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3rd Order FCs Calculation on LJ FCC crystal Comparing Finite Difference Method and Analytical One

1. Numerical Calculation

Generally, 3rd order force constants are described as the second order force derivation on atom i

$$\Phi_{ijk}^{\alpha\beta\gamma} = -\frac{\partial F_i^\alpha}{\partial r_j \partial r_k^\gamma} \tag{1}$$

where r_j^β is the atomic displacement of atom j for β component from equilibrium position. Numerically, this equation is driven into

$$\Phi_{ijk}^{\alpha\beta\gamma} \simeq -\frac{F_i^\alpha\left[\Delta r_j^\beta, \Delta r_k^\gamma\right] - F_i^\alpha\left[\Delta r_j^\beta\right] - F_i^\alpha\left[\Delta r_k^\gamma\right] + F_{i,eq}^\alpha}{\Delta r_j^\beta \Delta r_k^\gamma} \tag{2}$$

or

$$\Phi_{ijk}^{\alpha\beta\gamma} \simeq -\frac{F_i^\alpha\left[\Delta r_j^\beta, \Delta r_k^\gamma\right] - F_i^\alpha\left[\Delta r_j^\beta, -\Delta r_k^\gamma\right] - F_i^\alpha\left[-\Delta r_j^\beta, \Delta r_k^\gamma\right] + F_i^\alpha\left[-\Delta r_j^\beta, -\Delta r_k^\gamma\right]}{4\Delta r_j^\beta \Delta r_k^\gamma} \tag{3}$$

where $F_{i,eq}^\alpha$ is force on atom i for α component at equilibrium, so that this term is often omitted. Since LJ potential is a two body potential, two atoms displaced force is equivalent to the summation of each force which is loaded by one atom displaced. Thus, this linearity is expressed like this:

$$F_i^\alpha\left[\Delta r_j^\beta, \Delta r_k^\gamma\right] = F_i^\alpha\left[\Delta r_j^\beta\right] + F_i^\alpha\left[\Delta r_k^\gamma\right] \qquad (i \neq j \neq k) \tag{4}$$

Two atomic displaced force only valid when $(i,j,k) = (i,j,j),\ (i,j,k) = (i,i,k)$.

In numerical derivation, precision errors appear when Δr is too small. As for my calculation, using MATLAB, the order of precision errors are around 10^{-16} so that calculation accuracy decreases in the case the order of Δr is smaller than 10^{-8}. Especially self term values are strongly effected on this error. Thus we cannot use small Δr.

2. Analytical Method

The analytical force constants expression for LJ crystal is

$$\Psi_{ijk}^{\alpha\beta\gamma} = \frac{\partial}{\partial r_\gamma}\left(\Phi_{ijk}^{\alpha\beta}\right)$$

$$= \frac{r_\alpha r_\beta r_\gamma}{r^3}\left[\phi'''(r) - 3\frac{\phi''(r)}{r} + 3\frac{\phi'(r)}{r^2}\right] + \frac{\delta_{\beta\gamma}r_\alpha + \delta_{\gamma\alpha}r_\beta + \delta_{\alpha\beta}r_\gamma}{r^2}\left[\phi''(r) - \frac{\phi'(r)}{r}\right] \quad (5)$$

Equation (5) shows two body 3rd order force constants $\Phi_{ijj}^{\alpha\beta\gamma}$, and self term $\Phi_{iij}^{\alpha\beta\gamma}$ can be obtained with summation rule

$$\Phi_{iij}^{\alpha\beta\gamma} = \sum_k \Phi_{ijk}^{\alpha\beta\gamma} \quad (6)$$

To take Eq. (4) into consideration, every three body term should be zero. Therefore self term $\Phi_{iij}^{\alpha\beta\gamma}$ can be given as

$$\Phi_{iij}^{\alpha\beta\gamma} = -\Phi_{ijj}^{\alpha\beta\gamma} \quad (7)$$

and in the case of $j = i$, $\Phi_{iii}^{\alpha\beta\gamma}$ should be zero. It is easy to understand when you think about the summation of 3rd order force constants between j and j' which is point symmetry of j:

$$\Phi_{ijj}^{\alpha\beta\gamma} + \Phi_{ij'j'}^{\alpha\beta\gamma} = 0 \quad (8)$$

3. Results

I have developed a 3rd order force constants calculation program and put it on the dropbox, "https://www.dropbox.com/home/ald-si/ankit/FCs_calculation_by_Yusuke".

It takes only few seconds to obtain force constants with both schemes, numerical and analytical one. These two results shows a good agreement.