* **39** (1989) 12520.]

- **Tight-binding** (**TB**) models can be considered “minimal” quantum mechanical models. They are most often semi-empirical, and the quality of the results varies a lot. At best, one can achieve results comparable to DFT with a 100 times less computer capacity, at worst they are no better or even worse than semi-empirical models but a 100 times slower!

- In semi-empirical TB one starts with the *assumption* that total electronic energy E can be written as

$$E = \sum_{i=1}^{N} \varepsilon_i + \frac{1}{2}\sum_i \sum_j U(r_{ij})$$

where U is a repulsive classical pair potential acting between the atoms, and the ε_i are eigenvalues of some self-consists Schrödinger-like equation,

$$\hat{H}\psi_i(r) = \left[-\frac{1}{2}\nabla^2 + V(r)\right]\psi_i(r) = \varepsilon_i(r)$$

  - This resembles the DFT formalism, and can be derived with various approximations.

- The eigenvalues ε_i are negative, and the repulsive energy positive. $U(r)$ is either constructed by empirical fitting to give the desired total energy, or derived from DFT.

Tight-binding methods

- Bonding of H_2
  - Wave function: $|\psi\rangle = a_1|\phi_1\rangle + a_2|\phi_2\rangle$
  - Schrödinger equation
    $\hat{H}|\psi\rangle = E|\psi\rangle$
  - Project to states $|\phi_1\rangle$ and $|\phi_2\rangle$

$$\begin{cases}\langle\phi_1|\hat{H}|\psi\rangle = \langle\phi_1|E|\psi\rangle \\ \langle\phi_2|\hat{H}|\psi\rangle = \langle\phi_2|E|\psi\rangle\end{cases} \Rightarrow \begin{cases}E_0 a_1 + h a_2 = E a_1 \\ h a_1 + E_0 a_2 = E a_2\end{cases},$$

$h = \langle\phi_1|\hat{H}|\phi_2\rangle = \langle\phi_2|\hat{H}|\phi_1\rangle$ (We know (?) that $h < 0$.)

  - Let's shift energy origin so that $E_0 = 0 \Rightarrow$ we get the equation

$$\begin{bmatrix} 0 & -|h| \\ -|h| & 0 \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = E\begin{bmatrix} a_1 \\ a_2 \end{bmatrix}$$

  - Solutions $E = \pm|h|$, $|\psi\rangle = \frac{1}{\sqrt{2}}(\phi_1 \mp \phi_2)$

Tight-binding methods

- The TB Schrödinger is solved with the variational principle for some set of basis functions $\{\phi_\alpha\}$ which leads to a secular equation

  $|H - \varepsilon S| = 0$

  where

  $H_{\alpha\beta} = \langle\phi_\alpha|\hat{H}|\phi_\beta\rangle$

  and

  $S_{\alpha\beta} = \langle\phi_\alpha|\phi_\beta\rangle$
  - Often one still assumes that the set of basis functions is orthogonal, in which case S reduces to the unit matrix.

- Usually the basis set is put to contain only the outermost electrons, with all others treated with the repulsive potential $U(r)$. The elements in the basis function set are usually also fit to experimental data.
  - For instance, to treat a material where only the outer s and p electrons are important, one can get away with using only for basis functions (ssσ, spσ, ppσ and ppπ). If one want to also describe d electrons, one needs at least 10 basis functions.
  - Roughly speaking it seems that TB methods usually works well in materials with only covalent bonding. Systems where much work has been done and which have been found to work well are at least C, Si and their hydrogen compounds.

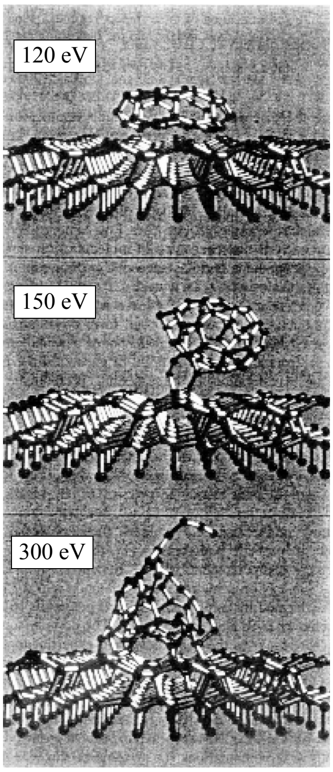
- See for example Foulkes *et al.*, *Phys. Rev. B* **39** (1989) 12520, and Sutton *et al.*, *J. Phys. C: Solid State Phys.* **21** (1988) 35. for the DFT foundations of the TB model

Tight-binding methods

- An example of a $O(N)$ TBMD application [G. Galli and F. Mauri, *Phys. Rev. Lett.* 73 (1994) 3471]
  - A fullerene C_{60} colliding with a diamond surface with different kinetic energies Ek (the surface is a reconstructed (111) surface with no dangling bonds):
  - When $E_k \leq 120$ eV no bonds are formed between the fullerene and the surface, and the fullerene simply bounces off it.

  - When 120 eV < E_k < 240 eV a few bonds are formed between the fullerene and the surface, and the fullerene may stick to the surface. The bonds may also be quickly broken again and the fullerene can bounce off again.

  - When $E_k \geq 240$ eV several bonds are formed between the fullerene and the surface, the fullerene breaks down almost completely, and sticks to the surface.



Very brief mention of a few other methods

- **Quantum Monte Carlo** (**QMC**) methods are a set of DFT-related methods where Monte Carlo simulation techniques are used to minimize the correlation term of DFT.
  - Computationally very expensive, but they can give very accurate results, especially for the correlation term which is difficult to treat otherwise.
  - The most common varieties: Diffusion Monte Carlo (DMC) and Variational Monte Carlo (VMC)
- Just an example on results [Grossman *et al., Phys. Rev. Lett.* **75** (1995) 3870]:

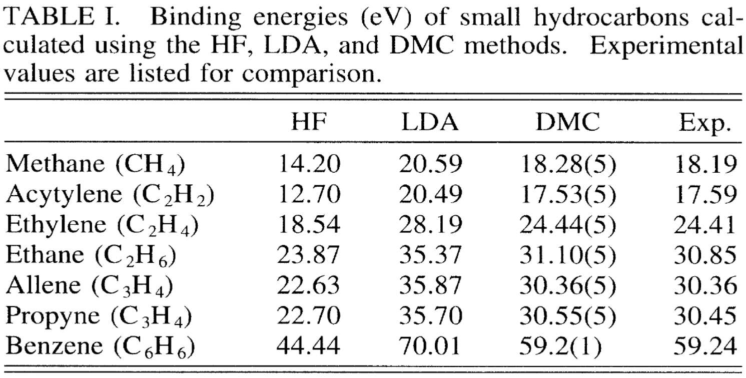


TABLE I. Binding energies (eV) of small hydrocarbons calculated using the HF, LDA, and DMC methods. Experimental values are listed for comparison.

	HF	LDA	DMC	Exp.
Methane (CH_4)	14.20	20.59	18.28(5)	18.19
Acytylene (C_2H_2)	12.70	20.49	17.53(5)	17.59
Ethylene (C_2H_4)	18.54	28.19	24.44(5)	24.41
Ethane (C_2H_6)	23.87	35.37	31.10(5)	30.85
Allene (C_3H_4)	22.63	35.87	30.36(5)	30.36
Propyne (C_3H_4)	22.70	35.70	30.55(5)	30.45
Benzene (C_6H_6)	44.44	70.01	59.2(1)	59.24

  - DMC gives all energies correct within the uncertainties, and clearly outshines HF and plain LDA.

Very brief mention of a few other methods

- What is the minimum-energy configuration of C_{20} [Grossman *et al.*, *Phys. Rev. Lett.* 75 (1995) 3870.]?

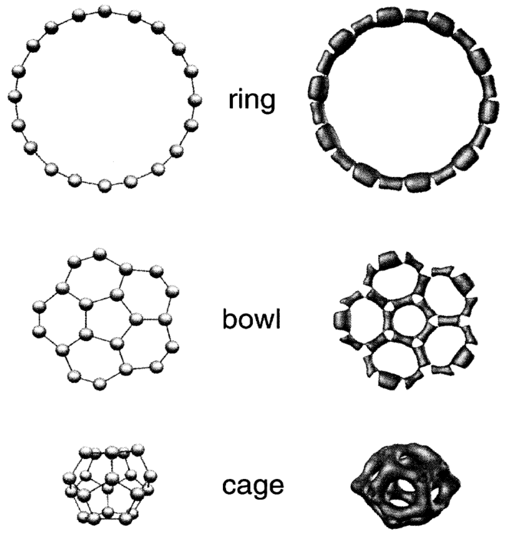


FIG. 1. The three isomers of C_{20} and their corresponding HF valence electron density isosurfaces. There are ten triple bonds in the ring and five in the bowl, and a much more covalent bonding character in the cage.

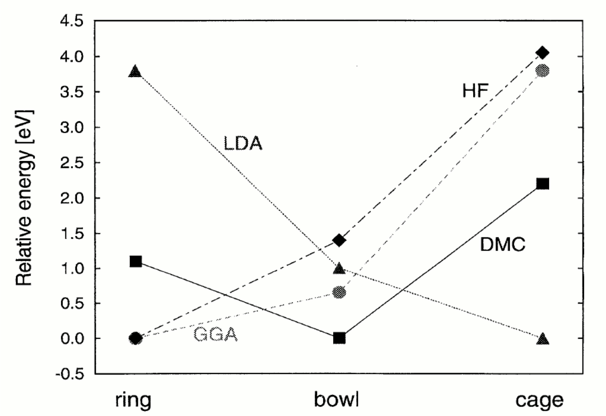
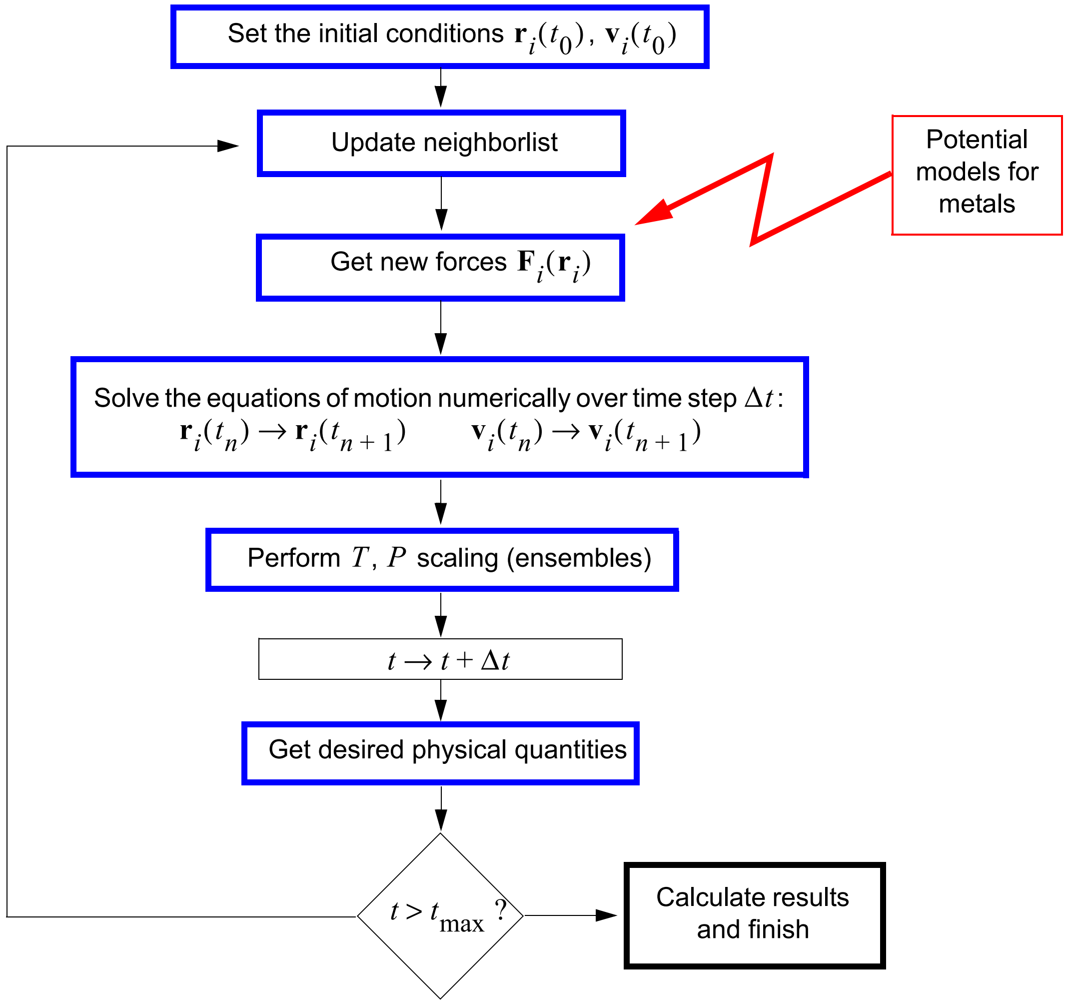


FIG. 2. The relative energy differences for the ring, bowl, and cage C_{20} isomers (DMC error bars are 0.2 eV). For each theory the lowest energy structure is taken as a reference. BLYP refers to calculations done with the Becke-Lee-Yang-Parr functional.

- According to QMC:n it is the “bowl” shape
- Note the large differences between the supposedly reliable DFT and HF methods, and that none of the agrees with the QMC behaviour.

Very brief mention of a few other methods

- **Path Integral Molecular Dynamics**
  - Path Integral MD (PIMD) is a DFT / Car-Parrinello type of method which uses a Feynman path integral representation of the density matrix.
  - Also hideously expensive computationally, but claimed to be the only really good method to describe water-related reactions.
  - A rough rule of thumb for both QMC and PIMD is that the number of atoms is limited to ~ 20 or so...
- **Time-dependent HF, DFT, TB**
  - The methods described until now are all normally used to obtain the ground state. This means one assumes that the electron system has time to come to rest before the processes of interest happen. Since electronic relaxation times are typically of the order of femtoseconds, this is often a very good approximation.
  - However, if one is interested in e.g. electronic excitation, this approximation is not valid, and one has to actually solve the time-dependent Schrödinger equation. This can be done by iterating over time.
  - Time-dependent (TD)-methods are somewhat of a hot topic in electronic structure calculations now, and there are TD variations of all the main methods: HF, DFT and TB.
  - A rough rule of thumb is that a TD-method is at least a factor of 100 slower than the corresponding ordinary method



Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Potential models for metals

Solve the equations of motion numerically over time step Δt:
$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1}) \qquad \mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$

Perform T, P scaling (ensembles)

$t \rightarrow t + \Delta t$

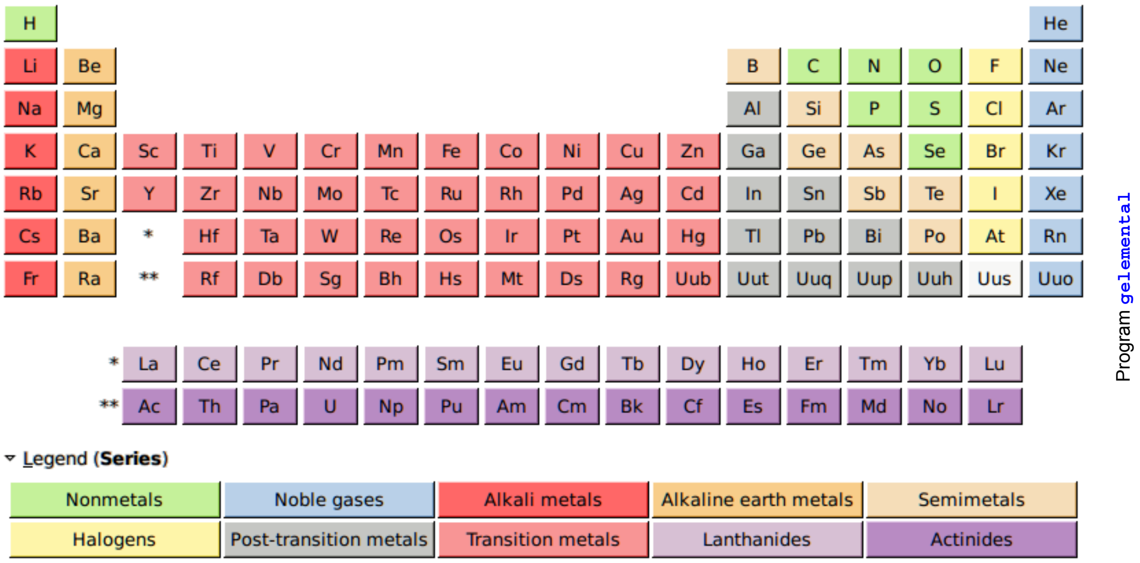
Get desired physical quantities

$t > t_{\max}$?

Calculate results and finish

Classical potentials for metals

- About 80 % of all elements are metals. The crystal structures of all the elements are distributed as follows:



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
	*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
	**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Legend (Series)

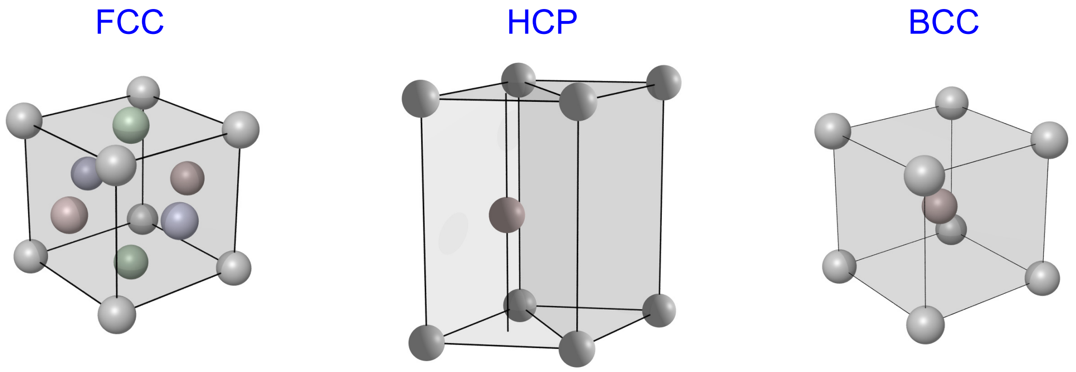
Nonmetals	Noble gases	Alkali metals	Alkaline earth metals	Semimetals
Halogens	Post-transition metals	Transition metals	Lanthanides	Actinides

FCC 19 HCP 26 BCC 15 (quick counting from inside cover of Ashcroft&Mermin)

- If we can describe the FCC, HCP- and BCC structures with interatomic potentials, already some 60 % of all stable elements are described well at least with respect to the structure.

Classical potentials for metals

- The crystal structures are as follows:



- FCC Face-Centered Cubic (close packed)
  atoms at the corners of the cube and in the center of each side face
  HCP Hexagonal Close-Packed (close packed)
  Angle between x and y unit cell axes is 120°.
  One atom at each corner of the unit cell,
  one (atom E) above the middle of the triangle ABC.
  BCC Body-Centered Cubic (not close packed)
  Cubic unit cell, atoms at the corners of the cube and in the center of the cube
  FCC and HCP are close packed $\Rightarrow$ can be stabilized with pair potentials (although getting the small HCP-FCC energy difference right is a bit tricky).

Effective medium theory

- The effective medium theory, EMT, is an approximation in which models based on density-functional theory are used to describe the properties of solids, usually metals.
  - Today there exist numerous many-body interatomic potentials which are based on EMT, in which the total energy is written in the form

$$E_{\text{tot}} = \sum_i F(n_i(\mathbf{R}_i)) + \frac{1}{2}\sum_{i,j} \Phi(\mathbf{R}_i - \mathbf{R}_j) \quad ,$$

  where F is a function of the electron density, and Φ is a (usually purely repulsive) pair potential.
  - Sort of a generalization of DFT: local electron density can be used to deduce the energy.

  - EMT can be used to directly derive a potential but many potentials only obtain the motivation of their functional form from EMT.

  - In EMT the real material is replaced by **jellium** which consists of
    1) a homogeneous electron gas, formed by the free electrons of the metal
    2) a constant positive background density (metal ions)

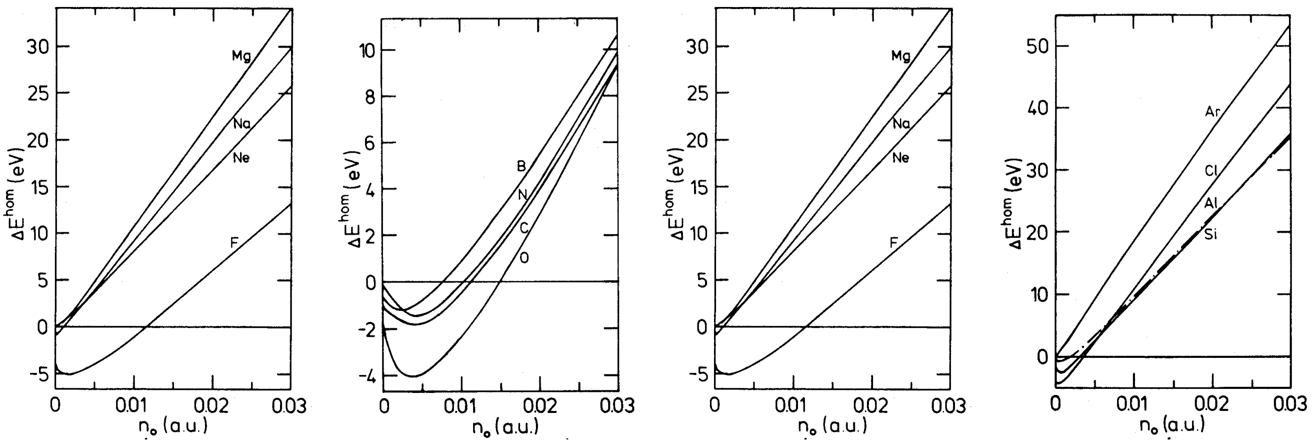
  - When an atom is 'embedded' into this medium in a position $\mathbf{r}$, the change in energy is as a first approximation

$$\Delta E(\mathbf{r}) = E_{\text{atom+jellium}} - (E_{\text{atom}} + E_{\text{jellium}}) \equiv \Delta E^{\text{hom}}(n_0(\mathbf{r})) \quad ,$$

  where $\Delta E^{\text{hom}}(n)$ is the **embedding energy** into a homogeneous electron gas with density n, and $n_0(\mathbf{r})$ is the electron density at $\mathbf{r}$.

Effective medium theory

- The embedding energy $\Delta E^{\text{hom}}(n)$ is a universal function of the electron density. Below is a list of examples [Puska, Nieminen, Manninen *Phys. Rev. B* **24** (1981) 3037].



- From the pictures we see that for noble gases $\Delta E^{\text{hom}}(n)$ is linear for all values of n, i.e. the closed electron shell only causes a repulsive interaction. (Some noble gases do have bonds, but this interaction derives from van der Waals effects which are not included in DFT/EMT).

- For other elements there is a minimum in the curves, which describes their propensity to form bonded materials.

Effective medium theory

- How do we get from this to the total energy of the whole system? [Manninen, *Phys. Rev. B* **34** (1986) 8486.]

  - The total energy of this “atoms in jellium” N-atom system is

    $$E^N_{\text{tot}} = E^N_R[n] \quad ,$$

    where n is the electron density of the ground state of the system.

  - The energy difference when an atom i is removed is

    $$\Delta E_i = E^N_{\text{tot}} - (E^{N-1}_{\text{tot}} + E_{\text{atom}}) = \Delta E_i[n_i] \quad ,$$

    where n_i is the electron density in the system *after* atom i has been removed.

  - **The idea of EMT** (motivated by DFT):
    Both E^N_{tot} and E^{N-1}_{tot} can be stated as a functional of the same electron density n_i.

  - The energy of the whole atom system can be stated as

    $$E_{\text{tot}} = E^{N-1}_{\text{tot}}[n_i] + \Delta E_i[n_i] + E_{\text{atom}}$$

Effective medium theory

- By removing more and more atoms, one at a time, we obtain for E_{tot}

$$E_{\text{tot}} = NE_{\text{atom}} + \sum_{i=1}^{N} \Delta E_i[n_{123\ldots i}] \quad .$$

  - Here $n_{123\ldots i}$ is an electron density in the system after atoms $1, 2, 3, \ldots, i$ all have been removed.
  - By rearranging the terms in the electron density this can be written as

$$\begin{aligned} E_{\text{tot}} &= NE_{\text{atom}} \\ &+ \sum_i \Delta E_i[n_i] \\ &+ \frac{1}{2}\sum_{ij} (\Delta E_j[n_{ij}] - \Delta E_j[n_j]) \\ &+ \frac{1}{6}\sum_{ijk} (\Delta E_k[n_{ijk}] - \Delta E_k[n_{ik}] - \Delta E_k[n_{jk}] - \Delta E_k[n_k]) \\ &+ \ldots \end{aligned}$$

In sums with many indices the terms with at least two same indices are left out.

  - Terms with distant atom pairs is are small, so the sums converge rapidly.

Effective medium theory

- The electron density $n_{123\ldots i}$ is approximated as a superposition of atom (or pseudo-atom) electron densities $n_{\text{a}}(\mathbf{r})$

$$n_{123\ldots i}(\mathbf{r}) = \sum_{j=i+1}^{N} n_{\text{a}}(\mathbf{r}_i - \mathbf{R}_j) \quad .$$

  - The atomic densities can be densities for free atoms or for atoms in the solid state where the surrounding compresses the electron shells.

- As mentioned above, in the first approximation

$$\Delta E_i[n_i] = \Delta E^{\text{hom}}(n_i(\mathbf{R}_i)) \quad ,$$

i.e. the functional is replaced by a function.

- By superposition the density n_{ij} is now

$$n_{ij}(\mathbf{R}_j) = n_j(\mathbf{R}_j) - n_{\text{a}}(\mathbf{R}_j - \mathbf{R}_i) \quad .$$

- The embedding energy $\Delta E^{\text{hom}}(n_{ij})$ can be calculated from $\Delta E^{\text{hom}}(n_j)$ by developing it as a Taylor series

$$\Delta E^{\text{hom}}(n_{ij}) = \Delta E^{\text{hom}}(n_i) - n_{\text{a}}(\mathbf{R}_i - \mathbf{R}_j)\frac{\partial \Delta E^{\text{hom}}(n_j)}{\partial n_j} + \ldots \quad .$$

Effective medium theory

- If the same is done with the other terms in the expression (*), we find that the total energy:

$$E_{\text{tot}} = \sum_{i=1}^{N} F^{\text{hom}}(n_i(\mathbf{R}_i)) \quad ,$$

where

$$F^{\text{hom}}(n) = E_{\text{atom}} + \Delta E^{\text{hom}}(n) - \frac{1}{2} n \frac{\partial \Delta E^{\text{hom}}(n)}{\partial n} + \frac{1}{6} n^2 \frac{\partial^2 \Delta E^{\text{hom}}(n)}{\partial n^2} \quad .$$

- Pair potential is completely missing!
- Can be used to some extent, but it is not completely satisfactory as it e.g. tends to lead to wrong values for the elastic constants [Daw, Baskes, *Phys. Rev. B* **29** (1984) 6443.]
- A better model is obtained by taking account of the electron density induced by an atom in the material

$$\Delta\rho(\mathbf{r}) = \Delta n(\mathbf{r}) - Z\delta(\mathbf{r})$$

and by considering the difference between the real external potential and the jellium external potential $\delta v^{\text{ext}}(\mathbf{r})$.

Effective medium theory

- By using perturbation theory one obtains

$$\Delta E^{(1)}(\mathbf{R}_i) = \int d\mathbf{r} \Delta\rho(\mathbf{r} - \mathbf{R}_i) \delta v^{\text{ext}}(\mathbf{r}) \quad ,$$

which can also be written as

$$\Delta E^{(1)}(\mathbf{R}_i) = \int d\mathbf{r} \Delta\rho(\mathbf{r} - \mathbf{R}_i) \phi(\mathbf{r}) \quad ,$$

where $\phi(\mathbf{r})$ is the electrostatic potential of the system (without the potential of the embedded atom).

- By the superposition principle this can be stated as a sum over single-atom potentials:

$$\Delta E^{(1)}(\mathbf{R}_i) = \sum_{i \neq j} \int d\mathbf{r} d\mathbf{r}' \frac{\Delta\rho(\mathbf{r} - \mathbf{R}_i) \Delta\rho(\mathbf{r}' - \mathbf{R}_j)}{|\mathbf{r} - \mathbf{r}'|}$$

- By using instead of the electron density at a point some average over the electron density in a region the model can also be improved. One suitable average is

$$\bar{n}_i(\mathbf{R}_i) = -\frac{1}{\alpha} \int d\mathbf{r} d\mathbf{r}' n_i(\mathbf{r}) \frac{\Delta\rho_i(\mathbf{r}' - \mathbf{R}_i)}{|\mathbf{r} - \mathbf{r}'|} \quad ,$$

where

$$\alpha = -\int d\mathbf{r} d\mathbf{r}' \frac{\Delta\rho_i(\mathbf{r}' - \mathbf{R}_i)}{|\mathbf{r} - \mathbf{r}'|} \quad .$$

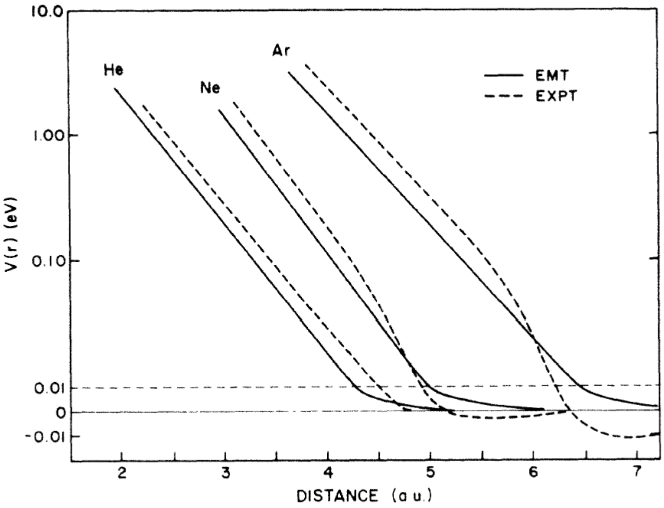
Effective medium theory

- Now the total energy of the system is of the form

$$E_{\text{tot}} = \sum_i F^{\text{hom}}(\bar{n}(\mathbf{R}_i)) + \frac{1}{2}\sum_{i\neq j}\int d\mathbf{r}\,d\mathbf{r}'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|}\ .$$

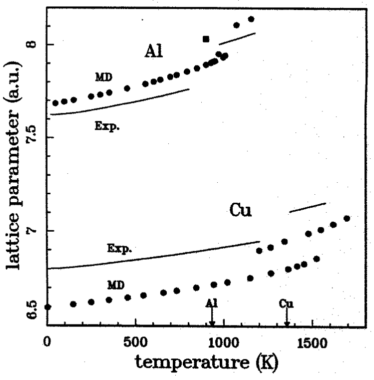
  - A density-dependent term and a pair potential term!
  - Changes in the single-electron states in the system ⇒ correction term $\Delta E_{1\text{el}}$.
    - Affects things mostly in the case of transition metals (unfilled d shell)

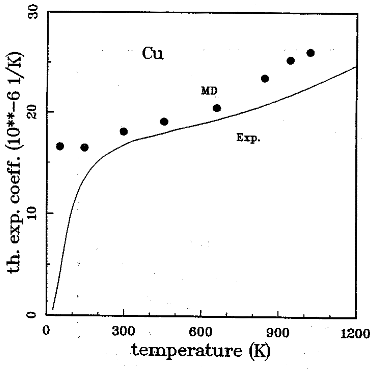
- As an example measured and simulated potentials for a few metals:



Effective medium theory

- As an example of an application to metals the properties of Al and Cu studied by constant pressure MD:





Embedded-Atom Method (EAM)

- The **EAM** method [Daw, Foiles and Baskes, *Mat. Sci. Rep.* **9** (1993) 251] is based on the same ideas as EMT.
  - The functional form has been deduced primarily semi-empirically and in part by fitting.
  - Despite its poorer physical motivation EAM usually works as well or better than EMT.
- The EAM total energy is written in the form

$$E_{\mathrm{tot}} = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{ij} V_{ij}(r_{ij}) \quad \text{(EAM 1)}$$

where

$\rho_i = \sum_{j \neq i} \rho_j^{\mathrm{a}}(r_{ij})$ is the electron density at atom i,

$\rho_j^{\mathrm{a}}(r)$ is the electron density of atom j and

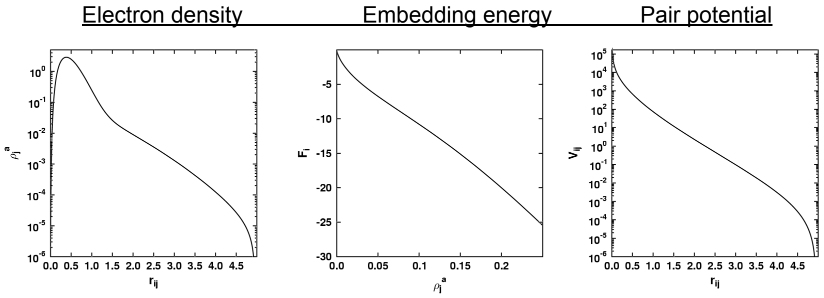
F_i is the embedding function.

Embedded-Atom Method (EAM)

- This resembles a lot the EMT total energy, the main difference being that the argument of F_i is the electron density in a given point.
  - Note that the embedding function F_i is universal in the sense that a same function can be used to embed the atom to different materials; material dependence only comes through the argument ρ.
  - Daw, Baskes and Foiles obtained the functions F_i and V_{ij} by fitting experimental results (lattice parameter, elastic constants, cohesive energy, vacancy formation energy and difference between fcc- and bcc- structures).

Embedded-Atom Method (EAM)

- Here is an example of all the terms in the original Foiles Cu EAM potential:



- Let's compare the expression above with the general expression for a many-body potential given earlier:

$$V = \sum_i V_1(\mathbf{r}_i) + \sum_{i,j} V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i,j,k} V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots$$

  - V_{ij} is clearly a pair potential V_2 . But what is the embedding term?
  - The embedding term is easiest to understand as a pair potential whose strength is affected by the local environment: an **environment-dependent pair potential.**
  - It can not be directly written in the form shown above.
  - Maybe, by Taylor expansion, it could be done. (Haven't tried it.) In that case the series in the above-mentioned would be infinite.

Embedded-Atom Method (EAM)

- The pair potential is further interpreted as

$$V_{ij}(r) = \frac{1}{4\pi\varepsilon_0}\frac{Z_i^a(r)Z_j^a(r)}{r}$$

where the $Z_i^a(r)$ are effective screened charges of the nuclei of atom type α.

  - This has the advantage that if instead of V_{ij} the $Z_i^a(r)$ are used as the starting point in evaluating the potential, forming the EAM potential for an alloy is straightforward:
    - The mixed V_{ij} is given by the equation above, and since $\rho_j^a(r)$ only depends on the type of atom j and F_i on the type of atom i, the embedding term can also be evaluated directly for the mixture.

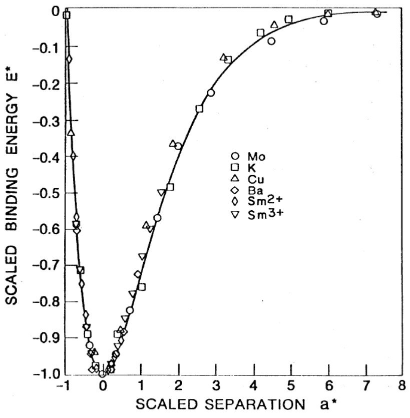
  - The electron densities $\rho_j^a(r)$ are obtained from modified HF electron densities for the outermost electrons of the material.

  - In many cases the embedding function $F(\rho)$ is obtained by fitting to universal binding energy relation [Rose *et al.*, *Phys. Rev. B* **29** (1984) 2963.]:

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

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

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



Embedded-Atom Method (EAM)

- So in practice the EAM potential has three 1-dimensional functions.
  - In analytical form or a set of points to be used with spline interpolation
  - The standard “Universal 3” format for elemental EAM potentials of Daw, Baskes and Foiles looks like:

```
Arbitrary comment line
Z1 m a latticename
nrho drho nr dr rcut
((nr points of F(rho) data))
((nr points of Z(r) data, V(r)=1/(4 pi epsilon_0) Z(r)^2/r))
((nrho points of rho data))
```

where `Z1` is the atomic number, m the mass and `a` the lattice constant.

  - A real example (Foiles Cu potential):

```
Cu functions (universal 3)
29     63.550          3.6150    FCC
500 5.0100200400801306e-04 500 1.000000000000009e-02  4.9499999999999886e+00
0.
-3.1561636903424350e-01
-5.2324876182494506e-01
```

and so on, with 1497 more data points.

  - The advantage of using a code which reads this format is that any potential which can be given in the functional form (EAM 1) can then be made into a set of spline points and read into the code without any modifications necessary in the code itself.

Embedded-Atom Method (EAM)

- Non-uniqueness of EAM-like potentials: Note that in EAM-like potentials the division of the energy into the pair potential and embedding term is not unique.
  - In the formalism (EAM 1) one obtains the same total potential energy for any configuration with the transformation $\begin{cases} V_{ij}(r) = V_{ij}(r) + 2\lambda\rho_j(r_{ij}) \\ F(\rho_i) = F(\rho_i) - \lambda\rho_i \end{cases}$, where λ is an arbitrary real number.

- Forces in EAM (embedding part; force on atom k):

$$\mathbf{F}_k = -\nabla_k \sum_i F(\rho_i) = -\nabla_k \sum_i F\left(\sum_{j \neq i} \rho(r_{ij})\right)$$

$$= -\nabla_k F\left(\sum_{j \neq k} \rho(r_{kj})\right) - \nabla_k \sum_{i \neq k} F\left(\sum_{j \neq i} \rho(r_{ij})\right)$$

$$= -F'(\rho_k) \sum_{j \neq k} \rho'(r_{kj}) \hat{\mathbf{r}}_{kj} - \sum_{i \neq k} F'(\rho_i) \rho'(r_{ik}) \hat{\mathbf{r}}_{ki}$$

$$= -\sum_{i \neq k} [F'(\rho_k) + F'(\rho_i)] \rho'(r_{ik}) \hat{\mathbf{r}}_{ki}$$

Glue models

- Like EAM but physical interpretation of the functions more or less thrown away

- For instance Ercolessi *et al.* gold potential: [*Phys. Rev. Lett.* **57** (1986) 719 , *Phil.Mag. A* **58** (1988) 213.]
  - Nearest neighbors only
  - Functions are usually polynomials

- In here instead of an embedding function a 'glue function' U is used, which depends on the atomic coordination

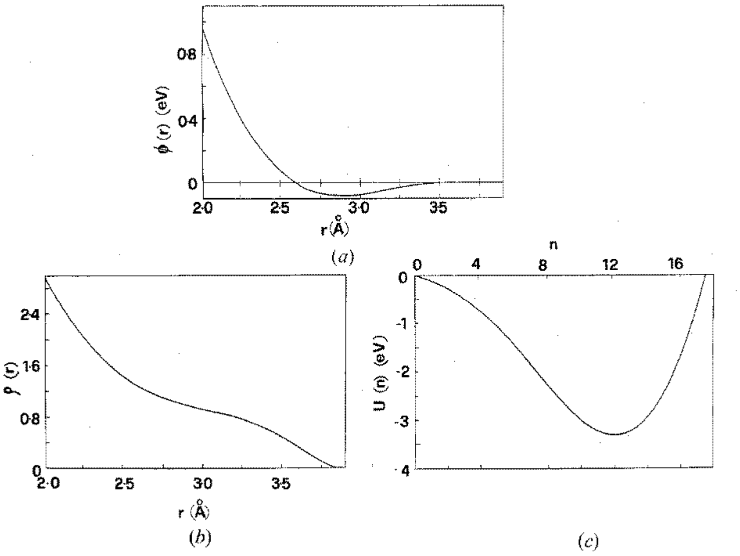
$$E_{\text{tot}} = \frac{1}{2}\sum_{i \neq j} \phi(r_{ij}) + \sum_{i} U(n_i) \quad ,$$

where

$$n_i = \sum_{i \neq j} \rho(r_{ij}) \quad .$$

Glue models

- Example: glue model for Au



(*a*) (*b*) (*c*)

The three functions $\phi(r)$ (*a*), $\rho(r)$ (*b*) and $U(n)$ (*c*) optimized for Au.

- Note that here the pair potential is no longer purely repulsive (Non-uniqueness of EAM-like potentials!)

Glue models

- A few properties of the potential:

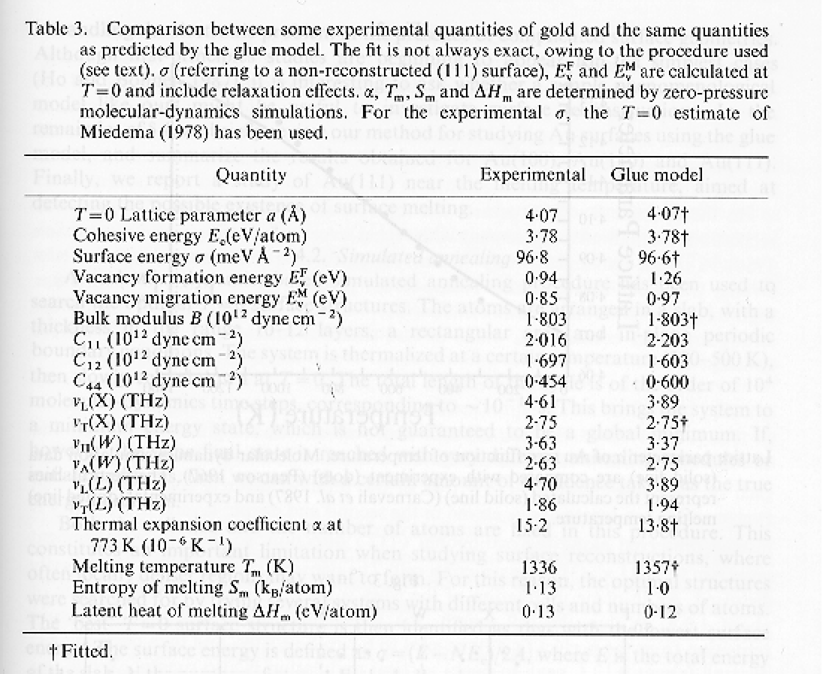
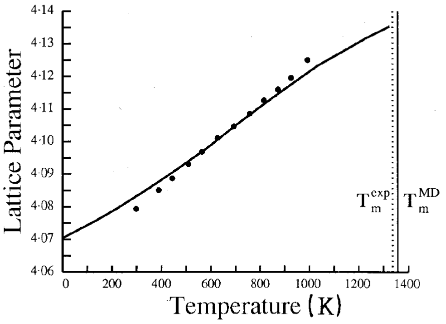


Table 3. Comparison between some experimental quantities of gold and the same quantities as predicted by the glue model. The fit is not always exact, owing to the procedure used (see text). σ (referring to a non-reconstructed (111) surface), E_v^F and E_v^M are calculated at $T=0$ and include relaxation effects. α, T_m, S_m and ΔH_m are determined by zero-pressure molecular-dynamics simulations. For the experimental σ, the $T=0$ estimate of Miedema (1978) has been used.

Quantity	Experimental	Glue model
$T=0$ Lattice parameter a (Å)	4·07	4·07†
Cohesive energy E_c(eV/atom)	3·78	3·78†
Surface energy σ (meV Å^{-2})	96·8	96·6†
Vacancy formation energy E_v^F (eV)	0·94	1·26
Vacancy migration energy E_v^M (eV)	0·85	0·97
Bulk modulus B (10^{12} dyne cm^{-2})	1·803	1·803†
C_{11} (10^{12} dyne cm^{-2})	2·016	2·203
C_{12} (10^{12} dyne cm^{-2})	1·697	1·603
C_{44} (10^{12} dyne cm^{-2})	0·454	0·600
$\nu_L(X)$ (THz)	4·61	3·89
$\nu_T(X)$ (THz)	2·75	2·75†
$\nu_\Pi(W)$ (THz)	3·63	3·37
$\nu_\Lambda(W)$ (THz)	2·63	2·75
$\nu_L(L)$ (THz)	4·70	3·89
$\nu_T(L)$ (THz)	1·86	1·94
Thermal expansion coefficient α at 773 K (10^{-6} K^{-1})	15·2	13·8†
Melting temperature T_m (K)	1336	1357†
Entropy of melting S_m (k_B/atom)	1·13	1·0
Latent heat of melting ΔH_m (eV/atom)	0·13	0·12

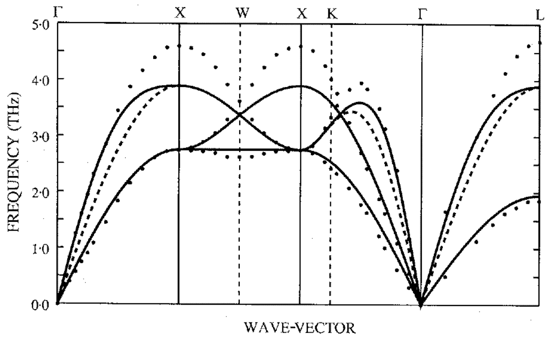
† Fitted.

- Thermal expansion from MD simulations



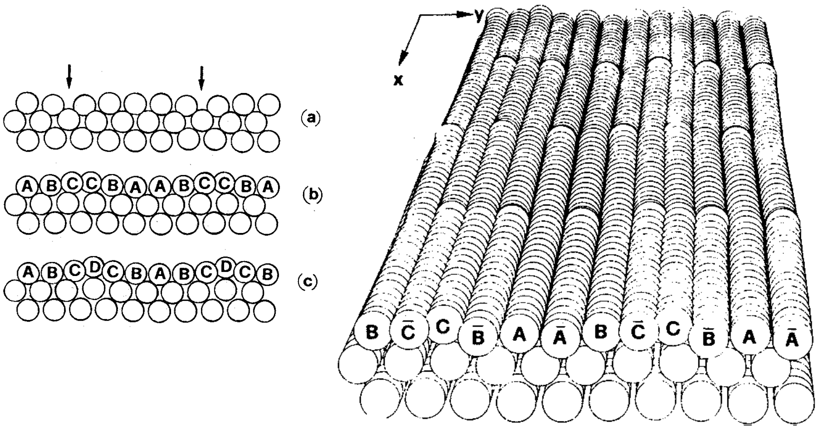
Glue models

- Phonon dispersion relation:



points: experiment
solid line: with glue function
dashed line: without glue function

- Gold (100) surface reconstruction



Rosato group potentials

- The group of Rosato *et al.* (first ones by Cleri and Rosato) has formulated a large group of potentials based on the second-moment approximation of the tight-binding Hamiltonian (TB-SMA). [Cleri and Rosato, Phys. Rev. B **48** (1993) 22]:
  - The method starts from the knowledge that a large set of properties of transition metals can be derived purely from the density of states of the outermost *d* electrons:
  - The second moment of the density of states is μ_2 , and experimentally it has been found that the cohesive energy of metals is roughly proportional to the width of the density of states, which in the second-moment approximation is simply $\sqrt{\mu_2}$.
  - When only the ddσ, ddπ and ddδ orbitals are taken into account, the band-energy of atom i can according to the model be written as:

$$E_B^i = -\sqrt{\sum_j \xi^2 \exp\left[-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right]}$$

which only depends on the distance and which formally is exactly the same as the $F(\rho)$ part of the EAM potentials (with the square root operation being the embedding function F).

Rosato group potentials

- In addition the model has a repulsive Born-Mayer-term:

$$E_R^i = \sum_j A \exp\left[-p\left(\frac{r_{ij}}{r_0} - 1\right)\right]$$

so the total energy of the system becomes

$$E_c = \sum_i (E_R^i + E_B^i)$$

- Here r_0 is the equilibrium distance between atoms, and A, ξ, p and q are fitted parameters. Despite its simple functional form, the model can be used to describe quite well elastic, defect and melting properties of a wide range of FCC- and HCP-metals.

- Later work in the Rosato group has given also extensions to alloys, e.g. [Mazzone *et al.*, Phys. Rev. B **55** (1997) 837].

- One practical caveat about the Cleri-Rosato potentials: at least in some of their papers they have been sloppy with factors of 1/2 and minus signs, you may have to correct these yourself.

Finnis-Sinclair potentials

- One more important group of EAM-like potentials are the so called Finnis-Sinclair potentials [*Phil.Mag. A* **50** (1984) 45; for an improvement see *Phil. Mag. A* **56** (1987) 15]. They model transition metals based on ideas derived from the tight binding method.
  - The form of a Finnis-Sinclair-potential is

$$E_{\mathrm{tot}} = \frac{1}{2}\sum_{i \neq j}\phi(r_{ij}) - A\sum_{i}\sqrt{n_i} \quad ,$$

where

$$n_i = \sum_{i \neq j}\rho(r_{ij}) \quad .$$

i.e. this is the same functional form as in EAM where the embedding function is simply $F(n_i) = -A\sqrt{n_i}$. The square root function can be motivated by the tight-binding model, as in the Rosato potentials.

  - The potential parameters are obtained purely by fitting to experimental data.

Vacancy formation energy revisited

See e.g. Rob Phillips, *Crystals, Defects and Microstructures*.

- Definition of the formation energy:

$$E^{\mathrm{f}}_{\mathrm{vac}} = E_{\mathrm{tot}}(\mathrm{vacancy}, N) - E_{\mathrm{tot}}(\mathrm{perfect}, N)$$

- EAM-type potential

$$E_{\mathrm{tot}} = \sum_{i} F(\rho_i) + \frac{1}{2}\sum_{ij} V(r_{ij}),$$

$$\rho_i = \sum_{j \neq i}\rho^{\mathrm{a}}(r_{ij})$$

Remember pair potentials:

$$E_{\mathrm{tot}}(\mathrm{vacancy}, N) = \frac{1}{2}[(N-12)12\phi + 12(12-1)\phi] = 6(N-1)\phi$$

$$E_{\mathrm{tot}}(\mathrm{perfect}, N) = \frac{1}{2}N12\phi = 6N\phi$$

$$\Rightarrow E^{\mathrm{f}}_{\mathrm{vac}} = -6\phi = -E_{\mathrm{coh}}/\mathrm{atom}$$

- Perfect fcc lattice atoms, only NN interaction, equilibrium bond length r_0:

$$E_{\mathrm{tot}}(\mathrm{perfect}, N) = NF(12\rho_0) + \frac{1}{2}12N\phi = NF(12\rho_0) + 6N\phi$$

$$E_{\mathrm{tot}}(\mathrm{vacancy}, N) = (N-12)F(12\rho_0) + 12F(11\rho_0) + \frac{1}{2}[(N-12)12\phi + 12 \times 11\phi],$$

where $\rho_0 = \rho^{\mathrm{a}}(r_0)$, $\phi = V(r_0)$

$$\Rightarrow E^{\mathrm{f}}_{\mathrm{vac}} = 12[F(11\rho_0) - F(12\rho_0)] - 6\phi$$

Vacancy formation energy revisited

- Note that now cohesion energy per atom is

$$E_{\mathrm{coh}} = \frac{E_{\mathrm{tot}}(\mathrm{perfect}, N)}{N} = F(12\rho_0) + 6\phi \Rightarrow 6\phi = E_{\mathrm{coh}} - F(12\rho_0)$$

- Substitute 6ϕ in expression for $E^{\mathrm{f}}_{\mathrm{vac}}$

$$\Rightarrow \quad E^{\mathrm{f}}_{\mathrm{vac}} = 12F(11\rho_0) - 11F(12\rho_0) - E_{\mathrm{coh}}$$

Element	$\lvert E_{\mathrm{coh}}\rvert$ (eV)	$E^{\mathrm{f}}_{\mathrm{vac}}$ (eV)
V	5.31	2.1 ± 0.2
Nb	7.57	2.6 ± 0.3
W	8.90	4.0 ± 0.2

Typically for metals
$E_{\mathrm{vac}}/E_{\mathrm{coh}} = 0.2\ldots0.4$

NOTE: Pure pair potential means that $F(\rho) = \alpha\rho$, i.e. linearity $\Rightarrow$

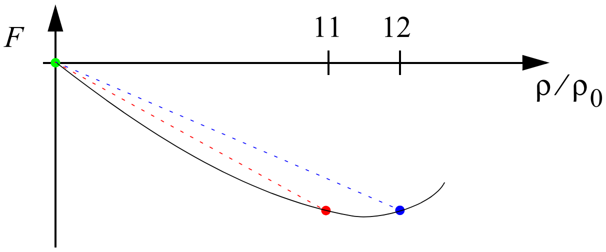
$$E^{\mathrm{f}}_{\mathrm{vac}} = 12(11\alpha\rho_0) - 11(12\alpha\rho_0) - E_{\mathrm{coh}} = -E_{\mathrm{coh}}$$

Vacancy formation energy revisited

- So now we at least have $E^{\mathrm{f}}_{\mathrm{vac}} \neq -E_{\mathrm{coh}}$
- To have $E^{\mathrm{f}}_{\mathrm{vac}} < -E_{\mathrm{coh}}$ requires

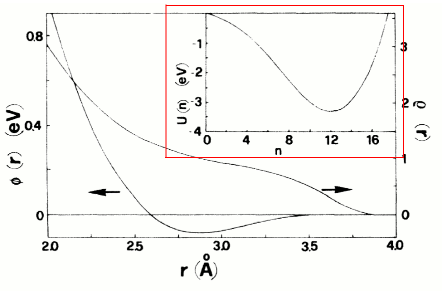
$$12F(11\rho_0) - 11F(12\rho_0) < 0 \Rightarrow \frac{F(11\rho_0)}{11} < \frac{F(12\rho_0)}{12},$$

i.e. positive curvature $\dfrac{d^2F}{d\rho^2} > 0$:

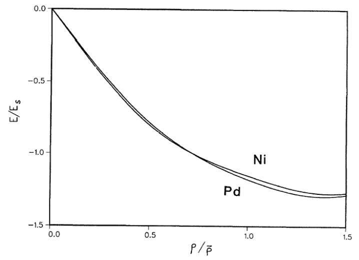


Vacancy formation energy revisited

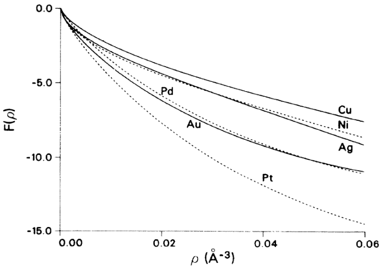
- Glue model for Au



Daw & Baskes for Ni, Pd



Foiles *et al.*



Some EAM-like potentials

- Below are listed some EAM potentials. It is impossible to list all of them, so this is just a list of some common ones.

- **FCC metals**
- "**Original" EAM**-potentials [S. M. Foiles, Phys. Rev. B **32** (1985) 3409; *ibid.* **33** (1986) 7983]:
  - Good potentials for Ni, Cu, Pd, Ag, Pt, Au and all dilute alloys of these. Good in many ways, surfaces the most commonly mentioned shortcoming. But surfaces tend to be a problem for most EAM potentials
  - Decent potential for Al.
  - Very widely used and tested, and almost no fatal shortcomings have been reported, so these can be used with good confidence.

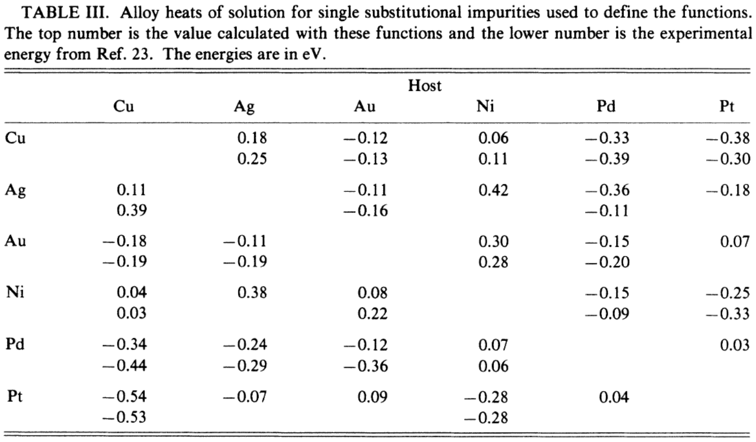


TABLE III. Alloy heats of solution for single substitutional impurities used to define the functions. The top number is the value calculated with these functions and the lower number is the experimental energy from Ref. 23. The energies are in eV.

			Host			
	Cu	Ag	Au	Ni	Pd	Pt
Cu		0.18 0.25	−0.12 −0.13	0.06 0.11	−0.33 −0.39	−0.38 −0.30
Ag	0.11 0.39		−0.11 −0.16	0.42	−0.36 −0.11	−0.18
Au	−0.18 −0.19	−0.11 −0.19		0.30 0.28	−0.15 −0.20	0.07
Ni	0.04 0.03	0.38	0.08 0.22		−0.15 −0.09	−0.25 −0.33
Pd	−0.34 −0.44	−0.24 −0.29	−0.12 −0.36	0.07 0.06		0.03
Pt	−0.54 −0.53	−0.07	0.09	−0.28 −0.28	0.04	

Foiles *et al.*, *Phys. Rev. B* **33** (1986) 7983.

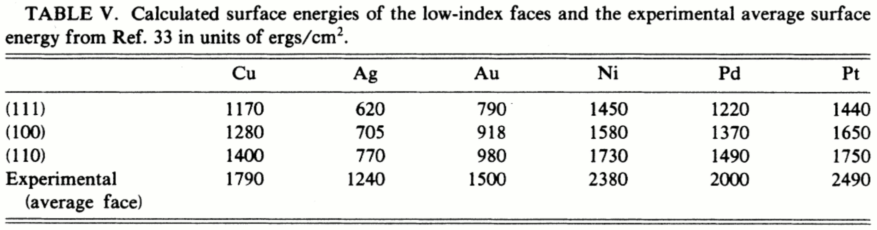


TABLE V. Calculated surface energies of the low-index faces and the experimental average surface energy from Ref. 33 in units of ergs/cm^2.

	Cu	Ag	Au	Ni	Pd	Pt
(111)	1170	620	790	1450	1220	1440
(100)	1280	705	918	1580	1370	1650
(110)	1400	770	980	1730	1490	1750
Experimental (average face)	1790	1240	1500	2380	2000	2490

Some EAM-like potentials

- Glue potentials: [Ercolessi, Adams: Europhys. Lett. 26 (1994) 583]: good potentials at least for Au and Al.
- [Cai and Ye, Phys. Rev. B **54** (1996) 8398]: Alternative EAM potentials for Al, Ag, Au, Cu, Ni, Pd and Pt. May be better than original EAM in particular for alloys and surfaces.
- [Johnson, Phys. Rev. B **37** (1988) 3924]: Analytical EAM model for most FCC metals
- [Sabochick, Lam, Phys. Rev. B **43** (1991) 5243]: Potential for Cu, Ti and their compounds
- [Zhou, Johnson, Wadley, Phys. Rev. B 69 (2004) 144113]: EAM potentials for numerous metals that can be mixed for a huge number of alloys using a special mixing rule.

Some EAM-like potentials

- The Cu part of this potential seems to be very good for point defects
  [Nordlund and Averback, Phys. Rev. Lett. 80 (1998) 4201] (see on the right).
- [Voter and Chen, Mat. Res. Soc. Symp. Proc. **82** (1989) 175]: NiAl system potentials
- Cleri-Rosato parameters (see above) for FCC metals exist at least for Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, Al and Pb.
- [Ackland and Vitek, Phys. Rev. B **41** (1990) 10324]: EAM potentials for Cu, Ag, Au and alloys. Improvements in [Deng and Bacon, Phys. Rev. B **48** (1993) 10022].

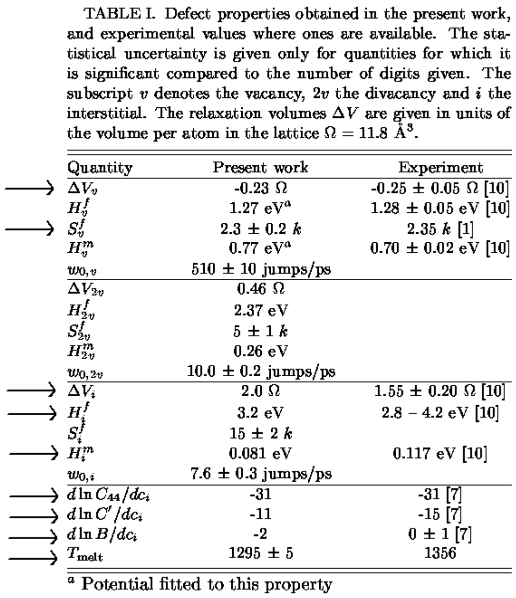


TABLE I. Defect properties obtained in the present work, and experimental values where ones are available. The statistical uncertainty is given only for quantities for which it is significant compared to the number of digits given. The subscript v denotes the vacancy, $2v$ the divacancy and i the interstitial. The relaxation volumes ΔV are given in units of the volume per atom in the lattice $\Omega = 11.8$ Å^3.

Quantity	Present work	Experiment
ΔV_v	-0.23 Ω	-0.25 ± 0.05 Ω [10]
H_v^f	1.27 eV^a	1.28 ± 0.05 eV [10]
S_v^f	2.3 ± 0.2 k	2.35 k [1]
H_v^m	0.77 eV^a	0.70 ± 0.02 eV [10]
$w_{0,v}$	510 ± 10 jumps/ps	
ΔV_{2v}	0.46 Ω	
H_{2v}^f	2.37 eV	
S_{2v}^f	5 ± 1 k	
H_{2v}^m	0.26 eV	
$w_{0,2v}$	10.0 ± 0.2 jumps/ps	
ΔV_i	2.0 Ω	1.55 ± 0.20 Ω [10]
H_i^f	3.2 eV	2.8 – 4.2 eV [10]
S_i^f	15 ± 2 k	
H_i^m	0.081 eV	0.117 eV [10]
$w_{0,i}$	7.6 ± 0.3 jumps/ps	
$d \ln C_{44}/dc_i$	-31	-31 [7]
$d \ln C'/dc_i$	-11	-15 [7]
$d \ln B/dc_i$	-2	0 ± 1 [7]
T_{melt}	1295 ± 5	1356

[a] Potential fitted to this property

Some EAM-like potentials

- **HCP-metals**

- Compared to both FCC and BCC metals, the HCP metals have been studied relatively little, both experimentally and with simulations.
- In fitting potentials for an HCP one should take care to ensure that the HCP phase is lower in energy than the FCC phase, and that one can obtain the required c/a ratio (which experimentally seldom equals exactly $\sqrt{8/3}$, which is the "ideal" value calculated for close packing of hard spheres)
- In addition there are 5 elastic constants, rather than 3 as in cubic metals.

- Pasianot and Savino [Phys. Rev. B **45** (1992) 12704] have made EAM-like potentials for HCP-metals Hf, Ti, Mg and Co. But they also showed that an EAM-like model **can not** reproduce all elastic constants correctly for those HCP metals which have

  $$c_{13} - c_{44} < 0 \quad \text{or} \quad \frac{1}{2}(3c_{12} - c_{11}) < c_{13} - c_{44}$$

  - Such metals are e.g. Be, Y, Zr, Cd and Zn.

- Cleri and Rosato (see above) derive parameters for the HCP metals Ti, Zr, Co, Cd, Zn and Mg.

- Oh and Johnson [J. Mater. Res. **3** (1988) 471] have also put their fingers here, for the HCP metals Mg, Ti and Zr.

Some EAM-like potentials

- **BCC-metals**

- When one constructs potentials for BCC metals, one has to take into account that the BCC structure is not closed packed. A pair potential would most likely make the BCC phase unstable compared to FCC and HCP, unless carefully constructed. Or one can attain unwanted effects such as a negative thermal expansion.

- In BCC metals the Finnis-Sinclair potentials (see above) have been much used. Originally they were formulated at least for Fe, V, Nb, Ta, Mo and W. In the five latter ones serious problems were later found, which were corrected in [Ackland and Thetford, Phil. Mag. A **56** (1987) 15].

- Johnson and Oh [J. Mater. Res. **4** (1989) 1195] have been active in BCC as well. They derived potentials at least for Li, Na, K, V, Nb, Ta, Cr, Mo, W and Fe.

- But in BCC metals one should take into account the recent theoretical work which showes that in them 4-body interactions can have an important role, and these can of course not be described well by EAM-like potentials [J. A. Moriarty, Phys. Rev. B **42** (1990) 1609].

  - Moriarty has developed 4-body potentials at least for a few metals [e.g. Phys. Rev. B **49** (1994) 12431]. These have shown for instance that the migration energies of the Finnis-Sinclair model are probably 3-15 times too large [Phys. Rev. B **54** (1996) 6941].

Some EAM-like potentials

- **Metal-hydrogen potentials**

- Finally, we mention that it is possible to construct a somewhat sensible EAM-like potential for metal-hydrogen interactions. Of course these can not describe delocalized hydrogen in metals, but they can still reproduce well e.g. the cohesive and migration energy of hydrogen in solid metals and hydrogen on solid surfaces.

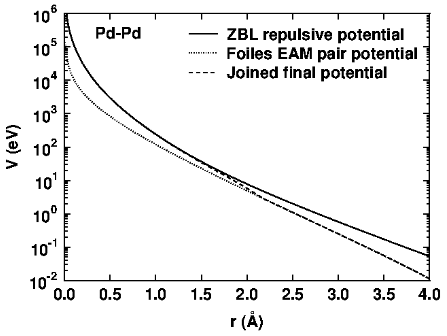
- Just one example: [Rice *et al.*, J. Chem. Phys. **92** (1990) 775]; EAM potential for Ni-H.

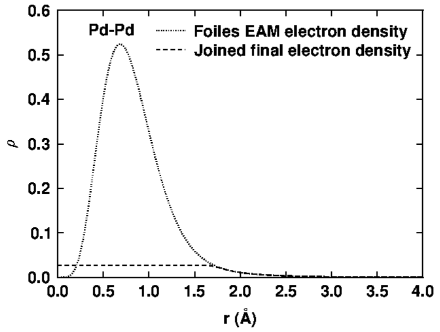
Fitting a repulsive potential to EAM models.

- When one wants to describe high-energy processes ($E_{kin} > 10$ eV) one almost always has to modify the repulsive part of the potential. One can for instance use the so called ZBL universal potential for this, which describes the repulsive part with ~ 10 % accuracy for all material combinations, or even better an accurate potential derived from *ab initio* - calculations.

- A special feature for EAM-like potentials is that one still has to remember that the electron density has to be set to a constant value in the same r range where the high-energy repulsive potential is fit to the pair potential part.

- Example: fitting the Foiles Pd-potential to the ZBL repulsive potential. With the same fit also the high-pressure properties and melting point of the potential was obtained almost exactly right, whereas the properties of the interstitial atom became worse. [Nordlund *et al.*, Phys. Rev. B **57** (1998) 13965].



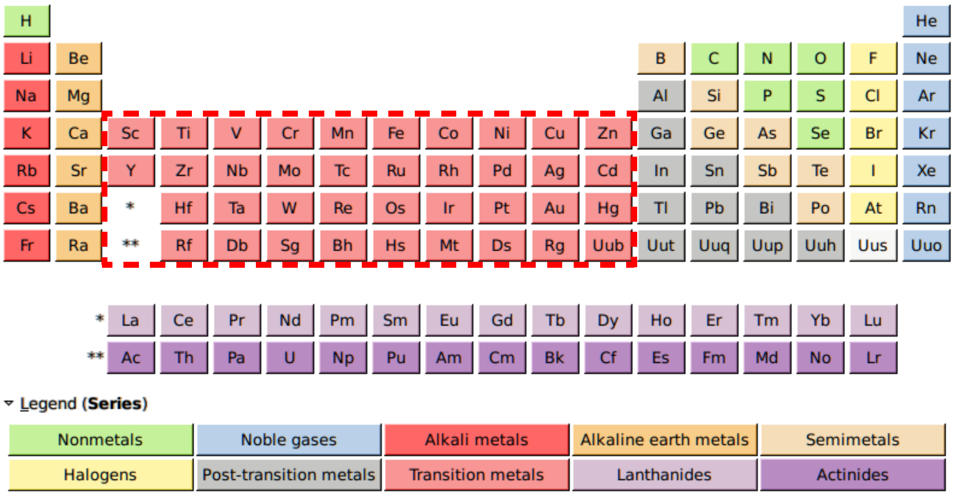


Two-band EAM model

- EAM is often used to model transition metals:
  - Their bonding is characterized by the free-electron-like s orbital and the narrow d orbital.
  - In the original EAM potential the effect of these two orbitals was taken into account by assuming the electron density be a sum of contributions from s and d shells:

$$\rho^a(r) = n_s\rho_s(r) + n_d\rho_d(r).$$

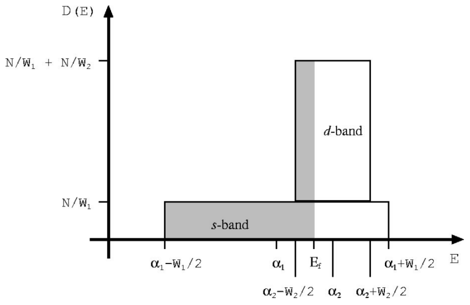
  - The ‘occupations’ n_s and n_d were obtained by e.g. fitting to H heat of solution or such.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
	*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
	**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Legend (Series)

Nonmetals	Noble gases	Alkali metals	Alkaline earth metals	Semimetals
Halogens	Post-transition metals	Transition metals	Lanthanides	Actinides



G.J.Ackland, S.K.Reed, *Phys. Rev. B* **67** (2003) 174108.

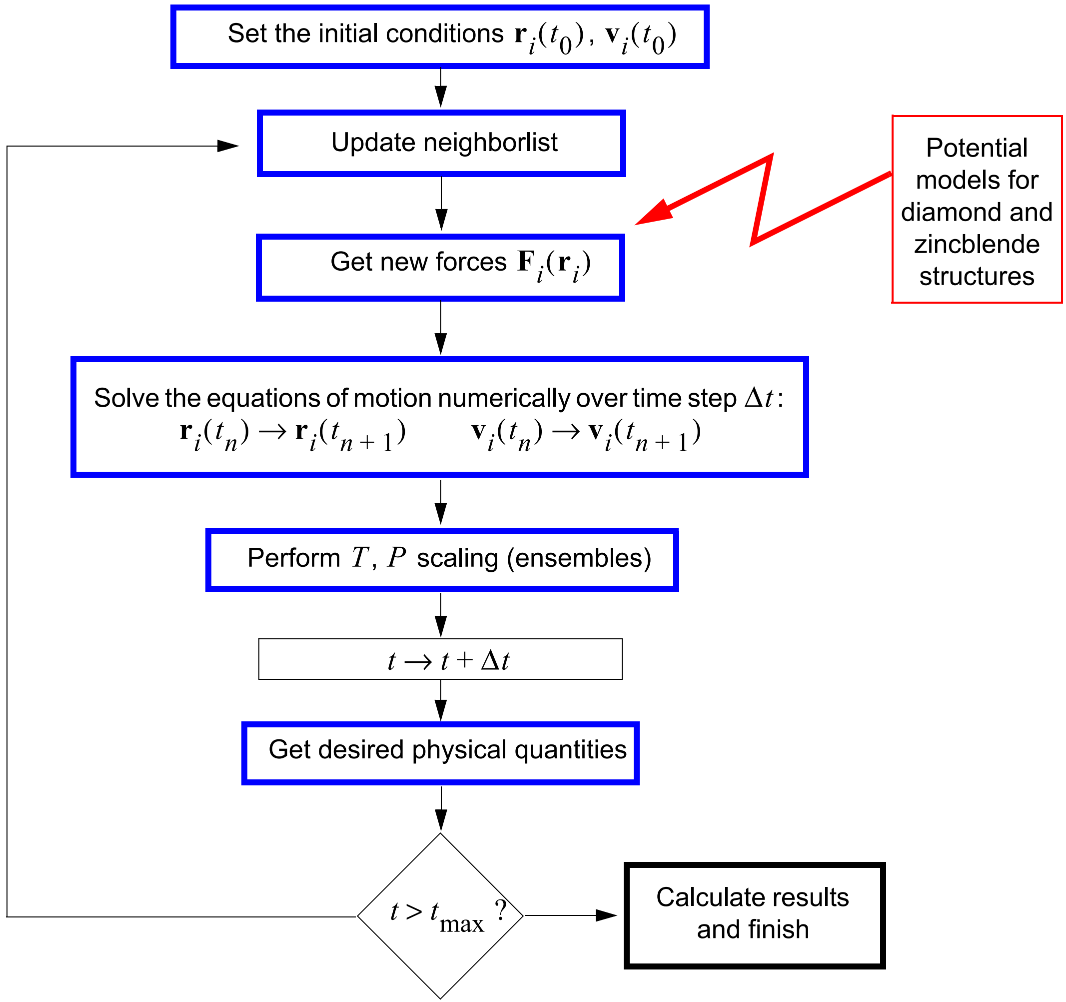
Two-band EAM model

- In the two-band EAM model the s and d orbitals (or bands) are explicitely taken into account.
  - Energy of atom i is written as

$$E_i = F_d(\rho_{i,d}) + F_s(\rho_{i,s}) + \frac{1}{2}\sum_j V(r_{ij}),$$

where $\rho_{i,b} = \sum_j \phi_b(r_{ij})$ is the electron density contribution from band b.

  - The original formulation of the EAM model in the form of fitting the s band density
  - A two-band EAM potential has been developed for elemental caesium [G.J.Ackland et al., *Phys. Rev. B* **67** (2003) 174108.] and for the binary alloy FeCr [P.Olsson et al., *Phys. Rev. B* **72** (2005) 214119.]
  - For many transition metals the cohesion is determined mainly by the d band but the s band affects the elastic properties by providing repulsion.
  - On the other hand for alkali and alkaline-earth metals are normally close-packed metals with bonding determined by the s electrons.
    - However, at large pressures electrons are transferred to d band which is — although higher in energy — more compact, allowing lower atomic volumes.
  - With these models the isostructural transition of Cs and the thermodynamical properties of Fe-Cr alloy were reasonably described.



Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Solve the equations of motion numerically over time step Δt:

$$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1}) \qquad \mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$$

Perform T, P scaling (ensembles)

$t \rightarrow t + \Delta t$

Get desired physical quantities

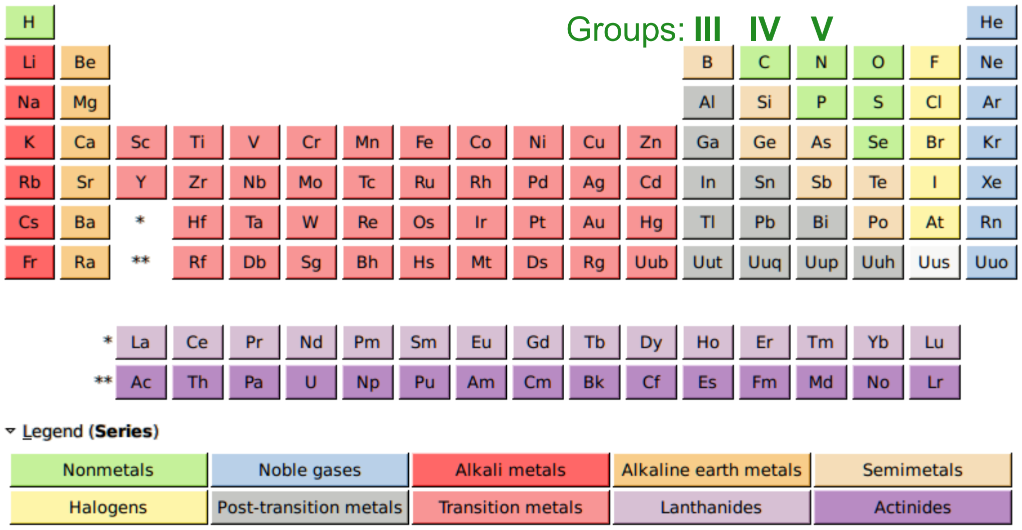
$t > t_{\max}$?

Calculate results and finish

Potential models for diamond and zincblende structures

Diamond and zincblende structure potentials

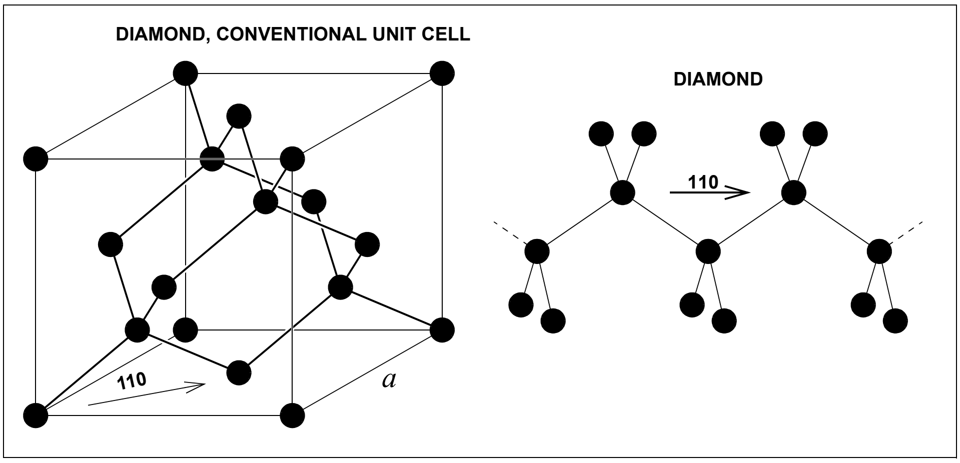
- Only three elements have the diamond (DIA) structure: C, Si, Ge
- However, since almost the whole semiconductor industry and micromechanical engineering industry is based on Si technology, the interest in studying diamond-structured semiconductors is immense.
- In addition, the most common compound semiconductors (GaAs, AlAs, InAs, etc.) have the zincblende structure, which is essentially the same as diamond except that there are 2 atom types. This further increases the interest in describing this crystal structure.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
	*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
	**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Diamond and zincblende structure potentials

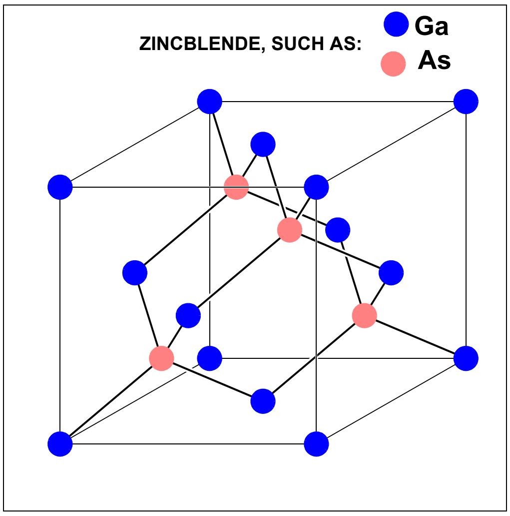
- The diamond structure is (2 ways of looking at the same thing)



- Essentially two FCC structures inside each other which have been displaced by $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$ from each other.
- The unit cell has 8 atoms
- **In terms of bonding the crucial feature is that every atom has exactly 4 neighbours.** The bonds are covalent or predominantly covalent, and the nearest neighbours are distributed such that one atom is in the middle of a regular tetrahedron
- The angle between any two bonds of the same atom becomes $\cos(-1/3) = 109.47°$. Chemically this corresponds to the **sp^3** hybridization of electrons.

Diamond and zincblende structure potentials

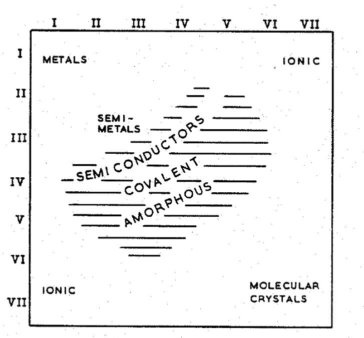
- The **zincblende** structure is the same except that one FCC sublattice has atoms of one type, the other of the other type. One unit cell thus has 4 atoms of type A and 4 of type B.



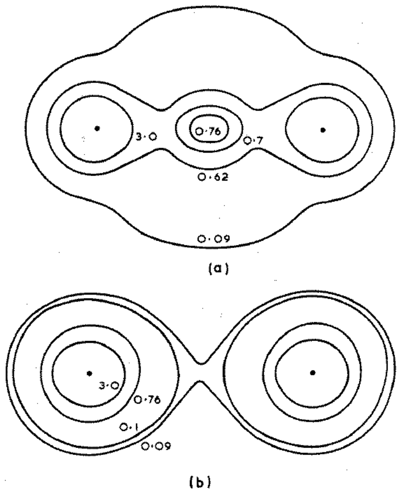
- If the (111) stacking is ...ABAB... instead of ..ABCABC... we have wurtzite

- Note the analogy: fcc ↔ hcp
  zincblende↔wurtzite

Diamond and zincblende structure potentials

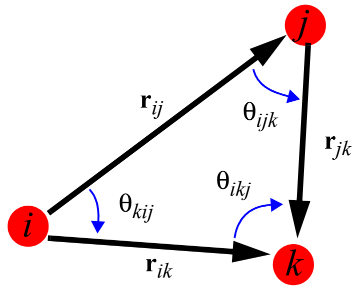


- Covalent bonds
- In a covalent bonds atoms share electrons and thus in some sense achieve a filled electron shell.
- In solids covalent bonds typically form between elements which have a similar outer electron structure.
  - Some elements: C, Si, Ge, S, Se, Te
  - III-V-componds (GaAs, InP, ...)
  - II-VI-compounds (ZnSe, CdTe, ...)
  - various compounds such as SiC
  - molecular crystals (e.g. oxygen where the basic element is the O_2 molecule, H_2O etc. etc.)
- The electrons extend to the space between the atoms.
  - The electron structure of the Si_2 dimer is compared to the superposition of the density of two Si atoms:



Diamond and zincblende structure potentials

- Because of the nature of the hybridization of the electron orbitals, the covalent bonds typically have a strong directional dependence, with some preferred angles between the bonds. For instance, the energy of three atoms will depend not only on the distances $\mathbf{r}_{ij}$, $\mathbf{r}_{ik}$ and $\mathbf{r}_{jk}$ but also on the angles between them θ_{kij}, θ_{ijk} and θ_{ikj}:



- Si has 4 outer electrons, and these can form 4 bonds with sp^3 hybridization, i.e. the angle of 109.47^o .
- From this directional dependence, it also follows that the crystal (or amorphous) structure of covalent solids is often fairly open:
  - Number of nearest neighbours only 2-4, (12 in close-packed structures!).
  - Packing fraction in diamond is only 0.34, whereas it in FCC is 0.74.

Diamond and zincblende structure potentials

- **Dealing with covalent bonding: explicit angles vs. bond order**

- Before we proceed with semiconductors, let us think quite generally about the angular properties of covalent bonds.
- Since we know for any given covalently bonded material that there is one or a few angles between the bonds which give a minimum in the energy, one can immediately see a **purely geometrically motivated** way of constructing a potential: simply put in an explicit angular term which gives a minimum at the equilibrium angle θ_0.
  - For instance, consider a single water molecule H_2O. We know that the angle between the two O-H bonds is about 105°. Thus if one wants to construct an interatomic potential to describe water, one could get the structure right simply by including an explicit angular energy term of the form

    $$E_{\text{angular}} = K_\theta (\theta - 105°)^2$$

    into the potential. (Let's call these potentials "**explicit angular**".)

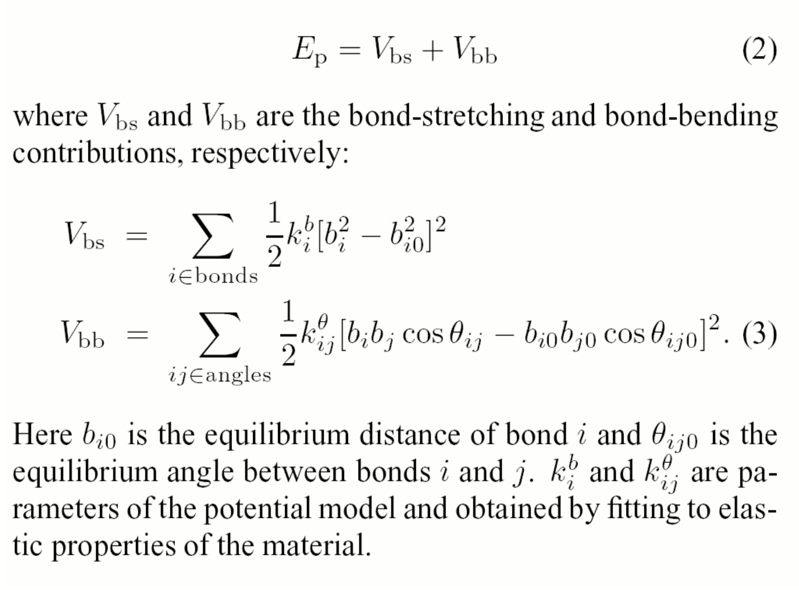
  - There is a problem: The minimum always at only one angle, and nowhere else.

  - However, for instance, consider the carbon allotropes graphite and diamond. In one the angle between bonds is 120°, in the other 109.47°. The energy difference between the two phases is vanishingly small. An explicit angular potential can not possibly describe carbon in both allotropes correctly.

  - Thus although it is easy to construct explicit angular potentials for a known geometry, they do not have a fundamental physical motivation.

Diamond and zincblende structure potentials

- The Keating potential



$$E_{\mathrm{p}} = V_{\mathrm{bs}} + V_{\mathrm{bb}} \qquad (2)$$

where V_{bs} and V_{bb} are the bond-stretching and bond-bending contributions, respectively:

$$V_{\mathrm{bs}} = \sum_{i \in \mathrm{bonds}} \frac{1}{2} k_i^b [b_i^2 - b_{i0}^2]^2$$

$$V_{\mathrm{bb}} = \sum_{ij \in \mathrm{angles}} \frac{1}{2} k_{ij}^\theta [b_i b_j \cos\theta_{ij} - b_{i0} b_{j0} \cos\theta_{ij0}]^2. \qquad (3)$$

Here b_{i0} is the equilibrium distance of bond i and θ_{ij0} is the equilibrium angle between bonds i and j. k_i^b and k_{ij}^θ are parameters of the potential model and obtained by fitting to elastic properties of the material.

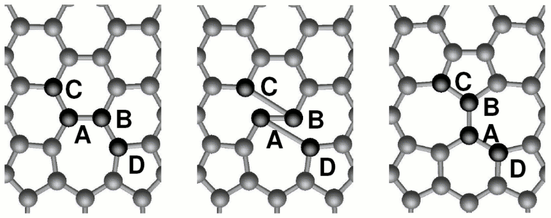


FIG. 1: The bond-switch move in a 2D example. *On the left:* The situation before the switch. *Center:* The bonds have been switched. *On the right:* The atoms have been moved to their minimum energy position.

  - Can be used when near to the equilibrium configuration and no bond breaking occurs.

  - Example of application: build amorphous Si and SiO_2 using bond-switching MC

Diamond and zincblende structure potentials

- An alternative, physically motivated approach to construct potentials for covalent systems is through the concept of “bond order”.
  - By bond order one means is that the strength of a single chemical bond is affected by the chemical neighbourhood: the more neighbours an atom has, the weaker are the bonds which are formed to these atoms. This can be described in potentials of the form

    $$V = V_{\text{repulsive}}(r_{ij}) + b_{ij}V_{\text{attractive}}(r_{ij})$$

    by constructing an environment-dependent term b_{ij} which weakens the pair interaction when the number of neighbours (**coordination number**) Z of an atom is increased.
    -
      - For simplicity we here deal with cases where only bonds to nearest-neighbour atoms are considered.
  - This idea is well motivated qualitatively from basic chemistry: if an atom has N outer electrons, these can form (with other atoms of the same type in a symmetric configuration):
    - a single (dimer) bond with N pairs of electrons
    - two bonds with $N/2$ pairs of electrons
    - three bonds with $N/3$ pairs of electrons

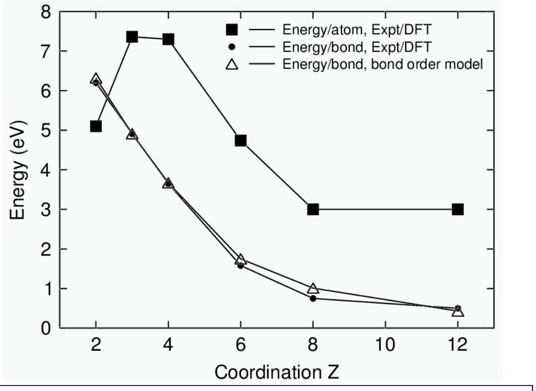
    and so forth
  - Since for every larger number of bonds one bond has less pairs of electrons, it is quite natural that the strength of a single bond tends to decrease.
  - However, the strength of the bond is not directly proportional to the number of electron pairs in it, and the behaviour of the energy/bond may vary quite a lot from one material to another.

Diamond and zincblende structure potentials

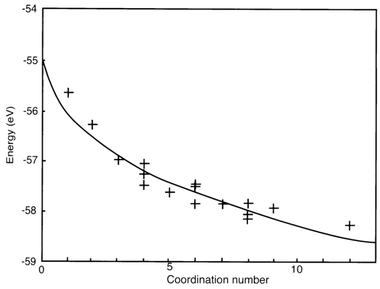
- If the energy/bond decreases very rapidly with the coordination number, the most stable form of the atom is a dimer. If, on the other hand, the dependence is weak, the material wants to maximize its coordination number and will end up in a close-packed configuration.
  - In the limiting case of b_{ij} = constant we get a pure pair potential.
- We can thus think that the strength of bond is a monotonously decreasing function of the coordination number. The equilibrium structure is determined by the balance between the number of bonds and the single bond strength, since the total energy is the product of the two.
  - This formalism allows us to adjust how many numbers of neighbours an atom “wants to have”. This now gives a physical motivation to the preferred angles between bonds: if e.g. the ideal coordination is 4, and the bonds are arranged symmetrically about an atom, one automatically gets the tetrahedral bonding configuration with an angle of 109.47° between the bonds.
- The great advantage here is that now the angle needs not be fixed, because it is perfectly possible to construct potentials which give the same energy for 2 different configurations. Thus one can (and as we shall se people have) constructed potentials which e.g. give local energy minima of equal depth for both the graphite and diamond configurations, thus solving the carbon problem!

Diamond and zincblende structure potentials

- Based on pseudopotential theory Abell [*Phys. Rev. B* **31** (1985) 6184.] has argued that the term b_{ij} should be of the form $b_{ij} \propto Z^{-\delta}$ where Z is the coordination number and δ some number. More specifically, in the so called second-moment approximation of tight binding one obtains $b_{ij} \propto Z^{-1/2}$.
- Let us make all this concrete with an example: carbon. The table below shows the energy/bond and energy/atom for a number of different coordinations of carbon. The values for $Z = 2, 3, 4$ are from experiment and the values for the hypothetical phases $Z > 4$ from a DFT calculation which also reproduces the experimental values well [Furthmüller *et al*, *Phys. Rev. B* **50** (1994) 15606; data compiled in Albe *et al*, *Phys. Rev. B* **65**, 195124].



Z	Phase	Energy/atom (eV)	Energy/bond (eV)	Energy/bond bond order model
2	dimer	5.10	6.20	6.32
3	graphite	7.36	4.91	4.91
4	diamond	7.30	3.65	3.67
6	simple cubic	4.74	1.58	1.75
8	BCC	3.00	0.75	1.01
12	FCC	3.00	0.50	0.43



For comparison: energy/atom for aluminium [Phillips, Fig. 4.5]. Curve is a fit of the form $E = E_0 + \alpha Z^{1/2} + \beta Z$.

Note the different sign convention!

Diamond and zincblende structure potentials

- The last column shows a fit to the data obtained with a bond order model of the $1/\sqrt{Z}$ form. As you can see, a quite good fit is obtained for all phases, and especially the most important ones are described very well.
- Note also that the bond order model correctly predicts that graphite and diamond are almost equal in energy.

Diamond and zincblende structure potentials

- The generality of this approach was shown by Brenner [*Phys. Rev. Lett.* **63** (1989) 1022.], who proved that this form is mathematically equivalent with the EAM formalism (after suitable transformations), and specifically that if $\delta = -1/2$ one can obtain exactly the Finnis-Sinclair / Cleri-Rosato-like metal potentials:

$$E = \sum_i E_i \ , \ E_i = \frac{1}{2}\sum_{j \neq i} [V_i^{\mathrm{pair}}(r_{ij}) + V_i^{\mathrm{mb}}]$$

- Tersoff: $V_i^{\mathrm{mb}} = -\frac{1}{2}\sum_{j \neq i} B b_{ij} e^{-\lambda_2 r_{ij}}$, $b_{ij} = \left[1 + \sum_{k, j \neq i} G(\theta_{ijk}) e^{-\lambda_3 (r_{ij} - r_{ik})}\right]^{-\eta}$

  (or $b_{ij} = \left[1 + \left(\sum_{k, j \neq i} G(\theta_{ijk}) e^{-\lambda_3^3 (r_{ij} - r_{ik})^3}\right)^n\right]^{-1/(2n)}$)

- EAM: $V_i^{\mathrm{mb}} = -F\left(\sum_{j \neq i} \rho(r_{ij})\right)$.

Diamond and zincblende structure potentials

- Assuming Finnis-Sinclair form $F(\rho) = -A\rho^{1/2}$, $\rho(r) = e^{-ar}$ we get

$$\begin{aligned}
V_i^{\mathrm{mb}} &= -A\left[\sum_{j \neq i} e^{-ar_{ij}}\right]^{1/2} = -A\left[\sum_{j \neq i} e^{-ar_{ij}}\right]\left[\sum_{k \neq i} e^{-ar_{ik}}\right]^{-1/2} \\
&= -A\left\{\sum_{j \neq i} e^{-ar_{ij}}\left[\sum_{k \neq i} e^{-ar_{ik}}\right]^{-1/2}\right\} \\
&= -A\left\{\sum_{j \neq i} e^{-ar_{ij}}\left[e^{-ar_{ij}} + \sum_{k \neq i, j} e^{-ar_{ik}}\right]^{-1/2}\right\} \\
&= -\sum_{j \neq i} A e^{-ar_{ij}/2}\left[1 + \sum_{k \neq i, j} e^{a(r_{ij} - r_{ik})}\right]^{-1/2}
\end{aligned}$$

Thus if $B = 2A$, $\lambda_3 = a = 2\lambda_2$, $\eta = 1/2$, $G(\theta) = 1$ we get the Tersoff potential!

Classical Si potentials

[One important source: Balamane, *Phys. Rev. B* **46** (1992) 2250]

- Because of the directional dependence of the bonds, all decent Si potentials have some sort of an angular dependence, and hence they are at least 3-body potentials.
- Some potentials have an explicit 3-body form, i.e. the potential has the shape:

$$V = \sum_{i,j} V_2(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_{i,j,k} V_3(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k)$$

  - These potentials are called by Balamane *cluster-potentials.* They typically also are *explicit angular* potentials.
  - In other potentials the angular dependence is hidden in the 2-body part so that there is no explicit V_3 part. These are called by Balamane *cluster functionals.*
- The philosophy of the cluster functionals is similar to the EMT/EAM potentials: calculate a pair potential, but let its strength be affected by the environment. A common formulation is

$$V = V_{\text{repulsive}}(r_{ij}) + b_{ij} V_{\text{attractive}}(r_{ij})$$

  which is the same as for *bond-order* potentials.

  - Here the attractive and repulsive parts themselves are pure pair potentials, but there is a coefficient b_{ij} which has an environment-dependence. The main difference to EAM is that although they can be cast in the form above, in them b_{ij} has no angular dependence, whereas in the Si potential there must be one.
  - Hence in the Si potentials there also has to be a three-body loop $\sum_{i,j,k} (\boldsymbol{r_{ij}}, \boldsymbol{r_{ik}})$ which gives the angles.

Efficiency of semiconductor vs. metal potentials

- Assume the number of atoms is N and the average number of neighbours per atom is M
- A pair potential and an EAM potential is then $O(NM)$
- A three-body potential is $O(NM^2)$
- So it would appear like the Si potentials are a factor of M slower than EAM potentials.

- But this is most of the time not true in reality. This is because for covalent bonding, long-range interactions are weak compared to the nearest neighbour-ones, so it is often enough to only include nearest-neighbour interactions. So for Si $M = 4$. But in metals long-range interactions are important (e.g. for surface properties and to get the difference between the FCC and HCP phases right), so often $M \sim 50$ in metals.

- Because $4^2 < 50$ the Si potentials with three-body terms may in fact be faster than EAM potentials without one!

- But there are additional funny effects. For some Si potentials the cutoff is set so that in the crystalline phase $M = 4$, but it increases strongly in a disordered (amorphous or liquid) phase. So the speed of the potential may be strongly affected by what phase of a material is simulated!

The Stillinger-Weber-potential

- Stillinger and Weber [*Phys. Rev. B*, **31** (1985) 5262] (**SW**) developed a potential, which describes fairly well both crystalline and liquid silicon - they in fact constructed it to give the melting temperature right. The potential has become quite popular over the years because it turned out to describe well several properties which it was not really designed to describe originally (such as point defect energies and surface properties).
- The potential is an explicit angular potential, and has the form

$$V = \sum_{i,j} V_2(r_i, r_j) + \sum_{i,j,k} V_3(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k)$$

$$V_2(r_{ij}) = \varepsilon f_2(r_{ij}/\sigma)$$

$$V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = \varepsilon f_3(\mathbf{r}_i/\sigma, \mathbf{r}_j/\sigma, \mathbf{r}_k/\sigma) \quad .$$

where V_2 is the pair potential and V_3 the three-body part. The f_i are

$$f_2(r) = \begin{cases} A(Br^{-p} - 1)\exp[(r-a)^{-1}], & r < a \\ 0, & r \geq a \end{cases}$$

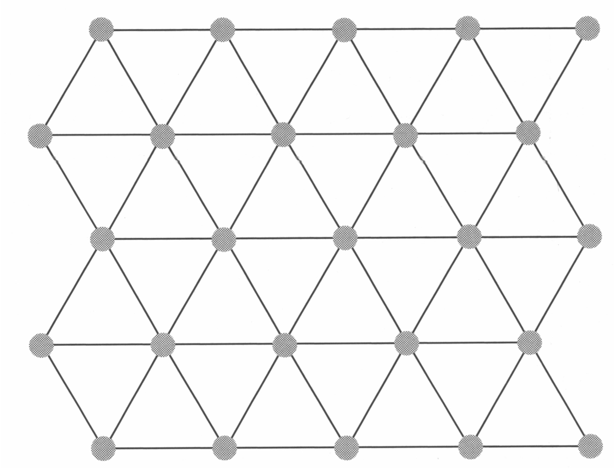
$$f_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}) \quad ,$$

where θ_{jik} is the angle, which the vectors $\mathbf{r}_{ij}$ and $\mathbf{r}_{ik}$ make at the atom i and the function h is

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \begin{cases} \lambda\exp[\gamma(r_{ij}-a)^{-1} + \gamma(r_{ik}-a)^{-1}]\left(\cos\theta_{jik} + \frac{1}{3}\right)^2, & r_{ij} < a \text{ and } r_{ik} < a \\ 0, & r_{ij} \geq a \text{ or } r_{ik} \geq a \end{cases} \quad .$$

The Stillinger-Weber-potential

- So, in practical calculation all atom triplets being within the cut-off radius from each other must be handled.
- As a hypothetical example take the triangular lattice:



- Here the potential energy for one atom term takes the form:

$$V = 3V_2(r_{\text{nn}}) + 6h(r_{\text{nn}}, r_{\text{nn}}, 60^{\text{o}}) + 6h(r_{\text{nn}}, r_{\text{nn}}, 120^{\text{o}}) + 3h(r_{\text{nn}}, r_{\text{nn}}, 180^{\text{o}}).$$

- Note that in this case the Stillinger-Weber would not work!
- However, in the diamond lattice all the bond pairs of a single atom have the same angle.

The Stillinger-Weber-potential

- The constants A, B, p, a, λ and γ are all positive and were determined by demanding that the diamond structure is the most stable one and that the melting point, cohesive energy and lattice parameter are about right.

- According to rumours the potential was also fit to the elastic constants (which are reproduced fairly well), although the authors never stated this in the paper!

- The actual parameter values are

$$\sigma = 2.0951\text{Å}, \varepsilon = 2.1672\text{eV},$$
$$A = 7.0496, B = 0.60222,$$
$$p = 4, \quad a = 1.80,$$
$$\lambda = 21.0 \text{ and } \gamma = 1.20 \quad .$$

- The melting point was fit to be almost exactly right with a rather dirty trick: the authors modified the cohesive energy to get the melting point close to the right value of 1685 K. The cohesive energy of the potential is 4.334 eV, when the right value is 4.63 eV. So this is a 7% mismatch. If this is corrected by direct scaling, the melting point will go wrong.

The Stillinger-Weber-potential

- The authors examined the structure of molten Si by comparing the maxima and minima of the structure factor $S(k)$ to measured values:

	MD	measured
1. maximum	2.53	2.80
1. minimum	3.25	3.25
2. maximum	5.35	5.75
3. maximum	8.16	8.50
4. maximum	10.60	11.20

- The potential describes fairly well melting and liquid Si. However, it is important to realize that the angle between bonds is ‘forced’ to the ideal tetrahedral angle with the cosine term $(\cos\theta_{jik} + (1/3))^2$. This is not a good feature, because of the reasons given above for “explicit angular” potentials.

The Stillinger-Weber-potential

- However, SW describes the Si (001) surface better than the Tersoff potentials [Nurminen *et al.*, *Phys. Rev. B* **67** (2003) 035405.]

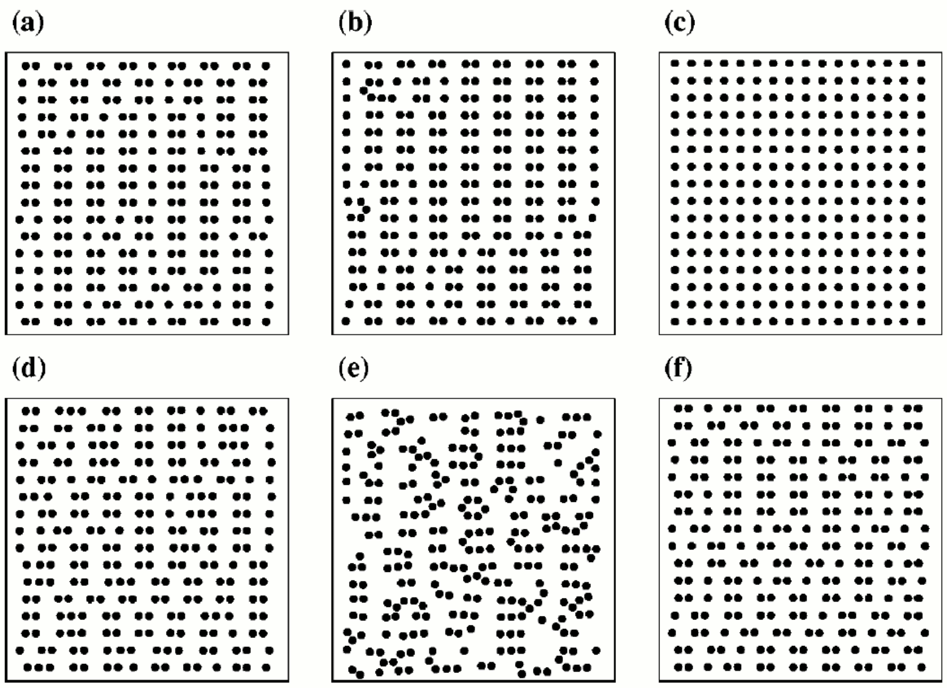


FIG. 2. Typical *metastable* surface configurations obtained from a regular MC run at $T=116$ K (upper row) and at $T=812$ K (lower row) using the SW potential (a) and (d), the $T2$ potential (b) and (e), and the $T3$ potential (c) and (f). The configurations are averages over 20 000 MC steps after initial run of 20 000 MC steps. All atoms were initially placed in diamond lattice positions.

The EDIP potential

- The EDIP-potential is fairly similar to the SW one, but it has been derived from an *ab initio*-calculated database of the cohesive properties of Si both in the diamond and graphite phases.

- The potential is:

$$E_i=\sum_{j\neq i} V_2(R_{ij},Z_i)+\sum_{j\neq i}\sum_{k\neq i,k>j} V_3(\vec{R}_{ij},\vec{R}_{ik},Z_i), \quad (1)$$

$$Z_i=\sum_{m\neq i} f(R_{im}) \quad (2)$$

$$f(r)=\begin{cases} 1 & \text{if } r<c, \\ \exp\left(\dfrac{\alpha}{1-x^{-3}}\right) & \text{if } c<r<a, \\ 0 & \text{if } r>a, \end{cases} \quad (3)$$

$$V_2(r,Z)=A\left[\left(\frac{B}{r}\right)^{\rho}-p(Z)\right]\exp\left(\frac{\sigma}{r-a}\right), \quad (4)$$

$$p(Z)=e^{-\beta Z^2}. \quad (5)$$

$$V_3(\vec{R}_{ij},\vec{R}_{ik},Z_i)=g(R_{ij})g(R_{ik})h(l_{ijk},Z_i), \quad (6)$$

$$g(r)=\exp\left(\frac{\gamma}{r-a}\right), \quad (7)$$

$$h(l,Z)=H\left(\frac{l+\tau(Z)}{w(Z)}\right), \quad (8)$$

$$h(l,Z)=\lambda[(1-e^{-Q(Z)(l+\tau(Z))^2})+\eta Q(Z)(l+\tau(Z))^2]. \quad (9)$$

$$\tau(Z)=u_1+u_2(u_3e^{-u_4Z}-e^{-2u_4Z}), \quad (10)$$

with the choice $w(Z)^{-2}=Q(Z)=Q_0e^{-\mu Z}$

The EDIP potential

- So the main difference to SW is the environment-dependence in the form of the effective coordination number Z, which modifies the terms.
- The potential is available in the web
  http://www-math.mit.edu/~bazant/EDIP/
  including Fortran and C codes by which it can be evaluated efficiently.
- The parameter-values are:

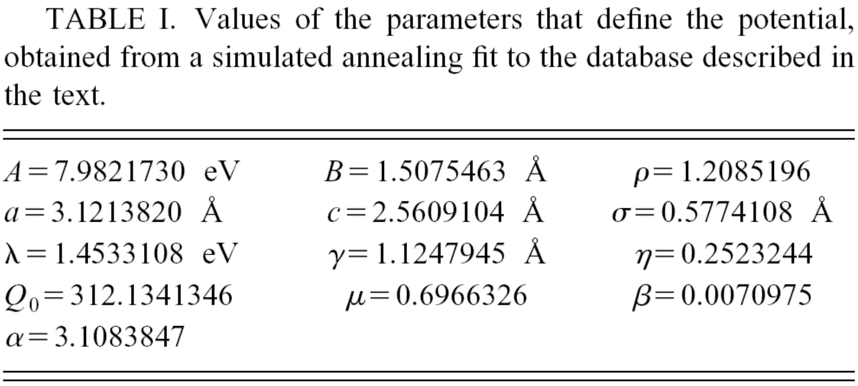


TABLE I. Values of the parameters that define the potential, obtained from a simulated annealing fit to the database described in the text.

$A = 7.9821730$ eV	$B = 1.5075463$ Å	$\rho = 1.2085196$
$a = 3.1213820$ Å	$c = 2.5609104$ Å	$\sigma = 0.5774108$ Å
$\lambda = 1.4533108$ eV	$\gamma = 1.1247945$ Å	$\eta = 0.2523244$
$Q_0 = 312.1341346$	$\mu = 0.6966326$	$\beta = 0.0070975$
$\alpha = 3.1083847$		

The EDIP potential

- As required in a good fit, a large number of other properties have also been tested in the potential, the most important of which is that the diamond structure is the minimum of several common crystal structures:
- But note that EDIP does overestimate the energy of many other phases fairly much compared to DFT.
- Among the best properties of the EDIP potential is that it reproduces the elastic constants very well, gives both good point defect, stacking fault and dislocation properties, and describes amorphous Si well. Also the melting point is described well, the potential predicts 1550 ± 50 K [Nord *et al, PRB* **65** (2002) 165329], quite close to the experimental value of 1685 K.
- The thermodynamical properties of EDIP-Si have been studied by P. Keblinski *et al.*,[*Phys. Rev. B* **66** (2002) 064104.]

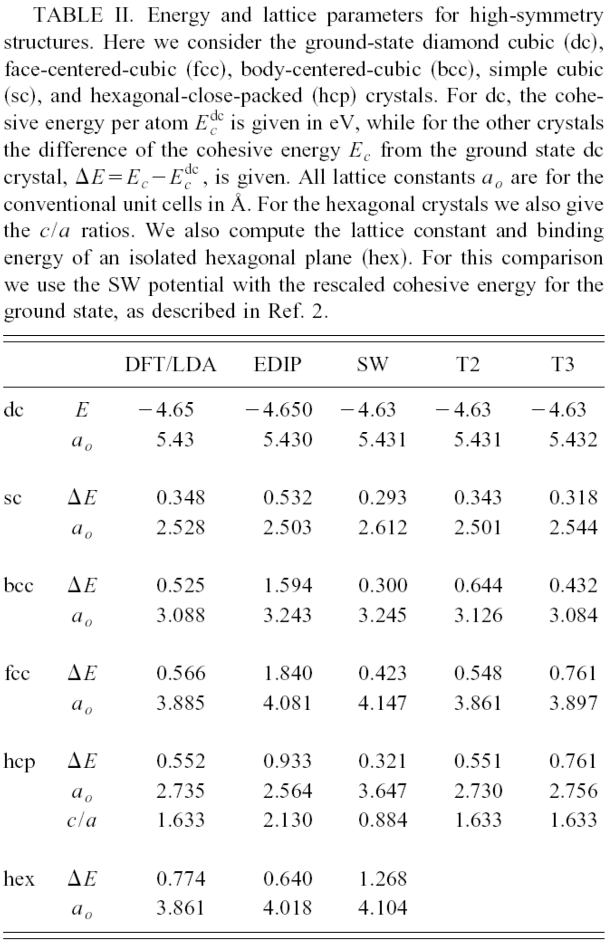


TABLE II. Energy and lattice parameters for high-symmetry structures. Here we consider the ground-state diamond cubic (dc), face-centered-cubic (fcc), body-centered-cubic (bcc), simple cubic (sc), and hexagonal-close-packed (hcp) crystals. For dc, the cohesive energy per atom E_c^{dc} is given in eV, while for the other crystals the difference of the cohesive energy E_c from the ground state dc crystal, $\Delta E = E_c - E_c^{\mathrm{dc}}$, is given. All lattice constants a_o are for the conventional unit cells in Å. For the hexagonal crystals we also give the c/a ratios. We also compute the lattice constant and binding energy of an isolated hexagonal plane (hex). For this comparison we use the SW potential with the rescaled cohesive energy for the ground state, as described in Ref. 2.

		DFT/LDA	EDIP	SW	T2	T3
dc	E	−4.65	−4.650	−4.63	−4.63	−4.63
	a_o	5.43	5.430	5.431	5.431	5.432
sc	ΔE	0.348	0.532	0.293	0.343	0.318
	a_o	2.528	2.503	2.612	2.501	2.544
bcc	ΔE	0.525	1.594	0.300	0.644	0.432
	a_o	3.088	3.243	3.245	3.126	3.084
fcc	ΔE	0.566	1.840	0.423	0.548	0.761
	a_o	3.885	4.081	4.147	3.861	3.897
hcp	ΔE	0.552	0.933	0.321	0.551	0.761
	a_o	2.735	2.564	3.647	2.730	2.756
	c/a	1.633	2.130	0.884	1.633	1.633
hex	ΔE	0.774	0.640	1.268		
	a_o	3.861	4.018	4.104		

The EDIP potential

- For example the radial distribution function of amorphous Si compared to experiments is reproduced fairly well:
- The EDIP potential clearly is one of the best Si potentials available now, most tests of its properties have been quite favourable to it.

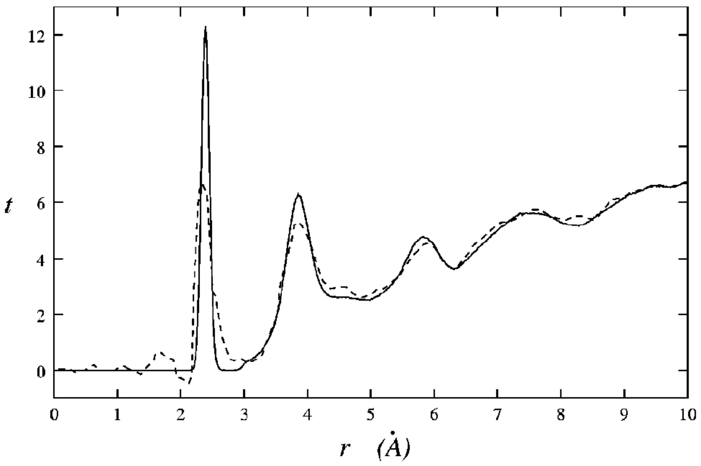


FIG. 11. Radial distribution function $t(r)=4\pi\rho r g(r)$ for the amorphous phase at room temperature and zero pressure using our model, compared with the results of neutron-scattering experiments on pure evaporated-beam-deposited a-Si thin films by Kugler *et al.* (Ref. 68).

- Another Si potential is [Lenosky *et al.*, *Modelling and Simulation in Materials Science and Engineering* **8** (2000) 825]. This is a combination of EAM and SW models, which gives truly excellent fits to a large number of elastic constants, different structures and defect properties. However, it contains some questionable features (such as a negative electron density for some distances r) so its transferability outside the parameter database to which it has been originally fit is questionable.

Tersoff potential

- The Tersoff potential [first good Si fit in *Phys. Rev. B* **38** (1988) 9902] is a cluster-functional and bond order potential which has an environment dependence and no absolute minimum at the tetrahedral angle. Tersoff based his potential on the ideas presented by Abell a few years earlier. The Tersoff or more appropriately **Tersoff-Abell formalism** is probably the most widely used bond order potential formalism and has become the basis or inspiration for a huge number of potentials developed since then.

  Tersoff-like potentials are pure bond order potential motivated by the approach presented a few pages back in these notes, i.e. of the form:

$$V = V_{\mathrm{repulsive}}(r_{ij}) + b_{ijk} V_{\mathrm{attractive}}(r_{ij})$$

- The original Tersoff potential has the following form. The total energy is

$$E = \frac{1}{2}\sum_{i \neq j} V_{ij} \quad ,$$

  where

$$V_{ij} = f_{\mathrm{C}}(r_{ij})[a_{ij} f_{\mathrm{R}}(r_{ij}) + b_{ij} f_{\mathrm{A}}(r_{ij})] \ .$$

Tersoff potential

- The various terms have the following forms:

repulsive part $f_R(r) = Ae^{-\lambda_1 r}$,

attractive part $f_A(r) = -Be^{-\lambda_2 r}$,

potential cutoff function

$$f_C(r) = \begin{cases} 1, & r \le R - D \\ \frac{1}{2} - \frac{1}{2}\sin\left(\frac{\pi}{2}\frac{(r-R)}{D}\right), & R - D < r < R + D \\ 0, & r \ge R + D \end{cases} ,$$

and

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-1/2n} ,$$

$$\zeta_{ij} = \sum_{k \ne i,j} f_C(r_{ik}) g(\theta_{jik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] ,$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2} ,$$

$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/2n}$ and $\eta_{ij} = \sum_{k \ne i,j} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3]$.

Tersoff potential

- Here, as above, the distance between atoms i and j is r_{ij} and the angle between bonds ij and ik is θ_{jik}.
- Inspection of the terms shows that there is an angular dependence, but because is embedded inside the b_{ij} term, it does not give a fixed minimum angle between bonds.
- The relation to the bond order potential basic formalism is as follows: if $n = 1$, $c = 0$, $\beta = 1$, and $\lambda_3 = 0$ we get the “pure” bond order potential with

$$b_{ij} = \left[1 + \sum_{k \ne i,j} f_C(r_{ik})\right]^{-1/2} \propto \frac{1}{\sqrt{Z_i}} .$$

Note that the sum excludes atom j that is taken into account by adding one.

- Tersoff could not find a parameter set $\{A, B, \lambda_1, \lambda_2, \alpha, \beta, n, c, d, h, \lambda_3, R, D\}$ which would describe well both the reconstructed Si surfaces and its elastic properties. Because of this he gave two parametrizations: Si C, which describes well elastic properties, and Si B, which gives good surface properties. Tersoff's Si A is the original potential which proved to be unstable. Si(B) is also known as Tersoff 2 and Si(C) as Tersoff 3.

	Si(B)/T2	Si(C)/T3
A (eV)	3264.7	1830.8
B (eV)	95.373	471.18
λ_1 (Å^{-1})	3.2394	2.4799
λ_2 (Å^{-1})	1.3258	1.3722
α	0.0	0.0
β	0.33675	1.0999×10^{-6}
n	22.956	0.78734
c	4.8381	1.0039×10^{5}
d	2.0417	16.218
h	0.0	-0.59826
λ_3 (Å^{-1})	1.3258	1.7322
R (Å)	3.0	2.85

	Si(B)/T2	Si(C)/T3
D (Å)	0.2	0.15

Tersoff potential

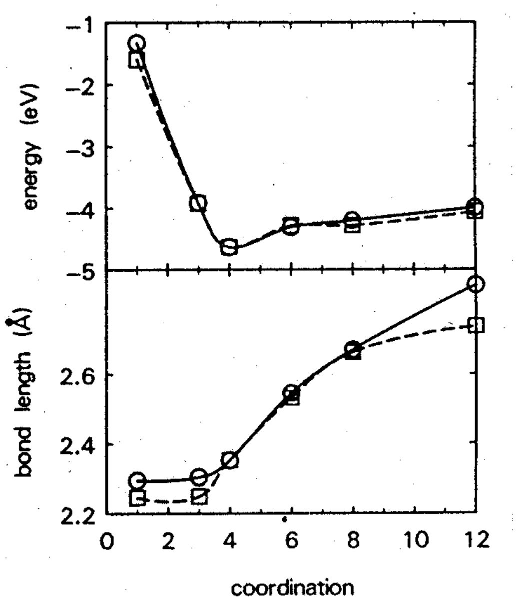
- The parameter λ_3 is an interesting case: it does not affect the equilibrium properties at all, only properties far from equilibrium. Tersoff himself said it can be set to 0, and this is often done. However, in far-from-equilibrium studies it has proven to be best to include λ_3.

- Note also that since $\alpha = 0$, the two last equations in the potential form are meaningless (give exactly 1). Although Tersoff have these two equations, I am not aware of any case where they would actually have been used.

Tersoff potential

- Below is a comparison of the energies and bond lengths obtained with Tersoff for different coordination numbers compared to experimental and *ab initio*-calculations.

Why should anyone care about e.g. 12-fold coordinated Si?
Although some coordination numbers may not exist in the ground state, they may still be present e.g. in defects, surfaces and metastable molecules.



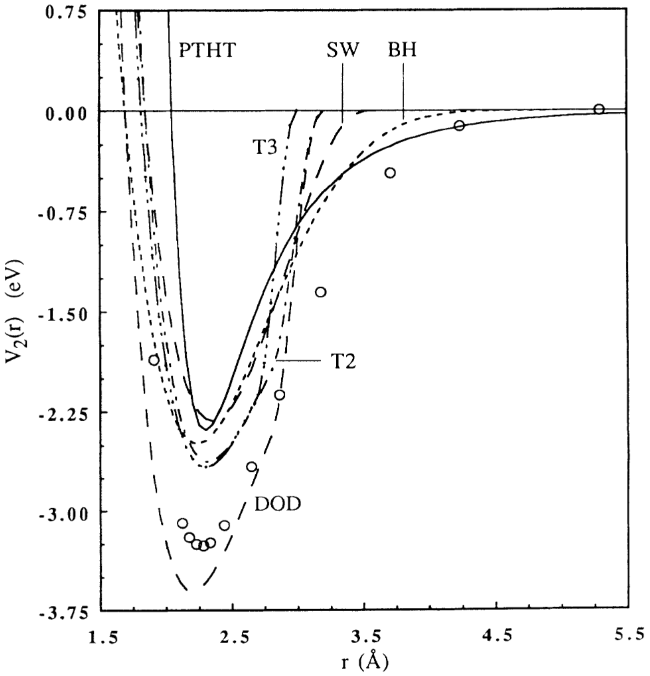
Comparison of Si potentials

- Balamane & co have done an extensive comparison of Si potentials, looking e.g. at bulk, surface, defect and small molecule properties. [H. Balamane, T. Halicioglu, W. A. Tiller, *Phys. Rev. B* **46** (1992) 2250.]. Unfortunately EDIP was not part of this comparison.

- Included were the SW, and Tersoff potentials Si(B) [T2] and Si(C) [T3]. Also included were the Biswas-Hamann potential (BH) [PRL 55 (1985) 2001, PRB 34 (1986) 895.], the Tersoff-like Dodson potential [DOD; *Phys. Rev. B* **35** (1987) 2795.] and the potential by Pearson *et al.* (PTHT; *Cryst. Growth.* **70** (1984) 33.].

Comparison of Si potentials

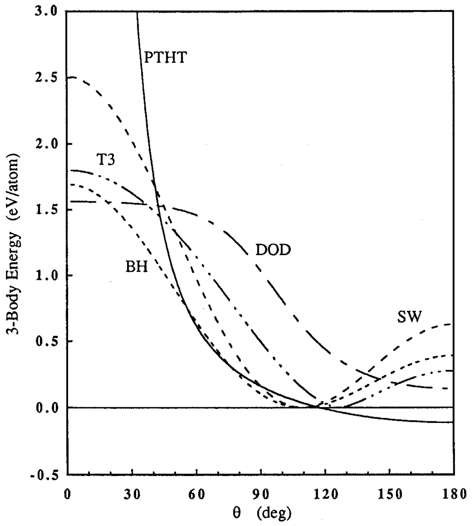
- Below is the pair term of the potentials $V_2(r)$. The spheres are *ab initio* results.

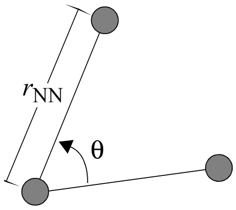


- We see that except for DOD the potentials are fairly similar. BH and PTPH have a long range compared to the others.

Comparison of Si potentials

- Here is the energy of three Si atoms/atom:



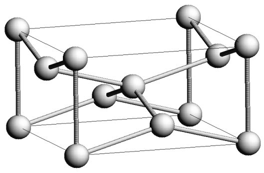


- Note that the energy becomes fairly large for small angles for all the potentials.

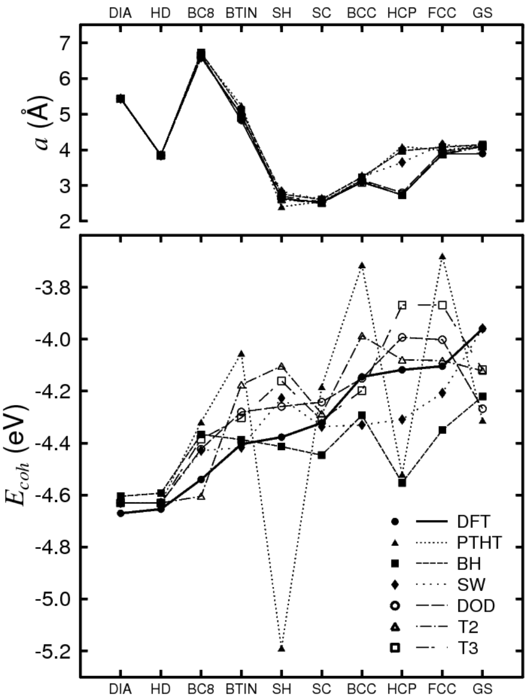
Comparison of Si potentials

- In the adjacent picture the cohesive energies of different structures are shown, compared to DFT calculations.
  - Note that PTHT predicts that the simple hexagonal structure is the most stable one.

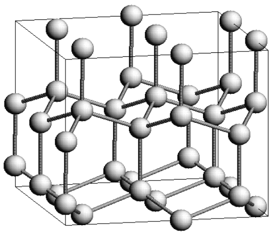
β-tin



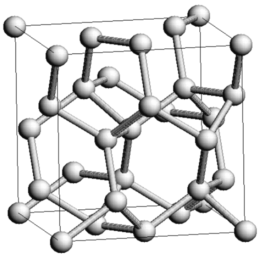
DIA = diamond
HD = hexagonal diamond
BC8 = bc-8
BTIN = β–tin
SH = hexagonal
SC = cubic
BCC = body-centered cubic
HCP = hexagonal close-packed
FCC = face-centered cubic
GS = graphite



HD (wurtzite)



BC8



Good source of crystal structures:
http://cst-www.nrl.navy.mil/lattice/index.html

Comparison of Si potentials

- And below are the elastic properties of the potentials

	experiment	PTHT	BH	SW	DOD	T2	T3
B	0.99	2.788	1.692	1.083	0.884	0.98	0.98
B'	4.2	7.82	5.66	2.93	4.27	4.58	4.30
c_{11}	1.67	2.969	2.042	1.616	1.206	1.217	1.425
c_{12}	0.65	2.697	1.517	0.816	0.722	0.858	0.754
c_{44}	0.81	0.446	0.451	0.603	0.659	0.103	0.690
c_{44}^0	1.11	2.190	1.049	1.172	3.475	0.923	1.188
ζ	0.74	1.03	0.74	0.63	1.06	0.83	0.67
$\nu_{TA}(X)$	4.4	4.5	5.6	6.7		2.7	9
$\nu_{TO}(X)$	13.9	19.3	14.5	15.9		15.3	16
$\nu_{LOA}(X)$	12.3	13.8	12.2	13.1		11.7	12
$\nu_{LTO}(\Gamma)$	15.3	18.3	16	18.1		16.5	16

$$[B], [c_{ij}] = \text{Mbar}, \; [\nu] = \text{THz}, \; B' = \frac{\mathrm{d}B}{\mathrm{d}P}$$

- We see that T3 and SW give good elastic properties. Lattice vibrations are described well by the BH potential.

Comparison of Si potentials

- And here are a bunch of energies for lattice defects.

	DFT	PTHT	BH	SW	DOD	T2	T3
V	3-4	0.77	2.12	2.82	2.57	2.81	3.70
	4.5	2.50	3.83	4.63	3.23	2.83	4.10
		38.5	-25.7	-24	14.7	1	10.5
V_S	4.19	2.83	2.30	3.36	4.17	1.40	3.50
	5.01	4.53	4.72	6.00	8.12	4.15	10.5
	-9.5	-15.9	-12.5	-11.8	-14.5	-14.9	-8.8
I_T	5-6	0.63	1.56	5.25	3.03	5.03	3.45
		1.91	4.57	12.21	5.00	5.85	6.92
		3.8	8	9	9.1	7.3	10.5
I_H	4-5	0.84	2.89	6.95	2.61	3.67	4.61
		5.32	9.31	17.10	5.1 1	5.39	8.22
		7.4	11.5	14.7	7.3	7.6	10.2
I_B	4-5	1.92	2.54	5.99	4.39	2.84	5.86
I_S		1.47	3.30	3.66*	3.49	2.32	4.70

V = vacancy

V_S=split vacancy

I_T=tetrahedral interstitial

I_H=hexagonal interstitial

I_B=bond-centered interstitial

I_S=split interstitial.

The first number is the energy of the ground state, the second the energy of the ideal (non-relaxed) structure, and the third gives the radial relaxation of the nearest neighbours in percent (negative value inwards, positive outwards).

* Note that Balamane had an error here, this is determined by K. Nordlund.

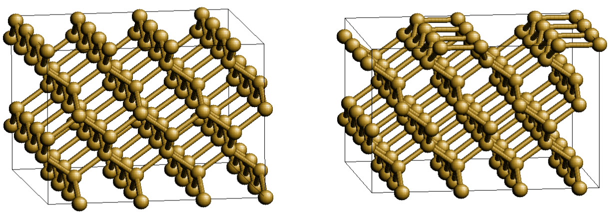
- The table tells predominantly that the short-range potentials (SW, DOD, T2, T3) describe defects best. SW is good in that it predicts that the simple vacancy and split interstitial are the ground state defects, which agrees with ab initio results for uncharged defects.

Comparison of Si potentials

- Finally a table of the properties of the Si (100) surface:

	DFT	PTHT	BH	SW	DOD	T2	T3
	1×1						
γ	2.5	1.805	2.080	2.315	1.779	2.015	2.126
σ_{xx}	2.535	1.176	1.421	0	0	0	0
σ_{yy}	0.855	2.363	1.683	0	0.145	0.625	-0.236
	1×1 relaxed						
$\Delta\gamma$	-0.03	-0.077	-0.027	0	-0.085	-0.004	-0.037
σ_{xx}		-0.427	0.848	0	0.515	0.023	0.076
σ_{yy}		-2.176	0.273	0	-2.775	0.080	-1.693
Δ	-5.1	-7.0	-5.5	0	-10.2	-2.3	-7.2
	2×1						
$\Delta\gamma$	-0.93	-0.690	-0.709	-0.899	-0.714	-1.258	-0.759
σ_{xx}	0.693	-0.808	0.669	1.167	-0.094	0.703	0.367
σ_{yy}	-1.945	-1.731	0.008	-0.051	-1.709	0.190	-1.236
Δ	-24.4	-23.3	-13.3	-8.3	-22.9	-14.6	-15.6

		DFT	PTHT	BH	DOD	T2	T3
	c2×2						
$\Delta\gamma$		-0.839	-0.703	-0.824	-0.720	-1.143	-0.753
σ_{xx}		-1.356	0.898	1.691	0.274	1.517	0.865
σ_{yy}		-1.419	0.851	0.574	-0.866	0.567	-0.344


Si 1×1

Si 2×1

Si c(2×2): buckling of dimers

γ=surface energy (eV)
$\Delta\gamma$=change in surface energy from 1x1
σ_{ii}=surface tension tensor (x in the direction of the dimer bond and y in the direction of the dimer row)
Δ= distance change between 1. and 2. layer (%).

Comparison of Si potentials

- The conclusions of the authors are that no potential is clearly superior. Different potentials describe different properties well.

  SW, **T3** and to some extent **DOD** are good for elastic properties

  T3, SW, DOD, T2 and **BH** give fairly good values for the point defects, to the extent this is possible to judge considering that the experimental values are not known very well either!

  The (100) surface is described best by **BH, SW** and **T3**. No potential describes the complicated reconstructions of the (111) surface.

- **EDIP** was not part of this comparison, but it is clear it would be among the best at least for the elastic and defect properties.

MEAM models

- There also exist so called MEAM (modified EAM) models for Si. This is basically EAM to which an angular term has been added:

$$E_{\text{tot}} = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{ij} V_{ij}(r_{ij})$$

$$\rho_i = \sum_{j \neq i} \rho^{\text{a}}(r_{ij}) + \sum_{k, j \neq i} \rho^{\text{a}}(r_{ij})\rho^{\text{a}}(r_{ik})g(\cos\theta_{ijk})$$

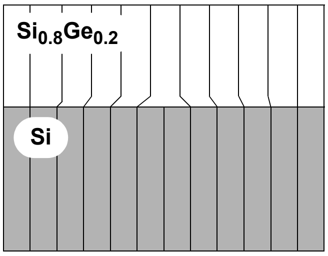
- Baskes has developed some models, but is apparently not quite satisfied with them.

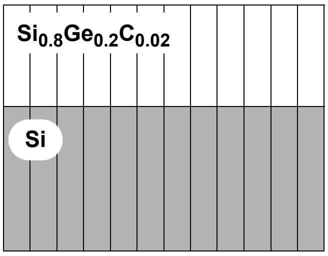
- Applied (in addition to metals) to e.g. silicides (TaSi, MoSi; electronic components!)

Potentials for semiconductor alloys

- The alloys of Si are something of a hot topic.

- Silicon carbide is interesting both for its mechanical hardness as well as its possibilities in high-voltage or high-current electronics.





- Silicon-germanium compounds ($Si_{1-x}Ge_x$) again are very interesting because by adding some 20 % Ge to Si one can get the electron mobility (and hence integrated circuit speed) about as high as in GaAs, about twice the value in Si. But because the device is still based on Si, one does not have to change to the more complicated GaAs manufacturing technology.

- In $Si_{1-x}Ge_x$-compounds there is, however, the problem that their lattice constant does not match that of Si (on top of which the SiGe is grown). The latest promising word is then $Si_{1-x-y}Ge_xC_y$ where x ~ 0.2 and y ~ x/10. That is, only a few years ago someone realized that by adding a little bit of carbon one can get a perfect lattice match to Si.

- For instance because of this it is interesting to have models for SiGe-, SiGeC and SiC-compounds.

Potentials for semiconductor alloys

- The Stillinger-Weber potential has two Ge-parametrizations [Ding and Andersen, *Phys. Rev. B* **34** (1986) 6987 and Wang and Stroud, *Phys. Rev. B* **38** (1988) 1384]. Out of these, the Ding and Andersen potential has: $\sigma = 2.181\ \text{Å}$ and $\varepsilon = 1.93\ \text{eV}$; the other parameters are identical to Si. Wang-Stroud is like Ding-Andersen except that $\lambda = 31$.
  - One can construct a SiGe compound potential simply by taking the geometric average of the Si and Ge parameters:

$$
\begin{aligned}
\sigma_{\mathrm{SiGe}} &= \sqrt{\sigma_{\mathrm{Si}}\sigma_{\mathrm{Ge}}} \\
\varepsilon_{\mathrm{SiGe}} &= \sqrt{\varepsilon_{\mathrm{Si}}\varepsilon_{\mathrm{Ge}}} \\
\lambda_{\mathrm{SiGe}} &= \sqrt{\lambda_{\mathrm{Si}}\lambda_{\mathrm{Ge}}}
\end{aligned}
$$

- There is also actually a SW-parametrization for C [Pailthorpe and Mahon, Thin Solid Films **192/ 193** (1990) 34], but this should normally not be used - since SW has a minimum for sp^3 bonding, but carbon also can be favourably in the triply bonded graphite sp^2 configuration, with bond angles of 120^{o}°, the SW parametrization is of very limited usability.
- But in describing the lattice compensation of $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ for y ~ 0.01 the combination of the three SW potentials actually does correctly reproduce the good lattice match to Si.

Potentials for semiconductor alloys

- Tersoff has also developed potentials for SiC and SiGe [*PRB* **39** (1989) 5566.]. The formalism is almost the same as for his Si potential:

$$
E = \frac{1}{2}\sum_{i \neq j} V_{ij} \quad , \quad V_{ij} = f_{\mathrm{C}}(r_{ij})[f_{\mathrm{R}}(r_{ij}) + b_{ij} f_{\mathrm{A}}(r_{ij})] \quad ,
$$

$$
f_{\mathrm{R}}(r_{ij}) = A_{ij} e^{-\lambda_{ij} r_{ij}} \quad , \quad f_{\mathrm{A}}(r_{ij}) = -B_{ij} e^{-\mu_{ij} r_{ij}} \quad ,
$$

$$
f_{\mathrm{C}}(r_{ij}) = \begin{cases} 1, & r_{ij} \le R_{ij} \\ \frac{1}{2} + \frac{1}{2}\cos\pi\left(\frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}\right), & R_{ij} < r_{ij} < S_{ij} \\ 0, & r \ge S_{ij} \end{cases} \quad ,
$$

$$
b_{ij} = \chi_{ij}(1 + \beta_i^{n_i} \zeta_{ij}^{n_i})^{-1/2n_i} \quad , \quad \zeta_{ij} = \sum_{k \neq i, j} f_{\mathrm{C}}(r_{ik}) \omega_{ik} g(\theta_{ijk}) \quad ,
$$

$$
g(\theta_{ijk}) = 1 + \left(\frac{c_i}{d_i}\right)^2 - \left(\frac{c_i}{d_i^2 + (h_i - \cos\theta_{ijk})}\right)^2
$$

Potentials for semiconductor alloys

- Here the indices i and j on the parameters denote the atom types. The mixed parameters $\lambda_{ij}, \mu_{ij}, A_{ij}, B_{ij}, R_{ij}, S_{ij}$ are obtained by interpolation from the elemental parameters:

$$\lambda_{ij} = \frac{\lambda_i + \lambda_j}{2} \ , \ \mu_{ij} = \frac{\mu_i + \mu_j}{2} \ , \ A_{ij} = \sqrt{A_i A_j} \ , \ B_{ij} = \sqrt{B_i B_j} \ , R_{ij} = \sqrt{R_i R_j} \ , \ S_{ij} = \sqrt{S_i S_j} \ .$$

- A new parameter is χ by which the mixed potential can be finetuned. Tersoff set $\chi_{ii} = 1$ and $\chi_{ij} = \chi_{ji}$, so there is only one free parameter for the mixed interactions, all the others are determined from the elemental parameters. Moreover, ω_{ik} could be used to finetune the mixed interactions but Tersoff set $\omega_{ik} = 1$

Potentials for semiconductor alloys

- The parameter values for C, Si and Ge were obtained from a fit to the properties of different structures, and the finetuning parameters χ were obtained from the cohesive energies of SiC and (hypothetical) zinc-blende SiGe. The Si parameters are just Si(C) without λ_3.

	C	Si	Ge
A (eV)	1393.6	1830.8	1769
B (eV)	346.7	471.18	419.23
λ (Å)	3.4879	2.4799	2.4451
μ (Å)	2.2119	1.7322	1.7047
β	1.5724×10^{-7}	1.1000×10^{-6}	9.0166×10^{-7}
n	0.72751	0.7873	0.75627
c	3.8049×10^{4}	1.0039×10^{5}	1.0643×10^{5}
d	4.384	16.217	15.652
h	-0.57058	-0.59825	-0.43884
R (Å)	1.8	2.7	2.8
S (Å)	2.1	3.0	3.1

$$\chi_{\text{C-Si}} = 0.9776 \quad \chi_{\text{Si-Ge}} = 1.00061$$

Potentials for semiconductor alloys

- The potential gives the following properties for SiC:

	Tersoff	Expt.
a (Å)	4.32	4.36
B (Mbar)	2.2	2.2
c_{11} (Mbar)	4.2	3.6
c_{12} (Mbar)	1.2	1.5
c_{44} (Mbar)	2.6	1.5

- Tersoff also calculated the energies for a few stoichiometric defects (eV):

	Tersoff	DFT
$V_{\mathrm{Si}} + V_{\mathrm{C}}$	7.4	12.7
$\mathrm{C}_{\mathrm{Si}} + \mathrm{Si}_{\mathrm{C}}$	7.2	8.4
$\mathrm{Si}_{TC} + \mathrm{C}_{T\mathrm{Si}}$	22.6	23.3
$\mathrm{Si}_{T\mathrm{Si}} + \mathrm{C}_{TC}$	23.2	26.0
$\mathrm{C}_{TC} - \mathrm{C}_{T\mathrm{Si}}$	3.0	2.4

Here

V_{Si} is the Si vacancy,

C_{Si} is a carbon atom on an Si site, and

$\mathrm{C}_{T\mathrm{Si}}$ a C atom on a tetrahedral site, surrounded by C atoms.

Potentials for semiconductor alloys

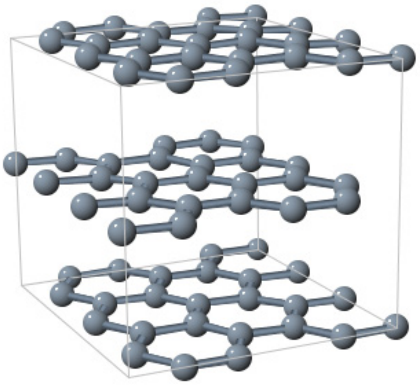
- The potential predicts the properties of SiC fairly well, especially considering that the potentials has only one parameter which is really fit to the properties of the compound (χ). And even this parameter is fairly close to 1. Only the shear modulus c_{44} and the formation energies of vacancies are pretty bad.

- One problem here is that in reality SiC is partly ionic in its bonding, which is not accounted for at all in the Tersoff potentials. One potential where this is taken into account is [Shimojo, *Phys. Rev. Lett.* **84** (2000) 3338] but this potential uses explicit angles so it is also problematic

- Nowadays also a wealth of reparametrizations exist for the Tersoff formalism SiC potential - it seems almost every group working on SiC has made their own parametrization...

C potentials

- Constructing a potential for elemental C is complicated (as noted above) because it has two structures which are practically identical in energy: diamond and graphite. Both have a cohesive energy of about 7.4 eV. The structure of graphite is:



- As noted above, this situation clearly can not be described with an explicit angle potential, but a bond order potential like Tersoff can handle this.

C potentials

- The Tersoff parametrization for C does, however, describe both bonding types well [Tersoff, *Phys. Rev. Lett.* **61** (1988) 2879], and is clearly the most used C potential in the materials physics community.
- But it describes the graphite-to-diamond potential poorly. But simply by increasing the parameter S in the potential to 2.46 Å [Nordlund *et al.*, *Phys. Rev. Lett.* **77** (1996) 699] one can make this transition much better described:

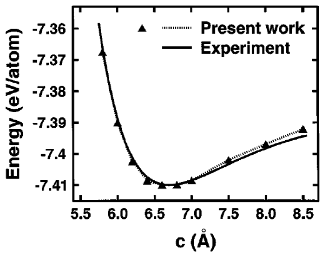


FIG. 1. Total energy per atom of graphite as a function of the graphite lattice c parameter. The solid line shows the experimental curve, the triangles and dotted line result from our potential.

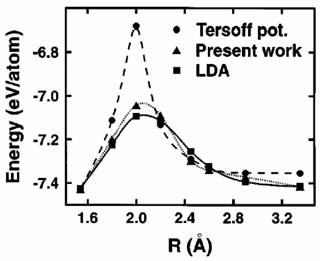


FIG. 2. Total energy per atom of the diamond to rhombohedral graphite transformation as a function of the interlayer distance R parameter. The squares show the energy given by *ab initio* calculations in Ref. [22], the circles the result of the original Tersoff potential, and the triangles the result of our potential. The lines are drawn to guide the eye.

C potentials

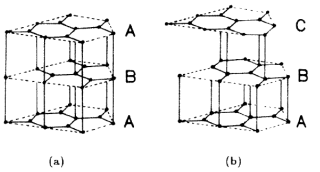


FIG. 1. The crystal structure of (a) hexagonal and (b) rhombohedral graphite showing the different stacking of the layers.

Fahy *et al.* *Phys. Rev. B* **34** (1986) 1191.

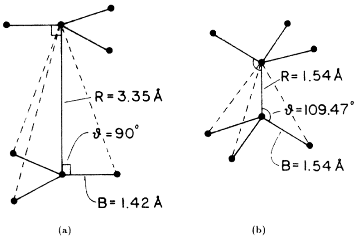


FIG. 2. The local structure of (a) rhombohedral graphite (b) diamond. The dashed lines indicate the basis vectors of the rhombohedral lattice. The [111] direction of the usual cubic description of the diamond lattice is vertical.

C potentials

- But there is a significant problem with the Tersoff C potential: because of its short cutoff, it does not describe the interaction between graphite layers at all.
- There are two good solutions to this.
  - Nordlund *et al.* have made an extension to the Tersoff potential which does describe the interaction between graphite layers well [*Phys. Rev. Lett.* **77** (1996) 699]. However, the additional terms are very weak except precisely for configurations very close to the flat graphite layers, and do not have a deep physical motivation
  - A more general formulation which includes Lennard-Jones-like long-range potentials for many carbon bonding types (including polymers) by Stuart *et al.* [*J. Chem. Phys.* **112** (2000) 6472].

Ge-potentials

- As we saw above, pure Ge has two almost identical SW-parametrizations, and the Tersoff parametrization, which are all fairly good in the crystalline phase.

- But they all severely overestimate the melting point of Ge, giving about 2500 - 3000 K when the experimental value is 1210 K.

- Nordlund *et al.* tried to solve this in the same way as Stillinger and Weber obtained the right melting point for Si, i.e. decreasing the cohesive energy [*Phys. Rev. B* **57** (1998) 7556]. By decreasing the cohesive energy in the SW potential by 18 % (i.e. setting $\varepsilon = 1.56$ eV) they obtained a melting point 1230 ± 50 K, and at the same time the threshold displacement energy and mixing coefficient (important in ion irradiation physics) obtained reasonable values.
  - But it is clear that this kind of solution is problematic.

Potentials for compound semiconductors

- Compound semiconductors are an interesting alternative to Si in some applications, especially opto-electronics.

- A Keating-type potential [Schabel and Martins, *Phys. Rev. B* **43** (1991) 11873] has been designed which can describe a large variety of semiconductors when the atoms are close to the ideal sites, but the model is absolutely terrible when the atoms are farther because it has a a harmonic ("r^2")-potential well.

- For GaAs there is the Smith potential, based on the Tersoff formalism [*Nucl. Instr. Meth. Phys. Res.* B **67** (1992) 335], which uses all the normal Tersoff parameters for Ga-Ga, Ga-As and As-As separately, except that $\lambda_3 = 0$. But this potential has a vanishingly small angular term, and hence all shear moduli are almost exactly 0.

- Sayed started from the Smith parametrizations, but fitted anew the Ga-As-interactions, and constructed an AlAs-potential. The GaAs potential is terrible because the zincblende-structure is not its ground state! However, by setting $\lambda_3 = 0$ it becomes fairly decent.

- Ashu made a potential for InAs following Sayed's approach, but this potential even has the wrong lattice spacing! However, Janne Nord has later made a reparametrization which describes InAs stably [Nordlund *et al., Comput. Mater. Sci.* **18** (2000) 283].

Potentials for compound semiconductors

- There also exist a tight-binding-based Tersoff-like parametrization by Conrad *et al,* [*Phys. Rev. B* **58** (1998) 4538] but this potential is terrible far from the ground state, it collapses into a state with at least a factor of 2 lower energy than the correct zincblende structure.

- The most recent approach is a modified Tersoff-like parametrization which gives the correct ground states for Ga, As and GaAs, as well as good melting properties for all three [Albe *et al.*, *Phys. Rev. B* **66**, 035205 (2002)]. The only major problem is As-rich surfaces and defects.

- There is also a potential for GaN in this formalism.
- Modeling also like-ion interactions: e.g. Ga and As has many complex structures

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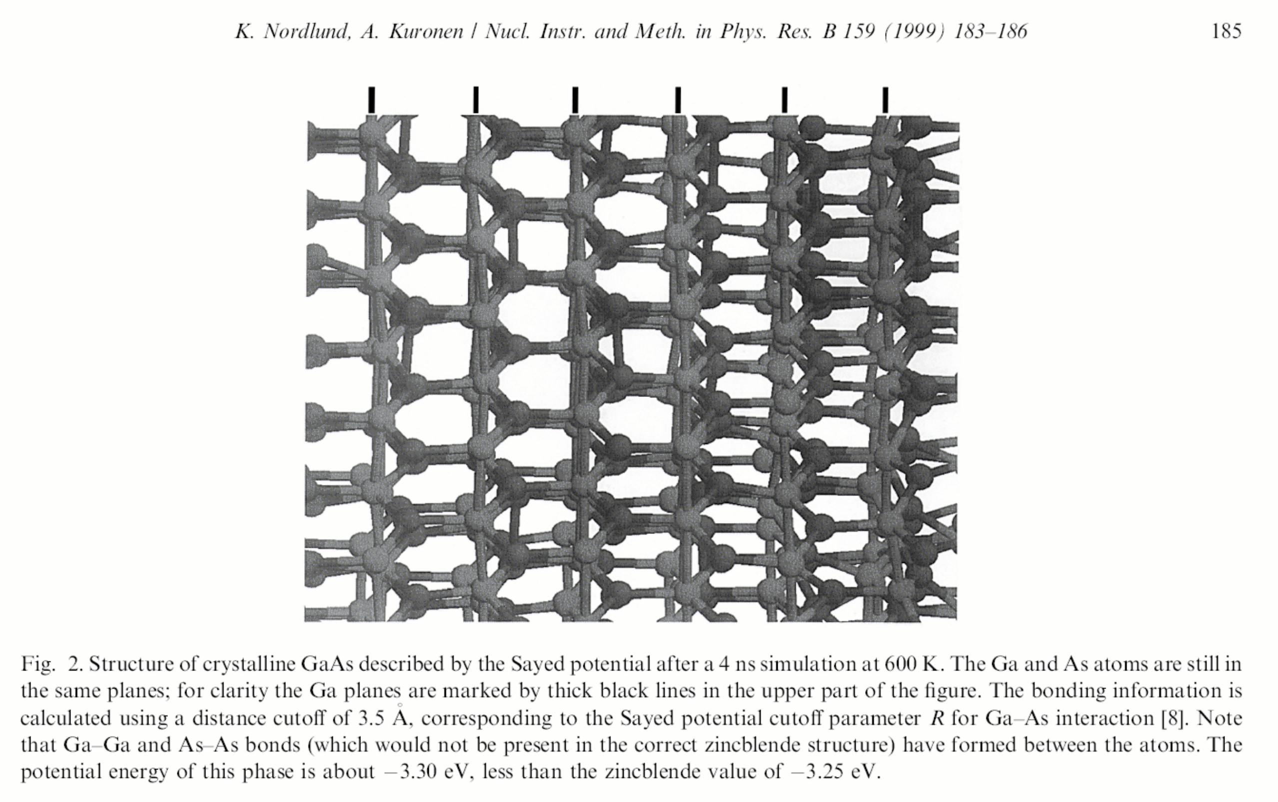
Potentials for compound semiconductors

- Ground state of the Sayed potential for GaAs:



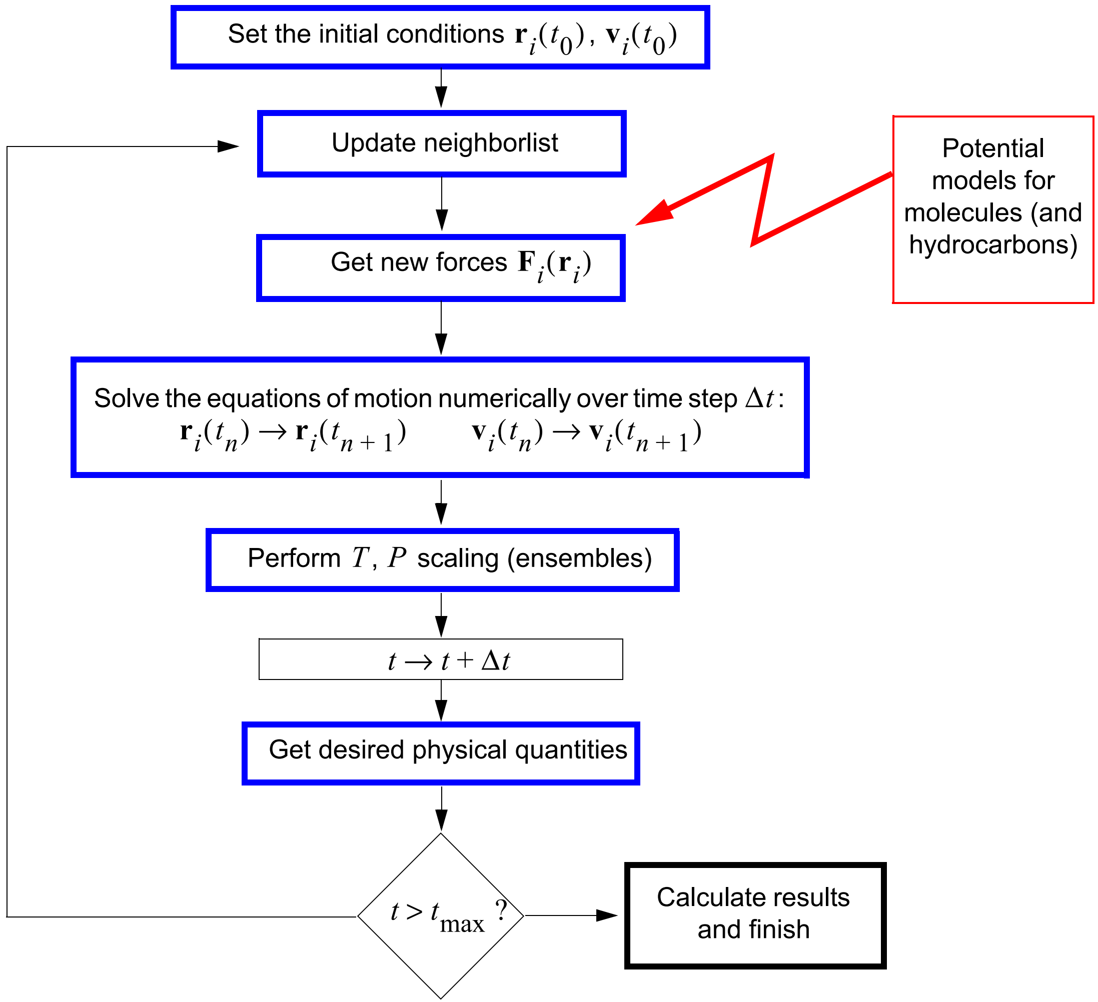
K. Nordlund, A. Kuronen / Nucl. Instr. and Meth. in Phys. Res. B 159 (1999) 183–186 185

Fig. 2. Structure of crystalline GaAs described by the Sayed potential after a 4 ns simulation at 600 K. The Ga and As atoms are still in the same planes; for clarity the Ga planes are marked by thick black lines in the upper part of the figure. The bonding information is calculated using a distance cutoff of 3.5 Å, corresponding to the Sayed potential cutoff parameter R for Ga–As interaction [8]. Note that Ga–Ga and As–As bonds (which would not be present in the correct zincblende structure) have formed between the atoms. The potential energy of this phase is about −3.30 eV, less than the zincblende value of −3.25 eV.

Bond order potentials for metals and compounds

- As noted in the description of bond-order potentials above, they are actually equivalent to the basic EAM form. Hence nothing actually prevents from constructing metals potentials from a bond order, e.g. Tersoff-like form.

- People in the Nordlund and Karsten Albe groups have done this, so far for Be, Fe, Cr, Au, Pt and W, obtaining potentials which are at least as good as the common EAM-like potentials for the same metals and a nunmber of their carbide and oxide compounds, showing that the bond order concept carries further even to complex compounds. The basic methodology and PtC part is published in [Albe *et al.*, *Phys. Rev. B* **65**, 195124 (2002)].
  - Other references to these mixed potentials:
    - Au: M. Backman, N. Juslin, and K. Nordlund. Eur. Phys. J. B, 85:317, 2012.
    - GaN: J. Nord, K. Albe, P. Erhart, and K. Nordlund, Journal of Physics: Condensed Matter 15, 5649 (2003).
    - WCH: N. Juslin et al, J. Appl. Phys. 98, 123520 (2005).
    - ZnO: P. Erhart, N. Juslin, O. Goy, K. Nordlund, R. Muller, and K. Albe, J. Phys.: Condens. Matter 18, 6585 (2006).
    - BeCWH: C. Björkas et al: : Condens. Matter 21, 445002 (2009); J. Phys.: Condens. Matter 22, 352206 (2010).
    - FeCrC: K. O. E. Henriksson, C. Björkas, and K. Nordlund, Enabling atomistic simulations of stainless steels: A bond-order potential for Fe-Cr-C system, J. Phys. Condens. Matt. 25, 445401 (2013).
    - FeH: Kuopanportti et al, Interatomic Fe–H potential for irradiation and embrittlement simulations, Comput. Mater. Sci. 111, 525 (2015).



Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Potential models for molecules (and hydrocarbons)

Solve the equations of motion numerically over time step Δt:
$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1})$ $\mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$

Perform T, P scaling (ensembles)

$t \rightarrow t + \Delta t$

Get desired physical quantities

$t > t_{\max}$?

Calculate results and finish

Molecular interaction models

- Since molecules are bonded by covalent bonds, at least angular terms are needed,
  - In many cases many more complicated terms as well: e.g. carbon chains the difference between “single” and “double” bonds often is important $\Rightarrow$ at least a four-body term is needed.

- To describe complex molecules a large set of **force fields** have been developed.
  - **Molecular mechanics**: use of force fields, no reactions (i.e. bond breaking or creation)
  - Fixed neighbor topology (except for so called non-bonded interactions).

  - The total energy of a molecule can be given as

$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{oop}} + E_{\text{cross}} + E_{\text{nonbond}}$$

E_{bond}: energy change related to a change of bond length (V_2)

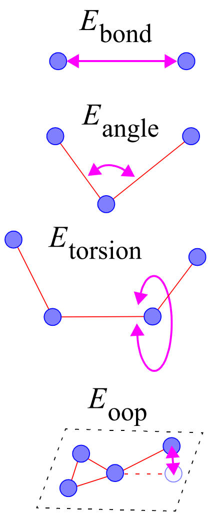
E_{angle}: energy change associated with a change in the bond angle,(V_3)

E_{torsion}: torsion, i.e. energy associated with the rotation between two parts of a molecule relative to each other (also termed dihedral)

E_{oop}: “out-of-plane” interactions, i.e. the energy change when one part of a molecule is out of the plane with another (keeps the molecule planar)

E_{cross}: cross terms between the other interaction terms

E_{nonbond}: interaction energies which are not associated with covalent bonding (e.g. ionic or van der Waals terms)



- In the following we describe the terms, using notation more common in chemistry rather than the physics notation used earlier on the course.

Molecular interaction models

- **The term E_{bond}**
  - This term describes the energy change associated with the bond length. It is a simple pair potential, and could be e.g. a Morse or LJ potential.
    - At its simplest, it is purely harmonic, i.e.

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

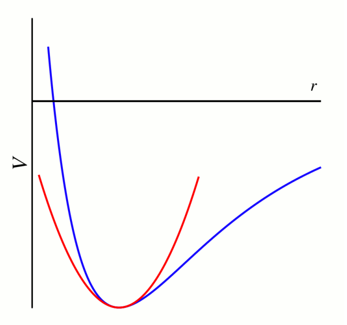
where b is the bond length.

    - If we write this term instead as

$$E_i = \sum_j \frac{1}{2} k (r_{ij} - r_0)^2$$

we see that it is the same thing as the pair potentials dealt with earlier.

    - Can be good enough in problems where we are always close to equilibrium, since any smooth potential well can always be to the first order approximated by a harmonic well.



    - But harmonic potentials obviously can not describe large displacements of atoms or bond breaking reasonably.
    - In solids, the harmonic approximation corresponds to the elastic regime, i.e. the one where stress is directly proportional to the strain (Hooke's law).
      - A historical footnote is that Hooke presented the law already in the 1678 as "*Ut tensio, sic vis.*"[1] so it did not originally have to do much with interatomic potentials...

Molecular interaction models

- To improve on the bond model beyond the elastic regime, one can add higher-order terms to it, e.g.

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

- Larger strain can be described, but not bond breaking: if here $b \to \infty$ thenalso $E \to \infty$ => bonds cannot break

- The familiar Morse potential

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

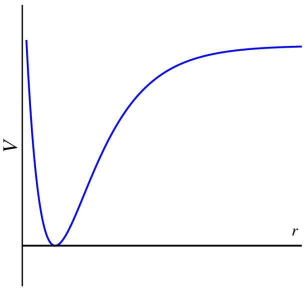
is much used to describe bond energies.

This is shifted in E axis so that $E_{\text{bond}}(b_0) = 0$.

---

[1] The Power of any spring is in the same proportion with the Tension thereof.

- It is good in that $E \rightarrow \text{constant}$ when $b \rightarrow \infty$ so it can describe bond breaking.
- But on the other hand it never goes fully to 0, which is not quite realistic either as in reality a covalent bond does break essentially completely at some interatomic distance.



Molecular interaction models

- **Angular terms** E_{angle}
  - The angular terms describe the energy change associated with two bonds forming an angle with each other. Most kinds of covalent bonds have some angle which is most favoured by them - for sp^3 hybridized bonds it is ~ 109^o, for sp^2 120^o and so on.
  - Like for bond lengths, the easiest way to describe bond angles is to use a harmonic term like

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

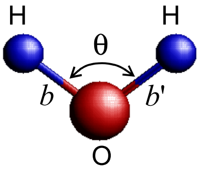
    where θ_0 is the equilibrium angle and H_θ a constant which describes the angular dependence well. This may work well up to 10^o or so, but for larger angles additional terms are needed.
  - A typical means for improvement is, surprise surprise, third-order terms and so forth, for instance

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

  - An example: by taking the simplest possible bond length and angular terms, it is already possible to describe one water molecule to some extent:

    $$E_{H_2O} = K_{\text{OH}}(b - b^0_{\text{OH}})^2 + K_{\text{OH}}(b' - b^0_{\text{OH}})^2 + K_{\text{HOH}}(\theta - \theta^0_{\text{HOH}})^2$$

    where b and b' are the lengths of the two bonds and θ the angle between them.

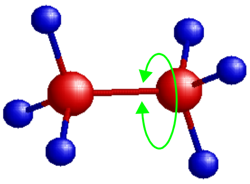


Molecular interaction models

- **Torsional terms** E_{torsion}

  - The bond and angular terms were already familiar from the potentials for solids. In the physics and chemistry of molecules there are many important effects which can not be described solely with these terms.

  - The most fundamental of these is probably torsion. By this, the rotations of one part of a molecule with respect to another is meant. A simple example is the rotation of two parts of the ethane molecule C_2H_6 around the central C-C carbon bond.



  - Torsional forces can be caused by e.g. dipole-dipole-interactions and bond conjugation.

  - If the angle between two parts is described by an angle ϕ, it is clear that the function f which describes the rotation should have the property $f(\phi) = f(\phi + 2\pi)$, because it is possible to do a full rotation around the central bond and return to the initial state. The trigonometric functions $\sin$ and $\cos$ of course fulfil this requirement, so it is natural to describe the torsional energy with a a few terms in a Fourier series

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

Molecular interaction models

- **Out-of-plane terms** E_{oop}
  - With the out-of-plane-terms one describes the energy which in (some cases) is associated with the displacement of atoms out of the plane in which they should be. This is relevant in some (parts of) molecules where atoms are known to lie all in the same plane. The functional form can be rather simple,

$$E_{\text{oop}} = \sum_{\chi} H_{\chi}\chi^2$$

    where χ is the displacement out of the plane.

- **Cross terms** E_{cross}
  - The cross-terms are functions which contain several of the above-mentioned quantities. They could e.g. describe how a stretched bond has a weaker angular dependence than a normal one. Or they can describe the relations between two displacements, an angle and a torsion and so one.

- **Non-bonding terms** E_{nonbond}
  - With the non-bonding terms all effects which affect the energy of a molecule but are not covalent bonds are meant. These are e.g. van der Waals-terms, electrostatic Coulomb interactions and hydrogen bonds. For this terms one could thus further divide

$$E_{\text{nonbond}} = E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{hbond}}$$

  - The van der Waals term is often a simple Lennard-Jones-potential, and E_{Coulomb} a Coulomb potential for some, usually fractional, charges q_i.

Molecular interaction models

- If all of the above are included except for hydrogen bonds, the total energy expression can for instance look like

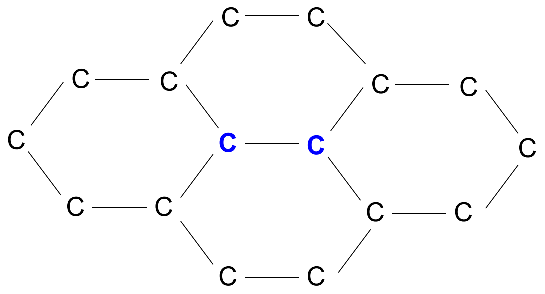
$$\begin{aligned} V(R) = {} & \overbrace{\sum_b D_b[1-\exp(-a(b-b_0))]^2}^{E_{bond}} + \overbrace{\sum_\theta H_\theta(\theta-\theta_0)^2}^{E_{angle}} + \overbrace{\sum_\phi H_\phi[1+s\cos(n\phi)]}^{E_{torsion}} \\ E_{oop}\ & \boxed{+\sum_\chi H_\chi \chi^2} + \sum_b\sum_{b'} F_{bb'}(b-b_0)(b'-b'_0) + \sum_\theta\sum_{\theta'} F_{\theta\theta'}(\theta-\theta_0)(\theta'-\theta'_0) \\ & + \sum_b\sum_\theta F_{b\theta}(b-b_0)(\theta-\theta_0) + \sum_\theta\sum_{\theta'} F_{\theta\theta'\phi}(\theta-\theta_0)(\theta'-\theta'_0)\cos\phi \quad E_{cross} \\ & + \sum_\chi\sum_{\chi'} F_{\chi\chi'}\chi\chi' + \sum_i\sum_{j>i}\left[\underbrace{\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}}}_{E_{vdW}} + \underbrace{\frac{q_iq_j}{r_{ij}}}_{E_{Coulomb}}\right] \end{aligned}$$

- There are many popular force fields in the literature:
  AMBER, CHARMM, MM2, MM3, MM4, ...

- **GROMACS** is a GPL'ed MD code able to use various force fields.
  - Home page: **http://www.gromacs.org/**

Brenner potential

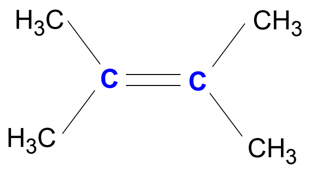
- The Brenner potential [D. W. Brenner, *Phys. Rev. B* **42** (1990) 9458] is a 'simple' potential for hydrocarbons, which is based on the Tersoff potential but developed further from this.
  - The ideas behind the potential show how information on chemical bonding can be added in a well-motivated way to a classical potential.
  - The Brenner potential is also attractive in that it can describe chemical reactions, which the potentials with harmonic terms can not.
  - The basic Tersoff potential contains a bonding term E_{bond} and an angular term E_{angle}. But these can not describe alone e.g. conjugated bonds.
  - The issue here can be understood as follows. Consider first graphite:



  - Here all the carbons have an identical local neighbourhood. Because carbon has 4 outer electrons, but only three bonds, every bond has 1 1/3 electrons.

Brenner potential

- Then consider the following molecule:



- Here there is a double bond between the two **C atoms marked in blue.** But the local neighbourhood of these two atoms is identical to the two **C atoms in blue** in graphite. Because the Tersoff potential only accounts for the nearest neighbours, it describes the middle bond here in the same way as the bonds in graphite, although in reality there is a clear difference in bond character, strength and length.

- To improve on problems like this, Brenner added terms which depend on the chemical environment into the Tersoff potential.

- Brenner starts with the Tersoff potential

$$E_b = \sum_i \sum_{j(>i)} [V_R(r_{ij}) - \bar{B}_{ij} V_A(r_{ij})]$$

and defines the repulsive and attractive parts V_R and V_A just like Tersoff. But the environment-dependence obtains additional parts.

Brenner potential

- $\bar{B}_{ij}$ is now:

$$\bar{B}_{ij} = (B_{ij} + B_{ji})/2 + F_{ij}(N_i^{(t)}, N_j^{(t)}, N_{ij}^{\mathrm{conj}})/2$$

where

$$B_{ij} = \left[1 + \sum_{k(\neq i,j)} G_i(\theta_{ijk}) f_{ik}(r_{ik}) e^{\alpha_{ijk}[(r_{ij} - R_{ij}^{(e)}) - (r_{ik} - R_{ik}^{(e)})]} + H_{ij}(N_i^{(\mathrm{H})}, N_i^{(\mathrm{C})}) \right]^{-\delta_i}$$

- The first part is almost as Tersoff's formulation (except no power of three in the exponential), but the H_{ij} and F_{ij} are new. Here $N_i^{(\mathrm{H})}$ are the number of H neighbours of one atom, $N_i^{(\mathrm{C})}$ the number of C neighbours of one atom, and $N_i^{(\mathrm{t})}$ the total number of neighbours. The number of neighbours is calculated by utilizing the normal Tersoff cutoff-function

$$f_{ij}(r) = \begin{cases} 1, & r < R_{ij}^{(1)} \\ \left[1 + \cos\left[\dfrac{\pi(r - R_{ij}^{(1)})}{(R_{ij}^{(2)} - R_{ij}^{(1)})} \right] \right] \Big/ 2, & R_{ij}^{(1)} < r < R_{ij}^{(2)} \\ 0, & r > R_{ij}^{(2)}. \end{cases}$$

Brenner potential

- The sums over f_{ij} thus gives an effective number of neighbours (coordination!):

$$N_i^{(\mathrm{H})} = \sum_{j(=\text{hydrogen})} f_{ij}(r_{ij}) \, ,$$

$$N_i^{(\mathrm{C})} = \sum_{j(=\text{carbon})} f_{ij}(r_{ij}) \, ,$$

- The values of $N_i^{(\mathrm{t})}$ can be used to deduce whether some C atom is part of a conjugated system. If any C atom has even one neighbour which does not have 4 neighbours, it is interpreted as conjugated. (because all quantities are continuous, the precise requirement is in fact $N_i^{(\mathrm{t})} < 4$)

Brenner potential

- The continuous quantity N_{ij}^{conj} which describes whether a bond ij is conjugated is calculated as

$$N_{ij}^{\mathrm{conj}} = 1 + \sum_{\text{carbons } k(\neq i,j)} f_{ik}(r_{ik}) F(x_{ik}) + \sum_{\text{carbons } l(\neq i,j)} f_{jl}(r_{jl}) F(x_{jl})$$

where

$$F(x_{ik}) = \begin{cases} 1, & x_{ik} \leq 2 \\ \{1 + \cos[\pi(x_{ik} - 2)]\}/2, & 2 < x_{ik} < 3 \\ 0, & x_{ik} \geq 3 \end{cases}$$

and

$$x_{ik} = N_k^{\mathrm{tot}} - f_{ik}(r_{ik}) \, .$$

- So if one carbon atom has exactly 4 bonds we get

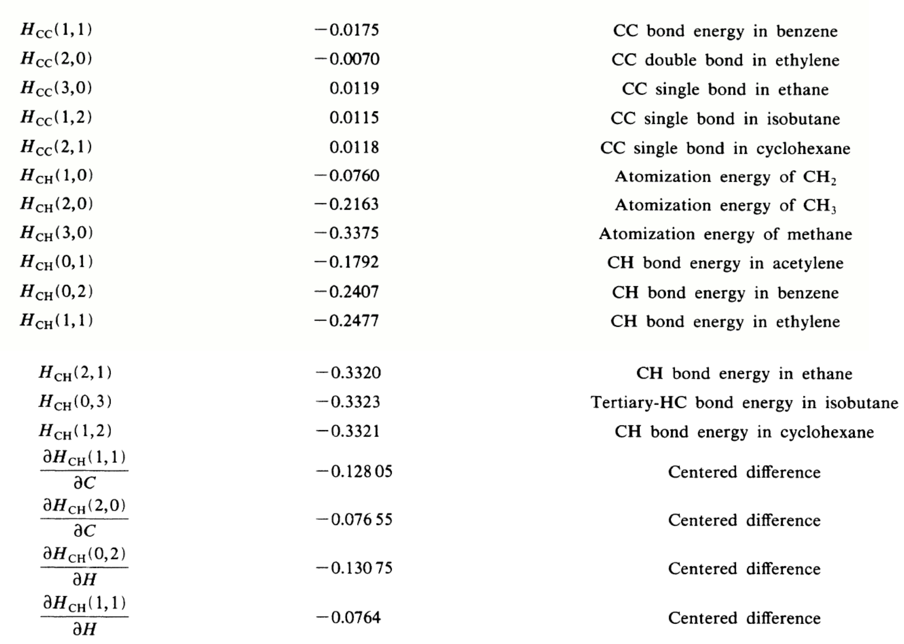
$$x_{ik} = 3 \Rightarrow F(x_{ik}) = 0 \Rightarrow N_{ij}^{\mathrm{conj}} = 1 \, .$$

- If the bond on the other hand is conjugated, $N_{ij}^{\mathrm{conj}} \geq 2$.

- The remaining question is how to form the functions $F_{ij}(N_i^{(\mathrm{t})}, N_j^{(\mathrm{t})}, N_i^{\mathrm{conj}})$ and $H_{ij}(N_i^{(\mathrm{H})}, N_i^{(\mathrm{C})})$?
- Brenner does this simply by fitting into a large set of experimental data. As many as possible of the values for integer indices are set to some values directly derived from experiments, and thereafter spline interpolation is used to interpolate values smoothly for non-integer arguments.

Brenner potential

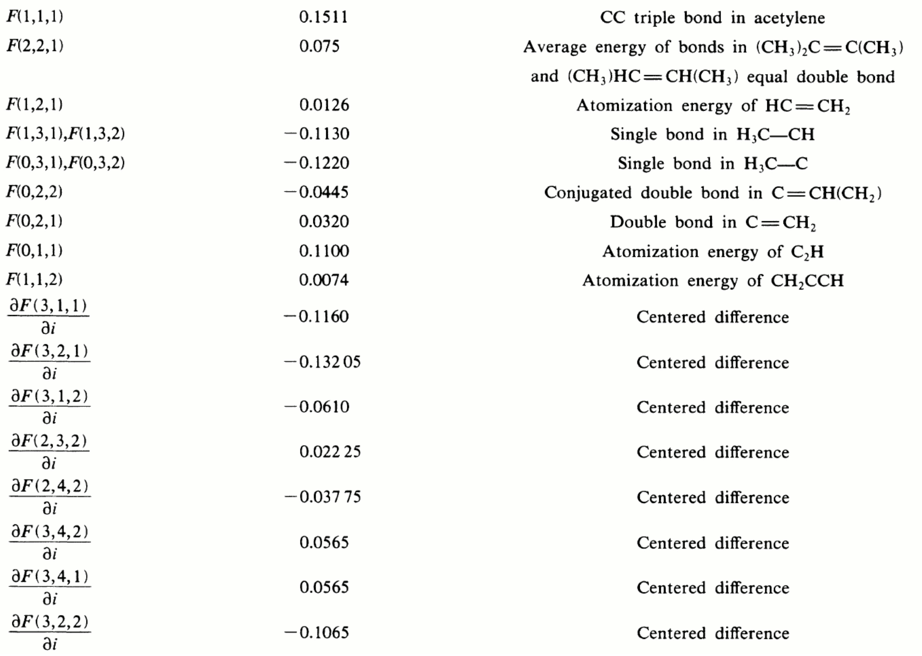
- For instance, the values for integer arguments determined in version 1 of the potential for the function H are:



$H_{CC}(1,1)$	-0.0175	CC bond energy in benzene
$H_{CC}(2,0)$	-0.0070	CC double bond in ethylene
$H_{CC}(3,0)$	0.0119	CC single bond in ethane
$H_{CC}(1,2)$	0.0115	CC single bond in isobutane
$H_{CC}(2,1)$	0.0118	CC single bond in cyclohexane
$H_{CH}(1,0)$	-0.0760	Atomization energy of CH_2
$H_{CH}(2,0)$	-0.2163	Atomization energy of CH_3
$H_{CH}(3,0)$	-0.3375	Atomization energy of methane
$H_{CH}(0,1)$	-0.1792	CH bond energy in acetylene
$H_{CH}(0,2)$	-0.2407	CH bond energy in benzene
$H_{CH}(1,1)$	-0.2477	CH bond energy in ethylene
$H_{CH}(2,1)$	-0.3320	CH bond energy in ethane
$H_{CH}(0,3)$	-0.3323	Tertiary-HC bond energy in isobutane
$H_{CH}(1,2)$	-0.3321	CH bond energy in cyclohexane
$\frac{\partial H_{CH}(1,1)}{\partial C}$	-0.12805	Centered difference
$\frac{\partial H_{CH}(2,0)}{\partial C}$	-0.07655	Centered difference
$\frac{\partial H_{CH}(0,2)}{\partial H}$	-0.13075	Centered difference
$\frac{\partial H_{CH}(1,1)}{\partial H}$	-0.0764	Centered difference

Brenner potential

- And for function F:



$F(1,1,1)$	0.1511	CC triple bond in acetylene
$F(2,2,1)$	0.075	Average energy of bonds in $(CH_3)_2C{=}C(CH_3)$ and $(CH_3)HC{=}CH(CH_3)$ equal double bond
$F(1,2,1)$	0.0126	Atomization energy of $HC{=}CH_2$
$F(1,3,1), F(1,3,2)$	-0.1130	Single bond in H_3C—CH
$F(0,3,1), F(0,3,2)$	-0.1220	Single bond in H_3C—C
$F(0,2,2)$	-0.0445	Conjugated double bond in $C{=}CH(CH_2)$
$F(0,2,1)$	0.0320	Double bond in $C{=}CH_2$
$F(0,1,1)$	0.1100	Atomization energy of C_2H
$F(1,1,2)$	0.0074	Atomization energy of CH_2CCH
$\frac{\partial F(3,1,1)}{\partial i}$	-0.1160	Centered difference
$\frac{\partial F(3,2,1)}{\partial i}$	-0.13205	Centered difference
$\frac{\partial F(3,1,2)}{\partial i}$	-0.0610	Centered difference
$\frac{\partial F(2,3,2)}{\partial i}$	0.02225	Centered difference
$\frac{\partial F(2,4,2)}{\partial i}$	-0.03775	Centered difference
$\frac{\partial F(3,4,2)}{\partial i}$	0.0565	Centered difference
$\frac{\partial F(3,4,1)}{\partial i}$	0.0565	Centered difference
$\frac{\partial F(3,2,2)}{\partial i}$	-0.1065	Centered difference

- In addition, Brenner also presented another parametrization of his potential.

Brenner potential

- Crucial here are not the exact values, but the principle used: that as many parameters as possible are set to well-defined experimental quantities. Also the H values are largely derived from experimental data:

Hydrogen	$R_{HH}^{(e)}$	0.74144 Å	Gas-phase diatomic
	$D_{HH}^{(e)}$	4.7509 eV	Gas-phase diatomic
	β_{HH}	1.9436 Å^{-1}	Gas-phase diatomic
	S_{HH}	2.3432	Barrier for reaction (19)
	δ_{HH}	0.804 69	Set equal to carbon value
	α_{HHH}	3.0	Remove spurious wells from (19)
	G_{HH}	4.0	Barrier for reaction (19)
	$R_{HH}^{(1)}$	1.1 Å	Near-neighbor interactions
	$R_{HH}^{(2)}$	1.7 Å	Near-neighbor interactions

- Also the parameters for pure carbon were refitted by Brenner.

- Brenner tested his potential by calculating atomization energies for a large group of simple hydrocarbons. The results are listed on the next page.

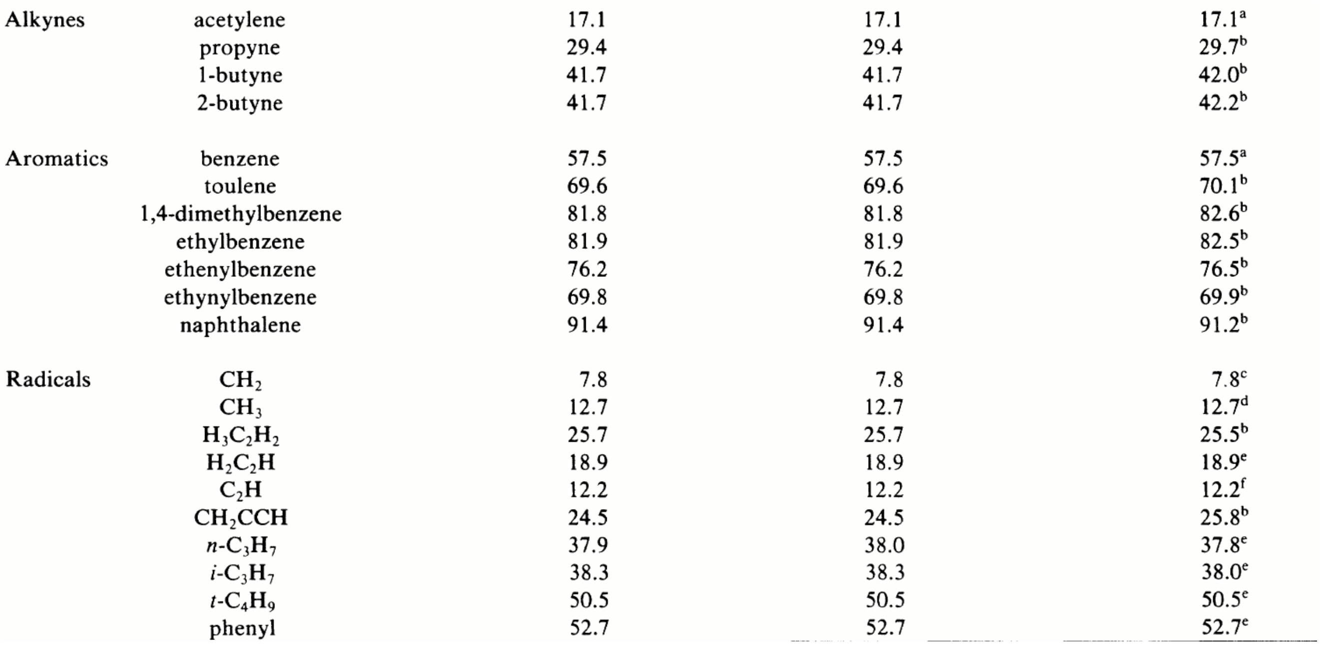
- The potential was also shown to describe well the reconstructed and H-terminated diamond (111) surface and molecules chemisorbed on the surface.

Brenner potential

TABLE IV. Atomization energies for various hydrocarbon molecules. Experimental values were derived from heats of formation using energies of 7.3768 eV for carbon and 2.375 eV for hydrogen.

	Molecule	Potential I (eV)	Potential II (eV)	Experimental value (eV)
Alkanes	methane	17.6	17.6	17.6[a]
	ethane	29.7	29.7	29.7[a]
	propane	42.0	42.0	42.0[a]
	n-butane	54.3	54.3	54.3[a]
	i-butane	54.3	54.3	54.4[a]
	n-pentane	66.5	66.5	66.6[a]
	isopentane	66.5	66.5	66.6[a]
	neopentane	66.8	66.8	66.7[a]
	cyclopropane	35.5	35.0	35.8[a]
	cyclobutane	48.7	48.5	48.2[a]
	cyclopentane	61.4	61.3	61.4[a]
	cyclohexane	73.6	73.6	73.6[a]
Alkenes	ethylene	23.6	23.6	23.6[a]
	propene	36.2	36.2	36.0[a]
	1-butene	48.5	48.5	48.5[b]
	cis-butene	48.8	48.9	48.6[b]
	isobutene	48.4	48.4	48.7[b]
	$(CH_3)_2C{=}C(CH_3)_2$	73.2	73.3	73.4[b]
	cyclopropene	28.2	27.3	28.8[b]
	cyclobutene	42.4	42.0	42.4[b]
	cyclopentene	55.7	55.7	55.6[b]
	1,4-pentadiene	55.0	55.0	54.8[b]
	$CH_2{=}CHCH{=}CH_2$	41.8	41.9	42.6[b]
	$CH_3CH{=}C{=}CH_2$	40.4	40.5	42.1[b]
	$H_2C{=}C{=}CH_2$	27.8	27.9	29.6[b]

Brenner potential



Alkynes	acetylene	17.1	17.1	17.1[a]
	propyne	29.4	29.4	29.7[b]
	1-butyne	41.7	41.7	42.0[b]
	2-butyne	41.7	41.7	42.2[b]
Aromatics	benzene	57.5	57.5	57.5[a]
	toulene	69.6	69.6	70.1[b]
	1,4-dimethylbenzene	81.8	81.8	82.6[b]
	ethylbenzene	81.9	81.9	82.5[b]
	ethenylbenzene	76.2	76.2	76.5[b]
	ethynylbenzene	69.8	69.8	69.9[b]
	naphthalene	91.4	91.4	91.2[b]
Radicals	CH_2	7.8	7.8	7.8[c]
	CH_3	12.7	12.7	12.7[d]
	$H_3C_2H_2$	25.7	25.7	25.5[b]
	H_2C_2H	18.9	18.9	18.9[e]
	C_2H	12.2	12.2	12.2[f]
	CH_2CCH	24.5	24.5	25.8[b]
	n-C_3H_7	37.9	38.0	37.8[e]
	i-C_3H_7	38.3	38.3	38.0[e]
	t-C_4H_9	50.5	50.5	50.5[e]
	phenyl	52.7	52.7	52.7[e]

Brenner potential

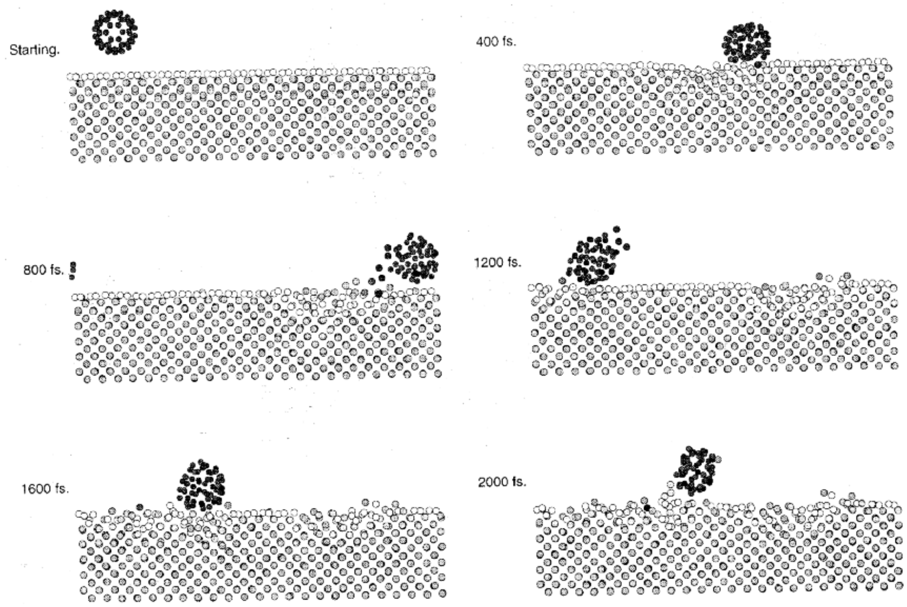
- Later Murty and Atwater [Phys. Rev. B 51 (1991) 4889] have made a Si-H version of the Brenner potential, and Beardmore and Smith [Phil. Mag. A 74 (1996) 1439] a combined C-Si-H-version.

- Brenner himself has later added a torsional term to the potential, and at least two groups have added long-range interactions (intermolecular interactions) into it: [Stuart *et al.,* J. Chem. Phys. **112** (2000) 6472] and [Che *et al.*, Theor. Chem. Acc. **102** (1999) 346].

Brenner potential

- Example application: Beardmore and Smith examined in their paper how a fullerene C_{60} hits an Si surface.
  - Case I: 250 eV $C_{60} \rightarrow$ virgin Si, incoming angle 80^{o} i.e. the fullerene forms bonds with the surface and rotates along it for a while (note the periodic boundary conditions).

Fig. 11

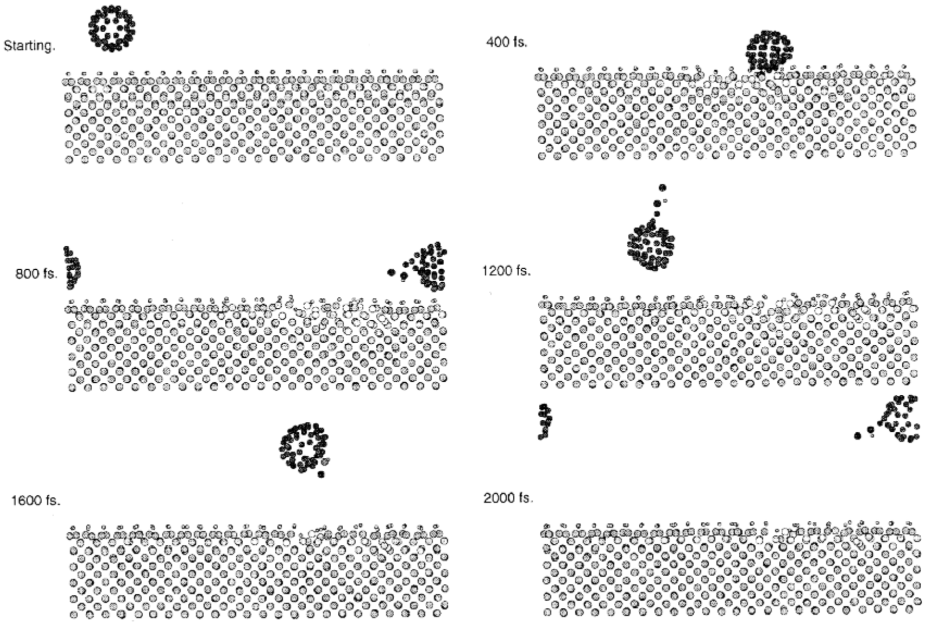


Atomic positions for a 250 eV C_{60} molecule incident at 80° to normal on bare Si{100} during a 2 ps simulation.

Brenner potential

- But if the Si-surface is H-terminated (all dangling bonds are filled with a H) the behaviour changes: Case II: 250 eV $C_{60} \rightarrow$ H-terminated Si, 80^{o}.

Fig. 12



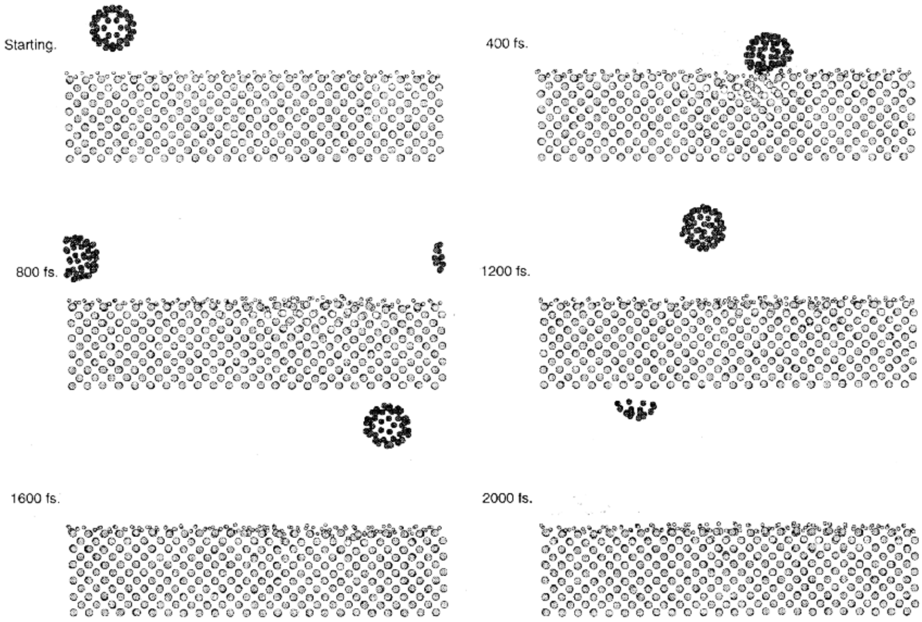
Atomic positions for a 250 eV C_{60} molecule incident at 80° to normal on 1 MLH Si{100} during a 2 ps simulation.

So the H protects the surface such that only a couple of bonds are formed with the surface, and the fullerene bounces back almost impact, having only taken up one Si atom.

Brenner potential

- Case III: 250 eV C_{60} → doubly H-terminated Si, 80^o

Fig. 13



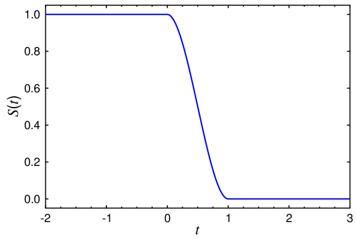
Atomic positions for a 250 eV C_{60} molecule incident at 80° to normal on 2 MLH Si{100} during a 2 ps simulation.

  - So now the protective H layer is so thick that there are no C-Si bonds formed at all, and the fullerene bounces back intact.

Stuart potential

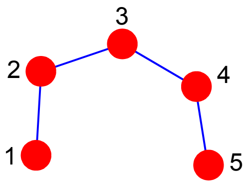
- Long range interactions are important also in graphite and in **multiwalled carbon nanotubes** (MWCNTs)
  - Stuart *et al.* [J. Chem. Phys. **112** (2000) 6472] used the Lennard-Jones potential to model the dispersion and intermolecular interaction:

$$V_{ij}^{\mathrm{LJ}}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$



  - However, LJ should be switched off when molecules approach
    - Switching depends on interatomic distance $[S(t_r(r_{ij}))]$, bond order $[S(t_b(b_{ij}))]$, and connectivity $[C_{ij}]$:

Connectivity: no LJ interaction among 1,2,3,4, LJ possible between 1 and 5



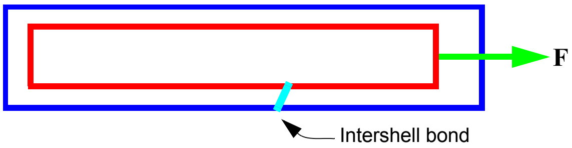
$$E_{\mathrm{b}} = \sum_i \sum_{j>i} [V_{\mathrm{R}}(r_{ij}) + \bar{B}_{ij} V_{\mathrm{A}}(r_{ij}) + E_{ij}^{\mathrm{LJ}}]$$

$$E_{ij}^{\mathrm{LJ}} = S(t_r(r_{ij}))S(t_b(b_{ij}))C_{ij}V_{ij}^{\mathrm{LJ}}(r_{ij}) + [1 - S(t_r(r_{ij}))]C_{ij}V_{ij}^{\mathrm{LJ}}(r_{ij})$$

  - For C-C interaction $\sigma_{ij} = 3.40$ Å (graphite interlayer distance) ⇒ large neighbor lists ($r_{\mathrm{cutoff}} \approx 11$ Å)!

Stuart potential

- Example: Load transfer between shells in MWCNTs [M. Huhtala *et al.*, *Phys. Rev. B* **70** (2004) 045404]



$$E = \varepsilon_i(\hat{n},\hat{m})\pi\tilde{d}(L-x) - A(\hat{n},\hat{m})\pi\tilde{d}(L-x)\cos\left[\frac{2\pi x}{\lambda(\hat{n},\hat{m})}\right].$$

No intershell bonds

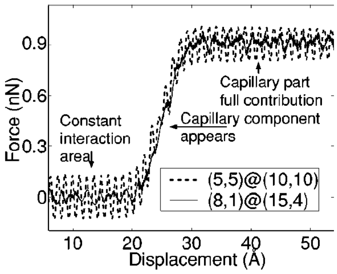
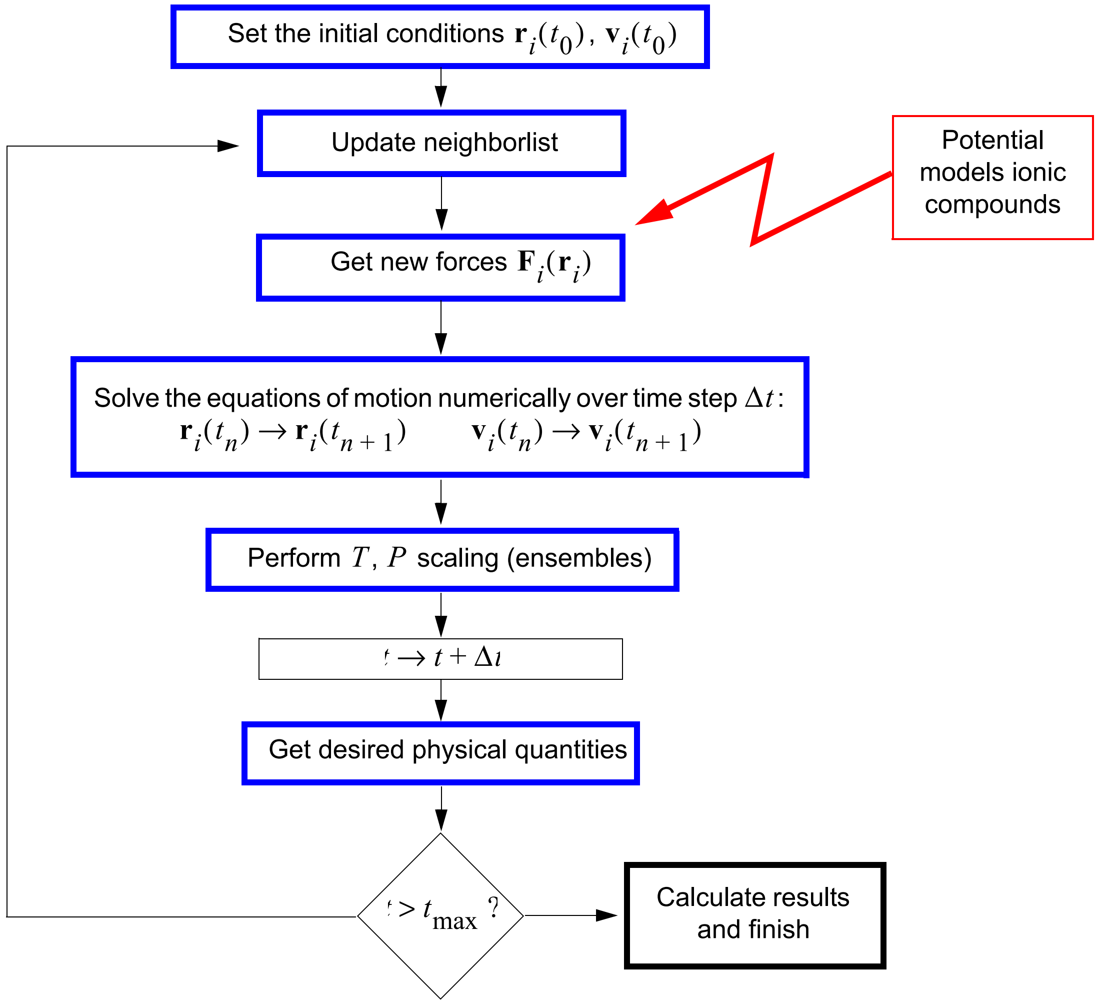


FIG. 1. Force vs displacement plotted for intact nanotube sliding. The displacement is measured from the point where the tube ends are even.

FIG. 2. Two views of a covalent intershell bond in tubes with different chiralities. Such bonds can be formed, for example, due to on-shell vacancies or intershell interstitials. The bonds shown are due to vacancy-pair reconstructions. As can be observed, the bond orientation is chirality dependent and there are several possible orientations in each particular tube.

Defect type	Force (nN)
Single vacancy	0.08—0.4
Two vacancies	6.4—7.8
Intershell interstitial	4.9—6.3
Intershell dimer	3.8—7.3



Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Solve the equations of motion numerically over time step Δt:
$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1}) \qquad \mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$

Perform T, P scaling (ensembles)

$t \rightarrow t + \Delta t$

Get desired physical quantities

$t > t_{\max}$?

Calculate results and finish

Potential models ionic compounds

Potentials for ionic compounds

- There is a wide range of materials where ionic interactions are important:
  - In hard condensed matter many, if not most, compounds have at least some degree of ionicity.
  - Partial ionic charges are also very important for organic materials

- In ionic compounds one can simply describe the long-range interaction with a Coulomb pair potential. But one should add a short-range interaction V_{SR} to describe repulsion at short distances:

$$V(r_{ij}) = V_{\mathrm{SR}}(r_{ij}) + \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{ij}};$$

  - The charges z_i are often fractional charges, depending on the degree of ionicity of a material (e.g. NaCl: 1, GaN: 0.5, GaAs: 0.2, Si 0.0).

  - V_{SR} contains the repulsion of the electron shells and possibly an attractive van der Waals-interaction. Common forms:
    - Buckingham: $V_{\mathrm{SR}}(r) = Ae^{-r/\rho} - \frac{C}{r^6}$
    - Born-Huggins-Mayer: $V_{\mathrm{SR}}(r) = Ae^{-B(r-\sigma)} - \frac{C}{r^6} - \frac{D}{r^8}$
    - Morse: $V_{\mathrm{SR}}(r) = De^{-2\alpha(r-r_0)} - 2De^{-\alpha(r-r_0)}$

Potentials for ionic compounds

- The repulsion is usually significant only for nearest neighbours, and the van der Waals interaction for the 2-nd neighbours. In oxides frequently the interaction between cations is assumed to be only the Coulomb repulsion.

- In many real compounds the interactions are a mixture of covalent, metallic and ionic interactions (e.g. many carbides and nitrodes).

Potentials for ionic compounds

- Such potentials have been formed for many ionic compounds. We present here briefly the potential by Vashista *et al.* for SiO_2, [*Phys. Rev. B* **41** (1990) 12197.] which comes up in many different contexts.
  - Silicon dioxide also has many different structures, which makes it difficult to model:

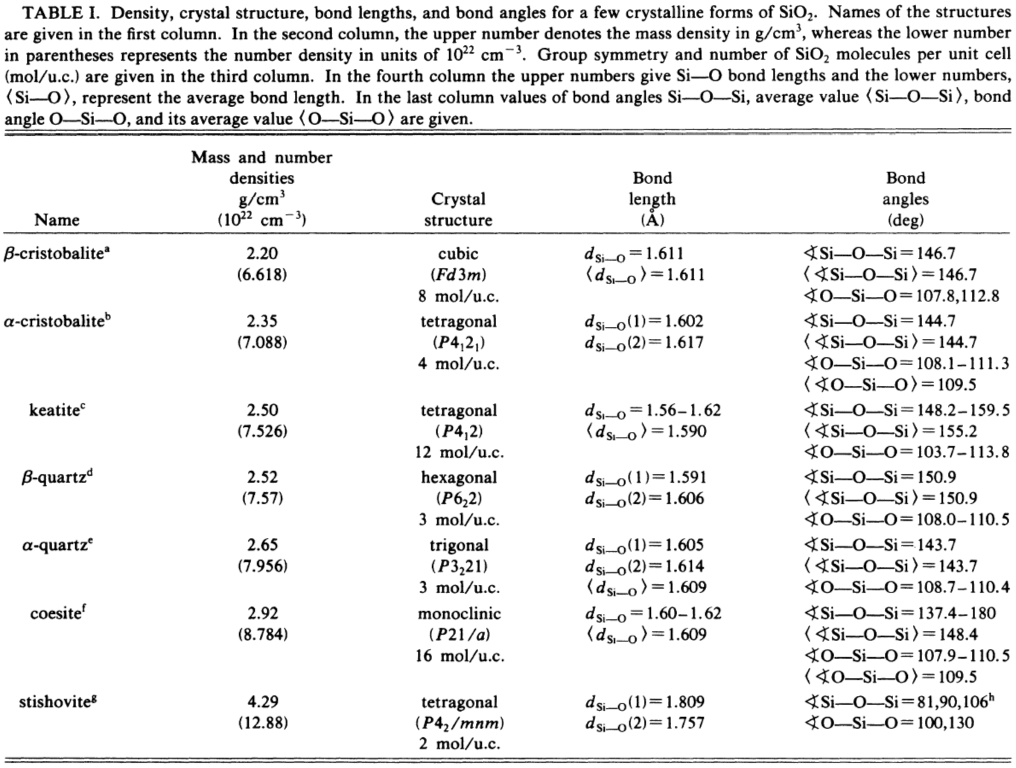


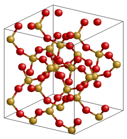
TABLE I. Density, crystal structure, bond lengths, and bond angles for a few crystalline forms of SiO_2. Names of the structures are given in the first column. In the second column, the upper number denotes the mass density in g/cm^3, whereas the lower number in parentheses represents the number density in units of 10^{22} cm^{-3}. Group symmetry and number of SiO_2 molecules per unit cell (mol/u.c.) are given in the third column. In the fourth column the upper numbers give Si—O bond lengths and the lower numbers, $\langle$Si—O$\rangle$, represent the average bond length. In the last column values of bond angles Si—O—Si, average value $\langle$Si—O—Si$\rangle$, bond angle O—Si—O, and its average value $\langle$O—Si—O$\rangle$ are given.

Name	Mass and number densities g/cm^3 (10^{22} cm^{-3})	Crystal structure	Bond length (Å)	Bond angles (deg)
β-cristobalite[a]	2.20 (6.618)	cubic ($Fd3m$) 8 mol/u.c.	$d_{\mathrm{Si—O}} = 1.611$ $\langle d_{\mathrm{Si—O}} \rangle = 1.611$	$\measuredangle$Si—O—Si = 146.7 $\langle \measuredangle$Si—O—Si$\rangle$ = 146.7 $\measuredangle$O—Si—O = 107.8,112.8
α-cristobalite[b]	2.35 (7.088)	tetragonal ($P4_12_1$) 4 mol/u.c.	$d_{\mathrm{Si—O}}(1) = 1.602$ $d_{\mathrm{Si—O}}(2) = 1.617$	$\measuredangle$Si—O—Si = 144.7 $\langle \measuredangle$Si—O—Si$\rangle$ = 144.7 $\measuredangle$O—Si—O = 108.1–111.3 $\langle \measuredangle$O—Si—O$\rangle$ = 109.5
keatite[c]	2.50 (7.526)	tetragonal ($P4_12$) 12 mol/u.c.	$d_{\mathrm{Si—O}} = 1.56–1.62$ $\langle d_{\mathrm{Si—O}} \rangle = 1.590$	$\measuredangle$Si—O—Si = 148.2–159.5 $\langle \measuredangle$Si—O—Si$\rangle$ = 155.2 $\measuredangle$O—Si—O = 103.7–113.8
β-quartz[d]	2.52 (7.57)	hexagonal ($P6_22$) 3 mol/u.c.	$d_{\mathrm{Si—O}}(1) = 1.591$ $d_{\mathrm{Si—O}}(2) = 1.606$	$\measuredangle$Si—O—Si = 150.9 $\langle \measuredangle$Si—O—Si$\rangle$ = 150.9 $\measuredangle$O—Si—O = 108.0–110.5
α-quartz[e]	2.65 (7.956)	trigonal ($P3_221$) 3 mol/u.c.	$d_{\mathrm{Si—O}}(1) = 1.605$ $d_{\mathrm{Si—O}}(2) = 1.614$ $\langle d_{\mathrm{Si—O}} \rangle = 1.609$	$\measuredangle$Si—O—Si = 143.7 $\langle \measuredangle$Si—O—Si$\rangle$ = 143.7 $\measuredangle$O—Si—O = 108.7–110.4
coesite[f]	2.92 (8.784)	monoclinic ($P21/a$) 16 mol/u.c.	$d_{\mathrm{Si—O}} = 1.60–1.62$ $\langle d_{\mathrm{Si—O}} \rangle = 1.609$	$\measuredangle$Si—O—Si = 137.4–180 $\langle \measuredangle$Si—O—Si$\rangle$ = 148.4 $\measuredangle$O—Si—O = 107.9–110.5 $\langle \measuredangle$O—Si—O$\rangle$ = 109.5
stishovite[g]	4.29 (12.88)	tetragonal ($P4_2/mnm$) 2 mol/u.c.	$d_{\mathrm{Si—O}}(1) = 1.809$ $d_{\mathrm{Si—O}}(2) = 1.757$	$\measuredangle$Si—O—Si = 81,90,106[h] $\measuredangle$O—Si—O = 100,130

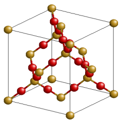
Potentials for ionic compounds

- But all of these have the common feature that they can be understood as tetrahedra with Si in the centre and O atoms in the joint corners:

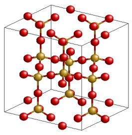
α cristobalite



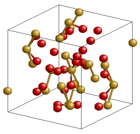
β cristobalite



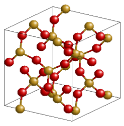
β tridymite



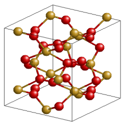
keatite



α quartz



β quartz



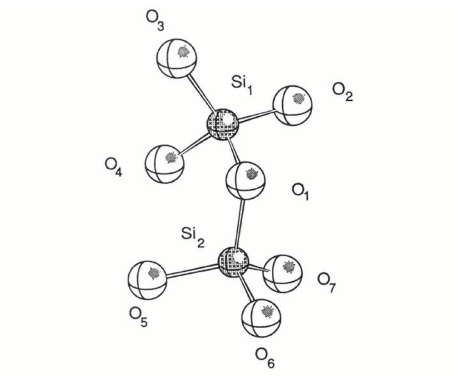
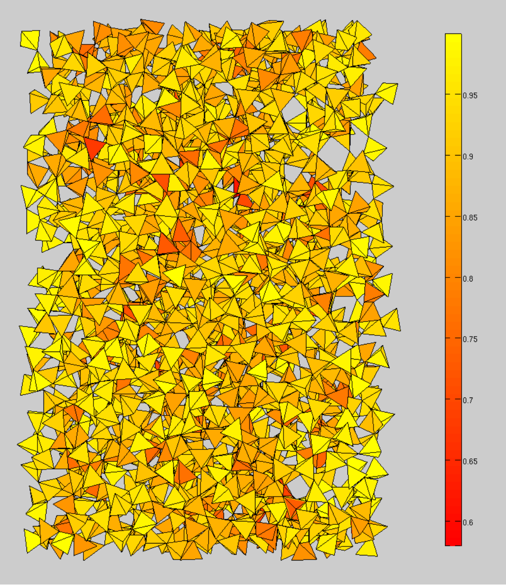
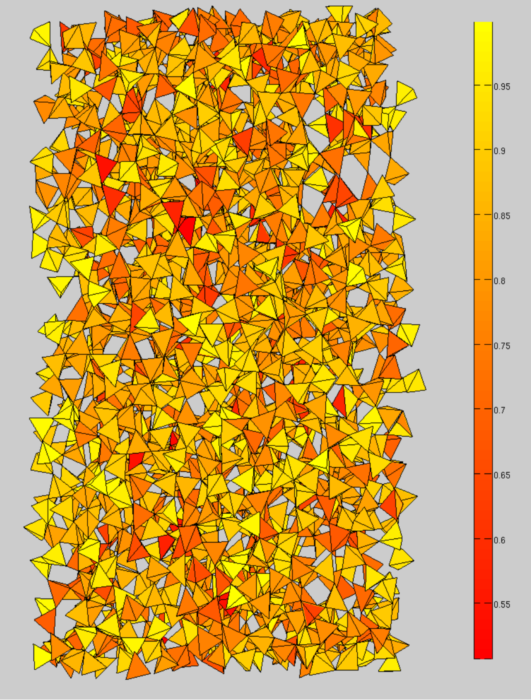


FIG. 9. A schematic view of corner-sharing tetrahedra in *a*-SiO_2.

Potentials for ionic compounds

- Simulation of a 40-Å diameter SiO_2 beam in equilibrium (left) and strained.
  - Colorcoded is the ratio between the shortest and longest edge of a face of a tetrahedron.





Potentials for ionic compounds

- The potential is of the familiar form:

$$V=\sum_{1\le i<j\le N} V_2(r_{ij})+\sum_{1\le i\le j\le k\le N} V_3(\mathbf{r}_{ij},\mathbf{r}_{jk},\mathbf{r}_{ik}) .$$

- The two-body part V_2:

$$V_2=\frac{H_{ij}}{r^{\eta_{ij}}}+\frac{Z_iZ_j}{r}-\frac{\frac{1}{2}(\alpha_i Z_j^2+\alpha_j Z_i^2)}{r^4}e^{-r/r_{4s}} ,$$

The first part is the “steric” repulsion due to the ion size, the second the Coulomb term and the third a charge-dipole term, which takes into account the large polarizability of O.

- The three-body term:

$$V_3=B_{jik}f(r_{ij},r_{ik})p(\theta_{jik},\bar{\theta}_{jik}) ,$$

where the f-function describes how the bond lengths and the p-term how a change of the bond angle affects the interaction.

Potentials for ionic compounds

- These are

$$f(r_{ij},r_{ik})=\begin{cases}\exp\left[\dfrac{l}{r_{ij}-r_0}+\dfrac{l}{r_{ik}-r_0}\right] & \text{for } r_{ij},r_{ik}<r_0\\ 0 \quad \text{for } r_{ij},r_{ik}>r_0 ,\end{cases}$$

$$p(\theta_{jik},\bar{\theta}_{jik})=(\cos\theta_{jik}-\cos\bar{\theta}_{jik})^2 ,$$

- Parameters are shown on the right.
  - *A* corresponds to Si and *X* to O in the three-body parts. Note that only the *AXA*- and *XAX*-three-body terms are defined - the potential would not describe sensibly e.g. pure Si since there is no *AAA*-term.

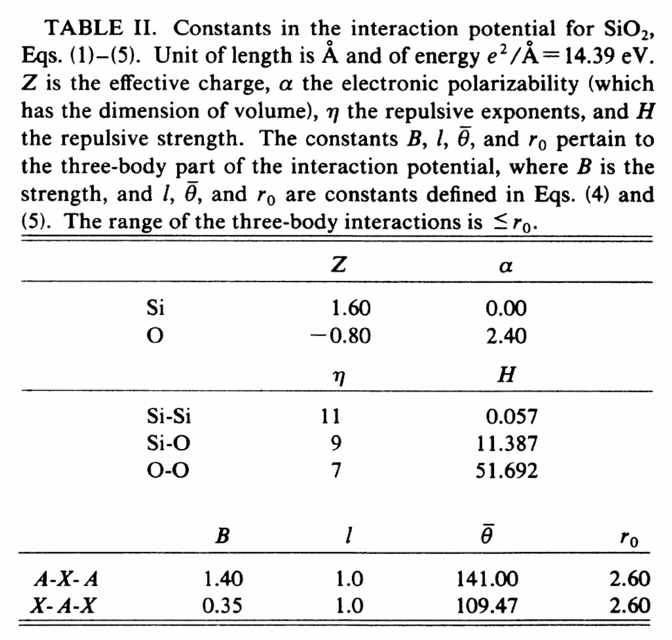


TABLE II. Constants in the interaction potential for SiO_2, Eqs. (1)–(5). Unit of length is Å and of energy $e^2/\text{Å}=14.39$ eV. Z is the effective charge, α the electronic polarizability (which has the dimension of volume), η the repulsive exponents, and H the repulsive strength. The constants B, l, $\bar{\theta}$, and r_0 pertain to the three-body part of the interaction potential, where B is the strength, and l, $\bar{\theta}$, and r_0 are constants defined in Eqs. (4) and (5). The range of the three-body interactions is $\le r_0$.

		Z	α	
Si		1.60	0.00	
O		−0.80	2.40	
		η	H	
Si-Si		11	0.057	
Si-O		9	11.387	
O-O		7	51.692	
	B	l	$\bar{\theta}$	r_0
A-X-A	1.40	1.0	141.00	2.60
X-A-X	0.35	1.0	109.47	2.60

Potentials for ionic compounds

- The Si-Si and O-O-interaction are just a purely repulsive pair potential:

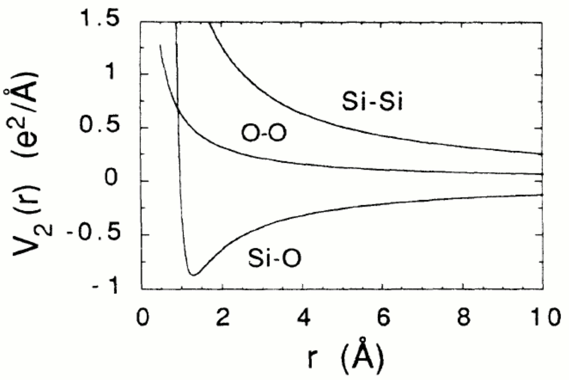


FIG. 1. Si-Si, Si-O, and O-O contributions to the two-body part of the interaction potentials, Eq. (2), for SiO_2. Total interaction potential is a sum of two-body, Eq. (2), and three-body contributions, Eq. (3). Unit of length is Å and of energy $e^2/\text{Å} = 14.39$ eV.

Potentials for ionic compounds

- The potential describes well the most common forms of SiO_2 :

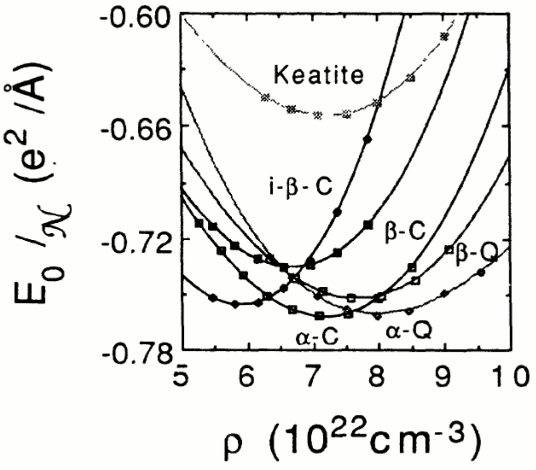


FIG. 2. Total potential energy (two plus three body) per particle, $E_0/\mathcal{N}$ in units of $e^2/\text{Å} = 14.39$ eV, for various crystalline phases of SiO_2 as a function of density: ideal β-cristobalite (i-β-C), β-cristobalite (β-C), α-cristobalite (α-C), β-quartz (β-Q), α-quartz (α-Q), and keatite.

Potentials for ionic compounds

- A newer potential was developed by Watanabe et al. [*Appl. Surf. Sci.* **234** (2004) 207.].
  - One of its strengths is the ability to describe also the so called sub-oxides of SiO_2; e.g. SiO.
  - Because of this it is suitable for describing interfaces between Si and SiO_2 and to be used in defect studies and ion bombardment simulations.
  - The potential is based on the Stillinger-Weber potential and the Si-Si interaction is the original Si-SW.
  - Examples of its use in nanocluster bombardment can be found in J. Samela's PhD thesis[1].
  - However, its elastic properties are not very good, strongly overestimates e.g. bulk modulus
- An SiO2 potential in the Tersoff formalism: [Munetoh et al, Comput. Mater. Sci. 39 (2007) 334]: better than Watanabe in some elastic and melting properties

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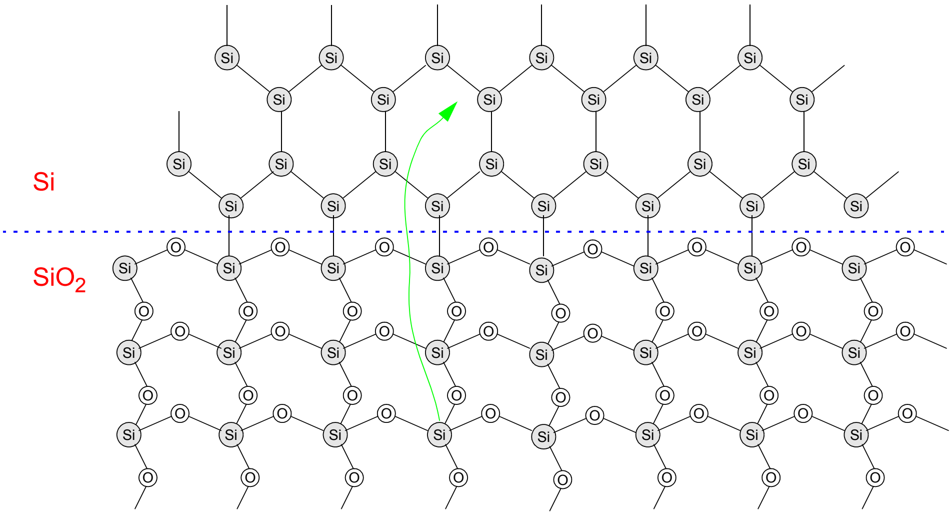
1. Electronically available at http://urn.fi/URN:ISBN:978-952-10-3927-0

Charge-transfer potential models

- There is a clear fundamental problem with the description of ionic bonding and covalent bonding described above.
  - Consider the following (schematic 2D representation) of an $Si\text{-}SiO_2$ interface system:



  - On the Si side of the interface, $z_{Si} = 0 \rightarrow$ ordinary Si potentials.
  - On the SiO_2 side $z_{Si} \approx 2 \rightarrow$ ionic model.

To be more precise, ab initio calculations give for SiO_2:

$$Z_{Si} \approx 1.4e, \; Z_O \approx -0.7e$$

- What happens if we move an Si atom from the SiO_2 to the Si side (green line). This could easily occur in reality by diffusion or a radiation process. Which model should be used to describe the interactions of this atom??

Charge-transfer potential models

- Here we get to the charge transfer model for the atoms, where the environment-dependence of the ionicity of the atom is built into the model.
  - There are extremely few models like this, since charge transfer processes are difficult to deal with and poorly understood.
  - One fairly well motivated approach is that of Alavi *et al.,* Phil. Mag. B **65** (1992) 489.
  - The idea is to formulate an environment-dependent term which gives the charge state of atoms:

$$z_i = Z\left(\sum_{j \neq i} f_{A_i B_j}(r_{ij})\right)$$

    - $f_{AB}(r_{ij})$ is some function of the atom distances and types A_i and B_j
    - $Z(x)$ is a function which could e.g. limit the charge state to reasonable values (like say between -4 and +4 for Si).
  - Some thought reveals that the f_{AB} functions would be likely to have the properties

$$\begin{aligned} f_{AA} &= 0 \\ f_{BB} &= 0 \\ f_{AB}(r_{ij}) &= -f_{BA}(r_{ij}) \end{aligned}$$

    - The first two criteria ensure charge neutrality in a pure elemental region, the latter one global charge neutrality.

Charge-transfer potential models

- Once the z_i have been determined, one could use an expression of e.g. the form

$$V_i = \sum_j \frac{z_i z_j e^2}{4\pi\varepsilon_0 r_{ij}} + g(z_i)\sum_{jk} V_{\text{manybody}}$$

to obtain the total interaction energy of an atom i.

- V_{manybody} could be some many-body potential for an uncharged system.
- The function $g(z_i)$ would be used to switch this potential on and off depending on the ionicity:

$$g(z_i)\ \begin{cases} = 1 \text{ when } z_i = 0 \\ \rightarrow 0 \text{ when } z_i \neq 0 \end{cases}$$

- The big and difficult question is how to choose $f(r_{ij})$. It should be constructed to ensure global charge neutrality, and give correct ionicities in known environments.

Charge-transfer potential models

- For instance in the SiO_2 case presented above, it obviously should be constructed such that if an Si atom has four O atoms at the equilibrium distance, it should give $z_i \approx 1.4e$. Since every Si atom has 4 O neighbours and every O atom 2 Si neighbours this would mean that in case only nearest-neighbour interactions are counted and the equilibrium atom distance is r_0, one could have

$$\begin{cases} f_{\text{Si-Si}} = 0 \\ f_{\text{O-O}} = 0 \\ f_{\text{Si-O}} = +0.35 \\ f_{\text{O-Si}} = -0.35 \\ Z(x) = x, \quad \text{when } x \le 4 \end{cases}$$

(remember: $Z_{\text{Si}} \approx 1.4e$, $Z_{\text{O}} \approx -0.7e$)

- One way to deduce the functional form could be to use quantum mechanical schemes to deduce ionicity, such as Mulliken charge analysis.

- Since little work has been done on this topic there is not much more to say, except that this is a wide-open topic with lots of room for new and interesting research.

- See also F. H. Streitz, J. W. Mintmire, *Phys. Rev. B* **50** (1994) 11996; X. W. Zhou *et al.*, *Phys. Rev. B* **69** (2004) 035402.

Potential models for ionic compounds

- Sometimes rather simple models may be sufficient.
  - An example: Si/SiO_2 interface (again!) [Y. Tu, J. Tersoff, *Phys. Rev. Lett.* **84** (2000) 4393.]
    - Simple VFF potential (sum over bonds; only Si-O and Si-Si bonds; no defects: continuous network of bonds):

$$E_{\{\mathbf{r}\}} = \frac{1}{2}\sum_i k_b (b_i - b_0)^2 + \frac{1}{2}\sum_{i,j} k_\theta (\cos\theta_{ij} - \cos\theta_0)^2 + U$$

- Suboxide penalty U allows to study other environments of Si atoms than the perfect SiO_2. It gives the energy cost of having less than 4 O neighbors:

Number of O neighbors	U/eV
0	0.00
1	0.47
2	0.51
3	0.24
4	0.00

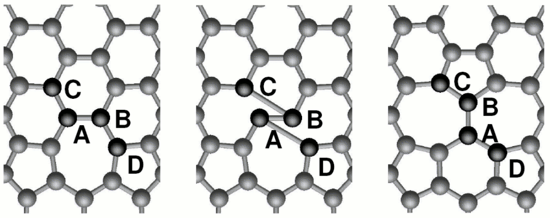


FIG. 1: The bond-switch move in a 2D example. *On the left:* The situation before the switch. *Center:* The bonds have been switched. *On the right:* The atoms have been moved to their minimum energy position.

- Interface structure was optimized using bond-switching Monte Carlo.

- For every **bond topology** the atom positions $\{\mathbf{r}\}$ were obtained by minimizing the potential energy

$$E = \min_{\{\mathbf{r}\}}(E_{\{\mathbf{r}\}})$$

Phase space = ensemble of bond topologies

Potential models for ionic compounds

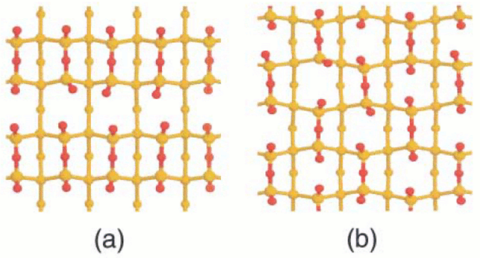


FIG. 1 (color). Plan view illustrating two Si-SiO$_2$ interface structures. The last three layers of Si are shown in gold, with atoms farther from the interface shown smaller. The first layer of O is shown in red. (a) Stripe phase, having (2 × 1) symmetry. (b) Check phase, having $c(2 \times 2)$ symmetry.

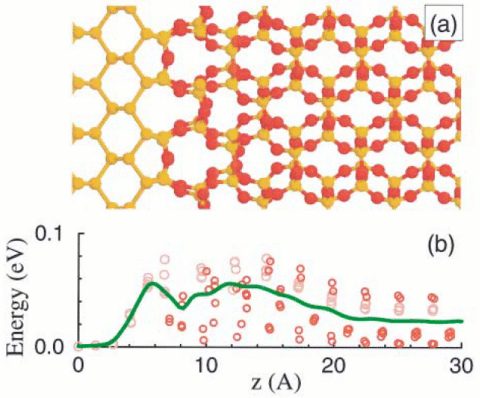


FIG. 4 (color). Interface between Si and tridymite, as in Fig. 3, to illustrate similarity of interface regions.

Results: interfaces Si—amorphous SiO2 and Si—tridymite

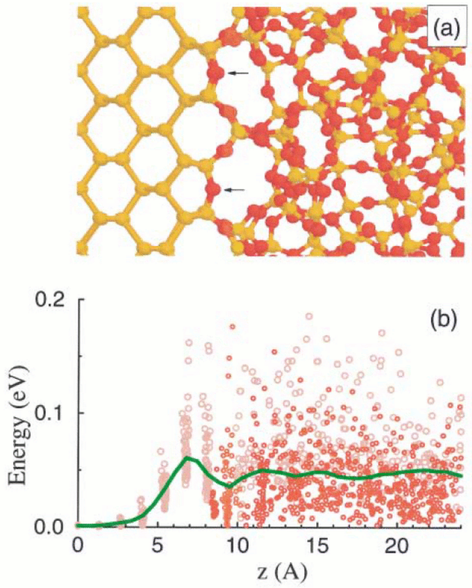
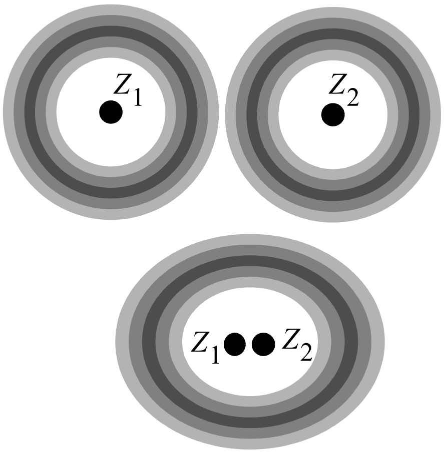


FIG. 3 (color). (a) Side view of canonical interface, for 4 × 4 cell of stripe phase, in [110] projection. The Si and O atoms are represented by gold and red spheres, respectively. Each arrow points to a row of oxygen atoms that form the bridges at the interface. Notice the substantial voids above each bridge bond. (b) Energy of each atom versus its z coordinate. Red circles represent oxygen atoms and gold circles represent silicon atoms. The green line is the local energy per atom, averaged over 20 configurations (and over a z range of ~1 Å for smoothness).

Repulsive potentials for high energies

- When talking about repulsive potentials there is first reason to clarify the concepts:
  - **Repulsive part** of equilibrium potentials: Constructed to obtain a minimum in the potential, and to describe states close to equilibrium, at energies ~ 0.1 - 100 eV above the minimum.
    - E.g. the short-range potentials V_{SR} mentioned above belong to this category.
  - Ion ion irradiation and nuclear physics one frequently is interested in very high-energy collisions.
    - An ion with a kinetic energy of 100 keV makes a head-on collision with a target atom → the C.M. energy is 50 keV
    - In this regime the equilibrium potentials are not valid, and there is a reason to fit a high-energy **repulsive potential** to them.



- Repulsive potentials are usually written in the form

$$V(r) = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 r}\Phi\left(\frac{r}{a}\right) \quad ,$$

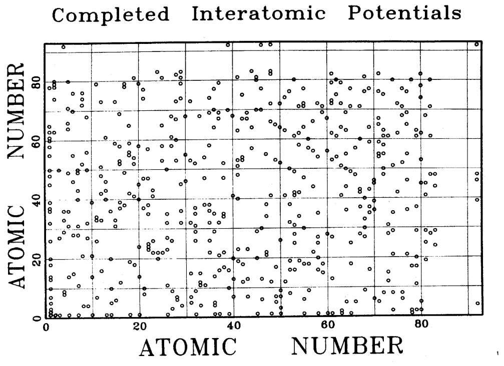
where $\Phi(x)$ is a **screening function** and $a = a(Z_1, Z_2)$ a **screening length**.
  - Φ is formed such that $\Phi \to 1$ when $x \to 0$, so the potential reduces to the Coulomb potential between the nuclei at high energies.
  - At normal interatomic distances the electron shells screen the nuclei so that the nucleus don't "see" each other almost at all ($\Phi \approx 0$).

Repulsive potentials for high energies

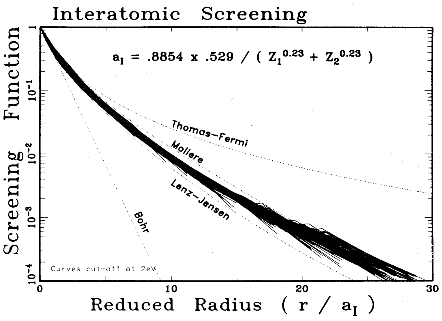
- At very small distances the nuclei are so close that the electron clouds do not screen them. The interaction is then purely Coulombic and $\Phi \approx 1$.

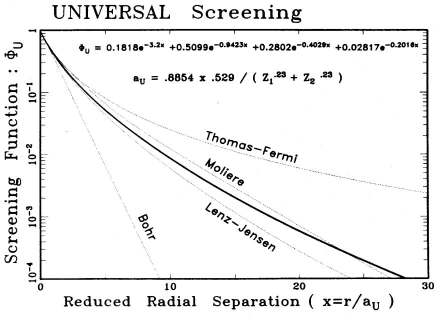
- The most used repulsive potential is that formulated by Ziegler, Biersack and Littmark (ZBL).
  - They used free-electron gas (FEG)-calculations to obtain the repulsive interatomic potential for 522 randomly chosen atom pairs, and sought a shape for the screening length which makes the screening function be as similar as possible for the different atoms:

$$a = \frac{0.8856 \times a_0}{Z_1^{0.23} + Z_2^{0.23}}$$, where $a_0 = 0.529\text{Å}$ is the Bohr length.



Repulsive potentials for high energies





- Onto these curves they fit a universal function (right figure above) of the form

$$\Phi(x) = \sum_{i=1}^{4} a_i e^{-b_i x} .$$

and obtained the parameter values shown on the right.

i	a_i	b_i
1	0.1818	3.2
2	0.5099	0.9423
3	0.2802	0.4029
4	0.02817	0.2016

- This potential is generally called the **ZBL universal potential**. The advantage of using it is that it is extremely easy: the only information needed of it are the atom numbers Z_1 and Z_2. The disadvantage is that this is an average potential, from which each specific case can vary easily 5-10 %.

- It is also possible to reproduce the FEG calculations for any atom pair based on information in the ZBL book *The Stopping and Range of Ions in Matter* (Pergamon, New York, 1985). This gives so called **ZBL pair-specific potentials.** These seem to be accurate to a few % or so.

Repulsive potentials for high energies

- In case the best possible accuracy is desired, one can use Hartree-Fock- or DFT-calculations of the energy of a dimer, or even better an atom inside a solid.
  - With dimer calculations by using certain HF- , HFS- and DFT methods it is possible to obtain the high-energy repulsive potential to ~ 1 % accuracy [Nordlund, Runeberg and Sundholm, *Nucl. Instr. Meth. Phys. Res. B* **132** (1997) 45].

Efficient ways to calculate ionic interactions

- So far we have assumed that the sum giving the energy of each atom always converges easily. This is not true always, however.
  - Let us consider potentials of the form $V \sim r^{-d}$. Far from the central atom in a homogeneous material the number of atoms in a thin shell dr is $4\pi r^2 \rho dr$, where ρ is the atom density, so the total potential in this layer is proportional to $4\pi r^2 \rho dr r^{-d}$. If we now integrate the total potential for all r, we obtain

$$V = \int_{r_{\min}}^{\infty} 4\pi\rho r^2 r^{-\mathrm{d}} dr = 4\pi\rho \frac{1}{3-d} r^{3-d} \Big|_{r_{\min}}^{\infty}$$

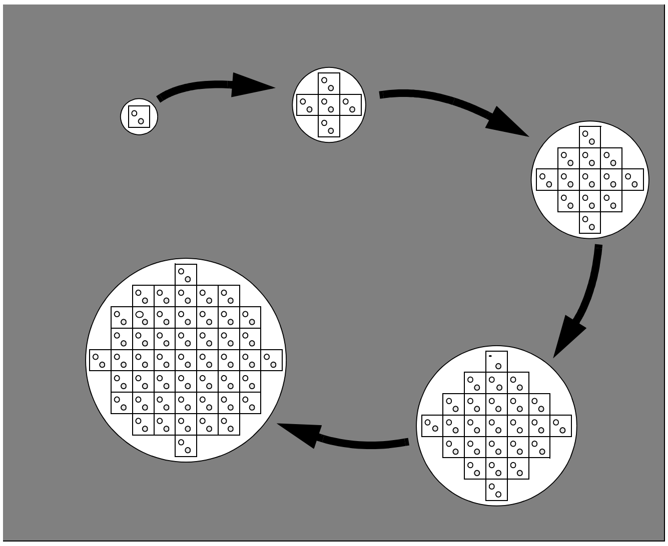
  - This vanishes in infinity only if $d > 3$. So in three dimensions we obtain convergence trivially only if the potential decays faster than r^{-3}.
  - Exponentially decaying potentials (Morse, Tersoff etc.), as well as LJ potentials are OK in this resprect, but not the Coulomb potential which is r^{-1}
$\rightarrow$ **When one simulates a periodic system with an ionic potential one can not use a simple cutoff distance < cell size/2.**
  - To circumvent this many methods have been developed: 1) Ewald summation [*Ann. Phys.* **64** (1921) 253]. It is much more efficient than direct summation, but is still an $O(N^2)$ method. 2) A newer method is the so called Fast Multipole Method, which can be parallelized and is $O(N)$.

Ewald-summation

- Take into account all interactions to an atom both from the MD cell itself as well as all the periodic image cells.
- The potential energy due to the Coulomb interaction is

$$V^{zz} = \frac{1}{2}\sum_{\mathbf{n}}\left[\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{z_1 z_2}{|\mathbf{r}_{ij}-\mathbf{n}|}\right]$$

Note: cgs units



- z_1 and z_2 are the atom charges, and cgs units are used for brevity. The vector $\mathbf{n}$ is now in principle a sum over all image cells $(n_x L, n_y L, n_z L)$, where $n_x = -\infty, \ldots, -1, 0, 1, \ldots, \infty$ and the indices i and j loop over atom pairs inside the cell (except of course not $i = j$ when $\mathbf{n} = 0$).

- This sum does not necessarily converge!
- Change the summation order: A natural way to achieve this is to add image cells radially outwards from the origin.
- Physically the reason this leads to convergence is easy to understand: since each cell has to be charge neutral the charges in it give at a long distance a dipole, quadrupole etc. interaction, which vanishes during symmetric summation.

Ewald-summation

- The surrounding medium also affects the energy of this ball. In a perfect conductor (metal) $(\varepsilon = \infty)$ and in vacuum $(\varepsilon = 1)$ the results are different; in vacuum a dipole layer will form at the surface. The correspondence between the two quantities is:

$$V^{zz}(\varepsilon = \infty) = V^{zz}(\varepsilon = 1) - \frac{2\pi}{3L^3}\left|\sum_i z_i \mathbf{r}_i\right|^2$$

- Ewald summation enables calculation of $V^{zz}(\varepsilon = \infty)$.

- If we want our system to be surrounded by vacuum, we can add the dipole term.

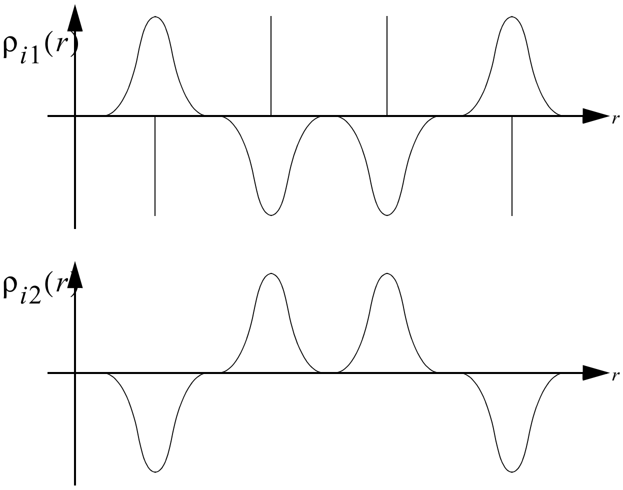
Ewald-summation

- In the Ewald method the charges z_i are given in the form of a charge density ρ_i^z . This ρ_i^z is given us the sum of a Gaussian and delta function electron density:

$$\rho_i^z(\mathbf{r}) = \rho_{i1}^z(\mathbf{r}) + \rho_{i2}^z(\mathbf{r})$$

$$\rho_{i1}^z(\mathbf{r}) = z_i[\delta(\mathbf{r}-\mathbf{r}_i) - \kappa^3\pi^{-3/2}e^{-\kappa^2(\mathbf{r}-\mathbf{r}_i)^2}]$$

$$\rho_{i2}^z(\mathbf{r}) = z_i\kappa^3\pi^{-3/2}e^{-\kappa^2(\mathbf{r}-\mathbf{r}_i)^2}$$



- ρ_{i1}^z is now a sum of delta functions located at the atom positions, and Gaussian-shaped densities of centered on the same position but of opposite signs, formed so that the integral is 0. Because ρ_{i1}^z now has a finite range, we can calculate the energy and force due to is using a cutoff radius.

- On the other hand, we also use the function ρ_{i2}^z to correct for the error made in introducing the Gaussian functions. But this function is now smooth, and can be calculated in reciprocal space: the Fourier-transformation of ρ are summed, and then an inverse Fourier transformation is used to obtain back the real-space answer.

Ewald-summation

- The result ("after a few steps of algebra") is an equation which has a real-space term $\mathbf{r}$, a $\mathbf{k}$-space term and the inverse value of the self-energy and the surface energy:
  - Term 1 is the short-range part. $\mathrm{erfc}(x) = (2/\pi^{1/2})\int_x^\infty e^{-t^2}dt$ is the complementary error function and L the side length of the MD-cell. We assume here that the cell is cubic. Again in the $\mathbf{n}$ sum the term $i = j$ when $\mathbf{n} = 0$.
  - Term 2 is the sum over reciprocal space vectors $\mathbf{k} = (2\pi/L)\mathbf{n}$.
  - Term 3 V_{self} is the self-energy of ρ_{i2}^z which has to be removed because it is included in the $V_{\mathrm{recipr.}}^{zz}$ part.
  - Term 4 is the surface term of the sphere.

$$V^{zz}(\varepsilon = 1) = V_{\mathrm{real}}^{zz} + V_{\mathrm{recipr.}}^{zz} - V_{\mathrm{self}}^{zz} + V_{\mathrm{surf}}^{zz}$$

$$= \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left[\sum_{|\mathbf{n}|=0}^{\infty} z_i z_j \frac{\mathrm{erfc}(\kappa|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|} \qquad 1\right.$$

$$\left. + \frac{1}{\pi L^3}\sum_{\mathbf{k}\neq 0} z_i z_j \frac{4\pi^2}{k^2} e^{-k^2/4\kappa^2}\cos(\mathbf{k}\cdot\mathbf{r}_{ij})\right] \qquad 2$$

$$- \frac{\kappa}{\pi^{1/2}}\sum_{i=1}^{N} z_i^2 \qquad 3$$

$$+ \frac{2\pi}{3L^3}\left|\sum_{i=1}^{N} z_i \mathbf{r}_i\right|^2 \qquad 4$$

- By setting κ (the width of the Gaussians) large enough we can restrict ourselves to the term $\mathbf{n} = 0$, which corresponds to the normal 'minimum image' convention.
- The real-space term can be calculated in the some loop as the short-range forces. Then V_{real}^{zz} is of the form

$$V_{\mathrm{real}}^{zz} = \sum_{i<j}\left[z_i z_j \frac{\mathrm{erfc}(\kappa r_{ij})}{r_{ij}}\right].$$

Ewald-summation

- Using complex numbers the reciprocal-space term can be written in the simpler form

$$V^{zz}_{\text{recip}} = \sum_{\mathbf{k}} A(\mathbf{k}) \left| \sum_i z_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \right|^2$$

$$A(\mathbf{k}) = \frac{2\pi}{L^3} \frac{\exp(-k^2/4\kappa^2)}{k^2}$$

- The force acting on atom i is

$$\mathbf{f}^i_{\text{recip}} = -2z_i \sum_{\mathbf{k}\neq 0} \mathbf{k} A(\mathbf{k}) \operatorname{Im}\left\{ e^{-i\mathbf{k}\cdot\mathbf{r}_i} \sum_j z_j e^{i\mathbf{k}\cdot\mathbf{r}_j} \right\}$$

- Note that the force calculation takes time as $O(N^2)$.

- Does this sound highly complicated? Fortunately there are several implementations of Ewald summation easily available, see e.g. Allen-Tildesley program **F.22** or N. Anastasiou and D. Fincham, *Comput. Phys. Commun.* **25** (1981)159.

- It is easy to generalize the equations to non-cubic cells.

Ewald-summation

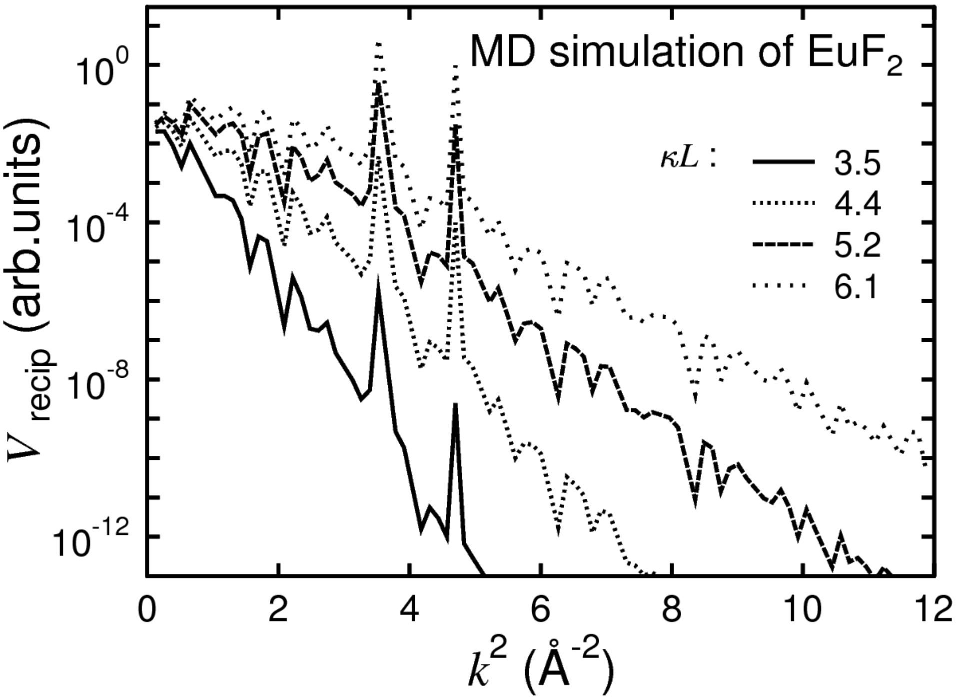
- In applying the method one has to choose three parameters:
  cutoff radius r_c
  width of Gaussian charge densities κ
  upper limit for $\mathbf{k}$ summation $|\mathbf{k}|^2_{\max}$.

  - It is best to start by setting r_c fairly large, e.g. $L/2$. From this a suitable value of κ can be obtained, on the basis of which a suitable limit for the $\mathbf{k}$-summation can be obtained. Typically $\kappa \sim 5/L$, in which case the calculation is concentrated in $\mathbf{k}$-space. The $\mathbf{k}$-summation would then involve 100-200 vectors.

Ewald-summation

- Example: EuF_2 :

$$N = 324$$
$$L = 17.4 Å$$
$$\kappa L = 5.2$$
$$r_c = L/2$$
$$|\mathbf{k}|^2_{\max} = 5 Å^{-2}$$



Ewald-summation

- Application of MD in neutrino-induced Doppler broadening (NID) [A. Kuronen, *et al. Phys. Rev. B* 52, (1995) 12640.]: *K* electron capture of ^{152}Eu → ν emission → 3.0-eV recoil energy to ^{152}Sm → γ rays Doppler broadened

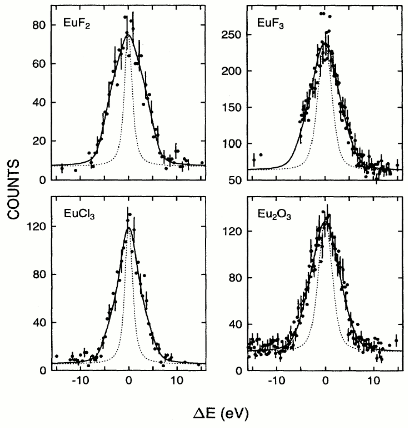


FIG. 1. Experimental (filled circles) and simulated (solid line) γ-ray line shapes for the 842-keV transition in ^{152}Sm measured in different target materials. The instrumental response function is also shown (dashed line). The simulations were performed with the recoil charge equal to the charge of the Eu atom in each lattice.

TABLE I. Parameters for the short-range potential (1) used in the simulations. For Sm, same values as for Eu were used.

Interaction	A (eV)	ρ (Å)	C (eVÅ^6)
Eu–Eu	1715.0	0.317	0.0
Eu–F	3429.1	0.280	14.0
F–F	369.1	0.280	12.5
Eu–Cl	3886.0	0.349	169.6
Cl–Cl	7911.5	0.383	2026.8
Eu–O	5045.4	0.290	34.0
O–O	22764.3	0.149	27.9

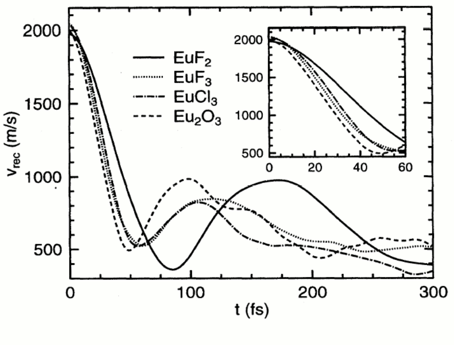


FIG. 2. Average magnitude of the velocity vector of the recoiling Sm ion as a function of time after the nuclear decay of ^{152}Eu as obtained from the MD simulations for different target materials.

TABLE II. Lifetime of the 963-keV state in ^{152}Sm obtained from NID measurements in different target materials using the equilibrium charges of Eu (2+ for EuF_2 and 3+ for the others) for the Sm ion in simulations. Lifetimes are weighted averages of the values for the 842- and 963-keV transitions. In addition to the statistical uncertainty, the quoted errors include uncertainties of the target temperature (0.9 fs), simulation statistics (2.0 fs), and instrumental response function (1.2 fs for EuF_3 and Eu_2O_3).

Target material	Lifetime (fs)
EuF_2	24.2±2.7
EuF_3	22.4±2.9
$EuCl_3$	36.8±2.8
Eu_2O_3	27.8±2.8

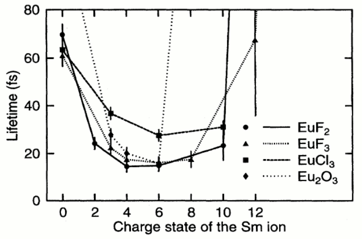


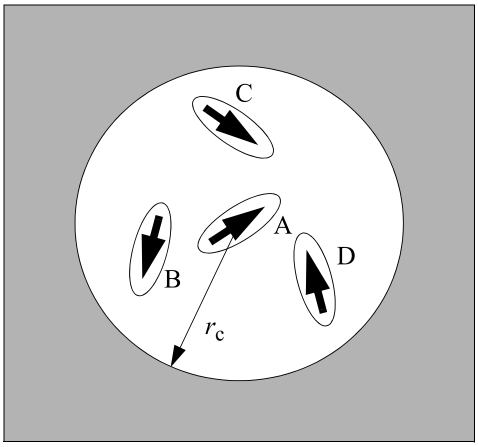
FIG. 3. Dependence of the fitted lifetime of the 963-keV level in ^{152}Sm on the charge state of recoiling ion in different target materials.

Ewald-summation

- If the periodicity of the Ewald summation causes trouble, one can use the particle-lattice (or particle-mesh) method:
  - The reciprocal space part is calculated by smoothing the ion charges in a regular lattice and solving the potential from the Poisson equation $\nabla^2\phi = -\rho/\varepsilon_0$ with Fourier methods.
    - The advantage is that this scales as $O(N)$.
    - The disadvantage is that the program gets more complicated
    -

Reaction field method

- In this method neighbours farther than r_c are approximated as continuous medium with some ε_s.
- The forces and energies inside the cavity are calculated normally.



- The continuous medium polarizes, which leads to a force on molecule i in the cavity R

$$E_i = \frac{2(\varepsilon_s - 1)}{2\varepsilon_s + 1}\frac{1}{r_c^3}\sum_{j \in R}\mu_j \text{ (sum includes } i\text{)}$$

- The problem here is ε_s, which has to be known in advance.

Field Multipole Method (FMM)

- The FMM method [Greengard and Rokhlin, *J. Comput. Physics* **73** (1987) 325.] is based on looking at different regions of space with different resolutions.
- The advantage of the method is that it is $O(N)$ and also can be parallelized [Nakano *et al*. *Comput. Physics Commun.* **83** (1994) 197.]
- The method uses an electrical multipole method to describe the influence of a region far away on an atom.
    - Potential outside a localized charge distribution $\rho(\mathbf{r})$ can be written as a multipole expansion:

$$\Phi(\mathbf{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \frac{4\pi}{2l+1} q_{lm} \frac{Y_{lm}(\theta,\phi)}{r^{l+1}},$$

where the multipole moments are defined as

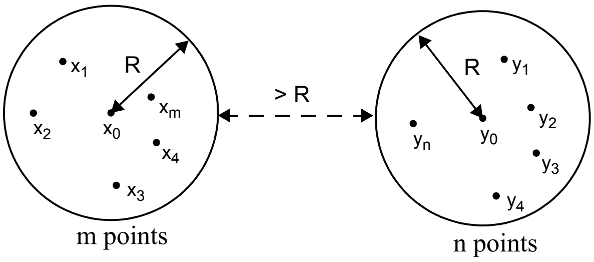
$$q_{lm} = \int Y^*_{lm}(\theta',\phi') r'^l \rho(\mathbf{r}') d\mathbf{r}'.$$

- In practice, the sum over l can be truncated to some finite value:

$$\Phi(\mathbf{r}) = \sum_{l=0}^{p}\sum_{m=-l}^{l} \frac{4\pi}{2l+1} q_{lm} \frac{Y_{lm}(\theta,\phi)}{r^{l+1}}$$

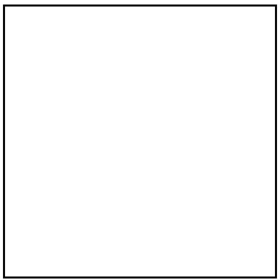
Field Multipole Method (FMM)

- Why is this useful, then ? Let us consider as a simple example two sets of points x_i and y_j which are inside two circles of radius R:



- Let the points x_i have charges q_i. If we now want to calculate the forces from points x_i on the points y_j we could of course calculate the Coulomb interaction from all the m y-points to all the n x-points. This would require nm interaction calculations, i.e. the algorithm is $O(nm)$.
- But if we, instead of this, first calculate the p^2 factors q_{lm}, requiring mp^2 operations. After this we could calculate the sum for all points y, which requires np^2 operations. Hence this method is $O(mp^2 + np^2)$. If the two circles are far away, p can be relatively small. If the number of points is large then clearly $mp^2 + np^2 \ll nm$, so we can gain lots of simulation time.

Field Multipole Method (FMM)


Level 0

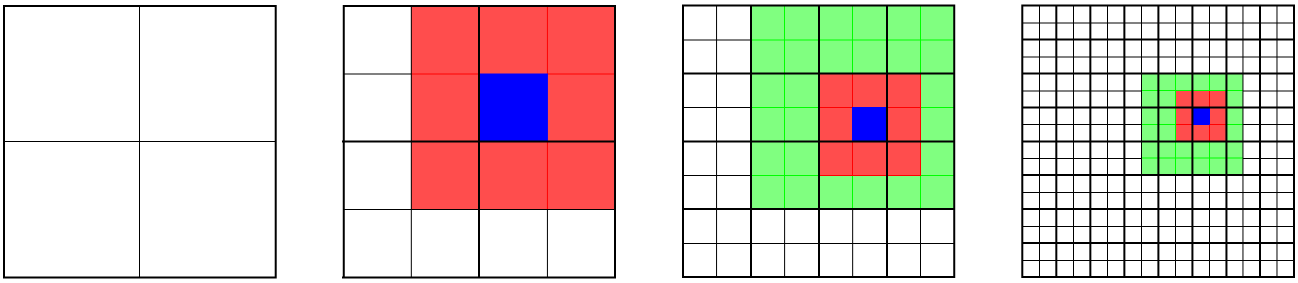
In the actual *FMM*-method space is divided into different levels of cell sizes.

🟦 cell b

🟥 b's **near neighbors**: cell at the same level as b that have a common point with b

🟩 b's **far neighbors**: cells at the same level as b that are children of b's parent's near neighbors but are not b's near neighbors

Cells that are not each others near neighbors are **well separated**.


Level 1 Level 2 Level 3 Level 4

- Level 0 is the normal, ordinary simulation cell, and the higher index levels finer divisions of it.
- Multipole expansion is used to calculate interactions between cells that are well separated.
- At level 1 (see above) there are no well separated cell pairs, so that we have to go to level 2 to be able to use the expansion.
- At level 2, in order to calculate interactions between a cell and its near neighbors, we divide the box further to smaller cells. Now each new cell has far neighbors for which the multipole expansion is applied. (Note that interaction between a cell and those cells that are not its near or far neighbors has been taken care of in previous levels.)
- At some stage division is so fine that interaction between near neighbors can be calculated by normal sum over atom pairs.

Field Multipole Method (FMM)

- This calculation scales as $O(N\log N)$ (where N is the number of atoms):
  1) at every level the calculation of multipole expansions scales as $O(p^2N)$
  2) number of levels is $O(\log N)$

- To obtain the $O(N)$ behavior multipole expansion is calculated from atom positions only at the smallest scale divisions.
  - These results can be compined to calculate the expansions in coarser levels by so called translation of a multipole expansion.

- An accurate algorithm, the equations and boundary condition solutions can be found from the paper of Greengard and Rokhlin.

- In practical calculations numerical noise may become a problem.

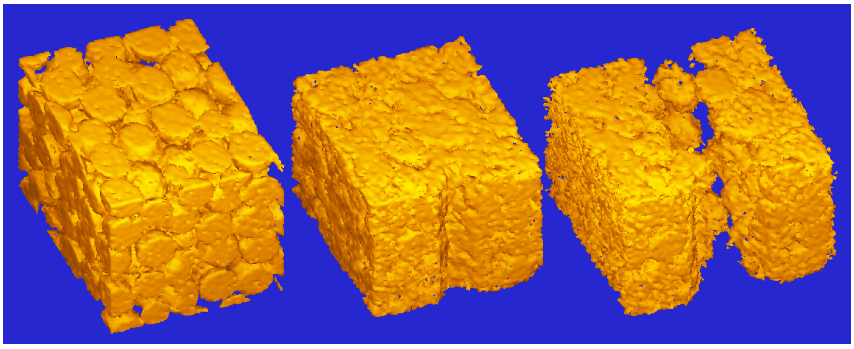
- In addition, as in Ewald summation it is also possible to take into account the effect of periodic image cells with the same principle.

- It is also evident that this algorithm can be parallelized well, since for the far cells it is enough to know only the multipole expansion, which is relatively easy to pass around.

- The FMM-model is also very general: in addition to the calculation of atomic interactions it can also be used in plasma dynamics, fluid mechanics and in astronomy!

Field Multipole Method (FMM)

- Sample application: R. Kalia et. al. simulated the fracture of about a million atom Si_3N_4 crystal [R. Kalia, TMS conference proceedings 1997].



Note that in the picture above the atoms are so small they can not be distinguished from each other!!

- After the original FMM formulation, variations often called **Fast Multipole Algorithms (FMA)** have been developed.
  - Basic idea same as in FMM, but tree-like data structures and FFT's are used to optimize the interactions even further.
  - E.g.: **dpmta** method, W. T. Rankin, PhD Thesis, Duke University, 1995
  - In principle better, but very complex leading to numerical accuracy problems ("numerical noise"

- A comparison: [J. A Board, C. W. Humphres, C. G. Lambert, W. T. Rankin and A. Y. Toukmaji, "Ewald and multipole methods for periodic N-body problems", "Proceedings of the Eighth SIAM Conference on Parallel Processing for Scientific Computing 1997]; says that for small numbers of particles and processors, PArticle-Mesh Ewald (PME) faster than dpmta

Energy minimization techniques

- The task of minimizing the energy of a set of atoms is a very common, yet surprisingly complex problem to solve efficiently.
  - N atoms, set of atomic coordinates $\mathbf{x} = (\mathbf{r}_{1x}, \mathbf{r}_{1y}, \mathbf{r}_{1z}, \mathbf{r}_{2x}, \ldots)$, system potential energy $V(\mathbf{x})$
  - Find $\mathbf{x}$ that minimizes $V(\mathbf{x})$
  - Examples: the equilibrium shape of a protein, the ground state configuration of an atom cluster, a minimum-energy configuration of a defect, ...
- A large variety of energy minimization techniques in numerical mathematics.
  - For large sets of atoms, one has to require that the memory requirement of the method scales as $O(N)$, which rules out many efficient techniques which require $O(N^2)$ memory.
    - In these $O(N^2)$ methods the Hessian matrix $\mathbf{A}$, $A_{ij} = \dfrac{\partial^2 V}{\partial x_i \partial x_j}$ is usually needed.

Energy minimization techniques

- At least the following approaches can be used to atomistic energy minimization:

  1. Monte Carlo simulation: Do an MC-simulation letting $T \to 0$.
  - Can be good e.g. in finding the equilibrium coordination in a liquid.
  - Not very efficient in finding the closest local minimum.
  - Good when non-physical moves needed to reach the equilibrium.

  2. MD simulation: Do an MD-simulation letting $T \to 0$.
  - Can be made more efficient by setting all $v = 0$ if the energy grows, or by setting $v_i = 0$ if the force $\mathbf{f}_i$ is in the opposite direction to $\mathbf{v}_i$
  - Sometimes quite efficient in finding a local minimum
  - Sometimes also good tool to find a global minimum: simulate at high T first, cooling down in cycles.

  3. Conjugate gradient
  - Very efficient method to find a local minimum.

  4. Genetic algorithm
  - Probably best method to find a global minimum from a random initial configuration.
- In this lecture package conjugate gradient and genetic algorithms are presented.

Simulated annealing

Energy minimization techniques

- A sidenote: optimization at 'constant pressure' : Usually the potential energy V is written as a function of the coordinates $\{x_i\}, \{y_i\}, \{z_i\}$ $(i = 1, \ldots, N)$ of the atoms in the system. When the cell edges are taken as variables it is easier to write the energy as a function of reduced coordinates $\{s_i\}, \{t_i\}, \{u_i\}$ and sizes of the simulation box in x, y, z directions: α, β, γ: $V = V(\{s_i\}, \{t_i\}, \{u_i\}, \alpha, \beta, \gamma)$ where $s_i = x_i/\alpha$, $t_i = y_i/\beta$, $u_i = z_i/\gamma$

- Now the gradient of the potential energy is $\nabla U = \begin{pmatrix} \partial V/\partial s_1 \\ \partial V/\partial s_2 \\ \ldots \\ \partial V/\partial t_1 \\ \partial V/\partial t_2 \\ \ldots \\ \partial V/\partial u_1 \\ \partial V/\partial u_2 \\ \ldots \\ \partial V/\partial \alpha \\ \partial V/\partial \beta \\ \partial V/\partial \gamma \end{pmatrix} = \begin{pmatrix} -F_{x1}\alpha \\ -F_{x2}\alpha \\ \ldots \\ -F_{y1}\beta \\ -F_{y2}\beta \\ \ldots \\ -F_{z1}\gamma \\ -F_{z2}\gamma \\ \ldots \\ -1/\alpha\sum_i F_{xi}x_i \\ -1/\beta\sum_i F_{yi}y_i \\ -1/\gamma\sum_i F_{zi}z_i \end{pmatrix} = \begin{pmatrix} -F_{x1}\alpha \\ -F_{x2}\alpha \\ \ldots \\ -F_{y1}\beta \\ -F_{y2}\beta \\ \ldots \\ -F_{z1}\gamma \\ -F_{z2}\gamma \\ \ldots \\ -W_{xx}/\alpha \\ -W_{yy}/\beta \\ -W_{zz}/\gamma \end{pmatrix}$

Conjugate gradient

- The conjugate gradient (CG) method is a general method to minimize function $f(\mathbf{x})$, where f can be any function of points $\mathbf{x}$ in N-dimensional space [Numerical Recipes, 2nd ed. ch. 10]
  - For N atoms we can write their coordinates $\mathbf{r}$ as a $3N$-dimensional vector $\mathbf{x}$ of the form

    $$\mathbf{x} = (\mathbf{r}_{1x}, \mathbf{r}_{1y}, \mathbf{r}_{1z}, \mathbf{r}_{2x}, \ldots)$$

  - The function $f(\mathbf{x})$ corresponds now to the potential energy function $V(\mathbf{r})$.
- In the CG method the gradient (force) of the function is used as a help in finding the minimum.
  - The gradient tells in which direction the function changes the most rapidly.

Conjugate gradient

- An obvious, but *not very efficient* way to minimize the energy is to always move in the direction of the negative gradient.
  - This is the so called **steepest descent method**, which for atoms can be described as follows:

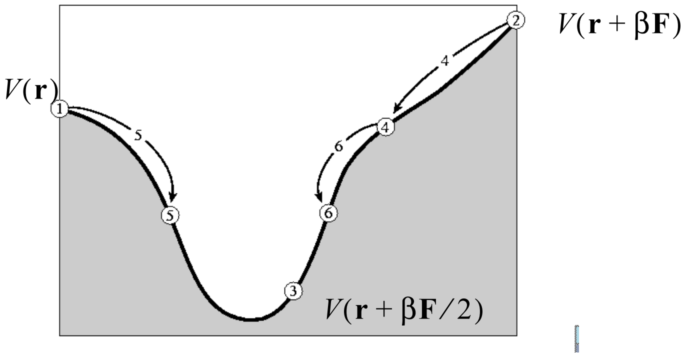
    0. Start from point $\mathbf{r}_0$, set $i = 0$.
    1. Calculate $V_i(\mathbf{r}_i)$, $\mathbf{F}_i = -\nabla V_i(\mathbf{r}_i)$.
    2. If $V_{i-1} - V_i < \varepsilon$ end.
    3. Minimize $V(\mathbf{r}_i + \alpha\mathbf{F}_i)$ with respect to the scalar quantity α.
    4. Set $\mathbf{r}_{i+1} = \mathbf{r}_i + \alpha\mathbf{F}_i$ and $i = i + 1$.
    5. Return to stage 1.

  - The algorithm resembles MD, but: no time, velocity or acceleration.
  - The line minimization in stage **3** a 1-dimensional operation in which the minimum of a function is sought by moving in a predetermined direction $\alpha\mathbf{F}_i$.
  - The line minimization is a relatively straightforward operation which is carried out in two steps.

    1. Make sure that there is a minimum and bracket it.
    2. Search it with a given accuracy.

Conjugate gradient

- Stage **1** is in principle easy to carry out. Starting from a point $\mathbf{r}$ and known direction $\mathbf{F}$, move forward some direction $\beta\mathbf{F}$. If $V(\mathbf{r} + \beta\mathbf{F}) > V(\mathbf{r})$ and in addition $V(\mathbf{r} + \beta\mathbf{F}/2) < V(\mathbf{r})$ and $V(\mathbf{r} + \beta\mathbf{F}/2) < V(\mathbf{r} + \beta\mathbf{F})$ the minimum is bracketed with the three points (1) $V(\mathbf{r})$ (3) $V(\mathbf{r} + \beta\mathbf{F}/2)$ and (2) $V(\mathbf{r} + \beta\mathbf{F})$. If these criteria are not fulfilled, increase β and try again.

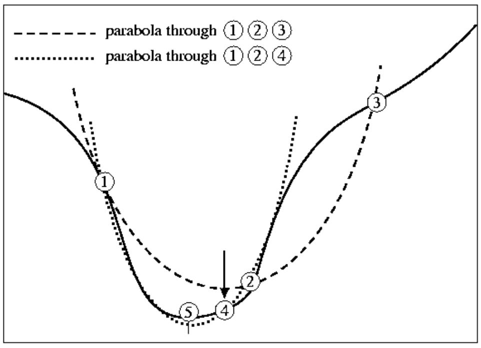


- After the minimum has been bracketed, one could of course use ordinary binary search to find it. A slightly better method turns out to be to use a golden section, i.e. let the new minimum be 0.38197 from either end.
- Often much better is to use so called inverse parabolic interpolation. In this method, a parabola is fit to the points a, b and c (corresponding to (1), (2) and (3) above), and the estimate of the minimum is the minimum of the parabola x:

$$x = b - \frac{1}{2}\frac{(b-a)^2[V(b) - V(c)] - (b-c)^2[V(b) - V(a)]}{(b-a)[V(b) - V(c)] - (b-c)[V(b) - V(a)]}$$

Conjugate gradient

- When the minimization is done once, either point a or c is replaced by point x (depending on which side of b x is), and the minimization step is repeated.



- The iteration is continued until the minimum has been found with the desired accuracy.
- A combined method: try the inverse parabolic search, but switch to the golden section if this fails.
  - One such method is the so called Brents method, which is presented in Numerical Recipes[1] (program `brent()`).

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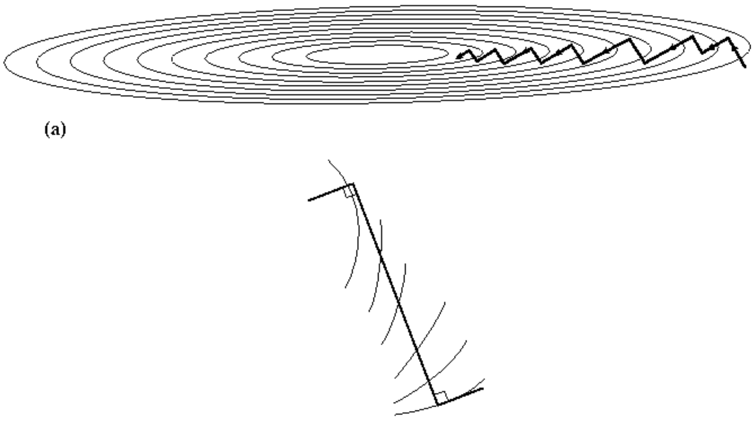
[1] http://www.nr.com/

Conjugate gradient

- By combining the Steepest descent (SD)-algorithm and the Brent line minimization the energy of an atom system can be minimized. But this is still not very efficient in many dimensions. The reason is that the SD method easily winds up in a zig-zag pattern which does not move towards the minimum efficiently as in the figure below:



Conjugate gradient

- In the Conjugate gradient (CG) method the problem is solved by choosing a new “conjugate” direction of movement so that it depends on the previous direction, and does not lead to the zig-zag-pattern above.
  - What is really meant by two directions being conjugate to each other? Consider an arbitrary function $f(\mathbf{x})$ of N dimensional argument, and construct its Taylor-series around a point $\mathbf{P}$:

$$f(\mathbf{x}) = f(\mathbf{P}) + \sum_{i} \frac{\partial f}{\partial x_i} x_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 f}{\partial x_i \partial x_j} x_i x_j + \ldots \approx c - \mathbf{b} \cdot \mathbf{x} + \frac{1}{2} \mathbf{x} \cdot \mathbf{A} \cdot \mathbf{x}$$

$$\text{where} \quad c \equiv f(\mathbf{P}) \qquad \mathbf{b} = -\nabla f\big|_{\mathbf{P}} \qquad \mathbf{A} = \left.\frac{\partial^2 f}{\partial x_i \partial x_j}\right|_{\mathbf{P}}$$

  - The matrix $\mathbf{A}$ is the so called Hessian matrix. In this approximation the gradient of f is $\nabla f = \mathbf{A} \cdot \mathbf{x} - \mathbf{b}$, and a change in the gradient ∇f over some distance $\delta \mathbf{x}$ is again $\delta(\nabla f) = \mathbf{A} \cdot (\delta \mathbf{x})$
  - The previous direction in which we have moved is $\mathbf{u}$, gradient is $\mathbf{g}$. How to construct the next direction $\mathbf{v}$?
  - In the current point: $\mathbf{g} \perp \mathbf{u}$
  - After the next step we still want $\mathbf{g}' \perp \mathbf{u}$ → the change in the gradient $\delta(\nabla f)$ should be perpendicular to $\mathbf{u}$: $\mathbf{u} \cdot \delta(\nabla f) = 0 \Rightarrow \mathbf{u} \cdot \mathbf{A} \cdot \mathbf{v} = 0$
  - If this is valid, the directions $\mathbf{u}$ and $\mathbf{v}$ are considered to be *conjugated*.

Conjugate gradient

- In the conjugate gradient method two vectors $\mathbf{g}$ and $\mathbf{h}$ are used to calculate the new direction into which to move. $\mathbf{h}$ is the actual direction into which the line minimization is carried out.
  - In solving linear equations, these are iterated as follows: $\mathbf{g}_{i+1} = \mathbf{g}_i - \lambda_i (\mathbf{A} \cdot \mathbf{h}_i)$ and $\mathbf{h}_{i+1} = \mathbf{g}_{i+1} + \gamma_i \mathbf{h}_i$

    where

$$\lambda_i = \frac{\mathbf{g}_i \cdot \mathbf{g}_i}{\mathbf{h}_i \cdot \mathbf{A} \cdot \mathbf{h}_i} = \frac{\mathbf{g}_i \cdot \mathbf{h}_i}{\mathbf{h}_i \cdot \mathbf{A} \cdot \mathbf{h}_i} \quad \text{ja} \quad \gamma_i = \frac{\mathbf{g}_{i+1} \cdot \mathbf{g}_{i+1}}{\mathbf{g}_i \cdot \mathbf{g}_i}$$

  - The vectors $\mathbf{g}$ and $\mathbf{h}$ fulfil the orthogonality and conjugation requirements:

$$\mathbf{g}_i \cdot \mathbf{g}_j = 0 \qquad \mathbf{h}_i \cdot \mathbf{A} \cdot \mathbf{h}_j = 0 \qquad \mathbf{g}_i \cdot \mathbf{h}_j = 0$$

  - Not suitable for atomistic systems: the $N \times N$ matrix $\mathbf{A}$!
  - The crucial, saving statement is the following: if we have just minimized f in the direction $\mathbf{h}$ to some point $\mathbf{x}_{i+1}$, the new $\mathbf{g}$ can be obtained simply with

$$\mathbf{g}_{i+1} = -\nabla f(\mathbf{x}_{i+1})$$

    and the end result corresponds to the above equations!

Conjugate gradient

- In principle this iteration algorithm gets one to an energy minimum in a system of N atoms with a memory requirement $O(N)$ and a number of iteration steps $O(N)$.

- This sounds like a problem for large numbers of atoms: if say $N = 100000$ we definitely do not want to iterate 100000 times.

- In practice the atom motion in large systems is almost always strongly correlated, and much fewer iteration steps are enough to get to a minimum.

- Typically ~ 200 steps in periodic systems and ~ 1000 steps in systems with a surface is enough to find an energy minimum with 15 digits of accuracy regardless of system size.

Conjugate gradient

- Using these equations we obtain the following algorithm for conjugate gradient energy minimization:

0. Start at point $\mathbf{r}_0$, set $i = 0$, $V_0 = V(\mathbf{r}_0)$, $\mathbf{x}_0 = -\nabla V(\mathbf{r}_0)$, $\mathbf{g}_0 = \mathbf{x}_0$, $\mathbf{h}_0 = \mathbf{x}_0$.

1. Minimize $V(\mathbf{r}_i + \alpha\mathbf{x}_i)$ with respect to the scalar α, then set $\mathbf{r}_{i+1} = \mathbf{r}_i + \alpha\mathbf{x}_i$ and evaluate $V_{i+1} = V(\mathbf{r}_{i+1})$.

2. If $V_{i+1} - V_i < \varepsilon$, quit.

3. Calculate $\mathbf{x}_i = -\nabla V(\mathbf{r}_{i+1})$ and $V_i = V(\mathbf{r}_{i+1})$.

4. Calculate $\gamma = (\mathbf{x}_i \cdot \mathbf{x}_i)/(\mathbf{g}_i \cdot \mathbf{g}_i)$

5. Set $\mathbf{g}_{i+1} = \mathbf{x}_i$.

6. Set $\mathbf{h}_{i+1} = \mathbf{g}_{i+1} + \gamma\mathbf{h}_i$ and $\mathbf{x}_{i+1} = \mathbf{h}_{i+1}$.

7. Set $i = i + 1$ and return to phase 1.

Conjugate gradient

- The above is the original, so called Fletcher-Reeves - algorithm. In some cases it is more efficient to use the so called Polak-Ribiere- version, which is identical to the above except that step 4 is:

4. Calculate $\gamma = \frac{(\mathbf{x}_i + \mathbf{g}_i) \cdot \mathbf{x}_i}{\mathbf{g}_i \cdot \mathbf{g}_i}$

Conjugate gradient

- The above algorithm is already a very efficient way to look for a local minimum. It also does not have anything specific to atomistic simulations; the function $V(\mathbf{r})$ can be any N-dimensional function $f(\mathbf{x})$ which has a well-defined gradient.

Material on the ACG variant of CG is from Kai Nordlund.

- In typical atomistic simulations there are special features (especially the knowledge that the atoms do have a smooth minimum) which can be utilized to optimize the algorithm, at the possible expense of generality.
- In atomistic simulations the calculation of the potential energy $V(\mathbf{r})$ is very slow, and the calculation of forces even slower.
  - In the above algorithm the line minimization-step **1** is the only step where forces are actually calculated. This step had two parts (see above):
    1. Make sure there is a minimum, and bracket it.
    2. Search it with the desired accuracy.

  - The bracketing requires at least 3 evaluations of the potential, and the Brent method line minimization typically 5-10 evaluations.

  - In atomistic systems we know, however, that the length scale is rather limited.
    - Unless the initial atom positions are really unphysical, the atoms are almost certain to be ~ 0.2 Å from the ground state position, or even closer. If we simply assume that the minimum is never farther than say 0.5 Å, we can simply get rid of step **1.** But this is clearly a bit dangerous, and still does not gain us more than 20 % or so of the efficiency.

  - It would be even better if we could get rid of the 5-10 potential evaluations needed in the Brent method. This can be achieved rather simply.

Conjugate gradient

- In this speed-up method (called ACG for reasons apparent below) we start by assuming that the 'minimum is out there'.

- The main point in the ACG method is the observation that when the original CG method line minimization of $V(\mathbf{r}_i + \alpha\mathbf{F}_i)$ with respect to the scalar α, for most steps the optimal value of the scalar α is about the same, ~ 0.05.
  - This is of course no natural constant, but seems to be valid for common Si and metal potentials. If the scalar α is almost the same in any case, it does not seem sensible to optimize it separately every time.

- So the method is as follows:
  - Set initially $\alpha = 0.05$.
  - For every step move forwards by $\alpha\mathbf{F}_i$.
  - If the potential energy goes down, increase optimistically α a bit.
  - If the potential energy goes up, disregard the previous step, decrease α and repeat the same iteration.

Conjugate gradient

- Because of the optimization of α the method might be called adaptive conjugate gradient, ACG:

0. Start from $\mathbf{r}_0$, set $i = 0$, $\mathbf{F}_0 = -\nabla V(\mathbf{r}_0)$, $\mathbf{g}_0 = \mathbf{F}_0$, $\mathbf{h}_0 = \mathbf{F}_0$, $\alpha = 0.05$
1. Store old $\mathbf{r}_i \rightarrow \mathbf{r}_i^{\mathrm{prev}}$
2. Set $\mathbf{r}_{i+1} = \mathbf{r}_i + \alpha\mathbf{F}_i$
3. Calculate $V_{i+1} = V(\mathbf{r}_{i+1})$, $\mathbf{F}_i = -\nabla V(\mathbf{r}_i)$.
4. If $V_{i+1} > V_i$ return $\mathbf{r}_i^{\mathrm{prev}} \rightarrow \mathbf{r}_i$, set $\alpha = \alpha/2$, return to step 2.
5. If $V_{i+1} - V_i < \varepsilon$, quit.
6. Calculate $\gamma = \dfrac{(\mathbf{x}_i + \mathbf{g}_i) \cdot \mathbf{x}_i}{\mathbf{g}_i \cdot \mathbf{g}_i}$ (Polak-Ribierre)
7. Set $\mathbf{g}_{i+1} = -\mathbf{F}_i$
8. Set $\mathbf{h}_{i+1} = \mathbf{g}_{i+1} + \gamma\mathbf{h}_i$ and $\mathbf{F}_{i+1} = \mathbf{h}_{i+1}$.
9. Increase $\alpha = 1.05\alpha$, set $i = i + 1$ and return to step 1.

- Here the constants 0.5 and 1.05 were optimized for Stillinger-Weber Si.

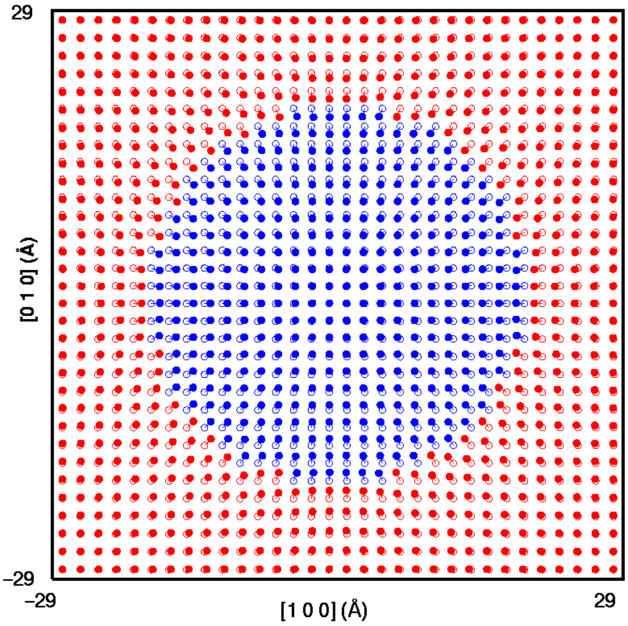
Conjugate gradient

- Written in this way the method usually needs only one potential evaluation per iteration step, except when the energy increases. In practice the energy decreases almost always, so on average the number of potential evaluations still is only about 1.1 / iteration. In the ordinary CG method this value is about 10, so in the ACG each iteration step is about 10 times faster than in CG!

- On the other hand, the ACG loses the perfect match of conjugate directions, so it needs more iterations. Still, the overall speedup of ACG vs. CG is almost always a factor of ~ 3-5.

Conjugate gradient

- As an example a 40 Å diameter Co-nanocluster in a 16×16×16 unit cell periodic Cu cell was created, and relaxed this system with EAM potentials with different methods. These calculations (in larger cells) are useful in understanding the energetics of Co nanoclusters.



- The figure above shows the atom displacements due to the minimization, but so that the displacements have been exaggerated by a factor of 3. The open circles are the original atom positions, the closed circles the final positions after minimization.
- The blue atoms are Co, red Cu. Because Co has a smaller equilibrium nearest-neighbour distance than Cu, the atoms move inwards.

Conjugate gradient

- The simulation results were as follows (computer ~ 400 Mhz Pentium[1] Linux):

```
Method                   Et (eV) Niter   Final E (eV)    Simulation time (s)
------                   ------- ------  -------------   -------------------
SD Plain                 0.001   227      -59927.160     2684.20
SD Adaptive              0.001   172      -59927.052      323.56

CG Plain                 0.001    27      -59927.193      363.03
CG No bracketing         0.001    27      -59927.193      251.98
ACG                      0.001    70     -59927.194      128.34

MD btctau=70 fs          -       250      -59927.169      390.25
```

SD= Steepest Descent
CG= Conjugate gradient
MD= Molecular dynamics.

`Et` is the energy tolerance
`Niter` the number of iterations

  - We see that all methods give essentially the same result, as they should. The 0.1 eV differences may be shifts in the position of a single atoms, and hence not likely to be a significant problem.

  - The SD method with line minimization is very slow, as expected. The number of iterations is clearly the smallest in the CG methods, but they are still ~ 3 times slower than ACG.

  - A bit surprising is that the adaptive SD method is in fact faster than straight CG, and that ordinary MD is almost as fast as straight CG or adaptive SD.

  - But the ACG method clearly beats all the others by a factor of 3 or more.

- However, in a new minimization problem it is best to first implement the full CG method. After that, one can check whether it can be optimized for the particular range of problems, e.g. by a scheme similar to the one above.

---

[1] I know, this should be updated :-)

Genetic algorithms

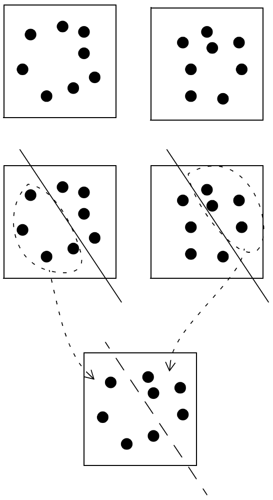
- Genetic algorithms (GA) are a popular method for looking for a global minimum, which have not been used too much in the physical sciences. They are, however, well suited at least for looking for the minimum of a fairly large set of atoms.
- Groups of atoms typically have a fairly large set of energy minima, so the ordinary methods are not well applicable for looking for a global minimum: CG only looks for the closest local minimum, and MD and Monte Carlo (simulated annealing) are fairly easily stuck to one minimum or a local region.
  - But the GA method is well suited for looking for global minima, at least for dilute atom systems.

- Genetic algorithms have obtained their inspiration from Darwin’s theory of evolution.
  - The idea is to perform natural selection for some group of parameters G which describes well the real system.
  - The group is allowed to breed by mating, after which natural selection is carried out (i.e. the poorest adapted species are killed).
  - The parameters G can be considered to correspond to a gene sequence, DNA.

- Here we present the Deaven and Ho approach to genetic algorithms for atoms [Deaven and Ho, *Phys. Rev. Lett.* **75** (1995) 288].
  - Let us state the problem as follows. We have N atoms in free space, and want to find their minimum-energy configuration. The parameter set is now simply the set of atom coordinates $G = \{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\}$.
  - We illustrate there the algorithm with 2D figures; in reality it of course usually is in 3D. The difference between 2D and 3D is trivial.

Genetic algorithms

- **Deaven and Ho genetic algorithm:**



0. Start. Create random initial positions for structures, each with exactly N atoms.
1. Mating and breeding. Select two well-adjusted parents for breeding. This is done by selecting a given parent i with state G_i with the probability

$$P(G_i) \propto e^{-E(G_i)/T_{\mathrm{m}}}$$

where the mating 'temperature' T_{m} is selected as the range of energies among the whole population $\{G_i\}$. Split the two parent structures along the same line. Take one half of one parent, and another half of another parent, and join them together.
Here the added complication that a child may have a different number of atoms than the parents comes in. In this case, the lines creating the two parents are moved in opposite directions until a state where the child has equal numbers of parents is found.
2. Mutation. With a probability μ perform a mutation on the child. There are two possible kinds of mutations:
  a) Move atoms in a random direction by a random distance a random number of times.
    The distance is of the order of the bond length, and the number of times ~ 5 - 50.
  b) Move an atom *up* along the potential energy function. (Try to move over potential barriers.)
3. Minimize the energy of the child to the closest local minimum. This is done by CG or MD.
4. Natural selection. If the child has lower energy than any of the parents, allow it to stay alive. Then check that its energy does not match the energy of any parent within an energy range δE. If this is true, include it in the population, and kill the least-well adapted parent (the one with the highest E).
5. Convergence test. If convergence has not been reached, return to stage 1.

Genetic algorithms

- The energy range δE is included to prevent the population from having several identical or very similar structures.
- The mutation operation can sometimes be completely left out.
- The mating temperature reduces the probability that poorly adjusted parents get to breed. Hence they are more likely to die without giving rise to any offspring.
  - If $T_{\mathrm{m}} \gg E_{\mathrm{max}}$ all parents get to breed by about the same probability. If on the other hand $T_{\mathrm{m}} \ll E_{\mathrm{max}}$ only the best adjusted parents get to breed. (Even this can be seen to have a biological interpretation, although not a very good one: in warm climates it is easier to survive, whereas in harsher, colder climates only the best adjusted individuals can survive and breed...)

- The size of the population does not have to be very large. With Deaven and Ho, who used TB, had it usually at 4. Jura Tarus found that somewhat larger numbers work better for the Tersoff C potential.

- Deaven and Ho used their code to find the equilibrium structure for a fullerene C_{60} and other small carbon clusters, starting from random atom coordinates.
  - No other simulation method had at that time been able to produce a fullerene 'from scratch' .
  - Chelikowsky got close with MD [*Phys. Rev. Lett.* **67** (1991) 2970.], but using a to-say-the least suspicious bond-bending part in his potential.
  - Simulated annealing (a Monte Carlo method) can find the structure of molecules of the order of C_{20} , but not larger than that.

- Deaven and Ho used a Tight Binding force model, which was known to describe fullerenes well.

- Parameters: mating temperature $T_{\mathrm{m}} = 0.2\ \mathrm{eV/atom}$, energy resolution $\delta E = 0.01\ \mathrm{eV}$, population $p = 4$.

Genetic algorithms

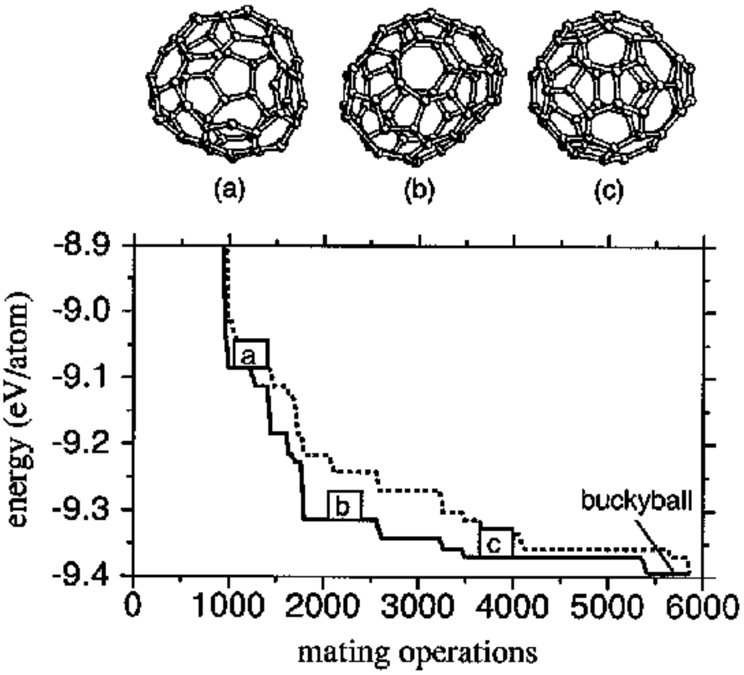
- **Fullerene C_{60} .** The algorithm finds a perfect fullerene after about 6000 mating operations starting from random coordinates, without mutations ($\mu = 0$) :

- The upper curve is the maximum energy of the population, the lower the minimun.

- We see that fairly fast (1000 mating operations) a fairly well-adjusted state (a) which still has defects (a 12-membered atom ring and two 7-membered atom rings).

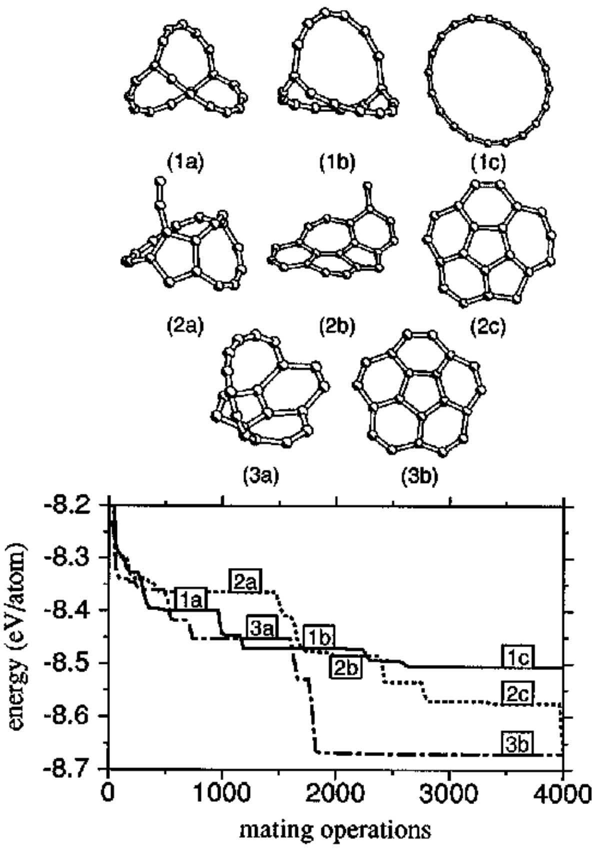
- A large fraction of the time, about 5000 mating operations, goes to removing the last defects.

- In stage (b) there is still left a 7-atom ring, and in state (c) there already is the correct amount of pentagons and hexagons, but two pentagons adjacent to each other.



Genetic algorithms

- **Carbon cluster C_{20}**. When the genetic algorithm is run for 20 carbon atoms, the effect of mutations becomes apparent:
  - States 1 a-c and the solid line describe the results when the code is ran without mutations.
    - The structure is stuck in a round carbon circle.
    - But some $\mu = 0$ -states do find the correct structure.
  - In states 2 a -c and 3 a-b $\mu = 0.05$.
    - Now the structures find fairly fast the lowest-energy bowl form.
    - State 2 c is already close to the ground state, but the rings on the side have 5 or 7 atoms.
    - State 3 b is the correct ground state, with only 6-membered atom rings.



Genetic algorithms

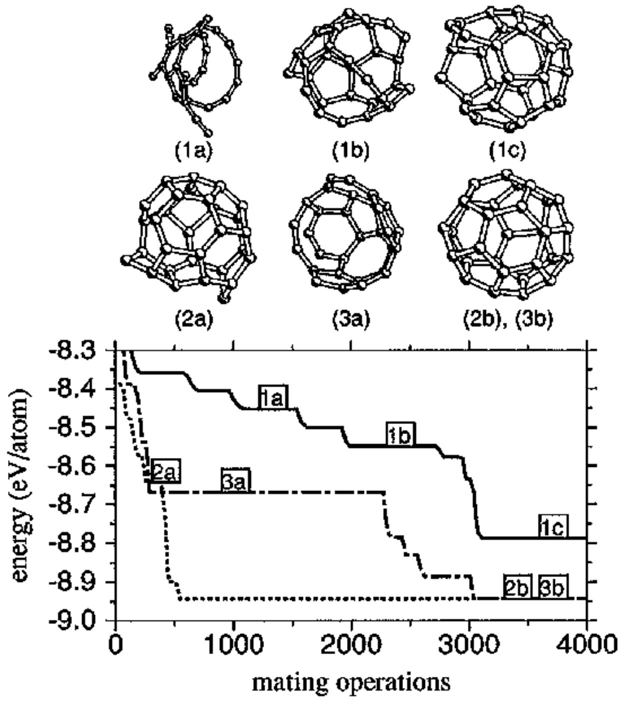
- **Carbon cluster C_{30}**

  - Most runs end up in the correct state, but some of the $\mu = 0$ states do not in 4000 mating operations found the ground state, but get stuck in state (1c).

  - With $\mu = 0.05$ almost all states end up in the correct cage structure (2b) and (3b).

  - The intermediate configurations (2a) and (3a) show that the correct final state can be reached in several different ways.

  - Only mutation, with no mating, does not lead to the correct state.



Genetic algorithms

- Here it is important to realize that the development of the GA minimization *process* does not necessarily contain any physically meaningful information.

  - The real path to the ground state probably has no relation to the GA path.

  - So only the ground state found by GA may correspond to real life (in case the experimental situation has had time to reach the ground state).

  - You probably remember: This same note applies to equilibrium MC simulations.

Genetic algorithms

- In the original way of realizing GA the information on the state is coded in a binary “gene sequence” which corresponds to DNA.
  - Let us consider the interaction between two molecules A and B [Xiao and Williams, *Chem. Phys. Lett.* **215** (1993) 17]. Both molecules can be described with a position and rotation angle, so the information needed $(x, y, z, \alpha, \theta, \phi)$.
  - If we now discretize the possible positions and angles, using e.g. 16 possibilities for each dimension, the state of the molecule can be described with 24 bits of information, for instance

    (4.5 Å,5.0 Å,9.0 Å,120^{o}, 100^{o},60^{o})=(1001:1010:1110:0110:0101:0011).

  - The breeding operation is defined such that the binary string is exchanged from some point forward (“crossover”). So if we have two parents

    P1 = (1001:1010:1110:0110:0101:0011)
    P2 = (1001:1010:1110:0100:1011:1110)

    and the exchange position is chosen to be 17, we get the children

    C1 = (1001:1010:1110:0110:0101: 1110)
    C2 = (1001:1010:1110:0100:1011: 0011)

Genetic algorithms

- In this case stage **1.** in the above algorithm simply becomes.

  1. Mating and breeding. Exchange the gene sequence of a parents with another starting from a random position.

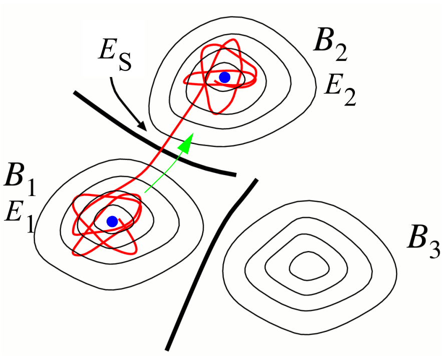
- The mutation operation now becomes simply

  2. Mutation. With a given probability μ exchange the state of a bit (0→1 or 1→0) for all bits in all individuals.

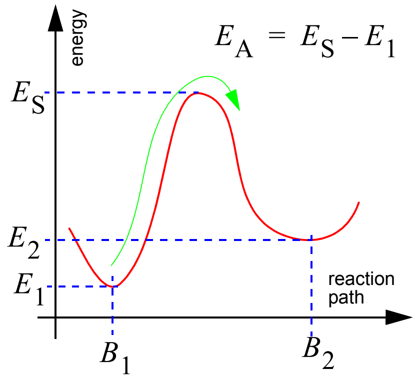
- Because a bit corresponds to a position or rotation angle, this directly changes the state of the individual.
- Otherwise the algorithm is essentially as that of Deaven and Ho.
- Xiao used the algorithm to search for the ground state configurations for simple hydrocarbon molecules such as the benzene dimer. He used a population of 100 and 8 bits to code each position or angle.
- But this approach has the problem that during the mating and mutation the state of the molecule can change quite radically, and the properties of the parents are not transferred to the children. Hence Deaven and Ho say that their method is better for optimizing atomic structure.

- GA has been applied in physics particularly in studying equilibrium structure of small clusters. [See e.g. K. M. Ho *et al.*, *Nature* **392** (1998) 582; D. M. Deaven *et al.*, *Chem. Phys. Lett.* **256** (1996)**;** J. Zhuang, *et al.*, *Phys. Rev. B* **69** (2004).]

Reaction (or minimum energy) path determination



- Thermally activated atomistic processes
  - Need to know the transition rate (events/unit time) for $B_1 \rightarrow B_2$.
  - If the probability for the event is not too low direct MD simulation is possible.
  - For really **rare events** transition state theory (TST) can be used.
    - Rate can be written in form $\nu = \nu_0 e^{-E_A/k_B T}$ → need to know the activation energy $E_A = E_S - E_1$, where E_S is so called saddle point energy.
    - From TST one can also get an estimate for the prefactor ν_0 based on vibrational properties: $\nu_0 = \prod_{i=1}^{N} \nu_i / \prod_{i=1}^{N-1} \nu'_i$, where ν_i, and ν'_i are the vibration frequencies at B_1 and the saddle point, respectively. Note that at the saddle point there is one less frequency compared to the local minimum B_1.
      - Quite often the prefactor is simply set to a typical vibration frequency in the system: $\nu_0 \approx 10^{12} s^{-1}$.



  - Exactly E_A is defined as the maximum energy along the path with lowest energy (minimum energy path; **MEP**) going from B_1 to B_2 (local minima; blue dots).
    - Path here means a line in the $3N$ dimensional configuration space.

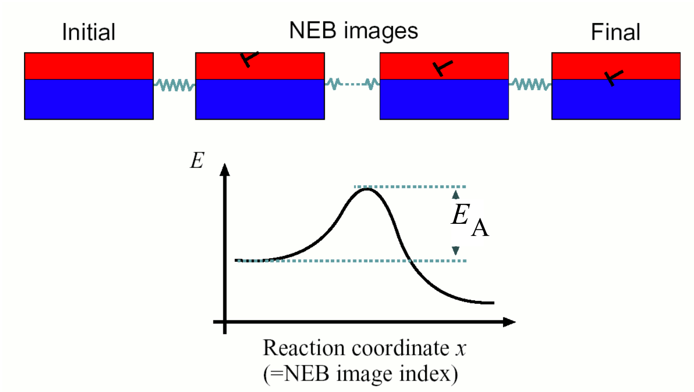
Reaction (or minimum energy) path determination

- There are many methods to do this; one of the most often used in atomistic systems is the Nudged Elastic Band method or NEB. [G. Henkelman, H. Jónsson, *J. Chem. Phys.* 113 (2000) 9901.; G. Henkelman, H. Jónsson, *J. Chem. Phys.* 113 (2000) 9978.]

- In NEB images of the system are created by interpolating the atomic coordinates between the initial and final configurations (that are usually local minima).

- Every image is connected by a spring force to its neighboring images. (End points are fixed.)

- The spring force prevents all images to fall to the nearest local potential energy minimum.



Reaction (or minimum energy) path determination

- The total force on the atoms in image i is calculated as

$$\mathbf{F}_i = \mathbf{F}^{\mathrm{S}}_{i,\parallel} - \nabla V(\mathbf{R}_i)_{\perp} ,$$

$\mathbf{R}_i$ is the $3N$ dimensional vector of atom coordinates in image i.

- The first term is the spring force which acts only in the tangential direction of the image chain:

$$\mathbf{F}^{\mathrm{S}}_{i,\parallel} = k[|\mathbf{R}_{i+1} - \mathbf{R}_i| - |\mathbf{R}_i - \mathbf{R}_{i-1}|]\hat{\tau}_i ,$$

where k is the spring constant and τ_i is the tangent vector of the image chain:

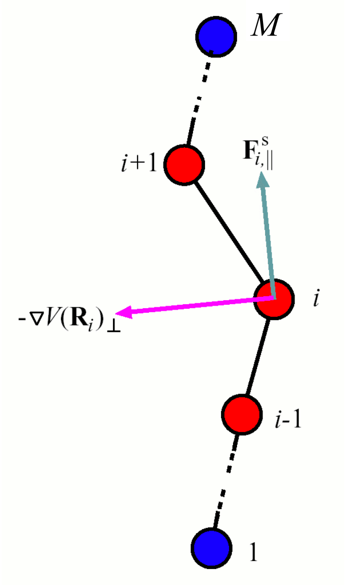
$$\tau_i = \begin{cases} \tau_i^{+} & \text{if } V_{i+1} > V_i > V_{i-1} \\ \tau_i^{-} & \text{if } V_{i+1} < V_i < V_{i-1} \end{cases} , \quad \tau_i^{+} = \mathbf{R}_{i+1} - \mathbf{R}_i, \quad \tau_i^{-} = \mathbf{R}_i - \mathbf{R}_{i-1}$$

- When the middle image is the minimum or maximum of the three the tangent is calculated as

$$\tau_i = \begin{cases} \tau_i^{+}\Delta V_i^{\max} + \tau_i^{-}\Delta V_i^{\min}, & \text{if } V_{i+1} > V_{i-1} \\ \tau_i^{+}\Delta V_i^{\min} + \tau_i^{-}\Delta V_i^{\max}, & \text{if } V_{i+1} < V_{i-1} \end{cases} ,$$

$$\Delta V_i^{\max} = \max(|V_{i+1} - V_i|, |V_{i-1} - V_i|)$$

$$V_i^{\min} = \min(|V_{i+1} - V_i|, |V_{i-1} - V_i$$



Every image has N atoms. Number of images M (including the end points).

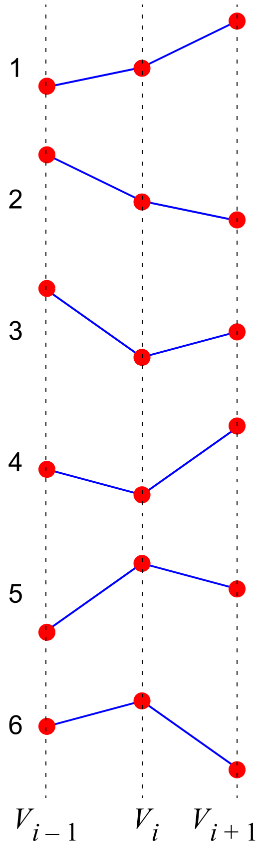
Reaction (or minimum energy) path determination

- The second term is calculated from the potential energy model of the system:

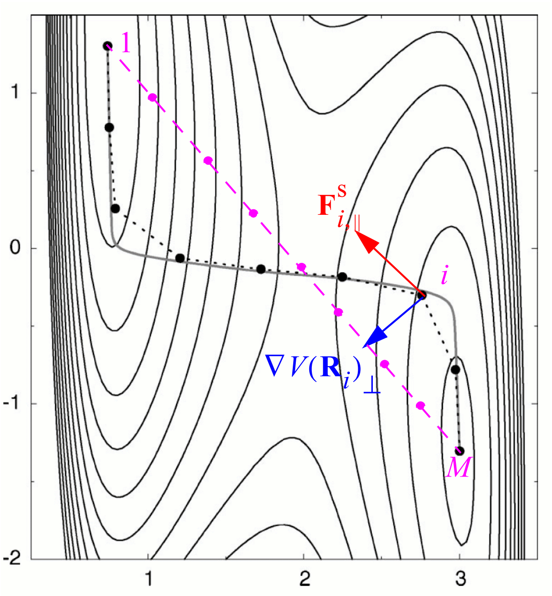
$$\nabla V(\mathbf{R}_i)_{\perp} = \nabla V(\mathbf{R}_i) - \nabla V(\mathbf{R}_i)\hat{\tau}_i \cdot \hat{\tau}_i$$

- When calculating the tangent on has to take into account all the six energy configurations of the three neighbor images shown on the right.

- The spring force tries to keep the images in the chain evenly spaced.
- The potential force is there to find the minimum energy of all images in the direction perpendicular to the image chain (=reaction path).



Reaction (or minimum energy) path determination



Let's illustrate NEB by a simple 2D potential energy surface shown on the left [G. Henkelman, H. Jónsson, *J. Chem. Phys.* **113** (2000) 9978.]

- Solid line: the real MEP
- Dashed line (magenta): initial configuration for NEB (interpolated)
- Dotted line with circles: the path obtained by NEB

Reaction (or minimum energy) path determination

- Running a NEB simulation:
  - Create the end points by optimizing the two configurations by e.g. CG of cooling-MD.
  - Interpolate the images and remove atom overlaps.
  - Find the minimum energy path by optimizing the image system by applying the forces described above.
- Modifying an existing MD code for NEB is not difficult:
  - Input the coordinates of the image chain.
  - When calculating neighbor list skip atom pairs that belong to different images.
  - Add the calculation of tangent τ_i,
    - The inter-image distance is calculated simply as

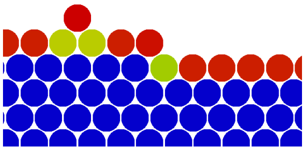
$$\left|\mathbf{R}_i - \mathbf{R}_{i-1}\right|^2 = \sum_{j=1}^{N} [(x_{i,j} - x_{i,j-1})^2 + (y_{i,j} - y_{i,j-1})^2 + (z_{i,j} - z_{i,j-1})^2],$$

    where $\mathbf{r}_{i,j}$ is the position of the jth atom in the ith image.

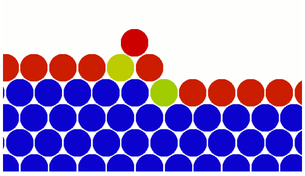
  - Add the calculation of the spring force.
  - Modify the force routine to calculate only the perpendicular component of the force.
  - The only parameter is the spring force constant k. Fortunately, calculation is rather insensitive to its value.

Reaction (or minimum energy) path determination

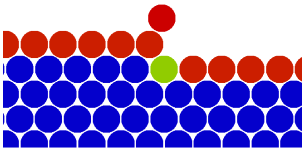
- A simple example: surface diffusion in a 2D Lennard-Jones system



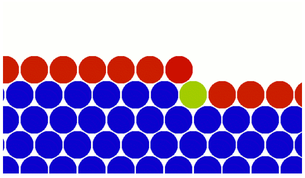
(a)



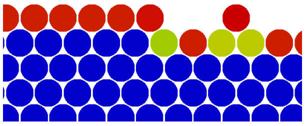
(b)



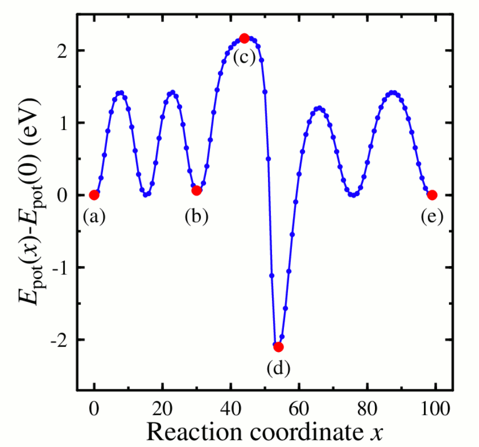
(c)



(d)



(e)



Difficult to jump down from the step: Erlich-Schwoebel barrier → surface growth instabilities.

Molecular dynamics 2015

Exercises 9 (not to any specific chapter): `mdmorse` : applications

1. (10p) Determine the bulk modulus

$$B = -V\frac{dP}{dV}$$

B of your Cu model. Is the excellent agreement you obtain with the experimental value of 1420 kbar surprising?

2. (10p) Test the melting of bulk Cu using the temperature and pressure controls. Simulate a block of Cu at different temperatures, using pressure control to keep the pressure at 0 kbar, and find the temperature at which the cell melts. Try to determine the melting temperature with an uncertainty less than 100 K. It is enough to estimate when the cell melts by visual inspection of the atom positions. How does the value compare with the experimental melting temperature?

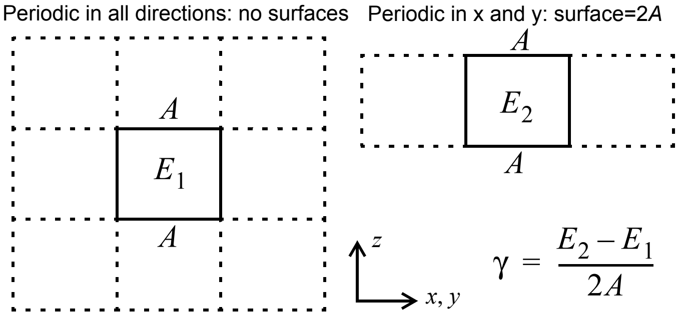
Note that since the initial kinetic energy of atoms is set to twice the temperature, the cell may melt instantaneously (within 1 ps or so) before it has time to equilibrate to a given temperature. You can circumvent this by using `initialT < desiredT` and let the temperature control set the cell to the correct temperature. Report the obtained melting temperature, compare the result to experiment and comment on the difference.

Molecular dynamics 2015

Exercises 10 (not to any specific chapter): `mdmorse` : surface and defect energies

1. (10 p) Surface energies of Cu.

Determine the surface energies γ of our Morse copper at 0 K for the (001) and (111) surfaces[1]. Surface energy can easily be calculated by comparing a simulation with periodic boundary conditions in all directions with one having e.g. z direction open.



Use system sizes of $5 \times 5 \times 5$ unit cells for the (001) surface and $7 \times 4 \times 4$ for the (111) surface. Give the result in units of J/m^2.

Compare the energies you obtained to experimental and *ab initio* results found in article[2]: Q Jiang, H M Lu and M Zhao, *J. Phys.: Condens. Matter* **16** (2004) 521-530.

What happens to the outermost atomic layers? What would happen if atoms only interacted with their nearest neighbors?

Plot the potential energy of atomic layers as a function of z (or distance from the surface). Do the systems seem to be large enough to be used in this kind of calculations? Check your result for (001) surface by doubling the system size[3] and calculating the surface energy for it.

Can you explain the possible difference or equality of the energies of the two surfaces?

2. (5 p) Vacancy formation energy of Cu.

Determine the vacancy formation energy of copper. How does it compare with the cohesion energy? Calculate how large is the effect of relaxation of atoms around the vacancy.

3. (5 p) FCC vs. HCP

a) How large must the pair potential cut-off radius be (in units of nearest-neighbor distance) in order to get differences in potential energy between the FCC and HCP lattices?
b) When only the nearest neighbors are included in energy calculation do the energies of the two lattices differ when the potential energy model is (i) EAM or (ii) a model with explicit angular dependence (i.e. has bond-angle dependence)?

---

[1] To build the (111) system use the program of exercise 1.

[2] The journal is available on-line from University computers at http://www.iop.org/EJ/abstract/0953-8984/16/4/001 .

[3] In which direction(s)? Decide yourself.

Molecular dynamics 2015

Exercise 11 (not to any specific chapter): `mdmorse` : melting temperature by the interface method

1. (14 p) Determine the melting point of Morse Cu by constructing a cell which has both liquid and solid parts, and finding the temperature at which these are more or less in equilibrium. The most accurate way to determine the melting point is to estimate the speed of the movement of the liquid-solid interface as a function of temperature and determine the temperature where it crosses zero. In this case, however, visual inspection is enough.

Use temperature and pressure control the way you think is physically best motivated. When done properly, this is the best possible way to determine the melting point by direct simulation.

Hint: create the liquid and solid part in separate simulations which end at the same temperature close to the expected melting point[1]*, then merge these into a joint simulation cell which you first equilibrate a little while before starting longer simulations.*

Comment on the difference to the result you obtained in exercise 9.2. Why is the answer you obtain here more reliable than the one you obtained previously?

2. (6 p) Assume a Finnis-Sinclair type EAM model of a metal with only nearest neighbor interaction. The energy of atom i is expressed as

$$E_i = \frac{1}{2}\sum_{j \neq i} \phi(r_{ij}) - A\sqrt{n_i}, \quad n_i = \sum_{j \neq i} \rho(r_{ij}).$$

Show that it is possible to parameterize the model such that it gives BCC lattice as the equilibrium structure instead of FCC. *Hint: When only nearest neighbor interaction is included the nearest neighbor distance is the same for all structures, only the coordination varies.*

---

[1] Note that this method should give a better value for T_m than the simple heating simulation of exercise 9.

Molecular dynamics 2015

Exercise 12 (not to any specific chapter): `mdmorse` : application to nanoclusters

Note: This is the last exercise.

1. (15 p) Spontaneous sintering of nanoclusters.

Simulate the spontaneous sintering of nanoclusters by creating two Cu spheres which are 20 Å in diameter. Rotate them by a random angle[1], and place them after that next to each other so that the minimum distance between atoms in the two is 4 Å[2]. After this simulate them for 100 ps at 600 K and cool after that slowly to 0 K. Repeat the whole process starting from picking a new random angle a few times to get a representative idea of what is going on.

Describe the behaviour of the system, and return a series of images which illustrates your description.

(The observed behaviour actually underlies the manufacturing of materials using powder sintering. See e.g H. Zhu, R. Averback, *Phil. Mag. Lett.* **73** (1996) 27).

2. (5 p) Stillinger-Weber potential for Si.

Express the energy of one silicon atom in a diamond lattice in the form given in the lecture notes (chapter 9, page 18).

---

[1] Euler angles; see e.g. http://mathworld.wolfram.com/EulerAngles.html

[2] I.e. less than the potential cut-off.

Repetitia mater studiorum

Atomistic simulation types

- **Molecular dynamics (MD)**

  - Simulates atom motion as a function of real time based on some interaction model

- **Monte Carlo (MC)**

  - Atomistic Monte Carlo: calculate thermodynamic averages by letting particles move randomly according to certain rules.

  - Metropolis algorithm for NVT ensemble
  - Metropolis-based algorithms for NVE, NPT, μVT

  - Energy minimization

- **Conjugate gradient energy minimization**

  - Efficient way to find a local minimum

- **Genetic algorithms for atoms**

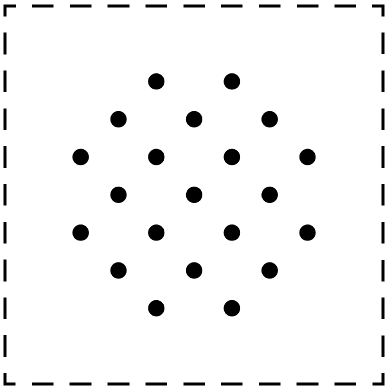
  - Possibly efficient way to find a global minimum

The basic MD algorithm

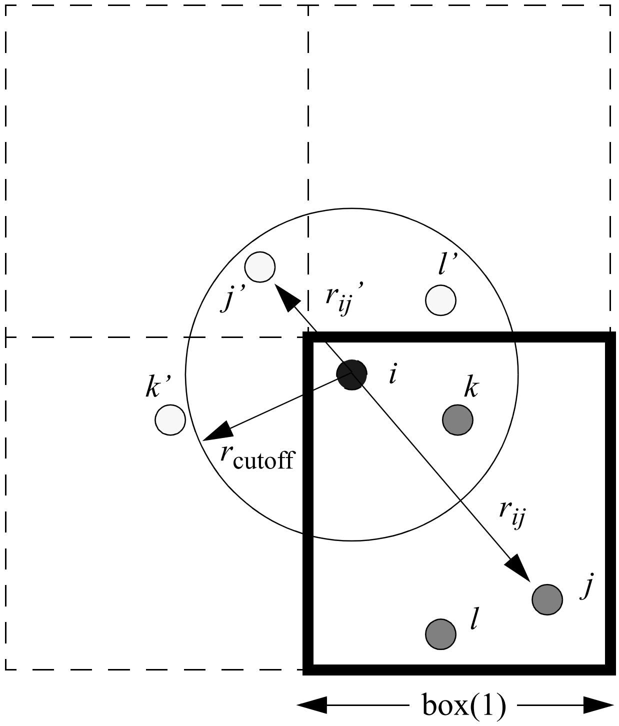
```
0. Set initial conditions $\boldsymbol{r}_i(t_0)$ and $\boldsymbol{v}_i(t_0)$

1. If necessary, calculate new neighbour list

2. Solve equations of motion over a short time step $\Delta t$
   (predictor phase)

       $\boldsymbol{r}_i(t_n) \rightarrow \boldsymbol{r}_i^{pred}(t_{n+1})$
       $\boldsymbol{v}_i(t_n) \rightarrow \boldsymbol{v}_i^{pred}(t_{n+1})$

3. Calculate new forces $\boldsymbol{F}_i(\boldsymbol{r}_i^{pred})$

4. Solve equations of motion over a short time step $\Delta t$
   (corrector phase)

       $\boldsymbol{r}_i^{pred}(t_{n+1}) \rightarrow \boldsymbol{r}_i(t_{n+1})$
       $\boldsymbol{v}_i^{pred}(t_{n+1}) \rightarrow \boldsymbol{v}_i(t_{n+1})$

5. Do temperature or pressure scaling, if appropriate

6. Calculate desired physical quantities

7. Set $t = t + \Delta t$, $n = n + 1$

8. If $t < t_{\max}$, return to phase 1.

9. Calculate final results and end simulation
```

Most common boundary conditions in MD

- Free boundaries: simulate matter in empty space



- Periodic boundaries: describes a continuous medium



  - Because here $r_{ij} > r_{ij}'$, the vector r_{ij}' is used for the distance between atoms *i* and *j* (minimum image convention)

```
if (periodic(1)) then
    dx = x(j) - x(i)
    if (dx  >  box(1)/2.0)  dx=dx-box(1)
    if (dx <= -box(1)/2.0)  dx=dx+box(1)
endif
```

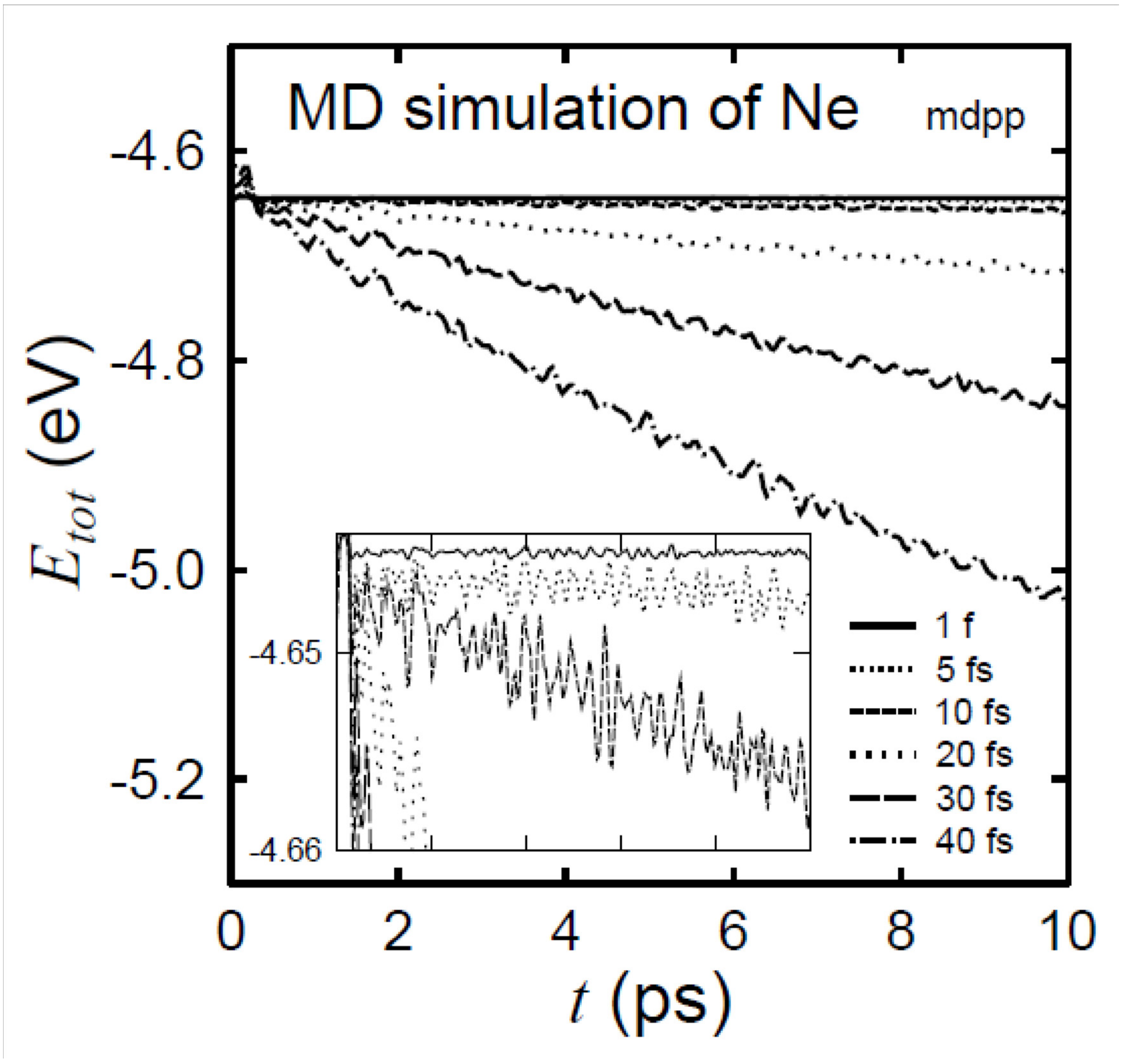
Choice of time step

- In choosing the time step one could rule of thumb is that an atom should not move farther than ~ 1/20 of the nearest-neighbour distance during one time step

- In practice for atoms with Z > 10 or so $\Delta t \sim 0.05 \times 10.18 \sqrt{m\ (\mathrm{u})}\ \mathrm{fs}$ has been found to work well for most materials in classical simulations with the Gear V - algorithm.
  - For very hard materials (Pt, W) slightly smaller time steps may be needed

- The choice of time step should still be checked by checking the conservation of energy (in NVE) **for every new type of system or interaction model.**

- If Δt is too large, energy is not conserved:



Construction of a neighbour list

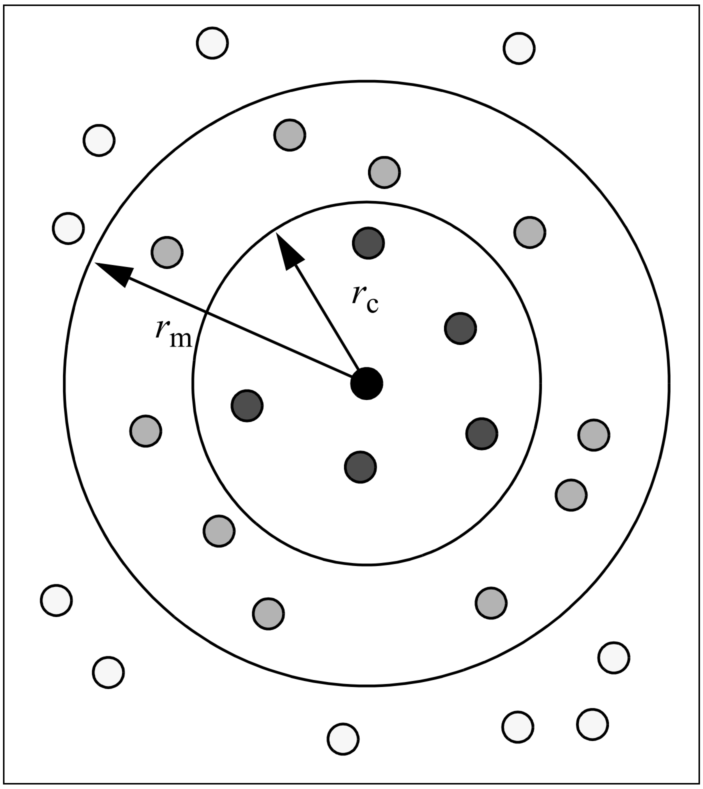
- To save time in classical MD, and often CG and MC as well, it is worth constructing a neighbour list. If there are more than ~ 1000 atoms, it is worth constructing it with a linkcell method.

- **Verlet neighbour list**

  - r_c is the potential cutoff radius

  - Construct a list which contains the atom indices for all neighbours within $r_m > r_c$.

  - The list should be updated as soon as two atoms may have moved further than $r_m - r_c$



- **Cellular method**

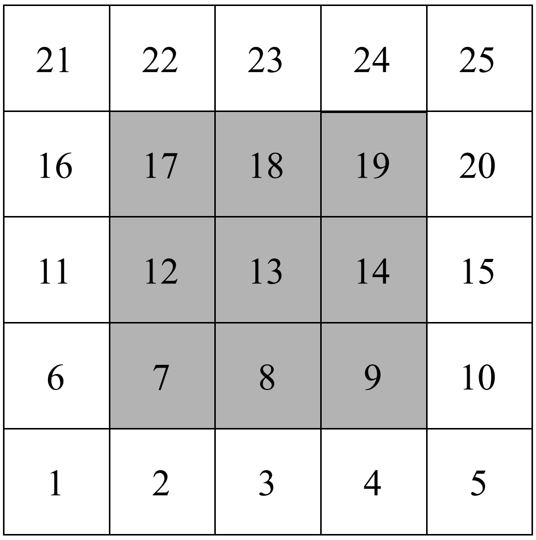
  - Divide the MD simulation cell into $M \times M \times M$ subcells

  - Neighbours for an atom in cell 13 is looked for only in the darker subcells.

  The size of the subcells l is chosen such that

$$l = \frac{L}{M} > r_m$$

  where L = the size of the whole MD cell.



21	22	23	24	25
16	17	18	19	20
11	12	13	14	15
6	7	8	9	10
1	2	3	4	5

Solving the MD equations of motion

- The basic idea of MD is to solve the motion of N atoms by numerical integration over a short time step Δt

  - The basic idea is:

$$\begin{aligned} a(t) &= \nabla V(r(t)) \\ r(t+\Delta t) &= r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 \\ v(t+\Delta t) &= a(t)\Delta t \end{aligned}$$

  but these equations are very inaccurate. A good general algorithm is velocity Verlet

$$\begin{aligned} \mathbf{r}(t+\delta t) &= \mathbf{r}(t) + \delta t\mathbf{v}(t) + \frac{1}{2}\Delta t^2\mathbf{a}(t) \\ \mathbf{v}(t+\delta t) &= \mathbf{v}(t) + \frac{1}{2}\delta t[\mathbf{a}(t) + \mathbf{a}(t+\delta t)] \end{aligned}$$

- A highly accurate algorithm for small time steps is 5th order Gear:

Denote $\mathbf{r}_i = \dfrac{\mathbf{r}^{(i)}(\delta t)^i}{i!}$

The the **predictor** is:

$$\begin{bmatrix} \mathbf{r}_0^{\mathrm{P}}(t+\delta t) \\ \mathbf{r}_1^{\mathrm{P}}(t+\delta t) \\ \mathbf{r}_2^{\mathrm{P}}(t+\delta t) \\ \mathbf{r}_3^{\mathrm{P}}(t+\delta t) \\ \mathbf{r}_4^{\mathrm{P}}(t+\delta t) \\ \mathbf{r}_5^{\mathrm{P}}(t+\delta t) \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 1 & 2 & 3 & 4 & 5 \\ 0 & 0 & 1 & 3 & 6 & 10 \\ 0 & 0 & 0 & 1 & 4 & 10 \\ 0 & 0 & 0 & 0 & 1 & 5 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{r}_0(t) \\ \mathbf{r}_1(t) \\ \mathbf{r}_2(t) \\ \mathbf{r}_3(t) \\ \mathbf{r}_4(t) \\ \mathbf{r}_5(t) \end{bmatrix}$$

and the **corrector**:

error term $\delta\mathbf{R}_2 = \mathbf{a} - \mathbf{a}^{\mathrm{p}}$

correction: $\mathbf{r}_n = \mathbf{r}_n^{\mathrm{P}} + \alpha\delta\mathbf{R}_2$ where $\alpha = \begin{bmatrix} 3/16 \\ 251/360 \\ 1 \\ 11/18 \\ 1/6 \\ 1/60 \end{bmatrix}$

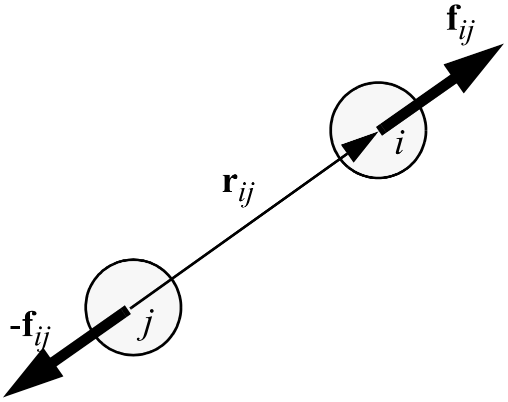
Force calculations

- In a classical model the potential between atoms can be written as:

$$V = \sum_{i} V_1(\boldsymbol{r}_i) + \sum_{i,j} V_2(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_{i,j,k} V_3(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k) + \dots$$

  where V_2 is a pair potential which only depends on the distance between atoms r_{ij} and V_3 is a three-body potential which may have an angular dependence, $V_3 = V_3\,(r_{ij}\,, r_{ik}\,, \theta_{\mathrm{ijk}})$

- **Force calculation for a pair potential:**



  Say we have a pair potential $V(r_{ij})$. The force acting from atom i on atom j is

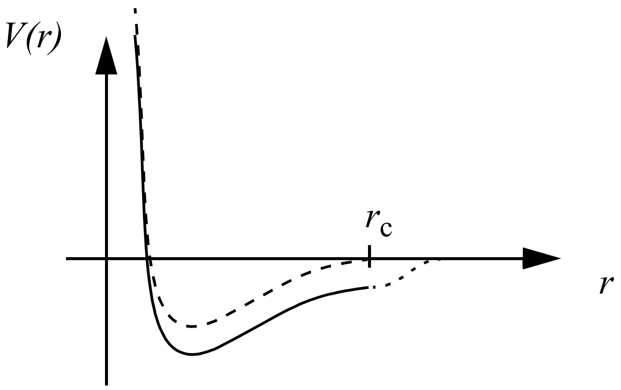
$$\mathbf{f}_{ij} = -\nabla_{\mathbf{r}_i} V(r_{ij}) = -\nabla_{\mathbf{r}_{ij}} V(r_{ij})$$

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$$

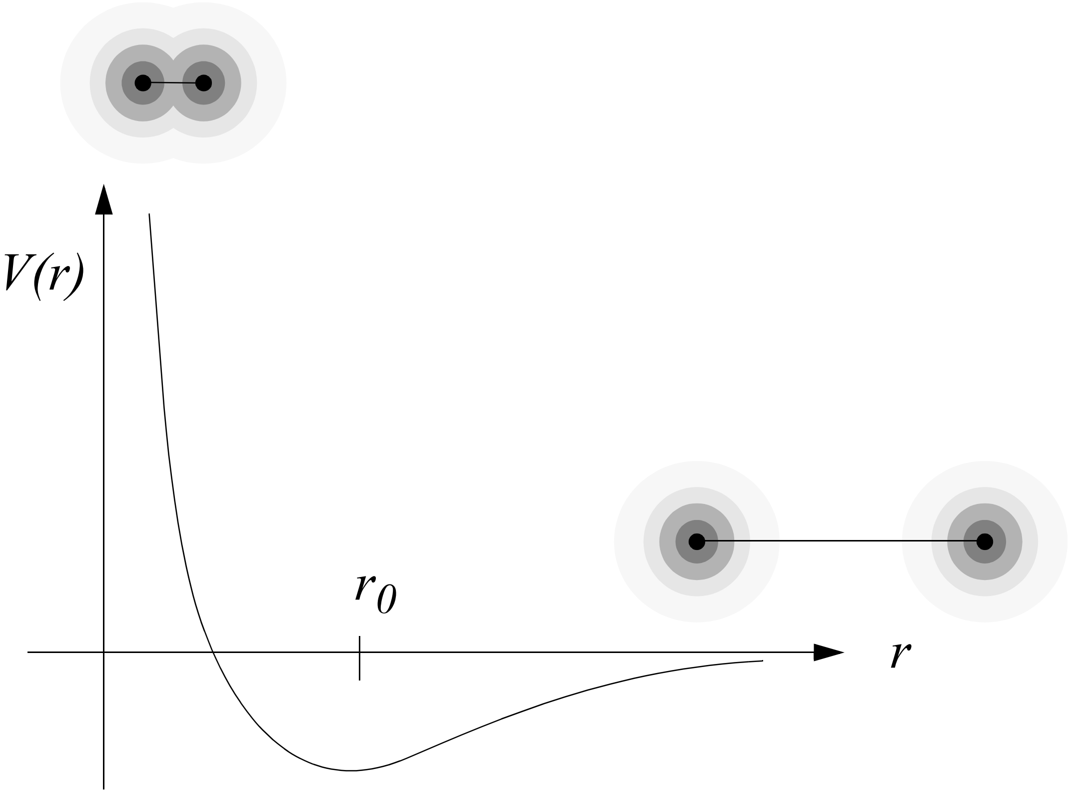
$$\mathbf{f}_{ij} = -\left[\frac{dV}{dr}\right]_{r = r_{ij}} \times \frac{\mathbf{r}_{ij}}{r_{ij}}$$

- The potentials usually have a cut-off radius r_c. Atoms separated by a distance $> r_c$ do not interact. Usually $r_c \approx$ a few Å .

  In a good potential both V and all its derivatives go continuously to zero when $r = r_c$(dashed lines in figure).



General form of the interaction



- At small separations there is a repulsive force due to the overlapping of electron shells (Pauli rule and electron-electron Coulomb repulsion) and at very small distances due to the Coulomb repulsion between the charges of the nuclei.

- At larger distances there may be an attractive interaction, which may have several different causes: van der Waals, Coulomb, metallic bonding, covalent bonding, hydrogen bonding

- Potential minimum is at a distance r_0.

Fitting of potential parameters.

- Important parameters to which a potential can be fit:

Physical property	**Atom-level property**
Crystal structure	Balance of atomic forces.
Cohesive energy	Potential energy at the equilibrium atom positions
Elastic constants $c_{\rho\sigma}$	Long-wavelength acoustic vibrations Elastic distortions of unit cell.
Equation of state P(V)	Compression or expansion of material
Neutron scattering	Phonon $\omega(\mathbf{k})$ in the Brillouin zone.
Dielectric constant ε_∞	Electronic polarizability
Dielectric constant ε_0	Polarization of electrons and lattice; long-wavelength optical vibration modes;
Infrared absorption	Long-wavelength vibrations with a dipole moment.
Raman scattering	Long-wavelength vibrations which change the polarizability.

- Out of these, the four first ones are usually the most important in solids.
- In addition, it is also possible to fit potentials to or even derive potentials from data obtained from (hopefully) realistic quantum mechanical calculations.

Pair potentials

- **Taylor expansions**

$$V(r) = K_2(r-r_0)^2 + K_3(r-r_0)^3 + K_4(r-r_0)^4$$

- No physical motivation whatsoever, but can work close to equilibrium separation r_0 since any smooth function can be approximated with a Taylor series.

- **Lennard-Jones (LJ)**

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

- The attractive $1/r^6$ - term can be derived by considering the induced dipole-dipole interaction of two electrically neutral spheres, or for quantum mechanical oscillators. It is also known as a Van der Waals or London interaction.

- The LJ potential describes well at least interactions between noble gases or dipole-dipole interactions between molecules.

- **Morse potential**

$$V(r) = De^{-2\alpha(r-r_0)} - 2De^{-\alpha(r-r_0)}$$

- Can describe fairly realistically chemical bonds and the breaking of chemical bonds.

- Parameters available e.g. for most metals in the solid state.

Potentials for ionic compounds

- The interactions between ions can of course be described with Coulomb interactions. To get a sensible short-range interaction one has to add a separate short-range potential.

- This gives a potential of the form

$$V(r_{ij}) = V_{\mathrm{SR}}(r_{ij}) + \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{ij}} \; ; \; z_i = \text{ionic charges}$$

  The short.-range potential V_{SR} can be e.g.

$$V_{\mathrm{SR}}(r) = A e^{-r/\rho} - \frac{C}{r^6}$$

- In modelling ionic compounds, the sum over neighbours does not converge automatically. Then it is best to use some special algorithms to form the sum efficiently. For small numbers of atoms the Ewald sum or Ewald mesh methods are probably fastest, for large number of atoms there are the truly O(N) scaling fast multipole algorithms (FMA’s).

Metal interaction models

- Metals can be described well by considering the atoms as positively charges ions which are embedded into a surrounding free electron gas. The density of the electron gas depends on the local environment.

- These models can be derived from effective medium theory (EMT).

- Most models used now are given in the Embedded Atom Method (EAM) functional form.

- In EAM the total energy is given as

$$E_{\text{tot}} = \sum_{i} F_i(\rho_i) + \frac{1}{2}\sum_{ii} V_{ij}(r_{ij})$$

  where

$$\rho_i = \sum_{i \neq i} \rho_j^{\mathrm{a}}(r_{ij}) \quad \text{is the electron density at atom } i \ ,$$

  $\rho_j^{\mathrm{a}}(r)$ is the electron density distribution of atom j,

  F_i is the embedding function and

  V_{ij} is a repulsive potential

- In Finnis-Sinclair and Rosato models $F_i(x) = \sqrt{x}$

- In glue models the functional form is the same as in EAM, but V_{ij} is not purely repulsive.

- EAM-models can describe quite well the basic mechanical and thermodynamic properties of most pure FCC metals, fairly well most BCC metals and fairly well those HCP metals for which

$$C_{13} - C_{44} > 0 \text{ and } 1/2\,(3\,C_{12} - C_{11}) > C_{13} - C_{44}$$

- Also many metal alloys can be described well with EAM models.

Semiconductor and carbon potentials

- For **Si** at least three good potentials exist:
- **Stillinger-Weber (SW)**
  - The potential has a pair term V_2 and a three-body term V_3 . The three-body term has an explicit minimum when the angles between the bonds correspond to ideal sp^3 bond hydridization, i.e. for the diamond crystal structure.
  - Describes well melting and surprisingly many other properties as well.
- **EDIP**
  - An SW-like formulation which is also environment dependent. Probably the best potential for bulk Si now.
- **Tersoff**
  - The form of the potential is

$$V_{ij} = f_C(r_{ij})[a_{ij}f_R(r_{ij}) + b_{ij}f_A(r_{ij})]$$

    where f_R is the repulsive and f_A the attractive pair potential part. b_{ij} modifies the strength of the pair interaction depending on the local environment and angles between bonds.
  - The Tersoff potential can also describe reasonably non-tetrahedral bonding configurations.
  - Two parametrizations, out of which Tersoff C or III best in non-equilibrium applications.
- **Ge**:
  - Two SW parametrizations, but terrible description of melting.
  - Also a Tersoff-parametrization, but also with bad description of melting.

- For **C** in the bulk states (graphite and diamond) as well as fullerenes several parametrizations exist.

    - **Tersoff** works fairly well in all of these.

    - The **Brenner** potential (based on the Tersoff formalism) also describes conjugated bonds and small hydrocarbon molecules well. But it is clearly slower than Tersoff.

Molecular interaction models (classical force fields)

- The total energy of a molecule can be written as

$$E = E_{bond} + E_{angle} + E_{torsion} + E_{oop} + E_{cross} + E_{nonbond}$$

E_{bond} describes the energy change related to a change of bond length, and thus is simply a pair potential V_2

E_{angle} describes the energy change associated with a change in the bond angle, i.e. is a three-body potential V_3

$E_{torsion}$ describes the torsion, i.e. energy associated with the rotation between two parts of a molecule relative to each other.

E_{oop} describes "out-of-plane" interactions, i.e. the energy change when one part of a molecule is out of the plane with another

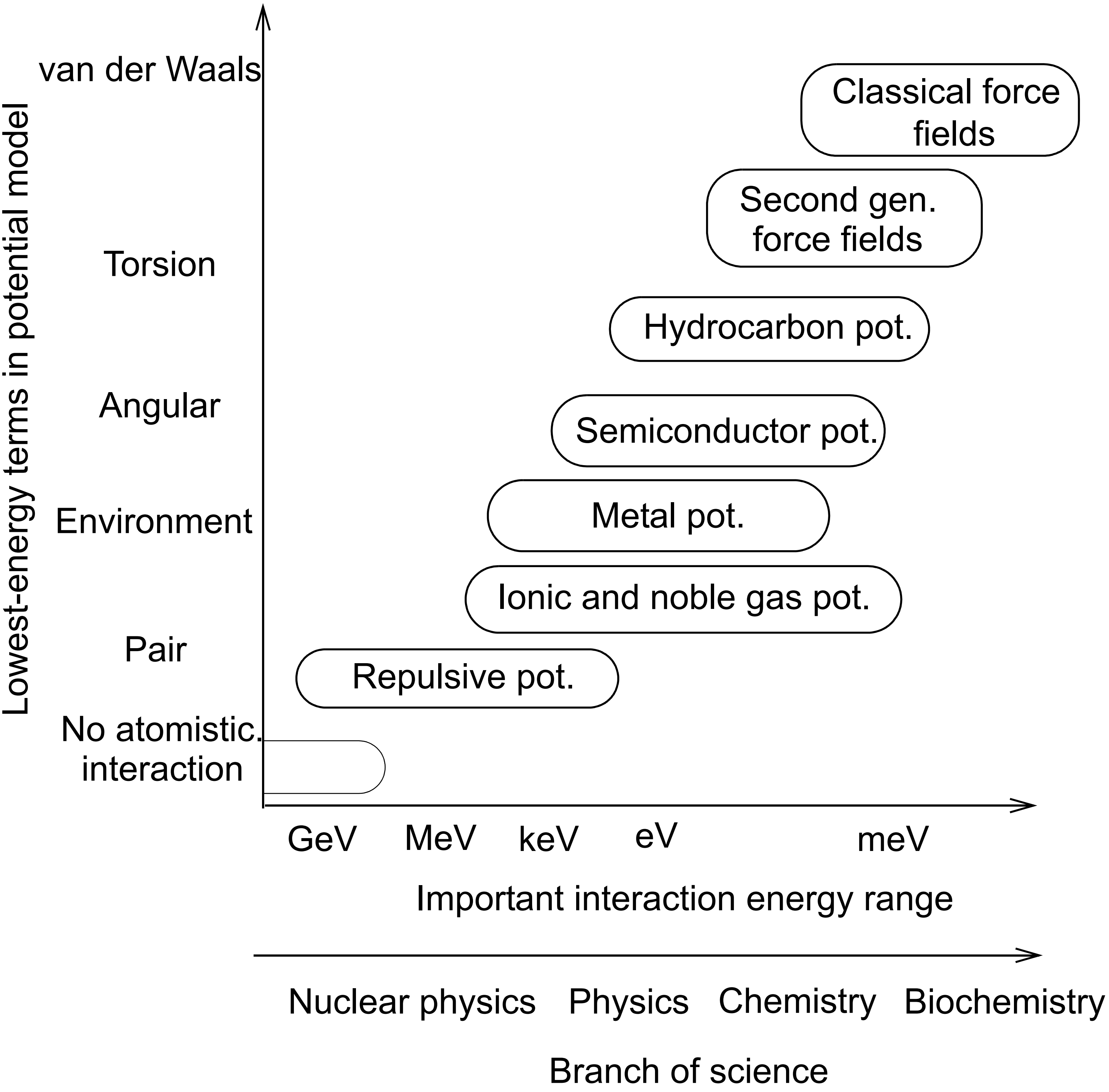
$\mathrm{E}_{\mathrm{cross}}$ - are cross terms between the other interaction terms.

$E_{nonbond}$ describes interaction energies which are not associated with covalent bonding. Can be ionic, hydrogen bonding or van der Waals terms.

- An example of a real molecular potential:

$$\begin{aligned}
V(R) = {} & \overbrace{\sum_b D_b \left[1 - \exp(-a(b-b_0))\right]^2}^{E_{bond}} + \overbrace{\sum_\theta H_\theta (\theta-\theta_0)^2}^{E_{angle}} + \overbrace{\sum_\phi H_\phi \left[1 + s\cos(n\phi)\right]}^{E_{torsion}} \\
& \underbrace{+ \sum_\chi H_\chi \chi^2}_{E_{oop}} + \underbrace{\begin{aligned} & \sum_b \sum_{b'} F_{bb'} (b-b_0)(b'-b'_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'} (\theta-\theta_0)(\theta'-\theta'_0) \\ & + \sum_b \sum_\theta F_{b\theta} (b-b_0)(\theta-\theta_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'\phi} (\theta-\theta_0)(\theta'-\theta'_0)\cos\phi \\ & + \sum_\chi \sum_{\chi'} F_{\chi\chi'} \chi\chi' \end{aligned}}_{E_{cross}} \\
& + \sum_i \sum_{j>i} \left[\underbrace{\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}}}_{E_{vdW}} + \underbrace{\frac{q_i q_j}{r_{ij}}}_{E_{Coulomb}} \right]
\end{aligned}$$

Overview of classical interatomic force models
as a function of the branch of science



Quantum mechanical models

- In the Schrödinger equation (7.1) the computationally most complicated part is the electron-electron interaction

  $$V_{ee} = \sum_i \sum_j \frac{e^2}{|\mathbf{r}_{ij}|^2}$$

  which is a sum from all electrons to all electrons. This can not be directly evaluated except for the very smallest system.

- The basic solution in both Hartree-Fock (HF) and density functional theory (DFT) is to create some sort of an “average” electron density, with which every electron interacts separately.
-
- HF- and DFT methods are much better motivated than classical models. Unfortunately they are also very much slower. The limit for common HF methods is maybe 50 atoms, and for DFT calculations maybe 200 atoms on ordinary computers.

- In the DFT method the so called **LDA-approximation** is often applied. In this approximation the electron exchange and correlation energy is calculated for small density elements as if the density were constant in this element.

- In the so called **Plane wave** methods the outermost electron wave function are written as the sum of periodic plane waves.

  $$\psi = \sum_l f_l(\boldsymbol{K}) e^{-i\boldsymbol{K} \cdot \boldsymbol{r}}$$

  These methods are well suited for describing periodic systems, i.e. bulk matter.

Tight binding-methods

- Tight-binding (TB) models are so called minimal quantum mechanical models. They are usually semi-empirical, and the quality of the results varies a lot. In the TB method the total electron energy *E* is

$$E = \sum_{i=1}^{N} \varepsilon_i + \frac{1}{2}\sum_i \sum_j U(r_{ij})$$

where U is a repulsive pair potential acting between atoms, and the ε_i are the eigenvalues of some Schrödinger-like equation

$$\hat{H}\psi_i(r) = \left[-\frac{1}{2}\nabla^2 + V(r)\right]\psi_i(r) = \varepsilon_i(r)$$

The TB-Schrödinger is solved in some set of basis functions $\{\phi_\alpha\}$ which only includes the outermost valence electrons.

Efficiency of different force models.

- Crucial in selecting a model is to find one which is efficient enough to do what you want, yet realistic enough to describe the essential physics in your problem correctly. Below is a summary of the situation today:

Model	Type	Scaling	N_{max}[1]
HF (Hartee-Fock)	quantum mechanical, ab initio	$O(N^{4-8})$	50
DFT (density functional theory	quantum mechanical	$O(N^3)$	200
TB (Tight-binding)	quantum mechanical (often semiempirical)	$O(N^3)$/ $O(N)$	1000 10000
Many-body potential	classical, semiempirical	$O(N)$	10^7
Pair potential	classical, semiempirical	$O(N)$	10^7

[1] This is a rough estimate of how many atoms can be simulated in a reasonable time, i.e. a week or so, on a single-processor machine.

- Hence, typical application areas:

  - The number of atoms of quantum mechanical models (HF and DFT) ~ 100 is enough to simulate e.g. small molecules, bulk properties of common phases, and point defect properties. HF and DFT can give information on the electronic structure of the material.

  - Tight-binding is a “minimal quantum mechanical” model which works well in a few materials (e.g. C, Si, Ge) but is problematic in many others. The O(N) tight-bonding works only in a very limited set of applications, such as a-Si.

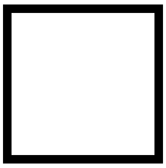
  - With classical models it is nowadays possible to simulate even very large systems, such as large protein molecules, 2- and 3-dimensional defects, whole nanoclusters, surface growth, grain boundaries etc. etc. The main limitation is that they do not usually directly give information on the electronic properties of the material.

MD Simulation of different ensembles

- Ensembles are denoted by the thermodynamical quantities which are conserved in them. N=number of atoms, V=volume, E=energy, P=pressure, T=temperature

- **microcanonical: NVE** (isolated)

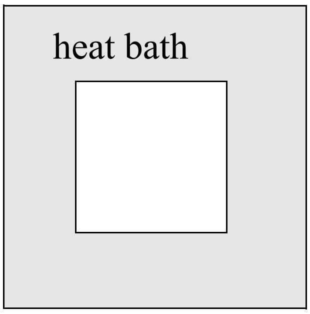
  - Algorithm: direct solution of equations of motion



- **canonical: NVT** (closed)

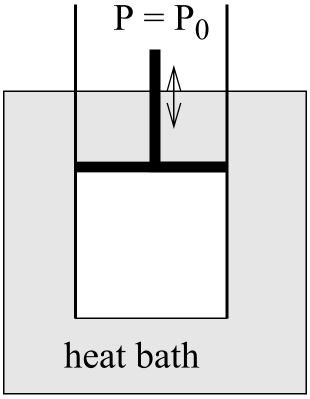
  - Algorithm: Berendsen “quick and dirty”, not true NVT ensemble.

    True NVT: Nosé-Hoover, or N-H chain or massive N-H chain.



- **isothermal-isobaric: NPT**

  - Heat control as above, pressure control:
  - Berendsen “quick and dirty”, not true NPT
  - Andersén-pressure control if pressure is hydrostatic (e.g. in liquid)
  - Parrinello-Rahman-pressure control for non-hydrostatic stress (e.g. in crystals)



- Berendsen temperature scaling: scale velocities every time step with

  $\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T}\left(\frac{T_0}{T} - 1\right)}$, where T_0 is the desired T.

- Berendsen pressure scaling: scale atom position and the box size every time step with a factor $\mu = \sqrt[3]{1 - \frac{\beta \Delta t}{\tau_P}(P_0 - P)}$, where P_0 is the desired pressure and $\beta = 1/B$

Energy minimization techniques.

- There are at least 4 ways to approach minimizing the energy of an atom system:

1. Monte Carlo-simulation:

- May be good in looking for a global minimum, if only one very strong minimum exists
- Not very efficient in looking for a local minimum

2. MD-simulation: Do an MD simulation letting T -> 0 K.

- Sometimes quite efficient in finding a local minimum, especially by using the trick of setting $\boldsymbol{v}_i = 0$ if $\boldsymbol{v}_i \bullet \boldsymbol{F}_i = 0$.
- May sometimes be good for looking for a global minimum, but tends to get stuck if a high barrier exists.

3. Conjugate gradients (CG)

- Very efficient way to reach the closest local minimum

- - Works by movement down a potential well, but so that the new direction is *conjugated* with respect to the previous to prevent zig-zag motion.

- The new direction $\boldsymbol{x}_{i+1}$ into which one moves is evaluated as

$\boldsymbol{x}_i = \nabla V(\boldsymbol{r}_{i+1})$;

$\boldsymbol{g}_{i+1} = -\boldsymbol{x}_i$; $\boldsymbol{h}_{i+1} = \boldsymbol{g}_{i+1} + \gamma \boldsymbol{h}_i$ and $\boldsymbol{x}_{i+1} = \boldsymbol{h}_{i+1}$

where $\gamma = ((\boldsymbol{x}_i + \boldsymbol{g}_i) \cdot \boldsymbol{x}_i)/(\boldsymbol{g}_i \cdot \boldsymbol{g}_i)$

- In the CG method for atoms it is often even more efficient to use an adaptive step length instead of line minimization.

4. Genetic algorithms

- An efficient way to look for a global minimum in dilute systems
- Not much tested in atom systems yet.

- The basic idea comes from evolution theory; a population is formed, this is allowed to breed, and the best-adjusted species are allowed to stay alive.

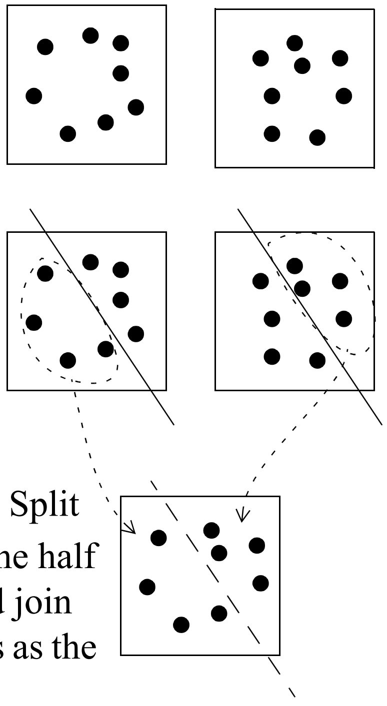
Deaven and Ho genetic algorithm for atoms, slightly simplified.

0. Start. Create random initial positions for p structures, each with exactly N atoms.

1. Mating and breeding. Select two well-adjusted parents for breeding. This is done by selecting a given parent i with state $\boldsymbol{G}_i$ with the probability

$$P(\boldsymbol{G}) \propto e^{-E(\boldsymbol{G})/T_m}$$

where the mating 'temperature' T_m is selected as the range of energies among the whole population $\{\boldsymbol{G}_i\}$. Split the two parent structures along the same line. Take one half of one parent, and another half of another parent, and join them together. Make sure the child has as many atoms as the parents.



2. Mutation. With a probability $\mu \geq 0$ perform a mutation on the child.

3. Minimize the energy of the child to the closest local minimum. This is done by CG or MD.

4. Natural selection. If the child has lower energy than any of the parents, allow it to stay alive. Then check that its energy does not match the energy of any parent within an energy range δE. If this is true, include it in the population, and kill the least-well adapted parent.

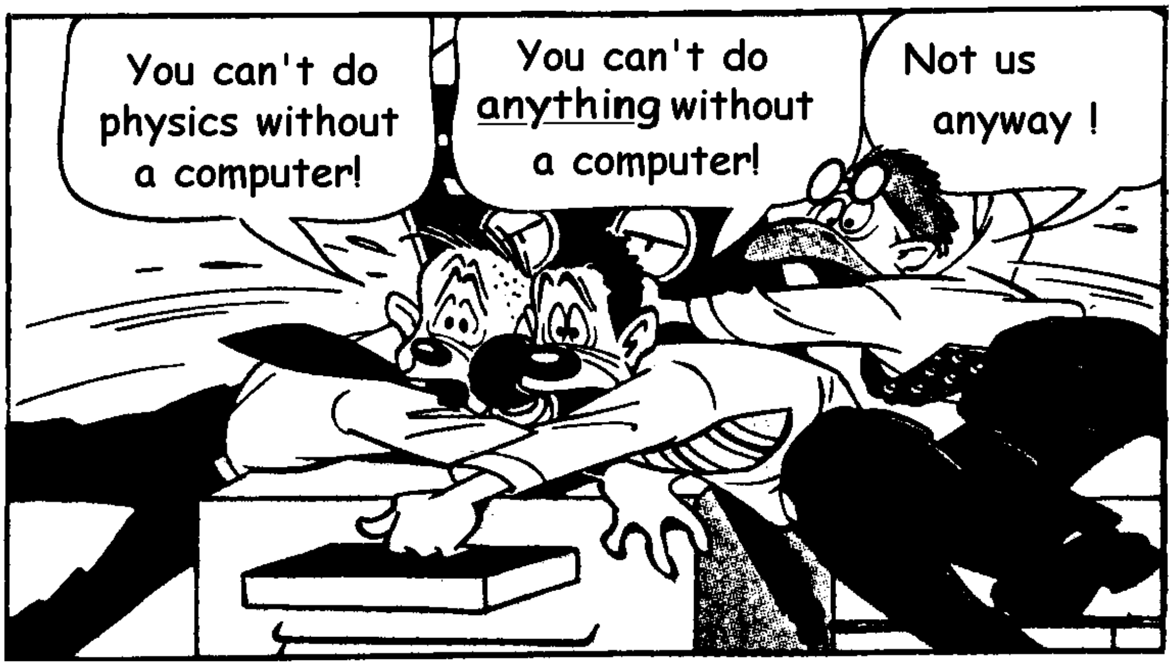
5. If convergence has not been reached, return to stage **1.**

Comparison to experiments

- Atomistic data can be seldom compared directly to experiments. Most often some intermediate analysis code is needed to enable a sensible comparison.

- A special caveat should be taken with STM and TEM: in both methods, what may look like an atom may in fact be something entirely different.

Final comment of the course



Hope you have enjoyed the materials
and have happy simulation-times !