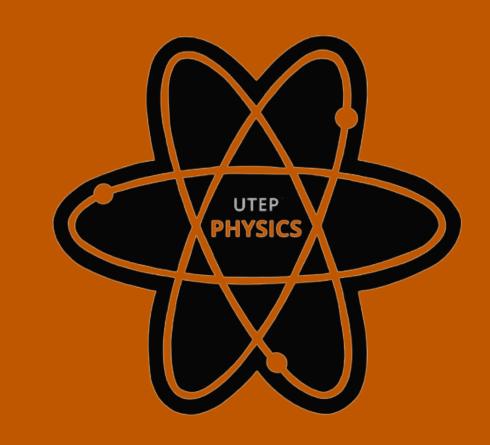


# Novel procedure to construct the displacement matrix of the atoms with thermal vibrations in a face-centered cubic crystal.



Diego Juarez <sup>1</sup>, Jorge Munoz<sup>1</sup>

<sup>1</sup>Department of Physics, The University of Texas at El Paso.

### **Abstract**

The potential energy  $\Phi$  of a crystal can be expanded in a Taylor series of the atomic displacements about their equilibrium positions  $\vec{u}_{\ell\kappa}^a = 0$ , where  $\ell$  is the unit cell index and  $\kappa$  is an atom in that unit cell. Orthogonal directions are indexed by a, b, and c, so:

$$\Phi = \Phi_0 + \sum_{a\ell\kappa} \Phi^a_{\ell\kappa} u^a_{\ell\kappa} + \frac{1}{2} \sum_{a\ell\kappa} \sum_{b\ell'\kappa'} \Phi^{ab}_{\ell\kappa\ell'\kappa'} u^a_{\ell\kappa} u^b_{\ell'\kappa'} + \dots , \qquad (1)$$

The second order term of Eq. 1 contains the displacements from equilibrium of pairs of atoms, and the coefficients can be accommodated in  $\hat{\Phi}$ , the  $3\times 3$  matrix of force constants for those pairs of atoms. The structure of  $\hat{\Phi}$  depends of the symmetry of the crystal. The force constants depend on the physics of the interatomic interactions, and in the current application we extracted them from molecular dynamics simulations. In this talk, we will describe how we build a displacement matrix  $\hat{\mathcal{U}}$  that minimizes the number of unknowns and hence the computational cost of computing the lattice dynamics.

We exploit the symmetries of the crystal and introduce two auxiliary matrices which separate the diagonal and off-diagonal components of the displacements:

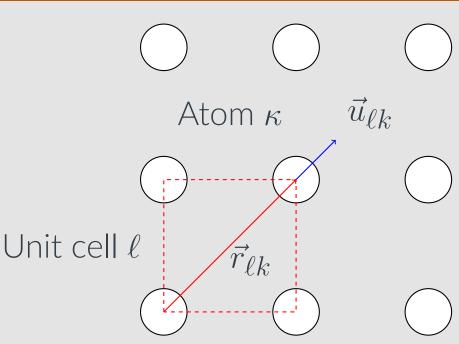
$$m_1 = \begin{pmatrix} U_{nx} & 0 & 0 \\ 0 & U_{ny} & 0 \\ 0 & 0 & U_{nz} \end{pmatrix} \tag{2}$$

$$m_2 = \begin{pmatrix} 0 & U_{ny} & U_{nz} \\ U_{nx} & 0 & U_{nz} \\ U_{nx} & U_{nz} & 0 \end{pmatrix} \tag{3}$$

### with n as time step.

We define matrix operations involving  $m_1$  and  $m_2$  for each of the five nearest neighbors to populate  $\hat{\mathcal{U}}$ , which has number of force constants (FC) rows and three times the number of atoms (3N) columns. The matrix multiplication of the pseudo-inverse of  $\hat{\mathcal{U}}$  times the forces acting on each orthogonal direction of each atom obtained from the physics simulations is the vector of force constants  $\hat{\mathcal{P}}$ . Finally, the dynamical matrix  $\hat{\mathcal{D}}$ , from which the lattice dynamics of the system are extracted, is obtained by taking the Fourier transforms of appropriate force constant matrices built using the elements of  $\hat{\mathcal{P}}$ . We will show results for face-centered cubic nickel.

# Statement of the problem



The equations of motion for the lattice follows (analogous to Hooke's law):

$$m_{\kappa}\ddot{\vec{u}}_{\ell\kappa}(t) = -\sum_{\ell'\kappa'} \underline{\Phi}_{\ell\kappa\ell'\kappa'}^{a,b} \vec{u}_{\ell'\kappa'}(t), \qquad (4)$$

where the dynamical matrix is defined as:

$$\underline{\mathbf{D}}_{\kappa\kappa'}(\vec{k}) = \frac{1}{\sqrt{m_{\kappa}m_{\kappa'}}} \sum_{\ell'} \underline{\Phi}_{0\kappa\ell'\kappa'}^{a,b,c} \exp\left(i\vec{k} \cdot (\vec{r}_{\ell'} - \vec{r}_0)\right), \tag{9}$$

yielding the following eigenvalue equation:

$$\underline{\mathbf{D}}(\vec{k})\vec{e}_{\kappa j}(\vec{k}) = \omega_{\vec{k}j}^2 \vec{e}_{\kappa j}(\vec{k}). \tag{6}$$

This corresponds to the dispersion relation for the crystal structure.

From equation 4, we can rewrite it as;

$$\hat{\mathcal{F}} = -\hat{\Phi} \, \hat{\mathcal{U}},\tag{7}$$

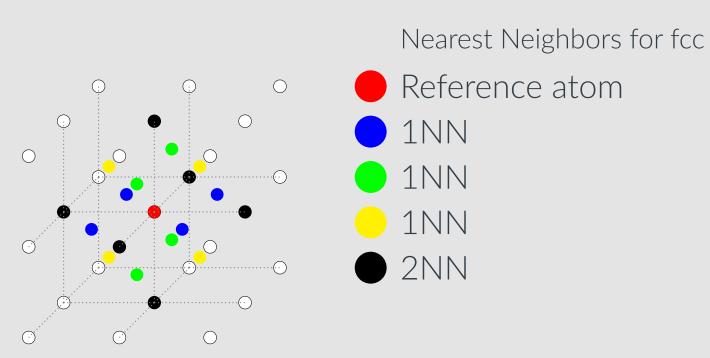
Where  $\hat{\mathcal{F}}$  is a vector of the forces (obtained from MD),  $\hat{\Phi}$  is the  $3 \times 3$  matrix of force constants for pairs of atoms (computed with HELD) and  $\hat{\mathcal{U}}$  is our **displacement matrix**.

### **Symmetries**

To look into the symmetries, lets first see which are the nearest neighbors of fcc:

Nearest Neighbors	1NN	2NN	3NN	4NN	5NN
Position $(\hat{p} = \frac{1}{2}a[x, y, z])$	[011]	[200]	[211]	[022]	[310]
Distance $(\frac{1}{2}a)$	$\sqrt{2}$	$\sqrt{4}$	$\sqrt{6}$	$\sqrt{8}$	$\sqrt{10}$
Frequency	12	6	24	12	24

Table 1. Nearest Neighbors, position, Distance and Frequency



With these considerations, we can classify the displacements of each atom according to its five distinct nearest neighbors. For each of these neighbors, the arrangement of the force constant matrix  $\hat{\Phi}$  will be different. Below are the force constant matrices for each nearest neighbor (ONN to 5NN)

ONN: 
$$\begin{pmatrix} \alpha_0 & 0 & 0 \\ 0 & \alpha_0 & 0 \\ 0 & 0 & \alpha_0 \end{pmatrix}$$
 1NN:  $\begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \beta_1 & \gamma_1 \\ 0 & \gamma_1 & \beta_1 \end{pmatrix}$  2NN:  $\begin{pmatrix} \alpha_2 & 0 & 0 \\ 0 & \beta_2 & 0 \\ 0 & 0 & \beta_2 \end{pmatrix}$  3NN:  $\begin{pmatrix} \alpha_3 & \gamma_3 & \gamma_3 \\ \gamma_3 & \beta_3 & \delta_3 \\ \gamma_3 & \delta_3 & \beta_3 \end{pmatrix}$  4NN:  $\begin{pmatrix} \alpha_4 & 0 & 0 \\ 0 & \beta_4 & \gamma_4 \\ 0 & \gamma_4 & \beta_4 \end{pmatrix}$  5NN:  $\begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \beta_5 & \gamma_5 \\ 0 & \gamma_5 & \delta_5 \end{pmatrix}$ 

For example for 5th nearest neighbor their 6 permutation and 4 sign combinations are:

ef/Rot		Rot(x-y)	Rot(x-z)	Rot(y-z)	Rot(z-x-y)	Rot(y-z-x)
	[310]	[130]	[013]	[301]	[031]	[103]
Refl(x)	[-310]	[-130]	[0-13]	[-301]	[0-31]	[-103]
efl(x,y)	[-3-10]	[-1-30]	[0-1-3]	[-30-1]	[0-3-1]	[-10-3]
Refl(v)	[3-10]	[1-30]	[01-3]	[30-1]	[03-1]	[10-3]

Table 2. 24 Permutations of positions

Ref/Rot		Rot(x-y)	Rot(x-z)	Rot(y-z)	Rot(z-x-y)	Rot(y-z-x)
	$ \begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \beta_5 & \gamma_5 \end{pmatrix} $	$ \begin{pmatrix} \beta_5 & 0 & \gamma_5 \\ 0 & \alpha_5 & 0 \end{pmatrix} $	$ \begin{pmatrix} \delta_5 & \gamma_5 & 0 \\ \gamma_5 & \beta_5 & 0 \end{pmatrix} $	$ \begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \delta_5 & \gamma_5 \end{pmatrix} $	$ \begin{pmatrix} \delta_5 & 0 & \gamma_5 \\ 0 & \alpha_5 & 0 \end{pmatrix} $	$\begin{pmatrix} \delta_5 & 0 & \gamma_5 \\ 0 & \alpha_5 & 0 \end{pmatrix}$
	$\begin{pmatrix} 0 & \gamma_5 & \delta_5 \end{pmatrix}$	$\begin{pmatrix} \gamma_5 & 0 & \delta_5 \end{pmatrix}$	$ \begin{bmatrix} \begin{pmatrix} \gamma_3 & \beta_3 & 0 \\ 0 & 0 & \gamma_5 \end{pmatrix} $	$\begin{pmatrix} 0 & \gamma_5 & \beta_5 \end{pmatrix}$	$\begin{pmatrix} \gamma_5 & 0 & \beta_5 \end{pmatrix}$	$\begin{pmatrix} \gamma_5 & 0 & \beta_5 \end{pmatrix}$
D ((/)	$\begin{pmatrix} \alpha_5 & 0 & 0 \end{pmatrix}$	$\left(\begin{array}{cccc} \beta_5 & 0 & -\gamma_5 \end{array}\right)$	$\left(\begin{array}{cccc} \delta_5 & -\gamma_5 & 0 \end{array}\right)$	$\left(\begin{array}{ccc} \alpha_5 & 0 & 0 \end{array}\right)$	$\int \delta_5  0  -\gamma_5$	$\left(\begin{array}{cccc} \delta_5 & 0 & -\gamma_5 \end{array}\right)$
Refl(x)	$ \left( \begin{array}{ccc} 0 & \beta_5 & \gamma_5 \\ 0 & \gamma_5 & \delta_5 \end{array} \right) $	$\left[\begin{array}{ccc} 0 & \alpha_5 & 0 \\ -\gamma_5 & 0 & \delta_5 \end{array}\right]$	$\begin{bmatrix} -\gamma_5 & \beta_5 & 0 \\ 0 & 0 & \gamma_5 \end{bmatrix}$	$ \left[ \begin{array}{ccc} 0 & \delta_5 & \gamma_5 \\ 0 & \gamma_5 & \beta_5 \end{array} \right] $	$\left[\begin{array}{ccc} 0 & \alpha_5 & 0 \\ -\gamma_5 & 0 & \beta_5 \end{array}\right]$	$\left[ \begin{array}{ccc} 0 & \alpha_5 & 0 \\ -\gamma_5 & 0 & \beta_5 \end{array} \right]$
Refl(x,y)	$ \begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \beta_5 & -\gamma_5 \\ 0 & -\gamma_5 & \delta_5 \end{pmatrix} $	$ \begin{pmatrix} \beta_5 & 0 & -\gamma_5 \\ 0 & \alpha_5 & 0 \\ -\gamma_5 & 0 & \delta_5 \end{pmatrix} $	$ \begin{pmatrix} \delta_5 & \gamma_5 & 0 \\ \gamma_5 & \beta_5 & 0 \\ 0 & 0 & \gamma_5 \end{pmatrix} $	$ \begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \delta_5 & -\gamma_5 \\ 0 & -\gamma_5 & \beta_5 \end{pmatrix} $	$ \begin{pmatrix} \delta_5 & 0 & -\gamma_5 \\ 0 & \alpha_5 & 0 \\ -\gamma_5 & 0 & \beta_5 \end{pmatrix} $	$ \begin{pmatrix} \delta_5 & 0 & -\gamma_5 \\ 0 & \alpha_5 & 0 \\ -\gamma_5 & 0 & \beta_5 \end{pmatrix} $
Refl(y)	$ \begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \beta_5 & -\gamma_5 \\ 0 & -\gamma_5 & \delta_5 \end{pmatrix} $	$\begin{pmatrix} \beta_5 & 0 & \gamma_5 \\ 0 & \alpha_5 & 0 \\ \gamma_5 & 0 & \delta_5 \end{pmatrix}$	$ \begin{pmatrix} \delta_5 & -\gamma_5 & 0 \\ -\gamma_5 & \beta_5 & 0 \\ 0 & 0 & \gamma_5 \end{pmatrix} $	$ \begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \delta_5 & -\gamma_5 \\ 0 & -\gamma_5 & \beta_5 \end{pmatrix} $	$\begin{pmatrix} \delta_5 & 0 & \gamma_5 \\ 0 & \alpha_5 & 0 \\ \gamma_5 & 0 & \beta_5 \end{pmatrix}$	$\begin{pmatrix} \delta_5 & 0 & \gamma_5 \\ 0 & \alpha_5 & 0 \\ \gamma_5 & 0 & \beta_5 \end{pmatrix}$

Table 3. 24 Permutations of force constants matrices

## Constructing $\hat{\mathcal{U}}$

Starting with a zero matrix with the follow structure:

where FC = number of force constants 17 in our case (BCC), n = number of atoms, in reality what we are constructing is a tensor of  $3n \times FC \times ts$ , where ts is the time step of each simulation, but we are focus in how we construct this matrix per just one time step.

To fill this matrix we used the next matrix operation applied to the auxiliary matrices  $m_1$  and  $m_2$ 

$$ext_{diag} \begin{bmatrix} \begin{pmatrix} U_{nx} & 0 & 0 \\ 0 & U_{ny} & 0 \\ 0 & 0 & U_{nz} \end{pmatrix} \end{bmatrix} = \begin{pmatrix} U_{nx} \\ U_{ny} \\ U_{nz} \end{pmatrix}, \quad sum_{rows} \begin{bmatrix} \begin{pmatrix} 0 & U_{ny} & U_{nz} \\ U_{nx} & 0 & U_{nz} \\ U_{nx} & U_{y} & 0 \end{pmatrix} \end{bmatrix} = \begin{pmatrix} U_{ny} + U_{nz} \\ U_{nx} + U_{nz} \\ U_{nx} + U_{ny} \end{pmatrix}$$

## Constructing $\hat{\mathcal{U}}$

**Zeroth nearest neighbor:** In this case we only applied the first operation  $ext_{diag}$  per time step filling the first column from the matrix  $\hat{\mathcal{U}}$ .

First and fourth nearest neighbor: In this case we have two different force constants,  $\alpha_1$ ,  $\beta_1$  and  $\gamma_1$  and 12 nearest neighbors with its different force constant matrix; lets begin with an matrix m1r which is initialized as a zero matrix of size  $3 \times 2$ :

$$m1r = \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{pmatrix}$$

If the atoms are in the same axis, that means x=y, x=z, or z=y, we add both displacement components  $U_{nx}$  and  $U_{ny}$ ,  $U_{nx}$  and  $U_{nz}$ , or  $U_{nz}$  and  $U_{ny}$  respectively, in the second column of  $\hat{\mathcal{U}}$ , while the remaining component is placed in the first column. So for example if the ideal distance equals to (101), m1r will be:  $\begin{pmatrix} 0 & U_{nx} \\ U_{ny} & 0 \\ 0 & U_{nx} \end{pmatrix}$ .

That was for the two first force constant for the third one, we use the same condition, so if  $x \neq y \neq z$  but y = z, we convert the first column and row of m2 in zeros and apply the matrix operation  $sum_{row}$ , finally adding this to the fourth column of  $\hat{\mathcal{U}}$ .

**Second nearest neighbor:** For this nearest neighbor we have two force constants elements  $\alpha_2$  and  $\beta_2$ , therefore to fill the column fifth and sixth of  $\hat{\mathcal{U}}$  we use the same procedure as for the previous  $\alpha_1$  and  $\beta_1$  force constants elements.

**Thrid nearest neighbors:** For the two first nearest neighbors  $\alpha_3$  and  $\beta_3$  is the same procedure as before so we fill the column 7 and 8, however for the next two force constants  $\gamma_3$  and  $\delta_3$  we start with a zero matrix,

$$m2r = \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{pmatrix}$$

If ideal distance equal to (211):

Ite 1. Set  $m2r[0,0] = U_{ny} + U_{nz}$  (sum of the first row of  $m_2$ );

Ite2. Set  $m2r[1,0] = U_{nx}$  and  $m2r[2,0] = U_{nx}$  from  $m_2[1,0]$  and  $m_2[2,0]$ ;

Ite 3. Set  $m2r[1,1] = U_{nz}$  and  $m2r[2,1] = U_y$  from  $m_2[1,2]$  and  $m_2[2,1]$ .

Thus, the resulting m2r is:  $\begin{pmatrix} U_{ny} + U_{nz} & 0 \ U_{nx} & U_{nz} \ U_{nx} & U_{y} \end{pmatrix}$ 

**Fifth Nearest Neighbor:** For the first three force constants, refer to Table 3. The arrangement of the three diagonal force constant elements depends on (xyz); thus, we can classify each of these three using matrix  $m_1$  and place them in their corresponding columns of  $\hat{\mathcal{U}}$ . and for the last force constant element we use the same procedure as for the 1NN.

With those classification we constructed the displacement matrix:

# Results

Second nearest neighbors, six force constants:

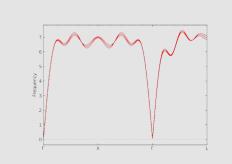


Figure 1. Temperature: 300K, lattice parameter: 3.52

Fifth nearest neighbors, seventeen force constants:

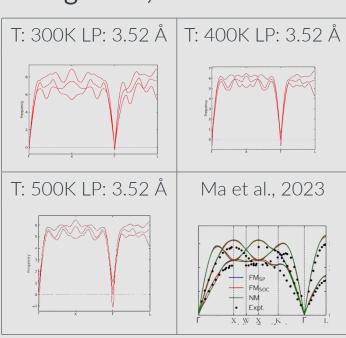


Table 4. Curves Dispersion for different temperatures and experimental data.

Force Constant	Value(eV/ Å <sup>2</sup> )
$\alpha_0$	9.33638127
$\alpha_1$	-0.7829288
$\beta_1$	-0.7861299
$\gamma_1$	-0.2772958
$\alpha_2$	0.07476799
$\beta_2$	-0.1673495

Force Constant	Value (eV/ Ų)
$\alpha_0$	9.187305888384765
$\alpha_1$	-0.213400041
$\beta_1$	-1.049554545
$\gamma_1$	-0.914702001
$\alpha_2$	0.23236519395809782
$\beta_2$	-0.14958012
$\alpha_3$	0.10811242708759967
$\beta_3$	0.1015043959192274
$\gamma_3$	0.067423216
$\delta_3$	-0.055964916
$\alpha_4$	0.007509247
$eta_4$	-0.27854021
$\gamma_4$	-0.274360198
$\alpha_5$	-0.013389585
$eta_5$	-0.001254429
$\gamma_5$	0.002723937
$\delta_5$	0.002916544