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://www.ch.ic.ac.uk/gale/Research/gulp.html

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.

Shell-dynamo (Lennard Jones, Buckingham potentials).

Steve Plimpton's codes (includes Lennard-Jones and Embedded Atom method)
http://www.cs.sandia.gov/~sjplimp/codes.html

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.

First, log into your account.

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Log into the computers.

```
Go ahead...make my day.>ssh -l mit3320 armageddon.mit.edu
The authenticity of host 'armageddon.mit.edu (18.82.0.217)'
can't be established.
RSA key fingerprint is
6b:55:b5:16:94:89:15:8a:ca:28:4c:6b:41:ac:a9:d1.
Are you sure you want to continue connecting (yes/no)? yes
Warning: Permanently added 'armageddon.mit.edu' (RSA) to
the list of known hosts.
mit3320@armageddon.mit.edu's password: password here
Last login: Mon Feb 10 10:48:40 2003 from
tcmpc18.phy.cam.ac.uk
mit3320@master:~$
```

Your TA's should have the password.

From here, you should log onto the node that the TA assigns to you.

For example

```
mit3320@master:~$ssh node6
    Last login: Mon Feb 10 10:47:38 2003 from
    master.cl.lanai.mit.edu
mit3320@node6:~$
```

Use the node the TA assigns to you.

Once you log in, you should make your own home directory, and cd to it.
For example

```
mit3320@node8:~$mkdir eric   (insert your name here)
mit3320@node8:~$cd eric (your name here)
```

Don't mess with somebody else's directory!

All of the files for this homework are located in the HW1 directory and bin directories.

Problem 1

Read over problem 1 of the homework.

To do this problem, you will use the gulp1a.in input file.
Copy this file to your directory. You may want to keep your directories organized so that it will be easier to find things later on. An example is something like this:

```
mit3320@node8:~/eric$mkdir HW1
mit3320@node8:~/eric$cd HW1
mit3320@node8:~/eric/HW1$mkdir P1
mit3320@node8:~/eric/HW1$cd P1
mit3320@node8:~/eric/HW1/P1$cp /home/mit3320/HW1/gulp1a.in .
                            (need the period at the end)
mit3320@node8:~/eric/HW1/P1$ls
gulp1a.in
mit3320@node8:~/eric/HW1/P1$
```

To view the gulp1a.in file type

```
mit3320@node8:~/eric/HW1/P1$less gulp1a.in
```

You can scroll through the file by typing space (to go forward), b (to go backwards) or q (to quit). The file gulp1a.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 conp
2       cell
3         3.0000000     3.0000000   3.0000000  90 90 90
4       fractional
5       Cu     0.0000000     0.0000000     0.0000000
6       Cu     0.0000000     0.5000000     0.5000000
7       Cu     0.5000000     0.0000000     0.5000000
8       Cu     0.5000000     0.5000000     0.0000000
9       lennard 12 6
10      Cu  core Cu core 3000.000 18.000 0.000 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. **conp** 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)
Cu           0.5000000        0.5000000        0.0000000
etc…
```

In this case, we have input the FCC copper 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:

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

The format of the Lennard-Jones line is:

```
(type 1)     (type 2)     (A)        (B)      (potential start) (potential cutoff)
Cu core      Cu core      3000.000   18.000     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 Cu atoms.

To run the program type

```
mit3320@node8:~/eric/HW1/P1$gulp<(input file)>(output file)
```

In this case,

```
mit3320@node8:~/eric/HW1/P1$gulp<gulp1a.in>gulp1a.out
```

Use "less" to read the output file (less gulp1a.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 occurance 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 "gulp1a.in" you will be using "gulp1b.in". Make sure to copy the gulp1b.in file into your directory:

```
mit3320@node8:~/eric/HW1/P1$cp /home/mit3320/HW1/gulp1b.in .
```

Problem 2.

Read over problem 2 on the homework.

You will need to copy over the gulp.wrap.cu.lj and gulp.wrap.cu.eam files. For example

mit3320@node8:~/eric/HW1/P1$**cd /home/mit3320/eric/HW1**
mit3320@node8:~/eric/HW1$**mkdir P2**
mit3320@node8:~/eric/HW1$**cd P2**
mit3320@node8:~/eric/HW1/P2$**cp /home/mit3320/HW1/gulp.wrap.cu.lj .**
mit3320@node8:~/eric/HW1/P2$**cp /home/mit3320/HW1/gulp.wrap.cu.eam .**
(don't forget to type the period at the end)

(if your directory is eric…if it is not, then change the name)

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
2…N (anything you want to appear in the gulp.in file
besides fractional corrdinates)
```

For example:

```
3.616817
opti dist comp conp
lennard 12 6
Cu  core Cu core  3000.0000 18.000  0.000 40.000 0 0
```

This file specifies a Lennard Jones potential with lattice constant of 3.616817.

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

```
mit3320@node8:~/eric/HW1/P2$ls
gulp.wrap.cu.eam  gulp.wrap.cu.lj
mit3320@node8:~/eric/HW1/P2$cp gulp.wrap.cu.lj gulp.wrap
```

and if you are doing problem 2B, type

```
mit3320@node8:~/eric/HW1/P2$cp gulp.wrap.cu.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

mit3320@node8:~/eric/HW1/P2$**buildcell**

4. The program will output:

```
Hello buddy.  Gimme number of cell in x,y, and z directions
```

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

```
Hello buddy.  Gimme number of cell in x,y, and z
                        directions
2 2 2
```

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

```
mit3320@node8:~/eric/HW1/P2$mv gulp.in gulp.in.lj.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. You can use emacs, vi, or any editor you wish. If you don't know how, ask one of the class instructors. 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.

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 2x1x1 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 2x2x2 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 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 Tildesly, which are on the web.

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.