

## 3rd-Order Force Constants Calculation for an LJ-fcc crystal

### 1. General expression

Force constants (FCs) are defined as derivatives of the potential energy with the respect to atomic displacement around their equilibrium position. The Taylor expansion of the potential energy is written as following form:

$$E = E_0 + \sum_i \Pi_i u_i + \frac{1}{2!} \sum_{ij} \Phi_{ij} u_i u_j + \frac{1}{3!} \sum_{ijk} \Psi_{ijk} u_i u_j u_k + \frac{1}{4!} \sum_{ijkl} \chi_{ijkl} u_i u_j u_k u_l + \dots \quad (1)$$

where  $u_i$  is the displacement of atom  $i$ , which is also expressed with a translation vector  $R$ , atom index within the primitive unit cell  $\tau$  and the Cartesian coordinate  $\alpha$ .  $\Phi$ ,  $\Psi$  and  $\chi$  are the harmonic, cubic and quartic FCs, respectively. The first and second terms in the right-hand side are zeros at equilibrium.

Each order of the term in the right-hand side correspond to their level of interaction, e.g., the harmonic term shows two-body interaction, the cubic one three-body, respectively. Although it is easy to obtain the first order derivative analytically which is used to calculate the force between atom  $i$  and  $j$ , it becomes more difficult to obtain FCs as the derivation order become higher. Thus, high order FCs are often calculated with the force derivation with displacement to atoms. Focusing on the harmonic and cubic term, I discuss this method in Sec. 2 in this report. And FCs of an LJ crystal can be analytically calculated by second order FCs. I also discuss the analytical expression of the 3rd order FCs.

### 2. Force derivation Approach

A force on an atom is the first derivative of the potential energy with respect to an atomic position,

$$F_{R\tau}^\alpha = - \frac{\partial E}{\partial r_{R\tau}^\alpha} \quad (2)$$

And the second order FCs are driven into

$$\Phi_{R_1\tau_1, R_2\tau_2}^{\alpha\beta} = \frac{\partial^2 E}{\partial r_{R_1\tau_1}^\alpha \partial r_{R_2\tau_2}^\beta} = \frac{\partial}{\partial r_{R_2\tau_2}^\beta} \left[ \frac{\partial E}{\partial r_{R_1\tau_1}^\alpha} \right] = - \frac{\partial F_{R_1\tau_1}^\alpha}{\partial r_{R_2\tau_2}^\beta} \quad (3)$$

With the numerical scheme, or finite differences, Eq. (3) is approximately calculated from the force on atom  $R_1\tau_1$  in the case the atom  $R_2\tau_2$  is slightly displaced to  $\beta$  component:

$$\Phi_{R_1\tau_1, R_2\tau_2}^{\alpha\beta} \simeq - \frac{F_{R_1\tau_1}^\alpha \left[ \Delta r_{R_2\tau_2}^\beta \right] - F_{R_1\tau_1}^{\alpha, eq}}{\Delta r_{R_2\tau_2}^\beta} \quad (4)$$

where superscript  $eq$  means “at equilibrium”, so  $F_{R_1\tau_1}^{\alpha,eq}$  in Eq. (4) should be ideally zero. Thus this term is often omitted [1] and finally expressed as

$$\Phi_{R_1\tau_1, R_2\tau_2}^{\alpha\beta} \simeq -\frac{F_{R_1\tau_1}^{\alpha} [\Delta r_{R_2\tau_2}^{\beta}]}{\Delta r_{R_2\tau_2}^{\beta}} \quad (5)$$

In the almost same manner, 3rd order FCs can be expressed as a form of 2nd order force derivatives,

$$\Psi_{R_1\tau_1, R_2\tau_2, R_3\tau_3}^{\alpha\beta\gamma} = -\frac{\partial^2 F_{R_i\tau_i}^{\alpha}}{\partial r_{R_2\tau_2}^{\beta} \partial r_{R_3\tau_3}^{\gamma}} \quad (6)$$

Using finite differences and Eq. (4),

$$\begin{aligned} \Psi_{R_1\tau_1, R_2\tau_2, R_3\tau_3}^{\alpha\beta\gamma} &\simeq \frac{\Phi_{R_1\tau_1, R_2\tau_2}^{\alpha\beta} [\Delta r_{R_3\tau_3}^{\gamma}] - \Phi_{R_1\tau_1, R_2\tau_2}^{\alpha\beta}}{\Delta r_{R_3\tau_3}^{\gamma}} \\ &= -\frac{F_{R_1\tau_1}^{\alpha} [\Delta r_{R_2\tau_2}^{\beta}, \Delta r_{R_3\tau_3}^{\gamma}] - F_{R_1\tau_1}^{\alpha} [\Delta r_{R_3\tau_3}^{\gamma}] - F_{R_1\tau_1}^{\alpha} [\Delta r_{R_2\tau_2}^{\beta}] + F_{R_1\tau_1}^{\alpha,eq}}{\Delta r_{R_2\tau_2}^{\beta} \Delta r_{R_3\tau_3}^{\gamma}} \end{aligned} \quad (7)$$

Instead of Eq. (4), Chaput et al introduced it with Eq. (5) [1],

$$\Psi_{R_1\tau_1, R_2\tau_2, R_3\tau_3}^{\alpha\beta\gamma} \simeq -\frac{F_{R_1\tau_1}^{\alpha} [\Delta r_{R_2\tau_2}^{\beta}, \Delta r_{R_3\tau_3}^{\gamma}] - F_{R_1\tau_1}^{\alpha} [\Delta r_{R_2\tau_2}^{\beta}]}{\Delta r_{R_2\tau_2}^{\beta} \Delta r_{R_3\tau_3}^{\gamma}} \quad (8)$$

But I doubt this equation is really accurate. For example, FCs are invariant about the turn of derivation, that is,  $\Psi_{R_1\tau_1, R_2\tau_2, R_3\tau_3}^{\alpha\beta\gamma} = \Psi_{R_1\tau_1, R_3\tau_3, R_2\tau_2}^{\alpha\beta\gamma}$  should always be satisfied. However, Eq. (8) cannot satisfy that because there are no symmetry about indices 1, 2, and 3 in this equation. I carried out calculating the 3rd order FCs with Eqs. (7) or (8), however, I failed to do it in both cases (the order of results quite depended on the atomic displacement). The reason of that is unknown.

Here, focusing on the Eq. (7), I discuss 3rd order FCs of an LJ-fcc crystal. Since LJ potential only assume two-body interactions, when  $R_1\tau_1 \neq R_2\tau_2 \neq R_3\tau_3$  3rd order FCs have the following relation:

$$F_{R_1\tau_1}^{\alpha} [\Delta r_{R_2\tau_2}^{\beta}, \Delta r_{R_3\tau_3}^{\gamma}] = F_{R_1\tau_1}^{\alpha} [\Delta r_{R_3\tau_3}^{\gamma}] + F_{R_1\tau_1}^{\alpha} [\Delta r_{R_2\tau_2}^{\beta}] \quad (9)$$

Thus, all FCs are zeros in this case. So all we only have to do is to calculate FCs when  $R_2\tau_2 = R_3\tau_3$ , this means that one atom moves twice, or  $R_1\tau_1 = R_2\tau_2 \neq R_3\tau_3$ , this also means both two atoms involved interaction move simultaneously. Each cubic FC matrix is  $3 \times 3 \times 3$ , once I roughly estimate the number of FCs (here I don't assume cutoff or symmetry operations), this is  $(3 \times 3 \times 3) \times (\#atoms)$ .

### 3. Analytical Approach

The harmonic FCs of an LJ potential is given as an analytical form

$$\Phi_{R_1\tau_1, R_2\tau_2}^{\alpha\beta} = \frac{r_\alpha r_\beta}{r} \left[ \phi''(r) - \frac{1}{r} \phi'(r) \right] + \frac{\delta_{\alpha\beta}}{r} \phi'(r) \quad (10)$$

where  $r = |\vec{r}_{R_2\tau_2} - \vec{r}_{R_1\tau_1}|$  [2]. The cubic FCs are analytically described as

$$\begin{aligned} \Psi_{R_1\tau_1, R_2\tau_2, R_3\tau_3}^{\alpha\beta\gamma} &= \frac{\partial}{\partial r_\gamma} \left( \Phi_{R_1\tau_1, R_2\tau_2}^{\alpha\beta} \right) \\ &= \frac{r_\alpha r_\beta r_\gamma}{r^3} \left[ \phi'''(r) - 3 \frac{\phi''(r)}{r} + 3 \frac{\phi'(r)}{r^2} \right] + \frac{\delta_{\beta\gamma} r_\alpha + \delta_{\gamma\alpha} r_\beta + \delta_{\alpha\beta} r_\gamma}{r^2} \left[ \phi''(r) - \frac{\phi'(r)}{r} \right] \end{aligned} \quad (11)$$

It should be noted that Eq. (11) can only show FCs when the triplet  $(R_1\tau_1, R_2\tau_2, R_3\tau_3)$  satisfy  $R_2\tau_2 = R_3\tau_3$ . I have checked the accuracy of Eq. (11) by comparing results of the numerical derivation of Eq. (10). It shows good agreement.

### Reference

[1] L. Chaput et al., PRB 84, 094302 (2011)