High-Throughput Prediction of Finite-Temperature Properties using the Quasi-Harmonic Approximation

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Abstract

In order to calculate thermal properties in automatic fashion, the Quasi-Harmonic Approximation (QHA) has been combined with the Automatic Phonon Library (APL) and implemented within the AFLOW framework for high-throughput computational materials science. As a benchmark test to address the accuracy of the method and implementation, the specific heats capacities, thermal expansion coefficients, Grüneisen parameters and bulk moduli have been calculated for 130 compounds. It is found that QHA-APL can reliably predict such values for several different classes of solids with root mean square relative deviation smaller than 28\% with respect to experimental values. The automation, robustness, accuracy and precision of QHA-APL enable the computation of large material data sets, the implementation of repositories containing thermal properties, and finally can serve the community for data mining and machine learning studies.

Keywords: High-throughput, materials genomics, Quasi-Harmonic Approximation, AFLOW

1. Introduction

The characterization and prediction of thermal properties of materials are amongst the key factors enabling a rational accelerated materials development [1]. Important properties include specific heat capacity at constant volume/pressure ($C_V$ or $C_p$), mode resolved and average Grüneisen parameters ($\gamma_{qj}$ and $\gamma$), thermal expansion coefficient ($\alpha_V$), Debye temperature ($\theta_D$), lattice thermal conductivity ($\kappa_L$), and vibrational entropy and Gibbs free energy ($S(p, T)$ and $G(p, T, V)$).

There are several computational techniques leading to the characterization of these thermal properties: i. First principles molecular dynamics (extremely time consuming and computationally impractical for creating large datasets); ii. The GIBBS approach [2] also implemented in the AFLOW-AGL (Automatic-Gibbs-Library) [3] (very fast and reasonably reliable especially for high-throughput screening [1]); iii. Anharmonic force constant calculations and Boltzmann Transport Equation solvers, as implemented in ShengBTE[4], PHONOPY [5] and in the AFLOW-APL2 Library [6] (computationally intensive but capable of giving very accurate values for $\kappa_L$); iv. approaches based on the QHA [7–14] which can rapidly characterize $C_V$, $C_p$, $\gamma$, and $\alpha_V$. Methods ii-iv. are based on phonon calculations as available in packages like AFLOW-APL [15, 16], PHONOPY [17], Phon [10], ALAMODE [18].
With the goal of creating large repositories of ab-initio calculated properties, such as in our AFLOW.org [19–21] online database, we have undertaken the task of implementing the quasi-harmonic method in the AFLOW software platform [15]. The quasi-harmonic method is based on the construction of a strain dependent free energy function in which each strained structure belongs to the harmonic regime. The strain dependent free energy contributes as a vibrational energy and introduces anharmonic effects into the system, including the temperature dependence. Although this method has been successfully applied for decades, it has limitations: the QHA loses predictive power when anharmonic forces play a major role in the dynamics (as in the case of thermal conductivity), under extreme conditions in term of temperature and pressure, [22, 23] or close to their melting point [24]. Despite these limitations, this model has been satisfactorily demonstrated to accurately and robustly predict many temperature-dependent properties for compounds of different nature [25–32].

Even if the QHA is a well-established approach, its implementation within an automatic framework requires addressing several challenges. Therefore, despite the availability of the previously mentioned packages (PHONOPY, and ALAMODE), to the best of our knowledge, there is not yet a high-throughput [1] framework able to predict temperature dependent properties using the QHA in a self-contained robust way. The high-throughput protocol should include: automatic generation of files, robust correction of errors and post-processing, and appropriate interface to a material database [19]. In this article, we show tests of our QHA implementation in AFLOW by computing temperature dependent thermodynamic properties for more than one hundred materials. For one case we assess the effect of improved electronic structure [33] on the thermal properties.

2. Methods

2.1. Ab initio thermodynamics

In the framework of the QHA, the Helmholtz free energy, $F$, for a fixed number of particles, is written as

$$F(V, T) = E_{0K}(V) + F_{vib}(V, T) + F_{elec}(V, T)$$  \hspace{1cm} (1)

where $E_{0K}$ is the total energy of the system at 0K and given volume, $V$. $F_{vib}$ represents the vibrational contribution to the free energy and $F_{elec}$ is the electronic contribution to the free energy as function of volume and temperature. The total energy at any volume and 0 K can be computed by using standard periodic quantum mechanical software such as Quantum Espresso [34] or the Vienna Ab-initio Simulation Package (VASP) [35] and properly relaxed structures. The vibrational free energy, which includes zero point energy contributions, can be obtained from the phonon density of states, $g(\nu)$, via:

$$F_{vib}(V, T) = \int_0^{\infty} g(\nu) \left[ \frac{\hbar \nu}{2} + k_B T \ln(1 - \exp(-\frac{\hbar \nu}{k_B T})) \right] d\nu \hspace{1cm} (2)$$

where $k_B$, $\hbar$, and $\nu$ are the Boltzmann constant, the Planck constant, and the vibrational frequency respectively. Frequencies for a given wave vector $q$ can be computed by diagonalizing the dynamical matrix. The phonon density of states, pDOS, can be computed by integrating the phonon dispersion in the Brillouin zone.

Similarly, $F_{elec}$, can be computed as:

$$F_{elec}(V, T) = \Delta E_{elec}(V, T) - T S_{elec}(V, T) \hspace{1cm} (3)$$

where $\Delta E_{elec}(V, T)$ and $S_{elec}(V, T)$ are the contribution to the electronic energy due to temperature changes and the electronic entropic contribution to the free energy. At low temperatures, $\Delta E_{elec}(V, T)$ is very small
and can be neglected. However, it may play a significant role at high temperatures. Both can be computed using the electronic density of states, eDOS,

\[ \Delta E_{\text{elec}}(V, T) = \int n(\epsilon) f(\epsilon) \, d\epsilon - \int^{e_{\text{F}}} n(\epsilon) \, d\epsilon \]

(4)

\[ S_{\text{elec}}(V, T) = -k_B \int n(\epsilon) \left[ f(\epsilon) \ln f(\epsilon) + (1 - f(\epsilon)) \ln(1 - f(\epsilon)) \right] \, d\epsilon \]

(5)

where the eDOS at energy, \( \epsilon \), is represented by \( n(\epsilon) \), and \( f \) is the Fermi distribution function.

Once \( F(V, T) \) is computed at different volumes and temperatures, extracting the thermodynamic data is a straightforward process using the equations of state. For instance, properties like equilibrium free energy, \( F_{\text{eq}} \), equilibrium volume, \( V_{\text{eq}} \), bulk modulus, \( B \), and the derivative of the bulk modulus with respect to pressure, \( B_p \), can be obtained by fitting \( F(V, T) \) at different volumes and temperatures to the Birch-Murnaghan (BM) function:

\[ F(V) = F_{\text{eq}} + \frac{BV_{\text{eq}}}{B_p} \left[ \left( \frac{V_{\text{eq}}}{V} \right)^{B_p} - B_p - 1 \right] \]

(6)

where, \( F_{\text{eq}}, B, V_{\text{eq}} \) and \( B_p \) are used as the fitting parameters.

The mode Grüneisen parameters, \( \gamma_{qj} \), for the wave vector \( q \) and the phonon branch \( j \) can be computed by taking the derivative of the dynamical matrix with respect to the volume, as [36]:

\[ \gamma_{qj} = \frac{V_{\text{eq}}}{2\pi^2} \sum_j \epsilon_{qj} \frac{\partial D_{qj}}{\partial V} e_{qj}^* \]

(7)

where \( D_{qj} \) is the dynamical matrix for a wave-vector, \( q \), \( \nu_{qj} \) vibrational frequency, and \( e_{qj} \) is the eigenvector for phonon branch, \( j \). An average Grüneisen parameter, \( \gamma(T) \), can be obtained using [37, 38]:

\[ \gamma(T) = \frac{\sum_{q, j} \gamma_{qj} C_{V_{qj}}}{C_V} \]

(8)

where \( C_{V_{qj}} \) is the isochoric specific heat:

\[ C_{V_{qj}} = k_B \sum_{q, j} \frac{(\hbar \nu_{qj}) \exp(\hbar \nu_{qj}/k_BT)}{(k_B T)^2(\exp(h \nu_{qj}/k_B T) - 1)^2} \]

(9)

Once \( \gamma(T) \) is calculated, other variables such as volumetric thermal expansion \( \alpha_V(T) \) and isobaric specific heat, \( C_p \) can be predicted using Eq. 10 and Eq. 11 respectively:

\[ \alpha_V(T) = \frac{C_V(T)\gamma(T)}{V(T)B(T)} \]

(10)

\[ C_p - C_V = \alpha^2(T)B(T)V(T)T \]

(11)

2.2. Computational details

In the QHA-APL we first perform a geometry optimization minimizing the forces acting on the atoms in the primitive cell and the stresses. The optimized geometry is used as starting point for the other calculations. The phonon dispersions are computed at three different volumes to determine the Grüneisen parameters, one at the equilibrium volume and the other two at slightly distorted volumes (less than ±5% of the volume). Finally, the data are used to fit the BM equation of state. These calculations are automatically generated, managed and monitored by the AFLOW [15, 20] package, facilitating and accelerating the prediction of all properties required by the user in the original input.
2.2.1. Geometry optimization

All structures are fully relaxed using the HT framework, AFLOW [15], and the DFT Vienna Ab-initio simulation package, VASP [35]. Optimizations are performed following the AFLOW standards [21]. We use the projector augmented wave (PAW) pseudopotentials [39] and the exchange and correlation functionals parametrized by the generalized gradient approximation proposed by Perdew-Burke-Ernzerhof (PBE) [40]. All calculations use a high energy-cutoff, which is 40% larger than the maximum recommended cutoff among all component potentials, and a k-points mesh of 8000 k-points per reciprocal atom. Primitive cells are fully relaxed (lattice parameters and ionic positions) until the energy difference between two consecutive ionic steps is smaller than $10^{-4}$ eV and forces in each atom are below $10^{-3}$ eV/Å.

2.2.2. Phonon calculations

Phonon calculations were carried out using the automatic phonon library, APL, as implemented in the AFLOW package, using VASP to obtain the interatomic force constants (IFCs) via the finite-displacement approach. The magnitude of this displacement is 0.015 Å. Non-analytical contributions to the dynamical matrix are also included using the formulation developed by Wang et al [41]. Frequencies and other related phonon properties are calculated on a $21 \times 21 \times 21$ mesh in the Brillouin zone, which is sufficient to converge the vibrational density of states, pDOS, and hence the values of thermodynamic properties calculated through it. The pDOS is calculated using the linear interpolation tetrahedron method available in AFLOW package. The derivative of dynamical matrix in Eq. 7 is obtained using the central difference method within a volume range of ±0.03%.

In order to balance accuracy and computational cost, the dimension of the supercell for IFCs calculations has been optimized. Since the average Grüneisen parameter is an important variable in our equations, we have evaluated this property for different cell size for Si. Results and comparison with experimental results are shown in Fig. 1. We note that a $3 \times 3 \times 3$ supercell, containing 54 atoms, predicts almost the same quantitative values as the $4 \times 4 \times 4$ supercell (128 atoms) in the 100-700 K range, while dramatically reducing the number of atoms and computational time. Therefore, we have built supercells with at least 27 atoms per reciprocal atom in the primitive cell homogeneously distributed in all directions.

2.2.3. Distorted volume single point calculations

To obtain $F(V, T)$ vs. $V(T)$ curves, phonon calculations have been performed for thirteen equally spaced configurations in which the volume of cell was compressed and expanded in the range from 98 % to 113 % of its fully relaxed value. $F_{\text{elec}}(V, T)$ is computed from static and band calculations of the expanded and compressed primitive cells following AFLOW standard [21] that are consistent with the setup used for the geometry optimizations.

There are limitations derived by the level of theory or functional. PBE could predict metallic behavior in semiconductors with a narrow band gap. This error would modify $F_{\text{elec}}(V, T)$ which is a small contribution at low and moderate temperatures. To verify that none of the materials included in the data set present this anomaly, we have compared the calculated band gaps with the experimental values (see Table 1 in Supplementary Information).

2.3. Analysis of Results

Different statistical parameters have been used to measure the qualitative and quantitative agreement of QHA-APL with experimental values. The Pearson correlation coefficient $r$ is a measure of the linear correlation between two variables, $X$ and $Y$. It is calculated by

$$ r = \frac{\sum_{i=1}^{n} (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^{n} (X_i - \bar{X})^2} \sqrt{\sum_{i=1}^{n} (Y_i - \bar{Y})^2}} $$

(12)

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where $\overline{X}$ and $\overline{Y}$ are the mean values of $X$ and $Y$.

The Spearman rank correlation coefficient $\rho$ is a measure of the monotonicity of the relationship between two variables. The values of the two variables $X_i$ and $Y_i$ are sorted in ascending order, and are assigned rank values $x_i$ and $y_i$ which are equal to their position in the sorted list. The correlation coefficient is then given by

$$\rho = \frac{\sum_{i=1}^{n} (x_i - \overline{x})(y_i - \overline{y})}{\sqrt{\sum_{i=1}^{n} (x_i - \overline{x})^2} \sqrt{\sum_{i=1}^{n} (y_i - \overline{y})^2}}. \quad (13)$$

It is useful for determining how well the ranking order of the values of one variable predict the ranking order of the values of the other variable.

We also investigate the root-mean-square relative deviation ($RMSrD$) of the calculated results from experiment. This gives a measure of the magnitude of the difference between the QHA-APL predictions and experiment. The root mean square relative deviation ($RMSrD$) is calculated using the expression

$$RMSrD = \sqrt{\frac{\sum_{i=1}^{n} \left(\frac{X_i - Y_i}{X_i}\right)^2}{N - 1}}, \quad (14)$$

Note that lower values of the $RMSrD$ indicate better agreement with experiment.

3. Results

A benchmark of 130 materials has been used to demonstrate the accuracy and robustness of this method (see Table 1). To maximize the heterogeneity of the data set, these compounds were selected to belong
to different crystallographic lattices (cubic, tetragonal, orthorhombic, hexagonal, rhombohedral and monoclinic) as well as different electronic properties (insulators, semiconductors and metals, see Supplementary Information for the computed and experimental energy gaps).
| Formula | ICSD | $B$ (GPa) | $\gamma$ | $\alpha$ | $C_p$ (Jmol$^{-1}$K$^{-1}$) |
|---------|------|-----------|---------|---------|---------------------------|
| AgCl | 157355 | 28.6(44.0)[43] | 2.30 | 114.0 | 53.3(53.0)[44] |
| Ag$_2$ | 18205 | 48.6 | 2.14 | 89.2 | 59.6 |
| Ag$_3$ | 58348 | 65.8 | 1.66 | 46.6 | 49.3 |
| Al$_2$ | 58322 | 58.1 | 2.41 | 86.9 | 102.7 |
| Al$_3$ | 606008 | 64.5(77.0)[49] | 0.57(0.66)[46] | 13.7 | 44.4(45.8)[44] |
| Al$_4$ | 159334 | 167.5 | 1.16 | 22.2 | 51.0(43.9)[44] |
| Al$_5$ | 241029 | 67.5 | 2.41 | 80.8(69.0)[47] | 24.3(24.2)[47] |
| Al$_6$ | 241012 | 47.6 | 1.54 | 69.1 | 44.5(48.9)[44] |
| Al$_7$ | 602459 | 180.0(201.0)[50] | 0.80(0.70)[51] | 10.1 | 31.0(30.1)[44] |
| Al$_8$ | 608085 | 147.1 | 1.93 | 40.5 | 45.9(45.9)[44] |
| Al$_9$ | 609019 | 80.6(86.0)[49] | 0.50(0.75)[51] | 10.3 | 41.5(42.0)[44] |
| Al$_{10}$ | 609290 | 47.3(58.2)[45] | 0.40(0.60)[46] | 11.7(12.6)[47] | 45.8 |
| Al$_{11}$ | 58098 | 63.6 | 1.83 | 52.9 | 47.0 |
| Al$_{12}$ | 162865 | 51.9 | 1.31 | 37.7 | 69.3 |
| Al$_{13}$ | 58173 | 45.9 | 0.51 | 16.2 | 96.5 |
| Al$_{14}$ | 187030 | 92.1 | 1.54 | 35.6 | 45.6(49.3)[44] |
| Al$_{15}$ | 609529 | 97.9 | 1.49 | 33.8 | 89.7 |
| As$_2$ | 161292 | 126.6 | 0.80 | 13.0 | 34.9 |
| As$_3$ | 56445 | 31.1 | 1.27 | 55.7 | 70.9 |
| As$_4$ | 53964 | 57.2(74.8)[49] | 0.76(0.75)[46] | 21.6(16.2)[47] | 46.9(46.8)[44] |
| As$_5$ | 165642 | 43.6(58.0)[49] | 0.64(0.57)[46] | 19.7(14.1)[47] | 43.6(47.8)[44] |
| B$_2$Sb | 184571 | 94.9 | 0.85 | 15.2 | 38.0 |
| B$_2$Te | 78847 | 231.4 | 1.27 | 15.3 | 45.7 |
| Be$_2$N$_2$ | 167794 | 265.9 | 1.35 | 15.8 | 48.5 |
| Be$_3$ | 52708 | 99.4 | 1.63 | 54.2 | 16.5(16.52)[44] |
| Be$_4$ | 58734 | 210.0 | 2.10 | 32.5 | 43.1 |
| Be$_5$ | 186889 | 89.7(105.0)[56] | 0.91 | 20.9 | 36.7(34.2)[44] |
| Be$_6$Se | 616419 | 70.8(92.0)[56] | 0.80 | 21.1 | 39.9 |
| Be$_7$Te$_2$ | 290068 | 53.8(67.0)[56] | 0.72 | 19.9 | 41.6 |
| Be$_8$C | 616184 | 179.3 | 1.17 | 20.2 | 38.9(33.4)[44] |
| Be$_9$C$_2$ | 616837 | 24.1 | 1.92 | 106.8 | 51.9 |
| Be$_{10}$N$_2$ | 30090 | 36.8 | 1.19 | 53.5(46.2)[47] | 49.5(54.8)[44] |
| Be$_{11}$K | 52243 | 11.0(15.4)[52] | 1.87(1.45)[46] | 170.5(116.1)[53] | 53.7(52.3)[53] |
| Be$_{12}$Li | 53819 | 19.4(26.0)[53] | 2.39 | 216.6(149.4)[53] | 59.4(48.9)[53] |
| Be$_{13}$Na$_2$ | 44278 | 16.0(19.6)[52] | 1.69(1.5)[46] | 148.0(126.9)[53] | 52.3(51.9)[53] |
| C | 182729 | 416.9(442.0)[45] | 0.73(0.75)[46] | 3.23(3.5)[47] | 6.4(6.0)[44] |
| C$_2$Si | 618777 | 211.0(211.0)[45] | 0.72(0.75)[46] | 7.3 | 27.7(27.1)[44] |
| C$_3$Ti | 183681 | 230.0 | 1.44 | 16.8 | 35.1(33.9)[44] |
| C$_4$Zr | 180599 | 212.0 | 1.58 | 17.9 | 38.2 |
| Ca$_2$C | 619188 | 27.3 | 1.57 | 78.6 | 50.4 |
| Ca$_3$ | 40938 | 68.3(84.0) | 1.78 | 68.7 | 68.7(68.7)[44] |
| Ca$_4$O | 180198 | 98.6(113)[58] | 1.57(1.57)[46] | 39.3 | 43.4(42.2)[44] |
| Ca$_5$S | 619530 | 69.6 | 1.46 | 34.1 | 47.0(47.4)[44] |
| Ca$_5$Se | 619570 | 46.0 | 1.50 | 47.8 | 48.4(48.1)[44] |
| Formula | ICSD | B   | γ   | α   | C_p | Formula | ICSD | B   | γ   | α   | C_p |
|---------|------|------|------|------|------|---------|------|------|------|------|------|
| Ca, Te | 619016 | 34.6 | 1.47 | 51.3 | 49.5(41.6)[44] | Ni, O | 166115 | 168.9 | 1.59 | 33.6 | 42.1(44.5)[44] |
| Cd, F | 28864 | 79.3 | 2.20 | 74.1 | 71.2 | Ni, Sb | 646431 | 107.3 | 1.73 | 36.2 | 48.6 |
| Cd, O | 181735 | 114.4 | 1.94 | 46.0 | 46.1(43.7)[44] | Ni, Se | 105333 | 96.2 | 1.86 | 45.6 | 48.7 |
| Cd, Pd | 620270 | 91.6 | 2.32 | 57.1 | 50.4 | Ni, X | 647134 | 129.5 | 1.86 | 46.8 | 48.1 |
| Cd, Pt | 620297 | 119.3 | 2.70 | 51.7 | 50.7 | Ni, Sn, Ti | 646777 | 138.5 | 2.17 | 41.3 | 97.2(98.0)[44] |
| Cd, S | 290009 | 46.8 | 0.53(0.75)[51] | 16.8 | 46.7 | O, Pd | 26598 | 142.3 | 1.51 | 19.8 | 39.1 |
| Cd, Sr | 102066 | 19.8 | 1.51 | 89.0 | 51.3 | O, Sr | 26960 | 76.4(91.2)[58] | 1.63(1.52)[46] | 44.8 | 46.2(45.4)[44] |
| Cd, Zr | 102093 | 71.8 | 1.99 | 50.5 | 100.2 | O, Zn | 182356 | 121.0 | 0.66(0.75)[51] | 15.7 | 40.3(41.17)[44] |
| Cl, Cu | 78270 | 35.6 | 0.86 | 46.2(36.3)[47] | 48.3(52.6)[44] | O, Zn | 647683 | 121.4(143)[45] | 0.66 | 15.7 | 40.3 |
| Cl, K | 240522 | 13.3(18.2)[52] | 1.77(1.45)[46] | 157.4(111.3)[53] | 52.7(51.7)[53] | O, Zn | 108733 | 65.6(71.4)[49] | 0.79(0.75)[46] | 23.1 | 45.5 |
| Cl, Li | 26909 | 38.9(32.9)[52] | 2.71 | 119.6(131.4)[53] | 50.0(48.1)[53] | Pt, Zn | 105852 | 159.4 | 2.13 | 37.6 | 49.2 |
| Cl, Na | 240600 | 19.7(25.1)[52] | 1.75(1.56)[46] | 145.7(119.1)[53] | 51.6(50.54)[53] | S, Zn | 108733 | 65.6(71.4)[49] | 0.79(0.75)[46] | 23.1 | 45.5 |
| Cl, Rb | 18016 | 10.2(16.2)[52] | 1.55(1.45)[46] | 156.5(108.0)[53] | 52.6(52.3)[53] | Sc, Zn | 164093 | 52.1 | 1.10 | 30.8 | 23.8(25.58)[44] |
| Cu, I | 163427 | 18.9 | 1.36 | 101.0 | 51.0 | Sc, Zn | 106041 | 65.1 | 1.39 | 42.3 | 48.3 |
| Cu, Sn | 627117 | 114.5 | 1.91 | 53.5 | 24.3(24.5)[44] | Si, Zn | 76268 | 84.9(100.0)[45] | 0.42(0.56)[51] | 8.0(7.8)[47] | 20.0(20.0)[44] |
| Cu, Zn | 629278 | 54.7 | 2.40 | 85.4 | 51.9 | Te, V | 106143 | 232.5 | 1.91 | 21.7 | 45.9 |
| Cu, Ni, Zn | 103079 | 124.7 | 1.93 | 50.5 | 96.7 | Te, Zn | 184485 | 39.4(51.0)[49] | 0.89(0.97)[46] | 30.7 | 48.6 |
| F, K | 52241 | 22.8(31.6)[52] | 1.59(1.5)[46] | 133.4(104.4)[53] | 50.5(49.0)[53] | Te, Zr | 653209 | 93.1 | 1.60 | 27.6 | 48.2 |
| F, Li | 53839 | 55.8(76.0)[52] | 1.63(1.5)[46] | 109.9(99.6)[53] | 42.8(42.0)[53] | Ti, Zr | 168830 | 109.3 | 1.62 | 30.1 | 23.5(25.1)[44] |
| F, Na | 52238 | 37.3(48.5)[52] | 1.52(1.5)[46] | 113.7(95.1)[53] | 47.8(46.9)[53] | Ti, Zr | 181734 | 44.8 | 2.47 | 144.8 | 26.8(25.41)[44] |
| Ga, P | 77088 | 74.8(88.7)[49] | 0.700(0.75)[46] | 16.2(15.9)[47] | 44.1(44.2)[44] | Zn, Zr | 181290 | 96.3 | 1.42 | 31.2 | 48.3 |
| Ga, Sb | 41675 | 42.7(45.1)[49] | 0.71(0.75)[46] | 21.9 | 47.9 | | | | | | |
For each temperature, we calculated the free energy ($F$) at different volumes ($V$). These $F$ vs. $V$ curves are initially fitted to a cubic function which is used as an initial guess to fit the Birch-Murnaghan equation of state (see “Method” and Eq. 6). As an example, the results of the final fitting for Si are depicted in Fig. 2. Automatic tests to ensure the correct fitting of the curves have been implemented to warn of possible errors, especially in magnetic systems or close to phase transition temperatures. The bulk modulus, $B$, at 300 K is obtained by the fitting procedure. Fig. 3 (a) illustrates the distribution of $B$ for the whole set of materials while Fig. 3 (b) compares experimental and predicted values of $B$ for those materials with available experimental data. The computed values range over two orders of magnitude, from C diamond (442 GPa) to K (3.2 GPa). To quantify the accuracy, precision and robustness of our results we have used different statistical quantities such as mean absolute deviation (MAD), root mean square deviation (RMSD), root mean square relative deviation (RMSrD), relative maximum absolute deviation (rMAX), and Pearson and Spearman correlation (see Table 2). Most of the predicted values are within a 20% error (dashed lines in Fig. 3 (b)), presenting a RMSrD of around 17% and a rMAX close to 22.9%. Values close to 1.0 for the Pearson and Spearman correlations also demonstrate that our implementation of the QHA is robust and that the results can be compared with experimental data.

![Figure 2](image-url)

Figure 2: Free energy and volume data fitted using Birch-Murnaghan function for different temperatures for Si. Points represent calculated data and solid lines indicate the fitted function. Equilibrium volumes at each temperature are connected by solid black line.

In the spirit of the QHA, the Grüneisen parameter, $\gamma(T)$, is often used to estimate the anharmonicity of the vibrations in the crystal. Methods such as AGL are able to predict reasonably accurate values for the Debye temperature or $B$ but fail to predict $\gamma(T)$ [3]. Our QHA-APL results are shown in Fig. 3 which includes, for comparison, the available results using AGL for the same compounds. Despite the higher computational cost of the QHA compared to the AGL methodology (one or two orders of magnitude higher than AGL depending on the size of the system), it is clear that results are tremendously improved. The MAD for QHA-APL is 0.13 for a property whose highest measured value is around 3 and the average values are...
between 1 and 2. Relative statistical indicators also demonstrate the high accuracy of the method obtaining a RMSrD below 16% and a rMAX lower than 29%. Values larger than 3 are especially interesting for their potential application as thermoelectrics. As we mentioned, $\gamma(T)$ is related to the anharmonicity of the crystal, so high values for this property usually [59] indicate lower values of the lattice thermal conductivity, $\kappa_L$, which increases the thermoelectric figure of merit, $ZT$. We have found two materials with $\gamma$ over 3, however both are metals (HgPd, HgPt). We have looked for other possible candidates with high values of $\gamma$ considering also that for a high thermoelectric figure of merit they should be semiconductors. K$_2$O and MnO are the best two candidates, with $\gamma$ around 1.8 and band gaps below 2 eV. There is no experimental data available for K$_2$O, although Gheribi et al. have predicted a lattice thermal conductivity for this material below 2 Wm$^{-1}$K$^{-1}$ [60].

The Grüneisen parameters for each vibrational mode, $\gamma_{iq}$, provide even more information than $\gamma$ about the anharmonicity of the crystal and the lattice thermal conductivity. High and low values of $\kappa_L$ in an insu-
Table 2: Mean absolute deviation (MAD), root mean square deviation (RMSD), root mean square relative deviation (RMSrD), relative maximum absolute deviation (rMAX), and Pearson and Spearman correlation for the material data set. Units: MAD and RMSD in the same units that are used in Table 1.

|       | B       | γ       | α       | Cp      |
|-------|---------|---------|---------|---------|
| MAD   | 11.09   | 0.13    | 20.22   | 1.63    |
| RMSD  | 12.89   | 0.17    | 28.15   | 2.45    |
| RMSrD | 17.38%  | 15.00%  | 28.0%   | 6.35%   |
| rMAX  | 22.9%   | 28.32%  | 46.5%   | 18.9%   |
| r     | 0.996   | 0.969   | 0.974   | 0.985   |
| ρ     | 0.990   | 0.891   | 0.927   | 0.929   |

Lato are usually linked to low and high values of γ_{iq} at low frequency. SiC (κ=360 Wm^{-1}K^{-1}) [51] and NaI (κ=1.8 Wm^{-1}K^{-1}) [51] are two good examples of this trend (see Fig. 4 (a) and (b)) that has been exploited in the literature to pinpoint anharmonic effects [61, 62]. We have studied the mode Grüneisen parameters of two other materials included in the benchmark whose κ_L has not been measured experimentally. We have already discussed the probable low thermal conductivity of K_{2}O which is in agreement with the very high mode Grüneisen parameter values at low frequencies (see Fig. 4 (d)). BeTe shows the opposite behavior to K_{2}O, presenting low values for γ_{iq} at low frequencies (see Fig. 4 (c)). This trend is in agreement with the AGL prediction of κ_L for BeTe, which is close to the value obtained for AlAs (κ=98 Wm^{-1}K^{-1}) [51]. These predictions validate the use of γ and γ_{iq} as a simple predictors for κ_L and demonstrates that the QHA-APL method can be used as a powerful method for the discovery of new interesting properties in well known materials.

The volumetric thermal expansion, α_V(T), has very important implications in engineering. However, it is not easy to predict accurately from first principles. Statistical parameters prove again that QHA-APL methodology is a reliable method to obtain this thermodynamic quantity. The uncertainty as described by RMSrD is below 28% and MAD is around 20.22 10^{-6}K^{-1} for the benchmark in which the range varies between 0 and 160 10^{-6}K^{-1}. Low thermal expansion coefficient materials deserve special attention because they are particularly interesting for a variety of applications. There are 5 materials in our benchmark that present a value of α below 10^{-5}K^{-1} (see Fig. 5 (b)). Three of them have been already reported, C, Si and CSi. However, to the best of our knowledge, the other two materials have not been experimentally measured or predicted: MnTe and MgSe.

Isobaric specific heat, C_p, can be considered another good test for our method because of the vast amount of available experimental data (see Fig. 5 (d)). The low MAD (9.84 Jmol^{-1}K^{-1}) is surprising for a property in which the average value of our data set is close to 50 Jmol^{-1}K^{-1}. This fact is also reflected in the relative statistical parameters (RMSrD = 6.35% and rMAX = 18.9%) and correlations close to 1.0. A caveat should be mentioned: this deviation grows slightly when comparing C_p at 1000 K instead of 300 K. This is due to higher anharmonicity at higher temperatures.

Some groups of materials are more likely to show larger deviations because of the exchange-correlation functional limitations. Inaccurate band gaps could lead to predict metallic behavior in semiconductor with a narrow band gap. This qualitative disagreement can modify the electronic terms in the free energy. To ensure that our description is correct, we have calculated the RMSrD for metals and semiconductors with a predicted band gap smaller than 1.0 eV. For metals, the RMSrD is 8.1% for C_p, which is below the RMSrD for the whole data set. We have also calculated this quantity for α_V(T) and C_p for low band gap semiconductors, obtaining 30.0% and 3.6% respectively. Both values are also close to the RMSrD obtained for the whole data set. Despite QHA limitations, we demonstrate that our implementation can predict the properties of different groups of materials.
We also computed the temperature dependence for selected materials in the data set (see Fig. 6). Our implementation predicts correctly the behavior of $\gamma(T)$, $B$, $\alpha_V(T)$ and $C_p$ below melting points for various types of materials (metals, insulators and semiconductors). The bulk modulus for insulators such as NaCl and KCl are shown in Fig. 6 (a) with errors smaller than 25%. QHA-APL also predicts $\alpha_V(T)$ for complex metals as Ni$_2$SnTi with a high accuracy below its melting point (see Fig. 6 (b)). Finally, $C_p$ for GaAs, a classic semiconductor, is depicted in Fig. 6 (c) presenting errors smaller than 2%.

More sophisticated electronic structure methods can be used to validate our data. Our framework can use different exchange correlation functionals such as the pseudo hybrid functional ACBN0 [33]. We have used K$_2$O as a test to study how a more accurate functional works compared to the results obtained with PBE (see Fig. 7). Despite the use of a more accurate approach, the band gap (1.8 eV compared to 1.71 eV for PBE), phonon dispersion curves and the average Grüneisen parameter for K$_2$O are only slightly modified by ACBN0.

4. Conclusions

The quasi-harmonic approximation has been combined with the Automatic Phonon Library in the AFLOW high-throughput framework in order to develop a tool to accurately and robustly predict some of the most important temperature dependent properties of solids such as $B$, $\gamma$, $\alpha$, and $C_p$. Lattice dynamics calculations at different volumes for fully relaxed structures are performed, managed, self-corrected, and post processed by the QHA-APL code, creating a unique workflow to populate material databases such as AFLOW. A benchmark of 130 materials has been used to test the precision and accuracy of the software.
Figure 5: (a) Histogram for the dispersion of predicted volumetric thermal expansion coefficient at 300 K for the selected set of systems. (b) Comparison of experimental $\alpha^{exp}$ and predicted $\alpha^{APL}$ for the selected set of systems. The red line represents equality between experimental and predicted values and the dashed black lines represent ±20% error. (c) Histogram for the dispersion of predicted isobaric specific heat at 300 K for the selected set of systems. (d) Comparison of experimental $C_p^{exp}$ and predicted $C_p^{APL}$ for the selected set of systems. The red line represents equality between experimental and predicted values and the dashed black lines represent ±20% error.

QHA-APL predicts results whose RMSrD is below 18% for any of the four quantities with respect to experimentally reported data. We confirm recent results on $K_2O$ and computed data for well known materials that have not been reported before. QHA-APL is useful not just for the prediction of properties for particular materials; its automation, robustness, accuracy and precision make it the perfect framework for the creation of material data sets that can be used for data mining or machine learning.

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Figure 6: (a) Predicted bulk modulus of NaCl and KCl compared to the available experimental data [63]. (b) Predicted volumetric thermal expansion coefficient of Ni2SnTi compared to the available experimental data [64]. (c) Predicted isobaric specific heat of GaAs compared to the available experimental data [65].

Figure 7: (a) Phonon dispersion curves and (b) average Grüneisen parameter for K2O using PBE and ACBN0 functionals.

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