

## **Lab 1: Handout**

### **GULP: an Empirical energy code**

We will be using the GULP code as our energy code. GULP is a program for performing a variety of types of simulations on 3D periodic solids, gas phase clusters, and defects in a bulk material. Further information (including online manual) can be found at the GULP website.

<http://gulp.curtin.edu.au>

GULP is free for academics

There are many other potentials codes one can use. These include:

Cerius2 (commercial). Includes Lennard Jones, Embedded atom, visualization, and much more.

Steve Plimpton's codes (includes Lennard-Jones and Embedded Atom method )

VEGA (various force fields for molecular systems)

<http://users.unimi.it/~ddl/vega/index.htm>

This is a tutorial on how to get **energies** and **lattice constants** using GULP. This will walk you through problem 1a of the homework. This will also show you parts of problem 2.

### Problem 1

Read over problem 1 of the homework.

To view the gulpl1a.in file type

```
hpcbeo2$ less gulpl1a.in
```

You can scroll through the file by typing space (to go forward), b (to go backwards) or q (to quit). The file gulpl1a.in contains a face-centered cubic structure, which has 4 atoms per unit cell.

The file will look something like this:

```

1      opti dist comp comp
2      cell
3      3.0000000      3.0000000      3.0000000      90 90 90
4      fractional
5      Au      0.0000000      0.0000000      0.0000000
6      Au      0.0000000      0.5000000      0.5000000
7      Au      0.5000000      0.0000000      0.5000000
8      Au      0.5000000      0.5000000      0.0000000
9      lennard 12 6
10     Au core Au core 214180.2000      625.482 40.000 0 0
```

Line numbers are added for reference.

*Line 1:*

“**opti**” means to optimize the structure (relax). The “**opti**” flag will calculate the energy of a structure, then change the structure (depending on resulting forces and stresses) and recalculate the energy of the structure. This is repeated until equilibrium is reached. **opti** can be replaced by “**single**” which means to do a single-point calculation. That is, calculate the energy of the structure, but don’t relax.

You will not change the other options, but here is what they mean. **dist** and **comp** give comparisons of lattice constants and neighbor distances before and after relaxation. **comp** means a constant pressure simulation

*Line 2,3:*

**cell** is a keyword that tells the program that you will be entering the cell in terms of a, b, c, alpha, beta, gamma (as opposed to Cartesian lattice vectors). Don't forget to type the numbers on a new line after **cell**. In this case, we have input a=b=c=3.0 and  $\alpha=\beta=\gamma=90$  as a starting configuration. All units are Angstroms.

*Lines 4-8*

**fractional** is a keyword that tells the program you will be entering the atoms in fractional coordinates. Don't forget to type the actual numbers on a new line after **fractional**.

The format is

(atom name)	(x pos)	(y pos)	(z pos)
Au	0.5000000	0.5000000	0.0000000
etc...			

In this case, we have input the FCC gold structure.

*Lines 9-10*

Line 9 specifies we will be using the Lennard-Jones potential with the 12-6 exponents (don't forget to type the actual numbers on a new line).

That is the potential form is:

$$U(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$$

The format of the Lennard-Jones line is:

(type 1)	(type 2)	(A)	(B)	(potential start)	(potential cutoff)
Au core	Au core	214180.2	625.482	0.000	40.000

The last two '0's are flags, and you can ignore them.

Don't worry about the words "core", they are just labels. This is a potential between two Au atoms.

To run the program type

```
hpcbeo2$ gulp<(input file)>(output file)
```

In this case,

```
hpcbeo2$ gulp<gulpla.in>gulpla.out
```

Use “less” to read the output file (less gulpla.out). Scroll through the file by typing space to go forward or ‘b’ to go backwards.

Look for something that says

```
Final energy = (number here)
```

Or else the LAST occurrence of

```
Total lattice energy = (number here)
```

There may be two occurrences of “Total lattice energy =” - there will be two if you have set “**opti**” in the input, one if you have set “**single**”

This will give you your energy.

To find the lattice constants after relaxation, look for something near the end of the file that looks like:

```
Final cell parameters and derivatives :
```

```
-----
a (number here) Angstrom dE/de1 (xx) -0.0007 eV/strain
b (number here) Angstrom dE/de2 (yy) -0.0005 eV/strain
c (number here) Angstrom dE/de3 (zz) -0.0005 eV/strain
alpha 90.000000 Degrees dE/de4 (yz) 0.0000 eV/strain
beta 90.000000 Degrees dE/de5 (xz) 0.0000 eV/strain
gamma 90.000000 Degrees dE/de6 (xy) 0.0000 eV/strain
```

Record the value for  $a_0$  (remember  $a_0=a=b=c$  for a cubic system).

Don’t worry if the “strain” values are different in your calculation and this example.

Problem 1b.

The procedure is the same. However, instead of using “gulpla.in” you will be using “gulp1b.in”. Make sure to copy the gulp1b.in file into your directory.

## Problem 2.

Read over problem 2 on the homework.

You will need the `gulp.wrap.cu.lj` and `gulp.wrap.cu.eam` files. For example

To build the supercell, which you will need to calculate vacancy formation energies and surface energies, you will use the program *buildcell*

### The way this program works is this:

*buildcell* will read a file `gulp.wrap`

It will build the cell in cubic directions, according to dimensions that you specify.

It is specific to fcc structures.

The format of `gulp.wrap` is:

```
1 lattice constant and atomic symbol
2...N (anything you want to appear in the gulp.in file
besides fractional coordinates)
```

For example:

```
4.0800 Au
opti dist comp conp
lennard 12 6
Au core Au core 214180.2000 625.482 0.000 40.000 0 0
```

This file specifies a Lennard Jones potential with lattice constant of 4.0800.

The program *buildcell* is specific to the face centered cubic structure. Thus, it knows where to put the atoms correctly.

### To run this program

First, create the appropriate `gulp.wrap` file, depending on which potential you will use. These have (mostly) been made for you.

If you are doing problem 2A, type (in your 3.320/LAB1/PROBLEM2 directory)

```
hpcbeo2$ cp gulp.wrap.au.lj gulp.wrap
```

and if you are doing problem 2B, type

```
hpcbeo2$ cp gulp.wrap.au.eam gulp.wrap
```

2. EDIT the first line of the `gulp.wrap` file to pick the lattice constant you want (lattice constant for a single unit cell) You can use `emacs`, `vi`, or any editor you wish. If you don't know how, ask one of the class instructors.

3. type

```
hpcbeo2$ buildcell
```

4. The program will output:

```
Please enter the number of cells in the x,y,z:
```

At this point, you type in 3 integers for the numbers you want, with a space in between. If you want a 2x2x2 supercell, type in

```
Please enter the number of cells in the x,y,z:  
2 2 2
```

5. The program will create a `gulp.in` file. If you want, you may rename this

```
hpcbeo2$ mv gulp.in gulp.in.1j.2x2x2
```

6. To find the vacancy formation energy (or surface energies) you will have to remove atoms from the cell. To do this, edit the file with `emacs`, `vi`, or any editor you wish. Remove an atom manually (just delete the line). Calculate the energy before and after removing the atom. Use these numbers to find calculate the vacancy formation energy.

## Visualizing

We will use a program called `gdis`. `Gdis` is a free visualizer, which can read a variety of input files. `Gulp` is one of the input types supported by `gdis`. The webpage is <http://gdis.seul.org>

`Gdis` is only on `xterminals`, or requires `Xwindows`. This means if you are using `secureCRT` from a PC, you need an `Xwindows` program like `X-Win32` (downloadable from MIT) running with `X-forwarding` enabled (in `secureCRT`, go to `Options->Session Options->X11` and select 'Forward x11 packets'. You may need to restart the session.).

Gdis reads gulp input files. All files read by gdis must end in “.gin”.  
You can copy any input file to gdis format by:

```
hpcbeo2$cp gulp.au.in gulp.au.gin
```

To run gdis, you must use a special account we have set up for you on a different computer.

```
hpcbeo2$: export DISPLAY=<your machine name here>:0.0
```

You can find your machine name by typing “uname -n”.

You may need to set the canvas type by selecting Display Properties->Toggles->OpenGL Canvas.

#### **To open a file:**

On the top row, go to File->load and open the file you want. Again, all input files for gdis must end in “.gin”.

#### **To rotate the picture**

Move the mouse to the picture, hold down the right mouse button, and move the mouse around

#### **To save and print**

Select the Display Properties button. Select the POVRay tab and select render image. In the window that pops up, right click and save. Click format and select ps for postscript. Pick a filename and press save. You will need to copy the postscript file somewhere else in order to print it.

## **FAQ for problem 1**

### **What dimensions of supercell should I use?**

*Remember periodic boundary conditions.* This is the most important thing.

For the surface energy calculation, the cell will be different in the x direction (or y, or z). Remember though, because of periodic boundary conditions, there is no need to build the cell in the y or z direction. So 5x1x1 (or 10x1x1) is a suitable supercell. You could also build a 10x2x2 cell; this will just take longer. There are

two convergence issues to think about, the slab (the part with the atoms) thickness, and the vacuum thickness.

Note, this cell dimension choice does not apply for all problems!!! Before you build your cell, you have to think about the problem you are working on. For instance, it does not apply to the vacancy problem! Think about why this is.

If your supercell is built in the  $x$ -direction for the surface energy problem, you should try viewing your system in a  $2 \times 1 \times 1$  system to get a better idea of this.

Lastly, you can not know for sure beforehand what a good size is. You must always test for convergence. For example, if you look for the vacancy formation energy in a  $2 \times 2 \times 2$  supercell, you **must** test a larger supercell to make sure that your supercell is big enough.

**In the vacancy problem, is the answer I get only applicable to the vacancy concentration that I have created? I do not understand the supercell convergence issues for the vacancy problem.**

Remember the objective is not to "simulate" the real material, but to compute the properties that are relevant for the real material. For example, say one has a metal with vacancy concentration  $10^{-6}$ , which is quite typical for real metals. Does this mean that one should study the vacancies in such a metal with a supercell with 1 million atoms and one vacancy? Of course not! At such low concentration the vacancies are isolated. (That means that they do not interact. They do not "see" each other). So any vacancy that behaves isolated is the same, whether it is at concentration  $10^{-8}$  or  $10^{-5}$ . What we need to do is find the smallest supercell where it is still a reasonable approximation that the vacancies in the different images of the cell do not interact. One way is to find is to make the cell systematically bigger and see if the energy converges. When the vacancy formation energy does not change much anymore as the cell gets bigger, one has found the formation energy for an isolated vacancy. In practice this occurs at much higher concentrations than  $10^{-6}$  (and hence for smaller supercells).

**I do not understand potentials at all. Do you have some supplementary reading materials?**

<http://www.fisica.uniud.it/~ercolessi/md/md/>

is a nice primer.

For now, skip the part on molecular dynamics.

Relevant parts are nodes 1-5, 7-9, 14-19, 44-52

Also the parts from Allen and Tildesley.

**My answers do not converge, and I am not sure if I used the correct formulas.**

You may have the wrong definition of vacancy formation energy or surface energy. The most common error is forgetting that thermodynamics requires conservation of mass. That is, you can not have a different number of atoms on each side of the equation. You can not expect to obtain a correct thermodynamic quantity (such as vacancy formation energy) if, for example, you take the difference between a cell with 5 atoms and a cell with 4 atoms.

**My answers seem strange, but I am sure I did everything correctly.**

Remember the definition of potentials, how they are derived, and how what they are used for. For example, a potential derived by fitting to lattice constants is not necessarily going to give correct melting temperatures. If you have more questions, talk with the professor.

**The total lattice energy results for the two methods are very different. Why?**

Usually we do not care about absolute energies. Instead, we care about energy differences. For example, we can always shift energies by a constant by taking difference reference states. So it is not that important if two energy methods show different absolute energies. On the other hand, it *is* significant if two energy method show energy differences that are very different. An example of a property obtained using energy differences is the vacancy formation energy.