

Elastic Constants and Mechanical Properties of Materials using DFT and VASP Software

Siby Thomas

Elastic constants are fundamental properties that play a crucial role in determining the mechanical stability of materials. In order to compute these properties using first-principles methods, such as Density Functional Theory (DFT), VASP software uses a finite difference scheme to generate the force constants matrix. This matrix is then utilized to compute the necessary elastic constants, such as bulk modulus (B), shear modulus (G), elastic modulus (E) and Poisson's ratio (ν), which are essential for characterizing the mechanical behavior of a material.

To ensure the mechanical stability of a given material, it must satisfy necessary and sufficient elastic stability criteria, which are different for different crystal systems (<http://dx.doi.org/10.1103/PhysRevB.90.224104>). These criteria are based on the elastic stiffness constants C_{ij} , which are calculated using DFT methods. **In the case of silicon, for example**, these constants are computed by applying small elastic strains to the equilibrium unit cell and then using the corresponding changes in energy to obtain a set of elastic constants $C_{\alpha\beta}$. The elastic constant tensors were calculated within the VASP software by performing finite distortions of the lattice and utilizing the relationship between stress and strain by Hooke's law, $\sigma_{ij} = C_{ijkl} \varepsilon_{ij}$, where C_{ijkl} represents the elastic constants.

Please see the attached INCAR, KPOINTS, POTCAR, POSCAR and OUTCAR. In the last portion of the OUTCAR, you can see TOTAL ELASTIC MODULI, as shown below.

Table 1:

TOTAL ELASTIC MODULI (kBar)

Direction	XX	YY	ZZ	XY	YZ	ZX

XX	1545.9969	560.1075	560.1075	0.0000	0.0000	0.0000
YY	560.1075	1545.9969	560.1075	0.0000	0.0000	0.0000
ZZ	560.1075	560.1075	1545.9969	0.0000	0.0000	0.0000
XY	0.0000	0.0000	0.0000	743.9285	0.0000	0.0000
YZ	0.0000	0.0000	0.0000	0.0000	743.9285	0.0000
ZX	0.0000	0.0000	0.0000	0.0000	0.0000	743.9285

Please note that X=1, Y=2, Z=3 and XX=11, YY=22, ZZ=33 (This is the standard notation in all the cases).

Figure 1.

$$C_{ijkl} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{pmatrix}$$

where 1 = xx, 2 = yy, 3 = zz, 4 = xz, 5 = yz, and 6 = xy.

If you compare Table 1 with Figure 1, you can see that $C_{11}=C_{22}=C_{33}=1545.9969$ kBar, which is equal to 154.599 GPa. This corresponds to bulk silicon in the cubic FCC format. The elastic constants, initially given in kBar, can be converted to GPa using a conversion tool such as <https://www.convertunits.com/from/kilobar/to/GPa>.

Note that for a symmetric elastic constants' tensor, there are at most 21 independent elements in the 6x6 matrix for a triclinic crystal, as shown in Figure 1. As the crystal symmetry increases, some of the matrix elements become related by symmetry, and the number of independent matrix elements is further reduced. Monoclinic systems have 13 independent elements, rhombohedral systems have 6 elements, hexagonal systems have 5, and cubic systems have only 3, as indicated in Table 1.

For mechanical stability, the elastic energy should always be positive, which is equivalent to the Born stability criterion that all the eigenvalues of the elastic stiffness matrix C should be positive. For symmetric systems, this condition can be expressed in terms of closed-form relationships between different elastic constants. The relevant relationships for the crystal classes of Ruthenium Carbides are provided in the reference (<http://dx.doi.org/10.1103/PhysRevB.90.224104>).

Cubic:

$$C_{11} > 0, C_{44} > 0, (C_{11} + 2C_{12}) > 0, (C_{11} - C_{12}) > 0$$

Rhombohedral I:

$$C_{11} > |C_{12}|, C_{44} > 0, (C_{11} + C_{12})C_{33} > 2C_{13}^2, (C_{11} - C_{12})C_{44} > 2C_{14}^2$$

Hexagonal:

$$C_{11} > |C_{12}|, \quad C_{44} > 0, \quad (C_{11} + C_{12})C_{33} > 2C_{13}^2$$

We can compute the bulk modulus, shear modulus, elastic modulus and Poisson's ratio using the Voigt-Reuss approximation, which is commonly used for the calculation of polycrystalline elastic moduli. For **cubic lattices**, there are three independent elastic constants C_{11} , C_{12} , and C_{44} . Then the bulk modulus (B) and shear modulus (G) using the Voigt (B_V and G_V) and Reuss approximations (B_R and G_R) are given as:

$$B_V = B_R = (C_{11} + 2C_{12})/3 \quad (1)$$

$$G_V = (C_{11} - C_{12} + 3C_{44})/5 \quad (2)$$

$$G_R = \frac{5(C_{11}-C_{12})C_{44}}{4C_{44}+3(C_{11}-C_{12})} \quad (3)$$

Similarly, the **trigonal/rhombohedral** systems have six independent elastic constants and are C_{11} , C_{12} , C_{13} , C_{14} , C_{33} , and C_{44} . Then

$$B_V = [2(C_{11} + C_{12}) + 4C_{13} + C_{33}]/9 \quad (4)$$

$$G_V = [C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{44} + 12C_{66}]/30 \quad (5)$$

$$C_{66} = (C_{11} - C_{12})/2 \quad (6)$$

$$B_R = \frac{[(C_{11}+C_{12})C_{33}-2C_{13}^2]}{[C_{11}+C_{12}+2C_{33}-4C_{13}]} \quad (7)$$

$$G_R = \frac{\frac{5}{2}\{[(C_{11}+C_{12})C_{33}-2C_{13}^2](C_{44}C_{66}-C_{14}^2)\}}{3B_V(C_{44}C_{66}-C_{14}^2)+[(C_{11}+C_{12})C_{33}-2C_{13}^2](C_{44}+C_{66})} \quad (8)$$

where B_V is given by Eq.(4) and C_{66} is given by Eq.(6).

In the case of an **orthorhombic** system, there are nine independent second order elastic constants which are C_{11} , C_{22} , C_{33} , C_{12} , C_{13} , C_{23} , C_{44} , C_{55} , and C_{66} . Then

$$B_V = \frac{1}{9}(C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) \quad (9)$$

$$G_V = \frac{1}{15} (C_{11} + C_{22} + C_{33} + 3C_{44} + 3C_{55} + 3C_{66} - C_{12} - C_{13} - C_{23}) \quad (10)$$

$$B_R = \frac{1}{(S_{11}+S_{22}+S_{33})+2(S_{12}+S_{13}+S_{23})} \quad (11)$$

$$G_R = \frac{15}{4(S_{11}+S_{22}+S_{33})-4(S_{12}+S_{13}+S_{23})+3(S_{44}+S_{55}+S_{66})} \quad (12)$$

Where the $S_{ij} = (C_{ij})^{-1}$ are the elastic compliance constants.

Then the effective bulk and shear moduli is the arithmetic average of the Voigt and Reuss bulk (B_V, B_R) and shear (G_V, G_R) moduli. Then the Hill approximation gives the average of the two:

$$B = B_H = (B_V + B_R)/2 \quad (13)$$

$$G = G_H = (G_V + G_R)/2 \quad (14)$$

From B and G values, Young's modulus Y and Poisson's ratio ν are calculated as:

$$Y = 9BG / (3B + G) \quad (15)$$

$$\nu = (3B - 2G)/[2(3B + G)] \quad (16)$$

This is a general approach and theoretical description of how to compute elastic constants for materials. For more information on computing elastic constants for 2D materials, please refer to our published papers

1. <https://doi.org/10.1039/D1CP05590A>;
2. <https://doi.org/10.1002/adts.202000250>;
3. <https://doi.org/10.1039/D0CP02973D>;
4. <https://doi.org/10.1016/j.carbon.2019.03.085>).

Task: Try to compute the elastic constants of diamond by yourself. To compute the elastic constants of diamond, we can use a Gamma centered KPOINTS and set IBRION=6 during the calculation. This will allow us to generate the force constants matrix, which can then be used to compute the necessary elastic constants such as bulk modulus, shear modulus, elastic modulus, and Poisson's ratio. It is important to verify that the results obtained from the computation match the expected values for diamond, to ensure that the calculation was performed correctly.

Additional Notes:

- For the calculation of total energy in bulk materials, it is recommended to use the tetrahedron method with Blöchl corrections (ISMEAR=-5). This method provides a good account for the electronic density of states (DOS). However, the method is not variational with respect to the partial occupancies, which can lead to errors of up to 5-10% in calculated forces and stress tensor for metals. For semiconductors and insulators, the forces are correct as the partial occupancies do not vary and are either zero or one.
- It is advised to avoid using ISMEAR>0 for semiconductors and insulators, as this can lead to incorrect results where the occupancies of some states might be smaller than 0 or larger than 1. For insulators, it is recommended to use ISMEAR=0 or ISMEAR=-5.
- The Gaussian smearing method usually provides reasonable results in most cases. If there is no a priori knowledge of the system, such as whether it is an insulator, semiconductor or metal, it is recommended to use Gaussian smearing ISMEAR=0 in combination with a small SIGMA=0.03-0.05.
- VASPKIT (<https://vaspkit.com/>) can also be used to automatically obtain elastic properties such as Bulk modulus, Shear modulus, Poisson's ratio, etc. from the OUTCAR file of VASP.

VASP INPUT files for the elastic constants' computation of Si

• POSCAR

Si8

```
1.0000000000000000
  5.4684574509260617    0.0000000000000000    0.0000000000000003
  0.0000000000000009    5.4684574509260617    0.0000000000000003
 -0.0000000000000000    0.0000000000000000    5.4684574509260617
```

Si

8

Direct

```
0.7500000000000000    0.7500000000000000    0.2500000000000000
0.0000000000000000    0.5000000000000000    0.5000000000000000
0.7500000000000000    0.2500000000000000    0.7500000000000000
```

```

0.000000000000000000  0.000000000000000000  0.000000000000000000
0.250000000000000000  0.750000000000000000  0.750000000000000000
0.500000000000000000  0.500000000000000000  0.000000000000000000
0.250000000000000000  0.250000000000000000  0.250000000000000000
0.500000000000000000  0.000000000000000000  0.500000000000000000

```

- **KPOINTS**

Si-elastic

0

Gamma

5 5 5

0 0 0

- **INCAR**

Note: During Elastic constants calculation, after relaxation, we should made changes in INCAR as:

```

IBRION = 6
ISIF = 3
POTIM = 0.01
and comment
#NSW = 200

```

and also chose Gamma centred KPOINTS, as shown above.

```

SYSTEM                = Si
#1 Startparameter for this Run
NWRITE                = 2          ! LPETIM=F      write-flag & timer
ISTART                = 0          ! job       : 0-new  1-contEcut  2-sameBS
INIWAV                = 1          ! 0-jellium  1-random
IWAVPR               = 1          ! prediction: 0-non 1-charg 2-wave 3-comb
ICHARG                = 2          ! 0-from WF  1-from CHGCAR  2-from atom
11-12-fixed

```

LWAVE = .FALSE. ! determines whether the wavefunctions are
written to the WAVECAR file

LCHARG = .FALSE.

#2 Electronic Relaxation 1

NELM = 100 ! number of iterations

EDIFF = 1E-05 ! stopping-criterion for ELM

BMIX = 3.00 ! sets the cutoff wave vector for Kerker
mixing for the magnetization density

ENCUT = 500 ! Cut-Off Energy

#3 Electronic Relaxation 1

IALGO = 38 ! algorithm for the e-relax

LDIAG = T ! sub-space diagonalisation

LREAL = auto ! real-space projection

PREC = Accurate ! accuracy

NBANDS = 30 ! number of bands for diagonalization

#4 Ionic Relaxation

#NSW = 200 ! number of steps for IOM

NBLOCK = 1 ! inner block

KBLOCK = 10 ! outer block

IBRION = 6 ! ionic relax: 0-MD 1-quasi-New 2-CG

ISIF = 3 ! ion&cell relax: 0-MD 2-ion&stress 3-
ion&cell&stress

ISYM = 2 ! switch symmetry stuff ON (1 or 2) or
OFF (0)

SYMPREC = 1e-6 !

LCORR = T ! Harris-correction to forces

EDIFFG = -1E-03 ! Criterion for geom opt (eV/Ang)

```
POTIM          = 0.01      ! time-step for ionic motion (fs)
SMASS          = 3.00      ! Nose mass-parameter (am)

#5 DOS related values

ISMEAR         = 0         ! Broadening methode -5-tet -1-fermi 0-
gaus 1-mp 2-mp2

SIGMA          = 0.05      ! Broadening in eV
LORBIT         = 11       ! l-decomposed DOS

#11 vdWcorrections

#IVDW          = 12       !
PSTRESS        = 0.0
NPAR           = 4
```