

Energy Minimization

Keonwook Kang and Wei Cai

February 16, 2007

1 Creating a Vacancy in a Perfect Crystal

A vacancy is a common and important type of point defect in solids. It is an empty site (i.e. a missing atom) in an otherwise perfect crystal structure. Here we discuss how to introduce a vacancy in a perfect crystal using MD++ and how to compute the vacancy formation energy. Consider the following MD++ input file, `movacancy.script`, that creates a vacancy in a perfect BCC Molybdenum crystal.

```
# -*-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 allocolors rotate saverot plot
sleep quit

```

We can run this script file by typing

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

First, MD++ creates a $5 \times 5 \times 5$ perfect cubic crystal of Mo with edges along $\langle 100 \rangle$ directions. Then it fixes atom 0 by

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

and

```
removefixedatoms
```

then removes this atom.

The first number in the `input` array specifies the number of atoms to be fixed. For example, if you would like to remove two atoms, say 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 indices
removefixedatoms   # remove fixed atoms

```

Sometimes, you may want to remove a specific atom you see in the graphic window. You can obtain the index of this atom by clicking the atom with your mouse. Depending on the setting of `plot_atom_info`, other information is also displayed when you click on the atom. If `plot_atom_info = 1`, the atom index number and its scaled coordinates are printed when the atom is clicked.

If `plot_atom_info = 2`, the atom index and its real coordinate (in Å) will be printed. If `plot_atom_info = 3`, the atom index and its local energy (in eV) will be printed.

The script file also sets up two color windows (`plot_color_windows`) to display the atoms. Atoms with local energy between -10 eV and -6.8 eV are shown in gray and the atoms whose energies lie between -6.7 eV and -6.0 eV are shown in orange. This will highlight the atoms near the vacancy because they usually have a higher local energy. Click the atoms and you will see the actual local energy of these atoms.

The command `eval` computes the potential energy of the simulation cell and prints it to the screen. **Question:** If we remove a different atom, say atom 10, instead of atom 0, do we expect the system to have a different potential energy?

2 Relaxation

When an atom is removed from a crystal, we expect the neighboring atoms to adjust its positions, e.g. to move toward the vacant site, to lower the potential energy. The relaxed structure can be obtained by an energy minimization algorithm, such as the conjugate gradient (CG) method. This can be done by uncommenting the following lines in the `movacancy.script`.

```
#-----  
# 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
```

The potential energy printed by the second `eval` should be lower than that printed by the first `eval`.

There are several variables controlling the CG relaxation. `conj_ftol` is the tolerance of the residual gradient and `conj_fevalmax` is the maximum number of calls to the potential function (effectively limiting the number of iterations). If `conj_fixbox = 1`, the shape and volume of simulation cell box is fixed and only the scaled coordinates of the atoms can change during the relaxation. If `conj_fixbox = 0`, then all 9 components of the **H** are allowed to change.¹ Sometimes, we want to fix some components of the **H** matrix while allowing other components to move. This can be done by specifying the `conj_fixboxvec` matrix. For example, if

```
conj_fixbox = 0
```

¹The definition of matrix **H** is given in Manual 02.

```

conj_fixboxvec = [ 0 1 1
                  1 0 1
                  1 1 0]

```

then only the diagonal components of \mathbf{H} are allowed to move (the corresponding entries in `conj_fixboxvec` are zero).

3 Vacancy Formation Energy

The vacancy formation energy E_v is the energy increase that is needed to create a vacancy in a perfect crystal. It can be used to predict the vacancy concentration at thermal equilibrium through,

$$[n] \approx \exp(-E_v/k_B T) \quad (1)$$

This is an approximation because we have ignored the vibration entropy contribution S_v of the vacancy. The exact expression is

$$[n] = \exp(-F_v/k_B T) \quad (2)$$

where $F_v = E_v - TS_v$ is the vacancy formation free energy. These expressions are similar to Boltzmann's distribution and will be derived in the Appendix.

Let E_1 be the energy of the perfect crystal with N atoms, and E_2 be the relaxed potential energy of the $(N - 1)$ -atom system (containing the vacancy). The vacancy formation energy is not simply the difference between the two, i.e.

$$E_v \neq E_2 - E_1 \quad (3)$$

because the two systems does not have the same number of atoms, whereas in a real crystal, no atom is destroyed when a vacancy forms. Instead, when a vacancy forms in a real crystal, the atom can go to the external surface of the crystal (or to grain boundaries), see Fig.2. Because we have a very small crystal in our simulation, which is subjected to the periodic boundary condition, there is no external surface. Therefore, we need to account for this effect in a different way. In the perfect crystal, all atoms contributes equally to the total energy. Therefore, we expect the energy contribution of $N - 1$ atoms in the perfect crystal structure to be $\frac{N-1}{N}E_1$ (even though we cannot fit a perfect crystal with $N - 1$ atoms in to a periodic simulation cell). The vacancy formation energy E_v can be computed from

$$E_v \equiv E_2 - \frac{N-1}{N} \cdot E_1 \quad (4)$$

The cohesive energy of the perfect crystal, $E_{\text{coh}} = E_1/N$, is the potential energy per atom. Hence the vacancy formation energy can also be expressed as,

$$E_v \equiv E_2 - (N-1)E_{\text{coh}} \quad (5)$$

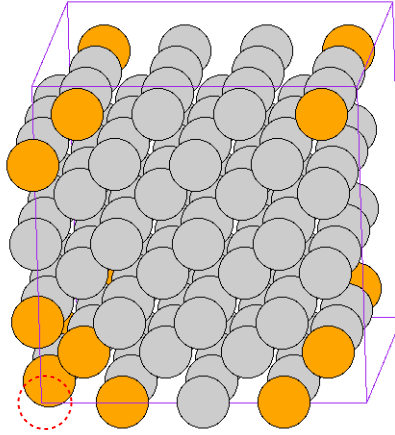


Figure 1: A vacancy formed BCC molybdenum crystal. $\mathbf{c}_1 = 4[100]$, $\mathbf{c}_2 = 4[010]$, and $\mathbf{c}_3 = 4[001]$ are the periodicity vectors. The red dotted circle designates the missing atom and the atoms around the vacant site are shown in different color due to their relatively high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

The result for BCC Mo using the FS potential is $E_v = 2.550$ eV,² which leads to $[n] \approx 1.43 \times 10^{-13}$ at $T = 1000$ K ($k_B = 8.621 \times 10^{-5}$ eV/K).

Question: Recompute E_v with larger and smaller simulation boxes. How does E_v depend on the number of atoms in the simulation cell?

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

²This is consistent with the more accurate tight-binding (TB) model which predicts $E_v = 2.46$ eV [2].

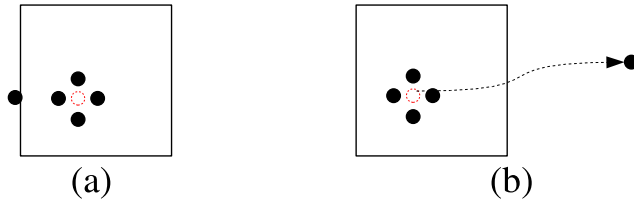


Figure 2: (a) In a real crystal, the atom that leaves the interior, thus creating a vacancy, moves to the surface of the crystal. (b) If we simply take the energy difference between E_2 ($N - 1$ atoms) and E_1 (N atoms), we are considering the process in which the atom leaves the crystal and moves so far away that it does not interact with any other atoms in the crystal. This will lead to a much higher potential energy and does not predict E_v correctly.

A Equilibrium Vacancy Concentration

Here we derive the equilibrium vacancy concentration, Eq. (2), given the formation energy of a single vacancy. Consider a crystal with N sites, n of which are occupied by vacancies. We can write the Gibbs free energy of the solid as

$$G = G_0 + nE_v - TS_c \quad (6)$$

where G_0 is the free energy of the perfect crystal ($n = 0$). Here we have ignored the interaction between the vacancies. This approximation is valid if $n \ll N$.³ S_c is the configurational entropy due to the fact that there are Ω different ways to arrange the n vacancies on N sites.

$$\begin{aligned} S_c &= k_B \ln \Omega = k_B \ln \frac{N!}{(N-n)!n!} \\ &= k_B [N \ln N - (N-n) \ln(N-n) - n \ln n] \end{aligned} \quad (7)$$

In the last step we have used Stirling's approximation. At equilibrium, the Gibbs free energy G reaches minimum, which means $\frac{\partial \Delta G}{\partial n} = 0$.

$$\begin{aligned} \frac{\partial \Delta G}{\partial n} &= E_v - T \frac{\partial S_c}{\partial n} \\ &= E_v - T k_B \ln \frac{N-n}{n} \\ &\simeq E_v - T k_B \ln \frac{N}{n} = 0 \\ \implies [n] &\equiv \frac{n}{N} = \exp\left(-\frac{E_v}{k_B T}\right) \end{aligned} \quad (8)$$

³We have also ignored the vibrational entropy S_v of the vacancies. Otherwise E_v should be replaced by $F_v = E_v - TS_v$.