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Editor's Choice

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 heat 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.

1. Introduction

The characterization and prediction of thermal properties of materials are among 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 (γ_{qj} and γ), thermal expansion coefficient (α_V), Debye temperature (θ_D), lattice thermal conductivity (κ_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], PHONO3PY [5] and in the AFLOW-APL2 Library [6] (computationally intensive but capable of giving very accurate values for κ_L). **iv.** Approaches based on the QHA [7–14] which can rapidly characterize C_V, C_p, γ, and α_V. Methods **ii.–iv.** are based on phonon calculations as available in packages like AFLOW-APL [15,16], PHONOPY [17], Phon [10], and 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

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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

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

where E_{0K} is the total energy of the system at 0 K 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:

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

where k_B, h, and ν are the Boltzmann constant, the Planck constant, and the vibrational frequency respectively. Frequencies for a given wave vector $\mathbf{q}$ 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:

$$F_{elec}(V,T) = \Delta E_{elec}(V,T) - TS_{elec}(V,T) \tag{3}$$

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,

$$\Delta E_{elec}(V,T) = \int n(\epsilon) f \epsilon d\epsilon - \int^{\epsilon_F} n(\epsilon)\epsilon d\epsilon \tag{4}$$

$$S_{elec}(V,T) = -k_B \int n(\epsilon)[f \ln f + (1-f)\ln(1-f)] d\epsilon \tag{5}$$

where the eDOS at energy, ϵ, 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_{eq}, equilibrium volume, V_{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:

$$F(V) = F_{eq} + \frac{BV_{eq}}{B_p}\left[\frac{(V_{eq}/V)^{B_p}}{Bp-1} + 1\right] - \frac{V_{eq}B}{Bp-1} \tag{6}$$

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

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

$$\gamma_{qj} = -\frac{V_{eq}^{0K}}{2\nu_{qj}^2}\sum_j e_{qj}\frac{\partial D_q}{\partial V}e_{qj}^* \tag{7}$$

where D_q is the dynamical matrix for a wave-vector, $\mathbf{q}$, ν_{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]:

$$\gamma(T) = \frac{\sum_{qj}\gamma_{qj}C_{V_{qj}}}{C_V} \tag{8}$$

where $C_{V_{qj}}$, is the isochoric specific heat:

$$C_{V_{q,j}} = k_B\sum_{q,j}\frac{(h\nu_{qj}^2)\exp(h\nu_{qj}/k_BT)}{(k_BT)^2(\exp(h\nu_{qj}/k_BT)-1)^2} \tag{9}$$

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 Eqs. (10) and (11) respectively:

$$\alpha_V(T) = \frac{C_V(T)\gamma(T)}{V(T)B(T)} \tag{10}$$

$$C_p - C_V = \alpha^2(T)B(T)V(T)T \tag{11}$$

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.*