Scripta Materialia xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular Article

High throughput combinatorial method for fast and robust prediction of lattice thermal conductivity

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ARTICLE INFO

Article history:
Received 18 July 2016
Received in revised form 7 September 2016
Accepted 26 September 2016
Available online xxxx

Keywords:
High-throughput
Accelerated materials development
Quasi-harmonic approximation
Lattice thermal conductivity

ABSTRACT

The lack of computationally inexpensive and accurate *ab-initio* based methodologies to predict lattice thermal conductivity, without computing the anharmonic force constants or time-consuming *ab-initio* molecular dynamics, is one of the obstacles preventing the accelerated discovery of new high or low thermal conductivity materials. The Slack equation is the best alternative to other more expensive methodologies but is highly dependent on two variables: the acoustic Debye temperature, θ_a, and the Grüneisen parameter, γ. Furthermore, different definitions can be used for these two quantities depending on the model or approximation. In this article, we present a combinatorial approach to elucidate which definitions of both variables produce the best predictions of the lattice thermal conductivity, κ_l. A set of 42 compounds was used to test the accuracy and robustness of all possible combinations. This approach is ideal for obtaining more accurate values than fast screening models based on the Debye model, while being significantly less expensive than methodologies that solve the Boltzmann transport equation.

1. Introduction

Lattice thermal conductivity, κ_l, plays an important role in multiple applications and technologies [1]. Thermoelectric materials [2], heat sink materials [3], rewritable density scanning-probe phase-change memories [4] or thermal medical therapies [5] are some examples in which thermal transport is the technological enabling property. During the last three decades, several theoretical models and methodologies have been developed to calculate κ_l [6–10]. It is a trade-off: while the quickest approaches can only predict trends, accurate methods are computationally expensive and can not be implemented in high throughput (HT) frameworks, hindering the discovery of new materials with better performance [1,11,12]. For instance, semi-empirical models predict thermal properties at reduced computational cost but require some experimental data [6–8]. Additionally, classical molecular dynamics combined with Green-Kubo equations also produces reliable results. Although this method includes high-order scattering processes, the use of semi-empirical potentials leads to errors on the order of 50% [13,14]. Furthermore, the extension of the Green-Kubo formalism to multiscale models has been shown to be nontrivial [15]. Characterization of the anharmonic forces constants and its use in the solution of the Boltzmann transport equation, BTE, is extremely expensive which makes it unfeasible in a HT approach. Thus, for an effective prediction of κ_l with HT methods, there is an advantage in approximated methods based on *ab-initio* characterization. **i.** *Ab-initio* is fully self-consistent and does not need experimental data or the use/generation of force fields; **ii.** There exists HT frameworks, such as AFLOW [16–18], that can monitor, manage, correct, and post-process the information obtained from different quantum mechanical codes.

There are three main families of approximated models based on first principles. They can be classified depending on performance, accuracy and robustness.

- The "GIBBS" quasiharmonic Debye model is the least computationally expensive approach to identify trends and simple descriptors for thermal properties, such as the Grüneisen parameters, γ, and the Debye temperature, θ_D [19]. The Automatic-GIBBS-Library (AGL) framework combines this model with the Slack equation [20] based on work with noble gas crystals by

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http://dx.doi.org/10.1016/j.scriptamat.2016.09.034
1359-6462/

Leibfried and Schlömann [21] and Julian [22] to predict κ_l [23]. It reproduces correctly the ordinal ranking of the thermal conductivity for several different classes of semiconductor materials using only energy-volume curves, but suffers in comparing families with different structures.

- More accurate Grüneisen parameters can be obtained using the quasiharmonic approximation, QHA, and then used in the Slack equation [24]. However, harmonic force constants have to be calculated to build the dynamical matrix that describe the vibrational modes of the system. An alternative method proposed by Madsen *et al.* [24] consists of the use of lattice dynamics calculations to compute approximate relaxation scattering times at θ_D. Both methods give κ_l in reasonable quantitative agreement with experiments.
- Third order interatomic force constants (3rd IFCs) are required to calculate the phonon scattering times included in the solution of the Boltzmann transport equation, BTE [9,10,25]. This is the most computationally expensive method but it is the most used for highly accurate results. Once scattering processes are computed using 3rd IFCs, different schemes have been proposed to solve the BTE. The relaxation time approximation, RTA, is the simplest and predicts values on average 10% smaller than experimental quantities. The full solution requires a self-consistent iteration, but produces values very close to experiment while adding only a small computational cost compared to RTA solutions [26]. The bottle neck of both methods comes from on the computation of the 3rd order IFCs. Recently, some authors have proposed the computation of these forces using compressive sensing. However, the cost to obtain reliable results is still high [27].

Despite the different approaches developed in the last few decades, there is a lack of inexpensive, accurate, and robust methods that can be used routinely. In this article, we use different definitions of θ_a and γ based on the Debye model and the QHA to obtain values for κ_l using the Slack equation. Using a phenomenological approach, we compare the results obtained with our combinatorial schema to available experimental data to decide which description of these two variables best predict values for κ_l with qualitative and quantitative accuracy in a high-throughput approach.

2. Methodology

2.1. Lattice thermal conductivity

The lattice thermal conductivity[1] is computed using the Slack equation (Eq. 1) because of its simplicity:

$$\kappa_l(\theta_a) = \frac{0.849 \times 3\sqrt[3]{4}}{20\pi^3\left(1-0.514\gamma^{-1}+0.228\gamma^{-2}\right)} \times \times\left(\frac{k_B\theta_a}{\hbar}\right)^2 \frac{k_B M_{av} V^{\frac{1}{3}}}{\hbar\gamma^2}. \quad (1)$$

This equation predicts κ_l at the acoustic Debye temperature (θ_a) using the Grüneisen parameter, γ, primitive cell volume, V, and the average atomic mass, M_{av}. The thermal conductivity at any temperature is estimated by [20,24,28]:

$$\kappa_l(T) = \kappa_l(\theta_a)\frac{\theta_a}{T}. \quad (2)$$

Eqs. (1) and (2) show that only the acoustic Debye temperature and the Grüneisen parameter are needed to calculate κ_l at any temperature. Various groups have used different models to predict this quantity using the Slack equation. It seems that Slack equation combined with the Debye model tends to underestimate κ_l [23], while when combined with lattice dynamics calculations, κ_l is overestimated [24]. We propose the combination of both models to offset the errors and obtain values closer to the experimental results.

Our implementation is based on a combinatorial approach where the lattice thermal conductivity is a function of two variables: acoustic Debye temperature, θ_a, and Grüneisen parameter, γ: $\kappa_l(\theta_a, \gamma)$. We use different formulations based on the Debye model and quasiharmonic approximation to compute these two variables and then combine them to obtain different values for $\kappa_l(\theta_a^x, \gamma^y)$ (see Fig. 1). We use a set of 42 materials, all belonging to different space groups and presenting a range of four orders of magnitude for κ_l, as a test to determine the best combination of variables from a quantitative point of view. This approach maximizes the flexibility of the method, optimizing the results without extra cost beyond the harmonic force constants calculations.

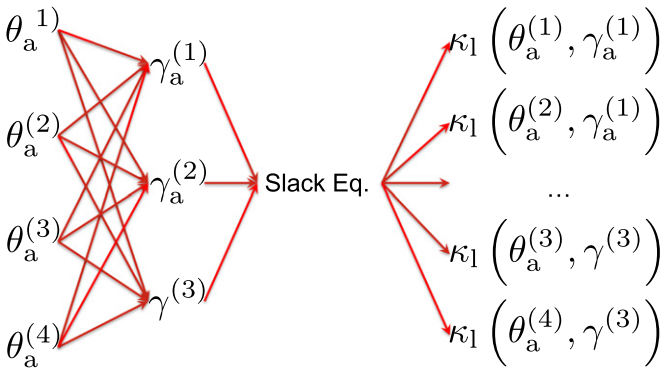

Fig. 1. Combinatorial diagram for lattice thermal conductivity.

The first definition for γ is extracted from Ref. [24]:

$$\gamma_a^{(1)} = \sqrt{\tilde{\gamma}_a^2} = \sqrt{\frac{\sum_q \sum_i^{\hbar\omega_{iq}<k_B\theta_a} \gamma_{iq}^2 C_{iq}}{\sum_q \sum_i^{\hbar\omega_{iq}<k_B\theta_a} C_{iq}}}, \quad (3)$$

where γ_{iq} is defined as:

$$\gamma_{iq} = -\frac{V_{eq}^{0K}}{2\omega_{qj}^2}\sum_i e_{iq}^* \frac{\partial D_q}{\partial V} e_{iq}. \quad (4)$$

Since the acoustic bands provide the majority of the contribution to κ_l, the sum is performed over the modes, i, and q-points, q, having an energy less than $k_B\theta_a$. We propose a second definition where the

[1] List of symbols: θ_a acoustic Debye temp.; γ Grüneisen parameter; κ_l lattice thermal cond.; θ_D Debye temp.; V prim. cell volume; M_{av} average atomic mass; ω_{iq} frequency mode i at q-point q; k_B Boltzmann constant; C_{iq} specific heat; V_{eq}^{0K}, prim. cell volume at 0 K; e_{iq} eigenvector; D_q dynamical matrix; n number atoms in prim. cell; ω_D Debye freq.; σ Poisson ratio; $F(V)$ free energy; F_{eq} eq. free energy; V_{eq} eq. volume; B bulk modulus; B_p derivative of B over P.

Please cite this article as: P. Nath et al., High throughput combinatorial method for fast and robust prediction of lattice thermal conductivity, Scripta Materialia (2016), http://dx.doi.org/10.1016/j.scriptamat.2016.09.034