

A-TDEP

Temperature Dependent Effective Potential for ABINIT

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Part I : Thermodynamic properties using second and third order Interatomic Force Constants

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Abstract

The capture of thermal effects in solid state physic is a long standing issue and several stand-alone or post-process computational codes are now available. Using different theoretical framework, they propose to provide some thermodynamic quantities involving the so called anharmonic effects. In this article, we show that A-TDEP can produce almost all the temperature dependent thermodynamic quantities you want, from a single *ab initio* molecular dynamic (AIMD) trajectory and by means of a Graphical User Interface (GUI) very easy to use.

We start by detailing how the originally "Temperature Dependent Effective Potential" method proposed by Hellman *al.* [1] is implemented in the *ab initio* code ABINIT. In particular, we present the various algorithms and schemes used in A-TDEP to obtain the Interatomic Force Constants (IFC). The 2nd and 3rd order IFCs are produced self-consistently using a least-square method fitting the AIMD forces on a model Hamiltonian function of the displacements. In addition, we stress that we face to a constrained least-square problem since all the IFCs have to fulfill the several symmetry rules imposed by the space group, by the translation or rotation invariances of the system...

Numerous thermodynamic quantities can be computed starting from the

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2nd order IFCs. The first one is the phonon spectra, from which a large number of other quantities flow : internal energy, entropy, free energy, specific heat... The elastic constants and other usual elastic moduli (the bulk, shear and Young moduli) can be also produced at this level. Using the 3rd order IFCs, we show how to extract the Grüneisen parameter, the thermal expansion, the sound velocities... and in particular, how to take into account the anisotropy of the system within.

As representative applications A-TDEP capabilities, we show the thermal evolution of the soft phonon mode of α -U, the thermal stabilization of the bcc phase of Zr and the thermal expansion of Si. All these features highlight the strong anharmonicity included in this system.

Keywords: Phonons; *ab initio*; Temperature; Thermodynamic; Elastic

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[1] Reference 1

[2] Reference 2

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Introduction

The study of thermal properties of materials has always been the subject of a significant research in solid state physics. Whatever the purpose, experiments and theory have brought together their discoveries to understand the mechanisms that governed temperature effects. A large number of fields of research are concerned, but also interested in a still better description of materials when they undergo some temperature variations : astrophysics, superconductivity, aerospace industry, electronics, geoscience... All of them require the building of phase diagrams, the refinement of Equation of States (EoS) and the characterization of thermodynamical quantities.

The theory of lattice dynamics has been developed for this purpose and specifies that thermal effects can be captured by describing precisely the lattice vibrations of the system. In this framework, the key quantity is the phonon frequencies $\omega(V, T)$ which depend on the volume V and the temperature T . Within the harmonic approximation (HA), the most famous approach based on the quantum harmonic crystal, the lattice vibrations are considered to be temperature independent. The HA phonon frequencies $\omega_{\text{HA}}(V, 0K)$ are assumed to be equal to the ones computed at $T=0K$ and the temperature effects are taken into account through the population of phonon states. If this approximation has encountered many success, nevertheless this one failed to describe the thermal expansion of materials. That's the reason why another approximation has been proposed : the quasi-harmonic approximation (QHA). This one considers that the phonon frequencies depend on the temperature through the variation of the volume : $\omega_{\text{QHA}}(V(T), 0K)$. Even if the temperature is not explicitly taken into account, the QHA is able to capture most of standard thermal effects encountered by materials.

However, the QHA reaches its limits when materials are strongly heated, when some crystalline phases are (de)stabilized wrt temperature, when thermodynamic conditions are close to phase transitions... In these cases, the implicit variation of temperature through the variation of volume is no longer sufficient. If the QHA already includes some effects going beyond to the harmonic approximations (ex : thermal expansion), this one is not able to account for thermal effects at constant volume. These ones will be called "anharmonic effects" in the following. Following Holzapfel [2], two kinds of anharmonicities can be distinguished :

- one described by the QHA, named **isothermal** or **extrinsic**, able to describe the thermal expansion but inefficient to depict the thermal

behaviour of materials at constant volume,

- another going beyond the QHA, named **isochoric** or **intrinsic**, which treats explicitly the dependency wrt the temperature and reproduces thermal effects at constant volume : $\omega_{\text{Anh}}(V(T), T)$.

One can formalize and synthesize this statement as follows :

$$\frac{d\omega}{dT} = \left(\frac{\partial\omega}{\partial T}\right)_V + \left(\frac{\partial\omega}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \quad (1)$$

The second term of the right hand side of the previous equation is included in the QHA, but not the first one only treated when the temperature dependency is explicit.

As well for material science as for theoretical issues, the calculation of lattice vibrations (whatever the thermodynamic conditions) is become one of the most important challenge in solid state physics. For this purpose, the *ab initio* calculations are well suited : both the effects of pressure and temperature can be taken into account, without any assumption about the interatomic potential. Some approaches have been developed in order to compute the phonon frequencies at 0 K : either by brute force using finite differences [3, 4] or employing more elegant method such as density functional perturbation theory (DFPT) [5, 6]. But it seems harder to pick up all the anharmonic effects using these techniques.

Since the beginning of the 60's, several microscopic formalisms has been developed in order to go beyond the simple quantum harmonic crystal and to deal with the anharmonic effects [7, 8, 9, 10, 11, 12, 13]. Not only do they offer a description of lattice vibrations going beyond the QHA (that is to say capturing thermal intrinsic effects) but also they give a comprehensive framework including anharmonicity in thermodynamic and elasticity. If these theoretical developments were very successful in the past sixty years, they were restricted to analytical results. Nowadays, due to the increasing power of supercomputers, they can be introduced in computational codes in order to access quantities unreachable in the past.

A large number of theoretical approaches have been developed during the 10 last years in order to capture the anharmonics effects starting from *ab initio* calculations. These ones have led to several computational codes which have recently emerged in the solid state physics community. Without claiming to make an exhaustive list, we can mention :

- the so-called "Self-Consistent Ab-Initio Lattice Dynamics" (SCAILD) method developed by Souvatzis and collaborators [14, 15, 16, 17],
- the famous python code for phonons calculations (PHONOPY) developed by Togo and Tanaka [4, 18, 19] and its new version (DynaPhoPy) able to extract phonon quasiparticles from AIMD simulations [20],
- the computational code named "Anharmonic LAttice MODEl" (ALAM-ODE) developed by Tadano and collaborators [21, 22, 23, 24]
- the "Stochastic Self-Consistent Harmonic Approximation" (SSCHA) developed by Errea and collaborators [25, 26, 27, 28, 29],
- the approach named "Compressive Sensing Lattice Dynamics" developed by Nelson, Zhou and collaborators [30, 31],
- the method proposed by Glensk and collaborators allowing to deduce the anharmonic contributions via a direct derivation of the Gibbs energy [32, 33, 34],
- the Automatic Anharmonic Phonon Library (AAPL) developed by Curtarolo and coworkers [35, 36]
- ...

In this work, we present an implementation of the method originally proposed by Esfarjani and Stokes [37, 38, 39] then developed by Hellman and collaborators [1, 40, 41, 42]. This one, named "Temperature Dependent Effective Potential" (TDEP), allows to extract the temperature-dependent interatomic force constants (IFCs) by means of AIMD simulations. As already highlighted by other authors, this method can be applied successfully to go beyond QHA and capture explicit thermal effects [43, 44, 45].

If a large number of equations and definitions are already published in the literature, few details are available concerning the implementation of this method. In the following, we propose to give them in the particular case of our home-made implementation in the ABINIT code [46]. In a first part... In a second part...

1. The Temperature Dependent Effective Potential

1.1. The Interatomic Forces Constants

Let us define a 3-dimensional crystal composed of only one chemical species and consider that a ground state energy U_0 is obtained when the N_a atoms i are in their equilibrium positions $\tau_i(0)$. Now, let us assume that the system evolves along an AIMD trajectory. At each time step t , we can define the new positions of the atoms $\tau_i(t)$, the displacements wrt the equilibrium positions $\mathbf{u}_i(t) = \tau_i(t) - \tau_i(0)$ and the forces $\mathcal{F}_i(t)$. The Hamiltonian of this system can be rewritten (using a perturbative expansion around the equilibrium) :

$$\begin{aligned}
 H = U_0 &+ \sum_{i,\alpha} \left(\frac{\partial U}{\partial u_i^\alpha} \right)_0 u_i^\alpha \\
 &+ \sum_{ij,\alpha\beta} \frac{1}{2!} \left(\frac{\partial^2 U}{\partial u_i^\alpha \partial u_j^\beta} \right)_0 u_i^\alpha u_j^\beta \\
 &+ \sum_{ijk,\alpha\beta\gamma} \frac{1}{3!} \left(\frac{\partial^3 U}{\partial u_i^\alpha \partial u_j^\beta \partial u_k^\gamma} \right)_0 u_i^\alpha u_j^\beta u_k^\gamma \\
 &+ \sum_{ijkl,\alpha\beta\gamma\delta} \frac{1}{4!} \left(\frac{\partial^4 U}{\partial u_i^\alpha \partial u_j^\beta \partial u_k^\gamma \partial u_l^\delta} \right)_0 u_i^\alpha u_j^\beta u_k^\gamma u_l^\delta + 0(u^5) \quad (2)
 \end{aligned}$$

In this equation, and in the rest of the article, the indices i, j, k, \dots and the superscripts $\alpha, \beta, \gamma, \dots$ will define the atoms and the cartesian directions, respectively. In Equation 2, the first term of the development is :

$$\Pi_i^\alpha = \left(\frac{\partial U}{\partial u_i^\alpha} \right)_0 \quad (3)$$

It defines the net force acting on the atom i . This term is generally null except for low-symmetry systems with several atoms in the unitcell. At the second order, the hamiltonian includes all pair interactions between atoms i and j . This quantity connecting forces and displacements is called "the second order IFC" (IFC₂^{tot}) :

$$\Phi_{ij}^{\alpha\beta} = \left(\frac{\partial^2 U}{\partial u_i^\alpha \partial u_j^\beta} \right)_0 \quad (4)$$

In the same way, the third and fourth order IFC ($\text{IFC}_3^{\text{tot}}$, $\text{IFC}_4^{\text{tot}}$), also called cubic and quartic force constants, are :

$$\Psi_{ijk}^{\alpha\beta\gamma} = \left(\frac{\partial^3 U}{\partial u_i^\alpha \partial u_j^\beta \partial u_k^\gamma} \right)_0 \quad \text{and} \quad \chi_{ijkl}^{\alpha\beta\gamma\delta} = \left(\frac{\partial^4 U}{\partial u_i^\alpha \partial u_j^\beta \partial u_k^\gamma \partial u_l^\delta} \right)_0 \quad (5)$$

These ones contain all the three and four body interactions between the i , j , k and l atoms. When the third and fourth order terms become significant, the system acquires a truly anharmonic behavior with an asymmetric shape of the potential [47, 48, 49].

In the framework of this Hamiltonian, expanded up to the fourth order wrt the displacements, the total force \mathcal{F}_H acting on each atom i and for each direction α is written as :

$$\mathcal{F}_{H,i}^\alpha = -\Pi_i^\alpha - \sum_{j,\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta - \frac{1}{2} \sum_{jk,\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma - \frac{1}{6} \sum_{jkl,\beta\gamma\delta} \chi_{ijk}^{\alpha\beta\gamma\delta} u_j^\beta u_k^\gamma u_l^\delta + 0(u^4) \quad (6)$$

In a more generic manner, with $\Theta_{ij\dots}^{\alpha\beta\dots}(p)$ the IFC matrix at the p^{th} order, the previous equation becomes :

$$\mathcal{F}_{H,i}^\alpha = - \sum_p \frac{1}{p!} \sum_{j\dots,\beta\dots} \Theta_{ij\dots}^{\alpha\beta\dots}(p) u_j^\beta \dots \quad (7)$$

1.2. The principles of the TDEP method

The goal of the TDEP method is to extract the IFCs from a molecular dynamic (MD) simulation, since this later includes all the temperature effects. Let us consider that N_t configurations are acquired along the MD trajectory, with a set of displacements $u_{MD,i}^\alpha(t)$ and forces $\mathcal{F}_{MD,i}^\alpha(t)$ for each time step t . Knowing the forces and displacements, it seems possible to extract the IFCs $\Theta_{ij\dots}^{\alpha\beta\dots}(p)$ from the previous equation by solving the following system of equations :

$$\mathcal{F}_{MD,i}^\alpha(t) = - \sum_p \frac{1}{p!} \sum_{j\dots,\beta\dots} \Theta_{ij\dots}^{\alpha\beta\dots}(p) u_{MD,j}^\beta(t) \dots \quad (8)$$

However, the forces being not linear wrt the displacements, this system becomes impossible to solve. The trick is to rewrite Eq. 8 as a function of all IFC coefficients (we will show in the following section how to achieve it) and no longer as a function of the displacements :

$$\mathcal{F}_{MD,i}^\alpha(t) = \sum_{p\lambda} f_{i,\lambda p}^\alpha(\mathbf{u}_{MD}(t)) \theta^{\lambda p} \quad (9)$$

with $\theta^{\lambda p}$ the λ^{th} coefficient of the IFC $_p^{tot}$ matrix and $f_{i,\lambda p}^\alpha(\mathbf{u}_{MD}(t))$ the function including all the displacements (but also the factorial and the minus sign).

The system of equations is now linear and has the form $A.x = b$, with A the function including all the displacements, b the forces and x the IFC coefficients to determine. When the MD trajectory is sufficiently long, this system is overdetermined; i.e. there are more equations than unknowns. One can solve this system of equations by searching its least squares solution. Let us define the residual :

$$\mathcal{R} = \mathbf{F}_{MD} - \mathbf{f}.\Theta \quad (10)$$

such as $\mathbf{F}_{MD} \equiv \mathcal{F}_{MD,i}^\alpha(t)$, $\mathbf{f} \equiv f_{i,\lambda p}^\alpha(\mathbf{u}_{MD}(t))$ and $\Theta \equiv \theta^{\lambda p}$. One measure of smallness of \mathcal{R} is to choose $\theta^{\lambda p}$ such that the sum of squares of residual \mathcal{S} is as small as possible :

$$\mathcal{S} = \min(\mathcal{R}^T.\mathcal{R}) = \|\mathbf{F}_{MD} - \mathbf{f}.\Theta\|^2 \quad (11)$$

The solution giving the lowest residual (i.e. the IFC coefficients giving the best fit of the MD forces) is the following least squares solution :

$$\Theta = \mathbf{f}^\dagger.\mathbf{F}_{MD} \quad (12)$$

with \mathbf{f}^\dagger the pseudoinverse of the \mathbf{f} matrix. This later is a generalization of the inverse matrix and we will see at the end of the next section how to compute it.

1.3. How many coefficients in the IFCs?

If the system is composed of N_a atoms, the IFCs contain $(3N_a)^p$ coefficients at the p^{th} order, so one has to compute $\sum_1^4 (3N_a)^p$ coefficients at the fourth order. On the other hand, at each time step of the MD simulation one accumulates $3N_a$ equations. Therefore, if one wants to acquire "at least" as many equations as unknowns, the MD trajectory have to contain $N_t = \sum_1^4 (3N_a)^{p-1}$ time steps. For instance, if one considers a supercell with 100 atoms, it is needed to have "at least" $N_t=90\ 301$ time steps in order to compute the 27 090 300 coefficients up to the third order.

These few lines unveil the problematic. The calculation of the whole IFC $_p^{tot}$ matrices is possible but at a prohibitive computational cost. Moreover, the goal is to have an overdetermined system of linear equations in order to solve it by means of a least-squares method.

Here, we show an expansion of the second order IFC, solution of the system of equations :

$$\begin{pmatrix} \mathcal{F}_1^x(t) \\ \mathcal{F}_1^y(t) \\ \mathcal{F}_1^z(t) \\ \mathcal{F}_2^x(t) \\ \mathcal{F}_2^y(t) \\ \mathcal{F}_2^z(t) \\ \vdots \\ \mathcal{F}_{N_a}^z(t) \end{pmatrix} = - \begin{pmatrix} \begin{pmatrix} \Phi_1 & 0 & 0 \\ 0 & \Phi_1 & 0 \\ 0 & 0 & \Phi_1 \end{pmatrix} & \begin{pmatrix} \Phi_2 & \Phi_3 & \Phi_4 \\ -\Phi_3 & \Phi_2 & \Phi_6 \\ \Phi_5 & \Phi_6 & \Phi_2 \end{pmatrix} & \dots \\ \begin{pmatrix} \Phi_2 & -\Phi_3 & \Phi_5 \\ \Phi_3 & \Phi_2 & \Phi_6 \\ \Phi_4 & \Phi_6 & \Phi_2 \end{pmatrix} & \begin{pmatrix} \Phi_7 & 0 & 0 \\ 0 & \Phi_7 & 0 \\ 0 & 0 & \Phi_7 \end{pmatrix} & \dots \\ \dots & \dots & \ddots \end{pmatrix} \begin{pmatrix} u_1^x(t) \\ u_1^y(t) \\ u_1^z(t) \\ u_2^x(t) \\ u_2^y(t) \\ u_2^z(t) \\ \vdots \\ u_{N_a}^z(t) \end{pmatrix}$$

The whole $3N_a \times 3N_a$ matrix is symmetric. Each 3×3 pair interaction (see for example the $\begin{pmatrix} \Phi_2 & \Phi_3 & \Phi_4 \\ -\Phi_3 & \Phi_2 & \Phi_6 \\ \Phi_5 & \Phi_6 & \Phi_2 \end{pmatrix}$ matrix) can exhibit some symmetric, antisymmetric, non-symmetric or null terms. Actually, the thousands of coefficients of the $\text{IFC}_p^{\text{tot}}$ can be reduced to tens. If a strong effort is made upstream the resolution process in order to take into account all the symmetries, the method shown previously then becomes tractable. The five symmetry rules, responsible for the decrease of several orders of magnitude, are detailed in the following.

2. How to reduce the number of IFCs coefficients?

2.1. The IFCs tensors are symmetric

The energy conservation law impose that the $\text{IFC}_p^{\text{tot}}$ tensors comply with the usual transposition rule :

$$\begin{aligned} \Phi_{ij}^{\alpha\beta} &= \Phi_{ji}^{\beta\alpha} \\ \Psi_{ijk}^{\alpha\beta\gamma} &= \Psi_{jki}^{\beta\gamma\alpha} = \Psi_{kij}^{\gamma\alpha\beta} = \Psi_{ikj}^{\alpha\gamma\beta} = \Psi_{jik}^{\beta\alpha\gamma} = \Psi_{kji}^{\gamma\beta\alpha} \\ \chi_{ijkl}^{\alpha\beta\gamma\delta} &= \chi_{jkli}^{\beta\gamma\delta\alpha} = \chi_{klij}^{\gamma\delta\alpha\beta} = \chi_{iklj}^{\alpha\gamma\delta\beta} = \chi_{jikl}^{\beta\alpha\gamma\delta} = \chi_{klji}^{\gamma\delta\beta\alpha} = \dots \end{aligned}$$

This invariance under the permutation of the indices is easy to implement. The total number of coefficients is divided by 2 for the $\text{IFC}_2^{\text{tot}}$, 6 for the $\text{IFC}_3^{\text{tot}}$ and 24 for the $\text{IFC}_4^{\text{tot}}$.

2.2. The acoustic sum rule

The momentum conservation principle implies that there is no mass center displacement. To write this condition properly we expand the atomic coordinates as follows : $\tau_i(a) = \mathbf{r}_i + \mathbf{R}(a)$ with \mathbf{r}_i the atomic position of the atom i in the cell 0 and $\mathbf{R}(a)$ the lattice vector of the cell a . In this framework, the acoustic sum rule writes :

$$\begin{aligned} \sum_i \Pi_i^\alpha(0) &= 0 \quad \forall (\alpha) \\ \sum_{jb} \Phi_{ij}^{\alpha\beta}(0, b) &= 0 \quad \forall (i, \alpha\beta) \\ \sum_{kc} \Psi_{ijk}^{\alpha\beta\gamma}(0, b, c) &= 0 \quad \forall (ijb, \alpha\beta\gamma) \\ \sum_{ld} \chi_{ijkl}^{\alpha\beta\gamma\delta}(0, b, c, d) &= 0 \quad \forall (ijkbc, \alpha\beta\gamma\delta) \end{aligned}$$

These equations lead to some relations between all the coefficients of each IFC. By using some mathematics (and contracting the summation index over atoms), it can be showed that the Equation 6 could be rewritten as :

$$\begin{aligned} \mathcal{F}_i^\alpha &= -\Pi_i^\alpha - \sum_{\beta, j \neq i} \Phi_{i,j}^{\alpha\beta} (u_j^\beta - u_i^\beta) \\ &\quad - \frac{1}{2} \sum_{\substack{\beta\gamma \\ j \neq i, k \neq i}} \Psi_{ijk}^{\alpha\beta\gamma} (u_j^\beta - u_i^\beta) (u_k^\gamma - u_i^\gamma) \\ &\quad - \frac{1}{6} \sum_{\substack{\beta\gamma\delta \\ j \neq i, k \neq i, l \neq i}} \chi_{ijkl}^{\alpha\beta\gamma\delta} (u_j^\beta - u_i^\beta) (u_k^\gamma - u_i^\gamma) (u_l^\delta - u_i^\delta) \end{aligned} \tag{13}$$

We can easily see that, at each order, the on-site coefficients are not involved in the calculation of the total force and that the invariance of the system under arbitrary translation is fully achieved. The constraints coming from the acoustic sum rules lead to a reduction of the IFCs coefficients and we will show in Section 2.7 how to proceed.

2.3. The rotational invariance

The system (force and energy) has to remain invariant after a rotation. This imposes some relations between the IFCs of different orders :

$$\begin{aligned}
0 &= \sum_{i,\alpha\beta} \Pi_i^\alpha(0) \tau_i^\beta \epsilon^{\alpha\beta\nu} \quad \forall (\nu) \\
0 &= \sum_{jb,\beta\gamma} \Phi_{ij}^{\alpha\beta}(0,b) \tau_j^\gamma \epsilon^{\beta\gamma\nu} + \sum_{\beta} \Pi_i^\beta(0) \epsilon^{\beta\alpha\nu} \quad \forall (i,\alpha\nu) \\
0 &= \sum_{\gamma} \Phi_{ij}^{\gamma\beta}(0,b) \epsilon^{\gamma\alpha\nu} + \sum_{\gamma} \Phi_{ij}^{\alpha\gamma}(0,b) \epsilon^{\gamma\beta\nu} \\
&+ \sum_{kc,\gamma\delta} \Psi_{ijk}^{\alpha\beta\gamma}(0,b,c) \tau_k^\delta \epsilon^{\gamma\delta\nu} \quad \forall (ijb,\alpha\beta\nu) \\
0 &= \sum_{\delta} \Psi_{ijk}^{\delta\beta\gamma}(0,b,c) \epsilon^{\delta\alpha\nu} + \sum_{\delta} \Psi_{ijk}^{\alpha\delta\gamma}(0,b,c) \epsilon^{\delta\beta\nu} + \sum_{\delta} \Psi_{ijk}^{\alpha\beta\delta}(0,b,c) \epsilon^{\delta\gamma\nu} \\
&+ \sum_{ld,\delta\mu} \chi_{ijkl}^{\alpha\beta\gamma\delta}(0,b,c,d) \tau_l^\mu \epsilon^{\delta\mu\nu} \quad \forall (ijklbc,\alpha\beta\gamma\nu)
\end{aligned}$$

with $\epsilon^{\alpha\beta\gamma}$ the Levi-Civita symbols. As for the acoustic sum rules defined in the previous subsection, one explains in Section 2.7 how to impose such constraints.

2.4. The crystal symmetries (I)

In the following, we no longer consider the whole IFC matrix and focus on a "reference" force constant matrix IFC_p^{ref} for each kind (or shell) of interaction. Using the crystal symmetry operations \mathcal{S} , it is then possible to pursue the reduction process of the IFCs coefficients: *i*) by deducing all the IFC_p connected to IFC_p^{ref} through a crystal symmetry (that's the subject of this section) and *ii*) by determining the nonzero coefficients really independent in the reference interaction (this will be the subject of the next section).

The "image" interaction, indexed by the $ijkl$ letters, can be deduced from the "reference" interaction, named (*ref*) in the following, using the

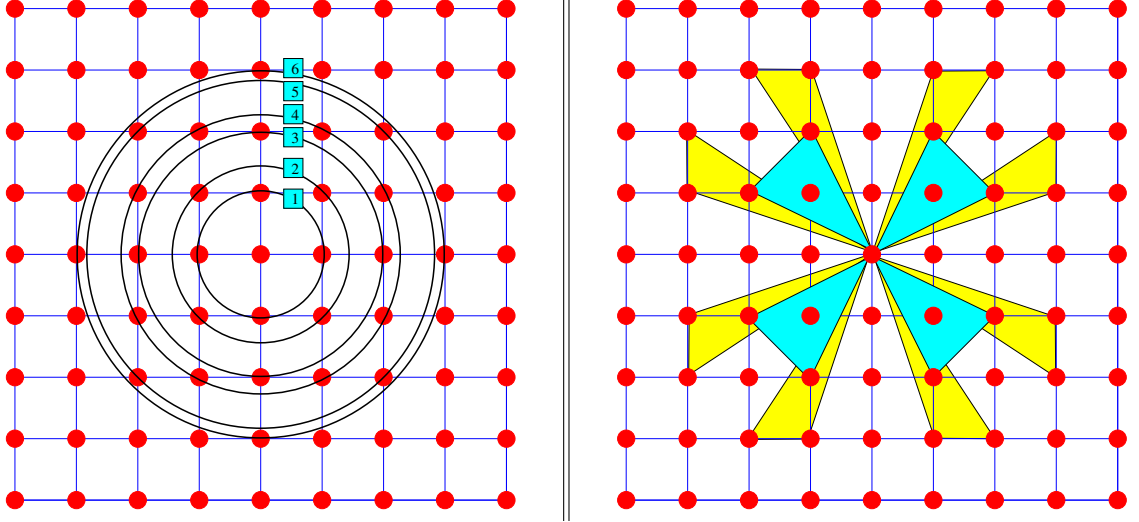


Figure 1: Sketch of interaction shells in 2-dimension. Left panel (second order) : six shells of pair interaction. The atoms belonging to each shell are connected through the crystal symmetries. Right panel (third order) : two kinds of triplet interactions.

symmetry operation \mathcal{S} , such as :

$$\begin{aligned}
 \Pi_i^\alpha &= \sum_{\mu} \mathcal{S}^{\alpha\mu} \Pi_{(ref)}^\mu \\
 \Phi_{ij}^{\alpha\beta} &= \sum_{\mu\nu} \mathcal{S}^{\alpha\mu} \mathcal{S}^{\beta\nu} \Phi_{(ref)}^{\mu\nu} \\
 \Psi_{ijk}^{\alpha\beta\gamma} &= \sum_{\mu\nu\xi} \mathcal{S}^{\alpha\mu} \mathcal{S}^{\beta\nu} \mathcal{S}^{\gamma\xi} \Psi_{(ref)}^{\mu\nu\xi} \\
 \chi_{ijkl}^{\alpha\beta\gamma\delta} &= \sum_{\mu\nu\xi\sigma} \mathcal{S}^{\alpha\mu} \mathcal{S}^{\beta\nu} \mathcal{S}^{\gamma\xi} \mathcal{S}^{\delta\sigma} \chi_{(ref)}^{\mu\nu\xi\sigma}
 \end{aligned}$$

The number of coefficients falls down significantly after this work. If 10 shells of pair interactions are present, there are at worst 90 coefficients to determine for the second order... and no longer 90 000 as before.

2.5. The crystal symmetries (II)

The last symmetry rule is probably the most subtle and tedious to carry out. This one permits to obtain the exact number of nonzero coefficients really independent in the reference matrices IFC_p^{ref} . For simplicity, let us

consider the point group of the crystal. A comprehensive treatment using the space group would burden the presentation without changing the result of the discussion.

The point group is a subgroup of the orthogonal group. Consequently, all the symmetry operations \mathcal{S} (in the cartesian space) belonging to this group have the following properties :

- The inverse equals its transpose : $\mathcal{S}^{-1} = \mathcal{S}^T$
- The norm of the (three) eigenvalues equals to 1: $\lambda = (\pm 1, \pm 1, \pm 1)$ when \mathcal{S} is symmetric, or $\lambda = (\pm 1, e^{i\theta}, e^{-i\theta})$ when \mathcal{S} is antisymmetric.
- The norm of the (three) eigenvectors equals to 1: $|p| = 1$

These properties will be used thereafter and will strongly simplify the development. We have to consider two peculiar cases : some symmetry operations \mathcal{S} may let the interaction invariant or reverse the interaction. This imposes some constraints on the IFCs and thus reduces the number of coefficients. Note that the symmetry operations leaving the interaction invariant (or reversed) form a subgroup of the point group, so a large set of constraints may consistently act on the IFCs.

In the following, we restrict the development to the second order. The reasoning is the same for all the others.

If the interaction is kept invariant... the IFC $_2^{ref}$ is not affected by the transformation, so :

$$\Phi_{(ref)}^{\alpha\beta} = \sum_{\mu\nu} \mathcal{S}^{\alpha\mu} \mathcal{S}^{\beta\nu} \Phi_{(ref)}^{\mu\nu}$$

We can apply the eigenvectors of the \mathcal{S} symmetry operation and obtain :

$$\sum_{\alpha\beta} p_r^\alpha p_s^\beta \Phi_{(ref)}^{\alpha\beta} = \lambda_r^* \lambda_s^* \sum_{\mu\nu} p_r^\mu p_s^\nu \Phi_{(ref)}^{\mu\nu} \quad \forall(rs)$$

By gathering the left and right members we get:

$$(\lambda_r^* \lambda_s^* - 1) \sum_{\alpha\beta} p_r^\alpha p_s^\beta \Phi_{(ref)}^{\alpha\beta} = 0 \quad \forall(rs)$$

The left hand-side of the equation equals to zero if *i*) the term between brackets is null or if *ii*) the summation is null. The eigenvalues of \mathcal{S} being

equal to ± 1 or $e^{\pm i\theta}$, it happens very frequently that their product equals to 1. Consequently, the condition $i)$ and the previous equality is naturally fulfilled in numerous cases. Otherwise, we have :

$$\sum_{\alpha\beta} p_r^\alpha p_s^\beta \Phi_{(ref)}^{\alpha\beta} = 0 \quad \text{if } \lambda_r^* \lambda_s^* \neq 1 \quad \forall(rs)$$

These equations impose some constraints on the IFC_2^{ref} (linear relation between the coefficients). We will see in the following how to extract the nonzero independent coefficients.

If the interaction is reversed.... the IFC_2^{ref} is also reversed by the transformation :

$$\sum_{\mu\nu} \mathcal{S}^{\alpha\mu} \mathcal{S}^{\beta\nu} \Phi_{(ref)}^{\mu\nu} = \Phi_{(ref)}^{\alpha\beta}$$

where (ref) means that the interaction (ref) is reversed. Using the symmetry properties of the IFCs then by applying the eigenvectors and gathering the left and right hand-side, one obtains :

$$\sum_{\alpha\beta} (\lambda_r^* \lambda_s^* p_r^\alpha p_s^\beta - p_r^\beta p_s^\alpha) \Phi_{(ref)}^{\alpha\beta} = 0 \quad \forall(rs)$$

As already highlighted when the interaction is kept invariant, these equations also impose some constraints if the term within brackets is not null.

2.6. All the symmetries together

For each shell, whether the interaction is kept invariant or reversed, a new equation (constraint) is obtained when a couple of eigenvalues/eigenvectors gives a nonzero contribution to the "term in brackets". At the end of the process, all the equations are collected then orthonormalized resulting in a system of Λ_2 independent homogeneous linear equations. This system may be rewritten as :

$$\sum_{\kappa=1}^9 \Upsilon_{\lambda_2}^\kappa \Phi_{(ref)}^\kappa = 0 \quad \text{with } \lambda_2 = 1, \dots, \Lambda_2$$

with the indices $\alpha\beta$ contracted in an only index κ , and the matrix $\Upsilon_{\lambda_2}^\kappa$ coming from all the nonzero terms between brackets. The solutions of such system

is obtained by computing the kernel of the application. The result has the following form :

$$\Phi_{(ref)}^\kappa = \sum_{\lambda_2=1}^{\Lambda_2} \Upsilon'_{\lambda_2}{}^\kappa \phi_{(ref)}^{\lambda_2} \quad \text{with } \kappa=1,\dots,9$$

with $\phi_{(ref)}^{\lambda_2}$ the Λ_2 nonzero coefficients of the IFC $_2^{ref}$. The $\Upsilon'_{\lambda_2}{}^\kappa$ matrix is built by gathering the column vectors orthogonal to the line vectors of $\Upsilon_{\lambda_2}^\kappa$. In a similar way, we can apply this process to the other p orders and obtain :

$$\Theta_{(ref)}^\kappa(p) = \sum_{\lambda_p=1}^{\Lambda_p} \Upsilon'_{\lambda_p}{}^\kappa \theta_{(ref)}^{\lambda_p p} \quad \text{with } \kappa = 1, \dots, 3^p$$

After taking into account all the interactions of each shell at each order, we finally recover Equation 9 : $\mathcal{F}_i^\alpha(t) = \sum_{\lambda_p p} f_{i,\lambda_p p}^\alpha(\mathbf{u}(t))\theta^{\lambda_p p}$. All the terms depending on the displacements $u_i^\alpha(t)$ and symmetries $S^{\alpha\beta}$ are hidden in the \mathbf{f} matrix. We obtain a system of linear equations with the nonzero coefficients of the IFCs $\{\theta^{\lambda_p p}\}$ as the unknown variables. Its expanded form is :

$$\begin{pmatrix} \mathcal{F}_1^x(1) \\ \mathcal{F}_1^y(1) \\ \mathcal{F}_1^z(1) \\ \vdots \\ \mathcal{F}_{N_a}^z(1) \\ \vdots \\ \mathcal{F}_{N_a}^z(N_t) \end{pmatrix} = \begin{pmatrix} f_{1,11}^x(1) & f_{1,21}^x(1) & \cdots & f_{1,\Lambda_p p}^x(1) \\ f_{1,11}^y(1) & f_{1,21}^y(1) & \cdots & f_{1,\Lambda_p p}^y(1) \\ f_{1,11}^z(1) & f_{1,21}^z(1) & \cdots & f_{1,\Lambda_p p}^z(1) \\ \vdots & \vdots & \vdots & \vdots \\ f_{N_a,11}^z(1) & f_{N_a,21}^z(1) & \cdots & f_{N_a,\Lambda_p p}^z(1) \\ \vdots & \vdots & \vdots & \vdots \\ f_{N_a,11}^z(N_t) & f_{N_a,21}^z(N_t) & \cdots & f_{N_a,\Lambda_p p}^z(N_t) \end{pmatrix} \begin{pmatrix} \theta^{11} \\ \theta^{21} \\ \theta^{31} \\ \vdots \\ \theta^{\Lambda_1 1} \\ \vdots \\ \theta^{\Lambda_p p} \end{pmatrix}$$

We stress that the \mathbf{f} matrix is really huge. At the second order, its size is $(3 * N_a * N_t) \times \Lambda_2$. If we consider $N_t=1000$ time steps, $N_a=100$ atoms and $\Lambda_2=20$ coefficients, this matrix has 300 000 lines and 20 columns.

2.7. The constrained least squares problem

The whole set of coefficients $\{\theta^{\lambda_p p}\}$ can be obtained by reversing the previous equation. An elegant way to perform such reversion is to compute the

Moore-Penrose pseudoinverse (marked with a † superscript in the following):

$$\begin{pmatrix} \theta^{11} \\ \vdots \\ \theta^{\Lambda_{pp}} \end{pmatrix} = \begin{pmatrix} f_{1,11}^x(1) & \cdots & f_{1,\Lambda_{pp}}^x(1) \\ \vdots & \ddots & \vdots \\ f_{N_a,11}^z(N_t) & \cdots & f_{N_a,\Lambda_{pp}}^z(N_t) \end{pmatrix}^\dagger \cdot \begin{pmatrix} \mathcal{F}_1^x(1) \\ \vdots \\ \mathcal{F}_{N_a}^z(N_t) \end{pmatrix}$$

The usual and mathematical definition of a pseudoinverse Γ^\dagger is :

$$\Gamma^\dagger = \Gamma^T(\Gamma\Gamma^T)^{-1} \quad (14)$$

This definition implies to carry out a reversion of the \mathbf{f} matrix. In practice, this method is proved to be numerically unstable and the computational cost turn out to be really expensive, due to the size of the matrix. A more simple and accurate way is possible, by performing a singular value decomposition :

$$\Gamma^\dagger = \mathcal{V}\Sigma^\dagger\mathcal{U}^T \quad (15)$$

with \mathcal{V} and \mathcal{U} some square matrices and Σ a diagonal matrix. Some linear algebra routines (`dgesdd`) enable to perform such decomposition easily. The Σ being diagonal, this one can be conveniently reversed, which makes this method much more stable and less expensive than the previous one.

We have seen previously that the acoustic sum rules and the rotational invariance of the system impose some constraints on the IFCs. In the same way, we will see in the following that the dynamical matrix and the elastic tensor also impose other constraints on IFCs. If one rewrites these Q linear constraints, function of the $\theta^i \equiv \theta^{\lambda_{pp}}$ coefficients, in a matrix \mathbf{C} , we obtain an homogeneous linear equation system :

$$\sum_{i=1}^{\Lambda_{pp}} C_{q,i}^T \theta^i = 0 \quad \text{with } q = 1, \dots, Q \quad (16)$$

In order to satisfy these constraints we have to :

1. minimize $\mathcal{S} = \|\mathbf{F}_{MD} - \mathbf{f}\cdot\Theta\|^2$, as previously performed by least squares method with Eq.11
2. subject to $\mathbf{C}\cdot\Theta = 0$.

That's could be done by building the Lagrangian function $\mathcal{L}(\theta, \zeta)$ with ζ the Lagrange multipliers :

$$\mathcal{L}(\theta, \zeta) = \mathcal{S}(\theta) + \sum_{q=1}^Q \zeta_q \sum_{i=1}^{\Lambda_{pp}} C_{q,i}^T \theta^i \quad (17)$$

The optimality conditions are :

$$\begin{cases} \frac{\partial \mathcal{L}}{\partial \theta^i} = 2 \sum_{j=1}^{\Lambda_{pp}} (\mathbf{f}^T \cdot \mathbf{f})_{ij} \theta^j - 2(\mathbf{f}^T \cdot \mathbf{F}_{MD})_i + \sum_{q=1}^Q \zeta_q C_{q,i} = 0 \\ \frac{\partial \mathcal{L}}{\partial \zeta_q} = \sum_{i=1}^{\Lambda_{pp}} C_{q,i}^T \theta^i = 0 \end{cases}$$

In matrix-vector form, these equations are more readable and are written :

$$\begin{pmatrix} 2\mathbf{f}^T \cdot \mathbf{f} & \mathbf{C}^T \\ \mathbf{C} & 0 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{\Theta} \\ \boldsymbol{\zeta} \end{pmatrix} = \begin{pmatrix} 2\mathbf{f}^T \cdot \mathbf{F}_{MD} \\ 0 \end{pmatrix}$$

As already carried out for the least square problem, the constrained least squares solution can be obtained by computing the pseudoinverse of the first matrix in the left hand-side member. Note that the matrix to invert is smaller than the one shown previously. At the second order, its size is $(\Lambda_2 + Q) \times (\Lambda_2 + Q)$. This one no longer depends on the number of time steps and atoms. For $\Lambda_2=20$ coefficients and $Q=30$ constraints this matrix has only 50 lines and columns.

3. What are the IFCs useful for?

In this section we show that the knowledge of IFCs allows us to calculate almost all the quantities that we want to characterize a material: phonon spectrum, free energy, elastic constants and moduli, sound speed, Grüneisen parameter, thermal expansion... Since the IFCs are temperature dependent, all the quantities resulting from them exhibit an explicit dependence with respect to temperature.

3.1. The phonon spectrum

In order to evaluate the phonon spectrum and the vibrational density of states, we need to split up again the index over atoms as follows : $\tau_i(a) = \mathbf{r}_i + \mathbf{R}(a)$ with \mathbf{r}_i the position of the atom i in the cell 0 and $\mathbf{R}(a)$ the lattice

vector going to cell a .

Once the $\Phi_{ij}^{\alpha\beta}(a, b)$ tensor is built (after the Moore-Penrose), it is quite direct to compute the phonons modes of the system by performing a Fourier Transform of the second order IFCs. We obtain the so-called dynamical matrix :

$$D_{ij}^{\alpha\beta}(\mathbf{q}) = \sum_b \frac{\Phi_{ij}^{\alpha\beta}(0, b)}{\sqrt{M_i M_j}} \exp(i\mathbf{q} \cdot [\mathbf{R}(b) - \mathbf{R}(0)]) \quad (18)$$

with \mathbf{q} a wave vector belonging to the Brillouin zone (BZ) and M_i the mass of atom i . Such equation of motion can be diagonalized in order to obtain the phonon eigen frequencies $\omega(\mathbf{q})$ and eigen modes $X_i^\alpha(\mathbf{q})$ of the lattice :

$$\sum_{\beta, j} D_{ij}^{\alpha\beta}(\mathbf{q}) X_{js}^\beta(\mathbf{q}) = \omega_s^2(\mathbf{q}) X_{is}^\alpha(\mathbf{q}) \quad (19)$$

In this equation (representative of an harmonic oscillator) the quantum number s refers to the quantification of the eigen frequencies $\omega_s(\mathbf{q})$, with $3 * N_a$ energy levels at all.

The vibrational Density Of States (vDOS) $g(\omega)$ is defined by :

$$g(\omega) = \frac{1}{3N_a} \sum_{s=1}^{N_a} \delta(\omega - \omega_s) \quad \text{such as} \quad \int_0^{\omega_{max}} g(\omega) d\omega = 1 \quad (20)$$

with ω_{max} the highest phonon frequency of the system.

3.2. The Free energy

When one wants to evaluate the free energy $F(V, T)$ of a system as a function of the temperature and the volume, the usual process is to split up the cold and vibrational contributions such as :

$$F(V, T) = U_0(V) + F_{\text{vib}}(V, T) \quad (21)$$

with $U_0(V)$ the zero temperature energy of the system and $F_{\text{vib}}(V, T)$ the vibrational free energy. If the cold contribution can be estimated through an independent ground state calculation, this one could be computed also

using the expression of the energy expanded up to the second order (see Equation 2) :

$$U_{\text{model}}(t) = U_0(V) + \frac{1}{2} \sum_{ij, \alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha(t) u_j^\beta(t) \quad (22)$$

and the total energy coming from the AIMD simulation $U_{\text{simul}}(t)$. In this case, the expression of the cold energy is just :

$$U_0(V) = \langle U_{\text{simul}}(t) - \frac{1}{2} \sum_{ij, \alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha(t) u_j^\beta(t) \rangle \quad (23)$$

If there is no strong modification of the equilibrium structure of the crystal due to temperature effects, these two approaches have to match.

Concerning the vibrational part of the free energy F_{vib} (see Equation 21) but also in a similar way for the internal vibrational energy U_{vib} , the constant-volume specific heat $C_{\text{vib},V} = (\frac{\partial U}{\partial T})_V$ and the entropy $S_{\text{vib}} = -(\frac{\partial F_{\text{vib}}}{\partial T})_V$, they can be evaluated in the framework of the three-dimensional quantum harmonic crystal using the vDOS [50] :

$$F_{\text{vib}} = \frac{3N_a}{\beta} \int_0^{\omega_{\text{max}}} \ln \left(2 \sinh \left(\frac{\beta \hbar \omega}{2} \right) \right) g(\omega) d\omega \quad (24)$$

$$U_{\text{vib}} = 3N_a \int_0^{\omega_{\text{max}}} \frac{\hbar \omega}{2} \coth \left(\frac{\beta \hbar \omega}{2} \right) g(\omega) d\omega \quad (25)$$

$$C_{\text{vib},V} = 3N_a k_B \int_0^{\omega_{\text{max}}} \left(\frac{\beta \hbar \omega}{2 \sinh \left(\frac{\beta \hbar \omega}{2} \right)} \right)^2 g(\omega) d\omega \quad (26)$$

$$S_{\text{vib}} = 3N_a k_B \int_0^{\omega_{\text{max}}} \left[\frac{\beta \hbar \omega}{2} \coth \left(\frac{\beta \hbar \omega}{2} \right) - \ln \left(2 \sinh \left(\frac{\beta \hbar \omega}{2} \right) \right) \right] g(\omega) d\omega \quad (27)$$

All these thermodynamic quantities display three kinds of dependence with respect to the temperature. The first one originates from the Bose-Einstein statistic and corresponds to the filling of the energy levels (including the zero-point energy), another one more implicit is provided by the thermal expansion of the volume $V(T)$, and a last one is due to the explicit dependence of the phonon frequencies with respect to the temperature $\omega(V, T)$. If the first one is taken into account in a quantum harmonic approach, the second one appears when considering the QHA approximation, and the third one comes from the explicit treatment of the temperature carried out in this work.

3.3. Elastic constants and moduli

The IFCs enable to obtain almost all the thermal elastic properties of a material. The elastic constants are defined using the Hooke law which relies on the strain tensor $\epsilon_{\alpha\beta}$ to the stress one $\sigma_{\gamma\delta}$, through the elastic tensor $C_{\alpha\beta\gamma\delta}$:

$$\sigma_{\alpha\beta} = C_{\alpha\beta\gamma\delta} \epsilon_{\gamma\delta} \quad (28)$$

The most famous way employed to compute the elastic tensor is the finite differences method. This approach, coupled with AIMD simulations, enable to take into account temperature effects. But numerous simulations have to be performed and the computational time can be prohibitive (in order to have long AIMD trajectories). Another approach is to compute phonons and to evaluate the elastic constants using the slopes of the acoustic branches. This one is connected to a more elegant formulation using the IFCs [7, 13]. Let us define the $A_{\alpha\beta\gamma\delta}$ quantity :

$$A_{\alpha\beta\gamma\delta} = \frac{1}{2V} \sum_{ij} \Phi_{ij}^{\alpha\beta} d_{ij}^{\gamma} d_{ij}^{\delta} \quad \text{with } d_{ij}^{\gamma} = \tau_i^{\gamma} - \tau_j^{\gamma} \quad (29)$$

The elastic constants are then obtained by using this simple following equation :

$$C_{\alpha\beta\gamma\delta} = A_{\alpha\gamma\beta\delta} + A_{\beta\gamma\alpha\delta} - A_{\alpha\beta\gamma\delta} \quad (30)$$

Using the Voigt notation and the Voigt formulation, we can define the isothermal Bulk K_T and Shear G moduli (but also the Young modulus E and the Poisson's ratio ν) as follows :

$$\begin{aligned} K_T &= ((C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{13} + C_{23}))/9 \quad (31) \\ G &= ((C_{11} + C_{22} + C_{33}) - (C_{12} + C_{13} + C_{23}) + 3(C_{44} + C_{55} + C_{66}))/15 \end{aligned}$$

It is important to note that this method needs to have long range IFCs in order to have converged quantities [51].

3.4. Grüneisen parameter & thermal expansion

As well known, the thermal expansion α_V , the thermodynamic Grüneisen parameter $\gamma = V \left(\frac{\partial P}{\partial U}\right)_V$, the isothermal compressibility $\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ ($= 1/K_T$, see Equation 31) and the specific heat C_V (see Equation 26) are connected to each other through the following equation:

$$\alpha_V = \frac{\gamma C_V}{\beta_T V} \quad (33)$$

In order to compute γ in the lattice dynamic framework, we introduce the Grüneisen parameters $\gamma_s(\mathbf{q})$ and the specific heat $C_{V,s}(\mathbf{q})$ per phonon mode $\omega_s(\mathbf{q})$:

$$\gamma_s(\mathbf{q}) = -\frac{V}{\omega_s(\mathbf{q})} \left(\frac{\partial \omega_s(\mathbf{q})}{\partial V} \right)_T \quad (34)$$

$$C_{V,s}(\mathbf{q}) = k_B \left(\frac{\beta \hbar \omega_s(\mathbf{q})}{2 \sinh(\frac{\beta \hbar \omega_s(\mathbf{q})}{2})} \right)^2 \quad (35)$$

It can be shown that the thermodynamic Grüneisen parameter γ is written :

$$\gamma = \frac{\sum_{s,\mathbf{q}} \gamma_s(\mathbf{q}) C_{V,s}(\mathbf{q})}{C_V} \quad (36)$$

If the system undergoes an anisotropic strain $\epsilon_{\gamma\delta}$, such as $\sum_{\kappa} \epsilon_{\kappa}^2 = 1$ in the Voigt notation, the displacement of atom k become $\mathbf{u}_k^{\gamma} = \sum_{\gamma} \epsilon_{\gamma\delta} \tau_k^{\delta}$. In this framework, the mode Grüneisen parameters rewrite [52] :

$$\gamma_s^{\gamma\delta}(\mathbf{q}) = -\frac{1}{3\omega_s(\mathbf{q})} \left(\frac{\partial \omega_s(\mathbf{q})}{\partial \epsilon_{\gamma\delta}} \right)_T = -\frac{1}{6\omega_s^2(\mathbf{q})} \left(\frac{\partial \omega_s^2(\mathbf{q})}{\partial \epsilon_{\gamma\delta}} \right)_T \quad (37)$$

Using Equations 19 and 18, we obtain :

$$\gamma_s^{\gamma\delta}(\mathbf{q}) = -\frac{1}{6\omega_s^2(\mathbf{q})} \frac{\partial}{\partial \epsilon_{\gamma\delta}} \left[\sum_{ij,\alpha\beta} X_{is}^{\star\alpha}(\mathbf{q}) \sum_b \frac{1}{\sqrt{M_i M_j}} \frac{\partial^2 U}{\partial u_i^{\alpha} \partial u_j^{\beta}} \exp(i\mathbf{q} \cdot \mathbf{R}(b)) X_{js}^{\beta}(\mathbf{q}) \right] \quad (38)$$

In this equation one has to compute the third derivative with respect to displacements and strain. This one can be evaluated using the expansion of the Hamiltonian up to the third order:

$$\frac{\partial}{\partial \epsilon_{\gamma\delta}} \left(\frac{\partial^2 U}{\partial u_i^{\alpha} \partial u_j^{\beta}} \right) = \frac{\partial}{\partial \epsilon_{\gamma\delta}} \left(\Phi_{ij}^{\alpha\beta} + \sum_{k\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_k^{\gamma} \right) = \sum_k \Psi_{ijk}^{\alpha\beta\gamma} \tau_k^{\delta} \quad (39)$$

We obtain the common definition of the mode Grüneisen parameters as a function of the interatomic force constants.

$$\gamma_s^{\gamma\delta}(\mathbf{q}) = -\frac{1}{6\omega_s^2(\mathbf{q})} \sum_{ijk,bc,\alpha\beta} \Psi_{ijk}^{\alpha\beta\gamma}(0,b,c) \frac{X_{is}^{\star\alpha}(\mathbf{q}) X_{js}^{\beta}(\mathbf{q})}{\sqrt{M_i M_j}} \tau_k^{\delta} \exp[i\mathbf{q} \cdot \mathbf{R}(b)] \quad (40)$$

Once these parameters obtained, the thermodynamic Grüneisen parameter γ (see Equation 36) and the the thermal expansion α_V (see Equation 33) can be computed directly. In the case of an anisotropic crystal, the thermal expansion matrix rewrites :

$$\alpha_V^{\alpha\beta} = \sum_{\gamma\delta} S_{\alpha\beta\gamma\delta} \sum_{\mathbf{q}s} C_{V,s}(\mathbf{q}) \gamma_s^{\gamma\delta}(\mathbf{q}) \quad (41)$$

with $S_{\alpha\beta\gamma\delta} \equiv C_{\alpha\beta\gamma\delta}^{-1}$ the compliance matrix (see Equation 30). The volumetric thermal expansion α_V can be obtained by summing up the linear thermal expansion coefficients $\alpha_V^{\alpha\alpha}$ arranged along the diagonal of the thermal expansion matrix : $\alpha_V = \sum_i \alpha_V^{\alpha\alpha}$.

3.5. Thermal pressure, isentropic quantities & sound speed

If the electronic contribution is not considered, the total stress tensor can be split into two parts (see Equation 21) :

$$\sigma_{\alpha\beta} = \frac{1}{V} \left(\frac{\partial F}{\partial \epsilon_{\alpha\beta}} \right)_T = \sigma_{0,\alpha\beta} + \sigma_{\text{vib},\alpha\beta} \quad (42)$$

the first part coming from the cold energy $U_0(V)$ and the second one being the thermal stress contribution deriving from the thermal free energy (see Equation 24) as :

$$\sigma_{\text{vib},\alpha\beta} = - \sum_{s,\mathbf{q}} \gamma_s^{\alpha\beta}(\mathbf{q}) \frac{U_{\text{vib},s}(\mathbf{q})}{V} \quad \text{with} \quad (43)$$

$$U_{\text{vib},s}(\mathbf{q}) = \frac{\hbar\omega_s(\mathbf{q})}{2} \coth\left(\frac{\beta\hbar\omega_s(\mathbf{q})}{2}\right) \quad (44)$$

This result is really important since it makes it possible to verify that the pressure computed along the AIMD trajectory $P = -\frac{1}{3}\text{Tr}[\sigma]$ is well reproduced by the sum of the cold and vibrational pressures. The later part being computed using the Grüneisen parameter, it's a good way to check its convergence.

The thermodynamic Grüneisen parameter and the thermal expansion are also useful to compute the isentropic (or adiabatic) compressibility β_S and the constant-pressure heat capacity C_P :

$$\beta_S = \beta_T(1 + \alpha_V\gamma T) = \frac{1}{K_S} \quad (45)$$

$$C_P = C_V(1 + \alpha_V\gamma T) \quad (46)$$

Note that β_T and C_V are already known (see Equations 31 and 26). Using the isentropic compressibility, the longitudinal V_p and transverse V_s sound speeds can be also obtained :

$$V_p = \sqrt{\frac{K_S + 4G/3}{\rho}} \quad (47)$$

$$V_s = \sqrt{\frac{G}{\rho}} \quad (48)$$

3.6. *Normal modes & mean square displacements*

3.7. *Limitations & perspectives*

Order 4 [47, 48, 49], Lifetime, phonon shift, lattice thermal conductivity

4. Examples illustrating the a-TDEP capabilities

4.1. *Failure of the QHA : the α -U*

4.2. *Thermal stabilization of the Zr bcc phase*

4.3. *Thermal expansion of Si*

For Si [53]

5. Conclusion

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