Step by step Tutorial

Day-3

Phonons

講師：政治大學應用物理研究所楊志開教授
協助人員：葉學舫

Introduction

hfyeh@cluster:~> **cd phonon/**
hfyeh@cluster:~/phonon> **ls**
0-relaxation 1-supercell 2-forces 3-dispersion 4-thermo EXPAL INPHON phon

0-relaxation: to relax FCC bulk Al to ground state

1-supercell: to generate a 2x2x2 supercell based on Al-FCC primitive cell and generate displacement of ions inasmuch as non-zero force might occur.

2-forces: to calculate forces acting on each ion in the supercell.

3-dispersion: to derive dispersion curve

4-thermo: to calculate thermodynamic properties such as free energy, specific heat

EXPAL: phonon dispersion experimental data

phon: phonon program

INPHON: input information and parameters of phon

0-Relaxation

hfyeh@cluster:~/phonon> **cd 0-relaxation**
hfyeh@cluster:~/phonon/0-relaxation> **ls**
INCAR KPOINTS POSCAR POTCAR run.sh
hfyeh@cluster:~/phonon> **cat POSCAR**

```
Al
      3.9688275000
  0.500000000000000   0.500000000000000   0.000000000000000
  0.000000000000000   0.500000000000000   0.500000000000000
  0.500000000000000   0.000000000000000   0.500000000000000
   1
 Direct
  0.000000000000000   0.000000000000000   0.000000000000000
```

hfyeh@cluster:~/phonon/0-relaxation> **cat KPOINTS**

```
4x4x4
0
Monkhorst
4 4 4
0 0 0
```

Use 4x4x4 k-points for primitive cell, and 2x2x2 for super cell, which we'll see later

hfyeh@cluster:~/phonon/0-relaxation> **cat INCAR**

```
System = Al
ISMEAR = 1
SIGMA = 0.05
NSW = 50
ISIF = 7
IBRION = 2
```

Relax cell volume

Relax the bulk Al until it reaches its minimum energy and its corresponding lattice constant, then go to next section.

1-Generating super cell


```
hfyeh@cluster:~/phonon/0-relaxation> cd ../1-supercell/
hfyeh@cluster:~/phonon/1-supercell>  cp ../0-relaxation/POSCAR .
hfyeh@cluster:~/phonon/1-supercell>  ls
INPHON  phon  POSCAR
hfyeh@cluster:~/phonon/1-supercell> cat POSCAR
```

Relaxed POSCAR

```
Al
   3.96882750000000
     0.5094932521529604    0.5094932521529604    0.0000000000000000
     0.0000000000000000    0.5094932521529604    0.5094932521529604
     0.5094932521529604    0.0000000000000000    0.5094932521529604
   1
Direct
  0.0000000000000000  0.0000000000000000  0.0000000000000000
hfyeh@cluster:~/phonon/1-supercell> cat INPHON
# number of ions types and masses
    NTYPES = 1; MASS =26.98

# displacement of ions
    DISP = 25

# generate superlattice
    LSUPER = .T.;   NDIM = 2 2 2;
    DXSTART = 1 -1 1
```

Displacement = 1/25 angst.

LSUPER: phon will generate super cell
NDIM: super cell dimensions

Direction of displacement in lattice coordinate. In this case, the displacement is along x-axis. Program would choose a proper direction automatically if this tag is absent.

1-Generating super cell


```
hfyeh@cluster:~/phonon/1-supercell> ./phon >  phon.out
hfyeh@cluster:~/phonon/1-supercell>  ls
DISP  INPHON  phon phon.out  POSCAR  SPOSCAR
hfyeh@cluster:~/phonon/1-supercell>  cat SPOSCAR
          super cell
               3.9688275000
            1.018986504305921   1.018986504305921   0.000000000000000
            0.000000000000000   1.018986504305921   1.018986504305921
            1.018986504305921   0.000000000000000   1.018986504305921
             8
           Direct
            0.000000000000000   0.000000000000000   0.000000000000000
            0.500000000000000   0.000000000000000   0.000000000000000
            0.000000000000000   0.500000000000000   0.000000000000000
            0.500000000000000   0.500000000000000   0.000000000000000
            0.000000000000000   0.000000000000000   0.500000000000000
            0.500000000000000   0.000000000000000   0.500000000000000
            0.000000000000000   0.500000000000000   0.500000000000000
            0.500000000000000   0.500000000000000   0.500000000000000
hfyeh@cluster:~/phonon/1-supercell> cat DISP
          "   1  0.00494538 -0.00494538  0.00494538 " \
```

Blocks are output files

2x2x2 FCC-Al super cell

Displacement of first ion would be record in DISP

Displacement of first ion, in basis vector (fractional coordinate)

2-Calculating forces on ions

hfyeh@cluster:~/phonon/1-supercell> **cd ../2-forces/**
hfyeh@cluster:~/phonon/2-forces> **cp ../1-supercell/SPOSCAR ./POSCAR**
hfyeh@cluster:~/phonon/2-forces> **cp ../1-supercell/DISP .**
hfyeh@cluster:~/phonon/2-forces> **vi DISP**

```
"   1  0.00494538 -0.00494538  0.00494538" \
```

Type ‘yy’ to yank this line

hfyeh@cluster:~/phonon/2-forces> **vi POSCAR**

```
super cell
     3.9688275000
  1.018986504305921   1.018986504305921   0.000000000000000
  0.000000000000000   1.018986504305921   1.018986504305921
  1.018986504305921   0.000000000000000   1.018986504305921
   8
 Direct
  0.000000000000000   0.000000000000000   0.000000000000000
  0.500000000000000   0.000000000000000   0.000000000000000
  0.000000000000000   0.500000000000000   0.000000000000000
  0.500000000000000   0.500000000000000   0.000000000000000
  0.000000000000000   0.000000000000000   0.500000000000000
  0.500000000000000   0.000000000000000   0.500000000000000
  0.000000000000000   0.500000000000000   0.500000000000000
  0.500000000000000   0.500000000000000   0.500000000000000
```

Type ‘p’ to past the information you yanked before, then type ‘dd’ to delete this line.

One needs to move ions in super cell to calculate the induced force. Yank the lattice coordinate in DISP and replace to first ion position in POSCAR.

2-Calculating forces on ions

hfyeh@cluster:~/phonon/2-forces> **cat POSCAR**

The resultant POSCAR would be like this

```
super cell
3.9688275000
1.018986504305921   1.018986504305921   0.000000000000000
0.000000000000000   1.018986504305921   1.018986504305921
1.018986504305921   0.000000000000000   1.018986504305921
8
Direct
0.004945380000000  -0.00494538000000    0.004945380000000
0.500000000000000   0.000000000000000   0.000000000000000
0.000000000000000   0.500000000000000   0.000000000000000
0.500000000000000   0.500000000000000   0.000000000000000
0.000000000000000   0.000000000000000   0.500000000000000
0.500000000000000   0.000000000000000   0.500000000000000
0.000000000000000   0.500000000000000   0.500000000000000
0.500000000000000   0.500000000000000   0.500000000000000
```

hfyeh@cluster:~/phonon/2-forces> **cat KPOINTS**

```
2x2x2
0
Monkhorst
2 2 2
0 0 0
```

Use 2x2x2 k-points for super cell

hfyeh@cluster:~/phonon/2-forces> **cat INCAR**

```
System = Al
ISMEAR = 1
SIGMA = 0.05
NSW = 0
```

Run electron self-consistent loops only

2-Calculating force on ions

hfyeh@cluster:~/phonon/2-forces> **ls**
INCAR KPOINTS POSCAR POTCAR run.sh
hfyeh@cluster:~/phonon/2-forces> **qsub run.sh**
(wait)
hfyeh@cluster:~/phonon/2-forces> **vi OUTCAR**

Type '/FORCE' to search this line

…

POSITION			TOTAL-FORCE (eV/Angst)		
0.04000	4.04418	4.04418	-0.167093	0.000000	0.000000
2.02209	2.02209	0.00000	0.060648	0.036092	0.000000
0.00000	2.02209	2.02209	-0.029221	0.000000	0.000000
2.02209	4.04418	2.02209	0.060648	0.000000	-0.036092
2.02209	0.00000	2.02209	0.060648	0.000000	0.036092
4.04418	2.02209	2.02209	-0.029221	0.000000	0.000000
2.02209	2.02209	4.04418	0.060648	-0.036092	0.000000
4.04418	4.04418	4.04418	-0.017057	0.000000	0.000000
total drift:			0.004241	-0.000185	-0.000181

…

Put cursor on this line then type '8yy' to yank the following 8 lines

The block shows the forces on ions in Cartesian coordinate. It's clear that the first ion suffers a relatively large negative force in x-axis since we shifted it along positive x.

2-Calculating force on ions

hfyeh@cluster:~/phonon/2-forces> **vi FORCES**

Generate FORCES by yourself

```
1
 1  0.00494538 -0.00494538  0.00494538
-0.167093     0.000000     0.000000
 0.060648     0.036092     0.000000
-0.029221     0.000000     0.000000
 0.060648     0.000000    -0.036092
 0.060648     0.000000     0.036092
-0.029221     0.000000     0.000000
 0.060648    -0.036092     0.000000
-0.017057     0.000000     0.000000
```

Number of displacements

First displacement, which is printed in DISP

Block region in previous page

FORCES is used to calculate dispersion relation, for phon, the force unit is eV/Angst

3-Dispersion

Note here one should use undisplaced super cell POSACR

```
hfyeh@cluster:~/phonon/2-forces> cd ../3-dispersion
hfyeh@cluster:~/phonon/3-dispersion> cp ../1-supercell/SPOSCAR ./POSCAR
hfyeh@cluster:~/phonon/3-dispersion> cp ../2-forces/FORCES .
hfyeh@cluster:~/phonon/3-dispersion> cat INPHON
```

```
# number of ions types and masses
   NTYPES = 1;  MASS =26.98

# displacement of ions
  DISP = 25

# generate superlattice
   LSUPER = .F.; NDIM = 2 2 2;
   DXSTART = 1 -1 1

# q points section
   LRECIP = .F.
   ND = 3;  NPOINTS = 51
   QI = 0.0      0.0      0.0 \
        1.0      1.0      0.0 \
        0.0      0.0      0.0

   QF = 1.0      0.0      0.0 \
        0.0      0.0      0.0 \
        0.5      0.5      0.5
```

Turn off super cell generation (and phon will calculate dispersion relation)

If LRECIP=.T., QI and QF are in unit of reciprocal space lattice vectors; otherwise, they are in Cartesian coordinate.

Number of QI-QF sets and number of points between them.

The first QI-QF set on dispersion curve

3-Dispersion

hfyeh@cluster:~/phonon/3-dispersion> **ls**
FORCES INPHON phon POSCAR
hfyeh@cluster:~/phonon/3-dispersion> **./phon > phon.out**
hfyeh@cluster:~/phonon/3-dispersion> **ls**
DOS DOS.cm DOS.meV FORCES FREQ FREQ1 FREQ.cm INPHON phon phon.out POSCAR

Density of states in THz, cm^{-1}, and meV

Dispersion curve in THz, and in cm^{-1}

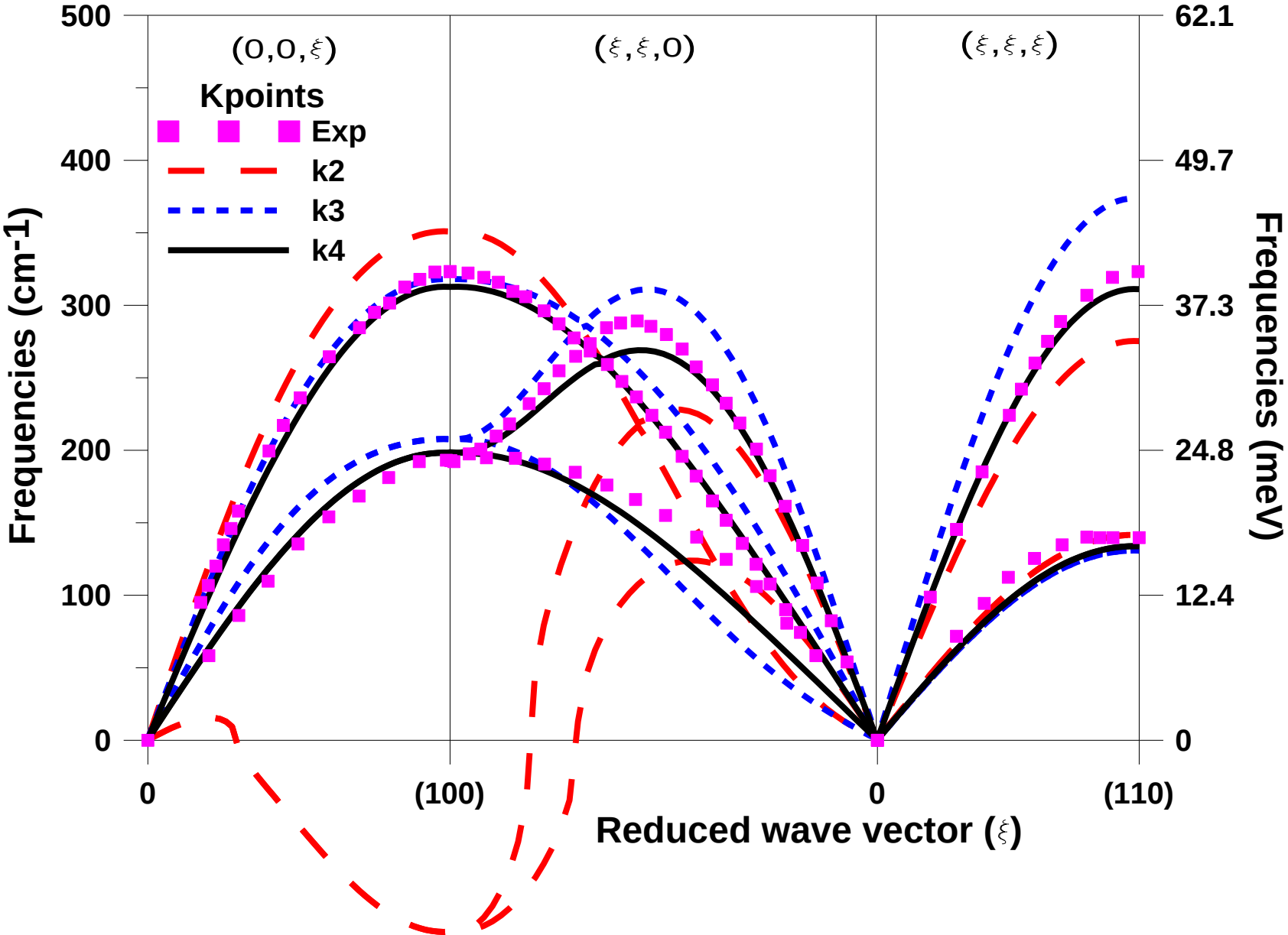
hfyeh@cluster:~/phonon/3-dispersion> **vi FREQ.cm**

0.00000000	-0.00001	-0.00001	-0.00001
0.02000000	4.55203	4.55203	10.65446
0.04000000	9.10731	9.10731	21.30137
0.06000000	13.66898	13.66898	31.93319
0.08000000	18.23998	18.23998	42.54230
0.10000000	22.82299	22.82299	53.12101
0.12000000	27.42028	27.42028	63.66153
0.14000000	32.03368	32.03368	74.15597
0.16000000	36.66447	36.66447	84.59628
…			

3 acoustic modes

Reciprocal spce length along the symmetry line your chosen

Dispersion curve



4-Thermodynamic properties

hfyeh@cluster:~/phonon/3-dispersion> **cd ../4-thermo/**
hfyeh@cluster:~/phonon/4-thermo> **cp ../3-dispersion/POSCAR .**
hfyeh@cluster:~/phonon/4-thermo> **cp ../3-dispersion/FORCES .**
hfyeh@cluster:~/phonon/4-thermo> **cat INPHON**

```
# number of ions types and masses
   NTYPES = 1;  MASS =26.98

# displacement of ions
  DISP = 25

# generate superlattice
   LSUPER = .F.;   NDIM = 2 2 2;
   DXSTART = 1 -1 1

# q points section
   LRECIP = .F.
   ND = 3;  NPOINTS = 51
   QI = 0.0       0.0       0.0 \
        1.0       1.0       0.0 \
        0.0       0.0       0.0

   QF = 1.0       0.0       0.0 \
        0.0       0.0       0.0 \
        0.5       0.5       0.5
```

(Next page)

4-Thermodynamic properties


```
# free energy calculation
   LFREE = .TRUE.; TEMPERATURE = 0
   LGAMMA = .True.
   QA=8; QB=8; QC=8
   PTEMP = 10 100
```

LFREE = .T., to turn on thermodynamic properties calculation.
TEMPERATURE = 0, initial temperature.

QA,QB and QC are the divisions for a Monkhorst-Pack special point grid generations. LGAMMA = .TRUE. means that the grid will pass through Γ.

Temperature increment, number of increments

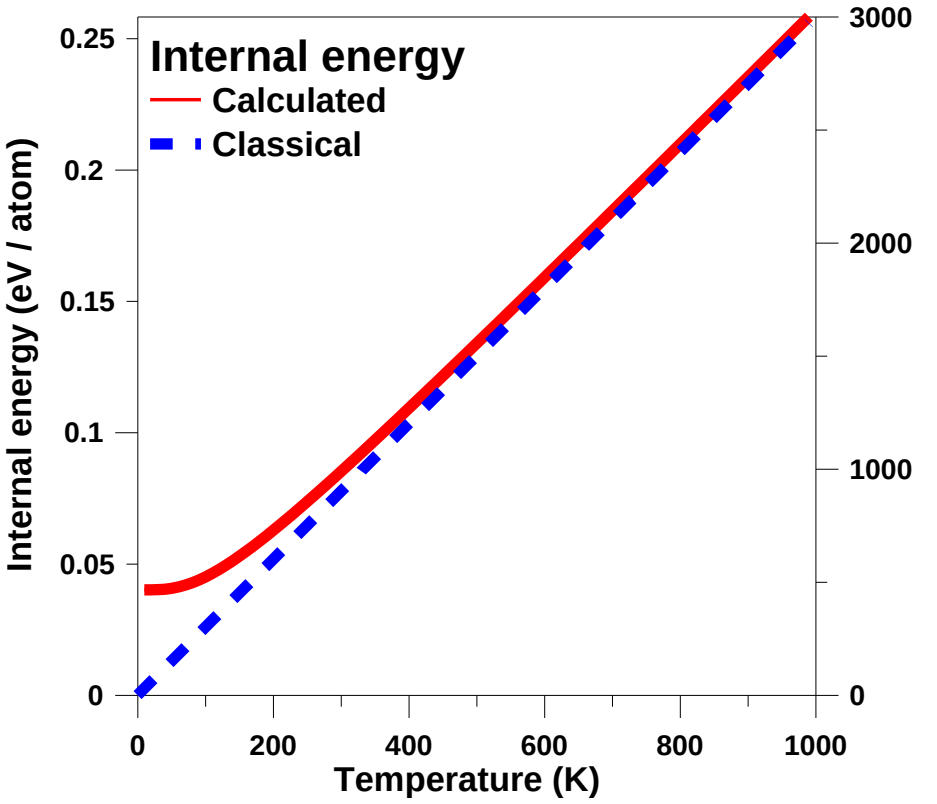
hfyeh@cluster:~/phonon/4-thermo> **ls**
FORCES INPHON phon POSCAR
hfyeh@cluster:~/phonon/4-thermo> **./phon > phon.out**
hfyeh@cluster:~/phonon/4-thermo> **ls**
DOS DOS.cm DOS.meV FORCES INPHON phon phon.out POSCAR QPOINTS THERMO

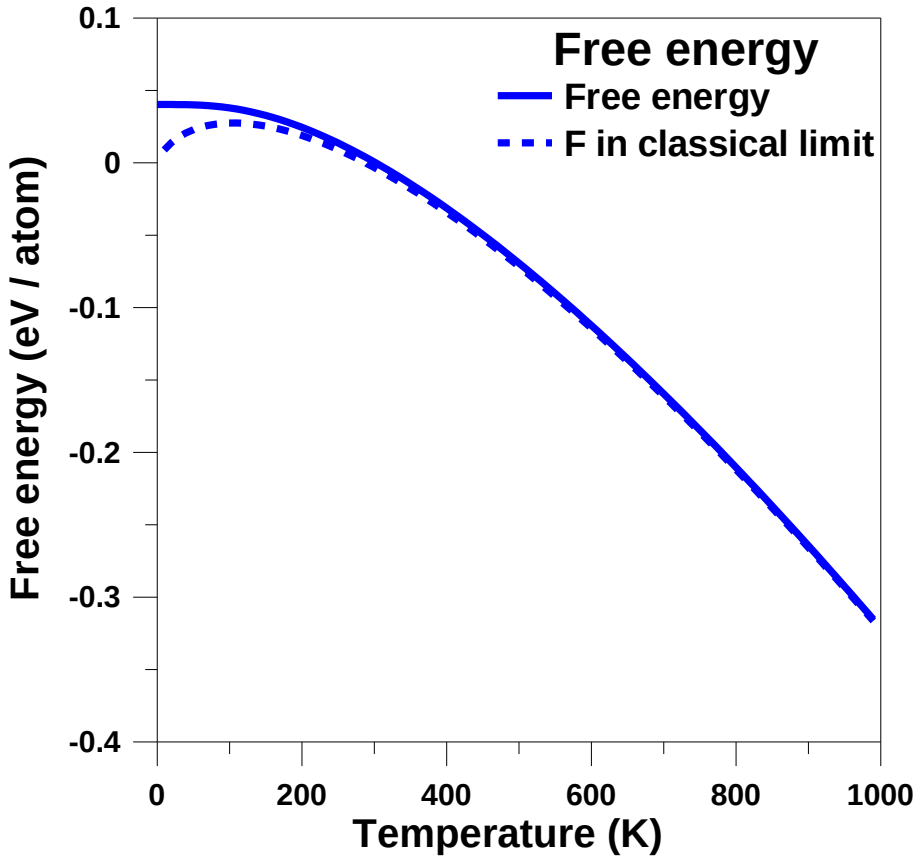
• 4-Thermodynamic properties

hfyeh@cluster:~/phonon/4-thermo> **vi THERMO**

# T(K)	E(eV/cell)	F(eV/cell)	Fc(eV/cell)	S(kB/cell)	Cv(kB/cell)
0.00	NaN	0.04112759	NaN	NaN	NaN
10.00	0.04112811	0.04112744	0.00879789	0.00077527	0.00248405
20.00	0.04113645	0.04112476	0.01401190	0.00678014	0.02129924
30.00	0.04117695	0.04111227	0.01787321	0.02501740	0.08243949
40.00	0.04129764	0.04107551	0.02085606	0.06444151	0.20873384
.....					

Temperature, internal energy, free energy, free energy in classical limit, entropy, and specific heat. Units are shown above, note the term ‘per cell’ means per primitive cell, which in our case is equivalent to per atom.


Internal energy
Calculated
Classical
Internal energy (eV / atom)
Internal energy (K / atom)
Temperature (K)
0.25
0.2
0.15
0.1
0.05
0
3000
2000
1000
0
0
200
400
600
800
1000


Free energy
Free energy
F in classical limit
Free energy (eV / atom)
Temperature (K)
0.1
0
-0.1
-0.2
-0.3
-0.4
0
200
400
600
800
1000

Entorpy and specific heat