September 29, 2020

1 Previous work:

Summarizing [**?**, **?**] for phonon-dispersion relations from X-ray scattering:

Refs:	Xu & Chiang	Wehringer,. . ., Bosak
DFT	No	Yes and obtain phonon spectra... then why TDS?
$a_{k,j}$	$\|a_{k,j}\|^2 = \frac{\hbar}{N\omega_{k,j}} coth\left(\frac{\hbar\omega_{k,j}}{k_B T}\right)$	Same expression but from DFT
(M_s)	Fit/compute TDS $M_s(\mathbf{q},T) = \frac{1}{\mu_s}\sum_{k,j}\|a_{k,j}\|^2 \|\mathbf{q}\cdot\mathbf{e}_{k,j,s}\|^2$	From DFT computations using CASTEP
Displacement Eq:	$D(\mathbf{k})\epsilon_{k,j} = \omega_{k,j}^2\epsilon_{k,j}$	$\tilde{C}_{ijlm}k_j k_l u_m = \rho\omega^2 u_i$ Contract $\tilde{C}_{ijlm}k_j k_l \rightarrow D(\mathbf{k})$
	Requires a lattice dynamics model (harmonic energy description that can be used to compute the dynamical matrix)	• DFT used to select $\mathbf{q}$, multiple phonon scattering, optical phonons. • Compute $D(\mathbf{k})$ and subsequently $M_s(\mathbf{q})$ • 1/2 temperature method • Guess $\tilde{C}$, solve for displacements, compute $I_1(\mathbf{q})$, etc • Minimize the difference between computed and measured values

Table 1: Notation: $\mathbf{q}$ be recorded Q, difference between incident and reflected momentum, $\mathbf{k}$ be momentum in reciprocal space, first Brillouin zone, s indicates s-th atom in the unit cell, while $j = 1, 2 \ldots 3n$ denote phonon modes.

- Latent variables of the observed intensities are dynamical matrices $D(\mathbf{k})$ of the first Brillouin zone.
- At the very least, we can establish one-to-one correspondence between $I_1(\mathbf{q})$ and dynamical matrix $D(\mathbf{k})$

The Bragg scattering is given by:

$$I_0 = NI_e \sum_{m,s,s'} f_s f_{s'} \exp(-M_s - M_{s'}) \exp\left[-i\mathbf{q} \cdot (\mathbf{R}_m + \tau_{s,s'})\right] \tag{1}$$

where:

$$M_s = \frac{1}{\mu_s} \sum_{k,j} |a_{k,j}|^2 |\mathbf{q} \cdot \mathbf{e}_{k,j,s}|^2 \tag{2}$$

where

$$\mathbf{q}_{1\times 3} \rightarrow \begin{bmatrix} \mathbf{q}_{1\times 3} \\ \mathbf{q}_{1\times 3} \\ \cdots \\ \mathbf{q} \end{bmatrix}_{s-atoms} \rightarrow \begin{bmatrix} \mathbf{q}_{1\times 3} & 0_{1\times 3} & 0_{1\times 3} & \cdots \\ 0_{1\times 3} & \mathbf{q}_{1\times 3} & 0_{1\times 3} & 0_{1\times 3} \\ 0_{1\times 3} & 0_{1\times 3} & \mathbf{q}_{1\times 3} & 0 \\ 0 & 0 & 0 & \mathbf{q} \end{bmatrix} = \begin{bmatrix} [\ldots q \ldots]_{atom\,1} \\ [\ldots q \ldots]_{atom\,2} \end{bmatrix} \tag{3}$$

where

$$\epsilon_{k,j} = \begin{pmatrix} \mathbf{e}_{k,j,s_1} \\ \mathbf{e}_{k,j,s_2} \\ \cdots \end{pmatrix} \tag{4}$$

and

$$\Phi^{ij}_{ms,m's'} = -\frac{\partial^2 U}{\partial r^i_{m,s} \partial r^j_{m's'}} \tag{5}$$

where i, j are x , y , z.

$$D^{i,j}_{s,s'}(\mathbf{k}) = -\sum_{m'} \frac{\Phi^{ij}_{m,s,m',s'}}{\sqrt{\mu_s \mu_{s'}}} \exp\left[i\mathbf{k} \cdot (\mathbf{R}_{m,m'} + \tau_{s,s'})\right] \tag{6}$$

which is $3n \times 3n$ where n denotes the number of atoms per unit cell.

$$D(\mathbf{k})\epsilon_{k,j} = \omega^2_{k,j} \epsilon_{k,j} \tag{7}$$

2 In tensorflow:

The Debye-Waller factor reformulated:

$$M_s(\mathbf{q}, T) = \frac{\hbar}{4N\mu_s} \langle \mathbf{q}(s)|_{1\times 3n} \left[\sum_{k,j} \frac{1}{\omega_{k,j}} coth\left(\frac{\hbar\omega_{k,j}}{2k_B T}\right) \underbrace{\epsilon^T_{k,j} \cdot \epsilon_{k,j}}_{3n\times 1 \cdot 1\times 3n} \right] |\mathbf{q}(s)\rangle_{3n\times 1} \tag{8}$$

$$M_s(\mathbf{q}, T) = \frac{\hbar}{4N\mu_s} \underbrace{\langle \mathbf{q}(s)|}_{1\times 3n} \underbrace{\sum_k M(k)}_{3n\times 3n} \underbrace{|\mathbf{q}(s)\rangle}_{3n\times 1} \tag{9}$$

- Decide on the discretization on the $\mathbf{k}$ in the first Brillouin zone. We use the Monkhorst-Pack discretization.
- Weight: initialize $D(\mathbf{k})$ randomly for $3 * N_{kpoints}$, which determines the batch-size, and the internal $D(\mathbf{k}_i)$ which is $3n \times 3n$ where n is the number of atoms per unit cell.
- Tensor of shape $N_{points} \times 3n \times 3n$

2.1 First order scattering

One-to-one map between observed intensity and phonon modes

$$I_1(\mathbf{q}) = \frac{\hbar N I_e}{2} \sum_j \frac{1}{\omega_{k,j}} coth\left(\frac{\hbar\omega_{k,j}}{2k_BT}\right) \sum_{ss'} \frac{f_s f_{s'}}{\sqrt{\mu_s \mu_{s'}}} \exp(-M_s - M_{s'}) \mathbf{q}_s^T (\epsilon_{k,j} \cdot \epsilon_{k,j}) \mathbf{q}_{s'} \, e^{-iK_L \cdot \tau_{ss'}}$$

$$I_1(\mathbf{q}) = \frac{\hbar N I_e}{2} \sum_{s,s'} e^{-iK_L \cdot \tau_{ss'}} \, \mathbf{q}_s^T \left(\frac{f_s \exp(-M_s)}{\sqrt{\mu_s}}\right) \mathbb{M}(k) \left(\frac{f_{s'} \exp(-M_{s'})}{\sqrt{\mu_{s'}}}\right) \mathbf{q}_{s'}$$

$$I_1(\mathbf{q}) = \frac{\hbar N I_e}{2} \sum_{s,s'} e^{-iK_L \cdot \tau_{ss'}} \underbrace{A(\mathbf{q}, s)}_{1\times 3n} \quad \underbrace{\mathbb{M}(k)}_{3n\times 3n} \quad \underbrace{A(\mathbf{q}, s')}_{3n\times 1}$$

where $\mathbf{q} = k + K_L$ where

- $k \in 1^{st}\, BZ$
- K_L is the closest reciprocal space vector.

Here, M_s and $M_{s'}$ depend on $\mathbf{q}$ and the sum over Brillouin zone, $\sum_k M(k)$. In the case of a single-atom unit cell, we can further simplify by using $\tau_{ss'} = 0$, and there is only one term in the sum over $\{s, s'\}$

$$I_1(\mathbf{q}) = \frac{\hbar N I_e}{2} \underbrace{A(\mathbf{q}, s = 1)}_{1\times 3n} \quad \underbrace{\mathbb{M}(k)}_{3n\times 3n} \quad \underbrace{A(\mathbf{q}, s' = 1)}_{3n\times 1}$$

References