Manual 04 for MD++

MD++ Tour with Sample Scripts

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1 Making a Vacancy

A vacancy is a type of frequently encountered point defects in solids and can be viewed as a missing atom from the perfect crystal strutcture. In this manual, we will learn how to introduce a vacancy into the perfect crystal and how to calculate the vacancy formation energy of the bulk material. Run the following example script by typing

```
$ bin/fs_gpp scripts/movacancy.script
```

```
# -*-shell-script-*-
setnolog
setoverwrite
dirname = runs/movacancy  # specify run directory
#-------------------------------------------
# Read in potential file
potfile = ~/Codes/MD++/potentials/mo_pot readpot
#-------------------------------------------
#Create Perfect Lattice Configuration
crystalstructure = body-centered-cubic latticeconst = 3.1472 #(A)
latticesize = [  1  0  0  5
                 0  1  0  5
                 0  0  1  5 ]
makecrystal finalcnfile = perf.cn writecn
eval # evaluate the potential of perfect crystal
#-------------------------------------------
# Create Vacancy
input = [ 1      # number of atoms to be fixed
          0 ]    # index of an atom to be fixed
fixatom_by_ID    # fix a set of atoms by their index
removefixedatoms # remove picked atoms
finalcnfile = movac.cn writecn
eval # evaluate the vacancy-formed crystal
```

```
#-------------------------------------------
# Plot Configuration
atomradius = 1.0  bondradius = 0.3  bondlength = 0
atomcolor = blue  highlightcolor = purple backgroundcolor = gray
bondcolor = red   fixatomcolor = yellow
plotfreq = 10  win_width = 600   win_height = 600
plot_atom_info = 3
color00 = "orange"  color01 = "purple" color02 = "green"
color03 = "magenta" color04 = "cyan"   color05 = "purple"
color06 = "gray80"  color07 = "white"
plot_color_windows = [ 2
                       -10  -6.8   6  #color06 = gray80
                       -6.7 -6.0   0  #color00 = orange
                       ]
rotateangles = [ 0 0 0 1 ]
openwin alloccolors rotate saverot plot
sleep quit
```

The script above shows how to create a vacancy from the perfect BCC Mo crystal.[1] First, a 5×5×5 perfect cubic crystal of Mo is generated with edges along ⟨100⟩ directions. Then atom 0 is fixed by

```
input = [ 1 0 ] fixatom_by_ID
```

and

```
removefixedatoms
```

removes this atom. Suppose, if you want to remove two atoms with indices 3 and 8, you can do so by

```
input = [ 2        # number of atoms to be fixed
          3 8 ]    # index of atoms to be fixed
fixatom_by_ID      # fix a set of atoms by their index
removefixedatoms   # remove fixed atoms
```

At this moment, you may wonder how do we know which atom has which index. If you click an atom in the graphic window with the mouse, it gives its index number and energy.[2] In the graphic window, you will see the atoms near the vacant site have different color than the others. In the script file, two color windows are set by the variable *plot_color_windows* according to atoms' energy. The atoms whose energies are between -10 and -6.8 (eV) are shown in gray and the atoms whose energies lie between -6.7 and -6.0 (eV) are shown in orange. So, the atoms near the vacancy have higher energy than the rest. Click the atoms and you will see the actual energy of each atom. If you also compare the potential energy of the perfect crystal and the vacancy-formed structure, you will know which structure has higher energy.

[1] Uploaded as "movacancy.script" to the coursework website.

[2] This is the case when *plot_atom_info* = 3 is specified in the script file. If *plot_atom_info* = 1, it gives its index number and the reduced coordinate. If *plot_atom_info* = 2, the index number of the atom and its real coordinate (in angstrom) will be displayed.

Q.1 If other atom is removed instead of the atom of index 0, do you still expect the final state has the same amount of energy? Explain the reason.

2 Relaxation

After introducing a vacancy, the atomistic structure is then relaxed to its locay energy minimum. For example, here we expect the atoms near the vacancy to relax toward the vacant site to lower the energy. MD++ uses a conjugate gradient relaxation algorithm. The corresponding section in the script file is given below.

```
#-------------------------------------------
# Conjugate-Gradient relaxation
conj_ftol = 1e-7     # tolerance on the residual gradient
conj_fevalmax = 1000 # max. number of iterations
conj_fixbox = 1      # fix the simulation box
relax                # CG relaxation
finalcnfile = relaxed.cn writecn
eval                 # evaluate relaxed structure
```

Copy the above script and paste it to the "movacancy.script" right before *sleep quit*.[3] You observe the reduction of potential energy of the simulation system during the relaxation process because the system was not in an energy minimum state after you just removed an atom from the perfect crystal.
There are several variables related with CG relaxation. *conj_ftol* is the tolerance of the residual gradient and *conj_fevalmax* is the maximum number of iterations. The relaxtion will stop if the tolerance becomes smaller than the specified *conj_ftol* or if the number of iteration reaches its maximum. If *conj_fixbox* is equal to 1, the shape and size of simulation cell box is fixed so that only the atoms can move during the relaxation. Sometimes you need to also relax the simulation box itself and in such a case you can add more degrees of freedom to the system by setting *conj_fixbox* = 0. For example, you can allow the box to expand or shrink due to the pressure by

```
conj_fixbox = 0
conj_fixboxvec = [ 0 1 1
                   1 0 1
                   1 1 0]
```

In this case, only the diagonal components of the box matrix **H** can relax and the other components are fixed by *conj_fixboxvec*. [4]

[3] The relaxation part is commented out in the "movacancy.script". To activate, simply uncomment these lines.

[4] See the manual M02_MD++.pdf for the definition of **H**.

3 Vacancy Formation Energy

We define the vacancy formation energy as the energy needed to form a vacancy from the bulk perfect crystal structure. This can be obtained by comparing the relaxed energy of a simulation cell with a vacancy and the energy of a perfect crystal structure. However, we need to make sure we are comparing two systems with the same number of atoms, because in reality an atom is never destroyed when a vacancy forms. We can think of is as moving to the external surface of a large crystal.(See Fig.2.) In our simulation with the periodic boundary condition, there is no external surface. So this effect will have to be accounted for in a different way. Let N be the total number of atoms in the original perfect crystal structure and let its energy be E_1 and let E_2 be the relaxed energy of the $(N-1)$ atom structure. Then the vacancy formation energy E_v can be expressed as

$$E_v \equiv E_2 - \frac{N-1}{N} \cdot E_1 \tag{1}$$

Q.2 What is the difference between the $E_2 - \frac{N-1}{N}E_1$ and $E_2 - E_1$? Explain the physical meaning of both terms.

Once the vacancy formation energy is obtained, we can use it to obtain the concentration of vacancy $[n]$ in the crystal strucutre using Boltzmans distribution function[1][5],

$$[n] \sim \exp(-E_v/k_BT) \tag{2}$$

For example, the vacancy formation energy for Mo is 2.550 (eV)[6] from the atomistic calculation and the concentration will be $[n] \sim$ 1.514E-43 at 300K.(k_B = 8.621E-5 eV/K)

Q.3 Calculate the vacancy formation energy while changing the simulation box size. Are all the obtained energies same irrelavant to the box size? You will observe the energy dramatically changes if the box is smaller than the certain size. Explain the reason.

References

[1] R. J. Stokes and D. F. Evans, "Fundamentals of Interfacial Engineering", Wiley-VCH 1997 pp.491-493

[2] M. J. Mehl and D. A. Papaconstantopoulos, "Applications of a tight-binding total-energy method for transition and noble metals: Elastic constants, vacancies, and surfaces of monatomic metals", Physical Review B **54** 4519-4530 1996

[5] See the appendix A.

[6] With the tight binding model, it is reported to be 2.46eV. See the reference [2]

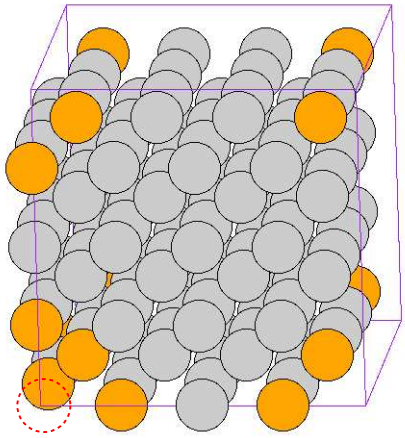

Figure 1: A vacancy formed BCC molybdenum crystal. $\mathbf{c}_1 = 4[100]$, $\mathbf{c}_2 = 4[010]$, and $\mathbf{c}_3 = 4[001]$ are the periodicity vectors. The red dotted circle designates the missing atom and the atoms around the vacant site are shown in different color due to their relatively high energy than the others.

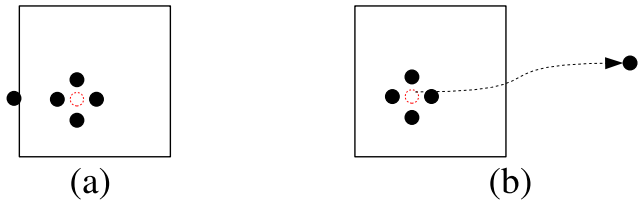

Figure 2: Two different concepts about vacancy-forming mechanism. (a) Rearrangement of atoms while the total number of atoms does not change. (b) Removal of an atom from the crystal, which is then located so far away that no more interatomic interaction exists.

A Derivation of the Equation (2)

Assume that there are n vacancies in the N candidate sites and $n \ll N$. The free energy of the solid G is

$$G = G_0 + n\Delta H_v - T\Delta S_v \tag{3}$$

where G_0 is the free energy of the perfect solid, H_v is the enthalpy required for forming a vacancy, and S_v is the configurational entropy related with vacancy formation. If every site has equal probability to be vacancy , the entropy is

$$\begin{aligned} \Delta S_v &= k_B \ln \Omega = k_B \ln \frac{N!}{(N-n)!n!} \\ &= k_B[N \ln N - (N-n)\ln(N-n) - n \ln n] \end{aligned} \tag{4}$$

where the number of states Ω is simply number of ways in choosing n out of N. Stirling's approximation is applied to get the last line of Eqn.(4).
At the equlibrium state, the free energy change ΔG is minimum, which means $\frac{\partial \Delta G}{\partial n} = 0$.

$$\begin{aligned} \frac{\partial \Delta G}{\partial n} &= \Delta H_v - T\frac{\partial \Delta S_v}{\partial n} \\ &= \Delta H_v - T k_B \ln \frac{N-n}{n} \\ &\simeq \Delta H_v - T k_B \ln \frac{N}{n} = 0 \\ \Longrightarrow \qquad & \frac{n}{N} = \exp\big(-\frac{H_v}{k_B T}\big) \end{aligned} \tag{5}$$

Generally, since there is additional term due to the nonconfigurational entropy contribution, we can say

$$[n] \sim \exp\big(-\frac{E_v}{k_B T}\big) \tag{6}$$