

# Vacancy Formation Energy

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A vacancy, one of point defects is introduced into a perfect crystal FCC (Al, Cu), BCC (Mo, Ta), and DC (Si) and the vacancy formation energy,  $E_v$  was calculated in each case using MD++ code.

## 1 Background Knowledge

A computation domain is usually taken to be simply shaped such as a unit cube shown as Fig. 1(a) for solving various problems of different coordinates or some other reasons.

MD++ code also has a similar transformation to easily implement periodic boundary condition (PBC). Since the crystal shows a periodic structure, it is natural to assume there are infinite number of image cells faced with a primary cell and periodically arranged in all 3 directions like Fig. 1(b). This primary cell is called as the simulation cell (or box) and the coordinate in the simulation cell as the reduced coordinate,  $\mathbf{s}$ . The relationship between the reduced coordinate,  $\mathbf{s}$  and the real coordinate,  $\mathbf{r}$  is defined with the transformation matrix  $\mathbf{H}$  like

$$\mathbf{s} = \mathbf{H}^{-1} \cdot \mathbf{r} \quad (1)$$

where  $\mathbf{H}$  is a matrix whose columns are 3 periodicity vectors, or  $\mathbf{H} = [\mathbf{c}_1 \mathbf{c}_2 \mathbf{c}_3]$ .

In this work, fortunately, it does not need to take the periodicity vectors  $\mathbf{c}_1$ ,  $\mathbf{c}_2$ , and  $\mathbf{c}_3$  different from the conventional  $x$ ,  $y$ , and  $z$  coordinate frame. So take as simple as

$$\mathbf{c}_1 = L_1[100], \mathbf{c}_2 = L_2[010], \mathbf{c}_3 = L_3[001]$$

where  $L_1 = L_2 = L_3 = L$  is the size of a cubic simulation box. (Actually, all the lengths are nondimensionalized by the lattice constant, which should be multiplied to get the real coordinate,  $\mathbf{r}$  in the above equation.)

## 2 Simulation Procedure

The simulation procedure in MD++ is outlined as the following items.

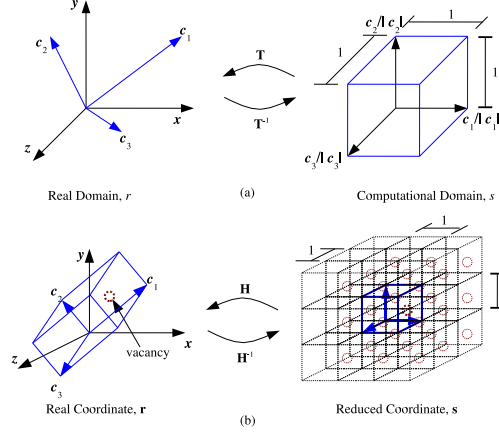


Figure 1: (a) Transformation between the real domain,  $r$  and the computational domain,  $s$ . (b) The relationship between the real coordinate and the reduced coordinate in MD++,  $\mathbf{r} = \mathbf{H} \cdot \mathbf{s}$  where  $\mathbf{H} = [\mathbf{c}_1 \mathbf{c}_2 \mathbf{c}_3]$

- Create a perfect crystal.
- Remove an atom.
- Relax the system using the conjugate gradient relaxation method.
- Evaluate the potential energy of the system.
- Calculate the vacancy formation energy,  $E_v$  for different box size,  $L$ .

The first four steps are so obvious that I will not mention all the steps in detail. If you read the MD++ manual<sup>1</sup>, you will know how to write a script file for each step.<sup>2</sup>

In the 2nd step, when you pick an atom to be removed, where do you think that atom is located? Corner or center of the box? Or the middle of an edge? If you see the Fig.2, you will clearly understand what the question is. The answer is the location of a vacancy does not affect the simulation result, because the periodic boundary condition is imposed, and whatever atoms you choose they are all the same.

At the last step, how to calculate the vacancy formation energy,  $E_v$  may be different according to what definition of  $E_v$  you propose. Our definition of the vacancy formation energy is how much cohesive energy is needed to form a vacancy. If this value is negative, that means energy is released when forming a vacancy. Cohesive energy,  $E_{coh}$ , can be said as the interatomic potential

<sup>1</sup><http://micro.stanford.edu/~caiwei/Forum/>

<sup>2</sup>See the appendix B.

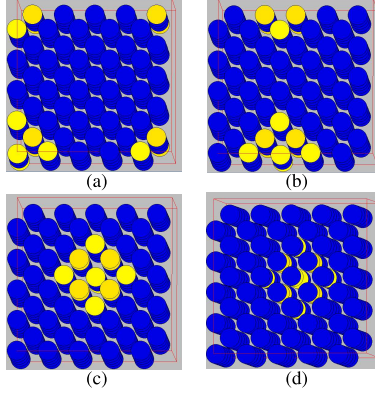


Figure 2: The BCC molybdenum with a vacancy. The atoms around a vacancy are highlighted with yellow. (a) Vacancy in the corner (b) Vacancy in the middle of an edge (c) Vacancy on the center of a surface (d) Vacancy in the center of the box. The vacancy formation energy is independent of the position of a vacancy.

energy per atom at most stable state. For example,  $E_{coh}$  in Lennard-Jones(LJ) potential between 2 atoms is shown as Fig.3.

We assume that the total potential energy,  $E_1$  in the perfect crystal has been reached to the cohesive state and so does the energy,  $E_2$  in the vacancy-formed structure after the relaxation. Then vacancy formation energy can be defined as Eqn.4. Note that it is not just the difference between  $E_1$  and  $E_2$  even if it can be assumed so in case that  $N$  is a very big number.

$$E_1 = \sum_i^N E_i \equiv N \cdot E_{coh}^1 \quad (2)$$

$$E_2 = \sum_i^{N-1} E_i \equiv (N-1) \cdot E_{coh}^2 \quad (3)$$

$$E_v \equiv (N-1) \cdot (E_{coh}^1 - E_{coh}^2) = E_2 - \frac{N-1}{N} \cdot E_1 \quad (4)$$

where  $N$  is the number of atoms in the simulation box.

Let us think more about what this definition implies. What really happens when a vacancy forms is not like just removing an atom from the perfect crystal as we did in the simulation. (See Fig.4(b)) Rather, it is more or less like the rearrangement of atoms within the crystal, with the number of atoms kept constant like Fig.4(a).

Once the vacancy formation energy is revealed, we can apply this knowledge to obtain the concentration of vacancy in the crystal with Boltzmann's probability,

$$\begin{aligned} \exp(-F_v/kT) &= \exp(-(E_v - TS_v)/kT) \\ &\simeq \exp(-E_v/kT) \quad \text{for low temperature.} \end{aligned} \quad (5)$$

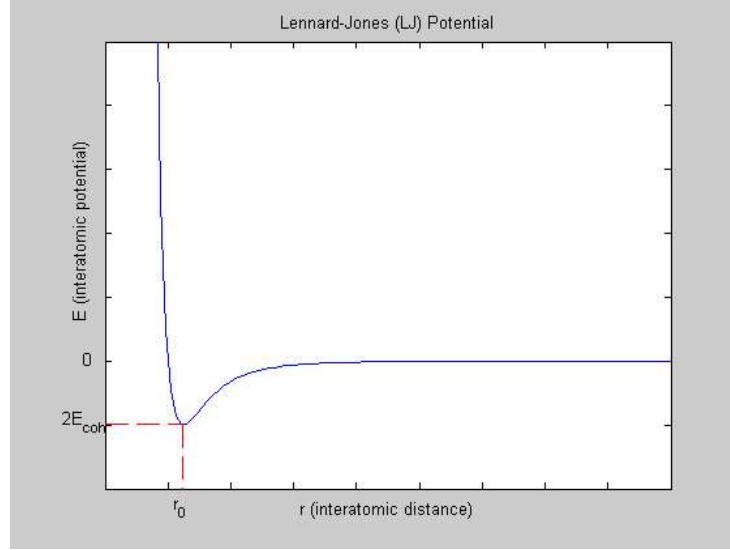


Figure 3: Cohesive energy,  $E_{coh}$  in Lennard-Jones(LJ) interatomic potential

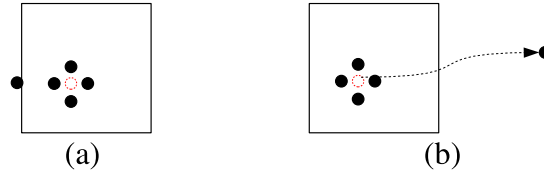


Figure 4: Two different concepts about vacancy-forming mechanism. (a) Rearrangement of atoms while the total number of atoms does not change. (b) An atom is removed from the crystal and located so far away that no more interaction exists. In this case, additional energy (e.g. evaporation energy or sublimation energy) is usually needed in addition to vacancy-forming energy.

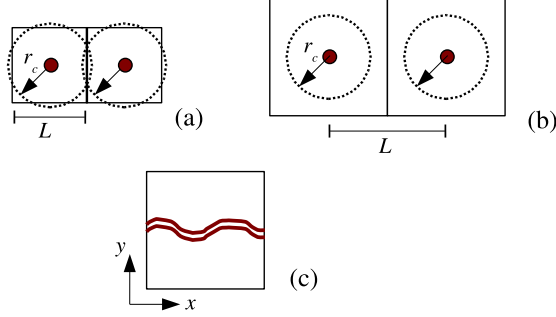


Figure 5: (a) Pseudo effect of the periodic images of defects exists in case of  $L < 2r_c$ . (b) The simulation cell can be considered as a supercell when  $L > 2r_c$ . In (c), supercell concept holds only along the  $y$  direction and the periodicity is imposed along the  $x$  direction.

where  $F_v$  is the free energy for the vacancy formation<sup>3</sup>.

The last thing to point out is the concept of “supercell”. Periodic boundary condition has a drawback that the unwanted effect of periodic images of a defect in Fig.1(b) can distort the solution. Because we want to focus one single vacancy in the infinite crystal, the effects of other image vacancies should be removed or at least mitigated. Thus the cell size,  $L$  is chosen larger than a critical radius,  $r_c$  where the potential of a vacancy is assumed to vanish.<sup>4</sup> According to the result, it is shown that vacancy formation energy gets constant once the simulation box size is larger than certain value. Sometimes this supercell is intentionally broken down along a certain direction where you want to impose periodic effect of images as shown in Fig.5(c), where the supercell is achieved only along  $y$ -direction.<sup>5</sup>

### 3 Numerical Result

#### 3.1 Aluminum (Al, lattice constant=4.05Å)

The vacancy formation energy of FCC aluminum is obtained to be 0.7381eV in the following table with the “Aluminum Glue Potential” or “Ercollesi-Adams potential”. The energy becomes constant above the box size 5 in Fig.6.

<sup>3</sup>R.J.Stokes and D.F.Evans, “Fundamentals of Interfacial Engineering”, Wiley-VCH 1997 pp.491-493

<sup>4</sup>see Appendix A.

<sup>5</sup>see. Rüdiger et al., Phy. Rev. Lett. **82** Num.1 (Jan.04.1999)

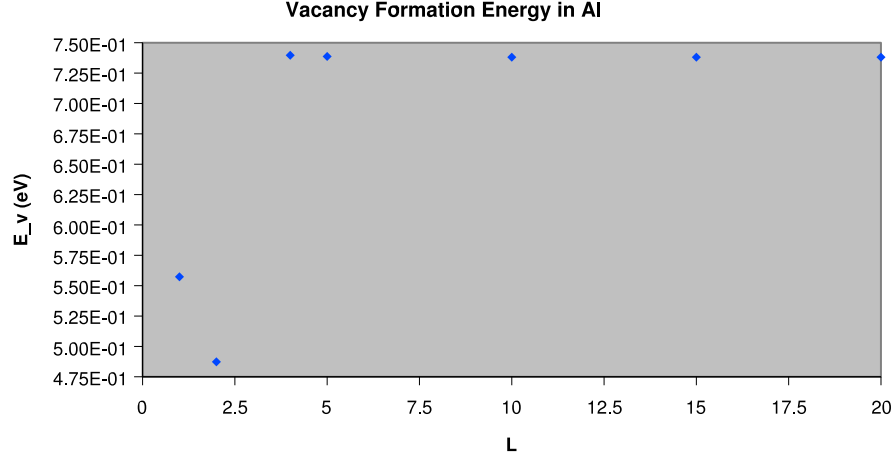


Figure 6: Vacancy Formation Energy,  $E_v$  of FCC Al is plotted for the different simulation box size,  $L$ . The energy gets constant after the box size is bigger than 5.

$L$	1	2	...	20
$N = 4L^3$	4	32	...	32000
$E_1$	-6.20844E+00	-9.98300E+01	...	-1.07497E+05
$E_2$	-4.09903E+00	-9.62230E+01	...	-1.07493E+05
$E_v$	5.57302E-01	4.87296E-01	...	7.38091E-01

### 3.2 Other Atoms

For other atoms like copper(Cu), molybdenum(Mo), tantalum(Ta), and silicon(Si), the vacancy formation energy is also calculated and shown in the following table.

Structure	FCC		BCC		DC
Element	Al	Cu	Mo	Ta	Si
Potential	Al glue	EAM	FS	FS	EDIP
Lattice Constant ( $\text{\AA}$ )	4.05	3.6030	3.1472	3.3058	5.4309
$E_v$ (eV)	0.739	1.308	2.250	2.906	3.224

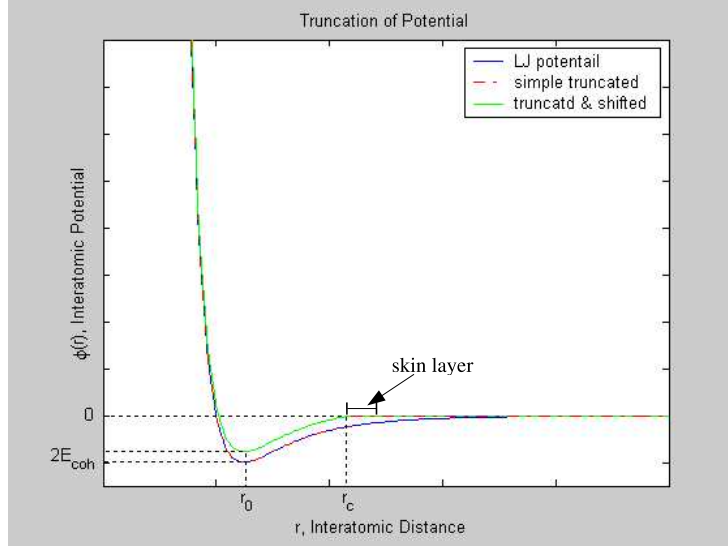


Figure 7: LJ potential (blue) and two models of its truncation: (a) simple truncated (red dot) and (b) truncated and shifted (green). Simple truncated potential has a discontinuity at cutoff radius.

## A Cut-off Radius and Truncation of Potential <sup>6</sup>

The periodic boundary condition means that infinite number of periodic structure repeat again and again in all x, y, z direction. This brings us an impossible mission to calculate potentials with innumerable atoms. To overcome this obstacle, we adopt an assumption that potential between atoms can be neglected beyond a certain range, so called “cut-off radius”,  $r_c$  just like Fig.7.

According to Frenkel and Smits, cutoff radius,  $r_c$  is chosen where the potential reduces to 1/60th of the energy well depth, or

$$r_c = 2.5r_0$$

for the LJ potential. If  $r_0$  is regarded as a lattice constant  $a$ , then we can approximately say

$$L > 2r_c \simeq 5a \quad \text{or} \quad L/a > 5$$

This can make it helpful for us to guess how large box size might be chosen for MD simulation, even though the potentials for Al, Cu, Mo, Ta, and Si are not LJ potential.

This truncated potential assumption makes finite number of calculation of interatomic potential possible by neglecting the atoms out of cutoff radius. Note

<sup>6</sup>See Frenkel & Smit, “Understanding Molecular Simulation: From Algorithm to Application” 2<sup>nd</sup>ed. Academic Press. pp.35-39

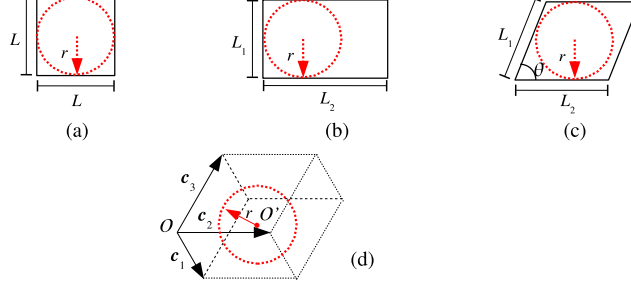


Figure 8: (a) square:  $L > 2r_c$ , (b) rectangle:  $\min(L_1, L_2) > 2r_c$ , (c) parallelogram:  $\min(L_1 \sin \theta, L_2 \sin \theta) > 2r_c$ , (d) general 3D case:  $\min(\frac{\det(\mathbf{H})}{|\mathbf{c}_3 \times \mathbf{c}_1|}, \frac{\det(\mathbf{H})}{|\mathbf{c}_1 \times \mathbf{c}_2|}, \frac{\det(\mathbf{H})}{|\mathbf{c}_2 \times \mathbf{c}_3|}) > 2r_c$ , where  $\mathbf{H} = [\mathbf{c}_1 \mathbf{c}_2 \mathbf{c}_3]$

that this can be justified only if long range interaction is dominated by dispersion force.

Fig.8 show some examples to get an idea of how to obtain the inequality,

$$L > 2r_c$$

given in the Fig.5 and how to generalize this inequality. The basic algorithm is that the minimum height of the simulation box should be larger than twice of the cutoff radius, and for general 3D case the height is given by the volume over the area in Fig.8(d).

For the general 3D case, first of all, the center of sphere  $O'$  is assumed to be located at the center of diagonal lines. From the point  $O'$ , make the orthogonal line to each three surfaces formed by the periodicity vectors,  $\mathbf{c}_1$ ,  $\mathbf{c}_2$ , and  $\mathbf{c}_3$ . The distances are

$$\begin{aligned} r_1 &= \frac{1}{2} \frac{\det(\mathbf{H})}{|\mathbf{c}_2 \times \mathbf{c}_3|} \\ r_2 &= \frac{1}{2} \frac{\det(\mathbf{H})}{|\mathbf{c}_3 \times \mathbf{c}_1|} \\ r_3 &= \frac{1}{2} \frac{\det(\mathbf{H})}{|\mathbf{c}_1 \times \mathbf{c}_2|} \end{aligned}$$

Since the radius of the biggest inner touching sphere is the smallest one among  $r_1$ ,  $r_2$ , and  $r_3$ , we can get the inequality,

$$2r_c < \min\left(\frac{\det(\mathbf{H})}{|\mathbf{c}_3 \times \mathbf{c}_1|}, \frac{\det(\mathbf{H})}{|\mathbf{c}_1 \times \mathbf{c}_2|}, \frac{\det(\mathbf{H})}{|\mathbf{c}_2 \times \mathbf{c}_3|}\right) \quad (6)$$

where  $\mathbf{H} = [\mathbf{c}_1 \mathbf{c}_2 \mathbf{c}_3]$ .

Another topic related with the cutoff radius is “minimum image convention”, which says the vector of the shortest distance between an atom  $i$  and an image



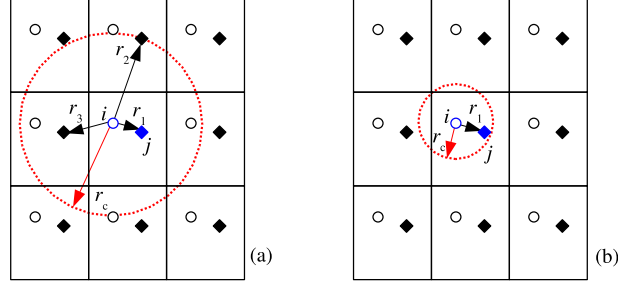


Figure 9: Minimum Image Convention. (a) Interatomic potential between atom  $i$  and  $j$ ,  $u_{ij} = u(r_1) + u(r_2) + u(r_3)$ . (b)  $u_{ij} = u(r_1)$ . If box size is large enough such that only one image of atom  $j$  or atom  $j$  itself exists within the cutoff radius of atom  $i$  as shown in (b), the minimum image convention holds.

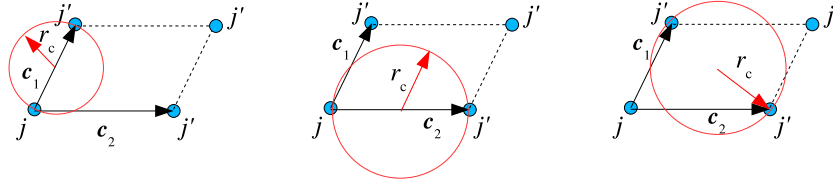


Figure 10: Condition for the minimum image convention in 2D case.  $j'$  is an image atom of the primary atom  $j$ . Two or more atoms including both image atoms and the primary atom are not located in the circle of the radius,  $r_c$ .

of atom  $j$  is taken as a relative position vector for calculating potential between atom  $i$  and  $j$ , if the simulation box size,  $L$ , is large enough such that only one image of atom  $j$  remains within the cutoff radius as shown in Fig.9. The condition for the minimum image convention for 2D is (See Fig.10)

$$r_c < \frac{1}{2} \min(|\vec{c}_1|, |\vec{c}_2|, |\vec{c}_1 + \vec{c}_2|, |\vec{c}_1 - \vec{c}_2|)$$

For the general 3D case, we can say

$$r_c \leq \frac{1}{2} |n_1 \vec{c}_1 + n_2 \vec{c}_2 + n_3 \vec{c}_3| \quad (7)$$

for any integer  $n_1$ ,  $n_2$ , and  $n_3$  except that  $n_1 = n_2 = n_3 = 0$ .

The atoms within the cutoff radius of an atom  $i$  are called “neighbor atoms” of the atom  $i$ , and potentials between the atom  $i$  and its neighbors are taken into consideration. At this point, we have another issue that the neighbor atoms do not stay at their original position but move and drift continuously due to thermal vibration or random walk during the simulation. This implies that the

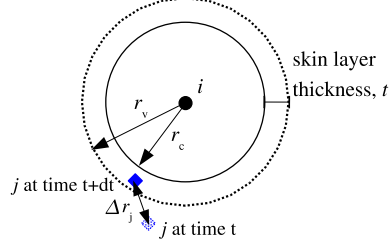


Figure 11: Skin Layer. As a buffer zone for adapting the movement of atoms in the neighbor list, a skin layer is introduced around the cutoff radius. If the maximum movement of a neighbor atom does not exceed the skin layer thickness,  $t$ , the neighbor list does not need be updated, which saves CPU time, but Verlet list algorithm is still  $O(N^2)$  operation due to the list update.  $N$  is so large that Verlet list algorithm does not show better performance than simple  $O(N^2)$  scheme. A fancy  $O(N)$  scheme is introduced in the book by Frenkel and Smit. In LJ potential, usually  $r_v = 2.7r_0 \sim 3.0r_0$ .

neighbor list has to be updated at every time step of MD simulation to make sure whether the atoms once belonged to neighbors of an atom still belong to its neighbors and vice versa. This confirming process costs a lot of computer resources and “skin layer” concept is adopted to reduce this cost. Skin layer is a buffer zone which is a thin layer right outside of the cutoff radius as shown in Fig.11, to accommodate the movement of neighbor atoms. The neighbor list or “Verlet list” contains atoms within the Verlet radius,  $r_v$ .

With the skin layer, the neighbor list does not need to be reconstructed at every time step if the maximum atom movement is less than skin layer thickness, or

$$\max(\Delta r_{ij}) < t/2 \quad (8)$$

where the factor of 2 is introduced to consider the movements of both atoms  $i$  and  $j$  together.

## B Sample Script

```
# Vacancy is introduced into BCC Mo
# Then it is relaxed via CGR method.
setnolog
setoverwrite
dirname = runs/movacancy_kw    # specify run directory
#-----
#Read in potential file
potfile = ~/private/MD/Codes/MD++/potentials/mo_pot readpot
#-----
#Create Perfect Lattice Configuration
latticestructure = body-centered-cubic
latticeconst = 3.1472 #(A) for Mo
makecnspec = [ 1 0 0 5 # c1 = 5*[1 0 0]
               0 1 0 5 # c2 = 5*[0 1 0]
               0 0 1 5 ] # c3 = 5*[0 0 1]
makecn finalcnfile = perf.cn writecn
eval # evaluate the potential of perfect crystal
#-----
# Create Vacancy
pickfixedatomspec = [ 1    # number of picked atoms in a cell
                      0 ] # index number of an atom to be picked
# Actually, which index number you choose doesn't matter
# due to the nature of Periodic Boundary Condition
removepickedatoms    # remove picked atoms
finalcnfile = makevac.cn writecn
eval # evaluate the potential of vacancy-formed crystal
#-----
#Plot Configuration
atomradius = 1.0 bondradius = 0.3 bondlength = 0
atomcolor = cyan highlightcolor = purple backgroundcolor = gray
bondcolor = red fixatomcolor = yellow
#hideatomenergy = [ 1 -6.725 -6 ]
energycolorbar = [ 1 -6.8 -6.55 ] highlightcolor = red
plot_select = 3 plot_highlight = [ 0 0 1 2 3 4 5 6 7 8 9 ]
plotfreq = 10
rotateangles = [ 0 0 0 1.5 ]
win_width = 600 win_height = 600
openwin alloccolors rotate saverot refreshnlist plot
#-----
#Conjugate-Gradient relaxation
conj_ftol = 1e-7 conj_fevalmax = 1000 conj_fixbox = 1
relax finalcnfile = relaxed.cn writecn
eval # evaluate vacancy formation energy after relaxation
sleep quit
```