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# Phonons and Anharmonic Lattice Effects in Iron Pnictide Superconductors

*Master of Science Thesis in the M.Sc. Programme Applied Physics*

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## Abstract

In the current thesis we investigate phonon behaviour in the $BaFe_2As_2$ crystal and the effect of anharmonicity in the interionic potential on the lattice. In the first part we treat the potential as harmonic and calculate the phonon spectrum and density of states for the crystal. The crystal has a unit cell with 5 ions in a body-centered tetragonal structure and correspondingly 3 acoustic and 12 optical phonon branches. We then consider anharmonicity by including a small cubic term in the potential. This introduces the phenomenon of lattice expansion, which we treat by using a variational method. This is demonstrated in the second part of the thesis for one-dimensional and three-dimensional monoatomic lattices, and then for the full problem of the $BaFe_2As_2$ crystal. The last part deals with the isotope substitution effect, where we alter the mass of iron to see how much the expansion changes, which should reflect how the actual lattice constants change due to isotope substitution. Experimental measurements of the $^{57}Fe$ to $^{54}Fe$ substitution showed a negligible expansion in the ab-plane and a $\delta_c = (3 \pm 1) \cdot 10^{-3}$ Å expansion in the c-plane [1]. This is in very good agreement with our result of $\delta_a = -1.13 \cdot 10^{-5}$ Å and $\delta_c = 1.73 \cdot 10^{-3}$ Å.

**Keywords:** phonons, barium iron arsenic, anharmonic, lattice expansion, isotope substitution, isotope effect

# Contents

# 1 Introduction

Iron pnictide superconductors were first discovered in 2008, when Kamihara et al. [2] reported that F-doped LaFeAsO superconducts at 26 K. This sparked considerable interest among physicists, and since then similar superconducting materials have been found [3, 4, 5]. LaFeAsO now constitutes one of the iron-based superconductor families, namely the 1111 family, which also holds the record of $T_c$ (critical temperature) is high as 55 K, which is only surpassed by cuprate superconductors [6, 3]. The name 1111 comes from the stoichiometry of the parental prototype. Other families currently known are the 122 $BaFe_2As_2$ family, the 111 LiFeAs family and the 11 FeSe family.

In all above-mentioned iron-based materials the key feature which makes them superconduct is the FeAs layer (or FeSe layer in case of the 11 family) with a tetragonal structure at room temperature. These layers are separated in space by a different layer. This structure is very similar to cuprates with, however, some differences — the FeAs layer is not purely planar like the $CuO_2$ layer, for example [4, 5, 7, 8].

The superconductivity mechanism itself is not yet entirely understood. While some calculations indicate than it cannot be explained by the conventional electron-phonon coupling [9], others say that it may still play an important role [10, 7]. In this thesis we present phonon calculations for $BaFe_2As_2$ crystal. While magnetism plays a significant role in iron-based superconductors [7], we will not discuss magnetic effects here.

The study itself is split into two parts. First, we calculate phonon modes assuming harmonic interactions within the crystal. The theoretical framework is fairly straightforward and has been outlined in several books [11, 12]. After acquiring frequencies and polarization vectors of the phonons, we use them in the second part of the thesis, where we use the variational method described by Feynman [13] to see how much the lattice constants change when anharmonic interactions are included. The lattice expansion is a purely quantum-mechanical effect, due to phonon zero-point motion.

# 2 Harmonic interactions

## 2.1 Method

To solve the harmonic problem we employ the Classical Theory described in [11]. Interionic interactions are modelled as simple springs and we use Newtonian mechanics. First, we need to extend Hooke's Law to 3 dimensions.
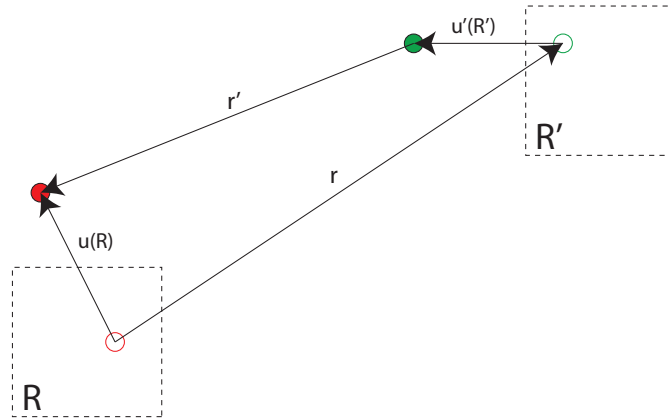
### 2.1.1 Derivation of Hooke's Law in 3 dimensions



Figure 1: Vector diagram for a general lattice. Ion 1 (red) in the unit cell with the absolute coordinate $\mathbf{R}$ deviates from the equilibrium position by vector $\mathbf{u}(\mathbf{R})$, while ion 2 (green) in the unit cell with the absolute coordinate $\mathbf{R}'$ deviates from the equilibrium position by vector $\mathbf{u}'(\mathbf{R}')$. Unit cell boundaries are not to scale but only for illustration.

Consider the situation depicted on Fig. 1. Ion 1 belongs to the unit cell with the absolute coordinate $\mathbf{R}$ and ion 2 belongs to the unit cell with the absolute coordinate $\mathbf{R}'$. When both ions are in the equilibrium position, the net force between them is zero and the distance between them can be described by a relative vector $\mathbf{r}$. Assume now that ion 1 deviates from equilibrium by $\mathbf{u}(\mathbf{R})$ and ion 2 does so by $\mathbf{u}'(\mathbf{R}')$. We can then denote the displacement of ion 1 relative to ion 2 by $\mathbf{r}'$ — the force on ion 1 by ion 2 will then be proportional to the difference of the magnitudes of $\mathbf{r}'$ and $\mathbf{r}$, and directed antiparallel to $\mathbf{r}'$ in case the former is larger

than the latter. This can be expressed as

$$\mathbf{F}(\mathbf{R}) = -K \left[ \frac{\mathbf{r}'}{|\mathbf{r}'|} \left( |\mathbf{r}'| - |\mathbf{r}| \right) \right] = -K \left[ \mathbf{r}' \left( 1 - \frac{|\mathbf{r}|}{|\mathbf{r}'|} \right) \right] \tag{1}$$

where $K$ is the force constant.

We can now start calculating vector magnitudes:

$$\mathbf{r}' = \mathbf{u}(\mathbf{R}) - \left( \mathbf{r} + \mathbf{u}'(\mathbf{R}') \right) \tag{2a}$$

$$|\mathbf{r}'|^2 = |\mathbf{u}(\mathbf{R})|^2 + |\mathbf{r} + \mathbf{u}'(\mathbf{R}')|^2 - 2 \left( \mathbf{r} + \mathbf{u}'(\mathbf{R}') \right) \cdot \mathbf{u}(\mathbf{R}) \tag{2b}$$
$$= |\mathbf{u}(\mathbf{R})|^2 + |\mathbf{r}|^2 + |\mathbf{u}'(\mathbf{R}')|^2 + 2\mathbf{r} \cdot \mathbf{u}'(\mathbf{R}') - 2\mathbf{r} \cdot \mathbf{u}(\mathbf{R}) - 2\mathbf{u}(\mathbf{R}) \cdot \mathbf{u}'(\mathbf{R}')$$

We are interested in the first approximation, so we will discard all terms non-linear in deviation functions $\mathbf{u}$ and $\mathbf{u}'$:

$$\frac{|\mathbf{r}'|}{|\mathbf{r}|} = \left( 1 + \frac{2\mathbf{r} \cdot \mathbf{u}'(\mathbf{R}')}{|\mathbf{r}|^2} - \frac{2\mathbf{r} \cdot \mathbf{u}(\mathbf{R})}{|\mathbf{r}|^2} \right)^{1/2} \tag{3}$$

and therefore

$$\frac{|\mathbf{r}|}{|\mathbf{r}'|} = \left( 1 + \frac{2\mathbf{r} \cdot \mathbf{u}'(\mathbf{R}')}{|\mathbf{r}|^2} - \frac{2\mathbf{r} \cdot \mathbf{u}(\mathbf{R})}{|\mathbf{r}|^2} \right)^{-1/2} \tag{4}$$

Since deviation functions are very small compared to the distance between the ions, we reduce this equation using $(1 + x)^{\alpha} = 1 + \alpha x + O(x^2)$:

$$\frac{|\mathbf{r}|}{|\mathbf{r}'|} = 1 - \frac{\mathbf{r} \cdot \mathbf{u}'(\mathbf{R}')}{|\mathbf{r}|^2} + \frac{\mathbf{r} \cdot \mathbf{u}(\mathbf{R})}{|\mathbf{r}|^2} \tag{5}$$

Inserting this into the force equation (1) we obtain

$$\mathbf{F}(\mathbf{R}) = -K \left[ \mathbf{r}' \left( 1 - \frac{|\mathbf{r}|}{|\mathbf{r}'|} \right) \right]$$
$$= -K \left[ \left( \mathbf{u}(\mathbf{R}) - \mathbf{u}'(\mathbf{R}') - \mathbf{r} \right) \left( \frac{\mathbf{r} \cdot \mathbf{u}'(\mathbf{R}')}{|\mathbf{r}|^2} - \frac{\mathbf{r} \cdot \mathbf{u}(\mathbf{R})}{|\mathbf{r}|^2} \right) \right] \tag{6}$$

Dropping non-linear terms again,

$$\mathbf{F}(\mathbf{R}) = -K \left[ \mathbf{r} \left( \frac{\mathbf{r} \cdot \mathbf{u}(\mathbf{R})}{|\mathbf{r}|^2} - \frac{\mathbf{r} \cdot \mathbf{u}'(\mathbf{R}')}{|\mathbf{r}|^2} \right) \right]$$
$$= -K \left[ \frac{\mathbf{r}}{|\mathbf{r}|} \left( \frac{\mathbf{r}}{|\mathbf{r}|} \cdot (\mathbf{u}(\mathbf{R}) - \mathbf{u}'(\mathbf{R}')) \right) \right] \tag{7}$$

9

Equation (7) is our final result — it describes the force on an ion in one unit cell by a different ion in another unit cell.

To solve a system of such equations it is favorable to express the dot product as a matrix operation to be able to explicitly separate coefficients of deviation functions. By assuming a column vector and using $\mathbf{a} \cdot \mathbf{b} = \mathbf{a}^T\mathbf{b}$ we can rewrite equation (7) as

$$\mathbf{F}(\mathbf{R}) = -K\tilde{R}\left[\mathbf{u}(\mathbf{R}) - \mathbf{u}'(\mathbf{R}')\right] \tag{8}$$

where

$$\tilde{R} = \frac{\mathbf{r}}{|\mathbf{r}|}\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right)^T \tag{9}$$

is a matrix.

### 2.1.2 Applying the Classical Theory

Now, when the form of Hooke's Law is established, we can apply the Classical Theory to our system. Assume deviation functions of the form $\mathbf{u}(\mathbf{R}, t) = \frac{1}{\sqrt{m}}e^{i(\mathbf{k}\cdot\mathbf{R}-\omega t)}\epsilon$ which represents simple plane waves, $\epsilon$ is the polarization vector that describes the direction in which the ions move . The mass coefficient is necessary to weigh the equation to make the solution matrix Hermitian. Using Newton's 2nd Law we obtain

$$m\ddot{\mathbf{u}} = -K\tilde{R}\left[\mathbf{u}(\mathbf{R}) - \mathbf{u}'(\mathbf{R}')\right] \tag{10a}$$

$$\sqrt{m}\omega^2 e^{i(\mathbf{k}\cdot\mathbf{R}-\omega t)}\epsilon = K\tilde{R}\left[\frac{1}{\sqrt{m}}e^{i(\mathbf{k}\cdot\mathbf{R}-\omega t)}\epsilon - \frac{1}{\sqrt{m'}}e^{i(\mathbf{k}\cdot\mathbf{R}'-\omega t)}\epsilon'\right] \tag{10b}$$

$$\omega^2\epsilon = K\tilde{R}\frac{1}{\sqrt{m}}\left[\frac{1}{\sqrt{m}}\epsilon - \frac{1}{\sqrt{m'}}e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}\epsilon'\right] \tag{10c}$$

Now, to find out $\omega$ we only need to write out the equation (10c) for each ion in the unit cell and its interacting neighbors, and solve the obtained system of equations. Considering a unit cell with $p$ ions, we will have $p$ vector equations of the form

$$\omega^2\epsilon_i = \sum_{j=1}^{p}\mathbf{M}_{ij}\epsilon_j \tag{11}$$

10

for $i^{\text{th}}$ of $p$ ions, where $\mathbf{M}_{ij}$ is a certain matrix. Denote now $n$ as a certain neighbor that the ion $i$ interacts with. Putting equations (11) together in one big matrix equation produces

$$\omega^2 \epsilon = \mathbf{M}\epsilon \tag{12}$$

$$\omega = \sqrt{\texttt{eig}(\mathbf{M})} \tag{13}$$

where

$$\mathbf{M}(i,j) = \mathbf{M}_{ij} = \begin{cases} \displaystyle\sum_{\forall n} \frac{1}{m_i} K_{in} \tilde{\boldsymbol{R}}_{in} - \sum_{\epsilon_n = \epsilon_i} \frac{1}{m_i} K_{in} \tilde{\boldsymbol{R}}_{in} e^{i\mathbf{k}\cdot(\mathbf{R}_n - \mathbf{R}_i)} & i = j \\[2ex] \displaystyle-\sum_{\epsilon_n = \epsilon_j} \frac{1}{\sqrt{m_i}} \frac{1}{\sqrt{m_n}} K_{in} \tilde{\boldsymbol{R}}_{in} e^{i\mathbf{k}\cdot(\mathbf{R}_n - \mathbf{R}_i)} & i \neq j \end{cases} \tag{14}$$

This means that summations in the diagonal entries of the matrix $\mathbf{M}$ go over all neighbors of $i$ and neighbors with the deviation function $\mathbf{u}_i$ (and consequently the polarization vector $\epsilon_i$), while the summations in the non-diagonal entries go only over neighbors with the deviation function $\mathbf{u}_j$. Terms like $K_{in}$ denote constants which correspond to the specific interaction between ions $i$ and $n$, e.g. the spring constant $K$ and the displacement matrix $\tilde{R}$.

As mentioned above, matrix $\mathbf{M}$ is Hermitian, because we included mass coefficients in the expressions of deviation functions. It will therefore yield real eigenvalues. Since we have $p$ vector equations in $\mathbb{R}^3$, the size of matrix $\mathbf{M}$ will be $3p \times 3p$ and will thus yield $3p$ solutions of $\omega$ for each $\mathbf{k}$.

We choose k-vectors according to the Born-von Karman periodic boundary condition, requiring that $\mathbf{u}(\mathbf{R} + N_i \mathbf{a}_i) = \mathbf{u}(\mathbf{R})$ for each of the three primitive vectors $\mathbf{a}_i$. which means k-vectors are restricted to the form

$$\mathbf{k} = \frac{n_1}{N_1}\mathbf{b}_1 + \frac{n_2}{N_2}\mathbf{b}_2 + \frac{n_3}{N_3}\mathbf{b}_3 \tag{15}$$

where $n_i$ are integers, $N_i$ — number of unit cells in each dimension, and $\mathbf{b}_i$ — the reciprocal lattice vectors. Since only k-vectors within a single primitive cell of the reciprocal lattice will yield distinct solutions ($e^{i\mathbf{K}\cdot\mathbf{R}} \equiv 1$, where $\mathbf{K}$ is a reciprocal lattice vector), integers $n_i$ only go up to $N_i$ and there will be $N = N_1 N_2 N_3$ non-equivalent values of $\mathbf{k}$.

## 2.2 Results

Since the key feature of the crystal is the FeAs plane, our method was first applied to it alone (Fig. 2(a)). The angle of incline is taken to be $35°$ [14, 15]. It is assumed that each Fe ion interacts with its 8 nearest neighbors (4 As and 4 Fe), while each As ion interacts with 4 nearest Fe ions and 4 nearest coplanar As ions. This is just enough to adequately describe the phonon dispersion and not run into unphysical zero energy modes problem. The force constants are
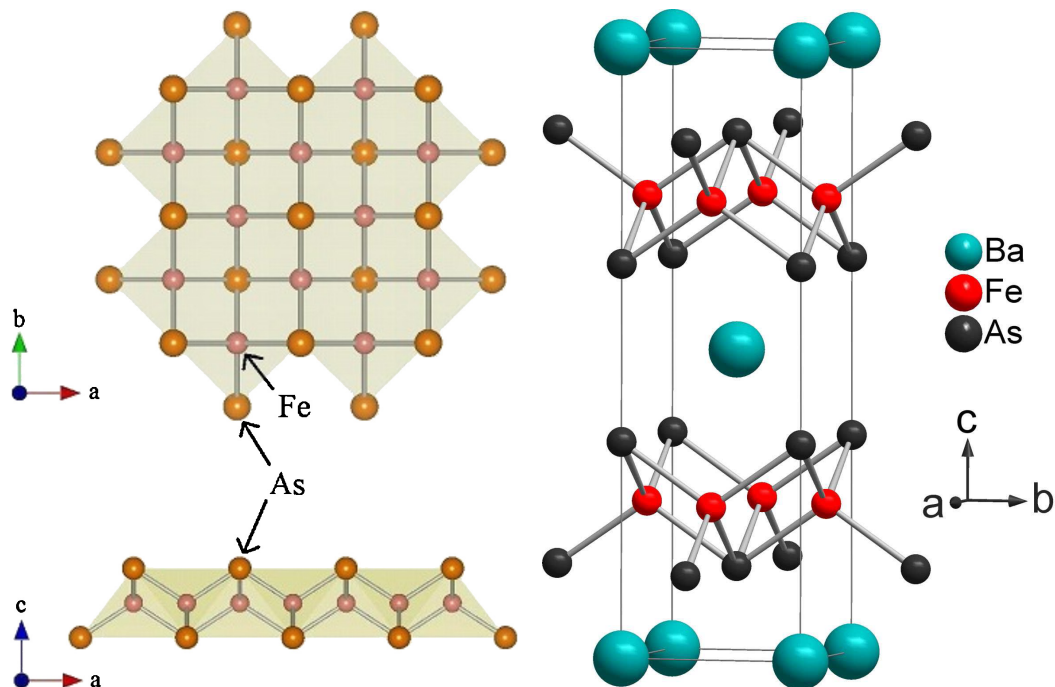


(a) Iron arsenic plane. *The material is the reproduction from J. Phys. Soc. Jpn. 78, 062001 (2009), K. Ishida, Yu. Nakai and H. Hosono. Copyright (2009) by the Physical Society of Japan.*

(b) Barium iron arsenic crystal. *Reprinted figure with permission from Rotter M., Tegel M. and Johrendt D., Phys. Rev. Lett. 101, 107006 (2008). Copyright (2008) by the American Physical Society. <http://link.aps.org/doi/10.1103/PhysRevLett.101.107006>*

Figure 2: The structures of FeAs plane and $BaFe_2As_2$ crystal.

| Pair | Force constant, eV/Å$^2$ [14] |
|---|---|
| Fe-As | 8.7 |
| Fe-Fe | 2.61 |
| As-As | 1.74 |

The lattice constant is taken to be $a$ = 3.96 Å in both directions [10]. Fig. **??** shows acquired normal modes along $(\zeta,0,0)$ and Fig. **??** — along $(\frac{\pi}{a},\zeta,0)$.
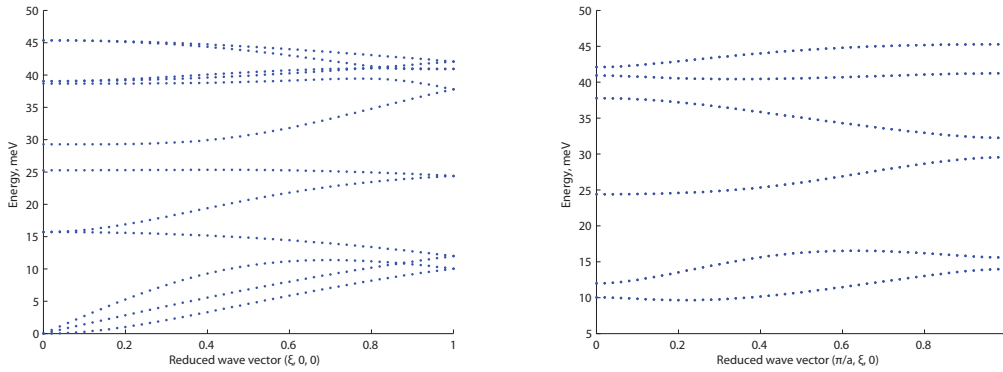


Figure 3: Phonon dispersion curves for the FeAs plane along reduced k-vectors $(\zeta,0,0)$ (left) and $(\frac{\pi}{a},\zeta,0)$ (right).

Same procedure was then applied to the complete BaFe$_2$As$_2$ crystal (Fig. 2(b)). Additional force which was included in the model is the interaction of Ba ion with its 8 closest As neighbors. Force constants used were different from the ones from the previous case and were taken to be

| Pair | Force constant, eV/Å$^2$ [6] |
|---|---|
| Fe-As | 4.37 |
| Fe-Fe | $8.11 \cdot 10^{-1}$ |
| As-As | $2.5 \cdot 10^{-1}$ |
| Ba-As | $5 \cdot 10^{-1}$ |

The c-axis lattice constant was taken to be $c$ = 13 Å [10]. Fig. 4 shows some phonon dispersion curves of BaFe$_2$As$_2$ together with the calculated phonon density of states. The discretization value for DOS was chosen as 1 $\mu$eV.

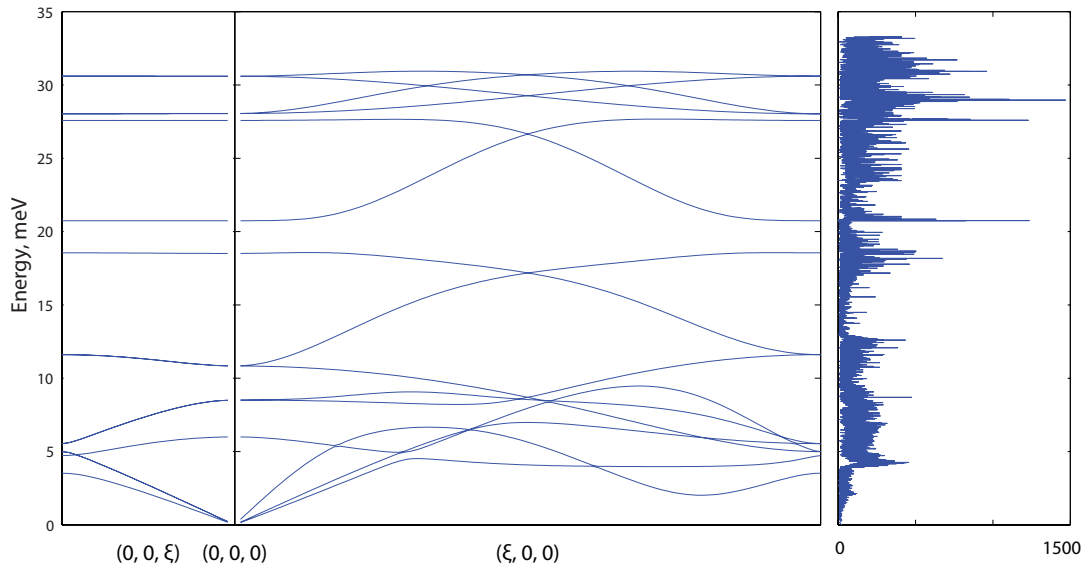For comparison, some published data is given in Appendix A.

Figure 4: Left: Phonon dispersion of $BaFe_2As_2$. Right: Phonon density of states of $BaFe_2As_2$.

# 3   Anharmonic interactions and lattice expansion

When anharmonicity of the interactions is considered, the potential additionally includes third and higher order terms. When this happens, lattice constants change to fit the anharmonic potential. Lattice expansion is a quantum-mechanical effect which exists even at zero temperature due to zero-point motion (Fig. 5), and we need to treat this problem quantum-mechanically (see Appendix B for the quantum-mechanical solution of a harmonic problem).

We follow the variational method outlined by Feynman [13]. Since a cubic potential cannot be diagonalized, we introduce a small variational parameter $\delta$ and compare the cubic potential with the diagonalizable harmonic potential. We then want the average of the difference between them to be minimal. To calculate this quantity, we need the energy spectrum of the harmonic potential. We can then differentiate the average with respect to $\delta$ to find $\delta$ that minimizes it.

We start with the one-dimensional case of identical particles, continue to the three-dimensional case of identical particles, then finally develop full theory for three dimensions and a unit cell, and apply it to the $BaFe_2As_2$ crystal.
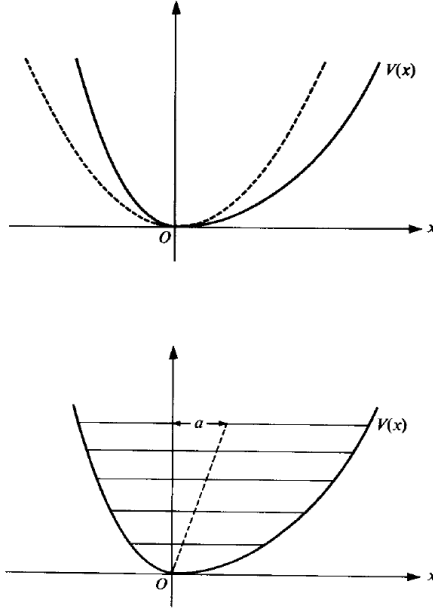
14

Figure 5: Potential shift when considering an anharmonic potential. Dashed curve represents harmonic potential, solid curve represents anharmonic potential. *a* shows the shift in the average. *Source: Statistical mechanics: a set of lectures / R.P. Feynman [13]*

## 3.1 One dimension

To begin, consider a one-dimensional chain of identical particles. The anharmonic potential energy of the chain can be written as

$$V = \sum_j \frac{K}{2}(r_{j+1} - r_j - a)^2 + \frac{G}{6}(r_{j+1} - r_j - a)^3 \tag{16}$$

Here, $a$ is the lattice constant and $r$ represents absolute particle coordinates. Our goal is to compare it to the harmonic potential $V_0 = \sum_j \frac{K}{2}(r_{j+1} - r_j - (a + \delta))^2$ and find out $\delta$, which makes the difference between them minimal.

First, we make the transformation

$$r_j = j(a + \delta) + x_j \tag{17}$$

15

where $x_j$ is now a quantum-mechanical position operator which represents particle deviation from equilibrium, to obtain

$$V = \sum_j \frac{K}{2}(x_{j+1} - x_j + \delta)^2 + \frac{G}{6}(x_{j+1} - x_j + \delta)^3 \tag{18a}$$

$$V_0 = \sum_j \frac{K}{2}(x_{j+1} - x_j)^2 \tag{18b}$$

We will now look for the minimum of $\langle V - V_0 \rangle$:

$$
\begin{aligned}
\langle V - V_0 \rangle &= \left\langle \sum_j \left( \frac{K}{2}\left((x_{j+1} - x_j + \delta)^2 - (x_{j+1} - x_j)^2\right) + \frac{G}{6}\left(x_{j+1} - x_j + \delta\right)^3 \right) \right\rangle \\
&= \left\langle \sum_j \left( \left(\frac{K}{2}\delta^2 + \frac{G}{6}\delta^3\right) + \left(K\delta + \frac{G}{2}\delta^2\right)(x_{j+1} - x_j) \right. \right. \\
&\quad \left. \left. + \frac{G}{2}\delta(x_{j+1} - x_j)^2 + \frac{G}{6}(x_{j+1} - x_j)^3 \right) \right\rangle \\
&= N\left(\frac{K}{2}\delta^2 + \frac{G}{6}\delta^3\right) + \left(K\delta + \frac{G}{2}\delta^2\right)\left\langle \sum_j (x_{j+1} - x_j) \right\rangle \\
&\quad + \frac{G}{2}\delta \left\langle \sum_j (x_{j+1} - x_j)^2 \right\rangle + \frac{G}{6}\left\langle \sum_j (x_{j+1} - x_j)^3 \right\rangle
\end{aligned}
\tag{19}
$$

Introducing the discrete Fourier transform (where $k$ is in units of $a$)

$$x_j = \frac{1}{\sqrt{N}} \sum_k e^{ikj} x_k \tag{20}$$

we see that

16

$$\sum_j \left( x_{j+1} - x_j \right) = \frac{1}{\sqrt{N}} \sum_k \left( (e^{ik} - 1) x_k \sum_j e^{ikj} \right) = 0 \tag{21a}$$

$$\sum_j \left( x_{j+1} - x_j \right)^2 = \sum_k 2 \left( 1 - \cos k \right) x_k x_{-k} \tag{21b}$$

$$\sum_j \left( x_{j+1} - x_j \right)^3 = \frac{1}{\sqrt{N}} \sum_{k,k'} \left( e^{ik} - 1 \right) \left( e^{ik'} - 1 \right) \left( e^{-ik - ik'} - 1 \right) x_k x_{k'} x_{-k-k'} \tag{21c}$$

since $\sum_j e^{ikj} = N\delta_{k,0}$ ($\delta$ with subscripts is the Kronecker delta). We then introduce ladder operators

$$x_k = \sqrt{\frac{\hbar}{2m\omega_k}} \left( a^\dagger_{-k} + a_k \right) \tag{22}$$

where $\omega_k = \sqrt{2(1 - \cos k)\frac{K}{m}} = \overline{\omega}\sqrt{\frac{K}{m}}$ are frequencies obtained by solving the harmonic problem, to get

$$
\begin{aligned}
\left\langle \sum_j \left( x_{j+1} - x_j \right)^2 \right\rangle &= \sum_k \frac{\hbar}{m\omega_k} (1 - \cos k) \left( \left\langle a^\dagger_{-k} a^\dagger_k \right\rangle + \left\langle a_k a_{-k} \right\rangle + 2 \left\langle a^\dagger_k a_k \right\rangle + 1 \right) \\
&= \sum_k \frac{\hbar}{m\omega_k} (1 - \cos k) \left( 2 \left\langle a^\dagger_k a_k \right\rangle + 1 \right) \\
&= \sum_k \frac{\hbar}{m\omega_k} (1 - \cos k) \left( \frac{2}{e^{\beta\hbar\omega_k} - 1} + 1 \right) \\
&= \sum_k \frac{\hbar}{m\omega_k} (1 - \cos k) \coth \frac{1}{2}\beta\hbar\omega_k \\
&= \frac{\hbar}{\sqrt{Km}} \sum_k \frac{1}{\overline{\omega}} (1 - \cos k) \coth \frac{\overline{\omega}}{T} \\
&= \frac{\hbar}{\sqrt{Km}} A
\end{aligned} \tag{23}
$$

and

$$\left\langle \sum_j (x_{j+1} - x_j)^3 \right\rangle = \frac{1}{\sqrt{N}} \sum_{k,k'} \left( \frac{\hbar}{2m} \right)^{3/2} \frac{1}{\sqrt{\omega_k \omega_{k'} \omega_{-k-k'}}} \left( e^{ik} - 1 \right) \left( e^{ik'} - 1 \right) \left( e^{-ik-ik'} \right.$$
$$\left. - 1 \right) \left\langle \left( a^\dagger_{-k} + a_k \right) \left( a^\dagger_{-k'} + a_{k'} \right) \left( a^\dagger_{k+k'} + a_{-k-k'} \right) \right\rangle$$
$$= 0 \tag{24}$$

Here we have used the fact that the averages of all operators involved, except $a^\dagger_k a_k$, are zero, since the state they make is orthogonal to the original state[1], and set temperature $\overline{T}$ in units of $\frac{\hbar\sqrt{\frac{K}{m}}}{2k_B}$. We therefore have

$$\langle V - V_0 \rangle = N \left( \frac{K}{2} \delta^2 + \frac{G}{6} \delta^3 \right) + \frac{1}{2} \frac{G\hbar}{\sqrt{Km}} A\delta \tag{25}$$

We assume that the cubic term is negligible and find the lattice expansion $\delta$ for which $\langle V - V_0 \rangle$ is minimal:

$$\frac{\partial}{\partial \delta} \langle V - V_0 \rangle = NK\delta + \frac{1}{2} \frac{G\hbar}{\sqrt{Km}} A = 0 \tag{26a}$$

$$\delta = -\frac{1}{2N} LA \tag{26b}$$

where $L = \frac{G\hbar}{\sqrt{K^3 m}}$ and $A$ is dimensionless. Constant $L$ is the length parameter and determines the scale of the problem.

## 3.2 Three dimensions

Similar to the one-dimensional case, we can now find the lattice expansion for three dimensions. Consider first the case of simple cubic lattice of identical particles.

In Fig. 6, $\mathbf{r}$ is now a vector of the expanded lattice, $\mathbf{r} = \mathbf{r}_0 + \delta(r_0)$, where $\mathbf{r}_0$ is a vector of the unexpanded lattice. Since we are interested in a uniform expansion, $\delta(\mathbf{r}_0)$ has to reflect directional symmetry and proportionality, and can

---

[1]Recall that the average of an operator $\hat{A}$ is $\langle \hat{A} \rangle = \sum_n p_n \langle n|\hat{A}|n \rangle$, where $n$ is a certain state and $p_n$ is the probability of that state.
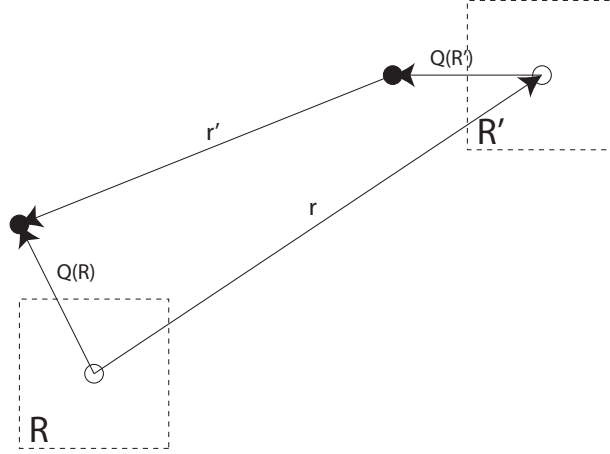
Figure 6: Vector diagram for a lattice of identical particles. Particle in the unit cell with the absolute coordinate **R** deviates from the equilibrium position by vector **Q(R)**, while another particle in the unit cell with the absolute coordinate **R**′ deviates from the equilibrium position by vector **Q(R**′**)**. Unit cell boundaries are not to scale but only for illustration.

be expressed as $\delta_\mu(\mathbf{r}_0) = c_\mu r_{0\mu}$, where $c_\mu$ is a constant and $\mu$ represents x-, y- or z-projection. Particle deviations are now expressed as **Q(R)**.

In this case the potential can be approximated with the form

$$V = \sum_{\mathbf{R}\mathbf{R}'} \left( \frac{k(\mathbf{r})}{2} \left( |\mathbf{r}'| - |\mathbf{r}_0| \right)^2 + \frac{g(\mathbf{r})}{6} (|\mathbf{r}'| - |\mathbf{r}_0|)^3 \right) \tag{27}$$

where $k$ (not to be confused with the wave vector **k**) and $g$ are force constants which depend on a particular interaction. Since we assume that the force constants don't change with the expansion, we can set $k(\mathbf{r}) = k(\mathbf{r}_0)$ and $g(\mathbf{r}) = g(\mathbf{r}_0)$.

We know that

$$
\begin{aligned}
|\mathbf{r}'| &= |\mathbf{R}' + \mathbf{Q}(\mathbf{R}') - \mathbf{R} - \mathbf{Q}(\mathbf{R})| \\
&= |\mathbf{r} - (\mathbf{Q}(\mathbf{R}) - \mathbf{Q}(\mathbf{R}'))| \\
&= |\mathbf{r}_0 + \delta(r_0) - (\mathbf{Q}(\mathbf{R}) - \mathbf{Q}(\mathbf{R}'))| \\
&= |\mathbf{r}_0 - (\mathbf{Q}(\mathbf{R}) - \mathbf{Q}(\mathbf{R}') - \delta(\mathbf{r}_0))| \\
&= |\mathbf{r}_0| - \frac{\mathbf{r}_0}{|\mathbf{r}_0|} \cdot (\mathbf{Q}(\mathbf{R}) - \mathbf{Q}(\mathbf{R}') - \delta(\mathbf{r}_0))
\end{aligned}
\tag{28}
$$

in the first approximation. Denoting $\mathbf{Q} = \mathbf{Q}(\mathbf{R})$, $\mathbf{Q}' = \mathbf{Q}(\mathbf{R}')$ and $\delta = \delta(\mathbf{r}_0)$ for brevity, and using Einstein notation, we therefore obtain

$$
\begin{aligned}
V &= \sum_{\mathbf{RR}'} \left( \frac{k(\mathbf{r}_0)}{2} \left( \frac{\mathbf{r}_0}{|\mathbf{r}_0|} \cdot (\mathbf{Q} - \mathbf{Q}' - \delta) \right)^2 - \frac{g(\mathbf{r}_0)}{6} \left( \frac{\mathbf{r}_0}{|\mathbf{r}_0|} \cdot (\mathbf{Q} - \mathbf{Q}' - \delta) \right)^3 \right) \\
&= \sum_{\mathbf{RR}'} \left( \frac{k(\mathbf{r}_0)}{2|\mathbf{r}_0|^2} \left( \mathbf{r}_{0\mu} (\mathbf{Q} - \mathbf{Q}' - \delta)_\mu \right)^2 - \frac{g(\mathbf{r}_0)}{6|\mathbf{r}_0|^3} \left( \mathbf{r}_{0\mu} (\mathbf{Q} - \mathbf{Q}' - \delta)_\mu \right)^3 \right) \\
&= \sum_{\mathbf{RR}'} \left( \frac{K_{\mu\nu}(\mathbf{r}_0)}{2} (\mathbf{Q} - \mathbf{Q}' - \delta)_\mu (\mathbf{Q} - \mathbf{Q}' - \delta)_\nu \right. \\
&\qquad\qquad \left. - \frac{G_{\mu\nu\sigma}(\mathbf{r}_0)}{6} (\mathbf{Q} - \mathbf{Q}' - \delta)_\mu (\mathbf{Q} - \mathbf{Q}' - \delta)_\nu (\mathbf{Q} - \mathbf{Q}' - \delta)_\sigma \right)
\end{aligned}
\tag{29}
$$

where we set $K_{\mu\nu}(\mathbf{r}_0) = \frac{k(\mathbf{r}_0)\mathbf{r}_{0\mu}\mathbf{r}_{0\nu}}{|\mathbf{r}_0|^2}$ and $G_{\mu\nu\sigma}(\mathbf{r}_0) = \frac{g(\mathbf{r}_0)\mathbf{r}_{0\mu}\mathbf{r}_{0\nu}\mathbf{r}_{0\sigma}}{|\mathbf{r}_0|^3}$ (not a summation).

We can now compare $V$ to an unperturbed harmonic potential

$$
V_0 = \sum_{\mathbf{RR}'} \frac{K_{\mu\nu}(\mathbf{r}_0)}{2} (\mathbf{Q} - \mathbf{Q}')_\mu (\mathbf{Q} - \mathbf{Q}')_\nu
\tag{30}
$$

20

$$
\begin{aligned}
V - V_0 &= \sum_{\mathbf{RR'}} \left( \frac{K_{\mu\nu}(\mathbf{r}_0)}{2} \left( \left( \mathbf{Q} - \mathbf{Q'} - \boldsymbol{\delta} \right)_\mu \left( \mathbf{Q} - \mathbf{Q'} - \boldsymbol{\delta} \right)_\nu - \left( \mathbf{Q} - \mathbf{Q'} \right)_\mu \left( \mathbf{Q} - \mathbf{Q'} \right)_\nu \right) \right. \\
&\qquad \left. - \frac{G_{\mu\nu\sigma}(\mathbf{r}_0)}{6} \left( \mathbf{Q} - \mathbf{Q'} - \boldsymbol{\delta} \right)_\mu \left( \mathbf{Q} - \mathbf{Q'} - \boldsymbol{\delta} \right)_\nu \left( \mathbf{Q} - \mathbf{Q'} - \boldsymbol{\delta} \right)_\sigma \right) \\
&= \sum_{\mathbf{RR'}} \frac{K_{\mu\nu}(\mathbf{r}_0)}{2} \left( -\delta_\mu \left( \mathbf{Q} - \mathbf{Q'} \right)_\nu - \delta_\nu \left( \mathbf{Q} - \mathbf{Q'} \right)_\mu + \delta_\nu \delta_\nu \right) \\
&\qquad - \frac{G_{\mu\nu\sigma}(\mathbf{r}_0)}{6} \left( \left( \mathbf{Q} - \mathbf{Q'} \right)_\mu \left( \mathbf{Q} - \mathbf{Q'} \right)_\nu \left( \mathbf{Q} - \mathbf{Q'} \right)_\sigma + \delta_\mu \delta_\nu \left( \mathbf{Q} - \mathbf{Q'} \right)_\sigma \right. \\
&\qquad\qquad + \delta_\nu \delta_\sigma \left( \mathbf{Q} - \mathbf{Q'} \right)_\mu + \delta_\mu \delta_\sigma \left( \mathbf{Q} - \mathbf{Q'} \right)_\nu - \delta_\mu \left( \mathbf{Q} - \mathbf{Q'} \right)_\nu \left( \mathbf{Q} - \mathbf{Q'} \right)_\sigma \\
&\qquad\qquad \left. - \delta_\nu \left( \mathbf{Q} - \mathbf{Q'} \right)_\mu \left( \mathbf{Q} - \mathbf{Q'} \right)_\sigma - \delta_\sigma \left( \mathbf{Q} - \mathbf{Q'} \right)_\mu \left( \mathbf{Q} - \mathbf{Q'} \right)_\nu - \delta_\mu \delta_\nu \delta_\sigma \right)
\end{aligned}
$$
$$(31)$$

As before, we use normal coordinates and ladder operator transformations:

$$
\begin{cases}
\mathbf{Q}(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} \mathbf{Q}_{\mathbf{k}} \\
\mathbf{Q}_k = \sum_\lambda \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}\lambda}}} \boldsymbol{\epsilon}_{\mathbf{k}\lambda} \left( a^\dagger_{-\mathbf{k}\lambda} + a_{\mathbf{k}\lambda} \right)
\end{cases}
\tag{32}
$$

$$
\begin{aligned}
\mathbf{Q}(\mathbf{R}) - \mathbf{Q}(\mathbf{R'}) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \left( e^{i\mathbf{k}\cdot\mathbf{R}} - e^{i\mathbf{k}\cdot\mathbf{R'}} \right) \mathbf{Q}_{\mathbf{k}} \\
&= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \left( e^{i\mathbf{k}\cdot\mathbf{R}} - e^{i\mathbf{k}\cdot(\mathbf{R}+\mathbf{r})} \right) \mathbf{Q}_{\mathbf{k}} \\
&= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \left( 1 - e^{i\mathbf{k}\cdot\mathbf{r}} \right) e^{i\mathbf{k}\cdot\mathbf{R}} \mathbf{Q}_{\mathbf{k}} \\
&= \frac{1}{\sqrt{N}} \sum_{\mathbf{k},\lambda} \left( 1 - e^{i\mathbf{k}\cdot\mathbf{r}} \right) e^{i\mathbf{k}\cdot\mathbf{R}} \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}\lambda}}} \boldsymbol{\epsilon}_{\mathbf{k}\lambda} \left( a^\dagger_{-\mathbf{k}\lambda} + a_{\mathbf{k}\lambda} \right)
\end{aligned}
\tag{33}
$$

Analogous to the one-dimensional case, we see that only even multiples of $\mathbf{Q}(\mathbf{R}) - \mathbf{Q}(\mathbf{R'})$ yield non-zero averages. We can also neglect the cubic $\delta_\mu \delta_\nu \delta_\sigma$ term and ob-

tain

$$\langle V - V_0 \rangle = \sum_{\mathbf{RR}'} \left( \frac{K_{\mu\nu}(\mathbf{r}_0)}{2} \delta_\mu \delta_\nu + \frac{G_{\mu\nu\sigma}(\mathbf{r}_0)}{6} \left( \delta_\mu \left\langle (\mathbf{Q} - \mathbf{Q}')_\nu (\mathbf{Q} - \mathbf{Q}')_\sigma \right\rangle \right. \right.$$

$$\left. \left. + \delta_\nu \left\langle (\mathbf{Q} - \mathbf{Q}')_\mu (\mathbf{Q} - \mathbf{Q}')_\sigma \right\rangle + \delta_\sigma \left\langle (\mathbf{Q} - \mathbf{Q}')_\mu (\mathbf{Q} - \mathbf{Q}')_\nu \right\rangle \right) \right)$$

$$= \sum_{\mathbf{R,r}} \frac{K_{\mu\nu}(\mathbf{r}_0)}{2} \delta_\mu \delta_\nu + \sum_{\mathbf{R,r}} \sum_{\mathbf{k,k}',\lambda,\lambda'} \frac{1}{N} \frac{G_{\mu\nu\sigma}(\mathbf{r}_0)}{6} \tag{34}$$

$$\cdot 2 \left(1 - \cos \mathbf{k} \cdot \mathbf{r}\right) \frac{\hbar}{2m\sqrt{\omega_{\mathbf{k}\lambda}\omega_{\mathbf{k}'\lambda'}}} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{R}} \left\langle \left( a^\dagger_{-\mathbf{k}\lambda} + a_{\mathbf{k}\lambda} \right) \left( a^\dagger_{-\mathbf{k}'\lambda'} \right. \right.$$

$$\left. \left. + a_{\mathbf{k}'\lambda'} \right) \right\rangle \left( \delta_\mu \epsilon_{\mathbf{k}\lambda\nu} \epsilon_{\mathbf{k}'\lambda'\sigma} + \delta_\nu \epsilon_{\mathbf{k}\lambda\mu} \epsilon_{\mathbf{k}'\lambda'\sigma} + \delta_\sigma \epsilon_{\mathbf{k}\lambda\mu} \epsilon_{\mathbf{k}'\lambda'\nu} \right)$$

Since we know that $\sum_{\mathbf{R}} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{R}} = N\delta_{\mathbf{k}',-\mathbf{k}}$ and $\left\langle a^\dagger_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda'} \right\rangle = \delta_{\lambda,\lambda'} \left\langle a^\dagger_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda} \right\rangle$ we can rewrite this as

$$\langle V - V_0 \rangle = N \sum_{\mathbf{r}} \frac{K_{\mu\nu}(\mathbf{r}_0)}{2} \delta_\mu \delta_\nu + \sum_{\mathbf{r}} \sum_{\mathbf{k},\lambda} \frac{G_{\mu\nu\sigma}(\mathbf{r}_0)}{3} (1$$

$$- \cos \mathbf{k} \cdot \mathbf{r}) \frac{\hbar}{2m\sqrt{\omega_{\mathbf{k}\lambda}\omega_{-\mathbf{k}\lambda}}} \coth \frac{1}{2}\beta\hbar\omega_{\mathbf{k}\lambda} \left( \delta_\mu \epsilon_{\mathbf{k}\lambda\nu} \epsilon_{-\mathbf{k}\lambda\sigma} + \delta_\nu \epsilon_{\mathbf{k}\lambda\mu} \epsilon_{-\mathbf{k}\lambda\sigma} \right.$$

$$\left. + \delta_\sigma \epsilon_{\mathbf{k}\lambda\mu} \epsilon_{-\mathbf{k}\lambda\nu} \right) \tag{35}$$

We also know that $\omega_{\mathbf{k}} = \omega_{-\mathbf{k}}$ and $\epsilon_{\mathbf{k}} = \epsilon^*_{-\mathbf{k}}$, therefore

$$\langle V - V_0 \rangle = N \sum_{\mathbf{r}} \frac{K_{\mu\nu}(\mathbf{r}_0)}{2} \delta_\mu \delta_\nu$$

$$+ \sum_{\mathbf{r}} \sum_{\mathbf{k},\lambda} \frac{G_{\mu\nu\sigma}(\mathbf{r}_0)}{3} (1 - \cos \mathbf{k} \cdot \mathbf{r}) \frac{\hbar}{2m\omega_{\mathbf{k}\lambda}} \coth \frac{1}{2}\beta\hbar\omega_{\mathbf{k}\lambda} \left( \delta_\mu \epsilon_{\mathbf{k}\lambda\nu} \epsilon^*_{\mathbf{k}\lambda\sigma} \right. \tag{36}$$

$$\left. + \delta_\nu \epsilon_{\mathbf{k}\lambda\mu} \epsilon^*_{\mathbf{k}\lambda\sigma} + \delta_\sigma \epsilon_{\mathbf{k}\lambda\mu} \epsilon^*_{\mathbf{k}\lambda\nu} \right)$$

We see here that no summation terms depend on vector $\mathbf{r}$ directly, which means that we can replace the summation on $\mathbf{r}$ by the summation on $\mathbf{r}_0$ (and

assume k-vectors generated from lattice vectors of the unexpanded lattice). The set of vectors $\mathbf{r}_0$ depends on the interactions considered. Assume that each particle interacts with nearest and next-nearest neighbors, which results in total of 9 interactions per particle. In this case the magnitude of each component of $\delta$ can only take one value, which leaves only the sign of the component variable: $\delta_\mu(\mathbf{r}_0) \to -\delta_\mu(\mathbf{r}_0)$ when $\mathbf{r}_{0\mu} \to -\mathbf{r}_{0\mu}$. Further, consider anharmonicity only in the $x$ direction, $\mathbf{r}_{anh} = (a, 0, 0)$. Equation 36 reduces to

$$
\begin{aligned}
\langle V - V_0 \rangle &= N \sum_{\mathbf{r}_0} \frac{K_{\mu\nu}(\mathbf{r}_0)}{2} \delta_\mu \delta_\nu \\
&\quad + \sum_{\mathbf{k},\lambda} G_{xxx}(\mathbf{r}_{anh}) \left(1 - \cos \mathbf{k} \cdot \mathbf{r}_{anh}\right) \frac{\hbar}{2m\omega_{\mathbf{k}\lambda}} \coth\left(\frac{1}{2}\beta\hbar\omega_{\mathbf{k}\lambda}\right) \epsilon_{\mathbf{k}\lambda x} \epsilon^*_{\mathbf{k}\lambda x} \delta_x \\
&= N \sum_{\mathbf{r}_0} \frac{K_{\mu\nu}(\mathbf{r}_0)}{2} \delta_\mu \delta_\nu + A\delta_x
\end{aligned}
$$

$$(37)$$

where A is a constant for a given temperature. Again, values of $\omega$ and $\epsilon$ are obtained by solving the harmonic problem.

To find out $\delta$ we now equate the derivatives of $\langle V - V_0 \rangle$ to zero:

$$
\begin{cases}
\frac{\partial}{\partial \delta_x} \langle V - V_0 \rangle = \sum_r \left(K_{xx}\delta_x + K_{xy}\delta_y + K_{xz}\delta_z\right) + A = 0 \\
\frac{\partial}{\partial \delta_y} \langle V - V_0 \rangle = \sum_r \left(K_{yx}\delta_x + K_{yy}\delta_y + K_{yz}\delta_z\right) = 0 \\
\frac{\partial}{\partial \delta_z} \langle V - V_0 \rangle = \sum_r \left(K_{zx}\delta_x + K_{zy}\delta_y + K_{zz}\delta_z\right) = 0
\end{cases}
$$

$$(38)$$

If we visualize $K_{\mu\nu}$ as elements of a matrix $\mathbf{K}$ with $\mu$ and $\nu$ representing indices, we can rewrite this as

$$
N \left(\sum_{\mathbf{r}_0} \mathbf{K}(\mathbf{r}_0)\right) \delta(\mathbf{r}_0) = - \begin{pmatrix} A \\ 0 \\ 0 \end{pmatrix}
$$

$$(39)$$

Determining $\delta$ now reduces to solving a linear system of equations. We know that $\delta_\mu(\mathbf{r}_0)$ changes sign whenever $\mathbf{r}_{0\mu}$ changes sign, which is analogous to fixing $c_\mu$ as positive and using absolute values of elements of $\mathbf{K}$ and $\mathbf{G}$. Since $\delta$ has the form $\delta_\mu(\mathbf{r}_0) = c_\mu r_{0\mu}$, positive values of $\delta$-components represent expansion and negative values represent contraction.

23

## 3.3 Three dimensions and a unit cell

We are now ready to construct the framework for the full problem.
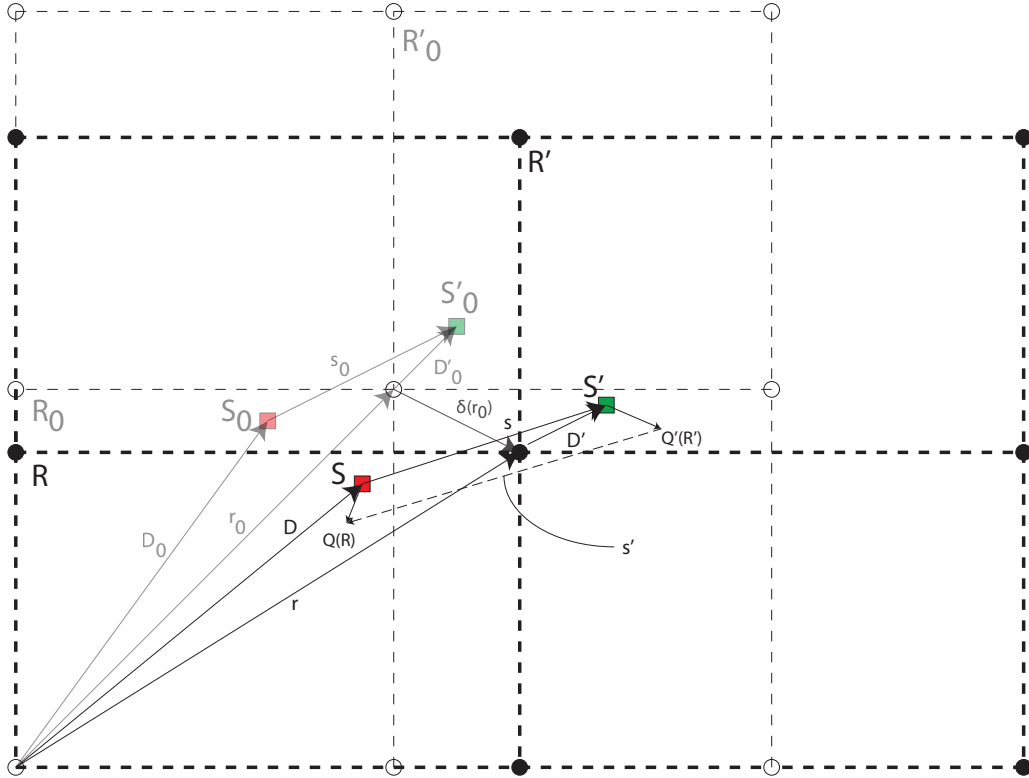


Figure 7: Vector diagram for two ions in an expanded lattice.

Consider an ion in an undistorted lattice which is located in the unit cell with absolute coordinate $\mathbf{R}_0$ (Fig. 7). The absolute coordinate of the ion's equilibtrium position is thus $\mathbf{S}_0 = \mathbf{R}_0 + \mathbf{D}_0$ where $\mathbf{D}_0$ is the displacement vector of the ion within the unit cell. The displacement between two ions is then

$$\mathbf{s}_0 = \mathbf{S}'_0 - \mathbf{S}_0 = (\mathbf{R}'_0 + \mathbf{D}'_0) - (\mathbf{R}_0 + \mathbf{D}_0) = (\mathbf{R}'_0 - \mathbf{R}_0) + (\mathbf{D}'_0 - \mathbf{D}_0) = \mathbf{r}_0 + \mathbf{d}_0 \quad (40)$$

When the lattice expands, the displacement between the equilibrium sites be-

comes

$$s = S' - S = (R' + D') - (R + D) = (R' - R) + (D' - D) = r + d \qquad (41)$$

where $S$ and $S'$ are absolute coordinates of ions' equilibrium sites, and $R$ and $R'$ are absolute coordinates of ions' unit cells. We will have the same uniformity constraints as before, $\delta_\mu(r_0) = c_\mu r_{0\mu}$. In particular, ions within the cell will move proportionally to the expansion, $\delta_\mu(D_0) = c_\mu D_{0\mu}$. Therefore,

$$
\begin{aligned}
d &= D' - D \\
&= D_0' + \delta(D_0') - (D_0 + \delta(D_0)) \\
&= (D_0' - D_0) + (\delta(D_0') - \delta(D_0)) \\
&= d_0 + \delta(d_0)
\end{aligned}
\qquad (42)
$$

Equation 41 becomes

$$s = S' - S = r + d = r_0 + \delta(r_0) + d_0 + \delta(d_0) = s_0 + \delta \qquad (43)$$

where we set $\delta = \delta(r_0) + \delta(d_0)$ for brevity.

Allow now ions to deviate from equilibrium by $Q = Q(R)$ and $Q' = Q'(R')$ respectively. The distance between them is expressed in the first approximation as

$$
\begin{aligned}
|s'| &= |S' - S + Q' - Q| \\
&= |s_0 - (Q - Q' - \delta)| \\
&= s_0 - \frac{s_0}{|s_0|} \cdot (Q - Q' - \delta)
\end{aligned}
\qquad (44)
$$

The potential spans over all interacting ions with assigned coordinates $S$ and $S'$ and has the form

$$
\begin{aligned}
V &= \sum_{s,s'} \left( \frac{k(s_0)}{2} \left( |s'| - |s_0| \right)^2 + \frac{g(s_0)}{6} (|s'| - |s_0|)^3 \right) \\
&= \sum_{s,s'} \left( \frac{k(s_0)}{2} \left( \frac{s_0}{|s_0|} \cdot (Q - Q' - \delta) \right)^2 - \frac{g(s_0)}{6} \left( \frac{s_0}{|s_0|} \cdot (Q - Q' - \delta) \right)^3 \right) \\
&= \sum_{s,s'} \left( \frac{k(s_0) s_{0\mu} s_{0\nu}}{2|s_0|^2} \left( Q - Q' - \delta \right)_\mu \left( Q - Q' - \delta \right)_\nu \right. \\
&\qquad \left. - \frac{g(s_0) s_{0\mu} s_{0\nu} s_{0\sigma}}{6|s_0|^3} \left( Q - Q' - \delta \right)_\mu \left( Q - Q' - \delta \right)_\nu \left( Q - Q' - \delta \right)_\sigma \right)
\end{aligned}
\qquad (45)
$$

25

Keep in mind that $\mathbf{s}_0 = \mathbf{r}_0 + \mathbf{d}_0$ depends on the choice of $\mathbf{S}$ and $\mathbf{S}'$. Similar to before, we set $K_{\mu\nu}(\mathbf{s}_0) = \frac{k(\mathbf{s}_0)s_{0\mu}s_{0\nu}}{|\mathbf{s}_0|^2}$ and $G_{\mu\nu\sigma}(\mathbf{s}_0) = \frac{g(\mathbf{s}_0)s_{0\mu}s_{0\nu}s_{0\sigma}}{|\mathbf{s}_0|^3}$ and compare $V$ to

$$V_0 = \sum_{\mathbf{S},\mathbf{S}'} \frac{K_{\mu\nu}(\mathbf{s}_0)}{2} \left(\mathbf{Q} - \mathbf{Q}'\right)_\mu \left(\mathbf{Q} - \mathbf{Q}'\right)_\nu \tag{46}$$

Notice that equations 45 and 46 have the same form as equations 29 and 30. We can therefore immediately write out $\langle V - V_0 \rangle$:

$$\langle V - V_0 \rangle = \sum_{\mathbf{S},\mathbf{S}'} \left( \frac{K_{\mu\nu}(\mathbf{s}_0)}{2}\delta_\mu\delta_\nu + \frac{G_{\mu\nu\sigma}(\mathbf{s}_0)}{6} \left( \delta_\mu \left\langle \left(\mathbf{Q} - \mathbf{Q}'\right)_\nu \left(\mathbf{Q} - \mathbf{Q}'\right)_\sigma \right\rangle \right. \right.$$
$$\left. \left. + \delta_\nu \left\langle \left(\mathbf{Q} - \mathbf{Q}'\right)_\mu \left(\mathbf{Q} - \mathbf{Q}'\right)_\sigma \right\rangle + \delta_\sigma \left\langle \left(\mathbf{Q} - \mathbf{Q}'\right)_\mu \left(\mathbf{Q} - \mathbf{Q}'\right)_\nu \right\rangle \right) \right) \tag{47}$$

As before, we omitted here odd multiples of $\mathbf{Q} - \mathbf{Q}'$ and the cubic $\delta$ term.

Next we use variable transformations

$$\begin{cases} \mathbf{Q}(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}}\mathbf{Q}_k \\ \mathbf{Q}_{\mathbf{k}} = \sum_\lambda \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}\lambda}}} \epsilon_{k\lambda} \left(a^\dagger_{-\mathbf{k}\lambda} + a_{\mathbf{k}\lambda}\right) \end{cases} \tag{48}$$

where $m$ and $\epsilon$ depend on a particular ion, to obtain

$$\mathbf{Q}(\mathbf{R}) - \mathbf{Q}'(\mathbf{R}') = \frac{1}{\sqrt{N}} \sum_{\mathbf{k},\lambda} e^{i\mathbf{k}\cdot\mathbf{R}} \left( \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}\lambda}}} \epsilon_{\mathbf{k}\lambda} - e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2m'\omega_{\mathbf{k}\lambda}}} \epsilon'_{\mathbf{k}\lambda} \right) \left(a^\dagger_{-\mathbf{k}\lambda} + a_{\mathbf{k}\lambda}\right) \tag{49}$$

Consider now

$$
\sum_{s,s'} \left\langle (\mathbf{Q} - \mathbf{Q}')_\mu (\mathbf{Q} - \mathbf{Q}')_\nu \right\rangle = \frac{1}{N} \sum_{\mathbf{R},\mathbf{D},\mathbf{R}',\mathbf{D}'} \sum_{\mathbf{k},\mathbf{k}',\lambda,\lambda'} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{R}} \left( \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}\lambda}}} \epsilon_{\mathbf{k},\lambda\,\mu} \right.
$$

$$
\left. - e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2m'\omega_{\mathbf{k}\lambda}}} \epsilon'_{\mathbf{k},\lambda\,\mu} \right) \left( \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}'\lambda'}}} \epsilon_{\mathbf{k}',\lambda'\,\nu} \right.
$$

$$
\left. - e^{i\mathbf{k}'\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2m'\omega_{\mathbf{k}'\lambda'}}} \epsilon'_{\mathbf{k}',\lambda'\,\nu} \right) \left\langle \left( a^\dagger_{-\mathbf{k}\lambda} + a_{\mathbf{k}\lambda} \right) \left( a^\dagger_{-\mathbf{k}'\lambda'} + a_{\mathbf{k}'\lambda'} \right) \right\rangle
$$

$$
= \sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} \sum_{\mathbf{k},\lambda} \left( \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}\lambda}}} \epsilon_{\mathbf{k},\lambda\,\mu} \right.
$$

$$
\left. - e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2m'\omega_{\mathbf{k}\lambda}}} \epsilon'_{\mathbf{k},\lambda\,\mu} \right) \left( \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}\lambda}}} \epsilon^*_{\mathbf{k},\lambda\,\nu} \right.
$$

$$
\left. - e^{-i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2m'\omega_{\mathbf{k}\lambda}}} \epsilon'^*_{\mathbf{k},\lambda\,\nu} \right) \coth \frac{1}{2} \beta\hbar\omega_{\mathbf{k}\lambda}
$$

$$
= \sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} \alpha^\sigma_{\mu\nu} \tag{50}
$$

$\mathbf{D}$ and $\mathbf{D}'$ represent specific ions in the unit cells and define values for $m$ and $\epsilon$, and $m'$ and $\epsilon'$. Here $\alpha^\sigma_{\mu\nu} = \alpha^\sigma_{\mu\nu}(\mathbf{s})$ is a term, which is acquired by summation over $\mathbf{k}$ and $\lambda$ using the harmonic results from the first part of the thesis. Superscript $\sigma$ is there to remind us that the Einstein summation goes over three indices, although the constant only depends on two.

Equation 47 therefore becomes

$$
\langle V - V_0 \rangle = \sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} \left( N \frac{K_{\mu\nu}(\mathbf{s}_0)}{2} \delta_\mu \delta_\nu + \frac{G_{\mu\nu\sigma}(\mathbf{s}_0)}{6} \left( \delta_\mu \alpha^\mu_{\nu\sigma} + \delta_\nu \alpha^\nu_{\mu\sigma} + \delta_\sigma \alpha^\sigma_{\mu\nu} \right) \right) \tag{51}
$$

Before we proceed, we would like to separate all units into a separate constant to see the length scale of this problem. We begin by changing the form of $K_{\mu\nu}$. We know that $s_{0\mu} = |\mathbf{s}_0| \Omega_\mu$ where

$$
\begin{cases} \Omega_x = \cos\theta \cos\phi \\ \Omega_y = \cos\theta \sin\phi \\ \Omega_z = \sin\theta \end{cases} \tag{52}
$$

27

Here $\theta$ is the elevation angle that $\mathbf{s}_0$ makes with the horizontal xy-plane and $\phi$ is the azimuth angle. Therefore,

$$
\begin{aligned}
K_{\mu\nu}(\mathbf{s}_0) &= k(\mathbf{s}_0)\Omega_\mu\Omega_\nu \\
&= k_0\overline{k}(\mathbf{s}_0)\Omega_\mu\Omega_\nu \\
&= k_0\overline{K}_{\mu\nu}(\mathbf{s}_0)
\end{aligned}
\tag{53}
$$

where $\overline{k}(\mathbf{s}_0)$ is the force constant in units of $k_0$. $\overline{K}_{\mu\nu}$ is the dimensionless counterpart of $K_{\mu\nu}$.

Similarly, we obtain

$$
\begin{aligned}
G_{\mu\nu\sigma}(\mathbf{s}_0) &= g\Omega_\mu\Omega_\nu\Omega_\sigma \\
&= g\overline{G}_{\mu\nu\sigma}(\mathbf{s}_0)
\end{aligned}
\tag{54}
$$

assuming there is only one value for anharmonic interactions. We have thus successfully replaced lengths of bonds' projections $s_{0\mu}$ with bonds' angles $\theta$ and $\phi$, keeping geometry intact.

The next step is to redefine the expansion terms. Recall that

$$
\delta_\mu = \delta_\mu(\mathbf{r}_0) + \delta_\mu(\mathbf{d}_0) = c_\mu r_{0\mu} + c_\mu d_{0\mu} = c_\mu(r_{0\mu} + d_{0\mu}) = c_\mu s_{0\mu}
\tag{55}
$$

We can rewrite this as

$$
\delta_\mu = c_\mu s_{0\mu} = c_\mu f_\mu l_\mu = f_\mu \Delta_\mu
\tag{56}
$$

Here $l_\mu$ is the lattice constant of the conventional unit cell, $l_x = l_y = a$, $l_z = c$, and $f_\mu$ is the length of $s_{0\mu}$ in units of $l_\mu$. $\Delta_\mu$ is therefore the expansion of the conventional unit cell, and is the value we're looking for.

The last step is to extract dimensional constants from the $\alpha$ terms:

$$\alpha_{\mu\nu}^{\sigma} = \sum_{\mathbf{k},\lambda} \left( \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}\lambda}}} \epsilon_{\mathbf{k},\lambda\,\mu} - e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2m'\omega_{\mathbf{k}\lambda}}} \epsilon'_{\mathbf{k},\lambda\,\mu} \right) \left( \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}\lambda}}} \epsilon^{*}_{\mathbf{k},\lambda\,\nu} \right.$$

$$\left. - e^{-i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2m'\omega_{\mathbf{k}\lambda}}} \epsilon'^{*}_{\mathbf{k},\lambda\,\nu} \right) \coth \frac{1}{2}\beta\hbar\omega_{\mathbf{k}\lambda}$$

$$= \frac{\hbar}{2\sqrt{k_0 m_0}} \sum_{\mathbf{k},\lambda} \frac{1}{\overline{\omega}_{\mathbf{k}\lambda}} \left( \frac{\epsilon_{\mathbf{k},\lambda\,\mu}}{\sqrt{\overline{m}}} - e^{i\mathbf{k}\cdot\mathbf{r}} \frac{\epsilon'_{\mathbf{k},\lambda\,\mu}}{\sqrt{\overline{m'}}} \right) \left( \frac{\epsilon^{*}_{\mathbf{k},\lambda\,\nu}}{\sqrt{\overline{m}}} - e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{\epsilon'^{*}_{\mathbf{k},\lambda\,\nu}}{\sqrt{\overline{m'}}} \right) \coth \frac{\overline{\omega}_{\mathbf{k}\lambda}}{\overline{T}}$$

$$= \frac{\hbar}{2\sqrt{k_0 m_0}} \overline{\alpha}_{\mu\nu}^{\sigma}$$

$$(57)$$

where $\overline{\omega}$ is in units of $\sqrt{\frac{k_0}{m_0}}$ (which is acquired when solving the harmonic problem with force constants in units of $k_0$ and masses in units of $m_0$), $\overline{m}$ and $\overline{m'}$ are in units of $m_0$ and $\overline{T}$ is in units of $\frac{\hbar\sqrt{\frac{k_0}{m_0}}}{2k_B}$.

The problem is thus reduced to

$$\langle V - V_0 \rangle = \sum_{\mathbf{D},\mathbf{R'},\mathbf{D'}} \left( \frac{Nk_0}{2} \overline{K}_{\mu\nu}(\mathbf{s}_0) f_\mu f_\nu \Delta_\mu \Delta_\nu \right.$$

$$(58)$$

$$\left. + \frac{g\hbar}{12\sqrt{k_0 m_0}} \overline{G}_{\mu\nu\sigma}(\mathbf{s}_0)(f_\mu \overline{\alpha}_{\nu\sigma}^{\mu}\Delta_\mu + f_\nu \overline{\alpha}_{\mu\sigma}^{\nu}\Delta_\nu + f_\sigma \overline{\alpha}_{\mu\nu}^{\sigma}\Delta_\sigma) \right)$$

We now look for values $\Delta_x, \Delta_y, \Delta_z$ for which this average is minimal. Setting the derivatives in each dimension to zero, we obtain[2]:

$$J_{\langle V-V_0 \rangle}(\Delta_x, \Delta_y, \Delta_z) = J_{f_1}(\Delta_x, \Delta_y, \Delta_z) + J_{f_2}(\Delta_x, \Delta_y, \Delta_z) = 0 \qquad (59a)$$

$$J_{f_1}(\Delta_x, \Delta_y, \Delta_z) = -J_{f_2}(\Delta_x, \Delta_y, \Delta_z) \qquad (59b)$$

where[3]

---

[2] $J$ is the Jacobian matrix, $J_F(x_1, \ldots, x_n) = \begin{pmatrix} \frac{\partial y_1}{\partial x_1} & \cdots & \frac{\partial y_1}{\partial x_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial y_m}{\partial x_1} & \cdots & \frac{\partial y_m}{\partial x_n} \end{pmatrix}$.

[3] Since $\langle V - V_0 \rangle$ is a scalar function, it's easier to work with the transpose of the Jacobian.

29

$$f_1 = \frac{Nk_0}{2} \sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} \overline{K}_{\mu\nu}(\mathbf{s}_0) f_\mu f_\nu \Delta_\mu \Delta_\nu \tag{60a}$$

$$J_{f_1}(\Delta_x, \Delta_y, \Delta_z) = Nk_0 \sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} \begin{pmatrix} \overline{K}_{xx} f_x^2 \Delta_x + \overline{K}_{xy} f_x f_y \Delta_y + \overline{K}_{xz} f_x f_z \Delta_z \\ \overline{K}_{xy} f_x f_y \Delta_x + \overline{K}_{xy} f_y^2 \Delta_y + \overline{K}_{xz} f_y f_z \Delta_z \\ \overline{K}_{xy} f_x f_z \Delta_x + \overline{K}_{xy} f_y f_z \Delta_y + \overline{K}_{xz} f_z^2 \Delta_z \end{pmatrix} \tag{60b}$$

$$f_2 = \frac{g\hbar}{12\sqrt{k_0 m_0}} \sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} \overline{G}_{\mu\nu\sigma}(\mathbf{s}_0)(f_\mu \overline{\alpha}_{\nu\sigma}^\mu \Delta_\mu + f_\nu \overline{\alpha}_{\mu\sigma}^\nu \Delta_\nu + f_\sigma \overline{\alpha}_{\mu\nu}^\sigma \Delta_\sigma)$$

$$= \frac{g\hbar}{12\sqrt{k_0 m_0}} \sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} A_x(\mathbf{s}_0)\Delta_x + A_y(\mathbf{s}_0)\Delta_y + A_z(\mathbf{s}_0)\Delta_z \tag{60c}$$

$$J_{f_2}(\Delta_x, \Delta_y, \Delta_z) = \frac{g\hbar}{12\sqrt{k_0 m_0}} \sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} \begin{pmatrix} A_x(\mathbf{s}_0) \\ A_y(\mathbf{s}_0) \\ A_z(\mathbf{s}_0) \end{pmatrix} = \frac{g\hbar}{12\sqrt{k_0 m_0}} \sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} \mathbf{A}(\mathbf{s}_0) \tag{60d}$$

$A_x$, $A_y$ and $A_z$ are terms, calculated from the Einstein summation. Putting equations 59b and 60 together gives

$$\sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} \begin{pmatrix} \overline{K}_{xx} f_x^2 & \overline{K}_{xy} f_x f_y & \overline{K}_{xz} f_x f_z \\ \overline{K}_{xy} f_x f_y & \overline{K}_{xy} f_y^2 & \overline{K}_{xz} f_y f_z \\ \overline{K}_{xy} f_x f_z & \overline{K}_{xy} f_y f_z & \overline{K}_{xz} f_z^2 \end{pmatrix} \begin{pmatrix} \Delta_x \\ \Delta_y \\ \Delta_z \end{pmatrix} = -L \frac{1}{12N} \sum_{\mathbf{D},\mathbf{R}',\mathbf{D}'} \mathbf{A}(\mathbf{s}_0) \tag{61}$$

Here we see that everything, except $L = \frac{g\hbar}{\sqrt{k_0^3 m_0}}$, is dimensionless. Constant $L$ is the length parameter and determines the scale of the problem.

The system of linear equations (61) can be solved for values of $\Delta_x, \Delta_y, \Delta_z$. As mentioned before, these are the expansions of the conventional unit cell, i.e. each dimension $\mu$ of the unit cell is increased by $\Delta_\mu$.

## 3.4   Results

Table 1 indicates some common values that were used for numerical calculations in the one- and three-dimensional cases with identical particles. $T$ and $g$ were also used in the full $BaFe_2As_2$ case.

---

[4]We took the temperature at which used lattice constants were measured [10].

| | | |
|---|---|---|
| Anharmonic interaction strength | $G$ or $g$ | $-103$ eV/Å$^3$ |
| Number of unit cells in each dimension | $N$ | 10 |
| Temperature[4] | $T$ | 175 K |
| Lattice constant | $a$ | 3.96 Å |

Table 1: Numerical values for constants in the one- and three-dimensional cases with identical particles

In the one-dimensional case numerical calculations with $K = 1.39 \cdot 10^2$ N/m produce

$$\delta = 1.20 \cdot 10^{-2}\text{Å} \tag{62}$$

In the three-dimensional case, with $k = 1.39 \cdot 10^2$ N/m for the nearest neighbor interaction and $k = 4.18 \cdot 10$ N/m for the next-nearest neighbor interaction, we calculate

$$\delta = \begin{pmatrix} 6.28 \\ -0.99 \\ -0.99 \end{pmatrix} \cdot 10^{-3}\text{Å} \tag{63}$$

For calculations on the BaFe$_2$As$_2$ crystal we used Fe-As interaction and mass of Fe ion as the reference constants: $k_0 = k_{\text{Fe-As}}$, $m_0 = m_{\text{Fe}}$. Magnitudes of the force constants were the same as in the harmonic problem with an additional anharmonic constant $g$ for the Fe-As interaction. The length parameter was calculated to be $L = -9.67 \cdot 10^{-2}$ Å. We found that the lattice expansion depends strongly on the Fe-Fe-As angle, i.e. the angle that the Fe-As bond makes with the horizontal and which controls how far the As ions are from the Fe plane. For a variable angle and the rest of the crystallographic data unchanged, Fig. 8 shows how much the lattice constants change. At a $0°$ angle we have a positive expansion in the xy-plane, which is expected since the FeAs plane is then purely horizontal. At a $58°$ angle, when As ions are in the same plane as Ba ions, we have no expansion in the xy-plane.

For the $35°$ angle we have

$$\delta_a = -5.65 \cdot 10^{-3}\text{Å} \tag{64a}$$

$$\delta_c = 8.63 \cdot 10^{-1}\text{Å} \tag{64b}$$

which is near a zero expansion in the xy-plane and a maximal expansion in the z-direction. These points are shown on Fig. 8 as black squares.
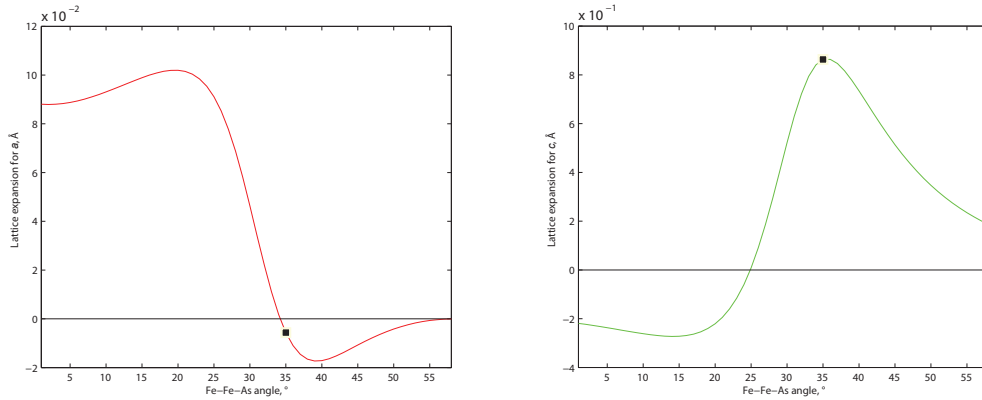
Figure 8: Left: Expansion of the lattice constant $a$. Right: Expansion of the lattice constant $c$. Black squares show the expansions for a $35°$ angle.

## 3.5 Isotope effect

One of the ways to compare our results with the experimental data is through the isotope effect. We know that the isotope substitution results in the change of lattice parameters [1], so we change the mass of Fe ions in our calculations and see how much the lattice expansions change. As expected, the change is proportional to the expansion itself. Fig. 9 shows the change of lattice expansions when we switch from $^{57}$Fe to $^{54}$Fe.

For the $35°$ angle, the mass change leads to $\delta_a$ changing by $-1.13 \cdot 10^{-5}$ Å and $\delta_c$ changing by $1.73 \cdot 10^{-3}$ Å. For comparison, it was experimentally measured [1] that there was no change in $a$ and a $(3 \pm 1) \cdot 10^{-3}$ Å change in $c$ when going from $^{57}$Fe to $^{54}$Fe.

# 4 Conclusions

The overall result of the work has been very satisfactory. Harmonic phonon dispersions are in excellent agreement with published data; almost reproducing the energy spectrum from [6]. While it is hard to check the validity of calculations for identical anharmonic particles (since the anharmonic effect is intrinsic to the material — there is no method to measure lattice constants in a real crystal without the anharmonic expansion), the anharmonic expansions obtained were of the an-
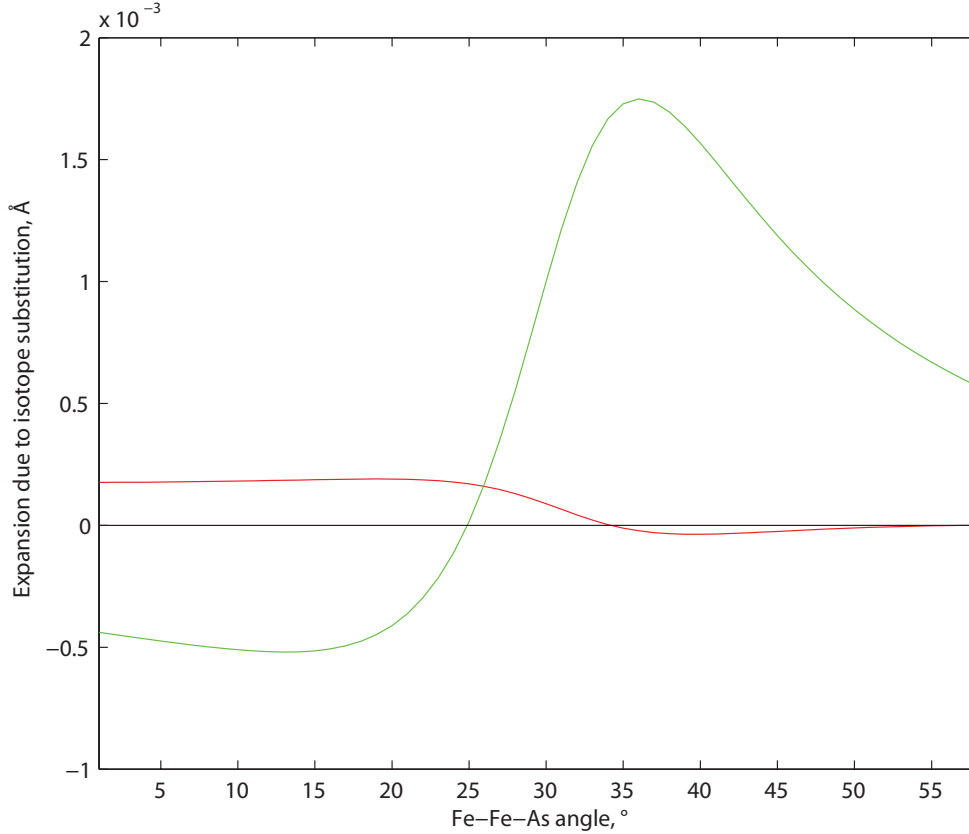
Figure 9: Change of the lattice expansions (red for $a$ and green for $c$) due to $^{57}$Fe to $^{54}$Fe substitution for different angles.

ticipated order of magnitude. The isotope expansion of the $BaFe_2As_2$ crystal also agrees with the experimental data very well. In this work we found that Fe-Fe-As angle, i.e. the As height, greatly affects both direction and magnitude of the expansion. It has been argued that $T_c$ is very sensitive to this height [15, 16]. As the calculated isotope expansion can be both positive and negative, depending on the Fe-Fe-As angle, it could possibly be related to the experimental observation of both positive and negative isotope effects in different materials [1, 17]. This, however, is an extensive topic and deserves a separate study as a natural continuation of this thesis.

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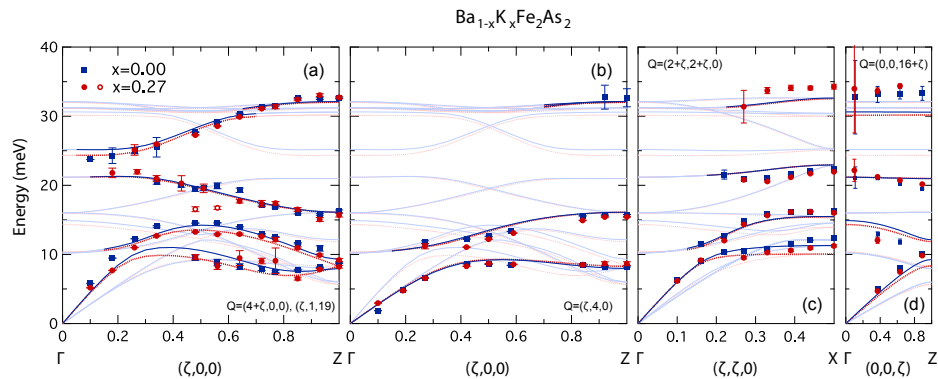
# A   Published data on BaFe$_2$As$_2$



Figure 10: Phonon dispersions measured by inelastic X-ray scattering at different scattering vectors **Q**. Light-colored lines depict modes that are unobservable with the chosen scattering vector. *The material is the reproduction from J. Phys. Soc. Jpn. 79, 014714 (2010), Ch. Lee, K. Kihou, K. Horigane, S. Tsutsui, T. Fukuda, H. Eisaki, A. Iyo, H. Yamaguchi, A. Baron, M. Braden and K. Yamada. Copyright (2010) by the Physical Society of Japan.*
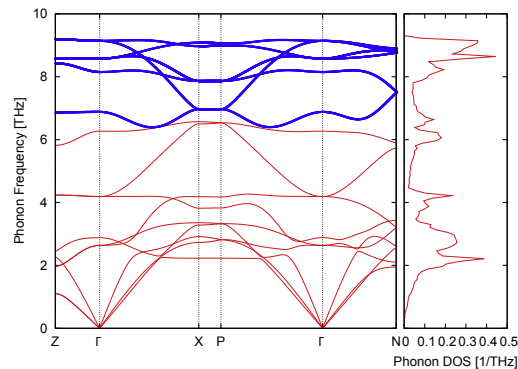


Figure 11: Phonon dispersions and density of states calculated from the first principles.
*Reprinted from Physica C: Superconductivity, Volume 469, Issues 15-20, Nakamura H., Hayashi N., Nakai N. and Machida M., First-principle calculation for the phonon structure on iron-based superconductors, Pages 1024-1026, Copyright (2009), with permission from Elsevier.*

35

# B  Quantum-mechanical treatment of a harmonic problem

Consider the Hamiltonian for a one-dimensional harmonic chain of N identical particles:

$$H = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \frac{m\omega^2}{2} \sum_j (x_{j+1} - x_j)^2 \tag{65}$$

We introduce discrete Fourier transforms of $x$ and $p$, assuming periodic boundary conditions:

$$x_j = \frac{1}{\sqrt{N}} \sum_k Q_k e^{ikja} \tag{66a}$$

$$p_j = \frac{1}{\sqrt{N}} \sum_k P_k e^{-ikja}. \tag{66b}$$

The Hamiltonian can thus be written in wave vector space as

$$H = \sum_k \frac{P_k P_{-k}}{2m} + \frac{m\omega_k^2}{2} Q_k Q_{-k} \tag{67}$$

where

$$\omega_k = \sqrt{2\omega^2(1 - \cos ka)}. \tag{68}$$

To see that $\omega_k$ really are the phonon frequencies, we introduce ladder operators that would diagonalize the Hamiltonian:

$$a_k = \sqrt{\frac{m\omega_k}{2\hbar}} (Q_k + \frac{i}{m\omega_k} P_{-k}) \tag{69a}$$

$$a_k^\dagger = \sqrt{\frac{m\omega_k}{2\hbar}} (Q_{-k} - \frac{i}{m\omega_k} P_k) \tag{69b}$$

They obey commutation relations

$$[a_k, a_{k'}^\dagger] = \delta_{kk'} \tag{70a}$$

$$[a_k, a_{k'}] = [a_k^\dagger, a_{k'}^\dagger] = 0 \tag{70b}$$

The Hamiltonian then reduces to

$$H = \sum_k \hbar\omega_k \left( a_k^\dagger a_k + \frac{1}{2} \right) \tag{71}$$

where $a_k^\dagger a_k$ behaves as the number operator, similar to the case of the simple harmonic oscillator. Here we see that the energy spectrum is characterized by quanta $\hbar\omega_k$. Essentially, frequencies $\omega_k$ are the same as the ones acquired by the Classical Theory.

For a more detailed discussion, see [18].

# C  Pseudocode

## C.1  Harmonic calculations

- Set all numerical constants

- Generate k-vectors (excluding the k-vector at the primitive cell boundary)

```
for n1 from 1 to N1-1
    for n2 from 1 to N2-1
        for n3 from 1 to N3-1
            add to k-array
                (n1/N1)*b1 + (n2/N2)*b2 + (n3/N3)*b3
```

- Generate displacement matrices

```
for each ion in the unit cell
    for each neighbor
        set
            r = vector from ion to neighbor
            R = transpose(r/norm(r))*(r/norm(r))
```

- Create matrix **M**

```
assign an <id> to each ion in the unit cell
for each ion <id>
    for each neighbor
        write the motion equation
    add the motion equations
    sort coefficients by <id>
    insert into row of M that corresponds to the <id>
```

- Solve the matrix for different k-vectors

```
for each k in the k-array
    solve for eigenvalues and eigenvectors of M
    assign <lambda> to each set of eigenvalue-eigenvector
    take square root of eigenvalues (omega)
    add the solutions to the spectrum-array
```

- Calculate density of states

```
round off spectrum-array to 1 micro-eV
count how many times each distinct omega occurs
```

## C.2   Anharmonic calculations

- Calculate constants $A_x$, $A_y$, $A_z$

```
for each ion <id>
    for each neighbor
        for mu from x to z
            for nu from x to z
                for sigma from x to z
                    for each k in the k
                        for each <lambda>
                            set
                                s = vector from ion to neighbor
                            calculate A_x, A_y, A_z
```

38

```
                                using values from spectrum-array
                     set
                         A = A + (A_x, A_y, A_z)
```

- Calculate the LHS sum of matrices

```
for each ion <id>
    for each neighbor
        calculate the LHS matrix <Kff>
set
    Kff_sum = sum of all matrices <Kff>
```

- Obtain final values of $\Delta_\mu$

```
Kff_sum \ (-L*(1/12N)*A)
```

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