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

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Abstract

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

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

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 3×3 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:

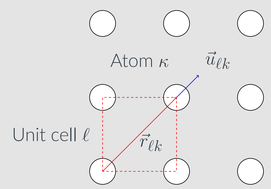
$$m_1 = \begin{pmatrix} U_{nx} & 0 & 0 \\ 0 & U_{ny} & 0 \\ 0 & 0 & U_{nz} \end{pmatrix} \tag{2}$$

and

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

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):

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

where the dynamical matrix is defined as:

$$\underline{\mathrm{D}}_{\kappa\kappa'}(\vec{k}) = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{\ell'} \Phi^{a,b,c}_{0\kappa\ell'\kappa'} \exp\left(i\vec{k} \cdot (\vec{r}_{\ell'} - \vec{r}_0)\right) , \tag{5}$$

yielding the following eigenvalue equation:

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

This corresponds to the dispersion relation for the crystal structure.
From equation 4, we can rewrite it as;

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

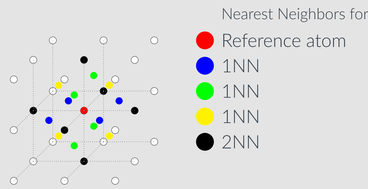
Where $\hat{\mathcal{F}}$ is a vector of the forces (obtained from MD), $\hat{\Phi}$ is the 3×3 matrix of force constants for pairs of atoms (computed with HELD) and $\hat{\mathcal{U}}$ is our **displacement matrix**.

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 $\hat{\Phi}$ wil be different. Below are the force constant matrices for each nearest neighbor (0NN to 5NN)

0NN: $\begin{pmatrix} \alpha_0 & 0 & 0 \\ 0 & \alpha_0 & 0 \\ 0 & 0 & \alpha_0 \end{pmatrix}$ 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: $\begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \beta_5 & \gamma_5 \\ 0 & \gamma_5 & \beta_5 \end{pmatrix}$

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

Ref/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]
Refl(x,y)	[-3-10]	[-1-30]	[0-1-3]	[-30-1]	[0-3-1]	[-10-3]
Refl(y)	[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)
	$\begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \beta_5 & \gamma_5 \\ 0 & \gamma_5 & \delta_5 \end{pmatrix}$	$\begin{pmatrix} \beta_5 & 0 & \gamma_5 \\ 0 & \alpha_5 & 0 \\ \gamma_5 & 0 & \delta_5 \end{pmatrix}$	$\begin{pmatrix} \delta_5 & \gamma_5 & 0 \\ \gamma_5 & \beta_5 & 0 \\ 0 & 0 & \gamma_5 \end{pmatrix}$	$\begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \delta_5 & \gamma_5 \\ 0 & \gamma_5 & \beta_5 \end{pmatrix}$	$\begin{pmatrix} \delta_5 & 0 & \gamma_5 \\ 0 & \alpha_5 & 0 \\ \gamma_5 & 0 & \beta_5 \end{pmatrix}$	$\begin{pmatrix} \beta_5 & 0 & \gamma_5 \\ 0 & \alpha_5 & 0 \\ \gamma_5 & 0 & \beta_5 \end{pmatrix}$
Refl(x)	$\begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \beta_5 & \gamma_5 \\ 0 & \gamma_5 & \delta_5 \end{pmatrix}$	$\begin{pmatrix} \beta_5 & 0 & -\gamma_5 \\ 0 & \alpha_5 & 0 \\ -\gamma_5 & 0 & \delta_5 \end{pmatrix}$	$\begin{pmatrix} \delta_5 & -\gamma_5 & 0 \\ -\gamma_5 & \beta_5 & 0 \\ 0 & 0 & \gamma_5 \end{pmatrix}$	$\begin{pmatrix} \alpha_5 & 0 & 0 \\ 0 & \delta_5 & \gamma_5 \\ 0 & \gamma_5 & \beta_5 \end{pmatrix}$	$\begin{pmatrix} \delta_5 & 0 & -\gamma_5 \\ 0 & \alpha_5 & 0 \\ -\gamma_5 & 0 & \beta_5 \end{pmatrix}$	$\begin{pmatrix} \delta_5 & 0 & -\gamma_5 \\ 0 & \alpha_5 & 0 \\ -\gamma_5 & 0 & \beta_5 \end{pmatrix}$
Refl(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:

$$\hat{\mathcal{U}} = \begin{pmatrix} 0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0 \\ 0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0 \\ 0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0 \\ \vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots\,\vdots \\ 0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0\,0 \\ \alpha_0\,\alpha_1\,\beta_1\,\gamma_1\,\alpha_2\,\beta_2\,\alpha_3\,\beta_3\,\gamma_3\,\delta_3\,\alpha_4\,\beta_4\,\gamma_4\,\alpha_5\,\beta_5\,\gamma_5\,\delta_5 \end{pmatrix}_{3n \times FC}$$

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 auxilary matrices m_1 and m_2

$$ext_{diag}\left[\begin{pmatrix} U_{nx} & 0 & 0 \\ 0 & U_{ny} & 0 \\ 0 & 0 & U_{nz} \end{pmatrix}\right] = \begin{pmatrix} U_{nx} \\ U_{ny} \\ U_{nz} \end{pmatrix}, \quad sum_{rows}\left[\begin{pmatrix} 0 & U_{ny} & U_{nz} \\ U_{nx} & 0 & U_{nz} \\ U_{nx} & U_y & 0 \end{pmatrix}\right] = \begin{pmatrix} U_{ny} + U_{nz} \\ U_{nx} + U_{nz} \\ U_{nx} + U_{ny} \end{pmatrix}$$

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, α_1, β_1 and γ_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 3×2:

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

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: $\begin{pmatrix} 0 & U_{nx} \\ U_{ny} & 0 \\ 0 & U_{nz} \end{pmatrix}$.
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 α_2 and β_2, therefore to fill the column fifth and sixth of $\hat{\mathcal{U}}$ we use the same procedure as for the previous α_1 and β_1 force constants elements.
Thrid nearest neighbors: For the two first nearest neighbors α_3 and β_3 is the same procedure as before so we fill the column 7 and 8, however for the next two force constants γ_3 and δ_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:

$$\hat{\mathcal{U}} = \begin{pmatrix} U_{1x} & U_{1x} & (U_{1y}+U_{1z}) & U_{nx} & 0 & U_{nx} & 0 & U_{nz} & U_{1x} & U_{1x} & (U_{1y}+U_{1z}) & U_{nx} & 0 & U_{nx} \\ U_{1y} & U_{1y} & (U_{1x}+U_{1z}) & 0 & U_{ny} & 0 & U_{ny} & U_{1y} & U_{1y} & (U_{1x}+U_{1z}) & 0 & U_{ny} & 0 & U_{ny} \\ U_{1z} & U_{1z} & (U_{1x}+U_{1y}) & 0 & U_{nz} & 0 & U_{nz} & U_{nz} & U_{1z} & U_{1z} & (U_{1x}+U_{1y}) & 0 & U_{nz} & 0 \\ U_{nz} & U_{nz} & & & & & & & & & & & & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ U_{nz} & U_{nz} & (U_{nx}+U_{1y}) & U_{nz} & U_{nz} & (U_{nx}+U_{1y}) & U_{nz} & U_{nz} & (U_{nx}+U_{1y}) & U_{nz} & U_{nz} & (U_{nx}+U_{1y}) & U_{nz} & U_{nz} \end{pmatrix}$$

Results

Second nearest neighbors, six force constants:

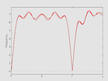


Figure 1. Temperature: 300K, lattice parameter: 3.52

Force Constant	Value(eV/ Å^2)
α_0	9.33638127
α_1	-0.7829288
β_1	-0.7861299
γ_1	-0.2772958
α_2	0.07476799
β_2	-0.1673495

Fifth nearest neighbors, seventeen force constants:

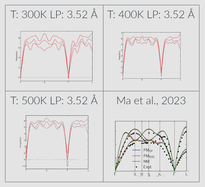


Table 4. Curves Dispersion for different temperatures and experimental data.

Force Constant	Value (eV/ Å^2)
α_0	9.187305888384765
α_1	-0.213400041
β_1	-1.049554545
γ_1	-0.914702001
α_2	0.23236519395809782
β_2	-0.14958012
α_3	0.10811242708759967
β_3	0.1015043959192274
γ_3	0.067423216
δ_3	-0.055964916
α_4	0.007509247
β_4	-0.27854021
γ_4	-0.274360198
α_5	-0.013389585
β_5	-0.001254429
γ_5	0.002723937
δ_5	0.002916544